Exploratory Research of Wintertime Aerosol Chemical Composition at a Ground Location in Fairbanks, Alaska

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EXECUTIVE SUMMARY

This report summarizes quantitative chemical composition data of ambient particulate matter of less than 2.5 μm (PM2.5) aerosol collected during a month-long study in Fairbanks, Alaska in February and March, 2011. The data collected include hourly measures of ions commonly found in aerosol, as well as hourly measurements of organic and elemental carbon. Daily filter samples were also collected for alternative chemical analyses. Data were collected in a small, insulated trailer that was located near the Fairbanks Borough North Star Administrative Office near 809 Pioneer Road.

Approximately 283 sets of ion samples were collected during this study, and just over 500 measurements of organic and elemental carbon were collected. 37 pairs of filters were collected as well, with one set consumed by analytical techniques and a second set collected for long-term storage and post-hoc analyses. Aerosol chemical composition appears to be dominated by organic carbon (mean = 6.5 μgC m^{-3}) and estimated organic matter, as well as elemental carbon (mean = 0.9 μgC m^{-3} and sulfate (mean = 2.02 μg m^{-3}). Lesser measurements included ammonium, nitrate, potassium, and several light organic acids.

The data show a clear diurnal profile that is likely attributed to anthropogenic activities. Wood burning appears the be a significant contributor to the high particle loading observed during the winter in Fairbanks as indicated by the enhanced levels of organic carbon and in the relative absence of other compounds that would indicate other emission sources of PM2.5. Ion information provides some confirmation of this, and a preliminary look at high time resolution XRF data provides additional confirmatory evidence in support of this hypothesis.

A particular focus of this work involved improving the understanding of sulfur in the Fairbanks airshed. Particulate sulfur (as sulfate) was detected throughout the study indicating that mechanisms that promote sulfur conversion (from gas phase to particle phase) are, in fact, present. We also examined chemical composition by complementary analytical methods – first by X-Ray Fluorescence (XRF) followed by ion chromatography for two measures of sulfur from the same filter. Results show that sulfur is measured at the same levels no matter the analytical method, which is in contrast to results reported by the United States Environmental Protection Agency (EPA) for chemical speciation measurements in Fairbanks. It is likely that a methodological difference explains the disagreement between the two methods of sulfur measurement used by the EPA speciation network.

INTRODUCTION AND RATIONALE FOR RESEARCH

Ambient fine particles are ubiquitous in the lower troposphere, and result from a variety of physical and chemical transformations. They can be formed as a primary pollutant through, among others, combustion and biogenic sources, as well as by resuspension of dust from crustal surfaces [1-3]. Secondary aerosol sources – that is, aerosol formed by a variety of secondary gas-phase chemical reactions in the atmosphere - are substantially more complex and can represent a significant fraction of ambient aerosol [2, 4]. The diversity of possible atmospheric reactions makes unequivocal identification of aerosol sources quite complex, and thus, our understanding of aerosol formation is also incomplete.

The Fairbanks region is an excellent example of unique and diverse chemical conditions that result in ambient particulates. The region is known to routinely exceed the National Ambient Air Quality Standards during the winter heating season. This is thought to arise both from significant local emissions, but also by meteorological enhancement due to strong inversions and poor regional ventilation. Aerosol source hypotheses include emissions from wood and fuel oil burning, and the formation of sulfur-containing particles from local coal-fired power generation. Because of its relatively remote location, regional transport of particle pollution is generally insignificant suggesting that most of the ambient pollution was generated within the local area. Thus, because of this unique complexity and the absolute need to maintain safe temperatures through residential heating during the winter, Fairbanks represents an excellent case for further study of ambient aerosol composition and formation.

Because of a history of demonstrated non-attainment for PM2.5 in the Fairbanks area, there exists a need for substantially increased expansion of fundamental understanding of aerosol chemical climatology for the community. This information will be useful in identifying suggested pathways to reduce air pollution levels in the most efficient and cost-effective manner, as well as reduce aerosol components of known health hazards for the citizens of the borough. Without this information, mitigation attempts are likely to be ineffective.
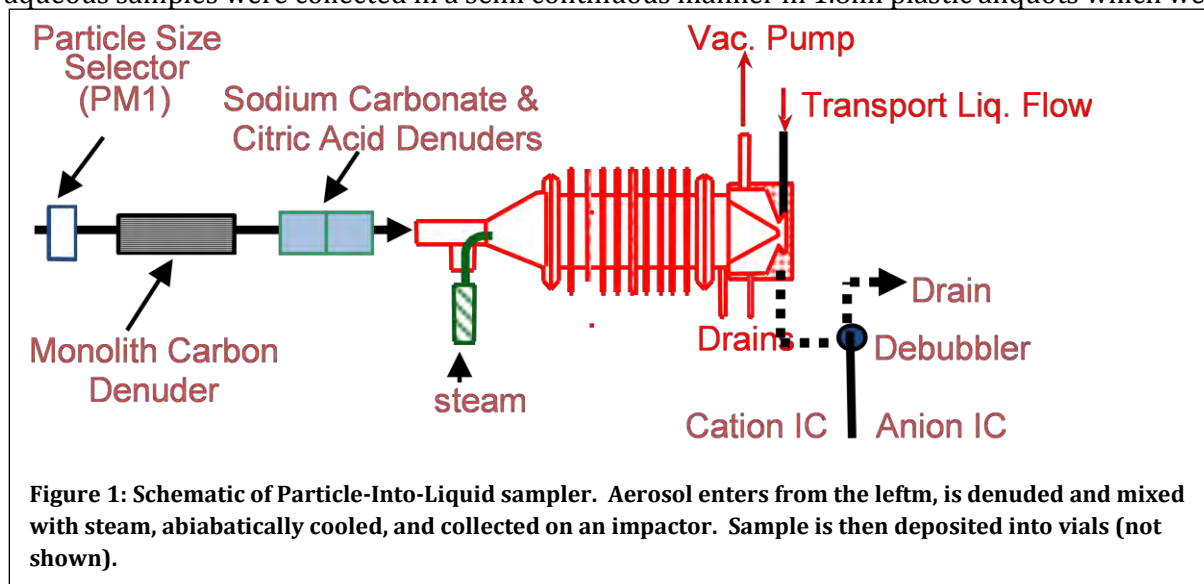

INSTRUMENTATION

A state-of-the-art instrumentation package was installed in a small, insulated utility trailer, which was situated near the NCORE site in Fairbanks, Alaska. Instrument integration was completed on February 6, 2011, and field data collection began on February 9th, 2011 at approximately 13:00 AST. The instrumentation package, described below, operated with periodic user intervention and maintenance, as described below. FNSB staff were immensely helpful in performing these duties for the duration of the study. The study continued until March 16th, 2011 at 07:05 AST when instruments were powered down and removed from the trailer.

PILS-IC

The Particle-Into-Liquid Sampler (PILS) is a device that captures all particles greater than ~10-15 nm by employing condensational growth of the particle in a supersaturated environment of water vapor. Prior to entering the PILS, a particle passes through a set of denuders which strip out gas phase organics, and any acidic or basic gases present in the aerosol stream. The particles and water vapor are adiabatically cooled, which promotes rapid particle growth to a size of 1-3 μm; these are then accelerated and collected on an impaction wall. This wall is continuously washed with a small amount of purified water, and the effluent is then diverted by syringe pump to any number of

analytical processes. Typical detection limits are described in Table 1, and a schematic representation of the PILS system is show in Figure 1. Rather than *in-situ* analytical chemistry, aqueous samples were collected in a semi continuous manner in 1.8ml plastic aliquots which were

Figure 1: Schematic of Particle-Into-Liquid sampler. Aerosol enters from the leftm, is denuded and mixed with steam, abiabatically cooled, and collected on an impactor. Sample is then deposited into vials (not shown).

mounted on a computer-controlled rotating carousel. Filled aliquots were periodically collected and frozen by local assisting staff.

Maintenance activities performed by local staff included emptying of wastewater tanks (containing a non-hazardous dilute solution), replacement of purified water, retrieval and storage of samples and replacement of new plastic vials, and inspection and removal of any ice buildup at the pump exhaust. The instruments were checked daily for normal operation. Collected samples were organized according to unique barcodes, and shipped to the investigator's lab in Massachusetts for chemical analysis.

Table 1: This is a summary of analyses of aerosol chemical composition useful for this study. Data include typical concentrations in Fairbanks, estimated liquid concentration in the PILS effluent, and typical detection limits by a variety of analytical techniques.

Compound	Typical Winter Air Concentration at Fairbanks (Jan-Feb, 2006-2009), $\mu g\ m^{-3}$	Estimated Liquid Concentration ($\mu g\ L^{-1}$)	Typical Detection Limit ($\mu g\ L^{-1}$)
Sulfate	4.498	3748.33	0.01[a]
Elemental sulfur	1.63	1358.33	0.1[b]
Ammonium	2.021	1684.17	0.1 [a]
Sodium	0.093	77.50	0.1 [a]
Nitrate	1.121	934.17	0.5 [a]
Potassium	0.150	125.00	0.2[a]
As	0.0015	1.25	0.1[c]
Se	0.0010	0.83	1.0 [c]
Oxalate	n/a	n/a	0.2 [a]
Zn	0.0520	43.33	0.2 [c]

[a] by ion chromatography
[b] by ICP-MS
[c] by Flame ionization/ Atomic Absorption

Once defrosted, collected aliquots were removed from field vials and diluted to 4ml with precision pipettes and placed into 5ml autosampler vials (Environmental Express, Model K4300). Dilution matrix was 18.2M-Ohm or better purified water. The samples were then analyzed by ion chromatographic separation for 18 ion species (as a total of 13 anion and 5 cation peak) using a Dionex ICS-3000 Ion Chromatography System. In order of elution, the anion peaks are fluoride, acetate, formate, methanesulfonate, chlorite, chloride, nitrite, sulfate, bromide, oxalate, nitrate, chlorate, and phosphate. The 5 cation peaks are sodium, ammonium, potassium, magnesium, and calcium.

SUNSET LABS EC AND OC
Because of the multicomponent complexity of aerosol in Fairbanks, we also operated a Sunset Labs Model 4 semi continuous Organic Carbon and Elemental Carbon (OC/EC) analyzer. This instrument simultaneously and directly measures fine particle organic and elemental carbon at hourly integrated measurements and is a standalone instrument that requires almost no user support.

The instrument includes a sharp-cut cyclone to remove particles greater than 2.5 μm. The inlet also includes a parallel plate denuder consisting of laminar paper sheets impregnated with activated carbon which effectively removes organic vapors. The sample cycle typically includes 45 minutes of sample collection that begins on the hour, and a 12-13 minute analysis cycle. The instrument goes through a cooling cycle and then repeats an analysis at the next hour. With typical operating parameters, the detection limits of this analyzer are approximately 0.3 μg m^{-3} for both organic carbon and elemental carbon. It requires several certified compressed gases for analysis, and this method is consistent with the NIOSH [5-7] method of OC and EC determination.

FILTER SAMPLES
37 filters samples (collected in duplicate, a total of 74 filters) were also collected for the duration of this study. The samples were collected over a nominal 24 hours (with filter changes initiated at approximately 13:00 AST), and were collected at ambient temperature and pressure and corrected to standard temperature and pressure. Samples were collected in conductive plastic filter holders than contained 37 mm ringed Teflon filters (Pall Corporation, model R2PJ037) that were sequentially labeled. Sample passed through a sharp-cut cyclone with a cut size of 2.5 μm, and through two stainless steel annular denuders in series, one of which was coated with a sodium carbonate/bicarbonate solution, and second coated with a citric acid solution. Sample flow was achieved by a 1/4hp vane pump that applied a strong vacuum to a critical orifice calibrated for choked flow at 15.0 l min^{-1}. After sampling, filters were returned to their original petri dish containers and sent to the investigator's lab in Massachusetts.

Filters were analyzed by high resolution X-ray Fluorescence Spectroscopy using analytical methods consistent with EPA speciation approaches. The method used in this analysis conforms to EPA Compendium Method IO-3.3: For the Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy.

Filters were then returned to the lab and sent for further analysis by ion chromatography. This is a destructive technique that renders the remaining filters unusable for any further testing. Chromatographic separation methods were consistent with those described above, but filters were first digested in a vial of purified water under sonication, and then cooled for an hour to room temperature prior to analysis.

RESULTS AND DISCUSSION

AEROSOL IONS

Approximately 280 unique, hourly samples were collected over the course of this study. A number of samples were invalidated due to issues of contamination and instrument failure.

Table 2: Univariate statistics for the range of ions measured during this study. Reported values include mean, median, standard deviation, range, and the number of measurements collected during this study. Llod denotes measurements below the limit of detection.

	Mean, $\mu g\ m^{-3}$	Median, $\mu g\ m^{-3}$	Std Dev, $\mu g\ m^{-3}$	Range, $\mu g\ m^{-3}$	n
Ammonium	0.39	0.24	0.46	(llod, 3.22)	278
Potassium	0.75	0.63	0.42	(0.24, 3.5)	278
Magnesium	0.17	0.07	0.39	(0.03, 2.65)	278
Calcium	0.93	0.56	1.16	(0.17, 7.37)	273
Acetate	1.06	0.51	1.23	(llod, 8.8)	285
Formate	0.21	0.09	0.25	(0.02, 1.55)	285
Chloride	0.83	0.28	2.12	(0.08, 25.1)	285
Nitrite	0.08	0.03	0.12	(llod, 0.62)	285
Sulfate	2.02	1.55	1.56	(0.12, 12.25)	285
Oxalate	0.03	0.01	0.08	(llod, 0.56)	285
Nitrate	0.59	0.41	0.51	(llod, 2.9)	285

Table 2 shows univariate statistics describing the data collected at this location. Dominant ions throughout this study included ammonium, calcium, and potassium, as well as sulfate, nitrate and some chloride. All ions were detected at times over the course of this study. A number of light organic acids were detected, including acetate and formate; these are discussed further in the next section.

Aerosol chemical composition during this study could be characterized by high variability, as seen in relatively high reported standard deviations (Table 2) and graphically as in Figure 2. Figure 2 plots sulfate, one of the more dominant ions measured during this campaign, plotted on hourly intervals. Superimposed on this graph are measured sulfate concentrations determined from collocated 24-hour filter samples which were also analyzed by ion chromatography. Of particular note, sulfate appears with a quasi-diurnal cycle (more discussion of this follows) with minima typically in the 1-2 $\mu g\ m^{-3}$ range, and short term maxima in the 4-5 $\mu g\ m^{-3}$ range; there are notable deviations from this with clear spikes in sulfate approaching 10-12 $\mu g\ m^{-3}$. 24 hour filter measures show some variability in concentration data, but they lack substantial texture clearly seen with the higher time resolution data.
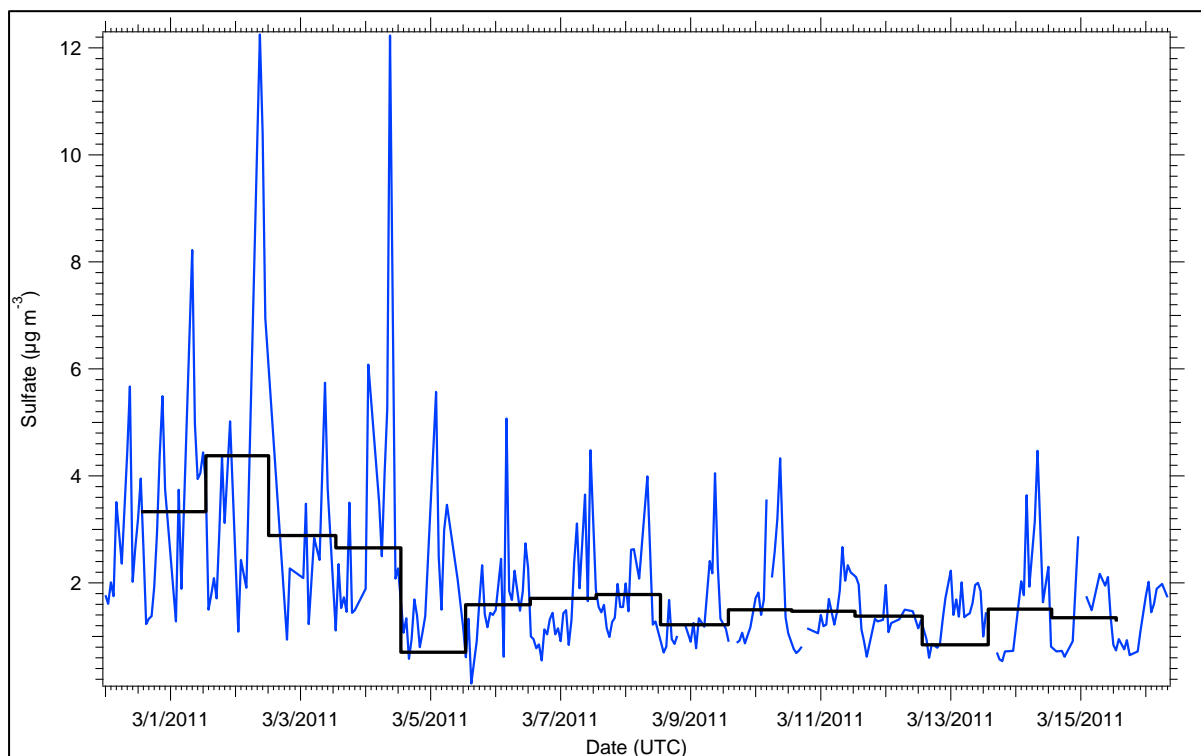
Figure 2: Time series of daily filter measures of sulfate (black lines) with hourly measures of sulfate by PILS (blue) superimposed on the figure.

Figure 3 depicts available ion data coupled with measured organic carbon, plotted against apparent charge, in microequivalents. Charge is calculated by taking the net valence charge for each measured ion, adjusted for molar concentration, and summing the positive and negative charges. This approach also includes (when available) the net charge resulting from a variety of measured light organic acids (including oxalate, formate, and acetate). If all elements are measured, one would expect a balanced charge of zero. Deviations towards a net negative charge indicate a missing cation; deviations towards a net positive charge indicate a missing anion. In typical studies, this missing cation (e.g. conditions with net negative charge) is presumed to be a hydrogen proton which can accompany acidic aerosol.

In the case of Figure 3, both positive and negative conditions appear in the data. While acidic conditions are often observed in air sheds that have significant influence from coal combustion (which normally leads to sulfuric acid formation in the aerosol), it is notable that these deviations occurred throughout a range of concentrations of OC – both high and low – and suggest that acidic influence is independent of OC concentration. Charge balance contributed by the measured light organic acids also appears to be relatively low during these periods suggesting that the aerosol climatology lacks a substantial light organic acid profile and further suggestion this acidity is linked more closely inorganic acids, such as sulfuric or nitric acid, rather than light organic acids. This does provide some weak evidence that inorganic acids are playing a role in determining aerosol charge in Fairbanks, but these results are not yet determinative; there are a number of possible explanations for this, though it does appears likely that the modest acidity results from a source unrelated to the source of organic carbon. It should also be noted that apparent acidity determined here is quite modest in the context of other studies which examined particle acidity arising from coal combustion. For example, in communities on the East Coast of the US, net charges are typically -0.25 μEq and lower [8, 9], which is twice as acidic as conditions observed here.

In contrast, a surprising result was that there were a number of cases where there were significant positive charges observed in the data, suggesting missing cations. This tended to occur during
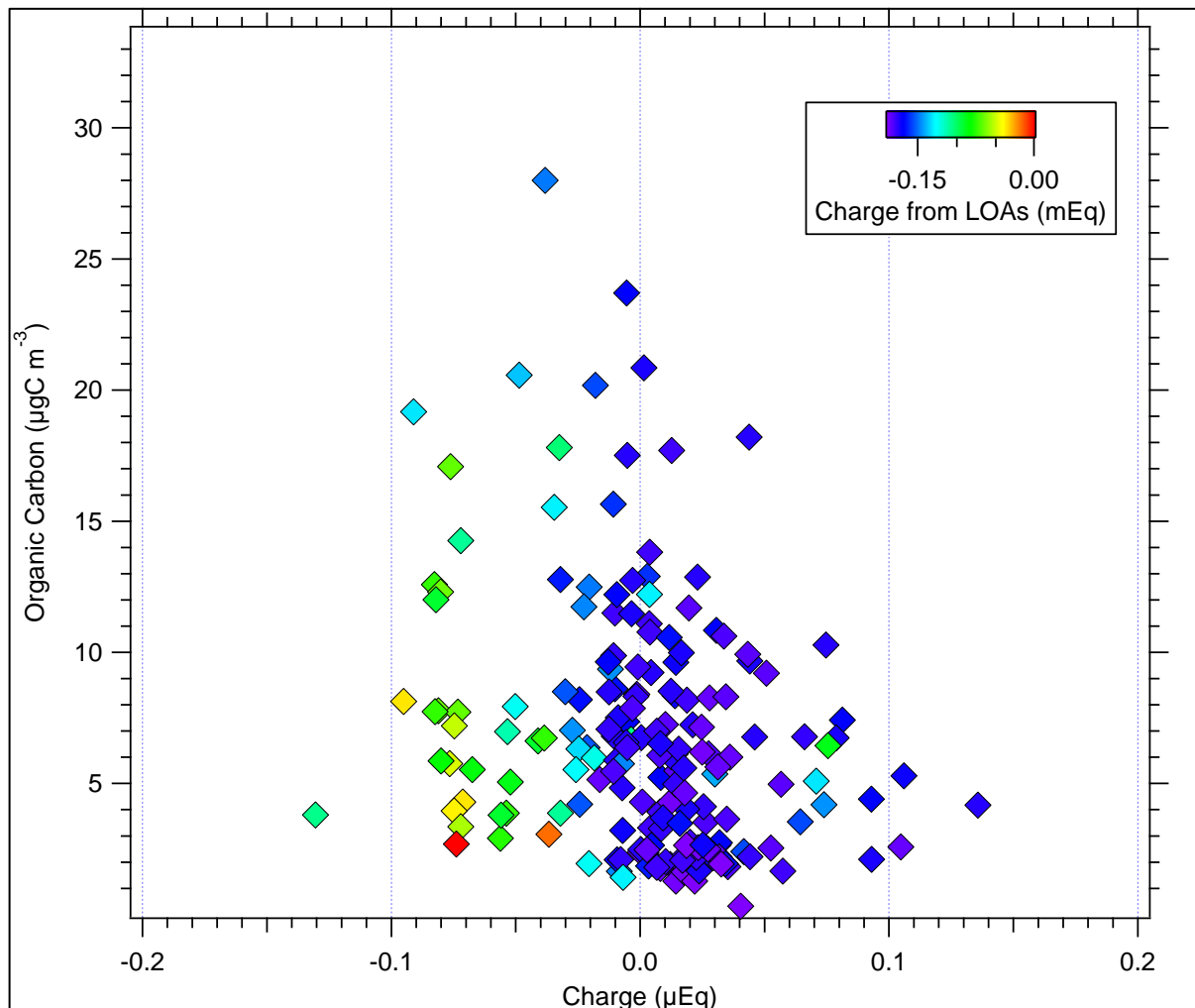

Figure 3: Net charge on aerosol plotted against organic carbon concentration. Markers are colored by apparent net charge resulting from three measured light organic acids, which include acetate, formate, and oxalate.

periods of lowest measured OC. While not yet determined, there are several possible explanations for this. For example, one explanation would be contamination of the system by a cation such as ammonium, though one would expect to see a systematic bias rather than only occasional influence. Another more likely explanation is that a negatively charged species, such as a light organic acid, may be present in aerosol only under conditions of limited OC, which is not accounted for in the charge calculation.

SULFUR STUDIES

Investigating the possible sources of sulfur was an a priori interest in this study and stems from the observation that local speciation measurements, which measure sulfate by chromatography and sulfur by XRF, suggest that there may be a non-sulfate source of sulfur present in the Fairbanks air shed. Of note, as illustrated by Figure 4, existing sulfate and sulfate data shows a substantially noisy
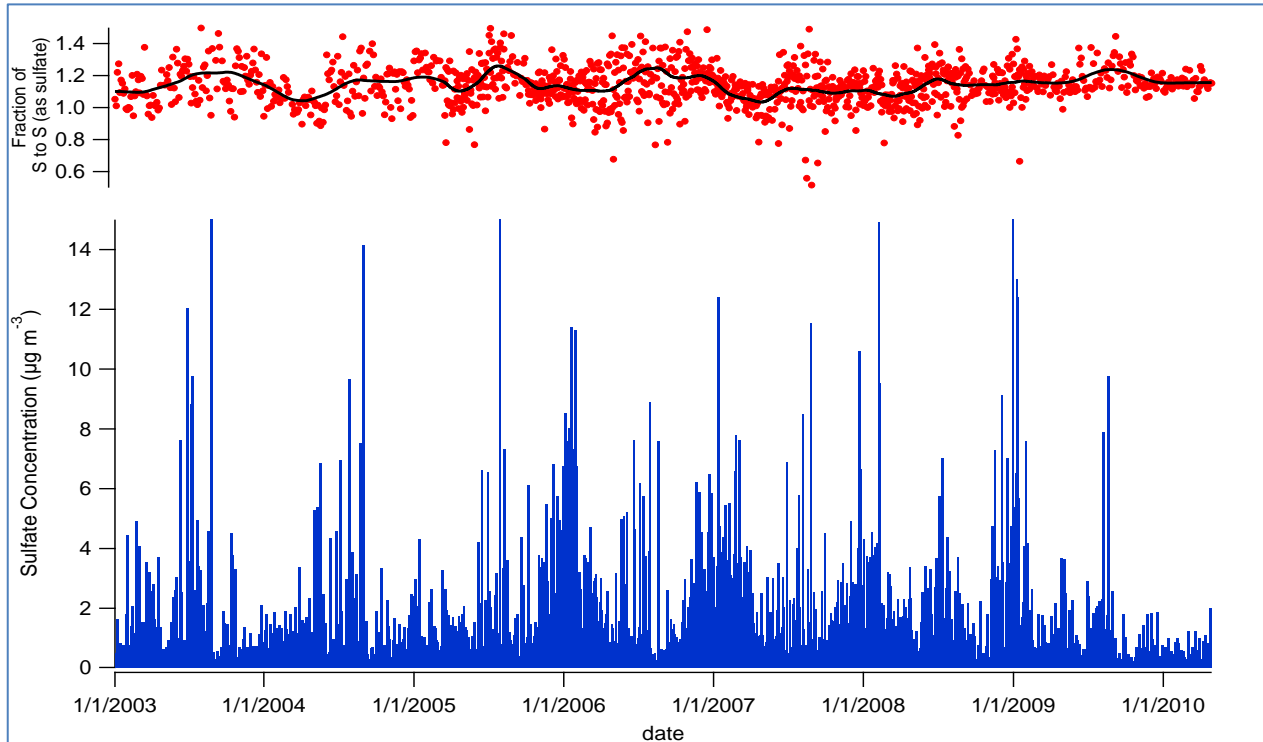

Figure 4: Time series of speciation data collected by FNSB staff since 2003. Data on bottom is daily sulfate measurements, and plot at top represents the fraction of total sulfur to sulfur calculated from measured sulfate. Total sulfur is measured directly by XRF, and sulfate is measured directly by ion chromatography.

pattern in the ratio of sulfur to sulfur (as sulfate). A clear divergence from unity can be observed suggesting that there is a possible unmeasured, stoichiometrically-adjusted sulfur source not captured in a collocated measure of sulfate. This ratio does have broad trends, but they do not appear to correspond with measured sulfate, which appears as highly variable in concentration and time.

Because this study collected its own filter measurements, we can empirically investigate the possibility of 'missing sulfur' by sequential analysis by non-destructive X-Ray Fluorescence Spectroscopy, followed by filter processing and chemical analysis of dissolved ions. The methods

Coefficient values ± 95% Confidence Interval
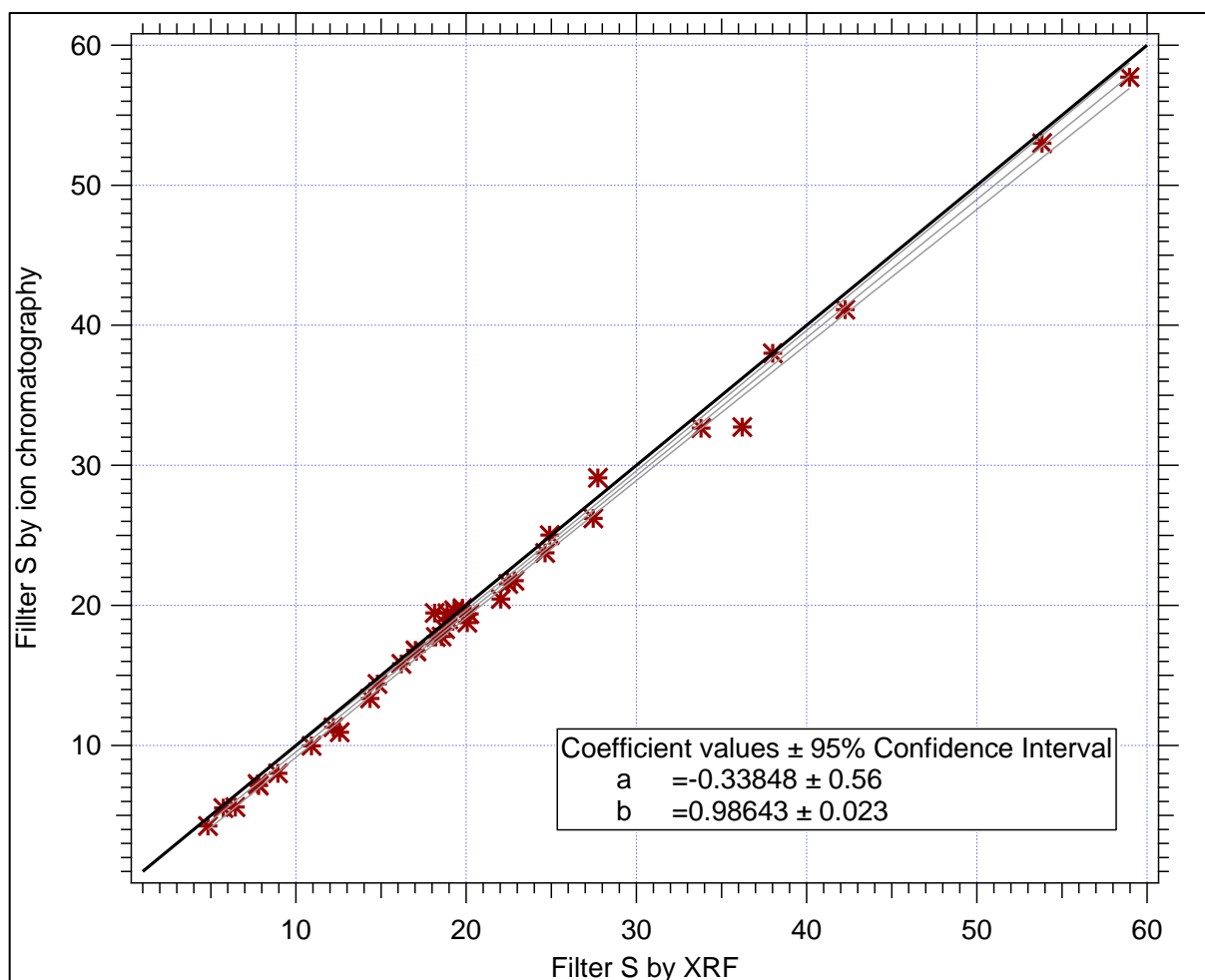a   =-0.33848 ± 0.56
b   =0.98643 ± 0.023

Figure 5: Regression plot of sequentially analyzed filters for sulfur concentration. Filters were first analyzed by XRF followed by ion chromatography for a measure of sulfate. Linear fit coefficients are also included and report a correlation coefficient of 0.97.

for this process were similar to the method used to analyze the aliquots collected by the PILS. The results, as shown in Figure 5, show a very high degree of correlation between measured S as sulfate and directly measured S by XRF. Regression slope approaches statistical unity, with a statistically insignificant intercept. These findings clearly suggest that any bias seen in the presence of sulfur across different measurements are not likely because of a unmeasured sources of ambient sulfur; the most likely explanation is that there is some bias introduced because of methodological reasons such as differential absorption related to different filter materials, systemic bias introduced by post-collection filter processing, or gas-phase intrusion resulting from the extreme cold experienced in Fairbanks. While the answer to this problem is still elusive, it should be noted that sulfur comprises a relatively small fraction of overall PM loading and this small bias, on average, may represent just a few tenths of percent of aerosol (by mass) in the Fairbanks region.

Further analysis follows in the section on preliminary analysis of XRF data.

EC AND OC

By mass, OC was one of the largest contributors to PM2.5 mass observed at this location during the study. EC, which was a much smaller fraction by mass, was well correlated with OC suggesting common sources. Of particular note as illustrated in Figure 6, OC and EC are generally well correlated with one another during this study. The OC to EC ratio was generally between 4-5,
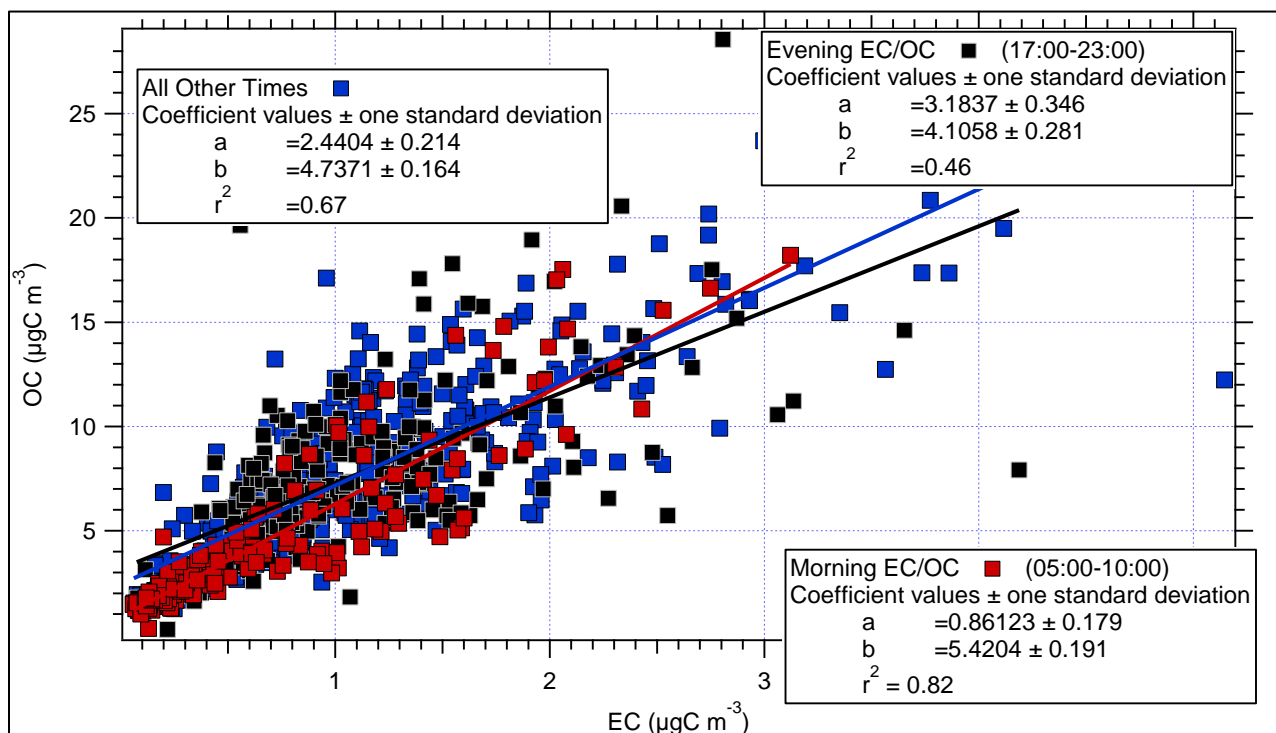

Figure 6: Measured organic carbon compared to measured elemental carbon (collected at same time). Data are binned to different time periods to show comparison between morning, evening, and all other times. Regression statistics are for a linear fit.

which is somewhat higher than urban values reported in the literature [10-14] and is more consistent with the higher values observed in biomass burning plumes [15-18], though this is an overly simplified analysis. More work is indicated to investigate these ratios further. A somewhat different regression was observed when the data were binned between morning, evening, and all other times. Tighter correlations and higher ratios were observed (Figure 6) in the morning compared to the evenings, suggested a different source process is occurring at this time. The lowest ratios and the less correlated data are observed in the evenings, with data from all other times falling between the two. This finding suggests that during morning periods, sources that are attributed to OC and EC (which themselves are tightly correlated) are more likely to emit OC per unit of EC than observed in the evenings. Possible explanations for this may include different combustion characteristics that emit OC and EC that are more conducive for OC formation in the morning compared to the evening. Likewise, combustion conditions in the evening appear to emit less OC per unit EC, providing another line of evidence suggesting different formation mechanisms.

Table 3: Univariate statistics for organic and elemental carbon measured during this study. Reported values include mean, median, standard deviation, range, and the number of measurements collected during this study. Llod denotes measurements below the limit of detection.

	Mean, $\mu g\ m^{-3}$	Median, $\mu g\ m^{-3}$	Std Dev, $\mu g\ m^{-3}$	Range, $\mu g\ m^{-3}$	n
Organic Carbon	6.47	5.92	4.62	(0.03, 33.4)	505
Elemental Carbon	0.90	0.78	0.69	(llod, 3.86)	509

While much remains to be analyzed, it appears that OC and EC in the Fairbanks region are most likely associated with biomass burning. A substantial residential heating demand is required in this community during the winter, and wood burning remains an economically efficient fuel source for the community. Unfortunately, this has resulting in a preponderance of OC and EC in the Fairbanks
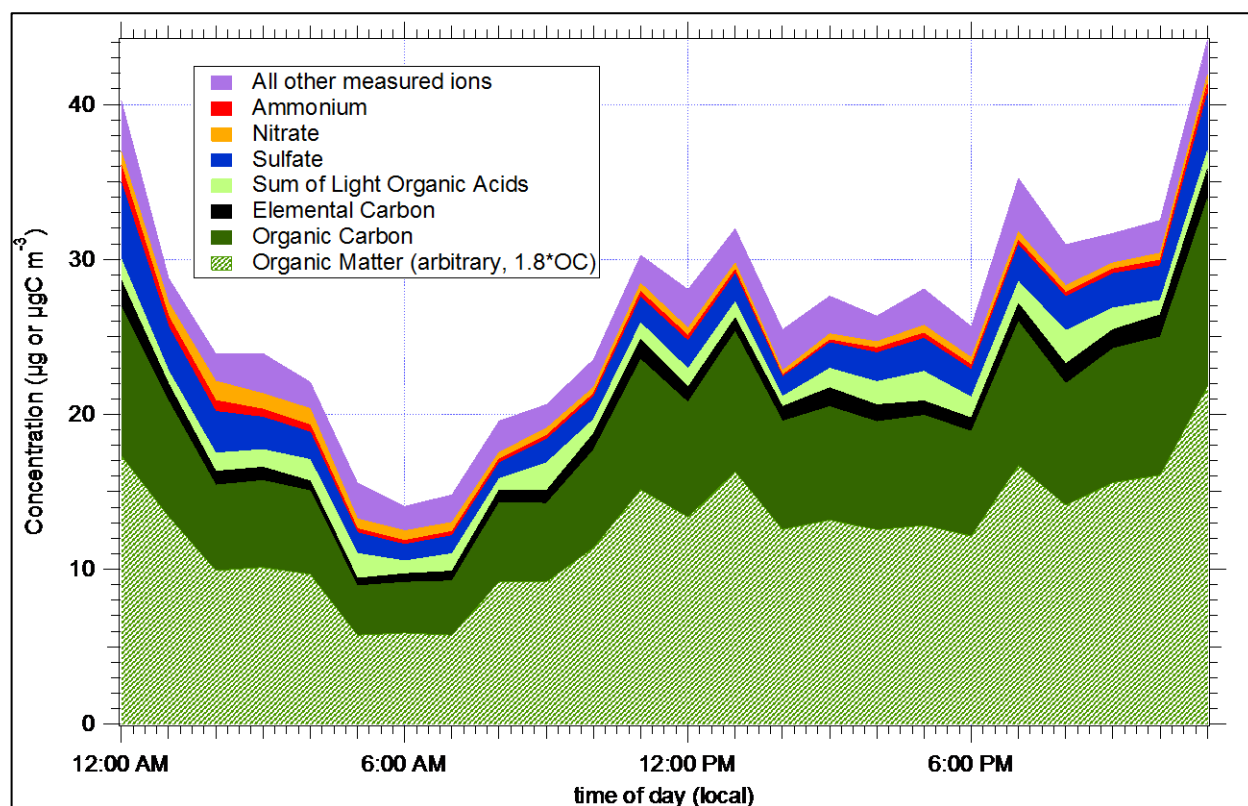

Figure 7: A composite diurnal profile for ~270 hourly measurements of OC, EC, and most ions. Organic matter is estimated as 1.8 times the measured OC value. Data are binned to each hour of the day and the mean value is presented here. Several lesser ions are binned into a separate composite group ('all other measured ions') to simplify this plot

air shed linked to these fuels, and it would be wise to investigate this issue further in hopes to better identify the mechanistic conditions leading to these different emissions profiles.

The data from this study were concatenated into a single, diurnal profile and plotted in Figure 7. While a number of components were measured during this study, organic matter – that is, the functional groups that are part of the organic particle, but not accounted for in the measure of carbon – is only estimated here. We use an arbitrary, but reasonable, value of 1.8 for the OM-to-OC ratio, and included this in the profile. Figure 7 shows a clear drop in concentration in the early

morning, with distinct peaks occurring around noon, 7PM, with highest observations around midnight local time. Ion composition is generally uniform throughout the day with some deviations in sulfate apparent throughout the day. Notable, however, is the dominance of OC and OM across the entire day, with these components reaching a minima around 6AM and a maxima at midnight.

This profile, at least subjectively, is consistent with wood burning as the dominant source of aerosol in this community. One might expect to see a declining emission rate between the evening and early morning as wood burning devices start to self-extinguish; a rapid increase in emissions follows in the morning as there is an increased demand for residential heating. The spike near midnight may be attributed to residential space heaters which are typically refueled to ensure continuous heating through the night and early morning.

XRF (PRELIMINARY)

As part of additional measurement efforts, the Borough has initiated a longer term study in the winter/spring of 2012 using a novel speciation instrument that provides hourly measurements of metal composition from PM2.5. This method is accomplished by way of a newly developed semicontinuous XRF installed at a ground location in Fairbanks. An initial look at this data is enclosed here, but does not represent a full analysis. Univariate statistics describing the dataset, as of 06 Jan 2012 are included in Table 4.

Table 4: Univariate statistics for the range of metals measured during the ongoing field study. Reported values include mean, standard deviation, max, and min values. All data are reported as nanograms per cubic meter, adjusted for standard temperature and pressure. Total number of measurements is 261 as of January 6, 2012, with data collection currently ongoing.

	Average	Stdev	Min	Max		Average	Stdev	Min	Max
SULFUR	868.169	760.360	0.076	3348.000	**ZINC**	42.448	42.982	0.116	254.743
POTASSIUM	158.202	100.821	0.941	568.123	**GERMANIUM**	0.129	0.102	*LLOD*	0.777
CALCIUM	24.719	93.944	*LLOD*	834.172	**ARSENIC**	0.117	0.500	*LLOD*	3.642
SCANDIUM	0.127	0.249	*LLOD*	1.486	**SELENIUM**	0.052	0.065	*LLOD*	0.372
TITANIUM	0.949	0.877	*LLOD*	4.754	**BROMINE**	3.291	3.250	0.049	24.975
VANADIUM	0.084	0.133	*LLOD*	0.729	**RUBIDIUM**	0.220	0.196	*LLOD*	1.122
CHROMIUM	0.087	0.240	*LLOD*	2.242	**STRONTIUM**	2.177	8.863	0.203	127.562
MANGANESIUM	0.525	0.821	*LLOD*	8.083	**SILVER**	54.473	178.273	0.204	1378.000
IRON	27.536	32.076	2.400	280.647	**CADMIUM**	19.157	52.453	1.096	588.461
COBALT	0.020	0.054	*LLOD*	0.504	**BARIUM**	0.930	1.547	*LLOD*	15.086
NICKEL	0.220	0.177	*LLOD*	1.645	**MERCURY**	0.001	0.010	*LLOD*	0.157
COPPER	3.997	3.263	0.918	46.591	**LEAD**	4.443	4.740	0.719	37.569

Transition metals are useful for source identification initiatives to provide quantitative information on elements that are released by specific sources, even if the overall concentrations of the elements are quite small. Figure 8 depicts a time series of concentration following elements with tracers through to mainly derive from coal combustion, although the important caveat that these
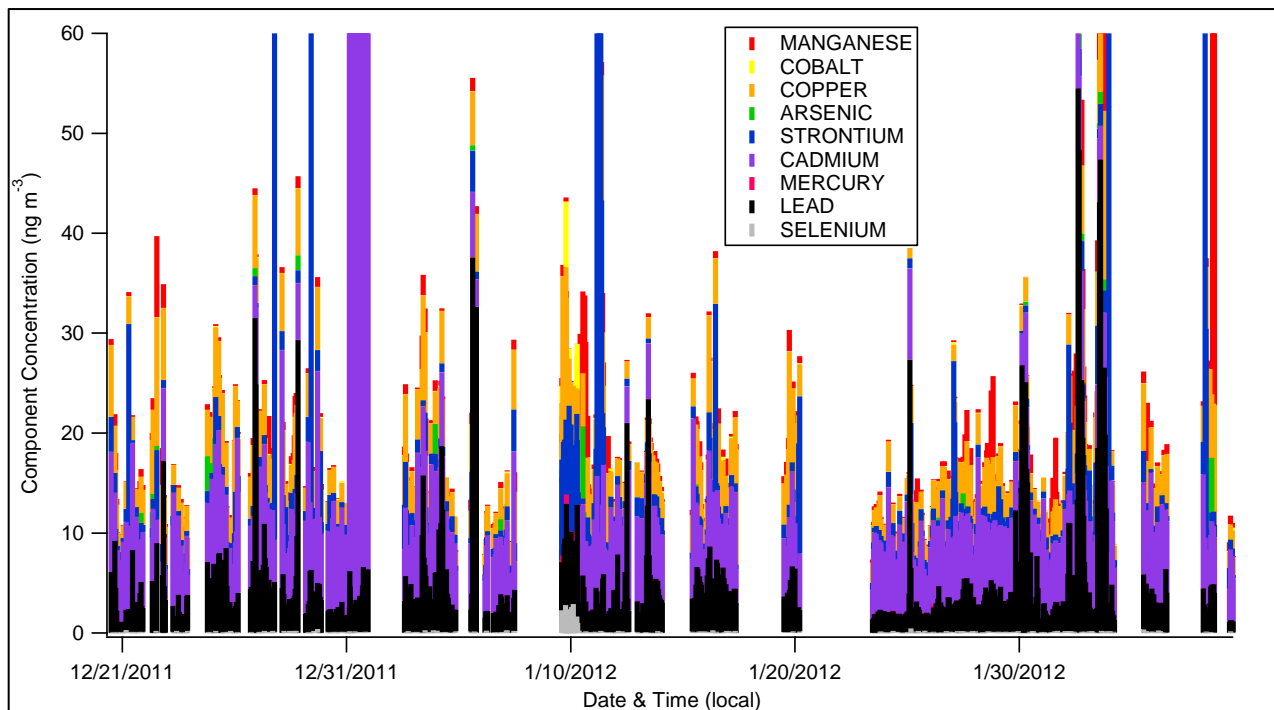

Figure 8: Time series of preliminary XRF data for selected metals thought to be linked to coal emissions. Gaps in data represent periods where the instrument was not reporting data.

components have not yet been confirmed as markers of coal combustion; further analyses to this effect are continuing.

Substantial texture in these elements suggests highly variable influence from coal combustion sources at this location. While overall elemental concentrations are in the single to 10's of nanogram per cubic meter range, some notable trends do appear in the data. For example, strontium has been anecdotally linked to spikes in PM concentration during times when air advection would suggest influence from the nearby coal power plant. Mercury and selenium also appear infrequently, but do so at clearly detectable levels well above a background concentration of less than ~0.5 ng m^{-3} and are generally throughy to be markers of coal combustion.

At least three distinct events are shown in this figure, occurring on January 1, January 12, and Feb 2-3 that warrant greater investigation. The event on January 1 was characterized by nearly 1 microgram per cubic meter of cadium; other elements were also substantially elevated during this time period. Because this event occurred just after midnight, it is likely that this is linked to local fireworks celebrations in the community. While this anecdote has little relevance for the broader air quality problems experienced by the borough, it does show the specificity and power of these measurements in the context of a complex aerosol setting. The other events are characterized by increases in strontium concentration, which is thought to be linked to coal emissions, though other sources may also be responsible for this emission.

It is important to point out that Figure 8 depicts a time series of densely-packed concentration for only a fraction of the elements. Though this approach provides a measure of concentration magnitude and temporal time scales, a more robust approach would be to use statistical modeling techniques to refine this data; such techniques include PMF, PCA, or other source apportionment approaches. It should also be noted that information on 13 additional elements (not plotted here) are also available, and these data are expected to be collected until the end of winter 2012. These approaches are forthcoming and not included in this report.

High time resolution data for sulfur was also exploited to begin investigating sulfur emissions and sulfate formation processes. The time period of study for this was from December 20th, 2011 through January 13th, 2012 and included 417 hourly data points measuring particulate sulfur by
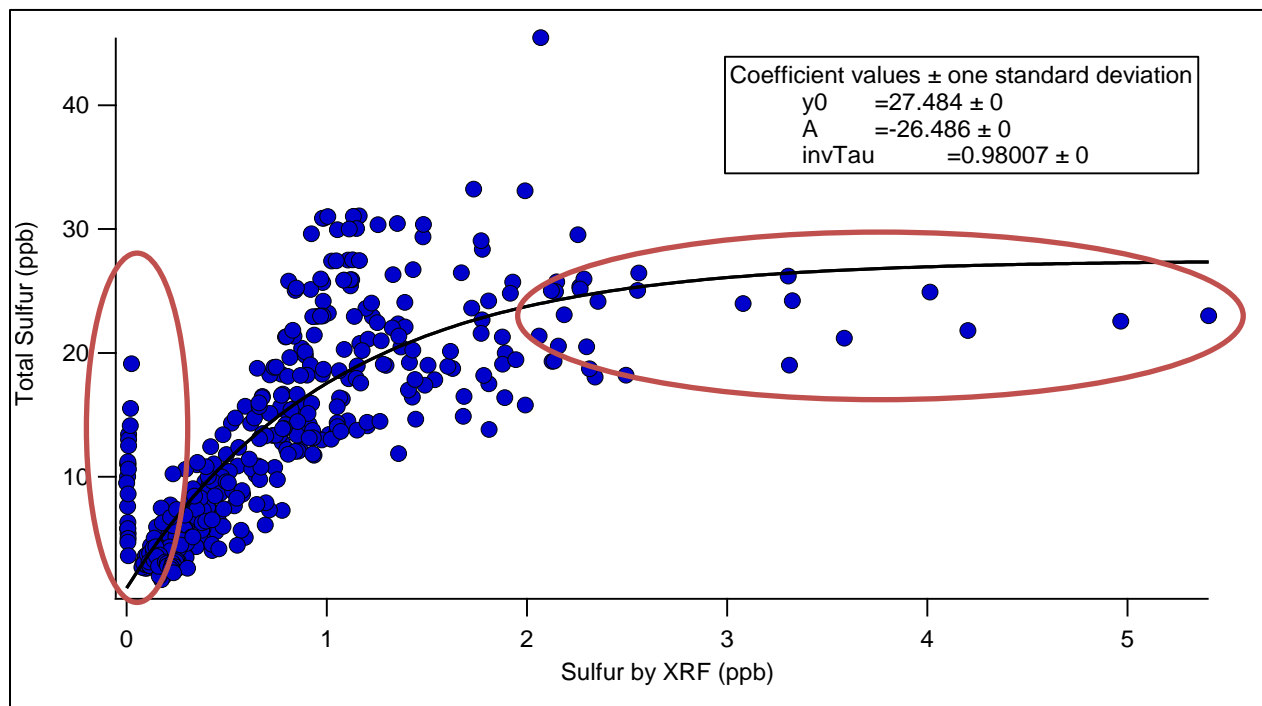

Figure 9: Total sulfur compared to sulfur measured by XRF. Total sulfur is defined as the sum of particulate sulfur by XRF with the sulfur observed in the gas phase as sulfur dioxide. Measurements are collocated. Circled regions highlight two distinct regimes; the left being a regime where particulate sulfate is absent even in the presence of gas-phase sulfur and the second regime (right) where total sulfur appears with a higher fraction in the particulate phase. This second regime may represent the most advantageous conditions for gas-to-particle conversion processes. Fit line is a simple exponential decay function.

XRF and sulfur as sulfur dioxide. Figure 9 plots total sulfur as defined by the sum of particulate sulfur by XRF and sulfur from SO2 compared against total particular sulfur by XRF. At least two different regimes are immediately apparent from this data; one that shows conditions where no aerosol is detected (presumably during precipitation events) and a second where sulfur conversion to particles is effective. In the latter case, an exponential decay appears to describe the latter where SO2 concentrations were generally limited to 25-30 ppb. An exponential curve fit to the data appears reasonable, but greater investigation is warranted. Under most conditions, sulfur conversion is a widely understand chemical process that occurs it he presence of sulfur dioxide, water vapor, and sunlight. The region lacks strong sunlight, and thus the typical mechanism for sulfate conversion is probably quite weak. Nonetheless, the presence of sulfate in the aerosol

stream in Fairbanks confirms that this conversion process exists, and appears to limit SO2 concentration to less than ~30ppb.

In terms of identification of sulfur sources, it is not yet clear where these sources can be attributed. Likely sources include coal power generation, coal residential heating, or combustion of fuel oils for residential heating. Much greater analysis is indicated to develop a more robust profile.

CONCLUSIONS AND FUTURE DIRECTIONS

While data from these studies continues to be collected at the time of writing this report, it is clear from the winter 2011 studies that aerosol chemical composition is complex and unlike any other air shed in the United States. With the exception of occupational environments, it is relatively rare that greater than 20 μgC m^{-3} are observed at any time in US, yet this is typical on cold winter days in Fairbanks. Thus, Fairbanks is subjected to unique and important stressors on its airshed.

The data are consistent with a profile that fits a primary influence from biomass burning. High levels of OC and EC are routinely observed, and follow a pattern one might expect from a community that relies on wood burning to meet sizeable demands for residential heating. EC is well correlated with OC suggesting common sources, and the OC to EC ratio is consistent with sources derived from biomass combustion.

High temporal resolution measurements of ion concentrations showed relatively low (when compared with OC and EC) levels and suggest only a limited influence. Measured ions were dominated by sulfate, ammonium, and nitrate, but only at levels of approximately 10-20% of observed PM2.5 mass. While ions derive from a number of sources, sulfate is mainly derived from coal and non-road distillate combustion, the latter being defined mainly by home heating oil. Because we observed modest concentrations of sulfate (typically 2-4 μg m^{-3}), we cannot exclude these sources as contributors to the air quality concerns in Fairbanks, but they likely play only a minor role in PM2.5 loading in the community.

Combining these measurements, a strong diurnal profile was observed providing further evidence of anthropogenic influence on aerosol composition in Fairbanks. While there was some hour-to-hour variability in ion concentration, the vast majority of the diurnal profile was driven by OC, and the estimated organic material component that was not measured in this study. Further limited analysis examined sulfur concentrations in both gas and particle forms and suggest that there are at least two regimes related to sulfur conversion: one where sulfur remains in the gas phase with only trivial particulate sulfur, and another where sulfur conversion to particulate form appears to follow an exponential decay pattern. This suggests that the conditions necessary for this conversion are, in fact, present.

Future work on this data is extensive. One project includes a comparative analysis with fuel source profiles collected during another investigation by FNSB. By incorporating updated fuel profiles, which provide detailed chemical component information from each type of fuel used in the region, we hope to be able to statistically connect those profiles with the observations in Fairbanks. Another project will incorporate these results into the Chemical Mass Balance modeling currently performed by investigators at the University of Montana. Additional planned analyses include investigating the high time resolution XRF data in much greater detail, with a focus on chemical mass balance and positive matrix factorization modeling, as well as coupling this data with in-progress modification of the CMAQ model for purposes of refining and validation.

REFERENCES

1. Kanakidou, M., et al., *Organic aerosol and global climate modelling: a review.* Atmospheric Chemistry and Physics, 2005. **5**: p. 1053-1123.
2. Seinfeld, J.H. and J.F. Pankow, *Organic atmospheric particulate material*, in *Annual review of physical chemistry, Volume 54, 2003*. 2003, Annual Review. p. 121-40.
3. USEPA. *Review of the national ambient air quality standards for particulate matter policy Assessment of scientific and technical information*. 2005; 514 p.]. Available from: Available online, Government web site, 2005: http://purl.access.gpo.gov/GPO/LPS62787
4. Jacobson, M.C., et al., *Organic atmospheric aerosols: review and state of the science.* Reviews of Geophysics, 2000. **38**(2): p. 267-94.
5. Schauer, J.J., et al., *ACE-Asia intercomparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon.* Environmental Science & Technology, 2003. **37**(5): p. 993-1001.
6. Chow, J.C., et al., *Comparison of IMPROVE and NIOSH carbon measurements.* Aerosol Science and Technology, 2001. **34**(1): p. 23-34.
7. NIOSH, *Elemental carbon (diesel particulate): method 5040*, in *NIOSH Manual of Analytical Methods*, P.M. Eller and M.E. Cassinelli, Editors. 1996, National Institute for Occupational Safety and Health: Cincinatti.
8. Peltier, R.E., et al., *Fine aerosol bulk composition measured on WP-3D research aircraft in vicinity of the Northeastern United States – results from NEAQS.*

Atmospheric Chemistry and Physics, 2007. **7**(12): p. 3231–3247.

9. Peltier, R.E., et al., *No evidence for acid-catalyzed secondary organic aerosol formation in power plant plumes over metropolitan Atlanta, Georgia.* Geophysical Research Letters, 2007. **34**(6): p. 5.

10. Heald, C.L., et al., *A large organic aerosol source in the free troposphere missing from current models.* Geophysical Research Letters, 2005. **32**(L18809): p. 4.

11. Heald, C.L., et al., *Concentrations and sources of organic carbon aerosols in the free troposphere over North America.* Journal of Geophysical Research, 2006. **111**(D23): p. D23S47.

12. Na, K., et al., *Primary and secondary carbonaceous species in the atmosphere of Western Riverside County, California.* Atmospheric Environment, 2004. **38**(9): p. 1345-1355.

13. Turpin, B.J., J.J. Huntzicker, and S.V. Hering, *Investigation of organic aerosol sampling artifacts in the Los Angeles basin.* Atmospheric Environment, 1994. **28**(19): p. 3061-3071.

14. Turpin, B.J. and H.J. Lim, *Species contributions to PM2.5 mass concentrations: Revisiting common assumptions for estimating organic mass.* Aerosol Science and Technology, 2001. **35**(1): p. 602-610.

15. de Gouw, J.A., et al., *Volatile organic compounds composition of merged and aged forest fire plumes from Alaska and western Canada.* Journal of Geophysical Research, 2006. **111**(D10): p. 20.

16. Maxwell-Meier, K., et al., *Inorganic composition of fine particles in mixed mineral dust-pollution plumes observed from airborne measurements during ACE-Asia.* Journal of Geophysical Research-Atmospheres, 2004. **109**(D19).

17. Sullivan, A.P., et al., *Airborne measurements of carbonaceous aerosol soluble in water over northeastern United States: Method development and an investigation into water-soluble organic carbon sources.* Journal of Geophysical Research, 2006. **111**(D23): p. 1-14.

18. Warneke, C., et al., *Biomass burning and anthropogenic sources of CO over New England in the summer 2004.* Journal of Geophysical Research, 2006. **111**(D23): p. 13.