calculation would overestimate light absorbing carbon by an additional, though probably very small, amount.[13]

At Page, the calculation yielded a mean extinction-derived absorbing carbon (with negative values included) of 0.283 $\mu g/m^3$. The means of the TOR and TMO absorbing carbon data for the same time periods are 0.432 and 0.092 $\mu g/m^3$, respectively. At Hopi Point, the extinction derived concentration was 0.039 $\mu g/m^3$, while means of TOR and TMO absorbing carbon are 0.126 and 0.027 $\mu g/m^3$, 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.

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 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 NO_2 is possible for Hopi Point. Since 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 5.16, 5.17, and 5.18. 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

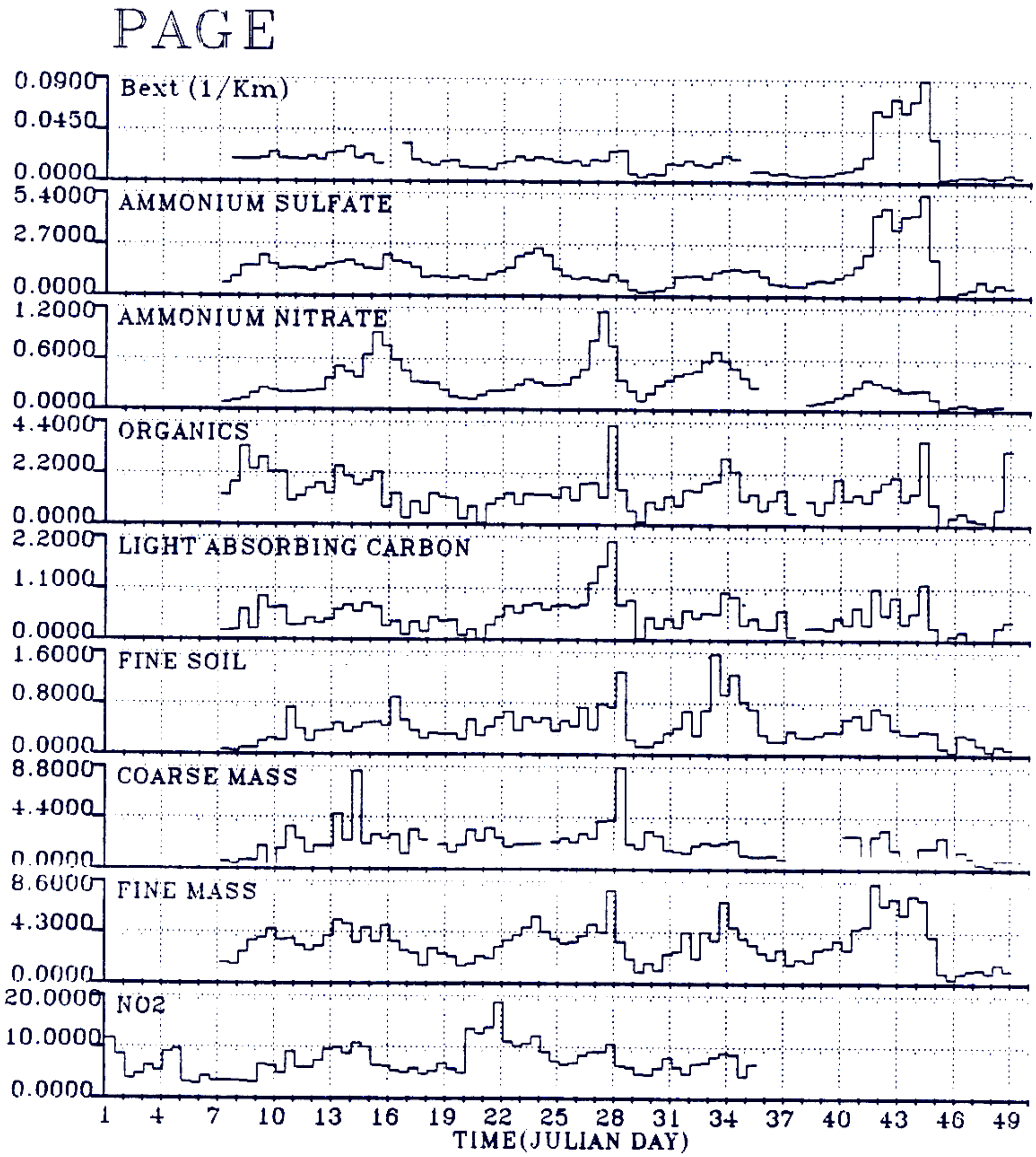

Figure 5.16: Time traces of particulate and NO_2 data ($\mu g/m^3$) at Page.

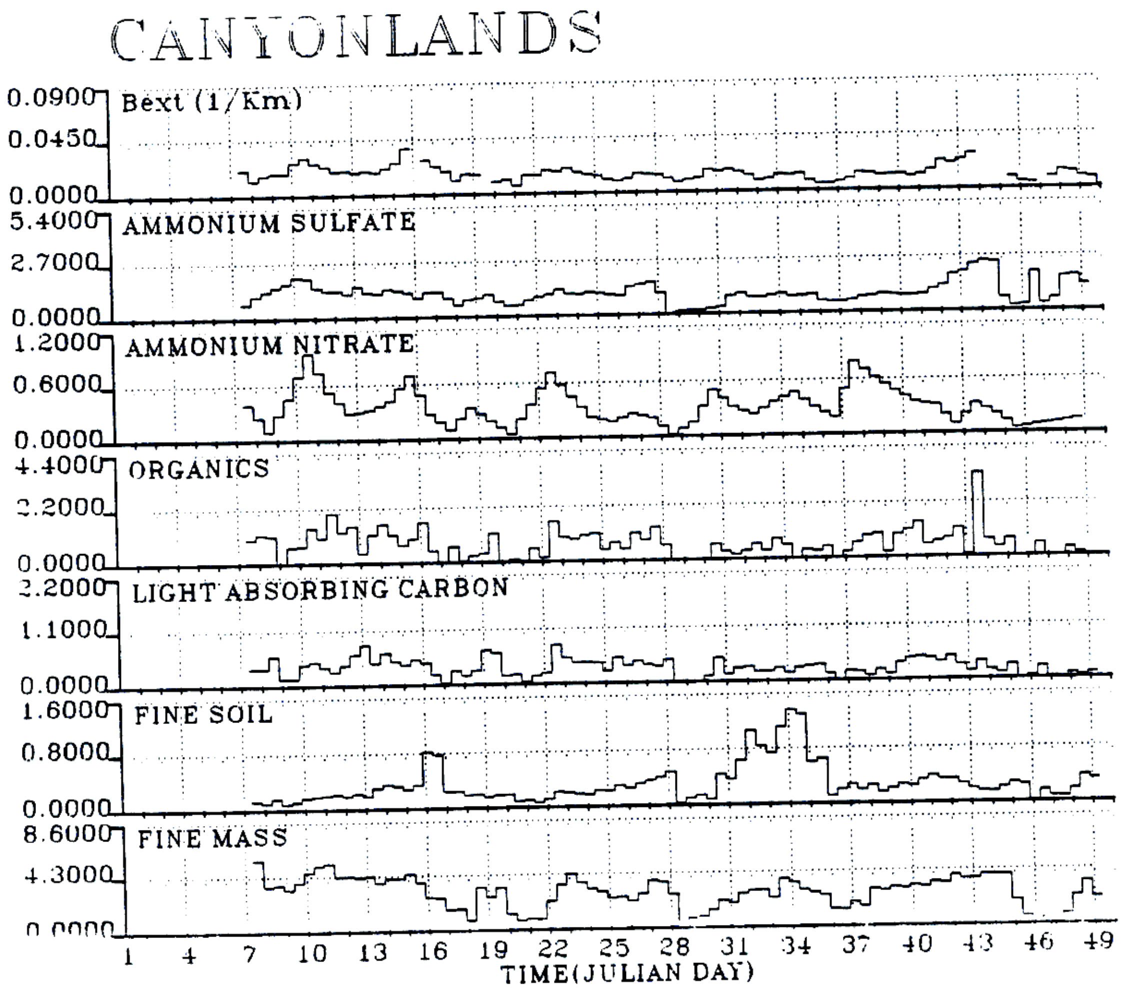

Figure 5.17: Time traces of particulate data ($\mu g/m^3$) at Canyonlands.

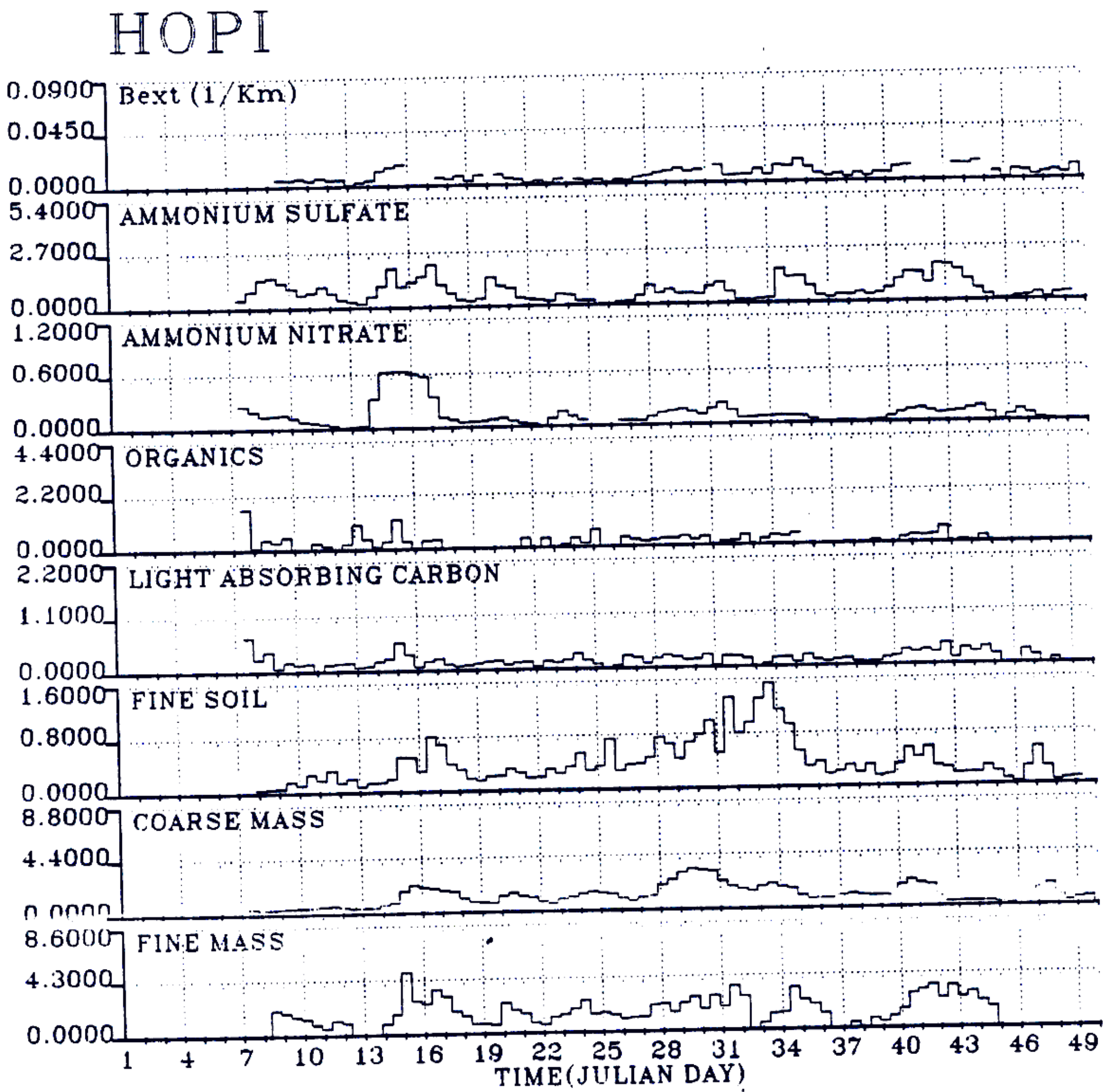

Figure 5.18: Time traces of particulate data ($\mu g/m^3$) at Hopi Point.

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 μm diameter. Coarse mass is 2.5–15 μm. Low RH is RH < 60%.

Humidity Subgroup	Variable	Mean	Standard Deviation	Minimum	Maximum	Number of Cases
All	sulfates	1.355	1.021	0.075	5.380	84
Low	sulfates	1.064	0.530	0.075	2.233	45
All	nitrates	0.316	0.215	0.028	1.157	78
Low	nitrates	0.241	0.180	0.028	0.911	39
All	organics	1.355	0.819	0.000	4.251	83
Low	organics	1.279	0.845	0.000	3.344	44
All	abs. carbon	0.507	0.355	0.000	2.107	82
Low	abs. carbon	0.405	0.254	0.000	0.921	43
All	fine soil	0.422	0.279	0.040	1.580	84
Low	fine soil	0.331	0.182	0.040	0.727	45
All	coarse mass	2.131	1.456	0.000	8.739	77
Low	coarse mass	2.096	1.506	0.000	8.427	38
All	fine mass	3.388	1.740	0.409	8.410	84
Low	fine mass	2.716	1.236	0.409	5.304	45
All	NO_2	7.347	2.984	2.900	18.607	69
Low	NO_2	7.473	2.934	2.900	13.810	33

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

Humidity Subgroup	Variable	Mean	Standard Deviation	Minimum	Maximum	Number of Cases
All	sulfates	1.020	0.520	0.023	2.438	84
Low	sulfates	0.934	0.424	0.023	1.937	51
All	nitrates	0.321	0.195	0.014	0.950	83
Low	nitrates	0.344	0.212	0.014	0.950	50
All	organics	0.643	0.571	0.000	3.332	84
Low	organics	0.633	0.527	0.000	2.000	51
All	abs. carbon	0.285	0.188	0.000	0.803	84
Low	abs. carbon	0.266	0.176	0.000	0.768	51
All	fine soil	0.301	0.267	0.000	1.357	84
Low	fine soil	0.321	0.304	0.000	1.357	51
All	fine mass	2.749	1.287	0.000	5.632	84
Low	fine mass	2.615	1.325	0.000	5.335	51

Table 5.18: Statistics for the 12-hour averaged particulate data at Hopi Point, ($\mu g/m^3$). All data are for particles < 2.5 μm diameter. Coarse mass is 2.5–15 μm. Low RH is RH < 60%.

Humidity Subgroup	Variable	Mean	Standard Deviation	Minimum	Maximum	Number of Cases
All	sulfates	0.675	0.513	0.023	2.100	84
Low	sulfates	0.525	0.424	0.023	1.906	61
All	nitrates	0.121	0.143	0.000	0.629	81
Low	nitrates	0.097	0.119	0.000	0.625	58
All	organics	0.197	0.279	0.000	1.663	83
Low	organics	0.209	0.306	0.000	1.663	61
All	abs.carbon	0.164	0.118	0.000	0.679	84
Low	abs. carbon	0.154	0.124	0.000	0.679	61
All	fine soil	0.384	0.313	0.020	1.539	83
Low	fine soil	0.364	0.326	0.020	1.539	60
All	coarse mass	1.137	0.729	0.131	3.278	85
Low	coarse mass	1.049	0.657	0.131	3.278	62
All	fine mass	1.420	1.089	0.000	4.932	83
Low	fine mass	1.159	0.982	0.000	4.932	60

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

	Page		Canyonlands		Hopi Point	
	Km^{-1}	% of Total	Km^{-1}	% of Total	Km^{-1}	% of Total
Scatter by Gases	.0103	32%	.0097	43%	.0095	55%
Absorption by Gases	unknown mean—not more than 5%					
Coarse Particle Scatter	.0010	3%	.0007	3%	.0005	3%
Fine Particle Scatter	.0159	50%	.0096	42%	.0059	34%
Particle Absorption	.0046	14%	.0026	12%	.0015	9%
Total	.0318	100%	.0226	100%	.0174	100%
Measured b_{ext}	.0291	92%	.0246	109%	.0161	93%

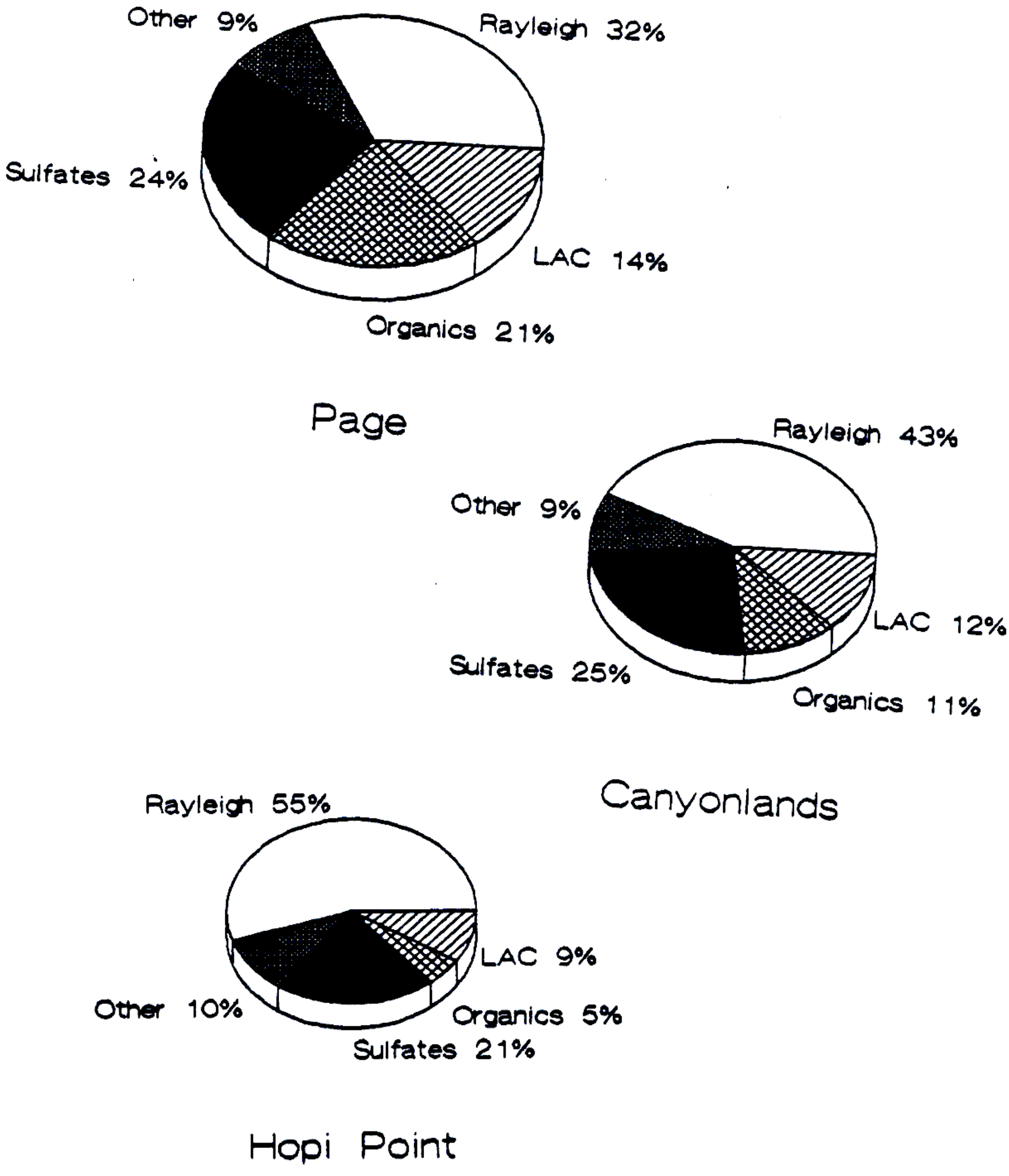

Figure 5.19: Mean light extinction budgets for the entire WHITEX time period. The areas of the wedges are proportional to the light extinction for each component. Mean reconstructed extinction is 0.0318 Km^{-1} at Page, 0.0226 Km^{-1} at Canyonlands, and 0.0174 Km^{-1} at Hopi Point.

scattering coefficients for wavelength 550 nm at each site are 0.0095 Km^{-1} at Hopi Point, 0.0097 Km^{-1} at Canyonlands, and 0.0103 Km^{-1} at Page.[3]

The fractions of the reconstructed extinction which were due to Rayleigh scattering were on average, 32% at Page, 43% at Canyonlands, and 55% at Hopi Point.

The minimum measured 6-hour average b_{ext} at Page was 0.0115 Km^{-1} and minimum measured b_{scat} was 0.0108 Km^{-1} indicating that even during the clearest time period there was measurable non- Rayleigh extinction at Page. Similarly at Canyonlands, the lowest measured 6-hour averages of b_{ext} and b_{scat} were 0.0133 and 0.0113 Km^{-1}, which are 37% and 16% greater than mean Rayleigh extinction for this site.

The minimum measured b_{ext} at Hopi Point was 0.0093 Km^{-1} which is slightly lower than the expected average Rayleigh extinction. This could be due to lower than average barometric pressure (air density) during this time period, so that the Rayleigh scattering was actually below average, or could be due to measurement error. Lowest measured b_{scat} at Hopi Point was 0.0109 Km^{-1}, 15% higher than mean Rayleigh scattering for this site. The apparent discrepancy between the b_{ext} and b_{scat} measurements at Hopi Point may be due to transmissometer and nephelometer data being missing for different time periods, or could be because the two instruments were located 30 Km apart.

5.3.2 Absorption by gases (NO_2 Absorption)

The only gas present in measurable amounts during WHITEX which could cause significant absorption of visible light is nitrogen dioxide (NO_2). The only site for which there are any NO_2 data is Page, and there were no NO_2 data during the high extinction episode in February.

The absorption efficiency of NO_2 at 550 nm is 0.332 Km^{-1} per ppm (Hodkinson, 1966). Based on this efficiency, for time periods when there are NO_2 data, the average extinction due to NO_2 is 0.0013 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 NO_2 concentrations are missing for a biased set of time periods, an accurate estimate of the mean extinction due to 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 NO_2 absorption to the mean light extinction is a maximum of 5%.

The fractions of extinction due to absorption by NO_2 are presumed to be less at the other sites, since they are farther from any sources of NO, the precursor to NO_2.

5.3.3 Coarse Particle Scattering

The scattering efficiency of coarse particles ($> 2.5\ \mu m$ 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 m^2/g, the extinctions due to coarse particle scattering at Page and Hopi Point are on average 0.0010 and 0.0005 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

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
Page	All	b_{ext}	1.1±0.6
Page	All	b_{scat}	*0.3±0.3
Page	Low	b_{ext}	*0.5±0.4
Page	Low	b_{scat}	*0.6±0.4
Hopi	All	b_{ext}	*0.3±0.5
Hopi	All	b_{scat}	*-0.1±0.5
Hopi	Low	b_{ext}	*-0.0±0.7
Hopi	Low	b_{scat}	*0.1±0.4
Both	All	b_{ext}	1.3±0.3
Both	All	b_{scat}	*0.2±0.2
Both	Low	b_{ext}	*0.6±0.3
Both	Low	b_{scat}	*0.3±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.

approximately 3% of the total extinction. Based on this assumption, the estimated mean coarse particle scattering coefficient for Canyonlands is 0.0007 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 1.14 ±0.55 m^2/g. Use of this scattering efficiency would result in a mean coarse mass scattering coefficient of 0.0024 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 m^2/g. The mean particle absorptions are 0.0046, 0.0026, and 0.0015 Km^{-1} for Page, Canyonlands, and Hopi Point, respectively. These values are 14%, 12% and 9% 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 expected or "reconstructed" fine particle scattering based on the concentrations of each of the species.

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[8] 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±0.2 m^2/g but when cases for all RH were used, the coefficient was inflated to 9.7±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, NO_2 absorption, and particle absorption estimates. Since 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

$$b_{scat,fm} = b_{scat} - b_{scat,gas} - 1/2 \times b_{scat,cm} + RH correction \tag{5.10}$$

where

$$\begin{aligned} RH\ correction &= sulfates \times E_S \times (fs(RH) - 1) \\ &+ nitrates \times E_N \times (fn(RH) - 1) \end{aligned} \tag{5.11}$$

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

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}	9.7±1.0
Page	All	fine, coarse	b_{scat}	3.8±0.2
Page	Low	(fine-abs. C), abs. C, coarse	b_{ext}	4.0±0.9
Page	Low	fine, coarse	b_{scat}	3.5±0.4
Hopi	All	(fine-abs. C), abs. C, coarse	b_{ext}	1.4±0.5
Hopi	All	fine, coarse	b_{scat}	2.6±0.3
Hopi	Low	(fine-abs. C), abs. C, coarse	b_{ext}	*0.6±0.5
Hopi	Low	fine, coarse	b_{scat}	2.3±0.3
Cany	All	(fine-abs. C), abs. C	b_{ext}	3.3±0.5
Cany	All	fine	b_{scat}	3.5±0.3
Cany	Low	(fine-abs. C), abs. C	b_{ext}	3.0±0.5
Cany	Low	fine	b_{scat}	3.7±0.3
All	All	(fine-abs. C), abs. C	b_{ext}	5.5±0.4
All	All	fine	b_{scat}	3.0±0.1
All	Low	(fine-abs. C), abs. C	b_{ext}	2.7±0.3
All	Low	fine	b_{scat}	2.9±0.2

*This value is statistically insignificant (t > 0.05).
†There were no RH corrections made to the data.

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 m^2/g. For nitrates, 2.55 m^2/g was used with 1/(1-RH) and 1.1 m^2/g was used with fn(RH). Coarse mass scattering was calculated using 0.45 m^2/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

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

	Site		
Method	Page	Canyonlands	Hopi Point
1	0.0159	0.0096	0.0059
2	0.0143	0.0092	0.0054
3	0.0132	0.0116	0.0046
4a	0.0183	0.0152	0.0094
4b	0.0242	0.0199	0.0133

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.

methods, reconstructed extinction is too high at Page and too low at Canyonlands. Measured extinction is reproduced quite well at Hopi Point.

Using results of method 1, mean fine particle scattering coefficients are 0.0159 Km^{-1} at Page, 0.0096 Km^{-1} at Canyonlands, and 0.0059 Km^{-1} at Hopi Point. These scattering coefficients are 50%, 42%, and 34%, respectively of the total reconstructed extinction at the three sites.

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 the 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 was 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