

## Top down Arsenic uncertainty measurement in water and sediments from Guarapiranga Dam (Brazil)

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**Abstract:** Total arsenic measurements assessment regarding legal threshold demands more than average and standard deviation approach. In this way, analytical measurement uncertainty evaluation was conducted in order to comply with legal requirements and to allow the balance of arsenic in both water and sediment compartments. A top-down approach for measurement uncertainties was applied to evaluate arsenic concentrations in water and sediments from Guarapiranga dam (São Paulo, Brazil). Laboratory quality control and arsenic interlaboratory tests data were used in this approach to estimate the uncertainties associated with the methodology.

**Keywords:** Top down estimation uncertainty, Guarapiranga Dam, Arsenic

### 1. INTRODUCTION

Despite the focus of interest, understanding some concepts can be worth and add value to the work. When analyte concentration is reported with its appropriate analytical method uncertainty, much more information is provided than a simple replicate standard deviation. It does not matter now, but analytical laboratories realized the benefits or were forced to apply the concepts of analytical measurement uncertainty in reporting analyte concentration. After several years of harmonization documents have been published, some measurement uncertainties approaches pop up such as bottom-up, top-down, based on validation studies, empiric and *ad-hoc* methods, the very popular control charts, manufacturers specifications, and others complex theoretical models. Some with general application, others targeting specific situation, and others as a time saving approach [1, 2]. In the TR 537 Ed. 3.1 handbook by Nordtest, Magnusson *et al.* [3] used

internal and external quality control data for ammonia assessment in water and estimated the analytical data uncertainties based on a top-down approach. That procedure also checked if the method performance is under control with no significant change or bias. In this study, the top-down uncertainty estimation approach was considered in analyzing analytical data from arsenic concentration in water and sediment from Guarapiranga dam, São Paulo, Brazil.

### 2. METHODS/EXPERIMENTAL

#### 2.1. Arsenic measurement and quality control

Sample preparation and analytical measurements were carried out at Laboratório de Análises Química e Ambiental, Centro de Química e Meio Ambiente in IPEN-CNEN, São Paulo, Brazil. Since 2010, this laboratory has been working under ISO 17025 standard principles. Total arsenic was measured by GF-AAS (AAAnalyst/HGA 400,

Perkin-Elmer, USA) at 193.7 nm as presented at [4] and [5].

## 2.2. Top down Uncertainty estimation

Based on the described in the handbook by Magnusson *et al.* (2011) [6], top-down approach was used to estimate the expanded uncertainty in measuring arsenic in water and sediment. Two components were considered:

### 2.2.1 Repeatability within laboratory

From 2011 to 2013, arsenic measurements were conducted in NIST 1643e Standard Reference Material – Trace Elements in Water with certified value of  $60.45 \pm 0.72 \mu\text{g L}^{-1}$  ( $U, k = 2$ ) for arsenic together with routine water samples analyses. Control chart with obtained arsenic results from this RM was part of laboratory quality system performance, and was used in the uncertainty estimation of repeatability standard uncertainty,  $u_{Rw}$ . In routine analyses, information from repeatability is attributed to short-term variations on uncertainty.

### 2.2.2 Method and Laboratory bias

Uncertainty second component used in this approach was the laboratory bias or bias standard uncertainty,  $u_{bias}$ , obtained from 2010 to 2013 performance in interlaboratory tests ( $n=10$ ), with a high number of participant laboratories ( $m = 50$ ). Z-score value is the most common tool to assess the laboratory technical competence no matter the target value is a conventional quantity value or an agreement to a consensus value between the reported values by the participant laboratories. All percentage bias results (not z-score values) for arsenic concentration were considered in this component, where  $RMS_{Bias}$  and  $u_{Cref}$  are calculated as in (1) and (2).

$$RMS_{Bias} = \sqrt{\sum (bias)^2 / n} \quad (1)$$

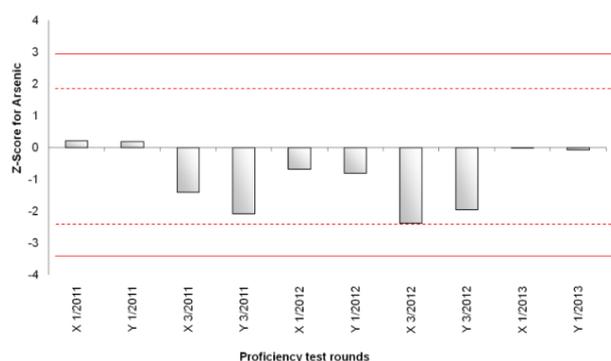
$$u_{Cref} = \frac{S_r}{\sqrt{m}} \quad (2)$$

## 2.3. Water and bottom sediment sample treatment

Water samples were acidified to  $\text{pH} < 2$  and directly measured. bottom sediment samples were dried for 5 days at 40-60 °C and 0.5g of each sample was twice digested accordingly US-EPA 3051 method [7] lead to 50 mL final volume. Sediment samples were treated as described by [5].

## 3. RESULTS AND DISCUSSION

Uncertainty component,  $u_{Rw}$ , associated to the repeatability within laboratory was obtained from the control chart of arsenic values in NIST 1643e ( $n=60, p=0.05$ ) measured before each sample batch with 15% control limits. The estimated  $u_{Rw}$  for that standard along three years of routine conditions measurements is  $4.5 \mu\text{g L}^{-1}$  (7.5%). Once the arsenic certified value is  $60.45 \mu\text{g L}^{-1}$  with an expanded uncertainty of  $0.72 \mu\text{g L}^{-1}$  ( $k=2$ ), the obtained  $u_{Rw}$  was considered in the uncertainty calculation. Measurement of total arsenic in water was evaluated by laboratory regular participation in proficiency tests (PT) organized by Rede Metrologica do Rio Grande do Sul [8]. Laboratory Z-score performance from PT, in two (X and Y) rounds, from 2010 to 2013, are present in figure 1.



**Figure 1:** Z-Score for arsenic measurements by GF-AAS in PT rounds from 2011 to 2013.

Consensus value, robust standard deviation and laboratory bias (in  $\mu\text{g L}^{-1}$  and %) are presented in table 1.

**Table 1.** Arsenic interlaboratory results.

Total As	Value	S <sub>R</sub>	Bias	Bias	Z-Score
	ug L <sup>-1</sup>	ug L <sup>-1</sup>	ug L <sup>-1</sup>	%	
X1/2011	40	8	7	18%	0.2
Y1/2011	60	6	0	0%	0.2
X3/2011	20	20	-10	-50%	-1.4
Y3/2011	45	25	-30	-67%	-2.1
X1/2012	30	15	-5	-17%	-0.7
Y1/2012	50	30	-10	-20%	-0.8
X3/2012	20	7	-17	-85%	-2.4
Y3/2012	50	11	-22	-44%	-1.9
X1/2013	40	20	0	0%	0.1
Y1/2013	80	20	0	0%	0.1
$\bar{X}$	43	16	9	26	0.9

From table 1 data, laboratory root means square bias ( $RMS_{Bias}$ ) was estimated as 5.9%. Reference value or nominal value uncertainty  $u_{Cref}$  was estimated as PT robust standard deviation ( $m=50$ ,  $p=0.05$ ) as the second  $u_{bias}$  component.  $u_{Cref}$  was estimated as 3.7% and this value was considered also adequate to the measurement purpose. It is important to mention that  $u_{Cref}$  component is very dependable of PT provider, how the provider establishes consensual average and robust standard deviation. If these components are evaluated as too large, the laboratory solely action must be the change of PT program to one with smaller  $S_R$ . These components combined uncertainty ( $u_c$ ) corresponded to 7.9%. To complete uncertainty estimation see table 2.

**Table 2.** Data from uncertainty estimation from As in water and bottom sediment by GF-AAS

Action	As in water and bottom sediment by GF-AAS
Specify measurand	Total As measurement by GF-AAS with a $\pm 7.5\%$ from LQM to $100\mu\text{g.L}^{-1}$ concentration range
Quantify $R_w$ component: A - Control Chart B - Steps not covered by Control Chart	A: Control limit set as $\pm 4.5 \text{ ug.L}^{-1}$ or $\pm 7.5\%$ (95% confidence limit) B: The control sample includes all analytical steps.
Quantify Bias component	Interlaboratory proficiency tests results from 2011 to 2013 are presented at table 1. The root mean square (RMS) of bias was 5.9%. The uncertainty of nominal values is $u_{Cref} = 3.7\%$
Convert components to Standard uncertainty $u(x)$	$u_{Rw} = \pm 7.5\%/2 = 3.75$ $u_{bias} = \text{Raiz}(RMS_{bias}^2 + u_{Cref}^2) = \text{Raiz}(5.9^2 + 3.7^2) = 6.96\%$
Calculate combined standard uncertainty, $u_c$	$u_c = \text{Raiz}(u_{Rw}^2 + u_{bias}^2) = \text{Raiz}(3.75^2 + 6.96^2) = 7.9\%$
Calculate Expanded uncertainty, $U = 2 \cdot u_c$	$U = 2 \cdot 7.9\% = 15.8\% \sim 16\%$

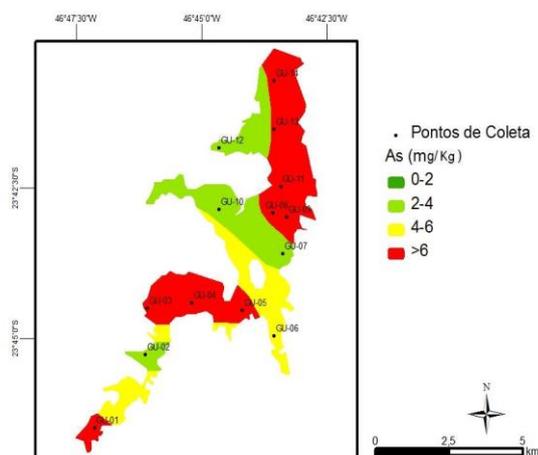
### 3.1 Total As content in water samples

In this study, total As measurement expanded uncertainty in water samples considering top-down approach in the concentration range of 20 to  $80 \mu\text{g L}^{-1}$  was estimated as 16% ( $U$ ,  $k=2$ ). Which is two to three times higher than expanded uncertainty found with bottom-up approach [2]. Water Framework Directive, European requirements and directives regarding drinking water, groundwater, freshwater, and coastal seawater, establishes that

the maximum standard expanded uncertainty with 10% precision and 10% trueness (As requirement conditions at  $10\mu\text{g.L}^{-1}$  concentration range) should be 15%. Therefore, according this requirement, the top-down uncertainty estimation approach would not be suitable. However, Magnusson et al. [6] present data that shows As requirements are frequently not met in several water sample PT.

### 3.2. Total As content in Bottom sediment

In 14 dried bottom sediments collected at Guarapiranga Dam presented a Total As concentration from 2.1 to 8.5 mg.kg<sup>-1</sup> (figure 2).



**Figure 2.** Total As in 14 sediment samples of Guarapiranga Dam.

With an associated expanded uncertainty of 0.2 mg.kg<sup>-1</sup> (95% confidence interval; 14 degrees of freedom and  $k=2$ ). For sediment samples, reproducibility within-laboratory standard deviation was considered a good uncertainty estimation. This uncertainty value was considered adequate to bottom sediment samples when compared with:

- Canadian Sediment Quality guidelines to fresh water sediments are ISQG-interim sediment quality guideline is 5.9 mg.kg<sup>-1</sup> and PEL – probable effect level is 17mg.kg<sup>-1</sup>.

The maximum As uncertainty associated with Guarapiranga 33 core sediment samples digestion and dilution step ( $u_{dil}$ ) was estimated as 12% ( $U$ ,  $k=2$ ) for the working range of 0.5 to 20 mg.kg<sup>-1</sup> [5].

### 3.3. Legal compliance

Considering that 10 µg.L<sup>-1</sup> of total As in water is the current legal limit [9], the concentration range (20 to 80 µg.L<sup>-1</sup>) must be improved to reach lower values in the range of 10 µg L<sup>-1</sup>. In addition, expanded uncertainty estimated by top-down

approach in the present scenario did not fit the purposed use of Total As in water measurement.

Considering As Interim Sediment Quality Guideline (ISQG) value of 5.9 mg kg<sup>-1</sup> in sediments [10] the current method expanded uncertainty of 0.2 mg L<sup>-1</sup> ( $U$ ,  $k=2$ ) is appropriated to the intended use of the Total As measurement. Any larger dispersion must be related to the sample inhomogeneity. The largest uncertainty contribution to  $u_c$  was by far  $RMS_{Bias}$ . Therefore, laboratory performance improvement in further PT's must be a goal to reduce total As measurement uncertainty.

## 4. CONCLUSIONS

Considering that water and sediment samples collection represent a good estimate of the entire Guarapiranga dam scenario for arsenic, top-down procedure to estimate uncertainty on total As measurement was much simpler than bottom-up approach. With top-down procedure, the measurement was proved stable and under controlled conditions. Estimated uncertainty to measure total As in bottom sediment was adequate to the concentration range found at Guarapiranga Dam and to meet Brazilian legal requirements and Canadian sediment quality guidelines. In order to comply with current legal requirements, uncertainty estimation on As measurement in water by top-down approach was not adequate, and the lower concentration range must be improved, once concentrations <20µg/L were not reached. However, this could be associated with top down uncertainty estimation procedure, which usually cover many more uncertainty components.

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