SINGLE PARTICLE ANALYSIS OF PARTICULATE POLLUTANTS IN YELLOWSTONE NATIONAL PARK DURING THE WINTER SNOWMOBILE SEASON.

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Introduction: Particulate, or aerosol, pollution is a complex mixture of organic and inorganic compounds which includes a wide range of sizes and whose composition can vary widely depending on the time of year, geographical location, and both local and long range sources. Aerosol are important because of participation in atmospheric electricity, absorption and scattering of radiation (i.e. sunlight and thus affecting climate and visibility), their role as condensation nuclei for water vapor (and thus affecting precipitation chemistry and pH), and health effects. Particles greater than 2 micrometers in diameter (coarse) are generally formed by mechanical processes while smaller particles (fine) are formed by gas to particle conversion and accumulation/coagulation of these smallest aerosol. Because particles smaller than 2.5 micrometers (USEPA PM2.5) can become trapped deep in the lungs, it is of particular interest to identify toxic substances, such as heavy metals and polyaromatic hydrocarbons, that may be present in particles of this size range. Epidemiological studies have typically used particle size as the metric for identifying adverse health effects of particulate matter (PM), largely because data on PM size is available. Data on particle composition or other characteristics are less well known, if known at all in many cases.

We are evaluating the potential for using Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) to study the composition of single particles from atmospheric aerosol. X-ray analysis has commonly been used to analyze the composition of single particles but it is useful only for elemental analysis and cannot be used to study organic compounds. It offers low sensitivity for light elements (C, O, N) common in particles. Microanalysis SIMS can provide higher sensitivity and molecular information but has lower spatial resolution than SEM [1].

For this study, samples of naturally occurring and anthropogenic atmospheric aerosol were collected at the west entrance to Yellowstone National Park (YNP) during the winter snowmobile season of 1998/99. During the winter snowmobile season, incomplete combustion products from snowmobile exhaust may be a predominant source of airborne particulate matter and carbon monoxide in YNP [2,3]. Two methods were used to collect aerosol. Total suspended particulate (TSP) matter was collected on 47 mm Millipore Fluoropore (PTFE) filters using a vacuum pump system. A Graseby/Anderson 8 stage cascade impactor was used to collect size segregated fractions of the aerosol onto aluminum disks. The cascade impactor separates aerosol according to aerodynamic diameter. Our impactor stages collect particles ranging from 10 to 0.7 micrometers diameter in 8 fractions. Sections of the PTFE filters and aluminum disks have been imaged using a PHI TRIFT I instrument with a Ga primary ion source. A large number of particles could be distinguished on both the filter and impactor surfaces. Multivariate statistical methods have been employed to enhance image resolution and aid in interpretation of the SIMS images. This paper will compare and contrast information obtained from the impactor samples using SEM/X-ray Microanalysis and imaging TOF-SIMS.

Experimental: This study was one part of a multi-investigator study of winter transportation and visitation impacts on YNP in winter 1998/1999. A sampling hut was installed at the West Yellowstone entrance to YNP. Our vacuum pump and flowmeter for the 47 mm TSP filters was installed within the hut, and the filter holder assembly was secured to a pole, supported by the hut, 3.2 meters above the ground to minimize problems from blowing ground snow. Samples were taken for intervals of 3 days to one week.

The 8 stage cascade impactor was loaded at MSU with 81 mm diameter aluminum substrates obtained from Anderson Instruments Inc. The impactor was deployed just outside the central kiosk at the West Yellowstone entrance. Location of the impactor close to the ground was intended to allow sampling of emissions from snowmobiles entering YNP. Sampling was typically for 6 to 8 hours.

Sections of the 47 mm Fluoropore filters and the aluminum cascade impactor substrates were imaged and analyzed using a PHI TRIFT I TOF-SIMS. Sections of the aluminum impactor substrates were also examined with a JEOL JSM-6100 Scanning Electron Microscope with a Noran Instrument Tracor Northern Z-Max 30 X- ray detector.

Data Analysis: The dark color of the TSP filter samples indicated the presence of elemental, or black, carbon. Particles on the PTFE filters could be clearly visualized as dark areas in the CF^+ SIMS image. Still, the filter sample included a very wide range of particle sizes and showed many overlapping particles, making data analysis difficult. Hence, we will focus in this paper on the size segregated impactor samples, using stage 6 of the sample taken January 23, 1999 11:25 AM to 5:27 PM, with light snow and moderate snowmobile traffic. The sample was analyzed first with SIMS. Two squares were etched with the Ga beam just outside the static SIMS analysis regions to serve as registration marks for the subsequent SEM analysis. We will discuss three regions. Region A shows many particles, overlapping each other. Region B is the etched region. Region C contains an area with relatively few particles and more substrate surface. The SEM images are treated first.

Figure 1: Images of Region A. From left to right: (a) SEM image (box shows area of SIMS analysis), (b) SIMS image of PC1, (c) SIMS image of 3 component latent profile.

SEM images

The SEM images show several apparently different types of particles. Figures 1 and 2 show regions A and B. The individual particles appear to be about 1or 2 micrometers in diameter, with some larger clumps, especially where there are many particles. Stage 6 is calibrated to collect particles of 0.7 to 1.1 micrometer aerodynamic diameter at unit specific gravity at sea level (our size cut will differ slightly due to elevation, particle specific gravity and particle shape). One type of particle , somewhat "amoeba" shaped, seems to

Figure 2: Images from Region B. SEM image shown on left. SIMS image of 6 latent variables on right.

resemble the oil soot shown by McCrone and Delly in The Particle Atlas [4] except that it is covered by a film. X-ray microanalysis showed C, O, S, and a little K. A strong Al signal showed that the beam was penetrating the particle into the substrate. Another type of particle was evidenced only by a very thin black layer, which showed no elements (except background Al) by X-ray microanalysis. It appears that we can see these "black spots" in the SEM solely because they reduce the background Al signal from the substrate. Likely, then, the black spots are made of a light element which gives only a poor X-ray signal. We expect that they are carbon or organic spots. These particles were readily erased by the electron beam.

SIMS images: Figure 3 shows the SIMS spectra of regions A, B and C. Region A shows a strong organic signature, and C a similar signature, though weaker due to lower number of particles. Some high mass peaks were seen, at fair ion yield, at 256.3, 419.4, 435.4, 441.4 and 455.4 amu. Region B, which was etched with the Ga beam, shows little but Al substrate and Ga from the beam. Clearly, etching the sample prior to analysis removes the organic layer from the particles, as does the electron beam in SEM. The raw spectra for region A showed only small peaks for elemental carbon (ions 12, 24, 36, etc.). The etched region B still showed only small amounts of elemental carbon, which could have formed from destruction of organics in the etching process. Clearly, the samples contain far more organic than elemental carbon, despite visual observation of black carbon on the TSP filters.

Several multivariate statistical data analysis methods were used to examine the SIMS data. Principal components analysis (PCA) separates the data into components showing covarying information. These components often reveal chemical information. Figure 1b shows an image of region A using principal component 1, describing 56 % of the variance in the data. Principal component 1 consisted of a strong organic component. The image shows light spots, indicating organic-rich particles, with dark patches of Al substrate. Principal component 2 gave similar information. Principal components 3 and 4 showed particles richer in Na, K and Ca with less organics. Principal components 5 and 6 correlated well with the SEM dark particles and contained mass spectral ions indicative of organic compounds. These included $C_2H_3^+$, $C_2H_5^+$, $C_3H_5^+$, $C_3H_7^+$, $C_4H_7^+$, $C_4H_9^+$, $C_5H_5^+$, $C_5H_7^+$, $C_5H_{11}^+$, $C_6H_5^+$, $C_6H_{11}^+$, $C_7H_{13}^+$, $C_7H_{16}^+$, $C_8H_{17}^+$, $C_{11}H_{23}^+$, $C_{12}H_{25}^+$ and some oxygenated species. Ions 83 ($C_6H_{11}^+$) and 97 ($C_7H_{13}^+$) were strongly associated with the dark spots, and somewhat less ions 55 and 57 ($C_4H_7^+$, $C_4H_9^+$). These six principal components together described 89.5% of the sample variance. Higher components described less than 1% of variance and look like noise.

The other multivariate method used was Latent Profile Analysis (LPA), a model based statistical method which accounts for the Poisson distribution of low count rate data and allows us to classify each pixel into classes and extract the spectra for each class as described by Willse et al [5]. Figure 1c shows a 3 component latent profile analysis of region A. The image is dramatically clearer than that provided by PCA (Figure 1b) and remarkably resembles the SEM image. The gray-scale latent profile analysis

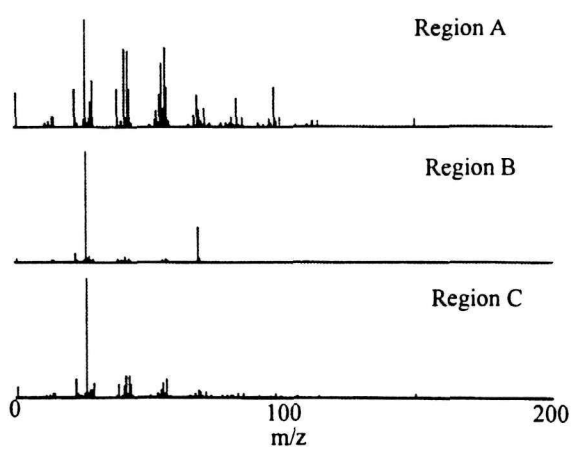

Figure 3: Spectra for the total image from regions A, B, and C.

image indicates Al substrate as white, "amoeba" shaped as gray, and the SEM dark spots as black. LPA indicates a somewhat different organic signature for the two particle types. The dark spots, as also indicated by PCA, have more $C_6H_{11}^+$, $C_7H_{13}^+$, $C_4H_7^+$ and $C_4H_9^+$. LPA also indicates enrichment of the dark spots in $C_3H_5^+$, $C_5H_7^+$ and $C_8H_{17}^+$. The "amoebas" have more Na, K, Ca, and a few probably oxygenated organic fragments including 149 (probably $C_8H_5O_3^+$, phthalate).

The two particle components of region A from LPA were examined with discriminant analysis to look for differences. This indicated more 83, 97 and 113 ($C_8H_{17}^+$) for the dark spots (and more Al showing through) and, interestingly, many even numbered ions (possibly indicating the presence of N) for the "amoebas".

LPA was also used to examine region B (Figure 2) and region C. Six components were found to describe region B. Two components are etched regions from the marking and are described by Al and Ga (from the beam). Another component describes the much higher organic concentrations outside the etched areas. The top and rims (two components) of the "amoebas" are indicated by Na, K, Ca, CaH and Fe. Finally, a few remaining organic particles in the etched area are described by fragments similar to the organic signatures previously described. Etched particles are somewhat higher in elemental carbon and metals than unetched particles. Region C, with its lower particle numbers, showed the same organic signature as region A. Significantly, the areas with no particles do not show the organic signature, indicating that the organics are indeed part of the particles and were not deposited by vapor phase over the whole substrate.

Negative ion spectra also indicated organic signatures and revealed the presence of bisulfate in the particles in the 1 micrometer size range.

Conclusion: This study indicates that SEM/X-ray microanalysis and SIMS imaging using multivariate data analysis are complementary techniques for single particle analysis. Latent profile analysis is a powerful tool to help resolve SIMS images and allow the elemental and molecular information available from SIMS to be utilized. Clear differences were seen between particle types using LPA, as well as imaging capabilities more similar to SEM.

Analysis showed a great predominance of organic aerosol, with differences in degree of oxidation, in the 1 micrometer size range of West Yellowstone winter air. Bisulfate was also clearly observed in the negative SIMS spectra. Etching revealed that many particles were composed of an inorganic core coated with an organic and bisulfate film. This layered structure was likely due to vapor phase deposition of fuel and combustion products. The particle composition was consistent with a snowmobile exhaust emission origin.

Etching of samples prior to SIMS analysis can remove valuable information. In our case, etching prohibited observation of the important organic portion of the aerosol.

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