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Concentration and Composition of Atmospheric Aerosols from the 1995 SEAVS Experiment and a Review of the Closure between Chemical and Gravimetric Measurements

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ABSTRACT

We summarize the results from the various measurements and the inter-sampler comparisons from Southeastern Aerosol and Visibility Study (SEAVS), a study with one of its objectives to test for closure among chemical, gravimetric and optical measurements of atmospheric aerosol particles. Sulfate and organics are the dominant components

IMPLICATIONS

PM_{2.5} consists of hundreds of compounds that are difficult to measure individually. Therefore, for almost two decades, PM_{2.5} composition has been expressed in terms of three broad constituent categories (ions; elemental carbon and organics; and crustal dust). Any lack of closure in PM_{2.5} mass (i.e., constituent concentrations not adding up to gravimetrically measured PM_{2.5}) was presumed to be due to water present in the samples and measurement error. Here we show that this presumption is not universally correct and that errors in extrapolating organic mass from organic carbon measurements may be plausible explanation. With the public and private sectors on the verge of investing substantial resources in fine PM characterization studies in the wake of new U.S. PM_{2.5} ambient standard, our results underscore the urgency for producing more reliable technology for measuring organics.

of the SEAVS fine particles (nominally, particles with aerodynamic diameter $\leq 2.5 \mu\text{m}$) but between 28 and 42% (range over various samplers) of the gravimetrically measured total fine particle concentration is unidentified by the chemical measurements. Estimates of water associated with inorganic components and measurement imprecision do not totally explain the observed difference between gravimetric and chemical measurements. We examine the theoretical and empirical basis for assumptions commonly made in the published literature to extrapolate total fine particle concentration on the basis of chemical measurements of ions, carbon and elements.

We then explore the more general question of closure using the SEAVS data as well as data from other, similar studies reported in the literature. In so combining the SEAVS measurements with other similar studies, we find a strong association between organic carbon and the unidentified component, that is, the fraction of the total fine particle concentration not identified by chemical measurements. We offer several tenable hypotheses for the relationship between the organic and unidentified components that deserve to be tested in future work. Specifically, we hypothesize that (1) errors in the sampling and analysis of organic carbon; (2) estimates of organic mass from measurements

of organic carbon; and/or (3) water absorption by organics may all contribute to the observed relationship.

INTRODUCTION

Over the past decade, a number of studies have attempted to fully characterize atmospheric fine particles by synthesizing gravimetric measurements of total fine particulate matter (PM) concentration with chemical measurements of constituent concentrations at a variety of urban and rural sites.¹⁻²² Using a mass closure test (a.k.a., a mass balance), the investigators determined whether the physical measurement of gravimetric fine PM concentration of a sample is equal to the summed concentrations of the individually identified chemical constituents in the sample. Mass closure is used to check data consistency although, if achieved, mass closure does not necessarily imply that all components of the aerosol have been identified and quantified. If closure is not achieved the instruments, methods, and assumptions used need to be evaluated to pinpoint areas which need further study.

In these prior studies,¹⁻²² the following five chemical constituents (measured or inferred) were typically able to account for a large percentage of the total fine PM: sulfates and nitrates (with their associated ammonium and hydrogen), elemental carbon, organics, and soil dust (in the form of selected metal oxides). However, despite advances in sampling and analytic techniques, mass closure tests have shown both positive and negative discrepancies between the two measures of concentration, that is, at some sites chemical concentration (estimate of total fine PM concentration derived from chemical measurements) was less than gravimetric fine PM concentration while at others it was greater. Of course some of these differences can be attributed to comparing fundamentally different quantities: typically, chemical measurements do not include water, which is included in the gravimetric fine PM concentration measurement.

In this paper we investigate mass closure using atmospheric measurements of atmospheric aerosol particles. While water content can contribute to differences between chemically and gravimetrically measured concentrations, we demonstrate in this paper that there may be other explanations, such as the assumptions required to calculate chemical concentration and accuracy of the measurements, that contribute to a lack of closure. We first examine data from the Southeastern Aerosol and Visibility Study (SEAVS), a study with one of its objectives to test for closure among chemical, gravimetric and optical measurements. We then explore the more general question of mass closure using the SEAVS data as well as data from other, similar studies reported in the literature.

During SEAVS, investigators used a wide array of instrumentation for measuring aerosol chemistry and mass. Thus

for the same aerosol, several independent data sets were acquired which can be compared to check for measurement accuracy and each can be tested for mass closure. We use the SEAVS mass and composition measurements to (1) determine the accuracy of the measurements, (2) characterize the relative contribution of different components to the fine PM, and (3) reassess the plausibility of common assumptions used in the literature to estimate particle composition from chemical measurements of a handful of ions and elements; specifically, little or untested assumptions concerning water and organic content.

EXPERIMENTAL

The goal of SEAVS was to characterize the aerosol's composition as completely as possible, particularly from the standpoint of relating chemical and optical properties. During the study, atmospheric gases and particles were sampled in the Great Smoky Mountains National Park using an array of instrumentation (see Tables 1a and 1b) and analyzed for mass, chemical composition, optical properties, particle size distributions, and particle diameter and optics as a function of relative humidity (RH) and size.²³ Here we discuss the measurements of fine particle mass concentration and composition.

The experiment was conducted from July 15 through August 25, 1995 (Julian dates 196-137) at Look Rock Ridge (84° W, 36° N; elevation 2700 ft) in the Great Smoky Mountains National Park in Tennessee. The focus of SEAVS was on daytime aerosol properties; all results we present here are for measurements over 12-hr sampling periods (7:00 a.m. to 7:00 p.m. EDT), except one sampler (MOUDI #3, see Table 1a) which was operated over that 12-hr period for five consecutive days in order to collect enough mass for analysis. Chemical and gravimetric concentrations were measured by six institutions: Stanford University, Harvard University, University of Minnesota, Massachusetts Institute of Technology (MIT), University of California at Davis (UCD) and the National Park Service (NPS). The samplers operated by NPS were part of their nationwide IMPROVE (Interagency Monitoring of Protected Visual Environments) network. Tables 1a and 1b summarize the samplers, collection methods, observables, and analytical methods for the particulate and gas measurements. The experiment emphasized redundant measurements to enable an assessment of the reliability of individual measurements as well as closure. Further information on the experimental design and measurement methods can be found in SEAVS field and project reports.^{23,24}

RESULTS

Tables 2a, 2b, and 2c summarize the chemical and gravimetric (i.e., total fine particle mass concentration, hereafter referred to as fine mass, gravimetric mass or fine PM

Table 1a. Summary of fine particulate samplers operated during SEAVS. Collection method, observables, and analytical method are listed. (These samplers were also used for gaseous collection.)

Sampler	Stanford	HEADS	MOUDI	IMPROVE
DESCRIPTION	two 2-stage filter samplers	Harvard-EPA annular denuder system (filter sampler)	micro-orifice uniform deposit impactor (multi-stage impactor)	filter sampler
sampling time	7am-7pm EDT	7am-7pm EDT	7am-7pm EDT	7am-7pm EDT
# of samplers (identity)	2 (Modules 1abc and 2abc) ^d	1	3 (MOUDIs #1, #2, #3)	1 (with Modules A, B, C, and D)
COMMENTS	identical co-located samplers	Two annular denuders in series with filter pack ^b	MOUDI #3 ran for five consecutive days	with annular denuder for HNO ₃
size cut	2.1 µm	2.1 µm	1.8 µm	2.1 µm
OBSERVABLES				
Fine particle mass sampler	Modules 1a & 2a		MOUDI #3: ^e	Module A ^c
(substrate)	(Teflon filters)		(Teflon film)	(Teflon filter)
analysis method	Microbalance (40% < RH < 55%)		Microbalance (35% < RH < 45%)	Microbalance (31% < RH < 45%)
Particulate ions sampler		Sulfate, Nitrate, Ammonium	Sulfate, Nitrate, Chloride	Sulfate, Nitrate, Ammonium
(substrate)		(Teflon filter)	MOUDI #1 ^e	Module B
analysis method		Ion Chromatog.	Ion Chromatog.	Ion Chromatog.
Particulate carbon ^d sampler	Modules 1 & 2		MOUDI #2: ^e	Module C
(substrate)	(quartz filters)		(RH cond) (aluminum foil)	(quartz filters)
analysis method	Thermal Optical Reflectance		Thermal Manganese Oxidation	Thermal Optical Reflectance
Particulate elements sampler	Module 1a		MOUDI #3	Module A
(substrate)	(Teflon filter)		(Teflon film)	(Teflon filter)
analysis method ^a	INAA		INAA	PIXE + XRF
Strong Acidity sampler		Strong Acidity (H ⁺)		
(substrate)		(Teflon filter)		
analysis method		Potentiometry		

^aINAA measures the following elements: Na, Mg, Al, Cl, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, As, Se, Br, Rb, Sr, Zr, Mo, Cd, In, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Au, Hg, Th, U. PIXE+XRF measures the following elements: Na, Mg, Al, Cl, K, Ti, V, Cr, Mn, Fe, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Si, P, S, Ca, Ni, Cu, Pb. ^bDenuders (NH₃, HNO₃, SO₂) followed by a Teflon filter followed by three glass fiber filters to collect volatilized nitrate and ammonium. ^cIMPROVE module D was used to measure PM₁₀ (particulate matter with aerodynamic diameter ≤ 10 µm). ^dSee discussion in text. ^eMOUDIs #1 and #2 were operated at a controlled RH (approximately between 70 & 80%); MOUDI #3 was operated at ambient RH.

mass) measurements from the particulate samplers. The first set of columns list the study average mass concentrations of the individual chemical components for each sampler while the remaining columns provide the inter-sampler coefficient of determination (r^2) (an indication of data correlation) for the concentration data. We discuss the results in these tables in more detail in the corresponding sections. Figure 1(a-f) shows time variation of the gravimetric fine particle concentration and concentrations of the specifically measured components. Figure 1g shows the time variation of the SEAVS crustal component; this was calculated, using measured elemental

concentrations, in conjunction with the sum of oxides method discussed later in this paper. These plots demonstrate the broad dynamic range of constituent concentrations over the study period and show that the concentration range of the individual observables varied by up to two orders of magnitude during the study period. Furthermore, it can be seen that while some of the components seem to rise and fall together (e.g., sulfate and ammonium) other components (e.g., soil dust) exhibit rather unique time fluctuations. These figures also give some idea of the inter-sampler agreement (or disagreement) for individual constituents, that is, the sulfate

Table 1b. Summary of gaseous samplers operated during SEAVS. Collection methodology, observables, and analytical methodology are listed. (These samplers are also used for particulate collection.)

Sampler	Stanford	HEADS	IMPROVE
DESCRIPTION	two 2-stage filter samplers	Harvard-EPA annular denuder system	filter sampler preceded by annular denuder
OBSERVABLES			
gaseous organics	Adsorbed organic gases		adsorbed organic gases
sampler (substrate)	Modules 1a & 2a, 1b & 2b (quartz filters and after-filters)		Module C (quartz filter and after-filter)
analysis method	Thermal Optical Reflectance		Thermal Optical Reflectance
gaseous inorganics		Nitric Acid and Sulfur Dioxide (gas)	Nitric acid gas
sampler(substrate)		(sodium carbonate coated denuder)	Module B (potassium carbonate coated denuder)
analysis method		Ion Chromatography	Ion Chromatography
		Ammonia (gas)	Ammonia gas
sampler(substrate)		(citric acid coated denuder)	Module A (citric acid impregnated quartz after-filter)
analysis method		Colorimetry	Automated colorimetry
			Sulfur Dioxide
sampler(substrate)			Module D (sodium carbonate impregnated quartz after-filter)
analysis method			Ion Chromatography

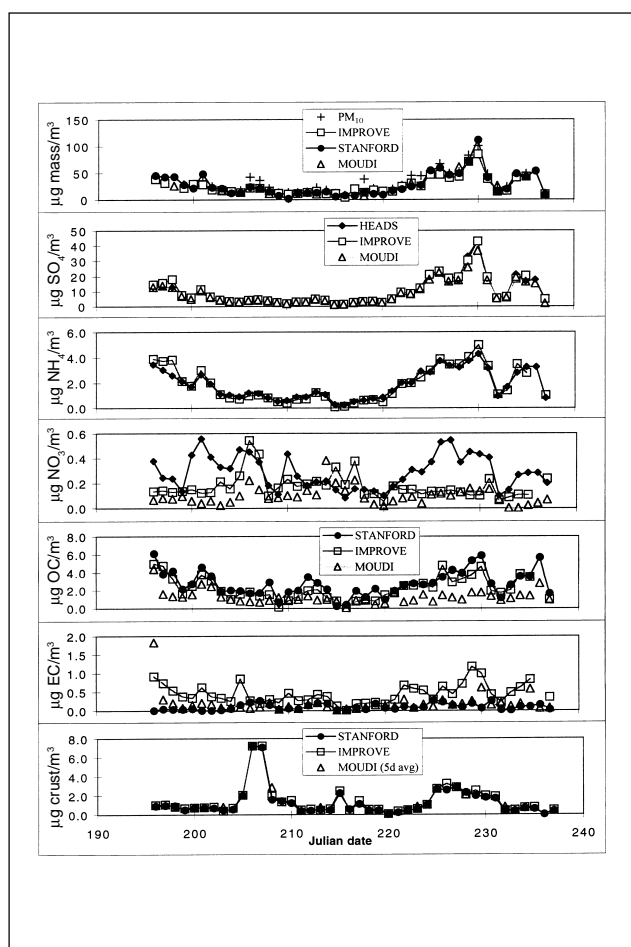


Figure 1. Time series of constituents concentration during SEAVS for (a) fine PM and PM_{10} , (b) sulfate, (c) ammonium, (d) nitrate, (e) elemental carbon, (f) organic carbon, (g) soil dust calculated as = $2.14^{\circ}Si + 1.89^{\circ}Al + 1.43^{\circ}Fe + 1.67Ti + 1.4^{\circ}Ca + 1.2^{\circ}K$.

measurements appear to lie on top of each other for the different samplers while the nitrate measurements do not. The details of the individual component measurements are discussed below.

Particulate Matter

Gravimetric Measurements—Particles. Here, fine mass is defined as the concentration of particles with aerodynamic diameters less than a nominal value of $2.5 \mu m$, with inlet size cuts for individual samplers during SEAVS being 1.8 and $2.1 \mu m$. SEAVS measurements showed that gravimetrically measured fine mass (Figure 1a) comprised, on average, approximately 80% of PM_{10} mass (total concentration of particles with aerodynamic diameters less than $10 \mu m$) measured in the Great Smoky Mountains National Park during the study. Average fine mass ranged from 23.5 to $28.0 \mu g/m^3$ depending on the sampler. Over the period of the study, there were wide variations in particulate matter concentrations (e.g., concentrations ranged from less than 10 to greater than $100 \mu g/m^3$). The fine mass measurements were well correlated ($r^2 \geq 0.92$) across four samplers (Table 2b), although study average mass differed by up to 20%. The differences in inter-sampler measurements may be due to cut-point differences of the individual samplers (MOUDI: $1.8 \mu m$; IMPROVE and Stanford: $2.1 \mu m$), differences in relative humidity of weighing (MOUDI: 35 to 45% humidity; IMPROVE: 31 to 45% humidity; Stanford: 40 to 55% humidity), differences in the filter collection or cyclone efficiencies, accuracy and precision of weighings, and/or volatilization or sorption of compounds with a substantial vapor pressure, including water, during or after sampling.

Table 2a. Study average fine particle concentrations for inorganic components and intersampler correlations.

Component	Mass Concentration ^a (μg/m ³)			Coeff. of Determination ^b (r ²)		
	IMPROVE	HEADS	MOUDI	IH	IM	MH
Sulfate	9.7	9.1	8.7	0.97	0.99	0.98
Nitrate	0.2	0.3	0.1	0.016	0.28	0.003
Ammonium	1.8	1.8	N/A	0.95	N/A	N/A

^aIMPROVE samples were analyzed at Research Triangle Institute, HEADS samples at Harvard and MOUDI samples at Desert Research Institute; ^bIH is the IMPROVE/HEADS comparison, IM is the IMPROVE/MOUDI comparison, MH is the MOUDI/HEADS comparison; N/A: Not available; all correlation coefficients are derived using Deming⁶⁵ regression model.

Table 2b. Study average fine particle concentrations for total gravimetric mass and carbon components and their intersampler correlations.

Component	Mass Concentration ^a (μg/m ³)				Coeff. of Determination ^b (r ²)			
	IMPROVE	Stanford1&2		MOUDI ^d	IS	IM ^e	MS ^e	SS
PM10	33.2	N/A		N/A	N/A	N/A	N/A	N/A
Fine PM	25.4	28.0	26.4	23.5	0.92	0.98	0.97	0.93
EC ^c	0.4	0.1	0.1	0.2	0.0	0.29	0.0	0.0
OC ^c	2.2	2.8	2.5	1.2	0.78	0.45	0.57	0.83
TC ^c	2.6	2.9	2.6	1.4	0.80	0.46	0.54	0.83

^aIMPROVE samples were weighed at UC Davis and analyzed for carbon at Desert Research Institute; Stanford samples were weighed and analyzed for carbon at Stanford; MOUDI samples were weighed at Harvard and analyzed for carbon at AtmAA; for all three samplers, gravimetric (Teflon) and carbon (quartz) measurements stem from two identical co-located samplers; ^bIS is the IMPROVE/Stanford1&2 average comparison, IM is the IMPROVE/MOUDI comparison, MS is the MOUDI/Stanford1&2 average comparison, and SS is Stanford 1&2 comparison; all correlation coefficients are derived using Deming⁶⁵ regression model; ^cEC is elemental carbon, OC is organic carbon, and TC is total carbon; ^dMOUDI data are 5-day sample for fine PM; ^eIM and MS are derived from 5-day averages of IMPROVE and Stanford1&2 average for comparison with MOUDI fine PM.

Table 2c. Study average mass concentrations for elemental components and intersampler correlations for elements used in sum of oxides calculation of crustal mass concentration.

	Mass Concentration ^a (ng/m ³)			r ²	
	IMPROVE	Stanford	MOUDI ^b	IS ^c	IM ^c
Fe	79.1	92.6	53.9	0.95	0.97
K	85.3	57.5	52.5	0.59	0.83
Al	216.	170.	171. (103.)	0.91	0.015 (0.98) ^d
Ti	44.4	21.6	5.5	0.64	0.79
Si	384.	-	-	-	-
Ca	62.4	-	-	-	-

^aStanford and MOUDI sampler were analyzed by INAA at MIT; IMPROVE samples were analyzed by PIXE+XRF at UCD; ^bMOUDI data are for a 5-day samples, we averaged IMPROVE over same 5-day periods and then compared; ^cAll correlation coefficients are derived using Deming⁶⁵ regression model; ^dValues in parentheses represent statistics for MOUDI after removing one outlier (n=7 instead of 8) for which no clear explanation was found.

Chemical Measurements—Particles. Table 2a summarizes the SEAVS study-average measurements for inorganic components. Inorganic components are, historically, the most widely studied constituents of the atmospheric aerosol,

and sampling and analysis methods for them are well characterized. Hence, agreement between the different samplers for inorganic ion measurements provides both some indication of the samplers’ ability to collect the same aerosol and the accuracy of the analytical method. Because many of the inorganics found in the atmosphere are hygroscopic and may contain water at humidities at which the filters are weighed,²⁵ it is necessary to be confident in the measured composition of the inorganic ions in order to determine the influence of associated water on gravimetric mass. Average inorganic component concentrations for SEAVS (range over different samplers) were 8.0 to 9.7 μg/m³ sulfate, 0.1 to 0.3 μg/m³ nitrate, and 1.8 μg/m³ ammonium. Sulfate and ammonium measurements agreed among the different samplers (sulfate: r² > 0.95; ammonium: r² = 0.95) while nitrate concentrations showed poorer agreement (r² < 0.28) probably because the measurements were close to or in the noise range (i.e., typically near or below the lower detection limit (LDL) of 0.12, 0.08 and 0.17 μg/m³ for HEADS, IMPROVE and MOUDI, respectively). Although volatilization of nitrate during collection or handling can be an important consideration for some locations and sampling techniques,²⁶ given the sample collection, storage and analysis procedures used by Harvard and NPS/UCD, it was probably not a factor in the observed lack of agreement.

Particulate sulfate was not completely neutralized by ammonium: study-average molar ratios of ammonium-to-sulfate ranged from 1.1 to 1.4. This is important as this ratio is indicative of the acidity and water content of the aerosol. The ion balance (from the HEADS sampler) was, on average, within $\pm 10\%$ and neither anions nor cations were systematically more abundant: this suggests no significant ionic components were missed.

Accurate measurement of the carbon content of particulate matter is notoriously difficult and previous studies^{1,27} have shown substantial scatter among the carbon measured by different co-located samplers as well as among total carbon apportioned into organic and elemental components by different laboratories. In this study (see Table 2b), while statistically meaningful relationships among the particulate organic carbon and total carbon values were found, the accuracy of the measurements (as gauged from the closeness to one another of the values derived from various samplers) was poorer than that for sulfate, even for two co-located samples collected and analyzed using identical hardware and procedures by Stanford. As we discuss next, scatter among the measurements, as well as biases (as much as a factor of two) contribute to these differences. Whereas the differences between the IMPROVE and Stanford samplers were randomly distributed, the MOUDI observations are approximately a factor of 2 less than the other samplers, for which we have no clear explanation. This is opposite to what was observed by Turpin et al.¹ at the Grand Canyon, where MOUDI derived total carbon concentrations were almost twice those measured by a co-located IMPROVE sampler. The average concentrations (range over the different samplers) were 1.2 to 2.8 $\mu\text{g}/\text{m}^3$ organic carbon and 0.1 to 0.4 $\mu\text{g}/\text{m}^3$ elemental carbon. (Note that the OC values given in the Table 2b are measured organic carbon, and not the measured mass of organics.) One potential cause of the inter-sampler differences could be differences in how the samples were collected and how the concentration of organic carbon was inferred. These are discussed below.

During SEAVS the investigators employed both filter-based samplers and impactors, each of which are subject to different limitations. Impactors and filters may both lose organics from the collected particles due to volatilization. There is currently no reliable means of characterizing the amount of particulate organic lost due to evaporation²⁸ and most studies (including our analysis) have assumed it negligible. In addition, quartz filters adsorb organic gases, and the particulate organic carbon concentration is deduced by subtracting an estimate of adsorbed gases. Both Stanford and IMPROVE collected daily samples of organic gases-plus-particles on quartz filters (Q1), however, their procedure to estimate adsorbed organic gases was different. Stanford used (in parallel with

Q1) a two stage filter pack with a Teflon filter first to remove particulates followed by a quartz after-filter (Qaf) to collect organic gases. The mass of organic carbon (presumed to be adsorbed gases) on Qaf was subtracted from the mass of organic particles-plus-gases on Q1 (i.e., mass of particulate organic carbon = $Q1 - Qaf$) for each day's sample. IMPROVE used a quartz after-filter (Qaf) in series with Q1 for each day's sample. The mass of organic gases collected on each day's after-filter was averaged over the study period and this average was subtracted from each day's measurement of the organic gas-plus-particle masses (i.e., mass of particulate organic carbon = $Q1 - \text{avg}(Qaf)$). The MOUDI measurements of OC were not adjusted for adsorbed organic gases as the aluminum foil substrates do not adsorb organic gases.

As mentioned above, gaseous organic compounds were measured to estimate the magnitude of the interference with the particulate organic measurements. It should be noted that the gas phase organic carbon quantified here is not representative of the atmospheric concentration of organic gases but rather that portion of atmospheric organic gases which interferes with organic particulate measurement. For the Stanford samplers, the study-average concentration of gas phase organics was 1.8 $\mu\text{g}/\text{m}^3$ (obtained from the Qaf above). This was calculated using the total air volume sampled (9.33 m^3) and the average OC mass on the back up filter (16.8 μg). A substantial portion of the total organic material sampled was gaseous (between 20 and 100%, with an average value of approximately 40%). For the IMPROVE sampler, the study average fraction of adsorbed gaseous OC was also approximately 40%; the study median concentration of gas phase organics was 1.6 $\mu\text{g}/\text{m}^3$ (total air volume sampled = approximately 16.6 m^3 ; median OC mass on the back up filter = 26.3 μg). For comparison, in the observations reported by Turpin et al.²⁹ for Claremont, CA (an urban area with much greater PM loading than SEAVS), the gas-phase organics ranged from approximately 10 to 40% of the total. In summary, the interference from organic gases is substantial, and although the particulate concentrations have been adjusted for this, the assumptions for doing so are ad hoc and can introduce substantial error. For instance, if volatilization of organics was substantial, then the carbon on the after-filter would represent particle phase carbon that evaporated during sampling rather than, or in addition to, gaseous phase compounds. These results underscore the message that the technology for measuring particulate organic and elemental carbon warrants improvements. Nonetheless, despite the inter-sampler differences and uncertainties in the organic carbon measurements, all carbon measurements suggest that organic carbon is an important component of particles sampled during SEAVS.

Since soil dust (also known as crustal material, that is, the inorganic material stemming from the earth's crust), is a mixture of many minerals, its concentration (and thus contribution to fine PM mass) cannot be measured directly and is usually estimated from elemental concentrations. For SEAVS two types of elemental analysis were done: instrumental neutron activation analysis (INAA) and proton induced X-ray emission and X-ray fluorescence (PIXE+XRF). These instruments measure different, though overlapping elements (see Table 1a). Table 2c lists study average mass concentrations and intersampler correlations found for elements used in the crustal calculation by the sum of oxides method described below. The dust concentrations can be estimated from measurements of specific elements using two techniques: the sum of oxides method^{12,13,30} and the principal component analysis (PCA) method.³¹ The sum of oxides method, in particular, is the method most commonly used to derive dust concentration from elemental data in atmospheric studies. We describe both techniques below and, because the sum of oxides method is so prevalent, we examine how effectively it estimates dust concentration. We discuss the suitability of each technique for mass closure tests in the mass closure section of this paper.

The sum of oxides method assumes that dust is composed solely of the oxides of six elements (SiO_2 , Al_2O_3 , Fe_2O_3 , TiO_2 , CaO and K_2O) as these oxides are six of the eight most significant compounds found in the continental crust^{32,33} and are typically used as crustal markers.³⁴ (Na_2O and MgO also contribute to the earth's crust [approximately 3% each], however, as they are also often associated with marine particles,⁹ they are excluded from the dust calculation.) The mass concentration of dust is thus given by the equation: $\text{dust} = 2.14 \cdot \text{Si} + 1.89 \cdot \text{Al} + 1.43 \cdot \text{Fe} + 1.67 \cdot \text{Ti} + 1.4 \cdot \text{Ca} + 1.2 \cdot \text{K}$, where Si, Al, Fe, Ti, Ca and K are the measured element concentrations. (Other researchers have used slightly different sets of elements, e.g., Salmon et al.⁸ also include Mn; while Malm et al.,^{12,13} estimate K from expected K/Fe ratios for soil; and Gone et al.,³⁵ use Mn instead of Ti.) The use of only six compounds to estimate dust concentrations may lead to underestimation, as other compounds may also contribute. In addition, not all metals come from dust, not all metals in dust are present as oxides, and some metal oxides may react with ions on the filter thus altering the contribution of dust to filter sample versus airborne particles. To check the effectiveness of the sum of oxides technique for estimating dust concentration, we applied it to measured elemental compositions for soil samples from a variety of locations across the United States³⁶ and found that only 50-90% of the measured sample mass (depending on the soil) is accounted for using the sum of oxides technique.

PCA uses a receptor model to combine co-varying variables into sets of factors. If source or region profiles

are known, then the factor can be attributed to a particular source type (e.g., crustal material) using marker elements or elemental ratios specific to the source and, hence, the source contribution to the sample can be estimated. For the SEAVS study, Gone et al.³⁵ identified the crustal factor by the predominance of Al and Fe, with Sc and Sm acting as additional markers for the Stanford and MOUDI samples (analyzed by INAA), and Si, K and Ca for the IMPROVE samples (analyzed by PIXE-XRF).

Using the sum of oxides technique, we estimated study average dust concentrations to be between 1.3 and 1.4 $\mu\text{g}/\text{m}^3$ (range over samplers). For PCA the study average range over the samplers was 2.2 to 2.8 $\mu\text{g}/\text{m}^3$.³⁵ The estimated dust concentrations using these two techniques were highly correlated ($r^2 \geq 0.95$), although the dust concentration calculated using PCA was approximately a factor of 2 greater than the concentration calculated using the sum of oxides method. The higher PCA dust concentration is not surprising as the sum of oxides method does not include all components known to contribute to dust; moreover, the PCA result will include other components which co-vary with crustal dust: for instance, organic soil constituents such as humic materials.³⁵ Thus using PCA may result in counting some components (e.g., some portion of organics) twice: first as "organics" as inferred from carbon measurements and second as "dust" as estimated by PCA. In summary, our best estimate is that the actual dust concentration is probably bounded by these two methods with PCA providing an upper bound and sum of oxides a lower bound.

Gaseous Measurements. SO_2 concentrations measured by the HEADS and IMPROVE samplers were correlated ($r^2 = 0.82$), although the values from HEADS were approximately a factor of four greater than those measured by IMPROVE. The average concentrations were 2.8 and 0.8 $\mu\text{g}/\text{m}^3$ for HEADS and IMPROVE, respectively. It is known that the IMPROVE aluminum tube inlet adsorbs SO_2 although the amount and mechanism is not certain (personal communication, Eldred, 1996) hence a reasonable hypotheses for the systematically lower value measured by IMPROVE is that the SO_2 reacted with the eight foot aluminum inlet tube used in that sampler. Such adsorption was demonstrated by Wohlers,³⁷ though for much higher SO_2 concentrations. Concentrations of ammonia gas were low, close to the LDLs (0.03 and 0.66 mg/m^3 for IMPROVE and HEADS, respectively) and have little relationship among the samplers; such an ammonia-deficient atmosphere is consistent with the measured acidity and incomplete neutralization of sulfate.

Mass Closure and Contributions to Fine Mass. In this section, we compare gravimetric mass with the sum of the concentrations of the various components inferred from

chemical measurements. This exercise, referred to as a test for mass closure, serves as a test of the mutual consistency of various observations. Moreover, it makes possible quantification of the contribution of various constituents (e.g., sulfate, organics) to total fine mass. We analyze the discrepancies between the gravimetric measurements and the mass estimated from chemical measurements and discuss their implications.

Two conceptual difficulties arise in comparing gravimetric and chemical measurements. First, the chemical measurements are incomplete: for some components such as sulfate, nitrate and ammonium, chemical methods measure the concentration of the component itself; however, for other components (e.g., organics and dust), chemical methods measure the concentration of a specific set of atoms in that component; and therefore, assumptions are necessary to relate the concentration of these atoms to their corresponding molecules. For crustal components there are the two methods mentioned previously: sum of oxides and PCA. For organic compounds, it is commonly assumed in the literature that, on an average, for every gram of carbon, organic compounds in fine particles contain 0.4 gram (sometime 0.2 gram) of other elements such as oxygen, hydrogen and nitrogen (e.g., 1, 5). In other words, the organics concentration is estimated by multiplying the measured organic carbon concentration by 1.4. This value was first derived by White and Roberts³⁸ on the basis of measurements by Grosjean and Friedlander.³⁹ Grosjean and Friedlander³⁹ sampled particulates in Pasadena, CA, extracted organic compounds from these particulates using various combinations of solvents (e.g., water, cyclohexane and a mixture of isooctane-isopropyl alcohol), fractionated them into different organic compound groups (e.g., aliphatics, aromatics, oxygenated, etc.) using the Tabor procedure⁴⁰ and analyzed the fractions for carbon, hydrogen, oxygen and nitrogen. Using Grosjean and Friedlander's data, White and Roberts estimated the average mass percentage of carbon in the measured organics to be 73%. The inverse gives the ratio of the weight of organics to organic carbon: 1.4. While this ratio is a useful estimate, it was derived from only two total suspended particulate (TSP) samples collected at one urban site 25 years ago. Therefore, the ratio of 1.4 is unlikely to be reliable as a universal factor for all locations and times. More recent studies have questioned this assumption^{41,42} (also, personal communication, B. Turpin, Rutgers University, 1998) although a reliable alternate is not available. The tenuousness of the 1.4 value must be kept in mind as we test for mass closure with SEAVS fine particle data.

Second, fine mass (as measured gravimetrically at relative humidities between 31 and 55%) contains an unknown contribution from water. According to solution theory, the fine particle water content would depend upon

the fine PM composition and relative humidity at which filters were weighed: since both of these quantities vary from day to day, the absolute and the relative quantity of water would also vary from day to day. Although, water content has been inferred using special instruments in SEAVS⁴³ and a few other studies⁴² for particles of specific sizes, the total water content of fine particles was not measured in SEAVS due to a lack of reliable technology.

We will test for mass closure by first keeping aside these conceptual difficulties and later by factoring them into our analysis. In the case of the SEAVS data, there are several choices of sampler for each observable when testing for mass closure. From all the possible combinations, we chose the five combinations in Table 3. Using these combinations, we compare fine mass measured using three samplers (i.e., MOUDI, Stanford, IMPROVE) with the corresponding chemical measurements from these samplers. If a chemical component was not measured by the individual sampler, concentration from a different sampler is used (e.g., HEADS inorganic ions measurements were used in conjunction with the Stanford fine mass, carbon and elemental data) or assumed on the basis of other samplers' measurements (e.g., the ammonium-to-sulfate ratio from HEADS was used to estimate the ammonium concentrations corresponding to the MOUDI sulfate data). Using these procedures, we compare fine mass obtained gravimetrically with the sum of component concentrations (ions, organics, elemental carbon, dust and other elements).

High correlation between fine mass and the sum of concentrations of measured and inferred components ($r^2 = 0.94, 0.92, 0.96, 0.94, 0.96$ for combinations 1 through 5, respectively) indicates a strong consistency among chemical and gravimetric measurements; however a clear bias is also evident (see Table 3 and Figure 2). The sum of the chemical components was consistently less than the gravimetrically measured fine mass for all five sampler combinations. We depict the excess of fine mass (or deficit in sum of component concentration) as an "unidentified component" (Figure 2). For individual days, the difference between gravimetric and chemical mass (i.e., sum of measured and inferred components) was the greatest toward the end of the study (Julian dates 225 to 231) when the meteorology suggested that the aerosol could be considered to be strongly influenced by anthropogenic emissions.⁴⁴ We also found substantial differences between gravimetric and chemical mass at the beginning of the study (Julian date 196-204): there were nearby forest fires observed during this time period.²⁴ For both periods, fine PM levels and elements indicative of anthropogenically influenced air (As, Se, Br and Sb)³⁵ were higher than those during other parts of the study. Depending upon the sampler combination, the study-average deficit in composition (the unidentified component in Figure 2) ranged

Table 3. Sampler combinations used in testing for fine PM mass closure.

Quantity	Sampler Combin. 1	Sampler Combin. 2	Sampler Combin. 3	Sampler Combin. 4	Sampler Combin. 5 ^a
gravimetric mass	IMPROVE	IMPROVE	Stanford	Stanford	MOUDI
ions	IMPROVE	IMPROVE	HEADS	HEADS	MOUDI ^b
carbon	IMPROVE	IMPROVE	Stanford	Stanford	MOUDI
dust	IMPROVE (oxides)	IMPROVE (PCA) ^d	Stanford ^c (oxides)	Stanford (PCA)	MOUDI ^c (oxides)
slope ^e	0.68	0.71	0.58	0.59	0.59
r ²	0.94	0.92	0.96	0.94	0.96

^a5-day averages; ^bUsing HEADS ammonium-to-sulfate ratio to calculate ammonium; ^cUsing IMPROVE Ca and Si elemental data for oxide calculation (Ca and Si are not measured by INAA); ^dPCA calculations were performed at MIT (Gore et al., 1997); ^eSlope is for regression line (sum of components = slope * grav. mass) constrained to pass through the origin; all correlation coefficients are derived using Deming⁶⁵ regression model.

between 28 and 42% of the fine mass, while for the individual (12-hr) samples the deficit in composition ranged from -290% to 70%. The large (-290%) unidentified extreme for the daily sample is most likely due to measurement noise as it was derived for a day when the concentrations of all measured components were low (Julian day 210).

We used error analysis as follows to determine whether the calculated unidentified component is within measurement uncertainties. Since the measurements of individual chemical components and the fine mass have some error associated with them, these can be used to calculate the overall uncertainty in the estimated concentration of the unidentified component for each day. First, we assume that the errors in the measurements of the individual components and in the fine mass are independent. Then, using propagation of error analysis, the error in the sum of components is found using the square root of the squared errors of the individual components making up the chemical mass concentrations

$$E_{\Sigma \text{ components}} = [(E_{\text{SO}_4})^2 + (E_{\text{NH}_4})^2 + (E_{\text{NO}_3})^2 + (E_{\text{org}})^2 + (E_{\text{EC}})^2 + (E_{\text{soil}})^2]^{1/2} \quad (1)$$

where E_j represents the uncertainty in component j . Similarly, the uncertainty of the difference between the total fine PM concentration and sum of chemical components (i.e., the unidentified component) can be estimated

$$\sigma = E_{\text{diff}} = [(E_{\Sigma \text{ components}})^2 + (E_{\text{fine mass}})^2]^{1/2}. \quad (2)$$

Errors in the concentration of individual chemical components as well as fine mass measurements were calculated by the experimentalists using replicate samples acquired during the study as follows. The variance for each set of replicate measurements was calculated and

these variances were then used to calculate the uncertainty in each measurement. Figure 3a compares the uncertainty ($\pm\sigma$) in the concentration of the unidentified component (E_{diff}) with the concentration of the unidentified component for sampler combination 3 (Table 3). Since the known measurement errors of the fine mass and sum of components represent random imprecision, statistically we would expect the concentration of unidentified component to be randomly distributed around a value of zero, if it stemmed solely from measurement uncertainties. Our error analysis, however, shows that the concentration of the unidentified component is positive for all 40 days for sampler combinations 1 and 2, for 41 out of 42 days for the sampler combinations 3 and 4, and for all eight 5-day periods for the sampler combination 5. Furthermore, the unidentified component is larger than its uncertainty for all 40 days for sampler combinations 1 and 2, 31 out of 42 days for the sampler combinations 3 and 4 and for all eight 5-day periods for the sampler combination 5. Hence, measurement errors alone do not explain our observed concentration of an unidentified component.

A large unidentified contribution to the total fine PM concentrations has implications for relating aerosol chemistry and composition to other properties such as optics, inhalation toxicity, or cloud formation. For instance, scientists often estimate light scattering in the atmosphere on the basis of measured concentration of various components, their size distribution, density, refractive index and water content.⁴³ If the unidentified component manifests a real uncertainty, then this uncertainty permeates all of these properties (composition, refractive index, etc.) and to calculations of scattering efficiencies and extinction coefficients. Hence, creating a tenable hypothesis to explain this unidentified component is our goal and the focus of the next section of this paper.

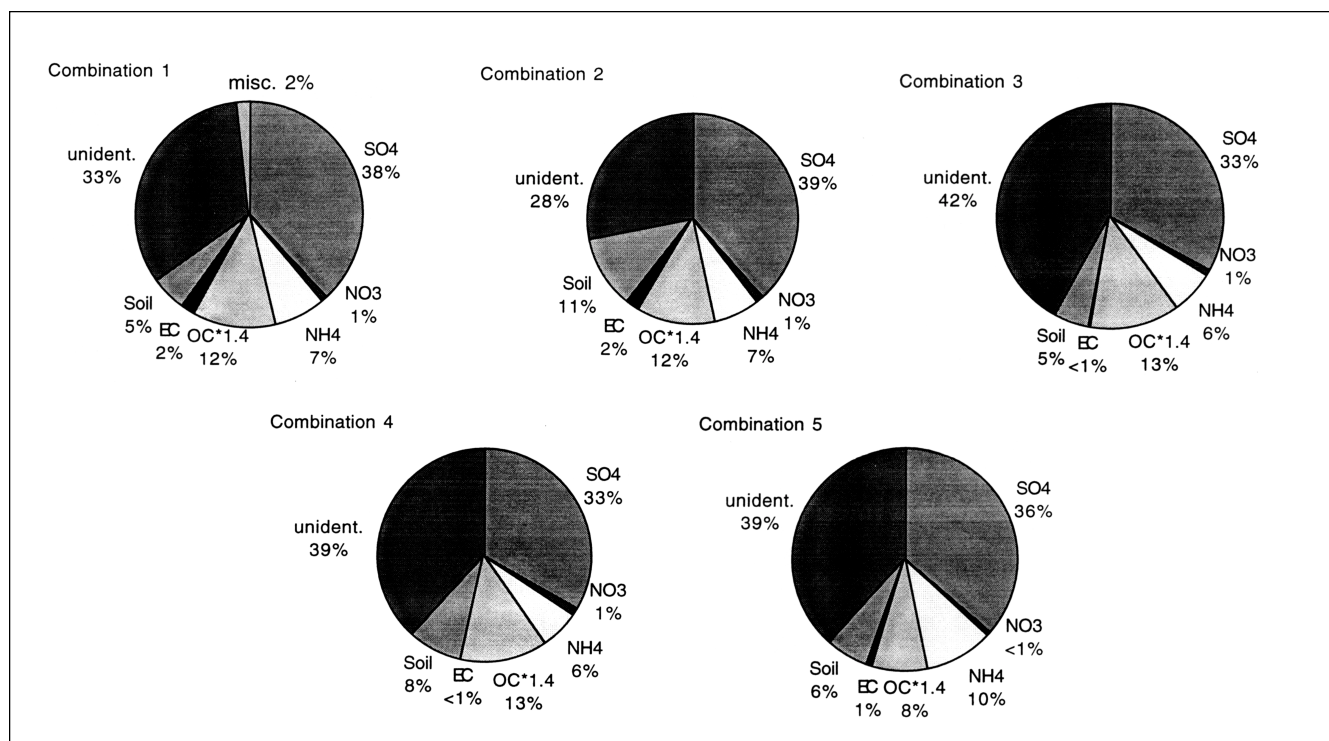


Figure 2. Consistency of chemical and gravimetric measurements of study average concentrations of total fine PM mass and particle composition (a) Combination 1 - IMPROVE samplers (using dust estimated by sum of oxides); miscellaneous is sum of concentration of remaining elements measured by PIXE+XRF not used in estimating dust concentration, (b) Combination 2 - IMPROVE samplers (using dust estimated by Principal Component Analysis), (c) Combination 3 - Stanford and Harvard samplers (using dust estimated by sum of oxides) miscellaneous is sum of concentration of remaining elements measured by PIXE+XRF not used in estimating dust concentration, (d) Combination 4 - Stanford and Harvard samplers (using dust estimated by Principal Component Analysis), (e) Combination 5 - MOUDI (Minnesota and MIT) samplers (using dust estimated by sum of oxides); NH₄ estimated using HEADS SO₄/NH₄ ratio.

Possible Sources of the Unidentified Component. In addition to measurement error, which we have discounted as the sole source of the unidentified component, other possible causes are:

- Contribution of dust being different than estimated from sum of oxides or PCA;
- The gravimetric measurement of fine mass does not accurately represent the samples analyzed chemically due to the differences in the inlet size cuts for different samplers, (e.g., filters used for gravimetric measurements collect more material than those used for chemical analysis);
- Contribution of water (associated with sulfate, organics and/or dust components) to total fine mass; and
- Contribution of organics being larger than what we estimated either due to sampling and analysis errors or due to the untested assumption that the total concentration of organic compounds is 1.4 times the concentration of organic carbon.

Below, we test our hypotheses about measurement differences, examine other plausible explanations for the unidentified component, and examine whether our results for SEAVS are peculiar compared with similar published results.

A possible (but unlikely to be substantial) explanation for the unidentified component is errors in the calculated crustal component for the following reasons. First, the contribution of dust to the aerosol may be underestimated by the sum of oxides method. The sum of oxides method uses only six compounds to estimate dust concentrations, while, as discussed previously, additional compounds may also contribute to dust concentrations. We found that, for specific soils, mass estimated using the sum of oxides technique could be lower than the actual soil mass by up to 50%. However, as we discussed before, the actual dust concentration probably lies between the results estimated by the sum of oxides technique and PCA; hence on average the dust contribution is limited to between 5 and 11% for SEAVS and its uncertainty cannot explain the magnitude of unidentified component. Second, some oxides used in the dust calculation are hygroscopic (i.e., K₂O which converts to KOH in water), so there may be some water associated with dust. Using composition and water activity data for KOH,⁴⁵ we calculate that there is approximately 4.3 g water/g K at 55% relative humidity. Study average concentrations of K were between 0.05 and 0.08 µg/m³ (range over different samplers); therefore, the average water content associated with K would

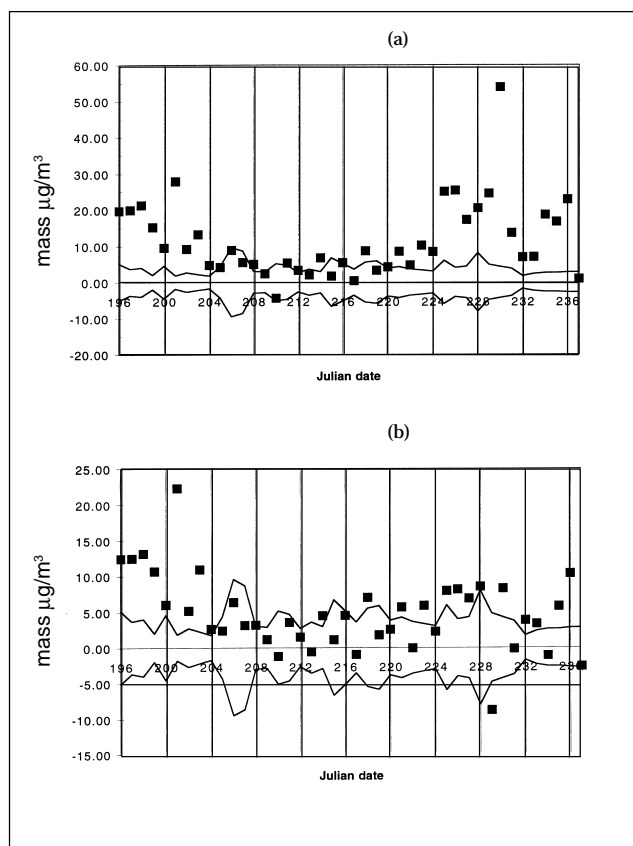


Figure 3. (a) Concentration of unidentified component versus its uncertainty for sampler combination 3. (Squares represent concentration of unidentified component; lines represent $\pm 1\sigma$ measurement uncertainty, i.e., $\pm 1\sigma$); (b) after accounting for the maximum amount of water associated with sulfate, versus its uncertainty for sampler combination 3. (Squares represent concentration of unidentified component; lines represent $\pm 1\sigma$ measurement uncertainty, i.e., $\pm 1\sigma$).

be equivalent to about 1% of the fine mass. Hence, we can also rule out water associated with dust as a major source of unidentified component.

The different inlet size cuts of the various samplers are unlikely to contribute to the mass closure discrepancy: in this paper, we used sampler combinations (see Table 1a and 3) that were consistent, (e.g., we subtracted the chemical mass measured and inferred from MOUDI measurements from the fine PM mass measured using the MOUDI).

Measurements during SEAVS and prior studies support the thesis that water contributes substantially to the unidentified component. Atmospheric particles contain water at relative humidity as low as 20% and, for a given aerosol, the amount of water absorbed by particles increases with increasing relative humidity.^{1,42,43,46} During gravimetric measurements, the filters are allowed to equilibrate and are weighed in a controlled relative humidity chamber; we expect that the humidity of the weighing chamber would influence the amount of water included in the gravimetric mass depending on the thermodynamic properties of the sampled particles. Stanford typically

weighed their filters between 40 and 55% relative humidity while the IMPROVE samples were weighed at humidities between 31 and 45%. When six of the Stanford samples were reweighed at lower humidity (between 20 and 30%), they showed a weight decrease of between 17 and 43%, suggesting a decrease in water content of the filters due to the lowered humidity. The question is how much of the unidentified component can be attributed to water and whether a combination of measurement error and particle water content can account for all of the unidentified component.

To estimate the contribution of water to fine mass, we assume (1) only sulfate compounds (e.g., H_2SO_4 , NH_4HSO_4 , $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$, and $(\text{NH}_4)_2\text{SO}_4$) absorb water in measurable quantity; and (2) the amount of water absorbed by sulfate compounds (g water/g sulfate) contained in atmospheric particles (which also contain other components such as organics) is equal to the amount of water absorbed by sulfate compounds in laboratory experiments. Such experiments have been performed for aqueous solutions of single (e.g., $(\text{NH}_4)_2\text{SO}_4$) and multicomponent (e.g., H_2SO_4 - NH_4HSO_4) electrolytes.^{47,48} In laboratory experiments conducted with aqueous solutions of specific components, it is feasible to measure water content of these sulfate compounds at equilibrium, as well as in the metastable state (e.g., supersaturation). In the metastable state deliquescent compounds (such as $(\text{NH}_4)_2\text{SO}_4$) will retain more water than in the equilibrium state at a relative humidity less than the relative humidity of deliquescence.

We estimated the particle water content using the measured concentrations of sulfate and ammonium and the extremes of weighing humidities (Stanford: 40 and 55%; IMPROVE: 31 and 45%) as input for a computer code developed by Clegg et al.⁴⁹ on the basis of laboratory observations. Results support allocation of some of the unidentified component to water (between 0 and 47% of the fine mass for individual samples; the range is over the two extremes of weighing humidities, sampler combinations and whether a metastable or equilibrium state is assumed). Including the calculated water content, however, does not account for all of the unidentified components. Even when using the largest estimates of water absorbed by inorganics (i.e., a supersaturated solution at the upper limit of the relative humidity range at which filters were weighed), the remaining unidentified component was positive for at least 75% of the study days (regardless of sampler combination) and was larger than the overall measurement uncertainty (E_{diff}) for over half of the study days (e.g., Figure 3b). This suggests that, some, but not all of the unidentified component may be water associated with the inorganics (practically all sulfate). There is still 15 to 23% of the study-average fine mass (depending on weighing humidities and sampler combinations) which remains unexplained. We

close the discussion by emphasizing that our estimates of water associated with sulfate are just that: estimates on the basis of laboratory experiments. Atmospheric particles (in suspended state as well as on filters) may not behave like pure aqueous electrolyte solutions either in equilibrium or in supersaturated state. For instance, water-insoluble compounds (e.g., organics, elemental carbon, dust) may provide sites for nucleation and thus obviate the existence of the supersaturated state.^{49,50} Moreover, the presence of organics would likely alter the thermodynamics of atmospheric particles from that of an aqueous electrolyte.^{51,52} For instance, the presence of completely miscible organics in atmospheric particles could provide an explanation for the retention of water by these particles at relative humidity below the relative humidity of deliquescence of sulfate and nitrate salts in an equilibrium state.

We have shown that measurement errors and inorganic constituents and water associated with sulfate do not totally account for the unidentified component. Next we investigate whether the unidentified component is specific to SEAVS or whether it is observed in other studies as well. To this end, we examined results from prior published studies for a wide range of locations (e.g., 1-21, see Table 4) and find a lack of closure among fine PM mass and composition measurements (i.e., the gravimetrically measured fine mass is not equal to the chemical mass, calculated by summing the concentration of measured and inferred constituents). We have used study or annual average concentrations reported in these publications¹⁻²¹ and assumed organics = 1.4*organic carbon, dust = sum of oxides. For most part, we have selected only post-1988 studies because the studies prior to 1988 did not utilize nitric acid denuders which minimize nitric acid adsorption on particulate samples, nor did they have any means of estimating particulate nitrate that volatilized during sampling.

We hypothesize that the unidentified component arises out of the errors in measurement and/or analysis of organics. Figure 4a shows the unidentified component as a function of organic component (both expressed as a percent of fine mass) for the studies listed in Table 4. Two things are obvious from this plot. First, the contribution of unidentified component to fine mass is often substantial and varies significantly, ranging from -30 to +50%. The negative percentage indicates cases where the sum of the constituents exceeds the measured fine mass. As discussed before, one possible explanation for the positive values (for unidentified component) is the presence of water associated with electrolytes (sulfates, nitrates and chlorides). A possible explanation for negative values is as follows. In many of these studies, fine mass was measured off a filter that may have lost some of the particle phase nitrate during or after sampling due to volatilization; however, nitrate concentrations were measured using filters or their

combination that minimized such volatilization. Therefore, for some studies, fine mass does not reflect all of the particle phase nitrate and associated ammonium.²⁶

Second, there is a strong negative correlation ($r^2 \sim 0.8$) between measured organic and estimated unidentified component for these studies which span the entire North American continent as well as other parts of the world.^{6,7,15} We find no strong correlations between the other major components of the aerosol: sulfate and unidentified component ($r^2 \sim 0.1$), sulfate and organic ($r^2 \sim 0.2$). If water associated with sulfate were a major explanation for the unidentified component, we would expect a stronger association between sulfate fraction and unidentified component fraction. Second, the organic-unidentified component relationship persists, albeit weaker, ($r^2 \sim 0.5$) even when the percentages of organic and unidentified component are limited to cases between where they contribute only 0-40% of the fine mass (i.e., neither component is dominant).

As we discussed earlier, the estimates of organic concentration have relatively large errors associated with them (compared to sulfate, for example). These errors transcend the known measurement errors we considered in constructing Figure 3. Appendix A provides a mathematical explanation for why relatively large random errors in concentration of organics could lead to a relatively large negative correlation coefficient (r) between the organic and unidentified fraction. Physical explanations are discussed in the next section.

DISCUSSION

We hypothesize that the relationship arises from one or more of the following: (1) errors in measurements of organic carbon; (2) estimates of total organic concentration from organic carbon measurements; and (3) water absorbed by organics. First, organics may contribute directly to the unidentified component. For instance, the quartz after-filter may contain adsorbed organic gases as well as organics that evaporated during sampling from particles collected on the front filter; therefore, estimating particulate organics as Q1 - Qaf would lead to overadjustment for gaseous interference and thus, underestimation of particulate organic carbon. Second, the assumed organics/organic carbon concentration ratio of 1.4 may be low, leading to underestimation of the true organic concentration in the samples. For many oxygenated organic compounds expected to be found in atmospheric particles, the ratio of average molecular weight to carbon weight ranges between 1.3 and 3.75.⁴² Recently Turpin et al. (personal communication, 1997) have re-examined this ratio and suggested higher numbers, particularly for non-urban areas where organic compounds are more oxidized. Using similar reasoning, Hegg et al.⁴¹ utilized a value of 1.7 for fine PM samples collected off the

Table 4. Summary of Studies used to construct Figures 4a and 4b.

Reference ^a	Site #s	Location	Season ^b	Type ^c	Sample Length ^d	Time of Day ^d	Duration ^e
This study	1-3	Smoky Mountains, TN	S	R	12 h	day	42 days
Turpin, 1997	4-5	Southwest U.S.	S	R	12 h	day	1.5 months
Chow, 1993	6-11	San Joaquin Valley, CA	S	RTU	24 h	-	1 year
Gray, 1986	12-22	Los Angeles, CA	A	RTU	24 h	-	1 year
Salmon, 1994	23	China	A	U	24 h	-	1 year
Salmon, 1995	24-25	Poland	A	U	24 h	-	1 year
Chow, 1996	26-35	San Joaquin Valley, CA	S	RTU	24 h	-	2 months
Chow, 1994	36-44	Los Angeles, CA	S/F	RTU	4-7 h	day and night	17 days
Salmon, 1997	45-49	Northeast U.S.	A	RTU	24 h	-	1 year
Pryor, 1997	50-52	Western Canada	S	RT	24 h	-	1 month
Dzubay, 1982	53	Houston TX	S	U	12+12 h	day and night	1 month
Malm, 1994a	54-55	Northwest U.S.	S	R	12 h	day	2.5 months
Tuncel, 1985	56	Shenandoah, WV	S	R	12 h	day	3 weeks
Stevens, 1984	57-59	Russia and WV	S	R	12 h	day & night	1 month
Wolff, 1982	60	Detroit, MI	S	U	4 h	day & night	1 week
Cahill, 1996	61	Mexico City	S	U	n/r	n/r	3 years
Tombach, 1996	62	Dallas, TX	W	U	4 h	8AM-noon	2 months
Watson, 1988	63-65	Denver, CO	W	U	7 h (am)	day & night 17 h (pm)	3 months
Watson, 1997	66	Chicago, IL	A	U	24 h	-	1 year
Dzubay, 1988	67	Camden, NJ	S	U	12 h	day and night	1 month
Ferman, 1981	68	Shenandoah, WV	S	R	12 h	day	1 week

^aReferences are listed by first author and date of publication; ^bA=Annual, S=Summer, F=Fall, W=Winter; ^cR=Rural, T=Transition, U=Urban; ^dn/r = not reported; ^eWe have used averages of all available experimental data and we report here "Duration" only to give the reader a notion of the period over which averages were derived in various studies. In many cases, samples were not collected every day: for instance, a 24-hr sample every 6 days for a period of 1 year was used in some studies to derive an annual average.

mid-Atlantic coast of the US. Second, water associated with organics may also contribute to the unidentified component.^{42, 43, 51, 52} In summary, our hypotheses (1) and (2) stem from our work as well as the work of others.

If part of the unidentified component is due to organic compounds and associated water, the following reasoning leads us to expect that rural areas would have a larger percentage of the total fine PM mass manifested as unidentified component in our analysis (Figure 4a). Rural areas are expected to contain relatively more polar and oxygenated compounds which have organics to organic carbon mass ratios greater than the value we assumed (1.4). Researchers have noted possible sources of such compounds to be oxidation of both anthropogenic and biogenic volatile organics as well as direct emission from vegetation.⁵³ Hence, as an aerosol is transported away from its source area, VOCs can undergo oxidation which results in particle phase secondary organics that are both hydrophilic and have an organics-to-organic carbon ratio higher than 1.4.

In prior studies, the contribution of secondary organics has been inferred from the ratio of organic carbon (OC)

to elemental carbon (EC).^{5, 54-56} The idea is that direct particle emissions (e.g., from automobiles and other sources) have a characteristic ratio (OC/EC); the ratio will increase as more organics are formed from oxidation of volatile organic compounds. An indication of the contribution of particulate organic compounds stemming from biogenic and secondary sources can likewise be inferred from the ratio of OC to total carbon (TC). We chose to use the OC/TC ratio, rather than OC/EC, because EC is a small fraction of the carbon measured during SEAVS (EC was often near the LDL) and a small amount of noise in the EC signal may result in a larger noise in the OC/EC ratio. (The two ratios can be related by: $(OC/EC)^{-1} = (OC/TC)^{-1} - 1$.) An OC/TC ratio greater than 0.69 (based on the OC/EC ratio of 2.2 used by Turpin and Huntzicker,⁽⁵⁶⁾) may be indicative of the presence of secondary organics. During SEAVS the OC/TC ratio has a median value of 0.97, 0.87, and 0.9 for the Stanford, IMPROVE and MOUDI samplers respectively. The high fraction of total carbon that was organic suggests that much of the particulate organics measured during SEAVS originated from VOC oxidation. A similar conclusion was also drawn by Turpin et al.¹ for

their Grand Canyon study; there OC/TC ratios of 0.80 to 0.90 were found.

Figure 4a suggests that for the rural locations (e.g., SEAVS and Meadview, points 1-5 on the plot) typically a greater percentage of fine mass remains unidentified than for the urban locations (e.g., Dallas and Denver, points 62-65 on the plot). Based upon these observations and the above discussion of primary and secondary organics, we test two additional hypotheses: (1) the unidentified component is proportional to the contribution of the secondary organics to the total organics in a sample; and (2) secondary compounds contribute more to the total organics in the rural areas than in the urban areas. In testing these hypotheses, we presume that the OC/TC ratio is a measure of the contribution of secondary organics to total organics. We differentiate between rural and urban areas by assuming that sites within 20 km of a city (or a metropolitan area) are urban, sites more than 50 km from a city are rural and sites between 20 and 50 km are transitional. Figure 4b shows that the dichotomy between urban vs. rural sites is unclear in terms of the range of OC/TC ratios as well as the range of the percent unidentified component. Therefore, neither of the two hypotheses, which taken together would lead us to expect higher OC/TC ratios and higher contribution of the unidentified component to fine mass at rural sites than urban sites, is borne out in Figure 4b. However, our test results are a product of the quality of the observations and our assumptions and we hope that these hypotheses can be retested with more reliable observations in the future.

CONCLUSIONS

Fine particles comprised, on average, approximately 80% of the PM_{10} concentration measured in the SEAVS study in Great Smoky Mountains National Park between July 15 and August 25, 1995. Over the period of study there were wide variations in fine mass and its components: for instance, fine mass ranged from less than 10 to greater than 100 $\mu\text{g}/\text{m}^3$ while the average concentration was 23.5 to 28.1 $\mu\text{g}/\text{m}^3$ (range over different samplers). Study average component concentrations (range over different samplers) were 8.7 to 9.7 $\mu\text{g}/\text{m}^3$ sulfate, 1.8 to 3.9 $\mu\text{g}/\text{m}^3$ organics (estimated as OC multiplied by 1.4), 1.8 to 2.3 $\mu\text{g}/\text{m}^3$ ammonium, 1.3 to 2.8 $\mu\text{g}/\text{m}^3$ soil dust, 0.1 to 0.4 $\mu\text{g}/\text{m}^3$ elemental carbon and 0.1 to 0.3 $\mu\text{g}/\text{m}^3$ nitrate. Sulfate was the dominant component accounting for more than 30% of the measured gravimetric mass, while organics, soil dust and elemental carbon each accounted for 5 to 13% of the total mass. Particulate nitrate was frequently near or below detection limits.

We tested the consistency of the measurements by comparing the sum of component concentrations derived from chemical measurements with the gravimetrically

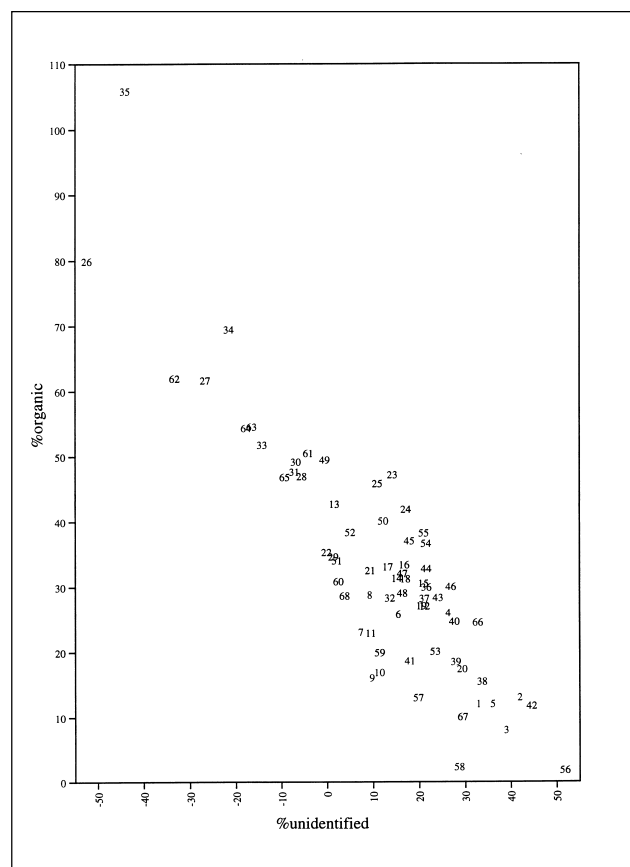


Figure 4a. Comparison of percent unidentified component and organic carbon for a number of different studies. (1-3 SEAVS, this paper; 4-5 (1); 6-11 (2); 12-22 (5); 23 (6); 24-25 (7); 26-35 (4); 36-44 (3); 45-49 (8); 50-52 (9); 53 (10); 54-55 (12); 56 (14); 57-59 (15); 60 (16); 61 (17); 62 (18); 63-65 (19); 66 (21); 67 (11); 68 (20)).

measured fine mass concentration. Although the sum of components is strongly correlated with fine mass, between 28 and 42% of the fine mass could not be attributed to specific components (study average contribution, range across different samplers and sets of assumptions). We found that the known measurement uncertainty may make the unidentified component (e.g., the difference between fine mass and the sum of chemically measured or inferred components) appear smaller or larger than what was observed, however, this uncertainty alone does not appear to be a sufficient explanation for the entire unidentified component.

We investigated other potential contributions to the unidentified component and found that errors associated with the dust contribution or water expected to be absorbed by sulfate could not account for all of the unidentified component. Combining the SEAVS measurements with results of other similar studies, we find a strong association between fractional contributions of organic carbon and the unidentified component. We offer several tenable hypotheses for the relationship between organic and unidentified mass fractions that

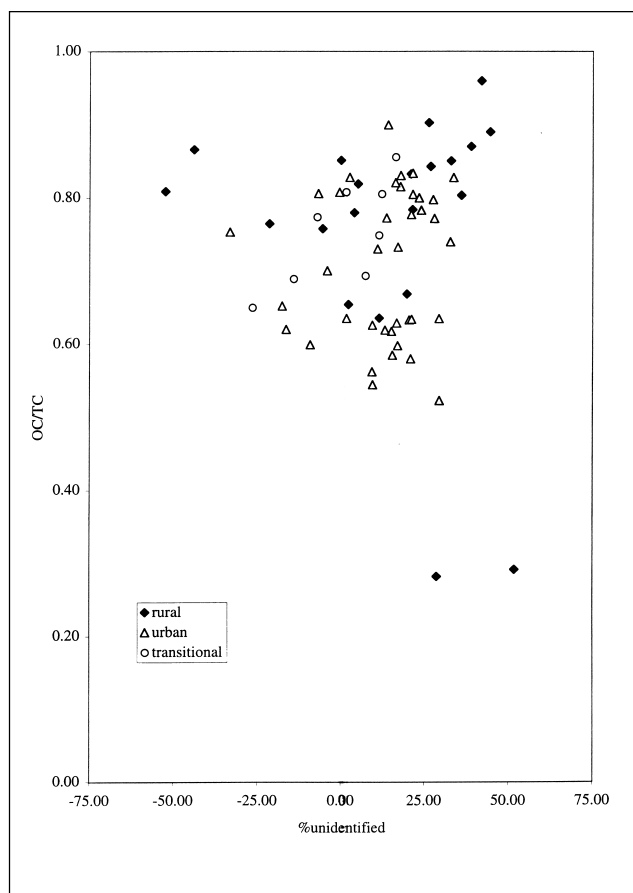


Figure 4b. Relationship between unidentified component and OC/TC ratio categorized by whether a location is urban, rural or transitional (the same data as in Figure 4a).

deserve to be tested in future work. Specifically, we hypothesize that (1) errors in the measurement of organic carbon; (2) estimates of organic concentration from measurements of organic carbon; and/or (3) water absorption by organics may all contribute to the observed relationship. These hypotheses can be tested in future studies that address the following: sampling improvement to minimize losses (e.g., denuders, concentrators),^{27,57,58} organic compound identification,⁵⁹⁻⁶¹ and laboratory studies of water absorption by individual organic compounds as well as organic-electrolyte mixtures.^{51,63,64}

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APPENDIX

On the Negative Correlation of Components in a Mixture

Figure 4a in the text suggests a strong negative correlation between organics and the unidentified component, while weak correlations were observed between other pairs of components. Using statistics we demonstrate how these observations can result from random measurement errors in one of the components.

Suppose we have a mixture of total mass, TM, such that

$$TM = M_1 + M_2 + \dots + M_N$$

(e.g., $TM = M_{\text{organics}} + M_{\text{sulfates}} + M_{\text{remainder}}$).

If we consider the relative contributions $C_i = M_i / TM$ then $C_1 + C_2 + \dots + C_N = 1$

We can then ask, what is the variance of the sum of the relative contributions to total mass, i.e., what is var

$(C_1 + C_2 + \dots + C_N)$? Since $C_1 + C_2 + \dots + C_N = 1$ is a constant and $\text{var}(\text{constant}) = 0$ we could simply write: $\text{var}(C_1 + C_2 + \dots + C_N) = 0$.

However, based on the definitions of variance and covariance and working through the algebra, we can also write

$$\text{var}(C_1 + C_2 + \dots + C_N) = \sum_i \text{var}(C_i) + \sum_{i,j=1, i \neq j}^N \text{cov}(C_i, C_j) \quad (\text{A1})$$

In more familiar terms, $\text{var}(C_i) = s_i^2$ and $\text{cov}(C_i, C_j) = s_i s_j r_{ij}$ where s_i is the standard deviation of C_i and r_{ij} is the correlation between C_i and C_j . (This is how s and r are defined.) Putting these various identities together yields the following constraint:

$$0 = \sum_i s_i^2 + \sum_{i,j=1, i \neq j}^N s_i s_j r_{ij} \quad (\text{A2})$$

Consider the special case of symmetry where the standard deviations and correlation coefficients are equal, that is, $s_i = s$ for all i and $r_{ij} = r$ for all $i \neq j$. Then eq A2 can be rewritten

$$0 = Ns^2 + N(N-1)s^2r \quad (\text{A3})$$

Solving for r yields

$$r = -1/(N-1) \quad (\text{A4})$$

For the example $\text{TM} = M_{\text{organics}} + M_{\text{sulfates}} + M_{\text{remainder}}$, we might thus expect negative correlations of order $r = -0.5$ between each species.

Now, suppose that C_1 is measured with random error e , and C_2, \dots, C_{N-1} and TM are measured exactly. This is plausible for the example $\text{TM} = M_{\text{organics}} + M_{\text{sulfates}} + M_{\text{remainder}}$, because errors in the quartz-filter carbon measurement do not affect the Teflon-filter measurements of sulfur and gravimetric mass. We can calculate what this error will do to the correlations.

Note, first, that the measurement noise inflates the observed variance

$$\begin{aligned} \text{var}(C_1 + e) &= \text{var}(C_1) + 2\text{cov}(C_1, e) + \\ \text{var}(e) &\equiv \text{var}(C_1) + \text{var}(e) = s_i^2 + s_e^2 \end{aligned} \quad (\text{A5})$$

This assumes that the error e in measurement is independent of the true composition C_1, C_2, \dots, C_N so that $\text{cov}(C_1, e) \neq 0$. For $j < N$, the observed covariance $\text{cov}(C_1 + e, C_j) = \text{cov}(C_1, C_j) + \text{cov}(e, C_j) \neq \text{cov}(C_1, C_j)$ is unaffected, again assuming that the error is independent of the true composition. The observed correlation is thus

$$r_{1j} = \frac{\text{cov}(C_1 + e, C_j)}{\sqrt{\text{var}(C_1 + e)\text{var}(C_j)}} \cong r_{1j} \sqrt{\frac{s_i^2}{s_i^2 + s_e^2}} \quad (\text{A6})$$

So the observed correlation r'_{1j} is closer to zero than the actual correlation r_{1j} .

The derived value for the residual component has error $-e$, so a similar argument yields

$$r'_{Nj} \cong r_{Nj} \sqrt{\frac{s_N^2}{s_N^2 + s_e^2}} \quad \text{for } j > 1 \quad (\text{A7})$$

Again the effect of the error is to attenuate the observed correlations.

The only covariance affected by the measurement error is the one between C_1 and C_N

$$\begin{aligned} \text{cov}(C_1 + e, C_N - e) &= \text{cov}(C_1, C_N) + \\ \text{cov}(C_1, -e) + \text{cov}(e, C_N) + \text{cov}(e, -e) &\cong \text{cov}(C_1, C_N) - \text{var}(e) \end{aligned} \quad (\text{A8})$$

The observed correlation is then

$$r'_{1N} \cong \frac{s_i s_N r_{1N} - s_e^2}{\sqrt{(s_i^2 + s_e^2)(s_N^2 + s_e^2)}} \quad (\text{A9})$$

In the special case of symmetry, this simplifies to

$$r'_{1N} \cong \frac{s^2 r - s_e^2}{(s_i^2 + s_e^2)} \cong \frac{r - f^2}{1 + f^2} \quad (\text{A10})$$

where $f = s_e/s$.

For the example $\text{TM} = M_{\text{organics}} + M_{\text{sulfates}} + M_{\text{remainder}}$, we found $r = -0.5$ for the symmetric case. If we suppose that half of the observed organic variance is attributable to measurement error, so that $s_e = s$ (and $f = 1$), then $r'_{13} \sim -0.75$. The correlations involving sulfate on the other hand, are then

$$r_{12} = r_{23} \cong r \sqrt{\frac{s^2}{s^2 + s_e^2}} = -0.5\sqrt{1/2} = -0.35 \quad (\text{A11})$$

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