

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 Hokpe (2006) evaluated the sources of ambient PM_{2.5} at two sampling sites in San Jose during a
81 large period of time 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 a combined chemical dataset from 2002 to
139 2013 was used as the input file when running the PMF model (Hasheminassab et al., 2014). In
140 the present study, in order to compare the results with those obtained for the rest of sampling
141 sites, we calculated the average source contributions between 2002 and 2007 from the output of
142 the 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 are tested, equilibrated, and weighted in the U.S. EPA
157 contract laboratories, and then they are shipped to the field. After sampling, filters bearing PM_{2.5}
158 deposits are 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.

179 To avoid double-counting of species, the linear correlations in each pair of S/SO₄²⁻,
180 Na/Na⁺, and K/K⁺ were examined. Depending on the goodness of fit and the percent number of
181 samples below detection limit (BDL) (threshold of 70%), either IC SO₄²⁻, Na⁺, K⁺ or ED-XRF S,

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

191 **2.3.2. PMF model**

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

202 Species with a signal-to-noise (S/N) ratio between 0.2-2, as well as those that have BDL
203 values more than 50% of total samples were considered as weak variables and their uncertainties
204 were increased by a factor of 3. In order to directly apportion the total PM mass, PM_{2.5} mass

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

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

217

218 **3. Meteorology**

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

228 and tables presented in this study, sampling sites were ranked according to their latitude, from
229 south to north (i.e. from El Cajon to Sacramento).

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

248

249 **4. Results and discussion**

250 **4.1. Particulate mass**

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

269 **4.2. Source characterization and apportionment**

270 **4.2.1. Overview**

271 Between five to nine particle sources were identified at each sampling site. Resolved
272 source profiles along with the explained variation (EV) of each species are shown in Figure S2 a-
273 h, for all studied sampling sites. Gray bars represent the normalized concentration of each

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

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

287 Year-to-year variability in the source contributions was overall quite small for almost all
288 identified sources. This can be deduced from the relatively small standard errors in the 6-year
289 seasonal average source contributions, as shown in Table S3 a-d (median relative standard error
290 of 8%, across all sites, seasons, and sources). Identified sources, on the other hand, displayed
291 distinct seasonal and spatial variability. The percent contributions from these sources to $PM_{2.5}$
292 mass are presented in Figure 1. Overall, secondary aerosols (including secondary ammonium
293 nitrate and ammonium sulfate) collectively comprised the largest fraction of ambient $PM_{2.5}$ at all
294 sampling sites (except for San Jose), accounting for 26 to 63% of total mass across all sites, on
295 an annual average basis. Vehicular emissions were the second major contributor to $PM_{2.5}$ at all
296 sites (11 to 25% annual average contribution, across the state), except for San Jose and Fresno, at

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

304 **4.2.2. Vehicular emissions**

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

320 the contributions from diesel and gasoline vehicles were combined together at Rubidoux and
321 referred to as vehicular emissions throughout the discussion.

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

329 Vehicular emissions displayed similar seasonal patterns at all sampling sites, with higher
330 contributions in fall and winter compared to spring and summer. In spring, summer, and fall,
331 highest vehicular emissions source contributions were observed at Rubidoux. In contrast, during
332 winter, when particulate pollution is confined within the emission area due to higher atmospheric
333 stability and lower mixing height, vehicular source contribution exhibited the highest value in
334 downtown LA. This trend is typical of the LA Basin, in which downwind “receptor” areas are
335 generally impacted by emissions from upwind “source” regions, when westerly/south-westerly
336 onshore winds prevail (Table S2) (Daher et al., 2013). Several previous studies have reported
337 similar trends in the LA Basin (Hasheminassab et al., 2013;Heo et al., 2013). It should be noted
338 that after 2007 until 2012, contributions of vehicular emissions to ambient PM_{2.5} in the LA Basin
339 statistically significantly decreased by 20 to 25%, following the implementation of major federal,
340 state, and local regulations on vehicular emissions, particularly on diesel trucks (Hasheminassab
341 et al., 2014).

342 Among the studied locations in the California's Central Valley, vehicular emissions
343 displayed the highest levels in Sacramento, while lowest in San Jose, accounting for nearly 30
344 and 10% of total mass, respectively, on an average over 6 years. Vehicular emissions were
345 comparable at Bakersfield and Fresno during spring and summer, whereas levels were slightly
346 higher at Bakersfield in fall and winter. Schauer and Cass (2000) conducted a 4-day sampling in
347 Bakersfield during the winter of 1995 to quantify the sources of ambient PM_{2.5}, using chemical
348 mass balance receptor model. Average wintertime level of vehicular emissions in our study at
349 Bakersfield (3.0±0.2 µg/m³) was about half of that reported by Schauer and Cass (2000) (6.3±0.4
350 µg/m³), whereas the percent contributions of this source to total mass were comparable in both
351 studies (10 and 12%, respectively). This finding suggests that vehicular emissions have
352 decreased by almost half after almost a decade in Bakersfield.

353 **4.2.3. Secondary aerosols**

354 Secondary ammonium nitrate source profile was identified by high concentrations of
355 NO₃⁻ and NH₄⁺ (Figure S2 a-h). Its contribution ranged from 0.2 to 16.8 µg/m³, accounting for 3
356 to 55% of ambient PM_{2.5} mass, among all sites and seasons, as displayed in Figure 3 and
357 tabulated in Table S3 a-d. Seasonally, the contribution of secondary ammonium nitrate was
358 largest in winter while lowest during summer, with statewide average contribution of 8.4 and 3.2
359 µg/m³, respectively. Elevated concentration of secondary ammonium nitrate during the cold
360 seasons is mainly due to the increased partitioning of ammonium nitrate into the particle phase,
361 favored by lower wintertime temperatures and higher RH (Ying, 2011). This source displayed
362 considerably higher contribution at Fresno and Bakersfield in winter (16.8±1.3 and 15.8±1.0
363 µg/m³, respectively). Ying and Kleeman (2006) stated that diesel engines and catalyst equipped
364 gasoline vehicles are important local sources that contribute to secondary nitrate in the SJV.

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

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

385 **4.2.4. Biomass burning**

386 Identified biomass burning source profiles consisted primarily of EC, OC, and either K or
387 K^+ (Figure S2 a-h). Biomass burning includes emissions from wildfires and residential wood

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

400 **4.2.5. Soil**

401 Resolved soil source profiles were dominated by crustal elements such as Al, Ca, Fe, Si,
402 and Ti (Figure S2 a-h). These profiles generally lacked the contributions from EC and OC,
403 indicating that they are not majorly impacted by emissions of road dust. As stated above, road
404 dust was partially apportioned in the resolved vehicular emissions source profiles. A distinct
405 source profile attributable to soil was not identified at Fresno. Instead, crustal elements
406 partitioned in a separate source profile, along with high loadings of sulfate, EC, and OC, which
407 was characterized as “sulfate-bearing road dust”. Across the state, soil exhibited lower
408 concentrations in northern regions, namely at San Jose and Sacramento (Figure 6). This is likely
409 attributed to increased precipitation and higher RH in this part of the state (Table S2), which
410 limit the wind-induced resuspension of soil (Harrison et al., 2001). Soil, in contrast, accounted

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

416 **4.2.6. Fresh and aged sea salt**

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

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

432

433 **4.2.7. Other sources**

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

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

455 At Fresno, a source profile with a high loading of sulfate along with road dust tracers,
456 such as OC, EC, Fe, Ca, Mn, Si and Ti, was resolved (Figure S2 f). These road dust tracers most

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

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

471

472 **5. Summary and conclusions**

473 Source apportionment analyses were conducted using PMF receptor model applied on
474 chemical speciation datasets, obtained from 8 different STN sampling sites throughout the state
475 of California, between 2002 and 2007. Five-to-nine major sources contributing to ambient $\text{PM}_{2.5}$
476 were identified at each site, with several of which being common in multiple locations. Overall,
477 secondary aerosols (including secondary ammonium nitrate and ammonium sulfate) were
478 collectively the main contributor to $\text{PM}_{2.5}$ mass at all sampling sites. Annual average source

479 contribution of secondary ammonium nitrate and ammonium sulfate ranged from 3.1 to 12 $\mu\text{g}/\text{m}^3$
480 (or 16 to 50% of total mass) and 1.3 to 4.6 $\mu\text{g}/\text{m}^3$ (or 10 to 23% of total mass) across the state,
481 respectively. On an annual average basis, vehicular emissions (including both diesel and gasoline
482 vehicles) were the largest primary sources of $\text{PM}_{2.5}$ at all sampling sites in the southern part of
483 the state (i.e. El Cajon, Rubidoux, LA, and Simi Valley), with 17-18% contribution total PM
484 mass. In Fresno and San Jose, on the other hand, biomass burning was the dominant primary
485 source of ambient $\text{PM}_{2.5}$, contributing to 27 and 35% of total mass, on average over all years. In
486 Bakersfield and Sacramento, biomass burning and vehicular emissions equally contributed to
487 $\text{PM}_{2.5}$ mass with near 12 and 25% annual contributions, respectively. Other sources commonly
488 identified at all sites were minor contributors to $\text{PM}_{2.5}$, including aged and fresh sea salt as well
489 as soil, which contributed to 0.5-13%, 2-27%, and 1-19% of total mass, respectively, across all
490 sites and seasons. Furthermore, a few sources (including chlorine sources, sulfate-bearing road
491 dust, and different types of industrial emissions), which overall accounted for a small fraction of
492 total mass (1 to 15%, on an annual average basis), were solely identified at some of the sites.

493

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497 **References**

- 498 Araujo, J. A., Barajas, B., Kleinman, M., Wang, X., Bennett, B. J., Gong, K. W., Navab, M.,
499 Harkema, J., Sioutas, C., Lulis, A. J., and Nel, A. E.: Ambient Particulate Pollutants in
500 the Ultrafine Range Promote Early Atherosclerosis and Systemic Oxidative Stress,
501 *Circulation Research*, 102, 589-596, 2008.
- 502 Arhami, M., Sillanpää, M., Hu, S., Olson, M. R., Schauer, J. J., and Sioutas, C.: Size-Segregated
503 Inorganic and Organic Components of PM in the Communities of the Los Angeles
504 Harbor, *Aerosol Science and Technology*, 43, 145-160, 2009.
- 505 Birch, M. E., and Cary, R. A.: Elemental Carbon-Based Method for Monitoring Occupational
506 Exposures to Particulate Diesel Exhaust, *Aerosol Science and Technology*, 25, 221-241,
507 1996.
- 508 Chen, L. W. A., Watson, J. G., Chow, J. C., and Magliano, K. L.: Quantifying PM_{2.5} Source
509 Contributions for the San Joaquin Valley with Multivariate Receptor Models,
510 *Environmental Science & Technology*, 41, 2818-2826, 2007.
- 511 Cheung, K., Daher, N., Kam, W., Shafer, M. M., Ning, Z., Schauer, J. J., and Sioutas, C.: Spatial
512 and temporal variation of chemical composition and mass closure of ambient coarse
513 particulate matter (PM_{10-2.5}) in the Los Angeles area, *Atmospheric Environment*, 45,
514 2651-2662, 2011.
- 515 Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L. W. A., Zielinska, B., Mazzoleni, L. R.,
516 and Magliano, K. L.: Evaluation of organic markers for chemical mass balance source
517 apportionment at the Fresno Supersite, *Atmospheric Chemistry and Physics*, 7, 1741-
518 1754, 2007.
- 519 Chow, J. C., Watson, J. G., Chen, L. W. A., Rice, J., and Frank, N. H.: Quantification of PM_{2.5}
520 organic carbon sampling artifacts in US networks, *Atmos. Chem. Phys.*, 10, 5223-5239,
521 2010.
- 522 Daher, N., Hasheminassab, S., Shafer, M. M., Schauer, J. J., and Sioutas, C.: Seasonal and
523 spatial variability in chemical composition and mass closure of ambient ultrafine
524 particles in the megacity of Los Angeles, *Environmental Science: Processes & Impacts*,
525 15, 283-295, 2013.
- 526 Dall'osto, M., Booth, M. J., Smith, W., Fisher, R., and Harrison, R. M.: A Study of the Size
527 Distributions and the Chemical Characterization of Airborne Particles in the Vicinity of
528 a Large Integrated Steelworks, *Aerosol science and technology*, 42, 981-991, 2008.
- 529 Dall'sto, M., Beddows, D. C. S., Gietl, J. K., Olatunbosun, O. A., Yang, X., and Harrison, R. M.:
530 Characteristics of Tyre Dust in Polluted Air: Studies by Single Particle Mass
531 Spectrometry (ATOFMS), *Atmospheric Environment*, 2014.
- 532 Davis, D. A., Akopian, G., Walsh, J. P., Sioutas, C., Morgan, T. E., and Finch, C. E.: Urban air
533 pollutants reduce synaptic function of CA1 neurons via an NMDA/NO pathway in vitro,
534 *Journal of Neurochemistry*, 127, 509-519, 2013a.
- 535 Davis, D. A., Bortolato, M., Godar, S. C., Sander, T. K., Iwata, N., Pakbin, P., Shih, J. C.,
536 Berhane, K., McConnell, R., Sioutas, C., Finch, C. E., and Morgan, T. E.: Prenatal
537 Exposure to Urban Air Nanoparticles in Mice Causes Altered Neuronal Differentiation
538 and Depression-Like Responses, *PLoS ONE*, 8, 2013b.
- 539 Delfino, R. J., Sioutas, C., and Malik, S.: Potential Role of Ultrafine Particles in Associations
540 between Airborne Particle Mass and Cardiovascular Health, *Environmental Health
541 Perspectives*, 113, 934-946, 2005.

542 DeNero, S. P.: Development of a source oriented version of the WRF-Chem model and its
543 application to the California Regional PM10/PM2.5 air quality study, UNIVERSITY OF
544 CALIFORNIA, DAVIS, 2012.

545 Fann, N., Lamson, A. D., Anenberg, S. C., Wesson, K., Risley, D., and Hubbell, B. J.:
546 Estimating the National Public Health Burden Associated with Exposure to Ambient
547 PM2.5 and Ozone, *Risk Analysis*, 32, 81-95, 2012.

548 Flanagan, J. B., Jayanty, R. K. M., Rickman, E. E., Jr., and Peterson, M. R.: PM2.5 Speciation
549 Trends Network: Evaluation of Whole-System Uncertainties Using Data from Sites with
550 Collocated Samplers, *Journal of the Air & Waste Management Association*, 56, 492-499,
551 2006.

552 Fujita, E. M., Watson, J. G., Chow, J. C., Robinson, N. F., Richards, L. W., and Kumar, N.:
553 Northern Front Range Air Quality Study. Volume C: Source apportionment and
554 simulation methods and evaluation. Prepared for Colorado State University. Cooperative
555 Institute for Research in the Atmosphere. Ft. Collins, CO, Desert Research Institute,
556 Reno, NV., 1998.

557 Gorin, C. A., Collett, J. L., and Herckes, P.: Wood Smoke Contribution to Winter Aerosol in
558 Fresno, CA, *Journal of the Air & Waste Management Association*, 56, 1584-1590,
559 2006.

560 Gutknecht, W., Flanagan, J., McWilliams, A., Jayanty, R. K. M., Kellogg, R., Rice, J., Duda, P.,
561 and Sarver, R. H.: Harmonization of Uncertainties of X-Ray Fluorescence Data for
562 PM2.5 Air Filter Analysis, *Journal of the Air & Waste Management Association*, 60,
563 184-194, 2010.

564 Ham, W. A., and Kleeman, M. J.: Size-resolved source apportionment of carbonaceous
565 particulate matter in urban and rural sites in central California, *Atmospheric
566 Environment*, 45, 3988-3995, 2011.

567 Harrison, R. M., Yin, J., Mark, D., Stedman, J., Appleby, R. S., Booker, J., and Moorcroft, S.:
568 Studies of the coarse particle (2.5-10 μ m) component in UK urban atmospheres,
569 *Atmospheric Environment*, 35, 3667-3679, 2001.

570 Hasheminassab, S., Daher, N., Schauer, J. J., and Sioutas, C.: Source apportionment and organic
571 compound characterization of ambient ultrafine particulate matter (PM) in the Los
572 Angeles Basin, *Atmospheric Environment*, 79, 529-539, 2013.

573 Hasheminassab, S., Daher, N., Ostro, B. D., and Sioutas, C.: Long-term source apportionment of
574 ambient fine particulate matter (PM2.5) in the Los Angeles Basin: A focus on emissions
575 reduction from vehicular sources, *Environmental Pollution*, 193, 54-64, 2014.

576 Held, T., Ying, Q., Kaduwela, A., and Kleeman, M.: Modeling particulate matter in the San
577 Joaquin Valley with a source-oriented externally mixed three-dimensional
578 photochemical grid model, *Atmospheric Environment*, 38, 3689-3711, 2004.

579 Heo, J., Dulger, M., Olson, M. R., McGinnis, J. E., Shelton, B. R., Matsunaga, A., Sioutas, C.,
580 and Schauer, J. J.: Source apportionments of PM2.5 organic carbon using molecular
581 marker Positive Matrix Factorization and comparison of results from different receptor
582 models, *Atmospheric Environment*, 73, 51-61, 2013.

583 Heo, J. B., Hopke, P. K., and Yi, S. M.: Source apportionment of PM2.5 in Seoul, Korea, *Atmos.
584 Chem. Phys.*, 9, 4957-4971, 2009.

585 Hopke, P. K.: Recent developments in receptor modeling, *Journal of Chemometrics*, 17, 255-
586 265, 2003.

587 Hu, J., Zhang, H., Chen, S., Ying, Q., Wiedinmyer, C., Vandenberghe, F., and Kleeman, M. J.:
588 Identifying PM_{2.5} and PM_{0.1} Sources for Epidemiological Studies in California,
589 Environmental Science & Technology, 48, 4980-4990, 2014.

590 Hu, S., Polidori, A., Arhami, M., Shafer, M. M., Schauer, J. J., Cho, A., and Sioutas, C.: Redox
591 activity and chemical speciation of size fractioned PM in the communities of the Los
592 Angeles-Long Beach harbor, Atmos. Chem. Phys., 8, 6439-6451, 2008.

593 Hughes, L. S., Allen, J. O., Kleeman, M. J., Johnson, R. J., Cass, G. R., Gross, D. S., Gard, E. E.,
594 GÃalli, M. E., Morrical, B. D., Ferguson, D. P., Dienes, T., Noble, C. A., Liu, D.-Y.,
595 Silva, P. J., and Prather, K. A.: Size and Composition Distribution of Atmospheric
596 Particles in Southern California, Environmental Science & Technology, 33, 3506-3515,
597 1999.

598 Hughes, L. S., Allen, J. O., Salmon, L. G., Mayo, P. R., Johnson, R. J., and Cass, G. R.:
599 Evolution of Nitrogen Species Air Pollutants along Trajectories Crossing the Los
600 Angeles Area, Environmental Science & Technology, 36, 3928-3935, 2002.

601 Hwang, I., and Hopke, P. K.: Comparison of source apportionments of fine particulate matter at
602 two San Jose speciation trends network sites, Journal of the Air & Waste Management
603 Association (1995), 56, 1287-1300, 2006.

604 Hwang, I., and Hopke, P. K.: Estimation of source apportionment and potential source locations
605 of PM_{2.5} at a west coastal IMPROVE site, Atmospheric Environment, 41, 506-518,
606 2007.

607 Katrinak, K. A., Anderson, J. R., and Buseck, P. R.: Individual Particle Types in the Aerosol of
608 Phoenix, Arizona, Environmental Science & Technology, 29, 321-329, 1995.

609 Kim, E., Hopke, P. K., and Qin, Y.: Estimation of Organic Carbon Blank Values and Error
610 Structures of the Speciation Trends Network Data for Source Apportionment, Journal of
611 the Air & Waste Management Association, 55, 1190-1199, 2005.

612 Kim, E., and Hopke, P. K.: Source characterization of ambient fine particles in the Los Angeles
613 basin, Journal of Environmental Engineering and Science, 6, 343-353, 2007.

614 Kim, E., Turkiewicz, K., Zulawnick, S. A., and Magliano, K. L.: Sources of fine particles in the
615 South Coast area, California, Atmospheric Environment, 44, 3095-3100, 2010.

616 Kleeman, M. J., and Cass, G. R.: A 3D Eulerian Source-Oriented Model for an Externally Mixed
617 Aerosol, Environmental Science & Technology, 35, 4834-4848, 2001.

618 Kleeman, M. J., Riddle, S. G., Robert, M. A., Jakober, C. A., Fine, P. M., Hays, M. D., Schauer,
619 J. J., and Hannigan, M. P.: Source Apportionment of Fine (PM_{1.8}) and Ultrafine
620 (PM_{0.1}) Airborne Particulate Matter during a Severe Winter Pollution Episode,
621 Environmental Science & Technology, 43, 272-279, 2009.

622 Laden, F., Neas, L. M., Dockery, D. W., and Schwartz, J.: Association of fine particulate matter
623 from different sources with daily mortality in six U.S. cities, Environmental Health
624 Perspectives, 108, 941-947, 2000.

625 Lee, E., Chan, C. K., and Paatero, P.: Application of positive matrix factorization in source
626 apportionment of particulate pollutants in Hong Kong, Atmospheric Environment, 33,
627 3201-3212, 1999.

628 Lee, H. J., Gent, J. F., Leaderer, B. P., and Koutrakis, P.: Spatial and temporal variability of fine
629 particle composition and source types in five cities of Connecticut and Massachusetts,
630 Science of The Total Environment, 409, 2133-2142, 2011.

631 Lim, S. S., Vos, T., Flaxman, A. D., Danaei, G., Shibuya, K., Adair-Rohani, H., AlMazroa, M.
632 A., Amann, M., Anderson, H. R., Andrews, K. G., and others: A comparative risk

633 assessment of burden of disease and injury attributable to 67 risk factors and risk factor
634 clusters in 21 regions, 1990-2010: a systematic analysis for the Global Burden of
635 Disease Study 2010, *The Lancet*, 380, 2224-2260, 2013.

636 Liu, W., Wang, Y., Russell, A., and Edgerton, E. S.: Enhanced source identification of southeast
637 aerosols using temperature-resolved carbon fractions and gas phase components,
638 *Atmospheric Environment*, 40, Supplement 2, 445-466, 2006.

639 Mar, T. F., Norris, G. A., Koenig, J. Q., and Larson, T. V.: Associations between air pollution
640 and mortality in Phoenix, 1995-1997, *Environmental Health Perspectives*, 108, 347-353,
641 2000.

642 Minguillón, M. C., Arhami, M., Schauer, J. J., and Sioutas, C.: Seasonal and spatial variations of
643 sources of fine and quasi-ultrafine particulate matter in neighborhoods near the Los
644 Angeles-Long Beach harbor, *Atmospheric Environment*, 42, 7317-7328, 2008.

645 Norris, G. A., Vedantham, R., Wade, K., Brown, S., Prouty, J., and Foley, C.: EPA positive
646 matrix factorization (PMF) 3.0 fundamentals & user guide. Prepared for the US
647 Environmental Protection Agency, Washington, DC, by the National Exposure Research
648 Laboratory, Research Triangle Park., 2008.

649 Ostro, B., Broadwin, R., Green, S., Feng, W.-Y., and Lipsett, M.: Fine Particulate Air Pollution
650 and Mortality in Nine California Counties: Results from CALFINE, *Environmental
651 Health Perspectives*, 114, 29-33, 2006.

652 Ostro, B., Feng, W.-Y., Broadwin, R., Green, S., and Lipsett, M.: The Effects of Components of
653 Fine Particulate Air Pollution on Mortality in California: Results from CALFINE,
654 *Environmental Health Perspectives*, 115, 13-19, 2007.

655 Ostro, B., Tobias, A., Querol, X., Alastuey, A., Amato, F., Pey, J., Pérez, N., and Sunyer, J.: The
656 Effects of Particulate Matter Sources on Daily Mortality: A Case-Crossover Study of
657 Barcelona, Spain, *Environmental health perspectives*, 119, 1781-1787, 2011.

658 Ostro, B., Malig, B., Broadwin, R., Basu, R., Gold, E. B., Bromberger, J. T., Derby, C.,
659 Feinstein, S., Greendale, G. A., Jackson, E. A., Kravitz, H. M., Matthews, K. A.,
660 Sternfeld, B., Tomey, K., Green, R. R., and Green, R.: Chronic PM_{2.5} exposure and
661 inflammation: Determining sensitive subgroups in mid-life women, *Environmental
662 Research*, 132, 168-175, 2014.

663 Özkaynak, H., and Thurston, G. D.: Associations Between 1980 U.S. Mortality Rates and
664 Alternative Measures of Airborne Particle Concentration, *Risk Analysis*, 7, 449-461,
665 1987.

666 Paatero, P., and Tapper, U.: Positive matrix factorization: A non-negative factor model with
667 optimal utilization of error estimates of data values, *Environmetrics*, 5, 111-126, 1994.

668 Paatero, P., Hopke, P. K., Song, X.-H., and Ramadan, Z.: Understanding and controlling
669 rotations in factor analytic models, *Chemometrics and Intelligent Laboratory Systems*,
670 60, 253-264, 2002.

671 Pant, P., and Harrison, R. M.: Estimation of the contribution of road traffic emissions to
672 particulate matter concentrations from field measurements: A review, *Atmospheric
673 Environment*, 77, 78-97, 2013.

674 Polissar, A. V., Hopke, P. K., Paatero, P., Malm, W. C., and Sisler, J. F.: Atmospheric aerosol
675 over Alaska: 2. Elemental composition and sources, *Journal of Geophysical Research:
676 Atmospheres*, 103, 19045-19057, 1998.

677 Reff, A., Eberly, S. I., and Bhave, P. V.: Receptor Modeling of Ambient Particulate Matter Data
678 Using Positive Matrix Factorization: Review of Existing Methods, *Journal of the Air &*
679 *Waste Management Association*, 57, 146-154, 2007.

680 Rohr, A. C., and Wyzga, R. E.: Attributing health effects to individual particulate matter
681 constituents, *Atmospheric Environment*, 62, 130-152, 2012.

682 RTI: Standard Operating Procedure for PM2.5 Anion Analysis. Research Triangle Park,NC.,
683 2009a.

684 RTI: Standard Operating Procedure for PM2.5 Cation Analysis. Research Triangle Park,NC.,
685 2009b.

686 RTI: Standard operating procedure for the X-ray fluorescence analysis of particulate matter
687 deposits on Teflon filters. Research Triangle Park,NC., 2009c.

688 Saffari, A., Daher, N., Shafer, M. M., Schauer, J. J., and Sioutas, C.: Seasonal and spatial
689 variation in reactive oxygen species activity of quasi-ultrafine particles (PM0.25) in the
690 Los Angeles metropolitan area and its association with chemical composition,
691 *Atmospheric Environment*, 79, 566-575, 2013.

692 Sardar, S. B., Fine, P. M., and Sioutas, C.: Seasonal and spatial variability of the size-resolved
693 chemical composition of particulate matter (PM10) in the Los Angeles Basin, *Journal of*
694 *Geophysical Research: Atmospheres*, 110 (D7), D07S08., 2005.

695 Sarnat, J. A., Marmur, A., Klein, M., Kim, E., Russell, A. G., Sarnat, S. E., Mulholland, J. A.,
696 Hopke, P. K., Tolbert, P. E., and others: Fine particle sources and cardiorespiratory
697 morbidity: an application of chemical mass balance and factor analytical source-
698 apportionment methods, *Environmental Health Perspectives*, 116, 2008.

699 Schauer, J. J., and Cass, G. R.: Source Apportionment of Wintertime Gas-Phase and Particle-
700 Phase Air Pollutants Using Organic Compounds as Tracers, *Environmental Science &*
701 *Technology*, 34, 1821-1832, 2000.

702 Shah, S. D., Cocker, D. R., Miller, J. W., and Norbeck, J. M.: Emission Rates of Particulate
703 Matter and Elemental and Organic Carbon from In-Use Diesel Engines, *Environmental*
704 *Science & Technology*, 38, 2544-2550, 2004.

705 Song, C. H., and Carmichael, G. R.: The aging process of naturally emitted aerosol (sea-salt and
706 mineral aerosol) during long range transport, *Atmospheric Environment*, 33, 2203-2218,
707 1999.

708 Stanek, L. W., Sacks, J. D., Dutton, S. J., and Dubois, J.-J. B.: Attributing health effects to
709 apportioned components and sources of particulate matter: An evaluation of collective
710 results, *Atmospheric Environment*, 45, 5655-5663, 2011.

711 Toledo, V. E., Júnior, P. B. d. A., Quiterio, S. L., Arbilla, G., Moreira, A., Escalera, V., and
712 Moreira, J. C.: Evaluation of levels, sources and distribution of toxic elements in PM10
713 in a suburban industrial region, Rio de Janeiro, Brazil, *Environmental Monitoring and*
714 *Assessment*, 139, 49-59, 2008.

715 von Schneidmesser, E., Stone, E. A., Quraishi, T. A., Shafer, M. M., and Schauer, J. J.: Toxic
716 metals in the atmosphere in Lahore, Pakistan, *Science of The Total Environment*, 408,
717 1640-1648, 2010.

718 Watson, J. G., Fujita, E. M., Chow, J. C., Zielinska, B., Richards, L. W., Neff, W., and Dietrich,
719 D.: Northern Front Range Air Quality Study. Final report. Prepared for Colorado State
720 University. Cooperative Institute for Research in the Atmosphere, Fort Collins, CO,
721 Desert Research Institute, Reno, NV., 1998.

722 Watson, J. G., Chow, J. C., Bowen, J. L., Lowenthal, D. H., Hering, S., Ouchida, P., and Oslund,
723 W.: Air quality measurements from the Fresno Supersite, *Journal of the Air & Waste*
724 *Management Association*, 50, 1321-1334, 2000.

725 Woodruff, T. J., Parker, J. D., and Schoendorf, K. C.: Fine Particulate Matter (PM_{2.5}) Air
726 Pollution and Selected Causes of Postneonatal Infant Mortality in California,
727 *Environmental Health Perspectives*, 114, 786-790, 2006.

728 Ying, Q., and Kleeman, M. J.: Source contributions to the regional distribution of secondary
729 particulate matter in California, *Atmospheric Environment*, 40, 736-752, 2006.

730 Ying, Q., and Kleeman, M.: Regional contributions to airborne particulate matter in central
731 California during a severe pollution episode, *Atmospheric Environment*, 43, 1218-1228,
732 2009.

733 Ying, Q.: Physical and chemical processes of wintertime secondary nitrate aerosol formation,
734 *Frontiers of Environmental Science & Engineering in China*, 5, 348-361, 2011.

735 Zhang, H., DeNero, S. P., Joe, D. K., Lee, H. H., Chen, S. H., Michalakes, J., and Kleeman, M.
736 J.: Development of a source oriented version of the WRF/Chem model and its
737 application to the California regional PM₁₀ / PM_{2.5} air quality study, *Atmos. Chem.*
738 *Phys.*, 14, 485-503, 2014.

739 Zhang, Y., Schauer, J. J., Shafer, M. M., Hannigan, M. P., and Dutton, S. J.: Source
740 Apportionment of in Vitro Reactive Oxygen Species Bioassay Activity from
741 Atmospheric Particulate Matter, *Environmental Science & Technology*, 42, 7502-7509,
742 2008.

743 Zhao, Z., Chen, S.-H., Kleeman, M. J., Tyree, M., and Cayan, D.: The impact of climate change
744 on air quality-related meteorological conditions in California. Part I: present time
745 simulation analysis, *Journal of Climate*, 24, 3344-3361, 2011.

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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

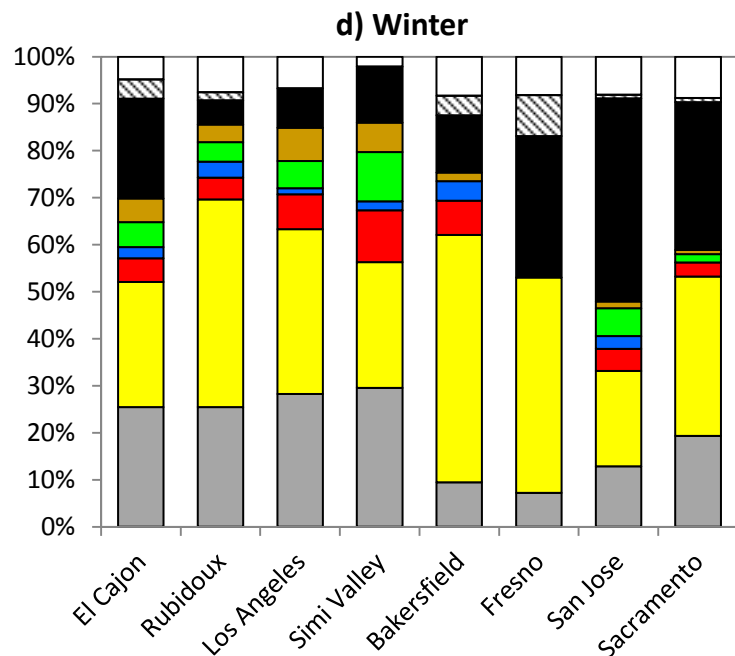
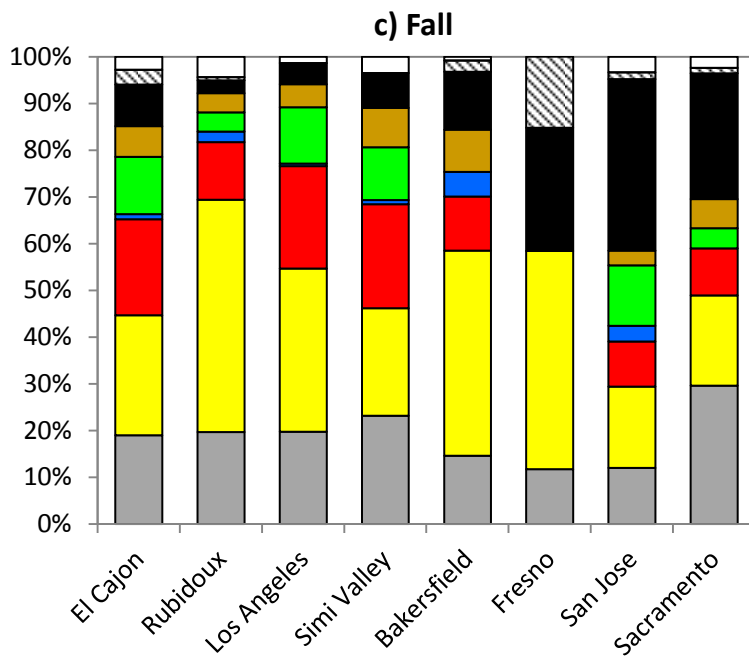
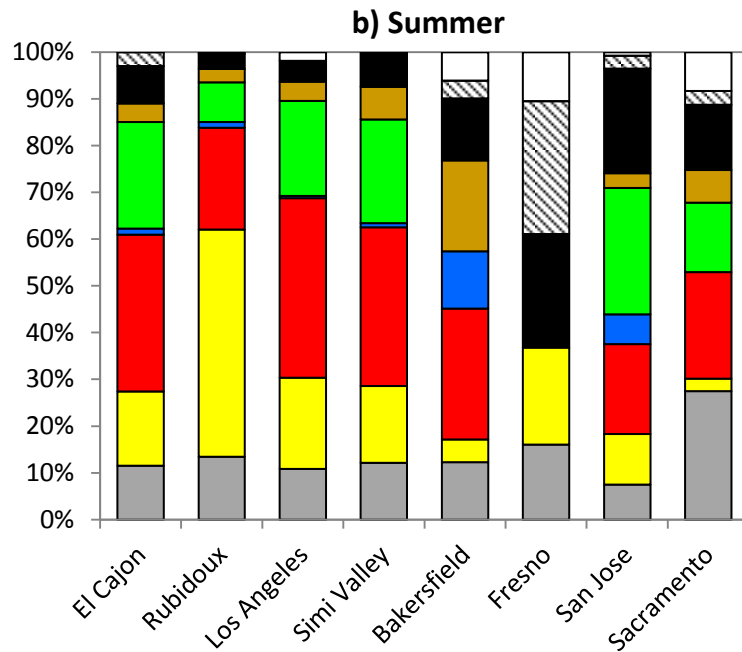
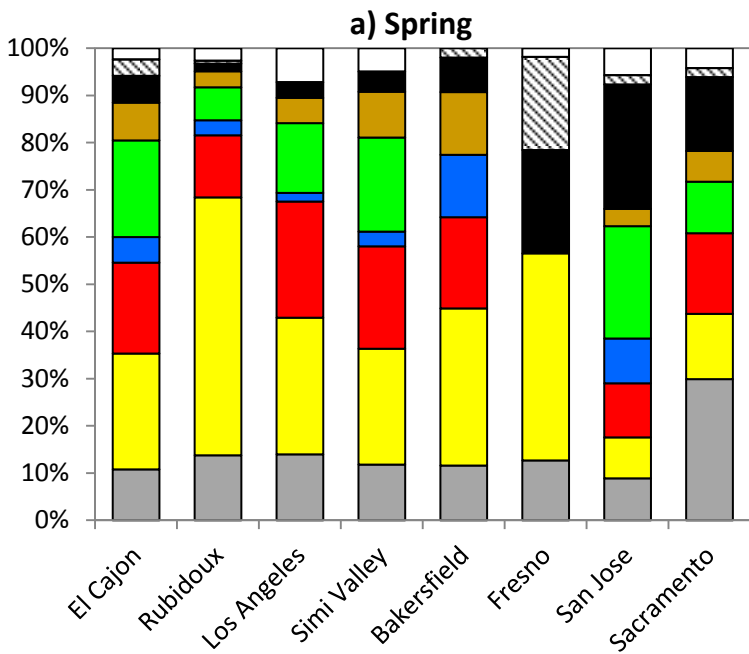
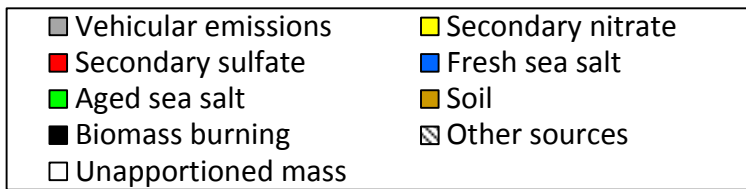


Figure 1 a-d. Seasonal variation in the percent contribution of identified sources to ambient $PM_{2.5}$, by site.

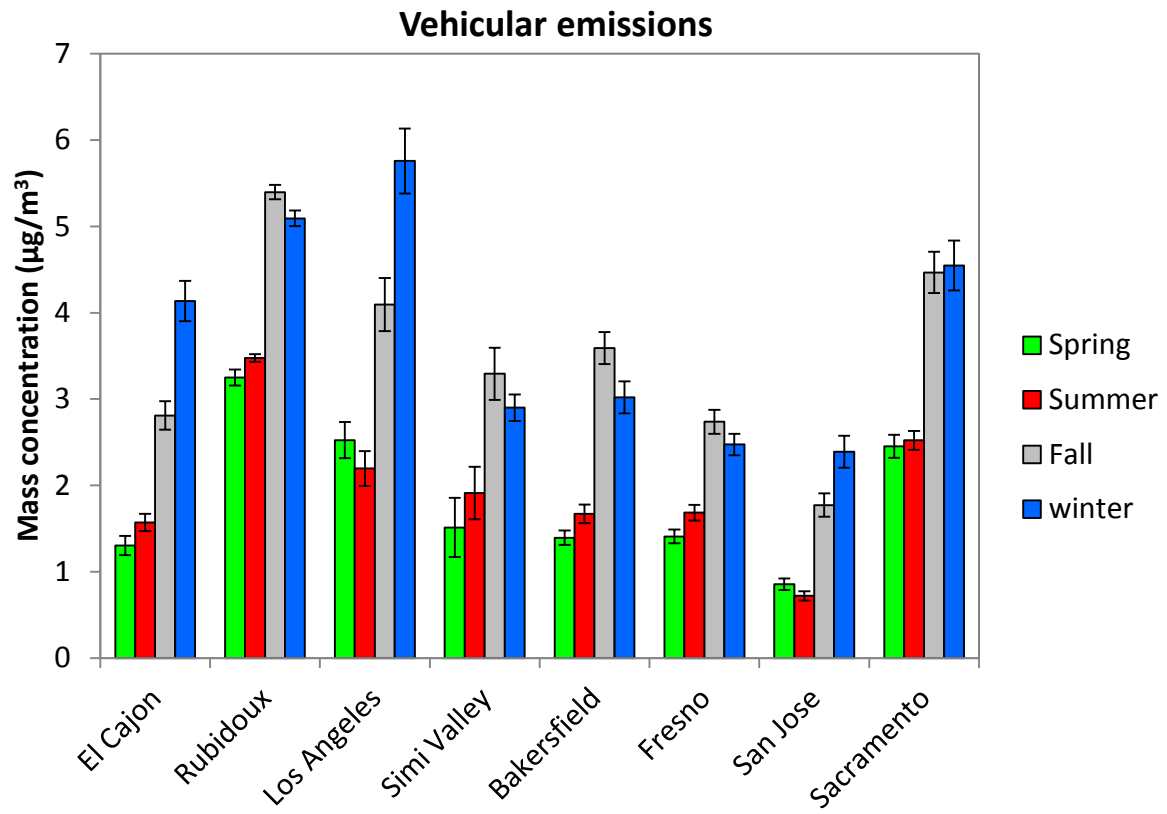


Figure 2. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of vehicular emissions to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

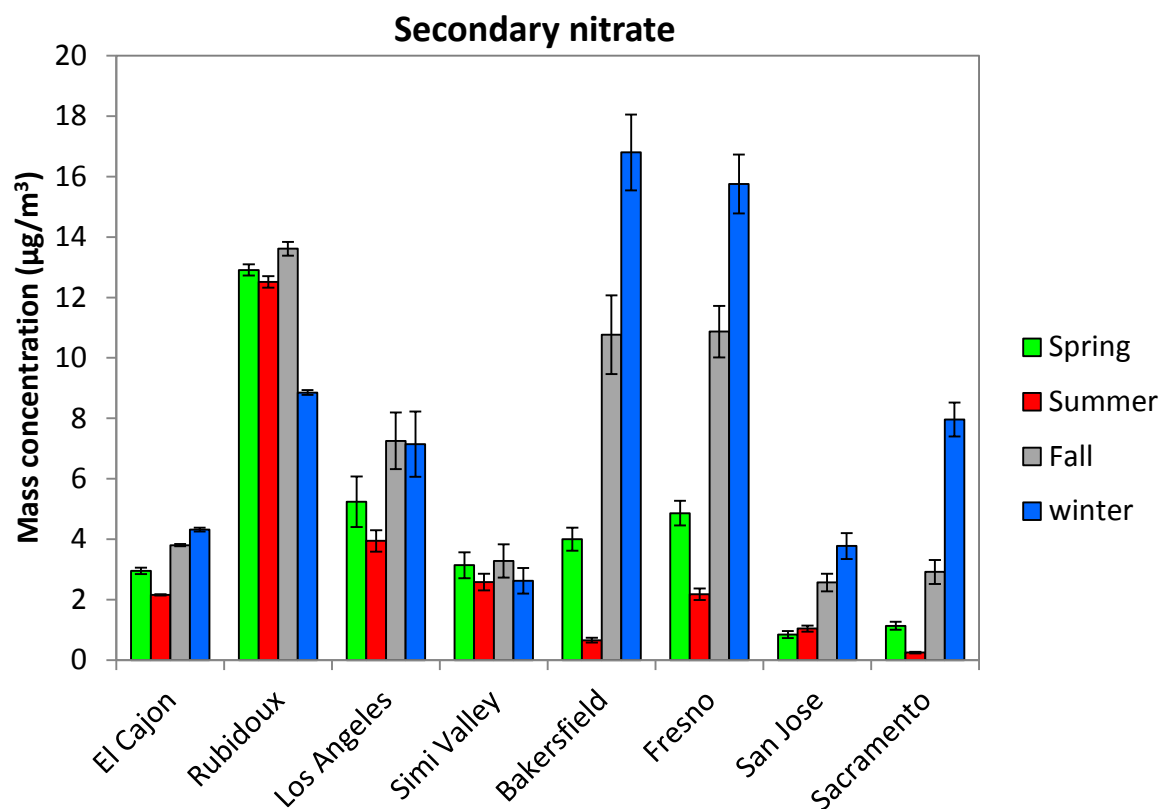


Figure 3. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of secondary ammonium nitrate to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

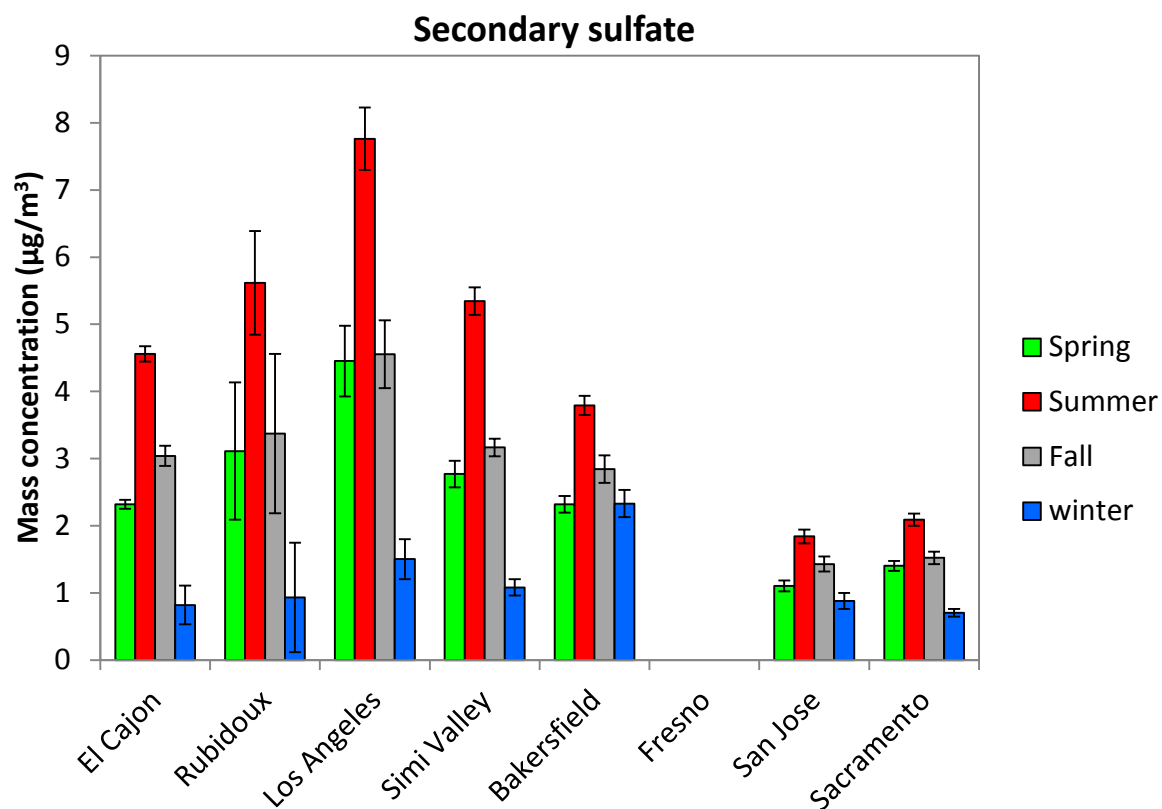


Figure 4. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of secondary ammonium sulfate to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

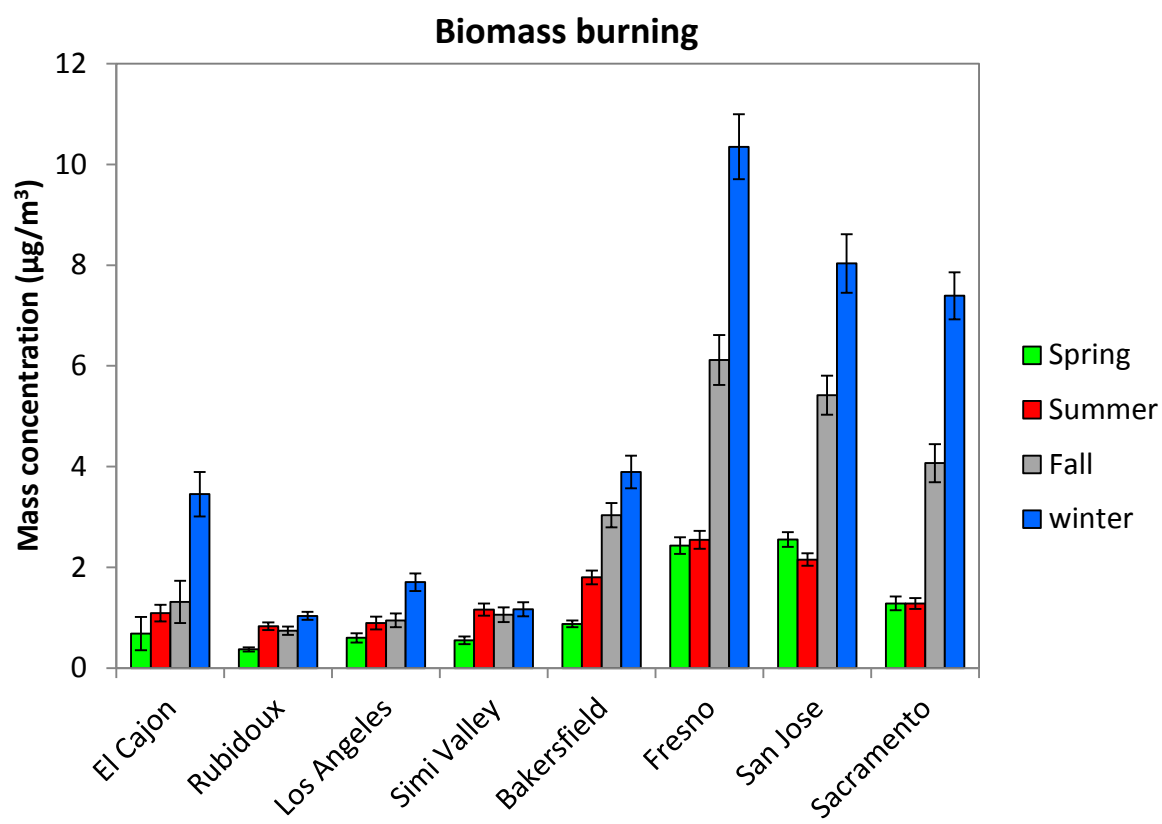


Figure 5. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of biomass burning to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

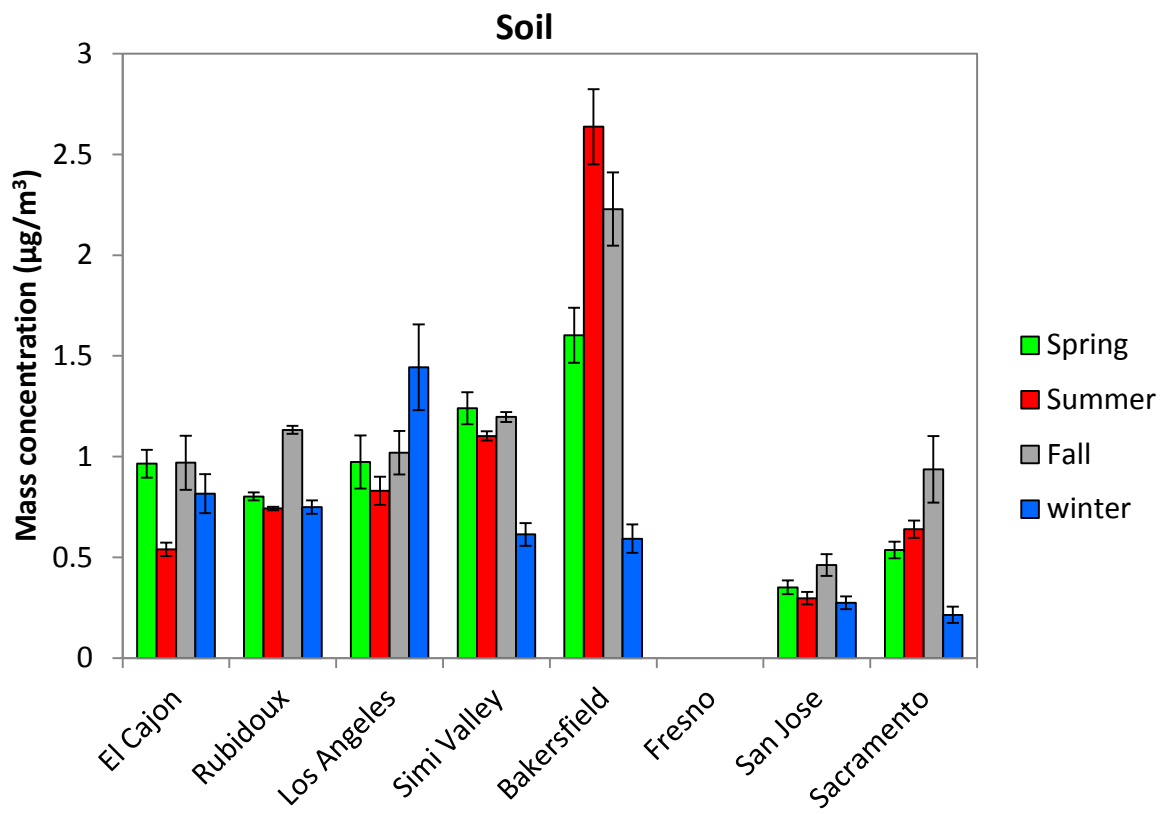


Figure 6. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of soil to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

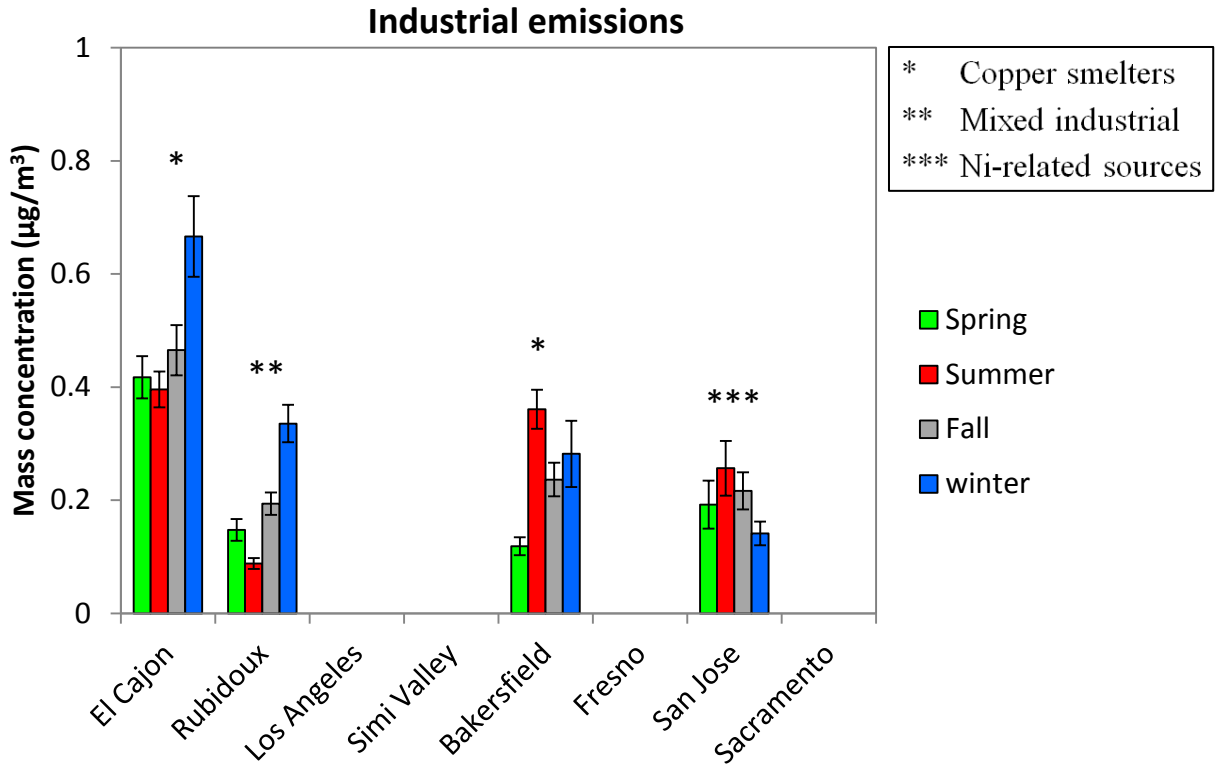


Figure 7. Seasonal average source contribution ($\mu\text{g}/\text{m}^3$) of industrial emissions to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.

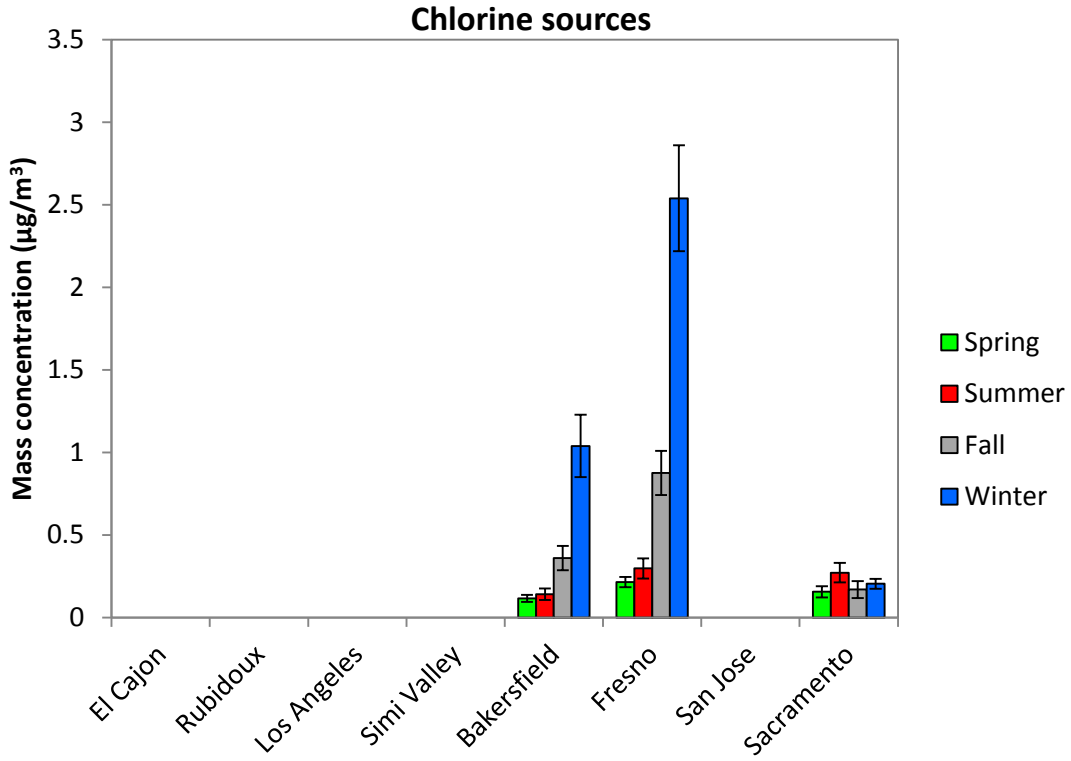


Figure 8. Seasonal average contribution ($\mu\text{g}/\text{m}^3$) of chlorine sources to ambient $\text{PM}_{2.5}$, by site. Error bars correspond to one standard error.