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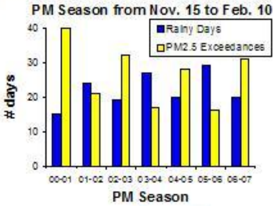
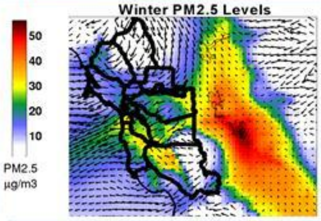
Sources of Bay Area Fine Particles: 2010 Update and Trends

December, 2012





Prepared by:

David Fairley, Statistician

Reviewers:

Brian Bateman, Health and Science Officer
Scott Beaver, Atmospheric Modeler
David Burch, Principal Environmental Planner
Philip Martien, Air Quality Engineering Manager

Approved by:

Saffet Tanrikulu, Research and Modeling Manager

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Summary

In recent years, the Bay Area has violated both State and national fine particulate matter ($PM_{2.5}$) ambient air quality standards. $PM_{2.5}$ is the air pollutant that constitutes the greatest threat to health in the region. Understanding its sources is key to developing control measures to reduce its ambient concentrations. This analysis estimates the contributions to ambient levels of $PM_{2.5}$ from various sources in the Bay Area.

This analysis uses data collected from 2009 through 2011. It updates a previous analysis (Fairley 2008) that used data from a decade earlier. Since the first analysis, there have been substantial reductions in emissions, largely as the result of California Air Resource Board (CARB) regulations governing diesel and gasoline engines and ship emissions, and Bay Area Air Quality Management District (District) rules for wood burning and charbroiling.

Filters containing PM from ambient air samples were analyzed to assess the respective contributions from various categories of sources. In each filter, a set of chemical PM species was measured, and the measurements were matched against the chemical profiles from various source categories. The Chemical Mass Balance (CMB) method was used to find the mix of source categories that best matched each ambient sample. The CMB results were combined with the District's $PM_{2.5}$ Emissions Inventory (EI) to make a final estimate of the contributions from individual sources.

S1. Ambient data and source profiles

In this analysis, ambient data were used from the four District monitoring sites where requisite data were available – Livermore, West Oakland, San Jose, and Vallejo – and from a non-District site, Point Reyes, part of the IMPROVE network, a set of National Park sites. Data were also analyzed from a set of eight Central Valley sites: Chico, Sacramento Del Paso, Sacramento T Street, Modesto-14th Street, Visalia, Fresno, Bakersfield, and Sequoia National Park. Analysis of Bay Area data excluded samples collected prior to July 2009 because of a CARB rule requiring the use of low-sulfur ship fuel that took effect July 1, 2009.

For each site, the set of chemical species measured included higher atomic weight elements; various ions including nitrate, sulfate, ammonium, chloride, sodium, and potassium; and elemental and organic carbon (EC and OC). These filter measurements were analyzed at three different labs; there were a few differences among the labs in terms of what was measured. Species chosen for CMB analysis were limited to those with a substantial fraction of concentrations greater than the estimated level of uncertainty of the measurement (that is, the standard deviation of the measurement error).

Source profiles were obtained from the California Regional Particulate Air Quality Study (CRPAQS) and EPA Speciate (Hsu *et al*. 2006) databases, along with a set that had been used in a previous analysis (Fairley 2008). These profiles were refined and updated for the Bay Area by comparing profiles from different sources and profiles against ambient measurements. The source categories used in this CMB analysis were: new and aged marine air[1], geological dust, residential woodsmoke, wildfire smoke, meat cooking, diesel emissions, gasoline emissions, tire/brake wear, and fireworks. Ammonium nitrate and ammonium sulfate were also included. These are compounds produced in the atmosphere; they constitute a large fraction of Bay Area $PM_{2.5}$ but largely derive from ammonia, NOx and SO_2 emitted from a variety of sources.

In addition to the measurements made on ambient filters, pieces of ambient filters were combined into 16 samples – four each from the four District sites to represent four periods: summer, spring/fall, winter off-peak, and winter peak. These 16 composite samples were analyzed for carbon-14 (C-14), a measurement that makes a bright-line distinction between "new" carbon sources – wood burning and cooking – and the old "fossil" carbon sources – e.g., diesel and gasoline exhaust.

S2. Methodology

The source apportionment was performed using a variant of the CMB model. The new approach involved fitting the ambient data with source profiles that were randomly generated. The fitting process was repeated 100,000 times for each daily sample (on the order of 150 samples for each of five Bay Area sites, and eight Central Valley sites), and a weighted average of the 25 best fits was used in each.

The CMB results for the four District sites were modified based on the carbon-14 analysis. The CMB model was run with the C-14 measurements as one of the chemical species and the original individual CMB fits were adjusted in some cases.

The CMB model apportions $PM_{2.5}$ concentrations to source *categories,* like diesel combustion. But the model cannot distinguish among individual sources like diesel trucks, construction equipment, farm equipment, and so on. Therefore, the District's Emissions Inventory, which has a detailed breakdown of emissions, was used to help apportion the contributions from each source category to individual sources.

This melding of the two data sources included factoring in the contributions of precursors to $PM_{2.5}$. The previous analysis (Fairley 2008) simply apportioned the ammonium nitrate source category proportional to NOx emissions, and ammonium sulfate proportional to SO_2 emissions. This analysis also takes into account the estimated sensitivity of these secondary PM compounds to ammonia reductions, based on results from the CMAQ model (a grid-based model utilized to simulate Bay Area PM concentrations). (See Appendices E and F in Fairley and Burch 2010.)

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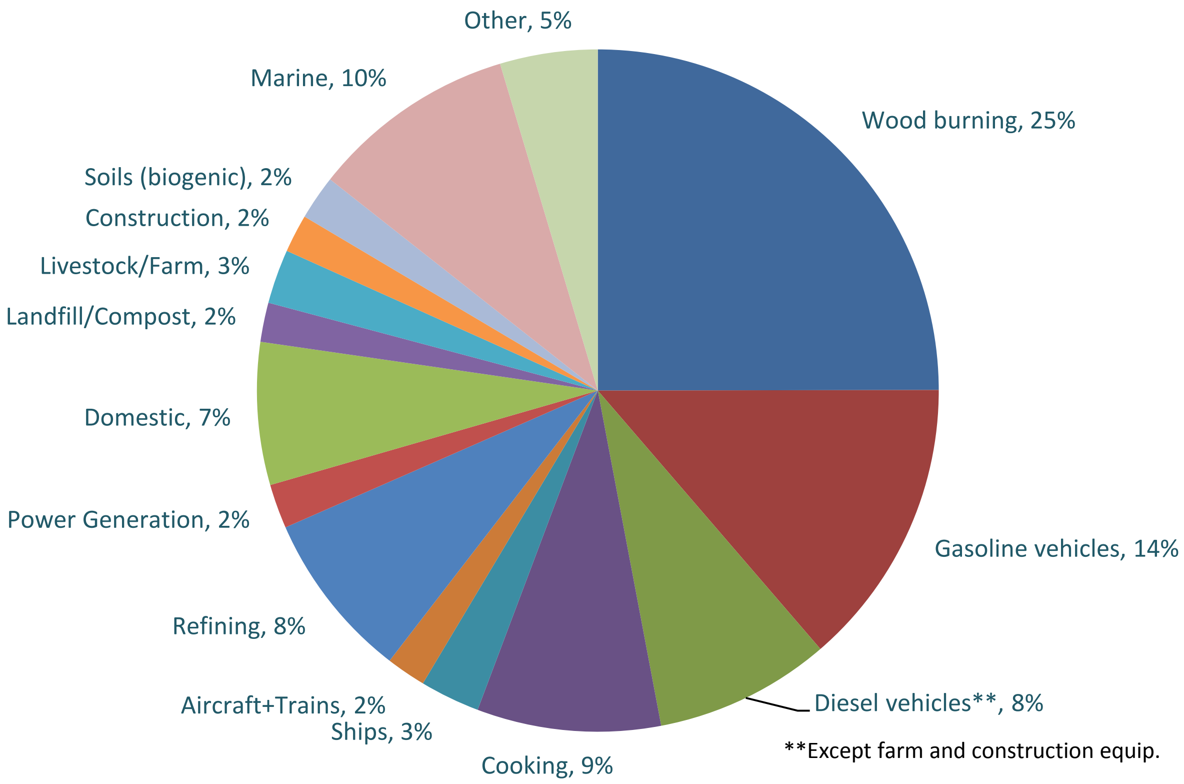
[1] Marine air is air off the ocean, new being fresh, aged having been modified by other pollutants as it drifted over an urban area.

S3. Results

The results are summarized for annual average and peak $PM_{2.5}$ concentrations to correspond with the annual average and 24-hour National Ambient Air Quality Standards.

Figure S1 shows the contributions from individual sources to annual Bay Area $PM_{2.5}$ concentrations. Wood burning stands out as the largest source, comprising 25% of the total. Much of this is from residential fireplaces and woodstoves, but it also includes contributions from wildfires, controlled burns, and secondary organic compounds (such as pinonic acid deriving from α–pinene, found in the oils of pines and other conifers). Gasoline and diesel vehicles add another 22%. These include both on- and off-road vehicles except farm and construction equipment. Cooking adds 9%. Refining adds 8%. Marine air (pure sea salt without ship emissions) adds another 10%. Ship emissions had contributed 10% previously, but currently contribute only 3% due to the CARB's low sulfur emissions for ships.

Figure S1. Estimated Source Contributions to Annual $PM_{2.5}$ Concentrations*



**Except farm and construction equip.

* These estimates derive from combining the source category contribution estimates from four sites: Livermore, San Jose, Vallejo, and West Oakland, for 2009-2011 with detailed emissions estimates from the Emissions Inventory.

Figure S2 shows the contributions from individual sources to peak Bay Area $PM_{2.5}$ concentrations; that is, contributions on days that exceed or nearly exceed the standard. Wood burning contributes 28%, larger than its annual contribution. This is not surprising, because peak days virtually always occur in winter. Gasoline and diesel vehicles contribute 30%, considerably larger than their annual contribution. This increase occurs mainly because vehicles are the primary contributors to NOx, a precursor of ammonium nitrate, which is a large component of peak $PM_{2.5}$ in the winter. Similarly, the domestic category, which includes cats and dogs and is estimated to be the largest single source of ammonia, the other ammonium nitrate precursor, contributes 9% of the total. By the same token, cooking and refining contribute a lower percentage to peak $PM_{2.5}$ because they contribute only a small fraction of the ammonium nitrate precursors. The marine air contribution drops to 3% because peak $PM_{2.5}$ conditions typically occur with easterly winds, where the air blows from observation stations toward the ocean.

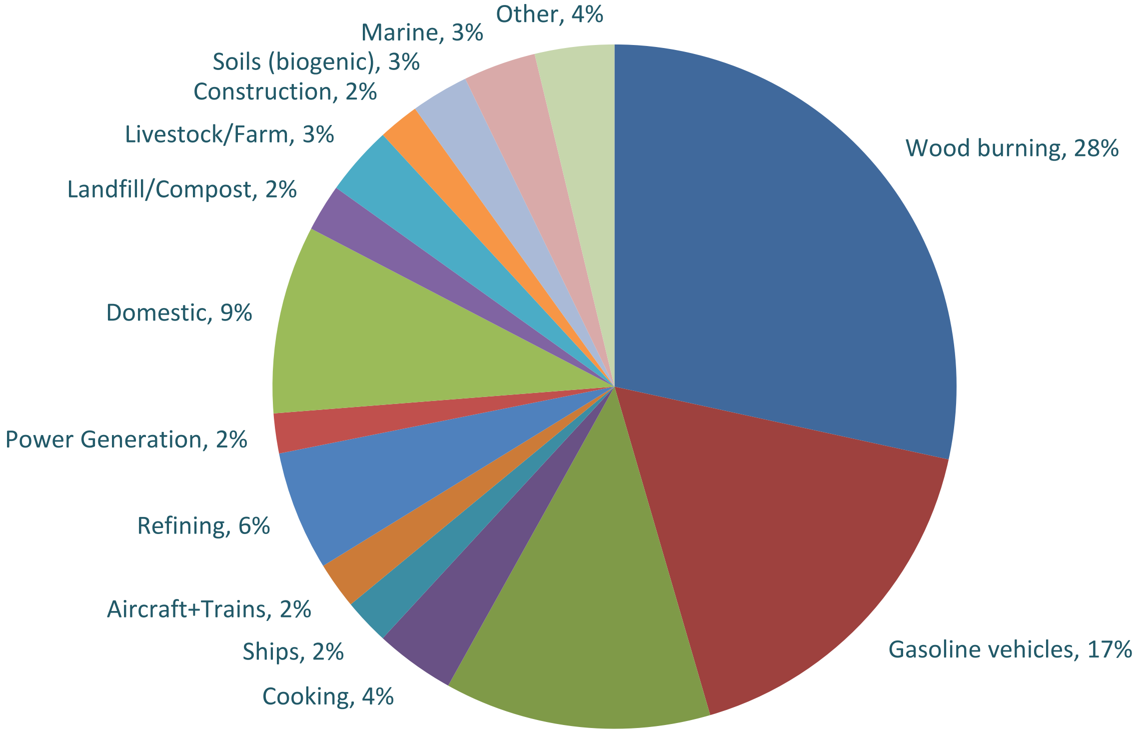


Figure S2. Estimated Source Contributions to Peak PM2.5 Concentrations*

**Except farm and construction equip.

* These estimates derive from combining the source category contribution estimates from four sites: Livermore, San Jose, Vallejo, and West Oakland, for 2009-2011 with detailed emissions estimates from the Emissions Inventory.

S3.1 Comparison with Emissions Inventory

The source contributions estimated by CMB were compared with the Emissions Inventory where they overlapped. This overlap excluded the secondary PM sources that CMB identified – ammonium nitrate and sulfate – and also marine air. The Emissions Inventory sources were summed to correspond to CMB categories. For example, residential fireplace and woodstove emissions were added to the emissions from the burning of waste material and wildfires to correspond to the wood-burning category in CMB.

There were consistencies between CMB and the EI, for example woodsmoke representing the largest contributor in each, and ships a relatively small contributor. But there were also some discrepancies. The largest differences were for geological dust and brake wear where the CMB percentage was less than one-third of the EI percentage. This continues a pattern where EI estimates of particles that are mainly in the coarse fraction are considerably larger than the corresponding CMB values. We posit this is in large part because the EI estimates what is emitted into the air, whereas CMB is based on the ambient concentrations of the particles that remain suspended in the air.

The EI shows larger contributions from diesel and gasoline, and correspondingly smaller emissions from woodsmoke and cooking. The Carbon-14 adjusted CMB values are generally closer than the unadjusted to the EI values.

S3.2 Trends

To estimate trends in the source categories, the new CMB method was applied to 1999-2001 data used in a previous study (Fairley 2008). The Livermore and Point Reyes sites were the same in the two studies but the other sites were different: San Francisco and Bethel Island rather than West Oakland and Vallejo. There was also a San Jose site, but at a different location with somewhat different nearby sources. Note that an analysis on trends in ambient $PM_{2.5}$ and several components (Fairley 2011) is also available.

Figure S3 compares the averages across the urban sites for 2000 and 2010. There were reductions in all anthropogenic sources, though the amount of reduction varied.

Perhaps most striking are the large reductions in the estimated diesel and gasoline contributions. There is some uncertainty in this finding because the sites selected in two studies aren't identical and because laboratory instruments and precision may have differed. But these reductions are large relative to the uncertainty and parallel reductions shown in the EI.

There is a similarly large reduction in ship emissions, undoubtedly the result of CARB's July 2009 low-sulfur fuel rule. There are also large reductions in estimated ammonium nitrate and cooking contributions.

Wood burning contributions are estimated to have been reduced a modest amount. It should be noted, however, that this includes wildfires, controlled burns and secondary carbonaceous PM. Limiting analysis to the wood burning season – November 15 through February 15, the estimated reduction in wood burning was about 40%.

Note that there are reductions in the marine contribution as well. Since this is not of anthropogenic origin, the difference is random, and suggests there is a substantial amount of uncertainty in the trend estimates.

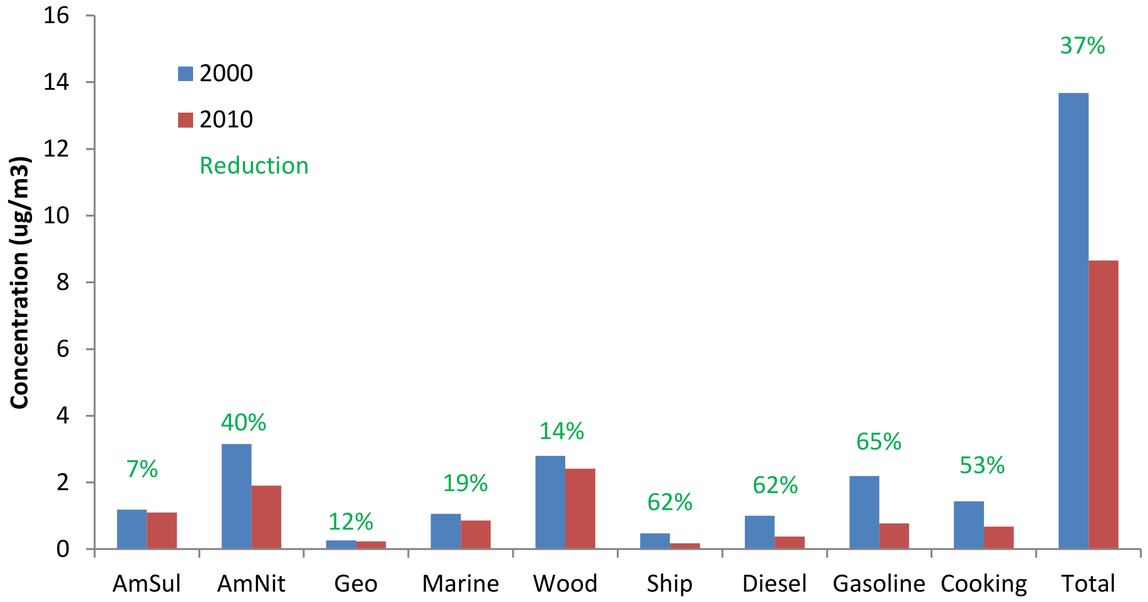


Figure S3. Trends in CMB-Estimated Source Contributions: 2010 vs. 2000

S3.3 Seasonality

Bay Area $PM_{2.5}$ concentrations are generally higher in the winter, reaching a peak in December and January. Several factors combine to produce this effect: Winter has periods where the air is relatively stable, allowing the $PM_{2.5}$ to build up; it is when most wood burning occurs; and a higher percentage of ammonium nitrate stays in the particulate phase in colder winter weather.

S3.4 Comparison with Central Valley

During the winter periods conducive to high $PM_{2.5}$ concentrations, the prevailing easterly winds put the Bay Area downwind of the Central Valley.

The CMB model was run for a set of Central Valley sites that had speciated data from 2009-2010. Many of the Central Valley sites had higher $PM_{2.5}$ concentrations than the Bay Area. Ammonium nitrate and woodsmoke account for almost all the difference. Ammonium nitrate averages about 2 $\mu g/m^3$ higher in the valley than the Bay Area on an annual basis, and peak values average 6.5 $\mu g/m^3$ higher. Woodsmoke also averages 2 $\mu g/m^3$ higher annually, with peak values 3 $\mu g/m^3$ higher.

Concentrations of ammonium sulfate, diesel, gasoline and brake wear are similar to Bay Area concentrations. The marine component is higher in the Bay Area, since the Bay Area is nearer the ocean. Geological dust is lower.

S4. Conclusions

Residential woodsmoke continues to be the largest source of Bay Area $PM_{2.5}$ concentrations, contributing about a quarter to the annual average and a greater percentage to peak $PM_{2.5}$. Woodsmoke concentrations have been reduced, presumably in part because of the District's wood burning rule (BAAQMD 2008).

Both gasoline and diesel concentrations appear to have fallen rapidly. Combined, they contribute about 20% to annual average and 30% to peak $PM_{2.5}$ compared with 30% of the annual average and 40% of the peak a decade ago. Ships were another large source, but the CARB rule requiring low sulfur fuel near ports dramatically reduced ship emissions, on the order of seventy-five percent, so that ships contribute only about 3% today.

Cooking emissions are estimated to contribute 9% to annual $PM_{2.5}$ concentrations and 4% to peak $PM_{2.5}$. The Emissions Inventory estimates commercial cooking emissions but not domestic; however, the contributions from both deposit on the filters used for CMB. Although the impact of domestic cooking on ambient levels may not be great, its impact on personal exposure is likely large as people spend time close to the stove while cooking.

A modeling study showed that both ammonium nitrate and ammonium sulfate were sensitive to changes in ammonia emissions (Fairley and Burch 2010, Appendix E). Using the District's new ammonia inventory (STI 2008) ammonia was included as a secondary $PM_{2.5}$ precursor for apportioning CMB-source categories to individual sources. Including ammonia added several new sources from the Emissions Inventory: farm animals, landfills and compost, domestic (cats, dogs, people), soil (biogenic emissions), that combined to contribute about 17% to the annual total.

Contributions from sources where $PM_{2.5}$ derives from abrasion processes – geological dust, tire and brake wear – were found to be smaller relative to their estimated fraction in the Emissions Inventory than sources derived from agglomeration – woodsmoke, engine exhaust, cooking. The overall contribution of these abrasion sources to ambient concentrations was only a few percent.

There continue to be some contributions from "smokestack" sources – refineries (6% to 8%) and power plants (about 2%). But, as Figures S1 and S2 suggest, the vast majority of the Bay Area's anthropogenic $PM_{2.5}$ now derives from millions of small sources, with more than half (fireplaces, wood stoves, cars, vans, SUVs, cats and dogs) under the purview of individual Bay Area residents.

1. Introduction

This analysis estimates the sources of fine particulate matter ($PM_{2.5}$) in ambient air of the Bay Area from July 2009 through December 2011. Understanding the sources that contribute to $PM_{2.5}$ is key to developing emissions control measures to reduce $PM_{2.5}$ concentrations. The Bay Area has violated both state and national $PM_{2.5}$ ambient air quality standards in recent years. $PM_{2.5}$ constitutes the greatest threat to health among all Bay Area air pollutants.

This report updates a previous analysis (Fairley 2008) that used data from 1999-2001. Since then there have been substantial changes in emissions from California Air Resource Board (CARB) regulations of diesel and gasoline engines and ship emissions, and the Bay Area Air Quality Management District's (District) rules for wood burning and charbroiling. July 2009 was chosen as the starting point so that the analysis better reflects current emissions; it was the first month of the implementation of a CARB rule that vastly reduced emissions from ocean-going ships.

The main tool used was a variant of the Chemical Mass Balance (CMB) model. Essentially, CMB estimates the contributions from various sources by comparing their chemical signatures with chemical measurements of particles in the ambient air. CMB determines the mix of source contributions that provides the best match with ambient measurements.

The CMB model identifies categories of sources, but not individual sources. For example, CMB can identify $PM_{2.5}$ from diesel combustion, but can't determine whether the diesel is from trucks or trains or construction equipment or diesel generators. The District's Emissions Inventory (EI) does have estimates of emissions by individual source. Therefore, the CMB results were combined with the Emissions Inventory to estimate the contributions from individual sources.

Section 2 discusses the chemical measurements made on ambient samples that serve as the basis of the CMB analysis. Section 3 discusses the set of source categories considered in the analysis. Section 4 discusses the CMB methodology used, which includes some innovations. Section 5 discusses the initial CMB results, including uncertainties, and comparisons with the Central Valley and earlier results for the Bay Area. Section 6 presents a synthesis of CMB and the Emissions Inventory, providing estimates of contributions from individual sources. Section 7 summarizes the results.

A note on terminology: *CMB analysis* refers to the specific method of estimating source categories using a computer program that matches ambient measurements with source profiles. *Source apportionment* is used in a more general sense to mean the estimation of the sources of fine particulate matter. The latter includes CMB analysis, but also the combination of its results with the information from the Emissions Inventory.

2. Measurements

CMB analysis uses measurements of chemical species made on fine particles from the ambient air. These particles are collected on filters and analyzed for a variety of chemical species. CMB analysis involves finding the mix of sources whose spectrum of species best matches that of the ambient sample. This section describes where the samples were collected and analyzed, and what species were measured, including some of their characteristics.

CMB analysis requires a large set of measurements. These measurements are routinely made only at a few sites. The District started collecting these measurements at two sites, Livermore and Vallejo, in September 2008 and added a third site in West Oakland in February 2009. Samples were collected every sixth day, and measurements were available through December 2011. Measurements of species that are used in the analysis are also made at the San Jose – Jackson St. site as part of the national Speciation Trends Network and the Point Reyes National Seashore site as part of the national IMPROVE network. Point Reyes data for 2011 were not available. Table 2.1 lists the sites, the date range, and numbers of samples used in the CMB analysis.

Table 2.1. Speciated sampling locations, dates and numbers of samples.

Site	Address	Lab*	Date Range		# of observations
Livermore	793 Rincon Avenue	DRI	July-2009	Dec-2011	152
Oakland West	1100 - 21st Street	DRI	July-2009	Dec-2011	151
Vallejo	304 Tuolumne St	DRI	July-2009	Dec-2011	152
San Jose	158-B E. Jackson St	RTI	July-2009	Dec-2011	235
Point Reyes	Pt. Reyes National Seashore	UC Davis	July-2009	Dec-2010	174

* DRI = Desert Research Institute, Reno, NV; RTI = RTI International, Research Triangle Park, NC.

The PM filter measurements were chemically analyzed at three different labs. Measurements for Livermore, Oakland and Vallejo were analyzed by Desert Research Institute (DRI); for San Jose by RTI labs; and for Point Reyes by UC Davis. The set of species measured is nearly, but not quite, identical, and there are some differences in the measurement characteristics among the labs, as explained below.

2.1 Ambient filter measurements

A sampler draws ambient air through filters that collect particles; the particles are limited to the fine ($PM_{2.5}$) fraction by a selective size inlet. The samples are drawn over a 24-hour period, midnight to midnight. Samples are collected on three different types of filters that are used for three categories of measurements:

- on filter 1, all the higher atomic weight elements are measured, starting with sodium or magnesium. The total $PM_{2.5}$ mass is also measured on this filter.
- on filter 2, ions, including nitrate, sulfate and sometimes chloride, sodium, potassium, and ammonium.
- on filter 3, elemental and organic carbon.

The measurements here are all converted to micrograms per cubic meter ($\mu g/m^3$).

In addition to the ambient measurements, CMB analysis requires estimates of measurement uncertainty, which the labs also provide.

2.2 Species summary statistics

Much information on $PM_{2.5}$ sources can be found by looking at the concentrations of individual species and their inter-relations. Figure 2.1 shows the means, 80% confidence intervals of $PM_{2.5}$ mass, and key species by site. Roughly speaking, the means are significantly different when the confidence intervals do not overlap. For most species shown, the measurement method is the same for every site. For these species the means and confidence intervals for a given species are comparable among sites. For sodium, the Point Reyes measurement is the ion; for the other sites, it's the element as measured by X-Ray fluorescence. For chlorine, the San Jose measurement is the element as measured by X-Ray fluorescence; for the other sites, it's the ion. Thus, for sodium and chlorine, apparent differences may stem from different quantities being measured rather than actual differences in concentrations.

The Point Reyes site is located in the midst of the Point Reyes National Seashore; the other sites are in urban areas. $PM_{2.5}$ mass at Point Reyes is significantly lower than at the other sites. Nevertheless, its sodium and chlorine concentrations are greater than at any of the other sites suggesting that it has a larger marine component than the urban sites. Vanadium, nickel and sulfate are key ship emissions. We see the greatest concentrations of these at the Point Reyes or West Oakland sites. The West Oakland site is near the Port of Oakland.

Silicon and aluminum are key species of geological dust, constituting close to 20% of its total mass. The relatively low silicon and aluminum concentrations at all sites indicate that geological dust is not present in high concentrations at any of the sites. Potassium is a key element of woodsmoke. Its higher concentrations at San Jose and Vallejo suggest that woodsmoke is a larger source at these sites than at West Oakland or Point Reyes. Elemental carbon (EC or soot) has several sources, but it typically forms the majority of diesel particulate matter. The West Oakland site, right next to West Grand Avenue – a key thoroughfare with many diesel trucks going to and from the Port of Oakland – has EC concentrations no higher than the other urban sites. It is unclear why its EC levels aren't higher.

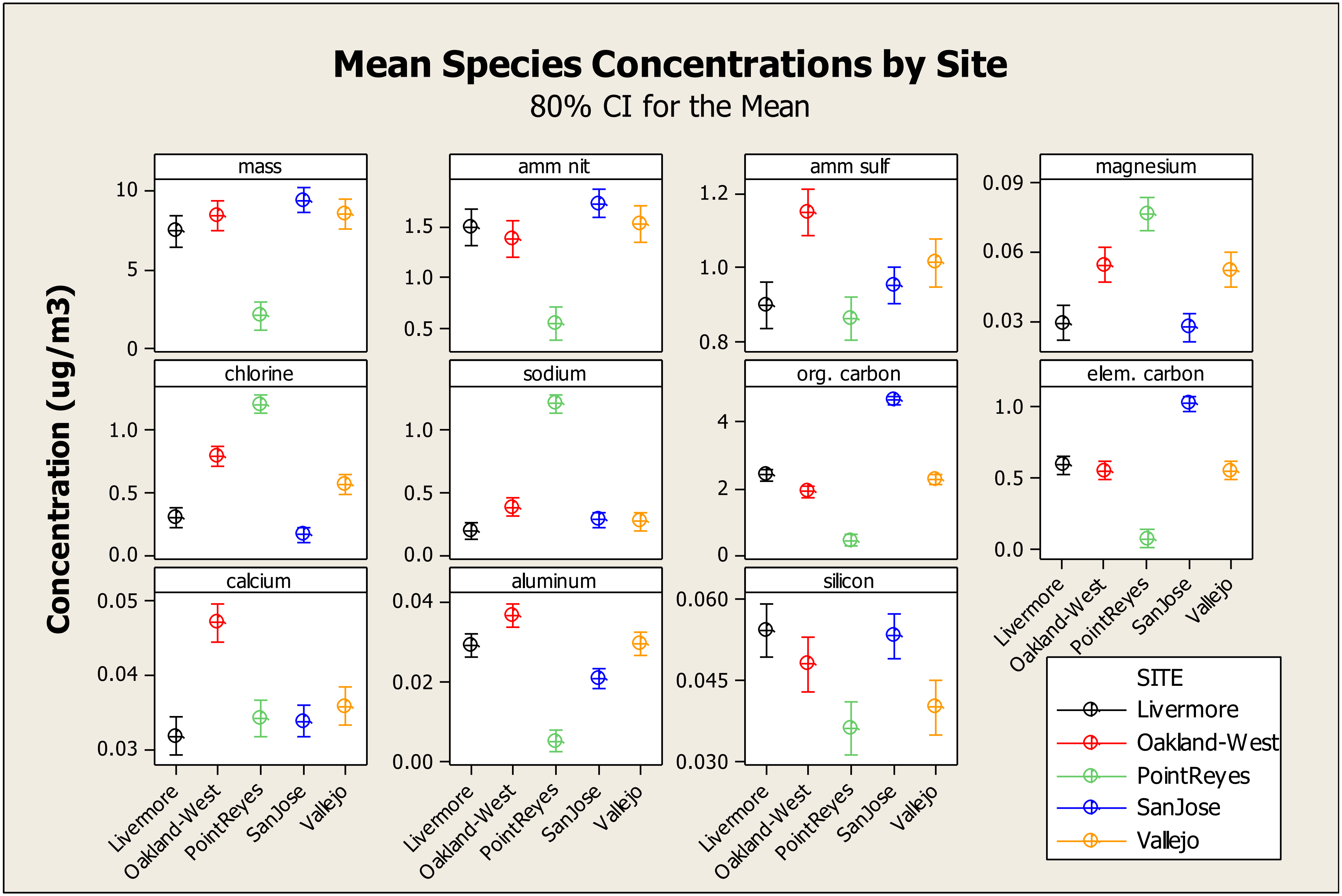


Figure 2.1. Mean species concentrations by site for total mass and key species. Also shown are 80% confidence intervals.

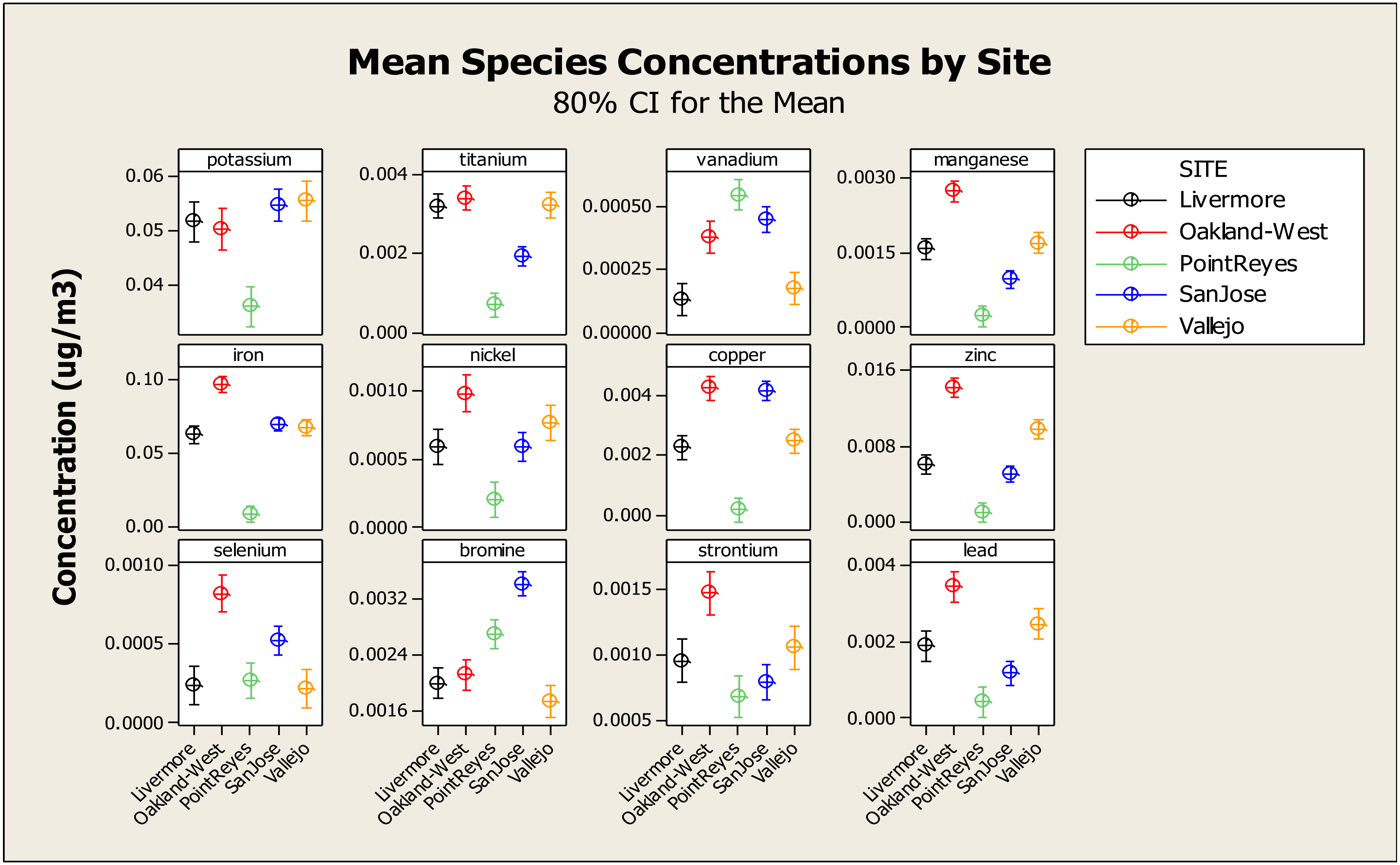


Figure 2.1 (continued)

2.3 Carbon-14 analysis

The largest sources of $PM_{2.5}$ emissions in the Bay Area derive from combustion: woodsmoke, gasoline and diesel exhaust, and charbroiling emissions. More than half the mass of each of these sources is carbonaceous – EC and OC – and there is considerable overlap in the other species among these sources. This overlap leads to considerable uncertainty in the amounts of $PM_{2.5}$ to apportion to each source. To reduce the uncertainty in apportionment, an additional measurement was made, namely the carbon-14 (C-14) of the carbon on the ambient filters.

C-14 is a radioactive isotope of carbon best known for its use in dating fossil remains. Ambient air has a certain fraction of C-14 which gets incorporated into living tissue, both plant and animal. Once there it begins to decay, with a half-life of 5,730 years. Thus, very little of the C-14 in wood or meat has decayed whereas all of the C-14 in millions-of-years-old fossil fuels has. So, the fraction of C-14 in $PM_{2.5}$ provides a clear demarcation between "new" carbon sources including woodsmoke and charbroiling, and old "fossil" carbon sources like gasoline and diesel exhaust.

Because of the expense of C-14 analysis and because a substantial amount of carbon is required for an accurate measurement, $PM_{2.5}$ filters from various days were composited. Specifically, the year was divided into three seasons based on typical $PM_{2.5}$ composition: "summer" (May-August), "winter" (November-February), and "spring/fall" (March-April + September-October). The winter season was split into "peak" and "off-peak" with the former having the high $PM_{2.5}$ days, the latter the remaining winter days.

A selection was made from filters for April 2009 through April 2010 for each of the four urban sites and sent for analysis by Accelerator Mass Spectrometry at the University of Arizona.

3. Sources

CMB analysis depends on the availability of a set of source profiles that represent the actual chemical composition of emissions from sources in the area being studied. This section provides a discussion of how source profiles were updated and improved for use in this analysis.

For CMB analysis to have practical utility, it is necessary to place sources into groups that are reasonably homogeneous within the group and distinguishable from other groups. What we refer to as "sources" for CMB should be thought of as source *categories*, i.e., groups of sources. For example, "geological dust" refers to any $PM_{2.5}$ from roads, playing fields, farms, or construction operations; "cooking" refers to frying foods, charbroiling meats, or baking in an oven.

The profiles of certain sources are similar: cooking and woodsmoke, for example, or gasoline and diesel. This leads to large uncertainties in source attribution. Therefore, in the previous analysis (Fairley 2008), the number of source categories analyzed was reduced: "woodsmoke" included cooking emissions and secondary organic $PM_{2.5}$; fossil included $PM_{2.5}$ from diesel, gasoline, the bunker fuel used in ships, and natural gas.

In the present analysis, we use a different CMB method to incorporate more source categories, as explained in Section 4. We have also systematically reviewed and revised the sources defined.

3.1 Development of source profiles

CMB uses *source profiles* to match against ambient samples. A source profile is a set of estimated fractions of chemical species from a given source category. For example, a woodsmoke profile might consist of 50% organic carbon, 15% elemental carbon, 1% potassium, 1.5% sulfate, and so on. The sum of the distinct species percentages should be at most 100%, typically less, because some elements like hydrogen and oxygen are not measured.

Source profiles are derived in one of two ways: measurement or theory. Measurements have been made for woodsmoke from fireplaces and woodstoves; cooking of various kinds; tailpipe emissions from automobiles and diesel trucks; brake wear; and a number of others. Theoretical estimates have been used here for ammonium nitrate, ammonium sulfate, and fireworks. For this analysis, we adjusted some of the theoretical profiles by comparing with measurements in the ambient air where the source was clearly present.

Each source profile fraction is accompanied with a percent uncertainty (standard error). This uncertainty includes measurement uncertainty, but typically also includes the estimated variation within the source category. For example, the organic carbon in a test of woodsmoke might be measured to within an uncertainty of 3%, say, but the variation from fire to fire using different wood, different burning conditions, and so on, might be 10%. This latter number would be used in what we will term a *composite* profile.

The approach of using composite profiles has limitations as discussed below. So, in some cases rather than a single composite profile, we use a set of *individual* profiles. The individual profiles were selected from the EPA Speciate Database (Hsu *et al*. 2006), and CRPAQS source profiles.

What follows is a list of profiles used in the CMB analysis, and some description of their development and modifications. For a fuller description, see Appendix A: Source Profile Development.

3.1.1 Ammonium Nitrate

Ammonium nitrate is among the largest components of Bay Area $PM_{2.5}$. Virtually all of it is *secondary* –formed in the atmosphere from other constituents, specifically ammonia and nitric acid. Thus, ammonium nitrate has no direct sources, so it itself is considered a source in the CMB model. The ammonium nitrate profile uses its theoretical composition.

Because of uncertainty and data gaps in measurements, ammonium was not used in the CMB model, and without it, it is not possible to estimate the fraction of nitrate that is ammonium nitrate vs. sodium nitrate, the latter deriving from non-anthropogenic sea salt. As a result, the CMB model may overestimate the anthropogenic contribution from this source.

3.1.2 Ammonium Sulfate

Unlike nitrate, there are significant primary sources of sulfate. The ammonium sulfate profile allows for the accounting of additional sulfate formed secondarily, deriving from the conversion of SO_2 from other sources, especially refineries and ships. As with ammonium nitrate, the ammonium sulfate profile uses its theoretical composition.

3.1.3 Marine Air Profile

Marine air contains a variety of salts found in sea water though not necessarily in the same ratios. Figure 3.1 shows the major constituents in sea water.

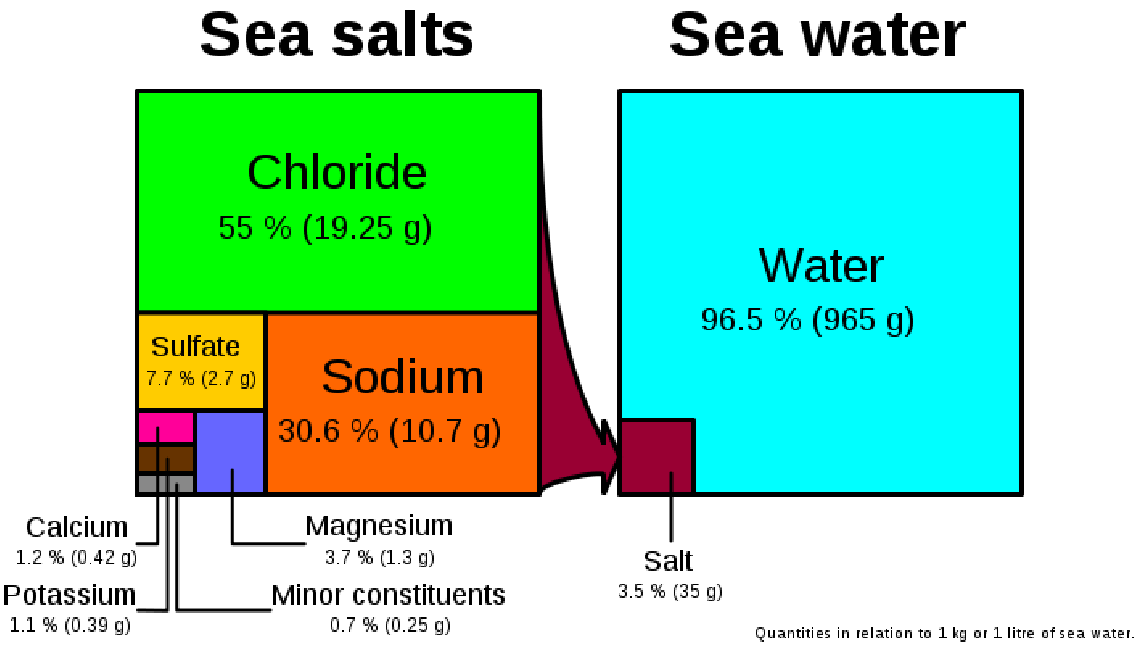


Figure 3.1. Salts in sea water. Source: Grobe (2008). Bromine and strontium are also present in smaller concentrations.[2]

This sea salt composition was compared with concentrations at the various air monitoring sites, for samples where marine air was likely present in significant amounts. For some samples the component fractions of species were similar to those of sea water. For other samples, there was a reduction of most marine species relative to sodium (see Appendix A1.) This appears to be the impact of *aging* of marine air, where the air traveling over urban areas loses chloride and bromine in particular, and gains nitrate, a process that has been identified elsewhere (see, e.g., Pio and Lopes 1998). The analysis indicated that other species were also lost – calcium, potassium, magnesium, and strontium. It is also possible that Grobe's data may not be representative of our area.

To account for the large transformation of marine air in some of the samples, we developed two marine profiles. One represented fresh marine air, with composition fractions equal to those in Figure 3.1 scaled to sum to 1. For uncertainty values we used a weighted average of ambient standard deviations from Point Reyes on days where the air was believed to contain a fresh marine component and standard deviations from a marine profile developed by Desert Research Institute.

The other marine profile represented aged marine air, where the species other than sodium were reduced by 50%, and the total rescaled to sum to 1. Although the aged air contains nitrate, it was decided to exclude it in the aged marine profile because nitrate is of anthropogenic origin. The intent was that the CMB source apportionment would account for this nitrate as part of its apportionment into ammonium nitrate while the amount accounted as "marine" would be of natural origin. (See Appendix A1 for more details.)

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[2] Wikipedia: http://en.wikipedia.org/wiki/Sea_salt#Composition (Accessed 6/6/12)

3.1.4 Geological Profile

A geological profile derived from a composite of measurements of dirt samples from around the Bay Area was taken from Chow *et al.* 1995. This had been found to be adequate previously so it was used in the present analysis.

3.1.5 Residential Woodsmoke Profile

A composite residential woodsmoke profile had been developed from filter samples collected in neighborhoods with considerable wood burning. The profile had been adjusted to remove contamination from marine and motor vehicle components.

A range of profiles was available from other studies (Chow *et al*. 2004). These were compared with the Bay Area profile, species by species. The Bay Area composite profile species were adjusted to be within one standard deviation of the profile distribution from other sources. If the Bay Area standard deviation for a given species was greater than the standard deviation of the profiles from the other studies, the latter standard deviation was used. (See Appendix A2 for details.)

3.1.6 Forest Fire Profile

Comparison between EC and OC at various sites showed that during periods with forest fires, OC was greatly elevated relative to EC. For residential wood burning, the OC/EC ratio was just over 3 to 1. But during forest fires, the OC/EC ratio appeared to be closer to 9 to 1. Since OC and EC are the two largest components of woodsmoke, we decided it would be useful to develop a separate profile for forest fires.

An analysis of other species showed that their ratio to EC was higher for forest fires than for residential woodsmoke, but their ratio to OC was similar. In other words, EC was a smaller fraction of the total mass in forest fires than in residential woodsmoke. Therefore, we decided to make the forest fire profile with a lower fraction of EC (from about OC/3.3 to OC/8.7), raising all other species fractions to compensate. (See Appendix A3.)

3.1.7 Ships

Oceangoing ship emissions have had a distinctive chemical signature. Although virtually all forms of motorized transportation equipment use fossil fuels, only ships have burned residual fuel oil. This is the only substantial source of vanadium (see Table 2.2), and also the largest source of nickel.

A profile was developed starting with published residual oil emission profiles and modified with an analysis of ambient data from Point Reyes. Specifically, regressions were performed with each of the other species as the dependent variable and with vanadium as one of the independent variables.[3] The vanadium slope was used to scale the other variables relative to

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[3] Where there were multiple possible sources for the species, other indicator species were included as independent variables.

vanadium, each slope multiplied by the estimated fraction of vanadium in ship exhaust (0.12%). The final profile was the simple average of the slope-derived estimate and the residual profile estimate. (See Appendix A4 for details. Note that this profile was developed based on emissions before the CARB rule requiring ships to use cleaner fuels.)

3.1.8 Cooking profiles

Cooking profiles were selected from the Speciate and CRPAQS databases. Analysis revealed large variation in some species. For example, the amount of sodium could vary by orders of magnitude: clearly some cooks use more salt than others. Because the distributions were not symmetric, but frequently with a long right tail, we decided to use individual profiles randomly selected, rather than a pooled profile. (See Section 4.)

3.1.9 Diesel and Gasoline Profiles

Both the Speciate and CRPAQS databases contained many diesel and gasoline profiles. Unfortunately, no subset could be considered representative of the emissions from current Bay Area motor vehicles, especially with newer regulations on fuels and engines. Although the CRPAQS profiles might in theory be more representative, since the cars and trucks sampled were from California, the profiles were challenging, with EC+OC fractions often considerably greater than 100%. Attempts to make adjustments in EC and OC failed.

As an alternative, these profiles were randomly sampled (as discussed in Section 4), with any profile the sum of whose components exceeded 100% scaled to 100%.

3.1.10 Fireworks Profile

Typically in the Bay Area potassium is well correlated with organic carbon. But occasionally potassium concentrations are much higher. We noticed that this occurred mostly on January 1 or July 4, suggesting fireworks. Initially, a profile was developed based on gunpowder. But fireworks may contain a range of elements for color, like strontium, copper and barium. Conversely, elevated potassium may be associated with other sources.

An analysis of ambient data was performed, identifying days with very high potassium. There did indeed appear to be a subset of these days associated with fireworks (all occurring within one day of January 1 or July 4) and another subset not associated with fireworks and not occurring near these dates.

Of the fireworks-related days, we saw considerably elevated values for copper, strontium and magnesium. On the other high potassium days, we saw elevated levels of iron, manganese, calcium, and elemental carbon. These latter may indicate brake wear.

The fireworks profile was developed using the ambient measurements on days with an obvious fireworks signature. We backed out the contributions of woodsmoke and marine air, and averaged the residuals, using their standard deviations for the profile standard deviations. (See Appendix A5 for details.)

3.1.11 Brake Profile

On some days with potassium outliers, we found elevated iron, copper, manganese, zinc, titanium, and strontium, all of which can be significant components of brake wear. To account for such days, we developed a brake profile based on a set of profiles from the Speciate and CRPAQS databases.

3.2 Completeness of source list

The range of possible sources is much wider than listed here. Nevertheless, we can check the completeness of our list of profiles in a couple of ways. One is to compare it to the BAAQMD Emissions Inventory. The inventory lists a total of 47 tons/day of directly emitted $PM_{2.5}$, of which 29 tons are carbonaceous (that is, from burning fossil fuels, wood or other biomass, and cooking), and another 6 tons are geological. Thus, our profiles encompass most of the inventory.

A second method is to examine the CMB analysis in cases where it does not fit well. This has led to the discovery of several missing sources, e.g., excess potassium was evidence of fireworks. A large discrepancy between the fitted and actual measured species concentration is reflected in the chi-square statistic. The fitting results are discussed in Section 5.4.

4. A Model for Source Apportionment -- CMB

In this analysis, we modified the EPA CMB model (EPA 1990). This modified model uses a Monte Carlo approach that simulates sets of sources and chooses the sets with the best fit.

The CMB model works as follows. Suppose we have a measurement from an ambient filter sample, $\mathbf{y} = (y_1, y_2, \ldots, y_i, \ldots, y_p)$, where y_i = concentration of species i in the sample. Let j = the index for a given source (e.g., geological dust or wood smoke), and let f_{ij} = the fraction of species i in source j. (For example, if woodsmoke is 15% elemental carbon, then $f_{ij} = 0.15$ for i = EC and j = woodsmoke). The goal of CMB modeling is to find concentration estimates, c_j, so that for each species, i,

$$c_1f_{i1} + c_2f_{i2} + \ldots + c_Jf_{iJ} \cong y_i \tag{1}$$

where J = number of source categories used in the CMB analysis. In EPA's CMB model, the measure of closeness between y_i and its source mix estimate, $c_1f_{i1} + c_2f_{i2} + \ldots + c_Jf_{iJ}$, is the estimated standard deviation of their difference. Symbolically, let u_i = standard deviation (measurement error) of y_i, and let v_{ij} be the standard error of f_{ij}. As discussed above, v_{ij} represents not only measurement error in the fraction f_{ij}, but also the variation in the source itself. The variance of the difference is estimated as:

$$u_i^2 + c_1^2v_{i1}^2 + c_2^2v_{i2}^2 + \ldots + c_J^2v_{iJ}^2 \tag{2}$$

and the CMB minimizes the sum over i of the squared differences in the pairs of terms in (1) divided by (2), that is, it finds the values of $c_1, c_2, \ldots, c_J$ that minimize:

$$\sum_{i=1}^{p} \frac{(y_i - \sum_{j=1}^{J} c_j f_{ij})^2}{u_i^2 + \sum_{j=1}^{J} c_j^2 v_{ij}^2}$$

4.1 A Monte Carlo approach to fitting CMB

In this analysis, we developed and used a new approach to fitting CMB. Rather than incorporating the variation in source profiles into the fit, as in (2) above, we repeatedly sample from the profile distributions. Specifically, to fit a given observation, our method is as follows:

1. Sample from each of the J source profile categories. If the category is represented by a vector of means and standard deviations, we sample these as normal random variables. If the category is represented as a set of profiles, we sample one of the profiles with uniform probability from the set and add a normal random error to represent its measurement error.

2. We fit the model minimizing the sum of squares of term (1) divided by u_i^2:

$$S = \sum_{i=1}^{p} \frac{\left(y_i - \sum_{j=1}^{J} c_j \tilde{f}_{ij}\right)^2}{u_i^2}$$

where $(\tilde{f}_{1j}, \tilde{f}_{2j}, \ldots, \tilde{f}_{pj})$ are the vectors of simulated source profiles.[4] In each simulation, if any coefficient, c_j, was negative then the source j with the most negative coefficient was eliminated and the model was refitted. The eliminations continued until all coefficients were ≥ 0.

Steps 1 and 2 were repeated 100,000 times, each time computing S + T, where T represents how closely the calculated mass matched the measured mass:

$$T = \min\left[\left(\frac{y_t - b_t}{u_t}\right)^2, \left(\frac{y_s - b_t}{u_s}\right)^2\right]$$

where y_t = total measured mass, u_t = its uncertainty, $b_t = c_1 + c_2 + \ldots + c_J$, $y_s = y_1 + y_2 + \ldots + y_p$, and $u_s^2 = u_1^2 + u_2^2 + \ldots + u_p^2$. The second term is included for the occasional case where the measured total mass is very different from the sum of the species, that is, y_t is very different from y_s.

Of these, for the 25 with the smallest values of S+T, the coefficients and also the simulated source profiles were saved.

3. For each source, j, the weighted average of these 25 coefficients was computed, weighting by $e^{-(S+T)/2}$. This estimate is somewhat ad hoc; there isn't a theoretical statistical justification for it, although it's the local mean around the maximum likelihood. We term this "localized mean likelihood" estimate.[5]

4.2 Choice of CMB species

Although a large number of species are measured, for some there are few or no observations that exceed the corresponding uncertainties.[6] Using them adds noise to the analysis rather than information so these species were excluded from the analysis.

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[4] The c_j's can be found directly without an iterative fit because S is of the form of a weighted multiple linear regression, which has a closed-form solution.

[5] We also tried taking the average across all 100,000 samples, again weighted by $e^{-(S+T)/2}$. This is basically the mean of the posterior distribution, the Bayesian solution assuming a flat prior on the original source profiles. This posterior mean did not perform as well as the localized mean likelihood approach by several measures, so we decided to adhere to the ad hoc approach.

[6] The measurements provided for CMB analysis include corresponding uncertainties but not limits of detection. The uncertainty is taken to be the standard deviation of the measurement error. Frequently, measurements smaller than the corresponding uncertainty are included, even though they can't be reliably distinguished from zero. If a given chemical species is found in most samples and several source profiles but falls below the uncertainty in some samples, this provides evidence of a lack of sources with that species in these particular samples. But if a species is almost always below its corresponding uncertainty, including the source uncertainties, then it basically can't be measured precisely enough to provide any real information.

Also, several species occur in more than one form: chlorine, sodium and potassium may be measured both as elements on filter 1 and ions on filter 2. Sulfur occurs both as an element on filter 1 and as part of sulfate on filter 2. To avoid double-counting, only one of the forms was used in any analysis. Sulfur was never used. For the other forms, the data quality appeared to vary by lab, and not all labs measured all forms. For the analysis of the data from each lab, the form with the better correlations with other species was chosen.

Table 4.1 shows a list of species, those used in the analysis shown with an asterisk. The table shows the percentage of ambient samples where the measured concentration exceeded its uncertainty; that is, where the measured concentration is larger than one standard deviation. It also shows the number of source categories where the species fraction exceeds the uncertainty of the fraction. Those species with high percentages were included, with the exceptions to avoid double-counting, as noted above.

For most species, the choice was the same for all sites. Exceptions included:

Chloride was used except for San Jose, where chlorine was used because chloride was not measured. **Ammonium** was used except for Point Reyes, where it was not measured. Elemental **sodium** was used except for Point Reyes, where it was not measured. **Chromium** was used except for Point Reyes, where it was not measured. **Rubidium** was used for Point Reyes, which uniquely had many observations above the corresponding uncertainty level.

The species excluded were those for which there were no sources.

Table 4.1. Species measured and species used in CMB, and percent of concentrations above uncertainty

	DRI			Used in CMB	IMPROVE	Used in CMB	RTI	Used in CMB	# of sour-ces*
	Livermore	OaklandW	Vallejo		PointReyes		SanJose		
# samples	**152**	**151**	**152**		**154**		**234**		
Mass	99%	99%	99%		97%		100%		
Chloride	86%	97%	96%	*	99%	*			7
Nitrate	100%	100%	100%	*	100%	*	100%	*	7
Sulfate	100%	100%	100%	*	100%	*	100%	*	10
Ammonium	86%	83%	84%	*			96%	*	8
Sodium Ion	92%	97%	95%				63%		7
Potassium Ion	99%	100%	99%				96%		10
Organic Carbon	91%	83%	80%	*	87%	*	100%	*	8
Elemental Carbon	81%	77%	66%	*	70%	*	60%	*	7
Magnesium	7%	17%	14%	*	79%	*	64%	*	6
Sodium	21%	41%	28%	*	95%	*	94%	*	7
Aluminum	41%	50%	38%	*	38%	*	59%	*	6
Silicon	76%	75%	71%	*	82%	*	97%	*	6
Phosphorus	0%	0%	0%		1%		0%		4
Sulfur	100%	100%	100%		97%		100%		10
Chlorine	78%	91%	88%		78%		92%	*	5
Potassium	97%	97%	96%	*	97%	*	100%	*	10
Calcium	78%	86%	81%	*	97%	*	100%	*	9
Titanium	28%	30%	31%	*	69%	*	36%	*	3
Vanadium	1%	5%	1%	*	74%	*	13%	*	2
Chromium	17%	21%	18%	*	6%		53%	*	6
Manganese	4%	15%	7%	*	40%	*	45%	*	6
Iron	95%	99%	95%	*	97%	*	100%	*	7
Cobalt	0%	0%	0%				30%		1
Nickel	1%	7%	3%	*	55%	*	38%	*	5
Copper	14%	26%	18%	*	37%	*	78%	*	6
Zinc	48%	72%	53%	*	92%	*	85%	*	4
Gallium	0%	0%	0%						0
Arsenic	0%	0%	0%		13%		6%		1
Selenium	3%	9%	5%	*	69%	*	19%	*	4
Bromine	30%	30%	22%	*	97%	*	85%	*	5
Rubidium	1%	2%	3%		12%	*	8%		3
Strontium	9%	19%	11%	*	89%	*	14%	*	9
Yttrium	10%	7%	6%						1
Zirconium	12%	19%	16%		12%		6%		3
Niobium	0%	0%	0%						2
Palladium	0%	0%	0%				0%		1
Silver	0%	0%	0%				8%		0
Cadmium	0%	0%	0%				7%		0
Indium	0%	0%	0%				7%		0
Tin	0%	0%	0%				6%		0
Antimony	0%	0%	0%				6%		2
Barium	0%	0%	0%				9%		4
Lanthanum	0%	0%	0%						0
Mercury	0%	0%	0%						0
Lead	17%	23%	24%	*	73%	*	21%	*	6

* Number of sources where species mean exceeded species uncertainty.

4.3 Using the Carbon-14 measurements

The species measurements for the filters selected for C-14 analysis were averaged for each site and period. For each of the sites and periods, the C-14 analysis provided an estimate of the fraction of modern carbon, f. New variables were then made by taking the total carbon measurement, TC = OC + EC, and computing a modern carbon value, f * TC, and a fossil carbon value, (1-f) * TC. These were used in place of the OC and EC measurements in the CMB analysis.

The CMB analysis was performed for these averaged filter measurements using the new variables, yielding adjusted fits and also using OC and EC measurements instead, yielding unadjusted fits. For each analysis, the fraction of modern carbon was estimated by summing the amount of modern carbon, mc, and fossil carbon, fc, attributed to each of the fitted sources, then computing the ratios mc/(mc+fc).

Figure 4.1 shows the results. For San Jose and, to a lesser extent for Livermore, the amount of modern carbon was over-represented in the unadjusted fits relative to the measured C-14 fraction, so that the CMB analysis appears to have attributed too much of the carbon to modern sources such as wood burning and cooking relative to the fossil sources, principally diesel and gasoline exhaust. The adjusted CMB fits had ratios consistently closer to the C-14 fraction for these sites. For Oakland, the ratios from the unadjusted fits were relatively close to the corresponding measured C-14 fraction; the adjusted values were not substantially closer to the C-14 ratios. For Vallejo, the unadjusted summer ratios were substantially higher than the corresponding C-14 ratio and the ratio for the adjusted fit was closer. For the other periods, the adjustment did not make a substantial improvement.

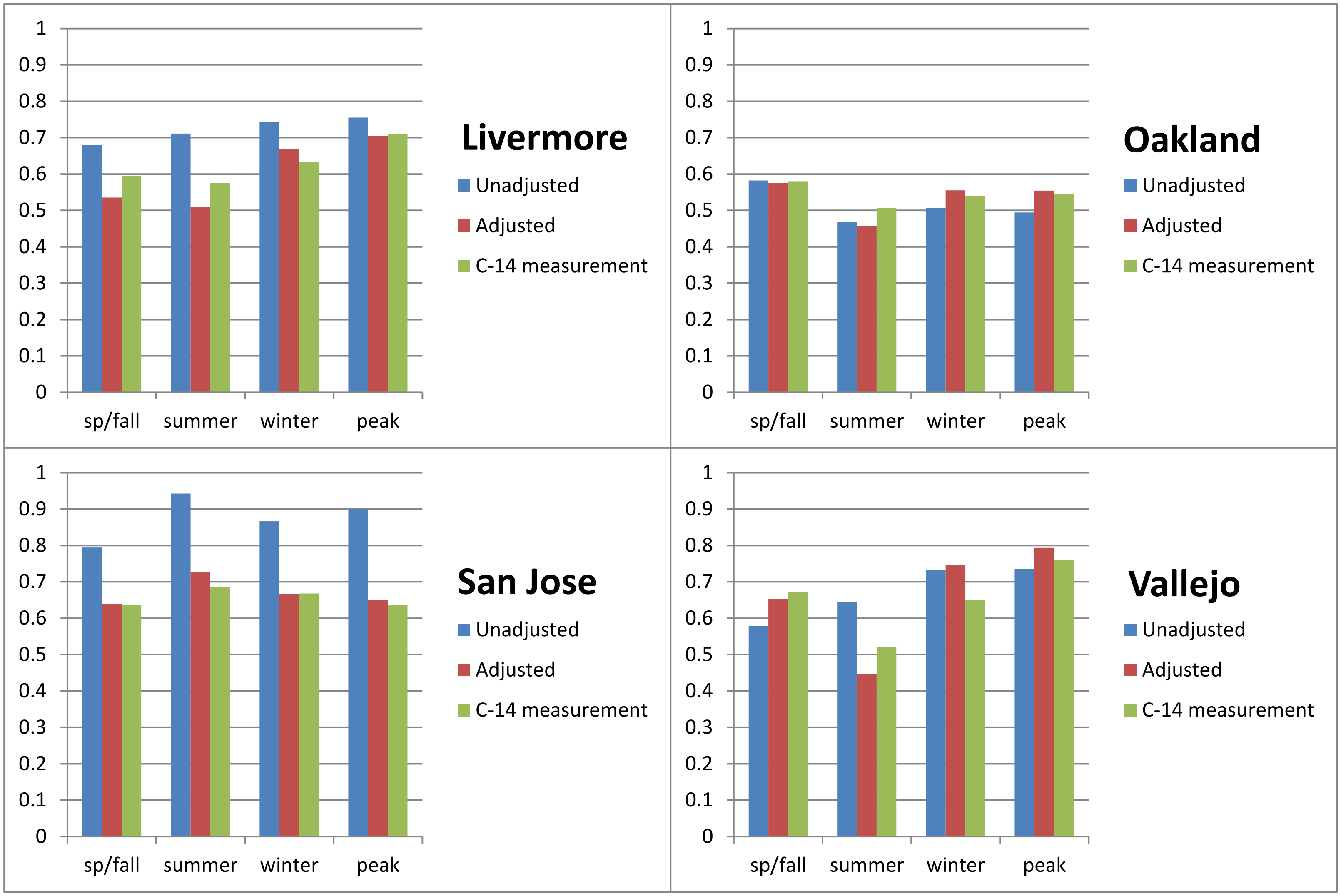


Figure 4.1. C-14 fraction of modern carbon and the fractions from CMB analysis adjusted and unadjusted for C-14.

Figure 4.2 shows the CMB results for wood, diesel, gasoline, and cooking with and without C-14 adjustments. The results are limited to the sources with substantial fractions of carbon, and totaled for the year. As with Figure 4.1, there are sizeable changes for Livermore and San Jose, but little change for Oakland and Vallejo. For Livermore and San Jose, the estimated woodsmoke and cooking concentrations have been adjusted downward and the diesel and gasoline increased. The amounts of decrease in the woodsmoke and cooking concentrations are approximately proportional as are the increases in gasoline and diesel exhaust.

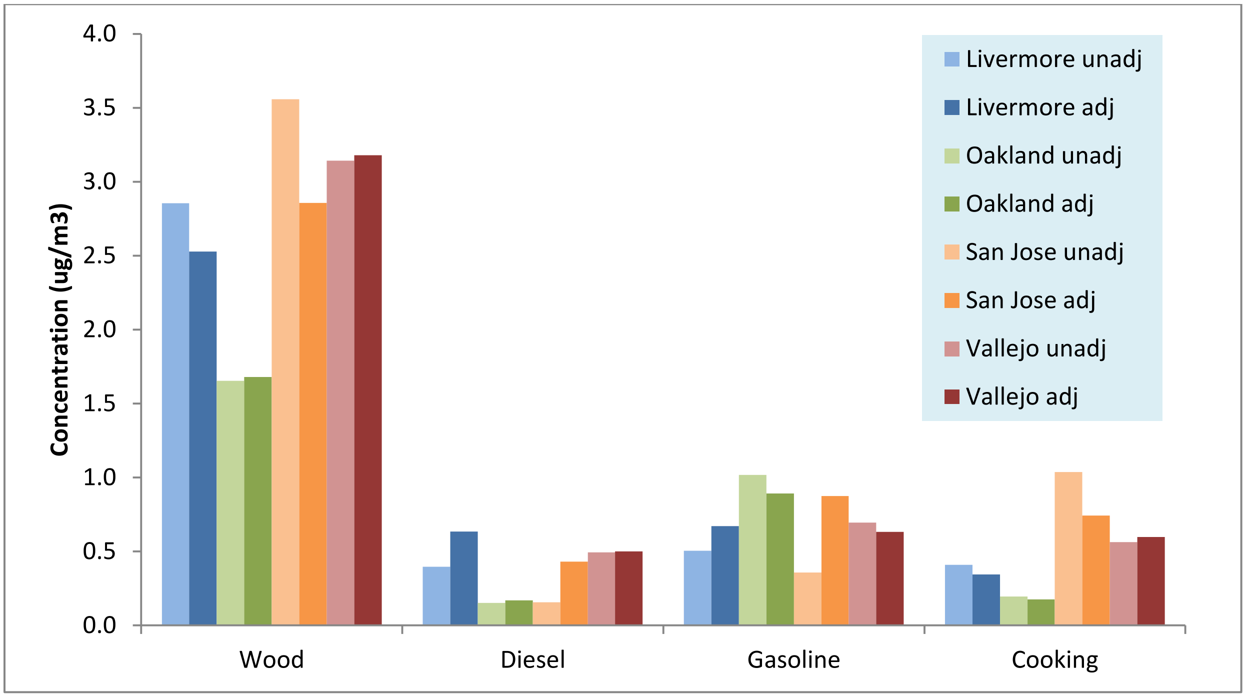


Figure 4.2. CMB-estimated annual average concentrations for carbonaceous sources, adjusted and unadjusted for C-14.

To summarize: 1. there are some substantial biases, 2. the degree of bias varies among sites, 3. the bias is in one direction for Livermore and San Jose, and 4. the proportional bias is roughly the same among new carbon sources and among fossil carbon sources. Therefore, the following adjustments were made to the individual CMB fits:

	Livermore	**Oakland**	**San Jose**	**Vallejo**
Rationale	consistent bias	little bias	consistent bias	bias
Adjustment	adjust all values to ratio*	no adjustment	adjust all values to ratio*	adjust summer values to ratio*

* Multiply new carbon sources by r and old carbon sources by 1 + (1-r)c_n/c_f, where c_n = new carbon concentration, c_f = fossil carbon concentration. Where r = f_a/f_u, f_a = (adjusted new carbon fraction + c-14 new carbon fraction)/2 and f_u = unadjusted new carbon fraction for a given season and site.

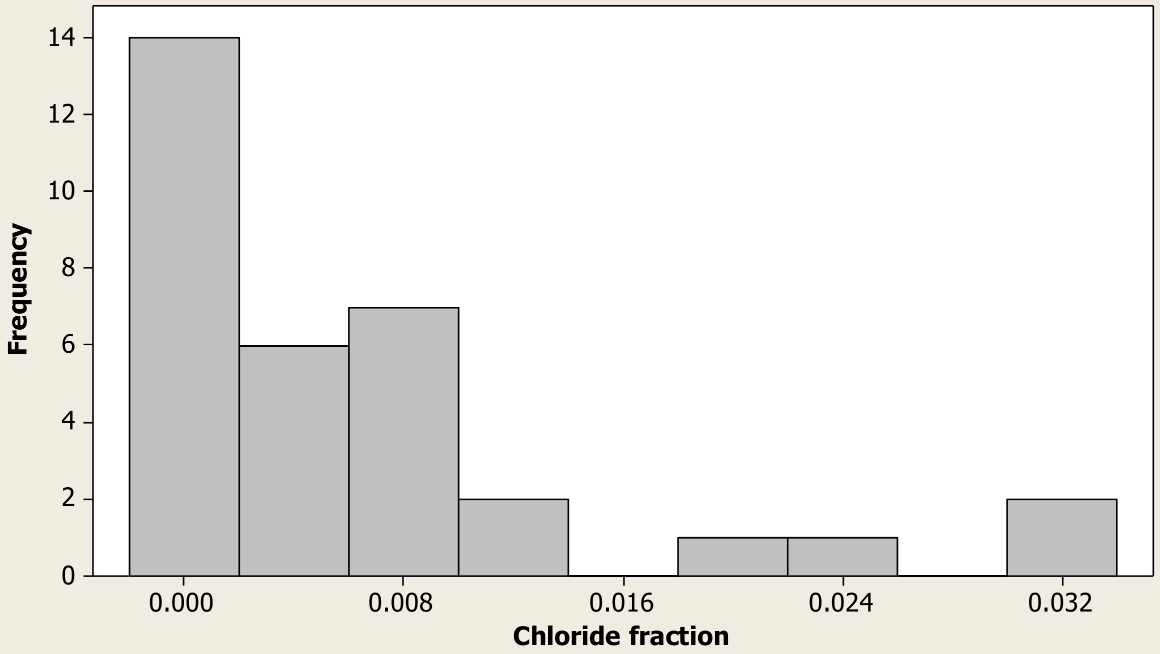
4.4 Strengths and limitations

Knowledge of sources must be brought in at some point in the source apportionment process. A strength of the CMB approach is that it incorporates prior knowledge of the composition of various sources as part of the model. As a result CMB is capable of differentiating pollutant contributions from multiple sources that may be confounded if they are highly correlated, e.g., brake wear and diesel exhaust.

An important weakness of the CMB model is that it requires source profiles specifically tailored to the ambient data. Due to changes in regulations, the profiles of diesel, gasoline, and perhaps brake and tire wear have changed in California significantly, especially over the past decade. Another key change occurred in July 2009 – the low sulfur fuel requirement for ships. Thus, the available source profiles, which were mostly developed earlier in the decade or even the past century, may differ significantly from the actual chemical composition of emissions from those sources.

A second weakness is the assumption that the source compositions are normally distributed, that is, with a bell shape and no large outliers. There is no reason this must be the case. For example, Figure 4.3 shows a histogram of chloride ion fractions from various cooking profiles, i.e., how much salt was used. The distribution is skewed, not bell-shaped: Many profiles have no salt, some have a small amount, and a few have quite a bit.

Figure 4.3. Histogram of chloride fraction in cooking profiles from EPA and CARB



This distribution is clearly non-normal (under the assumption that all samples are equally probable.) Thus, we believe that the use of the Monte Carlo approach, which samples the clearly non-normal distributions from individual source profiles, offers an advantage.

The use of the Monte Carlo approach offers another advantage. It selects those fits that best match the data within the likely ranges of the source distributions. If the actual source has altered systematically, e.g., contains more or less of one chemical species vis-à-vis the others than the source profile would suggest, then the Monte Carlo method will select those draws where the random error is in the direction of the actual source profile.

5. CMB Results

The results are presented with a focus on their connection with national and State $PM_{2.5}$ standards, which are set for annual and 24-hour average $PM_{2.5}$. The latter standard focuses on the highest daily $PM_{2.5}$ measurements. Therefore, we present the results in terms of annual average and peak $PM_{2.5}$ concentrations. We also present results by season. Note that in this section, we present results for source categories; section 6 provides estimates for individual sources.

5.1 Annual averages

Figure 5.1 shows annual averages of the quarterly averaged source contributions from 10 source categories by site. Table 5.1 shows the percentages for each site. Woodsmoke and ammonium nitrate are the two largest contributors at every urban site, averaging 25% and 22% of the total, respectively; marine air dominates at the Point Reyes background site, representing half its total.

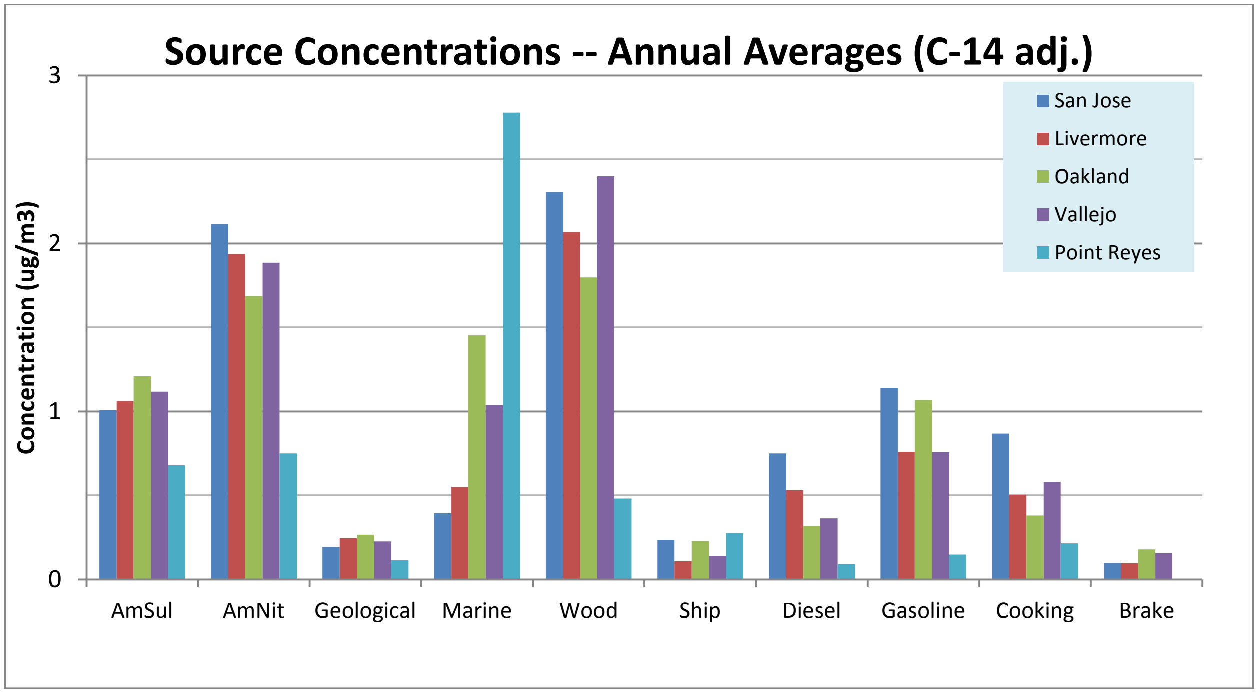


Figure 5.1. Annual averages of quarterly averaged CMB estimated concentrations for various source categories, adjusted for Carbon-14.

Table 5.1. Annual source category contribution percentages, by site.

	AmSul	AmNit	Geological	Marine	Wood	Ship	Diesel	Gasoline	Cooking	Brake
San Jose	11.1%	23.2%	2.1%	4.3%	25.3%	2.6%	8.2%	12.5%	9.5%	1.1%
Livermore	13.5%	24.6%	3.1%	7.0%	26.3%	1.4%	6.8%	9.7%	6.4%	1.2%
Oakland	14.1%	19.6%	3.1%	16.9%	20.9%	2.7%	3.7%	12.4%	4.4%	2.1%
Vallejo	12.9%	21.7%	2.6%	12.0%	27.7%	1.6%	4.2%	8.7%	6.7%	1.8%
4 Site Ave	**12.8%**	**22.3%**	**2.7%**	**10.0%**	**25.0%**	**2.1%**	**5.7%**	**10.9%**	**6.8%**	**1.5%**
Point Reyes	12.2%	12.4%	2.1%	53.7%	7.6%	5.7%	0.9%	2.2%	3.0%	0.1%

Among anthropogenic sources, ammonium sulfate is the third greatest urban source category, representing 13% of the total. Gasoline (non-diesel fossil) is next at 11%, followed by cooking (7%) and diesel (6%).

The contributions from the ship category are low about 2% at urban sites, and 6% at Point Reyes. These are about half the percentage estimated previously, due to reductions in emissions that started in July 2009.

Geological contributions averaged 3% at urban sites, and brake contributions averaged 1.5%. Fireworks were not shown, but averaged less than 0.1% at every site.

5.2 Comparison with the Emissions Inventory

The CMB analysis includes source categories for all $PM_{2.5}$ in the Bay Area, whereas the Emissions Inventory is largely limited to directly-emitted anthropogenic $PM_{2.5}$. The source contributions estimated by CMB were compared with the Emissions Inventory where they overlapped. This overlap excluded the secondary PM sources that CMB identified – ammonium nitrate and sulfate – and also marine air. The Emissions Inventory sources were summed to correspond to CMB categories. For example, residential fireplace and woodstove emissions were added to the emissions from the burning of waste material and wildfires to correspond to the wood-burning category in CMB. It was assumed that CMB apportioned natural gas PM into the "Gasoline" category.

Figure 5.2 shows a comparison of CMB and the 2010 Emissions Inventory for the seven source categories represented in the inventory. Shown are percentages of the total from those seven sources.

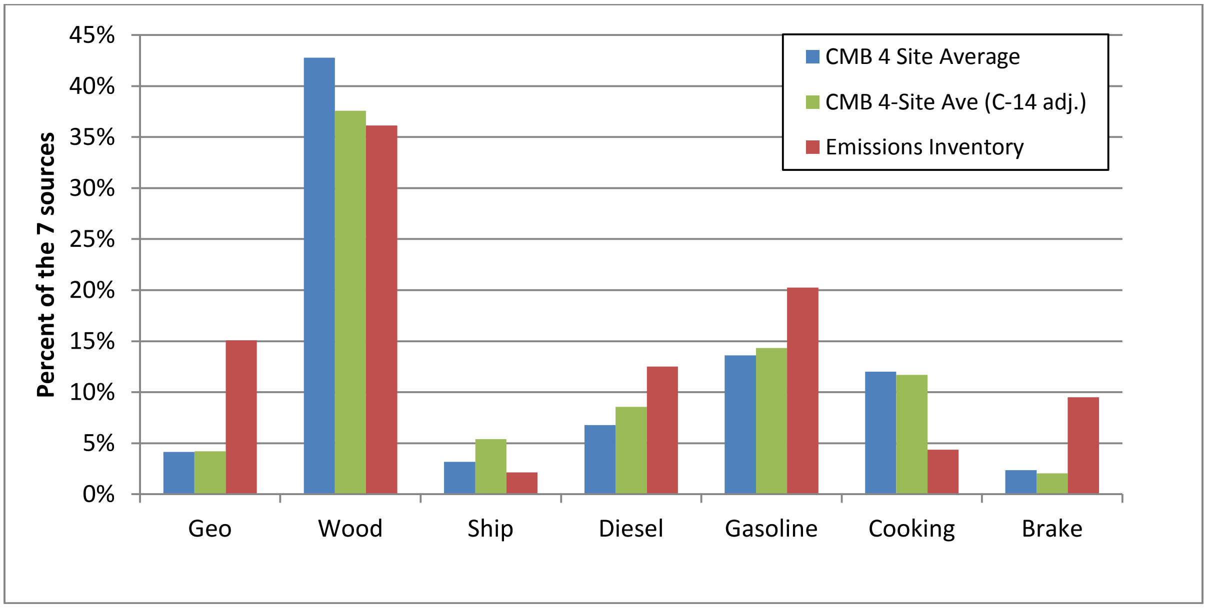


Figure 5.2. 4-site average percentages of annual CMB-estimated contributions from seven source categories vs. 2010 Emissions Inventory. The percentages are out of the total of the seven categories, not total $PM_{2.5}$. Shown are results from CMB analyses both adjusted and unadjusted for Carbon-14.

The figure shows a rough congruence between the EI and CMB: In both, woodsmoke is the largest source among the overlapped categories – as great as or greater than diesel and gasoline contributions combined. In both CMB and the EI, the ship emissions are only a few percent.

There are some significant discrepancies, however. Geological dust estimates are over three times as much of the $PM_{2.5}$ in the EI as in CMB. The CMB estimate is likely closer to the actual dust percentage in ambient concentrations. Geological dust has a clear chemical signature. Silicon and aluminum are two of its major components. The lack of high ambient concentrations of these elements implies that there is little geological dust in the air samples collected at the monitoring sites. Part of the discrepancy likely arises because the EI estimates what is emitted into the air, not what stays in the air. Geological dust is composed mainly of larger particles (> 2.5 microns) that settle out of the atmosphere in a matter of hours. Products of combustion are mostly smaller particles (< 1 micron) that can stay suspended for days. Thus, a larger proportion of the combustion emissions will remain suspended long enough to reach ambient monitors. The same explanation may apply to brake wear, which is also composed mainly of larger particles. As with geological dust the EI estimates are several times those of CMB.

The values for diesel and gasoline are both larger in the EI than with CMB. The "gasoline" EI category includes all natural gas emissions as well. The values for wood burning and cooking are correspondingly less in the EI than CMB.

The values for the ship contribution are close. Here, both the EI and CMB have considerable uncertainty. This is because the EI uses a somewhat arbitrary ocean boundary of 3 km beyond which ship emissions are not counted and CMB uses a ship profile based on a fuel that is no longer used near ports.

The EI cooking estimate is considerably lower than the CMB estimate. This is the opposite of the previous estimates; in the previous EI, where condensable particles were included, the cooking estimate was higher. If roughly half of condensable particles were included in the EI, the two estimates would be close.

The C-14 adjusted CMB percentages are closer to the EI for most categories, adding credence to the value of the adjustment.

5.3 Peak concentrations

Figure 5.3 and Table 5.2 show the CMB-estimated source contributions for the 10 days with the highest $PM_{2.5}$ concentrations at each site. The goal is to identify the PM sources on days when the 24-hour $PM_{2.5}$ concentrations are elevated.

At every urban site, the largest source is ammonium nitrate, contributing almost 40% of the total on average. Woodsmoke adds another 30%. These two sources contribute more to peak concentrations than to the annual average. Engine exhaust, diesel plus gasoline, contributes about 15%, similar to its annual average contribution. All other sources – ammonium sulfate, cooking, marine, geological and ship – contribute less to peak $PM_{2.5}$ than to annual.

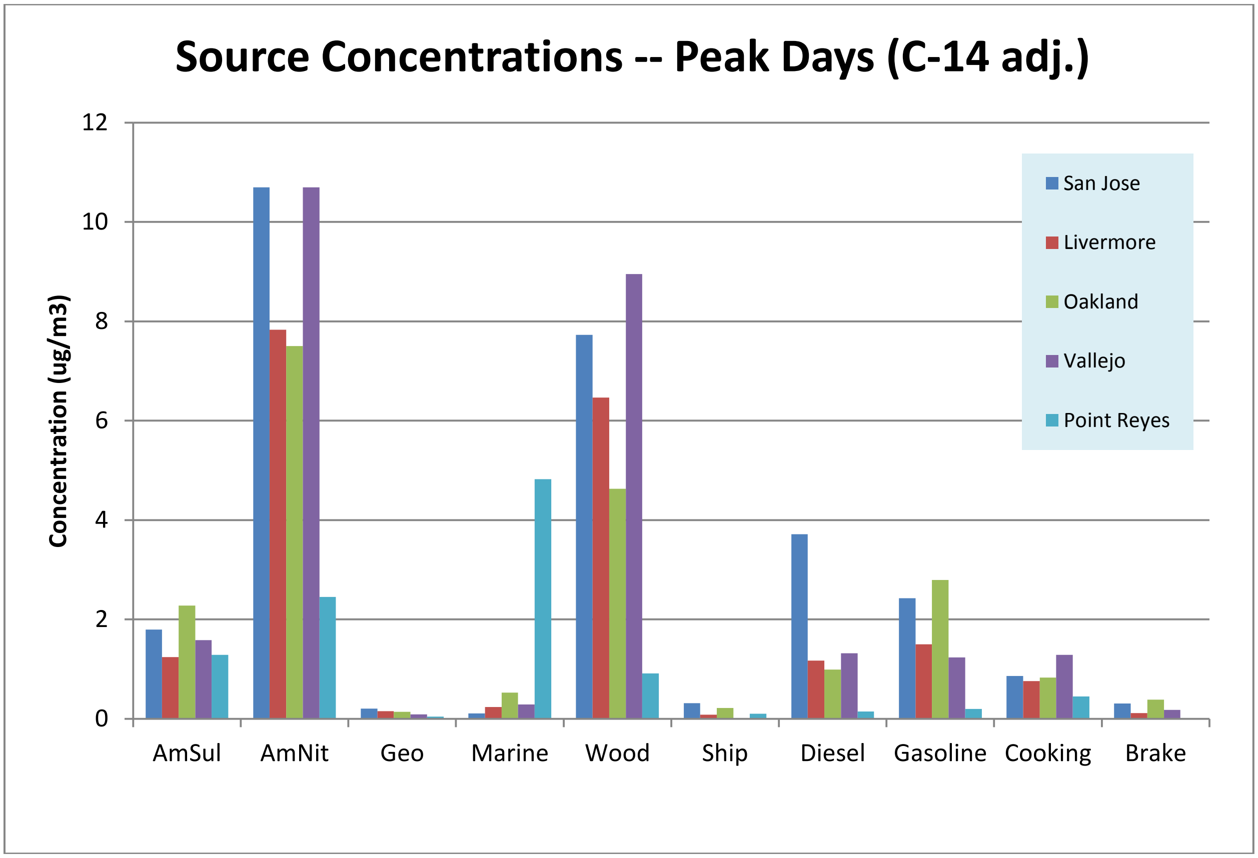


Figure 5.3. Average of concentrations from the 10 days with highest $PM_{2.5}$ concentrations at each site.

Table 5.2. Peak source percent contributions, by site.

	AmSul	AmNit	Geological	Marine	Wood	Ship	Diesel	Gasoline	Cooking	Brake
San Jose	6.4%	38.0%	0.7%	0.4%	27.5%	1.1%	13.2%	8.6%	3.1%	1.1%
Livermore	6.4%	40.1%	0.8%	1.2%	33.1%	0.4%	6.0%	7.7%	3.9%	0.6%
Oakland	11.2%	37.0%	0.7%	2.6%	22.8%	1.1%	4.9%	13.8%	4.1%	1.9%
Vallejo	6.2%	41.7%	0.3%	1.1%	34.9%	0.1%	5.1%	4.8%	5.0%	0.7%
4 Site Ave	**7.4%**	**39.2%**	**0.6%**	**1.2%**	**29.7%**	**0.7%**	**7.7%**	**8.5%**	**4.0%**	**1.1%**
Point Reyes	12.0%	23.6%	0.4%	46.2%	8.9%	1.0%	1.4%	1.9%	4.4%	0.1%

5.4 Goodness of fit

Evaluating goodness of fit is challenging. On the one hand, the fits appear very good because each CMB fit is based on the top 25 out of 100,000 trials. On the other hand, the chi-square statistic – a standard measure of goodness of fit – depends on a lab's evaluation of its precision. If the lab claims that its measurements are very precise, then the chi-square statistic will be larger. Thus, across the 864 fits from the five sites, a chi-square test found significant deviations in 141, or about one-sixth. All but eight of these "problems" were for Point Reyes or San Jose, where the reported lab error was much smaller.

Another way to estimate goodness of fit is to compare the observed and estimated values. The calculated mass and measured mass are compared in Figure 5.4.1. The calculated mass is the sum of the CMB source profile coefficients. Over 99% of the fits met the EPA CMB application criterion that the ratio of calculated mass to measured mass should be between 0.8 and 1.2 (EPA 1990, page 57), except for Livermore where it was 97% of the fits.

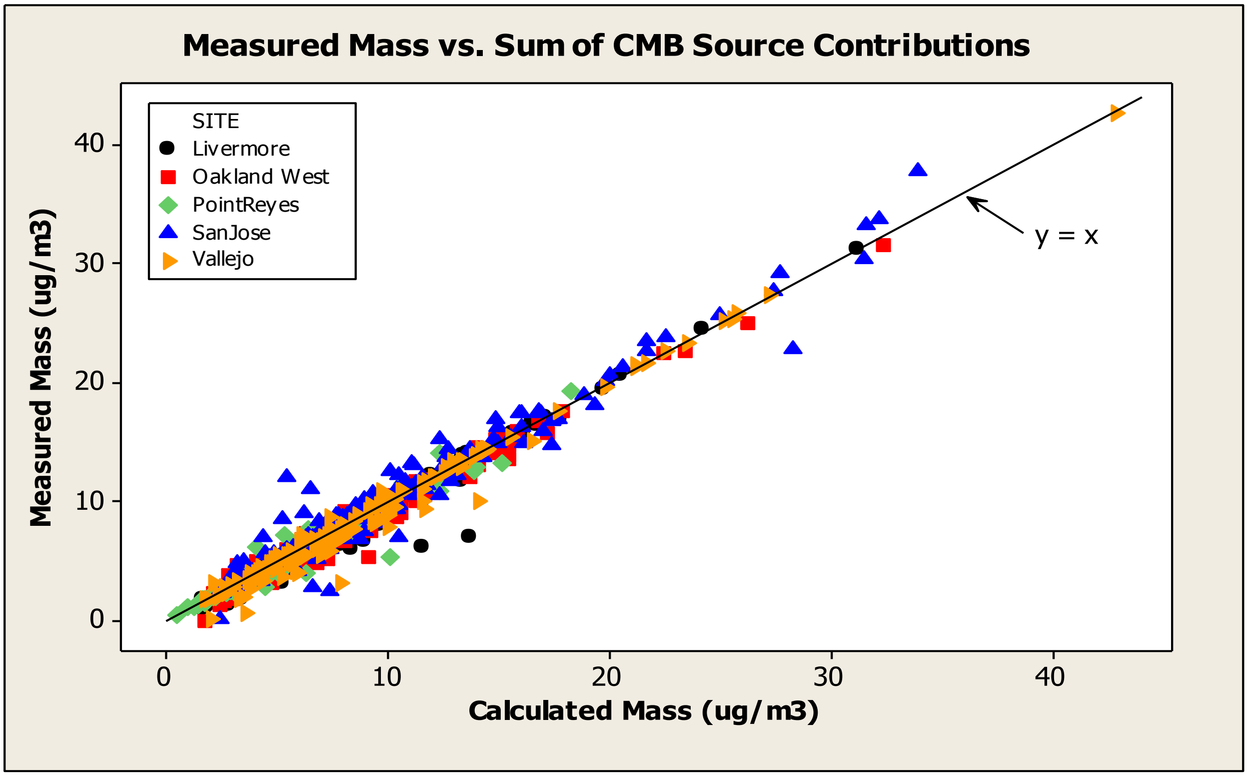


Figure 5.4.1. Measured mass vs. CMB-calculated mass. Calculated mass is the sum of CMB-estimated source contributions. Also shown is the line y=x where the measured mass = calculated mass.

We can compute an "R^2" statistic for each of the species by considering the ratio of the average squared residual with its sample variance, that is, if $y_{i1}, y_{i2}, \ldots, y_{in}$ are the measurements for species i, and the corresponding CMB-estimated values are $\hat{y}_{i1}, \hat{y}_{i2}, \ldots, \hat{y}_{in}$, define

$$R_i{}^2 = 1 - \frac{\sum_{k=1}^{n}(y_{ik} - \hat{y}_{ik})^2}{\sum_{k=1}^{n}(y_{ik} - \bar{y})^2}$$

for the R^2 of species i. Figure 5.4.2 shows these values for each site. For nitrate and sulfate, the values are virtually 1 because they are source categories themselves. Other species with high R^2 values include calcium, chlorine, iron, organic carbon, potassium, and silicon. All R^2 values for iron are over 0.995, perhaps because the very low uncertainty of iron measurements imparts a significant influence on the CMB fit. Conversely, low R^2 values found in some cases may be because of errors in species measurements. For example, manganese and nickel values are rarely above the corresponding measurement standard deviation for Livermore, West Oakland or Vallejo, just the sites with R^2 values less than 0.5. Point Reyes, with a high percentage of measurements above the corresponding standard deviations had an average R^2 of 0.92 across species, compared with 0.66 to 0.75 for the other sites.

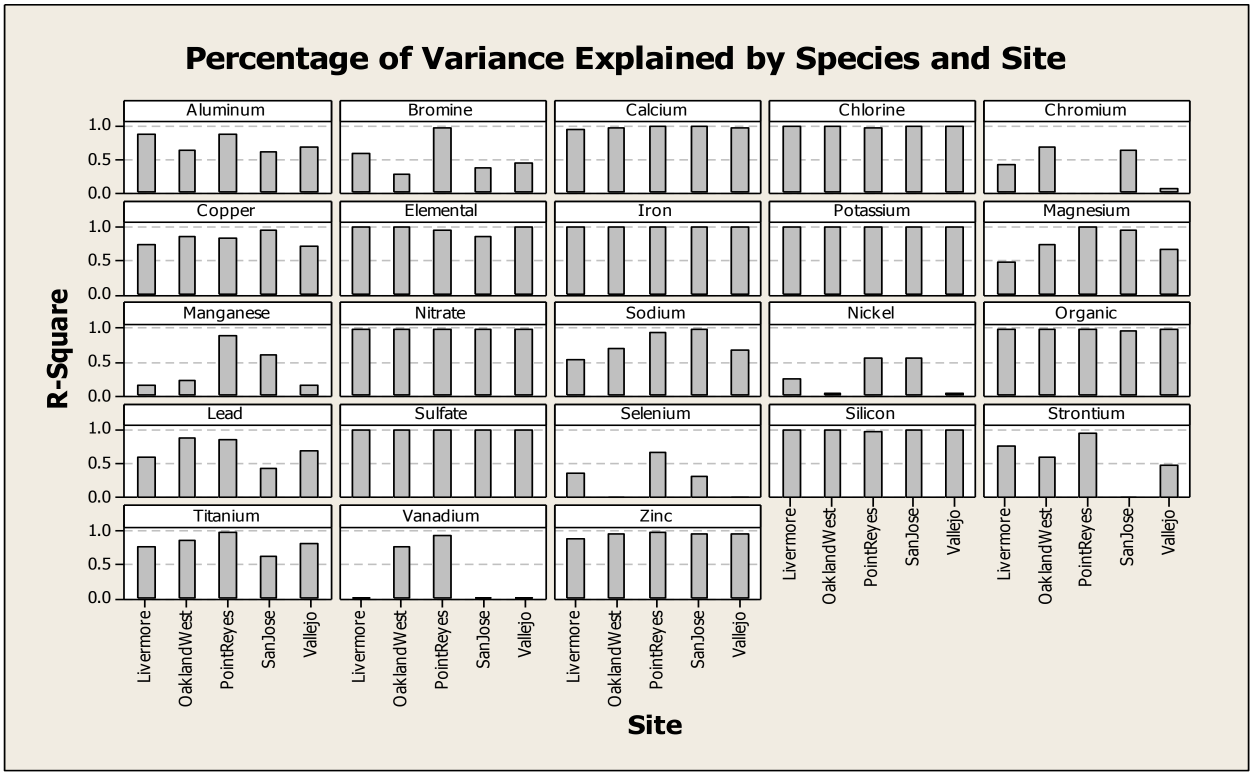


Figure 5.4.2. Percentage of variance explained. R^2 values for each site and species.

An examination of the residuals – the difference between the measured concentration and the concentration estimated from CMB – offers some clues to missing or misspecified source profiles. Figure 5.4.3 shows the mean of the residuals by species and site divided by the mean for that species. A positive residual indicates that the observed concentration was larger than the CMB prediction and a negative residual indicates the opposite. Also shown are 95% confidence intervals for the mean of the residuals.

For example, in the plot for aluminum in the upper left, the value for Oakland is 0.30 so that, on average, the measured values were 30% higher than the corresponding predicted value. The confidence interval was 0.18 to 0.41. In this case, the CMB model substantially underestimated aluminum concentrations.

Several features stand out: The Elemental Carbon concentrations were overestimated at every site – by several percent, except for San Jose where the overestimation was large. We suspect that this is a reflection of the cleaner-burning diesel engines. The San Jose anomaly may be a measurement issue.

Vanadium concentrations were also substantially overestimated except for Point Reyes. This is likely because of the new rules requiring ships along the California coast to switch from residual fuel oil to marine distillate, which has much lower vanadium concentrations than the ship profile used in the CMB analysis, which was developed for residual fuel oil; and it suggests Point Reyes gets a substantial fraction of its ship emissions from ships further from shore, where the CARB rule doesn't apply.

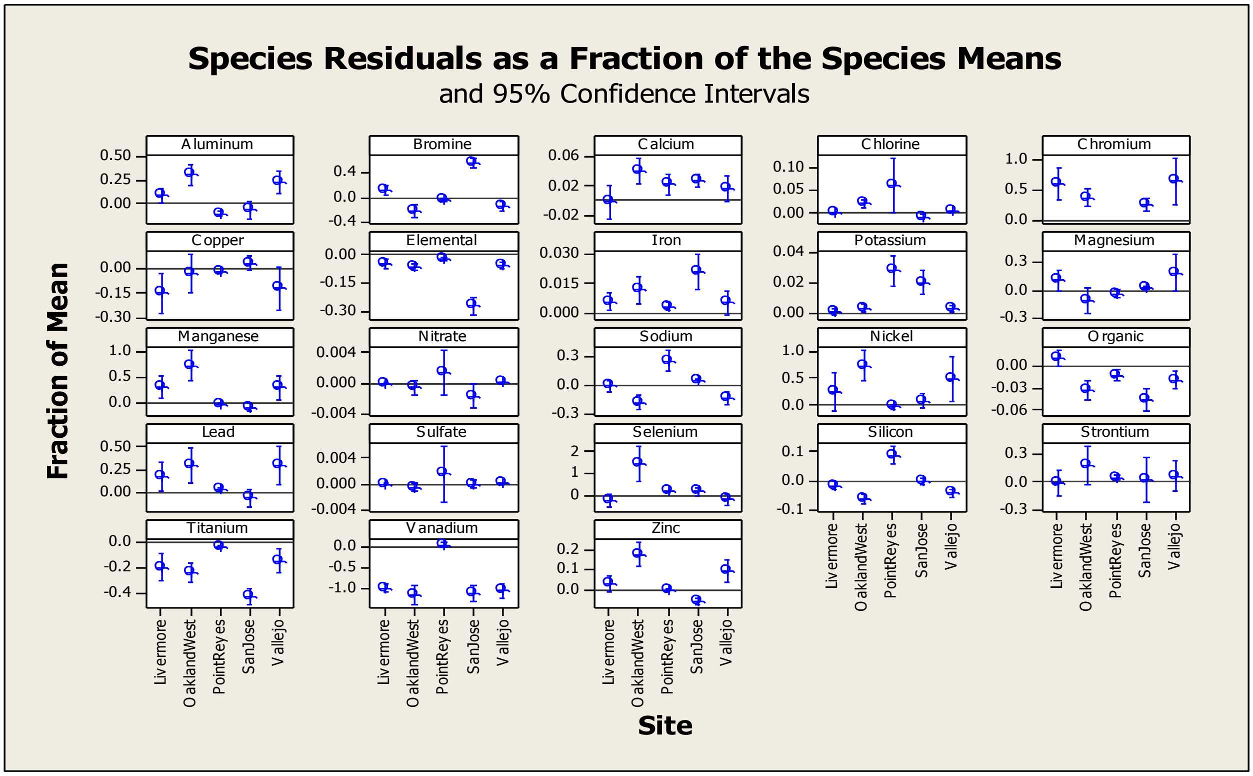


Figure 5.4.3. Mean residual error (observed – predicted) as a percent of mean for species in CMB. Also shown are 95% confidence intervals for the mean, and zero lines where observed = predicted.

Silicon is overestimated for Livermore, Vallejo and West Oakland, and underestimated for Point Reyes. The pattern with aluminum is the reverse. This may indicate a limitation with the geological profile and/or differences resulting from varying measurement accuracy among labs.

Chromium is underestimated for all sites where it was measured, possibly indicating an unidentified source or a lab measurement issue.

Selenium was vastly underestimated at West Oakland. A residual plot showed several residuals where the measured value was many times the predicted (although the median residual was actually negative). This suggests an omitted source that registers intermittently.

Note that there are large variations from species to species in the range of fractions. Examples include sulfate and nitrate, whose means differ by less than 0.4% from zero. On the other extreme are vanadium and selenium, where the mean residual is larger than the species mean in absolute value, i.e., the predicted values average more than double or less than half the measured values. In some species, very small relative differences were statistically significant, e.g., iron where the differences were about 1%-2% of the mean. These differences were so small that they lack practical significance.

Measurements may differ by lab. Livermore, West Oakland and Vallejo were measured by the same lab, while San Jose and Point Reyes were each measured by a different lab. Note a pattern for aluminum, manganese, nickel, lead, and zinc, where the former three sites have values that differ from the other two.

5.5 Analysis by season

Figures 5.5.1 – 5.5.5 show CMB results by season for each site. $PM_{2.5}$ concentrations are highest in Nov-Jan. We defined this period as the winter season. Other seasons are defined as follow: spring as February-April, summer as May-July, fall as August-October. At every site, ammonium nitrate and woodsmoke are much higher in the winter season, as expected. Diesel and gasoline are also highest in winter due to in part winter's greater atmospheric stability.

Marine is lowest in winter, peaking in summer. This reflects the fact that stagnant conditions with easterly drainage airflows are common in winter months. In contrast, the winds that blow the rest of the year are typically westerly, carrying marine air from the Pacific Ocean.

Ship emissions peak in the summer at West Oakland and Point Reyes, roughly paralleling marine emissions. Ammonium sulfate is less variable from season to season, but peaks in fall at every site except Point Reyes. Cooking peaks in fall or winter.

Geological dust and brake wear are low in every season. Geological dust is lowest in winter, which would make sense as a combination of winter conditions of rain and low winds when it is not raining.

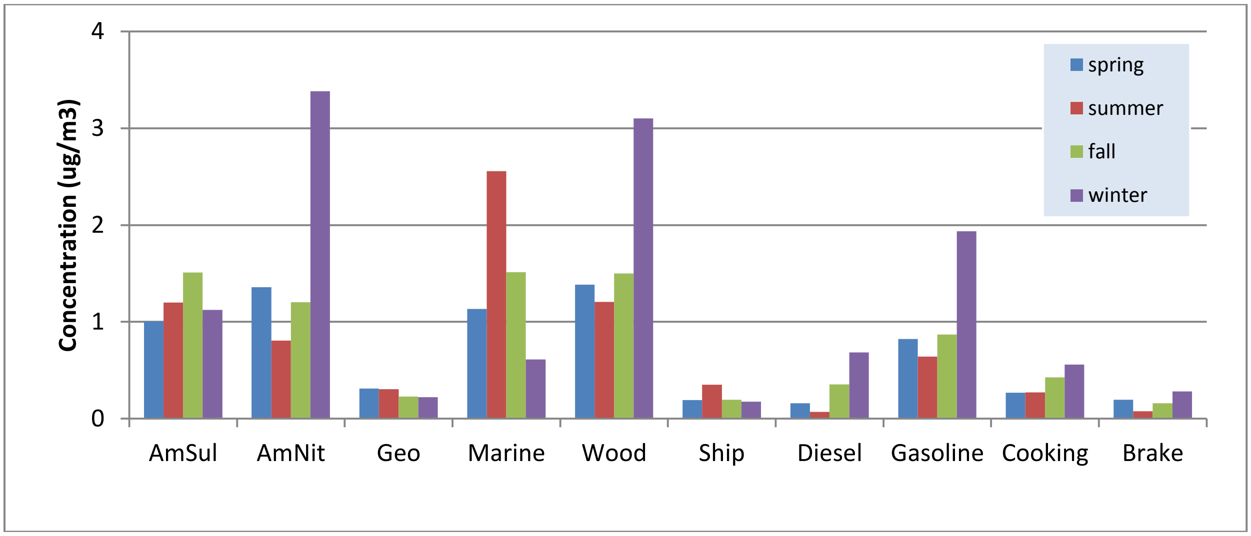


Figure 5.5.1. $PM_{2.5}$ source contributions by season, West Oakland, 2009-2011.

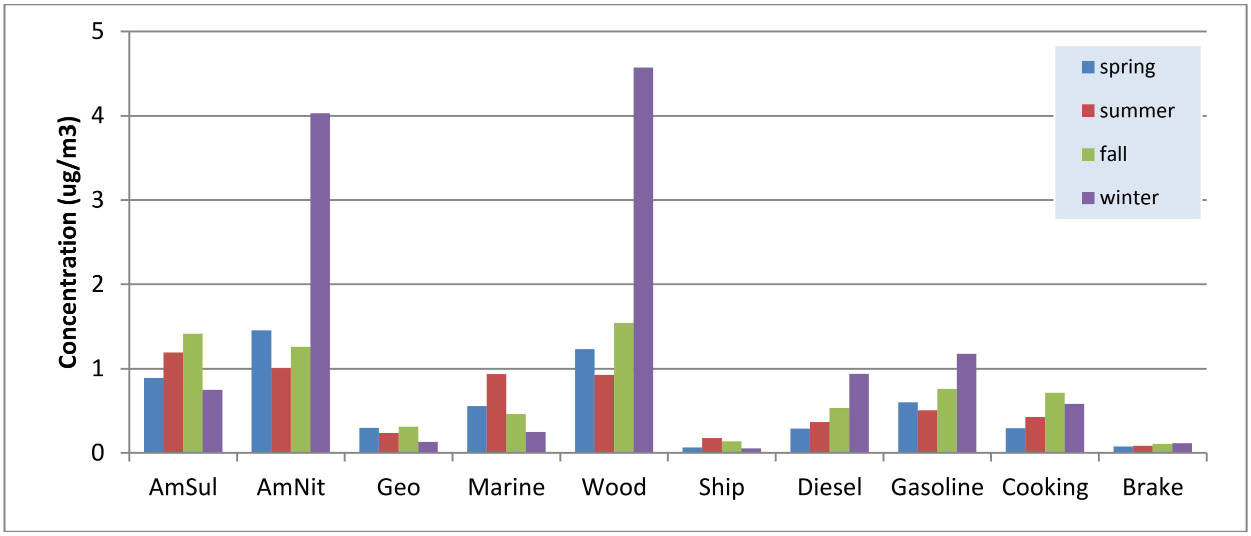


Figure 5.5.2. PM$_{2.5}$ source contributions by season, Livermore, 2009-2011.

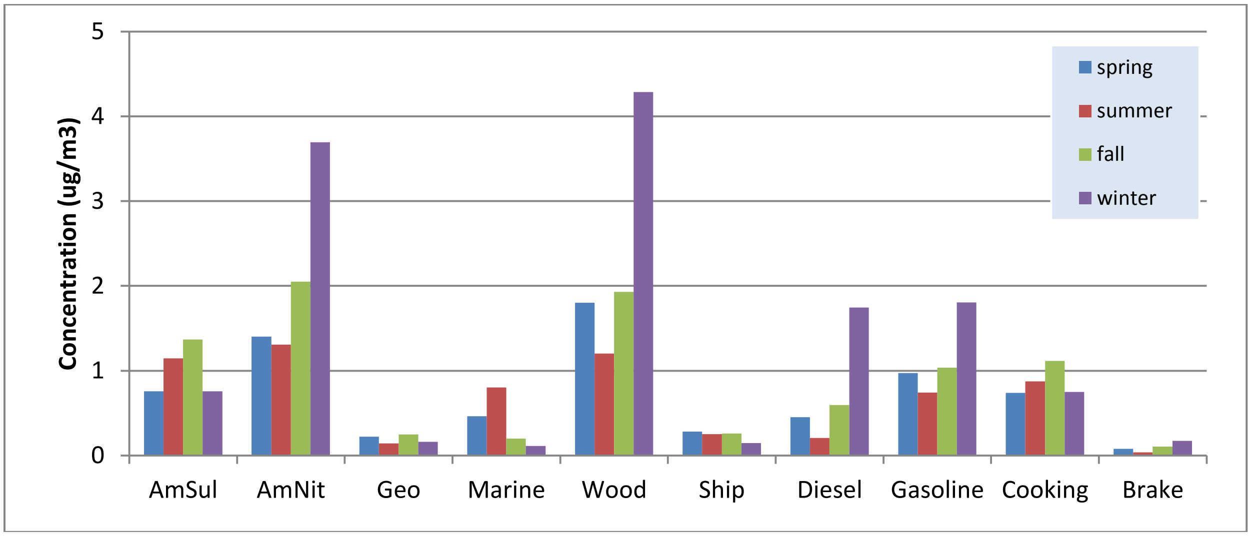


Figure 5.5.3. PM$_{2.5}$ source contributions by season, San Jose, 2009-2011.

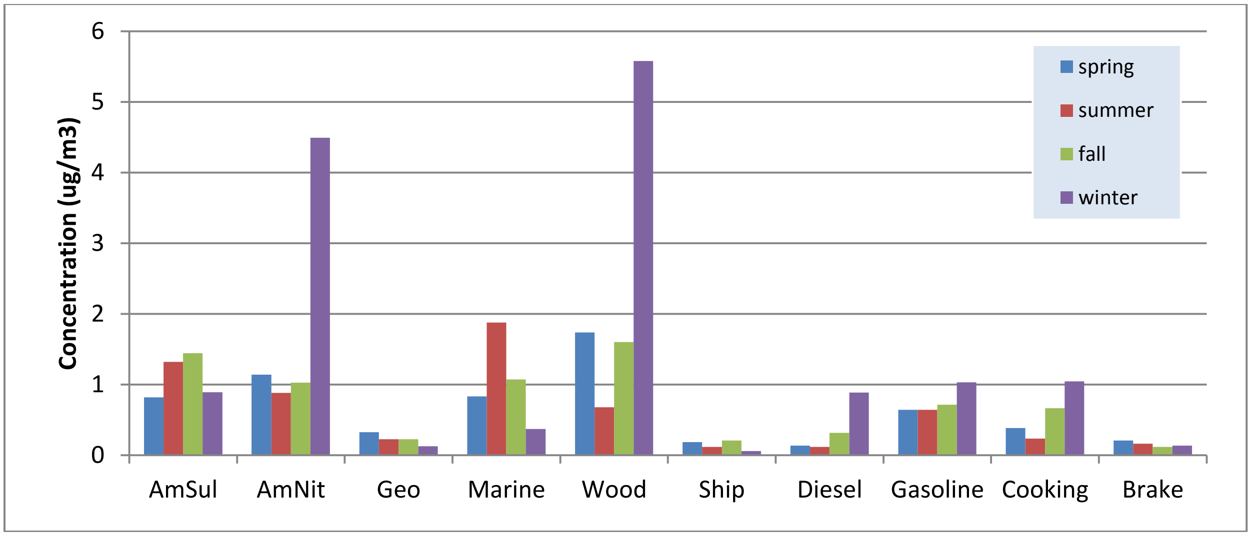


Figure 5.5.4. PM$_{2.5}$ source contributions by season, Vallejo, 2009-2011.

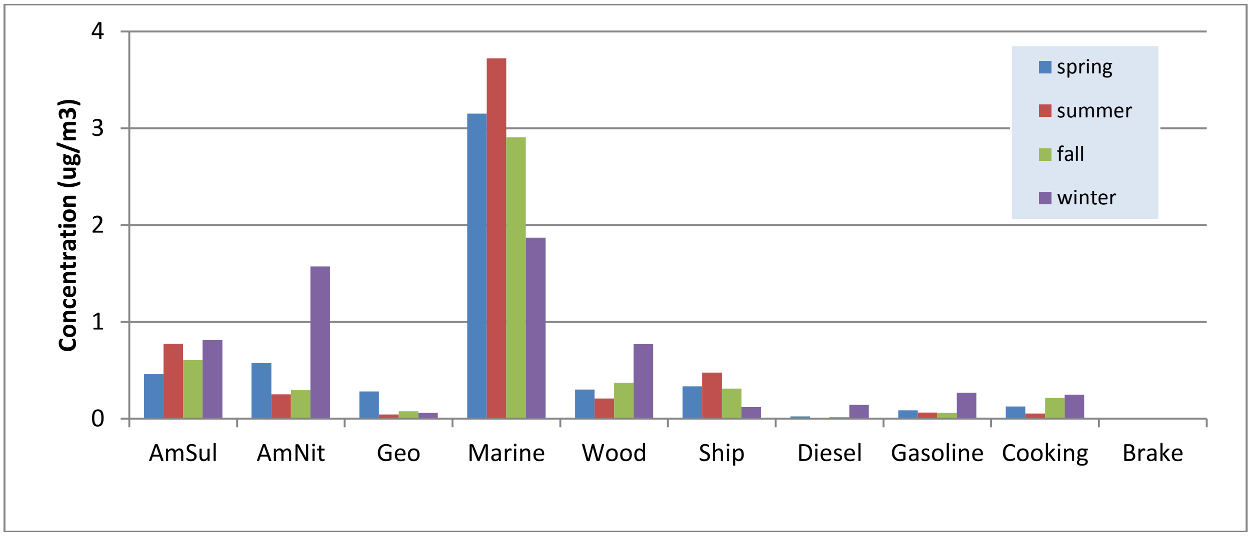


Figure 5.5.5. $PM_{2.5}$ source contributions by season, Point Reyes, 2009-2010.

5.6 Comparison with apportionment of data from 1999-2001

For the purpose of comparing the apportionment of data from 2009-2011 with data from 1999-2001, we applied the same methodology, computer program, and source profiles used for 2009-2011 to the 1999-2001 data. Because C-14 data for the 1999-2001 were unavailable, we used the unadjusted fits for both periods.

In each period, there were five sites, but the locations varied; the sites were paired as closely as possible. The sites at Livermore and Point Reyes were the same. San Jose Jackson (SJJ), operating in 2009-2011, was paired with San Jose 4th St. (SJ4), which operated in 1999-2001. Oakland was paired with San Francisco (both urban sites influenced by marine air), and Vallejo was paired with Bethel Island (both sites influenced by Central Valley $PM_{2.5}$, but clearly with Vallejo being an urban site). It is important to keep in mind that they are different in the following comparisons.

The periods compared are short and may be affected by different meteorology to some extent. The winter of 2000-2001, in particular, was more conducive to high $PM_{2.5}$. As a matter of fact it was the most conducive winter among all the years with data. The winter of 1999-2000, however, was moderate. Nevertheless, the comparison is based on annual averages, averaged by quarter; therefore, despite some impact from meteorology, the influence of meteorology is not expected to be substantial.

Figure 5.6 shows a source-by-source comparison of the apportionments in the two periods as discussed below:

Marine air is not impacted by trends in anthropogenic emissions. However, we did not find identical concentrations for this category for the two periods, even at Livermore and Point Reyes. This suggests that we might expect a considerable amount of variation just by chance as opposed to a systematic trend.

Geological dust shows an inconsistent pattern, though the difference between SJ4 and SJJ may represent a difference in the emissions in the immediate vicinity of each site.

Total PM$_{2.5}$ shows reductions for every pair, averaging about ⅓ at urban sites. Point Reyes shows only a marginal reduction, but in part this results from being heavily influenced by marine air.

The most dramatic and significant drops occurred with **diesel** and **gasoline** concentrations, each estimated to have dropped by 2/3 on average at urban sites. The sum of these fossil sources was comparable to ammonium nitrate or woodsmoke in the 1999-2001 period, but the combined contribution is apparently less in the 2009-2011 period. Comparing the 2000 values with the 2010 values fitted with Carbon-14, there is still a drop of more than ½ in diesel plus gasoline at every urban site.[7]

Ship concentrations show reductions similar to those of gasoline and diesel. This comports with reductions in ship emissions expected to result from a requirement for using cleaner burning fuels near the shoreline.

Ammonium nitrate dropped by about 40% at urban sites, 20% at Point Reyes.

Cooking concentrations dropped about 50% on average. Some of this decrease may be the result of the District's charbroiling rule.

Wood burning shows some reduction at Livermore, the only urban site with data from both periods. If analysis is limited to the period where most wood burning occurs, November 15 through February 15, however, the reductions at Livermore and Point Reyes were both 40%. (See Section 5.9) This finding is consistent with District wood-burning surveys, which also indicate a reduction in the amount of wood burning.

Ammonium sulfate remained essentially unchanged.

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[7] If anything, this underestimates the drop, since the 2000 data were fit without the C-14 measurements, and limited C-14 analysis in the previous study suggested that new carbon was over-represented there also.

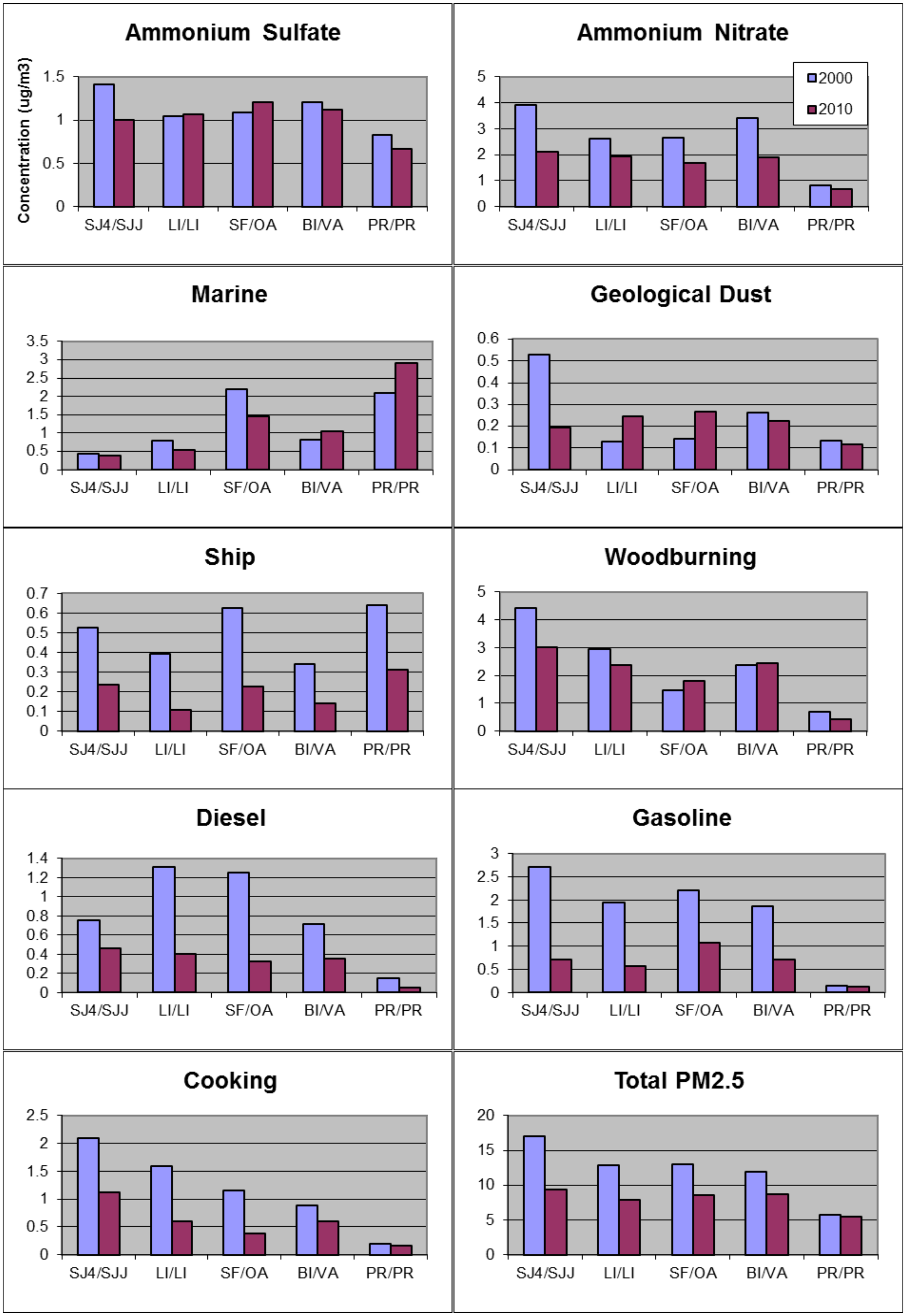

Figure 5.6. Comparison of 2000 and 2010 annual average source apportionment results.

5.7 Comparison with Central Valley sites

Estimating the sources of $PM_{2.5}$ in the Central Valley is useful for several reasons: to help validate the CMB model, to help validate the CMAQ PM simulations, which include the Central Valley, and to provide information on the composition of $PM_{2.5}$ from sites that may contribute to Bay Area pollution through transport.

Speciated $PM_{2.5}$ data were downloaded from AQS for selected Central Valley counties, from Butte in the north to Kern in the south. Samples with incomplete data were eliminated. The analysis was limited to 2009-2010. To ensure comparability, CMB analysis was done with OC/EC rather than C-14 for the Bay Area as well as the Central Valley sites. Table 5.3 lists the Central Valley sites analyzed.

Table 5.3. Sites with speciated $PM_{2.5}$ data from selected Central California counties.

Site	County	# samples analyzed	1st date	last date
Chico	Butte	85	4/1/2009	10/26/2010
Sacramento Del Paso	Sacramento	189	4/4/2009	11/7/2010
Sacramento T St	Sacramento	79	4/7/2009	10/26/2010
Modesto-14th St	Stanislaus	55	10/4/2009	10/26/2010
Visalia	Tulare	50	11/3/2009	10/26/2010
Fresno	Fresno	185	4/1/2009	11/7/2010
Bakersfield	Kern	103	7/21/2009	11/4/2010
Sequoia Nat'l Park-Ash Mountain #2	Tulare	119	1/1/2009	12/30/2009

The CMB model was run using the same methodology as for the Bay Area with the exception that the ship profile was excluded. The results are combined with those of the Bay Area and presented in the figures below, showing annual (average of quarterly averages) and peak (top 10) CMB-estimated source contributions. Several features stand out:

- There is generally a gradient of increasing annual $PM_{2.5}$ from north to south in the Central Valley driven by increasing concentrations of ammonium nitrate.
- Ammonium nitrate concentrations are higher in the valley than the Bay Area perhaps because of higher ammonia emissions from farming operations and the extensive use of fertilizer. Ammonium sulfate concentrations in the two areas are similar.
- Annual concentrations of woodsmoke are higher in the valley, which could be from residential wood burning, but also wildfires and/or secondary organic PM (PM formed in the atmosphere from gaseous carbonaceous molecules).
- Woodsmoke is a major factor in peak $PM_{2.5}$ at several Central Valley sites – Fresno, Sacramento-Del Paso, and especially, Chico.
- Diesel + gasoline + brake wear are relatively small across sites. This may be due, in part, to CMB underfit relative to new carbon sources.
- Although there was more geological dust in the Central Valley than the Bay Area, concentrations were well under 1 $\mu g/m^3$ except at the Bakersfield site.

- Ammonium sulfate is a small but consistent factor, yielding a not insignificant 1 µg/m^3 to 2 µg/m^3 across sites.

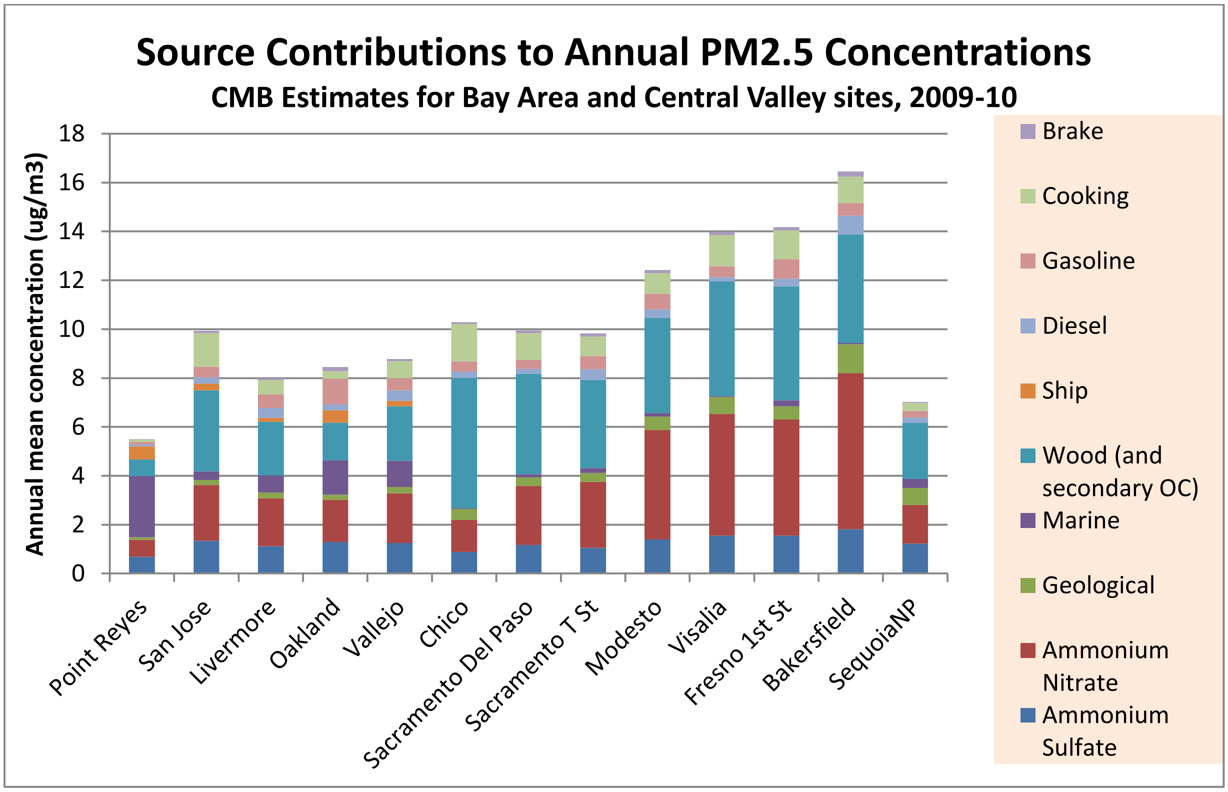

Figure 5.7.1. Source contributions to annual PM2.5 concentrations. CMB estimates for Bay Area and Central Valley sites, 2009-2010

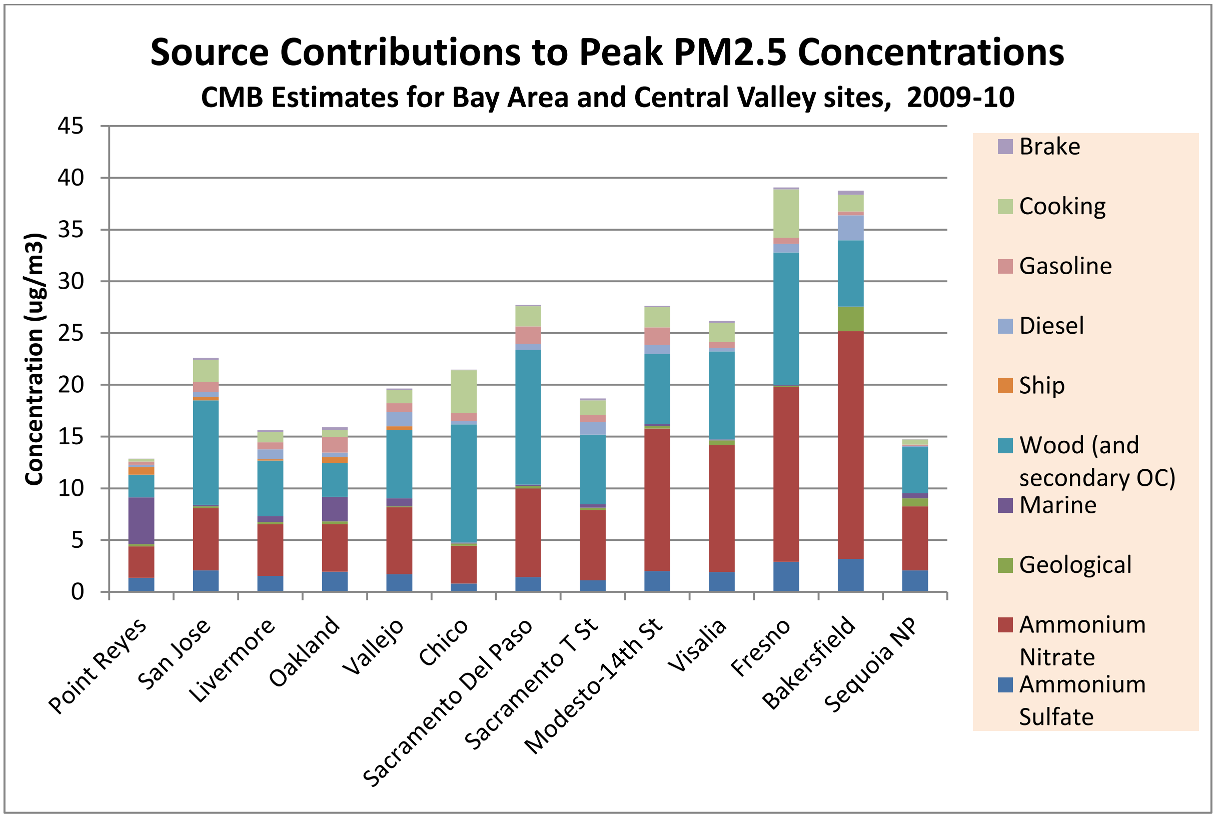

Figure 5.7.2 Source contributions to peak PM2.5 concentrations. CMB estimates for Bay Area and Central Valley sites, 2009-2010

5.8 Reduction in ship contributions

A CARB rule to reduce sulfur in ship fuel took effect in July 2009 that was expected to reduce $PM_{2.5}$ emissions from ships near the California coastline by 75% (CARB 2011). Figure 5.8 shows a plot of CMB-estimated contributions to annual ambient $PM_{2.5}$ from ship emissions before and since July 2009.[8] The estimated drop was considerable at four of the five sites and in line with the expected reductions from the rule despite the fact that the ship emissions source profile was based on the pre-July 2009 ship fuel formulation. The drop for Point Reyes was large, though less than for Livermore, Oakland or Vallejo. This may be because a significant fraction of the ship-derived $PM_{2.5}$ Point Reyes receives is emitted by ships beyond the limit of the CARB rule that continue to use residual fuel oil.

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[8] An effort was made to provide comparable pre- and post- estimates. Livermore and Vallejo each had a year's worth of data before and after July 2009, so quarterly averaged annual averages are shown. For San Jose, the data begin in the 2nd quarter of 2009, so we compared this quarter against the 2nd quarter of 2010. For Point Reyes, a full year was available before & after, and therefore used. For Oakland, the 1st and 2nd quarters of 2009 were available. We compared the average of these against the annual average since July 2009. A comparison with the 1st and 2nd quarters of 2010 suggests even a bigger drop in ship $PM_{2.5}$ concentrations.

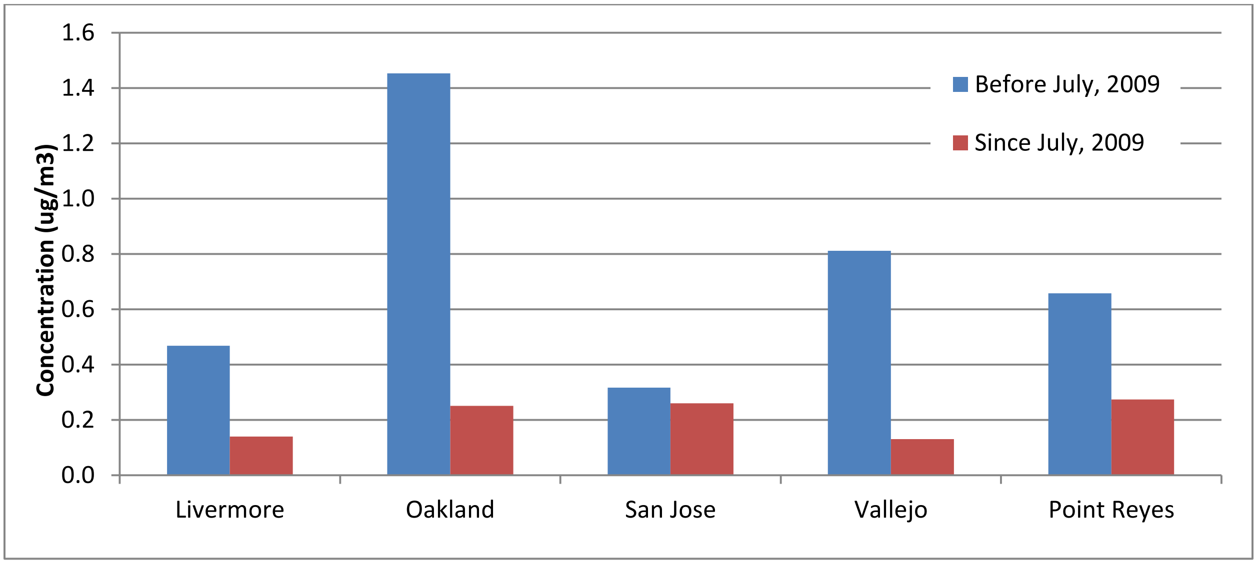

Figure 5.8. CMB-estimated annual $PM_{2.5}$ concentrations from ship emissions before and since July 1, 2009.

5.9 Trend in Residential Wood Burning

The District adopted a Wood Burning Rule in July 2008 (BAAQMD 2008) that prohibits wood burning on days that the District predicts the national 24-hour $PM_{2.5}$ ambient air quality standard will be exceeded. Responses to the District's annual wintertime Spare the Air Survey indicate that wood burning may have been reduced substantially overall.

To investigate whether the source apportionment analysis corroborates this trend, we analyzed the period when most wood burning occurs – November 15 through February 15. Data from just before 2008 were not available, so we again compared with data from 1999-2001. And, as in section 5.6, the comparisons were made for CMB analysis excluding C-14.

Figure 5.9 shows the mean concentrations for 2010 and 2000. There are substantial reductions for each comparison. The two sites that remained in the same location – Livermore and Point Reyes – both show reductions of about 40%; the other pairs show divergent reductions, but this could be because of divergent local conditions.

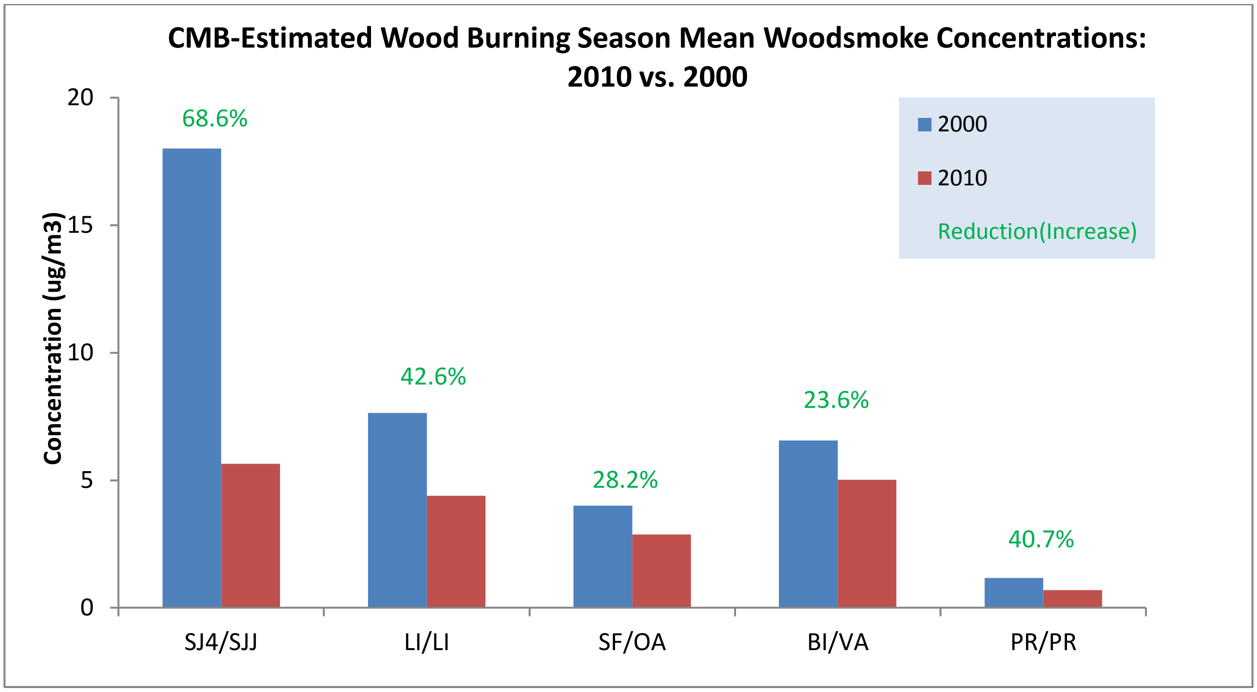

Figure 5.9. CMB-estimated Nov 15 through Feb 15 mean woodsmoke concentrations 2010 vs. 2000. The values above the bars represent the percent reduction from 2000 to 2010.

6. Apportionment to Individual Sources

The CMB analysis provides estimates of $PM_{2.5}$ contributions from source *categories*. To make an apportionment to individual sources, we need to incorporate information from elsewhere, namely the District's Emissions Inventory. The EI was used to provide breakdowns for several CMB categories of directly emitted $PM_{2.5}$–gasoline, diesel, and geological–into estimates for individual sources. For secondary $PM_{2.5}$, our PM air quality model was used to provide estimates of the contributions of various precursors, and the EI was then used to apportion contributors to those precursors.

6.1 Apportioning secondary PM

Secondary PM forms with the presence of precursors NOx and ammonia for ammonium nitrate, and SO2 and ammonia for ammonium sulfate. The District has simulated secondary $PM_{2.5}$ using the CMAQ model (Tanrikulu *et al*. 2009). The model shows that ammonium nitrate is reduced if either precursor is reduced, though not in equal proportion. The same holds true for ammonium sulfate.

The goal of source apportionment is to attribute the contribution of a certain amount of emissions to a certain amount of concentration. But how can the contribution of two precursors be quantified if both are necessary for the production of the secondary compound? The rate that the secondary compound is produced is, in general, dependent on the relative amounts of the precursors and also atmospheric conditions. Fortunately, the CMAQ model is capable of estimating the rates that secondary PM is reduced in response to reductions in precursor emissions.

Table 6.1 shows the reduction in population-weighted concentrations of ammonium nitrate and ammonium sulfate resulting from a 10% reduction in their precursors simulated by CMAQ. We used the ratios 52.9 to 35.8 and 25.2 to 15.7 to apportion ammonium nitrate and sulfate concentrations to their precursor emissions.

Table 6.1. Reduction in per capita exposure concentration (ng/m3) per 10% reduction in emissions*

	NOx	SO2	Ammonia
Ammonium Nitrate	52.9	0	35.8
Ammonium Sulfate	0	25.2	15.7

* Values computed using the District's Multipollutant Evaluation Method (Fairley & Burch 2010)

6.2 Apportionment to individual sources

Table 6.2 shows the apportionment of source categories to individual sources. This table represents contributions on an *annual* basis; thus, estimates of contributions to annual average $PM_{2.5}$. The largest individual source is wood burning, representing 25% of the total; residential wood burning represents about 80% of this, or 20% of the total. The next largest sources are on-road gasoline vehicles (10%), (non-anthropogenic) marine air (10%), cooking (9%), and refineries (8%).

Table 6.3 shows the apportionment to individual sources on days with high $PM_{2.5}$. Wood burning remains the largest individual source, representing about 28% of the total. On-road gasoline and diesel contribute 14% and 10% respectively, more than their annual totals. This greater contribution results from their being the major sources of NOx emissions, and hence major ammonium nitrate precursors. Domestic, landfills/compost and farm livestock also contribute more, being large sources of ammonia emissions. Other sources, including refineries and marine air contribute correspondingly less to peak $PM_{2.5}$ than to annual.

Table 6.2. Apportionment of annual average CMB source categories to individual sources.

		Annual average across four sites ($\mu g/m^3$)						Emissions from the Annual 2010 inventory (t/d)					Ammonia Inventory[c]
Sources	% of total	Total	Direct $PM_{2.5}$	Ammonium Nitrate[a]	Ammonium Sulfate[b]	Geological	Brake & Tire	Carbonaceous $PM_{2.5}$	Geological	Brake & Tire	NOx	SO2	Ammonia
Wood burning[d]	**25%**	2.18	2.14	0.018	0.017			14.82			2.57	0.53	320
Cooking	**9%**	0.76	0.76	0.000	0.000			1.79			0.00	0.00	0
On-Road									3.63				
On-Road gasoline	**10%**	0.90	0.09	0.456	0.083	0.140	0.132	0.80		3.90	100.56	0.78	4056
On-Road diesel	**7%**	0.58	0.27	0.306	0.002			2.70			91.17	0.08	6
Off-Road									0.39				
Off-Road gasoline	**3%**	0.29	0.19	0.094	0.000	0.007		1.62			28.09	0.00	
Off-Road diesel (except farm and construction)	**2%**	0.15	0.09	0.047	0.000	0.007		0.91			14.05	0.00	
Ships	**3%**	0.25	0.18	0.028	0.041			0.88			8.27	1.82	
Aircraft	**1%**	0.10	0.05	0.038	0.021			0.40			11.26	0.91	
Trains	**1%**	0.06	0.02	0.036	0.000			0.24			10.70	0.00	
Refining	**8%**	0.70	0.31	0.049	0.340			2.62			10.65	14.56	460
Power Generation	**2%**	0.18	0.14	0.034	0.014			1.16			8.63	0.49	164
Domestic[e]	**7%**	0.59	0.14	0.304	0.146			1.19			12.21	0.09	8962
Landfill	**1%**	0.06	0.02	0.021	0.017			0.17			0.81	0.31	617
Compost	**1%**	0.10		0.068	0.037								2307
Livestock/Farm	**3%**	0.22	0.03	0.125	0.058	0.009		0.31	0.24		5.92	0.00	3603
Construction	**2%**	0.16	0.07	0.045	0.000	0.042		0.69	1.10		13.45	0.00	
Soils (biogenic)	**2%**	0.18		0.119	0.065								4057
Marine	**10%**	0.85	0.85	0.000	0.000								
Other	**5%**	0.40		0.119	0.258	0.027			0.70		20.63	10.09	1703
Total	**100%**	8.72	5.35	1.91	1.10	0.23	0.13	30.30	6.06	3.90	338.97	29.66	26255

[a] Total from CMB, annual averages across four sites. Individual terms apportioned according to NOx and ammonia emissions in the ratio of 52.9 for NOx to 35.8 for ammonia.

[b] Total from CMB, annual averages across four sites. Individual terms apportioned according to SO2 and ammonia emissions in the ratio of 25.2 for SO2 to 15.7 for ammonia.

[c] Ammonia Inventory: STI 2008

[d] Includes residential fires, accidental fires, controlled burns, and cigarette smoke.

[e] Includes domestic natural gas for heating and cooking, plus dog, cat and human respiration.

Table 6.3. Apportionment of peak CMB source categories to individual sources.

		4-site average, annual average (µg/m^3)						Emissions from the Winter 2010 inventory (t/d)					Ammonia Inventory[c]
Sources	% of total	Total	Direct PM$_{2.5}$	Ammonium Nitrate[a]	Ammonium Sulfate[b]	Geological	Brake & Tire	Carbonaceous pm2.5	Geological	Brake & Tire	NOx	SO2	Ammonia[c]
Wood burning[d]	**28%**	7.04	6.94	0.076	0.017			18.47			1.94	0.25	320
Cooking	**4%**	0.93	0.93	0.000	0.000			1.75			0	0	0
On-Road									3.50				
On-Road gasoline	**14%**	3.45	0.20	2.265	0.130	0.088	0.770	0.80		3.90	107.29	0.77	4056
On-Road diesel	**10%**	2.53	1.05	1.479	0.003			2.70			93.68	0.08	6
Off-Road									0.40				
Off-Road gasoline	**3%**	0.78	0.33	0.443	0.000	0.005		1.32			28.09	0.00	
Off-Road diesel (except farm and construction)	**2%**	0.59	0.36	0.222	0.000	0.005		0.92			14.05	0.00	
Ships	**2%**	0.54	0.34	0.130	0.067			0.24			8.27	1.82	
Aircraft	**1%**	0.29	0.08	0.173	0.032			0.34			10.94	0.88	
Trains	**1%**	0.26	0.09	0.168	0.000			0.24			10.677	0	
Refining	**6%**	1.40	0.64	0.231	0.531			2.56			10.50	14.20	460
Power Generation	**2%**	0.47	0.29	0.160	0.022			1.15			8.65	0.49	164
Domestic[e]	**9%**	2.20	0.42	1.553	0.231			1.68			18.28	0.13	8962
Landfill	**1%**	0.17	0.04	0.100	0.027			0.17			0.81	0.31	617
Compost	**2%**	0.38		0.326	0.058								2307
Livestock/Farm	**3%**	0.81	0.12	0.601	0.091	0.005		0.30	0.20		5.89	0.00	3603
Construction	**2%**	0.48	0.27	0.184	0.000	0.025		0.69	1.00		11.67	0.00	
Soils (biogenic)	**3%**	0.67		0.573	0.102								4057
Marine	**3%**	0.85	0.85	0.000	0.000								
Other	**4%**	0.93		0.500	0.412	0.018			0.70		16.44	10.09	1703
Total	**100%**	24.77	12.94	9.18	1.72	0.15	0.77	33.33	5.80	1.25	347.18	29.02	26255

[a] Total from CMB, 4-site annual averages. Individual terms apportioned according to NOx and ammonia emissions in the ratio of 52.9 for NOx to 35.8 for ammonia.

[b] Total from CMB, 4-site annual averages. Individual terms apportioned according to SO2 and ammonia emissions in the ratio of 25.2 for SO2 to 15.7 for ammonia.

[c] Ammonia Inventory: STI 2008. Units are tons/year.

[d] Includes residential fires, accidental fires, controlled burns, and cigarette smoke.

[e] Includes domestic natural gas for heating and cooking, plus dog, cat and human respiration.

7. Summary and Conclusions

This analysis accounts for, and apportions to sources, all but a small fraction of the Bay Area's $PM_{2.5}$. The similarity between the CMB results and the Emissions Inventory strengthens the conclusion that the apportionment is approximately correct.

7.1 Source contributions

By combining the CMB model results with the Emissions Inventory, the contributions of individual sources to ambient $PM_{2.5}$ were estimated, including both directly emitted $PM_{2.5}$ and $PM_{2.5}$ created in the atmosphere from the precursors, NOx, SO_2 and ammonia. The results were:

- Wood burning remains the number one source of $PM_{2.5}$ in the Bay Area, contributing 25% of the annual average concentration and almost 30% of the peak $PM_{2.5}$ concentrations. Of this, most is residential wood burning, representing approximately 20% on an annual basis and 25% of peak $PM_{2.5}$.

- Gasoline emissions from on- and off-road vehicles and equipment contribute approximately 15% of the total. Diesel emissions from on- and off-road vehicles and equipment contribute approximately 10%.

- Marine air contributes 10% to annual $PM_{2.5}$ but only 3% to peak $PM_{2.5}$.

- Ships contribute only 2%-3% because of the new ship rule (CARB 2011).

- Domestic emissions – from space and water heaters, and ammonia from human and pet respiration – contribute 8%-9% of annual and peak $PM_{2.5}$.

- Refining contributes 8% of annual and 6% to peak $PM_{2.5}$.

- Cooking contributes 9% to annual and 4% to peak $PM_{2.5}$.

- Smaller sources include: livestock/farms (3%), construction (2%), power generation (2%), biogenic soil emissions (2%), landfills (1%), compost (1%), and aircraft (1%).

7.2 Reductions from 2000

One striking result is the dramatic reduction in contributions from motor vehicles, both diesel and gasoline. In the earlier report (Fairley 2008), which analyzed data from 2000, on- and off-road vehicles represented 30% of the contribution to annual $PM_{2.5}$ concentrations and 40% to peak. A decade later, these represent only 20% of annual $PM_{2.5}$ and 30% of the peak.

These reductions are due to reductions of emissions of both direct $PM_{2.5}$ and a key secondary PM precursor, NOx.

There has been a sizeable drop in ship emissions also, previously representing 10% of $PM_{2.5}$.

Other sources, including wood burning and cooking, have also declined, but because of the greater declines in motor vehicle contributions, the percentage contribution from these other sources has remained relatively constant.

7.3 CMB and Emissions Inventory roughly comparable

The percentages of CMB-estimated contributions to $PM_{2.5}$ concentrations are roughly comparable to the corresponding percentages of emissions in the Emissions Inventory. Both show woodsmoke as the largest single source of direct $PM_{2.5}$ emissions with the percentages for diesel and gasoline considerably smaller. Ship emissions are only a few percent in each.

One discrepancy is geological dust, where the EI estimates 15% compared to less than 5% for CMB. The identification of geological dust by CMB has little uncertainty and is likely to be closer to the true ambient fraction at the monitoring sites. One likely reason for the discrepancy is that the EI estimates what gets emitted into the air, whereas filters measure what stays in the air. In contrast to $PM_{2.5}$ from combustion, geological dust consists mostly of larger particles that settle out of the air relatively fast. There is a similar discrepancy for brake wear emissions, which also tend to be larger particles.

Another discrepancy is cooking, where emissions are much less than the CMB estimates. The current EI omits contributions from condensable vapors. Previously, these had been included and the EI cooking emission percentage was then considerably larger than the CMB estimates. This suggests that some of the condensable vapors become $PM_{2.5}$.

7.4 Comparison with Central Valley sites

Bay Area urban concentrations of $PM_{2.5}$ are similar to those in Sacramento but smaller than those for the San Joaquin Valley cities of Modesto, Fresno, Visalia, and Bakersfield. One major difference is that ammonium nitrate concentrations in these San Joaquin Valley cities are double to triple those of the Bay Area. Woodsmoke is a large component of Central Valley $PM_{2.5}$, as it is in the Bay Area. In fact, it is larger in several cities, notably Chico, where it accounts for half of its $PM_{2.5}$. It is possible that more of Central Valley woodsmoke derives from wildfires – the annual Central Valley woodsmoke percent contribution is over 30% compared with 25% for the Bay Area.

7.5 Changes to the previous source apportionment methodology

The key change from the source apportionment for 1999-2001 was the application of a new methodology – a Monte Carlo approach to fitting CMB. This facilitated the inclusion of several new source profiles.

The previous source apportionment used only wood, fossil, geological, fireworks, and marine profiles. This analysis divided “wood” into “residential woodsmoke”, “wildfire” and “cooking”; divided “fossil” into “diesel” and “gasoline”; and added tire/brake wear. Considerable effort went into refining the source profiles.

The results were partly successful. The splits between woodsmoke and cooking, and between diesel and gasoline appear reasonable. The concentrations of brake wear appear consistent with the EI. The split between “residential woodsmoke” and “wildfire” was not successful, yielding large sample-to-sample variability. Thus, these were combined into one “woodsmoke” total.

Another addition was to use ammonia from the EI in the apportionment to individual sources. This led to finding additional sources of Bay Area $PM_{2.5}$ including landfills and compost and suggesting that domestic emissions were among the larger sources.

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Appendix A. Source Profile Development

This appendix discusses refinements made in the source profiles used in the latest CMB analysis.

A1. Marine Air

Some of the ambient $PM_{2.5}$ in the Bay Area blows in from the ocean. It includes sea salts and also some ship emissions. This section focuses on developing profiles for the sea salts.

Figure 1.1 shows the major salt constituents.

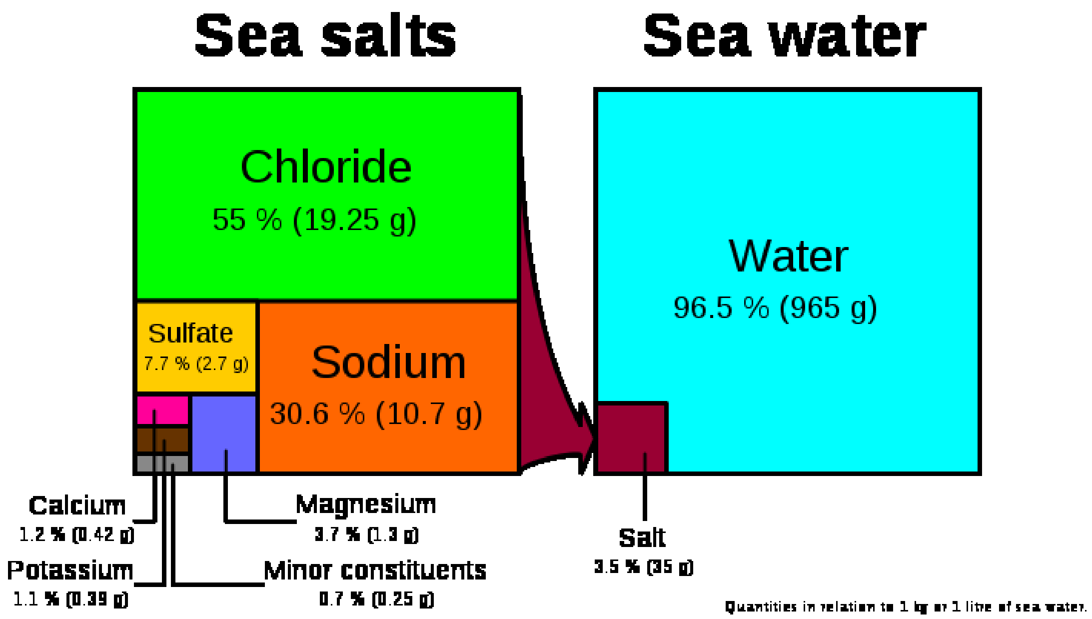

Figure 1.1 Major sea salt components. (Source: http://en.wikipedia.org/wiki/Seawater)

Table 1.1 has a more detailed breakdown.

Table 1.1. Sea water components

	mol/kg	Atomic weight	relative mass in ocean	% of salts
H2O	53.6	18	964.8000	
Cl-	0.546	35.453	19.3573	54.9924
Na+	0.469	22.9898	10.7822	30.6313
Mg2+	0.0528	24.312	1.2837	3.6468
SO42-	0.0282	96	2.7072	7.6909
Ca2+	0.0103	40.08	0.4128	1.1728
K+	0.0102	39.102	0.3988	1.1331
Br-	0.000844	79.909	0.0674	0.1916
Sr2+	0.000091	87.62	0.0080	0.0227
Sum of listed non-H20 species			35.02	99.4807
All non-H20 species			35.20	100.0000

We use the percentages in the last column for the assumed distribution of fresh marine air.

Measurements

Measurement precision and accuracy limit the identification of marine species. Sodium and chloride are well-identified even if the concentration of marine air is low. But some of the other species listed in Table 1.1 may not be well-identified. This limits their effectiveness in estimating the amount of marine air and also other sources that may share some of these species.

The Point Reyes IMPROVE site is near the ocean, with lower concentrations from non-marine sources with shared species. It also has the smallest reported uncertainties. In fact, at least 97% of its 176 observations had measurements above the uncertainty level for every one of the species listed in Table 1.1 except for elemental chlorine (82%), but including chloride (100%) (see next section). The correlations among the species were high with one exception, sulfate, which has several other sources, including ships and refineries. The correlations among chloride, chlorine, sodium, magnesium, calcium, and strontium were all over 0.75. The correlations with potassium were somewhat lower, but still at least 0.6; potassium is also a key species in woodsmoke.

For San Jose, sodium, sodium ion, chlorine, and magnesium all had correlations at least 0.6, but the correlations with other marine species were lower. Calcium concentrations were always above the uncertainty level, but it was only weakly correlated with other marine constituents. It is a component of geological dust and tire wear, but its values were poorly correlated with these sources also. Potassium was weakly correlated with marine species but had correlations above 0.6 with organic and elemental carbon and, interestingly, with copper. Organic carbon is the major constituent of woodsmoke. Bromine was only weakly correlated with other marine constituents and more strongly with several species including organic carbon and iron, indicating other sources predominate for this species. Strontium has few values above its uncertainty and no correlations above 0.2.

For Oakland and Vallejo, sodium and sodium ion, chloride and chlorine, and magnesium are all highly correlated. For Livermore, calcium is not highly correlated with marine species but is with silicon, suggesting most of its calcium is geological. As with San Jose, potassium is highly correlated with organic carbon at these sites, but not with marine species. Unlike San Jose, magnesium is not highly correlated with the other marine species, although the correlations are statistically significant; it is rarely above uncertainty levels at these sites. Bromine and strontium are also mostly below uncertainty levels. Bromine had significant correlations with sodium and chloride, but below 0.5. Strontium was also weakly correlated with marine species; at Oakland it was more strongly correlated with several others, including potassium and organic carbon, indicating other strontium sources.

Cl and Na measurements – ion or elemental

One complicating aspect of this analysis is the differences between datasets in terms of the species measured. (See Table 1.2.) The two key marine species, sodium and chloride, may be measured either as ions or elements. The three datasets differ on which combinations are measured, and there appear to be differences in the precision and accuracy of ions vis-à-vis the elemental measurement also.

Table 1.2. Which chlorine and sodium species are measured at which sites.

	Chloride	Chlorine	Sodium ion	Sodium
Point Reyes	x	x	x	
San Jose		x	x	x
Livermore	x	x	x	x
Oakland	x	x	x	x
Vallejo	x	x	x	x

For source apportionment purposes, one would choose chloride and sodium ion as being more appropriate for analysis of marine air, all else being equal. But, as can be seen in the table, San Jose lacks a chloride measurement. Figure 1.2 shows chloride vs. chlorine for the other sites. Note that, contrary to expectation, the chloride measurement is virtually always greater than the chlorine measurement. Most of the differences far exceed the joint uncertainties in the measurements. Thus, one or the other measurement has systematic biases.

Chloride and chlorine are measured separately from two different filters. One possibility is volatilization of chlorine-containing species in the vacuum environment of the elemental XRF measurements (Kohl 2010).

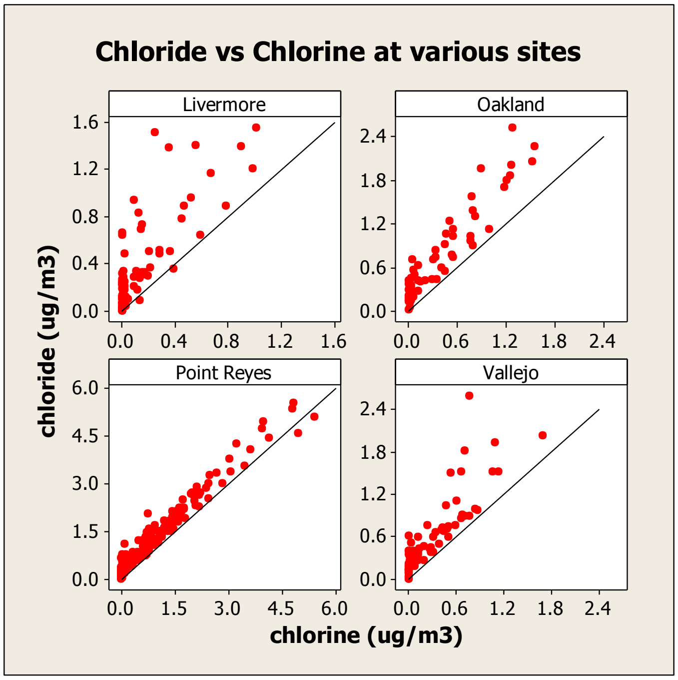

Figure 1.2. Chloride vs. chlorine at four sites. y=x lines are drawn for reference.

Figure 1.3 shows sodium ion vs. elemental sodium. As with chloride/chlorine, the ion form is generally larger, contrary to expectations. The difficulty is again with the elemental measurement. Apparently, the sodium atom produces only low-energy x-rays that the XRF instrument has difficulty measuring.

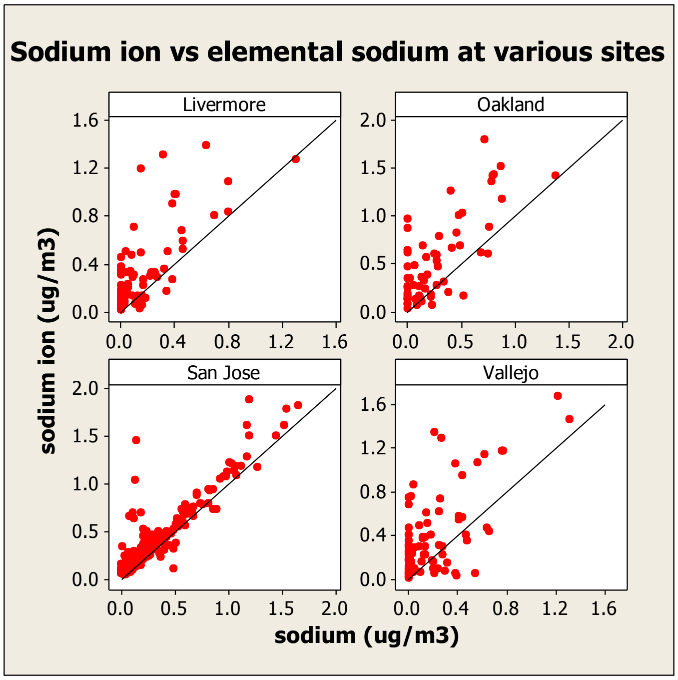

Figure 1.3. Sodium ion vs. elemental sodium at four sites. y=x lines are drawn for reference.

Figure 1.4 shows the correlations between sodium ion and element compared with chlorine ion and element. The correlation between sodium ion and chloride ion is better than the correlation between elemental sodium and chloride ion in the cases where both exist. Thus, it may be reasonable to use the sodium ion even for San Jose, where the correlation of the sodium ion with elemental chlorine is somewhat lower than the correlation of elemental sodium with elemental chlorine.

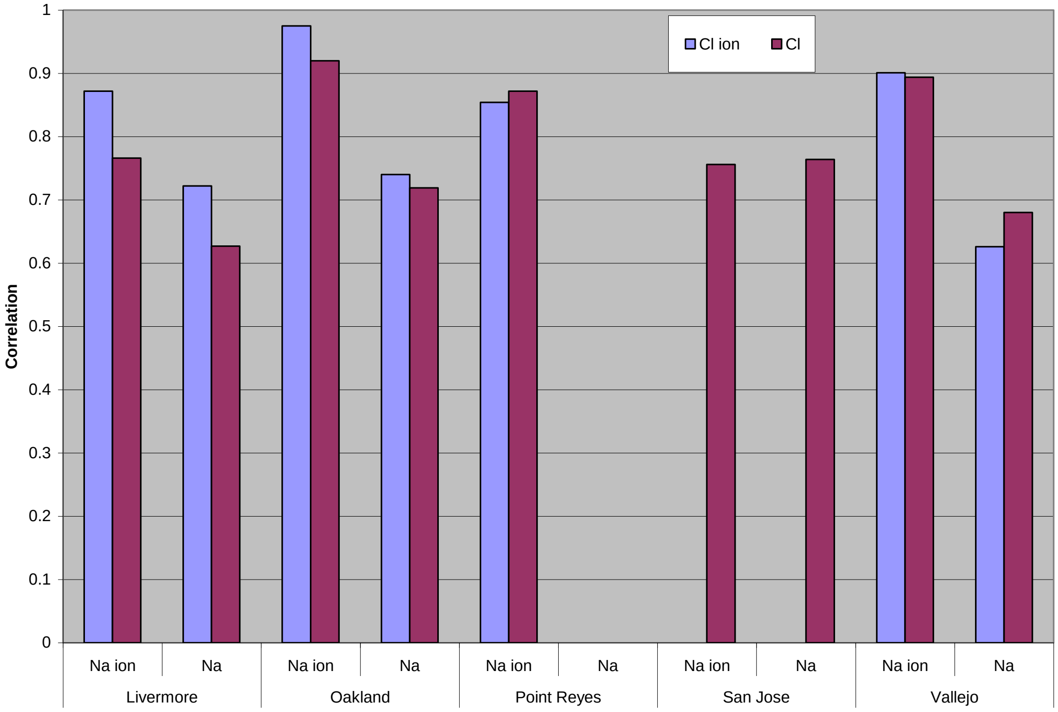

Figure 1.4. Correlations between sodium measurements and chlorine/chloride measurements.

Figure 1.5 shows the relationship between sodium and chloride ions at the sites that measure both. Most of the points for the urban sites are above the line of equal parts sodium and chloride, indicating the aging of the marine air, whereas at the Point Reyes site, subject to fresh marine air most of the time, the values are clustered more evenly around the line.

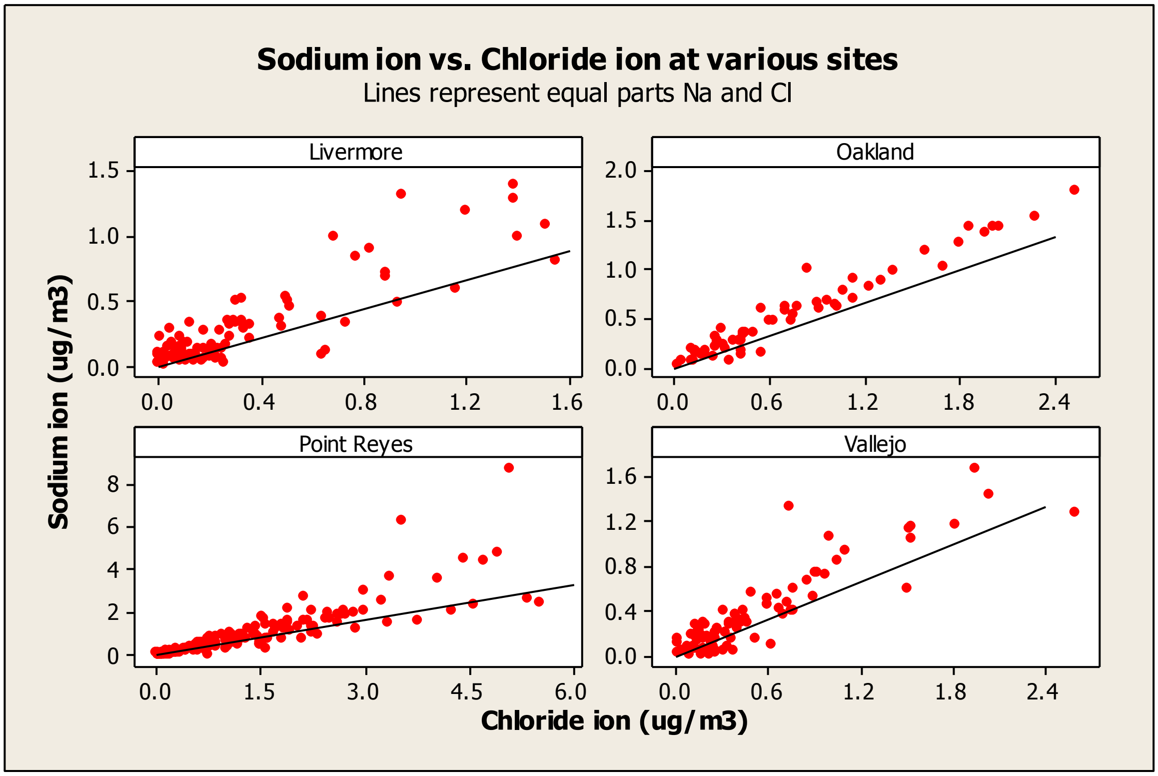

Figure 1.5. Sodium ion vs. chloride ion at various sites.

Figure 1.6 shows a similar plot for San Jose, only substituting elemental chlorine for the unmeasured chloride ion. We see more of a spread in the sodium values, as might be expected if chlorine is underestimating the chloride ion as shown in Figure 1.2.

Although we cannot be completely sure, Figure 1.6 is consistent with the assumption that San Jose elemental chlorine measurements also underestimate its chloride ion concentrations. It differs from the relationships in Figure 1.5 – with almost all points lying above the line for fresh marine air. To account for this we could either modify the marine source profiles with lower elemental chlorine values than chloride ion values, or we could approximate San Jose chloride ion concentrations from its chlorine values and its sodium based on the relationship we see at the other sites.

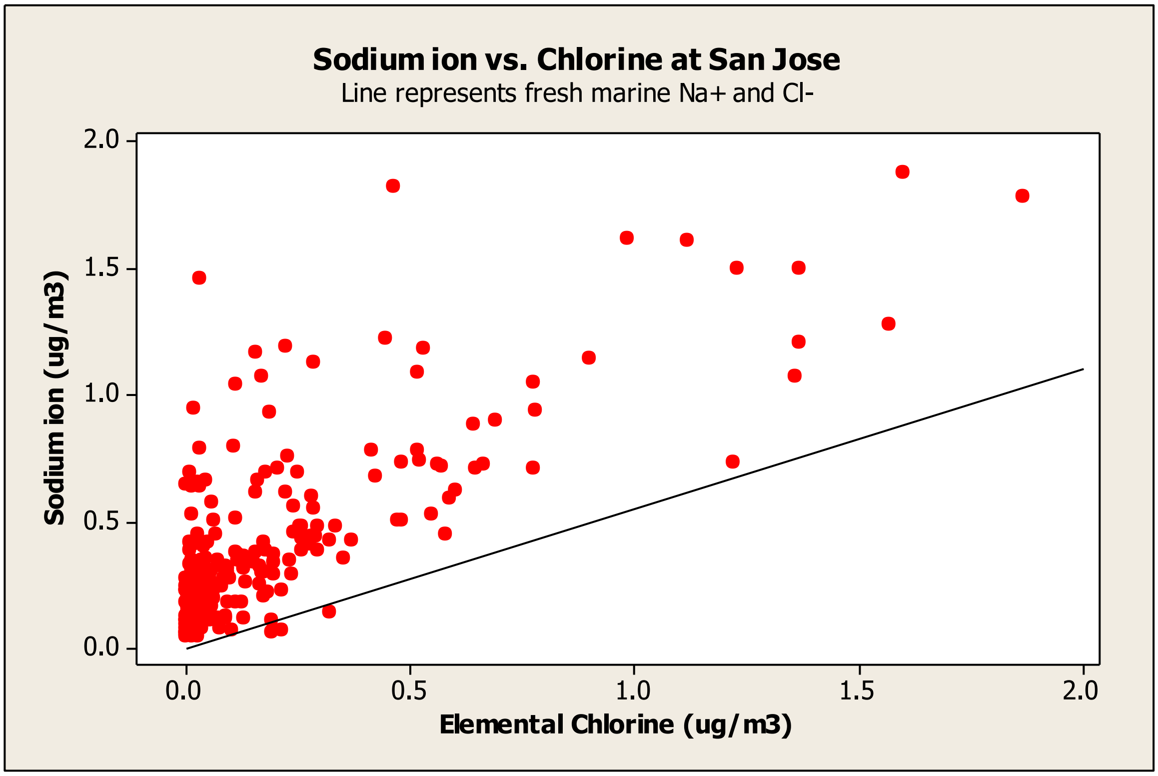

Figure 1.6. Sodium ion vs. elemental chlorine at San Jose.

Taking the latter course, we performed various linear regressions using the three urban sites. We excluded Point Reyes because the chloride/sodium relationship is likely to be different from that at San Jose – the Point Reyes site often seeing essentially fresh marine air. Based on an F-test, fitting separate slopes and/or intercepts did not improve the fit. The regression equation found was

Cl ion = .586 Cl + .785 (Na ion) + .065

where the units are µg/m^3. The standard errors of the coefficients were .069, .062 and .017, respectively – all highly significant. The R^2 was 89% and the regression standard deviation (s.d.) was 0.175 µg/m^3. Thus, we use this synthetic Cl ion value in our analysis. Figure 1.7 shows the relationship of Na ion to this synthetic Cl ion. This figure shows a Na/Cl relationship more similar to those in Figure 1.5.

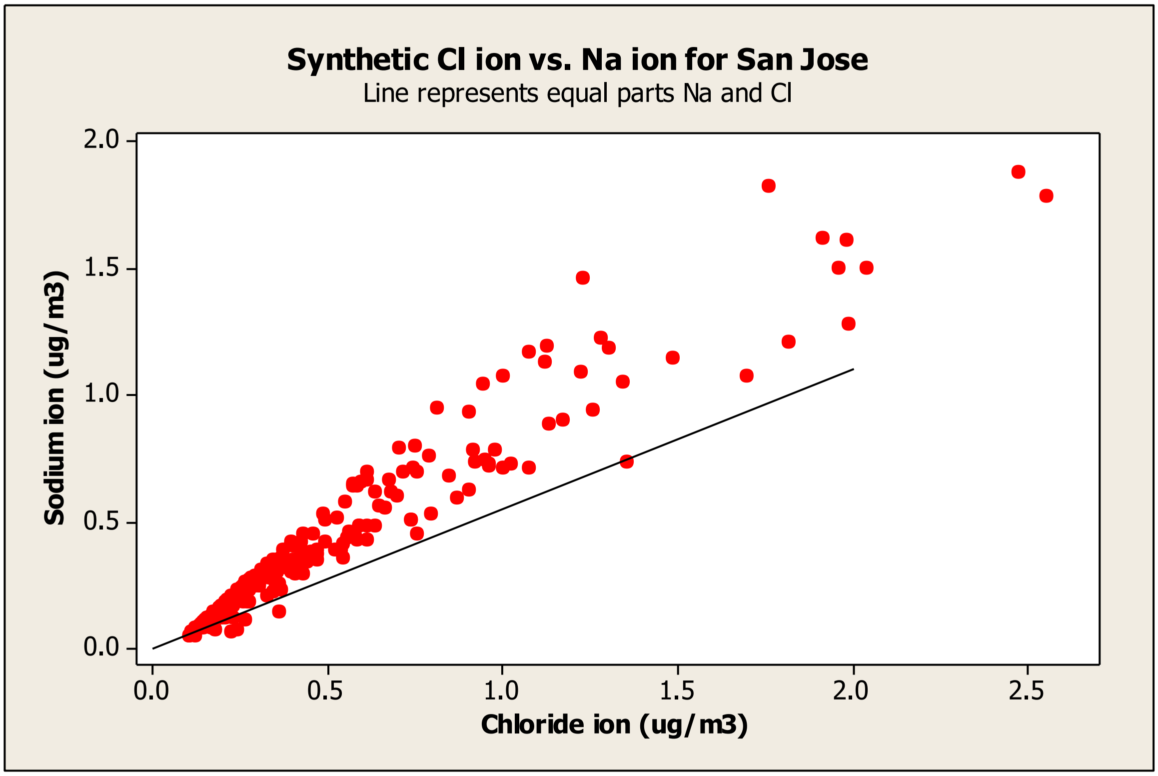

Figure 1.7. Sodium ion vs. synthetic chloride ion at San Jose.

Chemical transformations of marine air

As marine air combines with air containing ammonium sulfate and nitrate, some chloride and bromine are replaced by sodium sulfate and sodium nitrate (See e.g., Ayers *et al.* 1999). Thus, in the Bay Area, as marine air is mixed with ship emissions, which contain some ammonium sulfate, and with urban air containing some ammonium nitrate and ammonium sulfate, the marine air is transformed.

This transformation raises three questions. First, how far does this transformation travel? Second, how should the additional sulfate and nitrate be accounted for – as part of "marine origin" or as something separate? Third, should there be one marine profile with wide uncertainties for chloride and bromine, or two profiles, one representing fresh marine air, the other well aged?

Figure 1.8 is the same as Figure 1.5 with a dashed line showing a doubling of the sodium ion relative to the chloride ion. As can be seen, most Na/Cl pairs fall below the line except for a few outliers, or if Cl is small. On the other hand, a number of these values above the line are well above it, that is, not just measurement uncertainty. The causes of the large outliers are unclear. Nonetheless, we will use a simple transformation to create an aged marine profile by simply doubling the sodium relative to the chloride.

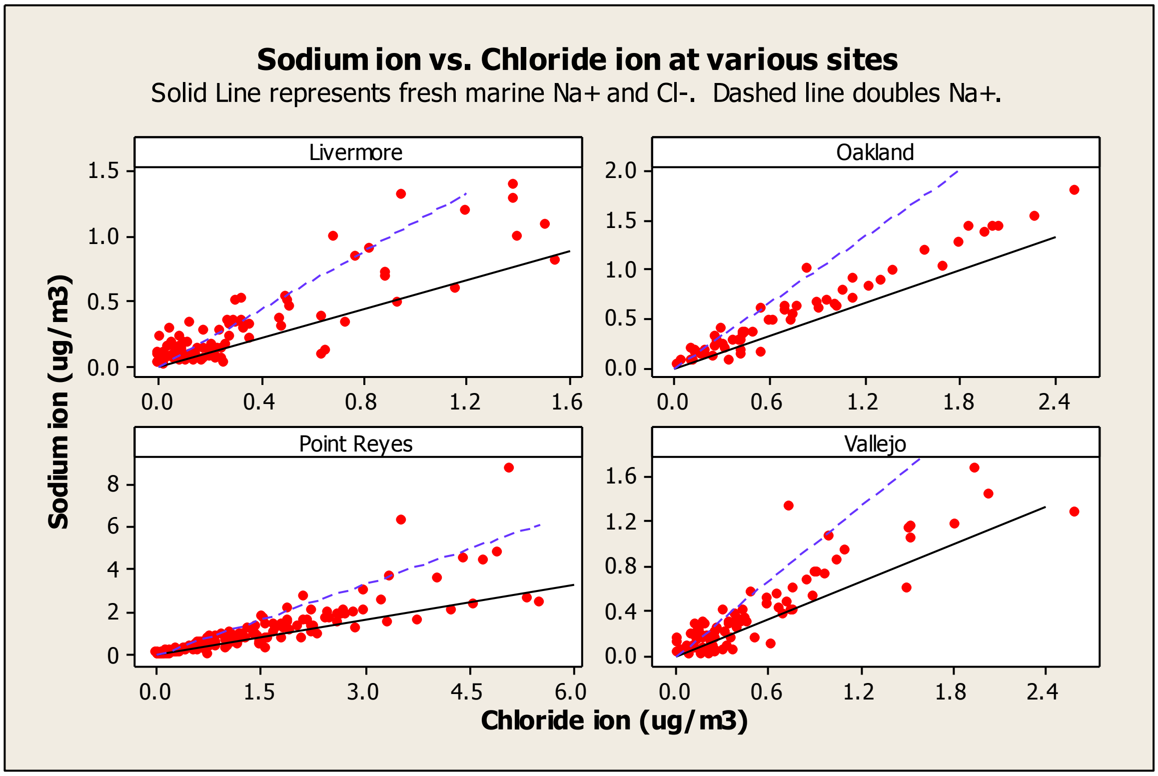

Figure 1.8. Sodium ion vs. chloride ion at various sites showing the line representing two parts sodium to one part chloride.

But what of the other marine constituents? According to Ayers (1999) bromine is also lost, in fact, perhaps more than chloride. We did not find a definitive reference, but the Point Reyes data provide interesting, and surprising, results. Figure 1.9 shows bromine versus sodium and chloride ions, differentiated between (relatively) fresh marine air (black circles) and aged marine air (red squares), as suggested by a chloride/sodium ion ratio of less than 1.1. In the plot versus sodium ion, the bromine in aged air clearly has a lower slope than it does in the fresh marine air. In the plot versus chloride, there is some evidence of a reduction in slope, but not as pronounced.

To investigate the effect of aging on each of the marine components in Table 1.1, we performed regressions of each against sodium and against chloride, with separate slope depending on whether Chloride was > 1.1*Sodium (“fresh marine air”) or < 1.1*Sodium (“aged marine air”). A number of these components may be found in other sources, like woodsmoke, geological dust, or ship emission particles. Thus, we checked whether certain covariate markers were statistically significant and, if so, added them to the regression.

We attempted regressions for all sites except San Jose, because it lacks chloride. In some cases, there was too much noise to find results of interest so these cases were excluded.

Bromine

For bromine, the results emerged roughly as expected, namely that there is a substantial reduction in aged marine air. There was marginal evidence that the reduction was greater than for chloride, although the difference was not large. For the Point Reyes regression, we found that organic carbon (OC) and Silicon (Si) were significant covariates; for Livermore, OC and Aluminum (Al) were the covariates; for Oakland, the regression was not useful; for Vallejo, OC and Vanadium (V) were the covariates.

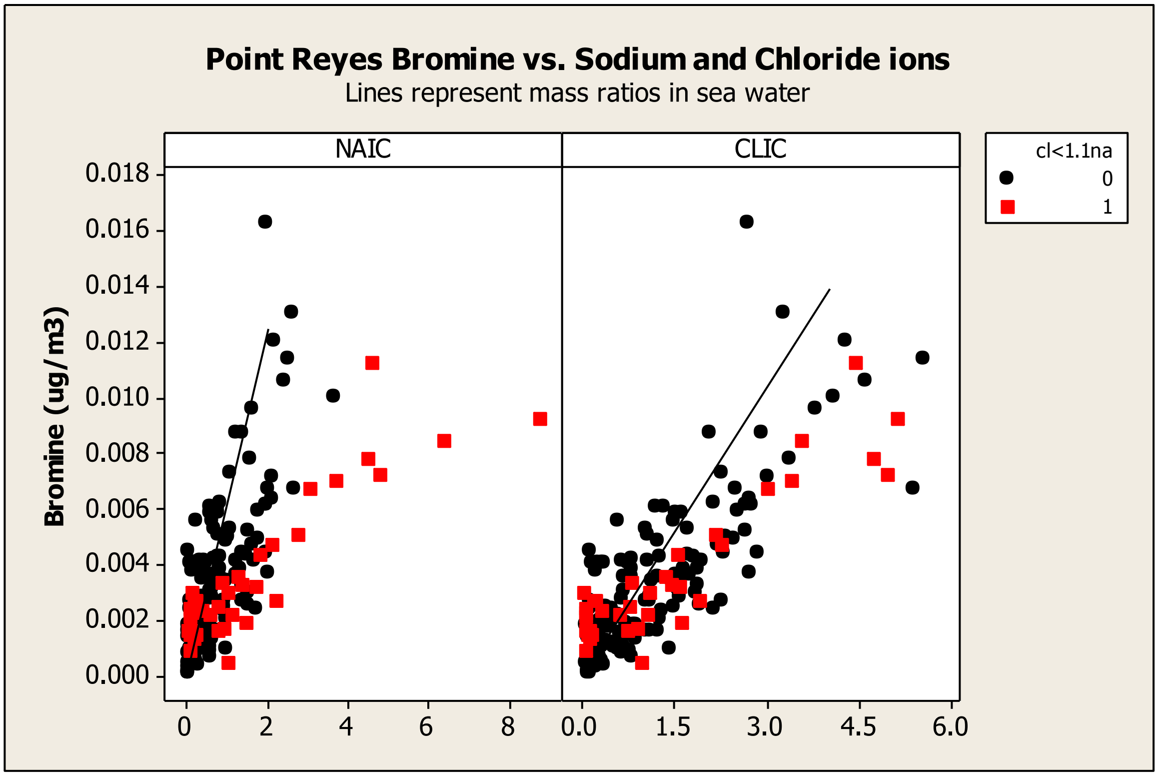

Figure 1.9. Bromine relative to sodium and chloride ions at Point Reyes. Black circles represent fresh marine air; red squares, aged marine air.

Figure 1.10 summarizes the regression results for bromine. The estimated bromine regression coefficients are shown, with fresh and aged coefficients contrasted. The error bars represent an 80% confidence range for the difference between the fresh and aged coefficients. Thus, the coefficients are different if and only if the aged coefficient lies between the bars. For example, the fresh coefficients are significantly larger than the aged coefficients for both sodium and chloride for Point Reyes and for sodium at Livermore, but not in the other cases.[9]

As can be seen, in the regressions versus sodium, the aged coefficient is roughly half the fresh coefficient at every site, whereas the coefficients for chloride are much more similar.

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[9] As discussed, regression results that were statistically insignificant were excluded, in this case, for Oakland-West.

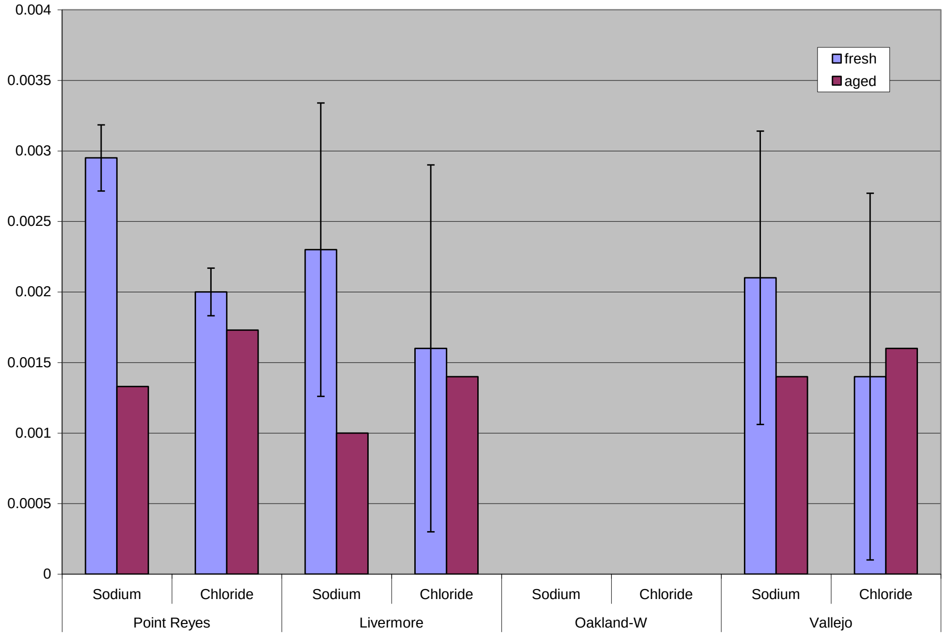

Figure 1.10. Bromine regression coefficients for aged vs. marine air for sodium and chloride, for various sites. Also shown is an 80% confidence interval for the *difference* between fresh and aged air.

Potassium

Potassium is also a component of woodsmoke and geological dust. To estimate the marginal relationship of potassium to chloride and sodium in the marine component, a multiple regression was performed for each site, with covariates for either woodsmoke, geological dust or both depending on the goodness of fit. The following covariates were used: Point Reyes (OC, Si); Livermore (OC, elemental carbon or EC); Oakland (OC); Vallejo (EC). Occasionally, very large values are seen on from fireworks or firecrackers (gunpowder). This may have been the case for Oakland on December 9, 2009. This outlier was removed for the Oakland regression.

Figure 1.11 shows the regression results. There are substantial reductions of potassium relative to sodium in aged marine air, but not relative to chloride. The results are consistent with a reduction of about 50% relative to sodium and no reduction relative to chloride.

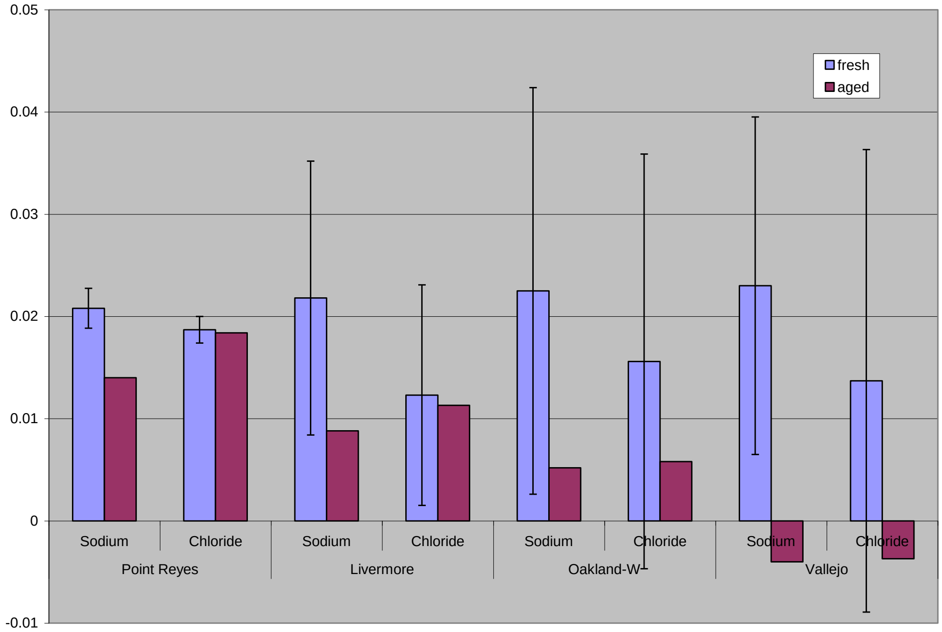

Figure 1.11. Potassium regression coefficients for aged vs. marine air for sodium and chloride, for various sites. Also shown is an 80% confidence interval for the *difference* between fresh and aged air.

Calcium

Calcium is also a constituent of geological dust and other sources. Again, multiple regressions were performed to estimate the marginal relationship of calcium with sodium and chloride. The following covariates were used: Point Reyes (OC, Si); Livermore (Si); Oakland (Si); Vallejo (Si, EC). Figure 1.12 shows a summary of the regression results for calcium. For Point Reyes, calcium acts similarly to potassium with a large reduction relative to sodium in aged air, but not relative to chloride. But the other sites show a different pattern, with little change relative to sodium and a statistically significant increase relative to chloride in aged air. This discrepancy is puzzling, suggesting the possibility that either Point Reyes or the other three sites are affected by another source containing calcium.

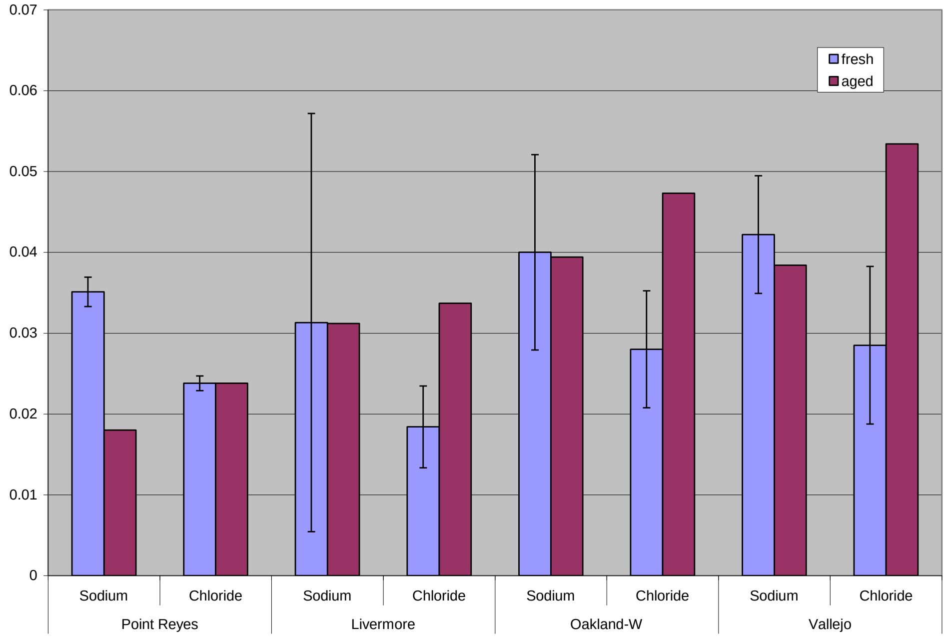

Figure 1.12. Calcium regression coefficients for aged vs. marine air for sodium and chloride, for various sites. Also shown is an 80% confidence interval for the *difference* between fresh and aged air.

Magnesium

Only Point Reyes had statistically significant results for magnesium. Also, no covariates were found to be significant though the correlations between magnesium and sodium and chloride were high. Figure1.13 shows that in aged marine air magnesium drops significantly relative to sodium but not to chloride.

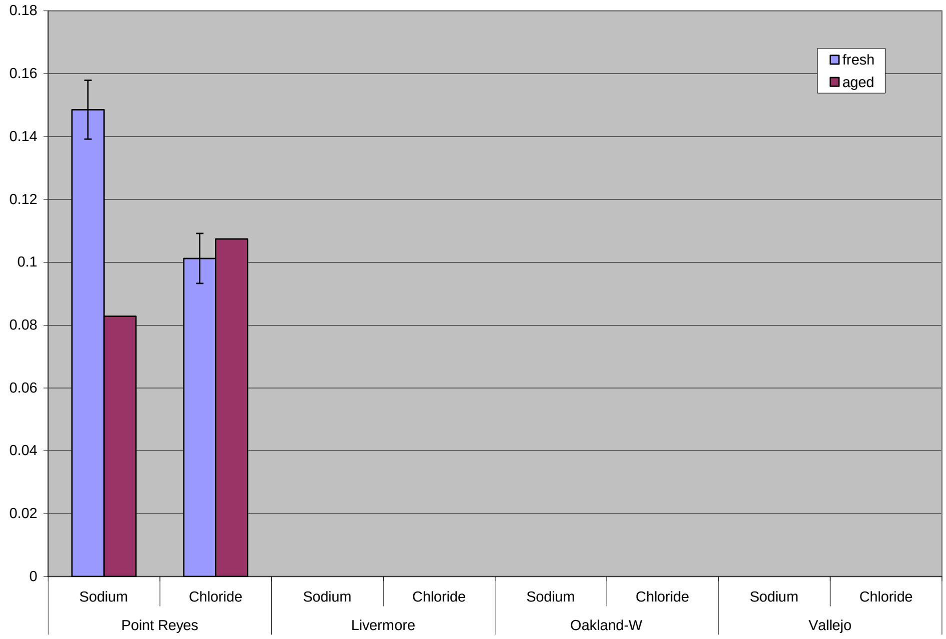

Figure 1.13. Magnesium regression coefficients for aged vs. marine air for sodium and chloride, for Point Reyes. Also shown is an 80% confidence interval for the *difference* between fresh and aged air.

Strontium

Point Reyes and Oakland had statistically significant results for strontium. The covariates were OC, Si and V for Point Reyes, and OC and Si for Oakland. Figure 1.14 shows that there is a highly significant drop in strontium relative to sodium, but not to chloride for Point Reyes. For Oakland, there appear to be drops in magnesium relative to both sodium and magnesium, but these are nowhere close to statistically significant.

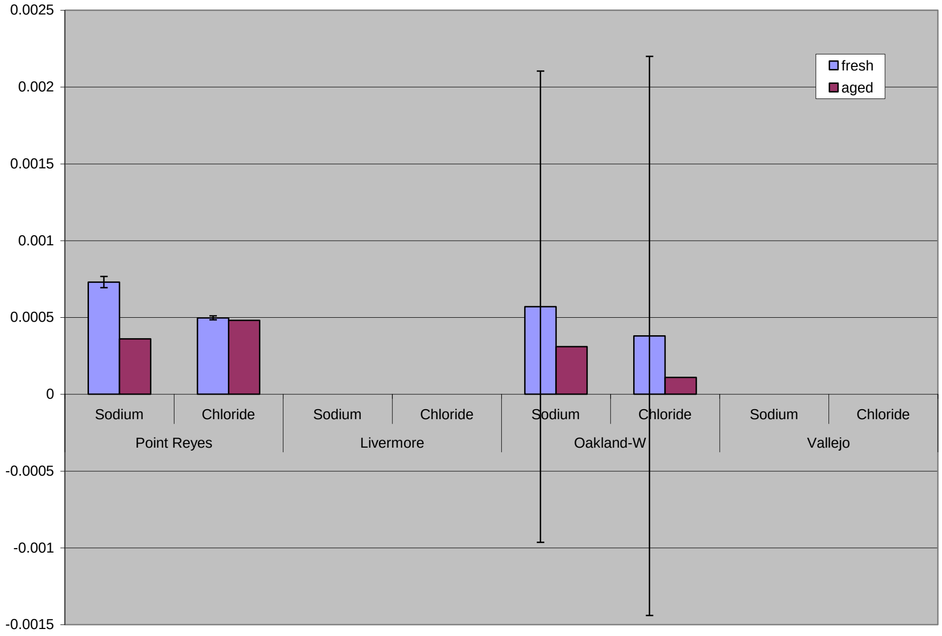

Figure 1.14. Strontium regression coefficients for aged vs. marine air for sodium and chloride, for Point Reyes and Oakland. Also shown is an 80% confidence interval for the *difference* between fresh and aged air.

Development of marine source profiles

A simple method for setting the means for the *fresh marine profile* is to take the percentages from the last column of Table 1.1. This would be appropriate provided that fresh marine aerosol matched. The development of uncertainties is more of a challenge. A fresh marine profile was available. To check the reasonableness of its uncertainties, we considered measurements for Point Reyes where the Cl measurement was greater than 1.1 times the Na measurement, and where the sum of the marine species times 1.077 was at least 3 $\mu g/m^3$.[10]

Figure 1.15 shows a comparison of the fresh marine profile – the "default" – with the mean and standard deviation from the sample, plotted on the log scale. There is good agreement between the mean values; and even some of the differences make sense, such as potassium and calcium having higher sample values, presumably because they're also significant constituents of woodsmoke and geological dust, respectively. Thus, there is no indication that marine aerosol differs substantially from the salts in sea water with the possible exception of

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[10] We excluded sulfate from the comparison because a large fraction is from other sources. To standardize, we divided all values by 1.077 times the sum of the species – the 0.077 to compensate for not including sulfate.

bromine. For simplicity, we thus assume marine aerosol has the same weight percentages as sea water.

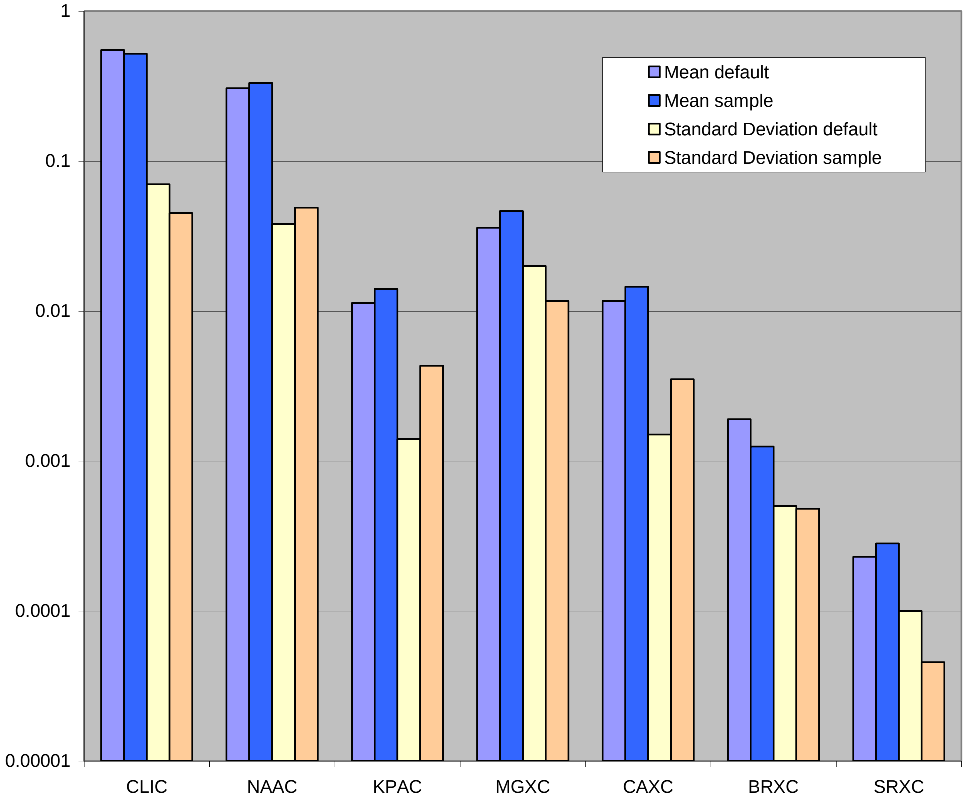

Figure 1.15. Comparison of theoretical marine air and Point Reyes sample fresh marine air means and standard deviations for key marine species.

The standard deviations are intended to represent the actual variability of marine air. The sample and default standard deviations are in the same ballpark but differ significantly in most cases based on an F-test. It is unknown where the default s.d.s come from. The sample s.d.s are based on only 36 data points; furthermore, the potassium and calcium s.d.s are likely inflated because they derive from more than one source. Somewhat arbitrarily, we took the geometric means of the sample and theoretical s.d.s except for potassium and calcium where, because the presence or absence of other sources would inflate the sample s.d., we weighted the result in the direction of the default s.d.

For the *aged marine profile*, based on the above analysis, we assume that all species except sodium are decreased by half. We also assume that the lost chloride is replaced by nitrate. Because the nitrate is largely from anthropogenic sources, we wish to account for it separately from marine air. Thus, we want a profile whose percentages add up to 100% excluding the percentage due to nitrate, the idea being to estimate the remaining mass deriving from marine salts.

Identifying the percentage mass of each element by its symbol, we have

$$Na + 0.5(Cl + K + Mg + Ca + Br + Sr) = 100\%,$$

keeping the ratios of the elements except sodium in the same ratios as in fresh marine air and the ratio to sodium equaling half the ratio in fresh marine air. The following is a table of the results for fresh and marine air.

Table 1.3. Source profiles for fresh and marine air

	Na	Nau	Cl	Clu	Mg	Mgu	K	Ku	Ca	Cau	Br	Bru	Sr	Sru
fresh	.306	.043	.550	.056	.036	.015	.0113	.0020	.0117	.0020	.0019	.0005	.00023	.00007
aged	.471	.029	.421	.028	.028	.008	.0087	.0010	.0090	.0010	.0015	.00025	.00018	.000034

References

Ayers, G.P., R.W. Gillett, J. McAiney, and A.L. Dick. 1999. “Chloride and bromide loss from sea-salt particles in Southern Ocean air.” *Journal of Atmospheric Chemistry*, 33: 299-319.

Kohl, Steve. 2010. Personal communication, 16 February.

A2. Residential Woodsmoke Profile

A woodsmoke profile was estimated for the previous CMB analysis (Fairley 2008) based on samples collected in three backyards over several days on PM_{10} filters. Efforts were made to "back out" other sources that might be contaminating the sample – marine air, geological dust and motor vehicle exhaust.

For this CMB analysis, we decided to test and compare this profile against a library of other profiles. Woodsmoke profiles were available from several studies (Table 2.1).

Table 2.1. Studies producing woodsmoke profiles.

Study	Location	Description	Year
Ca. Source Characterization (CARB)	Bakersfield, Mammoth Lakes	agricultural burning (wheat & barley stubble), fireplace/woodstove	1987
Denver Brown Cloud (Scenic)	Denver	fireplace & woodstove under various conditions	1987
State of Nevada Air Pollution Study (SNAPS)	Reno, Sparks	residential fireplace	1988?
Bay Area Winter PM	SF Bay Area	fireplace from residential chimneys	1993-94
Mt. Zirkel Visibility Study	Mt. Zirkel	forest fire, fireplace from residential chimneys	1994-95
Las Vegas Valley PM_{10}	Las Vegas	fireplace & woodstove from residences	1995-96
Northern Front Range	Denver	fireplace & woodstove in dilution tunnel, various wood species	1996-97
Big Bend National Park Regional Visibility (BRAVO)	Texas	simulated wildfire	1999-2000
Ca. Regional PM AQ Study (CRPAQS)	Fresno	fireplace in dilution tunnel, various wood species	2001

Source: Judy Chow *et al.* 2004

All profiles included measurements for 21 species: ions nitrate, sulfate, ammonium, and soluble potassium; organic and elemental carbon; and 15 elements from aluminum to lead.

As a first pass, a cluster analysis was performed on these measurements, where the profiles are identified as ag (agricultural burning), ff (forest fire), fp (residential fireplace), wf (wildfire), and ws (woodstove). A couple of odd profiles were eliminated a priori – two Texas fence post profiles, and a Duraflame log profile.

Figure 2.1 shows the cluster results. The focus is on finding Bay Area-relevant source profiles so the key categories are fireplaces and woodstoves. Generally, most fireplace profiles are similar and reasonably close to most woodstove profiles. The forest fire profiles are also similar. The ag profiles constitute most of the outlying observations and clearly differ systematically. The wildfire profiles also differ; therefore, in what follows, profiles are limited to fireplace, forest fire and woodstove.

Figure 2.2 shows a dendrogram of these source profiles. There are still some significant outliers. Observation 3 has an impossible EC value > 100%. Observation 57 has a very large nitrate value. Observations 22 and 23 were both from the Reno fireplace. These observations were eliminated. The next most extreme observation, 69, was actually from the Bay Area study. This was kept in the analysis because the goal is to adjust these profiles to eliminate contamination from other sources.

Source profile comparisons

Figure 2.3 shows boxplots of 20 species in the wood burning profiles from eight locations. Lines are drawn at the median of the eight medians. There are clear differences among the sites on virtually every species. The Bay Area profiles differ in a couple of systematic ways. They have above-average fractions of several species related to marine air: chlorine, calcium, bromine, and strontium. They also have elevated fractions of a set of metals: iron, copper zinc, and lead.

Of course, there is a possibility that the wood used in the Bay Area has a different composition. Only an analysis under controlled conditions can determine this for certain. In any case, marine air is present much of the time in San Jose, and a previous analysis has shown that San Jose has elevated concentrations of a range of metals some of which, at least, are related to the heavy motor vehicle traffic in the area (Fairley 2010). In the absence of other evidence, we assume that these represent contamination.

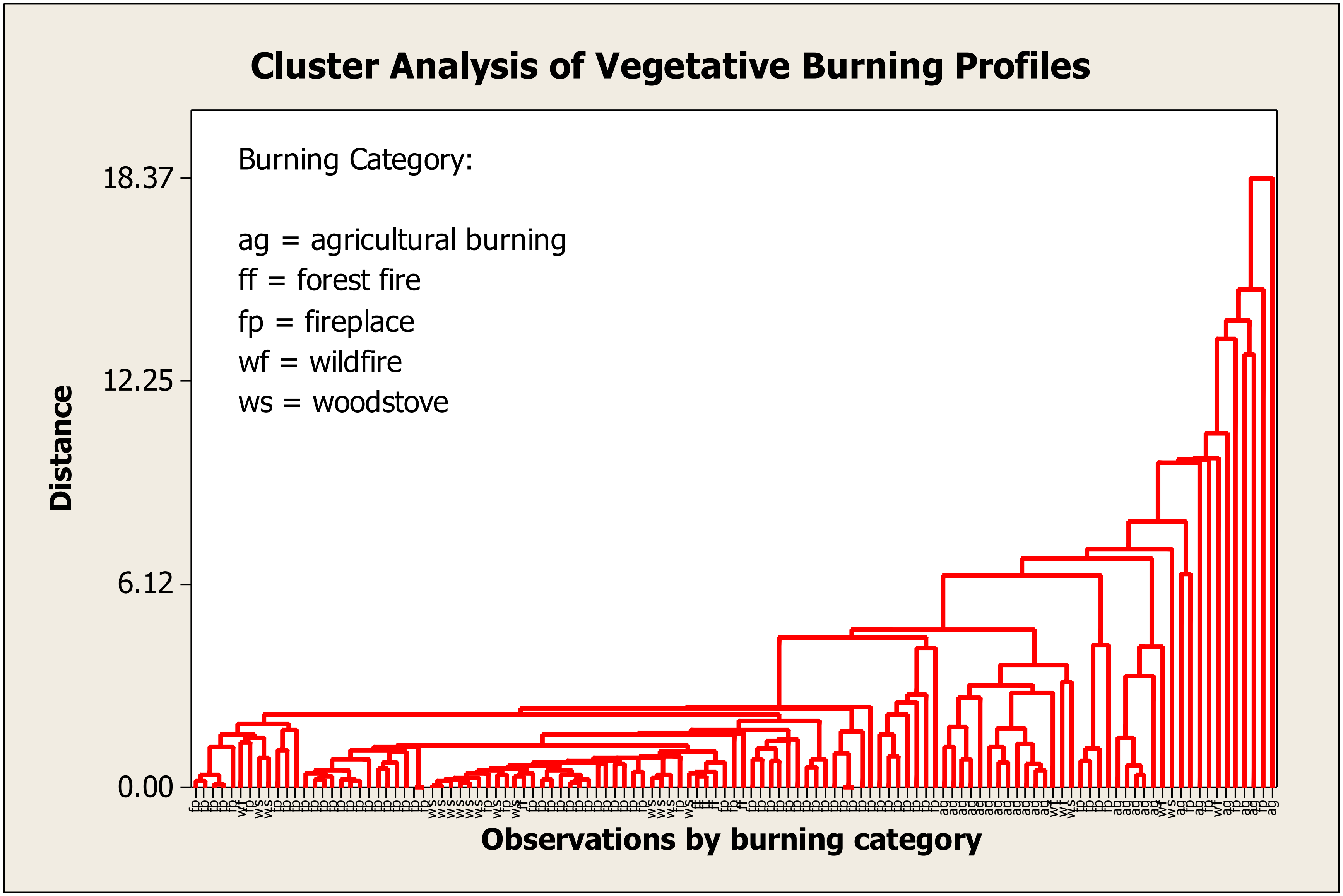

Figure 2.1. Dendrogram of wood and biomass burning profiles from library of Chow *et al.* 2004.

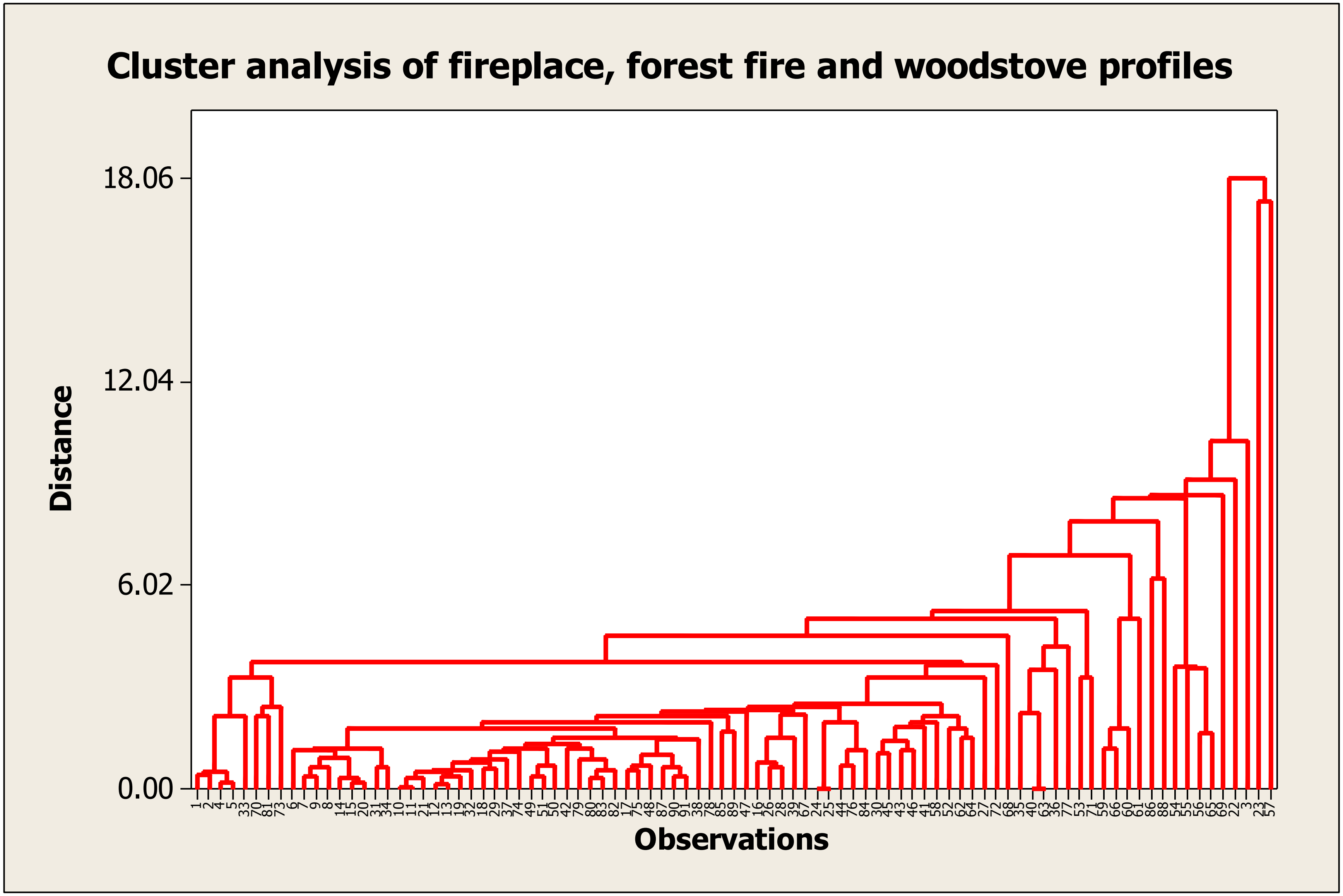

Figure 2.2. Dendrogram of fireplace, woodstove and forest fire profiles from library of Chow *et al.* 2004.

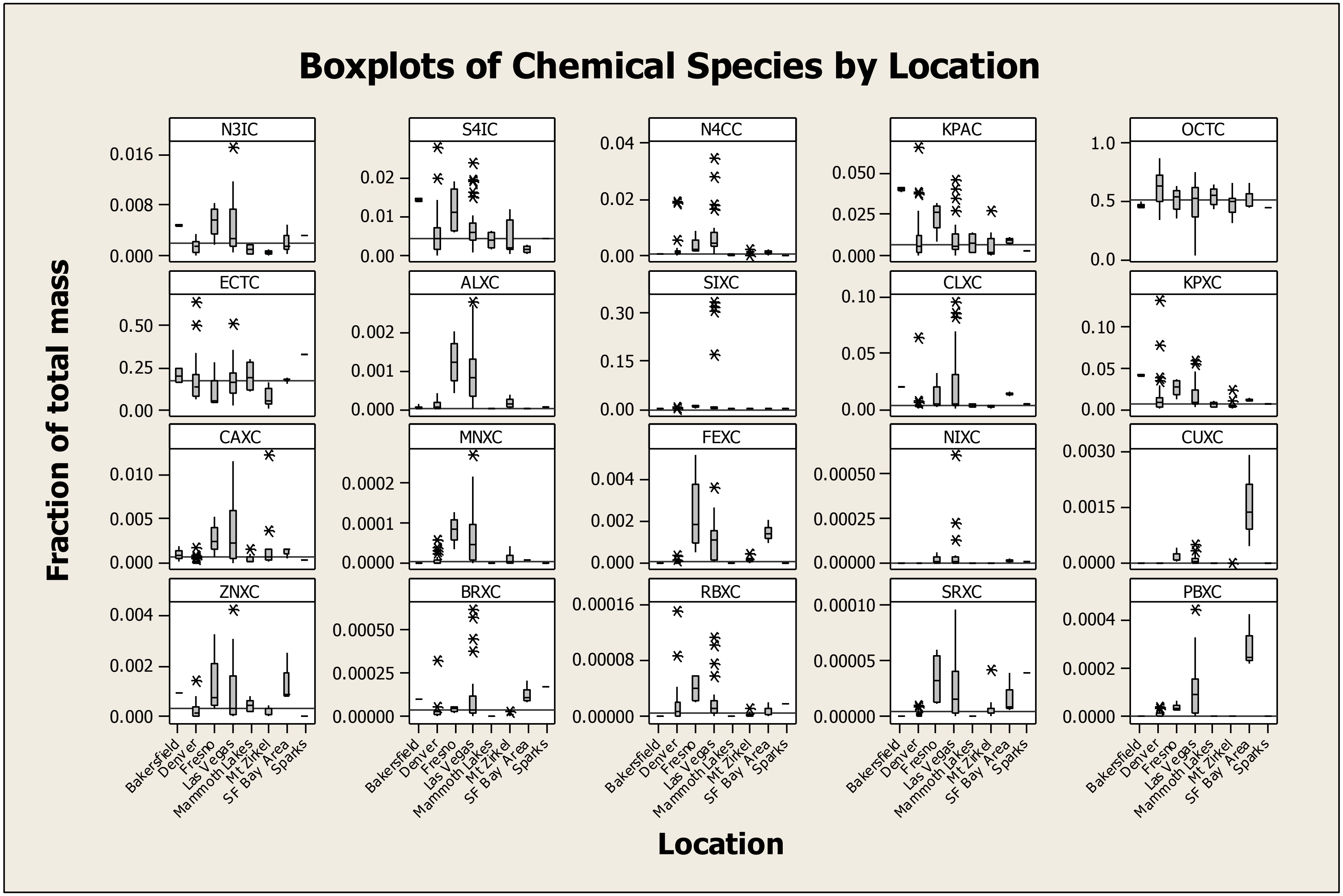

Figure 2.3. Boxplots of species by location. Reference line drawn at the median of the site medians.

Adjusted profile

Figure 2.4 compares the Bay Area medians with the trimmed mean of the medians from the other seven locations. Also shown are the trimmed standard deviations.

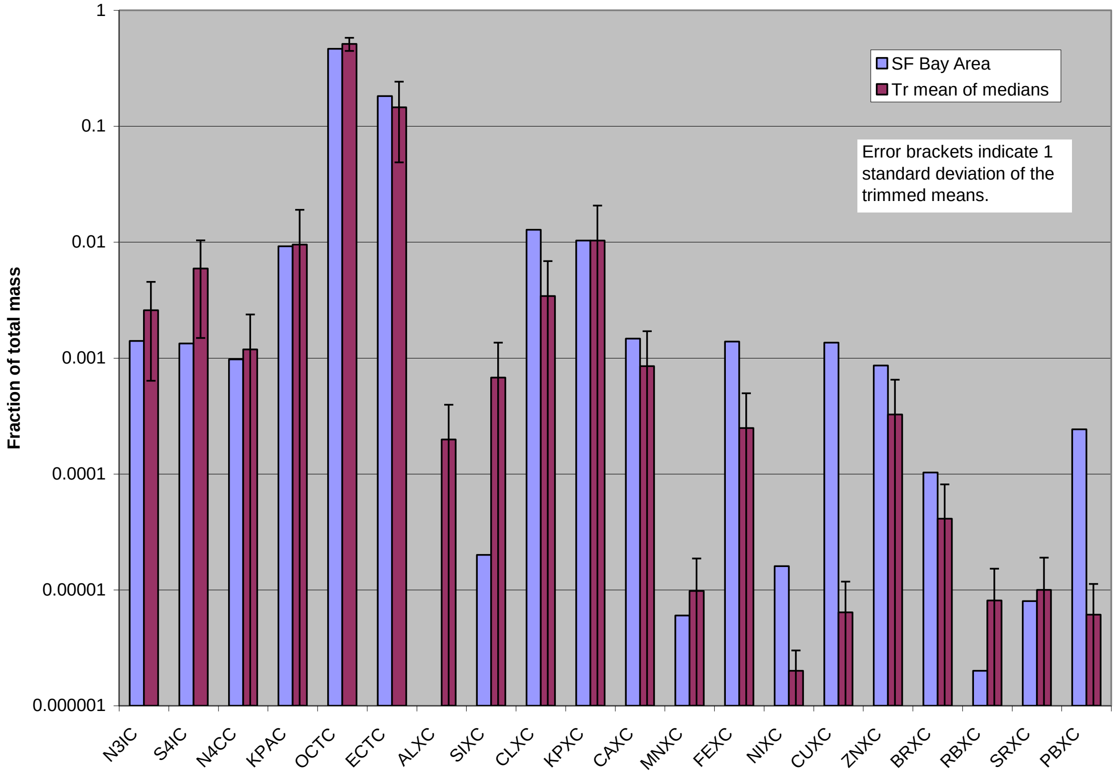

Figure 2.4. Comparison of SF Bay Area profile median by species with the trimmed mean of the medians of the other seven locations. Also shown is ±1 standard deviation of the medians.

We adjusted the Bay Area woodsmoke profile to be at or within one standard deviation of the trimmed mean of the medians from the other locations. This reduced the fractions of chlorine, bromine, and the metals mentioned above. It also actually raised the sulfate level somewhat.

The Bay Area uncertainties were compared with the standard deviation of all the observations pooled. In several cases, the Bay Area uncertainties were substantially greater. Since the pooled observations vary by region and probably because of contamination, it seemed reasonable that the Bay Area uncertainties should not be larger; therefore, we took the minimum of the two. The uncertainty for elemental potassium was lower than that for soluble potassium and considerably lower than the variation among the location medians. We raised this uncertainty to equal the Bay Area uncertainty for soluble potassium. The adjusted profile is presented in Table 2.2.

Table 2.2. Adjusted woodsmoke profile

	N3IC	S4IC	N4CC	KPAC	OCTC	ECTC	ALXC	SIXC	CLXC	KPXC	CAXC	MNXC	FEXC	NIXC	CUXC	ZNXC	BRXC	RBXC	SRXC	PBXC
fraction	0.0014	0.0015	0.0010	0.0092	0.465	0.149	0	0	0.0069	0.0103	0.0015	0	0.0005	0	0	0.0007	0.00004	0	0	0
uncertainty	0.0031	0.0058	0.0061	0.0044	0.15	0.043	0.0007	0.002	0.0084	0.0044	0.0008	0.00003	0.0009	0.00007	0.0004	0.0007	0.00010	0.00003	0.00002	0.0001

References

Fairley, D. 2008. "Sources of Bay Area fine particles." BAAQMD Technical Report 200804-001-PM. http://www.baaqmd.gov/Divisions/Planning-and-Research/~/media/A4FE23A2D4734DE4968FF4F2ED649D85.ashx

Fairley, D. 2010. "West Oakland Metals Analysis." BAAQMD memorandum.

Chow, J.D., J.G. Watson, and L.-W.A. Chen. 2004. "Contemporary Inorganic and Organic Speciated Particulate Matter Source Profiles for Geological Material, Motor Vehicles, Vegetative Burning, Industrial Boilers, and Residential Cooking." Draft Report, Desert Research Institute, Reno, NV.

A3. Wildfire Profile

Plots of OC as a function of EC from various sites revealed outliers where OC was considerably higher than EC. Figures 3.1 and 3.2 show these outliers along with the dates they occurred. The dates are all during periods with substantial wildfire activity. Because the ratio of OC to EC appeared exceptional, it seemed reasonable to create a wildfire source profile.

Our Bay Area woodsmoke profile has an OC/EC ratio of 3.3, shown in Figure 3.2. There were two periods in 2008 with heavy wildfire smoke in the Bay Area, June 23-28 and July 6-12. Figure 3.3 shows a dramatic satellite photo for July 8, 2008 where wildfire smoke covers not just the Bay Area but much of Northern California.

Figures 3.4 and 3.5 show OC as a function of EC at two coastal California IMPROVE sites, Point Reyes and Redwood National Park. These sites are less impacted by urban OC and EC sources. Unlike Figure 3.2, most of the points in the OC/EC line are near or above the line; however, there are several points far above the line. Some of these points also coincide with northern California wildfires, including October 12, 2004 and October 20, 1999 to October 23, 1999. Several other high points occurred between August 3, 2002 and August 12, 2002. There were no substantial wildfires in northern California in this period that we could determine.

Observations on known wildfire days were combined and shown in Figure 3.6. The OC/EC relationship appears quite linear. A simple linear regression has an R^2 of 94% with an insignificant intercept. A regression through the origin yields OC = 8.7EC with a slope standard error of 0.4. Figures 3.7a and 3.7b show the relationship of OC and EC to potassium (K) on these days. Also shown are the ratios of OC and EC to potassium from the District's woodsmoke profile. With the exception of October 20, 1999 for Redwood National Park and October 12, 2004 for Point Reyes, the OC/K relationship is similar to the ratio for District woodsmoke. But the ratios for EC to K in Figure 3.7b are well below the line, with one exception. This suggests that wildfires have less EC than regular woodsmoke as opposed to having more OC.

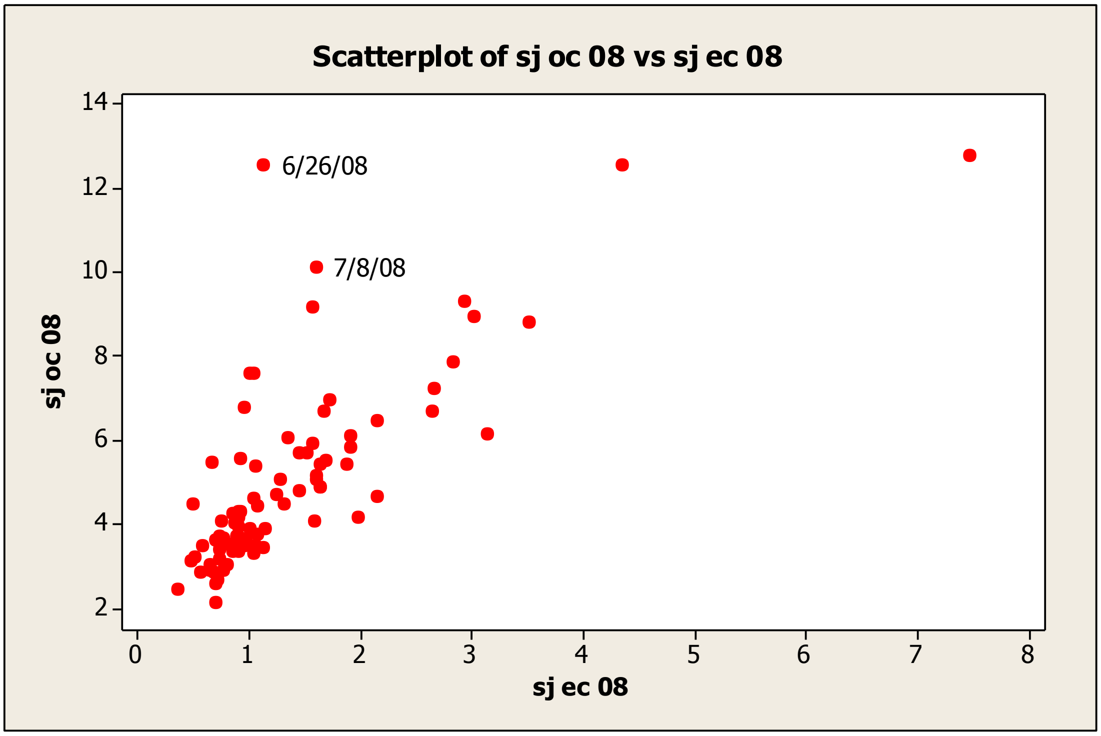

Figure 3.1. San Jose OC vs. EC for 2008 from STN measurements.

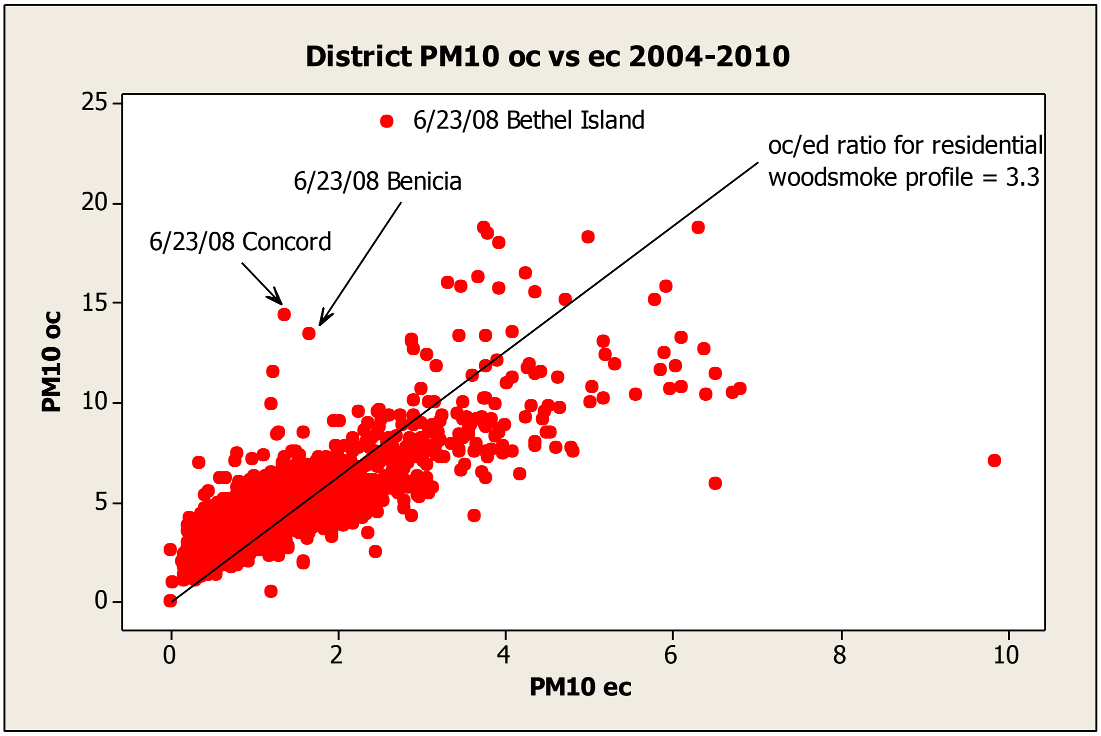

Figure 3.2. Organic vs. elemental carbon at various District sites, 2004-2010. A line representing the typical OC/EC residential woodsmoke ratio is also shown.

Figure 3.3. Satellite photo of Northern California 7/8/08. SF Bay Area in lower center.

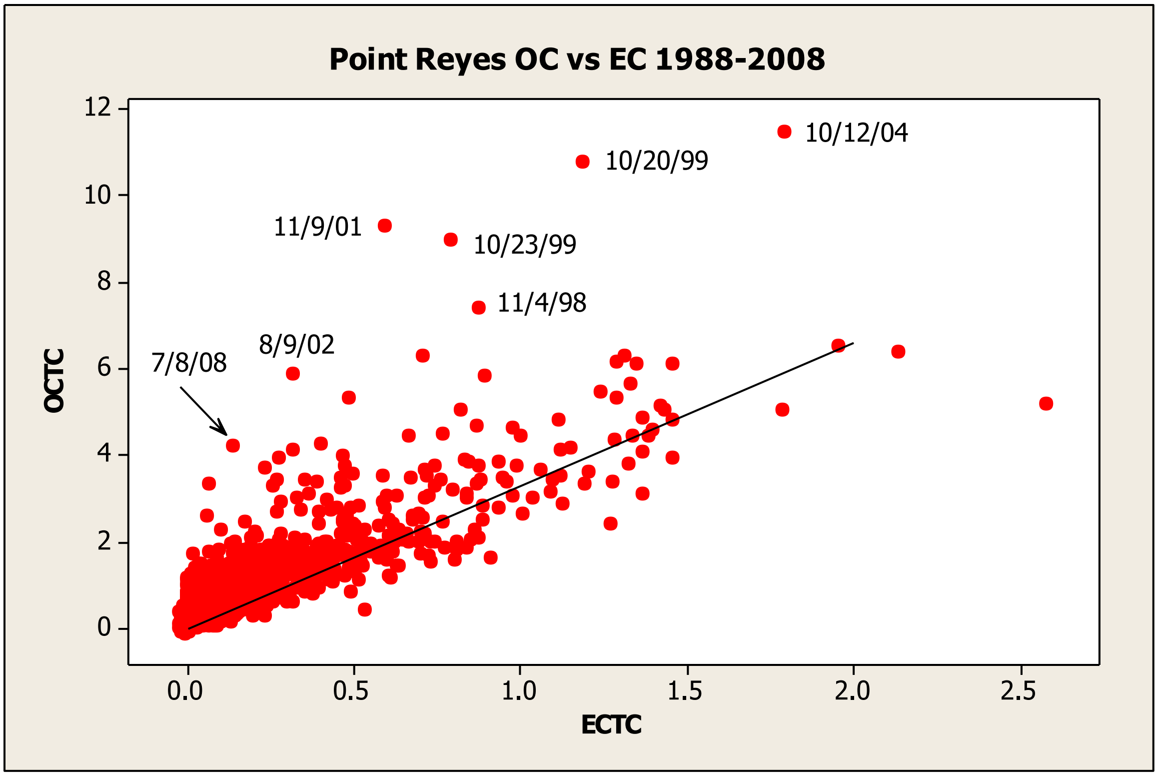

Figure 3.4. Organic vs. elemental carbon measurements at Point Reyes, 1988-2008.

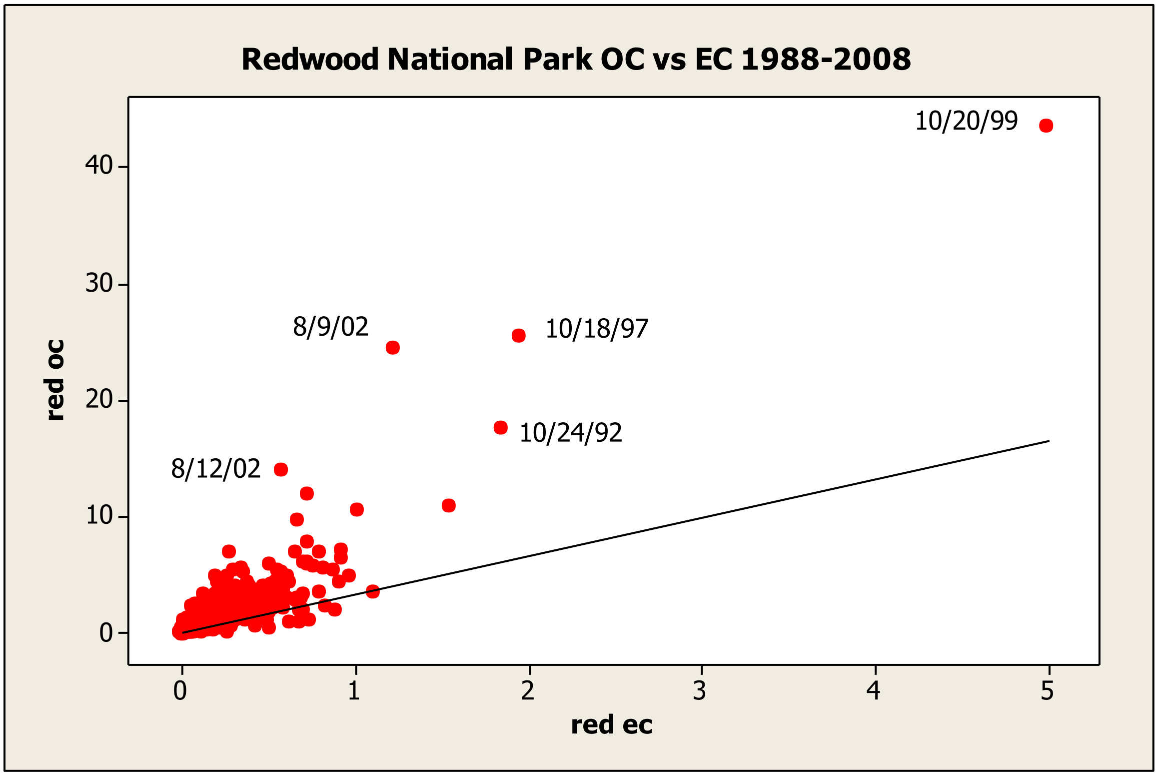

Figure 3.5. Organic vs. elemental carbon measurements at Redwood National Park, 1988-2008.

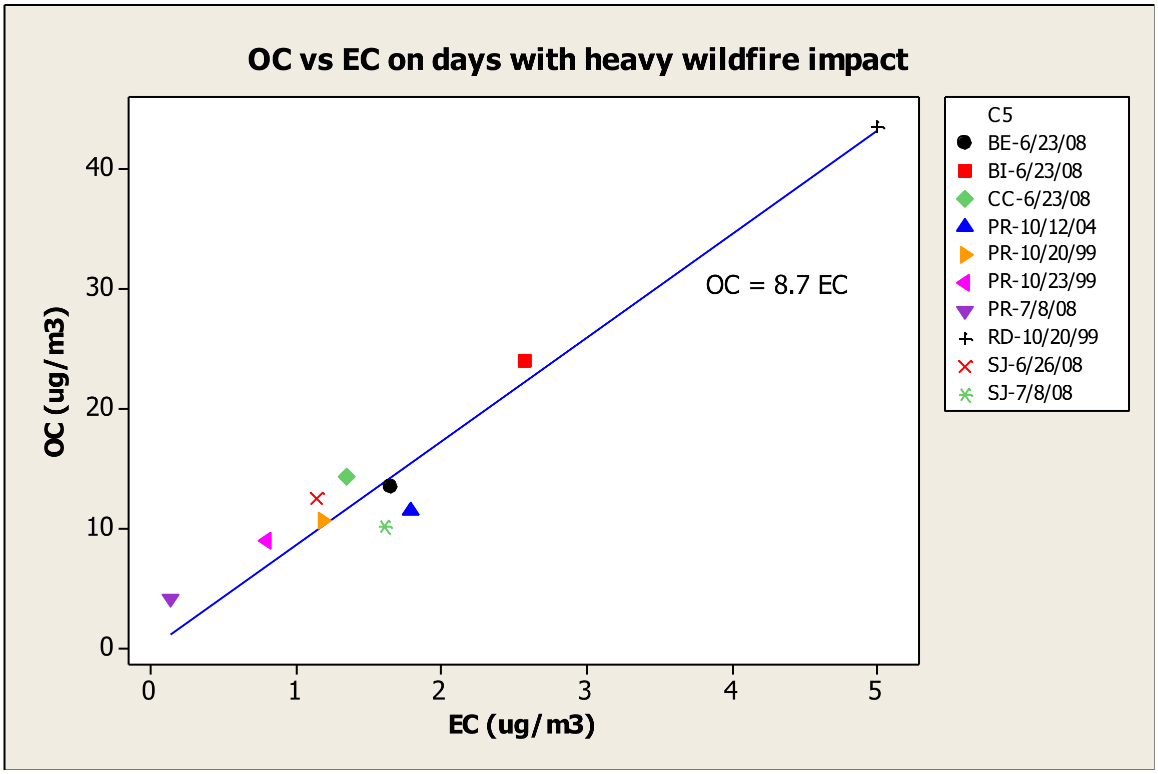

Figure 3.6. OC and EC measurements at various sites on days with known heavy wildfire impact.

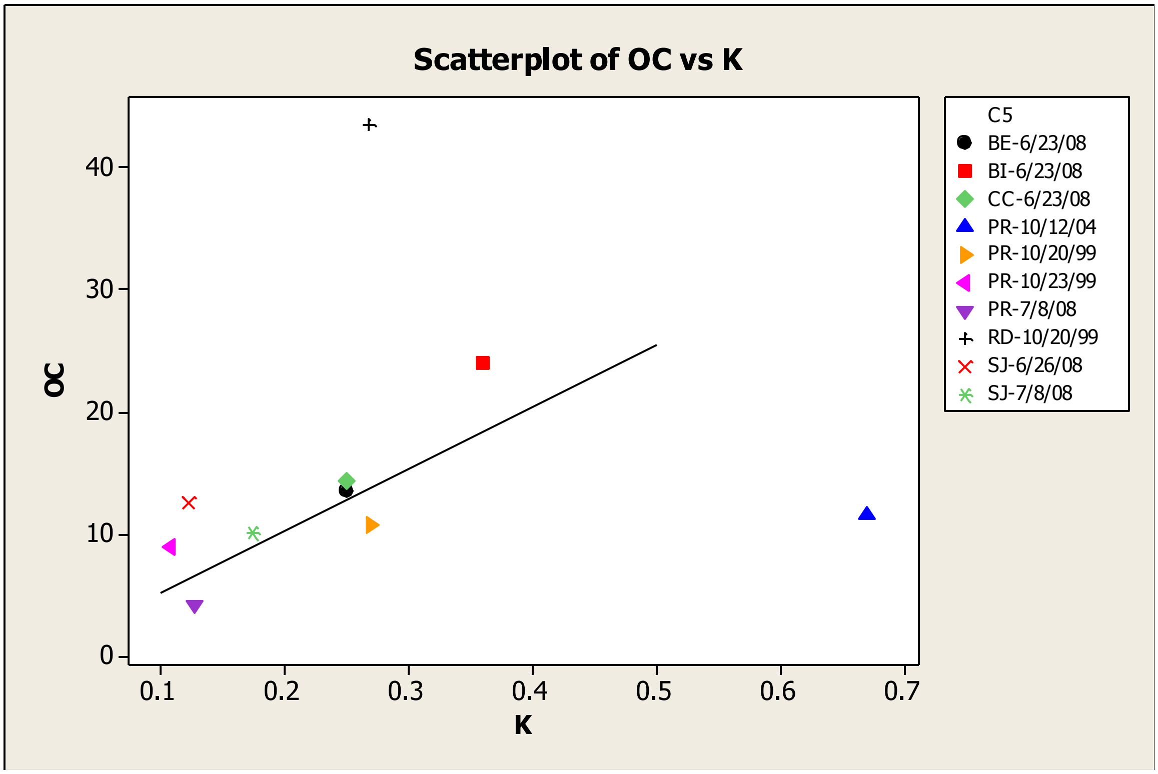

Figure 3.7a. Plot of organic carbon vs. potassium on days with heavy wildfire impact. Also shown, a line representing the OC/K ratio from the District's woodsmoke profile.

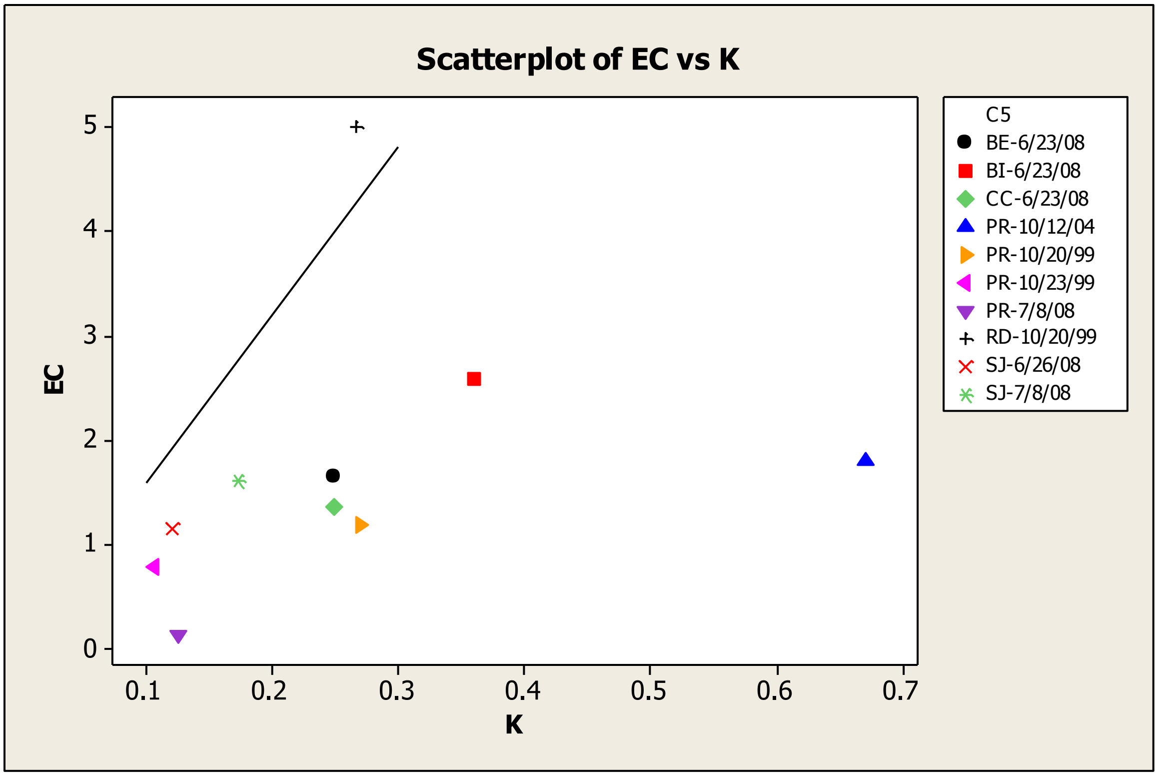

Figure 3.7b. Plot of elemental carbon vs. potassium on days with heavy wildfire impact. Also shown, a line representing the EC/K ratio from the District's woodsmoke profile.

Developing a wildfire profile

To make a wildfire profile, we took the residential woodsmoke profile and lowered the EC to be OC/8.7. This resulted in the sum of the element fractions dropping from 0.65 to 0.55. We made the assumption that the total fraction would be about the same, so we took the profile with the altered EC value and multiplied each term by 0.65/0.55, including the uncertainties.

Table 3.1 Wildfire profile

	N3IC	S4IC	N4CC	KPAC	OCTC	ECTC	ALXC	SIXC	CLXC	KPXC
fraction	0.0016	0.0018	0.0012	0.0108	0.5456	0.0627	0.0000	0.0000	0.0081	0.0121
uncertainty	0.0036	0.0068	0.0072	0.0052	0.1760	0.0181	0.0008	0.0023	0.0099	0.0052
	CAXC	MNXC	FEXC	NIXC	CUXC	ZNXC	BRXC	RBXC	SRXC	PBXC
fraction	0.0018	0.0000	0.0006	0.0000	0.0000	0.0008	0.00005	0.0000	0.0000	0.0000
uncertainty	0.0009	0.00004	0.0011	0.0001	0.0005	0.0008	0.0001	0.00004	0.00002	0.0001

A4. Constructing a ship emissions profile

Until July 2009, ships near or in San Francisco Bay largely used residual fuel oil for fuel. A residual oil profile (Resfuel) was available from a previous analysis (Fairley 2010). But information is also obtainable from ambient samples. In particular, much of the $PM_{2.5}$ collected at the Point Reyes IMPROVE site is marine, containing a substantial portion from ship emissions. These ambient data provide information about the source composition of locally emitted ship emissions. In this analysis, we combine the two datasets as explained below.

Ambient correlations and regressions

Point Reyes data from 2002 through 2008 were used to investigate the ship emissions component in ambient air. The start date was chosen because of a significant reduction in uncertainty in the measurement of vanadium, a key component of residual fuel oil (see Figure 4.1).

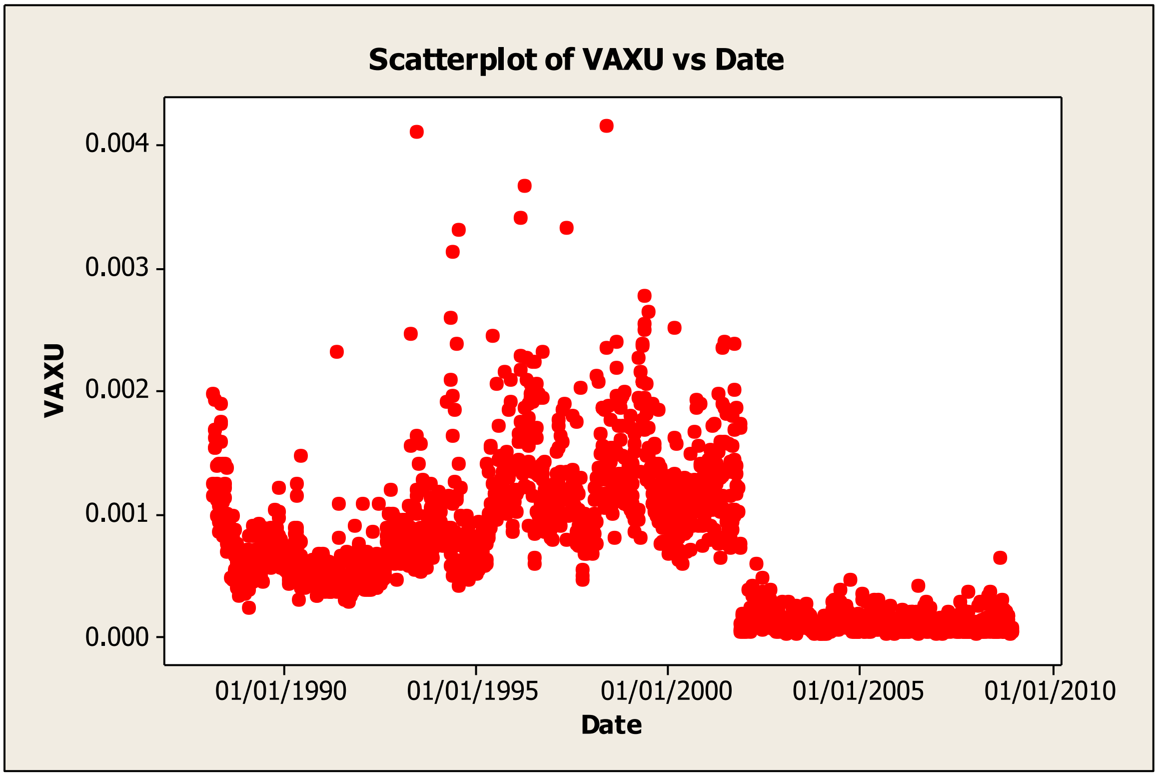

Figure 4.1. Uncertainties in Point Reyes vanadium measurements 1989-2009.

Vanadium at Point Reyes was strongly correlated with nickel and weakly correlated with a number of other species. It was decided to perform univariate regressions of vanadium on other species and compare the slopes to the ratio of these species to vanadium in the Resfuel source profile. For the latter, the ratios were simulated assuming the species were independent normal random variables with standard deviations equal to the Resfuel profile uncertainty.

Figure 4.2 compares the Resfuel profile with species fractions estimated from regressions on vanadium, assuming that vanadium makes up 0.12% of ship emissions, the percent of vanadium in the Resfuel profile. The profile and regression-derived fractions are largely in agreement both in terms of magnitude and order. Both show sulfate as the largest component; there is a discrepancy with nitrate but then comes organic carbon followed by elemental carbon. The error bars overlap in the majority of cases, indicating that the differences are not statistically significant.

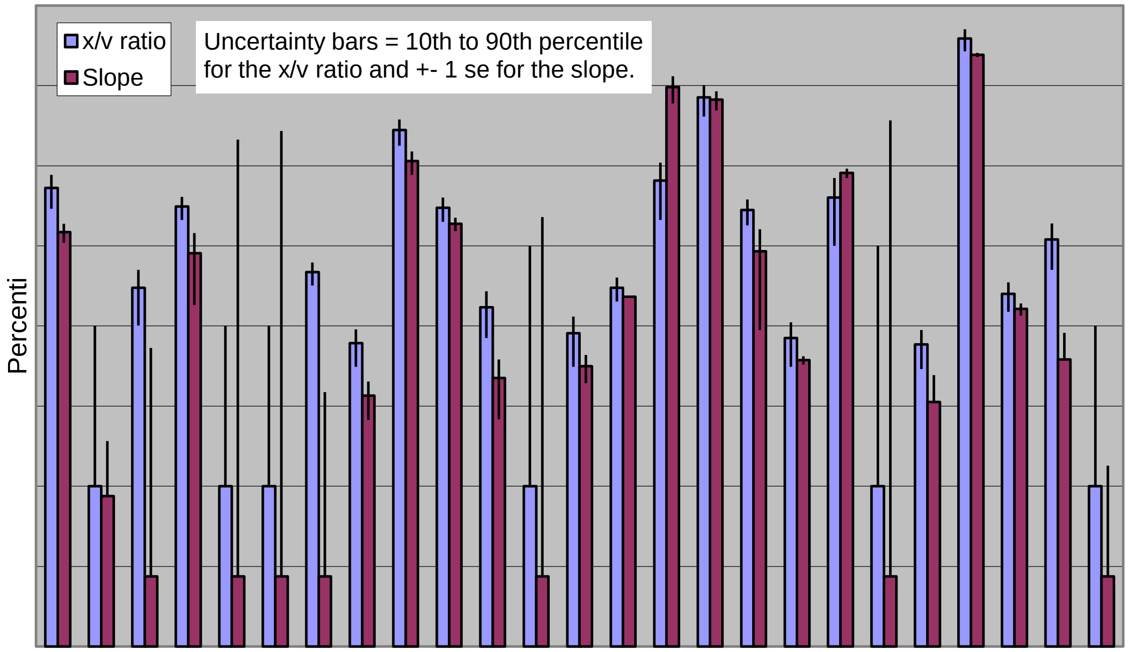

Figure 4.2. Comparison of Resfuel composition with Point Reyes species concentrations estimated from regressions on vanadium.

Note that the Resfuel values for the main constituents of sea salt, namely sodium and chloride and also magnesium, are effectively zero. The corresponding slopes were negative.

Sulfate in ship exhaust

Although some sulfate is directly emitted, most is likely formed from chemical reaction of SO_2 gas (Dominguez *et al*. 2008). Among the ratios of other constituents to vanadium, sulfate's ratio is by far the highest; it appears to be the largest single component of the $PM_{2.5}$ from ship emissions.

As an anion, sulfate needs cations to balance it. What these include is still an open question. Vanadium and other trace metals account for only a small fraction. Some cations are undoubtedly ammonium, but the amounts measured in one study (Ault 2010a) do not balance all the sulfate. Some of the remainder may be hydrogen ions or organic carbon (Ault 2010b).

Ship Profile

To estimate a Bay Area ship profile, we simply averaged the Resfuel profile with the profile derived from regressions on vanadium, that is, the two profiles shown in Figure 4.2. For the s.d., we took the median of three standard deviations: 1. the uncertainty from the Resfuel profile, 2. the s.d. from the regression slope multiplied by 0.12, and 3. the s.d. of the difference between the two profiles.

References

Ault, A., C.J. Gaston, Y. Wang, G. Dominguez, M. Thiemens, and K.A. Prather. 2010. “Characterization of the single particle mixing state of individual ship plume events measured at the Port of Los Angeles.” *Environmental Science and Technology* 44: 1954–1961.

Ault, Andrew. 2010. Personal communication, October 3.

Dominguez, G., T. Jackson, L. Brothers, B. Barnett, B. Nguyen, and M.H. Thiemens. 2008. “Discovery and measurement of an isotopically distinct source of sulfate in Earth's atmosphere.” Proceedings of the National Academy of Sciences, 105, 35: 12769-12773.

Fairley, D. 2010. Evidence for the Sources of Oceanic Background $PM_{2.5}$ in the Bay Area: Source Apportionment for two California Coastal Sites. Draft BAAQMD Report.

Hsu Y., R. Strait, S. Roe, and D. Holoman. 2006. “Speciate 4.0. Speciation database development documentation.” EPA/600/R-06/161.
http://www.epa.gov/ttnchie1/software/speciate/

A5. Fireworks Profile

The presence of fireworks or gunpowder was discovered by examining statistically outlying potassium measurements. In general potassium is a reliable marker for woodsmoke, with a relatively consistent relationship to woodsmoke's main constituent, organic carbon; however, some large potassium values had been discovered in an earlier analysis that didn't fit the above pattern. Figure 5.1a shows potassium and organic carbon, both measured at San Jose[11] from 2003 through 2009. Potassium values > 0.4 $\mu g/m^3$ are colored. All days within ±1 day of either January 1 or July 4 are shown in red. About half of these show a large impact of what appears to be fireworks. There are three other days shown in green which also exhibit anomalously high potassium levels. Figure 5.1b shows a plot of potassium versus organic carbon during the CRPAQS study. All of the outliers occurred on New Year’s Day.

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[11] San Jose was the only site where fireworks/gunpowder were noted in the past couple of years. Other sites showed fireworks/gunpowder evidence in data collected for the CRPAQS study 1999-2001.

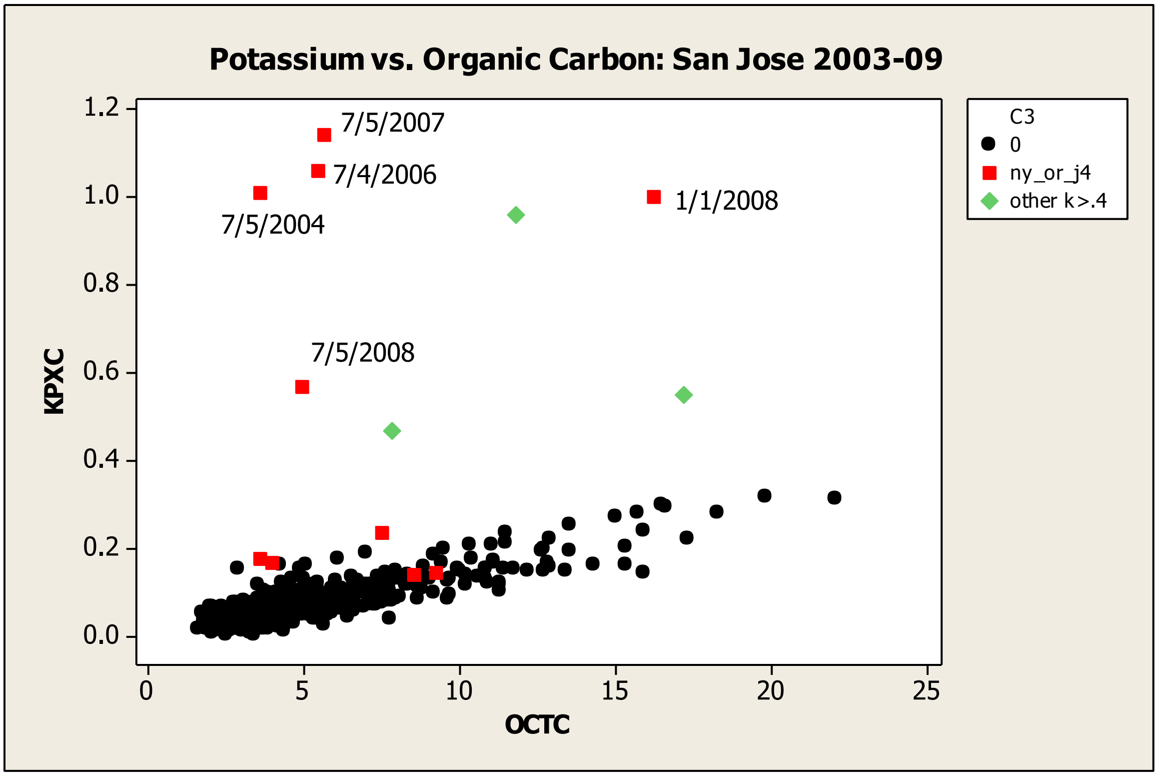

Figure 5.1a. Potassium vs. OC for San Jose-Jackson, 2003-2009. Measurements made within a day of New Year's or July 4 are denoted with red squares; outliers for other days are denoted with green diamonds.

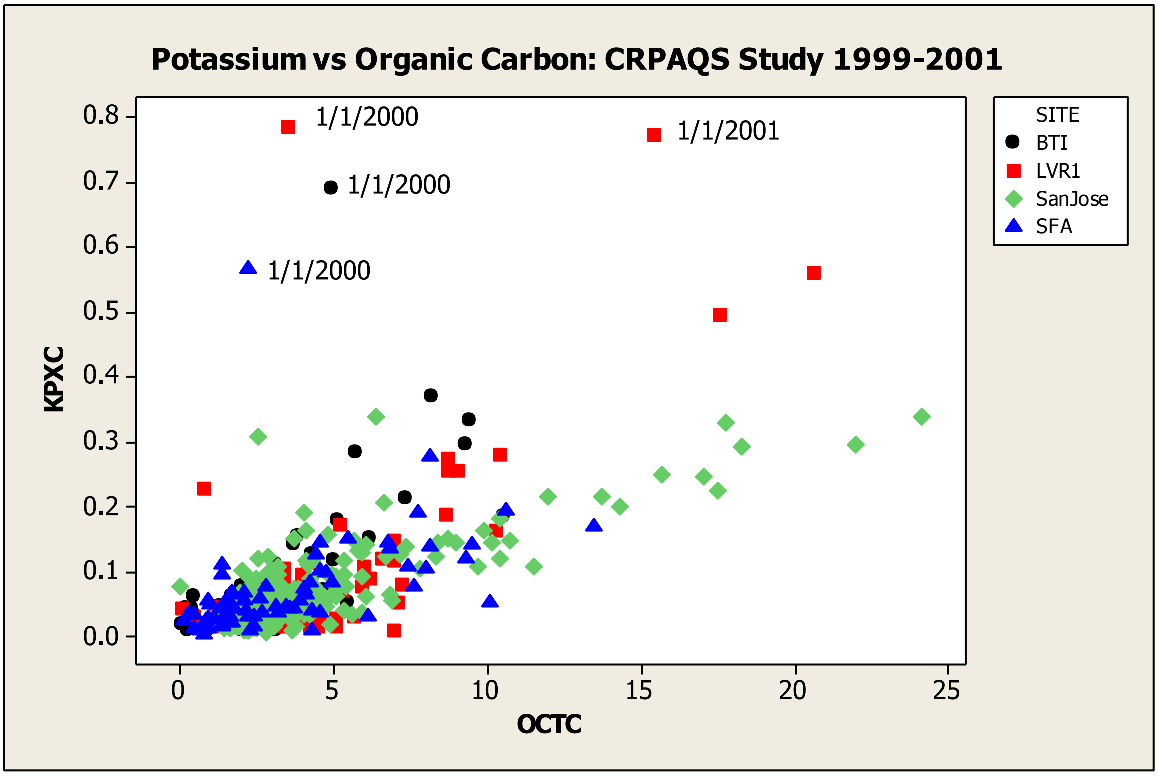

Figure 5.1b. Potassium vs. OC for measurements made during the CRPAQS study.

In a previous analysis, we assumed we were seeing gunpowder, which is approximately 75% charcoal (EC), 15% ammonium nitrate (or sulfate), and 10% sulfur. In this updated analysis, we noticed that high potassium seemed correlated with high values of some other elements. What is being measured on January 1 or July 4 may be fireworks instead of gunpowder. A web investigation of fireworks turned up this list of elements that may be included in fireworks: aluminum, antimony, barium, calcium, carbon, chlorine, copper, iron, lithium, magnesium oxygen, phosphorus, potassium, sodium, strontium, sulfur, titanium, and zinc. All but lithium and oxygen are measured, so we can make comparisons (Skylighter 2012, About.com 2012).

Figure 5.2 shows boxplots of these species and several others partitioned by whether the corresponding potassium concentration was ≤ or > 0.4 μg/m^3. The species listed in fireworks show elevated levels with the exception of antimony and barium, but vanadium and manganese are elevated also.

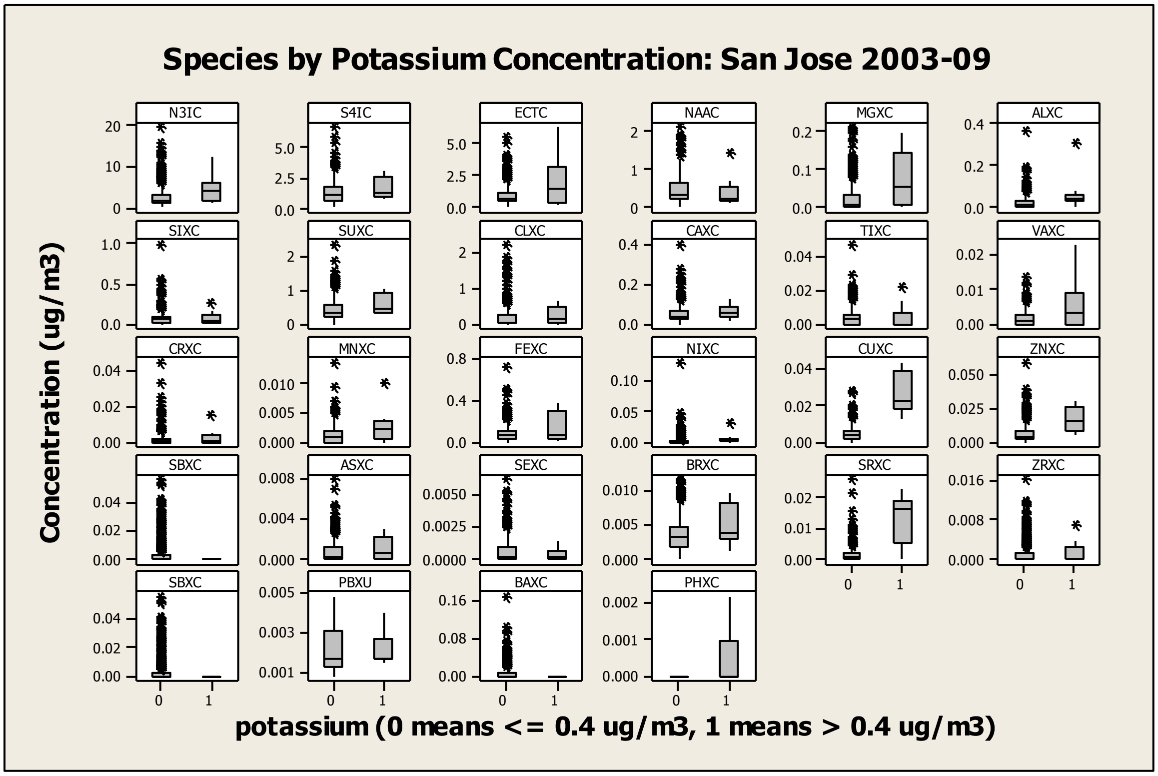

Figure 5.2. Boxplots of species concentrations at San Jose-Jackson, 2003-2009, partitioned by whether potassium was less than or equal to 0.4 μg/m^3, or greater.

Are all the elevated potassium values fireworks-related, or could there be other sources? To help untangle this question, many of the species in Figure 5.2 were plotted versus potassium, with the values colored as in Figures 5.1a and b. Figure 5.3a reveals a number of features. Iron – an element that is generally well measured – is elevated on the green observations but not the fireworks-related. The same with manganese, an element not identified with fireworks. With magnesium it is the reverse – red elevated, green not. Both red and green copper values are elevated; so are most strontium values.

The elevated iron and manganese values suggest the presence of another source. Among those that we have identified, brake wear is a possibility. Iron is its number one constituent, with elemental carbon as number three. Brake wear PM contains has a range of elements including all of those shown in Figure 5.3a except for antimony, chlorine and phosphorus. Note that the green values for these elements are low except for one chlorine observation which could be marine-related. We therefore assume that the green observations represent brake wear, not fireworks.

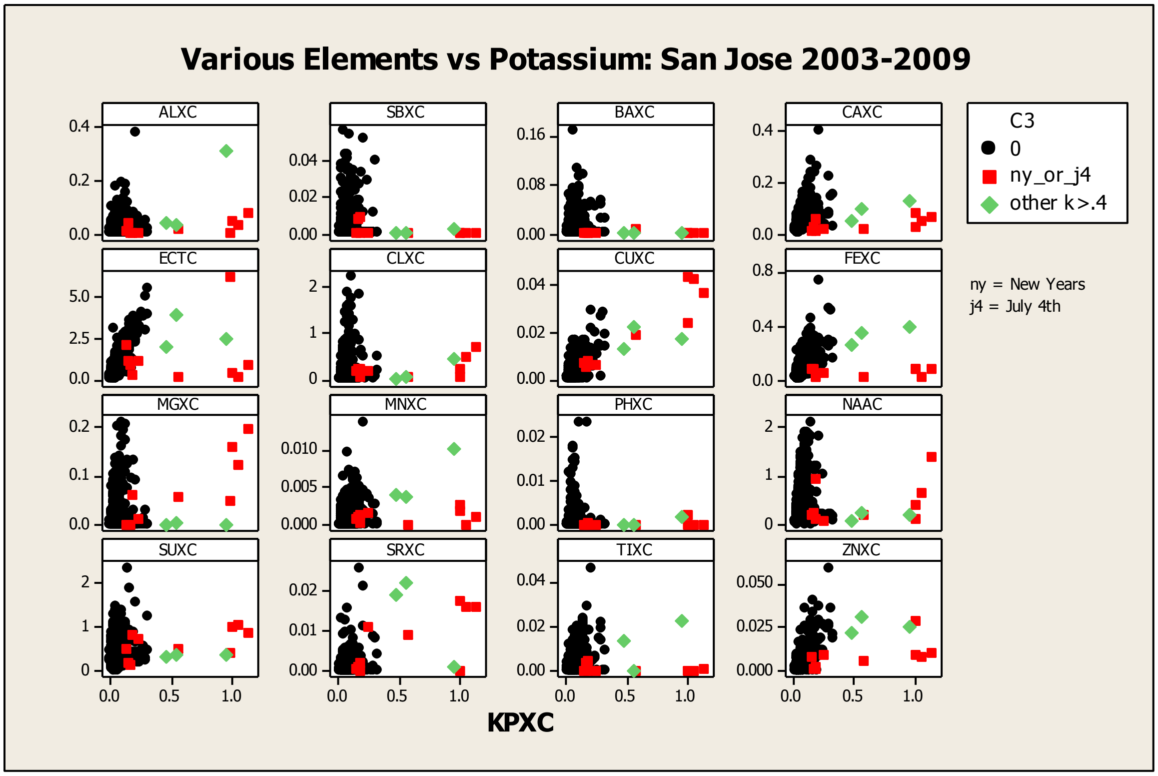

Figure 5.3a. Chemical species vs. potassium for San Jose-Jackson 2003-2009. Values where potassium was greater than 0.4 shown by colors: red squares for days within ±1 day of January 1 or July 4; green diamonds for other days.

We assume that the red observations with large potassium values do indeed represent mainly fireworks. In several cases (sulfur, strontium, and zinc) there are large variations, which suggests considerable variability in the fireworks themselves. This makes sense, as many of these elements are coloring agents that can be present in some fireworks but not others.

Figure 5.3b shows chemical species versus potassium at CRPAQS sites along with pooled San Jose-4th St. and San Jose-Jackson. Red values indicate January 1 or July 4 days. We see many of the same features at other sites: elevated copper, sulfur and strontium concentrations. (Magnesium observations were not readily available.) Iron concentrations are not elevated. Manganese is elevated in one case but not in the other three.

It is not clear how to treat sodium and chlorine since some or all of these could easily be marine-related. We see somewhat elevated sodium observations and chloride observations in Figure 5.3a, but the January 1 or July 4 values for Bethel Island and Livermore are not high, suggesting that the elevated sodium and chloride are indeed marine-related.

The high red elemental carbon observation at San Jose occurred on January 1, 2008, a day with very high organic carbon values also. A plot of EC versus OC shows a ratio that is above average (6/16 =

0.39, compared with a typical value of about 0.24), suggesting some additional EC, but mostly due to woodsmoke. Another occurred at Livermore on January 1, 2001, but the OC was also high and the relationship didn't appear out of line with other Livermore values.

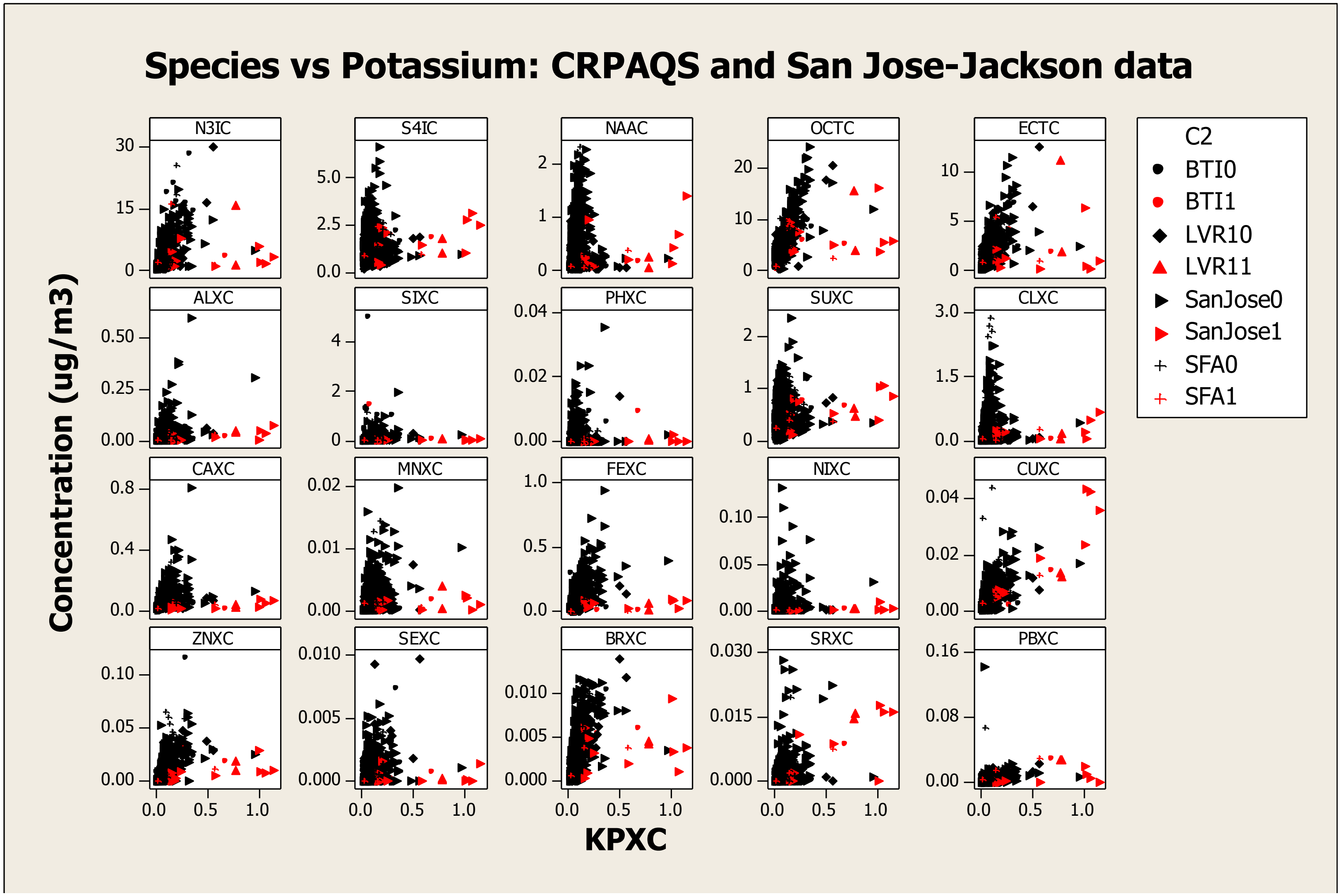

Figure 5.3b. Chemical species vs. potassium at CRPAQS sites, 1999-2001 and San Jose-Jackson 2003-2009. Symbols in red indicate days within ±1 day of 1/1 or 7/4.

Developing a fireworks profile

The five days with high potassium shown in Figure 5.3a that occurred around January 1 or July 4 were used to develop a fireworks profile. For most elements, this was accomplished as follows. For nitrate and sulfate, see the next section.

Because potassium is a key component of woodsmoke, we backed out an estimate of the woodsmoke component from these samples. We assumed that the woodsmoke was proportional to the organic carbon, and backed out the other elements in proportion to the OC concentration and used our woodsmoke profile. We then backed out marine air contributions, keying on sodium, assuming that all the sodium came from marine air and used our aged marine profile.

This gave us residuals for every element for each of the five days. We averaged these residuals, setting the value to zero if the sum was negative. We computed the standard deviations and used these for the uncertainties. Since the backed out residuals for OC and sodium were identically zero, we set their uncertainties to the EC and chlorine standard deviations, respectively.

Nitrate and Sulfate

Potassium nitrate and sulfate are used as oxidizers in fireworks, but both nitrate and sulfate have other sources in the Bay Area so it is not possible to determine how much of these originate from fireworks based on the ambient data. The ambient amount of either of these compounds is sufficient to balance the potassium. Figure 5.4 shows nitrate and sulfate versus potassium with lines drawn in to represent the amounts of nitrate and sulfate that would be required to use all the potassium in either potassium nitrate or potassium sulfate.

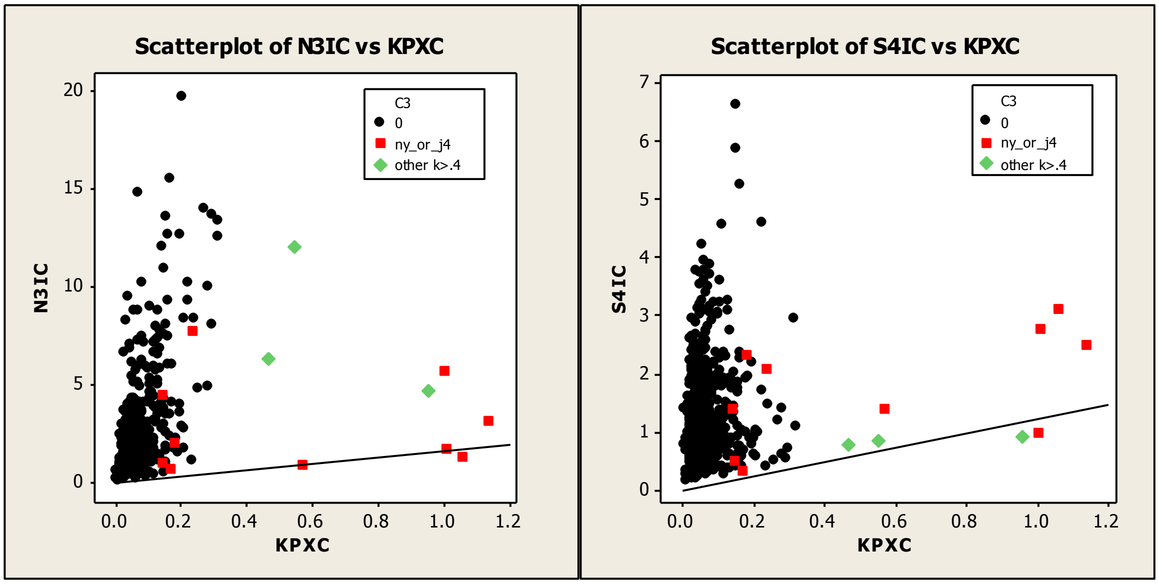

Figure 5.4. Nitrate and sulfate vs. potassium for San Jose-Jackson. Lines representing ammonium nitrate and ammonium sulfate are also shown.

Without prior knowledge of Bay Area fireworks composition, we assumed that fireworks used potassium nitrate with probability 2/3 and potassium sulfate with probability 1/3. For the nitrate component of the profile, then, we took the potassium mean and multiplied by 2/3 x 62/39.1, where the latter is the ratio of the atomic weight of NO_3 to K. For sulfate, we multiplied by 1/3 x (96.07/(2*39.1)), the latter being the ratio of the atomic weight of SO_4 to K_2. For the uncertainties, we used the standard deviation of distribution generated by the probability assumptions. Specifically, in each case we have a variable that takes a value k, with probability p, and a value of 0 with probability 1-p. The standard deviation of this random variable is k*sqrt[p(1-p)]. In either case here the s.d. is k*sqrt(2/3*1/3).

The profile is shown in Table 5.1.

Table 5.1. Fireworks profile.

	CLIC	N3IC	S4IC	N4CC	NAAC	KPAC	OCTC	ECTC	MGXC	NAXC	ALXC	SIXC	CLXC
fraction	0	0.3060	0.1184	0	0	0.2805	0	0.0723	0.1461	0	0.0122	0.0087	0
uncert	0.0791	0.2164	0.0837	0.0036	0.0723	0.0891	0.1808	0.4311	0.1509	0.1688	0.0099	0.0082	0.0791
	KPXC	**CAXC**	**TIXC**	**VAXC**	**CRXC**	**MNXC**	**FEXC**	**COXC**	**NIXC**	**CUXC**	**ZNXC**	**SEXC**	**BRXC**
fraction	0.2887	0.0046	0	0.0023	0.0007	0.0004	0.0180	0	0.0009	0.0119	0.0011	0	0.0004
uncert	0.0821	0.0116	0.0006	0.0037	0.0009	0.0004	0.0125	0.0001	0.0015	0.0041	0.0013	0.0005	0.0012
	RBXC	**SRXC**	**YTXC**	**ZRXC**	**MOXC**	**PDXC**	**AGXC**	**CDXC**	**SBXC**	**BAXC**	**LAXC**	**HGXC**	**PBXC**
fraction	0	0.0042	0	0	0	0	0	0	0	0	0	0.0001	0.0023
uncert	0.0001	0.0027	0.0001	0.00008	0.00004	0.0001	0.0015	0.0011	0.0012	0.0088	0.0115	0.0003	0.0030

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