

Source apportionment of PM_{2.5} and selected hazardous air pollutants in Seattle

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Abstract

The potential benefits of combining the speciated PM_{2.5} and VOCs data in source apportionment analysis for identification of additional sources remain unclear. We analyzed the speciated PM_{2.5} and VOCs data collected at the Beacon Hill in Seattle, WA between 2000 and 2004 with the Multilinear Engine (ME-2) to quantify source contributions to the mixture of hazardous air pollutants (HAPs). We used the ‘missing mass’, defined as the concentration of the measured total particle mass minus the sum of all analyzed species, as an additional variable and implemented an auxiliary equation to constrain the sum of all species mass fractions to be 100%. Regardless of whether the above constraint was implemented and/or the additional VOCs data were included with the PM_{2.5} data, the models identified that wood burning (24%–31%), secondary sulfate (20%–24%) and secondary nitrate (15%–20%) were the main contributors to PM_{2.5}. Using only PM_{2.5} data, the model distinguished two diesel features with the 100% constraint, but identified only one diesel feature without the constraint. When both PM_{2.5} and VOCs data were used, one additional feature was identified as the major contributor (26%) to total VOC mass. Adding VOCs data to the speciated PM_{2.5} data in source apportionment modeling resulted in more accurate source contribution estimates for combustion related sources as evidenced by the less ‘missing mass’ percentage in PM_{2.5}. Using the source contribution estimates, we evaluated the validity of using black carbon (BC) as a surrogate for diesel exhaust. We found that BC measured with an aethalometer at 370 nm and 880 nm had reasonable correlations with the estimated concentrations of diesel particulate matters ($r > 0.7$), as well as with the estimated concentrations of wood burning particles during the heating seasons ($r = 0.56–0.66$). This indicates that the BC is not a unique tracer for either source. The difference in BC between 370 and 880 nm, however, correlated well exclusively with the estimated wood smoke source ($r = 0.59$) and may be used to separate wood smoke from diesel exhaust. Thus, when multiple BC related sources exist in the same monitoring environment, additional data processing or modeling of the BC measurements is needed before these measurements could be used to represent the diesel exhaust. © 2007 Elsevier B.V. All rights reserved.

Keywords: Receptor modeling; Hazardous air pollutants; Aethalometer; Black carbon

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1. Introduction

The federal Clean Air Act Amendments of 1990 mandate that the U.S. EPA determine a set of urban hazardous air pollutants (HAPs, or ‘air toxics’) that potentially pose the greatest risks in urban areas, in terms of contribution to population health risk. The current set of 188 HAPs includes toxic metals and volatile organic compounds (VOCs). The U.S. EPA identified 33 urban HAPs based on emissions and toxicities in a 1995 ranking analysis (U.S. EPA, 1999a) and developed concurrent monitoring and modeling programs to evaluate potential exposures and risks to these top-ranked 33 HAPs. The National-scale Air Toxics Assessment (NATA) estimated potential cancer and non-cancer risks associated with the ambient concentrations of these urban HAPs (U.S. EPA, 2002a, 2006). Results from the NATA project, which rely heavily on HAPs emission inventories and modeling approaches, will be used to set priorities for the collection of additional emissions data, ambient concentration data, and information on adverse effects to health and the environment.

Developing effective control strategies to reduce population exposure to certain HAPs requires identifying sources and quantifying their contributions to the mixture of HAPs and the associated health risks. One approach is to use receptor-based source apportionment models to distinguish sources. Most source apportionment studies focus on analyzing either VOCs (e.g. Mukund et al., 1996; Jorquera and Rappengluck, 2004) or fine particle ($PM_{2.5}$) mass (e.g. Kim et al., 2003; Larsen and Baker, 2003; Kim et al., 2004a). Only few studies used source apportionment modeling to identify common sources of both VOCs and $PM_{2.5}$. However, in these studies, the monitored PM species were mostly organic compounds (Harrison et al., 1996; Schauer and Cass, 2000; Schauer et al., 2002; Larsen and Baker, 2003), rather than the metals, ions, and carbon constitutes that are more routinely measured at current PM monitoring network. In other source apportionment studies that included both non-organic trace elements on PM and gaseous pollutants (Swietlicki et al., 1996; Kim et al., 2005a; Zhou et al., 2005; Liu et al., 2006), the gaseous species usually were non-VOCs (such as CO, SO₂, and NO).

Among the HAP sources commonly found in urban areas, diesel engine exhaust is of special interest as it is a likely lung cancer hazard (U.S. EPA, 2002b). Emerging evidence has also indicated that diesel exhaust exacerbates existing allergies and asthma symptoms (U.S. EPA, 2002b). Another HAP source of interest is wood smoke,

which is a major contributor to the air pollution in the west coast of U.S. during winter months (Schauer and Cass, 2000; Maykut et al., 2003). Exposure to wood smoke has been linked to both acute and chronic illnesses (Naehrer et al., 2007). Both diesel exhaust and wood smoke contain a complex mixture of gases and particulates. In this paper, we apportioned the diesel exhaust and wood smoke sources using the speciated PM with and without additional VOC measurements. For diesel exhaust, it is also commonly characterized by diesel particulate matter through measurements of black carbon (BC). Aethalometers are increasingly used in the field to provide continuous BC measurements to represent diesel exhaust (e.g. Edgerton et al., 2006; Zanobetti and Schwartz, 2006). However, other sources, such as wood smoke, also contribute to BC. Thus, complications of using the BC measurements as diesel exhaust marker in high and low wood smoke seasons need to be addressed.

In this study we applied source apportionment models to a combination of VOCs and non-organic elemental $PM_{2.5}$ speciation measurements to identify sources of selected HAPs in Seattle, WA. We evaluated the performance of the models with and without the addition of VOCs data. Using the source apportionment results, we examined the validity of using BC as a marker for diesel exhaust during different seasons.

2. Methods

2.1. Sample collection and analysis

Speciated $PM_{2.5}$ and VOCs measurements at the Beacon Hill monitoring site in Seattle from 2000 to 2004 were used for modeling. This urban-scale site, located in a highly populated neighborhood, has been shown to represent average $PM_{2.5}$ concentrations in a typical Seattle residential neighborhood (Goswami et al., 2002). It is located within 2 km of two major interstate freeways and arterial roads, as well as within 4 km of a warehousing area and a major seaport. Thus it is impacted by a mixture of urban sources including vehicle emissions and wood burning. A map and photograph of the monitoring site and the surrounding area can be found in Maykut et al. (2003) and Larson et al. (2006). The Beacon Hill site, as part of the U.S. EPA Speciation Trends Network (STN), collects $PM_{2.5}$ samples using the URG (Chapel Hill, NC) sampler equipped with Teflon, Nylon, and quartz filters, which were analyzed for (1) $PM_{2.5}$ mass and elemental compositions; (2) sulfate (SO₄²⁻), and nitrate (NO₃⁻), and (3) organic carbon (OC) and elemental carbon (EC), respectively (Kim et al., 2005b). VOCs samples also were

collected at the Beacon Hill site by the Washington Department of Ecology. Formaldehyde and acetaldehyde were sampled with a DNPH cartridge and analyzed with HPLC-UV (EPA TO-11A) (U.S. EPA, 1999c). Benzene, 1,3-butadiene, carbon tetrachloride, chloroform, dichloromethane, tetrachloroethylene, and trichloroethylene, were collected with a SUMA canisters and analyzed with GC FID/ECD (EPA TO-14A) (U.S. EPA, 1999b). These VOCs were chosen for monitoring because they were on the list of the 33 urban HAPs with emissions from major, area and mobile sources (U.S. EPA, 1999a). Among them, acetaldehyde, benzene, 1,3-butadiene, and formaldehyde are mainly from combustion related sources. The other VOCs of the urban HAPs were not monitored because they were considered less stable or there were no approved sampling and analytical methods (PSCAA, 2003). An aethalometer (Magee Scientific Dual Channel Aethalometer™) with a PM_{2.5} cyclone inlet (SCC 1.829, BGI Inc., Waltham, MA), measuring optical absorption at $\lambda=880$ nm (BC_A) and at $\lambda=370$ nm (UV-BC) (Jeong et al., 2004), has been operated by the Puget Sound Clean Air Agency to measure real-time BC since March, 2003.

2.2. Models implementation

We applied the Multilinear Engine (ME-2) (Paatero, 1999) for source apportionment analyses. This model solves a positively constrained bilinear mass balance model using an explicit least-squares equation. The required input data include the mass concentrations and uncertainties of each measured species. The concentrations and uncertainties of the input PM_{2.5} elements and VOCs species were processed according to Polissar et al. (1998). Namely, concentrations below the method detection limit (MDL) values were replaced by half of the MDL values with uncertainties set at 5/6 of the MDL values. Missing concentrations were replaced by the geometric mean concentrations with uncertainties set at four times the geometric mean concentration. We further down-weighted the weak signals, defined as concentration values below 3 times the detection limit in this study, by a factor of five (Kim et al., 2005b). Note that uncertainty value for individual PM_{2.5} sample was not reported prior to 2003 in the STN. Kim et al. (2005b), examining a limited set of measurements in the STN and their associated uncertainties, derived a comprehensive set of error structures and uncertainty values for source apportionment studies of STN data. The uncertainty values for the speciated PM_{2.5} samples at Beacon Hill were thus calculated according to the information given in Kim et al. (2005b).

To investigate the benefits of adding VOCs data to the speciated PM_{2.5} data and its effects on source apportionment results, the model was applied to the PM_{2.5} speciated data with or without VOCs measurements. When the model included only the PM_{2.5} data, the measured PM_{2.5} mass concentration was used as the dependent variable in the post-hoc regression model that calculates the rescaling factors for converting the unitless ‘source contributions’ from the model outputs to the estimated source-specific mass concentrations. When both VOCs and PM_{2.5} data were used in the models, the measured PM_{2.5} mass concentrations and the sum of the measured VOCs concentrations were added as the dependent variable for the regression model.

We also applied a novel approach by Larson et al. (2006) that eliminated the need of the post-hoc regression process by including the ‘missing mass’ as another ‘specie’, which is defined as the concentration of the measured total particle mass minus the sum of all analyzed PM species. This step also provides an auxiliary equation for the model to constrain the sum of all species mass fractions in each source feature to be 100%. The uncertainty of the ‘missing mass’ is calculated as the square root of the sum of the variances of all species and measured mass. The ME model was ran with the 100% constraint (i.e. including the missing mass as one specie and not using the post-hoc regression process) and without the 100% constraint (i.e. not including the missing mass as one specie but using the post-hoc regression process) in this study to evaluate how this additional constraint affected the model performance. Finally, using the modeling results as the reference, we analyzed the correlations between the BC measurements and the combustion related source contribution estimates by seasons to evaluate the validity of using BC as a surrogate for diesel exhaust.

3. Results and discussion

3.1. Quality control

Concentrations of formaldehyde from July 8, 2003 to August 25, 2003 were almost 10 times higher than the rest of the measurements. In the 2004 Air Quality Data Summary Report (PSCAA, 2005) from the Puget Sound Clean Air Agency, it was stated that a local formaldehyde source, including solvents that are sometimes used in research projects, was possibly present at the Beacon Hill site during this period. As a regional increase of formaldehyde during this time was unlikely, these measurements were removed from the dataset. In addition, following the procedures of Kim et al. (2005b), we

estimated the OC blank concentrations to be $0.27 \mu\text{g}/\text{m}^3$ ($\text{OC} = 0.27 + 0.31 * \text{PM}_{2.5}$, $R^2 = 0.8$). This estimated blank value was consequently subtracted from all measured OC concentrations. This observed positive artifact is unique to the OC. Several studies have identified that it is mainly due to adsorption of gaseous organic compounds on the quartz filters or previously collected particles (Turpin et al., 1994; Kim et al., 2001, 2005b). In the STN samplers, no upstream carbon denuder was used to minimize the positive sampling artifact.

Table 1 summarizes the concentrations of the $\text{PM}_{2.5}$ species and VOCs used in the source apportionment model, and the percentage of samples below the MDL (BDL). HAPs were included in this study only when 30% or more of the values were above the MDL (Buzcu et al., 2007). Important PM species including OC, EC, Ca, Cu, Fe, nitrate, Si, Na, sulfate, and Zn are 94% or more above the MDL. The percentages of weak signals for these species are mostly below 12%, except for Cu

(=28%). Most VOCs measurements are above the MDL. Dichloromethane had 74% measurements below the MDL and was not included in the analysis.

3.2. Source apportionment results

3.2.1. $\text{PM}_{2.5}$ data only

When using $\text{PM}_{2.5}$ data only without the 100% constraint, the 9-feature ME model provides the best results. The 8-feature model failed to separate the commonly seen soil and gasoline features while the 10-feature model included a feature rich in OC and EC but lacked other identifiable characteristic. When using $\text{PM}_{2.5}$ data with the 100% constraint, the 9- and 10-feature solutions are both reasonable. The 9-feature model identified one diesel feature while the 10-feature model identified two diesel features. More discussion about the different diesel features are given later in this paper. In general, these three sets of solutions provide similar

Table 1

Average concentration of HAPs used for source apportionment modeling at the Beacon Hill site ($n=268$)

	Element	Abbrev	Mean (ng/m^3)	Number of missing values (%)	Number of BDL ^a values (%)	Number of weak ^b signals (%)
PM _{2.5}	Organic carbon ^c	OC	2600	1.1	0.0	1.1
	Elemental carbon	EC	610	1.1	0.0	6.0
	Ammonium	NH ₄	460	0.0	0.0	0.4
	Arsenic	As	0.97	0.0	60.1	96.3
	Bromine	Br	2.0	0.0	11.9	66.8
	Calcium	Ca	27	0.0	0.0	0.0
	Chlorine	Cl	60	0.0	34.3	46.6
	Chromium	Cr	1.6	0.0	28.0	73.1
	Copper	Cu	4.3	0.0	5.2	28.0
	Iron	Fe	52	0.0	0.0	0.0
	Lead	Pb	3.7	0.0	27.6	89.9
	Manganese	Mn	3.0	0.0	30.2	68.3
	Nickel	Ni	2.3	0.0	22.0	56.3
	Nitrate nonvolatile	NO ₃	460	0.0	0.0	0.0
	Potassium ion	K	30	0.4	42.2	44.0
	Silicon	Si	42	0.0	3.0	6.0
	Sodium ion	Na	150	0.0	2.2	11.9
	Sulfate	SO ₄	1200	0.0	0.0	0.0
	Tin	Sn	5.1	0.0	66.0	99.6
	Titanium	Ti	2.6	0.0	21.6	54.1
Vanadium	V	3.5	0.0	23.5	45.9	
Zinc	Zn	8.8	0.0	0.0	1.9	
VOCs	Acetaldehyde	Ace	1500	3.7	0.0	4.1
	Formaldehyde	For	1500	4.1	0.0	4.9
	Benzene	Ben	1300	0.0	0.4	0.4
	1,3-Butadiene	But	120	0.0	22.4	77.2
	Chloroform	Chl	240	0.4	0.4	35.1
	Carbon tetrachloride	Car	640	0.4	0.0	0.4
	Tetrachloroethylene	Tet	180	0.4	3.0	37.7
	Trichloroethylene	Tri	170	0.4	14.2	57.5

^a BDL: below detection limit.

^b The weak signal is defined as the concentration value below 3 times the detection limit.

^c After the OC correction.

estimates in terms of the source contribution estimates (SCE) with similar R^2 values (0.88–0.89, Table 2) between the observed and predicted mass concentrations. Since the 100% constraint helped separate two unique diesel features, only the results from the 10-feature model are discussed below. The goodness of fit variable, i.e. the Q -value, of this model is 3832. This value indirectly verified the model's performance since theoretically it should be approximately equal to or less than the product of the number of samples and the number of species, which is $268 * 23 = 6164$ in this case (Yakovleva et al., 1999; Liu et al., 2006). It is also close to the robust Q -value of 3694, indicating that the potential outliers did not affect the model's output significantly.

Fig. 1 shows the feature profiles using the speciated $PM_{2.5}$ data only. The soil feature was distinguished by the characteristic richness in crustal-derived materials such as Si and Ca (Kim et al., 2005b). The marine feature was identified by the high levels of Cl and Na. The wood burning feature was characterized by the high levels of OC, EC and K with relatively low portions of other trace elements (Maykut et al., 2003). The average SCE for wood burning is higher during the heating season than during the non-heating season due to the more frequent burning activities in the winter (Fig. 2a). The heating season is defined as Oct–Feb for Seattle area based on average temperature and observed ambient $PM_{2.5}$ levels (Liu et al., 2003).

Secondary sulfate and nitrate rich features were clearly marked by the high concentrations of sulfate and nitrate, respectively. Because the secondary sulfate levels are enhanced by photochemical activity in summer, the contribution in the non-heating season is slightly higher than in the heating season (Fig. 2a). The smaller than expected seasonal difference was attributed to the winter-time inversion in Seattle area. On the contrary, nitrate rich aerosol tends to form in the season with low temperature and high humidity (Kim et al., 2004b); therefore, the higher contribution in winter can be observed with the difference further enhanced by the winter-time inversions (Fig. 2a).

The fuel feature was characterized by its high proportion of V and Ni. It represented the residual oil burned by large industrial and commercial sources (Lee et al., 2002). Kim et al. (2004b) showed that the major contributors for the fuel source in Beacon Hill are from downtown Seattle and the Port of Seattle (e.g. ship emissions). Although diesel and gasoline features have similar carbon fractions, it is easy to separate diesel feature by its relatively high levels of Mn and Fe (Kim et al., 2004b). We identified two diesel features with high EC, OC, Fe and Mn as in Larson et al. (2006), in which the separation of the two features originally resulted from including the size distribution measurements as utilized by their ME model. By comparing the feature profiles in Larson et al. (2006), we interpreted

Table 2
Source contribution estimates from the ME models with $PM_{2.5}$ data only or with all available HAPs data

Source feature	$PM_{2.5}$ only						All available HAPs							
	PM contribution						PM contribution				VOC contribution			
	ME_{UC}^a		ME_C^b		ME_C^b		ME_{UC}^a		ME_C^b		ME_{UC}^a		ME_C^b	
	ng/m ³	%	ng/m ³	%	ng/m ³	%	ng/m ³	%	ng/m ³	%	ng/m ³	%	ng/m ³	%
Wood burning	2400	31	2300	29	2400	30	1500	27	1900	24	510	10	690	14
Secondary sulfate	1700	22	1800	22	1600	20	1200	21	1900	24	220	4	430	9
Nitrate rich	1200	15	1600	20	1300	16	770	14	1600	20	470	9	260	5
Diesel	890	11	610	8			560	10	700	9	720	14	710	14
Diesel 1					670	8								
Diesel 2					240	3								
Gasoline	180	2	400	5	270	4	290	5	240	3	280	5	360	7
Fuel	680	9	550	7	780	10	480	9	430	5	660	13	580	12
Marine	140	2	130	2	100	1	99	2	140	2	34	1	61	1
Soil	130	2	200	2	150	2	190	3	230	3	150	3	130	3
Aged sea salt	440	6	410	5	500	6	350	6	410	5	290	6	480	10
Other							160	3	400	5	1900	35	1300	26
R^2 ^c	0.89		0.88		0.89		0.88		0.88		0.77		0.72	
Slope	1.0		0.98		0.97		1.4		0.97		1.08		1.14	
Intercept (ng/m ³)	420		419		506		173		421		37		−99	

^a ME_{UC} : ME model without the 100%-constraint.

^b ME_C : ME model with the 100%-constraint.

^c Regression model with measured mass against predicted mass.

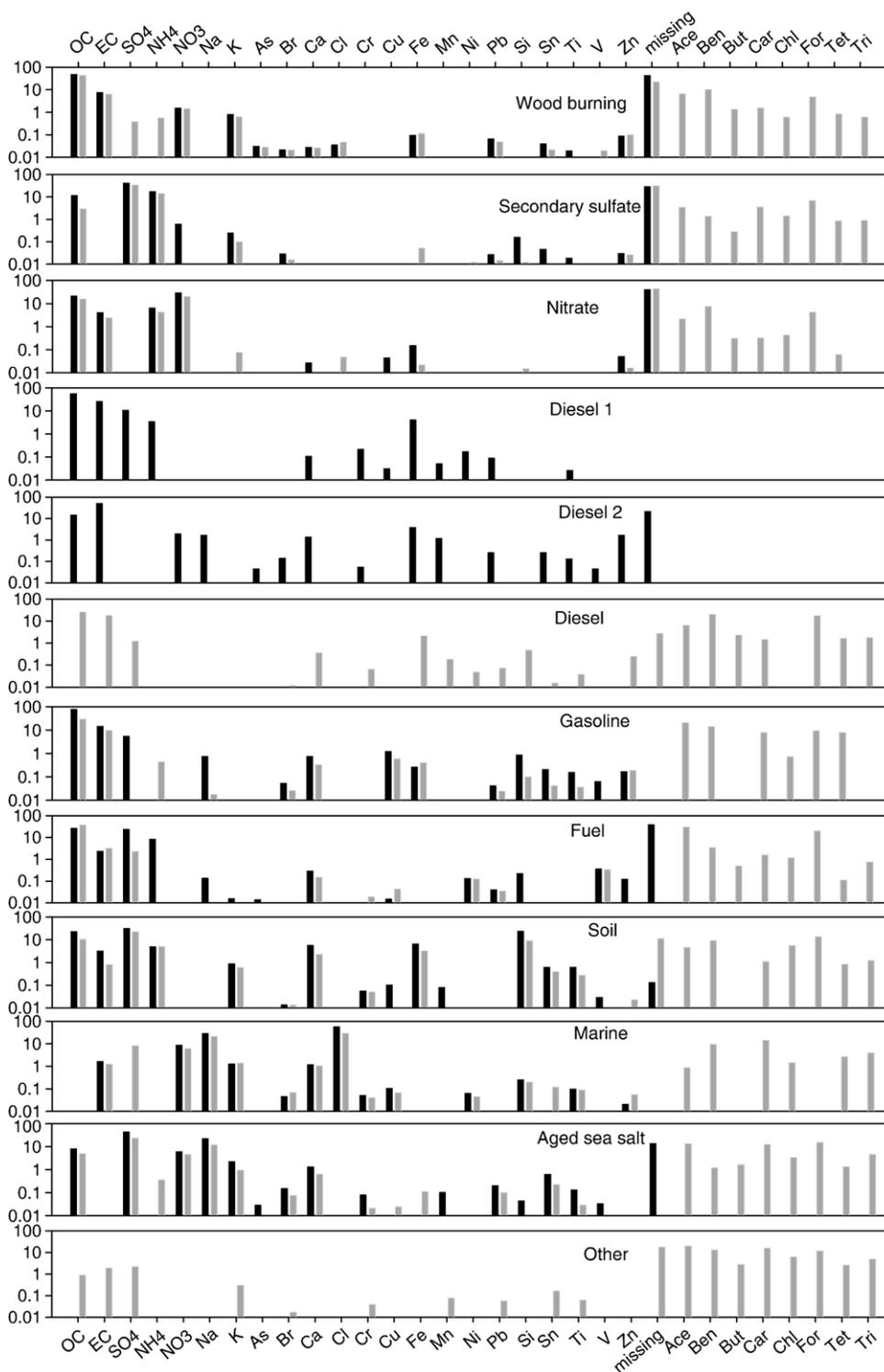


Fig. 1. Feature profiles from the ME models with the 100% constraint. The y-axis is the mass fraction (%) of each species in the feature profile. The dark bars represent the results from using PM_{2.5} data only, while the light bars represent the results from the combined PM_{2.5} and VOCs data.

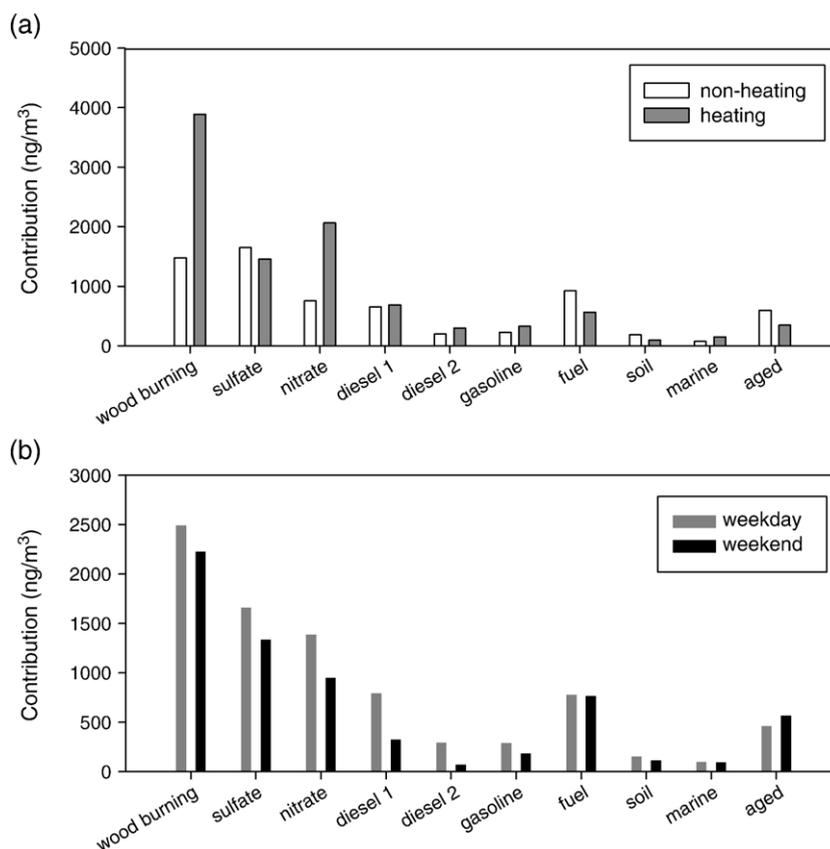


Fig. 2. Source contribution estimates (SCE) between heating/non-heating seasons and weekday/weekend. Results were from the ME model with the 100% constraint and using the $PM_{2.5}$ data only.

Diesel 1, less enriched in EC and Mn than the diesel feature identified in previous studies but enriched with SO_4^{2-} and NH_4^+ , representing the majority of the diesel contribution, as the aged and chemically processed tailpipe emission of diesel vehicles. Diesel 2 feature, which had highly enriched EC and Mn without SO_4^{2-} and NH_4^+ , represents possibly the freshly emitted diesel exhaust. The weekday and weekend variation of diesel and gasoline features also agreed with the traffic pattern (Fig. 2b). Aged sea salt is identified by its high mass fractions of sulfate, nitrate, Na, and K (Kim et al., 2004b). Wood burning, secondary sulfate, and nitrate rich features were the most abundant contributors to $PM_{2.5}$ in Seattle (Table 2).

3.2.2. $PM_{2.5}$ and VOCs

When both $PM_{2.5}$ and VOCs data were included in the ME model, the 10-feature solutions provided the most reasonable results, regardless of the 100% constraint. The 9-feature solutions without the 100% constraint failed to resolve the secondary sulfate and the

9-feature solutions with the 100% constraint resulted in an unusually high contribution (up to 13%) from the aged sea salt. The 11-feature solutions with or without the 100% constraint showed very little acetaldehyde, a common component of the diesel exhaust (Siegl et al., 1999), in the profile of the presumed diesel feature. Table 2 shows that the source contribution estimates from the model without the 100% constraint were generally lower than those from the model with the 100% constraint. This is because for several features in the no-constraint model, the sum of the contributions from all species was considerably smaller than the $PM_{2.5}$ mass concentration. Thus, for the $PM_{2.5}$ and VOCs data combined, only results from the constrained model are included in the discussion below. The Q -value of this model is 15,152, which is higher than the theoretical Q -value of 8308 ($=268 \times 31$). This is because we originally used the default ‘ $c3=0.05$ ’ setting in the ME model (i.e. adding additional 5% of the larger of the input and fitted concentration data to the uncertainty value) but did not find reasonable solutions. For example, the original 10-

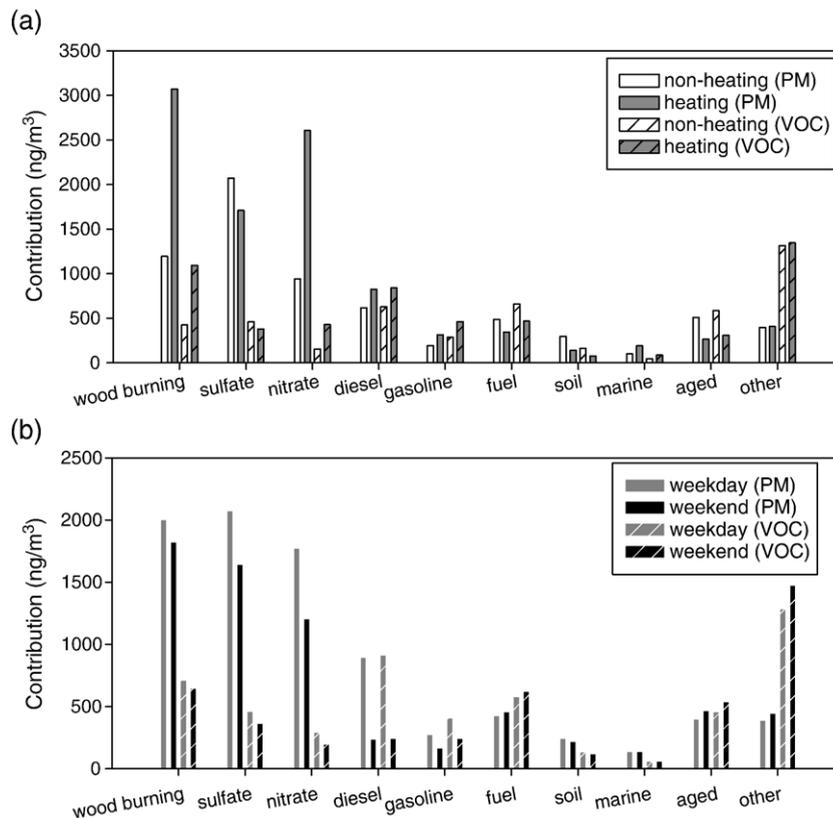


Fig. 3. Source contribution estimates (SCE) between heating/non-heating seasons and weekend/weekday. Results were from the ME model with the 100% constraint and using both the $PM_{2.5}$ and VOCs data.

feature solution did not give any ‘soil’ feature, which is a commonly identifiable one. Thus we changed the $c3$ to 0.01 and inevitably increased the Q -value. On the other hand, this Q -value is still similar to the robust Q -value of 13,173, indicating the minimal effects from the potential outliers.

The 10-source features derived from the ME model with the 100% constraint using both speciated $PM_{2.5}$ and VOCs data are presented as gray bars in Fig. 1. Two

main differences were observed in the modeling results with and without the addition of VOCs data. Only one diesel feature was identified when including both the $PM_{2.5}$ and VOCs data. In addition, one ‘Other’ feature enriched in VOCs and contributed 26% of the total VOCs (Table 2) was identified when both $PM_{2.5}$ and VOCs data were applied to the model. This feature probably represents the urban background concentrations of VOCs since the contribution for each VOC was

Table 3

Pearson’s correlation coefficients of aethalometer’s measurement vs. combustion related particles estimates from modeling PM and VOCs data

	Diesel		Gasoline		Motor vehicle ^a		Wood burning	
	Non-heating	Heating	Non-heating	Heating	Non-heating	Heating	Non-heating	Heating
BC_A^b	0.77**	0.71**	0.33*	0.56**	0.77**	0.74**	0.16	0.56**
UV- BC^c	0.8**	0.63**	0.39**	0.56**	0.81**	0.69**	0.32*	0.66**
BCdiff ^d	-0.12	-0.02	0.06	0.21	-0.10	0.07	0.36**	0.59**

** : $p < 0.01$.

* : $0.01 < p < 0.05$.

^a Motor vehicle = SCE for diesel particulate matter plus SCE for gasoline particles.

^b Aethalometer’s measurement at $\lambda = 880$ nm.

^c Aethalometer’s measurement at $\lambda = 370$ nm.

^d The difference between UV-BC and BC_A .

high and the reconstructed time series did not show obvious temporal variation. Other than the two dissimilarities, ME solutions with and without the VOCs data showed similar PM_{2.5} profiles for all other features (Fig. 1) and similar trend in the SCE for PM_{2.5} between heating and non-heating seasons and between weekends and weekdays (Figs. 2 vs. 3).

The SCE for PM_{2.5} were similar for diesel, gasoline, marine, soil and aged sea salt for the constrained solutions with or without the VOCs data (Table 2). In contrast, slightly larger differences were obtained for wood burning (30% vs. 24%), secondary sulfate (20% vs. 24%), nitrate rich (16% vs. 20%), and fuel features (10% vs. 5%). The regression curves of predicted versus measured PM_{2.5} mass from both sets of modeling results do not provide sufficient information to determine which sets of solutions are uniformly more accurate since they have similar R^2 (Table 2, 0.89 and 0.88) and slope estimates (0.97 and 0.97). However, for the wood burning, diesel, and fuel profiles the percentage of ‘missing mass’ in PM was lower when modeling the PM and VOCs data together (29.8%, 5.5%, and <0.01%) than when modeling only the PM data (42.2%, 21.1%, and 38.3%). On the other hand, for secondary sulfate and nitrate rich features, the ‘missing mass’ percentages were higher (37.9% vs. 28.8%; 50.9% vs. 39.4%) when modeling the PM and VOCs data than when modeling only the PM data. This is probably because the VOCs measured in this study were not sufficiently unique to these secondary aerosol features, thus introducing more uncertainty to the model.

For the VOCs portion, the model identified a separate feature (‘Other’) as a major contributor (26%) with wood burning (14%) and diesel exhaust (14%) as the next largest ones. The R^2 of the predicted versus measured mass for the VOCs portion is lower than the one for the PM_{2.5} portion (Table 2), indicating a better model fit for PM_{2.5} species than VOCs.

We further evaluated the modeling results by examining the feature-specific Pearson correlation coefficient between the SCE of PM_{2.5} from modeling with or without the VOCs data. The SCE of the two diesel features from modeling PM_{2.5} only were summed up to be compared with the one from modeling PM_{2.5} plus VOCs data. The feature-specific correlation coefficients ranged from 0.92 (secondary sulfate) to 0.99 (nitrate rich) with the median value of 0.96 (wood burning). These high correlations verified the robustness of the modeling results and indicated that the day to day variation of the SCE estimates was captured mostly by the models. This variation is important for conducting source-specific health effects studies (Hopke et al., 2006; Ito et al., 2006; Mar et al., 2006).

We originally hypothesized that adding VOCs data in the source apportionment analysis would enhance our ability to separate sources (e.g. the diesel). However, our results showed that most features were readily identifiable by using the PM_{2.5} species alone. The addition of the VOCs data to the ME model did not provide additional information for feature identification, based on known source features in the literature. This is probably due to the high impact of diesel exhaust at the Beacon Hill site. Thus assessing the utility of adding VOCs in the ME model to identify diesel features might be biased at this site. On the other hand, it is found that the SCE estimates for wood burning and diesel features from modeling both PM_{2.5} and VOCs data might be more accurate as evidenced by the less ‘missing mass’ percentage in PM. More importantly, the VOCs studied here are also HAPs and from a risk management perspective this approach is helpful for obtaining a more complete picture of the source-specific health risks.

3.3. Combustion related particles and black carbon

Table 3 shows the correlations between the daily time-averaged BC measurements from the aethalometer and the SCE for combustion related particles from modeling PM and VOCs data. Regardless of the season, BC_A was significantly correlated with the diesel particulate matter ($r > 0.7$) and gasoline particles ($r > 0.3$). Thus the SCE from the two features were summed up to represent the SCE from the motor vehicles for the following analysis. Note that the correlation was lower with the gasoline particles than with the diesel particulate matter. This is because that the diesel engine emits more BC comparing to spark ignition engines (Miguel et al., 1998; Zhu et al., 2002).

Table 3 shows that during the heating season the BC_A correlated well with not only the motor vehicle particles ($r = 0.74$) but also the wood burning particles ($r = 0.56$), indicating that it is not a unique tracer for traffic exhaust. Similar results were observed for UV-BC; i.e. during the heating seasons, it correlated with both the motor vehicle and wood burning particles ($r > 0.66$, Table 3). This observation is consistent with previous findings that BC, as measured by the aethalometer, represent light absorbance by black carbon originating from various sources including traffic exhaust and wood burning smoke (Polissar et al., 2001; Larosa et al., 2002). Therefore, one should be cautious with using aethalometer BC to represent traffic exhaust in exposure and epidemiologic studies, especially when other sources (e.g. wood burning smoke) exist in the same monitoring environment.

One possible way to separate the traffic exhaust and wood smoke signals is to use the difference between the UV-BC and BC_A values. During the heating season, the UV-BC was generally higher than the BC_A and the difference (mean \pm SD=144 \pm 170 ng/m³) correlated well with the SCE for wood burning particles ($r=0.59$, Table 3), but not that for motor vehicle particles ($r=0.07$, Table 3). It was previously suggested that the additional absorption of UV-BC is due to the UV-absorbing aromatic organic material in the wood smoke particles (Jeong et al., 2004; Park et al., 2006).

4. Conclusions

The major PM_{2.5} emission sources at the Beacon Hill site are wood burning, secondary sulfate and nitrate. The majority of our measured vapor phase HAPs come from wood burning, diesel exhaust, and the general urban background. Light absorption carbon (BC) measurements by an aethalometer at 370 and 880 nm correlated well with motor vehicle particles throughout the year and with wood burning particle during the heating season. This suggested that aethalometer BC came from both traffic exhaust and wood burning smoke, and more so during the heating season. Thus, additional data processing or modeling of the BC measurements (e.g. examining the difference between the BC_A and UV-BC) is needed to separate these two sources.

Compared to the traditional post-hoc regression process, the approach of including the ‘missing mass’ as one specie provided several advantages. The 100% constraint can be implemented so the sum of all species mass fractions in each source feature is 100%. When modeling the PM_{2.5} data, this constraint helped resolve two diesel-related features. When modeling the PM_{2.5} and VOCs data without this 100% constraint, the SCE tends to be underestimated relative to the measured mass concentration. We had hypothesized that the additional VOCs features derived from combined dataset would provide information for identifying additional sources (i.e. diesel). However, the potential benefits of adding the VOC data were undermined as major sources were readily identified using merely the PM_{2.5} data and the VOCs measured in this study might not be unique for certain sources. The latter explanation is consistent with the fact that the Q -value from modeling the PM_{2.5} and VOCs data was higher than the theoretical Q -value. Nevertheless, with the addition of the VOCs data, the ME model gave a more accurate SCE estimate for combustion related sources and provided a more complete set of exposure sources including the VOC source. This could be crucial when conducting source-specific risk assessment.

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