HHS Public Access

Author manuscript

Atmos Environ (1994). Author manuscript; available in PMC 2016 July 25.

Published in final edited form as:

Atmos Environ (1994). 2014 February ; 84: 65–77. doi:10.1016/j.atmosenv.2013.11.031.

Constrained Source Apportionment of Coarse Particulate Matter and Selected Trace Elements in Three Cities from the Multi-Ethnic Study of Atherosclerosis

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Abstract

$PM_{10\text{-}2.5}$ mass and trace element concentrations were measured in Winston-Salem, Chicago, and St. Paul at up to 60 sites per city during two different seasons in 2010. Positive Matrix Factorization (PMF) was used to explore the underlying sources of variability. Information on previously reported $PM_{10\text{-}2.5}$ tire and brake wear profiles was used to constrain these features in PMF by prior specification of selected species ratios. We also modified PMF to allow for combining the measurements from all three cities into a single model while preserving city-specific soil features. Relatively minor differences were observed between model predictions with and without the prior ratio constraints, increasing confidence in our ability to identify separate brake wear and tire wear features. Brake wear, tire wear, fertilized soil, and re-suspended soil were found to be important sources of copper, zinc, phosphorus, and silicon respectively across all three urban areas.

Keywords

source apportionment; coarse particulate matter; air pollution; positive matrix factorization; brake wear; tire wear; soil; agriculture; trace elements

1. Introduction

There is ample evidence that long-term exposure to fine airborne particles ($PM_{2.5}$) is detrimental to human health (Pope & Dockery 2006; U.S. EPA 2009). In contrast, our understanding of the long-term effects of the coarse particle fraction ($PM_{10\text{-}2.5}$) is more

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limited (Dockery et al. 1993; Pope et al. 2002; Brunekreef & Forsberg 2005; Weuve et al. 2012; Puett et al. 2009; Lippmann and Chen, 2009). One major challenge for chronic epidemiological studies is in accurately describing the long-term spatial gradients in coarse mode mass and species concentrations within urban areas. Recent work has focused on characterizing $PM_{10\text{-}2.5}$ spatial concentration gradients (Hwang et al. 2008; Godoy et al., 2009; Thornburg et al. 2009; Moore et al. 2010; Cheung et al. 2011; Eeftens et al., 2012, 2012a; Clements et al. 2012; Strak et al. 2011) and developing models to allow spatial interpolation (Yanosky et al. 2009; Peltier et al. 2011; Eeftens, et al. 2012a). Another challenge is to characterize the sources that influence these gradients as well as the species that are associated with these sources.

Prior source apportionment studies of $PM_{10\text{-}2.5}$ have relied on either fully constrained models such as chemical mass balance (CMB), principal component analysis (PCA) and mass closure, (Paode et al. 1999; Manoli et al. 2002; Almeida et al. 2006; Stone et al. 2010; Daher et al. 2012; Oliveira et al. 2010; Waheed et al. 2012; Pakbin et al. 2011; Cheung et al. 2011), partially constrained models such as the constrained physical receptor model (COPREM) (Wahlin et al. 2006; Schauer et al, 2006), or relatively unconstrained models such as factor analysis or positive matrix factorization (PMF) (Wang and Shooter, 2005; Gietl and Klemm 2009; Begum et al. 2011; Begum 2010; Kertész et al. 2010; J. S. Han et al. 2006; Oh, 2011; Tecer et al. 2012; Mazzei et al., 2007; Chan et al., 2008; Hwang et al., 2008; Godoy et al., 2009). Several of these studies have employed multiple sites within a city to capture spatial as well as temporal variability in the source contributions (Stone et al. 2010; Mazzei et al. 2007; Cheung et al. 2011; Chan et al. 2008; Hwang et al. 2008; Godoy et al. 2009; Pakbin et al. 2011).

While there has been a number of near-roadway studies examining the sources and components of non-exhaust $PM_{10\text{-}2.5}$ (Thorpe and Harrison 2008; Harrison et al., 2012; Apeagyei et al., 2011; Schauer et al. 2006; S. Han et al. 2011; Kennedy & Gadd, 2000; Garg et al. 2000; Iijima et al. 2008; Gietl et al., 2010; Grieshop et al., 2006; Bukowiecki et al., 2009; von Uexküll et al., 2005; Sternbeck, 2002; Adachi and Tainosho, 2004; Johansson et al., 2009; Amato et al., 2011; Wahlström et al., 2009; Bukowiecki et al., 2010), only a few of the urban-scale source apportionment studies cited earlier have attempted to separate “road dust” into its separate components, including brake wear and tire wear (Wahlström et al., 2009; Amato et al., 2011; Schauer et al, 2006; Bukowiecki et al., 2010; Harrison et al. 2012). The studies which did not separate road dust into its components commonly identified the dominant source of $PM_{10\text{-}2.5}$ as resuspended road dust for sites near roadways and as crustal material for non-roadway sites.

Here we use a partially constrained version of PMF (Amato et. al. 2009; Reche et. al. 2012; Brown et. al. 2012) in order to examine the sources of $PM_{10\text{-}2.5}$ collected simultaneously at multiple sites in three urban areas during two-week periods in two different seasons. We use PMF with constraints imposed by prior knowledge of several important, ubiquitous source profiles, namely brake and tire wear. We furthermore impose additional constraints on the source contributions in order to combine all measurements into a single model. To our knowledge, this is the first application of a combined-cities PMF modeling approach with profile-constraints to identify contributions of brake and tire wear in $PM_{10\text{-}2.5}$ across multiple urban areas. This work is part of a larger effort to examine the chronic health effects of $PM_{10\text{-}2.5}$ and selected species in these same cities under the auspices of the Multi-Ethnic Study of Atherosclerosis and Coarse Particulate Matter (MESA Coarse), an ancillary study of the Multi-Ethnic Study of Atherosclerosis and Air Pollution (MESA Air).

2. Materials and Methods

2.1 Filter sampling and analysis

The MESA Air study leveraged the National Heart, Lung, and Blood Institute's Multi-Ethinic Study of Atherosclerosis (MESA) cohort to provide data for assessing the relationship between long-term exposures to fine ambient particulates and related health effects. The MESA cohort (Kaufman et al. 2012) was comprised of 6,814 white, black, Hispanic, and Chinese participants located in six U.S. cities. As an ancillary study to MESA Air, MESA Coarse assesses the health implications associated with coarse mode particulate exposure in three of the MESA cohort cities, namely Chicago, Illinois, St. Paul, Minnesota, and Winston-Salem, North Carolina.

Paired, two-week average PM_{10} and $PM_{2.5}$ Teflon filter samples were simultaneously collected over two different two-week periods, in the winter and summer of 2009, in Chicago, IL, St. Paul, MN, and Winston-Salem, NC. The monitoring sites in each city (see Figure 1) were residential locations of the existing MESA cohort selected to maximize variability in geographic features expected to influence coarse particles including land use, roadways, and vegetation as well as representative community monitoring sites. $PM_{10\text{-}2.5}$ mass concentrations were computed by the difference in collocated PM_{10} and $PM_{2.5}$ measurements. This "difference method" has been shown to be a reliable approach in estimating $PM_{10\text{-}2.5}$ in urban areas by the U.S. Environmental Protection Agency (Chen et al. 2011). At affiliated field centers in each sampled city, the Teflon filters were loaded into Harvard personal environmental monitors (HPEMs, Harvard School of Public Health, Boston, MA). These monitors were connected to a Medo VP0125 (MEDO USA, Inc., Roselle, IL) vacuum pump drawing 1.8 L/min air sample and equipped with a timer valve system that obtained a 50% duty cycle sample, where the flow alternated between the PM_{10} and $PM_{2.5}$ filter every 5 minutes to avoid filter overload.

PM_{10} and $PM_{2.5}$ mass concentrations were gravimetrically determined from weighing of Teflon filters at the University of Washington in a temperature and humidity controlled environment (Allen et al, 2001), and from the total volumetric flow of air sampled through the HPEMs. A Mettler-Toledo UMT-2 balance was used to determine sample mass following standard filter weighing procedures. Overall, the precision of duplicate PM_{10}, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ samples as measured by the average Relative Percent Difference was 2%, 10% and 18%, respectively. The filter samples were analyzed for a suite of 48 elements by X-Ray Fluorescence (XRF) at Cooper Environmental Services (Portland, OR). Method sensitivity was defined by a set of acceptable detection levels for a subset of 21 key elements from the Method IO-3.3 analyte list. The quality assurance and quality control data are provided in Tables A7 and A8.

2.2 PMF Model Inputs

Measurement uncertainty for coarse mode species j, σ_j, was calculated by combining the uncertainties of the PM_{10} and $PM_{2.5}$ measurements using standard error propagation as follows.

$$(\sigma_j^2)_{\mathrm{PM}_{10-2.5}} = (\sigma_j^2)_{\mathrm{PM}_{10}} + (\sigma_j^2)_{\mathrm{PM}_{2.5}} \quad (1)$$

The measured coarse mode species concentrations were pre-processed to remove frequently below detection species and species with a signal to noise (Norris and Vedantham 2008), S/N, <10. In addition, pre-processing included removal of sulfur samples identified as outliers (exceeding 2 standard deviations from the mean). Four samples were removed based on this criterion. The S/N cutoff choice was motivated by the consistently high signal to noise ratios of a subset of species and relatively low and variable ratios for some species depending upon city. Enrichment of the coarse mode for certain elements is not unexpected and has been documented in other literature (Amato et. al., 2011b; Tecer et. al, 2012; Carvalho et. al., 2011). The S/N criteria eliminated the following species: Ag, As, Au, Cd, Ce, Co, Cs, Eu, Ga, Hf, Hg, In, Ir, La, Mo, Nb, Rb, S, Sc, Se, Sm, Sn, Ta, Tb, V, W, and Y (see Table A1 in Appendix A). Although Sb had S/N < 10, we chose to include it in the models because of its value as a brake wear constraint variable described in the next section. We retained $PM_{10\text{-}2.5}$ mass but increased its uncertainty by a factor of 30 to avoid redundancy with all other measured species. The retention of coarse mass allows for the production of feature profiles in a gram per gram $PM_{10\text{-}2.5}$ basis. There were no missing species measurements. We also ran the models including all species with S/N > 2 without any significant difference in our final results.

3. Theory/calculation

We implemented the Positive Matrix Factorization (PMF) receptor model using the Multilinear Engine version 2 (ME-2) (Paatero, 1999). The PMF model solves the basic mass balance equation (Equation 2) for source contributions, g_{ik}, source profiles, f_{kj}, and model error, e_{ij}, for i=1,n samples, j=1,m species, and k=1,p sources. Species concentrations, x_{ij}, corresponding uncertainties, σ_{ij}, and the user-defined number of sources, p, serve as the model input.

$$x_{\mathrm{ij}} = \sum_{k=1}^{p} g_{\mathrm{ik}} f_{\mathrm{kj}} + \varepsilon_{\mathrm{ij}} \text{where } g_{\mathrm{ik}}, f_{\mathrm{kj}} > 0 \quad (2)$$

and the g_{ik} are normalized by their average value across all samples such that

$$\overline{g}_{\mathrm{ik}} = \sum_{i=1}^{n} \frac{g_{\mathrm{ik}}}{n} = 1 \pm \delta \quad (3)$$

where δ = 0.01 in this case.

Equations 2 and 3 comprise the basic PMF model. To add prior source profile constraints, we have added an additional set of equations that are solved simultaneously with equations 2 and 3. In this case we have added equations representing each of t=1,v species constraints using prior knowledge of two sources: brake wear (k=1) and tire wear (k=2). The t^{th} constraint is shown in equation 4.

$$f_{\mathrm{kq}} - \lambda_t f_{\mathrm{kr}} = 0 \quad (4)$$

where the k^{th} source profile (k =1 or 2) is constrained using the r^{th} and q^{th} species, and λ_t represents the value of the species ratio for that source profile, f_{kq}/f_{kr}. The constraints were developed from a literature review of brake wear and tire wear source profiles (Table 1). The median values for each reported ratio were used.

We present, in equation 4, ratio constraints in the form of a difference with a target of zero. However, within the code of ME-2 we define sub-expressions to invert the denominator element for each ratio constraint and then define an auxiliary equation to represent the ratio. Thus, the ratio is constrained to the target value, λ_t, not zero. Due to the construct within ME-2 we applied error mode −12. The alternative, error mode −5, is limited to special cases where the target is zero (Paatero 2009). Through the use of error mode −12 and our ratio constraints we are able to control the order of the constrained model results. This approach differs from other similar studies which model the data unconstrained, identify source-like features, and then pull up or down (error mode −22) to a desired target.

In ME-2, equations 2 through 4 are solved by minimizing an object function, Q, through the use of a preconditioned conjugate gradient algorithm. The object function (equation 5) includes a penalty, q_t, associated with the applied constraints.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} [\varepsilon_{\mathrm{ij}}]^2 + \sum_{t=1}^{v} q_t \quad (5)$$

We implement this in ME-2 by specifying auxiliary equations for q_t using error mode −12 and penalty values of 0.1. For constraint t in equation 4, these penalty values define the maximum allowable error from the defined constraint. The penalty values associated with a given constraint are shown in Table 1.

In order to increase the number of measurements used in the model, we combined all samples into one larger combined-city model. We hypothesize that the brake and tire wear profiles are universally applicable across all three cities. However, we assume that the soil profiles differ by geographic region of the country and therefore differ by city. To address this issue, we modified the model to allow three separate soil profiles, one for each city, while keeping all other features in common across cities. For the three soil sources (k=3 to 5), we allowed only one unique source in each of the three cities (c=1 to 3) as follows:

$$g_{\mathrm{ik}}=\sum_{c=1}^{3}\beta_c g_{\mathrm{ikc}}$$

$$\text{where}\beta_c=\left\{\begin{array}{c}1 \text{ for } c=k-2\\ 0\pm 1x10^{-5} \text{ for } c\neq k-2\end{array}\right\} \quad (6)$$

We did this by enforcing hard constraints in the form of additional auxiliary equations with a target of zero and a tolerance for error of 1e-5 ug/m^3 on the contributions from the soil sources of two of the three cities. We also included additional upward pulling of Si on the sources to ensure the features were soil related (see Table 1); the pulling was limited by a maximum change in Q of 400. In addition, to insure that it is the soil profile that we are restricting with equation 6, we add additional profile constraints for k = 3 to 5 (see Table 1) based on prior knowledge of the soil-derived $PM_{10-2.5}$ from the literature as well as from the individual city model predictions.

$$f_{\mathrm{kq}}-\lambda_t f_{\mathrm{kr}}>0 \quad (7)$$

For an initial user-specified value of p, multiple model runs were conducted at 20 different starting points chosen randomly, and the chosen p-source baseline model was the one with the minimum value of Q (= Q_{min}). Separate model runs were then made assuming a range of values of p. The final value of p was chosen based on the following criteria: the ratio as a function of p between Q_{min} and $Q_{theoretical}$ = n*m_s +n*m_w/3 –n*p, where m_s is number of strong species and m_w is the number of weak species; changes in Q as a function of p (Comero, Capitani, and Gawlik, 2009), the relationship between each f_{kj} and prior knowledge of source profiles; the known source types within the modeled region; and user judgment. The values of Q/$Q_{theoretical}$, degrees of freedom, and the selected number factors for each model are presented in Table A9 and plots of Q/$Q_{theoretical}$ for various p are provided in Figure A1.

Blocked bootstrapping (Norris & Vedantham, 2008) was then applied to the baseline model results, providing an estimate of the confidence limits of the f_{kj} and the average values of g_{ik} by city. Given that the 2-week samples were collected simultaneously over space in each city only twice and only a fraction were re-sampled in both seasons, a sample block size of 5 was defined to contain samples within a season for a given city. Profile matching was done on the predicted contributions of Ba, Br, Cl, Cu, Fe, Mg, Na, Ni, P, Pb, Si, Zn and Zr, with an acceptable match defined as an R^2 > 0.6 across all contributions for a given model run.

To assess the effect of the prior profile constraints, the model was run with and without these constraints. In the latter case, q_t = 0. We also ran the constrained and unconstrained models for each city separately (in this case equations 6 and 7 were not used).

4. Results

In addition to the brake wear, tire wear, and city-specific soil features, the combined cities model was able to identify three additional source-related features: fertilized soil, road salt, and a feature enriched in Pb. For individual city models, the features in addition to brake and tire wear and soil were: fertilized soil in all cities, a metals-rich feature in Chicago, and a road salt feature in St. Paul. The source-related profiles are shown in Figures 2 to 5. The g_{ik} are normalized in such a way (equation 3) that the f_{kj} (vertical bars in each figure) represent the average species concentrations contributed by a given feature across all samples. Table A2 in Appendix A summarizes model performance statistics. Table A6 shows the estimated average $PM_{10\text{-}2.5}$ contributions percentages by feature, model and city. Table A3 provides the estimated average $PM_{10\text{-}2.5}$ contributions and associated bootstrapped errors. Table A4 shows the estimated contribution of selected species and Table A5 provides the correlations between the contributions of each feature. Table 2 summarizes the average ratio of tire wear to brake wear contributions to $PM_{10\text{-}2.5}$ by model and city. Finally, Table 3 shows the pairwise correlation coefficients between the g_{ik} and measured concentrations of selected species.

4.1 Brake Wear

The brake wear profiles for all models are shown in Figure 2. As expected, the Cu/Fe, Cu/Sb and Cu/Ba ratios are consistent with the prior constraints in all four constrained model-derived profiles (ad). An additional “Metals-rich” factor (e) was identified in the Chicago individual model that contributes significantly to both Cu and Ba, but not to Sb. The contribution to Zn is low in all profiles except the Chicago individual profile (b). The predicted average contributions of brake wear to $PM_{10\text{-}2.5}$ are generally higher for the individual city models than for the combined city model (see Table A6).

The effect of the prior brake wear profile constraints on the final brake wear profiles is relatively minor for the combined cities model (a) with the exception of Sb which is pulled to a larger value in the constrained case. The effect of the prior constraints on this profile is also small for the individual city models, with the exception of increasing the P concentration in Winston Salem (d). Comparing the constrained combined cities brake wear profile with its individual city counterparts, the differences are again small except for the absence on Al in the combined profile (a).

The brake wear contributions of Al, Ca, Fe, and Si are similar to the soil profiles across the individual city models. Within the combined model, the source contributions of these elements decreases and the bootstrapped variability of the contributions become significantly wider. The “Metals-rich” factor found in the Chicago individual model also contains these elements along with others found in the brake wear profile, but differentiates itself from brake wear due, not only to the differences in Sb mentioned above, but also due to a lack of Zn and the addition of P.

4.2 Tire Wear

The tire wear profiles are shown in Figure 3. The percent contribution to Zn is high in all tire wear profiles (a–d). The Pb to Zn ratio is consistent with prior constraints except for the Chicago individual model (b), where Pb/Zn is larger than specified by the soft constraint. In contrast, an additional “Pb-rich” factor is present in the combined model (e) that is distinctly separate from the accompanying tire wear profile (a). The effect of the prior profile constraints on other species is small for all models with the exception of Ca which is smaller in the constrained case for all profiles (a to d) and K which is smaller in St. Paul and Winston Salem (c and d). The predicted average contributions of tire wear to $PM_{10\text{-}2.5}$ are shown in Table A3. The confidence intervals for $PM_{10\text{-}2.5}$ from tire wear are generally smaller for the constrained, combined city model compared with the other models.

4.3 Soil

The soil profiles are shown in Figure 4. The effect of prior tire and brake wear constraints on the soil profile is small in all models. In addition, the combined versus individual city model profiles are similar with the exception of P in Chicago (a vs. b), and Mg and P and Pb in St Paul (c vs. d). Predicted average $PM_{10\text{-}2.5}$ contributions and their associated confidence intervals by city are generally lower for the individual city models than for the combined cities model (Tables A4 and A6)

4.4 Fertilized Soil

The fertilized soil profiles are shown in Figure 5. All four profiles (a–d) indicate that fertilized soil is a major contributor to P, Mg and K concentrations. The effect of prior tire and brake wear constraints on the fertilized soil feature is small in all models. Compared with the combined model (a), Ba is slightly enriched in the Chicago and St. Paul features (b and c) and Mg is enriched in St. Paul. The contribution of this feature to $PM_{10\text{-}2.5}$ is generally larger in the individual city models than the combined city model.

4.5 Other features

The road salt profiles are shown in Figure 5. The road salt feature is similar to that reported by Schauer and coworkers (2006) and contributed substantially to both Na and Cl levels. Its contributions were only observed in St. Paul during the winter sampling period but not in the summer nor in the other two cities. This city makes extensive use of NaCl as a road deicing agent during snowfall events (Sander et al. 2007). Such events occurred during our winter sampling campaign in St. Paul, but not during winter sampling campaigns in either Chicago or Winston-Salem. The effect of the tire and brake wear constraints is small. For the road salt model, the difference between the combined and individual cities model is also small. This is consistent with the fact that the predicted road salt contributions are negligible in Chicago and Winston Salem.

The Pb-rich profile is shown in Figure 3. The effect of tire and brake wear constraints on this profile is small. The Pb-rich profile was not identified in any of the individual cities models.

5. Discussion

5.1 Effect of constraints

A comparison of the constrained versus unconstrained brake wear and tire wear profiles and their bootstrapped confidence intervals from either the individual or combined city models shows that the application of species ratio constraints had a relatively minor impact. The constraints impact was minimal not only on the specified species values, but also on those species in the profile that were not explicitly specified in the constraints. The ratio constraints are “soft” constraints in that they are limited by a maximum increase in Q rather than “hard” constraints that are forced specifically to their target values without consideration of the effect on Q. Yet both the brake wear and tire wear constrained profiles achieved their target ratios specified by the constraints. In other words, these profiles were robust to the application of prior information about their presumed sources, providing strong evidence that these two derived features were strongly influenced by tire and brake wear and thus appropriately named.

In contrast to the soft ratio constraints, we applied hard constraints on the soil contributions in the combined cities model in order to increase the number of observations while also deriving independent soil features for each city (equations 6 and 7). A comparison of the combined-city versus the individual-city models reveal that these hard constraints appear to have had a more significant effect on the derived tire and brake wear profiles than the soft constraints mentioned earlier, although these same hard constraints did not significantly alter the city- specific soil profiles compared to those derived from the individual city models. One major difference was the ability to separate Zn from Pb using the combined-city model, resulting in separate tire wear and Pb-rich profiles. This latter source’s contributions to $PM_{10\text{-}2.5}$ are small but similar in magnitude to those from tire wear (see Table A3) and may be due in part to the abrasion of wheel weights (Root, 2000). Even though there is no evidence that tires themselves contain Pb, the individual-city tire wear profile in Chicago contained significant amounts of Pb. This may be driven by re-suspension of Pb from historically contaminated soil especially in southeast Chicago (Sweet et al. 1993) and the resuspension of soils contaminated with leaded house paint (Laidlaw et al., 2012). The larger number and diversity of samples in the combined-cities model allowed these Pb-rich sources to be separated from the Zn rich tire profile.

5.2 Tire to Brake Wear Ratios

The ratio of the PM10-2.5 contributions from tire wear relative to brake wear as predicted by the models can be compared with other independent estimates of this ratio. Based on a combination of particle size distribution and chemical species measurements in London at a heavily-trafficked curbside site and an urban background site, Harrison and coworkers (Harrison et al. 2012) found that brake wear and tire wear contributed 55.3(+-7) percent and 10.7(+-2.3) percent respectively to particle mass between 0.9 and 11.5 μm, corresponding to an average tire-to-break wear ratio of 0.19. The traffic mix at their curbside site was dominated by light duty vehicles (Charron & Harrison 2005). This estimate is consistent with our model predictions in Table 2 with the exception of those from the unconstrained, individual-city models. The relatively low absolute contributions of tire wear to $PM_{10\text{-}2.5}$

(see Table A4) is also consistent with those reported elsewhere by Kumata et al. (2011) using molecular markers.

The results in Table 2 can also be compared with emissions derived from the EPA MOVES model for 2009 across all vehicle and roadway categories in the relevant counties in the three cities. The MOVES tire wear to brake wear emission ratio estimate is 0.29, reasonably consistent with our model predictions with the exception of those from the unconstrained, individual-city models. The corresponding ratios used in the California EMFAC model are 0.61-0.63 depending upon vehicle category, somewhat higher than MOVES but still consistent with our combined-city model predictions. However, it should be noted that these MOVES and EMFAC emission estimates for tire wear and brake wear $PM_{10-2.5}$ are themselves uncertain (Coordinating Research Council 2010).

5.3 Soil Profiles

The relative proportions of Si, Fe, K, Al, Ti and Mn in the St. Paul and Chicago soil profiles are similar to the Minneapolis resuspended coarse particle soil profile (MPNSoil) reported by Watson and co-workers (Watson et al. 2008), the Chicago urban dust profile (UDUST) reported by Vermette and co-workers (Vermette et al. 1988), surface soil geochemistry of Chicago soils reported by Cannon and co-workers (Cannon & Horton 2009), and the surrounding surface layer geochemistry of upper Midwestern U.S. soils (mollisols and alfisols), (Shacklette & Boerngen 1984; USDA, 2013).

Winston-Salem soil particles have slightly higher mass fractions of Ti compared with the other two cities consistent with the composition of the soils surrounding Winston Salem (ultisols), predominant throughout Virginia, the Carolinas, Tennessee, Georgia and Alabama (Shacklette & Boerngen 1984).

The phosphorus-rich fertilized soil feature contributions are consistently higher during the summer versus winter sampling period in all three cities (not shown). Phosphorus is added as a fertilizer to the soils within the urban areas as well as to those in the agricultural areas surrounding all three cities (IPNI 2012). Such windblown soil is a major source of airborne phosphorus in agricultural areas in the spring and summer (Anderson & Downing 2006).

5.4 Sources of Selected Species

An interesting question is how well a given measured species concentration represents the contribution from a given source. We addressed this by examining for each feature the relative contributions of and pairwise correlations with selected indicator species of Cu, Zn, P and Si.

Our model results clearly indicate that tire wear is highly correlated with and also an important source of Zn. In Chicago, Zn was strongly associated with tire wear but also contributed to the soil and the Pb-rich features. Since Pb was present in the tire wear feature for the Chicago individual model but not the individual models for St. Paul and Winston-Salem, it is logical that it would be separated from the combined model to ensure a ubiquitous tire wear source across cities. As a result, the Pb-rich contributions are highly correlated with the tire wear contributions in Chicago (Table A5).

We also found that the brake wear feature is a major contributor to Cu in all three cities and that crustal soil material is highly correlated with and also an important source of Si in all three cities (see Table A4). The Metals-rich feature identified in the Chicago individual models are very similar to the brake wear profile and differs in only a few elements, potentially the result of artificially splitting the brake wear feature based on the subtle differences of brake wear composition. However, the combined model does not identify a Metals-rich feature. By using a multi-city approach we increase the number of samples and thereby improve the model's ability to separate these ubiquitous features.

A positive correlation between brake wear, tire wear, and soil contributions implies that re-suspension from roadways, or road dust, is involved. This idea is reinforced by the presence of Cu, Ba, and Sb in both the individual and combined model profiles (Figure 4). Interestingly, the road salt feature in St. Paul in the winter is also a major contributor to and also more highly correlated with the observed Cu than the brake wear feature in this season (Table 3). To the extent that road salt is acting as a tracer of re-suspended road particles, this would indicate that a measurable portion of Cu from brake wear is from re-suspended material, at least in St. Paul. This is consistent with the idea that some fraction of brake (and tire) wear dusts are deposited on or near the roadway and subsequently re-suspended, partially as coarse mode particles (P. Pant et al, 2013). This is suggested by the accompanying enrichment of Ba in the same road salt feature in both the combined and individual model results (Figures 5e and 5f respectively). The soil and road salt contributions associated with Cu could also be due to the model's inability to separate these sources from a truly independent brake wear feature, but the fact that the soil and road salt features contain both Ba and Cu suggest that re-suspension of road dust is also playing an important role. This idea is reinforced by positive correlations of brake wear contributions with contributions from soil and road salt during the summer and winter seasons respectively (Table A5). Additionally tire wear and Pb-rich were slightly correlated with the Chicago soil feature indicating that re-suspension of road dust is playing a role in these features.

The fertilized soil feature is well correlated with P in St. Paul and Winston-Salem, however, Chicago exhibited elevated P contributions within the fertilized soil as well as the Pb-rich feature. A positive correlation of contributions between the soil and Pb-rich feature (Table A5) dilutes the ability of P to act as a strong indicator for fertilized soil in Chicago.

6. Conclusions

We were able to successfully use a modified version of PMF to identify contributions from brake wear, tire wear, crustal material, fertilized soil and a small Pb-rich feature. Our modified PMF model allowed not only for inclusion of prior source profile information for selected species, but also for locally specific results for soil (crustal) contributions in addition to generally applicable results for the other features. The effect of prior source profile constraints on model predictions was relatively small, increasing our confidence in correctly identifying the tire and brake wear features. The modified model also allowed us to include measurements from different cities with different soil compositions. The locally specific soil profiles in this model were consistent with those derived from city-specific models. Elements Cu, Zn, P, and Si were identified as general indicators of brake wear, tire wear, fertilized soil, and soil for the combined city analysis.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was made possible by the U.S.EPA STAR Grant program R833741 and RD831697. Its contents are solely the responsibility of the grantee and do not necessarily represent the official views of the USEPA. Further, USEPA does not endorse the purchase of any commercial products or services mentioned in the publication. The MESA study is supported by contracts N01-HC-95159 through N01-HC-95169 from the National Heart, Lung, and Blood Institute (NHLBI). The authors acknowledge the other investigators, staff, and participants of MESA, MESA Coarse, and MESA Air for their valuable contributions to this work. A full list of MESA investigators and institutions is located at http://www.mesa-nhlbi.org. Additionally, this work was partially funded by the Joint Fire Science Program (09-1-03-1). The assumptions, findings, conclusions, judgments, and views presented herein are those of the authors and should not be interpreted as representing the National Park Service.

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Highlights

- Receptor-oriented source apportionment using the Multilinear Engine
- Modeled coarse particles sampled spatially across three urban regions
- Applied source profile constraints using prior information
- Separated ubiquitous and city-specific sources

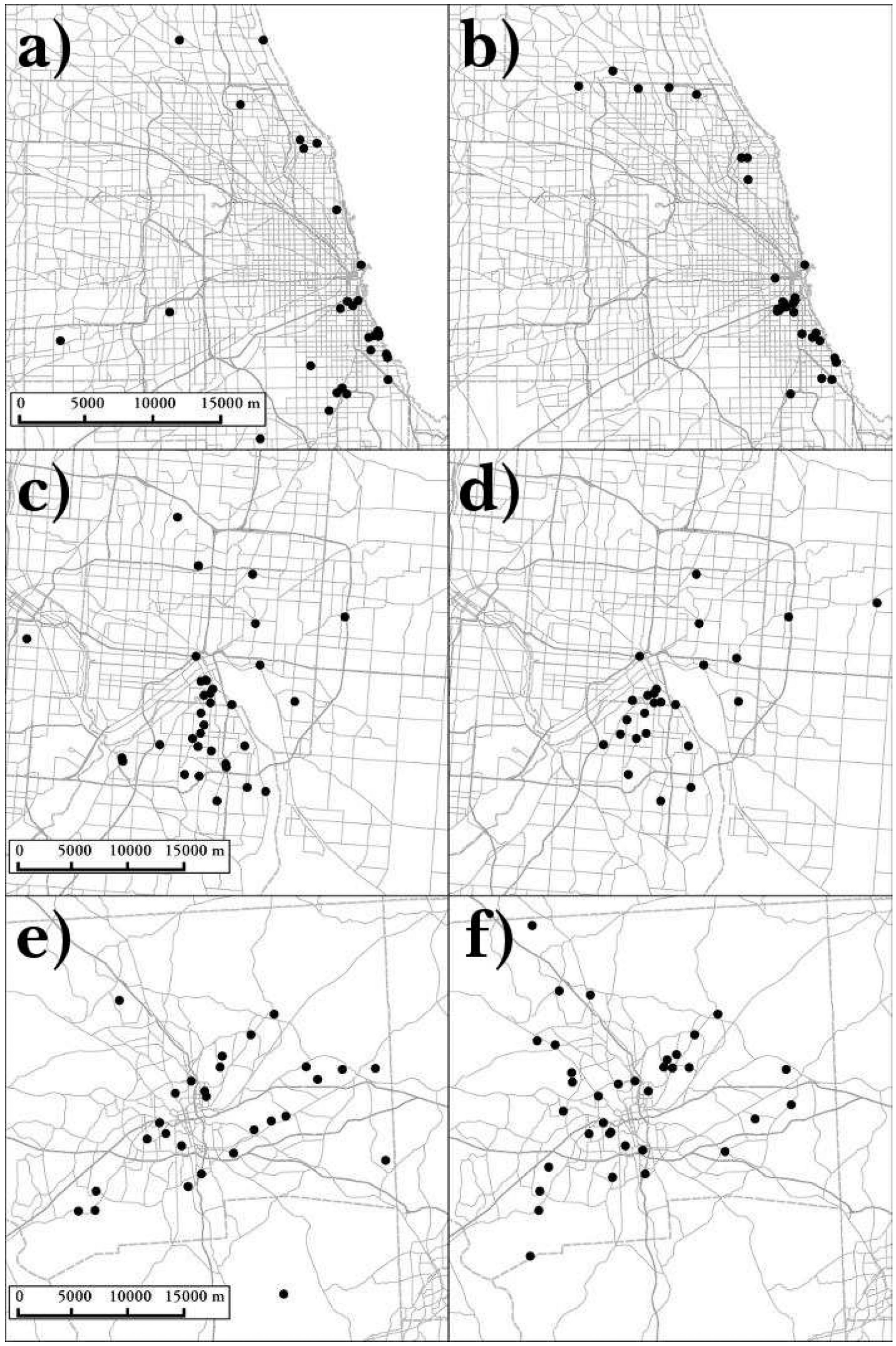

Figure 1.

Map of Sampling Locations in Chicago (a,b), St. Paul (c,d) and Winston-Salem (e,f). Samples were taken in the Winter or Early Spring (left panels) and in the Summer (right panels).

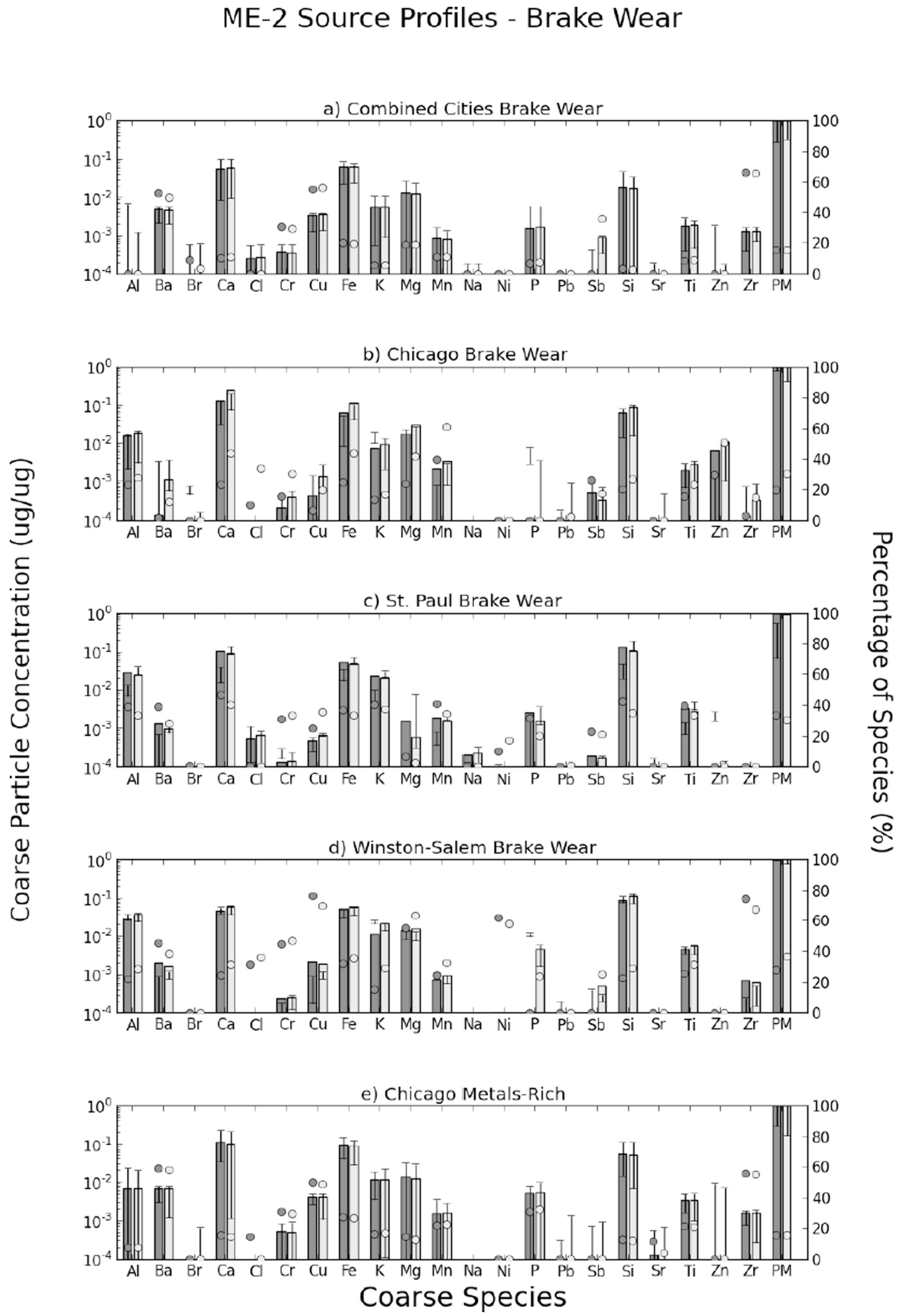

Figure 2.

PMF-derived features identified as brake wear (a–d). The black bars represent the average species contributions for the unconstrained models and the white bars represent the models with prior source profile constraints (see Table 1 and text). The bootstrapped 95% confidence limits are also shown. The circles refer to the percent of the total predicted concentration for a given species associated with that feature for the unconstrained (closed circles) and constrained (open circles) models. Also shown is an additional metals-rich source identified by the individual Chicago model (e) that is enriched in both Ba and Cu.

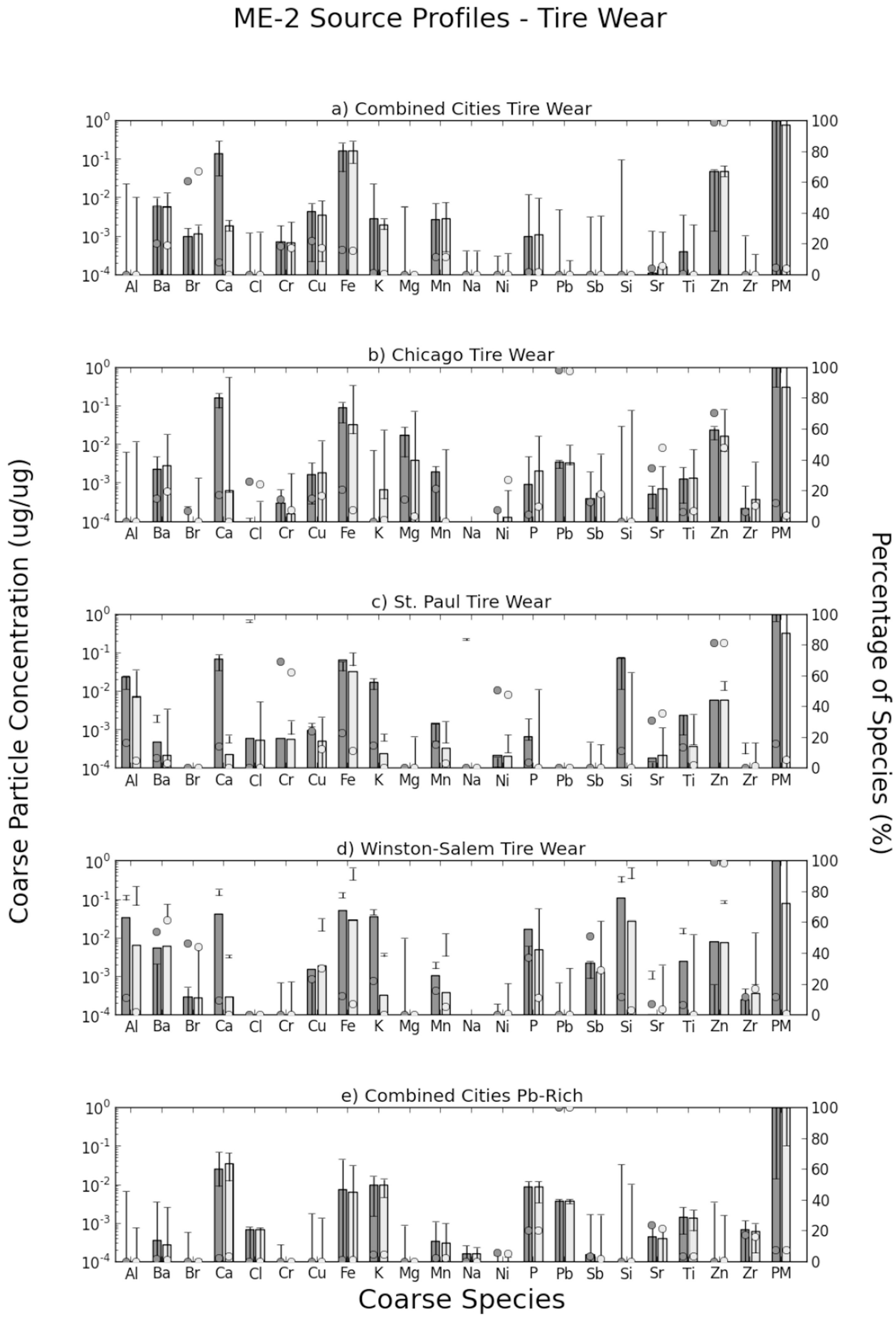

Figure 3.

PMF-derived features identified as tire wear (a–d). The black bars represent the average species contributions for the unconstrained models and the white bars represent the models with prior source profile constraints (see Table 1 and text). The bootstrapped 95% confidence limits are also shown. The circles refer to the percent of the total predicted concentration for a given species associated with that feature for the unconstrained (closed circles) and constrained (open circles) models. Also shown is an additional Pb-rich source identified by the combined-cities model (e).

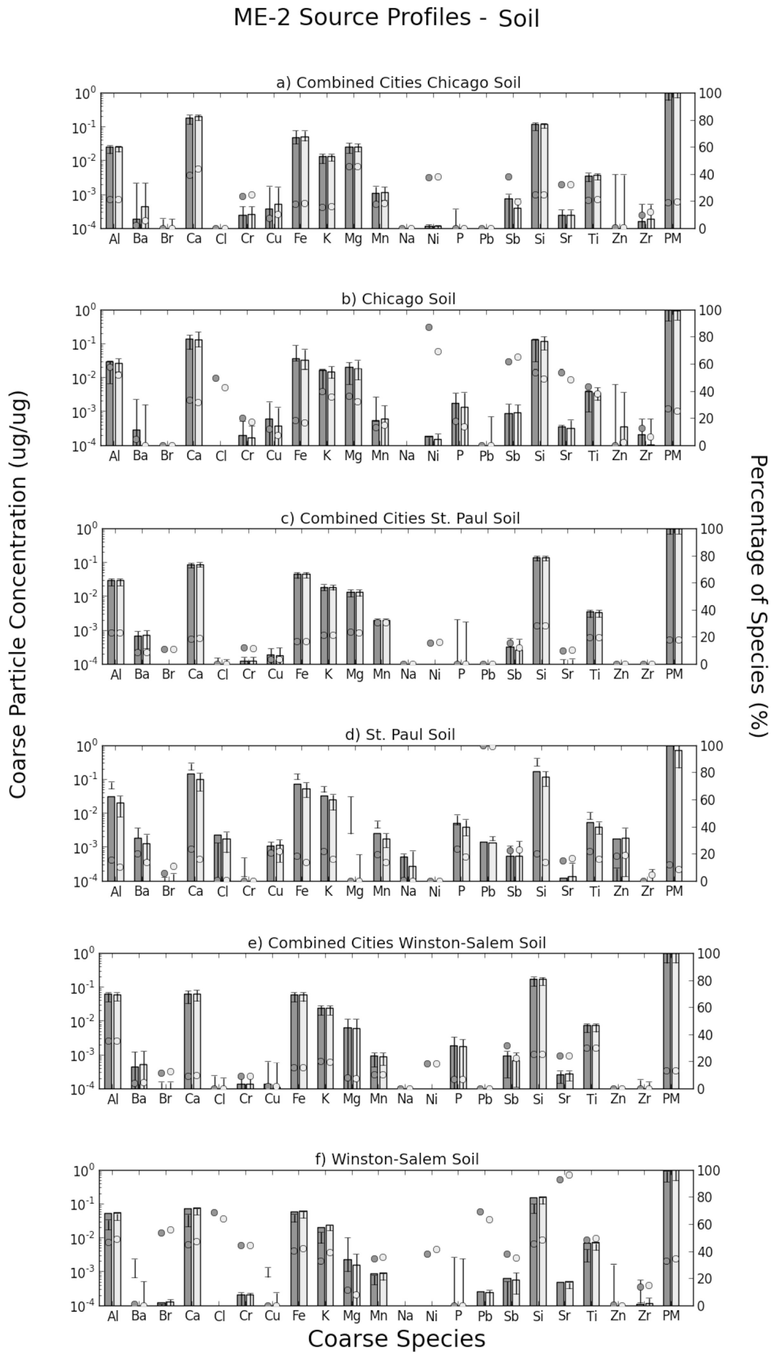

Figure 4.

PMF-derived features identified as soil. The black bars represent the average species contributions for the unconstrained models and the white bars represent the models with prior source profile constraints (see Table 1 and text). The bootstrapped 95% confidence limits are also shown. The circles refer to the percent of the total predicted concentration for a given species associated with that feature for the unconstrained (closed circles) and constrained (open circles) models. The predictions from the combined cities model (a, c, e) are shown by city along with the relevant predictions from the individual city models (b,d, f)

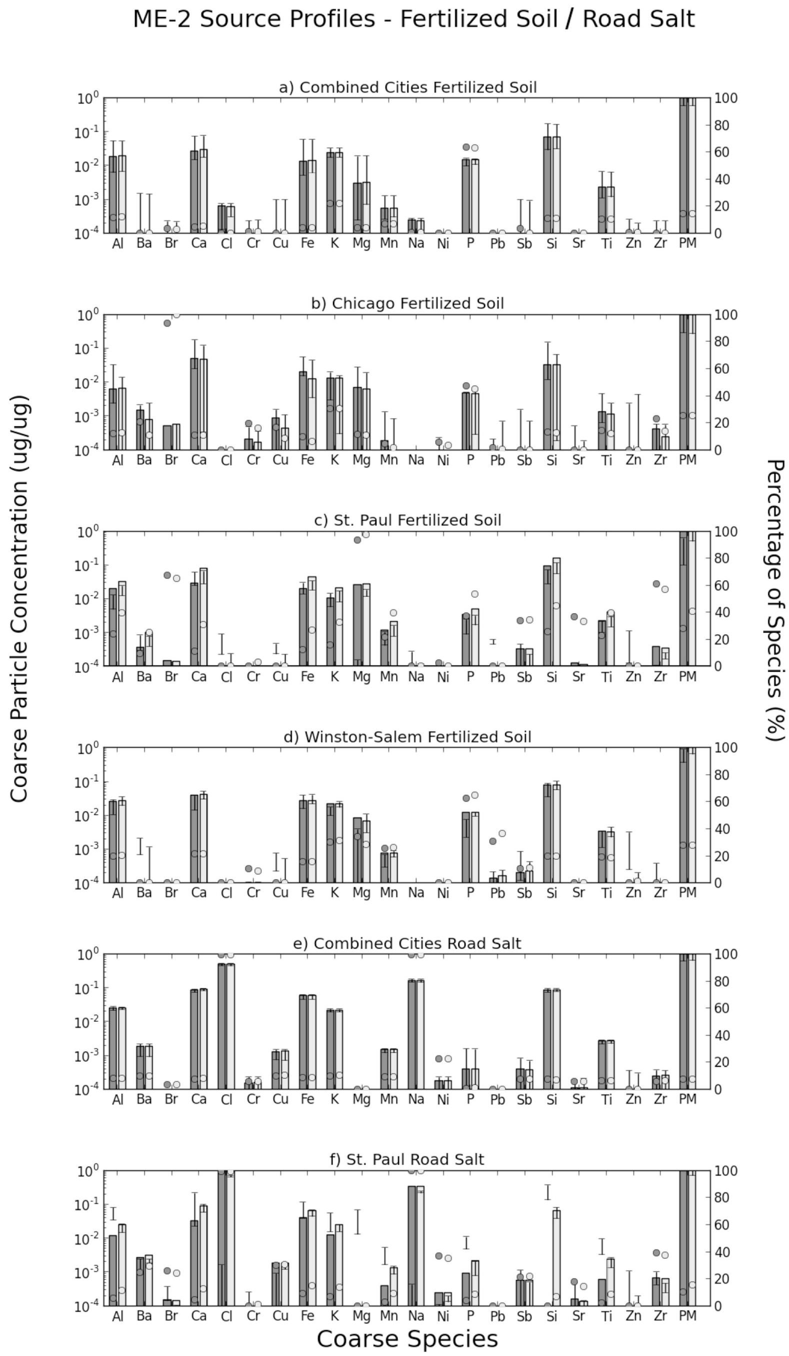

Figure 5.

PMF-derived features identified as fertilized soil (a–d) and road salt (e). The black bars represent the average species contributions for the unconstrained models and the white bars represent the models with prior source profile constraints (see Table 1 and text). The bootstrapped 95% confidence limits are also shown. The circles refer to the percent of the total predicted concentration for a given species associated with that feature for the unconstrained (closed circles) and constrained (open circles) models.

Table 1

Source Profile Constraints

Constraint Type	Species	Source				Literature Citations[e]
		Brake Wear	Tire Wear	Road Salt	Soil(s)	
Species Ratio (λ_t)[a]	Cu/Sb	3.9 (0.1)[b]				1-12
	Cu/Ba	1.2 (0.1)[b]				1-9, 12
	Cu/Fe	0.05 (0.1)[b]				1-8, 12
	Zn/Pb		1000 (0.1)[b]			13,14
	Zn/K		24 (0.1)[b]			13,14
	Zn/Ca		26 (0.1)[b]			13,14
Upper or Lower Limit Constraints on Average Species Concentration (ng/m^3)	Ba	>0.001				1-9, 12
	Cu	>0.001				1-9, 12
	Pb		<0.001			16
	Zn		>0.001			13-15
	Cl			>0.01		
	Na			>0.01		
	β_c				0 (1e-5)[c]	
Maximum Constraint on Q	Si				400[d]	

[a] see equation 4 in text;

[b] ( ) =maximum allowable constraint error;

[c] dimensionless value for c not equal to k-2 {see equation 6 in text};

[d] maximum allowable increase of Q for upward pulling of average species concentration using error mode −20 in ME2 {see also equation 5 in text}

[e] 1. Kennedy and Gadd, 2003; 2. Garg et al, 2000; 3. Iijima et al, 2007; 4. Geitel et al, 2010; 5. Schauer et al, 2006a; 6. Grieshop et al, 2005; 7. Bukoweicki et al, 2010; 8. von Uexkull et al, 2005; 9. Sternbeck et al, 2004; 10. Weckwerth, 2001; 11. Adachi and Tainosho, 2004, 12. Johansson et al, 2009; 13. Apeagyei et al 2011; 14. EPA, 2003; 15. Han et al, 2011. 16. Wahlin, 2006

Table 2

Ratio of Tire Wear to Brake Wear $PM_{10\text{-}2.5}$ Contributions

Model		Tire Wear to Brake Wear Median Ratio	
		With Profile Constraints	**Unconstrained**
Combined Cities Model	Combined Model	0.24 (0.00,1.38)[a]	0.31 (0.00,1.85)
	Chicago	0.30 (0.00,1.70)	0.37 (0.00,2.27)
	St. Paul	0.35 (0.00,1.88)	0.48 (0.00,2.96)
	Winston-Salem	0.09 (0.00,0.65)	0.11 (0.00,0.86)
Individual City Models	Chicago	0.13 (0.00,0.64)	0.48 (0.13,1.17)
	St. Paul	0.17 (0.00,1.26)	0.65 (0.17,12.66)
	Winston-Salem	0.03 (0.00,0.98)	1.18 (0.29,2.05)

[a]( ) 95% confidence limits from bootstrapping

Table 3

Combined-Cities Model with Profile Constraints: Pairwise Correlations between Predicted and Observed species by Feature, City and Season

	Feature	Pairwise Correlations[a] (Summer / Winter)			
		Cu	**Zn**	**P**	**Si**
Chicago	Brake Wear	**0.71 (0.68 / 0.76)**	0.15 (0.09 / 0.22)	0.23 (0.20 / 0.24)	0.23 (0.17 / 0.45)
	Tire Wear	**0.67 (0.70 / 0.67)**	**0.94 (0.93 / 0.97)**	0.51 (0.44 / **0.61**)	0.53 **(0.59 / 0.78)**
	Soil	**0.63 (0.60 / 0.75)**	**0.62 (0.61 / 0.80)**	0.29 (**0.56** / 0.51)	**0.97 (0.98 / 0.97)**
	Fertilized Soil	−0.48 (−0.58 / −0.35)	−0.52 (−0.78 / −0.24)	0.31 (−0.01 / 0.43)	−0.31 (−0.3 / −0.12)
	Pb-Rich	**0.57** (**0.63** / 0.52)	**0.89 (0.93 / 0.84)**	**0.59 (0.55 / 0.66)**	0.50 **(0.58 / 0.68)**
St. Paul	Brake Wear	0.33 (**0.90** / 0.39)	0.43 (**0.55** / −0.08)	0.54 (0.26 / −0.21)	**0.70** (0.44 / −0.04)
	Tire Wear	**0.57** (**0.75** / 0.41)	**1.00 (1.00 / 0.99)**	0.43 (0.54 / 0.50)	0.41 (**0.64 / 0.57**)
	Soil	−0.10 (**0.71** / −0.30)	0.37 (**0.70** / −0.24)	**0.79 (0.60 / −0.56)**	**0.98** (**0.97** / −0.14)
	Fertilized Soil	−0.21 (0.15 / −0.10)	0.29 (0.24 / 0.52)	**0.90 (0.78 / 0.87)**	**0.76** (0.50 / 0.28)
	Road Salt	0.49 (**0.65 / 0.88**)	−0.04 (**0.85** / 0.43)	**−0.65** (0.39 / 0.25)	**−0.78** (0.54 / **0.82**)
Winston-Salem	Brake Wear	**0.95 (0.98 / 0.92)**	0.31 (0.02 / **0.55**)	0.21 (0.17 / **0.57**)	0.44 (**0.58** / 0.37)
	Tire Wear	0.39 (0.13 / **0.62**)	**1.00 (1.00 / 1.00)**	0.03 (0.38 / 0.35)	0.40 (0.28 / 0.43)
	Soil	0.30 (0.47 / 0.25)	0.30 (0.21 / 0.27)	−0.28 (0.25 / 0.42)	**0.94 (0.95 / 0.96)**
	Fertilized Soil	0.07 (−0.05 / 0.37)	−0.01 (0.26 / 0.31)	**0.94 (0.84 / 0.78)**	−0.21 (0.07 / 0.14)

[a]Pearson correlation coefficient between measured species concentration and predicted source contribution from baseline model; values with $p < 0.05$ are shown in bold