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Characterization of atmospheric aerosols in the Adirondack Mountains using PIXE, SEM/EDX, and Micro-Raman spectroscopies

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ABSTRACT

We are making detailed measurements of the composition of atmospheric aerosols collected in the Adirondack Mountains as a function of particle size using proton-induced X-ray emission, scanning electron microscopy with energy-dispersive X-ray spectroscopy, and Micro-Raman spectroscopy. These measurements provide valuable data to help identify the sources and understand the transport, transformation, and effects of airborne pollutants in upstate New York. Preliminary results indicate significant concentrations of sulfur in small particles that can travel great distances, and that this sulfur may be in the form of oxides that can contribute to acid rain.

1. Introduction

A 1.1-MV tandem Pelletron accelerator (NEC Model 3SDH) has been used for many years at Union College, primarily as a teaching tool in a few courses and for some senior thesis projects. Over the last five years we have made a number of improvements to the accelerator and associated instrumentation [1], and have started an undergraduate research program in ion-beam analysis (IBA) of environmental materials such as aerosol, soil, plant, animal, and water samples [2]. One of our current projects is focused on the study of airborne pollution in the Adirondack Mountains of upstate New York.

Atmospheric aerosols consist of particulate matter (PM) suspended in the atmosphere. Some of the environmental effects of aerosols include reduction of visibility [3], climate change [4], acid rain [5], and dangerous health effects [6]. The effects are closely tied to the size of the particulate matter. For example, PM $\leqslant$0.1 μm in diameter are almost transparent to visible light while PM $\geqslant$0.5 μm are very efficient in scattering light. Also, PM $\leqslant$2.5 μm in diameter pose particular health risks because they can be inhaled into the lungs and transport toxic metals like Pb and Hg into the blood stream. The PM size distributions are also vital for understanding transport and removal processes and are very useful in identifying sources. For example, the lifetime of particles in the lower atmosphere ranges from minutes for PM $\approx$ 5 μm to around 8 days for PM $\approx$ 0.3 μm in diameter [7].

Of particular concern in the Adirondacks for the last 40 years is acid rain, believed to be caused by oxides of N and S from industry and coal combustion as far away as the Midwest. The acid rain problem has been abated somewhat over the last 20 years with new emission controls on industry and coal-fired power plants, but rain in the Adirondacks is still quite acidic [8].

In this paper, we report on some results of our study of airborne, particulate-matter pollution in the Adirondack Mountains as a function of particle size. The primary IBA technique used to characterize the aerosols is proton-induced X-ray emission (PIXE) [7]. We have also performed preliminary investigations using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM/EDX) to obtain elemental information on individual aerosol particles, and Micro-Raman spectroscopy (MRS) to extract chemical information.

2. Experimental methods

2.1. Sample collection

The samples discussed in this paper were collected at Piseco Lake in the Adirondack Mountains of upstate New York in July and September of 2012 and August of 2013. They were collected with a PIXE International, nine-stage, cascade impactor that separated the particulate matter by aerodynamic diameter and deposited it on thin

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(7.5 μm) Kapton foils. In each sampling period, air was drawn through the impactor at a rate of 1 L/min for approximately 48 h.

2.2. PIXE experiments

The PIXE experiments were performed in the Union College Ion-Beam Analysis Laboratory. Proton beams with energies of 2.2 MeV from the 1.1-MV tandem Pelletron accelerator were incident on the impacted Kapton foils positioned in the center of a multipurpose scattering chamber [1]. The beams had currents of 8–12 nA and diameters of 1–2 mm. A charge of 30 μC was collected on each sample and 1 μC was collected on Al, Ti, Fe, Cu, Ge, Au, and Pb MICROMATTER standards. The X-rays were detected with an Amptek silicon drift detector with a resolution of about 140 eV and an effective solid angle of approximately 0.74 msr. The X-ray energy spectra were analyzed using GUPIX software.

2.3. SEM/EDX measurements

Preliminary SEM/EDX measurements were performed on some of the samples to get elemental information on individual aerosol particles. The particles were imaged with a Zeiss EVO50XP SEM and X-ray energy spectra were measured using a Bruker Quantax 200 EDX system with a Peltier-cooled XFlash silicon detector. The aerosol samples were coated with a thin layer of conductive material before the measurements were performed.

2.4. Micro-Raman measurements

The MRS measurements were performed using a Senterra MRS system to obtain molecular information on the aerosol samples. The samples were illuminated with a diode laser with a power of 100 mW and a wavelength of 785 nm. The scattered light was dispersed with a 1200 ab grating and detected with a CCD detector. In addition to the aerosol samples, spectra were taken on a blank Kapton foil and a number of standards prepared to help us interpret the results.

3. Results

3.1. PIXE

Shown in Fig. 1 is a comparison of PIXE spectra taken on an aerosol sample consisting of particulate matter with an aerodynamic cutoff diameter of 1 μm (blue) and a blank Kapton foil (red). The measured concentrations in mass per unit area on the Kapton foils for each element and particle size group for the samples collected in July of 2012 are shown in Fig. 2. Significant concentrations of Si, P, S, K, Ca, and Fe were measured in many of the PM bins. Trace amounts of Cl, Ti, Mn, Cu, and Zn were also observed in several PM bins.

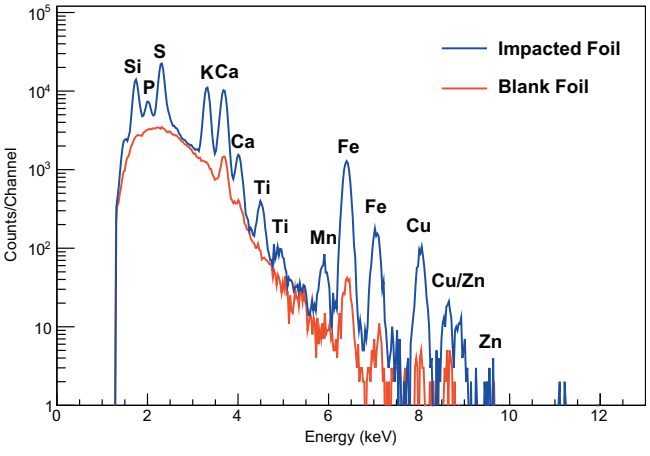

Fig. 1. A comparison of PIXE spectra taken on an aerosol sample consisting of particulate matter (PM) with an aerodynamic cutoff diameter of 1 μm (blue) and a blank Kapton foil (red).

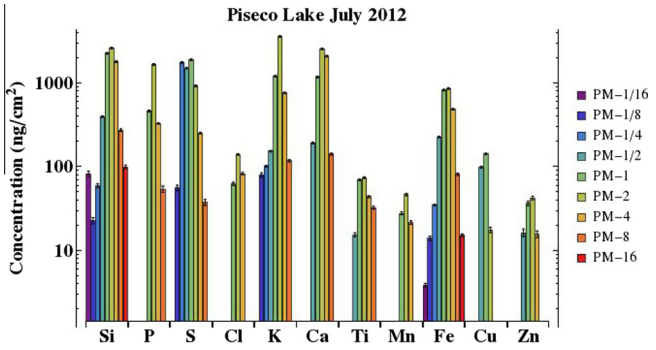

Fig. 2. A bar graph of the measured concentrations in mass per unit area on the Kapton foils for each element and particle size bin for samples collected in July of 2012.

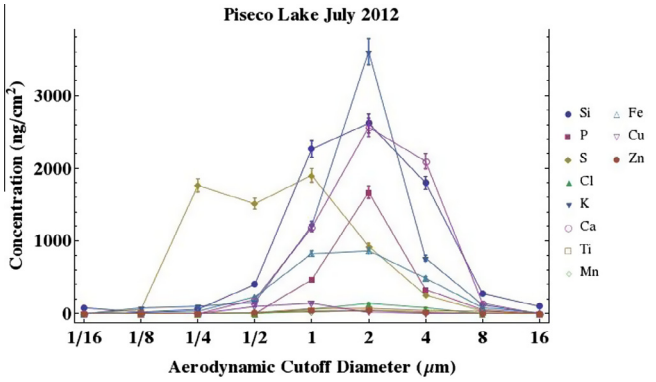

Fig. 3. A graph of the measured concentrations in mass per unit area as a function of aerodynamic cutoff diameter for each element.

The measured concentrations in mass per unit area as a function of aerodynamic cutoff diameter for each element in the July 2012 samples are shown in Fig. 3. This graph shows a characteristic bimodal distribution [7]. The sulfur concentration peaks at PM sizes between 1/4 and 1 μm, while the other elements with significant concentrations (Si, P, K, Ca, and Fe) peak between 1 and 4 μm in size. Primary sources of sulfur are coal combustion and industry, and the small sulfur-containing particles can be suspended in the air for long periods of time and may come from sources very far away. The elements in the larger particle size group suggest the source is most likely soil.

We measured the areas of the aerosol deposits on the Kapton foils from microscopic images for PM 1/4–4 μm. It was not possible to determine the areas for the two smallest and two largest PM bins because the deposits were not visible. Using the measured deposit areas, the flow rate through the impactor, the sampling time, the average temperature and pressure during the sampling period, and the concentrations in mass per unit area, we calculated the concentration in mass per unit volume of air for each element in PM 1/4–4 μm. The results are shown in Fig. 4.

The PIXE data taken on the samples collected in September of 2012 and August of 2013 show very similar distributions to those displayed in Figs. 2–4.

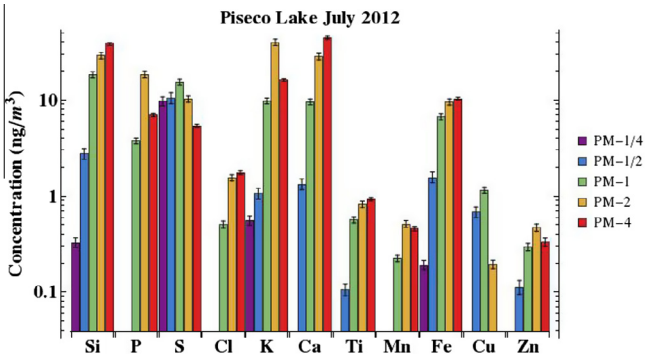

Fig. 4. A bar graph of the measured concentrations in mass per unit volume of sampled air for each element and particle size bin for samples collected in July of 2012.

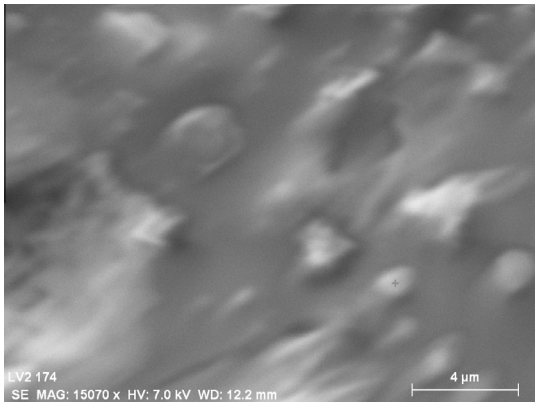

Fig. 5. An SEM image of aerosol particles with PM 1 µm on a Kapton impaction foil.

3.2. SEM/EDX

Shown in Fig. 5 is an SEM image of aerosol particles with PM 1 µm on a Kapton impaction foil. A typical EDX spectrum taken on one of the particles is shown in Fig. 6. Spectra taken on many of the particles in the PM-1 sample show sulfur and oxygen in approximately the same ratio suggesting the presence of sulfur oxides. A quantitative EDX analysis has yet to be performed to determine the oxygen to sulfur ratio in these particles.

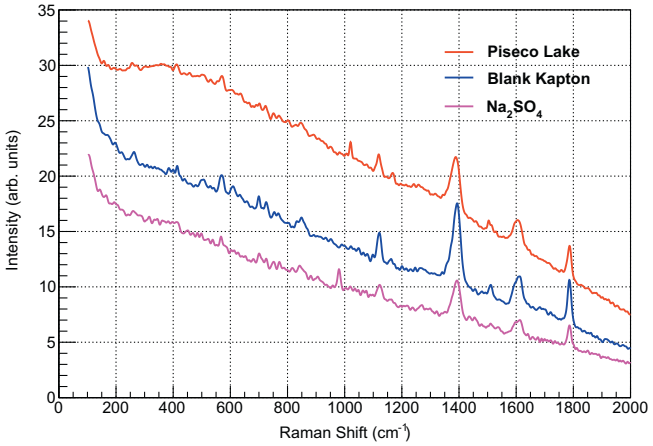

Fig. 7. Micro-Raman spectra taken on a PM-1 sample from Piseco Lake (red), a blank Kapton foil (blue), and a Na_2SO_4 solution dried on a Kapton foil (magenta).

3.3. Micro-Raman

Micro-Raman spectra taken on a PM-1 sample from Piseco Lake (red), a blank Kapton foil (blue), and a Na_2SO_4 solution dried on a Kapton foil (magenta) are shown in Fig. 7. Many of the peaks in the spectra from the Piseco Lake sample and the Na_2SO_4 standard clearly come from the Kapton foils. However, there is a peak around 1000 cm^{-1} that is present in the spectra from both the Piseco Lake sample and the Na_2SO_4 standard that is not in the spectrum taken on the Kapton foil. The peak just below 1000 cm^{-1} in the Na_2SO_4 spectrum is consistent with the strong peak at 980 cm^{-1} reported by Fung et al. [9] to correspond with the SO_4^{2-} sulfate ion. The peak in the Piseco spectrum is displaced slightly

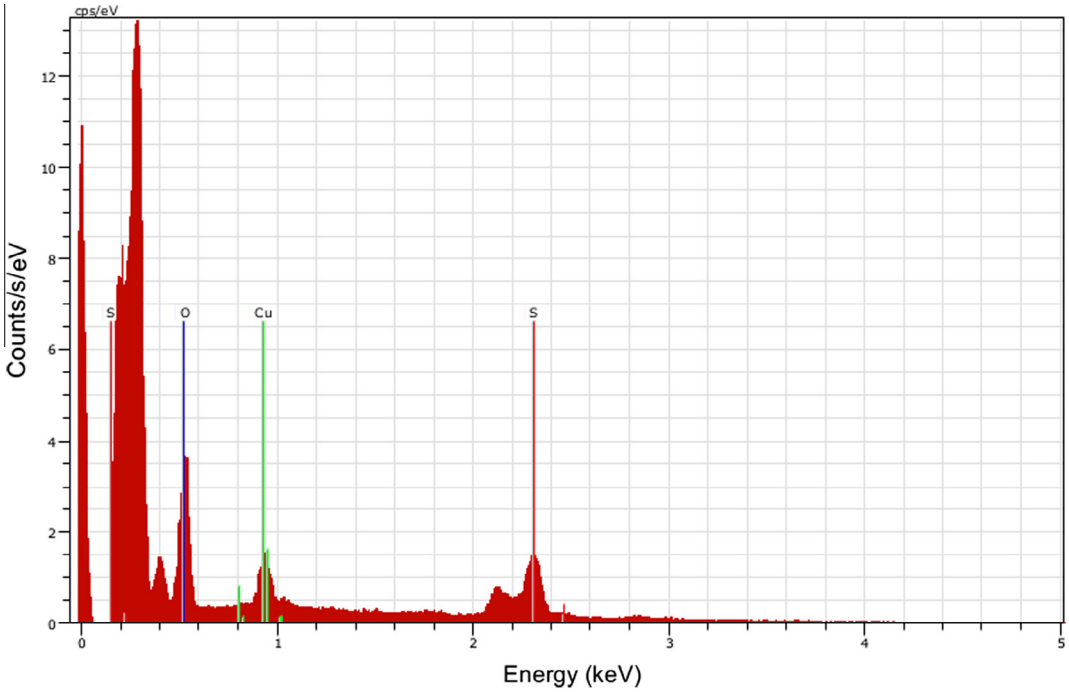

Fig. 6. An EDX spectrum taken on an individual aerosol particle.

to higher Raman shift but may well be due to the presence of this sulfate ion. Clearly more Micro-Raman work needs to be performed before firm conclusions can be drawn.

4. Summary

We are working on the characterization of atmospheric aerosols using PIXE, SEM/EDX, and MRS to study airborne pollution in the Adirondack Mountains as part of our active undergraduate research program in IBA at Union College. The aerosol samples were collected at Piseco Lake with a cascade impactor that separates the particulate matter into nine bins according to aerodynamic diameter. In the PIXE analysis, significant concentrations of Si, P, S, K, Ca, and Fe were measured in many of the PM bins, while trace amounts of Cl, Ti, Mn, Cu, and Zn were detected in a few. The sulfur concentration peaks at small particle sizes (0.25–1 μm), indicating that it could be suspended in the air for days and come from sources very far away. The other elements with significant concentrations peak at larger particle sizes (1–4 μm) and the distribution of elements suggests that the source is soil. Preliminary SEM/EDX measurements on individual aerosol particles with PM-1 show sulfur and oxygen in approximately the same ratio suggesting the presence of sulfur oxides. Initial MRS measurements on a PM-1 sample indicate the presence of a sulfate ion. These results show that there are significant concentrations of sulfur in atmospheric aerosols in the Adirondack Mountains and suggest that much of the sulfur may be in the form of oxides that could come from coal combustion and industry as far away as the Midwest and contribute to the acid rain problem.

Possible future work on this project includes:

- Collecting many more aerosol samples at Piseco Lake to investigate seasonal variations and gather enough data to make source appointments using positive matrix factorization.
- Applying some of the other IBA techniques such as proton-induced γ-ray emission, Rutherford backscattering, and proton elastic scattering analysis.
- Performing a quantitative SEM/EDX analysis to determine the ratio of oxygen to sulfur in individual aerosol particles.
- Continuing work on the MRS analysis.

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