

1 **A Regional Assessment of Marine Vessel PM_{2.5} Impacts in the U.S. Pacific Northwest Using a**
2 **Receptor Based Source Apportionment Method**

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8

9 **Abstract**

10 This work reports the results of a regional receptor-based source apportionment analysis using the
11 Positive Matrix Factorization (PMF) model on chemically speciated PM_{2.5} data from 36 urban and rural
12 monitoring sites within the U.S. Pacific Northwest. The approach taken is to model each site
13 independently, to treat monitor datasets with a common data handling and preparation protocol, and to
14 use a common modeling protocol. Complementary data from two monitoring networks, the urban
15 Chemical Speciation Network (CSN) and the rural Interagency Monitoring of Protected Visual
16 Environments (IMPROVE) Network, was modeled for the period of 2007-2011. 15 different factor types
17 were found for CSN network sites and 17 for IMPROVE network sites, however many factors occurred at
18 only a few locations. Only 3 factor types were common in both networks: sulfate/sulfur rich, nitrate rich,
19 and soil. However, for coastal and near coastal monitoring sites, there were three additional factors
20 common to both CSN and IMPROVE sites: sea salt, aged sea salt, and residual fuel oil combustion
21 (RFO). This work presents annual average PM_{2.5} mass impacts for all sites and factors found and the
22 results for RFO are explored in greater depth. The results for RFO are linked to marine vessel emissions
23 based on similarities between factor chemical profiles and published emissions profiles, comparisons with
24 emissions inventories, and the similarity in the spatial extent of RFO factor locations to that of the other
25 marine aerosols found in this study, sea salt and aged sea salt. All 14 monitoring sites with marine vessel
26 RFO factors showed a seasonal cycle of mass impacts, with lower impacts in winter months (monthly
27 average PM_{2.5} between 0.1 µg/m³ – 0.9 µg/m³ in January) and higher impacts in summer months (monthly
28 average PM_{2.5} between 0.3 µg/m³ – 2.7 µg/m³ in August). These results set a baseline to measure
29 progress in emissions reductions that are expected from implementation of the North American Emissions
30 Control Area (ECA) beginning in August 2012.

31 **1. Introduction**

32 Human health studies have shown that there is a relationship between exposure to fine particulate
33 matter (PM_{2.5}, particles with an aerodynamic diameter <2.5 µm) and adverse health effects such as

34 cardiovascular and pulmonary disease (Künzli et al., 2005), lung cancer and premature mortality (Pope
35 and Dockery, 2006). The preponderance of health studies has also shown that there is no PM exposure
36 threshold below which adverse health effects do not occur (Pope and Dockery, 2006), which suggests that
37 anthropogenic PM impacts should be of concern even in areas currently meeting national ambient air
38 quality standards. In addition to human health effects, deposition of anthropogenic PM has also been
39 linked to adverse effects on ecosystem health (Geiser et al., 2010).

40 $PM_{2.5}$ emissions from oceangoing marine vessels has been an active area of investigation because
41 these sources typically burn residual fuel oil (RFO), which has a very high sulfur content, produces large
42 amounts of $PM_{2.5}$, SO_2 , and NO_x (Moldanova et al., 2009), and these vessels are mobile sources that can
43 impact urban areas as well as rural and remote coastal areas that have few other direct sources of
44 anthropogenic emissions. Health studies targeted at seafarers have shown an increased rate of cancer
45 incidence depending on their length of time employed (Kaerlev et al., 2005), while globally among the
46 general population marine vessel emissions have been estimated to cause approximately 60,000
47 cardiopulmonary and lung cancer deaths annually (Corbett et al., 2007). Regulating the fuel sulfur
48 content of marine vessel fuels is a common approach to reducing emissions. Winebrake et al. (2009)
49 have shown that significant reductions in premature mortality from marine vessel emissions can be
50 achieved by regulating fuel sulfur content at amounts lower than the assumed average uncontrolled fuel
51 sulfur content of 2.7%.

52 Concerns over the health and ecological effects of marine vessel emissions led the United States
53 (U.S.) and Canadian governments in 2009 to propose to the International Maritime Organization (IMO)
54 the inclusion of North America in an Emissions Control Area (ECA). In March of 2010 the IMO
55 amended the International Convention for the Prevention of Pollution from Ships (MARPOL) to
56 designate specific portions of North American waters as an ECA (EPA, 2010). Beginning in August
57 2012, the ECA requires marine vessels within 200 nautical miles of North American coasts to use fuels
58 with sulfur content no higher than 10,000 ppm (1%) and worldwide no higher than 35,000 ppm (3.5%).

59 Starting in 2015, the ECA will require marine vessels within 200 nautical miles of North American coasts
60 to use fuels with sulfur content no higher than 1,000 ppm (0.1%).

61 ECA controls on fuel sulfur content are expected to significantly reduce marine vessel emissions.
62 Analysis of environmental aerosol data in coastal regions using receptor-based source apportionment
63 techniques has often been able to identify the impacts of marine vessels burning RFO due to high sulfur
64 and significant Ni and V trace metal content in their emissions (Agrawal et al., 2008). Previous source
65 apportionment studies in the U.S. Pacific Northwest have identified marine vessel RFO impacts at several
66 urban and rural locations (Maykut et al., 2003; Wu et al., 2007; Kim and Hopke, 2008a; Kim and Hopke,
67 2008b). Recent studies in Los Angeles (Minguillon et al., 2008) and the Netherlands (Mooibroek et al.,
68 2011) have used receptor-based techniques to analyze data from multiple monitoring sites and explored
69 the spatial extent and magnitude of marine vessel impacts, however, the number of sites analyzed in these
70 studies has been relatively small and within the same airshed.

71 Multi-site receptor-based studies have approached the source apportionment task by either grouping
72 the data together into one large dataset or analyzing the data from each site independently. When
73 monitoring sites share a common airshed and are expected to share the same aerosol sources, combining
74 the data from multiple sites can be an efficient approach that also increases the sample size, which can be
75 important for receptor models like Positive Matrix Factorization (PMF). However, if there is no
76 expectation of common aerosol sources, then combining data from multiple sites could lead to the
77 misidentification of source contributions at sites where they, in reality, do not contribute.

78 A regional assessment of aerosol source impacts is often addressed using source-oriented methods
79 like photochemical grid modeling that predict source impacts from emissions inventories, emissions
80 modeling, meteorological simulations, and a chemical transport model (Wagstrom et al., 2008). While
81 there are clear benefits to source-oriented methods, the results of such approaches are limited by
82 uncertainties in emissions, errors and biases in meteorological simulations, grid resolution, and
83 uncertainties and simplifications in the representation of atmospheric chemistry.

84 A regional assessment using receptor-based methods might be assembled from existing published
85 receptor modeling studies. However, while there are many of these studies, most report results for only a
86 single monitoring site or only a few sites, cover different time periods, and for many monitors there are no
87 published results. Also, when approaching a receptor-based source apportionment analysis there are
88 many decisions that need to be made with regards to data preparation and processing, which model to
89 choose, what modeling protocol to follow, and how to interpret results (Reff et al., 2007). Differences in
90 these choices between researchers can make it difficult to compare results between studies.

91 In this work a regional receptor-based source apportionment analysis is performed using the PMF
92 model on chemically speciated PM_{2.5} data from 36 sites within the U.S. Pacific Northwest. The approach
93 taken here is to model each site independently, to treat data from all sites with a common data handling
94 and preparation protocol, and to use a consistent modeling protocol. The benefits of this approach are
95 that results between sites are as comparable as possible since site-to-site data and modeling have
96 undergone the same treatments. Annual average results are presented for all sites and source factors and
97 the results for RFO from marine vessels are explored in more depth. Marine vessel emissions are perhaps
98 well suited to this approach because of their relatively unique chemical signature, they are a large regional
99 source, and are a mobile source with a wide geographic extent. The results presented here for marine
100 vessel impacts are timely because they cover data for a time period just prior to implementation of the
101 North American ECA, and therefore provide a baseline of source impacts from which ‘on the ground’
102 progress in emissions reductions can be assessed.

103 **2. Methods**

104 **2.1. PM_{2.5} Chemical Speciation Data**

105 Two monitoring networks in the U.S. Pacific Northwest routinely collect chemically speciated 24-
106 hour integrated PM_{2.5} mass: the Chemical Speciation Network (CSN) and the Interagency Monitoring of
107 Protected Visual Environments (IMPROVE) Network. The CSN is one of a number of urban and
108 suburban monitoring networks funded by the U.S. Environmental Protection Agency (EPA) and operated

109 by state and local agencies. CSN samplers are operated on a daily, once every third day, or once every
110 sixth day schedule depending on the site. Quality assured CSN data are housed in the EPA Air Quality
111 System (AQS) database. Detailed information about the CSN monitoring network and AQS database can
112 be found on the Technology Transfer Network, Ambient Monitoring Technology Information Center
113 section of EPA's web site (<http://www.epa.gov/ttn/amtic/>). The IMPROVE network is a chemically
114 speciated PM_{2.5} monitoring program associated with the Regional Haze Rule of the U.S. Clean Air Act,
115 which calls for state and federal agencies to work together to improve visibility in 156 national parks and
116 wilderness areas. IMPROVE samplers are typically sited at remote locations and are operated on a once
117 every third day schedule. Quality assured IMPROVE data are housed in a database that is part of The
118 Visibility Information Exchange Web System (VIEWS). Detailed information about the IMPROVE
119 monitoring network and VIEWS can be found on the IMPROVE network web site
120 (<http://vista.cira.colostate.edu/improve/>). While measurement and analytical techniques used to quantify
121 aerosol ionic and elemental concentrations are comparable between the two networks (Chen et al., 2010),
122 elemental and organic carbon data from these two networks has historically been difficult to compare
123 because of differences in carbon sampler design and analytical measurement protocols (Chow et al.,
124 2004). To address this problem and better harmonize the two monitoring networks, EPA conducted a
125 phased change out of all CSN carbon samplers between 2007 – 2009 to match those of the IMPROVE
126 program and also switched to IMPROVE-based carbon analytical measurement protocols at the same
127 time (EPA, 2009).

128 Information about the monitoring sites analyzed in this work is listed in Tables 1 and 2, for CSN
129 and IMPROVE sites, respectively, and also shown in Figure 1. The start date for data used from the
130 CSN monitors was based on when each site made the conversion to IMPROVE-based carbon sampling
131 methods and the start date for IMPROVE monitors was the beginning of 2007. The end date for both
132 networks represents the most recent data available at the time data were extracted. The date range for
133 data used in both monitoring networks was chosen to maximize both the total amount of available

134 samples from each monitor and to cover the broadest period of temporal overlap after the change in CSN
135 carbon sampler methods.

136 **2.2. Data Preparation and Treatment**

137 Prior to source apportionment analysis, the datasets were processed to correct for field blanks,
138 missing/negative values, data completeness issues, poor signal-to-noise (S/N) ratios, and species double
139 counting. The uncertainty of each reported measurement was also estimated.

140 **2.2.1. Blank Correction**

141 Analytical data from CSN monitors in the AQS database is not blank corrected, but sample blank
142 data are available. Field blanks were collected less frequently than the monitoring frequency, so many
143 samples did not have an associated field blank. For samples with coincident field blanks, the measured
144 blank concentration was subtracted from the reported concentration. For samples without coincident
145 blanks, the median value from the previous three blanks was used as an estimate for blank correction.
146 Analytical data from IMPROVE monitors in VIEWS is already blank corrected.

147 **2.2.2. Uncertainty Estimates**

148 For both CSN and IMPROVE monitors, most reported measurements also list the analytical
149 uncertainty. The overall measurement uncertainty was estimated from a combination of the analytical
150 uncertainty and the method detection limit (MDL). The uncertainty of measurements reported below the
151 MDL were set to either $5/6 * MDL$ or the reported uncertainty, whichever was larger. The uncertainty of
152 measurements above the MDL were set to the measured analytical uncertainty plus $1/3 * MDL$ (Reff et al.,
153 2007). If uncertainties were unavailable for a chemical species, the uncertainties were estimated based on
154 Kim et al. (2005).

155 **2.2.3. Treatment of Missing Data**

156 If the total $PM_{2.5}$ mass of a sample was missing or if an entire analytical channel was missing (e.g.,
157 carbon data, ions, metals), the sample was removed from the modeling dataset. In instances where

158 individual chemical species were missing, the missing observations were replaced with the species
159 median concentration and the uncertainty set to a very high value compared to measured data. Typically,
160 the uncertainty was set to four times the species median concentration to minimize the influence of the
161 replaced data on the model solution.

162 **2.2.4. Treatment of Negative Values**

163 The source apportionment model used in this analysis does not allow negative data, which can
164 sometimes be reported if species concentrations are close to zero. In these cases, the measured
165 concentration was reset to zero.

166 **2.2.5. Treatment of Chemical Species with Poor Data Completeness.**

167 Chemical species were removed from the modeling dataset if more than 50% of the samples had
168 missing data. Chemical species retained in the modeling datasets for IMPROVE monitors generally had
169 at or near 100% data completeness. Most chemical species retained in the modeling datasets for CSN
170 monitors had over 90% data completeness and many had 100% data completeness.

171 **2.2.6. Treatment of Data with low Signal-to-Noise Ratios**

172 Using data with excessive noise has been found to negatively impact that quality of receptor
173 modeling results (Paatero and Hopke, 2003). The signal-to-noise (S/N) ratio analysis proposed by
174 Paatero and Hopke is now often used to screen data for this problem (Reff et al., 2007).

175 In this study, chemical species were discarded from the CSN and IMPROVE datasets when $S/N <$
176 0.3 and $S/N < 0.2$, respectively. Removal of species with $S/N < 0.2$ was the S/N limit suggested by
177 Paatero and Hopke (2003), so was the default in this analysis. For the CSN datasets the limit was
178 increased to 0.3 to remove many trace level chemical species that were both not reported in the
179 IMPROVE datasets and not typically associated with known anthropogenic pollution sources. Examples
180 of trace level chemical species removed from CSN datasets because of this increased S/N limit are La,
181 Tb, Y, Nb, Hg, Eu, Ta, Ir, Au, Sc, Mo, and W.

182 **2.2.7. Removal or Adjustment of Chemical Species to Avoid Double Counting**

183 To avoid overweighting the influence of duplicate chemical species in the model results, one of the
184 duplicate species was removed or adjusted to avoid double counting. In both CSN and IMPROVE
185 datasets, the reported OP concentration is also a portion of the reported EC1 concentration. To account
186 for this, EC1 was recalculated as EC1-OP. In the CSN datasets, SO_4^{2-} , Na^+ , K^+ , and OP measured via the
187 Thermal Optical Transmittance (TOT) method were discarded and S, Na, K, and OP measured via the
188 Thermal Optical Reflectance (TOR) method retained. In the IMPROVE datasets, S and Cl^- were
189 discarded and SO_4^{2-} and Cl retained. The chemical species retained were generally chosen based on
190 higher data completeness and S/N ratio. Exceptions were that OP via TOR was selected in the CSN
191 datasets because this is the methodology that matches the IMPROVE method and SO_4^{2-} was selected over
192 S in the IMPROVE data because of a data advisory related to IMPROVE XRF-based sulfur data (White,
193 2009). Sulfur and SO_4^{2-} were well correlated in CSN datasets (average $r^2 = 0.88$), so the selection of S
194 instead of SO_4^{2-} in CSN network sites is not expected to adversely affect the comparability of source
195 apportionment results between the two networks.

196 **2.2.8. Other Data Treatments**

197 Measurements on July 4 and July 5 were removed from both network datasets to mitigate the
198 impact of fireworks on the source apportionment results.

199 **2.3. Source Apportionment**

200 PMF source apportionment modeling was performed using EPA PMF 3.0 (Norris et al., 2008). A
201 thorough discussion of the mathematical equations underlying EPA PMF can be found in Paatero &
202 Hopke (2003) and Norris et al. (2008). Data from each CSN and IMPROVE monitoring site was
203 modeled independently. In each case, the model was run in the robust mode using a non-random seed
204 value of 10 (so that results were reproducible) and 20 repeat runs to insure the model least-squares
205 solution represented a global rather than local minimum. The rotational FPEAK variable was held at the

206 default value of 0.0. The model solution with the optimum number of factors was determined somewhat
207 subjectively based on inspection of the factors in each solution, but also from the quality of the least-
208 squares fit (analysis of Q_{Robust} and Q_{True} values) in the model output. The scaled residuals for final model
209 solutions were generally normally distributed, falling into the recommended range of +3 to -3.

210 **3. Results and Discussion**

211 **3.1. Source Apportionment Results**

212 Tables 3 and 4 list the number of PMF factors determined for each monitoring site for CSN and
213 IMPROVE monitors, respectively, as well as factor names, annual average mass attribution for each
214 factor, and annual average measured $\text{PM}_{2.5}$. The annual averages presented in Tables 3 and 4 represent
215 multiyear averages based on the date range of data presented in Tables 1 and 2, respectively. Because
216 some sites had an uneven distribution of samples throughout the annual cycle, monthly average mass
217 attributions were computed and the annual average was calculated from the 12 monthly averages. A
218 description of factors and the rationale for factor names are described in the supplementary materials.

219 While the focus of this work is the RFO factor results and the connection to marine vessels, it is
220 worth briefly discussing some of the similarities and differences between PMF results for the CSN and
221 IMPROVE sites as a whole as well as comparing these results to those of other published studies. Tables
222 3 and 4 show that there were 15 different factor types found for CSN network sites and 17 different factor
223 types for IMPROVE network sites. This may seem counterintuitive because factors are usually related to
224 pollution sources and one would expect, conceptually, a larger variety of sources to impact urban sites
225 than the rural/remote sites. However, many factors in both networks occur at only a few locations and six
226 IMPROVE factors are various mixtures of sulfate, nitrate, OC, EC, and/or soil. If one considers the
227 number of factor types that commonly occur at CSN and IMPROVE sites, there are eight factor types that
228 occur at more than 50% of CSN sites and only five factor types that occur at more than 50% of
229 IMPROVE sites.

230 Between the two networks, there were nine factor types that had similar enough chemical profiles
231 to be given the same factor names in both the CSN and IMPROVE results (see supplementary materials).
232 Of these nine factor types, only three were commonly found at both CSN and IMPROVE sites throughout
233 the U.S. Pacific Northwest: sulfate/sulfur rich, nitrate rich, and soil. However, for coastal and near
234 coastal monitoring sites (sites west of the Cascade Mountain range), there were three additional factors
235 common to both CSN and IMPROVE sites: sea salt, aged sea salt, and RFO. RFO appears to be the only
236 factor commonly found at both CSN and IMPROVE monitoring locations in the U.S. Pacific Northwest
237 that can be clearly linked to a particular source of pollution, that is, marine vessels (see Section 3.2).

238 Previous studies have reported aerosol source apportionment results from data collected at some of
239 the monitoring locations also analyzed in this study. Source apportionment results for Seattle's Beacon
240 Hill monitoring site have been previously reported in a number of published studies. Maykut et al. (2003)
241 reported an 8 factor solution using PMF and found an average RFO contribution of $0.9 \mu\text{g}/\text{m}^3$ for data
242 from the period 1997 – 1999, Kim and Hopke (2008a) reported a 10 factor solution using PMF and found
243 an average RFO contribution of $0.47 \mu\text{g}/\text{m}^3$ for data from the period 2000 – 2005, and Wu et al. (2008)
244 reported a 10 factor solution using ME2 and found an average RFO contribution of $0.78 \mu\text{g}/\text{m}^3$ for data
245 from the period 2000 – 2004. In this work, RFO was found to contribute an average of $1.0 \mu\text{g}/\text{m}^3$ at the
246 Beacon Hill site for the period of 2007 – 2011. While the average mass contribution of RFO for the
247 Seattle Beacon Hill site is higher in this work than in previous studies, marine vessel activity data from
248 the Port of Seattle indicates that the number of annual vessel calls at the Port have increased an average of
249 39% from the periods of 2002 – 2005 to 2007 – 2011 and total tonnage of shipping has increased an
250 average of 29% for the same periods (Port of Seattle, 2012). The reported increase in vessel activity is
251 consistent with the increased RFO contribution found in this work.

252 Source apportionment results for the Seattle Duwamish monitoring site were reported by Kim and
253 Hopke (2008a) for data covering the period of 2000 – 2005. They reported 11 PMF factors and found an
254 average RFO contribution of $0.44 \mu\text{g}/\text{m}^3$. In this work, RFO was found to contribute an average of 1.1

255 $\mu\text{g}/\text{m}^3$ at the Duwamish site for the period of 2007 – 2011. The higher RFO contribution reported in this
256 work, over that of Kim and Hopke, can be partially explained by the increased port activity reported
257 above. Additionally, the slightly higher RFO impacts at the Duwamish site over the Beacon Hill site
258 reported in this work are consistent with the Duwamish site being both closer to Port of Seattle facilities
259 and sited in the Duwamish valley, nearer the same elevation as the Port, compared to the Beacon Hill site.

260 Kim and Hopke (2008b) reported PMF source apportionment results for the Olympic IMPROVE
261 monitoring site using data from 2001 – 2004. They report finding 8 factors, with RFO (oil combustion, in
262 that work) contributing an average of $0.50 \mu\text{g}/\text{m}^3$ to total $\text{PM}_{2.5}$. In this work, RFO was found to
263 contribute an average of $0.2 \mu\text{g}/\text{m}^3$ at the Olympic site for the period from 2007 – 2010. The smaller
264 attribution of RFO mass in this work for the more recent period, compared to Kim and Hopke, is
265 inconsistent with the previously discussed marine vessel port call data reported by the Port of Seattle as
266 well as annual total waterborne shipping tonnage data for Washington State (U.S. Corps of Engineers,
267 2012), which indicates that total tonnage shipped has increased 8.2% in Washington from the periods of
268 2001 – 2004 to 2007 – 2010. The discrepancy in results between this work and Kim and Hopke for the
269 Olympic site is not well understood.

270 Source apportionment results for the Portland Oregon CSN monitoring site were reported by Kim
271 and Hopke (2008b) for data covering the period of 2002 – 2005. They reported 10 PMF factors and, like
272 in this work, did not identify a factor related to RFO.

273 Hwang and Hopke (2007) reported PMF source apportionment results for the Kalmiopsis
274 IMPROVE site in southwestern Oregon. In that work they used data from 2000 – 2004 and found 9
275 factors, but did not identify a RFO factor. In this work RFO was found to contribute an annual average of
276 $0.7 \mu\text{g}/\text{m}^3$ to total $\text{PM}_{2.5}$ for the 2007 – 2010 period. The difference between Hwang and Hopke and this
277 work likely stems from differing interpretations of the source of the high sulfate factor. Hwang and
278 Hopke labeled their high sulfate factor secondary sulfate, but did not attribute that to RFO sources as in
279 this work.

280 **3.2. Results for RFO and Linkage to Marine Vessels**

281 **3.2.1. PMF Results for RFO and Comparison with Source Test Data**

282 Chemically speciated source profiles for primary PM_{2.5} emissions for a wide range of sources are
283 available through the EPA Speciate database Version 4.3 (Hsu and Divita, 2011). The Speciate database
284 has two emissions profiles for marine vessels using RFO, profile numbers 5676 and 5674. The V:Ni ratio
285 in these profiles is 2.6 and 2.3, the weight percent of the sum of V and Ni in the profiles is 2.5% and
286 2.2%, and the weight percent of sulfate in these profiles is 44% and 38%, respectively. Additionally, a
287 V:Ni ratio of 4.5 was reported by Agrawal et al. (2008) for marine vessels using RFO. While not
288 reported in the Speciate database, marine vessels using RFO also emit large amount of SO₂ due to the
289 very high fuel sulfur content (Agrawal et al., 2008; Moldanova et al., 2009). Downwind of marine vessel
290 emissions, it is expected that the ratio of V:Ni will be maintained but the absolute concentration of
291 sulfate, V, and Ni associated with this source may shift as SO₂ and other co-emitted gases undergo
292 photochemistry and gas-to-particle conversion.

293 Of the 36 sites analyzed in this study, 14 sites had factors that matched the chemical signature of
294 RFO. RFO factors were identified based on high sulfur content in the chemical profile, attribution of a
295 significant percentage of measured V and Ni to the factor, and a V:Ni ratio near that reported for RFO.
296 Figures 2 and 3 show the RFO PMF factor chemical profiles from CSN and IMPROVE sites,
297 respectively. The ratio of V:Ni in these factors ranged from 2.4 – 3.9 for CSN sites and 2.3 – 5.4 for
298 IMPROVE sites and had an average value of 3.0 and 3.2 for CSN and IMPROVE sites, respectively. A
299 map indicating the location of sites where RFO factors were found is shown in Figure 4.

300 **3.2.2. Comparison with 2008 Emissions Inventories**

301 In April of 2012 EPA published Version 2 of its 2008 National Emissions Inventory (NEI). The
302 NEI is a comprehensive and detailed county, state, and nationwide estimate of emissions for a wide range
303 of air pollutants and is prepared every three years by EPA in collaboration with State, Local, and Tribal
304 air agencies (U.S. EPA, 2012). Of particular interest for this study is that the 2008 NEI includes

305 estimates of primary particulate Ni emissions and SO₂ gaseous emissions (primary particulate V and
306 sulfate are not reported). 2008 NEI data indicate that Washington, Oregon and Idaho emitted 30017 lbs,
307 5617 lbs, and 1933 lbs of Ni, respectively. Of those statewide totals, commercial marine vessels
308 contributed 86% (25901 lbs), 55% (3107 lbs), and 0% (0 lbs), respectively. Similarly for SO₂, 2008 NEI
309 data indicate that Washington, Oregon and Idaho emitted 36902 tons, 26697 tons, and 20654 tons,
310 respectively. Of those statewide totals, commercial marine vessels contributed 38% (14094 tons), 6%
311 (1682 tons), and 0% (0 tons), respectively. The NEI data for both Ni and SO₂ indicate that in 2008
312 commercial marine vessel emissions were approximately an order of magnitude larger in Washington
313 State compared to Oregon, and nonexistent in Idaho. Additionally, on the county level, the majority of
314 commercial marine vessel emissions in Washington State are attributed to counties bordering the Puget
315 Sound, Strait of Juan de Fuca, and Strait of Georgia and for Oregon are mostly attributed to counties
316 bordering the Columbia River. This indicates that both the relative magnitude and spatial allocation of
317 commercial marine vessel emissions in the 2008 NEI is consistent with the number and location of
318 monitoring sites where PMF factors for RFO were found in Washington and Oregon (Figure 4).

319 Smaller sources of Ni in the 2008 NEI inventories for Washington State are oil fired industrial
320 boilers (1806 lbs, 6%) and petroleum refinery operations (546 lbs, 2%). The V:Ni ratio in the Speciate
321 emissions profiles for oil fired boilers range from 0.2 to 0.7 and the V:Ni ratio for petroleum refinery
322 operations is 1.6. Given these V:Ni ratios and the relatively small contribution to total Washington State
323 Ni emissions, it is unlikely that these sources significantly contribute to the PMF factors identified as
324 RFO.

325 Smaller sources of Ni in the 2008 NEI inventories for Oregon are coal fired electrical generation
326 (1113 lbs, 20%) and non-ferrous metal industrial processes (500 lbs, 9%). Oregon had one coal fired
327 power plant in operation from 2007 – 2011, the Portland General Electric plant in Boardman Oregon.
328 The Speciate database lists 5 emissions profiles from coal fired power plants using the same emissions
329 control technology as the Boardman plant. The V:Ni emissions ratio in these emissions profiles ranged

330 from 1.6 – 3.6, with an average value of 2.2. While these V:Ni ratios are similar to that of RFO, it is
331 unlikely that the Boardman plant is contributing to the factors identified as RFO because of its location.
332 Boardman Oregon lies along the Columbia river approximately 100 km east of the CORI IMPROVE
333 monitor and 200 km east of the COGO IMPROVE monitor (both CORI and COGO are also along the
334 Columbia river). However, no RFO factor was identified at the closer CORI site whereas RFO was
335 identified at the farther COGO site. Regarding the other smaller source of Ni in Oregon, non-ferrous
336 metal industrial processes, all of these emissions are attributed to one source located outside of Albany
337 OR. While there is no representative emissions profile for this source available in the Speciate database,
338 its location also suggests that is unlikely to be contributing to factors identified as RFO in this work. This
339 source lies 125 km southwest and 250 km north of the COGO and KALM IMPROVE monitors,
340 respectively, and closer monitors (Portland, MOHO, THSI, Oakridge, and CRLA) show no RFO impacts.

341 **3.2.3. Spatial Extent of Residual Fuel Oil Factors**

342 Figure 4 shows a map indicating the monitoring sites where RFO factors were identified and also
343 shows those sites where either sea salt or aged sea salt factors were identified. Figure 4 shows that the
344 spatial extent of sites impacted by RFO is very similar to the spatial extent of impacts from sea salt and
345 aged sea salt. The similarity in spatial extent between these three factors is consistent with the hypothesis
346 that the RFO originates from marine sources, namely, marine vessel emissions.

347 **3.2.4. Monthly Average Contributions from Marine Vessels using RFO**

348 Based on the evidence presented above, RFO factors identified in this work are attributed to marine
349 vessel emissions. Figure 5 shows the monthly average $PM_{2.5}$ mass attributed by PMF to RFO emissions
350 from marine vessels for the 14 monitoring sites where this factor was identified. The monthly averages
351 shown in Figure 5 represent multiyear averages based on the monitoring periods listed in Tables 1 and 2.
352 The bold lines in Figure 5 represent urban CSN monitors, generally have the highest mass impacts
353 throughout the annual cycle, and are consistent with the majority of these monitors being close to major
354 marine vessel ports where there is a higher density of marine vessel emissions compared to IMPROVE

355 monitors. All monitoring sites show a seasonal cycle in marine vessel impacts, with lower impacts in
356 winter months (monthly average $PM_{2.5}$ between $0.1 \mu\text{g}/\text{m}^3 - 0.9 \mu\text{g}/\text{m}^3$ in January) and higher impacts in
357 summer months (monthly average $PM_{2.5}$ between $0.3 \mu\text{g}/\text{m}^3 - 2.7 \mu\text{g}/\text{m}^3$ in August). This season pattern
358 is consistent with more photochemical production of secondary $PM_{2.5}$ from co-emitted gaseous emissions
359 in summer, but also to a smaller extent reflects an average summer increase in cargo traffic of 12% as
360 reported by the Port of Metro Vancouver and the Port of Tacoma (2008-2011 and 2009-2011 data,
361 respectively; Port Metro Vancouver, 2012; Port of Tacoma, 2012) and the exclusively summertime cruise
362 ship activity. Figure 6 shows the percent contribution of RFO emissions from marine vessels to total
363 monthly average $PM_{2.5}$ for the 14 monitoring sites where this factor was identified. As in Figure 5, the
364 urban CSN monitors are in bold lines and the seasonal cycle of percent contributions shows smaller
365 contributions from marine vessels in winter (between 3% – 23% of total monthly average $PM_{2.5}$ in
366 January) and larger contributions in summer (between 9% – 47% of total monthly average $PM_{2.5}$ in June).
367 The highest percent impacts from marine vessel emissions throughout the seasonal cycle occur at
368 comparatively clean IMPROVE sites. This is indicative of relatively few anthropogenic sources
369 impacting the remote IMPROVE sites compared to the urban CSN locations.

370 **4. Conclusions**

371 This work presents a novel regional-scale multisite source apportionment analysis of $PM_{2.5}$ using
372 PMF on data from 36 urban and rural monitoring sites in the U.S. Pacific Northwest covering the period
373 of 2007 - 2011. Results for 14 of the 36 sites indicated a factor linked to RFO from marine vessels. Most
374 sites west of the Cascade Mountains indicated some level of impact from marine vessel emissions. The
375 spatial extent of marine vessel emissions impacts was found to be similar to the other marine related
376 aerosols, sea salt and aged sea salt, and consistent with emissions inventories. Monitoring sites indicating
377 marine vessel emissions impacts show a seasonal cycle, with lower impacts in winter months (monthly
378 average $PM_{2.5}$ between $0.1 \mu\text{g}/\text{m}^3 - 0.9 \mu\text{g}/\text{m}^3$ in January) and higher impacts in summer months (monthly
379 average $PM_{2.5}$ between $0.3 \mu\text{g}/\text{m}^3 - 2.7 \mu\text{g}/\text{m}^3$ in August). The percent contribution to total monthly

380 average PM_{2.5} from marine vessels had a similar seasonal cycle, with smaller contributions in winter
381 (between 3% – 23% of total monthly average PM_{2.5} in January) and larger contributions in summer
382 (between 9% – 47% of total monthly average PM_{2.5} in June). These results for marine vessels,
383 representing data just prior to the implementation of the North American ECA, provide a baseline
384 assessment of marine vessel emissions impacts from which progress in ECA emissions reductions can be
385 assessed.

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388 seasonal marine shipping activity, Brandy Albertson, Phil Allen, Mark Fisher, Miyoung Park and Chris
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391 Islam, and Keith Rose at EPA Region 10 for their helpful insights.

392 **References**

393 Agrawal, H., Malloy, Q.G.J., Welch, W.A., Miller, J.W., Cocker, D.R. III, 2008. In-use gaseous and
394 particulate matter emissions from a modern ocean going container vessel. *Atmospheric Environment* 42,
395 5504–5510.

396

397 Chen, L.-W. A., Watson, J.G., Chow, J.C., DuBois, D.W., Herschberger, L., 2010. Chemical mass
398 balance source apportionment for combined PM_{2.5} measurements from U.S. non-urban and urban long-
399 term networks. *Atmospheric Environment* 44, 4908-4918.

400

401 Chow, J.C., Watson, J.G., Chen, L.-W.A., Arnott, W.P., Moosmuller, H., 2004. Equivalence of Elemental
402 Carbon by Thermal/Optical Reflectance and Transmittance with Different Temperature Protocols.
403 *Environmental Science and Technology* 38, 4414-4422.

404

405 Corbett, J.J., Winebrake, J.J., Green, E.H., Kasibhatla, P., Eyring, V., Lauer, A., 2007. Mortality from
406 Ship Emissions: A Global Assessment. *Environmental Science and Technology* 41, 8512-8518.

407

408 Geiser, L.H., Jovan, S.E., Glavich, D.A., Porter, M.K., 2010. Lichen based critical loads for atmospheric
409 nitrogen deposition in Western Oregon and Washington Forests, USA. *Environmental Pollution* 158,
410 2412-2421.

411

412 Hsu, Y., Divita, F., 2011. Speciate 4.3: Addendum to Speciate 4.2 Speciation Database Development
413 Documentation. U.S. Environmental Protection Agency, EPA/600/R-11/121.

414

415 Hwang, I., Hopke, P.K., 2007. Estimation of source apportionment and potential source locations of PM_{2.5}
416 at a west coastal IMPROVE site. *Atmospheric Environment* 41, 506–518.

417

418 Kaerlev, L., Hansen, J., Hansen, H.L., Nielsen, P.S., 2005. Cancer incidence among Danish seafarers: a
419 population based cohort study, *Occupational Environmental Medicine*, 62, 761-765.

420

421 Kim, E., Hopke, P.K., 2008a. Source characterization of ambient fine particles at multiple sites in the
422 Seattle area. *Atmospheric Environment* 42, 6047– 6056.

423

424 Kim, E., Hopke, P.K., 2008b. Characterization of Ambient Fine Particles in the Northwestern Area and
425 Anchorage, Alaska. *Journal of the Air & Waste Management Association* 58, 1328–1340.

426

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

430

431 Künzli, N., Jerrett, M., Mack, W.J., Beckerman, B., LaBree, L., Gilliland, F., Thomas, M., Peters, J.,
432 Hodis, H.N., 2005. Ambient air pollution and atherosclerosis in Los Angeles. Environmental Health
433 Perspectives, 113, 201-206.

434

435 Maykut, N., Lewtas, J., Kim, E., Larson, T., 2003. Source Apportionment of PM_{2.5} at an Urban
436 IMPROVE Site in Seattle, Washington. Environmental Science and Technology 37, 5135-5142.

437

438 Minguillon, M.C., Arhami, M., Schauer, J.J., Sioutas, C., 2008. Seasonal and spatial variations of sources
439 of fine and quasi-ultrafine particulate matter in neighborhoods near the Los Angeles–Long Beach harbor.
440 Atmospheric Environment 42, 7317–7328.

441

442 Moldanova, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto, A., Focsa, C.,
443 2009. Characterisation of particulate matter and gaseous emissions from a large ship diesel engine.
444 Atmospheric Environment 43, 2632–2641.

445

446 Mooibroek, D., Schaap, M., Weijers, E.P., Hoogerbrugge, R., 2011. Source apportionment and spatial
447 variability of PM_{2.5} using measurements at five sites in the Netherlands. Atmospheric Environment 45,
448 4180-4191.

449

450 Norris G., Vedantham R., Wade K., Brown S., Prouty J., Foley C., 2008. EPA Positive Matrix
451 Factorization (PMF) 3.0: fundamentals & user guide. U.S. Environmental Protection Agency. EPA
452 600/R-08/108.

453

454 Paatero, P., Hopke, P.K., 2003. Discarding or downweighting high-noise variables in factor analytic
455 models. *Analytica Chimica Acta* 490, 277–289.

456

457 Pope, C. A., III, Dockery, D.W., 2006. Health Effects of Fine Particulate Air Pollution: Lines that
458 Connect. *Journal of the Air & Waste Management Association* 56, 709–742.

459

460 Port Metro Vancouver, 2012. Port Metro Vancouver Container Statistics Report 2008 – 2011.
461 [http://www.portmetrovancover.com/Libraries/ABOUT_Facts_Stats/2008-](http://www.portmetrovancover.com/Libraries/ABOUT_Facts_Stats/2008-2011_Container_Statistics_Report.sflb.ashx)
462 [2011_Container_Statistics_Report.sflb.ashx](http://www.portmetrovancover.com/Libraries/ABOUT_Facts_Stats/2008-2011_Container_Statistics_Report.sflb.ashx), accessed 8/29/2012.

463

464 Port of Tacoma, 2012. Port of Tacoma Container Volumes 2009 – 2011.
465 <http://www.portoftacoma.com/stats>, accessed 8/29/2012.

466

467 Port of Seattle, 2012. Seattle Harbor 10 Year History of Cargo Volumes Handled: 2002 – 2011,
468 <http://www.portseattle.org/About/Publications/Statistics/Seaport/Pages/10-Year-History.aspx>, accessed
469 8/28/2012.

470

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

474

475 U.S. Army Corps of Engineers, 2012. Waterborne Commerce Statistics Center.
476 <http://www.ndc.iwr.usace.army.mil/wesc/wesc.htm>, accessed 8/7/2012.

477

478 U.S. Environmental Protection Agency, 2009. PM_{2.5} Speciation Network Newsletter, Issue 6, 2009.
479 <http://www.epa.gov/ttnamti1/files/ambient/pm25/spec/spnews6.pdf>, accessed 8/2/2012.

480

481 U.S. Environmental Protection Agency, 2010. Designation of North American Emission Control Area to
482 Reduce Emissions from Ships: Regulatory Announcement. EPA-420-F-10-015.

483

484 U.S. Environmental Protection Agency, 2010. 2008 National Emissions Inventory Version 2.0.
485 <http://www.epa.gov/ttnchie1/net/2008inventory.html>, accessed 7/26/2012.

486

487 Wagstrom, K.M., Pandis, S.N., Yarwood, G., Wilson, G.M., Morris, R.E., 2008. Development and
488 application of a computationally efficient particulate matter apportionment algorithm in a three-
489 dimensional chemical transport model. Atmospheric Environment 42, 5650– 5659.

490

491 White, W.H., 2009. Inconstant bias in XRF sulfur - Advisory Update to da0012.
492 http://vista.cira.colostate.edu/improve/Data/QA_QC/Advisory.htm, accessed 8/29/2012.

493

494 Winebrake, J.J., Corbett, J.J., Green, E.H., Lauer, A., Eyring, V., 2009. Mitigating the Health Impacts of
495 Pollution from Oceangoing Shipping: An Assessment of Low-Sulfur Fuel Mandates. Environmental
496 Science and Technology 43, 4776-4782.

497

498 Wu, C., Larson, T.V., Wu, S., Williamson, J., Westberg, H.H., Liu, L.-J.S., 2007. Source apportionment
499 of PM_{2.5} and selected hazardous air pollutants in Seattle. Science of the Total Environment 386, 42–52.

500

501 Table 1. CSN monitoring sites modeled in this study.

Site Name/City	Date Range Modeled	Number of Samples	State	AQS Number	Latitude	Longitude
Boise	5/3/07 - 9/12/11	532	ID	160010010	43.6003	-116.3479
Klamath Falls	7/6/09 - 3/28/11	88	OR	410350004	42.1889	-121.7225
Lakeview	10/4/09 - 3/28/11	83	OR	410370001	42.1889	-120.3519
Oakridge	7/6/09 - 3/28/11	100	OR	410392013	43.7444	-122.4805
Portland	5/3/07 - 8/4/11	513	OR	410510080	45.4965	-122.6034
Vancouver	4/1/09 - 9/6/11	149	WA	530110013	45.6483	-122.5869
Seattle_DW (Duwamish)	11/2/08 - 9/6/11	174	WA	530330057	47.5632	-122.3405
Seattle_BH (Beacon Hill)	5/3/07 - 9/12/11	435	WA	530330080	47.5683	-122.3081
Tacoma_SL (South L St.)	5/6/07 - 9/6/11	260	WA	530530029	47.1864	-122.4517
Tacoma_AL (Alexander Ave.)	11/2/08 - 9/6/11	174	WA	530530031	47.2656	-122.3858
Marysville	4/7/09 - 9/6/11	145	WA	530611007	48.0543	-122.1715
Yakima	11/8/07 - 9/6/11	202	WA	530770009	46.5968	-120.5122

502

Table 2. IMPROVE network monitoring sites modeled in this study.

Site Name	Date Range Modeled	Number of Samples	State	Class 1 Area	Latitude	Longitude
CRMO	1/6/07 - 12/31/10	452	ID	Craters of the Moon	43.4605	-113.5551
SAWT	1/3/07 - 12/31/10	414	ID	Sawtooth	44.1705	-114.9271
CABI	1/12/07 - 12/31/10	446	MT	Cabinet Mountains	47.9549	-115.6709
FLAT	1/3/07 - 12/31/10	451	MT	Flathead	47.7734	-114.2690
GLAC	1/3/07 - 12/28/10	441	MT	Glacier	48.5105	-113.9966
MONT	1/3/07 - 12/31/10	443	MT	Monture	47.1222	-113.1544
JARB	1/3/07 - 12/31/10	453	NV	Jarbidge Wilderness	41.8926	-115.4261
CRLA	1/3/07 - 12/31/10	432	OR	Crater Lake	42.8958	-122.1361
HECA	1/3/07 - 12/31/10	420	OR	Hells Canyon	44.9702	-116.8438
KALM	1/3/07 - 12/31/10	465	OR	Kalmiopsis	42.5520	-124.0589
MOHO	1/3/07 - 12/31/10	465	OR	Mount Hood	45.2888	-121.7837
STAR	1/6/07 - 12/31/10	478	OR	Starkey	45.2249	-118.5129
THSI	1/3/07 - 12/31/10	463	OR	Three Sisters Wilderness	44.2910	-122.0434
LABE	1/3/07 - 12/31/10	457	CA	Lava Beds	41.7117	-121.5068
REDW	1/3/07 - 12/31/10	420	CA	Redwood	41.5608	-124.0839
COGO	1/3/07 - 12/31/10	435	WA	Columbia Gorge	45.5693	-122.2103
CORI	1/3/07 - 12/31/10	475	WA	Columbia River Gorge	45.6644	-121.0008
MAKA	1/3/07 - 10/23/10	414	WA	Makah Tribe	48.3719	-124.5950
MORA	1/3/07 - 12/31/10	458	WA	Mount Rainier	46.7583	-122.1244
NOCA	1/6/07 - 12/31/10	450	WA	North Cascades	48.7316	-121.0646
OLYM	1/3/07 - 12/31/10	466	WA	Olympic	48.0065	-122.9727
PASA	1/3/07 - 12/31/10	453	WA	Pasayten	48.3877	-119.9275
SNPA	1/3/07 - 12/31/10	473	WA	Snoqualmie Pass	47.4220	-121.4259
WHPA	1/3/07 - 12/31/10	461	WA	White Pass	46.6243	-121.3881

505 Table 3. Annual average PM_{2.5} (µg/m³) and source apportionment results for PMF factors found at CSN
 506 monitoring sites in the U.S. Pacific Northwest.

Site Name	Number of Factors Found	Measured Average PM _{2.5}	Calcium Rich	Copper Rich	Gasoline Vehicles	Iron Rich	Nitrate Rich	Organic Pyrolysis (OP) Rich	Potassium Rich	Sea Salt	Aged Sea Salt	Soil	Sulfur Rich	Residual Fuel Oil	Urban Unidentified	Wood Smoke	Zinc Rich
Boise	8	6.9			0.9		1.3	0.9	0.3			1.0	0.9		0.4	1.2	
Klamath_Falls	5	10.7					0.7	2.1				1.1	0.6			6.4	
Lakeview	7	8.5					0.7	1.4	0.6			0.9	0.4		0.5	4.2	
Oakridge	7	8.0			1.3			1.5		0.3		0.4	0.8			3.8	
Portland	8	8.3			2.5		0.7	0.6		0.4		0.5	1.0		0.8	1.8	
Vancouver	8	7.1			0.1		0.6	1.0		0.3		0.4	1.2		1.6	2.2	
Seattle_DW	11	7.9	0.4		1.6	0.9	0.7	0.3		0.3	0.9	0.5		1.1		1.3	0.2
Seattle_BH	11	6.6		0.0	1.3	0.8	0.6	0.6		0.2	0.9	0.2		1.0	0.4	0.7	
Tacoma_SL	10	9.2			2.0	0.6	0.5	0.8		0.3	0.8	0.3		0.8	0.7	2.8	
Tacoma_AL	9	8.0			1.9	0.3	0.9	0.2		0.5		0.8		1.3	0.5	1.9	
Marysville	9	8.8			1.8		0.9	0.3		0.3	1.0	0.6		0.9	0.4	2.8	
Yakima	10	8.8			1.7	0.4	1.8	0.9		0.3		0.3	0.9		1.0	1.5	0.5

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509

Table 4. Annual average PM_{2.5} (µg/m³) and source apportionment results for PMF factors found at IMPROVE network monitoring sites in the U.S. Pacific Northwest.

Site Name	Number of Factors Found	Measured Average PM _{2.5}	Iron Rich	Mixed, Nitrate & Sulfate	Mixed, OC, EC & Sulfate	Mixed, OC & Nitrate	Mixed, OC & Soil (Ca Rich)	Mixed, Sulfate & Soil	Mixed, Sulfate & Soil (Ca Rich)	Nitrate Rich	Organic Pyrolysis (OP) Rich	Sea Salt	Aged Sea Salt	Secondary Organic Aerosol & Wood Smoke	Soil	Soil (Ca Rich)	Sulfate Rich	Residual Fuel Oil	Zinc Rich
CRMO	6	2.6								0.2	0.0			1.3	0.6		0.5		0.0
SAWT	6	3.1					0.1				0.1			2.0	0.6		0.3		0.0
CABI	5	2.7								0.1				1.5	0.5		0.6		0.1
FLAT	4	3.0								0.1				1.7	0.4		0.6		
GLAC	5	4.3	0.2							0.2				2.5	0.7		0.8		
MONT	4	3.4				0.2								2.0	0.6		0.6		
JARB	6	2.8								0.1				1.2	0.9	0.4	0.2		0.0
CRLA	4	2.2												1.4	0.3		0.4		0.1
HECA	5	3.6								0.2				2.1	0.3		0.8		0.0
KALM	6	3.1										0.3	0.5	1.5	0.2			0.7	0.0
MOHO	4	2.0		0.4				0.3	0.0					1.2					
STAR	5	3.0								0.2			0.2	1.8	0.3		0.4		
THSI	4	2.8											0.2	1.5	0.6		0.5		
LABE	7	2.8			0.1			0.1		0.1				1.7	0.4		0.4		0.0
REDW	5	3.4	0.1									1.2	0.2	1.2				0.9	
COGO	9	4.3			0.4					0.3		0.2	0.4	1.6	0.4		0.8	0.3	0.0
CORI	7	4.8	0.1							0.6			0.6	1.8	0.9		0.8		0.2
MAKA	7	4.6		0.2								0.7	0.6	1.9	0.2		0.9	0.5	
MORA	7	2.8								0.1			0.2	1.2	0.2		0.6	0.5	0.1
NOCA	5	2.2											0.2	1.1	0.2		0.1	0.7	
OLYM	7	2.7						0.2				0.2	0.4	1.2			0.6	0.2	0.1
PASA	5	2.1								0.0				1.3	0.3		0.5		0.0
SNPA	7	2.5								0.2			0.3	1.1	0.2		0.3	0.4	0.1
WHPA	5	1.8												0.8	0.2		0.4	0.4	0.0

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512 Figure captions:

513

514 Figure 1. CSN and IMPROVE PM_{2.5} monitoring sites in the U.S. Pacific Northwest.

515 Figure 2. Residual fuel oil combustion PMF factors for CSN monitoring sites. Vertical bars

516 indicate the fractional contribution (left vertical scale) of chemical species to factor composition,

517 grey dots indicate the percent of chemical species (right vertical scale) observed at each location

518 attributed to residual fuel oil.

519 Figure 3. Residual fuel oil combustion PMF factors for IMPROVE monitoring sites. Vertical

520 bars indicate the fractional contribution (left vertical scale) of chemical species to factor

521 composition, grey dots indicate the percent of chemical species (right vertical scale) observed at

522 each location attributed to residual fuel oil.

523 Figure 4. Monitoring sites where PMF factors for residual fuel oil were found and monitoring

524 sites where PMF factors for either sea salt or aged sea salt were found.

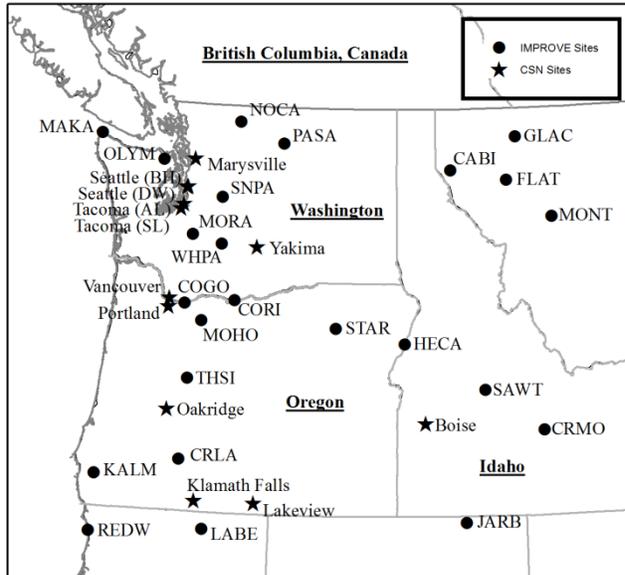
525 Figure 5. Monthly average PM_{2.5} (µg/m³) attributed to marine vessels using residual fuel oil for

526 14 monitoring sites in the U.S. Pacific Northwest.

527 Figure 6. Monthly average percent of total PM_{2.5} attributed to marine vessels using residual fuel

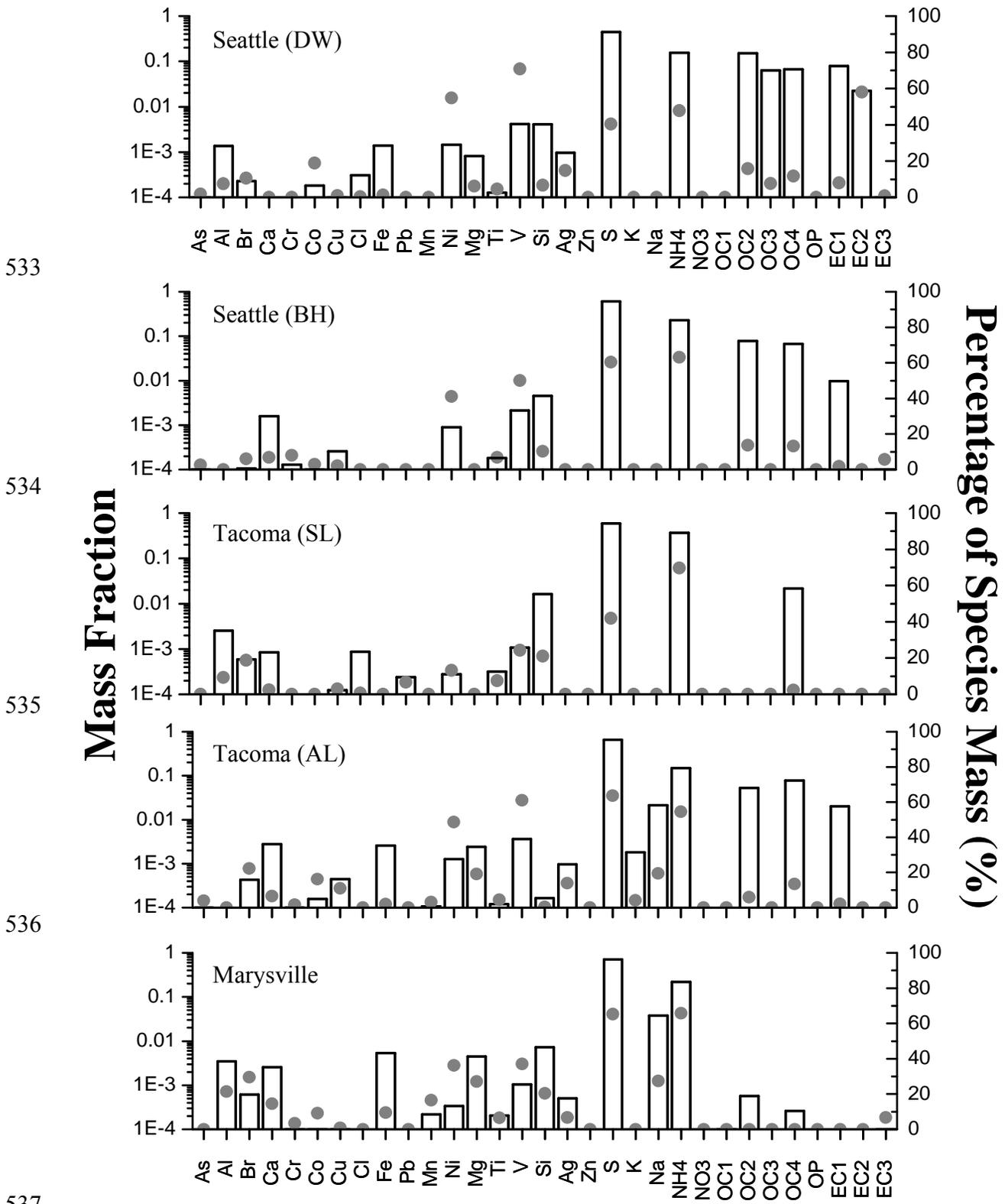
528 oil for 14 monitoring sites in the U.S. Pacific Northwest.

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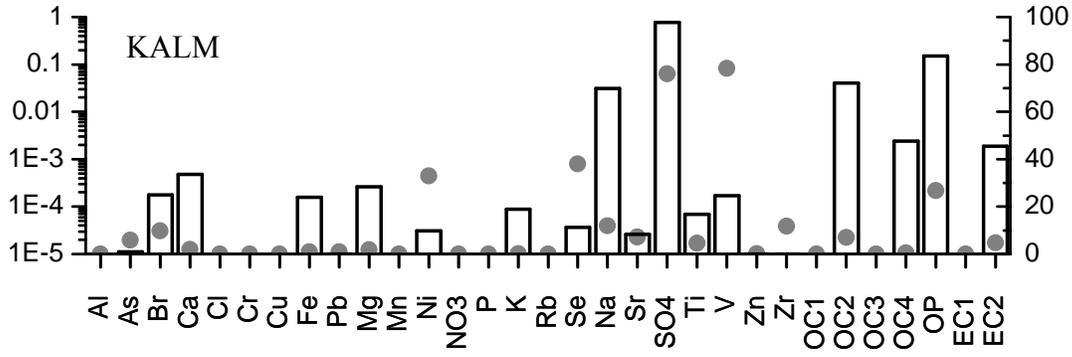


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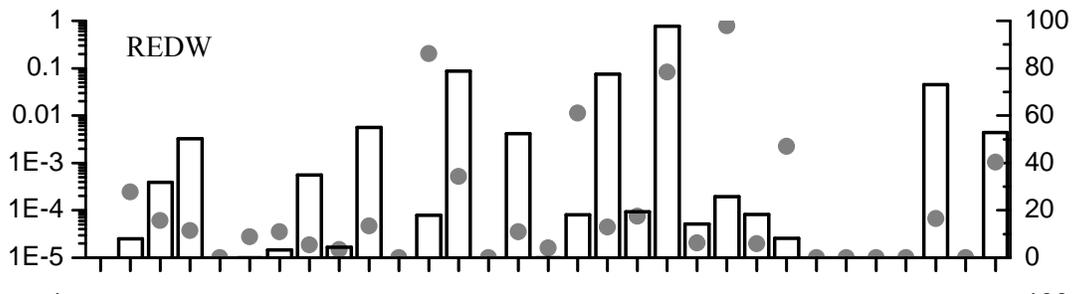
Figure 1.



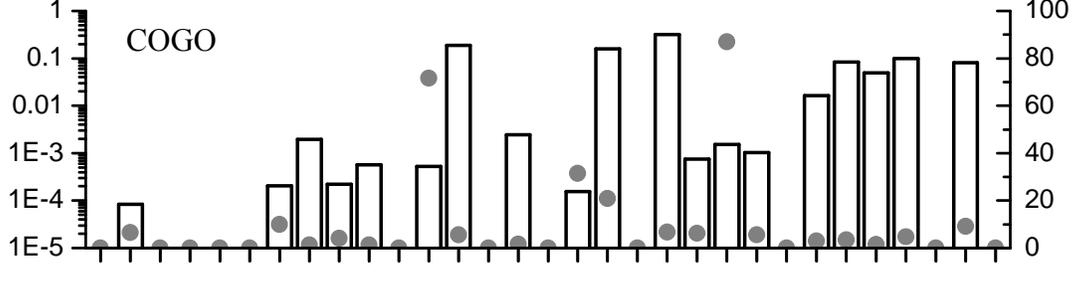
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 538 Figure 2.
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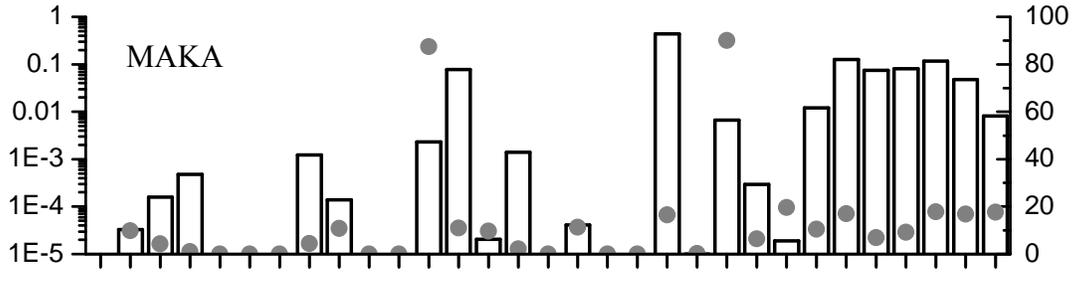
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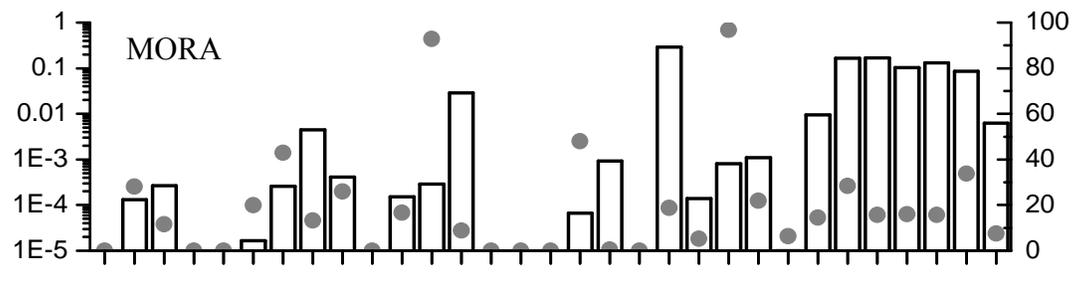
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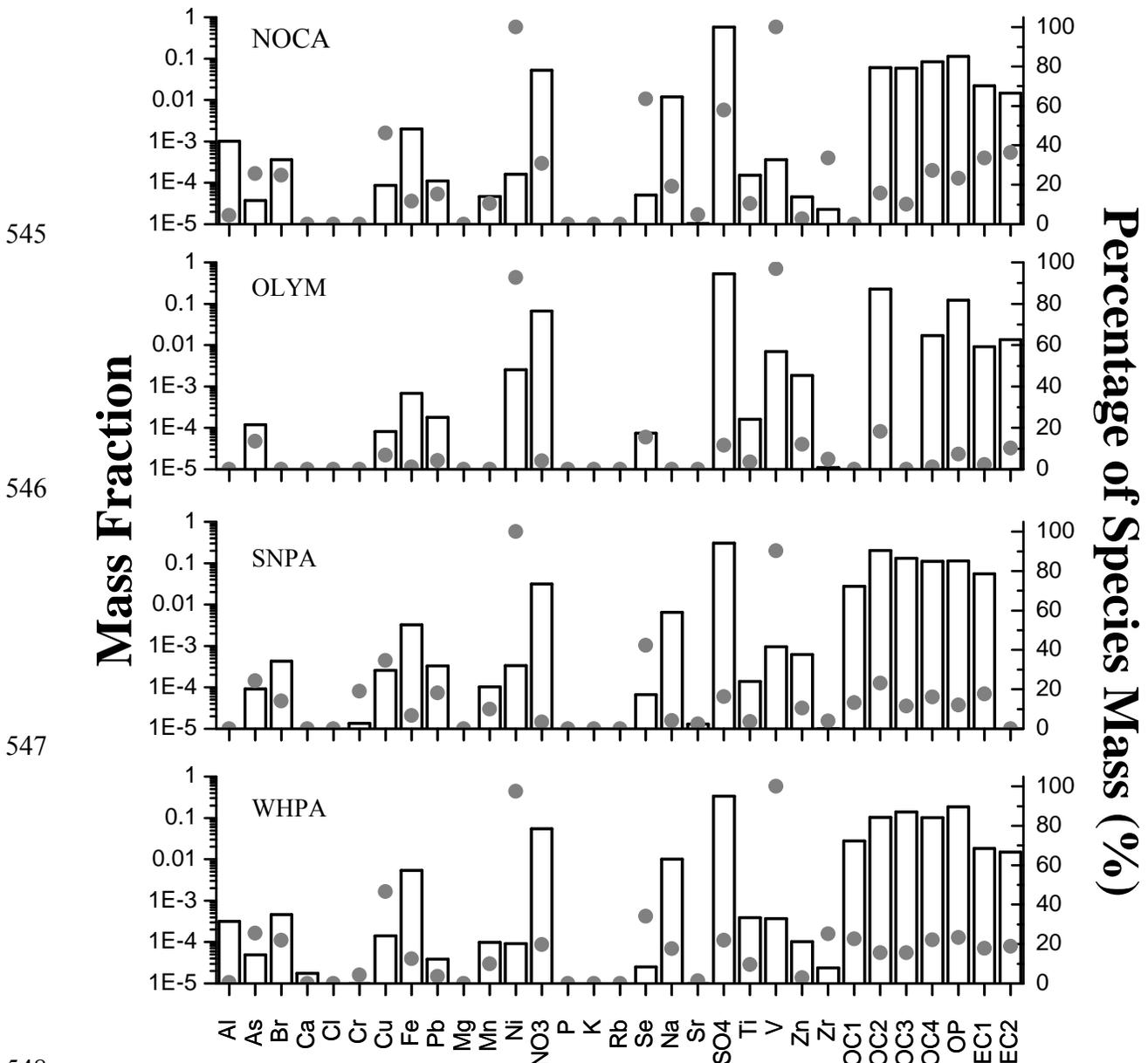
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Mass Fraction

Percentage of Species Mass (%)



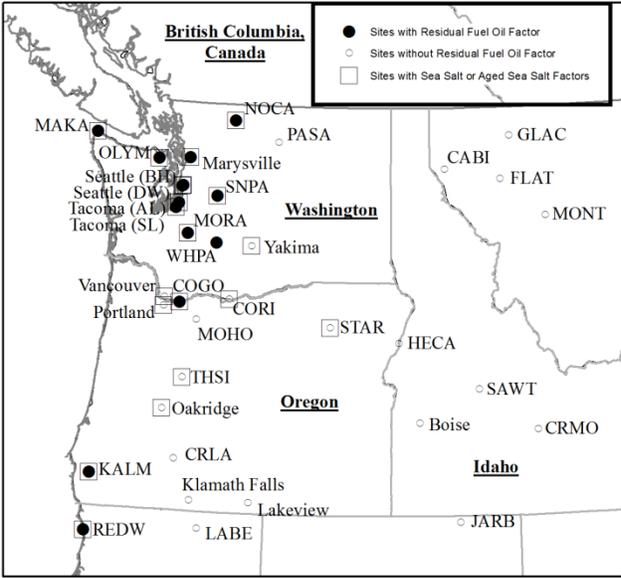
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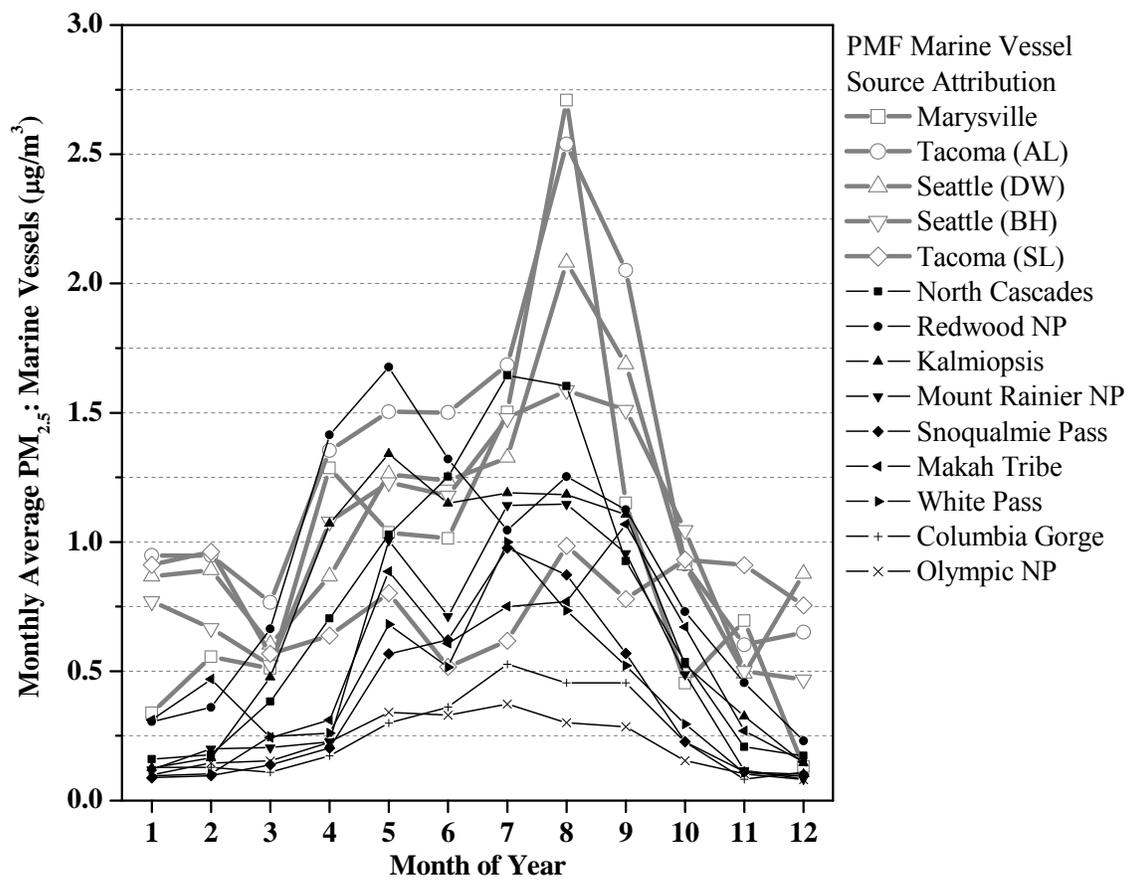
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Figure 3.

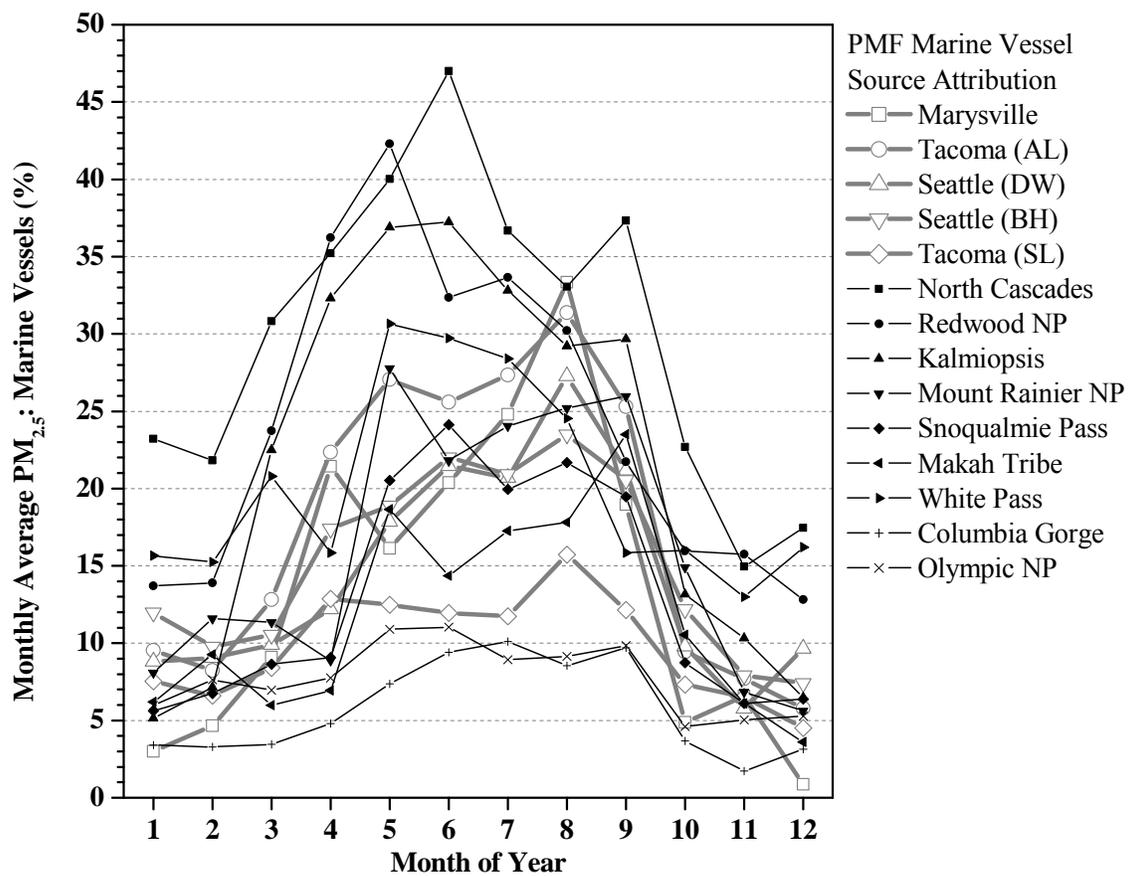


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Figure 4.



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 555 Figure 5.
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Figure 6.

561 **Kotchenruther, 2012. Supplementary Material: PMF Factor Names and Identification**

562 **S.1. Factors Found at Both CSN and IMPROVE Sites**

563 **S.1.1. Iron Rich**

564 Fe is important in the identification of this factor with concentrations ranging between 5 - 50% and
565 11 – 25% of total factor mass for CSN and IMPROVE sites, respectively. Factor also has variable
566 amounts of OC, EC, SO_4^{2-} (S in CSN datasets), and/or NO_3^- . Factor identification is unclear. Previous
567 studies have linked similar Fe rich factors to a variety of sources including diesel vehicles, heavy-duty
568 diesel, oil combustion, or industrial activity [Karanasiou et al., 2009 (oil combustion); Kim et al., 2004
569 (diesel); Maykut et al., 2003 (diesel); Ramadan et al., 2000 (heavy-duty diesel); Kim and Hopke, 2008a
570 (diesel); Kim and Hopke, 2008b (metal processing); Lee et al., 2008 (metal/industrial processing); Wu et
571 al., 2007 (diesel); Zhao and Hopke, 2006 (secondary sulfate); Zhou et al., 2004 (traffic); Amato and
572 Hopke 2011 (diesel); Kim et al., 2010 (diesel); Lewis et al., 2003 (diesel)].

573 **S.1.2. Nitrate Rich**

574 Factor mass dominated by the sum of NO_3^- and NH_4 for CSN sites and NO_3^- for IMPROVE sites.

575 **S.1.3. Organic Pyrolysis (OP) Rich**

576 Factor mass dominated by the sum of OC fractions (often > 95% of mass). OC fractions are
577 weighted to the higher temperature fractions (OC3, OC4, OP). OP is often the dominant mass of the OC
578 fractions. This factor likely has a significant contribution from secondary organic aerosols (Jang et al.,
579 2003). OP rich factors have been previously identified by Hwang and Hopke (2007), Kim et al. (2004),
580 and Zhao and Hopke (2006).

581 **S.1.4. Sea Salt**

582 Factor mass dominated by the sum of Na and Cl.

583 **S.1.5. Aged Sea Salt**

584 Sodium concentrations ranged between 5 – 13% and 9 – 53% of factor mass for CSN and
585 IMPROVE sites, respectively, with no associated Cl mass and about 1% Mg. Factor also associated with
586 variable amounts of SO_4^{2-} (S in CSN datasets), NO_3^- , and OC. Factor identified by the importance of Na
587 and Mg in chemical profile and the absence of Cl.

588 **S.1.6. Soil**

589 Factor mass dominated by the sum of Al, Ca, Fe, Ti, and Si, elements commonly found in the
590 earth's crust.

591 **S.1.7. Sulfur/Sulfate Rich**

592 Factor mass dominated by the sum of S and NH_4 for CSN sites and SO_4^{2-} for IMPROVE sites.

593 **S.1.8. Residual Fuel Oil (RFO)**

594 Factor mass dominated by S and NH_4 for CSN sites and SO_4^{2-} for IMPROVE sites, with Ni and V
595 playing a significant role in factor identification at trace levels. The ratio of V:Ni ranged between 2.4 –
596 3.9 for CSN sites and 2.3 – 5.4 for IMPROVE sites. OC and EC also can contribute to factor mass.
597 Previous studies have linked similar factors to RFO combustion from marine vessels due to V and Ni
598 tracer species and high sulfur content (Maykut et al., 2003; Kim and Hopke, 2008a; Kim and Hopke,
599 2008b).

600 **S.1.9. Zinc Rich**

601 Zn concentrations ranged from 3 – 7% and 1 – 9% of factor mass for CSN and IMPROVE sites,
602 respectively. The remaining mass is typically dominated by OC and EC, but at IMPROVE sites can also
603 have significant contributions from Si and/or SO_4^{2-} . Factor identification is unclear. Previous studies
604 have linked similar factors to a variety of sources including diesel vehicles and industrial activity [Hwang
605 and Hopke, 2007 (diesel); Kim and Hopke, 2006 (diesel); Kim and Hopke, 2008b (diesel); Kim et al.,
606 2010 (industrial)]. Zinc is widely used as an additive in lubricating oils for diesel engines, for gasoline-
607 powered engines in motor vehicles and other machines.

608 **S.2. Factors Found Only at CSN Sites**

609 **S.2.1. Calcium Rich**

610 Factor mass dominated by Ca and S. Previous studies have linked similar calcium rich factors to
611 cement production (Kim et al., 2004; Shi et al., 2009).

612 **S.2.2. Copper Rich**

613 Factor mass dominated by Cu and EC. Factor possibly linked to metal processing industry (Amato
614 and Hopke, 2011).

615 **S.2.3. Gasoline Vehicles**

616 Factor mass dominated by the sum of OC2, OC3 and OC4 species with an approximate ratio of
617 1:2:1 between OC2:OC3:OC4. Usually no OC1 or OP component. EC component usually 15 – 20 % of
618 total mass, and mostly EC1. Previous studies have linked similar factors to gasoline vehicles (Hwang and
619 Hopke, 2007; Kim et al., 2004; Maykut et al., 2003; Zhao and Hopke, 2004; Kim and Hopke, 2006; Kim
620 and Hopke, 2008b; Zhao and Hopke, 2006).

621 **S.2.4. Potassium Rich**

622 Factor mass has a high percentage of K and S. Previous studies have linked K rich sources to the
623 use of fireworks (Joly et al., 2010). However, this was ruled out here because data from July 4 and 5
624 were removed from the datasets and mass impacts did not show a particular bias to other days when
625 fireworks are more likely (e.g., near January 1).

626 **S.2.5. Urban Unidentified**

627 Factor dominated by a mixture of OC, EC, S and NO₃⁻. The EC2 is particularly important in the
628 identification of this factor. Factor identification is unclear. Previous studies have linked similar factors
629 to a variety of sources including railroad traffic and diesel vehicles [Kim et al., 2004 (railroad traffic);

630 Zhao and Hopke, 2004 (diesel); Kim and Hopke, 2006 (secondary sulfate); Han et al., 2007 (diesel)]. It is
631 thought likely that this factor is in some way connected to fuel combustion.

632 **S.2.6. Wood Smoke**

633 Factor dominated by the sum of OC and EC plus about 1% K. Usually OC dominated by the OC1
634 fraction, EC dominated by EC1, and no OP component. Majority of mass impacts were in winter. EC
635 can range between 10 – 30% of factor. Previous studies have linked similar factors to wood smoke
636 (Hwang and Hopke, 2007; Kim et al., 2004; Maykut et al., 2003; Kim and Hopke, 2008b; Zhao and
637 Hopke, 2006).

638 **S.3. Factors Found Only at IMPROVE Sites**

639 **S.3.1. Mixed, Nitrate & Sulfate**

640 Factor mass dominated by the sum of NO_3^- and SO_4^{2-} in roughly equal proportions.

641 **S.3.2. Mixed, Organic Carbon, Elemental Carbon & Sulfate**

642 Factor mass dominated by the sum of OC, EC, and SO_4^{2-} in variable amounts.

643 **S.3.3. Mixed, Organic Carbon & Nitrate**

644 Factor mass dominated by the sum of OC and NO_3^- in roughly equal amounts.

645 **S.3.4. Mixed, Organic Carbon & Soil (Ca Rich)**

646 Factor mass dominated by the sum of OC and soil elements in roughly equal amounts. Soil
647 elements have elevated Ca compared to the typical soil profile.

648 **S.3.5. Mixed, Sulfate & Soil**

649 Factor mass dominated by the sum of SO_4^{2-} and soil elements in roughly equal amounts.

650 **S.3.6. Mixed, Sulfate & Soil (Ca Rich)**

651 Factor mass dominated by the sum of SO_4^{2-} and soil elements in roughly equal amounts. Soil
652 elements have elevated Ca compared to the typical soil profile.

653 **S.3.7. Secondary Organic Aerosol & Wood Smoke**

654 Factor mass dominated by the sum of organic components. Usually OC3 is elevated above OC2,
655 OC4, and OP with OC1 usually the lowest component. Variable amount of EC, but usually less than
656 10%. K in trace amounts but usually significant for factor identification. Time series of mass impacts
657 often has a broad summer maximum with occasional elevated impacts of 5-10 $\mu\text{g}/\text{m}^3$. Previous studies
658 have linked similar factors to wood smoke (Hwang and Hopke, 2007; Kim et al., 2004; Maykut et al.,
659 2003; Kim and Hopke, 2008b; Zhao and Hopke, 2006). However, since factor time series have
660 ubiquitous summertime mass usually between 1-2 $\mu\text{g}/\text{m}^3$ with occasional elevated impacts, it is thought
661 likely that this factor is a combination of secondary organic aerosol and wood smoke from wild or
662 prescribed fires.

663 **S.3.8. Soil (Ca Rich)**

664 Factor mass dominated by the sum of Al, Ca, Fe, Ti, and Si. However, Ca concentration is elevated
665 compared to the other soil profile.

666 **S.4. Additional References for Supplementary Materials**

667 Amato, F., Hopke, P.K., 2012. Source apportionment of the ambient $\text{PM}_{2.5}$ across St. Louis using
668 constrained positive matrix factorization. *Atmospheric Environment* 46, 329-337.

669

670 Han, Y., Cao, J., Chow, J.C., Watson, J.G., An, Z., Jin, Z., Fung, K., Liu, S., 2007. Evaluation of the
671 thermal/optical reflectance method for discrimination between char- and soot-EC. *Chemosphere* 69, 569–
672 574.

673

674 Hwang, I., Hopke, P.K., 2007. Estimation of source apportionment and potential source locations of PM_{2.5}
675 at a west coastal IMPROVE site. *Atmospheric Environment* 41, 506–518.

676

677 Jang, M., Lee, S., Kamens, R.M., 2003. Organic aerosol growth by acid-catalyzed heterogeneous
678 reactions of octanal in a flow reactor. *Atmospheric Environment* 37, 2125–2138.

679

680 Joly, A., Smargiassi, A., Kosatsky, T., Fournier, M., Dabek-Zlotorzynska, E., Celso, V., Mathieu, D.,
681 Servranckx, R., D'amours, R., Malo, A., Brook, J. 2010. Characterisation of particulate exposure during
682 fireworks displays. *Atmospheric Environment* 44, 4325-4329.

683

684 Karanasiou, A.A., Siskos, P.A., Eleftheriadis, K., 2009. Assessment of source apportionment by Positive
685 Matrix Factorization analysis on fine and coarse urban aerosol size fractions. *Atmospheric Environment*
686 43, 3385–3395.

687

688 Kim, E., Hopke, P.K., 2006. Characterization of fine particle sources in the Great Smoky Mountains area.
689 *Science of the Total Environment* 368, 781–794.

690

691 Kim, E., Hopke, P.K., Edgerton, E.S., 2004. Improving source identification of Atlanta aerosol using
692 temperature resolved carbon fractions in positive matrix factorization. *Atmospheric Environment* 38,
693 3349–3362.

694

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

697

698 Lee, S., Liu, W., Wang, Y., Russell, A.G., Edgerton, E.S., 2008. Source apportionment of PM_{2.5}:
699 Comparing PMF and CMB results for four ambient monitoring sites in the southeastern United States.
700 Atmospheric Environment 42, 4126–4137.

701

702 Lewis, C.W., Norris, G.A., Henry, R.C., Conner, T.L., 2003. Source Apportionment of Phoenix PM_{2.5}
703 Aerosol with the Unmix Receptor Model. Journal of the Air & Waste Management Association 53, 325-
704 338.

705

706 Ramadan, Z., Song, X.-H., Hopke, P.K., 2000. Identification of Sources of Phoenix Aerosol By Positive
707 Matrix Factorization. Journal of the Air & Waste Management Association 50, 1308-1320.

708

709 Shi, G.-L., Li, X., Feng, Y.-C., Wang, Y.-Q., Wu, L.-H., Li, J., Zhu, T., 2009. Combined source
710 apportionment, using positive matrix factorization–chemical mass balance and principal component
711 analysis/multiple linear regression–chemical mass balance models. Atmospheric Environment 43, 2929–
712 2937.

713

714 Zhao, W. Hopke, P., 2004. Source apportionment for ambient particles in the San Gorgonio
715 wilderness. Atmospheric Environment 38, 5901–5910.

716

717 Zhao, W. Hopke, P., 2006. Source identification for fine aerosols in Mammoth Cave National Park.
718 Atmospheric Research 80, 309– 322.

719

720 Zhou, L., Hopke, P.K., Paatero, P., Ondov, J.M., Pancras, J.P., Pekney, N.J., Davidson, C.I., 2004.

721 Advanced factor analysis for multiple time resolution aerosol composition data. *Atmospheric*

722 *Environment* 38, 4909–4920.

723