CHAPTER 2

OPTICAL AND AEROSOL DATA

Monitoring of protected visibility areas is conducted on two complementary fronts: 1) optical monitoring of visibility in these areas; and 2) monitoring the concentration and composition of the aerosols in these areas. For optical monitoring, two measurements are possible, extinction (b_{ext}) measured by transmissometers and scattering (b_{scat}) measured by nephelometers. The IMPROVE particulate monitors provide measurements of PM_{10} mass and $PM_{2.5}$ mass. Chemical and elemental analysis of the $PM_{2.5}$ fraction is carried out to identify the fine aerosol species. What follows is a brief description of the IMPROVE monitoring instruments, their operating characteristics, and the data derived from them.

2.1 Transmissometers

Transmissometers are calibrated to measure the irradiance, at a wavelength of 550 nm, of a light source after the light has traveled over a finite atmospheric path. The transmittance of the path is calculated by dividing the measured irradiance at the end of the path by the calibrated initial intensity of the light source. Bouger's law is applied to calculate the extinction. Because of the relatively clean atmospheres found in the western United States, path lengths of a few kilometers are required to achieve the necessary sensitivity to resolve extinctions near the Rayleigh limit.

The transmissometers used in this study are the OPTEC, Inc., LPV-2 instruments, which have been in use since 1986. Their use in remote locations such as national parks is discussed by Molenar *et a1*. [1989], while their use in urban settings is presented by Dietrich *et al.* [1989]. Data processing algorithms that incorporate corrections for interferences are thoroughly discussed by Molenar and Malm [1992]. Basically, there are five checks the data must pass to be incorporated into a validated data set. They are:

1) relative humidity must be less than 90%;
2) maximum extinction cannot exceed a threshold value based on photometer sensitivity and path length;
3) variability in extinction readings taken over a period of one hour cannot exceed a threshold value;
4) rate of change of hourly average extinction measurements cannot exceed a threshold value; and
5) isolated data points. (By definition any hourly average data point passing the above four criteria but falling in between two hourly average data points that have failed the criteria is referred to as "isolated." It is conservatively assumed that it has also been affected by

interferences.)

Molenar *et al.* [1989] discuss the inherent uncertainties associated with the measurement. The accuracy of the transmission measurement, as determined by field and laboratory calibrations, is better than 1%. However, the accuracy of the derived extinction is dependent on the accuracy of the transmission measurement in field conditions. The transmission calculation is determined from an absolute (as opposed to relative) measurement of irradiance of a light source of known intensity that is located some known distance from the receiver. The measurement is made through optics that are exposed to the ambient atmosphere but are assumed to be free of dust or other films, which tend to build up on the optical surfaces. The uncertainties associated with these parameters contribute to the overall uncertainty of the measurement. For a typical 5 km path length the estimated uncertainty is about 4 Mm^{-1}.

2.2 Integrating Nephelometers

Integrating nephelometers measure the scattering of light over a defined band of visible wavelengths from an enclosed volume of air. Historically, integrating nephelometers used in most major field studies have underestimated scattering because of:

1) modification of the ambient aerosol by heating when a large fraction of the sampled aerosol is hygroscopic;
2) inlet, sampling train, and optical chamber design that limits the size of particles that make it into the sampling chamber;
3) optical geometry that causes a truncation of the true scattering volume; and
4) electronics that display large nonlinear drifts in zero and span values.

The OPTEC NGN-2 ambient integrating nephelometer was developed to minimize these limitations of integrating nephelometry. The instrument, which measures light scattering at an effective wavelength of 550 nm, is described in some detail by Molenar *et al.* [1989]. It is an "open air" design that has minimal heating characteristics, and because it is open air it tends to allow a wider spectrum of particles to pass through the instrument. However, the cutpoint of the instrument has not been characterized. It is also designed with solid-state electronics that are very stable over wide temperature and humidity shifts. It still has an inherent limitation of an abbreviated acceptance angle in that it only samples light scattered between 5 and 175^{o}. Calibration of the instrument and data validation and processing algorithms are also discussed in detail in Molenar and Malm [1992].

Unlike transmissometers, where an uncertainty in transmittance leads to an additive error in extinction, uncertainties in nephelometer calibration lead to a multiplicative error in measured scattering. Typical uncertainties for the OPTEC instrument are on the order of 5-10% [Molenar and Malm, 1992].

2.3 Particle Sampling System

The standard IMPROVE sampling module consists of: 1) a size selective inlet; 2) a cyclone to provide a particle size cutoff based on the flow rate; 3) collection substrates; 4) a critical orifice that provides the proper flow rate for the desired particle size cutoff; and 5) a vacuum pump that produces the flow. The system is described in some detail by Malm *et al.* [1994] and Eldred *et al.* [1988] and is only briefly described here.

The sampling system consists of four independent sampling modules. Three modules (denoted A, B, and C) employ a cyclone with a flow rate of 22.7 l/min that allows for collection of fine particles less than 2.5 ìm in diameter [John *et al.*, 1988]. The fourth module (D) is a PM_{10} sampler with a wind insensitive size selective inlet that collects particles less than 10 ìm in diameter. Table 2.1 summarizes the substrates used and aerosol species measured on each filter.

Table 2.1 Filter media and analysis techniques used to determine concentrations of particulate matter species from IMPROVE sampler modules.

Module	Filter Media	Analyses
A	Teflon	gravimetric analysis for mass < 2.5 ìm dia. [1]LIPM for optical absorption [2]PIXE for elements Na to Pb [3]PESA for H
B	nylon (denuded)	ion chromatography for NO_3 and SO_4
C	quartz	[4]TOR for organic and light-absorbing C
D	Teflon	gravimetric analysis for mass < 10 ìm dia.

[1]LIPM - Laser Integrating Plate Method
[2]PIXE - Particle Induced X-ray Emission
[3]PESA - Proton Elastic Scattering
[4]TOR - Thermal Optical Reflectance

Gravimetric mass (channel A fine mass, channel D PM_{10} mass) is measured as the difference between the weight of the substrates before and after sampling, using an electromicrobalance. The channel A Teflon substrates are analyzed for sulfur and other elements by Particle Induced X-ray Emission (PIXE), and simultaneously for hydrogen by Proton Elastic Scattering Analysis (PESA) [Cahill *et al.*, 1986].

The coefficient of light absorption for fine particles, b_{abs}, is also determined from the channel A Teflon substrates using a Laser Integrating Plate Method (LIPM) [Cahill *et al.*, 1986]. This involves direct measurement of the absorption of a laser beam by a sample over the area of the sample.

Extract from the channel B nylon substrates are analyzed by Ion Chromatography (IC) for sulfate and nitrate ions from which the sulfate and nitrate compounds can be estimated [Cahill *et al.*, 1986; Malm *et al.*, 1994].

The channel C quartz substrates are analyzed by Thermal Optical Reflectance (TOR) combustion for organic and elemental carbon [Chow *et al.*, 1993]. Because carbon derived from TOR analysis will be explored in some detail in Chapter 4, a more complete description of the analysis scheme is presented than for the other analytic procedures.

TOR involves: 1) heating a sample through a series of temperature increases or steps (in a pure helium atmosphere to which oxygen is added in the later stages to enable the volatilization of elemental carbon); 2) converting the carbon evolved at each step into CO_2, using an oxidizer (MnO_2 at 912^oC); and 3) reducing the CO_2 to methane, which is then quantified by passage through a flame ionization detector. Over the mid range of the TOR heating (between about 130^oC and 550^oC), charring of the sample occurs, due to pyrolysis of organic particles; this is monitored as a decrease in the reflectance from the sample surface. When the reflectance reaches a minimum, 2% oxygen is added to the atmosphere. This allows the elemental carbon in the sample, including the char produced by pyrolysis of organic matter, to oxidize and the reflectance of the sample increases as the char is removed. All carbon measured up to the point where the reflectance reattains its initial value is traditionally interpreted as organic carbon. Carbon evolved beyond this point is reported as elemental carbon. Overall, the peaks in the carbon evolution from the sample are operationally defined as O1 (25^oC-140^oC), O2 (140^oC-230^oC), O3 (230^oC-450^oC), and O4 (450^oC-550^oC). At 1100 seconds and at 550^oC, 2% oxygen is introduced. The carbon evolved between 1100 seconds and when the sample reflectance returns to its initial value is referred to as pyrolized carbon (OP). The remainder of the carbon evolved at 550^oC and 2% oxygen is labeled as E1. Temperatures are then ramped up to 800^oC in two steps. The evolved carbon is labeled as E2 (550^oC-700^oC) and E3 (700^oC-800^oC). Traditionally, O1, O2+O3+O4+OP, E1, and E2+E3 are referred to as OCLT, OCHT, ECLT, and ECHT, respectively. Organic carbon (OC) is assumed to be the sum of OCLT and OCHT. High temperature carbon, often referred to as elemental carbon or light-absorbing carbon (LAC), is the sum of ECLT and ECHT.

2.4 Determination of Aerosol Types

The fine aerosol species at most continental sites are classified into five major types: sulfates, nitrates, organics, light-absorbing carbon, and soil. Methods for apportionment of measured mass to the various aerosol species are detailed in Malm *et al.* [1994] and only a summary will be presented here. The major aerosol types are composites of the elements and ions measured in IMPROVE samplers, and their concentrations or masses are calculated from the masses of the

measured elements and ions according to their presumed or probable composition and are summarized by Table 2.2. The convention used here to denote the mass concentration of a measured element, ion, or species is to enclose its symbol in brackets ([ ]).

In the West, most sulfur is in the form of ammonium sulfate. In the East, or other environments where ammonia can be limited, it is recognized that acidic species such as ammonium bisulfate and sulfuric acid are not uncommon. However, for a first approximation, all elemental sulfur is interpreted as being in the form of ammonium sulfate, and ammonium sulfate concentrations are estimated by multiplying elemental sulfur concentrations by 4.125. For simplicity, ammonium sulfate is referred to as sulfate.

Table 2.2. The formulae and assumptions applied to IMPROVE sampler measurements to derive the principal fine aerosol species, reconstructed fine mass, and coarse mass. The brackets indicate the mass concentration of the aerosol species or element.

SPECIES	FORMULA	ASSUMPTIONS
SULFATE	4.125[S]	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.
EC (elemental carbon)	[ECLT] + [ECHT]	All high temperature carbon is elemental.
OMC (organic mass from carbon)	1.4{[OCLT]+[OCHT]}	Average organic molecule is 70% carbon.
SOIL (fine 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.
RCFM (reconstructed fine mass)	[SULFATE]+[NITRATE] +[LAC]+[OMC]+[SOIL]	Represents dry ambient fine aerosol mass for continental sites.
CM (coarse mass)	[PM_{10}] - [$PM_{2.5}$]	Consists only of insoluble soil particles.

Assuming, as is the case for sulfate, that the collected nitrate ion is associated with fully neutralized ammonium nitrate aerosol (NH_4NO_3). The mass of ammonium nitrate is estimated by using a multiplication factor of 1.29 and is referred to as simply nitrate.

Organic mass (organics) concentration is estimated by:

$$[OMC] = 1.4([OCLT] + [OCHT]\ ) \qquad (2.1)$$

The factor of 1.4 assumes that organic mass contains a constant fraction of carbon by weight [Watson *et al.,* 1988].

Light-absorbing carbon concentration, usually thought of as elemental carbon, is defined as the sum of E1+E2+E3 or more conventionally as:

$$[LAC] = [ECLT + ECHT] \qquad (2.2)$$

where ECLT and ECHT are the low and high temperature elemental carbon concentrations.

Soil mass concentration is estimated by summing the elements predominantly associated with soil, plus oxygen for the normal oxides (Al_2O_3, SiO_2, CaO, K_2O, FeO, Fe_2O_3, TiO_2), plus a correction for other compounds such as MgO, Na_2O, water, and carbonate. The final equation for fine soil is:

$$[SOIL] = 2.20[Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti] \qquad (2.3)$$

Components of these factors were confirmed in comparisons of local resuspended soils and ambient aerosols in the western United States [Cahill *et al.,* 1981; Pitchford *et al.,* 1981].

The sum of the above five composites should provide a reasonable estimate of the ambient fine mass concentration measured in the atmosphere (RCFM). The equation for RCFM concentration is therefore:

$$[RCFM] = [SULFATE] + [NITRATE] + [LAC] + [OMC] + [SOIL] \qquad (2.4)$$

Coarse mass (CM) is estimated gravimetrically by subtracting fine mass ($PM_{2.5}$) concentration from total aerosol mass (PM_{10}) concentration:

$$[CM] = [PM_{10}] - [PM_{2.5}] \qquad (2.5)$$

In the IMPROVE program additional chemical analysis is not carried out on the coarse fraction. However, it is known that in rural or remote areas of the country the primary constituent of coarse mass is naturally occurring wind-blown dust along with some vegetative material [Noll *et al.,* 1985; Noll, 1991].

The self consistency and overall quality of the aerosol measurements are assured by redundancy and intercomparisons between independently measured species. A detailed description of

validation and quality assurance procedures is available in Malm *et al.* [1994], Sisler *et al.* [1993], and Eldred *et al.* [1988]. In the most general sense, validation is a matter of comparing chemically-related species that have been measured in different channels. Fortunately, the design of the IMPROVE sampler allows for redundancy between certain channel A measurements and channel B and C measurements of the ions and carbons enabling quality control checks. For example, in the IMPROVE network, it was found that elemental sulfur mass times three agrees well with the sulfate ion measured in channel B; validating the assumption that concentrations of sulfate aerosols can be estimated by channel A PIXE analysis [Sisler et al., 1993]. However, when comparing measured fine mass to RCFM, two complicating factors must be dealt with. First, a large portion of the nitrates (≥50%) are presumed to volatilize from the channel A teflon filter; and second, it is presumed that there is residual water on the filters due to the soluble species.

2.5 References

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