

1 **Spatial and Temporal Variability of Sources of Ambient Fine**
2 **Particulate Matter (PM_{2.5}) in California**

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9

10 **Abstract**

11 To identify major sources of ambient fine particulate matter (PM_{2.5}, d_p < 2.5 μm) and
12 quantify their contributions in the state of California, positive matrix factorization (PMF)
13 receptor model was applied on Speciation Trends Network (STN) data, collected between 2002
14 and 2007 at 8 distinct sampling locations, including El Cajon, Rubidoux, Los Angeles, Simi
15 Valley, Bakersfield, Fresno, San Jose, and Sacramento. Between five to nine sources of fine PM
16 were identified at each sampling site, several of which were common among multiple locations.
17 Secondary aerosols, including secondary ammonium nitrate and ammonium sulfate, were the
18 most abundant contributor to ambient PM_{2.5} mass at all sampling sites, except for San Jose, with
19 an annual average cumulative contribution of 26 to 63%, across the state. On an annual average
20 basis, vehicular emissions (including both diesel and gasoline vehicles) were the largest primary
21 source of fine PM at all sampling sites in southern California (17-18% of total mass), whereas in
22 Fresno and San Jose, biomass burning was the most dominant primary contributor to ambient

23 PM_{2.5} (27 and 35% of total mass, respectively), in general agreement with the results of previous
24 source apportionment studies in California. In Bakersfield and Sacramento, vehicular emissions
25 and biomass burning displayed relatively equal annual contributions to ambient PM_{2.5} mass (12
26 and 25%, respectively). Other commonly identified sources at all sites included aged and fresh
27 sea salt as well as soil, which contributed to 0.5-13%, 2-27%, and 1-19% of the total mass,
28 respectively, across all sites and seasons. In addition, few minor sources were exclusively
29 identified at some of the sites (e.g. chlorine sources, sulfate-bearing road dust, and different types
30 of industrial emissions). These sources overall accounted for a small fraction of the total PM
31 mass across the sampling locations (1 to 15%, on an annual average basis).

32

33 **1. Introduction**

34 Exposure to ambient airborne particulate matter (PM) is one of the leading causes of
35 morbidity and mortality, contributing to more than 3 million premature deaths in the world
36 annually, based on a recent global burden of disease study (Lim et al., 2013). PM inhalation has
37 been linked to a wide range of adverse health effects, such as respiratory inflammation (Araujo et
38 al., 2008), cardiovascular diseases (Delfino et al., 2005;Ostro et al., 2014), and most recently
39 neurodegenerative and neurodevelopmental disorders (Davis et al., 2013b;Davis et al., 2013a).
40 During the past few decades, California has been constantly suffering from high concentrations
41 of ambient PM, among the highest levels recorded within the United States, with estimated rates
42 of PM-related morbidity and mortality exceeding any other state in the country (Fann et al.,
43 2012).

44 Ambient PM in California originates from a large number of diverse sources (Hu et al.,
45 2014) and is a complex mixture of different chemical components, the composition of which
46 may change drastically with PM size (Hu et al., 2008), location, and season (Cheung et al.,
47 2011;Daher et al., 2013). Current PM regulations in California target PM₁₀ and PM_{2.5} (particles
48 with aerodynamic diameter less than 10 and 2.5 μm, respectively) mass concentrations, with
49 PM_{2.5} being of major concern due to the higher rate of PM_{2.5}-related morbidity and mortality in
50 the state compared to PM₁₀ (Ostro et al., 2006;Woodruff et al., 2006). These regulations only
51 target PM mass concentration, regardless of their sources of emission and/or toxico-chemical
52 characteristics. There is, however, strong evidence that the level of toxicity and health-related
53 characteristics of PM are significantly affected by their chemical composition and therefore by
54 their emission sources (Rohr and Wyzga, 2012;Stanek et al., 2011;Zhang et al., 2008;Saffari et
55 al., 2013). Recently, there has been growing interest in using source apportionment data in
56 epidemiological health studies (Sarnat et al., 2008;Özkaynak and Thurston, 1987;Laden et al.,
57 2000;Mar et al., 2000;Ostro et al., 2011). These studies have provided significant evidence that
58 exposure to PM from certain sources is linked to mortality. In a recent study in Barcelona, Ostro
59 et al. (2011) found that exposure to several sources, including traffic emissions, sulfate from ship
60 emissions and long-range transport, as well as construction dust, is statistically significantly
61 associated with all-cause and cardiovascular mortality. Nonetheless, to draw firm conclusions
62 and develop more effective control strategies to reduce population exposure to harmful sources
63 of airborne PM, further epidemiological studies that use source apportionment data are
64 warranted.

65 To date, several source apportionment studies have been conducted in California, using
66 source-oriented (Hu et al., 2014;Kleeman and Cass, 2001;Zhang et al., 2014;DeNero, 2012) and

67 receptor models (Hasheminassab et al., 2013;Hwang and Hopke, 2006;Ham and Kleeman,
68 2011;Kim and Hopke, 2007;Kim et al., 2010;Schauer and Cass, 2000). Source-oriented models
69 focus on the transport, dilution, and transformation of pollutants from the source of emission to
70 the receptor site; thereby providing an overall estimation regarding the spatial distribution of
71 source contributions. Receptor models, on the other hand, focus on the behavior of ambient
72 environments at the point of impact (Hopke, 2003). Even though these studies have provided
73 important insights on the characteristics of sources of ambient PM as well as their relative
74 contributions, they have been mostly conducted in a limited number of sampling locations and/or
75 within a relatively short period of time. As a result, spatial and temporal variability of the
76 identified sources have not been extensively examined. For instance, Kim et al. (2010) analyzed
77 the PM_{2.5} speciation data collected between 2003 and 2005 at two sampling sites in southern
78 California (i.e. Los Angeles (LA) and Rubidoux) to identify and quantify major PM_{2.5} sources,
79 by application of a PMF model. Using similar source apportionment approach, Hwang and
80 Hopke (2006) evaluated the sources of ambient PM_{2.5} at two sampling sites in San Jose, using the
81 STN data collected between 2000 and 2005. In a more comprehensive study, Chen et al. (2007)
82 applied several receptor models to the chemically speciated PM_{2.5} measurements collected for
83 one year (between 2000 and 2001) at 23 sites, all located in California's San Joaquin Valley
84 (SJV), to estimate PM_{2.5} source contributions.

85 In this study, positive matrix factorization (PMF), one of the most widely-used receptor-
86 oriented source apportionment techniques (Paatero and Tapper, 1994), was employed in order to
87 provide a detailed and long-term (from 2002 to 2007) quantification of the contributions of
88 different emission sources to ambient PM_{2.5} mass concentration in California, at 8 distinct
89 locations spanning southern, central, and northern regions of the state. The association between

90 PM-related mortality and PM_{2.5} mass concentration as well as individual PM_{2.5} chemical
91 components has been investigated in previous epidemiological studies in California (Ostro et al.,
92 2006;Ostro et al., 2007). The results of this study will be used as an input for future
93 epidemiological studies conducted by California Environmental Protection Agency (Cal EPA),
94 in order to further expand the current epidemiological knowledge, by establishing the
95 relationship between PM-related adverse health effects and specific source contributions. These
96 findings will be crucial in establishing targeted and cost-effective regulations on PM_{2.5} emissions
97 in the state of California.

98

99 **2. Methodology**

100 **2.1. Sampling sites**

101 Sampling was conducted at eight Speciation Trends Network (STN) sampling sites,
102 established by the United States Environmental Protection Agency (U.S. EPA), located in
103 distinctly different cities all over California, including El Cajon, Rubidoux, Los Angeles, Simi
104 Valley, Bakersfield, Fresno, San Jose and Sacramento. The studied sampling sites comprise a
105 mixture of urban and semi-rural communities, with El Cajon and Rubidoux being located in
106 semi-rural areas, while the rest of sampling sites being situated in densely developed urban
107 regions of the state. Figure S1 shows the location of all sampling sites.

108 The Sacramento sampling site is located next to a park in a residential area with
109 commercial establishments and high-density residential homes in the surrounding neighborhood.
110 It is also about 3 km southeast of a major freeway (I-80). The sampling site in San Jose is located
111 46 km east of the Pacific Ocean and 14 km southeast of the San Francisco Bay. It is also
112 surrounded by primary commercial facilities (Hwang and Hopke, 2006). Cities of Fresno and

113 Bakersfield are located in California's heavily SJV (Zhao et al., 2011). These two cities are
114 relatively far from the Pacific Ocean and are mostly impacted by secondary aerosols formed by
115 emissions from upwind areas (Ying and Kleeman, 2006). Moreover, this part of the state usually
116 suffers from severe particulate pollution, especially during the colder seasons (Kleeman et al.,
117 2009). The northern parts of the SJV are dominated by agricultural activities, while the southern
118 regions are mostly impacted by oil production (Held et al., 2004). The sampling site in
119 Bakersfield is located about 6.5 km southwest of downtown, in a residential neighborhood and 2
120 km away from the nearest freeway (State Route (SR) 99). The sampling site in Fresno is about
121 5.5 km northeast of the downtown commercial district (Watson et al., 2000), next to a four-lane
122 artery with moderate traffic level. Simi Valley is located 50 km northwest of downtown LA, in
123 Ventura county, and the sampling site in this city is situated 500 m south of SR 118 (Kim and
124 Hopke, 2007). Two sampling locations in the South Coast Air Basin were considered in this
125 study; Los Angeles and Rubidoux. The sampling site in downtown LA is surrounded by three
126 major freeways (i.e. I-110, I-5, and US-101) and is 30 km away from the ports of LA and Long
127 Beach, both of which are the busiest ports in the U.S. (Minguillón et al., 2008). This sampling
128 site is therefore heavily impacted by primary emissions. Rubidoux is situated 60 km inland from
129 downtown LA and is typically subject to aged and photo-chemically processed particulate
130 plumes advected from upwind regions (Sardar et al., 2005). Previous studies have reported high
131 concentration of ammonium nitrate in this region, which is mostly formed by the atmospheric
132 reaction of nitric acid with ammonia from Chino dairy farms and livestock in upwind regions
133 (Hughes et al., 1999). Lastly, the El Cajon sampling site is located in an inland valley, downwind
134 of a heavily populated coastal zone, in San Diego County. This site is also impacted by
135 emissions from I-8 freeway, situated 500 m to its north.

136 2.2. Sampling schedule and chemical analysis

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

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

154 Filter weighing and chemical analyses were performed according to the U.S. EPA
155 Quality Assurance Project Plan (QAPP) (EPA-454/R-01-001) adopted for the STN field
156 sampling. According to the QAPP, filters were tested, equilibrated, and weighted in the U.S.
157 EPA contract laboratories, and then they were shipped to the field. After sampling, filters bearing
158 PM_{2.5} deposits were promptly shipped back to the laboratories for weight determination and other

159 [chemical analyses](#). PM_{2.5} mass concentration was determined gravimetrically by pre- and post-
160 weighing the Teflon filters. Concentration of elements on Teflon filter samples was quantified by
161 energy-dispersive X-ray fluorescence (ED-XRF) (RTI, 2009c). Major ions, including nitrate,
162 sulfate, ammonium, sodium, and potassium, were measured by Ion Chromatography (IC) (RTI,
163 2009a, b). Elemental carbon (EC) and organic carbon (OC) were quantified from quartz filters,
164 using Thermal Optical Transmittance (TOT) NIOSH 5040 carbon method (Birch and Cary,
165 1996).

166 **2.3. Source apportionment**

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

172 **2.3.1. Data screening**

173 The first step of data screening was correcting the OC data to account for sampling
174 artifacts, caused by adsorption and/or desorption of organic vapors on quartz filters (Chow et al.,
175 2010). For each sampling site, the OC artifact was estimated using the intercept of the linear
176 regression of OC against PM_{2.5} mass concentration (Kim et al., 2005). OC concentrations were
177 then corrected by subtracting the OC artifact concentrations. The estimated OC artifact values (\pm
178 standard errors) at each site are presented in Table S1. [In addition, a detailed discussion on the](#)
179 [year-to-year variability of the estimated OC artifacts is available in the supplemental text](#).

180 To avoid double-counting of species, the linear correlations in each pair of S/SO₄²⁻,
181 Na/Na⁺, and K/K⁺ were examined. Depending on the goodness of fit and the percent number of

182 samples below detection limit (BDL) (threshold of 70%), either IC SO_4^{2-} , Na^+ , K^+ or ED-XRF S,
183 Na, K data were included in the PMF analyses. Measured BDL concentrations were replaced by
184 half of the detection limit (DL) values, and their uncertainties were set as 5/6 of the DL values
185 (Polissar et al., 1998). Missing values were replaced by the geometric mean of the existing
186 concentrations, and their accompanying uncertainties were set as four times this geometric mean
187 concentration. Species with more than 70% BDL values as well as samples with missing mass
188 and/or all of the elemental concentrations were excluded from the model. Lastly, occasional
189 samples with unusually high concentrations of a few chemical species, such as those collected
190 around July 4th and/or New Year eves with extremely high concentrations of K and/or K^+ were
191 discarded.

192 **2.3.2. PMF model**

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

203 Species with a signal-to-noise (S/N) ratio between 0.2-2, as well as those that have BDL
204 values more than 50% of total samples were considered as weak variables and their uncertainties

205 were increased by a factor of 3. In order to directly apportion the total PM mass, PM_{2.5} mass
206 concentrations were included in the data matrix as a “total variable” in the PMF model (Lee et
207 al., 2011). To ensure that the inclusion of total PM mass concentration does not affect the
208 resulting PMF solution, their uncertainties were increased by a factor of 3, similarly to a weak
209 variable (Reff et al., 2007). The model was performed in the default robust mode to diminish the
210 influence of extreme values on the PMF solution, and the FPEAK parameter was applied to
211 control rotational ambiguity (Paatero et al., 2002). Furthermore, a value of 5% extra modeling
212 uncertainty was applied.

213 Uncertainties in the source profiles were estimated by a bootstrap procedure (Norris et
214 al., 2008). 500 runs were considered for the bootstrap analysis in this study, and a solution was
215 considered valid when the occurrence of unmapped factors was less than 10% of the total runs.
216 The final solutions were chosen based on the evaluation of the deduced source profiles and the
217 quality of the chemical species fits by testing different numbers of factors.

218

219 **3. Meteorology**

220 Select meteorological parameters data, including temperature, relative humidity (RH),
221 precipitation, as well as vector-average wind speed and direction were acquired from the online
222 database of the California Air Resources Board (CARB). Table S2 presents the seasonal
223 averages of these parameters at all studied sampling sites. In this study, seasons were defined as
224 spring (March–May), summer (June–August), fall (September–November) and winter
225 (December–February), and seasonal/annual averages of all parameters reported in the following
226 sections and shown in the figures and tables were calculated over all 6 years (i.e. 2002 to 2007).
227 In addition, [the standard errors accompanying the seasonal averages were calculated based on all](#)

228 daily-resolved source contributions that fall within a given season. Details regarding the
229 definition of standard error can be found in the supplemental text. Lastly, in all of the figures and
230 tables presented in this study, sampling sites were ranked according to their latitude, from south
231 to north (i.e. from El Cajon to Sacramento).

232 Most intense seasonality in temperature and RH was observed at the inland areas of the
233 SJV, in Fresno and Bakersfield. These two sites experience the hottest and driest summertime
234 weather across the state (temperature over 25°C and RH below 40%), while during winter, the
235 mean temperature in these cities is within the lowest levels among all sites (below 10°C) and the
236 RH reaches about 75%, comparable to levels in other sites in the northern region of the state (i.e.
237 San Jose and Sacramento). Unlike northern areas, RH exhibited more moderate seasonality in
238 southern California, displaying minima in fall/winter (50-71%) and maxima in spring/summer
239 (59-77%). At all sampling locations, the average of yearly total precipitation was negligible in
240 summer, but greatest in winter. During the studied period, Sacramento showed the highest total
241 precipitation in winter, followed by LA, San Jose, and Simi Valley (23.4±7.1, 21.7±17.1,
242 16.3±3.9, and 14.1±13.0 cm, respectively). Additionally, wind speeds were generally much
243 stronger in summer compared with fall/winter. During spring and summer, wind blows mostly
244 from coast to inland in the southern part of the state (i.e. El Cajon, Rubidoux, LA, and Simi
245 Valley), with a predominant westerly/southwesterly direction, while it shifts in winter and has a
246 predominantly northerly origin at all sites, with the exception of El Cajon. In Bakersfield and
247 Fresno, wind constantly blows from northwest throughout the year, except for Fresno in winter,
248 when wind has an easterly direction. Lastly, in Sacramento, the prevailing wind direction is
249 southerly/southwesterly throughout the year.

250

251 **4. Results and discussion**

252 **4.1. Particulate mass**

253 Seasonal average mass concentration of ambient PM_{2.5} at each sampling site is presented
254 in Table 1. Overall, mass concentrations spanned a broad range of 8.2 to 36.6 µg/m³ across the
255 studied sites and all seasons. PM_{2.5} mass concentration showed a very strong seasonality in
256 central and northern parts of the state (i.e. Bakersfield, Fresno, San Jose, and Sacramento), with
257 2 to 4 times higher concentrations in winter compared with summer. This trend is typical of the
258 California's Central Valley, which usually experiences the most severe particulate pollution
259 during winter in the U.S. (Ying and Kleeman, 2009). In winter, ambient PM_{2.5} mass
260 concentrations peaked at Bakersfield and Fresno (32.0±1.8 and 36.6±1.5 µg/m³, respectively).
261 Severe stagnation periods and decreased mixing height are mostly responsible for elevated
262 particulate pollution during winter in this part of the state. As it will be discussed in the
263 following section, secondary ammonium nitrate and emissions from biomass burning were
264 mainly responsible for elevated PM_{2.5} mass concentrations in these two cities during winter. In
265 summer, on the other hand, highest mass concentrations were observed in sampling sites located
266 in the Los Angeles Basin (i.e. LA and Rubidoux). Rubidoux displayed highest mass
267 concentration in fall, followed by summer and spring. In addition to local sources, this region of
268 the state is typically subject to transported plumes from upwind regions in west and central LA
269 (Daher et al., 2013; Sardar et al., 2005), particularly during the warm seasons when the westerly
270 wind prevails (Table S2).

271 **4.2. Source characterization and apportionment**

272 **4.2.1. Overview**

273 Between five to nine particle sources were identified at each sampling site. Resolved
274 source profiles along with the explained variation (EV) of each species are shown in Figure S2 a-
275 h, for all studied sampling sites. Gray bars represent the normalized concentration of each
276 species to the mass concentration of $PM_{2.5}$ apportioned to that factor, while the black dots
277 represent the percent of each species apportioned to that factor (Lee et al., 1999). Table 2
278 summarizes the marker species which were used to identify each source profile. Several sources,
279 including secondary ammonium nitrate, secondary ammonium sulfate, vehicular emissions,
280 biomass burning, soil, fresh and aged sea salt were commonly identified at multiple sites. Few
281 minor sources were exclusively identified at some of the sites, depending on the site location and
282 nearby emission sources. These sources, however, accounted for a small fraction of the total
283 mass (1 to 15% across the state, on an annual average basis).

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

289 Year-to-year variability in the source contributions was overall quite small for almost all
290 identified sources. This can be deduced from the relatively small standard errors in the 6-year
291 seasonal average source contributions, as shown in Table S3 a-d (median relative standard error
292 of 8%, across all sites, seasons, and sources). Identified sources, on the other hand, displayed
293 distinct seasonal and spatial variability. The percent contributions from these sources to $PM_{2.5}$
294 mass are presented in Figure 1. Overall, secondary aerosols (including secondary ammonium
295 nitrate and ammonium sulfate) collectively comprised the largest fraction of ambient $PM_{2.5}$ at all

296 sampling sites (except for San Jose), accounting for 26 to 63% of total mass across all sites, on
297 an annual average basis. Vehicular emissions were the second major contributor to $PM_{2.5}$ at all
298 sites (11 to 25% annual average contribution, across the state), except for San Jose and Fresno, at
299 which biomass burning was the dominant primary source of $PM_{2.5}$ (35 and 27% annual average
300 contribution, respectively). “Other sources” in Figure 1 are associated with those sources which
301 were exclusively identified at some specific locations. These contributed to < 15% of the mass,
302 on an annual average basis. The unapportioned mass, which is the difference between the
303 seasonal average $PM_{2.5}$ mass and the sum of the seasonal average source contributions from each
304 factor, accounted for 3 to 6% of total mass across the state, on an annual average basis. The
305 unapportioned mass represents the fraction that could not be resolved by the model.

306 **4.2.2. Vehicular emissions**

307 Vehicular emissions source profiles were identified by high concentrations of
308 carbonaceous species (i.e. EC and OC). Elevated loadings of several non-exhaust PM tracers
309 (e.g. Fe, Cu, Zn, Pb, Mn) indicate that these sources are affected by particles emitted from brake
310 and tire wear, road surface abrasion, and resuspension of road surface dust (Pant and Harrison,
311 2013;Dall'sto et al., 2014). Only at Rubidoux, the PMF model was able to determine two
312 separate source profiles for diesel and gasoline vehicles (Figure S2 b). These source profiles are
313 characterized by high loadings of EC and OC, respectively, with EC/OC ratios being 0.4 in
314 gasoline source profile, while 2.2 in diesel vehicles source profile. These ratios are within the
315 ranges reported in previous studies (Liu et al., 2006;Fujita et al., 1998;Watson et al., 1998;Heo et
316 al., 2009). Diesel vehicles operating at very low speed and in stop-and-go traffic usually produce
317 similar EC/OC ratios to typical gasoline vehicles (Shah et al., 2004). As a result, the diesel
318 emissions source profile that was obtained in Rubidoux may represent only diesel vehicles

319 driving in relatively constant speed in fluid traffic conditions and the diesel emissions from stop-
320 and-go traffic could be apportioned into the gasoline vehicles category. To overcome this
321 uncertainty and also be able to compare the results with those obtained at other sampling sites,
322 the contributions from diesel and gasoline vehicles were combined together at Rubidoux and
323 referred to as vehicular emissions throughout the discussion.

324 As can be seen in Figure 2, across the state, estimated $PM_{2.5}$ mass attributed to vehicular
325 sources (including diesel and gasoline vehicles) displayed highest levels at Rubidoux, LA, and
326 Sacramento, with annual average (\pm standard error) contributions of 4.3 ± 0.1 , 3.6 ± 0.1 , and
327 $3.5\pm 0.1 \mu\text{g}/\text{m}^3$, respectively. Spatial pattern of $PM_{2.5}$ emissions from mobile sources across the
328 state is in a good agreement with the findings of a recent study by Hu et al. (2014), in which they
329 applied a source-oriented air quality model to predict primary $PM_{2.5}$ source contributions across
330 the state of California between 2000 and 2006.

331 Vehicular emissions displayed similar seasonal patterns at all sampling sites, with higher
332 contributions in fall and winter compared to spring and summer. In spring, summer, and fall,
333 highest vehicular emissions source contributions were observed at Rubidoux. In contrast, during
334 winter, when particulate pollution is confined within the emission area due to higher atmospheric
335 stability and lower mixing height, vehicular source contribution exhibited the highest value in
336 downtown LA. This trend is typical of the LA Basin, in which downwind “receptor” areas are
337 generally impacted by emissions from upwind “source” regions, when westerly/south-westerly
338 onshore winds prevail (Table S2) (Daher et al., 2013). Several previous studies have reported
339 similar trends in the LA Basin (Hasheminassab et al., 2013;Heo et al., 2013). It should be noted
340 that after 2007 until 2012, contributions of vehicular emissions to ambient $PM_{2.5}$ in the LA Basin
341 statistically significantly decreased by 20 to 25%, following the implementation of major federal,

342 state, and local regulations on vehicular emissions, particularly on diesel trucks (Hasheminassab
343 et al., 2014).

344 Among the studied locations in the California's Central Valley, vehicular emissions
345 displayed the highest levels in Sacramento, while lowest in San Jose, accounting for nearly 30
346 and 10% of total mass, respectively, on an average over 6 years. Vehicular emissions were
347 comparable at Bakersfield and Fresno during spring and summer, whereas levels were slightly
348 higher at Bakersfield in fall and winter. Schauer and Cass (2000) conducted a 4-day sampling in
349 Bakersfield during the winter of 1995 to quantify the sources of ambient $PM_{2.5}$, using chemical
350 mass balance receptor model. Average wintertime level of vehicular emissions in our study at
351 Bakersfield ($3.0 \pm 0.2 \mu\text{g}/\text{m}^3$) was about half of that reported by Schauer and Cass (2000) (6.3 ± 0.4
352 $\mu\text{g}/\text{m}^3$), whereas the percent contributions of this source to total mass were comparable in both
353 studies (10 and 12%, respectively). This finding suggests that vehicular emissions have
354 decreased by almost half after almost a decade in Bakersfield.

355 **4.2.3. Secondary aerosols**

356 Secondary ammonium nitrate source profile was identified by high concentrations of
357 NO_3^- and NH_4^+ (Figure S2 a-h). Its contribution ranged from 0.2 to $16.8 \mu\text{g}/\text{m}^3$, accounting for 3
358 to 55% of ambient $PM_{2.5}$ mass, among all sites and seasons, as displayed in Figure 3 and
359 tabulated in Table S3 a-d. Seasonally, the contribution of secondary ammonium nitrate was
360 largest in winter while lowest during summer, with statewide average contribution of 8.4 and 3.2
361 $\mu\text{g}/\text{m}^3$, respectively. Elevated concentration of secondary ammonium nitrate during the cold
362 seasons is mainly due to the increased partitioning of ammonium nitrate into the particle phase,
363 favored by lower wintertime temperatures and higher RH (Ying, 2011). This source displayed
364 considerably higher contribution at Fresno and Bakersfield in winter (16.8 ± 1.3 and 15.8 ± 1.0

365 $\mu\text{g}/\text{m}^3$, respectively). Ying and Kleeman (2006) stated that diesel engines and catalyst equipped
366 gasoline vehicles are important local sources that contribute to secondary nitrate in the SJV.
367 Unlike all other sites, the seasonal trend of secondary ammonium nitrate was reverse at
368 Rubidoux, with higher concentration in summer compared to winter (12.5 ± 0.8 and 8.9 ± 0.8
369 $\mu\text{g}/\text{m}^3$, respectively). This is probably due to increased advection of ammonia from the upwind
370 Chino area, caused by stronger westerly/southwesterly wind speed during summer in the LA
371 Basin (Hasheminassab et al., 2013) combined with the increased photochemical production of
372 nitric acid in summer, which reacts with fugitive ammonia to produce high concentrations of
373 ammonium nitrate in summer in this area (Hughes et al., 2002;Sardar et al., 2005).

374 The characterized secondary ammonium sulfate source profiles have high loadings of
375 SO_4^{2-} and NH_4^+ (Figure S2 a-h). This source was identified at all sites, except at Fresno, where
376 sulfate largely partitioned in a source named “sulfate-bearing road dust” along with a few other
377 components, which will be discussed in further detail below. Annual average contributions of
378 this source ranged from 1.3 to 4.6 $\mu\text{g}/\text{m}^3$ (or 10 to 24% of total mass) among all sites, indicating
379 that this source is a smaller contributor to total mass compared with secondary ammonium
380 nitrate. Secondary ammonium sulfate exhibited a similar seasonal trend at all monitoring sites,
381 displaying wintertime minima while summertime peaks due to increased photochemical activity
382 that forms this species. Levels were also overall higher in the southern part of the state,
383 compared to the upper regions (Figure 4). As argued by Ying and Kleeman (2006), the majority
384 of secondary aerosols formed in southern California are formed from locally emitted precursors,
385 whereas in the SJV secondary PM is mostly impacted by emissions from upwind areas (i.e.
386 regional sources).

387 **4.2.4. Biomass burning**

388 Identified biomass burning source profiles consisted primarily of EC, OC, and either K or
389 K⁺ (Figure S2 a-h). Biomass burning includes emissions from wildfires and residential wood
390 combustion. This source showed distinct seasonal and spatial variability, with highest levels
391 observed during winter and also in upper parts of the state. Higher concentrations associated with
392 biomass burning in winter are mainly due to the higher residential wood burning during the
393 colder seasons. Central and northern parts of the state usually experience colder winters
394 compared to southern regions (Table S2), therefore higher biomass burning is expected in these
395 geographical locations, as shown in many previous studies (Hu et al., 2014;Chen et al., 2007).
396 Biomass burning was the major primary source of ambient PM_{2.5} at Fresno and San Jose during
397 all seasons, with levels ranging from 2.4 to 10.4 µg/m³ (or 22 to 30% of PM_{2.5}) at Fresno and
398 from 2.2 to 8.0 µg/m³ (or 22 to 43% of PM_{2.5}) in San Jose (Figure 5). This source was also the
399 dominant primary contributor to ambient PM_{2.5} in Bakersfield and Sacramento during winter (12
400 and 31% of PM_{2.5}, respectively), consistent with the findings of many previous studies in this
401 area (Chow et al., 2007;Gorin et al., 2006;Schauer and Cass, 2000).

402 **4.2.5. Soil**

403 Resolved soil source profiles were dominated by crustal elements such as Al, Ca, Fe, Si,
404 and Ti (Figure S2 a-h). These profiles generally lacked the contributions from EC and OC,
405 indicating that they are not majorly impacted by emissions of road dust. As stated above, road
406 dust was partially apportioned in the resolved vehicular emissions source profiles. A distinct
407 source profile attributable to soil was not identified at Fresno. Instead, crustal elements
408 partitioned in a separate source profile, along with high loadings of sulfate, EC, and OC, which
409 was characterized as “sulfate-bearing road dust”. Across the state, soil exhibited lower
410 concentrations in northern regions, namely at San Jose and Sacramento (Figure 6). This is likely

411 attributed to increased precipitation and higher RH in this part of the state (Table S2), which
412 limit the wind-induced resuspension of soil (Harrison et al., 2001). Soil, in contrast, accounted
413 for a large fraction of PM_{2.5} at Bakersfield, in concert with the findings of Chen et al. (2007).
414 During summer, in particular, contribution of soil to total mass was near 20% at Bakersfield,
415 which could be mainly due to the lack of precipitation and low RH in this area (Table S2). As
416 discussed by Chen et al. (2007), farm lands, pasture lands, and unpaved roads are major sources
417 of soil and windblown dust in the SJV.

418 **4.2.6. Fresh and aged sea salt**

419 Sources with high concentrations of Na⁺ and Cl⁻ were characterized as fresh sea salt
420 (Figure S2 a-h). Aged sea salt source profiles, on the other hand, were dominated by loadings of
421 Na⁺, SO₄²⁻, and NO₃⁻. Unlike fresh sea salt, chlorine has a negligible or near-zero contribution to
422 aged sea salt source profile. Chlorine is typically depleted due to reactions of sea salt with acidic
423 gases during the long range transport of sea salt aerosols from the point of emission (Song and
424 Carmichael, 1999). Aged sea salt overall accounted for a larger fraction (2 to 27%) of ambient
425 PM_{2.5} compared to fresh sea salt (1 to 13%), in all sites and seasons (Figures 1, S3, and S4).
426 Aged sea salt showed a clear seasonal pattern at all sites, with higher concentrations in summer,
427 consistent with increasing onshore winds (Table S 1), while lowest during winter.

428 It is also noteworthy that the PMF model did not apportion a separate factor for ship
429 emissions or a source related to ocean goods transport. However, high loadings of Ni and V
430 (tracers of ship emissions (Arhami et al., 2009)) in secondary ammonium sulfate and aged sea
431 salt source profiles for the sampling sites in the LA Basin, suggest that these sources are affected
432 in part by emissions from ships serving the ports of LA and Long Beach (Hwang and Hopke,
433 2007).

434

435 **4.2.7. Other sources**

436 As noted above, few sources were exclusively identified at some sites, with relatively low
437 annual contributions to total mass (1 to 15%, across the sites). At Rubidoux, a source profile was
438 deduced with high loadings of Zn, Pb, EC, and OC (Figure S2 b), which is most likely attributed
439 to local “mixed industrial” emissions in the surrounding areas. A similar source profile was also
440 obtained in previous studies in this area (Kim and Hopke, 2007;Kim et al., 2010). At San Jose, a
441 source profile dominated by Ni was identified, which likely indicates the contribution from
442 nearby Ni-related industrial sources. Hwang and Hopke (2006) reported similar findings at the
443 same sampling location, by application of the PMF model on STN data, collected between 2002
444 and 2005. This source, nonetheless, accounted for less than 2% of the total mass, on an annual
445 average basis. Copper smelters source profile, with a very high loading of Cu (>80%) and a
446 slight contribution of EC, was identified in El Cajon and Bakersfield sampling sites (Figure S2
447 a,e). This source accounted for about 1 and 4% of total mass, over all years, in Bakersfield and
448 El Cajon, respectively.

449 Figure 7 shows the seasonal trends of industrial emissions in locations where these
450 sources were identified. In El Cajon and Rubidoux, contributions of the identified industrial
451 sources peaked in winter, while in Bakersfield and San Jose, maximum emissions from copper
452 smelters and Ni-related sources were observed in summer. It is important to note that although
453 the contributions from the identified industrial sources to total PM mass were overall trivial
454 (<4%), these sources and the related elements may be important contributors to the overall
455 particle toxicity (Toledo et al., 2008;von Schneidemesser et al., 2010;Dall'osto et al.,
456 2008;Saffari et al., 2013).

457 At Fresno, a source profile with a high loading of sulfate along with road dust tracers,
458 such as OC, EC, Fe, Ca, Mn, Si and Ti, was resolved (Figure S2 f). These road dust tracers most
459 likely originate from the re-suspension of deposited soil and road dust enriched with vehicular
460 emissions and lubricating oils (Pant and Harrison, 2013; Dall'osto et al., 2014). This source was
461 therefore named “sulfate-bearing road dust” (Katrinak et al., 1995). As mentioned above,
462 separate source profiles for secondary ammonium sulfate and soil were not identified at Fresno.
463 Nonetheless, the relatively high loadings of sulfate and a few crustal elements (e.g. Al, Ca, Fe,
464 Si), along with the modest contribution of ammonium, suggest that these two sources are
465 partially apportioned into this source profile. On an average basis over all 6 years, “sulfate-
466 bearing road dust” accounted for about 15% of total mass at Fresno and its contribution was
467 highest in summer among all seasons ($2.7 \pm 0.1 \mu\text{g}/\text{m}^3$).

468 Relatively similar source profiles, with high loadings of chlorine, were obtained at
469 Fresno, Bakersfield, and Sacramento, with annual average contributions of about 5, 2, and 1% to
470 total mass, respectively (Figure S2 e, f, and h). This source, which was denoted as “chlorine
471 sources”, was mostly detected during fall and winter at Fresno and Bakersfield, in the SJV, while
472 it displayed the maximum seasonal average value in summer at Sacramento (Figure 8).

473

474 **5. Summary and conclusions**

475 Source apportionment analyses were conducted using PMF receptor model applied on
476 chemical speciation datasets, obtained from 8 different STN sampling sites throughout the state
477 of California, between 2002 and 2007. Five-to-nine major sources contributing to ambient $\text{PM}_{2.5}$
478 were identified at each site, with several of which being common in multiple locations. Overall,

479 secondary aerosols (including secondary ammonium nitrate and ammonium sulfate) were
480 collectively the main contributor to PM_{2.5} mass at all sampling sites. Annual average source
481 contribution of secondary ammonium nitrate and ammonium sulfate ranged from 3.1 to 12 µg/m³
482 (or 16 to 50% of total mass) and 1.3 to 4.6 µg/m³ (or 10 to 23% of total mass) across the state,
483 respectively. On an annual average basis, vehicular emissions (including both diesel and gasoline
484 vehicles) were the largest primary sources of PM_{2.5} at all sampling sites in the southern part of
485 the state (i.e. El Cajon, Rubidoux, LA, and Simi Valley), with 17-18% contribution total PM
486 mass. In Fresno and San Jose, on the other hand, biomass burning was the dominant primary
487 source of ambient PM_{2.5}, contributing to 27 and 35% of total mass, on average over all years. In
488 Bakersfield and Sacramento, biomass burning and vehicular emissions equally contributed to
489 PM_{2.5} mass with near 12 and 25% annual contributions, respectively. Other sources commonly
490 identified at all sites were minor contributors to PM_{2.5}, including aged and fresh sea salt as well
491 as soil, which contributed to 0.5-13%, 2-27%, and 1-19% of total mass, respectively, across all
492 sites and seasons. Furthermore, a few sources (including chlorine sources, sulfate-bearing road
493 dust, and different types of industrial emissions), which overall accounted for a small fraction of
494 total mass (1 to 15%, on an annual average basis), were solely identified at some of the sites.

495

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Tables and Figures

Table 1. Seasonal average mass concentration (\pm standard error) ($\mu\text{g}/\text{m}^3$) of ambient $\text{PM}_{2.5}$ at the 8 sampling sites in the period between 2002 and 2007.

	El Cajon	Rubidoux	Los Angeles	Simi Valley	Bakersfield	Fresno	San Jose	Sacramento
Spring	12.0 \pm 0.5	23.6 \pm 1.3	18.1 \pm 1.5	12.8 \pm 0.8	11.8 \pm 0.5	16.4 \pm 1.1	9.7 \pm 0.4	8.2 \pm 0.3
Summer	13.1 \pm 0.4	25.6 \pm 0.9	20.2 \pm 0.7	15.9 \pm 0.5	13.5 \pm 0.4	9.7 \pm 0.3	9.6 \pm 0.4	9.2 \pm 0.4
Fall	14.5 \pm 0.5	27.4 \pm 1.5	20.8 \pm 1.2	14.4 \pm 0.9	24.6 \pm 1.7	13.7 \pm 0.6	14.8 \pm 0.8	15.1 \pm 0.9
Winter	17.1 \pm 0.7	20.0 \pm 1.1	20.4 \pm 1.6	9.8 \pm 0.8	32.0 \pm 1.8	36.6 \pm 1.5	18.6 \pm 1.2	23.5 \pm 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 regressions between daily-resolved measured ambient PM_{2.5} and estimated PM_{2.5} mass concentrations obtained from the PMF model. Errors correspond to one standard error.

	R²	Slope	Intercept (µg/m³)
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

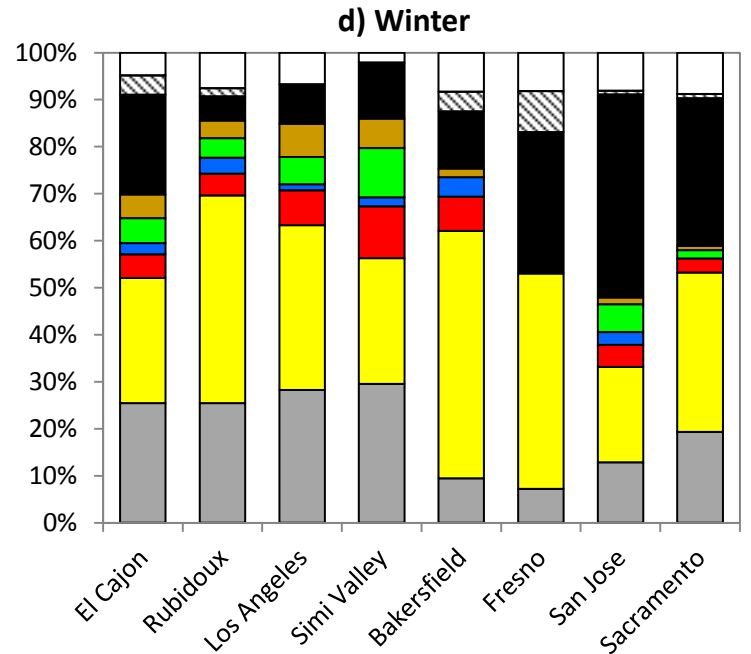
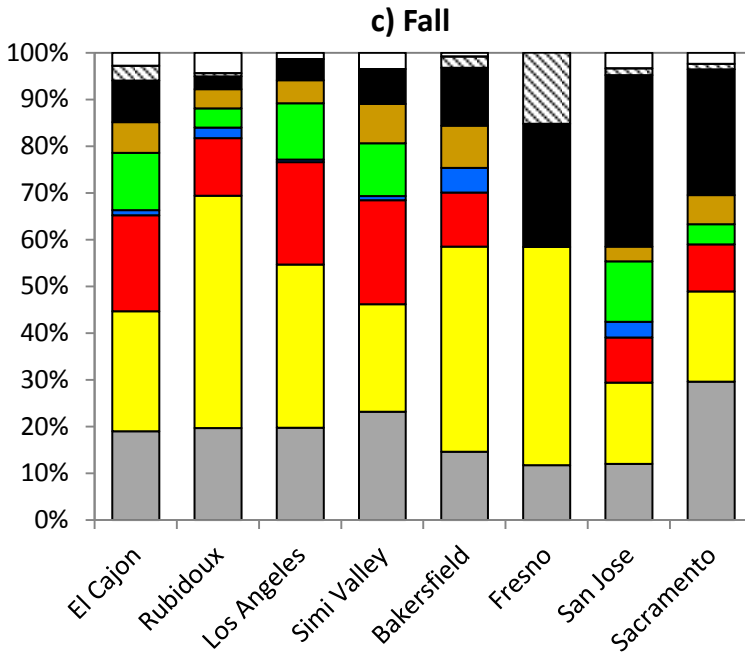
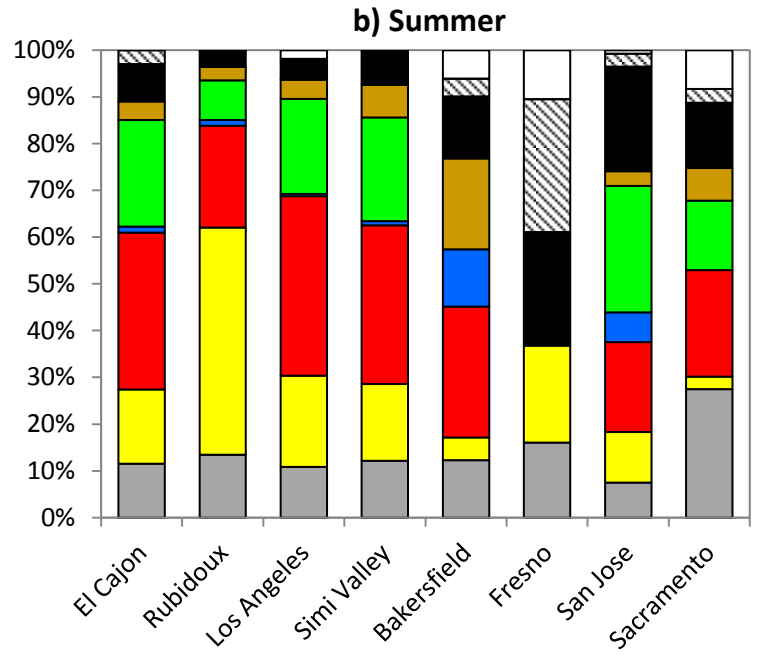
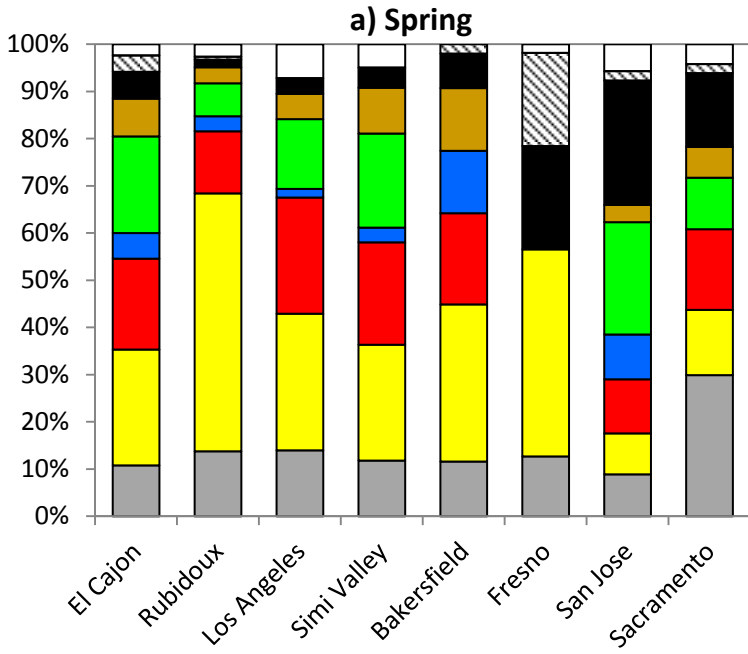
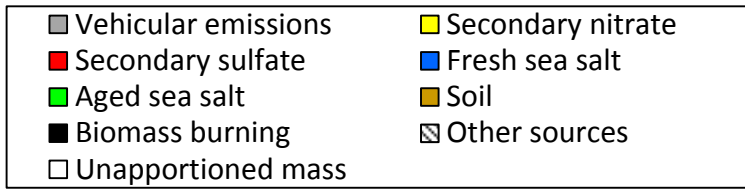


Figure 1 a-d. Seasonal variation in the percent contribution of identified sources to ambient $PM_{2.5}$, by site.

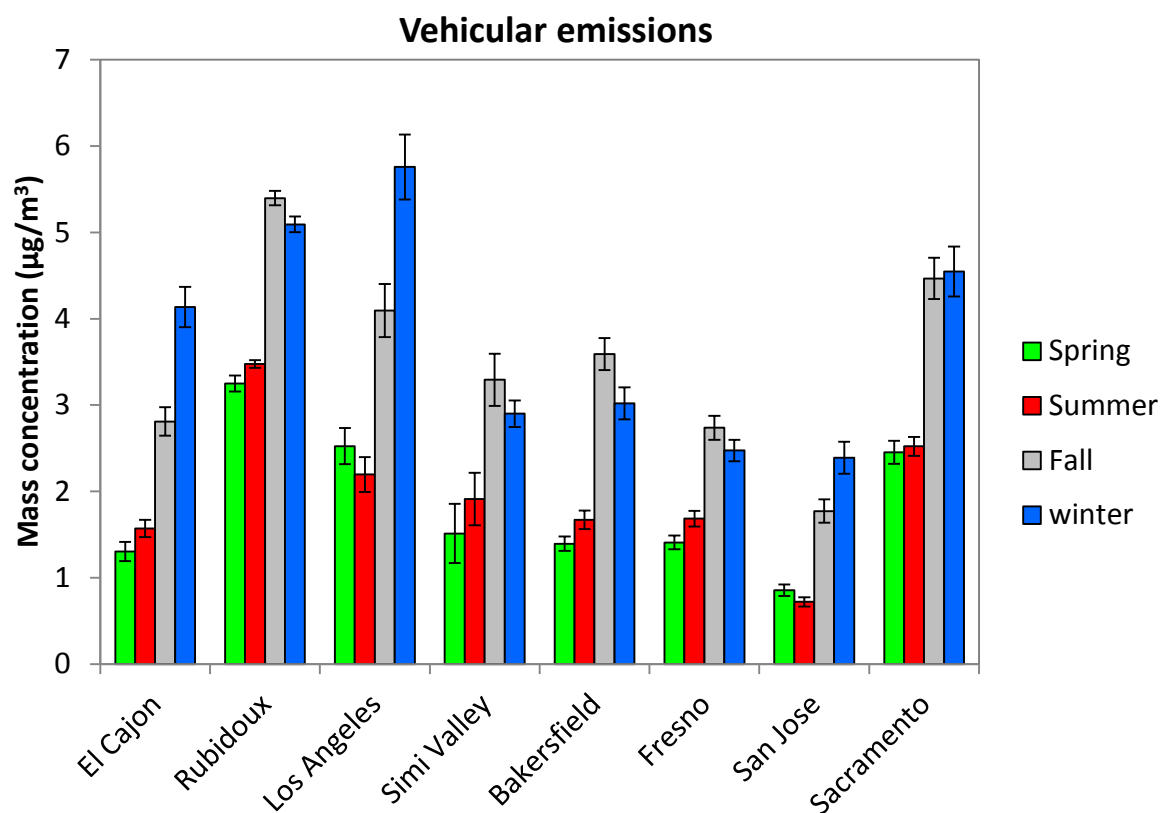


Figure 2. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of vehicular emissions to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

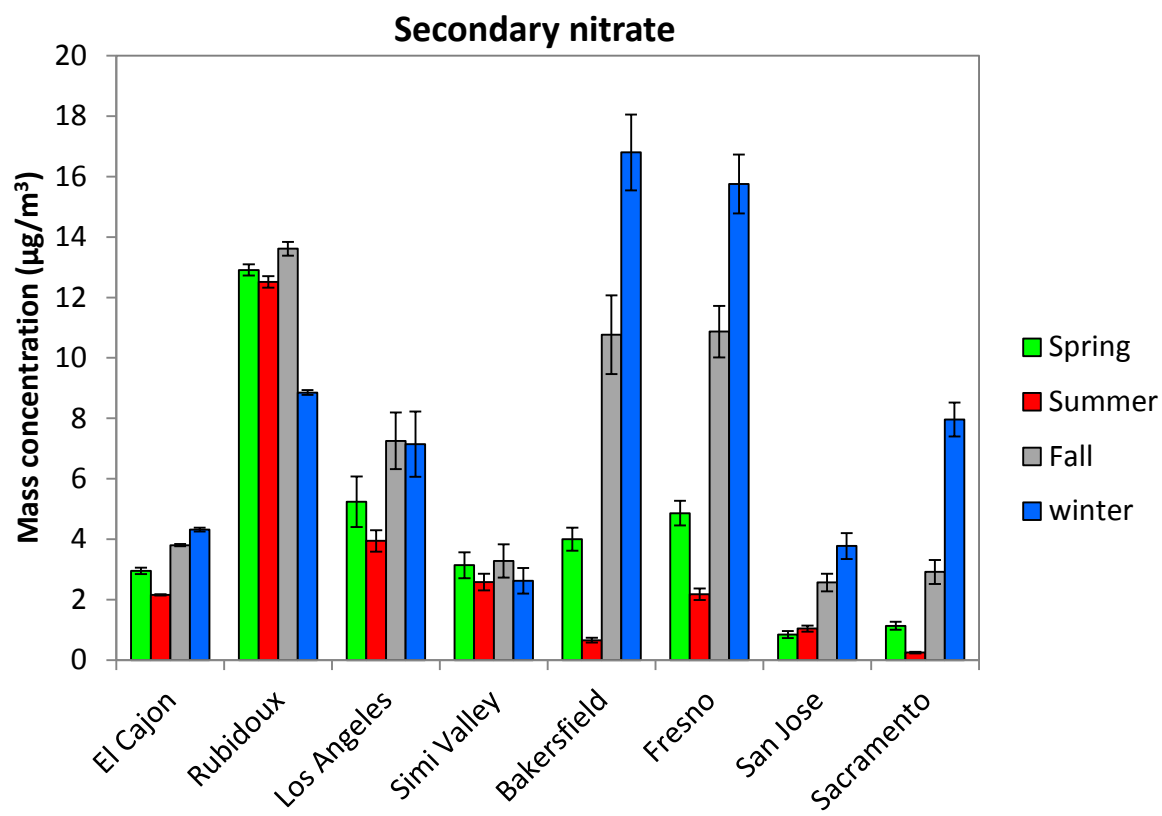


Figure 3. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of secondary ammonium nitrate to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

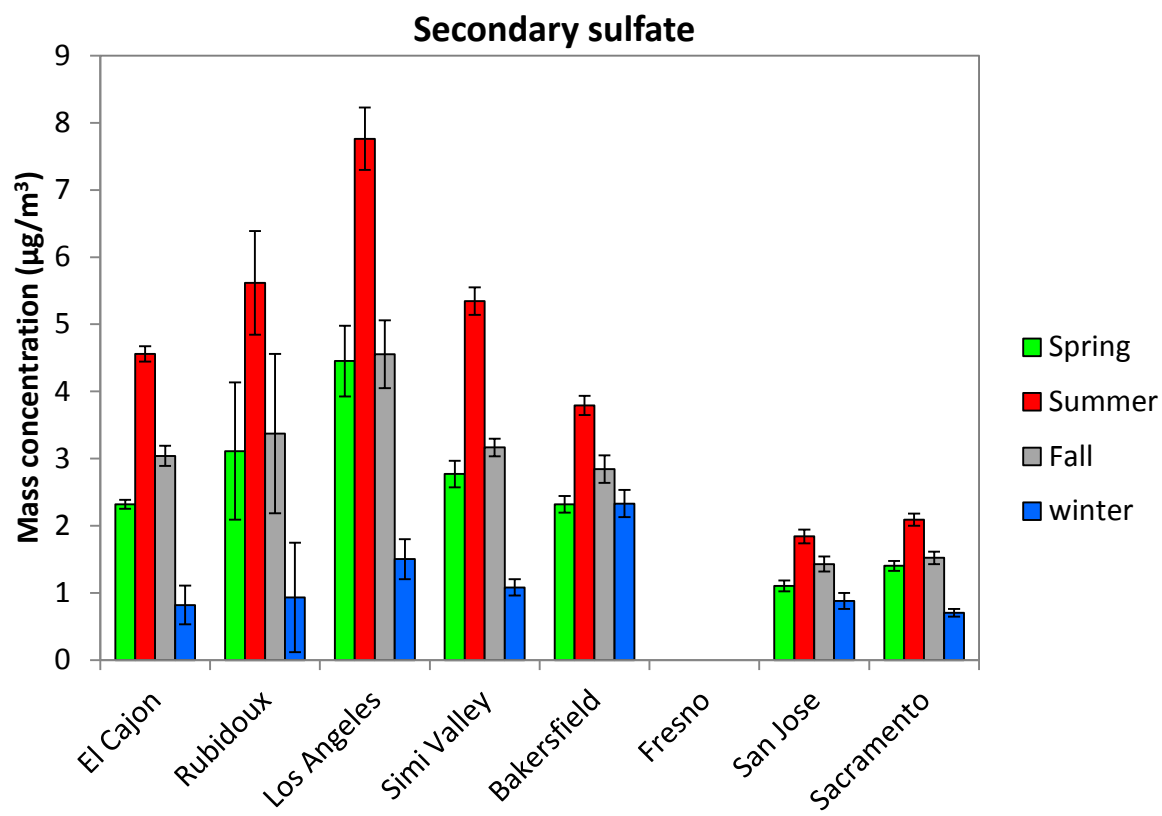


Figure 4. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of secondary ammonium sulfate to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

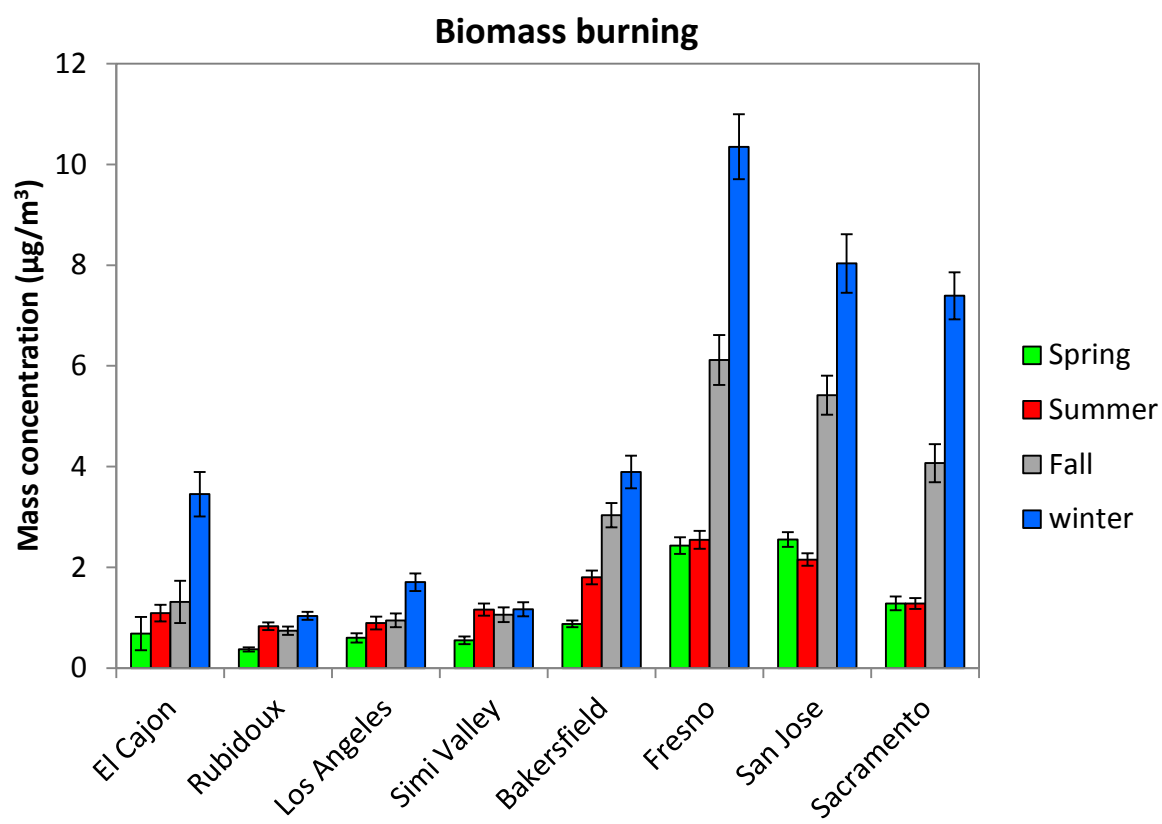


Figure 5. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of biomass burning to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

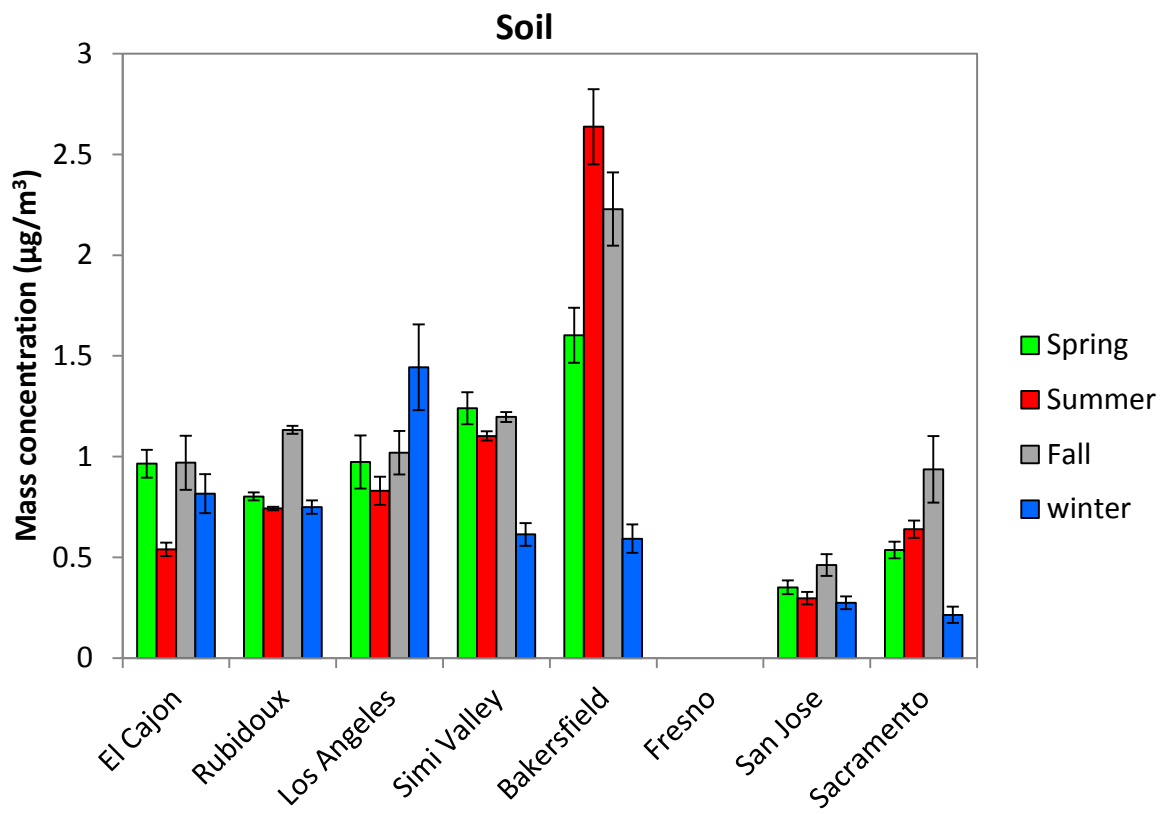


Figure 6. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of soil to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

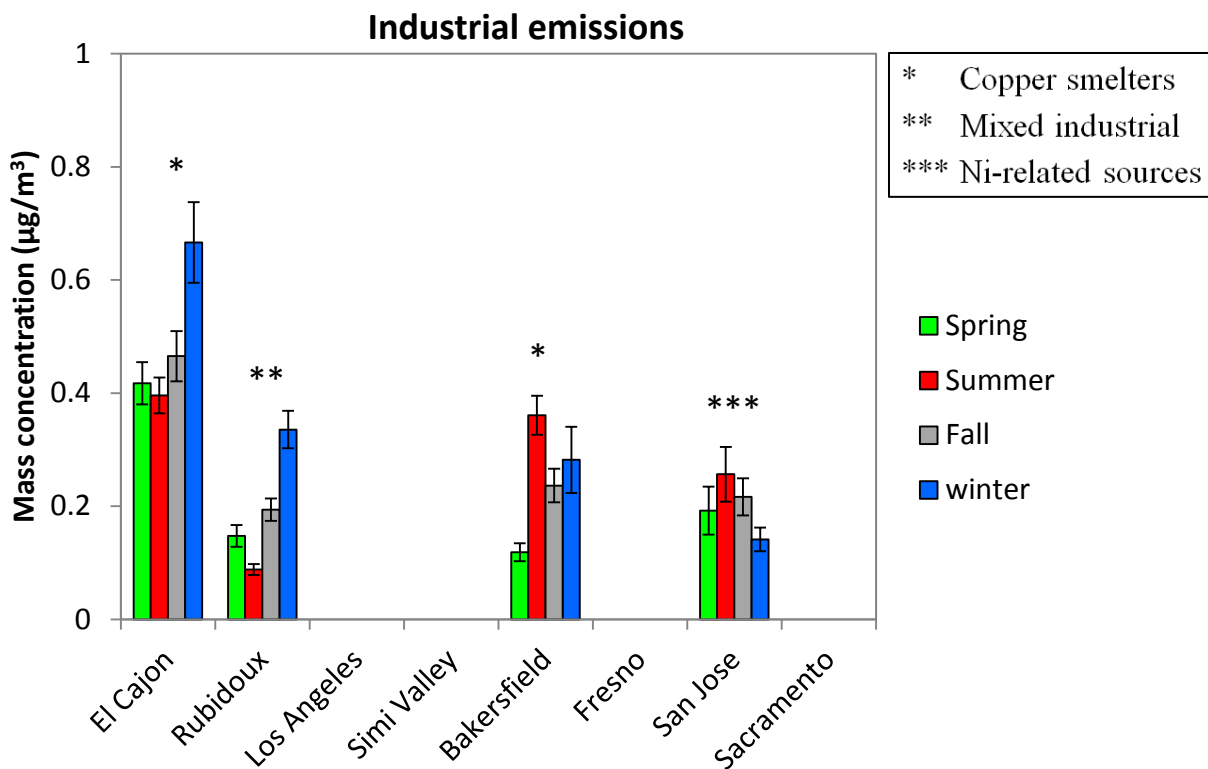


Figure 7. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of industrial emissions to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

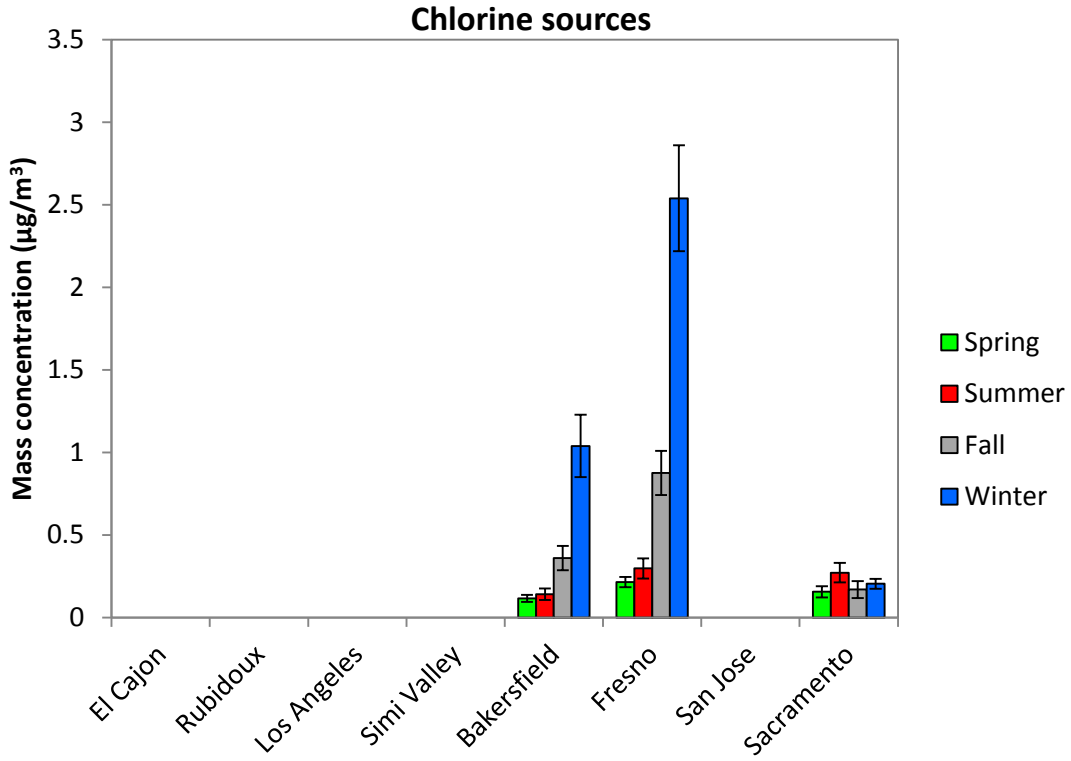


Figure 8. Seasonal average contribution ($\mu\text{g}/\text{m}^3$) of chlorine sources to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.