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Coarse particle speciation at selected locations in the rural continental United States

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Abstract

A few short-term special studies at National Parks have shown that coarse mass (CM) (2.5–10 μm) may not be just crustal minerals but may consist of a substantial amount (≈ 40–50%) of carbonaceous material and inorganic salts such as calcium nitrate and sodium nitrate. To more fully investigate the composition of coarse particles, a program of coarse particle sampling and speciation analysis at nine of the Interagency Monitoring of Protected Visual Environments (IMPROVE) sites was initiated 19 March 2003 and operated through the year 2004. Only the data for 2004 are reported here. Sites were selected to be representative of the continental United States and were operated according to IMPROVE protocol analytical procedures. Crustal minerals (soil) are the single largest contributor to CM at all but one monitoring location. The average fractional contributions range from a high of 76% at Grand Canyon National Park to a low of 34% at Mount Rainier National Park. The second largest contributor to CM is organic mass, which on an average annual fractional basis is highest at Mount Rainier at 59%. At Great Smoky Mountains National Park, organic mass contributes 40% on average, while at four sites organic mass concentrations contribute between 20% and 30% of the CM. Nitrates are on average the third largest contributor to CM concentrations. The highest fractional contributions of nitrates to CM are at Brigantine National Wildlife Refuge, Great Smoky Mountains, and San Gorgonio wilderness area at 10–12%. Sulfates contribute less than about 5% at all sites.
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1. Introduction

The Regional Haze Rule (U.S. Environmental Protection Agency, 1999) requires monitoring representative of 156 visibility-protected federal areas (VPFAs) beginning in January 2001. This entails particle sampling and analysis of the major aerosol components using methods patterned after those utilized since 1987 by the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Joseph et al., 1987; Malm et al., 1994).

In 1999, the IMPROVE network consisted of 30 monitoring sites in VPFAs, 20 of which began operation in 1988, with the others starting in the early 1990s. About this time the EPA provided supplemental support to expand the network to

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about 110 monitoring sites. Additional information about the site selection process is available elsewhere (Malm et al., 2000a; Colorado State University, http://vista.cira.colostate.edu/improve/).

The aerosol data collected in the IMPROVE program have been widely analyzed to better understand the seasonal and spatial patterns of fine aerosol components and their contribution to light extinction (Eldred et al., 1993; Malm et al., 1994, 2004; Sisler and Malm, 2000). The spatial patterns of trace elements, e.g., selenium, vanadium, zinc, and bromine, have also been examined (Eldred, 1997; Malm and Sisler, 2000). At sites where more than 10 years of data were collected, temporal trends in fine mass (FM) and its major aerosol components have been examined (Iyer et al., 2000; Malm and Sisler, 2000; Patterson et al., 2000; Malm et al., 2002).

However, fine particles (<2.5 μm) are speciated, while coarse particles (2.5–10.0 μm) are not. A few short-term special studies at national parks have shown that coarse mass (CM) is not just crustal minerals but consists of a substantial amount (≈ 40–50%) of carbonaceous material and inorganic salts such as calcium nitrate and sodium nitrate (Malm and Day, 2000; Lee et al., 2004; Malm et al., 2005). To more fully investigate the composition of coarse particles, a program of coarse particle sampling and speciation analysis at nine of the IMPROVE sites was initiated between 19 March 2003 and 23 December 2003 and operated through the year 2004. Only data from the year 2004 are reported here. Sites were selected to be representative of the continental United States and are listed in Table 1, along with the fine particle monitoring start date, elevation, and location of each of the sites. This paper reports on monthly trends in speciated FM and CM concentrations derived from data collected during 2004 at these sites and compares them to historical trends.

2. Particulate samplers

The basic IMPROVE sampler was designed for the IMPROVE network and has been operated extensively in the network and during field studies since the winter of 1987 (Malm et al., 1989, 1994). The IMPROVE sampler consists of four independent modules. Each module incorporates a separate inlet, filter pack, and pump assembly; however, all modules are controlled by the same timing mechanism. Every third day 24-h duration samples are collected using the same schedule as the national particulate matter (PM) monitoring network operated by state and local governments.

The sampler has a four-filter manifold for each module. Modules A, B, and C are each equipped with a 2.5 μm cyclone. The module A Teflon filter is analyzed for gravimetric FM, nearly all elements with atomic mass number ⩾11 (Na) and ⩽82 (Pb) by X-ray florescence (XRF), elemental hydrogen by proton elastic scattering analysis, and for light absorption. For module B, the sampled air is drawn through a sodium carbonate denuder tube in the inlet to remove gaseous nitric acid; the material collected on the Nylasorb substrate is extracted ultrasonically in a de-ionized water bath and subsequently analyzed by ion chromatography for the anions sulfate, nitrate, nitrite, and chloride. Module C utilizes quartz fiber filters for the collection of fine particles that are subsequently analyzed for carbon. At some sites, tandem quartz filters are used so that the second filter is available for estimating the organic carbon artifact associated with hydrocarbon gases trapped in the filter substrate. Thermal optical reflectance (TOR) is the

Table 1
Site description

Site	Elevation (m)	State	Latitude (degrees)	Longitude (degrees)	Start date
Bondville	211	Illinois	40.0514	−88.3719	3/5/2001
Bridger wilderness area	2607	Wyoming	42.9749	−109.757	3/2/1988
Brigantine National Wildlife Refuge	5	New Jersey	39.465	−74.4492	9/18/1991
Grand Canyon National Park	2267	Arizona	35.9731	−111.984	3/12/1988
Great Smoky Mountains National Park	815	Tennessee	35.6334	−83.9417	3/2/1988
Mount Rainier National Park	427	Washington	46.7579	−122.123	3/2/1988
San Gorgonio wilderness area	1705	California	34.1924	−116.901	3/2/1988
Sequoia National Park	535	California	36.4894	−118.829	3/4/1992
Upper Buffalo wilderness area	723	Arkansas	35.8259	−93.2029	12/18/1991

analytical technique used for determination of organic and elemental/light-absorbing carbon (LAC) (Chow et al., 1993). Finally, module D, fitted with a PM_{10} inlet, utilizes a Teflon filter that is gravimetrically analyzed for mass (PM_{10}). In this study, a second set of modules B and C was operated with a PM_{10} inlet (and denoted modules E and F). These and the Teflon filter from the D module were analyzed, allowing for an estimate of species mass in the 2.5–10.0 μm range as the difference between the PM_{10} and $PM_{2.5}$ measurements. It is this size range that will be referred to as the coarse mode.

2.1. Estimation of aerosol mass

The fine and coarse aerosol species concentrations at most continental sites can be classified into six major types: sulfates, nitrates, organics, LAC, crustal minerals (often referred to as soil), and sea salt. Details of standard methods for apportionment of measured mass to the various aerosol species concentrations are described in some detail in Malm et al. (1994), while Table 2 presents the standard equations currently used in the IMPROVE program for estimating the species concentrations.

A number of measurement programs have shown that, during summer months in the eastern United States, the average sulfate ammoniation is nearer ammonium bisulfate, with ammonium-to-sulfate molar ratios that can approach sulfuric acid (Gebhart et al., 1994; Malm et al., 2000b; Lefer and Talbot, 2001). Measurements at Big Bend, Texas, showed ammonium-to-sulfate molar ratios of about 1.4 on average (Malm et al., 2003). However, because the ammonium ion is not routinely measured in the IMPROVE program, sulfates will be assumed to be in the form of ammonium sulfate for the purpose of examining general spatial and temporal trends in sulfate mass concentrations.

Nitrates in the aerosol are assumed to be in the form of ammonium nitrate, but, again, special studies have shown that at some locations fine nitrates are the fine tail of the coarse particle nitrate size distribution, consisting of sodium nitrate or calcium nitrate, that has resulted from the reaction of nitric acid vapor with sea salt or crustal minerals (Malm et al., 2003). Assuming nitrates are in the molecular form of ammonium nitrate would underestimate nitrate mass concentrations by about 6% and by a factor of 2 if the true molecular

Table 2
Assumed molecular forms of each particulate species and method of estimation used

Species	Formula	Assumptions
Sulfate	$4.125[S]$ or $1.37*[SO_4^{=}]$	All elemental S is from sulfate. All sulfate is from ammonium sulfate
Nitrate	$1.29[NO_3^-]$	Denuder efficiency is close to 100%. All nitrate is from ammonium nitrate
LAC (light-absorbing carbon by channel C)	[EC1]+[EC2]+[EC3]-[OP]	All high temp carbon is elemental
OMC (organic mass from carbon)	1.8{[O1]+[O2]+[O3]+[O4]+[OP]}	Average organic molecule is 56% carbon
SOIL	2.2[Al]+2.19[Si]+1.63[Ca]+2.42[Fe]+1.94[Ti]	[Soil K] = 0.6[Fe]. FeO and Fe_2O_3 are equally abundant. A factor of 1.16 is used for MgO, Na_2O, H_2O, CO_2
Sea salt	$1.8*[Cl^-]$	1.8 accounts for other salts than NaCl
RCFM (reconstructed fine mass)	[SULFATE]+[NITRATE]+[LAC]+[OMC]+[SOIL]+[SEA SALT]	Represents dry ambient fine aerosol mass for continental sites
Coarse mass species	$[PM_{10}]$ species $-[PM_{2.5}]$ species	Difference between species found on the <10 and 2.5 μm substrates—coarse and fine species have same chemical form

compositions were sodium nitrate and calcium nitrate, respectively.

An average ambient particulate organic compound is assumed to have a constant fraction of carbon by weight. Particulate organic carbon mass concentration (POM) from module C is assumed to be [POM] = 1.8[OC], where OC is organic carbon as determined by TOR. The factor of 1.8 corrects the organic carbon mass for other elements associated with the assumed organic molecular composition (Turpin and Lim, 2001; Poirot and Husar, 2004; Malm et al., 2005; Malm and Hand, 2006).

Concentrations of crustal minerals, referred to as soil, are estimated by summing the elements predominantly associated with common crustal elements measured by XRF plus oxygen for the compounds (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, TiO_2) and applying an adjustment to account for other unmeasured compounds such as MgO, Na_2O, water, and carbonate.

Sea salt concentrations are typically computed from sea salt markers such as the sodium ion, chloride ion, or combination of ions (Quinn et al., 2001). Difficulties in computing sea salt from data from the IMPROVE network arise because positive ions are not analyzed; therefore sodium ion (the strongest indicator of sea salt) data are not available. Elemental sodium data are available from XRF analyses; however, sensitivity issues regarding poor detection of Na result in large uncertainties (White et al., 2004). Issues also arise when using the chloride ion or chlorine to estimate sea salt, because reaction of gaseous nitric acid with sea salt produces sodium nitrate particles and the release of gaseous HCl. The depletion of chloride during this reaction results in an underestimation of sea salt when using chloride to compute it. However, because the chloride ion is the only accurately measured marker for sea salt in the IMPROVE program, 1.8[Cl^-] will be used to estimate sea salt concentrations (sea salt is 55% Cl by weight as defined by the composition of sea water by Seinfeld and Pandis, 1998).

The self-consistency and overall quality of the measurements are assured by redundancy and intercomparisons between independently measured species. A description of validation and quality assurance procedures is available in Eldred et al. (1988), Sisler et al. (1993), and Malm et al. (1994). In the most general sense, validation is a matter of comparing chemically related species that have been measured in different modules. Fortunately, the design of the IMPROVE sampler allows for redundancy between certain module A measurements and modules B and C measurements of the ions and carbons, enabling quality control checks. For example, elemental sulfur mass × 3 should agree with the sulfate ion measured in module B. Reconstructed fine mass (RCFM), defined and used in this paper as the sum of the individual species described above, should agree with measurements of gravimetric mass. However, when comparing gravimetric FM to RCFM, a number of complicating factors must be dealt with. First, under some conditions, a large portion of the nitrates ($\geqslant$50%) can volatilize from the module A Teflon filter. Second, because of water retention by soluble aerosol species, the amount of residual water on the filter is a function of the relative humidity (RH) at which the filter was weighed and the history of the RH to which the aerosol was exposed.

3. The data set

The combined FM and CM concentration data sets for the 2004 year of monitoring at the nine sites are summarized in Tables 3 and 4 as the mean, standard deviation, maximum, and minimum for each species measured. Also shown in the last column is the fraction of gravimetric mass for each species. There are a total of 1014 data points. Reconstructed mass is the sum of all species. Negative values occur for the FM species because filter blanks exceed measured values, while for the CM species, negative values are also associated with reported PM_{10} mass concentrations for a given species that are less than $PM_{2.5}$ mass concentrations. For FM, the mean reconstructed value is 7% greater than the mean measured mass, while for CM the mean reconstructed value is 3% less than the

Table 3
Statistical summary of all fine mass and fine mass species concentrations

Variable ($\mu g\,m^{-3}$)	Mean	Std. dev.	Minimum	Maximum	% of FM
FM	6.64	5.44	0.09	39.75	
FM_{RECON}	7.12	5.49	0.19	36.00	107.2
$(NH_4)_2SO_4$	2.70	3.08	0.02	21.74	40.7
NH_4NO_3	1.19	2.07	0.00	27.97	17.9
POM	2.32	1.90	−0.03	14.17	34.9
LAC	0.27	0.20	0.01	2.07	4.1
SOIL	0.62	0.69	0.01	6.89	9.3
Sea salt	0.02	0.13	0.00	2.13	0.3

mean measured mass. Scatter plots of reconstructed versus measured FM and CM are presented in Figs. 1 and 2. For both data sets, the agreement is quite good. However, for the FM data set, reconstructed mass tends to be overestimated in the mid-range mass concentration values of 5–12 $\mu g\,m^{-3}$, and there is substantially more scatter around the 1:1 line for the CM than for the FM data set. With the intercept forced through 0, the ordinary least square (OLS) slopes for the data shown in Figs. 1 and 2 are 1.03 ± .004 and 0.95 ± .01, respectively. Corresponding R^2 values are 0.96 and 0.81.

On the average, sulfate interpreted as ammonium sulfate and POM make up 41% and 35% of the FM, respectively, while ammonium nitrate contributes another 18%. Soil mass concentration is less than 10% of measured mass, LAC about 4%, and sea salt is negligible. For the CM fraction, the sulfate contribution is negligible and LAC and sea salt are only 1% and 2%, respectively. As expected, crustal minerals (soil) are the major component at 61%, but POM and ammonium nitrate contribute significantly at 24% and 8%, respectively.

Table 4
Statistical summary of all coarse mass and coarse mass species concentrations

Variable ($\mu g\,m^{-3}$)	Mean	Std. dev.	Minimum	Maximum	% of CM
CM	5.24	5.81	−1.75	49.93	
CM_{RECON}	5.07	5.97	−3.47	46.70	96.8
$(NH_4)_2SO_4$	0.03	0.50	−4.23	4.54	0.6
NH_4NO_3	0.41	0.50	−1.72	2.97	7.8
POM	1.28	1.41	−3.35	15.29	24.4
LAC	0.07	0.13	−0.54	1.52	1.3
SOIL	3.19	4.87	−0.02	39.73	60.9
Sea salt	0.10	0.51	−0.11	6.99	1.9

4. Spatial variability of coarse and fine monthly patterns in species mass concentrations

Statistical summaries of FM and CM aerosol constituents in the form of averages, standard deviations, maximums, and minimums for data aggregations for the year 2004 are shown in Tables 5 and 6. Also presented in the tables are the percent contribution of each species to gravimetric mass and a comparison of gravimetric and reconstructed mass in the form of a percentage of reconstructed to gravimetric mass. These same summaries are available on a monthly basis at http://vista.cira.colostate.edu/IMPROVE/Data/Other/Data_CMSpeciation.htm. Figs. 3 and 4 present graphical summaries of these data in the form of average monthly concentrations as stacked bar plots, while Figs. 5 and 6 show the average fractional contribution of each species to gravimetric FM and CM. The sum of the fractional contributions of each species should sum to 1. Therefore, values greater or less than 1 show the over- or underestimation of reconstructed mass as compared to gravimetric mass. Also, for purposes of comparing the current data set to the

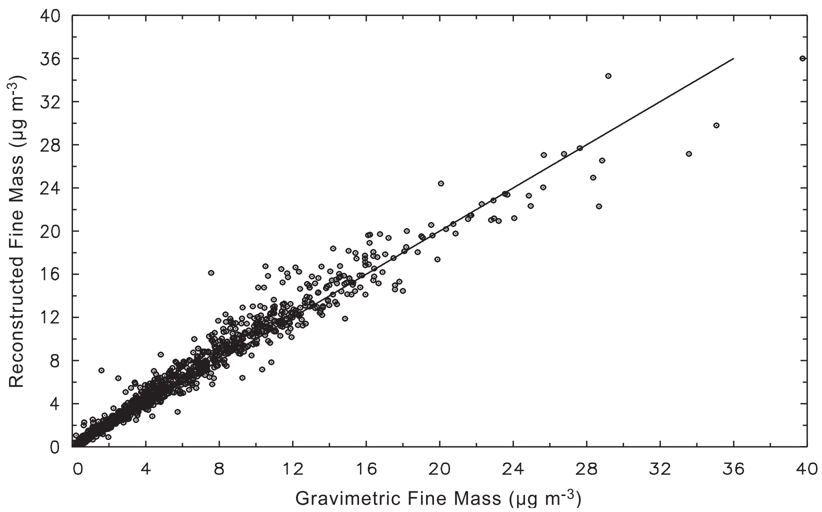

Fig. 1. Scatter plot of gravimetric and reconstructed fine mass. An ordinary least square slope with the intercept set equal to 0 is 1.03 ± 0.004 with an $R^2 = 96$.

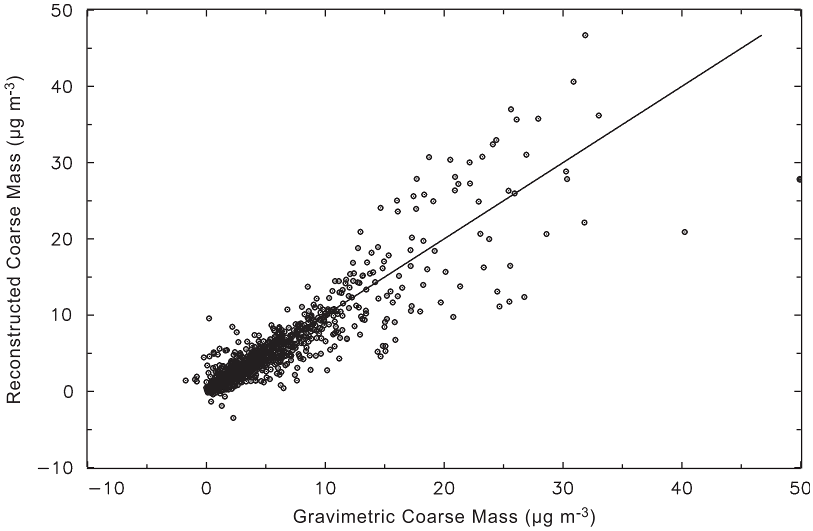

Fig. 2. Scatter plot of gravimetric and reconstructed coarse mass. An ordinary least square slope with the intercept set equal to 0 is 0.95 ± 0.01 with an $R^2 = 81$.

historical record, selected average species concentrations are also presented in Figs. 3 and 4. In the case of FM (Fig. 3), historical averages of gravimetric mass and the main constituents of FM—ammonium sulfate, POM, and, in some cases, ammonium nitrate—mass concentrations are plotted. Because only values of coarse gravimetric mass have been routinely measured, only historic values of this variable are presented (Fig. 4).

In general, the temporal variability, as well as composition of FM species collected during the year 2004, was similar to the grand average over all years. However, some differences are apparent. In most cases, FM concentrations during the year 2004 were generally less than the historical averages, perhaps reflecting the general reduction in species concentrations over the past 15 years (Malm et al., 2002). Sulfate concentrations have decreased across most of the United States, as have POM in the Northwest and nitrates in the coastal areas of California and inland at San Gorgonio wilderness area. Historical comparison at the Bondville site is less meaningful because routine monitoring was only initiated in the year 2001. At all monitoring sites, sulfates tend to be highest during the spring/summer/fall months when more sunlight is available and photochemistry is enhanced, while nitrates tend to be highest during the cooler winter months. This is especially true at Bondville and Sequoia National Park where nitrates are 40–50+ % of the FM from November to April. It interesting to note that at both Bondville and Upper Buffalo wilderness area FM concentrations tend to peak in February, then decrease, and peak again in late summer/fall months. Also, note the fine soil mass fraction (Fig. 5) increases during the month of April throughout most of the monitoring sites in the West and at Upper Buffalo. This trend is also observed at most IMPROVE monitoring sites in the western United States (Malm et al., 2002). Fine POM concentrations show less seasonal variability at the eastern sites, but Figs. 2 and 3 show large seasonal variability at those sites representing the interior West, the Colorado plateau, and the Northwest. At Mount Rainier National Park, the ratio of POM in July to that in January is almost a factor of 10 (8.6).

Fig. 5 shows that reconstructed and gravimetric FM compare quite well, as reflected in Fig. 1. There are, however, a variety of reasons why these two variables should not agree. First, average molecular structure is assumed for all species, and this may be most important in the R_{oc} factor, which scales organic carbon to mass of carbon plus other elements that make up the organic mass concentration. In this analysis, $R_{oc} = 1.8$ was used. In the East, sulfates tend to be acidic during summer months and therefore retain water at RH values found in laboratories where filters are weighed and gravimetric mass concentrations derived (about RH = 40%). Therefore gravimetric mass reflects retained water, as well as the mass of the sulfate aerosol. Another potentially important artifact is the loss of ammonium nitrate from the Teflon

Table 5
Statistical summary of annual fine mass and fine mass species concentrations by site

Variable ($\mu g\,m^{-3}$)	Mean	Std. dev.	Minimum	Maximum	% of FM
Mount Rainier fine mass, $N = 114$					
FM	3.69	2.79	0.09	15.47	
FM_{RECON}	3.92	3.03	0.2	17.45	106.2
$(NH_4)_2SO_4$	0.91	0.71	0.02	2.9	24.7
NH_4NO_3	0.2	0.23	0	1.13	5.4
POM	2.27	2.06	−0.03	12.98	61.5
LAC	0.26	0.2	0.01	0.89	7.0
SOIL	0.25	0.3	0.01	1.45	6.8
Sea salt	0.04	0.11	0	0.67	1.1
San Gorgonio fine mass, $N = 116$					
FM	5.82	3.48	0.21	14.57	
FM_{RECON}	7.41	4.47	0.63	16.76	127.3
$(NH_4)_2SO_4$	1.6	1.13	0.09	5.83	27.5
NH_4NO_3	2.66	2.22	0.03	9.28	45.7
POM	2.03	1.38	0.15	8.21	34.9
LAC	0.29	0.16	0.05	0.82	5.0
SOIL	0.83	0.69	0.01	3.35	14.3
Sea salt	0	0	0	0.03	0.0
Sequoia fine mass, $N = 112$					
FM	8.06	5.4	0.71	39.75	
FM_{RECON}	9.02	5.38	0.99	36	111.9
$(NH_4)_2SO_4$	1.99	1.39	0.13	6.69	24.7
NH_4NO_3	2.14	3.47	0.07	27.97	26.6
POM	3.49	1.94	0.55	8.85	43.3
LAC	0.33	0.16	0.04	0.83	4.1
SOIL	1.07	0.95	0.02	3.45	13.3
Sea salt	0	0	0	0.01	0.0
Grand Canyon fine mass, $N = 116$					
FM	2.58	1.94	0.27	14.2	
FM_{RECON}	2.71	2.38	0.19	18.38	105.0
$(NH_4)_2SO_4$	0.8	0.43	0.09	2.57	31.0
NH_4NO_3	0.22	0.26	0.02	2.19	8.5
POM	1.02	1.74	−0.01	14.17	39.5
LAC	0.12	0.22	0.01	2.07	4.7
SOIL	0.55	0.5	0.01	2.37	21.3
Sea salt	0	0	0	0.02	0.0
Upper Buffalo fine mass, $N = 106$					
FM	8.1	4.9	1.15	28.84	
FM_{RECON}	8.49	4.78	1.35	26.54	104.8
$(NH_4)_2SO_4$	3.42	2.37	0.38	11.01	42.2
NH_4NO_3	1.16	1.64	0.1	10.43	14.3
POM	2.88	2.25	0.56	13.83	35.6
LAC	0.27	0.16	0.07	1.05	3.3
SOIL	0.76	1.05	0.01	6.89	9.4
Sea salt	0	0	0	0.01	0.0
Bondville fine mass, $N = 102$					
FM	10.25	5.72	3.33	33.56	
FM_{RECON}	10.53	5.48	3.24	34.38	102.7
$(NH_4)_2SO_4$	4.26	3.26	0.68	19.84	41.6
NH_4NO_3	2.74	3.11	0.19	24.5	26.7
POM	2.59	1.5	0.51	9.52	25.3
LAC	0.37	0.19	0.11	0.98	3.6
SOIL	0.56	0.34	0.06	1.78	5.5
Sea salt	0	0.02	0	0.12	0.0
Great Smoky Mountains fine mass, $N = 112$					
FM	10.42	6.06	0.97	28.36	
FM_{RECON}	10.47	5.37	1.55	24.96	100.5
$(NH_4)_2SO_4$	5.87	4.09	0.72	17.64	56.3
NH_4NO_3	0.62	0.77	0.09	4.95	6.0
POM	3.04	1.58	0.37	9.8	29.2
LAC	0.33	0.15	0.07	0.87	3.2
SOIL	0.61	0.58	0.03	4.3	5.9
Sea salt	0	0	0	0	0.0
Bridger fine mass, $N = 122$					
FM	2.11	1.68	0.28	9.97	
FM_{RECON}	2.28	1.68	0.24	9.56	108.1
$(NH_4)_2SO_4$	0.62	0.39	0.09	2.65	29.4
NH_4NO_3	0.16	0.14	0.01	0.8	7.6
POM	0.98	0.93	0.03	6.98	46.4
LAC	0.08	0.07	0.01	0.57	3.8
SOIL	0.45	0.67	0.01	5.02	21.3
Sea salt	0	0	0	0.01	0.0
Brigantine fine mass, $N = 114$					
FM	9.74	5.79	3.43	35.06	
FM_{RECON}	10.18	5.87	3.66	29.8	104.5
$(NH_4)_2SO_4$	5.26	4.14	1.11	21.74	54.0
NH_4NO_3	1.07	1	0.18	5.23	11.0
POM	2.83	1.75	0.7	11.26	29.1
LAC	0.38	0.2	0.02	1.03	3.9
SOIL	0.55	0.43	0.03	1.94	5.6
Sea salt	0.09	0.36	0	2.13	0.9

substrate that is used for gravimetric analysis. Notice that, at Great Smoky Mountains National Park and Bondville, reconstructed mass is less than gravimetric mass during summer months, possibly reflecting retained water, while at San Gorgonio and Sequoia, where nitrates are a substantial fraction of FM, reconstructed mass is always higher than gravimetric mass, possibly reflecting loss of nitrate from the Teflon substrates. This is also true at some monitoring sites during the winter months, although one would expect that the nitrate loss artifact from Teflon filters would be lower because of lower ambient temperatures. At Mount Rainier and possibly Bridger and Sequoia, where POM is a significant fraction of FM and reconstructed mass is larger than gravimetric mass, the R_{oc} factor of 1.8 may be too high. In fact, an OLS regression with FM as the dependent variable and the species as independent variables suggests that the R_{oc} multiplier should be about 1.4 rather than the 1.8 used in this analysis.

Table 6
Statistical summary of annual coarse mass and coarse mass species concentrations by site

Variable ($\mu g\,m^{-3}$)	Mean	Std. dev.	Minimum	Maximum	% of CM
Mount Rainier coarse mass, N = 114					
CM	2.84	2.13	0.11	8.25	
CM_{RECON}	2.97	2.43	−3.47	10.09	104.6
$(NH_4)_2SO_4$	0.07	0.12	−0.31	0.59	2.5
NH_4NO_3	0.1	0.14	−0.06	0.67	3.5
POM	1.68	1.81	−3.33	8.38	59.2
LAC	0.08	0.15	−0.41	0.64	2.8
SOIL	0.95	1.42	−0.02	6.09	33.5
Sea salt	0.08	0.16	0	0.78	2.8
San Gorgonio coarse mass, N = 116					
CM	6.95	5.57	0.15	25.55	
CM_{RECON}	6.2	4.76	−0.31	18.53	89.2
$(NH_4)_2SO_4$	−0.07	0.19	−0.88	0.28	−1.0
NH_4NO_3	0.74	0.73	−0.34	2.97	10.6
POM	0.96	0.99	−2.81	5.7	13.8
LAC	0.05	0.11	−0.14	0.54	0.7
SOIL	4.51	3.67	0	16.13	64.9
Sea salt	0.01	0.02	0	0.08	0.1
Sequoia coarse mass, N = 112					
CM	10.33	8.6	−1.75	33	
CM_{RECON}	12.39	10.81	0.24	40.61	119.9
$(NH_4)_2SO_4$	0	0.28	−1.07	0.56	0.0
NH_4NO_3	0.69	0.65	−1.72	2.75	6.7
POM	2.52	1.44	0.38	6.78	24.4
LAC	0.06	0.08	−0.14	0.47	0.6
SOIL	9.28	9.46	0.04	32.72	89.8
Sea salt	0.02	0.04	0	0.3	0.2
Grand Canyon coarse mass, N = 116					
CM	2.55	2.22	0.08	10.31	
CM_{RECON}	2.41	2.26	−1.91	10.54	94.5
$(NH_4)_2SO_4$	0.09	0.12	−0.25	0.52	3.5
NH_4NO_3	0.14	0.11	0	0.43	5.5
POM	0.22	0.55	−3.35	2.64	8.6
LAC	0.01	0.06	−0.24	0.23	0.4
SOIL	1.94	1.81	0.04	8.86	76.1
Sea salt	0.01	0.04	−0.02	0.32	0.4
Upper Buffalo coarse mass, N = 106					
CM	8.03	6.48	0.28	40.24	
CM_{RECON}	6.49	5.12	0.48	27.85	80.8
$(NH_4)_2SO_4$	0.21	0.48	−1.03	1.81	2.6
NH_4NO_3	0.51	0.42	−0.15	2.04	6.4
POM	1.64	0.97	−0.22	5.86	20.4
LAC	0.09	0.12	−0.54	0.47	1.1
SOIL	4.03	4.25	0.06	23.47	50.2
Sea salt	0.02	0.04	0	0.24	0.2
Bondville coarse mass, N = 102					
CM	5.77	5.86	−0.81	31.88	
CM_{RECON}	6.03	6.35	0	46.7	104.5
$(NH_4)_2SO_4$	0.13	0.58	−1.08	3.71	2.3
NH_4NO_3	0.42	0.36	−0.65	1.59	7.3
POM	1.85	2.09	0.02	15.29	32.1
LAC	0.17	0.24	−0.15	1.52	2.9

Table 6 (*continued*)

Variable ($\mu g\,m^{-3}$)	Mean	Std. dev.	Minimum	Maximum	% of CM
SOIL	3.45	5.14	0.11	39.73	59.8
Sea salt	0	0.02	−0.11	0.07	0.0
Great Smoky Mountains coarse mass, N = 112					
CM	3.37	2.7	0.26	14.97	
CM_{RECON}	3.01	2.44	−0.28	12.91	89.3
$(NH_4)_2SO_4$	0	0.77	−4.23	1.51	0.0
NH_4NO_3	0.39	0.41	−0.07	2.24	11.6
POM	1.36	1.06	−0.17	4.29	40.4
LAC	0.08	0.11	−0.18	0.48	2.4
SOIL	1.43	1.4	−0.01	9.12	42.4
Sea salt	0.01	0.06	0	0.59	0.3
Bridger coarse mass, N = 122					
CM	1.81	2.07	−0.01	12.73	
CM_{RECON}	1.99	2.24	−1.34	14.31	109.9
$(NH_4)_2SO_4$	0.1	0.13	−0.1	0.81	5.5
NH_4NO_3	0.11	0.15	−0.14	1.06	6.1
POM	0.42	0.57	−1.51	4.63	23.2
LAC	0.03	0.06	−0.45	0.18	1.7
SOIL	1.33	1.72	0	11.23	73.5
Sea salt	0	0.01	0	0.1	0.0
Brigantine coarse mass, N = 114					
CM	6.11	6.37	1.02	49.93	
CM_{RECON}	4.67	3.88	−0.69	27.81	76.4
$(NH_4)_2SO_4$	0.14	0.86	−1.82	4.54	2.3
NH_4NO_3	0.6	0.49	−0.08	2.33	9.8
POM	1.08	0.93	−1.44	4.49	17.7
LAC	0.05	0.15	−0.5	0.67	0.8
SOIL	2.06	2.49	−0.02	18.69	33.7
Sea salt	0.74	1.35	0	6.98	12.1

Referring to Fig. 6 and Table 6, one can see that, for the most part, reconstructed and gravimetric CM compare quite favorably. This is also evident from Fig. 2, a scatter plot of reconstructed and gravimetric CM. However, it is evident from Fig. 2 that, although the data points scatter around the 1:1 line, there are a number of sampling periods where the two variables disagree by as much as a factor of 2.

It is clear that soil is the single largest contributor to CM at all but one monitoring location. The average fractional contributions range from a high of 76% at Grand Canyon National Park to a low of 34% at Mount Rainier. With the exception of Mount Rainier, the western United States generally has the highest fractional contributions, while the East has an average annual fractional contribution of 40–60%. The highest average concentration is found at Sequoia at 9.28 $\mu g\,m^{-3}$. Sequoia also has the highest average monthly contribution at near

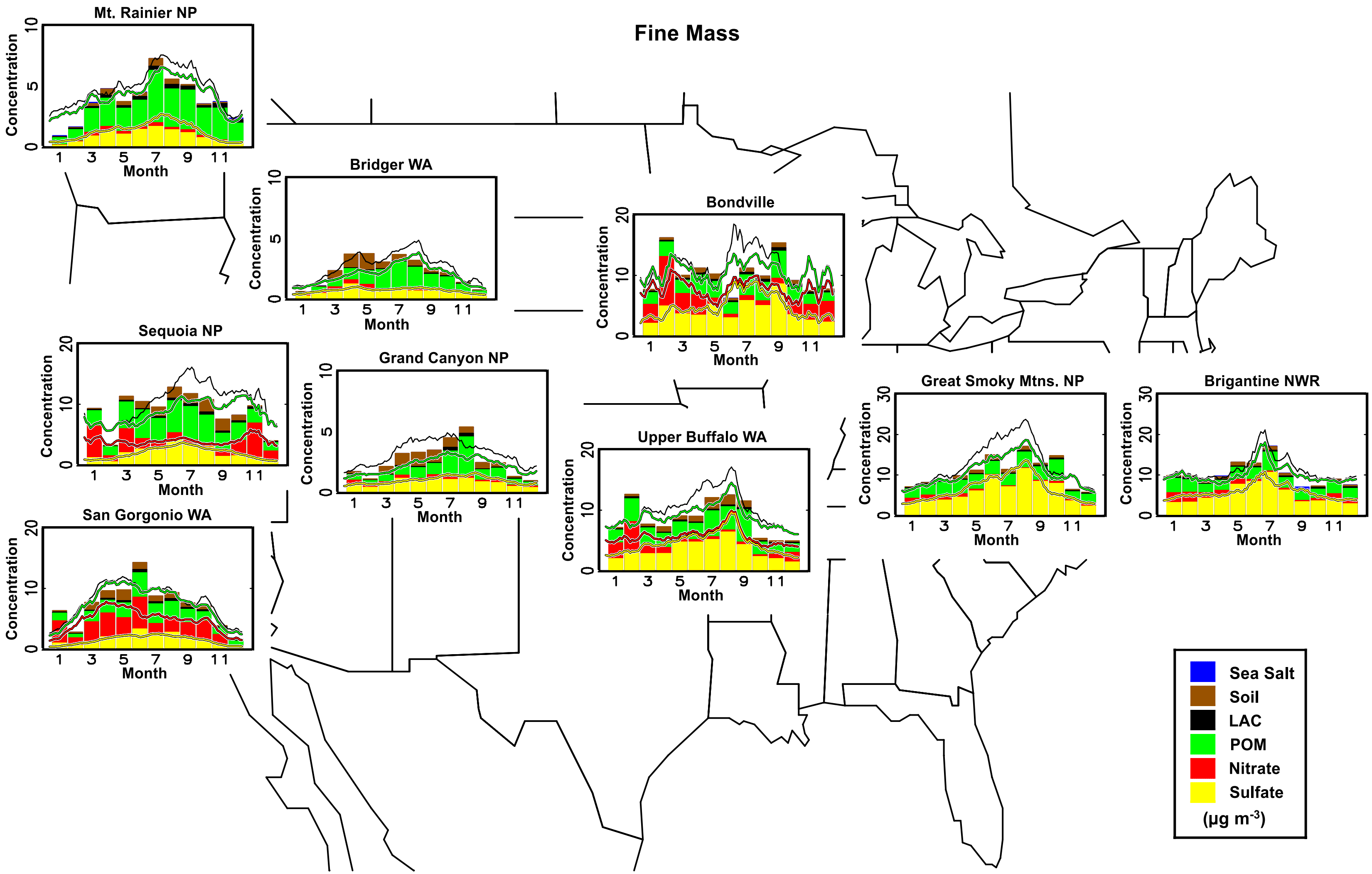

Fig. 3. A map of stacked bar charts showing the fine mass concentration of each species at each of the nine locations at which measurements were made. The continuous lines are running averages of the data collected historically at each monitoring site.

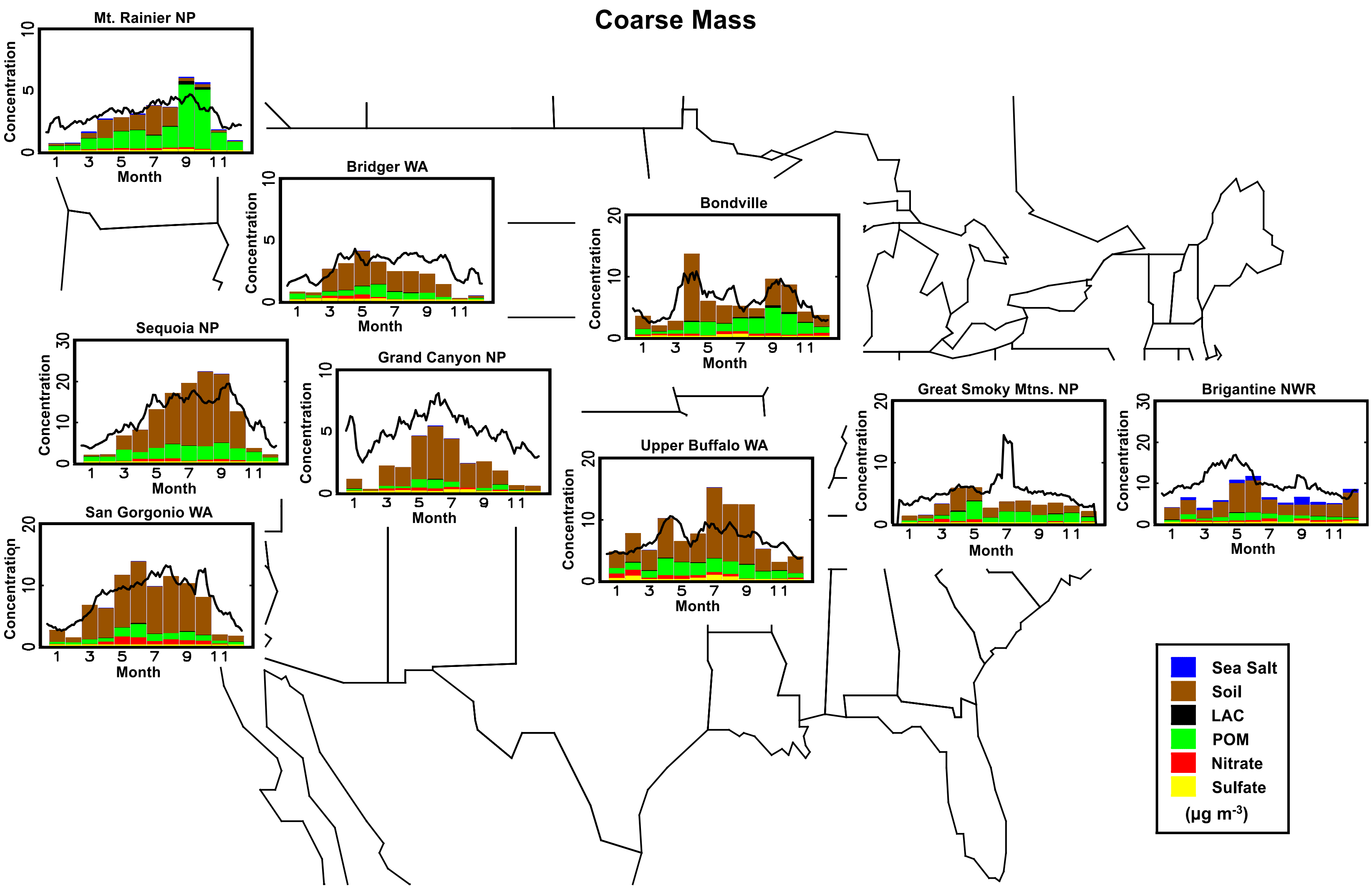

Fig. 4. A map of stacked bar charts showing the coarse mass concentration of each species at each of the nine locations at which measurements were made. The continuous lines are running averages of the data collected historically at each monitoring site.

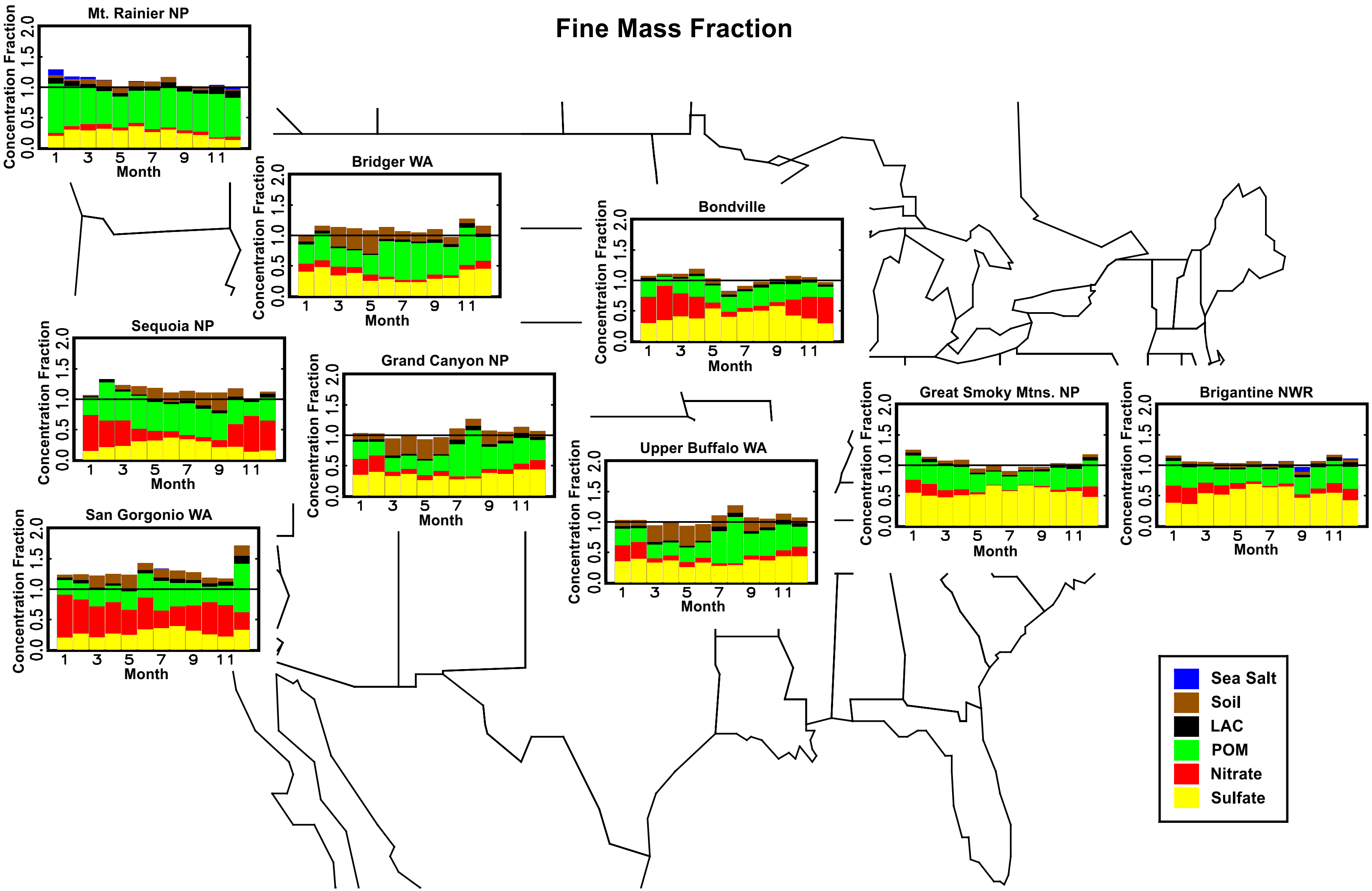

Fig. 5. A map of stacked bar charts showing the fractional contribution of each fine mass species to gravimetric mass at each of the nine locations at which measurements were made.

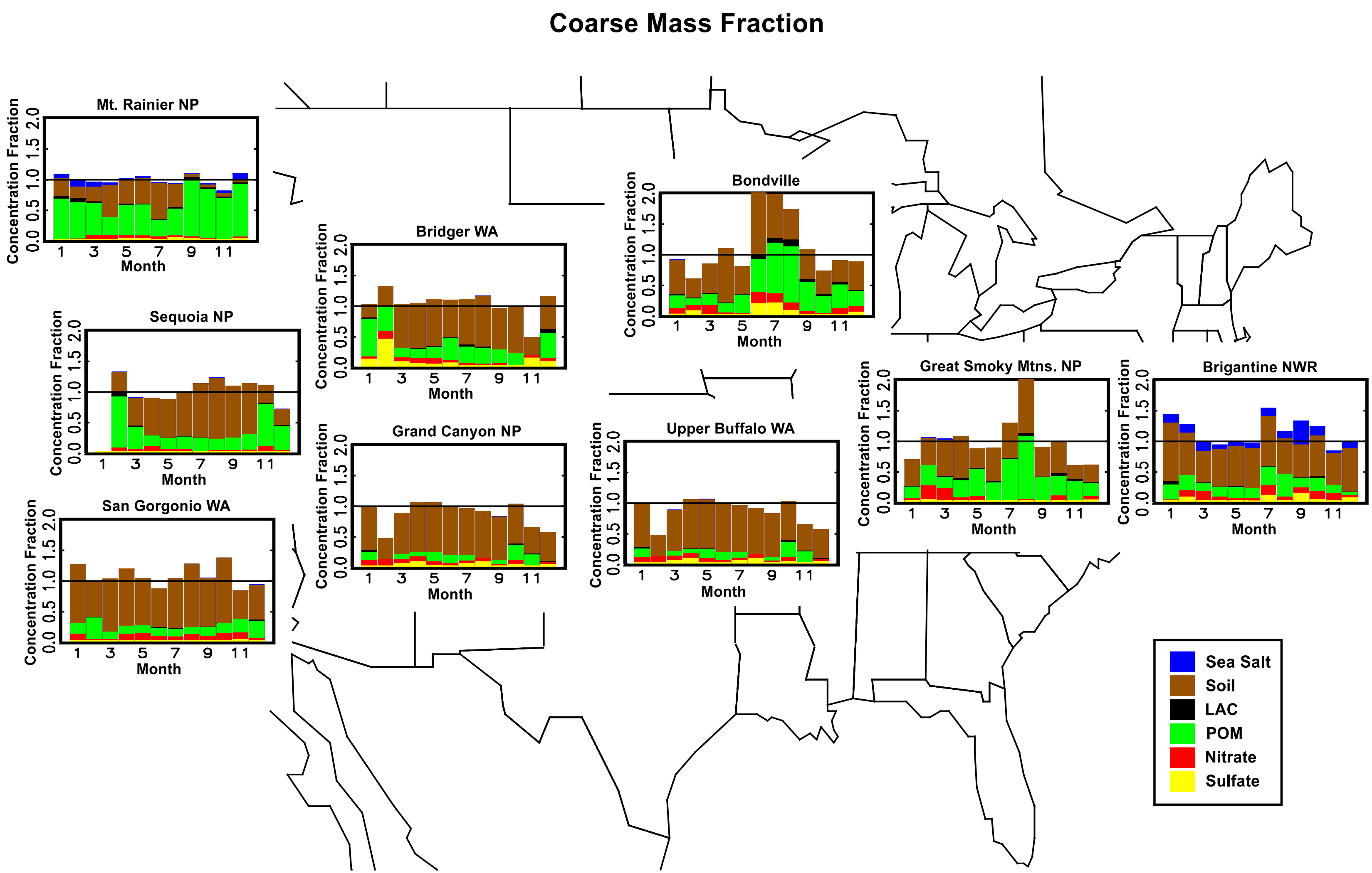

Fig. 6. A map of stacked bar charts showing the fractional contribution of each coarse mass species to gravimetric mass at each of the nine locations at which measurements were made. The stacked bar chart for the month of January is not shown for Sequoia National Park because of a large uncertainty in PM_{10} gravimetric mass.

$21.5\,\mu g\,m^{-3}$ for the month of August. San Gorgonio and Bondville have the second highest soil dust contributions at 4.5 and $3.5\,\mu g\,m^{-3}$, respectively, while Mount Rainier has the lowest average concentration of $0.95\,\mu g\,m^{-3}$.

Fig. 4 shows the lowest coarse soil concentrations tend to occur in the winter, as do most other species, while the months with maximum coarse soil contributions tend to vary from location to location. One interesting feature is the elevated soil concentrations during the month of April at Bondville and Upper Buffalo that are consistent with the historically high CM that occurs during this month. After this increase of CM in April, there is a decrease, followed by another increase in CM at Bondville and Upper Buffalo during the fall months. Whereas fine soil concentrations tend to peak across the entire western United States during the month of April, coarse soil concentrations do not show this trend. In the western United States, coarse soil concentrations tend to peak more toward mid-summer, and at Sequoia the highest concentrations are found in the fall.

The second largest contributor to CM is organic mass, which on an average annual fractional basis is highest at Mount Rainier at 59%. During the months of September and October, the fractional contribution of POM to CM was more than 80%. Even though POM contributes 59% of the CM on average at Mount Rainier, its average concentration is less than at the Sequoia and Bondville sites. The highest POM concentration occurs at Sequoia at $2.52\,\mu g\,m^{-3}$ and the second highest at Bondville at $1.85\,\mu g\,m^{-3}$. At Great Smoky Mountains, organic mass contributes 40% on average, while at four sites organic mass concentrations contribute between 20% and 30% of the CM. The lowest fractional contribution of organic mass occurs at Grand Canyon and San Gorgonio.

Nitrates are on average the third largest contributor to CM concentrations. The highest fractional contributions to CM by nitrates are at Brigantine, Great Smoky Mountains, and San Gorgonio at 10–12%. However, at coastal sites such as Brigantine, nitrates may well be in the form of sodium nitrate resulting from reactions of nitric acid with sea salt. San Gorgonio and Sequoia actually have the highest coarse nitrate contributions at 0.74 and $0.69\,\mu g\,m^{-3}$, respectively. Brigantine is nearly as high at $0.6\,\mu g\,m^{-3}$. Whereas nitrates at coastal sites may be in the form of sodium nitrate, in the interior West they are more likely to be associated with soil elements such as calcium. As with fine nitrates, coarse nitrate concentrations tend to be highest during the winter months.

At most sites sea salt concentrations are very low, the one exception being Brigantine where the average concentration is $0.74\,\mu g\,m^{-3}$ and is 12% of the CM budget. At Mount Rainier, sea salt contributes about 3% to the CM, and at the rest of the monitoring sites average concentrations are near 0.

Sulfates' contribution to CM is negligible on average at most sites, with its fractional contribution less than a few percent. This is also true on average for LAC.

It is interesting to contrast species mass concentrations that make up the fine and coarse modes. In the East, FM is dominated by sulfates, with organics contributing significantly less but in second place, while for CM soil is the biggest contributor, with organic mass again being in second place. In most of the rest of the United States, FM is made up of about equal amounts of sulfates, organics, and soil, with organics being the more significant contributor in the northwestern United States. Nitrates contribute little to FM except in southern California and the Midwest. In the coarse mode, soil is almost always the most significant fraction of mass, with organics being a distant second at about 24%. Other species on average are less than 10%.

5. Summary

To more fully investigate the composition of coarse particles, a nine-station coarse particle speciation network was initiated on 19 March 2003 and was completely operational by 23 December 2003. Sites were selected to be representative of the continental United States and were operated according to IMPROVE protocols for the year 2004. Both $PM_{2.5}$ (FM) and PM_{10} ($CM = PM_{10} - PM_{2.5}$) mass concentrations were speciated for sulfates, nitrates, organic and light-absorbing carbon, crustal minerals (soil), and sea salt. For FM, the sum of species mass concentrations values was 7% greater than gravimetric on average, while for CM the sum was 3% less than gravimetric mass on average. Scatter plots of reconstructed FM and CM versus gravimetric FM and CM show OLS slopes with the intercept set equal to 0 to be $1.03 \pm .004$ and $0.95 \pm .01$, respectively.

On average for the nine monitoring sites, sulfate (interpreted as ammonium sulfate) and POM make up 41% and 35% of the FM, respectively, while ammonium nitrate contributes another 18%. Soil mass concentration is less than 10% of measured mass, LAC about 4%, and sea salt is negligible.

For the CM fraction, the sulfate contribution is negligible, and LAC and sea salt are only 1% and 2%, respectively. As expected, soil is the major component at 61%, but POM and ammonium nitrate contribute significantly at 24% and 8%, respectively. The average fractional contributions of soil to CM range from a high of 76% at Grand Canyon to a low of 34% at Mount Rainier. With the exception of Mount Rainier, the western United States generally has the highest fractional contributions, while the East has an average annual fractional contribution of 40–60%. The lowest soil concentrations tend to occur in the winter, as do most other species, while the months with maximum soil contributions tend to vary from location to location.

The second largest contributor to CM is organic carbon mass, which on an average annual fractional basis is highest at Mount Rainier at 59%. During the months of September and October, the fractional contribution of POM to CM was more than 80%. The lowest fractional contribution of organic mass occurs at Grand Canyon and San Gorgonio.

Nitrates are on average the third largest contributor to CM concentrations. The highest fractional contributions to CM by nitrates are at Brigantine, Great Smoky Mountains, and San Gorgonio at 10–12%. However, at coastal sites such as Brigantine, nitrates may well be in the form of sodium nitrate, which results from reactions of nitric acid with sea salt. Whereas nitrates at coastal sites may be in the form of sodium nitrate, in the interior West they are more likely to be associated with soil elements such as calcium. As with fine nitrates, coarse nitrate concentrations tend to be highest during the winter months.

At most sites sea salt concentrations are very low, the one exception being Brigantine where the average contribution to CM is 12%. At Mount Rainier, sea salt contributes about 3% to the CM, and at the rest of the monitoring sites average concentrations are near 0. Sulfates' contribution to CM is negligible on average at most sites, with its fractional contribution less than a few percent. This is also true on average for LAC.

Disclaimer

The assumptions, findings, conclusions, judgments, and views presented herein are those of the authors and should not be interpreted as necessarily representing the National Park Service or the National Oceanic and Atmospheric Administration policies.

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