Sulfur isotopic composition and concentration in throughfall and precipitation samples from a suburban forest

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I. Statement of problem

Atmospheric sulfur is deposited into watersheds as both precipitation and as dry deposition. The NADP measures wet deposition of sulfate. High sulfate concentrations in Eastern U.S. are observed in the Ohio Valley.

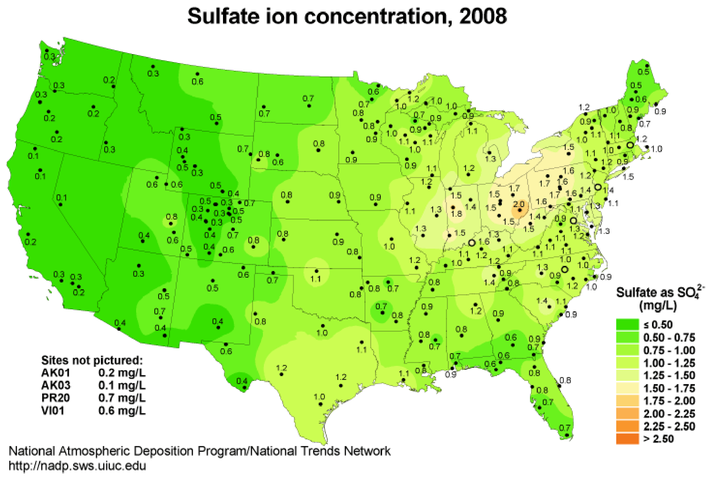

Fig. 1: 2008 Sulfate concentration map of the United States. Sulfate concentration of precipitation is shown in mg/L. From NADP

II. Hypotheses

1. **Measurements of sulfate in throughfall can be used to evaluate the amount and isotopic composition of dry deposition.**
2. **Dry deposition contributes to the sulfate concentration amounts.**
3. **Isotopic methods provide a way to constrain the relative contributions of wet and dry deposition**

III. Study Site and field methods

Throughfall and gross precipitation was measured at a Suburban site (fig. 2) in Univ. Park, Maryland. Throughfall was measured under the canopies of two *Liquidambar* trees and two *Quercus phellos* trees (fig. 3). Three precipitation gauges were used to measured gross precipitation. Canopy cover was determined by photography and visual estimation (fig. 4). Samples of precipitation and throughfall were collect on acid-washed Nalgene sheets (fig. 3)

Fig. 2: Site map showing A) open precipitation measurement site; B) forest canopy site. Image date: 3/1/2007; USGS air photo accessed through Google Earth

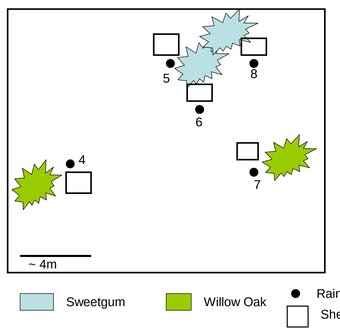

Fig. 3 Schematic diagram showing locations of the two different types of trees, rain gauge locations, numbering system, and locations of 2.5m² Nalgene sheets that were used to collect rainwater.

a b

Fig. 4: Photos show canopy above a plastic sheet photographed on a) Oct. 14, 2009 and on b) November 12, 2009.

IV. Methods

Samples of Rainwater and throughfall were collected for 6 storms (fig. 5) The samples were stored in Nalgene bottles and refrigerated or frozen.

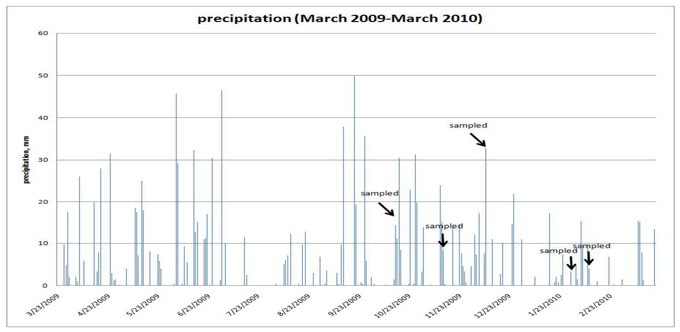

Fig 5 Precipitation values from March 2009 to March 2010, including samples from the study period. NADP and Weather Underground archived data were used to estimate the probability of finding an isolated small storm from April to November.

Sulfur concentration data were either measured by spectrophotometer with a 0.9 mg/L detection limit, which is near the NADP detection limit of 0.6 mg/L. or estimated from the Beltsville NADP data .

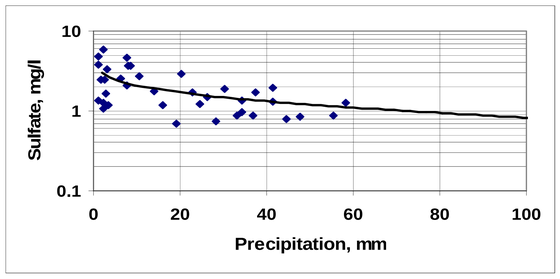

Fig. 6 The NADP sulfate concentration data in Beltsville, MD. This graph indicates that sulfate concentration is inversely proportional to precipitation in Beltsville.

The samples were prepared for isotopic analyses by precipitation of barium sulfate, then filtered. Barium chloride was reduced to barium sulfide using a reduction apparatus (fig. 7). 25 ml of a general reduction solution was added to a N_2 purged distillation line in order to chemically reduce $BaSO_4$ to H_2S. The H_2S is captured as ZnS and then converted to Ag_2S. The reduction solution is boiled under a N_2 atmosphere for 3 hours and then filtered to remove more impurities and precipitates (Johnston et al, 2007).

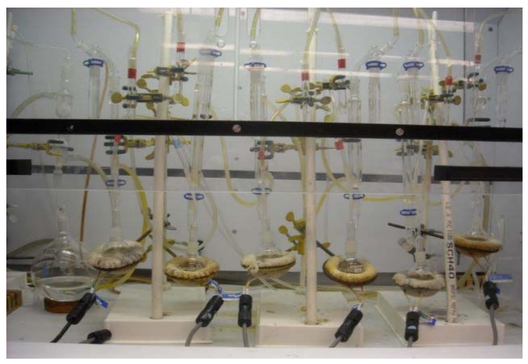

Fig. 7 Reduction apparatus used to chemically reduce $BaSO_4$ to H_2S, which in turn would be captured as ZnS and converted to Ag_2S.

The samples were then filtered and weighed. The 6 sufficiently large samples of silver sulfide were fluorinated with a manifold and the SF_6 was analyzed for isotope ratios with the mass spectrometer. A set of small samples were mixed with vanadium powder and wrapped in tin cups. The SO_2 method was used to combust and analyze the sulfur isotope ratios.

Storm trajectories can be used to evaluate source regions for storms. Therefore, I used a meterological program used to evaluate storm trajectories. NOAA's Hysplit model (Draxler et al., 2009) was used to evaluate storm trajectories.

V. Results

Gross Precipitation and Throughfall were measured for the 6 storms (fig. 7)The percentage of gross precipitation appearing as throughfall varied from storm to storm, but in general increased from 58% in October to 80% in December.

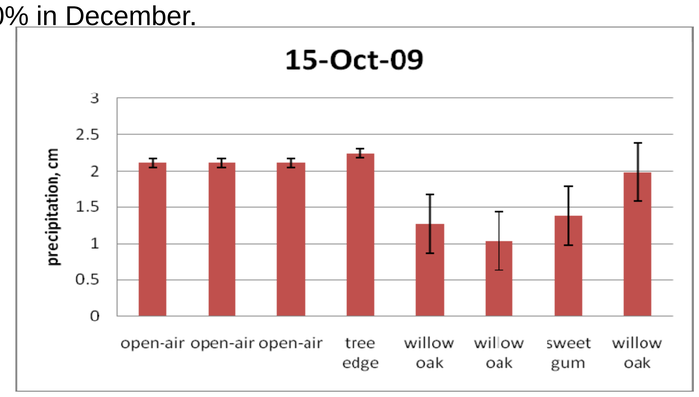

Fig. 7: Measurements of gross precipitation (open sites) and throughfall (tree sites) on October 15, 2009. Data from this sampling date will be discussed later in the isotope analysis section.

Table I: precipitation and sulfate concentrations

Storm date	Precipitation mm	Throughfall mm	Estimated sulfate (mg/l)	Measured sulfate (mg/l) (1σ)
14-Oct	17.6	10.1	2.16±1.90	
15-Oct	21.4	14.2	1±0.69	
11-Nov	101	71.7	1.3±0.6	
12-Nov	5.4	8.8	1±1.1	2±1.32
13-Nov	11.7	8.5	1±1	
9-Dec	50	40	0.78±0.75	1.3±1.32
1-Feb	*3.3		2.69±1.20	
10-Feb	*18		0.9±0.75	

Table II: Sulfur isotope measurements

Two samples were successfully analyzed; one throughfall and one gross precipitation sample from October 15th, 2009. Both samples have similar $\delta^{34}S$ values with estimated uncertainties. These are compared in Table II and fig. 8 with Mann's 1998 samples.

Sample	$\delta^{34}S$	$\Delta^{33}S$
10-15-09 #5 willow oak TF	5.41±0.40 ‰ (2σ)	-0.004±0.020 ‰ (2σ)
10-15-09 #1 open	6.07±0.40 ‰ (2σ)	-0.029±0.020 ‰ (2σ)
*07/23/95 open	3.5	
*03/30/96 open	4.8	
**07/23/95 TF	3.9	
*03/30/96	4	

*Mann, 1998

The $\delta^{34}S$ values indicate a mixing of sulfur sources (urban+ coal and Atlantic marine sulfate mixed would provide values less than +10 (Atlantic); but significantly larger than the negative values expected for coal or urban sources alone.

Mann, 1998, found higher values of sulfur in throughfall than in precipitation and both values were higher than observed in 2010 (fig. 9) . In another study of isotopic values of gross precipitation, Cooney, 2005 found that the $d^{34}S$ values do not vary seasonally (Cooney, 2005) and the isotopic values were similar to those measured in this study.

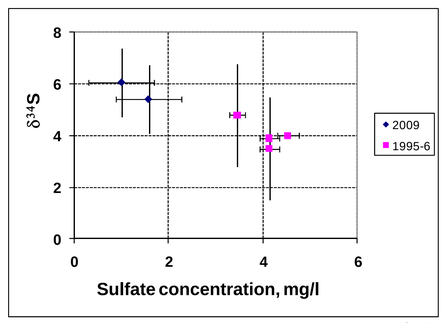

Fig. 8 As sulfate concentration decreases, $\delta^{34}S$ increases, indicating a decrease in fossil fuels in the mix of marine and coal sulfur in the atmosphere.

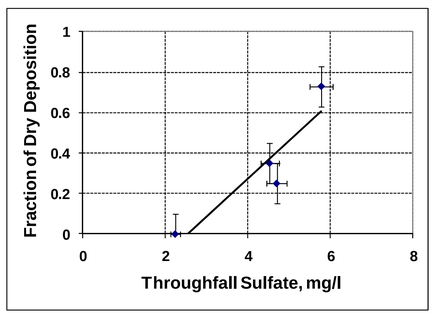

Fig. 9 As throughfall sulfate increases, dry deposition increases (from Mann, 1998).

Conclusions

Analysis of precipitation events in 2009-2010 suggests that only about 17% of the precipitation events can be used to evaluate dry deposition. The higher $\delta^{34}S$ values indicate a clean-up of the atmosphere between 1998 and 2009. Further tests should be done to see if dry deposition and wet deposition are similar or different in other precipitation events. I suggest doing further research on the leaf storage and the canopy saturation point during the summer in order to measure the minimal throughfall required to remove solutes from the leaves of the trees in this region.