CHAPTER 7

AEROSOL ACIDITY

It has been established by a number of investigators, that especially during the summer, aerosols along the coast of Washington are commonly acidic.[1-2] Although the measurements made during PREVENT were not explicitly designed for purposes of estimating aerosol acidity, a method for estimating acidity utilizing measurements made at the three major receptor sites is available.[3] The basis of this method derives from the concurrent measurements of fine particulate sulfur, organic matter, and hydrogen, and the reasonable assumption that the organic matter to hydrogen ratio is relatively constant. This last assumption is explored as part of the acidity estimation.

Typically, pH of aqueous extracts is measured to determine H^+ concentrations, and NH^+, NO_3, and SO_4 concentrations are obtained using appropriate analytic techniques such as ion chromatography. From these variables the acidity and the aerosols associated with the acidity are estimated.

An alternative technique for estimating the acidity of the sulfate aerosol is to regress the H concentration with S and OCM. OCM is the carbon associated with organic mass. Nitrates are not included in the regression because it is assumed that under a vacuum all nitrate aerosols would evaporate (H and S concentrations are derived from filters that are held under a vacuum during PIXE analysis). The form of the regression equation is:

$$H = a_o + a_1 S + a_2 OCM \qquad (7\text{-}1)$$

where a_0, a_1, and a_2 are the residual hydrogen, ratios of hydrogen to sulfur, and hydrogen to organic carbon, respectively. For ammonium sulfate, ammonium bisulfate, and sulfuric acid, the H/S ratios are 0.25, 0.156, and 0.063. The regression coefficient associated with sulfur is an estimate of the acidity of the sulfate aerosol.

For comparison, results of aerosol acidity estimates at four eastern sites will be presented. Multilinear regressions have been carried out at those sites for which measurements of organic carbon were made simultaneous with measurements of H and S. Results of the regressions are listed in Table 7-1.

Table 7-1. Results of multilinear regressions using hydrogen as the dependent variable and sulfur and OCM as independent variables for four eastern monitoring sites.

1989	r^2	Intercept	S	OCM
Acadia National Park	0.97	0.003±0.007	0.24±0.008	0.08±0.003
Whiteface Mountain	0.95	0.043±0.013	0.22±0.009	0.09±0.004
Quabbin Reservoir	0.89	0.07±0.022	0.22±0.016	0.058±0.007
Shenandoah National Park	0.89	0.095±0.02	0.16±0.011	0.09±0.01

First, all regressions are highly significant, with most r^2s varying from 0.80 to 0.97. Examination of the regression coefficients for sulfur show an increase in acidity as one moves from north to south. At Acadia National Park, the regression coefficient of 0.24 implies that the sulfate aerosol is nearly fully neutralized, while at Shenandoah National Park a coefficient of 0.16 implies the sulfate aerosol, on the average, is about half neutralized. The H/S ratio for ammonium bisulfate is 0.156. At the remaining sites, sulfate aerosols are more fully neutralized, with coefficients between 0.22 and 0.18. These results are consistent with average acidity measured in other studies.[1.2.4-13]

When sulfate is near full neutralization, the r^2s are greater than 0.9 implying that the H/OCM ratios are quite stable. If they were not the r^2s would be dramatically lowered.

The regression coefficient gives insight into the average acidity of the sulfate aerosol, but does not allow for specific identification of acid aerosol episodes or those time periods where the sulfate aerosol is fully neutralized. If it is assumed that the ratio H/OCM is constant, then it is possible to estimate on a sampling-period-by-sampling-period basis, the amount of H associated with the sulfate aerosol by using:
where H_s is the amount of elemental H associated with the sulfate aerosol and H_{OCM}/OCM is the

$$H_s = H - \frac{H_{ocm}}{OCM} OCM \qquad (7\text{-}2)$$

hydrogen-to-organic matter ratio which is derived from Equation 7-1. Knowing H_s amounts allows for calculation of the H/S ratio, from which the acidity of the sulfate aerosol can be estimated. Furthermore, the sulfate aerosol mass can be estimated from the known molecular structure of the various sulfate aerosol species. For instance, elemental sulfur is multiplied by 4.125, 3.6, and 3.06 for ammonium sulfate, ammonium bisulfate, and sulfuric acid, respectively.

A similar analysis was carried out on the PREVENT data set. Figures 7-1, 7-2, and 7-3 present, as temporal plots, the sulfur, hydrogen, OCLT, OCHT, ECLT, and ECHT concentrations along with the multiplication factor for estimating sulfate mass for the three data sets. Table 7-2 presents a statistical summary of these same data. The OLS regression following the form of Equation 7-1 yields H/S and H/OCM ratios of 0.33 and 0.08 and an r^2 of 0.88. The H/S ratio greater than 0.25 is physically impossible if the sulfur is a mixture of ammonium, sulfate, and free hydrogen. However, the H/OCM ratio is consistent with the ratios found at the five eastern sites and those reported by Eldred et al.[14]

Before returning to the hydrogen sulfur ratios, it is of interest to explore the hydrogen-derived organic carbon mass (OCMH) using Equation 7-1 and associated regression coefficients and measured OCM. Figure 7-4 is a scatter plot of OCM and OCMH along with the one-to-one line. The correlation between the two variables is high (0.87), however, there is an apparent offset with organics by evaporation (OCM) being higher than corresponding OCMH values by about 0.5 $\mu g/m^3$. There appears to be a positive artifact associated with most carbon data points. This problem has been reported by others and is discussed in more detail in Chapters 1 through 4. In the remainder of this chapter, estimates of organic carbon mass will be corrected for an apparent positive additive bias by subtracting 0.5 $\mu g/m^3$ from each data point.

The OLS regressions were repeated with the "corrected" carbon data set and the results are presented in Table 7-3. At both Tahoma Woods and Paradise the r^2s are high, 0.88 and 0.97, respectively. The somewhat lower r^2s at Marblemount are due to one or two "outliers." The H/OCM ratios at Tahoma Woods and Paradise are stable at 0.08, while the Marblemount ratio is 0.76. Scatter plots of OCM and OCMH for the three sites are shown in Figures 7-5, 7-6, and 7-7. The one-to-one line is shown for reference. In most cases the two variables compare quite favorably. The correlations between the two variables are 0.87, 0.96, and 0.72 for Tahoma Woods, Paradise and Marblemount, respectively. The lower correlation at Marblemount is due to a single outlying data point. There is not a significant multiplicative or additive bias between the two variables for any of the three data sets.

The H/S ratio at Paradise is 0.25, which suggests that on the average the sulfate aerosol is fully neutralized and in the form of ammonium sulfate. However, the H/S ratios at Tahoma Woods and Marblemount are greater than 0.25, which suggests that either an externally mixed hydrogen containing aerosol is highly collinear with sulfur, or that the sulfur aerosol is not externally mixed, but is a mixture of sulfur and hydrogen containing molecules such as organic material. It seems unlikely that another separate aerosol species could be sufficiently collinear with sulfur to maintain a relationship between H, S, and OCM that corresponds to an r^2 of 0.88 (see Table 7-3). Therefore, it is hypothesized that sulfur and hydrogen containing molecules, such as organics, are mixed within one particle to form an internally mixed aerosol. If this is the case, then one would expect correlations between sulfur and measured carbon. These relationships will be explored in Chapter 8.

Assuming a sulfur-organic aerosol model, the average carbon mass associated with the hypothesized organic sulfur mixture can be estimated by calculating the "excess" hydrogen:

$$H_{ex} = a_1 S - 0.25S \tag{7-3}$$

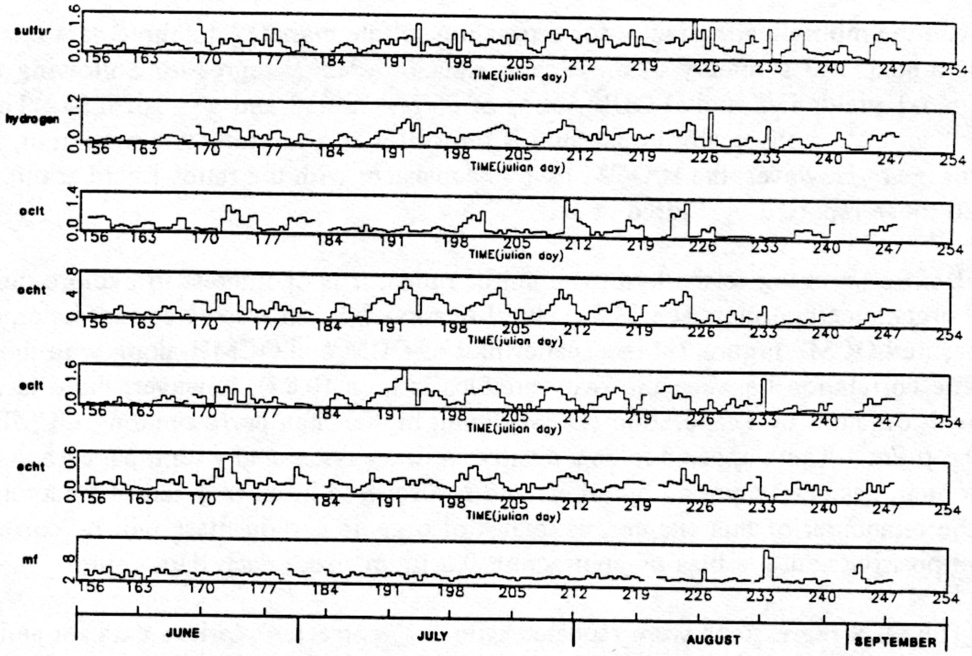

Figure 7-1. Tahoma Woods: Temporal plots of sulfur, hydrogen, OCLT, OCHT, ECLT, ECHT, and the sulfur multiplication factor (mf). Units on all aerosol concentrations are μg/m^3. The multiplication factor is an indication of sulfate acidity. If sulfur is in the form of ammonium sulfate, ammonium bisulfate, or sulfuric acid mf is 4.125, 3.6, or 3.06, respectively.

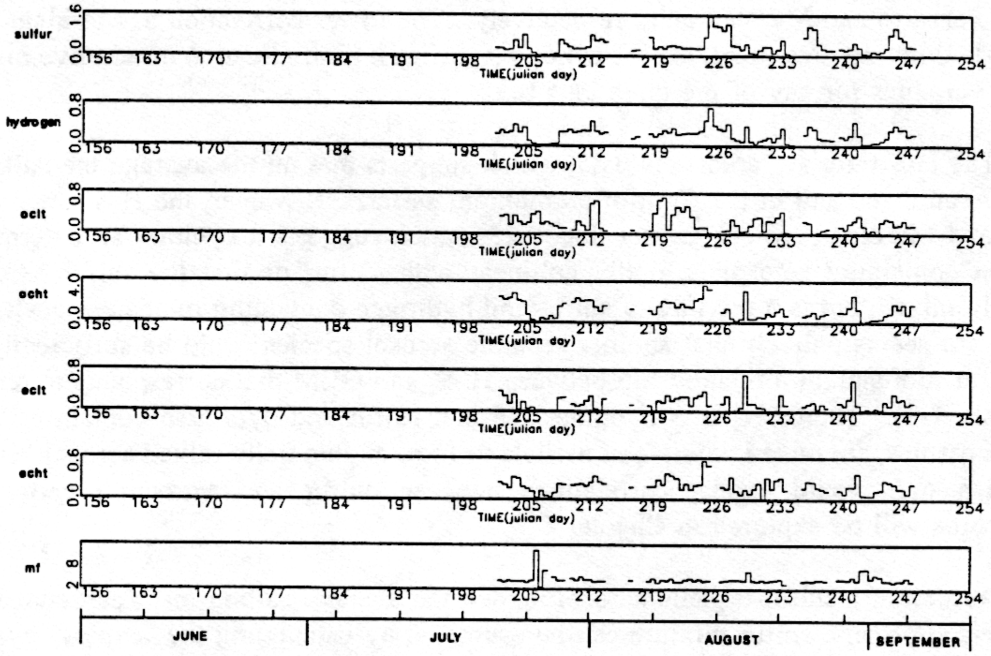

Figure 7-2. Paradise: Temporal plots of sulfur, hydrogen, OCLT, OCHT, ECLT, ECHT, and the sulfur multiplication factor (mf). Units on all aerosol concentrations are μg/m^3. The multiplication factor is an indication of sulfate acidity. If sulfur is in the form of ammonium sulfate, ammonium bisulfate, or sulfuric acid mf is 4.125, 3.6, or 3.06, respectively.

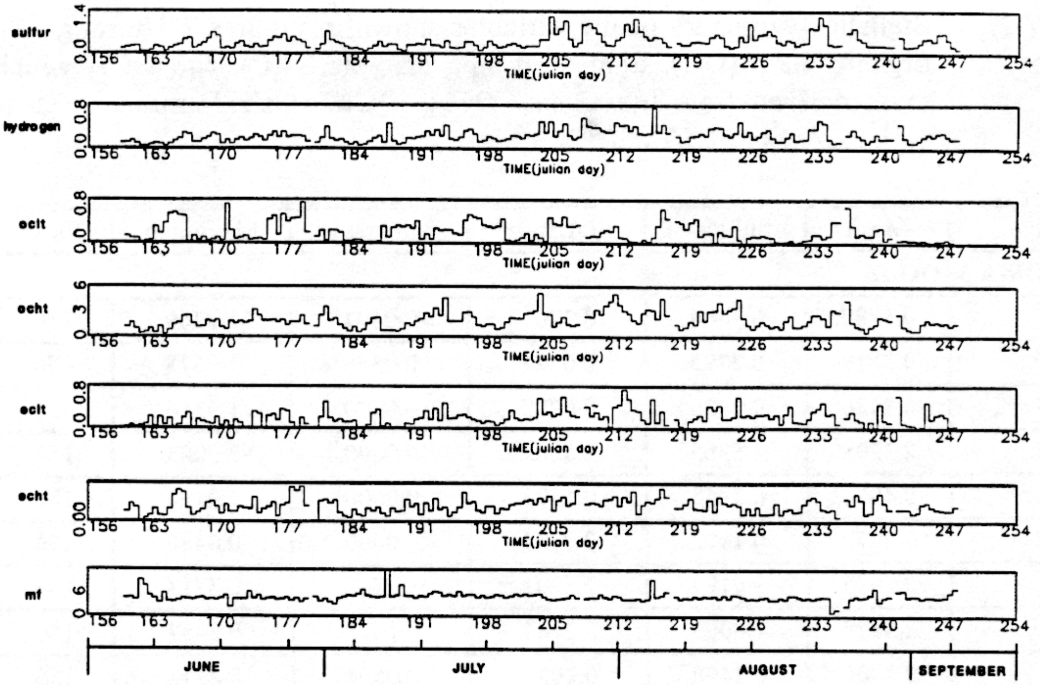

Figure 7-3. Marblemount: Temporal plots of sulfur, hydrogen, OCLT, OCHT, ECLT, ECHT, and the sulfur multiplication factor (mf). Units on all aerosol concentrations are μg/m^3. The multiplication factor is an indication of sulfate acidity. If sulfur is in the form of ammonium sulfate, ammonium bisulfate, or sulfuric acid mf is 4.125, 3.6, or 3.06, respectively.

where H_{ex} is the amount of hydrogen mass remaining after allocating hydrogen to sulfate, (assuming the sulfate is in the form of ammonium sulfate). a_1 is the H/S ratio found from the regression suggested by Equation 7-1, and 0.25 is the H/S ratio associated with ammonium sulfate. H_{ex} can then be used to estimate the carbon mass (OCM_s) in the organic-sulfur mixture using:

$$OCM_s = H_{ex}/0.08 \qquad (7\text{-}4)$$

where 0.08 is the H/OCM ratio from Table 7.3. Carrying out the calculation for Tahoma Woods and Marblemount yields 0.56 μg/m^3, and 0.28 μg/m^3, respectively. About 25% of the measured carbon mass may be internally mixed with sulfate particles.

The results of the regressions presented in the previous paragraphs yield average H/S ratios. Equation 7-2 explores the H/S ratios on a sampling-period-by-sampling-period basis. It should be emphasized that this equation assumes a constant H/OCM ratio. Figures 7-8, 7-9, and 7-10 show scatter plots of the hydrogen associated with sulfur on the ordinate, and sulfur mass concentration on the abscissa. The three lines on each graph correspond to H/S ratios associated with ammonium sulfate, ammonium bisulfate and sulfuric acid, respectively. Any data points above the ammonium sulfate line correspond to excess hydrogen while points below the line suggest an acid aerosol.

Table 7-2. Statistical summary of the variables shown in Figures 7-1 through 7-3 as well as organic mass (OC), light absorbing carbon (LAC), and OCH which is organic mass derived from hydrogen. OC is OCLT+OCHT minus a 0.5 μg/m^3 offset while LAC is ECLT+ECHT.

Variable	Mean	Std Dev	Variance	Minimum	Maximum	Valid	Missing
TAHOMA WOODS							
S	0.5789	0.3464	0.1200	0.0491	1.7369	156	28
H	0.3618	0.2295	0.0527	0.0376	1.2678	156	28
OCLT	0.3486	0.2826	0.0799	0.0000	1.5216	156	28
OCHT	2.3208	1.5383	2.3663	0.0000	7.0003	156	28
ECLT	0.4934	0.3963	0.1571	0.0000	1.9195	156	28
ECHT	0.2372	0.1122	0.0126	0.0000	0.6486	156	28
OC	2.1695	1.6187	2.6201	-0.4027	6.8713	156	28
OCH	2.3878	1.8095	3.2744	0.1629	9.8457	156	28
LAC	0.7305	0.4498	0.2023	0.0504	2.2372	156	28
MF	4.5881	1.1171	1.2479	2.0737	12.8752	156	28
PARADISE							
S	0.4597	0.3489	0.1217	0.0086	1.7735	76	108
H	0.2477	0.1492	0.0223	0.0148	0.8202	76	108
OCLT	0.2473	0.1866	0.0348	0.0000	0.8113	76	108
OCHT	1.6568	1.0655	1.1353	0.0000	4.5722	76	108
ECLT	0.1783	0.1547	0.0239	0.0000	0.8077	76	108
ECHT	0.2289	0.1163	0.0135	00.000	0.6601	76	108
OC	1.4042	1.0997	1.2093	-0.3324	4.2088	76	108
OCH	1.4605	1.0521	1.1069	0.1395	4.1447	76	108
LAC	0.4072	0.2173	0.0472	0.0370	1.1060	76	108
MF	4.5852	1.2048	1.4516	2.3745	12.4538	76	108
MARBLEMOUNT							
S	0.4510	0.2735	0.0748	0.0514	1.4225	171	13
H	0.2901	0.1465	0.0215	0.0457	0.9515	171	13
OCLT	0.2200	0.1911	0.0365	0.0000	0.8382	171	13
OCHT	1.9637	0.9788	0.9581	0.2180	5.2159	171	13
ECLT	0.2416	0.1854	0.0344	0.0000	0.9327	171	13
ECHT	0.2022	0.0919	0.0085	0.0000	0.4551	171	13
OC	1.6837	1.0140	1.0282	-0.1945	5.0042	171	13
OCH	1.9510	1.1851	1.4045	0.3487	8.7449	171	13
LAC	0.4438	0.2312	0.0534	0.0039	1.2618	171	13
MF	4.9603	1.1267	1.2695	0.9776	11.9279	171	13

Table 7-3. Results of multilinear regressions using hydrogen as the dependent variable and sulfur and "corrected" OCM as independent variables for Tahoma Woods, Paradise, and Marblemount.

	Intercept	Sulfur	OCM	r^2
Tahoma Woods	-0.009±0.012	0.33±0.02	0.08±0.004	0.88
Paradise	0.014±0.006	0.25±0.01	0.08±0.003	0.97
Marblemount	0.03±0.021	0.30±0.02	0.07±0.006	0.76

At Tahoma Woods and Marblemount, there are a preponderance of data points above the ammonium sulfate line, while a few scattered data points have H/S ratios consistent with acidic aerosols. Other data points fall below the sulfuric acid line. These data points may be a reflection of the measurement uncertainty, variability in the H/OCM ratios, or possibly the presence of crystalline sulfur. At Paradise, most data points correspond to H/S ratios consistent with ammonium sulfate, as the regression suggested. However, as in the Tahoma Woods and Marblemount data set there are a number of data points associated with zero or near zero hydrogen.

Summary

Ambient measurements of elemental sulfur, hydrogen, and organics were made at three monitoring sites. These measurements were used to estimate aerosol acidity and the stability of the H/OCM ratio. At two sites, Tahoma Woods and Paradise, the H/OCM ratio apparently is nearly constant in that the regression models relating the three variables had high r^2s and high significant coefficients. At Marblemount, the r^2 was lower indicating that the H/OCM and H/S ratios were more variable.

At all three sites the average H/S ratio is 0.25 or greater implying that there is enough hydrogen on the filters to be consistent with fully neutralized sulfate. At Paradise, the average ratio is 0.25±0.01, while at Tahoma Woods and Marblemount the ratio is about 0.33. This "inflated" H/S is suggestive of an organic-sulfur multicomponent aerosol.

Finally, at all three sites, there are a few time periods where the H/S ratios are suggestive of acidic aerosols.

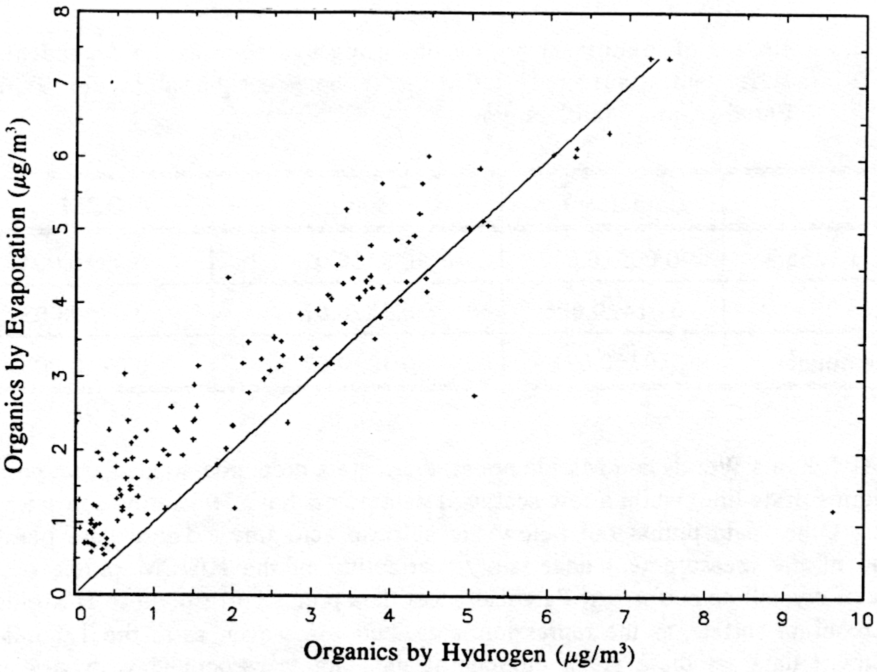

Figure 7-4. Tahoma Woods: Scatter plot of organics by evaporation (OCM) and organics from hydrogen (OCMH) without a 0.5 μg/m^3 offset subtracted from OCM. Units are μg/m^3.

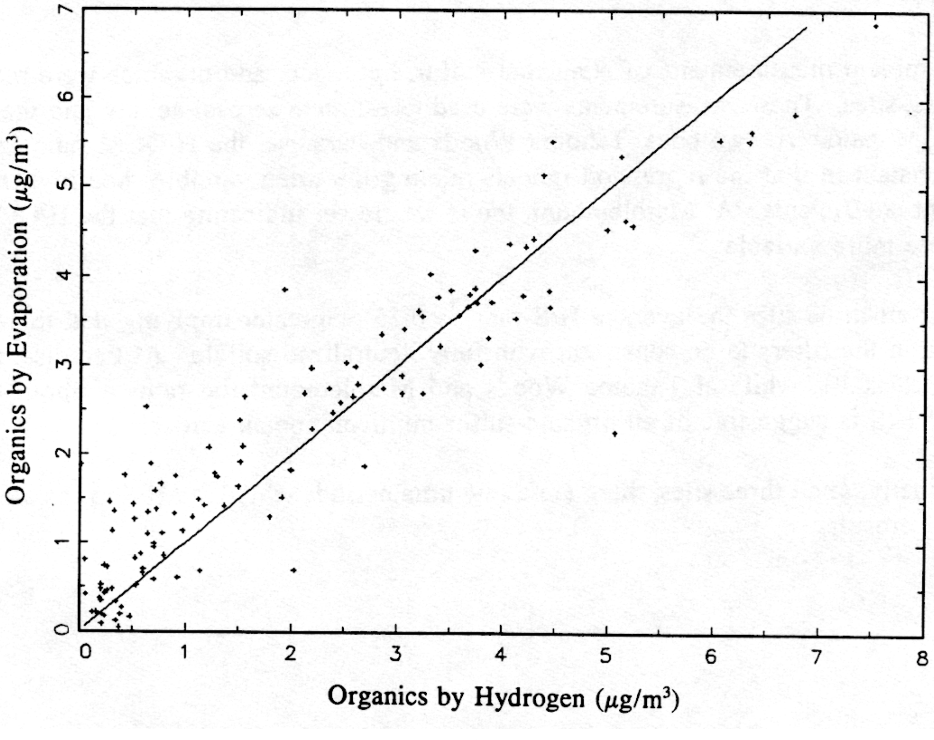

Figure 7-5. Tahoma Woods: Scatter plot of organics by evaporation (OCM) and organics from hydrogen (OCMH) with a 0.5 μg/m^3 offset subtracted from OCM. Units are μg/m^3.

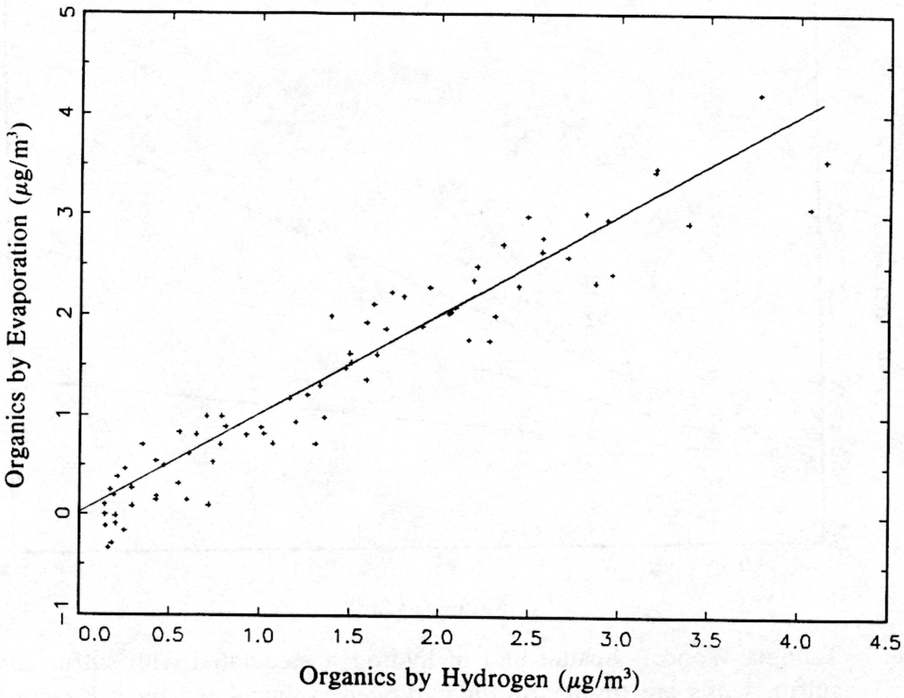

Figure 7-6. Paradise: Scatter plot of organics by evaporation (OCM) and organics from hydrogen (OCMH) with a 0.5 μg/m^3 offset subtracted from OCM. Units are μg/m^3.

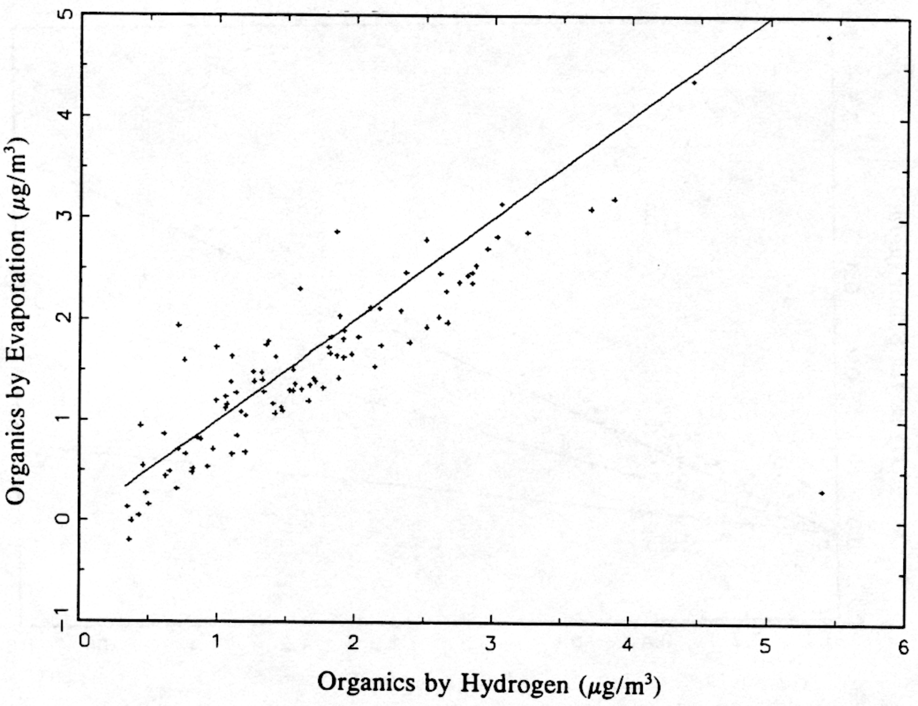

Figure 7-7. Marblemount: Scatter plot of organics by evaporation (OCM) and organics from hydrogen (OCMH) with a 0.5 μg/m^3 offset subtracted from OCM. Units are μg/m^3.

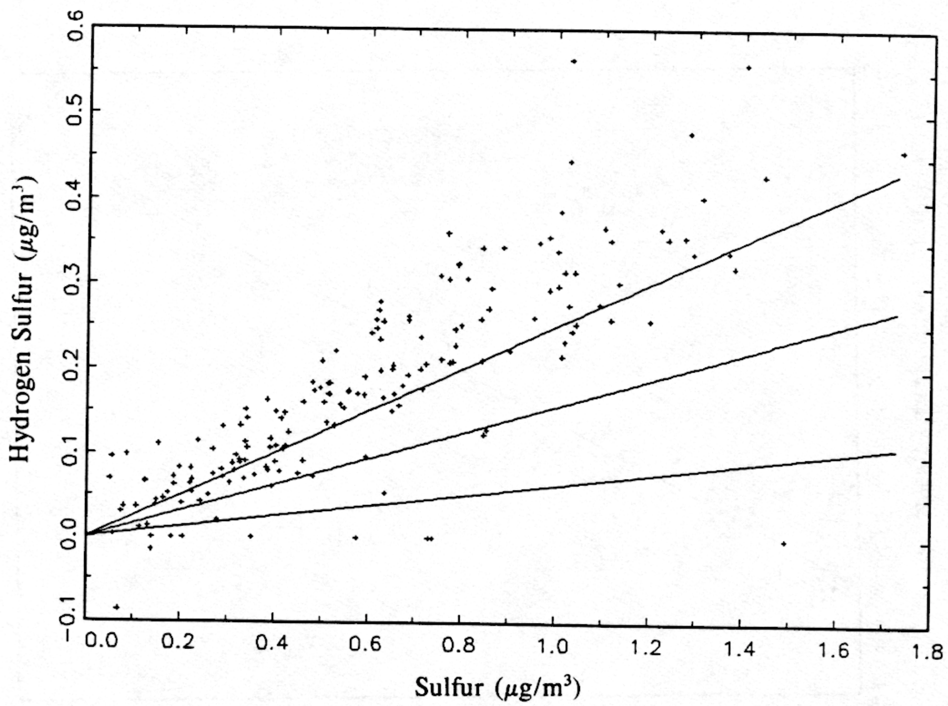

Figure 7-8. Tahoma Woods: Scatter plot of hydrogen associated with sulfur and elemental sulfur. Units are μg/m^3. Sulfur hydrogen is calculated by subtracting hydrogen associated with organics from total hydrogen. The hydrogen to sulfur ratio corresponding to ammonium sulfate, ammonium bisulfate, and sulfuric acid are shown for reference.

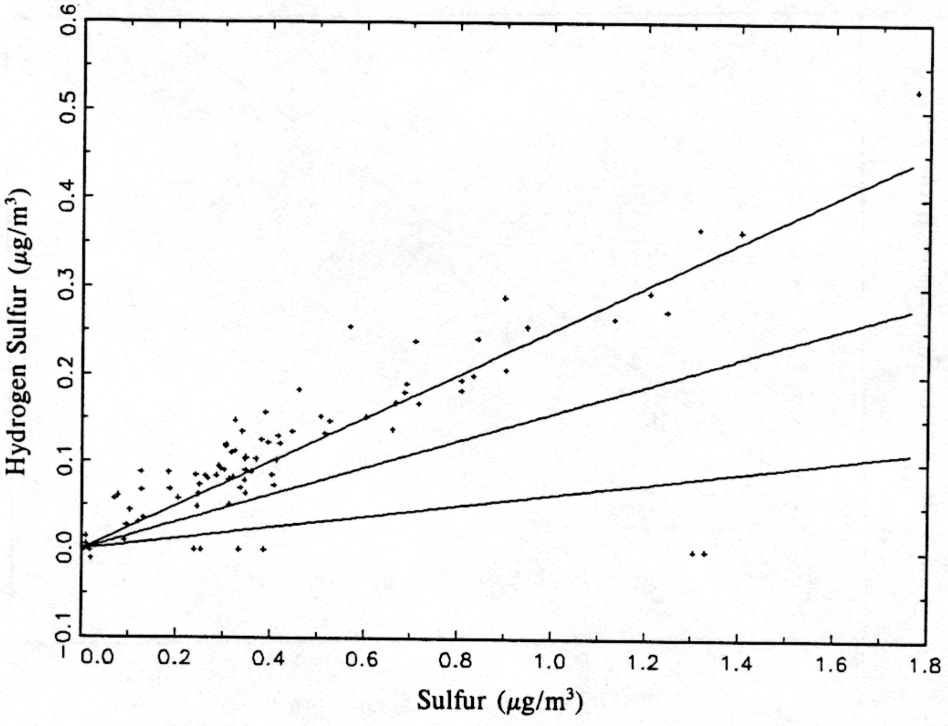

Figure 7-9. Paradise: Scatter plot of hydrogen associated with sulfur and elemental sulfur. Units are μg/m^3. Sulfur hydrogen is calculated by subtracting hydrogen associated with organics from total hydrogen. The hydrogen to sulfur ratio corresponding to ammonium sulfate, ammonium bisulfate, and sulfuric acid are shown for reference.

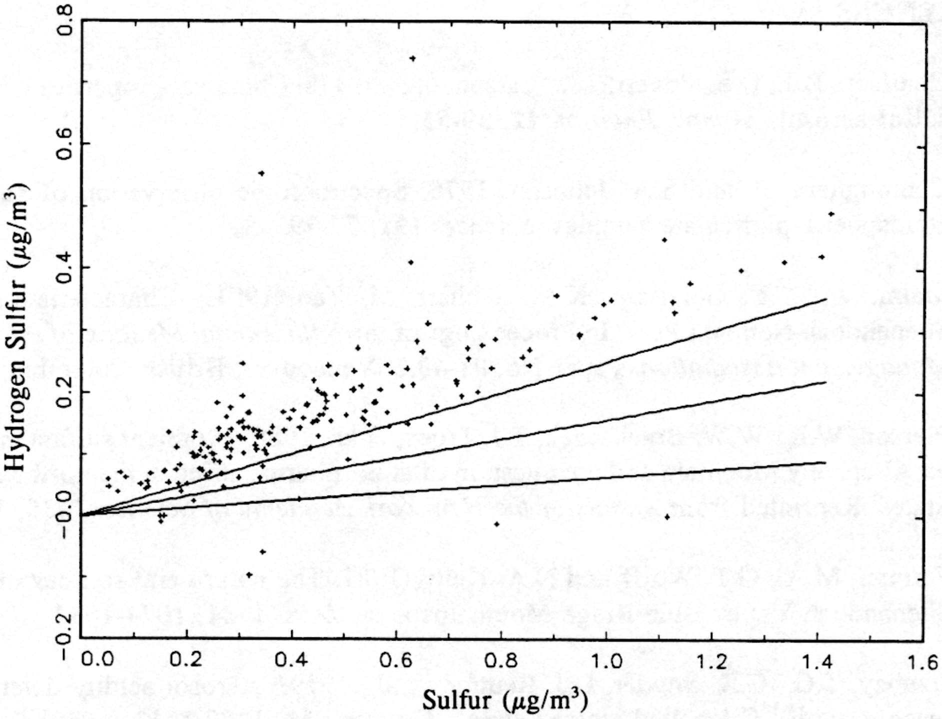

Figure 7-10. Marblemount: Scatter plot of hydrogen associated with sulfur and elemental sulfur. Units are μg/m^3. Sulfur hydrogen is calculated by subtracting hydrogen associated with organics from total hydrogen. The hydrogen to sulfur ratio corresponding to ammonium sulfate, ammonium bisulfate, and sulfuric acid are shown for reference.

REFERENCES

1. Charlson, R.J., D.S. Covert, T.V. Larson, et al., 1978. Chemical properties of tropospheric sulfur aerosols. *Atmos. Environ.* **12**, 39-53.

2. Cunningham, P. and S.A. Johnson, 1976. Spectroscopic observation of acid sulfate in atmospheric particulate samples. *Science*. **191**, 77-79.

3. Malm, W.C., Y. Golestani, K.A. Gebhart, M. Yao, 1991. Characteristics of haze in Shenandoah National Park. In Proceedings of the *84th Annual Meeting of the Air & Waste Management Association.* Paper No. 91-49.2. Vancouver, British Columbia, 16-21 June.

4. Pierson, W.R., W.W. Brachaczek, T.J. Truex, et al., 1980. Ambient sulfate measurements on Allegheny Mountain and the question of atmospheric sulfate in the northeastern United States. Reprinted from *Annals of the New York Academy of Sciences*. **338**, 145-173.

5. Ferman, M.A., G.T. Wolff and N.A. Kelly, 1981. The nature and sources of haze in the Shenandoah Valley/Blue Ridge Mountains area. *JAPCA*. **31**, 1074-1082.

6. Dzubay, T.G., G.K. Snyder, D.J. Reutter, et al., 1979. Aerosol acidity determination by reaction with ^{14}C labelled amine. *Atmos. Environ.*, **13**, 1209-1212.

7. Ferek, R.J., A.L. Lazrus, P.L. Haagenson, et al., 1983. Strong and weak acidity of aerosols collected over the northeastern United States. *Environ. Sci. Technol.*, **17**, 315-324.

8. Lioy, P.J. and M. Lippmann, 1985. Measurement of exposure to acidic sulfur aerosols. In *Proceedings of the Second U.S.-Dutch International Symposium on Aerosols: Research, Risk Assessment and Control Strategies*. Virginia, 743-752.

9. Stevens, R.K., T.G. Dzubay, R.W. Shaw, et al., 1978. Sampling and analysis of atmospheric sulfates and related species. *Atmos. Environ.*, **12**, 55-68.

10. Stevens, R.K., T.G. Dzubay, R.W. Shaw, et al., 1980. Characterization of the aerosol in the Great Smoky Mountains. *Environ. Sci. Technol.*, **14**, 1491-1498.

11. Stevens, R.K., T.G. Dzubay, C.W. Lewis, et al., 1980. Source apportionment methods applies to the determination of the origin of ambient aerosols that affect visibility in forested areas. *Atmos. Environ.*, **18**, 261-272.

12. *Acid aerosols issue paper.*, EPA/600/8-88/005A, U.S. Environmental Protection Agency, February, 1988, Review Draft.

13. Mueller, P.K. and G.M. Hidy, 1988. Personal Communication.

14. Eldred, R.A., T.A. Cahill, L.K. Wilkinson, et al., 1988. Measurement of fine particles and their chemical components in the IMPROVE/NPS networks. In *Proceedings of the 1988*

AWMA International Specialty Conference on Visibility and Fine Particles. Pittsburgh, 187-196.