Sensitivity of source apportionment results to mobile source profiles

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Abstract

The sensitivity of a source apportionment model to mobile source profiles was examined to determine the impact of using non-local mobile source profiles in chemical mass balance (CMB) models. We examined the impact of USA and Chinese mobile source profiles on source apportionment results in St. Louis, Missouri, and Beijing. The results showed that the use of non-local mobile source profiles did not impact the model apportionment results for vegetative detritus and biomass burning, but other primary source contributions were influenced by the use of non-local source profiles. Secondary organic carbon (SOC) contributions estimated by the CMB models with local and non-local profiles were compared to estimate of SOC from the EC tracer method and were found to be consistent with little bias. The results also showed that it is feasible to use the USA mobile profiles in China while model results were biased by using Chinese mobile profiles in the USA. Monthly and annual average concentrations of molecular markers in the source apportionment model showed lower sensitivity to source profiles than daily measurements, which has implications to the design of source apportionment studies.

Keywords: Mobile source; sensitivity; non-local profiles; CMB;

Capsule

Non-local mobile profiles may cause specific apportionment bias. Averaged samples are less affected than daily samples.

1 Introduction

Particulate matter (PM) is an important pollutant in the atmosphere on a global scale (Brunekreef and Holgate, 2002). A multitude of epidemiological studies show a positive correlation between morbidity and PM concentration (Fuks et al., 2011; Cesaroni et al., 2013; Madrigano et al., 2013). Vehicular emissions are a significant source of PM, and some studies have shown that mobile sources are responsible for 12.6% to 44% of total PM pollution (Maykut et al., 2003; Almeida et al., 2005; Lee and Hopke, 2006; Huang et al., 2015). Traffic-related air pollutants, such as elemental carbon (EC) and polycyclic aromatic hydrocarbons (PAHs)(Pearson et al., 2000; Vette et al., 2013), may increase the risk for leukemia, hypertension, and chronic obstructive pulmonary disease (COPD) (Pearson et al., 2000; Schikowski et al., 2005; Baumgartner et al., 2014). In recent years, many studies have focused on the effects of traffic-related exposure on health. However, a majority of these studies measure the exposure level as the distance between the point of exposure to a main road (i.e. distance to roadway) (Rivera et al., 2013; Batterman et al., 2014; Chart-asa and Gibson, 2015). However, these studies would be enhanced with more accurate quantification of mobile source contributions to atmospheric concentrations and exposures, so that the relationship between mobile source pollution and health levels can be analyzed.

Organic tracers, also called molecular markers, are widely used in molecular marker chemical mass balance models (MM-CMB) to determine air pollution

source contributions to particulate matter concentration, including biomass burning, coal combustion, and mobile sources (Schauer et al., 1996; Coulter, 2004; Zhang et al., 2009). Source profiles that provide “fingerprints” of molecular markers are necessary for three models. Although some published studies state that local source profile measurements are necessary for accurate source apportionment model results, many researchers use non-local source profiles when local profiles are unavailable (Lee et al., 2008; Duvall et al., 2012; Taiwo et al., 2014; Pirovano et al., 2015). Local and non-local mobile source profiles from urban regions may be similar because automotive emissions are largely comprised of fuel and lubricating oil, which must meet engine specification and have organic constituents that do not vary greatly in different regions of the world. Lough and Schauer (2007) demonstrated with a large set of mobile source profiles that the selection of source profile had a large impact on the split between gasoline and diesel vehicle emissions but that sum of mobile source contributions was not largely impacted by the selection of source profile. Pant et al. (2014) generally agrees with traffic profiles measured in the field and used different traffic profiles— including tests by dynamometer— that gave approximately similar estimates of traffic PM_{2.5} mass. However, Gillies and Gertler (2000) stated that similar mobile sources have distinctive characteristics, and caution should be exercised when selecting which profiles to use in source apportionment studies. The studies, however, mainly compare USA mobile source profiles and seldom consider PM sources from non-USA vehicles profiles.

As far as we know, this is the first study to compare the USA and Chinese mobile source profiles and test the sensitivity of them.

This paper has two goals. First, it presents the sensitivity of mobile source contributions from various mobile source profiles to determine whether non-local mobile source profiles are necessary. Second, it presents the sensitivity of non-mobiles source contributions that are determined by molecular marker CMB models to the use of non-local mobile source profiles.

2 Methods

2.1 Ambient data

The ambient data was collected from a published study that provided the USA daily PM_{2.5} samples from the St. Louis-Midwest Supersite (Bae et al., 2004). Measurements were obtained for 24-hour average samples every 6th day over the periods from May 1st, 2001 through April 30th, 2003. The remaining samples from the USA site were used in this study the 5-in-6 day samples were collected from May 2002 through April 2003 (Zhang et al., 2009). OC and EC were measured using a thermal-optical ECOC analyzer (Sunset Laboratory Inc., Forest Grove, OR) (NIOSH, 1996), and speciated organic markers were measured using solvent extraction and gas chromatography mass spectrometry (GCMS) (Schauer et al., 2002; Sheesley et al., 2007a). The 1-in-6 day samples were extracted using a mixture of methanol and dichloromethane, while the remaining samples were extracted using only dichloromethane. To eliminate

possible statistical bias caused by the measurement difference, only the 5-in-6 day samples from May 2002 through April 2003 were selected. Days with missing or invalid data were removed, and samples from 284 days were used in this study. Nine Chinese ambient samples were taken from three sites and analyzed using the same method (Table.1). Only organic markers and OC and EC were used to run the CMB model, so the apportionment model was set up to apportion atmospheric concentrations of OC.

All the measurements were blank corrected using field blanks that were handled, stored and shipped in the same manner as the samples. The uncertainties for molecular marker analysis was determined by:

$$\sqrt{(20\% \times Conc.)^2 + (STDEV_{blk})^2} \quad (1)$$

Where *Conc.* is the measured concentration and *STDEV_{Blk}* is the standard deviation of the measured concentrations of the field blanks, including all sample analysis batches.

2.2 Source profiles

Five molecular marker source profiles from the literature were used in the model, including vegetative detritus, biomass burning, coal burning, and two mobile source profiles (The USA one and a Chinese one). The vegetative detritus profile measured by Rogge et al. (1993) included samples of live and dead leaves from sixty-two individual plant species in the Los Angeles area. The biomass burning profile is an average of four wood burning profiles (Sheesley et al., 2007b). The coal burning profile used emissions from thirteen industrial boilers

and ten residential stoves, in order to represent real-world coal burning emission (Zhang et al., 2008).

2.2.1 USA mobile source profiles

The USA mobile source profiles are from Lough et al. (2007) that include an emissions testing of a vehicle fleet of fifty-three gasoline-powered and thirty-three diesel-powered vehicles. This study included seven of the gasoline cars that were identified as smoking vehicles (high-emitting). Vehicle fleet averages follow the LA diesel vehicle age distribution (Lough and Schauer, 2007). In order to match the species in the ambient data to the non-local mobile source profiles, twenty-five markers were chosen, including twenty-four organic markers and EC. The key tracers used in the model are shown in Figure 1. Levoglucosan is an effective tracer of biomass burning (Simoneit, 1999) and is widely used in both MM-CMB and PMF models (Sheesley et al., 2007b; Shrivastava et al., 2007). Hopanes and sterane are biomarkers of mobile source (Phuleria et al., 2007) and picene is a specific marker of coal burning source (Zhang et al., 2008). PAHs, like Benzo(β)fluoranthene, Indeno(1,2,3-cd)pyrene and Benzo(ghi)perylene, are produced from incomplete combustion so they are tracers of most combustion sources (Ravindra et al., 2008).

2.2.2 Chinese mobile source profiles

Eighteen Chinese vehicles (eight gasoline cars, five diesel cars, and five motorcycles) were analyzed for the non-local traffic profiles (Zhang and Zhang, 2010). To maintain consistency with USA mobile source profiles, motorcycles

were removed and the non-catalyst-equipped gasoline cars were regarded as smoker vehicles. Gasoline and diesel profiles both consisted of three light cars and two heavy cars. To match the local source profiles, the same compounds were chosen for the model input.

To express the USA and Chinese traffic profiles, the phrases “US case” and “CN case” will be utilized from now on.

2.3 CMB model

CMB 8.2 was developed by the U.S. Environmental Protection Agency (EPA) and used to apportion fine particle organic carbon (OC) in this study. As a receptor model, CMB 8.2 compares the chemical composition of ambient particles and pollutant source emissions and calculates the source contributions through an effective variance least squares solution (Schauer et al., 1996). This model takes the uncertainties of both ambient data and source profiles into account in the calculations and provide estimates of source contributions uncertainties (Pirovano et al., 2015). To meet performance standards, R^2 , χ^2 and percent mass must fall within the following parameters, respectively: greater than 0.8, less than 4, and between 80-120%.

3 Results

Forty-six samples were randomly chosen from all 284 US samples to test mobile source profile sensitivity. These samples were used to run the CMB model twice—once with the US case and another with the CN case.

3.1 Primary Sources Contributions

Four primary OC sources were considered in this study: vegetative detritus, biomass burning, mobile source, and coal burning. Biomass burning and mobile sources were the two major pollution sources in the study area, but coal combustion contribution was extremely high during some days, as well. Figure 2 shows the variation in results between the US and CN cases. The source contribution estimation (SCE) from the CN case is represented on the Y-axis, while the SCE for the US case is shown on the X-axis. When the slope of their regression line is close to one, the source contribution result may be insensitive to a change in the mobile source profile. Vegetative detritus and biomass burning are two insensitive sources, since the regression line for biomass burning is $y = 1.06x$ with an R^2 of 0.98 (Figure 2). The slope value shows that the SCE of biomass burning becomes approximately 1.06 times larger when a non-local mobile source profile is applied. However, the average uncertainty for biomass burning SCE is 40.3% for the US case, which is larger than the error caused by a change in mobile source profiles. High R^2 suggests that the biomass burning SCE was quite stable in the CMB model in both cases when non-local mobile profiles are used. Ratios between biomass burning SCE and parallel levoglucosan contribution in the atmosphere are shown in Figure 3. The regression lines for both cases have high R^2 values (>0.98), which means the SCE of biomass burning is strongly connected to the levoglucosan concentration in the CMB model. Since the levoglucosan/OC levels in mobile source profiles is negligible, the biomass

burning profile is not significantly affected when other mobile source profiles are applied. The slope of the vegetative detritus regression line is 0.96 and the R^2 is 0.98, which suggests that vegetative detritus is marginally influenced by other sources. The effectiveness for tracing vegetative detritus burning with n-nonacosane and n-hentriacontane is shown by the modified pseudoinverse matrix (MPIN, CMB output) (Sheesley et al., 2007b). The most approximate n-nonacosane/OC factor for Chinese diesel vehicle profiles was one tenth of that in vegetative detritus profiles.

Mobile SCE was influenced by mobile source profiles significantly. The regression line of the SCE in both cases was $y = 0.35x$ with an R^2 of 0.13 (Figure 2c). Therefore, significant underestimations exist when non-local mobile source profiles are used in the CMB model. Since mobile SCE is the sum of diesel, gasoline, and smoker vehicle SCE, its average uncertainty is large — 23.1%.

However, the bias for the non-local source profile was beyond the range of uncertainty, so the mobile SCE was sensitive to its profiles' variation. The relatively low R^2 for mobile sources (Figure 2c) suggests that they are not stable for running CMB models and may be affected by many factors. Hopanes and steranes found in $PM_{2.5}$ exhaust emission may help trace the diesel and gasoline exhaust in atmosphere (Schauer et al., 1999). Hopanes, such as 17 α (H)-22,29,30-trisnorhopane (TNO), 17 β (H)-21 α (H)-30-Norhopane (B17), and 17 α (H)-21 β (H)-Hopane (A17), along with other tracers, like EC, can also be used as diesel source tracers. Coal burning and other fossil fuels sources emit hopanes

as well, which may complicate source distinguishability in the CMB model. All these factors may influence the mobile SCE in the CMB outputs. Three kinds of hopanes, steranes and EC were used as mobile tracers in this study. Figure 4 shows the correlation between mobile SCE and hopane concentrations in the atmosphere for both cases. The sum of TNO, A17, and B17 concentrations is referred to as HP. It is clear that the R^2 values from the four regression lines in the US case, shown in Figure 4a (0.85, 0.75, 0.80 and 0.76), were much higher than those from the CN case, shown in Figure 4b (0.17, 0.11, 0.17 and 0.16). This suggests that using local mobile source profiles may explain mobile source contribution with greater accuracy, since mobile SCE increased with higher hopane concentrations in ambient samples. R^2 of regression between SCE and HP concentration in both cases were higher than correlations between SCE and singular hopane concentrations, so it is preferred to use a multitude of hopane concentrations as molecular markers rather than a singular hopane concentration.

Coal burning was a slightly influential source, with a slope of 1.16. The bias was smaller than its own average uncertainties of 24% and 33%, which were accepted in the CMB model according to the user manual. Along with hopanes, picene is a molecular marker of coal burning (Oros and Simoneit, 2000; Zhang et al., 2008). However, the tracers in common with mobile sources could influence the distinctiveness of these two sources. Relatively high uncertainty was reflected in the R^2 of coal burning regression (Figure 2d).

3.2 Secondary source

Secondary organic carbon (SOC) consists of organic particles formed in the atmosphere from volatile organic compounds (VOCs) and oxidants emitted by primary sources (Sheesley et al., 2004). Although several precursors of SOC have been identified by the smog chamber method (Baltensperger et al., 2005; Zhao et al., 2015), they are not widely used as tracers in MM-CMB models for secondary source estimations, since a limited number of known tracers leads to high uncertainty for SOC contribution (Lewandowski et al., 2008). An effective method is to calculate the difference-value between OC and primary OC (POC) that is aforementioned primary SCE. This value is also called “other” or “other OC” in many published studies (Schauer and Cass, 2000; Hasheminassab et al., 2013). The CMB model apportions a majority of POC to the “other” category, so it is nearly equal to the SOC contribution. The OC/EC minimum ratio method was used to determine SOC contribution, as well (Pio et al., 2011). The OC/EC minimum ratio $((OC/EC)_{pri})$ in a long data set was regarded as primary OC/EC, then SOC was estimated from the equation:

$$SOC = OC - \left(\frac{OC}{EC}\right)_{pri} \times EC \quad (2)$$

In this study, the OC/EC minimum ratio method was used as a reference to test SOC contributions, with an $(OC/EC)_{pri}$ of 1.91 from forty-six samples. Figure 5 presents three SOC contributions of filtered samples in a time series. The average SOC contributions during four seasons (summer, fall, winter, and spring) were 3240, 2628, 2263 and 2083 ng/m³, respectively. Higher temperatures

and increased sunlight during the summer caused a significant increase in SOC contribution. The similar trends of three lines showed the accuracy of both SOC estimated methods. The SOC contribution and OC/EC minimum ratio method results are more closely aligned in the CN case than in the US case. Between the two cases, the US apportions fewer SOC contributions than CN. Assuming the value calculated by $(OC/EC)_{pri}$ is standard, the CN case gives a better SOC result.

3.3 Case analysis

As stated previously, the SOC contribution and OC/EC minimum ratio method results agreed more favorably in the CN case. In the CMB model, secondary source contribution is calculated directly from the contributions of primary sources. CN's mobile source profile has higher emission ratios (normalized to OC), which is illustrated in Figure 1. The n-alkane factors in Chinese mobile source profiles are about ten times larger than those in American mobile source profiles and Chinese hopanes and steranes (mobile source tracers) factors were much greater. Although Chinese mobiles source profiles were measured three years later than American profiles (2004 and 2001, respectively), the vehicle emission standard implemented in China was still lower than that in the US. The equivalent of Euro II and Euro III emission standards (Wu et al., 2011) and "dirtier" mobile source profiles might result from lower fuel and vehicle qualities in China. The "dirtier" mobile source profiles, however, resulted in similar results between CMB model and OC/EC minimum ratio method.

Both mobile source profiles were measured using the chassis dynamometer-dilution tunnel method (Schauer et al., 1999). To carry out this technique, vehicle exhaust is mixed with carbon-filtered air in a pre-dilution tunnel connected to the tailpipe. Then, particles smaller than 2.5 μm in aerodynamic diameter are screened by a cyclone separator and collected via parallel teflon and quartz filters. The particles collected by this method are only those emitted from tailpipes, but real-world mobile sources include engine exhaust, fuel volatilization, lubrication oil volatilization, tire debris, and brake lining dust. Fuels volatilization in old vehicles may have similar organic compounds as engine exhaust, and hopanes and steranes are present in lubrication oils employed by most vehicles (Phuleria et al., 2007). The main deficiency of the chassis dynamometer method is the underestimation of total emissions from vehicles in source sampling. Thus, CMB models apportion a higher contribution of OC mass to traffic. Tunnel profiles that collect all particles generated by vehicles will result in less apportionment to mobile contribution than dynamometer profiles (Pant et al., 2014). The over-apportionment of mobile source contribution is analogous to that caused by missing primary sources (Subramanian et al., 2007). The distance between the two mobile source profiles may reduce the sampling underestimation from the chassis dynamometer-dilution tunnel method, so the SOC contribution in CN case was more close to OC/EC minimum ratio method results in this study.

Discussion

In previous sections, it was shown that daily mobile source contribution is sensitive to variation in mobile source profiles. However, some studies—especially those for policy-making—consider monthly or yearly source contribution. To test the sensitivity of monthly and yearly SCEs, ambient pollutant concentrations in 273 samples were averaged for twelve months, and the resulting annual mean was used in the CMB. The results are shown in Figure 6. Daily results of source contribution from vegetative detritus, biomass burning, and coal burning are not sensitive to traffic profile variation, with slopes of 0.96, 1.02 and 1.33, respectively. For mobile sources, the slope of average monthly samples is higher than that of daily samples, rising from 0.35 to 0.54. This suggests that averaging samples decreases mobile SCE sensitivity, which is confirmed by source apportionment results for the annual mean sample. The mobile SCE ratio (CN to US) is 0.82, and the ratios for the other three sources are all close to 1 (Figure 7). Non-local mobile source profiles can be utilized for studying the average source contribution during a long period.

Nine Chinese ambient samples were collected from a previous study of our group and were analyzed using the aforementioned method. The results are shown in Figure S1. Three insensitive primary sources are still little influenced by a change in mobile source profiles, and the slope of mobile SCE regression is 0.79. In this case, all source contribution, even daily samples, are insensitive to traffic source variation, which means USA mobile source profiles can be applied in source apportionment in China. However, these Chinese samples were taken

from three different sites, which means they represent a regional average and mobile SCE is less sensitive to traffic profile change.

4 Conclusion

Due to the lenient vehicle emission standards in China, most organic pollutant emission ratios (normalized to OC) for non-local Chinese mobile source profiles were higher than those in local USA profiles— especially n-alkanes and hopanes. Use of different mobile source profiles led to CMB results with significant differences in daily samples. In apportioned OC, vegetative detritus and biomass burning SCE were influenced slightly with slopes of 0.96 and 1.06 (R^2 were 0.98 in both cases) when vehicle profiles changed. The stability is mainly due to the specificity of levoglucosan, n-nonacosane, and n-hentriacontane in these two sources. The coal burning SCE was moderately affected by mobile source replacement with a linear ratio of 1.16 ($R^2 = 0.86$). The choice of mobile source profiles impacted mobile SCE significantly, with an average decrease of 65% when a non-local traffic profile was applied. In both cases, the correlation between mobile SCE and total hopane concentration is better than correlation between mobile SCE and a singular hopane concentration, which suggests simultaneously using all hopanes is more effective in mobile tracing. The SOC results calculated by the OC/EC minimum ratio method agreed more favorably with SOC contribution in the CN case than the US case, and it suggests that underestimated mobile profiles measured by the chassis dynamometer-dilution

tunnel method may cause over-apportioned mobile contributions.

When a greater number of samples are averaged, the influence caused by using non-local traffic profiles decreased. The influence of using non-local mobile source profiles lessened when ambient samples were averaged over timescales of months and a year. The results from this study suggest it is feasible to calculate source contributions with the USA mobile source profiles in China, while it will cause problems to use Chinese mobile source profiles in the USA.

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Figure 1. Comparison of organic tracers between American and Chinese mobile source profiles. (a) Diesel profiles; (b) smoking vehicle and Chinese gasoline car profiles; (c) American gasoline car profiles. The values for species mass were normalized to OC mass and represented in logarithmic terms.

Source contribution estimated in the US case (ng OC/m³)

Figure 2. Correlation of corresponding SCE in CN and US cases. Data for four sources and regression lines are shown in each figure. Y-axis and X-axis represent SCE in CN and US cases, respectively.

Figure 3. Correlation between biomass burning contributions and levoglucosan concentration. Solid and hollow dots represent the biomass burning source contributions in the US and CN cases, respectively.

Figure 4. Correlation between mobile contribution and molecular marker concentrations, including Trisnorhopane (TNO), 17 α (H)-21 β (H)-Hopane (A17), 17 β (H)-21 α (H)-30-Norhopane (B17), and the sum of both (HP). Regression lines are included for each tracer. (a) Correlations in the US case; (b) correlations in the CN case.

Figure 5. Time series of SOC contributions calculated by the CMB and OC/EC minimum ratio method, including filtered 137 samples from May 2002 to April 2003 (a) and the regression between two SOC contributions calculated (b).

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529 Figure 6. Correlation of corresponding SCE in the CN and US monthly cases. Data for four
530 sources and regression lines are shown in each figure. The Y-axis and X-axis represent SCE in
531 the CN and US cases, respectively.
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536 Figure 7. Source contribution comparison between the US and CN cases using yearly average

537 samples.

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Table 1 Information about nine Chinese ambient samples

Sample	Site	Date
1	EPSI of Guangzhou	10/6/2004
2	EPSI of Guangzhou	10/7/2004
3	The east gate of PKU	1/20/2005
4	The east gate of PKU	1/21/2005
5	UCAS	10/3/2013
6	UCAS	10/6/2013
7	UCAS	10/12/2013
8	UCAS	10/15/2013
9	UCAS	10/27/2013

540 EPSI: Environmental Protection Science Institute; PKU: Peking University; UCAS: The
541 University of Chinese Academy of Science, Yuquan Road, Beijing.

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