



Experimental characterization of sulfur interference in IMPROVE aluminum and silicon XRF data

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H I G H L I G H T S

- ▶ XRF is used to analyze Si and Al concentrations in ambient PM_{2.5} filter samples.
- ▶ Pure ammonium sulfate fine particles are added to the ambient filters.
- ▶ Si masses from XRF re-analysis are systematically higher. Al has large changes.
- ▶ Implication: IMPROVE Si and Al values have large uncertainties when S/Fe is high.
- ▶ Impacts 50% of IMPROVE data from 2002 to 2010.

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Silicon (Si) and aluminum (Al) are important elements for evaluating soil content in particulate matter. However, these elements are in some cases difficult to measure by X-ray fluorescence (XRF), the method used by the two large particulate matter networks in the U.S., the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network and the Chemical Speciation Network. The IMPROVE network has issued data advisories on Al and Si based on analysis of data from the network's ambient samples. The analysis shows that when sulfur concentrations are high, silicon concentrations can be larger than expected and aluminum may not be detected when it is likely to be present (vista.cira.colostate.edu/improve/data/QA_QC/Advisory.htm). In this research, a laboratory study was undertaken to determine the conditions and extent of measurement uncertainty in Al and Si when sulfur concentrations are high. Three possible causes of the uncertainty are spectral interference due to a low-energy tail on the S peak in the region of Al and Si peaks, attenuation of Si and Al fluorescence by S and the low instrument responses of Si and Al. Ambient samples encompassing the Al and Si mass range in the IMPROVE network and with low sulfur were collected. A layer of ammonium sulfate was sampled onto the deposit in the laboratory. Although the real Si concentrations were unchanged by the addition of pure ammonium sulfate, the Si concentrations reported by XRF were substantially higher. For samples with S/Fe ≥ 8 , Si is over-reported by 6–300% and the Al concentrations have large uncertainties. No sulfur interference is observed for samples with S/Fe < 8 . These measurement errors are expected to occur in 50% of IMPROVE data from December 1, 2001 through December 31, 2010. New XRF instruments with different hardware and software are being utilized by IMPROVE to measure elemental masses for samples beginning January 1, 2011.

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1. Introduction

The Interagency Monitoring of PROtected Visual Environments (IMPROVE) program (vista.cira.colostate.edu/improve/) reports PM_{2.5} (particles smaller than 2.5 μm in diameter) elemental, organic and elemental carbon and inorganic ion concentrations

from more than 160 sites in the U.S., primarily in National Parks and Wilderness areas (Class I areas). IMPROVE speciated PM_{2.5} data are available at the VIEWS website (views.cira.colostate.edu/web/) and serve the regulatory purpose of monitoring visibility at Class I areas in support of the Regional Haze Rule (Pitchford et al., 2007). An important use of elemental data is to determine the soil content in the particles and its impact on visibility. Each year, Crocker Nuclear Laboratory (CNL) at University of California Davis analyzes about 20,000 IMPROVE PM_{2.5} filter samples by energy-dispersive X-ray fluorescence spectrometry (XRF) to obtain concentrations of

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elements from sodium to lead. Summaries and analysis of IMPROVE elemental data can be found in IMPROVE Reports available at the IMPROVE website (vista.cira.colostate.edu/improve/Publications/improve_reports.htm).

Al and Si, which are two of the larger components in soil, may in some cases be difficult to measure by XRF because they can be subject to spectral interferences from the large, nearby sulfur peak, because they can be readily attenuated in the PM matrix and because they can have low instrument responses. One type of spectral interference caused by a large peak (such as sulfur in PM samples) is an incomplete charge effect in XRF detectors producing a non-Gaussian feature, namely a low-energy tail (Campbell, 1996). Low energy tails on intense peaks have been shown to make the determination of peak areas on smaller peaks difficult (Campbell et al., 1986). Si and Al peaks are located in the region of the spectra of the S low energy tail produced in the CNL XRF system (Fig. 1) and are often much smaller peaks than the sulfur peak, leading to difficulties in determining the peak areas of these elements. Non-Gaussian features are accounted for in some spectral software but are not in the software used by CNL. The second reason that Al and Si may be difficult to measure in XRF systems is due to attenuation caused by absorption of emitted fluorescence of low energy elements including Al and Si by the surrounding PM (Formenti et al., 2010). A third reason that Si and Al may be difficult to measure by XRF is that they produce less fluorescence (or have lower instrument response) from a given input of X-ray energy than more efficient elements like S when incoming X-rays are higher in energy than S as are typically used. Less fluorescence from low energy elements like Al and Si causes higher relative analytical uncertainties for these elements compared to higher energy elements with stronger fluorescence in many systems.

The IMPROVE network has issued advisories on Al and Si based on systematic analysis of data from the network's uncontrolled ambient samples. These advisories infer that aluminum goes undetected in many samples when it is present above the reported detection level (White, 2006a), and that aluminum and silicon values can be unreliable in the presence of elevated sulfur concentrations (White, 2006b, 2007). These and other Data Advisories are available on the IMPROVE website (vista.cira.colostate.edu/improve/data/QA_QC/Advisory.htm).

A useful parameter for evaluating the impact of sulfur on Si and Al is the amount of sulfur relative to the amount of soil in the sample. Fig. 2 compares the S/Fe ratio, which gives a measure of the

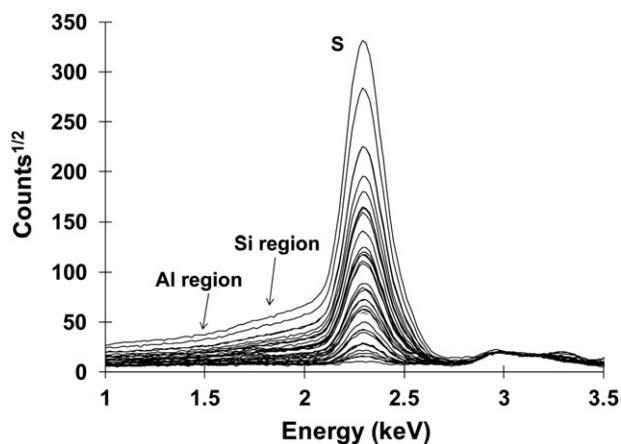


Fig. 1. The sulfur peak and low-energy tail to the left of the sulfur peak in pure ammonium sulfate reference materials analyzed in the CNL XRF system. Sulfur masses are in the range of masses observed in the IMPROVE network. Counts per bin are corrected for dead time and the square root of the counts per bin is plotted on the y-axis to highlight spectral features. The analysis time is 1000 s and the bin size 17 eV.

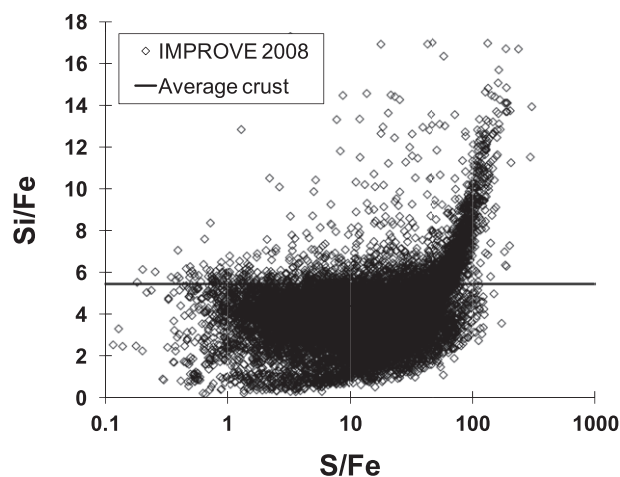


Fig. 2. The relationship between S and Si in IMPROVE network data during 2008. The average Si/Fe ratio in the earth's crust material is shown as a reference (Mason, 1982). Samples with Si/Fe between 18 and 100 are not shown (0.2% of data). Data for this plot was downloaded from the VIEWS website (views.cira.colostate.edu/web/), in September of 2011, and only data above the minimum detection limit (Table 1) are used.

sulfur to soil content, to the Si/Fe for IMPROVE samples in 2008. Since most of the IMPROVE sites are considered rural, and elements Si and Fe generally originate from crustal sources, Si/Fe is expected to be fairly constant at a given site. When estimated from the average amounts of elements in crustal material, the ratio of Si/Fe is 5.5 (Mason, 1982) and the Si/Fe ratio measured by XRF in several ambient soil dusts (PM_{2.5}) in the western US is on average 3.8 (Labban et al., 2004). In the IMPROVE network, the Si/Fe mass ratios are typically between 1 and 6 (Fig. 2). However, some IMPROVE samples have Si/Fe ratios well above six when S/Fe is high (Fig. 2) giving an indication that Si measurements could be incorrect. Si/Fe versus S/Fe IMPROVE data plots for 2002 through 2010 are in the supplemental material (Fig. S1), and are similar to Fig. 2.

The objectives of this work are to determine the conditions under which S concentrations influence the measurement of Si and Al in IMPROVE samples and the extent to which the measurements are compromised under those conditions. Ambient samples with low sulfur concentrations and a wide range of Si and Al concentrations are collected using an IMPROVE sampler and analyzed by XRF. In the laboratory, pure ammonium sulfate particles are layered on top of the ambient samples to create treated samples with a wide range of S/Fe ratios. Although no Si or Al is added to the filter when the sulfur is added, the Si and Al measurements by XRF are expected to change based on the statistical analysis of uncontrolled ambient measurements reported in the data advisories. The difference in reported Si and Al masses from XRF between the treated and untreated samples is calculated to quantify the measurement uncertainty due to sulfur over a wide range of S/Fe. For comparison, a subset of the samples was also analyzed by XRF at a different laboratory.

2. Methodology

Parallel ambient PM_{2.5} samples were collected using IMPROVE samplers at an inland site in Northern California. This site was chosen because it has high concentrations of soil elements but low concentrations of sulfur which produce samples that have Si and Al measurements that are not impacted by sulfur. A total of 143 filters were collected. The samples were analyzed by two different XRF methods and laboratories, namely the CNL XRF method used for

IMPROVE samples at the University of California, Davis, CA, USA and a commercial instrument (PANalytical Epsilon 5) located at the Desert Research Institute (DRI), Reno, NV, USA. Pure ammonium sulfate particles were deposited onto 119 of the ambient filters to generate a range of S to soil ratios equivalent to what is observed in the network. Twenty-four ambient samples were used as controls and had no ammonium sulfate added. Filters with (treated) and without (controls) added ammonium sulfate were re-analyzed by both XRF systems to evaluate the change in element concentrations due to addition of sulfur.

2.1. Sample collection

Eight parallel IMPROVE Type II PM_{2.5} modules (samplers that have been used in the network since 2000) were used to obtain aerosol samples on PTFE membrane filters (Teflo, 25 mm, 3.0 μm pore size, Pall Life Sciences). The PTFE membrane filters are the same filters used in the network for mass and elemental speciation. The samplers are located at a research site surrounded by agricultural fields about two miles west of Davis, CA. Nominal flow rates for all samples were 22.8 L per minute. Aerosol samples were collected from spring through fall of 2009 and 2010. The silicon concentrations in the collected samples (0.02–1.74 μg m⁻³ Si) are similar to that observed in the network (1st and 99th percentiles for 2008 are below MDL to 1.50 μg m⁻³ Si) and Al concentrations (0.01–0.76 μg m⁻³ Al) are similar to that observed in the network (1st to 99th percentiles for 2008 are below MDL to 0.52 μg m⁻³ Al). MDL values for the 2008 IMPROVE data are given in column 2 of Table 1. A few of the samples had larger amounts of Si compared to the network, up to 2.78 μg m⁻³ and larger amounts of Al, up to 1.18 μg m⁻³. All samples collected had S/Fe below 7, indicating that all samples had low S content.

2.2. Sample treatment

Ambient samples were grouped by similar Si and Al measurements and individual samples in each group assigned an amount of ammonium sulfate to be added to produce S/Fe ratios of 0.5–164. No ammonium sulfate was added to at least one sample from each group and these samples were used as control filters. Control filters were analyzed along with the filters with added sulfur and their Si concentrations ranged from 0.03 to 2.78 μg m⁻³ and their S/Fe ratios ranged from 0.3 to 7.

Ammonium sulfate was added to the ambient samples by sampling dry suspended sub-micrometer ammonium sulfate particles onto the filters. A solution of 0.0189 M pure ammonium sulfate (99.999%) and HPLC grade submicron filtered water (W5-4, Fischer Chemicals) was aerosolized by a TSI 3076 atomizer. The particles were dried in a diffusion dryer and mixed with clean dry air (TSI filtered air supply) in a 0.5 m³ mixing chamber before collection in an IMPROVE Type II PM_{2.5} sampler. Prior to adding ammonium sulfate to the ambient filters, the atomizer, chamber

and sampler were operated for 1 h to allow the particle concentration and relative humidity inside the chamber to stabilize. The relative humidity was monitored in the chamber and depositions were made when the relative humidity was 15 ± 3% in the mixing chamber. This relative humidity is well below the deliquescence point of ammonium sulfate aerosol (30–40%) (Onasch et al., 1999). A full description of the generation and sampling system can be found in Indresand et al. (submitted for publication). The system was calibrated so that the deposit mass of ammonium sulfate could be predicted by the sampling time. Ammonium sulfate was added to the ambient filters to obtain total sulfur masses on the filters between 1 and 200 μg. Sulfur above 200 μg/filter produces attenuation of the sulfur X-rays and therefore the sulfur mass is incorrectly measured (Indresand et al., submitted for publication). For samples with high Fe, high S/Fe could not be attained due to the limitation in the amount of sulfur mass that can be correctly measured. However, 200 μg/filter or 6 μg m⁻³ sulfur is near the 99th percentile in the IMPROVE network so lower ratios at high Fe masses is representative of what is observed in the network data.

Mass loadings of the collected PM in samples and the added ammonium sulfate layer were determined by gravimetric analysis with a Cahn 31 balance having a precision of ±2 μg. The balance is housed in an air-conditioned room where the set temperature and humidity in the room are 22 ± 3 °C and 35 ± 5%. Repeated gravimetric analysis confirmed that there was no loss or gain of materials on the samples due to XRF analysis or handling during the study. Samples were stored and transported in Petri dishes at ambient conditions.

A layer of ammonium sulfate on top of a sample with primarily soil components is not typical for ambient samples, but might occur under conditions of shifting wind pattern in a 24 h IMPROVE sample. However, the treated samples mimic what is presented to the XRF instrument detector by a sample with elevated sulfur content compared to soil and so is a reasonable basis for analyzing a sulfur interference.

2.3. X-ray fluorescence analysis

The XRF analysis on the collected and treated filters described above was done by an energy dispersive XRF system developed at CNL that includes a direct excitation from an X-ray tube with a Cu-anode, a Si(Li) detector with attached processing electronics and a chamber for analysis of the sample under vacuum. The copper anode X-ray tube instrument measures elements Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, and Fe. A more complete description of the CNL XRF system can be found in Indresand et al. (submitted for publication). Another XRF system with a Mo-anode system was used to analyze the filters for Pb and Br to correct peak overlap interferences in the S and Al measurements, respectively. The Cu XRF and Mo XRF instruments along with the spectral processing software used by CNL is identified in this paper as the CNL XRF system and was used to analyze IMPROVE samples from 2005 to

Table 1
Minimum detection limits (MDL) and relative uncertainties for the CNL and DRI XRF systems.

Element	CNL XRF system			DRI XRF system		
	MDL (μg m ⁻³)	5th percentile ^a relative uncertainty	50th percentile ^a relative uncertainty	MDL (μg m ⁻³)	5th percentile ^b relative uncertainty	50th percentile ^b relative uncertainty
Al	0.006	13.9%	3.5%	0.009	14.9%	5.7%
Si	0.02	4.1%	1.2%	0.002	3.7%	1.4%
S	0.003	3.4%	0.8%	0.0001	2.1%	0.9%
Fe	0.002	1.3%	0.5%	0.0001	0.3%	0.5%

^a This is the percentile of all filter measurements made for this study by the CNL system including samples prior to treatment, treated samples and controls.

^b This is the percentile of all filter measurements made by the DRI system for this study including samples prior to treatment, treated samples and controls.

2010 (Hand, 2011). An additional Cu-anode system, similar to the one described above, was also used for analyzing IMPROVE samples from 2005 to 2008. From December 1, 2001 until December 31, 2004, a Cu system with samples in a Helium environment was used for IMPROVE samples. Prior to 2001, elements Na through Mn were measured by PIXE. Only the system designated as the CNL XRF system was used to analyze the samples created for this research.

The CNL XRF system utilizes peak processing software called RACE that was developed in the early 1970's (Harrison and Eldred, 1974). Non-Gaussian spectral features such as the low-energy tail on sulfur which can cause spectral interference are not accounted for in RACE. The background subtraction method used for analysis of IMPROVE samples utilizes a very clean blank filter spectrum (Supplemental Material, Fig. S2) that is fit to non-peak regions of the sample spectrum through an iterative procedure prior to subtracting it from the sample spectrum. Matrix correction to account for attenuation of elements in the sample is included in RACE and is based on semi-empirical particle size distribution and sample thickness models. CNL has utilized the RACE software since the 1980's when the IMPROVE program began. As the IMPROVE network expanded and long term monitoring of atmospheric concentrations of PM became an objective, the continuity in spectral processing of samples was emphasized and the IMPROVE data from 2002 to 2010 which we are evaluating in this paper were obtained using RACE. With the weight of federal law-making as the ultimate usage of IMPROVE data, we prefer to be conservative in changing our analysis and we prefer to validate suggested changes to the measurement program based on a full disclosure of the problem. Recently we have taken steps to understand and correct problems with the analysis of important IMPROVE elements such as Al and Si, and our developments are two-fold. We are verifying suspicion cast from data analysis by experimental data as presented in this work and have changed the software and hardware (instruments) used for IMPROVE samples.

For each filter, the change in the Si and Al mass due to the addition of ammonium sulfate is calculated as the percent difference between the measured mass of the element after addition, X , compared to the measured element mass measured prior to addition, X_0 , or $[(X - X_0)/X_0] * 100\%$. X_0 is the "true" or best measurement of element X mass in the sample. Control filters, which do not have any added ammonium sulfate, are analyzed by XRF twice so X for control filters is the value of element X the second time the filters are analyzed and X_0 is the value obtained the first time they are analyzed.

Minimum detection limits (MDLs) for the data from the CNL XRF system, shown in Table 1, are based on the method developed by Hyslop and White (2008a) and are the 95th percentiles of IMPROVE field blanks from 2008.

Uncertainties for IMPROVE element data are reviewed in Hyslop and White (2008b) and include errors associated with X-ray counting statistics, calibration of XRF instruments, collected air volumes and sampling. The uncertainties presented in this paper for the percent differences calculated for Al, Si and Fe before and after addition of ammonium sulfate are propagated from the analytical uncertainties based on counting statistics uncertainties only. The uncertainty due to calibration is not included because the ambient and treated samples were analyzed using the same calibration and close in time. Air volume and sampling uncertainties are not included because we are reporting uncertainties due to the difference between two analyses (before and after treatment) of the same filter. The analytical uncertainty due to counting statistics uncertainty, σ_X , for each element mass, X , is the uncertainty in fitting Gaussian distributions to peaks as described by the Poisson distribution, and is determined for each measurement based on the counts in the sample and the blank. The uncertainty in the percent

difference between the reported concentrations before and after ammonium sulfate addition is defined as $[\sqrt{(\sigma_X^2 + \sigma_{X_0}^2)}]/X_0$, expressed as a percent. Relative analytical uncertainties are highest at the lowest mass concentrations and the values for the CNL system are shown in Table 1 for the 5th and 50th percentiles of all of the mass measurements in this work.

About 32% of the samples were analyzed by a PANalytical Epsilon 5 which employs tungsten X-rays that are irradiated onto a series of secondary targets that emit characteristic excitation X-rays and a germanium (Ge) detector. For elements Na through K, a CaF₂ target was used. Low-energy tails are accounted for in the spectral deconvolution software, Epsilon 5 version 2.0C. Each element is blank corrected using the average mass from a set of blanks. Matrix corrections are not applied. The instrument is optimized for routine analysis of 47 mm filters and any potential impacts of the custom 25 mm filter holders have not been assessed.

The ranges of masses detected in the DRI system for the subset of samples analyzed were 0.002–0.01 $\mu\text{g m}^{-3}$ for Al and 0.10–0.32 $\mu\text{g m}^{-3}$ for Si. Minimum detection limits for analysis of PM samples collected on PTFE membrane filters in the DRI instrument are based on three standard deviations of laboratory blank filters. Table 1 shows typical values for PTFE membrane filters calculated for 25 mm filters used in this study. A portion of the Al measurements was below the typical MDL for Al measurements given in Table 1.

The analytical uncertainty, σ_X , for each element X reported for the DRI data, is the counting statistics uncertainty for the sample plus one standard deviation of multiple laboratory blank measurements (personal communication, Steve Kohl, DRI). The relative counting statistics uncertainty used to calculate the counting uncertainty for each sample is obtained from multiple measurements of a low-mass standard of each element. The percent difference and the uncertainty in the percent difference calculated for each element in the DRI data is the same as for the CNL instrument data with the analytical uncertainty for each measurement σ_X defined for the DRI instrument. The analytical uncertainties from the DRI system for the 5th and 50th percentiles of the mass measurements in this work are shown in Table 1.

3. Results

3.1. X-ray fluorescence spectra

Elements commonly associated with soil (Na, Mg, Al, Si, K, Ca, Ti, Mn, Fe) and sea salt (Na, Mg, Cl) along with sulfur (S) were identified in XRF spectra collected from the ambient samples used in this study. Fig. 3 shows spectra of an ambient sample before and after sulfur addition (Fig. 3a CNL XRF system, Fig. 3b, DRI XRF system). No spectral manipulation such as background subtraction has been performed on these spectra. Only the spectral region near Al, Si and S is shown. (An example of a complete CNL XRF spectrum is shown in Fig. S2 in the Supplemental Material.) The detector counts corrected for dead time per channel are plotted as the square root as is commonly done to highlight spectral features. Fig. 3 shows that Al and Si peaks are located on the left side of the S peak and could be affected by the low-energy tail. The CNL XRF system spectrum of the ambient sample with ammonium sulfate layer (Fig. 3a) shows the low-energy tail to the left of the sulfur peak and the upward shift in the Si and Al peaks compared to the sample without the added sulfur. Although the change in peak height observed in the spectrum is suggestive of a change in the mass measurement, the measured Si (and all elements) mass is dependent on many factors including: spectral background subtraction, spectral deconvolution, calculation of the area of the peak fitted to a Gaussian curve, the calibration, and estimations to

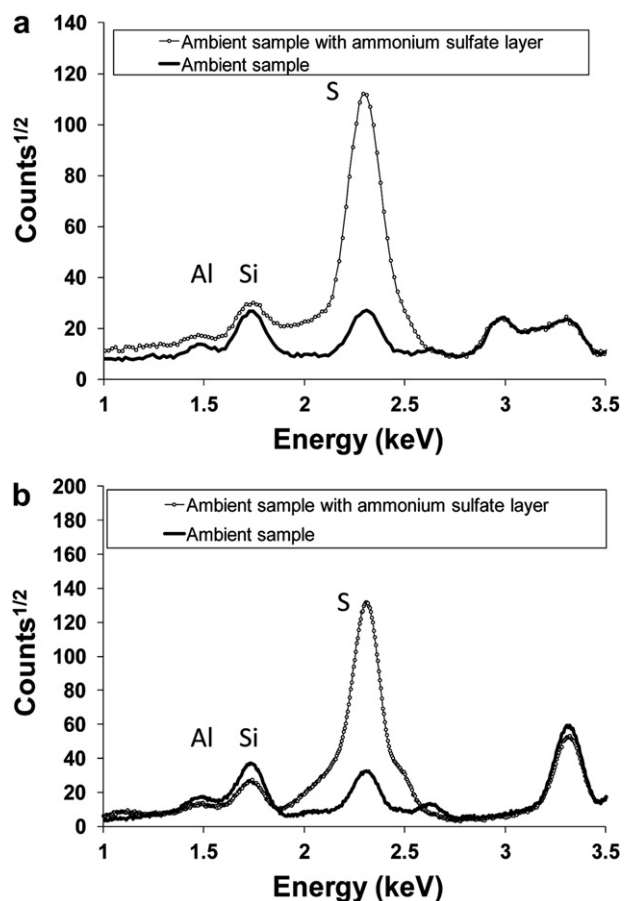


Fig. 3. Spectrum of ambient samples with (treated) and without (prior to treatment) the addition of a layer of ammonium sulfate from a) the CNL system and b) the DRI system. Only the spectral region near Al, Si and S is shown. Counts per bin are corrected for dead time and the square root of the counts per bin is plotted on the y-axis to highlight spectral features. Analysis time is 1000 s for the CNL system and 400 s for the DRI system. The detector bin size is 17 eV for the CNL XRF system and 5eV for the DRI XRF system.

correct for peak overlap and matrix effects (Harrison and Eldred, 1974). In comparison, Fig. 3b shows the spectra from the DRI PANalytical Epsilon 5 system. The sulfur tail shape is different, and a decrease in the Si and Al peak height after the addition of the sulfur is observed. For the PANalytical system, the final elemental mass measurements are dependent on: spectral deconvolution with peak overlap corrections, calculations of the area of the peak fitted to a Gaussian curve, the calibration, and subtraction of blank values. The observed changes in Al and Si mass after the addition of S reported below are based on spectra that have been processed using the spectral processing described above.

3.2. Change in element masses due to sulfur in CNL XRF system

Iron is used as a reference for soil content in the ambient samples because Fe has an XRF energy higher than S (6.5 keV, Fig. S2) and is not expected to be affected by addition of sulfur to the samples. Fig. 4 shows the percent change in Fe for treated and control ambient samples as a function of S/Fe ratios. The plot shows that there is no observed change in Fe in treated samples compared to controls which are on the order of $\pm 4\%$. Ninety four percent of the samples are within controls ($\pm 4\%$), and the rest of the data have differences that are within $\pm 9\%$. Furthermore, a linear regression of the Fe measurements before and after addition of sulfur has a slope of 0.99 and a correlation coefficient of 0.999. These results show

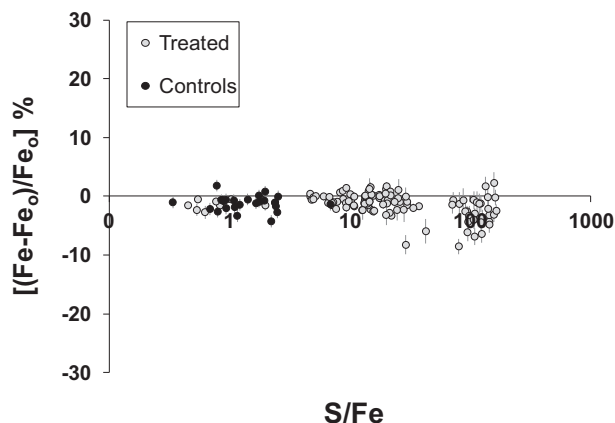


Fig. 4. Percent change in measured Fe mass as a function of S/Fe after addition of ammonium sulfate (sulfur) to ambient samples, as analyzed by the CNL XRF. Control filters are ambient samples that do not have ammonium sulfate added. All measured concentrations are above the MDLs given in Table 1. The vertical error bars are the uncertainty in the percent change determined from the analytical uncertainty in each measurement. The error in S/Fe is negligible.

that Fe is not affected by a sulfur interference and that the precision in the Fe measurement is good.

Large increases in the Si measurement are observed in the data from the CNL XRF system as shown in Fig. 5. The percent change in measured Si increases with increasing S/Fe and was shown to be up to 3 times higher than the initial Si measurement. These measurement uncertainties do not correlate with initial Si mass and are not accounted for by the analytical uncertainties shown as error bars in Fig. 5. When the S/Fe ratio is below 8, the change in Si is comparable to untreated filters ($\pm 6\%$) for most filters, and all are within $\pm 10\%$. These results show that the quantification of Si is compromised for filters with high sulfur compared to soil content, that the analytical uncertainties do not adequately account for the large observed differences and that for these samples an enhancement of Si mass is observed.

Aluminum's XRF peak is lower in energy than Si and is also affected by the sulfur tail. Fig. 6 shows the percent change in Al as a function of S/Fe ratios. When S/Fe is below 8 most of the samples are within the control levels ($\pm 13\%$) and all are within $\pm 20\%$. When S/Fe is 8 or above but less than 70, Al measurements after addition

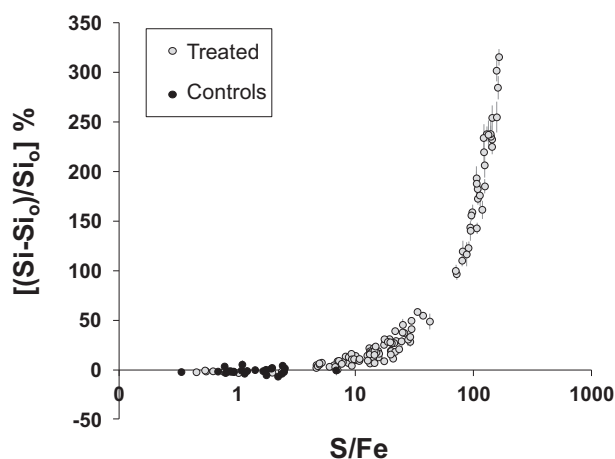


Fig. 5. Percent change in measured Si mass as a function of S/Fe after addition of ammonium sulfate (sulfur) to ambient samples, as analyzed by the CNL XRF. Control filters are ambient samples that do not have ammonium sulfate added. All measured concentrations are above the MDLs given in Table 1. The vertical error bars are the uncertainty in the percent change determined from the analytical uncertainty in each measurement. The error in S/Fe is negligible.

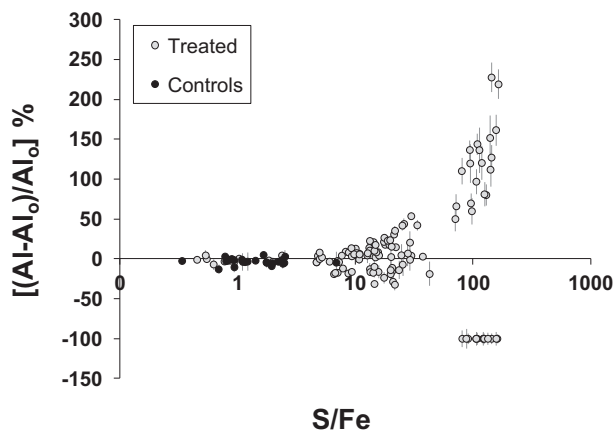


Fig. 6. Percent change in measured Al mass as a function of S/Fe after addition of ammonium sulfate (sulfur) to ambient samples, as analyzed by the CNL XRF. Control filters are ambient samples that do not have ammonium sulfate added. All measured concentrations are above the MDLs given in Table 1. The vertical error bars are the uncertainty in the percent change determined from the analytical uncertainty in each measurement. The error in S/Fe is negligible.

of sulfur are different by $\pm 50\%$ or more with no consistent trend as to the direction of the difference. At S/Fe greater than 70, the XRF analysis did not detect Al in some of the samples while other samples show increases of Al from 50% to over 200%. Because there are no samples with S/Fe between 45 and 70, it is possible that Al is not detected in samples with S/Fe as low as 45. The changes observed for Al are not a function of the initial Al mass. The inconsistent behavior of the Al results is due to measurement uncertainty not captured by the analytical uncertainties shown in Fig. 6. Like Si, these measurement uncertainties are due to the addition of sulfur and the behavior of the Al measurements is somewhat different than that observed for Si. Additional work is needed to fully understand the reason(s) for these differences.

3.3. Change in Si and Al mass due to S in another XRF instrument

Thirty-two percent of the samples were analyzed in a second XRF system, the PANalytical Epsilon 5 at DRI. XRF spectra are collected to compare responses for Si and Al due to high S in an instrument with

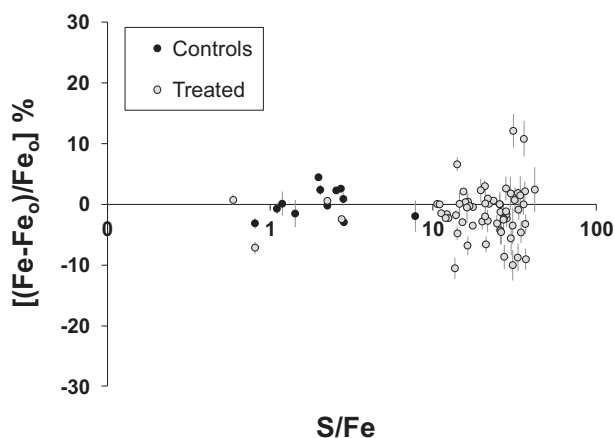


Fig. 7. Percent change in measured Fe mass as a function of S/Fe after addition of ammonium sulfate (sulfur) as analyzed by the DRI XRF of a subset of the samples shown in Figs. 4 through 6. Control filters are ambient samples that do not have ammonium sulfate added. All measured concentrations are above the MDL given in Table 1. The vertical error bars are the uncertainty in the percent change determined from the analytical uncertainty in each measurement. The error in S/Fe is negligible.

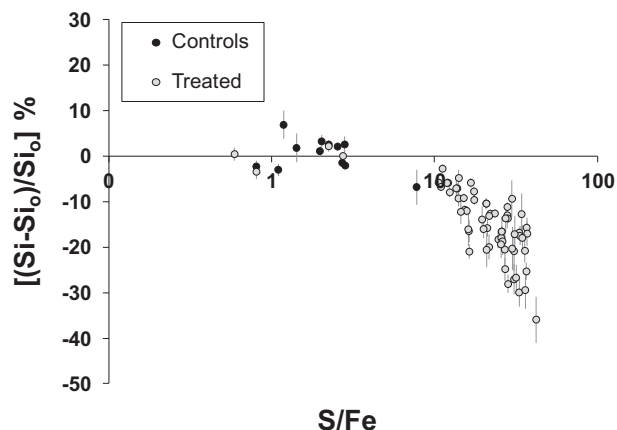


Fig. 8. Percent change in measured Si mass as a function of S/Fe after addition of ammonium sulfate (sulfur) as analyzed by the DRI XRF of a subset of the samples shown in Figs. 4 through 6. Control filters are ambient samples that do not have ammonium sulfate added. All measured concentrations are above the MDL given in Table 1. The vertical error bars are the uncertainty in the percent change determined from the analytical uncertainty in each measurement. The error in S/Fe is negligible.

very different hardware and software that accounts for tails. As with the analysis of IMPROVE data, Fe is used as a reference element. Fig. 7 shows the percent change in Fe as function of the S/Fe ratio. Seventy-nine percent of the data is within the reproducibility of the controls ($\pm 5\%$) and most is within 10%. Moreover, the correlation for Fe measured before and after sulfur addition is 0.98 with an $R^2 = 0.999$. Similar to the results from the CNL method used for IMPROVE, Fe is not affected by sulfur.

Fig. 8 shows the change in Si mass as a function of S/Fe ratios measured by the DRI method. For S/Fe < 8, Si masses are with controls ($\pm 7\%$). However, unlike the trend observed in the CNL XRF system, Si mass decreases with increasing S/Fe ratio. These results show that the low-energy element X-rays from Si can be attenuated by the layer of ammonium sulfate which produces an under-reporting of Si mass when the attenuation is not properly accounted for. The analytical uncertainties for Si (error bars in Fig. 8) do not predict the observed uncertainty in the Si data when the S/Fe ratio is large. The change to Al masses due to the addition of sulfur (Fig. 9) is similar to the change in CNL XRF masses for S/Fe < 70 (analysis was not done for higher ratios on the DRI instrument). Aluminum is

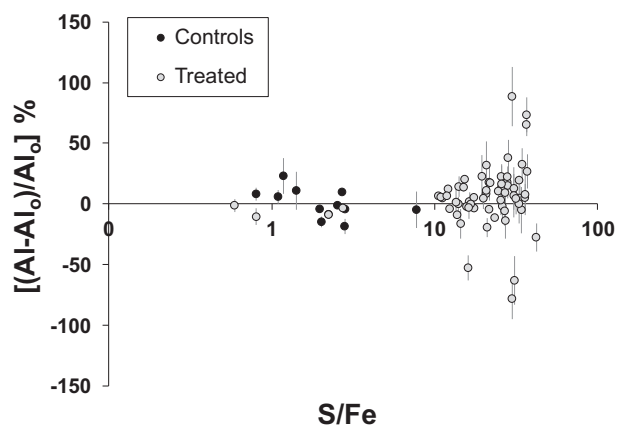


Fig. 9. Percent change in measured Al mass as a function of S/Fe after addition of ammonium sulfate (sulfur) as analyzed by the DRI XRF of a subset of the samples shown in Figs. 4 through 6. Control filters are ambient samples that do not have ammonium sulfate added. The vertical error bars are the uncertainty in the percent change determined from the analytical uncertainty in each measurement. The error in S/Fe is negligible.

within control values ($\pm 20\%$) for $S/Fe < 8$ but large differences occur for some samples at higher S/Fe ratios and they do not follow a consistent pattern. Further research is required to fully understand this behavior.

3.4. Study relevance and recommendations for using IMPROVE data

The results from this study are combined with 2008 data from IMPROVE in Fig. 10, to illustrate the relevance of this study to IMPROVE data. The Si_0/Fe ratios in ambient (prior to treatment) samples, denoted by Si_0 in the figure, collected in this study are on average 3 and the S/Fe ratios are below 7 which is within the range ($S/Fe < 8$) that Si mass measurements are not impacted by S. The treated ambient samples (denoted by Si in the figure) have S/Fe and Si/Fe ratios throughout the range observed in the network. The data from this study mimics the IMPROVE data which suggests that we have reproduced the effect of the sulfur interference on Si well.

The following specific recommendations are made for using IMPROVE Si and Al data from December 1, 2001 through the end of 2010. Samples with $S/Fe < 8$ are not affected by sulfur interference. This accounts for 49% of the data in 2008. Samples with $S/Fe > 70$ account for 4% of the data in 2008. For these data, Si is likely over-reported by a factor of 2 or more. Aluminum is either over-reported by 50% or more or erroneously reported as below the MDL. This data should be used with extreme caution. Samples with $8 \leq S/Fe < 70$ account for 47% of the data in 2008 and for this group, Si is over-reported by up to 100% and Al is misreported by $\pm 50\%$ or more. This data should be used with caution. Because Fe is used to represent the soil component in the atmosphere, these recommendations should not be applied to samples expected to have large impacts from urban sources of Fe.

An additional tool to evaluating IMPROVE Si and Al data is to plot S/Fe vs. Si/Fe as shown in Figs. 2 and 10. If the Si/Fe ratio is reasonably independent of S/Fe , as is shown by the Si_0 data in Fig. 10, then it is unlikely that the interference documented here is significant. However, if the Si/Fe ratio increases with increasing S/Fe (this is shown by the data labeled Si in the figure), then it is likely that these measurements are incorrect. This graphical technique is of limited value if the site(s) of interest are subject to soil-derived $PM_{2.5}$ from varied sources with greatly different Si/Fe or urban sources of Fe.

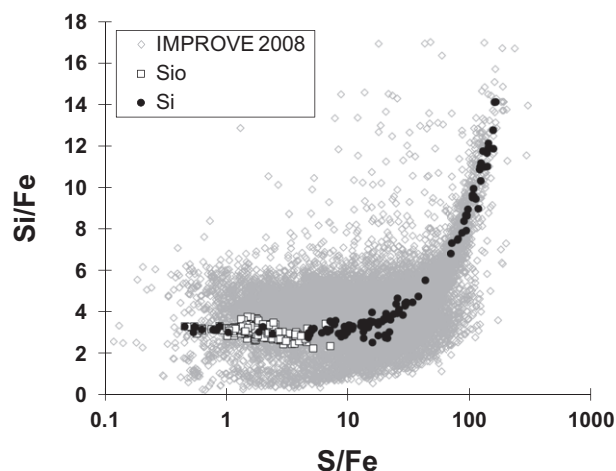


Fig. 10. IMPROVE network data for 2008 (the same data as shown in Fig. 2) plotted with results from ambient samples collected in this study. Values are shown for all filters both prior to treatment (Si_0) and after treatment (Si) by the addition of ammonium sulfate.

4. Conclusions

Experimental results show that Si and Al mass measurements are misreported when sulfur relative to soil content, evaluated using S/Fe , is high in IMPROVE samples. These uncertainties in Si and Al masses were measured by collecting ambient samples over a range of Si and Al masses and low sulfur content, analyzing them by XRF, modifying the samples by adding a layer of ammonium sulfate and re-analyzing the filters. For 50% of IMPROVE data from 2002 to 2010, the S/Fe is less than 8 and the measurement of Si and Al are not impacted by the sulfur content in the sample. For samples with higher sulfur relative to soil content (higher S/Fe) large uncertainties in both Si and Al are observed. For Si, the reported mass on the treated samples increases with increasing S/Fe and is higher than the untreated ambient samples by up to 300%. The enhancement in the Si data is likely due to the low-energy tail spectral interference by S in the CNL XRF instrument that is not accounted for in CNL's spectral processing software. Aluminum measurements on the treated samples have increasing uncertainty in the reported mass with increasing S/Fe but no pattern to predict when a result is over or under-reporting the ambient mass. Analyzing the same samples with a different XRF instrument shows that the low-energy X-rays from Si can be attenuated by the layer of ammonium sulfate causing an under-reporting of Si when the attenuation is not accounted for. This laboratory study confirms the existence of a sulfur interference in the CNL XRF system that had earlier been suggested by statistical analysis of uncontrolled ambient measurements in the IMPROVE network and reported to data users through data advisories. The results apply to IMPROVE data from December, 1, 2001 through December 31, 2010. CNL is utilizing PANalytical Epsilon 5 instruments for XRF analysis of IMPROVE samples beginning January 1, 2011.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.atmosenv.2012.06.079>.

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