Spatial and temporal variability of sources of ambient fine particulate matter (PM$_{2.5}$) in California

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Abstract. To identify major sources of ambient fine particulate matter (PM$_{2.5}$, dp < 2.5 μm) and quantify their contributions in the state of California, a positive matrix factorization (PMF) receptor model was applied on Speciation Trends Network (STN) data, collected between 2002 and 2007 at eight distinct sampling locations, including El Cajon, Rubidoux, Los Angeles, Simi Valley, Bakersfield, Fresno, San Jose, and Sacramento. Between five to nine sources of fine PM were identified at each sampling site, several of which were common among multiple locations. Secondary aerosols, including secondary ammonium nitrate and ammonium sulfate, were the most abundant contributor to ambient PM$_{2.5}$ mass at all sampling sites, except for San Jose, with an annual average cumulative contribution of 26 to 63 %, across the state. On an annual average basis, vehicular emissions (including both diesel and gasoline vehicles) were the largest primary source of fine PM at all sampling sites in southern California (17–18 % of total mass), whereas in Fresno and San Jose, biomass burning was the most dominant primary contributor to ambient PM$_{2.5}$ (27 and 35 % of total mass, respectively), in general agreement with the results of previous source apportionment studies in California. In Bakersfield and Sacramento, vehicular emissions and biomass burning displayed relatively equal annual contributions to ambient PM$_{2.5}$ mass (12 and 25 %, respectively). Other commonly identified sources at all sites included aged and fresh sea salt and soil, which contributed to 0.5–13 %, 2–27 %, and 1–19 % of the total mass, respectively, across all sites and seasons. In addition, a few minor sources were identified exclusively at some of the sites (e.g., chlorine sources, sulfate-bearing road dust, and different types of industrial emissions). These sources overall accounted for a small fraction of the total PM mass across the sampling locations (1 to 15 %, on an annual average basis).

1 Introduction

Exposure to ambient airborne particulate matter (PM) is one of the leading causes of morbidity and mortality, contributing to more than 3 million premature deaths in the world annually, based on a recent global burden of disease study (Lim et al., 2013). PM inhalation has been linked to a wide range of adverse health effects such as respiratory inflammation (Araujo et al., 2008), cardiovascular diseases (Delfino et al., 2005; Ostro et al., 2014), and most recently neurodegenerative and neurodevelopmental disorders (Davis et al., 2013b, 2013a). For the past few decades, California has been constantly suffering from high concentrations of ambient PM, among the highest levels recorded within the United States, with estimated rates of PM-related morbidity and mortality exceeding any other state in the country (Fann et al., 2012).

Ambient PM in California originates from a large number of diverse sources (Hu et al., 2014) and is a complex mixture of different chemical components, the composition of which may change drastically with PM size (Hu et al., 2008), location, and season (Cheung et al., 2011; Daher et al., 2013). Current PM regulations in California target PM$_{10}$ and PM$_{2.5}$ (particles with aerodynamic diameter less than 10 and 2.5 μm, respectively) mass concentrations, with PM$_{2.5}$ being of major concern due to the higher rate of PM$_{2.5}$-related morbidity and mortality in the state compared to PM$_{10}$ (Ostro

et al., 2006; Woodruff et al., 2006). These regulations only target PM mass concentration, regardless of their sources of emission and/or toxico-chemical characteristics. There is, however, strong evidence that the level of toxicity and health-related characteristics of PM are significantly affected by their chemical composition and therefore by their emission sources (Rohr and Wyzga, 2012; Stanek et al., 2011; Zhang et al., 2008; Saffari et al., 2013). Recently, there has been growing interest in using source apportionment data in epidemiological health studies (Sarnat et al., 2008; Özkaynak and Thurston, 1987; Laden et al., 2000; Mar et al., 2000; Ostro et al., 2011). These studies have provided significant evidence that exposure to PM from certain sources is linked to mortality. In a recent study in Barcelona, Ostro et al. (2011) found that exposure to several sources, including traffic emissions, sulfate from ship emissions and long-range transport, and construction dust, is statistically significantly associated with all-cause and cardiovascular mortality. Nonetheless, to draw firm conclusions and develop more effective control strategies for reducing population exposure to harmful sources of airborne PM, further epidemiological studies that use source apportionment data are warranted.

To date, several source apportionment studies have been conducted in California, using source-oriented (Hu et al., 2014; Kleeman and Cass, 2001; Zhang et al., 2014; DeNero, 2012) and receptor models (Hasheminassab et al., 2013; Hwang and Hopke, 2006; Ham and Kleeman, 2011; Kim and Hopke, 2007; Kim et al., 2010; Schauer and Cass, 2000). Source-oriented models focus on the transport, dilution, and transformation of pollutants from the source of emission to the receptor site, thereby providing an overall estimation regarding the spatial distribution of source contributions. Receptor models, on the other hand, focus on the behavior of ambient environments at the point of impact (Hopke, 2003). Even though these studies have provided important insights into the characteristics of sources of ambient PM as well as their relative contributions, they have been mostly conducted in a limited number of sampling locations and/or within a relatively short period of time. As a result, spatial and temporal variability of the identified sources have not been extensively examined. For instance, Kim et al. (2010) analyzed the $PM_{2.5}$ speciation data collected between 2003 and 2005 at two sampling sites in southern California (i.e., Los Angeles (LA) and Rubidoux) to identify and quantify major $PM_{2.5}$ sources, by application of a positive matrix factorization (PMF) model. Using a similar source apportionment approach, Hwang and Hopke (2006) evaluated the sources of ambient $PM_{2.5}$ at two sampling sites in San Jose using the Speciation Trends Network (STN) data collected between 2000 and 2005. In a more comprehensive study, Chen et al. (2007) applied several receptor models to the chemically speciated $PM_{2.5}$ measurements collected for 1 year (between 2000 and 2001) at 23 sites, all located in California's San Joaquin Valley (SJV), to estimate $PM_{2.5}$ source contributions.

In this study, PMF, one of the most widely used receptor-oriented source apportionment techniques (Paatero and Tapper, 1994), was employed in order to provide a detailed and long-term (from 2002 to 2007) quantification of the contributions of different emission sources to ambient $PM_{2.5}$ mass concentration in California, at eight distinct locations spanning the southern, central, and northern regions of the state. The association between PM-related mortality and $PM_{2.5}$ mass concentration as well as individual $PM_{2.5}$ chemical components has been investigated in previous epidemiological studies in California (Ostro et al., 2006; Ostro et al., 2007). The results of this study will be used as input for future epidemiological studies conducted by the California Environmental Protection Agency (Cal EPA) in order to further expand the current epidemiological knowledge by establishing the relationship between PM-related adverse health effects and specific source contributions. These findings will be crucial in establishing targeted and cost-effective regulations on $PM_{2.5}$ emissions in the state of California.

2 Methodology

2.1 Sampling sites

Sampling was conducted at eight STN sampling sites, established by the United States Environmental Protection Agency (US EPA), located in distinctly different cities all over California including El Cajon, Rubidoux, Los Angeles, Simi Valley, Bakersfield, Fresno, San Jose, and Sacramento. The studied sampling sites comprise a mixture of urban and semi-rural communities, with El Cajon and Rubidoux located in semi-rural areas while the rest of sampling sites are situated in densely developed urban regions of the state. Supplement Fig. S1 shows the location of all sampling sites.

The Sacramento sampling site is located next to a park in a residential area with commercial establishments and high-density residential homes in the surrounding neighborhood. It is also about 3 km southeast of a major freeway (I-80). The sampling site in San Jose is located 46 km east of the Pacific Ocean and 14 km southeast of the San Francisco Bay. It is also surrounded by primary commercial facilities (Hwang and Hopke, 2006). The cities of Fresno and Bakersfield are located in California's heavily SJV (Zhao et al., 2011). These two cities are relatively far from the Pacific Ocean and are mostly impacted by secondary aerosols formed by emissions from upwind areas (Ying and Kleeman, 2006). Moreover, this part of the state usually suffers from severe particulate pollution, especially during the colder seasons (Kleeman et al., 2009). The northern parts of the SJV are dominated by agricultural activities, while the southern regions are mostly impacted by oil production (Held et al., 2004). The sampling site in Bakersfield is located about 6.5 km southwest of downtown, in a residential neighborhood and 2 km away from the nearest freeway (State Route (SR) 99).

The sampling site in Fresno is about 5.5 km northeast of the downtown commercial district (Watson et al., 2000), next to a four-lane artery with moderate traffic levels. Simi Valley is located 50 km northwest of downtown LA, in Ventura County, and the sampling site in this city is situated 500 m south of SR 118 (Kim and Hopke, 2007). Two sampling locations in the South Coast Air Basin were considered in this study; Los Angeles and Rubidoux. The sampling site in downtown LA is surrounded by three major freeways (i.e., I-110, I-5, and US-101) and is 30 km away from the ports of LA and Long Beach, both of which are among the busiest ports in the US (Minguillón et al., 2008). This sampling site is therefore heavily impacted by primary emissions. Rubidoux is situated 60 km inland from downtown LA and is typically subject to aged and photochemically processed particulate plumes advected from upwind regions (Sardar et al., 2005). Previous studies have reported high concentrations of ammonium nitrate in this region, which is mostly formed by the atmospheric reaction of nitric acid with ammonia from Chino dairy farms and livestock in upwind regions (Hughes et al., 1999). Lastly, the El Cajon sampling site is located in an inland valley, downwind of a heavily populated coastal zone, in San Diego County. This site is also impacted by emissions from the I-8 freeway, situated 500 m to its north.

2.2 Sampling schedule and chemical analysis

Time-integrated 24 h $PM_{2.5}$ samples were collected between 2002 and 2007 at all sampling sites, except for LA and Rubidoux, where the STN data collected from 2002 to 2013 was used as the input file when running the PMF model (Hasheminassab et al., 2014). In the present study, in order to compare the results with those obtained for the rest of sampling sites, we calculated the average source contributions between 2002 and 2007 from the output of the same PMF runs which were originally conducted using the 2002–2013 chemical data set. By performing a sensitivity analysis, Hasheminassab et al. (2014) showed that the results of the PMF model performed on the entire chemical data set (i.e., 2002–2013) is comparable to the output of the PMF model conducted separately on the 2002–2006 and 2008–2012 data sets in terms of the sources identified (similar number of sources with almost identical compositions) and the absolute source contributions (less than 18 % difference in average source contributions among all sources). The outcome of the sensitivity analysis thus indicated that the daily resolved source contributions between 2002 and 2007 are not significantly biased when the chemical data between 2008 and 2013 are also included into the PMF input file.

During the studied period (i.e., 2002 to 2007), $PM_{2.5}$ samples were collected every third day in Sacramento, San Jose, Fresno, Bakersfield, Rubidoux, and El Cajon sites, while every sixth day in Simi Valley and Los Angeles sites.

Filter weighing and chemical analyses were performed according to the U.S. EPA Quality Assurance Project Plan (QAPP) (EPA-454/R-01-001) adopted for the STN field sampling. According to the QAPP, filters were tested, equilibrated, and weighted in the US EPA contract laboratories, and then they were shipped to the field. After sampling, filters bearing $PM_{2.5}$ deposits were promptly shipped back to the laboratories for weight determination and other chemical analyses. $PM_{2.5}$ mass concentration was determined gravimetrically by pre- and post-weighing the Teflon filters. Concentration of elements on Teflon filter samples was quantified by energy-dispersive X-ray fluorescence (ED-XRF) (RTI, 2009c). Major ions, including nitrate, sulfate, ammonium, sodium, and potassium, were measured by ion chromatography (IC) (RTI, 2009a, b). Elemental carbon (EC) and organic carbon (OC) were quantified from quartz filters, using the thermal/optical transmittance (TOT) NIOSH 5040 carbon method (Birch and Cary, 1996).

2.3 Source apportionment

In this study, the EPA PMF receptor model (version 3.0.2.2) was performed at each sampling site separately to identify the major sources of ambient $PM_{2.5}$ and quantify their relative contributions to total $PM_{2.5}$ mass. PMF is a factor analysis model that solves the chemical mass balance equations using a weighted least-squares algorithm and by imposing non-negativity constrains on the factors (Reff et al., 2007).

2.3.1 Data screening

The first step of data screening was correcting the OC data to account for sampling artifacts caused by adsorption and/or desorption of organic vapors on quartz filters (Chow et al., 2010). For each sampling site, the OC artifact was estimated using the intercept of the linear regression of OC against $PM_{2.5}$ mass concentration (Kim et al., 2005). OC concentrations were then corrected by subtracting the OC artifact concentrations. The estimated OC artifact values ($\pm$ standard errors) at each site are presented in Table S1. In addition, a detailed discussion on the year-to-year variability of the estimated OC artifacts is available in the Supplement.

To avoid double counting of species, the linear correlations in each pair of S/SO_4^{2-}, Na/Na^+, and K/K^+ were examined. Depending on the goodness of fit and the percent number of samples below detection limit (BDL) (threshold of 70 %), either IC SO_4^{2-}, Na^+, K^+ or ED-XRF S, Na, K data were included in the PMF analyses. Measured BDL concentrations were replaced by half of the detection limit (DL) values, and their uncertainties were set as five-sixths of the DL values (Polissar et al., 1998). Missing values were replaced by the geometric mean of the existing concentrations, and their accompanying uncertainties were set as 4 times this geometric mean concentration. Species with more than 70 % BDL values as well as samples with missing mass and/or all of the elemental concentrations were excluded from the model. Lastly, occasional samples with unusually

high concentrations of a few chemical species, such as those collected around 4 July and/or New Year's Eve with extremely high concentrations of K and/or K^+, were discarded.

2.3.2 PMF model

The uncertainties used in the PMF model were the estimated uncertainties reported in the Air Quality System (AQS) for the $PM_{2.5}$ chemical speciation network. The uncertainties reported by STN include both the analytical uncertainties and uncertainties associated with the field sampling component (Flanagan et al., 2006). The uncertainties of elements, measured by the ED-XRF method, go through a comprehensive calculation procedure that harmonizes the uncertainties between different instruments and accounts for filter matrix effect, in addition to the field sampling and handling uncertainty (Gutknecht et al., 2010). For the other species, uncertainty is estimated as the analytical uncertainty of the instrument, augmented by 5 % of the calculated concentration, assuming that this 5 % is representing the total "field" variability (Flanagan et al., 2006).

Species with a signal-to-noise (S / N) ratio between 0.2–2, as well as those that have BDL values more than 50 % of total samples, were considered as weak variables and their uncertainties were increased by a factor of 3. In order to directly apportion the total PM mass, $PM_{2.5}$ mass concentrations were included in the data matrix as a "total variable" in the PMF model (Lee et al., 2011). To ensure that the inclusion of total PM mass concentration does not affect the resulting PMF solution, their uncertainties were increased by a factor of 3, similarly to a weak variable (Reff et al., 2007). The model was performed in the default robust mode to diminish the influence of extreme values on the PMF solution, and the FPEAK parameter was applied to control rotational ambiguity (Paatero et al., 2002). Furthermore, a value of 5 % extra modeling uncertainty was applied.

Uncertainties in the source profiles were estimated by a bootstrap procedure (Norris et al., 2008). Five hundred runs were considered for the bootstrap analysis in this study, and a solution was considered valid when the occurrence of unmapped factors was less than 10 % of the total runs. The final solutions were chosen based on the evaluation of the deduced source profiles and the quality of the chemical species fits by testing different numbers of factors.

3   Meteorology

Select meteorological parameters data, including temperature, relative humidity (RH), precipitation, as well as vector-average wind speed and direction were acquired from the online database of the California Air Resources Board (CARB). Table S2 presents the seasonal averages of these parameters at all studied sampling sites. In this study, seasons were defined as spring (March–May), summer (June–August), fall

(September–November), and winter (December–February), and seasonal/annual averages of all parameters reported in the following sections and shown in the figures and tables were calculated over all 6 years (i.e., 2002 to 2007). In addition, the standard errors accompanying the seasonal averages were calculated based on all daily resolved source contributions that fall within a given season. Details regarding the definition of standard error can be found in the Supplement. Lastly, in all of the figures and tables presented in this study, sampling sites were ranked according to their latitude, from south to north (i.e., from El Cajon to Sacramento).

Most intense seasonality in temperature and RH was observed at the inland areas of the SJV, in Fresno and Bakersfield. These two sites experience the hottest and driest summertime weather across the state (temperatures over 25 °C and RH below 45 %), while during winter, the mean temperature in these cities is within the lowest levels among all sites (below 10 °C) and the RH reaches about 75 %, comparable to levels in other sites in the northern region of the state (i.e., San Jose and Sacramento). Unlike northern areas, in southern California RH exhibited more moderate seasonality, displaying minima in fall/winter (50–71 %) and maxima in spring/summer (59–77 %). At all sampling locations, the average of yearly total precipitation was negligible in summer but greatest in winter. During the studied period, Sacramento showed the highest total precipitation in winter, followed by LA, San Jose, and Simi Valley (23.4 ± 7.1, 21.7 ± 17.1, 16.3 ± 3.9, and 14.1 ± 13.0 cm, respectively). Additionally, wind speeds were generally much stronger in summer compared with fall/winter. During spring and summer, the wind blows mostly from the coast to inland in the southern part of the state (i.e., El Cajon, Rubidoux, LA, and Simi Valley), with a predominant westerly/southwesterly direction, while it shifts in winter and has a predominantly northerly origin at all sites with the exception of El Cajon. In Bakersfield and Fresno, the wind constantly blows from northwest throughout the year except for Fresno in winter, when wind has an easterly direction. Lastly, in Sacramento, the prevailing wind direction is southerly/southwesterly throughout the year.

4   Results and discussion

4.1   Particulate mass

Seasonal average mass concentration of ambient $PM_{2.5}$ at each sampling site is presented in Table 1. Overall, mass concentrations spanned a broad range of 8.2 to 36.6 $\mu g\,m^{-3}$ across the studied sites and all seasons. $PM_{2.5}$ mass concentration showed a very strong seasonality in central and northern parts of the state (i.e., Bakersfield, Fresno, San Jose, and Sacramento), with 2 to 4 times higher concentrations in winter compared with summer. This trend is typical of California's Central Valley, which usually experiences the most severe winter particulate pollution in the US (Ying

Table 1. Seasonal average mass concentration ($\pm$ standard error) ($\mu g\,m^{-3}$) of ambient $PM_{2.5}$ at the eight sampling sites in the period between 2002 and 2007.

	El Cajon	Rubidoux	Los Angeles	Simi Valley	Bakersfield	Fresno	San Jose	Sacramento
Spring	12.0 ± 0.5	23.6 ± 1.3	18.1 ± 1.5	12.8 ± 0.8	11.8 ± 0.5	16.4 ± 1.1	9.7 ± 0.4	8.2 ± 0.3
Summer	13.1 ± 0.4	25.6 ± 0.9	20.2 ± 0.7	15.9 ± 0.5	13.5 ± 0.4	9.7 ± 0.3	9.6 ± 0.4	9.2 ± 0.4
Fall	14.5 ± 0.5	27.4 ± 1.5	20.8 ± 1.2	14.4 ± 0.9	24.6 ± 1.7	13.7 ± 0.6	14.8 ± 0.8	15.1 ± 0.9
Winter	17.1 ± 0.7	20.0 ± 1.1	20.4 ± 1.6	9.8 ± 0.8	32.0 ± 1.8	36.6 ± 1.5	18.6 ± 1.2	23.5 ± 1.2

Table 2. Summary of the marker species for identified $PM_{2.5}$ sources, resolved by the PMF model.

Source	Marker species
Vehicular emissions	EC, OC, Fe, Cu, Zn, Pb, Mn
Secondary ammonium nitrate	NO_3^+, NH_4^+
Secondary ammonium sulfate	SO_4^{2-}, NH_4^+
Soil	Al, Si, Ca, Fe, Ti
Fresh sea salt	Na^+, Cl^-
Aged sea salt	Na^+, NO_3^+, SO_4^{2-}
Biomass burning	EC, OC, K/K^+
Copper smelters	Cu, EC
Mixed industrial	EC, OC, Zn, Pb
Chlorine sources	Cl^-
Sulfate-bearing road dust	EC, OC, SO_4^{2-}, Fe, Ca, Mn, Si, Ti
Ni-related industrial sources	Ni, Mn, Mg

Table 3. Summary statistics of the linear correlations between daily resolved measured ambient $PM_{2.5}$ and estimated $PM_{2.5}$ mass concentrations obtained from the PMF model. Errors correspond to 1 standard error.

	R^2	Slope	Intercept ($\mu g\,m^{-3}$)
El Cajon	0.85	0.91 ± 0.02	0.89 ± 0.26
Rubidoux	0.96	0.91 ± 0.01	1.30 ± 1.22
Los Angeles	0.86	0.88 ± 0.02	1.58 ± 0.47
Simi Valley	0.91	0.91 ± 0.02	0.84 ± 0.23
Bakersfield	0.95	0.91 ± 0.01	0.95 ± 0.24
Fresno	0.94	0.91 ± 0.01	1.01 ± 0.23
San Jose	0.88	0.85 ± 0.01	1.35 ± 0.23
Sacramento	0.91	0.83 ± 0.01	1.47 ± 0.18

and Kleeman, 2009). In winter, ambient $PM_{2.5}$ mass concentrations peaked at Bakersfield and Fresno (32.0 ± 1.8 and $36.6 \pm 1.5\,\mu g\,m^{-3}$, respectively). Severe stagnation periods and decreased mixing height are mostly responsible for elevated particulate pollution during winter in this part of the state. As it will be discussed in the following section, secondary ammonium nitrate and emissions from biomass burning were mainly responsible for elevated $PM_{2.5}$ mass concentrations in these two cities during winter. In summer, on the other hand, the highest mass concentrations were observed in sampling sites located in the Los Angeles Basin (i.e., LA and Rubidoux). Rubidoux displayed the highest mass concentrations in fall, followed by summer and spring. In addition to local sources, this region of the state is typically subject to transported plumes from upwind regions in west and central LA (Daher et al., 2013; Sardar et al., 2005), particularly during the warm seasons when the westerly wind prevails (Table S2).

4.2 Source characterization and apportionment

4.2.1 Overview

Between five to nine particle sources were identified at each sampling site. Resolved source profiles along with the explained variation (EV) of each species are shown in Fig. S2a–h for all studied sampling sites. Gray bars represent the normalized concentration of each species to the mass concentra-

tion of $PM_{2.5}$ apportioned to that factor, while the black dots represent the percent of each species apportioned to that factor (Lee et al., 1999). Table 2 summarizes the marker species which were used to identify each source profile. Several sources, including secondary ammonium nitrate, secondary ammonium sulfate, vehicular emissions, biomass burning, soil, and fresh and aged sea salt were commonly identified at multiple sites. A few minor sources were identified exclusively at some of the sites, depending on the site location and nearby emission sources. These sources, however, accounted for a small fraction of the total mass (1 to 15 % across the state, on an annual average basis).

Table 3 presents the slope, intercept, and R^2 of the linear regressions between daily resolved measured ambient $PM_{2.5}$ and estimated $PM_{2.5}$ mass concentrations, calculated by the sum of PM mass apportioned to each identified factor. It can be inferred that the PMF model was able to effectively estimate the measured $PM_{2.5}$ mass concentrations at all sites (slope varying from 0.83 to 0.91 and R^2 ranging from 0.85 to 0.96).

Year-to-year variability in the source contributions was overall quite small for almost all identified sources. This can be deduced from the relatively small standard errors in the 6-year seasonal average source contributions, as shown in Table S3a–d (median relative standard error of 8 %, across all sites, seasons, and sources). Identified sources, on the other hand, displayed distinct seasonal and spatial variability. The percent contributions from these sources to $PM_{2.5}$ mass are
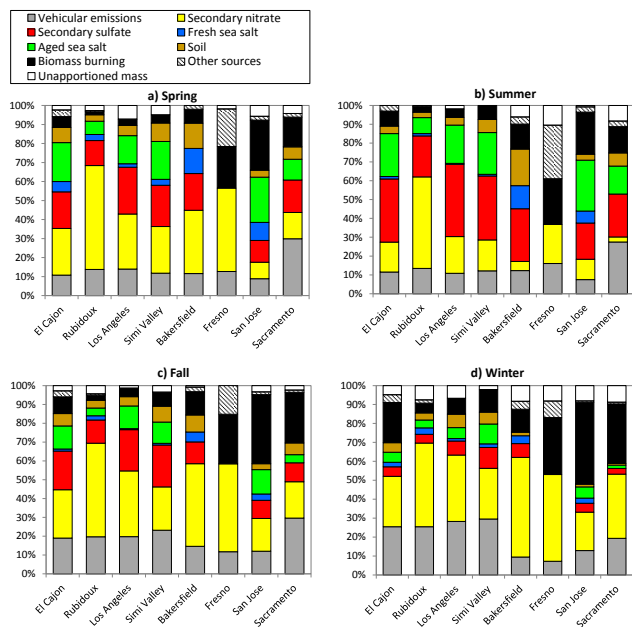
Figure 1. Seasonal variation in the percent contribution of identified sources to ambient PM$_{2.5}$, by site **(a–d)**.

Figure 2. Seasonal average source contribution (μg m^{-3}) of vehicular emissions to ambient PM$_{2.5}$, by site. Error bars correspond to 1 standard error.

presented in Fig. 1. Overall, secondary aerosols (including secondary ammonium nitrate and ammonium sulfate) collectively comprised the largest fraction of ambient PM$_{2.5}$ at all sampling sites (except for San Jose), accounting for 26 to 63 % of total mass across all sites, on an annual average basis. Vehicular emissions were the second major contributor to PM$_{2.5}$ at all sites (11 to 25 % annual average contribution, across the state), except for San Jose and Fresno, where biomass burning was the dominant primary source of PM$_{2.5}$ (35 and 27 % annual average contribution, respectively). "Other sources" in Fig. 1 are associated with those sources which were identified exclusively at some specific locations. These contributed to < 15 % of the mass, on an annual average basis. The unapportioned mass, which is the difference between the seasonal average PM$_{2.5}$ mass and the sum of the seasonal average source contributions from each factor, accounted for 3 to 6 % of total mass across the state, on an annual average basis. The unapportioned mass represents the fraction that could not be resolved by the model.

4.2.2 Vehicular emissions

Vehicular emissions source profiles were identified by high concentrations of carbonaceous species (i.e., EC and OC). Elevated loadings of several non-exhaust PM tracers (e.g., Fe, Cu, Zn, Pb, Mn) indicate that these sources are affected by particles emitted from brake and tire wear, road surface abrasion, and the resuspension of road surface dust (Pant and Harrison, 2013; Dall'sto et al., 2014). Only at Rubidoux was the PMF model able to determine two separate source profiles for diesel and gasoline vehicles (Fig. S2b). These source
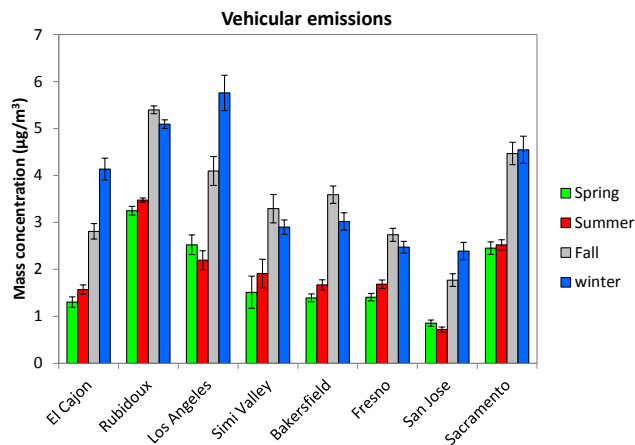
profiles are characterized by high loadings of EC and OC, respectively, with EC / OC ratios of 0.4 for the gasoline source profile and 2.2 for the diesel vehicles source profile. These ratios are within the ranges reported in previous studies (Liu et al., 2006; Fujita et al., 1998; Watson et al., 1998; Heo et al., 2009). Diesel vehicles operating at very low speed and in stop-and-go traffic usually produce similar EC / OC ratios to typical gasoline vehicles (Shah et al., 2004). As a result, the diesel emissions source profile that was obtained in Rubidoux may represent only diesel vehicles driving in relatively constant speed in fluid traffic conditions, and the diesel emissions from stop-and-go traffic could be apportioned to the gasoline vehicles category. To overcome this uncertainty and also be able to compare the results with those obtained at other sampling sites, the contributions from diesel and gasoline vehicles were combined together at Rubidoux and referred to as vehicular emissions throughout the discussion.

As can be seen in Fig. 2, across the state, estimated PM$_{2.5}$ mass attributed to vehicular sources (including diesel and gasoline vehicles) reached their highest levels at Rubidoux, LA, and Sacramento, with annual average ($\pm$ standard error) contributions of 4.3 ± 0.1, 3.6 ± 0.1, and $3.5 \pm 0.1\ \mu$g m^{-3}, respectively. The spatial pattern of PM$_{2.5}$ emissions from mobile sources across the state is in a good agreement with the findings of a recent study by Hu et al. (2014), in which they applied a source-oriented air quality model to predict primary PM$_{2.5}$ source contributions across the state of California between 2000 and 2006.

Vehicular emissions displayed similar seasonal patterns at all sampling sites, with higher contributions in fall and winter compared to spring and summer. In spring, summer, and fall, the highest vehicular emissions source contributions were observed at Rubidoux. In contrast, during winter, when particulate pollution is confined within the emission area due to higher atmospheric stability and lower mixing height, the
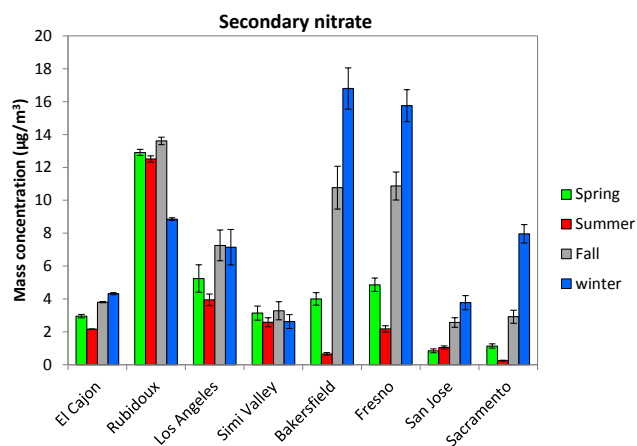
Figure 3. Seasonal average source contribution ($\mu g\, m^{-3}$) of secondary ammonium nitrate to ambient $PM_{2.5}$, by site. Error bars correspond to 1 standard error.

Figure 4. Seasonal average source contribution ($\mu g\, m^{-3}$) of secondary ammonium sulfate to ambient $PM_{2.5}$, by site. Error bars correspond to 1 standard error.

vehicular source contribution exhibited the highest value in downtown LA. This trend is typical of the LA Basin, in which downwind "receptor" areas are generally impacted by emissions from upwind "source" regions, when westerly/southwesterly onshore winds prevail (Table S2) (Daher et al., 2013). Several previous studies have reported similar trends in the LA Basin (Hasheminassab et al., 2013; Heo et al., 2013). It should be noted that after 2007 and until 2012, the contributions of vehicular emissions to ambient $PM_{2.5}$ in the LA Basin statistically significantly decreased by 20 to 25 % following the implementation of major federal, state, and local regulations on vehicular emissions, particularly on diesel trucks (Hasheminassab et al., 2014).

Among the studied locations in California's Central Valley, vehicular emissions displayed the highest levels in Sacramento and lowest in San Jose, accounting for nearly 30 and 10 % of total mass, respectively, on average over 6 years. Vehicular emissions were comparable at Bakersfield and Fresno during spring and summer, whereas levels were slightly higher at Bakersfield in fall and winter. Schauer and Cass (2000) conducted a 4-day sampling in Bakersfield during the winter of 1995 to quantify the sources of ambient $PM_{2.5}$ using chemical mass balance receptor model. The average wintertime level of vehicular emissions in our study at Bakersfield ($3.0 \pm 0.2\,\mu g\, m^{-3}$) was about half of that reported by Schauer and Cass (2000) ($6.3 \pm 0.4\,\mu g\, m^{-3}$), whereas the percent contributions of this source to total mass were comparable in both studies (10 and 12 %, respectively). This finding suggests that after almost a decade vehicular emissions have decreased by almost half in Bakersfield.
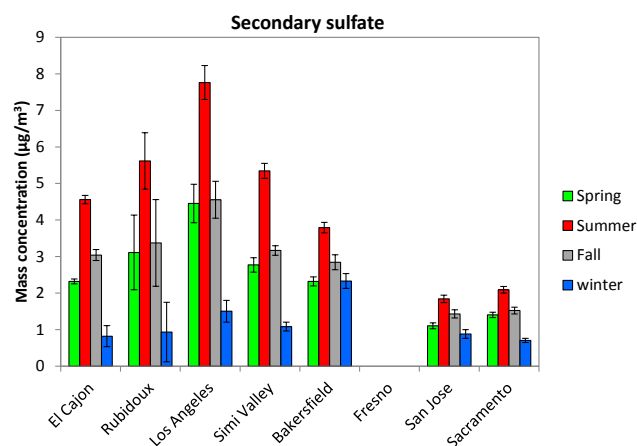
4.2.3 Secondary aerosols

Secondary ammonium nitrate source profile was identified by high concentrations of NO_3^- and NH_4^+ (Fig. S2a–h). Its contribution ranged from 0.2 to $16.8\,\mu g\, m^{-3}$, accounting for 3 to 55 % of ambient $PM_{2.5}$ mass, among all sites and seasons, as displayed in Fig. 3 and tabulated in Table S3a–d. Seasonally, the contribution of secondary ammonium nitrate was largest in winter and lowest during summer, with statewide average contribution of 8.4 and $3.2\,\mu g\, m^{-3}$, respectively. Elevated concentration of secondary ammonium nitrate during the cold seasons is mainly due to the increased partitioning of ammonium nitrate into the particle phase, favored by lower wintertime temperatures and higher RH (Ying, 2011). This source displayed considerably higher contributions at Fresno and Bakersfield in winter (16.8 ± 1.3 and $15.8 \pm 1.0\,\mu g\, m^{-3}$, respectively). Ying and Kleeman (2006) stated that diesel engines and catalyst equipped gasoline vehicles are important local sources that contribute to secondary nitrate in the SJV. Unlike all other sites, the seasonal trend of secondary ammonium nitrate was reversed at Rubidoux, with higher concentrations in summer compared to winter (12.5 ± 0.8 and $8.9 \pm 0.8\,\mu g\, m^{-3}$, respectively). This is probably due to increased advection of ammonia from the upwind Chino area, caused by stronger westerly/southwesterly winds during summer in the LA Basin (Hasheminassab et al., 2013) combined with the increased photochemical production of nitric acid, which reacts with fugitive ammonia to produce high concentrations of ammonium nitrate in this area.

The characterized secondary ammonium sulfate source profiles have high loadings of SO_4^{2-} and NH_4^+ (Fig. S2a–h). This source was identified at all sites, except at Fresno, where sulfate largely partitioned in a source named "sulfate-bearing road dust" along with a few other components, which
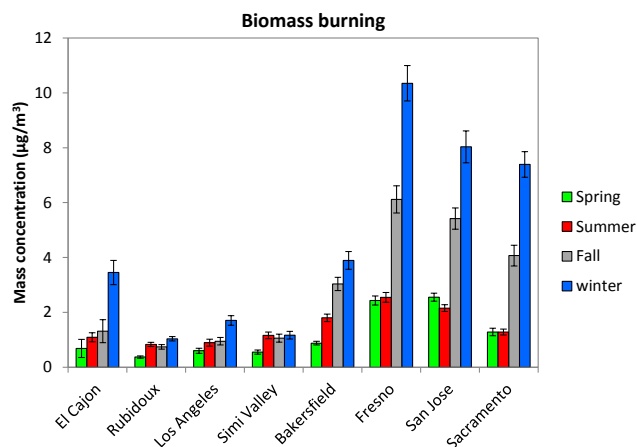
Figure 5. Seasonal average source contribution ($\mu g\,m^{-3}$) of biomass burning to ambient $PM_{2.5}$, by site. Error bars correspond to 1 standard error.

Figure 6. Seasonal average source contribution ($\mu g\,m^{-3}$) of soil to ambient $PM_{2.5}$, by site. Error bars correspond to 1 standard error.

will be discussed in further detail below. Annual average contributions of this source ranged from 1.3 to 4.6 $\mu g\,m^{-3}$ (or 10 to 24 % of total mass) among all sites, indicating that this source is a smaller contributor to total mass compared with secondary ammonium nitrate. Secondary ammonium sulfate exhibited a similar seasonal trend at all monitoring sites, displaying wintertime minima and peaks in summertime due to increased photochemical activity that forms this species. Levels were also overall higher in the southern part of the state compared to the upper regions (Fig. 4). As argued by Ying and Kleeman (2006), the majority of secondary aerosols formed in southern California are formed from locally emitted precursors, whereas in the SJV, secondary PM is mostly impacted by emissions from upwind areas (i.e., regional sources).

4.2.4   Biomass burning

Identified biomass-burning source profiles consisted primarily of EC, OC, and either K or K^+ (Fig. S2a–h). Biomass burning includes emissions from wildfires and residential wood combustion. This source showed distinct seasonal and spatial variability, with the highest levels observed during winter and also in upper parts of the state. Higher concentrations associated with biomass burning in winter are mainly due to higher residential wood burning during this season. Central and northern parts of the state usually experience colder winters compared to the southern regions (Table S2); therefore, higher biomass burning is expected in these geographical locations, as shown in many previous studies (Hu et al., 2014; Chen et al., 2007). Biomass burning was the major primary source of ambient $PM_{2.5}$ at Fresno and San Jose during all seasons, with levels ranging from 2.4 to 10.4 $\mu g\,m^{-3}$ (or 22 to 30 % of $PM_{2.5}$) at Fresno and from 2.2 to 8.0 $\mu g\,m^{-3}$ (or 22 to 43 % of $PM_{2.5}$) in San Jose (Fig. 5). This source was also the dominant primary contributor to ambient $PM_{2.5}$

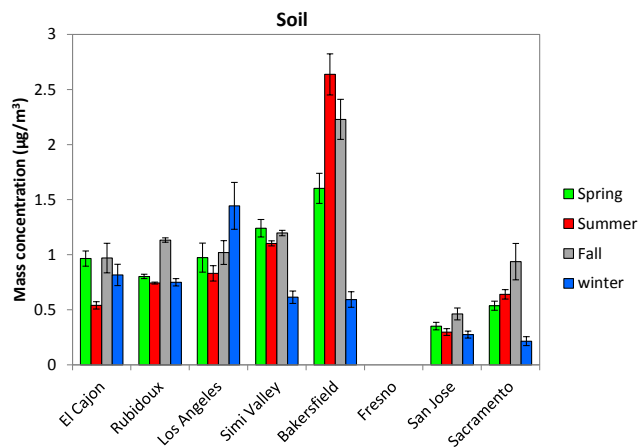in Bakersfield and Sacramento during winter (12 and 31 % of $PM_{2.5}$, respectively), consistent with the findings of many previous studies in this area (Chow et al., 2007; Gorin et al., 2006; Schauer and Cass, 2000).

4.2.5   Soil

Resolved soil source profiles were dominated by crustal elements such as Al, Ca, Fe, Si, and Ti (Fig. S2a–h). These profiles generally lacked the contributions from EC and OC, indicating that they are not majorly impacted by emissions of road dust. As stated above, road dust was partially apportioned to the resolved vehicular emissions source profiles. A distinct source profile attributable to soil was not identified at Fresno. Instead, crustal elements partitioned in a separate source profile, along with high loadings of sulfate, EC, and OC, which was characterized as "sulfate-bearing road dust". Across the state, soil exhibited lower concentrations in northern regions, namely at San Jose and Sacramento (Fig. 6). This is likely attributed to increased precipitation and higher RH in this part of the state (Table S2), which limit the wind-induced resuspension of soil (Harrison et al., 2001). Soil, in contrast, accounted for a large fraction of $PM_{2.5}$ at Bakersfield, in concert with the findings of Chen et al. (2007). During summer, in particular, the contribution of soil to total mass was near 20 % at Bakersfield, which could be mainly due to the lack of precipitation and low RH in this area (Table S2). As discussed by Chen et al. (2007), farm lands, pasture lands, and unpaved roads are major sources of soil and windblown dust in the SJV.

4.2.6   Fresh and aged sea salt

Sources with high concentrations of Na^+ and Cl^- were characterized as fresh sea salt (Fig. S2a–h). Aged sea salt source profiles, on the other hand, were dominated by loadings of Na^+, SO_4^{2-}, and NO_3^-. Unlike fresh sea salt, chlorine has
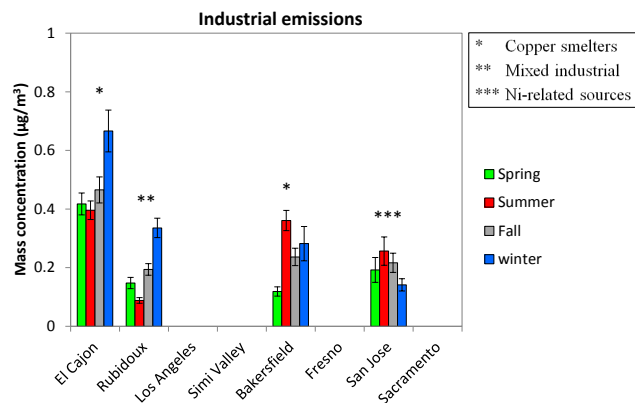
Figure 7. Seasonal average source contribution ($\mu g\,m^{-3}$) of industrial emissions to ambient $PM_{2.5}$, by site. Error bars correspond to 1 standard error.

Figure 8. Seasonal average contribution ($\mu g\,m^{-3}$) of chlorine sources to ambient $PM_{2.5}$, by site. Error bars correspond to 1 standard error.

a negligible or near-zero contribution to the aged sea salt source profile. Chlorine is typically depleted due to reactions of sea salt with acidic gases during the long-range transport of sea salt aerosols from the point of emission (Song and Carmichael, 1999). Aged sea salt overall accounted for a lager fraction (2 to 27 %) of ambient $PM_{2.5}$ compared to fresh sea salt (1 to 13 %), in all sites and seasons (Figs. 1, S3, and S4). Aged sea salt showed a clear seasonal pattern at all sites, with higher concentrations in summer, consistent with increasing onshore winds (Table S1), and lowest during winter.

It is also noteworthy that the PMF model did not apportion a separate factor for ship emissions or a source related to ocean goods transport. However, high loadings of Ni and V (tracers of ship emissions (Arhami et al., 2009)) in secondary ammonium sulfate and aged sea salt source profiles for the sampling sites in the LA Basin, suggest that these sources are affected in part by emissions from ships serving the ports of LA and Long Beach (Hwang and Hopke, 2007).

4.2.7 Other sources

As noted above, a few sources were identified exclusively at some sites, with relatively low annual contributions to total mass (1 to 15 %, across the sites). At Rubidoux, a source profile was deduced with high loadings of Zn, Pb, EC, and OC (Fig. S2b), which is most likely attributed to local "mixed industrial" emissions in the surrounding areas. A similar source profile was also obtained in previous studies in this area (Kim and Hopke, 2007; Kim et al., 2010). At San Jose, a source profile dominated by Ni was identified, which likely indicates the contribution from nearby Ni-related industrial sources. Hwang and Hopke (2006) reported similar findings at the same sampling location by application of the PMF model on STN data, collected between 2002 and 2005. This source, nonetheless, accounted for less than 2 % of the total mass, on an annual average basis. The copper smelter source
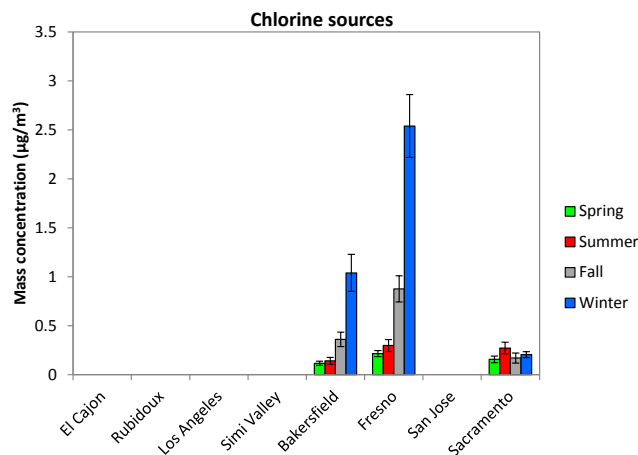
profile, with a very high loading of Cu (> 80 %) and a slight contribution of EC, was identified in El Cajon and Bakersfield sampling sites (Fig. S2a, e). This source accounted for about 1 and 4 % of total mass, over all years, in Bakersfield and El Cajon, respectively.

Figure 7 shows the seasonal trends of industrial emissions in locations where these sources were identified. In El Cajon and Rubidoux, the contributions of the identified industrial sources peaked in winter, while in Bakersfield and San Jose, maximum emissions from copper smelters and Ni-related sources were observed in summer. It is important to note that although the contributions from the identified industrial sources to total PM mass were overall trivial (< 4 %), these sources and the related elements may be important contributors to the overall particle toxicity (Toledo et al., 2008; von Schneidemesser et al., 2010; Dall'osto et al., 2008; Saffari et al., 2013).

At Fresno, a source profile with a high loading of sulfate along with road dust tracers, such as OC, EC, Fe, Ca, Mn, Si and Ti, was resolved (Fig. S2f). These road dust tracers most likely originate from the re-suspension of deposited soil and road dust enriched with vehicular emissions and lubricating oils (Pant and Harrison, 2013; Dall'sto et al., 2014). This source was therefore named "sulfate-bearing road dust" (Katrinak et al., 1995). As mentioned above, separate source profiles for secondary ammonium sulfate and soil were not identified at Fresno. Nonetheless, the relatively high loadings of sulfate and a few crustal elements (e.g., Al, Ca, Fe, and Si), along with the modest contribution of ammonium, suggest that these two sources are partially apportioned to this source profile. On an average basis over all 6 years, "sulfate-bearing road dust" accounted for about 15 % of total mass at Fresno and its contribution was highest in summer among all seasons ($2.7 \pm 0.1\,\mu g\,m^{-3}$).

Relatively similar source profiles, with high loadings of chlorine, were obtained at Fresno, Bakersfield, and Sacramento, with annual average contributions of about 5, 2, and 1 % to total mass, respectively (Fig. S2e, f, and h). This source, which was denoted as "chlorine sources", was mostly detected during fall and winter at Fresno and Bakersfield, in the SJV, while it displayed the maximum seasonal average value in summer at Sacramento (Fig. 8).

5   Summary and conclusions

Source apportionment analyses were conducted using a PMF receptor model applied on chemical speciation data sets, obtained from eight different STN sampling sites throughout the state of California, between 2002 and 2007. Five to nine major sources contributing to ambient $PM_{2.5}$ were identified at each site, with several of which being common in multiple locations. Overall, secondary aerosols (including secondary ammonium nitrate and ammonium sulfate) were collectively the main contributor to $PM_{2.5}$ mass at all sampling sites. Annual average source contributions of secondary ammonium nitrate and ammonium sulfate ranged from 3.1 to 12 $\mu g\,m^{-3}$ (or 16 to 50 % of total mass) and 1.3 to 4.6 $\mu g\,m^{-3}$ (or 10 to 23 % of total mass) across the state, respectively. On an annual average basis, vehicular emissions (including both diesel and gasoline vehicles) were the largest primary sources of $PM_{2.5}$ at all sampling sites in the southern part of the state (i.e., El Cajon, Rubidoux, LA, and Simi Valley), with 17–18 % contribution total PM mass. In Fresno and San Jose, on the other hand, biomass burning was the dominant primary source of ambient $PM_{2.5}$, contributing to 27 and 35 % of total mass, on average over all years. In Bakersfield and Sacramento, vehicular emissions and biomass burning displayed relatively equal annual contributions to ambient $PM_{2.5}$ mass (12 and 25 %, respectively). Other sources commonly identified at all sites were minor contributors to $PM_{2.5}$, including aged and fresh sea salt and soil, which contributed to 0.5–13 %, 2–27 %, and 1–19 % of total mass, respectively, across all sites and seasons. Furthermore, a few sources (including chlorine sources, sulfate-bearing road dust, and different types of industrial emissions), which overall accounted for a small fraction of total mass (1 to 15 %, on an annual average basis), were solely identified at some of the sites.

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