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An evaluation of interagency monitoring of protected visual environments (IMPROVE) collocated precision and uncertainty estimates

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Abstract

The Interagency Monitoring of Protected Visual Environments (IMPROVE) program is a cooperative measurement effort in the United States designed to characterize current visibility and aerosol conditions in scenic areas (primarily National Parks and Forests) and to identify chemical species and emission sources responsible for existing man-made visibility impairment. In 2003 and 2004, the IMPROVE network began operating collocated samplers at several sites to evaluate the precision of its aerosol measurements.

This paper presents the precisions calculated from the collocated data according to the United States Environmental Protection Agency's guidelines Code of Federal Regulations [CFR, 1997. Revised requirements for designation of reference and equivalent methods for $PM_{2.5}$ and ambient air quality surveillance for particulate matter: final rule, 1997. Code of Federal Regulations. Part IV: Environmental Protection Agency, vol. 40 CFR Parts 53 and 58, pp. 71–72. Available from ⟨http://www.epa.gov/ttn/oarpg/t1/fr_notices/pm-mon.pdf⟩]. These values range from 4% for sulfate to 115% for the third elemental carbon fraction. Collocated precision tends to improve with increasing detection rates, is typically better when the analysis is performed on the whole filter instead of just a fraction of the filter, and is better for species that are predominantly in the smaller size fractions. The collocated precisions are also used to evaluate the accuracy of the uncertainty estimates that are routinely reported with the concentrations. For most species, the collocated precisions are worse than the precisions predicted by the reported uncertainties. These discrepancies suggest that some sources of uncertainty are not accounted for or have been underestimated.

Keywords: Uncertainty; Collocated; Particulate matter; Air quality monitoring; Measurement error

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1. Introduction

Variations in a concentration series that arise from uncertainty in the measurements should not be interpreted as variations in the atmosphere. Accurate estimates of measurement uncertainty are thus important inputs to data analyses. Measurement uncertainty arises from all aspects of the measurement process including sample preparation, collection, analysis, data acquisition, and data processing (ISO, 1995). Some components of uncertainty are independent of the measured concentration, such as the uncertainty associated with blank correction or

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interferences. Other components of uncertainty are proportional to the magnitude of the concentration, such as uncertainty in sample volume. Yet other sources of uncertainty increase less proportionately than with concentration, such as the uncertainty in a spectroscopic background. The "bottom-up" approach for estimating overall measurement uncertainty involves combining these proportional and non-proportional uncertainties (ISO, 1995). Interagency Monitoring of Protected Visual Environments (IMPROVE) reports an uncertainty with each sample concentration based on this "bottom-up" approach.

Collocated sampling provides a "top-down" approach for estimating measurement uncertainty. Collocated sampling is the most comprehensive way to evaluate the uncertainty of measurements because it duplicates the bulk of the measurement process. Collocated aerosol sampling was introduced in the routine IMPROVE network in 2003. The different relationships between uncertainty and concentration are illustrated by the collocated $PM_{2.5}$ mass, PM_{10} mass, Se, S, sulfate, and nitrate data in Fig. 1. The graphs on the left side plot the scaled arithmetic differences between collocated measurement pairs, $(Y_i - X_i)/\sqrt{2}$, against their average concentration. The graphs on the right side plot the scaled relative difference, $\left(\frac{(Y_i - X_i)/\sqrt{2}}{(Y_i + X_i)/2}\right)$, against their average concentration. Here, Y_i and X_i represent the collocated and routine concentrations, and the differences are scaled by $\frac{1}{\sqrt{2}}$ to account for the presence of uncertainties in both measurements. Fig. 1 shows the differences in $PM_{2.5}$ mass, sulfate, and S to be less sensitive to concentration when expressed in relative terms instead of arithmetic terms. In contrast, the differences in Se appear to be less sensitive to concentration when expressed in terms of arithmetic differences. Nitrate exhibits two regimes, with constant arithmetic differences at lower concentrations and constant relative differences at higher concentrations. These different relationships demonstrate that no single number can characterize the method's uncertainty for any of these species independent of the concentrations actually encountered.

Despite the evident dependence on concentration, the uncertainty of a measurement method is often summarized by a single number. This number, referred to as *precision*, is a concentration-weighted measure of the method's uncertainty for the concentration distribution encountered in a given application. Published summaries of collocation results have employed various metrics for precision (Sickles and Shadwick, 2002; White et al., 2005; Flanagan et al., 2006; Nejedly et al., 1998; Rice, 2005). The United States Environmental Protection Agency (USEPA) specified a technique for reporting the precision of collocated measurements in the Speciation Trends Network (STN) network (USEPA, 2000; CFR, 1997). The IMPROVE network is very similar in structure and operations to the STN. Therefore, this paper presents IMPROVE collocated precisions in terms of the USEPA metric.

The collocated precisions, calculated using the USEPA metric, provide a "top-down" estimate of the precision. The uncertainties reported with the collocated data are combined to provide a "bottom-up" estimate of precision. These "bottom-up" predicted precisions are then compared to the "top-down" collocated precisions, and the differences between these precision estimates are explored using various analyses.

2. Measurements

The IMPROVE network collects particulate matter samples on filter media over 24-h periods from midnight to midnight every three days at approximately 170 sites across the United States. The IMPROVE aerosol samplers consist of four modules—referred to as the A, B, C, and D modules—each of which is used to collect a filter on each designated sampling day. The A module has a 2.5 μm cutpoint and utilizes a Teflon filter that is weighed for mass, analyzed by X-ray fluorescence (XRF) for most elements between Na and Zr, and analyzed by proton elastic scattering analysis (PESA) for H. Two separate XRF systems are used to measure the elements, one with a copper anode (Cu-anode) for the lower atomic number elements and another with a molybdenum anode (Mo-anode) for the higher atomic number elements. The B module has a 2.5 μm cutpoint and utilizes a nylon filter, preceded by a sodium carbonate denuder, for analysis of $PM_{2.5}$ anions—sulfate ($SO_4^{=}$), nitrate (NO_3^-), and chloride (Cl^-)—by ion chromatography (IC). The C module has a 2.5 μm cutpoint and utilizes a quartz filter for analysis of organic and elemental carbon (OCEC) by thermal optical reflectance (TOR). The D module has a 10 μm cutpoint and utilizes a Teflon filter that is weighed for mass. More details on the sampler and the analytical instrumentation can be found in the

IMPROVE SOPs (UC-Davis, 2002). An on-line archive of IMPROVE data and documentation is maintained by Colorado State University (http://vista.cira.colostate.edu/views/).

Collocated IMPROVE samplers were installed at different sites at different times beginning in 2003. At one site, Phoenix, a complete duplicate sampler was installed and operated. For logistical reasons,

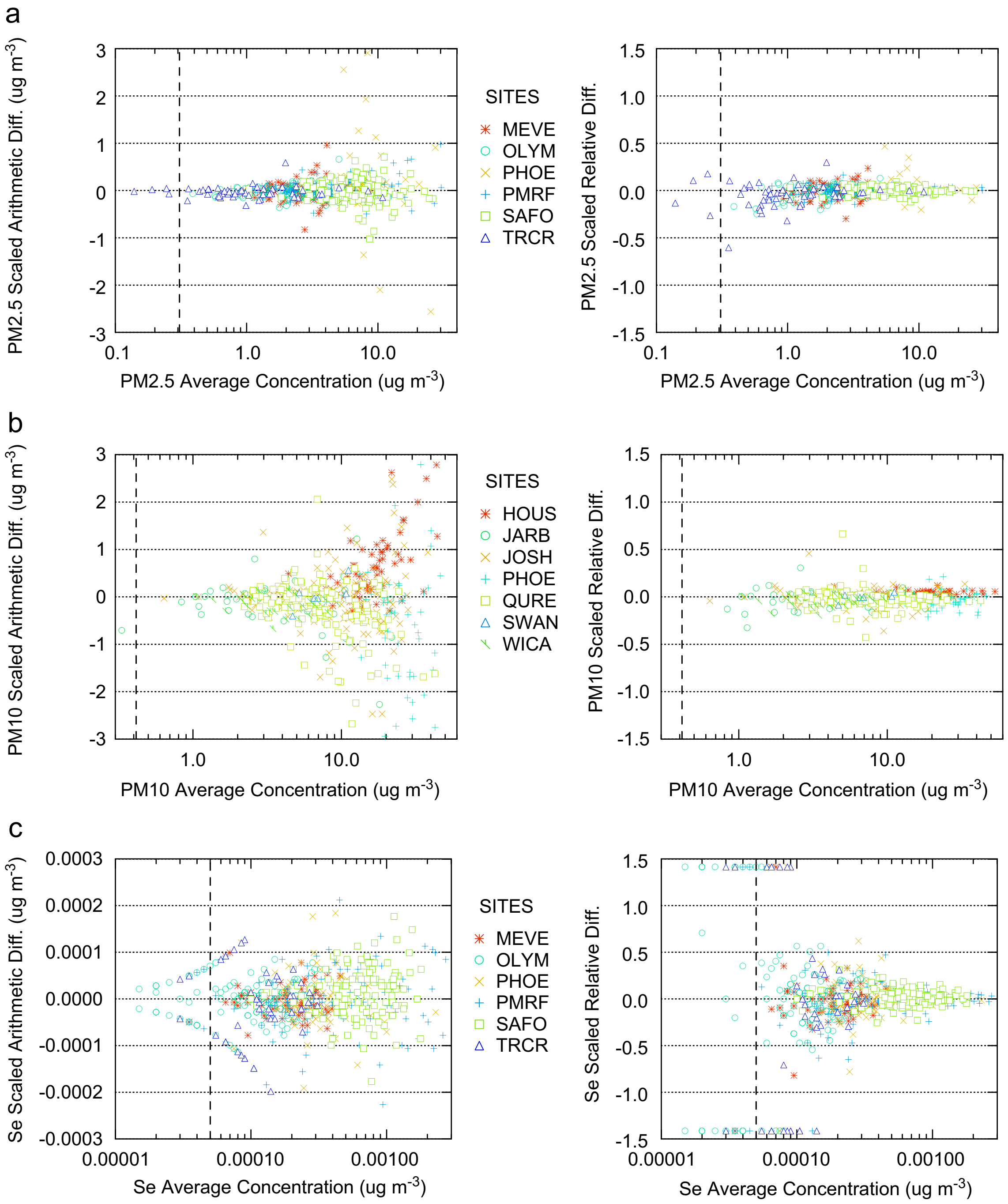

Fig. 1. Scaled arithmetic (left) differences, $([Y_i]-[X_i])/\sqrt{2}$, and scaled relative (right) differences, $\left(\frac{([Y_i]-[X_i])/\sqrt{2}}{([Y_i]+[X_i])/2}\right)$, versus average concentrations for the routine and collocated measurements of (a) $PM_{2.5}$ mass, (b) PM_{10} mass, (c) Se, (d) S, (e) sulfate, and (f) nitrate. If the mdl falls within the range of measured concentrations, it is indicated with a dashed vertical line. The different symbols represent different monitoring sites.

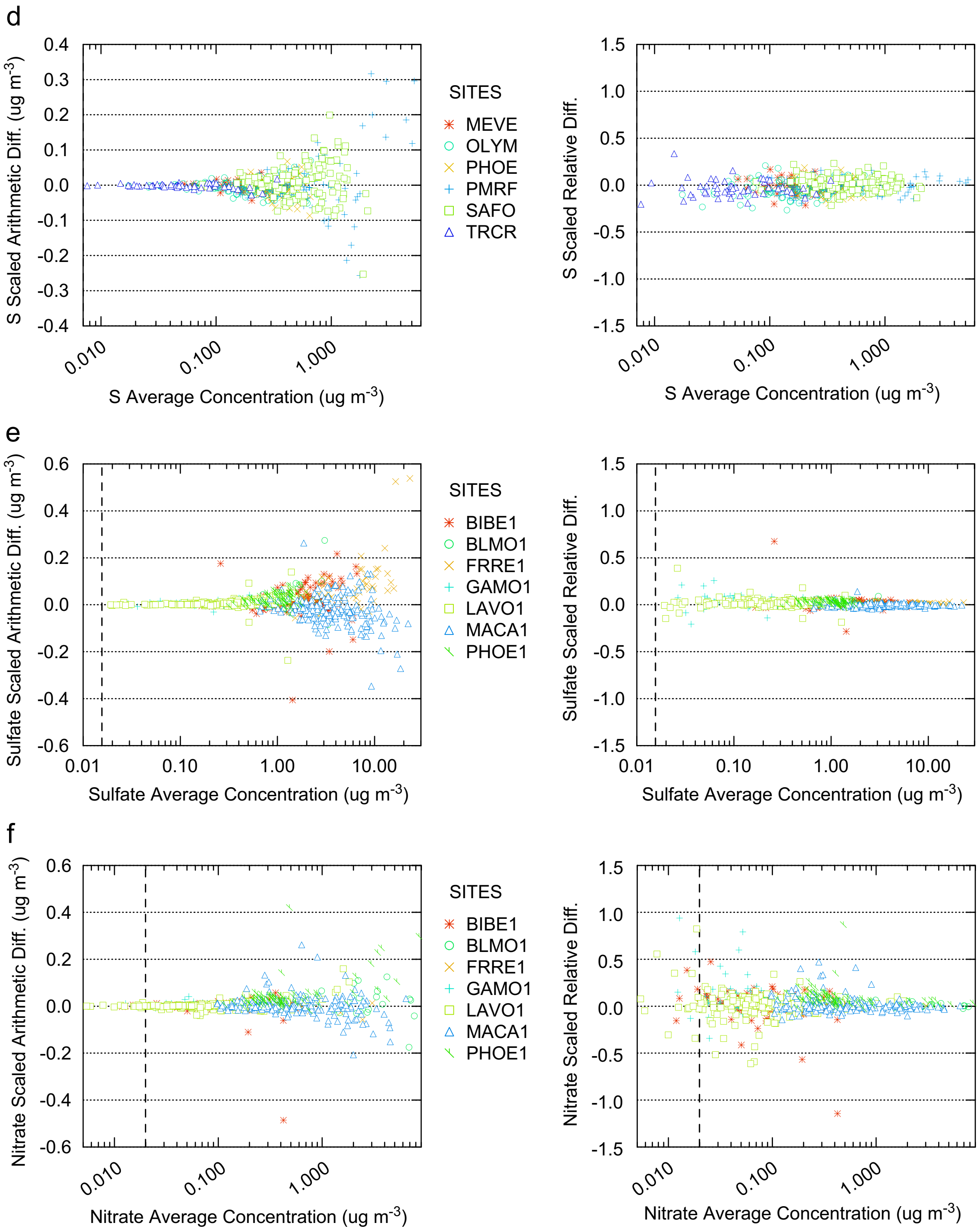

Fig. 1. (*Continued*)

the entire sampler was not duplicated at the other sites; instead a single module was duplicated. There are seven duplicate modules of each of the four types; since IMPROVE operates approximately 170 sites, this is equivalent to a 4% collocation rate. Table 1 lists the locations of the collocated modules along with the starting date for the data used in this analysis. At all sites, the first month of data was

Table 1
Collocated module locations and the start date for inclusion in this analysis

Module type	Site code	Site name	State	Start date
A, $PM_{2.5}$ mass and elements	MEVE	Mesa Verde NP	CO	5/12/04
	PMRF	Proctor Maple Research Facility	VT	10/3/03
	OLYM	Olympic NP	WA	12/8/03
	PHOE	Phoenix	AZ	4/30/04
	SAFO	Sac and Fox Nation	KS	12/20/03
	TRCR	Trapper Creek	AK	7/20/04
	SAMA	Saint Marks	FL	12/18/04
B, $PM_{2.5}$ anions	LAVO	Lassen Volcanic NP	CA	5/21/03
	MACA	Mammoth Cave NP	KY	6/14/03
	BIBE	Big Bend NP	TX	10/3/03
	GAMO	Gates of the Mountains WA	MT	10/24/03
	FRRE	Frostburg Reservoir	MD	5/18/04
	BLMO	Blue Mounds State Park	MN	10/18/04
	PHOE	Phoenix	AZ	4/30/04
C, $PM_{2.5}$ organic and elemental carbon	EVER	Everglades NP	FL	8/16/03
	SENE	Seney NWR	MI	9/12/03
	HOOV	Hoover WA	CA	9/15/03
	MELA	Medicine Lake NWR	MT	10/27/03
	PHOE	Phoenix	AZ	4/30/04
	SAWE	Saguaro NP West	AZ	5/3/04
	HEGL	Hercules-Glade WA	MO	10/15/04
D, PM_{10} mass	JOSH	Joshua Tree NP	CA	9/9/03
	QURE	Quabbin Reservoir	MA	10/3/03
	HOUS	Houston	TX	6/5/03
	JARB	Jarbridge WA	NV	8/1/04
	PHOE	Phoenix	AZ	4/30/04
	WICA	Wind Cave NP	SD	10/18/04
	SWAN	Swanquarter WA	NC	12/11/04

NP: National Park; WA: Wilderness Area; NWR: National Wildlife Refuge; NF: National Forest.

eliminated from the analysis to allow the operations to stabilize. The first nine months of data from MEVE were eliminated from the analysis because inequivalent equipment was inadvertently used. SAMA was not included in the analysis because only four samples were collected at the site in 2004.

The collocated module is semi-independent of the routine module. The collocated and routine modules have independent sample streams, including separate inlets, cyclones, pumps, and solenoid valves. Conversely, the collocated and routine modules are controlled and monitored by the same electronics (except at Phoenix), including a common timer, software, and data acquisition system. In addition, temperature is only measured once at the site and is used to adjust the measured mass flow rate to volumetric flow rate for both the collocated and routine modules. Therefore, this arrangement does not capture any uncertainty associated with the temperature measurement and may not capture all the variations resulting from electronics. Audits of temperature measurements suggest that temperature uncertainties could amount to a 1% uncertainty in the concentrations; the IMPROVE temperature measurements are being upgraded in the 2007 maintenance season to decrease this source of uncertainty.

Analytical calibration and data processing uncertainties are not thoroughly addressed by this type of evaluation. The routine and collocated samples are often analyzed on the same instrument within hours or at most days of each other, particularly XRF measurements. The analyzers are typically stable over this short time period. Uncertainty resulting from the range of acceptable calibration criteria could only be evaluated if the samples were analyzed at significantly different times (such that the instrument has drifted from its calibration or was using a different calibration) or if the routine and collocated samples were always analyzed using different instruments. The routine and collocated data are collected, processed, and validated using the same systems. Therefore, uncertainties resulting from calculations, such as rounding numbers, are not included in this assessment.

3. Results

The collocated sites are spread throughout the country to represent a variety of PM concentrations and compositions. As discussed in the Introduction, the collocated precision is dependent on the concentrations encountered; different collocated sites can have different concentration distributions and thus yield correspondingly different precisions. The goal of the collocated sampling is to determine the typical precision in the network. Thus, a concentration distribution at the collocated sites similar to that of the entire network is most desirable. Table 1 of the on-line materials lists the 2004 concentration percentiles in the entire network and at the collocated sites. The concentration percentiles (10th, 50th, and 90th) at the collocated sites are similar to those in the entire network. The only notable exceptions are that the collocated 90th percentile concentrations for Fe, Ti, and Ca are around 50% higher, PM_{10} mass concentration percentiles are between 20% and 40% higher, and chloride concentration percentiles are approximately 50% lower than the percentiles in the entire network. The collocated concentration distributions for most species can be considered at least qualitatively representative of the concentration distributions measured in the IMPROVE network.

To provide more robust statistics, data from all the collocated sites have been aggregated to estimate the network precision. The graphs in Fig. 1 plot the data from different sites using different symbols. Small concentration biases can be distinguished at many sites; these biases most likely result from biases in the flow rate calibrations which are accounted for by the uncertainty estimates. Therefore, the biases are included in the precision calculations. Precision estimates for the individual sites provide an indication of the variability in the precision.

Table 2 lists the collocated precision estimated from the difference between the routine and collocated measurements, predicted precision estimated from the reported uncertainties, ratio of collocated precision to predicted precision, and percent of sample pairs meeting the inclusion criterion specified by the USEPA (2000). The first number in each column is the aggregate value for all the collocated sites; the range in parentheses in each column lists the lowest and highest values calculated for the individual collocated sites. The precision values are only listed if at least one individual site had >10 sample pairs meeting the inclusion criteria. These metrics will be discussed in detail in the following sections. On-line Tables 2, 3, 4, and 5 list these metrics for each individual site. The precision estimates apply only to IMPROVE data from the corresponding time period (2003–2004). The IMPROVE network has undergone several operational and analytical changes over the years (DeBell et al., 2006) that may make the precision estimate for a particular species less representative of prior or future years.

3.1. Collocated precision

Table 2 shows the collocated precisions estimated from the collocated IMPROVE data collected in 2003 and 2004 using Eq. (1) (CFR, 1997).

$$\text{Collocated precision} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\frac{(Y_i - X_i)^2/2}{((Y_i + X_i)/2)^2}} * 100\%, \tag{1}$$

where X_i is the species concentration from the routine sampler and, Y_i the species concentration from the collocated sampler.

The difference in the numerator is divided by $\sqrt{2}$ because it arises from imprecision in both measurements, which add quadratically, and the desired result is the precision of one measurement. According to the STN documentation (USEPA, 2000), only sample pairs with an average concentration greater than three times the method detection limit (avg > 3*mdl)[1] are included in the calculation, and the precision is only calculated if at least 10 pairs meet this criterion. These are the only restrictions placed on the data for the initial precision calculations (i.e., quality control flags are ignored).

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[1] IMPROVE mdl's are estimated by different methods for different measurement types. Descriptions can be found in the Data Processing Standard Operating Procedures (UC-Davis, 2002).

Table 2
Collocated data statistics

Module	Analytical method	Species	Collocated precision (%)		Predicted precision (%)		Ratio collocated/ predicted		Percent >3*mdl (%)	
A, 577 valid sample pairs	Mass	$PM_{2.5}$	6	(4–11)	7	(4–10)	1.0	(0.6–2.5)	93	(47–100)
	PESA	H	8	(7–13)	6	(6–9)	1.3	(1.1–1.5)	100	(99–100)
	Cu-anode XRF	Na	$n<10$		–		–		3	
		Mg	$n<10$		–		–		2	
		Al	69	(46–94)	14	(9–18)	5.0	(4.4–5.5)	45	(20–87)
		Si	41	(19–61)	11	(6–14)	3.7	(2.4–4.5)	92	(78–100)
		P	$n<10$		–		–		4	
		S	8	(7–10)	5	(5–6)	1.6	(1.4–1.7)	100	(99–100)
		Cl	68	(60–67)	12	(9–11)	5.6	(5.8–6.5)	18	(24–69)
		K	13	(10–19)	6	(5–8)	2.3	(1.8–3.3)	100	(99–100)
		Ca	19	(12–32)	6	(5–9)	3.0	(1.8–5.9)	100	(99–100)
		Ti	30	(19–60)	11	(6–17)	2.6	(1.9–3.6)	92	(63–100)
		V	21	(11–29)	18	(9–26)	1.2	(1–1.4)	79	(64–99)
		Cr	56	(26–79)	28	(19–43)	2.0	(1.3–3.2)	19	(14–46)
		Mn	24	(16–41)	12	(6–17)	2.0	(1.7–2.8)	92	(61–100)
		Fe	18	(12–27)	5	(5–6)	3.3	(2.1–5.2)	100	(99–100)
	Mo-anode XRF	Ni	32	(13–111)	12	(10–13)	2.8	(1.1–10.2)	38	(17–86)
		Cu	30	(16–79)	12	(6–14)	2.5	(1.7–6)	86	(39–99)
		Zn	25	(13–56)	6	(5–11)	4.0	(2.4–5.4)	100	(96–100)
		As	15	(11–21)	14	(13–15)	1.1	(0.9–1.4)	10	(12–23)
		Se	15	(9–22)	14	(10–19)	1.1	(0.9–1.3)	70	(35–96)
		Br	8	(5–12)	7	(6–12)	1.2	(0.9–1.3)	100	(98–100)
		Rb	28	(27–28)	24	(21–22)	1.2	(1.2–1.3)	11	(21–48)
		Sr	23	(19–29)	11	(7–16)	2.1	(1.7–2.9)	46	(7–99)
		Zr	$n<10$		–				1	
		Pb	22	(14–35)	12	(10–17)	1.8	(1.4–2.1)	94	(53–100)
B, 823 valid pairs	IC	Cl^-	33	(8–55)	11	(9–14)	3.0	(0.8–3.9)	22	(6–92)
		NO_3^-	10	(3–15)	8	(4–10)	1.3	(0.6–2.9)	83	(62–100)
		$SO_4^=$	4	(2–7)	5	(4–6)	0.9	(0.5–1.7)	97	(92–100)
C, 775 valid sample pairs	TOR	OC1	44	(41–51)	33	(31–35)	1.3	(1.3–1.5)	9	(6–44)
		OC2	18	(14–26)	22	(21–24)	0.8	(0.7–1.2)	39	(14–96)
		OC3	24	(18–29)	17	(15–18)	1.4	(1–1.8)	33	(15–89)
		OC4	26	(21–36)	17	(17–19)	1.5	(1.3–1.9)	59	(27–95)
		OCP	45	(26–103)	29	(28–35)	1.5	(0.9–3)	27	(12–44)
		EC1	24	(18–29)	16	(15–17)	1.5	(1.2–1.8)	79	(57–99)
		EC2	37	(31–42)	30	(30–31)	1.2	(1–1.4)	28	(16–45)
		EC3	115	(101–133)	52	(50–55)	2.2	(2–2.4)	17	(8–37)
		OC	17	(11–29)	12	(9–14)	1.5	(0.9–2.1)	51	(27–100)
		EC	22	(11–47)	12	(10–15)	1.8	(0.8–3.5)	31	(7–100)
		TC	17	(10–23)	11	(8–14)	1.5	(0.9–1.8)	55	(27–100)
D, 502 pairs	Mass	PM_{10}	8	(4–10)	5	(3–8)	1.6	(1–2.4)	98	(86–100)

The first number in each column is the aggregate value for all the collocated sites; the range in parentheses lists the lowest and highest value calculated for the individual collocated sites.

3.2. Predicted precision based on reported uncertainties

The uncertainties reported with each IMPROVE concentration are intended to represent the standard deviation of the concentration measurement and are based on quadratic addition of estimated flow rate and analytical uncertainties. To compare these uncertainties to the collocated precisions, the individual uncertainties must be similarly aggregated for the collocated data set. For independent uncertainties in the collocated concentrations, the squared difference between the concentrations, $(Y_i-X_i)^2$, should be predicted by the sum of the squares of the reported uncertainties, $(\mathrm{U}_{X_i}^2+\mathrm{U}_{Y_i}^2)$. Making this substitution in Eq. (1) gives Eq. (2), which is used to estimate the predicted precisions in Table 2.

$$\text{Predicted precision} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\frac{(\mathrm{U}_{X_i}^2+\mathrm{U}_{Y_i}^2)/2}{(X_i+Y_i/2)^2}}*100\%, \tag{2}$$

where U_{X_i} is the reported uncertainty in the species concentrations from the routine sampler and U_{Y_i} the reported uncertainty in the species concentrations from the collocated sampler.

The focus herein is on the predicted precision appearing in Eq. (2), not on mechanistic details of the reported uncertainties. The reported uncertainty algorithms (model and inputs) have not been updated since the 1980s, and documentation on their development and evaluation is limited. However, a general knowledge of the estimation algorithms is of some value in interpreting the comparisons with the collocated precision. Eq. (3) shows the basic model for the reported uncertainty.

$$\mathrm{U}_X = \sqrt{X^2*(\mathrm{U}_{\text{proportion}}^2+\mathrm{U}_{\text{volume}}^2)+(\mathrm{U}_{\text{additive}})^2}, \tag{3}$$

where U_X is the uncertainty in the species concentration ($\mu\mathrm{g\,m^{-3}}$); X is the species concentration ($\mu\mathrm{g\,m^{-3}}$); $\mathrm{U}_{\text{proportion}}$ is the proportional analytical uncertainty and varies by species; $\mathrm{U}_{\text{volume}}$ is the proportional volume uncertainty and assumed to be 3% for all measurements; and $\mathrm{U}_{\text{additive}}$ is the additive analytical uncertainty ($\mu\mathrm{g\,m^{-3}}$) and varies by species and sample.

The reported uncertainties do not include possible uncertainties in deposit area, deposit non-uniformity, or cyclone collection efficiency. $\mathrm{U}_{\text{volume}}$ results from the uncertainty in the flow rate calibrations and is assumed to be 3% for all modules. The flow rate measurement technique for the PM_{10} modules was modified in 2000, and the current technique is less sensitive than the old technique. Therefore, the volume uncertainty for the PM_{10} measurement is probably $>3\%$ but the estimated uncertainty has not been updated since the measurement technique changed. The analytical uncertainties ($\mathrm{U}_{\text{proportion}}$ and $\mathrm{U}_{\text{additive}}$) are different for each analysis.

For the $\mathrm{PM}_{2.5}$ and PM_{10} mass measurements, $\mathrm{U}_{\text{additive}}$ is assumed to be $0.15\,\mu\mathrm{g\,m^{-3}}$ based on the historical precision of laboratory blanks. $\mathrm{U}_{\text{proportion}}$ is assumed to be zero for both gravimetric measurements. Therefore, as the mass concentrations increase, the relative uncertainty decreases and approaches $\mathrm{U}_{\text{volume}}$ (3%).

For the element concentrations, $\mathrm{U}_{\text{proportion}}$ is assumed to be 4% for all elements. $\mathrm{U}_{\text{additive}}$ results from the uncertainty in the peak fitting process, varies by element and sample, and is roughly proportional to the square root of the peak counts. $\mathrm{U}_{\text{additive}}$ varies by element because the scattering cross-section varies by element (by orders of magnitude); the scattering cross-section describes how effectively an incoming photon interacts with an atom of the element. $\mathrm{U}_{\text{additive}}$ also varies by sample because it is dependent on the peak and background counts in each sample spectrum.

The estimated $\mathrm{U}_{\text{proportion}}$ values for the ions and carbon fractions are listed in Tables 3 and 4. The ion and carbon concentrations are both

Table 3
The $\mathrm{U}_{\text{proportion}}$ estimates used to predict ion uncertainties (Eq. (3)), analytical precisions calculated from replicate ion measurements in 2004, and ratios of analytical precision to $\mathrm{U}_{\text{proportion}}$

Anion	Replicate precision (%)	$\mathrm{U}_{\text{proportion}}$ (%)	Precision/ $\mathrm{U}_{\text{proportion}}$
Cl^-	4	4	1.1
NO_3^-	1	3	0.4
$\mathrm{SO}_4^=$	1	2	0.5

Table 4
The $\mathrm{U}_{\text{proportion}}$ estimates used to predict carbon uncertainties (Eq. (3)), analytical precisions calculated from replicate carbon measurements in 2004, and ratios of analytical precision to $\mathrm{U}_{\text{proportion}}$

Carbon fraction	Replicate precision (%)	$\mathrm{U}_{\text{proportion}}$ (%)	Precision/ $\mathrm{U}_{\text{proportion}}$ (%)
OC1	41	27	1.5
OC2	17	16	1.1
OC3	19	11	1.7
OC4	20	13	1.5
OP	50	27	1.9
EC1	24	13	1.9
EC2	31	26	1.2
EC3	66	40	1.7
OC	11	–	–
EC	21	–	–

blank-corrected to account for contamination and sampling artifacts. The $U_{additive}$ values are based on the observed variability in the ion field blanks and carbon back-up filters from which the blank corrections are determined (UC-Davis, 2002).

3.3. *Collocated versus predicted precision*

The following sections discuss the precisions by analytical technique. Some commonalities within and between the techniques can be identified that provide clues about the sources of uncertainty. Table 2 lists the numerical values discussed herein. Throughout this discussion, the terms "good" and "poor" are used to describe the relative value of the precision; these terms are used to avoid the confusion of using high and low to describe a metric that has an inverse scale (e.g., high precision is a low number).

3.3.1. *$PM_{2.5}$ (A module) and PM_{10} (D module) gravimetric mass*

The aggregate $PM_{2.5}$ collocated precision is comparable to the predicted precision. The range of collocated to predicted precision ratios is large because the Phoenix site had a poor ratio (2.5); the range of ratios at the remaining five sites was 0.6–1.1. Phoenix experiences much higher coarse to fine particle ratios than the other sites with collocated A modules, and the anomalously high collocated to predicted precision ratio may be related to cyclone collection efficiency problems, which are not accounted for in the uncertainty estimates. Excluding Phoenix, the good comparability between the collocated and predicted precisions suggests that the components considered in the estimated uncertainty (i.e., volume and weighing uncertainties) are within their expected ranges and account for the observed collocated measurement differences. The $PM_{2.5}$ collocated precision thus places an upper bound on the volume uncertainty, and this bound should apply across all $PM_{2.5}$ species. The PM_{10} module uses a different flow measurement technique so this conclusion does not apply to the PM_{10} mass measurements.

The aggregate PM_{10} collocated precision is poorer than the predicted precision although the collocated precision range overlaps the predicted range. Possible causes of the discrepancy are the low resolution flow rate measurement on the PM_{10} modules or variations in the size-selective inlet collection efficiency as a result of fluctuations in flow rate or small differences in flow rate between the two modules.

3.3.2. *$PM_{2.5}$ XRF and PESA elements (A module)*

No element in Table 2 has an aggregate collocated precision better than predicted. Both the collocated and predicted precision estimates vary markedly for the elements. Variations in the predicted precisions are indicative of how well the peaks are resolved in the XRF spectra. Several elements have ratios of collocated to predicted precision <2 (H, S, V, As, Pb, Se, Br, Rb); these elements predominately exist in the fine mode (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000). The remaining elements have collocated to prediction precision ratios between 2.0 and 5.6. The ratios are particularly poor for the lightest elements measured by the Cu-anode XRF system (Al and Si); these elements are difficult to measure by XRF (Jenkins, 1999), and the predicted precisions are too optimistic. The differences between the collocated and predicted precision for the XRF elements vary markedly suggesting that a variety of sources are contributing to the differences. Some possible explanations for the discrepancies include filter area uncertainty, analytical uncertainty, filter deposit non-uniformity, contamination, and cyclone collection efficiency variations.

The filter area is assumed to be a constant for all sample filters, and all elements would be affected equally by filter area uncertainty. All elemental measurements are scaled according to the filter area, and it is thus a proportional uncertainty. Three elements stand out as having better collocated precisions than the others; H, S, and Br have precisions of 8%. This suggests that the filter area uncertainty is $<7\%$ ($\sqrt{8\%^2 - 3\%^2}$, total uncertainty minus 3% volume uncertainty) and is likely well below 7% since this includes the analytical uncertainties.

Two different types of analytical precision experiments have been performed that offer insight into the collocated precisions and the assumed analytical uncertainty. First, to check the analytical stability, a small batch of filters is re-analyzed every month prior to analyzing the routine filters. In 2004, the re-analysis batch consisted of 28 sample filters from June, July, and August 2003 at the Big Bend National Park site in Texas. These filters were re-analyzed 8 times on the Cu-anode XRF system and 10 times on the Mo-anode XRF system at approximately equal time intervals in 2004. The resulting data can be used to calculate a re-analysis precision. (The numerator and denominator in the summand of Eq. (1) are replaced, respectively, by the variance and squared mean of the 8 or 10 measurements instead of just 2.) Table 5 lists the re-analysis precisions and the predicted analytical uncertainties, which include both $U_{additive}$ and $U_{proportion}$. The uncertainty and precision were calculated if there was at least one sample with avg > 3*mdl. The re-analysis precisions are similar to (within 2% of) the analytical uncertainty estimates for some species (Si, S, K, Ca, Ti, V, and Fe) but are much worse than the uncertainty estimates for many species. Because of the limited number of samples, these precisions may not be representative of the entire network; nevertheless, they provide useful benchmarks. The re-analysis precision captures the calibration uncertainty because the filters are re-analyzed over several months; the calibration uncertainty is not included in the collocated precisions for the XRF species because the routine and collocated samples are analyzed on the same system within hours of each other.

XRF analytical precisions were also evaluated (White et al., 2004) by analyzing the same three filters hundreds of times each in close temporal succession. In these multi-analyses, the precisions ranged from 1% to 50% and were negatively correlated with the ratio of concentration to mdl. White et al. demonstrated that for elements with concentrations > 10*mdl, the multi-analysis precision was < 10% (Fe, Zn, Ca, S, K, Si, Br, Mn), whereas for elements with concentrations < 10*mdl, the precisions were 20–50%. Several XRF species are usually > 10*mdl in the collocated data set (Si, S, K, Ca, Ti, V, Mn, Fe, Zn, Br, Pb), but with the exception of S and Br, none has a collocated precision < 10%. Consistent with the re-analyses, these multi-analyses suggest that the analytical uncertainty is poorer than currently estimated for several elements (Na, Al, P, Cl, Cr, Ni, Cu, As, Se, Rb, Sr, Zr).

The elements associated with soil—Al, Si, K, Ca, Ti, Mn, and Fe—have collocated precisions exceeding 10% despite several of these elements having high detection rates and good re-analysis precisions (Si, K, Ca, Ti, Fe). Variations in cyclone collection

Table 5
XRF analytical precisions based on 28 filters that were re-analyzed 8 times on the Cu-anode XRF and 10 times on the Mo-anode XRF system in 2004

XRF anode	Element	Re-analysis precision (%)	Predicted analytical uncertainty (%)	Re-analysis precision/predicted	Count of samples > 3*mdl
Copper-anode XRF	Na	70	27	2.6	1
	Mg	–	–	–	0
	Al	51	10	5.3	26
	Si	7	5	1.3	28
	P	–	–	–	0
	S	5	4	1.2	28
	Cl	59	26	2.2	3
	K	5	4	1.1	28
	Ca	5	4	1.1	28
	Ti	7	6	1.2	28
	V	21	20	1.0	28
	Cr	42	29	1.5	2
	Mn	19	8	2.4	28
	Fe	3	4	0.8	28
Molybdenum-anode XRF	Ni	15	12	1.2	5
	Cu	20	15	1.3	7
	Zn	14	7	2.1	28
	As	–	–	–	0
	Se	35	14	2.5	28
	Br	18	7	2.7	28
	Rb	23	12	1.9	8
	Sr	20	10	2.0	24
	Zr	–	–	–	0
	Pb	43	19	2.3	26

efficiency between the modules may be the cause of these poor collocated precisions. The IMPROVE sampler uses cyclones based on the specifications of John and Reischl (1980) and passive flow control in the form of a critical orifice. With passive flow control, the flow rate changes due to variations in filter thickness, filter material uniformity, and sample loading. The cyclone was recently characterized by Turner et al. (2006); the characterization indicates that the cyclone cutpoint is only slightly sensitive to changes in flow rate but that the cyclone collection efficiency curve becomes broader (less steep) as the flow rate decreases. Perhaps more important for the coarse-mode elements, Turner et al. (2006) found negative collection efficiencies in tests with Arizona soil dust as a result of shattering (deagglomeration) of large particles to form small particles. The soil-derived elements are predominantly in the coarse mode (Seinfeld and Pandis, 1998), and the collection efficiency of soil particles are likely to be affected by both shifts in the cutpoint and shattering. More information about the particle size distributions and cyclone collection efficiency is necessary to characterize this source of uncertainty.

A final sampling-related uncertainty that is not considered in the uncertainty estimates is the possible non-uniformity of filter deposits. Unlike the $PM_{2.5}$ mass and ion measurements which analyze the entire filter, the XRF and PESA beams examine only a portion of the filter. If the sample loading is non-uniform, the location and size of the analysis area will affect the measurement. The re-analyses and multi-analyses are insensitive to non-uniformity because the location of the beam is very similar each time. No quantitative information is currently available to assess the uniformity of the sample loadings.

3.3.3. $PM_{2.5}$ ions (B module)

The collocated precisions for nitrate and sulfate are similar to the predictions. The chloride collocated precision is much worse than the nitrate and sulfate precisions and than its predicted precision; this is likely related to the low detection rates and high chloride blank loadings relative to the concentrations. As noted previously, the chloride concentrations measured at the collocated sites are low compared to the routine network. Also, the replicate ion measurements suggest that the chloride re-analysis uncertainty ($U_{proportion}$) is too low.

Approximately 10% of the ion analyses are replicated by the analytical laboratory—a second aliquot of the filter extract is analyzed by IC. Table 3 lists the replicate precisions for chloride, nitrate, and sulfate for 2004 samples. The replicate precisions should be better than the $U_{proportion}$ estimates because the estimates include the uncertainty associated with calibration tolerances, which are not included in the replicate analyses because the replicate analyses are performed on the same instrument and immediately follow the original analyses. The nitrate and sulfate replicate precisions are less than the estimated uncertainties but this is not the case for chloride, which suggests that the $U_{proportion}$ estimate is too low for chloride.

3.3.4. $PM_{2.5}$ OCEC (C module)

The carbon fractions have poor predicted aggregate precisions (16–52%) yet the collocated precisions for all the fractions, except OC2, are even worse than the predictions (18–115%). The discrepancies can be explained by the replicate analytical measurements. Similar to the XRF measurements, the OCEC measurements are performed on a small section of the filter; a $0.52\,cm^2$ sample punch is removed from the $3.53\,cm^2$ quartz filter and analyzed. Approximately 10% of OCEC analyses are replicated by the analytical laboratory—a second sample punch is taken from the filter and analyzed. In 2004, approximately 75% of the replicate analyses were performed on a different instrument than the original analyses; therefore, the replicate precision is expected to estimate the total analytical uncertainty because it includes the calibration uncertainty 75% of the time. The 2004 replicate precisions along with the proportional analytical uncertainties ($U_{proportion}$) are listed in Table 4 (the additive analytical uncertainty, $U_{additive}$, is based on variations in backup filter concentrations which do not affect the replicate analyses). The replicate precisions for every fraction are worse than the $U_{proportion}$ values. The poor replicate precisions may result from sample non-uniformity problems (DRI, 2000). In light of the replicate precisions, the collocated precisions are reasonable for the carbon fractions and sums. The carbon uncertainty estimates need to be revised accordingly.

4. Discussion

The scaled arithmetic and relative difference graphs in Fig. 1 provide insight into the sources of uncertainty and the impact of the inclusion criteria (avg >3*mdl) on the precisions. Graphs like these for all IMPROVE species are included in the on-line materials. The precisions are calculated based on the scaled relative difference in collocated concentrations. Fig. 2 contains graphs of the scaled relative differences versus concentration for H, V, Si, Fe, Cu, Zn, the third organic carbon fraction (OC3), and the first elemental carbon fraction (EC1). These figures illustrate three common issues that result in poorer precisions than predicted for several parameters: underestimated mdl, sampling discrepancies such as cyclone collection efficiency differences, and contamination.

The collocated data suggest that the reported mdl's for several parameters are too low. The plots of the Se, V, Si, and Cu differences have numerous points along the top and bottom edges (scaled relative difference $=\pm\sqrt{2}$); these points represent sample pairs where the element was detected on one filter but was not detected on the paired filter. In these cases, the average concentration shown in Figs. 1 and 2 is equal to one-half the detected concentration. These pairs strongly influence the precisions. The influence of these detect/non-detect pairs was quantified by recalculating elemental precisions using only pairs where the element was detected on both modules and dropping the original criterion (avg >3*mdl). Table 6 shows the ratios of collocated to predicted precision determined with the revised criterion (“Both Detected”), alongside the ratios determined with the “Original Criterion” (Table 6 lists a precision if there are 10 sample pairs in the collocated data set with average concentrations >3*mdl; in contrast to Table 2, the 10 pairs do not have to be at the same site). The “Both Detected” ratios are better for most elements and particularly for Na, Al, Si, Cl, Ti, Cr, Ni, Sr, and Cu. The dramatic improvements illustrate the sensitivity of the EPA precision metric to outliers and suggest that the reported mdl's are too low for many elements. Collocated to predicted precision ratios did not change for a few elements (H, Fe, K, S, Br) that are virtually always detected.

Four species (K, Ca, Fe, and Zn) still have ratios >2.0 even with this revised criterion. K, Ca, and Fe (which are associated with soil) have some of the best analytical precisions (Table 5), suggesting there is another uncertainty for coarse-mode particles that is not addressed by the current uncertainty model. Sampling discrepancies, such as may arise from differences in cyclone collection efficiency or sample deposit uniformity, are most likely to affect coarse-mode elements. Figs. 2(c) and 2(d) show the scaled relative differences for Si and Fe which are predominately from soil; the differences are high throughout the range of measured concentrations and the Si and Fe differences show similar patterns at the various sites. A few elements, including Fe and Ca, are measured by both the Cu-anode and Mo-anode XRF systems. For several filter pairs, both XRF measurements showed large differences in Fe and/or Ca. Large differences measured by these two independent XRF systems can be interpreted as actual differences between the sample deposits and not simply imprecise measurements. Further analyses need to be performed to assess the correlation between the soil differences.

The Cu and Zn collocated precisions appear to be degraded by contamination problems (White, 2006a, b). Figs. 2(e) and 2(f) show the relative differences for Cu and Zn. The Zn contamination source is suspected to be chaffing from the labels used on the filter holders, which contain a Zn whitening agent. Smaller labels were adopted in mid-2006, which should reduce the likelihood of label chaffing and thus contamination. Cu contamination has been observed at sites where a high-volume pump is operating close to the IMPROVE sampler; this is the case at Trapper Creek (TRCR). These pumps use brass brushes that abrade during use. Excluding the TRCR samples from the calculation reduces the collocated precision from 30% to 26%. Ni collocated precision may also be affected by contamination; a few sample pairs at MEVE and SAFO had large discrepancies in the Ni concentrations but no source of Ni contamination has been identified.

5. Conclusions

Six of the 41 measured species have collocated precisions $<10\%$ ($PM_{2.5}$, H, S, Br, $SO_4^{=}$, PM_{10}) based on the EPA precision metric (CRF, 1997). The collocated IMPROVE data demonstrate that current reported uncertainty estimates are too low for most species. In general, the collocated to predicted precision ratios are better for species that are predominantly in the fine mode and are measured at concentrations well above their mdl (H, S, V, Se, Br, Pb, sulfate, nitrate, $PM_{2.5}$ mass). The results suggest that the mdl estimates are too low for several XRF elements. In terms of analytical technique, the collocated precisions tend to be better

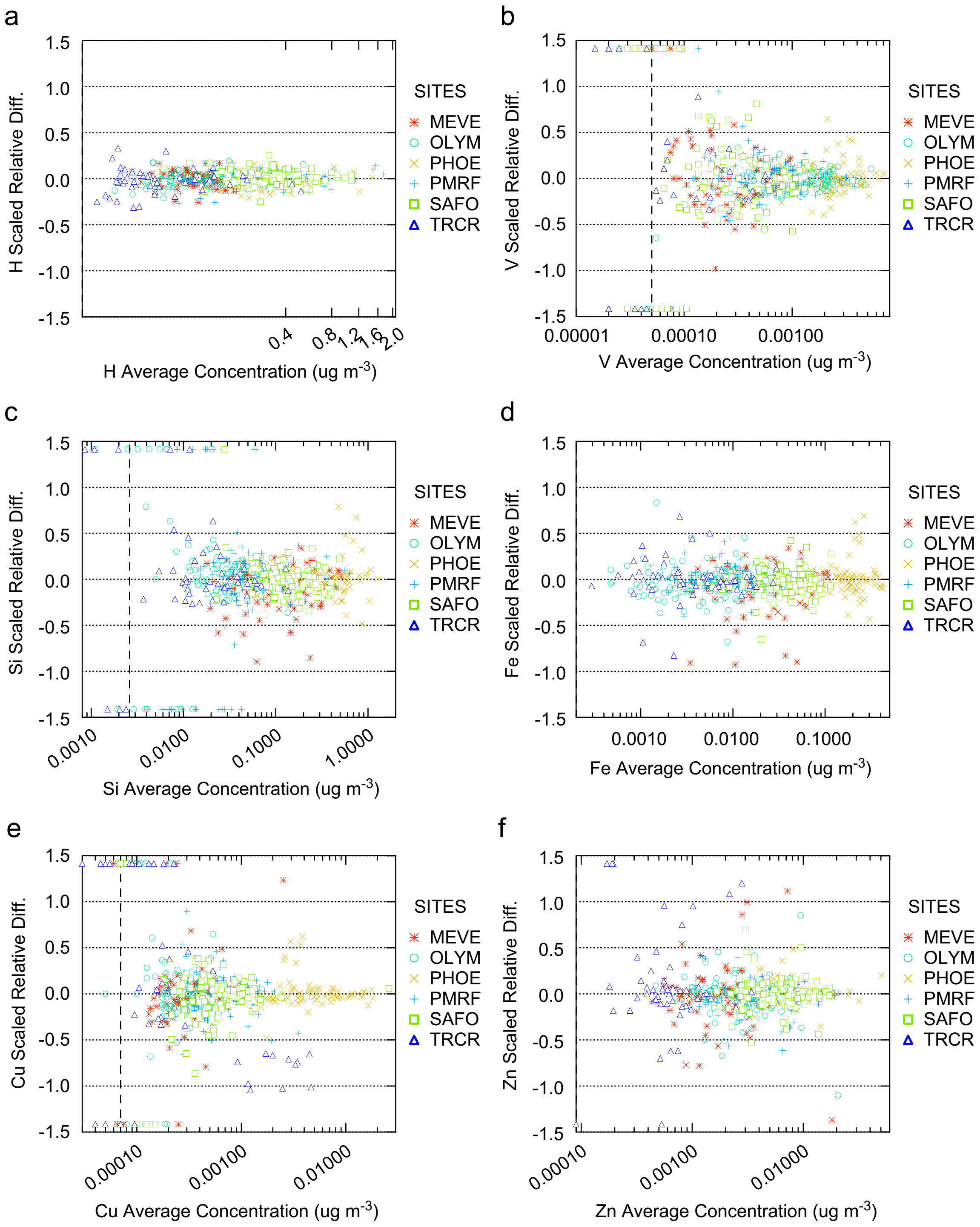

Fig. 2. Scaled relative difference versus average concentrations for the routine and collocated measurements of (a) H, (b) V, (c) Si, d) Fe, (e) Cu, (f) Zn, (g) third organic carbon fraction, and (h) first elemental carbon fraction. If the mdl falls within the range of measured concentrations, it is indicated with a vertical line in the graph. The different symbols represent different monitoring sites.

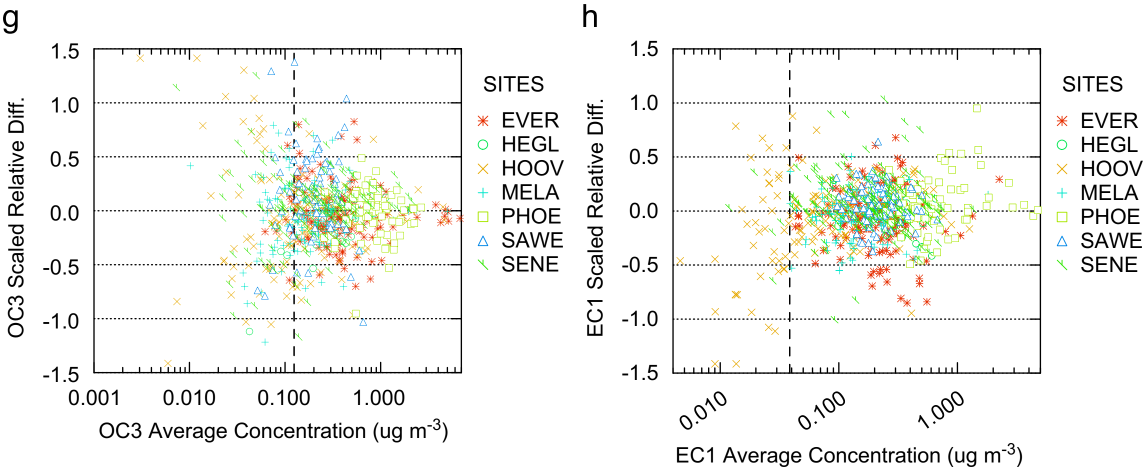

Fig. 2. (*Continued*)

Table 6
Collocated data statistics with alternative inclusion criteria: "Original Criterion" requires the average concentration on both filters to be >3*mdl, with undetected concentrations set to zero, and "Both Detected" requires that species be detected on both filters, at any multiple of the mdl

Species	Original Criterion		Both Detected	
	Count of pairs	Collocated/predicted	Count of pairs	Collocated/predicted
$PM_{2.5}$	539	1.0	577	0.6
H	577	1.3	577	1.3
Na	15	2.0	71	1.1
Mg	9	–	45	1.0
Al	257	5.0	212	1.7
Si	533	3.7	500	2.0
P	21	7.3	3	–
S	577	1.6	577	1.6
Cl	105	5.6	95	1.4
K	577	2.3	577	2.3
Ca	577	3.0	576	2.9
Ti	528	2.6	520	1.8
V	457	1.2	485	1.0
Cr	108	2.0	195	1.1
Mn	529	2.0	546	1.8
Fe	577	3.3	577	3.3
Ni	222	2.8	359	1.6
Cu	499	2.5	512	1.8
Zn	575	4.0	571	3.7
As	60	1.1	275	0.9
Se	406	1.1	500	1.1
Br	576	1.2	577	1.2
Rb	64	1.2	256	0.8
Sr	266	2.1	469	1.3
Zr	5	–	21	1.2
Pb	541	1.8	545	1.5

for techniques that are performed on the entire filter (gravimetry and IC) instead of just a portion of the filter (XRF and TOR), possibly indicating sample deposit uniformity problems.

The soil-related elements have poor precisions even though they are measured at concentrations well above their mdl's and their analytical precisions are within expectations. This suggests that sampling-related uncertainties such as filter deposit non-uniformity or cyclone collection efficiency variations are affecting the samples. The current element uncertainty estimates do not include any sampling-related uncertainties other than flow rate uncertainty.

A variety of experiments and analyses must be conducted to characterize the sources of uncertainty, improve the uncertainty estimates, improve the mdl estimates, and ultimately identify method changes to reduce the uncertainty. These experiments and analyses will be the topics of future publications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2007.06.053.

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