

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

Method	Site		
	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

Table 5.23: Average fine particle scattering due to each chemical species for Page, Canyonlands, and Hopi Point using both MLR derived and consensus literature values for the scattering efficiencies.

	Page		Canyonlands		Hopi Point	
	MLR	Literature	MLR	Literature	MLR	Literature
Sulfates	54%	48%	60%	58%	72%	62%
Organics	33%	41%	20%	27%	15%	16%
Nitrates	14%	6%	20%	9%	13%	5%
Fine Soil	0%	5%	0%	6%	0%	17%
Total (Km^{-1})	.0143	.0159	.0092	.0096	.0054	.0059

coefficients for low RH and when b_{scat} is the dependent variable. No RH corrections were applied to the sulfate and nitrate data for these analyses. This indicates two things 1) the nephelometer must not dry the particles completely since the regression coefficients for sulfates (and nitrates) which result when they are regressed against b_{scat} are too high to be the “dry” scattering efficiencies. 2) Some RH correction is needed for sulfates (and nitrates) for RHs lower than 60%. It seems physically reasonable that the RH correction should probably be extended down to RH of approximately 30%.

The percentages of reconstructed fine particle scattering due to sulfates are 48% at Page, 58% at Canyonlands, and 62% at Hopi Point if the MLR scattering efficiencies are used, and are 54% at Page, 60% at Canyonlands, and 72% at Hopi Point if the literature consensus efficiencies are used.

5.4.2 Organics

Table 5.25 summarizes the scattering efficiencies obtained for organics by MLR analyses. Many of the MLR scattering efficiencies for organic matter were statistically insignificant. With the exception of one result at Page, they were also lower than the consensus value of $4.0 m^2/g$.

The percent of reconstructed fine particle scattering due to organics is 33% at Page, 20% at Canyonlands, and 15% at Hopi Point if the MLR scattering efficiencies are used. The percent of fine particle scattering by organics is 41% at Page, 27% at Canyonlands, and 16% at Hopi Point if literature scattering efficiencies are used.

5.4.3 Nitrates

The scattering efficiency of nitrates is not well known, but according to Tang et al.¹² it should be between approximately 1.1 and $7.0 m^2/g$ at low relative humidities depending on the particle size distribution. The lowest efficiency corresponds to a highly polydisperse size distribution ($\sigma_g = 2.0$) and the highest efficiency corresponds to a monodisperse size distribution ($\sigma_g = 1.01$) assuming a mass median diameter of $0.98 \mu m$ which is based on measurements of Los Angeles aerosols. If the WHITEX nitrate particles actually had a smaller mean diameter, for example if they were similar in size to the sulfate particles, then the scattering efficiency would be higher. Results of the regression analyses indicate that this may be true. The RH corrected scattering efficiencies when b_{ext} is the dependent variable are 4.7 ± 1.6 at Hopi Point, 3.0 ± 1.3 at Canyonlands, and $2.3 \pm 0.9 m^2/g$ for all sites combined. The result for Page was smaller, but also not statistically significant.

Most of the nitrate scattering efficiencies estimated by the MLR analyses (see Table 5.26) were statistically significant, and physically reasonable. However, when the regressions were done using

Table 5.24: Summary of multiple linear regression analyses used to determine sulfate scattering efficiency for 0% RH. Results are in m^2/g .

Site	RH Subgroup	Dependent	†Result
		Variable	
Page	All	b_{ext}	2.8 ± 0.1
Page	All	b_{scat}	5.0 ± 0.4
Page	Low	b_{ext}	6.6 ± 1.2
Page	Low	b_{scat}	4.3 ± 1.6
Hopi	All	b_{ext}	1.4 ± 0.3
Hopi	All	b_{scat}	4.7 ± 0.4
Hopi	Low	b_{ext}	2.7 ± 0.9
Hopi	Low	b_{scat}	4.3 ± 0.5
Cany	All	b_{ext}	1.1 ± 0.5
Cany	All	b_{scat}	5.6 ± 0.7
Cany	Low	b_{ext}	2.0 ± 1.2
Cany	Low	b_{scat}	3.8 ± 1.3
All	All	b_{ext}	2.5 ± 0.1
All	All	b_{scat}	5.0 ± 0.2
All	Low	b_{ext}	3.7 ± 0.6
All	Low	b_{scat}	3.8 ± 0.6

The independent variables used for each MLR were sulfates, organics, nitrates, absorbing carbon, and coarse mass when the dependent variable was b_{ext} . When the dependent variable was b_{scat} , total carbon was used rather than organics and absorbing carbon.

†When b_{ext} was the dependent variable and all relative humidities were included, sulfates and nitrates were multiplied by the modified Tang relative humidity functions. No RH correction was applied to the other three cases for each site.

When "All" is the site, no coarse mass data are included in the regression since this would eliminate all Canyonlands data.

Table 5.25: Summary of multiple linear regression analyses used to determine the scattering efficiency for organics. Results are in m^2/g .

Site	RH Subgroup	Dependent Variable	Result
Page	All	b_{ext}	4.2 ± 1.2
Page	All	b_{scat}	1.7 ± 0.7
Page	Low	b_{ext}	* 2.0 ± 1.4
Page	Low	b_{scat}	* 1.6 ± 1.2
Hopi	All	b_{ext}	-3.0 ± 1.3
Hopi	All	b_{scat}	* -0.0 ± 0.8
Hopi	Low	b_{ext}	-2.9 ± 1.4
Hopi	Low	b_{scat}	* 0.5 ± 0.8
Cany	All	b_{ext}	* 1.7 ± 1.4
Cany	All	b_{scat}	* -0.0 ± 0.7
Cany	Low	b_{ext}	* 1.9 ± 1.2
Cany	Low	b_{scat}	* 1.0 ± 1.5
All	All	b_{ext}	2.7 ± 0.7
All	All	b_{scat}	1.6 ± 0.2
All	Low	b_{ext}	2.1 ± 0.8
All	Low	b_{scat}	2.1 ± 0.3

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

The independent variables used for each MLR were sulfates, organics, nitrates, absorbing carbon, and coarse mass when the dependent variable was b_{ext} . When the dependent variable was b_{scat} , total carbon was used rather than organics and absorbing carbon.

When b_{ext} was the dependent variable and all relative humidities were included, sulfates and nitrates were multiplied by the modified Tang relative humidity functions. No RH correction was applied to the other three cases for each site.

When the site is "All" no coarse mass data are included in the regression since this would eliminate all Canyonlands data.

Table 5.26: Summary of multiple linear regression analyses used to determine nitrate scattering efficiency for 0% RH. Results are in m^2/g .

Site	RH Subgroup	Dependent Variable	†Result
Page	All	b_{ext}	*-0.4±1.9
Page	All	b_{scat}	6.0±2.3
Page	Low	b_{ext}	*0.9±2.3
Page	Low	b_{scat}	*4.3±3.9
Hopi	All	b_{ext}	4.7±1.6
Hopi	All	b_{scat}	9.4±1.3
Hopi	Low	b_{ext}	*4.8±2.7
Hopi	Low	b_{scat}	8.8±2.2
Cany	All	b_{ext}	3.0±1.3
Cany	All	b_{scat}	12.0±1.6
Cany	Low	b_{ext}	5.0±1.9
Cany	Low	b_{scat}	11.5±2.3
All	All	b_{ext}	2.3±0.9
All	All	b_{scat}	9.8±0.9
All	Low	b_{ext}	5.6±1.1
All	Low	b_{scat}	10.0±1.1

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

The independent variables used for each MLR were sulfates, organics, nitrates, absorbing carbon, and coarse mass when the dependent variable was b_{ext} . When the dependent variable was b_{scat} , total carbon was used rather than organics and absorbing carbon.

†When b_{ext} was the dependent variable and all relative humidities were included, sulfates and nitrates were multiplied by the modified Tang relative humidity functions. No RH correction was applied to the other three cases for each site.

When the site is "All" no coarse data were included in the analysis since this would eliminate all Canyonlands data.

b_{scat} as the dependent variable, the results were higher than expected. No RH correction was used when b_{scat} was the dependent variable, but these results indicate that perhaps the nephelometer does not completely dry the particles and that some RH correction is needed. 60% RH may also be too high to use as "low" RH. Similar results were seen for sulfates.

When literature scattering efficiencies are used, the percents of fine particle scattering due to nitrates are 6% at Page, 9% at Canyonlands, and 5% at Hopi Point. When the mean MLR efficiencies are used, the scattering due to nitrates were 14% at Page, 20% at Canyonlands, and 13% at Hopi Point.

5.4.4 Fine Soil Dust

All fine soil regression coefficients but one were statistically insignificant (see Table 5.27). The sole significant estimate for the scattering efficiency of fine soil dust was $3.0 \pm 1.3 m^2/g$. This is approximately double the consensus efficiency of $1.3 m^2/g$.

Table 5.27: Summary of multiple linear regression analyses used to determine fine soil scattering efficiency. Results are in m^2/g .

Site	RH Subgroup	Dependent Variable	Result
Page	All	b_{ext}	*-0.1±3.1
Page	All	b_{scat}	*-1.6±1.6
Page	Low	b_{ext}	*-3.4±4.3
Page	Low	b_{scat}	*-5.2±3.8
Hopi	All	b_{ext}	*2.0±1.1
Hopi	All	b_{scat}	*0.8±0.7
Hopi	Low	b_{ext}	3.0±1.3
Hopi	Low	b_{scat}	*0.4±0.7
Cany	All	b_{ext}	*-0.9±2.2
Cany	All	b_{scat}	*-1.6±1.2
Cany	Low	b_{ext}	*-1.1±2.0
Cany	Low	b_{scat}	*-1.3±1.5
All	All	b_{ext}	*-0.5±1.2
All	All	b_{scat}	*-0.9±0.6
All	Low	b_{ext}	*0.0±1.0
All	Low	b_{scat}	*-0.7±0.7

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

The independent variables used for each MLR were sulfates, organics, nitrates, absorbing carbon, and coarse mass when the dependent variable was b_{ext} . When the dependent variable was b_{scat} , total carbon was used rather than organics and absorbing carbon.

When b_{ext} was the dependent variable and all relative humidities were included, sulfates and nitrates were multiplied by the modified Tang relative humidity functions. No RH correction was applied to the other three cases for each site.

When the site is "All" no coarse mass is included in the regression since this would eliminate all Canyonlands data.

Table 5.28: Number of 12-hour average particulate samples missing for each site. Total possible samples is 84.

	Page	Cany	Hopi
sulfates	0	0	0
organics	1	0	1
abs. C	2	0	0
nitrates	6	1	1
fine soil	0	0	1
coarse mass	8	84	0
NO_2	27	84	84

Using the literature scattering efficiency, the percentages of fine particle scattering due to fine soil are 5% at Page, 6% at Canyonlands, and 17% at Hopi Point. The MLR efficiency which was used to calculate reconstructed extinction was negative. Means of the scattering due to fine soil calculated using this efficiency are approximately -0.0002 Km^{-1} at all three sites.

5.5 Time Variations in the Light Extinction Budget

Time plots of 12-hour averaged measured and reconstructed scattering and absorption coefficients and the fractions due to each component are shown in Figures 5.20, 5.21, and 5.22 for each of the three sites. The scattering and absorption efficiencies used to produce the values for each component of extinction are the consensus literature values. The extinction due to missing particulate or NO_2 data was set to zero. This should not cause serious underestimation of the reconstructed extinction since with the exception of NO_2 at all sites and coarse mass at Canyonlands, there were very few missing data. Table 5.28 shows the number of missing values for each variable.

At all three sites, it can be seen that scattering by fine sulfates dominates when the extinction coefficient is high. When the extinction coefficient is below average, sulfate scattering is still important, but scattering by organics and absorption due to elemental carbon are also often large fractions of the total extinction. This is especially true for Page.

5.5.1 Budgets on Extreme Extinction Days

The maximum 24-hour averaged measured extinction at Page was 0.0769 Km^{-1} . This occurred on Julian day 43 (Feb. 12). The minimum measured extinction at Page occurred 2 days later on Julian day 45 (Feb 14) when it was 0.0129 Km^{-1} . These days were also near the extremes of the reconstructed extinction values at Hopi Point and Canyonlands. Although Julian day 42 (Feb 11) is used as the high extinction day at Hopi Point since the extinction at Hopi Point was higher on that day than on Feb 12 when it was not extremely high. A summary of the extinction budgets for these two days is shown in Table 5.29. On Feb. 12 (Feb 11 at Hopi Point), light extinction was dominated by scattering due to fine sulfates at all three sites. In contrast, Feb 14 was a near-Rayleigh day at all sites, with Rayleigh scattering accounting for 82%, 89%, and 96% of the light extinction at Page, Canyonlands, and Hopi Point, respectively. The pie charts in Figures 5.23, 5.24, and 5.25 illustrate these budgets. The relative sizes of the pies are proportional to the measured light extinction.