

A regional assessment of marine vessel PM_{2.5} impacts in the U.S. Pacific Northwest using a receptor-based source apportionment method

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HIGHLIGHTS

- ▶ PM_{2.5} source apportionment was performed for 36 sites in the northwest U.S.
- ▶ Residual fuel oil factors at 14 locations were linked to marine vessel emissions.
- ▶ Monthly average PM_{2.5} impacts from marine vessel emissions are quantified.
- ▶ Results are just prior to the start of the North American Emissions Control Area.
- ▶ Results set a baseline to measure progress in emissions reductions.

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ABSTRACT

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

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1. Introduction

Human health studies have shown that there is a relationship between exposure to fine particulate matter (PM_{2.5}, particles with

aerodynamic diameter <2.5 μm) and adverse health effects such as cardiovascular and pulmonary disease (Künzli et al., 2005), and lung cancer and premature mortality (Pope and Dockery, 2006). The preponderance of health studies suggest that there is no PM exposure threshold below which adverse health effects do not occur (Pope and Dockery, 2006), which implies that anthropogenic PM impacts should be of concern even in areas currently meeting national ambient air quality standards. In addition to human health

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effects, deposition of anthropogenic PM has also been linked to adverse effects on ecosystem health (Geiser et al., 2010).

PM_{2.5} emissions from commercial marine vessels has been an active area of investigation because these sources typically burn residual fuel oil (RFO), which has a very high sulfur content, produces large amounts of PM_{2.5}, SO₂, and NO_x (Moldanova et al., 2009), and are mobile sources that can impact urban areas as well as remote coastal areas having few other direct sources of anthropogenic emissions. Health studies targeted at seafarers have shown an increased rate of cancer incidence depending on length of time employed (Kaerlev et al., 2005), while globally among the general population marine vessel emissions have been estimated to cause approximately 60,000 cardiopulmonary and lung cancer deaths annually (Corbett et al., 2007). Regulating marine vessel fuel sulfur content is a common approach to reducing emissions. Winebrake et al. (2009) have shown that significant reductions in premature mortality from marine vessel emissions can be achieved by regulating fuel sulfur content at amounts lower than an assumed uncontrolled fuel sulfur content of 2.7%.

Concerns over health and ecological effects of marine vessel emissions led the United States (U.S.) and Canadian governments in 2009 to propose to the International Maritime Organization (IMO) the inclusion of North America in an Emissions Control Area (ECA). In March of 2010 the IMO amended the International Convention for the Prevention of Pollution from Ships (MARPOL) to designate specific portions of North American waters as an ECA (U.S. EPA, 2010). Beginning in August 2012, the ECA requires marine vessels within 200 nautical miles of North American coasts to use fuels with sulfur content no higher than 10,000 ppm (1%) and worldwide no higher than 35,000 ppm (3.5%). Starting in 2015, the ECA will require fuel sulfur content no higher than 1000 ppm (0.1%) within 200 nautical miles of North American coasts.

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

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

A regional assessment of aerosol source impacts is often addressed using source-oriented methods like photochemical grid modeling that predicts source impacts from emissions inventories, emissions modeling, meteorological simulations, and chemical transport modeling (Wagstrom et al., 2008). While there are clear benefits to source-oriented methods, the results are limited by uncertainties in emissions, errors and biases in meteorological

simulations, grid resolution, and uncertainties and simplifications in the representation of atmospheric chemistry.

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

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

2. Methods

2.1. PM_{2.5} chemical speciation data

Two monitoring networks in the U.S. Pacific Northwest routinely collect chemically speciated 24-h integrated PM_{2.5} mass: the Chemical Speciation Network (CSN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network. The CSN is one of several urban and suburban monitoring networks funded by the U.S. Environmental Protection Agency (EPA) and operated by state and local agencies. CSN samplers are operated on a daily, every third day, or every sixth day schedule depending on the site. Quality assured CSN data are housed in EPA's Air Quality System (AQS) database. Detailed information about the CSN network and AQS database can be found on the Technology Transfer Network, Ambient Monitoring Technology Information Center section of EPA's web site (<http://www.epa.gov/ttn/amtic/>). The IMPROVE network is a chemically speciated PM_{2.5} monitoring program associated with the Regional Haze Rule of the U.S. Clean Air Act. IMPROVE samplers are typically sited at remote locations and are operated on a once every third day schedule. Quality assured IMPROVE data are housed in The Visibility Information Exchange Web System (VIEWS). Detailed information about the IMPROVE network and VIEWS can be found on the IMPROVE web site (<http://vista.cira.colostate.edu/improve/>). While measurement and analytical techniques used to quantify aerosol ionic and elemental concentrations are comparable between the two networks (Chen et al., 2010), elemental and organic carbon (EC and OC, respectively) data have historically been difficult to compare because of differences in carbon sampler design and analytical measurement protocols (Chow et al., 2004). To address this problem and better harmonize the two monitoring networks, EPA replaced all CSN carbon samplers between 2007 and 2009 to match

those of the IMPROVE program and also switched to IMPROVE-based carbon analytical measurement protocols at the same time (U.S. EPA, 2009).

Information about the monitoring sites analyzed in this work is listed in Tables 1 and 2, for CSN and IMPROVE sites, respectively, and also shown in Fig. 1. The start date for data used from the CSN monitors was based on when each site converted to IMPROVE-based carbon sampling methods and the start date for IMPROVE monitors was January 2007. The end date for both networks represents the most recent data available at the time data were extracted. The date range for data from both monitoring networks was chosen to maximize the total amount of available samples from each monitor and to cover the broadest period of temporal overlap after the change in CSN carbon methods.

2.2. Data preparation and treatment

Prior to source apportionment analysis the downloaded datasets were processed to correct for field blanks (CSN only), missing/negative values, data completeness issues, poor signal-to-noise (S/N) ratios, and species double counting. The uncertainty of each reported measurement was also estimated. A detailed discussion of data preparation and treatment is provided in the supplementary materials Section S.1.

2.3. Source apportionment

PMF source apportionment modeling was performed using EPA PMF 3.0 (Norris et al., 2008). A discussion of the mathematical equations underlying EPA PMF can be found in Paatero and Hopke (2003) and Norris et al. (2008). Data from each CSN and IMPROVE monitoring site was modeled independently. In each case, the model was run in the robust mode with 20 repeat runs to insure the model least-squares solution represented a global rather than local minimum and the rotational FPEAK variable was held at the default value of 0.0. The model solution with the optimum number of factors was determined somewhat subjectively based on inspection of the factors in each solution, but also from the quality of the least-squares fit (analysis of Q_{Robust} and Q_{True} values) in the model output. The scaled residuals for final model solutions were generally normally distributed, falling into the recommended range of +3 to -3.

PMF is a receptor model that approaches the task source apportionment through 'factor analysis', that is, the use of mathematical constructs to reduce the overall dataset into a smaller number of 'factors' that can explain the majority of data variability. PMF 'factors' are then related to 'sources' by comparing the chemical composition of factors with chemical profiles from anthropogenic source test data or the natural environment (e.g., soil, sea salt). PMF does not typically provide an exact source

apportionment result because factors are often associated with multiple sources. A PMF factor could represent a single source (e.g., industrial point source), multiple sources with similar emissions profiles (e.g., gasoline vehicles), or multiple sources with insufficient variability in the observed dataset or insufficient chemical uniqueness to be separated by the model (e.g., sulfate rich, nitrate rich). PMF factors are also not necessarily mutually exclusive. For example, a factor identified as predominantly ammonium sulfate aerosol is likely from a combination of primary and secondary sources including diesel engines and industrial facilities, even though these sources may also have separately identified PMF factors. Hence, caution should be used in interpreting factor source classifications too literally or with exclusivity.

3. Results and discussion

3.1. Source apportionment results

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

The uncertainty and robustness of the PMF results were assessed through a bootstrap analysis, where the original data was resampled and the bootstrap PMF results are compared to the original. The number of bootstrap model runs that can be mapped back to the original result is a measure of solution robustness and the variability in bootstrap mass allocations is a measure of uncertainty. The PMF result for each monitoring site was subjected to 200 bootstrap model runs and the factor mapping results for all sites and factor types are provided in the supplementary materials Section S.5. The RFO factor results were found to be generally robust with an average of 96% of bootstrap results mapping back to the original RFO factor. The variability in bootstrap factor mass allocations and percentage of species allocations for RFO factors are provided in the supplementary materials Section S.6. Additionally, because the distribution of sulfur mass between factors will have a significant influence on the amount of mass attributed to RFO, the G-space plots between RFO and sulfur/sulfate rich factors were examined when both factors were identified at a monitoring site. Oblique edges in the G-space plot, if present, suggest that the solution obtained by the given rotation may not be the most

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

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	Jarbridge 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

plausible. Of the 7 sites indicating both RFO and sulfate rich factors, only the OLYM IMPROVE site had an apparent oblique edge in the G-space plot between these two factors (G-space plots for these 7 sites are provided in the supplementary materials Section S.7). This oblique edge was insensitive to variations in rotation using the model FPEAK variable, suggesting the original OLYM site solution has limited rotational freedom.

While the focus of this work is the RFO factor results and the connection to marine vessels, it is worth briefly discussing some of the similarities and differences between PMF results for CSN and IMPROVE sites as a whole as well as comparing these results to those of other published studies. Tables 3 and 4 show that there were 15 different factor types found for CSN sites and 17 different

factor types for IMPROVE sites. The larger number of factor types found across IMPROVE sites is understandable given that there are twice as many IMPROVE as CSN sites and the IMPROVE sites represent a wider geographic scope. That said, there were an average of 9 factors found at CSN sites compared to only 6 at IMPROVE sites, which is indicative of urban areas typically having a larger number of PM_{2.5} sources relative to the rural IMPROVE network.

Between the two networks, there were nine factor types that had similar enough chemical profiles to be given the same factor names in both the CSN and IMPROVE results (see supplementary materials Sections S.2–S.4). Of these nine factor types, only three were commonly found at both CSN and IMPROVE sites throughout the U.S. Pacific Northwest: sulfate/sulfur rich, nitrate rich, and soil. However, for coastal and near coastal monitoring sites (sites west of the Cascade Mountain range), there were three additional factors common to both CSN and IMPROVE monitoring locations in the U.S. Pacific Northwest that can be clearly associated with a particular source of pollution, that is, marine vessels (see Section 3.2).

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

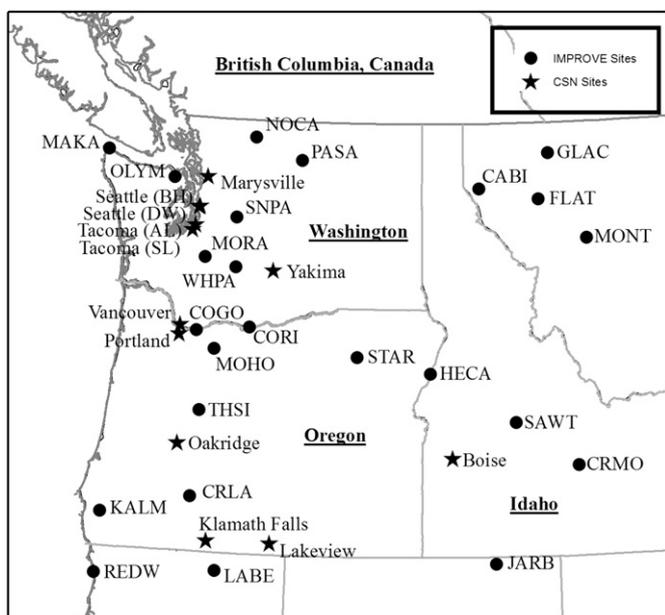


Fig. 1. CSN and IMPROVE PM_{2.5} monitoring sites in the U.S. Pacific Northwest.

Table 3Annual average PM_{2.5} (µg m⁻³) and source apportionment results for PMF factors found at CSN 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

Table 4Annual average PM_{2.5} (µg m⁻³) 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

of 29% for the same periods (Port of Seattle, 2012). The reported increase in vessel activity is consistent with the increased RFO contribution found in this work.

Source apportionment results for the Seattle Duwamish monitoring site were reported by Kim and Hopke (2008a) for data covering the period of 2000–2005. They reported 11 PMF factors and found an average RFO contribution of $0.44 \mu\text{g m}^{-3}$. In this work, RFO was found to contribute an average of $1.1 \mu\text{g m}^{-3}$ at the Duwamish site for the period of 2007–2011. The higher RFO contribution reported here, over that of Kim and Hopke, can be partially explained by the increased port activity reported above. Additionally, the slightly higher RFO impacts at the Duwamish site over Beacon Hill reported in this work are consistent with the Duwamish site being both closer to Port of Seattle facilities and sited in the Duwamish valley, nearer the same elevation as the Port, compared to the Beacon Hill site.

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

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

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

3.2. Results for RFO and linkage to marine vessels

3.2.1. PMF results for RFO and comparison with source test data

Chemically speciated source profiles of primary $\text{PM}_{2.5}$ emissions covering a wide range of sources are available through the EPA SPECIATE database Version 4.3 (Hsu and Divita, 2011). The SPECIATE database has two emissions profiles for marine vessels using RFO, profiles 5676 and 5674. The V:Ni ratio in these profiles is 2.6 and 2.3, the weight percent of the sum of V and Ni is 2.5% and 2.2%, the weight percent of sulfate is 44% and 38%, and the weight percent OC is 1.7% and 11.3%, respectively. Additionally, a V:Ni ratio of 4.5 was reported by Agrawal et al. (2008) for marine vessels using RFO. While not reported in the SPECIATE database, marine vessels using RFO also emit volatile organic compounds (VOCs), NO_x , and large amounts of SO_2 due to the very high fuel sulfur content (Agrawal et al., 2008; Moldanova et al., 2009). Downwind of marine vessel emissions, it is expected that the ratio of V:Ni will be maintained but the absolute concentration of sulfate, OC, V, and Ni associated with this source may shift as SO_2 , VOCs, and other co-

emitted gases undergo photochemistry and gas-to-particle conversion.

Of the 36 sites analyzed in this study, 14 sites had factors that matched the chemical signature of RFO based on high sulfur/sulfate content in the chemical profile, attribution of a significant percentage of measured V and Ni to the factor, and a V:Ni ratio near that reported for RFO. Figs. 2 and 3 show the RFO PMF factor chemical profiles from CSN and IMPROVE sites, respectively. The ratio of V:Ni in these factors ranged from 2.4 to 3.9 for CSN sites and 2.3–5.4 for IMPROVE sites and had an average value of 3.0 and 3.2 for CSN and IMPROVE sites, respectively. A map indicating the location of sites where RFO factors were found is shown in Fig. 4. It should be noted that while all RFO factors have a significant sulfur/sulfate mass attribution, there is large variability in the amount of OC, EC and nitrate attributed to the factors. Some of this variation can be attributed to differences in photochemistry effecting upwind RFO source emissions, but some is also likely associated with factor uncertainty.

3.2.2. Comparison with 2008 emissions inventories

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

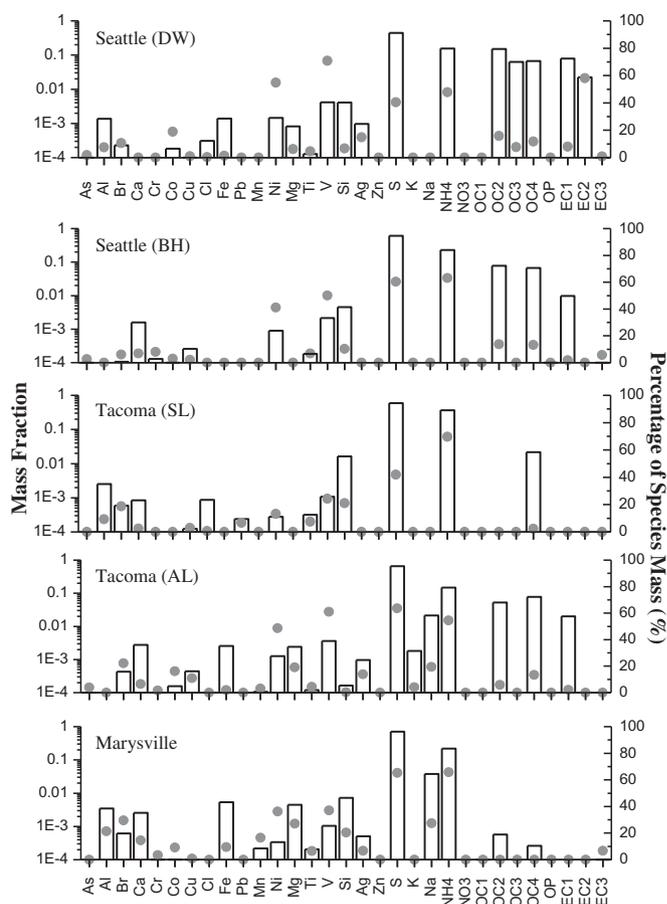


Fig. 2. Residual fuel oil combustion PMF factors for CSN monitoring sites. Vertical bars indicate the fractional contribution (left vertical scale) of chemical species to factor composition, gray dots indicate the percent of chemical species (right vertical scale) observed at each location attributed to residual fuel oil.

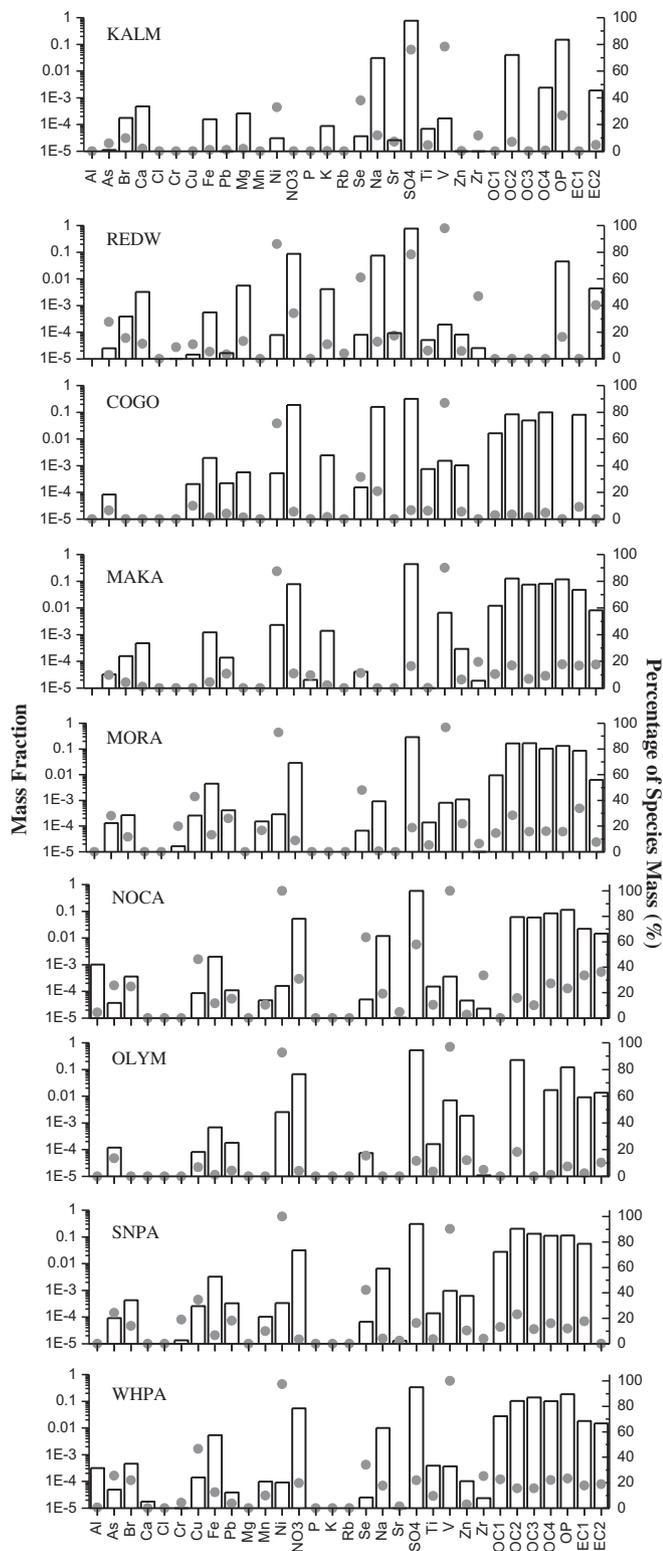


Fig. 3. Residual fuel oil combustion PMF factors for IMPROVE monitoring sites. Vertical bars indicate the fractional contribution (left vertical scale) of chemical species to factor composition, gray dots indicate the percent of chemical species (right vertical scale) observed at each location attributed to residual fuel oil.

estimates of primary particulate Ni emissions and SO₂ gaseous emissions (primary particulate V and sulfate are not reported). While comparison of county level emissions estimates with PMF results can be informative, it should also be noted that county level

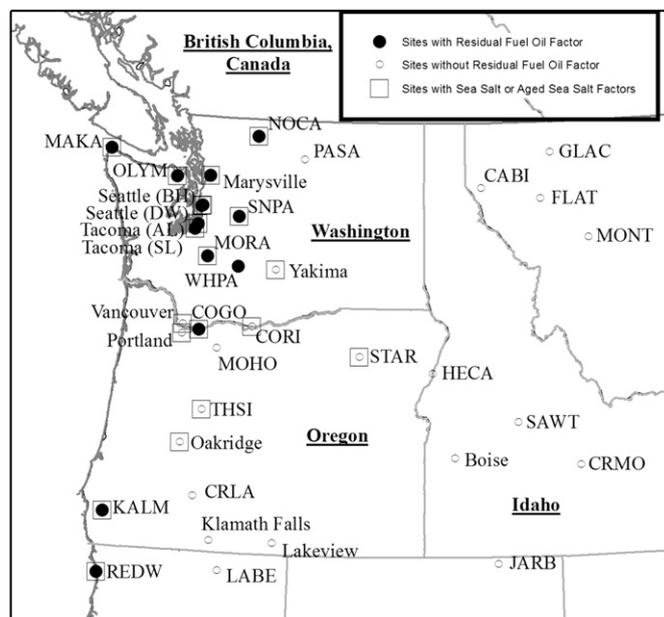


Fig. 4. Monitoring sites where PMF factors for residual fuel oil were found and monitoring sites where PMF factors for either sea salt or aged sea salt were found.

emissions represent a broad geographic area whereas the PMF results are specific to a particular monitoring station and the NEI represents emissions from 2008 whereas the PMF results are for 2007–2011. Differences between the two can also be caused by differences in the atmospheric lifetimes of emissions, uncertainties in the emissions estimates, and uncertainties in the PMF results.

For Ni emissions the 2008 NEI indicates that Washington, Oregon and Idaho emitted 30,017 lbs, 5617 lbs, and 1933 lbs, respectively. Of those statewide totals, commercial marine vessels contributed 86% (25,901 lbs), 55% (3107 lbs), and 0% (0 lbs), respectively.

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

Smaller sources of Ni in the 2008 NEI for Oregon are coal fired electrical generation (20%, 1113 lbs) and non-ferrous metal industrial processes (9%, 500 lbs). Oregon had one coal fired power plant in operation from 2007 to 2011, the Portland General Electric plant in Boardman Oregon. The SPECIATE database lists 5 emissions profiles from coal fired power plants using the same emissions control technology as the Boardman plant. The V:Ni emissions ratio in these profiles ranged from 1.6 to 3.6, with an average value of 2.2. While these V:Ni ratios are similar to that of RFO, it is unlikely that the Boardman plant is contributing to the factors identified as RFO because of its location. Boardman Oregon lies along the Columbia river approximately 100 km east of the CORI IMPROVE monitor and 200 km east of the COGO IMPROVE monitor (both CORI and COGO are also along the Columbia river). However, no RFO factor was identified at the closer CORI site whereas RFO was identified at the farther COGO site. Regarding the other smaller source of Ni in Oregon, non-ferrous metal industrial processes, all of these emissions are attributed to one source located outside of Albany OR. While there is no representative emissions profile for this source available in the SPECIATE database, its location also suggests that it is unlikely to be contributing to factors identified as RFO in this

work. This source lies 125 km southwest and 250 km north of the COGO and KALM IMPROVE monitors, respectively, and closer monitors (Portland, MOHO, THSI, Oakridge, and CRLA) show no RFO impacts.

For SO₂ emissions the 2008 NEI indicates that Washington, Oregon and Idaho emitted 36,902 tons, 26,697 tons, and 20,654 tons, respectively. Of those statewide totals, commercial marine vessels contributed 38% (14,094 tons), 6% (1682 tons), and 0% (0 tons), respectively.

Within the 12 Washington State counties bordering Puget Sound and the Strait of Juan de Fuca, commercial marine vessels contributed 49% (12,370 tons) of total SO₂ emissions. Smaller sources of SO₂ in these counties came from industrial point sources including non-ferrous metal facilities in Whatcom County (18%, 4523 tons), petroleum refineries in Whatcom and Skagit Counties (6%, 1552 tons), and industrial oil boilers in Whatcom, Skagit, Clallam and Jefferson Counties (5%, 1389 tons). On-road and non-road mobile sources contributed a combined 8% (1968 tons) of SO₂ emissions in these counties.

In the 5 Oregon and Washington counties bordering the Columbia River near Portland Oregon, commercial marine vessels contributed 39% (2551 tons) of total SO₂ emissions. Smaller sources of SO₂ in these counties came from industrial sources including pulp and paper manufacturing (29%, 1891 tons) and industrial boilers using biomass fuel (7%, 481 tons). On-road and non-road mobile sources contributed a combined 9% (564 tons) of SO₂ emissions in these counties.

For the 3 coastal counties in Oregon and California in the proximity of the KALM and REDW IMPROVE monitoring sites, commercial marine vessels contributed only 6% (114 tons) of total SO₂ emissions. The majority of SO₂ emissions in these counties were attributed to wild and prescribed fires (83%, 1625 tons). While commercial marine vessel SO₂ contributions for these counties is in apparent disagreement with the PMF results at the KALM and REDW sites, it should be noted that the 2008 NEI attributes only near-coastal commercial marine emissions to states and counties (default is emissions within 3 nautical miles, U.S. EPA, 2012b). Hence, the coastal county emissions inventories do not fully account for all commercial marine vessel activity off coastal waters.

The NEI data for both Ni and SO₂ indicate that 2008 commercial marine vessel emissions were approximately an order of magnitude larger in Washington State compared to Oregon, and nonexistent in Idaho. These emissions inventory data indicate that both the relative magnitude and spatial allocation of commercial marine vessel emissions in the 2008 NEI are consistent with the number and location of monitoring sites where PMF factors for RFO were found in Washington and Oregon (Fig. 4).

3.2.3. Spatial extent of residual fuel oil factors

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

3.2.4. Monthly average contributions from marine vessels using RFO

Based on the evidence presented above, RFO factors identified in this work are attributed to marine vessel emissions. Fig. 5 shows the monthly average PM_{2.5} mass attributed by PMF to RFO emissions from marine vessels for the 14 monitoring sites where this factor was identified. The monthly averages shown in Fig. 5

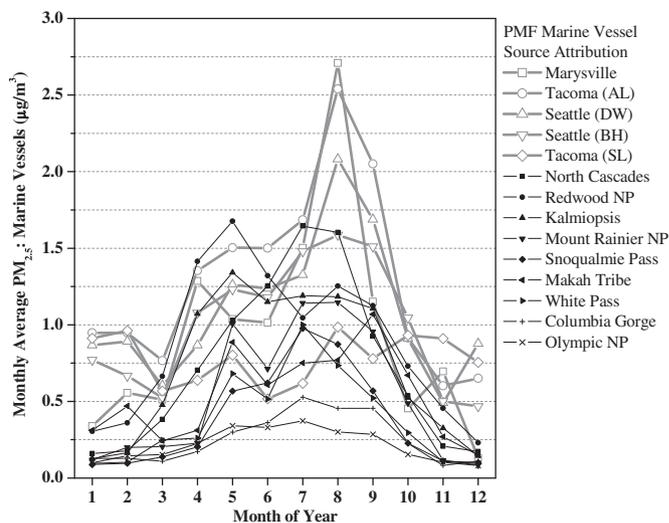


Fig. 5. Monthly average PM_{2.5} (µg m⁻³) attributed to marine vessels using residual fuel oil for 14 monitoring sites in the U.S. Pacific Northwest.

represent multiyear averages based on the monitoring periods listed in Tables 1 and 2. The bold lines in Fig. 5 represent urban CSN monitors, generally have the highest mass impacts throughout the annual cycle, and are consistent with the majority of these monitors being close to major marine vessel ports where there is a higher density of marine vessel emissions compared to IMPROVE monitors. All monitoring sites show a seasonal cycle in marine vessel impacts, with lower impacts in winter months (monthly average PM_{2.5} between 0.1 µg m⁻³ and 0.9 µg m⁻³ in January) and higher impacts in summer months (monthly average PM_{2.5} between 0.3 µg m⁻³ and 2.7 µg m⁻³ in August). This seasonal pattern is consistent with more photochemical production of secondary PM_{2.5} from co-emitted gaseous emissions in summer, but also to a smaller extent reflects an average summer increase in cargo traffic of 12% as reported by the Port of Metro Vancouver and the Port of Tacoma (2008–2011 and 2009–2011 data, respectively; Port Metro Vancouver, 2012; Port of Tacoma, 2012) and summertime cruise ship activity. The seasonal pattern may also be influenced by seasonal changes in the prevailing wind patterns. Fig. 6 shows the percent contribution of RFO emissions from marine

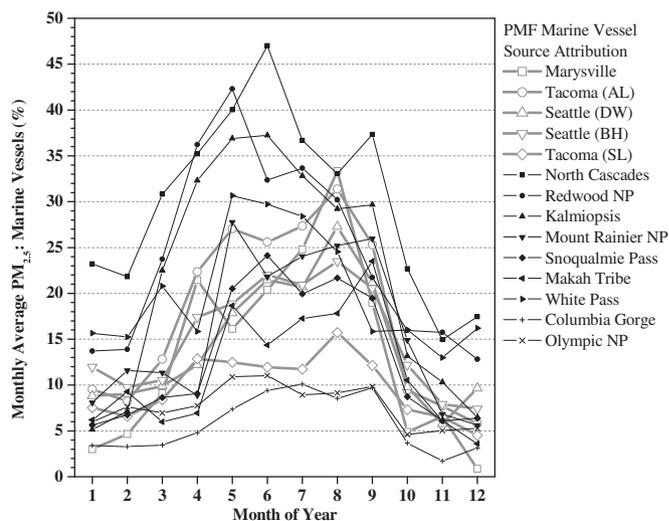


Fig. 6. Monthly average percent of total PM_{2.5} attributed to marine vessels using residual fuel oil for 14 monitoring sites in the U.S. Pacific Northwest.

vessels to total monthly average PM_{2.5} for the 14 monitoring sites where this factor was identified. The seasonal cycle of percent contributions shows smaller contributions from marine vessels in winter (between 3% and 23% of total monthly average PM_{2.5} in January) and larger contributions in summer (between 9% and 47% of total monthly average PM_{2.5} in June). The highest percent impacts from marine vessel emissions throughout the seasonal cycle occur at comparatively clean IMPROVE sites, which is indicative of relatively few anthropogenic sources impacting the remote IMPROVE sites compared to the urban CSN locations.

4. Conclusions

This work presents a regional-scale multi-site source apportionment analysis of PM_{2.5} using PMF on data from 36 urban and rural monitoring sites in the U.S. Pacific Northwest covering the period 2007–2011. Results for 14 of the 36 sites indicated a RFO factor that is associated with marine vessel emissions. Most sites west of the Cascade Mountains indicated some level of impact from marine vessel emissions. The spatial extent of marine vessel emissions impacts was found to be similar to the other marine related aerosols, sea salt and aged sea salt, and consistent with emissions inventories. Monitoring sites indicating marine vessel emissions impacts show a seasonal cycle, with lower impacts in winter months (monthly average PM_{2.5} between 0.1 µg m⁻³ and 0.9 µg m⁻³ in January) and higher impacts in summer months (monthly average PM_{2.5} between 0.3 µg m⁻³ and 2.7 µg m⁻³ in August). The percent contribution to total monthly average PM_{2.5} from marine vessels had a similar seasonal cycle, with smaller contributions in winter (between 3% and 23% of total monthly average PM_{2.5} in January) and larger contributions in summer (between 9% and 47% of total monthly average PM_{2.5} in June). These results for marine vessels, representing data just prior to the implementation of the North American ECA, provide a baseline assessment of marine vessel emissions impacts from which progress in ECA emissions reductions can be assessed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2012.11.067>.

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