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Application of an Ensemble-Trained Source Apportionment Approach at a Site Impacted by Multiple Point Sources

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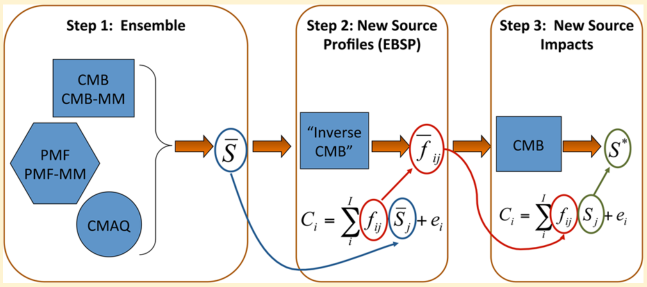
Supporting Information

ABSTRACT: Four receptor models and a chemical transport model were used to quantify $PM_{2.5}$ source impacts at the St. Louis Supersite (STL-SS) between June 2001 and May 2003. The receptor models used two semi-independent data sets, with the first including ions and trace elements and the second including 1-in-6 day particle-bound organics. Since each source apportionment (SA) technique has limitations, this work compares results from the five different SA approaches to better understand the biases and limitations of each. The source impacts calculated by these models were then integrated into a constrained, ensemble-trained SA approach. The ensemble method offers several improvements over the five individual SA techniques at the STL-SS. Primarily, the ensemble method calculates source impacts on days when individual models either do not converge to a solution or do not have adequate input data to develop source impact estimates. When compared with a chemical mass balance approach using measurement-based source profiles, the ensemble method improves fit statistics, reducing chi-squared values and improving $PM_{2.5}$ mass reconstruction. Compared to other receptor models, the ensemble method also calculates zero or negative impacts from major emissions sources (e.g., secondary organic carbon (SOC) and diesel vehicles) for fewer days. One limitation of this analysis was that a composite metals profile was used in the ensemble analysis. Although STL-SS is impacted by multiple metals processing point sources, several of the initial SA methods could not resolve individual metals processing impacts. The results of this analysis also reveal some of the subjectivities associated with applying specific SA models at the STL-SS. For instance, Positive Matrix Factorization results are very sensitive to both the fitting species and number of factors selected by the user. Conversely, Chemical Mass Balance results are sensitive to the source profiles used to represent local metals processing emissions. Additionally, the different SA approaches predict different impacts for the same source on a given day, with correlation coefficients ranging from 0.034 to 0.65 for gasoline vehicles, −0.54−0.48 for diesel vehicles, −0.29−0.81 for dust, −0.34−0.89 for biomass burning, 0.38−0.49 for metals processing, and −0.25−0.51 for SOC. These issues emphasize the value of using several different SA techniques at a given receptor site, either by comparing source impacts predicted by different models or by using an ensemble-based technique.



■ INTRODUCTION

Epidemiologic studies have linked fine particulate matter ($PM_{2.5}$) with adverse health outcomes, including cardiovascular disease and asthma. Ambient $PM_{2.5}$ is a mixture of pollutants emitted from multiple sources whose respective contributions to $PM_{2.5}$ levels cannot be directly measured. Therefore, scientists and policy-makers are interested in understanding how individual emissions sources impact $PM_{2.5}$ concentrations and human health. Researchers have developed various source apportionment (SA) models to quantify the impacts of emissions sources on pollutant concentrations (e.g., Positive Matrix Factorization (PMF),[1] Chemical Mass Balance (CMB),[2] and the Community Multiscale Air Quality Model (CMAQ[3])). Some approaches have also been used to provide $PM_{2.5}$ source inputs for epidemiological analyses.[4−8] Several issues limit the use of current SA approaches in epidemiological analyses, particularly those evaluating acute health effects and relying on day-to-day changes in exposures. Some models appear to introduce excessive day-to-day variability in source impact estimates whereas other models do the opposite. For example, receptor models, such as PMF and CMB, suggest little-to-no (or even negative) impacts from major emissions sources (e.g., gasoline vehicles) on certain days and high impacts on other days.[9] Conversely, SA methods based on chemical transport models (CTMs), such as CMAQ, utilize meteorological and emissions inventory data that do not appear to adequately capture day-to-day fluctuations in emissions source contributions.[5,10] Moreover, different SA techniques tend to predict different $PM_{2.5}$ impacts for the same source on the same day.[9]

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Since source impacts cannot be directly measured, it is difficult to evaluate which model provides the most accurate results.

Further, each commonly used SA technique (e.g., CMB, PMF, CMAQ) has known advantages and disadvantages.[9] For example, CMB requires the user to identify and characterize the chemical composition of each emissions source affecting the receptor location in the form of user-input, measurement-based source profiles (MBSPs). This can be particularly difficult if the receptor is impacted by local sources that have not been subject to source testing. While PMF does not require user-input MBSPs, the user must select an appropriate number of factors and link these factors to real-world emissions sources. In addition to other potential limitations and biases when using such approaches,[11,12] this process adds subjectivity to PMF-based SA analyses. Lastly, SA approaches based on CTMs are time-consuming to run.

One method of dealing with the limitations of individual SA techniques is to use multiple models at a single receptor site. Model results may then be compared to better understand the biases and uncertainties associated with each technique. While consistency between methods does not necessarily indicate accurate results, evaluation of the circumstances in which the model results converge or diverge is informative. Alternatively, Lee et al.[9] developed an ensemble-trained SA approach that combines the results of several different SA methods to calculate ensemble-based source profiles (EBSPs) that may be used in CMB to estimate optimized source contributions.

In theory, the ensemble-trained SA technique should minimize the errors associated with any single SA method.[9] Lee et al.[9] demonstrated that the ensemble method reduced the frequency of zero-impacts days for major emissions sources (e.g., gasoline vehicles) at the Jefferson Street site in Atlanta, GA. Performance metrics, such as the chi-squared value (χ^2) and ratio of predicted-to-observed $PM_{2.5}$ mass, also indicated that the ensemble method outperformed CMB at that site.[9] Since the ensemble method calculates EBSPs from source impacts estimated by a number of different models, this method should also reduce the uncertainty associated with identifying representative source profiles for a given receptor location and can be applied to large data sets even if the overlap among SA methods is limited to a shorter time period.

The current work evaluates the emissions sources contributing to $PM_{2.5}$ at the St. Louis Supersite (STL-SS), located in East St. Louis, Illinois. While the STL-SS data has been used in previous SA analyses,[13−16] prior work has focused on individual SA methods without intermethod comparison. The STL-SS presents a challenging and informative case for comparing methods and applying an ensemble technique because it is impacted by urban emissions, such as automobile exhaust, road dust, and local point sources (e.g., metals industries). Additionally, emissions measurements were not available for the point sources and prior work found that PMF results were very sensitive to inputs.[17] We consider five different SA techniques to (1) identify and characterize emissions sources affecting the STL-SS; (2) quantify contributions from these emissions sources to $PM_{2.5}$ concentrations at the STL-SS; (3) assess uncertainties associated with predicted source contributions; and (4) combine individual SA results into an ensemble-trained SA approach.

■ METHODS

Monitoring Data. The USEPA-funded STL-SS is located in a low-density, urban residential/light commercial area in East St. Louis, approximately 3 km east of the St. Louis central business district. This site was impacted by numerous industrial sources, including an integrated steelworks facility, and copper, lead, and zinc smelters.[13,18] Daily, filter-based $PM_{2.5}$ samples were collected at the STL-SS between June 2001 and May 2003. These samples were collected from midnight-to-midnight Central Standard Time, and analyzed for $PM_{2.5}$ mass, ions (sulfate, nitrate, ammonium), organic and elemental carbon (OC/EC) using the NIOSH protocol for thermal optical transmittance (TOT) and the IMPROVE protocol for thermal optical reflectance (TOR), and 40 trace elements by X-ray fluorescence (XRF).[13,14,19] One-in-six day samples were also collected and analyzed for particle-bound organic tracers using solvent extraction gas chromatography/mass spectroscopy. Target analytes for the 1-in-6 day samples included *n*-alkanes, cycloalkanes, alkanoic acids, resin acids, aromatic diacids, alkanedioic acids, steranes, hopanes, polycyclic aromatic hydrocarbons, phthalates, levoglucosan, and cholesterol.[20]

Modeling Approach. This work used five different receptor and chemical transport models for SA at the STL-SS: CMB using speciated (e.g., metals, ions, OC/EC) $PM_{2.5}$ data (CMB), PMF using speciated $PM_{2.5}$ data (PMF), CMB using organic molecular markers (CMB-MM),[14] PMF using organic molecular markers (PMF-MM),[15] and a CMAQ tracer method (CMAQ-TR).[21] Source impacts from these methods were then used to develop EBSPs and calculate optimized source impacts in CMB.[9]

CMB. CMB assumes that the measured concentration of a chemical species on a given day may be expressed as the linear combination of source profiles and source impacts:

$$C_i = \sum_{i=1}^{I} f_{ij} \cdot S_j + e_i \tag{1}$$

where C_i is the observed concentration of species *i*, f_{ij} is the mass fraction of species *i* in source *j* (source profile), S_j is the contribution of source *j* to measured $PM_{2.5}$ concentrations (source impact), and e_i is the error term. User inputs to CMB consist of ambient concentration data (C_i), MBSPs (f_{ij}), and associated uncertainties, whereas outputs consist of daily source contributions to measured $PM_{2.5}$ concentrations (S_j).[22]

The initial CMB analysis at the STL-SS utilized measurements of 16 species: IMPROVE total OC/EC, major ions (sulfate, nitrate, and ammonium), and 11 XRF species (aluminum, arsenic, calcium, copper, iron, potassium, manganese, lead, selenium, silicon, and zinc). Observational data was processed for input into CMB using the procedures outlined in Reff et al.[23,24] Days with missing OC/EC, XRF, and sulfate measurements were excluded from the analysis. Missing nitrate and ammonium measurements were replaced with the geometric mean of the measured values, and the associated uncertainties were set equal to four times the geometric mean.[23,24] Ultimately, we included 686 days (of 730 days during the June 2001−May 2003 period) of measurement data in this analysis.

In addition to ambient concentration data, CMB requires source profiles to describe the chemical composition of the emissions impacting the receptor location. This analysis used MBSPs for gasoline vehicles, diesel vehicles, biomass burning, dust, ammonium sulfate, ammonium bisulfate, and ammonium nitrate from Marmur et al.[25] Since the STL-SS monitor is also impacted by metals emitted by local industries (e.g., zinc, copper, iron, manganese, lead),[13,24] it was necessary to develop representative metals processing profiles for use in CMB. However, source testing data for these specific industrial sources were not available, so metals processing profiles were developed from the composite copper, steel, and lead processing profiles in EPA's Speciate database (Profiles 91008, 900042.5, and 293302.5).[26] An appropriate profile for the zinc smelter south of the STL-SS was not identified in Speciate and was therefore not included in the CMB analysis; however, the lead profile contained approximately 35% zinc by mass. Speciate provided measurement uncertainties for the composite lead smelting profile. Uncertainties for the steel and copper profiles were set equal to 50% of the mass fraction of each species. Recognizing that the measurement-based copper, steel, and lead processing profiles (MBSPs with individual metals profiles or MBSPs-MI) may not fully characterize the metals processing emissions impacting the STL-SS, three additional sets of metals processing profiles were developed for a sensitivity analysis. A composite, measurement-based metals processing profile (MBSPs with composite metals profiles or MBSPs-MC) was developed as a weighted average of source profiles and source impacts from the initial CMB results (CMB-MBSPs-MI or CMB). Individual and composite metals processing profiles were also developed from the PMF profiles for industrial lead, copper, zinc, and steel (PMF-MI and PMF-MC).

CMB results using MBSPs-MI were incorporated into the ensemble method; CMB results using MBSPs-MC, PMF-MI, and PMF-MC were compared to the ensemble results. Daily source impacts and associated uncertainties were calculated in EPA CMB8.2 using an effective variance approach and source elimination to prevent negative source impacts.[22]

PMF. Like CMB, factor analytic methods, such as EPA's PMF, also assume that the ambient concentration of a chemical species, *i*, can be expressed as the linear combination of the mass of species *i* in source *j* and the contribution of source *j* to $PM_{2.5}$ concentrations. PMF uses a mathematical approach to decompose sample data into factors and contributions; therefore the user is not responsible for specifying the chemical composition of the emissions sources impacting the monitor. The user must, however, choose an appropriate number of factors and relate these factors to real-world emissions sources. Although the selection of an appropriate number of factors is guided by the use of fitting statistics (e.g., the *Q* value) this process can still be subjective.

The only difference between the concentration and uncertainty data used in CMB and PMF was the use of temperature-resolved IMPROVE OC/EC fractions, rather than total OC/EC measurements. The analysis also excluded days with missing ion measurements, resulting in 655 (of 730) days of measurement data for input into PMF. Calculations were performed using EPA PMF v3.0.2.2.[27] Species with signal-to-noise ratios (S/N) less than two were considered weak species:

$$\frac{S}{N} = \sum_{k=1} \frac{|S_k^2|}{N_k^2} \tag{2}$$

where S is the signal and N is the noise for each measurement k. The uncertainties associated with these species were multiplied by a factor of 3 to lower their influence on the final 11-factor PMF solution. A bootstrapping analysis was performed to estimate the stability and uncertainty of the PMF solution. Factor contributions were determined from the average of 100 bootstrapping runs, and uncertainties were set equal to the standard deviation of 100 bootstrapping runs.

Molecular Marker Methods. 1-In-6 day, particle-bound organic data and the NIOSH OC/EC measurements were used in both CMB and PMF to estimate source contributions to OC rather than $PM_{2.5}$ at the STL-SS between June 2001 and May 2003. For CMB-MM, we used source contributions to OC, source impact uncertainties, and model fit statistics for 148 (of 730) days at the STL-SS reported in Bae et al.[14] Since Bae et al. considered all unapportioned OC to be from secondary sources, the model did not calculate source impact uncertainties for SOC.

Jaeckels et al.[15] previously used PMF-MM to estimate source contributions to OC concentrations at the STL-SS between June 2001 and May 2003. Since Jaeckels et al. did not provide daily source contributions to OC concentrations, we reran PMF-MM using their input files, which consisted of ambient concentration data and associated measurement uncertainties for 107 particle-bound organic compounds, NIOSH OC/EC, silicon, and aluminum for 93 (of 730) days.[15,28] We added 11 days of measurement data to the original data set, including 4 days in July 2001. We estimated measurement uncertainties for the 11 additional days by regressing the initial 93 days of ambient concentration data by their associated measurement uncertainties. Species with S/N less than two were treated as "weak" species and 9-hexadecenoiacid was excluded from the analysis.[15] The resulting eight-factor PMF solution was similar to the eight-factor PMF solution reported by Jaeckels et al.

CMAQ-TR. CMAQ-TR uses the CTM, CMAQ, and the direct decoupled method in three dimensions to investigate the sensitivity of $PM_{2.5}$ concentrations to emissions from 28 source categories. Baek et al. previously ran CMAQ-TR for a domain covering the contiguous United States, for 29 days in July 2001and 29 days in January 2002.[21] CMAQ-TR does not estimate source impact uncertainties, which is a limitation of this method.

Ensemble Method. Ensemble-average source impacts at the STL-SS were calculated from the PMF, PMF-MM, CMB, CMB-MM, and CMAQ-TR results for July 2001 and January 2002. This study considered nine categories of $PM_{2.5}$ emissions: gasoline vehicle exhaust and resuspended road dust (GV), diesel vehicle exhaust (DV), dust (DUST), biomass burning (BURN), metals processing (METALS), secondary organic carbon (SOC), secondary sulfate, secondary nitrate, and ammonium. These nine source categories comprise about 70% of the inventoried primary $PM_{2.5}$ sources and the dominant sources that contribute to secondary pollutant formation.[21] The individual emissions sources identified by CMB, PMF, CMB-MM, PMF-MM, and CMAQ-TR were binned into the five primary source categories (i.e., GV, DV, BURN, DUST, and METALS) and SOC (see Supporting Information (SI) Table S1). Secondary sulfate, nitrate, and ammonium source categories were estimated using only the 11-factor PMF results. The secondary sulfate and nitrate factors accounted for the majority of the modeled sulfate (86%), nitrate (81%), and ammonium (81%) mass in PMF. However, these secondary species were also present at low levels in the primary source factors (i.e., gasoline vehicles). Thus, secondary sulfate, nitrate, and ammonium contributions were calculated by summing the modeled sulfate, nitrate, and ammonium mass across the 11 PMF factors. Sulfate was left in the PMF steel processing factor, since it comprised a significant percentage (40% by mass) of the steel processing MBSP used in CMB.

Table 1. Comparison of Average $PM_{2.5}$ Source Impacts Estimated by CMB, PMF, CMB-MM, PMF-MM, and CMAQ-TR for June 2001−May 2003

	PMF[a]	CMB[b]	CMAQ-TR[c]	PMF-MM[a]	CMB-MM[b]
$\%PM_{2.5}$ or OC mass ratio, %[d]	100 ± 12	91 ± 15	77 ± 26[e] 118 ± 34[f]	229 ± 116	84 ± 48[g]
mean measured $PM_{2.5}$ or OC mass, $\mu g/m^3$ [d]	18.0	17.9	22.1[e] 17.8[f]	3.8	3.9
N	655	433[h]	29[e]	123	148
			average $PM_{2.5}$ source impacts, $\mu g/m^3$		
GV	2.2 ± 1.4	4.0 ± 0.56	2.5	0.62 ± 0.39	5.1 ± 0.65
DV	1.4 ± 1.1	0.78 ± 0.56	0.89	0.75 ± 0.48	0.31 ± 0.05
DUST	0.96 ± 0.64	0.34 ± 0.17	1.3	1.3 ± 0.61	0.28 ± 0.03
BURN	1. ± 0.62	1.2 ± 1.1	3.0	0.64 ± 0.42	1.3 ± 0.28
SOC	0.29 ± 0.01	0.21 ± 0.63	1.3	0.59 ± 0.33	1.7[c]
METALS	1.9 ± 0.97	1.7 ± 0.54	1.0		

[a] Source impact uncertainties were calculated from the standard deviation of 100 bootstrapping runs. [b] Source impact uncertainties were calculated by CMB. [c] Source impact uncertainties were not calculated by the model. [d] Modeled-to-measured $PM_{2.5}$ mass ratios and mean measured $PM_{2.5}$ mass provided for PMF, CMB, and CMAQ-TR. Modeled-to-measured OC mass ratios and mean measured OC (NIOSH/TOT) mass provided for PMF-MM and CMB-MM. [e] July 2001. [f] January 2002. [g] Does not consider SOC. Since Bae et al. considered all unapportioned OC to be from secondary sources, modeled-to-measured mass ratio is 100% with SOC. [h] CMB failed to converge to a solution on 253 of the 686 days with valid measurement data.

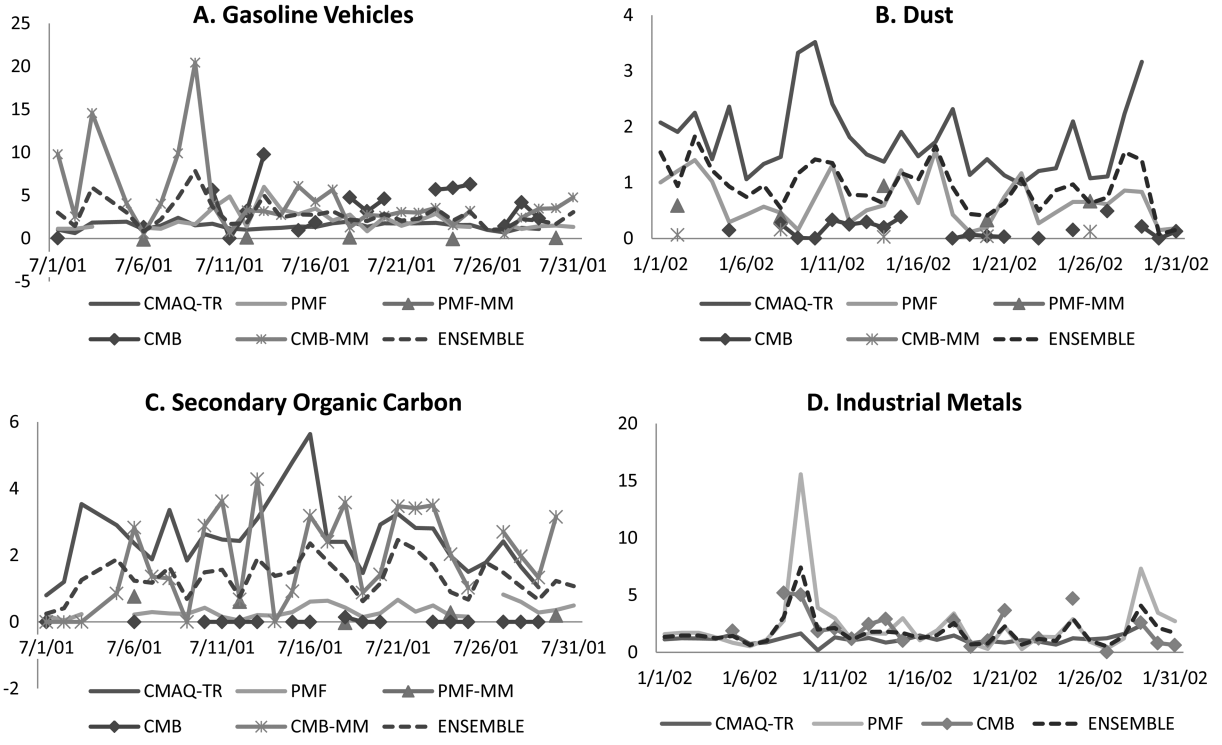

Figure 1. Comparison of ensemble average source impacts in $\mu g/m^3$ to selected SA results from PMF, CMB, PMF-MM, CMB-MM, and CMAQ-TR for July 2001 and January 2002: (a) GV, (b) DUST, (c) SOC, (d) METAL.

Although PMF did not resolve an SOC factor, the OC in the secondary sulfate and nitrate factors was considered to be from secondary formation. As such, the OC from these two PMF factors was combined with the SOC estimated by CMAQ-TR, CMB-MM, and PMF-MM to calculate ensemble-average SOC impacts.

PMF-MM and CMB-MM calculate source contributions to OC rather than $PM_{2.5}$ mass. Source contributions from these methods were scaled by source-specific $OC/PM_{2.5}$ ratios provided in the literature[14,29−31] (see SI Table S2). Since PMF-MM did not resolve separate gasoline and diesel vehicle factors, the combined mobile source factor was split into a gasoline and diesel component using the ratio of gasoline to diesel vehicle impacts estimated in CMAQ-TR.

Ensemble-average source impacts were calculated by averaging the daily source impacts predicted by each model for two one-month periods in July 2001 and January 2002. Since each SA approach uses a different method for estimating source impact uncertainties, all methods were given an equal weighting during the averaging. However, to prevent ensemble-average source contributions from being biased by the availability (or unavailability) of model results on a particular day, source contributions were mean-centered prior to averaging.

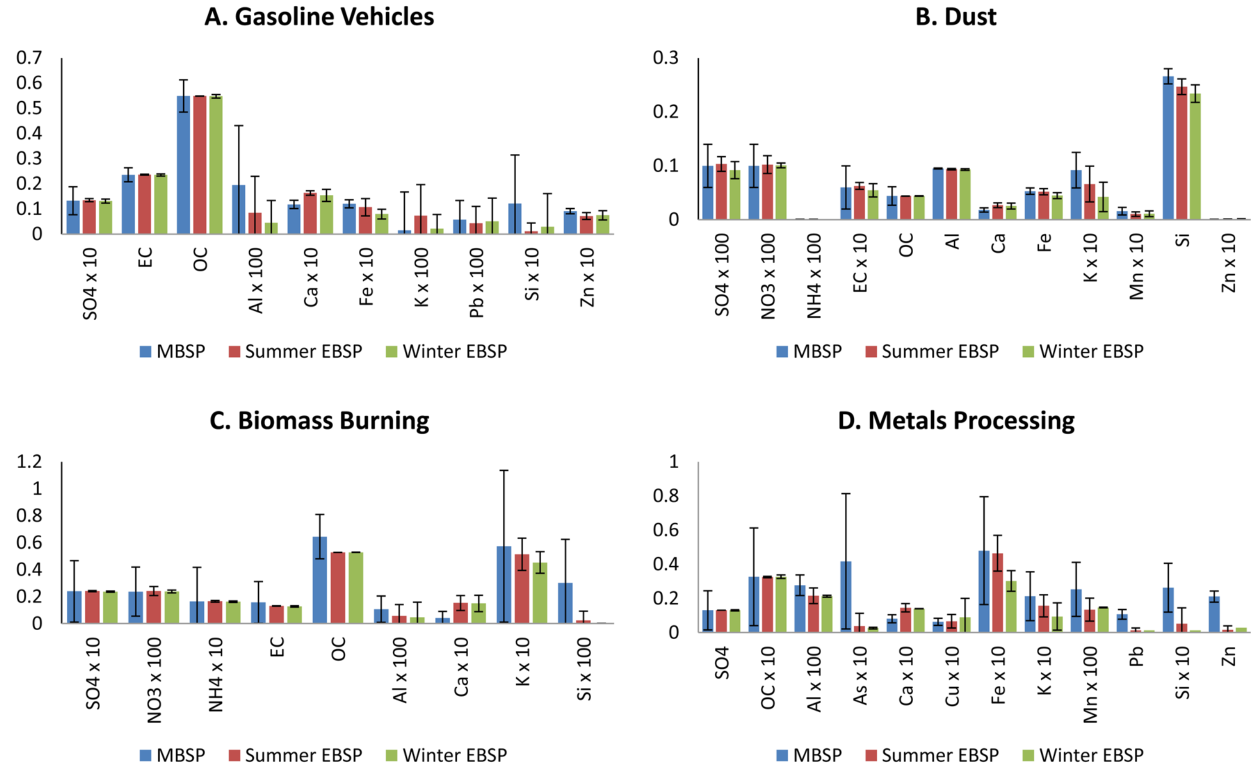

Figure 2. Comparison of winter and summer EBSPs to MBSPs: (a) GV, (b) DUST, (c) BIOMASS, (d) METAL.

The ensemble-average source impacts were used to understand how source impacts from each of the five initial SA approaches deviated from the mean during July 2001 and January 2002:[32]

$$\hat{\sigma}_{jl}^2 = \frac{1}{N}\sum_{k=1}^{N}(\bar{S}_{jkl} - S_{jkl})^2 \tag{3}$$

Here, $\hat{\sigma}_{jl}$ is the deviation of source j from the mean or updated source impact uncertainty for each SA method l (i.e., CMB, PMF, CMB-MM, PMF-MM, or CMAQ-TR), $\bar{S}_{jkl}$ is the ensemble-average impact for source j on day k, S_{jkl} is the contribution from source j from method l on day k, and N is the number of days included in the calculation. N ranged from 9 for PMF-MM to 55 for CMAQ-TR and PMF. $\hat{\sigma}_{jl}$'s were then compared to initial uncertainty estimates from PMF and CMB and used for intermethod comparison.

Ensemble-average source impacts for July 2001 and January 2002 were then used to calculate summer and winter EBSPs (f_{ij}'s) using a reverse CMB approach that minimized χ^2:

$$\chi^2 = \sum_{i=1}^{N}\frac{(C_{ik} - \sum_{j=1}^{J} f_{ij}S_{jk})^2}{\sigma_{C_{ik}}^2} \tag{4}$$

where C_{ik} is the observed concentration of species i on day k, f_{ij} is the mass fraction of species i in source j, S_{jk} is the contribution of source j to $PM_{2.5}$ concentrations on day k, and $\sigma_{C_{ik}}^2$ is the uncertainty associated with the measured concentration. Calculations were performed in Excel, using a nonlinear solver package developed by Frontline Systems.[33] During each optimization, the source profiles were initially set to the MBSPs, and constrained to the MBSP $\pm 3 \times \sigma_{\mathrm{MBSP}}$ as long as these values were between 0 and 1. Additionally, the total mass fractions of the species in the source profiles were restricted to values less than or equal to one. This calculation specified a primary organic matter to OC (OM/OC) ratio of 1.2 for GV, DV, DUST, and METALS, and an OM/OC ratio of 1.4 for BURN. OC/EC ratios for GV and DV were constrained to values between 0.80 and 4.0 and 0.17 and 1.25, respectively.[34] The OC/EC ratio for the BURN profile was constrained to values greater than or equal to 3. Lastly, the total carbon fractions (OC + EC) in the GV, DV, and BURN profiles were constrained to values greater than or equal to 0.5.

Daily source profiles were averaged for July 2001 and January 2002 to calculate the summer and winter EBSPs. The source profile uncertainties were set equal to the standard deviation of the daily profiles. The summer profiles were used to estimate source impacts in CMB between April and October, while the winter profiles were applied to daily measurements collected between November and March.

■ RESULTS AND DISCUSSION

A comparison of the CMB, PMF, CMAQ-TR, CMB-MM, and PMF-MM results demonstrate that these techniques can calculate very different source impacts for the same receptor location (Table 1, Figure 1). Pairwise Pearson correlation coefficients between the five methods ranged 0.034−0.65 for GV, −0.54−0.48 for DV, −0.29−0.81 for DUST, −0.34−0.89 for biomass burning, −0.25−0.51 for SOC, and 0.38−0.49 for METALS (see SI Tables S3A−G). Correlation coefficients between CMB and PMF ranged from 0.11 for SOC to 0.81 for DUST, whereas correlation coefficients between CMB-MM and PMF-MM ranged from 0.10 for SOC to 0.89 for BURN.

PMF, CMB, PMF-MM, CMB-MM, and CMAQ-TR results were then combined to calculate ensemble-average source impacts for July 2001 and January 2002 (Figure 1). Since the ensemble method used information from five different methods, source impacts could be resolved on days when

Table 2. Comparison of CMB-EBSPs, CMB-MBSPs-MC, and PMF Results for May 2001−June 2003[a]

	CMB-EBSPs	CMB-MBSPs-MC[b]	PMF
χ^2	11400 ± 38900	41000 ± 390000	126 ± 245
% mass[c]	93.8 ± 16.2	87.8 ± 13.6	99.7 ± 11.6
N[d]	673	341	655

	average PM$_{2.5}$ contributions, μg/m^3 [e]			correlation coefficients	
	CMB-EBSPs	CMB-MBSPs-MC	PMF	CMB-EBSPs v. CMB-MBSPs-MC	CMB-EBSPs v. PMF
GV	3.8 ± 0.84	3.6 ± 0.60	2.2 ± 1.4	0.61	0.66
DV	1.2 ± 0.38	0.56 ± 0.58	1.4 ± 1.1	0.82	0.15
DUST	0.42 ± 0.09	0.67 ± 0.13	0.96 ± 0.64	0.76	0.76
BURN	0.98 ± 0.39	2.2 ± 1.2	1.3 ± 0.62	0.53	0.87
SOC	1.3 ± 0.60	0.14 ± 0.53	0.29 ± 0.01	0.59	0.093
METAL	2.1 ± 0.60	0.17 ± 0.11	1.9 ± 0.97	0.42	0.69

[a] Uncertainties shown are either calculated by the model or derived using traditional approaches. [b] Composite measurement-based metals processing profiles were compared with the EBSPs, since the EBSPs also consider a composite metals-processing source. [c] Ratio of modeled-to-measured PM$_{2.5}$ mass. [d] 686 days with valid measurement data were input into the CMB-based models. Both models failed to converge on certain days, limiting the number of days on which CMB-EBSPs and CMB-MBSPs-MC estimated source impacts. [e] Table does not show secondary sulfate, nitrate, or ammonium contributions, which typically comprised nearly half of modeled PM$_{2.5}$ mass.

individual methods did not provide results. This was an improvement over CMB, which failed to converge to a solution on over 35% of the 686 days with valid measurements (due to colinearity between source profiles), and the molecular markers methods, which only had adequate sample data to resolve source impacts on approximately one-sixth of the days during the time period of interest (Table 1). The ensemble method also eliminated negative and zero impact estimates for major emissions sources, such as vehicles and SOC. This was an issue for both the CMB- and PMF-based methods. CMB, for example, calculated no impact from DV on 141 days and no impact from SOC on 336 days between June 2001 and May 2003, including during the summer.

CMAQ-TR and ensemble results generally exhibited less day-to-day variability in source impacts than the other receptor-based approaches. For example, CMB-MM calculated spikes in GV impacts on 7/3/2001 (14.6 μg/m^3) and 7/9/2001 (20.4 μg/m^3). While the ensemble method also calculated elevated GV impacts for these days (5.9 and 7.9 μg/m^3 on 7/3/2001 and 7/9/2001, respectively), they were lower than those estimated by CMB-MM. A similar dampening effect was observed for the ensemble-average DV, DUST, and BURN impacts in July (results not shown). Conversely, the ensemble results for the composite metals processing source exhibited the day-to-day variability expected from a point source or combination of point sources. CMAQ-TR, however, did not capture the elevated metals processing impacts estimated by other methods in July and January (e.g., July 10 and January 9).

Prior to developing summer and winter EBSPs, the ensemble-average source impacts were used to understand how source impacts for the five initial SA methods deviated from the mean in July 2001 and January 2002 (eq 3). This technique provides uncertainty estimates for SA methods that did not previously calculate source impact uncertainties (i.e., CMAQ-TR and SOC in CMB-MM). Additionally, since different methods use different techniques to calculate uncertainties (e.g., bootstrapping, effective variance), $\hat{\sigma}_{jl}$ allowed for a better comparison between methods. Updated relative uncertainties, defined as the deviation from the mean divided by the average source impact ($\hat{\sigma}/\overline{S}$), range 0.49−6.9 for CMB, 0.57−2.6 for PMF, 0.66−4.4 for CMB-MM, 0.46−20 for PMF-MM, and 0.49−1.2 for CMAQ-TR (SI Tables S4A−F). $\hat{\sigma}_{jl}$'s were generally higher than the source impact uncertainties calculated in CMB and PMF. However, $\hat{\sigma}_{jl}$ was lower than the initial source impact uncertainty for PMF for DV and METAL (SI Tables S4A−F).

Ensemble-average source impacts for July 2001 and January 2002 were then used to calculate summer and winter EBSPs, using a constrained inverse CMB model (eq 4). In general, the EBSPs and MBSPs-MI showed greater interprofile variability in the weight percentages of the XRF species than the ionic species, EC, and OC (Figure 2). The EC/OC ratios and total carbon fractions for the ensemble- and measurement-based GV and DV profiles were identical to two significant figures. EC/OC ratios were 0.43 for the GV profiles and 3.7 for the DV profiles. It should be noted that DV profile EC/OC ratios reflect vehicles moving at intermediate to highway speeds, but may vary substantially depending upon operational mode.[35] The ensemble-based DUST and BURN profiles contained smaller mass fractions of most XRF species than the MBSPs, particularly Si, Al, and K (Figure 2). The 16 fitting species used in this analysis also tended to explain a smaller mass fraction of the EBSPs than the MBSPs. For example, the MBSPs accounted for 92% of the mass of the DUST source, whereas the summer and winter EBSPs accounted for 89% and 84% of the DUST source.

The greatest differences between the EBSPs and MBSPs were observed for the metals processing source. This was expected, since the metals processing source was a composite of multiple industrial point sources, and the composition of this source was expected to be more variable than the other sources. For example, the METALS EBSPs contained substantially less As, Si, and Zn than the METALS MBSP. As with the other sources, the 16 fitting species accounted for a smaller mass fraction of the METALS EBSPs than the METALS MBSP. The summer and winter EBSPs explained 33% and 31% of the METALS profile mass, while the METALS MBSP explained 71%. The finding that the EBSPs consistently explained less of the emissions source mass than the MBSPs is due, in part, to the lower bound on the total mass fraction of the EBSPs being unconstrained.

The summer and winter EBSPs were used to calculate optimized source impacts at the STL-SS between June 2001 and May 2003 using CMB (CMB-EBSPs). Correlation coefficients between source impacts estimated using CMB-EBSPs and the five initial SA methods ranged 0.16−0.66 for

GV, 0.02−0.85 for DV, −0.19−0.86 for DUST, 0.07−0.87 for BURN, −0.22−0.72 for SOC, and 0.21−0.69 for METALS (see SI Tables S3A−G). The metals processing impacts estimated by PMF and CMB were better correlated with impacts estimated using the ensemble method than with impacts estimated using CMAQ-TR. This result was expected since the emissions inventory and meteorological data used in CMAQ-TR are thought to underestimate day-to-day variability in local point source emissions and pollutant transport to the receptor.[5]

CMB-EBSPs offered several advantages over CMB-MBSPs. Primarily, CMB-EBSPs calculated source impacts on more days than CMB-MBSPs. CMB-EBSPs also reduced zero impact days for major emissions sources, such as DV and SOC. Further, goodness of fit statistics, such as χ^2 and the ratio of modeled-to-measured $PM_{2.5}$ mass, were improved using CMB-EBSPs. CMB-EBSPs also resulted in a higher estimate of average metals processing impacts and the fewest zero impact days for this source (Table 2). This indicates that $PM_{2.5}$ from industrial point sources impacted the STL-SS on most days during the time period of interest, which is likely due to the proximity of those sources; however, this result could also indicate that CMB-EBSPs apportion too much $PM_{2.5}$ mass to the composite industrial metals source. The ensemble technique offers an alternative method for developing representative metals processing profiles. This is advantageous since the speciate MBSPs may not adequately characterize the industrial point sources affecting the STL-SS due to operational differences between facilities (e.g., furnace types, purity of the raw material, emissions controls) and other factors. For example, the steel MBSP was approximately 40% sulfate; however, a comparison of sulfate concentrations measured near the steel facility fence line (Granite City Monitor) and at a distal monitor (Blair Street) does not indicate primary sulfate impacts from the facility.[36] Lastly, while the MBSPs did not consider the nearby zinc smelter, the metal EBSPs contain information from the industrial zinc factor identified during the PMF analysis.

Compared to CMB-EBSPs, PMF had a better modeled-to-measured $PM_{2.5}$ mass ratio and lower χ^2. This is expected since PMF adjusts source profiles to improve fit over the entire time period. However, there are still several advantages to the constrained ensemble method, which considers information from multiple SA models, including PMF. First, PMF requires several semisubjective decisions, such as selecting an appropriate number of factors and relating these factors to real-world emissions sources. For example, a previous PMF analysis at the STL-SS found that ten factors produced a robust solution, which corresponded well with known $PM_{2.5}$ sources in East St. Louis.[13] The current study found that an additional factor (11 factors) was required to distinguish gasoline from diesel vehicle impacts. Additionally, this work found that the PMF results were sensitive to the selection of XRF fitting species, especially in the resolution of separate gasoline and diesel vehicle factors. Similarly, Christensen and Schauer found that the gasoline factor was the least stable PMF factor for this data set.[12] In contrast, the ensemble method utilizes gasoline and diesel vehicle profiles developed from the results of several different SA methods, circumventing some of the issues associated with distinguishing mobile source factors. Lastly, the ensemble method does not rely on fractionated OC/EC data, which may not be available for all receptor locations of interest (e.g., earlier Chemical Speciation Network data).

While the ensemble method offers several advantages over other SA approaches at the STL-SS, this method is also subject to several limitations. First, CMB-EBSPs used a composite metals processing source to incorporate the CMAQ-TR results, which consider only industry-wide impacts. Since the smelters are located south of the site and the steelworks is located north of the site, impacts from these sources may not always covary and the composite METALS profile may not adequately characterize industrial metals emissions for all wind directions and pollutant transport conditions.

Additionally, results from a number of different SA methods are needed to calculate the EBSPs. This makes the ensemble method more time-consuming to implement than other receptor-based SA techniques, especially if previous SA results are unavailable. This work considered five SA models based primarily on data availability; however, Lee et al. and Balachandran et al. found that removing individual methods from the ensemble calculation (i.e., CMAQ and CMB-MM) changed predicted source contributions by less than 3%.[9] Additionally, while the EBSPs outperform the MBSPs at the STL-SS based on goodness of fit statistics and reductions in zero impact days, actual source impacts at the STL-SS cannot be directly measured. Thus, it is impossible to conclusively determine which method is most accurate. However, since the ensemble method incorporates results from a number of different SA strategies, each with its own biases and limitations, this method should limit the inaccuracies associated with any single method. Further, Balachandran et al. found that ensemble average source impact uncertainties were lower than individual method uncertainties using an iterative approach to calculate source impact uncertainties and ensemble-average source impacts for the Jefferson St. site in Atlanta.[32]

In addition to testing the newly developed ensemble-based SA technique, this work also highlights some of the difficulties associated with using traditional SA approaches at a monitor impacted by multiple point sources. Since the composition of the metals processing sources affecting the STL-SS are not well-characterized and the composite METALS EBSP may not fully capture compositional variations in metals processing emissions, a sensitivity analysis was conducted using five different sets of metals processing profiles: MBSPs-MI, MBSPs-MC, PMF-MI, PMF-MC, and EBSPs. CMB-derived source impacts using these different profiles were correlated, with correlation coefficients ranging 0.39−0.93 for GV, 0.80−0.96 for DV, 0.53−0.94 for DUST, 0.38−0.85 for BURN, 0.58−0.91 for SOC, and 0.37−0.84 for metals processing (see SI Tables S5A−G). However, average $PM_{2.5}$ contributions for all sources varied somewhat depending upon the metals processing profiles. For example, average BURN impacts ranged from 0.98 for CMB-EBSPs to 3.4 for CMB-PMF-MC, and average GV impacts ranged from 2.5 for CMB-PMF-MI to 4.0 for CMB-MBSPs-MI (see SI Table S6). This analysis suggests that estimated source impacts were somewhat sensitive to the metal processing profile or set of profiles, even though metals processing impacts accounted for less than 15% of reconstructed $PM_{2.5}$ mass.

This sensitivity analysis indicates that decisions made in the application of the various methods, such as the characterization of local point sources, can impact SA results. This elucidates the benefits of using several different SA models since there are limitations, subjectivities, and uncertainties associated with all available approaches. In particular, if the sources impacting a particular receptor location are not well-characterized, it may be useful to consider both a factor analytic and a CMB approach.

PMF allows the user to investigate source impacts at the receptor site without quantitatively characterizing the composition of important emissions sources. CMB avoids the need to select an appropriate number of factors and link these factors to real-world sources. Additionally, while CMAQ-TR results may not be available for the entire time period of interest, these results may be used to understand whether receptor model results are consistent with meteorological and emissions inventory data, and potentially identify emissions inventory deficiencies. Conversely, receptor models may better characterize the day-to-day variability in source impacts at a specific site missed by CTMs, such as CMAQ. Lastly, organic molecular marker methods provide SA results using a semi-independent data set that is not influenced by trace metals; however, molecular marker data are not widely available and must be scaled by source specific $PM_{2.5}$/OC ratios, adding uncertainty to the analysis. It is therefore advantageous to use several different SA techniques at a given receptor site, either by comparing source impacts predicted by different models using different data sets or by utilizing an ensemble-trained SA technique.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables S1, S2, S3A−G, S4A−F, S5A−G, and S6, as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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