Chapter 5

Light Extinction Budget

5.1 Assumptions and Data Analysis Techniques

Throughout this chapter several data analysis techniques will be used repeatedly. These techniques, including calculations of reconstructed scattering and reconstructed extinction and multiple linear regression (MLR) analyses are summarized in this subsection.

5.1.1 Available Data

The data necessary to calculate a light extinction budget for a given site are measurements of light extinction and concentrations of fine and coarse particulate matter. Three of the WHITEX sites, Page, Canyonlands, and Hopi Point, had sufficient data for extinction budget calculations. Each site was equipped with both a transmissometer to measure extinction (b_{ext}) and a nephelometer to measured scattering (b_{scat}). The optical and particulate data are discussed in more detail in Chapters 3 and 4.

5.1.2 Chemical Composition of Particulate Matter

The following assumptions were made about the chemical composition of the fine particulate matter: sulfates are ammonium sulfate ($(NH_4)_2SO_4$), nitrates are ammonium nitrate ($(NH_4)NO_3$), and organics have a mean carbon to hydrogen ratio of 3:4. Since the quantities which were measured by the particulate samplers were SO_4 ion, NO_3 ion, and organic carbon, to account for the mass of associated ions, the following definitions will be used throughout the chapter:

$$
\begin{aligned}
sulfates &= 1.4 \times [SO_4] && (5.1)\\
nitrates &= 1.3 \times [NO_3] && (5.2)\\
organics &= 1.4 \times [organic\ C] && (5.3)\\
total\ carbon &= 1.4 \times [organic\ C] + [light\ absorbing\ C] && (5.4)
\end{aligned}
$$

SO_4 ion concentrations used are from the IMPROVE sampler module B which is the teflon filter analysed by ion chromatography. NO_3 ion concentrations are from IMPROVE module E (nylon filter analysed by ion chromatography). Coarse mass was calculated by subtracting the fine mass from the total mass measured by the SCISAS sampler. Discussions about choice of which carbon data to use in the extinction budgets are given in a following section.

Fine mass is 0–2.5 μm diameter. Coarse mass is 2.5–15 μm. All data were averaged to 12-hour time periods beginning at 0800 and 2000 local time each day.

The mass of fine soil is calculated from the mass of soil-related elements by

$$\begin{aligned} soil &= 2.20 \times [Al] + 2.49 \times [Si] + \\ &\quad 1.63 \times [Ca] + 1.94 \times [Ti] + 2.56 \times [Fe] \end{aligned} \tag{5.5}$$

where the multipliers include the oxide present plus the 14% of the soil not associated with elements measured by x-ray methods. The factor for iron includes the component of K expected in the soil. Concentrations of the soil elements are from IMPROVE module F, a teflon filter analysed by PIXE.

5.1.3 Relative Humidity Considerations

It is known that pure ammonium sulfate aerosol will rapidly undergo deliquescence (condensation of water vapor onto the solid particles) at approximately 80% relative humidity (RH). The reverse phase change, when the liquid evaporates from the 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% and 80%.[12] Since high RH complicates the relationship between particle concentrations and light scattering, some analyses were done for "low" RH cases only as well as all time periods. "Low" RH is defined as less than 60%.

The growth and phase change of the particles, of course, affects 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 sulfate scattering efficiency, referred to as fs(RH), is parameterized by a curve shown in Figure 5.1 based on one published by Tang et al.[12] A similar curve for nitrates, also based on one from Tang et al.[12] and referred to as fn(RH) is shown in the same figure. Tang's curves, calculated theoretically for aerosols of different size distributions have sharp discontinuities at 62% RH for nitrates and at 80% for sulfates, the deliquescence points for these species. However, since both ammonium nitrate and ammonium sulfate are hygroscopic at 30% RH[9, 11, 12] and since the growth factor and light scattering efficiency for ambient aerosols has previously been observed to be rather smooth,[9, 10] for WHITEX, Tang's curves were smoothed between the respective deliquescence points and 30% RH. 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. Similarly, the scattering efficiency of ammonium nitrate varies between approximately 1.1 and 7.0 m^2/g at low relative humidities depending on the size distribution.

For comparison, a curve showing 1/(1-RH) which has often been used in previous visibility studies[13] is shown in the same figure. In the following analyses both 1/(1-RH) and the modified Tang curves will be used.

The nephelometers used in the WHITEX study dry the aerosols, thus reducing their scattering efficiency. Therefore the scattering coefficients measured by the nephelometers should be considered the "dry" scattering only. This is discussed further in the next section.

5.1.4 Multiple Linear Regression Analysis

One method of determining the scattering or absorbing efficiency of particulate matter is multiple linear regression (MLR). The dependent variable can be either the measured light extinction (b_{ext}) from the transmissometer or the measured light scattering (b_{scat}) from the nephelometer. The independent variables are the concentrations of particulate matter for each chemical species. The regression coefficients which result from such an analysis are estimates of the scattering or

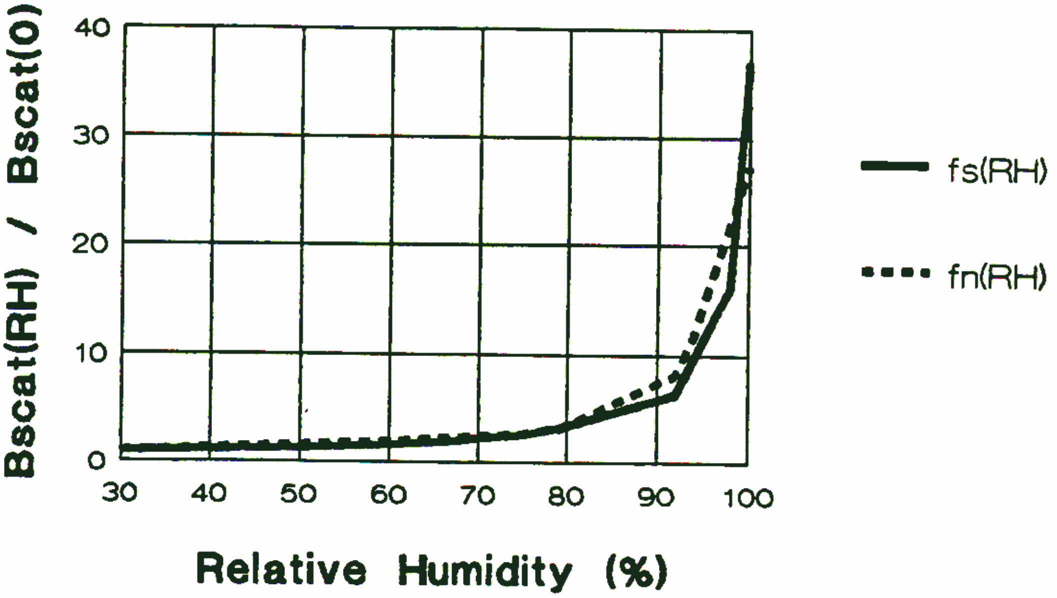

Figure 5.1: Relative light scattering coefficients for ammonium sulfate and ammonium nitrate aerosols.

absorption efficiencies of the associated chemical species. When sulfates and nitrates are regressed against b_{ext} they are multiplied by the relative humidity function fs(RH) and fn(RH), respectively, as discussed above.

Collinearities between any two or more "independent" variables used in an MLR analysis would suggest that the variables were not in fact independent, leading to unstable regression coefficients with large standard errors. If the collinearities were very strong, then in addition to the large standard errors, there would be numerical difficulty in inverting the matrix which would lead to regression coefficients which were inaccurate. To check for collinearities in the WHITEX data, the particulate concentrations at Page, Canyonlands, and Hopi Point were subjected to three diagnostic tests. The first was to generate a correlation matrix, second was a factor analysis followed by Varimax rotation, and third a collinearity test suggested by Belsley et al.[1]

The correlation matrices for all the relevant data are shown in Tables 5.1, 5.2, 5.3, and 5.4. They show that at Page, nitrates are fairly highly correlated with both carbonaceous material and fine soil. At Canyonlands, humidity corrected sulfates and nitrates are somewhat correlated. As expected, light absorbing carbon correlates fairly well with organic carbon, and fine soil is somewhat correlated with coarse mass at all sites.

Although the correlation matrices suggest there may be some problems with collinearities, the two diagnostic tests based on eigenvector extraction do not. Varimax rotation forces each variable to load as strongly as possible onto a single factor, while loading lightly on all other factors. If collinearities exist, the collinear variables would load onto the same factor. Results of the factor analyses for the three sites are shown in Tables 5.5, 5.6, 5.7, and 5.8. Since none of the variables except organics and elemental carbon at Canyonlands loaded strongly together, the results suggest no collinearity problems.

The Belsley collinearity test shows the amount each eigenvector of the sums of cross products and squares data matrix contributes to the variance of each regression coefficient. If an eigenvector

Table 5.1: Pearson correlation coefficients for data at Page.

	b_{ext}	sulfates ×fs(RH)	nitrates ×fn(RH)	organics	abs. C	fine soil	coarse mass	NO_2
b_{ext}	1.000	0.927	0.470	0.409	0.406	0.238	0.006	0.056
sulfates×fs(RH)	0.927	1.000	0.401	0.245	0.263	0.130	-0.134	0.009
nitrates×fn(RH)	0.470	0.401	1.000	0.418	0.627	0.474	0.174	0.054
organics	0.409	0.245	0.418	1.000	0.714	0.234	0.140	0.044
abs. C	0.406	0.263	0.627	0.714	1.000	0.348	0.311	0.235
fine soil	0.238	0.130	0.474	0.234	0.348	1.000	0.404	0.364
coarse mass	0.006	-0.134	0.174	0.140	0.311	0.404	1.000	0.342
NO_2	0.056	0.009	0.054	0.044	0.235	0.364	0.342	1.000

Table 5.2: Pearson correlation coefficients for Canyonlands.

	b_{ext}	sulfates ×fs(RH)	nitrates ×fn(RH)	organics	abs. C	fine soil
b_{ext}	1.000	0.516	0.440	0.452	0.417	0.043
sulfates×fs(RH)	0.516	1.000	0.685	0.206	0.003	-0.014
nitrates×fn(RH)	0.440	0.685	1.000	0.246	0.146	0.133
organics	0.452	0.206	0.246	1.000	0.540	-0.104
abs. C	0.417	0.003	0.146	0.540	1.000	-0.015
fine soil	0.043	-0.014	0.133	-0.104	-0.015	1.000

Table 5.3: Pearson correlation coefficients for data at Hopi Point.

	b_{ext}	sulfates ×fs(RH)	nitrates ×fn(RH)	†organics	abs. C	fine soil	coarse mass
b_{ext}	1.000	0.711	0.716	0.017	0.580	0.349	0.303
sulfates×fs(RH)	0.711	1.000	0.654	-0.027	0.178	-0.015	-0.059
nitrates	0.716	0.654	1.000	0.089	0.323	0.058	0.236
†organics	0.017	-0.027	0.089	1.000	0.472	-0.135	-0.065
abs. C	0.580	0.178	0.323	0.472	1.000	0.021	0.059
fine soil	0.349	-0.015	0.058	-0.135	0.021	1.000	0.634
coarse mass	0.303	-0.059	0.236	-0.065	0.059	0.634	1.000

†organics less than the minimum detection limit set to zero

Table 5.4: Pearson correlation coefficients for Page, Canyonlands, and Hopi Point combined.

	b_{ext}	sulfates ×fs(RH)	nitrates ×fn(RH)	organics	abs. C	fine soil	coarse mass
b_{ext}	1.000	0.857	0.566	0.515	0.522	0.175	0.233
sulfates×fs(RH)	0.857	1.000	0.538	0.257	0.245	0.062	-0.022
nitrates×fn(RH)	0.566	0.538	1.000	0.376	0.448	0.213	0.321
organics	0.515	0.257	0.376	1.000	0.745	0.118	0.372
abs. C	0.522	0.245	0.448	0.745	1.000	0.197	0.441
fine soil	0.175	0.062	0.213	0.118	0.197	1.000	0.482
coarse mass	0.233	-0.022	0.321	0.372	0.441	0.482	1.000

Table 5.5: Rotated factor pattern for Page.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
b_{ext}	$\boxed{0.951}$	0.220	0.133	-0.001	0.060	0.043
sulfates×fs(RH)	$\boxed{0.968}$	0.046	0.155	-0.114	0.006	0.030
nitrates×fn(RH)	0.252	0.218	$\boxed{0.905}$	0.054	0.239	0.096
organics	0.184	$\boxed{0.954}$	0.185	0.062	0.108	0.079
abs. carbon	0.134	0.563	0.530	0.189	0.092	$\boxed{0.583}$
fine soil	0.044	0.106	0.198	0.192	$\boxed{0.954}$	0.034
coarse mass	-0.095	0.080	0.064	$\boxed{0.972}$	0.182	0.055

Table 5.6: Rotated factor pattern for Canyonlands

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
b_{ext}	0.248	0.296	0.197	0.019	$\boxed{0.875}$
sulfates×fs(RH)	-0.025	$\boxed{0.841}$	0.215	0.018	0.359
nitrates×fn(RH)	0.130	0.167	$\boxed{0.957}$	0.069	0.172
organics	$\boxed{0.705}$	0.627	0.035	-0.123	0.002
abs. carbon	$\boxed{0.904}$	-0.064	0.140	-0.030	0.244
fine soil	-0.063	-0.017	0.062	$\boxed{0.995}$	0.015

Table 5.7: Rotated factor pattern for Hopi Point

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6
b_{ext}	$\boxed{0.634}$	0.534	0.349	0.262	-0.090	0.080
sulfates×fs(RH)	$\boxed{0.964}$	0.190	0.112	0.030	0.031	-0.004
nitrates×fn(RH)	0.319	$\boxed{0.844}$	0.309	0.039	0.175	0.179
†organics	0.001	0.091	0.120	-0.047	$\boxed{0.985}$	-0.002
abs. carbon	0.193	0.285	$\boxed{0.915}$	0.008	0.158	0.124
fine soil	0.100	0.063	0.011	$\boxed{0.931}$	-0.052	0.329
coarse mass	0.010	0.150	0.126	0.352	0.000	$\boxed{0.914}$

†organics less than the minimum detection limit set to zero

Table 5.8: Rotated factor pattern for Page, Canyonlands, and Hopi Point combined.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
b_{ext}	$\boxed{0.879}$	0.248	0.253	0.070	0.170
sulfates×fs(RH)	$\boxed{0.957}$	0.105	0.127	0.033	0.088
nitrates×fn(RH)	0.281	0.194	$\boxed{0.899}$	0.131	0.240
organics	0.249	$\boxed{0.900}$	0.185	0.039	0.302
abs. carbon	0.211	0.442	0.319	0.088	$\boxed{0.806}$
fine soil	0.058	0.035	0.100	$\boxed{0.991}$	0.055

Table 5.9: Consensus literature light extinction efficiencies in m^2/g.

	Trijonis and Pitchford[13]	Used for WHITEX
sulfates	2.55/(1-RH)	2.55× fs(RH)
nitrates	same as sulfates	†1.1× fn(RH)
organics	3.75	4.0
absorbing carbon	9.0	9.0
coarse mass	0.6	0.45
fine soil	1.25	1.25

†This extinction efficiency was taken from Tang et al.[12] and is based on a mass median diameter of 0.98 μm and a highly polydisperse size distribution.

with a small eigenvalue contributes strongly to the variance of two or more components, then a collinearity problem exists. The results of the Belsley test also showed no collinearity problems in the particulate data.

The three diagnostic tests indicate that collinearities in the WHITEX data are not strong enough to cause numerical difficulties with matrix inversion in the MLR analyses. However, they may be large enough to cause large standard errors in some regression coefficients. Standard errors for all regression coefficients are reported in the following sections.

5.1.5 Consensus Scattering and Absorption Efficiencies

In some of the following analyses "consensus literature" scattering and absorption efficiencies for different chemical species are used. These values are based on a literature review by Trijonis and Pitchford.[13] The values suggested by them in m^2/g are shown in Table 5.9 along with the values used for the WHITEX study. The scattering efficiency for organics which was suggested by Trijonis and Pitchford was scaled by 1.5/1.4 since they assumed that organics were $1.5 \times [organic\ C]$ while 1.4 was used as the mass multiplier for WHITEX. The coarse mass scattering efficiency suggested by Trijonis and Pitchford is for particles 2.5–10 μm in diameter. Since WHITEX coarse mass data are 2.5–15 μm, Trijonis[14] suggested reducing the efficiency to 0.45 m^2/g for this data set. Best estimates for the scattering efficiencies of ammonium sulfate and ammonium nitrate are those given by Tang[12] for highly polydisperse particle size distributions, although reconstructed scattering was also calculated using the Trijonis and Pitchford[13] efficiencies for these species.

5.1.6 Reconstructed Scattering and Extinction

For each time period the light extinction due to each chemical species (sulfates, nitrates, organics, light absorbing carbon, fine soil, coarse particles, and NO_2) can be calculated by

$$B_{i,j} = E_{i,j} \times C_{i,j} \tag{5.6}$$

where B is the light extinction, E is the extinction to mass ratio and C is the concentration of the species. The subscripts i and j refer to time periods and chemical species, respectively. The uncertainty in the extinction for each species for each time period is calculated by

$$BU_{i,j} = \sqrt{(E_{i,j} \times CU_{i,j})^2 + (C_{i,j} \times EU_{i,j})^2} \tag{5.7}$$

where BU, CU, and EU are the 1 standard deviation uncertainties for extinction, concentration, and extinction to mass ratio, respectively. When consensus literature extinction to mass ratios were used an uncertainty of 10% is assumed. If MLR derived efficiencies are used, then the standard error of each regression coefficient is its uncertainty. For sulfates and nitrates the uncertainty in the relative humidity factor is also included in the extinction to mass uncertainty. Reconstructed extinction for each time period is calculated by

$$B_{i,tot} = \sum_{j=1}^{J} B_{i,j} \tag{5.8}$$

Reconstructed scattering is the same except that absorption by NO_2 and LAC would not be included in the sum. Rayleigh scattering can also be included by including it in the sum. The uncertainty in the reconstructed extinction for each time period is

$$BU_{i,tot} = \sqrt{\sum_{j=1}^{J} BU_{i,j}^2} \tag{5.9}$$

where J is the total number of chemical species. The fraction of extinction due to each species for each time period is

$$F_{i,j} = B_{i,j}/B_{i,tot} \tag{5.10}$$

and the uncertainty in these fractions are calculated by

$$FU_{i,j} = \sqrt{\frac{BU_{i,j}^2}{B_{i,tot}^2} + \frac{B_{i,j}^2 BU_{i,tot}^2}{B_{i,tot}^4}} \tag{5.11}$$

The mean extinction for the entire WHITEX study due to each chemical species is calculated by

$$B_{mean,j} = \frac{1}{I}\sum_{i=1}^{I} B_{i,j} \tag{5.12}$$

where I is the total number of time periods. and the mean reconstructed extinction is

$$B_{mean,tot} = \frac{1}{I}\sum_{i=1}^{I} B_{i,tot} \tag{5.13}$$

The mean fractions of extinction due to each species were calculated by

$$F_{mean,j} = \frac{B_{mean,j}}{B_{mean,tot}} \tag{5.14}$$

and the uncertainties in the mean fractions are

$$FU_{mean,j} = \sqrt{\frac{BU_{mean,j}^2}{B_{mean,tot}^2} + \frac{B_{mean,j}^2 BU_{mean,tot}^2}{B_{mean,tot}^4}} \tag{5.15}$$

5.2 Preliminary Data Analysis

Before attempting the estimation of light extinction efficiencies and budgets with WHITEX data, some preliminary analyses of the data were performed. These included (1) an investigation of extinction coefficients measured by the transmissometer compared to scattering coefficients measured by the integrating nephelometer for the full range of relative humidity conditions; and (2)