

# **IMPROVE Data Guide**

University of California Davis

August 1995

# A GUIDE TO INTERPRET DATA

## Introduction

The National Park Service (NPS) and other Federal Land Managers are required by the Clean Air Act to protect visibility at Class I areas, which include most national parks and wilderness areas. This is being accomplished through the Interagency Monitoring of Protected Visual Environments (IMPROVE) program, which has representatives from the NPS, the Forest Service (USFS), the Bureau of Land Management, the Fish and Wildlife Service (FWS), the Environmental Protection Agency, and regional-state organizations. The IMPROVE program includes the characterization of the haze by photography, the measurement of optical extinction with transmissometers and nephelometers, and the measurement of the composition and concentration of the fine particles that produce the extinction and the tracers that identify emission sources.

Figure 1 shows the locations all particulate monitoring sites using IMPROVE samplers through August 1995. Funding agencies include the IMPROVE committee, the NPS, the USFS, the FSW, the Tahoe Regional Planning Agency, the Department of Energy, the Northeast States Cooperative Air Use Management, the state of Vermont, and the Regional District of Fraser Cheam (British Columbia). All of all sites are operated by the University of California, Davis. Table 1 gives the start and end months for each site.



Figure 1. Particulate sampling sites using IMPROVE samplers through August 1995.

Table 1: Start and end dates of IMPROVE particulate sampling.

Site name	Start	End	Site name	Start	End
Abbotsford, British Columbia.....	4/94	6/95	Lone Peak Wilderness .....	11/93	
Acadia National Park .....	3/88		Lye Brook Wilderness .....	3/91	
Arches National Park .....	3/88	5/92	Mammoth Cave National Park .....	3/91	
Badlands National Park .....	3/88		Meadview National Recreation Area...	9/91	9/92
Bandelier National Monument .....	3/88		Mesa Verde National Park .....	3/88	
Big Bend National Park .....	3/88		Mohawk Mountain, CT .....	9/88	11/93
Bliss State Park, CA.....	11/90		Moosehorn NWR.....	12/94	
Boundary Waters Canoe Area .....	3/91		Mount Rainier National Park .....	3/88	
Bridger Wilderness .....	3/88		Mount Zirkel Wilderness.....	11/93	
Bridgton, ME .....	9/88	11/93	Okefenokee NWR.....	3/91	
Brigantine National Wildlife Refuge...	3/91		Petrified Forest National Park.....	3/88	
Brooklyn Lake, WY.....	4/94		Pinnacles National Monument .....	3/88	
Bryce Canyon National Park .....	3/88		Point Reyes National Seashore .....	3/88	
Canyonlands National Park .....	3/88		Proctor Maple Research Farm, VT ....	09/88	
Cape Romain NWR .....	8/94		Quabbin Reservoir, MA.....	12/88	11/93
Chassahowitzka NWR.....	3/93		Redwood National Park .....	3/88	
Chilliwack, British Columbia .....	4/94	6/95	Ringwood State Park, NJ.....	9/88	11/93
Chiricahua National Monument.....	3/88		Rocky Mountain National Park .....	3/88	
Columbia River Gorge NSA.....	6/93		Saguaro National Monument .....	6/88	
Crater Lake National Park .....	3/88		Salmon National Forest .....	11/93	
Craters of the Moon NM.....	5/92		San Geronio Wilderness .....	3/88	
Death Valley National Monument ....	10/93		Sawtooth National Forest.....	1/94	
Denali National Park.....	3/88		Scoville, ID .....	5/92	
Dolly Sods /Otter Creek Wilderness ...	3/91		Sequoia National Park .....	9/92	
Dome Lands Wilderness.....	8/94		Shenandoah National Park.....	3/88	
Everglades National Park.....	9/88		Shining Rock Wilderness .....	8/94	
Gila Wilderness .....	4/94		Sipsy Wilderness .....	2/92	
Glacier National Park .....	3/88		Snoqualmie National Forest.....	7/93	
Grand Canyon National Park			South Lake Tahoe, CA .....	3/89	
Hopi Point.....	3/88		Sula (Selway Bitterroot Wilderness)....	8/94	
Indian Gardens.....	10/89		Sunapee Mountain, NH .....	12/88	11/93
Great Basin National Park .....	5/92		Sycamore Canyon Wilderness .....	9/91	9/92
Great Gulf Wilderness .....	6/95		Three Sisters Wilderness .....	7/93	
Great Sand Dunes NM.....	5/88		Tonto National Monument .....	3/88	
Great Smoky Mountains NP .....	3/88		Upper Buffalo Wilderness .....	6/91	
Guadalupe Mountains National Park ..	3/88		Virgin Islands National Park.....	10/90	
Haleakala National Park .....	2/91		Voyageurs National Park .....	3/88	
Hawaii Volcanoes National Park.....	3/88	4/93	Washington D.C. ....	3/88	
Isle Royale National Park .....	6/88	8/91	Weminuche Wilderness .....	3/88	
Jarbidge Wilderness.....	3/88		Whiteface Mountain, NY.....	9/88	11/93
Jefferson/James River Face Wild.....	8/94		White River National Forest.....	7/93	
Joshua Tree National Monument .....	9/91	9/92	Yellowstone National Park .....	3/88	
Lassen Volcanic National Park .....	3/88		Yosemite National Park .....	3/88	

## Sample Collection and Analysis

The standard IMPROVE sampler has four sampling modules, listed in the Table 2: A, B, and C collect fine particles (0-2.5  $\mu\text{m}$ ), and D collects PM10 particles (0-10  $\mu\text{m}$ ). Module A Teflon is the primary filter, providing most of the fine particle data. Module B, with a denuder before the

nylon filter to remove acidic gases, is used primarily for nitrate. Module C, with tandem quartz filters, measures carbon in eight temperature fractions. At many sites, the Module A or D Teflon filter is followed by a quartz filter impregnated with  $K_2CO_3$  that converts  $SO_2$  gas to sulfate on the filter. Some sites have a single Module A Teflon.

Table 2: Measurements by full IMPROVE sampler.

module:	A	B	C	D	A2 or D2
size:	fine	fine	fine	PM10	gas
filter:	Teflon	nylon	quartz	Teflon	impregnated
analysis:	gravimetric PIXE/PESA XRF absorption	IC	TOR combustion	gravimetric	IC
variables:	mass H, Na - Pb $b_{abs}$	nitrate sulfate chloride	carbon in 8 temperature fractions	PM10 mass	$SO_2$

Each module is independent, with separate inlet, sizing device, flow measurement system, critical orifice flow controller, and pump. All modules have a common controller clock. The flow rate is measured before and after the collection by a primary method using an orifice meter system and a secondary method using the pressure drop across the filter and the equation of flow rate through a critical orifice. The particle sizing depends on the flow rate; the standard deviation of annual flow rates is 2% to 3%. The average particle cut point for the fine modules has averaged  $2.6 \mu m$ , with a standard deviation of  $0.2 \mu m$ . All concentrations are based on local volumes. Two 24-hour samples are collected each week, on Wednesday and Saturday. The filter cassettes are changed weekly by on-site personnel and shipped to Davis for processing and analysis. All filter handling is done in clean laboratory conditions. The recovery rate for validated data since 1991 has been 96%.

Teflon A and D: The five analytical methods used at Davis to analyze the Teflon A filters are listed in Table 3. All PM10 (Teflon D) filters were analyzed by gravimetric analysis; 4% were analyzed by all five methods. The elemental concentrations (H, Na-Pb) are obtained by PIXE, PESA, XRF. XRF was added for samples collected after May 1992; this affected the precision, minimum detectable limits and fraction found for elements between Fe and Pb.

The coefficient of absorption ( $b_{abs}$ ) was measured either by an integrating plate or an integrating sphere system. Comparisons between the two methods verify that they accurately determine the absorption for the filter. However, because of shielding by other particles, this is less than the atmospheric coefficient. Based on separate experiments, an empirical equation has been derived using the areal density of all particles on the filter that corrects for the effect. The reported  $b_{abs}$  and the precision include this correction factor. Collocated samplers with differing collection areas verify that the expression is reasonable. The coefficient of absorption is an optical measurement with units of  $10^{-8} m^{-1}$  in the database. To convert to inverse megameters ( $10^{-6} m^{-1}$ ), divide the value by 100. (For the seasonal summaries, the units are written in inverse megameters.)

Because of volatilization of nitrate and organics during sampling, the gravimetric mass measurements on Teflon filters may be slightly less than the actual mass. Studies comparing nitrate collected on Teflon filters with that collected on nylon indicate that one-half to three-quarters of the nitrate volatilizes from the Teflon filter during sampling. At most sites and seasons, ammonium nitrate is approximately 5% of the fine mass, so this loss is only a small fraction of the mass. At some western sites near major cities, such as San Geronio, the ammonium nitrate may be one-half of the fine mass in summer, resulting in major underestimates of fine mass.

Table 3. Analytical methods used for A and D Teflon filters.

gravimetric (electromicrobalance)	mass
LIPM: Laser Integrating Plate Method	coefficient of absorption ( $b_{abs}$ )
PIXE: Particle Induced X-ray Emission XRF: X-ray Fluorescence	Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Pb
PESA: Proton Elastic Scattering Analysis	H

Nylon B: The nylon filters were analyzed by ion chromatography (IC) at Research Triangle Institute or Global GeoChemical for nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{CL}^-$ ), sulfate ( $\text{BSO}_4$ ), and nitrite ( $\text{NO}_2^-$ ). Nitrate vapors are removed prior to collection, so that the measured nitrate concentration represents only particulate nitrate. Chloride ion ( $\text{CL}^-$ ) is useful for sites near marine sources, but elsewhere the ambient concentrations are below than the minimum detectable limit. Sulfate on nylon ( $\text{BSO}_4$ ) is used as a quality assurance check of the sulfur measured by PIXE on the Teflon A filter. However, we strongly recommend using the Teflon sulfur as the measurement of ambient sulfate, because of possible adsorption of  $\text{SO}_2$  on the nylon filter. The nitrite concentrations are generally below the minimum detectable limit.

Quartz C: The quartz filters were analyzed at Desert Research Institute for carbon using the Thermal Optical Reflectance (TOR) combustion method. The sample is heated in steps and the evolved  $\text{CO}_2$  measured. The atmosphere is 100% He until part way through the  $550^\circ\text{C}$  step, when 2%  $\text{O}_2$  is introduced. The reflectance of the sample is monitored throughout. It decreases at  $120^\circ\text{C}$  and returns to the initial value during the  $550^\circ\text{C}$  step after oxygen is added. All carbon before this return of initial reflectance is considered organic carbon and the remainder elemental carbon. The eight carbon fractions in the database are defined in Table 4. OP is the portion of E1, E2, or E3 before the reflectance returns to the initial value.

Table 4. Carbon components as a function of temperature and added oxygen.

<i>Fraction</i>	<i>pyrolyzed fraction</i>	<i>temperature range</i>	<i>atmosphere</i>	<i>reflectance vs. initial</i>
O1		ambient to 120°C	100% He	at initial
O2		120 - 250°C		under initial
O3		250 - 450°C		
O4		450 - 550°C		
E1	OP	remains at 550°C	98% He 2% O <sub>2</sub>	over initial
E2		550 - 700°C		
E3		700 - 800°C		

The primary interest is in two fractions, organic carbon and elemental or light-absorbing carbon (LAC). The equations are:

$$\begin{aligned} \text{total organic carbon} &= \text{OC1} + \text{OC2} + \text{OC3} + \text{OC4} + \text{OP} \\ \text{total elemental carbon} &= \text{EC1} + \text{EC2} + \text{EC3} - \text{OP} \end{aligned}$$

Preliminary statistical comparisons between the coefficient of absorption and the carbon measured by TOR suggest that the carbon evolved at 550°C without added oxygen (OC4) may be light-absorbing. The comparison also suggests that much of the OP may not be pyrolyzed organic. The carbon in question (OC4+OP) could be either light-absorbing organic carbon or elemental carbon. If it is organic, then the current organic and elemental measurements are correct, but there is approximately three times as much absorbing carbon than would be estimated by elemental carbon alone. If it is elemental, then the current organic carbon concentrations are approximately 30% too large. Until we determine otherwise, we will assume that the equations above correctly determine the organic and elemental fractions.

SO<sub>2</sub> gas: The sulfate on the impregnated quartz filter following a Teflon filters were analyzed by ion chromatography at Desert Research Institute or Research Triangle Institute to give the concentration of SO<sub>2</sub>.

### Concentration and Precision of Measured Variables

The general equation for the concentration of a given variable is

$$c = \frac{A - B}{V},$$

where A is the measured mass of the variable, B is the artifact mass determined from field blanks or secondary filters, and V is the volume determined from the average flow rate and the sample

duration. The artifact B may be produced by contamination in the filter material, and in handling and analysis, and by adsorption of gas during collection. The artifact is negligible for all Teflon measurements, including gravimetric analysis. It is determined from designated field blanks for ions and from secondary filters for carbon.

The precision in each concentration is included in the data base. The overall precision is a quadratic sum of four components of precision. These are:

- (1) Fractional volume precision,  $f_v$ , primarily from the flow rate measurement. A value of 3% is used, based on third-party audits.
- (2) Fractional analytical precision associated with calibration or other factors,  $f_a$ . This is zero for gravimetric analysis. The values for all other methods are determined from replicate analyses. Most variables have an fractional analytical precision of around 4%, so that the combined volume and analytical precision is around 5%.

For the eight carbon fractions, the primary source of fractional uncertainty is the separation into temperature fractions. This may be associated with temperature regulation, but it may also be from inherent variability of the species involved. The fractional uncertainty of the sum of all carbon species is around 3% to 4%. The fractional uncertainty for the fractions range from 11% to 40%, averaging 22%. Thus for sums of fractions, such as total organic, the uncertainties are less than would be estimated from the individual fractions. This will be discussed in the section of carbon composites.

- (3) Constant mass per filter precision,  $\sigma_a$ , from either the analysis or artifact subtraction. These are determined from the standard deviations in the designated field blanks, secondary filters, or system control filters. For large concentrations, this is small compared to the fractional terms. This is zero for XRF, PIXE, and PESA.
- (4) Statistical precision based on the number of counts in the spectrum,  $\sigma_{stat}$ . This is used for XRF, PIXE, and PESA. For large concentrations, this is small compared to the fractional terms.

The equation for the total precision is:

$$[\sigma(c)]^2 = [f_v c]^2 + [f_a c]^2 + \left[ \frac{\sigma_a}{V} \right]^2 + \left[ \frac{\sigma_{stat}}{V} \right]^2$$

The relative precision depends on the concentrations. For large concentrations, only the fractional terms (1 and 2) are important, so the relative precision is around 5%. For small concentrations, the constant analysis/artifact term (3) or the statistical term (4) is important. At the mdl, the precision increases to 50%.

Table 5 separates the relative precisions of key measured variables into three groups. This is defined as the ratio of the mean precision from all sources divided by the mean concentration. Most variables are in the most precise group, 4% to 7%.

The average minimum detectable limits (mdl) are provided with each concentration in the database. A concentration is assumed to be statistically significant only if it is larger than the mdl. For ion chromatography and carbon the mdl corresponds to twice the precision of the field blanks or secondary filters. For mass and absorption, the minimum detectable limit corresponds to twice the analytical precision determined by controls. For PIXE, XRF, and PESA, the minimum detectable limit is based on the background under the peaks in the spectrum and is calculated separately for each case. The assumption for all elements except As is that there are no interference from other elements. Because the measurement for arsenic requires subtracting the value for lead, the mdl for As depends on the Pb concentration, and is generally larger than the value estimated from the background. When calculating averages, if the value is below the minimum detectable limit, we use one-half of the minimum detectable limit as the concentration and the precision in the concentration. In all cases, the relative precisions are around 50% at the mdl.

Table 5: Relative precision of key measured variables. Ratio of mean precision divided by mean concentration.

range	before 6/1/92	after 6/1/92
4% to 6%	PM <sub>2.5</sub> , PM <sub>10</sub> , H, S, Si, K, Ca, Fe, Zn, SO <sub>4</sub> <sup>=</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>2</sub>	PM <sub>2.5</sub> , PM <sub>10</sub> , S, Si, K, Ca, Fe, Cu, Zn, SO <sub>4</sub> <sup>=</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>2</sub>
8% to 15%	Na, Al, Ti, Cu, Br, Pb	H, Na, Ti, Se, As, Br, Sr, Pb, O4, E1
> 15%	V, Mn, Se, As, Sr, all carbon fractions	V, Mn, O1, O2, O3, OP, E2, E3

The minimum detectable limits of many elements changed in June 1992, with the addition of XRF. Figure 2 shows the mdl's for each season for sulfur and selenium. The minimum detection limits for Fe decreased by a factor of nearly 10. The minimum detection limits for elements below Fe increased slightly, because of a reduction in cyclotron time to compensate for the extra cost of XRF analysis.

The minimum detectable limits of standard network samples for elements measured by PIXE and XRF are given in Table 6. Arsenic is not included because the mdl depends on the lead concentration. Also important is the fraction of cases with statistically significant concentrations (above the mdl). This depends on the relationship between the mdl and the ambient concentrations. Table 7 separates these into four ranges. A significant change for aluminum occurred with samples beginning 2/93. Because of detector problems, Al, which is on the shoulder of the Si peak, was often not detected. Before this date, Al was observed on 65% of all samples; afterwards it was found on almost every sample. Sodium, chlorine, and chloride ion were observed in significant amounts only at sites with marine influences.



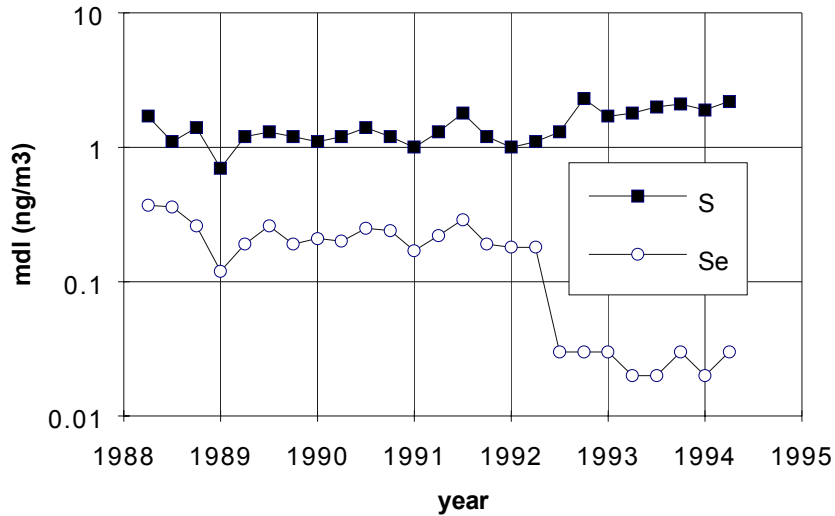


Figure 2: Minimum detectable limits of sulfur and selenium by season.

Table 6: Minimum detectable limits of elements in ng/m<sup>3</sup>.

dates	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn
6/88-5/92	8.7	2.9	1.8	1.4	1.3	1.2	1.3	0.83	0.64	0.57	0.50	0.41	0.39
6/92-5/94	13.	4.8	3.0	2.2	1.9	1.9	2.0	1.2	0.90	0.81	0.69	0.57	0.52
	Fe	Ni	Cu	Zn	Ga	Se	Br	Rb	Sr	Zr	Pb		
6/88-5/92	0.34	0.24	0.24	0.21	0.20	0.22	0.25	0.37	0.42	0.65	0.57		
6/92-5/94	0.11	0.05	0.05	0.05	0.03	0.03	0.03	0.06	0.07	0.11	0.06		

Table 7: Fraction of cases with statistically significant concentrations.

range	before 6/1/92	after 6/1/92
90% to 100%	PM <sub>2.5</sub> , PM <sub>10</sub> , S, H, Si, K, Ca, Ti, Fe, Zn, Br, SO <sub>4</sub> <sup>=</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>2</sub> , OP, E1	PM <sub>2.5</sub> , PM <sub>10</sub> , S, H, Si, K, Ca, Fe, Cu, Zn, Br, Pb, SO <sub>4</sub> <sup>=</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>2</sub> , O4, OP, E1
70% to 90%	Cu, Pb, O2, O3, O4, E2	Ti, Se, Sr, O2, O3, E2
60% to 70%	Mn	Mn, As, Rb
less than 40%	P, V, Ni, Se, As, Rb, Sr, Zr, O1, E3	P, V, Ni, Zr, O1, E3

Level I validation procedures for sample collection include comparison of the two measurements of flow rate. Level I validation procedures for sample analysis include comparison to recognized standards and periodic replicate measurements. Level II validation procedures include comparison of selected variables measured by different methods. This includes comparison of the PIXE and XRF measurements, comparison of sulfur by PIXE on Teflon with sulfate by ion chromatography on nylon, comparison of OMC and OMH, comparison of LAC and BABS, and comparison of MF with RCMA and RCMC.

Collocated sampling is an important part of the quality assurance program. These are conducted routinely at Davis and periodically at field locations. All collocated sampling has indicated that the precision estimates in the database are accurate representations of the actual differences.

## Composite Variables

The database contains only measured variables. The composite variables listed in Table 8 can be derived from the measured variables based on reasonable assumptions.

Table 8: Composite Variables

NHSO	ammonium sulfate, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>2</sub> : 4.125 * S
NHNO	ammonium nitrate, (NH <sub>4</sub> )NO <sub>3</sub> : 1.29 * NO <sub>3</sub> <sup>-</sup>
OC	total organic carbon (quartz): OC1+OC2+OC3+OC4+OP
OMC	organic mass by carbon (quartz): 1.4 * OC
OMH	organic mass by hydrogen (Teflon): assumes all sulfur is ammonium sulfate and no there is hydrogen from nitrate 13.75 * (H - 0.25 * S)
LAC	light absorbing carbon (quartz): EC1+EC2+EC3-OP
TC	total carbon (quartz): OC1+OC2+OC3+OC4+EC1+EC2+EC3
SOOT	light absorbing carbon from optical measurement: If BABS in 10 <sup>-8</sup> m <sup>-1</sup> , and SOOT and SOIL in ng/m <sup>3</sup> , SOOT = BABS - 0.11 * SOIL
SOIL	soil: 2.20*Al + 2.49*Si + 1.63*Ca + 2.42*Fe + 1.94*Ti
KNON	nonsoil potassium: K - 0.6 * Fe
RCMC	reconstructed mass without nitrate, carbon from quartz filter C: NHSO + SOIL + 1.4*KNON + 2.5*Na + LAC + OMC
RCMA	reconstructed mass without nitrate, carbon from Teflon filter A: NHSO + SOIL + 1.4*KNON + 2.5*Na + BABS/2 + OMH

For the uncertainty in all composites except for the four involving the quartz measurements, we recommend quadratically adding the uncertainties of the constituent terms times the appropriate multiplicative constant. For example, the uncertainty for soil would be:

$$[\sigma(\text{SOIL})]^2 = [2.20 \sigma(\text{Al})]^2 + [2.49 \sigma(\text{Si})]^2 + [1.63 \sigma(\text{Ca})]^2 + [2.42 \sigma(\text{Fe})]^2 + [1.94 \sigma(\text{Ti})]^2$$

Because of the fact that temperature separation plays a much larger role for carbon fractions than for the composites, and because the fractions are not independent, we cannot follow the above method for OC, OMC, LAC, and TC. For these we recommend the following equations for 24-hour samples:

$$\begin{aligned} \sigma(OC) &= \sqrt{(120)^2 + (0.05 * OC)^2} & \sigma(OMC) &= \sqrt{(168)^2 + (0.05 * OMC)^2} \\ \sigma(LAC) &= \sqrt{(34)^2 + (0.07 * LAC)^2} & \sigma(TC) &= \sqrt{(133)^2 + (0.05 * TC)^2} \end{aligned}$$

The constant terms (120, 168, 34, 133) are appropriate for volumes near 32.4 m<sup>3</sup>, which is typical for 24-hour samples. For other volumes they should be multiplied by (32.4/V). For typical 12-hour samples, the constant terms should be multiplied by 2.

ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>): The sulfur on the Teflon filter is always present as sulfate. In most cases the sulfate is fully neutralized ammonium sulfate, which is 4.125 times the sulfur concentration. The sulfate at eastern sites during the summer is not always fully neutralized, but overall the occurrences are rare. If 100% of the sulfur were sulfuric acid, the correct sulfate

mass would be 74% of the calculated NHSO. The uncertainty in NHSO is 1.4 times the uncertainty in S. The calculate sulfate ion from sulfur, multiply by 3.0.

ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ): As with sulfate, the nitrate is expected to be fully neutralized ammonium nitrate. This is 1.29 times the nitrate ion concentration. The uncertainty in NHNO is 2.9 times the uncertainty in  $\text{NO}_3^-$ .

total organic carbon (OC) and organic mass by carbon (OMC): The total organic carbon concentration is assumed to be the sum of the four organic fractions plus the pyrolyzed fraction, OP. To obtain organic mass, we recommend multiplying the total carbon by 1.4, which assumes that carbon accounts for 71% of the organic mass. The ratios for various typical compounds range from 1.2 to 1.8.

organic mass by hydrogen (OMH): The hydrogen on the Teflon filter is associated with sulfate, organics, nitrate, and water. Since the analysis is done in vacuum, all water will volatilize. We also assume that no significant hydrogen from nitrate remains. If we assume that the sulfate is fully neutralized ammonium sulfate, we can estimate the organic concentration by subtracting the hydrogen from sulfate and multiplying the difference by a constant representing the fraction of hydrogen. (We suggest a constant of 13.75. This gives the best comparison with OMC for the network samples. However, a value near 10 is suggested by various typical organic compounds.) The OMH variable is defined only when both H and S are valid measurements.

The OMH calculation is invalid when (1) there is high nitrate relative to sulfate, as at sites near Los Angeles and San Francisco, and (2) the sulfur is not present as ammonium sulfate. This latter includes sites with marine sulfur, and sites in the eastern United States with unneutralized sulfate. For the western sites except San Geronio, Sequoia, Pinnacles, Point Reyes, Redwoods, and Hawaii Volcanoes, the correlation coefficient ( $r^2$ ) between OMH and OMC for the first two years was 0.89 and the slope was  $0.98 \pm 0.02$ . For 1992,  $r^2$  was 0.87 and the slope was  $1.07 \pm 0.01$ . The main advantage of using OMH at these sites is that its precision is better than that for OMC during periods of low organic, as winter in the West. At sites in the East, OMH is often low because of unneutralized sulfate, and imprecise because of the high sulfate relative to organic. For 10 eastern sites in 1992, the average OMH was one-half the average OMC, and one-half of the OMH values were less than the minimum quantifiable limit.

An organic artifact was found on a batch of Teflon filters used between September 1990 and November 1991. Approximately 7% of the samples had OMH significantly larger than OMC. The artifact was apparently completely organic (there was no elevated sulfur) and appeared during collection. For these samples, both H and MF (fine mass) were invalidated. These variables were not invalidated on the remaining 93%, but flagged as less reliable than normal. No other variables were invalidated.

light-absorbing carbon (LAC): This is the sum of elemental carbon fractions. The pyrolyzed fraction is subtracted. Preliminary analyses indicate that some of the O4 fraction may absorb light, and that OP may overestimate the pyrolytic mass.

light-absorbing carbon (SOOT): This is estimated from the coefficient of absorption assuming absorption efficiencies of  $10 \text{ m}^2/\text{g}$  for elemental carbon and  $0.11 \text{ m}^2/\text{g}$  for soil.

soil (SOIL): This is a sum of the soil derived elements (Al, Si, K, Ca, Ti, Fe) along with their normal oxides. The variable does not depend on the type of soil, such as sediment, sandstone, or limestone. One fine element, K, however, may partly derive from smoke as well as soil. We have eliminated this from the calculation and used Fe as a surrogate. This is discussed in nonsoil potassium below.

nonsoil potassium (KNON): Fine potassium has two major sources, soil and smoke, with the smoke potassium on much smaller particles than the soil potassium. The potassium in coarse particles will be solely produced from soil. The soil potassium is estimated from the measured concentration of Fe and the ratio of K/Fe of 0.6 measured on coarse samples ( 2.5 to 15  $\mu\text{m}$ ) collected between 1982 and 1986. This ratio depends on the soil composition and varies slightly from site to site. If the ratio were slightly smaller (say 0.5), the KNON values will be negative when there is no smoke influence. The residual potassium,  $K - 0.6*Fe$ , is then assumed to be produced by smoke. The burning of most organic fuels will produce potassium vapor. During transport, this vapor will transform into fine particles. The KNON parameter is not a quantitative measure of the total smoke mass, since the ratio of nonsoil potassium to total smoke mass will vary widely, depending on the fuel type and the transport time. However, the KNON parameter can be used as an indicator of a nonsoil contribution for samples with large KNON. In some situations there may be some fine Fe from industrial sources which could cause occasional smoke episodes to be lost.

reconstructed mass (RCMC and RCMA): We use two estimates of reconstructed mass, which differ only in the estimation of organic mass and light-absorbing carbon. RCMC uses the quartz C measurements, while the RCMA uses the Teflon A measurements. The RCMC estimate should be used at sites where the OMH calculation is invalid, while the RCMA estimate should be used when the organic and LAC concentrations are small. It can also be used when there is no quartz measurement, as with a single Module A sampler.

Neither reconstructed mass estimate includes nitrates. The Teflon filter does not collect any nitrate in the vapor state, and loses one-half to three-quarters of the particulate nitrate by volatilization during sampling. At most sites this is a few percent the reconstructed mass.

Precision: The precisions of the composite variables are estimated by quadratically adding the precisions of the components. This assumes that the precisions are independent. Since this is not quite valid, the calculated precisions for composites formed by adding (SOIL, OMC, LAC, RCMC, RCMA) are slightly smaller than they should be. For example, the average calculated precision for SOIL of 4% should probably be closer to 5%. The composite formed by subtraction (OMH) may have a slightly smaller precision than reported.

### **Major Components of Fine Mass**

ammonium sulfate: Sulfate is generally the major component of the fine mass throughout the United States, accounting for 20-40% of the mass in the West to 45-60% in the East. (It is less than organic at most sites in the Northwest and less than nitrate at San Geronio.) Sulfur primarily enters the atmosphere as  $\text{SO}_2$  gas. The  $\text{SO}_2$  converts in the atmosphere to sulfuric acid, which reacts with ammonia gas to form ammonium sulfate. There are periods at some sites when there is too much sulfuric acid to be neutralized by ammonia; some of it may remain as

sulfuric acid. The rate of transformation and the size of the resulting particle depends on the relative humidity. This has a significant impact on visibility, because in high humidity the sulfate particles are larger and scatter light much more efficiently relative to the mass of sulfur. That is, the scattering per unit mass of sulfur is greater at high humidity than at low humidity. This growth can occur anytime during the lifetime of the particle. If the relative humidity later decreases the particle will shrink, but not immediately. Therefore the particle size and scattering efficiency depends on the relative humidity of the past as well as the present. The scattering efficiency for a small sulfate particle is less than that for a large one, but still significant. Because sulfate is such an efficient scatterer of light, its contribution to the extinction budget is even larger than its contribution to the mass budget.

ammonium nitrate: Nitrate is generally a minor component of the particulate mass and the extinction budget. At half of the sites, ammonium nitrate is less than 6% of the mass, compared to 32% for ammonium sulfate. The main exceptions are on the West Coast, where the average nitrate concentration can be more than the average sulfate concentration. In the east, it is 15% of ammonium sulfate.

soil: Most of this component is produced by soil dust. At some sites in the West, soil can be one of the largest components of the mass. Its effect on visibility is less per unit mass than sulfate, because the particles are generally larger than the optimum size. Soil emission is significantly enhanced by disturbances to the soil: off-road and dirt-road vehicular traffic, agricultural activities, bison stampedes. A smaller source of these elements can come from industrial and mining activities.

organic: Organic material is the largest components at most sites in the northwest, and elsewhere the second largest component. Possible sources are fires (wildfires, controlled burns, slash and field burning, incineration, household heating), industrial emissions, and biogenic emissions.

elemental carbon or light-absorbing carbon: This component accounts for 5% to 10% of the fine mass, depending on whether LAC or BABS is used.

reconstructed mass: The reconstructed mass by either definition generally correlates well with the gravimetric mass, accounting for almost all of the fine mass. About 20% of the unaccounted mass may be nitrate, with the remainder primarily residual water on the particles.