Harmonization of Interlaboratory X-ray Fluorescence Measurement Uncertainties

Overview

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Introduction

It is essential that there be general consistency in the precision of any one type of environmental measurement if the results of this measurement are to be used for source attribution, modeling, or some other data treatment requiring statistical analysis. Currently there is a wide disparity between methods for calculating the precision (uncertainty) of x-ray fluorescence (XRF) measurements of $PM_{2.5}$ trace metals from different XRF laboratories, including those used by the STN and IMPROVE networks. The principle contributors to total uncertainty of XRF values include: field sampling; filter deposit area; XRF calibration; attenuation or loss of the x-ray signals due to the other components of the particulate sample; and determination of the analyte x-ray emission peak areas by curve fitting. Because it is difficult to measure calibration and field sampling uncertainty components accurately and consistently, the STN program has assumed estimated values of 5% for each component. The uncertainty of determining a peak area is dependent upon the XRF instrument, the software used, and the size of the peak; of course, the larger the peak above the background, the smaller is the uncertainty of the peak area determination. This leaves attenuation, which can be a significant factor for the lighter elements. Attenuation of x-rays arises from (1) the excitation source x-rays being absorbed by the sample components and therefore not reaching the atoms of interest, and (2) the fluorescence x-rays not escaping the sample mass for detection.

Attenuation Uncertainty

The uncertainty (variability) of the attenuation arises from the variability of the composition of the deposit on each filter, including the amount of each element present (other than the element of interest) and the sample structure, with a homogeneous layer of very small particles absorbing differently than a layer of larger particles. For example, the attenuation of the x-ray signal for a given amount of sulfur will be different for a sample consisting principally of fine, high organic "soil" as compared to a sample which consists principally of oxides or crustal minerals. It is this variation that gives rise to the attenuation uncertainty. Some researchers, including John Cooper (CES), argue that we do not have sufficient information about these variations in composition and physical structure to model the uncertainty. Others such as Robert Kellogg (Alion Science and Technology), Bob Eldred (UC-Davis) and Tom Dzubay/Robert Nelson (EPA) have used first principles of physics to estimate this uncertainty. The work of Dzubay and Nelson has lead to the use of two models, the homogeneous layer model and the particle model. The first is applied to

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elements that are found principally in particles that are less than 2.5 μm in aerodynamic diameter and are considered to be part of a homogeneous layer. The second is applied to elements that are found principally in coarse particles, that is, from about 2.5 μm in aerodynamic diameter to about 10 μm in aerodynamic diameter. It is proposed that the methods and results of these latter researchers be used to define XRF attenuation uncertainty for the harmonization process.

Robert Kellogg refined the early work of Dzubay/Nelson and followed the same procedures described by Eldred. He assumed that the high end of the size distribution of the $PM_{2.5}$ contains principally coarse particles. He applied the particle size model to elements with Z = 11 to 14 and the homogeneous layer model to elements with Z > 14. To estimate uncertainty for the elements, Na, Mg, Al, and Si, Kellogg and Dzubay/Nelson assumed that the sample is composed of a wide variety of common crustal minerals; the uncertainty for each element has been defined by the range of attenuation values determined by this range of potential minerals. For Z > 14, they assumed the composition of the portion of the sample not measured by XRF varied from $C_6H_{10}O_5$ to C_6H_6 to O (oxygen only), which defines the uncertainty for each of the elements. The values for attenuation (A) and attenuation uncertainty ($δ_a$) from Kellogg are presented in Table 1.

Table 1. Attenuation and attenuation uncertainty values

Element, Z	Kellogg Models			
	Homogeneous Layer		Particle Size	
	A	$δ_a$	A	$δ_a$
Na, 11	---	---	0.62	0.035 (5.6%)
Mg, 12	---	---	0.65	0.044 (6.8%)
Al, 13	---	---	0.76	0.032 (4.2%)
Si, 14	---	---	0.80	0.032 (4.0%)
P, 15	0.99	0.003 (0.3%)	---	---
S, 16	0.99	0.002 (0.2%)	---	---
Cl, 17	0.99	0.001 (0.1%)	---	---
K, 19	0.99	0.001 (0.1%)	---	---
Ca, 20	0.99	0.001 (0.1%)	---	---

Harmonization Procedure

The generally-accepted model for calculating total uncertainty is:

$$\delta_{tot} = (\delta_f{}^2 + \delta_a{}^2 + \delta_c{}^2 + \delta_v{}^2)^{1/2}$$

where, δ_f = fitting uncertainty (XRF-specific, all elements; from ~2 to 100+%)

δ_a = attenuation uncertainty (XRF-specific, light elements only; see Table 1 above for values)

δ_c = calibration uncertainty (combined lab uncertainty, assumed by STN as 5%)

δ_v = volume/deposition size uncertainty (combined field uncertainty, assumed by STN as 5%)

To harmonize the total uncertainties, mutually acceptable values for each of the four contributors shown in the equation above will be used to calculate new, total uncertainty values for the XRF results from each laboratory. In the case of Chester LabNet, it will be necessary to replace their relatively high attenuation uncertainty values with new values. As an illustration of this procedure, calculations were performed to harmonize values for Si and S for the two STN XRF laboratories (RTI and Chester LabNet). The procedures were as follows:

- For RTI data, the values for attenuation uncertainty, 5% for calibration uncertainty, and 5% for combined field uncertainty were used.

- For Chester LabNet data, the relatively high values for attenuation uncertainty were extracted and the new values for attenuation uncertainty substituted, along with addition of 5% for combined field uncertainty.

The tables below present the uncertainty values that have been used by the RTI and Chester LabNet laboratories for silicon and sulfur. (The percentages shown in the tables are to be multiplied by the measured concentrations.) As to the new values for attenuation uncertainty, it was first thought that the best choice would be to accept the values of Kellogg as calculated with his chosen set of minerals. As an improvement of this proposal, Kellogg agreed to and then calculated the range of attenuation values (i.e., attenuation uncertainties) for the elements Na, Mg, Al, and Si that would be measured on the XRF's used at RTI and Chester LabNet for a set of pre-chosen mineral particles. These newly calculated values are presented in the table below. With the mineral set being comprehensive, it is reasonable to assume the range of values is between 2 and 3 σ as done by Kellogg. As noted, the changes in attenuation uncertainty with the different XRF instruments are minimal. Also, the

small differences in attenuation uncertainties will not be significant when these uncertainties are combined with the fitting uncertainty, the calibration uncertainty, and the field sampling uncertainty.

Silicon:

	Original (Fig 1)				Revised (Fig 2)			
Lab	δ_f[1]	δ_a	δ_c	δ_v	δ_f[1]	δ_a	δ_c	δ_v
RTI	-	0	0	0	-	4.3%	5%	5%
Chester LabNet	-	10%[2]	5%	0	-	4.7%	5%	5%

Sulfur:

	Original (Fig 3)				Revised (Fig 4)			
Lab	δ_f[1]	δ_a	δ_c	δ_v	δ_f[1]	δ_a	δ_c	δ_v
RTI	-	0	0	0	-	0.2%	5%	5%
Chester LabNet	-	10%[2]	5%	0	-	0.2%	5%	5%

Notes:
[1] – Fitting uncertainty is determined by the instrument and is not modified.
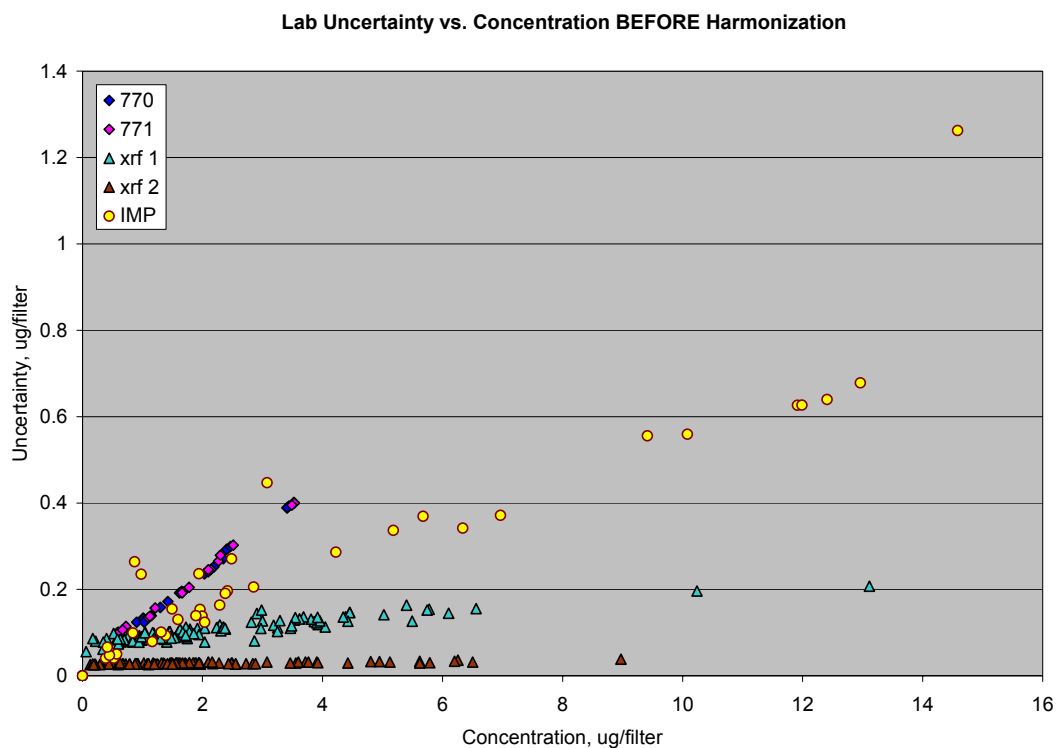[2] – The original value of δ_a for Chester LabNet data is assumed to be 10% based on analysis of historical data. The values provided to RTI by Chester LabNet for δ_a, 13.1% and 12.4% for silicon and sulfur, respectively (see Table 18 in White Paper), appear too large, and may have been truncated to 10% within the Chester LabNet software.
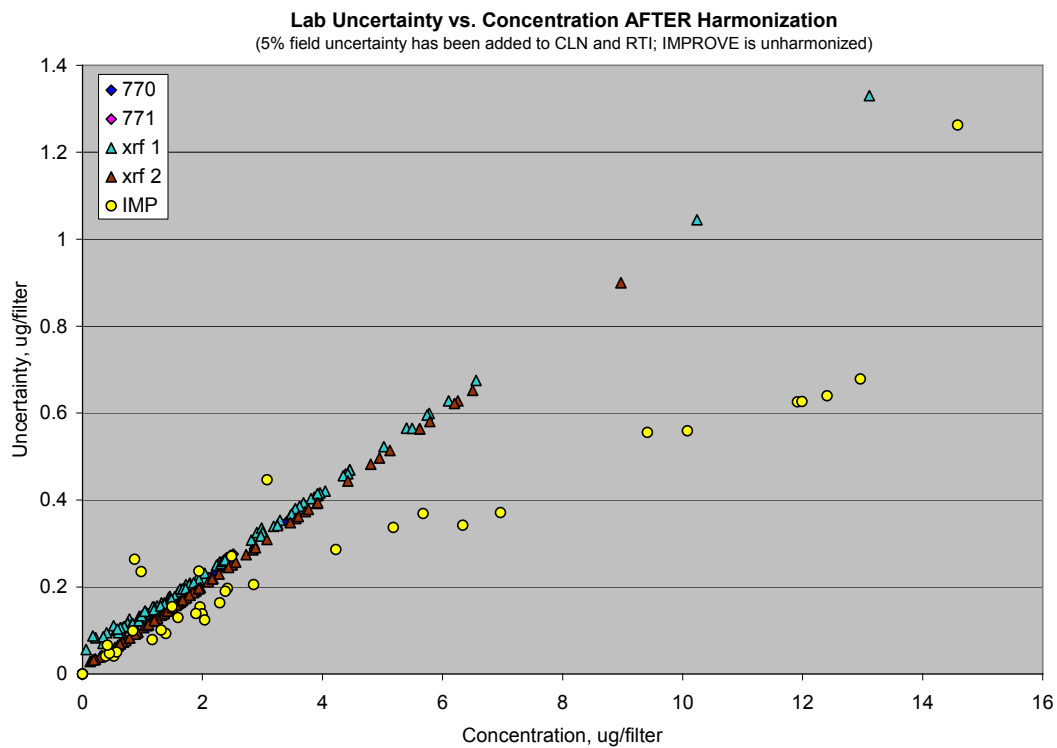
Illustration of Effects of Harmonization

Figures 1 through 4 below illustrate the effects of recalculating the total uncertainties for sample data from RTI [XRF 1 and XRF 2] and Chester LabNet [XRF 770 and XRF 771]. IMPROVE [IMP] XRF uncertainty data that are not harmonized are shown for comparison purposes. The IMPROVE concentration and uncertainty values shown are taken from the VIEWS website; data was taken from randomly chosen sites in order to illustrate the dependency between concentration and reported uncertainty. Figures 1 and 3 show the uncertainties as originally reported by the respective laboratories. Figures 2 and 4 show total uncertainty for RTI and Chester Labnet data with the proposed changes and additions; as in Figures 1 and 3, the IMPROVE data are shown without harmonization. It should be noted that the total uncertainty of the IMPROVE XRF data is based on the uncertainty of the determination of the analyte x-ray emission peak areas and 4% for calibration uncertainty and does not include attenuation uncertainty. Harmonization of the IMPROVE data using the proposed approach would bring the IMPROVE uncertainty values close to those of the harmonized RTI and Chester LabNet values, as shown in Figures 5 and 6. It is our

understanding that Warren White of UC-Davis is reevaluating the IMPROVE method for determining uncertainties and may propose changes in the future.

The figures show a considerable improvement in the comparability of the total uncertainties as a result of this approach to harmonization. Values for δ_a vary between laboratories, and these values could potentially be refined using improved estimates of the composition and structure of the $PM_{2.5}$ samples. However, the effects of these revisions on overall uncertainty will be small.

Lab Uncertainty vs. Concentration BEFORE Harmonization

Figure 1. Silicon Laboratory Uncertainty before Harmonization.

Lab Uncertainty vs. Concentration AFTER Harmonization
(5% field uncertainty has been added to CLN and RTI; IMPROVE is unharmonized)

Figure 2. Silicon Total Uncertainty after Harmonization (IMPROVE data not harmonized).

Lab Uncertainty vs. Concentration BEFORE Harmonization
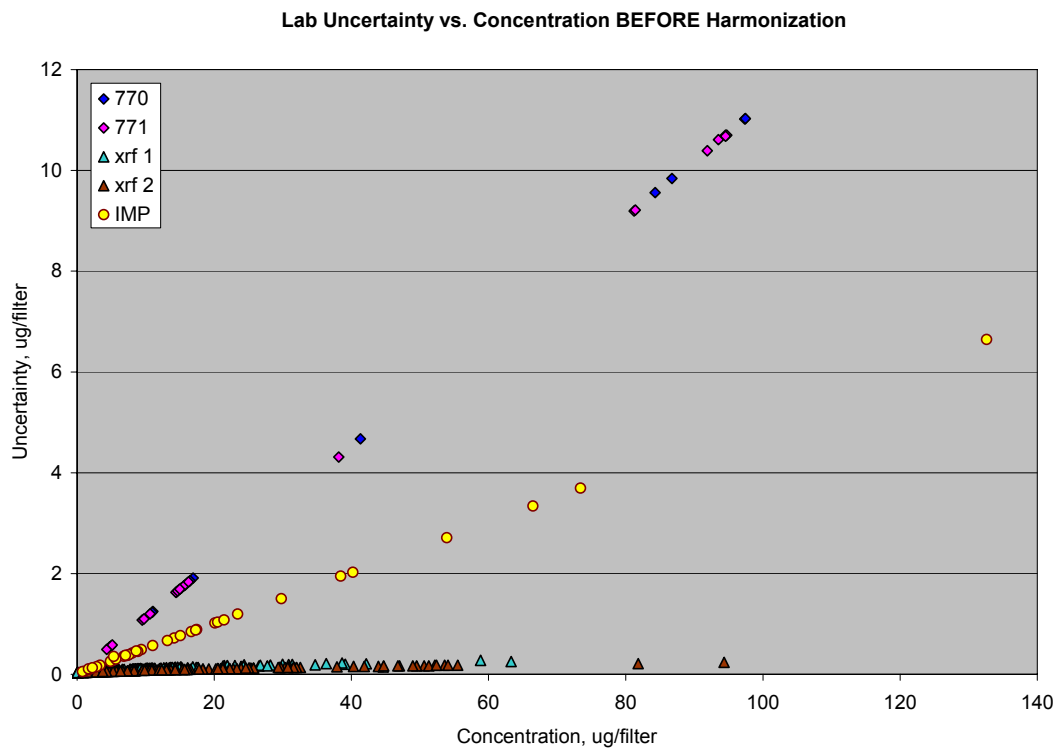
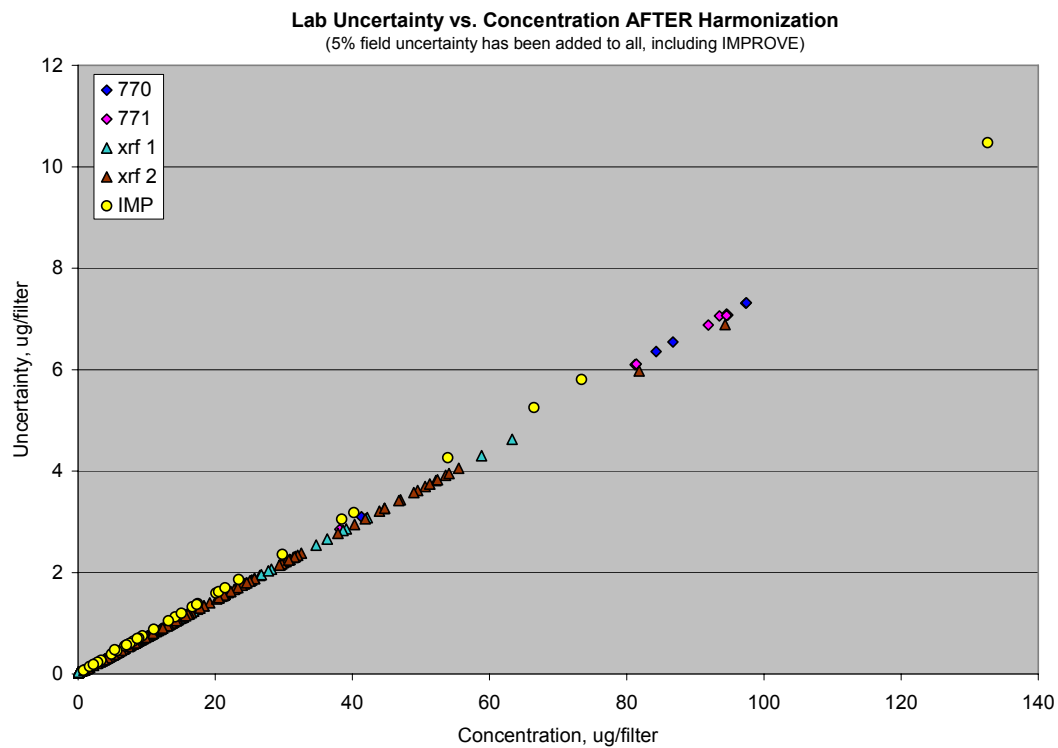**Figure 3. Sulfur Laboratory Uncertainty before Harmonization.**

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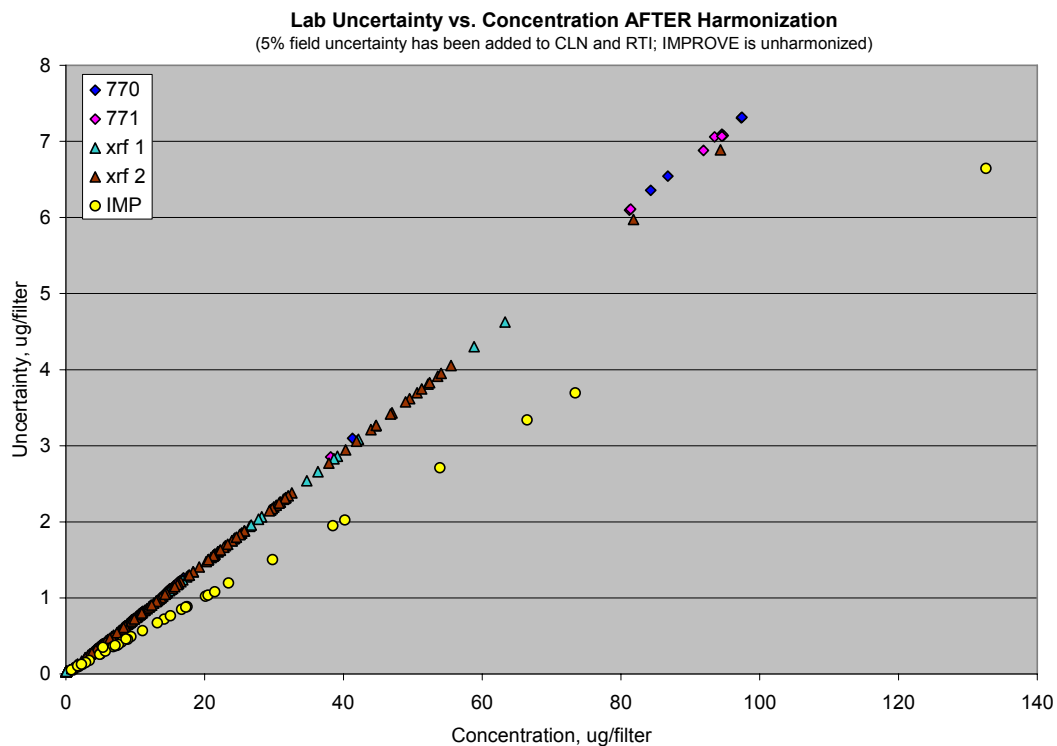
Figure 4. Sulfur Total Uncertainty after Harmonization (IMPROVE data not harmonized).
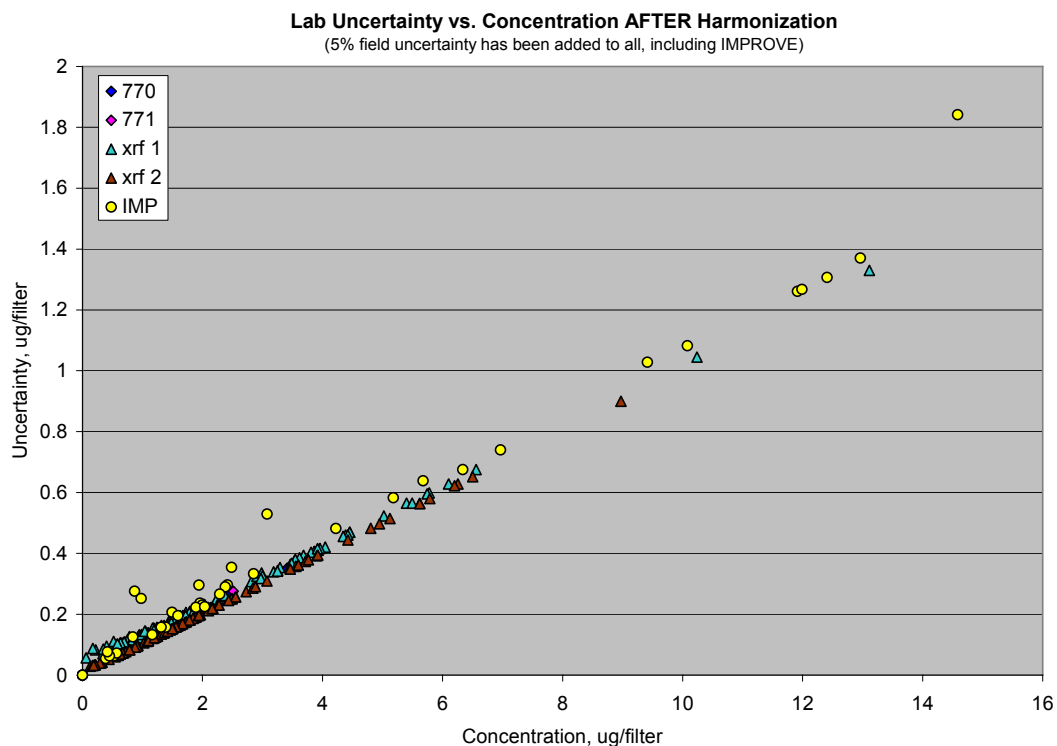
Figure 5. Silicon Total Uncertainty after Harmonization (IMPROVE data harmonized).

Figure 6. Sulfur Total Uncertainty after Harmonization (IMPROVE data harmonized).