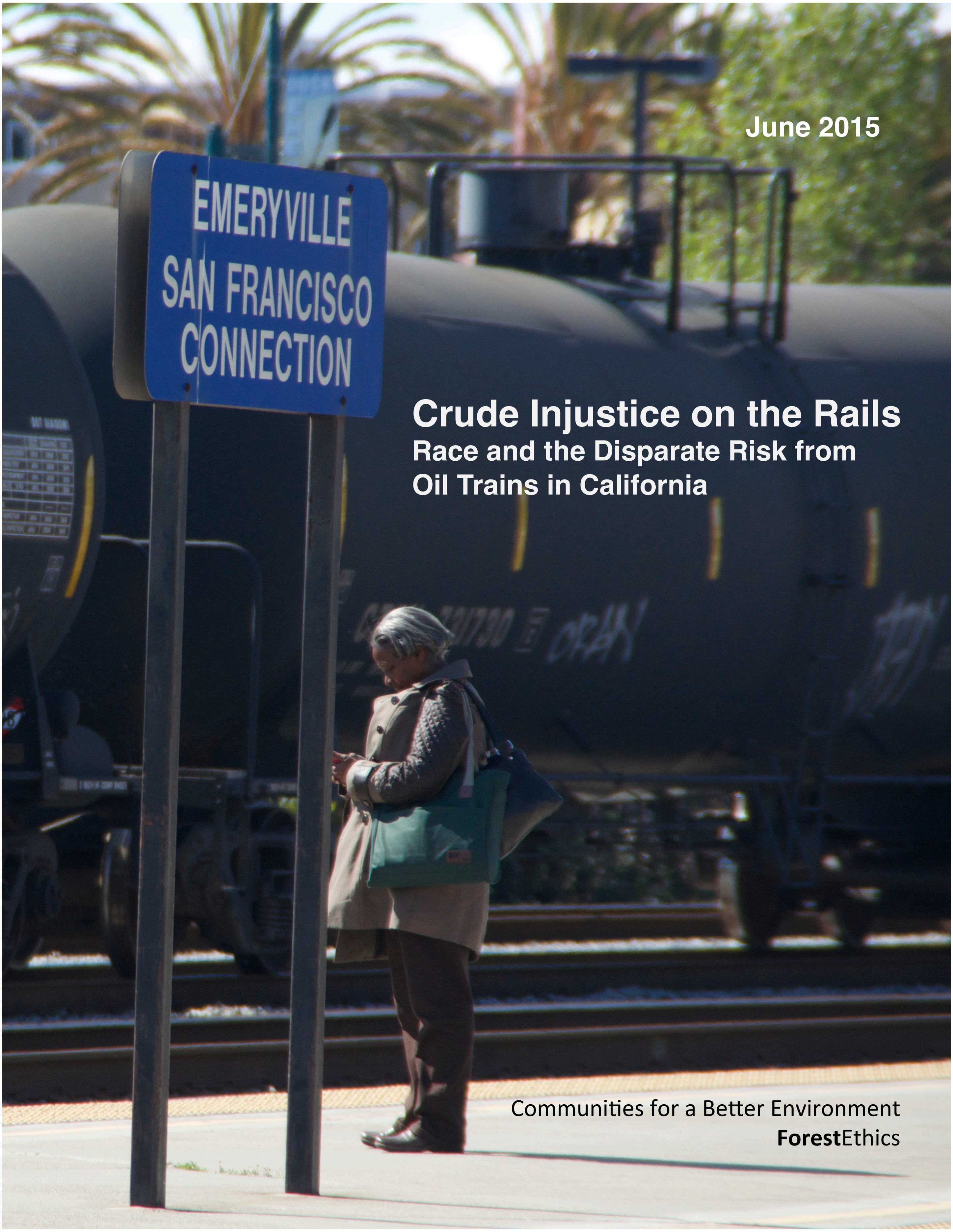
# CBE Attachments 33 through 53

Attachment 33



June 2015

# Crude Injustice on the Rails

## Race and the Disparate Risk from Oil Trains in California

Communities for a Better Environment
**Forest**Ethics

Lac Megantic, Quebec, July 6, 2013, the day of the fatal oil train derailment. Photo: Sûreté du Québec
http://commons.wikimedia.org/wiki/File:Lac_megantic_burning.jpg#/media/File:Lac_megantic_burning.jpg

# Crude Injustice on the Rails

## Race and the Disparate Risk from Oil Trains in California

# INTRODUCTION

The principles of environmental justice say that access to clean air, water and soil, and to a healthy, safe, livable community, are intrinsic human rights.

ForestEthics and Communities for a Better Environment (CBE) evaluated oil train routes and US Census data to investigate disparities in the hazards that Californians face from oil trains. This data is presented in maps showing the oil train blast zone, environmental justice census block groups, and racial profile of the ten largest cities in California with current and probable oil train routes, and four urban core areas where CBE works for environmental justice.

We conclude that oil trains contribute to environmental racism in California. Californians of color are more likely to live in the oil train blast zone, the dangerous one-mile evacuation zone in the case of an oil train derailment and fire.

Sixty percent of Californians live in environmental justice communities.[1] Yet 80 percent of the 5.5 million Californians with homes in the blast zone live in environmental justice communities. Nine out of ten of California's largest cities on oil train routes have an even higher rate of discriminatory impact than the state average. In these cities, 82–100 percent of people living in the blast zone are in environmental justice communities.

**Percentage of people in the oil train blast zone that live in environmental justice communities in the ten largest California cities on oil train routes:**

| | | | |
|---|---|---|---|
| Los Angeles | 82% | San José | 91% |
| Fresno | 85% | Sacramento | 89% |
| Long Beach | 85% | Oakland | 92% |
| Bakersfield | 77% | Stockton | 94% |
| Fremont | 100% | San Bernardino | 100% |

We document a racial component of this injustice statewide, in cities and in communities. People of color comprise a greater percentage of populations in the blast zone than outside the blast zone statewide, within each major California city on oil train routes except for Sacramento, and within each environmental justice community—except for the City of Huntington Park, where the comparison is not applicable. The exception to the pattern is Sacramento where the blast zone crosses the State Capital and its local urban renewal. The situation in Huntington Park also describes deep racial injustice, because nearly all residents are people of color *and* in the blast zone.

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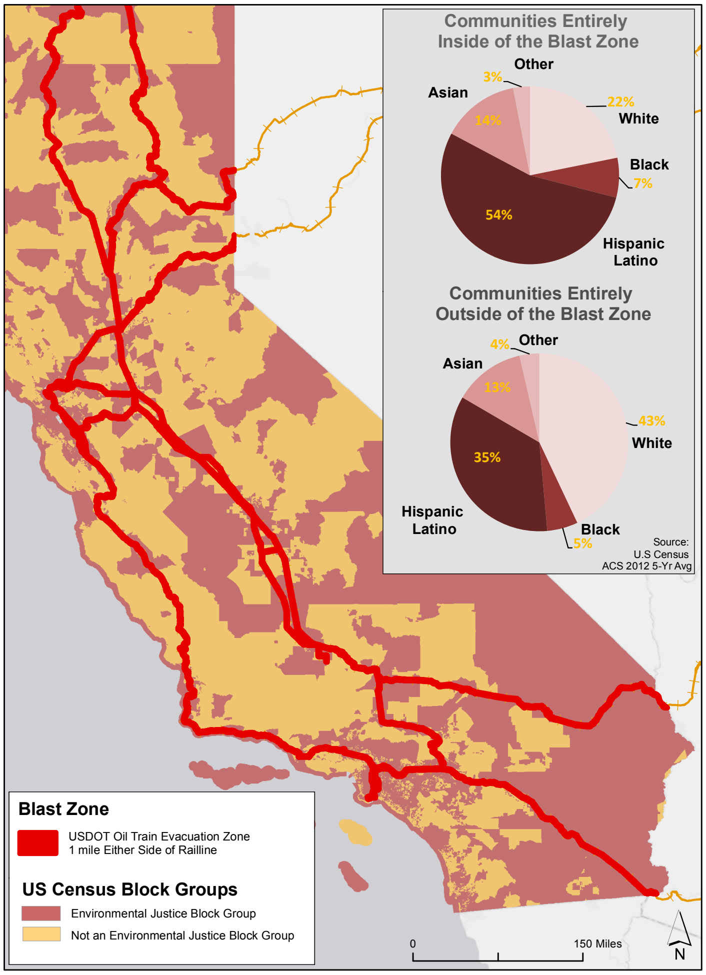
[1] Environmental Justice Communities, in this analysis, are census block groups that meet one or more of three criteria: more than 25% of residents are people of color (non-white); median household income is less than 65% of statewide median household income; more than 25% of households are linguistically isolated (no English speaker older than 14).

## Environmental Justice and Race Inside of the California Blast Zone



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**People of color* as a percentage of populations inside *versus* outside of the oil train blast zone in California, by political jurisdiction:**

|  | Inside the blast zone | Outside the blast zone |  | Inside the blast zone | Outside the blast zone |
|---|---|---|---|---|---|
| Los Angeles | 90% | 69% | San José | 76% | 70% |
| Fresno | 74% | 66% | Sacramento | 61% | 65% |
| Long Beach | 88% | 63% | Stockton | 85% | 66% |
| Bakersfield | 78% | 64% | Oakland | 91% | 64% |
| San Bernardino | 88% | 78% | Richmond | 89% | 70% |
| Modesto | 58% | 49% | Wilmington | 97% | 95% |
| Fremont | 73% | 71% | Huntington Park | 99% | NA |
| California | 78% | 57% |  |  |  |

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*Latino/Hispanic, Black, Asian, and other non-white Census categories; _see_ pages 4, and 7–20 for detail.

## RECOMMENDED ACTION

Federal, state, and local officials must consider environmental justice in oil train safety protections and the review of any proposed infrastructure projects that will permit or expand oil train traffic.

Federal, state and local officials must take immediate action to address the flawed and discriminatory safety protections and permits that allow oil trains to exacerbate already-serious cumulative health and safety hazards in our most vulnerable communities. There is great urgency because every oil train brings with it the potential for catastrophe and a guarantee of air pollution exposure leading to chronic risks.

Based on the severe potential environmental health, safety, and climate impacts of oil trains in California, the lack of necessity for trains to deliver the oil refined for fuels used here, and the environmental injustice and racism documented in this report, ForestEthics and Communities for a Better Environment (CBE) recommend the following actions.

- **A moratorium on oil imports into California by train and an immediate halt to permitting of proposed projects that would enable new or expanded use of oil trains in the state.**

- **Immediate action to root out systemic and institutional environmental discrimination and racism. Actions to investigate and correct the oil train-related public disclosure, public participation, monitoring, standard setting, and permitting actions that contribute to the environmental and racial injustice observed in California's oil train blast zone, including but not limited to the following:**
    - **The California Attorney General should open an investigation and inquiry, with state and local agencies, regarding oil train infrastructure permitting.**
    - **The US EPA Office of Civil Rights should enforce federal statutes prohibiting racial discrimination in the protection of people from oil trains.**
    - **The US Department of Justice Division of Civil Rights should enforce federal statutes prohibiting racial discrimination, to protect all people from oil trains.**

- **Public support of CBE and ForestEthics to protect our health, safety, and climate, and win on environmental justice. Join our local efforts to stop oil trains and prevent oil train projects, and join us to collaborate together across California's communities in the blast zone.**

# MAPPING ENVIRONMENTAL INJUSTICE IN THE BLAST ZONE

Fireball from the derailment of a crude oil train outside Casselton, ND. Photo: US PHMSA

Interpreting the blast zone maps:

- The **blast zone** shown is the one-mile evacuation area that the US Department of Transportation recommends in the case of an oil train derailment, spill and fire. While one-mile is a guideline for initial response to a multi-car accident with fire, the toxic cloud from the December 2013 Casselton, ND, oil train disaster (above) required a five-mile evacuation zone downwind.
- **Environmental justice communities** as defined in this analysis are based on a method from the State of Massachusetts, and are census block groups that meet one or more of three criteria: (1) greater than 25 percent of residents are people of color (non-white); (2) median household income is less than 65 percent of statewide median household income; (3) linguistically isolated households (no English speaker older than 14) are more than 25 percent of households.
- **Race** is broken out in charts for each area mapped.
- The estimates shown in these maps and charts were calculated from US Census block group[2] data. Data and methods are detailed at the end of this report.
- ForestEthics calculates[3] that 25 million Americans and 5.5 million Californians live in the blast zone. ForestEthics built the blast zone map tool using train routing information from the rail industry, current and proposed rail terminals, expert reporting, and eyewitness accounts. Blast-zone.org allows anyone to search addresses in the US and Canada and see if they are in the blast zone.

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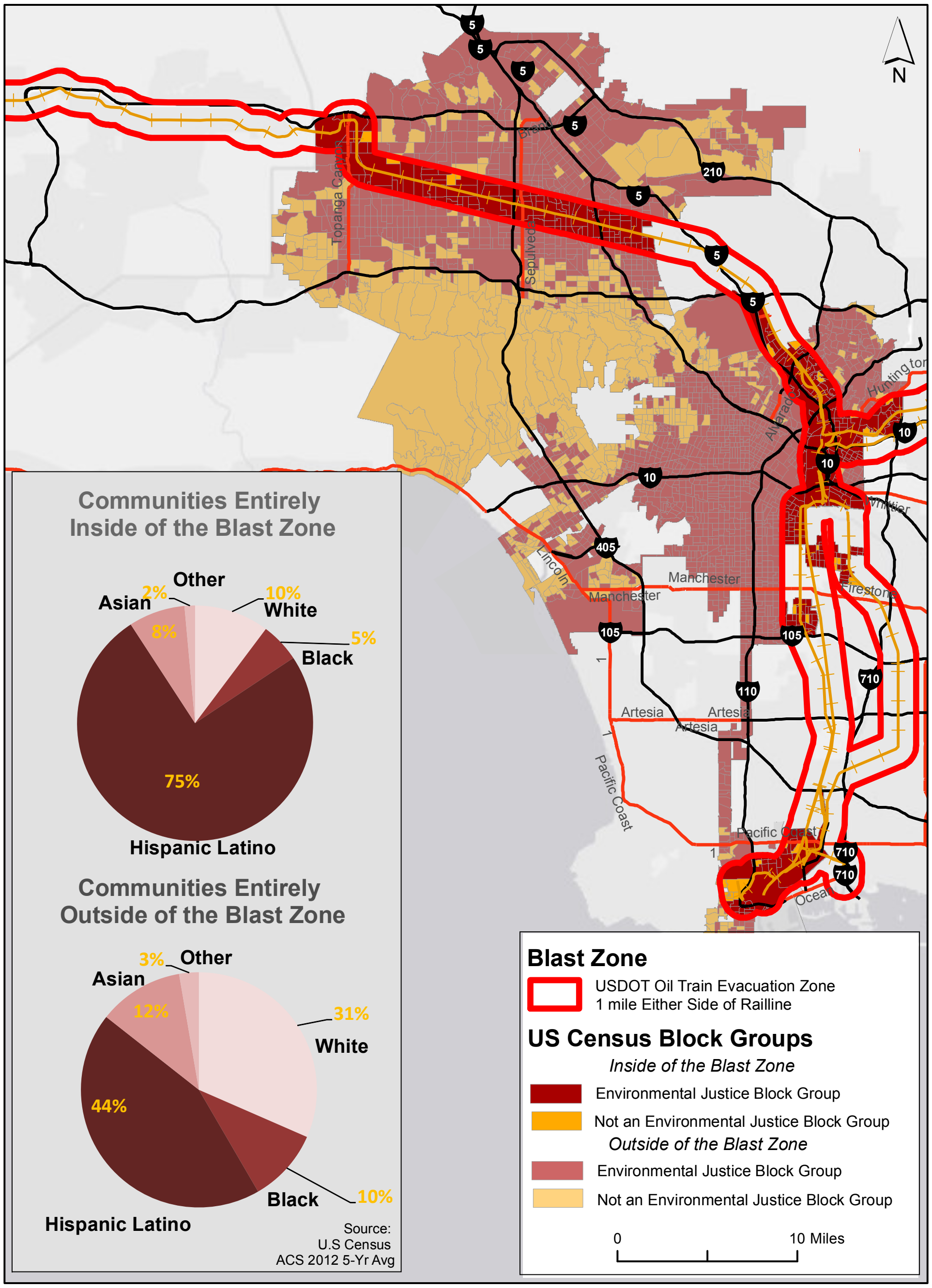
[2] https://www.census.gov/geo/reference/gtc/gtc_bg.html

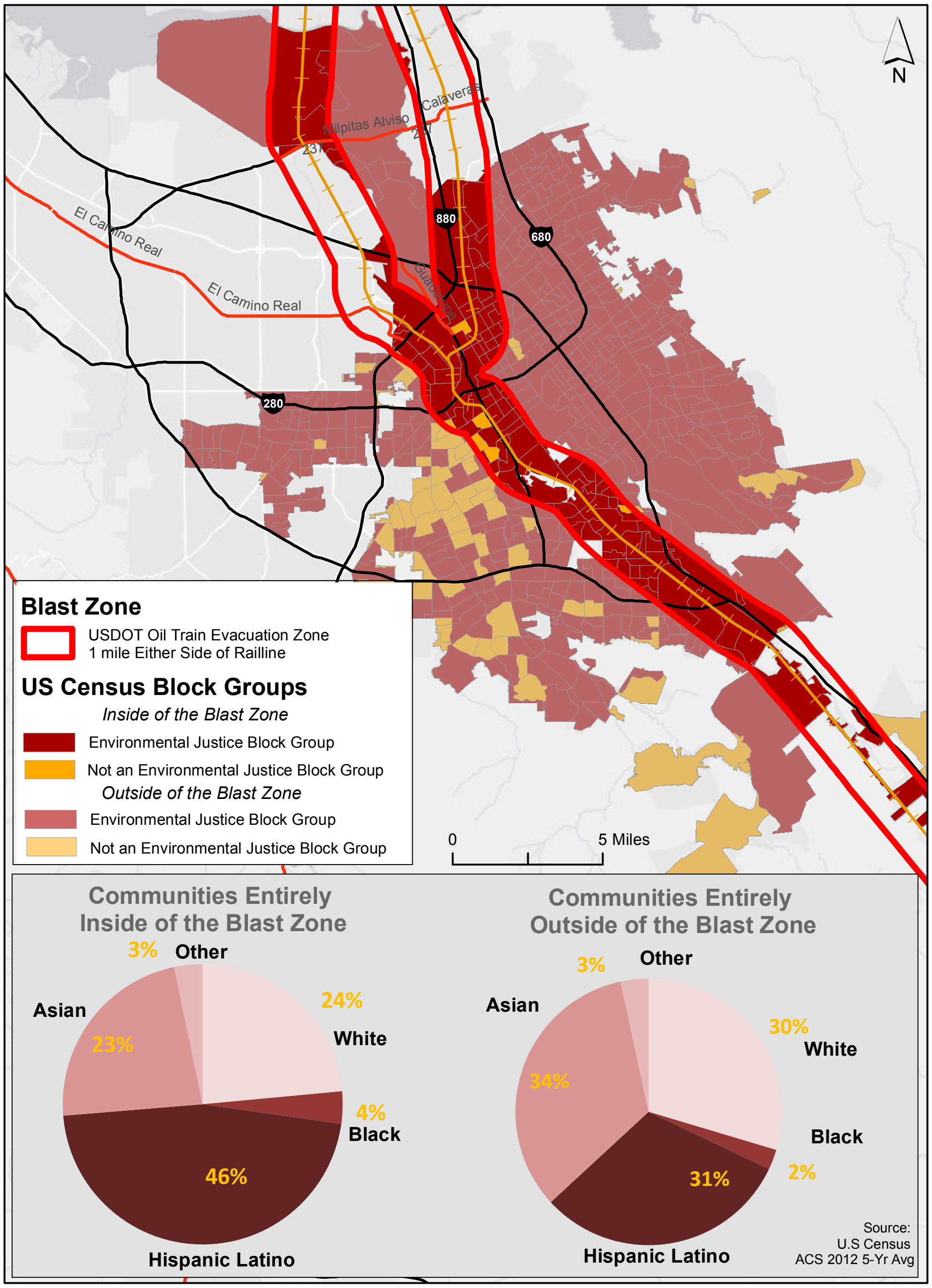
[3] http://tinyurl.com/orzncca

# Environmental Justice and Race
# Inside of the Los Angeles, CA Blast Zone



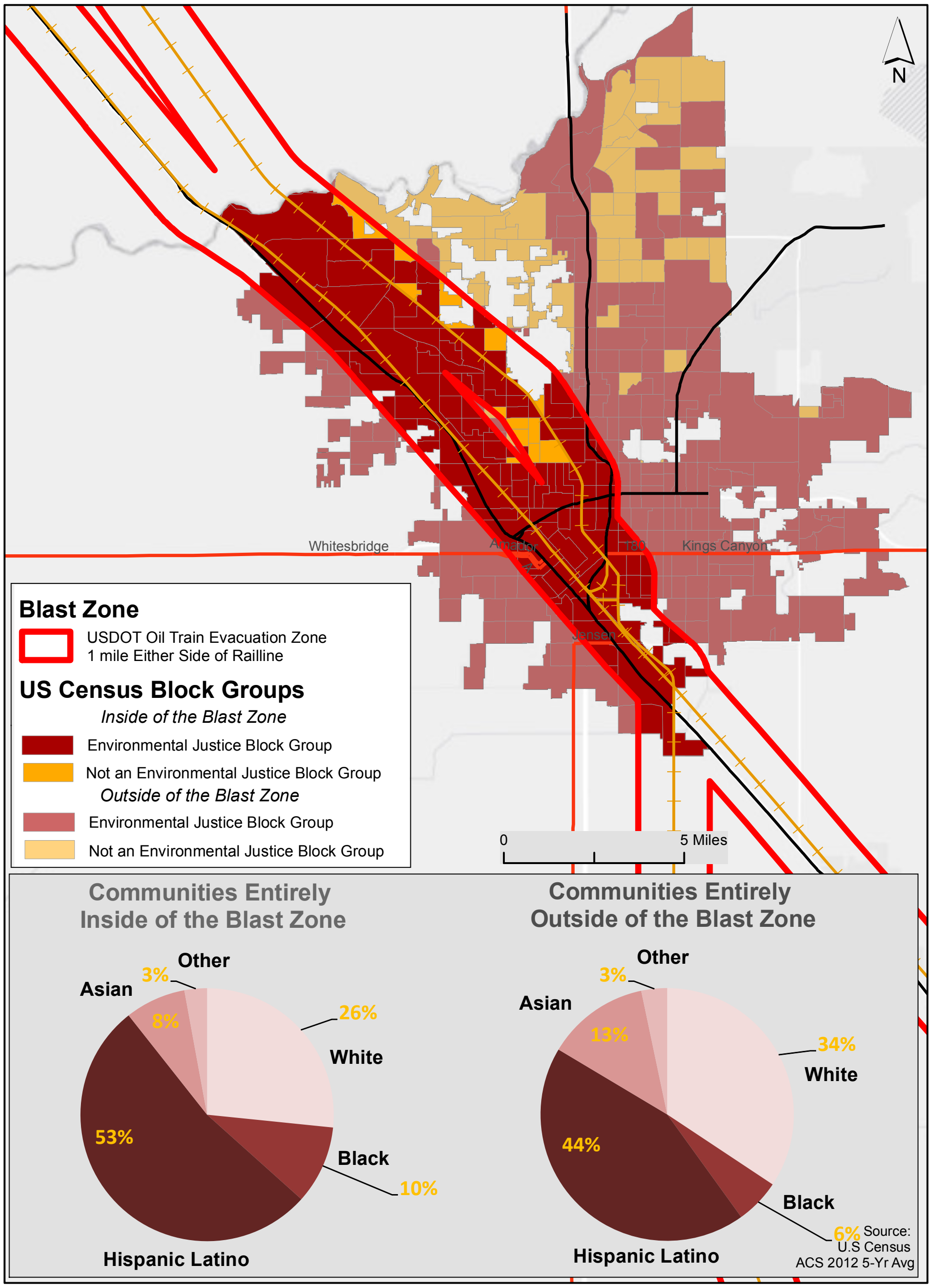
Source:
U.S Census
ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the San Jose, CA Blast Zone



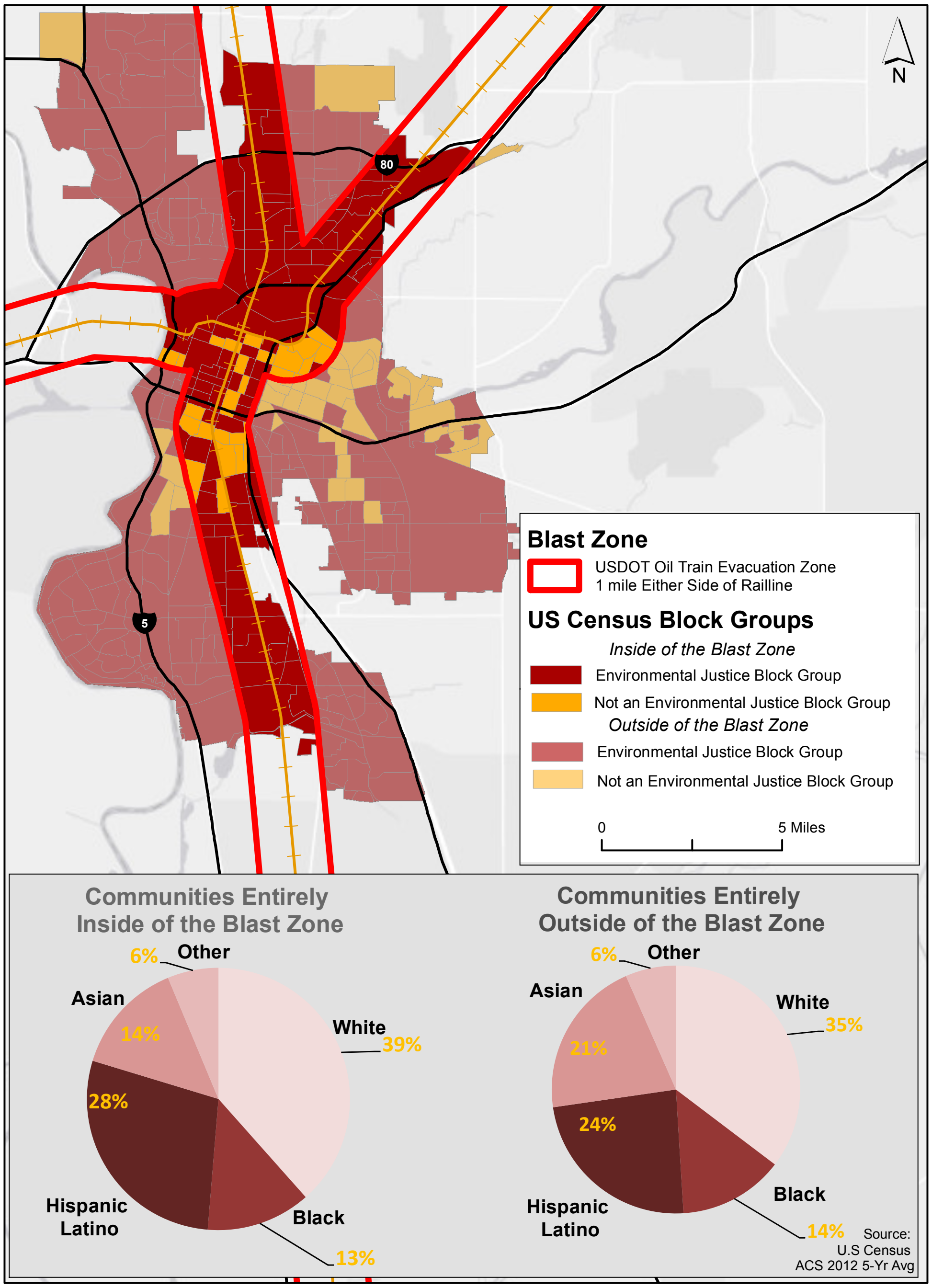
Source:
U.S Census
ACS 2012 5-Yr Avg

# Environmental Justice and Race Inside of the Fresno, CA Blast Zone



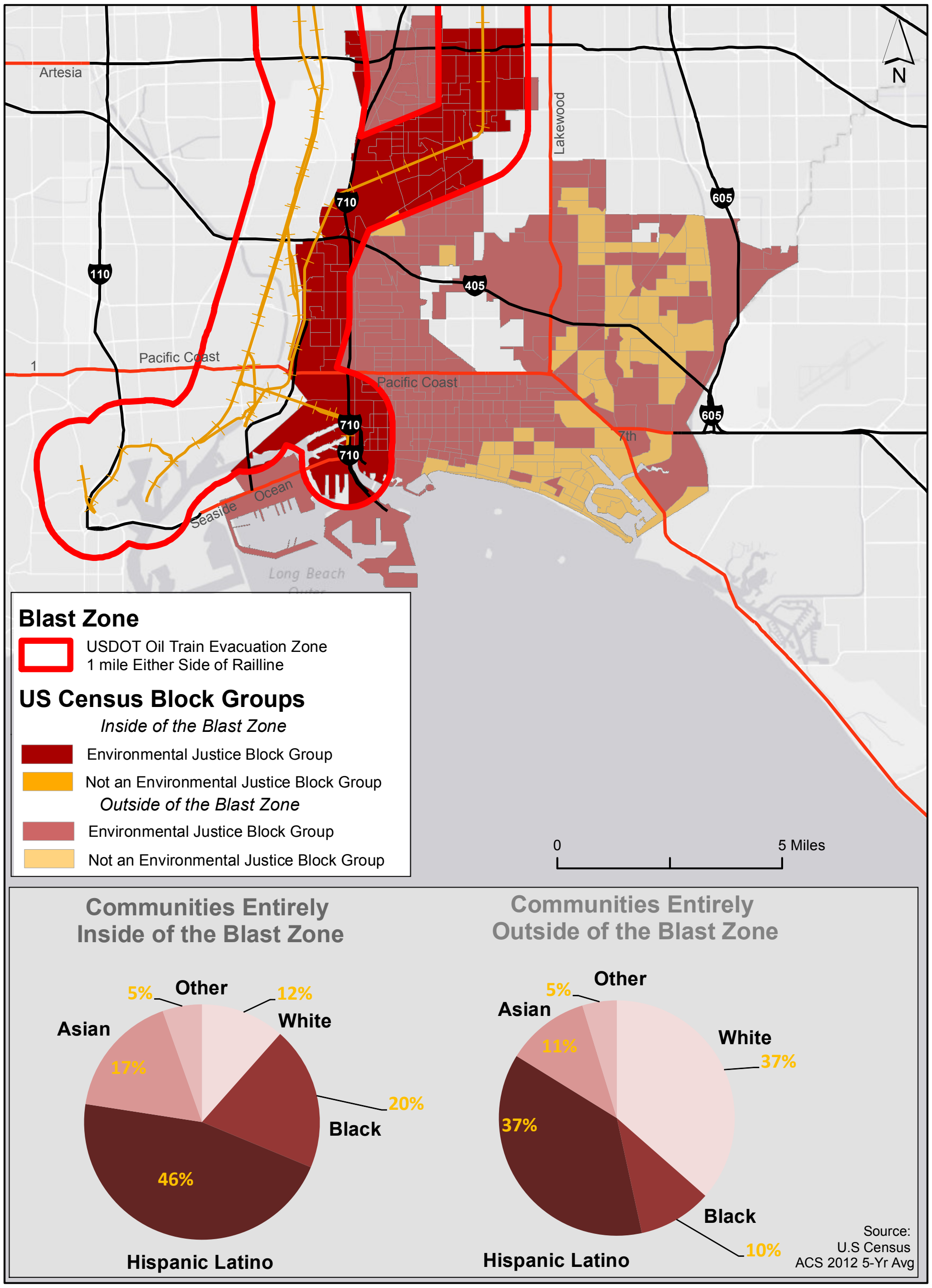
Source: U.S Census ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the Sacramento, CA Blast Zone



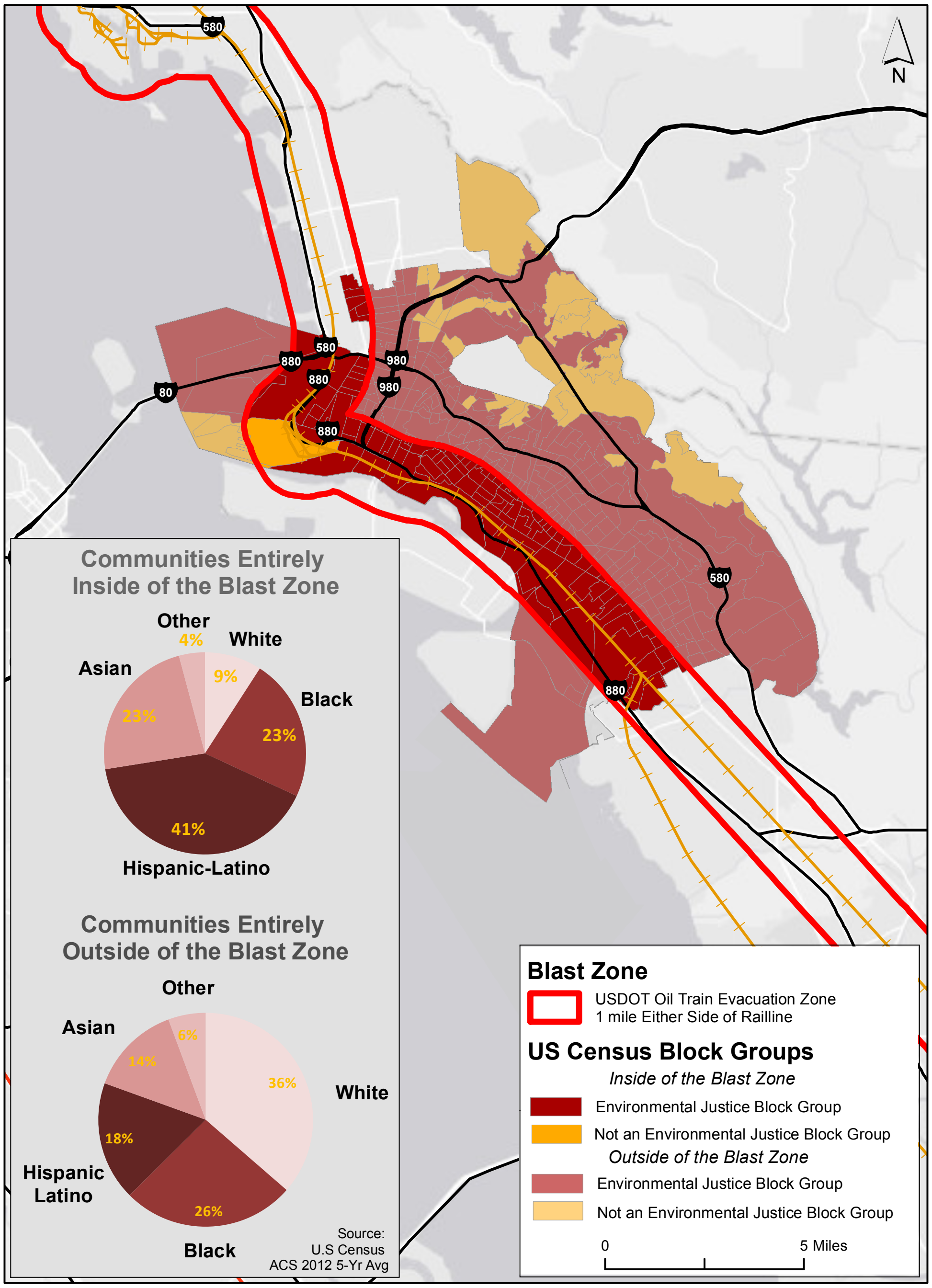
Source: U.S Census ACS 2012 5-Yr Avg

## Environmental Justice and Race
## Inside of the Long Beach, CA Blast Zone



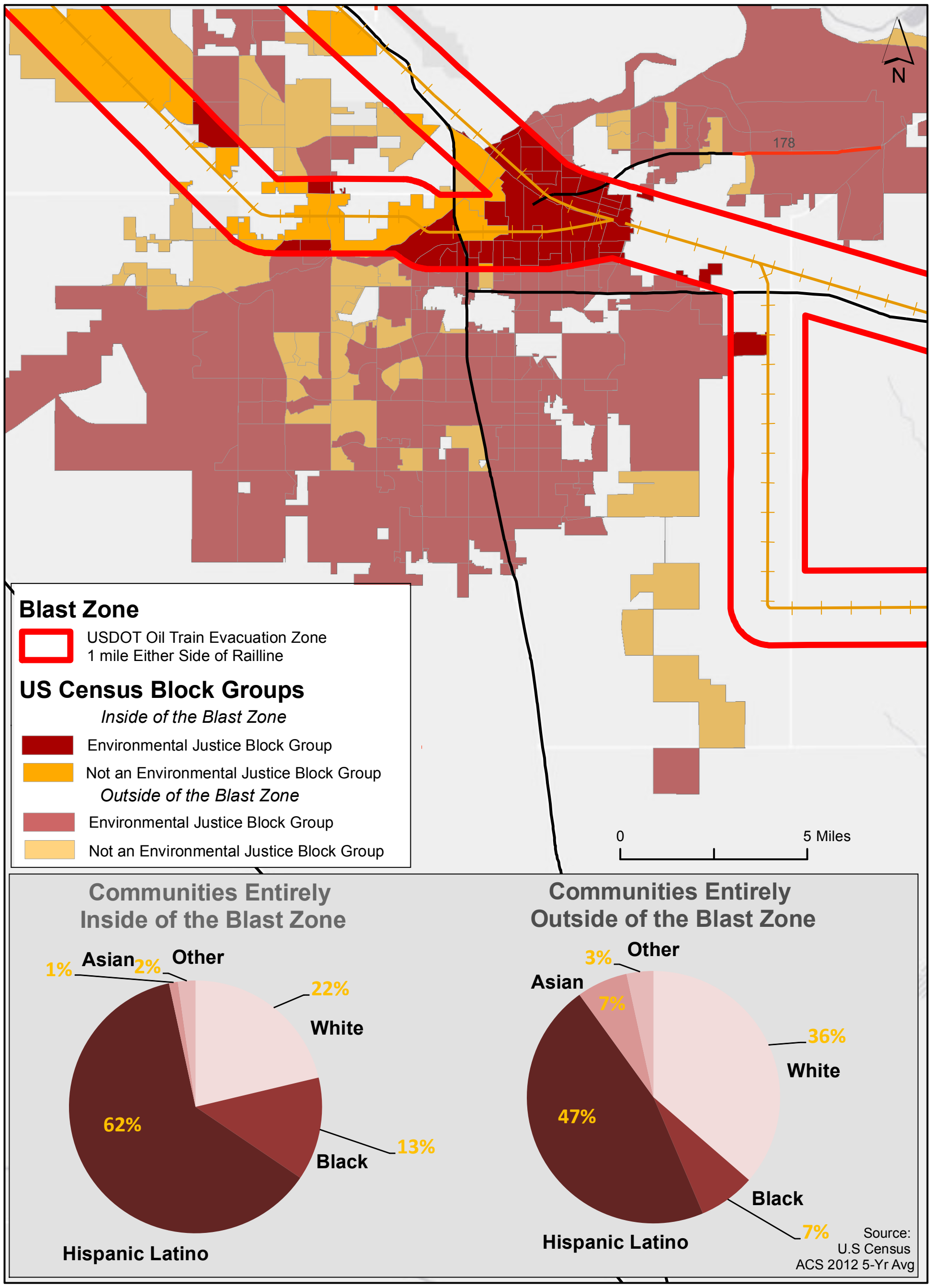
Source: U.S Census ACS 2012 5-Yr Avg

# Environmental Justice and Race inside of the Oakland, CA Blast Zone



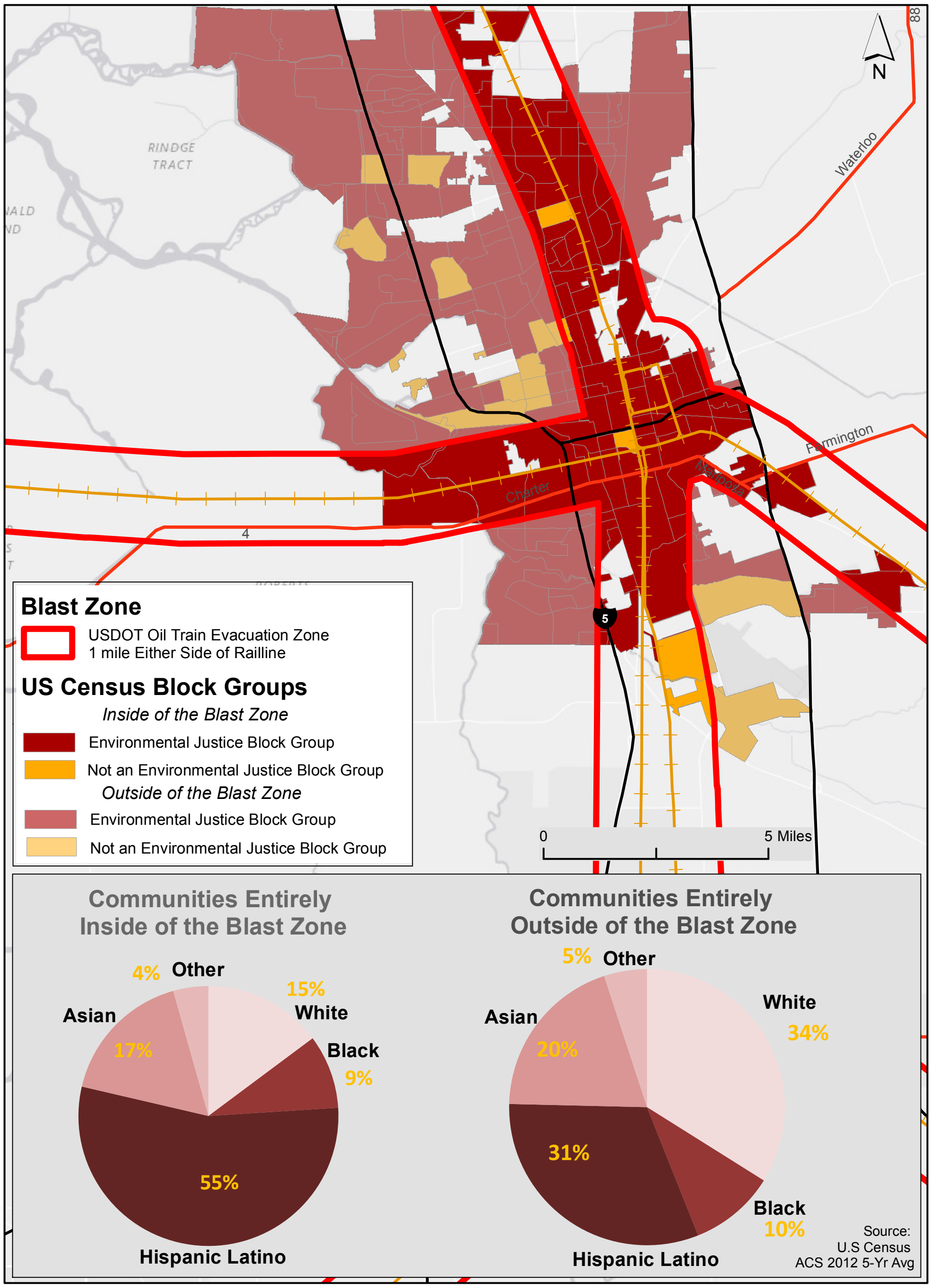
Source: U.S Census ACS 2012 5-Yr Avg

# Environmental Justice and Race Inside of the Bakersfield, CA Blast Zone



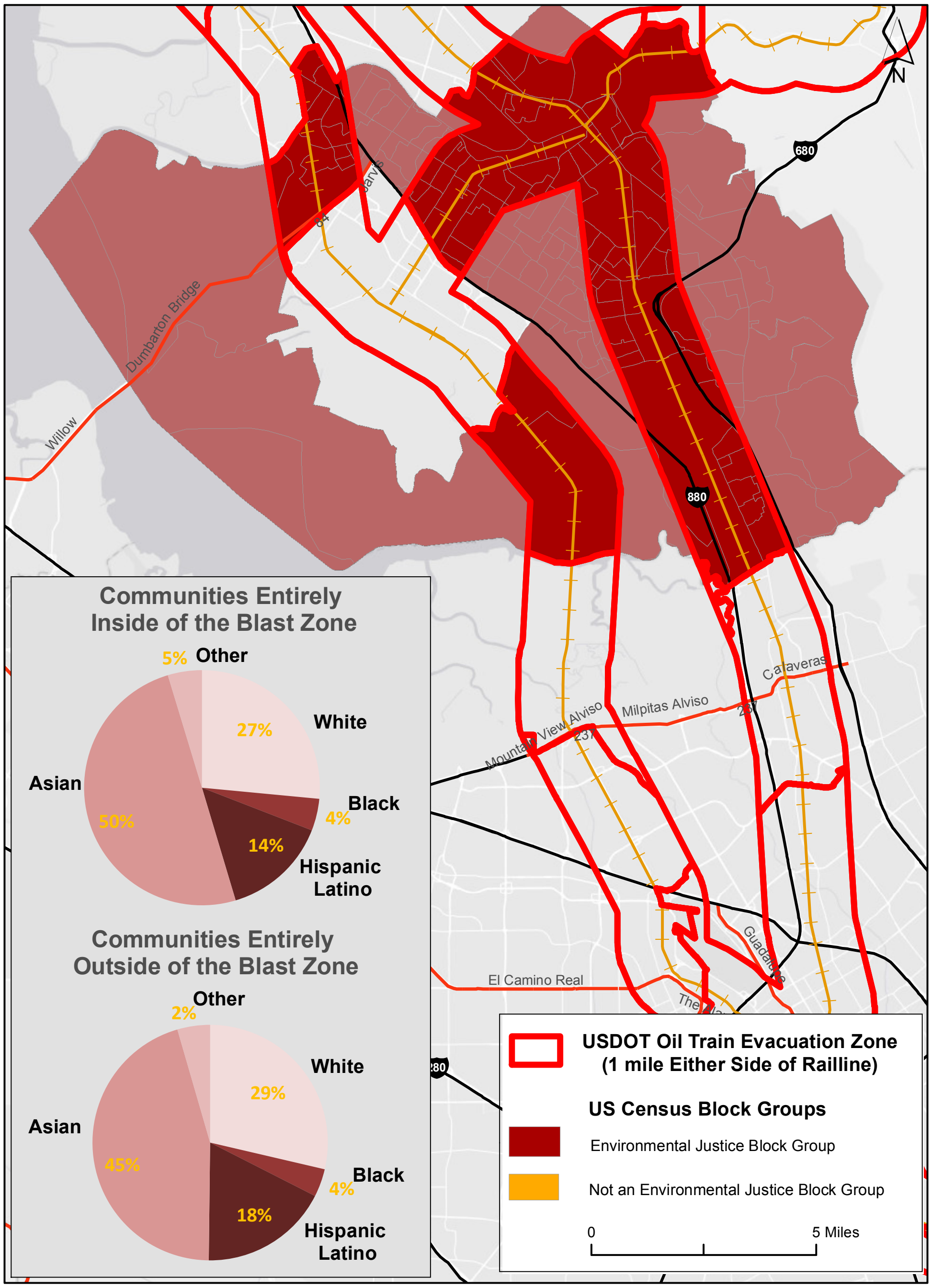
Source: U.S Census ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the Stockton, CA Blast Zone

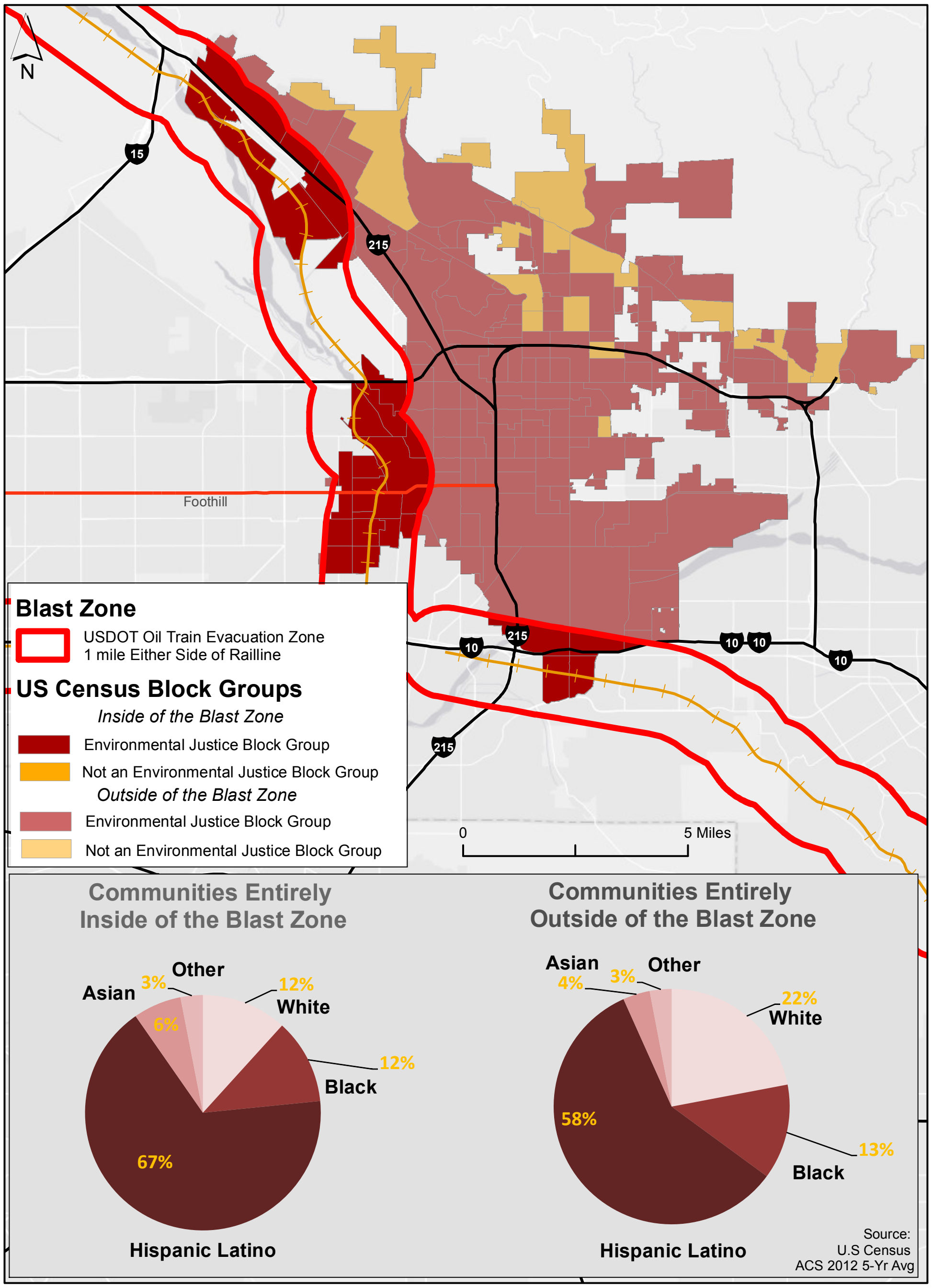


Source:
U.S Census
ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the Fremont, CA Blast Zone

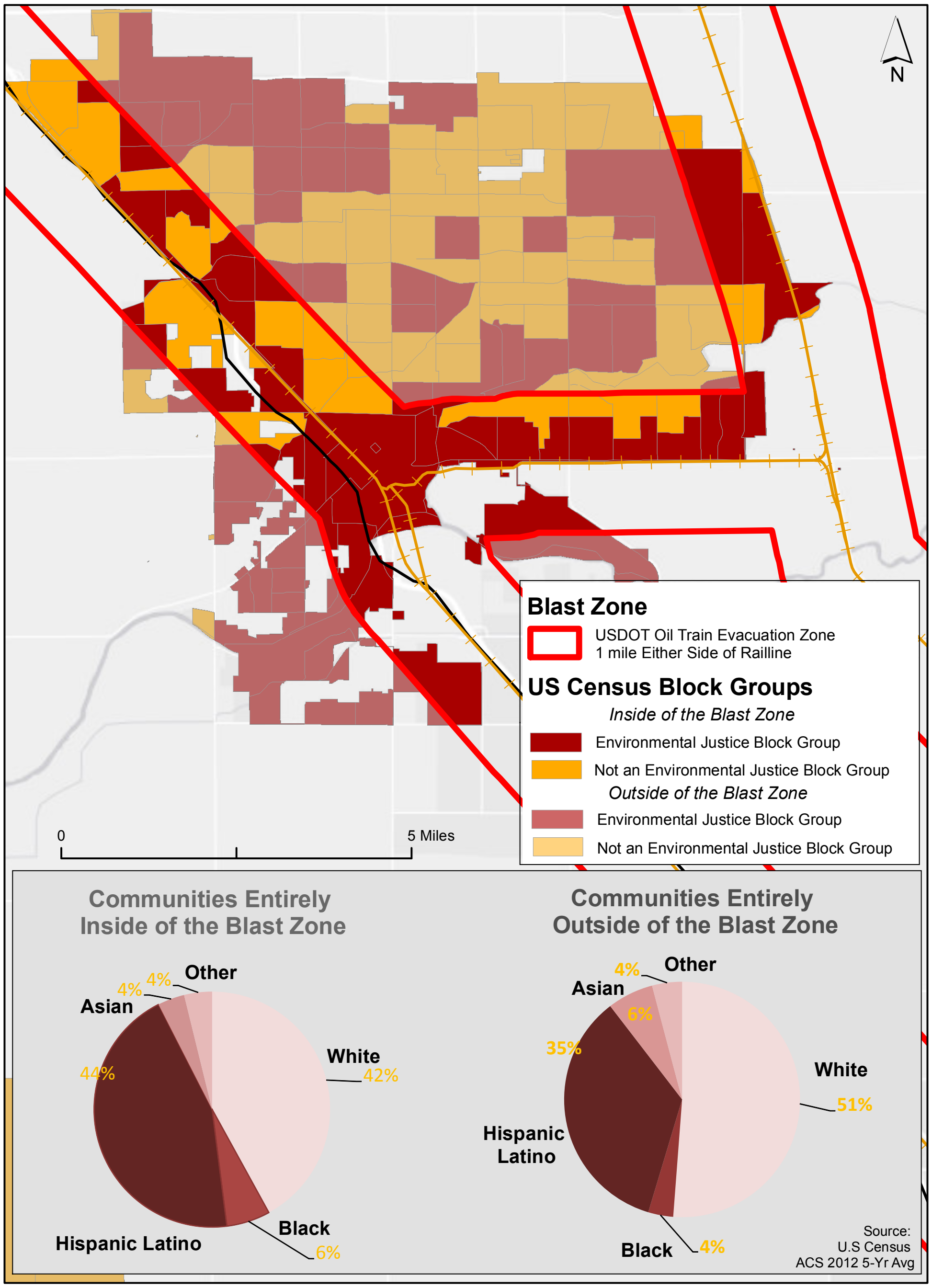


# Environmental Justice and Race
# Inside of the San Bernardino, CA Blast Zone



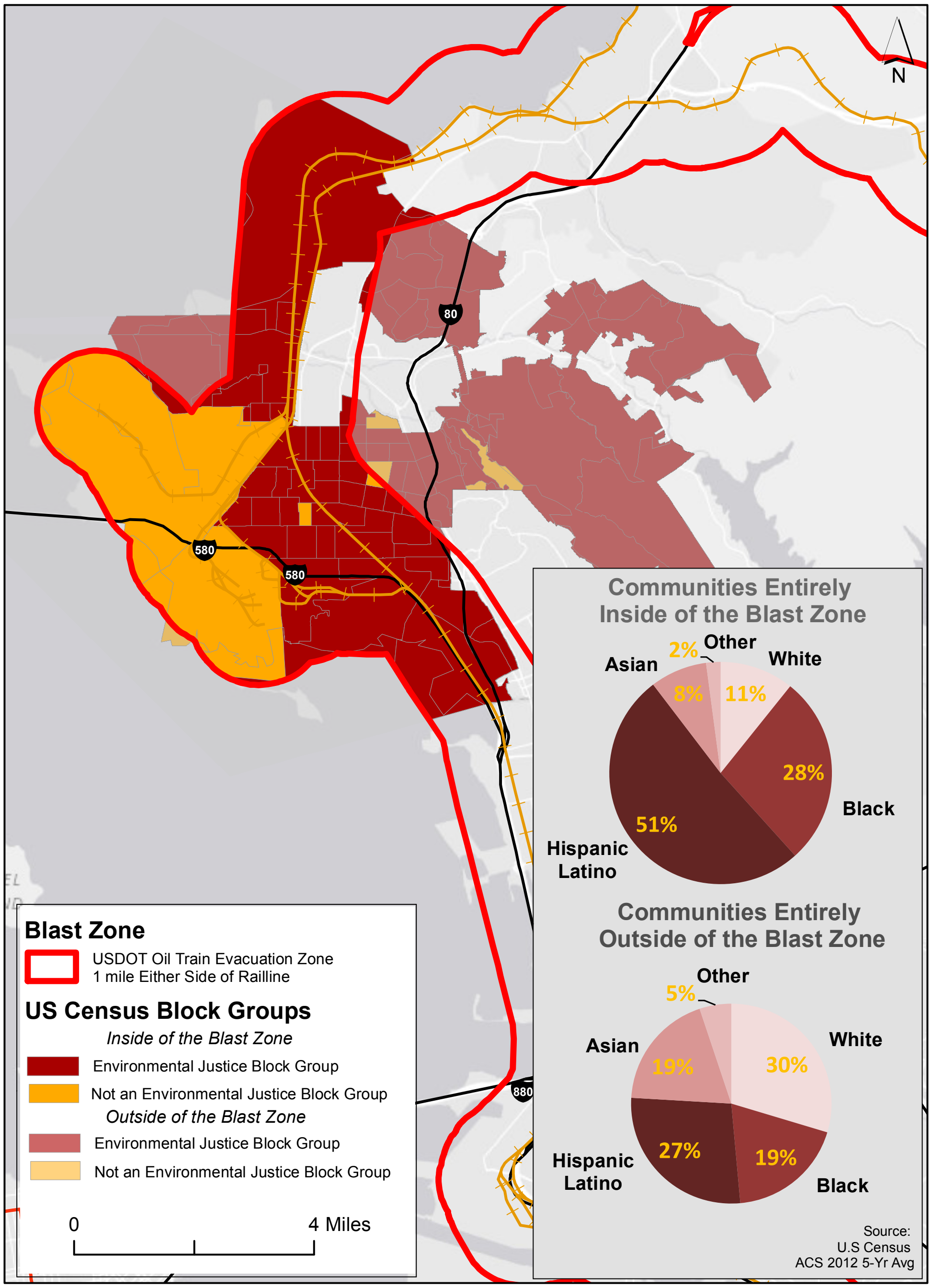
Source:
U.S Census
ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the Modesto, CA Blast Zone



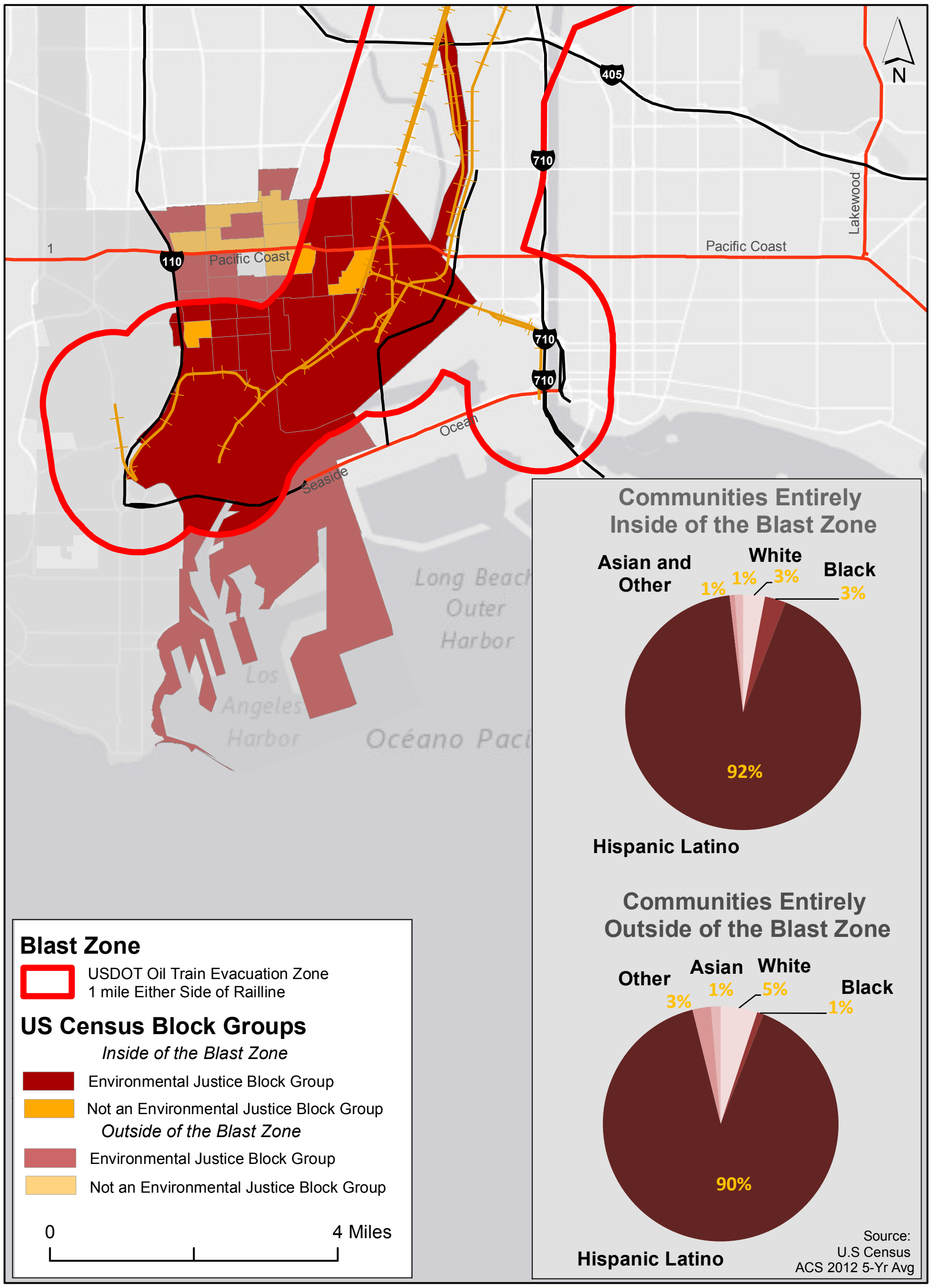
Source:
U.S Census
ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the Richmond, CA Blast Zone

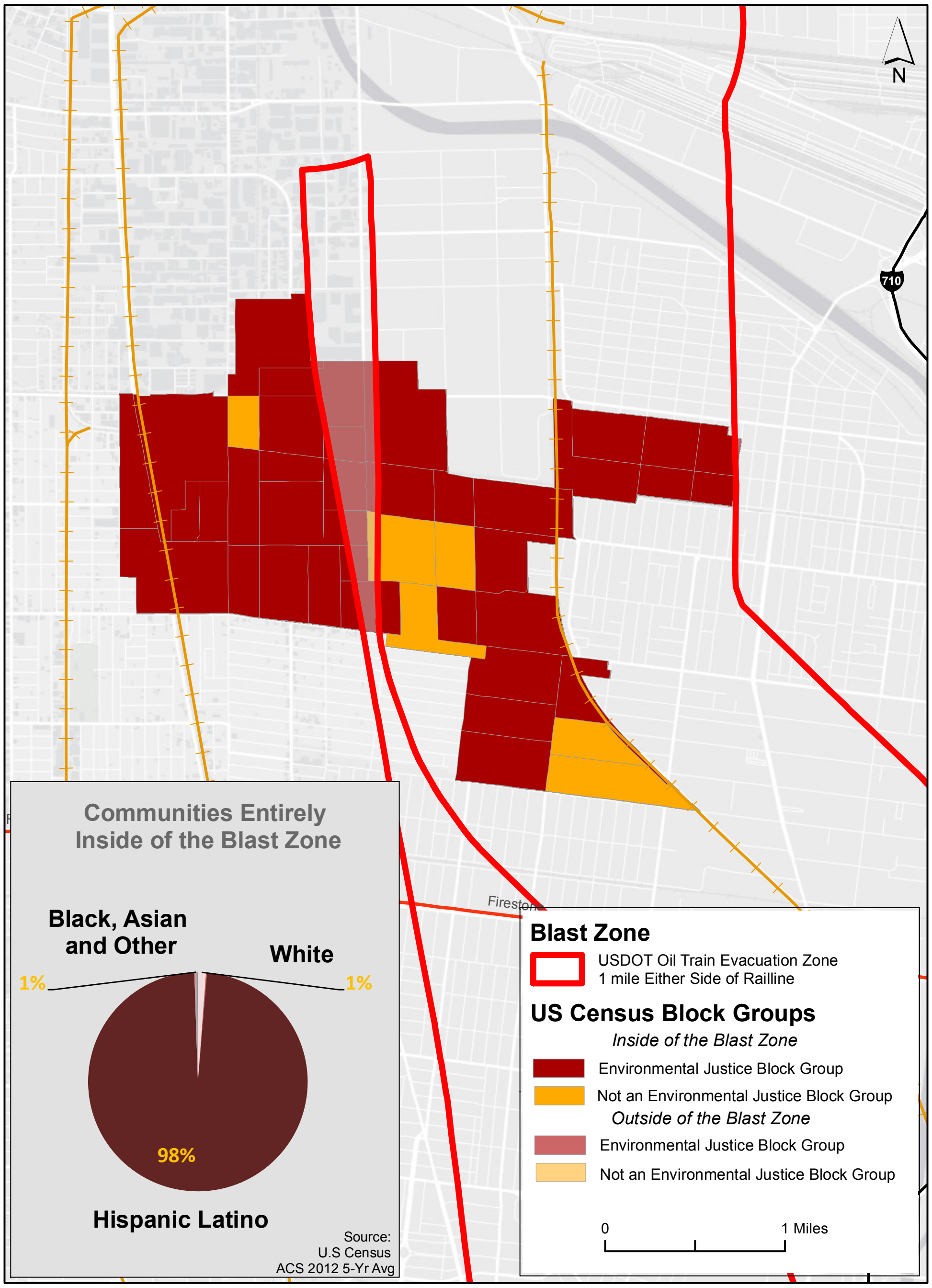


Source:
U.S Census
ACS 2012 5-Yr Avg

# Environmental Justice and Race
# Inside of the Los Angeles-Wilmington, CA Blast Zone



# Environmental Justice and Race
# Inside of the Los Angeles -- Huntington Park, CA Blast Zone



Source: U.S Census ACS 2012 5-Yr Avg

# BACKGROUND: EXTREME OIL ON THE RAILS

The oil and rail industries are moving to turn California's railways into deadly crude oil superhighways.

Government officials cited by Reuters[4] on April 7, 2015, reported oil industry plans to increase oil moving by train from about one percent of California imports in 2014 to 25 percent. Based on proposed California oil train infrastructure expansion projects cited in the table on page 26, the oil industry could bring up to 660,000–900,000 barrels per day (which would be 40–50 percent of refinery inputs statewide) of crude oil by rail. That would mean nine or more oil trains, each carrying 70,000 barrels—about three million gallons in each train—of explosive crude oil on California rails every day.

The increase in oil train traffic nationally over the past seven years has been rapid and poorly regulated. In 2008 the oil industry moved 9,500 carloads of crude oil. In 2014 approximately 500,000 carloads of crude moved on US tracks. In 2013, more crude oil spilled from trains than in the previous 30 years combined. According to the California Energy Commission oil imports by rail into California grew from 45,491 barrels in 2009[5] to 6.3 million barrels in 2013.[6]

In the first five months of 2015 five major oil train disasters resulted in spills and fires that burned for days, forcing evacuations, polluting waterways, and putting rail workers and emergency responders at risk. These incidents, in West Virginia, Illinois, North Dakota, and two in Ontario, were all in rural, relatively unpopulated areas. However, each of these trains passed through heavily populated areas before derailing and exploding. Each would have passed through many more cities and towns, and over critical water supplies, before reaching its final destination.

Our railways are not designed to carry hazardous materials. Railways connect population centers and our cities grew around rail lines. Moving oil by train means that hazardous oil train routes now cross through eight of the state's ten largest cities and through the downtowns of many smaller cities and towns. Increased oil train traffic is a threat to all Californians but brings greatest risk to environmental justice communities that already live with elevated health and safety risk from industrial spills, fires and explosions, as well as, chronic, daily air and water pollution.

## Fueling the Fires of Injustice

Low-income communities of color that are threatened by oil trains already are forced to carry heavy environmental burdens. For example, the California Office of Environmental Health Hazard Assessment estimates[7] the relative environmental health of communities based on indicators of cumulative health hazard: pollutant exposures, environmental effects, population vulnerability, and socio-economic vulnerability. A comparison of these state estimates with the state's Rail Risk & Response map[8] reveals that:

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[4] http://af.reuters.com/article/commoditiesNews/idAFL2N0X425Y20150407

[5] http://www.energyalmanac.ca.gov/petroleum/statistics/2009_crude_by_rail.html

[6] http://www.energyalmanac.ca.gov/petroleum/statistics/2013_crude_by_rail.html

[7] http://oehha.ca.gov/ej/ces2.html

[8] http://california.maps.arcgis.com/home/gallery.html

- Communities near oil train routes in Wilmington, Huntington Park, Oakland, Richmond and North Richmond already face disparate impacts, often facing a total environmental health hazard that is in the highest (worst) 20 percent among all communities statewide.
- Communities near oil train routes and oil refineries in Carson, Paramount, Torrance, Wilmington, Bakersfield, Martinez, Richmond and North Richmond face an environmental health hazard in the highest (worst) 20 percent statewide.
- Urban core communities near oil train routes in the Sacramento, Oakland, San José, Stockton, Modesto, Fresno, Bakersfield, Los Angeles, and San Bernardino–Riverside areas also score in the highest (worst) 20 percent for environmental health hazard statewide.

Disparities in environmental health exist now. Further increasing oil train traffic would make this environmental injustice even more severe. In Huntington Park, Wilmington, Fremont, and Richmond, ***most of the population*** faces the potential for direct impacts of an oil train derailment, explosion and fire, as most people living in each area live in the blast zone.

## State and Federal Officials Ignore Race and Environmental Justice

Authorities are required by state and federal law to consider the disparate impacts on environmental justice communities in their review of projects that would expand oil train traffic in California. Oil trains disproportionately threaten the health and safety of environmental justice communities. Yet, federal, state and local authorities have systematically failed to consider environmental justice, disproportionate impacts, and cumulative health impacts that result from discrimination in safety regulations or reviews of oil train projects.

On May 4, 2015, the US Department of Transportation released new regulations for trains hauling liquid hazardous materials, including crude oil. These rules include new tank standards, but long phase-out of hazardous cars, inadequate speed limits, deficient tanker shells, and secrecy leave communities at risk of catastrophe.[9] These rules allow unnecessary harm and will not protect public health and the environment. They also fail to consider the disproportionate impacts on environmental justice communities residing in the blast zone.

The Obama Administration failed to address two critical areas of federal law requiring that impacts on environmental justice communities and communities of color be addressed in federal rulemaking and funding decisions. The 1994 Executive Order, which remains in effect, requires that federal agencies and state agencies that take federal funds consider environmental justice in decisions about health and public safety. Likewise, Title VI of the 1964 Civil Rights Act prevents federal funds from being used to encourage racial discrimination. Yet the Department of Transportation and other federal rail safety agencies have developed new oil train rules that fail to consider disparate risk from oil trains to environmental justice communities.

California law also prohibits such discrimination, and further, requires that agencies and other regulatory bodies consider environmental justice and the cumulative impacts on health and safety when considering a project to “avoid over-concentrating these uses in proximity to schools or residential dwellings.”

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[9] http://earthjustice.org/news/press/2015/obama-administration-leaves-explosive-oil-trains-on-the-rails-for-years

## Explosion and Pollution: The Acute and Chronic Threat from Oil Trains

The fatal derailment, Bakken crude spill and fire in Lac-Mégantic, Quebec, on July 6, 2013 was a wakeup call to the severe threat from oil trains carrying toxic, explosive crude oil. At least 47 people lost their lives and an entire downtown was incinerated in a fire that lasted for days. Both North Dakota Bakken and Canadian tar sands crude oil have been involved in many rail explosions and spills, despite earlier claims that tar sands crude was expected to be safer than Bakken during transport.

Much of the crude oil carried by train in California is tar sands from Canada, with that proportion anticipated to increase in the future. Tar sands are an asphalt-like substance mined from rock that requires the addition of light petroleum diluent so that it can be loaded into tank cars. Once mixed with diluent the resulting mixture, called diluted bitumen or "dilbit," is not only toxic but also highly corrosive, flammable and explosive,[10] and bitumen oil spills sink in waterbodies, causing chronic pollution.

### *Chronic Pollution, Cumulative Health Impacts, and Disruption*

Even without derailment, spill, and fire, oil trains create hazardous air pollution from diesel exhaust and emit volatile pollutants. This air pollution is dangerous to anyone, but especially hazardous in communities that already suffer a significantly higher burden of airborne toxics and accompanying respiratory disease.

The antiquated tank cars currently used to move crude oil leak. They were not designed to carry volatile chemicals or contain chemicals at high pressure. The unpressurized DOT 111 and CPC 1232 tank cars currently permitted to carry crude under federal rules vent carcinogens and other toxic gases into the atmosphere.

In a process called shrinkage, one oil company calculated a loss of one percent of volume from oil tank cars on a journey from North Dakota to the Gulf Coast from off gassing through pressure relief valves and anticipated leakage. At this rate a 100 car, three-million-gallon train, may lose as much as 30,000 gallons of volatile, cancer-causing chemicals as it rolls down the tracks past homes and schools on the way to coastal refineries. New federal requirements announced in April 2015 will do nothing to improve containment of volatile air pollutants.

In an October 2014 environmental review for a Phillips 66 refinery oil train unloading project, San Luis Obispo County admits[11] that the proposed project will create "significant and unavoidable" levels of air pollution, including toxic sulfur dioxide and cancer-causing chemicals. This project's air pollution would impact communities near that refinery and along the rails in many California counties. The review cites increased health risks -- particularly for children and the elderly -- of cancer, heart disease, respiratory disease, and premature death.

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[10] *See* Andrews, 2014. Congressional Research Service; www.hsdl.org/?view&did=751042.

[11] http://www.slocounty.ca.gov/Assets/PL/Santa+Maria+Refinery+Rail+Project/Phillips+66+Company+Rail+Spur+Extension+Project+%28Oct+2014%29/Individual+EIR+Section/0_3_Executive+Summary.pdf

In 2012, The Whatcom Docs, a group of more than 180 physicians from Whatcom County, WA, outlined[12] their conclusions on the potential health impacts from increased coal train traffic based on research published in major medical journals. Their findings on the chronic health threat from coal trains are also directly relevant to anyone living along oil train routes, and in particular environmental justice communities where air emissions from industrial facilities, road traffic, and other sources are higher than average.

Research[13] compiled by the Whatcom Docs establishes:

**Diesel particulate matter from passing and idling trains, and increased road traffic due to delays at road crossings, is associated with**:

- Impaired pulmonary development in adolescents;
- Increased cardiopulmonary mortality and all-cause mortality;
- Measurable pulmonary inflammation;
- Increased severity and frequency of asthma attacks, ER visits, and hospital admissions in children;
- Increased rates of myocardial infarction (heart attack) in adults;
- Increased risk of cancer.

**Noise pollution exposure from train traffic causes:**

- Cardiovascular disease, including increased blood pressure, arrhythmia,
- Stroke, and ischemic heart disease;
- Cognitive impairment in children;
- Sleep disturbance and resultant fatigue, hypertension, arrhythmia, and increased rate of accidents and injuries;
- Exacerbation of mental health disorders such as depression, stress and anxiety, and psychosis.

**Frequent long trains at rail crossings will mean:**

- Delayed emergency medical service response times;
- Increased accidents, traumatic injury and death.

Other medical authorities[14] are sounding the alarm about the health hazards posed by oil trains as well.

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[12] http://www.coaltrainfacts.org/whatcom-docs-position-statement-and-appendices

[13] http://www.coaltrainfacts.org/whatcom-docs-position-statement-and-appendices - appendixA

[14] http://www.truth-out.org/news/item/31258-oil-trains-don-t-have-to-derail-or-explode-to-be-hazardous-doctors-warn

## *Oil Trains Undermine California Climate Policy*

Oil trains threaten California's climate protection goals. The oil industry wants to move more tar sands crude from Alberta, Canada, to California—the largest oil refining center in Western North America. This would require switching California refineries over to fundamentally different crude that causes the most extreme extraction and refining impacts of any petroleum known, undermining California's climate initiative.

The tar sands crude that trains could bring in increasing volumes emits more greenhouse gas per barrel. A study[15] published in 2015 by the Carnegie Endowment for International Peace showed that a switch from conventional light crude to tar sands could increase total well-to-wheel carbon pollution by as much as 80 percent. A 2010 study[16] published in *Environmental Science and Technology* by Greg Karras, Communities for a Better Environment (a co-author of this report), estimated that a switch from the average US refinery crude slate to tar sands could double or triple the average emission intensity of oil refining. If the oil industry is allowed to increase the importation of tar sands into the state, and that results in a full-blown switch to processing tar sands bitumen in California, refinery emissions alone could approach or exceed California's year-2050 target for GHG emissions from all sources statewide.

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[15] http://carnegieendowment.org/2015/03/11/know-your-oil-creating-global-oil-climate-index

[16] http://pubs.acs.org/doi/abs/10.1021/es1019965

# ACTIVE OIL TRAIN PROPOSALS IN CALIFORNIA

**Planned and recently permitted oil train projects in California as of June 2015.**

| Oil Train Project | Status as of June 2015 |
|---|---|
| Bakersfield: Alon<br>Location: 6451 Rosedale Hwy, Bakersfield<br>Proposed capacity: 140,000 barrels/day | Construction delayed, ongoing challenge of secrecy in environmental permit review, uncertainty over crude price forecasts |
| Bakersfield: Plains All-American<br>Location: South Lake Road, Taft<br>Capacity: 140,000 barrels/day | Operating despite ongoing challenge of secrecy in environmental permit review |
| Benicia: Valero<br>Location: 3400 East 2nd Street, Benicia<br>Proposed capacity: 70,000 barrels/day | Delayed since 2013 by public pressure, revised draft Environmental Impact Report (EIR) scheduled for release August 31, 2015 |
| Pittsburg: WesPac<br>Location: 690 West 10th Street, Pittsburg<br>Proposed capacity: 242,000 b/d rail+marine | Delayed since 2013 by public pressure and shifting proposals regarding the project's rail component, revised EIR expected in 2015 |
| Richmond: Kinder Morgan<br>Location: 303 S. Garrard Blvd., Richmond<br>Capacity: 70,000 barrels/day | Operating despite ongoing challenge of permit that was issued in secret, actual oil throughput appears to vary with crude price |
| San Luis Obispo County: Phillips 66<br>Location: 2555 Willow Road, Arroyo Grande<br>Proposed capacity: 52,000 barrels/day | Opposed by community, environment groups and 16 city and county governments, revised final EIR expected in summer or fall 2015 |
| Stockton: TARGA<br>Location: Port of Stockton<br>Proposed capacity: 70,000 b/d rail+marine | Proposed, seeking permits |
| Whitewater, CA: Questar<br>Location: Unknown<br>Proposed capacity: 120,000 b/d | No permit application found yet; trains would feed a pipeline from near Palm Springs to Long Beach and Los Angeles Area refineries |

Data from CBE and ForestEthics reviews of project documents. Additional new or secretly permitted (see Kinder Morgan above) proposals may be anticipated.

## *Oil Trains are Not Needed in California*

The planned statewide oil infrastructure listed in the table above could enable 660,000–900,000 barrels of oil to roll through California on trains every day—enough to supply 40–50 percent of total statewide refinery crude inputs. Today, however, despite their exponential growth since 2009, oil train imports to California still supply less than two percent of the crude refined statewide.[17] Meanwhile, Californians are steadily using less oil—statewide gasoline sales declined by 15 percent from 2006–2014[18]—and this trend is expected to continue as State climate policies move toward sustainable transportation.  Oil trains are not necessary to supply the feedstock for the fuels used in California.

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[17] http://www.energyalmanac.ca.gov/petroleum/statistics/2014_crude_by_rail.html

[18] http://tonto.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=C100050061&f=A

# DATA AND METHODS

### *Route selection and data*

The Blast Zone map uses data from Oak Ridge National Laboratory's publicly available rail map data set[19], their railroad network. There are many more possible rail lines than shown on the map. A three-step process was used to identify the most likely routes oil trains will travel:

1. Base routes were identified in the article ***All Oiled Up***[20] in the March 2014 issue of Trains Magazine. The article, by rail freight expert Fred Frailey, shows the most likely rail routes used for oil trains.
2. We compared estimates in the Frailey article with Oil Change International's map of known oil train offloading terminals.[21] We then connected major routes to known terminals. Where multiple connecting routes are possible we preferentially chose the Category 1 rail line owned by the railroad operating the main trunk line. Where multiple routes were possible with no Category 1 line, we chose the most direct route.
3. After publication of the Blast Zone website we have used first person accounts and feedback from site users to add rail routes. Any individual providing a first person account was asked to verify that they had seen the appropriate 1267 HAZMAT placard, and verify that they were observing crude oil unit trains. Often, individuals responded with unsolicited photographs of trains and their placards. Of the more than 100 additions and revisions we have received, only about five percent indicated areas that incorrectly showed oil train routes.

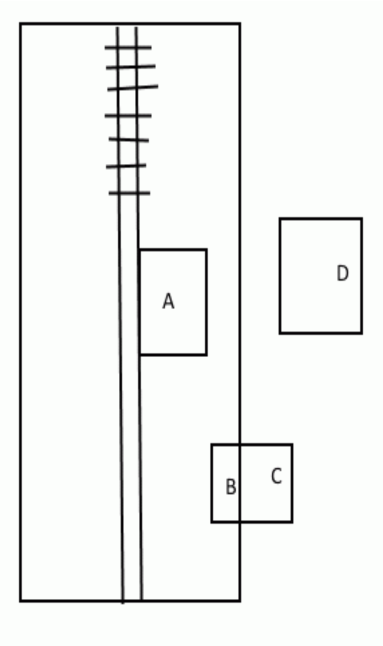
A fourth step, comparing our results against State of California oil train route mapping, (*see* 'Fueling the Fires of Injustice' above) also served as an informal spot-check on this method.

### *Calculating populations*

In July 2014 ForestEthics calculated that 25 million Americans live in the blast zone. We believe this is a conservative estimate. Whether for California or for individual communities where we have created environmental justice or racial makeup screens, we used the same methodology to calculate a range of estimates and create a 'best-estimate,' as follows.

Populations were calculated using US Census data at the block group level. Using the one-mile evacuation or blast zone buffer, we calculated our best guess number as A + B below.

A = Block groups wholly within Blast Zone
B = Areal interpolated population estimate for fractions of blocks within the Blast Zone
C = Areal interpolated population estimate for fractions of blocks outside the Blast Zone
D = Block groups wholly outside of the Blast Zone



With higher concentrations of populations near tracks in major urban areas, as well as smaller rail towns, it is a fundamentally conservative assumption to use an areal interpolated estimate of population based on even distribution across the block group. Our use of areal interpolation in this case meant an assumption of even distribution such that if 30 percent of the area of the block group lies within the blast zone, we assumed that 30 percent of the population of that block group resides in the blast zone. To validate our methodology, we compared numbers to other data sources using the "places" GIS layer available through the US Census, and American Fact Finder (2011-2012). A spot check of 24 California cities showed that our estimates are consistently from 1 to 5 percent lower than population estimates in the American Fact Finder.

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[19] http://www-cta.ornl.gov/transnet/RailRoads.html

[20] http://trn.trains.com/issues/2014/march-2014

[21] http://priceofoil.org/rail-map/

The most conservative and precise number would be to only use counts of A. Allowable methodologies for geographic analysis of these types of ranges include only A, our choice of A + B, and the high end methodology of all of A+B+C. We believe that the less precise, but potentially more accurate, choice of A+B is superior to using the much higher A+B+C number, or the lower number shown by A alone.

### *Identifying Environmental Justice Communities*

We identified Environmental Justice (EJ) Block Groups (communities) using the 2008-2012 American Community Survey 5-yr average demographic and economic data (2012-ACS 5-Yr Avg). A method used by the State of Massachusetts was chosen as the screening tool for this analysis. This method uses three criteria to identify EJ communities: the impacts of race, income, and linguistic isolation. Any Block Group that meets at least one of the three EJ criteria is flagged as an EJ community:

- To evaluate race, we calculated percent minority population and flagged an EJ community for US Census Block Groups where percent minority is greater than 25% of the population.
- To evaluate income, we compared Median Household Income for each Block Group to the statewide Median Household Income. Where the Block Group Median Household Income is less than 65% of the State's Median Household Income, the Block Group is flagged as an EJ community.
- To evaluate linguistic isolation we identified the total number of households without English speakers older than 14-years old by Block Group. Where the number of households without English speakers older than 14-years old is greater than 25% of the Block Group, that Block Group is flagged as an EJ community.

Our mapping of EJ communities uses the 'A+B' counts method described above.

### *Identifying Racial Make up of Communities*

To identify the racial make up of communities, the 2012-ACS 5-Yr Avg. B03002 Table for Hispanic or Latino Origin by Race was used. Within the U.S Census and the ACS, Hispanic and Latino origin information is not taken as a separate racial category, so a person can have Hispanic or Latino origin and be of multiple races, according to the Census. For our purpose of estimating population composition by race, anyone of Hispanic or Latino Origin from the ACS data was included in the Hispanic Latino community. The other racial communities were taken from the ACS data for the Non-Hispanic and Latino Origin population.

From the B03002 table, we estimated population counts for the categories Hispanic-Latino Origin, and from the Non-Hispanic Latino Origin population data we estimated White Alone, Blacks Alone, Asian Alone, American Indian Alone, Native Hawaiian-Pacific Islander Alone, Other races Alone, and Two or More Races. In our pie charts, American Indian, Native Hawaiian-Pacific Islander, Other races and Two or More Races are grouped together as 'other' (this was done for clarity of presentation only).

### *About the ½ mile (800m) and 1 mile (1,600m) "blast zone" buffers*

As represented on various maps and the blast-zone.org website, the 800 meter and 1,600 meter oil train incident and fire evacuation zones are simplified versions of what in practice is a highly complex set of potential responses by first responders and other safety personnel. In practice, these evacuation and impact zones may be much smaller (a single tipped car with no puncture in Seattle led to no evacuation) and much larger (the Casselton, ND explosion and ensuing toxic cloud led to a five mile evacuation zone to the south and east of the incident in the dead of winter.)

Various agencies including the Department of Transportation's Pipeline and Hazardous Materials Safety Administration have issued initial response guidelines codified in the Emergency Response Guidebook. For an incident involving a single oil tank car (whether truck or train), the primary set of responses is codified under response protocol 128 for petroleum crude oil, or UN hazmat code 1267. That guideline recommends initial evacuation range of 800 meters for a single burning car.

The 800 meter zone of evacuation and impact could be the result of multiple scenarios: high volumes of tar sands crude spilled and the toxic inhalation hazard it represents, or per the PHMSA guide a single burning tank car that doesn't impinge on other cars. Likewise, the 1,600 meter zone of evacuation and impact is recommended for multiple burning cars, leading to risk of a boiling liquid expanding vapor explosion (BLEVE).

However, additional response protocols may be called for with crude oils with high levels of hydrogen sulfide, a deadly toxic inhalation hazard (TIH), or extremely high vapor pressures and high percentages of explosive gases during commonly experienced temperatures of transport, such as tar sands-derived (Canadian Heavy) oils, condensates, and Bakken shale oils.

The 800 meter and 1,600 meter evacuation and impact zones also fail to take into account geography. Incidents involving pour points into waterways, such as the 1999 Olympic pipeline disaster in Bellingham, WA, can result in a plume of toxic smoke more than two miles long.

### *Coverage limitation*

We focused our limited resources on analysis of communities in California's major urban centers crossed by oil train routes. A strength of this choice is its focus on high-density populations where catastrophic and chronic hazards in the blast zone, if manifest, will harm the greatest number of people. A limitation is that detailed analysis for communities in low-density rural areas, smaller cities and towns is left to future work. Every community should have access to environmental justice information—and such future work might shed additional light on questions such as why, in California, Latinos appear to be disproportionately concentrated in the oil train blast zone.

### *Additional Data References:*

2012 TIGER Line Polygon Feature Classes of Block Groups by State and County; ftp://ftp2.census.gov/geo/tiger/TIGER2012/BG/

2012 TIGER Line Polygon Feature Classes of Places (Cities, Towns, Etc.) by State; ftp://ftp2.census.gov/geo/tiger/TIGER2012/PLACE/

2008-2012 5-Year Average Selected Demographic and Economic Data from the American Community Survey (ACS); ftp://ftp.census.gov/geo/tiger/TIGER_DP/2012ACS

CTA North American Railroad Network Lines; http://www-cta.ornl.gov/transnet/RailRoads.html

Open Street Map Rail Data; http://download.geofabrik.de/north-america.html

All Oiled Up: A Special Report by Fred Frailey; http://trn.trains.com/issues/2014/march-2014

MassGIS Data - 2010 U.S. Census - Environmental Justice Populations; http://www.mass.gov/anf/research-and-tech/it-serv-and-support/application-serv/office-of-geographic-information-massgis/datalayers/cen2010ej.html

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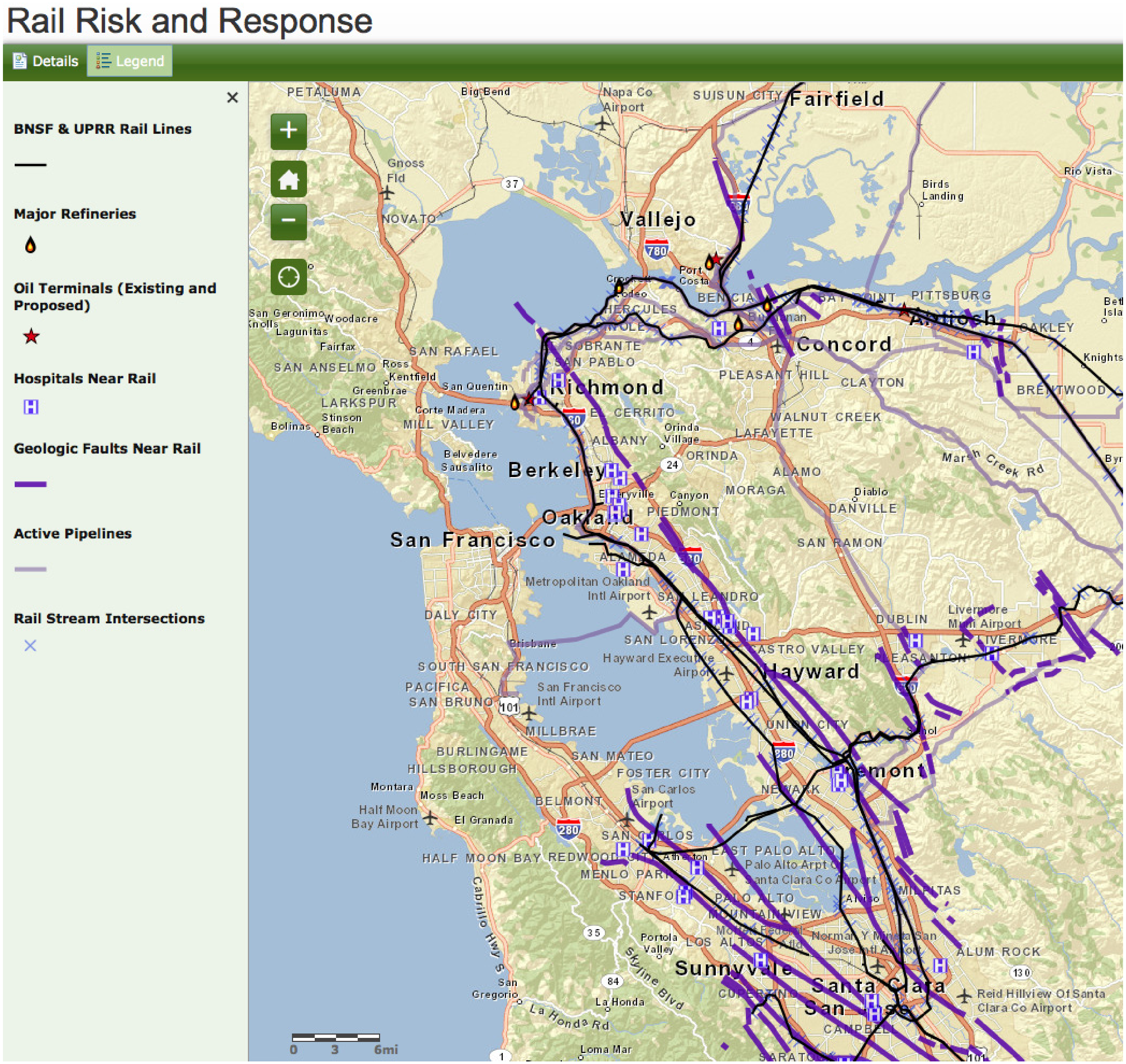
**Attachment 34**

**Attachment 34.** Image copied from State Interactive Rail Risk and Response map; http://california.maps.arcgis.com/apps/OnePane/basicviewer/index.html?appid=928033ed043148598f7e511a95072b89



Attachment 35

# SUBMISSION TO
# THE REGIONAL WATER QUALITY CONTROL BOARD
# SAN FRANCISCO BAY REGION

**Prepared on Behalf of Shell Oil Company**

December 1992

John H. Vautrain

*Purvin & Gertz, Inc.*
*Dallas - Houston - Los Angeles*

## Table of Contents

TABLES

FIGURES

# I: INTRODUCTION

The Regional Water Quality Control Board, San Francisco Bay Region will receive testimony in public hearing with respect to the Proposed Amendment to the Water Quality Control Plan: Mass Emission Strategy for Selenium. Shell Oil Company (Shell) will provide expert testimony on number of different selenium issues at this hearing.

One specific issue to be addressed is the suggestion that Bay Area refineries processing crude oils which are high in selenium content be required to substitute other crudes containing less selenium. Purvin & Gertz, Inc. has been retained by Shell to provide independent expert testimony addressing the technical practicality and economic impact of this suggested crude oil substitution.

Purvin & Gertz is a firm of consulting engineers which was founded in 1947 and is wholly owned by its member consultants. The firm has no affiliation with any operating company, process licensor, equipment manufacturer, or design and construction contractor.

Our staff is comprised primarily of chemical engineers with extensive industrial and commercial experience including marketing and economic analysis. We concentrate on understanding the interrelationships between the technical and economic aspects of the energy and chemical industries. Offices are maintained in Dallas, Houston, Los Angeles, Calgary and London.

Clients of the firm include many major oil company refiners, but the vast majority of our work is performed for government agencies, financial institutions, investors, public utilities, and smaller independent companies in the oil and chemical Industry. In all of our work, we provide objective advice and opinions based upon impartial analysis. Our analysis of the heavy crude replacement suggestion is discussed in three parts. First, some of the characteristics of crude petroleum are reviewed to illustrate the unique properties of San Joaquin Valley heavy crude which affect its transportation and refining. Next, the logistical impacts of curtailing the usage of this crude in the Bay Area are discussed. Finally, the impact of heavy crude substitution upon Bay Area refineries is described.

# II: CHARACTERISTICS OF CRUDE PETROLEUM

Thousands of different crude oils are produced throughout the world. Each individual crude oil is a unique mixture of thousands of different petroleum compounds. Therefore, it is not surprising that different crude oils have very different physical and chemical properties. These properties affect the ease of crude oil transportation and the type of refinery processing which is required to manufacture finished products from the crude. (Except in very rare cases, crude petroleum is unsuitable for any end use and must be transformed into useful products by the appropriate refining processes.)

Crude oils are often characterized very generally in terms of their density and are called "heavy" or "light". Crude oil density is measured numerically in terms of degrees on the API (American Petroleum Institute) gravity scale. In this scale, less dense materials have higher numbers than denser materials. Thus, a 30° API crude would be lighter or less dense than a 15° API heavy crude.

Both light and heavy crudes are produced in the San Joaquin Valley, which is the region of interest in the current discussion of selenium regulation. The heavy San Joaquin Valley crudes are those which are acknowledged to be relatively higher in selenium content than other crude oils refined in the Bay Area.

The U.S. Department of Energy (DOE) has performed laboratory analyses of crude oils from various producing fields since the early 1920's and its collection of about 9,000 comparable crude oil analyses is probably the largest in the world. A 1978 DOE report published the analyses of 800 important crude oils produced in the United States, including twenty-seven individual crudes produced in Kern and Fresno counties of California (the San Joaquin Valley).

This DOE data, along with data for selected Alaskan North Slope and West Texas crudes, is summarized in Table I and is used to illustrate some of the differences in crude oil properties which impact the ability to substitute other crudes for San Joaquin Valley heavy crude in Bay Area refineries.

## RANGE OF DENSITY AND SULFUR CONTENT

The density of the 27 San Joaquin Valley crudes analyzed by the DOE range from about 12.5° API to about 37° API. The crudes are listed in order of increasing density in Table I. Those above 20° API are grouped together in Table I as light and medium crude, and those below 20° API are grouped as heavy crude.

The table shows the average properties for each of these groups, giving equal weight to each of the fields analyzed.

There are additional producing fields in the San Joaquin Valley for which no DOE analyses are available. (The Conservation Committee of California Oil & Gas Producers lists 53 "principal fields" in the San Joaquin Valley.) Also, some fields produce more crude than others. (The Fruitvale field at 17.5° API produces about 1,500 barrels per day, while the Kern River field at 12.6° API produces about 125,000 barrels per day.) For both of these reasons, the computed average properties shown in Table I are only indicative of the actual weighted average properties of heavy and light San Joaquin crudes. Typical San Joaquin heavy crude shipments are normally closer to 13° API than to 15° API and would be more similar to the crudes in the lower half of the heavy crude block of Table I.

As the crudes in Table I become heavier, their sulfur content generally increases. The average heavy crude contains nearly twice as much sulfur as the average light crude. Sulfur must be removed from many petroleum products in order to meet quality specifications, so sulfur content affects the design and operation of refining equipment and may limit the selection of crudes for a particular refinery.

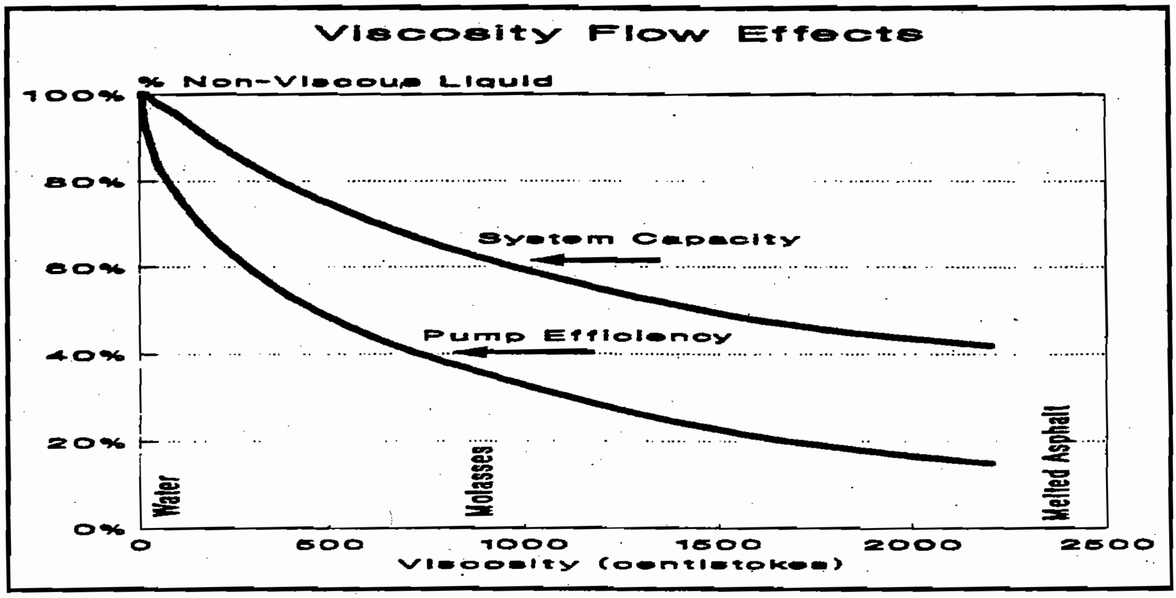
It is normal for heavy crudes to contain more sulfur than light crudes of a similar character because the sulfur is more easily accommodated in large hydrocarbon molecules than in small hydrocarbon molecules. Octane is a hydrocarbon with a "skeleton" made up of eight carbon atoms and is in the range of motor gasoline hydrocarbons. Asphaltenes, which are in the range of heavy fuel oil or asphalt hydrocarbons, have very complex skeletons with more than 80 carbon atoms and have many more active sites for sulfur attachment. Since heavy crudes have relatively more of the very large complex hydrocarbons, they generally contain more sulfur.

Chemists group the chemical elements into "families" based upon their atomic structure, and elements in the same family tend to react similarly. Selenium is in the same family as oxygen and sulfur, so it is not surprising that heavy crudes might contain more selenium than light crudes from the same region.

## VISCOSITY

Viscosity is defined as the resistance to flow, and is a very critical physical property of San Joaquin crudes. Resistance to flow is best explained by an example. Water is relatively non-viscous and flows easily in garden hoses, drinking straws and squirt guns. Molasses is very viscous and would be very difficult to move through any of these devices.

Pushing higher viscosity liquids through a pipeline requires much more work, and viscosity also affects the efficiency and capacity of the centrifugal pumps used to do the pushing. This is illustrated in the following figure which shows the percentage decline in both pipeline system capacity and pumping efficiency with increasing viscosity. For reference, the figure shows the approximate positions of water, molasses at 100 ° Fahrenheit, and hot melt paving asphalt at 300 ° Fahrenheit.



If a pipeline operator attempted to transport San Joaquin Valley heavy crudes at a temperature of 100° Fahrenheit, he would find them truly to be slower than molasses. His system capacity would decline by thirty to fifty percent and his monthly power bill would double or quadruple. If the crude ever stopped flowing because of an unintentional or unavoidable pump shutdown, its behavior would approach that of paving asphalt which is normally moved with a steam roller.

Because of its viscosity, San Joaquin Valley heavy crude is never transported alone at normal ambient temperatures. It is either diluted with light San Joaquin crudes to achieve a pumpable blend or it is pumped at high temperatures through special heated pipelines. (Heating reduces the crude oil viscosity to manageable levels.)

This need for blending or heating has an important effect upon transportation logistics, discussed in the second section of this presentation.

## DISTILLATION YIELD

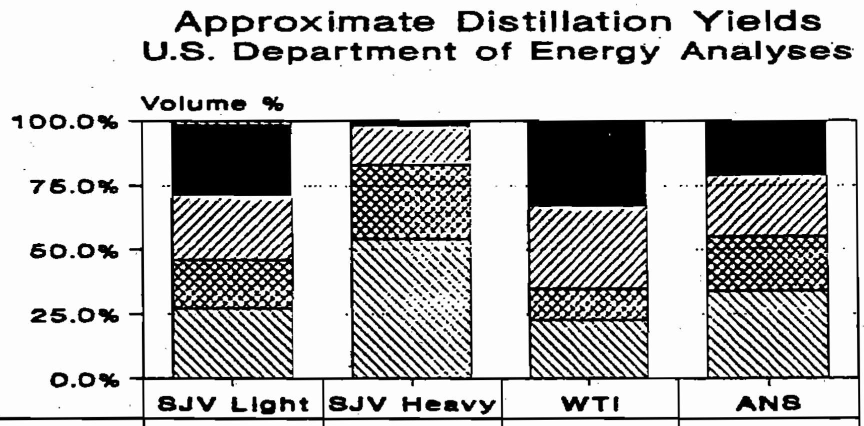
A petroleum refinery is an interrelated group of processing units. Each unit accomplishes a particular function of separating the crude oil components, improving component properties, or converting less valuable components into more valuable components. The last stage of refining is the reblending of these processed materials into finished products which meet the relevant quality specifications.

The initial separation of crude oil into its various components is accomplished by distillation. The distillation yield is determined almost entirely by the type of crude being processed, although the refiner has some limited flexibility in selecting the "cut point" between adjacent fractions of the crude.

In the DOE analyses, the distillation yield of each crude oil sample is measured for each of 16 laboratory "cuts" or bands of distillation temperature. These cuts are then combined into broader subdivisions of boiling range such as gasoline & naphtha or kerosene & gas oil. These broader boiling ranges represent typical practice in commercial refineries. The DOE data for the 27 San Joaquin crudes are summarized on Table I and graphed in Figure I.

Heavier crude oils generally yield relatively more asphalt, residual fuel oil and heavy distillate products while lighter crudes yield relatively more light transportation fuels and petrochemical feedstocks. This is illustrated by the steeply sloping trend lines in Figure I for gasoline/naphtha and for asphalt/resid. The heaviest crudes contain more than 50% asphalt/resid compared with 20% for the lightest crudes. The lightest crudes contain more than 30% gasoline/naphtha compared with less than 2% for the heaviest crudes. The trend lines for jet fuel/diesel and for lubes/gas oil also show a significant slope.

The following bar chart shows the computed average distillation yields for San Joaquin light and heavy crudes as well as for West Texas Intermediate and Alaskan North Slope crudes. The impact of these very different distillation yields upon refinery design and utilization is discussed in the third section of this presentation.


Approximate Distillation Yields
U.S. Department of Energy Analyses

| | | SJV Light | SJV Heavy | WTI | ANS |
|---|---|---|---|---|---|
| Light Ends & Loss | ▧ | 1.4 | 1.2 | 0.3 | 0.7 |
| Gasoline & Naphtha | ■ | 27.2 | 0.8 | 32.6 | 20.4 |
| Jet Fuel & Diesel | ▨ | 25.3 | 15.0 | 32.2 | 23.7 |
| Lubes & Gas Oil | ▩ | 18.8 | 28.7 | 12.3 | 21.4 |
| Asphalt & Resid | ▧ | 27.3 | 54.3 | 22.6 | 33.8 |

# III: LOGISTICAL IMPACTS OF HEAVY CRUDE SUBSTITUTION

Although California oil production has fallen for six consecutive years, the state still placed five of its fields in the top ten producing fields in the United States and supplied about 12% of total United States domestic crude. The San Joaquin Valley (Fresno and Kern County) accounts for nearly 85% of California on-shore production according to California Division of Oil & Gas statistics, and the Valley contains four of those five top U.S. producers. Therefore, the San Joaquin Valley is an extremely important production region, providing nearly 700,000 barrels per day of crude oil and natural gas liquids. About 550,000 barrels per day or more than three fourths of the total Valley production is heavy crude.

## SAN JOAQUIN VALLEY CRUDE BALANCE

A small amount of San Joaquin Valley production is used locally as fuel for steam generation in enhanced oil recovery and as feedstock for local refineries. This regional usage accounts for about 90,000 barrels per day or around 13% of total production. The balance of production is "exported" to other refineries, primarily by direct pipeline connections.

Figure II shows the system of crude oil pipelines in California. From the San Joaquin Valley (around Bakersfield) crude can flow north, west, south or east.

## MOVEMENTS NORTH AND WEST

There are three proprietary pipelines flowing north to the San Francisco Bay area; Texaco, Chevron and Union.

The Texaco pipeline is the only heated pipeline capable of transporting undiluted heavy crude, and has a capacity of about 215,000 barrels per day.

Light and heavy crudes are blended for transportation through the Chevron pipeline which has a capacity of about 95,000 barrels per day. Chevron also operates a heated pipeline flowing eastward to Estero Bay where San Joaquin and coastal crudes can be loaded for tanker shipment to either San Francisco or Los Angeles. The Estero Bay pipeline has a capacity of about 60,000 barrels per day.

The Union pipeline to San Francisco is also unheated and transports a blend of crudes and unfinished feedstock. Union operates a coastal refinery at Santa Maria and a marine terminal at Avila, primarily for partial processing of local on-shore and off-shore crudes including Point Pedernales and Point Arguello crudes. Two branch pipelines connect the Santa Maria refinery with the main Union pipeline to San Francisco. One of the branch pipelines is heated and reversible so that Pt. Pedernales crude can be moved to San Francisco or, alternatively, San Joaquin heavy crude can be moved to the Santa Maria refinery. The second unheated branch pipeline transports unfinished product from the Santa Maria refinery for use as diluent for blending with heavy crude. Recent estimates are that less than 10,000 barrels per day of San Joaquin heavy crude is moved to the Santa Maria refinery, and about 20,000 barrels per day of unfinished diluent is received from the refinery. Capacity of the main pipeline to San Francisco is about 72,000 barrels per day.

## MOVEMENTS SOUTH

Two pipeline systems allow movement of San Joaquin Valley crudes south to Los Angeles. Mobil operates a heated pipeline with a capacity of about 63,000 barrels per day. The Four Corners pipeline is an unheated system with a capacity of about 135,000 barrels per day of blended light and heavy crude. Because there is essentially no spare pipeline capacity -- particularly for heavy crudes -- about 30,000 barrels per day of heavy San Joaquin Valley crude is moved to Los Angeles by train.

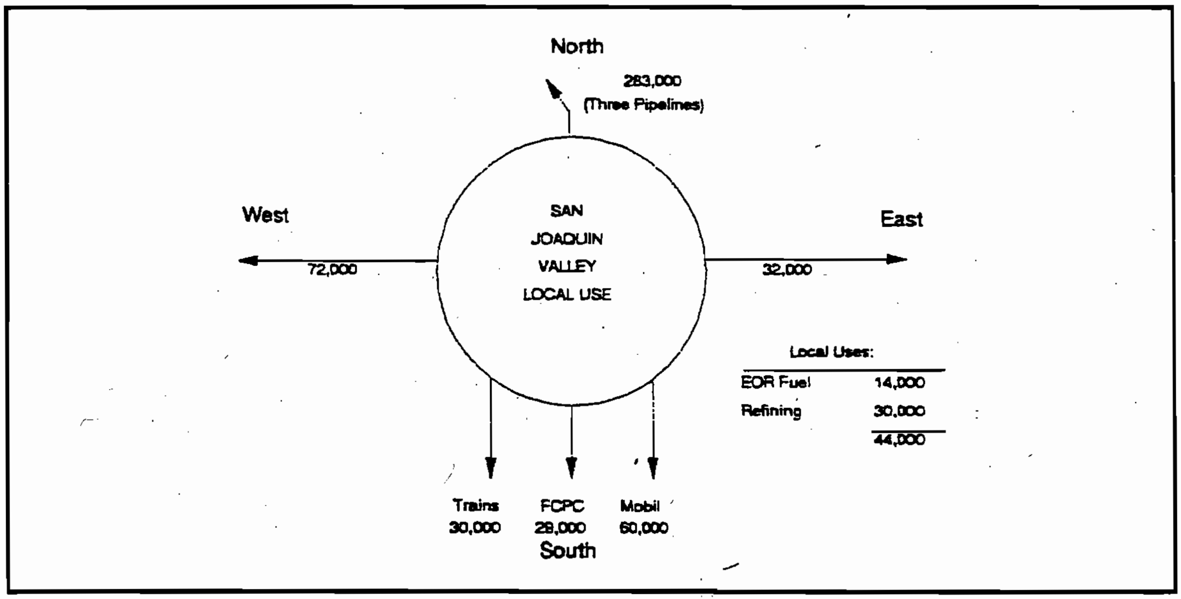
## MOVEMENTS EAST

With the commissioning of the All American pipeline, the movement of California crude eastward from the San Joaquin Valley became possible. This pipeline was initially intended to facilitate the transportation of heavy off-shore crudes to the major U.S. Gulf Coast refining centers, and a heated pipeline extending all the way to Houston was planned. With substantially slower development of off-shore California fields, the initial plans were revised and the heated pipeline terminates in West Texas, hundreds of miles short of the major refining centers. There are connections to other pipelines in West Texas, but all of the connecting systems are unheated so it is necessary to transport crude blends rather than undiluted heavy crude.

Data for 1990, the most recent year for which all data is available, showed about 55,000 barrels per day of West Coast crude moving into the All-American pipeline. The volume includes Alaskan North Slope crude received into Los Angeles terminals and moved by Four Corners pipeline to the junction in eastern California. Total volume of West Coast crude leaving California to the east was about 40,000 barrels per day of 27° API West Coast Blend plus about 15,000 barrels per day of 22° API West Coast Heavy. At 22° API, this "West Coast Heavy" obviously was much lighter than 15° API San Joaquin heavy, reflecting dilution with lighter California and Alaskan crude.

## SUMMARY OF HEAVY CRUDE MOVEMENTS

The historical movement of heavy crude oil production from the San Joaquin Valley is summarized in Table II and illustrated below:



Local consumption and movements eastward to non-California refineries account for about 76,000 barrels per day or only 14% of San Joaquin Valley production of heavy crude. Movements westward account for about 72,000 barrels per day or about 13% of heavy crude production. However, as noted above, a substantial portion of this crude is loaded on coastal tankers for delivery to Los Angeles or the Bay Area refineries, and the heavy crude which actually is refined on the west coast provides diluent for heavy crude shipments to the north. Therefore, most of the 13% moving westward from the San Joaquin Valley actually ends up in Los Angeles or Bay Area refineries.

**Movements directly to Los Angeles area refineries by pipeline and rail account for about 119,000 barrels per day or about 22% of heavy crude production. Pipeline movements of San Joaquin crude north to the Bay Area account for 283,000 barrels per day or about 52% of total Valley production.**

In the Bay Area, San Joaquin Valley heavy crude can be loaded for export or shipment to other domestic markets at the Wickland Oil Martinez terminal. This heavy crude outlet has existed for about ten years, and has been used routinely to balance production with deliveries to Los Angeles refiners. These balancing movements are relatively small, accounting for only about 10,000 barrels per day or about 4% of the total heavy crude received by pipeline into the Bay Area.

The markets for San Joaquin Valley heavy crude are virtually all in California. Export licenses have been issued for this crude, but sellers have been unable to identify any attractive foreign markets. Refiners in Texas do not favor even the lighter San Joaquin Valley crudes. Historically, there have been very few regular purchasers -- mainly Exxon and Lyondell. Other Gulf Coast refiners have tried the crude but ceased using it.

## SAN JOAQUIN VALLEY LOGISTICAL IMPACTS

The Bay Area is the most important market for San Joaquin Valley heavy crude, accounting for more than half of all production. The inability to access this important market would be a stunning blow to heavy crude producers.

If alternative markets could not be developed (along with pipeline capacity to serve those markets) half of the heavy crude oil production in the state's most important oil producing region would be shut in. This would eliminate production revenue for the producers, as well as royalty income for the land owners and tax revenue for the state.

If heavy crude production were not shut in, it would be necessary to impose significant price discounts to encourage waterborne exports, probably from the Martinez terminal. Waterborne movements would be necessary because heated pipeline capacity to alternative destinations is already fully utilized, as demonstrated by the current use of trains and ships to serve Los Angeles refineries.

The required price discounting may be several dollars per barrel, amounting to a million dollars per day or more. Landowner royalties and state tax revenues would also be affected. The combined effect would cause severe economic disruption in the San Joaquin Valley region.

## BAY AREA LOGISTICAL IMPACTS

The San Joaquin Valley is the only source of crude which can be delivered by pipeline to the Bay Area. Therefore, loss of this crude source would require Bay Area refiners to replace the curtailed heavy crude with alternative crudes delivered by water. (This assumes that suitable replacement crude could be acquired: the effects of crude quality are discussed in a subsequent part of the presentation.)

San Joaquin heavy crude accounts for about a third of all crude oil refined in the Bay Area. At a minimum, the curtailed heavy crude would need to be replaced "barrel for barrel" to provide the refined product market currently served by Bay Area refiners. (If refinery throughput is curtailed to avoid crude oil replacement, then waterborne product imports will be necessary to make up the shortfall.)

A substantial portion of the heavy crude is shipped in blends with light crude, and it is impossible to "un-mix" the light and heavy crude without refining. It will be necessary to replace more than one barrel of San Joaquin blend to eliminate one barrel San Joaquin heavy if curtailments exceed the deliveries by heated pipeline.

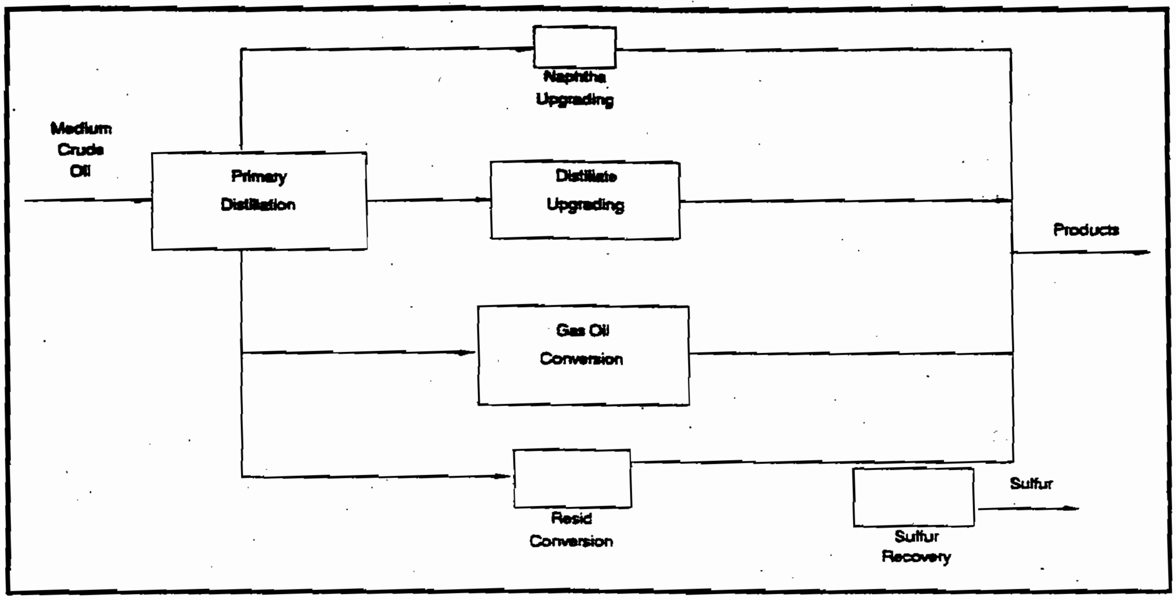
Heavy crude exports and replacement crude or replacement product imports (both magnified by the presence of light crude diluents) will cause a tremendous increase in oil tanker traffic in Carquinez Strait.

# IV: BAY AREA REFINERY IMPACTS OF HEAVY CRUDE SUBSTITUTION

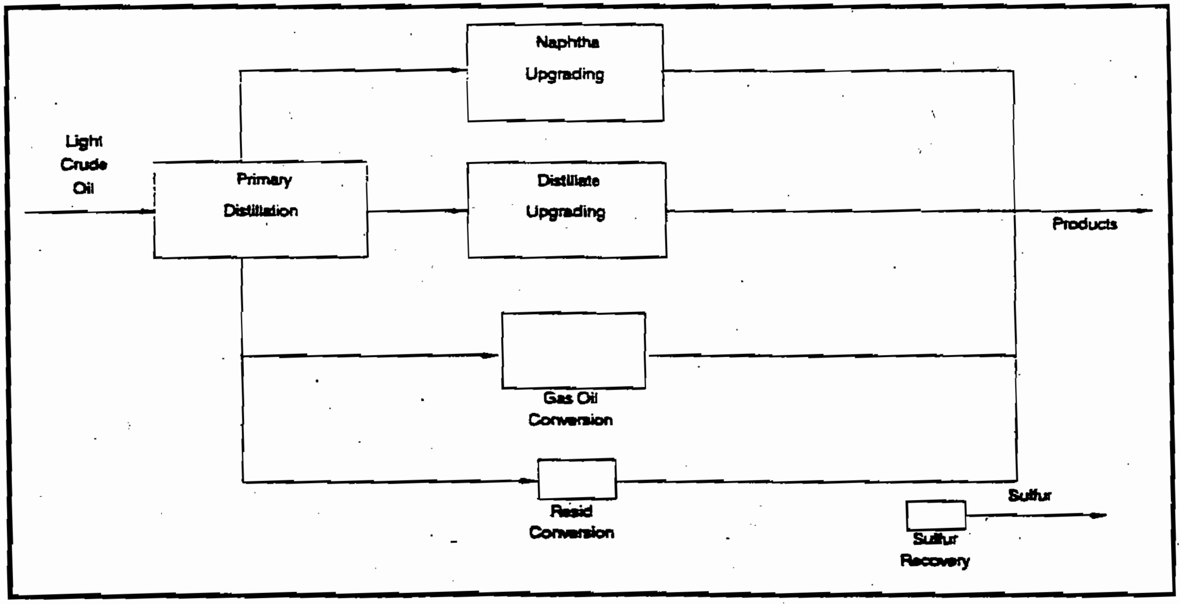
As noted above, there are significant differences in the distillation yields of heavy and light crude oils. Distillation is just the first stage of refining. The distillation cuts are further processed to improve their quality or to convert heavy materials into light products.

Several types of refinery processes are employed in the Bay Area and in other refineries throughout the world. Naphtha is processed to remove sulfur contaminants and to improve its octane rating for use as gasoline. Jet fuel and diesel fractions are processed in other units for sulfur removal and improvement of burning characteristics. Some of the gas oil fraction is processed intensively for the production of high quality lubricating oils and greases; the balance is converted into gasoline and other transportation fuels in different process units which break large hydrocarbon molecules into smaller molecules. The heavy residuum fraction supplies the asphalt and heavy fuel market, but these markets are relatively small in relation the amount of residuum contained in heavier crudes. Another type of refining process is applied to the surplus residuum in order to convert it into gasoline, jet fuel and diesel.

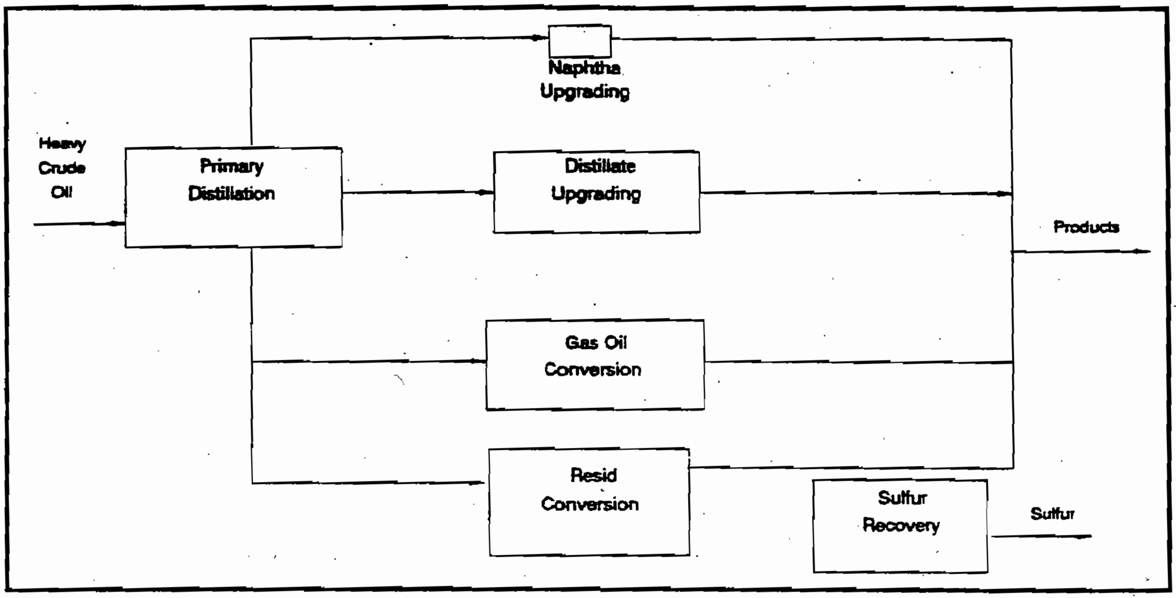
Refineries cannot easily adapt to other crudes because the various processing units are sized to handle the distillation yields for which the refinery was designed. The following figure illustrates the relative sizing of process units for a "medium gravity" crude oil. The size of the processing blocks are roughly proportional to the amount of processing capacity which is required. This is the base case for illustration.



The next figure shows a refinery designed for light crude. Compared with the base case, the naphtha processing block is much larger because considerably more processing capacity is needed to accommodate the higher distillation yield of naphtha. Very little residuum conversion capacity is needed because the light crudes contain much less of this asphalt type material.



The third figure illustrates a refinery designed for heavy crude oil. Very little naphtha processing capacity is required because these crudes do not contain much naphtha. However, this refinery would have a very large residuum processing unit to accommodate the high distillation yield of residuum.



Refineries designed for one type of crude cannot effectively utilize the other types of crude in significant quantities because their processing units are the wrong size. A "heavy crude" refinery designed for 100,000 barrels of crude might have naphtha processing units sized for 10,000 barrels per day, for example. If that refinery tried to process 100,000 barrels per day of light crude, the naphtha production would be several times larger than 10,000 barrels per day. In order to stay within the naphtha processing capacity, the refiner would have to drastically reduce the amount of crude oil being processed. The very large residuum conversion unit installed in the heavy crude refinery would be essentially empty, and probably could not run at such low rates.

Forcing a very dissimilar crude into an existing refinery is like forcing a square peg into a round hole. It is possible, but the square peg must be very much smaller than the round peg which is removed from the hole.

San Joaquin Valley heavy crude is unique, and similar crudes are not produced anywhere in the world except for the San Joaquin Valley. There are foreign sources of heavy crude in the Middle East and South America, but these foreign crudes are sufficiently different in chemical character to require significantly different processing.

Bay Area refineries have been supplied by the San Joaquin Valley for their entire existence, and their design has evolved to handle the specific mix of crudes. The Bay Area has several refineries in the "heavy crude" category described above. These refineries are very complex by industry standards and employ sophisticated processing to enable the production of more than 60% light transportation fuels from a heavy mix of crude oil feedstocks. The operating cost of these complex refineries is very high, but they are able to manufacture refined product at competitive price because heavy crude prices are lower. (In 1991, the average posted price of 13° API Kern River crude was $12.07 per barrel, compared with $15.65 for 28° API Ventura Avenue crude from Ventura County and $17.30 for Belgian Anticline crude from Kern County.)

If Bay Area refineries were unable to process the heavy San Joaquin Valley crudes for which they were designed, it would certainly cause severe technical and economic disruption.

# TABLE I

# COMPARISON OF CRUDE OIL PROPERTIES AND DISTILLATION YIELDS

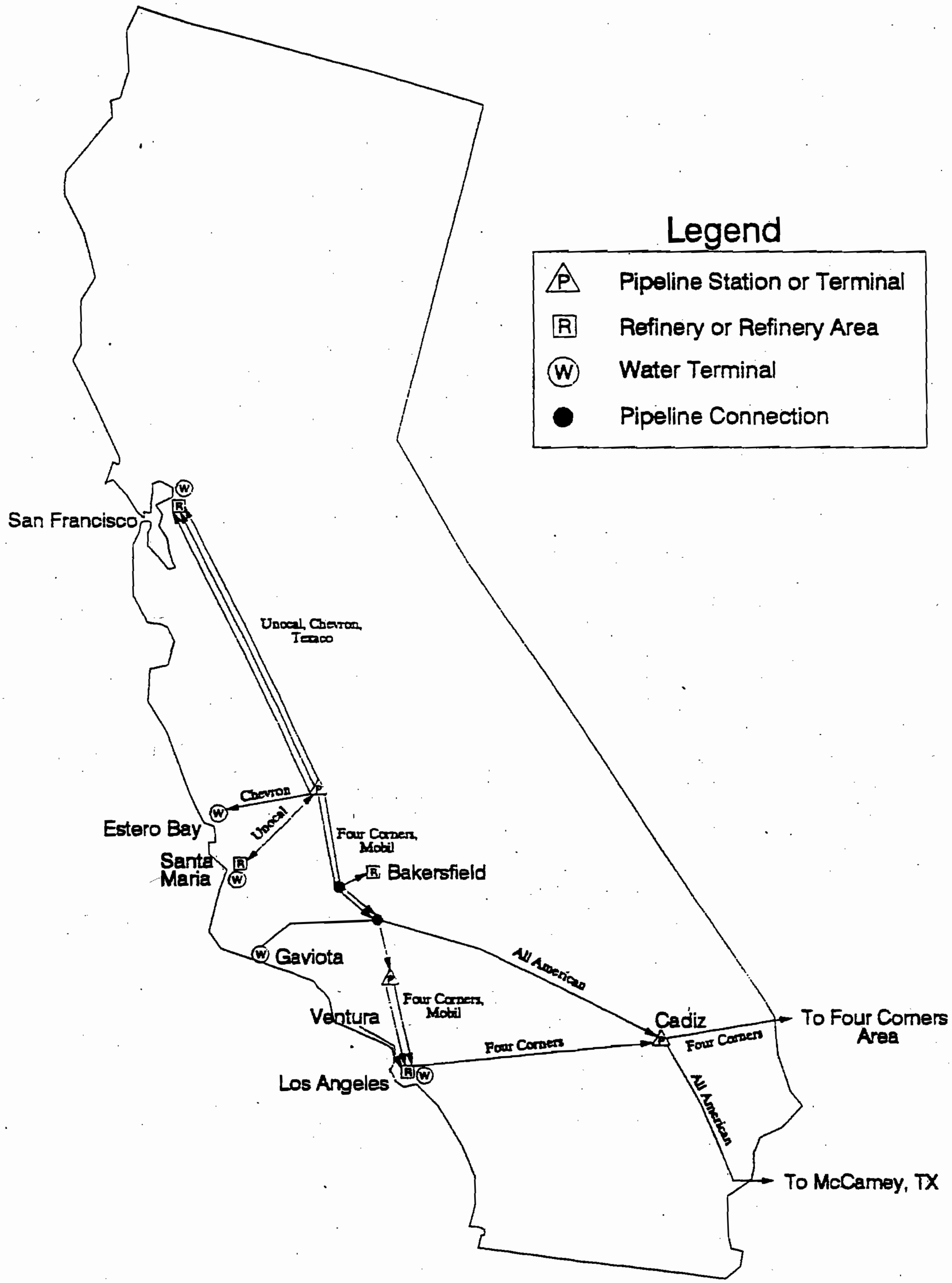
| Sample # & Field Name | Physical Properties | | | Summary of Approximate Distillation Yields (vol %) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Density (deg API) | Sulfur (wt %) | Viscosity @ 100 deg (CST) | LPG & Loss | Gasoline & Naphtha | Jet Fuel & Diesel | Lubes & Gas Oil | Asphalt & Residuum | Total |
| **San Joaquin Valley (Kern County & Fresno County)** | | | | | | | | | |
| 54 Greeley | 37.2 | .3 | 4.6 | 2.7 | 37.3 | 23.6 | 16.5 | 19.9 | 100.0 |
| 92 Wheeler Ridge | 37.0 | .3 | 3.7 | 2.5 | 34.9 | 28.1 | 17.2 | 17.3 | 100.0 |
| 27 Asphalto | 35.2 | .4 | 4.9 | 1.9 | 34.4 | 23.4 | 18.0 | 22.3 | 100.0 |
| 28 Belgian Anticline | 35.0 | .6 | 4.3 | .1 | 35.5 | 26.7 | 15.5 | 22.2 | 100.0 |
| 70 Mountain View | 35.0 | .4 | 20.5 | 2.5 | 35.0 | 23.0 | 16.0 | 23.5 | 100.0 |
| 89 Ten Section | 34.2 | .5 | 5.2 | 1.8 | 33.5 | 23.7 | 16.0 | 25.0 | 100.0 |
| 40 Coles-Levee | 34.0 | .4 | 5.2 | 2.4 | 35.0 | 21.0 | 16.3 | 25.3 | 100.0 |
| 53 Gosford | 34.0 | .6 | 7.7 | 4.2 | 34.6 | 19.6 | 16.6 | 25.0 | 100.0 |
| 60 Kettleman | 34.0 | .4 | 5.5 | .2 | 33.5 | 26.7 | 20.5 | 19.1 | 100.0 |
| 64 Lost Hills | 33.2 | .3 | 8.0 | .2 | 35.0 | 24.3 | 16.4 | 24.1 | 100.0 |
| 38 Coalinga Nose | 31.5 | .3 | 6.8 | 1.7 | 25.1 | 32.2 | 16.2 | 24.8 | 100.0 |
| 33 Buena Vista | 30.6 | .6 | 6.3 | 1.9 | 33.9 | 21.2 | 15.0 | 28.0 | 100.0 |
| 88 Tejon-Grapevine | 29.9 | .3 | 6.3 | .5 | 15.4 | 41.6 | 22.5 | 20.0 | 100.0 |
| 80 San Emidio | 29.7 | .8 | 10.0 | .7 | 27.3 | 22.6 | 19.1 | 30.3 | 100.0 |
| 37 Coalinga East | 28.8 | .3 | 12.4 | .8 | 23.2 | 26.0 | 21.6 | 28.4 | 100.0 |
| 48 Edison | 25.2 | .2 | 24.0 | .2 | 20.8 | 21.5 | 19.5 | 38.0 | 100.0 |
| 75 Raisin City | 23.8 | .5 | 30.8 | .6 | 17.0 | 21.1 | 21.9 | 39.4 | 100.0 |
| 49 Elk Hills | 22.8 | .7 | 28.6 | .8 | 11.1 | 28.7 | 22.0 | 37.4 | 100.0 |
| 66 Midway-Sunset | 22.6 | .9 | 34.2 | .5 | 15.4 | 23.5 | 20.8 | 39.8 | 100.0 |
| 39 Coalinga West | 20.2 | .6 | 42.0 | 1.2 | 6.9 | 26.5 | 28.9 | 36.5 | 100.0 |
| Avg Light/Medium Crude San Joaquin Valley | 30.5 | .5 | 8.9 | 1.4 | 27.2 | 25.3 | 18.8 | 27.3 | 100.0 |
| 51 Fruitvale | 17.5 | .9 | 378.0 | .5 | .7 | 19.0 | 25.4 | 54.4 | 100.0 |
| 69 Mount Poso | 16.0 | .7 | 410.0 | .6 | .0 | 13.6 | 33.8 | 52.0 | 100.0 |
| 65 McKittrick | 15.6 | 1.0 | 327.0 | 1.7 | 2.8 | 18.8 | 33.0 | 43.7 | 100.0 |
| 30 S Belridge | 15.0 | .2 | 527.0 | 1.7 | 2.1 | 17.2 | 29.6 | 49.4 | 100.0 |
| 58 Kern Front | 14.8 | .9 | 1,101.0 | 1.4 | .0 | 13.7 | 29.1 | 55.8 | 100.0 |
| 44 Cymric | 12.7 | 1.2 | 1,300.0 | 1.0 | .0 | 13.0 | 26.6 | 59.4 | 100.0 |
| 59 Kern River | 12.6 | 1.2 | 1,300.0 | 1.4 | .0 | 9.6 | 23.3 | 65.7 | 100.0 |
| Avg Heavy Crude San Joaquin Valley | 14.9 | .9 | 650.0 | 1.2 | .8 | 15.0 | 28.7 | 54.3 | 100.0 |
| **Alaskan North Slope** | | | | | | | | | |
| 6 Kuparuk | 28.2 | .7 | 13.6 | .3 | 21.8 | 24.7 | 21.9 | 31.3 | 100.0 |
| 9 Prudhoe Bay | 27.0 | .8 | 16.7 | 1.1 | 19.0 | 22.7 | 20.9 | 36.3 | 100.0 |
| Avg ANS | 27.6 | .7 | 15.2 | .7 | 20.4 | 23.7 | 21.4 | 33.8 | 100.0 |
| **Typical West Texas Intermediate** | | | | | | | | | |
| 567 Lea Field | 40.9 | .3 | 4.3 | .30 | 32.6 | 32.2 | 12.3 | 22.6 | 100.0 |

Reference: U.S. Department of Energy, Technical Information Center, "Analyses of 800 Crude Oils from United States Oilfields", November 1978.

RGA
December 1992
W-2219

# FIGURE II

## CALIFORNIA CRUDE OIL PIPELINES



**Attachment 36**

BAY AREA AIR QUALITY
MANAGEMENT DISTRICT

A HEALTHY BREATHING ENVIRONMENT FOR EVERY BAY AREA RESIDENT

# Air Quality Standards and Attainment Status

iew state and federal standards for 11 air pollutants and see the Bay
rea's attainment status for each pollutant.

ederal and state ambient air quality standards have been set to protect public health and the imate. "Attainment" status for a pollutant means that the Air District meets the standard set / the U.S. Environmental Protection Agency (federal) or California Environmental Protection gency (state). Continuous air monitoring ensures that these standards are met and aintained.

| Pollutant | Averaging Time | California Standards[1] | | National Standards[2] | |
|---|---|---|---|---|---|
| | | Concentration | Attainment Status | Concentration[3] | Attainment Status |
| Ozone | 8 Hour | 0.070 ppm (137$\mu$g/m$^3$) | N[9] | 0.075 ppm | N[4] |
| | 1 Hour | 0.09 ppm (180 $\mu$g/m$^3$) | N | | See Note #5 |
| Carbon Monoxide | 8 Hour | 9.0 ppm (10 mg/m$^3$) | A | 9 ppm (10 mg/m$^3$) | A[6] |

| | | | | | |
|---|---|---|---|---|---|
| | 1 Hour | 20 ppm (23 mg/m$^3$) | A | 35 ppm (40 mg/m$^3$) | A |
| Nitrogen Dioxide | 1 Hour | 0.18 ppm (339 µg/m$^3$) | A | 0.100 ppm<br>*See Note #11* | U |
| | Annual Arithmetic Mean | 0.030 ppm (57 µg/m$^3$) | | 0.053 ppm (100 µg/m$^3$) | A |
| Sulfur Dioxide<br>*See Note #12* | 24 Hour | 0.04 ppm (105 µg/m$^3$) | A | 0.14 ppm (365 µg/m$^3$) | A |
| | 1 Hour | 0.25 ppm (655 µg/m$^3$) | A | 0.075 ppm (196 µg/m$^3$) | A |
| | Annual Arithmetic Mean | | | 0.030 ppm (80 µg/m$^3$) | A |
| Particulate Matter (PM10) | Annual Arithmetic Mean | 20 µg/m$^3$ | N[7] | | |
| | 24 Hour | 50 µg/m$^3$ | N | 150 µg/m$^3$ | U |
| Particulate Matter - Fine (PM2.5) | Annual | 12 µg/m$^3$ | N[7] | 12 µg/m$^3$<br>*See Note #15* | U/A |

| | | | | | |
|---|---|---|---|---|---|
| | Arithmetic Mean | | | | |
| | 24 Hour | | | 35 $\mu$g/m$^3$<br>See Note #10 | N |
| Sulfates | 24 Hour | 25 $\mu$g/m$^3$ | A | | |
| Lead<br>See Note #13 | 30 day Average | 1.5 $\mu$g/m$^3$ | | - | A |
| | Calendar Quarter | - | | 1.5 $\mu$g/m$^3$ | A |
| | Rolling 3 Month Average$^{14}$ | - | | 0.15 $\mu$g/m$^3$ | See Note #14 |
| Hydrogen Sulfide | 1 Hour | 0.03 ppm (42 $\mu$g/m$^3$ | U | | |
| Vinyl Chloride (chloroethene) | 24 Hour | 0.010 ppm (26 $\mu$g/m$^3$ | No information available | | |
| Visibility Reducing particles | 8 Hour (10:00 to 18:00 PST) | See Note #8 | U | | |
| **A=Attainment N=Nonattainment U=Unclassified** | | | | | |

| | | |
|---|---|---|
| mg/m$^3$=milligrams per cubic meter | ppm=parts per million | $\mu$g/m$^3$=micrograms per cubic meter |

## NOTES

1. California standards for ozone, carbon monoxide (except Lake Tahoe), sulfur dioxide (1-hour and 24-hour), nitrogen dioxide, suspended particulate matter - PM10, and visibility reducing particles are values that are not to be exceeded. The standards for sulfates, Lake Tahoe carbon monoxide, lead, hydrogen sulfide, and vinyl chloride are not to be equaled or exceeded. If the standard is for a 1-hour, 8-hour or 24-hour average (i.e., all standards except for lead and the PM10 annual standard), then some measurements may be excluded. In particular, measurements are excluded that ARB determines would occur less than once per year on the average. The Lake Tahoe CO standard is 6.0 ppm, a level one-half the national standard and two-thirds the state standard.
2. National standards shown are the "primary standards" designed to protect public health. National standards other than for ozone, particulates and those based on annual averages are not to be exceeded more than once a year. The 1-hour ozone standard is attained if, during the most recent three-year period, the average number of days per year with maximum hourly concentrations above the standard is equal to or less than one. The 8-hour ozone standard is attained when the 3-year average of the 4th highest daily concentrations is 0.075 ppm (75 ppb) or less. The 24-hour PM10 standard is attained when the 3-year average of the 99th percentile of monitored concentrations is less than 150 $\mu$g/m3. The 24-hour PM2.5 standard is attained when the 3-year average of 98th percentiles is less than 35 $\mu$g/m3.

   Except for the national particulate standards, annual standards are met if the annual average falls below the standard at every site. The national annual particulate standard for PM10 is met if the 3-year average falls below the standard at every site. The annual PM2.5 standard is met if the 3-year average of annual averages spatially-averaged across officially designed clusters of sites falls below the standard.
3. National air quality standards are set by US EPA at levels determined to be protective of public health with an adequate margin of safety.
4. Final designations effective July 20, 2012.
5. The national 1-hour ozone standard was revoked by U.S. EPA on June 15, 2005.
6. In April 1998, the Bay Area was redesignated to attainment for the national 8-hour carbon monoxide standard.
7. In June 2002, CARB established new annual standards for PM2.5 and PM10.
8. Statewide VRP Standard (except Lake Tahoe Air Basin): Particles in sufficient amount to produce an extinction coefficient of 0.23 per kilometer when the relative humidity is less than 70 percent. This standard is intended to limit the frequency and severity of visibility impairment due to regional haze and is equivalent to a 10-mile nominal visual range.
9. The 8-hour CA ozone standard was approved by the Air Resources Board on April 28, 2005 and became effective on May 17, 2006.
10. On January 9, 2013, EPA issued a final rule to determine that the Bay Area attains the 24-hour PM2.5 national standard. This EPA rule suspends key SIP requirements as long as monitoring data continues to show that the Bay Area attains the standard. Despite this EPA action, the Bay Area will continue to be designated as “non-attainment” for the national 24-hour PM2.5 standard until such

time as the Air District submits a “redesignation request” and a “maintenance plan” to EPA, and EPA approves the proposed redesignation.

11. To attain this standard, the 3-year average of the 98th percentile of the daily maximum 1-hour average at each monitor within an area must not exceed 0.100ppm (effective January 22, 2010).
12. On June 2, 2010, the U.S. EPA established a new 1-hour SO2 standard, effective August 23, 2010, which is based on the 3-year average of the annual 99th percentile of 1-hour daily maximum concentrations. The existing 0.030 ppm annual and 0.14 ppm 24-hour SO2 NAAQS however must continue to be used until one year following U.S. EPA initial designations of the new 1-hour SO2 NAAQS. EPA expects to designate areas by June 2012.
13. ARB has identified lead and vinyl chloride as ‘toxic air contaminants’ with no threshold level of exposure below which there are no adverse health effects determined.
14. National lead standard, rolling 3-month average: final rule signed October 15, 2008. Final designations effective December 31, 2011.
15. In December 2012, EPA strengthened the annual PM 2.5 National Ambient Air Quality Standards (NAAQS) from 15.0 to 12.0 micrograms per cubic meter (µg/m3). In December 2014, EPA issued final area designations for the 2012 primary annual PM 2.5 NAAQS. Areas designated “unclassifiable/attainment” must continue to take steps to prevent their air quality from deteriorating to unhealthy levels. The effective date of this standard is April 15, 2015.

Last Updated: 10/31/2015

**Attachment 37**

# WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide

*Global update 2005*

## Summary of risk assessment

World Health
Organization

WHO/SDE/PHE/OEH/06.02

# WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide

## Global update 2005

### Summary of risk assessment

World Health
Organization

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# Contents

# Preface

Clean air is considered to be a basic requirement of human health and well-being. However, air pollution continues to pose a significant threat to health worldwide. According to a WHO assessment of the burden of disease due to air pollution, more than 2 million premature deaths each year can be attributed to the effects of urban outdoor air pollution and indoor air pollution (caused by the burning of solid fuels). More than half of this disease burden is borne by the populations of developing countries[1].

The WHO air quality guidelines are designed to offer guidance in reducing the health impacts of air pollution. First produced in 1987[2] and updated in 1997,[3] these guidelines are based on expert evaluation of current scientific evidence. Given the wealth of new studies on the health effects of air pollution that have been published in the scientific literature since the completion of the second edition of the *Air quality Guidelines for Europe*, including important new research from low-and middle-income countries where air pollution levels are at their highest, WHO has undertaken to review the accumulated scientific evidence and to consider its implications for its air quality guidelines. The result of this work is presented in this document in the form of revised guideline values for selected air pollutants, which are applicable across all WHO regions. These guidelines are intended to inform policy-makers and to provide appropriate targets for a broad range of policy options for air quality management in different parts of the world.

The new information included in this latest update of the *Air quality guidelines* relate to four common air pollutants: particulate matter (PM), ozone ($O_3$), nitrogen dioxide ($NO_2$) and sulfur dioxide ($SO_2$). The scope of this review reflects the availability of new evidence on the health effects of these pollutants and their relative importance with regard to current and future health effects of air pollution in each of the WHO regions. For air pollutants not considered in the present document the conclusions presented in the WHO *Air quality guidelines for Europe*[3] remain in effect.

The process leading to the present revision of the air quality guidelines is summarized in the report of the WHO Working Group Meeting, which convened in Bonn, 18–20 October 2005[4]. This report lists the members of the Working Group who reviewed the available evidence and who recommended the guideline values presented here. A full report, to include a detailed assessment of the available scientific evidence, as well as the revised introductory chapters of the WHO *Air quality guidelines* will be published later in 2006.

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[1] World health report 2002. Reducing risks, promoting healthy life. Geneva, World Health Organization, 2002.

[2] Air quality guidelines for Europe. Copenhagen, World Health Organization Regional Office for Europe, 1987 (WHO Regional Publications, European Series, No. 23).

[3] Air quality guidelines for Europe, 2nd ed. Copenhagen, World Health Organization Regional Office for Europe, 2000 (WHO Regional Publications, European Series, No. 91).

[4] Available at http://www.euro.who.int/Document/E87950.pdf.

## Role of the guidelines in protecting public health

The WHO air quality guidelines (AQGs) are intended for worldwide use but have been developed to support actions to achieve air quality that protects public health in different contexts. Air quality standards, on the other hand, are set by each country to protect the public health of their citizens and as such are an important component of national risk management and environmental policies. National standards will vary according to the approach adopted for balancing health risks, technological feasibility, economic considerations and various other political and social factors, which in turn will depend on, among other things, the level of development and national capability in air quality management. The guideline values recommended by WHO acknowledge this heterogeneity and, in particular, recognize that when formulating policy targets, governments should consider their own local circumstances carefully before adopting the guidelines directly as legally based standards.

The WHO AQGs are based on the now extensive body of scientific evidence relating to air pollution and its health consequences. Although this information base has gaps and uncertainties, it offers a strong foundation for the recommended guidelines. Several key findings that have emerged in recent years merit special mention. Firstly, the evidence for ozone ($O_3$) and particulate matter (PM) indicates that there are risks to health at concentrations currently found in many cities in developed countries. Moreover, as research has not identified thresholds below which adverse effects do not occur, it must be stressed that the guideline values provided here cannot fully protect human health.

Secondly, an increasing range of adverse health effects has been linked to air pollution, and at ever-lower concentrations. This is especially true of airborne particulate matter. New studies use more refined methods and more subtle but sensitive indicators of effects, such as physiological measures (e.g. changes in lung function, inflammation markers). Therefore the updated guidelines could be based both on these sensitive indicators, in addition to the most critical population health indicators, such as mortality and unscheduled hospitalizations.

Thirdly, as our understanding of the complexity of the air pollution mixture has improved, the limitations of controlling air pollution through guidelines for single pollutants have become increasingly apparent. Nitrogen dioxide ($NO_2$), for example, is a product of combustion processes and is generally found in the atmosphere in close association with other primary pollutants, including ultrafine (UF) particles. It is itself toxic and is also a precursor of ozone, with which it coexists along with a number of other photochemically generated oxidants. Concentrations of $NO_2$ are often strongly correlated with those of other toxic pollutants, and being the easier to measure, is often used as a surrogate for the pollutant mixture as a whole. Achieving guideline concentrations for individual pollutants such as $NO_2$ may therefore bring public health benefits that exceed those anticipated on the basis of estimates of a single pollutant's toxicity.

The present revision of the WHO *Air quality guidelines for Europe* provides new guideline values for three of the four pollutants examined. For two of them (particulate matter and ozone), it is possible to derive a quantitative relationship between the concentration of the pollutant as monitored in ambient air and specific health outcomes (usually mortality). These relationships are invaluable for health impact assessments and allow insights into the mortality and morbidity burdens from current levels of air pollution, as well as what health improvements could be expected under different air pollution reduction scenarios. The burden-of-disease estimates can also be used for the purpose of estimating the costs and benefits of interventions that reduce air pollution. Approaches to, and the limitations of, health impact assessments are summarized in the full report supporting the updated guidelines.

Air pollutant concentrations should be measured at monitoring sites that are representative of population exposures. Air pollution levels may be higher in the vicinity of specific sources of air pollution, such as roads, power plants and large stationary sources, and so protection of populations living in such situations may require special measures to bring the pollution levels to below the guideline values.

The following sections of this document present the WHO AQGs for PM, ozone, $NO_2$ and $SO_2$, and in each case give the rationale for the decision to revise the guideline value or to retain the existing value. As noted above, the epidemiological evidence indicates that the possibility of adverse health effects remains even if the guideline value is achieved, and for this reason some countries might decide to adopt lower concentrations than the WHO guideline values as their national air quality standards.

In addition to guideline values, **interim targets** are given for each pollutant. These are proposed as incremental steps in a progressive reduction of air pollution and are intended for use in areas where pollution is high. These targets aim to promote a shift from high air pollutant concentrations, which have acute and serious health consequences, to lower air pollutant concentrations. If these targets were to be achieved, one could expect significant reductions in risks for acute and chronic health effects from air pollution. Progress towards the guideline values should, however, be the ultimate objective of air quality management and health risk reduction in all areas.

# Air quality guidelines and their rationale

## Particulate matter

Guidelines

**$PM_{2.5}$:** **10 μg/m³ annual mean**
**25 μg/m³ 24-hour mean**

**$PM_{10}$:** **20 μg/m³ annual mean**
**50 μg/m³ 24-hour mean**

## Rationale

The evidence on airborne particulate matter (PM) and its public health impact is consistent in showing adverse health effects at exposures that are currently experienced by urban populations in both developed and developing countries. The range of health effects is broad, but are predominantly to the respiratory and cardiovascular systems. All population is affected, but susceptibility to the pollution may vary with health or age. The risk for various outcomes has been shown to increase with exposure and there is little evidence to suggest a threshold below which no adverse health effects would be anticipated. In fact, the low end of the range of concentrations at which adverse health effects has been demonstrated is not greatly above the background concentration, which for particles smaller than 2.5 μm ($PM_{2.5}$) has been estimated to be 3–5 μg/m³ in both the United States and western Europe. The epidemiological evidence shows adverse effects of PM following both short-term and long-term exposures.

As thresholds have not been identified, and given that there is substantial inter-individual variability in exposure and in the response in a given exposure, it is unlikely that any standard or guideline value will lead to complete protection for every individual against all possible adverse health effects of particulate matter. Rather, the standard-setting process needs to aim at achieving the lowest concentrations possible in the context of local constraints, capabilities and public health priorities. Quantitative risk assessment offers one way of comparing alternative control scenarios and of estimating the residual risk associated with a particular guideline value. Both the United States Environmental Protection Agency and the European Commission have recently used this approach to revise their air quality standards for PM. Countries are encouraged to consider adopting an increasingly stringent set of standards, tracking progress through the monitoring of emission reductions and declining concentrations of PM. To assist this process, the numerical guideline and interim target values given here reflect the concentrations at which increased mortality responses due to PM air pollution are expected based on current scientific findings.

The choice of indicator for particulate matter also requires consideration. At present, most routine air quality monitoring systems generate data based on the measurement of $PM_{10}$ as opposed to other particulate matter sizes. Consequently, the majority of epidemiological studies use $PM_{10}$ as the exposure indicator. $PM_{10}$ represents the particle mass that enters the respiratory tract and, moreover, it includes both the coarse (particle size between 2.5 and 10 μm) and fine particles (measuring less than 2.5 μm, $PM_{2.5}$) that are considered to contribute to the health effects observed in urban environments. The former is primarily produced by mechanical processes such as construction activities, road dust re-suspension and wind, whereas the latter originates primarily from combustion sources. In most urban environments, both coarse and fine mode particles are present, but the proportion of particles in these two size ranges is likely to vary substantially between cities around the world, depending on local geography, meteorology and specific PM sources. In some areas, the combustion of wood and other biomass fuels can be an important source of particulate air pollution, the resulting combustion particles being largely in the fine ($PM_{2.5}$) mode. Although few epidemiological studies have compared the relative toxicity of the products of fossil fuel and biomass combustion, similar effect estimates are found for a wide range of cities in both developed and developing countries. It is, therefore, reasonable to assume that the health effects of $PM_{2.5}$ from both of these sources are broadly the same. By the same token, the WHO AQG for PM can also be applied to the indoor environment, specifically in the developing world, where large populations are exposed to high levels of combustion particles derived from indoor stoves and fires.

Although $PM_{10}$ is the more widely reported measure, and also the indicator of relevance to the majority of the epidemiological data, for reasons that are discussed below, the WHO AQGs for PM are based on studies that use $PM_{2.5}$ as an indicator. The $PM_{2.5}$ guideline values are converted to the corresponding $PM_{10}$ guideline values by application of a $PM_{2.5}/PM_{10}$ ratio of 0.5. A $PM_{2.5}/PM_{10}$ ratio of 0.5 is typical of developing country urban areas and is at the bottom of the range found in developed country urban areas (0.5–0.8). When setting local standards, and assuming the relevant data are available, a different value for this ratio, i.e. one that better reflects local conditions, may be employed.

Based on known health effects, both short-term (24-hour) and long-term (annual mean) guidelines are needed for both indicators of PM pollution.

*Long-term exposures*

An annual average concentration of 10 μg/m$^3$ was chosen as the long-term guideline value for $PM_{2.5.}$ This represents the lower end of the range over which significant effects on survival were observed in the American Cancer Society's (ACS) study (Pope et al., 2002). Adoption of a guideline at this level places significant weight on the long-term exposure studies that use the ACS and the Harvard Six-Cities data (Dockery et al., 1993; Pope et al., 1995; HEI, 2000, Pope et al., 2002, Jerrett, 2005). In all of these studies, robust associations were reported between long-term exposure to $PM_{2.5}$ and mortality. The historical mean $PM_{2.5}$ concentration was 18 μg/m$^3$ (range, 11.0–29.6 μg/m$^3$) in the Six-Cities study and 20 μg/m$^3$ (range, 9.0–33.5 μg/m$^3$) in the ACS study. Thresholds were not apparent in any of these studies, although the precise period(s) and pattern(s) of relevant exposure could not be ascertained. In the ACS study, statistical uncertainty in the risk estimates becomes apparent at concentrations of about 13 μg/m$^3$, below which the confidence bounds significantly widen since the concentrations are relatively far from the mean. According to the results of the Dockery et al. (1993) study, the risks are similar in the cities with the lowest long-term $PM_{2.5}$ concentrations (i.e. 11 and 12.5 μg/m$^3$). Increases in risk are apparent in the city with the next-lowest long-term $PM_{2.5}$ mean (i.e. 14.9 μg/m$^3$), indicating that health effects can be expected when annual mean concentrations are in the range of 11–15 μg/m$^3$. Therefore, an annual mean concentration of 10 μg/m$^3$ can be considered, according to the available scientific literature, to be below the mean for most likely effects. Selecting a long-term mean $PM_{2.5}$ concentration of 10 μg/m$^3$ also places some weight on the results of daily exposure time-series studies that examine the relationships between exposure to $PM_{2.5}$ and acute adverse health outcomes. In these studies, long-term (i.e. three- to four-year) means are reported to be in the range of 13–18 μg/m$^3$. Although adverse effects on health cannot be entirely ruled out below these levels, the annual average WHO AQG value represents that concentration of $PM_{2.5}$ that has not only been shown to be achievable in large urban areas in highly developed countries, but also the attainment of which is expected to significantly reduce the health risks.

Besides the guideline value, three interim targets (IT) are defined for $PM_{2.5}$ (see Table 1). These have been shown to be achievable with successive and sustained abatement measures. Countries may find these interim targets particularly helpful in gauging progress over time in the difficult process of steadily reducing population exposures to PM.

An annual mean $PM_{2.5}$ concentration of 35 μg/m³ was selected as the IT-1 level. This level corresponds to the highest mean concentrations reported in studies of long-term health effects, and may also reflect higher but unknown historical concentrations that may have contributed to observed health effects. This level has been shown to be associated with significant mortality in the developed world.

The IT-2 interim level of protection is set at 25 μg/m³ and relies, as its basis, on the studies of long-term exposure and mortality. This value is greater than the mean concentration at which effects have been observed in such studies, and is likely to be associated with significant health impacts from both long-term and daily exposures to $PM_{2.5}$. Attainment of this IT-2 value would reduce the health risks of long-term exposure by about 6% (95% CI, 2–11%) relative to the IT-1 value. The recommended IT-3 level is 15 μg/m³ and places even greater weight on the likelihood of significant effects associated with long-term exposures. This value is close to the mean concentrations that are reported in studies of long-term exposure and provides an additional 6% reduction in mortality risk relative to the IT-2 value.
Corresponding AQGs and interim targets are also recommended for $PM_{10}$ (Table 1). This is because a $PM_{2\cdot5}$ guideline alone would not provide protection against the harmful effects of coarse PM (the fraction between 10 and 2.5 μm). However, the quantitative evidence on coarse PM is considered insufficient to derive separate guidelines. In contrast, there is a large body of literature on effects of short-term exposures to $PM_{10}$, which has been used as a basis for the development of WHO AQGs and interim targets for 24-hour concentrations of PM (see below).

**Table 1**

**WHOair quality guidelines and interim targets for particulate matter: annual mean concentrations[a]**

| | **$PM_{10}$ (μg/m³)** | **$PM_{2.5}$ (μg/m³)** | **Basis for the selected level** |
|---|---|---|---|
| Iinterim target-1 (IT-1) | 70 | 35 | These levels are associated with about a 15% higher long-term mortality risk relative to the AQG level. |
| Interim target-2 (IT-2) | 50 | 25 | In addition to other health benefits, these levels lower the risk of premature mortality by approximately 6% [2–11%] relative to theIT-1 level. |
| Interim target-3 (IT-3) | 30 | 15 | In addition to other health benefits, these levels reduce the mortality risk by approximately 6% [2-11%] relative to the -IT-2 level. |
| Air quality guideline (AQG) | **20** | **10** | These are the lowest levels at which total, cardiopulmonary and lung cancer mortality have been shown to increase with more than 95% confidence in response to long-term exposure to $PM_{2.5}$. |

[a] The use of $PM_{2.5}$ guideline value is preferred.

*Short-term exposures*

Whether the 24-hour or the annual average AQG, is the more restrictive tends to vary between countries, this being largely dependent on the specific characteristics of pollutant sources and their location. When evaluating the WHO AQGs and interim targets, it is generally recommended that the annual average take precedence over the 24-hour average since, at low levels, there is less concern about episodic excursions. Meeting the guideline values for the 24-hour mean will however protect against peaks of pollution that would otherwise lead to substantial excess morbidity or mortality. It is recommended that countries with areas not meeting the 24-hour guideline values undertake immediate action to achieve these levels in the shortest possible time.

Multi-city studies conducted in Europe (29 cities) and in the United States (20 cities) reported short-term mortality effects for $PM_{10}$ of 0.62% and 0.46% per 10 μg/m$^3$ (24-hour mean), respectively (Katsouyanni et al., 2001; Samet et al., 2000). A meta-analysis of data from 29 cities located outside western Europe and North America found a mortality effect of 0.5% per 10 μg/m$^3$ (Cohen et al., 2004), very similar in fact to that derived for Asian cities (0.49% per 10 μg/m$^3$)(HEI International Oversight Committee, 2004). These findings suggest that the health risks associated with short-term exposures to $PM_{10}$ are likely to be similar in cities in developed and developing countries, producing an increase in mortality of around 0.5% for each 10 μg/m$^3$ increment in the daily concentration. Therefore, a $PM_{10}$ concentration of 150 μg/m$^3$ would be expected to translate into roughly a 5% increase in daily mortality, an impact that would be of significant concern, and one for which immediate mitigation actions would be recommended. The IT-2 level of 100 μg/m$^3$ would be associated with approximately a 2.5% increase in daily mortality, and the IT-3 level with a 1.2% increase (Table 2). For $PM_{10}$, the AQG for the 24-hour average is 50 μg/m$^3$, and reflects the relationship between the distributions of 24-hour means (and its 99th percentile) and annual average concentrations.

**Table 2**

**WHO air quality guidelines and interim targets for particulate matter: 24-hour concentrations[a]**

| | $PM_{10}$ (μg/m$^3$) | $PM_{2.5}$ (μg/m$^3$) | Basis for the selected level |
|---|---|---|---|
| Interim target-1 (IT-1) | 150 | 75 | Based on published risk coefficients from multi-centre studies and meta-analyses (about 5% increase of short-term mortality over the AQG value). |
| Interim target-2 (IT-2) | 100 | 50 | Based on published risk coefficients from multi-centre studies and meta-analyses (about 2.5% increase of short-term mortality over the AQG value). |
| Interim target-3 (IT-3)* | 75 | 37.5 | Based on published risk coefficients from multi-centre studies and meta-analyses (about 1.2% increase in short-term mortality over the AQG value). |
| Air quality guideline (AQG) | **50** | **25** | Based on relationship between 24-hour and annual PM levels. |

[a] 99th percentile (3 days/year).

* For management purposes. Based on annual average guideline values; precise number to be determined on basis of local frequency distribution of daily means. The frequency distribution of daily $PM_{2.5}$ or $PM_{10}$ values usually approximates to a log-normal distribution.

Ultrafine particles (UF), i.e. particles smaller than 0.1 µm in diameter, have recently attracted significant scientific and medical attention. These are usually measured as a number concentration. While there is considerable toxicological evidence of potential detrimental effects of UF particles on human health, the existing body of epidemiological evidence is insufficient to reach a conclusion on the exposure–response relationship of UF particles. Therefore no recommendations can be provided as to guideline concentrations of UF particles at this point in time.

## Ozone

Guideline

**$O_3$: 100 μg/m³ 8-hour mean**

### Rationale

Since the publication of the second edition of the WHO Air quality guidelines for Europe (WHO, 2000) which sets the guideline value for ozone levels at 120 μg/m³ for an 8-hour daily average, little new information about the health effects of ozone has been obtained from either chamber studies or field studies. Significant additions to the health effects evidence base have, however, come from epidemiological time-series studies. Collectively these studies have revealed positive, small, though convincing, associations between daily mortality and ozone levels, which are independent of the effects of particulate matter. Similar associations have been observed in both North America and Europe. These latest time-series studies have shown health effects at ozone concentrations below the previous guideline of 120 μg/m³ but without clear evidence of a threshold. This finding, together with evidence from both chamber and field studies that indicates that there is considerable individual variation in response to ozone, provides a good case for reducing the WHO AQG for ozone from the existing level of 120 μg/m³ to 100 μg/m³ ( daily maximum 8-hour mean).

It is possible that health effects will occur below the new guideline level in some sensitive individuals. Based on time-series studies, the increase in the number of attributable deaths brought forward is estimated to be 1–2% on days when the 8-hour mean ozone concentration reaches 100 μg/m³ over that when ozone levels are at a baseline level of 70 μg/m³ (the estimated background ozone level; see Table 3). There is some evidence that long-term exposure to ozone may have chronic effects but it is not sufficient to recommend an annual guideline.

Ozone is formed in the atmosphere by photochemical reactions in the presence of sunlight and precursor pollutants, such as the oxides of nitrogen (NOx) and volatile organic compounds (VOCs). It is destroyed by reactions with $NO_2$ and is deposited to the ground. Several studies have shown that ozone concentrations correlate with various other toxic photochemical oxidants arising from similar sources, including the peroxyacyl nitrates, nitric acid and hydrogen peroxide. Measures to control tropospheric ozone levels focus its precursor gas emissions, but are likely to also control the levels and impacts of a number of these other pollutants.

Hemispheric background concentrations of tropospheric ozone vary in time and space but can reach 8-hours average levels of around 80 μg/m³. These arise from both anthropogenic and biogenic emissions (e.g. VOCs from vegetation) of ozone precursors and downward intrusion of stratospheric ozone into the troposphere. Indeed, the proposed guideline value may occasionally be exceeded due to natural causes.

As ozone concentrations increase above the guideline value, health effects at the population level become increasingly numerous and severe. Such effects can occur in places where concentrations are currently high due to human activities or are elevated during episodes of very hot weather.

The 8-hour IT-1 level for ozone has been set at 160 μg/m³ at which measurable, though transient, changes in lung function and lung inflammation have been recorded in controlled chamber tests in healthy young adults undertaking intermittent exercise. Similar effects were observed in summer camp studies, involving exercising children. Although some would argue that these responses may not necessarily be adverse, and that they were seen only with vigorous exercise, these views are counterbalanced by the possibility that there are substantial numbers of persons in the general population that might be more susceptible to the effects of ozone than the relatively young and generally healthy individuals who participated in the chamber study. Furthermore, chamber studies provide little information about repeated exposures. Based on time-series evidence, exposures at the IT-1 level are associated with an increase in the number of attributable deaths brought forward of 3–5% (see Table 3).

At 8-hour concentrations exceeding 240 µg/m$^3$, significant health effects are considered likely. This conclusion is based on the findings of a large number of clinical inhalation and field studies. Both healthy adults and asthmatics would be expected to experience significant reductions in lung function, as well as airway inflammation that would cause symptoms and alter performance. There are additional concerns about increased respiratory morbidity in children. According to time-series evidence, exposure to concentrations of ozone of this magnitude, would result in a rise in the number of attributable deaths brought forward of 5–9%, relative to exposures at the estimated background level (see Table 3).

## Table 3

**WHO air quality guideline and interim target for ozone: 8-hour concentrations**

| | **Daily maximum 8-hour mean ($\mu$g/m$^3$)** | **Basis for selected level** |
|---|---|---|
| High levels | 240 | Significant health effects; substantial proportion of vulnerable populations affected. |
| Interim target-1 (IT-1) | 160 | Important health effects; does not provide adequate protection of public health. Exposure to this level of ozone is associated with:<br>• physiological and inflammatory lung effects in healthy exercising young adults exposed for periods of 6.6 hours;<br>• health effects in children (based on various summer camp studies in which children were exposed to ambient ozone levels).<br>• an estimated 3–5% increase in daily mortality[a] (based on findings of daily time-series studies). |
| **Air quality guideline (AQG)** | **100** | Provides adequate protection of public health, though some health effects may occur below this level. Exposure to this level of ozone is associated with:<br>• an estimated 1–2% increase in daily mortality[a] (based on findings of daily time-series studies).<br>• Extrapolation from chamber and field studies based on the likelihood that real-life exposure tends to be repetitive and chamber studies exclude highly sensitive or clinically compromised subjects, or children.<br>• Likelihood that ambient ozone is a marker for related oxidants. |

[a] Deaths attributable to ozone. Time-series studies indicate an increase in daily mortality in the range of 0.3–0.5% for every 10 $\mu$g/m$^3$ increment in 8-hour ozone concentrations above an estimated baseline level of 70 $\mu$g/m$^3$.

# Nitrogen dioxide

Guidelines

**$NO_2$:** **40 $\mu g/m^3$ annual mean**
**200 $\mu g/m^3$ 1-hour mean**

## Rationale

As an air pollutant, nitrogen dioxide ($NO_2$) has multiple roles, which are often difficult or sometimes impossible to separate from one another:

i. Animal and human experimental studies indicate that $NO_2$ – at short-term concentrations exceeding 200 µg/$m^3$ – is a toxic gas with significant health effects. Animal toxicological studies also suggest that long-term exposure to $NO_2$ at concentrations above current ambient concentrations has adverse effects.

ii. Numerous epidemiological studies have used $NO_2$ as a marker for the cocktail of combustion-related pollutants, in particular, those emitted by road traffic or indoor combustion sources. In these studies, any observed health effects could also have been associated with other combustion products, such as ultrafine particles, nitrous oxide (NO), particulate matter or benzene. Although several studies – both outdoors and indoors – have attempted to focus on the health risks of $NO_2$, the contributing effects of these other, highly correlated co-pollutants were often difficult to rule out.

iii. Most atmospheric $NO_2$ is emitted as NO, which is rapidly oxidized by ozone to $NO_2$. Nitrogen dioxide, in the presence of hydrocarbons and ultraviolet light, is the main source of tropospheric ozone and of nitrate aerosols, which form an important fraction of the ambient air $PM_{2.5}$ mass.

The current WHO guideline value of 40 µg/$m^3$ (annual mean) was set to protect the public from the health effects of gaseous $NO_2$. The rationale for this was that because most abatement methods are specific to $NO_x$, they are not designed to control other co-pollutants, and may even increase their emissions. If, however, $NO_2$ is monitored as a marker for complex combustion-generated pollution mixtures, a lower annual guideline value should be used (WHO, 2000).

*Long-term exposures*

There is still no robust basis for setting an annual average guideline value for $NO_2$ through any direct toxic effect. Evidence has emerged, however, that increases the concern over health effects associated with outdoor air pollution mixtures that include $NO_2$. For instance, epidemiological studies have shown that bronchitic symptoms of asthmatic children increase in association with annual $NO_2$ concentration, and that reduced lung function growth in children is linked to elevated $NO_2$ concentrations within communities already at current North American and European urban ambient air levels. A number of recently published studies have demonstrated that $NO_2$ can have a higher spatial variation than other traffic-related air pollutants, for example, particle mass. These studies also found adverse effects on the health of children living in metropolitan areas characterized by higher levels of $NO_2$ even in cases where the overall city-wide $NO_2$ level was fairly low.

Recent indoor studies have provided evidence of effects on respiratory symptoms among infants at $NO_2$ concentrations below 40 µg/$m^3$. These associations cannot be completely explained by co-exposure to PM, but it has been suggested that other components in the mixture (such as organic carbon and nitrous acid vapour) might explain part of the observed association.

Taken together, the above findings provide some support for a lowering of the current annual $NO_2$ guideline value. However, it is unclear to what extent the health effects observed in epidemiological studies are attributable to $NO_2$ itself or to the other primary and secondary combustion-related products with which it is typically correlated. Thus it can be argued that the available scientific literature has not accumulated sufficient evidence to justify revising the existing WHO AQG for annual $NO_2$ concentrations. Nevertheless, since $NO_2$ concentrations in ambient air are routinely measured but those of other correlated combustion-derived pollutants are not, it seems reasonable to retain a prudent annual average limit value for $NO_2$. Such a limit allows for the fact that there may be direct toxic effects of chronic $NO_2$ exposure at low levels. In addition, maintaining the annual guideline value may help to control complex mixtures of combustion-related pollution (mainly from road traffic)

*Short-term exposures*

A number of short-term experimental human toxicology studies have reported acute health effects following exposure to 1-hour $NO_2$ concentrations in excess of 500 $\mu g/m^3$. Although the lowest level of $NO_2$ exposure to show a direct effect on pulmonary function in asthmatics in more than one laboratory is 560 $\mu g/m^3$, studies of bronchial responsiveness among asthmatics suggest an increase in responsiveness at levels upwards from 200 $\mu g/m^3$.

Since the existing WHO AQG short-term $NO_2$ guideline value of 200 $\mu g/m^3$ (1-hour) has not been challenged by more recent studies, it is retained.

In conclusion, the guideline values for $NO_2$ remain unchanged in comparison to the existing WHO AQG levels, i.e. 40 $\mu g/m^3$ for annual mean and 200 $\mu g/m^3$ for 1-hour mean.

## Sulfur dioxide

Guidelines

**$SO_2$:** **20 $\mu g/m^3$ 24-hour mean**
**500 $\mu g/m^3$ 10-minute mean**

### Rationale

*Short-term exposures*
Controlled studies involving exercising asthmatics indicate that a proportion experience changes in pulmonary function and respiratory symptoms after periods of exposure to $SO_2$ as short as 10 minutes. Based on this evidence, it is recommended that a $SO_2$ concentration of 500 $\mu g/m^3$ should not be exceeded over averaging periods of 10 minutes duration. Because short-term $SO_2$ exposure depends very much on the nature of local sources and the prevailing meteorological conditions, it is not possible to apply a simple factor to this value in order to estimate corresponding guideline values over longer time periods, such as one hour.

*Long-term exposures (over 24-hours)*
Early estimates of day-to-day changes in mortality, morbidity or lung function in relation to 24-hour average concentrations of $SO_2$ were necessarily based on epidemiological studies in which people are typically exposed to a mixture of pollutants. As there was little basis for separating the contributions of individual pollutants to the observed health outcomes, prior to 1987, guideline values for $SO_2$ were linked to corresponding values for PM. This approach led to the setting of an AQG value for $SO_2$ of 125 $\mu g/m^3$ as a 24-hour average, after applying an uncertainty factor of 2 to the lowest-observed-adverse-effect level (WHO, 1987). In the second edition of the WHO *Air quality guidelines for Europe* (WHO, 2000), it was noted that later epidemiological studies documented separate and independent adverse public health effects for PM and $SO_2$, and this led to a separate WHO AQG for $SO_2$ of 125 $\mu g/m^3$ (24-hour mean). The latest evidence to emerge includes a study conducted in Hong Kong (Hedley et al., 2002) where a major reduction in the sulfur content of fuels has been achieved over a very short period of time. This has been linked to substantial reductions in health effects (e.g. childhood respiratory disease and all-age mortality). Recent time-series studies on hospital admissions for cardiac disease in Hong Kong and London, produced no evidence of a threshold for health effects at 24-hour $SO_2$ concentrations in the range of 5–40 $\mu g/m^3$ (Wong et al., 2002). Twenty-four hour $SO_2$ levels were significantly associated with daily mortality rates in 12 Canadian cities, which had an average concentration of only 5 $\mu g/m^3$ (the highest mean $SO_2$ level was below 10 $\mu g/m^3$) (Burnett et al., 2004). In the American Cancer Society (ACS) study (see Particulate matter), significant associations between $SO_2$ and mortality were observed for the 1982–1998 cohort in 126 United States metropolitan areas, in which the mean $SO_2$ concentration recorded was 18 $\mu g/m^3$, and the highest mean, 85 $\mu g/m^3$ (Pope et al., 2002). If there were a threshold for effects in either of these two studies, it would have to be very low.

There is still considerable uncertainty as to whether $SO_2$ is the pollutant responsible for the observed adverse effects or whether it is a surrogate for ultrafine particles or some other correlated substance. Both Germany (Wichmann et al., 2000) and the Netherlands (Buringh, Fisher & Hoek, 2000) have experienced a strong reduction in $SO_2$ concentrations over a decade, but although mortality also decreased with time, the association between $SO_2$ and mortality was not judged to be causal in either case the fall in mortality and was instead attributed to a similar time trend in a different pollutant (PM).

In consideration of: a) the uncertainty of $SO_2$ in causality; b) the practical difficulty of attaining levels that are certain to be associated with no effects; and c) the need to provide a greater degree of protection than that provided by the present AQG, and assuming that reduction in exposure to a causal and correlated substance is achieved by reducing $SO_2$concentrations, there is a basis for revising the 24-hour guideline for $SO_2$ downwards adopting a prudent precautionary approach to a value of 20 µg/m$^3$.

## Table 4

**WHO air quality guidelines and interim targets for $SO_2$: 24-hour and 10-minute concentrations**

| | 24-hour average (µg/m$^3$) | 10-minute average (µg/m$^3$) | Basis for selected level |
|---|---|---|---|
| Interim target-1 (IT-1)[a] | 125 | – | |
| Interim target-2 (IT-2) | 50 | – | Intermediate goal based on controlling either motor vehicle emissions, industrial emissions and/or emissions from power production. This would be a reasonable and feasible goal for some developing countries (it could be achieved within a few years) which would lead to significant health improvements that, in turn, would justify further improvements (such as aiming for the AQG value). |
| **Air quality guideline (AQG)** | **20** | **500** | |

[a] Formerly the WHO Air Quality Guideline (WHO, 2000).

An annual guideline is not needed, since compliance with the 24-hour level will assure low annual average levels. These recommended guideline values for $SO_2$ are not linked to those for PM. Since the revised 24-hour guideline may be quite difficult for some countries to achieve in the short term, a stepped approach using interim goals is recommended (see Table 4). For instance, a country could move towards compliance with the guideline by controlling emissions from one major source at a time, selecting from among motor vehicle sources, industrial sources and power sources (which would achieve the greatest effect on $SO_2$ levels for the lowest cost), and follow this up with monitoring of public health and $SO_2$ levels for health effect gains. Demonstrating health benefits should provide an incentive to mandate controls for the next major source category.

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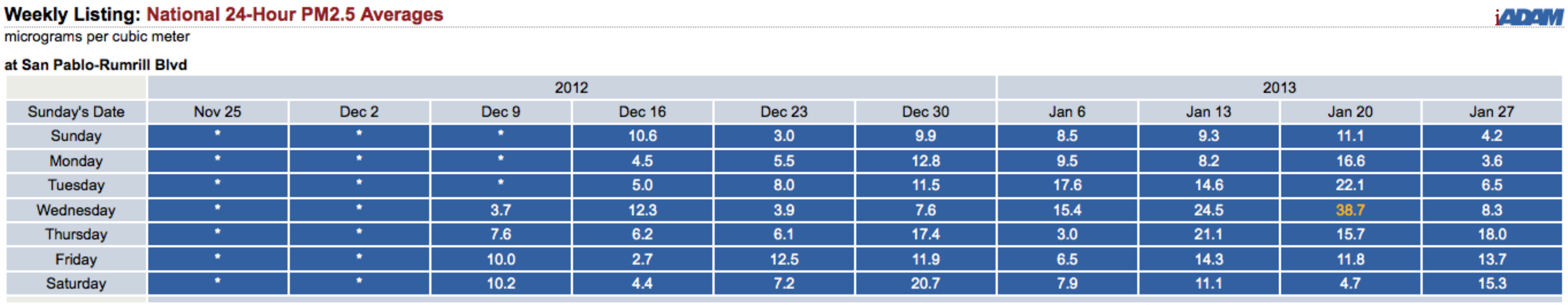
The WHO air quality guidelines are designed to offer guidance in reducing the health impacts of air pollution. Based on a review of the accumulated scientific evidence, the revised guideline values for the most common air pollutants are presented in this document. These guidelines are applicable across all WHO regions and inform policy-makers considering various options for air quality management in different parts of the world about the targets for air quality.

**Attachment 38**

**Attachment 38.** PM$_{2.5}$ ambient air concentrations exceeding EPA and WHO health criteria at the five NAAQS monitoring stations nearest to Bay Area oil refineries, from May 2012 through April 2015: Ambient air concentrations in micrograms per cubic meter as 24-hour averages; the EPA NAAQS and WHO 24-hour criteria are 35 and 25 µg/m$^3$, respectively.

Data are from Air Resources Board; http://www.arb.ca.gov/adam/weekly/weekly2.php; accessed 16 November 2015. Data shown include ten-week periods including periods when health criteria were exceeded. For comparison among stations, note that San Pablo Station data were not reported before 12 December 2012, and West Oakland Station data were not reported before 18 December 2012.

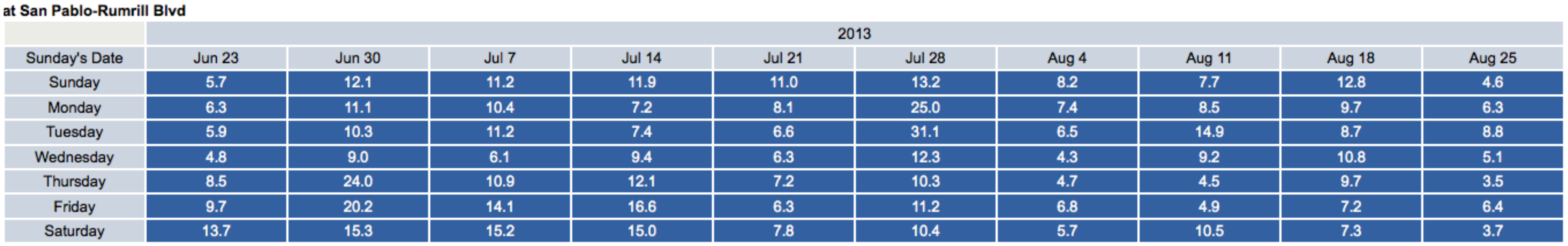


**Weekly Listing:** National 24-Hour PM2.5 Averages

micrograms per cubic meter

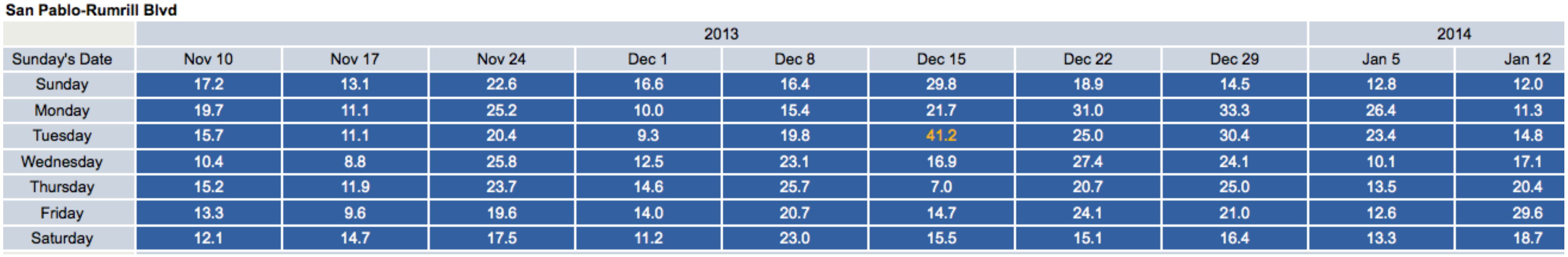
**at San Pablo-Rumrill Blvd**

| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | * | * | * | 10.6 | 3.0 | 9.9 | 8.5 | 9.3 | 11.1 | 4.2 |
| Monday | * | * | * | 4.5 | 5.5 | 12.8 | 9.5 | 8.2 | 16.6 | 3.6 |
| Tuesday | * | * | * | 5.0 | 8.0 | 11.5 | 17.6 | 14.6 | 22.1 | 6.5 |
| Wednesday | * | * | 3.7 | 12.3 | 3.9 | 7.6 | 15.4 | 24.5 | 38.7 | 8.3 |
| Thursday | * | * | 7.6 | 6.2 | 6.1 | 17.4 | 3.0 | 21.1 | 15.7 | 18.0 |
| Friday | * | * | 10.0 | 2.7 | 12.5 | 11.9 | 6.5 | 14.3 | 11.8 | 13.7 |
| Saturday | * | * | 10.2 | 4.4 | 7.2 | 20.7 | 7.9 | 11.1 | 4.7 | 15.3 |



**at San Pablo-Rumrill Blvd**

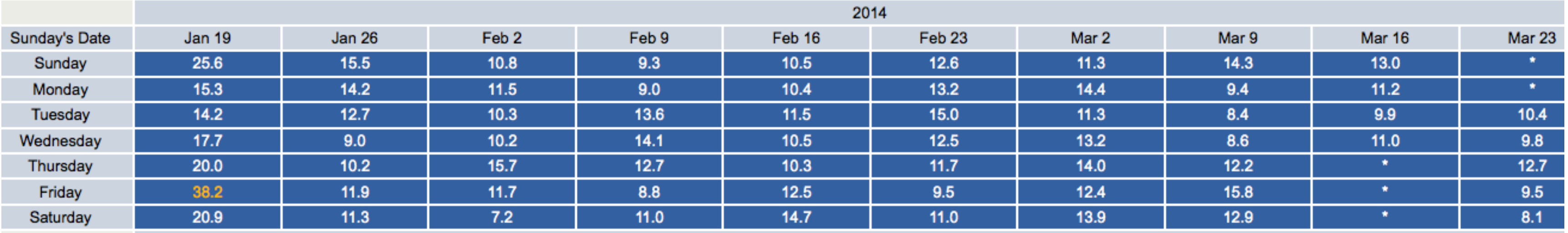
| | 2013 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jun 23 | Jun 30 | Jul 7 | Jul 14 | Jul 21 | Jul 28 | Aug 4 | Aug 11 | Aug 18 | Aug 25 |
| Sunday | 5.7 | 12.1 | 11.2 | 11.9 | 11.0 | 13.2 | 8.2 | 7.7 | 12.8 | 4.6 |
| Monday | 6.3 | 11.1 | 10.4 | 7.2 | 8.1 | 25.0 | 7.4 | 8.5 | 9.7 | 6.3 |
| Tuesday | 5.9 | 10.3 | 11.2 | 7.4 | 6.6 | 31.1 | 6.5 | 14.9 | 8.7 | 8.8 |
| Wednesday | 4.8 | 9.0 | 6.1 | 9.4 | 6.3 | 12.3 | 4.3 | 9.2 | 10.8 | 5.1 |
| Thursday | 8.5 | 24.0 | 10.9 | 12.1 | 7.2 | 10.3 | 4.7 | 4.5 | 9.7 | 3.5 |
| Friday | 9.7 | 20.2 | 14.1 | 16.6 | 6.3 | 11.2 | 6.8 | 4.9 | 7.2 | 6.4 |
| Saturday | 13.7 | 15.3 | 15.2 | 15.0 | 7.8 | 10.4 | 5.7 | 10.5 | 7.3 | 3.7 |



**San Pablo-Rumrill Blvd**

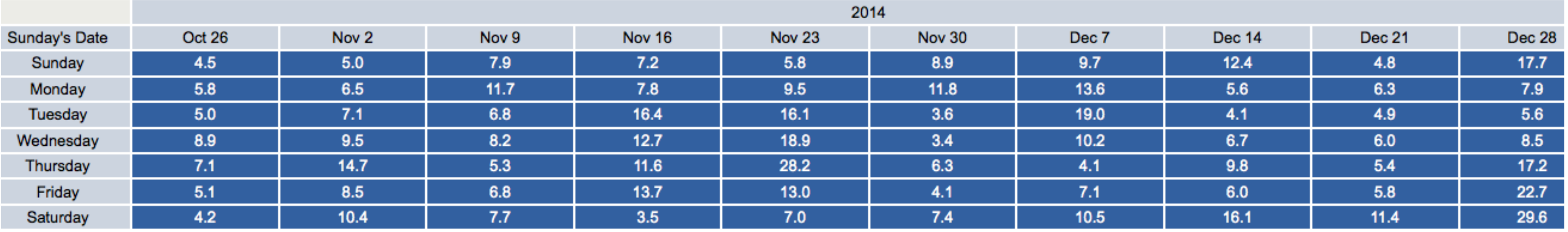
| | 2013 | | | | | | | | 2014 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 10 | Nov 17 | Nov 24 | Dec 1 | Dec 8 | Dec 15 | Dec 22 | Dec 29 | Jan 5 | Jan 12 |
| Sunday | 17.2 | 13.1 | 22.6 | 16.6 | 16.4 | 29.8 | 18.9 | 14.5 | 12.8 | 12.0 |
| Monday | 19.7 | 11.1 | 25.2 | 10.0 | 15.4 | 21.7 | 31.0 | 33.3 | 26.4 | 11.3 |
| Tuesday | 15.7 | 11.1 | 20.4 | 9.3 | 19.8 | 41.2 | 25.0 | 30.4 | 23.4 | 14.8 |
| Wednesday | 10.4 | 8.8 | 25.8 | 12.5 | 23.1 | 16.9 | 27.4 | 24.1 | 10.1 | 17.1 |
| Thursday | 15.2 | 11.9 | 23.7 | 14.6 | 25.7 | 7.0 | 20.7 | 25.0 | 13.5 | 20.4 |
| Friday | 13.3 | 9.6 | 19.6 | 14.0 | 20.7 | 14.7 | 24.1 | 21.0 | 12.6 | 29.6 |
| Saturday | 12.1 | 14.7 | 17.5 | 11.2 | 23.0 | 15.5 | 15.1 | 16.4 | 13.3 | 18.7 |

**San Pablo-Rumrill Blvd**



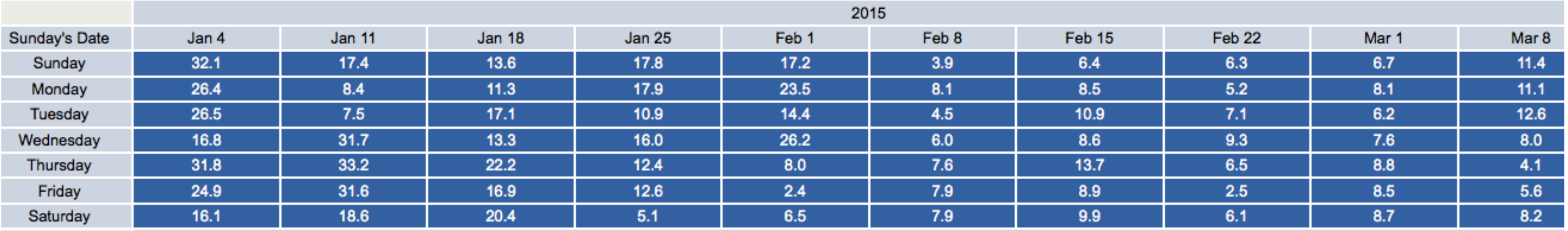
| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 19 | Jan 26 | Feb 2 | Feb 9 | Feb 16 | Feb 23 | Mar 2 | Mar 9 | Mar 16 | Mar 23 |
| Sunday | 25.6 | 15.5 | 10.8 | 9.3 | 10.5 | 12.6 | 11.3 | 14.3 | 13.0 | * |
| Monday | 15.3 | 14.2 | 11.5 | 9.0 | 10.4 | 13.2 | 14.4 | 9.4 | 11.2 | * |
| Tuesday | 14.2 | 12.7 | 10.3 | 13.6 | 11.5 | 15.0 | 11.3 | 8.4 | 9.9 | 10.4 |
| Wednesday | 17.7 | 9.0 | 10.2 | 14.1 | 10.5 | 12.5 | 13.2 | 8.6 | 11.0 | 9.8 |
| Thursday | 20.0 | 10.2 | 15.7 | 12.7 | 10.3 | 11.7 | 14.0 | 12.2 | * | 12.7 |
| Friday | 38.2 | 11.9 | 11.7 | 8.8 | 12.5 | 9.5 | 12.4 | 15.8 | * | 9.5 |
| Saturday | 20.9 | 11.3 | 7.2 | 11.0 | 14.7 | 11.0 | 13.9 | 12.9 | * | 8.1 |

**San Pablo-Rumrill Blvd**



| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Oct 26 | Nov 2 | Nov 9 | Nov 16 | Nov 23 | Nov 30 | Dec 7 | Dec 14 | Dec 21 | Dec 28 |
| Sunday | 4.5 | 5.0 | 7.9 | 7.2 | 5.8 | 8.9 | 9.7 | 12.4 | 4.8 | 17.7 |
| Monday | 5.8 | 6.5 | 11.7 | 7.8 | 9.5 | 11.8 | 13.6 | 5.6 | 6.3 | 7.9 |
| Tuesday | 5.0 | 7.1 | 6.8 | 16.4 | 16.1 | 3.6 | 19.0 | 4.1 | 4.9 | 5.6 |
| Wednesday | 8.9 | 9.5 | 8.2 | 12.7 | 18.9 | 3.4 | 10.2 | 6.7 | 6.0 | 8.5 |
| Thursday | 7.1 | 14.7 | 5.3 | 11.6 | 28.2 | 6.3 | 4.1 | 9.8 | 5.4 | 17.2 |
| Friday | 5.1 | 8.5 | 6.8 | 13.7 | 13.0 | 4.1 | 7.1 | 6.0 | 5.8 | 22.7 |
| Saturday | 4.2 | 10.4 | 7.7 | 3.5 | 7.0 | 7.4 | 10.5 | 16.1 | 11.4 | 29.6 |

**San Pablo-Rumrill Blvd**



| | 2015 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 4 | Jan 11 | Jan 18 | Jan 25 | Feb 1 | Feb 8 | Feb 15 | Feb 22 | Mar 1 | Mar 8 |
| Sunday | 32.1 | 17.4 | 13.6 | 17.8 | 17.2 | 3.9 | 6.4 | 6.3 | 6.7 | 11.4 |
| Monday | 26.4 | 8.4 | 11.3 | 17.9 | 23.5 | 8.1 | 8.5 | 5.2 | 8.1 | 11.1 |
| Tuesday | 26.5 | 7.5 | 17.1 | 10.9 | 14.4 | 4.5 | 10.9 | 7.1 | 6.2 | 12.6 |
| Wednesday | 16.8 | 31.7 | 13.3 | 16.0 | 26.2 | 6.0 | 8.6 | 9.3 | 7.6 | 8.0 |
| Thursday | 31.8 | 33.2 | 22.2 | 12.4 | 8.0 | 7.6 | 13.7 | 6.5 | 8.8 | 4.1 |
| Friday | 24.9 | 31.6 | 16.9 | 12.6 | 2.4 | 7.9 | 8.9 | 2.5 | 8.5 | 5.6 |
| Saturday | 16.1 | 18.6 | 20.4 | 5.1 | 6.5 | 7.9 | 9.9 | 6.1 | 8.7 | 8.2 |

# CBE Attachment 11

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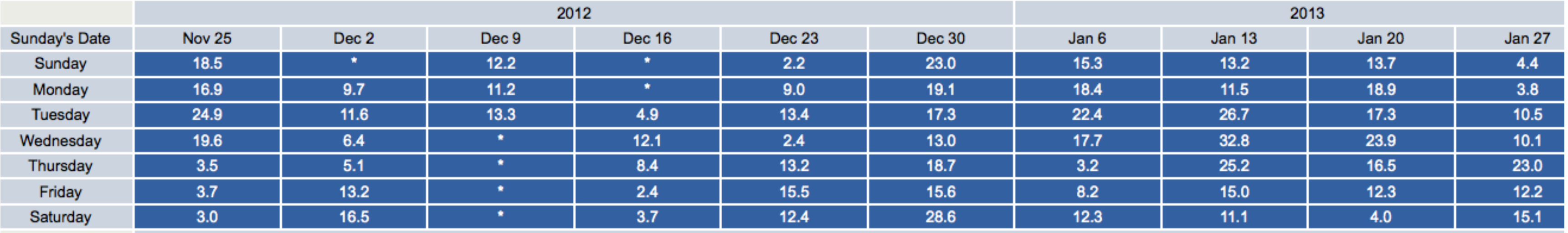
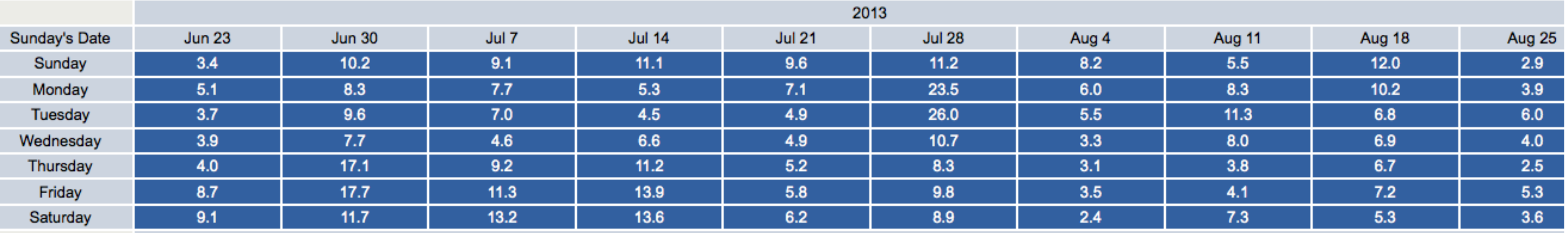
**Vallejo-304 Tuolumne Street**



| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | 18.5 | * | 12.2 | * | 2.2 | 23.0 | 15.3 | 13.2 | 13.7 | 4.4 |
| Monday | 16.9 | 9.7 | 11.2 | * | 9.0 | 19.1 | 18.4 | 11.5 | 18.9 | 3.8 |
| Tuesday | 24.9 | 11.6 | 13.3 | 4.9 | 13.4 | 17.3 | 22.4 | 26.7 | 17.3 | 10.5 |
| Wednesday | 19.6 | 6.4 | * | 12.1 | 2.4 | 13.0 | 17.7 | 32.8 | 23.9 | 10.1 |
| Thursday | 3.5 | 5.1 | * | 8.4 | 13.2 | 18.7 | 3.2 | 25.2 | 16.5 | 23.0 |
| Friday | 3.7 | 13.2 | * | 2.4 | 15.5 | 15.6 | 8.2 | 15.0 | 12.3 | 12.2 |
| Saturday | 3.0 | 16.5 | * | 3.7 | 12.4 | 28.6 | 12.3 | 11.1 | 4.0 | 15.1 |

**Vallejo-304 Tuolumne Street**

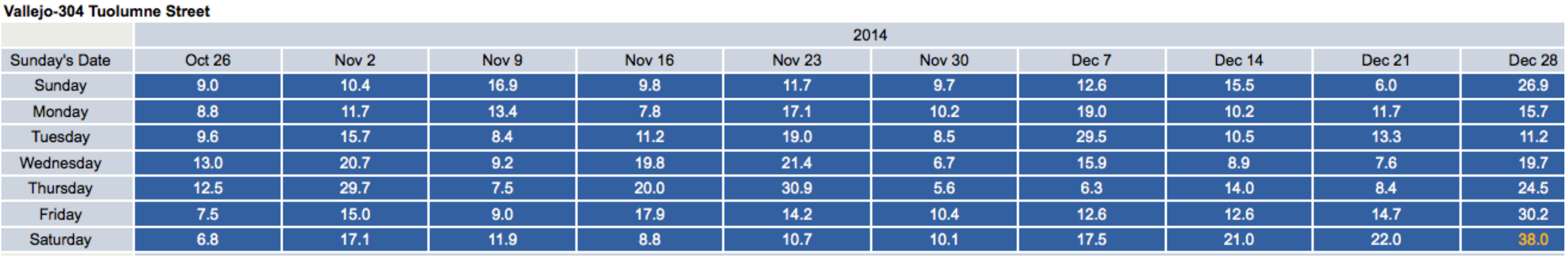


| | 2013 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jun 23 | Jun 30 | Jul 7 | Jul 14 | Jul 21 | Jul 28 | Aug 4 | Aug 11 | Aug 18 | Aug 25 |
| Sunday | 3.4 | 10.2 | 9.1 | 11.1 | 9.6 | 11.2 | 8.2 | 5.5 | 12.0 | 2.9 |
| Monday | 5.1 | 8.3 | 7.7 | 5.3 | 7.1 | 23.5 | 6.0 | 8.3 | 10.2 | 3.9 |
| Tuesday | 3.7 | 9.6 | 7.0 | 4.5 | 4.9 | 26.0 | 5.5 | 11.3 | 6.8 | 6.0 |
| Wednesday | 3.9 | 7.7 | 4.6 | 6.6 | 4.9 | 10.7 | 3.3 | 8.0 | 6.9 | 4.0 |
| Thursday | 4.0 | 17.1 | 9.2 | 11.2 | 5.2 | 8.3 | 3.1 | 3.8 | 6.7 | 2.5 |
| Friday | 8.7 | 17.7 | 11.3 | 13.9 | 5.8 | 9.8 | 3.5 | 4.1 | 7.2 | 5.3 |
| Saturday | 9.1 | 11.7 | 13.2 | 13.6 | 6.2 | 8.9 | 2.4 | 7.3 | 5.3 | 3.6 |

**Vallejo-304 Tuolumne Street**

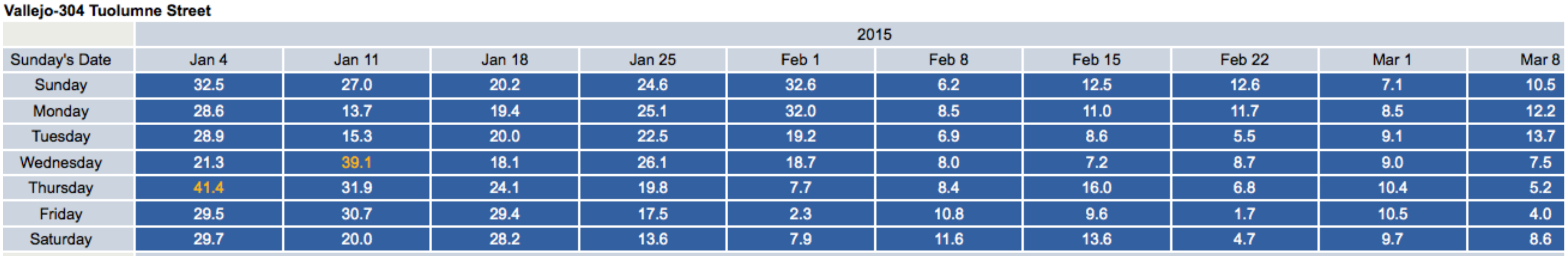
| | 2013 | | | | | | | | 2014 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 10 | Nov 17 | Nov 24 | Dec 1 | Dec 8 | Dec 15 | Dec 22 | Dec 29 | Jan 5 | Jan 12 |
| Sunday | 12.5 | 8.7 | 31.7 | 21.5 | 13.9 | 33.7 | 31.9 | 18.6 | 11.7 | 5.3 |
| Monday | 19.4 | 8.3 | 29.9 | 11.6 | 11.2 | 28.8 | 39.3 | 35.5 | 23.0 | 5.5 |
| Tuesday | 13.0 | 7.0 | 17.3 | 6.5 | 17.2 | 38.7 | 31.3 | 42.6 | 18.2 | 13.6 |
| Wednesday | 7.7 | 1.8 | 16.4 | 13.1 | 21.7 | 16.4 | 36.5 | 39.6 | 5.2 | 20.1 |
| Thursday | 11.0 | 9.4 | 14.7 | 26.2 | 23.5 | 6.0 | 18.3 | 24.0 | 3.5 | 23.4 |
| Friday | 6.9 | 8.2 | 20.2 | 19.7 | 25.2 | 12.2 | 18.4 | 30.7 | 11.4 | 31.8 |
| Saturday | 5.2 | 17.4 | 20.5 | 7.0 | 38.0 | 17.4 | 19.2 | 22.3 | 9.8 | 17.9 |

# CBE Attachment 11



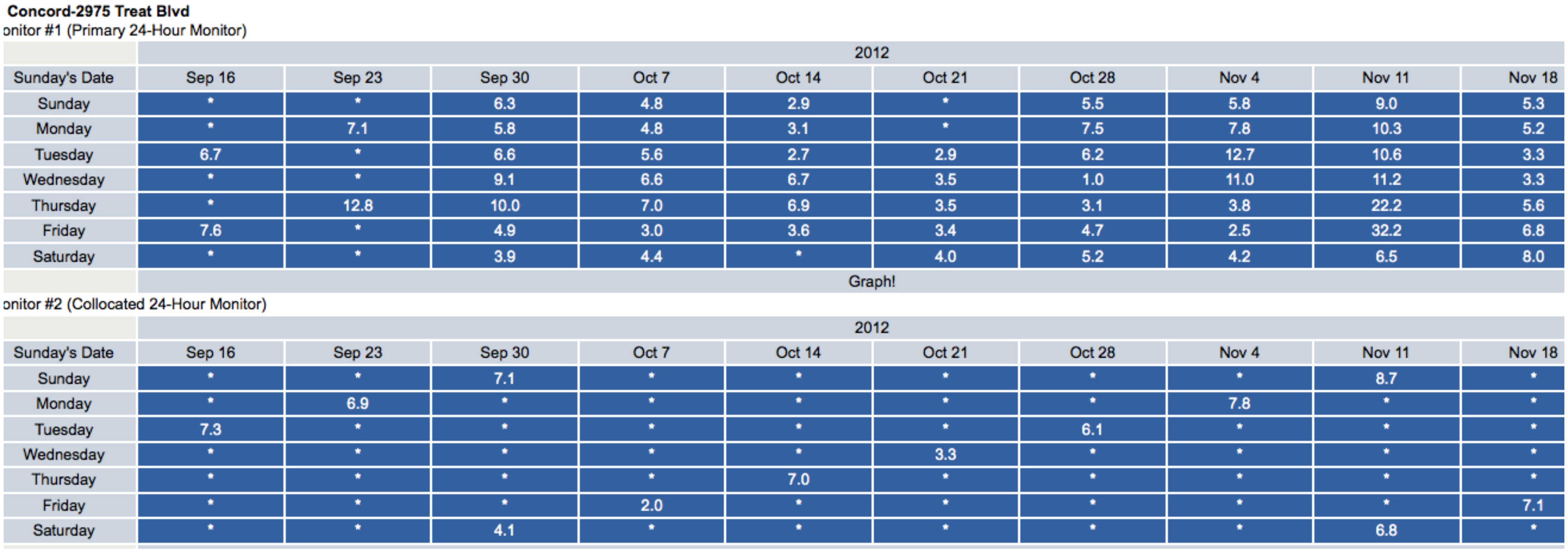
**Vallejo-304 Tuolumne Street**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Oct 26 | Nov 2 | Nov 9 | Nov 16 | Nov 23 | Nov 30 | Dec 7 | Dec 14 | Dec 21 | Dec 28 |
| Sunday | 9.0 | 10.4 | 16.9 | 9.8 | 11.7 | 9.7 | 12.6 | 15.5 | 6.0 | 26.9 |
| Monday | 8.8 | 11.7 | 13.4 | 7.8 | 17.1 | 10.2 | 19.0 | 10.2 | 11.7 | 15.7 |
| Tuesday | 9.6 | 15.7 | 8.4 | 11.2 | 19.0 | 8.5 | 29.5 | 10.5 | 13.3 | 11.2 |
| Wednesday | 13.0 | 20.7 | 9.2 | 19.8 | 21.4 | 6.7 | 15.9 | 8.9 | 7.6 | 19.7 |
| Thursday | 12.5 | 29.7 | 7.5 | 20.0 | 30.9 | 5.6 | 6.3 | 14.0 | 8.4 | 24.5 |
| Friday | 7.5 | 15.0 | 9.0 | 17.9 | 14.2 | 10.4 | 12.6 | 12.6 | 14.7 | 30.2 |
| Saturday | 6.8 | 17.1 | 11.9 | 8.8 | 10.7 | 10.1 | 17.5 | 21.0 | 22.0 | 38.0 |



**Vallejo-304 Tuolumne Street**

| | 2015 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 4 | Jan 11 | Jan 18 | Jan 25 | Feb 1 | Feb 8 | Feb 15 | Feb 22 | Mar 1 | Mar 8 |
| Sunday | 32.5 | 27.0 | 20.2 | 24.6 | 32.6 | 6.2 | 12.5 | 12.6 | 7.1 | 10.5 |
| Monday | 28.6 | 13.7 | 19.4 | 25.1 | 32.0 | 8.5 | 11.0 | 11.7 | 8.5 | 12.2 |
| Tuesday | 28.9 | 15.3 | 20.0 | 22.5 | 19.2 | 6.9 | 8.6 | 5.5 | 9.1 | 13.7 |
| Wednesday | 21.3 | 39.1 | 18.1 | 26.1 | 18.7 | 8.0 | 7.2 | 8.7 | 9.0 | 7.5 |
| Thursday | 41.4 | 31.9 | 24.1 | 19.8 | 7.7 | 8.4 | 16.0 | 6.8 | 10.4 | 5.2 |
| Friday | 29.5 | 30.7 | 29.4 | 17.5 | 2.3 | 10.8 | 9.6 | 1.7 | 10.5 | 4.0 |
| Saturday | 29.7 | 20.0 | 28.2 | 13.6 | 7.9 | 11.6 | 13.6 | 4.7 | 9.7 | 8.6 |



**Concord-2975 Treat Blvd**

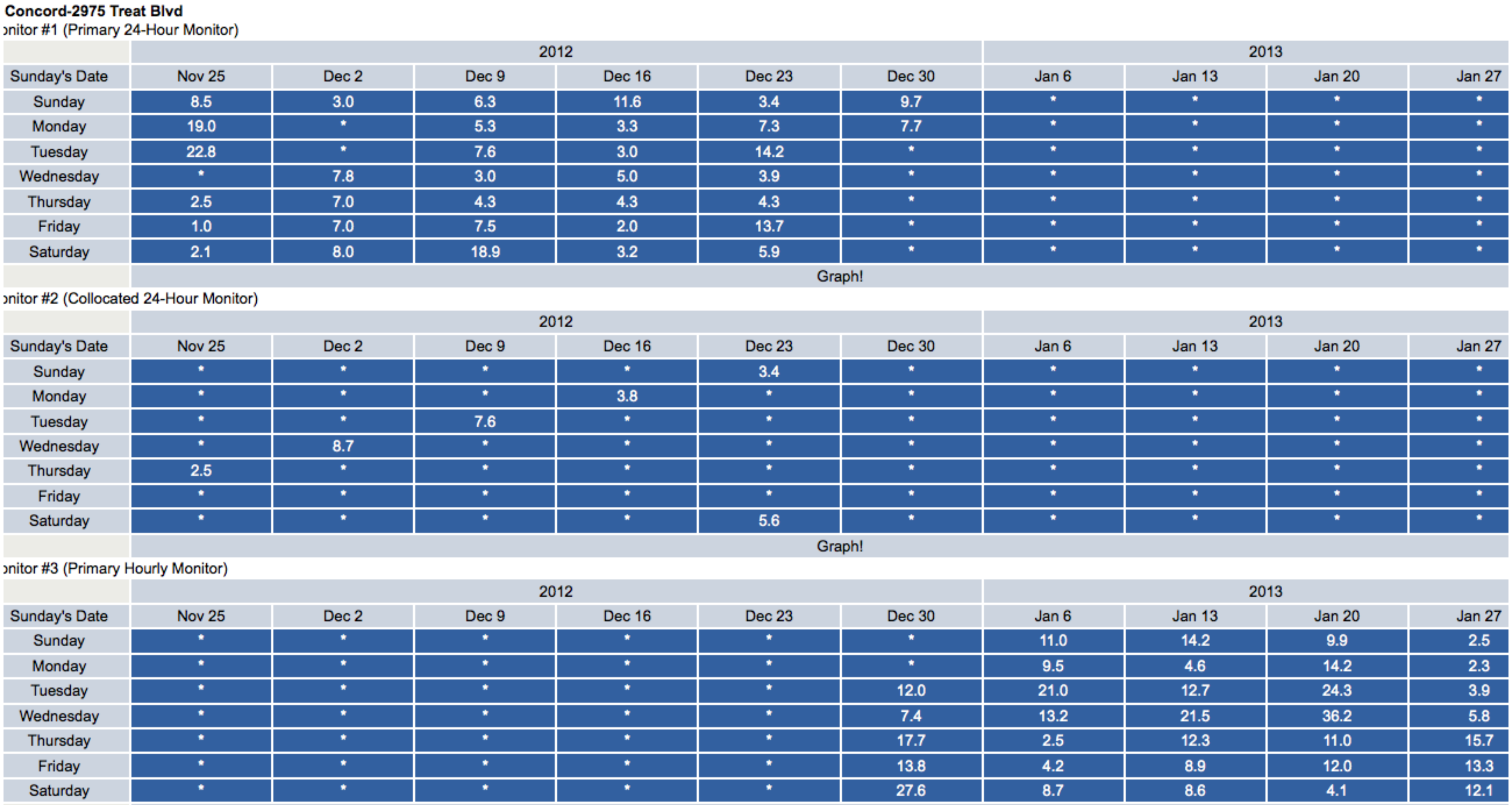
onitor #1 (Primary 24-Hour Monitor)

| | 2012 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Sep 16 | Sep 23 | Sep 30 | Oct 7 | Oct 14 | Oct 21 | Oct 28 | Nov 4 | Nov 11 | Nov 18 |
| Sunday | * | * | 6.3 | 4.8 | 2.9 | * | 5.5 | 5.8 | 9.0 | 5.3 |
| Monday | * | 7.1 | 5.8 | 4.8 | 3.1 | * | 7.5 | 7.8 | 10.3 | 5.2 |
| Tuesday | 6.7 | * | 6.6 | 5.6 | 2.7 | 2.9 | 6.2 | 12.7 | 10.6 | 3.3 |
| Wednesday | * | * | 9.1 | 6.6 | 6.7 | 3.5 | 1.0 | 11.0 | 11.2 | 3.3 |
| Thursday | * | 12.8 | 10.0 | 7.0 | 6.9 | 3.5 | 3.1 | 3.8 | 22.2 | 5.6 |
| Friday | 7.6 | * | 4.9 | 3.0 | 3.6 | 3.4 | 4.7 | 2.5 | 32.2 | 6.8 |
| Saturday | * | * | 3.9 | 4.4 | * | 4.0 | 5.2 | 4.2 | 6.5 | 8.0 |

Graph!

onitor #2 (Collocated 24-Hour Monitor)

| | 2012 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Sep 16 | Sep 23 | Sep 30 | Oct 7 | Oct 14 | Oct 21 | Oct 28 | Nov 4 | Nov 11 | Nov 18 |
| Sunday | * | * | 7.1 | * | * | * | * | * | 8.7 | * |
| Monday | * | 6.9 | * | * | * | * | * | 7.8 | * | * |
| Tuesday | 7.3 | * | * | * | * | * | 6.1 | * | * | * |
| Wednesday | * | * | * | * | * | 3.3 | * | * | * | * |
| Thursday | * | * | * | * | 7.0 | * | * | * | * | * |
| Friday | * | * | * | 2.0 | * | * | * | * | * | 7.1 |
| Saturday | * | * | 4.1 | * | * | * | * | * | 6.8 | * |



**Concord-2975 Treat Blvd**

onitor #1 (Primary 24-Hour Monitor)

| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | 8.5 | 3.0 | 6.3 | 11.6 | 3.4 | 9.7 | * | * | * | * |
| Monday | 19.0 | * | 5.3 | 3.3 | 7.3 | 7.7 | * | * | * | * |
| Tuesday | 22.8 | * | 7.6 | 3.0 | 14.2 | * | * | * | * | * |
| Wednesday | * | 7.8 | 3.0 | 5.0 | 3.9 | * | * | * | * | * |
| Thursday | 2.5 | 7.0 | 4.3 | 4.3 | 4.3 | * | * | * | * | * |
| Friday | 1.0 | 7.0 | 7.5 | 2.0 | 13.7 | * | * | * | * | * |
| Saturday | 2.1 | 8.0 | 18.9 | 3.2 | 5.9 | * | * | * | * | * |
| | Graph! | | | | | | | | | |

onitor #2 (Collocated 24-Hour Monitor)

| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | * | * | * | * | 3.4 | * | * | * | * | * |
| Monday | * | * | * | 3.8 | * | * | * | * | * | * |
| Tuesday | * | * | 7.6 | * | * | * | * | * | * | * |
| Wednesday | * | 8.7 | * | * | * | * | * | * | * | * |
| Thursday | 2.5 | * | * | * | * | * | * | * | * | * |
| Friday | * | * | * | * | * | * | * | * | * | * |
| Saturday | * | * | * | * | 5.6 | * | * | * | * | * |
| | Graph! | | | | | | | | | |

onitor #3 (Primary Hourly Monitor)

| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | * | * | * | * | * | * | 11.0 | 14.2 | 9.9 | 2.5 |
| Monday | * | * | * | * | * | * | 9.5 | 4.6 | 14.2 | 2.3 |
| Tuesday | * | * | * | * | * | 12.0 | 21.0 | 12.7 | 24.3 | 3.9 |
| Wednesday | * | * | * | * | * | 7.4 | 13.2 | 21.5 | 36.2 | 5.8 |
| Thursday | * | * | * | * | * | 17.7 | 2.5 | 12.3 | 11.0 | 15.7 |
| Friday | * | * | * | * | * | 13.8 | 4.2 | 8.9 | 12.0 | 13.3 |
| Saturday | * | * | * | * | * | 27.6 | 8.7 | 8.6 | 4.1 | 12.1 |

# CBE Attachment 11

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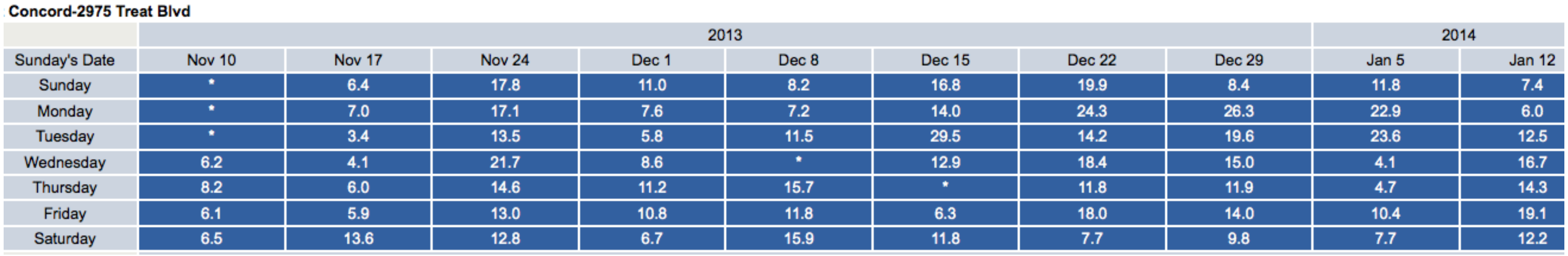
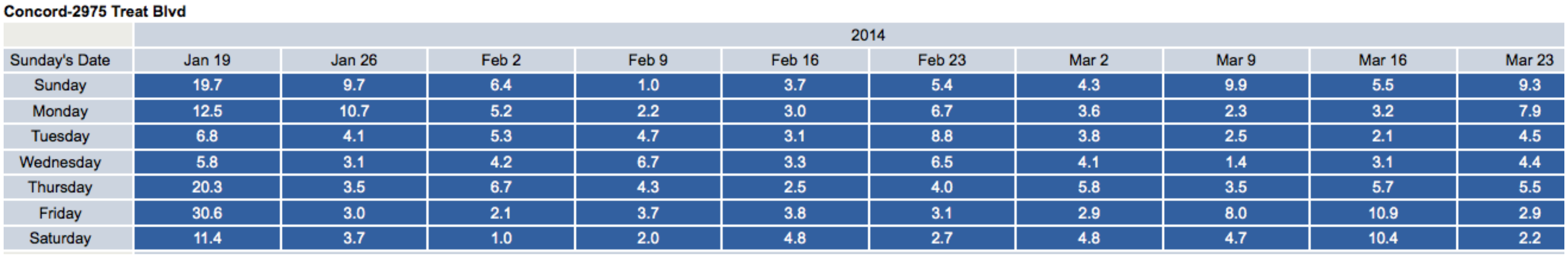


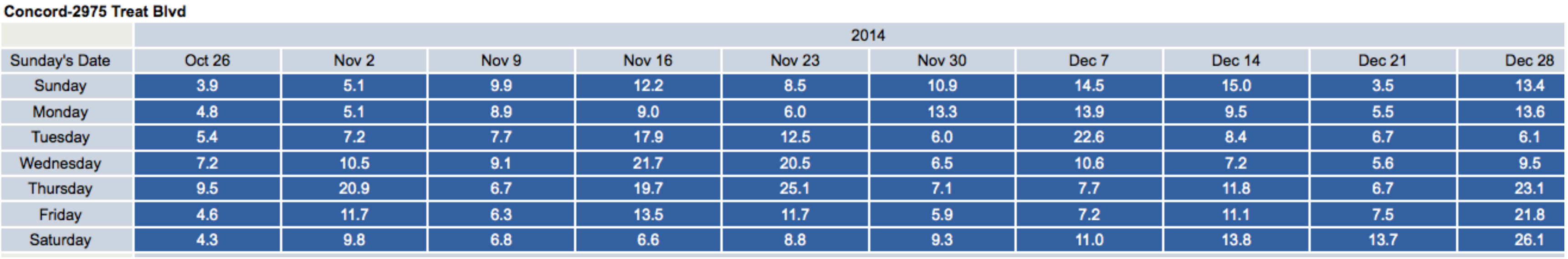
**Concord-2975 Treat Blvd**

| | 2013 | | | | | | | | 2014 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 10 | Nov 17 | Nov 24 | Dec 1 | Dec 8 | Dec 15 | Dec 22 | Dec 29 | Jan 5 | Jan 12 |
| Sunday | * | 6.4 | 17.8 | 11.0 | 8.2 | 16.8 | 19.9 | 8.4 | 11.8 | 7.4 |
| Monday | * | 7.0 | 17.1 | 7.6 | 7.2 | 14.0 | 24.3 | 26.3 | 22.9 | 6.0 |
| Tuesday | * | 3.4 | 13.5 | 5.8 | 11.5 | 29.5 | 14.2 | 19.6 | 23.6 | 12.5 |
| Wednesday | 6.2 | 4.1 | 21.7 | 8.6 | * | 12.9 | 18.4 | 15.0 | 4.1 | 16.7 |
| Thursday | 8.2 | 6.0 | 14.6 | 11.2 | 15.7 | * | 11.8 | 11.9 | 4.7 | 14.3 |
| Friday | 6.1 | 5.9 | 13.0 | 10.8 | 11.8 | 6.3 | 18.0 | 14.0 | 10.4 | 19.1 |
| Saturday | 6.5 | 13.6 | 12.8 | 6.7 | 15.9 | 11.8 | 7.7 | 9.8 | 7.7 | 12.2 |



**Concord-2975 Treat Blvd**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 19 | Jan 26 | Feb 2 | Feb 9 | Feb 16 | Feb 23 | Mar 2 | Mar 9 | Mar 16 | Mar 23 |
| Sunday | 19.7 | 9.7 | 6.4 | 1.0 | 3.7 | 5.4 | 4.3 | 9.9 | 5.5 | 9.3 |
| Monday | 12.5 | 10.7 | 5.2 | 2.2 | 3.0 | 6.7 | 3.6 | 2.3 | 3.2 | 7.9 |
| Tuesday | 6.8 | 4.1 | 5.3 | 4.7 | 3.1 | 8.8 | 3.8 | 2.5 | 2.1 | 4.5 |
| Wednesday | 5.8 | 3.1 | 4.2 | 6.7 | 3.3 | 6.5 | 4.1 | 1.4 | 3.1 | 4.4 |
| Thursday | 20.3 | 3.5 | 6.7 | 4.3 | 2.5 | 4.0 | 5.8 | 3.5 | 5.7 | 5.5 |
| Friday | 30.6 | 3.0 | 2.1 | 3.7 | 3.8 | 3.1 | 2.9 | 8.0 | 10.9 | 2.9 |
| Saturday | 11.4 | 3.7 | 1.0 | 2.0 | 4.8 | 2.7 | 4.8 | 4.7 | 10.4 | 2.2 |



**Concord-2975 Treat Blvd**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Oct 26 | Nov 2 | Nov 9 | Nov 16 | Nov 23 | Nov 30 | Dec 7 | Dec 14 | Dec 21 | Dec 28 |
| Sunday | 3.9 | 5.1 | 9.9 | 12.2 | 8.5 | 10.9 | 14.5 | 15.0 | 3.5 | 13.4 |
| Monday | 4.8 | 5.1 | 8.9 | 9.0 | 6.0 | 13.3 | 13.9 | 9.5 | 5.5 | 13.6 |
| Tuesday | 5.4 | 7.2 | 7.7 | 17.9 | 12.5 | 6.0 | 22.6 | 8.4 | 6.7 | 6.1 |
| Wednesday | 7.2 | 10.5 | 9.1 | 21.7 | 20.5 | 6.5 | 10.6 | 7.2 | 5.6 | 9.5 |
| Thursday | 9.5 | 20.9 | 6.7 | 19.7 | 25.1 | 7.1 | 7.7 | 11.8 | 6.7 | 23.1 |
| Friday | 4.6 | 11.7 | 6.3 | 13.5 | 11.7 | 5.9 | 7.2 | 11.1 | 7.5 | 21.8 |
| Saturday | 4.3 | 9.8 | 6.8 | 6.6 | 8.8 | 9.3 | 11.0 | 13.8 | 13.7 | 26.1 |

# CBE Attachment 11

**Concord-2975 Treat Blvd**

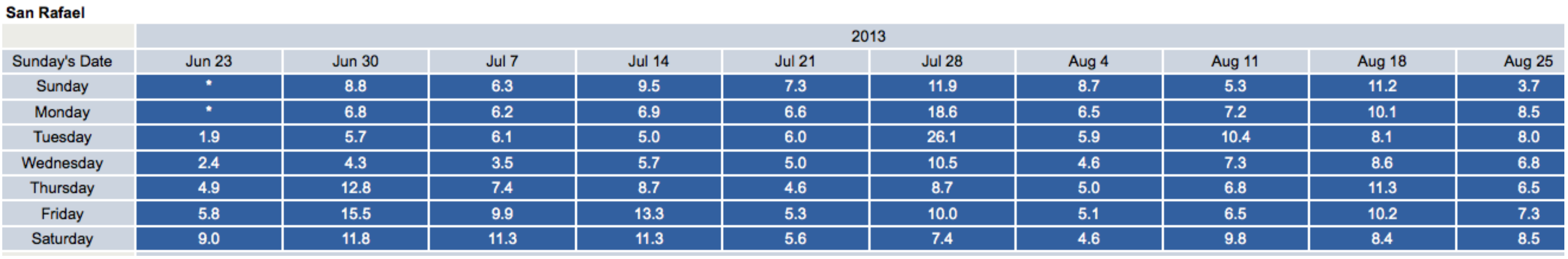
| | 2015 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 4 | Jan 11 | Jan 18 | Jan 25 | Feb 1 | Feb 8 | Feb 15 | Feb 22 | Mar 1 | Mar 8 |
| Sunday | 27.4 | 22.1 | 19.5 | 17.6 | 19.4 | 8.4 | 7.6 | 9.4 | * | * |
| Monday | 19.0 | 9.4 | 10.9 | 16.9 | 24.6 | 10.6 | 11.2 | 6.2 | 9.9 | * |
| Tuesday | 21.8 | 9.1 | 11.0 | 17.7 | 18.6 | 5.5 | 17.5 | * | * | * |
| Wednesday | 12.8 | 28.3 | 12.1 | 13.9 | 25.6 | 7.3 | 12.4 | * | * | * |
| Thursday | 31.0 | 29.6 | 18.8 | 15.1 | 12.7 | 8.9 | 19.2 | * | * | * |
| Friday | 24.5 | 28.1 | 17.6 | 10.4 | 6.5 | 12.0 | 12.0 | * | * | 9.6 |
| Saturday | 19.9 | 18.5 | 21.4 | 8.0 | 7.7 | 11.2 | 13.0 | * | * | 10.2 |

**San Rafael**

| | 2012 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Sep 16 | Sep 23 | Sep 30 | Oct 7 | Oct 14 | Oct 21 | Oct 28 | Nov 4 | Nov 11 | Nov 18 |
| Sunday | 7.0 | 8.8 | 9.3 | 7.0 | 4.4 | 8.3 | 5.8 | 6.6 | 12.1 | 8.2 |
| Monday | 8.1 | 8.5 | 11.5 | 8.9 | 6.1 | 5.6 | 7.4 | 10.2 | 13.3 | 9.0 |
| Tuesday | 7.9 | 8.6 | 11.7 | 8.6 | 5.0 | 7.6 | 5.9 | 17.2 | 14.5 | 6.0 |
| Wednesday | 11.7 | 12.2 | 11.7 | 10.1 | 8.4 | 5.8 | 3.9 | 12.2 | 15.3 | 10.1 |
| Thursday | 10.9 | 9.6 | 12.6 | 10.4 | 9.1 | 6.5 | 5.8 | 9.9 | 19.4 | 10.2 |
| Friday | 10.5 | 6.4 | 11.8 | 8.4 | 3.8 | 8.5 | 9.2 | 8.1 | 25.9 | 10.4 |
| Saturday | 12.3 | 6.4 | 9.5 | 6.7 | 7.8 | 6.8 | 6.3 | 9.3 | 6.3 | 10.6 |

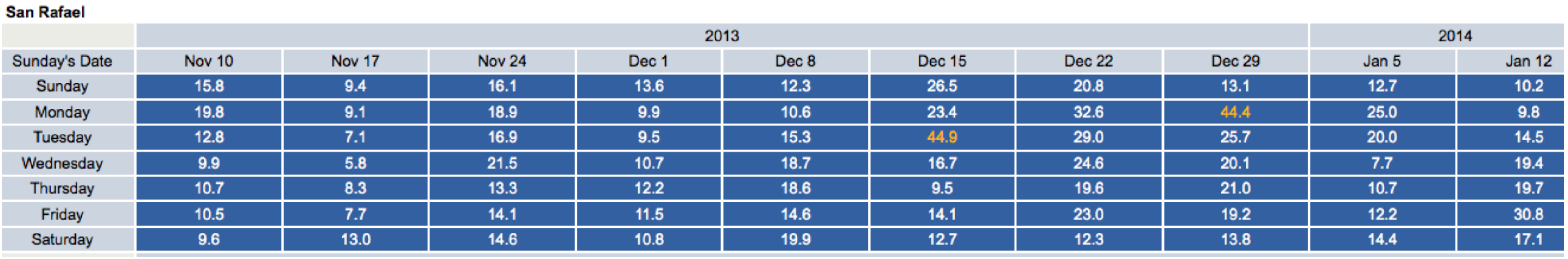
**San Rafael**

| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | 7.9 | 7.0 | 13.0 | 12.8 | 6.4 | 14.6 | 12.4 | 13.2 | 11.4 | 7.5 |
| Monday | 12.9 | 10.1 | 11.5 | 9.0 | 12.8 | 13.4 | 14.2 | 8.7 | 16.9 | 8.5 |
| Tuesday | 14.9 | 9.6 | 11.7 | 9.9 | 12.5 | 15.0 | 24.0 | 16.6 | 26.5 | 7.2 |
| Wednesday | 8.2 | 8.3 | 7.3 | 11.9 | 9.5 | 11.0 | 20.0 | 26.3 | 31.5 | 9.7 |
| Thursday | 7.5 | 7.2 | 10.9 | 10.2 | 8.3 | 18.5 | 7.4 | 25.5 | 21.1 | 18.9 |
| Friday | 4.5 | 10.4 | 13.0 | 7.8 | 15.0 | 17.9 | 10.9 | 17.2 | 12.7 | 16.0 |
| Saturday | 6.0 | 15.5 | 12.2 | 6.6 | 10.8 | 28.5 | 11.5 | 12.1 | 8.7 | 14.4 |



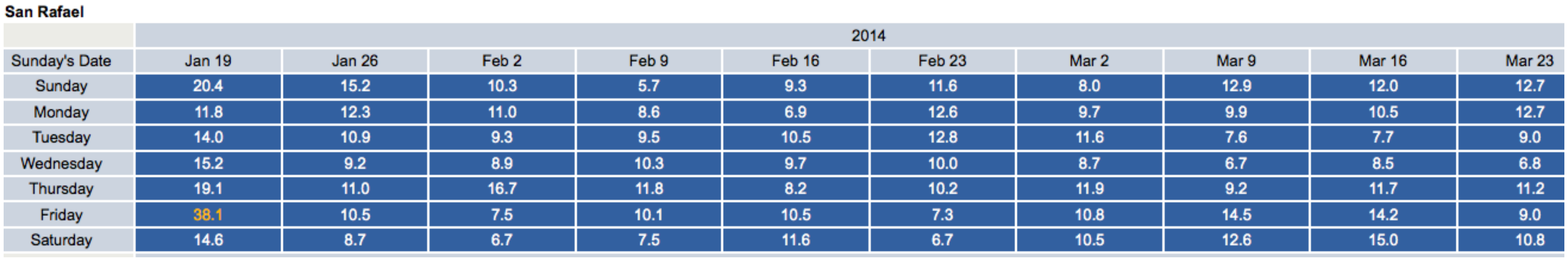
**San Rafael**

| | 2013 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jun 23 | Jun 30 | Jul 7 | Jul 14 | Jul 21 | Jul 28 | Aug 4 | Aug 11 | Aug 18 | Aug 25 |
| Sunday | * | 8.8 | 6.3 | 9.5 | 7.3 | 11.9 | 8.7 | 5.3 | 11.2 | 3.7 |
| Monday | * | 6.8 | 6.2 | 6.9 | 6.6 | 18.6 | 6.5 | 7.2 | 10.1 | 8.5 |
| Tuesday | 1.9 | 5.7 | 6.1 | 5.0 | 6.0 | 26.1 | 5.9 | 10.4 | 8.1 | 8.0 |
| Wednesday | 2.4 | 4.3 | 3.5 | 5.7 | 5.0 | 10.5 | 4.6 | 7.3 | 8.6 | 6.8 |
| Thursday | 4.9 | 12.8 | 7.4 | 8.7 | 4.6 | 8.7 | 5.0 | 6.8 | 11.3 | 6.5 |
| Friday | 5.8 | 15.5 | 9.9 | 13.3 | 5.3 | 10.0 | 5.1 | 6.5 | 10.2 | 7.3 |
| Saturday | 9.0 | 11.8 | 11.3 | 11.3 | 5.6 | 7.4 | 4.6 | 9.8 | 8.4 | 8.5 |



**San Rafael**

| | 2013 | | | | | | | | 2014 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 10 | Nov 17 | Nov 24 | Dec 1 | Dec 8 | Dec 15 | Dec 22 | Dec 29 | Jan 5 | Jan 12 |
| Sunday | 15.8 | 9.4 | 16.1 | 13.6 | 12.3 | 26.5 | 20.8 | 13.1 | 12.7 | 10.2 |
| Monday | 19.8 | 9.1 | 18.9 | 9.9 | 10.6 | 23.4 | 32.6 | 44.4 | 25.0 | 9.8 |
| Tuesday | 12.8 | 7.1 | 16.9 | 9.5 | 15.3 | 44.9 | 29.0 | 25.7 | 20.0 | 14.5 |
| Wednesday | 9.9 | 5.8 | 21.5 | 10.7 | 18.7 | 16.7 | 24.6 | 20.1 | 7.7 | 19.4 |
| Thursday | 10.7 | 8.3 | 13.3 | 12.2 | 18.6 | 9.5 | 19.6 | 21.0 | 10.7 | 19.7 |
| Friday | 10.5 | 7.7 | 14.1 | 11.5 | 14.6 | 14.1 | 23.0 | 19.2 | 12.2 | 30.8 |
| Saturday | 9.6 | 13.0 | 14.6 | 10.8 | 19.9 | 12.7 | 12.3 | 13.8 | 14.4 | 17.1 |



**San Rafael**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 19 | Jan 26 | Feb 2 | Feb 9 | Feb 16 | Feb 23 | Mar 2 | Mar 9 | Mar 16 | Mar 23 |
| Sunday | 20.4 | 15.2 | 10.3 | 5.7 | 9.3 | 11.6 | 8.0 | 12.9 | 12.0 | 12.7 |
| Monday | 11.8 | 12.3 | 11.0 | 8.6 | 6.9 | 12.6 | 9.7 | 9.9 | 10.5 | 12.7 |
| Tuesday | 14.0 | 10.9 | 9.3 | 9.5 | 10.5 | 12.8 | 11.6 | 7.6 | 7.7 | 9.0 |
| Wednesday | 15.2 | 9.2 | 8.9 | 10.3 | 9.7 | 10.0 | 8.7 | 6.7 | 8.5 | 6.8 |
| Thursday | 19.1 | 11.0 | 16.7 | 11.8 | 8.2 | 10.2 | 11.9 | 9.2 | 11.7 | 11.2 |
| Friday | 38.1 | 10.5 | 7.5 | 10.1 | 10.5 | 7.3 | 10.8 | 14.5 | 14.2 | 9.0 |
| Saturday | 14.6 | 8.7 | 6.7 | 7.5 | 11.6 | 6.7 | 10.5 | 12.6 | 15.0 | 10.8 |

**San Rafael**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Oct 26 | Nov 2 | Nov 9 | Nov 16 | Nov 23 | Nov 30 | Dec 7 | Dec 14 | Dec 21 | Dec 28 |
| Sunday | 7.5 | 6.9 | 9.8 | 8.3 | 7.0 | 10.0 | 13.2 | 18.6 | 10.2 | 18.7 |
| Monday | 8.0 | 7.9 | 10.3 | 9.8 | 10.5 | 20.3 | 17.2 | 11.6 | 8.7 | 9.7 |
| Tuesday | 6.5 | 10.0 | 11.2 | 15.1 | 13.3 | 6.9 | 25.0 | 9.5 | 11.2 | 5.9 |
| Wednesday | 10.1 | 11.4 | 9.9 | 14.2 | 18.5 | 6.2 | 17.8 | 10.0 | 11.6 | 13.3 |
| Thursday | 11.0 | 18.1 | 7.9 | 11.4 | 26.8 | 8.9 | 6.2 | 13.5 | 8.5 | 23.9 |
| Friday | 7.1 | 9.4 | 10.4 | 13.2 | 16.1 | 10.0 | 8.8 | 11.7 | 11.2 | 26.7 |
| Saturday | 7.5 | 9.4 | 9.7 | 10.3 | 11.5 | 9.4 | 14.5 | 17.0 | 14.2 | 30.2 |

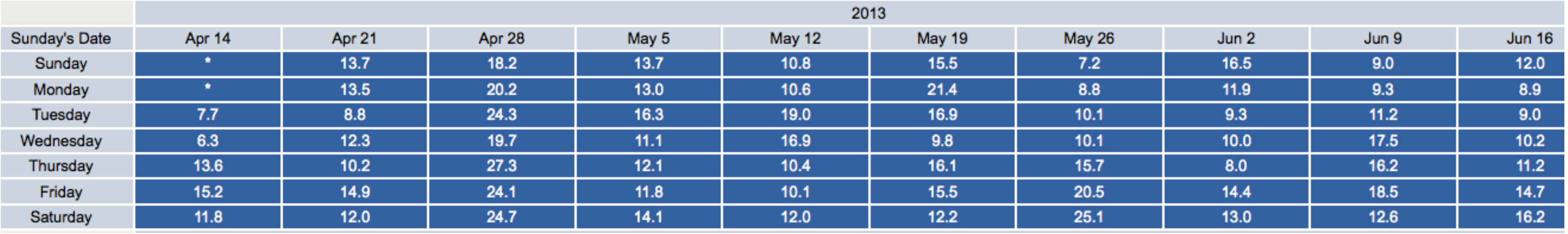
**San Rafael**

| | 2015 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 4 | Jan 11 | Jan 18 | Jan 25 | Feb 1 | Feb 8 | Feb 15 | Feb 22 | Mar 1 | Mar 8 |
| Sunday | 31.3 | 16.2 | 19.2 | 23.7 | 19.2 | 11.0 | 10.3 | 7.7 | 8.1 | 15.4 |
| Monday | 24.9 | 10.7 | 14.9 | 24.4 | 29.5 | 14.2 | 11.9 | 7.2 | 10.3 | 15.3 |
| Tuesday | 27.7 | 11.3 | 14.4 | 11.2 | 17.9 | 9.0 | 14.5 | 10.0 | 10.1 | 17.7 |
| Wednesday | 17.7 | 35.1 | 16.9 | 16.4 | 31.0 | 10.7 | 13.1 | 13.2 | 9.3 | 13.5 |
| Thursday | 34.8 | 36.3 | 24.5 | 13.3 | 9.8 | 11.8 | 17.4 | 13.0 | 10.9 | 8.0 |
| Friday | 21.5 | 36.0 | 23.3 | 14.2 | 7.5 | 12.7 | 12.6 | 8.5 | 13.3 | 11.0 |
| Saturday | 19.0 | 21.0 | 30.5 | 10.1 | 11.6 | 11.5 | 13.6 | 6.3 | 13.4 | 11.5 |

**Oakland-West**

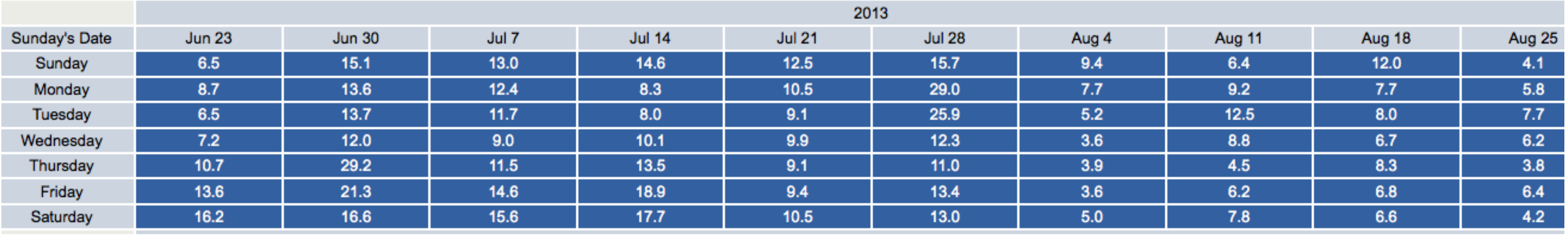
| | 2012 | | | | | | 2013 | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 25 | Dec 2 | Dec 9 | Dec 16 | Dec 23 | Dec 30 | Jan 6 | Jan 13 | Jan 20 | Jan 27 |
| Sunday | * | * | * | * | 3.7 | 11.2 | 13.0 | 7.0 | * | * |
| Monday | * | * | * | * | 7.6 | 12.4 | 15.5 | 8.3 | 22.4 | * |
| Tuesday | * | * | * | 5.0 | 8.5 | 12.6 | 21.9 | 14.0 | 28.1 | 9.1 |
| Wednesday | * | * | * | 5.9 | 3.6 | 15.3 | 16.9 | 33.2 | 37.4 | 13.4 |
| Thursday | * | * | * | 6.2 | 6.6 | 23.2 | 2.5 | 29.8 | * | 24.1 |
| Friday | * | * | * | 2.3 | 12.3 | 20.5 | 6.0 | * | * | 28.5 |
| Saturday | * | * | * | 4.6 | 10.1 | 18.9 | 8.9 | * | * | 22.0 |

**Oakland-West**



| | 2013 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Apr 14 | Apr 21 | Apr 28 | May 5 | May 12 | May 19 | May 26 | Jun 2 | Jun 9 | Jun 16 |
| Sunday | * | 13.7 | 18.2 | 13.7 | 10.8 | 15.5 | 7.2 | 16.5 | 9.0 | 12.0 |
| Monday | * | 13.5 | 20.2 | 13.0 | 10.6 | 21.4 | 8.8 | 11.9 | 9.3 | 8.9 |
| Tuesday | 7.7 | 8.8 | 24.3 | 16.3 | 19.0 | 16.9 | 10.1 | 9.3 | 11.2 | 9.0 |
| Wednesday | 6.3 | 12.3 | 19.7 | 11.1 | 16.9 | 9.8 | 10.1 | 10.0 | 17.5 | 10.2 |
| Thursday | 13.6 | 10.2 | 27.3 | 12.1 | 10.4 | 16.1 | 15.7 | 8.0 | 16.2 | 11.2 |
| Friday | 15.2 | 14.9 | 24.1 | 11.8 | 10.1 | 15.5 | 20.5 | 14.4 | 18.5 | 14.7 |
| Saturday | 11.8 | 12.0 | 24.7 | 14.1 | 12.0 | 12.2 | 25.1 | 13.0 | 12.6 | 16.2 |

**Oakland-West**



| | 2013 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jun 23 | Jun 30 | Jul 7 | Jul 14 | Jul 21 | Jul 28 | Aug 4 | Aug 11 | Aug 18 | Aug 25 |
| Sunday | 6.5 | 15.1 | 13.0 | 14.6 | 12.5 | 15.7 | 9.4 | 6.4 | 12.0 | 4.1 |
| Monday | 8.7 | 13.6 | 12.4 | 8.3 | 10.5 | 29.0 | 7.7 | 9.2 | 7.7 | 5.8 |
| Tuesday | 6.5 | 13.7 | 11.7 | 8.0 | 9.1 | 25.9 | 5.2 | 12.5 | 8.0 | 7.7 |
| Wednesday | 7.2 | 12.0 | 9.0 | 10.1 | 9.9 | 12.3 | 3.6 | 8.8 | 6.7 | 6.2 |
| Thursday | 10.7 | 29.2 | 11.5 | 13.5 | 9.1 | 11.0 | 3.9 | 4.5 | 8.3 | 3.8 |
| Friday | 13.6 | 21.3 | 14.6 | 18.9 | 9.4 | 13.4 | 3.6 | 6.2 | 6.8 | 6.4 |
| Saturday | 16.2 | 16.6 | 15.6 | 17.7 | 10.5 | 13.0 | 5.0 | 7.8 | 6.6 | 4.2 |

**Oakland-West**

| | 2013 | | | | | | | | 2014 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Nov 10 | Nov 17 | Nov 24 | Dec 1 | Dec 8 | Dec 15 | Dec 22 | Dec 29 | Jan 5 | Jan 12 |
| Sunday | 14.9 | 8.0 | 15.4 | 19.7 | 9.1 | 31.8 | 25.1 | 14.0 | 11.8 | 10.0 |
| Monday | 21.2 | 8.8 | 25.7 | 9.0 | 9.2 | 25.7 | 32.5 | 26.2 | 25.8 | 8.1 |
| Tuesday | 13.6 | 8.1 | 21.7 | 5.8 | 17.2 | 42.7 | 32.2 | 26.2 | 25.2 | 14.7 |
| Wednesday | 11.4 | 5.6 | 29.1 | 7.3 | 20.2 | 18.2 | 30.0 | 38.8 | 8.2 | 15.0 |
| Thursday | 13.5 | 8.2 | 21.0 | 14.9 | 25.7 | 5.2 | 26.1 | 25.7 | 8.7 | 22.2 |
| Friday | 11.4 | 5.2 | 17.7 | 9.8 | 26.9 | 12.9 | 29.6 | 25.7 | 10.4 | 33.8 |
| Saturday | 11.4 | 10.1 | 17.4 | 7.9 | 22.2 | 16.5 | 18.4 | 19.5 | 10.8 | 23.4 |

**CBE Attachment 11**

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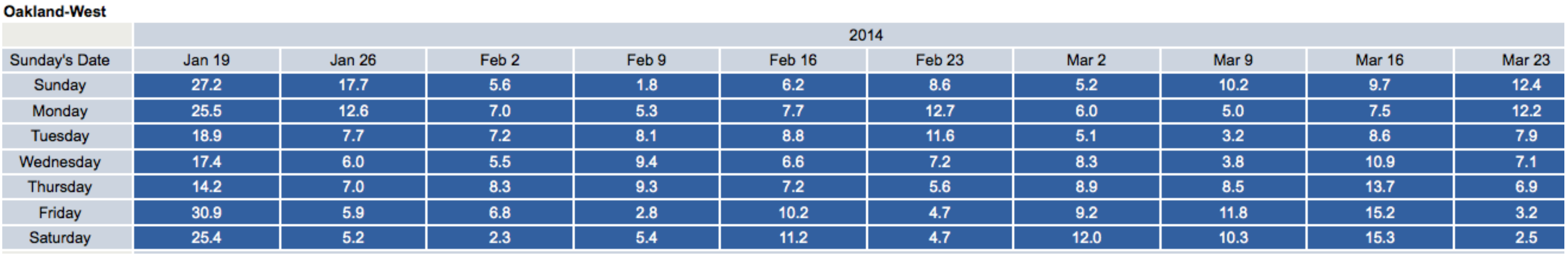
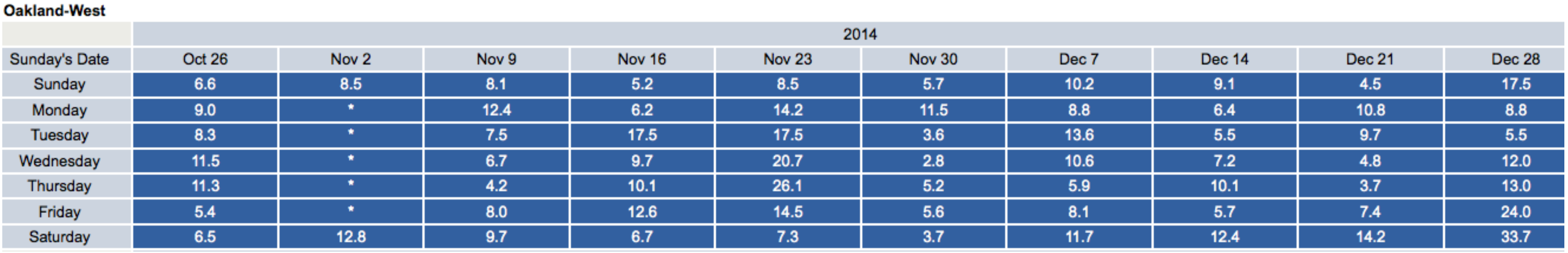


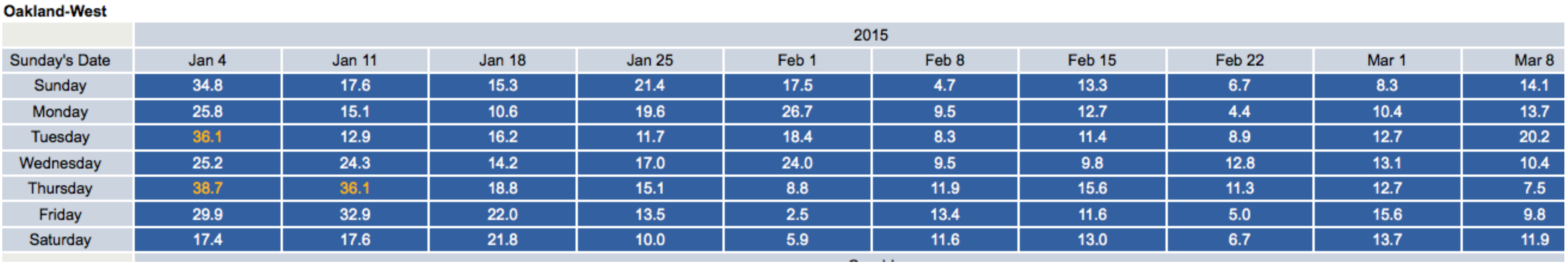
**Oakland-West**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 19 | Jan 26 | Feb 2 | Feb 9 | Feb 16 | Feb 23 | Mar 2 | Mar 9 | Mar 16 | Mar 23 |
| Sunday | 27.2 | 17.7 | 5.6 | 1.8 | 6.2 | 8.6 | 5.2 | 10.2 | 9.7 | 12.4 |
| Monday | 25.5 | 12.6 | 7.0 | 5.3 | 7.7 | 12.7 | 6.0 | 5.0 | 7.5 | 12.2 |
| Tuesday | 18.9 | 7.7 | 7.2 | 8.1 | 8.8 | 11.6 | 5.1 | 3.2 | 8.6 | 7.9 |
| Wednesday | 17.4 | 6.0 | 5.5 | 9.4 | 6.6 | 7.2 | 8.3 | 3.8 | 10.9 | 7.1 |
| Thursday | 14.2 | 7.0 | 8.3 | 9.3 | 7.2 | 5.6 | 8.9 | 8.5 | 13.7 | 6.9 |
| Friday | 30.9 | 5.9 | 6.8 | 2.8 | 10.2 | 4.7 | 9.2 | 11.8 | 15.2 | 3.2 |
| Saturday | 25.4 | 5.2 | 2.3 | 5.4 | 11.2 | 4.7 | 12.0 | 10.3 | 15.3 | 2.5 |



**Oakland-West**

| | 2014 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Oct 26 | Nov 2 | Nov 9 | Nov 16 | Nov 23 | Nov 30 | Dec 7 | Dec 14 | Dec 21 | Dec 28 |
| Sunday | 6.6 | 8.5 | 8.1 | 5.2 | 8.5 | 5.7 | 10.2 | 9.1 | 4.5 | 17.5 |
| Monday | 9.0 | * | 12.4 | 6.2 | 14.2 | 11.5 | 8.8 | 6.4 | 10.8 | 8.8 |
| Tuesday | 8.3 | * | 7.5 | 17.5 | 17.5 | 3.6 | 13.6 | 5.5 | 9.7 | 5.5 |
| Wednesday | 11.5 | * | 6.7 | 9.7 | 20.7 | 2.8 | 10.6 | 7.2 | 4.8 | 12.0 |
| Thursday | 11.3 | * | 4.2 | 10.1 | 26.1 | 5.2 | 5.9 | 10.1 | 3.7 | 13.0 |
| Friday | 5.4 | * | 8.0 | 12.6 | 14.5 | 5.6 | 8.1 | 5.7 | 7.4 | 24.0 |
| Saturday | 6.5 | 12.8 | 9.7 | 6.7 | 7.3 | 3.7 | 11.7 | 12.4 | 14.2 | 33.7 |



**Oakland-West**

| | 2015 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Sunday's Date | Jan 4 | Jan 11 | Jan 18 | Jan 25 | Feb 1 | Feb 8 | Feb 15 | Feb 22 | Mar 1 | Mar 8 |
| Sunday | 34.8 | 17.6 | 15.3 | 21.4 | 17.5 | 4.7 | 13.3 | 6.7 | 8.3 | 14.1 |
| Monday | 25.8 | 15.1 | 10.6 | 19.6 | 26.7 | 9.5 | 12.7 | 4.4 | 10.4 | 13.7 |
| Tuesday | 36.1 | 12.9 | 16.2 | 11.7 | 18.4 | 8.3 | 11.4 | 8.9 | 12.7 | 20.2 |
| Wednesday | 25.2 | 24.3 | 14.2 | 17.0 | 24.0 | 9.5 | 9.8 | 12.8 | 13.1 | 10.4 |
| Thursday | 38.7 | 36.1 | 18.8 | 15.1 | 8.8 | 11.9 | 15.6 | 11.3 | 12.7 | 7.5 |
| Friday | 29.9 | 32.9 | 22.0 | 13.5 | 2.5 | 13.4 | 11.6 | 5.0 | 15.6 | 9.8 |
| Saturday | 17.4 | 17.6 | 21.8 | 10.0 | 5.9 | 11.6 | 13.0 | 6.7 | 13.7 | 11.9 |

Attachment 39

# Minding the Climate Gap

## What's at Stake if California's Climate Law isn't Done Right and Right Away

Manuel Pastor, Ph.D. | Rachel Morello-Frosch, Ph.D., MPH | James Sadd, Ph.D. | Justin Scoggins, M.S.

## Acknowledgments

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# Introduction

The California Global Warming Act (AB 32) – a cutting edge policy that no one expected to pass so quickly and with so much bipartisan support – proposes to cut green house gas emissions to 1990 levels by 2020. The successful implementation of such a standard would mean reducing carbon emissions from major polluters around the state – cement refineries, power plants, and oil refineries top among them. It's a clear victory for all Californians, it would seem – but the underlying picture may be a bit more complicated.

As we have shown in a recent report entitled *The Climate Gap* (Morello-Frosch, et al. 2009), climate change is not affecting all people equally: communities of color and low-income communities suffer the greatest negative health and economic consequences. Among the many disparate impacts, these communities are more vulnerable to heat incidents, more exposed to air pollution, and may be more affected by the economic dislocations of ongoing climate change.

While reducing greenhouse gas emissions will benefit all Californians, a carbon reduction system that does not take co-pollutants into account could likely result in significantly varying benefits for different populations. Those who are most likely to suffer the negative consequences of a short-sighted carbon trading system are the communities of color and the low-income communities already facing the greatest impacts of climate change – widening instead of narrowing the climate gap.

Consider the La Paloma power plant and the Exxon Mobil refinery in Torrance. The La Paloma power plant sits about 35 miles west of Bakersfield in an abandoned oil field just outside the small town of McKittrick (population 160) with less than 600 residents in the surrounding six miles, and no other facilities in the immediate vicinity. The Exxon Mobil refinery, on the other hand, is one of many facilities affecting nearly 800,000 people in the encircling six miles. While these facilities share one similarity – according to recently released 2008 GHG emissions data from the California Air Resources Board, they both emit between 2.5 and 3 million tons of carbon dioxide each year – La Paloma releases 48.6 tons of asthma and cancer causing particulate matter per year while Exxon Mobil emits 352.2 tons. This staggering health risk is important to people who live in Torrance's dense neighborhoods, yet this fact is often ignored in the debates about how we might best implement AB 32.

Why is the difference between reducing emissions at La Paloma and in Torrance overlooked in the discussion about mitigating climate change? Part of the reason is that too much of the discussion stays at the macro-level: climate change is imagined as ozone layer erosion, heat waves, and sea level rises. So while the catastrophic potential of climate change is well documented, the story of the climate gap – the often unequal impact the climate crisis has on people of color and the poor in the United States – is just starting to be told. Until recently, systemic efforts to combat climate change have focused primarily on reducing carbon with little, if any, regard for where the reductions take place and who they might affect. In this view, reducing greenhouse gas emissions – no matter where it occurs – is the central objective of policy change.

People, however, do live somewhere – and it is at the local and not the macro level where changes from new policy will be most immediately felt. When smoke stacks in low-income communities belch less carbon, they also emit less particulate matter, sulfuric oxides, and nitrous oxides. When truck operators retrofit their units to reduce emissions, children's asthma rates are likely to fall along the traffic corridors that they impact. Paying attention to the climate gap – focusing on the co-pollutants and the potential co-benefits of greenhouse gas reductions – is important for public health. And lifting this issue up can give California not only a chance to address its historic pattern of environmental inequity but also the opportunity to implement a climate change policy that will be replicated throughout the nation.

Additionally, the economic opportunity that could be realized by reducing air pollution in dense neighborhoods is also enormous. All Californians are affected by higher insurance premiums, medical costs and lost productivity due to the many illnesses caused by air pollution, and all stand to benefit from an equitable system that would work toward minimizing these costs as opposed to adding to this growing burden. Not only does it make economic sense, but the text of AB 32 itself also requires CARB in designing any market-based mechanisms for GHG reductions to consider the localized impacts in communities that are already impacted by air pollution, prevent any increase in co-pollutants, and maximize the co-benefits of co-pollutant reductions.[1]

This report seeks to analyze co-pollutants and co-benefits, with an eye toward thinking through policy designs that could help maximize public health and close the climate gap. We begin below by discussing why geographic inequality in greenhouse gas (GHG) reduction is likely under any market-based scheme and why it matters for public health. We then describe the necessary baseline for any analysis, indicating how some major facilities that emit significant GHGs – power plants, petroleum refineries, and cement plants – affect their neighbors, and who (and how many) those neighbors are. We then take on a trickier task: assessing the potential impacts of a cap-and-trade program in California. Because we cannot see into the market's future, we take a simpler approach: we identify which industries and their associated facilities are driving environmental inequity, and use this to suggest how policy-makers could take this into account in fulfilling AB 32's requirement to both reduce overall emissions *and* protect climate gap neighborhoods.

AB 32 has heralded a new era of regulatory action to reduce greenhouse gas emissions, and California finds itself once again leading the country in the area of environmental protection. As proud as we should be of that, we must be mindful that the state is deeply plagued by issues of environmental inequity, and that if our new climate change regulations are not designed to address the growing climate gap, the suffering of those who bear the brunt of this burden may grow. Numerous studies demonstrate that air pollution burdens tend to fall disproportionately on those who are the least privileged and the most vulnerable. We do not need to perpetuate and worsen this trend. Instead, we can lift up issues of public health and fair environmental policies to ensure that the implementation of AB 32 is a success for all Californians and a model for the nation and a world looking for viable paths to environmental, social and economic sustainability.

## The Problem

California is at the forefront of dealing with climate change, by setting new standards, driving toward energy efficiency, encouraging renewables, and even working to rebalance the mix of land uses and transportation that have produced our well-documented sprawl. Within the context of our myriad efforts, the state has committed to the development of a "cap-and-trade" system in which GHG emissions from the facilities of certain polluting industries would be capped and emissions permits or "allowances" would be allocated (through auction, a fee, for free, or otherwise) to create a market for carbon emissions. In such a system, once the allowances are distributed for any compliance period, emitters of greenhouse gases whose emissions exceed their allowances may purchase allowances from other facilities – those who are reducing emissions beyond their own goals – rather than taking on the cost of reducing emissions from their own facilities. Another option, though highly controversial, is that they could cover their excess GHG emissions through the purchase of "offsets," which are basically projects or activities that yield a net GHG emissions reduction for which the ownership of the reduction can be transferred.

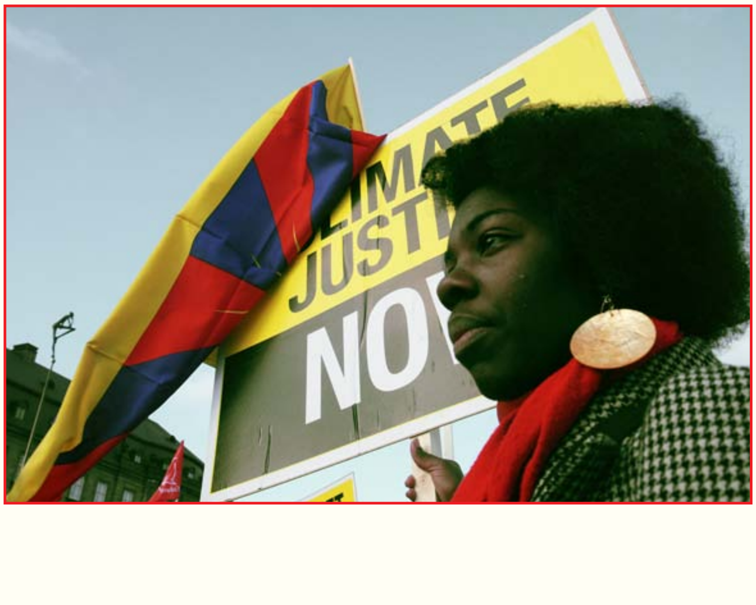
The arguments for cap-and-trade revolve around a narrow concept of industrial efficiency – if it is less costly for some firms to meet reduction goals, they should move first and fastest, and this will reduce the overall burden of compliance and perhaps speed the attainment of stricter GHG emissions targets overall (i.e. “the cap”). Some also argue that such a system could encourage technological innovation as firms seek to either buy fewer permits or chase the profit opportunities inherent in reducing their own emissions and offering their unused permits to other firms that cannot reduce as quickly. In this view, the market is being harnessed for public good, with the incentive structure providing businesses a positive reason to participate in making the intentions of AB 32 real as well as the flexibility to meet goals.

Opponents of cap-and-trade worry that enforcement of such a market system is not feasible and that the market will inevitably be gamed, leading to a sinkhole of financial resources with little regulatory oversight; opponents point to the subprime mortgage crisis and the recent economic meltdown as examples of trading markets that went haywire with little accountability. Others have noted that some experiences with cap-and-trade, as in the early implementation in the European Union, did not lead to significant GHG reductions. Still others object to program design, particularly the notions of handing out allowances *gratis* to polluting firms – something that is *de facto* a mass transfer of wealth from the general public to private polluters – and the use of offsets, which could displace actual emissions reductions in California through, for example, slowing deforestation somewhere across the globe.

While these are legitimate concerns this report explores a more limited and focused issue: whether or not implementation of cap-and-trade in California might fail to capture public health benefits, or even make an already inequitable situation worse, thereby failing to maximize the social good to the same extent that might be obtained from a different or better-designed system.

To see this, it is important to recognize that cap-and-trade is inherently unequal. The cap part is, of course, equal: everyone gains from a regional reduction in GHG and the slowdown in climate change that might be induced. But the trade part is inherently unequal – or why would anyone trade? Indeed, trading is justified on the grounds that reducing pollution is more efficient in some locations compared to others, and thus *where* reductions will occur is a decision such a system leaves in the hands of the market and businesspeople – neither of which have any incentive to lower emissions in order to benefit the low-income and minority communities hit hardest by concentrated pollution.

Some argue that the location of the emissions reduction is not important – reductions in GHG benefit the planet no matter where they occur. But since GHG emissions are usually accompanied by releases of other pollutants, there could be very different impacts on the health of residents living near plants that choose, under cap-and-trade, to either reduce emissions or purchase their way out of that requirement. Therefore, the reductions made at the lowest marginal price might be efficient in



terms of the costs and benefits to the industrial economy, but would likely be enormously inefficient in a real sense if they fail to completely account for all external costs such as health impacts. Any carbon trading plan blind to the effects of co-pollutants would be deeply flawed in ignoring significant health impacts and the associated costs, such as the economic burden that could be shifted to other sectors, such as the healthcare system.

This public health concern has been among the arguments made by members of the Environmental Justice Advisory Committee (EJAC) – a group made up of leaders representing the communities most impacted by pollution in the state and itself a product of the AB 32 legislation intended to advise the California Air Resources Board (CARB). EJAC has, among other things, been concerned that the Scoping Plan for AB 32 calls for a cap-and-trade regulatory mechanism, which on its own, has no way to ensure the protection or improvement of environmentally degraded or stressed neighborhoods.

The public health issue arises in part because while cap-and-trade tries to price in one externality – carbon and other GHG emissions – it does not price in all externalities, including the health and other impacts of co-pollutants. While quantifying such economic externalities is not our focus, Groosman et al. (2009) have found the health co-benefits alone from co-pollutant reductions due to a nationwide cap on carbon emissions *may be greater than the cost of making such reductions itself* – without even considering the large-scale benefits of slowing climate change. In a study of the co-benefits of carbon emissions reductions in the European Union, Berk et al. (2006) reached similar conclusions.

There are reasonable arguments that other regulations, such as the Clean Air Act, can tame co-pollutant emissions and that one does not want to overload a new carbon trading system. Yet it is not clear why the introduction of a whole new market in carbon trading is not in and of itself sufficiently complicated that building in a few safeguards to protect stressed communities would be the straw that breaks the regulatory camel's back. Moreover, given the well-founded skepticism of existing regulations that is held by many Environmental Justice (EJ) communities based on historical experiences, it is also not clear why the inclusion of safeguards would not make political sense as well.

Of course, whether one wants to think about such safeguards at all depends on whether or not a market system actually does have the realistic potential to introduce uneven benefits in public health – and the rest of this document is devoted to assessing whether such a scenario is possible. Thus, we need to investigate the current distribution of plants with regard to race, income and population density in order to see whether this is a concern worthy of public policy (and not just academic) consideration. Although we believe it is, we would also offer a few caveats to the case we will make.

First, some have dismissed concerns around uneven emissions reductions, arguing that because of other regulations, cap-and-trade will never produce "hot spots" – that is, places where emissions of both GHG and co-pollutants actually increase (an outcome that actually occurred in Southern California, for example, in a poorly designed system that allowed $NO_x$ emissions trading between mobile and stationary sources, and led refineries to purchase and decommission "clunkers" rather than clean up near fenceline communities; see Drury, et al. 1999). Thus, any form of trading should meet the limited requirement in AB 32 that any market system should "prevent any increase in the emissions of toxic air contaminants or criteria air pollutants."[2]

We do think that there is a possibility of "hot spots," particularly if plants below current regulatory emissions requirements for co-pollutants might eventually be sunsetted and so operators step up production (and emissions) in the interim (just as one might run an aging appliance past its prime knowing that it will soon be replaced). This is by no means an extreme view: the potential for "hot spots" is acknowledged by some who are against imposing any sort of health- or EJ-based constraints on the cap-and-trade system. Schatzki and Stavins (2009), for example, argue for mechanisms to address EJ concerns over cap-and-trade that are external to the the sytem itself (and particularly stress the use of traditional regulations for co-pollutants) but do concur that cap-and-trade could lead to an increase in local co-pollutant emissions, even if there is a net reduction statewide. However, we do not contend that this is the most likely outcome and believe that the main problem is one of missed opportunity: that we will fail to achieve and target public health benefits from GHG reductions in the communities that need them the most.

Second, while we focus here on cap-and-trade, the concerns we raise are equally applicable to the carbon fee system proposed by some cap-and-trade opponents. Although regulatory oversight is more straightforward in a fee-based system, here too, polluters can decide whether to reduce emissions or pay to pollute. We focus on cap-and-trade because it is the primary mechanism being discussed on both the state and federal policy agendas. The issues raised here are relevant to the potential gaps left by any market-based tool – cap-and-trade, carbon fee or a hybrid – and CARB must assess the potential for market-based mechanisms to worsen existing public health disparities before it develops such a regulatory framework.

Finally, we are *not* suggesting that considering inequitable health impacts in the development of a market-based carbon reduction plan is the only (or even the most important) piece of the puzzle in addressing the "climate gap". There are many other areas of concern – such as the economic impacts on consumers, the job opportunities for low-skill workers, the role of urban heat islands, and the nature of our logistic and social preparation for extreme weather events. Still, we think that the public health piece is an important component within a larger climate justice debate.

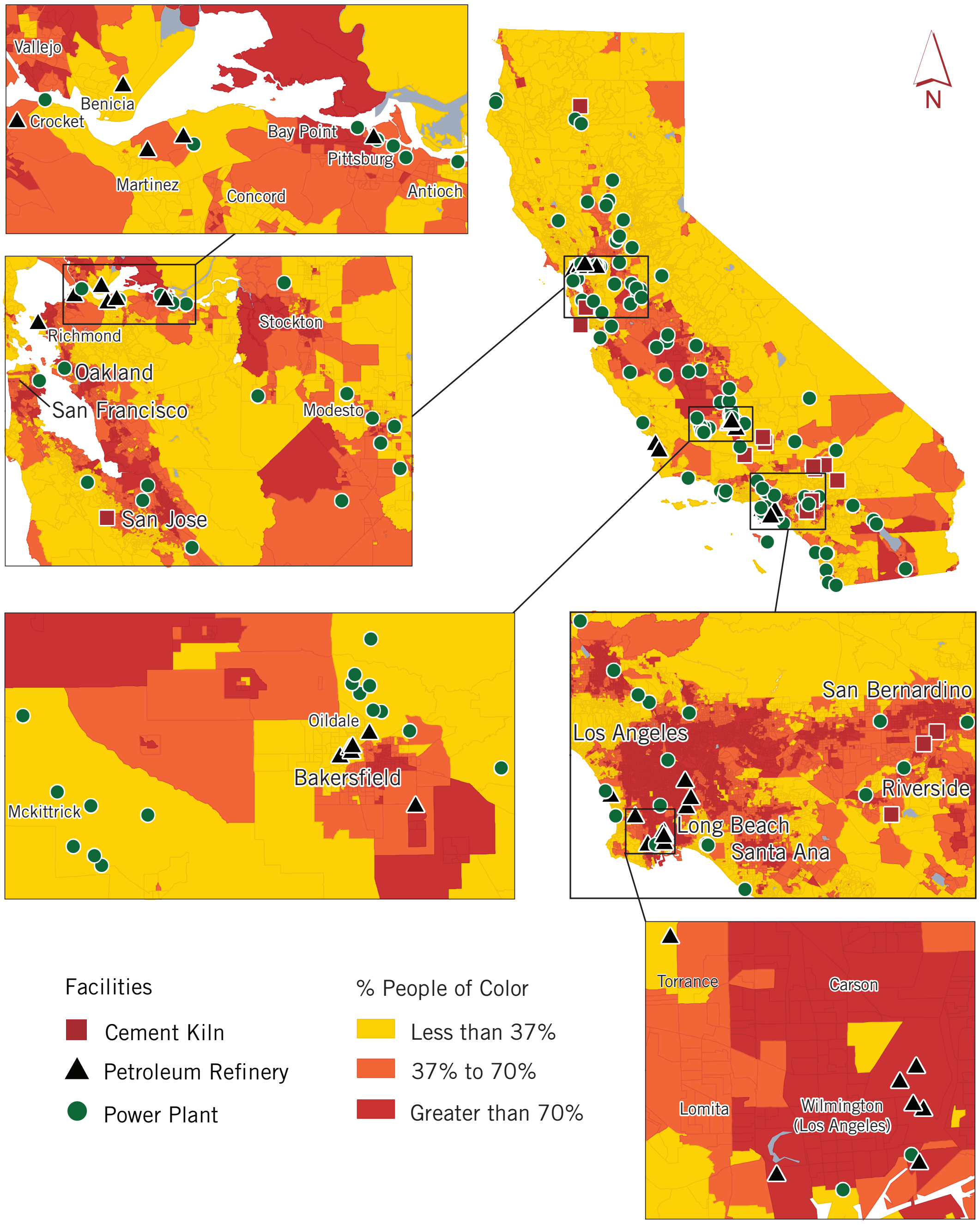
## The Data

To connect climate change indicators with neighborhood disparities, we combined several data sources. We specifically performed GIS spatial analysis using demographic and emissions data, working down to detailed neighborhood measures needed to understand local health impacts.

Following a method developed by the Natural Resources Defense Council (NRDC) (Bailey et al. 2008), we pulled together emissions data on industries that are known to emit large quantities of $CO_2$ – petroleum refineries, cement plants, and power plants.[3] Together, the facilities included in our analysis from these sectors account for about 20 percent of the state's GHG emissions and will be the first group to come under regulation. We extracted data from two sources: the 2006 CARB Emissions Inventory[4] for information on co-pollutants ($NO_x$ and $PM_{10}$) and the 2008 GHG emission from CARB's first annual release under the state's mandatory GHG Reporting Program.[5] The power plant data only includes those oil and natural gas plants who reported to the California Energy Commission (CEC) in 2007 that they produced at least 50 online megawatts, and all other plants that may not have met that criteria but were either coal-fired or among the top 20 polluters of nitrous oxides ($NO_x$), particulate matter ($PM_{10}$), or carbon dioxide equivalent (CO2e). Petroleum refineries and cement plants data are from 2006, and the resulting overall dataset includes 146 facilities, once restricted to those for which co-pollutant emissions information could be obtained from a total of 154 facilities considered. This set of facilities overlaid on racial demographics can be seen in Figure 1.

The process of attaching emissions to the facility location is similar to that followed by NRDC using an earlier version of the data to understand the regional health benefits of reducing emissions from these sources. Because we were interested in local health impacts, we conducted two additional steps in the preparation of this new iteration of the data.

**Figure 1: Major GHG-Emitting Facilities in California**



First, we used a variety of means to verify the address locations of the facilities indicated in the databases – a vital step since the purpose here is to consider local effects. While addresses were provided in the CARB Emissions Inventory for all facilities, these didn't always match the actual locations, sometimes because they were for the company headquarters instead of the actual refinery or plant. To determine correct locations, we cross-referenced the addresses given by CARB Emissions Inventory with data from the GHG Reporting Program, the CEC power plants database, and a dataset of facility locations from the U.S. Environmental Protection Agency (EPA), which provided geographic coordinates in addition to addresses, and then used aerial imagery[6] in Google Earth to visually confirm that the deduced coordinates were correct; in cases where they were not, we used the air photos to first find the facilities and then derive a set of coordinates that matched the emissions source at the facility. For a few facilities that seemed to be nowhere near their given coordinates or given address, we found their actual physical location through web-research, official documentation (e.g. permit history), and making phone calls to the parent companies.

Second, we verified NRDC's calculations of how the facilities impact the health of their neighbors, and updated it with more recent, 2006 data. NRDC researchers had created a "health impacts index" (for the formula, see the Technical Appendix) that quantifies, using health endpoint factors, how each facility's $NO_x$ and $PM_{2.5}$ emissions increases premature mortality in the region, or more specifically, the local air basin.[7] The index is quite useful as a broader geographic measure of health impacts posed by a facility. At smaller scales, it must be used carefully. We use it in combination with population-weighted $NO_x$ and $PM_{10}$ emissions at varying distances from a facility for facility level analysis. For neighborhood level analysis, we use only proximity at various distances along with total co-pollutant emissions as indicators of health risk or burden.

We then gathered demographic and socioeconomic data on the neighborhoods surrounding facilities, using the 2000 Census data (Summary Files 1 and 3). We used block groups as the unit of analysis because it is the lowest level at which income information is available. Block groups consist of some number of similar blocks and in California have an average population of about 1,500. They are drawn to represent fairly homogenous populations in terms of demographic and economic characteristics, making them a good approximation of a neighborhood. They are more geographically detailed than census tracts, which are the next higher level of geographic aggregation in the census, and less detailed than census blocks, which are the lowest level of geography but one at which only basic demographic information is available.

Matching people in block groups with facilities is complicated. Facility addresses are a single point on a map but block groups are polygonal "aerial units" – that is, they have dimension. Thus, there are many instances in which a block group is only partially contained within a given distance of a facility (e.g., with a portion that is within one mile of a facility but with the remainder more than one mile away from that facility). A further complication is that block groups do not have evenly distributed populations – just think of a typical neighborhood wherein there might be several residential blocks adjacent to a mini-mall. Given that proximity is a central component to how co-pollutants affect people's health, how do we determine a definite measure of proximity?

We settled this dilemma in two ways. First, we considered where people were situated within each block group, attempting to gauge how many were within the specified distance of a facility, and second, we varied these distances to test the sensitivity of our measurements. On the first consideration, we created circular buffers around each facility and used them to capture census blocks – the components of block groups – to determine neighborhood proximity. Blocks that fell completely inside the buffer circle were counted as being proximate to the facility. Blocks that fell only partially inside the buffer circle were only considered proximate to the facility if the buffer circle captured the geographic center of the block (usually encompassing about half its area). We then tallied up the populations of the captured blocks to get the total share of the block group's population that was within the buffer circle, and used that number to appropriately "down-weight" any association between a facility and a block group that was only partially captured by a buffer circle. If, for example, six of a block groups' ten blocks were inside a facility's buffer circle and they accounted for 75 percent of the block group's population, then only 75 percent of the block group's population was associated with the facility and 75 percent of the facility's emissions were associated with the block group. This approach ensured a focus on where people actually live in relation to a facility and its emissions.

We also varied the perimeters to test for sensitivity. We specifically utilized half mile, one mile, two and a half mile, five mile, and six mile buffers to account for whether the inclusion of additional block groups moving away from the facility made a difference in terms of our analytical results. The broadest of these distances, six miles, is used by the California Energy Commission when it attempts to determine whether or not there are environmental justice communities located nearby any proposed location for a power plant. The other tighter distances have been utilized in much of the environmental justice literature to determine which neighborhoods might be considered proximate to, say, a facility listed in the Toxic Release Inventory maintained by the U.S. Environmental Protection Agency.

While we do not, in this report, delve into how tight the relationship is between distance and co-pollutant effect, one reason for drawing multiple buffers of different radii is because of the large variation in the size of the facilities subject to analysis. While they are represented as points on a map, some facilities may cover a large area and may have multiple points of emission, in which case a one mile buffer drawn from the center of the identified stack or plant address may, in reality, barely reach the perimeter of the lot containing the facility. By running all analyses under various distances and identifying consistent conclusions, we can discount the distorting effect that variation in facility size may have on our findings.

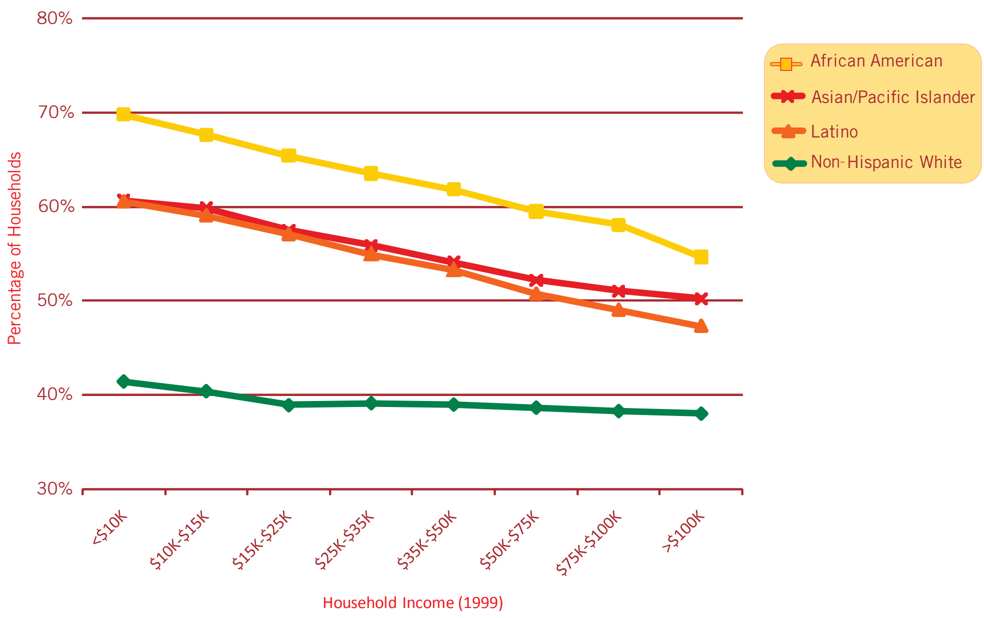
We use these geographic procedures to provide a picture of what each community looks like in terms of co-pollutant burden, and what each facility looks like in terms of the socioeconomic characteristics of its neighbors. Where a block falls within the reach of several faculties, its share of the block group is associated with each of those facilities to paint a cumulative picture. These aggregate portrayals enable us to examine neighborhood level patterns of environmental disparity and the facilities driving such patterns, the extent to which the co-pollutants of facilities burden nearby populations, and the effect of changes in emissions that might be anticipated under a cap-and-trade program.

## The Neighborhoods

Unequal emissions burdens from this set of large GHG emitting facilities by race or ethnicity may seem like an obvious point given that existing environmental justice analyses of other sources of pollution in California and Southern California have already shown disparities for stationary as well as mobile sources of air toxics (see, for example Pastor, Sadd, and Morello-Frosch 2004). However, the large GHG emitters subject to this analysis are a different kind of air pollution source and one cannot presume that patterns will hold without empirical verification.

As it turns out, we find a familiar story: the neighborhood analysis reveals the facilities are unevenly distributed across space, with a disproportionate share in communities that include more people of color and more poor families.

**Figure 2: Percentage Households Within 6 Miles of any Facility by Income and Race/Ethnicity, California**



However, the data shows an interesting nuance not always shown in other studies. With regard to large GHG emitters, in California, there are distinct differences by ethnicity that seem to trump income differences.

Figure 2 shows the order of burden with the six mile distance range across income brackets and race. The likelihood of proximity is highest for African-Americans, then Asians, then Latinos, and finally non-Hispanic white. At the lower end of the income distribution, racial disparities are the largest, with African Americans having more than two-thirds of their lower-income households located near a facility. It is not much better for Latinos or Asians, particularly when compared to whites, whose share of households within six miles of a facility hovers around 40 percent across all income levels. Figure 2 makes clear that while it is true for all groups that the likelihood of living near a facility declines as income rises (as does the racial disparity between groups), there remain difference by race at each and every level of income. And while the focus here is on the six mile distance, this pattern is the same at other distances.

While Figure 2 looks at the likelihood of a particular group living within six miles of a facility, Table 1 offers a more nuanced view: the composition of the neighborhoods within each of the buffers. The first five columns of the table present statistics for sets of block groups near any large GHG emitting facility by various distances; the same set of statistics is calculated for all block groups further than six miles away from a facility for purposes of comparison (column six). As discussed above, considering the results at a variety of distances helps ensure that conclusions are based on actual trends instead of statistical flukes.

The table shows that nearly half of all Californians live within six miles of a facility (46 percent), but they

## Table 1: Average Characteristics by Distance from a Facility

| | < Half Mile | < 1 Mile | < 2.5 Miles | < 5 Miles | < 6 Miles | > 6 Miles |
|---|---|---|---|---|---|---|
| Total Population | 96,362 | 575,014 | 4,368,581 | 12,844,279 | 15,492,631 | 18,226,753 |
| % of California Population | 0.3% | 1.7% | 13.3% | 38.8% | 45.9% | 54.1% |
| People Per Square Mile | 1,002 | 1,325 | 1,841 | 1,802 | 1,779 | 125 |
| | | | | | | |
| Non-Hispanic White | 42.6% | 41.2% | 37.4% | 37.5% | 38.0% | 54.0% |
| People of Color | 57.4% | 58.8% | 62.6% | 62.5% | 62.0% | 46.0% |
| African American | 8.7% | 8.2% | 8.3% | 8.5% | 8.6% | 4.6% |
| Latino | 35.0% | 38.1% | 40.2% | 38.6% | 37.5% | 28.1% |
| Asian/Pacific Islander | 10.2% | 8.9% | 10.6% | 12.0% | 12.6% | 9.7% |
| 1980's and 1990's Immigrants | 19.1% | 20.3% | 20.9% | 21.3% | 21.4% | 15.4% |
| People Below Poverty Level | 16.5% | 16.3% | 16.8% | 16.9% | 16.6% | 12.2% |
| Children (under 18 years) | 24.0% | 26.8% | 28.5% | 28.1% | 27.7% | 27.0% |
| | | | | | | |
| Renters | 56.0% | 52.8% | 50.3% | 49.6% | 49.4% | 37.8% |
| Per Capita Income (1999) | $21,399 | $20,794 | $20,043 | $20,950 | $21,186 | $24,013 |
| Relative Median Household Income (CA median = 100) | 87.7 | 87.7 | 90.4 | 93.5 | 94.0 | 105.0 |

are disproportionately people of color – 62 percent of nearby residents are people of color as compared to the 38 percent who are non-Hispanic white. African Americans live disproportionately close to facilities; their share of the population within half a mile of a facility is about twice their share of the population living outside of the six-mile range. The Latino community share is highest at the two and a half mile range, where they make up about 40 percent of that proximate population as compared to only 28 percent of those more than six miles away. Asian Pacific Islanders are also overrepresented within six miles of a facility, with the disproportionality most marked in the farthest reaches.

Beyond race and ethnicity, there are troubling trends for other vulnerable populations: immigrants, youth and the poor. Immigrants from the 1980's and 1990's are overrepresented within the six mile range, with a pattern similar to that seen in the "people of color" category.  Children in poverty (not shown), along with all people in poverty, are both disproportionately near facilities – around 23 percent and 17 percent within six miles versus 16.3 percent and 12.2 percent more than six miles away, respectively, with only slight variation within the six mile radius. Though not shown in the table, we also examined figures utilizing 150 percent of the poverty line (since some argue this is a better measure of low income for a high-cost state like California) and found the same pattern. As for other income measures, there are more renters, lower per capita incomes, and lower household incomes near polluting facilities.

In looking at the pattern, the two and a half mile radius is, we think, of special interest, partly because it captures a much more reasonable share of the overall California population (just over 13 percent) and represents a balance between stretching too far (six miles) and too tight (the half mile radius in which we capture very few people and are not allowing for the ways in which co-pollutants can travel well beyond plant boundaries). It is also the distance at which the highest correlation was found between the population-weighted co-pollutant emissions (person-tons of co-pollutants) we later consider and the air basin-wide health impacts index utilized by NRDC. The snapshot reveals that this is also a distance at which many of the disparities are the most pronounced.

While the demographic indicators in Table 1 are useful, they do not account for the relative burdens the neighborhoods carry. Columns one through

**Table 2: Average Characteristics by $PM_{10}$ Emissions from Facilities Within 6 Miles**

| | High Emissions | Middle Range | Low Emissions | No Facilities Within 6 Miles |
|---|---|---|---|---|
| Total Population | 2,317,884 | 10,940,640 | 2,234,107 | 18,226,753 |
| % of California Population | 6.9% | 32.4% | 6.6% | 54.1% |
| People Per Square Mile | 2,638 | 1,746 | 1,425 | 125 |
| | | | | |
| Non-Hispanic White | 34.4% | 37.7% | 43.5% | 54.0% |
| People of Color | 65.6% | 62.3% | 56.5% | 46.0% |
| African American | 15.9% | 7.8% | 4.9% | 4.6% |
| Latino | 34.5% | 38.8% | 33.9% | 28.1% |
| Asian/Pacific Islander | 11.7% | 12.5% | 14.3% | 9.7% |
| 1980's and 1990's Immigrants | 18.7% | 22.2% | 20.2% | 15.4% |
| People Below Poverty Level | 17.5% | 16.3% | 16.8% | 12.2% |
| Children (under 18 years) | 31.1% | 30.5% | 30.5% | 29.4% |
| | | | | |
| Renters | 50.6% | 49.6% | 47.3% | 37.8% |
| Per Capita Income (1999) | $20,986 | $21,482 | $19,945 | $24,013 |
| Relative Median Household Income (CA median = 100) | 90.8 | 95.8 | 88.4 | 105.0 |

five, for example, only break up neighborhoods according to whether they have *any* facility inside the specified distance, but some neighborhoods are within range of several facilities, and not all facilities emit the same amount of pollution. Because in-depth emissions modeling is beyond the scope of this project – although the results we offer up suggest it might be useful for a next phase – we instead employ a fairly simple methodology in which we sum up the tons of co-pollutant emissions for each co-pollutant by neighborhood (block group) from all facilities within six miles, and classify these neighborhoods into three categories: High Emissions (greater than average), Middle Range (about average) and Low Emissions (less than average), with the breaks derived through looking at the mean and what is called a standard deviation (see the appendix for details). The results of this approach are shown in Table 2. The comparison group, here, is the same used in Table 1, those neighborhoods in the greater than six mile range. We focus here on $PM_{10}$ because is it a well known co-pollutant with serious health effects including respiratory problems, cardiovascular disease and premature death.[8]

Gauging relative emissions burdens by breaking up the neighborhoods by total emissions from *all* facilities rather than by proximity to *any* facility, we find some differences, particularly in racial composition, that did not show up in the first part of Table 1, while others that did show up are strengthened and still others change in different ways. African Americans are drastically overrepresented in the High Emission group of neighborhoods, making up about 16 percent of the population – more than three times their share in either the Low Emissions group of neighborhoods or neighborhoods outside the six mile range of any facility. Latinos have their highest population representation in the middle range of emissions, and while Asians are over represented at each emissions level, their share is the highest in the places with lower emissions. As a group, there is a disparate pattern for all people of color: they make up about 46 percent of the population outside the six mile range, 57 percent of those in Low Emission areas, and 66 percent of those in High Emission areas. Again, while we only show the results at the six mile range, they are similar at other distances, including the two and a half mile distance which becomes the focus below.

While all the areas with emissions have lower income levels than in the rest of the state, and poverty generally rises with the level of emissions, one result may seem surprising: both the High Emissions *and* the Low Emissions neighborhoods have slightly lower levels of per capita and household income than the Middle Range neighborhoods. The reason seems to be that the Low Emissions areas – which have facilities but less clustering of facilities and/or facilities with lower emissions – tend to be more rural, which is geographically associated with lower-income.

In any case, the data suggests that, on average, communities of color tend to be situated near the facilities with the highest emissions, or clusters of facilities whose combined emissions add up, while pre-dominantly Anglo or mixed communities tend to live either around facilities with less emissions or beyond the range altogether. Place matters, and existing residential patterns leave communities of color more exposed to facilities that are responsible for the greatest share of co-pollutant emissions. The question, now, is how to ensure that emissions are reduced where the burdens are the largest (i.e. those neighborhoods in the High Emissions category), and in so doing, ensure that "co-benefits" go to communities on the least advantaged side of the climate gap. To begin answering this question, we try to determine which industries are driving the emission trends.

## The Industries

To understand what cap-and-trade could mean for environmental justice, we assessed which sectors and which facilities pose the greatest threat to their neighbors' health and where emissions reductions would accordingly provide the greatest benefit. This analysis reveals the distribution of responsibility by sector and facility. Such an analysis may inform the debate by helping to quantify the worst case and best case scenarios for environmental justice with regard to these facilities. For example, if the responsibility for the inequity is spread evenly across sectors and facilities, then exactly which ones curb their GHG emissions is less important for promoting environmental justice; therefore, cap-and-trade is unlikely to be a cause for public health concern because reductions anywhere would ameliorate the overall disparate pattern. If, on the other hand, the inequity is largely due to a small set of facilities, or largely restricted to a particular sector, then those facilities or that sector's purchase of allowances or failure to make reductions could significantly exacerbate existing inequalities. Trades among these facilities would be of highest concern.

Of course, the real gold standard in this task would involve forecasting how and where trades would occur (or, in the case of fees, predicting which firms would choose to pay rather than reduce emissions). However, this kind of predicting would require good financial and economic data on firms that is difficult to acquire and complicated to model. Further, it would mean making assumptions about the details of AB 32 implementation that have yet to be determined, such as how many allowances would be auctioned and at what price to which sectors. While this analysis can have value, it is beyond the scope of this report. Instead we focus on the disparities that facilities are already causing and what policy makers and regulators should take into account when creating safeguards against health-impacting trades that could widen the climate gap.

To measure the contribution of each facility to environmental disparities, we account for three measures. First, we determine how many Californians are impacted by any particular facility, utilizing information on the density of surrounding neighborhoods. Second, we take into account the total tons of co-pollutant emissions from the facility as a gauge of relative health burden. Third, we measure the racial/ethnic composition of the impacted population. These three factors in combination help us gauge the magnitude of disparity by sector, and later by facility; we focus here on $PM_{10}$ emissions due to the regulatory emphasis on the established adverse health effects of particulates (and since the results for $NO_x$ are similar to those of PM, they are omitted from reporting for the sake of brevity).

**Figure 3: Average Population per Facility (in Thousands) By Distance from Facility in California**

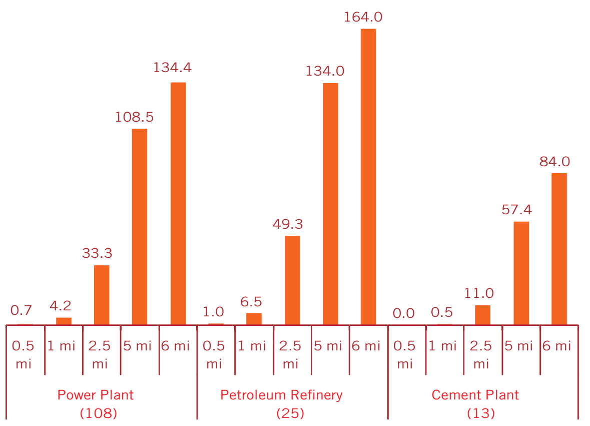
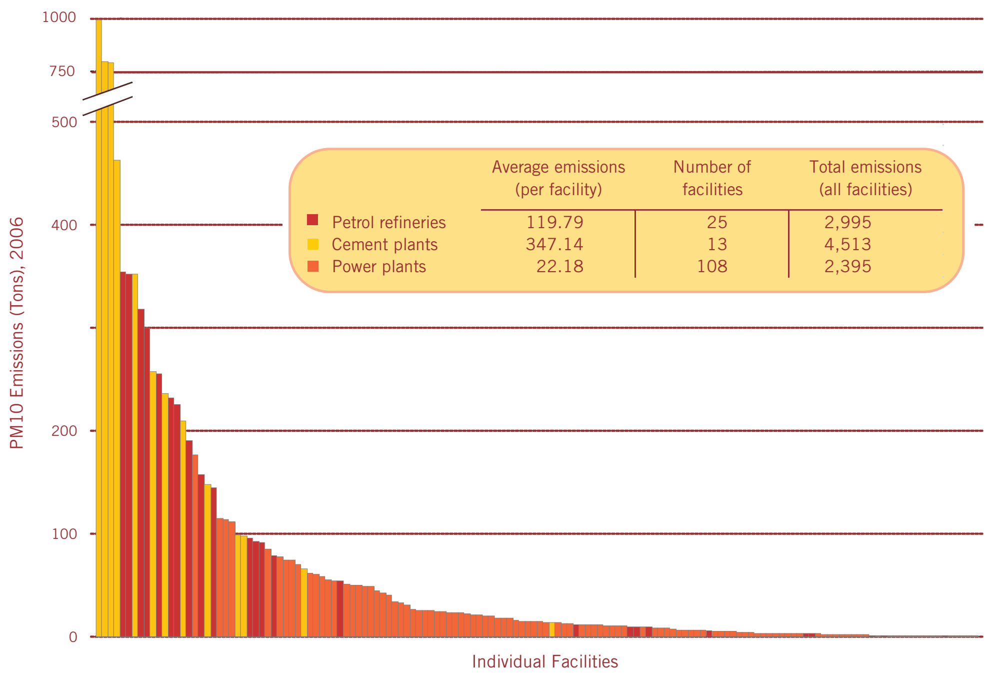


Figure 3 starts the analysis by counting up the populations within ranges of facilities and giving the total for sectors. Note that while power plants will affect more people overall due to their sheer number, refineries generally have the highest proximate population within the different ranges for the average facility. Power plants in California may also be the least harmful in terms of health impacts and least inequitably distributed by race. Despite the fact that there are more people living within a six mile radius of power plants than other facilities – primarily because there are so many more power plants than refineries or cement kilns – the 108 plants release the lowest tonnage of co-pollutants (see Figure 4

**Figure 4: $PM_{10}$ Emissions (Tons) by Facility**

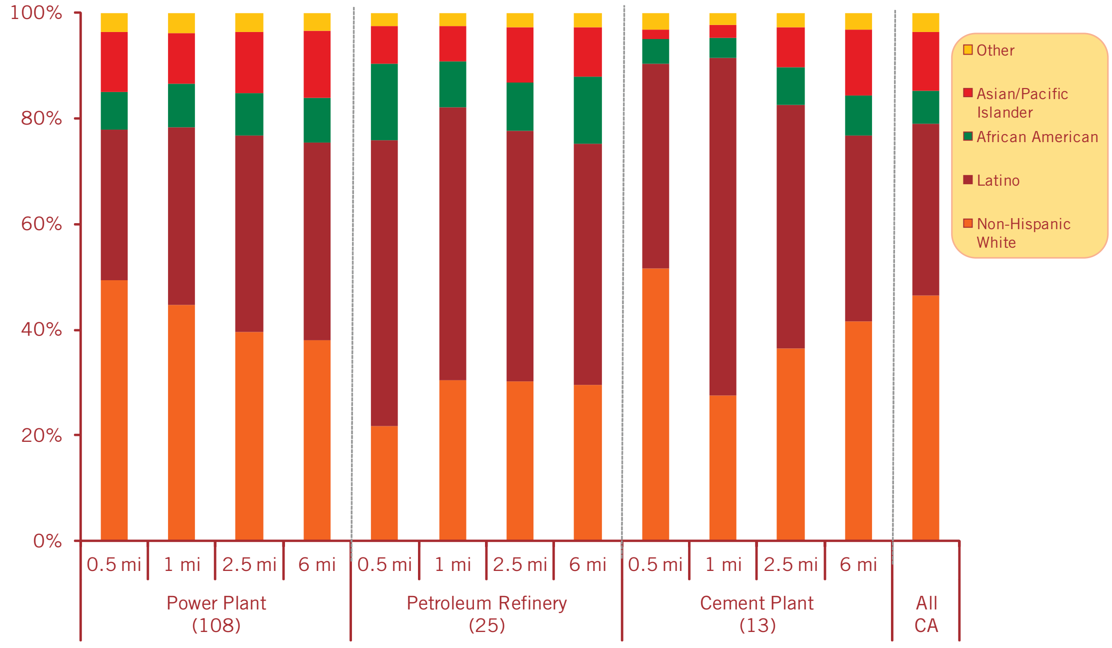


| | Average emissions (per facility) | Number of facilities | Total emissions (all facilities) |
|---|---|---|---|
| 🟥 Petrol refineries | 119.79 | 25 | 2,995 |
| 🟨 Cement plants | 347.14 | 13 | 4,513 |
| 🟧 Power plants | 22.18 | 108 | 2,395 |

in which we order the various types of facilities by their PM emissions from most to least – the power plants show up most frequently in the long tail of the distribution where emissions are lowest while cement plants and refineries show up more frequently in the early part of the distribution where emissions are much higher, resulting in combined emission by sector being highest for cement plants, followed by refineries, and lowest for power plants). Power plants also affect the lowest share of non-white residents, particularly at the nearer distances (Figure 5).[9] This is not to deny rather spectacular cases, including the recent attempt to expand a power plant in Vernon that gave rise to significant resistance from adjoining communities. Such resistance made sense: the current Vernon plant is the top power plant contributor to environmental inequity by race in California, due partly to its proximity to a predominantly immigrant population living in an area of high population density.

Petroleum refineries offer a more problematic picture. They are, on average, located in more densely populated areas (Figure 3) that are consistently home to communities of color (Figure 5). The total minority share ranges between 70 and 78 percent (depending on the particular distance) within six miles of the facility – on average, easily the most disproportionate of the three sectors. Particularly notable, blacks make up a large share in the closest distance buffers, more so than for cement plants and power plants. At the half mile distance, the African American share is more than double their share of the state population (14 percent as compared to 6 percent) and at the one mile distance it is one and a half times as high. Refineries are also unique in that their associated demographics are quite consistent

**Figure 5: Racial/Ethnic Composition of Population by Distance from Facility California**



throughout the surrounding geography, at least beyond the immediate half mile range. They tend to have much higher co-pollutant emissions than power plants, but lower than cement plants (Figure 4).

Although cement plants are few and affect few (Figure 3), they are by far the dirtiest (again, see the distribution as well as the average emissions figures in Figure 4). At the closest range of half a mile, non-Hispanic Whites are actually slightly overrepresented as compared to the state. However, the number of people in this range of cement plants is very small (about 300 people in all). When we consider the much larger population within one mile (about 6,500 people) the minority population is large, due almost exclusively to the high concentration of Latinos who make up 64 percent of the population (Figure 5). The percentage minority declines rapidly moving further away from cement facilities due exclusively to a steep decline in the Latino share of the population, supplemented by a steep increase in the non-Hispanic White share, and despite both a steep increase in the Asian/Pacific Islander share and a more modest increase in the African American share.

## The Disparities

Closing the climate gap requires measuring the factors that contribute to any disparity in environmental burdens. To evaluate the contribution of each facility to the overall pattern of environmental disparity, we developed a single metric of disparity that combines the total impacted population, PM emissions, and the racial/ethnic composition of the surrounding neighborhoods.  Such a measure can characterize the individual impact of one facility, but it also allows us to aggregate by sector or across all facilities in the state. It captures the difference in relative impact between a facility located in a sparsely populated area with a population that is 90 percent minority but whose emissions are moderate, and a facility in a densely populated area that is 70 percent minority, but with very high emissions.

The index we developed – the "pollution disparity index" – measures the relative co-pollutant burden on communities of color, as compared with non-Hispanic white communities. We start our calculations at the facility level. Using the socioeconomic neighborhood characteristics that have been attached to each facility, we approximate the local $PM_{10}$ emissions burden as the population-weighted $PM_{10}$ emissions (i.e. total person-tons of $PM_{10}$) for people of color and non-Hispanic whites. Using such a population-weighted emissions measure means that a facility may have a higher score for people of color even if it has a lower share of people of color in the vicinity because, although the community of color is a lower percentage, it is larger in population and around a facility with higher emissions. We then subtract the population-weighted $PM_{10}$ emissions for non-Hispanic whites from those for people of color (after adjusting the weights by dividing by the number of each group in the state), which gives us the pollution disparity index for that facility, or a measurement of environmental injustice (See the Technical Appendix for details). If the pollution disparity index is added up across all facilities in the state, the result is equal to the statewide difference – or disparity – in average $PM_{10}$ emissions burden between people of color and non-Hispanic whites.

Every facility in our data set is given a pollution disparity index at the varying buffer distances used throughout this analysis (half mile, one mile, two and a half mile, five mile, and six mile), with the characteristics of the "neighborhood" determined by the distance from the facility. The pollution disparity index can then be used to aggregate (at discrete distances bands) for different levels of analysis – it can be combined by sector or across the facilities in a particular region to get the combined contribution of that group of facilities to the statewide disparity in average $PM_{10}$ emissions burden between people of color and non-Hispanic whites caused by all facilities under analysis.

While we cover many technical details of this calculation in the Technical Appendix, a few are worth noting here. First, the measure of population-weighted $PM_{10}$ emissions upon which the pollution disparity index is based should be viewed only as a relative measure that compares the impact of facilities and their disparity within each buffer distance and not across them (similar to the Risk Screening Environmental Indicators risk score developed by the U.S. EPA; see Ash, et al. 2009). Second, the pollution disparity index can have positive and negative values. This depends on the demographics of the neighborhood near the facility; if the share of the state's people of color residing near the facility is greater than the share of the state's non-Hispanic white population residing near the facility, then the score will be positive (if reverse is true, it will be negative). Third, we are effectively assuming in this calculation that beyond six miles, there are no emissions. In practice this is not true, but as mentioned earlier, doing complex emissions dispersion modeling is beyond the scope of this report. Finally, the pollution disparity index is just that – an index of demographic disparity in local pollution burden and not a pure measure of local pollution burden. Thus, while it is useful for highlighting the most disparate facilities, it should be considered in practice along with overall local pollution burden (e.g. population-weighted $PM_{10}$ for all people) as we do below.

The formula for the pollution disparity index also allows for determining average emissions burdens for individual ethnic groups. To do this, we calculate the population-weighted $PM_{10}$ emissions for each ethnic group around each facility, divide it by the state population for each group, and then sum it up to the California level, at each buffer distance. The resulting average burdens are summarized in Table 3; there, the emissions burdens rise with distance because we are "allowing" a wider range of facilities to have an impact on any particular community.

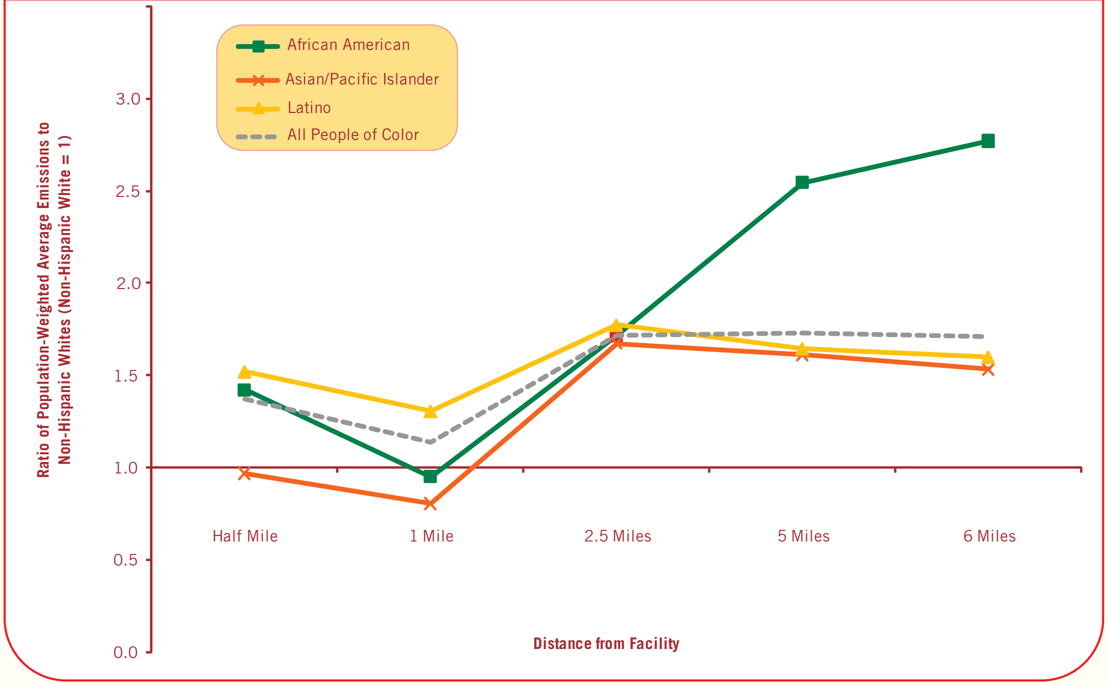
The difference between the average value for each group and that for non-Hispanic whites at each distance in Table 3 is a measure of statewide disparity in $PM_{10}$ emissions burden between that group and non-Hispanic whites at that particular distance. To determine relative differences in emissions burden, which allows us to compare the degree of disparity across the distances, we simply divide the average value for each racial/ethnic group by that for non-Hispanic whites at each distance. The resulting relative $PM_{10}$ emissions burdens are reported in Figure 6.

With the exceptions of Asians at the half and one mile distances, and African Americans at the one mile distance, there are persistent gaps at each level; the relative emissions burden for all people of color combined is always above that for non-Hispanic whites (which is always equal to one in the graph). The trend for Latinos is similar to the trend for all people of color, which is not surprising given that Latinos constitute the overwhelming majority of non-

**Table 3: Population-Weighted Average Annual $PM_{10}$ Emissions (Tons) Burden by Race/Ethnicity**

| | Half Mile | 1 Mile | 2.5 Miles | 5 Miles | 6 Miles |
|---|---|---|---|---|---|
| Non-Hispanic White | 0.07 | 0.67 | 6.73 | 29.55 | 41.51 |
| African American | 0.10 | 0.64 | 11.55 | 75.23 | 115.03 |
| Latino | 0.11 | 0.88 | 11.93 | 48.61 | 66.37 |
| Asian/Pacific Islander | 0.07 | 0.54 | 11.26 | 47.62 | 63.57 |
| All People of Color | 0.10 | 0.77 | 11.54 | 51.08 | 70.98 |

Figure 6: Relative Racial/Ethnic Inequities Compared to Non-Hispanic Whites in $PM_{10}$ Emissions Burden from Large GHG-Emitting Facilities by Buffer Distance



whites. They have the greatest emissions burden of any group up to the two and a half mile range where it levels off and declines slightly, while the emissions burden for African Americans soars dramatically to nearly three times the level for non-Hispanic whites at the six mile range. As for Asians, once we move beyond the one mile range, there are also persistent differences. Following the pattern for Latinos, as distance increases beyond the two and a half mile range, the disparity for all people of color combined levels off.

## The Sectors

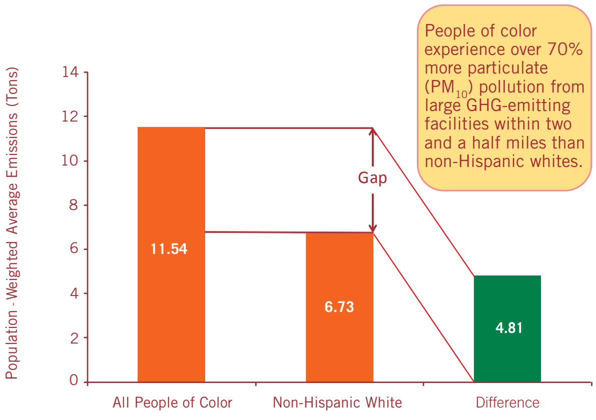
Given the disparity in PM emissions burdens for people of color seen in Figure 6, we decided to examine whether power plants, refineries, or cement plants were driving the overall trend. For this analysis, we focus on the two and a half mile distance threshold. We think this is a reasonable distance for portraying our results in terms of emissions burden – and it is also the case that the population-weighted emissions burden at two and a half miles is the most highly correlated among the different buffer distances with the air basin-wide Health impacts index, giving us some confidence in this choice of radius. In any case, the relative contribution of the various sectors and facilities to statewide inequity as measured by the pollution disparity index is not particularly sensitive to the buffers (with the exception of the half mile distance due to the very small populations captured in that range), so focusing in on one distance illustrates the overall pattern and allows for brevity in the presentation.

Figure 7 begins this analysis by graphically displaying the difference in emissions burdens between people of color and non-Hispanic whites seen in the third column of Table 3. Figure 8 then calculates which sectors are accounting for the PM emissions loads of each group and for the difference between them. From this, we can see that while refineries account for the majority of $PM_{10}$ emissions burden for all people, they account for a much larger share (about 93 percent) of the difference in emissions burden between people of color and non-Hispanic whites.

Which facilities are driving this difference in emissions burden? Because the statewide difference is simply the sum of the pollution disparity index across all facilities, we are able to rank the facilities by the index in Figure 9. The ranking confirms that refineries are driving the difference, as they are eight of the top ten contributors to co-pollutant emissions disparity. Moreover, the top eight facilities overall actually add up to the entire difference; if you took all the facilities below that, you'd have an even distribution of $PM_{10}$ emissions burden by race, since some facilities (displayed at the bottom of the distribution in that figure) disproportionately burden whites. The full distribution also shows that a vast majority of facilities have a score near zero. In short, a few facilities, mostly petroleum refineries, account for most of the observed inequity.

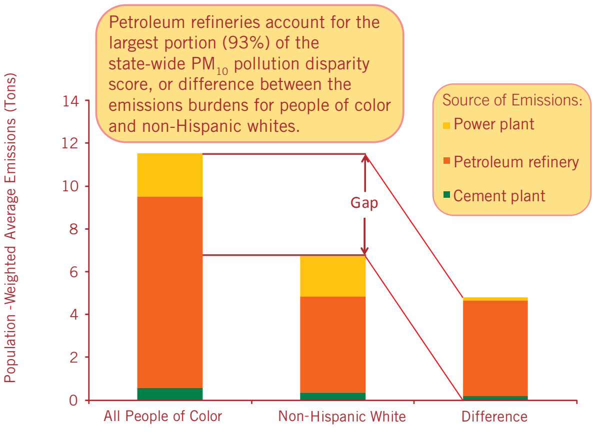
The geographic location of the top ten facilities is depicted in Figure 10. There we can see that nearly all are in Southern California, with only one in the San Francisco Bay Area – the Chevron refinery in Richmond, which ranks sixth in pollution disparity. In Southern California, we see that it is mainly a cluster of refineries around the Los Angeles and Long Beach ports that are driving the pattern of disparity, with five of the remaining top ten facilities located in or adjacent to the port-side neighborhood of Wilmington (part of Los Angeles City). These include the BP refinery in Carson, which takes first place in disparity, and the Tesoro Wilmington Refinery, which comes in second. The rest of the top ten facilities include two refineries (the Paramount Refinery in Paramount and the ExxonMobil Torrance Refinery in Torrance), one power plant (the Malburg Generating Station in Vernon), and one cement plant (the California Portland Cement Company Colton Plant in Colton).

**Figure 7: Population-Weighted Average Annual Particulate ($PM_{10}$) Emissions Burden (Tons) by Race/Ethnicity for Facilities within 2.5 Miles**



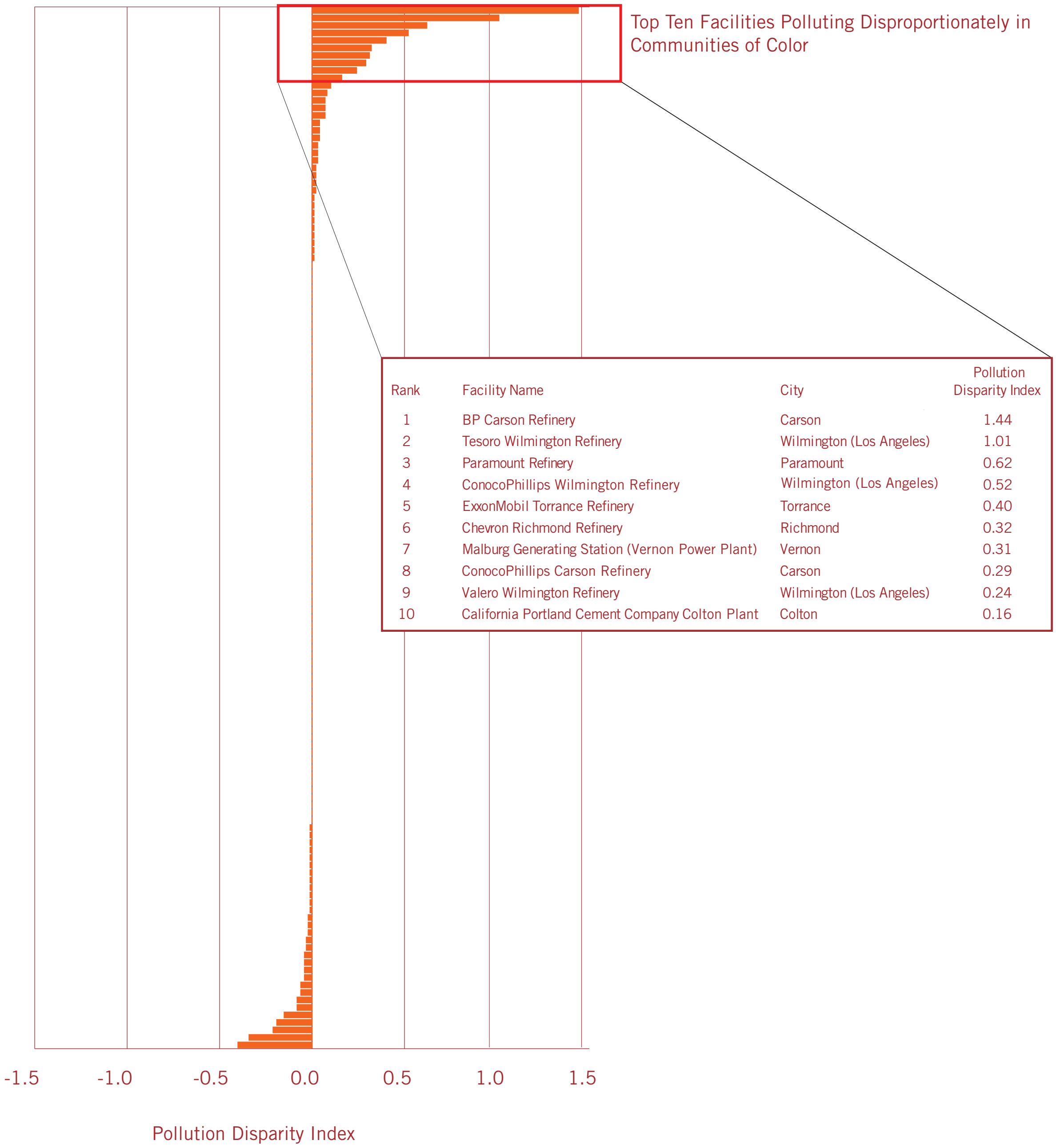
People of color experience over 70% more particulate ($PM_{10}$) pollution from large GHG-emitting facilities within two and a half miles than non-Hispanic whites.

**Figure 8: Population-Weighted Average Annual Particulate ($PM_{10}$) Emissions Burden (Tons) by Facility Category and Race/Ethnicity for Facilities within 2.5 Miles**



Petroleum refineries account for the largest portion (93%) of the state-wide $PM_{10}$ pollution disparity score, or difference between the emissions burdens for people of color and non-Hispanic whites.

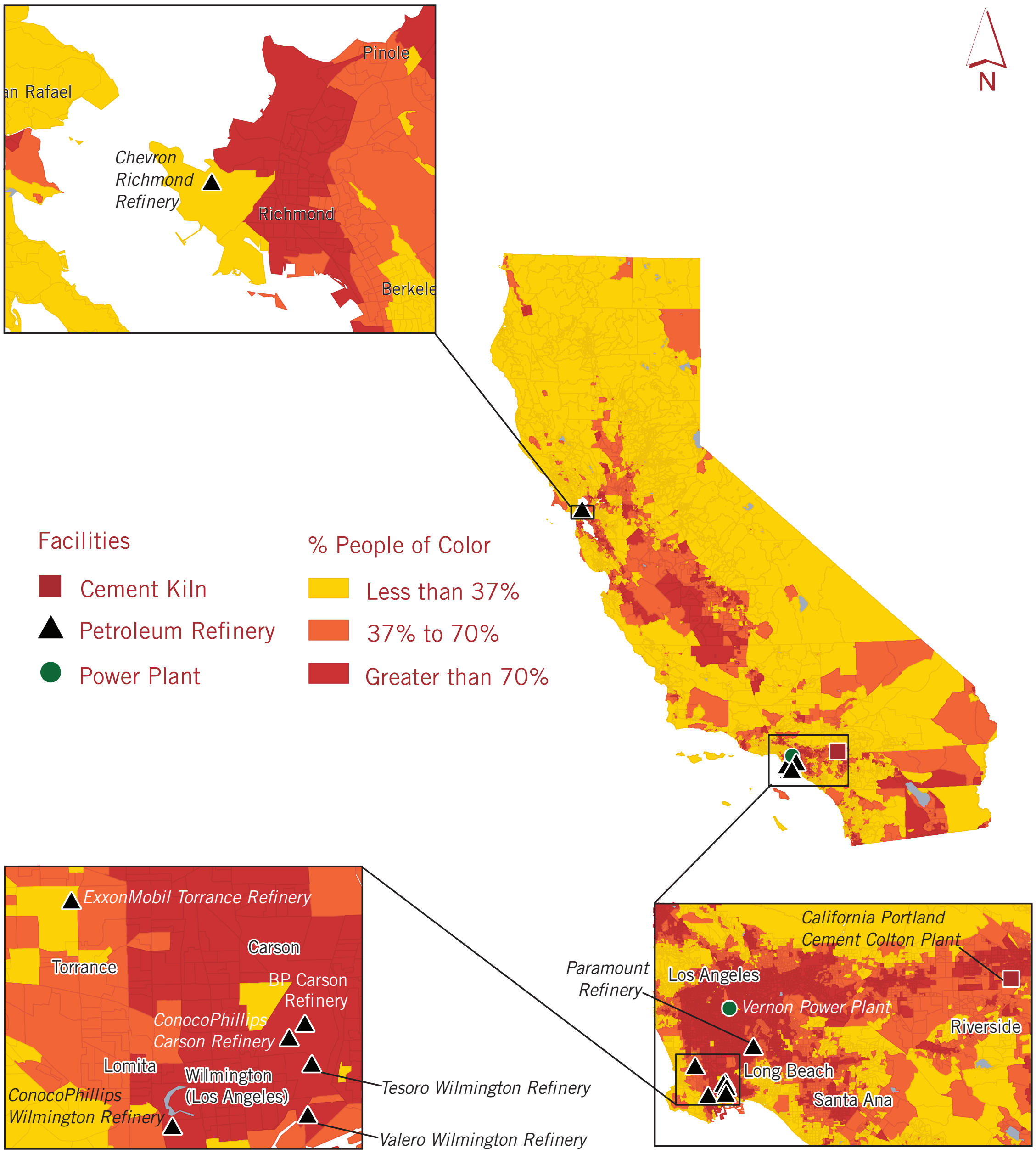
**Figure 9: Distribution of the Pollution Disparity Index for $PM_{10}$ at 2.5 Miles Across All Major GHG-Emitting Facilities**



Top Ten Facilities Polluting Disproportionately in Communities of Color

| Rank | Facility Name | City | Pollution Disparity Index |
|---|---|---|---|
| 1 | BP Carson Refinery | Carson | 1.44 |
| 2 | Tesoro Wilmington Refinery | Wilmington (Los Angeles) | 1.01 |
| 3 | Paramount Refinery | Paramount | 0.62 |
| 4 | ConocoPhillips Wilmington Refinery | Wilmington (Los Angeles) | 0.52 |
| 5 | ExxonMobil Torrance Refinery | Torrance | 0.40 |
| 6 | Chevron Richmond Refinery | Richmond | 0.32 |
| 7 | Malburg Generating Station (Vernon Power Plant) | Vernon | 0.31 |
| 8 | ConocoPhillips Carson Refinery | Carson | 0.29 |
| 9 | Valero Wilmington Refinery | Wilmington (Los Angeles) | 0.24 |
| 10 | California Portland Cement Company Colton Plant | Colton | 0.16 |

**Figure 10: Map of Top Ten Facilities in Pollution Disparity**



## The Risks

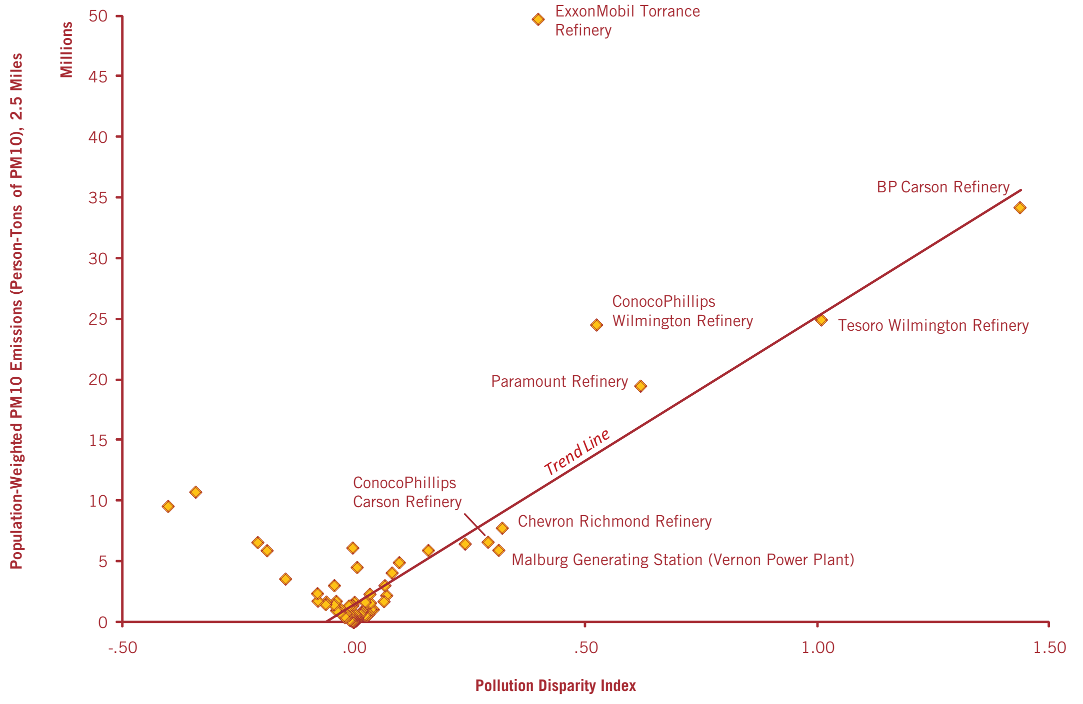
What does all this mean for lowering carbon emissions, protecting public health and closing the climate gap? How should these findings affect CARB's implementation of AB 32? What are the broader implications for market-oriented policies that might eventually emerge at the national level?

The first point made by this analysis is that some trades or allowance allocations *could* widen the climate gap by worsening disparities in emissions burdens by race/ethnicity. The second point is that while there are legitimate concerns about outcomes resulting from trades or the distribution of allowances *within* a sector – such as when a power plant that impacts a large number of people in low-income communities of color eschews reductions in favor of buying credits from a power plant that is nowhere near any population of size or outbidding that power plant in an allowance auction – the real concern might be trade and allowance distribution *between* sectors.

The third point that emerges from this work is the fact that it is a relatively small number of facilities that are driving most of the disparity in emissions; while this could be a problem, the concentration of "bad actors" also suggests that regulatory efforts could be carried out in an administratively feasible and cost efficient way to maximize public health benefits of GHG reduction strategies in the communities that need them the most.

Another point, which is of great importance for policy, is that targeting these facilities would help everyone. Recall, for example, that we employed the two and a half mile distance buffer in our analysis partly because of the strong correlation between population-weighted co-pollutant emissions at that distance and the health impacts index for the air basin derived using the measure indicated in Bailey et al. (2008). In Figure 11, we plot that measure

**Figure 11: $PM_{10}$ Emissions Burden and Racial/Ethnic Inequity by Facility**



against the pollution disparity index. There we can see that the two measures generally have a positive relationship – the higher the emissions burden the higher the inequity – and it is a handful of facilities with extreme values that are really driving the positive correlation (as they did in our analysis of disparity by race). The pattern suggests both that these are the sites of concern *and* that focusing on disproportionality will also have strong impacts on overall health (or vice versa). For example, in absence of the top eight facilities in terms of the pollution disparity index (labeled in Figure 11), co-pollutant emissions would be more or less evenly distributed by race/ethnicity *and* overall emissions burden would be significantly reduced.

Table 4 illustrates this in a slightly different way by showing the top ten percent of the facilities studied ranked by the aforementioned health impacts index (which is more regional in scope). There we see many of the same facilities that were identified as the most disparate by race/ethnicity in Figure 9, with eight of the ten most disparate facilities also ranking highly in terms of potential health impacts.

Clearly, facilities have to be located somewhere and not all sites will find it cost-efficient to be the first to reduce their emissions. These facilities will be among those purchasing relatively more credits and the last to realize co-pollutant reductions in their neighborhoods. While we have not demonstrated conclusively that the disparity by race *will* sharpen, we have shown that this type of disparity *could* sharpen.

The text of AB 32 unmistakably lifts up health benefits from reduced co-pollutants as an important objective of the legislation, and the California Air Resources Board has long indicated a serious concern about promoting equitable environmental outcomes as part of its overall program of activities. With the issues of overall burden and disproportionate burden intimately related, CARB could craft safeguards that ensure market strategies address these concerns and help close the climate gap.

## The Policy Choices

So what would an environmentally just GHG reduction strategy look like? We suggest a menu of market-based and regulatory approaches that could work toward a more equitable outcome.

**Table 4: Top Ten Percent of California's Major Greenhouse Gas-Emitting Facilities Ranked by the Health Impacts Index**

| Rank | Facility Name | City | Health Impacts Index |
|---|---|---|---|
| 1 | ExxonMobil Torrance Refinery | Torrance | 54.4 |
| 2 | Tesoro Wilmington Refinery | Wilmington (Los Angeles) | 50.0 |
| 3 | BP Carson Refinery | Carson | 46.3 |
| 4 | Chevron El Segundo Refinery | El Segundo | 41.2 |
| 5 | ConocoPhillips Wilmington Refinery | Wilmington (Los Angeles) | 30.3 |
| 6 | Shell Martinez Refinery | Martinez | 27.1 |
| 7 | Valero Benicia Refinery | Benicia | 19.1 |
| 8 | Mountainview Power Plant | San Bernardino | 17.5 |
| 9 | Chevron Richmond Refinery | Richmond | 17.3 |
| 10 | California Portland Cement Company Colton Plant | Colton | 14.1 |
| 11 | Paramount Refinery | Paramount | 13.8 |
| 12 | Valero Wilmington Refinery | Wilmington (Los Angeles) | 13.0 |
| 13 | Cemex Victorville/White Mountain Quarry | Apple Valley | 12.5 |
| 14 | Tesoro Golden Eagle Refinery | Martinez | 12.1 |
| 15 | Etiwanda Generating Station | Rancho Cucamonga | 11.1 |

First, one theoretically ideal but perhaps logistically challenging approach would entail pricing in the co-pollutants along with carbon. In this case, allowances might get extra credit (or carbon fees might be priced differently) depending on the ratio of co-pollutants to GHG. Suppose, for example, that a carbon fee was higher (or allowances were more expensive) if co-pollutants were more prevalent and/or population densities were greater; this could induce deeper GHG reductions in locations where health benefits would be maximized.

This is an elegant idea but one that would involve significant complexity in allowance design, could create problems in a trading system (which is easier if allowances are homogenous units measured only by their carbon emissions), and could significantly complicate the administration and compliance for either a trading or fee system. A simpler approach might be to vary permit prices (or fees) by the average relationship between co-pollutants and GHGs in different sectors, but this would be highly inefficient because it does not consider the substantial variation in marginal health co-benefits from GHG reduction that appears to exist at the facility level.

We see four other strategies that might make sense and be easier to implement.

The first strategy involves identification of those facilities that either have very high co-pollutant levels or make a very significant contribution to the pattern of environmental disparity in the state. These facilities – which should be small in number – would be restricted in allowance allocations, purchases of allowances from other facilities, and use of offsets, required instead to reduce emissions locally to meet their contribution to achieving the statewide carbon cap. While this might limit the market, it would be a small imposition on the system as a whole and would target only a handful of facilities. In a fee system, these facilities could be restricted in their capacity to pay fees rather than change operations.

A second strategy involves the creation of trading zones, based not on whether the facility imposes a significant burden but whether the adjacent areas are currently overburdened by emissions. Zonal restrictions on trading were used in the second phase of the RECLAIM program in Southern California, in which inland facilities were allowed to purchase credits from coastal facilities (where pollution was highest) as well as other inland facilities but coastal facilities were prohibited from making out-of-zone buys (Fowlie, Holland and Mansur 2009). This imposes some inefficiency but it is not administratively complex and it could be justified by the associated environmental benefits. However, as Kaswan (2009) suggests, certainty in achieving actual reductions in prioritized areas would largely depend on how allowances were distributed, with trading playing a small role, for example, if facilities are able to purchase all the allowances they need for any compliance period at auction or if they are able to rely on offsets to make up the difference between allowances holding and emissions. Thus, for this strategy to be effective it would have to be coupled with limits on overall allowance allocations and use of offsets in such zones to ensure that the total quantity of emissions allowed in the zonal market amounted to a net reduction of sufficient size. The zonal restrictions on trading would then prevent any increase above that level and likely lead to further reductions.

A third strategy involves the imposition of surcharges on allowances or fees in highly impacted areas, with the funds being returned for environmental and other improvements in those same areas. In this case, some facilities that are not the worst offenders – but share responsibility for the highest impacts because of their location – would be forced to contribute as well. This would create a tight nexus between the surcharge and the improvement and would be justified by the potential health benefits that could be realized (Boyce 2009).

A fourth strategy involves the creation of a community benefits fund, based as a share of all the monies collected from allowance auctions or fees that could target emissions improvements in neighborhoods that are overburdened, regardless of whether they are in the same location as the sources. Such neighborhoods could be identified through examining dimensions such as the proximity to hazards, exposure to various sorts of air pollution, and community-based social vulnerability; we have been working with the support of the California Air Resources Board to develop exactly such a typology. While the geographic nexus between the emitters and the communities receiving benefits might be looser in this scheme – unlike in the surcharge approach – it would be more efficient in achieving health and other benefits (money collected is spent where it is most needed not only where it is collected). Neighborhoods need not be limited to pollution issues in how they spend the funds but could rather improve park space, job training, and other identified needs.

The basic concept of a community benefits fund finds support even amongst some who are critical of any tinkering with carbon market mechanisms (e.g. Schatzki and Stavins 2009). A benefits fund is also aligned with the notion of compensating lower-income consumers for the higher energy prices that will be triggered by limiting carbon (Boyce and Riddle 2007). All of this would be made more possible if the state was to take up the recommendation of the Economic and Allocation Advisory Committee (EAAC 2010) that indicated that the Air Resources Board “rely principally, and perhaps exclusively, on auctioning as the method for distributing allowances.” A full auction would make the system much closer to a carbon fee system and, as EAAC notes, have several other attractive features. Finally, legislation currently in progress in the state legislature (AB 1405) could make a community benefits fund real: it would force the state to direct a portion of any revenues generated under AB 32 – whether from fees or auction revenues – to communities that are historically disadvantaged in terms of both economic and environmental health.

There are therefore real policy opportunities to close the climate gap. At the very least, CARB needs to create a mechanism for monitoring allowance allocations and trades or fee payments, and assess the impact on co-pollutants as facilities make their choice about how to contribute to achieving the overall cap. The research above has demonstrated a point that is really quite obvious: cap-and-trade is inherently unequal – and if it weren’t, no trades would take place. Given that, we should all be interested in exactly the pattern of geographic inequality that will emerge and whether it will exacerbate or ameliorate the pattern of environmental disparity that has marked the state and helped to produce the climate gap.

## Minding the Gap

California is at a crossroads. With a world in peril and public health at risk, the state has chosen to lead in the global fight to reduce greenhouse gas emissions, rescue our economy, and protect the planet for generations to come.

The state has also chosen to make equitable environmental outcomes central to its approach to these issues. An Environmental Justice Advisory Committee (EJAC) was written explicitly into the AB 32 legislation and while there have been tensions between the committee and the state, particularly related to cap-and-trade as a viable GHG reduction strategy, there is clearly a shared concern that implementation of AB 32 be done in a way that is fair to all communities.

As California takes steps to respond to the climate crisis, closing the climate gap needs to be a higher priority, starting with making sure GHG reduction policies don't leave anyone behind and don't unintentionally widen the climate gap.

The research reviewed here suggests that the concerns of environmental justice advocates about the unequal impacts of cap-and-trade are not misplaced. The major facilities that will be regulated under any carbon reduction program are more frequently located near people of color and lower-income communities, with a handful of petroleum refineries making a significant contribution to the pattern of inequity. While we cannot predict the exact direction of trades, we do know that it is quite possible that an unconstrained market system will, at a minimum, fail to realize the full benefits of co-pollutant reduction and, at a maximum, worsen the current pattern of inequality.

Ensuring that a market-oriented regulatory system – either cap-and-trade or fees – avoids widening the climate gap is essential. A series of simple strategies – prohibit facilities from making trades with and restrict allowance allocations and offset uses with significant health impacts, impose a surcharge in locations where health benefits could be high, limit trades by zone depending on overall pollution burden, or develop a compensation system that could redirect revenues to climate gap communities to address health and other concerns – are all relatively simple to design and implement and should be considered as part of the policy menu. In addition, the state should consider the development of a monitoring system that tracks trades and offset use (or fee payments) to ensure that a market system does not contribute to the inequities depicted here, and to enable other mitigation policies to be triggered as needed.

The stakes are high and the time is now. In order to successfully make the monumental economic and social shifts required to address the climate change challenge, we need to engage diverse constituencies in ways that take into account everyone's needs and health concerns. New and more inclusive GHG reduction policies can protect our communities and the planet. California faces a big challenge but also a big opportunity. We are poised to lead not only in curbing climate change, but also in closing the climate gap. As other states and the nation move forward, the impact of this work will multiply. We should get this right – and fair – from the beginning.

# Notes

[1] See California Health & Safety Code §38570(b).

[2] Ibid. §38570(b)(2).

[3] For a description of how the dataset was constructed, see "Appendix A: Co-Benefits Analysis Methods" at: http://www.nrdc.org/globalWarming/boosting/boostinga.pdf

[4] The emissions inventory can be accessed at: http://www.arb.ca.gov/ei/emissiondata.htm

[5] The 2008 GHG emissions data can be accessed at: http://www.arb.ca.gov/cc/reporting/ghg-rep/ghg-reports.htm

[6] TeleAtlas, 2007.

[7] Health endpoint factors are the estimated number of tons per year of a particular pollutant that can be associated with each case of a health endpoint (in this case premature mortality) in within a particular geographic area (in this case air basins). See www.arb.ca.gov/planning/gmerp/march21plan/docs/health_analysis_supplement.pdf for the more information, including the health endpoint factors for each air basin.

[8] See USEPA, AIRTrends 1995 Summary at: http://www.epa.gov/airtrends/aqtrnd95/pm10.html

[9] For Figure 5, in order to simplify the graph, the racial composition of people living near the different facility types at the five mile distance is not shown. It was chosen as the distance band to omit because it had a racial composition that was nearly identical to the composition at the six mile distance band, which is shown.

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## Photo Credit

Photos on the front cover from left to right:

Photo by Jesse Marquez.

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Photo of Communities for a Better Environment (CBE) Wilmington Lead Organizer by PERE.

Executive Summary, Page 1: La Paloma power plant and Exxon Mobile Refinery in Torrance, CA, TeleAtlas, 2010.

Executive Summary, Page 3: Tesoro Wilmington Refinery, 9/25/09, Photo by Jesse Marquez.

# Technical Appendix

## Constructing the Health Impact Index

Based on Bailey et al. (2008), we used the $NO_X$ and $PM_{10}$ emissions to calculate a health impacts index for each facility, which represents the relative potential health impact of the facilities included in the analysis (see Bailey et al. 2008 for assumptions and limitations). The only difference is that we used $PM_{10}$ rather than total PM because it is considered more closely tied to health endpoints. The NOX and $PM_{10}$ data come from the 2006 ARB Emissions Inventory for stationary sources and can be accessed at: http://www.arb.ca.gov/app/emsinv/emssumcat.php. The index also relies on health endpoint factors which are the estimated number of tons per year of a particular pollutant (here, $NO_x$ and $PM_{10}$) that can be associated with each case of a health endpoint (here, premature mortality) within a particular geographic area (here, air basins). The formula for the health impacts index is:

$$HI_i = \left( NO_x / HEP_{AB} \right) + \left( PM_{2.5} / HEP_{AB} \right)$$

Where: $HI_i$ = Health Impacts Index

$NO_x$ = $NO_x$ emissions in 2006

$PM_{2.5}$ = $PM_{10}$ emissions in 2006 divided by the ratio of $PM_{10}$ to $PM_{2.5}$

$HEP_{AB}$ = Air basin specific health endpoint factor for premature mortality

## Matching Block Groups and Facilities

The challenge of matching neighborhoods and facilities is this: facilities are points in space and block groups are areal units. Mohai and Saha (2006) found in their study of geographic methodology that the method employed to describe the spatial relationship of point-location environmental hazards and surrounding populations is the primary reason for the varied results found in many studies relying on similar data and geographic coverage. The "classic" approach, used in most studies, connects census tracts to a hazardous waste treatment, storage, or disposal facility (TSDF) if such a facility is located within the boundaries of the tract itself, making it a "host tract." This approach does not account for people residing in nearby, but non-host tracts, that could well possibly live, on average, about the same distance from the facility. These discrepancies are particularly important given the tendency for TSDFs to be located near tract boundaries (which are often defined by roads) and the large variation in the size and spatial distribution of populations within census tracts.

Instead, Mohai and Saha recommend a distance-based approach where tracts become associated with a facility if they fall within a specified distance of the facility as measured by either one of the tract boundaries, its centroid, or half of its geographic area. We employ a distance-based approach at the block group level that incorporates population weighing. We specifically drilled down to census block level to get the most geographically detailed population information publicly available and, as noted in the text, estimated the share of each block group's population that fell within each buffer distance of each facility. Thus, rather than expressing the block group-facility association in binary terms (i.e., proximate or not), in cases where a buffer intersects the boundaries of a block group, it is expressed as a percentage or fractional association that is equivalent to the share of the block group population captured. In our opinion, such "population weighting" using block-level population information is important because even at the relatively detailed block group level of geography, an evenly distributed population within the block group is uncommon; half of the area of a block group does not necessarily include half the population. Thus, this method should result in a more accurate representation of the number of people and the characteristics those who live near facilities.

## Emissions Categorizations

We chose the $PM_{10}$ emission categories shown in Table 2 based on standard deviations from the mean. The means and standard deviations used were calculated at the block group level for the natural log of the summed emissions from all facilities within six miles of each block group, across all block groups within six miles of any facility. The natural log function is commonly used to normalize measures that exhibit a "long tail" or exponential distribution – which describes the measure of summed emissions.

Among all block groups within six miles of any facility, we defined High Emissions block groups as those with emissions over one standard deviation above, Middle Range block groups as those with emissions within one standard deviation of the mean (plus or minus), and Low Emissions block groups as those with emissions under one standard deviation below the mean.

## Constructing the Pollution Disparity Index

The pollution disparity index used in this report, which was calculated at the facility level, can be described as a measure of the contribution each facility makes to the statewide difference in average co-pollutant emissions burden between people of color and non-Hispanic whites from the facilities included in our analysis, for a particular distance from the facilities. The derivation below describes how the statewide difference in emissions burden can be decomposed into the facility-level index. Note that while we used $PM_{10}$ as the pollutant and people of color and non-Hispanic whites as the population groups, by making slight adjustments to the below equation, the index and associated statewide difference in emissions burden could be calculated to reflect disparity in emissions of any other pollutant and/or between any other two population groups defined by race/ethnicity, income, or any other measurable characteristic.

In the derivation shown below, POC stands for total people of color, NHW stands for total non-Hispanic whites, d is distance, i is any facility in California included in the analysis, and CA means for the entire state of California.

Total statewide $PM_{10}$ emissions burden associated with the facilities included in our analysis can be calculated as the population-weighted sum of $PM_{10}$ emissions across all facilities i within a certain distance d (i.e. total person-tons of $PM_{10}$). Average local $PM_{10}$ emissions burden at distance d, calculated separately for each group, is measured essentially as a simple population-weighted average of $PM_{10}$ emissions across all facilities i, using the population within distance d of each facility as the weight, but with one modification: the sum of the weights (the denominators above) is set to the total California population for each group rather than the sum across facilities. This weighting scheme implicitly sets the $PM_{10}$ emissions to zero for all people beyond distance d of any facility, and is

$$\textit{CA difference in average PM10 burden}_{(POC-NHW)d}$$

$$= [\textit{average } POC\ PM10\ \textit{burden}_d] - [\textit{average } NHW\ PM10\ \textit{burden}_d]$$

$$= \left[\frac{\sum_{i=1}^{n} POC_i \times PM10_{i,d}}{POC_{CA}}\right] - \left[\frac{\sum_{i=1}^{n} NHW_i \times PM10_{i,d}}{NHW_{CA}}\right]$$

$$= \sum_{i=1}^{n}\left[\frac{POC_i \times PM10_{i,d}}{POC_{CA}}\right] - \sum_{i=1}^{n}\left[\frac{NHW_i \times PM10_{i,d}}{NHW_{CA}}\right]$$

$$= \left[\frac{POC_{1,d} \times PM10_{1,d}}{POC_{CA}} + \frac{POC_{2,d} \times PM10_{2,d}}{POC_{CA}} + \ldots \frac{POC_{n,d} \times PM10_{n,d}}{POC_{CA}}\right] - \left[\frac{NHW_{1,d} \times PM10_{1,d}}{NHW_{CA}} + \frac{NHW_{2,d} \times PM10_{2,d}}{NHW_{CA}} + \ldots \frac{NHW_{n,d} \times PM10_{n,d}}{NHW_{CA}}\right]$$

$$= \left[\frac{POC_{1,d} \times PM10_{1,d}}{POC_{CA}} - \frac{NHW_{1,d} \times PM10_{1,d}}{NHW_{CA}}\right] + \left[\frac{POC_{2,d} \times PM10_{2,d}}{POC_{CA}} - \frac{NHW_{2,d} \times PM10_{2,d}}{NHW_{CA}}\right] + \ldots \left[\frac{POC_{n,d} \times PM10_{n,d}}{POC_{CA}} - \frac{NHW_{n,d} \times PM10_{n,d}}{NHW_{CA}}\right]$$

imposed so that disparities are figured relative to the statewide population rather than to the population within distance d of any facility.

While this is not a realistic assumption – in reality $PM_{10}$ and other emissions disperse and de-concentrate at varying rates around a facility – in lieu of "fate-and-transport" modeling, this is our best estimate. Our method tests a variety of distances under the assumption that the $PM_{10}$ concentration is constant within each buffer and zero outside the buffer. If similar disparities are found across distance bands and there is a similar composition of sectors and facilities that are driving disparity at each distance, then we expect a more sophisticated model would draw similar conclusions to those drawn from this methodology.

In the last line of the derivation, each bracketed term represents the contribution (positive or negative) of each facility i to the overall statewide difference in person-tons of $PM_{10}$ between people of color and non-Hispanic whites, and is what we have termed the pollution disparity index. A positive or negative index value is determined by the representation of each group near the facility; if the share of the state's people of color residing near the facility is greater than the share of the state's non-Hispanic white population residing near the facility, then term will be positive. If reverse is true, it will be negative.

While the statewide difference expresses environmental disparity in co-pollutant emissions from the facilities included in our analysis at the state level, the pollution disparity index tells of each facility's contribution to that measure of statewide disparity, which is experienced at the local level. The facility-level index can be summed up across any group of facilities by type or locale (e.g., across all power plants in the state or across all facilities in a particular county, city, or neighborhood) to get a measure of the contribution that group of facilities makes to the statewide difference.

Finally, we emphasize that the approximation of "emissions burden" we use here is just that – an approximation. "Exposure" as used in the public health field typically implies modeling of emissions to determine concentrations at the neighborhood level, taking into account distance from the facility, how emissions are released, and local wind and atmospheric patterns, among other factors. Instead, emissions burden and the pollution disparity index rely on a rough approximation based on total co-pollutant emissions and the number of people within a particular distance from the facility.

# About the Research Team

**DR. RACHEL MORELLO-FROSCH** is Associate Professor in the Department of Environmental Science, Policy and Management and the School of Public Health at the University of California, Berkeley. Dr. Morello-Frosch's research examines race and class determinants of environmental health among diverse communities in the United States. A focus of her work is the relationship between segregation and environmental health inequalities associated with air pollution, children's environmental health, and the intersection between economic restructuring and community environmental health. Currently, Dr. Morello-Frosch collaborates with colleagues and environmental justice organizations to research and address climate justice issues, including the social equity implications of proposed greenhouse gas reduction strategies in California associated with the AB 32 Scoping Plan; and disparities in community capacity to adapt to environmental impacts of climate change. Her work is funded by the National Institutes of Health, the National Science Foundation, the California Environmental Protection Agency, the California Wellness Foundation, and the California Endowment, among others. Dr. Morello-Frosch currently serves on the Health Impacts Assessment Advisory Committee for the implementation of the AB 32 Scoping Plan.

**DR. MANUEL PASTOR** is Professor of Geography and American Studies & Ethnicity at the University of Southern California where he also serves as Director of the Program for Environmental and Regional Equity (PERE) and co-Director of USC's Center for the Study of Immigrant Integration (CSII). Pastor holds an economics Ph.D. from the University of Massachusetts, Amherst, and has received fellowships from the Danforth, Guggenheim, and Kellogg foundations and grants from the Irvine Foundation, the Rockefeller Foundation, the Ford Foundation, the National Science Foundation, the Hewlett Foundation, the MacArthur Foundation, the California Environmental Protection Agency, the California Wellness Foundation, and many others. His most recent book, co-authored with Chris Benner and Martha Matsuoka, is *This Could Be the Start of Something Big: How Social Movements for Regional Equity are Reshaping Metropolitan America* (Cornell University Press, 2009). Dr. Pastor served on the Regional Targets Advisory Committee, a group advising the California Air Resources Board on methods to set goals for the reduction of greenhouse gas emissions through better land use planning.

**DR. JAMES L. SADD** is Professor of Environmental Science at Occidental College, Los Angeles, California. He earned his doctorate in geology at the University of South Carolina, Columbia. His research includes spatial analysis using geographic information systems and remote sensing tools, particularly to evaluate questions related to environmental exposure. His recent research is supported by contracts and grants from the Andrew W. Mellon Foundation, US Army Corps of Engineers, US Navy Office of Naval Research, NOAA SeaGrant. Dr. Sadd served on the Nationally Consistent Environmental Justice Screening Approaches Work Group, advising on the EPA's Environmental Justice Strategic Enforcement Screening Tool (EJSEAT).

**JUSTIN SCOGGINS** is a data analyst at the Program for Environmental and Regional Equity at the University of Southern California. Since graduating with an MS in applied economics and finance from the University of California, at Santa Cruz, he has been assisting with research around issues of social justice, specializing in statistical analysis of patterns of environmental injustice, labor market intermediaries, and regional equity. He has published articles in both the Journal of Urban Affairs and the Journal of Planning Education and Research.

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**Minding the Climate Gap Report**

**Attachment 40**

**Attachment 40. Areal Refinery Source Strength Calculation Details.**

| | (units) | Data and calculations | | | | |
|---|---|---|---|---|---|---|
| Source area boundary (radius) from Attachment 39: | miles | **0.5** | 1 | **2.5** | 5 | **6** |
| Refinery source area (A) within radius ($r$) from $A = \pi r^2$: | square miles | 0.786 | 3.146 | 19.66 | 78.65 | 113.3 |
| Corresponding refineries source area (all 5 refineries): | square miles | 3.932 | 15.730 | 98.31 | 393.24 | 566.3 |
| BAAQMD jurisdiction area from DEIR at 1-5:<br>(source: DEIR SCH#2015032008 at 1-5) | square miles | 5,600 | 5,600 | 5,600 | 5,600 | 5,600 |
| **Primary PM$_{2.5}$ emissions (from attachments 3 and 4)** | | | | | | |
| Refineries—5 refineries collectively, in 2010: | short tons/y | 985 | 985 | 985 | 985 | 985 |
| **Source strength in boundary area** | t-yr/mile$^2$ | **250.48** | **62.62** | **10.02** | **2.50** | **1.74** |
| All sources in the region collectively, in 2010, annual: | short tons/y | 17,155 | 17,155 | 17,155 | 17,155 | 17,155 |
| All sources in the region collectively, in 2010, winter: | short tons/y | 17,885 | 17,885 | 17,885 | 17,885 | 17,885 |
| **Source strength in boundary area** | t-yr/mile$^2$ | **3.06** | **3.06** | **3.06** | **3.06** | **3.06** |
| **Source strength in boundary area** | t-yr/mile$^2$ | **3.19** | **3.19** | **3.19** | **3.19** | **3.19** |
| Refineries/regional average t-yr/mile$^2$ (%) | | 7843% | 1961% | 314% | 78.4% | 54.5% |
| **NOx emissions (from attachments 3 and 4)** | | | | | | |
| Refineries—5 refineries collectively, in 2010: | short tons/y | 4,271 | 4,271 | 4,271 | 4,271 | 4,271 |
| **Source strength in boundary area** | t-yr/mile$^2$ | **1,080** | **271** | **43.44** | **10.86** | **7.54** |
| All sources in the region collectively, in 2010, winter: | short tons/y | 126,655 | 126,655 | 126,655 | 126,655 | 126,655 |
| **Source strength in boundary area** | t-yr/mile$^2$ | **22.62** | **22.62** | **22.62** | **22.62** | **22.62** |
| Refineries/regional average t-yr/mile$^2$ (%) | | 4775% | 1200% | 192% | 48.0% | 33.3% |
| **SO$_2$ emissions (from attachments 3 and 4)** | | | | | | |
| Refineries—5 refineries collectively, in 2010: | short tons/y | 5,439 | 5,439 | 5,439 | 5,439 | 5,439 |
| **Source strength in boundary area** | t-yr/mile$^2$ | **1,380** | **346** | **55.32** | **13.83** | **9.604** |
| All sources in the region collectively, in 2010, winter: | short tons/y | 10,585 | 10,585 | 10,585 | 10,585 | 10,585 |
| **Source strength in boundary area** | t-yr/mile$^2$ | **1.89** | **1.89** | **1.89** | **1.89** | **1.89** |
| Refineries/regional average t-yr/mile$^2$ (%) | | 73009% | 18292% | 2927% | 732% | 508% |

**Attachment 41**

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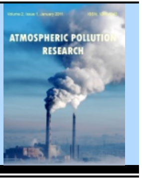

# Concentration and source origin of lanthanoids in the Canadian atmospheric particulate matter: a case study

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## ABSTRACT

Ambient $PM_{2.5}$ and $PM_{2.5–10}$ samples collected at selected urban and rural sites within the Canadian National Air Pollution Surveillance (NAPS) $PM_{2.5}$ Speciation Program were analyzed for lanthanoids and other elements. The average concentrations of total lanthanoids (calculated as sum of concentrations of all elements) in $PM_{2.5}$ ranged from 0.059 to 0.334 ng $m^{-3}$. These concentrations were two times lower than in $PM_{2.5–10}$ samples and generally lower than values reported for industrial and urban areas around the world. The highest concentrations of lanthanoids were found in $PM_{2.5}$ samples collected at the Halifax NS site, located near a petroleum refining complex. In addition, La/Ce and La/Sm ratios at this site were significantly higher than their natural values. Increased La–enrichment factors were also found in Wallaceburg ON, which is located in a rural area, about 50 km downwind of two major petrochemical complexes. The results of this study demonstrate that La–enrichment factors are reliable tracers of emissions from oil refining industry.

***Keywords:***
*Lanthanoids*
*Metals*
*Particulate matter*
*Industrial sources (petrochemical)*
*Source apportionment*

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## 1. Introduction

Lanthanoid elements (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) have been traditionally used as tracers for a variety of geochemical processes in hydrosphere and lithosphere due to their very distinctive geochemical properties (Munksgaard et al., 2003; Borrego et al., 2005; Kamber, 2009). As a result of the lanthanoids contraction phenomenon, lighter lanthanoid elements are more abundant in the Earth's crust whereas heavier ones are more concentrated in the Earth's mantle. Also, concentrations of lanthanoids in the upper continental crust (UCC) follow the Oddo–Harkins rule whereby the odd–numbered elements are less abundant than their even–numbered neighbors (Oddo, 1914; Harkins, 1917). The chemical properties of these elements are so similar that their natural distribution pattern will not change by natural and anthropogenic processes unless material with already altered composition is released into the natural environment.

Today, the oil–refining industry extensively uses fluid catalytic cracking units (FCC) for the process of converting petroleum crude oils into gasoline or other commercial products. The FCC catalysts are zeolites that usually contain excessive amounts of La. Although the catalyst is re–cycled and re–used during the refining process, there is a small amount that is unintentionally released into the atmosphere which will change the natural concentration pattern of lanthanoids in air particulate matter (PM). In 1985, Olmez and Gordon suggested for the first time that the concentrations of lanthanoids in fine particulate matter ($PM_{2.5}$, particles smaller than 2.5 μm in aerodynamic diameter) can be used as unique tracers for emissions from oil refining industry (Olmez and Gordon, 1985). Since the concentration patterns are not affected by chemical and physical transformations that take place after emission and during transportation of particles in the atmosphere, these elements are ideal tracers for both long–range and point source emissions on an urban and a regional scale. Following this paper, several studies confirmed that the natural distribution patterns of lanthanoids in $PM_{2.5}$ were greatly distorted due to zeolite catalysts used in oil refining industry and released to the atmosphere either accidentally or during routine operations of petrochemical facilities (Kitto et al., 1992; Wang et al., 2001; Kulkarni et al., 2006; Kulkarni et al., 2007; Moreno et al., 2008a; Moreno et al., 2008b; Moreno et al., 2010).

Major sources for anthropogenic emissions of $PM_{2.5}$ in the atmosphere include the products of fossil fuels combustion used for industrial and domestic heating, power generation, transportation and other purposes, as well as emissions from oil refining industry. During 2009, the $PM_{2.5}$ released from fuel used for electricity, heating, transportation (road, rail, air, marine), and oil and gas industry accounted for 18% of total $PM_{2.5}$ emissions in Canada (Environment Canada, 2009b). Since fossil fuels are normally rich in Ni and V, PM emissions related to oil–based domestic and industrial applications have been traditionally traced by high levels and significant correlations of concentrations of Ni and V in $PM_{2.5}$ (Celo and Dabek–Zlotorzynska, 2010 and references therein). The inclusion of lanthanoids in source apportionment studies adds one parameter that can be used to distinguish oil combustion from oil refining sources.

In this study we report the concentrations and distribution patterns of lanthanoids in fine ($PM_{2.5}$) and coarse ($PM_{2.5–10}$, particles with aerodynamic diameter between 2.5 µm and 10 µm) atmospheric PM samples collected at selected sites across Canada as a part of the National Air Pollution Surveillance (NAPS) $PM_{2.5}$ Speciation Program. The objective of this research is to track the PM emission sources related to oil refineries by monitoring concentrations of lanthanoids at several sites located in urban areas that are affected by various anthropogenic sources of PM.

## 2. Experimental

### 2.1. Site location and description

The NAPS network sampling sites included in this study were selected to represent both urban and rural settings, and were located from East to West Coast of Canada as shown in Figure 1 and described in Table 1.

The Toronto, Montreal and Halifax sites are located in downtown areas of highly populated metropolitan cities that are heavily influenced by local transportation emissions. In addition to other industrial facilities and power plants located nearby, two oil refining complexes are situated about 15 km northeast of the Montreal site and a major facility operates less than 2 km southeast of the Halifax site. The Abbotsford sampling site is located less than 0.5 km north of one of the runways of the Abbotsford International Airport. The Windsor and Burnaby sites are both located in residential areas close to major traffic arteries. Windsor is one of the major industrial cities in Canada where air quality is heavily affected by industries (mainly automotive and metal processing) located on both sides of the border (Gilbertson and Brophy, 2001). This sampling site is located less than 2 km northwest of two power generation plants, less than 6 km west of several automotive manufacturing facilities and within 1 km from the Ambassador Bridge which is the busiest international border crossing between Canada and the US. Burnaby is a coastal city and major seaport, located close to the Port of Vancouver which is the largest and busiest port in Canada. The sampling site is located about 8 km south of a refinery and within 15 km from the Port of Vancouver. The Canterbury and Wallaceburg sites are both located in rural–undeveloped areas. While there is no industrial facility located close to the Canterbury site, the Wallaceburg site is situated about 50 km south of the industrial town of Sarnia where several industrial facilities of metal producing and processing, a power generation plant and two major petrochemical refining complexes operate.

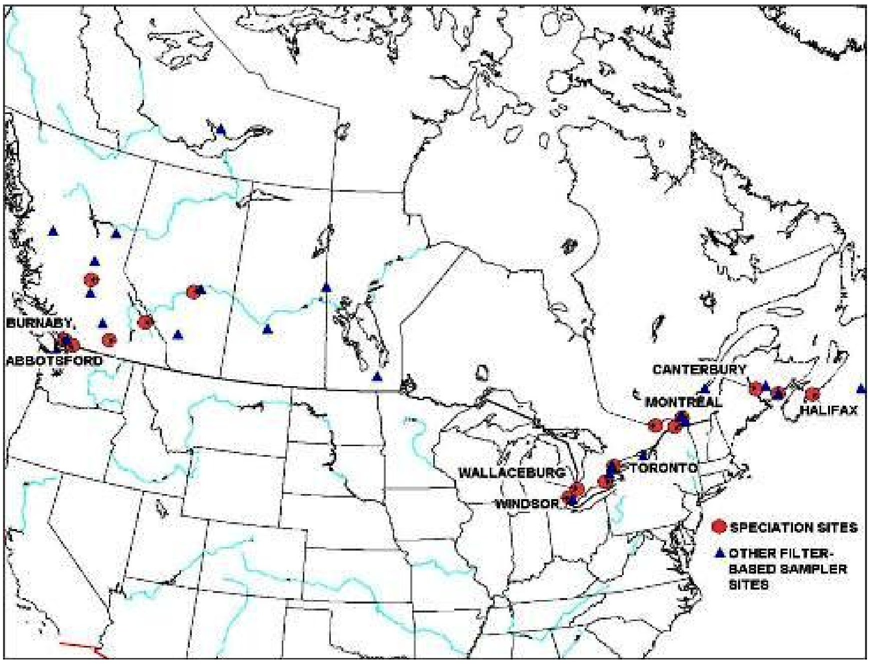


***Figure 1.*** *Locations of the Canadian NAPS monitoring sites selected for this study.*

***Table 1.*** *Brief description of the NAPS sampling sites (Dabek–Zlotorzynska et al., 2011)*

| City (NAPS ID) | Province | Site Description | Major Source Influences | Sampling period |
|---|---|---|---|---|
| Halifax (30113) | Nova Scotia (NS) | Urban–core | Oil refining, oil–fired power plant, marine vessels, traffic | 2006–2008 |
| Canterbury (40801) | New Brunswick (NB) | Rural–undeveloped | | 2005–2007 |
| Montreal (50104) | Quebec (QC) | Urban–core | Traffic, heating, oil refining | 2005–2007 |
| Windsor (60211) | Ontario (ON) | Urban–residential | Steel manufacturing, auto manufacturing, traffic | 2005–2008 |
| Toronto (60427) | Ontario (ON) | Urban–core | Traffic, heating | 2005–2008 |
| Wallaceburg (61902) | Ontario (ON) | Rural–undeveloped | | 2006–2008 |
| Abbotsford (101004) | British Columbia (BC) | Suburban–residential | Traffic, heating, airport | 2005–2008 |
| Burnaby (100119) | British Columbia (BC) | Urban–commercial | Traffic, heating, oil refining, marine vessels | 2006–2008 |

### 2.2. Sampling and chemical analysis

Samples were collected as a part of the NAPS $PM_{2.5}$ Speciation program, following procedures described elsewhere (Dabek–Zlotorzynska et al., 2011; Jeong et al., 2011). Aerosol $PM_{2.5}$ samples selected for this study were collected using the Partisol Model 2300 sequential speciation samplers and $PM_{2.5–10}$ samples were collected simultaneously using R&P Partisol–Plus Model 2025–D sequential dichotomous samplers. Samples were collected over 24 hours on 47–mm PTFE filters (PALL Corporation, NY, USA). All filters were weighed before and after sample collection using a Mettler Microbalance (MT–5, Mettler–Toledo Inc., Highstown, NJ), under controlled relative humidity (40 ± 5%) and temperature (23 ± 3 °C). The data reported in this case study are from analysis of about thirty $PM_{2.5}$ and ten $PM_{2.5–10}$ samples collected at each site during the 2005–2008 sampling period. There is no data reported for $PM_{2.5–10}$ samples from the Canterbury and Halifax sites because they were either not collected or not available for analysis.

Both fine and coarse PM samples were treated and analyzed by ICP–MS following a previously reported method (Celo et al., 2011). Briefly, samples were digested for 20 min at 200 °C with a $HNO_3/H_2O_2/HF/HCl$ mixture using a MARS Xpress microwave oven (CEM Corporation, Matthews, NC). After digestion, samples were evaporated to almost dryness in presence of concentrated HCl and diluted to 15 mL with 4% (v/v) $HNO_3$ prior to ICP–MS analysis. Reagent blanks, filter blanks and other QA/QC samples were prepared in the same manner. Standard reference materials 1648a (Urban Particulate Matter) and BRC estuarine sediment reference material 667 (Institute for Reference Materials and Measurements, Geel, Belgium) were used for validation of analytical results. Recoveries ranged from 85 to 115% for La to Ho, from 75 to 85% for the heavier lanthanoids, and from 80 to 120% for other elements. All measurements were performed using an Agilent Technologies 7500ce ICP–MS system (Agilent Technologies, Wilmington, DE, USA), equipped with a high matrix introduction (HMI) system, MicroMist nebulizer, an octopole collision/reaction system (ORS), a Peltier cooled (2 °C) quartz Scott–type double pass spray chamber and an Agilent I–AS integrated autosampler. The HMI system was used to minimize the oxide and hydroxide interferences associated with the analysis of lanthanoids (Celo et al., 2011). The ORS was pressurized with He gas for analysis of V, As and Cr, and with $H_2$ for analysis of Fe and Se. Internal standardization with 1 mg $L^{-1}$ solution of $^{103}Rh$ and $^{115}In$ was used to correct for the instrumental drifts and non–spectral interferences.

### 2.3. Limits of detection and statistical data analysis

Limits of detection (LOD) were determined as 3 times standard deviation of 30 filter blanks, which were digested and treated through all the steps of analysis as samples. The LOD for analysis of PM samples ranged from 1–30 pg $m^{-3}$. Typically, the heavier lanthanoids had the lowest LOD. In general, concentrations of La, Ce and Pr were above their respective LOD in 70–100% of $PM_{2.5}$ samples, Nd, Dy, Er, Gd and Yd were above LOD in 10–70% and the other elements were detected at less than 25% of analyzed samples from each site. The percentage of $PM_{2.5–10}$ samples with concentrations of lanthanoids above LOD was 70–100% for La, Ce, Pr and Nd, 50–80% for Sm, Gd, Dy, Er and Yb and less than 25% for the other elements.

STATISTICA ver. 8 software (StatSoft Inc., Tulsa, OK, USA) was used for statistical analyses. Summary statistics were calculated by substitution of concentrations below LOD with half of LOD. Unless otherwise stated, median with interquartile range (IQR) were reported.

## 3. Results and Discussion

### 3.1. $PM_{2.5}$ and $PM_{2.5–10}$ concentrations

The median $PM_{2.5}$ mass concentration for samples included in this study was 11.8 µg $m^{-3}$ (IQR 7.7 to 17.1 µg $m^{-3}$) (see the Supporting Material, SM, Tables S1A and S1B), with the highest values recorded at the Toronto, Windsor and Montreal sites. This result agrees with previous reports of $PM_{2.5}$ concentration in Canadian cities, and is consistent with the fact that these sites are affected by a number of anthropogenic emission sources, mainly manufacturing industries and transportation (Dabek–Zlotorzynska et al., 2011; Jeong et al., 2011). The rural site of Canterbury had the lowest concentration of $PM_{2.5}$ whereas relatively high levels were recorded at the Wallaceburg rural site. Spatial distribution of $PM_{2.5–10}$ concentrations showed a similar pattern, with the lowest values recorded at the rural sites (median 3.4 µg $m^{-3}$ at the Wallaceburg site) and the highest at the urban sites (see the SM, Table S2). Median $PM_{2.5–10}$ concentration was 5.1 µg $m^{-3}$ (IQR 3.4 to 7.6 µg $m^{-3}$).

*Table 2. Median [a] concentrations of lanthanoids (pg $m^{-3}$) in $PM_{2.5}$ samples (N = 30 for each site)*

| | LOD | Burnaby | Abbotsford | Windsor | Toronto | Wallaceburg | Montreal | Canterbury | Halifax |
|---|---|---|---|---|---|---|---|---|---|
| La | 20 | 86 (56–163) | 24 (10–58) | 53 (38–85) | 49 (35–62) | 50 (25–104) | 44 (25–94) | 15 (10–32) | 227 (96–270) |
| Ce | 30 | 115 (91–194) | 47 (27–61) | 70 (49–110) | 71 (57–91) | 36 (18–68) | 64 (38–101) | 18 | 44 (18–67) |
| Pr | 2.2 | 6.3 (3.8–10) | 2.7 (1.1–3.4) | 4.3 (2.9–6.3) | 4.6 (2.8–6.5) | 3.8 (3.0–8.5) | 4.2 (3.0–7.0) | 1.1 (1.1–3.5) | 2.8 (1.1–5.2) |
| Nd | 15 | 19 (8–27) | 8 | 8 (8–23) | 8 (8–20) | 8 (8–26) | 13 (8–26) | 8 | 8 (8–17) |
| Sm | 8.9 | 4.5 | 4.4 | 4.5 (4.5–7.5) | 4.4 (4.4–7.1) | 4.4 (4.4–6.0) | 4.4 | 4.4 | 4.7 (4.4–4.8) |
| Eu | 2.9 | 1.5 | 1.4 | 1.4 | 1.4 | 1.4 (1.4–2.5) | 1.4 | 1.4 | 1.4 |
| Gd | 5.0 | 2.5 | 2.5 | 3.0 (2.5–6.1) | 2.5 | 3.0 (2.5–5.3) | 2.5 | 2.5 | 3.0 (2.5–5.1) |
| Tb | 1.9 | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 (0.9–3.1) | 0.9 | 0.9 | 0.9 |
| Dy | 2.8 | 1.4 | 1.4 (1.4–3.5) | 3.4 (1.4–4.3) | 3.3 (1.4–3.4) | 1.4 (1.4–3.4) | 2.3 (1.4–3.4) | 1.4 (1.4–3.3) | 2.2 |
| Ho | 4.7 | 2.3 | 2.3 | 2.3 | 2.3 | 2.3 (2.3–21) | 2.3 | 2.3 | 2.3 |
| Er | 2.1 | 1.1 | 1.1 | 1.1 (1.1–2.5) | 1.1 (1.1–2.5) | 1.1 (1.1–2.0) | 1.2 (1.1–2.3) | 1.1 (1.1–2.4) | 1.1 (1.1–1.5) |
| Tm | 1.4 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 (0.7–2.9) | 0.7 | 0.7 | 0.7 |
| Yb | 3.1 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 (1.6–5.3) | 1.6 | 1.6 | 1.6 |
| Lu | 1.2 | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 (0.6–1.5) | 0.6 | 0.6 | 0.6 |
| Sum | | 244 | 99 | 155 | 152 | 116 | 144 | 59 | 300 |

*[a] Values in brackets are IQR, which are reported only when the number of samples with concentrations above LOD was more than 30%*

***Table 3.*** *Median [a] concentrations of lanthanoids (pg $m^{-3}$) in $PM_{2.5–10}$ samples (N = 10 for each site)*

| | Burnaby | Abbotsford | Wallaceburg | Toronto | Windsor | Montreal |
|---|---|---|---|---|---|---|
| La | 193 (97–257) | 57 (55–58) | 57 (71–105) | 60 (14–52) | 93 (81–146) | 107 (96–140) |
| Ce | 350 (114–639) | 86 (83–87) | 86 (39–104) | 188 (54–240) | 146 (92–200) | 192 (141–228) |
| Pr | 11 (7–17) | 5.6 (5.6–5.7) | 7 (2–9) | 14 (1–20) | 9 (6–13) | 18 (11–23) |
| Nd | 39 (18–53) | 21 (20–23) | 24 (18–21) | 45 (5–81) | 44 (26–65) | 62 (50–72) |
| Sm | 6 (6–19) | 5 (4–8) | 6 (4–6) | 6 | 6 (6–18) | 11 (6–12) |
| Eu | 3.5 (1.3–6.1) | 1.5 (1.4–1.8) | 1.5 | 1.3 (1.3–5.7) | 1.3 | 3.2 (2.5–4.2) |
| Gd | 9.5 (2.6–13.2) | 5.5 (4.8–5.2) | 3.2 (2.1–3.6) | 6.8 (2.6–15) | 5.0 (2.6–11) | 12.3 (9.6–16) |
| Tb | 1.5 | 0.6 | 1.6 | 1.7 | 1.6 | 1.7 (1.0–2.4) |
| Dy | 7.3 (4–9.8) | 3.8 (3.7–3.9) | 1.7 (1.7–3.8) | 6.7 (1.7–14) | 5.9 (2.9–7.2) | 7.5 (5.9–10) |
| Ho | 2.5 | 0.7 | 2.5 | 3.3 (2.5–6.6) | 3.7 | 2.2 (1.4–2.5) |
| Er | 3.7 (3.7–8) | 2.8 (2.7–2.9) | 3.0 (2.4–3.2) | 3.5 (1.0–5.9) | 4.0 (2.4–5.0) | 4.1 (2.2–6.1) |
| Tm | 1.4 | 0.2 | 1.5 | 1.5 | 1.5 | 0.6 (0.3–1.1) |
| Yb | 2.7 (2.7–7.3) | 2.3 (2.0–2.7) | 2.7 (2.7– 3.1) | 2.7 (2.7–6.5) | 2.7 | 3.5 (1.8–5.8) |
| Lu | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.6 |
| Sum | 774 | 192 | 212 | 354 | 432 | 434 |

[a] *Values in brackets are IQR, reported only when the number of samples with concentrations above LOD was more than 30%*

The contribution of $PM_{2.5}$ to the mass concentration of $PM_{10}$ (which includes particles with diameter ≤ 10 μm) is one parameter that is used frequently as an indicator of the PM origin (Querol et al., 2001; Charron and Harrison, 2005; Wojas and Almquist, 2007; Morawska et al., 2008; Moreno et al., 2008a; Perez et al., 2008). It is generally agreed that the fine portion of PM usually originates from various local and regional anthropogenic sources such as emissions related to industrial and vehicle combustion and few mechanical processes. The coarse portion is mostly derived from sea spray aerosol formation processes, re–suspension of local sediments and soils into the atmosphere by wind or vehicular traffic, and by mechanical processes such as wear and tear of materials, grinding, milling, mining, and construction industries. As a result, a high $PM_{2.5}/PM_{10}$ ratio signifies an important contribution of anthropogenic sources to PM emissions whereas lower ratios are expected for areas where the main PM input is dust re–suspension. In this study, the $PM_{2.5}/PM_{10}$ ratios were calculated as $PM_{2.5}/(PM_{2.5}+PM_{2.5–10})$ for each sample. The average ratio for all samples was 0.612 ± 0.14 indicating a significant contribution of fine particulates to total particulate mass at all sites. The Windsor and Abbotsford urban sites had the highest $PM_{2.5}/PM_{10}$ ratios (0.68 and 0.67 respectively) which suggest a significant contribution of anthropogenic particles to total particulate matter emitted at these sites. This result was expected for the Windsor site which is located close to several industrial facilities and high traffic roads that contribute to $PM_{2.5}$ emissions. High $PM_{2.5}/PM_{10}$ ratios found at the Abbotsford site are most probably due to aviation emissions that are typically the major source of $NO_x$ and $PM_{2.5}$ air pollution in the vicinity of airports (Arunachalam et al., 2011; Kurniawan and Khardi, 2011; Mazaheri et al., 2011; Woody et al., 2011). Contribution of $PM_{2.5}$ to $PM_{10}$ was slightly lower at the Toronto and Halifax sites where this ratio was ca. 0.60 which is typical for urban environments that are influenced by vehicular traffic (Charron and Harrison, 2005; Morawska et al., 2008). At the Burnaby and Montreal sites the average $PM_{2.5}/PM_{10}$ ratio was ca. 0.5 indicating that, compared to other urban sites included in this study, the contribution of coarse particles in the mass concentration of PM was higher.

The mass concentration, particle size fractionation and chemical composition of particulate matter at a given site, were also affected by the wind speed and prevailing direction (Charron and Harrison, 2005). As $PM_{2.5–10}$ is less easily transported in the atmosphere than $PM_{2.5}$, high $PM_{2.5}/PM_{10}$ ratios are expected at rural sites where, compared to local sources, the contribution of regional scale emissions is significant. Hence, the elevated $PM_{2.5}/PM_{10}$ ratios at the Wallaceburg site (average 0.69 ± 0.15) are most probably related to the fine particles emitted from the industrial facilities operating in the city of Sarnia, and transported at this site by the northerly winds which were typical for the sampling days included in this study (Environment Canada, Weather Office, 2011).

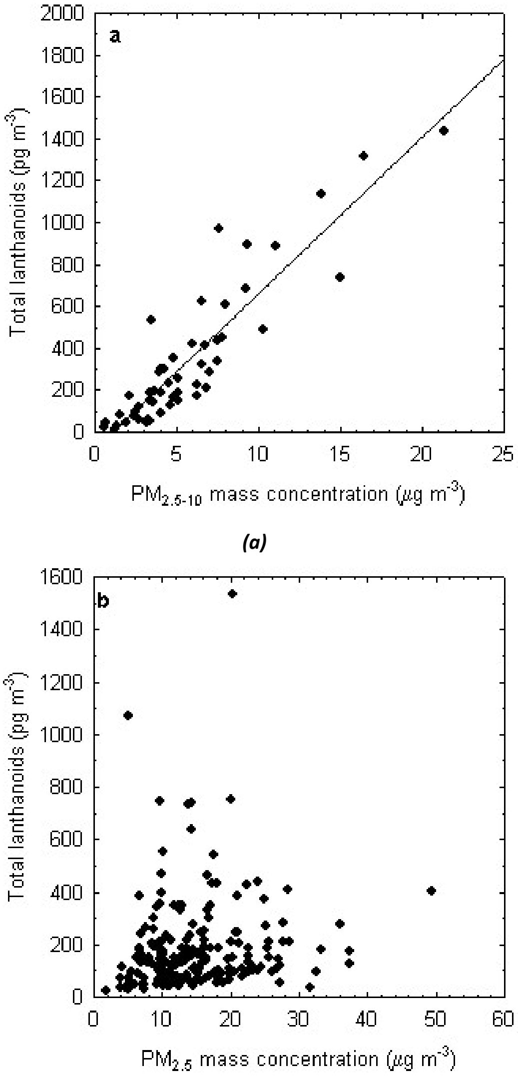
### 3.2. Concentrations and spatial distribution of lanthanoids

The median concentrations of total lanthanoids (calculated as sum of La to Lu concentrations) in $PM_{2.5}$ samples analyzed in this study ranged from 59 to 300 pg $m^{-3}$ (Table 2).

Maximum total concentrations were found at the Halifax (300 ± 15 pg $m^{-3}$) and Burnaby sites (244 ± 12 pg $m^{-3}$). It is worth noting that concentrations of lanthanoids in $PM_{2.5}$ at all Canadian sites included in this study were lower than values reported for other regions around the world. For example, typical background concentration of total lanthanoids reported for urban areas around Houston, Texas was ca. 1.6 ng $m^{-3}$ (Kulkarni et al., 2007). Moreno et al. (2008a) reported average total lanthanoids concentration in $PM_{2.5}$ ranging from 0.47 to 1.39 ng $m^{-3}$ for a site that is close to several industrial facilities in Puertollano, Spain, and from 1 to 10 ng $m^{-3}$ for $PM_{2.5}$ collected during a sampling campaign in Mexico City (Moreno et al., 2008b). More recently, total lanthanoids concentrations reported for $PM_{2.5}$ samples collected at five industrial towns in Spain varied from 0.64 to 3.62 ng $m^{-3}$ (Moreno et al., 2010). For comparison, the maximum total concentration of lanthanoids in this study was 1.5 ng $m^{-3}$ recorded at the Halifax site.

As expected, the most abundant lanthanoids in all PM samples were La and Ce. These elements were above respective LODs in more than 90% of analyzed samples and accounted for 60 to 80% of total lanthanoids in both $PM_{2.5}$ and $PM_{2.5–10}$. The highest median concentrations of La in $PM_{2.5}$ were 227 pg $m^{-3}$ (IQR 96 to270 pg $m^{-3}$) and 86 pg $m^{-3}$ (IQR 56 to 163 pg $m^{-3}$) at the Halifax and Burnaby sites, respectively. Burnaby site had also the highest concentration of Ce (115 pg $m^{-3}$) followed by the Toronto, Montreal, Windsor and Halifax sites which had similar concentrations, at *ca*. 70 pg $m^{-3}$.

Concentrations of total lanthanoids in $PM_{2.5–10}$ samples were typically two times higher than $PM_{2.5}$ at each site (Table 3), with the highest levels present at the Burnaby site where the median value was 774 pg $m^{-3}$ (with IQR 284 to 969 pg $m^{-3}$). At the other sites, total lanthanoids concentrations in $PM_{2.5–10}$ ranged from 192 to 434 pg $m^{-3}$.



***(a)***

***(b)***

***Figure 2**. Total lanthanoids concentrations vs. PM mass for **(a)** PM$_{2.5-10}$ and **(b)** PM$_{2.5}$ samples.*

Also, the concentrations of lanthanoids in PM$_{2.5–10}$ showed a significant correlation with particulate mass concentration (Spearman rank correlation 0.86, $p$<0.05) (Figure 2a), which suggests that the natural and/or anthropogenically induced re–suspension of local soils and sediments, and various mechanical processes that contribute to PM$_{2.5–10}$ emissions have a considerable effect on the presence of lanthanoids in the coarse fraction of air particulate matter. In contrary, the lack of correlation for PM$_{2.5}$ samples (Figure 2b) implies that the emission sources of lanthanoids do not have a significant impact on the mass of fine particles.

### 3.3. Concentration patterns of lanthanoids and La enrichment factors in FCC and air particulate samples

Fluid catalytic cracking is the major conversion process used in oil refineries to produce valuable hydrocarbons from crude oil fractions. Fluid cracking catalysts (FCC) commonly contain La–enriched zeolites and there is evidence showing the presence of La–enriched particles in the flue gas emitted from the refineries, despite attempts to minimize the loss of FCC through the process (Niccum, 2010). As a result, concentration patterns of lanthanoids and especially La–enrichment factors (ratios of La to other lanthanoids, mainly Ce and Sm) are often used as reliable indicators for tracing emissions of oil–refining industries (Table 4). Several studies have demonstrated that PM emitted by such sources had La–enrichment factors that were significantly higher than natural distribution values and showed distorted concentration patterns of lanthanoids.

The concentration patterns of lanthanoids for the Upper Continental Crust (UCC) composition (Taylor and McLennan, 1986) and for PM samples analyzed in this study are depicted in Figure 3.

Unlike the commonly used PM$_{10}$ fraction, PM$_{2.5–10}$ reflects the chemical composition of coarse particles with minimal contribution from the finer fraction. Since the coarse particles are mainly related to re–suspension processes and cannot travel in long distances in the atmosphere (Charron and Harrison, 2005), lanthanoid patterns of PM$_{2.5–10}$ typify the local soil and sediments composition and consequently can be considered as the background pattern for each site. As shown in Figure 3b, the PM$_{2.5–10}$ samples analyzed in this study had natural distribution patterns at each site. Median and IQR of La/Ce and La/Sm ratios for all samples were 0.57 (0.44–0.78) and 5.9 (3.9 – 6.9) with no significant differences between sites (Kruskal–Wallis test at $p$<0.05) (Kruskal and Wallis, 1952). Although the Burnaby site had the highest concentrations of lanthanoids in PM$_{2.5–10}$, the distribution patterns and the insignificant La–enrichment factors suggest that the oil–refining facility located nearby has no significant impact on PM$_{2.5–10}$ emissions and its chemical composition.

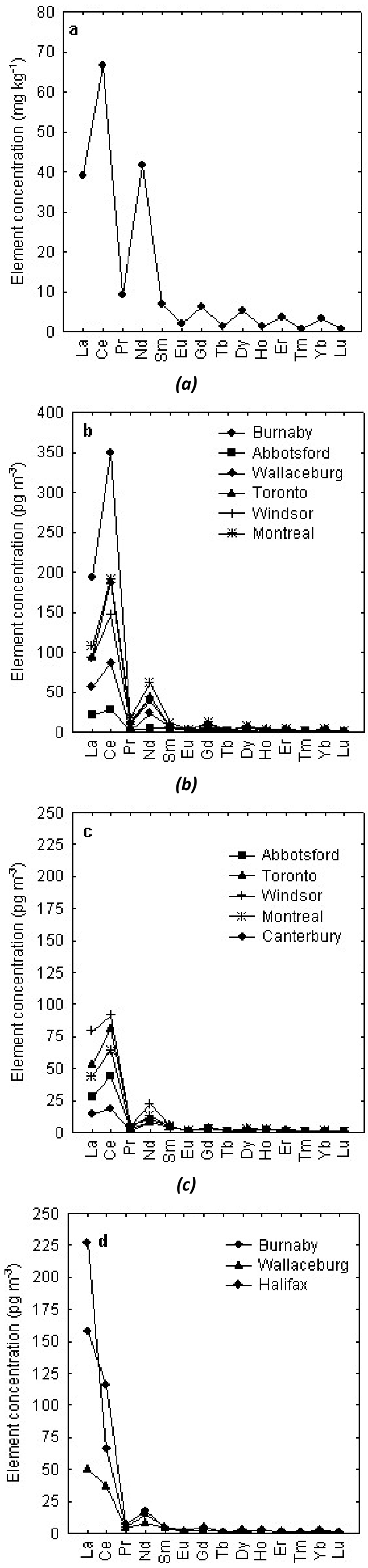
The distribution patterns of lanthanoids for PM$_{2.5}$ samples at the Abbotsford, Windsor, Toronto, Montreal and Canterbury sites were similar and quite close to the UCC distribution patterns (Figure 3c). La enrichment factors at these sites were not significantly different from each other (Kruskal–Wallis test at $p$<0.05). Median and IQR values for La/Ce and La/Sm ratios were respectively, 0.69 (0.54–0.83) and 5.0 (3.9–7.9). Although slightly higher than what is expected for natural composition of particles in the atmosphere, these values are very close to ratios found for the PM$_{2.5–10}$ composition and are much lower than what is reported for PM$_{2.5}$ emissions that were influenced by FCC–oil–refining operations (Table 4). This implies that the oil–refining industry does not have a significant effect on the PM$_{2.5}$ emissions at these sites during the sampling periods of this study. While these results were expected for the Abbotsford, Windsor, Toronto and Canterbury sites, this was not the case for the Montreal site which is located about 15 km southwest of two major oil refining facilities. However, most of the sampling days at the Montreal site were either calm (wind speed below 30 km h$^{-1}$) or characterized by southwesterly winds (Environment Canada, Weather Office, 2011) which explains why the oil refineries located north of the sampling site did not show any significant effect on the chemical composition and concentration of PM$_{2.5}$–lanthanoids at this site.

The concentrations of lanthanoids in PM$_{2.5}$ samples collected at the Halifax, Burnaby and Wallaceburg sites showed a different pattern (Figure 3d). The enrichment factors of La compared to Ce, and Sm at Halifax were 4.9 (2.1–6.9) and 39 (21–51), respectively. These values are much higher than natural ratios and similar to what is reported for PM$_{2.5}$ emissions related to the loss of zeolite catalysts from the FCC units (Kulkarni et al., 2006; Kulkarni et al., 2007; Moreno et al., 2008a). Hence, the refinery which is located about 2 km southeast of the Halifax site is a major source of PM$_{2.5}$–lanthanoids. Actually, this facility processes about 82 000 barrels of crude oil per day (Dartmouth Refinery, 2011) and releases about 210 tonnes of PM$_{2.5}$ per year (Environment Canada, 2009), which explains its significant contribution to the composition of PM$_{2.5}$ at this site. La/Ce and La/Sm ratios at the Burnaby site were 1.7 (0.5–2.1) and 26 (14–42), which are lower than values found at the Halifax site but still much higher than the natural enrichment factors. It is worth noting that the petrochemical complex located close to the Burnaby site processes 50 000 to 55 000 barrels per day (Chevron in Canada, 2011) and releases not more than 25 tonnes of PM$_{2.5}$ per year (Environment Canada, 2009a). As a result, a less prominent effect of these emissions was found at the Burnaby site as compared to the Halifax site. La enrichment factors at the Wallaceburg site were 1.3 (0.7–1.6) and 9 (6–21) for La/Ce and La/Sm, respectively. These results are consistent with values reported for urban areas where the emissions of lanthanoids are partly due to oil–refining sources (Wang et al., 2000; Moreno et al., 2006; Kulkarni et al., 2007). Since this site is located about 50 km south of two major oil–refining complexes, the contribution of $PM_{2.5}$ emissions from these facilities is less significant than at the Halifax and Burnaby sites, albeit remaining quite distinguishable from other natural and/or anthropogenic sources of PM at this rural site.

***Table 4.*** *Enrichment factors reported for $PM_{2.5}$ and $PM_{10}$ composition in different regions of the world*

| Sampling site | La/Ce | La/Sm | Reference |
|---|---|---|---|
| **$PM_{10}$ samples coming from non–refinery sources** | | | |
| Beijing, China | 0.44 – 0.51 | 6.0 – 6.9 | Wang et al. (2001) |
| Puertollano, Spain | 0.63 –1.07 | 7.7 – 12.8 | Moreno et al. (2008a) |
| Mexico City, Mexico | 0.81 – 0.93 | 14.0 – 20.0 | Moreno et al. (2008b) |
| Bailen, Spain | 0.58 | NR | Moreno et al. (2010) |
| Algeciras, Spain | 0.74 | NR | |
| **$PM_{2.5}$ samples coming from non–refinery sources** | | | |
| Camden, NJ | 0.51 | 5.2 | Olmez and Gordon (1985) |
| Houston, TX | 0.70 | 3.9 | Kulkarni et al. (2006) |
| Puertollano, Spain | 0.73 – 1.37 | 10.2 – 16.4 | Moreno et al. (2008a) |
| Mexico City, Mexico | 0.67 | 11.6 | Moreno et al. (2008b) |
| Bailen, Spain | 0.59 | NR | Moreno et al. (2010) |
| Algeciras, Spain | 0.79 | NR | |
| **$PM_{10}$ samples coming from refinery sources** | | | |
| Delft, The Netherlands | 1.11 | 12.6 | Wang et al. (2000) |
| Puertollano, Spain | 2.33 | 40.9 | Moreno et al. (2008a) |
| Puertollano, Spain | 0.77 | NR | Moreno et al. (2010) |
| La Linea, Spain | 0.85 | NR | |
| **$PM_{2.5}$ samples coming from refinery sources** | | | |
| Camden, NJ | 1.25 | 20.0 | Olmez and Gordon (1985) |
| Philadephia, PA | 1.23 – 1.62 | 17.4 – 32.0 | Kitto et al. (1992) |
| Houston, TX | 2.90 | 53.7 | Kulkarni et al. (2006) |
| Puertollano, Spain | 1.09 – 5.38 | 14.6 – 35.0 | Moreno et al. (2008a) |
| Mexico City, Mexico | 1.56 | 20.4 | Moreno et al. (2008b) |
| La Linea, Spain | 0.98 | NR | Moreno et al. (2010) |
| Puertollano, Spain | 0.93 | NR | |
| **Comparison/reference values** | | | |
| Fluid Cracking Catalysts (FCC) | 1.22 | 19.4 | Kitto et al. (1992) |
| | 4.30 | 55.2 | Kulkarni et al. (2006) |
| | 4.54 | 63.0 | This study |
| Upper Continental Crust (UCC) | 0.59 | 5.5 | Taylor and McLennan (1986) |

*NR–Non reported*



*(a)* *(b)* *(c)* *(d)*

***Figure 3**. Distribution patterns of lanthanoids for **(a)** Earth's Crust; **(b)** $PM_{2.5-10}$ samples; **(c)** $PM_{2.5}$ at the Abbotsford, Toronto, Windsor, Montreal and Canterbury sites; **(d)** $PM_{2.5}$ at the Burnaby, Wallaceburg and Halifax sites.*

### 3.4. Vanadium, nickel and lanthaniods

V and Ni are known to be reliable tracers of emission sources that are related to fossil fuels combustion and/or processing in the refining facilities. The concentrations of these elements at sites where $PM_{2.5}$ composition is affected by such sources are high, and are strongly correlated with slopes of linear regression lines (or V/Ni ratios) that can be used to typify the fossil fuels (Lopez et al., 1995; Saganic and Gilroy, 2002; Moreno et al., 2010; Jeong et al., 2011). In addition, V–rich emissions coming from oil and petroleum coke combustion usually have La/V ratios less than 0.1, which is much lower than what is expected by the uncontaminated crustal materials (La/V = 0.2 to 0.3), whereas La/V >1 values are expected for $PM_{2.5}$ coming by FCC emission sources (Kulkarni et al., 2006; Moreno et al., 2008a; Danadurai et al., 2011). Since most of the industrial areas with petrochemical complexes involve multiple air emission sources, using La/V ratio as the single marker of FCC–related emissions is not sufficient and using other parameters such as concentration of Ce and the three–component La–Ce–V diagram, is needed.

Median and IQRs for concentrations of V and Ni in $PM_{2.5}$ samples analyzed in this study were 1.37 ng $m^{-3}$ (1.21–3.03) and 0.87 ng $m^{-3}$ (0.80–1.48), respectively, with the Burnaby, Toronto and Halifax sites having the highest levels (5.2, 4.9 and 3.9 ng $m^{-3}$ V, and 1.7, 2.6 and 1.9 ng $m^{-3}$ Ni, respectively) (see the SM, Table 1S). In addition, V and Ni concentrations at these sites were strongly correlated (Spearman rank correlation 0.75, 0.90 and 0.95, $p<0.05$, respectively), suggesting that the fossil fuels used for domestic, transportation or industrial processes, have a significant contribution to the chemical composition of $PM_{2.5}$ emitted at these sites (Kulkarni et al., 2006; Moreno et al., 2008a; Moreno et al., 2008b; Moreno et al., 2010). Further on, the slopes of V *vs.* Ni linear regression lines at Burnaby and Halifax sites were 2.7 ± 0.2 and 2.9 ± 0.2, respectively which are comparable with average V *vs.* Ni ratios that are typical for PM emissions from combustion of heavy fuel oil used by marine transportation vessels (Querol et al., 2007; Moreno et al., 2010; Jeong et al., 2011). Hence, V and Ni emissions at these sites are related to the burning of heavy oils by marine vessels operating in the harbors located close to these sites. The slope of V *vs.* Ni linear regression line at the Toronto site, was 1.9 ± 0.1 which is similar to values reported for $PM_{2.5}$ emitted close to high traffic roadways (Saganic and Gilroy, 2002). Compared to $PM_{2.5}$, V and Ni median concentrations in $PM_{2.5-10}$ for all sites were about 5 times lower and did not show any correlation.

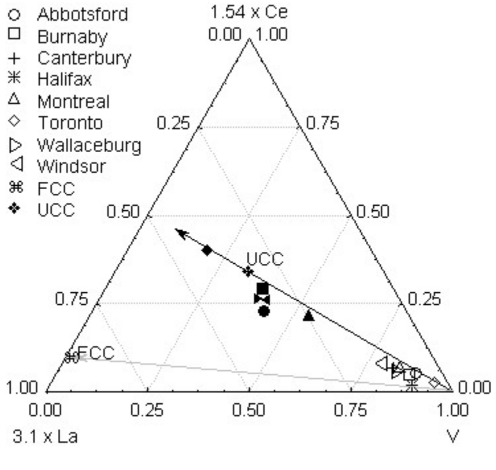


***Figure 4**. LaVCe tertiary plots for $PM_{2.5-10}$ (closed symbols), $PM_{2.5}$ (open symbols) samples. The FCC sample was provided from one supplier of FCC catalysts in Canada. The V–UCC and V–FCC lines represent La/Ce ratios for UCC and FCC respectively; the arrows show the direction of increasing La/V ratio.*

The La/V ratios in all $PM_{2.5}$ samples were not higher than 0.04, implying that a significant amount of V in this fraction of PM is coming from combustion processes. In contrary, the median La/V ratio for $PM_{2.5–10}$ was 0.28 (with IQR 0.15–0.39) which is very close to the uncontaminated crustal material composition (Moreno et al., 2008a). The three–component diagrams (or ternary plots) which are traditionally utilized by geologists to illustrate the compositional variations in minerals and rocks, have also been used to show geochemical patterns in atmospheric PM (Moreno et al., 2008a; Moreno et al., 2010). In the ternary La–V–Ce plot shown in Figure 4, La and Ce concentrations are adjusted so that the UCC point is placed in the center of the triangle. This plot shows a distinctive grouping of $PM_{2.5}$ samples close to V– apex and $PM_{2.5–10}$ samples close to UCC composition point.

Further on, the $PM_{2.5}$ samples were clustered in two groups: the Halifax site is plotted closer to V–FCC line and the other sites are plotted closer to the V–UCC line. These results imply that the presence of V in $PM_{2.5–10}$ samples is mostly due to fugitive dust suspended in the atmosphere while the emissions of V–rich fine aerosols are coming mainly from fossil fuel combustion processes. Unlike the other sites, emissions from petrochemical industrial complexes close to Halifax show some contribution to the presence of V in $PM_{2.5}$.

## 4. Conclusion

The data presented in this study support the previous reports that the distribution patterns of lanthanoids in air $PM_{2.5}$ are sensitive and reliable tracers for emissions related to oil–refining industry. The average concentrations of total lanthanoids in $PM_{2.5}$ samples from the Canadian urban and rural sites included in this study, ranged from 59 to 334 pg $m^{-3}$ and were typically two times lower than $PM_{2.5–10}$. The lowest concentrations of lanthanoids were found at the Canterbury site which has a minimal anthropogenic impact. Compared to this site, concentrations of lanthanoids at the Windsor, Toronto and Montreal urban sites were 2.5 to 4 times higher. However, the La enrichment factors were comparable to the natural composition and to the $PM_{2.5–10}$ values indicating that the main source of lanthanoids present in $PM_{2.5}$ at these sites is the wind and/or traffic induced re–suspension of local road dust. The highest concentrations of all lanthanoids were found at the Halifax site which is located less than 2 km southeast of a major petrochemical complex. La/Ce and La/Sm ratios at this site were respectively 4.1 and 39 which indicate that the oil refining facility has a significant effect on the emissions of lanthanoids at this site. The second highest concentrations and enrichment factors were found at the Burnaby site, which is located close to a smaller petrochemical complex, which results in less significant contribution of this facility on $PM_{2.5}$ composition. Compared to urban sites included in this study, concentrations of lanthanoids at the Wallaceburg site were about 2 times lower whereas La–enrichment factors were almost double and consistent with values reported for areas where the emissions of lanthanoids are partly due to oil–refining sources. These results confirm that the lanthanoids distribution patterns and La enrichment factors are useful indicators for tracking PM emissions from oil–refining facilities located as far as 50 km from the sampling site.

Finally, our results show that La, Ce and V can be used to identify three classes of particles: particles of crustal origin which are mostly found in the coarse fraction of PM, fine particles highly enriched in La which are related to the refinery emissions, and V–enriched fine particles originating from heavy oil combustion.

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## Supporting Material Available

Median mass and trace metal concentrations for $PM_{2.5}$ samples from urban sites (Table S1A), Median mass and trace metal concentrations for $PM_{2.5}$ samples from rural sites (Table S1B), Median mass and trace metal concentrations for $PM_{2.5–10}$ samples from urban and rural sites (Table S2). This information is available free of charge via Internet at http://www.atmospolres.com.

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**Attachment 42**

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# Variations in vanadium, nickel and lanthanoid element concentrations in urban air

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ABSTRACT

The emission of trace metal pollutants by industry and transport takes place on a scale large enough to alter atmospheric chemistry and results in measurable differences between the urban background of inhalable particulate matter (PM) in different towns. This is particularly well demonstrated by the technogenic release into the atmosphere of V, Ni, and lanthanoid elements. We compare PM concentrations of these metals in large datasets from five industrial towns in Spain variously influenced by emissions from refinery, power station, shipping, stainless steel, ceramic tiles and brick-making. Increased La/Ce values in urban background inhalable PM, due to La-contamination from refineries and their residual products (fuel oils and petcoke), contrast with Ce-rich emissions from the ceramic related industry, and clearly demonstrate the value of this ratio as a sensitive and reliable tracer for many point source emissions. Similarly, anomalously high V/Ni values (>4) can detect the influence of nearby high-V petcoke and fuel oil combustion, although the use of this ratio in urban background PM is limited by overlapping values in natural and anthropogenic materials. Geochemical characterisation of urban background PM is a valuable compliment to the physical monitoring of aerosols widely employed in urban areas, especially given the relevance of trace metal inhalation to urban health issues.

## 1. Introduction

Over the last 25 years there has been unprecedented anthropogenic contamination of the atmosphere by metalliferous particulate matter (PM) released during the combustion of the residual products from crude oil refining (Pacyna and Pacyna, 2001). Much of this PM has emanated from oil-fired power stations and petrochemical complexes, although shipping transport and a range of other industries utilising these residual oils and petroleum cokes in boilers and furnaces have also contributed their share. The metals most implicated in this global-scale atmospheric pollution event are V and Ni which are the most abundant metals present in crude oil, commonly in concentrations that exceed 1000 ppmV and 100 ppmNi (Barwise, 1990; Ali and Abbas, 2006). As a direct consequence, atmospheric emissions of Ni have around doubled and V tripled since the early 1980s, with an estimated 240 000 tonnes of V being globally emitted annually by 1995. These striking increases may be contrasted with overall decreases in emissions of most heavy metal PM (e.g. As, Cd, Cr, Cu, Hg, In, Mn, Mo, Pb, Sb, Se, Sn, Tl, Zn) over the same period (Pacyna and Pacyna, 2001).

Although less well publicised, another relatively recent consequence of the dependence of an increasing world population on crude oil refining has been higher atmospheric emissions of the “rare earth” metal La. Lanthanum is used in the form of La-concentrates (derived from the ore minerals bastnasite and monazite) in zeolitic fluid catalytic cracking units (FCC) which crack heavier crude oil distillation fractions into lighter compounds such as petrol (gasoline) and liquid petroleum gas (LPG). Because specifically La is concentrated rather than other “rare earth” elements belonging to the lanthanoid series La to Lu, release of La particles in FCC regenerator flue gas drives atmospheric lanthanoid chemistry away from natural ratios typical of rocks and minerals in the upper continental crust (UCC) (Olmez and Gordon, 1985; Kulkarni et al., 2006, 2007; Moreno et al., 2008a,b). The release of these metal pollutants into the atmosphere is not uniformly distributed, but instead focussed on areas exposed to pollution plumes derived from appropriate industrial (e.g refineries, oil power stations) or transport (e.g. large shipping ports) activities. Given the magnitude of the pollution involved, this has the potential to produce prominent spatial variations in atmospheric chemistry. In this paper we demonstrate the reality of such variations by reporting on the chemistry of air filter samples collected from urban areas with

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contrasting V, Ni and lanthanoid element atmospheric contamination sources. Specifically, we compare large chemical datasets of urban background levels of inhalable particulate matter ($PM_{10}$ and $PM_{2.5}$) collected over a period of 1–2 years in five Spanish towns variously contaminated by emissions from refineries, shipping, stainless steel industry, and brick and ceramic tiles manufacture.

## 2. Methodology

The five towns chosen for this study, Puertollano, La Línea, Algeciras, Bailén and L'Alcora (Fig. 1), are each distinctively different in their industrial character. *Puertollano* lies in inland Spain south of Madrid and has a major petrochemical refinery complex (capacity 140 000 b/d) and an opencast mine which supplies coal to two nearby power stations. One of these stations is the largest integrated gasification combined-cycle (IGCC) plant in the world, utilising a 50:50 mixture of high volatile bituminous coal and petcoke manufactured at the nearby refinery, whereas the other uses conventional pulverised coal combustion (PCC) (Font et al., 2009). *La Línea* is a coastal town situated on the NE side of the Bay of Algeciras adjacent to Gibraltar (Fig. 2), one of the most heavily industrialised areas in Spain. Like Puertollano, this site is influenced by a nearby major petrochemical complex which includes the San Roque refinery, the largest in Spain (capacity 240 000 b/d). Other important sources of industrial emissions include an oil fired power station and a major steelworks (Fig. 2). *Algeciras* lies on the SW side of the same bay, diametrically opposite and 9 km distant from La Línea (Fig. 2). Algeciras port is the busiest shipping area in Spain, with more than 80 000 registered ships (http://www.apba.es). Local meteorological conditions peculiar to the bay area result in dominant winds being either easterly (SSE) or westerly (WNW), producing highly localised atmospheric contamination patterns (Fig. 2). Thus WNW winds bring plumes from the refinery complex, metallurgical plant, and oil power station to La Línea but not Algeciras, easterly winds bring shipping emissions from Algeciras port directly to Algeciras but not La Línea (Pandolfi et al., in press).

*Bailén* is an inland town located at 39 km from the city of Jaén in the north of Andalucía (Fig. 1), with nearly half of the working population being linked to the brick and pottery manufacturing industry. The brick firing is performed in tunnel and Hoffman furnaces using agricultural wastes (from the olive industry) and especially petroleum coke as major fuels, and there is generally a relatively low level of smoke emission abatement applied so that the area is commonly highly polluted (Sánchez de la Campa et al., submitted). *L'Alcora*, located in eastern Spain, is another town strongly dependent on one industry, in this case the production of ceramic tiles, frits and pigments (used in ceramic glazes), but here the dominant fuel type utilised is natural gas and PM pollution levels are consequently much lower and mainly a consequence of production, handling and transport of raw materials used for ceramic tiles production (Querol et al., 2007; Minguillón et al., 2007; 2009). The locations and altitudes of each of the five urban background monitoring sites are presented in Table 1.

The data were obtained using manual gravimetric $PM_{10}$ and $PM_{2.5}$ high-volume samplers and quartz micro-fibre filters during different monitoring campaigns between the period 2003–2006. Two daily filters per week in accordance with a systematic programme were collected on alternative days for at least one year at each site. Thus although sampling was done during different years at each site, the sampling period and protocol were similar, making results intercomparable. Once the gravimetric determination was performed the filters were treated and analyzed for the determination of the chemical composition of PM. One half of each filter was acid digested ($HF{:}HNO_3{:}HClO_4$), kept at 90 °C in a Teflon reactor during 6 h, driven

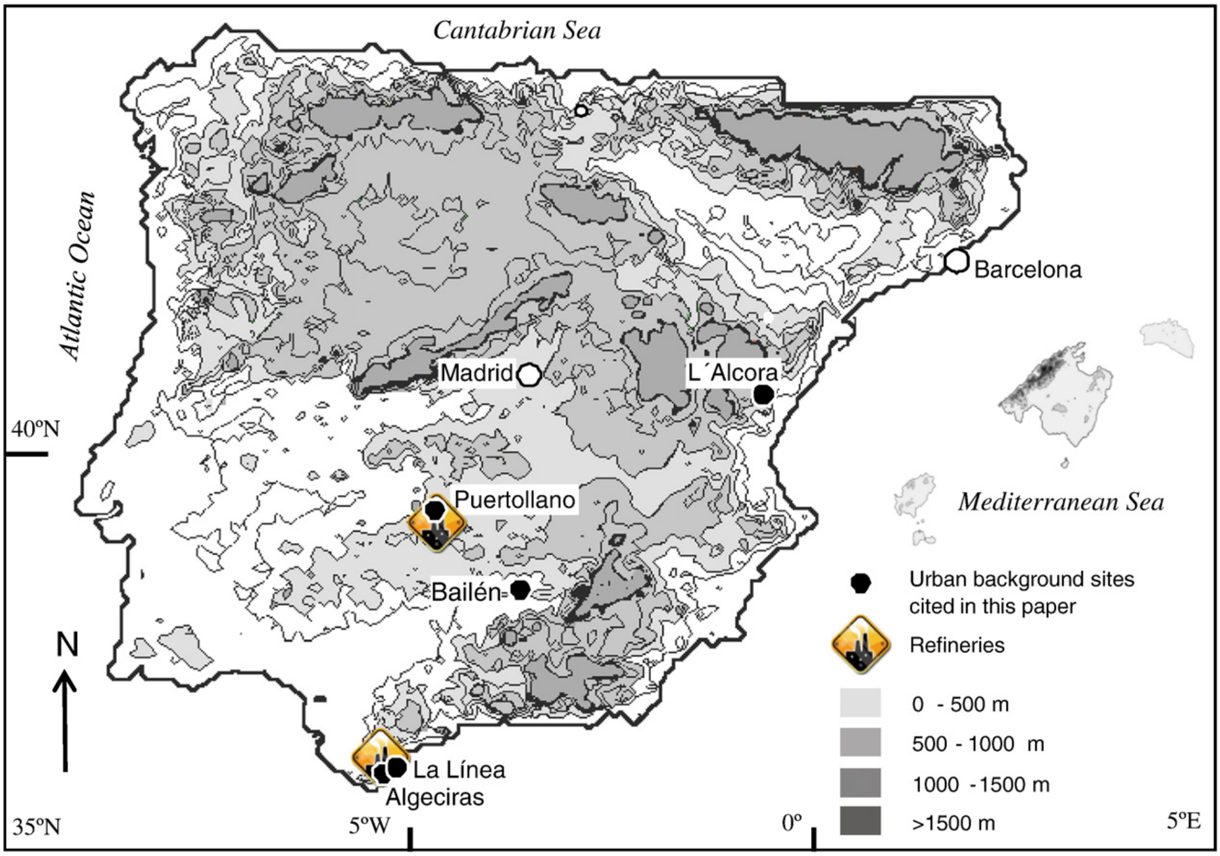

**Fig. 1.** Location map of the five monitoring sites(black circles).

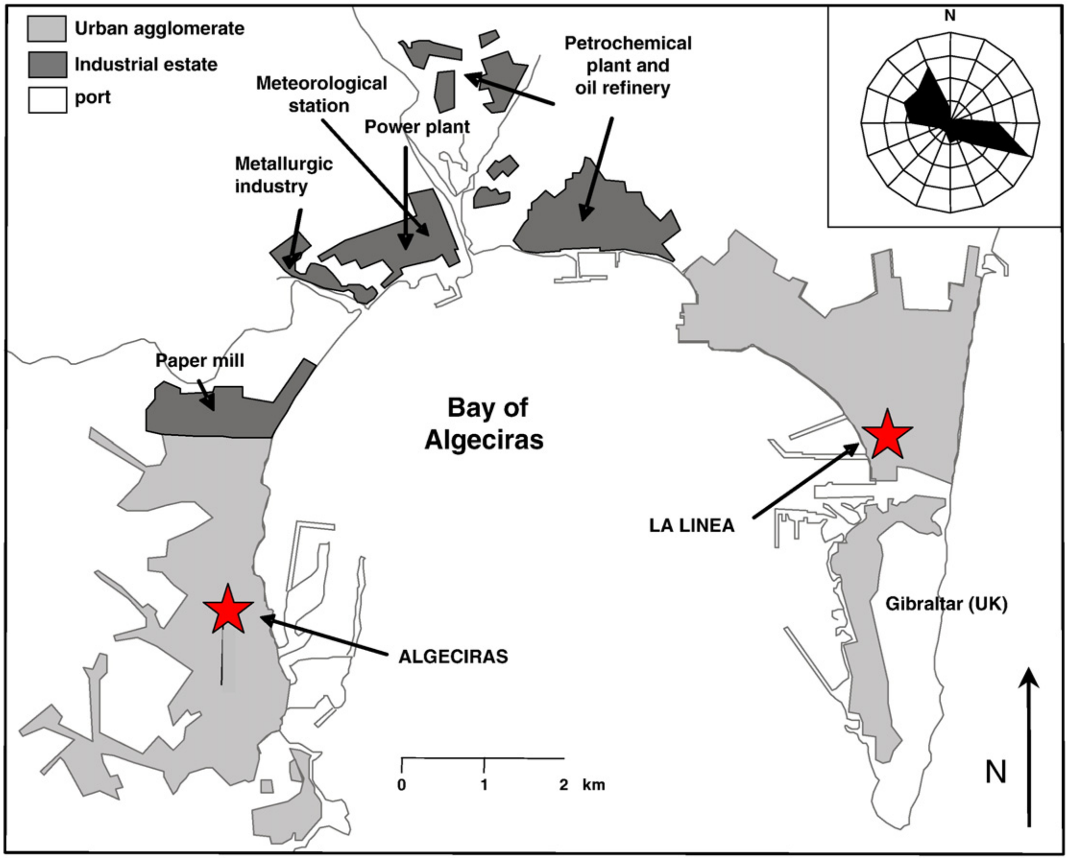

**Fig. 2.** Map of Algeciras Bay area, showing location of the La Línea and Algeciras monitoring sites, main contamination sources (San Roque refinery complex, metallurgical plant, oil power station, and port areas), and a rose diagram with prevailing wind directions.
Modified from Pandolfi et al., in press.

to dryness and re-dissolved with $HNO_3$ to make up a volume of 50 ml with water for the chemical analysis using Inductively Coupled Plasma Atomic Emission Spectrometry and Mass Spectrometry. Another quarter of each filter was water leached (6 h at 60 °C, preceded by an ultrasound bath during ten minutes, in 50 ml sealed PVC bottles) for the determination of soluble ion concentrations by ion chromatography (sulphate, nitrate and chloride) and ion selective electrode (ammonium). A portion of 1.5 $cm^2$ of the remaining quarter of each filter was used for the analysis of OC + EC (organic and elemental carbon) by a thermal-optical transmission technique using a Sunset Laboratory OCEC Analyzer.

$SiO_2$ and $CO_3^{2-}$ were indirectly determined on the basis of empirical factors ($Al*1.89 = Al_2O_3$, $3*Al_2O_3 = SiO_2$ and $1.5*Ca + 2.5\ Mg = CO_3^{2-}$, mass ratios, see Querol et al., 2001). The addition of the above determinations accounted for 75 to 85% of the $PM_{10}$ mass. The remaining undetermined mass is mainly attributed to the structural and adsorbed water that was not removed during the sample conditioning. To assure the quality of the analytical procedure a small amount (15 mg) of the NIST-1633b (fly ash) reference material loaded on a 1/4 quartz micro-fibre filter was also analysed. These reached values <10% for most elements, with the exception of P and K (<15%).

**Table 1**
Location and characteristics of the monitoring stations.

| Site | Longitude | Latitude | Altitude (m.a.s.l.) | Station type | Sampling period |
|---|---|---|---|---|---|
| Algeciras | 05°27′07″W | 36°08′16″N | 24 | Urban–industrial | 2003–2004 |
| Bailén | 03°46′00″W | 38°06′00″N | 350 | Industrial | 2003–2006 |
| L'Alcora | 00°12′43″W | 40°04′07″N | 175 | Urban–industrial | 2003–2005 |
| La Línea | 05°20′54″W | 36°09′33″N | 1 | Urban–industrial | 2003–2004 |
| Puertollano | 04°05′19″W | 38°41′64″N | 670 | Urban–industrial | 2004–2005 |

## 3. Results

The averaged chemical data for a total of 846 ICPMS analyses of PM from the five aforementioned urban background monitoring sites are presented in Table 2, along with average PM mass concentrations. It can be seen that Bailén was the most contaminated site both in terms of mass ($PM_{10} > 67\ \mu g/m^3$, $PM_{2.5} > 62\ \mu g/m^3$) and in the dominance of finer, more deeply inhalable PM ($PM_{2.5/10} = 0.93$), followed in turn by Puertollano, La Línea, Algeciras (each between 38–43 $\mu gPM_{10}/m^3$, and 24–29 $\mu gPM_{2.5}/m^3$ with $PM_{2.5/10} = 0.6–0.7$), and L'Alcora (33 $\mu g\ PM_{10}/m^3$). There is considerable chemical variation in major element concentrations, the most notable extremes being elevated levels of mainly coarse NaCl at the coastal sites of La Línea and Algeciras (around 3–5 $\mu gPM_{10}/m^3$), carbonaceous material (OM + EC) at the inland sites of Bailén and Puertollano (around 13–16 $\mu gPM_{10}/m^3$), $CaCO_3$ and K at Bailén (around 10 and 4 $\mu gPM_{10}/m^3$ respectively), and $NH_4^+$ at Puertollano (2.4 $\mu gPM_{10}/m^3$). The major chemical components of the PM are grouped into four categories in Table 2: (a) crustal or mineral (sum of $Al_2O_3$, $SiO_2$, $CO_3^{2-}$, Ca, Fe, K, Mg, Ti and P); (b) marine (sum of $Cl^-$ and $Na^+$); (c) organic matter and elemental carbon, OM + EC (OM obtained applying a 1.6 factor to the OC concentrations, Turpin et al., 2001); and (d) secondary inorganic compounds, SIC (sum of $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$). This grouping further emphasises the importance of sea spray in the coarser PM fraction at Algeciras and La Línea, crustal mineral matter at Bailén and L'Alcora,

**Table 2**
Average chemical compositions and standard deviations of PM filter samples collected from each monitoring station. Total number of samples at each site are as follows: Puertollano 112 $PM_{10}$ and 113 $PM_{2.5}$; La Línea 95 $PM_{10}$ and 86 $PM_{2.5}$; Algeciras 80 $PM_{10}$ and 83 $PM_{2.5}$; Bailén 96 $PM_{10}$ and 78 $PM_{2.5}$; L'Alcora 103 $PM_{10}$ (no $PM_{2.5}$ collected).

| | Puertollano | | | | La Línea | | | | Algeciras | | | | Bailén | | | | L'Alcora | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | |
| | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. |
| *$\mu g/m^3$* | | | | | | | | | | | | | | | | | | |
| PM | 42.9 | 19.7 | 28.6 | 14.3 | 41.5 | 20.2 | 24.4 | 9.9 | 37.7 | 19.2 | 24.6 | 11.9 | 67.3 | 27.3 | 62.9 | 26.2 | 33.2 | 16.4 |
| $PM_{2.5/10}$ | 0.7 | | | | 0.6 | | | | 0.7 | | | | 0.9 | | | | | |
| Cnm | 9.1 | 5.2 | 7.2 | 4.6 | 4.3 | 2.5 | 3.9 | 1.9 | 4.8 | 2.3 | 4.3 | 2.6 | 11.4 | 5.8 | 10.0 | 5.0 | 4.2 | 2.2 |
| OM+EC | 13.2 | 7.6 | 10.4 | 6.7 | 6.2 | 3.6 | 5.6 | 2.8 | 7.7 | 3.4 | 6.2 | 3.8 | 16.3 | 8.6 | 14.1 | 7.5 | 6.0 | 3.1 |
| $CO_3$= | 1.7 | 1.2 | 0.3 | 0.2 | 2.5 | 1.7 | 0.4 | 0.3 | 1.7 | 1.5 | 0.4 | 0.5 | 5.9 | 3.1 | 3.6 | 3.3 | 2.2 | 1.4 |
| $SiO_2$ | 6.1 | 5.5 | 1.2 | 1.3 | 3.3 | 3.8 | 1.1 | 1.3 | 2.5 | 4.7 | 1.0 | 1.7 | 10.2 | 6.7 | 6.8 | 6.4 | 6.2 | 4.4 |
| $Al_2O_3$ | 2.0 | 1.8 | 0.4 | 0.4 | 1.1 | 1.3 | 0.3 | 0.3 | 0.8 | 1.6 | 0.3 | 0.6 | 3.4 | 2.2 | 2.3 | 2.1 | 2.1 | 1.5 |
| Ca | 1.1 | 0.8 | 0.2 | 0.1 | 1.7 | 1.1 | 0.3 | 0.2 | 1.1 | 1.0 | 0.3 | 0.3 | **3.9** | 2.1 | **2.4** | 2.2 | 1.5 | 0.9 |
| K | 0.5 | 0.4 | 0.3 | 0.2 | 0.3 | 0.3 | 0.1 | 0.1 | 0.3 | 0.3 | 0.1 | 0.1 | 3.8 | 2.1 | 3.6 | 2.0 | 0.7 | 0.4 |
| Na | 0.5 | 0.3 | 0.2 | 0.3 | **2.3** | 2.1 | 0.4 | 0.4 | **1.6** | 1.0 | 0.4 | 0.2 | 0.5 | 0.4 | 0.3 | 0.3 | 0.5 | 0.4 |
| Mg | 0.3 | 0.2 | 0.1 | 0.1 | 0.4 | 0.3 | 0.1 | 0.1 | 0.3 | 0.2 | 0.1 | 0.1 | 0.5 | 0.3 | 0.3 | 0.3 | 0.2 | 0.1 |
| Fe | 0.7 | 0.5 | 0.1 | 0.1 | 0.5 | 0.4 | 0.1 | 0.1 | 0.4 | 0.5 | 0.1 | 0.2 | 1.2 | 0.7 | 0.8 | 0.7 | 0.5 | 0.4 |
| $SO_4$= | 4.7 | 4.2 | 3.7 | 2.9 | 6.5 | 4.2 | 4.7 | 2.8 | 5.0 | 3.5 | 3.9 | 2.8 | 8.6 | 3.3 | 7.9 | 3.1 | 3.9 | 2.7 |
| $NO_3$− | 2.9 | 2.6 | 2.0 | 2.3 | 3.6 | 3.1 | 1.0 | 1.0 | 3.5 | 2.5 | 1.2 | 1.5 | 3.4 | 3.1 | 3.2 | 3.3 | 0.9 | 0.8 |
| Cl− | 0.6 | 0.4 | 0.4 | 0.2 | **2.1** | 2.7 | 0.3 | 0.3 | **1.6** | 1.3 | 0.5 | 0.4 | 1.0 | 1.0 | 0.9 | 0.9 | 0.2 | 0.2 |
| $NH_{4+}$ | 2.4 | 2.2 | 2.5 | 2.4 | 1.3 | 1.0 | 1.8 | 1.3 | 1.4 | 1.2 | 1.5 | 1.3 | 1.4 | 1.0 | 1.6 | 1.2 | 0.6 | 0.5 |
| Mineral | 12.4 | | 2.7 | | 9.9 | | 2.3 | | 7.1 | | 2.4 | | 28.8 | | 19.9 | | 13.5 | |
| SIC | 10.0 | | 8.2 | | 11.4 | | 7.5 | | 10.0 | | 6.7 | | 13.4 | | 12.6 | | 5.4 | |
| OM+EC | 13.2 | | 10.4 | | 6.2 | | 5.6 | | 7.7 | | 6.2 | | 16.3 | | 14.1 | | 6.0 | |
| Marine | 1.1 | | 0.7 | | 4.5 | | 0.7 | | 3.2 | | 0.8 | | 1.5 | | 1.2 | | 0.7 | |
| Metals | 0.3 | | 0.1 | | 0.3 | | 0.2 | | 0.2 | | 0.1 | | 0.5 | | 0.4 | | 0.6 | |
| *$ng/m^3$* | | | | | | | | | | | | | | | | | | |
| Li | 1.00 | 0.90 | 0.26 | 0.22 | 0.60 | 0.55 | 0.18 | 0.13 | 0.43 | 0.80 | 0.12 | 0.21 | 1.94 | 1.03 | 1.37 | 0.96 | 1.41 | 1.06 |
| P | 32.65 | 23.91 | 12.25 | 13.32 | 25.43 | 28.20 | 6.11 | 5.70 | 18.29 | 17.12 | 8.92 | 17.12 | **64.72** | 27.91 | **45.89** | 30.79 | 14.04 | 15.23 |
| Sc | 0.22 | 0.19 | 0.05 | 0.07 | 0.21 | 0.32 | 0.09 | 0.17 | 0.11 | 0.16 | 0.04 | 0.06 | 0.32 | 0.24 | 0.21 | 0.21 | 0.14 | 0.14 |
| Ti | 62.04 | 53.78 | 12.42 | 12.75 | 35.83 | 40.69 | 7.19 | 6.07 | 30.55 | 65.87 | 6.32 | 7.34 | 77.58 | 54.45 | **53.81** | 52.82 | 51.80 | 34.92 |
| V | 9.85 | 10.08 | 5.54 | 6.19 | 27.67 | 17.93 | 22.40 | 14.01 | 24.84 | 22.68 | 20.37 | 20.81 | **133.51** | 80.45 | **95.29** | 73.43 | 3.53 | 2.43 |
| Cr | 3.46 | 2.03 | 1.73 | 1.05 | **24.60** | 29.18 | **14.33** | 18.86 | 6.25 | 7.92 | 3.69 | 4.99 | 5.64 | 4.37 | 4.23 | 2.99 | 5.70 | 4.22 |
| Mn | 11.34 | 8.61 | 3.20 | 2.76 | 16.90 | 14.71 | 8.54 | 8.75 | 8.39 | 9.17 | 4.10 | 4.30 | 20.06 | 11.93 | 13.77 | 11.70 | 5.96 | 3.33 |
| Co | 0.76 | 0.82 | 0.28 | 0.27 | 0.56 | 0.37 | 0.29 | 0.23 | 0.31 | 0.29 | 0.24 | 0.40 | 0.65 | 0.34 | 0.47 | 0.34 | 0.72 | 0.57 |
| Ni | 4.40 | 3.77 | 3.09 | 2.27 | 20.27 | 13.92 | 13.54 | 9.07 | 11.00 | 9.22 | 8.69 | 7.89 | 23.84 | 12.62 | 17.20 | 10.19 | 2.94 | 2.00 |
| Cu | 26.48 | 22.90 | 12.13 | 15.72 | 11.41 | 7.41 | 6.13 | 3.81 | 23.24 | 12.43 | 11.81 | 8.15 | 52.30 | 89.16 | 26.31 | 13.64 | 4.50 | 3.10 |
| Zn | 53.88 | 71.32 | 30.07 | 27.00 | 72.85 | 82.91 | 48.80 | 55.69 | 38.80 | 42.40 | 26.96 | 36.14 | 43.23 | 71.63 | 26.40 | 20.39 | **242.28** | 201.92 |
| Ga | 0.38 | 0.29 | 0.12 | 0.08 | 0.24 | 0.17 | 0.09 | 0.05 | 0.15 | 0.20 | 0.06 | 0.07 | **1.77** | 2.20 | **1.05** | 0.99 | 0.34 | 0.21 |
| Ge | 0.20 | 0.26 | 0.29 | 0.42 | 0.32 | 0.51 | 0.25 | 0.39 | 0.22 | 0.25 | 0.16 | 0.20 | 0.19 | 0.33 | 0.15 | 0.28 | 0.15 | 0.27 |
| As | 1.95 | 6.94 | 1.03 | 3.40 | 0.89 | 0.72 | 0.54 | 0.49 | 0.53 | 0.40 | 0.39 | 0.34 | 1.36 | 1.49 | 0.91 | 0.60 | **6.66** | 6.28 |
| Se | 0.60 | 0.48 | 0.46 | 0.59 | 0.83 | 0.60 | 0.41 | 0.32 | 0.51 | 0.27 | 0.30 | 0.22 | 2.26 | 1.03 | 1.94 | 1.04 | **3.08** | 2.71 |
| Rb | 1.55 | 1.20 | 0.46 | 0.28 | 0.78 | 0.78 | 0.22 | 0.13 | 0.65 | 1.01 | 0.24 | 0.28 | **5.65** | 2.64 | **4.69** | 2.49 | 2.89 | 1.79 |
| Sr | 4.60 | 4.46 | 0.84 | 1.02 | 5.68 | 4.40 | 1.18 | 0.90 | 4.40 | 4.59 | 1.32 | 1.69 | **10.10** | 9.28 | **5.99** | 4.67 | 4.24 | 2.66 |
| Y | 0.22 | 0.24 | 0.07 | 0.08 | 0.32 | 0.25 | 0.13 | 0.14 | 0.20 | 0.21 | 0.11 | 0.11 | **0.79** | 0.66 | **0.52** | 0.39 | 0.18 | 0.21 |
| Zr | 6.70 | 5.36 | 9.40 | 6.03 | 4.88 | 4.38 | 3.31 | 3.64 | 3.92 | 3.98 | 2.77 | 2.90 | 5.27 | 3.91 | 4.60 | 4.14 | **23.89** | 26.04 |
| Nb | 0.28 | 0.33 | 0.10 | 0.08 | 0.17 | 0.20 | 0.05 | 0.04 | 0.11 | 0.28 | 0.03 | 0.06 | 0.33 | 0.23 | 0.24 | 0.21 | 0.17 | 0.16 |
| Mo | 3.09 | 3.96 | 2.03 | 3.54 | 15.16 | 22.30 | 9.73 | 11.91 | 7.34 | 7.45 | 4.57 | 4.59 | 4.70 | 9.55 | 2.01 | 4.64 | 1.80 | 3.21 |
| Cd | 0.14 | 0.11 | 0.13 | 0.09 | 0.26 | 0.23 | 0.18 | 0.19 | 0.15 | 0.09 | 0.12 | 0.07 | 0.33 | 0.33 | 0.26 | 0.16 | **1.70** | 2.40 |
| Sn | 1.82 | 1.67 | 1.62 | 1.77 | 1.36 | 1.29 | 0.96 | 0.82 | 1.84 | 1.71 | 0.89 | 1.05 | <dl | 0.00 | <dl | 0.00 | 1.94 | 2.41 |
| Sb | 4.20 | 12.78 | 3.18 | 12.25 | 1.39 | 1.06 | 0.52 | 0.48 | 1.50 | 1.20 | 0.61 | 0.48 | <dl | 0.00 | <dl | 0.00 | **5.10** | 8.45 |
| Cs | 0.22 | 0.19 | 0.05 | 0.03 | 0.05 | 0.05 | 0.01 | 0.01 | 0.04 | 0.05 | 0.02 | 0.01 | 0.47 | 0.32 | 0.34 | 0.26 | 0.46 | 0.30 |
| Ba | 13.28 | 9.03 | 6.07 | 4.85 | 15.35 | 15.43 | 8.79 | 21.78 | 11.04 | 9.90 | 8.28 | 6.52 | 20.03 | 9.61 | 15.72 | 8.91 | 31.69 | 40.94 |
| La | 0.89 | 0.77 | 0.27 | 0.25 | 0.58 | 0.53 | 0.20 | 0.22 | 0.40 | 0.41 | 0.20 | 0.20 | 1.23 | 0.74 | 0.86 | 0.78 | 0.51 | 0.36 |
| Ce | 1.16 | 0.98 | 0.29 | 0.25 | 0.68 | 0.63 | 0.21 | 0.15 | 0.55 | 0.73 | 0.25 | 0.31 | 2.11 | 1.28 | 1.45 | 1.36 | 2.23 | 4.11 |
| Pr | 0.16 | 0.12 | 0.06 | 0.05 | 0.09 | 0.08 | 0.03 | 0.02 | 0.07 | 0.09 | 0.03 | 0.04 | 0.27 | 0.18 | 0.18 | 0.18 | 0.16 | 0.13 |
| Nd | 0.55 | 0.49 | 0.14 | 0.15 | 0.33 | 0.33 | 0.09 | 0.06 | 0.25 | 0.39 | 0.11 | 0.13 | 0.94 | 0.60 | 0.62 | 0.58 | 0.42 | 0.31 |
| Sm | 0.09 | 0.08 | 0.02 | 0.02 | 0.05 | 0.05 | 0.02 | 0.03 | 0.04 | 0.05 | 0.02 | 0.02 | 0.20 | 0.14 | 0.13 | 0.11 | 0.06 | 0.05 |
| Eu | 0.01 | 0.03 | 0.04 | 0.01 | 0.02 | 0.02 | 0.01 | 0.02 | 0.01 | 0.02 | 0.02 | 0.02 | 0.04 | 0.05 | 0.02 | 0.02 | <dl | 0.00 |
| Gd | 0.09 | 0.08 | 0.04 | 0.04 | 0.08 | 0.07 | 0.03 | 0.03 | 0.06 | 0.07 | 0.04 | 0.04 | 0.20 | 0.15 | 0.13 | 0.11 | 0.07 | 0.07 |
| Tb | <dl | 0.01 | <dl | 0.00 | 0.02 | 0.02 | <dl | 0.00 | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.03 | <dl | 0.01 | <dl | 0.00 |
| Dy | 0.06 | 0.06 | 0.04 | 0.04 | 0.06 | 0.06 | 0.02 | 0.02 | 0.04 | 0.04 | 0.03 | 0.03 | 0.16 | 0.13 | 0.11 | 0.09 | 0.04 | 0.04 |
| Ho | <dl | 0.01 | <dl | 0.00 | 0.01 | 0.02 | <dl | 0.00 | 0.01 | 0.02 | <dl | 0.00 | 0.01 | 0.02 | <dl | 0.01 | <dl | 0.00 |
| Er | 0.04 | 0.05 | 0.05 | 0.03 | 0.02 | 0.02 | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.07 | 0.06 | 0.05 | 0.04 | 0.05 | 0.04 |
| Tm | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | <dl | 0.01 | <dl | 0.02 | <dl | 0.00 |
| Yb | 0.05 | 0.06 | 0.04 | 0.04 | 0.02 | 0.02 | 0.01 | 0.01 | 0.02 | 0.02 | 0.01 | 0.01 | 0.07 | 0.05 | 0.04 | 0.03 | 0.06 | 0.05 |
| Lu | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | <dl | 0.00 | 0.02 | 0.12 | 0.02 | 0.07 | 0.02 | 0.06 | <dl | 0.00 |
| Ta | 0.07 | 0.12 | 0.04 | 0.06 | 0.02 | 0.03 | 0.01 | 0.02 | 0.02 | 0.07 | 0.01 | 0.02 | 0.02 | 0.00 | 0.01 | 0.00 | 0.04 | 0.06 |
| W | 0.04 | 0.08 | 0.04 | 0.08 | 0.15 | 0.17 | 0.09 | 0.13 | 0.05 | 0.15 | 0.03 | 0.06 | 0.17 | 0.10 | 0.14 | 0.09 | 0.33 | 0.34 |
| Tl | 0.06 | 0.09 | 0.07 | 0.07 | 0.04 | 0.03 | 0.04 | 0.03 | 0.03 | 0.03 | 0.04 | 0.03 | **2.73** | 3.06 | **2.47** | 2.41 | **3.03** | 1.84 |
| Pb | 11.98 | 13.90 | 9.30 | 13.16 | 12.97 | 11.39 | 9.74 | 8.96 | 7.58 | 6.58 | 6.32 | 6.45 | 33.89 | 24.41 | 23.91 | 14.10 | **183.93** | 185.38 |
| Bi | 0.08 | 0.08 | 0.06 | 0.07 | 0.12 | 0.12 | 0.09 | 0.10 | 0.08 | 0.13 | 0.07 | 0.10 | 0.12 | 0.15 | 0.09 | 0.10 | 0.18 | 0.24 |
| Th | 0.12 | 0.14 | 0.06 | 0.08 | 0.10 | 0.10 | 0.03 | 0.03 | 0.06 | 0.07 | 0.06 | 0.06 | 0.40 | 0.29 | 0.28 | 0.26 | 0.10 | 0.11 |
| U | 0.15 | 0.12 | 0.21 | 0.21 | 0.11 | 0.11 | 0.09 | 0.08 | 0.08 | 0.06 | 0.16 | 0.18 | 0.29 | 0.30 | 0.20 | 0.17 | 0.14 | 0.09 |

**Table 2** (*continued*)

| | Puertollano | | | | La Línea | | | | Algeciras | | | | Bailén | | | | L'Alcora | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{10}$ | |
| | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. | Mean. | Sta. Dev. |
| ΣLoid | 3.11 | *2.49* | 0.98 | *0.70* | 1.98 | *1.69* | 0.64 | *0.46* | 1.49 | *1.85* | 0.76 | *0.72* | 5.36 | *3.23* | 3.62 | *3.26* | 3.60 | *4.46* |
| La/Ce | 0.77 | *0.55* | 0.93 | *0.88* | 0.85 | *0.59* | 0.98 | *0.83* | 0.74 | *0.22* | 0.79 | *0.59* | 0.58 | *0.07* | 0.59 | *0.11* | 0.23 | *0.13* |
| V/Ni | 2.24 | *1.62* | 1.79 | *0.89* | 1.37 | *1.01* | 1.65 | *1.19* | 2.26 | *1.01* | 2.34 | *1.02* | 5.60 | *2.40* | 5.54 | *2.38* | 1.20 | *1.02* |
| V/Rb | 6.34 | *8.33* | 12.11 | *16.44* | 35.64 | *48.88* | 101.95 | *89.48* | 38.22 | *55.13* | 86.16 | *135.24* | 23.62 | *11.83* | 20.31 | *10.83* | 1.22 | *0.94* |

and C at Bailén and Puertollano. In the case of Bailén note that K is not only a crustal mineral component but also sources from combustion of biomass commonly used as fuel in brick manufacture. With regard to trace metals, there are anomalous concentrations of Cr and Ni at La Línea, P, V, Ni, Ga, Rb, Sr, Ti, Tl and Y at Bailén, and Zn, As, Se, Zr, Cd, Sb, Tl, Ce and Pb at L'Alcora (see elements highlighted in bold in Table 2).

### *3.1. Lanthanoid elements*

Concentrations of average total lanthanoids (ΣLoid: La to Lu) in our five PM samples range up to 5.4 ng/m$^3$, with the highest levels present in the Bailén and L'Alcora samples (Table 2). Lanthanoid elements are more strongly fractionated into the coarser particles ($PM_{10}$) at Puertollano and La Línea ($PM_{2.5/10}$ = 0.3), whereas this is not the case at Algeciras (0.5), and the reverse is true for Bailén (0.7) where the finer particles contain most of the total lanthanoid content. The commonest lanthanoid (Ce) is typically around twice as abundant as its lighter immediate neighbour La, producing natural La/Ce values of 0.4–0.6 in uncontaminated rocks, soils and minerals (Rudnick and Gao, 2004). In our database presented here, the PM samples from Bailén show La/Ce lying just within this 0.4–0.6 window of crustal compositions but in all other samples this ratio is clearly influenced by technogenic emissions. In the case of L'Alcora $PM_{10}$ La/Ce values drop to 0.2, due to excess Ce, whereas at the other three sites this ratio rises to >0.7 due to excess La in ambient air (Table 2). Furthermore, whereas there is no appreciable difference between La/Ce values in coarser and finer particles at Bailén, there is a very well defined fractionation of La relative to Ce in the finer ($PM_{2.5}$) fraction at Puertollano and La Línea (Table 2).

These differences in La/Ce patterns are clarified in Fig. 3 which provides a running plot of this ratio for $PM_{10}$ during each sampling period ($PM_{2.5}$ not shown but follow the same trends). Puertollano has already been documented as a typical refinery-contaminated site, with spikes in ambient PM La-concentrations produced in response to pollution plumes emanating from fluid catalytic converter (FCC) emissions sourcing 3–4 km from the monitoring site (Moreno et al., 2008b). The frequent occurrence of these La-day (LAD) spikes at Puertollano is demonstrated in Fig. 3a, with La/Ce rising from crustal values of 0.5 to reach peaks up to 8 times this value. A similar pattern of La spikes is displayed by the data from La Línea, again indicating the presence of LAD events, in this case from the San Roque refinery 4 km to the NW of the monitoring site (Fig. 2). In contrast, the Algeciras data, while still showing slightly enhanced La/Ce values (0.7–0.8) lack the prominent LAD spikes of the other two refinery-influenced sites. We attribute this difference between La/Ce signatures at La Línea and Algeciras to reflect the fact that La Línea lies downwind of the refinery on many days of the year, whereas Algeciras does not (Fig. 2). The background levels of La present at Algeciras reflect the contaminated nature of the highly industrialised bay area, which includes not just the petrochemical complex but also abundant fine PM from shipping emissions and an oil fired power station, rather than specific transient FCC plume events (Fig. 2).

The PM data from Bailén, in striking contrast to the previous sites discussed, maintain a constant La/Ce value of 0.5–0.6 for virtually all sampling days (Fig. 3). This geological lanthanoid signature derives from the use of argillaceous crustal materials in brick manufacture. Locally quarried red, yellow, black and white clays all have typically sedimentary rock La/Ce signatures of 0.50–0.55. The slightly higher background levels of La/Ce at Bailén (0.58–0.59) are likely to be related to the use of petroleum coke as the dominant fuel in the brick firing process: analysis of such fuels typically shows La/Ce>1. However, the concentration of lanthanoid elements in these fuels is very low (<<0.1 ppm La) so that only relatively minor increases in background atmospheric La/Ce values are produced despite the highly polluted nature of the area. Another difference displayed by the Bailén data is that the lanthanoid elements are more prevalent in the finer PM ($PM_{2.5/10}$ La + Ce = 0.7: Table 2). This prevalence simply reflects the fact that most ambient PM at Bailén are <2.5 µm in size, due to the abundant smoke emanating from the brick-firing ovens scattered across the area. Finally, the data from L'Alcora display the opposite pattern to those of Puertollano, La Línea and Algeciras (Fig. 3). In this case departures from crustal values are due to high Ce levels in ceramic (use and manufacture of pigments) industry emission plumes (Minguillón et al., 2007), producing a series of negative spikes in La/Ce $PM_{10}$ which regularly interrupt the normal "geological" background values of 0.5 (Fig. 3).

### *3.2. Vanadium and Nickel*

Average urban background V concentrations were very low in L'Alcora (4 ngPM$_{10}$/m$^3$), higher in Puertollano (10 ng PM$_{10}$/m$^3$), still higher at Algeciras and La Línea (25–28 ng PM$_{10}$/m$^3$), and by far the highest at Bailén (134 ng PM$_{10}$/m$^3$) (Table 2). This wide range in levels is controlled by the type of hydrocarbon being combusted by local industry. At Bailén high V refinery petcoke was the dominant fuel in a majority of the low stack brick ovens, and contains V levels >1500 ppm (*Plan de Mejora de Calidad del Aire de Bailén*; Sánchez de la Campa et al., submitted). In contrast much of the V pollution around the Bay of Algeciras is due to the burning (by abundant shipping not only in Algeciras Bay but crossing the Strait of Gibraltar, as well as a local power station) of heavy residual fuel oils which typically contain >100 ppm V (Hays et al., 2009; Moldanova et al., 2009). Puertollano is less polluted by V-rich emissions: the IGCC power plant in particular, although combusting petcoke and therefore a potential source of atmosphere V, is very clean (Font et al., 2009). Finally, the dominant fuel used by the ceramic industry in L'Alcora is natural gas, which has a negligible V content.

Comparing V concentrations with those of Ni (Table 2) we see that urban background levels measured at Bailén are again the highest, with average Ni content approaching 24 ng/m$^3$ (this exceeding the mean annual limit of 20 ng/m$^3$ established by the European Union, directive 2008/50/EC). This is also attributable directly to the chemistry of the locally combusted petcoke fuel, which typically contains >300 ppm Ni. Both this petcoke and background urban $PM_{10}$ and $PM_{2.5}$ have similar V/Ni values (5–6, Table 2), further implicating the petcoke fuel as the source of these metals. Such V/Ni values are much higher than those of natural geological materials such as the

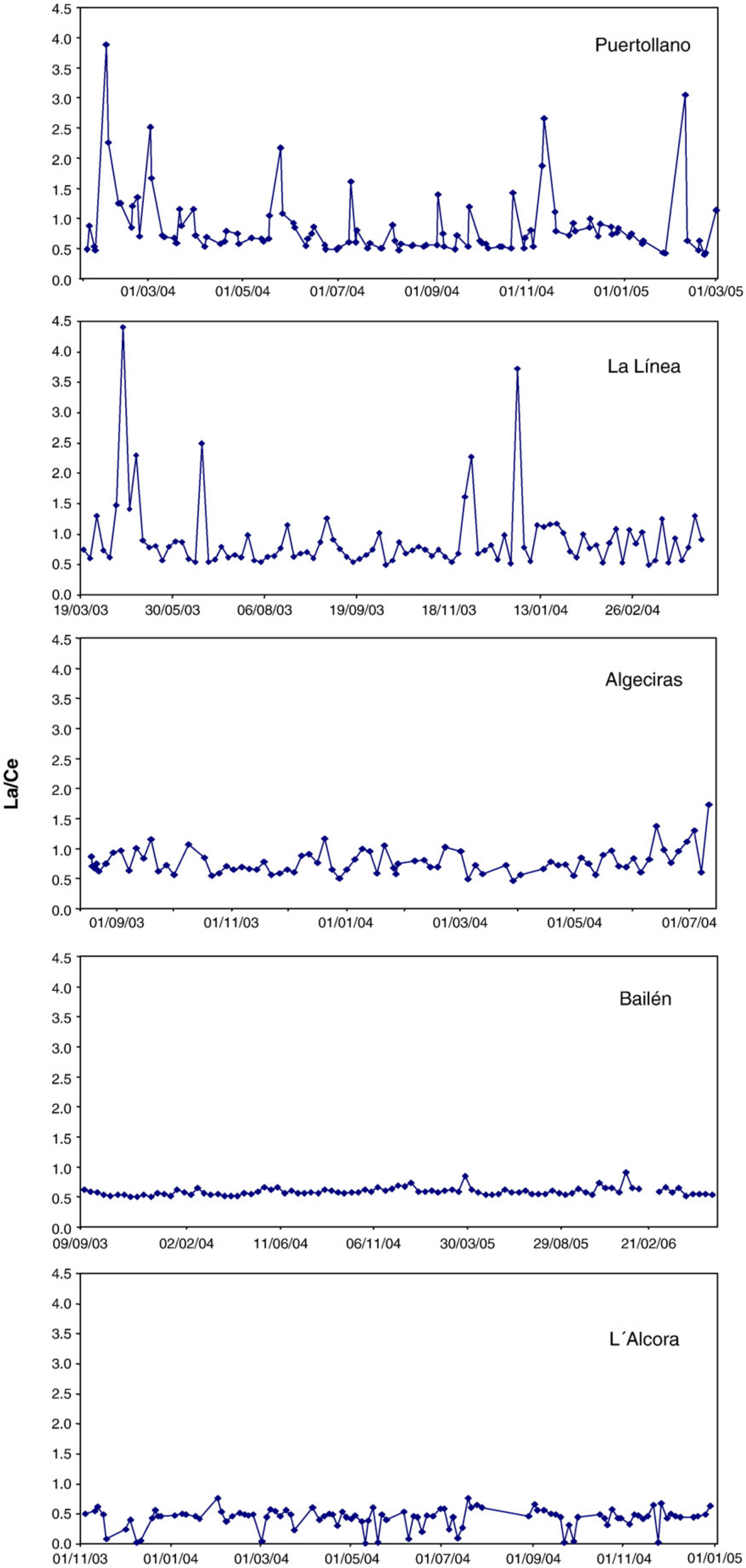

**Fig. 3.** Variations in La/Ce during sampling period for $PM_{10}$. Refinery contamination causes upward spikes whereas Ce-bearing ceramic emissions produce downward spikes (see text for details).

local clays quarried for the brick industry (V/Ni = 2–3, *Plan de Mejora de Calidad del Aire de Bailén*; Sánchez de la Campa et al., submitted).

There are also relatively high average Ni contents in the PM samples analysed at La Línea, which, at 20 ng/$m^3$ are only slightly below those registered at Bailén. However, a clear difference is that V/Ni levels at La Línea are anomalously low (<2: Table 2), indicating the presence of a specifically Ni-rich atmospheric pollution source. The obvious candidate for such a source is the large metallurgical plant lying upwind to the NW (Fig. 2). Given the meteorological conditions in the Bay of Algeciras mentioned earlier, much less of this metallurgical air pollution reaches the town of Algeciras itself, so that urban background Ni levels in both $PM_{10}$ and $PM_{2.5}$ drop to nearly half of those at La Línea (Table 2), and V/Ni consequently rises considerably above 2 (Table 1). As demonstrated in a recent atmospheric PM source apportionment study in the Bay of Algeciras by Pandolfi et al. (in press), the urban background V/Ni values at Algeciras and La Línea are highest on days when the winds are blowing from the east from shipping port and vessel routes to town. Filter samples collected during such days are characterised by V/Ni values of around 3 due to shipboard heavy fuel oil combustion which adds an estimated 4–5 µg/$m^3$ to daily urban background inhalable PM mass, much of which will be <2.5 µm in size ($PM_{2.5/10}$ = 0.89; Pandolfi et al., in press). The abundance of fine PM resulting from oil combustion appears to be characteristic of background PM across the entire Bay of Algeciras area, given the unusually high average $PM_{2.5/10}$ values of 0.82 for V at both the La Línea and Algeciras monitoring sites.

The different concentration signatures of V and Ni in urban background $PM_{10}$ are displayed in Fig. 4 ($PM_{2.5}$ not shown but follow the same patterns). Puertollano shows a strong positive correlation between these two metals, suggesting the presence of one major V–Ni source, with a slight preferential enrichment in V as compared to natural levels in average UCC. The data from La Línea, in contrast, demonstrate a clear upward scatter into Ni-enrichment due to the metallurgical plant emissions which can directly reach this site under westerly winds. The V/Ni pattern displayed by the Algeciras site is more mixed, demonstrating both a tendency towards a linear correlation (c.f. Puertollano) as well as the overprint of Ni-enrichment (c.f. La Línea), reflecting the mixed sources contaminating this area (shipping, power plant, petrochemical complex, metallurgical plant). The widest scatter of all five sites is exhibited by Bailén, with most data points recording exceptional V enrichment due to petcoke smoke. Finally, the L'Alcora data plot within a highly limited field which reflects low metal content and relative Ni enrichment, the latter being attributed to the use of this metal in calcinations of metalliferous raw materials during ceramic pigment preparation (Minguillón et al., 2007).

### 3.3. V/Rb v La/Ce

The Rb content of ambient PM is a useful surrogate for crustally-derived (i.e. natural) mineral particles, this being an element typically present in aluminous and potassic felsic silicates (notably K-feldspars, micas and clay minerals) lofted into the atmosphere from eroded rocks and soils. There are very few industrial applications for this element (Reimann and de Caritat, 1998), and, although abundantly present in the human body, it has no known negative health effects (Chemical Atlas of Europe, 2006). We can therefore use Rb to further demonstrate the departure of our industrially contaminated ambient PM samples from natural chemical compositions. Fig. 5 plots average $PM_{10}$ and $PM_{2.5}$ V/Rb values against those of La/Ce, and compares these with natural ratios typical of rocks and uncontaminated soils.

Several observations may be made concerning the geochemical variations between each of the industrially contaminated sites illustrated in Fig. 5. Firstly, the FCC refinery-related La-enrichment characteristic of Puertollano is more obvious in the finer ($PM_{2.5}$) fraction (Table 2; Fig. 5). Secondly, the same refinery signature also occurs at La Línea but is modified by higher V-enrichment, with this latter metal once again being preferentially concentrated within the $PM_{2.5}$. Thirdly, the Algeciras data show a similar V enrichment pattern to that at La Línea, reflecting the widespread effect of fuel oil combustion in the bay area, but, given the local wind directions, there is less refinery-related La-enrichment. Fourthly, while similarly enriched overall in V, the Bailén data show fractionation of neither V nor lanthanoid elements into the finer PM fraction, this presumably reflecting the very high levels of smoke which contributes most of the urban background PM mass ($PM_{2.5/10}$ = 0.93). Finally, the Ce-enrichment registered by the L'Alcora data places them to the left of

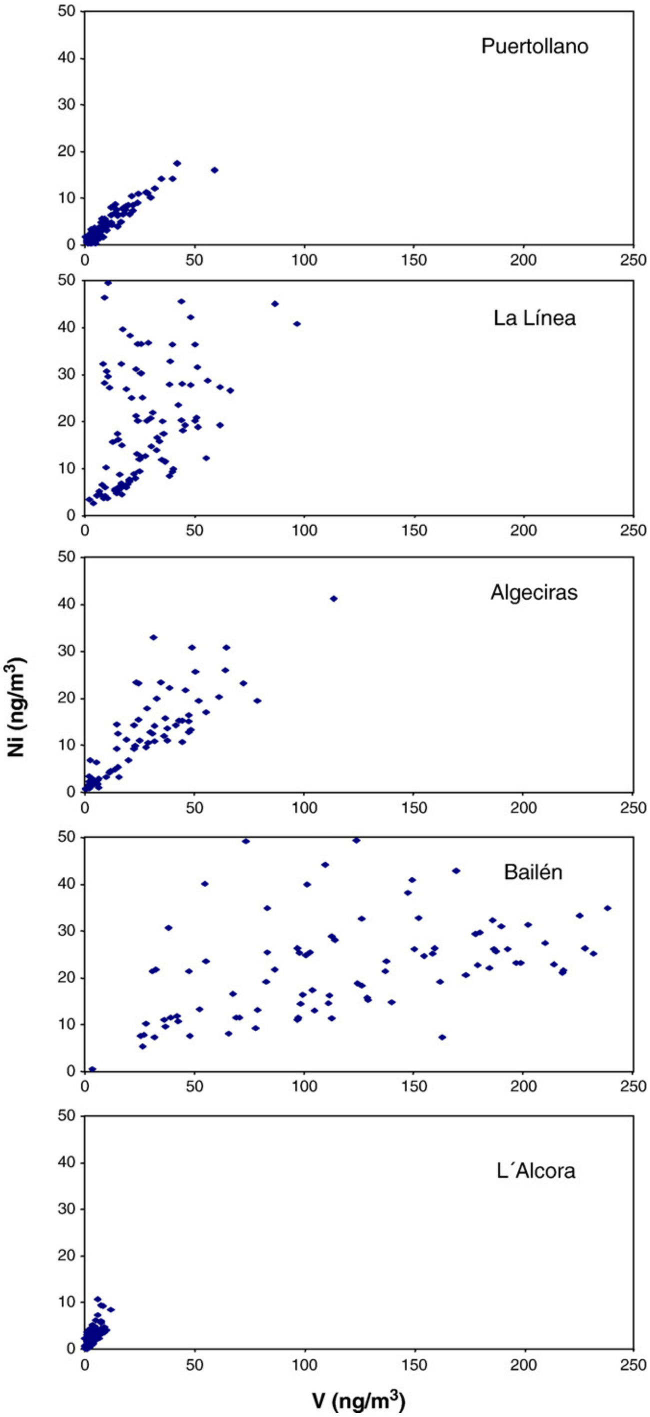

**Fig. 4.** Nickel v vanadium plot demonstrating variations between urban background monitoring stations (see text for details).

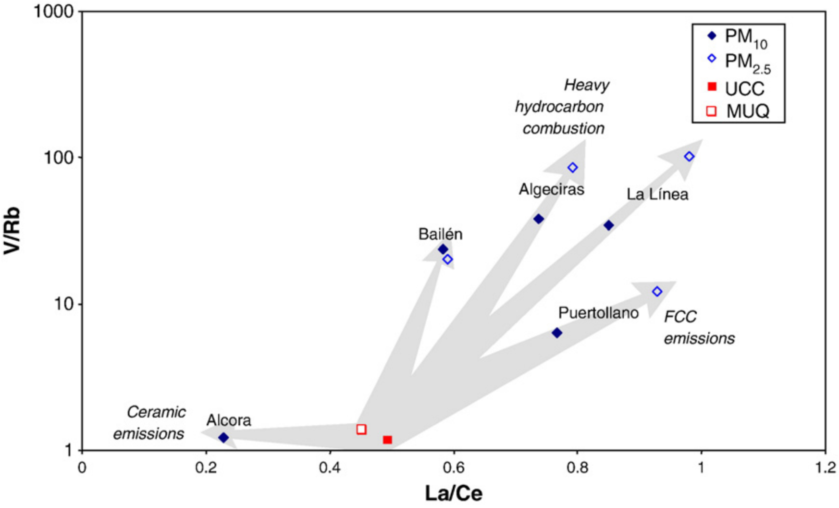

**Fig. 5.** Plot showing V/Rb v La/Ce and revealing contrasting patterns of La, Ce and V contamination (see text for details). Filled square = upper crustal compositions (UCC); open square = MUQ standard for unconsolidated argillaceous sedimentary rocks (Kamber et al., 2005).

natural compositions, and the lack of V-rich emissions at this site produces low V/Rb values more typical of crustal compositions than hydrocarbon combustion contamination.

## 4. Discussion and conclusions

The effect of FCC refinery emissions on atmospheric lanthanoid element chemistry can be further illustrated on three-component diagrams such as Fig. 6, which compares La, Ce and Sm concentrations at the five sites under examination. Triangular diagrams such as these are commonly used to illustrate compositional variations in lithospheric minerals and rocks, and, as we have demonstrated in previous publications, can equally usefully be employed to show geochemical patterns in atmospheric PM (e.g. Moreno et al., 2006; 2008a,b). In Fig. 6 we have adjusted the La and Sm values to place natural (i.e. geological) abundances of the three elements in the centre of the triangle (marked as a grey ellipse). Fluid catalytic converter refinery-contaminated PM, such as those recorded in Houston by Kulkarni et al. (2007) and at Dunkerque by Gaudry et al. (2008), deviate away from natural lanthanoid ratios towards the left vertex which represents 100% La. This FCC refinery pattern is displayed by our datasets from both Puertollano and La Línea, and can be contrasted with the unfractionated crustal lanthanoid chemistry of Bailén emissions, and the Ce-rich emissions recorded at L'Alcora (Fig. 6). For added comparison, and to demonstrate the geographic reach of the San Roque FCC refinery pollution plume, we include in Fig. 6 lanthanoid element compositions of three 24-hour filter samples of $PM_{10}$ collected onboard ship during a 2008 Mediterranean cruise westwards from Tunisia to Gibraltar (Moreno et al., 2010; Pérez et al., 2010). The first of these samples (C1) was collected off the Tunisian coast under westerly winds when the ship lay 1200 km east of Gibraltar and shows uncontaminated crustal La/Ce values (0.4). This ratio increases to 0.7 in the sample taken the next day (C2), off the Algerian coast 600 km further west, and reached 1.5 in the sample C3 collected as the ship reached Gibraltar. Although other refineries are present in the general area (e.g. Cartagena in Spain, Arzew in Algeria) these are relatively small and lack La-catalysed cracking facilities. We therefore attribute the progressive increase in La/Ce ratio recorded on this traverse across the SW Mediterranean to regional scale contamination from the Bay of Algeciras industrial and shipping pollution hotspot. The fact that such subtle chemical changes to the atmosphere can be detected over 600 km away from the pollution source emphasises the potency of using lanthanoid element ratios as anthropogenic pollution tracers.

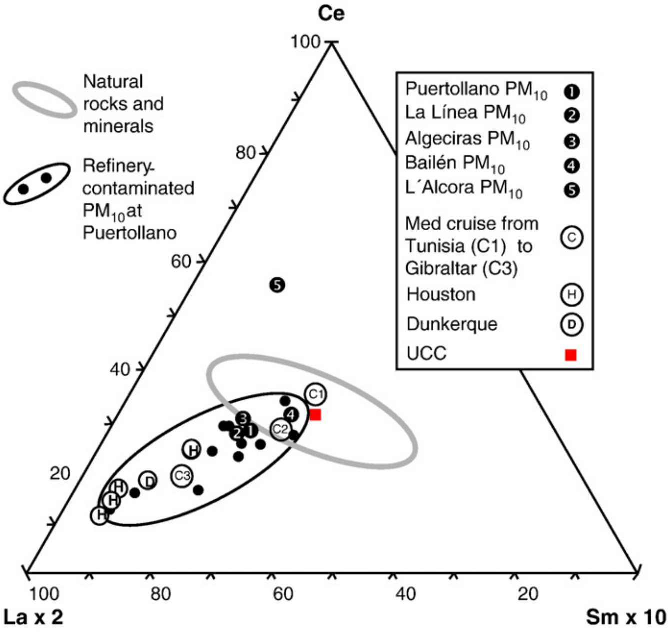

**Fig. 6.** Lanthanoid element ternary plot demonstrating the deviation away from crustal compositions (UCC) in refinery-contaminated (La-rich) and ceramic industry-contaminated (Ce-rich) aerosol samples. The grey oval represents crustal rocks and minerals (Moreno et al., 2008b) whereas the black oval includes samples contaminated by refineries. This includes individual samples from Houston (Kulkarni et al., 2006), Dunkerque (Gaudry et al., 2008), Puertollano and offshore from Gibraltar (Moreno et al., 2008b; 2010), as well as plots for averages from Puertollano, La Línea and Algeciras (see text for further details).

Compared to lanthanoid elements, the interpretation of V/Ni ratios as tracers for technogenic emissions is more complex. The average value for V/Ni in UCC is around 2 (Rudnick and Gao, 2004), with most sedimentary rocks and the finer fractions of soils exhibiting values confined within a range of 1–4. The natural mineral content of airborne particles derived from rocks and soils predictably shows V/Ni values within this range, with most of the content of these two metals residing in Fe oxides and oxyhydroxides, clay minerals and, in the case of Ni, detrital ferromagnesian silicates. Atmospheric intrusions of uncontaminated desert dust emanating from North Africa (NAF episodes), for example, typically show PM V/Ni values of 2–4, whether measured at sea level in the Mediterranean or Atlantic (Moreno et al., 2010; Pérez et al., 2010), or at Izaña meteorological observatory on Tenerife in the free troposphere (Alastuey et al., 2005). At regional background air monitoring sites across Europe the V/Ni value is normally lower, measuring 0.5–2.0 (Pey et al., 2009, and references therein).

The V and Ni contents (and the ratio between them) of crude oils are more variable than in most upper crustal rocks and minerals. These metals are present for the most part in the heavier asphaltene and (to a lesser extent) resin fractions of the crude oil, occurring as nickel and vanadyl porphyrins and non-porphyrins. Some oils (such as some Chinese deposits) are relatively rich in Ni and correspondingly have V/Ni values below 0.1, whereas in others (such as some North Sea and Venezuelan oils) the ratio can exceed 5.0 and in the most V-rich oil even reach 10 (Barwise, 1990; Speight, 1998). This variation in V/Ni is primarily controlled by the pH and Eh conditions present during the deposition of the source rock (Lewan, 1984). When these crude oils are refined, the residual heavy fuel oils and petcokes contain a similarly wide range in V/Ni values. The highest V/Ni values, typically ranging from 4–8, are characteristic of high sulphur residues such as the petcoke burnt at Bailén and the cheaper bunker oils commonly used as fuel by shipping on the open seas where harbour controls on sulphurous emissions do not apply. In less sulphurous petcoke and heavy oil fuels V/Ni values more typically lie within a range of V/Ni = 1–3 (Costa and Dreher, 1997; Bosco et al., 2005; Moldanova et al., 2009). Thus there is considerable overlap between V/Ni values in natural mineral dusts and those in emissions from the combustion of refinery-produced materials, and this hinders use of this ratio in pollution source identification. In exceptional cases, as we have demonstrated in Bailén and during easterly winds in Algeciras (Pandolfi et al., in press), a notable rise in V/Ni is clearly related to petcoke/fuel oil combustion. Conversely, a prominent source of Ni contamination, such as the steel plant NW of La Línea, will produce an anomalously low V/Ni value when it lies upwind of the monitoring station. However, away from such obvious proximal sources, V/Ni in background PM will be less useful in differentiating between technogenic contamination and the presence of V + Ni-bearing rock forming minerals.

An overview of the differences between the V, Ni and La content of aerosols collected at the 5 sites discussed in this paper is provided in Fig. 7. We use this plot to contrast crustal emissions, which lie towards the La vertex, with those more strongly influenced by V-rich hydrocarbon combustion. Thus Fig. 7 plots the compositions of natural “geological” surface and atmospheric materials (represented by UCC, MUQ, and average $PM_{10}$ at the free troposphere site of Izaña in the Canary Islands) versus those of petcoke, fuel oil and residual oil fly ash (ROFA) (Obrusník et al., 1989, Alastuey et al., 2005, Bosco et al., 2005; Moldonova et al., 2009; Hays et al., 2009). The data from the 5 Spanish sites are represented both as averages and as ellipsoidal fields within which plot at least 85% of the individual datapoints (Fig. 7). The Puertollano field defines a trend which includes both UCC and FCC-contaminated fuel oil compositions, indicating the mixed PM contributions from crustal and anthropogenic sources at this locality (Moreno et al., 2008b). In contrast, the trend displayed by data from La Línea reflects the importance of fuel oil combustion and metalliferous steel plant emissions to background $PM_{10}$ chemistry at this site. Note that in both of these fields the low mass of FCC La emissions results in a negligible effect as compared to crustal contributions: in atmospheric PM it is the crustal aerosols which account for most of the lanthanoid content and usually only La/Ce will reveal the refinery influence. Most of the data within the Algeciras field lie close to the V–Ni line, although there is considerable scatter which reflects the mixed provenance of background PM in the Bay of Algeciras (Pandolfi

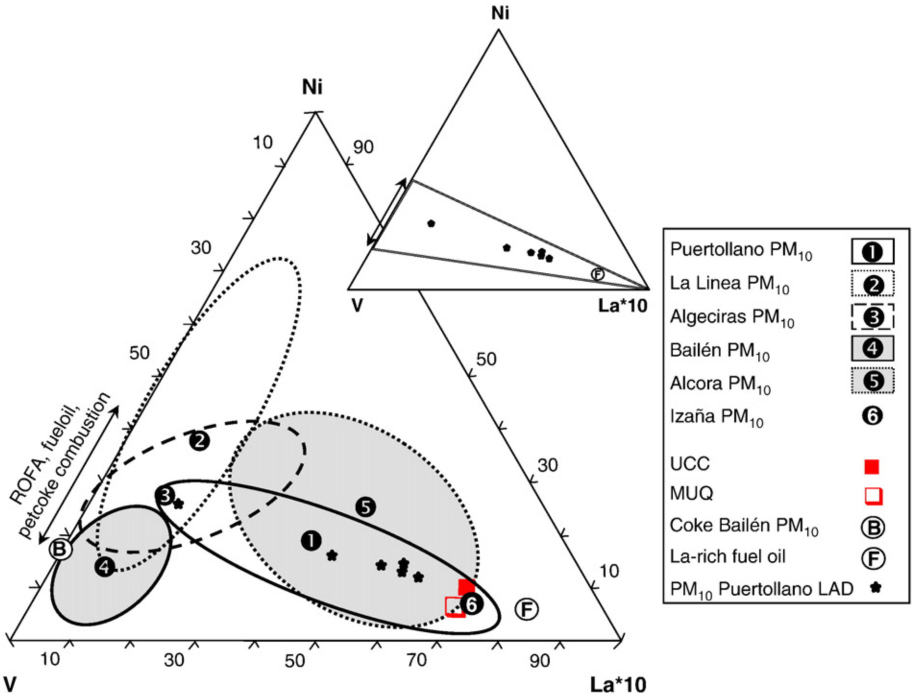

**Fig. 7.** Ternary plot comparing Ni, V and La (×10) compositional fields for each of the five monitoring stations. Uncontaminated crustal compositions (UCC) are represented by upper continental crust (filled square), MUQ standard for unconsolidated argillaceous rocks (MUQ: Kamber et al., 2005), and ambient concentrations at Izaña Astronomical Observatory, Tenerife (Alastuey et al., 2005). Averages for each site are shown as numbered circles. Compositional range for V/Ni in most oil refinery petcokes, fuel oils and their fly ashes (ROFA), as well as the composition of the petcoke combusted at Bailén (B), are also shown (see text for further discussion). The smaller triangle (with inner sub-triangle) plots compositions of samples collected during La-contaminated days (LAD) at Puertollano, and the La-contaminated fuel oil analysis published by Hays et al. (2008). Atmospheric PM enriched in FCC refinery La and/or V and Ni from fuel oil/petcoke combustion will plot within the sub-triangle.

et al., in press). The Bailén field is the most V-rich, reflecting the dominance of emissions from petcoke combustion, whereas the L'Alcora data scatter across a broadly defined field which ranges from crustal to more anthropogenically contaminated metal compositions (Fig. 7).

One of the primary objectives of this paper is to illustrate the considerable chemical variation in urban background air in different towns and cities, using V, Ni and lanthanoid elements as markers for technogenic emissions. We view our approach of geochemical characterisation of urban background PM as complimentary to the physical monitoring and interpretation of aerosols more widely employed in urban areas. In its widest sense, PM mass concentration ($\mu g/m^3$) can be considered as a human health biomarker, representing a precursor stressor linked to potential inflammation and oxidative stress after inhalation (Risom et al., 2005). Thus one may reasonably predict that in 2004–5 the population of Bailén suffered an above average risk of illness resulting from atmospheric pollution, given the high average mass levels (67 $\mu g/m^3$ $PM_{10}$). However, when average annual PM levels in industrialised areas are not anomalously high, as is the case at Puertollano, La Línea and Algeciras (38–43 $\mu g/m^3$ $PM_{10}$) measurement of mass alone is not enough to discern differences in air pollution-related health effects between different towns. The Bay of Algeciras area, for example, is known to be relatively unhealthy, with epidemiologically proven enhanced general mortality and premature mortality in both males and females (Benach et al., 2003; Cruz Rojo and Almisas, 2009). If this increased health risk is linked to air pollution, then it is the specific chemistry of background PM, rather than mass, which is likely to be the problem.

Trace metals are especially valuable as a surrogate for mapping variations in atmospheric chemistry not least because many of them are themselves of environmental concern (e.g. Adamson et al., 2000; Pope et al., 2002; Schaumann et al., 2004; Nawrot et al., 2006). With regard to the metals under review in this paper, both V and Ni released in particulate form during hydrocarbon combustion are well known to induce toxicological effects, both separately and synergistically (Campen et al., 2001; Ghio et al., 2002; Lippmann et al., 2006). Both these metals appear in the priority list of hazardous substances published by the U.S. Agency for Toxic Substances and Disease Registry (ATSDR), and although Ni emissions are regulated legislatively this is not the case for V. Lanthanoid elements, in contrast, are not normally considered as potentially toxic exposure (Hirano and Suzuki 1996), although concern has been raised over bioaccumulation in the food chain (e.g. Chua, 1998), and there are as yet no data on possible effects of chronic inhalation such as lifelong inhalation of La-rich FCC emissions in urban background aerosols.

We view the technogenic mobilisation of metals in the atmosphere, displayed *par excellence* by V, Ni and the lanthanoid elements, not only as an important process in the global recycling of trace elements (Nriagu and Pacyna, 1988; Wang et al., 2006) but also as having a more local dimension. Point source emission of these industrial pollutants takes place on a scale large enough to alter the atmospheric chemistry over whole towns and cities. These various cocktails of metalliferous aerosols are typically extremely fine in size and therefore potentially bioavailable, making a clear case for basing urban background PM characterisation not only on physical parameters such as mass but also on sample chemistry and with special emphasis on trace metal content.

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**Attachment 43**

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# Ultrafine particle and fine trace metal (As, Cd, Cu, Pb and Zn) pollution episodes induced by industrial emissions in Huelva, SW Spain

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## HIGHLIGHTS

- ► We studied how industrial emissions contribute to ultrafine particles (UP).
- ► Traffic and industrial UP episodes are identified from the relation of UP and $PM_{2.5}$.
- ► Road traffic emissions, in the morning rush hours, are associated with OM and BC.
- ► Industrial plumes, during daylight, are related with heavy metals.
- ► Industrial emissions are the first cause of high UP in Huelva city.

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## ABSTRACT

Urban air quality impairment by ultrafine particles has become a matter of concern due to the adverse effects on human health. Most of the studies of ultrafine particles in urban air quality have focused on vehicle exhaust emissions. We studied how industrial emissions contribute to ultrafine particle concentrations in downwind urban ambient air. This research is based on experimental data collected in the ambient air of the industrial city of Huelva (SW Spain) over April 2008–December 2009 period (particle number, gaseous pollutants and black carbon concentrations and levels and chemical composition of $PM_{10}$ and $PM_{2.5}$ with daily and hourly resolution). This city is affected by emissions from the second largest Cu-smelter in Europe, phosphoric acid and fertilizer production plants and an oil refinery and petrochemical plant. Industrial emissions are the main cause of ultrafine particle episodes. When vehicle exhaust emissions are the main source, ultrafine particles typically show (24-h mean) concentrations within the range 14,700–5000 $cm^{-3}$ (50th–1st), with 60% of these linked to this source and 30% to industrial emissions. In contrast, when daily mean levels of N are within the range 50,000–25,500 $cm^{-3}$ (100th–70th), industrial and vehicle exhaust emissions accounted for 49 and 30%, respectively. High concentrations of toxic trace metals (As, Cu, Cd, Zn and Pb) were recorded when the study city suffered fumigations of the Cu-smelter plumes (e.g. 10–25 ng $m^{-3}$ As, 1–2 ng $m^{-3}$ Cd and $>10^5$ $cm^{-3}$ of ultrafine particles). Because of these industrial emissions, ultrafine particle concentrations during daylight are about two times higher than those observed in other European cities. Recently, ultrafine particle emissions in vehicle exhausts have been subject to limit values in a recent stage of the EURO standards. Industrial emissions should also be considered.

## 1. Introduction

Epidemiological studies performed during recent decades have shown that in urban areas there is a relationship between the mass concentration of particles smaller than 10 and 2.5 μm aerodynamic

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diameter ($PM_{10}$ and $PM_{2.5}$, respectively) and cardiovascular and respiratory morbidity (WHO, 2005). Because of this, standards for $PM_{10}$ and $PM_{2.5}$ have been set in many countries. More recent studies reveal that some of the cardiovascular effects attributed to exposure to $PM_{2.5}$ may be due to ultrafine particles (diameter smaller than 0.1 μm; Araujo & Nel, 2009). Ultrafine particles typically account for 80–90% of the total number concentrations and for <10% of the $PM_{2.5}$ particle mass concentration (Putaud et al., 2010 and references therein). Most of the $PM_{2.5}$ mass concentrations (≥90%) occur in the accumulation mode (0.1–1 μm). As a consequence ultrafine particles are not properly monitored using $PM_{10}$ and $PM_{2.5}$ as air quality assessment metrics. The total number concentration of particles coarser than a given size (usually 2 or 10 nanometres) has been used as a metric representative of ultrafine particles (e.g. Puustinen et al., 2007). Size-resolved measurements have been used to study the sources and processes contributing to ultrafine particles (e.g. Casati et al., 2007). The correlation between particle number and $PM_{2.5}$ concentrations in urban ambient air is rather weak (Putaud et al., 2010). In urban areas it has been observed that organic matter and elemental carbon are the only two $PM_{2.5}$ components that may significantly correlate with the particle number, with this being attributed to vehicle exhaust emissions (Rodríguez et al., 2007). Because of the concern linked to ultrafine particle ambient air pollution, standards for particle number emissions have been set in EURO-5b (Regulation 692/2008).

Although biogenic SOA emissions may in general contribute to ultrafine and organic carbon concentrations, the high correlation between OC and BC in the study area points to anthropogenic emissions (industrial plus vehicle exhaust emissions) as dominant source. Particles emitted by this source tend to be bimodal, exhibiting a nucleation mode (<30 nm), constituted by sulphuric acid droplets that may be covered by condensed hydrocarbons, and a soot mode (50–200 nm; Kittelson, 1998). The formation rate of the nucleation mode particles is significantly influenced by ambient air conditions (e.g. wind speed, temperature and humidity; Casati et al., 2007). The soot mode is constituted by light-absorbing elemental carbon, primary organic carbon, condensed metals and sulphates and some carcinogenic organic pollutants (e.g. polycyclic aromatic hydrocarbons; Morawska and Zhang, 2002).

Up to the present date, modest attention has been paid to other potential major anthropogenic sources of ultrafine particles, even though it is well known that some activities may release large amounts of gaseous precursors. This is the case of some industrial activities that release large amounts of $SO_2$ and/or hydrocarbons. Sulphuric acid plays a key role in nucleation and new particle formation processes (Kulmala et al., 2004). These emissions result in gas-to-particle conversion processes that may prompt ultrafine and accumulation mode (0.1–1 μm) particle pollution. Nucleation of sulphur gases followed by particle growth by condensation and/or coagulation may result in the formation of ultrafine and fine particles and both (especially the latter) result in $PM_{2.5}$ pollution. These particles may be externally or internally mixed with trace elements linked to industrial emissions.

The development of techniques or methods for identifying the sources contributing to ultrafine particles is a major challenge in urban air quality nowadays. Several attempts have been made, by studying the relationship between particle number and $PM_{2.5}$ composition (Pey et al., 2009), by performing speciation of organic compounds (Kleeman et al., 2009) and by using the relationship between black carbon and particle number with a high time resolution (Rodríguez and Cuevas, 2007).

In this study we focused on identifying the sources and processes contributing to the number concentration of particles coarser than 2.5 nm in an urban area affected by industrial emissions. Different methods were used. Particle number concentrations were analysed using: 1) 1-h data of black carbon, trace gases and meteorological parameters measured over two years, 2) 1-h resolution data of $PM_{2.5}$ elemental composition, and 3) receptor-modelling techniques based on 2-years' data of 24-h average $PM_{2.5}$ chemical composition. Results show that the contribution of industrial emissions to ultrafine particles in the urban ambient air of industrial cities is comparable to that of vehicle exhausts.

## 2. Methodology

### 2.1. Study area

The study city (Huelva; 37°15′0″N, 6°57′0″W, 54 m.a.s.l) is located in SW Spain (Fig. 1). Air pollutants are mostly emitted by vehicle exhausts and by industrial activities in two estates to the south of Huelva: Punta del Sebo and Nuevo Puerto (Fig. 1). The second largest Cu-smelter factory in Europe (which emits $SO_2$, $H_2SO_4$, As, Sb, Pb, Zn and Sn) and a fertilizer and phosphoric acid production plant (which emits $NH_4^+$ and Na phosphate, phosphoric acid, sulphuric acid and sodium silicate) are located in Punta del Sebo. A crude oil refinery and a petrochemical complex (which

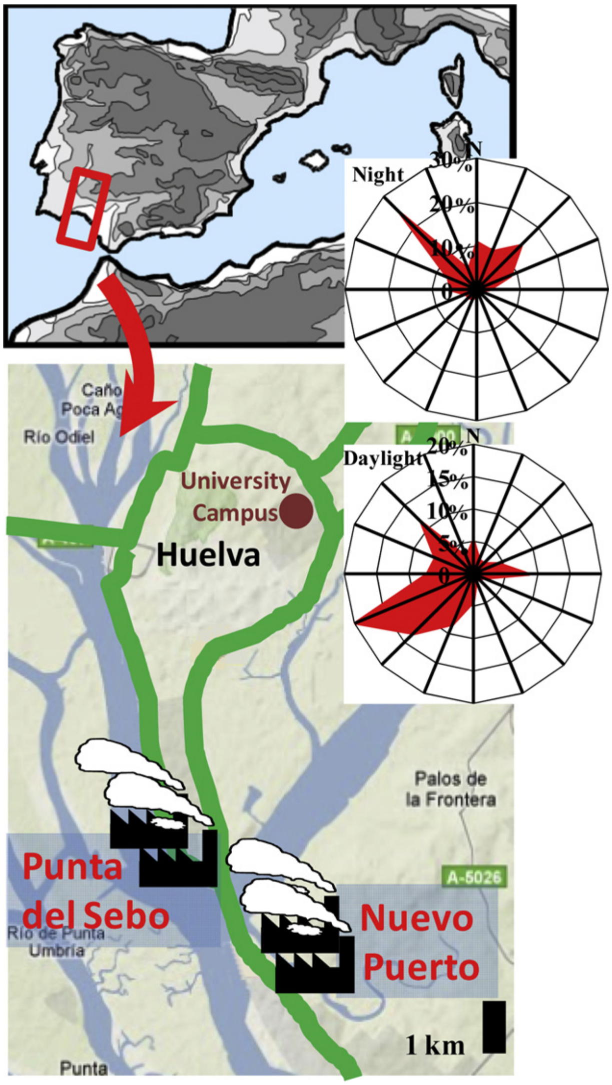

**Fig. 1.** Map of Huelva. Green lines indicate main roads and motorways around Huelva city. Punta del Sebo and Nuevo Puerto Industrial Estates and the University Campus measurement site are highlighted. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

emits $SO_2$, $NO_x$, $NH_3$, Ni, V and a wide variety of hydrocarbons) are to be found in Nuevo Puerto. Pollutants emitted by these industries are described in previous works (De la Rosa et al., 2010; Fernández-Camacho et al., 2010a; Sánchez de la Campa et al., 2011) and in the European Pollution and Emission Register (http://eper.ec.europa.eu/eper/). These industrial emissions can reach the city of Huelva on the southerly winds episodically linked to specific synoptic conditions or on an almost daily basis linked to the development of coastal breezes during daylight (Castell et al., 2010).

## 2.2. Experimental data

Concentrations of gaseous pollutants and levels and composition of atmospheric particulate matter were monitored in an urban background station (37°16′13.1″, 6°55′30.9″ m.a.s.l) located at the University Campus on the northern side of the city. The site is situated about 7 km from Punta del Sebo Estate and about 14 km from Nuevo Puerto Estate. Moreover, two entry roads to the city are located about 500 m to the west and about 1000 m to the east of the measurement site. The measurements used for this study were collected from April 2008 to December 2009.

### 2.2.1. Particle number, black carbon, $PM_{10}$ and $PM_{2.5}$ concentrations

Details of the experimental methods have been presented by Fernández-Camacho et al. (2010b). Thus a brief summary is performed here. The particle number (PN) was monitored using a TSI™ 3776 model Ultrafine Condensation Particle Counter (UCPC). The instrument records data averaged at 1-min intervals and detects particles coarser than 2.5 nanometres (nm) operating in high-flow mode (1.5 $l\ m^{-1}$). Because 80–90% of particles in urban air are <0.1 μm, PN is considered representative of ultrafine particle number concentration. Black carbon (BC) concentration was monitored using a Thermo™ Carusso model 5012 Multi-Angle Absorption Photometer (MAAP). BC concentrations were calculated using a mass-specific attenuation cross-section equal to 10.31 $m^2\ g^{-1}$ (Fernández-Camacho et al., 2010b). Instruments were intercompared before the measurement campaign and calibrated for airflow on a weekly basis using a Gilibrator™ bubble-flow meter. Data availability was 90% for BC and 70% for particle number.

$PM_{10}$ and $PM_{2.5}$ were sampled (24-h) using EU reference methods: a Graseby Andersen™ sampler (68 $m^3\ h^{-1}$, EN-12341) for $PM_{10}$ and a MCV™ (30 $m^3\ h^{-1}$, EN-14907) for $PM_{2.5}$. The sampling frequency was 1 sampling day (00:00–00:00 GMT) every four days in 2008 and every eight days in 2009. MUNKELL™ microquartz fibre filters were used. Filters were conditioned at 20 °C and 25% RH before weighting previous and after sampling. Blank field filters were also used.

Hourly levels of $PM_{10}$ and $PM_{2.5}$ were monitored using a GRIMM™ optical particle counter. Their concentrations were converted to the gravimetric equivalent by comparing with the EU (gravimetric) reference method using the EU standardized method (EC Working Group on Particle Matter report, 2002).

### 2.2.2. Gaseous pollutants, meteorology and road traffic data

Concentrations of gaseous pollutants ($SO_2$, $NO_x$ and $O_3$) were monitored with 1-h resolution using the reference methods of the European air quality directives (2008b/50/EC). Meteorological parameters (wind speed and direction, temperature, relative humidity, pressure and global radiation), monitored in a station less than 2 km away managed by the Meteorological State Agency (AEMET), and road traffic intensity data (number of vehicles·$h^{-1}$), recorded on the two roads close to the measurement site, were also used. These data were obtained during 2008 and 2009 with 1-h resolution.

### 2.2.3. Bulk chemical composition of particles: 24-h resolution

Samples of $PM_{10}$ and $PM_{2.5}$ collected on the microquartz fibre filters were chemically analysed using the method of Querol et al. (2008). This method includes ICP-OES and ICP-MS for elemental composition, Ion Chromatography for ions ($SO_4{}^{2-}$, $NO_3{}^{-}$, $Cl^-$ and $NH_4{}^{+}$) and the LECO SC-144 DR instrument for total carbon. Average precision and accuracy are within the range of 3–10% for most elements and compounds. Silica and carbonate were estimated by stoichiometry using the Ca, Mg and Al data (Querol et al., 2001).

A set of 62 samples of $PM_{10}$ and 59 samples of $PM_{2.5}$ were selected for the analysis of organic carbon (OC) and elemental carbon (EC), using the Thermo Optical Transmittance technique (Birch and Cary, 1996) and a Sunset Laboratory™ instrument with the default temperature steps of the EUSAAR2 program. The filters were selected in a homogeneous way, covering a representative range of concentrations of the area of study during the four seasons. The EC data were used to determine the mass-specific attenuation cross-section by comparison with the absorption coefficient measured by the MAAP. Then, mean black carbon (BC) concentrations were determined for each $PM_{10}$ and $PM_{2.5}$ sample. To determine the BC load in $PM_{2.5}$, the mean ratio of BC in $PM_{2.5}$/BC in $PM_{10}$ was used. A mass-absorption efficiency of 10.31 ± 0.25 $m^2\ g^{-1}$ and a mean BC in $PM_{2.5}$/BC in $PM_{10}$ ratio equal to 0.74 ± 0.025 was obtained (see details in Fernández-Camacho et al., 2010b). Then, the organic carbon in each $PM_{10}$ and $PM_{2.5}$ sample was determined as the difference between TC and BC. Finally, the organic matter was estimated by multiplying OC concentrations by 1.8 to take the contribution of other atoms into account (Turpin and Lim, 2001).

A total of 136 samples of $PM_{10}$ and 134 samples of $PM_{2.5}$ collected from April 2008 to December 2009 were analysed using this method (Table 1).

### 2.2.4. Elemental composition of particles: 1-h resolution

A ‘streaker’ sampler (PIXE International Corporation) was employed to collect samples of fine (<2.5 μm aerodynamic diameter) and coarse (2.5–10 μm) particles with one hour resolution (D’Alessandro et al., 2003). A paraffin-coated kapton foil was used as an impaction surface for coarse particles and a Nuclepore filter as a fine particle collector. Elemental composition was determined by PIXE in the LABEC laboratory at INFN in Florence (Italy): Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Sr and Pb as trace elements and Na, Mg, Al, Si, P, S, Cl, K and Ca as major elements. Concentration uncertainties were around 5%. Detection limits were about 10 ng $m^{-3}$ for low-Z elements and 1 ng $m^{-3}$ (or below) for medium-high Z elements. (Chiari et al., 2006). The sampling was performed from 15th to 22nd October 2009.

## 2.3. Data treatment

### 2.3.1. Components of ultrafine particles

In order to identify the sources and processes that contribute to the particle number concentrations, PN was split into two components (Rodríguez and Cuevas, 2007):

$$PN1 = S1 \cdot BC \qquad (1)$$

$$PN2 = PN - PN1 \qquad (2)$$

where $S1 = 6.9\ 10^6$ particlesng$^{-1}$ BC is the minimum slope observed in the PN vs BC plot in our measurement site and represents the minimum number of particles formed/emitted per nanogram of BC emitted by vehicle exhausts (Fig. 2).

In cities where black carbon is dominated by vehicle exhaust emissions, this method allows to segregate the contribution of this source from that of other sources to the ultrafine particle

**Table 1**
Mean chemical composition of $PM_{10}$ and $PM_{2.5}$ in Huelva from April 2008 to December 2009. NS: number of samples. OM: organic matter. SIC: secondary inorganic compounds.

| NS | $PM_{10}$ | | $PM_{2.5}$ | | $PM_{2.5-10}$ | |
|---|---|---|---|---|---|---|
| | 136 | | 134 | | 134 | |
| | $\mu g\ m^{-3}$ | % | $\mu g\ m^{-3}$ | % | $\mu g\ m^{-3}$ | % |
| PM | 32.7 ± 13.0 | | 19.3 ± 10.6 | | 13.4 ± 8.0 | |
| OM | 5.8 ± 3.6 | 18 | 5.8 ± 3.6 | 30 | 0.0 ± 1.9 | 0 |
| BC | 0.8 ± 0.4 | 2 | 0.6 ± 0.4 | 3 | 0.2 ± 0.2 | 2 |
| nss-$SO_4^{2-}$ | 3.0 ± 2.0 | 9 | 2.7 ± 1.6 | 14 | 0.3 ± 0.6 | 2 |
| $NO_3^-$ | 2.6 ± 1.7 | 8 | 1.0 ± 1.1 | 5 | 1.6 ± 1.2 | 12 |
| $NH_4^+$ | 0.8 ± 0.6 | 3 | 0.8 ± 0.7 | 4 | 0.0 ± 0.6 | 0 |
| Na | 1.3 ± 1.0 | 4 | 0.5 ± 0.3 | 3 | 0.8 ± 0.6 | 6 |
| $Cl^-$ | 1.2 ± 1.4 | 4 | 0.2 ± 0.4 | 1 | 1.0 ± 1.1 | 7 |
| ss-$SO_4^{2-}$ | 0.3 ± 0.2 | 1 | 0.1 ± 0.1 | 1 | 0.2 ± 0.2 | 1 |
| $CO_3^{=}$ | 2.2 ± 1.2 | 7 | 0.8 ± 0.4 | 4 | 1.5 ± 1.0 | 11 |
| $SiO_2$ | 4.6 ± 2.7 | 14 | 1.3 ± 0.8 | 6 | 3.3 ± 2.3 | 25 |
| $Al_2O_3$ | 1.5 ± 0.9 | 5 | 0.4 ± 0.3 | 2 | 1.1 ± 0.8 | 8 |
| Ca | 1.0 ± 0.6 | 3 | 0.4 ± 0.2 | 2 | 0.7 ± 0.6 | 5 |
| K | 0.4 ± 0.2 | 1 | 0.2 ± 0.2 | 1 | 0.2 ± 0.1 | 1 |
| Mg | 0.3 ± 0.1 | 1 | 0.1 ± 0.1 | 0 | 0.2 ± 0.1 | 1 |
| Fe | 0.6 ± 0.3 | 2 | 0.2 ± 0.1 | 1 | 0.4 ± 0.3 | 3 |
| $PO_4^{3-}$ | 0.2 ± 0.2 | 1 | 0.1 ± 0.1 | 0 | 0.1 ± 0.2 | 1 |
| | $ng\ m^{-3}$ | ‰ | $ng\ m^{-3}$ | ‰ | $ng\ m^{-3}$ | ‰ |
| Ti | 46.5 ± 30.1 | 1.4 | 17.8 ± 29.9 | 0.9 | 28.7 ± 25.0 | 2.1 |
| V | 5.3 ± 4.2 | 0.2 | 3.4 ± 3.2 | 0.2 | 1.9 ± 1.5 | 0.1 |
| Cr | 2.3 ± 2.0 | 0.1 | 1.6 ± 4.4 | 0.1 | 0.7 ± 1.8 | 0.1 |
| Mn | 9.6 ± 5.2 | 0.3 | 4.0 ± 2.0 | 0.2 | 5.6 ± 3.7 | 0.4 |
| Co | 0.3 ± 0.2 | <0.1 | 0.2 ± 0.1 | <0.1 | 0.1 ± 0.3 | <0.1 |
| Ni | 3.7 ± 2.8 | 0.1 | 2.3 ± 1.7 | 0.1 | 1.4 ± 2.0 | 0.1 |
| Cu | 45.3 ± 30.2 | 1.4 | 31.2 ± 20.4 | 1.6 | 14.1 ± 17.5 | 1.1 |
| Zn | 47.4 ± 42.9 | 1.4 | 37.3 ± 49.5 | 1.9 | 10.1 ± 40.4 | 0.8 |
| As | 6.2 ± 7.8 | 0.2 | 5.1 ± 7.6 | 0.3 | 1.1 ± 4.1 | 0.1 |
| Se | 2.1 ± 2.8 | 0.1 | 1.7 ± 2.8 | 0.1 | 0.4 ± 1.6 | <0.1 |
| Rb | 1.2 ± 0.7 | <0.1 | 0.4 ± 0.4 | <0.1 | 0.8 ± 0.5 | 0.1 |
| Sr | 6.2 ± 2.5 | 0.2 | 1.3 ± 0.7 | 0.1 | 4.9 ± 1.3 | 0.4 |
| Mo | 12.2 ± 1.6 | 0.4 | 0.7 ± 0.9 | <0.1 | 11.5 ± 1.9 | 0.9 |
| Cd | 0.7 ± 0.9 | 0.0 | 0.6 ± 1.0 | <0.1 | 0.1 ± 0.6 | <0.1 |
| Sn | 2.6 ± 2.0 | 0.1 | 1.5 ± 1.3 | 0.1 | 1.1 ± 0.8 | 0.1 |
| Sb | 1.6 ± 0.9 | <0.1 | 0.8 ± 0.6 | <0.1 | 0.8 ± 0.5 | 0.1 |
| Ba | 31.9 ± 48.4 | 1.0 | 19.7 ± 36.7 | 1.0 | 12.2 ± 57.2 | 0.9 |
| Pb | 14.4 ± 15.2 | 0.4 | 10.8 ± 14.3 | 0.6 | 3.6 ± 4.3 | 0.3 |
| Bi | 0.9 ± 1.1 | <0.1 | 0.8 ± 1.0 | <0.1 | 0.1 ± 0.5 | <0.1 |
| | $\mu g\ m^{-3}$ | % | $\mu g\ m^{-3}$ | % | $\mu g\ m^{-3}$ | % |
| PM | 32.7 ± 13.0 | | 19.3 ± 10.6 | | 13.4 ± 8.0 | |
| $\sum$ chemistry | 26.9 ± 5.5 | 82.1 | 15.2 ± 3.3 | 78.5 | 11.7 ± 2.3 | 87.3 |
| SIC | 6.4 ± 1.2 | 19.6 | 4.5 ± 1.0 | 23.4 | 1.9 ± 0.8 | 14.2 |
| OM | 5.8 ± 3.6 | 17.8 | 5.8 ± 3.6 | 30.0 | 0.0 ± 1.9 | 0.2 |
| BC | 0.8 ± 0.4 | 2.5 | 0.6 ± 0.4 | 3.1 | 0.2 ± 0.2 | 1.5 |
| Mineral dust | 10.8 ± 1.4 | 32.9 | 3.3 ± 0.4 | 17.0 | 7.5 ± 1.0 | 55.9 |
| Marine | 2.9 ± 0.5 | 8.7 | 0.9 ± 0.2 | 4.4 | 2.0 ± 0.4 | 15.0 |

concentrations. PN1 accounts for the minimum primary emissions of vehicle exhausts and is constituted by the previously described soot mode (light-absorbing elemental carbon, carbonaceous material, trace metals, etc.) and those components nucleating and condensing immediately after emission (e.g. sulphates, condensed hydrocarbons and unburned oil). PN2 accounts for those particles resulting from enhancement in new particle formation processes in several contexts: during the dilution and cooling of vehicle exhausts or in ambient air linked to photochemical processes and/or in gas-to-particle conversion processes in precursor plumes. This method has successfully been applied in European cities (Reche et al., 2011).

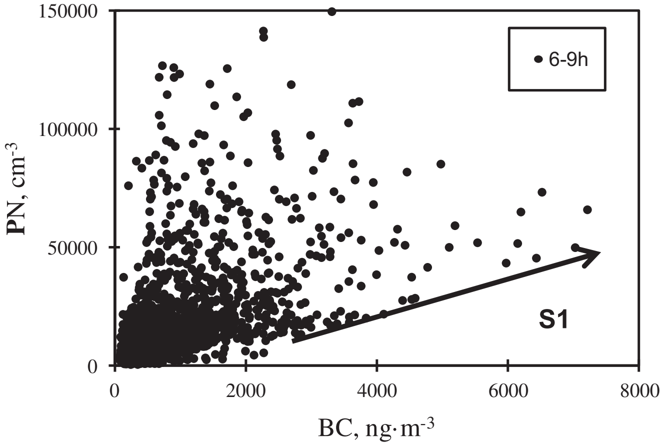

**Fig. 2.** Hourly average values of the particle number (PN) versus black carbon (BC) concentrations between 06:00 and 09:00 h. S1 indicates the line of minimum slope which contains N-vs.-BC data.

### 2.3.2. Source apportionment

The sources that contribute to particle concentration were identified by performing Principal Component Analysis (PCA) followed by varimax rotation. Because the results of the PCA depend on the data set analysed, several combinations of variables were tested. The contribution of each source was quantified by Multi-Linear Regression Analysis (Thurston and Spengler, 1985). The sources contributing to particle number were identified using the number concentration and $PM_{2.5}$ composition data. For $PM_{10}$, $PM_{2.5}$ and $PM_{2.5-10}$, bulk levels and composition data were analysed. Saharan events were excluded from the database in order to prevent the influence of external sources of sulphate, nitrate and other pollutants mixed with dust (Rodríguez et al., 2011).

## 3. Results and discussion

### 3.1. Chemical composition of particles

The mean chemical composition of $PM_{10}$ and $PM_{2.5}$ is shown in Table 1. An average value equal to 32.7 ± 13 μg $PM_{10}$ $m^{-3}$ and 19.3 ± 11 μg $PM_{2.5}$ $m^{-3}$ was observed. The most important contributors to $PM_{2.5}$ were secondary inorganic compounds (sulphate, nitrate and ammonium) and organic matter, which accounted for 23% and 30% of $PM_{2.5}$, respectively. The sulphate load was large, accounting for 14% of $PM_{2.5}$. Because these compounds mostly occur in the <2.5 μm fraction, their absolute concentrations in $PM_{10}$ and $PM_{2.5}$ are close. As expected, the mineral dust and sea salt mostly occur in the coarse 2.5–10 μm fraction. The mean contribution of major species to $PM_{10}$ and $PM_{2.5}$ is similar to that observed in other cities in Spain (Querol et al., 2004a, 2008). The most significant feature of the $PM_{10}$ and $PM_{2.5}$ composition in Huelva is the high content of toxic trace metals of environmental interest. Concentrations of As, Cu, Zn, Se and Bi are 3–5 times higher than those typically observed in other European cities (Querol et al., 2004b, 2008; Rodríguez et al., 2007; Putaud et al., 2004). Mean concentration of As (6.2 ng $m^{-3}$) is slightly higher than the annual target value of the European standard (6 ng $m^{-3}$ in $PM_{10}$; 2004/107/EC).

### 3.2. Influence of industrial emissions on composition and daily evolution of particles

#### 3.2.1. Ultrafine particles and gaseous pollutants

Figure 3 shows the hourly average values for particle number (PN, PN1 and PN2), BC concentrations and gaseous pollutant concentrations, road traffic intensity, road traffic intensity/wind speed and some meteorological parameters and $PM_{2.5}$ and $PM_{2.5-10}$ concentrations. Working days (Monday to Friday) and weekends are segregated. The influence of vehicle exhaust and industrial emissions on the particle number concentration tends to occur at

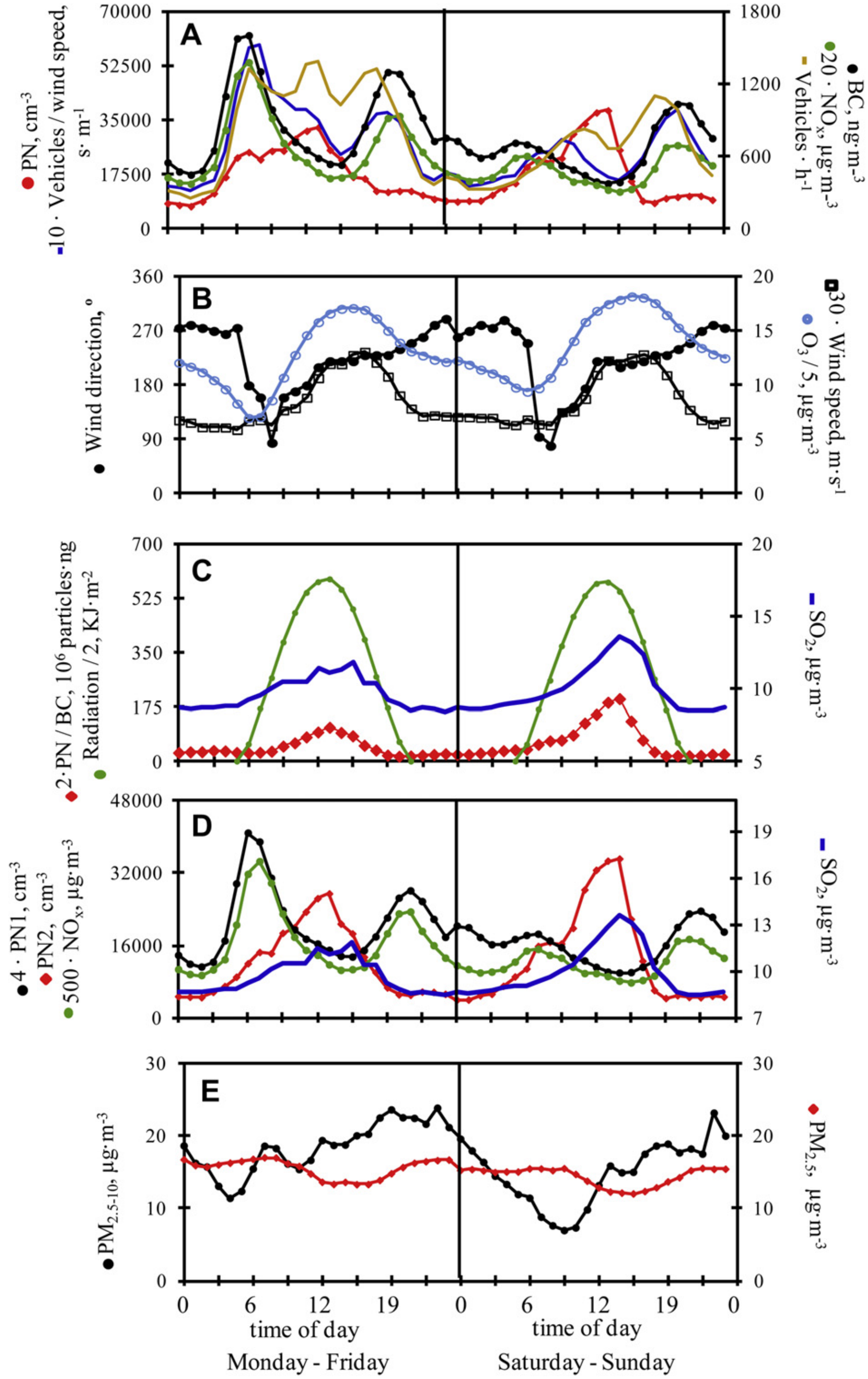

**Fig. 3.** Hourly average values of particles (PN, PN1 and PN2), BC concentrations and gaseous pollutant ($NO_x$ and $SO_2$) concentrations, and of road traffic intensity, the road traffic intensity (number of vehicles/h)/wind speed ratio, of the PN/BC ratio and solar radiation and of $PM_{2.5}$ and $PM_{2.5-10}$ concentrations, for working days, Saturdays and Sundays during 2008–2009.

different times of day. The sharp increase in road traffic intensity in the morning results in an abrupt rise in PN, BC and $NO_x$ concentrations due to vehicle exhaust emissions. The enhancement in the dilution conditions and air mass renewal due to the development of inland sea breeze after 09:00 GMT, results in a decrease in the concentration of these vehicles exhaust pollutants, even if the road traffic intensity does not decrease. The correlated weekly evolution of road traffic intensity / wind speed ratio and BC and $NO_x$ concentrations indicates that fresh vehicle exhaust emissions and dilution/ventilation conditions modulate the behaviour of these pollutants (Fig. 3A).

The inland sea breeze blowing from 09:00 to 17:00 GMT is associated with an increase in the sulphur dioxide concentrations (Fig. 3B and C). This is attributed to the inland transport of plumes from the industrial estates located to the south of Huelva (Fig. 1). Observe the correlation between the daily evolution of $SO_2$, wind speed and solar radiation. The increase in the PN/BC ratio and in PN2 concentrations observed during the inland blowing period is attributed to ultrafine particle formation in the $SO_2$ plumes. Fernández-Camacho et al. (2010b) showed that there is a strong statistical relationship between PN2 and $SO_2$, and between PN1 and $NO_x$, in such a way that PN2 tends to show high values during fumigations of industrial plumes, whereas PN1 shows high values linked to vehicle exhaust emissions. Stanier et al. (2004) and Cheung et al. (2011) observed that high particle number concentration in industrial $SO_2$ plumes was due to nucleation burst linked to the sulphuric acid/sulphate particles. During the morning $NO_x$ maximum period, when ultrafine particles were linked to vehicle exhaust emissions, PN is higher on average value than 23,000 $cm^{-3}$, and PN2 accounted for 53% of PN, whereas during the noon – afternoon $SO_2$ maximum due to the impact of the industrial plumes, PN is typically higher on average value than 29,000 $cm^{-3}$, and PN2 accounted for 70% of PN.

### 3.2.2. Ultrafine particles and elemental composition

The mean daily evolution (hourly values) of PN, $SO_2$ and $NO_x$ and of $PM_{2.5}$ elemental composition observed during the weekdays (Monday to Friday) and weekends (Saturday and Sunday) of the streaker campaign (15th to 22nd October 2009) is shown in Figure 4. The two types of ultrafine particle episodes are recognized:

- *Fresh road traffic emissions.* These are observed during the morning rush hours of the working days and are associated with high concentrations of typical road dust elements (Si, Al, Fe, Mg, K, Ca, Ti and Mn; Amato et al., 2009).
- *Fresh industrial plumes.* These events are associated with high concentrations of trace metals (As, Cu, Zn, Se, Pb and P) during the central hours of daylight (10:00–17:00 GMT) due to inland transport of the industrial plumes both during weekdays and weekends. The Fig. 4B shows the highest concentrations of PN, trace metals and $SO_2$ occurring during weekends. This fact can probably be due to the work regime of industrial estates, as during weekends and holidays, the electric cost is cheaper (by 60–70%).

The occurrence of high PN and trace metal concentrations due to the impact of the industrial plumes (containing $SO_2$) is clearly observed in Figure 5A. Observe that several events of N and As concentrations as high as $10^5$ $cm^{-3}$ and 18 ng $m^{-3}$ occurred during the streaker campaign. Because the stacks of the Cu-smelter and fertilizer plants are very close together in Punta del Sebo Estate (Fig. 1), simultaneous high As and P events occurred due to mixing of the plumes during inland transport.

The hourly evolution of S (in $PM_{2.5}$) and bulk $PM_{2.5}$ is compared with that of N and Zn (in $PM_{2.5}$) in Fig. 5B. It can clearly be observed that the $PM_{2.5}$ and S concentrations do not properly detect the fumigations of the industrial plumes. Only in the fumigations that occurred on 18th October is an increase in S concentrations observed. Moreover, high S and bulk $PM_{2.5}$ concentrations were observed during periods of non-fumigation or fresh emissions, e.g. 17th October at night. This indicates that S and $PM_{2.5}$ concentrations are linked to aged emissions, i.e. they are aged grown particles occurring in the accumulation mode (0.1–1 μm). In contrast, the high PN and $SO_2$ concentrations are attributed to fresh ultrafine sulphuric acid/sulphate formation in the industrial plumes (Fig. 5A). The contribution of this ultrafine sulphuric acid/sulphate to bulk S (in $PM_{2.5}$) is so low that it does not result in significant increases in the concentration of the S (Fig. 5B). Similar behaviour was identified in Milan (Italy) and Barcelona (Spain) by Rodríguez et al. (2007); they observed that high $PM_{2.5}$ concentrations were associated with particle growth due to condensation of ammonium nitrate and ammonium sulphate in aged air, whereas fresh emissions resulted in much larger increases in ultrafine than in $PM_{2.5}$ particles. The streaker data showed that S, V, Ni, Cr and Br did not show a daily pattern, and high concentrations of these elements were recorded linked to specific events.

Observe in Fig. 5C how PN exhibits a high correlation with elements linked to the fresh industrial Cu-smelter emissions (e.g. Zn, Cu and Pb, $r$: 0.48–0.64) and the phosphoric acid-based fertilizer plant (e.g. P, $r = 0.44$). In contrast, $PM_{2.5}$ shows high correlation with compounds linked to aged emissions from the oil refinery (S, V and Ni; $r$: 0.4–0.6) and road dust (Fe, Ca, K, Al and Sr; $r$: 0.3–0.4).

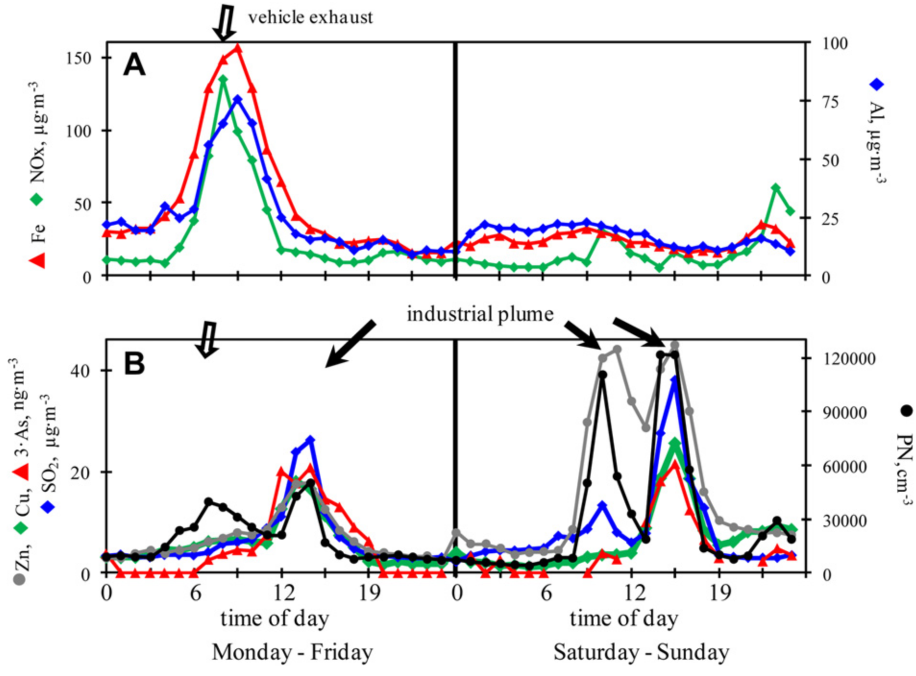

**Fig. 4.** Daily evolution (hourly values) of particle number (PN), gaseous pollutants ($NO_x$ and $SO_2$) and Fe, Al, Zn, Cu and As in $PM_{2.5}$ averaged during weekdays (Monday–Friday) and weekends (Saturday–Sunday) of the streaker campaign.

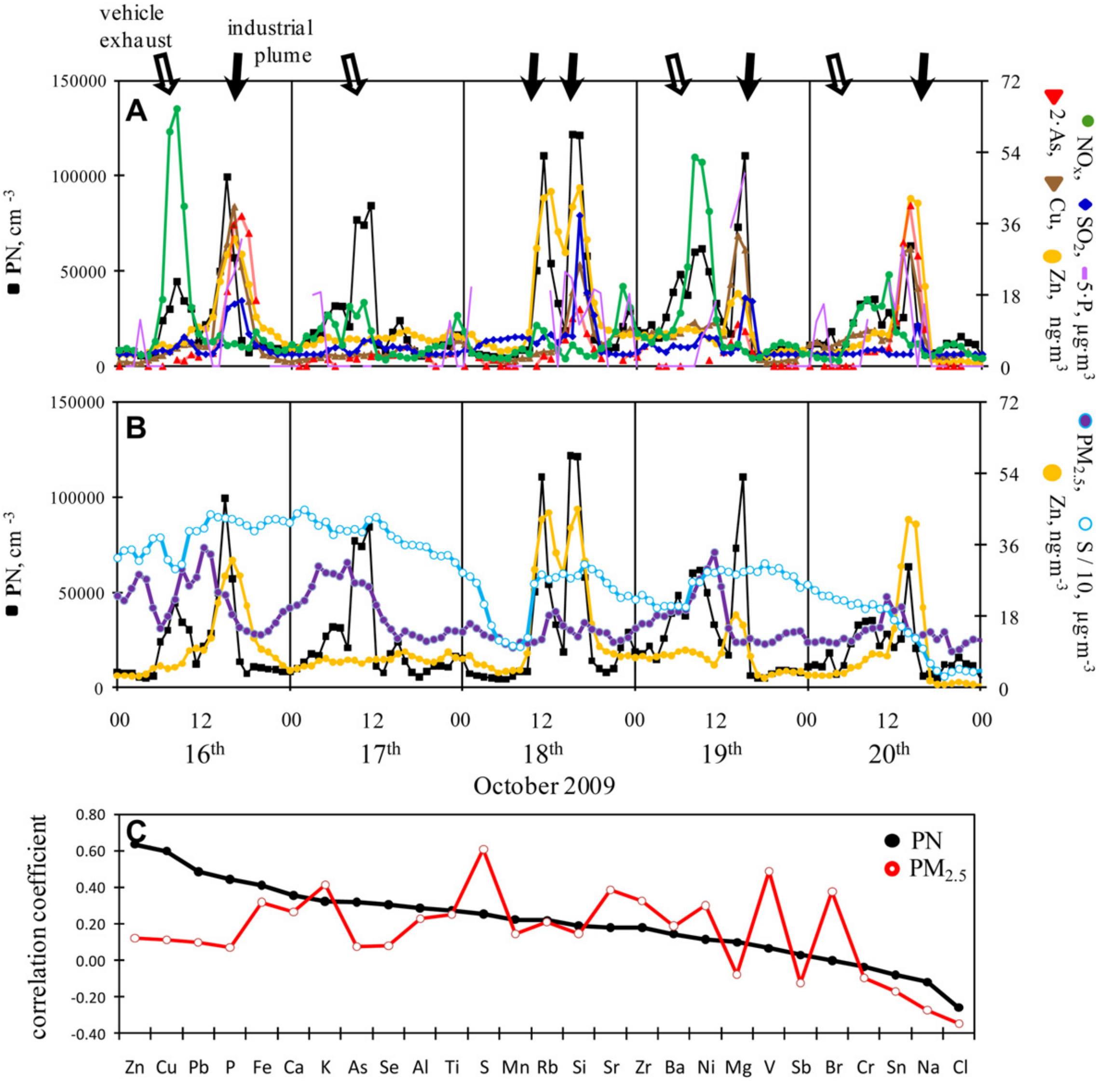

Figure 5

**Fig. 5.** A–B) Hourly average values of particle number (PN), $SO_2$, $NO_x$, some trace metals (P, As, Cu and Zn) and sulphur (S) in $PM_{2.5}$. C) Correlation coefficient between PN and all the elements analysed in $PM_{2.5}$. All data have hourly time resolution. Scale factor has been applied for some elements (*x* 2 for As, *x* 5 for P,/10 for S) in order to adjust the scale of the graphic.

### 3.3. Ultrafine particles episodes

A classification of ultrafine particle events was performed. This was done by identifying the pollutants that tend to increase simultaneously with hourly particle number concentration N. This classification allows the most frequent scenarios in which ultrafine particle events occur to be identified. Eight types of event, in which N experiences simultaneous increases with $NO_x$, $SO_2$, BC and/or solar radiation, were considered (Table 2). The most frequent time of occurrence and mean concentrations of the measured parameters are included in the analysis. The overall results show that:

- 29% of the peak events in hourly PN concentrations occurred in the morning (08:00 GMT) with concurrent increase of $NO_x$ and BC concentrations. These type-1 events are attributed to vehicle exhaust emissions.
- 31% of the peak events in PN were simultaneous with increases in $SO_2$ concentrations (type 2, 4, 6 and 8). Most of these events occurred from 13:00 to 14:00 GMT, when industrial plumes typically reach the measurement site. In most of these events (21% of all PN increases) $NO_x$ was the only pollutant that experienced a simultaneous increase with $SO_2$ and PN (type-6).
- In ~20% of the events, no increase in the measured pollutants was observed during the increases in PN concentrations. These type-3 events mostly occurred at noon, when simultaneous increases in PN and in solar radiation were observed.

Fig. 6A and B show the mean PN versus $SO_2$ and $O_3$ concentrations recorded in all types of events (data included in Table 2). It can clearly be observed how particle number tends to increase with $SO_2$ and $O_3$ concentrations. In fact, the highest PN concentrations are recorded during type-6 ($N = 80{,}891\ \mathrm{cm}^{-3}$) events, which are associated with the highest $SO_2$ ($28\ \mu\mathrm{g\ m}^{-3}$) and $O_3$ ($98\ \mu\mathrm{g\ m}^{-3}$) concentrations. This result suggests the significant involvement of photochemistry in the processes involved in the

**Table 2**
Classification of ultrafine particle events. Type, characteristic, frequency, most frequent time of occurrence (GMT), and concentrations of the considered pollutants.

| Type of events | PN peak correlated with | F | Time | PN | PN1 | PN2 | $NO_x$ | $SO_2$ | BC | $O_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $cm^{-3}$ | % | % | $\mu g\ m^{-3}$ | $\mu g\ m^{-3}$ | $ng\ m^{-3}$ | $\mu g\ m^{-3}$ |
| **$NO_x$ involved** | | **36%** | | | | | | | | |
| Type-1 | $NO_x$ and BC | 29% | 8:00 | 22,352 | 37 | 63 | 52 | 8 | 1351 | 50 |
| Type-5 | $NO_x$ | 7% | 13:00 | 45,989 | 7 | 93 | 33 | 8 | 497 | 74 |
| **$SO_2$ involved** | | **31%** | | | | | | | | |
| Type-2 | $SO_2$, BC and $NO_x$ | 5% | 13:00 | 33,828 | 16 | 84 | 30 | 20 | 807 | 81 |
| Type-4 | $SO_2$ | 4% | 14:00 | 71,989 | 6 | 94 | 20 | 25 | 622 | 82 |
| Type-6 | $SO_2$ and $NO_x$ | 21% | 13:30 | 80,891 | 5 | 95 | 32 | 28 | 608 | 98 |
| Type-8 | $SO_2$ and BC | 1% | 11:00 | 23,466 | 14 | 86 | 6 | 12 | 472 | 75 |
| **Only BC involved** | | **14%** | | | | | | | | |
| Type-7 | BC | 14% | 11:00 | 18,080 | 20 | 80 | 18 | 7 | 603 | 69 |
| **Non primary pollutants** | | **20%** | | | | | | | | |
| Type-3 | Only solar radiation | 20% | 12:00 | 36,994 | 9 | 91 | 20 | 9 | 505 | 76 |

conversion of $SO_2$ to ultrafine particles within the industrial plumes during inland transport prompted by sea breeze. Observe how the PN2 contribution to PN increases with $O_3$ concentrations (Fig. 6D). The contribution of PN1 to PN is only significant during type-1 events (primary vehicle exhaust emissions), when it reaches 37% (Table 2). The contribution of PN2 particles to PN is also high during type-3 and 5 events, even if $SO_2$ concentrations are rather low (8–9 $\mu g\ m^{-3}$). The relationship between PN2 and $O_3$ during these events (a linear trend similar to that observed in all events) suggests the involvement of photochemical processes (Fig. 6D). The fact that increases in $SO_2$ concentrations were not observed in these events could be due to the fact that $SO_2$ is consumed by conversion to sulphate, or species other than $SO_2$ are involved in the nucleation and subsequent particle growth (e.g. organic species; Metzger et al., 2010; Sipilä et al., 2010).

### 3.4. Sources that contribute to ultrafine particles

The sources that contribute to ultrafine particles were identified by applying PCA and varimax rotations to data for particle number concentration data and $PM_{2.5}$ chemical composition. Different combinations of variables were tested (e.g. PN and $PM_{2.5}$ composition, PN1, PN2 and $PM_{2.5}$ composition, including trace gases and/or meteorological parameters). A PCA with 45 cases and 27 variables was considered using the software package STATISTICA 7. Three Principal Components (PCs) were persistently observed (Table 3):

- APC-1, showing a high association with species linked to industrial emissions from the Cu-smelter (nss-$SO_4^{=}$, As, Sb, Pb, Zn and Sn), the phosphoric acid and fertilizer plant (nss-$SO_4^{=}$, P and $NH_4^{+}$) and the oil refinery (nss-$SO_4^{=}$, $NO_3^{-}$, $NH_4^{+}$, V and Ni), was persistently observed. The presence of PN2 in this PC is attributed to ultrafine sulphate particle formation in the plume during inland transport prompted by sea breeze. The association of PN2 in this factor is in agreement with the results above obtained using the streaker, which showed high concentrations of PN and trace metals during fumigations of the industrial $SO_2$ plumes (Figs. 4B and 5A).
- APC-2 associated with road traffic emissions: vehicle exhaust emissions (OM and PN1) plus road dust (Al, Ca, Fe, Ti, Mn and K). The association of this PC with particle number (PN1) is due to vehicle exhaust emissions, with the contribution of road

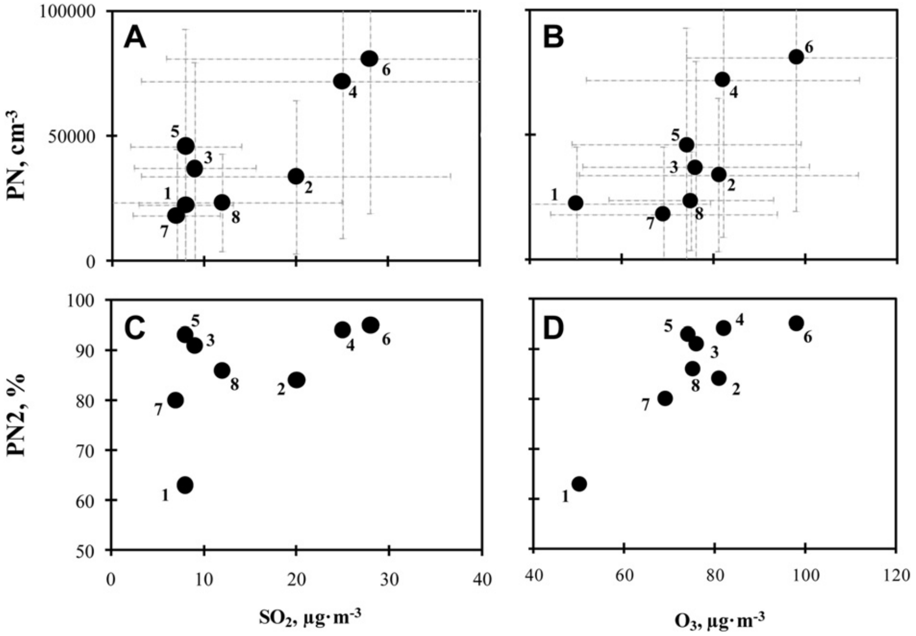

**Fig. 6.** Contributions of PN in absolute concentrations ($cm^{-3}$; A and B) and of PN2 in relative concentrations (%, C and D) versus $SO_2$ and $O_3$ concentrations. The number near each dot indicates the type of event described in Table 2. A and B) Dotted lines indicate plus/minus one standard deviation.

**Table 3**
Factor loading of the Principal Components Analysis (followed by a varimax rotation) obtained using daily data of $PM_{2.5}$ chemical composition and of PN1 and PN2 particles.

| | PC-1 | PC-2 | PC-3 |
|---|---|---|---|
| | Industrial | Road traffic | Sea salt |
| OM | 0.37 | **0.57** | −0.10 |
| PN1 | 0.52 | **0.59** | −0.10 |
| PN2 | **0.57** | 0.26 | −0.06 |
| nss-$SO_4^{2-}$ | **0.84** | −0.02 | −0.14 |
| $NO_3^-$ | 0.51 | 0.26 | −0.14 |
| $NH_4^+$ | **0.87** | 0.05 | −0.29 |
| Na | −0.08 | −0.06 | **0.86** |
| $Cl^-$ | 0.15 | −0.03 | **0.81** |
| Mg | −0.13 | 0.33 | **0.83** |
| Al | 0.13 | **0.76** | −0.21 |
| Ca | −0.07 | **0.89** | 0.14 |
| Fe | 0.14 | **0.95** | 0.05 |
| Ti | 0.14 | 0.46 | 0.25 |
| Mn | 0.26 | **0.83** | 0.12 |
| K | 0.29 | **0.71** | 0.13 |
| P | **0.67** | 0.10 | 0.10 |
| As | **0.83** | 0.26 | 0.16 |
| Pb | **0.86** | 0.21 | 0.28 |
| Cd | **0.88** | 0.18 | 0.32 |
| V | **0.82** | 0.25 | −0.09 |
| Ni | **0.74** | 0.29 | 0.02 |
| Zn | **0.61** | 0.11 | 0.31 |
| Cu | 0.44 | 0.13 | −0.05 |
| Bi | **0.81** | 0.07 | 0.39 |
| Mo | 0.53 | −0.01 | 0.21 |
| Sn | **0.71** | 0.44 | 0.20 |
| Sb | 0.41 | 0.30 | −0.29 |
| % Var | 39.20 | 12.00 | 11.70 |

Factor loadings with absolute values $> 0.5$ are in bold.

dust considered being almost negligible (road dust is mostly coarse, with a high contribution to mass, but a low contribution to number concentrations). The association of road dust in this PC is attributed to the simultaneous (correlated) increases in road dust and vehicle exhaust components during the morning rush hours (e.g. Fig. 4A). The presence of PN1 in this PC is in agreement with the weekly cycles of $NO_x$ and PN1 particles described above, which exhibited high values during working-day rush hours (Fig. 3).

- APC-3 showing high factor loading for typical sea salt components (Cl, Na and Mg). As expected, neither of the particle number components, PN1 or PN2, was associated with this factor.

Only two sources contributed significantly to the particle number PN: road traffic accounted for 50 ± 9%, whereas industrial emissions accounted for 44 ± 7% of PN (Fig. 7). The contribution of sea salt was negligible (<1%), whereas the undetermined fraction (the difference between measured PN and the sum of the identified sources) accounted for 4% (Fig. 7). The contribution of these two sources to ultrafine particle concentration in ambient air is of a comparable magnitude: the daily mean contribution of each of these sources to the particle number concentration exhibits values within the range 10,000–30,000 $cm^{-3}$ (Fig. 8). Observe how industrial emissions can frequently contribute 20,000–30,000 $cm^{-3}$ to the particle number and can result in As concentrations within the range 10–25 ng $m^{-3}$ (Fig. 8B). Fig. 9 shows the daily mean

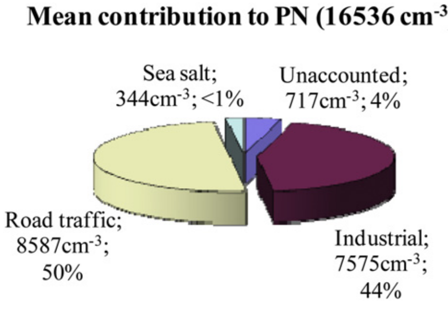

**Fig. 7.** Mean daily contribution to PN ($cm^{-3}$ and %) of the different factors identified by the PCA analysis.

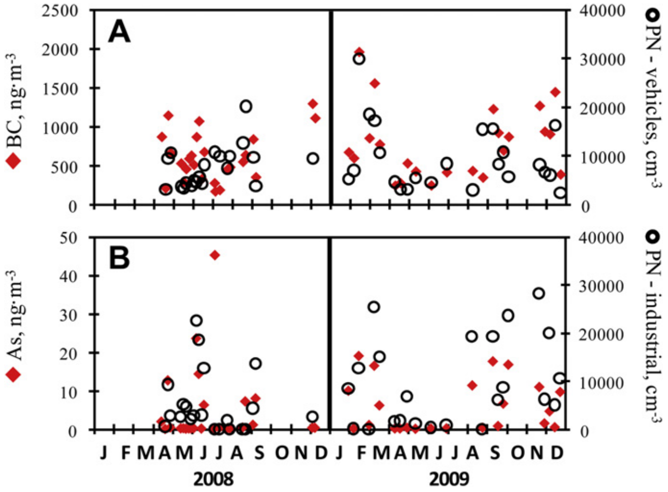

**Fig. 8.** Daily averaged values of BC, As and of the particle number PN linked to vehicle exhaust and industrial emissions.

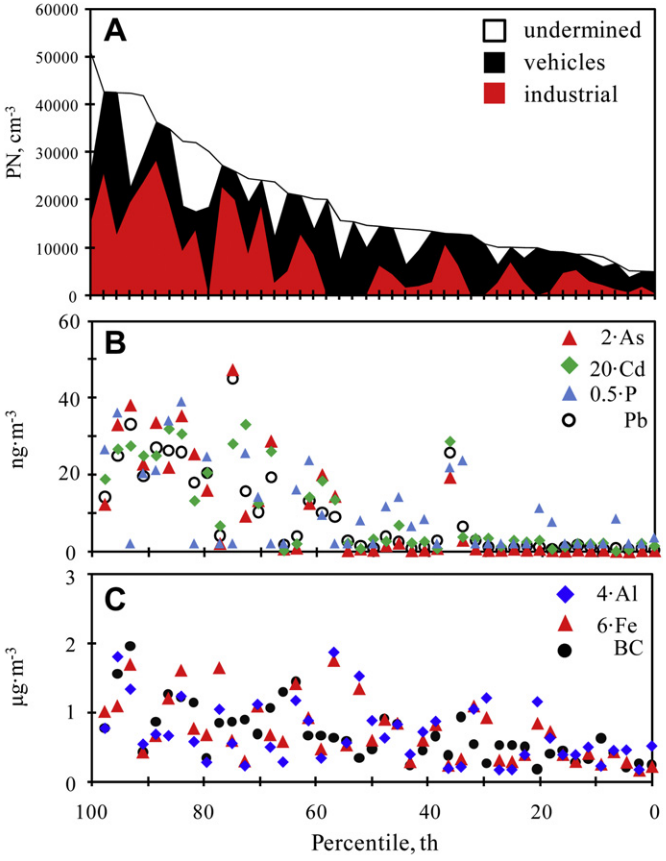

**Fig. 9.** A) Daily averaged values of PN classified from the highest to the lowest concentration (100th to 1st percentile) highlighting the contribution of the industrial, vehicle exhaust and undetermined fraction contributions. The associated concentrations of As, Cd, P, Pb, Al, Fe and BC are plotted in B and C.

averaged values of the particle number PN, classified from the highest to the lowest concentration (100th to 1st percentile), and the contribution of the identified sources. Observe how PN values $>25{,}500\ \mathrm{cm}^{-3}$ (70th P) are mainly induced by industrial emissions, whereas for PN values $<14{,}700\ \mathrm{cm}^{-3}$ (50th P) the vehicle exhaust contribution is greater:

- For daily mean levels of PN within the range 50,000–25,500 $\mathrm{cm}^{-3}$ (100th–70th) industrial and vehicle exhaust emissions accounted for 49 and 30%, respectively.
- For daily PN values within the range 14,700–5000 $\mathrm{cm}^{-3}$ (50th–1st), vehicle emissions accounted for 60% of PN, with only 30% of PN being linked to industrial emissions.

These results suggest that high PN concentrations, about 25,000 $\mathrm{cm}^{-3}$, are mostly due to industrial emissions. Observe the sharp increase in the concentrations of As, Cd, Pb and P (linked to the Cu-smelter and fertilizer production plants) when PN concentrations higher than the 70th P are recorded (Fig. 9B). In contrast, compounds linked to vehicle exhaust and road dust emissions increase progressively from low to high PN events (Fig. 9C).

The potential contribution of new particle formation in ambient air linked to photochemical processes, typically occurring with low concentrations of primary pollutants (e.g. $NO_x$ and $SO_2$; Rodríguez et al., 2009), was not identified in our PCA, with this being attributed to the fact that any chemical tracer of such a process was analysed. The features of the type-3 events we observed in the time series analysis suggest that these events occur in our study area. In fact, these events could account for the unexplained variance in the PCA (∼37%) and for the unaccounted-for fraction in the source contribution (4%; Fig. 7). Pey et al. (2009) identified such photochemically induced new particle formation events in Barcelona, and concluded that they accounted for 3% of the number of particles >10 nm and for 23% of 10–20 nm particles.

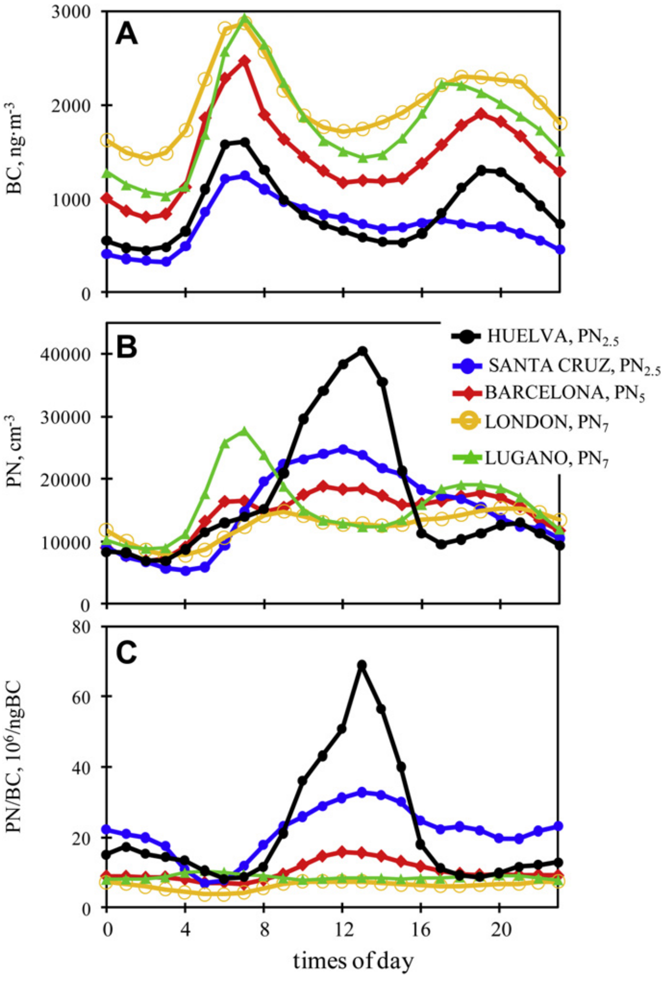

**Fig. 10.** Daily evolution of black carbon (BC), particle number (PN) and the number to black carbon ratio (PN/BC) in several European cities. $PN_x$: number concentrations of particles with a size higher than $x$ nanometers. Data from Santa Cruz (Spain), Barcelona (Spain), London (UK) and Lugano (Switzerland) provided by Reche et al. (2011).

The high impact of these industrial emissions on the ultrafine particle concentration is clearly observed in Fig. 10, where the number and black carbon concentration in several European cities is plotted (Reche et al., 2011). In Huelva, BC concentrations exhibit a maximum during the morning rush hours, as in other EU cities due to the dominant role of vehicle exhaust emissions. However, the particle number concentration in Huelva shows a distinct maximum during the noon–afternoon due to the impact of the industrial plumes over the city. Because of this, PN concentrations in Huelva are much higher than in other cities, even though BC levels in Huelva are significantly lower.

## 4. Conclusions

Urban air pollution by ultrafine particles is a matter of concern due to the adverse effects on human health. Studies performed during the last decade showed that vehicle exhausts are a major source of ultrafine particles in urban ambient air. Thus, ultrafine particle emissions in vehicle exhaust have recently been subject to limit values in a recent stage of the EURO standards.

The results of this study show that some industrial emissions result in high concentrations of ultrafine particles. This is the case of the industrial city of Huelva, where the second largest Cu-smelter plant in Europe, phosphoric acid and fertilizer plants, an oil refinery and a petrochemical plant are located. These sources release $SO_2$, toxic metals and hydrocarbons, among other pollutants. The results of this study show that industrial emissions are the main cause of ultrafine particle episodes. When vehicle exhaust is the main source, ultrafine particles typically show (24-h mean) concentrations within the range 14,700–5000 $\mathrm{cm}^{-3}$ (50th–1st), with 60% of these being linked to this source and 30% to industrial emissions. In contrast, when daily mean levels of PN are within the range 50,000–25,500 $\mathrm{cm}^{-3}$ (100th–70th), industrial and vehicle exhaust emissions accounted for 49 and 30%, respectively. High concentrations of toxic trace metals (As, Cu, Cd, Zn and Pb) are recorded during these ultrafine particle pollution events linked to industrial emissions (e.g. 10–25 ng $\mathrm{m}^{-3}$ As and 1–2 ng $\mathrm{m}^{-3}$ Cd). Because of these industrial emissions, ultrafine particle concentrations during daylight are about two times higher than those observed in other European cities.

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**Attachment 44**

# Linking Exposure Assessment Science With Policy Objectives for Environmental Justice and Breast Cancer Advocacy: The Northern California Household Exposure Study

Julia Green Brody, PhD, Rachel Morello-Frosch, PhD, MPH, Ami Zota, ScD, Phil Brown, PhD, Carla Pérez, BA, and Ruthann A. Rudel, MS

*Objectives.* We compared an urban fence-line community (neighboring an oil refinery) and a nonindustrial community in an exposure study focusing on pollutants of interest with respect to breast cancer and environmental justice.

*Methods.* We analyzed indoor and outdoor air from 40 homes in industrial Richmond, California, and 10 in rural Bolinas, California, for 153 compounds, including particulates and endocrine disruptors.

*Results.* Eighty compounds were detected outdoors in Richmond and 60 in Bolinas; Richmond concentrations were generally higher. Richmond's vanadium and nickel levels indicated effects of heavy oil combustion from oil refining and shipping; these levels were among the state's highest. In nearly half of Richmond homes, $PM_{2.5}$ exceeded California's annual ambient air quality standard. Paired outdoor–indoor measurements were significantly correlated for industry- and traffic-related $PM_{2.5}$, polycyclic aromatic hydrocarbons, elemental carbon, metals, and sulfates ($r=0.54$–$0.92$, $P<.001$).

*Conclusions*. Indoor air quality is an important indicator of the cumulative impact of outdoor emissions in fence-line communities. Policies based on outdoor monitoring alone add to environmental injustice concerns in communities that host polluters. Community-based participatory exposure research can contribute to science and stimulate and inform action on the part of community residents and policymakers. (*Am J Public Health.* 2009;99:S600–S609. doi: 10.2105/AJPH.2008.149088)

With a sprawling oil refinery in the background, Marleen Quint, Wanna Wright, and Etta Lundy stood on a hill overlooking Richmond, California, holding up a photograph of Quint's mastectomy scars.[1] The women were propelled by their breast cancer diagnoses to ask whether their own cancers as well as neighborhood problems with asthma, sore throats, rashes, other cancers, and children's development were related to chemical exposures from nearby industry and rail, truck, and marine shipping corridors. Their question is part of an emerging crossover of interests between environmental justice and breast cancer advocacy[2–5] that is driven not only by personal experiences but also by breast cancer statistics for ethnic minority women; environmental hypotheses that link the same pollutants to breast cancer and to health issues of concern in low-income, minority communities; and new partnerships between communities and scientists.[6–9]

In the United States, the breast cancer incidence rate is higher among African American women younger than 40 years than among White women in the same age group,[10,11] and mortality rates among African American women are higher in all age groups, even when access to mammography and treatment are equivalent.[12] Among older women, the incidence rate is lower in the African American population than in the White population,[11] but the gap may be closing.[13,14] Meanwhile, incidence rates are rising rapidly among US immigrants[15–17] and in industrializing nations.[18]

Environmental chemical pollutants hypothesized to cause breast cancer include some that have been associated with higher breast cancer risk in several human studies, for example polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs); animal mammary gland carcinogens, including PAHs, pesticides such as chlorothalonil, and flame retardants such as tris(2,3-dibromo-1-propyl) phosphate; and endocrine-disrupting compounds (EDCs), including bisphenol A, alkylphenols, phthalates, and pesticides such as dichlorodiphenyltrichloroethane (DDT) and pyrethroids.[19–21] Thus, the chemicals of interest in breast cancer research include urban air pollutants, industrial chemicals, and pesticides to which low-income, minority populations are disproportionately exposed.[6,22] Such exposures are also hypothesized to affect health outcomes such as premature puberty, asthma, obesity, and cognitive development that disproportionately affect low-income, minority populations.[23–26]

## NORTHERN CALIFORNIA HOUSEHOLD EXPOSURE STUDY COLLABORATIVE

Through the National Institute of Environmental Health Sciences environmental justice grants program, we established a community-based participatory research (CBPR) collaboration involving the Silent Spring Institute, which focuses on the environment and women's health, especially breast cancer[27]; Communities for a Better Environment (CBE), the environmental justice organization in which Quint, Wright, and Lundy are active[28]; and faculty at Brown University and the University of California, Berkeley. We addressed breast cancer and environmental justice concerns in an exposure study that expanded the Silent Spring Institute Household Exposure Study (part of the Cape Cod Breast Cancer and Environment Study)[29] to neighborhoods bordering an oil refinery in Richmond, where CBE has an active environmental justice campaign, and rural Bolinas, California, which provided a regional comparison.

We decided to conduct an exposure study because an epidemiological breast cancer study within Richmond probably would not have been informative, given the community's size and lack of relevant historical exposure measurements. An exposure study of compounds of toxicological concern can assess the extent of a problem and inform exposure reduction efforts.[30] We focused on household exposures because people spend 90% of their time indoors, often at home, and household environments have not been well characterized.[31,32] We tested for compounds hypothesized to affect breast cancer and additional products of oil combustion and refining that serve as indicators for the large number of uncharacterized emissions from oil refineries.

Our study included several goals related to policy, exposure science, and community education. Our policy goals were to provide data that would inform local decisions about the Richmond oil refinery, California state biomonitoring and chemicals policies,[33,34] and national debates regarding the use of EDCs in consumer products.

Our exposure science goals were to test for chemical markers of oil refinery emissions in homes, characterize the cumulative effects of emissions in an environmental justice community by measuring an exceptionally large and diverse set of pollutants from outdoor and indoor sources, assess geographic and sociodemographic differences in EDC exposures by comparing Cape Cod, Massachusetts, with an industrial neighborhood in California, and describe outdoor EDC levels. (An environmental justice community is composed of low-income or ethnic minority residents disproportionately affected by environmental pollution.) To our knowledge, no previous reports on these issues have been published.

Finally, one of our educational goals was to inform community members about important determinants of their indoor air quality. The other goal was to inform them about current scientific knowledge on potential relationships between indoor exposures and health, including breast cancer.

## RESEARCH SETTING

To inform CBE's organizing and advocacy, we focused on the Liberty and Atchison Village neighborhoods of Richmond, in Contra Costa County: 66 acres that border a Chevron oil refinery and truck, rail, and marine shipping corridors[35] (see Figure S1, available as a supplement to the online version of this article at http://www.ajph.org). The area's uniform 1- and 2-story housing was constructed for shipyard workers during World War II. According to the 2000 census, the community was 61% Latino (many residents were monolingual Spanish speakers), 18% African American, and 3% Asian American; 26% of residents had incomes below the federal poverty level ($17 603 for a family of 4), and half had incomes below 200% of the poverty level.[36] Richmond has high cancer and respiratory risks associated with toxic industrial releases.[37] Contra Costa's 15% asthma prevalence rate is among the state's highest,[38] and its breast cancer incidence rate is higher than the statewide rate.[39] These statistics highlight Richmond's enhanced vulnerability to multiple pollutant exposures.

The Richmond Chevron refinery is one of the nation's largest, covering 2900 acres and processing more than 240 000 barrels of crude oil a day[40] into gasoline, jet fuel, diesel fuel, and lubricants. It employs approximately 1000 workers.[41] CBE was concerned about air pollution from flaring (venting and uncontrolled burning of gaseous emissions in routine operations and emergencies)[42] and about requested permit changes to replace and add equipment[43] that reportedly would increase overall throughput[44] and increase emission of sulfur dioxide, sulfates, and metals[45] through refining of lower grade crude oil with higher sulfur content.

## FOCUS ON INDOOR POLLUTANTS WITH OUTDOOR SOURCES

Here, in our first report on the CBPR process and study design, we focus on results that pertain most directly to environmental justice. We describe the compounds detected (as an indication of cumulative impact) and pollutants with significant outdoor sources, as evidenced by higher outdoor concentrations in industrial Richmond than in rural Bolinas. We include for comparison an indoor-source chemical (dibutyl phthalate) to demonstrate the contrast between outdoor- and indoor-source compounds.

Results of additional analyses focusing on indoor-source chemicals, many of which are EDCs, will be published in a subsequent article, and analyses of questionnaire responses and refinery emergency releases as predictors of pollutant levels are under way. We previously reported dramatic geographic differences in brominated flame retardants (polybrominated diphenyl ethers), with the higher levels observed in California than other areas probably due to the state's strict furniture flammability standard.[46] We have written elsewhere about our methods for reporting personal exposure results to participants.[47,48]

## METHODS

After a CBPR collaborative process[49,50] designed to consider what data would address mutual goals of the project partners, we sampled air and dust from 40 homes in Richmond and 10 in Bolinas, as well as outdoor air near each home. Samples were analyzed for industrial and traffic pollutants, such as particulates, metals, PAHs, ammonia, and sulfates, and for many EDCs, including pesticides, flame retardants, phthalates, and phenols.

### CBPR Strategy

We gathered information on community health concerns, drew on CBE's relationships with public officials, held annual community meetings, and convened an advisory council that included neighborhood activists, breast cancer and biomonitoring activists, a state health official, and an academic researcher. On the basis of this input, we designed research to assess the cumulative effects and specific sources of indoor pollution originating from outdoor emissions.

The advisory council requested a comparison with rural northern California that would supplement the comparison with Cape Cod and maximize the contrast for assessing the cumulative impact of Richmond outdoor emissions. This request led to an additional community partnership with the Commonweal Biomonitoring Resource Center in Bolinas,[51] a nonindustrial coastal community. We deliberated how our results would affect refinery expansion plans. We expected to detect compounds associated with oil refining in Richmond homes; however, we were mindful that if we did not, our results might undermine CBE's refinery campaign, even though any negative findings might be due to inadequacies in our methods.

The research protocol was approved by Brown University's institutional review board in a novel agreement that covered both academic and community-based researchers, representing a significant accomplishment for our collaborative. Traditionally, university institutional review boards do not cover outside organizations, leaving community groups with the expense of contracting with an independent review board and diminishing the academic–community partnership. All individuals with access to personally identifiable data were formally trained with respect to ethics in human subjects research.

### Selection of Households for Sampling

Balancing the goals of collecting representative neighborhood data and creating opportunities to involve CBE members, we recruited 40 nonsmoking households in the Atchison Village and Liberty neighborhoods of Richmond through door knocks at randomly selected addresses (22 participants) and announcements at community meetings (18 participants). We obtained a list of all 550 eligible residential addresses from the county tax assessor's office and the management of the Liberty Village Apartments. We mailed a letter describing the study in English and Spanish to each home.

Using a randomized address list, a CBE researcher approached 132 nonvacant residences, contacting a resident at 74 (56%); 31% of contacted eligible homes participated. Six residents agreed but could not be scheduled, 3 were ineligible, and 43 declined; we were unable to contact 58 residents. We used snowball sampling to recruit 10 participants in Bolinas; the sample size was constrained by costs (for a chart of the sampling procedure, see Figure S2, available as a supplement to the online version of this article at http://www.ajph.org).

### Data Collection and Chemical Analysis

CBE staff were equipped and trained to collect samples and conduct interviews. Samples were collected between June and October 2006. EDC indoor sampling and analytical methods have been described elsewhere.[29] Paired indoor and outdoor air samplers collected parallel 24-hour integrated samples. University Research Glassware (Chapel Hill, NC) personal pesticide samplers (polyurethane foam plus sorbent XAD2) were used to collect semivolatile compounds at a flow rate of approximately 8 L per minute (as described by Rudel et al.[29]). For the 42 homes sampled between August and October 2006, respirable particulate ($PM_{2.5}$, particulate matter less than 2.5 microns in diameter) samples were also collected at a flow rate of approximately 5 L per minute on Teflon filters alongside the semivolatile sampler attached to the same high-volume pump. A parallel sample was collected on a quartz filter for carbon fractions and water-soluble ions.[52,53] Field blanks and duplicate samples were collected for quality assurance and quality control purposes.

A researcher observed characteristics of the home, including room size, open and closed windows, and rugs and carpets, and interviewed participants about demographic characteristics, consumer product use, and expectations about the study. The Southwest Research Institute (San Antonio, TX) and the Desert Research Institute (Las Vegas, NV) analyzed the samples for 153 analytes, including phthalates, alkylphenols, other phenols, parabens, banned and contemporary-use pesticides, PAHs, polybrominated diphenyl ethers, PCBs, particulates, metals, water-soluble ions, carbon fractions, and ammonia.

We obtained 24-hour integrated measurements from all 15 California Environmental Protection Agency monitors where $PM_{2.5}$ speciation data were gathered during the time of our data collection[54] (Figure S3 shows monitor locations, available as a supplement to the online version of the article at http://www.ajph.org). Comparison data from state monitors were available for $PM_{2.5}$, elemental and organic carbon, sulfates, nitrates, and metals. We selected $PM_{2.5}$, elemental and organic carbon, sulfates, vanadium, nickel, and sodium for comparison because they are indicators of specific emission source categories. We calculated summary measures for August through October 2006.

### Data Analysis

In addition to comparing Richmond data and Bolinas data, we compared outdoor measurements with indoor measurements and with state monitors. For each analyte, the method reporting limit was defined as the maximum of the analytical detection limit and the 90th percentile of the field blank concentrations. Values below the method reporting limit were not included in the percentage detected but were treated as estimated values to allow visualization of distributions (e.g., in box plots) and comparison of medians. We used the Fisher exact test to evaluate differences in the numbers of compounds detected between Richmond and Bolinas and the Wilcoxon rank-sum test to assess differences in pollutant levels.

To address environmental justice concerns about outdoor emissions sources in Richmond, we evaluated the contribution of outdoor sources to indoor pollution by comparing outdoor with indoor concentrations and calculating Spearman rank correlations between outdoor and indoor levels for compounds that had higher concentrations or were more frequently detected in Richmond outdoor air than in Bolinas outdoor air. For these compounds, measured or estimated values were available for at least 70% of indoor–outdoor pairs. The level of statistical significance was set at $P < .05$.

## RESULTS

Participants were predominantly middle-aged women. With respect to race/ethnicity (participants were allowed to select more than one option), 41% of the participants in Richmond self-identified as Hispanic, 54% self-identified as White, and 11% selected another race/ethnicity; 38% were interviewed in Spanish. In Bolinas, none of the participants were Hispanic, 80% were White, and 40% selected another race/ethnicity. In Richmond, 37% had a college education, as compared with 100% in Bolinas (see Table S1, available as a supplement to the online version of the article at http://www.ajph.org).

### Cumulative Effects

Chemical exposures in Richmond were greater than those in Bolinas. We detected 80 compounds in Richmond outdoor air and 60 in Bolinas outdoor air. Differences in indoor air were more pronounced, with 104 compounds detected in Richmond and 69 in Bolinas (detection frequencies are shown in Table S2, available as a supplement to the online version of the article at http://www.ajph.org). In the case of the 56 compounds detected in both communities, outdoor levels were significantly higher for 33 in Richmond and 1 (diethyl phthalate) in Bolinas (Wilcoxon $P \leq .05$). Median and maximum concentrations of these 33 compounds are shown in Table 1.[52,55–62] Richmond outdoor levels were significantly

**TABLE 1—Outdoor and Indoor Air Concentrations ($\mu g/m^3$) and Correlations for Compounds Detected at Higher Levels in Richmond Than in Bolinas, CA: 2006**

| | Outdoor Air | | | | Indoor Air | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Richmond | | Bolinas | | Richmond | | Bolinas | | Outdoor–Indoor Correlation[a]: |
| Chemical | Median | Maximum | Median | Maximum | Median | Maximum | Median | Maximum | Richmond |
| **Particulate matter and related carbon fractions[d]** | | | | | | | | | |
| $PM_{2.5}$ | 10 | 17 | 5.5 | 9.5 | 11 | 28 | 7.1 | 18 | 0.54* |
| Elemental carbon fraction 1 | 0.32 | 0.85 | 0.11 | 0.47 | 0.56 | 2.1 | 0.35 | 1.8 | 0.52* |
| Elemental carbon fraction 2 | 0.15 | 0.57 | <MRL | 0.45 | 0.23 | 0.70 | 0.088 | 0.46 | 0.78* |
| Total elemental carbon | 0.35 | 0.94 | 0.067 | 0.63 | 0.54 | 1.6 | 0.20 | 0.95 | 0.58* |
| Organic carbon fraction 1 | <MRL | 0.79 | <MRL | 1.1 | 2.1 | 6.3 | 1.8 | 3.5 | 0.03 |
| Organic carbon fraction 2 | 0.88 | 1.9 | <MRL | 1.4 | 3.4 | 5.2 | 2.6 | 6.5 | 0.20 |
| Organic carbon fraction 3 | 0.87 | 1.9 | 0.55 | 1.2 | 3.2 | 8.0 | 2.8 | 9.0 | <0.01 |
| Organic carbon fraction 4 | 0.32 | 0.77 | 0.11 | 0.61 | 1.1 | 2.9 | 0.87 | 2.3 | 0.01 |
| Total organic carbon | 2.1 | 4.8 | <MRL | 4.7 | 10 | 17 | 8.3 | 22 | 0.08 |
| Total carbon | 2.7 | 5.7 | <MRL | 5.3 | 11 | 19 | 8.5 | 23 | 0.14 |
| **Metals and ions[e]** | | | | | | | | | |
| Aluminum | 0.021 | 0.090 | 0.0092 | 0.086 | 0.023 | 0.11 | 0.030 | 0.25 | 0.50* |
| Calcium | 0.090 | 0.37 | <MRL | 0.053 | 0.093 | 0.28 | 0.045 | 0.11 | 0.81* |
| Copper | <MRL | 0.055 | <MRL | 0.0094 | <MRL | 0.054 | <MRL | 0.023 | 0.05 |
| Iron | 0.063 | 0.24 | <MRL | 0.034 | 0.055 | 0.32 | 0.028 | 0.15 | 0.79* |
| Lead | 0.0010 | 0.0040 | <MRL | 0.0017 | 0.0012 | 0.0041 | <MRL | 0.0015 | 0.62* |
| Manganese | 0.0020 | 0.0080 | <MRL | 0.0012 | 0.0015 | 0.0062 | 0.0013 | 0.0030 | 0.78* |
| Nitrates | 1.0 | 3.2 | 0.34 | 0.84 | 0.95 | 3.3 | 0.25 | 1.1 | 0.62* |
| Potassium | 0.051 | 0.11 | 0.018 | 0.062 | 0.050 | 0.21 | 0.033 | 0.11 | 0.46* |
| Sulfates | 2.2 | 3.9 | 1.3 | 2.5 | 1.6 | 3.6 | 1.4 | 3.4 | 0.91* |
| Vanadium | 0.0050 | 0.023 | 0.0018 | 0.0028 | 0.0035 | 0.020 | 0.0016 | 0.0023 | 0.93* |
| **Polycyclic aromatic hydrocarbons[f]** | | | | | | | | | |
| 1-methylphenanthrene | 0.00042 | 0.0010 | <MRL | 0.00068 | 0.0013 | 0.0041 | 0.0010 | 0.0030 | 0.17 |
| 2-methylphenanthrene | 0.00076 | 0.0020 | <MRL | 0.0012 | 0.0021 | 0.0060 | 0.0015 | 0.0047 | 0.30 |
| 3-methylphenanthrene | 0.00069 | 0.0020 | <MRL | 0.0012 | 0.0019 | 0.0066 | 0.0017 | 0.0048 | 0.27 |
| 9-ethylphenanthrene | 0.00034 | 0.00091 | <MRL | 0.00046 | 0.0013 | 0.0043 | 0.0012 | 0.0032 | 0.27 |
| Acenaphthene | 0.0048 | 0.011 | 0.00081 | 0.0046 | 0.0061 | 0.029 | 0.0034 | 0.0089 | 0.57* |
| Fluoranthene | 0.0010 | 0.0027 | <MRL | 0.0038 | 0.00098 | 0.012 | 0.00068 | 0.0015 | 0.49* |
| Fluorene | 0.0055 | 0.011 | 0.0011 | 0.0056 | 0.0081 | 0.028 | 0.0052 | 0.012 | 0.54* |
| Phenanthrene | 0.0086 | 0.017 | 0.0022 | 0.015 | 0.012 | 0.044 | 0.0097 | 0.018 | 0.48* |
| Pyrene | 0.00063 | 0.0019 | <MRL | 0.0019 | 0.00090 | 0.028 | 0.00071 | 0.00097 | 0.22 |
| **Phthalates[g]** | | | | | | | | | |
| Bis(2-ethylhexyl) adipate | 0.0023 | 0.0087 | 0.0015 | 0.0021 | 0.032 | 0.075 | 0.023 | 0.069 | 0.13 |
| Bis(2-ethylhexyl) phthalate | 0.017 | 0.24 | <MRL | 0.024 | 0.079 | 0.21 | 0.056 | 0.11 | –0.02 |
| **Other** | | | | | | | | | |
| Ammonia[b] | 3.0 | 32 | 0.67 | 2.0 | 24 | 180 | 7.9 | 32 | 0.03 |
| O-phenylphenol[c] | 0.0012 | 0.0048 | 0.00052 | 0.0010 | 0.0083 | 0.061 | 0.013 | 0.019 | –0.04 |

*Note*. MRL = method reporting limit (defined as the maximum of the analytical detection limit and the 90th percentile of the field blanks. Estimated values (i.e., quantified by the laboratory but below the MRL) were used in the calculation of summary statistics. Sources listed for each chemical class are based on cited literature and not specifically characterized in this study. Included are compounds measured at significantly ($P \leq .05$; Wilcoxon rank-sum test) higher concentrations in Richmond outdoor air than in Bolinas outdoor air.

[a] Spearman rank correlation coefficients.

[b] Sources: petroleum refining, agricultural activity, human and pet metabolic processes, and household cleaning products.[57,58]

[c] Sources: pesticides, disinfectants, preservatives, and other uncharacterized sources.[60,62]

[d] Sources: combustion sources including traffic, home heating, cigarette smoke, cooking, and candle burning.[52,55,56]

[e] Sources: petroleum refining, shipping, power generation, and other industrial activity; traffic; and crustal/soil.[52]

[f] Sources: combustion sources including traffic, power generation, home heating, cigarette and incense smoke, and cooking.[59]

[g] Sources: plastics, consumer products including cosmetics and pesticides, and other uncharacterized sources.[60,61]

*$P \leq .05$.

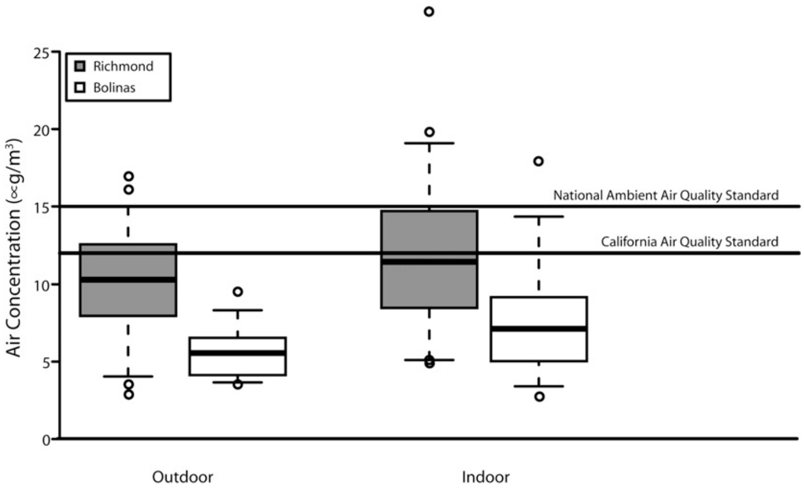
higher for refinery-related sulfates, vanadium, and ammonia and other industry- and transportation-related pollutants, including $PM_{2.5}$, PAHs, carbon fractions, and metals. Outdoor levels of 2 phthalates and *o*-phenylphenol were also significantly higher in Richmond (detailed results for EDCs will be published in an upcoming article).

Indoor air in nearly half of Richmond homes exceeded California's annual ambient air quality standard for $PM_{2.5}$, often considered an aggregate measure of air pollution; indoor levels were higher than outdoor levels in both communities (Figure 1). EDCs were detected more frequently indoors than outdoors in both communities.

### Indoor Penetration of Outdoor Pollutants

To examine the impact of outdoor pollutant emissions on indoor air, we evaluated relationships between paired outdoor and indoor measurements for the 33 chemicals measured at higher levels outdoors in Richmond. Figure 2 illustrates outdoor and indoor concentrations for an example outdoor-source and an example indoor-source pollutant. In the case of sulfates, a frequent by-product of industrial pollution with few indoor sources (Figure 2ab), there was a strong correlation ($r=0.92$; $P<.001$) between paired outdoor and indoor measurements, and outdoor concentrations were consistently higher than indoor concentrations, indicating that outdoor sulfates were penetrating indoors. Strong correlations between outdoor and indoor concentrations were observed for vanadium, selenium, calcium, iron, and manganese (Spearman $\rho$ range: 0.7–0.9; $P<.001$), and outdoor concentrations were higher than indoor concentrations.

Outdoor–indoor levels and correlations for $PM_{2.5}$, many of the PAHs (e.g., acenaphthene, fluorene, and fluoranthene), lanthanum, and elemental carbon (Spearman $\rho$ range: 0.4–0.6; $P<.05$) suggested both outdoor and indoor sources and indicated that outdoor air is an important source of these pollutants indoors. By contrast, there were high indoor levels of di-*n*-butyl phthalate, commonly found in personal care products, and a lack of correlation between paired outdoor and indoor measurements, indicating that indoor sources dominate (Figure 2cd). A similar pattern was observed for other EDCs, including bis(2-ethylhexyl) phthalate, bis(2-ethylhexyl) adipate, and *o*-phenylphenol, and for organic carbon fractions, ammonia, and some PAHs (e.g., pyrene and methylphenanthrenes).



*Note.* Solid lines are medians; boxes are interquartile ranges; vertical lines are 5th and 95th percentiles; circles are extreme data points below the 5th percentile and above the 95th percentile; and horizontal dotted lines represent annual federal and state ambient air quality standards for $PM_{2.5}$.

**FIGURE 1—Levels of fine particulate matter ($PM_{2.5}$) in homes in Richmond and Bolinas, CA: 2006.**

### Comparison With State Monitors

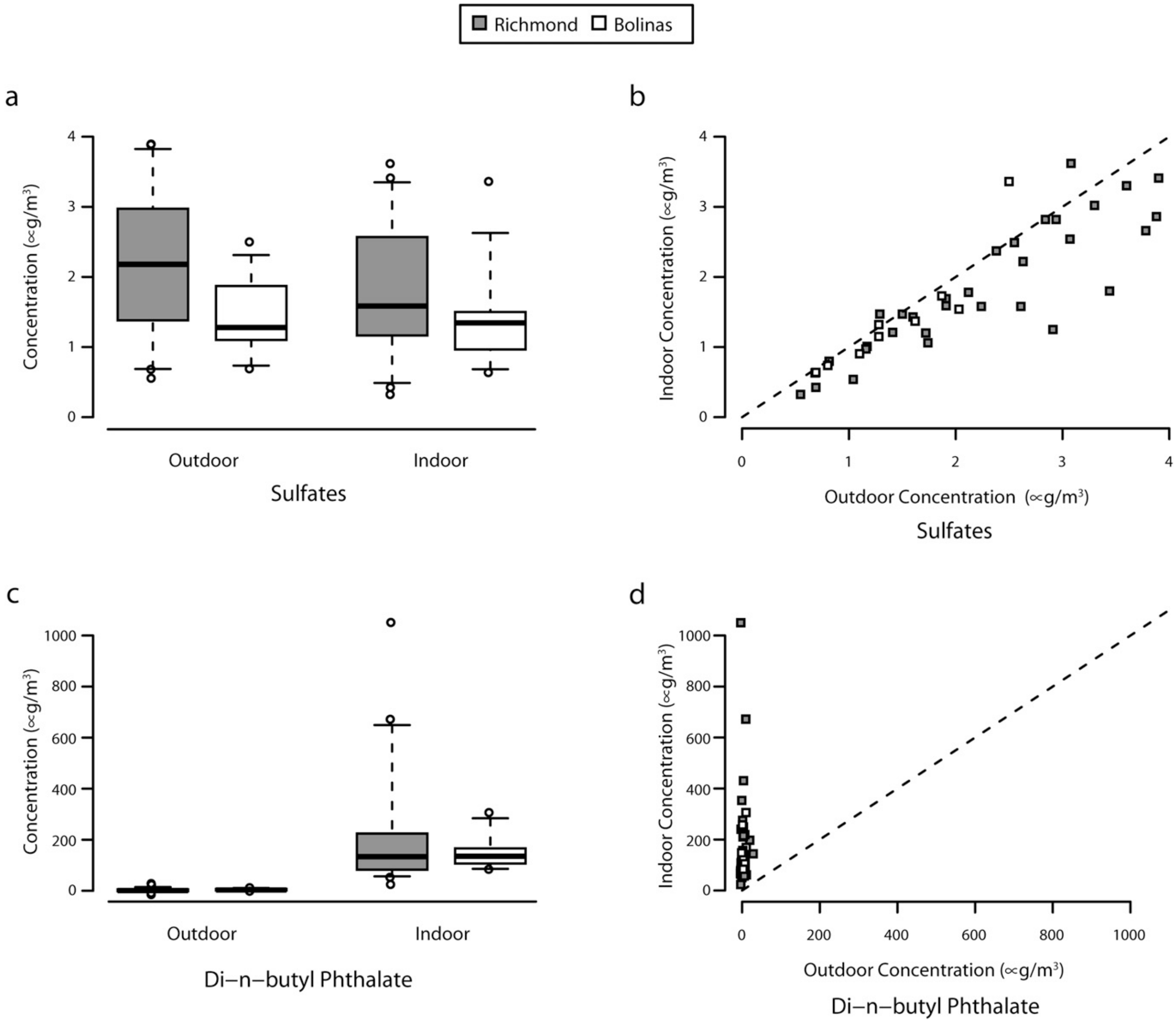
In another approach to analyzing the influence of local and regional outdoor sources, we compared outdoor measurements in Richmond and Bolinas with California Environmental Protection Agency monitoring data for the same time period as our study. For vanadium and nickel (which are markers of heavy oil combustion, especially from oil refineries and marine ports[52,63,64]), Richmond was near the top of the distribution, with the second-highest 95th percentile concentration. For sulfates, which tend to be influenced by both regional and local sources, including power plants, automobiles, and oil refineries, Richmond levels were in the top third.

In the case of pollutants such as $PM_{2.5}$, elemental and organic carbon, and nitrates deriving primarily from mobile sources, Richmond was in the lower half of the distribution. For sodium, a marker of ocean air, Richmond levels were among the highest of all monitoring sites. In Bolinas, levels for all pollutants were low, whereas sodium levels were comparable to those in Richmond. Results for vanadium, nickel, $PM_{2.5}$, and sulfates are shown in Figure 3, ordered according to 95th percentile concentrations.

## DISCUSSION

Our results provide evidence regarding 3 important environmental justice concerns: the character and magnitude of cumulative exposures in urban fence-line communities (communities that neighbor polluting facilities), the limitations of outdoor ambient monitoring as an indicator of personal exposure, and the impact of specific local sources on air quality in proximate neighborhoods. As expected, more pollutants and higher outdoor concentrations were detected in Richmond than in Bolinas. Heavy oil combustion was a more prominent factor than traffic in differences between the 2 communities. Despite high traffic in Richmond, outdoor concentrations of $PM_{2.5}$ and traffic-related pollutants were in the low half of the range reported by state monitors, perhaps as a result of meteorological effects of the study neighborhood's proximity to the coast.

By contrast, Richmond levels of nickel and vanadium (known to come from heavy oil combustion, especially in refinery operations



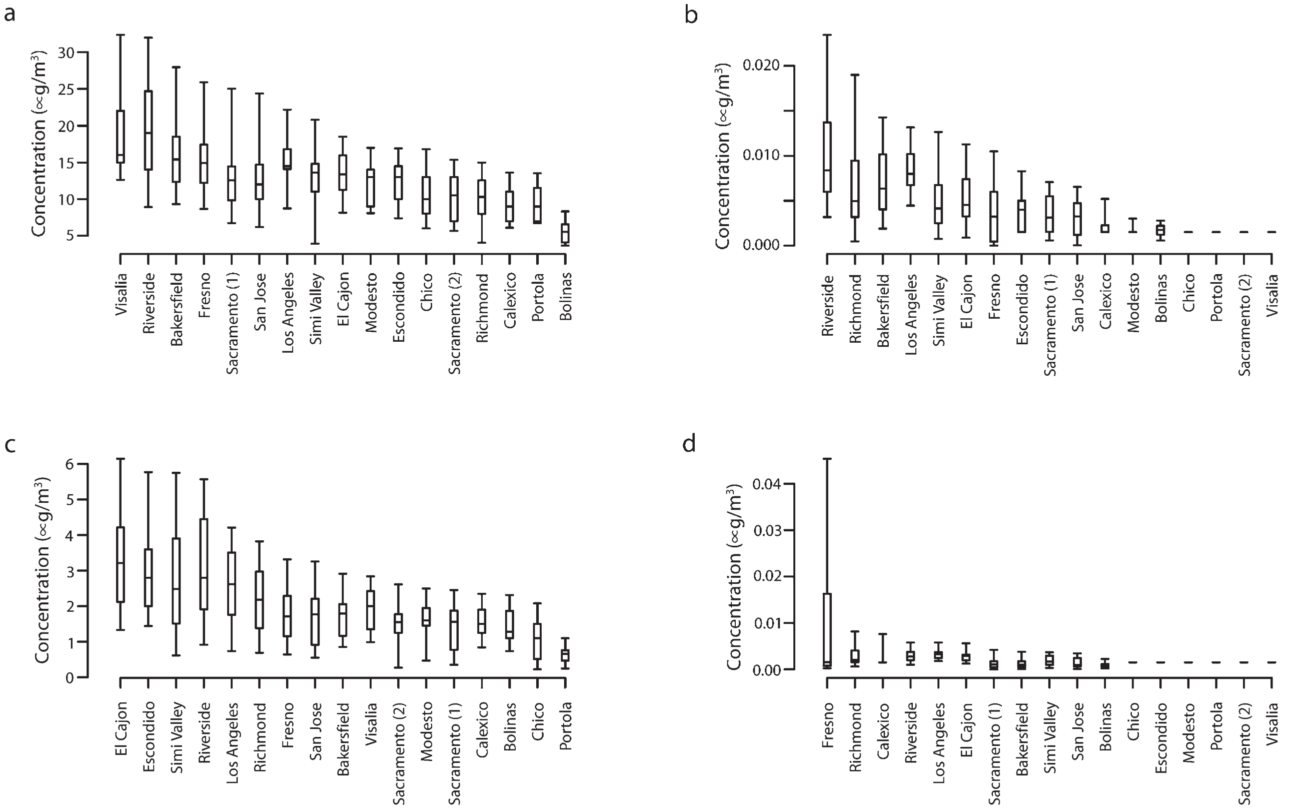
*Note*. Panels a and c are box plots comparing distributions for sulfates and di-*n*-butyl phthalate, respectively. Panels b and d show the correlations between indoor and outdoor concentrations across both communities. The dotted line represents 1:1.

**FIGURE 2—Relationships between (a) sulfates, (b) indoor and outdoor concentrations of sulfates, (c) di-*n*-butyl phthalate, and (d) indoor and outdoor concentrations in di-*n*-butyl phthalate: Richmond and Bolinas, CA, 2006.**

and marine shipping) were among the highest in the state. These compounds, along with sulfates (also associated with refineries), penetrated into Richmond homes, as demonstrated by correlations between outdoor and indoor concentrations. Health studies have shown that sulfates, nickel, and vanadium are some of the most harmful PM$_{2.5}$ components.[65,66] Furthermore, these compounds are indicators of probable exposures to hundreds of unmeasured compounds given that refinery emissions are complex and poorly characterized.[67,68]

The significant correlations we observed between outdoor and indoor levels of PM$_{2.5}$, sulfates, and other pollutants are consistent with the results of other studies showing that outdoor air pollution is an important determinant of indoor exposures.[31,59,69,70] The finding that local outdoor emissions penetrate indoors bears directly on Richmond refinery permits for activities that increase or decrease outdoor emissions, and our observations have implications for facility reviews elsewhere as well.

The much higher levels of pollutants indoors than outdoors indicate that traditional environmental impact assessments based on outdoor air quality are inadequate to represent personal exposures. California's ambient air quality standard is not intended to be applied to indoor air; however, it is of concern that



*Note*. Monitor locations are ranked according to the 95th percentile concentration in order of highest to lowest from left to right. Solid lines are medians; boxes are interquartile ranges; and vertical lines are 5th and 95th percentiles.

**FIGURE 3—Comparison of study site outdoor air pollution levels in Richmond and Bolinas, CA, with California state monitors, 2006.**

nearly half of Richmond homes exceeded this standard for $PM_{2.5}$ during the summer, when outdoor $PM_{2.5}$ levels are markedly lower than in winter. Epidemiological studies have consistently linked this pollutant to respiratory and cardiovascular problems, including premature death.[71] In addition, the PAHs and other compounds we detected may be associated with breast cancer.[20,21] Socioeconomic stressors in Richmond may amplify the detrimental health effects of chemicals we observed.[8,72]

Our results also have implications for policies concerning EDCs in consumer products. Outdoor levels were lower than and not correlated with indoor levels for chemicals coming primarily from consumer products, such as di-*n*-butyl phthalate. We observed few differences in EDC levels between our 2 markedly different communities. These results suggest that consumer products contribute substantially to indoor air quality and indicate the need for state or national remedies, such as the efforts of breast cancer organizations to secure proactive chemical policies and launch consumer campaigns to reduce the use of EDCs.[73,74]

Limitations of our study include the small number of homes sampled in Bolinas. Also, as a result of financial constraints, we sampled each home only once. Multiseason sampling would better characterize long-term, typical exposures and capture higher wintertime $PM_{2.5}$ levels. We were unable to collect samples directly representing emissions from refineries or other sources to compare with household contaminant profiles. In addition, although our study focused on a poor, largely Latino community, members of racial/ethnic minority groups and less educated residents were underrepresented in our sample. Finally, given the large number of comparisons of individual chemicals, some of our findings may be attributable to chance.

The strengths of the study include the use of a standard protocol in Richmond and Bolinas, the inclusion of paired indoor and outdoor samples and a broad range of analytes, comparability with state monitoring data, collaboration between diverse academic and community partners, and attention to individual and community communications regarding the study. Unlike environmental justice investigations of industrial and transportation pollution that typically rely on ambient air monitoring or facility emissions data, we collected unique local data on personal exposures in the home.

## Public Health Applications

During our study, refinery permit changes were proposed that could increase harmful pollutant emissions[45] in Richmond via the refining of higher sulfur crude oil. CBE mobilized testimony against the plan before the Richmond Planning Commission and the city council, urging them to consider the existing cumulative pollutant burdens documented in our study. News stories highlighted our results,[75,76] and city council members asked us to testify.[77] Study participants used their individual data and aggregate results in their own testimony, vividly demonstrating how our study helped activate and expand community engagement in environmental justice issues. At community meetings, discussions spontaneously turned to ways to use results to negotiate health protections from the oil company.

Testimony and media coverage of our findings led the Richmond Planning Commission to attempt to restrict high-sulfur crude oil refining. However, as gasoline prices climbed and the company offered Richmond $60 million in mitigation benefits, the city council reversed the planning commission's recommendation and approved the Chevron proposal in July 2008.[44] Thus, although our study influenced deliberations, the company's socioeconomic and political muscle in this cash-strapped city wielded a stronger influence. Later, the November 2008 election of new council members changed the balance again, and Richmond residents also passed a ballot measure that would require Chevron to pay the city an annual business license fee estimated at $26.5 million.

Although we cannot yet assess the significance of this study for CBE, we now have empirical results to support concerns about the effects of refinery emissions, and we know that CBE valued the study's process. As CBE staff conducted interviews and set up sampling equipment, the study helped demystify science by moving the data-gathering process into people's homes. That experience encouraged community members to think in new ways about sources of chemicals around them. These discussions enabled CBE to connect its organizing work with technical analysis—each central to environmental justice—and may strengthen CBE's long-term organizing and advocacy capacity.

This experience illustrates the CBPR view that both scientific outcomes and the research process are important. The future of the refinery expansion continues to unfold as CBE pursues a long-term mobilization effort that includes disseminating results from our study, engaging in litigation, and conducting a health symptoms survey with other neighborhood and environmental justice groups.

## Conclusions

Environmental justice assessments should consider indoor exposures from local polluters. In this study, we found that cumulative air pollution burdens were more pronounced indoors than outdoors in an urban industrial environmental justice community in comparison with a rural community. Indoor air in nearly half of the environmental justice community homes in our study exceeded the California ambient air quality standard for respirable particulates, even though the residents were nonsmokers. High levels of contaminants associated with oil refining and marine shipping were detected both outdoors and indoors. Participation in this CBPR study mobilized and supported community efforts to block permits for the neighboring oil refinery. Our results also can inform a variety of individual- and policy-level exposure reduction efforts and the design of future studies focusing on air pollutants and breast cancer and other health outcomes. ■

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## Contributors

J. Green Brody, R. Morello-Frosch, P. Brown, C. Pérez, and R.A. Rudel planned and supervised the study. J. Green Brody led the writing, with substantial contributions from the other authors. A. Zota conducted the statistical analysis and reported results to participants. All of the authors helped to conceptualize ideas and review drafts of the article.

## Acknowledgments

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We thank Jessica Tovar, Wanna Wright, Marleen Quint, and Andrea Samulon for contributions to planning the study, community organizing, and data collection and Allan Just, Sarah Dunagan, and Laura Perovich for additional research and outreach assistance. We thank the following advisory council members for their significant contributions to study design and communications: Asa Bradman of the University of California, Berkeley; Barbara Brenner of Breast Cancer Action; Raymond Neutra (then with the California Department of Public Health); Sharyle Patton of Commonweal; Jeanne Rizzo of the Breast Cancer Fund; and community members Marleen Quint and Wanna Wright, who also participated in conducting the study.

## Human Participant Protection

The research protocol was approved by Brown University's institutional review board. Participants provided informed consent prior to initiation of sample collection in their homes.

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## ERRATUM

In: Brody JG, Morello-Frosch R, Zota A, Brown P, Pérez C, Rudel RA. Linking exposure assessment science with policy objectives for environmental justice and breast cancer advocacy: the Northern California Household Exposure study. *Am J Public Health.* 2009;99(S3):S600–S609. doi: 10.2105/AJPH.2008.149088.

Figures and tables were improperly edited. On page S603, Table 1 should read:

**TABLE 1—Outdoor and Indoor Air Concentrations (μg/m$^3$) and Correlations for Compounds Detected at Higher Levels in Richmond Than in Bolinas, CA: 2006**

| | Outdoor Air | | | | Indoor Air | | | | Outdoor–Indoor Correlation[a]: Richmond |
|---|---|---|---|---|---|---|---|---|---|
| | Richmond | | Bolinas | | Richmond | | Bolinas | | |
| Chemical | Median | Maximum | Median | Maximum | Median | Maximum | Median | Maximum | |
| **Particulate matter and related carbon fractions[d]** | | | | | | | | | |
| PM$_{2.5}$ | 10 | 17 | 5.5 | 9.5 | 11 | 28 | 7.1 | 18 | 0.54* |
| Elemental carbon fraction 1 | 0.32 | 0.85 | 0.11 | 0.47 | 0.56 | 2.1 | 0.35 | 1.8 | 0.52* |
| Elemental carbon fraction 2 | 0.15 | 0.57 | < MRL | 0.45 | 0.23 | 0.70 | 0.088 | 0.46 | 0.78* |
| Total elemental carbon | 0.35 | 0.94 | 0.067 | 0.63 | 0.54 | 1.6 | 0.20 | 0.95 | 0.58* |
| Organic carbon fraction 1 | < MRL | 0.79 | < MRL | 1.1 | 2.1 | 6.3 | 1.8 | 3.5 | 0.03 |
| Organic carbon fraction 2 | 0.88 | 1.9 | < MRL | 1.4 | 3.4 | 5.2 | 2.6 | 6.5 | 0.20 |
| Organic carbon fraction 3 | 0.87 | 1.9 | 0.55 | 1.2 | 3.2 | 8.0 | 2.8 | 9.0 | < 0.01 |
| Organic carbon fraction 4 | 0.32 | 0.77 | 0.11 | 0.61 | 1.1 | 2.9 | 0.87 | 2.3 | 0.01 |
| Total organic carbon | 2.1 | 4.8 | < MRL | 4.7 | 10 | 17 | 8.3 | 22 | 0.08 |
| Total carbon | 2.7 | 5.7 | < MRL | 5.3 | 11 | 19 | 8.5 | 23 | 0.14 |
| **Metals and ions[e]** | | | | | | | | | |
| Aluminum | 0.021 | 0.090 | 0.0092 | 0.086 | 0.023 | 0.11 | 0.030 | 0.25 | 0.50* |
| Calcium | 0.090 | 0.37 | < MRL | 0.053 | 0.093 | 0.28 | 0.045 | 0.11 | 0.81* |
| Copper | < MRL | 0.055 | < MRL | 0.0094 | < MRL | 0.054 | < MRL | 0.023 | 0.05 |
| Iron | 0.063 | 0.24 | < MRL | 0.034 | 0.055 | 0.32 | 0.028 | 0.15 | 0.79* |
| Lead | 0.0010 | 0.0040 | < MRL | 0.0017 | 0.0012 | 0.0041 | < MRL | 0.0015 | 0.62* |
| Manganese | 0.0020 | 0.0080 | < MRL | 0.0012 | 0.0015 | 0.0062 | 0.0013 | 0.0030 | 0.78* |
| Nitrates | 1.0 | 3.2 | 0.34 | 0.84 | 0.95 | 3.3 | 0.25 | 1.1 | 0.62* |
| Potassium | 0.051 | 0.11 | 0.018 | 0.062 | 0.050 | 0.21 | 0.033 | 0.11 | 0.46* |
| Sulfates | 2.2 | 3.9 | 1.3 | 2.5 | 1.6 | 3.6 | 1.4 | 3.4 | 0.91* |
| Vanadium | 0.0050 | 0.023 | 0.0018 | 0.0028 | 0.0035 | 0.020 | 0.0016 | 0.0023 | 0.93* |
| **Polycyclic aromatic hydrocarbons[f]** | | | | | | | | | |
| 1-Methylphenanthrene | 0.00042 | 0.0010 | < MRL | 0.00068 | 0.0013 | 0.0041 | 0.0010 | 0.0030 | 0.17 |
| 2-Methylphenanthrene | 0.00076 | 0.0020 | < MRL | 0.0012 | 0.0021 | 0.0060 | 0.0015 | 0.0047 | 0.30 |
| 3-Methylphenanthrene | 0.00069 | 0.0020 | < MRL | 0.0012 | 0.0019 | 0.0066 | 0.0017 | 0.0048 | 0.27 |
| 9-Methylphenanthrene | 0.00034 | 0.00091 | < MRL | 0.00046 | 0.0013 | 0.0043 | 0.0012 | 0.0032 | 0.27 |
| Acenaphthene | 0.0048 | 0.011 | 0.00081 | 0.0046 | 0.0061 | 0.029 | 0.0034 | 0.0089 | 0.57* |
| Fluoranthene | 0.0010 | 0.0027 | < MRL | 0.0038 | 0.00098 | 0.012 | 0.00068 | 0.0015 | 0.49* |
| Fluorene | 0.0055 | 0.011 | 0.0011 | 0.0056 | 0.0081 | 0.028 | 0.0052 | 0.012 | 0.54* |
| Phenanthrene | 0.0086 | 0.017 | 0.0022 | 0.015 | 0.012 | 0.044 | 0.0097 | 0.018 | 0.48* |
| Pyrene | 0.00063 | 0.0019 | < MRL | 0.0019 | 0.00090 | 0.028 | 0.00071 | 0.00097 | 0.22 |
| **Phthalates[g]** | | | | | | | | | |
| Bis(2-ethylhexyl) adipate | 0.0023 | 0.0087 | 0.0015 | 0.0021 | 0.032 | 0.075 | 0.023 | 0.069 | 0.13 |
| Bis(2-ethylhexyl) phthalate | 0.017 | 0.24 | < MRL | 0.024 | 0.079 | 0.21 | 0.056 | 0.11 | −0.02 |
| **Other** | | | | | | | | | |
| Ammonia[b] | 3.0 | 32 | 0.67 | 2.0 | 24 | 180 | 7.9 | 32 | 0.03 |
| o-Phenylphenol[c] | 0.0012 | 0.0048 | 0.00052 | 0.0010 | 0.0083 | 0.061 | 0.013 | 0.019 | −0.04 |

*Note.* MRL = method reporting limit (defined as the maximum of the analytical detection limit and the 90th percentile of the field blanks. Estimated values (i.e., quantified by the laboratory but below the MRL) were used in the calculation of summary statistics. Sources listed for each chemical class are based on cited literature and not specifically characterized in this study. Included are compounds measured at significantly ($P \leq .05$; Wilcoxon rank-sum test) higher concentrations in Richmond outdoor air than in Bolinas outdoor air.

[a] Spearman rank correlation coefficients.

[b] Sources: petroleum refining, agricultural activity, human and pet metabolic processes, and household cleaning products.[57,58]

[c] Sources: pesticides, disinfectants, preservatives, and other uncharacterized sources.[60,62]

[d] Sources: combustion sources including traffic, home heating, cigarette smoke, cooking, and candle burning.[52,55,56]

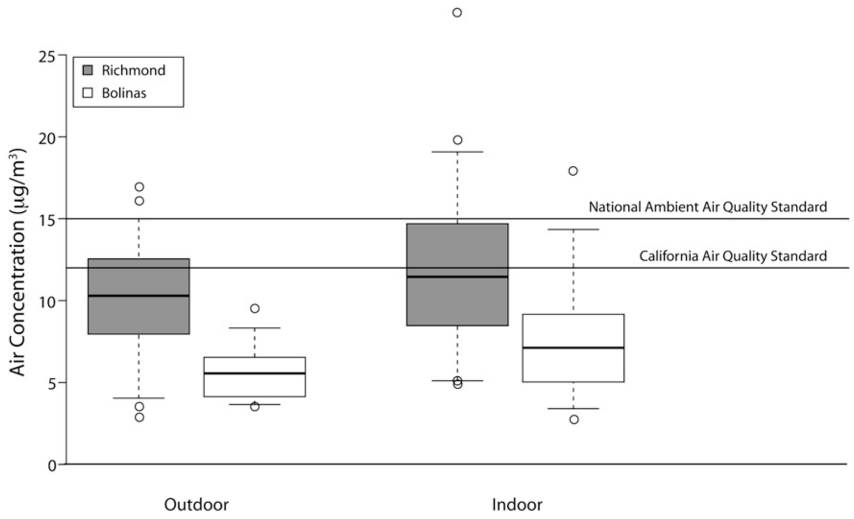
[e] Sources: petroleum refining, shipping, power generation, and other industrial activity; traffic; and crustal/soil.[52]

[f] Sources: combustion sources including traffic, power generation, home heating, cigarette and incense smoke, and cooking.[59]

[g] Sources: plastics, consumer products including cosmetics and pesticides, and other uncharacterized sources.[60,61]

*$P \leq .05$.

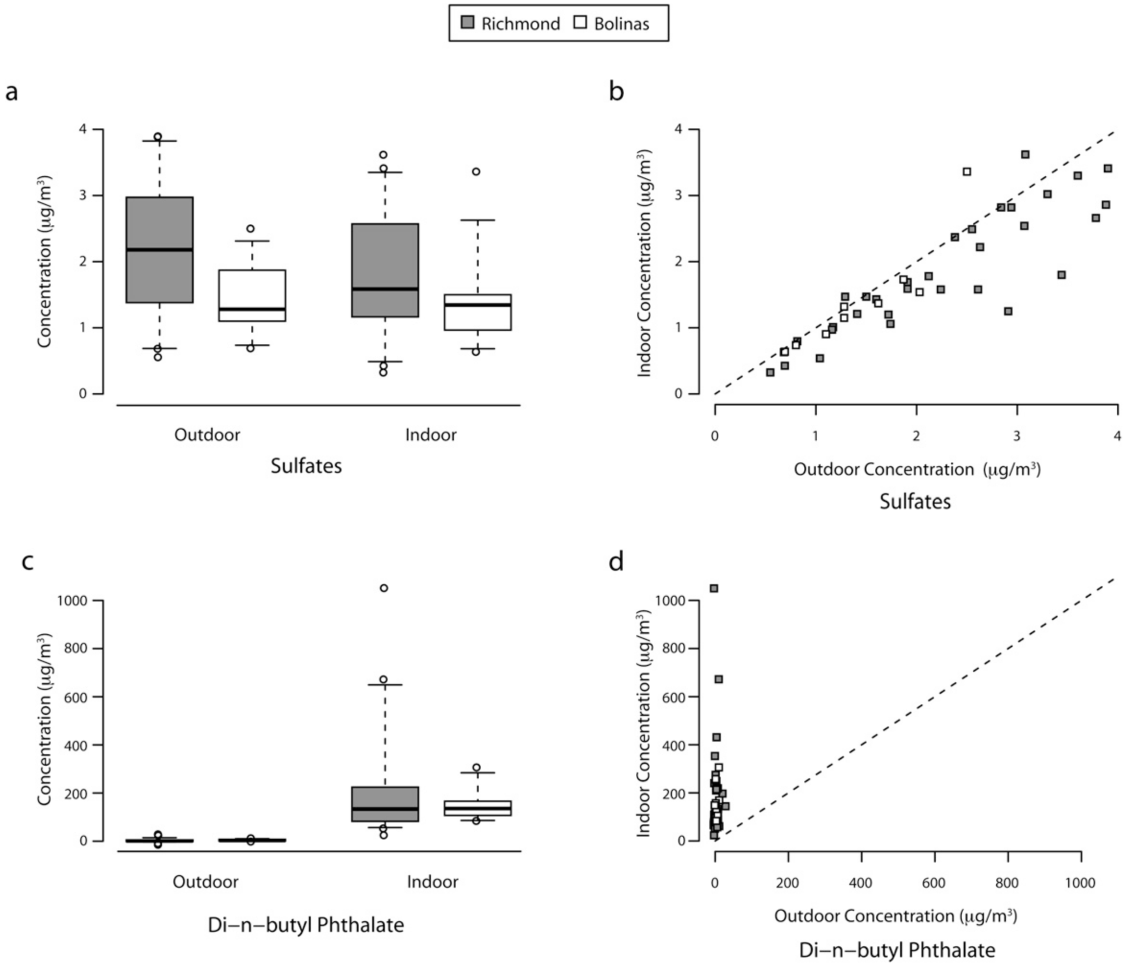
On page S604, Figure 1 should be:



*Note.* Solid lines are medians; boxes are interquartile ranges; vertical lines are 5th and 95th percentiles; circles are extreme data points below the 5th percentile and above the 95th percentile; and horizontal dotted lines represent annual federal and state ambient air quality standards for $PM_{2.5}$.

**FIGURE 1—Levels of fine particulate matter ($PM_{2.5}$) in homes in Richmond and Bolinas, CA: 2006.**

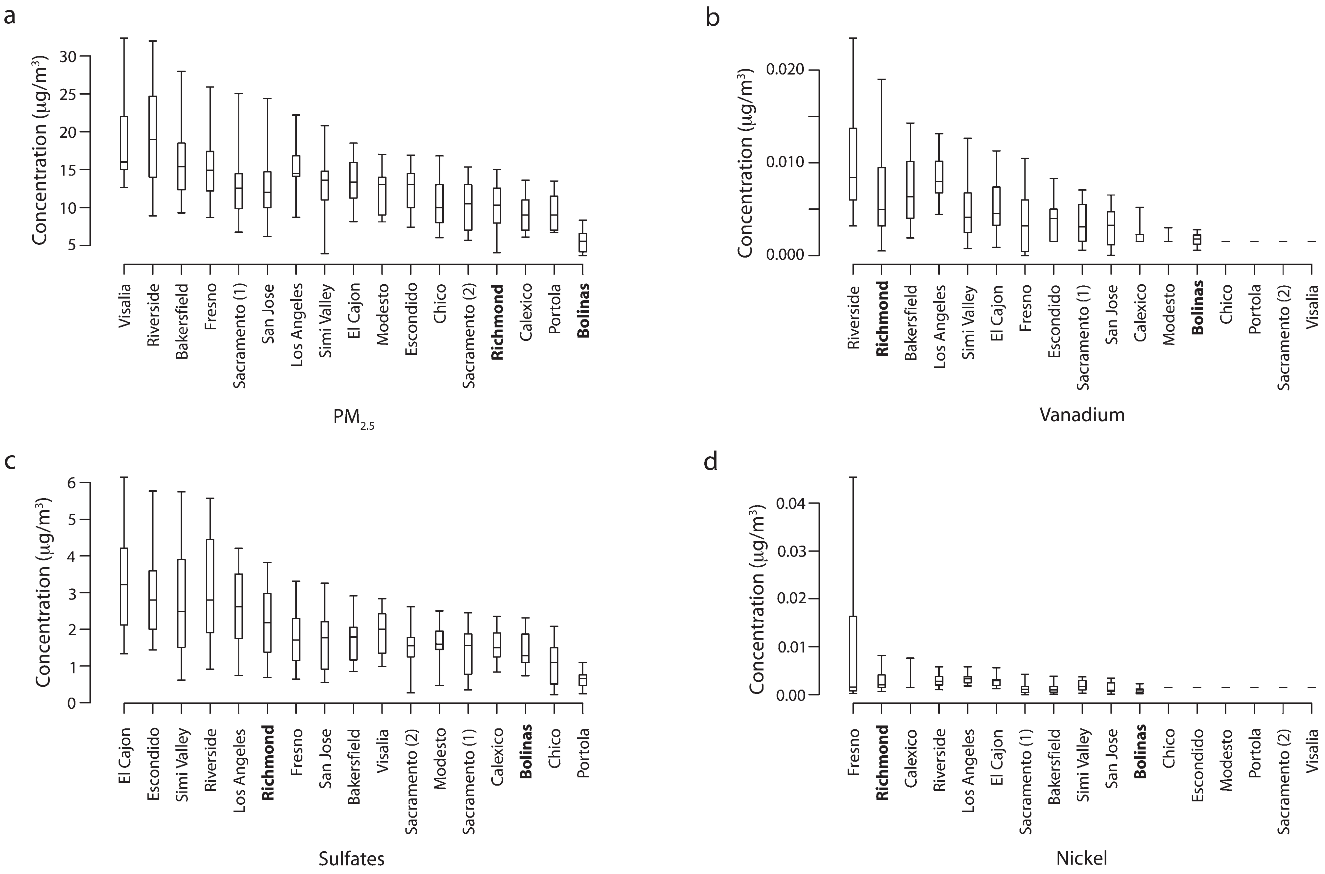
On page S605, Figure 2 should be:



*Note*. Panels a and c are box plots comparing distributions for sulfates and di-*n*-butyl phthalate, respectively. Panels b and d show the correlations between indoor and outdoor concentrations across both communities. The dotted line represents 1:1.

**FIGURE 2—Relationships between (a) sulfates, (b) indoor and outdoor concentrations of sulfates, (c) di-*n*-butyl phthalate, and (d) indoor and outdoor concentrations in di-*n*-butyl phthalate: Richmond and Bolinas, CA, 2006.**

On page S606, Figure 3 should be:



*Note*. Monitor locations are ranked according to the 95th percentile concentration in order of highest to lowest from left to right. Solid lines are medians; boxes are interquartile ranges; and vertical lines are 5th and 95th percentiles.

**FIGURE 3—Comparison of Richmond and Bolinas, CA, with California state monitor outdoor air pollution levels of (a) $PM_{2.5}$, (b) vanadium, (c) sulfates, and (d) nickel: 2006.**

doi:10.2105/AJPH.2008.149088e

**Attachment 45**

# Flaring Hot Spots

## A CBE Report

Assessment of episodic local air pollution associated with oil refinery flaring using sulfur as a tracer

July 2005

# Flaring Hot Spots

## Assessment of episodic local air pollution associated with oil refinery flaring using sulfur as a tracer.

A CBE report
July 2005

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Julia May initiated the research effort this report builds upon, wrote CBE's 2004 report *Refinery Flaring in the Neighborhood,* and continues to support CBE's flare campaign with her technical expertise. CBE also thanks the staffs of the Bay Area Air Quality Management District and California Air Resources Board for their cooperation and guidance in accessing public documents with detailed refinery flaring and air quality data. CBE is responsible for all findings and conclusions of the report.

### CBE

Founded in 1978, **Communities for a Better Environment** (CBE) is an environmental health and justice organization that works with urban communities directly affected by industrial pollution. CBE provides organizing skills and legal, technical and scientific resources that assist communities in taking control of the decisions that affect their quality of life. We believe that environmental health is a human right, fundamental change comes from the grass roots up, and that environmental solutions can only be sustained in concert with social and economic justice.

## Contents

## Appendices

Data tables bound separately or available electronically:

Appendix 1. Chevron-Richmond data. Daily maximum-hour concentrations at ground-level monitors (GLMs) and 7th Street-Richmond, standard cubic feet of gas flared and flare SOx emissions.

Appendix 2. ConocoPhillips-Rodeo data. Daily maximum-hour concentrations at GLMs and Crockett-Rodeo stations, standard cubic feet of gas flared and flare SOx emissions.

Appendix 3. Shell-Martinez data. Daily maximum-hour $SO_2$ concentrations at Jones Street station, standard cubic feet of gas flared and SOx emissions.

Appendix 4. Tesoro-Avon data. Daily maximum-hour concentrations at GLMs, standard cubic feet of gas flared and SOx emissions.

Appendix 5. Valero-Benicia data. Daily maximum-hour concentrations at GLMs, standard cubic feet of gas flared and SOx emissions.

Appendix 6. Hourly $SO_2$ concentrations at Chevron GLMs and 7th Street-Richmond, and data reported by Chevron to BAAQMD for hourly total volumes and daily percent hydrogen sulfide in vent gases sent to three flares during April 21-22, 2004.

## Tables

## Figures

## Summary and discussion

This report documents localized episodic air pollution associated with flaring by Bay Area oil refineries. The new findings are timely, because on July 20, 2005, the Bay Area Air Quality Management District plans to consider adopting what could become the first rule in the nation that comprehensively targets refinery gas disposal in flares.

When refineries flare, nearby residents report foul odors, burning eyes and asthma attacks, among other symptoms of exposure to episodic air pollution. Oil refiners, however, dispute the need for enforceable flare control rules. Their spokespeople point to smog problems in areas miles from the refineries and say that automobile emissions, not refinery flares, cause most of that smog. Meanwhile, data from years of continuous monitoring at refinery fence lines for two pollutants emitted by flares–sulfur dioxide and hydrogen sulfide–sit ready for comparison with the new monitoring of flare emissions that has been required by the Air District in recent years.

This report assesses whether newly available data 1) support community observations of episodically elevated air pollutant exposures associated with flaring, 2) identify changes in flaring that affect local air quality, and 3) support a quantitative estimate of locally increased episodic air pollution caused by flaring. Its purpose is to provide new information on these issues to the public and public officials as the Air District considers its proposed flare control rule. Flare data needed for comprehensive comparisons across the five refineries were reported only recently. CBE first received the fence line air data analyzed here in June, 2005. To our knowledge, this is the first assessment pairing these emission and air quality data.

The report assesses flare data over a cumulative five-refinery total of 3,233 days during parts of 2001 and 2002 and from January 1, 2004–March 31, 2005. It matches these data with 510,978 hourly data from 35 ground-level monitors at the refinery fence lines and 3,675 daily maximum-hour data from five ambient air monitoring network stations near three refineries. It assesses whether this official monitoring record supports community observations of an episodic pollution problem caused by flaring, by comparing changes in flare emissions with changes in sulfur dioxide and hydrogen sulfide concentrations at the two types of monitoring locations using analysis of maxima, percentiles, ranks, probability analysis, and regression analysis.

These data and analyses support five major findings:

Finding 1. During major flaring at two refineries, ambient monitoring network stations in nearby communities, but set away from the refinery fence lines, measured sulfur gases in the air at record-high levels for those stations while ground-level monitors closer to the flares measured even higher levels at the refinery fence lines. These fence line monitors consistently recorded higher maximum levels of sulfur gases than the ambient network stations. This evidence documents episodic air pollution hot spots near the fence lines of these refineries, and implicates flaring as a major source of episodic air pollution.

Finding 2. Each refinery flared on the very day when sulfur pollution reached its record-high level in the air near that particular refinery. At four refineries, the 28 highest daily maximum-hour concentrations were all recorded on days when the refinery near that monitor flared. The probability that this occurred because of random chance alone is less than one in a billion.

Finding 3. Increasing sulfur dioxide concentrations in the air near four refineries are associated with increasing sulfur emissions from their flares. This association is significant at the 99% confidence level for flare emissions concentration ($p = 0.0001$) and mass ($p = 0.0013$), and applies to the highest eight percent of daily maximum-hour concentrations during 2004 and early 2005 at the Chevron, ConocoPhillips, Tesoro and Valero refineries.

Finding 4. Continued flaring at current rates can be predicted to increase highest daily maximum-hour sulfur dioxide concentrations near refinery fence lines by an average of about 50%. This estimate is based on the findings above, and on a comparison of the highest hourly concentrations measured near four refineries when no flaring occurred with the higher levels measured on days the refinery flared.

Finding 5. Except for sulfur dioxide and hydrogen sulfide, present monitoring can not detect and quantify any of the other toxic pollutants in episodic flare plumes at most refinery fence lines–and health risk can not be estimated accurately while ignoring unmeasured pollutants. Until these other pollutants are monitored continuously at refinery fence lines, sulfur can be used as a tracer for the short-term movement of flare plumes to the refinery fence line. This analysis suggests that flares cause episodic local exposures to many pollutants.

The findings support the adoption of enforceable requirements to prevent and reduce flaring as a matter of environmental justice for disproportionately impacted low-income communities on refinery fence lines. Bay Area refinery flaring impacts local air quality. Analysis based on data from 2004 and early 2005 shows that these impacts are ongoing.

This report sheds new light on key policy details as well. The analysis supporting Finding 3 found that pollutant mass and concentration in flare emissions predicts changes in local air quality caused by a flaring episode more reliably than does the volume of gases flared. Requirements based on flare gas volume alone–such as the proposed 500,000 cubic feet/day trigger for remedial investigation (root cause analysis) of flare episodes–are not a reliable substitute for a limit on the concentration of sulfur in the fuel gas that is flared. This supports requirements to limit the sulfur concentration allowed in fuel gas flared, and to perform root cause analysis of high-mass emission flaring–especially at low gas flows.

Lastly, the findings suggest an issue for future assessment. The data might be used to confirm the effectiveness of efforts to stop unnecessary flaring in cleaning up local air quality. CBE received the ground-level monitor data assessed in this report recently, and could not complete this last assessment before the July 20, 2005 policy decision.

## Scope, data, methods and limitations

This report compares measurements of flaring activity and intensity at five major Bay Area refineries with the continuous monitoring of two pollutants in the air near the plants to assess flaring impacts on local air quality. It assesses whether these data 1) support community observations of episodically elevated air pollutant exposures associated with flaring, 2) identify changes in flaring that affect local air quality, and 3) support a quantitative estimate of locally increased episodic air pollution caused by flaring.

The purpose of the report is to provide new information on these issues to the public and public officials as the Bay Area Air Quality Management District (BAAQMD) considers adoption of the first emission control rule comprehensively targeting the use of flares for refinery gas disposal. Flare data needed for comprehensive comparisons across the five refineries were reported only recently, and the fence line air data in this report were first obtained by CBE in June, 2005. To our knowledge, this is the first assessment pairing these emission and air quality data.

Data are from four sources. Flare data for the period from January 1, 2004 through March 31, 2005 are from refiners' reports under new BAAQMD Rule 12-11. Flare data for the period before Rule 12-11 are from the BAAQMD Technical Assessment Document for further study of flares. Hourly average ambient air monitoring data from sulfur dioxide ($SO_2$) and hydrogen sulfide ($H_2S$) measurements at ground-level monitors (GLMs) around the refinery fence lines are from BAAQMD documents provided for CBE's review pursuant to the California Public Records Act. Daily maximum-hour data for these pollutants that were collected at ambient air quality monitoring network stations, established by air quality agencies, operating near three of the refineries during the period studied are from Air Resources Board (ARB) public data reports.

Descriptive statistics summarizing these data are shown in Table 1 below. Air data from monitors near each refinery are included for the same dates when daily data on flare gas flow and sulfur content are available from that refinery. The period of this comparison starts earlier for the Chevron-Richmond and ConocoPhillips-Rodeo/Crockett comparisons because flare data reporting including sulfur data began earlier for these plants.

Review of Table 1 reveals large data sets. Flare activity and nearby ambient concentrations of $SO_2$ and $H_2S$ were monitored continuously across five refineries and 40 monitors for a cumulative total of 3,233 days. Flaring was reported on 1,895 of these days. Volumes of refinery gases flared, flare sulfur data, and hourly average air concentrations are used in the comparisons.

Data were compared across the entire time periods shown in Table 1, and for the period from January 1, 2004 through March 31, 2005. These daily flaring data are matched with the

**Table 1. Summary description of data used in this report.**

| | **Chevron** | **ConocoPhillips** | **Shell** | **Tesoro** | **Valero** |
|---|---|---|---|---|---|
| **Period flare gas & sulfur data reported** | 5/1/01-7/8/02 & & 1/1/04-3/3105 | 1/1/02-8/31/02 & 1/1/04-3/3105 | 6/1/02-8/31/02` & 1/1/04-3/3105 | 6/1/02-8/31/02 & 1/1/04-3/3105 | 6/1/02-8/31/02 & 1/1/04-3/3105 |
| **Total days** | 890 | 699 | 548 | 548 | 548 |
| **Flare days** | 317 | 238 | 548 | 350 | 442 |
| **Ground-level $SO_2$ monitors** | 3 | 7 | 1 | 3 | 3 |
| **Hourly data** | 61,448 | 85,593 | — | 38,889 | 38,705 |
| **Ground-level $H_2S$ monitors** | 3 | 4 | 4 | 4 | 3 |
| **Hourly data** | 61,584 | 80,811 | 52,414 | 52,078 | 39,456 |
| **Ambient network $SO_2$ stn.** | 7th Street Richmond | Kendall Ave.. Crockett | Jones Street Martinez | None nearby | None nearby |
| **Max/day data** | 890 | 695 | 546 | 0 | 0 |
| **Ambient network $H_2S$ stn.** | 7th Street Richmond | Crockett &/or Rodeo 3rd St. | None nearby | None nearby | None nearby |
| **Max/day data** | 882 | 662 | 0 | 0 | 0 |

Flare data from BAAQMD Technical Assessment Document and Rule 12-11 reports. GLM data from BAAQMD response to Public Records Act request. Network monitoring data from ARB. Daily data in appendices 1-6.

daily maximum-hour $SO_2$ and $H_2S$ concentrations measured near each refinery. All data inputs to this analysis are data as reported in the four data sources discussed above. Data inputs were double-checked for accuracy. All data inputs for each analysis were checked by the primary researcher. A random sample of the input data base was then checked independently by a second researcher. Both checks supported the accuracy of data inputs to the analysis. The daily data are shown for each refinery in appendices 1-5. Hourly data assessed for one flaring episode are shown in Appendix 6.

Analysis was done in three ways. First, air concentrations at ground-level monitors were compared with those at nearby ambient network stations to identify patterns in air quality related to flaring. Second, air concentrations measured at monitors near each refinery on days when the refinery flared were compared with those measured at the same location on days when no flaring was reported at the plant. Patterns identified from this second comparison were assessed for significance using probability analysis. Third, changes in $SO_2$ concentrations near each refinery were compared with changes in its flare gas flow, sulfur mass emission, and emission concentration using regression analysis. This third comparison was performed on the highest 10th Percentile of air concentration data, to elucidate effects at high pollution levels. $SO_2$ is the major sulfur compound expected in flare emissions, and results of the other analyses suggest that limitations in the data are less likely to mask any real effects of changes in flaring on $SO_2$ than on $H_2S$.

The data are limited by the number of air monitoring locations, the accuracy of the flare emission estimates, and the number of pollutants measured. Too few nearby monitors are in place to ensure that all the flare plumes are detected. There is no appropriately situated ambient monitoring network station near the Tesoro or Valero plants. No network station near Shell measures hydrogen sulfide, and the Shell refinery has only one $SO_2$ GLM. False-negative results are apparent in the data for some periods during large flaring episodes, and the association between flaring and air quality appears less robust at refineries with fewer monitors. In the most extreme case, the lone ground-level $SO_2$ monitor at Shell never detected measurable $SO_2$ despite episodically elevated $H_2S$ concentrations at Shell's $H_2S$ GLMs, episodically-elevated $SO_2$ at the nearby network station, and occasional major flaring. Shell's flare emission pattern also differs from those of other refiners, and it flared virtually every day in the flare data period. Since there is no other $SO_2$ GLM at Shell, these apparently conflicting data for Shell are difficult to interpret.

Because of these limitations, the comparison of GLMs with corresponding network stations is limited to the Chevron-Richmond and ConocoPhillips-Rodeo/Crockett data sets, and data on nearby air quality could not be analyzed for days when Shell did not flare.

Flare data accuracy for the period before January 2004 is inconsistent, and though flare gas volume is reported hourly starting in 2004, data for fuel gas quality and sulfur are reported as daily averages throughout the flare data period in most cases. Due to these limitations regression is performed using the 2004-2005 data, and using daily rather than hourly data.

Lack of flare combustion efficiency measurements–a problem in estimating hydrocarbon emissions–is not a significant limitation for this analysis because flare combustion does not destroy sulfur. Both $SO_2$ and $H_2S$ emit from flares, with $SO_2$ the major sulfur compound emitted unless combustion efficiency is very poor. While a drop from 98% to 96% combustion efficiency results in doubling hydrocarbon emissions, it should cause only a small drop in the percentage of sulfur compounds emitted as $SO_2$, and no change in total sulfur emissions.

The ground-level monitors do not measure any other pollutant in flare emissions besides $SO_2$ and $H_2S$. Flares emit smog-forming hydrocarbons, nitrogen oxides, and toxic chemicals such as benzene, toluene, xylenes, carbon-disulfide, PAHs, mercury, carbon monoxide, particulate matter and other air pollutants. The health threat from flaring is the cumulative toxicity of all the pollutants emitted, and it is not appropriate to ignore unmeasured pollutants, so this is a significant limitation in the data. Fortunately, this limitation can be mitigated because different gases may be expected to move initially from a stack to a nearby receptor along similar paths–and $SO_2$ and $H_2S$ are measured at fence line as gases. The crucial point: sulfur gases can serve as a tracer for other toxic gases in flare plumes at the fence line.

## Concentrated episodic air pollution near refineries

Maximum hourly-average air pollutant levels (highest hour of the day) are higher at refinery fence line monitors than at comparable nearby ambient monitoring network stations.

Table 2 below compares statistics describing the highest daily maximum-hour concentrations measured at two refiners' ground-level monitors with those measured at the network station near each refinery. It compares sulfur dioxide ($SO_2$) concentrations, then compares levels of hydrogen sulfide ($H_2S$). Chevron GLM levels are three times network monitor levels for both pollutants. ConocoPhillips GLM levels are twice the network levels for $SO_2$ and 50-254% higher for $H_2S$. Averaged across all statistics in Table 2, the fence line monitor levels are 248% higher than the network monitor levels.

These data reveal episodically elevated maximum pollution levels at the refiners' fence lines.

A pollution gradient extends from the fence lines of these two refineries to the ambient network stations. On 16 of the 20 days when the highest daily maximum-hour $SO_2$ levels were found at the Richmond and Crockett stations, maximum-hour $SO_2$ levels were higher at the GLMs, and on 12 of these days the refinery near the station flared. These 12 days include the single highest maximum daily hour for $SO_2$ at each network station, as detailed below.

**Table 2. Highest daily maximum-hour sulfur dioxide and hydrogen sulfide concentrations at ground-level monitors and ambient air quality monitoring network stations where both types of stations are located near a refinery.**

| **Sulfur dioxide** | **Chevron GLMs** | **7th Street Richmond** | **Percent change** |
|---|---|---|---|
| **95th Percentile** | 50.55 ppb | 12.00 ppb | 321% |
| **99th Percentile** | 71.11 ppb | 19.00 ppb | 274% |
| **Maximum** | 125 ppb | 39 ppb | 221% |
| | **ConocoPhillips GLMs** | **Kendall Ave.-Crockett** | **Percent change** |
| **95th Percentile** | 55.00 ppb | 15.00 ppb | 267% |
| **99th Percentile** | 90.10 ppb | 33.06 ppb | 173% |
| **Maximum** | 215 ppb | 50 ppb | 330% |

| **Hydrogen sulfide** | **Chevron GLMs** | **7th Street Richmond** | **Percent change** |
|---|---|---|---|
| **95th Percentile** | 8.00 ppb | 2.00 ppb | 300% |
| **99th Percentile** | 14.00 ppb | 3.00 ppb | 367% |
| **Maximum** | 22 ppb | 6 ppb | 267% |
| | **ConocoPhillips GLMs** | **Crockett / Rodeo[a]** | **Percent change** |
| **95th Percentile** | 3.00 ppb | 2.00 ppb | 50% |
| **99th Percentile** | 10.00 ppb | 4.00 ppb | 150% |
| **Maximum** | 46 ppb | 13 ppb | 254% |

Based on continuous monitoring for 890 days ($SO_2$) and 882 days ($H_2S$) in Richmond and for 695 days ($SO_2$) and 662 days ($H_2S$) in Rodeo-Crockett during the periods shown in Table 1, and data from BAAQMD and ARB. See appendices 1-5. [a] $H_2S$ site shifted from Crockett-Pomona to Rodeo-Third St. station during the period.

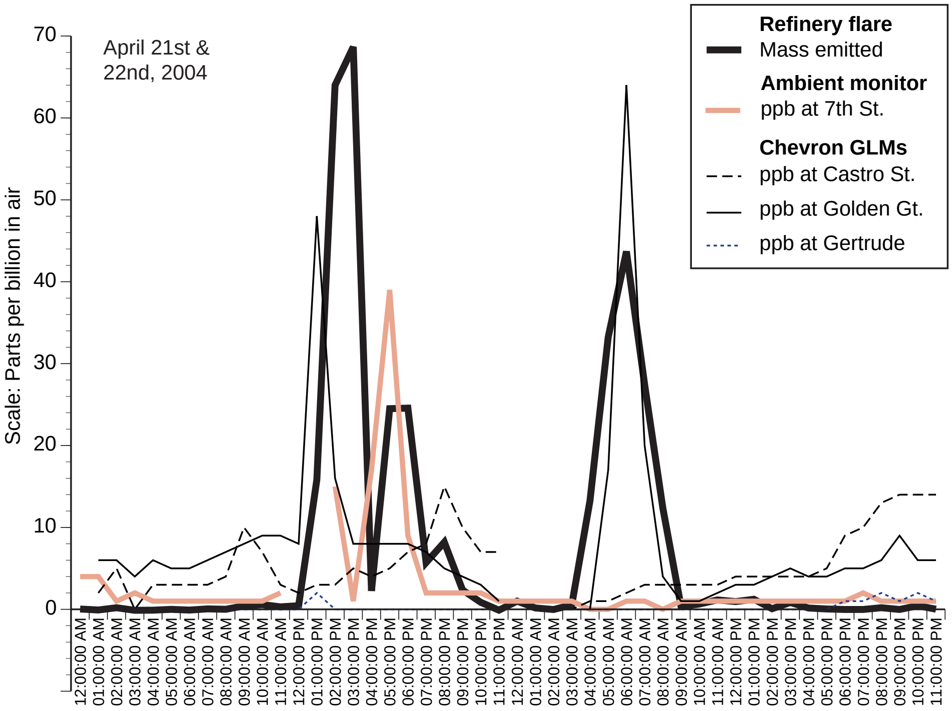
## Highest-hour air pollution on flaring days

All the worst hours of air pollution with sulfur compounds, near every refinery and throughout the flare data period, were on days when the refinery near the monitor flared.

Figure 1 below illustrates one example of this finding. The figure plots the hourly change in flare sulfur emissions (thick black line), and sulfur dioxide concentrations in air (other lines). It shows two days including the highest maximum hour recorded during the flare data period at the 7th Street-Richmond ambient monitoring network station. The ambient monitor peaked at 39 ppb on April 21, 2004 while Chevron's flares emitted 7,500 pounds of $SO_2$ that day. Hourly concentrations of $SO_2$ in air are plotted for each ground-level monitor at the refinery as well as for the 7th Street monitor. High concentrations appear in the chart as vertical peaks.

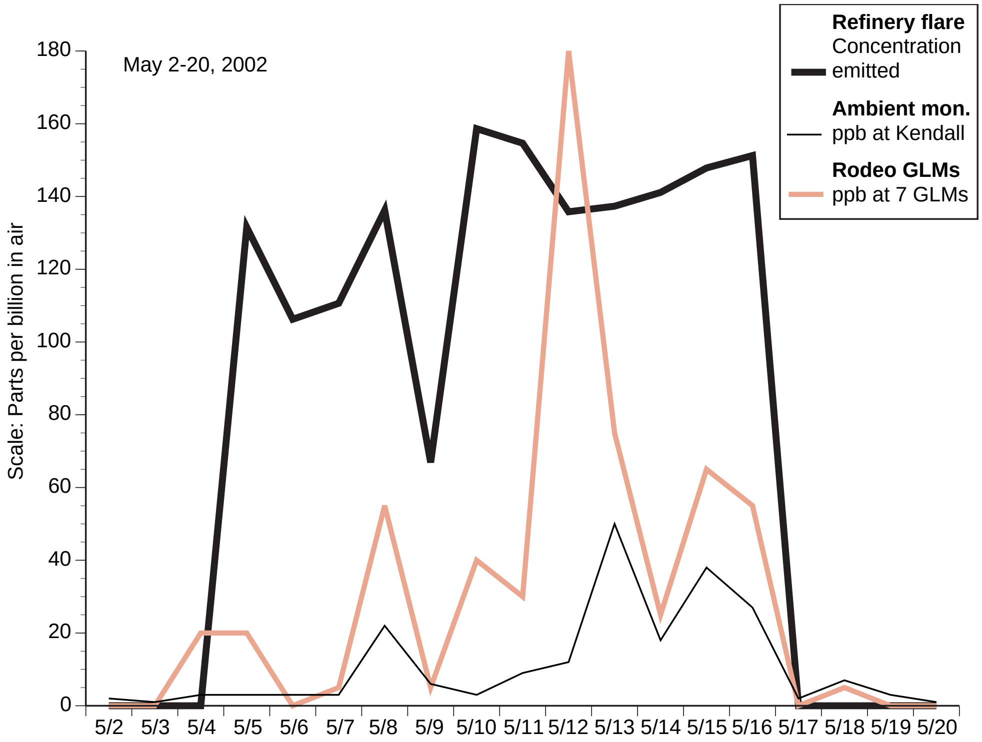
Review of Figure 1 shows that air concentrations for one monitor or another peak during part or all of every peak in flare emissions. Fence line concentrations peak earlier and higher than those measured at the network monitor. Different monitors peak at different levels and at different times. These observations describe a large, changing emission plume that is more concentrated near the refinery than further away, and shifts in the wind to hit or miss various monitors over the duration of the flaring episode.

**Figure 1. Hourly profile of flare sulfur emissions and $SO_2$ concentration in air at fence line and ambient monitors when the ambient monitor hit its highest hour: Chevron**



Data from BAAQMD: Rule 12-11 report, and response to Public Records Act request. Data shown in Appendix 6.

**Figure 2. Daily profile of flare sulfur emissions and $SO_2$ concentration in air at fence line and ambient monitors when the ambient monitor hit its highest hour: ConocoPhillips.**



Daily maximum-hour $SO_2$ concentration data from BAAQMD response to Public Records Act request and ARB air quality data reports. Flare data from BAAQMD Technical Assessment Document. Data shown in Appendix 2.

Figure 2 illustrates a similar pattern of observations in a second example, based on daily measurements around the flaring episode associated with the record-high 50 ppb hourly $SO_2$ concentration measured at the Crockett-Kendall Avenue network station on May 13, 2002. Sulfur dioxide peaked at the Rodeo GLMs on May 12, 2002 during flaring at the ConocoPhillips refinery – the day before the May 13, 2004 maximum hour reached at the network station. The 180 ppb hourly $SO_2$ concentration on May 12th is the second-highest recorded at the Rodeo GLMs in the flare data period. Hydrogen sulfide (not shown) also reached the second-highest level recorded at the Rodeo GLMs for that pollutant on May 12th, at 18 ppb.

The highest daily maximum-hour $SO_2$ and $H_2S$ levels on days of flaring near four refineries are listed in Table 3 below. The table also lists the maximum hour recorded on all days when the nearby refinery did not flare for each refinery, pollutant and monitoring location.

All the flaring day concentrations in the right-hand column of Table 3 are higher than any hourly level recorded at the same location on a day the refinery did not flare. For example, the maximum-hour concentration on all days in the flare data period when the Chevron refinery did not flare was 85 ppb for $SO_2$ at the Chevron ground-level monitors, 21 ppb for $SO_2$ at 7th Street-

Table 3. Twenty-eight observations of maximum-hour sulfur dioxide or hydrogen sulfide concentrations at nearby monitors on days when the refinery flared.

| **Refinery** | **Pollutant** | **Monitor** | **Max-hour all days with no flaring** | **Days with higher hourly levels when the refinery flared** |
|---|---|---|---|---|
| Chevron | $SO_2$ | GLMs | 85 ppb | 125 ppb on May 29, 2002 |
| Chevron | $SO_2$ | GLMs | 85 ppb | 93 ppb on March 21, 2004 |
| Chevron | $SO_2$ | GLMs | 85 ppb | 91 ppb on July 18, 2001 |
| Chevron | $SO_2$ | GLMs | 85 ppb | 90 ppb on January 4, 2004 |
| Chevron | $SO_2$ | GLMs | 85 ppb | 88 ppb on July 27, 2001 |
| Chevron | $SO_2$ | 7th Street | 21 ppb | 39 ppb on April 21, 2004 |
| Chevron | $SO_2$ | 7th Street | 21 ppb | 34 ppb on May 15, 2001 |
| Chevron | $SO_2$ | 7th Street | 21 ppb | 31 ppb on April 12, 2002 |
| Chevron | $SO_2$ | 7th Street | 21 ppb | 28 ppb on September 10, 2001 |
| Chevron | $SO_2$ | 7th Street | 21 ppb | 27 ppb on May 14, 2001 |
| Chevron | $SO_2$ | 7th Street | 21 ppb | 24 ppb on May 30, 2004 |
| Chevron | $H_2S$ | 7th Street | 5 ppb | 6 ppb on October 10, 2001 |
| ConocoPhillips | $SO_2$ | GLMs | 110 ppb | 215 ppb on April 10, 2004 |
| ConocoPhillips | $SO_2$ | GLMs | 110 ppb | 180 ppb on May 12, 2002 |
| ConocoPhillips | $SO_2$ | GLMs | 110 ppb | 140 ppb on March 20, 2004 |
| ConocoPhillips | $SO_2$ | GLMs | 110 ppb | 120 ppb on September 8, 2004 |
| ConocoPhillips | $SO_2$ | Kendall Ave. | 45 ppb | 50 ppb on May 13, 2002 |
| ConocoPhillips | $H_2S$ | GLMs | 13 ppb | 46 ppb on October 31, 2004 |
| ConocoPhillips | $H_2S$ | GLMs | 13 ppb | 18 ppb on May 12, 2002 |
| Tesoro | $SO_2$ | GLMs | 80 ppb | 220 ppb on July 10 , 2002 |
| Tesoro | $SO_2$ | GLMs | 80 ppb | 212 ppb on August 9, 2002 |
| Tesoro | $H_2S$ | GLMs | 16 ppb | 21 ppb on October 6, 2004 |
| Valero | $SO_2$ | GLMs | 3 ppb | 6 ppb on March 15, 2004 |
| Valero | $SO_2$ | GLMs | 3 ppb | 4 ppb on March 16, 2004 |
| Valero | $SO_2$ | GLMs | 3 ppb | 4 ppb on June 24, 2004 |
| Valero | $H_2S$ | GLMs | 13 ppb | 18 ppb on June 24, 2002 |
| Valero | $H_2S$ | GLMs | 13 ppb | 16 ppb on June 4, 2004 |
| Valero | $H_2S$ | GLMs | 13 ppb | 15 ppb on October 3, 2004 |

Air quality data from June 21, 2005 BAAQMD response to Public Records Act request, and ARB reports for Richmond-7th St. and Crockett-Kendall stations. Flare data from BAAQMD Technical Assessment Document and Rule 12-11 reports. See appendices 1-5 for daily data.

Richmond ambient network station, and 5 ppb for $H_2S$ at 7th Street-Richmond. Chevron flared on five days when the GLMs recorded hourly $SO_2$ concentrations higher than 85 ppb, on six more days when the network station recorded $SO_2$ concentrations higher than 21 ppb, and on one day when the network station recorded a hydrogen sulfide level higher than 5 ppb.

Review of Table 3 shows that the 28 highest daily maximum-hour concentrations were all recorded on a day when the refinery near that monitor flared. The significance of this finding is confirmed by the probability calculation shown in Table 4 below. Given the number of days when air quality was monitored continuously while flare activity was monitored at each refinery,

**Table 4. Probability table for 28 observations of maximum-hour concentrations across the refineries and pollutant-monitors shown in Table 3.**

| Pollutant & location | Chance of one max. level on a flare day | # max. levels on flare days | Probability this occurred randomly: within that location | across locations |
|---|---|---|---|---|
| Richmond $SO_2$ GLMs | 890 days ÷ 317 days refinery flared | 5 | 0.0056[a] | |
| 7th St. $SO_2$ Network Stn | 890 days ÷ 317 days refinery flared | 6 | 0.0019 | 1.1E-05 |
| 7th St. $H_2S$ Network Stn. | 882 days ÷ 317 days refinery flared | 1 | 0.3564 | 4.0E-06 |
| Rodeo $SO_2$ GLMs | 699 days ÷ 238 days refinery flared | 4 | 0.0132 | 5.3E-08 |
| Rodeo $H_2S$ GLMs | 699 days ÷ 238 days refinery flared | 2 | 0.1156 | 6.1E-09 |
| Kendall Ave.. $SO_2$ | 695 days ÷ 238 days refinery flared | 1 | 0.3424 | 2.1E-09 |
| Avon $SO_2$ GLMs | 547 days ÷ 350 days refinery flared | 2 | 0.4090 | 8.5E-10 |
| Avon $H_2S$ GLMs | 547 days ÷ 350 days refinery flared | 1 | 0.6398 | 5.6E-10 |
| Benicia $SO_2$ GLMs | 548 days ÷ 442 days refinery flared | 3 | 0.5240 | 2.9E-10 |
| Benicia $H_2S$ GLMs | 548 days ÷ 442 days refinery flared | 3 | 0.5240 | **1.5E-10** |

Based on the BAAQMD and ARB data summarized in tables 1 and 3 and shown for each day in appendices 1-5. Shell Martinez refinery data not shown in this table or table 3 because this refinery flared every day.

[a] Example calculation for $SO_2$ at Richmond GLMs: (317÷890) x ((317-1)÷(890-1)) x ((317-2)÷(890-2)) x ((317-3)÷(890-3)) x ((317-4)÷(890-4)) = 0.0056.

and the number of these days when each refinery flared, the probability of observing all 28 of the highest daily maximum-hours on flaring days because of random chance alone is 1.5E-10, or less than one in a billion. Accordingly, the null hypothesis–that maximum pollution hours occur when refineries flare by random chance–must be rejected. The data support a significant association between flaring and the highest daily maximum-hour $SO_2$ and $H_2S$ concentrations in air near four of the Bay Area refineries.

Maximum pollution hours continued to occur on days refineries flared throughout the flare data period. Half of the 28 observations in Table 3 were recorded in 2004. In addition, four of the five highest $SO_2$ daily maximum-hours and three of the five highest $H_2S$ hours recorded by monitors near the Shell refinery on days Shell flared were recorded in 2004 or 2005.

## Increase in highest-hour pollution associated with flaring

Changes in flare emissions that can be compared with pollutant levels in air near the refineries to explore flare impacts on air quality are summarized in Table 5 below. The table shows refinery-specific data for the volume of gases flared (in million standard cubic feet or MMSCF), sulfur emission (lbs expressed as $SO_2$), and emissions concentration (expressed as lbs/MMSCF).

Significant differences between flare episodes exist for each refinery. The 99th Percentile highest day of flare gas volume, sulfur emissions mass, and emission concentration is between 250% and 2,200% greater than the average in the 15 comparisons for these three emission factors across the five plants. This shows emissions differ between flaring episodes at each plant. The Shell refinery flaring pattern appears significantly different from that of the other refineries. Its flare gas flow is 600-2,600% higher than those of the other refineries, but its flare emissions mass and concentration are only 2-40% as high as those of the other plants, in the 36 comparisons in the table. Shell's flaring may affect air quality differently from that of the other plants.

It should be noted that the statistics in Table 5 represent the days in each refinery monitoring period when the refinery actually flared, not long-term averages of all days in the period.

Regression analysis was performed for the highest 10th Percentile of daily maximum-hour $SO_2$ concentrations, on days the refinery near the monitor flared, during the period from January 1, 2004 through March 31, 2005. This analysis pairs each daily maximum-hour near a refinery

**Table 5. Average, 95th Percentile and 99th Percentile gas volume disposed, pounds sulfur emitted, and emission concentration for flare episodes.[a]**

| | **Chevron** | **ConocoPhillips** | **Shell** | **Tesoro** | **Valero** |
|---|---|---|---|---|---|
| Days of flaring | 317 | 238 | 548 | 350 | 442 |
| <u>MMSCF gases flared</u> | | | | | |
| Average by day: | 3.260 | 2.762 | 12.78 | 3.059 | 1.002 |
| 95th Percentile: | 10.47 | 10.38 | 153.0 | 9.650 | 5.673 |
| 99th Percentile: | 21.38 | 16.76 | 153.0 | 16.55 | 13.55 |
| <u>Lbs SOx emitted</u> | | | | | |
| Average by day: | 1,765 | 3,350 | 176 | 6,126 | 662 |
| 95th Percentile: | 8,849 | 20,570 | 1,181 | 20,680 | 2,977 |
| 99th Percentile: | 18,490 | 38,030 | 1,850 | 32,480 | 14,070 |
| <u>Lbs SOx/MMSCF</u> | | | | | |
| Average by day: | 1,213 | 1,059 | 47 | 1,775 | 1,330 |
| 95th Percentile: | 5,808 | 4,019 | 123 | 3,663 | 2,669 |
| 99th Percentile: | 12,830 | 9,583 | 967 | 17,185 | 4,745 |

[a] For the periods when flare data are available for each refiner, as shown in Table 1 (no data excluded to force start- and end-dates of refinery periods to match). Data from BAAQMD Technical Assessment Document and Rule 12-11 reports. Daily data shown in appendices 1-5. MMSCF = million standard cubic feet.

with that refiners' flare gas flow, sulfur mass emission, and sulfur emission concentration for that day. The air concentration is expressed as a percentage of the mean for the monitoring location to allow analysis across refineries.[1] However, regression was performed separately for the Shell-Martinez data set because Shell flares differently from the other refiners. Results suggest that increasing air concentrations may be associated with increasing flare sulfur emissions concentration at the Shell refinery, but the results are not statistically significant ($p = 0.31$).

Table 6 below summarizes results of the regression on the paired data from the Chevron-Richmond, ConocoPhillips-Rodeo/Crockett, Tesoro-Avon, and Valero-Benicia data sets. The intercept value shown in the table (212 which represents 212% of the mean air concentration) approximates the lowest $SO_2$ air concentrations within the top 10th Percentile of the refiners' data sets. For flare gas volume, the positive coefficient indicates a positive association between increasing flare gas flow and increasing air concentration. However, the lower bound of the 99% confidence interval dips below zero, and the result is not statistically significant ($p = 0.8$). Flare gas flow may not be a reliable predictor of local air quality impacts from flaring. Thus, data assessed here support the need to address *sulfur concentration* in addition to *gas volume* for effective protection against local air quality impacts from flaring episodes.

In contrast, increasing flare sulfur mass emission is positively associated with increasing $SO_2$ air concentrations *and* this association is significant at the 99% confidence level ($p = 0.0013$). Similarly, increasing flare sulfur emission concentration is associated with increasing $SO_2$ in air, and this association is significant at the 99% confidence level ($p = 0.0001$). The 10th Percentile of highest $SO_2$ daily maximum hours includes eight percent of the days in this data set. Increasing sulfur dioxide concentration is associated with increasing flare sulfur emission on the worst eight percent of bad air days near these four refineries.

**Table 6. Results of regression analysis: y = change in daily maximum-hour from mean, in percent v. $x_1$ = flare gas volume, in SCF, $x_2$ = flare sulfur mass emission, in lbs, and $x_3$ = flare sulfur emission concentration, in tons/MMSCF.[a]**

| | | | | |
|---|---|---|---|---|
| **Multiple R** | 0.5030067 | | | |
| **Observations** | 141 | | | |
| | **Coefficients** | **P-value** | **Lower 99.0%** | **Upper 99.0%** |
| **Intercept** | 212.304095 | 4.2247E-45 | 186.148023 | 238.460167 |
| **Gas flared (SCF)** | 7.5699E-07 | 0.8381816 | -8.907E-06 | 1.0421E-05 |
| **Mass $SO_2$ emitted (lbs)** | 0.006869 | 0.00131099 | 0.00140061 | 0.01233738 |
| **Concentration (lbs/MMSCF)** | 18.3729555 | 0.0001182 | 6.26518883 | 30.4807223 |

[a] Based on daily maximum-hour $SO_2$ measurements near the Chevron, ConocoPhillips, Tesoro and Valero refineries on days the refineries flared during the period from January 1, 2004–March 31, 2005. Regression performed on those data at or above the 90th Percentile in each refinery data set.

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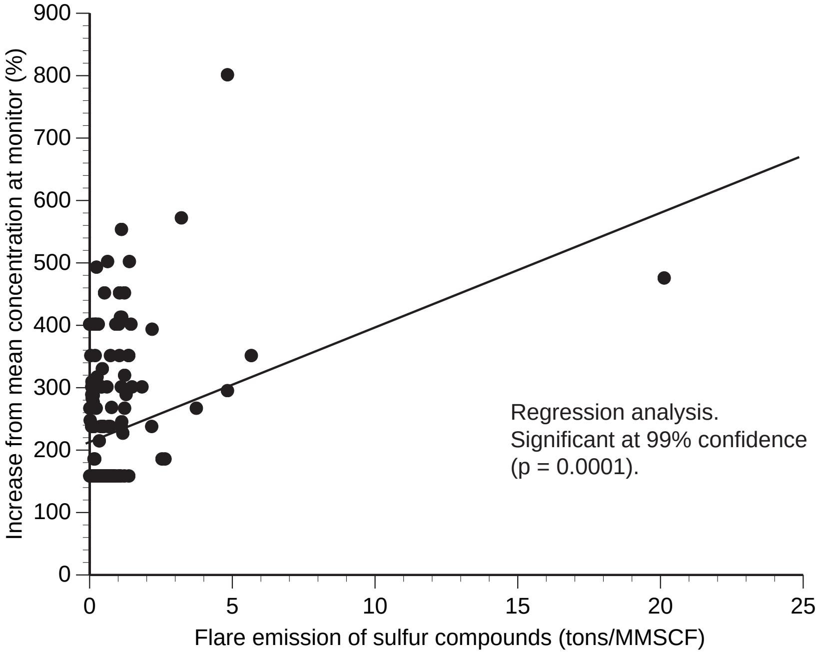
[1] For example, a daily maximum-hour of 2 ppb at a station where the mean is 1 ppb is expressed as 200, for 200%. This transformation was checked in trial runs of individual refinery data sets and did not change the results.

Figure 3. Association of highest 10th Percentile daily maximum-hour sulfur dioxide levels with flare sulfur concentration.



Based on daily maximum-hour $SO_2$ measurements near the Chevron, ConocoPhillips, Tesoro and Valero refineries on days the refineries flared. Regression performed on 141 paired observations during January 2004 through March 2005 including all data at or above the 90th Percentile value in each refinery-specific data set. Data shown in appendices 1-5.

The line fit plot for $SO_2$ emission concentration (as tons/MMSCF) is shown in Figure 3 above. The broad scatter of observations suggests that other factors–changing winds carrying plumes away from the few existing monitors, other pollution sources in or near the refineries, and flare mass emissions–can cause different pollution levels than those that the regression line predicts on any given day.

There is more than one way to estimate the increase in maximum episodic pollution levels associated with flaring from these data. The regression line prediction in the figure above shows one method (if the impact of mass emission is added). Another method would simply calculate the difference between direct measurements of the highest levels near each refinery when it flared and did not flare. These direct measurements are available, as shown in Table 3. Given the variability shown in Figure 3, the more straightforward, transparent approach seems appropriate.

Accordingly, the direct observations of highest levels with and without flaring at each location are compared for the estimate presented here. The percentage increase is calculated directly

**Table 7. Change in daily maximum-hour sulfur dioxide concentration in air near four refineries that is associated with flaring.**

| Monitor location | Highest hour when refinery does not flare | Higher daily maximum-hours when refinery flares | Percent increase |
|---|---|---|---|
| **Chevron-$SO_2$ GLMs** | 85 ppb | 125 ppb | 47% |
| **Chevron-$SO_2$ GLMs** | 85 ppb | 93 ppb | 9% |
| **Chevron-$SO_2$ GLMs** | 85 ppb | 91 ppb | 7% |
| **Chevron-$SO_2$ GLMs** | 85 ppb | 90 ppb | 6% |
| **Chevron-$SO_2$ GLMs** | 85 ppb | 88 ppb | 4% |
| **Chevron-$SO_2$ 7th St.** | 21 ppb | 39 ppb | 86% |
| **Chevron-$SO_2$ 7th St.** | 21 ppb | 34 ppb | 62% |
| **Chevron-$SO_2$ 7th St.** | 21 ppb | 31 ppb | 48% |
| **Chevron-$SO_2$ 7th St.** | 21 ppb | 28 ppb | 33% |
| **Chevron-$SO_2$ 7th St.** | 21 ppb | 27 ppb | 29% |
| **Chevron-$SO_2$ 7th St.** | 21 ppb | 24 ppb | 14% |
| **ConocoPhillips-$SO_2$ GLMs** | 110 ppb | 215 ppb | 95% |
| **ConocoPhillips-$SO_2$ GLMs** | 110 ppb | 180 ppb | 64% |
| **ConocoPhillips-$SO_2$ GLMs** | 110 ppb | 140 ppb | 27% |
| **ConocoPhillips-$SO_2$ GLMs** | 110 ppb | 120 ppb | 9% |
| **ConocoPhillips-$SO_2$ Kendall** | 45 ppb | 50 ppb | 11% |
| **Tesoro-$SO_2$ GLMs** | 80 ppb | 220 ppb | 175% |
| **Tesoro-$SO_2$ GLMs** | 80 ppb | 212 ppb | 165% |
| **Valero-$SO_2$ GLMs** | 3 ppb | 6 ppb | 100% |
| **Valero-$SO_2$ GLMs** | 3 ppb | 4 ppb | 33% |
| **Valero-$SO_2$ GLMs** | 3 ppb | 4 ppb | 33% |

**Estimated increase in highest 20 daily maximum hours associated with flaring: 50%**

Observations from Table 3 used in calculation as reported from monitor measurements provided by BAAQMD and ARB. Estimate by CBE in ***Flaring Hot Spots,*** based on BAAQMD and ARB data included and analyzed in the report.

from each paired observation, and it is conservatively assumed that the average of these percentages, rather than the maximum, is a representative estimate. An advantage of this method is that every data input is measured, and can be confirmed by direct comparison of measurements to be a higher value than any observed in a comparable period when the refinery did not flare, as detailed in the discussion of Table 3.

This assessment predicts a 50% increase in the highest daily maximum-hour sulfur dioxide concentration associated with flaring at emission rates observed in the period examined. The calculation is shown in Table 7 above.

## Closing

Findings are summarized on page 5 above. This report documents localized episodic air pollution associated with flaring by Bay Area oil refineries. Its findings support the adoption of enforceable requirements to prevent and reduce flaring as a matter of environmental justice for disproportionately impacted low-income communities on refinery fence lines.

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**Attachment 46**

# Bay Area Air Quality Management District

939 Ellis Street
San Francisco, CA 94109

# Staff Report

## Proposed Amendments
## to
## Regulation 12, Miscellaneous Standards of Performance
## Rule 12, Flares at Petroleum Refineries

March 3, 2006

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# I. EXECUTIVE SUMMARY

On July 20, 2005, the Bay Area Air Quality Management District (District) adopted a ground breaking refinery flare control rule (Regulation 12: Miscellaneous Standards of Performance, Rule 12: Flares at Petroleum Refineries). The new rule is intended to reduce emissions from flares at petroleum refineries by reducing the magnitude and duration of flaring events.

The new rule requires each Bay Area refinery to develop and implement a Flare Minimization Plan (FMP) for each flare subject to the rule and to update the plan annually. In addition, the refiners must conduct a causal analysis when significant flaring occurs and develop and submit an annual report to provide information about the cause of flaring at lower flow rates. Refiners must operate their flares in accordance with the FMP except for flaring in emergency situations. The initial FMP for each refinery must be submitted to the District by August 1, 2006.

The rule embodies a continuous improvement process focused on reducing all air pollutants from all flaring. A fundamental requirement of the regulation is the investigation to determine primary cause and contributing factors for flaring (causal analysis) in order to develop prevention measures to avoid or minimize flaring. The rule includes two requirements for submitting an analysis of the cause(s) of flaring depending on the amount of vent gas flared.

The first reporting requirement calls for submission of a causal analysis report to the District within 60 days following the end of the month in which a reportable flaring event occurs. A reportable flaring event is currently defined as any flaring where more than 500,000 standard cubic feet per day (scfd) of vent gas is flared. The second reporting provision requires an annual report to the Air Pollution Control Officer (APCO) that summarizes the use of a flare at rates less than 500,000 scfd where sulfur dioxide emissions are greater than 500 pounds per day. The summary must include the reasons for the flaring and prevention measures considered or implemented. Reporting of flaring resulting in sulfur dioxide emissions in excess of 500 pounds (regardless of the flow rate) is required twelve months after approval of the initial FMP and annually thereafter. Both provisions require determination of cause, identification of prevention measures and incorporation of prevention measures into the FMP.

These provisions are the subject of the proposed rule amendments. The proposal is to change the annual reporting requirement for lower-volume flaring (less than 500,000 scfd) where emissions of sulfur dioxide exceed 500 pounds per day. The change would require the analysis and reporting of this lower-volume flaring to occur on the same schedule specified for flaring events greater than 500,000 scfd, i.e., within 60 days following the end of the month in which a reportable flaring event occurs. The proposed change would take effect upon adoption by the District Board of Directors. There have been 49 of these lower-volume flaring events over the past two years; 28 in 2004 and 21 in 2005.

The reason for the proposed amendment is to ensure that the prevention measures developed from the investigations into lower-volume flaring with sulfur dioxide emissions greater than 500 pounds per day are incorporated into the initial FMPs.

In addition, the proposal would specify that the report of causal analysis for a reportable flaring event must include the volume of vent gas flared and the calculated emissions (methane, non-methane hydrocarbon and sulfur dioxide). This information is necessary to provide the context necessary for a comprehensive report. The proposal would also clarify the application of the causal analysis provision for refineries with cascade and backup systems.

## II. BACKGROUND

The District's flare control rule, Regulation 12, Rule 12, recognizes that a flare is first and foremost a safety device. Specifically, the rule allows flaring in an emergency if necessary to prevent an accident, hazard or release of vent gas directly to the atmosphere. All other flaring must be consistent with the FMP developed by each refinery.

The FMP includes information about the flare system or systems at the refinery and a list of feasible prevention measures to be implemented on an expedited schedule. The prevention measures are to be developed in conjunction with the causal analysis of reportable flaring events and the annual reports of the analysis of lower-volume flaring with sulfur dioxide emissions in excess of 500 pounds per day.

The current regulation includes a requirement to conduct an investigation to evaluate any reportable flaring event, i.e., flaring where more than 500,000 scfd of vent gas is combusted. The purpose of the investigation is to identify the cause (or causes) of the flaring and the means to avoid flaring from that cause in the future if feasible. In addition to the causal analyses for reportable flaring events, beginning 12 months after approval of the initial FMP, each facility is required to submit an annual report to the District that includes an evaluation of flaring at volumes less than 500,000 scfd where the calculated sulfur dioxide emissions are greater than 500 pounds per day. These formal evaluation processes will ensure that each refinery makes continuous improvement and progress toward minimizing flaring from any cause.

All feasible prevention measures identified through either of the reporting methods described above are to be incorporated in the FMP with a schedule for expeditious implementation of those measures. The FMP must be updated annually to incorporate the prevention measures identified during the previous year as well as any significant changes in process equipment or operational procedures related to flares. Any flaring that occurs after submission of the initial

FMP must be consistent with the current plan.

The requirement to conduct an investigation into the reasons for flaring was originally proposed in Regulation 12, Rule 11: Flare Monitoring at Petroleum Refineries. Under that regulation, for any 24-hour period during which more than 1 million standard cubic feet (scf) of vent gas is flared, a description of the flaring including the cause, time of occurrence and duration, the source or equipment from which the vent gas originated, and any measures taken to reduce or eliminate flaring must be submitted to the District in a monthly report. This provision was effective on the date of rule adoption, June 4, 2003. The data included in the monthly report became more encompassing as other provisions in the rule became effective; specifically the requirements to continuously monitor vent gas flow and to sample vent gas and analyze for composition. These data were used to consider various thresholds of a causal analysis in the development of the flare control rule.

A lower threshold to conduct a causal analysis was proposed for the new flare control rule, Regulation 12, Rule 12: Flares at Petroleum Refineries. Two reporting requirements were developed to cover all significant flaring events in an efficient and thorough manner. The first reporting requirement calls for a causal analysis to be completed where more than 500,000 scfd of vent gas is flared. This report is due 60 days following the end of the month in which the flaring event occurs. The second reporting provision requires a summary of the use of a flare at rates less than 500,000 scfd of vent gas where sulfur dioxide ($SO_2$) emissions are greater than 500 pounds per day. This report is due annually effective 12 months after approval of the original FMP.

A breakdown of the number of flaring events for 2004 and 2005 is shown in Table 1. This data was obtained from the monthly reports required by the flare monitoring rule. The 2005 data incorporates January through November 2005. Also, the Tesoro data excludes the Ammonia Plant flare, because of an ongoing verification audit.

**Table 1. Summary of Flaring Events at Bay Area Refineries**

| Facility | Events Less than 500,000 scfd and Greater than 500 lbs SO2 per day | | Events Greater than 500,000 scfd | |
|---|---|---|---|---|
| | 2004 | 2005[a] | 2004 | 2005[a] |
| Chevron | 0 | 2 | 38 | 21 |
| ConocoPhillips | 8 | 9 | 12 | 38 |
| Shell | 0 | 1 | 89 | 30 |
| Tesoro[b] | 4 | 2 | 72 | 64 |
| Valero | 16 | 7 | 90 | 21 |
| Total | 28 | 21 | 301 | 174 |

[a] Data through November 2005

[b] Excludes Ammonia Plant Flare

The data in the table shows that most flaring would require a causal analysis under the existing threshold for causal analysis (greater than 500,000 scfd vent gas). The lower threshold represents a small portion of all flaring, but these lower-flow events with sulfur dioxide emissions at levels of concern may have different causes than the greater than 500,000 scfd events. Staff has concluded that requiring analysis of certain lower-volume flaring (greater than 500 pounds per day $SO_2$) for inclusion in the initial FMP will insure that each refinery is creating a flare minimization strategy that will best address the causes of all flaring of concern at each refinery.

## III. PROPOSED AMENDMENTS

The proposed amendments will change the annual reporting provision for the flaring events of less than 500,000 scfd but greater than 500 lbs $SO_2$ per day. The change would require the analysis and reporting of this lower-volume flaring to occur on the same schedule specified for reportable flaring events, i.e., within 60 days following the end of the month in which the flaring occurs. The proposed change would take effect upon adoption by the District Board of Directors.

Specifically, the proposal would amend the current definition of “reportable flaring event” for which a causal analysis is required within 60 days of the end of the month in which the flaring occurs, i.e., any flaring of more than 500,000 scfd vent gas, to include any flaring at rates below 500,000 scfd where the calculated $SO_2$ emissions are greater than 500 pounds per day. The current rule requires the owner or operator of a flare subject to the rule to submit an annual report covering such lower-volume flaring beginning 12 months after approval of a refinery’s initial FMP. By moving up the schedule for analysis of lower-volume flaring with emissions of $SO_2$ in excess of 500 pounds per day, the District will insure that the initial FMPs will account for and address the causes of all significant flaring.

The proposal also includes an amendment specifying that the causal analysis must include the calculated methane, non-methane and sulfur dioxide emissions. The reports currently submitted include this information or the data necessary to calculate this information. This amendment will insure that all refineries submit this information a manner most efficient for staff use.

Finally, the definition of a reportable flaring event has been amended to clarify that the total volume is calculated on a cumulative basis for flare systems. This clarification is necessary to identify when a reportable flaring event begins and ends for systems that are operated as a backup or staged flares or flares in a cascade (common piping configured either in series or parallel where the flare vent gas may be distributed to more than one flare).

# IV. Emissions

Flares produce air pollutants through two primary mechanisms. The first mechanism is incomplete combustion of a gas stream, because like all combustion devices, flares do not combust all of the fuel directed to them. The second mechanism of pollutant generation is the oxidation of flare gases to form other pollutants. As an example, the gases that are burned in flares typically contain sulfur in varying amounts. Combustion oxidizes these sulfur compounds to form sulfur dioxide, a criteria pollutant. In addition, combustion also produces relatively minor amounts of nitrogen oxides through oxidation of the nitrogen in flare gas or atmospheric nitrogen in combustion air. The flare control rule adopted by the District last year will reduce emissions from flaring as described in the staff report for Regulation 12, Rule 12: Flares at Petroleum Refineries.

The proposed amendments are administrative in nature and will not have a significant emissions impact. The amendments will require a causal analysis for the lower-volume events with $SO_2$ emissions in excess of 500 pounds per day on the same schedule as the higher volume events. This will insure that prevention measures for these lower-volume events are incorporated into the initial FMPs. In addition, the proposed amendments include a clarification of the application of the requirements to cascade, staged or backup flare systems and a provision to ensure that the report to the District providing the causal analysis for a flaring event includes calculated emissions for that event. No change in the amount of emission reductions from implementation of the flare control rule as adopted July 20, 2005 are expected as a result of the proposed amendments; however, some reductions may occur earlier than under the current rule if prevention measures for these lower-volume flaring events are identified and implemented through the initial FMPs.

## Current Flare Emission Estimate

The estimated emissions from flares, on an average daily basis for all facilities in 2004, are approximately 2 tons/day of total organic compounds (approximately 1.5 tons/day of non-methane organic compounds and 0.5 tons/day methane). The daily emissions range from 0 to 12 tons/day of total organic compounds. For sulfur dioxide, the average daily emission rate is approximately 4 tons/day and ranges from 0 to 61 tons/day.

To illustrate the offsite impact of emissions associated with lower-volume flaring, staff modeled two days (April 21 and 22, 2004) of flaring at the Chevron refinery where the volume of vent gas flared was less than one-million standard cubic feet per calendar day and the calculated sulfur dioxide emissions were greater than 500 pounds per day. The results of the modeling are illustrated in the Figure 1.

### Figure 1. Modeled Lower-Volume Flaring Event

April 21 and 22, 2004 Chevron Flaring Event
Maximum 1-hour SO2 Air Concentration (ppb)

SO2 Ambient Air Quality Standard
California 1-hour: 250 ppb

In Figure 1, above, Richmond area monitoring stations (Gertrude, Richmond - 7th Street, Castro Street, and Golden Gate) are indicated by the white dots. The boxes next to each station contain the recorded concentration of $SO_2$ in parts per billion (ppb) at that station for April 21 (upper, purple) and April 22 (lower, blue). The areas within the 10 ppb isopleths (April 21 near the Richmond - 7th Street Station in purple and April 22 southeast of the Golden Gate Station in blue) show the modeled ground level concentration of $SO_2$ in ppb. Chevron's flares are located directly west of the Gertrude Station (in red).

On each of the two days several flares were in operation at rates less than one-million standard cubic feet per day with calculated $SO_2$ emissions of over 7500 and 2500 pounds per day, respectively. The isopleths show that the modeling estimates concentrations consistent with data from nearby ambient air quality monitors. The modeling shows a one-hour maximum concentration of 72 ppb for April 21 and 32 ppb for April 22. The ambient air quality standard for a one-hour concentration of $SO_2$ is 250 ppb. Nevertheless, these isopleths show an impact on the nearby community. For this reason, the inclusion of prevention measures directed at lower-volume flaring with $SO_2$ emissions greater than 500 pounds per day in the initial FMP will lessen the emissions impact of flaring on those who live and work within affected areas.

## V. ECONOMIC IMPACTS

### A. Introduction

This section discusses the estimated costs associated with the proposed amendments. The California Health & Safety Code states, in part, that districts shall endeavor to achieve and maintain State ambient air quality standards for ozone, carbon monoxide, sulfur dioxide, and nitrogen dioxide by the earliest practicable date. In developing regulations to achieve this objective, districts shall consider the cost-effectiveness of their air quality programs, rules, regulations, and enforcement practices in addition to other relevant factors, and shall strive to achieve the most efficient methods of air pollution control. However, priority shall be placed upon expeditious progress toward the goal of healthful air.[1]

Regulation 12-12 requires refineries to develop the prevention measures they will implement to reduce flaring. The regulation by design ensures that the most cost effective means for achieving this goal will be implemented. That is, it is reasonable to expect that each refinery, given the flexibility provided by the structure of the rule, will include the most cost-effective prevention measures available for each iteration of the flare minimization plan, thus insuring the continuous improvement at the least cost.

This was the determination of the District in adopting the current flare control rule. The conclusion is equally applicable to the proposed amendments.

### B. Discussion

### Determination and Reporting of Cause

The cost for the determining and reporting of cause is dependant on the number of reportable flaring events and the complexity of each event. The data from the flare monitoring monthly reports, which was used in the cost analysis for Regulation 12-12, shows 243 occurrences where the volume of vent gas flared was greater than 500,000 scfd in 2004 for all facilities. In the development of Regulation 12-12, staff estimated costs of determining and reporting cause at an hourly rate of $50.00 per hour for 12 hours per event. The total was approximately $145,800 for all facilities per year. The cost for an individual refinery will be much less. Moreover, staff expected this cost to drop in time as

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[1] California Health and Safety Code section 40910

facilities minimize the number of events and become more proficient in investigations.

The initial cost analysis was based on a hypothetical 67 events per facility. A review of Table 1 shows that, even including lower-volume flaring where sulfur dioxide emissions exceed 500 pounds per day, no facility would have had reportable flaring events in excess of 67 events in 2005. Staff anticipates the downward trend in the number of reportable flaring events to continue, with a concomitant drop in these costs. Therefore, although there may be additional causal analyses required in the first year (or two) of implementation of the flare control rule under this proposal, the additional causal analyses required by these amendments will create no significant increase in the costs assumed for the current version of Regulation 12, Rule 12: Flares at Petroleum Refineries when adopted in July of 2005.

### Prevention Measures

The cost effectiveness analysis for Regulation 12, Rule 12 was estimated for two scenarios selected to represent the range of options among prevention measures. The first estimate, representing a costly prevention measure, considered an example of a refinery that had performed a hazard analysis for Contra Costa County and had upgraded the flare gas recovery system. A less costly prevention measure was also considered where startup and shutdown schedule adjustments resulted in a reduction of flaring, which included cost of lost production. The costs of these prevention measures were estimated to vary from $1,603 to $1,527 per ton of all pollutants for the first year and from $800 to $1500 per ton thereafter.

Currently, Regulation 12, Rule 12 requires the prevention measures developed for the lower-volume events to be included in the FMPs following inclusion in an annual report. While the proposed amendments may result in earlier implementation of one or more prevention measures, the costs of those measures would not exceed those identified when Regulation 12-12 was originally proposed and adopted.

### Annual Reports and Updates

The proposed administrative amendments merely change the scheduling of the analysis and reporting of lower-volume flaring. Under the current rule, all flaring with sulfur dioxide emissions in excess of 500 pounds per day per day is addressed in a report to be submitted 12 months after approval of the initial FMP and annually thereafter. As amended, these events will have to be analyzed in a report submitted within 60 days following the end of the month in which the flaring occurs, consistent with the high volume events. Although, as discussed above, there may be more causal analyses required in the first year (or two) under the program, and prevention measures associated with these events may be scheduled for implementation earlier, the costs will not exceed the costs estimated for implementation of the current rule. Refineries will not, however, incur the costs of preparing the annual report.

### C. Socioeconomic Impacts

Section 40728.5 of the Health and Safety Code requires an air district to assess the socioeconomic impacts of the adoption, amendment, or repeal of a rule if the rule is one that "will significantly affect air quality or emissions limitations." Applied Economic Development of Berkeley, California, prepared a socioeconomic analysis for the initial proposed Regulation 12, Rule 12: Flares at Petroleum Refineries. The analysis concludes that the affected refineries should be able to absorb the costs of compliance with the proposed rule without significant economic dislocation or loss of jobs.

The proposed amendments are administrative changes; they expedite reporting of lower-volume events so that any prevention measures specifically developed for this type of flaring can be incorporated into the initial FMP. The affect on air quality and emissions will result from the various measures refineries put into place to reduce flaring, not from these administrative requirements. In any event, the proposed amendments would not change the conclusion of the socioeconomic analysis for the initial proposed Regulation 12, Rule 12: Flares at Petroleum Refineries.

### D. District Staff Impacts

In the staff report for the adopted Regulation 12-12, staff identified that it will take a total of 1.5 FTE at an average staff level of a Senior Engineer to implement the rule. The total cost was estimated to exceed $250,000. The proposed amendments do not add significantly to staff impacts, and in some cases may reduce those impacts. By specifying that the refinery must provide the volume of vent gas and calculated emission data, staff resources necessary to perform the calculations from raw data will not be needed. In addition, staff time will no longer be required to review annual reports.

## VI. ENVIRONMENTAL IMPACTS

Pursuant to the California Environmental Quality Act, the District prepared an Initial Study during the development of the original flare control rule (Regulation 12, Rule 12) to determine whether it would result in any significant environmental impacts. The study and subsequent Environmental Impact Report discussed certain potential significant environmental impacts, but ultimately concluded that the proposed rule would not have any significant adverse environmental impacts. Based on this determination (and others), the District adopted the flare control rule in July of 2005.

The amendments now proposed are administrative changes to the original flare control rule; they expedite reporting and development of prevention measures and incorporation of lower-volume events into the initial FMP. The District has determined that there is no possibility the proposed amendments could cause any significant environmental effect; therefore, they are exempt from the provisions of CEQA in accordance with State CEQA Guidelines section 15061(b)(3). In fact, the amendments would not constitute a "project" under CEQA because they do not have the potential to result in either a direct physical change in the environment or a reasonably foreseeable indirect physical change in the environment. (Public Resource Code section 21065; State CEQA Guidelines section 15378.)

## VII. REGULATORY IMPACTS

Section 40727.2 of the Health and Safety Code requires an air district, in adopting, amending, or repealing an air district regulation, to identify existing federal and district air pollution control requirements for the equipment or source type affected by the proposed change in district rules. The district must then note any differences between these existing requirements and the requirements imposed by the proposed change. Table 2 is a matrix of the thresholds and reporting requirements, including the responsible agency.

**Table 2. Reporting Thresholds and Requirements**

| Agency | Regulation | Requirement | Threshold | Responsible Agency |
|---|---|---|---|---|
| BAAQMD | Reg. 12-12 | Causal Analysis | > 500,000 scfd | BAAQMD |
| EPA | Emergency Planning and Community Right-to-Know Act (EPCRA) and Section 112(r) of the Clean Air Act | Notification to Local Emergency Response Committee/Agency | 500 lbs $SO_2$<br>100 lbs Hydrogen Sulfide | Local Emergency Response Committee/Agency |
| BAAQMD | Reg. 12-12 Proposed Amendments | Causal Analysis | Any flaring greater than 500 lbs/day of $SO_2$ | BAAQMD |

### Federal Requirements

Federal Title 3 requirements include reporting and planning provisions at specified thresholds. The focus of these requirements is emergency response and community right to know. Adequate release response plans and timely notification to responsible agencies are required.

EPA has entered into consent decrees with all Bay Area refineries. These decrees, among other requirements, contain increments of progress for the application of New Source Performance Standards (NSPS) to all flares. NSPS limit sulfur oxides in vent gases combusted in a flare installed after June 11, 1973 (40 CFR Part 60, Subpart J, Section 60.104). Flaring caused by upset gases or fuel gas from relief valve leakage or other emergency malfunctions is exempt from the standard.

## VIII. RULE DEVELOPMENT PROCESS

### A. Introduction

Staff posted a request for comments on the proposed amendments to Regulation 12-12 on December 23, 2005. Three written comments were received in support of the proposed amendments.

As part of the development of the original regulation staff had undertaken an extensive rule development process in order to receive input from all affected parties. These efforts included the formation of a technical working group, public meetings, workshops and presentations to the District Board of Directors Stationary Source Committee. This process is described in the staff report for Regulation 12, Rule 12: Flares at Petroleum Refineries.

Staff has formed an implementation team to ensure thorough review of and compliance with the causal analyses and prevention measures submitted to the District by each facility. The team consists of District staff from the Engineering, Enforcement, Planning and Legal Divisions. The team meets regularly to evaluate submittals and make recommendations, which have been incorporated into the proposed amendments. In addition, the team meets with refinery staff as questions and the need for clarification and consistency arise.

### B. Stationary Source Committee Reports

At the flare control rule adoption hearing on July 20, 2005, staff was directed to provide an update to the Stationary Source Committee on the cumulative impacts of a lower threshold for causal analysis. The minutes of that meeting can be found at on the District's web site at the following address, (http://www.baaqmd.gov/brd/brddirectors/agendas_minutes.htm).

Staff has reported to the Stationary Source Committee at each meeting since rule adoption. At the meeting of November 28, 2005 the Committee recommended consideration of amendments to include a causal analysis of lower-volume flaring where 500 pounds per day of $SO_2$ is emitted on the same schedule as for events involving flaring of vent gas at flow rates in excess of 500,000 scfd. The agenda of that meeting can be found on the District's web site at the same address.

### C. Public Comment

The proposed rule amendments were made available for public comment and posted on the District's web site. Two comments expressed concern over proposed language in the definition of a reportable flaring event. The proposed language, which was intended to define the end of a reportable flaring event by specifying a volume of vent gas as the endpoint, was deemed confusing. As suggested, it has been deleted. The definition as proposed identifies the end of an event as either a specified rate or when water seal integrity is established and explains that for certain systems where more than one flare may burn vent gas, the total volume is calculated on a cumulative basis.

## IX. CONCLUSION

The proposed amendments to Regulation 12, Rule 12: Flares at Petroleum Refineries, are intended to ensure that information about lower-volume flaring where sulfur dioxide emissions are greater than 500 pounds per day is available for inclusion in the initial Flare Minimization Plans. Pursuant to Health and Safety Code Section 40727, new regulations must meet standards of necessity, authority, clarity, consistency, non-duplicity and reference. The proposed amended regulation is:

- Necessary to protect public health by reducing ozone precursor emissions, and to reduce exposures to toxic air contaminants, sulfur dioxide and particulate matter by insuring that feasible prevention measures to reduce or avoid use of flares at petroleum refineries are identified and scheduled for implementation on an expedited schedule;
- Authorized by California Health and Safety Code section 40702;
- Clear, in that the new regulation specifically delineates the affected industry, compliance options and administrative requirements for industry subject to this rule;
- Consistent with other District rules, and not in conflict with State or federal law;
- Non-duplicative of other statutes, rules or regulations; and
- The proposed regulation properly references the applicable District rules and test methods and does not reference other existing law.

The proposed amendments are not subject to CEQA because they do not constitute a "project" as defined in State law and the CEQA Guidelines and because it can be determined with certainty that the amendments have no possibility of causing any significant environmental effects.

The proposed amendments will not increase the costs of implementing Regulation 12, Rule 12: Flares at Petroleum Refineries. Staff has analyzed the cost of the additional causal analysis and found them to be within the total number of analysis projected in the original adoption of Regulation 12, Rule 12 and the potential for early implementation of one or more prevention measures would not increase the costs estimated for the adoption of the current rule.

Staff recommends the adoption of the proposed amendments to Regulation 12: Miscellaneous Standards of Performance, Rule 12: Flares at Petroleum Refineries, and approval of the filing of a CEQA Notice of Exemption.

**Attachment 47**

U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD

# INTERIM INVESTIGATION REPORT

## CHEVRON RICHMOND REFINERY FIRE

CHEVRON RICHMOND REFINERY

RICHMOND, CALIFORNIA

AUGUST 6, 2012

## KEY ISSUES

- INHERENTLY SAFER DESIGN
- DAMAGE MECHANISM HAZARD REVIEW
- EFFECTIVE ANALYSIS OF PROCESS SAFEGUARDS IN PROCESS HAZARD ANALYSIS

# Summary

On August 6, 2012, the Chevron U.S.A. Inc. Refinery in Richmond, California, experienced a catastrophic pipe failure in the #4 Crude Unit. The pipe ruptured, releasing flammable, hydrocarbon process fluid which partially vaporized into a large vapor cloud that engulfed nineteen Chevron employees. All of the employees escaped, narrowly avoiding serious injury. The flammable portion of the vapor cloud ignited just over two minutes after the pipe ruptured. The ignition and subsequent continued burning of the hydrocarbon process fluid resulted in a large plume of unknown and unquantified particulates and vapor traveling across the Richmond, California, area. In the weeks following the incident, approximately 15,000 people from the surrounding area sought medical treatment due to the release. Testing commissioned by the U.S. Chemical Safety and Hazard Investigation Board (CSB) and the California Division of Occupational Safety and Health (Cal/OSHA) determined that the pipe failed due to thinning caused by sulfidation corrosion, a common damage mechanism in refineries. As a result of the incident, the Chevron Richmond Refinery crude unit remains out of commission over eight months later. In addition, Cal/OSHA issued the refinery 17 citations related to the incident and eight additional citations, with a total proposed fine of nearly one million dollars. In this interim report, the CSB is issuing recommendations to Chevron, the City of Richmond, Contra Costa County, Cal/OSHA, the State of California, and the U.S. Environmental Protection Agency, addressing the need for inherently safer design, rigorous and documented damage mechanism hazard reviews, and thorough analyses of process safeguards.

This interim investigation report contains detailed analyses of and makes recommendations to Chevron and regulatory bodies at the local, state, and federal level. The CSB believes the findings and recommendations presented in this report can be applied to refineries, chemical plants, and other industries nationwide to improve process safety.

The CSB plans to release a comprehensive Final Investigation Report later in 2013 that will include analyses and recommendations relating to technical and regulatory investigation findings which are not included in this interim report. The Final Investigation Report will cover topics including: the importance of having a competent, well-funded regulator and an adaptable regulatory regime; Chevron safety culture; process safety indicator data collection and reporting; emergency planning and response; stop work authority; and recommendations for improvement of petroleum industry standards and recommended practices. Some of these issues are previewed at the end of this interim report under *Additional Issues Currently Under Investigation*.

# Table of Contents

# Figures

# Acronyms and Abbreviations

| | |
|---|---|
| ALARP | As Low As Reasonably Practicable |
| API | American Petroleum Institute |
| ASTM | American Society for Testing and Materials |
| BIN | Business Improvement Network |
| bpd | Barrels Per Day |
| BPTC | BP Texas City |
| CAA | Clean Air Act |
| Cal/OSHA | California Division of Occupational Safety and Health |
| CCPS | Center for Chemical Process Safety |
| CCR | California Code of Regulations |
| Chevron ETC | Chevron Energy Technology Company |
| CML | Condition Monitoring Locations |
| CSB | U.S. Chemical Safety and Hazard Investigation Board |
| CSHO | Compliance Safety and Health Officer |
| CWS | Community Warning System |
| EPA | Environmental Protection Agency |
| °F | degree Fahrenheit |
| HSE | Health and Safety Executive |
| ISO | Industrial Safety Ordinance |
| ISS | Inherently Safer Systems |
| IST | Inherently Safer Technology |
| KPI | Key Process Indicator |

| | |
|---|---|
| LEPC | Local Emergency Planning Committee |
| LOPA | Layers of Protection Analysis |
| MOC | Management of Change |
| NEP | National Emphasis Program |
| OEM | U.S. EPA Office of Emergency Management |
| OSHA | Occupational Safety and Health Administration |
| P&P | Policy and Procedures |
| PHA | Process Hazard Analysis |
| PMI | Positive Materials Identification |
| psig | Pounds Per Square Inch Gauge |
| PSM | Process Safety Management |
| RISO | City of Richmond Industrial Safety Ordinance |
| RLOP | Richmond Lube Oil Project |
| RMP | Risk Management Plan |
| SIP | Shelter-In-Place |
| TML | Thickness Monitoring Location |
| UK | United Kingdom |
| USW | United Steelworker International Union |
| wt. % | Weight Percent |

# Background and Findings

1. On August 6, 2012, the Chevron U.S.A. Inc. Refinery in Richmond, California (Chevron Richmond Refinery), experienced a catastrophic pipe rupture in the #4 Crude Unit (crude unit). The ruptured pipe released a flammable hydrocarbon process fluid which then partially vaporized into a large vapor cloud that engulfed nineteen Chevron U.S.A. Inc. (Chevron) employees. At 6:33 pm, approximately two minutes after the release, the flammable portion of the vapor cloud ignited.[i] Eighteen of the employees safely escaped from the cloud just before ignition; one employee, a firefighter, was inside a fire engine that caught fire when the vapor cloud ignited (Figure 1). Because he was wearing full body fire-fighting protective equipment, he was able to make his way to safety. Six Chevron employees suffered minor injuries during the incident and subsequent emergency response efforts.

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[i] Surveillance footage provided by Chevron. Chevron clarified to CSB that video time is approximately 5 minutes out of sync. The video can be found at http://www.csb.gov/videoroom/detail.aspx?VID=69 (accessed February 8, 2013).

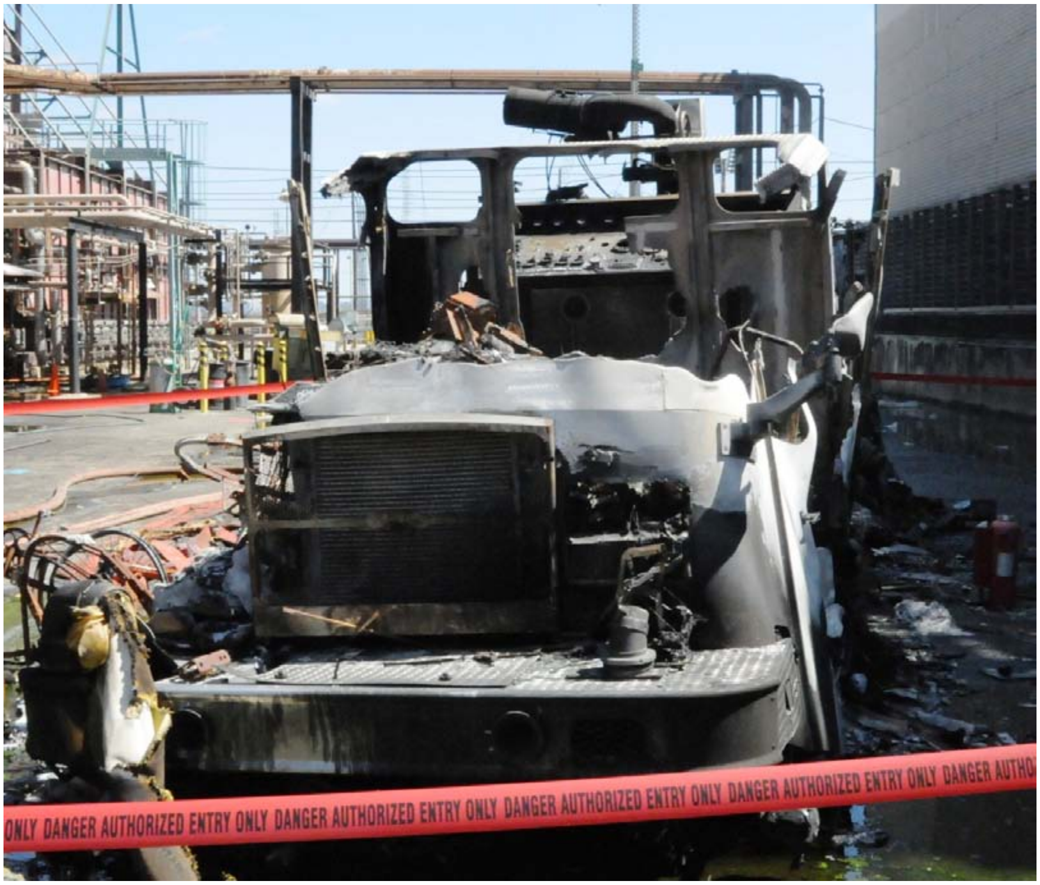

**Figure 1. The burned remains of the fire truck that was consumed by the fire. A firefighter was in the cab when the vapor cloud ignited. The fire truck was positioned approximately 65 feet from the leak location.**

2. The ignition and subsequent continued burning of the hydrocarbon process fluid resulted in a large plume of unknown and unquantified particulates and vapor traveling across the Richmond, California, area (Figures 2 and 3). This resulted in a Community Warning System (CWS) Level 3 alert,[i] and a shelter-in-place[ii] (SIP) was issued at 6:38 pm[1] for the cities of Richmond, San Pablo, and North Richmond. It was lifted later that night at 11:12 pm after the fire was fully under control. In the weeks following the incident, nearby medical facilities received over 15,000 members of the public seeking treatment for ailments including breathing problems, chest pain, shortness of breath, sore throat, and headaches. Approximately 20 people were admitted to local hospitals as inpatients for treatment.

**Figure 2. Vapor cloud (white) over Richmond area and smoke (black) from Chevron Richmond Refinery fire as seen from San Rafael in Marin County.[2]**

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[i] A Community Warning System Level 3 alert indicates that a facility within Contra Costa County has had a release that has offsite impact and is categorized by any of the following:

1. Off-site impact that may cause eye, skin, nose and/or respiratory irritation to the general population.
2. Fire, explosion, heat, or smoke with an off-site impact. Example: On a process unit/storage tank where mutual aid is requested to mitigate the event and the fire will last longer than 15 minutes.
3. Hazardous material or fire incident where the incident commander or unified command, through consultation with the Contra Costa Health Services Hazardous Material Incident Response Team, requests that sirens should be sounded.

*See* http://cchealth.org/hazmat/pdf/incident_notification_policy.pdf (accessed April 9, 2013).

[ii] Contra Costa County considers a shelter-in-place to include going inside a home or nearest building, closing doors and windows, and turning off heating, ventilation, and air conditioning. *See* http://cchealth.org/emergencies/shelter-in-place.php (accessed February 6, 2013).

**Figure 3. Initial vapor cloud formation (white cloud) and subsequent ignition (black smoke) as seen from a pier in San Francisco, California.**

3. The incident occurred from the piping referred to as the “4-sidecut” stream, one of several process streams exiting the C-1100 Crude Unit Atmospheric Column (Figure 4).[i] A plot plan of the crude unit shows the leak location relative to C-1100 (Figure 5). As shown in Figure 6, light gas oil (the crude unit 4-sidecut process fluid) exits the atmospheric column via a 20-inch nozzle and is split into a 12-inch line and an 8-inch line. The August 6, 2012, pipe rupture (Figure 7) occurred on a 52-inch long component[ii] of the 4-sidecut 8-inch line (the 52-inch component). The line operated at a temperature of 640 degrees Fahrenheit (°F)[iii] and had an operating pressure of approximately 55 pounds per square inch gauge (psig) at the rupture location. At the

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[i] The atmospheric column separates crude oil feed into different streams through distillation. These streams are further processed in other units in the refinery.

[ii] The term “component” refers to a portion of piping between welds or flanges. It includes straight run piping and pipe fittings.

[iii] The auto-ignition temperature for this process, the temperature at which a material will combust in the presence of sufficient oxygen without an ignition source, was also 640 °F. This number is based on the Chevron Light Gas Oil Material Safety Data Sheet. Chemical testing of 4-sidecut samples following the incident indicated lower auto-ignition temperatures; however, these samples may not have been representative of typical 4-sidecut process fluid.

time of the incident, light gas oil was flowing through the 8-inch line at a rate of approximately 10,800 barrels per day (bpd).[i]

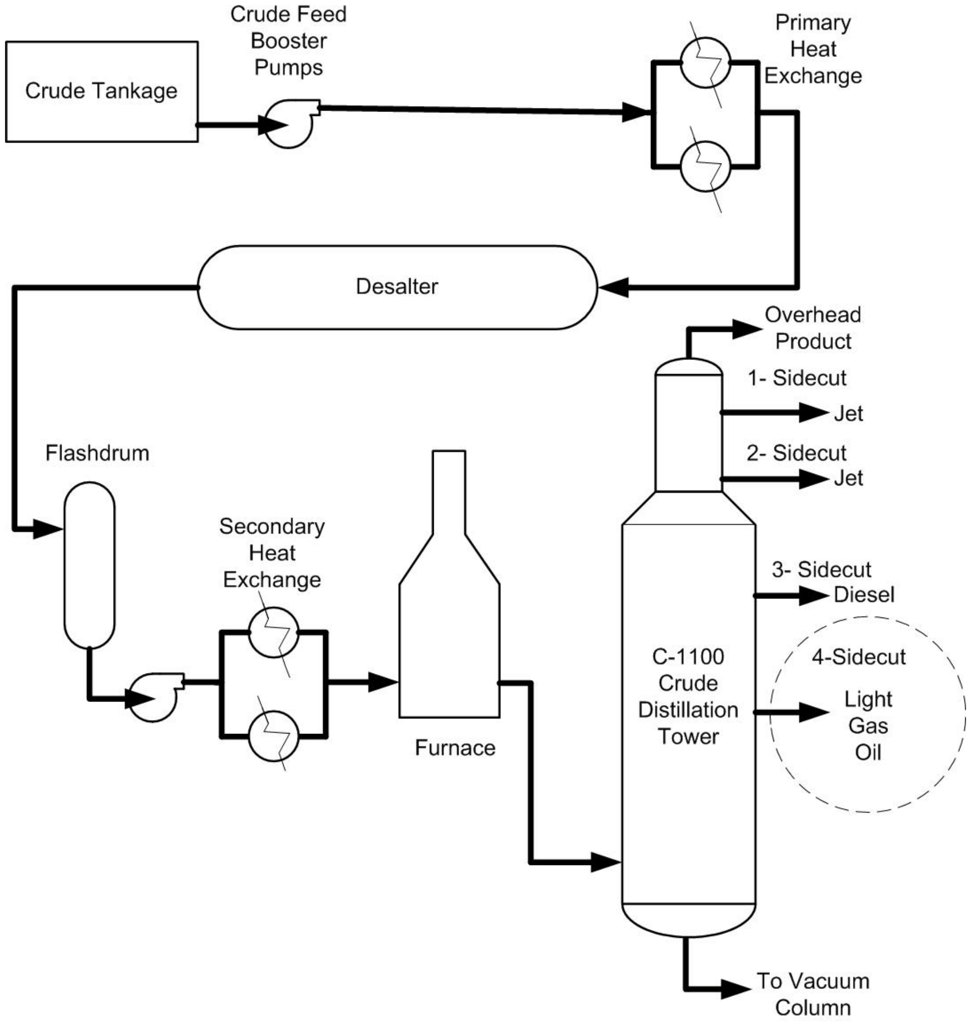

**Figure 4. C-1100 Crude Unit Atmospheric Column and Upstream Process Equipment.**

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[i] This is the equivalent of 315 gallons per minute (gpm). A barrel equals 42 gallons.

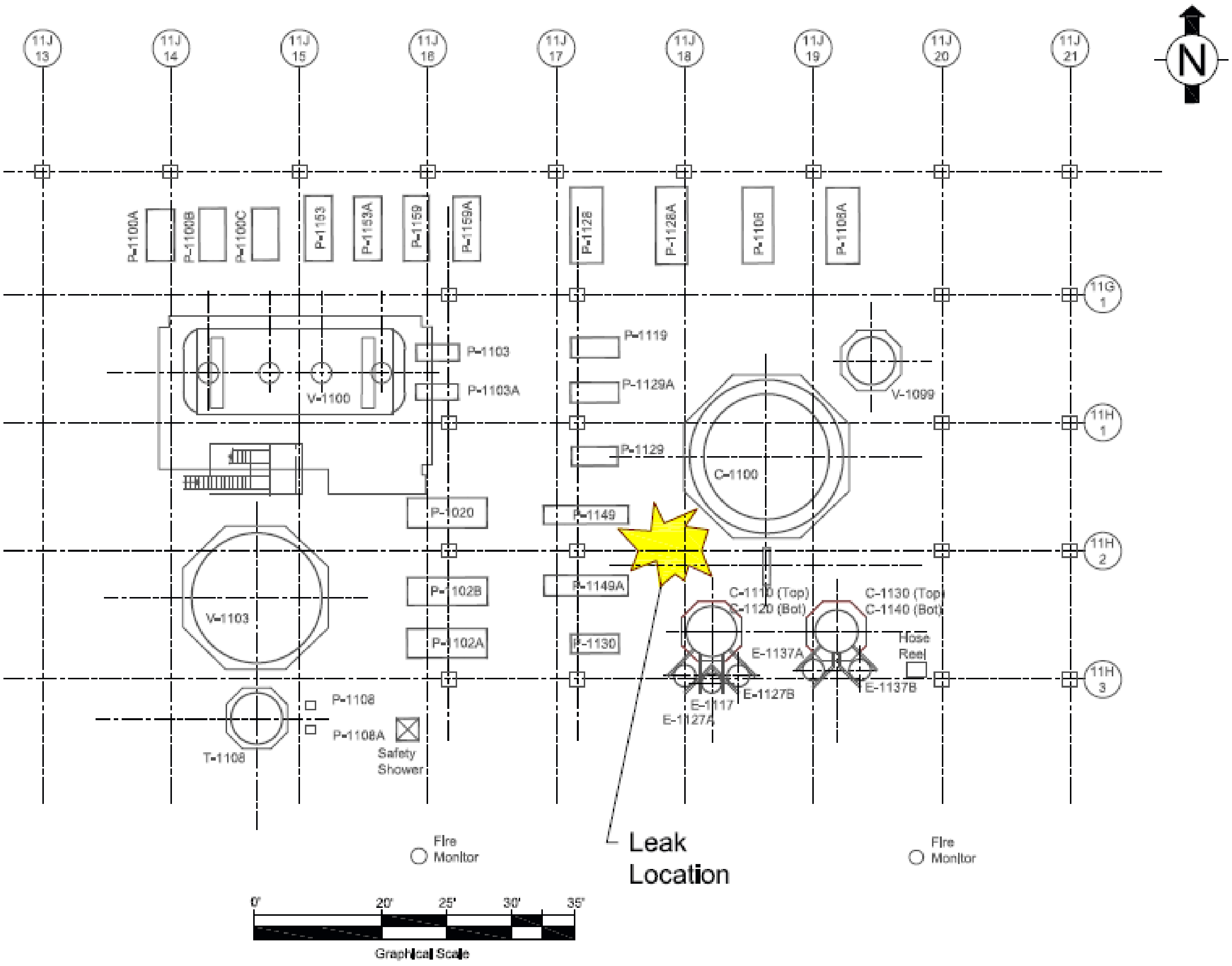

Figure 5. Overhead view of the equipment in the #4 Crude Unit showing the leak location, commonly referred to as a plot plan.

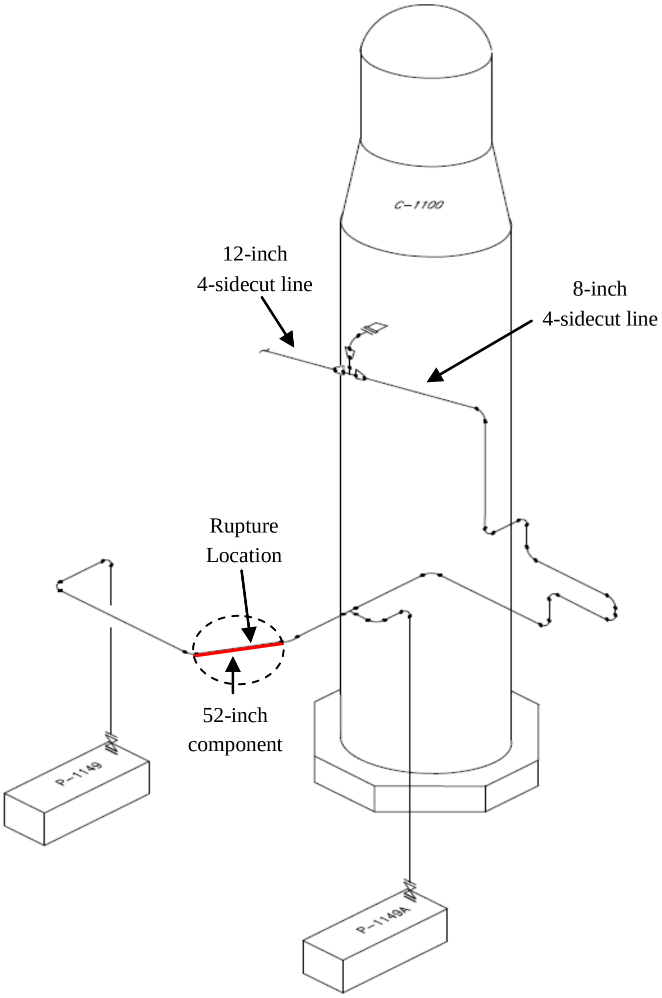

**Figure 6. 4-sidecut line configuration and rupture location.**

4. The CSB commissioned Anamet, Inc., a materials engineering and laboratory testing company, to conduct testing of the 4-sidecut pipe, including the failed 52-inch component. The testing concluded that the rupture was due to pipe wall thinning caused by sulfidation corrosion,[3] which is discussed below.

5. Anamet's metallurgical analysis found that the 52-inch component where the rupture occurred had experienced extreme thinning; the average wall thickness near the rupture location was approximately 40 percent thinner than a dime[i] (the thinnest American coin). Between 1976 and 2012, the 52-inch piping component had lost, on average, 90 percent of its original wall thickness in the area near the rupture. The piping had an initial nominal wall thickness of 0.322-inch[ii] when it was installed in 1976.

**Figure 7. Photo of rupture on 4-sidecut 52-inch component.**

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[i] The U.S. Mint reports that a dime has a thickness of 1.35 mm, or 0.053 inches. Information can be found at http://www.usmint.gov/about_the_mint/?action=coin_specifications (accessed February 14, 2013).

[ii] This portion of the 4-sidecut line was constructed of 8-inch Schedule 40 carbon steel piping.

# Sulfidation Corrosion

6. Sulfidation corrosion is a damage mechanism[i] that is well understood in the refining industry. The sulfidation corrosion industry guidance document, American Petroleum Institute (API) Recommended Practice (RP) 939-C *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*[ii] notes:

> [Sulfidation] …is not a new phenomenon, but was first observed in the late 1800s in a pipe still (crude separation) unit, due to the naturally occurring sulfur compounds found in crude oil. When heated for separation, the various fractions in the crude were found to contain sulfur compounds that corroded the steel equipment.[4]

7. Sulfidation corrosion, also known as sulfidic corrosion,[5] is a damage mechanism that causes thinning in iron-containing materials, such as steel, due to the reaction between sulfur compounds and iron at temperatures ranging from 450 °F to 800 °F.[6] This damage mechanism causes pipe walls to gradually thin over time. Sulfidation corrosion is common in crude oil distillation[iii] where naturally occurring sulfur and sulfur compounds found in crude oil feed, such as hydrogen sulfide,[iv] are available to react with steel piping and equipment. Process variables that affect corrosion rates include the total sulfur content of the oil, the sulfur species present, flow conditions, and the temperature of the system. Virtually all crude oil feeds contain sulfur compounds and, as a result, sulfidation corrosion is a damage mechanism present at every refinery that processes crude oil. Sulfidation corrosion can cause thinning to the point of pipe failure when not properly monitored and controlled.

8. The reaction between sulfur and iron produces a layer of iron sulfide scale[v] on the inside surface of piping.[7] This reaction can be compared to that of oxygen and iron which also produces a scale, commonly known as rust. The type of scale formed by sulfidation corrosion is dependent upon the components contained in the steel. Certain scales formed are protective and actually reduce the reaction rate between sulfur compounds and iron, minimizing sulfidation corrosion

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[i] Piping damage mechanisms are any type of deterioration encountered in the refining and chemical process industry that can result in flaws/defects that can affect the integrity of piping (e.g. corrosion, cracking, erosion, dents, and other mechanical, physical or chemical impacts). *See* API 570. "Piping Inspection Code: In-Service Inspection, Rating, Repair, and Alteration of Piping Systems." 3rd ed., Section 3.1.1.5, November 2009.

[ii] API RP 939-C is one of several relevant American Petroleum Institute recommended practices and standards under evaluation by the CSB as part of this investigation. To the casual observer API RP 939-C appears to obligate the industry to take significant actions. However, the CSB concluded it was written to be permissive so that industry compliance with specific provisions would not be required. The complete findings from this evaluation will be included in the CSB's Final Report.

[iii] Distillation separates mixtures into broad categories of its components by heating the mixture in a distillation column where different products boil off and are recovered at different temperatures. *See* http://www.eia.gov/todayinenergy/detail.cfm?id=6970 (accessed April 4, 2013).

[iv] Hydrogen sulfide is the most aggressive sulfur compound that causes sulfidation corrosion.

[v] Scale is a nonmetallic layer on the surface of metals and is often a result of corrosion.

rates. For instance, sulfidation corrosion affecting steel alloys containing greater than two weight percent (wt. %) chromium produces a protective scale that inhibits the reaction between the iron and sulfur compounds, thereby reducing corrosion rates.[i] With increasing percentages of chromium, the reaction is further slowed, greatly diminishing corrosion rates.[8,ii] For example, stainless steel (an 18 wt. % chromium alloy) is nearly 15 times more resistant to sulfidation corrosion than 9-Chrome (a 9 wt. % chromium alloy).[9] Conversely, sulfidation corrosion rates are significantly higher in steels containing very little chromium. Carbon steel, the Chevron 4-sidecut line material of construction, was manufactured with a maximum concentration of 0.40 % chromium.[10] The scale formed on carbon steel is less protective and allows continued reaction between the sulfur compounds and iron.[11] Thus, carbon steel corrodes at a rate that is significantly faster than other materials of construction, such as high chromium steels.

9. In addition to its inherently faster rate of sulfidation corrosion when compared with higher chromium steels, carbon steel also experiences significant variation in corrosion rates due to variances in silicon content, a component used in the steel manufacturing process. Carbon steel piping containing silicon content less than 0.10 wt. % can corrode at accelerated rates,[12] up to sixteen times faster than carbon steel piping containing higher percentages of silicon as shown in Figure 8. This figure shows how carbon steel corrosion rates can greatly vary depending on silicon content.

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[i] At greater than two wt. % chromium, sulfur compounds react with the steel to form $FeCr_2S_4$ scale. This scale provides more protection than the FeS scale that forms on carbon steel piping. *See* Niccolls, E. H., J. M. Stankiewicz, J. E. McLaughlin, and K. Yamamoto. "High Temperature Sulfidation Corrosion in Refining." *17th International Corrosion Congress.* Las Vegas: NACE International, 2008.

[ii] It has also been found that chromium “poisons” the decomposition of sulfur compounds to hydrogen sulfide which also slows down the sulfidation corrosion rate. *See* Couper, A.S. “High Temperature Mercaptan Corrosion of Steels.” *19th Annual Conference of the National Association of Corrosion Engineers*. Pages 396t-401t, New York: March 1963.

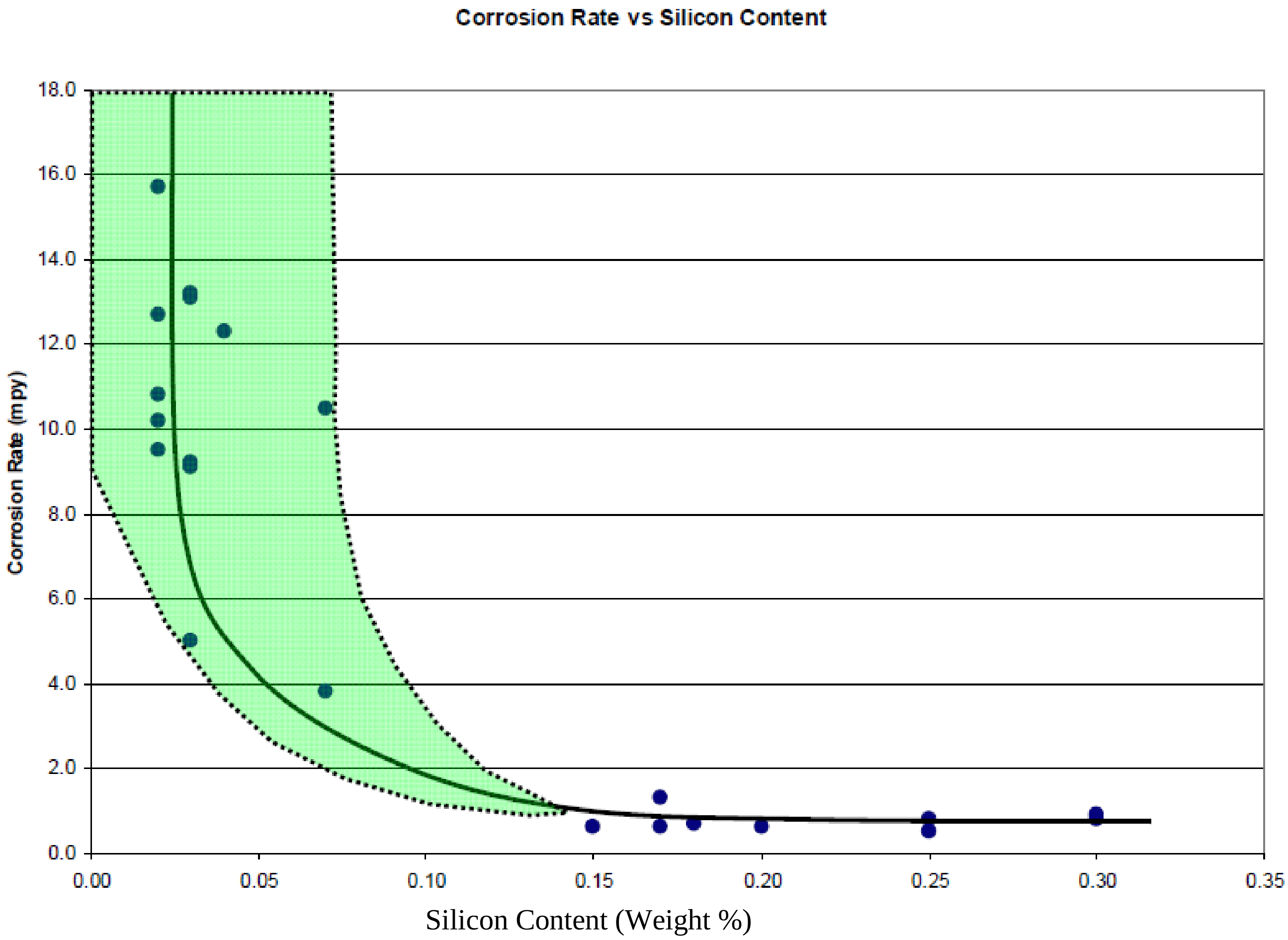

**Figure 8. This graph shows how corrosion rates increase in carbon steel containing decreasing percentages of silicon. This information can be found in Annex C of API RP 939-C.**[i]

10. The refining industry has been aware of increased rates of sulfidation corrosion in low-silicon carbon steel piping since as early as 1974,[13] nearly 40 years before the August 6, 2012, incident and two years before the Chevron crude unit was constructed. Prior to the incident, Chevron documented its understanding of the significant consequences of sulfidation corrosion. This is reflected in Chevron's *Corrosion Prevention and Metallurgy Manual*, which states:

> Sulfidation corrosion has caused severe fires and fatalities in the refining industry, primarily because it causes corrosion over a relatively large area, so failures tend to involve ruptures or large leaks rather than pinhole leaks. It can be insidious in that moderately high corrosion rates can go undetected for years before failure. Finally, process changes that increase the temperature or sulfur content can creep up over time and

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[i] The y-axis of this figure is in units of mils per year (mpy). A "mil" is 1/1000 inch.

> multiply corrosion rates so that what was thought to be a low corrosion rate system becomes corrosive enough to fail before the increased corrosion rate is recognized.

11. Carbon steel piping is manufactured to meet certain specifications, including American Society for Testing and Materials (ASTM) A53B,[14] ASTM A106,[15] and API 5L.[16] ASTM A53B and API 5L do not contain minimum silicon content requirements for carbon steel piping,[17] while ASTM A106 requires the piping to be manufactured with a minimum silicon content of 0.10 wt. %. As a result, manufacturers have used different levels of silicon in the carbon steel pipe manufacturing process. Thus, depending on the manufacturing specification for carbon steel susceptible to sulfidation corrosion, corrosion rates could vary depending on the silicon content within the steel.

12. In the mid 1980s, pipe manufacturers began to simultaneously comply with all three manufacturing specifications (ASTM A53B, ASTM A106, and API 5L) when manufacturing carbon steel piping. The majority of carbon steel piping purchased following this time period likely has a minimum of 0.10 wt. % silicon content. However, piping purchased and installed prior to the mid-1980s could still contain low silicon components that are susceptible to high, variable sulfidation corrosion rates.

13. Over 95 percent of the 144 refineries in operation in the U.S., including the Chevron Richmond Refinery,[i] were built before 1985,[18] and thus before piping manufacturers began producing carbon steel in compliance with all three manufacturing specifications. Therefore, the original carbon steel piping in these refineries is likely to contain varying percentages of silicon content and may experience highly variable sulfidation corrosion rates.

14. The Chevron Richmond Refinery 4-sidecut piping circuit containing the 52-inch component that failed was constructed of ASTM A53B carbon steel, which had no minimum specification for silicon content. Post-incident testing of samples of the 4-sidecut piping from the Chevron Richmond Refinery identified silicon content ranging from 0.01 wt. % to 0.2 wt. %. Of twelve samples taken from the 8-inch and 12-inch 4-sidecut line, six had a silicon concentration of less than 0.10 wt. %. The 52-inch pipe component that ruptured on the day of the incident had a silicon content of only 0.01 wt. %. The elbow component directly upstream of the 52-inch component that failed had a silicon concentration of 0.16 wt. % and showed considerably less thinning (Figure 9).

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[i] The Chevron Richmond Refinery was constructed in 1902.

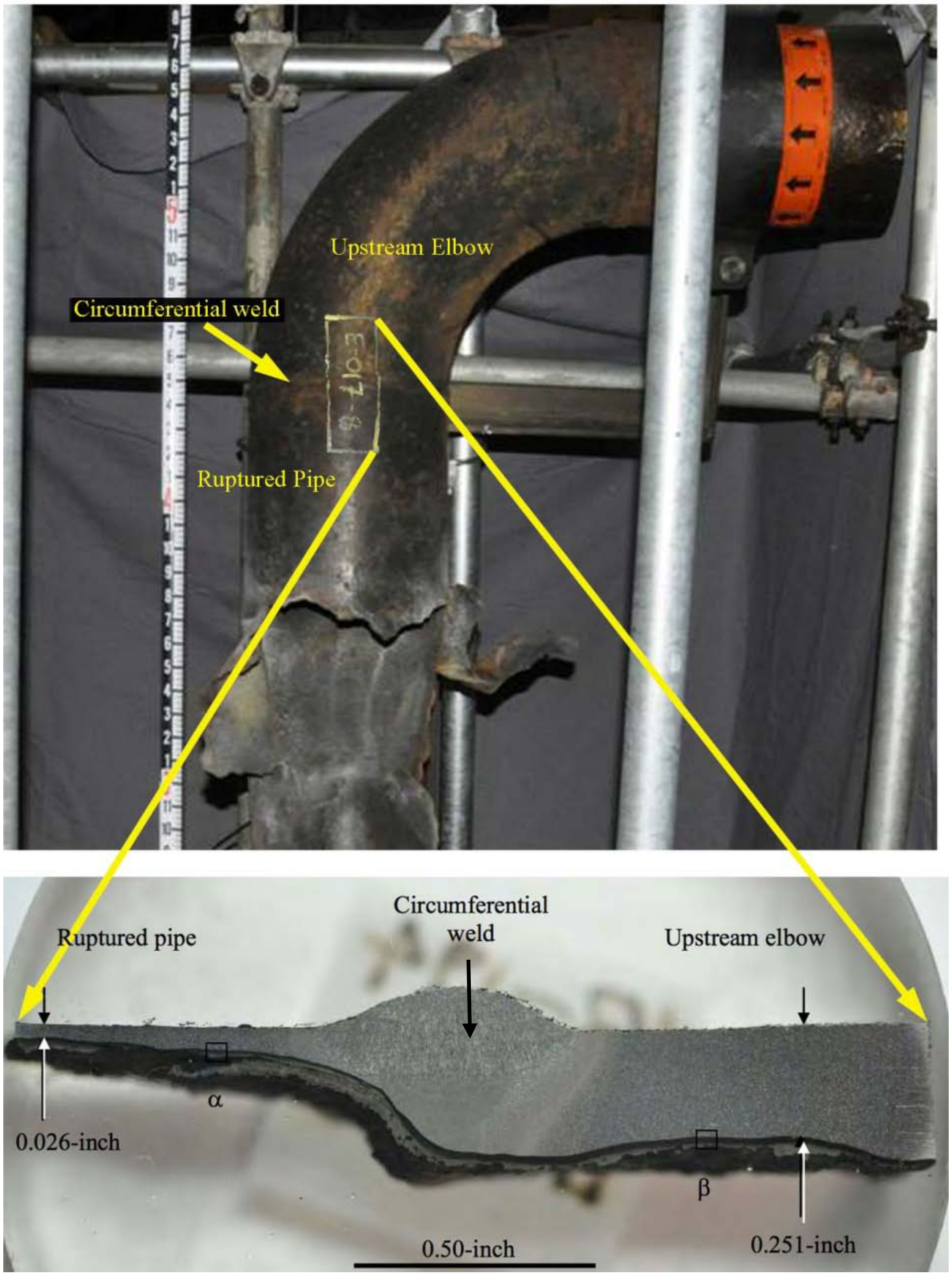

**Figure 9. 4-sidecut piping sample (E-017-8) analyzed by Anamet Labs showing the relative thickness of low silicon piping on the left and the high silicon piping on the right. The ruptured pipe component (left) contained 0.01 % silicon and the upstream elbow component (right) contained 0.16 % silicon.[19] The initial nominal thickness of this piping was 0.322-inch.**

# Sulfidation Corrosion Inspection Techniques

15. As evidenced by the chemical analysis performed on the Chevron 4-sidecut piping post-incident, carbon steel piping components within a single circuit[i] can contain varying percentages of silicon, resulting in a large variation in sulfidation corrosion rates by component. Historically, sulfidation corrosion monitoring techniques required the measurement of pipe thickness at only a minimal number of permanent Condition Monitoring Locations (CMLs)[ii] along the piping. These CMLs are most frequently placed on elbows and fittings.[iii] However, due to details of the manufacturing process, carbon steel pipe fittings generally contain high percentages of silicon.[20] When measurements are only taken at high-silicon containing fittings, the measurements can fail to identify high corrosion rates within a pipe circuit caused by low-silicon components. At the Chevron Richmond Refinery, the 4-sidecut piping had a total of 24 CMLs[iv] on piping and fittings. The CSB found that there were no CMLs placed on the low silicon piping component that failed. Chevron identified accelerated corrosion in the 52-inch component in a 2002 inspection. However, no CML was added to ensure future monitoring, and the 52-inch component was not inspected again. Instead, the CSB found that Chevron relied on inspection data gained primarily from high silicon pipe-fitting components, such as elbow components. This inspection data did not reflect the corrosion rates of the lower-silicon components of the 4-sidecut piping. Relying on the limited inspection data from the CMLs on the high silicon components, Chevron management denied multiple recommendations to replace the 4-sidecut line. As illustrated by the Chevron incident, inspection techniques alone may not accurately identify the most aggressive corrosion rates throughout an entire circuit of carbon steel piping. Low-silicon components can remain uninspected and unidentified until failures such as the August 6, 2012, Chevron incident occur. As will be discussed below, upgrading metallurgy is a more effective means of managing sulfidation corrosion.

16. Determining silicon content in existing carbon steel piping and equipment in the field is a difficult undertaking. To properly characterize the silicon content in each component in a piping circuit, every component must be inspected. This is known as 100 percent component inspection. Two techniques are currently used to determine silicon content in existing carbon steel piping circuits with unknown chemical composition: performing chemical analysis and pipe wall thickness measurements of every component.

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[i] A piping circuit is a length of pipe and the fittings associated with a particular process service that operate at similar conditions. A circuit usually begins and ends at either a branch or a piece of process equipment such as a vessel or a pump. Reference to piping by circuits allows piping to be grouped conveniently by proximity and operating service. Piping circuits may also be referred to as piping runs.

[ii] A condition monitoring location (CML) is a designated area where periodic thickness examinations are conducted. Each CML represents as many as four inspection locations located circumferentially around the pipe. CMLs are also referred to as thickness monitoring locations (TMLs). CML was historically referred to as corrosion monitoring locations (CMLs) and that terminology is sometimes still used within the industry.

[iii] A fitting is a piping component usually associated with a change in direction or diameter.

[iv] Many of these CMLs were added during the 2011 turnaround.

17. Many field-portable instruments used for positive material identification cannot adequately identify silicon content.[21] If original manufacturing quality assurance data[i] are not available, as is generally the case with older plants, then chemical verification requires destructive testing. Metal shavings must be taken from each carbon steel piping component for chemical analysis in a laboratory.[22] This method requires that the insulation be removed for access to the piping so that each individual piping component can be sampled and verified.

18. Carbon steel components containing low concentrations of silicon can also potentially be identified by performing thickness measurements of every component within a carbon steel circuit.[23] This practice is only useful if the piping circuit has been exposed to sulfidation corrosion for a long enough time period so that variances in corrosion rate caused by differences in silicon content may be detected. Chemical analysis is therefore the most accurate technique to identify low-silicon carbon steel components. As with chemical analysis, the thickness measurement method requires that each individual piping component be identified by removing insulation (so every weld seam can be located), a time consuming and costly undertaking, or by using non-destructive examination techniques. Thickness measurements on high temperature piping typically can only be done accurately and safely during unit turnarounds.[ii] Although these various methods were available to detect the location of the field welds, Chevron had not used them to identify the 4-sidecut pipe segment locations.

19. API Recommended Practice 939-C *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries* describes the challenges faced when attempting to thoroughly inspect carbon steel lines susceptible to sulfidation corrosion. The recommended practice states that older ASTM A53 piping, such as the Chevron piping that failed on August 6th, creates a "major inspection challenge"[24] and that "unless the refinery is fortunate enough to have located an inspection point on that particular [low silicon] section of pipe or fitting, it is very difficult to detect the thinning component."[25] It states that in some applications, carbon steel will appear to be adequate based on measured corrosion rates until failure occurs at some undocumented or unidentified low-silicon component.[26]

20. Unlike silicon concentration, the chromium concentration of steel can easily be verified in the field using portable positive material identification instruments. In addition, steel alloys containing at least 9 wt. % chromium are more resistant to sulfidation corrosion and do not run the risk of extreme variations in corrosion rates within components in the same piping circuit.[iii] This makes alloys with higher chromium content an inherently safer choice in high temperature

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[i] Manufacturing quality assurance data, also known as mill data, provides the chemical composition of the steel.

[ii] A "turnaround" is a scheduled shutdown of a process unit to perform maintenance, repairs, upgrades, and inspection of process equipment.

[iii] The protective scale, $FeCr_2S_4$, begins to be the dominant scale formed in steels containing a chromium content of five wt. %. The 5Cr steel alloy can be manufactured to contain anywhere from 4% to 6% chromium. Thus, "the sulfidation corrosion rate can vary dramatically in 5Cr steels even in the same operating environment." *See* Niccolls, E. H., J. M. Stankiewicz, J. E. McLaughlin, and K. Yamamoto. "High Temperature Sulfidation Corrosion in Refining." *17th International Corrosion Congress.* Las Vegas: NACE International, 2008.

sulfidation corrosion environments.[i] As shown in the Modified McConomy Curves[ii] from API RP 939-C (Figure 10), 9-Chrome[iii] corrodes 15 times faster than stainless steel,[iv] and carbon steel[v] corrodes 125 times faster than stainless steel.[27]

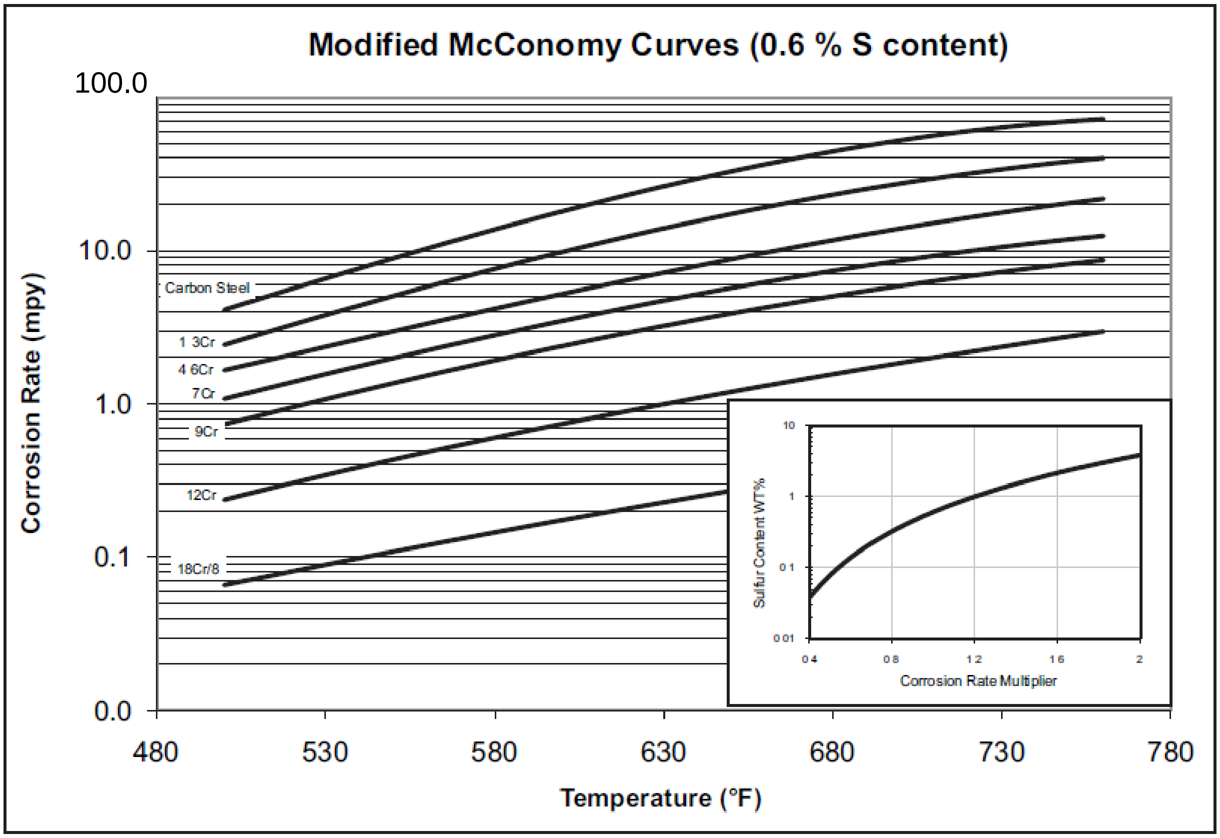

Figure 10. Modified McConomy Curves from API RP 939-C.

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[i] Steels with higher chromium content are inherently safer than carbon steel with respect to sulfidation corrosion. However, analysis is still required to ensure that the best material of construction is selected.

[ii] Modified McConomy Curves are the set of curves API RP 939-C uses to predict sulfidation corrosion rates versus temperature for several steel alloys.

[iii] 9-Chrome contains 9 wt. % chromium.

[iv] Stainless steel contains 18 wt. % chromium.

[v] ASTM A53B carbon steel contains a maximum of 0.40 wt. % chromium.

# Chevron Sulfidation Corrosion Knowledge and Expertise

21. Figure 11 shows a timeline of Chevron's key sulfidation events. Chevron technical staff has considerable knowledge and expertise regarding sulfidation corrosion, specifically with respect to corrosion rate variations caused by differing silicon concentration in carbon steel piping. Chevron employees have authored industry papers on sulfidation corrosion and had significant influence in the development of the industry sulfidation corrosion recommended practice, API RP 939-C. This recommended practice, first published in 2009, was developed under Chevron leadership. At the approximate time of publication of API RP 939-C, Chevron Energy Technology Company (Chevron ETC)[i] created an internal document on the subject of sulfidation corrosion. Chevron ETC metallurgists released a formal report dated September 30, 2009 (nearly 3 years prior to the incident) to Chevron refinery-based reliability managers and chief inspectors entitled *Updated Inspection Strategies for Preventing Sulfidation Corrosion Failures in Chevron Refineries*.

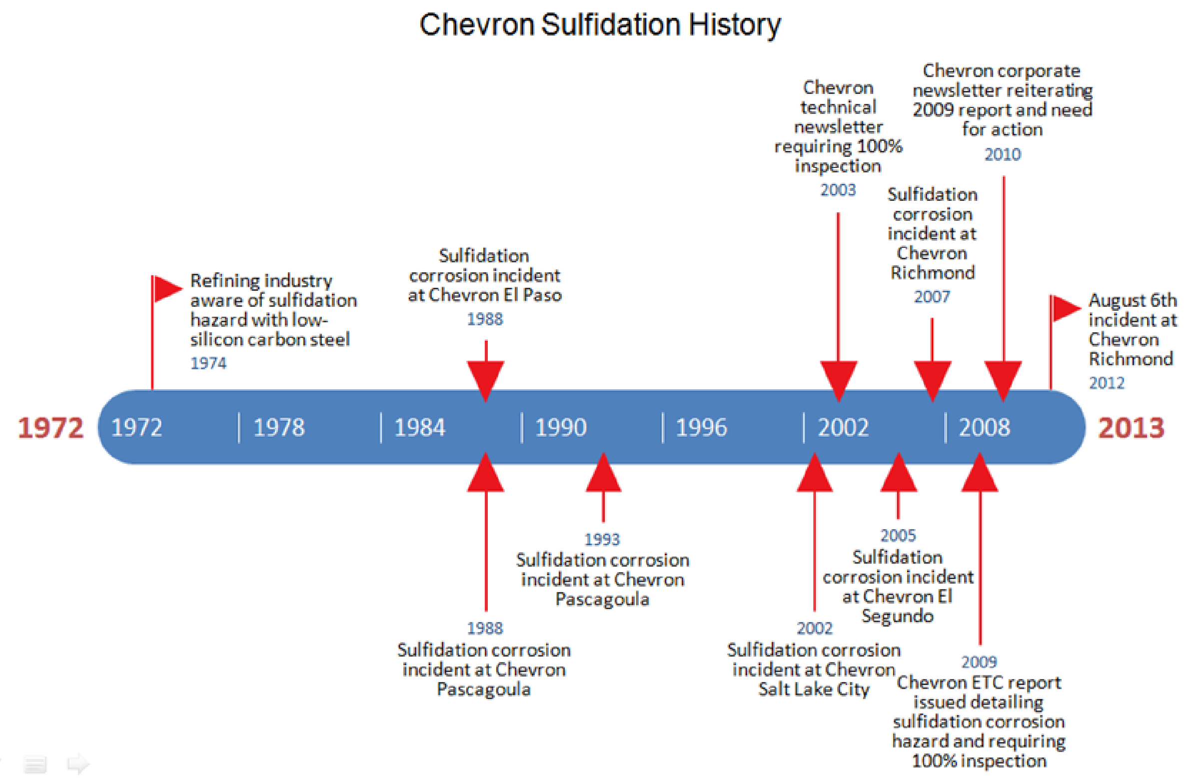

**Figure 11. Chevron's key sulfidation events between 1974 and 2013.**

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[i] The Chevron Energy Technology Company is a separate business unit within the Chevron Corporation that provides technology solutions and technical expertise for Chevron operations worldwide. *See* http://richmond.chevron.com/home/aboutchevronrichmond.aspx (accessed April 4, 2013)

22. Sulfidation experts acknowledged in the Chevron ETC report that, “Until now, Chevron has not directly addressed the risk of low Si[licon] carbon steel…”[i] and that the report lays out a program that “seeks to close these gaps, and to maximize the effectiveness of our inspection.” The report clearly indicates that Chevron understood both the potential consequence and the high likelihood of a rupture or catastrophic failure from sulfidation corrosion and calls out Chevron’s need for action:

> Sulfidation corrosion failures are not common in Chevron or in the industry but they are of great concern because of the comparatively high likelihood of blowout or catastrophic failure […] . This can happen because corrosion occurs at a relatively uniform rate over a broad area so a pipe can get progressively thinner until it actually bursts rather than leaking at a pit or local thin area. In addition the process fluid is often above its autoignition temperature. The combination of these factors means that sulfidation corrosion failures frequently result in large fires. […] [S]everal case histories of sulfidation corrosion failures that have occurred in Chevron or in the industry several of which are blowouts.

This Chevron ETC report specifically recommends that inspectors perform 100 percent component inspection on high temperature carbon steel piping susceptible to sulfidation corrosion. However, this 100 percent component inspection program was not implemented at the Richmond refinery prior to the August 6, 2012 incident. The Chevron ETC report defines a priority ranking system to help focus the inspection implementation efforts. The process conditions of the 4-sidecut stream placed it in the highest priority for inspection.

23. Chevron ETC technical experts issued a corporate newsletter in 2010 that again warned of the potential consequence of sulfidation failures. In this newsletter, the 100 percent component inspection recommendation from the 2009 report was reiterated for piping systems such as the crude unit 4-sidecut piping. The newsletter states:

> Sulfidation corrosion failures … are of great concern because of the comparatively high likelihood of “blowout” or catastrophic failure. This typically happens because corrosion occurs at a relatively uniform rate over a broad area, so a pipe can get progressively thinner until it actually bursts rather than leaking at a pit or local thin area. In addition, the process fluid is often above its autoignition temperature. The combination of these factors means that sulfidation corrosion failures frequently result in large fires. Chevron and the industry have experienced numerous failures from this mechanism and recent incidents have reinforced the need for revised inspection strategies and a robust PMI (Positive Materials Identification) program.

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[i] A 2003 corporate technical newsletter recommended 100 percent component inspection of carbon steel piping susceptible to sulfidation corrosion following a 2002 Chevron Salt Lake City sulfidation corrosion incident.

The Chevron ETC 100 percent component inspection recommendation for high risk piping systems, established in 2009, was not implemented at Richmond; therefore, the thin-walled low silicon 4-sidecut piping component remained in service until it catastrophically failed on August 6, 2012.

24. Chevron and Chevron ETC metallurgists, materials engineers, and piping inspectors had expertise regarding sulfidation corrosion. They educated personnel and advocated for identification and control of damage mechanisms, including sulfidation corrosion. However, they had limited practical influence to implement their recommendations. These individuals did not participate in the crude unit Process Hazard Analysis (PHA)[i] and did not affect decisions concerning control of sulfidation corrosion during the crude unit turnaround process.[ii]

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[i] A process hazard analysis is a hazard evaluation to identify, evaluate, and control the hazards involved in a process. Facilities that process a threshold quantity of hazardous materials, such as the Chevron Richmond refinery, are required to conduct a process hazard analysis per the California Code of Regulations Title 8 Section 5189. Process Safety Management of Acutely Hazardous Materials (1992). PHAs are also required by the California Accidental Release Prevention Program and the federal EPA Risk Management Program.

[ii] The turnaround process includes both the planning stage prior to the shutdown and the activities staged during the shutdown.

# Other Significant Sulfidation Occurrences

25. The refining industry has experienced numerous sulfidation corrosion failures, primarily in piping.[28] API RP 939-C identifies 45 sulfidation corrosion failures, one third of which were found to have occurred in carbon steel piping containing low levels of silicon.[29]

26. The August 6, 2012, Chevron Richmond Refinery 4-sidecut pipe rupture was not the first sulfidation corrosion-related incident to occur at a Chevron refinery. In 1988, a low silicon carbon steel (0.02 wt. % silicon) piping component failed at the Chevron's former El Paso Refinery[i] in El Paso, Texas. In addition, two sulfidation corrosion incidents occurred at the Chevron Pascagoula refinery in Pascagoula, Mississippi: one in 1993 and one in 1988 on a low-silicon carbon steel component.

27. In 2002, the Chevron Salt Lake City Refinery experienced a fire when process piping failed as a result of sulfidation corrosion in a low silicon ASTM A53 carbon steel piping component. Chevron communicated the incident throughout the company in a technical newsletter. Chevron experts found that despite regular monitoring of the line for 30 years in compliance with industry standards, their inspection program failed to prevent the failure. Corrosion rates at the unmonitored failure location were found to be five times greater than corrosion rates at the monitored piping locations. The monitored locations were constructed of high silicon ASTM A106 piping (Figure 12). Chevron also found that in the years preceding the failure, both the temperature[ii] and hydrogen sulfide concentration in the process had been increasing. Each of these factors increased corrosion rates and contributed to the failure. In 2003, following this incident, Chevron experts recommended that refineries inspect every piping component (100 % component inspection) in all high-risk piping systems: those operating above 550 °F and containing hydrogen sulfide.

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[i] The El Paso Refinery is now owned by Western Refining.

[ii] The temperature in the line had been increased by over 170 °F throughout the life of the unit. During the two years prior to failure, temperatures of the line exceeded the measurement capabilities of the temperature measurement device and so the actual temperature increase cannot be determined.

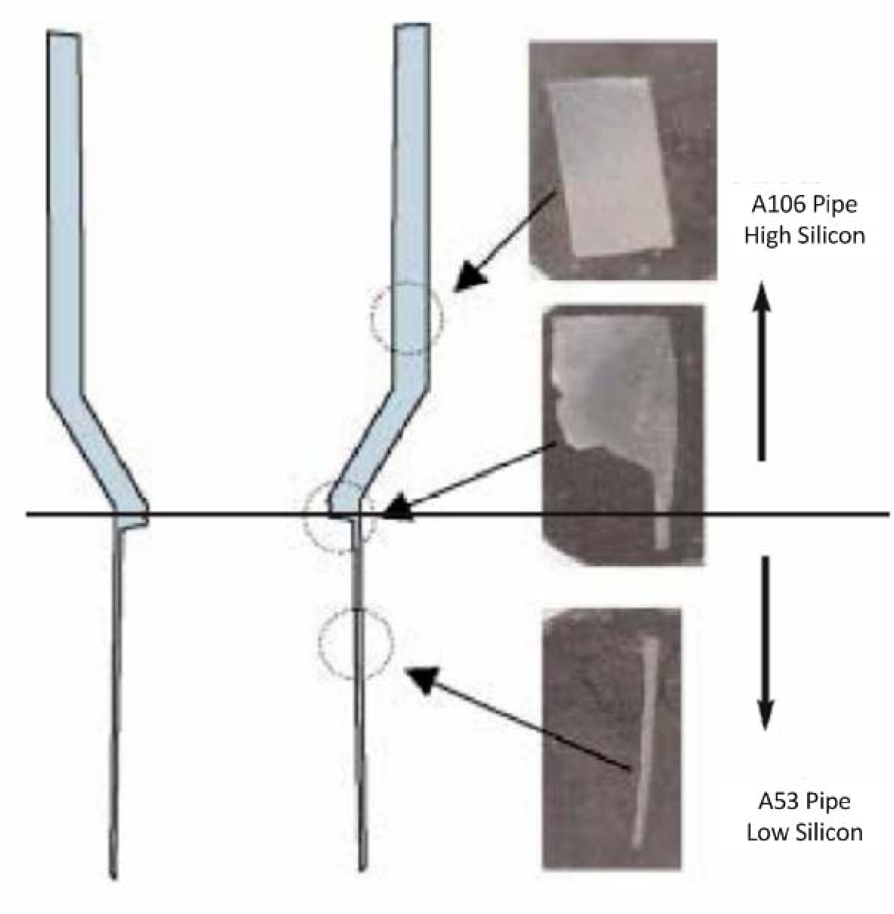

**Figure 12. Schematic of failed piping from the Chevron Salt Lake Refinery. Similar to the Chevron Richmond Refinery incident, the failed piping contained low amounts of silicon and corroded significantly faster than adjacent piping components.**

28. In January 2007, a failure due to sulfidation corrosion caused a serious fire in the Chevron Richmond Refinery crude unit resulting in a CWS Level 3 alert, initiating a shelter-in-place for the surrounding community. A carbon steel piping spool[i] failed catastrophically during operation (Figure 13). The carbon steel piping contained a low percentage of silicon (<0.005 wt. %). The process fluid ignited, injuring a nearby worker. Chevron informed Contra Costa Health Services' Hazardous Materials Program[ii] (Contra Costa County) in a letter that the metallurgy had been upgraded following this incident as an inherently safer solution. However, the CSB learned that this upgrade was limited to only the immediate piping spool that failed. The inherently safer, more corrosion resistant metallurgy was not implemented more broadly in crude unit high temperature service as a result of this incident.

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[i] A piping spool is a small, removable section of piping. In some cases, a piping spool is installed or removed in order to provide a temporary connection or complete disconnection between two piping circuits.

[ii] Contra Costa Health Services' Hazardous Materials program is designed to respond to emergencies and monitor hazardous materials within Contra Costa County. *See* http://cchealth.org/hazmat/ (accessed April 17, 2013).

**Figure 13. Failed piping component that resulted in the 2007 Richmond crude unit fire. This carbon steel piping was found to contain less than 0.005 percent silicon.**

29. Following the August 6, 2012, incident, personnel at the Chevron El Segundo, California, refinery, a near duplicate of the Richmond refinery, inspected their refinery's crude unit 4-sidecut piping. Significant thinning was discovered in the line; the piping from the atmospheric crude column to the pumps was removed and substituted with 9-Chrome, an upgraded and inherently safer material of construction.

30. On November 9, 2009, the Silver Eagle refinery in Woods Cross, Utah, experienced a catastrophic piping failure due to sulfidation corrosion in a 10-inch pipe, while conducting a temporary operation at higher than normal operating temperature. The pipe was located on the

bottom of a reactor in the de-waxing unit. The failed pipe released hydrogen which subsequently exploded, damaging over 100 homes in the nearby neighborhood.

31. On October 6, 2011, an explosion and fire resulted from a catastrophic piping failure at a Canadian refinery in Regina, Saskatchewan, injuring 52 workers. The piping component that failed was substantially thinner than neighboring components. Prior to the incident, the company's inspection data indicated that wall thickness in the overall piping system was within acceptable limits. However, the specific component that failed was not inspected. Although Canadian authorities are still investigating, metallurgical testing has indicated that hydrogen sulfide corrosion contributed to the catastrophic failure.

32. In February 2012, the BP refinery crude unit in Cherry Point, Washington, suffered a failure due to sulfidation corrosion, causing a large fire. This incident demonstrates that even when applying inherently safer concepts to reduce the potential for major hazards, it is still vital to fully understand all processes and piping configurations and incorporate a rigorous inspection program. The piping that failed was constructed of 9-Chrome. The line was used only during start-up operations and otherwise remained in-service and non-flowing. Such lines that do not have regular process flow yet remain in contact with process fluids are commonly referred to as "dead legs." The failure location was a high-point in the piping connected to the top of an operating process line. Hydrogen sulfide evolved from the process fluid and collected in the 9-Chrome piping. The concentrated vapor-phase hydrogen sulfide severely corroded the 9-Chrome, causing the failure. CMLs were located on adjacent elbow components; however, no CMLs were placed on the straight-run piping component where the failure occurred. The Cherry Point sulfidation failure demonstrates that even with more corrosion-resistant, inherently safer metallurgy, failure from sulfidation corrosion still may occur if piping is not effectively inspected or piping configurations are not adequately evaluated. In addition it is important to conduct a thorough analysis to determine the best material of construction for the process conditions.

# Process Hazard Analysis

33. Chevron personnel analyze numerous deviations[i] for each portion of a process when conducting a Process Hazard Analysis (PHA). These include conditions such as changes in flow and temperature and pressure extremes. Specifically of interest, one of the deviations analyzed was "leak/rupture" of the particular vessel or pipe. For each deviation, the team's responsibility was to identify causes, consequences, safeguards, and recommendations. The 4-sidecut line was analyzed in the most recent crude unit PHA. Corrosion was *not* identified as a potential cause of a leak/rupture in the piping (emphasis added).

34. Sometimes referred to as a corrosion review, a damage mechanism hazard review analyzes risks presented by all process failure mechanisms such as corrosion and cracking. Common process failure mechanisms are described in API 571: *Damage Mechanisms Affecting Fixed Equipment in the Refining and Petrochemical Industries*.[30] Such a review ensures that potential hazards caused by process conditions, process materials, and external mechanisms are properly identified, analyzed, and systems are put in place to control or eliminate the hazard. Despite Chevron knowledge and expertise of potential damage mechanisms (such as sulfidation corrosion), the CSB found these hazards are only identified in a PHA if the participants conducting the PHA happen to have personal knowledge of the relevant mechanism. The Chevron PHA teams do not typically seek assistance from corrosion experts.[ii] The inclusion of a damage mechanism hazard review as part of the PHA is not required by the state of California, the California Division of Occupational Safety and Health (Cal/OSHA),[iii] Contra Costa County, the City of Richmond,[iv] or Chevron standards. Because Chevron does not conduct, and is not required to conduct, a formal damage mechanism hazard review, damage mechanisms are only identified when the PHA team happens to have some knowledge of the mechanism. As a result, many damage mechanisms which occur in various processes are not properly addressed.

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[i] Deviations using guide words (such as no, more, less, as well as) and process parameters (such as flow, pressure, temperature) are analyzed in PHAs. *See* Center for Chemical Process Safety (CCPS). "Guidelines for Hazard Evaluation Procedures." 2nd ed., Page 132, 1992.

[ii] The Crude Unit Business Improvement Network (BIN) Leader, a crude unit expert, reviews portions of the PHA with the PHA team. However, this review did not identify the potential for sulfidation corrosion failures in the 4-sidecut piping. A rigorous review of corrosion and damage mechanisms present in the crude unit was not performed during the PHA process.

[iii] The state of California, under an agreement with the federal Occupational Safety and Health Administration, or OSHA, operates an occupational safety and health program in accordance with Section 18 of the Occupational Safety and Health Act of 1970. *See* http://www.osha.gov/dcsp/osp/stateprogs/california.html (accessed April 17, 2013). The Department of Industrial Relations administers the California Occupational Safety and Health Program, commonly referred to as Cal/OSHA. The program applies to all public and private sector places of employment in the state, with some exceptions. *See* http://www.dir.ca.gov/dosh/dosh1.html (accessed April 17, 2013).

[iv] The City of Richmond adopted an ordinance on Industrial Safety, Richmond Municipal Code Chapter 6.43 (also known as the RISO), on December 18, 2001, "for the purposes of protecting public health and safety by prevention of accidental release of hazardous materials and to assure protection of the environment." Richmond Municipal Code §6.43.040 (February 5, 2013). There are two facilities, including Chevron, that are located in the City of Richmond and subject to this ordinance. More information about the RISO is provided later in the report.

35. During a hazard analysis process such as a PHA, the evaluation team has to determine the likelihood of a hazardous consequence occurring. Then the team must identify safeguards which will reduce the risk of the hazard to an acceptable level. A recognized methodology for consistently and objectively making these determinations could include the use of quantitative, semi-quantitative, or qualitative tools.[31] Chevron does not employ a prescribed methodology for determining the likelihood that an incident will occur or whether a safeguard will be effective. Instead, Chevron relies upon the judgment of the people on the PHA team, who base their conclusions upon their collective experiences, beliefs, and areas of expertise. In its 2009 crude unit PHA, Chevron simply cited non-specific, judgment-based qualitative safeguards such as: utilizing metallurgy to minimize corrosion, having effective maintenance and inspection programs, and providing pipe wall corrosion allowances.[i] The effectiveness of these safeguards was neither evaluated nor documented; instead the safeguards were merely listed in the PHA. Had the adequacy of these safeguards been verified, improved safeguards intended to protect against sulfidation-induced failure of carbon steel piping could have been recommended.

36. Following the August 6th incident, Cal/OSHA inspected the Chevron facility and issued citations. Only one citation related to PHAs, and it was not associated with evaluating the effectiveness of safeguards. Rather, the emphasis was that Chevron's PHA did not adequately account for hazards caused by other units associated with the crude unit. The citation stated "The Employer [Chevron] failed to perform an effective Process Hazard Analysis [PHA] of the crude unit. Specifically, it failed to identify, evaluate, and control potential hazards caused by upstream and downstream units that provide and receive feed from the crude unit."[32] Had the Cal/OSHA regulation required documentation of the effectiveness of safeguards, Chevron would have been obligated to conduct this analysis and Cal/OSHA inspectors could rely on the regulation for support during inspections.

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[i] Corrosion allowance refers to extra wall thickness added as a safety factor to the design of a piece of equipment beyond that needed solely for mechanical considerations such as design temperature and pressure. This extra thickness is provided to accommodate for expected loss of wall thickness due to corrosion over the life of the equipment.

# Operational Changes

37. The original design of the 4-sidecut circuit included equipment which had the effect of removing dissolved hydrogen sulfide, the most aggressive sulfur compound associated with sulfidation corrosion, from the 4-sidecut light gas oil process fluid. As a result, the 4-sidecut equipment was effective in reducing the sulfidation corrosion rate. This allowed the 4-sidecut equipment to be constructed of carbon steel. In 1991, this 4-sidecut equipment was taken out of service. No management of change[i] (MOC) was performed to analyze the effect of the elimination of this hydrogen sulfide-removing equipment on 4-sidecut corrosion rates. Such an MOC would have ensured that the increase in sulfur concentration on the carbon steel 4-sidecut piping was reviewed prior to removing the equipment.

38. Crude oil feedstock used at the Chevron Richmond Refinery is obtained from a variety of different sources that are blended before processing. These various crudes have different compositions, such as varying sulfur compounds and concentrations. These crudes can have differing corrosion effects on process equipment and piping. There is an increasing trend in crude oil refining to process less expensive "opportunity crudes" because they can provide significant cost savings to the company.[ii] However, these crudes may contain more undesirable characteristics such as high sulfur content, high naphthenic acid content, or very heavy hydrocarbons[33] that a refinery may not have been originally designed to process. Refinery equipment may not be the proper material of construction to achieve the design life of the equipment when exposed to the different operating conditions. Additional mitigation may be needed to reduce risk. In 1984, the Chevron Richmond Refinery crude oil feed contained approximately 85 volume % Alaskan North Slope (1 wt. %) crude oil. As the refinery began running more high-sulfur content crudes, the sulfur content in the 4-sidecut line steadily increased (Figure 14), as discussed below.

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[i] Management of change requires that employers have procedures to manage changes to process chemicals, technology, equipment, and procedures. The procedures must address the technical basis for the change, the impact on safety and health, and training required for employees affected by the change.

[ii] Crude oil costs can account for up to 90% of the operating costs in a refinery. *See* Qu, Dingrong, Xiaohui Liu, Xiu Jiang, Zhenggui Lan, and Guangbin Shan. "Setting Critical Operational TAN and Sulfur Level for Crude Distillation Units." *Corrosion 2011 Conference & Expo.* Paper No. 11362. NACE International, 2011.

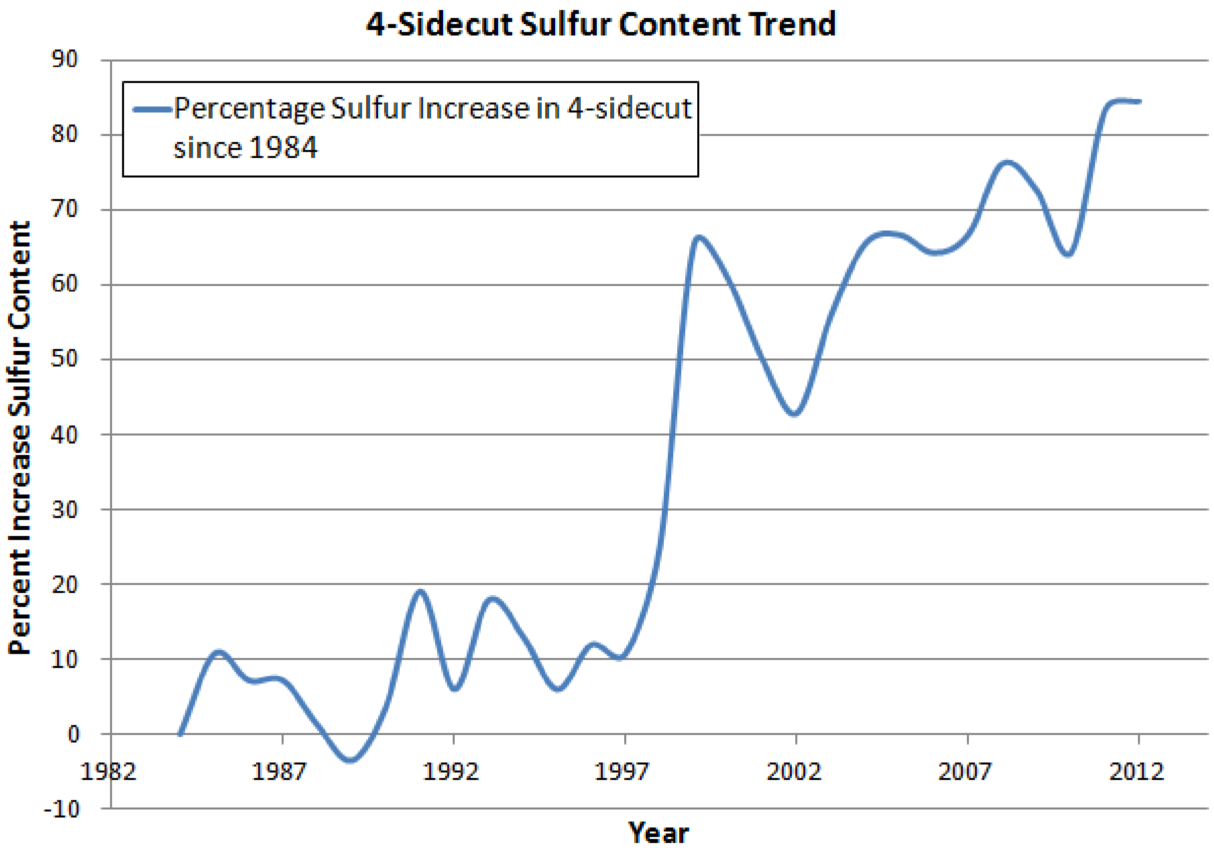

**Figure 14. Graph shows the percentage increase from 1984 values of the sulfur content in the 4-sidecut.**

39. When Chevron introduces a new crude, an MOC is generated to evaluate the potential impact on the refinery.[i] While Chevron stayed under its established crude unit design basis for total wt. % sulfur of the blended feed to the crude unit, the sulfur composition significantly increased over time. Historic data indicates that the sulfur in the 4-sidecut stream has increased from 0.8 to 1.6 wt%. This increase in sulfur composition likely increased corrosion rates in the 4-sidecut line. Chevron did not conduct an MOC analyzing the impact that increases in sulfur composition would have on corrosion in the crude unit. Chevron also did not change its corrosion monitoring programs in response to the increased sulfur content.

40. The CSB found that increased Chevron Richmond usage of non-domestic crude feed stock over time resulted in higher sulfur content in the process fluid passing through the 4-sidecut piping. Specifically, the percentage of sulfur in the Richmond refinery crudes increased nearly 85% between 1984 and 2012, including a significant jump of 32% from 1998 to 1999. This increase in sulfur content corresponded with a simultaneous increase in the usage of non-domestic crude feed at the Richmond refinery.

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[i] Chevron MOCs on new crudes considered general operational issues but did not analyze corrosion effects from sulfidation corrosion.

41. Sulfidation corrosion rates increase in piping circuits as temperature and sulfur content increase. Accordingly, the 4-sidecut sulfidation corrosion rate increased between 1984 and 2012 due to the increase in sulfur content in the line. The CSB found that for the 26-year period from the installation of the piping in 1976 through 2002, the 52-inch 4-sidecut component had lost approximately 33 percent of its wall thickness. From the single inspection of the 52-inch component in 2002 to the incident in 2012 – just ten years – an additional 57 percent of the original component nominal wall thickness was lost near the rupture location due to sulfidation corrosion.[i] In addition to the sulfur content increase, the 4-sidecut draw temperature increased from 625 °F in 1992 to 680 °F in 2002. Corrosion rates and remaining life calculations based on past sulfur content and temperatures may not accurately reflect current corrosion rates if process conditions have changed. Inspection based on historical corrosion rates may be too infrequent to detect an increase in corrosion caused by adverse changes in process conditions, potentially leading to equipment failure.

42. API RP 939-C states that refinery feed stock changes reduce the relevance of past inspection data when predicting future corrosion rates:

> Oil refineries that processed a consistent diet of a particular crude oil or crude blend could often base future predictions on past experience. However, over the past 20+ years, global economics have resulted in many refineries processing tens of different crudes in any given year; thus, minimizing the accuracy, or even feasibility, of predictions based on historical data. Additionally, the verification of the actual corrosion rate experienced while processing a specific crude oil is very difficult.[34]

43. API 570 *Piping Inspection Code: In-service Inspection, Rating, Repair, and Alteration of Piping Systems*, the API standard for inspecting piping, recommends companies to incorporate process changes into inspection programs. The standard states:

> The owner/user is … responsible for implementing an effective MOC process that will review and control changes to the process and to the hardware. An effective MOC process is vital to the success of any piping integrity management program in order that the inspection group will be able to anticipate changes in corrosion or other deterioration variables and alter the inspection plan to account for those changes. The MOC process shall include the appropriate materials/corrosion experience and expertise in order to effectively forecast what changes might affect piping integrity. The inspection group shall be involved in the approval process for changes that may affect piping integrity.

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[i] The 4-sidecut 52-inch component had an original wall thickness of 0.322 inches. Metallurgical analysis found the thinnest portion of the 52-inch 4-sidecut component was 0.03 inches.

> *Changes to the hardware and the process shall be included in the MOC process to ensure its effectiveness* [emphasis added].[35]

Chevron failed to comply with the requirements of API 570 when it did not conduct an MOC to thoroughly evaluate the change of increasing sulfur weight percentage in crude oil feed and to assess how it might affect corrosion rates within the 4-sidecut piping circuit. After the August 6, 2012, incident, Cal/OSHA inspected the Chevron Richmond Refinery and issued citations.[i] However, Cal/OSHA did not issue any citations for failing to perform an MOC when sulfur composition in the crude oil feed was increased.

## Chevron Sulfidation Corrosion Inspection and Mitigation

44. In the ten years prior to the incident, a small number of Chevron personnel with knowledge and understanding of sulfidation corrosion made at least six recommendations (listed in the following six paragraphs and included in Figure 15) to increase inspections or upgrade the metallurgy in the 4-sidecut piping. The recommendations made by these personnel were not implemented by Chevron management.

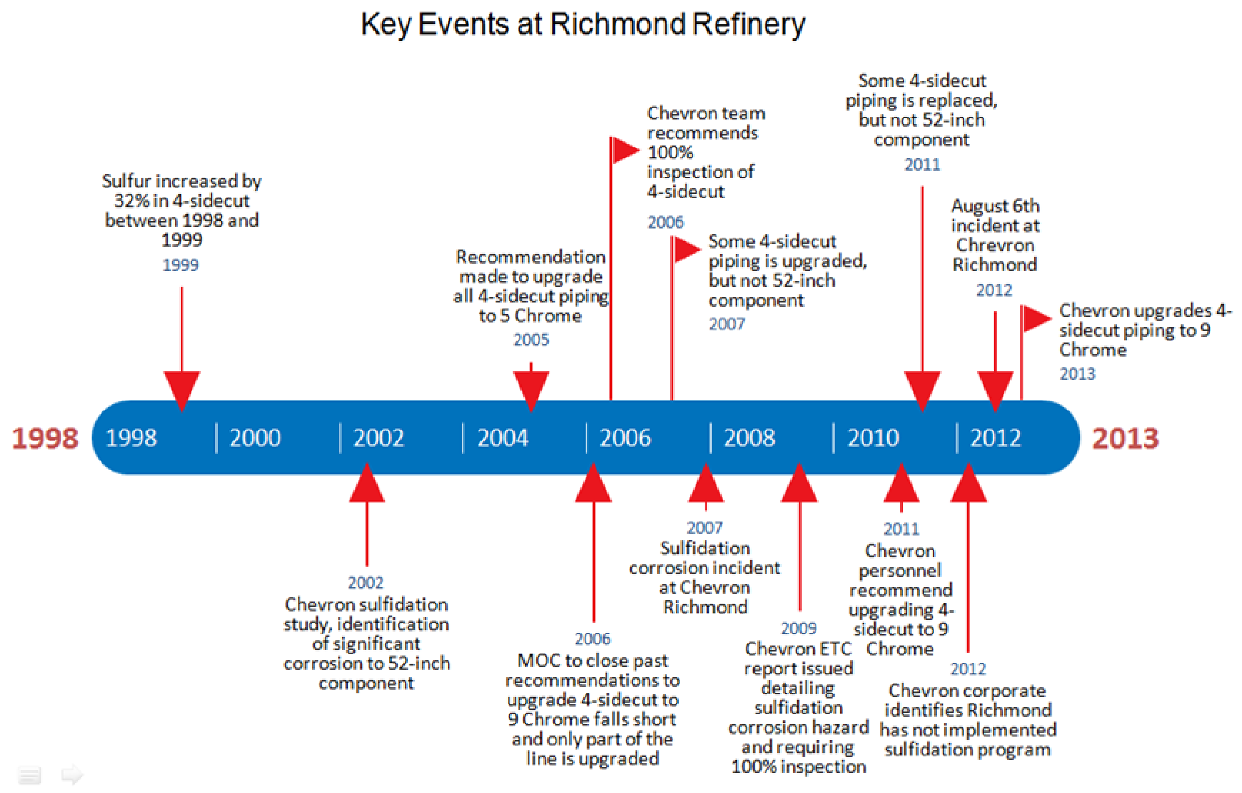

**Figure 15. Key events at the Richmond refinery between 1998 and 2013.**

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[i] Cal/OSHA citations issued January 30, 2013.

45. In August 2002, a Chevron Richmond Refinery employee performed a study analyzing sulfidation corrosion rates in the crude unit and identifying potentially vulnerable areas. The employee discovered that the 4-sidecut operating temperature had been increased and concluded that this increase would cause more hydrogen sulfide to evolve, leading to increased sulfidation corrosion rates. As a result of these findings, the employee recommended increased inspection of the 4-sidecut piping and noted that this piping might need to be upgraded from carbon steel to 5-Chrome, a steel alloy that is more resistant to sulfidation corrosion. In 2002, proactively following up on this study, the crude unit inspector conducted additional piping inspection and identified accelerated corrosion in the 52-inch 4-sidecut component. The inspector recommended upgrading this piping during the next shutdown in 2007. In the inspector's 2002 accomplishments, Chevron management acknowledged this effort to prevent a significant incident; it was characterized as "a save." However, during the 2007 turnaround the recommendation was not implemented, and because a CML was not added to the inspection program, the 52-inch component was not inspected after 2002.

46. In February 2006, a team consisting of a materials and corrosion engineer, an inspector, a process engineer, a metallurgist, and a design engineer issued a Corrosion Mitigation Plan for the Chevron Richmond Refinery crude unit. The report specifically identified the 4-sidecut piping to be at risk for high temperature sulfidation corrosion. The report described that low silicon carbon steel can corrode faster than carbon steel manufactured with higher silicon content, and recommended that 100 percent inspection be performed on the 4-sidecut line using continuous monitoring technology. During the 2007 crude unit turnaround, continuous monitoring probes were only installed on a segment of the 4-sidecut line that did not include the 52-inch component that ultimately failed. The 100 percent inspection recommended in the 2006 Corrosion Mitigation Plan was not performed.

47. During the 2007 turnaround, the crude unit inspector recommended that the refinery upgrade the entire 4-sidecut piping with 5-Chrome. The recommendation was based on findings obtained during the 2002 crude unit turnaround, where the crude unit inspector found that the 52-inch 4-sidecut component had lost one-third of its wall thickness due to corrosion. However, after evaluation, this recommendation was not accepted by the turnaround planning team. Basing its decision on limited inspection data, Chevron determined that the 8-inch portion of the 4-sidecut piping that ran from the atmospheric column to the pump, the portion which included the 52-inch component, had sufficient wall thickness to last to the next turnaround scheduled for Fall 2011.[i] The piping downstream of the pump, which operates at a higher pressure, was determined not to have sufficient wall thickness to last to the next turnaround. This piping was removed and replaced with 9-Chrome, an upgraded and inherently safer metallurgy. The 52-inch component of the 8-inch piping between the atmospheric column and the pump was not replaced during the 2007 turnaround even though it had been identified as thinned in 2002.

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[i] This decision was made without reinspecting or evaluating the thickness of the thinned 52-inch component identified in 2002 that prompted the recommendation.

Furthermore, a permanent CML was not placed on the 52-inch component, and it was not entered into the inspection database. As a result, the component was not inspected again.

48. In September 2009, Chevron ETC corrosion experts released a formal technical report discussing sulfidation corrosion and the specific issues associated with carbon steel, including the potential for high corrosion rates in carbon steel piping containing low percentages of silicon. In its report, Chevron ETC issued recommendations for inspection and provided guidelines for prioritizing piping circuits susceptible to sulfidation corrosion so that high-risk lines could be evaluated first. It was recommended that 100 percent component thickness testing be completed on all high priority lines one time to identify thin, low-silicon components to establish a baseline of corrosion rate and risk for failure. Following the release of the report, the Chevron Richmond Refinery materials group completed the risk-ranking of the carbon steel piping in the Richmond Lube Oil Project (RLOP) and in the crude unit, two units known to be susceptible to sulfidation corrosion. The group identified the crude unit 4-sidecut line as a high risk line per the report ranking guidance. Instead of completing the 100 percent component inspection, the 4-sidecut was recommended for replacement with 9-Chrome. However, the replacement recommendation was denied because the available, limited inspection data indicated the piping would last until the next turnaround. Subsequently, the alternative 100 percent component inspection was also never performed.

49. Five months prior to the incident in March 2012, a Chevron corporate review of Richmond identified that inspection of all carbon steel components susceptible to sulfidation corrosion was not being performed at the Richmond refinery. In addition to identifying that CMLs were not in the proper locations, this corporate review found that critical inspection recommendations were being submitted to the shutdown planning process, but were being denied. Chevron corporate identified that Richmond refinery leadership needed to review and implement the 2009 Chevron ETC report recommendations.

50. Chevron conducts “Intensive Process Reviews” prior to turnarounds. This process involves knowledgeable individuals including Business Improvement Network leaders, process engineers, metallurgical engineers, design engineers, and turnaround planners. The purpose of the review is to identify key unit issues that should be addressed and repaired during the unit turnaround. Prior to the 2011 crude unit turnaround, Chevron personnel conducted an Intensive Process Review of the crude unit and specifically recommended that the 4-sidecut carbon steel piping “should be upgraded to 5 Cr [5-Chrome]… due to sulfidation.” Although the Intensive Process Review identified sulfidation problems in the 4-sidecut line, this activity was ineffective. The 4-sidecut piping was not upgraded during the 2011 crude unit turnaround.

51. In preparation of the work list for the 2011 crude unit turnaround, the crude unit inspector and crude unit metallurgist recommended that the 4-sidecut line be replaced with an upgraded metallurgy, 9-chrome, the metallurgy recommended in the Chevron new construction guidelines for piping in high temperature and high sulfur service. The recommendation was based on the

high priority ranking of the 4-sidecut line, corrosion history, and both Chevron and industry recommended best practice. However, the turnaround management team determined that the inspection data available for the 4-sidecut piping, from CMLs on elbow components which are less prone to sulfidation corrosion, did not support a material upgrade during the 2011 turnaround.[i, ii] The lack of data on the more susceptible 4-sidecut straight-run piping components was not considered.

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[i] This decision was made without reinspecting or evaluating the thickness of the 52-inch component identified in 2002.

[ii] A portion of the 4-sidecut 12-inch line was replaced during the 2011 turnaround with carbon steel due to thinning caused by sulfidation corrosion.

# Inherently Safer Systems

52. The Center for Chemical Process Safety (CCPS) is a corporate membership organization that identifies and addresses process safety needs within the chemical, pharmaceutical, and petroleum industries.[36] Chevron is a corporate member of CCPS.[37] The CCPS book *Inherently* Safer *Chemical Processes, 2nd ed.* defines inherently safer design as the process of identifying and implementing inherent safety in a specific context that is permanent and inseparable.[38] In the book *Guidelines for Engineering Design for Process Safety, 2nd ed.*, CCPS states "inherently safer design solutions eliminate or mitigate the hazard by using materials and process conditions that are less hazardous."[39]

53. Inherently safer technologies are relative; a technology can only be described as inherently safer when compared to a different technology with regard to a specific hazard or risk.[40] A technology may be inherently safer with respect to one risk but not safer from another risk. For this reason, it is important to carry out a comprehensive, documented hazard analysis to determine the individual and overall risks in a process and assess how the risks can be effectively minimized to control hazards. An inherently safer systems review details a list of choices offering various degrees of inherently safer implementation. The review should include risks of personal injury, environmental harm, and lost production, as well as evaluating economic feasibility.[41]

54. It is simpler, less expensive, and more effective to introduce inherently safer features during the design process of a facility rather than after the process is already operating.[42] Process upgrades, rebuilds, and repairs are additional opportunities to implement inherent safety concepts. Conducting a comprehensive hazard review to determine risks and identify ways to eliminate or reduce risks is an important step in implementing an inherently safer process. Chevron training programs on inherently safer systems reflect this approach, stating "we have the greatest opportunity to eliminate or minimize hazards during the development phase of new projects or major revamps of existing facilities."

55. After a 2007 incident caused by a pipe failure in the Richmond refinery crude unit, Chevron implemented an "Inherently Safer Solution" by upgrading the piping to metallurgy that was less susceptible to sulfidation corrosion. However, the change was implemented intuitively without a supporting inherent safety review or failure mechanism hazard review to provide a detailed documented technical rationale for the metallurgy selection. Without such a review, the material selected cannot be analyzed to determine if it is the best inherently safer solution for the process in order to minimize risk.

56. Following the August 6, 2012, incident, the 4-sidecut piping circuit at the Richmond refinery was upgraded from carbon steel to 9-Chrome.[i] However, Chevron did not produce a documented inherently safer hazard review before commencing the rebuild of the crude unit. The crude unit at the Chevron El Segundo refinery is nearly identical in construction and design to the Richmond refinery crude unit. Chevron informed the CSB that piping *downstream* of the 4-sidecut pumps in the 4-sidecut piping circuit at the El Segundo refinery was upgraded in 2001[ii] from carbon steel to stainless steel. As stated previously, after the August 6, 2012, Richmond incident, the 4-sidecut piping *upstream* of the 4-sidecut pumps at the El Segundo refinery was upgraded from carbon steel to 9-Chrome. Had a comprehensive inherently safer systems review been conducted at the Richmond refinery following the August 6th incident, a different metallurgy, such as stainless steel which was installed at the Chevron El Segundo Refinery, may have been identified as inherently safer than 9-Chrome with respect to sulfidation corrosion.

57. An effectiveness ranking of techniques used to control hazards and the risk they represent can be described as a hierarchy of controls. The further up the hierarchy, the more effective the risk reduction achieved (Figure 16). All concepts in the hierarchy of controls should be included in the process of risk assessment and reduction. Upgrading metallurgy to a more corrosion resistant material may be a high ranking, inherently safer choice for certain corrosion mechanisms, such as sulfidation corrosion. Holding other variables constant, upgrading the material of construction may reduce the severity of corrosion and the likelihood of a failure.

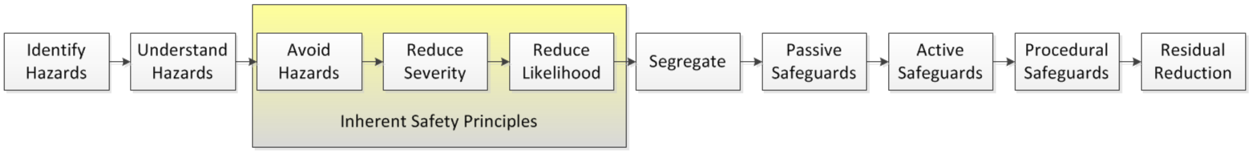

**Figure 16. Hierarchy of controls. The boxes reflect inherently safer controls from left to right, based on *Process Plants: A Handbook for Inherently Safer Design Second Edition*; Kletz, Trevor Amyotte, Paul; CRC Press 2010.**

58. Chevron employees have recommended implementing inherently safer designs through the MOC process, incident investigations, technical reports, and recommendations from employees in the past. However, the CSB has not identified any documented, thorough analysis of the proposed inherently safer solutions. In addition, Chevron has repeatedly failed to implement proposed inherently safer recommendations. For example, following the discovery of significant 4-sidecut piping sulfidation corrosion in 2002, a Chevron inspector issued the following recommendation to replace the piping in the 2007 turnaround:

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[i] After the 2012 incident, the Richmond refinery stated that stainless steel was susceptible to chloride stress corrosion cracking and should not be used.

[ii] Chevron verbal estimate for date of piping installation. No MOC was conducted to review and document this change.

> INFORMATION
>
> The #4 sidecut piping from C-1100 to P-1149/A to E-1113 was RT (x-ray) inspected for hot H2S [sulfidation] corrosion. The piping is actively corroding, particularly on the section on the discharge line from the pumps near the exchanger; the line upstream of the P-1149/A pumps is corroding as well. Corrosion rates indicate that the piping has 4 years of remaining life until the refinery throwaway thickness of 0.14” [inch] is reached. The carbon steel piping is currently running at temperatures between 650 °F on the pump suction line to 641 °F on the line just before E1113; the upper limit for carbon steel piping in this service is 550 °F. A materials upgrade to 5 chrome would raise the upper limit to between 650-750 °F. Additionally, the ABCR piping loop from the same sidecut draw line off of the column to P-1148/A to E-1111 is also carbon steel and operates at the same temperatures, rendering the ABCR piping system to E-1111 susceptible to hot H2S corrosion as well.
>
> Recommendation
>
> Replace the existing #4 sidecut piping noted above from C-1100 through P-1149/A to E1113 and P-1148/A to E-1111 (approximately 700’[feet] of 12”, 10”, 8” and 6”piping, plus some 4”and 3” at the P-1149/P-1148 suction/discharge headers). Upgrade the pipe material from carbon steel to 5 chrome.

To implement this recommendation, Chevron initiated an MOC in 2006 to replace the piping during the 2007 Turnaround. However, the MOC supporting documents had a narrowed scope to only replace the section of piping from P-1149/A pumps to the E-1113 heat exchanger because Chevron reduced the work scope during the 2007 turnaround planning process. The Description of Change in the MOC stated:

> Existing line is carbon steel in a hot service that operates in the range where high temperature sulfadation [sic] occurs. The line has been ut[i] inspected and found to be nearing tmin[ii] requiring replacement. Due to the higher temperature 9CR [9-Chrome] would be the prefered [sic] material.

Contradicting this Description of Change detailing a replacement of the entire 4-sidecut piping circuit, the MOC Summary Review and attached documentation only authorized replacement of the piping from the P-1149’s to E-1113. The MOC states:

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[i] UT is an abbreviation used to indicate ultrasonic thickness testing inspection technique.
[ii] Tmin is an abbreviation used to indicate minimum required piping wall thickness.

> 4 S/C piping has been operating hotter in recent years. The hotter temperatures 550 °F are in the high temperature sulfadation [sic] range. Additionally the section of 4 S/C piping from P-1149' s to E-1113 has been found to be nearing tmin.
>
> The section of pipng [sic] from P-1149's to E-1113 will be replaced with 9 Cr [9-Chrome] piping.

As a result, the portion of the piping containing the 52-inch component that failed on August 6th remained in service. Although the recommendation was intended to more broadly apply inherently safer materials of construction, the final implementation by the MOC limited the application of this more corrosion resistant metallurgy.[i] Again, the inherently safer, more corrosion resistant, metallurgy was not implemented more broadly in crude unit high temperature service. Other examples are discussed above in the section entitled *Chevron Sulfidation Corrosion Inspection and Mitigation*.

59. In 2007, the Chevron Richmond Refinery conducted training to teach employees about the importance of complying with the City of Richmond's Industrial Safety Ordinance (RISO)[ii] inherent safety guidance. The training states "we should always strive to implement inherently safer strategies to the greatest extent feasible." However, Chevron did not regularly or rigorously[iii] apply inherently safer design strategies in opportunities including PHAs, MOCs, incident investigation recommendations, and during turnarounds.[iv]

60. Chevron uses an inherently safer design checklist[v] for PHAs to meet inherently safer systems analysis requirements of the RISO. The checklist, provided by Contra Costa County, is intended to aid identification of opportunities to implement inherently safer design during the PHA process. The checklist was intended to stimulate discussion and analysis of potential opportunities to implement inherently safer design. Contra Costa County's guidance on the IST checklist states that some items may need to be reviewed by a team that is outside the PHA team in order to involve people with the required expertise. Chevron utilized the Contra Costa County inherently safer technologies checklist (IST Checklist) during the 2009 crude unit PHA.

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[i] As discussed earlier, only the section of piping downstream of the pumps was replaced with 9-Chrome.

[ii] The RISO will be discussed in more detail in the *Regulatory Oversight* section below.

[iii] Chevron does not utilize inherent safety guidewords or checklists during the MOC or incident investigation process. Inherently safer guidewords help direct the inherently safer review process. Examples of guidewords include minimization, substitution, moderation, and simplification. These words may be applied to materials, product inventory, process controls, process piping, and siting, among others. *See* Center for Chemical Process Safety (CCPS). "Inherently Safer Chemical Processes – A Life Cycle Approach." 2nd ed., Table 8.3, 2009.

[iv] As stated in the *Regulatory Oversight* section below, Chevron is only required to conduct inherently safer design strategies during PHAs and for the construction of new processes.

[v] Contra Costa County's guidance document entitled "Attachment C: Inherently Safer Systems Checklist" is provided as a tool for facilities to utilize during the PHA process. The actual use of the checklist is not required. *See* http://cchealth.org/hazmat/pdf/iso/attachment_c.pdf (accessed April 17, 2013).

However, only three permissively worded[i] inherently safer system recommendations were made, none of which addressed sulfidation corrosion or piping metallurgy. In addition, Chevron performed the checklist analysis using the same individuals who conducted the PHA despite Contra Costa County's guidance to involve other personnel with additional expertise. Performing a superficial analysis, Chevron failed to adequately consider inherently safer systems like improved metallurgy for corrosion resistance. For instance, the checklist prompted: "Use corrosion resistant material?" In response, Chevron stated that "vessel specifications and piping classifications include a conservative wall thickness and an appropriate corrosion allowance for each service." No mention is given to improving metallurgy to reduce corrosion. There is also no documented analysis regarding potential materials with enhanced corrosion resistance. There was no documentation of the inherently safer technologies analysis, and no inherently safer alternatives were documented. The checklist as applied by Chevron was a "check-the-box" exercise. Chevron Richmond PHAs were thus not an effective means of driving inherent safety. The table below gives a sample of the IST checklist questions along with the associated Chevron responses.[ii]

| **Contra Costa County Checklist Question** | **Chevron IST Analysis** |
|---|---|
| Use Corrosion resistant materials? | Vessel specifications and piping classifications include a conservative wall thickness and an appropriate corrosion allowance for each service. |
| Use smallest diameter piping? | Piping sizes are the smallest possible for the capacity of the unit. |
| Substitute less hazardous raw materials? | Raw materials in use are of minimal hazard. |
| Dilute hazardous raw materials? | Raw materials currently dilute where applicable. |
| Minimize off-site impacts? | #4 Crude Unit is located at a distance from public areas. |
| Easy operation of valves designed to prevent inadvertent error? | In general, valves are arranged in a logical manner. |
| Increasing wall strength? | Piping classifications include a conservative wall thickness and an appropriate corrosion allowance for each service. |

61. Contra Costa County inspected the Chevron Richmond Refinery in 2011, auditing Chevron's implementation of the county's inherently safer systems analysis requirements in the PHA process. The inspectors determined that Chevron's PHAs "follows the requirements specified by … ISS [inherent safety systems] guidelines." This approval by Contra Costa County

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[i] All began with "consider" and two began with "consider evaluating" which does not require any action by Chevron.

[ii] The comprehensive list of IST checklist questions and Chevron's corresponding answers are provided separately on the CSB website.

conveyed to Chevron that the regulator considered that Chevron's minimal analysis of opportunities to implement inherently safer design, its "check-the-box" exercise, was sufficient.

62. Effectively implementing inherently safer technology provides an opportunity for preventing major chemical incidents. The August 6, 2012, incident at Chevron and other incidents[43] throughout the refining industry highlight the difficulty in preventing failure caused by sulfidation corrosion in low silicon carbon steel piping solely through inspection, a procedural safeguard that is low on the hierarchy of controls. Using inherently safer design concepts to avoid issues such as variation in corrosion rate in carbon steel piping due to hard-to-determine silicon content will reduce future similar failures in refineries. Chevron and other process plants' implementation of inherently safer systems to the greatest extent feasible would provide a higher degree of protection from incidents like the one that occurred on August 6, 2012.

63. It is essential that MOCs incorporate hazard analyses and the assessment of opportunities to implement inherently safer systems. This process can be assisted through the use of guidewords to trigger the thought process. CCPS states that "by including inherent safety guidewords in a management of change program, the MOC protocol recognizes inherent safety as both a driving force for - and as an opportunity during - implementation."[44]

64. Layer of Protection Analysis (LOPA) is a well-recognized hazard analysis methodology that is intended to determine if a sufficient number of safeguards or layers of protection exist to protect against a particular hazard or accident scenario.[45] As the potential consequence of a particular scenario increases, the number of safeguards or protection layers must increase to reduce the risk of the scenario to what is considered an acceptable or tolerable level.[46] LOPA can be used to help an organization decide if the risk of a scenario or hazard has been reduced to a level that is "as low as reasonably practicable" (ALARP).[47] ALARP is a risk reduction goal, where risk reduction efforts are continued until the incremental effort to further reduce risk becomes grossly disproportionate to the level of additional risk reduction.[48] By rigorously reviewing accident or hazard scenarios, evaluating the potential consequence of the scenario, and identifying the safeguards or layers of protection necessary to drive risk to as low as reasonably practicable, LOPA becomes an effective organizational tool for implementing a Process Safety Management (PSM) mechanical integrity program.[49] LOPA also helps an organization decide which safeguards to focus on during operation, maintenance, and training.[i, 50] In addition, the LOPA methodology includes provisions allowing an organization to determine the availability[ii] and effectiveness of a safeguard or layer of protection in reducing the risk of a potential scenario.[51]

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[i] Chevron is a member of CCPS and peer-reviewed the CCPS LOPA publication. *See* Center for Chemical Process Safety (CCPS). "Layer of Protection Analysis – Simplified Process Risk Assessment," page xiv, 2001.

[ii] The probability that a system will be able to perform its designated function when required for use. Another term frequently used is *Probability of Failure on Demand* (PFD). Availability = 1 - PFD. *See* Center for Chemical Process Safety (CCPS), "Guidelines for Safe Automation of Chemical Processes," page XIX, 1993.

# Regulatory Oversight

65. The Contra Costa County Industrial Safety Ordinance (ISO) requires that regulated facilities[i] within the county implement safety programs to prevent chemical incidents. Since the ISO took effect in January 1999, Contra Costa County has continued to make improvements to the implementation of the prevention program's elements.

66. The purpose of the ISO is to "prevent accidental release of hazardous chemicals; improve accident prevention by soliciting participation from industry and the community; require industry to submit a Safety Plan; and conduct audits of the plan and inspections of the industrial plants."[52]

67. Although the City of Richmond is located in Contra Costa County, the county does not have jurisdiction over industrial facilities located within the city limits. Thus, the ISO is not enforceable within the City of Richmond. On December 18, 2001, the City of Richmond adopted its own industrial safety ordinance (RISO), based on the ISO.[ii, 53] The RISO covers the two facilities located within the City of Richmond: Chevron and General Chemical West Richmond Works.[54] Pursuant to an agreement between the two parties, Contra Costa County inspects these two facilities and implements the RISO for the City of Richmond.[55]

68. The ISO and RISO contain identical provisions that address the use of inherent safety concepts. Each defines "inherently safer systems" as "feasible alternative equipment, processes, materials, lay-outs and procedures meant to eliminate, minimize, or reduce the risk of a major chemical accident or release by modifying a process rather than adding external layers of protection."[56] Both regulations also require that:

> For all covered processes, the stationary source shall consider the use of inherently safer systems in the development and analysis of mitigation items resulting from a process hazard analysis and in the design and review of new processes and facilities. The stationary source shall select and implement inherently safer systems to the greatest extent feasible. If a stationary source concludes that an inherently safer system is not feasible, the basis for this conclusion shall be documented in meaningful detail.[57]

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[i] The ISO applies to oil refineries and chemical plants within the county jurisdiction that are required to submit a Risk Management Plan to EPA and are program level 3 stationary sources as defined by the California Accidental Release Prevention (CalARP) Program. There are seven facilities covered by the ISO, five of which are refineries. *See* http://cchealth.org/hazmat/iso/ (accessed April 17, 2013).

[ii] At the time of the August 6th incident, the RISO did not include amendments made to the ISO in 2006. The 2006 amendments required an expansion of human factors programs, expanded management of organizational change reviews, security vulnerability analyses, and safety culture assessments. These amendments were subsequently adopted by the City of Richmond in February 2013. *See* http://cchealth.org/hazmat/iso/ (accessed on April 9, 2013).

69. The apparent intent of the ISO and RISO regulations is to require companies to evaluate their processes in order to identify opportunities to implement inherently safer systems. However, the plain language contained within these regulations conflicts with this intent. Both regulations contain the following permissive language: “the stationary source *shall consider* the use of inherently safer systems…”[58] This language does not require companies to conduct a comprehensive analysis and implement inherently safer systems even where feasible. It only requires such an analysis be considered. The regulations allow companies to merely engage in an activity contemplating the potential use of inherently safer systems.

70. The language within the ISO and RISO regulations also requires effective action to implement inherently safer systems “to the greatest extent feasible.”[59] If an inherently safer system is not implemented, the regulations require that the basis for this decision be “documented in meaningful detail.”[60] However, these regulations do not require documentation supporting the adequacy of existing “inherently safer”[61] claims. Chevron’s compliance with the RISO is indicative of this deficiency. In its inherently safer systems checklist, Chevron simply concluded that its systems were inherently safer to the extent that no modifications were necessary. However, the company offered no documentation to substantiate these claims. Had the ISO and RISO regulations required analysis of inherently safer systems regardless of what the site already had in place, Chevron may have implemented the inherently safer recommendations made by technical staff to replace the 4-sidecut with an inherently safer metallurgy.

71. The inherently safer systems requirements of the ISO and RISO are only triggered by the conduct of a PHA or the construction of a new process.[62] Rebuilds, repairs, MOCs, and the implementation of incident investigation corrective actions do not require the analysis and application of inherently safer systems.

72. The Contra Costa County PHA guidance document presents four categories of risk reduction:[i] inherent, passive, active, and procedural (Figure 15).[ii] It states that all four categories should be used in the development of recommendations from process hazard analyses.[63] It reiterates the CCPS statement that all may contribute to the overall safety of a process, but that inherent safety is the most effective.[64] It goes on to state “The inherent and passive categories should be implemented when feasible for new processes and facilities and used during the review of Inherently Safer Systems for existing processes if these processes could cause incidents that could result in a Major Chemical Accident or Release.”[65] This wording in the guidance

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[i] The guidance document uses CCPS definitions for the identified categories of risk reduction.

[ii] Inherent risk reduction involves eliminating the hazard by using materials and process conditions that are non-hazardous. Passive risk reduction is defined as minimizing the hazard through process and equipment design features that reduce the frequency or consequence of the hazard without active functioning of any device. Active risk reduction includes using controls, alarms, safety instrumented systems, and mitigation systems to detect and respond to process deviations from normal operation. Procedural risk reduction achieves the lowest level of risk reduction and involves using policies, operating procedures, training, administrative means, emergency response, and management approaches to prevent incidents and minimize the effects of an incident.

document demonstrates the importance Contra Costa County places on risk reduction and prevention such as metallurgy upgrades; however, as a guidance document, it is non-mandatory.

73. The California Division of Occupational Safety and Health (Cal/OSHA) has jurisdiction over employee safety in California.[66] Cal/OSHA is a division of the California Department of Industrial Relations and has operated a state plan industrial health and safety program since 1973 under a delegation from the U.S. Occupational Safety and Health Administration (OSHA). Cal/OSHA conducts inspections of California workplaces in response to industrial accidents, safety complaints, or as part of an inspection program targeting specific industries.[67] Consideration of inherently safer processes is not currently a required component of any Cal/OSHA (or federal OSHA) standard or regulation.[i]

74. The State of California has promulgated process safety regulations similar to OSHA[68] for the prevention or minimization of the consequences of the accidental release of acutely hazardous chemicals.[69] These regulations require that covered employers perform a PHA to identify, evaluate and control hazards involved in the process using recognized methodologies.[70]

75. California regulations, however, do not provide for a specific review of the effectiveness of the proposed safeguards to control the hazards identified in the PHA using recognized methodologies such as Layers of Protection Analysis (LOPA).[71] Additionally, California regulations do not have any requirements for the use of inherently safer systems analysis and the hierarchy of controls for establishing safeguards for identified process hazards. Cal/OSHA, like federal OSHA, also does not require damage mechanism hazard reviews as part of the PHA process.

76. The Energy Institute, an industry technical working group[ii] organized in the United Kingdom (UK), with contributions from regulators including the UK's Health and Safety Executive (HSE),[iii] as well as other entities,[iv] developed a document in 2008[v] that provides guidance on damage mechanism hazard reviews in the UK's offshore petrochemical industry. The guidance states that effective management of corrosion will contribute to equipment integrity and reduce risk from safety and environmental hazards.[72] In addition, during the design of a process, a corrosion review can be used to eliminate risks and achieve inherent safety.[73] The guidance also

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[i] This is also the case for US EPA Risk Management Program and the California Accidental Release Prevention Program regulations.

[ii] The Energy Institute is the leading chartered professional membership body supporting individuals and organizations across the energy industry. With a combined membership of over 13,500 individuals and 300 companies in 100 countries, it provides an independent focal point for the energy community and a powerful voice to engage business and industry, government, academia and the public internationally. *See* http://www.energyinst.org/about-us (accessed April 17, 2013).

[iii] HSE is an independent regulator that is tasked with securing the health, safety and welfare of workers within the UK. *See* http://www.hse.gov.uk/aboutus/index.htm (accessed April 17, 2013).

[iv] Chevron Energy Technology Company (ETC) was one of roughly 30 entities recognized in the guidance document as providing contributions to the institute that were "key to the development of this publication…". *See* http://www.energyinstpubs.org.uk/pdfs/815.pdf (accessed April 17, 2013).

[v] *Ibid.*

notes that damage mechanism hazard reviews should provide a structured framework for identifying risks associated with corrosion and developing suitable risk reduction measures.[74] These reviews should cover failure mechanisms including, but not limited to corrosion, environmental cracking, erosion, and mechanical damage, such as vibration induced fatigue.[75] Finally, this guidance states that a formal, documented quantitative and logic based assessment should be used when conducting corrosion reviews.[76]

77. Under a rule issued by the U.S. Environmental Protection Agency (EPA),[77] a facility with a tank, drum, pipe, or other process[i] that contains an extremely hazardous toxic or flammable substance listed at 40 CFR §68.130 in an amount above the "threshold quantity" specified for that substance, is required to conduct a hazard assessment as well as develop a prevention program and an emergency response program. These requirements are documented in a Risk Management Plan (RMP) that is submitted to EPA. Covered facilities must implement the RMP and update their RMPs periodically or when certain changes occur. The goal of EPA's Risk Management Program is to prevent accidental releases of substances that can cause serious harm to the public and the environment from short-term exposures, and to mitigate the severity of releases that do occur.[78]

78. The EPA RMP program provisions build on the planning and preparedness groundwork laid by the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA). EPCRA establishes requirements for federal, state, and local governments, as well as industry, regarding emergency planning and "Community Right-to-Know" reporting on hazardous toxic chemicals. EPCRA "help[s] increase the public's knowledge and access to information on chemicals at individual facilities, their uses, and releases into the environment."[79] According to the U.S. EPA's Chemical Emergency Preparedness and Prevention Office,[ii] transparency between industry and the public will improve community safety:

> Both EPCRA and the CAA [Clean Air Act] section 112(r) Risk Management Program encourage communication between facilities and the surrounding communities about chemical safety and chemical risks. Regulatory requirements, by themselves, will not guarantee safety from chemical accidents. Information about hazards in a community will allow local emergency officials and the public to work with industry to prevent accidents.[80]

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[i] "Process" means "any activity involving a regulated substance including any use, storage, manufacturing, handling, or on-site movement of such substances, or combination of these activities…" 40 CFR §68.3 (1997).

[ii] In 2004, the U.S. EPA's Chemical Emergency Preparedness and Prevention Office was merged with the Superfund Emergency Response Program and Oil Spill Prevention Program to form the Office of Emergency Management, or OEM. OEM works with other EPA partners, federal, state, and local agencies, and industry to prevent accidents and maintain and provide superb response capabilities. *See* http://www.epa.gov/oem/about.htm (accessed April 17, 2013).

The CCPS also notes that governments and advocacy organizations have been successful in driving performance improvement by using public disclosure to make safety information available to the public.[81]

79. Under the RMP program's hazard assessment requirement, a facility must prepare a worst-case release scenario analysis[82] and complete a five-year accident history.[83] A covered facility must also develop and implement an emergency response program that includes procedures for informing the public and local agencies about accidental releases and procedures and measures for emergency response after an accidental release.[84] Officials and the public, including local emergency planning committees (LEPCs) can use this information to understand the chemical hazards in the community and then work with industry to address and mitigate those hazards. With both EPCRA and the Risk Management Program, the regulatory purpose and substantive provisions emphasize the importance of transparency, sharing of process safety data, and public participation to prevent chemical accidents. The CSB notes that post-incident, during the decision-making related to piping repairs to the crude unit, the public, worker representatives, regulators, and governmental bodies played a key role driving transparency, accountability, and improved risk reduction.

80. Workforce involvement is a key element of process safety and effective chemical accident prevention. In the Center for Chemical Process Safety publication, *Guidelines for Risk Based Process Safety*, it lists workforce involvement as one of 20 essential management systems necessary to reduce process safety risks and prevent chemical accidents.[85] CCPS states that:

> …workers are potentially the most knowledgeable people with respect to the day-to-day details of operating the process and maintaining the equipment and facilities and may be the sole source for some types of knowledge gained through their unique experiences. Workforce involvement provides management a mechanism for tapping into this valuable expertise.[86]

This CCPS publication discusses general areas of workforce involvement in risk assessments, inspections, audits, and performance reviews. The CCPS notes that participation leads to empowerment, management responsiveness, and process safety performance improvement.[87] The OSHA PSM Standard emphasizes the importance of participation by workers and their representatives. It requires employers to develop a written plan of action, consult with employees, and make available all process safety information.[88] In previous investigation reports, the CSB has identified that workers and their representatives play a very important role in major incident prevention. For example, in the BP Texas City oil refinery investigation report, the CSB recommended that BP and the United Steelworkers International Union (USW) establish a joint program to report incidents and near misses, and to ensure that recommendations made during investigations were implemented. The CSB also recommended that API and the USW work together to develop a safety standard addressing leading and lagging process safety indicators. [i]

81. In July 2012, the CSB held a public hearing on process safety indicators[ii] to explore how companies and regulators use process safety metrics to manage risks and drive continuous safety improvements. During this hearing the CSB stated that, following the 2005 BP Texas City accident, both the CSB and Baker Panel[iii] reports noted the lack of focus by BP on process safety and inadequate performance measurement indicators. The CSB also noted that one goal of process safety indicators is to drive continuous process safety improvement, and that regulators can utilize these indicators to focus inspections, audits, and investigations.

82. Process safety management systems are critical for reducing process safety incidents. Process safety indicators are a significant element of these systems. Indicators measure the strengths and weaknesses of process safety management systems, to achieve and maintain safe and reliable operations. [89] Properly selected and managed indicators will identify the successes and point out the flaws of the system.[90]

83. In 2008, the CCPS published a guidance document for the development of leading[iv] and lagging[v] process safety indicators to assist industry in avoiding catastrophic chemical incidents.[91] While process safety indicators are an important tool for major accident prevention, the simple activity of identifying and recording process safety metrics will not drive process safety improvement. CCPS notes that these metrics must be "collected, analyzed, communicated, understood, and *acted upon.*"[92]

84. The UK HSE has published a guidance document to help chemical and major hazard industries develop process safety indicators. HSE states that:

> Most systems and procedures deteriorate over time, and system failures discovered following a major incident frequently surprise senior managers, who sincerely believed that the controls were functioning as designed. Used effectively, process

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[i] Process safety indicators are also referred to as safety performance indicators, metrics, key process indicators (KPI), performance measures, indicators, etc…

[ii] *See* http://www.csb.gov/assets/1/19/CSB_20Public_20Hearing.pdf (accessed April 17, 2013).

[iii] *See* http://www.bp.com/liveassets/bp_internet/globalbp/globalbp_uk_english/SP/STAGING/local_assets/assets/pdfs/Baker_panel_report.pdf (accessed April 12, 2013).

[iv] Leading indicators are measurements that predict future performance to ensure that safety protection layers and operating discipline are being maintained, including unsafe behaviors or insufficient operating discipline equipment selection, engineering design, specification of inspection frequency, and technique. *See* Center for Chemical Process Safety (CCPS), *Guidelines for Process Safety Metrics*, Page 20. 2010.

[v] Lagging indicators are facts about previous events, such as process safety incidents, that meet the threshold of severity and should be reported as part of the process safety metric. *See* Center for Chemical Process Safety (CCPS), "Guidelines for Process Safety Metrics," 2010; Page 20.

> safety indicators can provide an early warning, before catastrophic failure, that critical controls have deteriorated to an unacceptable level. [93]

85. The public can play an important role in monitoring safety management systems. In its recent guidelines, the CCPS promoted the sharing of process safety indicators with the public:

> Sharing performance metrics and results broadly can engage the public as a partner in holding the organization accountable for process safety performance. Making metrics and performance public can be an especially powerful way of maintaining upper management commitment since it will likely be the CEO or other senior managers who will be called to account by the public if goals are not met or performance declines. Communicating process safety successes also demonstrates to employees and the public that positive change can be, and are being, made within an organization. [94]

# Recommendations

Under 42 U.S.C. 7412(r)(6)(C)(ii), the U.S. Chemical Safety and Hazard Investigation Board is charged with "recommending measures to reduce the likelihood or the consequences of incidental releases and proposing corrective steps to make chemical production, processing, handling and storage as safe and free from risk of injury as possible …." The CSB makes recommendations based on the findings and conclusions of the investigation. Recommendations are made to parties that can affect change to prevent future incidents, which may include the company, contractors, industry organizations responsible for developing good practice guidelines, regulatory bodies, and/or organizations that have the ability to broadly communicate lessons learned from the incident, such as trade associations or professional societies.

**Chevron U.S.A (Urgent)**

2012-03-I-CA-R1

At all Chevron U.S. refineries, engage a diverse team of qualified personnel to perform a documented damage mechanism hazard review. This review shall be an integral part of the Process Hazard Analysis cycle and shall be conducted on all PSM-covered process piping circuits and process equipment. The damage mechanism hazard review shall identify potential process damage mechanisms and consequences of failure, and shall ensure safeguards are in place to control hazards presented by those damage mechanisms. Analyze and incorporate into this review applicable industry best practices, Chevron Energy Technology Company findings and recommendations, and inherently safer systems to the greatest extent feasible.

2012-03-I-CA-R2

At all California Chevron U.S. refineries, report leading and lagging process safety indicators, such as the action item completion status of recommendations from damage mechanism hazard reviews, to the federal, state, and local regulatory agencies that have chemical release prevention authority.

**Mayor and City Council,**
**City of Richmond, California**

2012-03-I-CA-R3

Revise the Industrial Safety Ordinance (ISO) to require that Process Hazard Analyses include documentation of the recognized methodologies, rationale and conclusions used to claim that safeguards intended to control hazards will be effective. This process shall use established qualitative, quantitative, and/or semi-quantitative methods such as Layers of Protection Analysis (LOPA).

2012-03-I-CA-R4

Revise the Industrial Safety Ordinance (ISO) to require the documented use of inherently safer systems analysis and the hierarchy of controls to the greatest extent feasible in establishing safeguards for identified process hazards. The goal shall be to drive the risk of major accidents to As Low As Reasonably Practicable (ALARP). Include requirements for inherently safer systems analysis to be automatically triggered for all Management of Change and Process Hazard Analysis reviews, prior to the construction of new processes, process unit rebuilds, significant process repairs, and in the development of corrective actions from incident investigation recommendations.

2012-03-I-CA-R5

Ensure the effective implementation of the damage mechanism hazard review program (2012-03-I-CA-R1 and 2012-03-I-CA-R2), so that all necessary mechanical integrity work at the Chevron Richmond Refinery is identified and recommendations are completed in a timely way.

**Board of Supervisors**
**Contra Costa County, California**

2012-03-I-CA-R6

Revise the Industrial Safety Ordinance (ISO) to require that Process Hazard Analyses include documentation of the recognized methodologies, rationale and conclusions used to claim that safeguards intended to control hazards will be effective. This process shall use established qualitative, quantitative, and/or semi-quantitative methods such as Layers of Protection Analysis (LOPA).

2012-03-I-CA-R7

Revise the Industrial Safety Ordinance (ISO) to require the documented use of inherently safer systems analysis and the hierarchy of controls to the greatest extent feasible in establishing safeguards for identified process hazards. The goal shall be to drive the risk of major accidents to As Low As Reasonably Practicable (ALARP). Include requirements for inherently safer systems analysis to be automatically triggered for all Management of Change and Process Hazard Analysis reviews, prior to the construction of new processes, process unit rebuilds, significant process repairs, and in the development of corrective actions from incident investigation recommendations.

2012-03-I-CA-R8

Monitor and confirm the effective implementation of the damage mechanism hazard review program (2012-03-I-CA-R1 and 2012-03-I-CA-R2), so that all necessary mechanical integrity work at the Chevron Richmond Refinery is identified and recommendations are completed in a timely way.

**California State Legislature,**
**Governor of California**

2012-03-I-CA-R9

Revise the California Code of Regulations, Title 8, Section 5189, Process Safety Management of Acutely Hazardous Materials, to require improvements to mechanical integrity and process hazard analysis programs for all California oil refineries. These improvements shall include engaging a diverse team of qualified personnel to perform a documented damage mechanism hazard review. This review shall be an integral part of the Process Hazard Analysis cycle and shall be conducted on all PSM-covered process piping circuits and process equipment. The damage mechanism hazard review shall identify potential process damage mechanisms and consequences of failure, and shall ensure safeguards are in place to control hazards presented by those damage mechanisms. Require the analysis and incorporation of applicable industry best practices and inherently safety systems to the greatest extent feasible into this review.

2012-03-I-CA-R10

For all California oil refineries, identify and require the reporting of leading and lagging process safety indicators, such as the action item completion status of recommendations from damage mechanism hazard reviews, to state and local regulatory agencies that have chemical release prevention authority. These indicators shall be used to ensure that requirements described in 2012-03-I-CA-R9 are effective at improving mechanical integrity and process hazard analysis performance at all California oil refineries and preventing major chemical incidents.

2012-03-I-R11

Establish a multi-agency process safety regulatory program for all California oil refineries to improve the public accountability, transparency, and performance of chemical accident prevention and mechanical integrity programs. This program shall:

1. Establish a system to report to the regulator the recognized methodologies, findings, conclusions and corrective actions related to refinery mechanical integrity inspection and repair work arising from Process Hazard Analyses, California oil refinery turnarounds and maintenance-related shutdowns;
2. Require reporting of information such as damage mechanism hazard reviews, notice of upcoming maintenance-related shutdowns, records related to proposed and completed mechanical integrity work lists, and the technical rationale for any delay in work proposed but not yet completed;

3. Establish procedures for greater workforce and public participation including the public reporting of information; and
4. Provide mechanisms for federal, state and local agency operational coordination, sharing of data (including safety indicator data), and joint accident prevention activities. The California Department of Industrial Relations will be designated as the lead state agency for establishing a repository of joint investigative and inspection data, coordinating the sharing of data and joint accident prevention activities.

2012-03-I-CA-R12

Require that Process Hazard Analyses required under California Code of Regulations, Title 8, Section 5189 Section (e) include documentation of the recognized methodologies, rationale and conclusions used to claim that safeguards intended to control hazards will be effective. This process shall use established qualitative, quantitative, and/or semi-quantitative methods such as Layers of Protection Analysis (LOPA).

2012-03-I-CA-R13

Require the documented use of inherently safer systems analysis and the hierarchy of controls to the greatest extent feasible in establishing safeguards for identified process hazards. The goal shall be to drive the risk of major accidents to As Low As Reasonably Practicable (ALARP). Include requirements for inherently safer systems analysis to be automatically triggered for all Management of Change and Process Hazard Analysis reviews, prior to the construction of new process, process unit rebuilds, significant process repairs and in the development of corrective actions from incident investigation recommendations.

2012-03-I-CA-R14

Monitor and confirm the effective implementation of the damage mechanism hazard review program (2012-03-I-CA-R9 and 2012-03-I-CA-R10), so that all necessary mechanical integrity work at all California Chevron Refineries is identified and recommendations are completed in a timely way.

**The U.S. Environmental Protection Agency**

2012-03-I-CA-R15

Jointly plan and conduct inspections with Cal/OSHA, California EPA and other state and local regulatory agencies with chemical accident prevention responsibilities to monitor the effective implementation of the damage mechanism hazard review and disclosure requirements under 2012-03-I-CA-R9 and R10 above.

**The Board of Supervisors, Contra Costa County, California,** 2012-03-I-CA-R16;
**The Mayor and City Council, City of Richmond, California**, 2012-03-I-CA-R17;
**The California Air Quality Management Divisions,** 2012-03-I-CA-R18;
**The U.S. Environmental Protection Agency,** 2012-03-I-CA-R19; and
**The California Environmental Protection Agency,** 2012-03-I-CA-R20;

Participate in the joint regulatory program described in recommendation 2012-03-I-CA-R11. This participation shall include contributing relevant data to the repository of investigation and inspection data created by the California Department of Industrial Relations and jointly coordinating activities.

# Additional Issues Currently Under Investigation

The following section highlights additional issues which the CSB has identified to date in its investigation of the Chevron Richmond Refinery fire and major hydrocarbon release that occurred on August 6, 2012. These issues relate to the ongoing CSB investigation of the management and regulation of health and safety at refineries. The CSB final report will make additional recommendations consistent with this interim report and will present additional detailed findings and analyses in a final report on the incident, to be released later in 2013.

## Regulatory Oversight

The CSB noted in its BP Texas City (BPTC) Final Investigation Report (issued in March 2007) the importance of having a well-resourced, competent regulator consisting of individuals with the necessary training, education, and experience to conduct planned comprehensive and robust inspections of facilities with the goal of preventing catastrophic accidents. In a 1992 compliance directive[i] the federal Occupational Safety and Health Administration (OSHA) stated that the primary enforcement model for the Process Safety Management of Highly Hazardous Chemicals (PSM) standard would be planned, comprehensive, and resource-intensive Program Quality Verification (PQV) inspections to help prevent catastrophic accidents.[95] However, the CSB report noted that for the 10-year period prior to the Texas City incident, federal OSHA had conducted no planned PQV inspections in oil refineries. Regular planned inspections appropriately emphasize the prevention of accidents that are potentially catastrophic. Issuing fines and prosecuting companies post-incident are not acceptable substitutes for prevention. As a result, CSB recommended in its report that OSHA strengthen the planned enforcement of the OSHA Process Safety Management (PSM) standard by developing more highly trained and experienced inspectors to conduct more comprehensive inspections similar to those under OSHA's PQV program at facilities presenting the greatest risk of a catastrophic accident.

Spurred in part by the CSB's recommendations, OSHA issued the Petroleum Refinery Process Safety Management National Emphasis Program (NEP) on June 7, 2007.[ii] The NEP was a federal program that established guidelines for inspecting petroleum refineries to assure compliance with the PSM standard, 29 CFR §1910.119.[96] Unlike the PQV approach to inspections, which "employs a broad, open-ended inspection strategy and uses a more global approach to identify compliance deficiencies…,"[97] the NEP "provide[d] a specific tool to evaluate compliance with the [PSM] standard…[which] identifies a particular set of requirements from the PSM standard from which CSHOs [Compliance Safety and Health Officers] are to review documents, interview employees, and verify implementation for specific processes, equipment, and procedures."[98] While the CSB called for an ongoing comprehensive inspection

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[i] Compliance directives are the main method OSHA uses to communicate plans, inspection methods, and compliance expectations to their Compliance Safety and Health Officers (CSHOs) for enforcing a new regulation.

[ii] Originally Directive Number CPL 03-00-004. Extended August 18, 2099 as Directive Number CPL 03-00-010 to allow more time to complete NEP inspections under the original CPL 03-00-004.

program, inspections being conducted pursuant to the NEP were terminated in 2011. The CSB recommendation to OSHA remains Open.[i]

OSHA State Plan States[ii] were strongly encouraged but not required to implement the NEP. California's Division of Occupational Safety and Health (Cal/OSHA) did not adopt the NEP "because of its dedicated PSM Unit."[99] Cal/OSHA informed the CSB that federal OSHA approved this decision in 2007. In lieu of conducting NEP inspections, Cal/OSHA's PSM Unit has conducted and continues to conduct a full range of programmed, accident, complaint, and referral inspections of PSM-covered facilities in the state of California pursuant to the California Labor Code, Title 8 regulations, and Cal/OSHA's Policy and Procedures (P&P) Manual C-17 "Process Safety Management,"[iii] to ensure these facilities are complying with PSM requirements.

Between 2006 and August 6, 2012, Cal/OSHA conducted three planned inspections of the Chevron Richmond facility, totaling only 150 inspector hours of effort. None of these inspections resulted in citations or fines. In contrast, according to statistics provided by OSHA, federal NEP refinery inspections conducted between 2007 and the end of 2011 lasted roughly 1,000 inspector hours each and resulted in an average of 11.2 violations and $76,821 in penalties per inspection. OSHA noted that hours spent on a typical federal refinery NEP inspection were 40 times greater than the average OSHA inspection. These numbers indicate a major disparity in thoroughness and comprehensiveness between the planned inspections conducted by Cal/OSHA and the NEP inspections conducted by OSHA and other OSHA State Plan States.

The safety case is a rigorous prescriptive and goal-setting regulatory regime that is highlighted by its adaptability and requirements for continuous improvements in risk reduction for high hazard industrial facilities. The approach is used widely overseas but is not used currently for U.S. process industries. The CSB is currently examining whether the implementation of the safety case regime could be a more effective regulatory tool for Cal/OSHA in its effort to ensure that California refineries are identifying and controlling hazards and ultimately driving risk to as low as reasonably practicable (ALARP). Utilizing the safety case requires effective implementation by an independent, competent, well-funded regulator. Experience and competence of the regulator in technical areas such as chemical engineering, human factors, and process safety are necessary to provide effective auditing and regulatory oversight for prevention. To ensure effective implementation of the safety case, industry standards and guidelines must be rigorous and up-to-date as well. The CSB notes that relevant and applicable industry standards and guidelines – such as API RP 939-C – currently contain voluntary and permissive language. The CSB will be examining the need for more effective good practice standards and guidelines containing the necessary requirements to prevent catastrophic accidents.

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[i] Open - Awaiting Response or Evaluation/Approval of Response (O - ARE/AR) - The recipient has not submitted a substantive response, or the evaluation by CSB staff of a response is pending, or the Board has not yet acted on staff recommendation of status.

[ii] Section 18 of the Occupational Safety and Health Act of 1970 encourages States to develop and operate their own job safety and health programs, referred to informally as an OSHA State Plan. OSHA approves and monitors State plans and provides up to 50 percent of an approved plan's operating costs.

[iii] Issued June 6, 1994. Revised August 1, 1994 and May 19, 2007.

In addition to the issues discussed above, the CSB will also be examining the need for the reporting of leading and lagging process safety indicators to the regulator; the regulator's effective use of these process safety indicators; workforce and stakeholder involvement in regulatory oversight of refineries; and the thoroughness of Contra Costa County's safety auditing of the Chevron facility.

## Emergency Planning and Reporting

According to information provided by Contra Costa Emergency Medical Services, 15,213 individuals sought emergency medical attention between August 6 and August 23, 2012, due to the Chevron refinery major hydrocarbon release and fire.

CSB Investigation Team members visited local hospitals the week of the incident to better understand the impact on the surrounding community. Officials at Doctor's Medical Center (DMC) in San Pablo, California, informed the CSB that in the days following the incident they were inundated with emergency room visits and found it difficult to handle the influx due to a lack of funding and staffing. Officials at both DMC and Kaiser Permanente Hospital (KP) in Richmond told the CSB that they lacked specific knowledge of the chemicals released as a result of the incident, complicating efforts to evaluate and treat individuals.

The California Code of Regulations (CCR) requires that owners and operators of hazardous waste facilities make "arrangements to familiarize local hospitals with the properties of hazardous waste handled at the facility and the types of injuries or illnesses which could results from fires, explosions, or releases at the facility."[100] The CSB is currently evaluating ways to ensure that hospitals have the information necessary to properly evaluate and treat individuals that may be exposed to releases from facilities in Contra Costa County.

Following the incident, Contra Costa County's Community Warning System (CWS) notified the surrounding community of a hazardous material incident and ordered a shelter-in-place (SIP). The CWS uses sirens, the news media, and phone calls to residents in order to initiate the SIP. Contra Costa County issued the SIP on August 6, 2012, at 6:38 pm for the cities of Richmond, San Pablo, and North Richmond, California, and lifted the SIP later that evening at 11:12 pm. However, the CSB has learned that some phone calls notifying residents of the SIP did not occur until over four hours after the release.

It is essential that responders, community residents, and hospitals in the areas surrounding industrial facilities be aware of what hazardous materials exist at these facilities, what specific chemicals are released into the community in the event of an incident, and what is known about the potential acute and chronic health impacts. The CSB will be analyzing ways to strengthen current regulations and policies to ensure there is proper emergency planning and reporting for industrial facilities in Contra Costa County and the state of California.

## Emergency Response

OSHA provides guidance on emergency response in its *Hazardous Waste Operations and Emergency Response* standard, known as HAZWOPER, under 29 CFR §1910.120 (p) and (q). Under 29 CFR §1910.120(q)(6), the HAZWOPER standard contains requirements for training and qualification of all individuals involved in emergency response related to their roles and responsibilities.

Good safety practice dictates that individuals responding to emergencies should have the technical knowledge to give input into shutdown decisions, set up an incident command structure, establish boundary limits, and evaluate the "hot zone." Access to the hot zone must be strictly limited to personnel with higher degrees of specific training, experience, and appropriate personal protective equipment; all others must be removed to a safe location away from chemical hazards. Hot zone boundaries must be established to anticipate the possible escalation of releases and the positioning of firefighting equipment such as fire trucks.

The CSB will be looking at the sufficiency of regulatory requirements, industry standards, and good practices, in addition to evaluating emergency response decision-making following the leak and subsequent pipe rupture (including the training and qualification of responders) to determine whether improvements are needed in these areas.

## Safety Culture

The Center for Chemical Process Safety (CCPS) defines process safety culture as the "combination of group values and behaviors that determines the manner in which process safety is managed."[101] As the CSB noted in its BP Texas City Report, safety culture can be influenced by management changes, historical events, and economic pressures. After reviewing evidence and decisions made relating to materials of construction and mechanical integrity within the crude unit at the Chevron refinery, as well as the response to the leak on August 6, 2012, the CSB has determined that issues relating to safety culture are relevant to this incident. The CSB will examine the Chevron Richmond Refinery's approach to safety, its safety culture and any organizational deficiencies, to determine how to best prevent future incidents.

The CSB notes that on August 6, 2012, following discovery of the leak on the 4-sidecut piping, Chevron hoped to forestall a shutdown by installing a leak repair clamp.[i] Chevron's mechanical integrity management system has not been fully successful in detecting and replacing deteriorated piping components prior to failure, resulting in the company's frequent use of leak repair clamps[ii] to externally stop process fluid leaks. Chevron's reliance on such clamps to mitigate process piping component leaks identifies serious questions about its mechanical integrity program. The CSB determined that Chevron

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[i] Chevron's leak repair clamp vendor was called out to the scene of the leak to help determine potential clamping options.

[ii] Leak repair clamps are mechanical devices designed and installed to stop a leak from a piping component such as piping, valves, flanges, and instrumentation. These devices are typically intended to provide a temporary repair while a process continues operation until a plant shutdown takes place and a permanent repair can be made.

has more than 100 clamps on hydrocarbon and other process piping components at the Richmond refinery. The leak repair clamp is typically relied upon to prevent further leaking until the next unit turnaround, when the deteriorated piping component can be repaired. However, Cal/OSHA citations following the August 6, 2012, fire in the crude unit identified that Chevron has not always replaced these clamps during unit turnarounds and these devices then remain in service significantly longer than originally intended. The CSB determined that Chevron has leak repair clamps in place on piping components containing hazardous flammable process fluids including applications where the process material is above the autoignition temperature. Some of these leak repair clamp applications are in locations where a permanent repair would not have required a unit shutdown. The CSB will further evaluate the frequent use of leak repair clamps by Chevron and the potential that the deviance of a weak mechanical integrity management system has been normalized.[i]

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[i] Normalization of deviance is a long-term phenomenon in which individuals or work teams gradually accept a lower standard of performance until the lower standard becomes the norm. It is typically the result of conditions slowly changing and eroding over time. *See* Center for Chemical Process Safety (CCPS), Recognizing Catastrophic Incident Warning Signs in the Process Industries, Page 4. 2012.

BY THE

U.S. Chemical Safety and Hazard Investigation Board

Rafael Moure-Eraso
Chair

Mark Griffon
Member

Beth Rosenberg
Member

Date of Approval April __, 2013.

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Attachment 48

## Attachment 48. Statistical Analysis Report on Comparison of Actual Refinery Fuel Combustion Energy Intensity *versus* Actual Refinery CO2 Emission Intensity Observed Across 97% of the U.S. Oil Refining Industry: Annual Observations From 1999–2008.[a]

| Petroleum Administration Defense District (PADD) # | Year | Observations | |
|---|---|---|---|
| | | **$CO_2$ emission intensity**[b] (kg/$m^3$) | ***Fuel energy intensity***[c] (GJ/$m^3$) |
| 1 | 1999 | 281 | 3.451 |
| 1 | 2000 | 276 | 3.430 |
| 1 | 2001 | 288 | 3.518 |
| 1 | 2002 | 278 | 3.426 |
| 1 | 2003 | 274 | 3.364 |
| 1 | 2004 | 278 | 3.416 |
| 1 | 2005 | 277 | 3.404 |
| 1 | 2006 | 277 | 3.440 |
| 1 | 2007 | 288 | 3.499 |
| 1 | 2008 | 296 | 3.551 |
| 2 | 1999 | 263 | 3.368 |
| 2 | 2000 | 261 | 3.361 |
| 2 | 2001 | 263 | 3.396 |
| 2 | 2002 | 264 | 3.393 |
| 2 | 2003 | 257 | 3.298 |
| 2 | 2004 | 261 | 3.376 |
| 2 | 2005 | 270 | 3.496 |
| 2 | 2006 | 284 | 3.738 |
| 2 | 2007 | 287 | 3.800 |
| 2 | 2008 | 289 | 3.858 |

| | | | |
|---|---|---|---|
| 3 | 1999 | 326 | 4.546 |
| 3 | 2000 | 328 | 4.563 |
| 3 | 2001 | 315 | 4.348 |
| 3 | 2002 | 322 | 4.434 |
| 3 | 2003 | 319 | 4.381 |
| 3 | 2004 | 309 | 4.204 |
| 3 | 2005 | 308 | 4.205 |
| 3 | 2006 | 324 | 4.367 |
| 3 | 2007 | 317 | 4.226 |
| 3 | 2008 | 325 | 4.361 |
| 5 | 1999 | 345 | 4.908 |
| 5 | 2000 | 358 | 5.189 |
| 5 | 2001 | 350 | 5.039 |
| 5 | 2002 | 338 | 4.881 |
| 5 | 2003 | 339 | 4.885 |
| 5 | 2004 | 340 | 4.861 |
| 5 | 2005 | 334 | 4.774 |
| 5 | 2006 | 337 | 4.862 |
| 5 | 2007 | 352 | 5.091 |
| 5 | 2008 | 338 | 4.939 |

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[a] Data from Karras (2010); appended to CBE's 21 October Supplemental Comment at Attachment 13.

[b] Average refinery emission intensity for carbon dioxide, in kilograms per cubic meter oil refined.

[c] Average refinery fuel consumption energy intensity, in Gigaljoule per cubic meter oil refined.

XLSTAT 2009.4.01 - Linear regression - on 11/21/2015 at 5:48:31 PM
Y / Quantitative: Workbook = Att 48 Refinery fuel energy v CO2 emissions.xls / Sheet = Data / Range = Data!$C$7:$C$47 / 40 rows and 1 column
X / Quantitative: Workbook = Att 48 Refinery fuel energy v CO2 emissions.xls / Sheet = Data / Range = Data!$D$7:$D$47 / 40 rows and 1 column
Confidence interval (%): 95

Summary statistics:

| Variable | Observations | with missing | ithout missin | Minimum | Maximum | Mean | Std. deviation |
|---|---|---|---|---|---|---|---|
| CO2 emissior | 40 | 0 | 40 | 257.272 | 358.488 | 303.303 | 30.824 |
| Fuel energy i | 40 | 0 | 40 | 3.298 | 5.189 | 4.066 | 0.644 |

**Regression of variable CO2 emission intensityb (kg/m3):**

Goodness of fit statistics:

| | |
|---|---|
| Observations | 40.000 |
| Sum of weigh | 40.000 |
| DF | 38.000 |
| R² | 0.960 |
| Adjusted R² | 0.959 |
| MSE | 38.678 |
| RMSE | 6.219 |
| MAPE | 1.691 |
| DW | 0.743 |
| Cp | 2.000 |
| AIC | 148.159 |
| SBC | 151.537 |
| PC | 0.044 |

Analysis of variance:

| Source | DF | um of square | Mean squares | F | Pr > F |
|---|---|---|---|---|---|
| Model | 1 | 35585.935 | 35585.935 | 920.063 | < 0.0001 |
| Error | 38 | 1469.753 | 38.678 | | |
| Corrected To | 39 | 37055.687 | | | |

*Computed against model Y=Mean(Y)*

Model parameters:

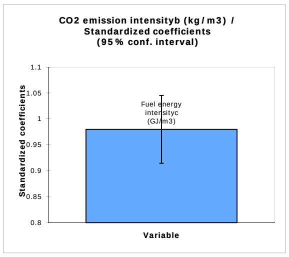
| Source | Value | Standard erro | t | Pr > \|t\| | ver bound (95 | er bound (95%) |
|---|---|---|---|---|---|---|
| Intercept | 112.655 | 6.362 | 17.708 | < 0.0001 | 99.777 | 125.534 |
| Fuel energy i | 46.886 | 1.546 | 30.333 | < 0.0001 | 43.757 | 50.015 |

Equation of the model:

CO2 emission intensityb (kg/m3) = 112.655255279842+46.8862304655538*Fuel energy intensityc (GJ/m3)

Standardized coefficients:

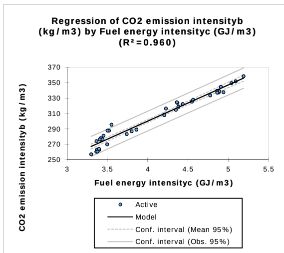
| Source | Value | Standard erro | t | Pr > \|t\| | ver bound (95 | er bound (95%) |
|---|---|---|---|---|---|---|
| Fuel energy i | 0.980 | 0.032 | 30.333 | < 0.0001 | 0.915 | 1.045 |

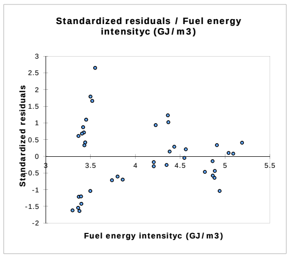


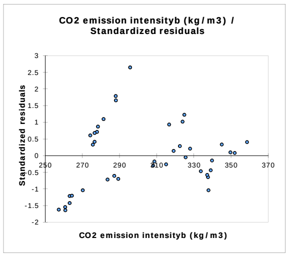
Predictions and residuals:

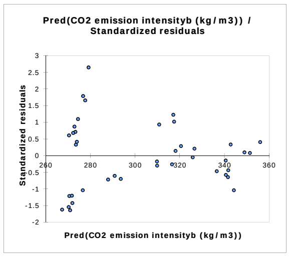
| Observation | Weight | rgy intensityc | sion intensityb | ission intensi | Residual | Std. residual | ev. on pred. ( | bound 95% ( | bound 95% ( | on pred. (Ob | und 95% (Ob | und 95% (Obs |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Obs1 | 1 | 3.451 | 281.318 | 274.443 | 6.875 | 1.105 | 1.368 | 271.673 | 277.213 | 6.368 | 261.552 | 287.334 |
| Obs2 | 1 | 3.430 | 275.573 | 273.483 | 2.090 | 0.336 | 1.390 | 270.669 | 276.298 | 6.373 | 260.583 | 286.384 |
| Obs3 | 1 | 3.518 | 287.974 | 277.615 | 10.359 | 1.666 | 1.298 | 274.988 | 280.242 | 6.353 | 264.754 | 290.476 |
| Obs4 | 1 | 3.426 | 277.776 | 273.290 | 4.486 | 0.721 | 1.395 | 270.466 | 276.114 | 6.374 | 260.387 | 286.193 |
| Obs5 | 1 | 3.364 | 274.194 | 270.374 | 3.820 | 0.614 | 1.465 | 267.408 | 273.339 | 6.389 | 257.439 | 283.308 |
| Obs6 | 1 | 3.416 | 278.292 | 272.831 | 5.461 | 0.878 | 1.406 | 269.985 | 275.677 | 6.376 | 259.924 | 285.739 |
| Obs7 | 1 | 3.404 | 276.504 | 272.248 | 4.256 | 0.684 | 1.420 | 269.374 | 275.122 | 6.379 | 259.334 | 285.162 |
| Obs8 | 1 | 3.440 | 276.533 | 273.920 | 2.613 | 0.420 | 1.380 | 271.126 | 276.715 | 6.370 | 261.024 | 286.817 |
| Obs9 | 1 | 3.499 | 287.908 | 276.725 | 11.183 | 1.798 | 1.317 | 274.058 | 279.391 | 6.357 | 263.855 | 289.594 |
| Obs10 | 1 | 3.551 | 295.652 | 279.138 | 16.514 | 2.655 | 1.266 | 276.576 | 281.700 | 6.347 | 266.290 | 291.986 |
| Obs11 | 1 | 3.368 | 263.053 | 270.566 | -7.513 | -1.208 | 1.460 | 267.610 | 273.521 | 6.388 | 257.633 | 283.498 |
| Obs12 | 1 | 3.361 | 260.647 | 270.225 | -9.578 | -1.540 | 1.468 | 267.252 | 273.197 | 6.390 | 257.289 | 283.161 |
| Obs13 | 1 | 3.396 | 263.061 | 271.883 | -8.822 | -1.418 | 1.428 | 268.991 | 274.774 | 6.381 | 258.965 | 284.801 |
| Obs14 | 1 | 3.393 | 264.279 | 271.721 | -7.442 | -1.197 | 1.432 | 268.822 | 274.621 | 6.382 | 258.802 | 284.641 |
| Obs15 | 1 | 3.298 | 257.272 | 267.301 | -10.029 | -1.613 | 1.541 | 264.181 | 270.421 | 6.407 | 254.330 | 280.272 |
| Obs16 | 1 | 3.376 | 260.770 | 270.932 | -10.162 | -1.634 | 1.451 | 267.995 | 273.870 | 6.386 | 258.004 | 283.861 |

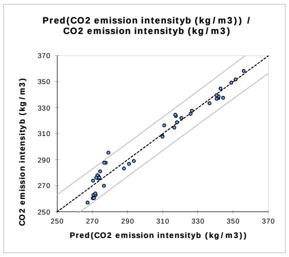
| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Obs17 | 1 | 3.496 | 270.168 | 276.583 | -6.415 | -1.031 | 1.320 | 273.910 | 279.255 | 6.358 | 263.712 | 289.453 |
| Obs18 | 1 | 3.738 | 283.503 | 287.929 | -4.426 | -0.712 | 1.106 | 285.689 | 290.168 | 6.317 | 275.141 | 300.716 |
| Obs19 | 1 | 3.800 | 287.096 | 290.822 | -3.726 | -0.599 | 1.066 | 288.665 | 292.980 | 6.310 | 278.049 | 303.596 |
| Obs20 | 1 | 3.858 | 289.261 | 293.554 | -4.293 | -0.690 | 1.035 | 291.460 | 295.648 | 6.305 | 280.791 | 306.317 |
| Obs21 | 1 | 4.546 | 325.512 | 325.788 | -0.276 | -0.044 | 1.231 | 323.295 | 328.281 | 6.340 | 312.954 | 338.623 |
| Obs22 | 1 | 4.563 | 327.920 | 326.580 | 1.340 | 0.215 | 1.247 | 324.055 | 329.105 | 6.343 | 313.739 | 339.420 |
| Obs23 | 1 | 4.348 | 314.956 | 316.532 | -1.576 | -0.253 | 1.076 | 314.354 | 318.710 | 6.311 | 303.755 | 329.309 |
| Obs24 | 1 | 4.434 | 322.370 | 320.540 | 1.830 | 0.294 | 1.136 | 318.241 | 322.840 | 6.322 | 307.742 | 333.339 |
| Obs25 | 1 | 4.381 | 318.979 | 318.059 | 0.920 | 0.148 | 1.097 | 315.838 | 320.280 | 6.315 | 305.274 | 330.843 |
| Obs26 | 1 | 4.204 | 308.703 | 309.768 | -1.065 | -0.171 | 1.006 | 307.731 | 311.805 | 6.300 | 297.014 | 322.521 |
| Obs27 | 1 | 4.205 | 308.000 | 309.829 | -1.829 | -0.294 | 1.007 | 307.791 | 311.866 | 6.300 | 297.075 | 322.583 |
| Obs28 | 1 | 4.367 | 323.832 | 317.430 | 6.402 | 1.029 | 1.088 | 315.228 | 319.633 | 6.314 | 304.649 | 330.212 |
| Obs29 | 1 | 4.226 | 316.652 | 310.797 | 5.855 | 0.941 | 1.014 | 308.744 | 312.849 | 6.301 | 298.041 | 323.553 |
| Obs30 | 1 | 4.361 | 324.799 | 317.122 | 7.677 | 1.234 | 1.084 | 314.928 | 319.316 | 6.313 | 304.343 | 329.902 |
| Obs31 | 1 | 4.908 | 344.912 | 342.788 | 2.124 | 0.342 | 1.631 | 339.485 | 346.090 | 6.430 | 329.772 | 355.804 |
| Obs32 | 1 | 5.189 | 358.488 | 355.932 | 2.556 | 0.411 | 1.994 | 351.895 | 359.970 | 6.531 | 342.711 | 369.154 |
| Obs33 | 1 | 5.039 | 349.565 | 348.901 | 0.664 | 0.107 | 1.796 | 345.264 | 352.537 | 6.473 | 335.796 | 362.006 |
| Obs34 | 1 | 4.881 | 337.531 | 341.513 | -3.982 | -0.640 | 1.598 | 338.277 | 344.748 | 6.421 | 328.514 | 354.512 |
| Obs35 | 1 | 4.885 | 338.983 | 341.679 | -2.696 | -0.434 | 1.602 | 338.435 | 344.923 | 6.422 | 328.678 | 354.680 |
| Obs36 | 1 | 4.861 | 339.686 | 340.546 | -0.860 | -0.138 | 1.573 | 337.361 | 343.730 | 6.415 | 327.559 | 353.532 |
| Obs37 | 1 | 4.774 | 333.622 | 336.507 | -2.885 | -0.464 | 1.471 | 333.528 | 339.486 | 6.391 | 323.569 | 349.445 |
| Obs38 | 1 | 4.862 | 337.071 | 340.627 | -3.556 | -0.572 | 1.575 | 337.439 | 343.816 | 6.416 | 327.640 | 353.615 |
| Obs39 | 1 | 5.091 | 351.911 | 351.367 | 0.544 | 0.087 | 1.865 | 347.592 | 355.142 | 6.493 | 338.223 | 364.511 |
| Obs40 | 1 | 4.939 | 337.788 | 344.225 | -6.437 | -1.035 | 1.669 | 340.845 | 347.605 | 6.439 | 331.189 | 357.261 |

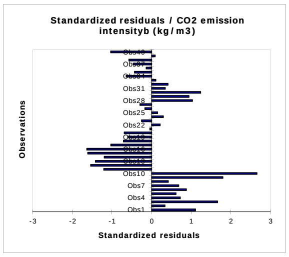

Regression of CO2 emission intensityb (kg/m3) by Fuel energy intensityc (GJ/m3) (R²=0.960)


Standardized residuals / Fuel energy intensityc (GJ/m3)


CO2 emission intensityb (kg/m3) / Standardized residuals


Pred(CO2 emission intensityb (kg/m3)) / Standardized residuals


Pred(CO2 emission intensityb (kg/m3)) / CO2 emission intensityb (kg/m3)


Standardized residuals / CO2 emission intensityb (kg/m3)

servation)

XLSTAT 2009.4.01 - Normality tests - on 11/21/2015 at 5:50:09 PM
Data: Workbook = Att 49 Refinery fuel energy v CO2 emissions.xls / Sheet = Linear regression / Range = '
Significance level (%): 5

Summary statistics:

| Variable | Observations | with missing | without missin | Minimum | Maximum | Mean | Std. deviation |
|---|---|---|---|---|---|---|---|
| Residual | 40 | 0 | 40 | -10.162 | 16.514 | 0.000 | 6.139 |

Shapiro-Wilk test (Residual):

| | |
|---|---|
| W | 0.979 |
| p-value | 0.664 |
| alpha | 0.05 |

Test interpretation:
H0: The sample follows a Normal distribution.
Ha: The sample does not follow a Normal distribution.
As the computed p-value is greater than the significance level alpha=0.05, one should accept the null hypo
The risk to reject the null hypothesis H0 while it is true is 66.39%.

Anderson-Darling test (Residual):

| | |
|---|---|
| A² | 0.158 |
| p-value | 0.947 |
| alpha | 0.05 |

Test interpretation:
H0: The sample follows a Normal distribution.
Ha: The sample does not follow a Normal distribution.
As the computed p-value is greater than the significance level alpha=0.05, one should accept the null hypo
The risk to reject the null hypothesis H0 while it is true is 94.71%.

Lilliefors test (Residual):

| | |
|---|---|
| D | 0.060 |
| D (standardiz | 0.381 |
| p-value | 0.972 |
| alpha | 0.05 |

Test interpretation:
H0: The sample follows a Normal distribution.
Ha: The sample does not follow a Normal distribution.
As the computed p-value is greater than the significance level alpha=0.05, one should accept the null hypo
The risk to reject the null hypothesis H0 while it is true is 97.22%.

Jarque-Bera test (Residual):

| | |
|---|---|
| JB (Observed | 0.938 |
| JB (Critical va | 5.991 |
| DF | 2 |
| p-value | 0.626 |
| alpha | 0.05 |

Test interpretation:
H0: The sample follows a Normal distribution.

Ha: The sample does not follow a Normal distribution.
As the computed p-value is greater than the significance level alpha=0.05, one should accept the null hypo
The risk to reject the null hypothesis H0 while it is true is 62.56%.

Linear regression'!$G$80:$G$120 / 40 rows and 1 columr

thesis H0

thesis H0

thesis H0

thesis H0

**Attachment 49**

**OFFICE OF ENVIRONMENTAL HEALTH HAZARD ASSESSMENT**

# Air Toxics Hot Spots Program

## Appendices A-F

## Guidance Manual for Preparation of Health Risk Assessments

Air, Community, and Environmental Research Branch

Office of Environmental Health Hazard Assessment

California Environmental Protection Agency

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# Table of Contents

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# Appendix A:

# Air Toxics Hot Spots Program List of Substances*

*The List of Substances presented in Appendix A is periodically updated by the California Air Resources Board (ARB). The most recent update at the time of preparation of this document was August 27, 2007. Future updates may be obtained from the ARB web site (http://www.arb.ca.gov/ab2588/2588guid.htm).

# Appendix A-I

## Substances For Which
## Emissions Must Be Quantified

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| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 75070 | Acetaldehyde | | c | 20 | 1 | 2 | 3 | 4 | | | | |
| 60355 | Acetamide | | c | 2 | 1 | 2 | 3 | 4 | | | | |
| 75058 | Acetonitrile | 06/91 | | 200 | 1 | 2 | | | | | | |
| 98862 | Acetophenone | 06/91 | | 100 | 1 | 2 | | | | | | |
| 53963 | 2-Acetylaminofluorene [PAH-Derivative, POM] | | c | 100 | 1 | 2 | | 4 | 5 | | | |
| 107028 | Acrolein | | | 0.05 | 1 | 2 | | | | | | |
| 79061 | Acrylamide | | c | 0.01 | 1 | 2 | 3 | 4 | | | | |
| 79107 | Acrylic acid | 06/91 | | 5 | 1 | 2 | | | | | | |
| 107131 | Acrylonitrile | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 107051 | Allyl chloride | | c | 5 | 1 | 2 | | 4 | | | | |
| 7429905 | Aluminum | 06/91 | | 100 | 1 | | | | | | | |
| 1344281 | Aluminum oxide (fibrous forms) | 06/91 | | 100 | | | | | | | 7 | |
| 117793 | 2-Aminoanthraquinone [PAH-Derivative, POM] | | c | 5 | 1 | 2 | | 4 | 5 | | | |
| 92671 | 4-Aminobiphenyl [POM] | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| 61825 | Amitrole | | c | 0.1 | | | 3 | 4 | 5 | | | |
| 7664417 | Ammonia | | | 200 | 1 | 2 | | | | | | |
| 6484522 | Ammonium nitrate | 06/91 | | 100 | 1 | | | | | | | |
| 7783202 | Ammonium sulfate | 06/91 | | 100 | 1 | | | | | | | |
| 62533 | Aniline | 09/90 | c | 5 | 1 | 2 | | 4 | | | | |
| 90040 | o-Anisidine | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| - | Anthracene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 7440360 | Antimony | 06/91 | | 1 | | | | | | | 7 | |
| * | Antimony compounds including but not limited to: | 06/91 | | 1 | 1 | 2 | | | | | | [7] |
| 1309644 | Antimony trioxide | 09/90 | c | 1 | 1 | 2 | 3 | 4 | | | | [7] |
| 7440382 | Arsenic | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 1016 | Arsenic compounds (inorganic) including but not limited to: | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | [7] |
| 7784421 | Arsine | | | 0.01 | 1 | 2 | | | | | 7 | [7] |
| 1017 | Arsenic compounds (other than inorganic) | 06/91 | | 0.1 | 1 | | | | | | | [7] |
| - | Asbestos (see Mineral fibers) | | | | | | | | | | | |
| 7440393 | Barium | 06/91 | | 1 | | | | | | | 7 | |
| * | Barium Compounds | 06/91 | | 1 | 1 | | | | | | | [7] |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| - | Benz[a]anthracene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 71432 | Benzene | | c | 2 | 1 | 2 | 3 | 4 | 5 | | | |
| 92875 | Benzidine (and its salts) [POM] | | c | 0.0001 | 1 | 2 | 3 | 4 | 5 | | | |
| 1020 | Benzidine-based dyes [POM] including but not limited to: | | c | 0.0001 | 1 | 2 | 3 | | | | | |
| 1937377 | Direct Black 38 [PAH-Derivative, POM] | | c | 0.0001 | 1 | 2 | | 4 | 5 | | | |
| 2602462 | Direct Blue 6 [PAH-Derivative, POM] | | c | 0.0001 | 1 | 2 | | 4 | 5 | | | |
| 16071866 | Direct Brown 95 (technical grade) [POM] | 09/89 | c | 0.0001 | 1 | 2 | | 4 | | | | |
| - | Benzo[a]pyrene [PAH, POM], (see PAH) | | | | | | | | | | | |
| - | Benzo[b]fluoranthene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 271896 | Benzofuran | 06/91 | c | 100 | | | | 4 | | | | |
| 98077 | Benzoic trichloride {Benzotrichloride} | | c | 10 | 1 | 2 | | 4 | 5 | | | |
| - | Benzo[j]fluoranthene [PAH, POM] (see PAH) | | | | | | | | | | | |
| - | Benzo[k]fluoranthene [PAH, POM] (see PAH) | | | | | | | | | | | |
| 98884 | Benzoyl chloride | 06/91 | | 100 | 1 | | | | | | | |
| 94360 | Benzoyl peroxide | 06/91 | | 100 | | | | | | | 7 | |
| 100447 | Benzyl chloride | | c | 1 | 1 | 2 | | 4 | | | | |
| 7440417 | Beryllium | | c | 0.001 | 1 | 2 | 3 | 4 | 5 | | | |
| * | Beryllium compounds | 09/89 | c | 0.001 | 1 | 2 | 3 | 4 | 5 | | | [7] |
| 92524 | Biphenyl [POM] | 06/91 | | 0.5 | 1 | 2 | | | | | | |
| 111444 | Bis(2-chloroethyl) ether {DCEE} | 09/89 | c | 0.05 | 1 | 2 | | 4 | | | | |
| 542881 | Bis(chloromethyl) ether | | c | 0.001 | 1 | 2 | 3 | 4 | 5 | | | |
| 103231 | Bis(2-ethylhexyl) adipate | 06/91 | | 100 | 1 | | | | | | | |
| 7726956 | Bromine | | | 0.5 | | 2 | | | | | | |
| * | Bromine compounds (inorganic) including but not limited to: | | | 100 | 1 | 2 | | | | | | [7] |
| 7789302 | Bromine pentafluoride | 11/06 | | 100 | | | | | | | 7 | |
| 10035106 | Hydrogen bromide | 11/06 | | 20 | | | | | | | 7 | |
| 7758012 | Potassium bromate | | | 0.1 | 1 | | 3 | 4 | | | | [7] |
| 75252 | Bromoform | 06/91 | | 100 | 1 | 2 | | 4 | | | | |
| 106990 | 1,3-Butadiene | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 540885 | t-Butyl acetate | 11/06 | | 200 | | | | | | | 7 | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 141322 | Butyl acrylate | 06/91 | | 100 | 1 | | | | | | | |
| 71363 | n-Butyl alcohol | 06/91 | | 100 | 1 | | | | | | | |
| 78922 | sec-Butyl alcohol | 06/91 | | 100 | 1 | | | | | | | |
| 75650 | tert-Butyl alcohol | 06/91 | | 100 | 1 | | | | | | | |
| 85687 | Butyl benzyl phthalate | 06/91 | | 100 | 1 | | | | | | | |
| 7440439 | Cadmium | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| * | Cadmium compounds | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | [7] |
| 156627 | Calcium cyanamide | 06/91 | | 100 | 1 | 2 | | | | | | |
| 105602 | Caprolactam | 06/91 | | 100 | 1 | 2 | | | | | | |
| 2425061 | Captafol | 09/89 | c | 100 | | | | 4 | | | | |
| 133062 | Captan | 09/90 | c | 100 | 1 | 2 | | 4 | | | | |
| 63252 | Carbaryl [PAH-Derivative, POM] | 06/91 | | 100 | 1 | 2 | | | | | | |
| 1050 | Carbon black extracts | | c | 2 | 1 | | 3 | 4 | | | | |
| 75150 | Carbon disulfide | 09/89 | | 200 | 1 | 2 | | 4 | | | | |
| 56235 | Carbon tetrachloride | | c | 1 | 1 | 2 | 3 | 4 | 5 | | | |
| 463581 | Carbonyl sulfide | 06/91 | | 100 | 1 | 2 | | | | | | |
| 1055 | Carrageenan (degraded) | | c | 100 | | | 3 | 4 | | | | |
| 120809 | Catechol | 06/91 | | 100 | 1 | 2 | | | | | | |
| 133904 | Chloramben | 06/91 | | 100 | 1 | 2 | | | | | | |
| 57749 | Chlordane | 09/89 | c | 10 | 1 | 2 | | 4 | | | | |
| 108171262 | Chlorinated paraffins (average chain length, C12; approximately 60% Chlorine by weight) | 09/89 | c | 2 | | | 3 | 4 | 5 | | | |
| 7782505 | Chlorine | | | 0.5 | 1 | 2 | | | | | | |
| 10049044 | Chlorine dioxide | 06/91 | | 1 | 1 | | | | | | | |
| 79118 | Chloroacetic acid | 06/91 | | 100 | 1 | 2 | | | | | | |
| 532274 | 2-Chloroacetophenone | 06/91 | | 0.1 | 1 | 2 | | | | | | |
| 106478 | p-Chloroaniline | 07/96 | c | 100 | | | | 4 | | | 7 | |
| 1058 | Chlorobenzenes including but not limited to: | 06/91 | | 100 | 1 | | | | | | | |
| 108907 | Chlorobenzene | | | 200 | 1 | 2 | | | | | | |
| 25321226 | Dichlorobenzenes (mixed isomers) including: | 06/91 | | 100 | 1 | | | | | | 7 | |
| 95501 | 1,2-Dichlorobenzene | 06/91 | | 200 | 1 | | | | | | 7 | |
| 541731 | 1,3-Dichlorobenzene | 06/91 | | 100 | 1 | | | | | | 7 | |

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| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 106467 | p-Dichlorobenzene {1,4-Dichlorobenzene} | | c | 5 | 1 | 2 | 3 | | 5 | | | |
| 120821 | 1,2,4-Trichlorobenzene | 06/91 | | 200 | 1 | 2 | | | | | | |
| 510156 | Chlorobenzilate [POM] {Ethyl-4,4'-dichlorobenzilate} | 09/90 | c | 100 | 1 | 2 | | 4 | | | | |
| 67663 | Chloroform | | c | 10 | 1 | 2 | 3 | 4 | 5 | | | |
| 107302 | Chloromethyl methyl ether (technical grade) | | c | 100 | 1 | 2 | | 4 | 5 | | | |
| 1060 | Chlorophenols including but not limited to: | | c | 100 | 1 | | 3 | | | | | |
| 95578 | 2-Chlorophenol | 11/06 | | 10 | 1 | | 3 | | | | | |
| 120832 | 2,4-Dichlorophenol | 06/91 | c | 100 | 1 | | | | | | 7 | |
| 87865 | Pentachlorophenol | 09/90 | c | 10 | 1 | 2 | | 4 | | | | |
| 25167833 | Tetrachlorophenols including but not limited to: | 11/06 | | 10 | | | | | | | 7 | |
| 58902 | 2,3,4,6-Tetrachlorophenol | 07/96 | c | 100 | 1 | | | | | | 7 | |
| 95954 | 2,4,5-Trichlorophenol | 06/91 | c | 100 | 1 | 2 | | | | | | |
| 88062 | 2,4,6-Trichlorophenol | | c | 2 | 1 | 2 | | 4 | | | | |
| 95830 | 4-Chloro-o-phenylenediamine | | c | 10 | | | 3 | 4 | 5 | | | |
| 76062 | Chloropicrin | | | 2 | | | | | | | 7 | |
| 126998 | Chloroprene | | | 5 | 1 | 2 | | | | | | |
| 95692 | p-Chloro-o-toluidine | | c | 0.5 | | | 3 | 4 | | | | |
| 7440473 | Chromium | 06/91 | | 0.001 | | | | | | | 7 | |
| * | Chromium compounds (other than hexavalent) | 06/91 | | 0.001 | 1 | 2 | | | | | | [7] |
| 18540299 | Chromium, hexavalent (and compounds) including but not limited to: | | c | 0.0001 | 1 | 2 | 3 | 4 | 5 | | | [7] |
| 10294403 | Barium chromate | 06/91 | c | 0.001 | 1 | 2 | | | 5 | | | [7] |
| 13765190 | Calcium chromate | 06/91 | c | 0.001 | 1 | 2 | | | 5 | | | [7] |
| 1333820 | Chromium trioxide | 06/91 | c | 0.0001 | 1 | 2 | | | 5 | | | [7] |
| 7758976 | Lead chromate | 06/91 | c | 0.001 | 1 | 2 | | | 5 | | | [7] |
| 10588019 | Sodium dichromate | 06/91 | c | 0.0001 | 1 | 2 | | | 5 | | | [7] |
| 7789062 | Strontium chromate | 06/91 | c | 0.001 | 1 | 2 | | | 5 | | | [7] |
| - | Chrysene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 7440484 | Cobalt | 06/91 | | 0.5 | | | | | | | 7 | |
| * | Cobalt compounds | 06/91 | | 0.5 | 1 | 2 | | | | | | [7] |
| 1066 | Coke oven emissions | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |

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| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 7440508 | Copper | | | 0.1 | | 2 | | | | | | |
| * | Copper compounds | 09/89 | | 0.1 | 1 | 2 | | | | | | [7] |
| 1070 | Creosotes | | c | 0.05 | 1 | | 3 | 4 | | | | |
| 120718 | p-Cresidine | | c | 1 | | | 3 | 4 | 5 | | | |
| 1319773 | Cresols (mixtures of) {Cresylic acid} including: | | | 5 | 1 | 2 | | | | | | |
| 108394 | m-Cresol | 06/91 | | 5 | 1 | 2 | | | | | | |
| 95487 | o-Cresol | 06/91 | | 5 | 1 | 2 | | | | | | |
| 106445 | p-Cresol | 06/91 | | 5 | 1 | 2 | | | | | | |
| 4170303 | Crotonaldehyde | 07/96 | c | 50 | | | | | | | 7 | |
| 98828 | Cumene | 06/91 | | 200 | 1 | 2 | | | | | | |
| 80159 | Cumene hydroperoxide | 06/91 | | 100 | 1 | | | | | | | |
| 135206 | Cupferron | | c | 0.5 | | | | 4 | 5 | | | |
| 57125 | Cyanide compounds (inorganic) including but not limited to: | 06/91 | | 0.05 | 1 | 2 | | | | | | [8] |
| 74908 | Hydrocyanic acid | | | 10 | | 2 | | | | | | |
| 110827 | Cyclohexane | 06/91 | | 200 | 1 | | | | | | | |
| 108930 | Cyclohexanol | 07/96 | | 200 | | | | | | | 7 | |
| 66819 | Cycloheximide | | | 2 | | | | | | 6 | | |
| | Decabromodiphenyl oxide [POM] (see Polybrominated diphenyl ethers) | 06/91 | | | | | | | | | | |
| 1075 | Dialkylnitrosamines including but not limited to: | | | 0.001 | 1 | | | | | | | |
| 924163 | N-Nitrosodi-n-butylamine | | c | 0.0001 | 1 | | 3 | 4 | 5 | | | |
| 1116547 | N-Nitrosodiethanolamine | | c | 100 | 1 | | 3 | 4 | 5 | | | |
| 55185 | N-Nitrosodiethylamine | | c | 0.001 | 1 | | 3 | 4 | 5 | | | |
| 62759 | N-Nitrosodimethylamine | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 621647 | N-Nitrosodi-n-propylamine | | c | 0.01 | 1 | | 3 | 4 | 5 | | | |
| 10595956 | N-Nitrosomethylethylamine | | c | 0.001 | 1 | | 3 | 4 | | | | |
| 615054 | 2,4-Diaminoanisole | | c | 5 | | | 3 | 4 | | | | |
| 1078 | Diaminotoluenes (mixed isomers) including but not limited to: | 09/90 | c | 100 | 1 | | | 4 | | | | |
| 95807 | 2,4-Diaminotoluene {2,4-Toluene diamine} | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |
| 334883 | Diazomethane | 06/91 | c | 5 | 1 | 2 | | | | | | |
| 226368 | Dibenz[a,h]acridine [POM] | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 224420 | Dibenz[a,j]acridine [POM] | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| - | Dibenz[a,h]anthracene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 194592 | 7H-Dibenzo[c,g]carbazole | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |
| - | Dibenzo[a,e]pyrene [PAH, POM], (see PAH) | | | | | | | | | | | |
| - | Dibenzo[a,h]pyrene [PAH, POM], (see PAH) | | | | | | | | | | | |
| - | Dibenzo[a,i]pyrene [PAH, POM], (see PAH) | | | | | | | | | | | |
| - | Dibenzo[a,l]pyrene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 132649 | Dibenzofuran [POM] | 06/91 | | 100 | 1 | 2 | | | | | | |
| - | Dibenzofurans (chlorinated) (see Polychlorinated dibenzofurans) [POM] | | | | | | | | | | | |
| 96128 | 1,2-Dibromo-3-chloropropane {DBCP} | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 96139 | 2,3-Dibromo-1-propanol | 07/96 | c | 50 | | | | 4 | | | | |
| 84742 | Dibutyl phthalate | 06/91 | | 100 | 1 | 2 | | | | | | |
| - | p-Dichlorobenzene (1,4-Dichlorobenzene) (see Chlorobenzenes) | | | | | | | | | | | |
| 91941 | 3,3'-Dichlorobenzidine [POM] | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 72559 | Dichlorodiphenyldichloroethylene {DDE} [POM] | 09/89 | c | 100 | 1 | 2 | | 4 | | | | |
| 75343 | 1,1-Dichloroethane {Ethylidene dichloride} | 09/90 | c | 20 | 1 | 2 | | 4 | | | | |
| 94757 | Dichlorophenoxyacetic acid, salts and esters {2,4-D} | 06/91 | | 100 | 1 | 2 | | | | | | |
| 78875 | 1,2-Dichloropropane {Propylene dichloride} | 09/90 | c | 20 | 1 | 2 | | 4 | | | | |
| 542756 | 1,3-Dichloropropene | | c | 10 | 1 | 2 | 3 | 4 | 5 | | | |
| 62737 | Dichlorovos {DDVP} | 09/89 | c | 0.5 | 1 | 2 | | 4 | | | | |
| 115322 | Dicofol [POM] | 06/91 | | 100 | 1 | 2 | | | | | | |
| -- | Diesel engine exhaust | 09/90 | c | | 1 | | 3 | 4 | | | | [9] |
| 9901 | Diesel engine exhaust, particulate matter **{**Diesel PM**}** | 09/90 | c | 0.1 | 1 | | 3 | 4 | | | | [9] |
| 9902 | Diesel engine exhaust, total organic gas | 09/90 | c | 10 | 1 | | 3 | 4 | | | | [9] |
| # | Diesel fuel (marine) | 06/91 | c | | | | | | | | | |
| 111422 | Diethanolamine | 06/91 | | 20 | 1 | 2 | | | | | | |
| 117817 | Di(2-ethylhexyl) phthalate {DEHP} | | c | 20 | 1 | 2 | 3 | 4 | 5 | | | |
| 64675 | Diethyl sulfate | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| 119904 | 3,3'-Dimethoxybenzidine [POM] | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| 60117 | 4-Dimethylaminoazobenzene [POM] | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 121697 | N,N-Dimethylaniline | 06/91 | | 200 | 1 | 2 | | | | | | |
| 57976 | 7,12-Dimethylbenz[a]anthracene [PAH-Derivative, POM] | 09/90 | c | 0.0001 | 1 | 2 | | 4 | | | | |
| 119937 | 3,3'-Dimethylbenzidine {o-Tolidine} [POM] | | c | 10 | 1 | 2 | 3 | 4 | 5 | | | |
| 79447 | Dimethyl carbamoyl chloride | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| 68122 | Dimethyl formamide | 09/90 | c | 100 | 1 | 2 | 3 | | | | | |
| 57147 | 1,1-Dimethylhydrazine | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 131113 | Dimethyl phthalate | 06/91 | | 50 | 1 | 2 | | | | | | |
| 77781 | Dimethyl sulfate | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 534521 | 4,6-Dinitro-o-cresol (and salts) | 06/91 | | 100 | 1 | 2 | | | | | | |
| 51285 | 2,4-Dinitrophenol | 06/91 | | 100 | 1 | 2 | | | | | | |
| 42397648 | 1,6-Dinitropyrene [PAH-Derivative, POM] | 06/91 | c | 0.001 | 1 | 2 | 3 | 4 | | | | |
| 42397659 | 1,8-Dinitropyrene [PAH-Derivative, POM] | 06/91 | c | 0.05 | 1 | 2 | 3 | 4 | | | | |
| 25321146 | Dinitrotoluenes (mixed isomers) including but not limited to: | 06/91 | | 100 | | | | | | | 7 | |
| 121142 | 2,4-Dinitrotoluene | 09/89 | c | 0.5 | 1 | 2 | | 4 | | | | |
| 606202 | 2,6-Dinitrotoluene | 06/91 | | 100 | | | | | | | 7 | |
| 123911 | 1,4-Dioxane | | c | 5 | 1 | 2 | 3 | 4 | 5 | | | |
| - | Dioxins (Chlorinated dibenzodioxins) (see Polychlorinated dibenzo-p-dioxins) [POM] | | | | | | | | | | | |
| 630933 | Diphenylhydantoin [POM] | | c | 100 | 1 | 2 | | 4 | | | | |
| 122667 | 1,2-Diphenylhydrazine {Hydrazobenzene} [POM] | | c | 100 | 1 | 2 | | 4 | 5 | | | |
| 1090 | Environmental Tobacco Smoke | | c | 2 | 1 | | 3 | 4 | | | | |
| 106898 | Epichlorohydrin | | c | 2 | 1 | 2 | 3 | 4 | 5 | | | |
| 106887 | 1,2-Epoxybutane | 06/91 | | 100 | 1 | 2 | | | | | | |
| 1091 | Epoxy resins | 09/89 | | 100 | | | | | | 6 | | |
| 140885 | Ethyl acrylate | | c | 200 | 1 | 2 | 3 | 4 | 5 | | | |
| 100414 | Ethyl benzene | 06/91 | | 200 | 1 | 2 | | | | | | |
| 75003 | Ethyl chloride {Chloroethane} | | | 200 | 1 | 2 | | 4 | | | | |
| - | Ethyl-4,4'-dichlorobenzilate (see Chlorobenzilate) | | | | | | | | | | | |
| 74851 | Ethylene | 06/91 | | 200 | | | | | | | 7 | |
| 106934 | Ethylene dibromide {EDB, 1,2-Dibromoethane} | | c | 0.5 | 1 | | 3 | 4 | 5 | 6 | | |
| 107062 | Ethylene dichloride {EDC, 1,2-Dichloroethane} | | c | 2 | 1 | 2 | 3 | 4 | 5 | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 107211 | Ethylene glycol | 06/91 | | 200 | 1 | 2 | | | | | | |
| 151564 | Ethyleneimine {Aziridine} | 06/91 | | 100 | 1 | 2 | | | | | | |
| 75218 | Ethylene oxide | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 96457 | Ethylene thiourea | | c | 2 | 1 | 2 | 3 | 4 | 5 | | | |
| 1101 | Fluorides and compounds including but not limited to: | 09/89 | | 100 | | 2 | | | | | | |
| 7664393 | Hydrogen fluoride | | | 50 | 1 | 2 | | | | | 7 | |
| 1103 | Fluorocarbons (brominated) | | | 200 | | | | | | 6 | | [10] |
| 1104 | Fluorocarbons (chlorinated) including but not limited to: | | | 200 | 1 | | | | | 6 | | [10] |
| 76131 | Chlorinated fluorocarbon {CFC-113} {1,1,2-Trichloro-1,2,2-trifluoroethane} | | | 200 | 1 | 2 | | | | 6 | | |
| 75456 | Chlorodifluoromethane {Freon 22} | 07/96 | | 200 | 1 | | | | | 6 | 7 | |
| 75718 | Dichlorodifluoromethane {Freon 12} | 11/06 | | 200 | | | | | | | 7 | |
| 75434 | Dichlorofluoromethane {Freon 21} | 07/96 | | 200 | 1 | | | | | 6 | 7 | |
| 75694 | Trichlorofluoromethane {Freon 11} | 07/96 | | 200 | 1 | | | | | 6 | 7 | |
| 50000 | Formaldehyde | | c | 5 | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 110009 | Furan | 07/96 | c | 5 | | | | 4 | | | | |
| -- | Gasoline engine exhaust including but not limited to: | 09/89 | c | | | | 3 | | | | | [9] |
| -- | Gasoline engine exhaust (condensates & extracts) | 06/91 | c | | | | | 4 | | | | [9] |
| 9910 | Gasoline engine exhaust, particulate matter | 09/90 | c | 100 | | | 3 | 4 | | | | [9] |
| 9911 | Gasoline engine exhaust, total organic gas | 09/90 | c | 100 | | | 3 | 4 | | | | [9] |
| 1110 | Gasoline vapors | | c | 200 | 1 | 2 | 3 | 4 | | | | [11] |
| 111308 | Glutaraldehyde | | | 0.1 | 1 | | | | | 6 | | |
| 1115 | Glycol ethers and their acetates including but not limited to: | | | 100 | 1 | 2 | | | | 6 | | |
| 111466 | Diethylene glycol | 09/90 | | 100 | 1 | | | | | 6 | | |
| 111966 | Diethylene glycol dimethyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 112345 | Diethylene glycol monobutyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 111900 | Diethylene glycol monoethyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 111773 | Diethylene glycol monomethyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 25265718 | Dipropylene glycol | 09/90 | | 100 | 1 | | | | | 6 | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 34590948 | Dipropylene glycol monomethyl ether | 09/90 | | 100 | 1 | | | | | 6 | | |
| 629141 | Ethylene glycol diethyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 110714 | Ethylene glycol dimethyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 111762 | Ethylene glycol monobutyl ether | 09/90 | | 200 | 1 | 2 | | | | 6 | | |
| 110805 | Ethylene glycol monoethyl ether | 09/89 | | 50 | 1 | 2 | | | | 6 | | |
| 111159 | Ethylene glycol monoethyl ether acetate | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 109864 | Ethylene glycol monomethyl ether | 09/89 | | 10 | 1 | 2 | | | | 6 | | |
| 110496 | Ethylene glycol monomethyl ether acetate | 09/90 | | 200 | 1 | 2 | | | | 6 | | |
| 2807309 | Ethylene glycol monopropyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 107982 | Propylene glycol monomethyl ether | 09/90 | | 200 | 1 | | | | | 6 | | |
| 108656 | Propylene glycol monomethyl ether acetate | 09/90 | | 100 | 1 | | | | | 6 | | |
| 112492 | Triethylene glycol dimethyl ether | 09/90 | | 100 | 1 | 2 | | | | 6 | | |
| 76448 | Heptachlor | 09/89 | c | 100 | 1 | 2 | | 4 | | | | |
| 118741 | Hexachlorobenzene | | c | 0.1 | 1 | 2 | 3 | | 5 | | | |
| 87683 | Hexachlorobutadiene | 06/91 | | 0.1 | 1 | 2 | | | | | | |
| 608731 | Hexachlorocyclohexanes (mixed or technical grade), including but not limited to: | | c | 0.05 | 1 | | 3 | 4 | 5 | | | |
| 319846 | alpha-Hexachlorocyclohexane | 07/96 | c | 0.1 | 1 | | 3 | 4 | 5 | | 7 | |
| 319857 | beta-Hexachlorocyclohexane | 07/96 | c | 0.1 | 1 | | 3 | 4 | 5 | | 7 | |
| 58899 | Lindane {gamma-Hexachlorocyclohexane} | 09/90 | c | 0.1 | 1 | 2 | | 4 | | | | |
| 77474 | Hexachlorocyclopentadiene | | | 2 | 1 | 2 | | | | | | |
| 67721 | Hexachloroethane | 09/90 | c | 200 | 1 | 2 | | 4 | | | | |
| 680319 | Hexamethylphosphoramide | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| 110543 | Hexane | 06/91 | | 200 | 1 | 2 | | | | | | |
| 302012 | Hydrazine | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 7647010 | Hydrochloric acid | | | 20 | 1 | 2 | | | | | | |
| - | Hydrocyanic acid (see Cyanide compounds) | | | | | | | | | | | |
| 7783064 | Hydrogen sulfide | | | 5 | 1 | 2 | | | | | | |
| 123319 | Hydroquinone | 06/91 | | 100 | 1 | 2 | | | | | | |
| - | Indeno[1,2,3-cd]pyrene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 13463406 | Iron pentacarbonyl | 07/96 | | 5 | | | | | | | 7 | |
| 1125 | Isocyanates including but not limited to: | | | 0.05 | | | | | | 6 | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 822060 | Hexamethylene-1,6-diisocyanate | 06/91 | | 0.05 | 1 | 2 | | | | | | |
| 101688 | Methylene diphenyl diisocyanate {MDI} [POM] | 06/91 | | 0.1 | 1 | 2 | | | | | | |
| 624839 | Methyl isocyanate | | | 1 | 1 | 2 | | | | | | |
| - | Toluene-2,4-diisocyanate (see Toluene diisocyanates) | | | | | | | | | | | |
| - | Toluene-2,6-diisocyanate (see Toluene diisocyanates) | | | | | | | | | | | |
| 78591 | Isophorone | 06/91 | | 200 | 1 | 2 | | | | | | |
| 78795 | Isoprene, except from vegetative emission sources | 07/96 | c | 200 | | | 3 | | | | | |
| 67630 | Isopropyl alcohol | 06/91 | | 200 | 1 | | | | | | | |
| 80057 | 4,4'-Isopropylidenediphenol [POM] | 06/91 | | 100 | 1 | 2 | | | | | | |
| 7439921 | Lead | | c | 0.5 | 1 | | | 4 | | 6 | | |
| 1128 | Lead compounds (inorganic) including but not limited to: | | c | 0.5 | 1 | | 3 | | | | | [7] |
| 301042 | Lead acetate | | c | 1 | 1 | 2 | | 4 | 5 | | | [7] [12] |
| - | Lead chromate (see Chromium, hexalent) | | | | | | | | | | | |
| 7446277 | Lead phosphate | | c | 2 | 1 | | | 4 | 5 | | | [7] |
| 1335326 | Lead subacetate | 09/90 | c | 2 | 1 | 2 | | 4 | | | | [7] [12] |
| 1129 | Lead compounds (other than inorganic) | 06/91 | | 5 | 1 | 2 | | | | | | [7] |
| 108316 | Maleic anhydride | | | 0.5 | 1 | 2 | | | | | | |
| 7439965 | Manganese | | | 0.1 | 1 | 2 | | | | | | |
| * | Manganese compounds | 09/89 | | 0.1 | 1 | 2 | | | | | | [7] |
| 7439976 | Mercury | | | 1 | 1 | 2 | | 4 | | 6 | | |
| * | Mercury compounds including but not limited to: | 09/89 | | 1 | 1 | 2 | | 4 | | | | [7] |
| 7487947 | Mercuric chloride | | | 1 | | 2 | | | | | | [7] |
| 593748 | Methyl mercury {Dimethylmercury} | | | 1 | | 2 | | | | | | [7] |
| 67561 | Methanol | | | 200 | 1 | 2 | | | | | | |
| 72435 | Methoxychlor [POM] | 06/91 | | 100 | 1 | 2 | | | | | | |
| 75558 | 2-Methylaziridine {1,2-Propyleneimine} | | c | 100 | 1 | 2 | 3 | 4 | | | | |
| 74839 | Methyl bromide {Bromomethane} | | | 20 | 1 | 2 | | | | 6 | | |
| 74873 | Methyl chloride {Chloromethane} | 06/91 | | 20 | 1 | 2 | | | | | | |
| 71556 | Methyl chloroform {1,1,1-Trichloroethane} | | | 200 | 1 | 2 | | | | 6 | | |
| 56495 | 3-Methylcholanthrene [PAH-Derivative, POM] | 09/90 | c | 0.001 | 1 | 2 | | 4 | | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3697243 | 5-Methylchrysene [PAH-Derivative, POM] | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |
| 101144 | 4,4'-Methylene bis(2-chloroaniline) {MOCA} [POM] | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 75092 | Methylene chloride {Dichloromethane} | | c | 50 | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 101779 | 4,4'-Methylenedianiline (and its dichloride) [POM] | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 78933 | Methyl ethyl ketone {2-Butanone} | 06/91 | | 200 | 1 | 2 | | | | | | |
| 60344 | Methyl hydrazine | 06/91 | | 100 | 1 | 2 | | | | | | |
| 74884 | Methyl iodide {Iodomethane} | | c | 100 | 1 | 2 | | 4 | 5 | | | |
| 108101 | Methyl isobutyl ketone {Hexone} | 06/91 | | 20 | 1 | 2 | | | | | | |
| 75865 | 2-Methyllactonitrile {Acetone cyanohydrin} | 07/96 | | 50 | | | | | | | 7 | |
| 80626 | Methyl methacrylate | | | 200 | 1 | 2 | | | | 6 | | |
| 109068 | 2-Methylpyridine | 07/96 | | 100 | | | | | | | 7 | |
| 1634044 | Methyl tert-butyl ether | 06/91 | | 200 | 1 | 2 | | | | | | |
| 90948 | Michler's ketone [POM] | | c | 0.1 | 1 | 2 | | 4 | 5 | | | |
| 1136 | Mineral fibers (fine mineral fibers which are man-made, and are airborne particles of a respirable size greater than 5 microns in length, less than or equal to 3.5 microns in diameter, with a length to diameter ratio of 3:1) including but not limited to: | 06/91 | c | 100 | 1 | 2 | | | | | 7 | |
| 1056 | Ceramic fibers | 09/89 | c | 100 | 1 | 2 | 3 | 4 | | | | |
| 1111 | Glasswool fibers | 09/89 | c | 100 | 1 | 2 | 3 | 4 | | | | |
| 1168 | Rockwool | 09/89 | c | 100 | 1 | 2 | 3 | | | | | |
| 1181 | Slagwool | 09/89 | c | 100 | 1 | 2 | 3 | | | | | |
| 1135 | Mineral fibers (other than man-made) including but not limited to: | | | 100 | | 2 | | | | | 7 | |
| 1332214 | Asbestos | | c | 0.0001 | 1 | 2 | 3 | 4 | 5 | | | |
| 12510428 | Erionite | | c | 100 | | 2 | 3 | 4 | | | | |
| 1190 | Talc containing asbestiform fibers | | c | 100 | | 2 | 3 | 4 | | | | |
| 1313275 | Molybdenum trioxide | 06/91 | | 100 | 1 | | | | | | | |
| - | Naphhthalene [PAH, POM], (see PAH) | | | | | | | | | | | |
| 7440020 | Nickel | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| * | Nickel compounds including but not limited to: | | c | 1 | 1 | 2 | 3 | 4 | 5 | | | [7] |
| 373024 | Nickel acetate | 06/91 | c | 0.1 | 1 | 2 | | | 5 | | | [7] |
| 3333673 | Nickel carbonate | 06/91 | c | 0.1 | 1 | 2 | | | 5 | | | [7] |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13463393 | Nickel carbonyl | | c | 0.1 | 1 | 2 | | 4 | 5 | | | [7] |
| 12054487 | Nickel hydroxide | 06/91 | c | 0.1 | 1 | 2 | | | 5 | | | [7] |
| 1271289 | Nickelocene | 06/91 | c | 0.1 | 1 | 2 | | | 5 | | | [7] |
| 1313991 | Nickel oxide | 06/91 | c | 0.1 | 1 | 2 | | | 5 | | | [7] |
| 12035722 | Nickel subsulfide | | c | 0.1 | 1 | 2 | | 4 | 5 | | | [7] |
| 1146 | Nickel refinery dust from the pyrometallurgical process | 09/89 | c | 0.1 | | | | 4 | | | | |
| 7697372 | Nitric acid | 06/91 | | 50 | 1 | | | | | | | |
| 139139 | Nitrilotriacetic acid | | c | 100 | 1 | | | 4 | 5 | | | |
| 602879 | 5-Nitroacenaphthene [PAH-Derivative, POM] | 11/06 | c | 2 | 1 | 2 | 3 | 4 | | | | |
| 98953 | Nitrobenzene | | | 0.5 | 1 | 2 | | | | | | |
| 92933 | 4-Nitrobiphenyl [POM] | 09/89 | c | 100 | 1 | 2 | | 4 | | | | |
| 7496028 | 6-Nitrochrysene [PAH-Derivative, POM] | 06/91 | c | 0.001 | 1 | 2 | 3 | 4 | | | | |
| 607578 | 2-Nitrofluorene [PAH-Derivative, POM] | 06/91 | c | 5 | 1 | 2 | 3 | 4 | | | | |
| 302705 | Nitrogen mustard N-oxide | | c | 0.05 | | | 3 | 4 | | | | |
| 100027 | 4-Nitrophenol | 06/91 | | 100 | 1 | 2 | | | | | | |
| 79469 | 2-Nitropropane | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 5522430 | 1-Nitropyrene [PAH-Derivative, POM] | 06/91 | c | 0.5 | 1 | 2 | 3 | 4 | | | | |
| 57835924 | 4-Nitropyrene [PAH-Derivative, POM] | 11/06 | c | 1 | | | | 4 | | | | |
| 86306 | N-Nitrosodiphenylamine | 11/06 | c | 10 | 1 | 2 | 3 | 4 | | | | |
| 156105 | p-Nitrosodiphenylamine [POM] | | c | 5 | 1 | 2 | | 4 | 5 | | | |
| 684935 | N-Nitroso-N-methylurea | | c | 100 | 1 | 2 | | 4 | 5 | | | |
| 59892 | N-Nitrosomorpholine | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | | | |
| 100754 | N-Nitrosopiperidine | | c | 1 | | | 3 | 4 | 5 | | | |
| 930552 | N-Nitrosopyrrolidine | | c | 0.05 | | | 3 | 4 | 5 | | | |
| * | Oleum (see Sulfuric acid and oleum) | | | | | | | | | | | |
| -- | PAHs (Polycyclic aromatic hydrocarbons) [POM] including but not limited to: | | | | 1 | 2 | | | | | | [13] |
| 1151 | PAHs, total, w/o individ. components reported [PAH, POM] | | | 50 | 1 | 2 | | | | | | |
| 1150 | PAHs, total, with individ. components also reported [PAH, POM] | | | 50 | 1 | 2 | | | | | | |
| 83329 | Acenaphthene [PAH, POM] | 07/96 | | 50 | 1 | | | | | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 208968 | Acenaphthylene [PAH, POM] | 07/96 | | 50 | 1 | | | | | | | |
| 120127 | Anthracene [PAH, POM] | 06/91 | | 50 | 1 | 2 | | | | | 7 | |
| 56553 | Benz[a]anthracene [PAH, POM] | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| 50328 | Benzo[a]pyrene [PAH, POM] | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |
| 205992 | Benzo[b]fluoranthene | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| 192972 | Benzo[e]pyrene [PAH, POM] | 07/96 | | 0.5 | 1 | | | | | | | |
| 191242 | Benzo[g,h,i]perylene [PAH, POM] | 07/96 | | 0.5 | 1 | | | | | | | |
| 205823 | Benzo[j]fluoranthene [PAH, POM] | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| 207089 | Benzo[k]fluoranthene [PAH, POM] | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| 218019 | Chrysene [PAH, POM] | 09/90 | c | 5 | 1 | 2 | | 4 | | | | |
| 53703 | Dibenz[a,h]anthracene [PAH, POM] | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 192654 | Dibenzo[a,e]pyrene [PAH, POM] | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |
| 189640 | Dibenzo[a,h]pyrene [PAH, POM] | | c | 0.001 | 1 | 2 | 3 | 4 | 5 | | | |
| 189559 | Dibenzo[a,i]pyrene [PAH, POM] | | c | 0.001 | 1 | 2 | 3 | 4 | 5 | | | |
| 191300 | Dibenzo[a,l]pyrene [PAH, POM] | | c | 0.001 | 1 | 2 | 3 | 4 | 5 | | | |
| 206440 | Fluoranthene [PAH, POM] | 07/96 | c | 0.5 | 1 | | | | | | | |
| 86737 | Fluorene [PAH, POM] | 07/96 | c | 0.5 | 1 | | | | | | | |
| 193395 | Indeno[1,2,3-cd]pyrene [PAH, POM] | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| 91576 | 2-Methyl naphthalene [PAH, POM] | 07/96 | c | 50 | 1 | | | | | | | |
| 91203 | Naphthalene [PAH, POM] | | c | 0.1 | 1 | 2 | | | | | | |
| 198550 | Perylene [PAH, POM] | 07/96 | c | 0.5 | 1 | | | | | | | |
| 85018 | Phenanthrene [PAH, POM] | 07/96 | c | 0.5 | 1 | | | | | | | |
| 129000 | Pyrene [PAH, POM] | 07/96 | c | 0.5 | 1 | | | | | | | |
| # | PAH-Derivatives (Polycyclic aromatic hydrocarbon derivatives) [POM] (including but not limited to those substances listed in Appendix A with the bracketed designation [PAH-Derivative, POM]) | 06/91 | | | | | | | | | | [14] |
| 56382 | Parathion | 06/91 | | 100 | 1 | 2 | | | | | | |
| 1336363 | PCBs (Polychlorinated biphenyls), total [POM] including but not limited to: | | c | 0.01 | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 32598133 | 3,3',4,4'-Tetrachlorobiphenyl (PCB 77) | 11/06 | c | 0.01 | | 2 | 3 | 4 | 5 | | | |
| 70362504 | 3,4,4',5-Tetrachlorobiphenyl (PCB 81) | 11/06 | c | 0.01 | | 2 | 3 | 4 | 5 | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 32598144 | 2,3,3',4,4'-Pentachlorobiphenyl (PCB 105) | 11/06 | c | 0.01 | | 2 | 3 | 4 | 5 | | | |
| 74472370 | 2,3,4,4',5-Pentachlorobiphenyl (PCB 114) | 11/06 | c | 0.002 | | 2 | 3 | 4 | 5 | | | |
| 31508006 | 2,3',4,4',5-Pentachlorobiphenyl (PCB 118) | 11/06 | c | 0.01 | | 2 | 3 | 4 | 5 | | | |
| 65510443 | 2,3',4,4',5'-Pentachlorobiphenyl (PCB 123) | 11/06 | c | 0.01 | | 2 | 3 | 4 | 5 | | | |
| 57465288 | 3,3',4,4',5-Pentachlorobiphenyl (PCB 126) | 11/06 | c | 0.00001 | | 2 | 3 | 4 | 5 | | | |
| 38380084 | 2,3,3',4,4',5-Hexachlorobiphenyl (PCB 156) | 11/06 | c | 0.002 | | 2 | 3 | 4 | 5 | | | |
| 69782907 | 2,3,3',4,4',5'-Hexachlorobiphenyl (PCB 157) | 11/06 | c | 0.002 | | 2 | 3 | 4 | 5 | | | |
| 52663726 | 2,3',4,4',5,5'-Hexachlorobiphenyl (PCB 167) | 11/06 | c | 0.1 | | 2 | 3 | 4 | 5 | | | |
| 32774166 | 3,3',4,4',5,5'-Hexachlorobiphenyl (PCB 169) | 11/06 | c | 0.0001 | | 2 | 3 | 4 | 5 | | | |
| 39635319 | 2,3,3',4,4',5,5'-Heptachlorobiphenyl (PCB 189) | 11/06 | c | 0.01 | | 2 | 3 | 4 | 5 | | | |
| 82688 | Pentachloronitrobenzene {Quintobenzene} | 06/91 | | 100 | 1 | 2 | | | | | | |
| 79210 | Peracetic acid | 06/91 | | 100 | 1 | | | | | | | |
| 127184 | Perchloroethylene {Tetrachloroethene} | | c | 5 | 1 | 2 | 3 | 4 | 5 | 6 | | |
| 2795393 | Perfluorooctanoic acid {PFOA} and its salts, esters, and sulfonates | 11/06 | | 10 | | | | | | | 7 | |
| 108952 | Phenol | | | 200 | 1 | 2 | | | | | | |
| 106503 | p-Phenylenediamine | 06/91 | | 100 | 1 | 2 | | | | | | |
| 90437 | 2-Phenylphenol [POM] | 06/91 | | 100 | 1 | 2 | | | | | | |
| 75445 | Phosgene | | | 2 | 1 | 2 | | | | | | |
| 7723140 | Phosphorus | | | 0.1 | 1 | 2 | | | | | | |
| -- | Phosphorus compounds: | 09/89 | | | | 2 | | | | | | |
| 7803512 | Phosphine | | | 0.01 | 1 | 2 | | | | | 7 | |
| 7664382 | Phosphoric acid | 09/89 | | 50 | 1 | 2 | | | | | | |
| 10025873 | Phosphorus oxychloride | 09/89 | | 0.1 | | 2 | | | | | | |
| 10026138 | Phosphorus pentachloride | 09/89 | | 0.1 | | 2 | | | | | | |
| 1314563 | Phosphorus pentoxide | 09/89 | | 0.1 | | 2 | | | | | | |
| 7719122 | Phosphorus trichloride | 09/89 | | 0.1 | | 2 | | | | | | |
| 126738 | Tributyl phosphate | 09/89 | | 100 | | 2 | | | | | | |
| 78400 | Triethyl phosphine | 09/89 | | 100 | | 2 | | | | | | |
| 512561 | Trimethyl phosphate | 09/89 | | 100 | | 2 | | | | | | |
| 78308 | Triorthocresyl phosphate [POM] | 09/89 | | 0.5 | 1 | 2 | | | | | | |
| 115866 | Triphenyl phosphate [POM] | 09/89 | | 100 | 1 | 2 | | | | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 101020 | Triphenyl phosphite [POM] | 09/89 | | 100 | 1 | 2 | | | | | | |
| 85449 | Phthalic anhydride | | | 0.01 | 1 | 2 | | | | | | |
| 2222 | Polybrominated diphenyl ethers {PBDEs}, including but not limited to: | 11/06 | | 1 | | | | | | | 7 | |
| 1163195 | Decabromodiphenyl oxide [POM] | 06/91 | | 1 | 1 | 2 | | | | | | |
| -- | Polychlorinated dibenzo-p-dioxins {PCDDs or Dioxins} [POM], including but not limited to: | | c | | 1 | 2 | | | | | | |
| 1086 | Dioxins, total, w/o individ. isomers reported {PCDDs} [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 1085 | Dioxins, total, with individ. isomers also reported {PCDDs} [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 1746016 | 2,3,7,8-Tetrachlorodibenzo-p-dioxin {TCDD} [POM] | | c | 0.000001 | 1 | 2 | 3 | 4 | 5 | | | |
| 40321764 | 1,2,3,7,8-Pentachlorodibenzo-p-dioxin [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 39227286 | 1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin [POM] | | c | 0.000001 | 1 | 2 | | 4 | | | | |
| 57653857 | 1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 19408743 | 1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 35822469 | 1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 3268879 | 1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 41903575 | Total Tetrachlorodibenzo-p-dioxin [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 36088229 | Total Pentachlorodibenzo-p-dioxin [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 34465468 | Total Hexachlorodibenzo-p-dioxin [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 37871004 | Total Heptachlorodibenzo-p-dioxin [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| -- | Polychlorinated dibenzofurans {PCDFs or Dibenzofurans} [POM], including but not limited to: | | c | | 1 | 2 | | | | | | |
| 1080 | Dibenzofurans (Polychlorinated dibenzofurans) {PCDFs} [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 51207319 | 2,3,7,8-Tetrachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 57117416 | 1,2,3,7,8-Pentachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 57117314 | 2,3,4,7,8-Pentachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 70648269 | 1,2,3,4,7,8-Hexachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 57117449 | 1,2,3,6,7,8-Hexachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 72918219 | 1,2,3,7,8,9-Hexachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 60851345 | 2,3,4,6,7,8-Hexachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 67562394 | 1,2,3,4,6,7,8-Heptachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 55673897 | 1,2,3,4,7,8,9-Heptachlorodibenzofuran [POM] | | c | 0.000001 | 1 | 2 | | | | | | |
| 39001020 | 1,2,3,4,6,7,8,9-Octachlorodibenzofuran [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 55722275 | Total Tetrachlorodibenzofuran [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 30402154 | Total Pentachlorodibenzofuran [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 55684941 | Total Hexachlorodibenzofuran [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| 38998753 | Total Heptachlorodibenzofuran [POM] | 07/96 | c | 0.000001 | 1 | 2 | | | | | | |
| # | POM (Polycyclic organic matter) (including but not limited to those substances listed in Appendix A with the bracketed designation of [POM], [PAH, POM], or [PAH-Derivative, POM]) | 09/89 | | | 1 | 2 | | | | | | [15] |
| 1120714 | 1,3-Propane sultone | | c | 0.05 | 1 | 2 | 3 | 4 | 5 | | | |
| 57578 | beta-Propiolactone | | c | 10 | 1 | 2 | 3 | 4 | 5 | | | |
| 123386 | Propionaldehyde | 06/91 | | 200 | 1 | 2 | | | | | | |
| 114261 | Propoxur {Baygon} | 06/91 | | 100 | 1 | 2 | | | | | | |
| 115071 | Propylene | | | 200 | 1 | 2 | | | | | | |
| 75569 | Propylene oxide | | c | 10 | 1 | 2 | 3 | 4 | 5 | | | |
| - | 1,2-Propyleneimine (see 2-Methylaziridine) | | | | | | | | | | | |
| 110861 | Pyridine | 06/91 | | 100 | | | | | | | 7 | |
| 91225 | Quinoline | 06/91 | | 100 | 1 | 2 | | | | | | |
| 106514 | Quinone | 06/91 | | 100 | 1 | 2 | | | | | | |
| 1165 | Radionuclides including but not limited to: | | c | 100 | 1 | 2 | | 4 | | | | [16] |
| 24267569 | Iodine-131 | 09/89 | c | 100 | 1 | 2 | | 4 | | | | |
| 1166 | Radon and its decay products | 09/89 | c | 100 | 1 | | | 4 | | | | |
| 50555 | Reserpine [POM] | | c | 100 | 1 | 2 | | 4 | 5 | | | |
| # | Residual (heavy) fuel oils | 06/91 | c | | | | | | | | | |
| 7782492 | Selenium | | | 0.5 | | 2 | | | | | | |
| * | Selenium compounds including but not limited to: | | | 0.5 | 1 | 2 | | | | | | [7] |
| 7783075 | Hydrogen selenide | 11/06 | | 0.1 | | | | | | | 7 | |
| 7446346 | Selenium sulfide | 09/90 | c | 0.1 | | 2 | | 4 | 5 | | | [7] |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1175 | Silica, crystalline (respirable) | | | 0.1 | 1 | | 3 | 4 | | | | |
| 7440224 | Silver | 06/91 | | 2 | | | | | | | 7 | |
| * | Silver compounds | 06/91 | | 2 | 1 | | | | | | | [7] |
| 1310732 | Sodium hydroxide | | | 2 | 1 | 2 | | | | | | |
| 100425 | Styrene | | c | 100 | 1 | 2 | 3 | | | 6 | | |
| 96093 | Styrene oxide | | c | 100 | 1 | 2 | 3 | 4 | | | | |
| * | Sulfuric acid and oleum | | | | | | | | | | | |
| 8014957 | Oleum | 11/06 | | 100 | | | | | | | 7 | |
| 7446719 | Sulfur trioxide | 11/06 | | 100 | | | | | | | 7 | |
| 7664939 | Sulfuric acid | 06/91 | | 2 | 1 | | | | | | | |
| 100210 | Terephthalic acid | 06/91 | | 100 | 1 | | | | | | | |
| 79345 | 1,1,2,2-Tetrachloroethane | 09/90 | c | 1 | 1 | 2 | | 4 | | | | |
| - | Tetrachlorophenols (see Chlorophenols) | | | | | | | | | | | |
| 7440280 | Thallium | 06/91 | | 100 | | | | | | | 7 | |
| * | Thallium compounds | 06/91 | c | 100 | | | | | | | 7 | [7] |
| 62555 | Thioacetamide | | c | 0.01 | | | 3 | 4 | 5 | | | |
| 62566 | Thiourea | | c | 0.1 | 1 | | 3 | 4 | 5 | | | |
| 7550450 | Titanium tetrachloride | 06/91 | | 100 | 1 | 2 | | | | | | |
| 108883 | Toluene | | | 200 | 1 | 2 | | 4 | | 6 | | |
| - | 2,4-Toluenediamine (see 2,4-Diaminotoluene) | | | | | | | | | | | |
| 26471625 | Toluene diisocyanates including but not limited to: | 06/91 | c | 0.1 | 1 | | 3 | | | | | |
| 584849 | Toluene-2,4-diisocyanate | | c | 0.1 | 1 | 2 | 3 | | 5 | | | |
| 91087 | Toluene-2,6-diisocyanate | | c | 0.1 | 1 | 2 | 3 | | 5 | | | |
| 95534 | o-Toluidine | | c | 10 | 1 | 2 | 3 | 4 | 5 | | | |
| 8001352 | Toxaphene {Polychlorinated camphenes} | | c | 100 | 1 | 2 | 3 | 4 | 5 | | | |
| - | 1,1,1-Trchloroethane (see Methyl chloroform) | | | | | | | | | | | |
| 79005 | 1,1,2-Trichloroethane {Vinyl trichloride} | 06/91 | c | 1 | 1 | 2 | | 4 | | | | |
| 79016 | Trichloroethylene | | c | 20 | 1 | 2 | | 4 | | | | |
| - | 2,4,6-Trichlorophenol (see Chlorophenols) | | | | | | | | | | | |
| 96184 | 1,2,3-Trichloropropane | 07/96 | c | 200 | | | 3 | 4 | | | 7 | |
| 121448 | Triethylamine | 06/91 | | 20 | 1 | 2 | | | | | | |
| 1582098 | Trifluralin | 06/91 | | 100 | 1 | 2 | | | | | | |

## Substances for Which Emissions Must Be Quantified

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Applicable Degree of Accuracy (lb/yr)** [Note 5] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---:|---|:-:|:-:|:-:|:-:|:-:|:-:|:-:|:-:|:-:|:-:|:-:|
| 25551137 | Trimethylbenzenes including but not limited to: | 11/06 | | 100 | 1 | | | | | | | |
| 95636 | 1,2,4-Trimethylbenzene | 06/91 | | 5 | 1 | | | | | | | |
| 540841 | 2,2,4-Trimethylpentane | 06/91 | | 100 | 1 | 2 | | | | | | |
| 51796 | Urethane {Ethyl carbamate} | | c | 0.1 | 1 | 2 | 3 | 4 | 5 | | | |
| 7440622 | Vanadium (fume or dust) | 06/91 | | 10 | | | | | | | 7 | [17] |
| 1314621 | Vanadium pentoxide | 11/06 | | 10 | | 2 | | | | | | |
| 108054 | Vinyl acetate | 06/91 | | 200 | 1 | 2 | | | | | | |
| 593602 | Vinyl bromide | | c | 20 | 1 | 2 | 3 | 4 | | | | |
| 75014 | Vinyl chloride | | c | 0.5 | 1 | 2 | 3 | 4 | 5 | | | |
| 100403 | 4-Vinylcyclohexene | 07/96 | c | 5 | | | 3 | | | | | |
| 75025 | Vinyl fluoride | 07/96 | c | 200 | | | 3 | | | | | |
| 75354 | Vinylidene chloride | | | 20 | 1 | 2 | | | | | | |
| 1206 | Wood preservatives (containing arsenic and chromate) | 09/89 | | 100 | | | | | | 6 | | |
| 1330207 | Xylenes (mixed) including: | | | 200 | 1 | 2 | | | | 6 | | |
| 108383 | m-Xylene | 06/91 | | 200 | 1 | 2 | | | | | | |
| 95476 | o-Xylene | 06/91 | | 200 | 1 | 2 | | | | | | |
| 106423 | p-Xylene | 06/91 | | 200 | 1 | 2 | | | | | | |
| 7440666 | Zinc | | | 2 | | 2 | | | | | | |
| * | Zinc compounds including but not limited to: | 09/89 | | 2 | 1 | 2 | | | | | | [7] |
| 1314132 | Zinc oxide | | | 2 | | 2 | | | | | | [7] |

# Appendix A-II

## Substances for Which Production, Use, or Other Presence Must Be Reported

## Substances for Which Production, Use, or Other Presence Must be Reported

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 26148685 | A-alpha-C {2-Amino-9H-pyrido[2,3-b]indole} | 09/89 | c | | | 3 | 4 | | | | [18] |
| 34256821 | Acetochlor | 09/89 | c | | | | 4 | | | | |
| 62476599 | Acifluorfen [POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 3688537 | AF-2 | | c | | | 3 | 4 | | | | |
| 1000 | Aflatoxins | | c | | | 3 | 4 | 5 | | | |
| 15972608 | Alachlor | 09/89 | c | | | | 4 | | | | |
| 309002 | Aldrin | 09/89 | c | | | | 4 | | | | |
| 107186 | Allyl alcohol | 06/91 | | | | | | | | 7 | |
| 60093 | p-Aminoazobenzene {4-Aminoazobenzene} [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 97563 | o-Aminoazotoluene [POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 6109973 | 3-Amino-9-ethylcarbazole hydrochloride [POM] | 09/89 | c | 1 | 2 | | 4 | 5 | | | |
| 125848 | Aminoglutethimide | 09/90 | | | | | 4 | | | | |
| 82280 | 1-Amino-2-methylanthraquinone [PAH-Derivative, POM] | | c | 1 | 2 | | 4 | 5 | | | |
| 68006837 | 2-Amino-3-methyl-9H-pyrido(2,3-b) indole {MeA-alpha-C} | 09/89 | c | | | 3 | 4 | | | | |
| 712685 | 2-Amino-5-(5-nitro-2-furyl)-1,3,4-thiadiazole | | c | | | 3 | 4 | | | | |
| 134292 | o-Anisidine hydrochloride | | c | | | | 4 | 5 | | | |
| 104949 | p-Anisidine | 06/91 | | | | | | | | 7 | |
| 140578 | Aramite | | c | | | 3 | 4 | | | | |
| 492808 | Auramine [POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 446866 | Azathioprine | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 103333 | Azobenzene [POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 98873 | Benzal chloride | 06/91 | | | | | | | | 7 | |
| 55210 | Benzamide | 06/91 | | | | | | | | 7 | |
| 1694093 | Benzyl violet 4B [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 1025 | Betel quid with tobacco | | c | | | 3 | 4 | | | | |
| 494031 | N-N-Bis(2-chloroethyl)-2-naphthylamine {Chlornaphazine} [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 108601 | Bis(2-chloro-1-methylethyl) ether | 06/91 | | | | | | | | 7 | |
| 1030 | Bitumens, extracts of steam-refined and air-refined bitumens | | c | | | 3 | 4 | | | | |
| 1035 | Bleomycins | | c | | | 3 | | | | | |
| 75274 | Bromodichloromethane | 09/90 | c | | | | 4 | | | | |

## Substances for Which Production, Use, or Other Presence Must be Reported

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1689845 | Bromoxynil | 06/91 | | | | | 4 | | | | |
| 25013165 | Butylated hydroxyanisole {BHA} | | c | | | 3 | 4 | | | | |
| 123728 | Butyraldehyde | 06/91 | | | | | | | | 7 | |
| 3068880 | beta-Butyrolactone | | c | | | 3 | 4 | | | | |
| 630080 | Carbon monoxide | 09/89 | | | | | 4 | | | | |
| 143500 | Chlordecone {Kepone} | | c | | | 3 | 4 | | | | |
| 6164983 | Chlordimeform | 09/89 | c | | | | 4 | | | | |
| 115286 | Chlorendic acid | 09/89 | c | | | 3 | 4 | 5 | | | |
| 124481 | Chlorodibromomethane | 09/90 | c | | | | 4 | | | | |
| 563473 | 3-Chloro-2-methylpropene | 09/89 | c | | | | 4 | 5 | | | |
| 1065 | Chlorophenoxy herbicides | | c | | | 3 | | | | | |
| 1897456 | Chlorothalonil | 09/89 | c | | | | 4 | | | | |
| 1059 | p-Chloro-o-toluidine (strong acid salts) | 06/91 | c | | | 3 | | | | | |
| 4680788 | C. I. Acid Green 3 [POM] Note: "C.I." means "color index" | 06/91 | | 1 | 2 | | | | | 7 | |
| 569642 | C. I. Basic Green 4 [POM] | 06/91 | | 1 | 2 | | | | | 7 | |
| 989388 | C. I. Basic Red 1 [POM] | 06/91 | | 1 | 2 | | | | | 7 | |
| 569619 | C. I. Basic Red 9 monohydrochloride [POM] | 09/89 | c | 1 | 2 | | 4 | 5 | | | |
| 2832408 | C. I. Disperse Yellow 3 [POM] | 06/91 | | 1 | 2 | | | | | 7 | |
| 87296 | Cinnamyl anthranilate [POM] | 09/89 | c | 1 | 2 | | 4 | 5 | | | |
| 6358538 | Citrus Red No. 2 [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 8007452 | Coal tars | 09/89 | c | | | 3 | 4 | 5 | | | |
| 21725462 | Cyanazine | 09/90 | | | | | 4 | | | | |
| 14901087 | Cycasin | | c | | | 3 | 4 | | | | |
| 13121705 | Cyhexatin | 09/89 | | | | | 4 | 5 | | | |
| 3468631 | D and C Orange No. 17 [PAH-Derivative, POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 81889 | D and C Red No. 19 [POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 2092560 | D and C Red No. 8 [PAH-Derivative, POM] | 06/91 | c | 1 | 2 | | 4 | | | | |
| 5160021 | D and C Red No. 9 [PAH-Derivative, POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 1596845 | Daminozide | 09/90 | c | | | | 4 | | | | |
| 50293 | DDT {1,1,1-Trichloro-2,2-bis(p-chlorophenyl)ethane} [POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 613354 | N,N'-Diacetylbenzidine [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 2303164 | Diallate | 06/91 | | | | | | | | 7 | |
| 39156417 | 2,4-Diaminoanisole sulfate | | c | | | | 4 | 5 | | | |

## Substances for Which Production, Use, or Other Presence Must be Reported

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 101804 | 4,4'-Diaminodiphenyl ether [POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 764410 | 1,4-Dichloro-2-butene | 09/90 | c | | | | 4 | | | | |
| 28434868 | 3,3'-Dichloro-4,4'-diaminodiphenyl ether [POM] | 09/89 | c | 1 | 2 | 3 | 4 | | | | |
| 72548 | Dichlorodiphenyldichloroethane {DDD} [POM] | 09/89 | c | 1 | 2 | | 4 | | | | |
| 540590 | 1,2-Dichloroethylene | 06/91 | | | | | | | | 7 | |
| 78886 | 2,3-Dichloropropene | 06/91 | | | | | | | | 7 | |
| 60571 | Dieldrin | 09/89 | c | | | | 4 | | | | |
| 1464535 | Diepoxybutane | | c | | | 3 | 4 | 5 | | | |
| 1615801 | 1,2-Diethylhydrazine | | c | | | 3 | 4 | | | | |
| 84662 | Diethyl phthalate | 06/91 | | | | | | | | 7 | |
| 101906 | Diglycidyl resorcinol ether {DGRE} | | c | | | 3 | 4 | 5 | | | |
| 94586 | Dihydrosafrole | | c | | | 3 | 4 | | | | |
| 20325400 | 3,3'-Dimethoxybenzidine dihydrochloride [POM] | 06/91 | c | 1 | 2 | | 4 | | | | |
| 55738540 | trans-2-[(Dimethylamino)methylimino]-5-[2-(5-nitro-2-furyl)vinyl-1,3,4-oxadiazol | | c | | | 3 | 4 | | | | |
| 540738 | 1,2-Dimethylhydrazine | | c | | | 3 | 4 | | | | |
| 105679 | 2,4-Dimethylphenol {2,4-Xylenol} | 06/91 | | | | | | | | 7 | |
| 513371 | Dimethylvinylchloride {DMVC} | 09/89 | c | | | | 4 | 5 | | | |
| 25154545 | Dinitrobenzenes (mixtures of) including: | 09/90 | | | | | 4 | | | 7 | |
| 99650 | m-Dinitrobenzene | 06/91 | | | | | | | | 7 | |
| 528290 | o-Dinitrobenzene | 06/91 | | | | | | | | 7 | |
| 100254 | p-Dinitrobenzene | 06/91 | | | | | | | | 7 | |
| 39300453 | Dinocap | 09/90 | | | | | 4 | | | | |
| 88857 | Dinoseb | 09/89 | | | | | 4 | | | | |
| 117840 | n-Dioctyl phthalate | 06/91 | | | | | | | | 7 | |
| 2475458 | Disperse Blue 1 [PAH-Derivative, POM] | 06/91 | c | 1 | 2 | 3 | 4 | | | | |
| 541413 | Ethyl chloroformate | 06/91 | | | | | | | | 7 | |
| 62500 | Ethyl methanesulfonate | | c | | | 3 | 4 | | | | |
| 2164172 | Fluometuron | 06/91 | | | | | | | | 7 | |
| 133073 | Folpet | 09/89 | c | | | | 4 | | | | |
| 3570750 | 2-(2-Formylhydrazino)-4-(5-nitro-2-furyl)thiazole | | c | | | 3 | 4 | | | | |
| 60568050 | Furmecyclox | 09/90 | c | | | | 4 | | | | |
| 67730114 | Glu-P-1 {2-Amino-6-methyldipyrido[1,2-a:3',2'-d]imidazole} | | c | | | 3 | 4 | | | | |

## Substances for Which Production, Use, or Other Presence Must be Reported

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 67730103 | Glu-P-2 {2-Aminodipyrido[1,2-a:3',2'-d]imidazole} | | c | | | 3 | 4 | | | | |
| 765344 | Glycidaldehyde | | c | | | 3 | 4 | | | | |
| 556525 | Glycidol | 09/90 | c | | | | 4 | | | | |
| 16568028 | Gyromitrin {Acetaldehyde methylformylhydrazone} | | c | | | | 4 | | | | |
| 2784943 | HC Blue 1 | 09/89 | c | | | | 4 | 5 | | | |
| 1024573 | Heptachlor epoxide | 09/89 | c | | | | 4 | | | | |
| 1335871 | Hexachloronaphthalene [PAH-Derivative, POM] | 06/91 | | 1 | 2 | | | | | 7 | |
| 10034932 | Hydrazine sulfate | | c | | | | 4 | 5 | | | |
| 76180966 | IQ {2-Amino-3-methylimidazo[4,5-f]quinoline} | | c | | | 3 | 4 | | | | |
| 78842 | Isobutyraldehyde | 06/91 | | | | | | | | 7 | |
| 120581 | Isosafrole | 09/90 | c | | | | 4 | | | | |
| 4759482 | Isotretinoin | | | | | | 4 | | | | |
| 77501634 | Lactofen [POM] | 09/89 | c | 1 | 2 | | 4 | | | | |
| 1131 | Lubricant base oils and derived products, specifically vacuum distillates, acid treated oils, aromatic oils, mildly solvent-refined oils, mildly hydrotreated-oils and used engine oils. | 09/89 | c | | | 3 | 4 | 5 | | | |
| 8018017 | Mancozeb | 09/90 | c | | | | 4 | | | | |
| 12427382 | Maneb | 09/90 | c | | | | 4 | | | | |
| 59052 | Methotrexate | 09/89 | | | | | 4 | | | | |
| 96333 | Methyl acrylate | 06/91 | | | | | | | | 7 | |
| 590965 | Methylazoxymethanol | 09/90 | c | | | | 4 | | | | |
| 592621 | Methylazoxymethanol acetate | 09/89 | c | | | 3 | 4 | | | | |
| 101611 | 4,4'-Methylene bis (N,N-dimethyl) benzenamine [POM] | | c | 1 | 2 | | 4 | 5 | | | |
| 838880 | 4,4'-Methylene bis(2-methylaniline) [POM] | 09/89 | c | 1 | 2 | 3 | 4 | | | | |
| 74953 | Methylene bromide | 06/91 | | | | | | | | 7 | |
| 66273 | Methyl methanesulfonate | | c | | | 3 | 4 | | | | |
| 129157 | 2-Methyl-1-nitroanthraquinone (uncertain purity) [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 70257 | N-Methyl-N'-nitro-N-nitrosoguanidine | | c | | | 3 | 4 | | | | |
| - | N-Methyl-N-nitrosourethane (see N-Nitroso-N-methylurethane) | | | | | | | | | | |
| 924425 | N-Methyloacrylamide | 09/90 | c | | | | 4 | | | | |
| 9006422 | Metiram | 09/90 | | | | | 4 | | | | |
| 1140 | Mineral oils (untreated and mildly treated oils; and those used in occupations such as mulespinning, metal machining, and jute | | c | | | 3 | 4 | 5 | | | |

## Substances for Which Production, Use, or Other Presence Must be Reported

| Emittent ID [Note 1] | Substance Name [Note 2] | Add Date [Note 3] | Carcinogen [Note 4] | Source List(s) [Note 6] | | | | | | | Other Note(s) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | processing). | | | | | | | | | | |
| 2385855 | Mirex | | c | | | 3 | 4 | 5 | | | |
| 315220 | Monocrotaline | | c | | | 3 | 4 | | | | |
| 505602 | Mustard gas {Sulfur mustard} | | c | | | 3 | 4 | 5 | | | |
| 134327 | 1-Naphthylamine [PAH-Derivative, POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 91598 | 2-Naphthylamine [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 54115 | Nicotine | 09/90 | | | | | 4 | | | | |
| 1148 | Nitrilotriacetic acid (salts) including but not limited to: | 06/91 | c | | | 3 | | | | | |
| 18662538 | Nitrilotriacetic acid, trisodium salt monohydrate | 06/91 | c | | | | 4 | | | | |
| 99592 | 5-Nitro-o-anisidine | | c | | | | 4 | 5 | | | |
| 1836755 | Nitrofen (technical grade) | | c | | | 3 | 4 | 5 | | | |
| 51752 | Nitrogen mustard {Mechlorethamine} | 09/89 | c | | | 3 | 4 | 5 | | | |
| 55867 | Nitrogen mustard hydrochloride | 06/91 | c | | | | 4 | 5 | | | |
| 55630 | Nitroglycerin | 06/91 | | | | | | | | 7 | |
| 88755 | 2-Nitrophenol | 06/91 | | | | | | | | 7 | |
| 57835924 | 4-Nitropyrene [PAH-Derivative, POM] | 09/89 | c | 1 | 2 | 3 | 4 | | | | |
| 759739 | N-Nitroso-N-ethylurea | 09/89 | c | | | | 4 | 5 | | | |
| 60153493 | 3-(N-Nitrosomethylamino)propionitrile | 09/89 | c | | | 3 | 4 | | | | |
| 64091914 | 4-(N-Nitrosomethylamino)-1-(3-pyridyl)-1-butanone {NNK} | | c | | | 3 | 4 | | | | |
| 615532 | N-Nitroso-N-methylurethane | | c | | | 3 | 4 | | | | |
| 4549400 | N-Nitrosomethylvinylamine | | c | | | 3 | 4 | 5 | | | |
| 16543558 | N-Nitrosonornicotine | | c | | | 3 | 4 | 5 | | | |
| 13256229 | N-Nitrososarcosine | | c | | | 3 | 4 | 5 | | | |
| 303479 | Ochratoxin A [POM] | 09/90 | c | 1 | 2 | | 4 | | | | |
| 2234131 | Octachloronaphthalene [PAH-Derivative, POM] | 06/91 | | 1 | 2 | | | | | 7 | |
| 2646175 | Oil Orange SS [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 20816120 | Osmium tetroxide | 06/91 | | | | | | | | 7 | |
| 794934 | Panfuran S {Dihydroxymethylfuratrizine} | | c | | | 3 | 4 | | | | |
| 122601 | Phenyl glycidyl ether | 09/90 | c | | | 3 | 4 | | | | |
| 57410 | Phenytoin [POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |
| 88891 | Picric acid | 06/91 | | | | | | | | 7 | |
| 1155 | Polybrominated biphenyls {PBBs{ [POM] | | c | 1 | 2 | 3 | 4 | 5 | | | |

## Substances for Which Production, Use, or Other Presence Must be Reported

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3] | **Carcinogen** [Note 4] | **Source List(s)** [Note 6] | | | | | | | **Other Note(s)** |
|---:|---|---|---|---|---|---|---|---|---|---|---|
| 53973981 | Polygeenan | 09/89 | c | | | | 4 | | | | |
| 3761533 | Ponceau MX [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 3564098 | Ponceau 3R [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 36791045 | Ribavirin | 09/90 | | | | | 4 | | | | |
| 94597 | Safrole | | c | | | 3 | 4 | 5 | | | |
| 1180 | Shale oils | | c | | | 3 | 4 | | | | |
| 132274 | Sodium o-phenylphenate [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 128449 | Sodium saccharin | 09/89 | c | | | | 4 | | | | |
| 1185 | Soots | | c | | | 3 | 4 | | | | |
| 10048132 | Sterigmatocystin [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 95067 | Sulfallate | | c | | | 3 | 4 | 5 | | | |
| 5216251 | p-alpha,alpha,alpha-Tetrachlorotoluene | 09/90 | c | | | | 4 | | | | |
| 961115 | Tetrachlorvinphos | 06/91 | | | | | | | | 7 | |
| 509148 | Tetranitromethane | 09/90 | c | | | | 4 | | | | |
| 139651 | 4,4'-Thiodianiline [POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 1314201 | Thorium dioxide | | c | | | | 4 | 5 | | | |
| 1200 | Tobacco products, smokeless | | c | | | 3 | 4 | | | | |
| 1205 | alpha-chlorinated Toluenes | | c | | | 3 | | | | | |
| 636215 | o-Toluidine hydrochloride | | c | | | | 4 | 5 | | | |
| 106490 | p-Toluidine | 09/90 | c | | | | 4 | | | | |
| 52686 | Trichlorfon | 06/91 | | | | | | | | 7 | |
| 68768 | Tris(aziridinyl)-p-benzoquinone {Triaziquone} | 09/90 | c | | | | 4 | | | | |
| 52244 | Tris(1-aziridinyl) phosphine sulfide {Thiotepa} | | c | | | 3 | 4 | 5 | | | |
| 126727 | Tris(2,3-dibromopropyl)phosphate | 09/89 | c | | | | 4 | | | | |
| 62450060 | Trp-P-1 {3-Amino-1,4-dimethyl-5H-pyrido[4,3-b]indole} | | c | | | 3 | 4 | | | | |
| 62450071 | Trp-P-2 {3-Amino-1-methyl-5H-pyrido[4,3-b]indole} | | c | | | 3 | 4 | | | | |
| 72571 | Trypan blue [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | | | | |
| 106876 | 4-Vinyl-1-cyclohexene diepoxide {Vinyl cyclohexene dioxide} | 09/90 | c | | | | 4 | | | | |
| 81812 | Warfarin [POM] | | | 1 | 2 | | 4 | | | | |
| 87627 | 2,6-Xylidene | 06/91 | | | | | 4 | | | | |
| 12122677 | Zineb | 09/90 | c | | | | 4 | | | | |

# Appendix A-III

## Substances Which Need Not Be Reported Unless Manufactured By the Facility

## Substances Which Need Not Be Reported Unless Manufactured By the Facility

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3]) | **Carcinogen** [Note 4] | **Source Lists** [Note 6] | | | | | **Other Note(s)** |
|---:|---|:-:|:-:|:-:|:-:|:-:|:-:|:-:|---|
| 546883 | Acetohydroxamic acid | 09/90 | | | | | 4 | | |
| 50760 | Actinomycin D | 09/90 | c | | | | 4 | | |
| 23214928 | Adriamycin [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | 5 | |
| 28981977 | Alprazolam [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 39831555 | Amikacin sulfate | 09/90 | | | | | 4 | | |
| 54626 | Aminopterin | | | | | | 4 | | |
| 1005 | Analgesic mixtures containing phenacetin | | c | | | 3 | 4 | 5 | |
| 1010 | Androgenic (anabolic) steroids including but not limited to: | | c | | | 3 | 4 | | |
| 58184 | Methyltestosterone | 09/90 | | | | | 4 | | |
| 434071 | Oxymetholone | | c | | | | 4 | 5 | |
| 58220 | Testosterone and its esters including but not limited to: | 09/89 | | | | | 4 | | |
| 315377 | Testosterone enanthate | 09/90 | | | | | 4 | | |
| 50782 | Aspirin | 06/91 | | | | | 4 | | |
| 115026 | Azaserine | | c | | | 3 | 4 | | |
| 5411223 | Benzphetamine hydrochloride [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 154938 | Bischloroethyl nitrosourea | | c | | | 3 | 4 | | |
| 55981 | 1,4-Butanediol dimethanesulfonate {Busulfen/Myleran} | | c | | | 3 | 4 | 5 | |
| 41575944 | Carboplatin | 09/90 | | | | | 4 | | |
| 474259 | Chenodiol | 09/90 | | | | | 4 | | |
| 305033 | Chlorambucil | | c | | | 3 | 4 | 5 | |
| 56757 | Chloramphenicol | | c | | | 3 | 4 | | |
| 1620219 | Chlorcyclizine hydrochloride [POM] | | | 1 | 2 | | 4 | | |
| 13010474 | 1-(2-Chloroethyl)-3-cyclohexyl-1-nitrosourea {CCNU} | | c | | | 3 | 4 | 5 | |
| 13909096 | 1-(2-Chloroethyl)-3-(4-methylcyclohexyl)-1-nitrosourea {Methyl CCNU} | | c | | | 3 | | | |
| 15663271 | Cisplatin | | c | | | 3 | 4 | | |
| 50419 | Clomiphene citrate [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 50180 | Cyclophosphamide | | c | | | 3 | 4 | | |
| 147944 | Cytarabine | 09/89 | | | | | 4 | | |
| 4342034 | Dacarbazine | | c | | | 3 | 4 | 5 | |
| 17230885 | Danazol | 09/90 | | | | | 4 | | |
| 20830813 | Daunomycin [PAH-Derivative, POM] | | c | 1 | 2 | 3 | 4 | | |
| 23541506 | Daunorubicin hydrochloride [PAH-Derivative, POM] | 09/90 | | 1 | 2 | | 4 | | |
| 84173 | Dienestrol [POM] | 09/90 | c | 1 | 2 | | 4 | | |

## Substances Which Need Not Be Reported Unless Manufactured By the Facility

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3]) | **Carcinogen** [Note 4] | **Source Lists** [Note 6] | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|
| 564250 | Doxycycline | 09/90 | | | | | 4 | | |
| 379793 | Ergotamine tartrate [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 1095 | Estrogens, non-steroidal including but not limited to: | | c | | | 3 | | 5 | |
| 56531 | Diethylstilbestrol [POM] | | c | 1 | 2 | 3 | 4 | 5 | |
| 1100 | Estrogens, steroidal including but not limited to: | | c | | | 3 | | 5 | |
| 1068 | Conjugated estrogens | 09/90 | c | | | | 4 | | |
| 50282 | Estradiol 17 beta | | c | | | | 4 | 5 | |
| 53167 | Estrone | | c | | | | 4 | 5 | |
| 57636 | Ethinyl estradiol | | c | | | | 4 | 5 | |
| 72333 | Mestranol | | c | | | 3 | 4 | 5 | |
| 33419420 | Etoposide [POM] | 09/90 | | | 2 | | | | |
| 54350480 | Etretinate | | | | | | 4 | | |
| 51218 | Fluorouracil | 09/89 | | | | | 4 | | |
| 76437 | Fluoxymesterone | 09/90 | | | | | 4 | | |
| 13311847 | Flutamide | 09/90 | | | | | 4 | | |
| 67458 | Furazolidone | 09/90 | c | | | | 4 | | |
| 126078 | Griseofulvin | | c | | | 3 | 4 | | |
| 23092173 | Halazepam [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 3778732 | Ifosfamide | 09/90 | | | | | 4 | | |
| 9004664 | Iron dextran complex | | c | | | 3 | 4 | 5 | |
| 303344 | Lasiocarpine | 09/89 | c | | | 3 | 4 | | |
| 554132 | Lithium carbonate | 06/91 | | | | | 4 | | |
| 919164 | Lithium citrate | 06/91 | | | | | 4 | | |
| 846491 | Lorazepam [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 595335 | Megestrol acetate | 06/91 | | | | | 4 | | |
| 148823 | Melphalan | | c | | | 3 | 4 | 5 | |
| 9002680 | Menotropins | 09/90 | | | | | 4 | | |
| 6112761 | Mercaptopurine | 09/90 | | | | | 4 | | |
| 531760 | Merphalan | 09/89 | c | | | | 4 | | |
| 3963959 | Methacycline hydrochloride | 06/91 | | | | | 4 | | |
| 60560 | Methimazole | 09/90 | | | | | 4 | | |
| 15475566 | Methotrexate sodium | 09/90 | | | | | 4 | | |
| 484208 | 5-Methoxypsoralen | | c | | | 3 | | | |

## Substances Which Need Not Be Reported Unless Manufactured By the Facility

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3]) | **Carcinogen** [Note 4] | **Source Lists** [Note 6] | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|
| 56042 | Methylthiouracil | | c | | | 3 | 4 | | |
| 443481 | Metronidazole | | c | | | 3 | 4 | 5 | |
| 59467968 | Midazolam hydrochloride [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 62015398 | Misoprostol | 09/90 | | | | | 4 | | |
| 50077 | Mitomycin C | | c | | | 3 | 4 | | |
| 70476823 | Mitoxantrone hydrochloride [PAH-Derivative, POM] | 09/90 | | 1 | 2 | | 4 | | |
| 139913 | 5-(Morpholinomethyl)-3-[(5-nitrofurfurylidene)amino]-2-oxazolidinone | | c | | | 3 | 4 | | |
| 86220420 | Nafarelin acetate [PAH-Derivative, POM] | 09/90 | | 1 | 2 | | 4 | | |
| 3771195 | Nafenopin [POM] | | c | 1 | 2 | 3 | 4 | | |
| 1405103 | Neomycin sulfate | 09/90 | | | | | 4 | | |
| 56391572 | Netilmicin sulfate | 09/90 | | | | | 4 | | |
| 61574 | Niridazole | | c | | | 3 | 4 | | |
| 67209 | Nitrofurantoin | 06/91 | c | | | | 4 | | |
| 59870 | Nitrofurazone | 09/90 | c | | | | 4 | | |
| 555840 | 1-[(5-Nitrofurfurylidene)amino]-2-imidazolidinone | | c | | | 3 | 4 | | |
| 531828 | N-[4-(5-Nitro-2-furyl)-2-thiazolyl]acetamide | | c | | | 3 | 4 | | |
| 6533002 | Norgestrel | 09/90 | | | | | 4 | | |
| 79572 | Oxytetracycline | 06/91 | | | | | 4 | | |
| 115673 | Paramethadione | 09/90 | | | | | 4 | | |
| 52675 | Penicillamine | 06/91 | | | | | 4 | | |
| 57330 | Pentobarbital sodium | 09/90 | | | | | 4 | | |
| 63989 | Phenacemide | 09/90 | | | | | 4 | | |
| 62442 | Phenacetin | | c | | | 3 | 4 | 5 | |
| 94780 | Phenazopyridine hydrochloride | | c | | | 3 | 4 | 5 | |
| 3546109 | Phenesterin | 09/89 | c | | | | 4 | 5 | |
| 50066 | Phenobarbital | | c | | | 3 | 4 | | |
| 59961 | Phenoxybenzamine [POM] | 09/89 | c | 1 | 2 | | 4 | | |
| 63923 | Phenoxybenzimide hydrochloride [POM] | 09/90 | c | 1 | 2 | 3 | 4 | 5 | |
| 54911 | Pipobroman | 09/90 | | | | | 4 | | |
| 18378897 | Plicamycin [PAH-Derivative, POM] | 09/90 | | 1 | 2 | | 4 | | |
| 366701 | Procarbazine hydrochloride | | c | | | 3 | 4 | 5 | |
| 57830 | Progesterone | | c | | | 3 | 4 | 5 | |
| 1160 | Progestins including but not limited to: | | c | | | 3 | | | |

## Substances Which Need Not Be Reported Unless Manufactured By the Facility

| **Emittent ID** [Note 1] | **Substance Name** [Note 2] | **Add Date** [Note 3]) | **Carcinogen** [Note 4] | **Source Lists** [Note 6] | | | | | **Other Note(s)** |
|---|---|---|---|---|---|---|---|---|---|
| 71589 | Medroxyprogesterone acetate | | c | | | 3 | 4 | | |
| 68224 | Norethisterone | | c | | | | 4 | 5 | |
| 51525 | Propylthiouracil | | c | | | 3 | 4 | 5 | |
| 302794 | all-trans-Retinoic acid | 09/89 | | | | | 4 | | |
| 1167 | Retinol/retinyl esters | 09/89 | c | | | | 4 | | |
| 81072 | Saccharin | | c | | | 3 | 4 | 5 | |
| 3810740 | Streptomycin sulfate | 06/91 | | | | | 4 | | |
| 18883664 | Streptozotocin | | c | | | 3 | 4 | 5 | |
| 54965241 | Tamoxifen citrate [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 846504 | Temazepam [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 64755 | Tetracycline hydrochloride | 06/91 | | | | | 4 | | |
| 50351 | Thalidomide | | | | | | 4 | | |
| 154427 | Thioguanine | 09/90 | | | | | 4 | | |
| 49842071 | Tobramycin sulfate | 09/90 | | | | | 4 | | |
| 299752 | Treosulfan | | c | | | 3 | 4 | | |
| 28911015 | Triazolam [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 13647353 | Trilostane | 09/90 | | | | | 4 | | |
| 127480 | Trimethadione | 06/91 | | | | | 4 | | |
| 66751 | Uracil mustard | | c | | | 3 | 4 | | |
| 26995915 | Urofollitropin | 09/90 | | | | | 4 | | |
| 99661 | Valproate | | | | | | 4 | | |
| 143679 | Vinblastine sulfate [POM] | 09/90 | | 1 | 2 | | 4 | | |
| 2068782 | Vincristine sulfate [POM] | 09/90 | | 1 | 2 | | 4 | | |

## NOTES TO APPENDIX A:

[ 1] Emittent ID (the emittent identification number) is the Chemical Abstract Service (CAS) number where available, or an ARB-assigned 4-digit emittent ID code.

A dash ("-") is shown for the Emittent ID for substances which are alphabetized under a group header or synonym elsewhere on the list. Refer to the cross reference indicated in parenthesis, "( )".

A double dash ("- -") is shown for the Emittent ID to indicate that the entry is a non-reportable group header for the substances immediately following it.

An asterisk ("*") is shown for the Emittent ID to indicate that the emissions of unspecified metal compounds shall be reported as the metal atom equivalent. See Note [7].

A pound sign ("#") is shown for the Emittent ID to indicate that the individual, component listed substances must be reported for this mixture or group.

[ 2] Individual substances listed under a group heading must be reported individually. Other, unspecified substances in the group must be summed and reported using the emittent ID of the group heading.

The square bracket designation, "[ ]", indicates that the substance is a component of the chemical group heading(s) within the brackets.

The braces designation, "{ }", indicates a synonym for the substance listed.

[ 3] The date the Board approved addition of the substance to the original list. The original list was approved by the Board in July 1988.

[ 4] The letter "c" indicates that for purposes of this section the substance shall be treated as a human carcinogen or potential human carcinogen.

[ 5] Applicable degree of accuracy (in lbs/year except where noted). Radionuclides must be reported in Curie units, and the accuracy must be considered accordingly. Refer to section VII.E. and Appendix B.

[ 6] Substances are required to be included on the Hot Spots list based on the following lists cited in Health & Safety Code section 44321:

1 = California Air Resources Board (44321(c));

2 = Environmental Protection Agency (44321(e));

3 = International Agency for Research on Cancer;

4 = Governor's List of Carcinogens and Reproductive Toxicants; (44321(a); Labor Code section 6382(b)(1)): (44321(b); HSC section 25249.8):

5 = National Toxicology Program (44321(a));

6 = Hazard Evaluation System and Information Service (44321(d));

7 = Added pursuant to HSC section 44321 (f).

[ 7] Emissions of unspecified metal compounds shall be reported as the amount of the metal atom equivalent, using the metal emittent identification number for the metal itself (or the emittent identification number indicated on the table, such as for reporting inorganic versus other-than-inorganic arsenic compounds).

For unspecified metal compounds which contain two or more listed metals (e.g., zinc chromate), each component metal shall be reported as the amount of the appropriate metal atom equivalent (i.e., the zinc portion of the weight as zinc equivalent and the chromate portion as hexavalent chromium equivalent.

For specific, individually listed metal compounds (e.g., Lead chromate), emissions shall be reported for the compound (as pounds of whole compound), using the emittent identification number for that compound.

[ 8] Compounds of the form "X-CN", where formal dissociation can occur. Report as the amount of Cyanide equivalent in the compound using an emittent identification code of 1073.

[ 9] Emissions of these mixtures shall be reported as emissions of total particulate matter and total organic gas, using the following emittent identification numbers:

9901 Diesel exhaust, particulate matter 9910 Gasoline exhaust, particulate matter

9902 Diesel exhaust, total organic gas

9911 Gasoline exhaust, total organic gas

Individually listed substances from gasoline exhaust must also be reported. Emissions of diesel engine exhaust particulate matter (diesel PM), shall be reported as diesel PM using emittent ID 9901.

[10] The emittent identification number 1105 has been discontinued for all facilities reporting for the first time and for all updates. Use the listed replacement emittent identification codes 1103 and 1104.

[11] Emissions of the individual, component listed substances must be reported in addition to the total gasoline vapors emissions.

[12] These lead compounds are listed here so that the inorganic lead fraction will be quantified and reported if these individual compounds cannot be quantified.

[13] PAH: (Polycyclic Aromatic Hydrocarbon) - An organic compound consisting of a fused ring structure containing at least two (2) benzene rings, and which may also contain additional fused rings not restricted exclusively to hexagonal rings.

The structure does not include any heteroatoms or substituent groups. The structure includes only carbon and hydrogen.

PAHs are a subgroup of POM and have a boiling point of greater than or equal to 100 C.

[14] PAH-DERIVATIVE: (Polycyclic Aromatic Hydrocarbon Derivative) - An organic compound consisting of a fused ring structure containing at least two (2) benzene rings, and which may also contain additional fused rings not restricted exclusively to hexagonal rings. The fused ring structure does not contain heteroatoms. The structure does contain one or more substituent groups.

PAH-Derivatives are a subgroup of POM and have a boiling point of greater than or equal to 100 C.

[15] POM: (Polycyclic Organic Matter) - Includes organic compounds with more than one benzene ring, and which have a boiling point of greater than or equal to 100 C.

[16] Radionuclides and other radioactive substances shall be reported in units of Curies per year (for annual average emissions) and in units of milliCuries per hour (for maximum hourly emissions).

[17] Emissions of Vanadium (fume or dust) shall be reported as the amount of the vanadium atom equivalent, using the identification number 7440622.

[18] The emittent identification number 1001 has been replaced with the CAS number 26148685.

NOTE: The notation “11/06” indicates most recently added substances.

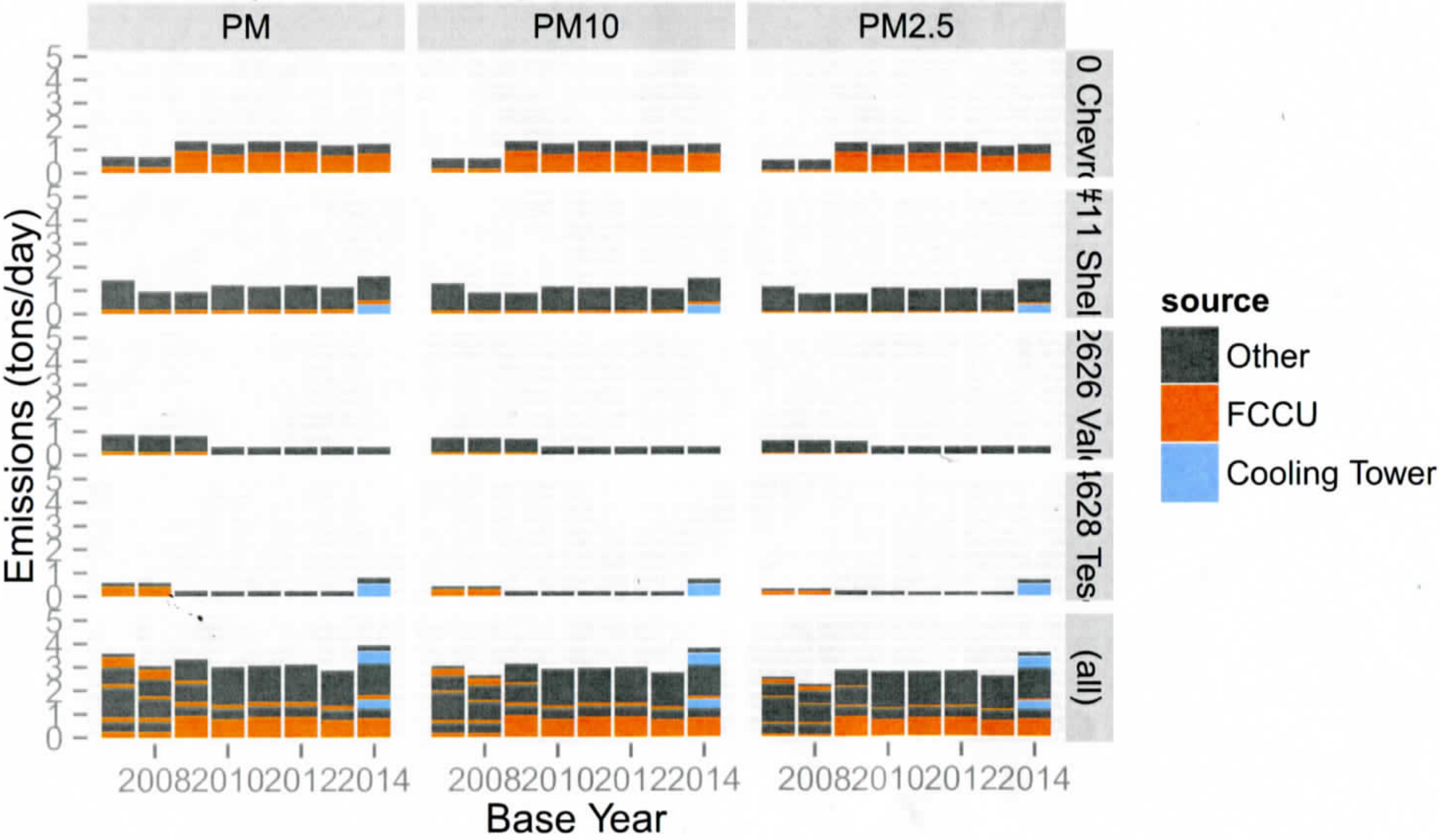
**Attachment 50**

| Facility Name | Air District Plant No. | ARB ID | Refining GHG Emissions Reported to ARB (MT $CO_2e$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
| Chevron | 10 | 101384 | 4,798,282 | 4,522,383 | 4,511,882 | 4,462,878 | 3,945,970 | 3,915,488 | 4,120,931 |
| Shell | 11 | 100914 | 4,570,475 | 4,322,192 | 4,446,565 | 4,262,144 | 4,056,522 | 4,191,585 | 3,968,978 |
| Valero | 12626 | 100372 | 2,796,057 | 2,889,804 | 2,627,977 | 2,638,405 | 2,939,902 | 2,738,051 | 2,710,549 |
| Tesoro | 14628 | 101331 | 2,703,145 | 2,291,909 | 2,028,587 | 2,400,813 | 2,089,720 | 2,445,615 | 2,334,466 |
| Phillips 66 | 21359 | 100303 | 1,888,895 | 1,873,464 | 1,638,946 | 1,502,353 | 1,320,965 | 1,363,918 | 1,276,578 |

| Facility Name | Air District Plant No. | ARB ID | Fuel Supplier/Associated Processes GHG Emissions Reported to ARB (MT $CO_2e$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
| Eco Services (Sulfuric Acid Plant) | 11661 | 100258 | 28,879 | 12,691 | 7,189 | 9,940 | 10,259 | 10,982 | 21,366 |
| Air Products (Hydrogen Plant) | 10295 | 101017 | 220,179 | 285,442 | 250,564 | 258,497 | 217,135 | 270,753 | 255,203 |
| Phillips 66 (Carbon Plant) | 21360 | 100351 | 168,132 | 13,441 | 14,881 | 243,283 | 169,892 | 163,775 | 217,492 |
| Martinez Cogen | | 101332 | 397,537 | 399,676 | 410,886 | 421,152 | 413,261 | 386,217 | 411,584 |
| Air Liquide (Hydrogen Plant) | 17419 | 101749 | 0 | 0 | 609,557 | 645,397 | 770,858 | 884,931 | 815,746 |

| Facility Name | Air District Plant No. | ARB ID | TOTAL GHG Emissions Reported to ARB (MT $CO_2e$) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
| Chevron | 10 | 101384 | 4,798,282 | 4,522,383 | 4,511,882 | 4,462,878 | 3,945,970 | 3,915,488 | 4,120,931 |
| Shell | 11 | 100914 | 4,982,451 | 4,728,214 | 4,861,045 | 4,688,267 | 4,474,912 | 4,583,293 | 4,391,245 |
| Valero | 12626 | 100372 | 2,810,497 | 2,896,149 | 2,631,572 | 2,643,375 | 2,945,032 | 2,743,542 | 2,721,232 |
| Tesoro | 14628 | 101331 | 2,923,324 | 2,577,351 | 2,279,151 | 2,659,310 | 2,306,855 | 2,716,367 | 2,589,669 |
| Phillips 66 | 21359 | 100303 | 2,057,027 | 1,886,906 | 2,263,384 | 2,391,033 | 2,261,715 | 2,412,625 | 2,309,816 |
| **Total** | | | **17,571,582** | **16,611,003** | **16,547,034** | **16,844,862** | **15,934,483** | **16,371,315** | **16,132,893** |

PM (t1132, t088x), speciated (via t0324)



**Attachment 51**

## Attachment 51. Excerpts from BAAQMD files regarding the Chevron Richmond Refinery Fluid Catalytic Cracking Unit (FCCU; S-4285):

- Evaluation Report (1993) and Status Letter (1998) re: FCC expansion.
- Current Emission Factor for Richmond FCC (2.3 lb PM/ton coke burned).
- Annual Source Update showing 1999 FCC oil feed rate (18,832,000 barrels) and coke burn rate (234,214 tons) for year.
- Emission Inventory Data for year ending 12/31/2009 showing FCC oil feed rate (27,600,000 barrels) and coke burn rate (299,000 tons).

FCC Unit PM emission increase from 1999–2009 based on these data:

| Year | | 1999 | 2009 | Increase (%) |
|---|---|---|---|---|
| Oil feed | b/y | 18,832,000 | 27,600,000 | 47% |
| Oil feed | b/d | 51,595 | 75,616 | 47% |
| Coke burn | t/y | 234,214 | 299,000 | 28% |
| Coke burn | t/d | 642 | 819 | 28% |
| | | *(at 2.3 lb/ton emission factor)* | | |
| PM emitted | lb/d | 1,476 | 1,884 | 28% |
| PM emitted | t/d | 0.74 | 0.94 | 28% |
| PM emitted | t/y | 269 | 344 | 28% |

PM: Particulate matter
FCC: Fluid Catalytic Cracking

[redacted]

# NEW/MODIFIED INDUSTRIAL PERMIT APPLICATION WORKSHEET

Company Name Chevron USA Products Co.
Equipment Address 841 Chevron Way
City, State, Zip Code Richmond, CA 94802

Application No. 611068
Plant No. 10
Assigned Engineer GDS

**Fill in all blanks in these columns:**

No Yes
☑ ☐ Regulation 10, Rule ____ (NSPS)
☑ ☐ Regulation 11, Rule ____ (NESHAPS)
☑ ☐ Air Quality Analysis
☑ ☐ PSD

**This Application Involves:**

No Yes
☑ ☐ Banking No. ________
☑ ☐ Violation No. ________
☑ ☐ Docket No. ________
☑ ☐ Bubble/AECP

☑ ☐ **NEW SOURCE REVIEW**
Preliminary Decision Due ________
To APCO For Preliminary Decision ________
To Public Notice ________
End of Public Notice ________
To APCO For Approval ________

FCC Feedrate Increase

☑ ☐ **TOXICS REVIEW**

| | Date | Initials | Results |
|---|---|---|---|
| Screening Analysis Complete | | | |
| Risk Assessment Complete | | | |
| Review Complete | | | |

**STATUS**

**Preliminary Review**

| | Date | Initials |
|---|---|---|
| Application Received | 4/23/93 | D.W |
| Permit Operations Review | | |
| Assigned to Engineer | 4/28 | |
| Additional Data Requested | | |
| Fee Request | | |
| Data and/or Fee Received | | |
| Application Deemed Complete | | |

**A/C Application Review**

| | Date | Initial | Recommended Action |
|---|---|---|---|
| Engineer | 7/20/93 | GDS | |
| Supervisor | 7/20/93 | | |
| Manager | | | |
| Permit Operations | | | |

**P/O Review**

| | Date | Initial | Recommended Action |
|---|---|---|---|
| Start-up Letter Received | | | ME 8/24/93 |
| Start-up Date | | | |
| Start-up Inspection | | | Offload. |
| Permit Operations | 8-20-93 | | |
| Engineer | 7/20/93 | GDS | P/O |
| Supervisor | 7/20/93 | TDA | P/O - Change of Cond. |
| Manager | 7/21/93 | WDB | Approved |

PSC 8/9/93

Comments:

**Emission Change(s) - This Application**

| | PM | POC | NOX | SO2 | CO | NPOC |
|---|---|---|---|---|---|---|
| Ann Avg. (lb/day) (+) | — | — | — | — | — | — |
| Banked (t/year) (−) | | | | | | |
| Offset [illegible] (−) | | | | | | |
| RACT Red. [illegible] | | | | | | |
| Max Oper [illegible] | | | | | | |

June, 1988

# EVALUATION REPORT
# Chevron USA, Plant #10
# Application Number 11068

## Background

Chevron is proposing to increase the throughput at S-4285 Fluid Catalytic Cracking Unit at its refinery located in Richmond, CA. The increase in daily throughput will be 19,000 bbls/day (to 80,000 bbls/day total). Chevron claims that this increase in throughput will not increase emissions of any criteria pollutants.

Chevron continuously monitors SOx and NOx levels from this FCC Plant. Chevron claims that it will not exceed the baseline levels for SOx and NOx. Chevron will meet the SOx baseline limit by hydrotreating (feed desulfurization) and/or the use of catalyst additives. The NOx baseline limit will be achieved by hydrotreating, ammonia injection, and/or reducing the steam generator firing.

The CO and VOC baselines were established based on source test data provided by Chevron. Chevron will meet these baselines by accepting permit conditions limiting the coke burn rate in the FCC Regenerator. Chevron claims that POC and CO emissions are dependent on boiler coke burn rate almost exclusively. A source test and continuous emission monitors will also be required to prove compliance under worst case conditions.

Particulate emissions are also dependent on coke burn and are not expected to increase beyond baseline levels. Additionally, the electrostatic precipitators are oversized and have capacities to handle greater quantities of flue gas and particulate matter.

## BACT

Baselines were established to prevent BACT from being triggered on an annual basis. On a daily basis there may be an increase of greater than 5 pounds per day. Therefore BACT will be required for the FCC Unit.

It should be noted that the NOx baseline used in this application (1504.7 tpy) was established using the average of the highest 12 one year baselines over the past 5 years. The five year average was approximately 1000 tpy, the previous 12 month average was 1150 tpy, and the highest 12 month average over the past 5 years was 1650 tpy. The 1650 tpy was cause by a four month spike in NOx emissions. District Staff could not determine the cause of the high NOx months. The established baseline of 1504.7 tpy uses the four high months, but does not use the highest 12 month period.

NOx emissions from the FCC regenerator will be controlled through the injection of ammonia upstream of the CO boiler. Ammonia is added as a conditioner to reduce dust resistivity and increase the electrostatic precipitator efficiency. The ammonia causes a thermal "deNOx" reaction in the CO Boiler which converts the $NH_3$ and $NO_x$ to $N_2$ and $H_2O$. No other form of BACT has been adequately demonstrated for this operation.

SOx emissions will be controlled through the use of deSOx catalyst and hydrotreating the feed.

The CO Boiler acts as a large afterburner converting regenerator CO and POC's to $CO_2$ and $H_2O$.

TSP will be controlled through the use of an electrostatic precipitator.

## Emission Calculations

Emissions were not calculated for this application since baseline levels will not be exceeded.

## Plant Cumulative Increase

There will be no increase in the Plant Cumulative Increase from this application.

## Toxic Risk Screening Analysis

There will be no increase in annual emissions from this modification and there for a risk analysis is not required. Toxic emissions are assumed to be a function of coke burn rate. NO increase in coke burn equals no increase in toxics.

## Statement of Compliance

This application will comply with 9-1-310.1, which requires that SO2 emissions not exceed 1000 ppmv.

This application will not be subject to NSPS Section 60.14 because this modification will be accomplished without a capital expenditure.(see attached NSPS 60.14)

The project is considered to be exempt under the District's CEQA Regulation 2-1-312.1, which states that permit applications that do not increase emissions are exempt as defined by CEQA.

This application triggers BACT, daily emissions increase will be greater than 5 pounds per day. BACT was not triggered on an annual basis. See BACT section for more detail.

This project is over 1000 feet from the nearest school and is therefore not subject to the public notification requirements of Reg.2-2-412.

A Toxics Risk Screening Analysis was not required for this application.

**Recommendation**

Recommend that a change in conditions be granted to:

**S-4285 Fluidized Catalytic Cracking Unit, 80,000 BPD**

**Conditions**

1. Feed rate to the FCC reactor S-4285 shall not exceed 80,000 BPD averaged over any calendar year nor 90,000 BPD over any calendar day.

2. The owner/operator shall conduct a District approved source test on every fifteenth day that S-4285 throughput exceeds 80,000 BPD. The test shall analyze for CO, POC, and TSP.

3. The following conditions shall apply at all times after the FCC plant feedrate exceeds 61,000 bbl/day averaged over any calendar year or 67,000 bbl/day over any calendar day.

    a. SOx, NOx, CO, POC and TSP emissions shall not exceed the following limits in any consecutive 12 month period beginning on the first day that the throughput levels in condition #2 are exceeded:

        SOx: 2205.4 tpy
        NOx: 1504.7 tpy
        CO: 258.4 tpy
        POC: 6.1 tpy
        TSP: 111 tpy

        The emission baselines used in this permit condition are only applicable for the purpose of limiting emissions to pre-project (non-modified) levels and are not necessarily acceptable for purposes of emissions banking pursuant to District Regulation 2, Rule 4.

b. The owner/operator of S-4285 shall continuously monitor and record SOx, NOx, and CO emissions from the FCC flue gas stack (P-133). The CO monitor shall be installed and operational within 90 days of triggering condition #3. Any new continuous emission monitors shall be reviewed and pre-approved by District Source Test Staff.

c. Whenever both the FCC Regenerator and Steam Generator are operating, the minimum ammonia feed rate to the FCC flue gas shall be 60 #/hr, averaged over any consecutive 24 hour period.

d. The owner/operator of S-4285 shall use a combination of SOx controlling catalyst additive and/or feed hydrotreating to maintain compliance with the SOx limitation in condition #3.a.

e. The owner/operator shall conduct a District approved source test for Sox, NOx, CO, POC, and TSP within 30 days of the of the installation of any new continuous emissions monitors in order to demonstrate compliance with condition #3.a.

f. The owner/operator of S-4285 shall maintain a District approved daily log of all SOx, NOx, and CO emissions, total throughput, source test data, and ammonia feed. This log shall be kept on site for two years and made available to District Staff upon request.

4. The following conditions shall remain in effect until the FCC plant feedrate exceeds 61,000 bbl/day averaged over any calendar year or 67,000 bbl/day over any calendar day.

a. The feedrate to the reactor (S-4285) shall not exceed 61,000 BPD on a calendar year average nor exceed 67,000 BPD on any calendar day.

b. The District's Inspection Section Personnel shall have 24 hours per day access to the following control, indicating, and recording instruments located in FCC unit control room:

1. FCC feed meter
2. Main air flow to regenerator
3. Oxygen analyzer on regenerator flue gas
4. Regenerator temperature

c. Recording charts shall be kept available for District for a period of 2 months and the daily log shall be kept available for District inspection for a period of 1 year.

d. The baseline for particulate emissions from the FCC Unit (S-4285) shall be 25.4 pounds per hour, averaged over one year.

by Gregory Solomon date 7/21/93
Gregory Solomon
Air Quality Engineer II

Attachment #3

September 2, 1998

**Chevron Products Company**
P. O. Box 1272
Richmond, CA 94802-0272

**M. A. Gilles**
Manager
Environmental and Safety Division
Phone 510 242 1400

Mr. Barry Young
Permit Services Division
Bay Area Air Quality Management District
939 Ellis Street
San Francisco, CA 94109

**Authority to Construct Status (Application # 9978)**

Dear Mr. Young:

In response to your letter dated April 27, 1998, the table below shows the construction status of each of the sources included in the Reformulated Gasoline and FCC Modernization Project. Since the Project was given a single authority to construct, and a substantial number of the sources included in the Project have been constructed, substantial use of the authority to construct has begun for all of the sources not yet in operation.

| | | |
|---|---|---|
| S-4291 | H2SO4 Alkylation Plant | Equipment is in operation |
| S-4355 | Butamer Section of the DIB/Butamer Plant* | Substantial use of the A/C has begun |
| S-4355 | DIB Section of the DIB/Butamer Plant* | Equipment is in operation |
| S-4357 | C4 Treating Plant | Substantial use of the A/C has begun |
| S-4356 | TAME Plant | Equipment is in operation |
| S-6053 | Alky/TAME Plant Cooling Tower | Equipment is in operation |
| S-6016 | FCC Flare | Equipment is in operation |
| S-6019 | Alky/Poly Flare | Equipment is in operation |
| S-3202* | Tank, Methanol (was S-3205) | Equipment is in operation |
| S-3201* | Tank, Whole Alkylate (was S-3206) | Equipment is in operation |
| S-3203* | Tank, FCC Heavy Gasoline (was S-3207) | Substantial use of the A/C has begun |
| S-4285 | Fluid Catalytic Cracker | Equipment is in operation |
| S-4358 | FCC Gasoline Hydrotreater | Substantial use of the A/C has begun |
| S-4346 | Gas Recovery Unit | Substantial use of the A/C has begun |
| S-4348 | H2 Recovery Plant | Substantial use of the A/C has begun |
| S-4282 | Aromatics Saturation Plant | Equipment is in operation |

* Corrected source numbers or source descriptions

Please call Mr. Bob Chamberlin at (510) 242-1546 with any questions or concerns.

Very truly yours,

**ORIGINAL SIGNED BY**
R.T. Chamberlin for MAG

## *Bay Area Air Quality Management District*
## *Emission Inventory for the Chevron Richmond Refinery*

## *Chevron Products Company - Current Emission Factors*

```
-------------------- ---- ------------- ---------- ----  ----  ---- ---------
Organics (part not s  990    1.00E-04     General    8              02-03-84


SOURCE #:  4282, PENHEX ISOMERIZATION UNIT

  Source Code: G5004342        Material Processed: Cat reformer fresh feed, r
  Train: /,S6015,

                     Pol. Emiss. Factor            Basis Repl.
Pollutant Name       Code lb/thou barre  EF File   Code  Code  Empl Eff. Date
-------------------- ---- ------------- ---------- ----  ----  ---- ---------
Organics (part not s  990    1.00E-04     General    8              02-03-84


SOURCE #:  4283, NO. 4 CATALYTIC REFORMER, 28,000 BPD

  Source Code: G5004342        Material Processed: Cat reformer fresh feed, r
  Train: /,S6015,

                     Pol. Emiss. Factor            Basis Repl.
Pollutant Name       Code lb/thou barre  EF File   Code  Code  Empl Eff. Date
-------------------- ---- ------------- ---------- ----  ----  ---- ---------
Organics (part not s  990    1.00E-04     General    8              02-03-84


SOURCE #:  4285, FCC PLANT

  Source Code: C573?080        Fuel Burned: Coke
  Train: /,A14,

                     Pol. Emiss. Factor            Basis Repl.
Pollutant Name       Code lb/tons        EF File   Code  Code  Empl Eff. Date
-------------------- ---- ------------- ---------- ----  ----  ---- ---------
Organics (part not s  990    1.94E-01    Specific    5          BGY  01-09-97
Particulates (portio 1990    2.30E+02    Specific    2     2    GDS  11-18-10
Nitrogen Oxides (par 2990    6.72E-01    Specific   67     2    GDS  08-10-10
Sulfur Dioxide (SO2) 3990    1.17E+00    Specific   67     2    GDS  08-10-10
Carbon Monoxide (CO) 4990    3.13E-01    Specific   67     2    GDS  08-10-10
Carbon Dioxide, non- 6960    6.79E+03     General    7          HIL  03-06-08
Methane (CH4)        6970    1.98E-01     General    7          HIL  03-15-08
Nitrous Oxide (N2O)  2030    3.96E-02     General    7          HIL  03-15-08


  Source Code: G5007344        Material Processed: FCC fresh feed, refinery
  Train: /,A14,

                     Pol. Emiss. Factor            Basis Repl.
Pollutant Name       Code lb/thou barre  EF File   Code  Code  Empl Eff. Date
-------------------- ---- ------------- ---------- ----  ----  ---- ---------
Benzene                41    2.80E-03    Specific    1          BN   07-25-90
Arsenic (all)        1030    1.30E-03    Specific    1          BN   07-25-90
Chromium             1090    1.40E-03    Specific    1          BN   07-25-90
Manganese            1160    2.70E-01    Specific    1          BN   07-25-90
Nickel pollutant     1180    1.50E-03    Specific    1          BN   07-25-90
Zinc pollutant       1320    2.40E-01    Specific    1          BN   07-25-90
PAH's (non-speciated 1840    4.04E-04    Specific    1          BN   07-25-90
Particulates (portio 1990    0.00E+00    Specific    1     2    GDS  08-10-10
Nitrogen Oxides (par 2990    0.00E+00    Specific    5          BGY  08-17-94
Sulfur Dioxide (SO2) 3990    0.00E+00    Specific    5          BGY  08-17-94
Ammonia (NH3) pollut 6990    6.30E-02    Specific    1          BN   07-25-90
```

Chevron

June 1, 2000

**Chevron Products Company**
P. O. Box 1272
Richmond, CA 94802-0272

**J. W. Hartwig**
Manager
Environmental and Safety
510 242 1400

Mr. Gregory D. Solomon
Bay Area Air Quality Management District
Permit Services Division
939 Ellis Street
San Francisco, CA 94109

**Chevron Richmond Refinery Submittal of Annual Source Update for the 1999 Operating Year**

Dear Mr. Solomon:

As requested, enclosed is the completed BAAQMD Annual Source Update for the operating year - 1999. Data Form-X changes are included to update information in the District database. A list of sources with X-form changes is included as Attachment #1.

If you have any questions or need more information, please contact Mr. Ross N. Eagar at (510) 242-2903.

Sincerely,

for JWH

Attachment: Attachment #1 - List of Sources with X-Form Changes
Attachment #2 - 1999 Source Update Submittal

cc: Inspector Jeremy Kimball w/o Attachments

gds

APR 10, 2000 BAY AREA AIR QUALITY MANAGEMENT DISTRICT 10-88

Chevron Products Company
841 Chevron Way
Richmond, CA 94802

ANNUAL DATA UPDATE FORM

S# 4285 FCC PLANT ****************************************

Coke (4285-C573?080)

12-month consumption, ton . . . . . . . . . . . . . 234,214

For period ending (date) . . . . . . . . . . DEC 31 1999
Sulfur content of this fuel (typical): .516 wt %
Ash content of this fuel (typical): 0 wt %
Max usage rate for this fuel: 40 ton/hr

Complete Form X, Part 1, for any other fuel burned at this source.

S# 4285 FCC PLANT ****************************************

FCC fresh feed, refinery (4285-G5007344)

12-month throughput, thou barrels . . . . . . . . 18,832

For period ending (date) . . . . . . . . . . DEC 31 1999
Max throughput rate: 2.792 thou barrels/hr

Complete Form X, Part 2, for any other material used in this source.

S# 4315 POINT ORIENT WHARF *******************************

*** ERR 301-32-4315

S# 4315 POINT ORIENT WHARF *******************************

Xylene (301-TB8?2307)

*** ERR 102-31-301-TB8?2307

# APPENDIX 4.3 - EI

EI: Bay Area Air Quality Management District Emission Inventory Data

BAY AREA AIR QUALITY MANAGEMENT DISTRICT Printed: AUG 1, 2013
CRITERIA POLLUTANTS - ABATED
P/O APPROVED (2010)
Chevron Products Company (P# 10)

| | | | | | | | <----------- Emissions in lbs/day ----------> | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| S# | Name | Material | SourceCode | ThruPut | Units | Date | PM | Org | NOx | SO2 | CO |
| 4193 | F-2270 TAIL GAS HEATER #2 SRU | Natural gas | C1520189 | -6.42E+05 | therms/yr | 12/31/2009 | 0.5 | 1 | 23.5 | 0.1 | 5.9 |
| 4193 | F-2270 TAIL GAS HEATER #2 SRU | Chevron refinery fuel gas | C1540708 | 0.00E+00 | thou cu ft/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4194 | F-2370 TAIL GAS HEATER #3 SRU | Bunker C fuel oil | C1520242 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4194 | F-2370 TAIL GAS HEATER #3 SRU | Natural gas | C1540189 | -8.58E+05 | therms/yr | 12/31/2009 | 0.7 | 1.3 | 31.4 | 6.1 | 7.8 |
| 4226 | Hydrotreater for gasoline, jet fuel diesel fuel and | Refinery feedstock - other/not | G5022239 | -5.95E+03 | thou barre/yr | 12/31/2009 | 0 | 16.3 | 0 | 0 | 0 |
| 4227 | SRU #1 TRAIN | Sulfur | G7055267 | -4.28E+04 | tons/yr | 12/31/2009 | 0 | 0 | 0 | 247.5 | 0 |
| 4228 | SRU #2 TRAIN | Sulfur | G7055267 | -4.04E+04 | tons/yr | 12/31/2009 | 0 | 0 | 0 | 233.4 | 0 |
| 4229 | SRU #3 TRAIN | Sulfur | G7055267 | -6.89E+04 | tons/yr | 12/31/2009 | 0 | 0 | 0 | 398.2 | 0 |
| 4230 | LUBE OIL FILLING AT PACKAGE & GREASE PLANT | Lube oil | G7013419 | -2.48E+04 | thou gallo/yr | 12/31/1997 | 0 | 0 | 0 | 0 | 0 |
| 4233 | #1 Jet Hydrotreater | Refinery feedstock - other/not | G5022239 | -2.17E+04 | thou barre/yr | 12/31/2009 | 0 | 59.4 | 0 | 0 | 0 |
| 4234 | NO. 5 NAPHTHA HYDROTREATER | Refinery feedstock - other/not | G5022239 | -1.80E+04 | thou barre/yr | 12/31/2009 | 0 | 49.4 | 0 | 0 | 0 |
| 4235 | Diesel Hydrotreater | Refinery feedstock - other/not | G5022239 | -1.01E+04 | thou barre/yr | 12/31/2009 | 0 | 8.3 | 0 | 0 | 0 |
| 4236 | NO. 4 CRUDE UNIT, 175,000 BPD | Crude oil | G5027089 | -8.05E+04 | thou barre/yr | 12/31/2009 | 0 | 220.5 | 0 | 0 | 0 |
| 4237 | NO. 5 RHENIFORMER, 23,000 BPD | Refinery feedstock - other/not | G5993239 | -7.74E+03 | thou barre/yr | 12/31/2009 | 0 | 31.8 | 0 | 0 | 0 |
| 4238 | LIQUID PETROLEUM GAS LOADING RACK #4238 | LPG | T98?2160 | -1.08E+05 | thou gal/yr | 12/31/2009 | 0 | 47.3 | 0 | 0 | 0 |
| 4239 | MAIN TANK CAR LOADING RACKS #4239 | Distillate oil | T9812315 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4239 | MAIN TANK CAR LOADING RACKS #4239 | Hydrocarbon - mixtures, other/ | T9812318 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4239 | MAIN TANK CAR LOADING RACKS #4239 | Crude oil | T9832089 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4239 | MAIN TANK CAR LOADING RACKS #4239 | Gasoline - leaded | T9832128 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4239 | MAIN TANK CAR LOADING RACKS #4239 | Gasoline - unleaded | T9832551 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4240 | ASPHALT TANK TRUCK LOADING RACK | Asphalt | T9811030 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4241 | ASPHALT TANK CAR LOADING RACKS 4241 | Asphalt | T9711030 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4250 | HYDROGEN MANUFACTURING PLANT, 150 MM SCF/DAY | Hydrogen (gas) | G5026759 | -5.79E+04 | million cu/yr | 12/31/2009 | 0 | 8.1 | 0 | 0 | 87.2 |
| 4251 | Solvent Deasphalting (SDA) Plant | Refinery feedstock - other/not | G5029239 | -1.10E+04 | thou barre/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4251 | Solvent Deasphalting (SDA) Plant | Bunker C fuel oil | G5029242 | -2.14E+05 | thou gallo/yr | 12/31/2009 | 0 | 58.7 | 0 | 0 | 0 |
| 4252 | TKN ISOCRACKER | Cat reformer fresh feed, refin | G5004342 | -1.73E+04 | thou barre/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4253 | TKC Plant | Cat reformer fresh feed, refin | G5004342 | -1.22E+04 | thou barre/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4282 | Penhex Isomerization Unit | Cat reformer fresh feed, refin | G5004342 | -8.67E+03 | thou barre/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4283 | NO. 4 CATALYTIC REFORMER, 28,000 BPD | Cat reformer fresh feed, refin | G5004342 | -9.30E+03 | thou barre/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4285 | FCC Plant | Coke | C573?080 | -2.99E+05 | tons/yr | 12/31/2009 | 1881.5 | 158.7 | 582.1 | 957.1 | 256 |
| 4285 | FCC Plant | FCC fresh feed, refinery | G5007344 | -2.76E+04 | thou barre/yr | 12/31/2009 | 0.4 | 0.2 | 0 | 0 | 0 |
| 4286 | LIGHT ENDS RECOVERY | Refinery feedstock - other/not | G5028239 | -1.78E+04 | thou barre/yr | 12/31/2009 | 0 | 0.5 | 0 | 0 | 0 |
| 4291 | H2SO4 ALKYLATION PLANT, 21,000 BPD | Refinery feedstock - other/not | G5030239 | -9.40E+03 | thou barre/yr | 12/31/2009 | 0 | 12.9 | 0 | 0 | 0 |
| 4292 | FCC POLYMER PLANT | Refinery feedstock - other/not | G5024239 | -2.23E+03 | thou barre/yr | 12/31/2009 | 0 | 9.2 | 0 | 0 | 0 |
| 4315 | POINT ORIENT WHARF | Benzene | TB8?2041 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4315 | POINT ORIENT WHARF | Xylene | TB8?2307 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4315 | POINT ORIENT WHARF | Distillate oil | TB8?2315 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4315 | POINT ORIENT WHARF | Hydrocarbon - mixtures, other/ | TB8?2318 | 0.00E+00 | thou gal/yr | 12/31/2009 | 0 | 0 | 0 | 0 | 0 |
| 4329 | RLOP Cooling Tower | Fresh water | G5005415 | -1.39E+05 | thou gallo/yr | 12/31/2009 | 0 | 0.3 | 0 | 0 | 0 |
| 4330 | HNHF Reactor Furnace, F-1610 | Chevron refinery fuel gas | C1540708 | -5.14E+04 | thou cu ft/yr | 12/31/2009 | 1.4 | 0.4 | 1.2 | 0.5 | 2.4 |
| 4331 | LNHF Reactor Furnace, F-1310 | Chevron refinery fuel gas | C1540708 | -8.13E+04 | thou cu ft/yr | 12/31/2009 | 2.3 | 0.7 | 2 | 0.8 | 3.8 |
| 4332 | Hot Oil Furnace, F-1360 | Chevron refinery fuel gas | C1540708 | -2.01E+05 | thou cu ft/yr | 12/31/2009 | 5.6 | 1.7 | 4.8 | 1.9 | 9.4 |
| 4333 | TKC Vacuum Furnace, F-1750 | Chevron refinery fuel gas | C1540708 | -1.04E+06 | thou cu ft/yr | 12/31/2009 | 0.2 | 8.1 | 25.1 | 9.7 | 48.6 |
| 4334 | LNC Atmos Furnace, F-1200 | Chevron refinery fuel gas | C1540708 | -1.29E+05 | thou cu ft/yr | 12/31/2009 | 3.6 | 1.1 | 3.1 | 1.2 | 6 |
| 4335 | LNC Vacuum Furnace, F-1250 | Chevron refinery fuel gas | C1540708 | -1.03E+05 | thou cu ft/yr | 12/31/2009 | 2.9 | 0.9 | 2.5 | 1 | 4.8 |
| 4336 | HNC Reactor Furnace, F-1410 | Chevron refinery fuel gas | C1540708 | -1.16E+05 | thou cu ft/yr | 12/31/2009 | 3.2 | 1 | 2.8 | 1.1 | 5.4 |
| 4337 | HNC Atmos Furnace, F-1500 | Chevron refinery fuel gas | C1540708 | -1.18E+05 | thou cu ft/yr | 12/31/2009 | 3.3 | 1 | 2.8 | 1.1 | 5.5 |
| 4338 | HNC Vacuum Furnace, F-1550 | Chevron refinery fuel gas | C1540708 | -1.58E+05 | thou cu ft/yr | 12/31/2009 | 4.4 | 1.3 | 3.8 | 1.5 | 7.4 |
| 4339 | LNC Reactor Furnace, F-1110 | Chevron refinery fuel gas | C1540708 | -1.04E+06 | thou cu ft/yr | 12/31/2009 | 29 | 8.6 | 25.1 | 9.7 | 48.6 |
| 4340 | Light Neutral Hydrocracker (LNC) | Hydrocarbon - mixtures, other/ | G5021318 | -6.74E+05 | tons/yr | 12/31/2009 | 0 | 0.7 | 0 | 0 | 0 |
| 4341 | Light Neutral Hydrofinisher (LNHF) | Refinery feedstock - other/not | G5022239 | -5.44E+03 | thou barre/yr | 12/31/2009 | 0 | 0.7 | 0 | 0 | 0 |
| 4342 | Heavy Neutral Hydrocracker (HNC) | Hydrocarbon - mixtures, other/ | G5021318 | -1.19E+06 | tons/yr | 12/31/2009 | 0 | 1.2 | 0 | 0 | 0 |
| 4343 | Heavy Neutral Hydrofinisher (HNHF) | Hydrocarbon - mixtures, other/ | G5022318 | -3.17E+05 | tons/yr | 12/31/2009 | 0 | 0.3 | 0 | 0 | 0 |

**Attachment 52**

# Increasing GHG emissions from dirty crude

Analysis of publicly available data for one of the oil refining processes expanding for more contaminated oil in California: Hydrogen steam reforming.

**Communities for a Better Environment (CBE)**
Research & analysis: Greg Karras, Senior Scientist
Technical review: Julia May, Senior Scientist
Anna Yun Lee, Staff Scientist

December 8, 2008.

**Contents**

The mission of **Communities for a Better Environment** (CBE) is to achieve environmental health and justice by building grassroots power in and with communities of color and working class communities. Founded in 1978, CBE combines in-house scientific, legal and organizing expertise to leverage plant-specific pollution prevention and regional policy progress that could not be achieved using science, organizing or legal advocacy alone. Thousands of CBE members and supporters live in the greater Los Angeles and San Francisco Bay Areas.

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# Increasing GHG emissions from dirty crude

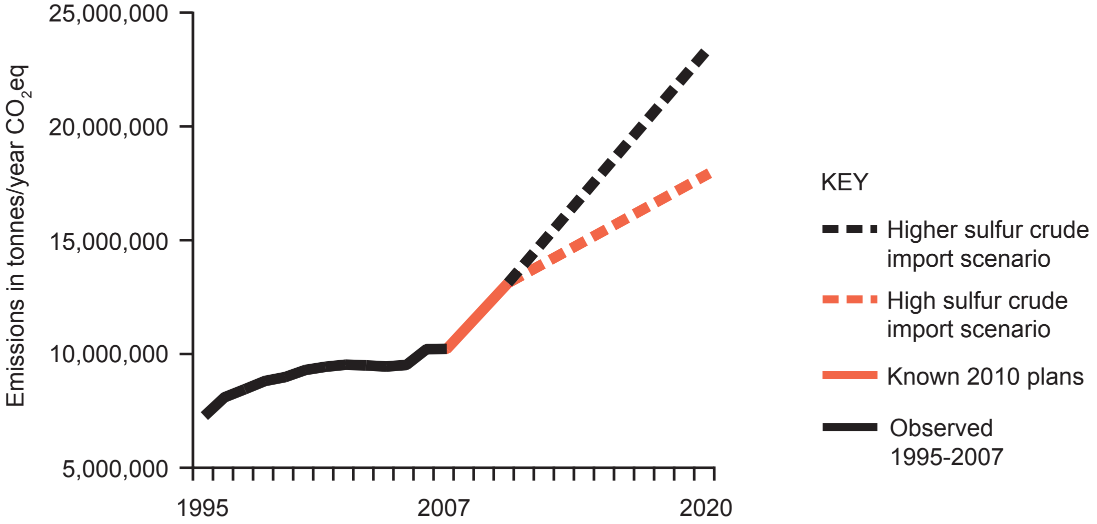
## Introduction

As government officials debate long-term plans for climate protection the next generation of oil refining infrastructure is being built. Communities near refineries are grappling with the toxic threats posed by these plans. This analysis of publicly available data focuses on California oil refineries, greenhouse gases (GHGs) and one refining process: hydrogen steam reforming.

## Findings and recommendations

Steam reforming for the extra hydrogen needed to refine more contaminated oil in California has already increased greenhouse gas emissions substantially, by approximately three million metric tonnes per year since 1995 ($CO_2$eq). Plans to feed much more hydrogen to even dirtier oil refining could further **increase statewide GHG emissions by another eight million to thirteen million tonnes per year** between 2008 and 2020, from steam reforming alone. See Figure 1.

**Figure 1. Increasing greenhouse gas emissions from hydrogen steam reforming by California oil refineries, 1995-2020**



Source: Analysis of data in Figure 2 (1995-2007) and Table 7 (2008-2020).

Emissions are increasing as steam reforming production increases to feed more hydrogen to the expanding hydroprocessing of more contaminated refinery crude oil inputs. Crude inputs to California refineries are getting dirtier as refiners shift to imports that include some of the higher-sulfur oils produced worldwide. This shift is accelerating as domestic supply dwindles.

Plans for GHG emission reductions that are needed by 2020 and 2050 in order to avoid severe global warming should address refinery feedstock quality. Steam reforming is only one of many types of oil infrastructure that is expanding for lower quality oil, and emitting more GHGs. A full-blown switch to dirtier oil threatens to overwhelm and thwart climate protection efforts.

We should treat refinery feedstock like we treat power plant feedstock. California is phasing out coal as a source of electricity served by its public utilities. We must now limit, and then phase out, dirtier oil refinery feedstock as well.

# Increasing GHG emissions from dirty crude

## Emission source

Oil refining is the world's second largest user of hydrogen. Steam reforming is the U.S. refining industry's technology of choice for add-on hydrogen plants. Steam reforming produces hydrogen from light hydrocarbons such as methane and superheated steam, in contact with a catalyst. The process reactions proceed at extremely high temperature, about 1,500 ºF, which is achieved by burning fossil fuel. *(1)* Burning this fossil fuel emits GHGs, among other pollutants.

It takes approximately 459 British thermal units (Btu) of heat to make one cubic foot of hydrogen by steam reforming. *(1)* Burning natural gas emits approximately 53.1 kilograms of GHG per million Btu. *(2)* Thus, steam reforming emits approximately 24.37 tonnes of GHG for each million cubic feet of hydrogen produced–if it burns natural gas, the least dirty fuel refineries burn, and the fuel assumed in this analysis. These emissions are expressed as $CO_2$ equivalent ($CO_2$eq) accounting for the potency of carbon dioxide, methane and nitrous oxide emissions.

**Table 1. Typical hydrogen steam reforming inputs and GHG emission factors.**

| | |
|---|---|
| Process feeds: | Methane or naphtha<br>Water (for steam) |
| Energy input: | 459 Btu/scf<br>(heat per standard cubic foot of hydrogen produced) |
| Emissions: | 53.1 kg/MMBtu*<br>24.37 tonnes/MMscf hydrogen* |

* Carbon dioxide equivalents of $CO_2$, $CH_4$ and $N_2O$ emissions from natural gas fuel.

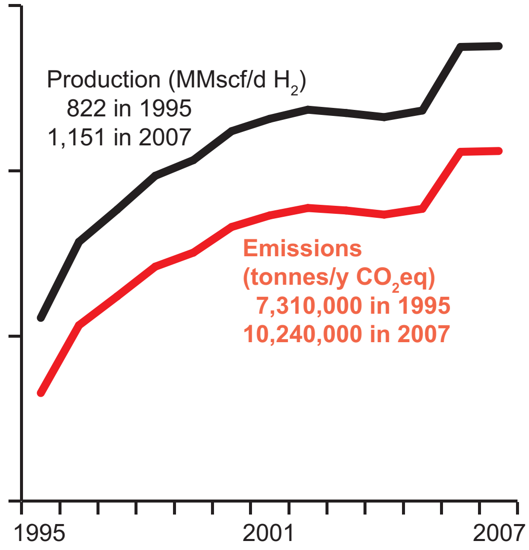
From USDOE (Ref. 1) and CARB Compendium of Emission Factors (Ref. 2; natural gas default factor).

## Observations from 1995-2007

Emissions from steam reforming increased from 1995-2007. See Figure 2. In 2007 California refiners' steam reformers produced approximately 1,151 million cubic feet of hydrogen per day, an increase of 329 million cf/d over their 1995 production. *(3)* At 24.37 tonnes/million cf, this indicates a GHG emissions increase of 2.93 million tonnes/year. This estimate is for steam reforming alone, and includes steam reforming by all refineries in California that produce California on-road gasoline and/or diesel.

Steam reforming increased with hydroprocessing. California refiners added 116,000 barrels/day of hydrocracking since 1995, and now have capacity to hydrocrack more than twice as much of their crude input as the average US refinery. *(3)*

**Figure 2. Steam reforming production and emissions, California refineries, 1995-2007**



Data from Oil & Gas Journal Worldwide Refining surveys (Ref. 3) and CARB (Ref. 2 and Table 1). Based on 90% of available production capacity.

# Increasing GHG emissions from dirty crude

California refiners also added 272,000 b/d of hydrotreating since 1995, and 84,100 b/d of that was hydrotreating of heavy oil streams such as gas oils. *(3)* Using this increased hydroprocessing capacity required more hydrogen.

Typical hydrogen demands for hydroprocessing various oil streams are shown in Table 2. Processing heavier streams such as gas oil requires several times more hydrogen per barrel than processing lighter streams such as naphtha (gasoline-sized hydrocarbons). Total hydrogen demand in California refineries, as estimated from these hydrogen requirements and the annual production capacities reported for these processes, is shown in Figure 3.

California refiners' hydroprocessing increased their hydrogen use by approximately 387 million cf/d since 1995. No such increase occurred, however, in catalytic naphtha reforming, which creates hydrogen as a byproduct. Cat-naphtha reforming declined by 7% since 1995 *(3)* and is not likely to increase because it creates volatile toxic chemicals limited by fuel standards.

The net result of increased hydrogen demand from more hydroprocessing while hydrogen byproduction from cat-naphtha reforming did not increase drove an increase in steam reforming to supply that extra hydrogen. See Figure 3.

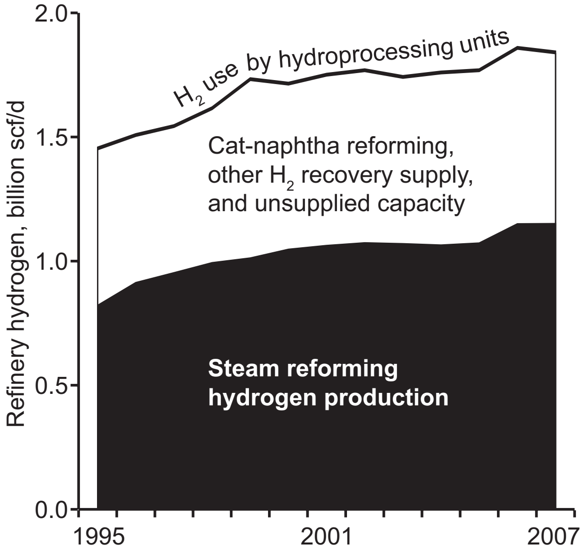
Refining more contaminated crude causes increased hydrogen demand in at least three related ways. First, hydrogen is bonded to contaminants to remove them from the oil (this avoids poisoning process catalysts and violating vehicle fuel standards); so removing more contaminants from dirtier oil takes more hydrogen. Second, sulfur and other catalyst poisons concentrate in the denser and heavier components of crude such as gas oil and residua; so refining dirtier crude requires more of the types of hydroprocessing that require the most hydrogen.

**Table 2. Typical hydrogen requirements for hydroprocessing different feeds.[a,b]**

| Process | Feed | Hydrogen per barrel of feed |
|---|---|---|
| Hydrotreating | naphtha[c] | 350 scf/b |
| Hydrotreating | kerosine, jet fuel | 450 scf/b |
| Hydrotreating | diesel oil | 800 scf/b |
| Hydrotreating | gas oil | 1,200 scf/b |
| Hydrotreating | residua | >3,000 scf/b |
| Hydrocracking to produce: | | |
| diesel | gas oil | 1,730 scf/b |
| jet fuel | gas oil | 1,870 scf/b |
| naphtha | gas oil | 2,050 scf/b |

[a] From Robinson and Dolbear, 2007 (Ref. 4).
[b] Hydrogen use capacities estimated from these data herein conservatively assign the kerosine/jet value to all "other distillate" hydrotreating; the naphtha value to unspecified "other" hydrotreating; and the diesel production value to all hydrocracking.
[c] Naphtha is a stream of mainly of gasoline-sized hydrocarbons; hydrotreating gasoline to meet fuel sulfur standards is a type of naphtha hydrotreating.

**Figure 3. Hydrogen supply and demand, California refineries, 1995-2007**



Data from Oil & Gas Journal (Ref. 3) and Table 2 (Robinson and Dolbear, 2007; Ref. 4). Hydroprocessing requirements applied per Table 2 note. Based on 90% of available production capacity.

# Increasing GHG emissions from dirty crude

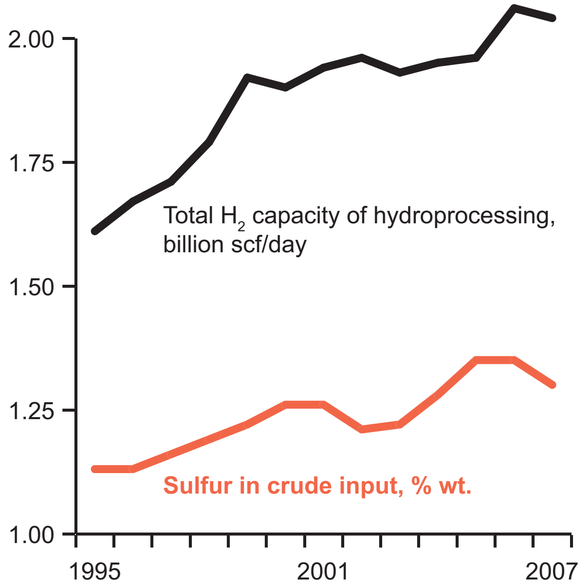
Third, the contaminants are embedded in the molecular structures of the large hydrocarbons in these heavier streams: removing them requires breaking up (“cracking”) those large compounds at higher temperatures and pressures. That more severe processing, in turn, requires more hydrogen to pressurize, quench and control the process reactions; so hydroprocessing each barrel of the more contaminated and heavier oil streams requires more hydrogen.

Sulfur contamination of the crude input to California refineries is estimated along with the total hydrogen capacity of their hydroprocessing units from 1995-2007 in Figure 4. As the sulfur content of their crude input increased from approximately 1.13% to 1.35%, their total hydrogen usage capacity increased from 1.61 billion to 2.04 billion cubic feet per day. Further, their hydrogen demand capacity is positively correlated with the sulfur content of their crude input (R-squared = 0.77; $p < 0.001$).

Sulfur increased in California refiners’ crude because they refined higher-sulfur imports in larger amounts as Californian and Alaskan supplies declined. See Table 3. Between 1995 and 2007 crude inputs from in-state and Alaska dropped by 70 million and 163 million barrels/year, respectively, while foreign crude inputs grew by 230 million b/y. This was a shift to dirtier crude. The foreign crude refined in California from 2005-2007 had an average of 1.55% sulfur as compared with 0.86% for Alaskan crude and 1.3% for San Joaquin Valley Heavy (SJVH)–the highest sulfur stream from California’s dominant remaining crude oil resource. *(5,6)*

The oil industry’s choice to replace dwindling domestic crude supplies with more contaminated sources of foreign crude has caused its hydrogen demand, hydrogen steam reforming production, and GHG emissions to increase.

**Figure 4. Sulfur content of crude input and hydrogen demand, California refineries, 1995-2007**



Crude quality data from USEIA (Ref. 5); and assay data for Alaskan and California crude oils (Ref. 6). Californian, Alaskan and imported crude volumes processed from Table 3. California crude input is conservatively assumed to be 100% San Joaquin Valley Heavy. All (100%) of available $H_2$ capacity is shown, based on references in Table 2 & Figure 3.

**Table 3. Domestic and foreign crude inputs to California refineries, 1995-2025**

*thousands of barrels*

| | California | Alaska | Imports |
|---|---|---|---|
| 1995 | 320,824 | 264,520 | 56,864 |
| 1996 | 322,238 | 267,492 | 77,628 |
| 1997 | 322,198 | 244,444 | 78,108 |
| 1998 | 317,817 | 221,983 | 104,653 |
| 1999 | 306,856 | 188,743 | 140,599 |
| 2000 | 326,371 | 163,233 | 169,105 |
| 2001 | 323,583 | 139,829 | 191,843 |
| 2002 | 317,321 | 143,685 | 199,994 |
| 2003 | 289,416 | 160,164 | 232,477 |
| 2004 | 274,396 | 141,967 | 238,484 |
| 2005 | 266,052 | 135,906 | 272,318 |
| 2006 | 254,498 | 105,684 | 295,306 |
| 2007 | 251,445 | 100,900 | 286,844 |
| 2015 | 197,923[b] | 79,422[b] | 361,844 |
| 2025 | 151,536[b] | 60,809[b] | 426,844 |

From the California Energy Commission (Refs. 7, 8).
[b] Calculated from 2007 total and state proportions.

## Projection for 2008-2020

Current industry plans would further increase the steam reforming rates observed from 1995-2007.

Crude input basis: Refinery crude input quality provides one basis for estimating potential future emissions. The average sulfur content of imported crude with similar density to medium-heavy (146-153 kg/b) California crude that was processed by US refiners in 2007 was 2.76%. *(5)* Import streams with known capacity to expand as domestic supply declines include, among others, Western Canadian Heavy from Alberta's vast tar sands (WCH; ~3.3% sulfur), and Arab Heavy (~2.93% sulfur). *(6)* WCH and Arab Heavy are refined in-state already. *(5)* Assuming projected domestic supply declines and the necessary processing capacity, a mix of these and similar oils with 2.76-3.3% sulfur is likely to be half of the new imports refined by 2020. Calculations for this estimate are shown in Table 4.

Sulfur in the total 2020 statewide crude input could range from 1.78% if half the new imports are as contaminated as the current same-gravity US average, to 1.83% if they are Arab Heavy, to 1.96% if half the new imports are WCH.

Hydrogen use predicted with this potential sulfur contamination of the future crude input is shown by extrapolation from 1995-2007 observations in Figure 5. The 1995-2007 data predict 1.69 billion cf/d of refinery hydrogen capacity for each 1% increase in statewide crude sulfur content (R-squared = 0.77; p < 0.001). Predictions a, b and c are the same-gravity average (2.8 billion cf/d), Arab Heavy (2.89 bcf/d) and WCH (3.11 bcf/d) scenarios, respectively.

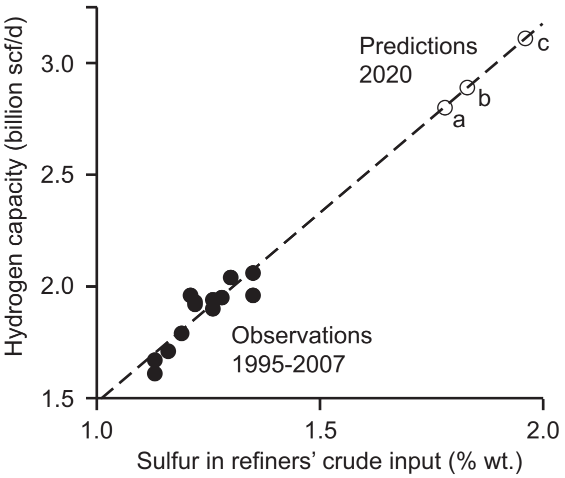
This information suggests that refinery hydrogen capacity could increase by 0.76-1.07 billion cf/d over the 2.04 billion cf/d of total hydroprocessing capacity to use hydrogen statewide in 2007.

**Table 4. Estimated 2020 crude input sulfur**

| Oil to be 50% of new imports: | Gravity-average[a] | Arabian Heavy[b] | W. Canadian Heavy[c] |
|---|---|---|---|
| Crude (kg/b) | | | |
| Imports[d] | 145 | 142 | 145 |
| California[e] | 148 | 148 | 148 |
| Alaska[f] | 137 | 137 | 137 |
| Sulfur (% wt) | | | |
| Imports[d] | 2.15 | 2.24 | 2.44 |
| California[e] | 1.30 | 1.30 | 1.30 |
| Alaska[f] | 0.86 | 0.86 | 0.86 |
| Crude (MM t/y)[g] | | | |
| Imports[d] | 57.3 | 55.9 | 57.2 |
| California[e] | 25.9 | 25.9 | 25.9 |
| Alaska[f] | 9.6 | 9.6 | 9.6 |
| Total | 92.8 | 91.4 | 92.7 |
| Sulfur (MM t/y) | | | |
| Imports[d] | 1.23 | 1.25 | 1.40 |
| California[e] | 0.34 | 0.34 | 0.34 |
| Alaska[f] | 0.08 | 0.08 | 0.08 |
| Total | 1.65 | 1.67 | 1.81 |
| **Weighted av. sulfur (% wt.)** | **1.78** | **1.83** | **1.96** |

[a] Average 2007 US imports with gravity from 146-153 kg/b (2.76% sulfur; Ref. 5).
[b] Arabian Heavy is 2.93% sulfur, 141 kg/b (Ref. 6).
[c] Western Canadian Heavy, 3.3% S, 148 kg/b. (Ref. 6).
[d] 50/50 blend of new import with 2005-2007 imports.
[e] All Calif. input conservatively set to SJVH (Ref. 6).
[f] ANS/Trans Alaska Pipeline (Ref. 6).
[g] From interpolation of 2015 & 2025 volumes in Table 3.

**Figure 5. Hydrogen capacity predicted by crude input sulfur, Calif. refineries**



Data for 1995-2007 observations from figures 3 and 4 (Refs. 3-6). Predictions from Table 4 and correlation line (R-squared = 0.77; p < 0.001).

Hydroprocessing capacity basis: Processing capacity provides another basis for estimating future emissions. In addition to the 116,000 b/d of hydrocracking capacity added by California refiners since 1995 *(3)*, at least 73,150 b/d of expanded hydrocracking capacity is planned by 2010. *(9,10,11)* More important, competition is likely to drive further expansion as refiners with less intensive hydroprocessing capacity per barrel of crude input "catch up" with those who are leading the trend. Calculations for this potential statewide increase in hydrogen demand by hydroprocessing are shown in Table 5.

The four California plants with the highest hydroprocessing capacities for hydrogen use/barrel of crude input–Chevron Richmond, Valero Wilmington, Tesoro Wilmington and ConocoPhillips Rodeo/Santa Maria–will have an estimated collective capacity to use approximately 1,534 cubic feet of hydrogen per barrel crude as of 2010. The two highest users will have a collective capacity of 1,755 cf/b. If other refiners match these levels, and accounting for other hydrogen recovery, this could result in 2.48-2.92 billion cf/d of total statewide capacity for hydrogen produced by steam reforming in 2020.

This 2.48-2.92 bcf/d estimate based on hydroprocessing capacity compares with 2.24-2.55 bcf/d based on crude input sulfur, when the predictions in Figure 5 are adjusted to account for other hydrogen recovery.

Steam reforming capacity basis: Steam reforming capacity provides another basis for estimating potential future emissions. At least three Bay Area refiners now plan new steam reforming plants, and the entire northern California industry could soon be linked by new hydrogen pipelines. See Figure 6. Based on plans announced publicly as of 2008 ConocoPhillips *(11)*, Chevron *(12)* and Valero *(13,14)* plan to add a net total of 320 million cf/d in steam reforming capacity; and pipe-

**Table 5. Predicted 2020 hydroprocessing capacity for hydrogen statewide**

| High-use plants | $H_2$ bscf/d | Crude b/d | $H_2$ scf/b |
|---|---|---|---|
| Chevron-Richmond[a] | 0.452 | 243,000 | 1,860 |
| Valero-Wilmington | 0.115 | 80,000 | 1,438 |
| Tesoro-Wilmington | 0.124 | 100,000 | 1,240 |
| ConPh.-Rodeo/S.M.[a] | 0.142 | 120,000 | 1,183 |

| Scaled statewide to: | Top 4 plants | Top 2 plants |
|---|---|---|
| Subtotal bscf/d | 0.833 | 0.567 |
| Subtotal b/d | 543,000 | 323,000 |
| Hydrogen scf/b | 1,534 | 1,755 |
| Adjusted $H_2$ scf/b[b] | 1,253 | 1,474 |
| **Statewide $H_2$ bscf/d[c]** | **2.48** | **2.92** |

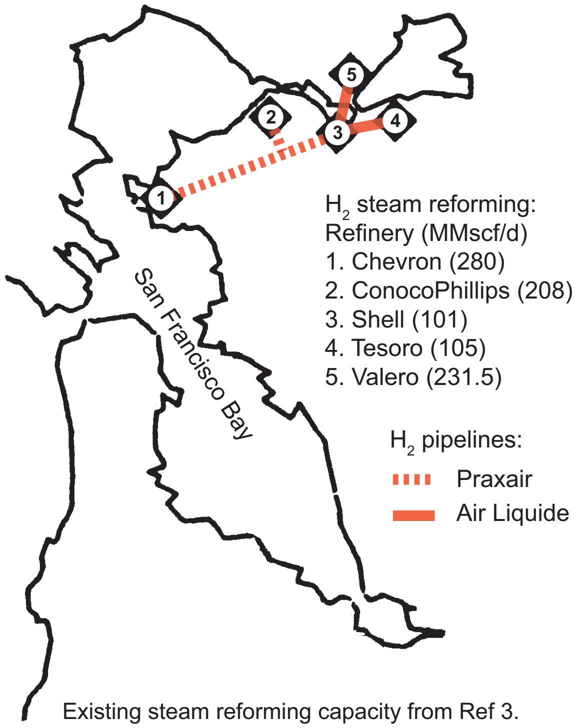
Data from Oil & Gas Journal (2007; Ref. 3); Chevron 6/29/06 BAAQMD Permit App. & 4/17/08 Title V Permit (Refs. 9, 10); ConocoPhillips EIR SCH #2005092028 (Ref. 11); Robinson and Dolbear, 2007 (Ref. 4) applied per Table 2 notes. Based on 100% of available capacity.

[a] Includes near-term capacity expansions (Refs. 9-11).

[b] Adjusted by subtracting cat-reforming & other recovery of 281 cf/b (statewide average in 2007; see Figure 3).

[c] From 1.983 MMb/d 2007 statewide input cap. (Ref. 3).

**Figure 6. Northern California refiners' steam reforming and $H_2$ pipeline plans**



Existing steam reforming capacity from Ref 3.
Planned 2010 SR capacity from Refs. 11-14.
Planned 2010 $H_2$ pipelines from Refs. 15, 16.

lines proposed by Praxair *(15)* and Air Liquide *(16)* would link hydrogen production and use by all five northern California refineries. This new infrastructure could be in place by 2010. Statewide capacity could grow to match it by 2020.

Calculations for estimated total statewide 2020 steam reforming capacity in this case are shown in Table 6. The 2010 northern California capacity totals an estimated 1,126 cubic feet per barrel of crude input capacity. Scaling this capacity to the 1,983,000 b/d statewide total crude capacity indicates that by 2020, California refineries could have steam reforming capacity totaling 2,232 million cubic feet per day.

Emissions projection: Table 7 shows projected emissions from hydrogen steam reforming. These are based on the same GHG emission factor used in the 1995-2007 estimate above ($CO_2$eq of carbon dioxide, methane and nitrous oxide), and 90% utilization of predicted capacity. Known steam reforming expansion proposals at just three plants could add 2.6 million tonnes of emissions per year by 2010. By 2020 steam reforming emissions from California refineries could total between 17.9 million and 23.4 million tonnes per year. That represents an increase of 7.63 million to 13.14 million tonnes/year above the 10.24 million t/y estimated in 2007.

## Discussion

This projection is for potential statewide emissions in the absence of effective policy intervention. Estimates based on steam reforming capacity, hydroprocessing capacity to use hydrogen produced by steam reforming, and oil input contamination that requires this more intensive hydroprocessing consistently predict increased emissions. Together with observed increases in the same causal factors from 1995-2007, this provides evidence for a very large ongoing increase in pollution from refining dirtier oil. The range of

**Table 6. Predicted 2020 statewide steam reforming capacity**

| N. California plant | $H_2$ bscf/d | Crude b/d | $H_2$ scf/b |
|---|---|---|---|
| Chevron-Richmond[a] | 0.2800 | 243,000 | 1,152 |
| ConPh.-Rodeo/S.M.[a] | 0.2080 | 120,000 | 1,733 |
| Shell-Martinez | 0.1010 | 158,600 | 637 |
| Tesoro-Golden Eagle | 0.1050 | 161,000 | 652 |
| Valero-Benicia | 0.2315 | 139,500 | 1,659 |
| Subtotal N.C. plants | 0.9255 | 822,100 | 1,126 |
| **Scaled statewide** | **2.2320** | **1,983,000** | **1,126** |

Existing steam reforming (billions of standard cubic feet per day) and crude capacities (barrels/day) from Ref 3.
Planned 2010 SR capacity from Refs. 11-14.
Based on 100% available capacity.

**Table 7. GHG emissions from steam reforming by California refineries in 2010 and 2020, projection scenarios based on seven estimate cases**

| Estimate case | Production rate (bscf/d)[a] | Emissions (MM t/y)[b] |
|---|---|---|
| Steam Reforming in 2010[c] | 1.439 | 12.8 |
| **2020 cases** | | |
| Steam Reforming[d] | 2.009 | 17.9 |
| Similar-gravity avg. crude[e] | 2.018 | 18.0 |
| Arabian Heavy crude[e] | 2.099 | 18.7 |
| Hydroprocessing, highest 4[f] | 2.232 | 19.9 |
| W. Canadian Heavy crude[e] | 2.297 | 20.4 |
| Hydroprocessing, highest 2[f] | 2.628 | 23.4 |
| **2020 projection** | | |
| **High sulfur scenario** | | **17.9** |
| **Higher sulfur scenario** | | **23.4** |

[a] Steam reforming production of hydrogen in billions of standard cubic feet/day, estimated based on production at 90% of available capacity.
[b] Million tonnes/year, Carbon dioxide equivalent of $CO_2$, $CH_4$ and $N_2O$, based on an emission factor of 24.37 tonnes/MMscf (Refs. 1, 2).
[c] Based on 320 MMscfd net increase from Refs. 11-14.
[d] Based on steam reforming capacity (Table 6).
[e] Based on crude input quality (Table 4, Figure 5).
[f] Based on hydroprocessing capacity (Table 5).

emissions projected reflects uncertainty about the extent to which refinery feedstock could become more contaminated, hydroprocessing could expand to refine the dirtier oil, and steam reforming could expand to feed this hydroprocessing.

Uncertainty: Hydrogen use by a specific hydroprocessing unit may vary from the typical $H_2$ requirements in Table 2. *(4)* Hydrogen needs are affected by plant-specific oil input quality and process-specific feed, products, operating temperature and pressure, catalysts, hydrogen purity and hydrogen recovery. Estimates based on hydroprocessing capacity in Table 7 address this uncertainty by assigning the typical hydrogen requirements conservatively (see the notes in Table 2), applying them to all California plants on average, and checking those estimates against estimates based on crude quality and steam reforming capacity. The range of estimates based on hydroprocessing capacity overlaps with that based on oil quality and, at its low end (19.9 MMt/y), is within 11% of the estimate based on steam reforming capacity.

The estimate based on steam reforming capacity may be conservative. This estimate assumes that Los Angeles area plants will not use more hydrogen in 2020 than Bay Area plants use in 2010. LA area plants refine imports as a larger portion of their total crude input than Bay Area plants now *(3,5)*, and they have less access to the dominant remaining California crude resource, in the San Joaquin Valley, than the Bay Area plants. With high sulfur imports, by 2020 steam reforming per barrel of crude refined in the LA area might exceed that planned for 2010 in the Bay Area.

Crude input quality might worsen more than is estimated. Chevron plans to retool the largest Bay Area refinery for 3% sulfur crude. *(12)* Statewide crude input might exceed 2% sulfur by 2020 if new high-sulfur imports are more than half of new imports (a third of all crude input), lower sulfur domestic supplies decline more quickly, and/or the sulfur content of Arabian Heavy, Western Canadian Heavy or other major streams increases. In addition, contaminants such as nitrogen, nickel and vanadium further increase hydrogen use in hydroprocessing. Some high-sulfur crude imports have high levels of these other contaminants.

Combustion emissions will increase with the amount of steam reforming capacity utilized. The emission estimates in Table 7 are based on production at 90% of available capacity. This assumption is consistent with worldwide conditions *(3)* but California refineries tend to run closer to maximum capacity than the world average, and could further maximize their use of available steam reforming capacity by sharing hydrogen via existing and planned pipelines.

Emissions are estimated at 24.37 tonnes $CO_2$eq emission per million cubic feet of hydrogen produced, based on DOE and CARB data. *(1,2)* This emission factor falls within the range of emissions from new state-of-the-art steam reforming plants. *(11,12)* It may, however, underestimate actual emissions. It accounts for emissions from direct combustion in steam reformers but not the emissions from their electricity requirements or "fugitive" leaks. Recent work suggests fugitive emissions of methane could be significant. *(17)* This emission factor also assumes natural gas fuel, but refiners burn dirtier fuels along with natural gas. In addition, less efficient older steam reforming plants that have higher emissions may remain in service along with the new plants that are built.

Lastly, this projection assumes no increase in the total volume of crude refined beyond 2007. This also is a conservative assumption. *(8)*

Taken together, these considerations suggest that the projection in Table 7 is conservative.

Root cause: Analysis of data from 1995-2007 shows that refining higher sulfur crude increased hydrogen needs for hydroprocessing the lower quality oil, steam reforming to produce this extra hydrogen, and emissions from that increased production.

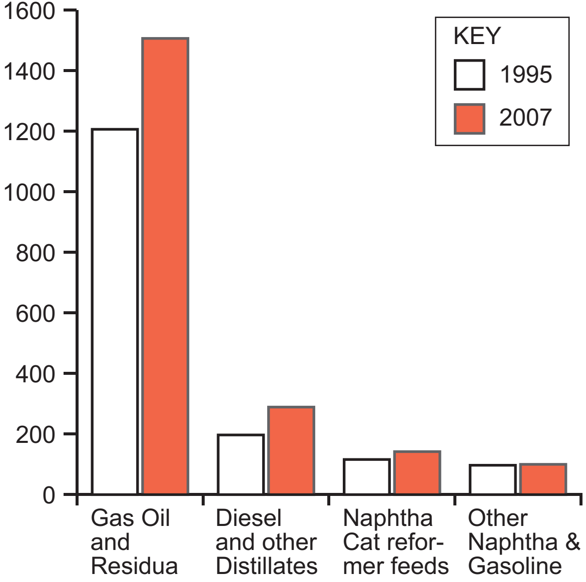
The need for severe hydroprocessing of the heavier streams from more contaminated crude, where the sulfur and other process catalyst poisons were concentrated, drove this increased hydrogen demand. See Figure 7. (Incidentally, this is also how we can know the industry's claim that new fuel standards drive its new hydrogen production is misleading.) Refining inherently dirtier feedstock is the root cause of the emissions increase observed now, and threatens to cause the future increase in emissions projected.

In this context, it is useful to consider the other major fossil energy user–electricity. Inherently dirtier power plant feedstock is acknowledged as a matter of policy. California requires public utilities to phase out use of electricity from coal-fired power plants. *(18)*

Other oil quality impacts: Making gasoline and diesel from low quality oils increases inputs of many pollutants *(6)*, requires more intensive conversion and conditioning by many refining processes, and requires more intensive extraction and pre-processing before the oil reaches refineries. *(19)* It requires more energy, burns more fossil fuel, and emits more toxic, smog-forming and climate-disrupting pollutants for each gallon of transportation fuel produced.

Elevated selenium in refinery inputs was associated with a tenfold increase in selenium discharge/barrel crude refined in the 1990s. *(20)*

**Figure 7. Hydrogen use for hydroprocessing various feeds, California refineries, 1995 and 2007 (MMscf/d)**



Data from References 3 and 4. Hydrogen requirements applied as described in Table 2 notes. Based on 100% of available capacity.

In 2007, an EPA study estimated that if high mercury oils become 0.5% of refinery inputs, potential mercury emissions from U.S. refineries might double. *(21)* In 2008, comparisons of recent Bay Area data found that increased flaring frequency and emissions concentrations were associated with increased sulfur in refinery crude inputs. *(22,23)* Hydroprocessing higher sulfur oil produces more hydrogen sulfide, a toxic gas that forms other toxic sulfur compounds when burned. This contributed to the increased flaring observed *(22)*, and may also increase toxic fugitive and combustion emissions from various refinery processes.

Brandt and Farrel estimated that a switch from conventional crude to extra-heavy oil and/or tar sands may cause GHG emissions by oil production and refining to increase from the current 22% to as much as 44% of total emissions from oil production, refining and vehicle tailpipes combined. *(19)* If this occurs, it may preclude the emission reductions necessary by 2020 and 2050 if we are to avoid the worst potential impacts from global warming.

Thus, other observed and predicted impacts of lower quality oil on releases of GHGs and other pollutants are consistent with those found here for steam reforming and point to a larger threat to our environmental health in communities near refineries, and to our global climate.

Policy implications: If public policy continues to allow it, an accelerating switch to more contaminated, lower quality oil could increase $CO_2$ equivalent emissions by 8-13 million tonnes/year by 2020 from hydrogen steam reforming alone. It might further increase toxic pollution impacts in communities near refineries and cause total emissions from transportation fuel production that overwhelm climate protection efforts. Inherently dirtier feedstock is the root cause of this problem.

Harnessing the chemical energy in low quality fossil resources creates more pollution per unit of useful energy produced. That is as true for vehicle fuels made from low quality oil as it is for electricity made from coal. California is addressing the feedstock problem for electricity by phasing out the use of coal-fired power. This solution–in the form of restrictions on oil input quality–can be applied to oil refineries.

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## Appendices

### Appendix A-1. Sulfur and specific gravity data for selected oil streams.

| Named Stream | Sulfur % wt. | Gravity | Reference |
|---|---|---|---|
| Alaska North Slope (ANS) | 0.86 | 0.860 | Chevron (4/3/08 Subm. re. EIR SCH #2005072117) |
| San Joaquin Valley Heavy (SJVH) | 1.30 | 0.934[a] | Sulfur from Ref. 12; see note a below for gravity |
| Arabian Heavy | 2.87 | 0.889 | www.caplinepipeline.com (3/1/02) |
| Arabian Heavy | 2.99 | 0.889 | www.caplinepipeline.com (10/22/06) |
| Access Western Blend (WCH) | 3.99 | 0.924 | www.crudemonitor.ca (July 2008) |
| Albian Heavy Synthetic (WCH) | 2.54 | 0.936 | www.crudemonitor.ca (3/07; 10/07; 5/08) |
| Albian Residual Blend (WCH) | 2.69 | 0.933 | www.crudemonitor.ca (9/06; 5/08) |
| Borealis Heavy Blend (WCH) | 3.66 | 0.925 | www.crudemonitor.ca (October 2007) |
| Bow River North (WCH) | 2.89 | 0.928 | www.crudemonitor.ca (8/06; 10/07; 5/08) |
| Bow River South (WCH) | 2.80 | 0.914 | www.crudemonitor.ca (10/07; 5/08) |
| Christina Synbit (WCH) | 2.91 | 0.935 | www.crudemonitor.ca (October 2007) |
| Cold Lake (WCH) | 3.61 | 0.929 | www.crudemonitor.ca (4/07; 10/07; 5/08) |
| Cold Lake Blend (WCH) | 3.69 | 0.927 | www.exxonmobil.com/apps/crude_oil (1/18/08) |
| Fosterton (WCH) | 3.13 | 0.931 | www.crudemonitor.ca (10/07; 5/08) |
| Lloyd Blend (WCH) | 3.38 | 0.928 | www.crudemonitor.ca (10/06; 10/07; 5/08) |
| Lloyd Kerrobert (WCH) | 3.08 | 0.929 | www.crudemonitor.ca (11/06; 10/07; 5/08) |
| Lloydminster (WCH) | 3.15 | 0.930 | www.crudemonitor.ca (October 2007) |
| Long Lake Heavy (WCH) | 3.06 | 0.934 | www.crudemonitor.ca (July 2008) |
| Mackay River (WCH) | 2.78 | 0.936 | www.crudemonitor.ca (10/07; 5/08) |
| Peace River Heavy (WCH) | 4.76 | 0.930 | www.crudemonitor.ca (10/07; 5/08) |
| Seal Heavy (WCH) | 4.58 | 0.929 | www.crudemonitor.ca (8/06; 5/08) |
| Smiley-Coleville (WCH) | 2.95 | 0.934 | www.crudemonitor.ca (11/06; 5/08) |
| Surmont Heavy Blend (WCH) | 2.86 | 0.938 | www.crudemonitor.ca (July 2008) |
| Wabasca Heavy (WCH) | 3.79 | 0.928 | www.crudemonitor.ca (4/06; 10/07; 5/08) |
| Western Canadian Blend (WCH) | 3.03 | 0.929 | www.crudemonitor.ca (6/06; 10/07; 5/08) |
| Western Canadian Select (WCH) | 3.28 | 0.930 | www.crudemonitor.ca (5/07; 5/08) |

WCH is Western Canadian Heavy. [a] Gravity estimated conservatively based on the lightest crude classified as "heavy" by the Calif. Div. Oil and Gas and the Division's 2006 Annual Report finding that statewide crude production, which is dominated by production from several very large San Joaquin Valley oil fields, has become lighter in recent years.

### Appendix A-2. 2007 hydroprocessing and steam reforming capacities[a] of California refineries[b]

| Refinery | Crude | Hydrocracking | Hydrotreating | $H_2$ Steam Reforming |
|---|---|---|---|---|
| *Bakersfield area plants* | | | | |
| Big West Refining Bakersfield | 65,000 | 23,500 | 21,900 | 24.7 |
| Kern Oil Bakersfield | 25,000 | 0 | 13,000 | 0.0 |
| San Joaquin Refining Bakersfield | 24,300 | 0 | 3,000 | 4.2 |
| *Bay Area plants* | | | | |
| Chevron Richmond | 243,000 | 154,250 | 177,000 | 150.0 |
| ConocoPhillips Rodeo & Santa Maria | 120,000 | 37,000 | 73,000 | 88.0 |
| Shell Martinez | 158,600 | 37,900 | 117,950 | 101.0 |
| Tesoro Golden Eagle | 161,000 | 32,000 | 172,500 | 105.0 |
| Valero Benicia | 139,500 | 36,000 | 146,000 | 131.5 |
| *Los Angeles area plants* | | | | |
| Alon USA Paramount | 54,000 | 0 | 29,000 | 0.0 |
| BP Carson | 264,500 | 45,000 | 244,700 | 105.0 |
| Chevron El Segundo | 260,000 | 46,000 | 201,000 | 217.0 |
| ConocoPhillips Carson & Wilmington | 138,700 | 24,750 | 135,850 | 100.8 |
| ExxonMobil Torrance | 149,500 | 20,500 | 143,500 | 146.0 |
| Tesoro Wilmington | 100,000 | 32,000 | 101,250 | 55.0 |
| Valero Wilmington | 80,000 | 0 | 139,500 | 50.0 |

[a] In barrels/calendar day ($H_2$ in MMscf/d) from Ref. 3. [b] California plants producing California gasoline and/or diesel.

Attachment 53

**Attachment 53. Preliminary comparison of estimates for total $CO_2$e emissions from refining in California**

| | PIIRA data | ARB data |
|---|---|---|
| **Avg from 1990–1992:** | **35.93** | **32.46** |
| **Avg from 2007–2009** | **39.63** | **34.34** |
| **Avg from 2011–2013** | **--** | **34.55** |

| ***Data in*** | California Air Resources Board emission estimates | | | | Based on PIIRA fuel data[d] | | UCS (2011)[e] | ARB MRR[f] |
|---|---|---|---|---|---|---|---|---|
| ***Megatons*** | ARB Inv. 1[a] | ARB Inv. 2[b] | ARB–MRR[c] | All years | All fuels | Onsite only | Table S2-2 | (see PRA file) |
| 1990 | 32.13 | | | 32.13 | 35.95 | 31.77 | | |
| 1991 | 32.65 | | | 32.65 | 36.49 | 32.25 | | |
| 1992 | 32.59 | | | 32.59 | 35.35 | 31.46 | | |
| 1993 | 33.31 | | | 33.31 | 35.57 | 32.10 | | |
| 1994 | 32.35 | | | 32.35 | 34.90 | 31.43 | | |
| 1995 | 31.16 | | | 31.16 | 34.32 | 30.84 | | |
| 1996 | 34.02 | | | 34.02 | 36.37 | 33.09 | | |
| 1997 | 33.90 | | | 33.90 | 35.48 | 32.49 | | |
| 1998 | 34.76 | | | 34.76 | 35.84 | 32.67 | -- | |
| 1999 | 32.71 | | | 32.71 | 34.01 | 30.90 | -- | |
| 2000 | 34.31 | 33.25 | | 33.25 | 35.99 | 32.77 | -- | |
| 2001 | 33.24 | 33.07 | | 33.07 | 35.52 | 32.35 | -- | |
| 2002 | 33.38 | 33.87 | | 33.87 | 36.37 | 33.26 | -- | |
| 2003 | 34.59 | 34.80 | | 34.80 | 37.18 | 34.31 | -- | -- |
| 2004 | 33.78 | 34.06 | | 34.06 | 36.67 | 33.61 | 36.82 | -- |
| 2005 | | 35.31 | | 35.31 | 38.22 | 34.98 | 38.32 | -- |
| 2006 | | 36.09 | | 36.09 | -- | -- | 39.98 | -- |
| 2007 | | 36.07 | | 36.07 | -- | -- | 40.73 | -- |
| 2008 | | 35.65 | 34.74 | 34.74 | 38.37 | 35.02 | 39.96 | -- |
| 2009 | | | 32.20 | 32.20 | 36.51 | 33.28 | 38.19 | -- |
| 2010 | | | | -- | 37.13 | 33.92 | -- | -- |
| 2011 | | | | | -- | -- | -- | 34.81 |
| 2012 | | | | | -- | -- | -- | 34.39 |
| 2013 | | | | | -- | -- | -- | 34.44 |

-- = Not available

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[a] Inventory Archive (arb.ca.gov/cc/inventory/data). Includes refinery gen/cogen, process losses and transformation.

[b] Inventory 2000–2008 (arb.ca.gov/cc/inventory/data). Excludes cogeneration, other process emissions.

[c] Mandatory GHG Reporting Rule public reports. Excludes production of H2 purchased by refiners.

[d] Refinery fuel consumption data like those reported for the US by USEIA are reported for California under PIRRA. Emissions are based on these data and the fuel-specific energy and emission factors given in Karras (2010). "Onsite only" emissions shown exclude emissions from purchased electricity and steam.

[e] *See* Attachment 16 to CBE's 21 October 2015 Supplemental Comment in this matter.

[f] *See* www.arb.ca.gov/cc/reporting/ghg-rep/reported-data/ghg-reports.htm (data for non-biogenic $CO_2$e).