

Appendix C

PM2.5 Source Apportionment in Georgia

PM_{2.5} SOURCE APPORTIONMENT IN GEORGIA

Receptor models are useful tools for identifying the source contributing to measured levels of pollutants. One of the most recently used source-apportionment models in recent years is the Positive Matrix Factorization (PMF) model. PMF is a factor analytic method that distinguishes correlation patterns among speciated PM_{2.5} measurements in a given location. As such, it does not rely on *a priori* knowledge concerning chemical composition of sources to generate source contribution estimates. An often noted limitation of using factor analysis methods is the inability to directly link observed factors in the analysis with actual sources. Since these methods are based on statistical patterns of correlations, rather than empirical chemical source profiles, naming the factors as specific sources is somewhat subjective. However, based on data on typical source-compositions for major sources, as well as researcher experience, very useful information on PM_{2.5} contributions can be derived from PMF. These include both total mass contributions for given factors/sources, as well as temporal patterns in such contributions, allowing to investigate the seasonal and weekly patterns, as well as specific days of interest.

GA EPD applied the EPA version of Positive Matrix Factorization (EPA-PMF1.1) in a novel way, using all available STN data for Georgia in one analysis. This allows for a more accurate spatial comparison of source contributions throughout the state, avoiding potential issues, such as breakdown of OC between SOA and primary OC sources, leading, for example, to erroneous conclusions about spatial patterns associated with biomass burning impacts (the inclusion of more data in the analysis assists in the breakdown between primary and secondary OC). Such an approach would be valid based on the rationale that many of the factors affecting PM_{2.5} levels are regional in nature, such as sulfate, nitrate, SOA and biomass-burning (hence, all sites are affected by the same sources), and for other sources, such as mobile sources, we do not expect a major difference in composition between different sites. However, some bias may be introduced for unique local sources of primary PM_{2.5}, and these may require further investigation using site-specific PMF analyses. However, a comparison between the combined analysis and site-specific ones show fairly minor differences between the two approaches (main differences are related to breakdown of OC mass between primary and secondary factors, as expected, and emphasize the advantage of the combined analysis approach).

Here, we will focus on the four STN sites within the GA PM_{2.5} NAA: Atlanta, Chattanooga, Rome (Floyd county) and Macon. Unfortunately, the Chattanooga STN site (on the TN side, 47-065-4002, was not included in the combined spatial PMF analysis, and results for that site are presented for the stand-alone analysis. At the time of the analyses, 468 samples were available for Atlanta (March 01 – May 05); 269 for Chattanooga (January 02 – December 06), 167 for Rome (May 02 – May 05) and 162 for Macon (June 02 – May 05). Sample uncertainties were developed, incorporating both analytical uncertainties and detection limits for each species. Samples to be included in the analysis, and which species should be given more weight in the optimization process within PMF were determined based on the average signal-to-noise ratio (average of ratios of concentration-to-uncertainty for each species), and the percent of samples below

detection limit (Table 1). In general, species with relatively high S/N ratios were chosen as “Strong” species is PMF (given more weight compared to “Weak” species), however, user judgment was used for species that serve as unique traces (such as Ni, V for oil burning) or species that were relatively elevated at specific site/s (such as Na⁺, Ni, V and the coastal Savannah site, not shown here; Cu at the Coffee county site, not shown here). OC levels were blank-corrected using the intercept point of the regression between PM_{2.5} and OC, for each site individually. Blank values, however, were applied to PMF results post analysis, since when blank corrected OC values were analyzed in PMF directly, all carbon was apportioned to an “OC” factor, and was not broken into individual categories (mobile source, biomass burning etc.).

Table 1: Species included in the PMF analysis, along with average concentrations (for each site separately), % of samples below detection limit (BDL), signal to noise ratio (S/N, defined here as the average of concentration-to-uncertainty ratios per species), and classification within PMF (%BDL, S/N and classification reported for the entire dataset used in the combined analysis).

Species	Atlanta avg. ($\mu\text{g}/\text{m}^3$)	Floyd co. avg. ($\mu\text{g}/\text{m}^3$)	Macon avg. ($\mu\text{g}/\text{m}^3$)	% BDL	S/N	Classification
SO ₄ ²⁻	4.5E+00	4.9E+00	4.6E+00	0.0	14.1	Strong
NO ₃ ⁻	8.3E-01	8.9E-01	6.6E-01	0.0	13.2	Strong
NH ₄ ⁺	1.3E+00	1.5E+00	1.3E+00	0.4	13.2	Strong
EC	9.6E-01	5.1E-01	6.7E-01	2.0	7.63	Strong
OC	5.1E+00	5.0E+00	5.5E+00	0.1	12.9	Strong
Al	2.3E-02	5.1E-02	7.2E-02	41	3.72	Weak
As	1.4E-03	1.4E-03	1.1E-03	45	2.38	Bad
Br	3.3E-03	3.5E-03	3.6E-03	4.5	7.59	Weak
Ca	3.2E-02	1.3E-01	3.2E-01	0.8	7.12	Strong
Cu	4.6E-03	2.1E-03	1.5E-03	29	5.41	Strong
Fe	8.1E-02	8.8E-02	8.1E-02	0.1	17.7	Strong
K	5.8E-02	7.5E-02	8.0E-02	0.3	8.14	Strong
K ⁺	3.5E-02	3.5E-02	3.7E-02	60	3.40	Weak
Mn	1.4E-03	1.9E-03	1.8E-03	37	3.53	Weak
Na	4.8E-02	6.9E-02	6.1E-02	54	2.48	Bad
Na ⁺	1.6E-01	1.5E-01	1.2E-01	16	6.02	Strong
Ni	4.2E-04	4.0E-04	5.4E-04	80	1.50	Strong
Pb	2.7E-03	2.6E-03	2.9E-03	50	2.67	Weak
Se	1.2E-03	1.4E-03	1.3E-03	60	1.94	Weak
Si	9.8E-02	2.0E-01	2.2E-01	2.3	7.75	Strong
Ti	5.2E-03	9.6E-03	9.1E-03	16	6.15	Weak
V	1.0E-03	1.2E-03	1.2E-03	59	2.46	Strong
Zn	8.9E-03	8.8E-03	9.3E-03	1.5	10.3	Strong
PM _{2.5}	1.55E+01	1.70E+01	1.64E+01	0.1	12.8	Weak

* - Ag, Au, Ba, Cd, Ce, Cl, Co, Cr, Cs, Eu, Ga, Hf, Hg, In, Ir, La, Mo, Nb, P, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, W, Y, and Zr were excluded from the analysis (classified as “Bad”), due to the majority of samples being below the MDL

Using the species in Table 1, several solutions based on a varying number of factors were investigated. A combination of twelve factors was chosen, as these factors seem to best represent identifiable source categories. The identification of sources was conducted based both on the composition of factors (Figure 2) and their correlation with the ambient concentrations of trace metals, carbon and major ions (Table 1). Determination of the total PM_{2.5} mass associated with each factor was carried out using several methods, such as regression of the factors against total PM_{2.5} mass, inclusion of PM_{2.5} as a weak variable in PMF, or by summation of the various components in the obtained factors (using an OM/OC ratios and metal oxides mass for crustal elements). While each of these approaches is valid, we focused on the “summation” approach, as it seemed most physically meaningful in terms of mass conservation (the other two approaches may assign high amounts of mass to factors containing only trace elements/mass). The drawback of the summation approach is the uncertainty related to the choice of the OM/OC ratio. One can chose the commonly used ratio of 1.4, however recent evidence suggest this ratio to be low, especially for biogenic aerosol. We used an optimization mechanism to minimize the error between factor-reconstructed and measured PM_{2.5} levels, by changing the OM/OC ratio for the three carbon containing factors: mobile-sources, biomass burning, and SOA. A combination of 1.2, 2.1 and 1.4, respectively, yielded the optimal solution.

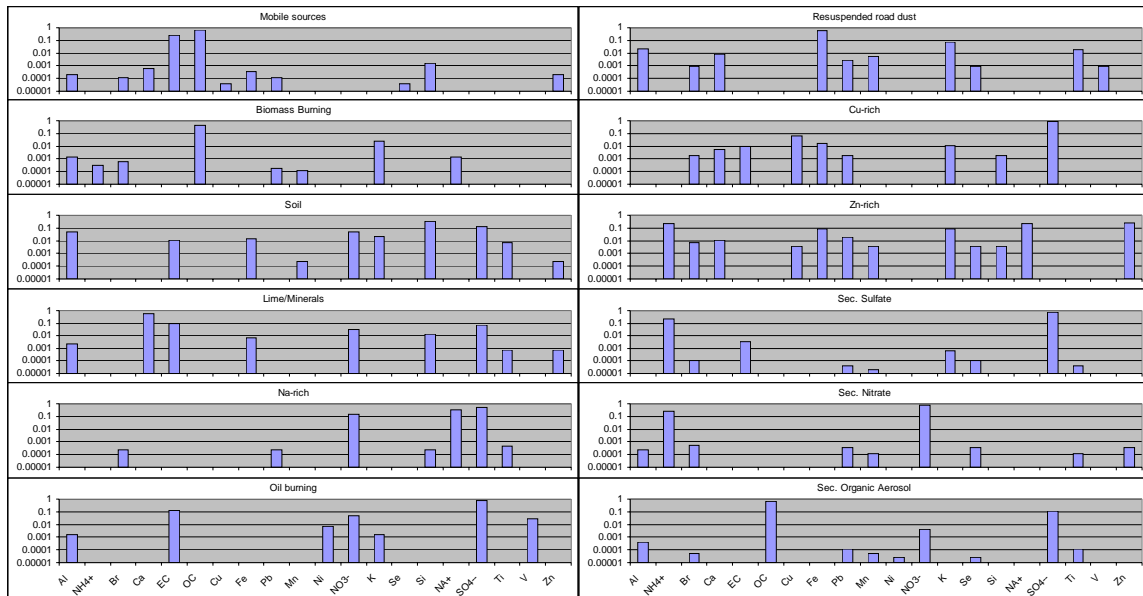


Figure 2: Compositions (factor loadings, $\mu\text{g}/\text{m}^3$) of the twelve factors identified by PMF

Table 1: Correlations (R) between factors and species

Species	Mobil e- sourc es	Biomass burning	Soil	Lime/ Minerals	Na-rich	Oil burning	Road- dust	Cu-rich	Zn-rich	Sec. Sulfate	Sec. Nitrate	SOA
SO ₄ ²⁻	0.07	-0.01	0.11	0.03	0.03	0.05	0.14	0.03	0.13	0.98	- 0.07	0.49
NO ₃ ⁻	0.13	0.24	-0.11	-0.02	0.10	-0.04	0.02	-0.08	0.20	-0.04	0.99	-0.10
NH ₄ ⁺	0.13	0.06	0.03	-0.01	-0.05	-0.03	0.13	0.01	0.21	0.95	0.26	0.40
EC	0.99	0.25	-0.01	0.08	0.04	-0.01	0.56	0.13	0.47	0.11	0.12	-0.10
OC	0.64	0.49	0.20	0.14	0.11	0.01	0.51	0.06	0.43	0.33	0.07	0.64
Al	-0.02	0.09	0.85	0.20	0.05	0.06	0.55	-0.05	0.04	0.00	- 0.11	0.21
As	0.28	0.13	0.00	-0.01	-0.06	-0.03	0.21	0.09	0.27	0.20	0.07	0.09
Br	0.32	0.50	0.01	0.09	0.17	0.00	0.23	0.05	0.34	0.20	0.41	0.10
Ca	0.01	0.22	0.20	1.00	0.03	0.01	0.12	-0.07	0.02	0.00	- 0.04	0.12
Cu	0.16	-0.02	-0.03	-0.07	-0.07	-0.07	0.08	1.00	0.05	0.03	- 0.06	-0.04
Fe	0.52	0.25	0.70	0.18	0.04	0.05	0.99	0.08	0.40	0.12	- 0.02	0.16
K	0.30	0.90	0.48	0.27	0.12	0.06	0.57	0.00	0.37	0.09	0.14	0.21
K ⁺	0.30	0.62	0.05	0.09	0.25	-0.01	0.22	0.02	0.24	0.00	0.17	0.06
Mn	0.22	0.30	0.32	0.17	0.03	0.01	0.53	-0.05	0.28	0.10	0.11	0.09
Na	-0.01	0.22	0.14	0.07	0.36	0.13	0.05	-0.02	-0.04	-0.05	- 0.04	0.02
Na ⁺	0.06	0.15	0.04	0.03	0.99	0.10	0.06	-0.07	0.01	-0.06	0.01	0.07
Ni	-0.04	0.04	0.06	0.00	0.14	0.91	0.05	-0.06	0.00	0.00	- 0.03	0.06
Pb	0.25	0.14	0.03	0.03	-0.03	-0.04	0.19	0.09	0.36	0.05	0.09	0.03
Se	0.16	0.06	0.02	0.00	-0.04	-0.03	0.15	-0.02	0.22	0.38	0.30	0.09
Si	-0.01	0.12	0.99	0.24	0.05	0.07	0.65	-0.03	0.08	0.07	- 0.14	0.28
Ti	0.06	0.13	0.72	0.25	0.11	0.18	0.59	-0.06	0.11	0.08	- 0.08	0.21
V	-0.03	0.05	0.08	0.02	0.11	0.99	0.07	-0.06	0.00	-0.01	- 0.06	0.06
Zn	0.52	0.30	0.08	0.07	-0.02	0.00	0.42	0.03	1.00	0.14	0.24	0.07
PM _{2.5}	0.37	0.33	0.28	0.20	0.04	0.02	0.46	0.06	0.38	0.77	0.06	0.58

The following factors were identified based on:

1. Mobile-sources - carbon loadings, and correlations with EC, OC, Fe and Zn (lubricating oil additive). Contributions are generally substantial, ranging from 1.6-2.8 $\mu\text{g}/\text{m}^3$ on average.
2. Biomass burning - loading and correlations with OC and K. Contributions are generally substantial, ranging from 1.1-1.5 $\mu\text{g}/\text{m}^3$ on average.
3. Soil – correlations and loadings of crustal elements such as Al, Si, Fe, Ti. Contributions are relatively small, ranging from 0.3-0.7 $\mu\text{g}/\text{m}^3$ on average.
4. Lime/minerals operations/processing– loading and correlation with Ca. Contributions are generally negligible on average in Atlanta (0.05 $\mu\text{g}/\text{m}^3$), but are higher at Rome (0.2 $\mu\text{g}/\text{m}^3$) and Macon (0.6 $\mu\text{g}/\text{m}^3$).
5. Na-rich – based on loadings and correlation with sodium ions. Could represent a mixture of sea-salt (elevated at the coastal Savannah site and/or pulp/paper industry emissions). Contributions are relatively small, ranging from 0.3-0.4 $\mu\text{g}/\text{m}^3$ on average.
6. Oil burning – based on correlations and loadings of Ni and V. Contributions are generally negligible (<0.05 $\mu\text{g}/\text{m}^3$) on average.

7. Resuspended road dust – based on correlation with crustal elements, as well as EC and OC. Contributions are relatively small ($0.1 \mu\text{g}/\text{m}^3$) on average.
8. Cu-rich factor – based on correlations and loading of Cu. Could be an indicator of metal smelting operations. Contributions are relatively small ($<0.7 \mu\text{g}/\text{m}^3$) on average.
9. Zn-rich – based on loading and correlation with Zn. Could be an indicator for industrial operations or “smoking” vehicles (Zn is a lubricating oil additive). Contributions are generally negligible ($<0.05 \mu\text{g}/\text{m}^3$) on average.
10. Secondary sulfate factor – based on correlations and loadings of sulfate and ammonium, as well as peak contributions occurring during summertime. Contributions are very substantial, ranging from $4.7\text{-}5.1 \mu\text{g}/\text{m}^3$ on average.
11. Secondary nitrate – based on the nitrate loading and correlation, as well as peak contributions occurring during wintertime. Contributions are fairly substantial, ranging from $0.7\text{-}1.0 \mu\text{g}/\text{m}^3$ on average.
12. Secondary organic aerosols – based on the high OC loading, accompanied by a smaller sulfate content, as well as peak contributions occurring during summertime. Contributions are very substantial, ranging from $1.8\text{-}3.0 \mu\text{g}/\text{m}^3$ on average.

For consistency across site, presented here are source-apportionment results for 2003-2004 (Figure 3 and Table 2). These once again show the regional nature of PM_{2.5}, given the similarities between the PMF results for the three sites. The major impacting factors at all sites are secondary sulfates, secondary nitrates, SOA, mobile sources and biomass burning. The Atlanta area, as expected, has higher levels of mobile-source PM_{2.5}, compared to Floyd county and Macon. On the other hand, these latter two sites exhibit higher levels of soil dust, and the Macon site exhibits a relatively high contribution of Lime/Minerals PM_{2.5}. This may be due to local sources in the industrial area where the site is located.

These results are also useful for a preliminary assessment of control strategies. Given the large contributions to PM_{2.5} from the secondary-sulfate factor, it is evident that controlling SO₂ emissions (mainly from coal-burning EGUs) would reduce PM_{2.5} levels throughout the state. Controlling emissions of SOA precursors would also be useful, unfortunately these are not yet well understood, and limited available knowledge suggest biogenic sources as the primary SOA precursors. Reducing primary PM_{2.5} may be best achieved by regulations on mobile-source emissions and biomass-burning. The efficiency of NO_x controls on PM_{2.5} was addressed via a photochemical modeling study, as was found to be inefficient. Contributions from all other source-categories were small in general, though the Macon and Rome sites seem to be affected by local sources related to lime/minerals processing and soil dust resuspension.

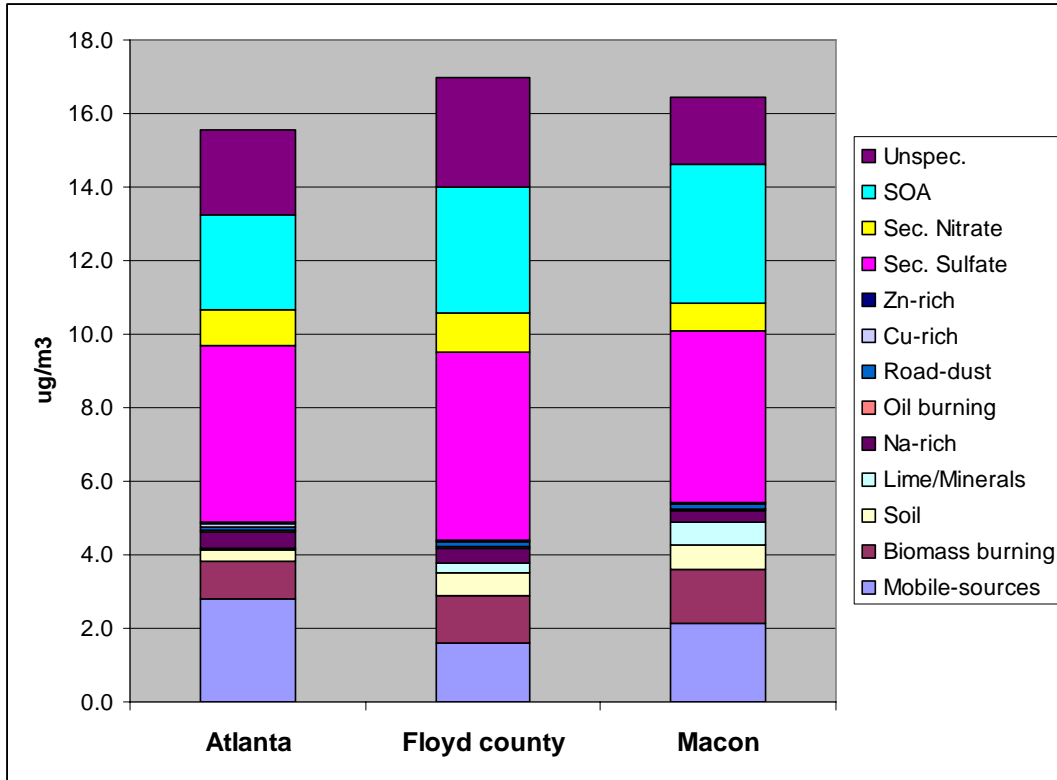


Figure 3: Average factor contributions for 2003-04 at the Atlanta, Floyd county, and Macon STN sites using PMF

Table 2: Average factor contributions to PM_{2.5} (μg/m³) for 2003-04 at the Atlanta, Floyd county, and Macon STN sites using PMF

Factor	Atlanta	Floyd county	Macon
Mobile-source	2.78	1.61	2.12
Biomass burning	1.06	1.31	1.50
Soil	0.29	0.61	0.67
Lime/Minerals	0.05	0.24	0.59
Na-rich	0.43	0.42	0.33
Oil	0.03	0.04	0.04
Road-dust	0.12	0.13	0.11
Cu-rich	0.07	0.03	0.02
Zn-rich	0.03	0.03	0.03
Sec. Sulfate	4.82	5.10	4.67
Sec. Nitrate	0.99	1.05	0.74
SOA	2.55	3.46	3.81
Unspecified	2.32	2.97	1.81

Chattanooga PMF analysis

A standalone PMF analysis was conducted for the Hamilton county STN monitor (47-065-4002) using data from 2002-2006. Table 3 provides a summary of species used in the analysis.

Table 3: Species included in the PMF analysis, along with average concentrations, % of samples below detection limit (BDL), signal to noise ratio (S/N, defined here as the average of concentration-to-uncertainty ratios per species), and classification within PMF

Species	Atlanta avg. ($\mu\text{g}/\text{m}^3$)	% BDL	S/N	Classification
SO_4^{-2}	5.0E+00	14.1	0.0	Strong
NO_3^-	1.1E+00	13.5	0.0	Strong
NH_4^+	1.7E+00	13.5	0.0	Strong
EC	6.9E-01	8.0	0.0	Strong
OC	5.0E+00	12.9	0.0	Strong
OC1	1.2E+00	7.0	0.0	Weak
OC2	1.4E+00	7.4	0.0	Weak
OC3	1.0E+00	6.7	0.0	Weak
OC4	1.2E+00	6.9	0.0	Weak
OP	1.5E-01	2.4	0.0	Weak
Al	3.1E-02	2.1	61.3	Weak
As	1.8E-03	1.6	65.1	Weak
Ba	2.1E-02	1.5	77.7	Bad
Br	3.5E-03	4.3	26.4	Weak
Ca	6.7E-02	5.9	2.2	Strong
Cl	1.3E-02	1.7	71.4	Weak
Cr	2.8E-03	2.4	61.3	Weak
Cu	4.1E-03	3.7	37.5	Weak
Fe	1.1E-01	16.7	0.0	Strong
K	6.2E-02	6.5	0.4	Strong
K^+	4.1E-02	3.7	55.0	Weak
Mn	4.2E-03	4.0	34.9	Weak
Na	6.8E-02	1.4	76.2	Bad
Na^+	1.0E-01	4.7	24.5	Strong
Ni	1.5E-03	1.7	70.3	Weak
Pb	4.3E-03	2.0	64.3	Weak
Se	1.7E-03	1.1	81.8	Bad
Si	1.1E-01	5.6	11.2	Strong
Ti	5.5E-03	2.4	53.5	Weak
V	1.9E-03	1.0	84.0	Bad
Zn	1.8E-02	9.3	3.0	Strong
$\text{PM}_{2.5}$	1.53E+01	13.3	0.0	Weak

* - Ag, Au, Cd, Ce, Co, Cs, Eu, Ga, Hf, Hg, In, Ir, La, Mo, Nb, P, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, W, Y, and Zr were excluded from the analysis (classified as "Bad"), due to the majority of samples being below the MDL

Using the species in Table 3, several solutions based on a varying number of factors were investigated. A combination of ten factors was chosen, as these factors seem to best represent identifiable source categories. The identification of sources was conducted based both on the composition of factors (Figure 4) and their correlation with the ambient concentrations of trace metals, carbon and major ions (Table 4). Determination of the total PM_{2.5} mass associated with each factor was carried out by including PM_{2.5} as a “weak” variable in the PMF analysis.

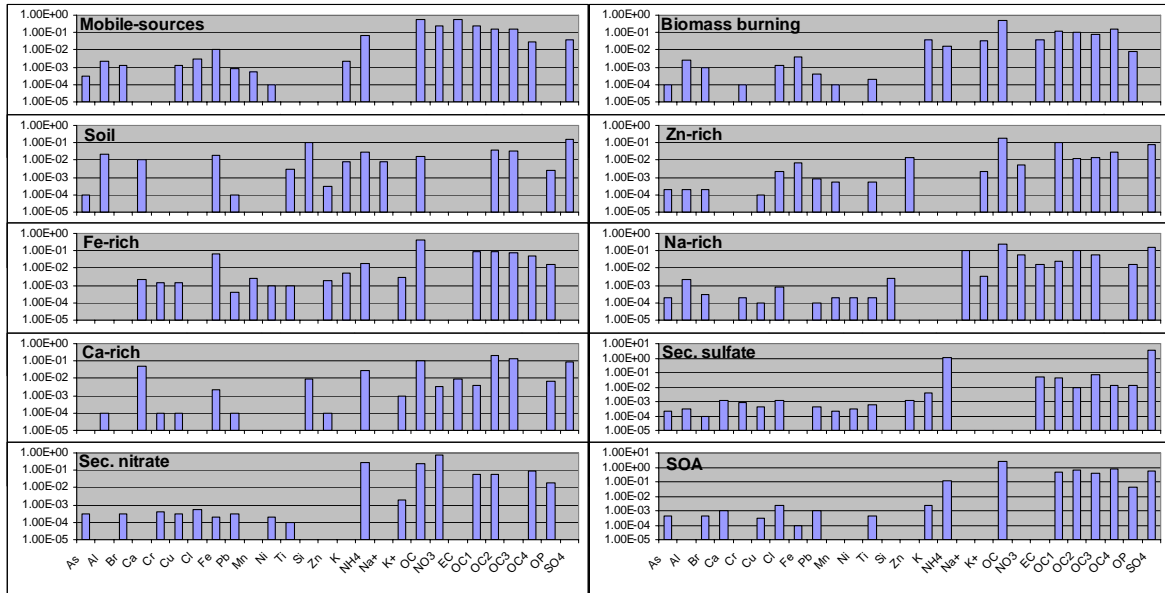


Figure 4: Compositions (factor loadings, $\mu\text{g}/\text{m}^3$) of the twelve factors identified by PMF

Table 4: Correlations (R) between factors and species

Species	Mobil e- source s	Bioma ss- burnin g	Soil	Zn- rich	Fe- rich	Na- rich	Ca- rich	Sec. Sulfat e	Sec. Nitrate	SOA
SO ₄ ⁻²	-0.06	0.02	0.06	-0.10	0.11	0.02	0.10	0.97	-0.13	0.49
NO ₃ ⁻	0.36	0.30	-0.08	0.40	0.12	0.14	-0.05	-0.13	0.98	-0.07
NH ₄ ⁺	0.08	0.14	0.01	0.06	0.16	-0.01	0.06	0.91	0.25	0.45
EC	0.99	0.37	0.03	0.61	0.54	0.04	0.04	-0.01	0.20	0.44
OC	0.68	0.47	0.13	0.44	0.44	0.10	0.15	0.25	0.14	0.83
OC1	0.70	0.35	0.04	0.48	0.41	0.04	0.04	0.17	0.11	0.60
OC2	0.59	0.36	0.09	0.34	0.34	0.10	0.04	0.18	-0.01	0.63
OC3	0.58	0.35	0.09	0.33	0.35	0.07	0.05	0.23	-0.03	0.60
OC4	0.55	0.37	0.04	0.31	0.27	0.05	0.03	0.24	0.11	0.66
OP	0.08	0.11	-0.03	0.05	0.08	0.04	0.00	-0.02	0.10	0.15
Al	-0.02	0.07	0.90	-0.07	0.23	0.03	0.23	-0.12	-0.10	-0.07
As	0.36	0.17	0.10	0.34	0.22	0.05	-0.03	-0.06	0.24	0.10
Br	0.55	0.51	-0.01	0.43	0.26	0.17	-0.03	0.04	0.35	0.32
Ca	-0.03	-0.01	0.43	-0.01	0.04	0.03	1.00	-0.06	-0.07	-0.05
Cl	0.29	0.36	0.00	0.29	0.03	0.13	0.00	-0.02	0.30	0.13

Cr	-0.03	-0.04	0.05	0.00	0.32	-0.02	0.13	0.08	-0.02	-0.14
Cu	0.48	0.07	0.11	0.40	0.51	0.01	0.14	-0.03	0.13	0.18
Fe	0.51	0.23	0.67	0.43	0.87	0.01	0.28	-0.02	0.04	0.15
K	0.33	0.92	0.46	0.30	0.33	0.18	0.09	0.05	0.18	0.23
K ⁺	0.31	0.72	0.13	0.32	0.22	0.26	0.08	0.00	0.27	0.14
Mn	0.53	0.19	0.23	0.53	0.81	0.05	0.04	0.01	0.06	0.12
Na ⁺	-0.02	0.23	0.16	-0.02	0.02	0.99	0.07	-0.04	0.05	-0.08
Ni	0.22	-0.04	-0.06	0.20	0.44	0.05	-0.01	-0.04	0.05	-0.14
Pb	0.33	0.11	0.01	0.29	0.24	-0.09	0.05	0.08	0.09	0.25
Si	-0.02	0.11	0.98	-0.06	0.25	0.05	0.55	-0.08	-0.10	-0.02
Ti	0.03	0.15	0.88	0.03	0.38	0.04	0.27	-0.02	-0.06	-0.01
Zn	0.64	0.30	0.00	0.99	0.53	-0.02	0.03	-0.07	0.29	0.14
PM _{2.5}	0.34	0.27	0.15	0.21	0.32	0.03	0.15	0.75	0.05	0.71

The following factors were identified based on:

1. Mobile-sources - carbon loadings, and correlations with EC, OC, Fe and Zn (lubricating oil additive). The average contribution is 1.1 $\mu\text{g}/\text{m}^3$.
2. Biomass burning - loading and correlations with OC and K. The average contribution is 0.7 $\mu\text{g}/\text{m}^3$.
3. Soil – correlations and loadings of crustal elements such as Al, Si, Fe, Ti. The average contribution is 0.5 $\mu\text{g}/\text{m}^3$.
4. Zn-rich – based on loading and correlation with Zn. Could be an indicator for industrial operations (metals processing etc.) or “smoking” vehicles (Zn is a lubricating oil additive). This factor is also rich in carbon. The average contribution is 0.6 $\mu\text{g}/\text{m}^3$.
5. Fe-rich – based on correlation with Fe, as well as Mn and carbon fractions. Likely an indicator for resuspended soil. The average contribution is 0.5 $\mu\text{g}/\text{m}^3$.
6. Na-rich – based on loadings and correlation with sodium ions. Could be an indicator of pulp/paper industry emissions. The average contribution is 0.2 $\mu\text{g}/\text{m}^3$.
7. Lime/minerals operations/processing – loading and correlation with Ca. The average contribution is 0.2 $\mu\text{g}/\text{m}^3$.
8. Secondary sulfate factor – based on correlations and loadings of sulfate and ammonium. Contributions are very substantial, 6.3 $\mu\text{g}/\text{m}^3$ on average.
9. Secondary nitrate – based on the nitrate loading and correlation. The average contribution is 0.2 $\mu\text{g}/\text{m}^3$.
10. Secondary organic aerosols – based on the high OC loading, accompanied by a smaller sulfate content, as well as peak contributions occurring during summertime. Contributions are very substantial, 4.4 $\mu\text{g}/\text{m}^3$ on average.

These results are useful for a preliminary assessment of control strategies. Given the large contributions to PM_{2.5} from the secondary-sulfate factor, it is evident that controlling SO₂ emissions (mainly from coal-burning EGUs) would reduce PM_{2.5} levels in the Chattanooga MSA. Controlling emissions of SOA precursors would also be useful, unfortunately these are not yet well understood, and limited available knowledge suggest biogenic sources as the primary SOA precursors. Reducing primary PM_{2.5} may be best achieved by regulations on mobile-source emissions and biomass-burning. The efficiency

of NO_x controls on PM_{2.5} was addressed via a photochemical modeling study, as was found to be inefficient. Contributions from all other source-categories were small in general.

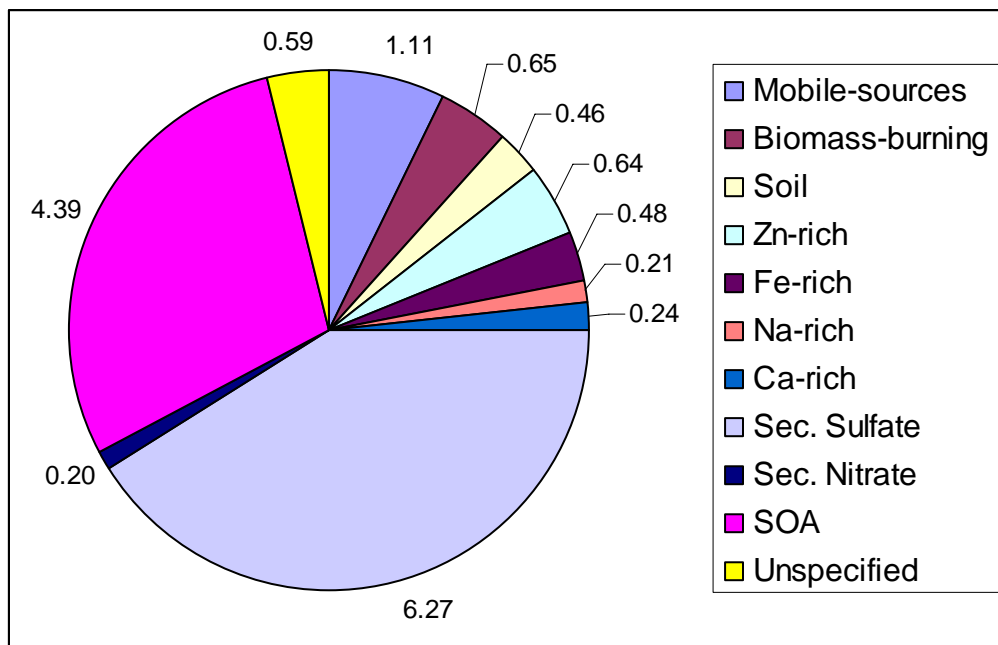


Figure 5: Average factor contributions to PM_{2.5} (µg/m³) for 2002-06 at the Chattanooga STN site using PMF

FIRE-STATION #8 ANALYSIS

PM_{2.5} levels at the Fire-Station #8 (FS#8) site are substantially higher than any of the other Atlanta NAA sites. Higher PM_{2.5} levels have been observed consistently ever since such measurements have become available (Figure 6). Compared to all other Atlanta PM_{2.5} NAA sites for the 1999-2006 period, FS#8 PM_{2.5} levels are 2.4 µg/m³ higher on average. Of interest, two sites are located within 3 miles of FS#8, the E. Rivers sites (2.9 miles NE of FS#8) and the Jefferson Street (JST) SEARCH site (2.2 miles SE of FS#8) (Figure 7), yet PM_{2.5} levels at FS#8 are substantially higher than at these two sites as well, by an average increment of 2.1 µg/m³ for the 1999-2006 period. This is an indication that the PM_{2.5} increment at FS#8 is likely due to a local source. To further investigate the nature of the local PM_{2.5} increment, PM_{2.5} concentrations at FS#8, E.Rivers and JST were plotted against wind-direction (measured at JST, the only site of the three at which such measurement were available) (Figure X-X). These data clearly indicate that PM_{2.5} levels are the highest during southern winds at all sites, which is expected due to their location with respect to downtown Atlanta. In fact, these data can serve as an additional method for estimating the urban increment in PM_{2.5} levels, comparing PM_{2.5} levels from the SW and SE quadrants to those from the NE and NW quadrants. Such an analysis yields an urban increment of 2.2-3.0 µg/m³ (for these three sites), which is fairly consistent with the estimate based on spatial patterns within the Atlanta NAA. Further analyzing Figure 8, a peak in PM_{2.5} is observed on days of

southwestern winds at the FS#8 site, but not at the other two sites. As shown in Figure 9, a large rail-yard is located southwest of FS#8, which may be contributing to the local increment in PM_{2.5} levels.

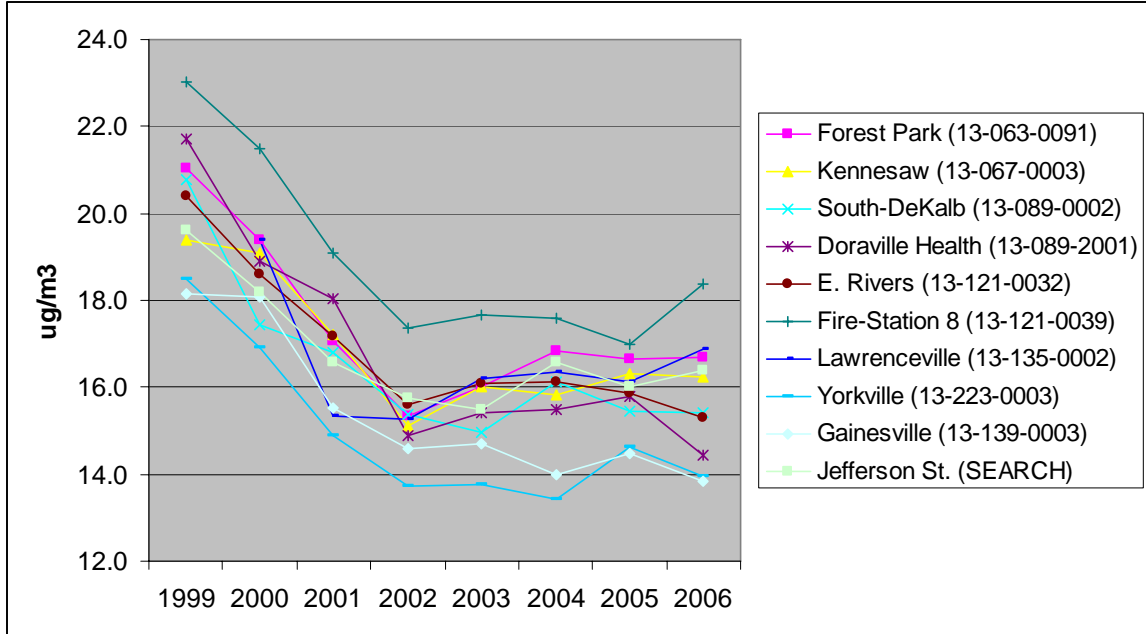


Figure 6: Annual averages of PM_{2.5} at Atlanta NAA sites for 1999-2006



Figure 7: Location of the FS#8 monitor compared to other Atlanta monitors.

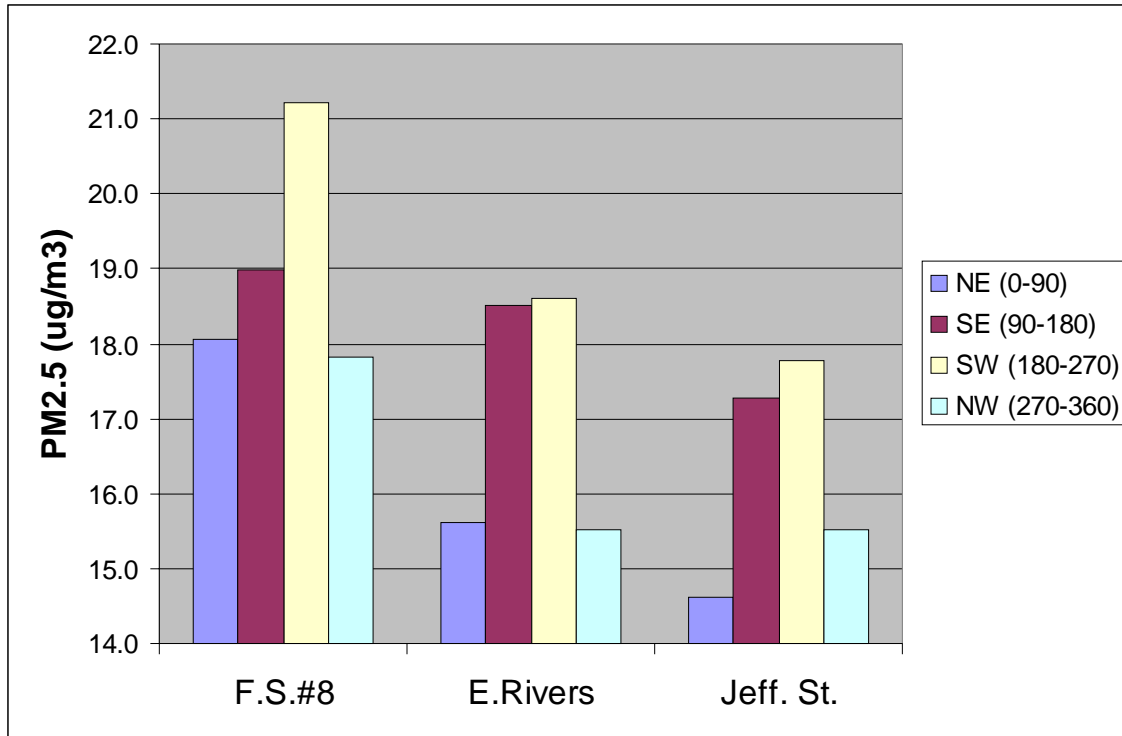


Figure 8: PM_{2.5} concentrations at FS#8, E.Rivers and Jeff. St. as a function of wind-direction (measured at the Jeff. St. site).



Figure 9: Location of the FS#8 monitor compared to the adjacent rail-yard and Marietta Boulevard

To further investigate the possible sources of the local PM_{2.5} increment at FS#8, we used the PMF model. Since the FS#8 site is not a STN site, no speciation data were readily

available. However, selected collected PM_{2.5} filters from 2002-2004 were analyzed by X-ray fluorescence (XRF) to quantify ambient trace metals concentrations. However, ions and carbon data were not available. Hence PMF was run using metals data only. 118 samples for January 2002- January 2005 were available for the analysis. Only metals for which the majority of samples were above the minimum detection limit (MDL), and the average signal-to-noise ratio (S/N, defined here as the average of concentration-to-uncertainty ratios per species) was greater than 2.0 were included in the analysis (Table 5). The metals were classified as “Strong” or “Weak” in PMF, with the “Weak” species being down-weighted in the PMF optimization process, hence giving more emphasis to the “Strong” species. Species classified as “Bad” were excluded from the analysis. The classification was based on the S/N values. However, user judgment was used for specific species: V was classified as “strong” and Ni kept in the analysis, to attempt to identify oil combustion particles; Cu downgraded to “weak” as it worsened the overall fit, and Br and Pb excluded for the same reason.

Table 5: Species included in the PMF analysis, along with average concentrations, minimum detection limits (MDL), % of samples below detection limit (BDL), signal to noise ratio (S/N, defined here as the average of concentration-to-uncertainty ratios per species), and classification within PMF.

Species	Avg. Conc. ($\mu\text{g}/\text{m}^3$)	MDL ($\mu\text{g}/\text{m}^3$)	% BDL	S/N	Classification
Ca	4.75E-02	1.79E-03	0.0	32.5	Strong
Cl	2.29E-02	2.12E-03	7.6	13.7	Strong
Fe	1.28E-01	4.42E-04	0.0	118	Strong
K	5.84E-02	1.48E-03	0.0	45.7	Strong
S	1.58E+00	2.82E-03	0.0	259	Strong
Si	9.79E-02	5.21E-03	0.8	17.7	Strong
V	2.94E-03	1.05E-03	11.8	3.8	Strong
Zn	1.05E-02	5.73E-04	0.0	22.4	Strong
Al	4.47E-02	1.10E-02	12.6	4.4	Weak
As	1.29E-03	6.59E-04	31.9	2.3	Weak
Cu	4.16E-03	4.68E-04	0.8	10.7	Weak
Mg	1.20E-02	4.52E-03	34.5	3.0	Weak
Mn	2.69E-03	6.15E-04	7.6	5.2	Weak
Na	6.60E-02	1.62E-02	5.9	4.9	Weak
Ni	6.25E-04	4.10E-04	47.9	2.1	Weak
Se	1.62E-03	7.09E-04	19.3	2.9	Weak
Br	3.26E-03	6.40E-04	2.5	6.0	Bad
Pb	3.59E-03	1.72E-03	31.1	2.5	Bad

* - Ag, Au, Ba, Cd, Ce, Co, Cr, Cs, Eu, Ga, Hf, Hg, In, Ir, La, Mo, Nb, P, Rb, Sb, Sc, Sm, Sn, Sr, Ta, Tb, Ti, W, Y, and Zr were excluded from the analysis (classified as “Bad”), due to the majority of samples being below the MDL

Using the species in Table 5, several solutions based on a varying number of factors were investigated. A combination of six factors was chosen, as these factors seem to best

represent identifiable source categories. The identification of sources was conducted based both on the composition of factors (Figure 10) and their correlation with the ambient concentrations of trace metals (Table 6). The factors were identified as representing the following source categories:

Factor A: Soil/fugitive dust, due to the high loading of crustal elements (Si, Al, and Fe), and high correlations with Al and Si.

Factor B: Cement operations (kiln, crushing), due to the high Ca loading, and correlations with Ca and V (an additive to tires, often used as fuel in cement kilns).

Factor C: Biomass burning, due to the high loading and correlation with K (OC was not available for the analysis, but would typically account for most of the mass is a biomass burning factor).

Factor D: Steel particles, due to the high Fe loading and correlations with steel components such as Fe, Cu, Mn, Ni and Zn.

Factor E: Zn-rich aerosol, possibly representing mobile sources. Zn is an additive to lubricating oil used in mobile sources, and in lieu of industrial sources of Zn in Atlanta, may serve as a tracer for mobile sources. In lieu of EC and OC data, these are not included in this factor, though would typically be.

Factor F: Sulfur rich aerosol, likely representing secondary sulfate.

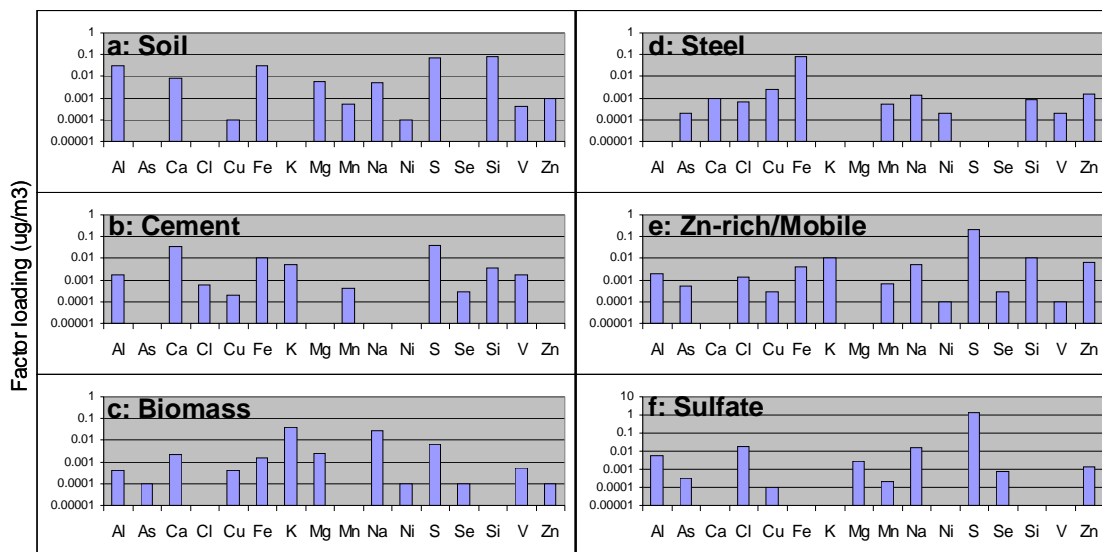


Figure 10: Compositions of the six factors identified by PMF for FS#8

Table 6: Correlations (R) between factors and species at FS#8

Species	Soil	Cement	Biomass	Sulfate	Steel	Zn-rich
Al	0.96	0.11	0.31	0.23	0.09	-0.01
Ca	0.34	0.95	0.07	-0.04	0.27	0.41
Cl	0.15	0.04	0.26	0.94	0.13	0.04
Cr	0.06	0.14	0.20	-0.02	0.38	0.33
Cu	0.09	0.16	0.26	-0.10	0.93	0.38
Fe	0.34	0.27	0.35	-0.02	0.96	0.47
K	0.30	0.14	0.95	0.10	0.41	0.28
Mn	0.26	0.39	0.19	-0.02	0.66	0.56
Na	0.29	-0.15	0.68	0.32	0.19	-0.11
Ni	0.11	0.08	0.25	-0.08	0.79	0.28
S	0.15	-0.02	0.14	0.99	0.00	-0.08
Si	0.99	0.18	0.32	0.09	0.17	0.08
V	0.37	0.88	0.24	-0.04	0.37	0.44
Zn	0.14	0.39	0.18	0.01	0.71	0.92

To further investigate the sources contributing to the local PM_{2.5} increment at FS#8, these factors were regressed against the difference in PM_{2.5} levels at FS#8 and the average of the JST and E. Rivers sites (to quantify and represent the local increment). We used a multiple linear regression model, assuming the local FS#8 PM_{2.5} increment can be explained by the sum of increments associated with each of these six factors. The average contribution of each factor to the local PM_{2.5} increment (Table 7) was represented by the regression slope. The correlations between the reconstructed (modeled) increment and the observed one was R=0.76, and the average ratio of modeled to observed concentrations was 0.97. The two factors with the highest contribution to the local PM_{2.5} increment at FS#8 are the steel and Zn-rich factors, contributing 1.2 and 0.6 $\mu\text{g}/\text{m}^3$, respectively (together explaining 60% of the increment). These two factors were also the only ones found to be statistically significant in the regression process, with p-values of 5×10^{-8} and 0.025, respectively. The daily contributions of these two factors to the local PM_{2.5} increment at FS#8 are shown in Figure 11. Average contributions from the soil, cement and biomass burning were in the range of 0.21-0.25 $\mu\text{g}/\text{m}^3$ each, but none were statistically significant. As expected, the contribution of the sulfate factor to the local PM_{2.5} increment was low (0.08 $\mu\text{g}/\text{m}^3$), as sulfate is a secondary, regional pollutant. Of note, it was not possible to characterize all sources affecting local PM_{2.5} levels, as ions and carbon data were not available for the analysis.

Table 7: Contribution of each factor to the local PM_{2.5} increment at FS#8

Factor	Avg. contribution ($\mu\text{g}/\text{m}^3$)	p-value
Soil	0.25 ± 0.17	0.138
Cement	0.21 ± 0.19	0.279
Biomass burning	0.23 ± 0.20	0.247
Secondary sulfate	0.08 ± 0.18	0.646
Steel	1.18 ± 0.18	5E-08
Zn-rich / Mobile sources	0.60 ± 0.26	0.025

Investigating further into the source of steel particles represented by the steel factor, we estimate the source to be related to activity at the adjacent rail-yard. This is supported by a study conducted in the New-York city subway (Chilrud et al, 2004), in which Fe, Mn, Cr levels at the subway were 100 times greater than those in the outside ambient air. In comparison, Fe, Mn, and Cu levels at FS#8 are more than twice of those at JST. The difference in magnitude (>100 compared to >2) is due to the subway being an enclosed “micro” environment, as opposed to two ambient measurements at JST and FS#8. However, an increment in the levels of metals associated with steel is evident. The increment in Fe, Mn and Cr at the subway was associated with the friction between the rails and the subway trains. It is reasonable to assume the same for the rail-yard adjacent to FS#8. It is, however, important to note that the steel particles themselves do not account for most of the mass emissions leading to the local increment in PM_{2.5} levels. Most mass associated with locomotive emissions are in the form of engine-generated carbon (mainly EC, or “soot”) emissions. However, these EC emissions are accompanied by friction-generated steel particles from movement of the locomotives on the rail. These co-emitted metals were identified by PMF as a factor (as carbon data were not available for the analysis). Hence, the metals associated with steel serve, in this case, as a tracer or proxy for activity at the rail-yard, and were found highly correlated with the local PM_{2.5} increment at FS#8. The Zn-rich factor may be an indicator of local traffic on Marietta Boulevard (which has a high percentage of diesel traffic), idling fire trucks at the fire-station, or idling locomotives at the nearby rail-yard.

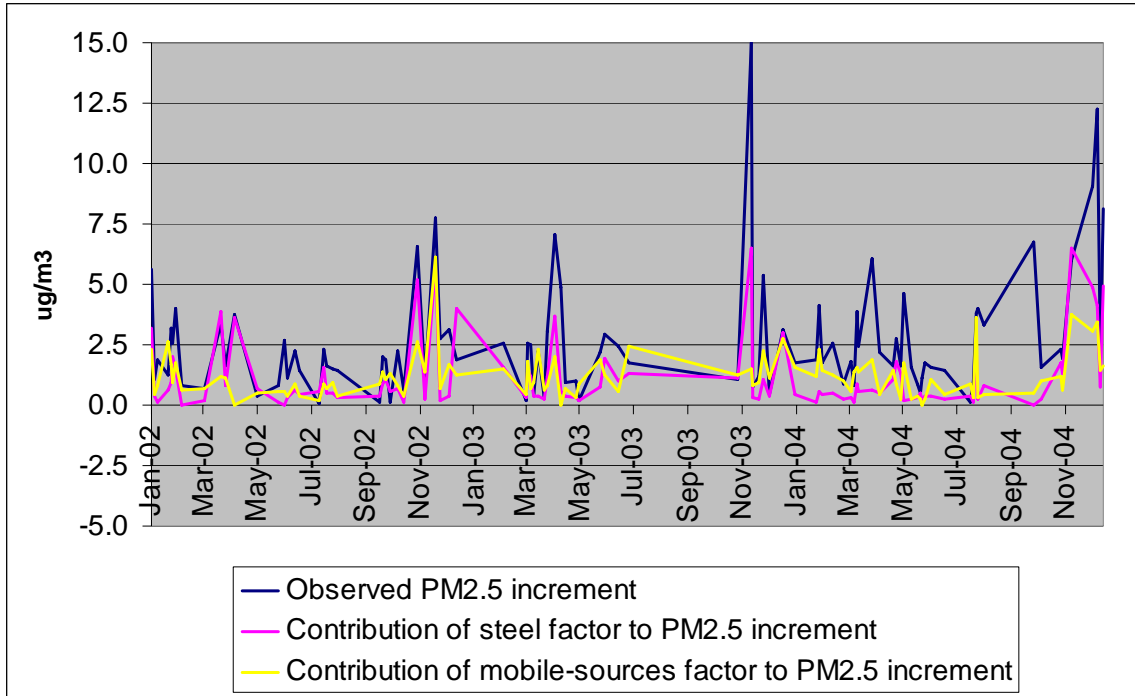


Figure 11: Daily contributions of the “steel” and “Zn-rich/Mobile” factors to the observed local PM2.5 increment at FS#8.