

same time periods are 0.441 and 0.090  $\mu\text{g}/\text{m}^3$ , respectively. At Hopi Point, the extinction derived concentration was 0.039  $\mu\text{g}/\text{m}^3$ , while means of TOR and TMO absorbing carbon are 0.137 and 0.025  $\mu\text{g}/\text{m}^3$ , respectively. Based on this analysis, it appears that the TMO derived absorbing carbon measurements, on average, are too low and TOR concentrations are too high.

## Recommendations

Evidence from the three preliminary analyses is inconclusive. The reconstructed extinction analysis shows that using TOR concentrations gives more reasonable results at Hopi Point, but TMO gives better results at Page. Use of multiple linear regression analysis to estimate the absorption efficiency indicates that TOR carbon is more reasonable. And finally, calculation of the mean extinction derived light absorbing carbon shows that TMO carbon is probably too low, while TOR is too high.

Though the preliminary analyses are inconclusive, it was decided that when calculating the WHITEX extinction budgets, TOR carbon concentrations would be used rather than TMO. Because there are so many TOR organic carbon concentrations which are less than the minimum detection limit at Hopi Point, all analyses for that site were done with both "maximum organics" (organics less than the minimum detection limit set to the detection limit) and "minimum organics" (organics less than the detection limit set to zero).

## 5.3 Light Extinction Budget By Extinction Type

For each of the sites for which there are adequate data, light extinction is apportioned into absorption by gases, absorption by particles, scattering due to gases, and scattering by fine and coarse particles.

There are no coarse mass data for Canyonlands and gaseous  $\text{NO}_2$  concentrations exist only for Page. Consequently, a full extinction budget by type can be explicitly calculated only for Page. A budget by type for all constituents except absorption by  $\text{NO}_2$  is possible for Hopi Point. Since  $\text{NO}_2$  concentrations were low at Page and probably lower at all other WHITEX sites, this is not a serious obstacle. Coarse mass scattering as well as gaseous absorption must be estimated for Canyonlands. Time plots of all the relevant particulate and gaseous data for Page, Canyonlands, and Hopi Point are shown in Figures 5.18, 5.19, and 5.20. Statistics for the same data are shown in Tables 5.16, 5.17, and 5.18.

To generate the extinction budgets by type for each site, the mean extinction coefficients for each extinction type were estimated independently. The details of these calculations are discussed in the following subsections. Not unexpectedly, the sums of the components do not exactly equal the means of the measured extinction coefficients. The fractions of light extinction allocated to each component are determined by dividing the estimated mean coefficient for each type by the sum of the means for all types. Rayleigh scattering is included in the total. Table 5.19 summarizes the extinction budgets by type for each of the three sites. The budgets for the three sites are also illustrated by the pie charts shown in Figure 5.3.

### 5.3.1 Scattering by gases (Rayleigh Scattering)

Scattering of light by air molecules is referred to as Rayleigh scattering. The amount of Rayleigh scattering or "clean" air scattering is dependent on the wavelength of the light and on the density of air molecules. Assuming that air density depends mostly on altitude, the average Rayleigh

# PAGE

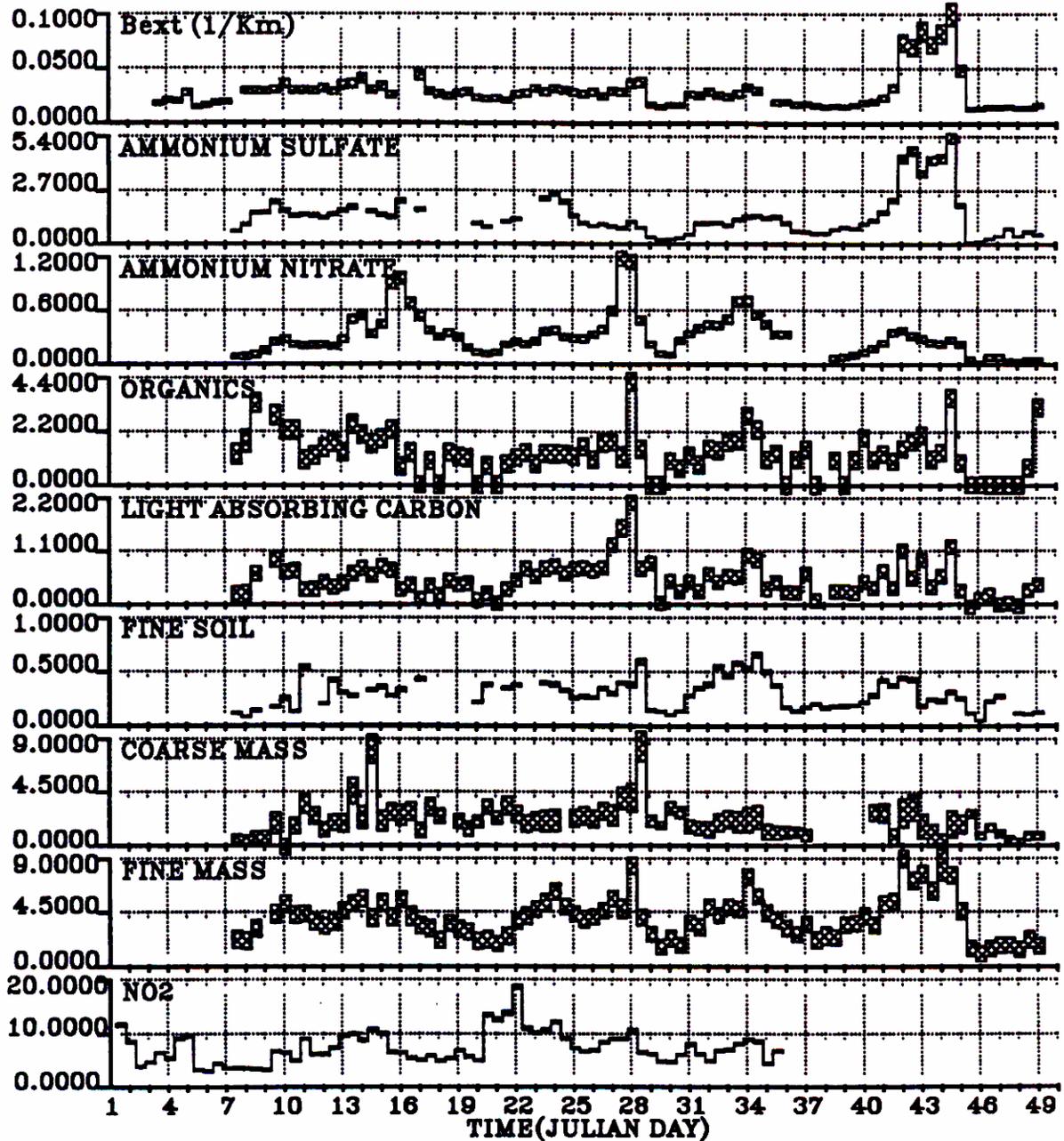


Figure 5.18: Time traces of particulate and NO<sub>2</sub> data ( $\mu\text{g}/\text{m}^3$ ) at Page.

# CANYONLANDS

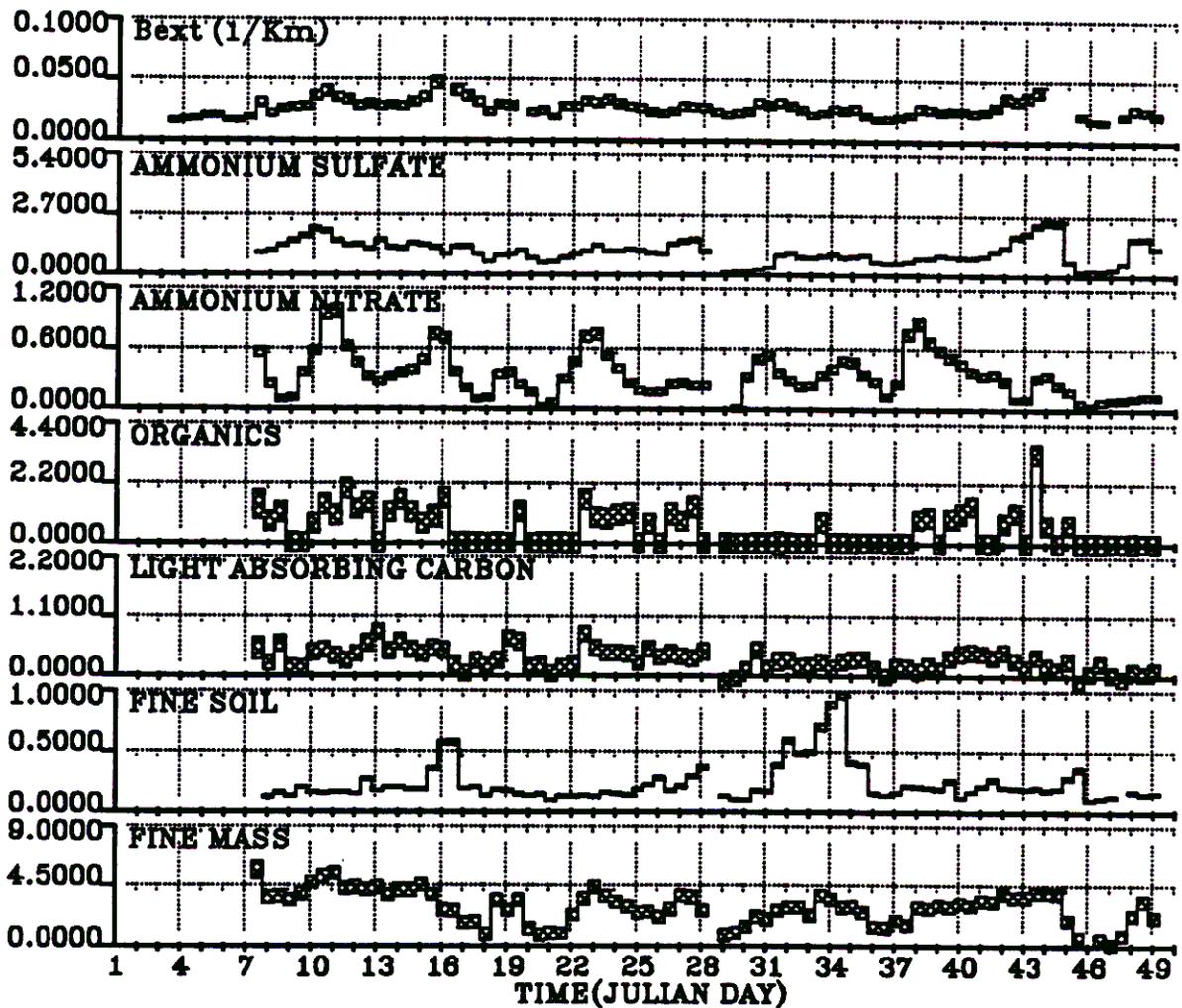


Figure 5.19: Time traces of particulate data ( $\mu\text{g}/\text{m}^3$ ) at Canyonlands.

# HOPI POINT

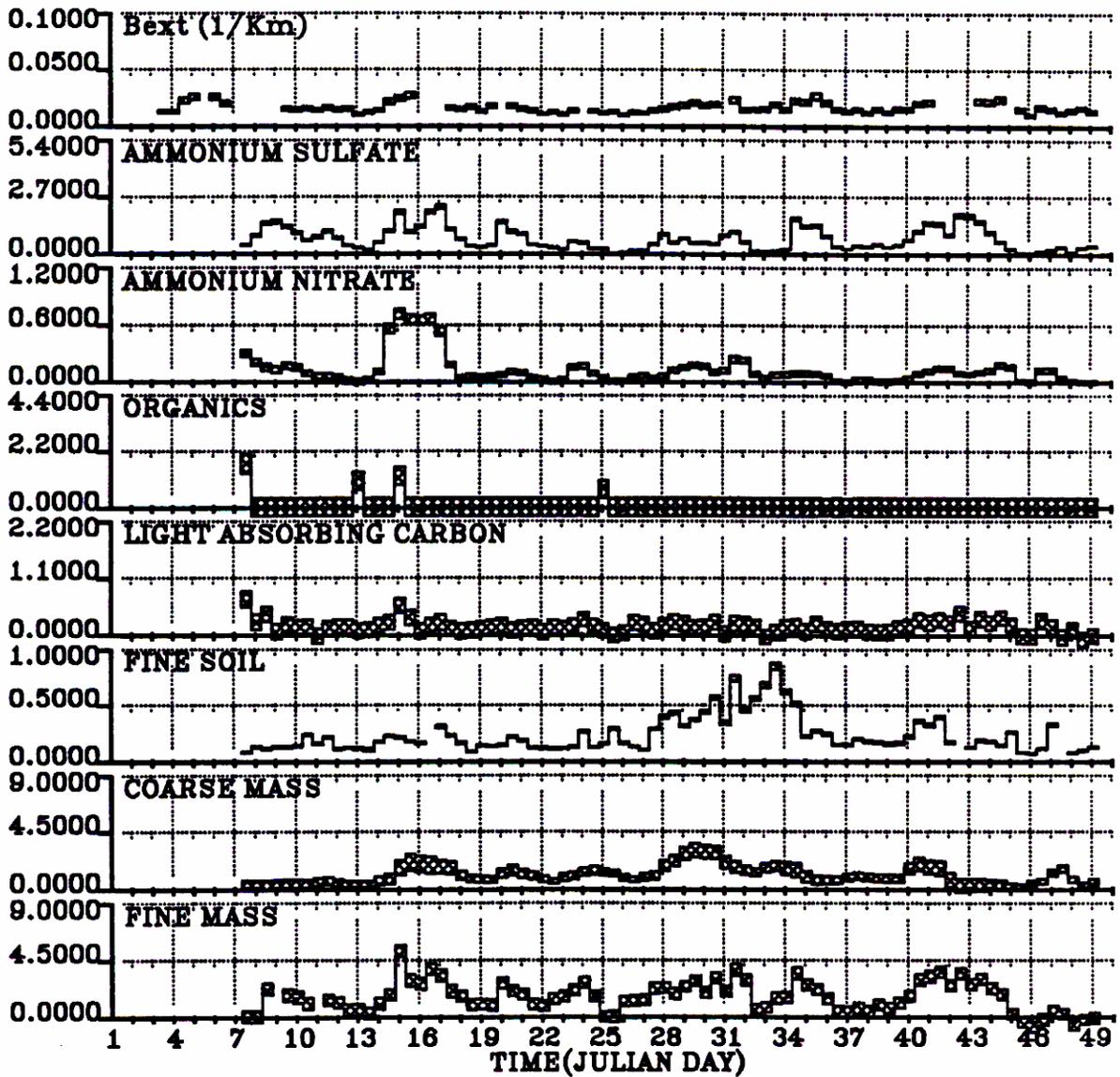


Figure 5.20: Time traces of particulate data ( $\mu\text{g}/\text{m}^3$ ) at Hopi Point.

Table 5.16: Statistics for the 12-hour averaged particulate and  $NO_2$  data at Page, ( $\mu g/m^3$ ). All data except coarse mass and  $NO_2$  are for particles  $< 2.5 \mu m$  diameter. Coarse mass is  $2.5-15 \mu m$ . Low RH is  $RH < 60\%$ .

Humidity Subgroup	Variable	Mean	Standard Deviation	Minimum	Maximum	Number of Cases
All	sulfates	1.361	1.071	0.074	5.341	74
Low	sulfates	1.061	0.563	0.074	2.285	40
All	nitrites	0.314	0.236	0.010	1.179	78
Low	nitrites	0.223	0.168	0.010	0.903	39
All	organics	1.284	0.891	0.000	4.241	82
Low	organics	1.170	0.937	0.000	3.359	43
All	abs. carbon	0.502	0.360	-0.068	2.102	82
Low	abs. carbon	0.397	0.266	-0.068	0.924	43
All	fine soil	0.287	0.138	0.047	0.652	71
Low	fine soil	0.244	0.121	0.047	0.543	37
All	coarse mass	2.064	1.411	-0.301	8.355	76
Low	coarse mass	2.053	1.464	-0.188	8.112	37
All	fine mass	3.980	1.746	1.004	8.980	83
Low	fine mass	3.269	1.239	1.004	5.292	44
All	$NO_2$	7.610	2.953	3.198	18.607	57
Low	$NO_2$	7.738	2.979	3.198	13.810	27

Table 5.17: Statistics for the 12-hour averaged particulate data at Canyonlands, ( $\mu g/m^3$ ). All data are for particles  $< 2.5 \mu m$  diameter. Low RH is  $RH < 60\%$ .

Humidity Subgroup	Variable	Mean	Standard Deviation	Minimum	Maximum	Number of Cases
All	sulfates	1.021	0.511	0.115	2.431	83
Low	sulfates	0.924	0.401	0.115	1.944	50
All	nitrites	0.337	0.220	0.005	0.975	80
Low	nitrites	0.351	0.233	0.019	0.975	48
All	organics	0.503	0.660	0.000	3.329	83
Low	organics	0.491	0.620	0.000	2.003	50
All	abs. carbon	0.287	0.197	-0.121	0.811	83
Low	abs. carbon	0.268	0.183	-0.121	0.778	50
All	fine soil	0.232	0.166	0.089	0.964	81
Low	fine soil	0.239	0.189	0.089	0.964	50
All	fine mass	2.836	1.231	0.065	5.633	82
Low	fine mass	2.733	1.246	0.463	5.404	49

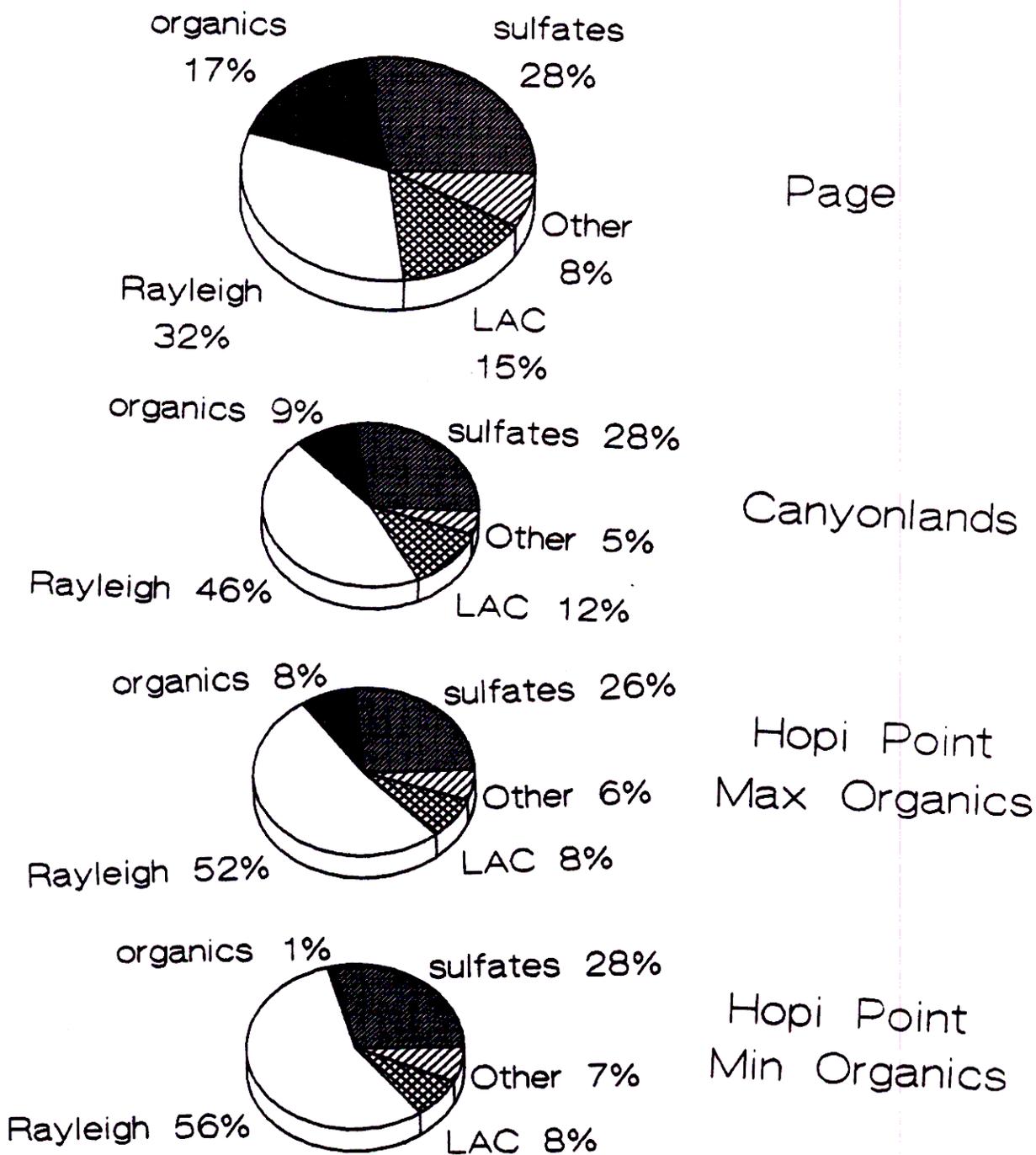


Figure 5.21: Mean light extinction budgets for the entire WHITEX time period. The areas of the wedges are proportional to the light extinction for each component. Mean reconstructed extinction is  $0.0317 \pm 0.0004$  at Page,  $0.0220 \pm 0.0004$  at Canyonlands,  $0.0168 \pm 0.0002$  with minimum organics at Hopi Point, and  $0.0182 \pm 0.0004 \text{ Km}^{-1}$  with maximum organics at Hopi Point.

Table 5.19: Mean extinction budgets by type for Page, Canyonlands, and Hopi Point for the 6-week WHITEX study period.

	Page		Canyonlands	
	$Km^{-1}$	% of Total	$Km^{-1}$	% of Total
Scatter by Gases	.0103±0.0001	32±1%	.0097±0.0001	44±1%
Absorption by Gases	unknown mean—not more than 5%			
Coarse Particle Scatter	.0092±0.0000	3±0%	.0007±0.0002†	3±1†
Fine Particle Scatter	.0155±0.0004	50±1%	.0091±0.0004	41±2%
Particle Absorption	.0046±0.0002	14±1%	.0026±0.0001	12±1%
Total	.0317±0.0004	100±2%	.0220±0.0004	100±3%
Measured $b_{ext}$	.0291±0.0004	93±2%	.0247±0.0003	112±3%

†Estimated based on Page and Hopi Point.

	Hopi Point Minimum Organics		Hopi Point Maximum Organics	
	$Km^{-1}$	% of Total	$Km^{-1}$	% of Total
Scatter by Gases	0.0095±0.0001	56±1%	0.0095±0.0001	52±1
Absorption by Gases	unknown mean—not more than 5%			
Coarse Particle Scatter	0.0005±0.0000	3±0%	0.0005±0.0000	3±0
Fine Particle Scatter	0.0055±0.0004	34±3%	0.0068±0.0004	37±2
Particle Absorption	0.0014±0.0001	8±1%	0.0014±0.0001	8±1
Total	0.0168±0.0002	100±4%	0.0182±0.0004	100±3
Measured $b_{ext}$	0.0161±0.0002	96±3%	0.0161±0.0002	88±2

0.0013  $\text{Km}^{-1}$ . This is 5% of the mean extinction measured during the same time periods, and 4% of the  $b_{ext}$  averaged over the entire WHITEX period. There are significant differences between the extinction budgets on high extinction days vs low extinction days (see section on time variations in the extinction budget) with sulfates accounting for a much larger fraction than average on dirty days. Therefore, since  $\text{NO}_2$  concentrations are missing for a biased set of time periods, an accurate estimate of the mean extinction due to  $\text{NO}_2$  is difficult. Because scattering by sulfates is dominant during dirty days, all other components contribute a lower than average fraction during these time periods. Thus it seems likely that the contribution of  $\text{NO}_2$  absorption to the mean light extinction is a maximum of 5%.

The fractions of extinction due to absorption by  $\text{NO}_2$  are presumed to be less at the other sites, since they are farther from any sources of  $\text{NO}$ , the precursor to  $\text{NO}_2$ .

### 5.3.3 Coarse Particle Scattering

The scattering efficiency of coarse particles ( $> 2.5 \mu\text{m}$  diameter) can be determined by at least three methods. 1) a review of literature to find a consensus coarse particle scattering efficiency; 2) regression of measured extinction vs fine and coarse mass; and 3) Mie theory applied to giant particle and Drum data. Mie scattering calculations were not done because there were not sufficient data.

Using the literature efficiency of  $0.45 \text{ m}^2/\text{g}$ , the extinctions due to coarse particle scattering at Page and Hopi Point are on average  $0.0009 \pm 0.0000$  and  $0.0005 \pm 0.0000 \text{ Km}^{-1}$ . These values are both 3% of the average measured extinction at the respective sites. Although there are no coarse particle data for Canyonlands, it is reasonable to assume that the coarse particle scattering there is also approximately  $3 \pm 1\%$  of the total extinction. Based on this assumption, the estimated mean coarse particle scattering coefficient for Canyonlands is  $0.0007 \pm 0.0002 \text{ Km}^{-1}$ .

Use of the second method, MLR analyses of transmissometer derived extinction vs fine mass by species and coarse mass for each site, which is summarized in Table 5.20 resulted in statistically insignificant regression coefficients at Hopi Point. At Page, the result was  $1.0 \pm 0.6 \text{ m}^2/\text{g}$ . Use of this scattering efficiency would result in a mean coarse mass scattering coefficient of  $0.0021 \text{ Km}^{-1}$  at Page. However, since reconstructed extinction is higher than measured at Page, even when the lower literature efficiency is used for coarse mass, the mean budget was calculated using the literature value.

### 5.3.4 Particle Absorption

Average particle absorption was estimated by multiplying the TOR absorbing carbon concentrations by the consensus absorption efficiency  $9.0 \text{ m}^2/\text{g}$ . The mean particle absorptions are  $0.0046 \pm 0.0002$ ,  $0.0026 \pm 0.0001$ , and  $0.0014 \pm 0.0001 \text{ Km}^{-1}$  for Page, Canyonlands, and Hopi Point, respectively. These values are  $14 \pm 1\%$ ,  $12 \pm 1\%$  and  $8 \pm 1\%$  of the mean reconstructed extinction for these sites.

### 5.3.5 Fine Particle Scattering

Several methods could potentially be used to estimate the amount of fine particle scattering at each site. In order of decreasing level of confidence in the results produced, they include:

1. Using consensus literature values for the scattering efficiencies of each of the important chemical species (sulfates, organics, nitrates, and soil dust) calculate the reconstructed fine particle scattering based on the concentrations of each of the species.

Table 5.20: Summary of multiple linear regression analyses for coarse mass. Results are scattering efficiencies in  $m^2/g$ .

Site	RH Subgroup	Dependent Variable	Result for Min Organics	Result for Max Organics
Page	All	$b_{ext}$	$1.0 \pm 0.6$	
Page	All	$b_{scat}$	$*0.3 \pm 0.3$	
Page	Low	$b_{ext}$	$*0.0 \pm 0.4$	
Page	Low	$b_{scat}$	$*0.3 \pm 0.4$	
Hopi	All	$b_{ext}$	$*-0.0 \pm 0.5$	$*-0.1 \pm 0.6$
Hopi	All	$b_{scat}$	$*-0.1 \pm 0.3$	$*-0.1 \pm 0.3$
Hopi	Low	$b_{ext}$	$*0.1 \pm 0.7$	$*0.1 \pm 0.7$
Hopi	Low	$b_{scat}$	$*0.0 \pm 0.4$	$*0.1 \pm 0.4$
Both	All	$b_{ext}$	$1.1 \pm 0.4$	$1.2 \pm 0.4$
Both	All	$b_{scat}$	$*0.2 \pm 0.2$	$*0.3 \pm 0.2$
Both	Low	$b_{ext}$	$*0.2 \pm 0.3$	$*0.4 \pm 0.3$
Both	Low	$b_{scat}$	$*0.2 \pm 0.2$	$*0.3 \pm 0.2$

\* These values are statistically insignificant ( $t > 0.05$ ).

The dependent variables used were sulfates, nitrates, organics, light absorbing carbon, fine soil and coarse mass. Sulfates and nitrates were corrected by the modified Tang curves when  $b_{ext}$  was used as the dependent variable for all RH.

2. Calculate reconstructed scattering as described above except use the scattering efficiencies derived from MLR analyses of scattering or extinction coefficients vs the chemical species concentrations.
3. Subtract the scattering by gases, absorption by gases, particle absorption, and coarse particle scattering from the  $b_{ext}$  measurements.
4. Subtract the coarse particle scattering and mean Rayleigh scattering from the  $b_{scat}$  measurements. Also need to add in an estimate of the additional scattering due to water.
5. Determine a scattering efficiency for fine mass by MLR analyses of  $b_{ext}$  or  $b_{scat}$  vs fine and coarse mass concentrations. Then multiply this by the fine mass concentrations.
6. Using a fine mass scattering efficiency based on consensus of previous studies, multiply by fine mass concentrations.

### Discussion of the Methods

Although some previous studies (Mathai and Tombach<sup>8</sup> list several) have attempted to determine the scattering efficiency for total fine mass (methods 5 and 6), unless the time periods are limited to low RH conditions only, the light extinction due to scattering by all fine particles can only be determined by separately finding the scattering efficiency for each chemical species, then summing the scattering due to each (methods 1 or 2). This is because the scattering due to ammonium sulfate and ammonium nitrate is strongly dependent on ambient relative humidity, while the scattering due to species which are less hygroscopic will not have the same RH dependence. Therefore, there is no relative humidity adjustment for fine mass as a whole. The relative humidity dependence of fine mass scattering can be illustrated by the MLR results which were obtained when WHITEX

fine mass data were regressed against the optical measurements. These analyses are summarized in Table 5.21. Note especially the results for Page when  $b_{ext}$  was the dependent variable. For the low RH data subset, the regression coefficient for fine mass was  $3.8 \pm 1.1 \text{ m}^2/\text{g}$  but when cases for all RH were used, the coefficient was inflated to  $9.9 \pm 1.0$ . The problem is not apparent at Canyonlands and Hopi Point because  $b_{ext}$  data were missing there on most high RH days.

Method 3, subtracting absorption by gases, scattering by gases, absorption by particles, and coarse particle scattering from the transmissometer measurements of  $b_{ext}$  is physically reasonable (no RH problems). However, the accuracy of this method depends on the accuracy of the coarse particle scattering,  $\text{NO}_2$  absorption, and particle absorption estimates. Since  $\text{NO}_2$  data are sparse, there are no coarse mass data at Canyonlands, and the absorbing carbon concentrations are controversial, methods 1 and 2 are probably better.

The scattering efficiencies for each chemical species used in methods 1 and 2 are discussed in detail in the section on extinction budget by species which follows.

For method 4, the scattering due to fine particles was calculated for each time period by

$$b_{scat, fm} = b_{scat} - b_{scat, gas} - 1/2 \times b_{scat, cm} + RH \text{ correction} \quad (5.17)$$

where

$$\begin{aligned} RH \text{ correction} &= \text{sulfates} \times E_S \times (fs(RH) - 1) \\ &+ \text{nitrates} \times E_N \times (fn(RH) - 1) \end{aligned} \quad (5.18)$$

and  $b_{scat}$  is the scattering coefficient measured by the nephelometer,  $b_{scat, gas}$  is Rayleigh scattering,  $b_{scat, cm}$  is the scattering due to coarse particles and all other variables are as defined previously. The calculation was also carried out with  $1/(1-RH)$  substituted for  $fs(RH)$  and  $fn(RH)$ . The scattering efficiency used for sulfates was  $2.55 \text{ m}^2/\text{g}$ . For nitrates,  $2.55 \text{ m}^2/\text{g}$  was used with  $1/(1-RH)$  and  $1.1 \text{ m}^2/\text{g}$  was used with  $fn(RH)$ . Coarse mass scattering was calculated using  $0.45 \text{ m}^2/\text{g}$  as the scattering efficiency.

## Results

Results for methods 1, 2, 3 and 4 are shown in Table 5.22. At each site, the method which produced the largest estimate of fine particle scattering, was method 4. Based on the comparison of reconstructed extinction to measured extinction, results from method 4 are too high, especially when  $1/(1-RH)$  was used as the relative humidity correction. The results indicate that both relative humidity corrections are too high to be applied to nephelometer data. These results along with some of the MLR results which will be discussed in the next section, indicate that the drying of the particles by the nephelometer is not complete and that some of the scattering measured by the nephelometer must be due to water.

The lowest estimate of mean fine particle scattering was from method 3. Because method 3 forces the reconstructed extinction to exactly match the measured extinction, the mean fine particle scattering from this method would be expected to be too low at Canyonlands and Hopi Point, since  $b_{ext}$  data at these sites were often missing when RH was high. Data at Page indicate that high RH days are often high  $b_{ext}$  days also.

Reconstructed extinction based on methods 1 and 2 were compared to measured extinction to determine which would result in a better fit. Both give relatively good fits, however, for both methods, reconstructed extinction is too high at Page and too low at Canyonlands. Measured extinction is reproduced quite well at Hopi Point.

Table 5.21: Summary of multiple linear regression analyses for fine mass. Results are scattering efficiencies in  $m^2/g$ . Low RH is  $RH < 60\%$ . (fine-abs. C) is the fine mass remaining after absorbing carbon has been subtracted.

Site	RH Subgroup	Independent Variables	Dependent Variable	†Result
Page	All	(fine-abs. C), abs. C, coarse	$b_{ext}$	$9.9 \pm 1.0$
Page	All	fine, coarse	$b_{scat}$	$3.7 \pm 0.2$
Page	Low	(fine-abs. C), abs. C, coarse	$b_{ext}$	$3.8 \pm 1.1$
Page	Low	fine, coarse	$b_{scat}$	$3.5 \pm 0.4$
Cany	All	(fine-abs. C), abs. C	$b_{ext}$	$2.7 \pm 0.6$
Cany	All	fine	$b_{scat}$	$3.7 \pm 0.3$
Cany	Low	(fine-abs. C), abs. C	$b_{ext}$	$2.6 \pm 0.5$
Cany	Low	fine	$b_{scat}$	$4.1 \pm 0.3$
Hopi	All	(fine-abs. C), abs. C, coarse	$b_{ext}$	$1.8 \pm 0.5$
Hopi	All	fine, coarse	$b_{scat}$	$2.7 \pm 0.3$
Hopi	Low	(fine-abs. C), abs. C, coarse	$b_{ext}$	$*0.9 \pm 0.6$
Hopi	Low	fine, coarse	$b_{scat}$	$2.4 \pm 0.3$
All	All	(fine-abs. C), abs. C	$b_{ext}$	$6.0 \pm 0.5$
All	All	fine	$b_{scat}$	$3.3 \pm 0.2$
All	Low	(fine-abs. C), abs. C	$b_{ext}$	$3.1 \pm 0.4$
All	Low	fine	$b_{scat}$	$3.3 \pm 0.2$

\*This value is statistically insignificant ( $t > 0.05$ ).

†There were no RH corrections made to the data.

Table 5.22: Scattering coefficients ( $Km^{-1}$ ) for fine mass for each site as estimated by 4 different methods

Method	Page	Canyonlands	Minimum Organics Hopi Point	Maximum Organics Hopi Point
1	0.0155±0.0004	0.0091±0.0004	0.0055±0.0004	0.0068±0.0004
2	0.0143±0.0004	0.0096±0.0004	0.0060±0.0004	0.0062±0.0004
3	0.0136±0.0005	0.0118±0.0004	0.0048±0.0003	
4a	0.0206±0.0033	0.0152±0.0026	0.0096±0.0021	
4b	0.0275±0.0039	0.0201±0.0037	0.0134±0.0057	

1. Reconstructed scattering using literature efficiencies for each chemical species.
2. Reconstructed scattering using MLR efficiencies for each chemical species.
3. Measured  $b_{ext}$  corrected by subtracting Rayleigh scattering, coarse particle scattering, particle absorption, and gaseous absorption.
4. Measured  $b_{scat}$  corrected by subtracting Rayleigh and coarse mass scattering and adding a relative humidity correction. 4a is using the modified Tang curves. 4b is using  $1/(1-RH)$  for the relative humidity correction.

Using results of method 1, mean fine particle scattering coefficients are  $0.0155±0.0004$  at Page,  $0.0091±0.0004$  at Canyonlands,  $0.0055±0.0004$  for minimum organics at Hopi Point, and  $0.0068±0.0004$   $Km^{-1}$  for maximum organics at Hopi Point. These scattering coefficients are  $50±1%$ ,  $41±2%$ ,  $32±1%$ , and  $37±2%$  respectively of the total reconstructed extinction.

## 5.4 Extinction Budget by Species

The only extinction type which can be apportioned by chemical species with the available data is fine particle scattering. Two methods were used to determine the scattering efficiencies for each species: consensus values from previous studies (see Table 5.9) and MLR analyses with  $b_{ext}$  and  $b_{scat}$  as the dependent variable and the chemical species as the independent variables. These analyses were done for each site for both the low relative humidity subgroup and for all data. The results of the MLR analyses are discussed below in each subsection.

To determine the fraction of fine particle scattering due to each species, the expected scattering due to each was calculated using both the MLR and the literature scattering efficiencies. Then the mean calculated scattering for each species was divided by the mean of the total reconstructed fine particle scattering. These results are summarized in Table 5.23. Although the results of all the regressions are reported in the following sections, the reconstructed fine particle scattering was calculated only using the MLR results obtained when data from all sites were regressed together using  $b_{ext}$  as the dependent variable for all relative humidities. This was done for two reasons, 1) increasing the sample size reduced the standard errors for most regressors by reducing the correlation between them; and 2) the results were more physically reasonable.

### 5.4.1 Sulfates

As can be seen in Table 5.24, the scattering efficiency estimates for sulfates calculated by MLR analyses were all statistically significant and physically reasonable. The literature consensus scattering efficiency for sulfates is  $2.55$   $m^2/g$  times a relative humidity factor. Note the inflated regression coefficients for low RH and when  $b_{scat}$  is the dependent variable. No RH corrections were applied to