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Estimating Precision Using Duplicate Measurements

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ABSTRACT

Precision is a concept for which there is no universally accepted metric. Reports of precision vary depending on the formula and inclusion criteria used to calculate them. To properly interpret and utilize reported precisions, the user must understand exactly what the precision represents. This paper uses duplicate Interagency Monitoring of Protected Visual Environments (IMPROVE) measurements to illustrate distinctions among different approaches to reporting precision. Three different metrics are used to estimate the precision from the relative differences between the duplicate measurements: the root mean square (RMS), the mean absolute value, and a percentile spread. Precisions calculated using the RMS relative difference yield wide distributions that tend to overestimate most of the observed differences. Precisions calculated using percentiles of the relative differences yield narrower distributions that tend to fit the bulk of the observed differences very well. Precisions calculated using the mean absolute relative difference lie between the other two precision estimates. All three approaches underestimate the observed differences for a small percentage of outliers.

INTRODUCTION

Precision is defined by the International Standardization Organization (ISO) as “the closeness of agreement between quantity values obtained by replicate measurements of a quantity, under specified conditions...precision is usually expressed numerically by measures of imprecision, such as standard deviation, variance, or coefficient of variation under the specified conditions of measurement.”¹ As noted by the ISO definition, there is no single prescribed formula for reporting precision. The quantitative expression of precision is subjectively chosen, and multiple issues must be considered when choosing a method, including whether to express the precision in dimensional or nondimensional terms, what range of concentrations to include in the precision calculations, and how to aggregate measurements made under differing conditions.

IMPLICATIONS

Measurement precisions are provided to indicate the confidence that can be placed in any data analysis and the associated decision-making. Precision values reported for the same dataset can vary widely depending on the exact formula and inclusion criteria used to calculate them. Analysts must be aware of the procedure used to calculate reported precisions and how to use those precisions in their analyses.

These issues must be considered in the context of the intended use of the precision.

Precision is typically expressed as a single number. ISO suggests standard deviation (SD), variance, and coefficient of variation (CV) as measures of precision, yet these three metrics express the “closeness of agreement” in different terms. SD and variance are dimensional quantities whereas CV is a dimensionless quantity. A precision of 0.1 g is the same as a precision of 10% for a mass of 1 g but is an order of magnitude different at a mass of 10 g. The choice of how to express precision is dependent on whether the precision in the range of interest is limited by additive or multiplicative uncertainties.

This paper will use the term “uncertainty” to describe expected or predicted differences among multiple measurements and reserve “precision” to describe the observed differences. Expected measurement uncertainties are typically modeled using two types of uncertainty as shown in eq 1: uncertainties that are constant throughout the range of measurements (additive) and uncertainties that scale with the magnitude of the measurement (multiplicative).²

$$Unc = \text{Expected uncertainty} = \sqrt{Unc_{\text{add}}^2 + Unc_{\text{mult}}^2 * C^2} \quad (1)$$

where Unc_{add} is the additive uncertainty (e.g., blank or zero uncertainty), Unc_{mult} is the multiplicative uncertainty, (e.g., volume or analytical uncertainty), and C is the concentration.

At low concentrations, additive uncertainties usually dominate the overall expected uncertainty, whereas at high concentrations, multiplicative uncertainties usually dominate the total expected uncertainty and $\frac{Unc}{C} \approx Unc_{\text{mult}}$. The transition from one regime to the other is dependent on the values of the additive and multiplicative uncertainties. Air monitoring is usually concerned with high concentrations and its practitioners thus express precision in relative, dimensionless terms.^{3–10}

To obtain a stable estimate of relative precision, the concentration range with uncertainties dominated by additive uncertainties must be eliminated from the estimates; however, exactly which concentrations to exclude is not clear. The additive and multiplicative uncertainties are unknown and can vary by species, site, filter lot, and even analysis date. To avoid the complications of trying to determine the additive and multiplicative uncertainties, simple criteria based on the detection limit are often used to exclude low concentration data. Minkinen⁶ recommends using concentrations above 5–10 times the detection limit, and Speciation Trends Network (STN) documentation¹¹ specifies using only sample pairs with a

mean concentration greater than 3 times the detection limit in the precision calculations. These criteria obviously depend on the exact definition of the detection limit, and detection limit is another concept for which there is no universally accepted metric.¹² On the basis of the uncertainty model in eq 1, if the multiplicative uncertainty is 10% (or 5%) and the detection limit is equal to 2 times the additive uncertainty term, the precision will approach to within 10% of its asymptotic value above a concentration of 10 (or 20) times the detection limit, respectively. The precision estimates are also sensitive to whether the threshold criterion is applied to each individual concentration or the mean of a pair. Depending on the measured concentrations, the selection criteria may exclude a large or small fraction of the dataset from the precision calculations.

Lastly, an approach for summarizing observed measurement differences to compute precision must be developed. The idealized model imagines many measurements at the same concentration C , yielding values C_1, C_2, \dots, C_n . The differences $C_i - \bar{C}$ are commonly assumed to follow a normal (Gaussian) probability distribution, $N(0, \sigma)$, with a mean of zero and a width parameter equal to σ . The dimensional precision is then defined as some multiple of σ , which can be estimated from the SD

$$\sigma \approx s = \sqrt{\frac{1}{n} \sum_{i=1}^n (C_i - \bar{C})^2}, \quad (2)$$

and the relative precision is reported as the ratio $\%c$. Because of the expenses involved in field studies, measurement precision is often determined by only two measurements (duplicates) at a time, made at multiple sites over multiple time periods. This setup provides a more comprehensive evaluation across a range of concentrations and operating conditions, as opposed to measuring a single concentration multiple times, but complicates the interpretation of the results because the mean value changes for each pair of measurements. It is now the relative differences $X_i = \frac{C_{i1} - C_{i2}}{\bar{C}_i}$ that are assumed homogeneous across concentration and are modeled by the normal distribution. Here C_{i1} and C_{i2} are the routine and duplicate concentrations, \bar{C}_i is the mean concentration for measurement pair i , and the mean relative difference is assumed to be zero, $\bar{X} = 0$. Note that the relative differences cannot be truly normal because the ratio must lie between -2 and $+2$ for non-negative concentrations.

The σ value for an assumed normal distribution can be estimated by different statistics. For a truly normal distribution, these different statistics yield identical σ estimates; for a non-normal distribution, the σ estimates will vary. Observed distributions often fail statistical tests for normality because of the presence of outliers, or anomalously large measurement differences. Outliers arise from sporadic errors such as contamination, interference, or mishandling, and from exceptional events such as local source activities that cause spatial gradients. Eliminating outliers using a statistical test is a possible solution although decisions made using these tests can be

considered arbitrary without independent evidence to document that the points are invalid. Alternatively, using a more robust approach to estimate σ , such as percentiles, can also reduce the influence of outliers.

Particular statistics are more or less sensitive to deviations from normality, and the appropriate statistic for the precision calculation may vary depending on the desired application. If the precision is intended to describe differences for most of the measurements, the influence of outliers may need to be minimized in the calculations. If the precision is intended to reflect the maximum possible uncertainty, the outliers may need to be emphasized in the calculations.

Data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) program are used to illustrate the issues presented above. IMPROVE 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 responsible for existing man-made visibility impairment.¹³⁻¹⁵ IMPROVE measures suspended particulate matter concentrations by collecting 24-hr filter samples at approximately 170 sites every 3 days.

In this paper, the U.S. Environmental Protection Agency (EPA) approach to estimating precision along with two other approaches will be applied to duplicate IMPROVE data. Our desired precision estimate is one that describes the differences between the bulk of the pairs well. Plots of the IMPROVE data illustrate discrepancies between the expected uncertainty model in eq 1 and actual duplicate measurement differences. Distributions of the duplicate IMPROVE measurement differences are compared with the differences modeled by the precision estimates; these plots show the effect of outliers and other departures from normality on the precision estimates.

DATA

In 2003 and 2004, the IMPROVE network began operating collocated (duplicate) samplers at several sites. Precision estimates using EPA guidelines for collocated data have been previously published.^{16,17} For logistical reasons, the entire sampler is not duplicated at the collocated sites; instead, a single sampling train is duplicated. There are six duplicate sampling trains of each of the four types in the network. The four types of IMPROVE sampling trains are referred to as A, B, C, and D modules and each one collects a filter on the designated sampling days.¹⁸ This analysis only uses data from the A and B modules. The A module has a 2.5- μm cut point (PM_{2.5}) and utilizes a Teflon filter that is weighed for mass and analyzed by X-ray fluorescence (XRF) for most elements between sodium and zirconium. Many of the elements measured by XRF are considered trace elements and are only present at very low concentrations. The B module has a 2.5- μm cut point and utilizes a nylon filter, preceded by a sodium carbonate denuder, for analysis of anions by ion chromatography—sulfate (SO₄²⁻), nitrate (NO₃⁻), and chloride (Cl⁻). This analysis uses data from the duplicate sampling sites collected from 2004 through 2006. The collocated A modules are located at Mesa Verde (MEVE) National Park (NP) in

Colorado, Proctor Maple Research Facility (PMRF) in Vermont, Olympic NP (OLYM) in Washington, Sac and Fox Nation (SAFO) in Kansas, Trapper Creek (TRCR) in Alaska, and Saint Marks (SAMA) in Florida. The collocated B modules are located at Lassen Volcanic NP (LAVO) in California, Mammoth Cave NP (MACA) in Kentucky, Big Bend NP (BIBE) in Texas, Gates of the Mountains (GAMO) in Montana, Frostburg Reservoir (FRRE) in Maryland, and Blue Mounds State Park (BLMO) in Minnesota. The data were downloaded from <http://vista.cira.colostate.edu/views> in April 2008.

Figure 1 illustrates the relationships between precision and concentration for PM_{2.5} mass and vanadium measurements in dimensional and dimensionless terms. Figure 1, a and c, plot the scaled arithmetic differences between duplicate measurement pairs, $(C_{i1} - C_{i2})/\sqrt{2}$, against their mean concentration; these differences are in dimensional terms. Figure 1, b and d, plot the scaled relative difference, $\left(\frac{(C_{i1} - C_{i2})/\sqrt{2}}{\bar{C}_1}\right)$, against their mean concentration; these differences are in dimensionless terms. The differences are divided by $\sqrt{2}$ because they arise from imprecision in both measurements, which adds quadratically, and the desired result is the precision of one measurement. The PM_{2.5} mass and vanadium scaled absolute differences increase with increasing concentration, but the scaled relative differences decrease with increasing concentration. Either type of differences could be

used to estimate precision, but as discussed in the introduction, the scaled relative differences (Figure 1, b and d) are commonly used in air quality work and will be used in this paper. Figure 2 illustrates the relationships between scaled relative difference and concentration for six more species. The dashed vertical line in each graph in Figures 1 and 2 indicates the mean critical limit (L_c) for 2004–2006.¹⁹ L_c is the lowest concentration that can be interpreted as indicating the presence of the analyte with 95% confidence. L_c values are estimated by the 95th percentile field blank concentrations.¹⁹ The L_c values for the elements were calculated for two groups, pre-2005 and post-2005, because significant changes were made to the XRF systems at the beginning of 2005. The L_c values for the ions were determined for each filter lot. For the elements, the L_c values are much greater than the reported minimum detectable limits (MDL) provided with the IMPROVE data; for the ions, the L_c values are similar to the reported MDL.

The species in Figures 1 and 2 show various relationships between relative difference and concentration. The sulfur and SO₄²⁻ scaled relative differences appear to be constant throughout their measurement range, whereas the PM_{2.5} mass, arsenic, vanadium, and lead scaled relative differences tend to decrease with increasing concentration throughout their measurement range. The calcium and potassium scaled relative differences are relatively constant throughout the measurement range,

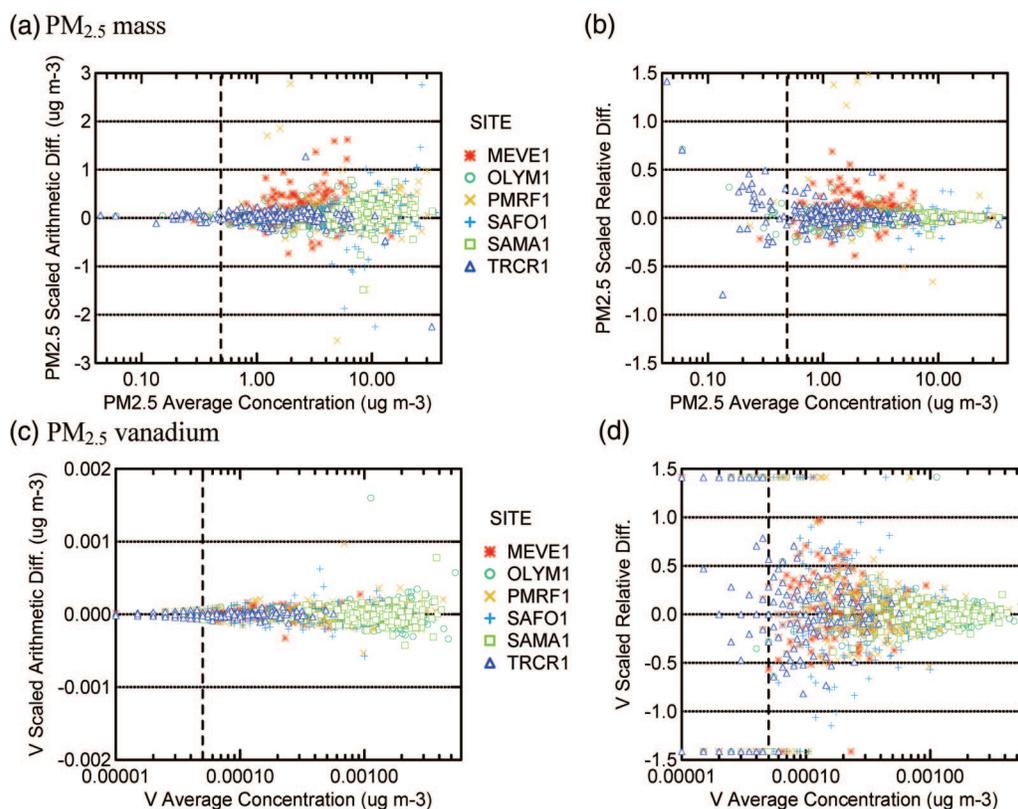


Figure 1. (a and c) Scaled arithmetic difference, $(C_{i1} - C_{i2})/\sqrt{2}$, and (b and d) scaled relative difference, $\left(\frac{(C_{i1} - C_{i2})/\sqrt{2}}{\bar{C}_1}\right)$, vs. mean concentration for the routine and collocated measurements of (a and b) PM_{2.5} mass and (c and d) vanadium. The dashed vertical line indicates L_c . The different symbols represent different monitoring sites.

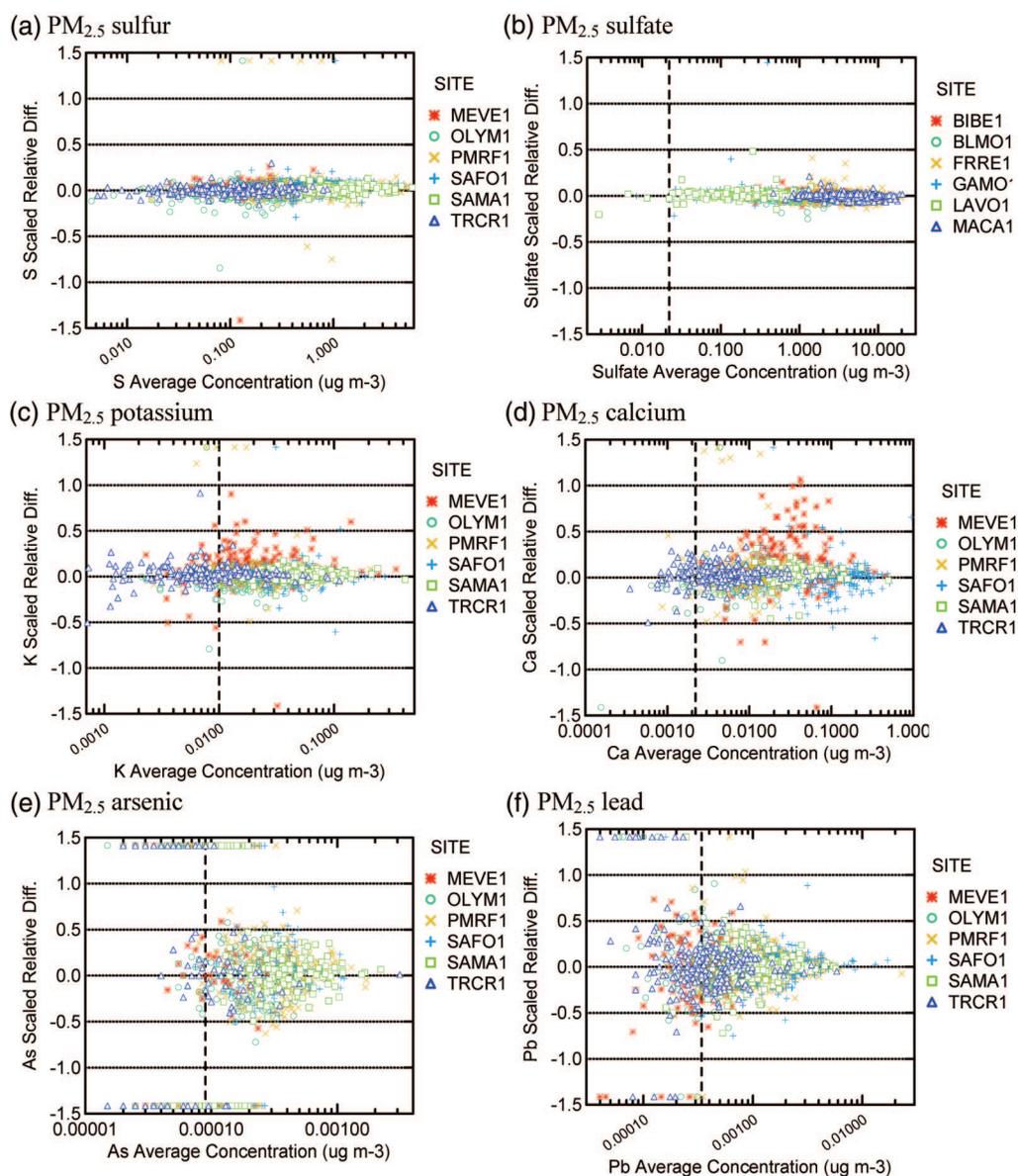


Figure 2. Scaled arithmetic relative differences vs. mean concentrations for the routine and collocated measurements of (a) sulfur, (b) SO_4^{2-} , (c) potassium, (d) calcium, (e) arsenic, and (f) lead. If the L_c falls within the range of measured concentrations, it is indicated with a dashed vertical line. The different symbols represent different monitoring sites.

except for several data pairs from the MEVE1 site that have unusually large differences. These different relationships illustrated in Figures 1 and 2 highlight the difficulty of representing precision with a single number and of developing a standard method for estimating precision.

METRICS

The individual relative differences shown in Figures 1 and 2 must be summarized to compute a single precision for each species. As discussed in the introduction, several different statistics can be used to express the precision. If the scaled relative differences are normally distributed, these precision estimates will be equivalent. The magnitude of the differences between the estimates indicates the magnitude and severity of deviations from normality. In this paper, the goal is to

estimate a σ for a normal distribution that best describes the bulk of the observed relative differences. A 1σ estimate of precision provides a concentration range within which the concentration is expected to occur 68% of the time.

The EPA-recommended formula for calculating precision of collocated Federal Reference Method samplers identifies σ with the root mean square (RMS) of the scaled relative differences, as shown in eq 3.¹³

$$\text{RMS Precision} = \sqrt{\frac{1}{n} \sum_{i=1}^n D_i^2} * 100\%, \text{ where} \quad (3)$$

$$D_i = \frac{(C_{i1} - C_{i2})/\sqrt{2}}{\bar{C}_i}$$

Table 1. Three different estimates of precision for several species measured in the IMPROVE network.

Species	Collocated Pair Count (<i>n</i>)	RMS Precision (%)	Mean Precision (%)	Percentile Precision (%)	Bias (%)
PM _{2.5}	1488	7	5	4	2
Sodium	315	22	20	17	4
Magnesium	53	14	13	11	-3
Aluminum	600	18	15	12	7
Silicon	918	15	13	9	4
Phosphorus	13	12	12	11	-2
Sulfur	1570	7	6	5	1
Chlorine	126	22	16	12	2
Potassium	1244	9	8	6	3
Calcium	1291	16	12	8	4
Titanium	662	14	12	10	5
Vanadium	963	14	13	11	1
Manganese	1356	16	15	13	3
Iron	1207	14	11	8	4
Nickel	153	11	8	7	1
Copper	220	14	10	9	1
Zinc	306	10	8	6	1
Arsenic	597	21	21	20	2
Selenium	952	11	10	9	2
Bromine	1586	9	8	6	4
Rubidium	107	18	18	17	-1
Strontium	379	15	15	13	4
Lead	715	11	10	9	1
Cl ⁻	72	10	8	7	0
NO ₃ ⁻	1477	7	6	5	2
SO ₄ ²⁻	1808	4	3	3	1

Notes: The precision estimates are based on concentrations greater than three times the critical limit.

Equation 3 is a modified version of the SD calculation shown in eq 2 for the situation in which the measurements are only repeated once. RMS precisions are sensitive to deviations from normality; the sensitivity results from the square of the differences term in the numerator. Data pairs with large differences (outliers) will be weighted heavily when they are squared compared with most pairs with moderate or small differences.

An alternative approach to determining precision identifies σ with the scaled mean absolute difference (MAD), as shown in eq 4.

$$\text{MAD Precision} = \sqrt{\frac{\pi}{2}} \frac{1}{n} \sum_{i=1}^n |D_i| * 100\% \quad (4)$$

The $\sqrt{\frac{\pi}{2}}$ factor in eq 4 arises from the relationship between the mean absolute difference and σ in a normal distribution.⁹ This approach does not square the differences and is therefore less sensitive to outliers. The STN and Clean Air Status and Trends Network report precisions using a metric similar to eq 4.^{5,20,21}

A third approach is to use percentiles to determine σ . Distribution percentiles can minimize the influence of outliers by excluding the outer edges of the distribution. For a normal distribution, 68% of the values are within 1 SD of the mean; therefore, the precision can be estimated as one-half of the range between the 16th and 84th percentiles.

$$\text{Percentile Precision} = \frac{1}{2}(P_{84}(D_i) - P_{16}(D_i)) * 100\% \quad (5)$$

P_{84} and P_{16} are the 84th and 16th percentiles in the scaled relative difference distribution. This approach completely ignores the outer one-third of the distribution and is therefore the least sensitive to outliers.

The RMS and MAD precision calculations include any bias existing in the measurements. Small biases (<3%) are expected at individual sites as a result of operational differences such as flow calibration. These biases are expected to be random and vary over long time scales (e.g., annually when new flow calibrations are performed). The site-specific biases are expected to average out to zero in the overall bias and precision calculations, which include six sites over 2 yr. The mean overall bias is estimated from eq 6.

$$\text{Bias} = \frac{1}{n} \sum_{i=1}^n D_i * 100\% \quad (6)$$

The criterion used to include data in the precision calculations is that both concentrations must be greater than 3 times the L_c . No further criterion is used to remove outlying differences from the dataset. All data above the minimum threshold, irrespective of the validation flag, were used in the precision calculations.

RESULTS

Table 1 shows the precision estimates based on the three different methods shown in eqs 3–5 for the duplicate

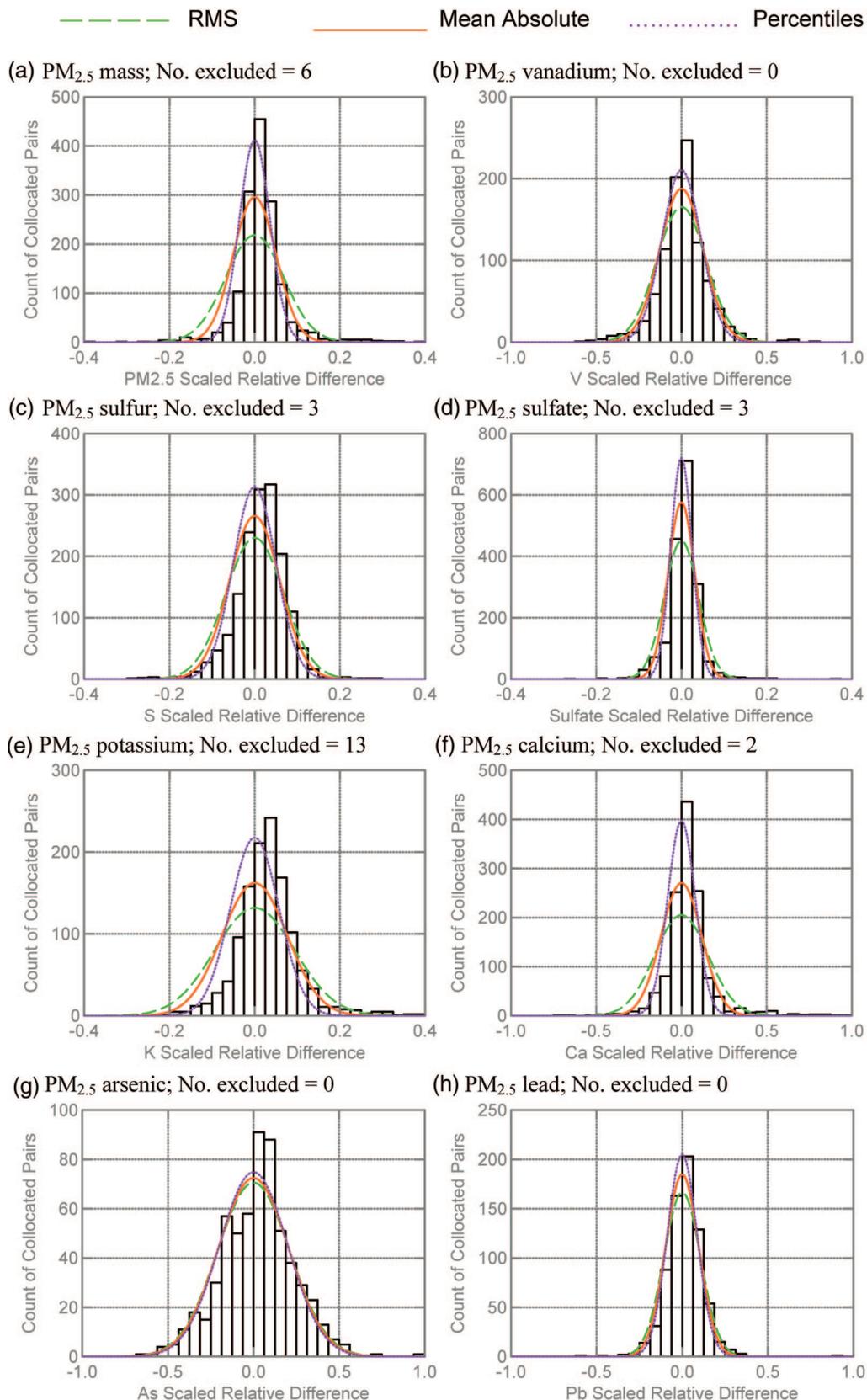


Figure 3. Histograms of scaled relative differences along with normal curves for three different estimates of precision based on the (1) RMS from eq 3, (2) MAD from eq 4, and (3) half of the difference between 84th and 16th percentiles from eq 5 for PM_{2.5} (a) mass, (b) vanadium, (c) sulfur, (d) SO₄²⁻, (e) potassium, (f) calcium, (g) arsenic, and (h) lead. The number of observed differences excluded from the graph by making the graph range less than the data range is listed next to each label (these differences are included in the calculations).

IMPROVE data collected from 2004 through 2006. Although there are over 1500 collocated filter pairs in the dataset, the "Collocated Pair Count" column in Table 1 illustrates that many species are rarely measured above 3 times the L_c . The three precision estimates in Table 1 are in a consistent order for all species with the RMS precisions being loosest (highest values) and percentile precisions being tightest (lowest values). Throughout this discussion of precisions, the terms "tight" and "loose" are used to qualitatively describe the precision estimates and shape of the curves; 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). The RMS precision estimates are sensitive to outlying differences because the RMS equation squares the differences. Therefore, the difference between the RMS and the other precision estimates indicates the prevalence and severity of outlying differences. Outlying differences can be observed for every species in Figures 1 and 2, except possibly arsenic. The source of these outliers could be contamination, interference, or mishandling, but there is no way to determine the exact source.

The last column in Table 1 lists the mean bias for the measurements (eq 6). Most of the biases are small, but some elements, and particularly those associated with soil (iron, silicon, aluminum, manganese, titanium, potassium), have relatively large biases ranging from 3 to 7%. It is unknown whether these bias are random or a result of some unintentional operational difference between the duplicate and routine samplers. The bias will inflate the RMS and MAD precision estimates but not the percentile precision estimates. Special measurements have been established to further investigate these biases, but results are not available at this time.

Figure 3 illustrates the different precisions listed in Table 1 by showing the actual distribution of differences as bars and the predicted distributions based on the three precision estimates as curves. Figure 3 shows these distributions for the same eight elements shown in Figures 1 and 2. The normal distribution curves are based on the three precision estimates in eqs 3–5. The three normal curves are centered on zero, which emphasizes that the actual difference distributions are biased to the right (histograms are not centered on zero). The RMS precisions are consistently looser, as illustrated by the wider normal curves. The percentile precisions are consistently tighter, as illustrated by the narrower curves. The MAD precisions consistently lie between the other two precision estimates.

The goodness of fit of the three precision estimates can be evaluated qualitatively using Figure 3. The RMS precisions predict fewer measurement pairs with small differences than are in the actual distributions; for example, the $PM_{2.5}$ RMS predicted that maximum counts are around 220, whereas the maximum counts in the actual distribution are over 400. This illustrates that the RMS precisions underestimate the frequency of small differences and overestimate the frequency of larger differences. All three precision estimates fail to predict the largest differences (outliers) observed in the data. The percentile precision estimates tend to do the best job of describing the most frequent measurement differences for

all of the species in Figures 2 and 3. The three precision estimates are very similar for arsenic, indicating that the arsenic differences are well described by a normal distribution.

CONCLUSIONS

Precision is a concept rather than a well-defined quantity. The goal of most precision evaluations is to characterize the performance of most of the measurements. When choosing a method for estimating precision, the homogeneity of the precision over the measurement range and normality of the distribution of differences must be considered, along with the desired purpose of the precision estimates. Particular methods tend to provide more or less conservative estimates of precision. Nondimensional precision estimates based on the relative differences of measurements are commonly used in the air quality field but may not sufficiently describe the data, particularly if the measured concentrations do not routinely exceed 5–10 times the detection limit. Outliers are hard to avoid and predict. The RMS precision estimates place disproportionate weight on these outliers and may provide poor estimates of precision for more typical measurements. The MAD and percentile precision estimates are more robust to outliers and better fit most of the differences. More quantitative analyses need to be performed to further understand the goodness of fit of these three estimates. Data users should be aware of the exact approach used to calculate precision, particularly when comparing published precision estimates for different monitoring programs.

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