

Allegheny County Health Department Air Quality Program 301 39th St., Bldg. #7 Pittsburgh, PA 15201

Allegheny County PM_{2.5} Source Apportionment Results using the Positive Matrix Factorization Model (PMF Version 1.1)



Model Timeframe: July 2003 through August 2005

January 13, 2006 Prepared By Jason Maranche APC Engineer II

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1. Executive Summary

The Positive Matrix Factorization Model (PMF Version 1.1)¹ is a Windows-based software tool developed by EPA as a method to estimate source contributions based on actual monitored results. PMF performs a least-squares fit over an array of species measured simultaneously at a monitoring site.

The Allegheny County Health Department operates $PM_{2.5}$ speciation monitors at Lawrenceville in the City of Pittsburgh and at Liberty Borough near the southeastern tip of Allegheny County. Each speciation monitor measures 54 different species of $PM_{2.5}$, including total mass concentration.

Sample concentrations were entered into PMF along with date-matched uncertainties. Source factors were then calculated by the model as a result of iterative methods that converge on possible solutions to the array of variables. Modeled source factors were then matched to possible actual source types according to known species profiles, previous source apportionment studies, and a conceptual model of the area. A conceptual model is a fundamental understanding of how pollutants behave based on emissions inventory, monitored results, meteorological conditions, and transport phenomena.

This report is based on preliminary results using PMF Version 1.1. It is anticipated that future receptor modeling will be performed at a later date using a larger array of samples for the Lawrenceville and/or Liberty sites. This may also include wind direction or trajectory analysis for specific factors.

PMF modeling resulted in the following 11 source factors for Lawrenceville:

						Gasoline	Airborne			
Secondary	Secondary	Diesel Vehicles	Diesel Vehicles +		Gasoline	Vehicles +	Crustal	Airborne	Road Dust	Misc.
Ammonium	Ammonium	+ Misc. Road	Ferromanganese-		Vehicles +	Selenium-Rich	(Silicon-	Crustal	(Road Salt-	Burning and
Sulfate	Nitrate	Dust	Rich Industrial	Incinerators	Tire Wear	Industrial	Rich)	(Other)	Rich)	Cooking
5.49	2.81	0.42	0.26	0.45	0.79	0.58	0.28	0.52	0.38	2.40

PMF modeling also resulted in the following 12 source factors for Liberty:

I									Airborne			
	Secondary	Secondary		Selenium-		Halogen-			Crustal	Airborne		
	Ammonium	Ammonium	Carbon-Rich	Rich	Zinc-Rich	Rich	Diesel	Gasoline	(Silicon-	Crustal		Vegetative
	Sulfate	Nitrate	Industrial	Industrial	Sources	Sources	Vehicles	Vehicles	Rich)	(Other)	Road Dust	Burning
Ι	4.33	1.75	4.00	0.12	0.46	1.03	1.35	1.11	0.28	0.52	0.15	1.37

The values shown above are concentrations for each factor in units of μ g/m³. Detailed results for Lawrenceville and Liberty are given in <u>Section 4</u> and <u>Section</u> <u>5</u>, respectively.

¹ PMF 1.1 is currently under peer review and is not yet available for distribution. See disclaimer at the end of this document.





2. Sites

The Lawrenceville monitor site is an urban residential site, downwind from the Pittsburgh Central Business District (Downtown). Monitored data shows that Lawrenceville is affected by both regional flow and urban excess for $PM_{2.5}$. The regional flow is presumably due to upwind power plant emissions, but may also include $PM_{2.5}$ from biogenic sources such as trees. The urban excess sources should be anthropogenic sources such as light industry, mobile source emissions residential and commercial burning/heating.

The Liberty Borough monitor site is located in the Monongahela Valley, which contains a mix of urban residential, heavy industrial, and rural areas. Monitored data shows that regional flow is evident for some $PM_{2.5}$ species, while concentrations of other species do not follow regional flow. It is assumed that species that do not follow regional flow may be originating at sources resident to the area, both stationary and mobile.

Uncertainties for speciation data were uploaded to AQS beginning with July 2003 data. Data used in this PMF modeling spans the dates July 2003 through August 2005.

Over this timeframe, 206 samples were modeled for the Lawrenceville site (a 1in-3 sampling frequency). Dates on or near the Fourth of July were removed due to outliers in the concentrations due to fireworks. Potassium nitrate and other ingredients can lead to abnormal concentration levels of trace elements, some of which rarely exceed minimum detection limits (MDLs) on average days.

Since Liberty is a 1-in-6 sampler and only began operation in October 2003, only 91 samples were modeled for the Liberty site. Independence Day firework outliers were also observed at this site, and corresponding dates were removed from the modeling input file.



3. Methodology

Model operation was followed according the user's guide and modeling workbook. The PMF model was tested under many different species and factor combinations. Species are excluded if they exhibit low signal-to-noise ratios, are frequently below the minimum detection limit (MDL), or do not easily fit into a least-squares solution.

The <u>major species</u> measured from the speciation monitors show the highest concentrations, strongest signal-to-noise ratios, and are usually a sign of specific sources. These species can strongly affect the model. These species include:

Sulfate Nitrate Ammonium Organic Carbon Elemental Carbon Total PM_{2.5}

The following <u>trace element species</u> also had significant concentrations and strong signal-to-noise ratios. They may also be important tracer elements, associated with specific sources. These species include:

Aluminum	Copper	Potassium
Arsenic	Iron	Selenium
Bromine	Lead	Silicon
Calcium	Manganese	Titanium
Chlorine	Mercury	Vanadium
Chromium	Nickel	Zinc

Over half of the trace element species available were *excluded* from the modeling based on frequent concentrations that were less than the MDL. These elements provide little weight in the fit of a solution. These species include:

Antimony	Gold	Phosphorus	Terbium
Barium	Hafnium	Rubidium	Tin
Cadmium	Indium	Samarium	Tungsten
Cobalt	Iridium	Scandium	Yttrium
Cerium	Lanthanum	Silver	Zirconium
Cesium	Magnesium	Sodium	
Europium	Molybdenum	Strontium	
Gallium	Niobium	Tantalum	

Sulfur as a trace element has also been excluded from the model, since nearly all sulfur as a component of $PM_{2.5}$ in the Pittsburgh region is accounted for by sulfate.



Total $PM_{2.5}$ was used PMF an strength indicator for each factor but was down weighted in order to lower its influence on the fit of the model. Down weighting increases the uncertainty by a factor of 3.

Trace element species with low signal-to-noise ratios (less than 3.0) were down weighted. Low signal-to-noise ratios mean that a species' concentrations and uncertainties are nearly equal.

Trace element species that fit less perfectly than other species into a convergent solution were also down weighted. A poor fit is reflected by poor diagnostics from regression, standard deviation, and residual statistics.

Additionally, a 5% uncertainty was applied to the entire model (based on EPA recommendation) for samples taken from Speciation Trends Network (STN) speciation monitoring sites, used by Allegheny County.

The number of <u>source factors</u> in the model are increased or decreased based on the performance of the model and the rationality of the results. A source factor does not necessarily represent a single source but rather a source type or scenario (or combination thereof) that leads to contributions at the monitor site. Too few sources factors indicate a lack of uncertainty and creates profiles with species that are clustered. Too many source factors indicate too much uncertainty and leads to profiles that cannot be characterized or are too small in overall concentration to have significance.

The goodness-of-fit parameter (Q) for a perfect theoretical model is calculated as:

Q = (# samples * # good species) + [(# samples * # weak species)/3] – (# samples * # factors being estimated)

Source factors are varied in the model until the modeled Q converges on a solution that approaches the perfect theoretical Q. The source factor profiles for near-perfect model runs are then examined for physical validity.²

Some factors may be associated with a similar source type but are separated into more specific source factors by the model. For example, a source type of road dust may comprise a source factor that has a strong year-round presence and another factor that is seasonal. There may also be overlap of some source types. For example, a factor dominated by secondary ammonium sulfate may also include carbons and trace elements that may or may not be originating from the sulfate sources but are peaking simultaneously with sulfate.

² Results were compared to previously-compiled source profiles. See the References section of this document.

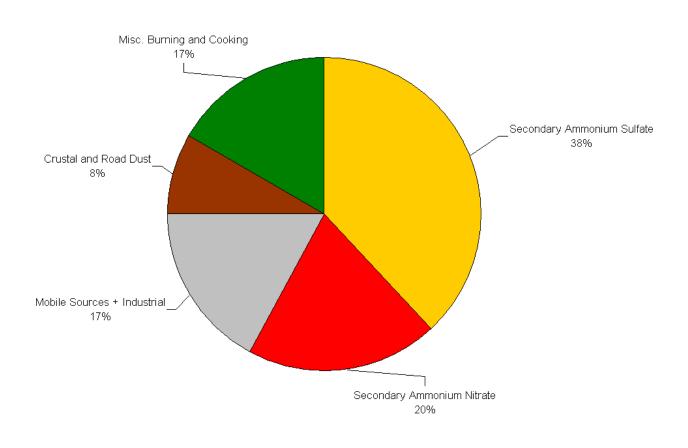


4. Modeled Results: Lawrenceville

A total of 206 Lawrenceville samples were input into the model. The best model runs were able to resolve 11 source factors. The following trace elements were down weighted in the model runs: Al, As, Br, Cr, Hg, K, Ni, Ti, and V.

In addition to Fourth of July samples removed on account of trace element outliers, the sample taken on 4/10/2005 has been removed from the modeling. An exceptional event was identified on this date in which crustal elements (geological dust, or airborne soil) were higher than the norm.

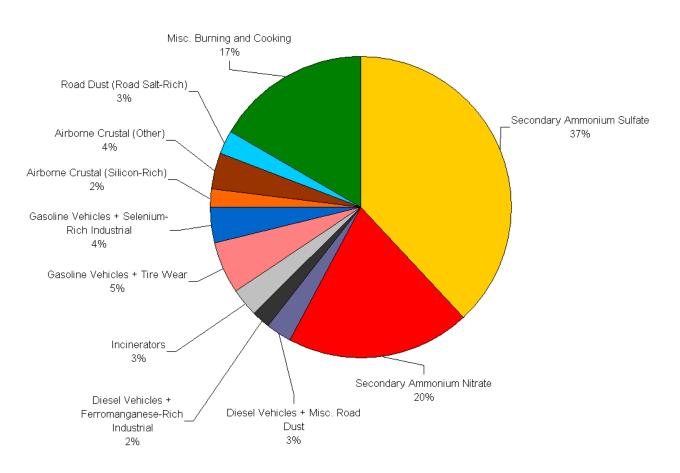
Lawrenceville results exhibited source factors that are common to urban areas. A simplified pie chart of the best-guess source types (by percentage of summed concentrations) is shown below.



Lawrenceville Pie Chart - Simplified Source Types



An expanded pie chart of the source types is also shown below.



Lawrenceville Pie Chart - Expanded Source Types



Lawrenceville source factor profiles and associated source types are given in the table below. Species concentrations that were considered to be indicators of the specific source types are shown in bold.

		1		1		1				i.	1
											Misc.
		ndary /Nitrate		Mobile and I	ndustrial Sou	weee		Crus	Burning and Cooking		
	Sullate	VINITALE				lices	Gasoline	Airborne			
	Secondary	Secondary	Diesel Vehicles	Diesel Vehicles +		Gasoline	Vehicles +	Crustal	Airborno	Road Dust	Misc.
	Ammonium	, ,	+ Misc. Road	Ferromanganese-		Vehicles +		(Silicon-	Crustal	(Road Salt-	
	Sulfate	Nitrate	Dust	Rich Industrial	Incinerators		Industrial	Rich)	(Other)	Rich)	Cooking
Factor	1	8		2		7	9	<u> </u>	<u>``</u>		
Total	6.4161	2.5224	0.2664	0.3167	0.5161	1.0412	0.7419	0.5796	0.4859	0.4923	2.8246
Ammonium	1.1737	0.5381	0.0702	0.0304	0.0728	0	0	0.0572	0	0.0799	0.0530
Nitrate	0.0497	1.3083	0	0	0	0	0	0.0083	0.1195	0.1390	0
Sulfate	3.7984	0.4717	0.0688	0.0748	0.2202	0.0531	0.1002	0.1150	0.0001	0.0662	0.4070
Org_Carbon	0.4347	0.4330	0	0	0.0834	0.6498	0.4265	0	0.3544	0.0522	1.6817
Elem Carbon	0.0312	0.0416	0.2051	0.1017	0.0540	0.0599	0.0365	0.0327	0	0.0181	0.2118
AI	0	0.0029	0	0.0011	0	0.0003	0.0003	0.0001	0.0048	0	0.0014
As	0.0003	0	0	0.0001	0	0.0003	0.0009	0.0001	0	0.0002	0.0012
Br	0.0004	0.0009	0.0005	0	0	0.0004	0.0004	0.0002	0.0001	0.0002	0.0010
Ca	0.0044	0	0	0.0061	0	0	0.0022	0	0.0280	0.0023	0
CI	0	0.0004	0	0	0.0003	0	0.0001	0	0	0.0180	0
Cr	0.0002	0.0003	0.0005	0.0005	0.0007	0.0006	0.0005	0	0	0	0
Cu	0.0002	0	0.0036	0	0	0.0006	0.0002	0.0001	0	0	0
Fe	0	0.0020	0.0649	0.0373	0.0100	0	0	0	0.0049	0.0017	0.0126
Pb	0	0	0	0	0.0094	0	0.0021	0	0	0	0
Mn	0	0	0	0.0065	0	0.0001	0.0004	0.0001	0	0.0002	. 0
Hg	0.0001	0.0003	0.0001	0	0	0	0.0004	0	0	0	0.0004
Ni	0	0.0004	0.0009	0.0001	0	0.0001	0	0	0	0	0.0002
К	0	0.0075	0.0045	0	0.0003	0.0057	0.0062	0.0028	0.0083	0.0009	0.0247
Se	0.0003	0.0003	0	0	0	0	0.0047	0.0002	0	0.0002	. 0
Si	0	0.0008	0	0	0.0010	0	0.0016	0.0639	0.0026	0.0009	0
Ti	0.0004	0.0004	0.0014	0	0.0001	0.0005	0	0.0003	0.0011		0.0000
V	0.0002	0.0002	0	0	0	0	0	0	0	0.0002	0.0005
Zn	0	0.0021	0	0.0047	0.0026	0.0162	0		0.0009		
SUM (exc. total)	5.4942	2.8112	0.4205	0.2633	0.4548	0.7876	0.5832	0.2818	0.5247	0.3828	2.3958

Analysis and graphical results for each factor are given on subsequent pages. Graphical results are copied directly from the model output and include the following for each factor:

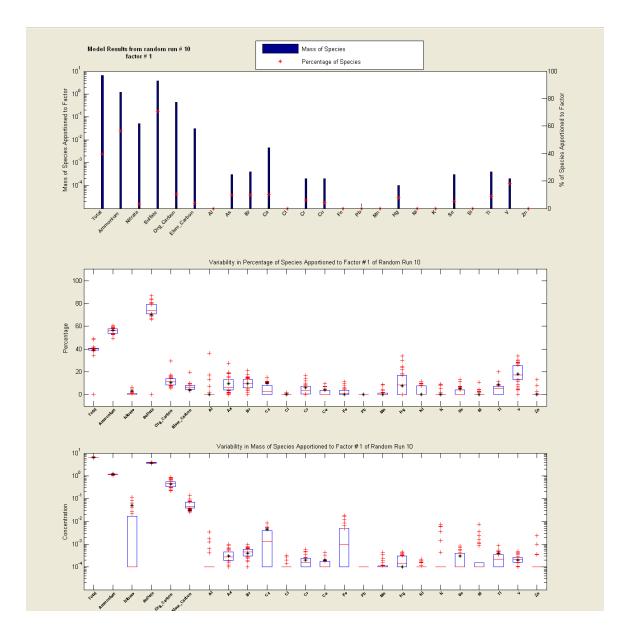
- Concentration by value and percentage of total for each species
- Variability (bootstrapping) for each concentration and percentage
- Time series plot by overall factor concentration
- Contribution aggregates according to season and day of the week

Note: Factors and runs are generated randomly by PMF and are not ranked according to any one species.

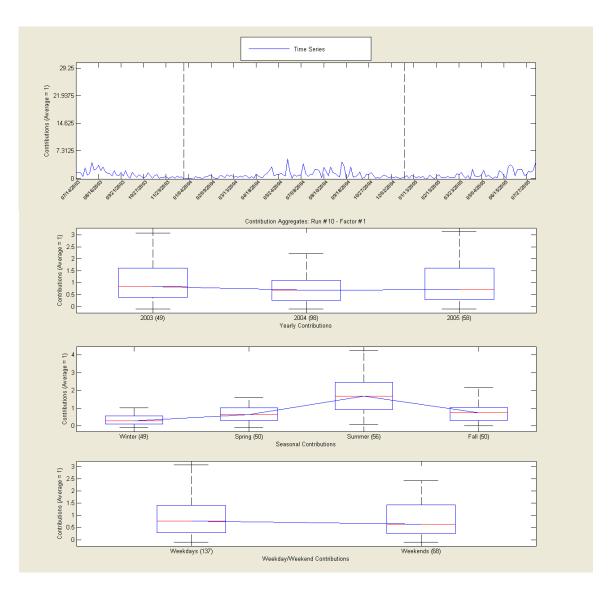


Lawrenceville Source Factor 1: Secondary Ammonium Sulfate

Factor 1 is the largest source factor by summed concentration and comprises the majority of ammonium sulfate at Lawrenceville. Contributions are highest in summer, when sulfate is most prevalent. Sulfate exists as secondary $PM_{2.5}$ in the Pittsburgh region, formed from upwind SO₂ sources such as coal-fired power plants. Factor 1 also contains some carbons and trace elements that are likely peaking concurrently with the sulfate. The organic carbon may be secondary in nature as well. Graphical results are shown below.



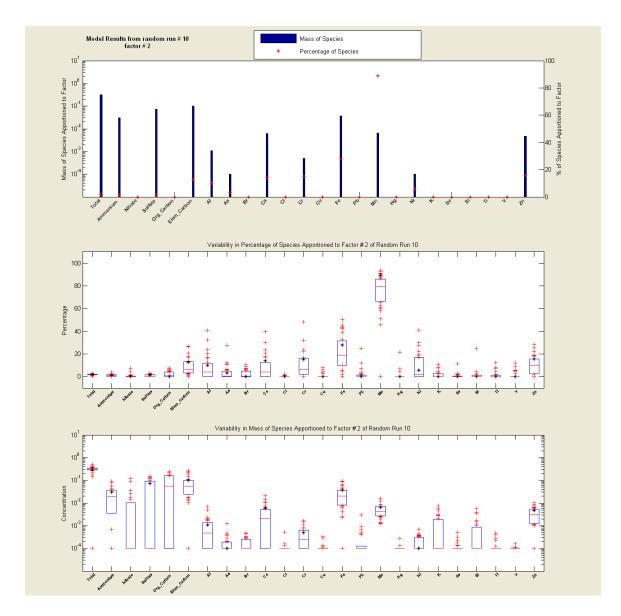




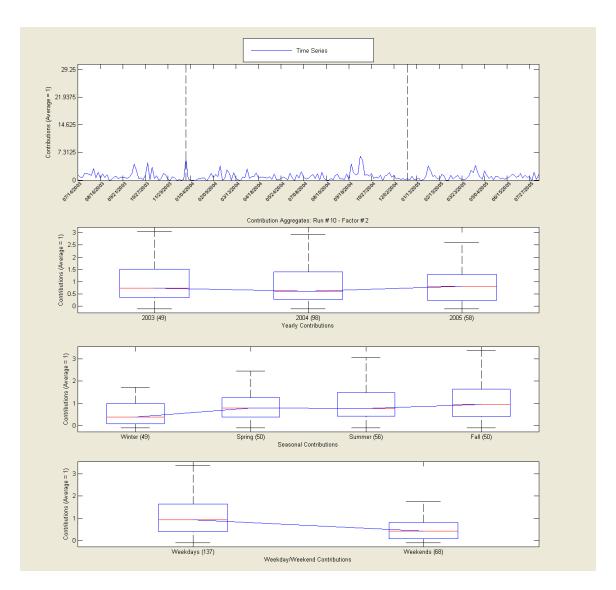


Lawrenceville Source Factor 2: Diesel Vehicles + Ferromanganese-Rich Industrial

High elemental carbon and weekday contributions are indicative of diesel vehicles for Factor 2. There is also a strong presence of iron and manganese associated with this factor, which may be related to steel industry operations. Diesel and steel emissions may be originating from the same wind direction for this factor.



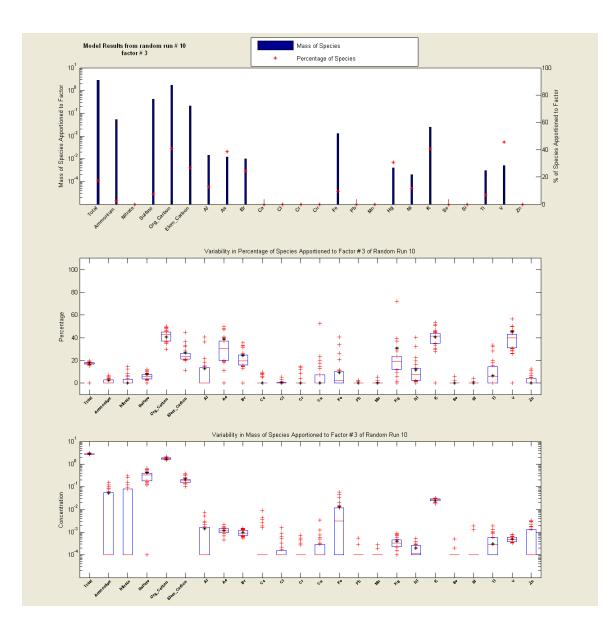




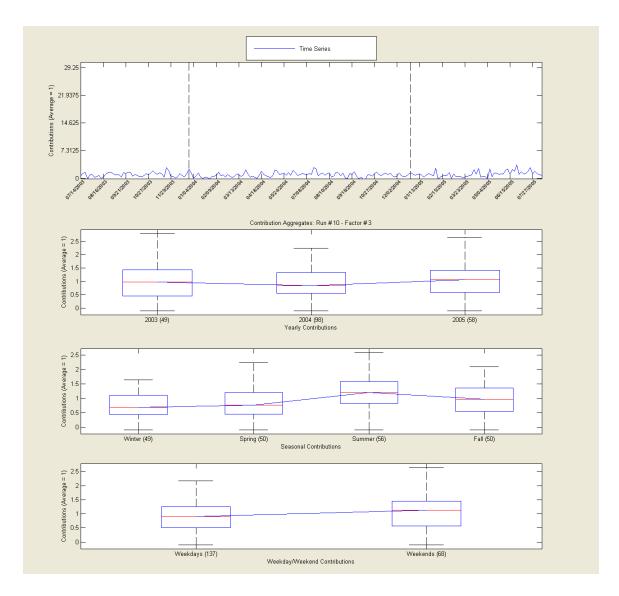


Lawrenceville Source Factor 3: Miscellaneous Burning and Cooking

Factor 3 contains high amounts of carbons together with potassium, which are usually indicators of vegetative burning and cooking. This factor is slightly higher on weekends and in summer, perhaps due to recreational open burning and cooking. Arsenic, bromine, mercury, and vanadium are also high in percentage, perhaps due to oil/coal burning, either residential or commercial.



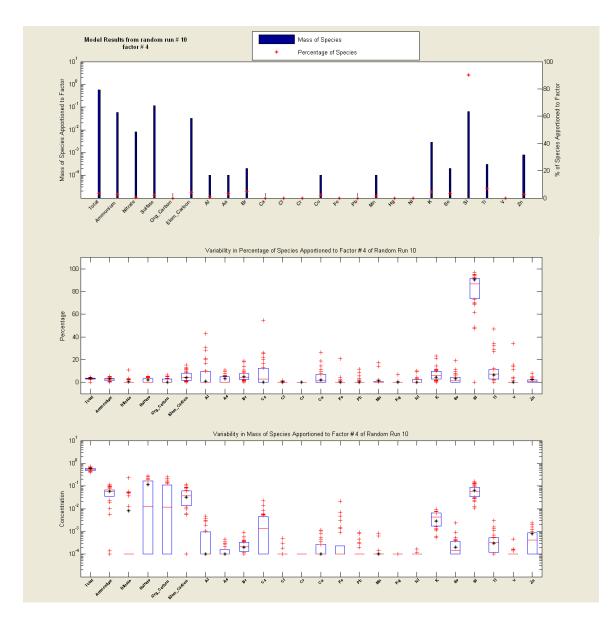






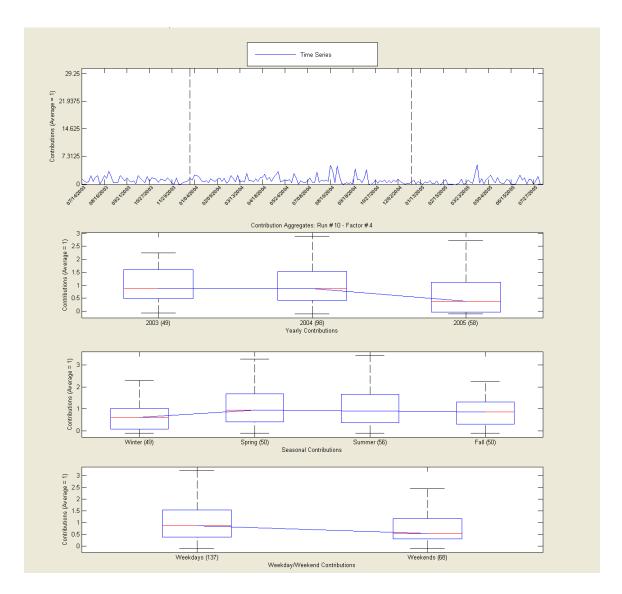
Lawrenceville Source Factor 4: Airborne Crustal (Silicon-Rich)

Crustal elements include aluminum, calcium, iron, silicon, and titanium. These elements are the basic make-up of fine airborne soil. Factor 4 is best attributed as the silicon portion of airborne crustal component. Contributions are slightly higher during weekdays, possibly due to traffic forcing up road and crustal dust. Springtime contributions are also slightly higher. Some silicon may be also due to primary power plant emissions.





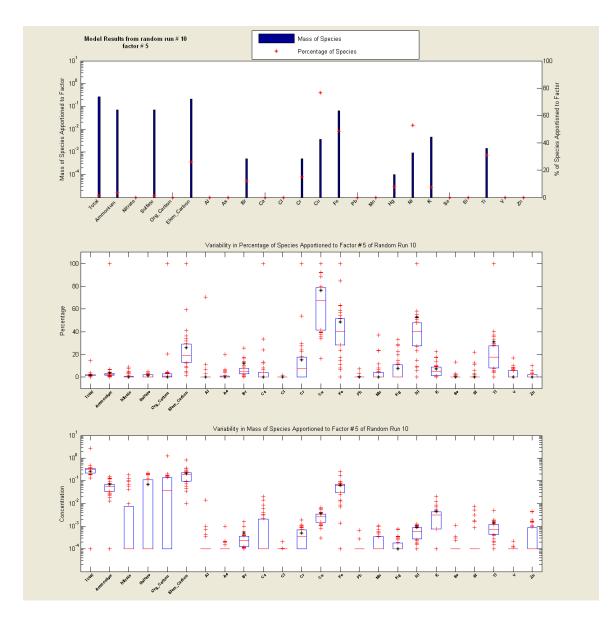




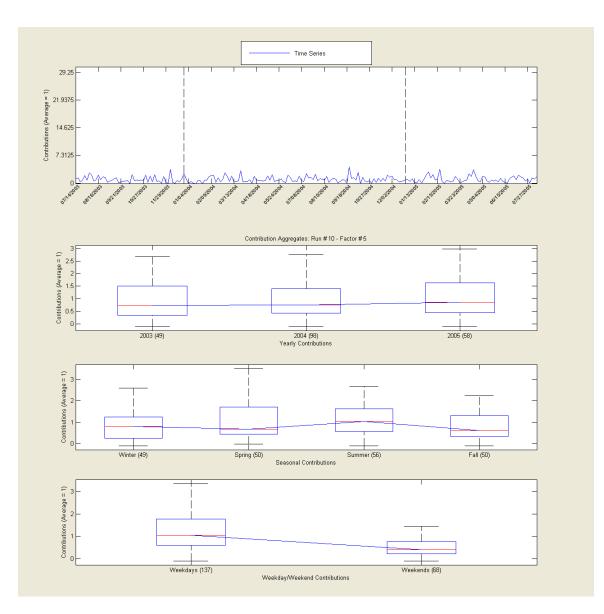


Lawrenceville Source Factor 5: Diesel Vehicles + Miscellaneous Road Dust

Factor 5 contains a large percentage of elemental carbon with high weekday contributions. Large percentages of copper and nickel are also present, along with crustal iron and titanium. These trace elements have been grouped as miscellaneous road dust.



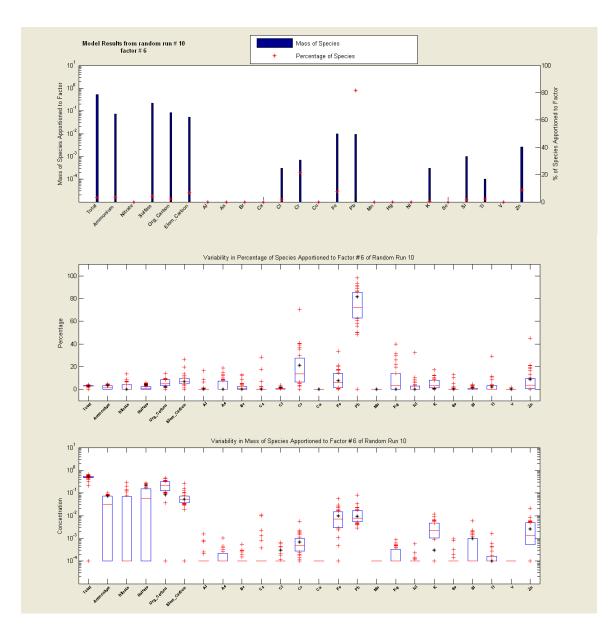




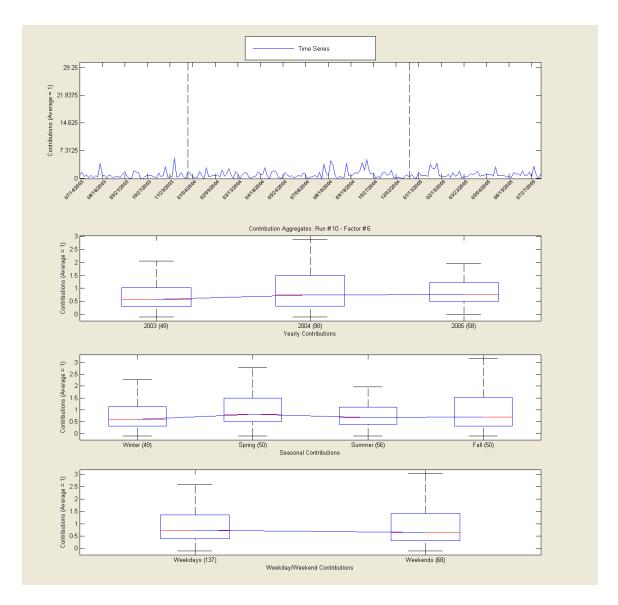


Lawrenceville Source Factor 6: Incinerators

Factor 6 has a high percentage of lead, along with significant percentages of carbons and zinc. The carbon ratios are different from most vehicle profiles, and there is little variation between weekday/weekend contributions. Source factors with these characteristics are associated with municipal waste incinerators and sewage sludge incinerators.





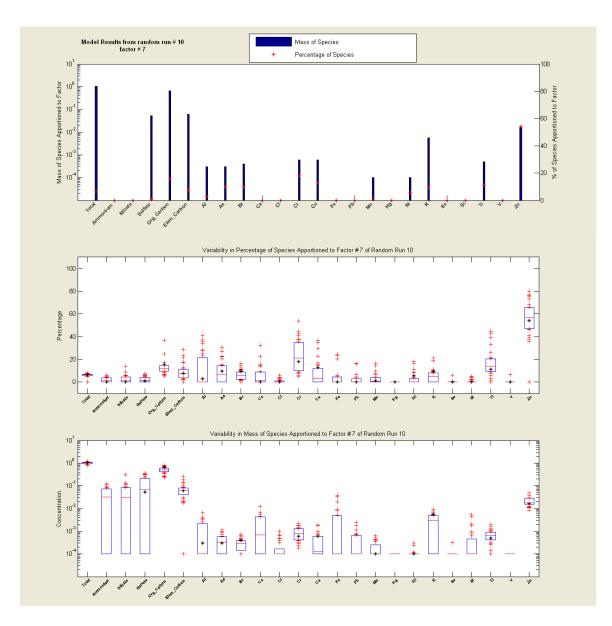




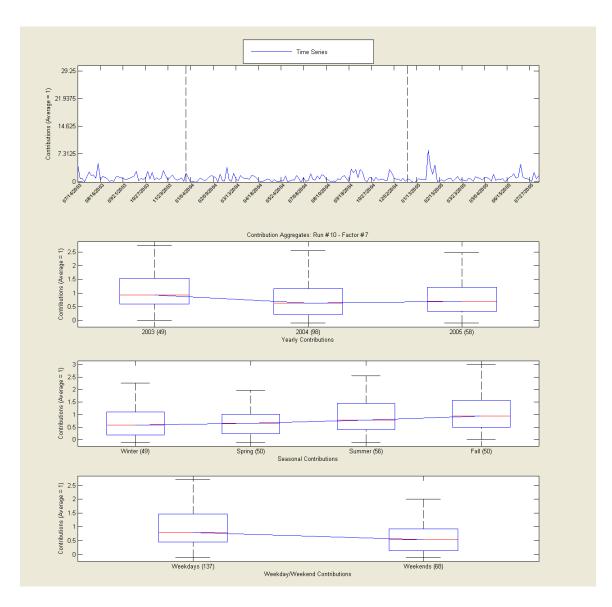


Lawrenceville Source Factor 7: Gasoline Vehicles + Tire Wear

Factor 7 has high percentages of organic and elemental carbons and zinc, showing high contributions on weekdays. The carbon ratio is indicative of gasoline vehicles, and zinc is associated with tire wear from vehicles. Minor concentrations of other trace elements are also present.



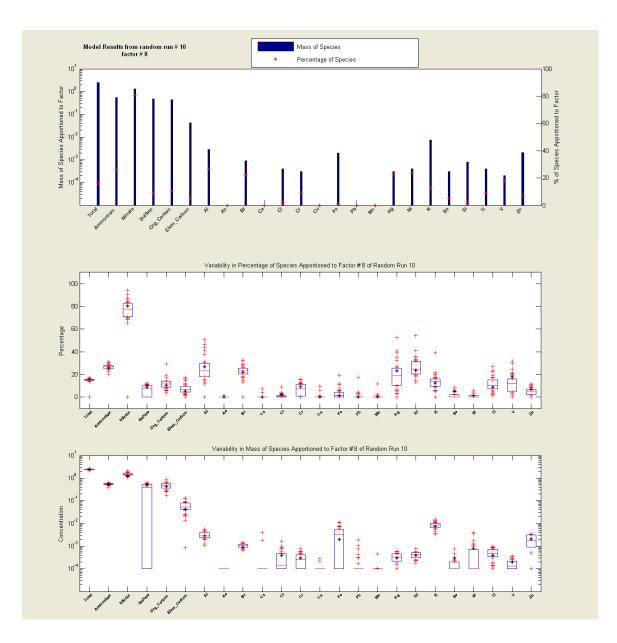






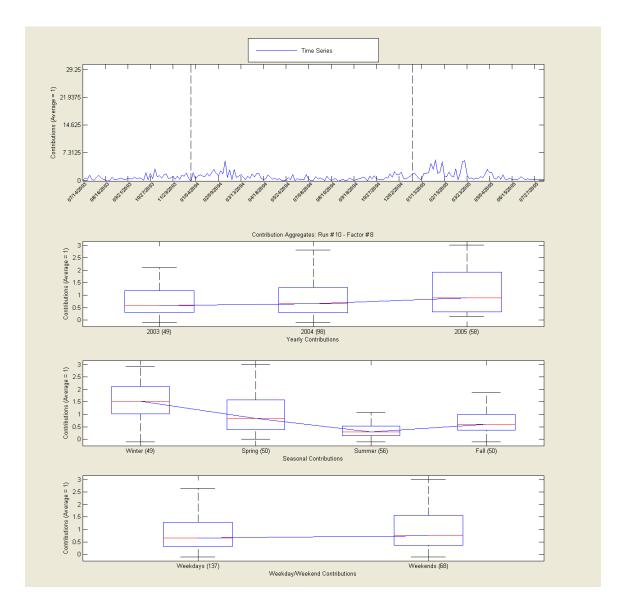
Lawrenceville Source Factor 8: Secondary Ammonium Nitrate

Factor 8 is the majority of secondary ammonium nitrate at the monitor, dominant in cold weather. Nitrate is a secondary species created by upwind NOx sources such as fossil fuel-fired boilers. Other species such as carbons and aluminum are grouped with this factor as well, perhaps representing cold-weather fractions of their total contribution.







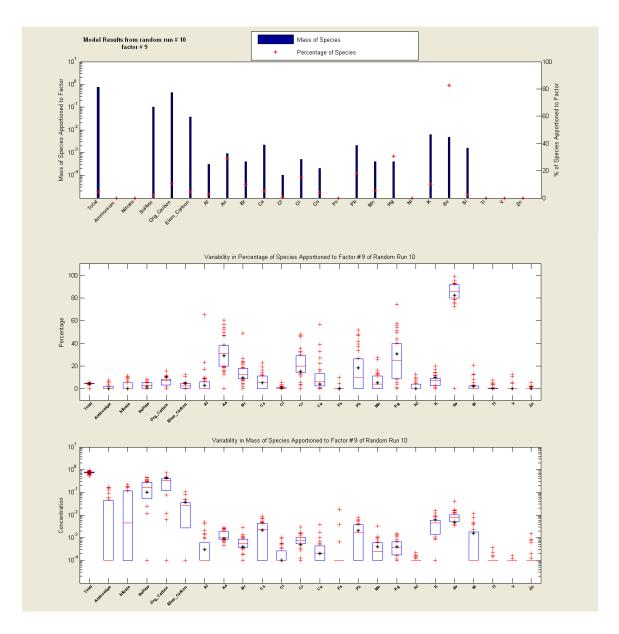




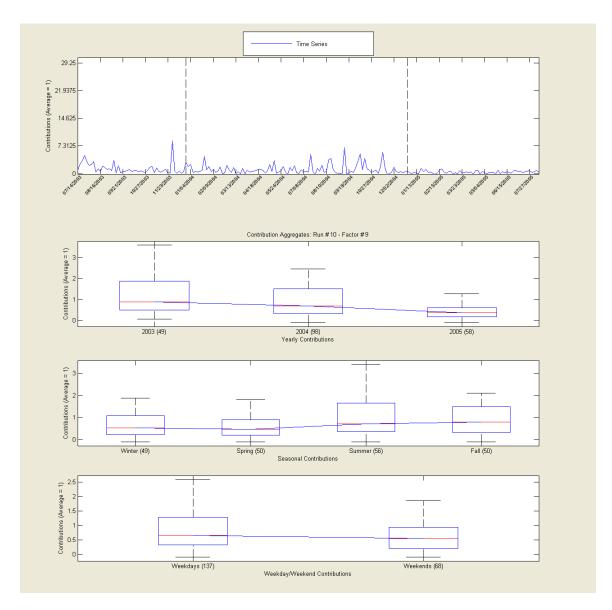


Lawrenceville Source Factor 9: Gasoline Vehicles + Selenium-Rich Industrial

Factor 9 shows strong weekday organic and elemental carbon concentrations, indicating light-duty gasoline vehicle emissions. Also peaking with this factor is selenium, perhaps originating from the same area as the vehicle emissions. Selenium is sometimes associated with primary coal-fired boiler emissions but is also present in some glass manufacturing emissions. Total factor emissions decreased noticeably in 2005.





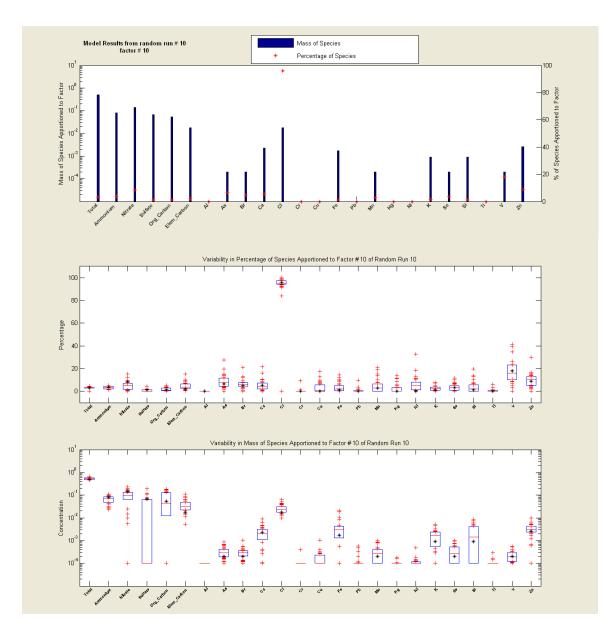




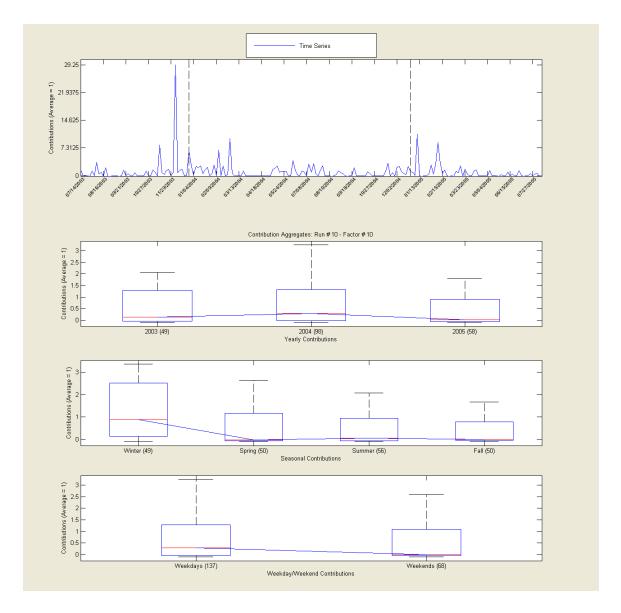


Lawrenceville Source Factor 10: Road Dust (Road Salt-Rich)

Factor 10 contributes almost all of the chlorine at Lawrenceville. Since it peaks on winter weekdays, it is likely due to airborne road salt along with other miscellaneous road dust compounds.





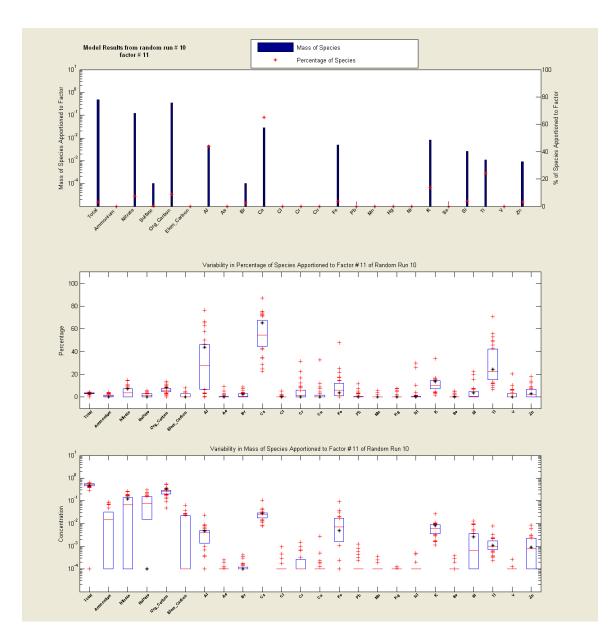




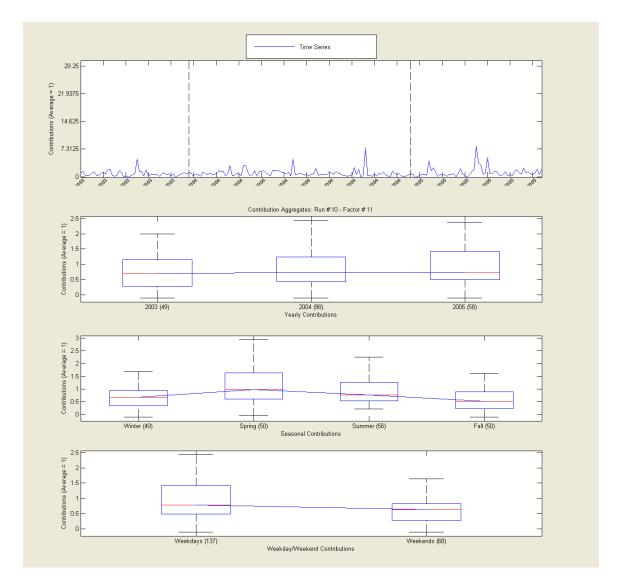


Lawrenceville Source Factor 11: Airborne Crustal (Other)

Like Factor 4 (silicon-rich crustal), Factor 11 is composed of crustal elements and is higher on weekdays and in spring. Aluminum, calcium, and titanium show the highest percentages for this factor.







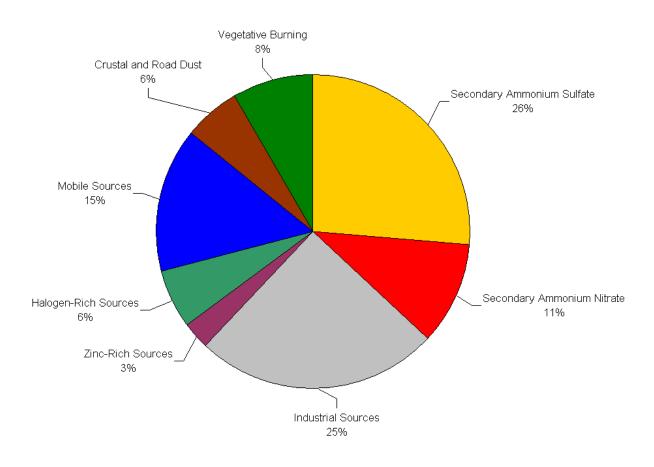


5. Modeled Results: Liberty

A total of 91 Liberty samples were input into the model. The best model runs were able to resolve 12 source factors. The following trace elements were down weighted in the model runs: AI, As, Cr, Hg, Mn, Ni, Ti, and V.

In addition to Fourth of July samples removed on account of trace element outliers, the samples taken on 2/3/2005 and 5/10/2005 were removed from the modeling. An exceptional event was identified on these dates in which crustal elements (geological dust, or airborne soil) were higher than the norm.

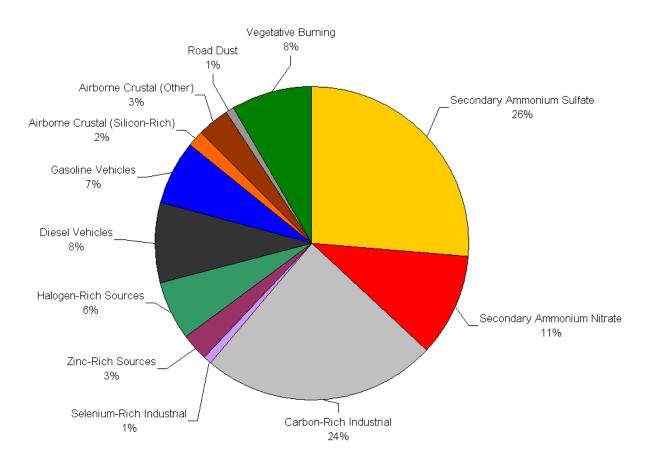
Liberty results revealed many of the same source factors that were evident at Lawrenceville, while also indicating additional sources specific to the Liberty area. A simplified pie chart of the best-guess source types (by percentage of summed concentrations) is shown below.



Simplified Pie Chart - Liberty Source Types



An expanded pie chart of the source types is also shown below.



Expanded Pie Chart - Liberty Source Types



Liberty source factor profiles and associated source types are given in the table below. Species concentrations that were considered to be indicators of the specific source types are shown in bold.

	Seco	ndary			Zinc-Rich	Halogen- Rich						Vegetative
	Sulfate	/Nitrate	Industrial	Sources	Sources	Sources	Mobile S	Sources	Crust	Burning		
									Airborne			
	Secondary	Secondary		Selenium-		Halogen-			Crustal	Airborne		
	Ammonium	Ammonium	Carbon-Rich	Rich	Zinc-Rich	Rich	Diesel	Gasoline	(Silicon-	Crustal		Vegetative
	Sulfate	Nitrate	Industrial	Industrial	Sources	Sources	Vehicles	Vehicles	Rich)	(Other)	Road Dust	Burning
Source Factor	3	11	2	8	7	6	4	1	5	10	9	12
Total	4.8529	1.4586	4.7404	0.2820	0.0000	0.9354	1.1247	1.4644	0.3113	0.5434	0.6755	2.0641
Ammonium	0.8185	0.4406	0.3981	0.0341	0.0672	0.1845	0.1705	0.1142	0.0474	0	0	0
Nitrate	0.1455	0.9814	0	0.0040	0	0.0369	0.1301	0	0	0	0	0.0872
Sulfate	2.8271	0.3140	0.0268	0.0491	0.3188	0.2365	0.3232	0.4012	0	0.1023	0.0410	0.2162
Org_Carbon	0.4784	0	2.0157	0.0205	0.0526	0.2387	0.3288	0.5657	0.1092	0.3292	0.0621	0.9952
Elem_Carbon	0.0508	0	1.5418	0	0	0.0340	0.3706	0	0.0383	0.0379	0	0.0421
Al	0.0039	0	0	0	0	0	0	0	0.0006	0.0031	0.0010	0
As	0.0002	0	0.0030	0	0.0013	0	0	0	0.0002	0	0	0.0004
Br	0	0.0007	0.0057	0.0002	0.0004	0.0020	0	0	0	0.0004	0.0006	0
Ca	0	0	0	0.0008	0.0003	0.0022	0	0.0035	0.0030	0.0244	0	0
CI	0	0.0024	0	0.0036	0	0.2813	0.0001	0	0.0017	0	0.0016	0.0082
Cr	0.0001	0	0	0	0	0	0.0002	0	0	0.0004	0.0009	0.0004
Cu	0	0	0	0	0	0	0.0004	0.0044	0	0.0002	0	0
Fe	0.0028	0	0.0099	0.0006	0.0029	0	0	0.0156	0.0017	0.0048	0.0384	0
Pb	0.0002	0	0	0.001	0	0.0024	0.0095	0.0004	0	0	0	0.0004
Mn	0	0.0004	0	0	0.0007	0	0	0.0001	0	0	0.0012	0.0003
Hg	0	0.0001	0	0	0.0002	0.0006	0	0.0017	0.0005	0	0	0
Ni	0.0001	0	0	0	0	0.0001	0.0001	0	0	0	0.0009	0.0002
К	0	0.0041	0	0.0003	0.0035	0.0020	0		0.0031	0.0129	0.0005	0.0226
Se	0.0002	0	0.0009	0.0079	0.0003	0	0.0007	0	0	0.0002	0	0.0004
Si	0	0	0	0	0	0.0090	0.0084	0	0.0728	0	0	0
Ti	0.0001	0.0001	0	0.0002	0	0.0001	0	0.0003	0.0001	0.0019	0.0005	0
V	0.0002	0.0002	0	0.0001	0	0	0	0.0004	0.0001	0	0.0001	0
Zn	0	0.0012	0.0005	0	0.0144	0.0013	0.0098	0	0	0.0004	0	0
SUM (exc. total)	4.3281	1.7452	4.0024	0.1224	0.4626	1.0316	1.3524	1.1120	0.2787	0.5181	0.1488	1.3736

Analysis and graphical results for each factor are given on subsequent pages. Graphical results are copied directly from the model output and include the following for each factor:

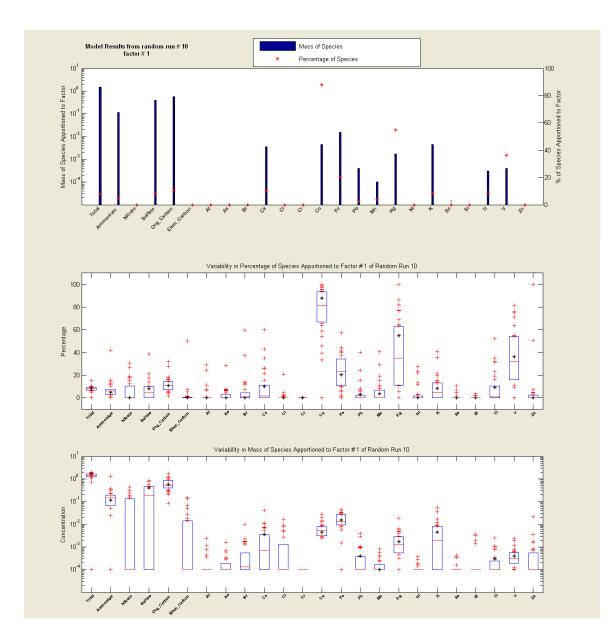
- Concentration by value and percentage of total for each species
- Variability (bootstrapping) for each concentration and percentage
- Time series plot by overall factor concentration
- Contribution aggregates according to season and day of the week

Note: Factors and runs are generated randomly by PMF and are not ranked according to any one species.

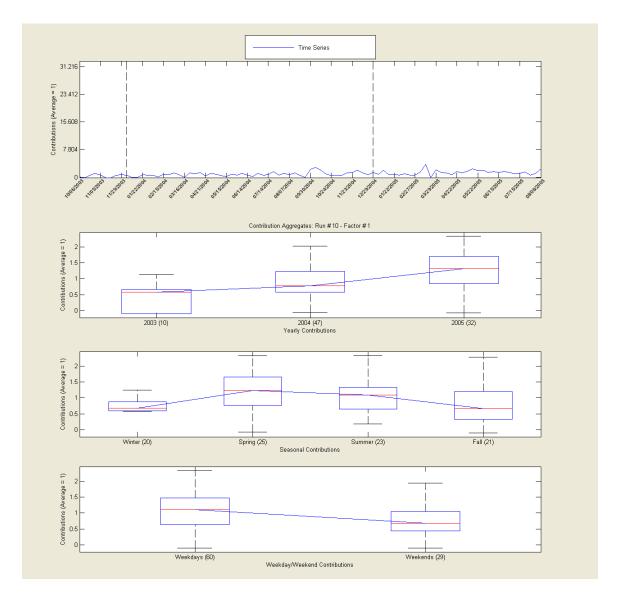


Liberty Source Factor 1: Gasoline Vehicles

Factor 1 is high in weekday organic carbon, indicating light-duty gasoline vehicle emissions. Copper, mercury, vanadium, and copper also have high percentages with this factor.



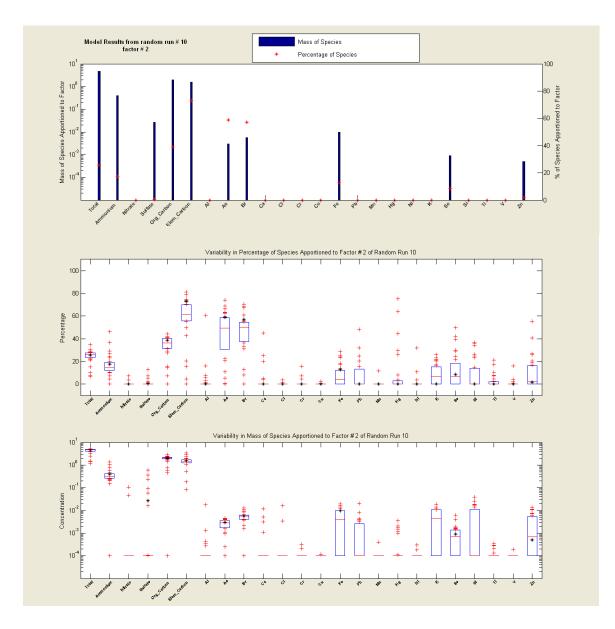




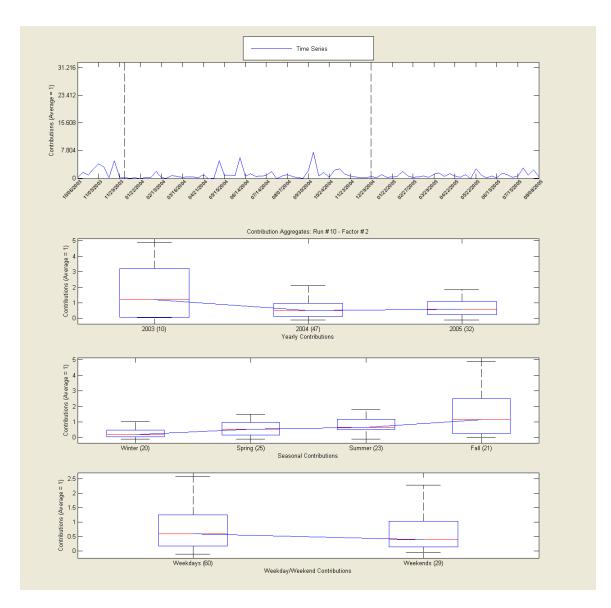


Liberty Source Factor 2: Carbon-Rich Industrial

Factor 2 contains high percentages of elemental and organic carbon, as well as noticeable percentages of arsenic, bromine, and ammonium. Contributions are slightly higher in fall and on weekdays, perhaps due to background mobile source emissions or secondary organic carbons. It is assumed that the majority of this factor represents a constant source, best classified as a carbon-rich industrial source or combination of sources.



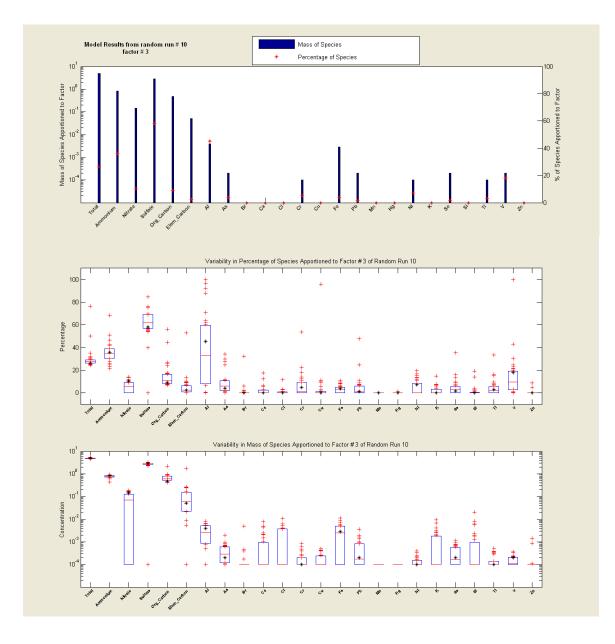




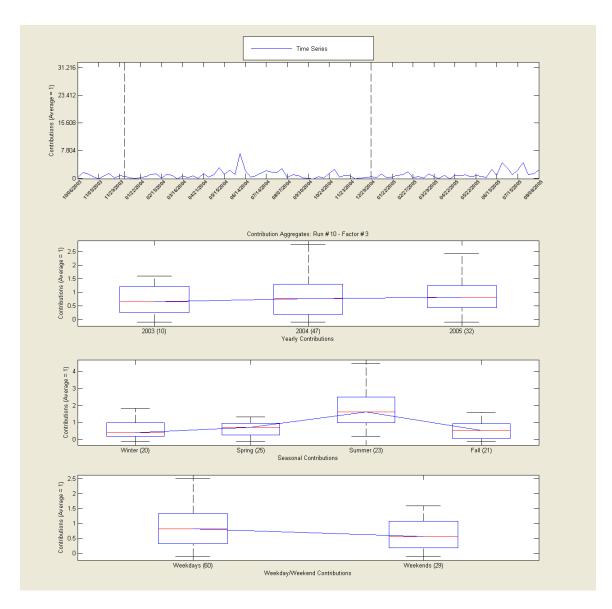


Liberty Source Factor 3: Secondary Ammonium Sulfate

Factor 3 is comprises the majority of ammonium sulfate at Liberty. Contributions are highest in summer, when sulfate is most prevalent. Sulfate exists as secondary $PM_{2.5}$ in the Pittsburgh region, formed from upwind SO_2 sources such as coal-fired power plants. Factor 3 also contains some carbons and trace elements that are likely peaking concurrently with the sulfate. The organic carbon may be secondary in nature as well. Aluminum may be a result or either airborne crustal dust or primary coal-fired power plant emissions.



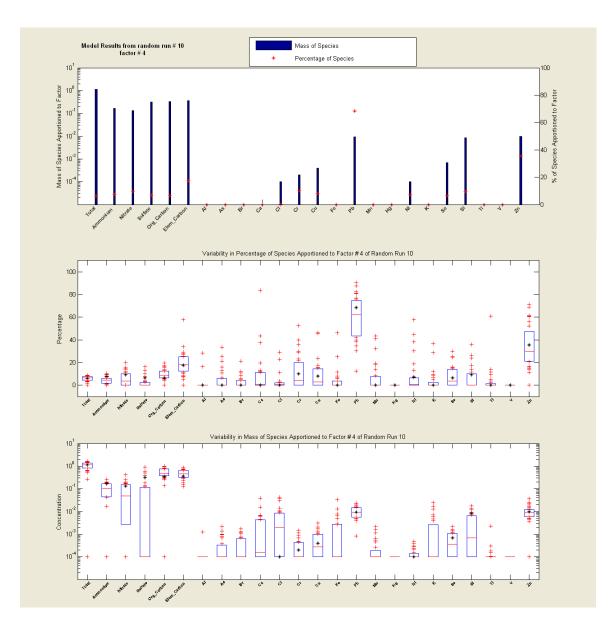




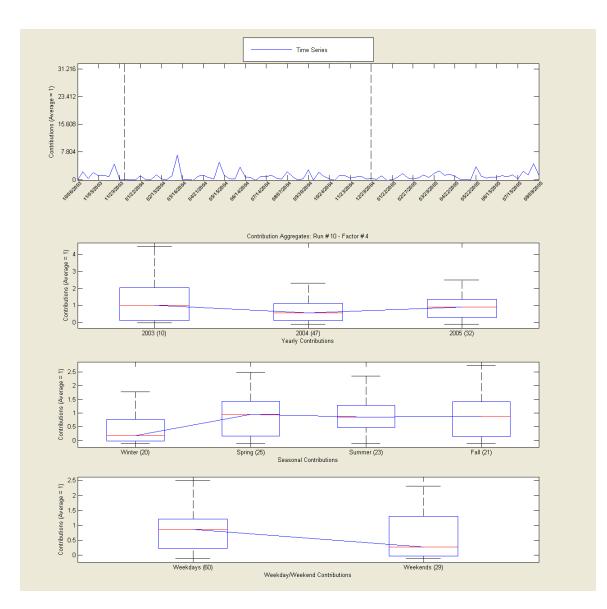


Liberty Source Factor 4: Diesel Vehicles

Factor 4 is assumed to be primarily diesel vehicle emissions due to the strong presence of weekday elemental carbon. High percentages of lead and zinc are also present, possibly due to tire wear, municipal waste incinerators, or other sources. Minor percentages of ammonium, nitrate, and sulfate are also included in this factor.



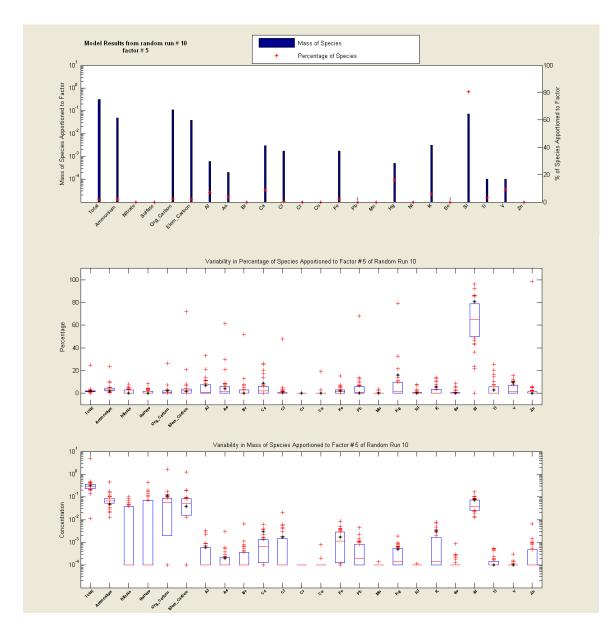




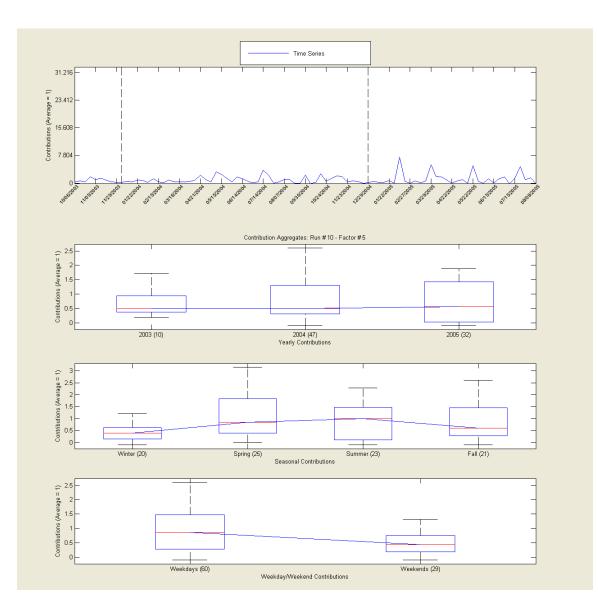


Liberty Source Factor 5: Airborne Crustal (Silicon-Rich)

Crustal elements include aluminum, calcium, iron, silicon, and titanium. These elements are the basic make-up of fine airborne soil. Factor 5 is best attributed as the silicon portion of airborne crustal component. Contributions are slightly higher during weekdays, possibly due to traffic forcing up road and crustal dust. Springtime contributions are also slightly higher. Some silicon may be also due to primary power plant emissions.



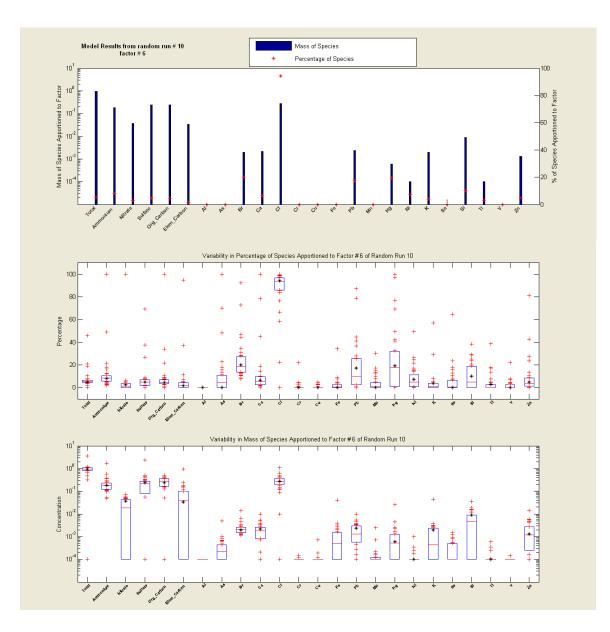




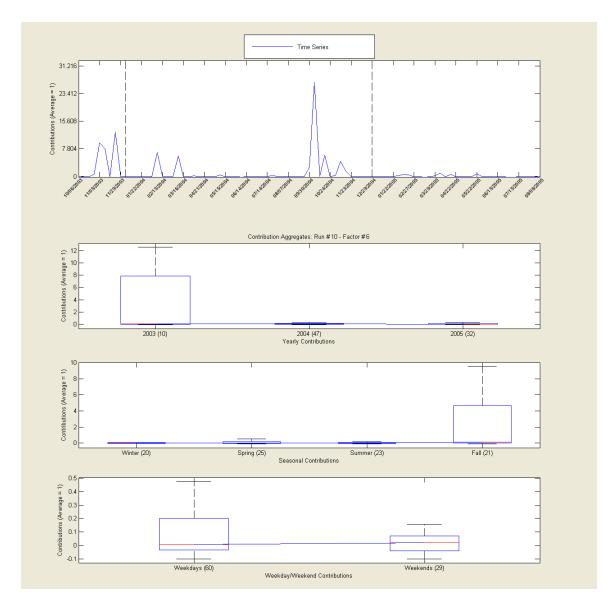


Liberty Source Factor 6: Halogen-Rich Sources

Factor 6 contains high percentages of chlorine and bromine, and contributions are highest in fall. Contributions from this factor are extremely specific, as only a few large peaks are evident throughout the year. Previous analysis of speciation data has shown that chlorine tracks the carbons during cold weather only. This may indicate that the halogens are originating from the same wind direction.



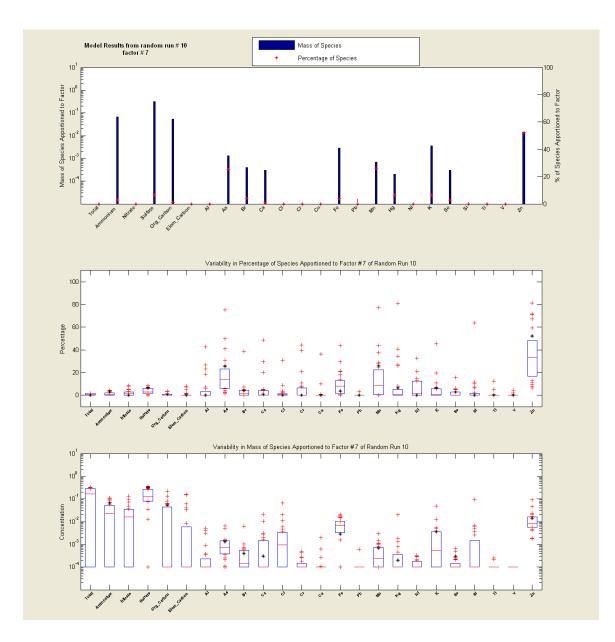




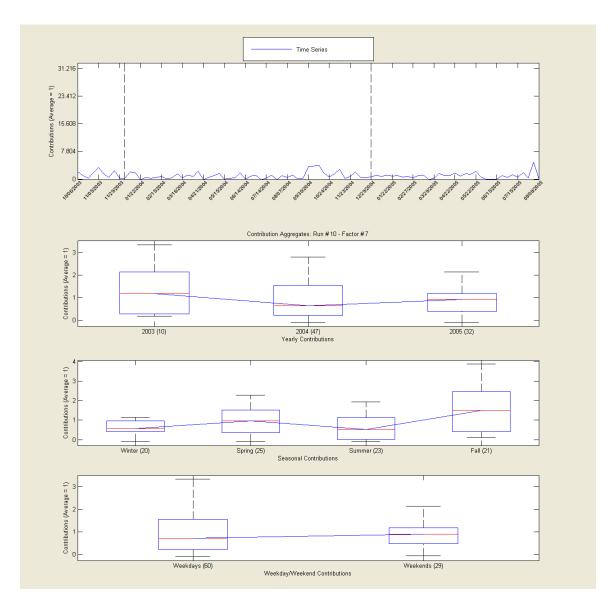


Liberty Source Factor 7: Zinc-Rich Sources

Factor 7 contains a high percentage of zinc, along with smaller percentages arsenic, manganese, and sulfate. Factors with these characteristics are often classified as municipal waste incinerators or metallurgical (galvanizing) facilities.



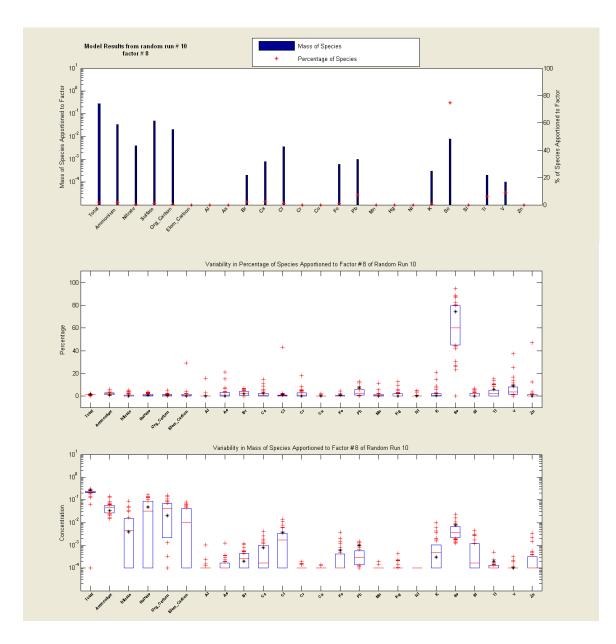




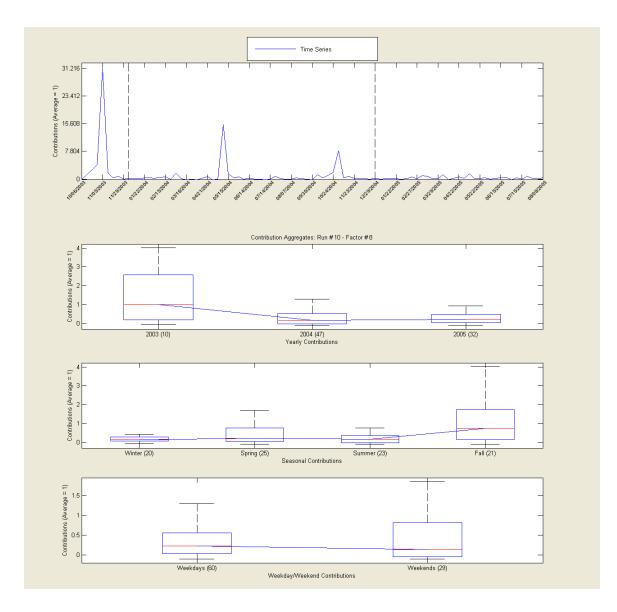


Liberty Source Factor 8: Selenium-Rich Industrial

Factor 8 contains a high percentage of selenium, with nearly negligible percentages of all other species. Selenium is sometimes associated with primary coal-fired boiler emissions but is also present in some glass manufacturing emissions.



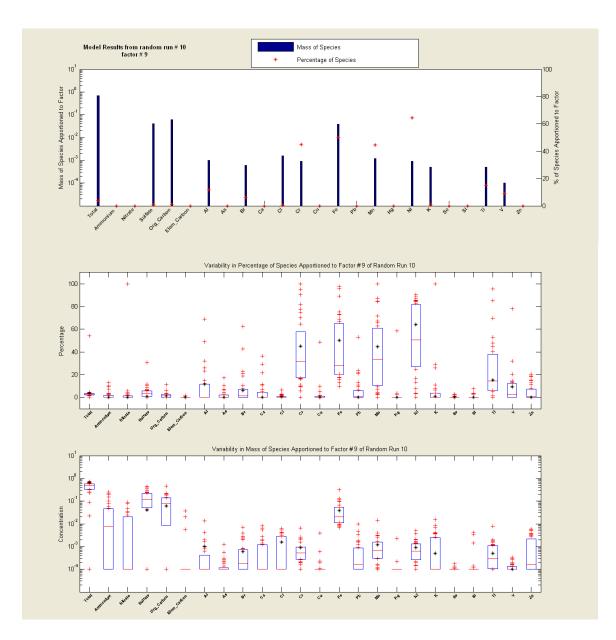






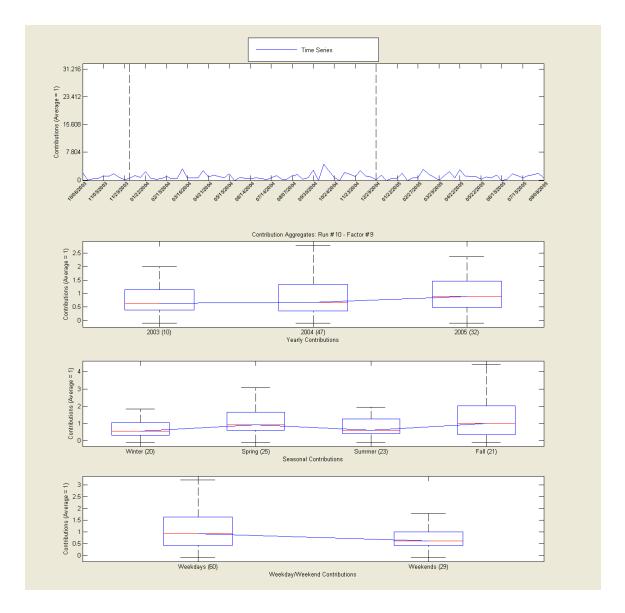
Liberty Source Factor 9: Road Dust

Factor 9 contains percentages of iron, aluminum, and titanium, as well as chromium, nickel, and manganese, and is higher on weekdays. It is best classified as miscellaneous road dust, with some contributions possibly from metallurgical facilities.





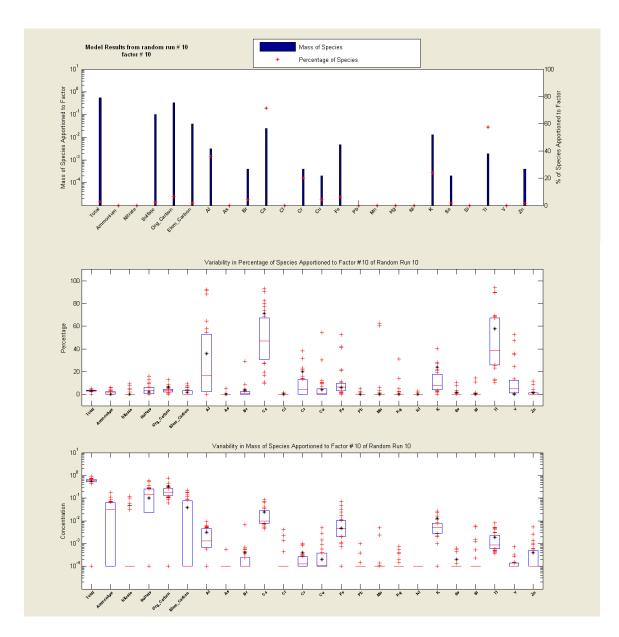




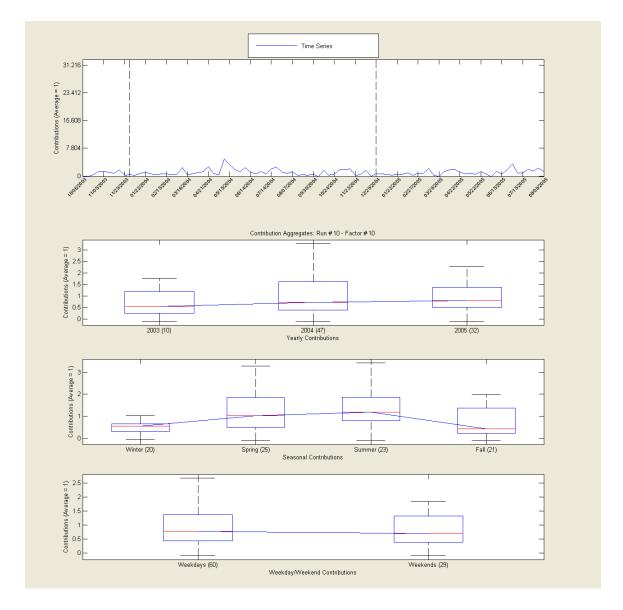


Liberty Source Factor 10: Airborne Crustal (Other)

Like Factor 5 (silicon-rich crustal), Factor 10 is composed of crustal elements and is higher on weekdays and in spring. Aluminum, calcium, and titanium show the highest percentages for this factor.



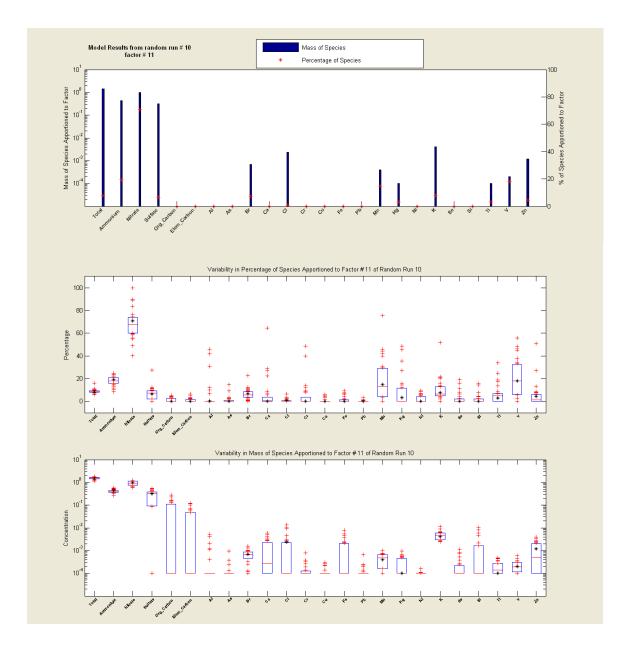






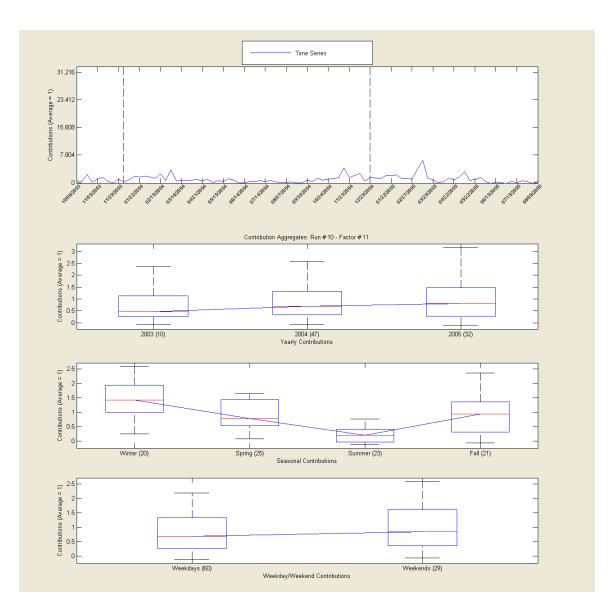
Liberty Source Factor 11: Secondary Ammonium Nitrate

Factor 11 is the majority of secondary ammonium nitrate at the Liberty, dominant in cold weather. Nitrate is a secondary species created by upwind NOx sources such as fossil fuel-fired boilers.





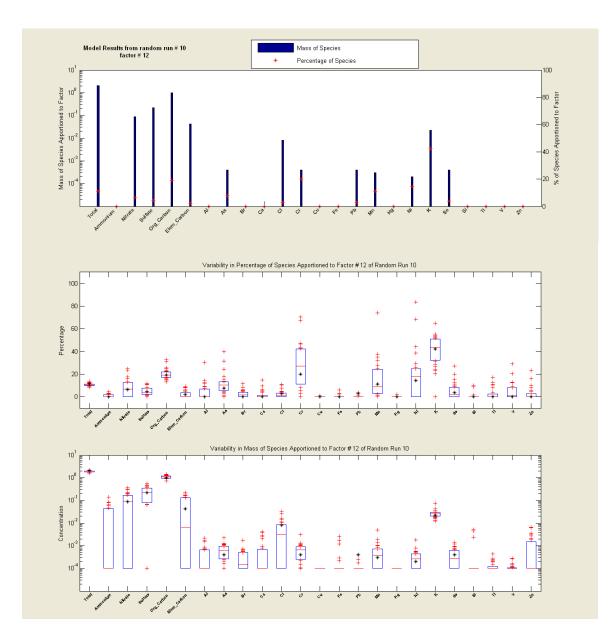




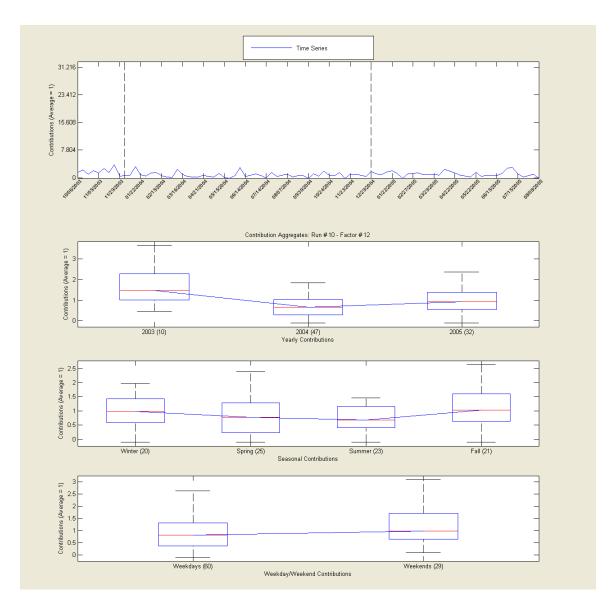


Liberty Source Factor 12: Vegetative Burning

Factor 12 contains high percentages of organic carbon and potassium and is highest in fall and winter. This is indicative of vegetative burning, most likely for residential-heating in the Liberty area. This differs from the miscellaneous burning factor at Lawrenceville, which is highest in summer and is most likely due to recreational burning and cooking.









6. Model Diagnostics

Lawrenceville Diagnostics:

Factors = 11 Random Run #10 Perfect Theoretical Q = 1305

______ ANALYSIS START Number of random starting points: 10 Number of factors: 11 Seed: Used random seed. c3 Modeling Constant (Percent): 5.00 Species included: Strong - Ammonium, Nitrate, Sulfate, Org Carbon, Elem_Carbon,Ca,Cl,Cu, Fe, Pb, Mn, Se, Si,Zn, Weak (down-weighted) - Total, Al, As, Br, Cr, Hg, Ni, K, Ti,V, Species not included: Bad (not included) - No "Bad" variables Q Values for random-start runs Random Run Q(Robust) Q(True) Converged(Y/N) #Steps 1 1571.85 1578.03 Yes 1289 2 1571.84 1578.03 Yes 1313 3 1571.88 1578.03 Yes 1320 1571.83 1578.01 Yes 1358 4 1578.04 Yes 5 1571.88 1471 1571.87 1578.04 Yes 6 1135 1578.01 Yes 1480 7 1571.81 8 1571.88 1578.03 Yes 1228 1571.81 1578.01 Yes 1571.84 1578.02 Yes 9 1177 10 1018





_____START BASE FACTOR ANALYSIS______

Regression diagnostics of run# 10

Species	Intercept	Slope	RMSE	r^2
Total	0.34	0.97	1.41	0.97
Ammonium	0.02	0.98	0.12	0.99
Nitrate	-0.01	1.01	0.08	1.00
Sulfate	0.12	0.97	0.34	0.99
Org Carbon	0.21	0.94	0.38	0.95
Elem Carbon	0.13	0.82	0.17	0.82
Al –	0.01	0.09	0.01	0.10
As	0.00	0.33	0.00	0.26
Br	0.00	0.41	0.00	0.46
Ca	0.00	0.98	0.00	1.00
Cl	0.00	0.97	0.00	1.00
Cr	0.00	0.19	0.00	0.27
Cu	0.00	0.82	0.00	0.83
Fe	0.01	0.93	0.02	0.96
Pb	0.00	0.98	0.00	0.99
Mn	0.00	0.93	0.00	0.97
Hg	0.00	0.04	0.00	0.02
Ni	0.00	0.27	0.00	0.32
K	0.03	0.38	0.02	0.44
Se	0.00	0.99	0.00	1.00
Si	0.00	1.00	0.00	1.00
Ti	0.00	0.34	0.00	0.41
V	0.00	0.14	0.00	0.13
Zn	0.00	1.00	0.00	1.00

Dates (residuals) beyond 3 Std. Dev.

Species	Dates (residuals)				
Al -	- 03/25/2004(3.2)			
As -	- 08/31/2004(3.1)			
Cr -	- 10/09/2003(3.0),	02/21/2005(4.1)
Cu -	- 07/23/2003(3.0),	08/25/2003(3.5),
	09/21/2003(3.5),	12/17/2003(-4.0),
	05/30/2004(4.3),	05/22/2005(3.4),
	07/09/2005(4.9)			
Fe -	- 11/23/2003(3.1),	12/17/2003(3.2)
Ni -	- 02/21/2005(3.6)			
К -	01/01/2005(3.1)			



Species (residuals) beyond 3 Std. Dev. Species (residuals) Dates (3.0) 07/23/2003 - Cu (3.5) 08/25/2003 - Cu (3.5) 09/21/2003 - Cu 10/09/2003 - Cr (3.0) 11/23/2003 - Fe (3.1) (3.2) 12/17/2003 - Cu (-4.0), Fe 03/25/2004 - Al (3.2) (4.3) 05/30/2004 - Cu 08/31/2004 - As (3.1) (3.1) (4.1), Ni 01/01/2005 - к (3.6) 02/21/2005 - Cr 05/22/2005 - Cu (3.4) 07/09/2005 - Cu (4.9) END BASE FACTOR ANALYSIS START BOOT STRAP ANALYSIS Number of bootstrap runs: 30 Minimum correlation between base and boot factors : 0.600000 Factor Map Frequency table Number of bootstrap runs :30 Minimum R-Value for base-boot factor mapping: 0.6 Seed: rand Number of bootstrap runs that converged and are summarized: 30 Number of bootstrap runs that did not converge and are therefore excluded from the summary: 0 Number of bootstrapped factors mapped to original factor 1 : 30 Number of bootstrapped factors mapped to original factor 2 : 30 Number of bootstrapped factors mapped to original factor 3 : 28 Number of bootstrapped factors mapped to original factor 4 : 30 Number of bootstrapped factors mapped to original factor 5 : 31 Number of bootstrapped factors mapped to original factor 6 : 30 Number of bootstrapped factors mapped to original factor 7 : 30 Number of bootstrapped factors mapped to original factor 8 : 30 Number of bootstrapped factors mapped to original factor 9 : 30 Number of bootstrapped factors mapped to original factor 10 : 30 Number of bootstrapped factors mapped to original factor 11 : 30 Number of bootstrapped factors mapped to no original factor : 1



Q(Robust) Pe Min 1342.28	ercentile Repo 25th 1466.54	Median	75th 1531.55	Max 1693.6	8
* * * * * * * * * * * *	* * * * * * * * * * * * * * *	* * * * * * * * * * * *	******	* * * * * * * * * *	
-	in Factor Str **************	J ,		11 2	
Factors	5th	25t	:h	75th	95th
Factor 1 Factor 2 Factor 3 Factor 4 Factor 5 Factor 6 Factor 7 Factor 8 Factor 9 Factor 10 Factor 11	0.860 0.451 0.617 0.441 0.673 0.279 0.486 0.547 0.281 0.40 0.38	.8 0.92 .76 0.83 .3 0.68 .32 0.95 .97 0.56 .97 0.56 .91 0.67 .1 0.47 .003 0.55	284 2. 341 1. 344 1. 509 1. 571 1. 124 1. 790 0. 717 0. 5116 1	3494 0731 7348 9119 6461 1508 8878	1.1832 4.7239 1.2811 4.7941 3.7830 2.3106 1.4861 1.0852 1.1209 1.5941 2.4260
	END	BOOT STRAP	ANALYSIS		
	ANAI	LYSIS END			



Liberty Diagnostics:

Factors = 12Random Run #10 Perfect Theoretical Q = 546

________ ANALYSIS START Number of random starting points: 10 Number of factors: 12 Seed: Used random seed. c3 Modeling Constant(Percent): 5.00 Species included: Strong - Ammonium, Nitrate, Sulfate, Org Carbon, Elem Carbon, Br, Ca, Cl, Cu, Fe, Pb, K, Se,Si,Zn, Weak (down-weighted) - Total, Al, As, Cr, Mn, Hg, Ni, Ti, V, Species not included: Bad (not included) - No "Bad" variables Q Values for random-start runs Random Run Q(Robust) Q(True) Converged(Y/N) #Steps 1 573.79 573.79 Yes 1887 2 573.79 1916 573.79 Yes 3 573.81 573.81 Yes 2070 573.77 Yes 4 573.77 1672 573.76 573.76 Yes 5 1776 573.93 Yes 573.93 6 1746 573.77 7 573.77 Yes 1672 8 573.80 573.80 Yes 1317 9 573.76 573.76 Yes 1813 10 573.76 573.76 Yes 1749



_____START BASE FACTOR ANALYSIS______

Regression diagnostics of run# 10

Species	Intercept	Slope	RMSE	r^2		
Total Ammonium Nitrate Sulfate Org_Carbon Elem_Carbon Al As Br Ca Cl Cr Cu Fe Pb Mn Hg Ni K Se Si Ti	0.16 0.08 0.03 -0.04 0.20 -0.00 0.01 0.00 -0.00 -0.00 -0.00 -0.00 0.00	0.97 0.95 0.97 1.01 0.94 0.97 0.09 0.87 1.01 1.00 0.99 0.23 1.00 1.01 0.99 0.23 1.00 1.01 0.99 0.29 0.27 0.31 0.97 0.98 1.00 0.40	2.44 0.18 0.08 0.25 0.60 0.43 0.01 0.00	0.96 0.99 0.99 0.99 0.99 0.98 0.97 0.20 0.77 0.20 0.77 0.99 1.00 1.00 1.00 0.24 1.00 1.00 0.40 0.57 0.39 0.98 1.00 1.00 0.40		
V Zn	0.00 0.00	0.16 1.00	0.00	0.16		
Dates (residuals) beyond 3 Std. Dev.						
Species	Dates (resid	duals)				
		3.6), 05/15 3.1)	/2004(3.9)		

-						
Dates S	pecies (resid	uals)				
04/21/2004 - 05/15/2004 - 10/06/2004 -	Al (3.6) 3.9) 3.1)				
END BASE FACTOR ANALYSIS						



START BOOT STRAP ANALYSIS

Number of bootstrap runs: 30 Minimum correlation between base and boot factors : 0.600000 Number of bootstrap runs :30 Minimum R-Value for base-boot factor mapping: 0.6 Seed: rand Number of bootstrap runs that converged and are summarized: 30 Number of bootstrapped factors mapped to original factor 1 : 30 Number of bootstrapped factors mapped to original factor 2 : 29 Number of bootstrapped factors mapped to original factor 3 : 31 Number of bootstrapped factors mapped to original factor 4 : 28 Number of bootstrapped factors mapped to original factor 5 : 31 Number of bootstrapped factors mapped to original factor 6 : 32 Number of bootstrapped factors mapped to original factor 7 : 25 Number of bootstrapped factors mapped to original factor 8 : 30 Number of bootstrapped factors mapped to original factor 9 : 32 Number of bootstrapped factors mapped to original factor 10 : 28 Number of bootstrapped factors mapped to original factor 11 : 30 Number of bootstrapped factors mapped to original factor 12 : 28 Number of bootstrapped factors mapped to no original factor : 6 Q(Robust) Percentile Report 75th Min 25th Median Max 461.76 506.43 540.53 560.06 591.49 Variability in Factor Strengths, Based on Bootstrapping 5th 25th 75t.h 95t.h Factors Factor 1 0.2080 0.4489 1.2264 1.5371 Factor 2 0.1891 0.6002 0.9719 1.6770 Factor 3 0.7942 0.8733 1.0212 1.0781 Factor 4 0.3861 0.6458 1.4760 2.1156 Factor 5 0.5246 0.9082 2.6555 4.0411 0.8355 1.4045 Factor 6 0.4377 2.5626 2.1890 Factor 7 0.3114 0.9239 4.2387 Factor 8 0.5044 1.0210 3.6669 4.8345 Factor 9 0.2280 0.6735 2.2953 3.5172 1.1254 Factor 10 2.5904 0.2869 4.0050 0.8371 1.6004 1.3037 Factor 11 0.6189 Factor 12 0.5059 0.6783 0.9834 1.2985 END BOOT STRAP ANALYSIS ANALYSIS END



7. References

<u>EPA PMF 1.1 User's Guide</u>. June 30, 2005. Eberly, S., U.S. Environmental Protection Agency.

<u>Multivariate Receptor Modeling Workbook</u>. Sept. 2005. Brown, S.G. and Hafner, H.R., Sonoma Technology, Inc., prepared for U.S. EPA.

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Sources of Fine Particle Concentration and Composition in Northern Vermont. <u>Poirot</u>, R.L., et al. For presentation at the International Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, Sept. 12-14, 2000.

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Source Apportionment Analysis of Air Quality Monitoring Data: Phase II. March 2005. Prepared by Desert Research Institute for the Mid-Atlantic/Northeast Visibility Union and Midwest Regional Planning Organization.

<u>PM_{2.5} Chemical Speciation and Related Comparisons at Lawrenceville and</u> <u>Liberty: 18-Month Results Comparison</u>. Maranche, J., Allegheny County Health Department, June 2005.



Additional Information

For more information concerning this report or Allegheny County PM_{2.5} data analysis, contact Jason Maranche at the ACHD Air Quality Program at 412-578-8104 or at <u>imaranche@achd.net</u>.

With regard to the development of the PMF 1.1 model, the EPA disclaimer is reproduced below:

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