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Allegheny County PM_{2.5} Source Apportionment Results using the Positive Matrix Factorization Model (PMF Version 3.0) and Conditional Probability Function (CPF)



Model Timeframe: January 2005 through December 2010

December 13, 2011

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1. Executive Summary

The Positive Matrix Factorization Model (PMF Version 3.0) is a Windows-base 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} Chemical Speciation Network (CSN) speciation monitors at Lawrenceville, in the City of Pittsburgh, and at Liberty Borough, near the southeastern tip of Allegheny County. Each speciation monitor measures 38 different component species of PM_{2.5}, along with total mass concentration. [Note: 53 species were measured until early 2009.]

Sample concentrations were entered into PMF along with concurrent uncertainties for each species. Source factors were then calculated by the model as a result of iterative method that converges 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, wind probability, and a conceptual model of Pittsburgh and the Monongahela Valley. 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 results using PMF Version 3.0. The species and pollutant comparisons between Lawrenceville and Liberty are over the timeframe of January 2005 through December 2010. All figures and tables represent the six-year period unless otherwise noted.

Wind direction data were also available at Liberty during the same timeframe, along with Lawrenceville since mid-2009. Wind directions were used to apply Conditional Probability Function (CPF) to the factor contributions. CPF reveals the frequency of wind directions for each modeled source factor during highest contributions.



PMF modeling resulted in the following 10 source factors for Lawrenceville:

Key Species/Tracers	Nitrate	Carbons, Cu, Fe	CI	Al, Ca, Fe, Si, Ti	Carbons, Pb, Zn	Cr, Ni	Se	Mn	Carbons, As, K, V	Sulfate, Carbons
Possible Source(s)	Secondary Ammonium Nitrate	Diesel Vehicles + Metals Processing	Road Salt/Dust	Crustal Component	Gasoline Vehicles + Tire Wear/ Incinerators	Metals Processing	Coal Combustion or Glass Manufacturing	Steel Manufacturing/ Processing	Burning/Cooking	Secondary Ammonium Sulfates + Gasoline Vehicles
Sum Conc. (µg/m³)	2.70851	0.34454	0.28995	0.54494	0.45208	0.08650	0.27532	0.49470	2.19307	5.18959

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

Key Species/Tracers	Cr, Ni	Carbons, As	Se	Carbons, Cu	Nitrate	Carbons, Sulfate	Sulfate, Carbons	Elemental Carbon, Si	Carbons, K	CI, Br	Fe, Mn, Zn	Al, Ca, Fe, Ti
Possible Source(s)	Metals Processing	Organic Industrial Carbons	Coal Combustion or Glass Manufacturing	Gasoline Vehicles + Metals Processing	Secondary Ammonium Nitrate	Elemental Industrial Carbons + Localized Sulfates	Secondary Ammonium Sulfates + Gasoline Vehicles	Coal/Coke Dust	Burning/ Cooking	Chlorine	Steel Manufacturing/ Processing	Crustal Component
Sum Conc. (µg/m³)	0.07132	1.93877	0.07281	0.73231	1.29450	2.87059	5.90173	0.56702	1.17206	1.02878	0.28750	0.09344

The values shown above are summed concentrations for each factor in units of $\mu g/m^3$. Detailed results for Lawrenceville and Liberty are given in <u>Section 4</u> and <u>Section 5</u>, respectively.

The modeled results reveal that Lawrenceville and Liberty share several similar source factors. Comparing the common factors and combining some results, a generalized view of the urban and localized nature of each site can be examined. A column chart of the common grouped source factors for both sites is given on the following page.







Lawrenceville shows larger amounts of urban components of $PM_{2.5}$, such as mobile sources, commercial/residential cooking, and light industry. Liberty shows a localized excess due to heavy industry specific to the area, strongly influenced by meteorological conditions.



2. Sites

The Lawrenceville monitor site is an urban residential site, downwind from the Pittsburgh Central Business District (Downtown). Elevation is 847 feet above mean sea level (MSL), 135 feet above the Allegheny River valley. The 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. The urban excess sources are anthropogenic sources such as light or heavy industry, mobile source emissions, and residential and commercial cooking/heating.

The Liberty Borough monitor site is located in the Monongahela Valley, which contains a mix of urban residential, heavy industrial and rural areas. The elevation is 1066 feet MSL, 340 feet above the Monongahela River valley. Monitored speciation data suggests that some $PM_{2.5}$ species are consistent with other sites in SW PA, while other species are more localized to the Liberty area. It is assumed that species that do not follow regional flow may be originating at sources resident to the area, both stationary and mobile.

Data used in this PMF modeling spans the dates January 2005 through December 2010 as uploaded to EPA's Air Quality System (AQS) by RTI International, which processes the CSN data for Allegheny County.

Over this timeframe, 564 samples were modeled for the Lawrenceville site. Lawrenceville has a (1-in-3) speciation sampling frequency.

Liberty has a (1-in-6) speciation sampling frequency, and 287 samples were modeled for the Liberty site. Samples for the periods 11/14/2008-2/24/2009, 12/21/2009-3/9/10, and 12/4/10-12/22/10 were removed from the Liberty modeling input, due to unknown errors with the samples. The speciation results showed poor correlation with the filter-based (FRM) and continuous (TEOM) monitors at the Liberty site. These samples have been indicated as outliers in AQS with a code of "5," for unknown outlier.

Dates on or near the Fourth-of-July were removed due to outliers in the concentrations of firework ingredients. Potassium nitrate and other ingredients can lead to abnormal concentration levels of trace elements, some of which rarely exceed the method detection limits (MDL) on average days.

Additional outlier samples removed from the model for a better modeled solution are given in the model <u>Diagnostics</u> section.



3. Methodology

Model operation was followed according the PMF 3.0 user's guide. The PMF model was tested under different species and factor combinations. Species are excluded if they exhibit low signal-to-noise ratios, are frequently below the method detection limit (MDL), or do not easily fit into a least-squares solution. Any samples with missing data for one or more species are not modeled.

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

Sulfate	Organic Carbon
Nitrate	Elemental Carbon
Ammonium	Total PM _{2.5}

Many trace element species also have significant concentrations and strong or moderate signalto-noise ratios. They may also be important tracer elements, associated with specific sources. These species include:

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

Trace element species with frequent concentrations less than the MDL were excluded from the modeling. These elements provide little weight in the fit of a solution. These species include:

Antimony	Cesium	Rubidium
Barium	Indium	Tin
Cadmium	Magnesium	Silver
Cobalt	Phosphorus	Zirconium
Cerium	Strontium	

Additionally, several trace elements were removed from the RTI lab analysis in early 2009. These species include:

Europium	Lanthanum	Scandium
Gallium	Mercury	Tantalum
Gold	Molybdenum	Terbium
Hafnium	Niobium	Tungsten
Iridium	Samarium	Yttrium

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. Additionally, potassium and sodium are measured by both ion chromatography and x-ray fluorescence. The x-ray fluorescence samples were used due to higher signal-to-noise ratios.



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

Trace element species with low signal-to-noise ratios (less than 3.5) were down-weighted. Low signal-to-noise ratios mean that a species' concentration 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. Based on EPA recommendation, an additional 5% uncertainty was applied to the entire model for all samples in the CSN network.

The number of source factors in the model is 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 source factors indicate a lack of uncertainty and create 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. Profile results were also compared to previously compiled source profiles (see the <u>References</u> section of this document).

Some factors may be associated with similar source types but are separated into more specific source factors by the model. For example, a source type that is representative of vehicle emissions may comprise one source factor based on year-round contributions and another factor based on specific traffic conditions.

There may also be overlap of some source types. For example, a factor dominated by ammonium sulfate may also include carbons and trace elements that may or may not be originating from the sulfate sources but are peaking simultaneously in the monitor data.

Conditional Probability Function (CPF) analysis was used to determine the high-day wind directions of each modeled factor. For this analysis, the hourly wind directions were first separated into 30-degree sectors for each 24-hour sample. All hourly directions from 16-45 degrees are assigned to the 30 degree sector, 46-75 degrees to the 60 degree sector, and so on. The total hourly count for each sector is used for the dominator in the CPF equation (shown below).



Conditional Probability Function (CPF)

CPF uses wind direction rather than trajectories to determine likely direction of sources. CPF compares these highest concentration days to the average transport pattern (i.e., the climatology)



For each modeled factor, the top 25% days based on daily contributions were assigned as high days. The hourly count of wind sectors on these days was then used for the numerator in the CPF equation.

The result of the equation provides a frequency for which the number of times the factor showed a high contribution in each wind sector. Each sector is then plotted on a radar chart, representing the predominant direction of the high days of the modeled source factor.

Upper air soundings¹ were also examined for the occurrences of 12Z temperature inversions on high contribution days for each factor. Temperature inversions frequently occur in SW PA and can greatly affect the dispersion characteristics in river valleys. Both gaseous and particulate pollutants can show elevated levels during nighttime inversion periods.

Potential Source Contribution Function (PSCF) is an additional analysis that can be used for source apportionment, based on long-range back-trajectories generated by the HYPLIT model. PSCF was not performed for this report due to the smaller-scale conceptual model of PM_{2.5} in Allegheny County, specifically in the Liberty area.

¹ Upper air soundings were taken from the University of Wyoming, College of Engineering, Department of Atmospheric Science web site: <u>http://weather.uwyo.edu/upperair/sounding.html</u>



4. Modeled Results: Lawrenceville

The best-fit model runs for Lawrenceville were able to resolve 10 source factors. The following species were down-weighted in the model runs: Elemental Carbon, Al, As, Na, Ti, V, and Total $PM_{2.5}$. Federal Reference Method (FRM) values were used for missing Total PM2.5 for two dates: 11/13/06 and 6/23/07.

Lawrenceville results exhibited source factors that are common to urban areas. Lawrenceville source factor profiles and associated source types are given in the table below. Species average concentrations that were considered to be indicators of the specific source types are shown in bold.

Factor	1	2	3	4	5	6	7	8	9	10
Key	Nitrate	Carbons,	CI	Al, Ca, Fe,	Carbons,	Cr, Ni	Se	Mn	Carbons, As, K, V	Sulfate,
Species/Tracers		Cu, Fe		Si, Ti	Pb, Zn	,				Carbons
Possible Source(s)	Secondary Ammonium Nitrate	Diesel Vehicles + Metals Processing	Road Salt/Dust	Crustal Component	Gasoline Vehicles + Tire Wear/ Incinerators	Metals Processing	Coal Combustion or Glass Manufacturing	Steel Manufacturing/ Processing	Burning/Cooking	Secondary Ammonium Sulfates + Gasoline Vehicles
Ammonium	0.53361	0.03588	0.07164	0.03502	0.02694	0	0.04244	0.01889	0.04900	1.02000
Nitrate	1.24560	0.03980	0.10552	0.03270	0.01385	0.01832	0.04364	0.07586	0	0
Sulfate	0.49256	0.04470	0.03314	0.13432	0.10375	0.01300	0.12948	0.03154	0.27690	3.14470
Org_Carbon	0.34376	0.08715	0.02019	0.14004	0.20581	0.03034	0	0.26879	1.58250	0.87877
Elem_Carbon	0.07234	0.06668	0.01724	0.06603	0.05431	0.00704	0.03885	0.06017	0.23596	0.12085
AI	0.00180	0.00074	0.00060	0.01382	0	0.00205	0	0	0.00010	0.00187
As	0	0.00013	0.00006	0	0.00010	0.00003	0.00005	0.00021	0.00084	0.00026
Br	0.00090	0.00013	0.00037	0.00006	0	0.00004	0.00032	0.00019	0.00142	0.00055
Са	0.00241	0	0.00181	0.02736	0.00062	0	0.00183	0.00394	0.00061	0
CI	0	0	0.02286	0	0.00049	0	0	0	0	0
Cr	0	0	0	0.00028	0.00009	0.00299	0.00003	0	0	0
Cu	0.00017	0.00201	0.00026	0.00021	0.00037	0.00043	0.00018	0.00031	0.00086	0.00038
Fe	0	0.06487	0.00374	0.02925	0.00966	0.01020	0.00327	0.02044	0	0.00686
Pb	0.00034	0.00101	0	0	0.00289	0	0.00218	0	0.00205	0
Mn	0.00014	0.00043	0.00007	0.00021	0	0.00004	0.00006	0.00500	0.00002	0
Ni	0.00012	0.00028	0.00002	0	0	0.00103	0	0	0.00002	0.00011
к	0.00893	0	0.00192	0.00710	0.00139	0.00076	0.00384	0	0.03357	0.00583
Se	0	0	0.00017	0	0	0	0.00303	0	0	0.00027
Si	0	0.00015	0.00370	0.05006	0	0	0.00294	0.00277	0.00281	0.00426
Na	0.00536	0.00057	0.00416	0.00696	0.00815	0.00001	0.00254	0.00264	0.00616	0.00192
Ті	0.00035	0	0	0.00153	0.0008	0.00008	0.00025	0.00005	0	0.00061
V	0.00011	0	0	0	0.00002	0.00001	0.00002	0.00020	0.00025	0.00023
Zn	0	0	0.00249	0	0.02356	0.00014	0.00038	0.00370	0	0.00212
Sum Conc. (µg/m³)	2.70851	0.34454	0.28995	0.54494	0.45208	0.08650	0.27532	0.49470	2.19307	5.18959

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



A pie chart of the best-guess source types, by percent of summed concentrations, is shown below.



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
- · Variable (bootstrapping) for each concentration and percentage
- Time series plot by overall factor concentration
- Contribution aggregates according to year, season, and day of week



Conditional Probability Functions (CPF) plots are also included for each factor for Lawrenceville. Below is the wind rose for Lawrenceville, showing wind direction frequencies plotted in vector grid form and also plotted in Google Earth.² Lawrenceville wind data were available only for July 2009 through Dec. 2010.



Average wind speed = 4.33 knots

Lawrenceville shows large frequencies of moderate wind speeds from the southwest and light wind speeds from the north. The light northerly winds generally occur at night, likely due to drainage from the Allegheny River valley.

² Wind rose generated by Lakes Environmental's WRPLOT View 7.0.0 software.



2008 annual average daily traffic volumes³ for the Lawrenceville vicinity are shown on the map below. Penn Ave. (count: 14,000), Butler St. (15,000), and 40th St. (27,000) are the roadways nearest the Lawrenceville site.



³ 2008 Traffic Volumes, Pennsylvania Department of Transportation (PennDOT), Bureau of Planning and Research.



Lawrenceville Source Factor 1: Secondary Ammonium Nitrate

Factor 1 contains the majority of secondary ammonium nitrate at Lawrenceville, dominant in cold weather. Ammonium nitrate (NH_4NO_3) is a secondary species created from nitrogen oxide (NO_x) sources such as fossil fuel-fired boilers and motor vehicles. Factor 1 is a large component of $PM_{2.5}$ at Lawrenceville, representing 22% of the total concentration.









The CPF plot for Factor 1 is shown below. High days showed the highest frequencies from the west and south. This may indicate that upwind sources along with local vehicle traffic (Butler St., Penn Ave.) are the largest contributors of wintertime NO_x at Lawrenceville.





Lawrenceville Source Factor 2: Diesel Vehicles + Metals Processing

Factor 2 contains elemental carbon with high weekday contributions, indicative of diesel exhaust. High percentages of copper and iron are also present, which may indicate metals processing. Factor 2 is a small factor overall (3% of total) and shows peak contributions during inversions.









The CPF plot for Factor 2 is shown below. High days showed the highest frequencies from the north and, to a lesser extent, the southwest and southeast. This may be due to traffic on nearby roadways (40th St., Penn Ave., Butler St.), along with local metals processing sources.







Lawrenceville Source Factor 3: Road Salt/Dust

Factor 3 contributes nearly all of the chlorine at Lawrenceville. It shows high peaks on winter days and is likely due to airborne road salt along with other miscellaneous road dust compounds. Factor 3 has small overall contributions, representing 2% of total PM_{2.5}.

Both sodium chloride and calcium chloride are used on the grounds of the Lawrenceville site. The signal-to-noise ratio is very low for sodium, however, and it does not fit well in the model. Calcium is apportioned mostly with Factor 4 as crustal material.









The CPF plot for Factor 3 is shown below. High day frequencies are distributed throughout all sectors, with the highest from the east and southeast. Traffic from 39th St., Penn Ave., and the ACHD Clack Center parking lot is likely contributing the salt dust along with other surrounding roadways.





Lawrenceville Source Factor 4: Crustal Component

Factor 4 is composed primarily of crustal elements that make up airborne fine soil: aluminum, calcium, iron, silicon, and titanium. Other miscellaneous elements likely due to road dust are also grouped with this factor. Factor 4 is highest during weekday activity and in spring, when the ground is drier and not covered by leaves or snow. It also contains carbons, which indicates that some vehicle emissions are also included in this factor. Factor 4 represents 4% of the total $PM_{2.5}$.















The CPF plot for Factor 4 is shown below. High days showed the highest frequencies from the north and from the south. Light winds from the north may be transporting crustal elements from Arsenal Park and roadways adjacent to the Lawrenceville site. Winds from the south may be transporting crustal elements from higher elevations to the south.





Lawrenceville Source Factor 5: Gasoline Vehicles + Tire Wear/Incinerators

Factor 5 contains carbons with a bias toward weekday contributions, indicative of vehicle emissions. Elemental carbon is higher by percentage, but the ratio of organic carbon to elemental carbon by concentration most likely represents gasoline vehicle emissions. A high percentage of lead and zinc is also present, which can be an indicator of tire wear or incinerators. Factor 5 represents 4% of the total $PM_{2.5}$.









The CPF plot for Factor 5 is shown below. High day frequencies from the south, east, and north may be due to traffic on adjacent roadways (39th St., Penn Ave, 40th St.), specifically at intersections. Frequencies from the south may also be due to medical waste incinerators.





Lawrenceville Source Factor 6: Metals Processing

Factor 6 has a high percentage of chromium and nickel, which is associated with metals processing such as electroplating or scrap-cutting. This factor is small in overall contributions (1% of total) and contains few additional species. It shows the highest contributions during inversions.









The CPF plot for Factor 6 is shown below. High day frequencies are high from the north, possibly due to local metals processing sources, but high days also occur in other sectors. This factor may be more affected by inversions than by wind directions.





Lawrenceville Source Factor 7: Coal Combustion or Glass Manufacturing

Factor 7 contributes nearly all of the selenium at Lawrenceville. Selenium is associated with primary coal-fired boilers and/or glass manufacturing. Some lead is also associated with this factor. Factor 7 is small overall (2% of total) and peaks during inversions.









The CPF plot for Factor 7 is shown below. High days showed the highest frequencies from the north/northeast and from the south. This can be due to local and distant fossil fuel-combustion or glass facilities. [Not shown on the map: Gallery G Glass on Liberty Ave., a few blocks south of the Lawrenceville site, creates hand-blown art glass.]





Lawrenceville Source Factor 8: Steel Manufacturing/Processing

Factor 10 has a strong presence of manganese, which is related steel manufacturing or processing. There is a strong weekday contribution from this factor, indicating weekday-only production. Smaller amounts of other species are also grouped with this factor. Factor 10 is small overall (4% of total), and it peaks during inversions but shows fairly steady contributions overall on a time-series basis.










Weekday/Weekend Contributions





The CPF plot for Factor 8 is shown below. High-day frequencies from the north and southeast may be due to nearby steel facilities. Frequencies from the southwest may be due to lesser components that are grouped with this factor.





Lawrenceville Source Factor 9: Burning/Cooking

Factor 9 contains high amounts of carbons along with potassium, which are indicators of vegetative burning and cooking. This factor shows high weekend contributions and is lowest in spring, possibly due to recreational burning and cooking in summer and wood-burning in winter. Arsenic and vanadium also show high percentages with this factor, which can be associated with wood burning and oil combustion, respectively. Some vehicle emissions may also be present with this factor. Factor 9 represents a significant portion of total PM_{2.5} (17%). It can peak during inversions but shows fairly steady contributions overall on a time-series basis.











Weekday/Weekend Contributions





The CPF plot for Factor 9 is shown below. High days showed the highest frequencies from the north and southwest, likely due to cooking and wood-burning from surrounding community.





Lawrenceville Source Factor 10: Secondary Ammonium Sulfates + Gasoline Vehicles

Factor 10 is the largest source factor and contributes nearly all of the ammonium sulfates $(NH_4HSO_4 \text{ or } (NH_4)_2SO_4)$ at Lawrenceville. Contributions are highest in the summer, when sulfates are most prevalent. Ammonium sulfates generally exist as secondary $PM_{2.5}$ in the Pittsburgh region, formed by upwind SO_2 from sources such as coal-fired power plants. Factor 10 also contains carbons that are peaking concurrently with sulfate, possibly from light-duty vehicle exhaust. Factor 10 is the largest component of $PM_{2.5}$ at Lawrenceville (41%).









The CPF plot for Factor 10 is shown below. High days showed the highest frequencies from the south and southeast. This could be due to a combination of sulfates from distant upwind sources along with nearby sources to the south.



Lawrenceville Source Descriptions

Below are descriptions of the sources shown on the aerial maps of the Lawrenceville area.

McConway & Torley	Manufacturer of steel rail and mining castings including steel melting, casting, heat treating, and finishing.
Jersey Chrome	Manufacturer of chromium metal for deposition on metals.
Pressure Chemical	Fine chemical, polymer, and specialty material manufacturing.
Pittsburgh Brewing	Malt beverage brewing and packaging facility.
Barber Spring	Steel spring manufacturing.
Bay Valley Foods	Boilers for food production.
Sun Oil-Pittsburgh	Terminal that transfers gasoline and ethanol to/from tanks.
NRG Energy Center	Steam generation for district steam heating.
PACT	Pittsburgh Allegheny County Thermal. Steam generation for district steam heating.
Bellefield Boiler	Steam generation for district steam heating.
UPMC Facilities	Hospitals, medical laboratories, and incinerators.
VA Medical Center	Intermediate and long term health care facility.
Allegheny Asphalt	Now Lindy Paving. Processes coal and mineral aggregates.
MetalTech	Produces galvanized steel strips from untreated steel coils.
GenOn Cheswick	Coal-fired electric generation.
Kelman Bottles	Manufacturer of glass bottles.
ALCOSAN	Allegheny County Sanitary Authority. Domestic sewage treatment plant.
US Steel Edgar Thompson	Steel blast furnace and slab manufacturing using coke, iron- bearing materials, and fluxes.
Neville Island	Upwind/background industrial area. Includes Shenango, Calgon Carbon, Ashland, Neville Chemical, and other facilities.



5. Modeled Results: Liberty

The best-fit model runs for Liberty were able to resolve 12 source factors. The following species were down-weighted in the model runs: Al, Na, Ti, V, and Total $PM_{2.5}$.

Liberty results revealed many of the same source factors that were evident at Lawrenceville, while also indicating additional sources specific to the Liberty area. Liberty source factor profiles and associated source types are given in the table below. Species average concentrations that were considered to be indicators of the specific source types are shown in bold.

Factor	1	2	3	4	5	6	7	8	9	10	11	12
Key Species/Tracers	Cr, Ni	Carbons, As	Se	Carbons, Cu	Nitrate	Carbons, Sulfate	Sulfate, Carbons	Elemental Carbon, Si	Carbons, K	CI, Br	Fe, Mn, Zn	Al, Ca, Fe, Ti
Possible Source(s)	Metals Processing	Organic Industrial Carbons	Coal Combustion or Glass Manufacturing	Gasoline Vehicles + Metals Processing	Secondary Ammonium Nitrate	Elemental Industrial Carbons + Localized Sulfates	Secondary Ammonium Sulfates + Gasoline Vehicles	Coal/Coke Dust	Burning/ Cooking	Chlorine	Steel Manufacturing/ Processing	Crustal Component
Ammonium	0	0	0.01388	0	0.30660	0.49492	1.27130	0.11616	0	0.20768	0	0.01033
Nitrate	0.02778	0.11853	0	0.07862	0.86571	0	0	0	0.14222	0	0.04303	0
Sulfate	0	0.00104	0.04091	0.16674	0	0.70900	3.91310	0	0.25534	0.14854	0.03032	0
Org_Carbon	0.01208	1.35170	0	0.38930	0.11800	0.72348	0.55460	0.10176	0.67784	0.23764	0.11525	0
Elem_Carbon	0.01137	0.42962	0.00828	0.05282	0	0.89370	0.15473	0.22997	0.03921	0.19885	0.02511	0
AI	0.00060	0	0	0.00222	0	0.00186	0	0.00209	0.00364	0.00066	0	0.01518
As	0	0.00314	0.00006	0	0	0.00062	0	0.00015	0	0.00040	0	0.00005
Br	0.00013	0.00021	0.00015	0	0.00045	0.00478	0.00008	0.00020	0.00134	0.00246	0	0.00060
Ca	0	0.00737	0.00056	0	0.00102	0.00494	0	0	0	0	0.00217	0.02762
CI	0.00293	0.00039	0	0.01200	0	0	0	0.00000	0.00340	0.22105	0.00758	0
Cr	0.00146	0	0	0	0	0.00008	0.00009	0	0	0	0	0.00014
Cu	0	0	0	0.00552	0.00097	0.00014	0	0	0	0	0	0.00048
Fe	0.01323	0.00604	0.00005	0.01415	0	0	0.00695	0.00186	0	0.00028	0.03176	0.02123
Pb	0	0	0	0.00093	0	0.01048	0.00002	0.00077	0.00071	0.00208	0.00045	0.00062
Mn	0.00020	0	0	0	0.00005	0.00006	0	0	0.00018	0	0.00179	0.00046
Ni	0.00142	0	0	0.00001	0	0.00003	0	0.00003	0	0.00002	0.00001	0
K_xrf	0	0.01188	0	0.00679	0	0	0	0	0.03436	0.00058	0.00426	0.00736
Se	0.00000	0	0.00861	0.00070	0	0	0.00001	0.00019	0.00029	0.00000	0.00008	0
Si	0	0.00062	0	0	0.00092	0	0	0.11349	0.00580	0.00605	0.00945	0.00169
Na_xrf	0	0.00398	0.00007	0.00019	0	0.01637	0.00022	0	0.00767	0	0.00341	0.00624
Ti	0.00011	0.00053	0	0	0.00007	0	0.00036	0.00034	0	0	0	0.00144
V	0	0.00021	0.00002	0.00006	0.00019	0	0.00028	0	0.00006	0	0.00016	0
Zn	0	0.00352	0.00022	0.00226	0.00052	0.01014	0	0	0	0.00248	0.01267	0
Sum Conc. (µg/m³)	0.07132	1.93877	0.07281	0.73231	1.29450	2.87059	5.90173	0.56702	1.17206	1.02878	0.28750	0.09344



A pie chart of the best-guess Liberty source types, by percent of summed concentrations, is shown below.



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
- Variable (bootstrapping) for each concentration and percentage
- Time series plot by overall factor concentration
- Contribution aggregates according to year, season, and day of week

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





Conditional Probability Functions (CPF) plots are also included for each factor for Liberty. Below is the wind rose for Liberty, showing wind direction frequencies plotted in vector grid form and also plotted in Google Earth. Liberty wind data were available for the full modeled timeframe (Jan. 2005 through Dec. 2010).



Average wind speed = 4.45 knots

Liberty shows the largest frequencies of wind directions from the southwest. The strongest winds are from the west and west-southwest



2008 annual average daily traffic volumes for the Liberty vicinity are shown on the map below. Washington Blvd. (count: 2,800) and Liberty Way (3,300) are the roadways nearest the Liberty site. Larger roadways at lower elevations to the southwest (the predominant wind direction) may also be significant to the Liberty site.





Liberty Source Factor 1: Metals Processing

Factor 1 has a high percentage of chromium and nickel, which can be associated with metals processing such as electroplating or scrap-cutting. Weekday contributions are slightly higher than weekend, which may indicate weekday production schedules at local facilities. Factor 1 is small overall (less than 1% of total $PM_{2.5}$) and shows the highest contributions on days with no inversions.









The CPF plot for Factor 1 is shown below. High days showed the highest frequencies from the northeast.





Liberty Source Factor 2: Organic Industrial Carbons

Factor 2 is largely composed of organic and elemental carbons, along with the majority of arsenic at Liberty. Weekday/weekend contributions are similar, indicating continuous activity. Yearly contributions are the lowest in 2009, with an increase in 2010, which may be attributed to industrial facilities with low production levels in 2009. Factor 2 is a significant factor (12% of total) and is strongly affected by inversions. Organic carbons may be primary or secondary in nature, possibly from coke production, chemical processing, and/or other sources. Arsenic may be attributed to coal combustion, coking, or wood burning. Smaller concentrations of other species are also grouped with this factor.















The CPF plot for Factor 2 is shown below. High days showed the highest frequencies from the southwest.







Liberty Source Factor 3: Coal Combustion or Glass Manufacturing

Factor 3 contains a high percentage of selenium, with nearly negligible percentages of all other species. High peaks occur during inversions, with the highest levels occurring in 2010. Selenium can be associated with coal-fired boilers or glass manufacturing operations. Factor 3 is a small factor overall (less than 1% of the total).









The CPF plot for Factor 3 is shown below. High days showed the highest frequencies from the southwest.





Liberty Source Factor 4: Gasoline Vehicles + Metals Processing

Factor 4 is high in weekday organic carbon, indicating light-duty gasoline vehicle emissions. Copper also shows a high percentage for this factor, possibly indicating metals processing near the Liberty site. Factor 4 represents about 5% of total PM_{2.5}.













Weekday/Weekend Contributions





The CPF plot for Factor 4 is shown below. High days showed nearly identical frequencies from all sectors. This may be indicative of light-duty vehicle emissions from all directions around the Liberty site.







Liberty Source Factor 5: Secondary Ammonium Nitrate

Factor 5 is the majority of secondary ammonium nitrate at Liberty, dominant in cold weather. Ammonium nitrate is a secondary species created by upwind NO_x sources such as fossil fuel-fired boilers and nearby vehicle emissions. Factor 5 represents 8% of the total $PM_{2.5}$.









The CPF plot for Factor 5 is shown below. High day frequencies are distributed throughout all sectors, indicating contributions from distant and nearby NO_x sources in all directions.





Liberty Source Factor 6: Elemental Industrial Carbons + Localized Sulfates

Factor 6 shows high amounts of elemental carbon, organic carbon, and ammonium sulfates (primary or secondary), along with several trace elements. The factor is continuous with little day of the week differences and is best attributed to a "mix" of continuous industrial activity in the Monongahela River valley. This may include coke production, mobile diesel use (trucks, railroads, tug boats), and/or electric power generation. This factor makes up 18% of the total PM_{2.5} and, along with Factor 2, represents the majority of the excess PM_{2.5} at Liberty in comparison to other SW PA sites. Factor 6 shows the highest levels during inversions, although at lesser extremes in contributions than other factors. High percentages of lead and zinc are also present, which can be due to tire wear or incinerators.















The CPF plot for Factor 6 is shown below. High days showed the highest frequencies from the south and southwest. Diesel emissions from school buses may contribute a small portion of elemental carbon at Liberty, but only for a few minutes during school days.





<u>Liberty Source Factor 7</u>: Secondary Ammonium Sulfates + Gasoline Vehicles

Factor 7 comprises the majority of secondary ammonium sulfates at Liberty. Contributions are highest in summer, when sulfates are most prevalent. Sulfates exist as secondary $PM_{2.5}$ throughout SW PA, formed by upwind SO₂ from sources such as coal-fired power plants. This factor also contains carbons that are peaking concurrently with sulfate, possibly from light-duty vehicle exhaust. Factor 7 is the largest factor by percentage of total (37%).

















The CPF plot for Factor 7 is shown below. High days showed the highest frequencies from the southwest, south, and southeast.





Liberty Source Factor 8: Coal/Coke Dust

Factor 8 shows a high amount of silicon and elemental carbon, which can be associated with coal and coke dust. It is a small factor overall (4% of total) and shows the highest contributions during inversions.










The CPF plot for Factor 8 is shown below. High days showed the highest frequencies from the south and southwest.





Liberty Source Factor 9: Burning/Cooking

Factor 9 contains high percentages of organic carbon and potassium and is highest in winter and on weekends. This is indicative of vegetative burning and cooking, most likely for winter heating and for summer recreational burning/cooking in the Liberty area. Cooking at the school cafeteria at the Liberty site may also be contributing a small portion to this factor. Factor 9 represents 7% of the total PM_{2.5} and shows the highest contributions during inversions.

















The CPF plot for Factor 9 is shown below. High days showed the highest frequencies from the east, likely due to residential burning and cooking in the Liberty area.





Liberty Source Factor 10: Chlorine

Factor 10 contains high percentages of chlorine, existing possibly as inorganic chlorides or as chlorinated organic compounds. Bromine and elemental carbon are also present with this factor. Contributions from this factor are specific, usually appearing as very large peaks during cool-weather inversions. Unlike the road salt factor for Lawrenceville, this factor is present in fall and spring and at much higher concentrations than road salt. Although road salt may be contributing a portion of the chlorine on winter days, the majority of this factor likely due to industrial activity that is emitting or utilizing chlorine. Sodium chloride and magnesium chloride are used for de-icing at the Liberty site, but no sodium is present with the factor (magnesium was not modeled due to low signal strength). Factor 10 makes up 6% of the total PM_{2.5}.









The CPF plot for Factor 10 is shown below. High days showed the highest frequencies from the southwest.







Liberty Source Factor 11: Steel Manufacturing/Processing

Factor 11 shows high amounts of iron, manganese, and zinc. The presence of iron and manganese is likely associated with steel manufacturing, while zinc may be due to galvanizing activities from similar wind directions. This factor shows higher weekday contributions, possibly pointing to weekday production schedules or a presence of some vehicle emissions. Factor 11 is a minor factor (2% of total) and usually peaks during inversions.











Weekday/Weekend Contributions





The CPF plot for Factor 11 is shown below. High days showed the highest frequencies from the north and northeast.





Liberty Source Factor 12: Crustal Component

Factor 12 is composed primarily of crustal elements that make up airborne fine soil: aluminum, calcium, iron, and titanium. The silicon portion of crustal component is low, since the majority of silicon is included in Factor 8 (Coal/Coke Dust). Factor 12 is highest during weekday activity and in spring/summer. It is a small factor overall (1% of total) and often peaks during inversions.









The CPF plot for Factor 12 is shown below. High day frequencies are distributed throughout all sectors, with the highest frequencies from the south.



Liberty Source Descriptions

Below are descriptions of the sources shown on the aerial maps of the Liberty area.

US Steel Clairton	Manufacturing of metallurgical coke for use in steel-making. Includes recovery and other processes.
US Steel Edgar Thomson	Steel blast furnace and slab manufacturing using coke, iron- bearing materials, and fluxes.
US Steel Irvin	Performs finishing processes to steel slabs, including hot and cold rolling, continuous pickling, annealing, galvanizing, and terne coating.
Tube City IMS	Formerly CJ Langenfelder and Son. Iron and steel furnace slag handling and processing at US Steel Edgar Thomson.
Braddock Recovery	Uses mill scale, flue dust, coke breeze, and sludge to produce briquettes for use in the BOP shop and blast furnace at US Steel Edgar Thomson.
Koppers	Distillation of crude tar into pitch, oils, and various other products.
Mid-Continent Coal & Coke	Metallurgical coke breeze screening.
Clairton Slag	Manufacturing of bituminous concrete mixes from raw materials for supply to asphalt paving companies and municipalities.
Kinder Morgan	Storage and handling of petroleum and chemical products.
Pennsylvania Electric Coil	Manufacturing and repair of high voltage and specialty coils.
Gardner Denver Nash	Manufactures and designs engineered vacuum and compressor systems.
Eastman	Manufactures polymer resins and pure monomers derived from cracked petroleum distillates.
Sanyo	Processes aromatic monomers into resins using batch suspension and solution polymerization.
Guardian	Manufacturing of float glass.
Kelly Run	Municipal landfill with a landfill gas (LFG) collection system.
ELG Metals	Scrap cutting, shearing, and bundling, burning and cutting of stainless and alloy steel with burning bars.



CP Industries	Manufacturing of seamless high pressure vessels.				
Dura-Bond	Cleaning and applying protective coating to steel pipes.				
Precoat Metals	Pretreatment, painting, curing and quenching of galvanized and cold-rolled steel materials. Closed 3/31/09.				
GenOn Elrama	Coal-fired electric generation.				
Allegheny Energy Mitchell	Coal-fired electric generation.				
20 km Background	Background sources within a 20 km (near-field) domain around the Liberty site. Includes Tube City IMS-West Mifflin, WHEMCO, Jefferson and McKeesport Hospitals, National Energy Technology Laboratory, Bettis Atomic Laboratory, and others.				



6. Model Diagnostics

Lawrenceville Diagnostics

Factors = 10 Random Run # 9

Valid samples not used in model due to outliers:

4/10/05 – crustal outliers 5/5/06 – Na, Zn outliers 7/28/06 – Al, Si outliers 12/10/06 – Pb outlier 4/21/07 – mass balance outliers 5/6/07 – Cr, Ni outliers 5/9/07 – Cr, Ni outliers 10/24/07 – major species outliers 11/14/07 – Ca outlier 7/5/08 – K outlier 7/6/09 – K outlier 7/4/10 – K outlier

Input Data Statistics:

Species	Category	S/N	Min	25th	Median	75th	Max
Ammonium	Strong	13.096	0.119	0.953	1.620	2.440	7.210
Nitrate	Strong	12.590	0.105	0.538	0.972	1.952	12.431
Sulfate	Strong	12.869	0.565	2.256	3.518	5.328	21.700
Org_Carbon	Strong	7.623	0.558	2.360	3.476	4.920	11.300
Elem_Carbon	Weak	2.368	0	0.469	0.721	1.027	4.000
AI	Weak	2.905	0	0	0.019	0.040	0.233
As	Weak	1.483	0	0	0.001	0.003	0.013
Br	Strong	4.024	0	0.002	0.004	0.006	0.016
Ca	Strong	11.326	0	0.020	0.033	0.050	0.275
CI	Strong	7.821	0	0	0.009	0.024	0.484
Cr	Strong	6.542	0	0	0.002	0.004	0.111
Cu	Strong	6.223	0	0.002	0.004	0.007	0.033
Fe	Strong	13.106	0.015	0.065	0.102	0.185	1.640
Pb	Strong	4.578	0	0.003	0.007	0.013	0.087
Mn	Strong	6.977	0	0.002	0.004	0.009	0.040
Ni	Strong	6.124	0	0	0.001	0.002	0.055
K_xrf	Strong	11.936	0.008	0.039	0.057	0.084	0.285
Se	Strong	4.662	0	0.001	0.002	0.004	0.053
Si	Strong	8.188	0	0.032	0.059	0.092	0.431
Na_xrf	Weak	1.978	0	0	0.028	0.073	0.381
Ti	Weak	3.116	0	0	0.001	0.005	0.102
V	Weak	1.272	0	0	0	0.001	0.011
Zn	Strong	12.515	0	0.013	0.024	0.040	0.478
Total	Weak	17.903	1.700	9.400	13.600	19.650	48.300



Base Run Summary:

Run #	Q(Robust)	Q(True)	Converged	# Steps
9	9978.47	10345.10	Yes	1034

Regression Diagnostics:

					KS Test	KS Test
Species	Intrcpt	Slope	SE	r^2	Stat	P Value
Ammonium	0.066	0.945	0.181	0.975	0.066	0.014
Nitrate	0.000	1.001	0.109	0.995	0.155	0.000
Sulfate	0.169	0.954	0.412	0.983	0.108	0.000
Org_Carbon	0.421	0.827	0.931	0.727	0.037	0.420
Elem_Carbon	0.291	0.563	0.261	0.516	0.075	0.004
AI	0.014	0.242	0.012	0.308	0.065	0.018
As	0.001	0.239	0.001	0.262	0.055	0.070
Br	0.001	0.575	0.001	0.602	0.036	0.440
Ca	0.006	0.804	0.010	0.877	0.068	0.010
CI	0.000	0.970	0.002	0.997	0.121	0.000
Cr	0.000	0.957	0.001	0.982	0.043	0.240
Cu	0.001	0.787	0.002	0.803	0.048	0.145
Fe	0.029	0.763	0.052	0.849	0.123	0.000
Pb	0.004	0.418	0.005	0.511	0.058	0.047
Mn	0.000	0.991	0.000	0.995	0.032	0.610
Ni	0.001	0.430	0.002	0.481	0.073	0.005
K_xrf	0.012	0.783	0.013	0.848	0.100	0.000
Se	0.000	0.924	0.001	0.959	0.060	0.032
Si	0.011	0.786	0.024	0.798	0.051	0.110
Na_xrf	0.030	0.183	0.020	0.241	0.079	0.002
Ti	0.003	0.125	0.002	0.169	0.119	0.000
V	0.001	0.085	0.000	0.093	0.178	0.000
Zn	0.003	0.906	0.005	0.978	0.148	0.000
Total	0.356	0.957	1.840	0.943	0.044	0.220

Scaled Residuals Beyond 3 Standard Deviations:

Species	Dates	Residuals
Ammonium	12/1/2010	5.673
Nitrate	10/5/2010	3.468
Sulfate	10/5/2010	3.576
Org_Carbon	2/27/2005	3.029
Org_Carbon	5/28/2005	3.204
Org_Carbon	6/18/2005	3.536
Org_Carbon	10/13/2005	3.126
Org_Carbon	10/22/2005	3.344
Org_Carbon	4/15/2007	4.380
Org_Carbon	9/12/2007	3.871
Org_Carbon	11/2/2007	4.742
Org_Carbon	8/25/2008	3.044
Org Carbon	8/28/2008	5.087
Org Carbon	1/13/2009	3.032
Org Carbon	2/15/2009	5.394
Org Carbon	5/1/2009	5.043
Org Carbon	9/10/2009	5.176
Br	1/4/2005	-3.863
Br	3/26/2005	3.054
Br	6/18/2005	-3.270
Br	6/30/2005	-3.339
Br	7/9/2005	-4.171
Br	11/12/2005	3.454
Br	2/19/2006	3.644
Br	3/12/2006	3.533
Br	3/21/2006	3.763
Br	5/17/2006	-3.025
Br	5/29/2006	-3.351
Br	6/16/2006	3.617
Br	6/25/2006	-3.920
Br	7/10/2006	-3.518
Br	11/13/2006	3.169
Br	1/12/2007	3.795
Br	2/17/2007	3.072
Br	3/31/2007	3.035
Br	5/27/2007	-4.273
Br	6/20/2007	-3.761
Br	6/23/2007	-5.992
Са	1/25/2005	3.030
Са	1/31/2005	3.766
Ca	2/3/2005	4.298
Ca	4/4/2005	3.357
Ca	4/19/2005	6.556
Ca	5/4/2005	3 054
Ca	6/21/2005	3 105
Ca	8/11/2005	6 022
04	0/11/2000	0.022



Species	Dates	Residuals
Ca	9/19/2005	3.247
Ca	9/22/2005	3.847
Са	5/20/2006	5.131
Са	9/8/2006	6.027
Са	2/21/2008	3.405
Са	7/14/2008	3.601
Са	3/2/2009	4,646
Ca	10/25/2009	3 191
Ca	7/10/2010	3 728
Cu	5/19/2005	-3.085
Cu	7/9/2005	1 283
Cu	11/27/2005	4.200
Cu	12/6/2005	4.042
Cu	12/0/2005	5.017
Cu	1/20/2006	5.191
Cu	1/29/2006	4.056
Cu	2/4/2006	4.162
Cu	2/10/2006	4.410
Cu	6/7/2006	3.572
Cu	9/26/2006	3.846
Cu	10/26/2006	-3.232
Cu	12/16/2006	4.270
Cu	1/27/2007	4.604
Cu	1/30/2007	6.136
Cu	3/4/2007	3.017
Cu	11/29/2007	3.021
Cu	12/8/2007	4.398
Cu	1/1/2008	5.076
Cu	12/24/2009	-3.359
Cu	1/20/2010	-3.189
Cu	6/19/2010	-3.307
Cu	9/17/2010	3.090
Cu	10/14/2010	3.462
Fe	11/2/2007	3.678
Fe	11/8/2007	6 306
Fe	1/22/2008	3 397
Fe	3/7/2008	3 046
Fe	10/6/2008	5 263
Fe	1/20/2010	3 691
Ph	2/6/2015	3 135
Dh	2/0/2005	3 015
Pb	5/22/2005	3.915
г и Dh	3/22/2003	5.070
	1/30/2005	0.792
	11/12/2005	-3.211
PD	4/5/2006	5.060
PD	8/9/2006	3.148
Pb	9/26/2006	3.536
Pb	10/2/2006	4.654
Pb	11/4/2006	4.075
Pb	12/16/2006	3.806



Species	Dates	Residuals
Pb	1/24/2007	4.026
Pb	1/30/2007	5.775
Pb	6/17/2007	6.458
Pb	7/29/2007	4.645
Pb	11/8/2007	-3.416
Pb	3/19/2008	-3.136
Pb	5/6/2008	3,526
Pb	5/24/2008	3 070
Ph	8/7/2008	-3 631
Ph	8/31/2008	4 405
Ph	9/3/2008	3 256
Ph	9/21/2008	3 952
Pb	3/21/2000	2 422
	10/12/2008	3.422
PD Dh	10/24/2008	3.314
PD	11/5/2008	3.082
PD	3/17/2009	3.486
Pb	5/19/2009	4.690
Pb	11/15/2009	3.206
Pb	1/20/2010	-3.072
Pb	2/1/2010	5.876
Pb	4/14/2010	5.575
Pb	9/17/2010	3.435
Pb	9/23/2010	-3.762
Ni	1/25/2005	3.358
Ni	9/7/2005	3.559
Ni	12/15/2005	3.019
Ni	7/13/2006	3.449
Ni	11/28/2006	4.007
Ni	1/3/2007	4.145
Ni	12/11/2007	4,650
Ni	4/30/2008	6.386
Ni	3/17/2009	-3 097
Ni	3/21/2010	6 172
Ni	4/8/2010	7 151
Ni	9/23/2010	7 346
K vrf	1/1/2005	1.540 1.11
K_xrf	7/0/2005	3 1//
K_xrf	5/20/2006	2 474
N_XII K_yrf	3/29/2000 9/12/2006	3.474 2.444
N_XII	0/12/2000	5.441
K_XII	1/1/2006	0.322
K_XII	11/6/2009	4.015
K_XIT	4/11/2010	3.118
Si	3/26/2005	4.118
Si	5/7/2005	3.396
Si	5/19/2005	-3.216
Si	6/21/2005	-5.436
Si	7/15/2005	-4.220
Si	8/8/2005	-3.117
Si	8/11/2005	-3.095



Species	Dates	Residuals
Si	8/14/2005	3.776
Si	9/10/2005	-3.126
Si	9/19/2005	-4.474
Si	9/22/2005	-3.756
Si	9/25/2005	-3.004
Si	9/28/2005	-3.018
Si	10/1/2005	-3.263
Si	12/9/2005	3.650
Si	5/2/2006	3.097
Si	7/13/2006	4.999
Si	10/17/2006	3.211
Si	2/9/2008	3.560
Si	7/8/2008	4.108
Si	8/29/2009	5.092
Si	5/2/2010	4.508
Si	7/25/2010	4.647
Ti	11/15/2009	3.169



Liberty Diagnostics

Factors = 12 Random Run # 2

Valid samples not used in model due to outliers:

2/3/05 – crustal outliers 5/10/05 – crustal outliers 8/14/05 – Ti outlier 11/25/06 – K outlier 6/5/07 – Ca outlier 9/27/07 – Fe outlier 10/3/07 – Ca outlier 10/9/07 – Ca outlier 7/5/08 – K outlier 3/25/08 – elemental carbon outlier

Input Data Statistics:

Species	Category	S/N	Min	25th	Median	75th	Max
Ammonium	Strong	13.108	0	1.140	2.017	3.280	10.600
Nitrate	Strong	12.246	0.032	0.601	0.972	1.650	6.975
Sulfate	Strong	12.872	0	2.450	4.170	6.586	29.300
Org_Carbon	Strong	8.912	0.586	1.994	3.354	5.582	27.700
Elem_Carbon	Strong	7.024	0.069	0.583	1.160	2.830	16.700
AI	Weak	3.273	0	0	0.020	0.054	0.206
As	Strong	3.707	0	0.001	0.003	0.007	0.047
Br	Strong	9.489	0	0.003	0.006	0.014	0.133
Са	Strong	11.398	0.001	0.018	0.033	0.059	0.236
CI	Strong	13.042	0	0.002	0.020	0.096	7.230
Cr	Strong	4.041	0	0	0.001	0.003	0.041
Cu	Strong	7.009	0	0.004	0.006	0.010	0.029
Fe	Strong	11.838	0	0.049	0.081	0.129	0.518
Pb	Strong	6.508	0	0.004	0.009	0.023	0.098
Mn	Strong	4.197	0	0.001	0.002	0.004	0.024
Ni	Strong	3.827	0	0	0.001	0.002	0.020
K_xrf	Strong	11.806	0	0.033	0.060	0.085	0.325
Se	Strong	11.455	0	0.001	0.003	0.007	0.377
Si	Strong	10.005	0	0.042	0.083	0.177	0.986
Na_xrf	Weak	1.843	0	0	0.026	0.065	0.514
Ti	Weak	1.870	0	0	0.002	0.004	0.015
V	Weak	1.225	0	0	0	0.002	0.008
Zn	Strong	12.131	0	0.013	0.024	0.042	0.185
Total	Weak	18.557	0.400	10.600	16.300	27.100	88.100



Base Run Summary:

Run #	Q(Robust)	Q(True)	Converged	# Steps
2	3870.23	3965.98	Yes	2825

Regression Diagnostics:

					KS Test	KS Test
Species	Intrcpt	Slope	SE	r^2	Stat	P Value
Ammonium	-0.007	0.991	0.212	0.987	0.050	0.465
Nitrate	-0.001	1.002	0.054	0.997	0.186	0.000
Sulfate	0.053	0.982	0.440	0.988	0.174	0.000
Org_Carbon	0.120	0.935	0.811	0.943	0.033	0.922
Elem_Carbon	0.161	0.875	0.599	0.922	0.033	0.909
AI	0.013	0.371	0.017	0.449	0.063	0.199
As	0.000	0.898	0.002	0.892	0.076	0.071
Br	0.001	0.835	0.004	0.887	0.041	0.707
Ca	0.000	0.987	0.004	0.988	0.068	0.143
CI	0.004	0.970	0.050	0.996	0.248	0.000
Cr	0.001	0.575	0.001	0.734	0.108	0.002
Cu	0.000	0.954	0.001	0.979	0.071	0.113
Fe	0.005	0.912	0.020	0.912	0.076	0.072
Pb	0.001	0.913	0.004	0.946	0.056	0.337
Mn	0.001	0.631	0.001	0.778	0.052	0.419
Ni	0.000	0.899	0.001	0.821	0.084	0.034
K_xrf	0.003	0.938	0.006	0.981	0.083	0.039
Se	0.000	1.017	0.001	0.999	0.171	0.000
Si	0.001	0.995	0.004	0.999	0.101	0.006
Na_xrf	0.028	0.212	0.026	0.227	0.086	0.029
Ti	0.002	0.444	0.002	0.454	0.108	0.003
V	0.001	0.100	0.001	0.082	0.168	0.000
Zn	0.003	0.867	0.009	0.901	0.100	0.007
Total	0.183	0.973	2.194	0.972	0.068	0.140

Scaled Residuals Beyond 3 Standard Deviations:

Species	Dates	Residuals
Nitrate	11/16/2010	3.015
Sulfate	10/13/2005	3.710
Sulfate	11/16/2010	8.181
Org_Carbon	6/15/2005	3.302
Elem_Carbon	11/12/2005	3.057
Br	11/2/2007	5.051
Br	1/25/2008	-3.482
Br	11/10/2010	4.263
Br	11/16/2010	3.307
Cr	3/5/2005	-6.504
Cr	5/16/2005	3.372
Cr	6/9/2005	3.481
Cr	8/20/2005	4.795
Cr	2/16/2006	-3.409
Cr	5/17/2006	4.889
Cr	5/29/2006	4.865
Cr	11/7/2006	-3.166
Cr	7/29/2007	4.435
Cr	5/8/2010	3.018
Cr	5/20/2010	3.271
Cr	11/4/2010	3.175
Fe	10/13/2005	-3.037
Fe	2/16/2006	3.166
Fe	6/18/2009	4.858
Pb	12/12/2005	3.626
Pb	5/23/2006	3.463
Pb	6/10/2006	3.124
Pb	8/9/2006	3.073
Mn	4/22/2005	4.822
Mn	1/23/2006	3.073
Mn	12/1/2006	3.167
Mn	12/13/2006	3.061
Mn	2/11/2007	5.368
Mn	8/16/2007	-3.247
Mn	8/12/2010	3.261
Mn	10/11/2010	3.078
Ni	3/5/2005	3.780
Ni	9/25/2005	3.899
Ni	10/13/2005	3.506
Zn	5/5/2006	5.639
Zn	5/18/2007	3.855

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Additional Information

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