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Source characterization of ambient fine particles at multiple sites in the Seattle area

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ABSTRACT

To identify major PM_{2.5} (particulate matter $\leq 2.5 \mu\text{m}$ in aerodynamic diameter) sources with a particular emphasis on the ship engine emissions from a major port, integrated 24 h PM_{2.5} speciation data collected between 2000 and 2005 at five United State Environmental Protection Agency's Speciation Trends Network monitoring sites in Seattle, WA were analyzed. Seven to ten PM_{2.5} sources were identified through the application of positive matrix factorization (PMF). Secondary particles (12–26% for secondary nitrate; 17–20% for secondary sulfate) and gasoline vehicle emissions (13–31%) made the largest contributions to the PM_{2.5} mass concentrations at all of the monitoring sites except for the residential Lake Forest site, where wood smoke contributed the most PM_{2.5} mass (31%). Other identified sources include diesel vehicle emissions, airborne soil, residual oil combustion, sea salt, aged sea salt, metal processing, and cement kiln. Residual oil combustion sources identified at multiple monitoring sites point clearly to the Port of Seattle suggesting ship emissions as the source of oil combustion particles. In addition, the relationship between sulfate concentrations and the oil combustion emissions indicated contributions of ship emissions to the local sulfate concentrations. The analysis of spatial variability of PM_{2.5} sources shows that the spatial distributions of several PM_{2.5} sources were heterogeneous within a given air shed.

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1. Introduction

Increased trade with the countries on the Pacific Rim and transport of crude oil from Alaska have resulted in significant ship traffic along the west coast of the United States (US) (Corbett and Fishbeck, 2000). There is relatively little reported on the impacts of the particulate emissions from compression–ignition ship engines. Ship engines typically use the lowest cost fuel available and thus commonly use residual oil (also referred to as no. 6 or Bunker-C oil) as their primary fuel. Residual oil contains significant concentrations of sulfur as well as trace metals, particularly V and Ni (Osan et al., 2000).

Primary ship emissions have been previously examined for sulfur dioxide (SO₂) and nitrogen oxides (NO_x) because of their potential for cloud formation in ship trails. There are a number of modeling efforts to estimate the impacts of ship emissions (e.g., Corbett et al., 1999; Corbett and Fishbeck, 2000; Endresen et al., 2003). However, all of the results were based on emission models and there was no direct information on the elemental composition of typical ship emissions.

The US Environmental Protection Agency in conjunction with state and local air quality agencies have been operating multiple Speciation Trends Network (STN) PM_{2.5} (particulate matter $\leq 2.5 \mu\text{m}$ in aerodynamic diameter) monitoring sites in Seattle since 2000, with several of them deployed around the Port of Seattle. Therefore, there are data available for receptor modeling that could potentially resolve contributions from combustion sources including ship engine emissions to the measured PM_{2.5} concentrations.

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PM_{2.5} chemical speciation data collected at the Beacon Hill monitoring site in Seattle have been used for several source apportionment studies. PM_{2.5} speciation data collected by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network were analyzed by positive matrix factorization (PMF2) (Maykut et al., 2003) and multilinear engine (ME2) (Kim et al., 2004). ME2 (Paatero, 1999) was applied to the analyses of PM_{2.5} speciation data collected by STN combined with particle size distribution data (Larson et al., 2006) and volatile organic carbon compound concentration data (Wu et al., 2007). However, PM_{2.5} speciation data collected at the other multiple STN sites in Seattle area have not been utilized in the source apportionment studies. It was the objective of this study to identify major PM_{2.5} sources with a particular emphasis on the ship engine emissions by analysis of the data collected at the multiple STN monitoring sites located in the Seattle area using PMF2.

2. Experiment

2.1. Data collection

The analyzed PM_{2.5} samples were collected by Reference Ambient Air Sampler (Andersen Instruments, Smyrna, GA) on a one-in-six day schedule at the four STN monitoring sites (Lake Forest, Olive St., Duwamish, Georgetown) and by a Mass Aerosol Speciation Sampler (URG, Chapel Hill, NC) on a one-in-three day schedule at Beacon Hill monitoring sites located in Seattle, WA and the surrounding area as shown in Fig. 1.

The Lake Forest monitoring site (AIRS code: 530330024) is located 20 km north of downtown Seattle. The area to the north and west of the site is residential. Local roads are situated to the southeast and northeast of

the site. The Olive St. monitoring site (AIRS code: 530330048) is located at downtown Seattle. Interstate highway 5 is located to the east of the site. The Beacon Hill monitoring site (AIRS code: 530330080) is located on a hilltop, 99 m above sea level. This monitoring site is located 5 km southeast of downtown Seattle. The area to the immediate north and east is residential. Highways 90 and 5 are situated about 2 km north and 1 km west of the site, respectively. The Duwamish (AIRS code: 530330057) and Georgetown (AIRS code: 530330032) monitoring sites are located within an industrial area 6 and 8 km south of the downtown Seattle, respectively. The Port of Seattle, container shipping, and warehousing areas are located north, northwest, and west of these sites and highways 5 and 99 are situated close to these sites.

Wind data measured at each site were used except for the Olive St. and Georgetown sites. For the Olive St. and Georgetown sites, wind data measured at the Beacon Hill and Duwamish sites, respectively, were used. The chemical analyses of the STN PM_{2.5} filters were described in detail by Kim et al. (2005a).

The OC artifact concentration was estimated following the method of Tolocka et al. (2001), in which the intercept of the regression of OC concentrations against PM_{2.5} concentrations is used as the blank value. Carbon denuders that minimize positive sampling artifact caused by adsorption of gaseous organic materials were not included upstream of the quartz filters in the STN samplers and the original STN data were not blank collected. For the OC artifact estimation, samples for which PM_{2.5} or OC data were not available were excluded before the regression between PM_{2.5} and OC concentration. Outliers in the measured mass concentrations were identified by comparing co-located PM_{2.5} data measured by STN and Federal Reference Method (FRM) samplers. The intercept in PM_{2.5} regression against OC concentration was considered to be

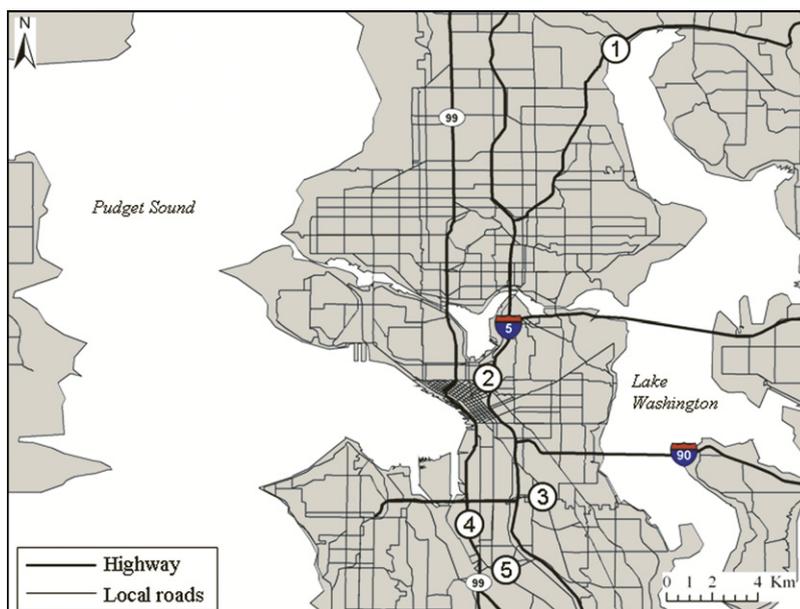


Fig. 1. Location of the STN monitoring sites: (1) Lake Forest, (2) Olive St., (3) Beacon Hill, (4) Duwamish, and (5) Georgetown.

OC artifact concentrations (Lake Forest: $0.51 \mu\text{g m}^{-3}$; Olive St.: $1.51 \mu\text{g m}^{-3}$; Beacon Hill: $0.33 \mu\text{g m}^{-3}$; Duwamish: $0.27 \mu\text{g m}^{-3}$; Georgetown: $0.08 \mu\text{g m}^{-1}$) and the reported STN OC concentrations were corrected by subtracting the estimated OC artifact concentrations. Since prior to July 2003 the STN data were not accompanied by uncertainties, a comprehensive set of errors were estimated using the method of Kim et al. (2005a).

2.2. Source apportionment

PMF2 is a multivariate receptor model that estimates the source profiles and their contributions based on a weighted least square approach (Paatero, 1997). Detailed explanations and equations have been presented previously (Kim and Hopke, 2004a). To decrease the rotational ambiguity that produces an infinite number of possible combinations of source contribution and profile, PMF2 uses non-negativity constraint on the source contribution and profile. Also, the parameter FPEAK and index matrix Fkey, are used to control the rotations (Paatero et al., 2002). To determine the optimal solution, PMF2 is run with different values of parameter FPEAK as well as matrix Fkey within which the sum of scaled residuals remains relatively constant (Paatero et al., 2002, 2005).

For the application of PMF2, the measured concentrations below the method detection limit (MDL) values were replaced by half of the MDL values and their uncertainties were set at 5/6 of the MDL values. Missing concentrations were replaced by the geometric mean of the species and their accompanying uncertainties were set at four times of this geometric mean concentration (Polissar et al., 1998). In this study, samples for which $\text{PM}_{2.5}$ or OC data were not available or were below zero, or for which $\text{PM}_{2.5}$ or OC mass concentration had error flag were excluded from data set. To obtain a reasonable model fit, the fireworks samples collected at Beacon Hill site on 5 July, 2000, 1 January, 2001, 4 July, 2002, and 5 July, 2003 in which K, Ba, Ca, Cu, Pb, and Sr mass concentrations were unusually high were excluded. For the Georgetown data, the fireworks-impacted sample on 1 January, 2001 in which K and Sr concentrations were high was excluded. Overall,

11.1% of the original Lake Forest data, 4.5% of the Olive St data, 9.4% of the Beacon Hill data, 9.4% of the Duwamish data, and 20.3% of the Georgetown data were not included in this study.

To prevent double counting of species, S measured by X-ray fluorescence (XRF) was included since XRF S and ion chromatography (IC) SO_4^{2-} showed good correlations (slope = 2.5, $r^2 = 0.93$ for Lake Forest data; slope = 2.5, $r = 0.97$ for Olive St. data; slope = 2.7, $r^2 = 0.96$ for Beacon Hill data; slope = 2.5, $r^2 = 0.95$ for Duwamish data; slope = 2.7, $r = 0.97$ for Georgetown data). Also, IC Na^+ and IC K^+ were chosen due to the higher analytical precision compared to XRF Na and XRF K. Chemical species that have below MDL values more than 90% were excluded. For the Beacon Hill data, the mass concentrations of Ba, Ce, Cu, Eu, Ga, and La show step changes on March 2002 caused by the change of the analytical instrument from Chester Labnet to Research Triangle Institute. Those chemical species were not included in the analysis for the Beacon Hill data. Thus, a total of 185 samples and 30 species, 128 samples and 35 species, 546 samples and 28 species, 154 samples and 35 species, and 235 samples and 32 species collected between 2000 and 2005 were used for the Lake Forest, Olive St., Beacon Hill, Duwamish, and Georgetown, respectively.

$\text{PM}_{2.5}$ concentration from Teflon filter was included in the data as an independent variable to directly obtain the mass apportionment without the usual multiple regression. The utilization of $\text{PM}_{2.5}$ concentration as a variable is explained in Kim et al. (2003). To reduce the weight in the solution, the estimated uncertainties of species that have signal-to-noise (S/N) ratio between 0.2 and 2 (weak variable) and species that have below MDL values more than 50% were increased by a factor of five and a factor of three, respectively (Paatero and Hopke, 2003). The estimated uncertainties were increased by a factor of thirty for the samples for which mass concentration had error flags. In addition, to obtain physically reasonable PMF2 solution, the estimated uncertainties of OC, EC, and NH_4^+ (Lake Forest); OC, EC, and Zn (Olive St); OC and Zn (Georgetown) were increased three times. A summary of $\text{PM}_{2.5}$ speciation data and S/N ratios are provided in Tables S1–S5 in the Supporting Information.

Table 1
Average source contributions ($\mu\text{g m}^{-3}$) to $\text{PM}_{2.5}$ mass concentration

Sources	Average source contribution (standard error)				
	Lake Forest	Olive St.	Beacon Hill	Duwamish	Georgetown
Secondary nitrate	1.19(0.10)	2.70(0.25)	1.53(0.07)	2.87(0.25)	2.00(0.17)
Secondary sulfate	1.70(0.10)	1.84(0.15)	1.51(0.05)	2.48(0.18)	1.77(0.09)
Wood smoke	3.07(0.27)	0.75(0.05)	0.67(0.03)	1.21(0.10)	1.86(0.13)
Motor vehicle	2.67(0.17)				
Gasoline vehicle		1.38(0.09)	2.61(0.09)	1.59(0.13)	1.80(0.12)
Diesel emissions		0.91(0.06)	0.45(0.02)	0.65(0.06)	0.18(0.02)
Airborne soil	0.23(0.03)	0.99(0.07)	0.23(0.01)	0.70(0.08)	0.49(0.06)
Oil combustion		0.39(0.04)	0.47(0.03)	0.44(0.08)	
Aged sea salt	0.93(0.05)	0.59(0.05)	0.55(0.02)	0.48(0.03)	1.15(0.06)
Sea salt	0.27(0.04)	0.40(0.09)	0.17(0.02)	0.44(0.04)	0.24(0.04)
Metal processing		0.50(0.05)	0.20(0.01)	0.78(0.07)	0.14(0.04)
Cement kiln				0.57(0.05)	

The conditional probability function (CPF) (Kim and Hopke, 2004b) analysis is a method to estimate the potential directions of the local source impacts and has been shown to be useful in various source apportionment studies (Zhou et al., 2005; Kim and Hopke, 2006; Xie and

Berkowitz, 2007). In this study, CPF was calculated for each source using the PMF2 source contributions coupled with wind information. To minimize the averaging effect of diurnal wind changes, the same daily contribution was assigned to each hour of a given day to match the hourly

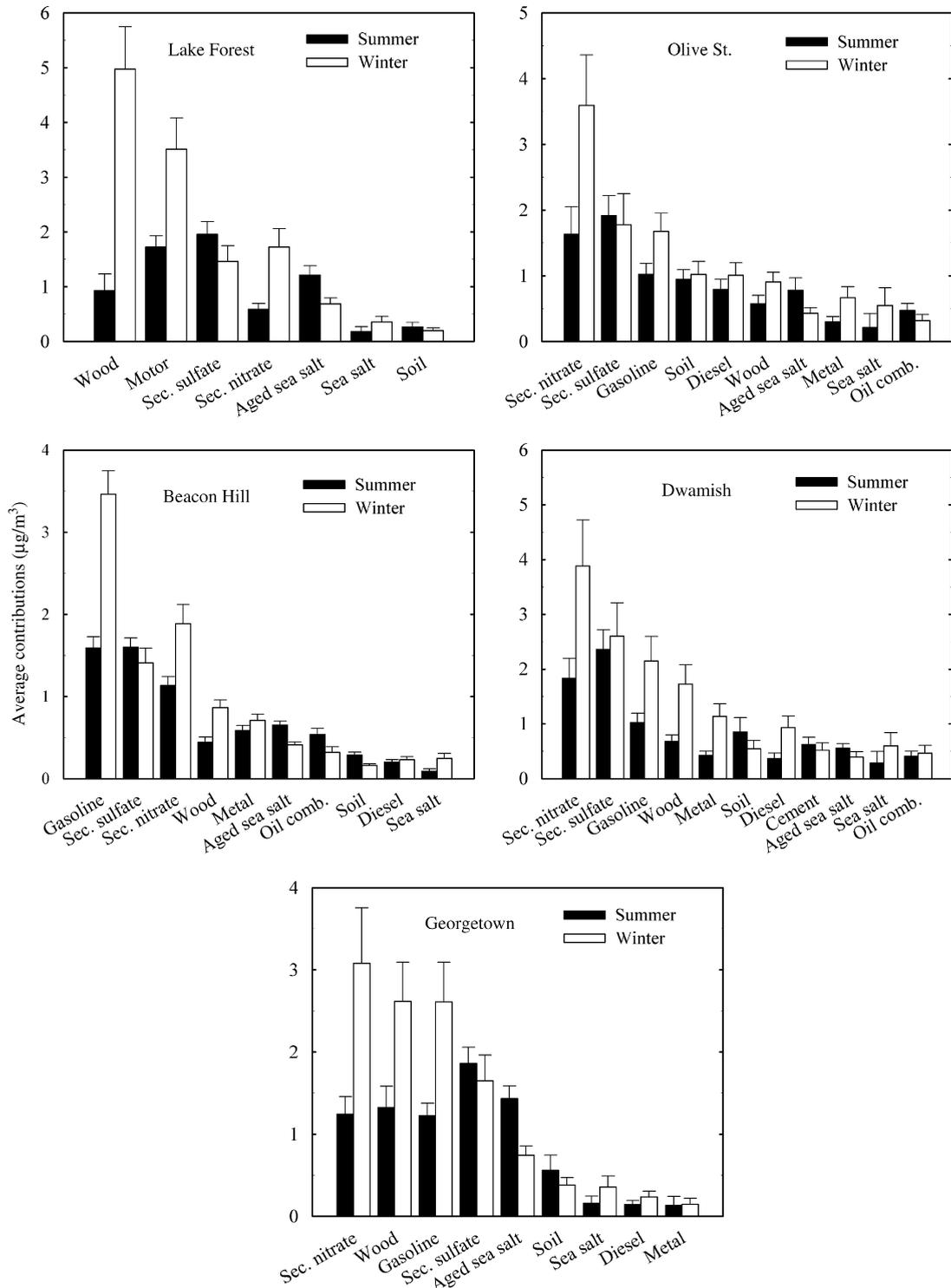


Fig. 2. Seasonal comparison of source contributions to PM_{2.5} mass concentration (mean ±95% distribution).

wind data. Calm winds ($<1 \text{ m s}^{-1}$) were excluded from this analysis. A threshold criterion of the upper 50% and 24 wind sectors of the 15° were chosen to show the potential direction of the sources based on the tests with different percentiles of the contribution and different azimuths of wind sectors.

3. Results and discussion

To obtain interpretable PMF2 solutions, different numbers of sources, FPEAK values, and Fkey matrices were tested with the final choice based on the evaluation of the resulting source profiles as well as the quality of the chemical species fits. Also, the global optimum of the

solutions were tested by using multiple random starts in the iterative fitting process.

Seven- and ten-source models with values of FPEAK = 0 provided the most physically interpretable solutions for the Lake Forest and Olive St. data, respectively. A ten-source model with values of FPEAK = 0 and an Fkey matrix, an eleven-source model with FPEAK = -0.1, and a nine-source model with FPEAK = 0 and an Fkey matrix provided final solutions for the Beacon Hill, Duwamish, and Georgetown data, respectively. In the Fkey matrix for the Beacon Hill data, values of all elements were set to zero, except for a value of 5 for OC in diesel emissions. Values of all elements were set to zero in the Fkey matrix for the Georgetown data, except for a value of 4 for OC in diesel emissions. The average source

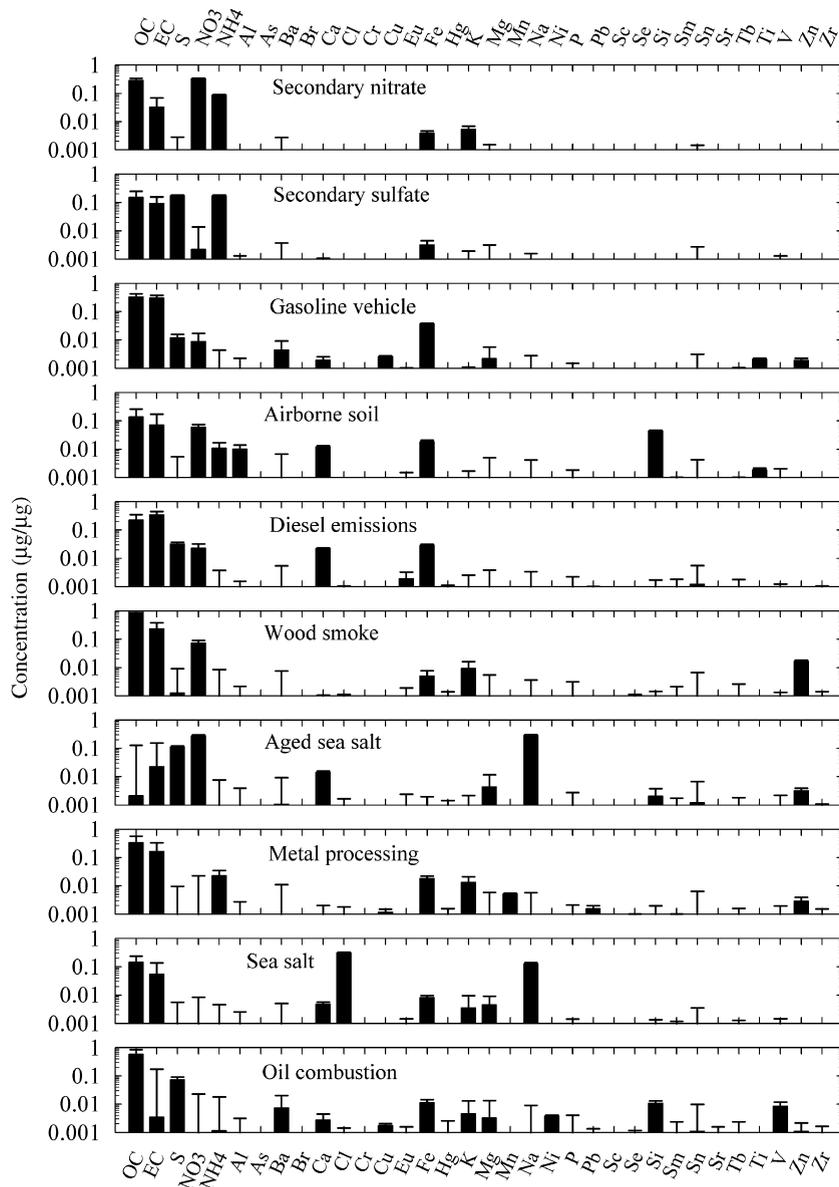


Fig. 3. Source profiles deduced from PM_{2.5} samples measured at Olive St. (prediction ± standard deviation).

contributions of each source to the $PM_{2.5}$ concentrations are provided in Table 1.

As shown in Fig. S1 in the Supporting Information, comparisons of the daily reconstructed $PM_{2.5}$ contributions from all sources with $PM_{2.5}$ concentrations from Teflon filter show that the resolved sources effectively reproduce the measured values and account for most of the variation in the $PM_{2.5}$ concentrations. The averaged seasonal contributions from each source are compared (summer: April–September; winter: October–March) in Fig. 2. Source profiles and contributions deduced from the PMF analysis of the $PM_{<}$ samples measured at Olive St. are shown in Figs. 3 and 4, respectively, as typical results. The other source profiles, corresponding source contributions, weekday/weekend variations, and CPF plots are presented in Figs. S2–S19 in the Supporting Information.

The secondary nitrate particles contain high concentrations of NO_3^- and NH_4^+ . They account for 12–26% of the $PM_{2.5}$ concentration at five monitoring sites. As shown in Fig. 2, the secondary nitrate has a seasonal variation with maxima in winter when low temperature and high relative humidity help the formation of secondary nitrate particles. Secondary sulfate has a high concentration of SO_4^{2-} and NH_4^+ account for 17–20% of the $PM_{2.5}$ concentration at the five monitoring sites. The secondary sulfate shows seasonal variations with higher concentrations in summer when the photochemical activity is highest at all monitoring sites except Duwamish site. The winter-high seasonal variation at Duwamish site and the higher values of the averaged contribution of secondary sulfate particle than other sites shown in Table 1 suggest the existence of the local sulfate sources near the Duwamish site.

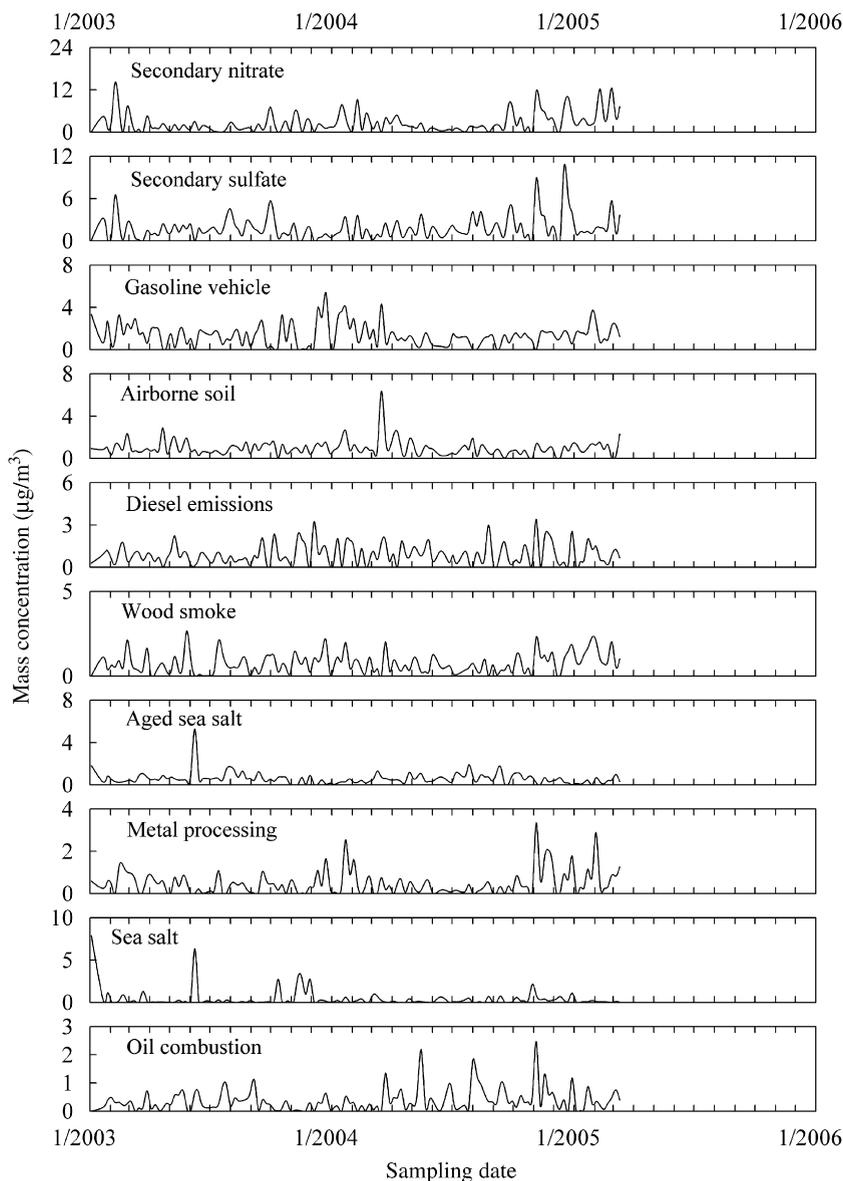


Fig. 4. Time series plot of source contributions at Olive St.

Wood smoke is characterized by OC, EC, and K contributing 7–31% to the $PM_{2.5}$ concentration. Wood smoke contributed the most at the residential Lake Forest site. This source has a winter-high seasonal trend shown in Fig. 2. There are no clear weekday/weekend variations in the wood smoke contributions.

It was possible to separate gasoline vehicle emissions from diesel emissions in Olive St., Beacon Hill, Duwamish, and Georgetown data. At the residential Lake Forest site, gasoline vehicle and diesel emissions were not separated and only a motor vehicle source profile was identified. It is likely that there was a sufficiently low impact of diesel emissions at this site, which precludes the separation of the two factors. Gasoline vehicle and diesel emissions are represented by high carbon concentrations: Gasoline vehicle and diesel emissions were identified on the basis of high OC concentration and high EC concentration, respectively. However, it was reported that diesel emissions from very slow speeds and in stop-and-go traffic have similar OC/EC ratios to typical gasoline vehicle emissions (Shah et al., 2004). There was significantly more EC than OC in the diesel emissions only for continuous traffic movement at higher speeds. Therefore, the diesel emissions extracted by PMF2 may represent only those emissions from diesel vehicles moving at high speed and diesel emissions from stop-and-go or slow-moving traffic are likely to be apportioned into the gasoline emissions. The average contributions from gasoline vehicles to $PM_{2.5}$ mass concentration were 13–31% and diesel emissions were 2–9%. Motor vehicle contributed 27% to $PM_{2.5}$ concentration measured at Lake Forest. The contributions from gasoline vehicle were higher at Beacon Hill than at the other sites. Diesel emissions contributed more at the Olive St. and Duwamish sites as shown in Table 1.

As shown in Figs. S10–S14 (Supporting Information), gasoline vehicle and diesel emissions show a weekday-high trend at most sites and this trend is stronger in diesel

emissions than in gasoline vehicle emissions. The CPF plot for motor vehicle identified in Lake Forest shown in Fig. S15 (Supporting Information) likely points to local roads located northwest and southeast of the site. For the Olive St., CPF plots pointing southeast suggest that gasoline and diesel emissions appear to have high contributions from interstate highway 5. The CPF plots for the Beacon Hill data indicate the gasoline emission impacts from mostly residential area (northeast, east, and southeast) and the diesel emission impacts from I-5 (west). The CPF plots for the gasoline and diesel emissions at Duwamish and Georgetown similarly point Port of Seattle (north) and highway 5 (southeast).

Airborne soil represented by Si, Fe, Al and Ca contributed 2–9% to the $PM_{2.5}$ concentration. Crustal particles could include wind-blown soil dust and dust re-suspended by road traffic that made carbon to be associated with airborne soil profile. Airborne soil contributed the most at Olive St. and Duwamish sites. Airborne soil does not show clear seasonal variation. At Olive St., Beacon Hill, and Duwamish sites, this source shows clear weekday-high variation. The elevated airborne soil contributions on 20 April, 2002 were identified at Lake Forest, Beacon Hill, and Georgetown sites. The backward trajectories in Fig. 5 showed that the elevated airborne soil contribution on 20 April, 2002 and two other peaks identified at Beacon Hill (12 April, 2000 and 22 April, 2001) were likely caused by Asian dust storm.

Oil combustion is characterized by high concentrations of carbons, S, V, and Ni, reflecting residual oil combustion for the utilities and industries. This source was identified at Olive St., Beacon Hill, and Duwamish sites and contributed 4–6% to the $PM_{2.5}$ concentrations. As shown in Fig. 6, the CPF plots of this source point to the Port of Seattle, suggesting the sources of the oil combustion are likely cargo ships, tugs, commercial harbor craft, and ferries. Oil combustion does not show strong seasonal variations. There are no clear weekday/weekend variations in this

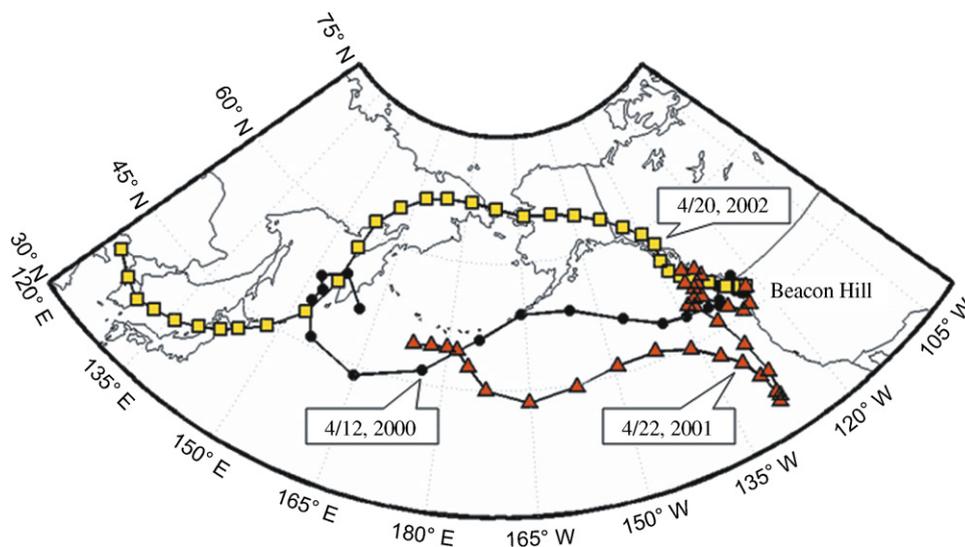


Fig. 5. Backward trajectories for days with high impacts of airborne soil arriving at Beacon Hill on 12 April, 2000 (circle), 22 April, 2001 (triangle), and 20 April, 2002 (square) calculated by the HYSPLIT model (NOAA Air Resource Laboratory).

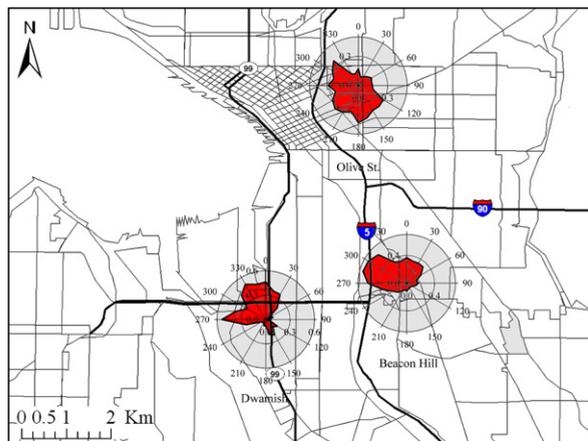


Fig. 6. Source directions of oil combustion identified by PMF and CPF analyses.

source at Beacon Hill and Duwamish sites. At Olive St. site, oil combustion shows weekend-high variation. The CPF at Olive St. also points toward the area in the harbor where cruise ships are boarded as compared with the cargo-loading areas at the south end of the port area.

The plots of source contributions are used to help identify the need for rotations in PMF2 (Paatero et al., 2005). Normally the assumption is made that the source contributions of the various sources should be independent of one another. However, in this case, correlations were found. Fig. 7 shows the oil combustion contributions plotted against the corresponding secondary sulfate particle contributions at three of the monitoring sites, Beacon Hill, Duwamish, and Olive Street. It can be seen that there is a relationship between the secondary sulfate particles and the primary V–Ni bearing oil combustion particles. The solid line represents an “edge” that demonstrates this relationship: the contribution of oil combustion source to the secondary sulfate formation (Henry, 2003). This edge does not appear in the plots for the other two sites. It is unlikely that the identical rotation would be required for all of these three sites. The slope of these edge lines is about 1.21 so that there appears to be $0.83 \mu\text{g m}^{-3}$ of sulfate for every $1 \mu\text{g m}^{-3}$ of primary oil combustion particles. It is suggested that this sulfate represents direct SO_3 emissions from the ship that appear as particulate sulfate at these three sites. Ship diesels typically burn high sulfur content residual oil (Bunker-C), and thus primary sulfate emissions can be anticipated. Modeling studies of oil combustion (Schneider and Bogdan, 2003) have suggested that between 2% to 9% of the emitted S could be in the form of SO. Combustion of residual oil will also produce particles containing vanadium (V) and nickel (Ni). Vanadium reacts with the oxygen from the combustion air surplus creating V_2O_5 that forms layers on the heat exchanger and other boiler and stack surfaces. The vanadium pentoxide acts as a catalyst in the temperature range of 500–800 °C, accelerating the SO_3 formation. SO_3 formed by this mechanism can exceed the amount produced in the flame by a factor of two or three (Adrian and Sonneschein, 1980). These

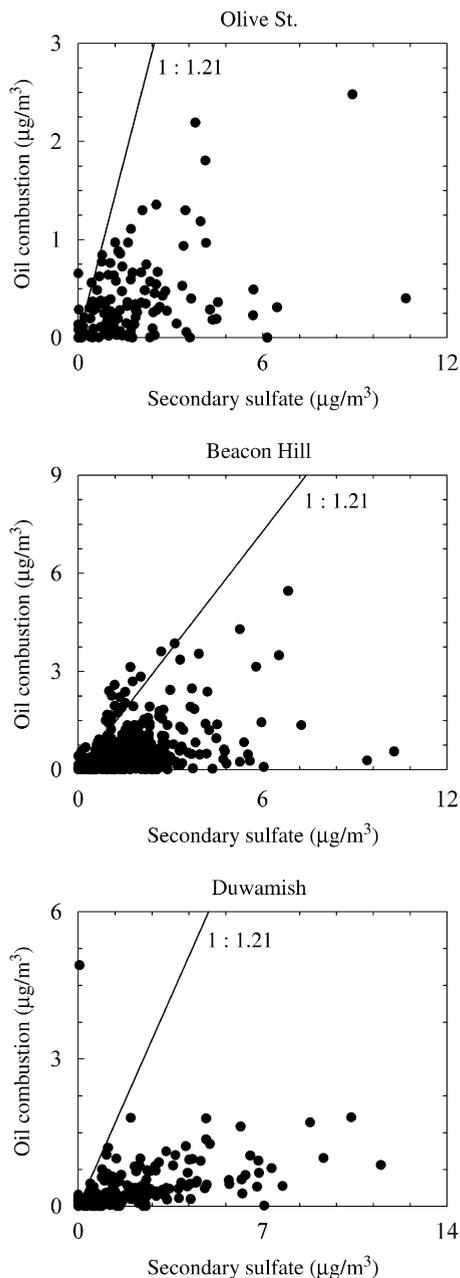


Fig. 7. The oil combustion contributions plotted against the secondary sulfate contributions obtained at the Olive St., Beacon Hill, and Duwamish STN sites in Seattle, WA.

plots for the three sites suggest the relative amounts of primary V–Ni bearing particles and sulfate coming from the ship emissions.

Sea salt is represented by its high concentration of Na^+ and Cl^- , accounting for 2–4% of the $\text{PM}_{2.5}$ concentration. This source shows a winter-high seasonal pattern, and does not show clear weekday/weekend variation. The CPF plot shows the contributions from the southwest, which is consistent at all five sites. Aged sea salt is characterized by its high concentration of Na^+ , SO_4^{2-} , and NO_3^- . The lack of Cl^- in the profile is caused by Cl^- displacement by acidic

gases. Aged sea salt accounts for 4–12% of the $PM_{2.5}$ concentrations at all monitoring sites. This particle shows a summer-high seasonal pattern. Aged sea salt identified at Duwamish shows a weekend-high variation.

A metal processing source characterized by carbons, Fe, and Zn was identified at Olive St., Beacon Hill, Duwamish, and Georgetown. This source accounts for 2–6% of the $PM_{2.5}$ concentration and has a strong winter-high seasonal pattern at Olive St. and Duwamish. A cement kiln identified by Ca and Si (US EPA, 2007) contributed 5% to the $PM_{2.5}$ concentration at the Duwamish site. Both metal processing and cement kiln show clear weekday-high trends.

The spatial relationships between source contributions at pairs of sites were determined using coefficients of divergence (COD) (Kim et al., 2005b). The COD are defined as

$$COD_{fh} = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{x_{if} - x_{ih}}{x_{if} + x_{ih}} \right)^2}$$

where x_{if} is the i th concentration measured at the f th site. f and h represent two monitoring sites, and n is the number of observations. The COD is a coefficient used to determine the degree of uniformity between monitoring sites. For the spatial distribution, the COD approaches zero if the source contributions at two monitoring sites are similar. The COD for identified $PM_{2.5}$ sources obtained at the five monitoring sites are shown in Fig. 8. It can be seen that secondary particles and aged sea salt show the smallest spatial variability, reflecting in large part their distant origins and transport into and across the monitored area. Other source contributions are more locally variable.

Gasoline vehicle emissions and airborne soil represent the next most highly correlated source components. Interestingly, contributions from wood smoke and diesel emissions belong to the least well-correlated source types. For the wood smoke, the COD between Lake Forest and Beacon Hill is the highest (0.75). Closely located Duwamish and Georgetown also show a high COD value

(0.63). For the diesel emissions, Olive St. and Georgetown show the highest COD (0.77). The emission schedules coupled with the transport conditions produce differences among the contributions at different sites that are reflected in the COD. It suggests that there is the potential for exposure misclassification in time-series epidemiological studies when regressing health outcomes against wood smoke or diesel contributions estimated at a monitoring site in Seattle.

4. Conclusions

Source apportionment studies were conducted for the 24 h averaged $PM_{2.5}$ speciation data collected between 2000 and 2005 from five STN monitoring sites located in Seattle, WA and vicinity area. Seven and ten major $PM_{2.5}$ sources were identified using PMF2, including secondary sulfate, secondary nitrate, gasoline vehicle emissions, diesel emissions, wood smoke, airborne soil, oil combustion, sea salt, aged sea salt, metal processing, and cement kiln. Secondary particles and gasoline vehicle emissions contributed the most to the $PM_{2.5}$ at all monitoring sites except for the residential Lake Forest site, where wood smoke contributed the most.

Although the impacts of residual oil combustion were relatively small compared to other sources (4–6% of $PM_{2.5}$), clear influence of ship emissions was found in downtown Seattle area, where multiple site results point clearly to the Port of Seattle as a likely source area. Also, the edge between the secondary sulfate particles and the oil combustion particles indicated the contribution of ship emissions to the secondary sulfate formation at multiple sites.

This study provided a unique chance to evaluate the spatial variability of $PM_{2.5}$ sources across an urban area with modern particle composition data. The COD analysis indicated that the spatial distributions of several $PM_{2.5}$ sources such as wood smoke and diesel emissions were heterogeneous within a given air shed. Therefore, in

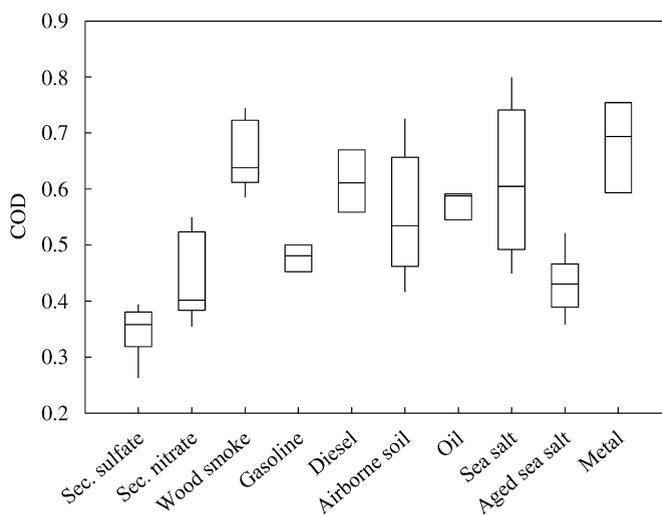


Fig. 8. Coefficients of divergence (COD) for identified $PM_{2.5}$ sources obtained at the 5 monitoring sites in Seattle, WA.

health effects studies, it is important that the spatial variation in ambient PM_{2.5} source contributions within a study area be taken into consideration so as to reduce the exposure misclassification.

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Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.atmosenv.2008.03.032](https://doi.org/10.1016/j.atmosenv.2008.03.032).

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