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.

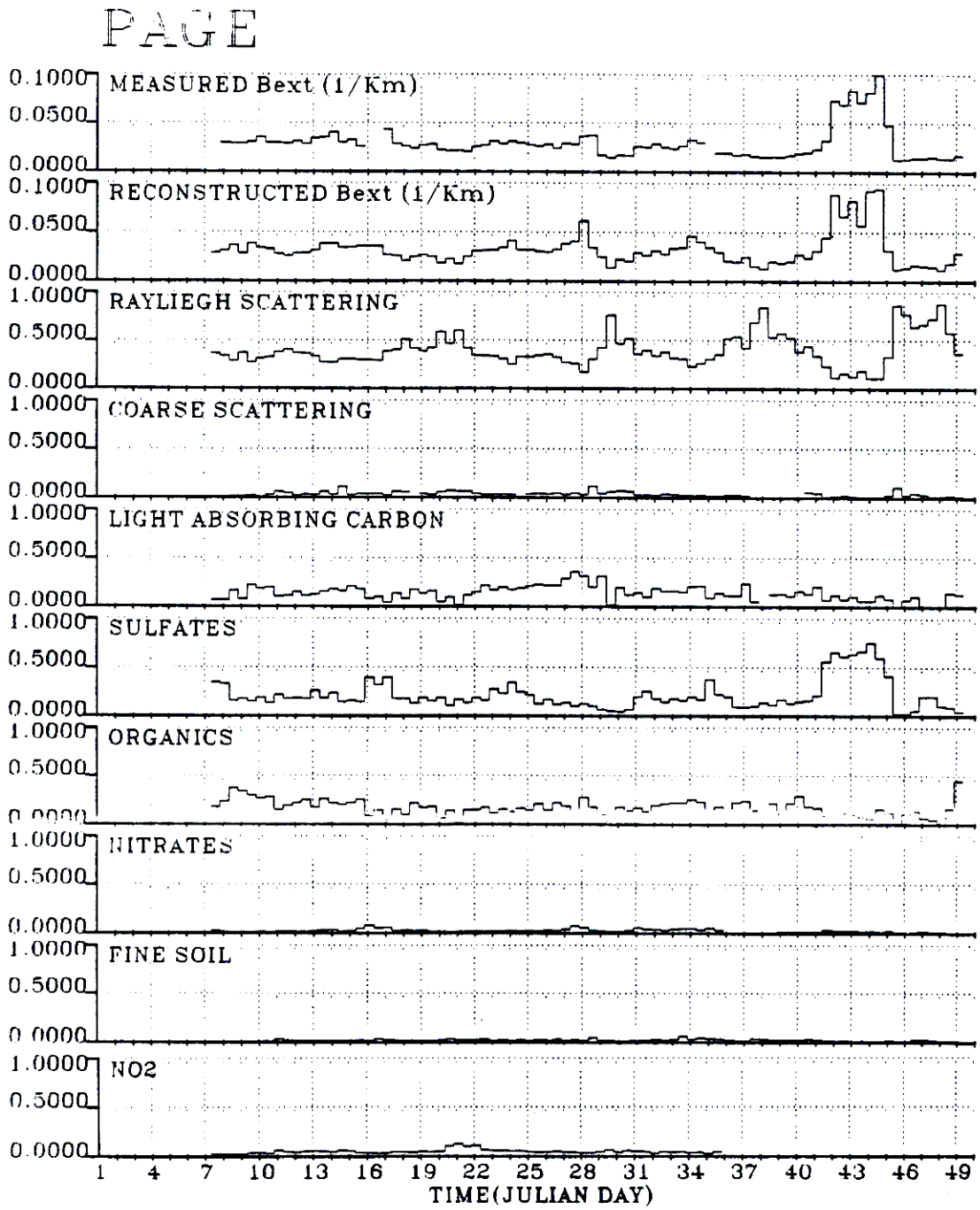


Figure 5.20: Measured and reconstructed 12-hour averaged extinction coefficients (Km^{-1}) and the fraction due to each component at Page. Extinction includes Rayleigh scattering.

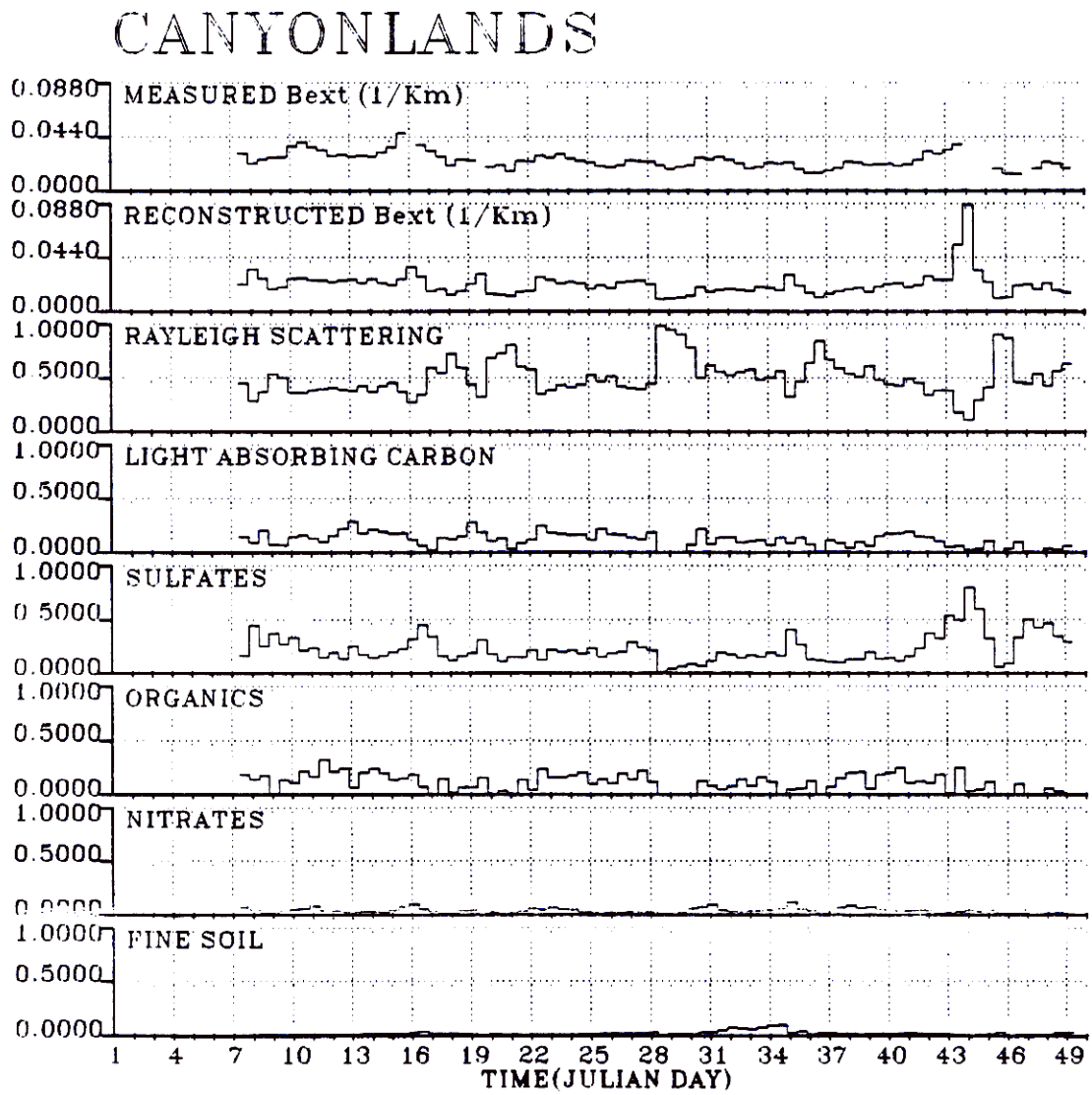


Figure 5.21: Measured and reconstructed 12-hour averaged extinction coefficients (Km^{-1}) and the fraction due to each component at Canyonlands. Extinction includes Rayleigh scattering.

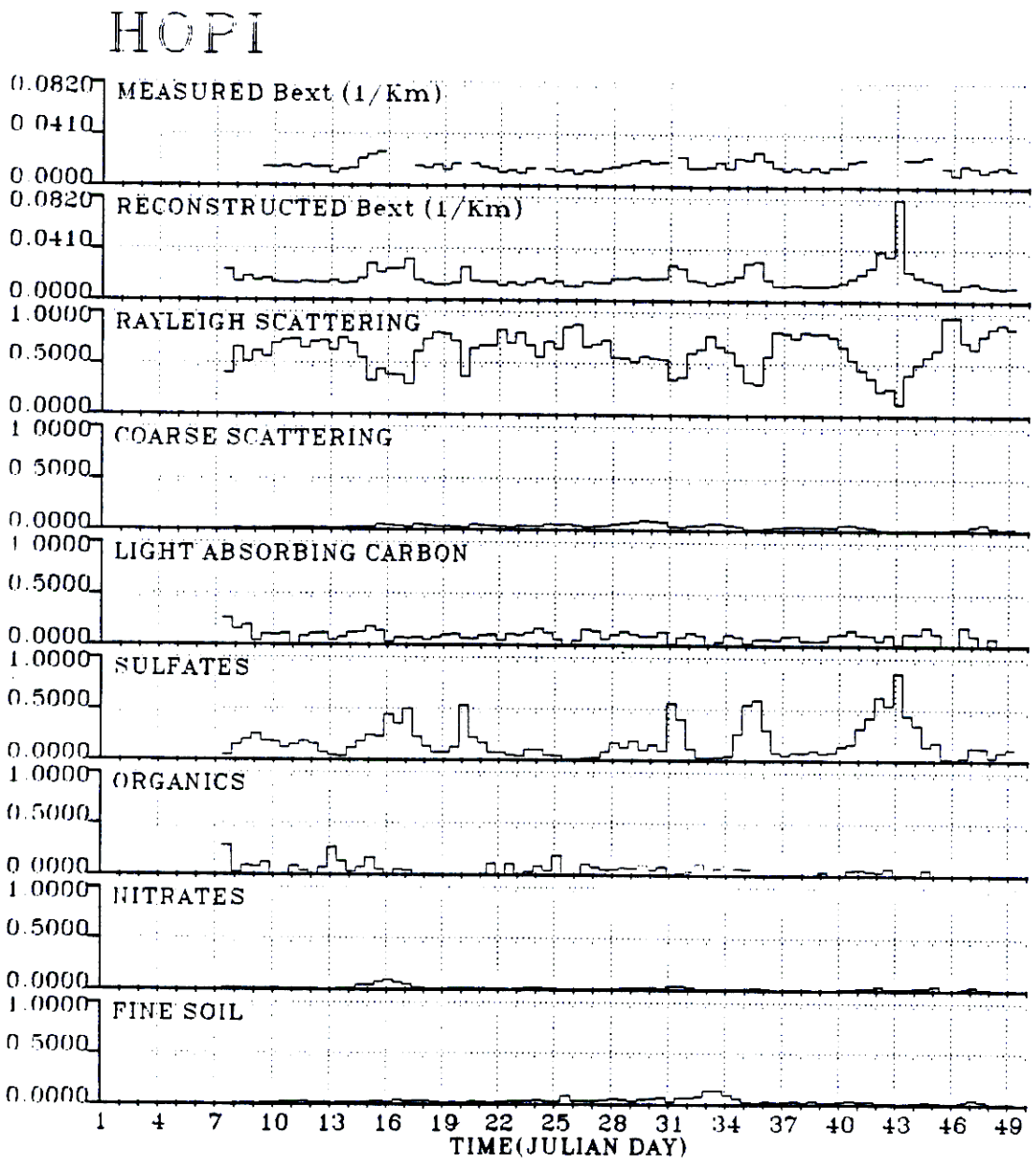
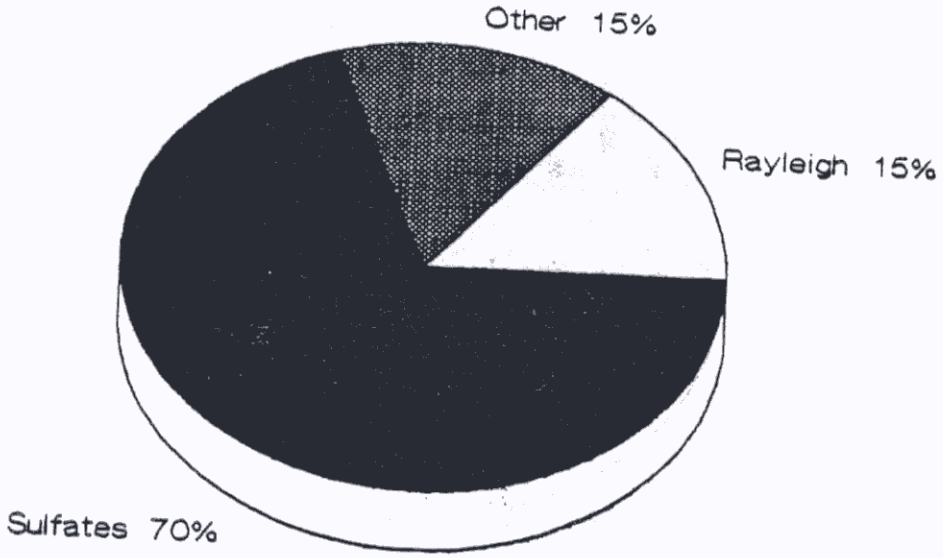
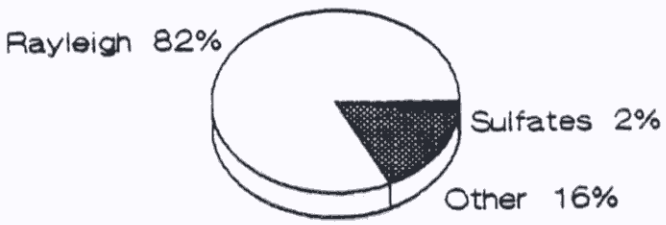


Figure 5.22: Measured and reconstructed 12-hour averaged extinction coefficients (Km^{-1}) and the fraction due to each component at Hopi Point. Extinction includes Rayleigh scattering.

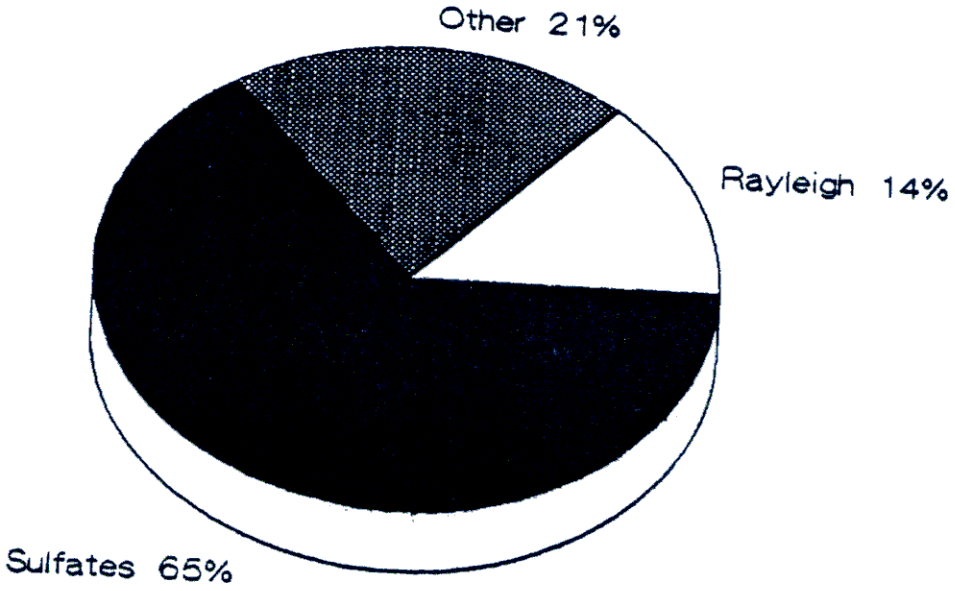


Feb 12

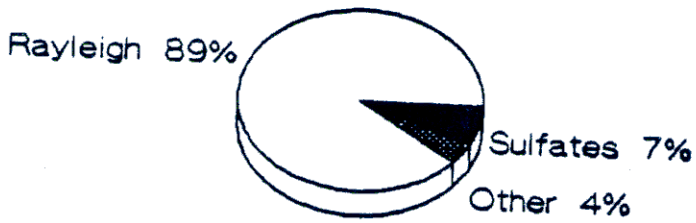


Feb 14

Figure 5.23: Extinction budgets on extreme days at Page. Areas of the wedges are proportional to the light extinction for each component. Total reconstructed extinction is 0.0749 Km^{-1} on Feb 12 (Julian day 43) and 0.0126 Km^{-1} on Feb 14 (Julian day 45).

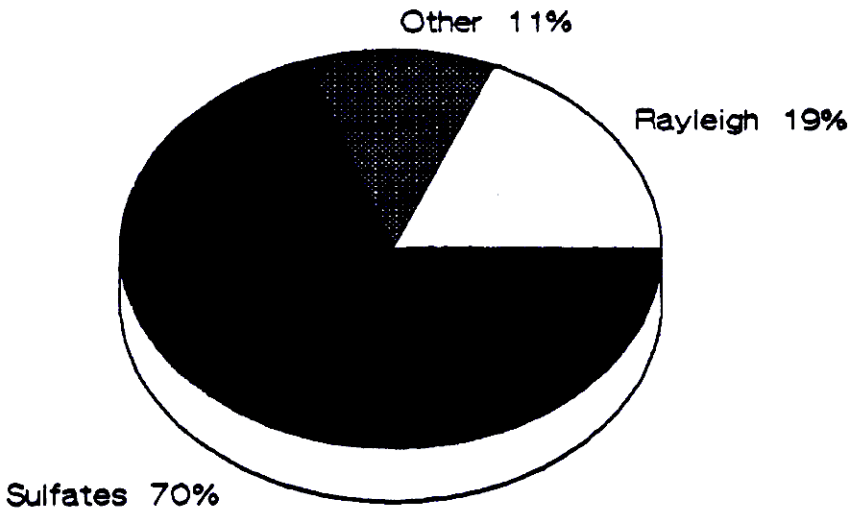


Feb 12



Feb 14

Figure 5.24: Extinction budgets on Feb 12 and 14 at Canyonlands. Areas of the wedges are proportional to the light extinction for each component. Total reconstructed extinction is 0.0708 Km^{-1} on Feb 12 (Julian day 43) and 0.0110 Km^{-1} on Feb 14 (Julian day 45).



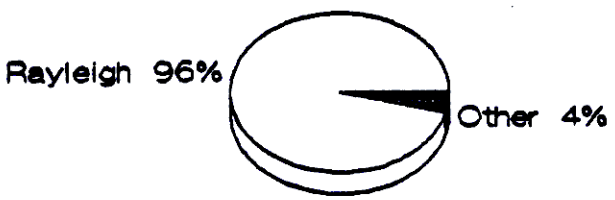


Figure 5.25: Extinction budgets on Feb 11 and 14 at Hopi Point. Areas of the wedges are proportional to the light extinction for each component. Total reconstructed extinction is 0.0588 Km^{-1} on Feb 11 (Julian day 42) and 0.0099 Km^{-1} on Feb 14 (Julian day 45).

Table 5.29: 24-hour average extinction budgets for extreme extinction days. Feb 12 is Julian day 43. Feb 14 is Julian day 45.

	Feb. 12			Feb 14		
	Page	Cany	†Hopi	Page	Cany	Hopi
Scatter by Gases (%)	15	14	19	82	89	96
Coarse Particle Scattering (%)	0	ND	0	7	ND	1
Scatter by Fine Sulfates (%)	70	65	70	2	7	2
Scatter by Fine Organics (%)	7	14	3	5	0	0
Scatter by Fine Nitrates (%)	2	3	1	0	1	0
Scatter by Fine Soil (%)	1	0	1	1	1	1
Particle Absorption (%)	6	4	6	3	2	0
Reconstructed (Km^{-1})	.0749	.0708	.0588	.0126	.0110	.0099
Measured (Km^{-1})	.0769	*.0378	ND	.0129	.0161	.0126

ND = No Data.
†Data is for Feb 11 (Julian day 42) at Hopi Point.
*One of the 12-hour time periods had missing b_{ext}.

5.5.2 Daily And Weekly Averaged Budgets

Tables 5.30, 5.31 and 5.32 show the means, standard deviations, and extremes for the fractions of extinction due to each component for the 12-hour, daily, and weekly averaged extinction budgets. As expected, the standard deviations decrease and the extremes moderate as the averaging time is lengthened. The largest fraction other than Rayleigh scattering at each site is scattering due to fine sulfates. If Rayleigh scattering is included in the budget, the range of the fraction of light extinction due to sulfates at Page was 2-75 percent for the 12- hour averages, and 21-31 percent for the weekly averages. Organics contribute 0-45 percent to the 12-hour averages and 17-25 percent to the weekly means. Absorption by absorbing carbon was 0-35 percent for the 12-hour means and 7-21 percent for the weekly averages.

It should be noted that the means in these tables do not exactly equal the means in Table 5.19. This is because the values in Tables 5.30, 5.31, and 5.32 were generated by taking the mean fractions for each extinction type for each time period. This is not the same as calculating the mean extinction for each component, then dividing by the mean total extinction as was done for Table 5.19. The reason for the difference is most easily explained by an example. Suppose on day 1 the total extinction was 0.010 Km^{-1} which was 90% sulfate scattering and on day 2 total extinction was 0.002 Km^{-1} which was 20% sulfate scattering. The two ways of generating the mean percent sulfate scattering for this hypothetical two-day period are

- Method 1:

$$100\% \times \frac{(0.9)(.010) + (0.2)(.002)}{.010 + .002} = 78\% \tag{5.12}$$

- Method 2:

$$100\% \times \frac{(0.9 + 0.2)}{2} = 55\% \tag{5.13}$$

The first method, which was used for Table 5.19, gives a more accurate representation of the mean scattering for each component because the fractions are weighted by the extinction for each

time period. The second method, used for Tables 5.30, 5.31, 5.31 is more useful for examining the extremes and standard deviations of fractions which exist for each component, which is the purpose of this section.

5.6 Comparison to Previous Studies at Grand Canyon

WHITEX extinction budgets are similar to the results of at least two previous studies which have reported light extinction budgets for Grand Canyon National Park (Hopi Point) (Malm, et al.[5] and Malm and Johnson[7]). Scattering by fine ammonium sulfate was found to be the dominant factor in the non-Rayleigh light extinction budget in all three studies even though WHITEX was during the winter, another study was for summertime data, and the third included data for a full two year time period. During WHITEX, the percent of the non-Rayleigh scattering at Hopi Point due to fine sulfates was 68%. Malm et al. found that 47–48% of the scattering during a two week period in August 1984 was due to fine sulfates and Malm and Johnson attributed 63% of the scattering during two years from December 1979 to November 1981 to fine sulfates.

5.7 Summary

The findings of this chapter are summarized below:

- The nephelometer underestimates the actual scattering coefficient by as much as a factor of three when the relative humidity is very high (> 90%). However there is evidence that it does not dry the particles completely.
- TOR light absorbing carbon measurements appear to be slightly too high and TMO concentrations are too low, but the TOR values are closer to what is expected based on the optical measurements.
- The largest fraction of mean non-Rayleigh extinction at Page, Canyonlands, and Hopi Point is scattering by fine sulfates. The two next largest fractions are absorption by light absorbing carbon and scattering by organics, with organics being more important at Page and particle absorption more important at Canyonlands and Hopi Point. (See Figure 5.3.)
- The extinction budgets vary considerably from time period to time period. Scattering by sulfates dominates on high extinction days. (See Figures 5.20, 5.21, and 5.22).
- Extinction budget results for the WHITEX time period are similar to those obtained in previous studies for the same area.