CHAPTER 6

CHARACTERISTICS OF PARTICULATE CONCENTRATIONS AND THEIR OPTICAL PROPERTIES

6.1 AVAILABLE DATA

The data necessary to calculate a light-extinction budget for a given site are measurements of extinction and/or independent measurements of ambient scattering and optical absorption, and concentrations of the various aerosol species contributing to extinction. This includes relative humidity (RH). At three of the sites in PREVENT, data were collected for purposes of making extinction budget calculations. These are Marblemount, Paradise, and Tahoma Woods. The measurement of the various aerosol species and light scattering and absorption were covered in Chapters 1 through 4. Extinction was not measured directly in the PREVENT study, however, at two sites (Tahoma Woods and Marblemount) nephelometers were operated at near ambient conditions. The nephelometer sampling chamber temperature was monitored at all three sites for purposes of estimating chamber RH.

6.2 CHEMICAL COMPOSITION OF PARTICULATE MATTER

Because ions and elements were measured, the molecular form of the aerosol species responsible for light extinction must be inferred or assumed. Elemental sulfur was measured; therefore, the molecular form of the sulfate aerosol must be estimated. Elemental sulfur was associated with marine aerosols and secondary sulfate species, such as ammonium bisulfate and ammonium sulfate.

Chlorine and sodium make up about 90% of the mass identified with elements present in solution in sea water. The third and fourth most abundant elements are magnesium and sulfur.[1] Therefore, at the monitoring sites it is expected that sodium be in the form of NaCl, Na_2SO_4, or $NaHSO_4$. An upper bound of marine derived sulfur is estimated by assuming all of the measured sodium and magnesium are in the form of Na_2SO_4 or $NaHSO_4$ and $MgSO_4$.

Based on the average sodium concentration (46.3 ng/m^3) for the three monitoring sites, the maximum amount of sodium-derived sulfur is 32-64 ng/m^3, depending on whether Na is in the form of Na_2SO_4 or $NaHSO_4$. The average sulfur associated with magnesium is 1 ng/m^3 (average magnesium concentration is 0.8 ng/m^3) and the average total particle sulfur concentration is 540 ng/m^3. Therefore, the average upper bound of marine sulfur is estimated between 6% and 12% of the total particulate sulfur. Because marine sulfur cannot be directly estimated and (the correlation between Na and S is low, and CMB analysis attributes most Na either to lime kilns or pulp and

paper mills, see Chapter 9), all sulfur will be assumed to be in some form of ammonium sulfate. However, the reader should keep in mind that average estimates of ammonium sulfate concentrations may be somewhat overestimated.

A remaining question is whether the sulfate aerosol is fully or partially neutralized. A full discussion of aerosol acidity is presented in Chapter 7. However, an abbreviated analysis will be presented for purposes of justifying the assumed form of ammonium-based sulfate. Malm *et al.*[2] have shown that an alternative technique for estimating the acidity of the sulfate aerosol is to regress the H concentration with S and organic carbon. Nitrates are not included in the regression because it is assumed that under a vacuum all nitrate aerosols evaporate. The form of the regression equation is:

$$H = a_o + a_1 S + a_2(OCLT + OCHT) \quad \textbf{(6-1)}$$

where a_0, a_1, and a_2 are the residual hydrogen, elemental ratios of hydrogen to sulfur, and hydrogen to organic carbon, respectively. For ammonium sulfate, ammonium bisulfate, and sulfuric acid, the hydrogen-sulfur ratios are 0.25, 0.156, and 0.063, respectively. The regression coefficient associated with sulfur is an estimate of the acidity of the sulfate aerosol. This procedure has compared favorably with other independent aerosol acidity measurements in the eastern United States.[2]

Regressions using Equation 6-1 were carried out on data collected at the three monitoring sites. r^2s were greater than 0.80, and sulfur coefficients were greater than 0.25. Sulfur coefficients greater than 0.25 imply that there was more than enough hydrogen for sulfate to be in the form of ammonium sulfate, and are suggestive of fully neutralized sulfate and organic carbon mixtures. However, others, such as Covert[3], have made independent measurements of NH_4 and SO_4 ions along the Pacific Coast and have concluded that the sulfate is only half neutralized. However, it seems quite possible that the sulfate could be fully neutralized after having moved inland to the Cascade Range.

Based on the foregoing analysis, and as a first approximation, all elemental sulfur is assumed to be in the form of ammonium sulfate. The nitrate ion is assumed to be associated with ammonium nitrate, (NH_4NO_3). OCLT and OCHT are assumed to be in the form of organic carbon, and ECLT and ECHT are assumed to be light-absorbing carbon. Therefore, the following definitions will be used throughout the paper:

$$(NH_4)_2 SO_4 = 4.125(S) \quad \text{(6-2)}$$

$$(NH_4)_2 SO_4 = 4.125(S) \quad NH_4 NO_3 = 1.3(NO_3) \quad \textbf{(6-3)}$$

$$OC = 1.4(OCLT + OCHT) \quad (6\text{-}4)$$

$$LAC = ECLT + ECHT \quad (6\text{-}5)$$

$$Soil = 18(Fe) \quad (6\text{-}6)$$

where Fe is elemental iron. Coarse mass (CM) is calculated by subtracting the fine mass (FM) from the total mass.

Table 6-1 is a statistical summary of the aerosol mass concentrations for the three monitoring sites. Even though the Marblemount monitoring site is about 150 miles north of Paradise and Tahoma Woods, and Paradise is thousands of feet higher in elevation than the other two sites, the average fine mass concentrations (8-10 $\mu g/m^3$) are similar at all three stations. The Tahoma Woods site has the highest average fine and coarse mass concentrations, while the higher elevation site at Paradise has the lowest average coarse mass value.

Figures 6-1 to 6-3 show temporal plots of fine mass and the various aerosol types. Examination of the time lines suggests that fine mass concentrations tend to be more episodic at the southern sites than at Marblemount. The fine mass variance at Marblemount is about 14, while at Tahoma Woods it is approximately 32. Much of the difference in variance between the two sites is associated with changes in carbon concentrations. The variance of organic mass at Marblemount is 2 while at Tahoma Woods it is more than a factor of 2.5 higher at 5.2.

Figures 6-4, 6-5, and 6-6 are scatter plots of reconstructed and measured fine mass. Reconstructed fine mass is the sum of the mass associated with each aerosol type:

$$Recon.\,Fine\,Mass = (NH_4)_2SO_4 + NH_4NO_3 + OC + LAC + Soil. \quad (6\text{-}7)$$

One obvious trend in these graphs is that measured fine mass can be considerably larger than reconstructed fine mass but rarely less. There are many sampling periods where measured fine mass is a factor of two or more higher than predicted fine mass. On the other hand, in many sampling periods, reconstructed and measured fine mass compare quite favorably.

The relationships between various aerosol types can be further explored by examining intercorrelations between variables. Figures 6-7, 6-8, and 6-9 are scatter plots of the various aerosol species scattered against each other, while Table 6-2 presents the associated correlation tables. The correlations between fine mass and all the fine mass species are highly significant at all sites, while the correlation between fine mass and coarse mass is low at every site. The fine mass to fine mass species correlations are typically between 0.5 and 0.7.

The intercorrelation between variables can be further explored using factor analysis. To force each variable to load as strongly as possible onto a single factor, a varimax rotation was performed. Table 6-3 presents the rotated factor patterns associated with a varimax rotation for the three monitoring sites. At Tahoma Woods and Marblemount there were only two meaningful

Table 6-1. Summary statistics of fine and coarse mass and aerosol species concentrations for Tahoma Woods, Paradise, and Marblemount. Units are $\mu g/m^3$.

VARIABLE	MEAN	STD DEV	MINIMUM	MAXIMUM	VALID
TAHOMA WOODS					
FINE MASS ($\mu g/m^3$)	9.72	5.66	0.86	28.18	177
RECON FINE MASS ($\mu g/m^3$)	7.52	4.09	0.50	18.47	164
$(NH_4)_2SO_4$ ($\mu g/m^3$)	2.16	1.47	-0.26	7.16	177
NH_4N0_3 ($\mu g/m^3$)	0.44	0.38	0.00	2.28	170
OC ($\mu g/m^3$)	3.56	2.26	0.14	10.32	170
LAC ($\mu g/m^3$)	0.70	0.44	0.05	2.24	170
SOIL ($\mu g/m^3$)	0.48	0.44	0.02	2.43	177
CM ($\mu g/m^3$)	9.57	7.63	0.65	43.63	163
PARADISE					
FINE MASS ($\mu g/m^3$)	8.19	3.97	1.03	19.39	78
RECON FINE MASS ($\mu g/m^3$)	5.65	3.06	0.75	15.35	77
$(NH_4)_2SO_4$ ($\mu g/m^3$)	1.75	1.47	-0.05	7.32	84
$NaSO_4$ ($\mu g/m^3$)	0.04	0.04	0.00	0.16	84
NH_4N0_3 ($\mu g/m^3$)	0.24	0.18	0.00	1.06	82
OC ($\mu g/m^3$)	2.65	1.54	0.24	6.59	77
LAC ($\mu g/m^3$)	0.40	0.22	0.03	1.11	77
SOIL ($\mu g/m^3$)	0.48	0.46	0.00	1.69	84
CM ($\mu g/m^3$)	7.43	5.71	0.29	32.07	69
MARBLEMOUNT					
FINE MASS ($\mu g/m^3$)	8.01	3.73	1.36	18.44	171
RECON FINE MASS ($\mu g/m^3$)	6.33	2.71	0.87	13.97	171
$(NH_4)_2SO_4$ ($\mu g/m^3$)	1.74	1.15	-0.23	5.81	174
$NaSO_4$ ($\mu g/m^3$)	0.06	0.08	0.00	0.42	174
NH_4N0_3 ($\mu g/m^3$)	0.39	0.33	0.03	1.54	173
OC ($\mu g/m^3$)	3.06	1.42	0.43	7.71	171
LAC ($\mu g/m^3$)	0.44	0.23	0.00	1.26	171
SOIL ($\mu g/m^3$)	0.45	0.39	0.03	1.96	174
CM ($\mu g/m^3$)	9.34	7.00	0.10	40.97	161

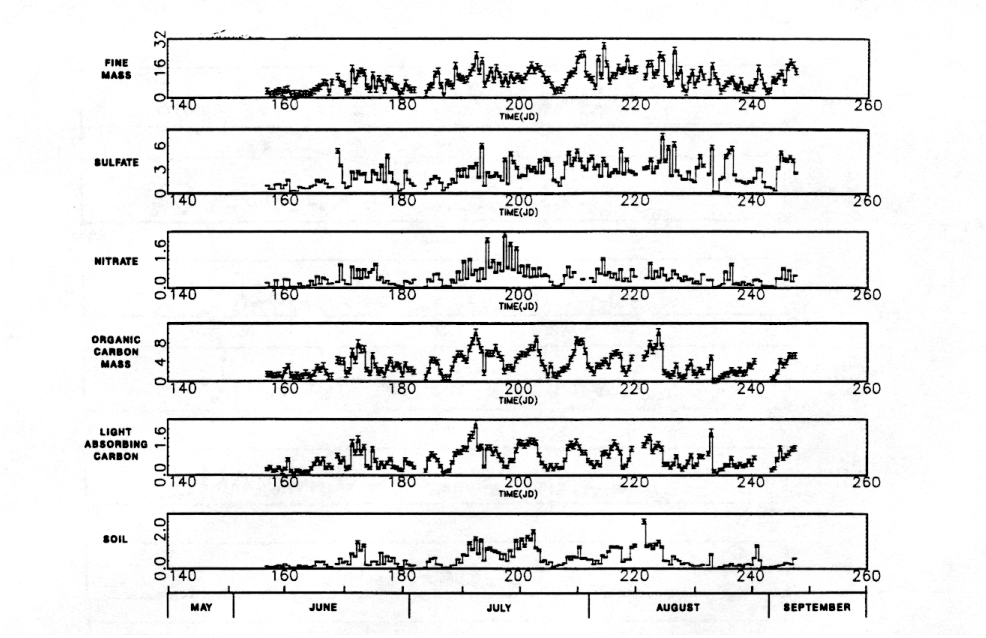

Figure 6-1. Tahoma Woods: Temporal plot of fine mass, ammonium sulfate, ammonium nitrate, organics, light-absorbing carbon and soil mass concentrations. Time is presented as Julian day for the year 1990 while units on concentration are $\mu g/m^3$. Also presented are the measurement uncertainties associated with each data point.

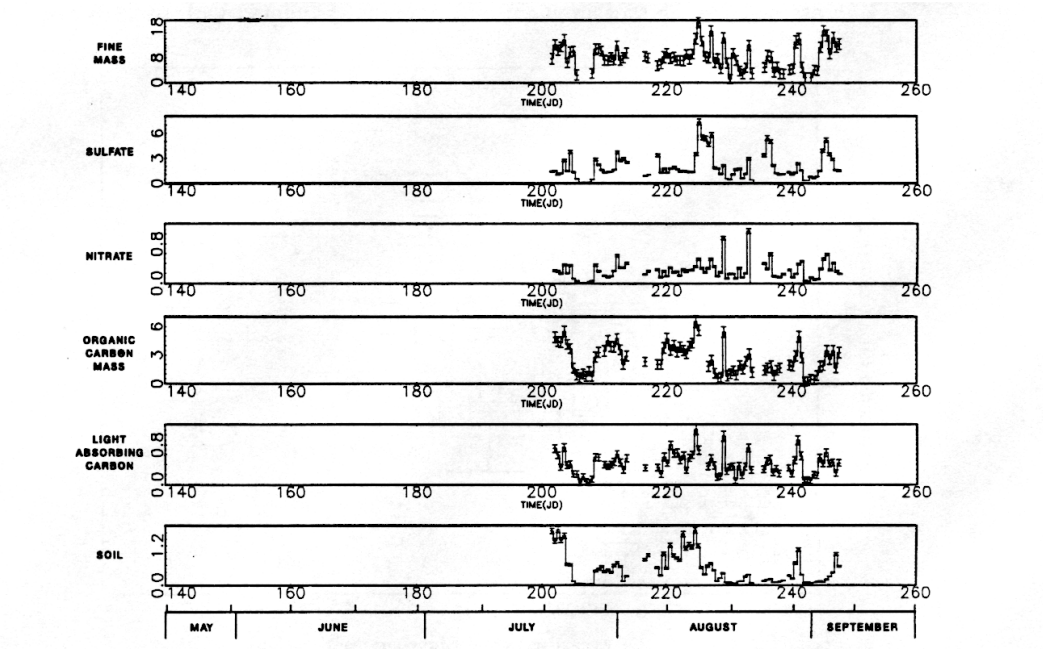

Figure 6-2. Paradise: Temporal plot of fine mass, ammonium sulfate, ammonium nitrate, organics, light-absorbing carbon and soil mass concentrations. Time is presented as Julian day for the year 1990 while units on concentration are $\mu g/m^3$. Also presented are the measurement uncertainties associated with each data point.

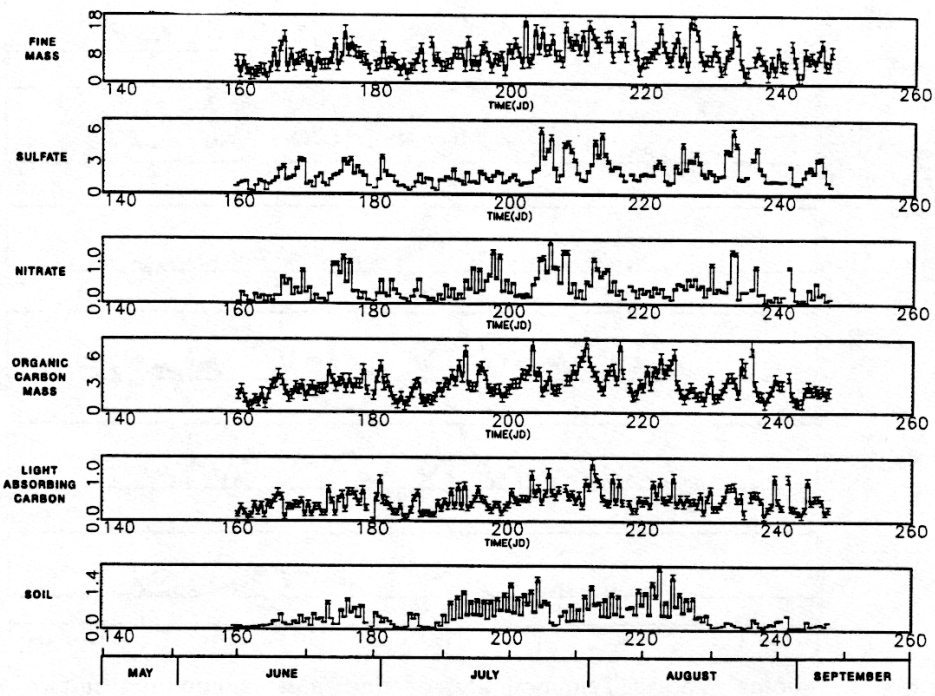

Figure 6-3. Marblemount: Temporal plot of fine mass, ammonium sulfate, ammonium nitrate, organics, light-absorbing carbon and soil mass concentrations. Time is presented as Julian day for the year 1990 while units on concentration are $\mu g/m^3$. Also presented are the measurement uncertainties associated with each data point.

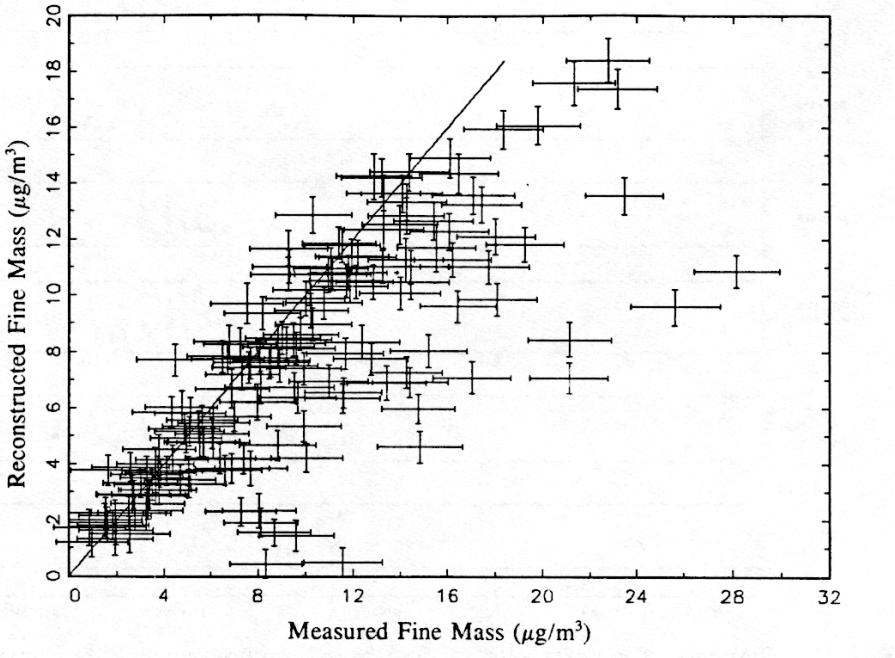

Figure 6-4. Tahoma Woods: Scatter plot of reconstructed and measured fine mass along with associated uncertainties. Units are $\mu g/m^3$. The one-to-one line is also shown for reference.

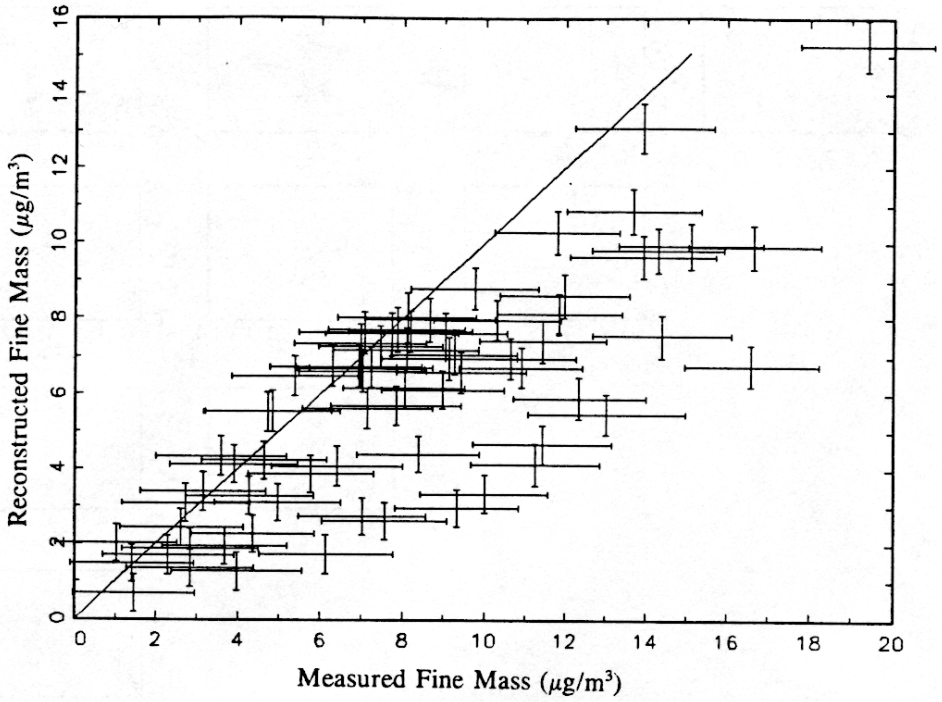

Figure 6-5. Paradise: Scatter plot of reconstructed and measured fine mass along with associated uncertainties. Units are $\mu g/m^3$. The one-to-one line is also shown for reference.

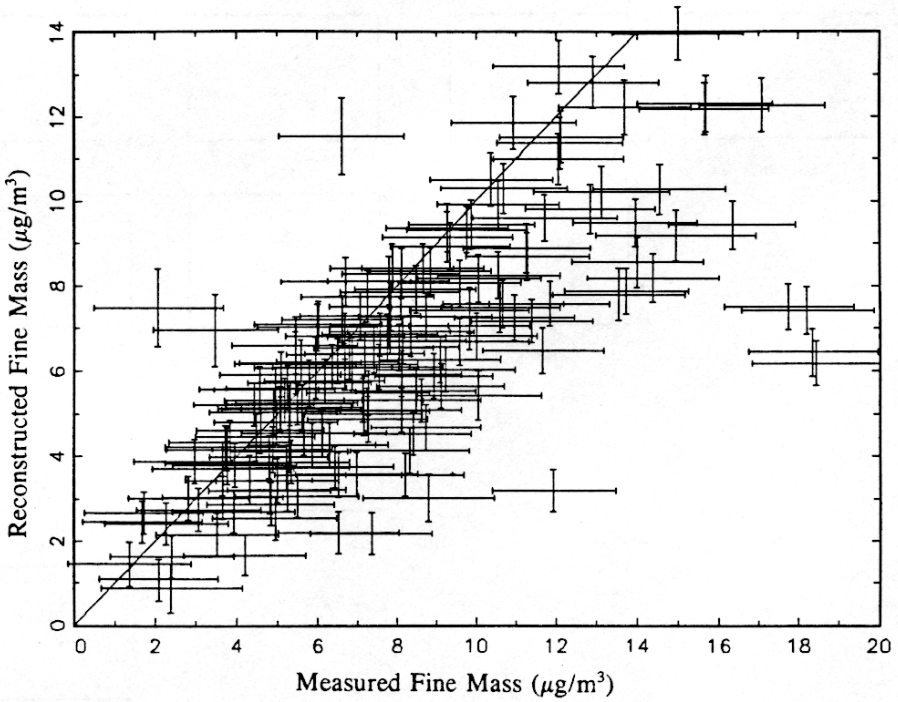

Figure 6-6. Marblemount: Scatter plot of reconstructed and measured fine mass along with associated uncertainties. Units are $\mu g/m^3$. The one-to-one line is also shown for reference.

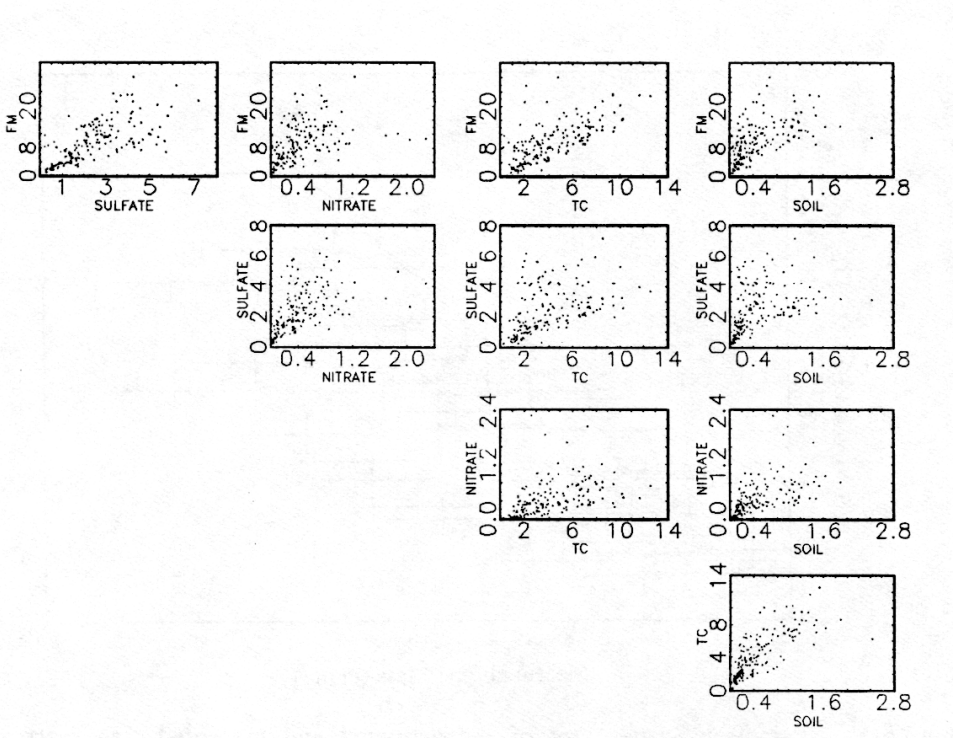

Figure 6-7. Tahoma Woods: Draftsman plot of fine mass and various aerosol species' concentrations. Units are $\mu g/m^3$.

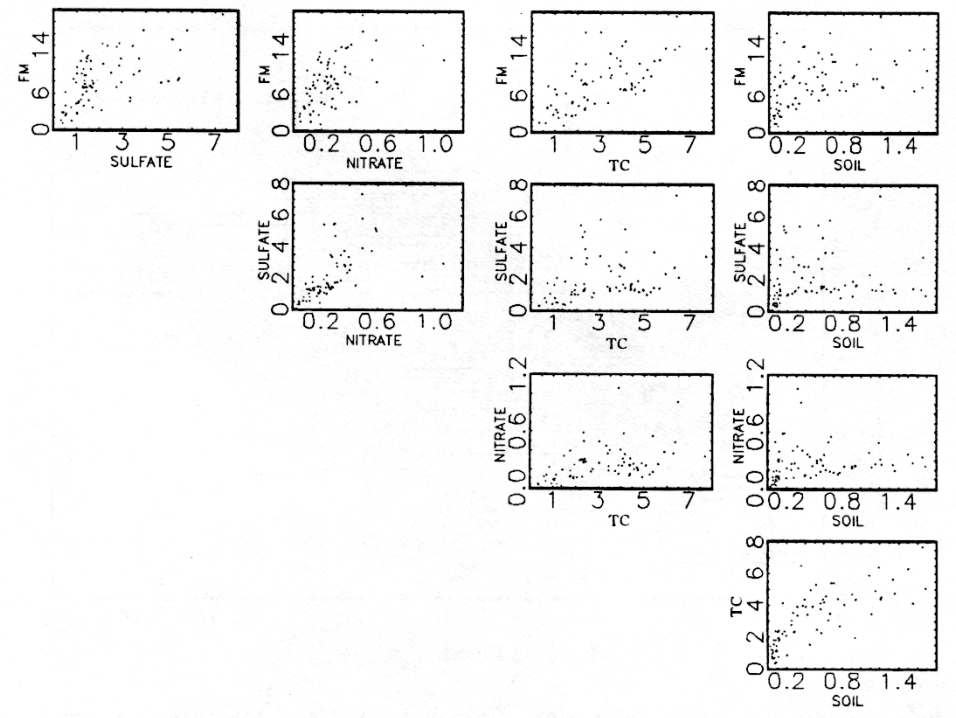

Figure 6-8. Paradise: Draftsman plot of fine mass and various aerosol species' concentrations. Units are $\mu g/m^3$.

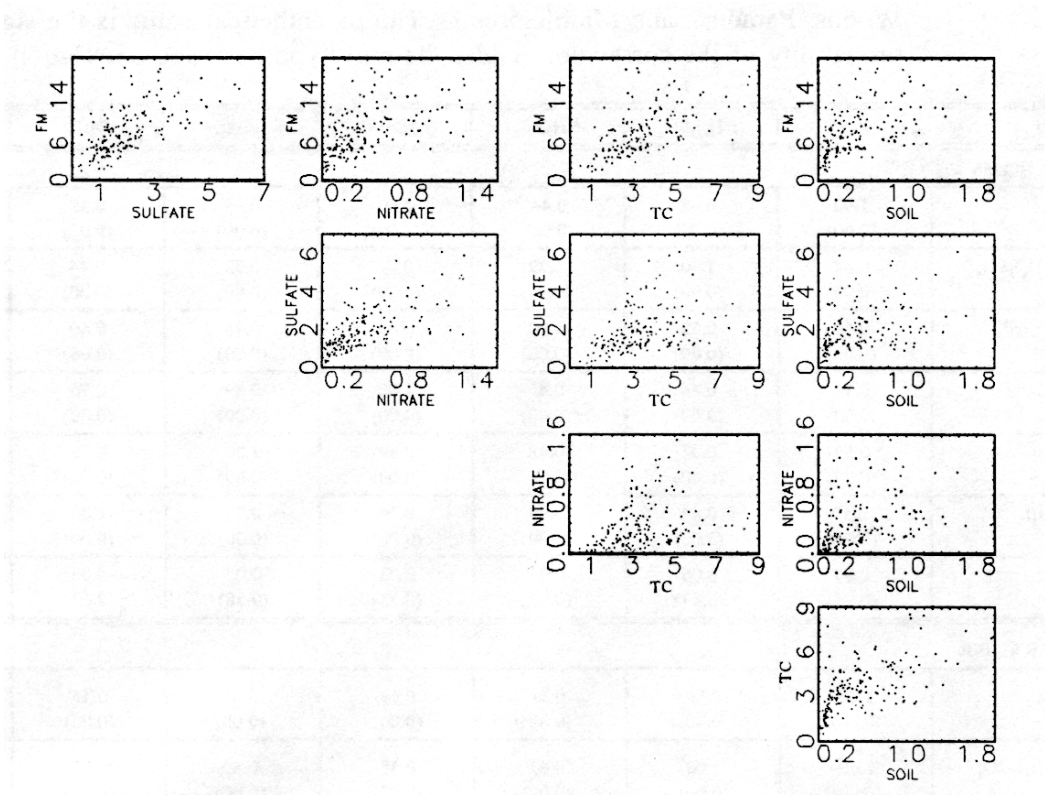

Figure 6-9. Marblemount: Draftsman plot of fine mass and various aerosol species' concentrations. Units are $\mu g/m^3$.

factors with the factors being similar but not identical for each site. At Tahoma Woods, fine mass and fine mass species all load into factor 1 with factor loadings of about 0.7 or higher while coarse mass loads into factor 2. At Marblemount fine mass, sulfates, nitrates, and light-absorbing carbon load into factor 1, while OC, soil, and coarse mass load into factor 2. At Paradise, there are three factors. Factor 1 contains organics, light-absorbing carbon, and soil. Factor 2 is primarily associated with fine mass, sulfates, and nitrates. And factor 3 again is associated with coarse mass.

When aerosol species load into one factor it suggests a high degree of collinearity between those variables. Therefore, the origin of those species may be from the same source or source area. Furthermore, species that load into one factor may not be independent, and multivariate techniques that attempt to independently characterize physical or chemical features of these species should be used with caution.

Multilinear regressions using fine mass as the dependent variable and composite variables suggested by factor analysis as independent variables can yield some insight into assumptions associated with Equations 6-2 through 6-6, and the relationship between reconstructed and measured fine mass. The form of the regression equation used is:

Table 6-2. Pearson correlation table for fine and coarse mass and aerosol species for Tahoma Woods, Paradise, and Marblemount. The parenthetical value is the significance probability of the correlation, under the null hypothesis the correlation is zero.

	FM	$(NH_4)_2SO_4$	NH_4NO_3	OC	LAC	SOIL	CM
TAHOMA WOODS							
FM	1.00 (0.00)	0.68 (0.00)	0.44 (0.00)	0.69 (0.00)	0.69 (0.00)	0.59 (0.00)	0.00 (0.99)
$(NH_4)_2SO_4$	0.68 (0.00)	1.00 (0.00)	0.52 (0.00)	0.44 (0.00)	0.52 (0.00)	0.44 (0.00)	0.06 (0.47)
NH_4NO_3	0.44 (0.00)	0.52 (0.00)	1.00 (0.00)	0.45 (0.00)	0.48 (0.00)	0.60 (0.00)	-0.02 (0.79)
OC	0.69 (0.00)	0.44 (0.00)	0.45 (0.00)	1.00 (0.00)	0.89 (0.00)	0.76 (0.00)	0.03 (0.73)
LAC	0.69 (0.00)	0.52 (0.00)	0.48 (0.00)	0.89 (0.00)	1.00 (0.00)	0.79 (0.00)	0.05 (0.58)
SOIL	0.59 (0.00)	0.44 (0.00)	0.60 (0.00)	0.76 (0.00)	0.79 (0.00)	1.00 (0.00)	0.03 (0.69)
CM	0.00 (0.99)	0.06 (0.47)	-0.02 (0.79)	0.03 (0.73)	0.05 (0.58)	0.03 (0.69)	1.00 (0.00)
PARADISE							
FM	1.00 (0.00)	0.60 (0.00)	0.58 (0.00)	0.64 (0.00)	0.66 (0.00)	0.45 (0.00)	0.03 (0.83)
$(NH_4)_2SO_4$	0.60 (0.00)	1.00 (0.00)	0.63 (0.00)	0.35 (0.00)	0.49 (0.00)	0.17 (0.12)	0.11 (0.36)
NH_4NO_3	0.58 (0.00)	0.63 (0.00)	1.00 (0.00)	0.45 (0.00)	0.69 (0.00)	0.24 (0.03)	-0.16 (0.20)
OC	0.64 (0.00)	0.35 (0.00)	0.45 (0.00)	1.00 (0.00)	0.82 (0.00)	0.77 (0.00)	0.08 (0.52)
LAC	0.66 (0.00)	0.49 (0.00)	0.69 (0.00)	0.82 (0.00)	1.00 (0.00)	0.66 (0.00)	-0.03 (0.83)
SOIL	0.45 (0.00)	0.17 (0.12)	0.24 (0.03)	0.77 (0.00)	0.66 (0.00)	1.00 (0.00)	0.22 (0.08)
CM	0.03 (0.83)	0.11 (0.36)	-0.16 (0.20)	0.08 (0.52)	-0.03 (0.83)	0.21 (0.08)	1.00 (0.00)
MARBLEMOUNT							
FM	1.00 (0.00)	0.62 (0.00)	0.50 (0.00)	0.52 (0.00)	0.61 (0.00)	0.52 (0.00)	0.16 (0.05)
$(NH_4)_2SO_4$	0.62 (0.00)	1.00 (0.00)	0.68 (0.00)	0.30 (0.00)	0.62 (0.00)	0.37 (0.00)	0.25 (0.00)
NH_4NO_3	0.50 (0.00)	0.68 (0.00)	1.00 (0.00)	0.23 (0.00)	0.50 (0.00)	0.37 (0.00)	0.12 (0.15)
OC	0.52 (0.00)	0.30 (0.00)	0.23 (0.00)	1.00 (0.00)	0.69 (0.00)	0.57 (0.00)	0.19 (0.02)
LAC	0.61 (0.00)	0.62 (0.00)	0.50 (0.00)	0.69 (0.00)	1.00 (0.00)	0.58 (0.00)	0.15 (0.05)
SOIL	0.52 (0.00)	0.37 (0.00)	0.37 (0.00)	0.57 (0.00)	0.58 (0.00)	1.00 (0.00)	0.35 (0.00)
CM	0.16 (0.05)	0.25 (0.00)	0.12 (0.15)	0.19 (0.02)	0.15 (0.05)	0.35 (0.00)	1.00 (0.00)

Table 6-3. Rotated factor patterns for specified variables for Tahoma Woods, Paradise, and Marblemount. Varimax rotation was assumed.

TAHOMA WOODS	FACTOR 1	FACTOR 2
FM	0.88	0.01
$(NH_4)_2SO_4$	0.71	0.06
NH_4N0_3	0.68	-0.12
OC	0.90	0.06
LAC	0.92	0.07
SOIL	0.88	-0.01
CM	0.01	0.99
Variance explained by each factor		
	FACTOR 1	FACTOR 2
	4.14	1.01

PARADISE	FACTOR 1	FACTOR 2	FACTOR 3
FM	0.54	0.72	0.01
$(NH_4)_2SO_4$	0.04	0.91	0.18
NH_4N0_3	0.20	0.84	-0.25
OC	0.91	0.25	0.01
LAC	0.78	0.48	-0.14
SOIL	0.91	-0.03	0.19
CM	0.08	-0.01	0.97
Variance explained by each factor			
	FACTOR 1	FACTOR 2	FACTOR 3
	2.60	2.35	1.09

MARBLEMOUNT	FACTOR 1	FACTOR 2
FM	0.76	0.41
$(NH_4)_2SO_4$	0.85	0.16
NH_4N0_3	0.85	-0.01
OC	0.38	0.71
LAC	0.72	0.47
SOIL	0.39	0.73
CM	-0.06	0.70
Variance explained by each factor		
	FACTOR 1	FACTOR 2
	2.83	1.94

$$FM = \sum_{1}^{N} a_i M_i \qquad (6\text{-}7)$$

where FM is fine mass and M_i is the mass concentrations of composite variables. Composite variables are formed by summing the mass concentrations associated with each factor but without regard to their factor loadings. Table 6-4 shows the results of this analysis for the Paradise data set. Sulfates and nitrates were combined into one variable, while total carbon (TC) plus soil is the sum of organic and light-absorbing carbon, and soil formed a second variable. Presented in the table are the results of both ordinary least square (OLS) and variance weighted (VW) regressions. Variance weighted regressions accounted for measurement uncertainties.[4] A similar analysis was not carried out on data from the other sites because of the high degree of collinearity between variables.

If the assumptions associated with Equations 6-2 to 6-7 are correct and the variables are independent of each other, then the regression coefficients should be equal to one and the intercept equal to zero. The regression analysis suggests that sulfate-nitrate mass has been underestimated by about 20-30%, while the regression coefficient associated with total carbon is near one, showing the mass estimate for organic and light-absorbing carbon and soil may be close to correct. Intercepts for both the OLS and VW regressions are between 1 and 2 $\mu g/m^3$. Variance weighted regressions are similar to OLS results; however, coefficients associated with organics tend to be higher because of the larger measurement uncertainty associated with that variable. The r^2s are approximately 0.60, indicating something less than a "perfect" fit.

The large positive intercepts and the inflated regression coefficients, along with a general underprediction of reconstructed fine mass using the sum of estimated species mass, imply that a significant fraction of the measured fine mass is not being accounted for.

Table 6-4. Paradise: This table presents the results of ordinary least square and variance weighted regressions, with fine mass as the dependent variable and aerosol species as independent variables. Results of ordinary least square and variance weighted regressions with fine mass as the dependent variable and composite parameters as the dependent variables. Sulfates and nitrates are summed to form one variable, while organics, light-absorbing carbon, and soil are summed to form a second variable.

$r^2 = 0.63$	Ordinary Least Square			Variance Weighted Regression		
Variable	Estimate	Std Error	t-value	Estimate	Std Error	t-value
CONSTANT	1.67	0.68	2.48	1.44	0.70	2.07
SO_4+NO_3	1.27	0.20	6.25	1.25	0.21	5.95
TC+SOIL	0.99	0.15	6.48	1.06	0.17	6.41

Although water associated with hygroscopic aerosols was not explicitly measured, it is

expected that a significant amount of water was retained on the filter when the filters were weighed. The filters were equilibrated in the laboratory at approximately 50% relative humidity, a value which is well above the relative humidity at which ammonium sulfate particles dry out.[5] Because average relative humidities observed in the field were around 80%, it is to be expected that measured fine mass be larger than the sum of individual mass species if water is not accounted for. The inflated regression coefficient associated with the hygroscopic salt species is consistent with this hypothesis. On the other hand, the regression coefficient of near one associated with organics suggests that organics may not be highly water soluble.

Table 6-5 presents the fine mass budgets, based on Equations 6-1 through 6-6, for the three monitoring sites. The fractions presented for each species are their fraction relative to reconstructed fine mass. The missing mass fraction is the percent difference between reconstructed and measured fine mass. In other words, rows 1-5 (not 1-6) sum to 100%. There is very little variation in the mass budgets between sites. The missing mass fraction (may be due to water associated with hygroscopic species), calculated by summing masses associated with each individual species and comparing this sum to measured-fine mass, is around 20% at both low elevation sites and slightly over 30% at Paradise. The ammonium sulfate mass fraction (fraction of calculated fine mass) is about 30-35%, while the organic mass fraction is about 45-50%. Nitrates, light-absorbing carbon, and soil each make up about 7-9% of the fine mass.

Table 6-5. Fine mass budgets for Tahoma Woods, Paradise, and Marblemount.

	TAHOMA WOODS	PARADISE	MARBLEMOUNT
Sulfate mass fraction	0.32	0.34	0.32
Nitrate mass fraction	0.06	0.04	0.06
OC mass fraction	0.47	0.46	0.48
LAC mass fraction	0.09	0.07	0.07
Soil mass fraction	0.06	0.09	0.07
Missing mass fraction	0.23	0.32	0.21

6.3 EXTINCTION COMPONENTS

The extinction coefficient, b_{ext}, is the sum:

$$b_{ext} = b_{sp} + b_{ap} + b_{sg} + b_{ag} \quad (6\text{-}8)$$

where b_{sp} is scattering by particles, b_{ap} is absorption by particles, b_{sg} is scattering by gases, b_{ag} is absorption by gases, and all terms are wavelength dependent. Light scattering by gases in the atmosphere, b_{sg}, is described by the Rayleigh scattering theory[6] and will be referred to as Rayleigh scattering. The only gas that is normally found in the atmosphere and absorbs light is nitrogen

dioxide.

In most instances, particle scattering and absorption are primarily responsible for visibility reduction. Single particle scattering and absorption properties can, with a number of limiting assumptions, be calculated theoretically using Mie theory[6] or estimated using statistical multivariate techniques.[4,7,8] However, before such calculations are carried out, suitable boundary conditions must be specified. Typically aerosol models assume:

- External mixtures - particles exist in the atmosphere as pure chemical species which are mixed without interaction;

- Multi-component aerosols - single particles are made up of two or more species. If the chemical species is combined in fixed proportions independent of particle size, then the aerosol is referred to as internally mixed. Other models assume solid cores with deposited shells of various thickness and composition.

If an aerosol is mixed externally or if in an internally mixed aerosol the index of refraction is not a function of composition or size, then the aerosol density is independent of volume. Aerosol extinction due to particles can be related in a linear fashion to particle mass concentration:[9]

$$b_{ext} = \sum_{i}^{N} \alpha_i m_i \qquad (6\text{-}9)$$

where α_i and m_i are the extinction efficiencies and mass concentrations, respectively.

A number of investigators have taken advantage of the form of Equation 6-9 to construct a multilinear regression model with b_{ext} as the independent variable and the measured aerosol mass concentrations of species i as the independent variables. The regression coefficients are then interpreted as extinction to mass efficiencies.[7,8] The use of multivariate regression models to apportion mass concentrations to scattering and absorption requires that the model meet a number of limiting assumptions and should be used with caution. White[4] discusses some of the issues associated with this problem.

Any apportionment of aerosol mass to extinction is only approximate. The assumptions required for extinction-mass relationships implied by Equation 6-9 probably were never exactly met. The appropriateness of any apportionment scheme can only be judged within the context of whether the model is physically "reasonable," and whether independent apportionment of mass to extinction is consistent with measurements of scattering and absorption.

Because mass size distributions were not available at all sites for all time periods, theoretical calculation of scattering and absorption efficiencies were not attempted. The strategy used to construct extinction budgets in this report will be to use Equation 6-9 and nominal dry particle scattering efficiencies that have been synthesized from a variety of estimates and prorated scattering associated with condensed water among hygroscopic aerosols.[10] Regression analysis will be used to investigate the validity of assumptions used in the apportionment scheme.

6.3.1 Estimating Aerosol Absorption

Table 6-6 presents a simple statistical summary of the various carbon categories. OC, which is the sum of OCLT and OCHT, is interpreted as organic carbon, while LAC, the sum of ECLT and ECHT, is assumed to be light-absorbing carbon (see Chapter 7 for definitions of the various carbon species). OC is typically assumed to scatter but not absorb light. Units on b_{abs} are Mm^{-1}, while masses are $\mu g/m^3$. Figures 6-10, 6-11, and 6-12 are scatter plots of b_{abs} and the four carbon variables scattered against each other. b_{abs} has been multiplied by a factor of 10. Table 6-7 presents the associated correlations.

One interesting feature associated with Figure 6-10 is the bifurcated relationship between b_{abs} and OCLT, and between OCLT and OCHT. At times OCLT correlates very well with b_{abs} and OCHT and at other times there is no apparent relationship between OCLT and these two variables. Different origins of OCLT or different aerosol formation mechanisms are possible explanations.

Because b_{abs} is an independent optical measurement it is expected that it should be related to light-absorbing carbon species in a way similar to Equation 6-7 but with b_{abs} being equal to the sum of absorption efficiencies multiplied by carbon mass concentrations. Traditionally, it has been assumed that high temperature carbon (ECLT and ECHT) is elemental carbon and is primarily responsible for aerosol absorption. Therefore, one would expect a high degree of correlation between b_{abs} and the two high temperature carbon species, and possibly very little correlation between b_{abs} and the OCHT and OCLT. However, a cursory look at Figures 6-10, 6-11, and 6-12 and the associated correlation in Table 6-7 show that this is not the case. b_{abs} is correlated with OCHT as well as with ECLT and better than with ECHT. On the other hand, the sum of ECLT and ECHT correlate better with b_{abs} than either variable alone. This is also true for OCLT and OCHT.

The relationship between these variables suggests that light-absorbing carbon is not associated just with ECLT and ECHT. Apparently, there is some absorbing carbon associated with OCLT and OCHT, the variables traditionally interpreted, and organic carbon.

This hypothesis can be further explored by examining the quantitative relationships between b_{abs} and LAC and OC. If LAC was the only variable associated with light absorption, then the ratio b_{abs}/LAC, the absorption efficiency of LAC, should be between 8 and 12 m^2/g.[10] For Tahoma Woods, Paradise, and Marblemount these ratios are 14.2, 18.7, and 16.9, respectively. The inflated b_{abs}/LAC ratios further suggest that there is also some light absorption associated with the low temperature carbon species. However, some caution must be exercised. The b_{abs} values have been adjusted upward (see Chapter 4) to compensate for absorbing particles that "screen" each other. Therefore, there may be some upward bias in the optical absorption numbers.

Table 6-6. Summary statistics of b_{abs}, and various carbon aerosol concentrations for Tahoma Woods, Paradise, and Marblemount. Units for b_{abs} are Mm^{-1} while carbon species concentrations are $\mu g/m^3$.

VARIABLE	MEAN	STD DEV	MINIMUM	MAXIMUM	VALID
TAHOMA WOODS					
b_{abs} (Mm^{-1})	9.96	5.80	0.82	28.67	170
OCLT ($\mu g/m^3$)	0.34	0.28	0.00	1.52	170
OCHT ($\mu g/m^3$)	2.20	1.53	0.00	7.00	170
ECLT ($\mu g/m^3$)	0.47	0.39	0.00	1.92	170
ECHT ($\mu g/m^3$)	0.23	0.11	0.00	0.65	170
OC ($\mu g/m^3$)	2.55	1.61	0.10	7.37	170
LAC ($\mu g/m^3$)	0.70	0.44	0.05	2.24	170
PARADISE					
b_{abs} (Mm^{-1})	7.52	4.25	0.20	18.79	77
OCLT ($\mu g/m^3$)	0.25	0.19	0.00	0.81	77
OCHT ($\mu g/m^3$)	1.65	1.06	0.00	4.57	77
ECLT ($\mu g/m^3$)	0.18	0.16	0.00	0.81	77
ECHT ($\mu g/m^3$)	0.23	0.12	0.00	0.66	77
OC ($\mu g/m^3$)	1.89	1.10	0.17	4.71	77
LAC ($\mu g/m^3$)	0.40	0.22	0.03	1.11	77
MARBLEMOUNT					
b_{abs} (Mm^{-1})	7.50	3.30	1.10	22.88	171
OCLT (ng/m^{-1})	0.22	0.19	0.00	0.84	171
OCHT (ng/m^{-1})	1.96	0.98	0.22	5.22	171
ECLT (ng/m^{-1})	0.24	0.19	0.00	0.93	171
ECHT (ng/m^{-1})	0.20	0.09	0.00	0.46	171
OC (ng/m^{-1})	2.18	1.01	0.31	5.50	171
LAC (ng/m^{-1})	0.44	0.23	0.00	1.26	171

Table 6-7. Pearson correlation table for various carbon species for Tahoma Woods, Paradise, and Marblemount. The parenthetical value is the significance probability of the correlation, under the null hypothesis the correlation is zero.

	b_{abs}	OCLT	OCHT	ECLT	ECHT
TAHOMA WOODS					
b_{abs}	1.00 (0.00)	0.28 (0.00)	0.87 (0.00)	0.88 (0.00)	0.53 (0.00)
OCLT	0.28 (0.00)	1.00 (0.00)	0.21 (0.01)	0.11 (0.15)	0.54 (0.00)
OCHT	0.87 (0.00)	0.21 (0.01)	1.00 (0.00)	0.87 (0.00)	0.53 (0.00)
ECLT	0.88 (0.00)	0.11 (0.15)	0.87 (0.00)	1.00 (0.00)	0.37 (0.00)
ECHT	0.53 (0.00)	0.54 (0.00)	0.53 (0.00)	0.37 (0.00)	1.00 (0.00)
PARADISE					
b_{abs}	1.00 (0.00)	0.21 (0.06)	0.81 (0.00)	0.79 (0.00)	0.53 (0.00)
OCLT	0.21 (0.06)	1.00 (0.00)	0.10 (0.39)	0.07 (0.57)	0.23 (0.04)
OCHT	0.81 (0.00)	0.10 (0.39)	1.00 (0.00)	0.71 (0.00)	0.59 (0.00)
ECLT	0.79 (0.00)	0.07 (0.56)	0.71 (0.00)	1.00 (0.00)	0.29 (0.01)
ECHT	0.53 (0.00)	0.23 (0.04)	0.59 (0.00)	0.29 (0.01)	1.00 (0.00)
MARBLEMOUNT					
b_{abs}	1.00 (0.00)	0.07 (0.38)	0.69 (0.00)	0.79 (0.00)	0.42 (0.00)
OCLT	0.07 (0.38)	1.00 (0.00)	0.09 (0.24)	-0.05 (0.49)	0.42 (0.00)
OCHT	0.69 (0.00)	0.09 (0.24)	1.00 (0.00)	0.61 (0.00)	0.51 (0.00)
ECLT	0.79 (0.00)	-0.05 (0.49)	0.61 (0.00)	1.00 (0.00)	0.31 (0.00)
ECHT	0.42 (0.00)	0.42 (0.00)	0.51 (0.00)	0.31 (0.00)	1.00 (0.00)

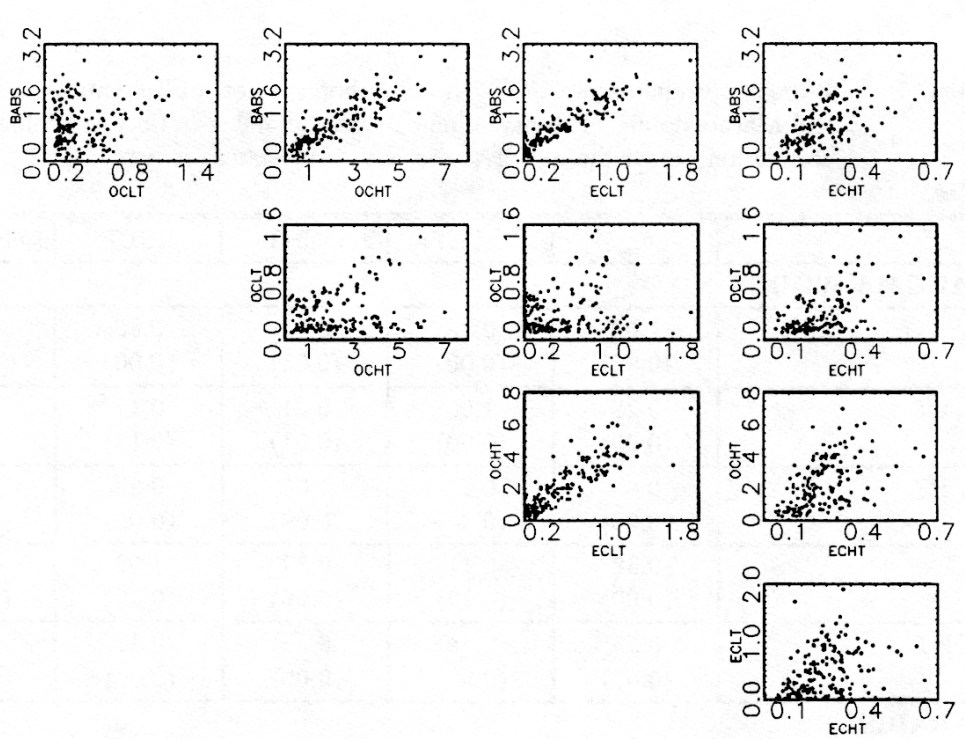

Figure 6-10. Tahoma Woods: Draftsman plot of b_{abs}, OCLT, OCHT, ECLT, and ECHT concentrations. Units on b_{abs} are $10^{-5}m^{-1}$ while carbon species concentrations are $\mu g/m^3$.

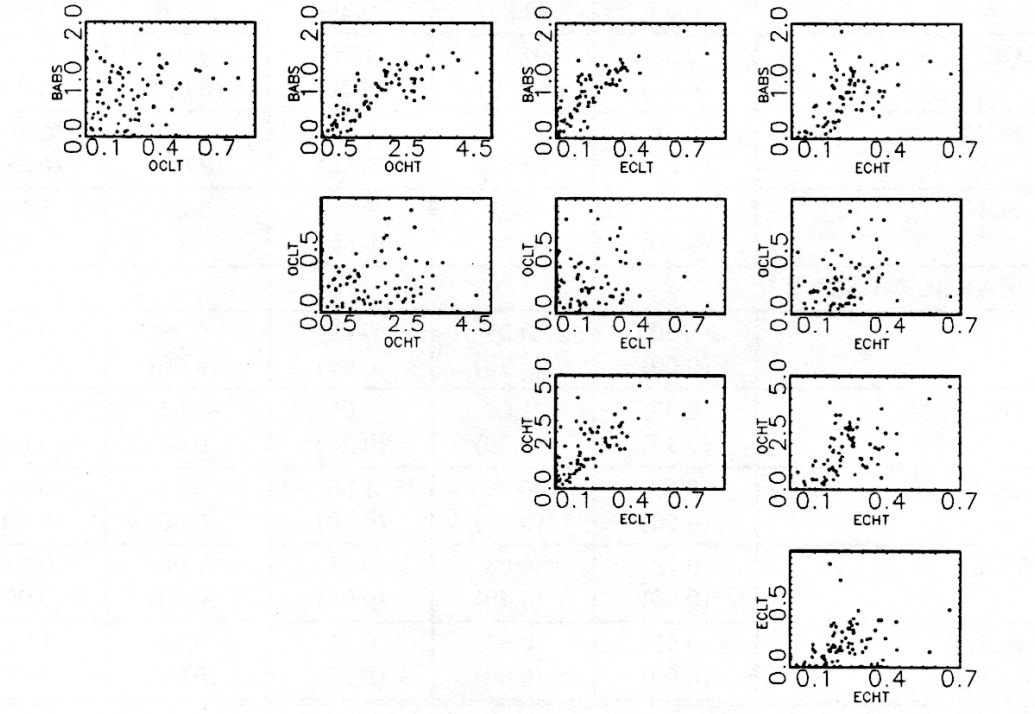

Figure 6-11. Paradise: Draftsman plot of b_{abs}, OCLT, OCHT, ECLT, and ECHT concentrations. Units on b_{abs} are $10^{-5}m^{-1}$ while carbon species concentrations are $\mu g/m^3$.

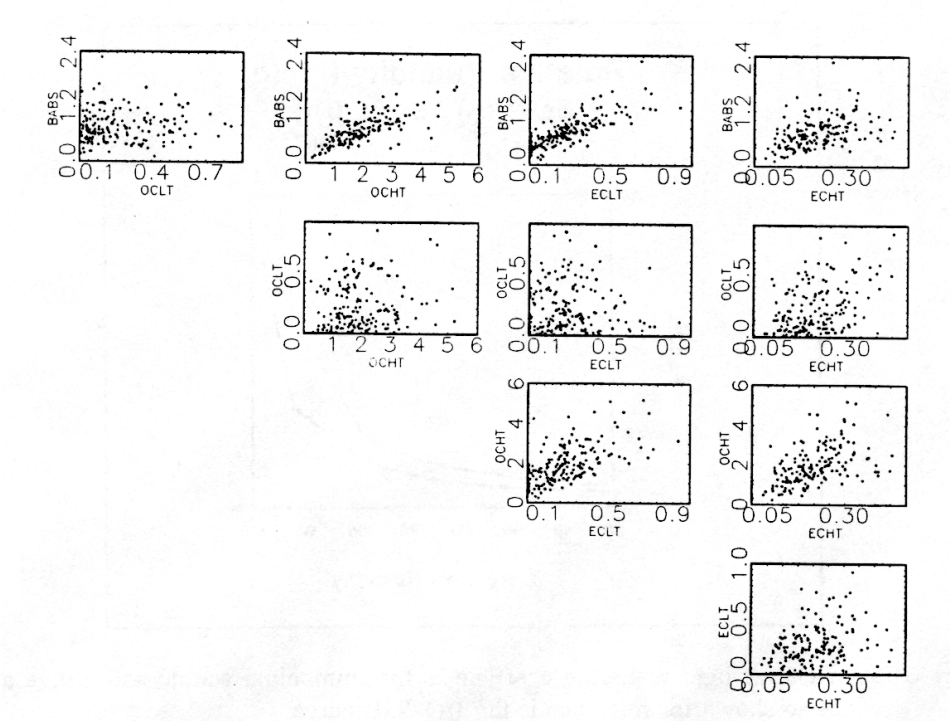

Figure 6-12. Marblemount: Draftsman plot of b_{abs}, OCLT, OCHT, ECLT, and ECHT concentrations. Units on b_{abs} are $10^{-5}m^{-1}$ while carbon species concentrations are $\mu g/m^3$.

The amount of absorption attributable to organic carbon (OCLT+OCHT) can be estimated by assuming an 8-12 m^2/g absorption efficiency for LAC and assigning the difference between measured b_{abs} and LAC absorption to organic carbon. The fraction of absorption attributed to organic carbon using this technique is 12-42%, 36-57%, and 29-53%, respectively, for Tahoma Woods, Paradise, and Marblemount.

The traditional scheme for apportioning absorption is to assume all absorption is associated with LAC and the absorption efficiency of LAC is about 10 m^2/g. Because the data gathered in this study does not definitely prove that this assumption is wrong, the "traditional" approach will be used for apportioning extinction. However, the reader is cautioned that absorption may be underestimated by as much as 50%.

6.3.2 Relative Humidity Effects

It is known that sulfate aerosols will rapidly undergo deliquescence (condensation of water vapor onto solid particles). The reverse phase change, when the liquid evaporates from droplets, occurs more slowly over a much broader range of RH. This is referred to as hysteresis. In the atmosphere, the situation is further complicated by internally mixed aerosols which may go through several stages of growth. The RHs at which these stages occur depend on the mixture, but in general are between 60% to 80%.[5]

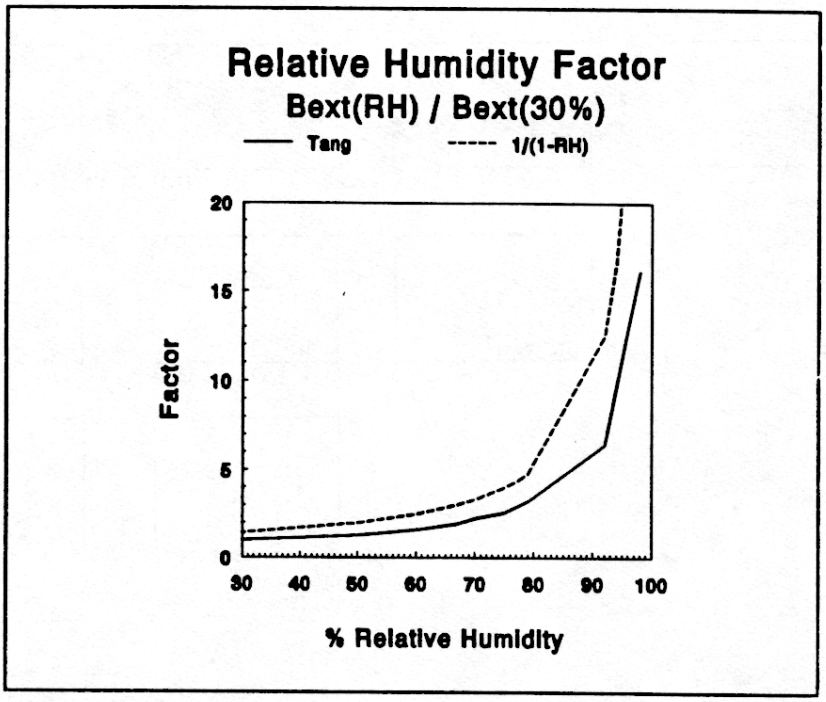

Figure 6-13. Relative light scattering coefficients for ammonium sulfate and nitrate aerosols. Also shown for reference is the 1/(1-RH) curve.

The growth and phase changes of the particles, of course, affect their light scattering efficiency. In general, the higher the RH, the greater the scattering efficiency of sulfate and nitrate aerosols. The relationship between RH and scattering efficiency, referred to as *f*(RH), is parameterized from curves published by Tang.[5] Tang's curves, calculated theoretically for aerosols of different size distributions have sharp discontinuities at 62% RH for nitrates and at 80% for sulfates, which are the deliquescence points for these species. However, because both ammonium nitrate and ammonium sulfate species have been shown to be hygroscopic at below these values[5,11] and because the size and light scattering efficiency of ambient aerosols as a function of RH has previously been observed to be rather smooth,[10,12] Tang's curves were smoothed between the deliquescence points and 30% RH (see Figure 6-13). Tang's results also show that the scattering efficiency of ammonium sulfate at low relative humidities is quite sensitive to the particle size distribution and can vary between approximately 1.4 and 3.5 m^2/g. For comparison, a curve showing 1/(1-RH), which has often been used in previous visibility studies,[7-8] is shown in the same Figure 6-13.

6.3.3 Estimating Aerosol Scattering

The following equation was used to estimate reconstructed particle scattering:

$$b_{sp} = (0.003)f(RH)[(NH_4)_2SO_4] + (0.003)f(RH)[NH_4NO_3] + 0.003[OC] + 0.001[soil] + 0.0006[CM] \quad (6\text{-}10)$$

where 0.003 is the dry scattering efficiencies of sulfates, nitrates and organic carbon, while 0.001

and 0.0006 are the respective efficiencies for soil and coarse mass. The brackets [ ] indicate concentrations of the various species. The units of the scattering efficiencies are $km^{-1}/\mu g/m^3$. The scattering efficiencies for soil and coarse mass are taken from a literature review by Trijonis *et al.*[13] It should be noted that the 0.006 $km^{-1}/\mu g/m^3$ efficiency associated with coarse mass is a "pseudo-coarse scattering efficiency" representing scattering by all coarse particles but scaled to only those particles measured below 10 μm. Because particle size measurements weren't made in this study the dry scattering efficiencies are unknown for sulfates, nitrates and organics. Therefore, a nominal value of 0.003 $km^{-1}/\mu g/m^3$ was used for all three species. It is expected that the dry efficiencies varied from near 0.001 to greater than 0.003 $km^{-1}/\mu g/m^3$. Furthermore, the f(RH) curve shown in Figure 6-13 was applied to both ammonium sulfate and ammonium nitrate.

Because the comparison of measured and reconstructed-fine mass suggest that organics are not strongly hygroscopic the initial scattering apportionment will only consider "dry" organics. The validity of this assumption will be examined by comparing reconstructed and measured scattering using regressional techniques.

Tables 6-8 and 6-9 are statistical summaries of the scattering associated with each variable for all data and just for the daytime samples. The sum of the scattering attributed to individual aerosol species is labeled as reconstructed scattering. Also presented in Tables 6-8 and 6-9 are summary statistics for measured b_{scat}, ambient relative humidity (RH_a), estimated relative humidity in the nephelometer chamber (RH_c), $f(RH_a)$, and $f(RH_c)$.

The chamber relative humidity is estimated from chamber temperature using:

$$RH_c = RH_a e^{\frac{5210.5(T_a - T_c)}{T_a T_c}} \qquad (6\text{-}11)$$

where RH_a, RH_c, T_a and T_c are the ambient and chamber relative humidities and temperatures respectively.

In spite of only about a 1 to 2°C difference between chamber and ambient temperature at the Marblemount and Tahoma Woods sites the corresponding difference in chamber and ambient RH is about 6% RH at Marblemount and 10% RH at Tahoma Woods. This translates into an overall average difference between $f(RH_a)$ and $f(RH_c)$ of about 3 and 6 at Marblemount and Tahoma Woods, respectively. The implication of these differences is that in spite of best efforts to modify nephelometers to measure ambient b_{scat}, the scattering associated with hygroscopic species was still substantially underestimated.

At Paradise, no effort was made to modify the nephelometer for purposes of making ambient measurements, and the estimated difference between ambient and chamber RH is greater than 40% RH. The average ambient RH was 72% while the estimated chamber RH is 31%. The corresponding average f(RH) values were 7.9 and 1.05. An unmodified nephelometer apparently was insensitive to the scattering associated with absorbed water in hygroscopic aerosols.

Figures 6-14, 6-15, and 6-16 are temporal plots of measured b_{scat}, ambient RH, and scattering associated with the various aerosol species. One outstanding feature associated with

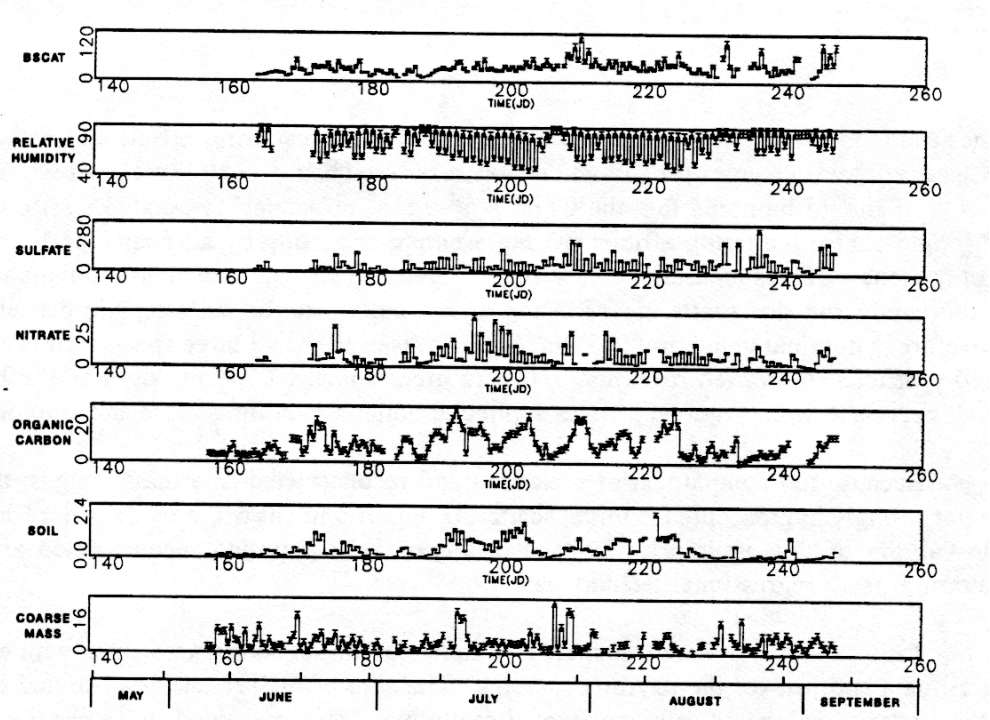

Figure 6-14. Tahoma Woods: Temporal plot of b_{scat}, ambient relative humidity, ammonium sulfate, ammonium nitrate, organic, soil and coarse mass scattering. Time is presented as Julian day for the year 1990 while units on scattering are Mm^{-1}. Also presented are the uncertainties associated with each data point.

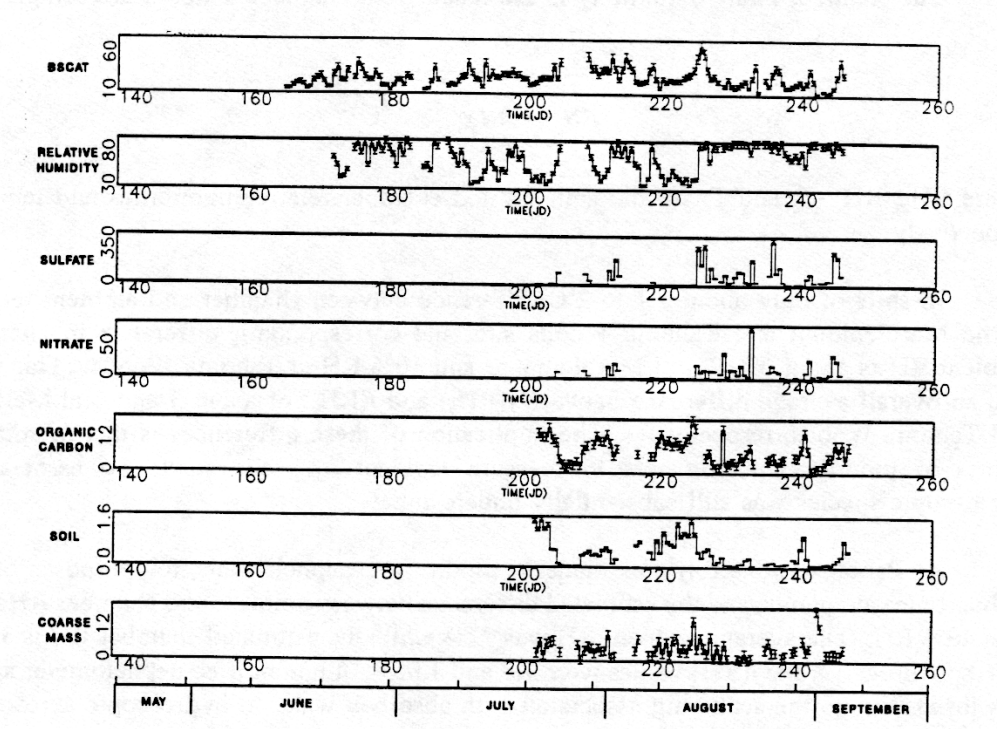

Figure 6-15. Paradise: Temporal plot of b_{scat}, ambient relative humidity, ammonium sulfate, ammonium nitrate, organic, soil and coarse mass scattering. Time is presented as Julian day for the year 1990 while units on scattering are Mm^{-1}. Also presented are the uncertainties associated with each data point.

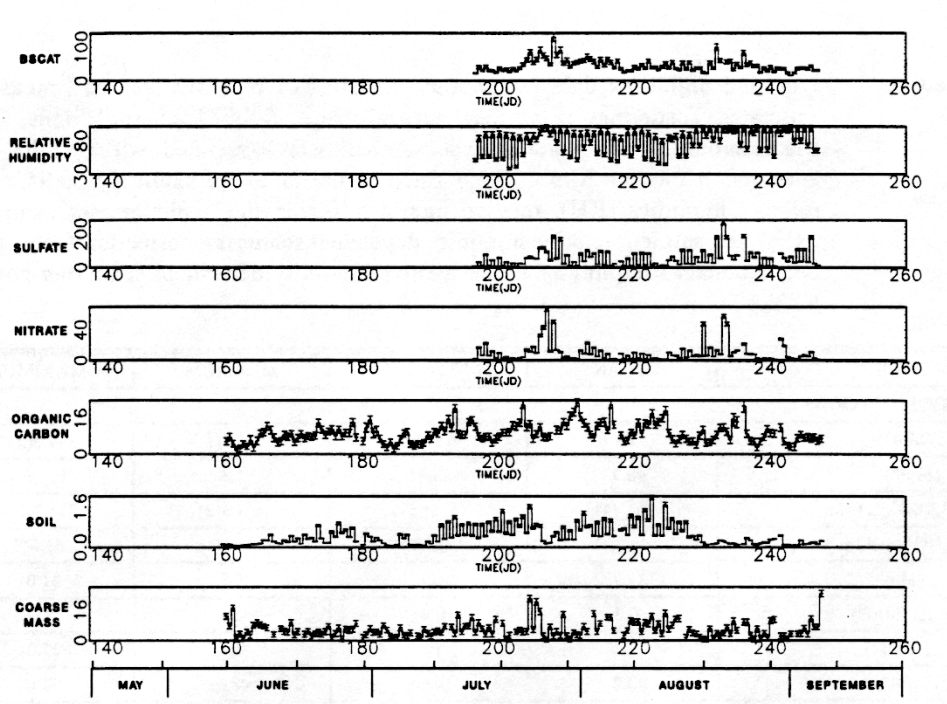

Figure 6-16. Marblemount: Temporal plot of b_{scat}, ambient relative humidity, ammonium sulfate, ammonium nitrate, organic, soil and coarse mass scattering. Time is presented as Julian day for the year 1990 while units on scattering are Mm^{-1}. Also presented are the uncertainties associated with each data point.

each of these figures is the large diurnal variation in relative humidity at the two low elevation sites, while at Paradise the relative humidity shows very little diurnal change. Furthermore, as with fine mass the variance of reconstructed extinction is greater at Paradise than the two lower elevation sites. (Measured b_{scat} cannot be compared between sites because the nephelometer at Paradise was not modified to run in an ambient mode.) The large swings in relative humidity are reflected in the changes in scattering of the hygroscopic aerosol species.

Comparing Tables 6-8 and 6-9 shows that because of significantly reduced daytime relative humidities the ambient daylight extinctions are significantly reduced. For instance, the daytime and nighttime mean extinction at Tahoma Woods is 88.7 Mm^{-1} while the mean daytime extinction is 52.8 Mm^{-1}. Therefore, daytime visibilities are better just because the relative humidity is lower.

Figures 6-17, 6-18, and 6-19 are scatter plots of reconstructed b_{scat} using ambient RH and measured b_{scat} along with the one-to-one line. Not surprisingly, because of the humidity difference between the nephelometer chamber and ambient, reconstructed and measured b_{scat} do not agree very well. At all three monitoring sites reconstructed b_{scat} is, at times, significantly larger than measured values. The disparity is largest at the Paradise site where the difference between chamber and ambient relative humidity is greatest. However, predicted scattering is never more than a few percent lower than the measured values.

Table 6-8. Day and nighttime data: Summary statistics of reconstructed and measured b_{scat} and estimated scattering of various aerosol species for Tahoma Woods, Paradise, and Marblemount. The parenthetical numbers are associated with results of regression analysis. Units are Mm^{-1}. Also listed in the table are summary statistics for ambient relative humidity (RH), relative humidity inside the nephelometer sampling chamber (RH_c), the ambient relative humidity dependent scattering correction factor f(RH), and the nephelometer sampling chamber relative humidity dependent scattering correction factor $f(RH_c)$.

VARIABLE	MEAN	STD DEV	MINIMUM	MAXIMUM	VALID
TAHOMA WOODS					
$b_{scat,r}$ (Mm^{-1})	88.7(65)	61.6(42)	16.1(15)	347.3(240)	118
b_{scat} (Mm^{-1})	40.7	23.4	2.4	121.6	118
$(NH_4)_2SO_{4,scat}$ (Mm^{-1})	61.7(41)	55.5(37)	3.3(2)	321.2(220)	118
$NH_4NO_{3,scat}$ (Mm^{-1})	9.3(6)	8.1(5)	0.8(1)	41.6(30)	118
OC_{scat} (Mm^{-1})	11.7	6.9	1.5	31.0	118
$SOIL_{scat}$ (Mm^{-1})	0.5	0.4	0.0	1.9	118
CM_{scat} (Mm^{-1})	5.5	4.2	0.4	22.0	118
RH_a (%)	83.2	14.6	48.6	98.8	156
RH_c (%)	73.9	14.1	40.4	94.2	156
f(RH)	9.2	6.5	1.5	24.8	156
$f(RH_c)$	3.9	2.5	1.1	20.2	156
PARADISE					
$b_{scat,r}$ (Mm^{-1})	91.5(130)	103.4(150)	14.8(20)	453.1(650)	59
b_{scat} (Mm^{-1})	23.3	12.3	2.0	63.3	59
$(NH_4)_2SO_{4,scat}$ (Mm^{-1})	68.1(100)	93.2(130)	2.8(4)	418.6(600)	59
$NH_4NO_{3,scat}$ (Mm^{-1})	9.5(14)	14.2(21)	0.00(0)	85.1(123)	59
OC_{scat} (Mm^{-1})	8.9(12)	4.5(6)	0.07(1)	19.8(27)	59
$SOIL_{scat}$ (Mm^{-1})	0.6(1)	0.5(1)	0.0(0)	1.7(2)	59
CM_{scat} (Mm^{-1})	4.5	3.6	0.2	19.2	59
RH_a (%)	72.2	22.4	36.9	99.0	59
RH_c (%)	30.8	7.4	17.9	42.7	59
f(RH)	7.9	8.0	1.1	26.7	59
$f(RH_c)$	1.1	0.1	1.0	1.2	59
MARBLEMOUNT					
$b_{scat,r}$ (Mm^{-1})	77.1(46)	51.1(25)	16.8(11)	242.1(13)	90
b_{scat} (Mm^{-1})	34.1	17.2	4.7	89.6	90
$(NH_4)_2SO_{4,scat}$ (Mm^{-1})	51.3(25)	44.0(21)	3.0(1.4)	185.0(89)	90
$NH_4NO_{3,scat}$ (Mm^{-1})	9.2(4.4)	11.4(6)	0.6(3)	67.9(23)	90
OC_{scat} (Mm^{-1})	10.1	4.6	2.8	23.1	90
$SOIL_{scat}$ (Mm^{-1})	0.6	0.4	0.0	2.0	90
CM_{scat} (Mm^{-1})	6.0	4.4	0.0	21.8	90
RH_a (%)	79.3	17.2	37.6	98.9	102
RH_c (%)	73.2	16.6	35.0	96.4	102
f(RH)	7.7	5.7	1.1	25.8	102
$f(RH_c)$	4.3	2.8	1.1	14.0	102

Table 6-9. Daytime hours: Summary statistics of reconstructed and measured b_{scat} and estimated scattering of various aerosol species for Tahoma Woods, Paradise, and Marblemount. The parenthetical numbers are associated with results of regression analysis. Units are Mm^{-1}. Also listed in the table are summary statistics for ambient relative humidity (RH), relative humidity inside the nephelometer sampling chamber (RH_c), the ambient relative humidity dependent scattering correction factor f(RH), and the nephelometer sampling chamber relative humidity dependent scattering correction factor $f(RH_c)$.

VARIABLE	MEAN	STD DEV	MINIMUM	MAXIMUM	VALID
TAHOMA WOODS					
$b_{scat,r}$ (Mm^{-1})	52.8 (41.2)	20.5 (14.4)	16.1 (14.1)	103.2 (71.7)	62
b_{scat} (Mm^{-1})	33.4	16.4	3.0	75.0	82
$(NH_4)_2SO_4$ (Mm^{-1})	29.6 (19.9)	20.4 (13.3)	3.0 (2.2)	106.0 (55.4)	76
NH_4NO_3 (Mm^{-1})	5.3 (3.6)	3.1 (2.1)	0.0 (0.5)	13.0 (9.0)	72
OC (Mm^{-1})	10.8	6.7	0.0	21.0	85
$Soil_{scat}$ (Mm^{-1})	0.6	0.5	0.0	2.0	88
CM_{scat} (Mm^{-1})	5.5	3.9	0.0	21.0	81
RH_a (%)	72.1	12.7	48.6	97.6	79
RH_c (%)	63.9	12.1	40.4	89.3	79
f(RH) (%)	4.2	3.4	1.5	16.3	79
$f(RH_c)$ (%)	2.4	1.3	1.1	6.7	79
PARADISE					
$b_{scat,r}$ (Mm^{-1})	69.1 (96.8)	63.5 (93.1)	14.1 (17.2)	306.3 (443.6)	30
b_{scat} (Mm^{-1})	23.9	12.1	3.2	49.4	27
SO_4 (Mm^{-1})	49.2 (71.8)	57.2 (83.5)	2.8 (4.1)	263.9 (385.3)	30
NO_3 (Mm^{-1})	7.1 (10.3)	8.4 (12.3)	0.0 (0.0)	31.3 (45.7)	30
OC (Mm^{-1})	7.8 (9.5)	4.4 (5.3)	0.7 (0.9)	19.1 (23.2)	30
Soil (Mm^{-1})	0.6 (0.7)	0.5 (0.6)	0.0 (0.0)	1.7 (2.1)	30
CM (Mm^{-1})	4.4	2.9	0.2	12.6	30
RH_a (%)	71.2	22.6	36.9	99.0	27
RH_c (%)	40.0	7.6	20.0	42.0	27
$f(RH)$ (%)	7.1	6.8	1.10	26.7	27
$f(RH_c)$ (%)	1.1	0.1	1.0	1.2	27
MARBLEMOUNT					
$b_{scat,r}$ (Mm^{-1})	53.9 (35.3)	41.3 (20.6)	17.1 (11.8)	242.4 (125.2)	46
b_{scat} (Mm^{-1})	30.0	15.4	11.0	24.3	46
SO_4 (Mm^{-1})	29.1 (14.0)	32.4 (15.6)	3.0 (1.4)	177.7 (85.3)	46
NO_3 (Mm^{-1})	6.6 (3.2)	9.6 (4.6)	0.8 (0.4)	47.7 (22.9)	46
OC (Mm^{-1})	11.1	4.9	4.1	23.5	46
Soil (Mm^{-1})	0.7	0.5	0.0	2.0	46
CM (Mm^{-1})	6.4	5.1	0.1	21.8	46
RH_a (%)	66.5	15.9	37.6	97.8	46
RH_c (%)	61.0	14.4	34.9	89.5	46
f(RH) (%)	3.7	3.4	1.1	16.0	46
$f(RH_c)$ (%)	2.4	1.4	1.1	6.1	46

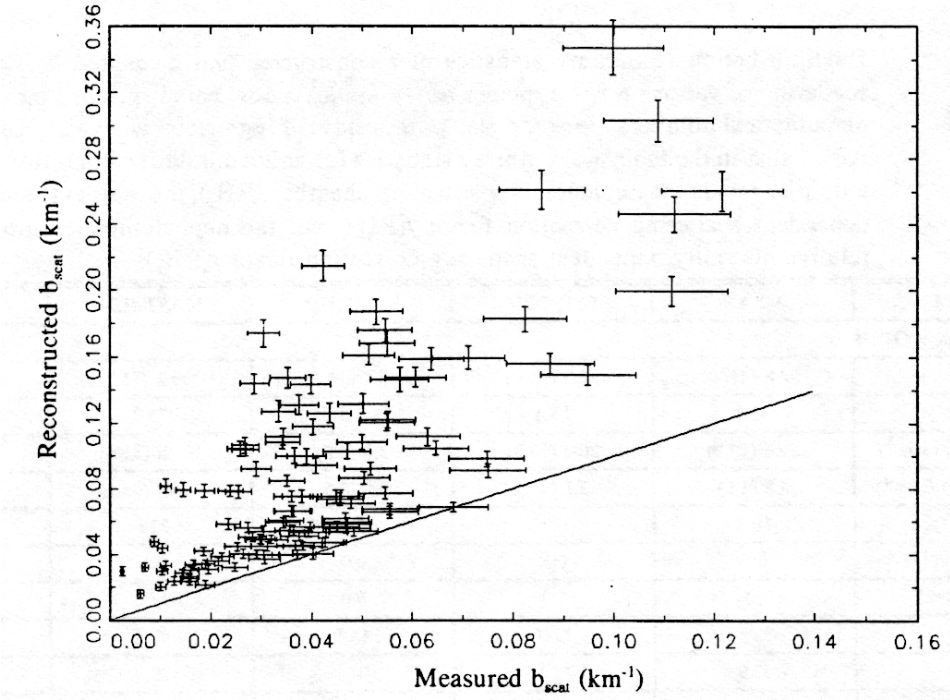

Figure 6-17. Tahoma Woods: Scatter plot of measured and reconstructed scattering. Reconstructed scattering was calculated using ambient RH values to estimate the scattering associated with hygroscopic species.

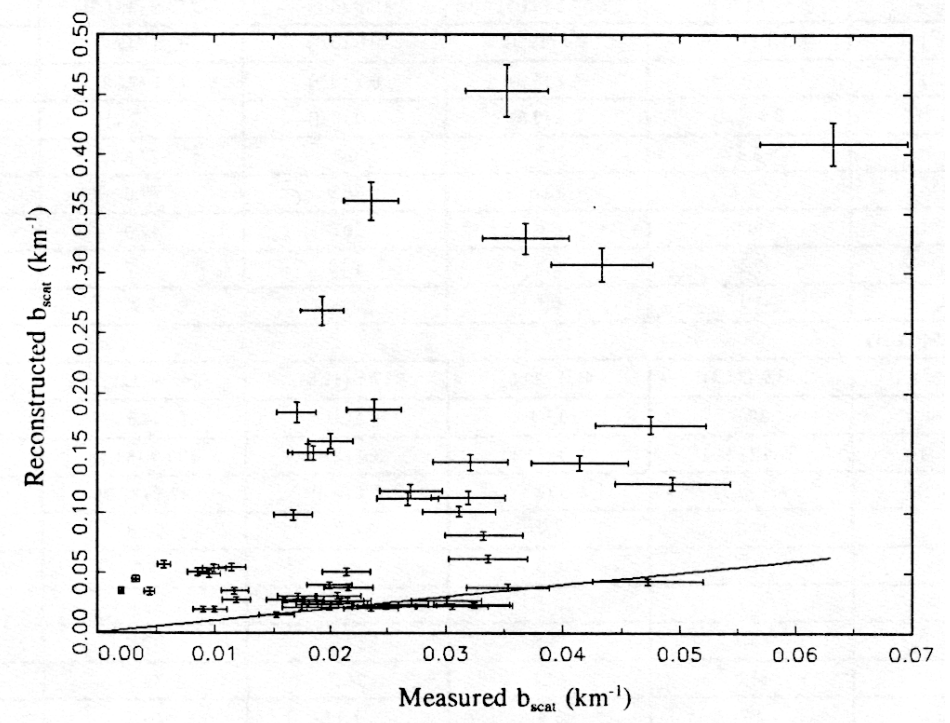

Figure 6-18. Paradise: Scatter plot of measured and reconstructed scattering. Reconstructed scattering was calculated using ambient RH values to estimate the scattering associated with hygroscopic species.

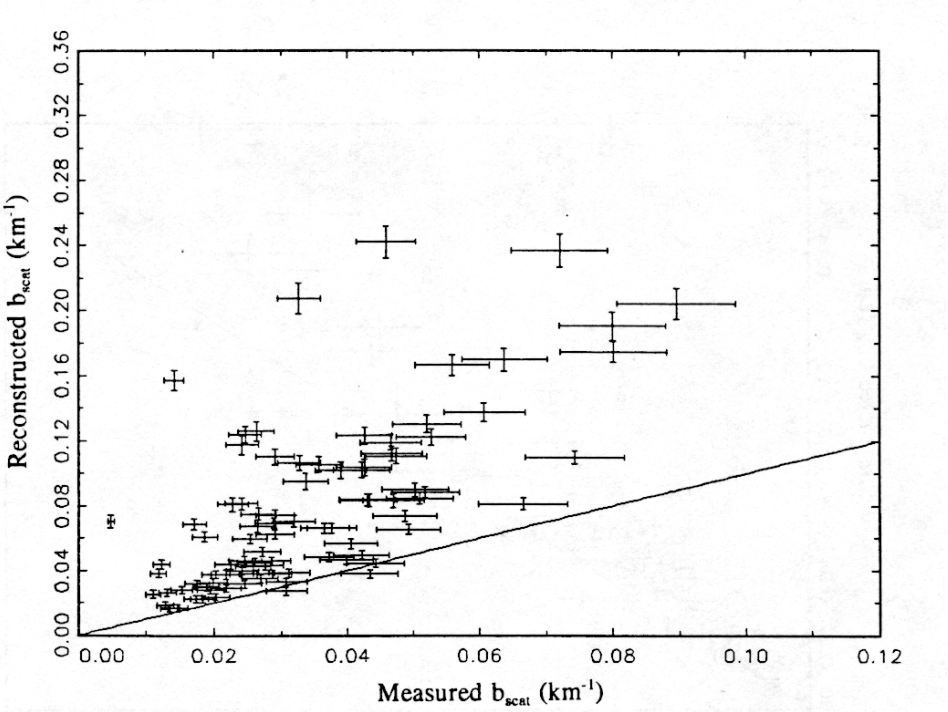

Figure 6-19. Marblemount: Scatter plot of measured and reconstructed scattering. Reconstructed scattering was calculated using ambient RH values to estimate the scattering associated with hygroscopic species.

A similar analysis can be carried out using chamber relative humidities. Figures 6-20, 6-21, and 6-22 show the comparisons between measured and reconstructed b_{scat} when $f(RH_c)$, rather than $f(RH_a)$, is used to estimate scattering from hygroscopic species. For the comparisons shown in these figures it is assumed that only ammonium sulfate and ammonium nitrate were hygroscopic. The comparisons are quite favorable at the Tahoma Woods site (r^2 = 0.77), while at Paradise and Marblemount the correspondence between reconstructed and measured scattering is not quite as high (r^2 = 0.62-0.66). At both the Marblemount and Tahoma Woods site reconstructed scattering is still somewhat overpredicted.

Similar analyses were carried out assuming a fraction of the organics in addition to sulfates and nitrates were also water soluble. However, in all cases the correlations between reconstructed and measured scattering lessened. Reconstructed scattering was further biased toward values that overshoot measured scattering.

The agreement between reconstructed and measured scattering when $f(RH_c)$ is used to estimate scattering from hygroscopic species is encouraging. The assumption that the scattering associated with individual species can be summed to yield total scattering does not seem to be grossly violated, and the scheme for calculating scattering from hygroscopic aerosols appears to be reasonable.

The assumptions concerning the scattering properties of the aerosols can be further examined using regression analysis with b_{scat} as the dependent variable and the various aerosol species as independent variables. Before the regression analysis is carried out collinearities will be examined by carrying out a factor analysis of pertinent variables. Table 6-10 presents the

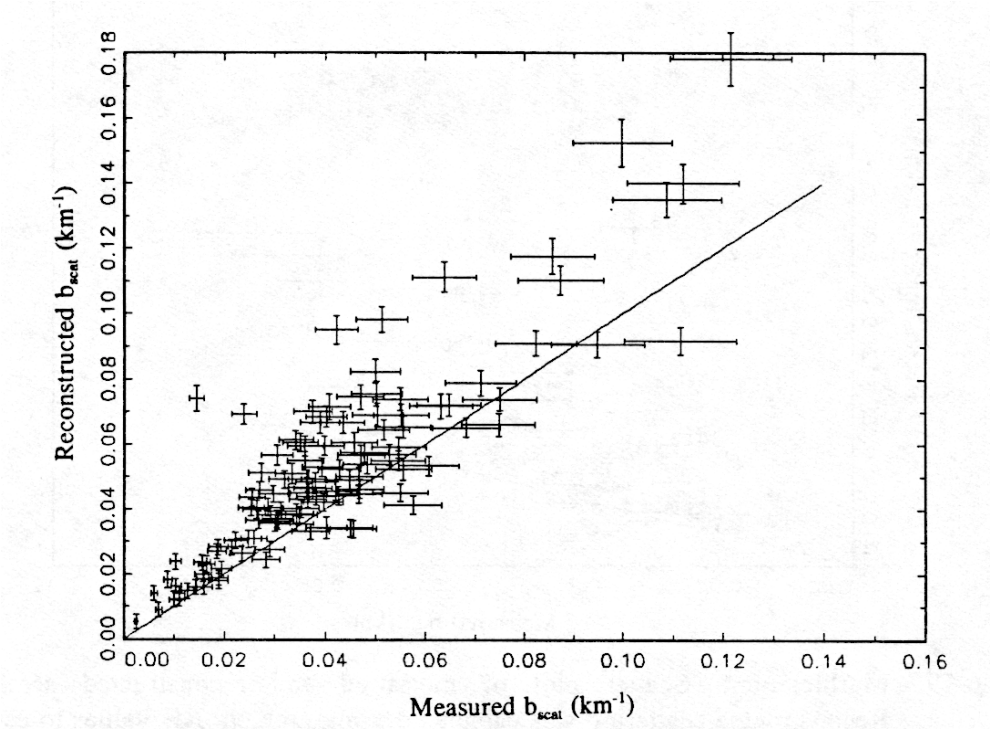

Figure 6-20. Tahoma Woods: Scatter plot of measured and reconstructed scattering. Reconstructed scattering was calculated using chamber RH values to estimate the scattering associated with hygroscopic species.

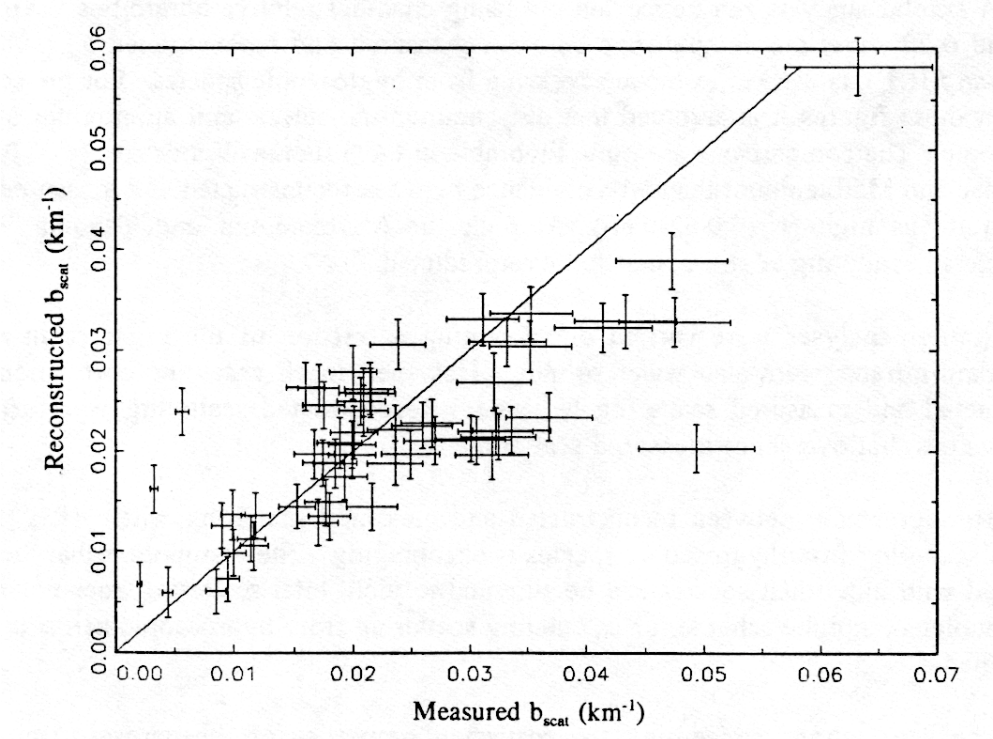

Figure 6-21. Paradise: Scatter plot of measured and reconstructed scattering. Reconstructed scattering was calculated using chamber RH values to estimate the scattering associated with hygroscopic species.

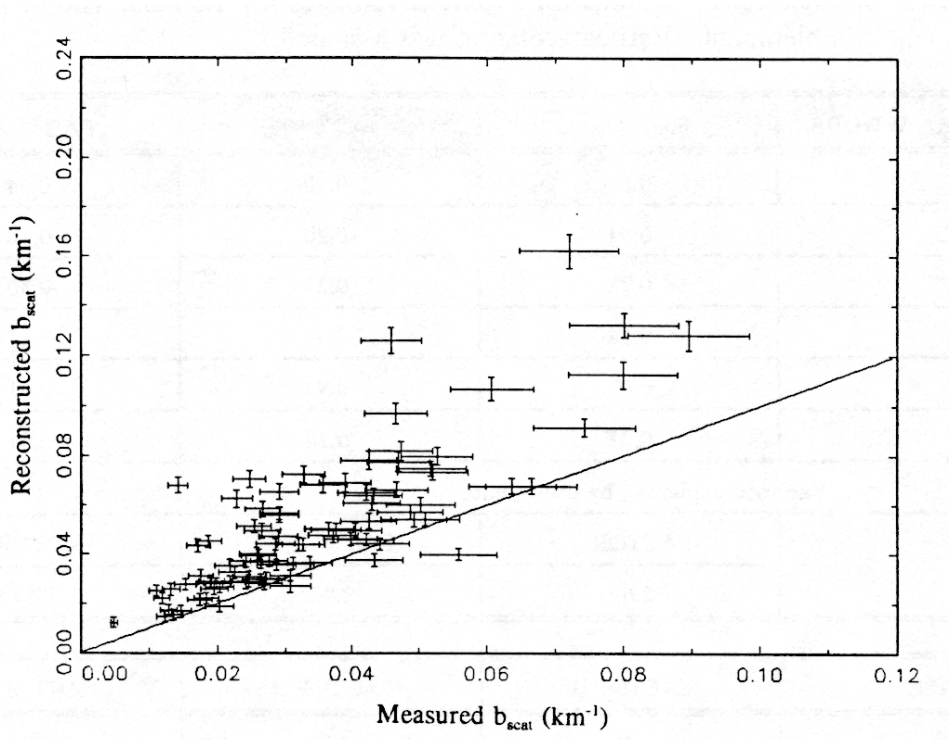

Figure 6-22. Marblemount: Scatter plot of measured and reconstructed scattering. Reconstructed scattering was calculated using chamber RH values to estimate the scattering associated with hygroscopic species.

results of this analysis. At all three sites ammonium sulfate and ammonium nitrate group into one factor. At Tahoma Woods and Paradise, organics and soil group into one factor and coarse mass into a third. At Marblemount, organics, soil, and coarse mass all group into a factor.

Accordingly, for the regression analysis, composite variables were formed by combining sulfates and nitrates into one variable, organics and soil into a second, and coarse mass was treated as a third. Both OLS and VW regressions were carried out. The results of this analysis are presented in Table 6-11. If the dry scattering efficiencies and growth curves used to estimate aerosol scattering and assumptions required for a regression analysis are met, then the coefficients should be equal to one.

At both the Tahoma Woods and Marblemount sites, results of both OLS and VW regression strongly suggest that the contribution of the combination sulfate and nitrate have been overestimated. At Tahoma Woods, the overestimation may be approximately 30% while at Marblemount it apparently is about 50%. On the other hand, the coefficient associated with organics is not statistically different from one suggesting that the assumption of dry organic scattering may not be unreasonable. In fact any attempt to add the effect of an f(RH) correction on OC or a fraction of OC results in a depression of both the r^2 and the associated regression coefficient. Apparently, organics at these two sites are not hygroscopic or if they are, only weakly so.

Table 6-10. Rotated factor patterns for specified variables for Tahoma Woods, Paradise, and Marblemount. Varimax rotation was assumed.

TAHOMA WOODS	FACTOR 1	FACTOR 2	FACTOR 3
b_{scat}	0.84	0.10	0.34
$(NH_4)_2SO_4$	0.91	-0.20	0.18
NH_4NO_3	0.73	0.25	-0.30
OC	0.18	0.93	0.11
SOIL	0.02	0.93	0.01
CM	0.07	0.10	0.94
Variance explained by each factor			
	FACTOR 1	FACTOR 2	FACTOR 3
	2.69	2.03	1.13

PARADISE	FACTOR 1	FACTOR 2	FACTOR 3
b_{scat}	0.49	0.77	0.09
$(NH_4)2SO_4$	0.01	0.92	0.16
NH_4NO_3	0.11	0.81	-0.29
OC	0.96	0.23	-0.02
SOIL	0.88	-0.07	0.18
CM	0.07	-0.00	0.97
Variance explained by each factor			
	FACTOR 1	FACTOR 2	FACTOR 3
	2.82	2.24	1.09

MARBLEMOUNT	FACTOR 1	FACTOR 2
b_{scat}	0.82	0.28
$(NH_4)_2SO_4$	0.94	-0.07
NH_4NO_3	0.75	-0.08
OC	0.21	0.73
SOIL	-0.29	0.85
CM	0.09	0.72
Variance explained each factor		
	FACTOR 1	FACTOR 2
	2.87	1.85

Table 6-11. Results of ordinary least square and variance weighted regressions with b_{scat} as the dependent variable and composite aerosol scattering variable as independent variables. Sulfate and nitrate scattering are summed to form one variable, organics plus soil form a second variable while coarse mass is a third.

TAHOMA WOODS

$r^2 = 0.77$	Ordinary Least Square			Variance Weighted Regression		
Variable	Estimate	Std Error	t-value	Estimate	Std Error	t-value
CONSTANT	2.89	2.56	1.13	1.80	2.72	0.66
$SO_4 + NO_3$	0.67	0.04	17.47	0.67	0.05	14.70
OC + SOIL	0.95	0.15	6.50	1.00	0.16	6.24
CM	0.62	0.25	2.47	0.71	0.32	2.23

PARADISE

$r^2 = 0.74$	Ordinary Least Square			Variance Weighted Regression		
Variable	Estimate	Std Error	t-value	Estimate	Std Error	t-value
CONSTANT	0.78	2.21	0.36	-0.37	2.56	-0.14
$SO_4 + NO_3$	1.46	0.16	8.92	1.44	0.18	8.00
OC + SOIL	1.22	0.18	6.86	1.37	0.20	6.71
CM	0.00	0.24	0.00	-0.02	0.31	-0.06

MARBLEMOUNT

$r^2 = 0.68$	Ordinary Least Square			Variance Weighted Regression		
Variable	Estimate	Std Error	t-value	Estimate	Std Error	t-value
CONSTANT	4.59	2.97	1.54	3.09	3.25	0.95
$SO_4 + NO_3$	0.48	0.04	12.35	0.48	0.04	11.13
OC + SOIL	0.98	0.23	4.34	1.10	0.26	4.20
CM	0.43	0.25	1.72	0.44	0.30	1.48

The inflated estimates of "empirical" sulfate and nitrate scattering may have its roots in a number of assumptions. The assumed dry scattering efficiency may have been too high, the shape of the hygroscopic growth curve may not have been appropriate for the aerosol species, aerosols may not have been externally mixed, or the chamber relative humidity may have been inflated. Chamber relative humidity was scaled from ambient values which were in turn measured by a RH sensor. Discussions with the manufacturers of the sensor suggested that at high relative humidity the sensors tended to saturate and overestimate RH results. Therefore, the relative humidity sensor was one sure source of error that would directly cause an overestimation of hygroscopic aerosol species scattering.

At Paradise, the regression results were somewhat different. The regression results indicated that both organics, and the combination of sulfates and nitrates were underestimated. However, no attempt was made to operate the Paradise nephelometer in an ambient mode and as such the chamber heating was rather drastic. Because of the difference in procedure used for operating nephelometers, the b_{scat} measurements at Paradise cannot be directly compared to measurements at Tahoma Woods and Marblemount.

6.4 APPORTIONMENT OF AEROSOL EXTINCTION

Aerosol extinction budgets were estimated in two different ways: first, Equation 6-9 was used to estimate scattering associated with each aerosol species; and second, the estimates were made using Equation 6-9, but modified to be consistent with the regressions presented in the previous section. At Tahoma Woods sulfate and nitrate efficiencies were multiplied by 0.67. At Paradise sulfates, nitrates, organics, and soil efficiencies were multiplied by 1.4, and at Marblemount sulfate and nitrate efficiencies were multiplied by 0.48. The effect of decreasing sulfate and nitrate efficiencies while leaving other efficiencies unchanged was to increase the fraction of extinction attributed to the unchanged species efficiencies.

Aerosol absorption was estimated from the product of LAC and an assumed absorption efficiency (10 m^2/g). Because NO_2 was not measured, its contribution to absorption cannot be estimated. However, based on previous measurements and studies, it is likely to be 5% or less (see Addendum).

Tables 6-8 and 6-9 also present a statistical summary of reconstructed and measured scattering along with estimated scattering associated with each species. The numbers in parentheses are to be associated with the regression modified efficiencies. Tables 6-12 and 6-13 present the fraction of extinction associated with various types of aerosols and again the numbers in parentheses reflect the effect of efficiencies modified to be consistent with the regression analysis. Table 6-12 shows averages for day and night, while Table 6-13 shows only daylight hours.

First, Rayleigh or clear blue sky scatter is responsible for only about 10-20% of the extinction. Of the remaining extinction about 80-90% is associated with fine particle scattering, 5-10% with coarse particle scattering, and 5-10% with light absorption.

Table 6-12. Daytime and nighttime extinction budgets for Tahoma Woods, Paradise, and Marblemount. The first third of the table shows the fraction of extinction attributable to Rayleigh scattering. It also presents the fraction of extinction associated with non-Rayleigh scattering as a function of fine particle and coarse particle scattering and particle absorption. The second third presents the budget for particle scattering while the remaining third presents the non-Rayleigh extinction budget.

	TAHOMA WOODS	PARADISE	MARBLEMOUNT
Rayleigh fraction of extinction	0.12 (0.16)	0.12 (0.07)	0.13 (0.20)
Fraction of non-Rayleigh extinction			
FM scattering fraction	0.86 (0.82)	0.91 (0.93)	0.87 (0.78)
b_{abs} extinction fraction	0.08 (0.11)	0.05 (0.03)	0.06 (0.10)
CM scattering fraction	0.06 (0.08)	0.05 (0.03)	0.07 (0.12)
Scattering budget by species			
Sulfate scattering fraction	0.70 (0.63)	0.75 (0.76)	0.67 (0.54)
Nitrate scattering fraction	0.11 (0.10)	0.10 (0.11)	0.12 (0.10)
OC scattering fraction	0.13 (0.18)	0.10 (0.09)	0.13 (0.22)
Soil scattering fraction	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
CM scattering fraction	0.06 (0.08)	0.05 (0.04)	0.08 (0.13)
Extinction budget by species			
Sulfate extinction fraction	0.64 (0.57)	0.71 (0.73)	0.62 (0.49)
Nitrate extinction fraction	0.10 (0.09)	0.10 (0.10)	0.11 (0.09)
OC extinction fraction	0.12 (0.16)	0.10 (0.09)	0.12 (0.20)
b_{abs} extinction fraction	0.08 (0.11)	0.05 (0.03)	0.06 (0.10)
Soil extinction fraction	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)
CM extinction fraction	0.06 (0.08)	0.05 (0.03)	0.07 (0.12)

Table 6-13. Daytime extinction budgets for Tahoma Woods, Paradise, and Marblemount. The first third of the table shows the fraction of extinction attributable to Rayleigh scattering. It also presents the fraction of extinction associated with non-Rayleigh scattering as a function of fine particle and coarse particle scattering and particle absorption. The second third presents the budget for particle scattering while the remaining third presents the non-Rayleigh extinction budget.

	TAHOMA WOODS	PARADISE	MARBLEMOUNT
Rayleigh fraction of extinction	0.19 (0.24)	0.14 (0.10)	0.19 (0.28)
Fraction of non-Rayleigh extinction			
FM scattering fraction	0.78 (0.73)	0.88 (0.91)	0.80 (0.70)
b_{abs} extinction fraction	0.13 (0.16)	0.06 (0.04)	0.10 (0.14)
CM scattering fraction	0.09 (0.11)	0.06 (0.04)	0.11 (0.16)
Scattering budget by species			
Sulfate scattering fraction	0.56 (0.48)	0.71 (0.74)	0.54 (0.40)
Nitrate scattering fraction	0.10 (0.09)	0.10 (0.11)	0.12 (0.09)
OC scattering fraction	0.22 (0.28)	0.11 (0.10)	0.21 (0.31)
Soil scattering fraction	0.01 (0.02)	0.01 (0.01)	0.01 (0.02)
CM scattering fraction	0.10 (0.13)	0.06 (0.05)	0.12 (0.18)
Extinction budget by species			
Sulfate extinction fraction	0.49 (0.41)	0.67 (0.71)	0.49 (0.34)
Nitrate extinction fraction	0.09 (0.07)	0.10 (0.10)	0.11 (0.08)
OC extinction fraction	0.19 (0.24)	0.11 (0.10)	0.19 (0.27)
b_{abs} extinction fraction	0.13 (0.16)	0.06 (0.04)	0.10 (0.14)
Soil extinction fraction	0.01 (0.01)	0.01 (0.01)	0.01 (0.02)
CM extinction fraction	0.09 (0.11)	0.06 (0.04)	0.11 (0.16)

The second part of Table 6-12 and 6-13 presents the percent of total scattering associated with each species while the remaining third of the table shows the estimated fraction of non-Rayleigh extinction attributed to each aerosol component. At the two low elevation sites sulfates are estimated to be associated with about 50-60% of the extinction while at Paradise the sulfate extinction fraction climbs to about 70%. Nitrates are about 10% of the extinction at all three sites. Organics contribute between 10-20% of the extinction while absorption accounts for another 5-10%. Taken together aerosols associated with all types of carbon are estimated to contribute between 15% and 35% of the extinction. Soil and coarse mass most likely contribute less than 10% of the extinction.

6.5 SUMMARY

Measurements of aerosol concentrations, atmospheric scattering, and absorption were made at Mount Rainier and North Cascades National Parks. A number of conclusions can be drawn from the analysis. From a data summary perspective, characteristics of mass concentrations are:

- At both parks the average fine mass concentration for the summer of 1990 were about 8-10 $\mu g/m^3$ with maximums of 20-30 $\mu g/m^3$.

- About 20-30% of the measured fine mass cannot be accounted for by the summation of masses associated with individual aerosol species. Presumably, much of the unexplained mass was residual water associated with hygroscopic aerosol species.

- Of the mass accounted for by summing the individual species' mass (reconstructed mass), about 45-50% was organic carbon and 10% light-absorbing carbon. Therefore, 55-60% of the fine mass was associated with carbon. Organic carbon contributed about 20-30% of the fine mass in most other parts of the United States.

- About 30% of reconstructed mass was sulfates, 5% was nitrates, 5-10% was soil related, and less than 1% was associated with sodium presumed to be in the form of sodium sulfate.

- About one-half of PM_{10} mass was less than 2.5 μm.

Characteristics of the optical properties are:

- The estimated average (day and night) reconstructed non-Rayleigh extinction coefficients are between 65-90, 90-130, and 45-80 Mm^{-1} at Tahoma Woods, Paradise, and Marblemount, respectively. This corresponds to standard visual ranges of approximately 45, 33, and 54 km.

- Rayleigh scattering is 10-20% of total extinction.

- During daylight hours the reconstructed non-Rayleigh extinctions are 40-50, 70-90, and 35-55 Mm^{-1} at Tahoma Woods, Paradise, and Marblemount, respectively.

Average daylight visual ranges corresponding to these extinctions are approximately 70, 40, and 70 km.

- Even though sulfates account for only 20-30% of the fine mass it is estimated that they are over 50% of the non-Rayleigh extinction budget.

- Organics contribute between 10-20% of the extinction while light-absorbing carbon contributes another 5-10%.

- All other species contribute less than 10% of estimated extinction.

Considerable insight into error associated with making scattering measurements using commercial nephelometers was made as well as hints into the chemical-physical nature of the aerosols.

- Operation of a commercial nephelometer without taking precautions to maintain the sampling chamber at ambient temperatures resulted in gross underestimations of the ambient scattering coefficient in an environment with hygroscopic aerosols and high relative humidities.

- It is estimated that hygroscopic aerosol scattering was underestimated by a factor of seven at the Paradise monitoring site. Even when substantial efforts to maintain nephelometers at ambient temperatures were made the hygroscopic aerosol may have been underestimated by a factor of two or more.

- b_{abs} correlated well with organics as well as "light-absorbing carbon" and the implied absorption efficiency associated with b_{abs}/LAC was so large as to be physically unreasonable. Apparently, light-absorbing carbon was present in all types of carbon aerosol species.

- No evidence was found to support the notion that a fraction of the organics were hygroscopic. Any assumption of organic aerosol hygroscopicity resulted in a reduction of the correlation between fine and reconstructed mass, and between measured and reconstructed b_{scat}.

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