CHAPTER 4

FINE PARTICLE MASS CONCENTRATION FREQUENCY DISTRIBUTIONS

The contributions of sulfates, carbon (organic plus light-absorbing carbon), soil, and nitrate particles to the fine mass concentration at various points of the fine mass concentration frequency distribution are summarized and displayed to illustrate which components are principal contributors during high and low concentration periods. Maps of chemical species' contribution to the mean and upper percentiles of particle fine mass show spatial trends in extreme contribution at IMPROVE (or IMPROVE protocol) sites across the contiguous United States. The chemical species contribution to extremes in fine mass is relevant to emissions control scenarios for the Class I areas represented by monitoring sites in which improvement is sought for the most impaired conditions as well as for more typical conditions.

4.1 DATA

Reconstructed fine mass (RCFM) concentrations were calculated following the procedures described in Section 2.1 using data from 51 monitoring sites. The site names and locations used for these assessments are indicated in Figure 1.3 and Table 1.2.

Unlike the analysis in Chapter 2, which displayed annual and seasonal means of reconstructed fine mass and its components, this chapter presents information at a number of points in the reconstructed fine mass frequency distributions for the selected monitoring sites. The chemical species contribution was calculated based upon the reconstructed fine mass rather than the gravimetric fine mass. This ensures that the sum of the components are always equal to 100% of the reconstructed fine mass. However, sample periods where all of the data needed to calculate fine mass components are not available and cannot be used because the reconstructed fine mass cannot be determined. This could result in a data analysis bias if missing data are not randomly distributed across the fine mass distribution. For example, the IMPROVE module B nylon filter clogs more readily under high fine mass loading than during average or low mass loading levels, so the nitrate data are more prone to be missing on days of high fine mass loading. To determine whether calculating species contributions to reconstructed rather than to gravimetric fine mass biased this analysis, the two approaches were compared. While the magnitude of species contribution changed somewhat between the two methods, general trends displayed in the frequency distributions and maps of species contributions to the mean and upper extremes of fine mass were similar.

4.2 RESULTS AND DISCUSSION

4.2.1 Fine Mass Frequency Distributions

Frequency distributions of fine mass at selected sites are shown in Figures 4.1a, 4.2a, 4.3a, and 4.4a, with mass concentration plotted as the abscissa on a logarithmic scale, and the number of samples per mass concentration bin, or *N per bin*, as the ordinate. Figures 4.1b, 4.2b, 4.3b, and 4.4b show the fractional contribution of individual chemical species to fine mass by mass concentration bin. The fine mass frequency distributions are separated into mass concentration bins covering three orders of magnitude, from 0.1 to 100 μg/m^3, with approximately equal bins widths on a logarithmic plot. The frequency distributions incorporate data from the entire period of record for selected sites. Color versions of the annual and seasonal frequency distributions for all sites listed in Table 1.2 are available on the internet (http://alta_vista.cira.colostate.edu /summary~data/fd.htm).

Figure 4.1a shows the fine mass frequency distribution at Shenandoah National Park. Data span the time period March 1988 through August 1999, as indicated by the Start and End dates on Figure 4.1a. *N Total* is the total number of sampling days included in the fine mass frequency distribution. Figure 4.1b shows the individual chemical species fraction of fine mass in each frequency distribution bin. Sulfates (solid line), have a steadily increasing contribution with increasing fine mass concentration at Shenandoah, and contribute in excess of 80% to fine mass on the days with highest fine mass concentration. On the cleanest days, when fine mass concentrations are less than approximately 3 μg/m^3, the particle carbon (dash-dot line) contribution is of approximately equal magnitude to sulfates. Soil (dashed line) and particle nitrate (dash-dot-dot line) are minor components of fine mass regardless of fine mass concentration, contributing approximately 10% or less over the entire range of fine mass concentration.

The fine mass frequency distribution at Big Bend National Park is shown in Figure 4.2a. The chemical species contribution to fine mass (Figure 4.2b) shows that sulfates and carbon are major contributors at low-to-mid-fine mass concentrations. However, the soil contribution increases with increasing fine mass concentration. On the days when fine mass concentrations at Big Bend are highest, soil dominates the fine mass fraction.

At Yellowstone National Park (Figure 4.3), particle carbon contributes about 50% at all but the highest fine mass concentrations. When the fine mass concentration at Yellowstone is greater than approximately 7 μg/m^3 the carbon contribution increases and can exceed 80%. At low fine mass concentrations (below approximately 2 μg/m^3), the relative contribution of the major chemical species to fine mass remains essentially constant.

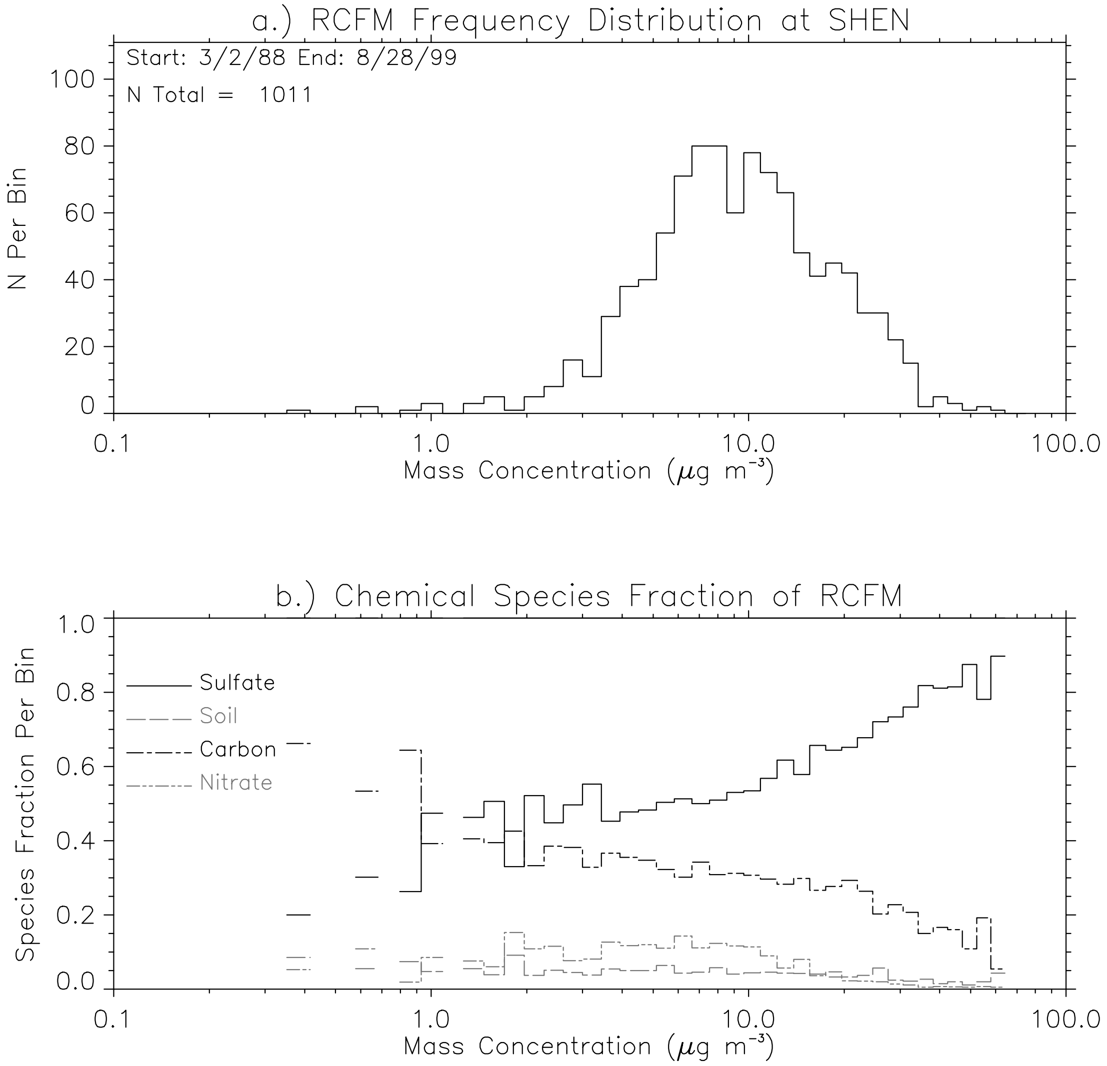

Figure 4.1 *(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Shenandoah National Park.*

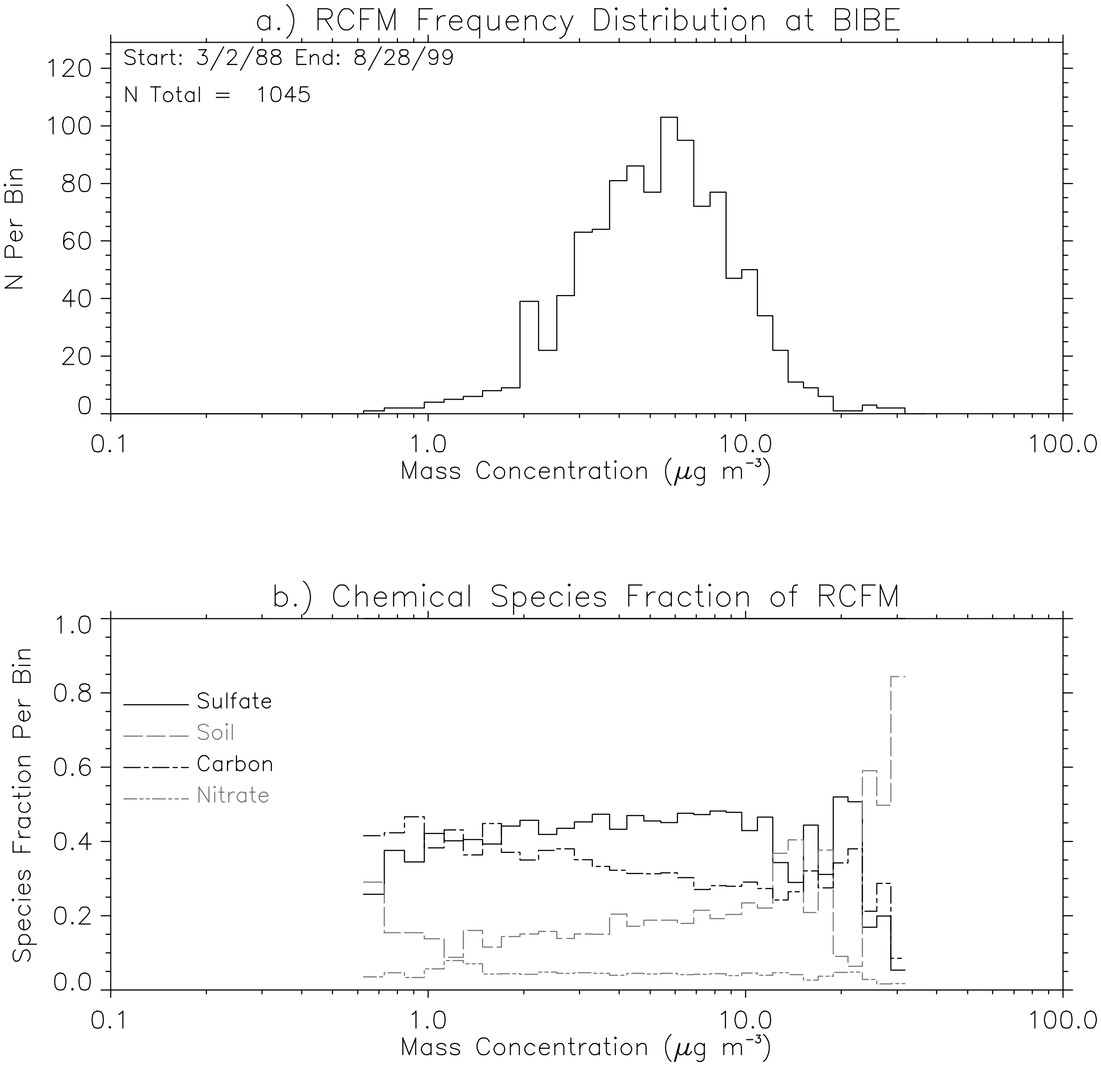

Figure 4.2 *(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Big Bend National Park.*

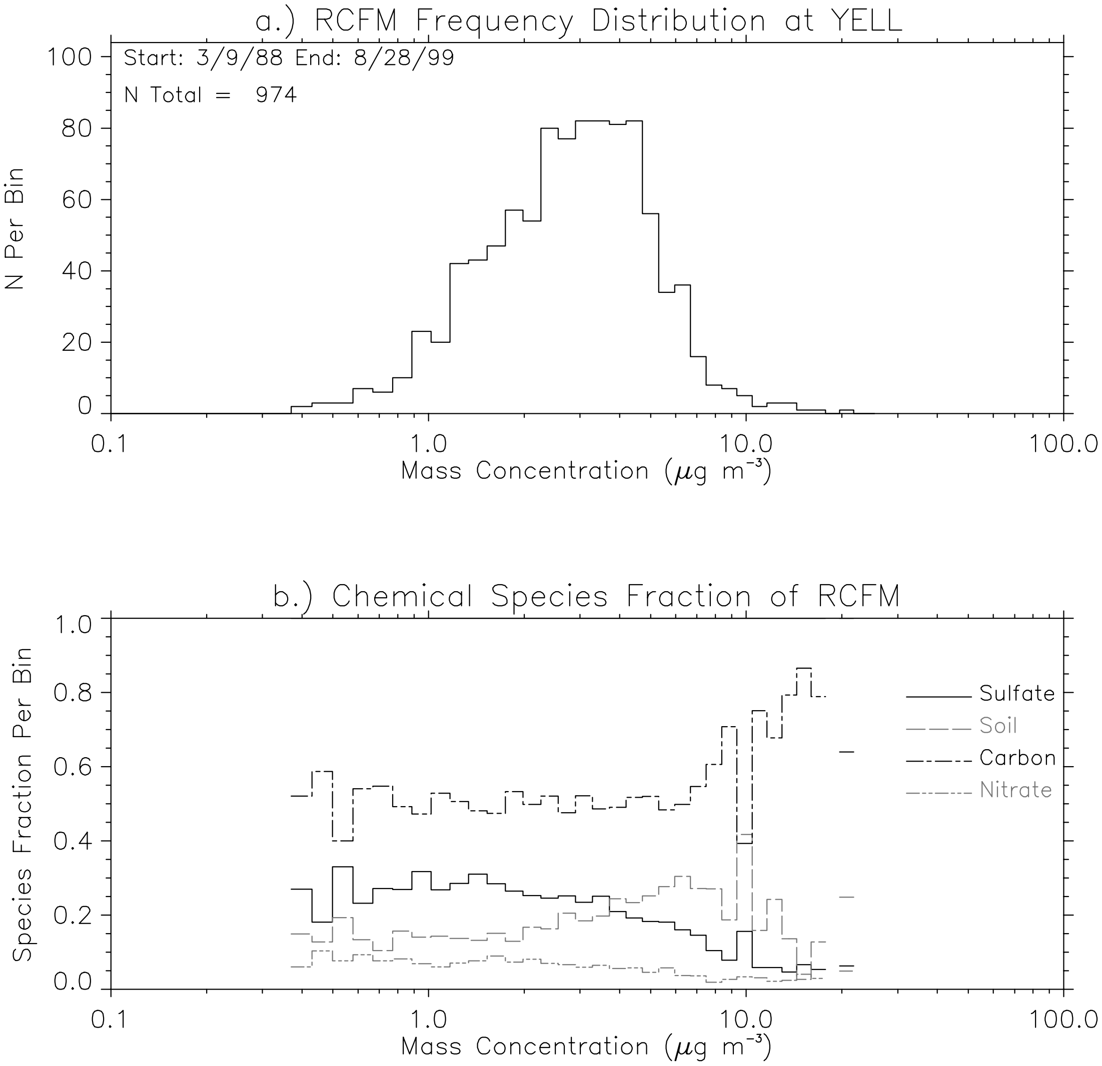

***Figure 4.3** (a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Yellowstone National Park.*

Figure 4.4a shows the wintertime fine mass frequency distribution at Yosemite National Park. During the winter at Yosemite, particle carbon has a majority contribution at most fine mass concentrations. However, when fine mass concentrations are high (in excess of 4 μg/m^3) the particle nitrate contribution to fine mass increases and can reach 50%.

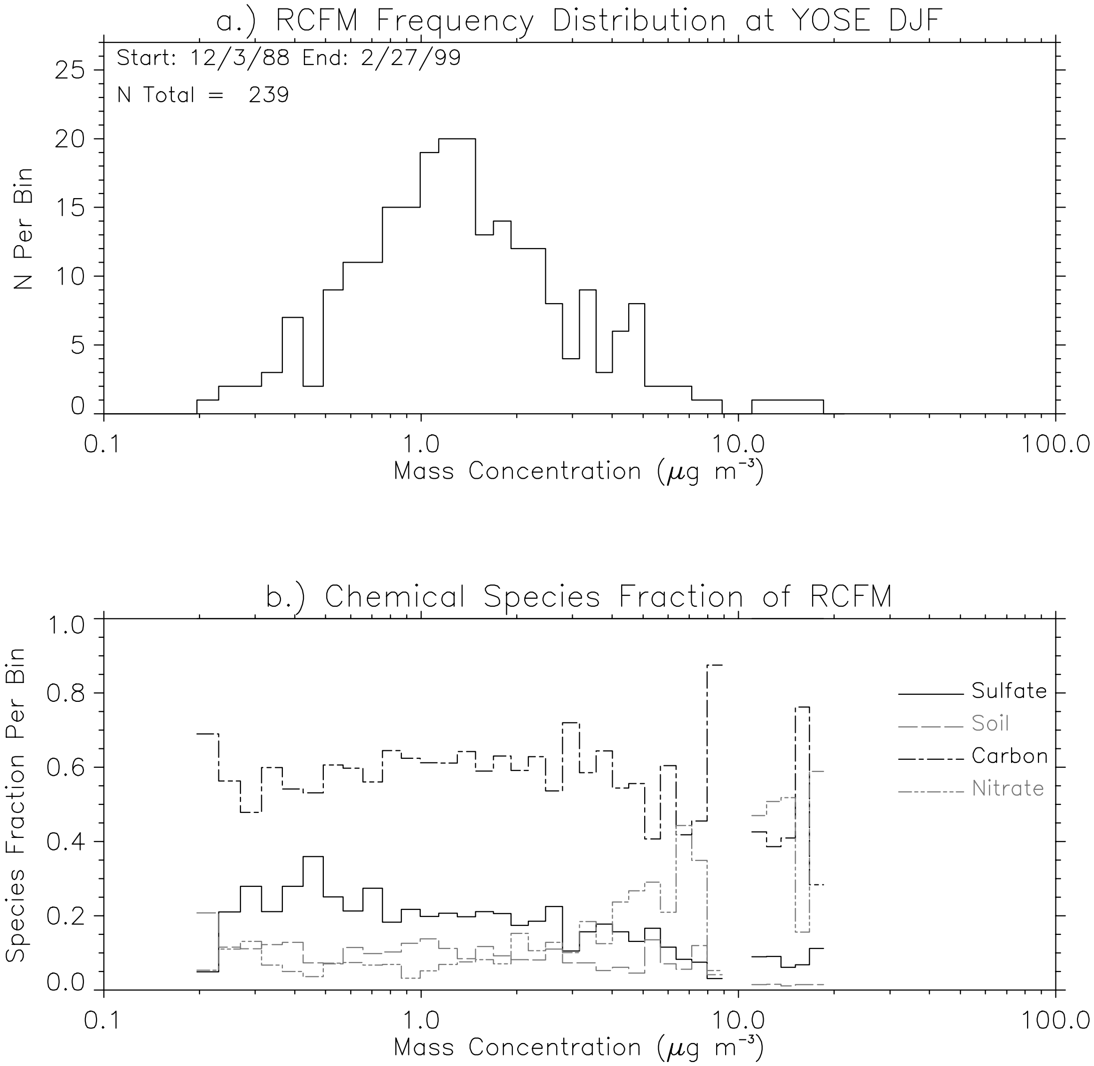

Figure 4.4 *(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Yosemite National Park. Data shown are for winter only.*

Figure 4.5a shows the wintertime fine mass frequency distribution at Rocky Mountain National Park, with similar high particle nitrate contributions to the upper percentiles of fine mass as observed at Yosemite. At Rocky Mountain, particle nitrate contributes in excess of 25% fine mass when fine mass concentrations are greater than 4 μg/m^3. Particle carbon is the largest single contributor to wintertime mean fine mass at Rocky Mountain, although sulfates and nitrates have comparable contributions to particle carbon at both the upper and lower extremes of fine mass.

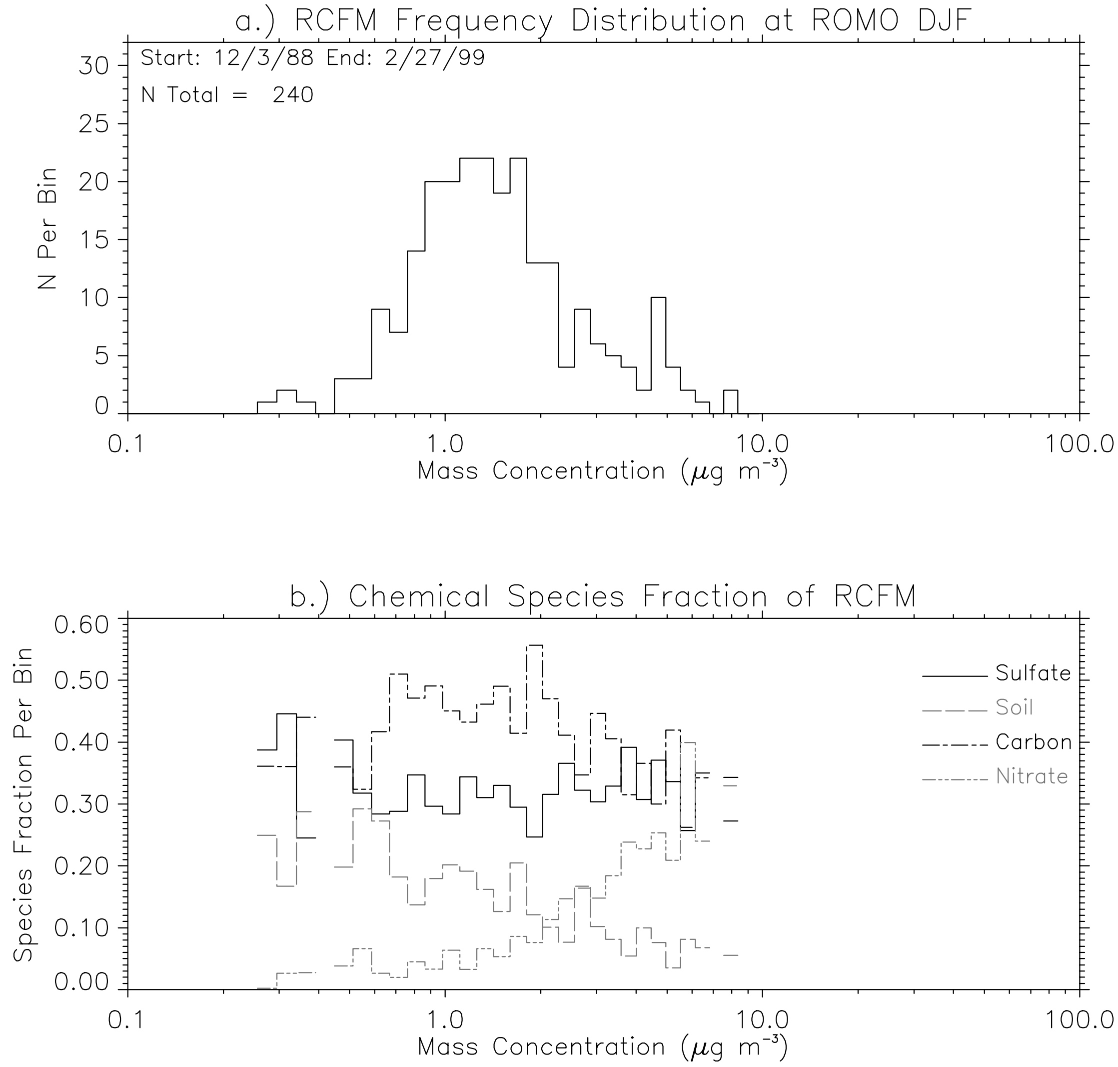

Figure 4.5 *(a) RCFM frequency distribution and (b) chemical species fractional contribution to RCFM by mass concentration bin at Rocky Mountain National Park.*

4.2.2 Maps of Chemical Species Contributions to Fine Mass (1994-1998)

Maps of mean chemical species percent contribution to reconstructed fine mass during December 1993 through November 1998 are shown in this section. A five-year period was chosen as a common period of record for all sites to display results on maps to show spatial patterns. Two maps are shown for each chemical species; the mean contribution during the specified time period, and the species contribution to an upper extreme, or percentile, of (reconstructed) fine mass. We represent the haziest days by the upper two percentiles of fine mass. The extreme contribution maps show the mean species contribution subtracted from the species contribution during the highest fine mass concentration days. In order to highlight regions where individual chemical species tend to dominate the highest fine mass concentration days, contours on the extreme contribution maps are shown for positive values only. We point out that all contours serve as guides to the eye and should be interpreted as approximations of spatial trends over large areas.

Discussion of chemical species contribution to low extremes of fine mass concentration is also included in this section. We represent the low fine mass concentration days, or clear days, by the lowest 20th percentile of fine mass. A larger percentile bracket is chosen for the low than high mass concentration days because the analytical measurements are less accurate at low mass concentrations, and incorporating more samples into the low extreme reduces uncertainty in the mean of those measurements. Clear day contributions can be inferred from the site specific frequency distribution plots.

An example of the chemical species contribution to the upper two percentiles of fine mass is the mean of the species pairwise contribution during the ten sampling days with highest fine mass concentration, based on 500 twice weekly IMPROVE samples available during a five-year period. A minimum of 70% of all possible sample periods must have complete chemical composition data for sites on the maps in this chapter except at Sipsey Wilderness where the criteria is relaxed to 64% to increase spatial coverage in the eastern United States.

The mean ammonium sulfate contribution to fine mass, expressed as a percent of fine mass, at IMPROVE monitoring sites across the United States, shown in Figure 4.6a, reaches a maximum of approximately 55% in the eastern United States. Note that values in Figure 4.6a are lower throughout much of the eastern United States sites than analogous values shown in Chapter 2, with discrepancies between the two chapters due to the different time periods, different averaging methods, and use of sulfur times three in place of the sulfate ion for calculations in this chapter.

Figure 4.6b shows sulfate contribution to the fine mass upper two percentiles, expressed as the mean contribution subtracted from the upper extreme contribution. By comparing Figures 4.6a and 4.6b we see that throughout much of the eastern United States the sulfate contribution to the upper extreme of fine mass exceeds the mean sulfate contribution. For example, the difference between the mean and upper two percentiles of sulfate contribution at Dolly Sods is 29%, or the contribution to the upper extreme is 84%, or the sum of the values for that site as given by Figures 4.6a and 4.6b. Figure 4.6b indicates that the spatial extent of high sulfate contribution (sites greater than 20% in Figure 4.6b) to upper extremes of fine mass encompasses

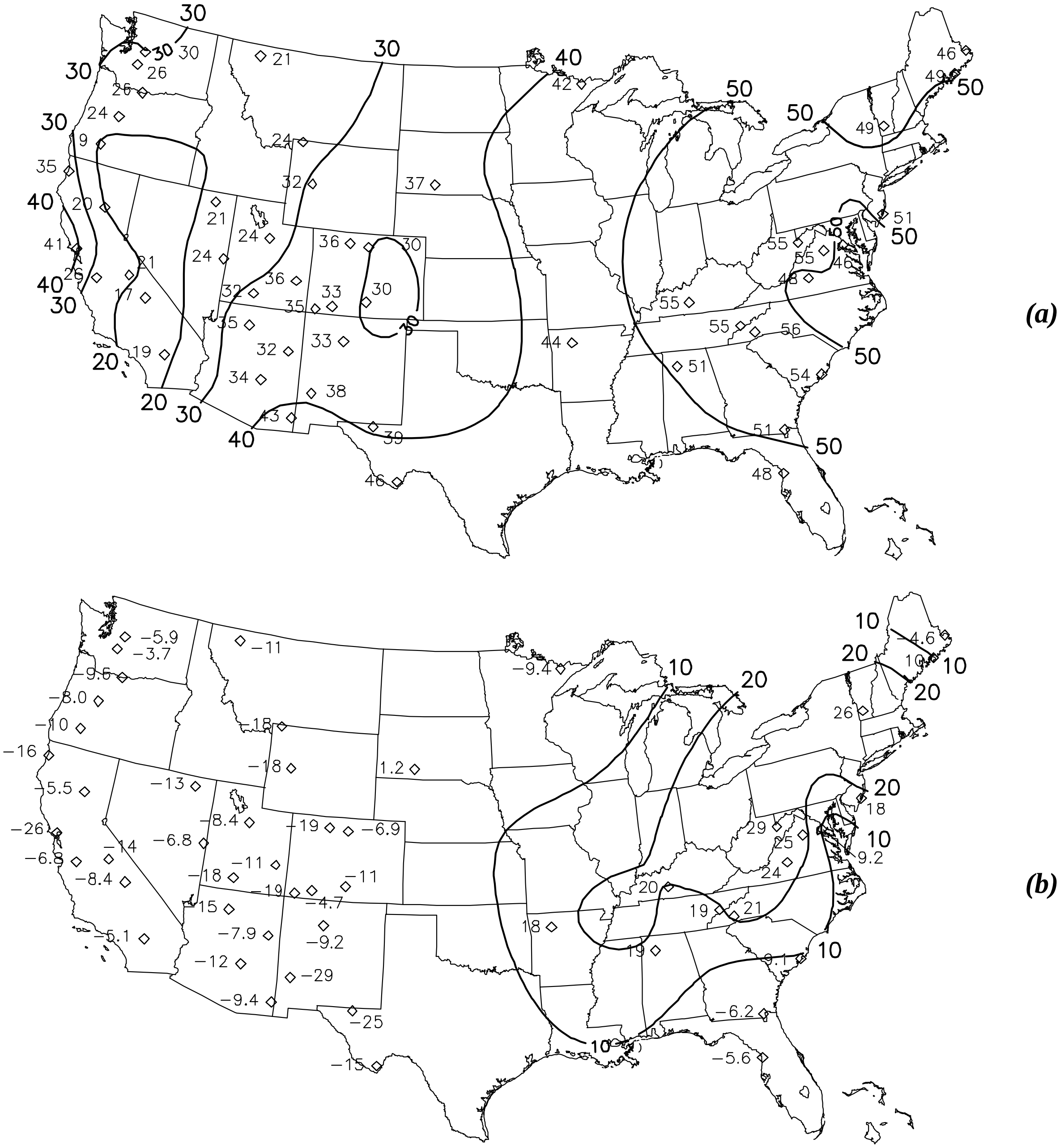

Figure 4.6 *(a) Map of mean sulfate contribution (%) to RCFM at IMPROVE monitoring sites across the United States. (b) Map of sulfate contribution to the upper two percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution).*

a region along the Ohio River Valley and northeast of Lye Brook. The true region of high sulfate contribution to the upper extreme of fine mass is likely more localized than the rather broad region in the eastern United States, where the mean sulfate contribution to fine mass exceeds approximately 50%. Negative values in Figure 4.6b indicate that the sulfate contribution to the upper extreme of fine mass is less than the mean for IMPROVE sites in the western United States and the most northerly and most southerly reaches of the eastern United States. In these regions, chemical species other than sulfate are major contributors to fine mass when particle fine mass concentrations are high.

The sulfate contribution to the lowest 20th percentile fine mass concentration days, or clean days, is about 5 to 10% less than the mean sulfate contribution (Figure 4.6a) in the eastern United States, and about 0 to 5% lower than the mean sulfate contribution in the western United States This translates to sulfate contributions on clean days of approximately 50% in the East and about 30% in the West.

The mean particle carbon contribution to fine mass, shown in Figure 4.7a, exhibits a general north-south gradient across the United States, with the highest values in the northwest United States. The difference between the carbon contribution to the mean and upper extreme of fine mass is shown in Figure 4.7b. At most western United States sites, the carbon contribution to the upper extremes is higher than the mean, while in the eastern United States only Moosehorn National Wildlife Refuge has a positive difference between the mean and upper extreme contributions. In the West, the carbon contribution to upper extremes of fine mass can be characterized by sporadic high values. For example, a 41% difference at Gila Wilderness Area in Figure 4.7b changes magnitude and location from year to year. These carbon 'hot spots' in the western United States may be related to wildland fires.

The particle carbon contribution to clean days is about 0 to 5% greater than the mean carbon contribution to fine mass at all IMPROVE sites shown in Figure 4.7a. Higher carbon contributions, approximately 15% in excess of the mean, are observed on clean days at monitoring sites in southern California.

The mean soil contribution to fine mass (Figure 4.8a) is about 5–10% along the eastern and western United States' coasts, and about 10–25% in the interior west. The soil contribution to the upper extremes of fine mass (Figure 4.8b) increases substantially from the mean in the southeast and throughout the southwest. Long-range dust transport from North African deserts may explain the large contribution of soil to the upper fine mass percentiles in the southeast states [Perry et al., 1997]. This source region is further evidenced by approximately 80% contribution of soil to the upper extremes of fine mass at Virgin Islands (not shown) during the summer and fall. High soil contributions to upper extremes of fine mass are also seen at sites in the southwest, particularly at Sequoia National Park (a difference of 35% from the mean) and Guadalupe Mountains National Park (a difference of 41% from the mean) in Figure 4.8b, which may be related to wind-blown dust originating in nearby arid regions.

Contributions of fine soil to clean days is generally within a few percent of the mean, therefore spatial patterns and magnitude of clean day fine soil contributions are roughly analogous to Figure 4.8a.

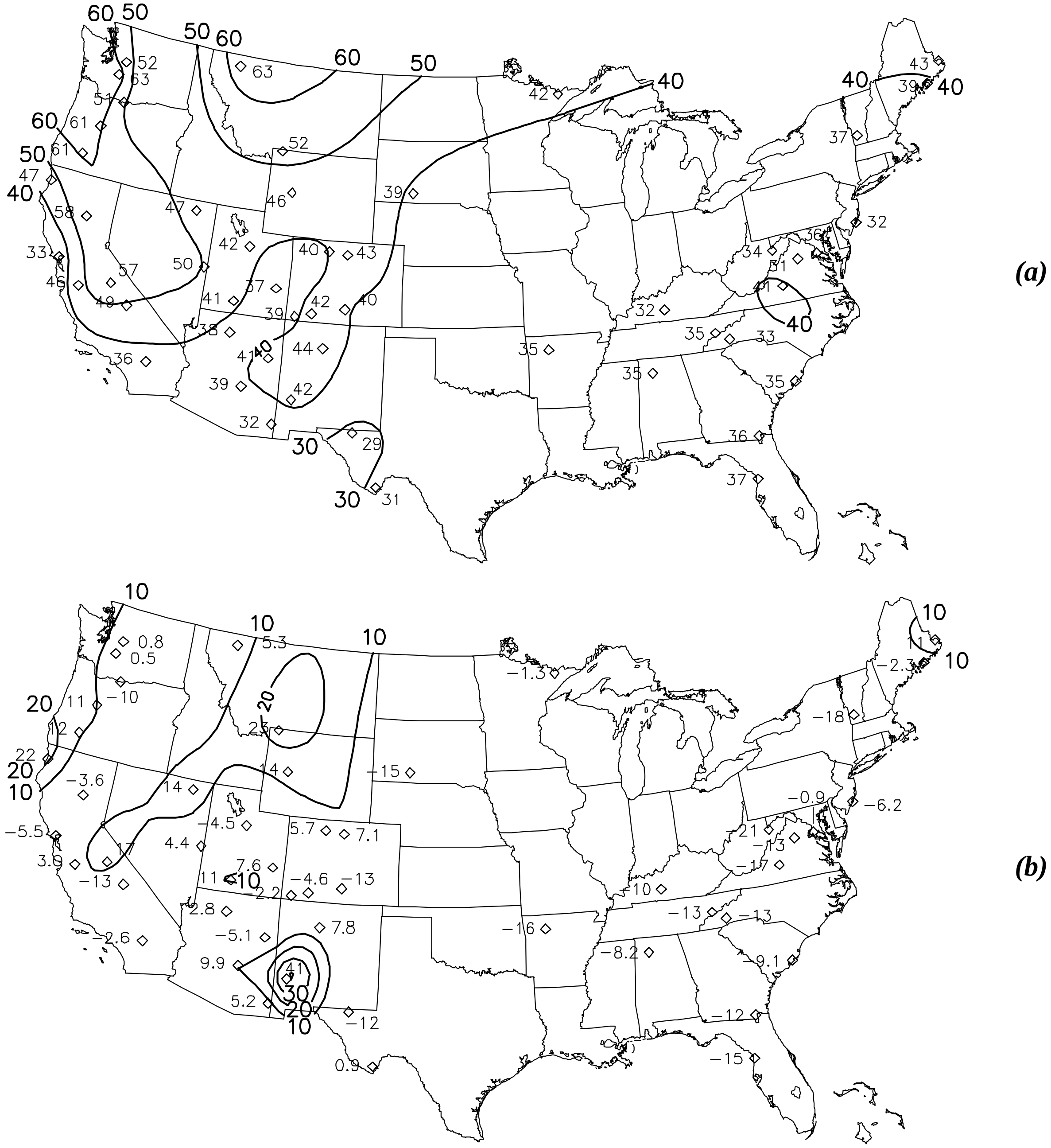

Figure 4.7 *(a) Map of mean particle carbon contribution to RCFM (%) at IMPROVE monitoring sites across the United States. (b) Map of particle carbon contribution to the upper two percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution).*

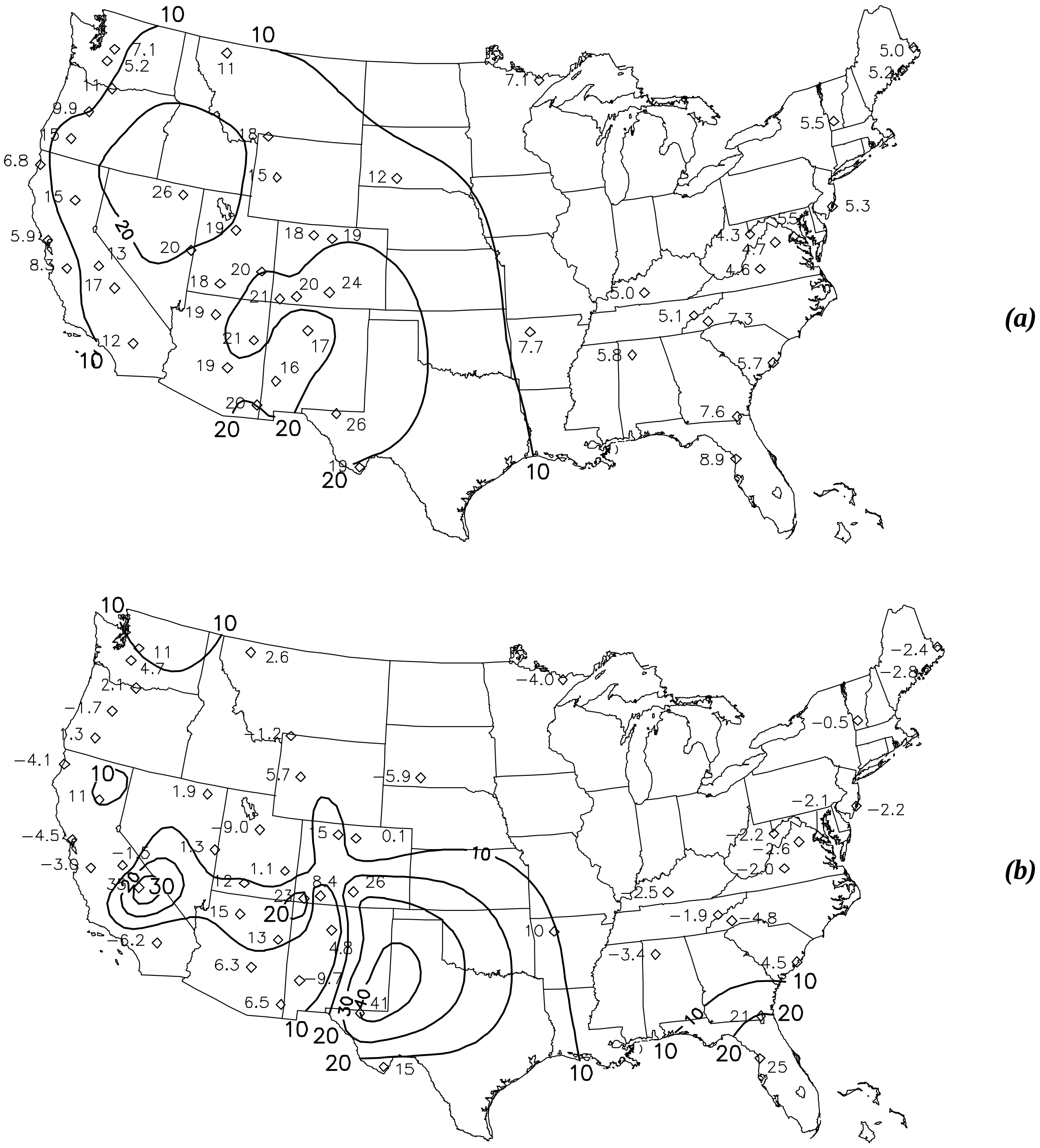

Figure 4.8 *(a) Map of mean soil contribution to RCFM (%) at IMPROVE monitoring sites across the United States. (b) Map of soil contribution to the upper two percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution).*

Because wintertime is generally the season when fine particle nitrate mass concentrations are at a maximum, and particle nitrate mass concentrations are often overwhelmed by other fine mass species during non-winter seasons, we show wintertime contributions to the mean (Figure 4.9a) and the upper extreme of fine mass (Figure 4.9b). The upper five percentiles are used to display the upper extreme for the wintertime maps so that statistics of the extreme values are derived from a sufficiently large number of data points.

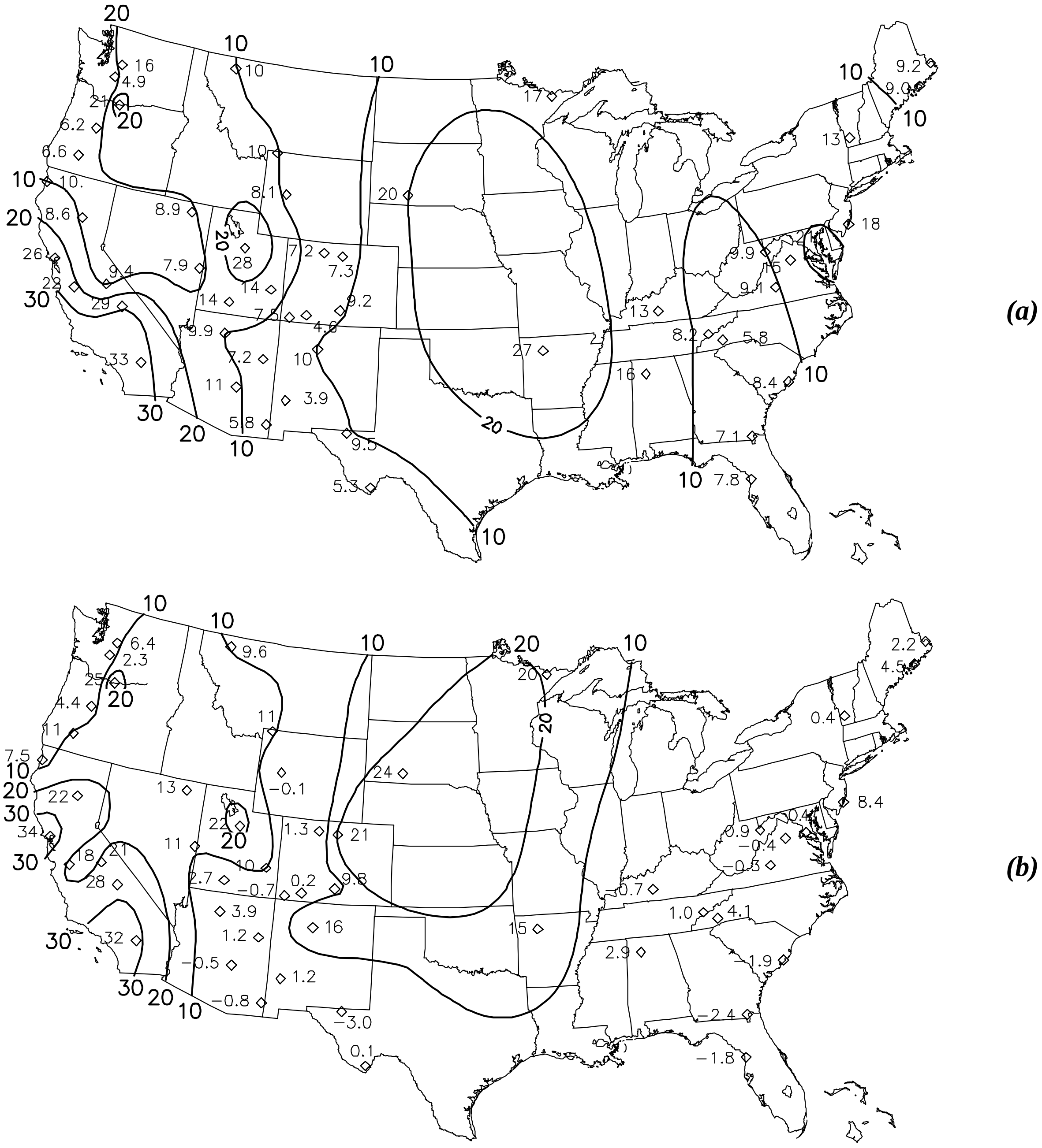

Figure 4.9 *(a) Map of mean particle nitrate contribution to RCFM (%) at IMPROVE monitoring sites across the United States. (b) Map of particle nitrate contribution to the upper five percentiles of RCFM (shown as the mean contribution subtracted from the upper extreme contribution). Data are shown for winter only.*

Figure 4.9b shows that many IMPROVE sites with high wintertime particle nitrate contributions to mean fine mass also have nitrate contributions to the upper extreme of fine mass well in excess of the mean. For example, Point Reyes National Seashore has a 26% contribution to mean fine mass concentration, with an additional 34% contribution to the upper extreme of fine mass, or 60% particle nitrate contribution to the upper extreme of fine mass. Similar examples can be found at nearly all IMPROVE sites in California. Sites where the difference between the mean and upper extreme particle nitrate contribution to fine mass is 20% or more include most California sites, Columbia River, Lone Peak, Rocky Mountain, Boundary Waters, and Badlands. Among Midwest and eastern sites mean wintertime particle nitrate contributions to fine mass in excess of 27% and 21% occur at Upper Buffalo and Washington, D.C., respectively, although the contribution to upper extreme of fine mass at these sites is less than 20% in excess of the mean. In the eastern United States the nitrate contribution to the upper extremes of wintertime fine mass is typically very similar to the mean, with the exception of Edwin B. Forsythe (Brigantine), where particle nitrate contributes 26% of fine mass on high fine mass days, or a difference of 8% from the mean.

Particle nitrate contribution to fine mass on clear wintertime days is generally only a few percent less than the mean wintertime nitrate contribution shown in Figure 4.9a, including the central and eastern United States sites where mean particle nitrate contributions are greater than 10%. Exceptions are the particle nitrate impacted sites mentioned above, where clean day wintertime particle nitrate contribution to fine mass is approximately 5 to 20% below the mean. This is expected at the particle nitrate impacted sites because the mean nitrate contribution is strongly influenced by the large particle nitrate contribution on high fine mass concentration days.

For the wintertime maps shown in Figure 4.9, the minimum data requirement of 70% was relaxed to 60% at Mount Zirkel, Sipsey, and Shining Rock so that the nitrate maps included the same IMPROVE sites as the other chemical species maps.

4.3 SUMMARY

The particle sulfate, carbon, soil, and nitrate contributions to the fine mass frequency distribution are shown at selected IMPROVE monitoring sites to illustrate departures in the respective chemical species mean contributions to fine mass from the contribution of those species to the extremes of observed fine mass concentration. Maps of the mean and upper extremes of chemical species contribution are shown to illustrate spatial patterns in chemical species contributions to fine mass. Spatial patterns in chemical species contributions to extremes of observed fine mass concentration may be indicative of source regions for visibility reducing particles. In addition, the extreme value maps indicate the magnitude of chemical species contribution to what are likely the haziest days in a given region.

On the haziest days, or upper percentiles of observed fine mass, all major components of fine mass; sulfates, nitrates, carbon, and soil, can have large contributions to fine mass depending on region and time of year. Sulfate is a major contributor to both the mean and upper extremes of fine mass in the eastern United States, with largest contributions to the upper extremes clustered in regions of high sulfur emissions. Particle carbon exhibits a general increasing south-to-north gradient in mean contribution to fine mass, with sporadic high contributions to the upper extremes of fine mass in the western United States that may be related to wildland fires. The mean soil contribution to fine mass is largest in the western United States, with high soil contributions to upper extremes in the southwest and southeast coastal regions likely related to regional and long-range transport of wind-blown dust. Particle nitrate contributions to fine mass are generally largest during the winter, and have substantially increased contributions to upper extremes of fine mass near urban areas.

On clear days, or the lowest 20th percentile of fine mass concentrations, sulfate and carbon are the largest contributors to fine mass. The sulfate contribution to fine mass on clear days is approximately 50% in the eastern United States, and approximately 20 to 30% in the western United States. Particle carbon contribution on clear days is approximately 40% in the East and from 40 to 60% in the West. Fine soil contributes a maximum of 20% to fine mass on clear days in the southwest United States, with contributions of only 5 to 10% during clear days in other regions of the United States. Particle nitrate contribution to fine mass on clear wintertime days is less than 10% at most IMPROVE sites, except for some monitoring locations near urban areas, and nearly all monitoring locations in the central United States, where particle nitrates contribute from 10 to 20% of fine mass on clean wintertime days.

4.4 REFERENCES

Perry K. D., Cahill T. A., Eldred R. A., Dutcher D. D., and Gill T. E., (1997) Long-range transport of North African dust to the eastern United States, *J. Geophys. Res.* 102(D10):11,225-11,238.