



Draft Report

**An Inter-Laboratory Comparison of
Arsenic Analysis in Bangladesh**

Prepared by

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Summary

The International Atomic Energy Agency (IAEA) conducted an evaluation of the quality of arsenic analysis in Bangladesh through an inter-laboratory comparison of the analysis of synthetic standards and field samples. A set of 8 synthetic standards with arsenic concentrations ranging from 0 to about 500 $\mu\text{g}/\text{kg}$, traceable to an internationally recognized standard solution of arsenic, were prepared by the IAEA and provided to the participating laboratories. In addition, two samples of drinking water were collected from near Dhaka by the local office of the World Health Organization (WHO) and provided to all participating laboratories and the IAEA for analysis. Out of the 25 laboratories who received the synthetic standards and field samples, 17 laboratories submitted results to the IAEA for comparison. The reported arsenic concentrations have a wide range with values much higher or much lower than the expected value. Analysis of field samples shows a range of values from 0 to 396 $\mu\text{g}/\text{kg}$. Less than one third of the participating laboratories obtained results that were within about 20% of the expected values (about 60 $\mu\text{g}/\text{kg}$) obtained by a laboratory cooperating with the IAEA (University of Rochester). Results of this inter-laboratory comparison point to a lack of consistency in the analytical results that have been and are being obtained in Bangladesh. More importantly, drinking water wells where elevated arsenic concentrations have been found may in fact have low concentrations. Similarly, wells that have been found to be free of arsenic may in fact have substantially higher arsenic concentrations. The quality and reliability of arsenic analysis needs to be established and continually evaluated in order to identify all affected areas and to provide appropriate mitigation.

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1. Introduction

The presence of elevated arsenic concentrations in ground water used for drinking has emerged as a major public health issue in many parts of the world, especially in adjoining regions of Bangladesh and India. Large-scale surveys have been initiated in the affected countries to identify tube wells in which arsenic concentrations are above the safe drinking water standards. The results of these surveys are used to determine if a given household or community is to be asked to discontinue the use of their drinking water source, potentially resulting in severe hardship for the affected population. The surveys of arsenic concentrations are being conducted with a variety of different analytical techniques by laboratories ranging from research institutions to commercial firms. While individual manufacturers or laboratories have tested the accuracy and precision of the analytical techniques that they use, a systematic effort has not been made to ascertain the quality and comparability of analytical data. Policy decisions based on inaccurate or inconsistent data could have unintended and adverse social and economic impacts.

Responding to a request from several UN agencies involved in the arsenic mitigation efforts in Bangladesh, the International Atomic Energy Agency (IAEA) initiated an inter-laboratory comparison of arsenic analysis. The inter-laboratory comparison was conducted in close collaboration with WHO-Dhaka, through its Environmental Health Advisor, and the Bangladesh Atomic Energy Commission (BAEC). The objective of this exercise was to determine the quality of arsenic analysis of water being provided by laboratories in the public and private sectors. The ultimate beneficiaries of this exercise are expected to be public and the government agencies through a better quality of analytical results provided by the participating laboratories.

2. Procedures

The inter-laboratory comparison was conducted with synthetic standards and drinking water samples collected from a well in Bangladesh. Synthetic standards were prepared by the IAEA in de-ionized water and in a solution whose chemical composition was modified to simulate that of typical groundwaters in Bangladesh. The two sets of standards were expected to help in result evaluation under variable chemical composition of solutions, as may be expected in natural waters. Arsenic concentrations in these standards ranged from approximately 0 to 500 $\mu\text{g}/\text{kg}$. This concentration range was achieved by diluting different amounts of a certified arsenic solution from the United States National Institute of Standards and Technology (NIST) into distilled water and simulated groundwater. A detailed description of the procedures used for preparing synthetic standards is given in Appendix A. Aliquots of synthetic standards were assigned randomized identification numbers for distribution to participating laboratories. The BAEC and WHO-Dhaka identified and distributed the synthetic standards to each laboratory. In addition, two groundwater samples were collected from wells near Dhaka by WHO-Dhaka. These samples were labeled PW-1 and PW-5, acidified in the field, and supplied to each participating laboratory and to the IAEA for analysis.

Synthetic standards were supplied by the IAEA in sets of 10 (five each of de-ionized water and simulated groundwater). However, only 8 standards were distributed to each laboratory because the number of laboratories interested in participating in this exercise was greater than anticipated. As a result, the initial sets were randomly split among all the

laboratories and the complete concentration range of the synthetic standards was not always analyzed by each of the participating laboratories. This mix-up, however, did not impact the integrity of the standards or this exercise, because each of the synthetic standard aliquot had a unique identification number that was traceable to its reference value.

Laboratories participating in this submitted their analytical results to the IAEA on prescribed forms. Identification numbers of aliquots of synthetic standards were converted back to the original standards to determine the reference values. The IAEA's laboratories in Monaco and Seibersdorf, Austria, and the trace element laboratory of the Department of Geology, University of Rochester, New York, USA, participated in this exercise on behalf of the IAEA. Arsenic concentrations at these laboratories were determined by using an Inductively Coupled Plasma – Mass Spectrometer (ICP/MS).

3. Reference Values

The synthetic standards were prepared by gravimetric dilution of a certified standard solution. The concentration of arsenic in the synthetic standards was calculated by accounting for the various dilution steps (Appendix A) and taken as the reference value. The uncertainty in the reference value was calculated by combining the uncertainty in the NIST standard solution and in the dilution procedure (Appendix B). These reference values and their uncertainties are given in Table 1.

Blank stock solutions of de-ionized water and simulated groundwater and synthetic standards spiked with arsenic were analyzed at the laboratories participating on behalf of the IAEA (Monaco, Seibersdorf, and Rochester) before the standards were shipped to Bangladesh for distribution. The blank stock solutions were analyzed at Seibersdorf. All three of the laboratories analyzed synthetic standards in de-ionized water. Simulated groundwater standards were analyzed only at the Monaco laboratory. These measurements were consistent with the reference values (Table 1).

Table 1. Reference and IAEA-analyzed concentrations of arsenic in synthetic standards.

	Arsenic Concentration (µg/kg)							
	Reference		Monaco		Seibersdorf		Rochester	
Standard	Conc.	Uncert.	Conc.	Uncert.	Conc.	Uncert.	Conc.	Uncert.
De-ionized Water								
DI-1	0	0			<2			
DI-2	17.7	0.1	18.0	0.9	20.5	0.1	16.1	0.8
DI-3	63.3	0.5	64.6	2.9	66.5	0.5	60.2	3.0
DI-4	101.3	0.8	102	7	102	1	96.1	5.0
DI-5	506.4	4.1	507	33	511	4	495	25
Simulated Groundwater								
G-1	0	0			<2			
G-2	22.5	0.2	23.4	1.9				
G-3	56.3	0.5	58.4	4.7				
G-4	90.1	0.7	90	7				
G-5	450.5	3.6	444	36				

4. Results

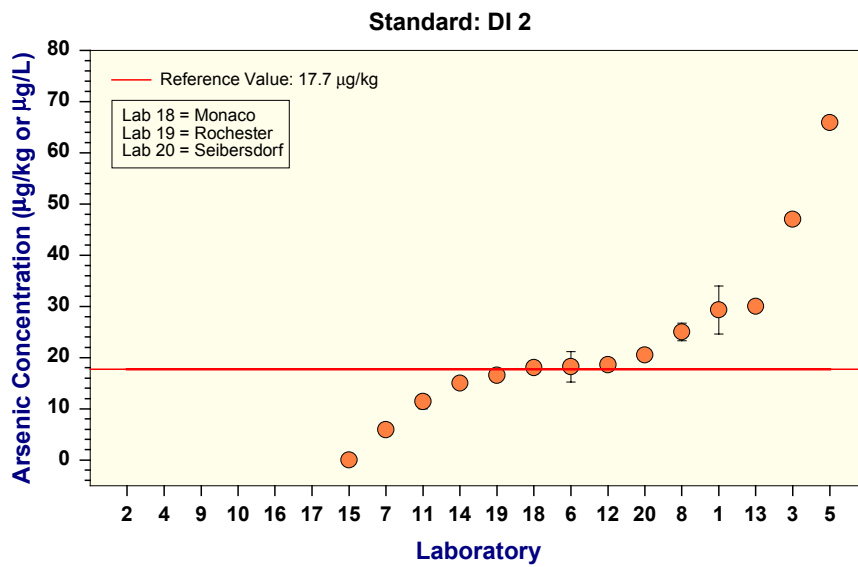
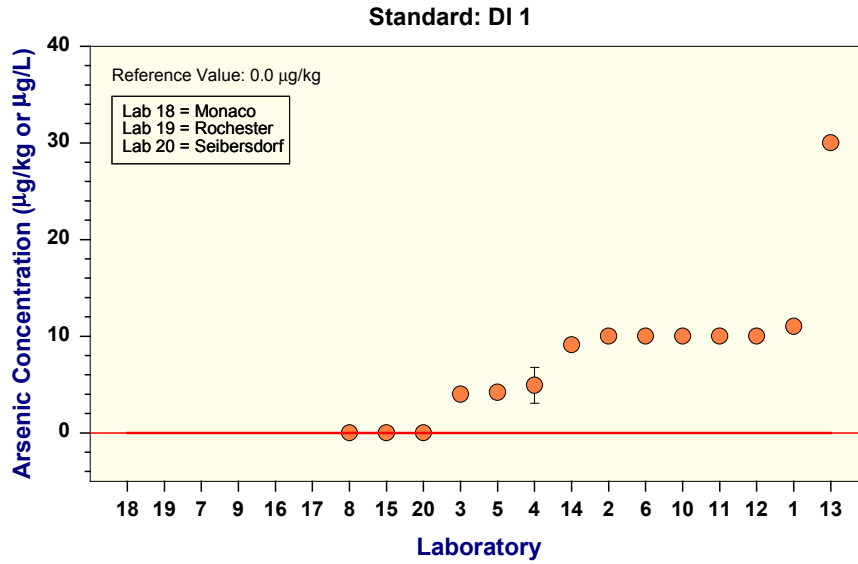
Analytical results received from 17 laboratories (Appendix C) are listed in Appendix D. Results for the synthetic standards are shown in Figures 1 - 10. There is a wide range of values obtained by the different laboratories. There does not appear to be a co-relation between the analytical method and deviation from the reference value or between the values for de-ionized versus simulated groundwater standards. Laboratory 6 consistently had very good results with sufficient accuracy and precision. Some of the laboratories have consistently poor performance. In general, there are linear off-sets for all concentration ranges, indicating that calibration errors may be significant.

Analyzed concentrations for the two groundwater samples collected from near Dhaka (PW-1 and PW-5) range from 0 to 396 $\mu\text{g}/\text{kg}$ or $\mu\text{g}/\text{L}$ (Figures 11 – 12). The results of the University of Rochester are 67.7 (± 1.3) $\mu\text{g}/\text{kg}$ for PW-1 and 60.9 (± 1.5) $\mu\text{g}/\text{kg}$ for PW-5. These samples had very high chloride concentrations (probably due to acidification with HCl). During the ICP/MS analysis of these samples, there was significant interference for mass 75 resulting from the formation of ArCl in the Ar plasma. This interference was a major problem as mass 75 is measured for As. To avoid the interference with ArCl, 5 g of the water sample was dried with nitric acid to allow for Cl to evaporate as HCl. The As concentrations were then measured again and these re-measured results are provided in this report. While the precision of these measurements is as low as for other measurements, the accuracy is less certain than that for the standards. The total uncertainty in the measurements for PW-1 and PW-5, therefore, may be as much as 10%. Significant ArCl – As interference was not encountered in the analysis of synthetic standards. Only one set of samples from the field tests could be analyzed as the second set was received with obvious damage to the integrity of the sample due to leakage.

5. Conclusions and Recommendations

Analytical results from 17 participating laboratories show a wide range of values in synthetic standards that are much higher or much lower than the reference value. Analysis of field samples shows that less than one third of the participating laboratories obtained results that were within about 20% of the value obtained by a specialized laboratory with state-of-the-art facilities. These results point to a lack of consistency in the analytical results that have been and are being obtained in Bangladesh. More importantly, drinking water wells where elevated arsenic concentrations have been found may in fact have low concentrations. Similarly, wells that have been found to be free of arsenic may in fact have substantially higher arsenic concentrations. The quality and reliability of arsenic analysis needs to be established and continually evaluated in order to identify all affected areas and to provide appropriate mitigation.

Figures 1 - 2. Comparison of analytical results for synthetic arsenic standard DI-1 and DI-2 in de-ionized water. The reference value for the standard is shown by the solid line.



Figures 3 - 4. Comparison of analytical results for synthetic arsenic standard DI-3 and DI-4 in de-ionized water. The reference value for the standard is shown by the solid line.

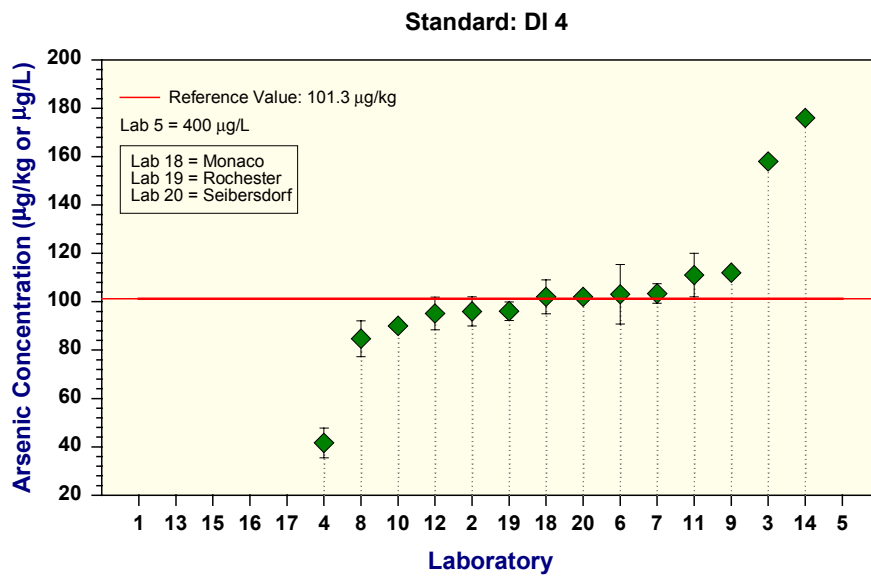
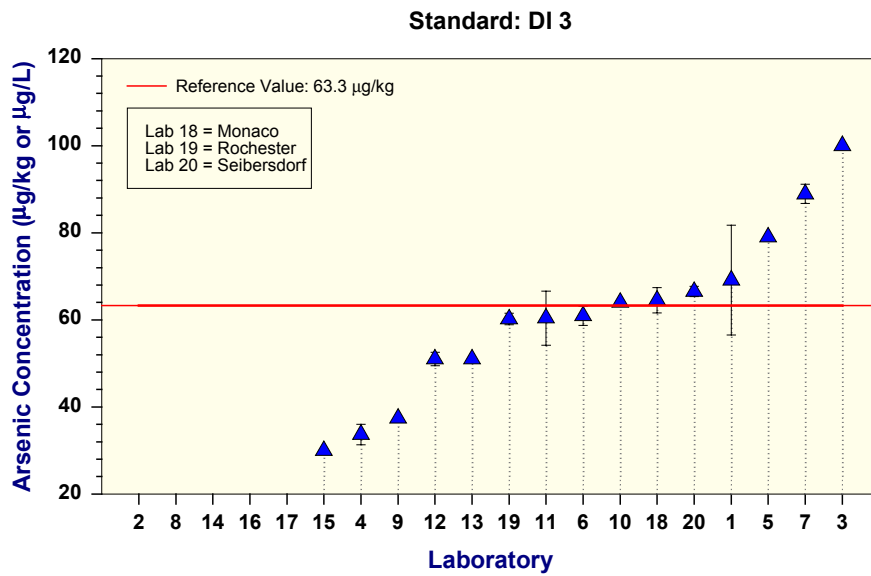


Figure 5. Comparison of analytical results for synthetic arsenic standard DI-5 in de-ionized water. The reference value for the standard is shown by the solid line.

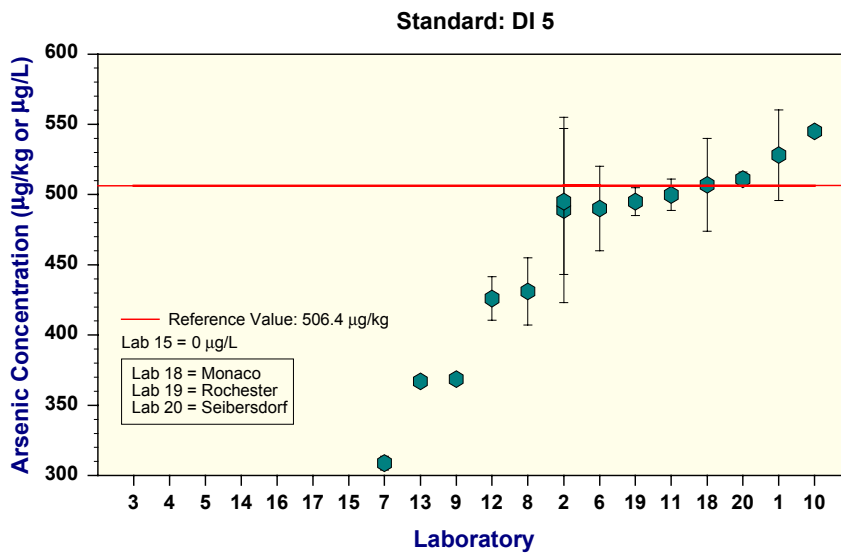
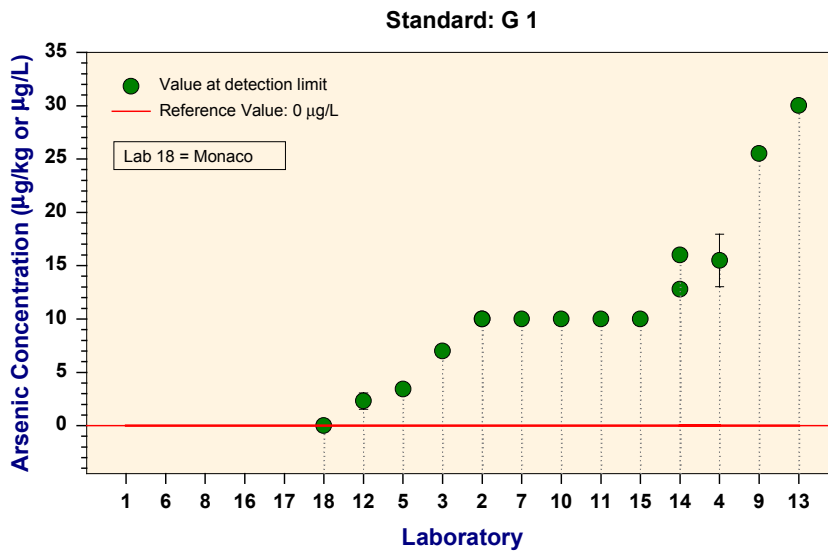
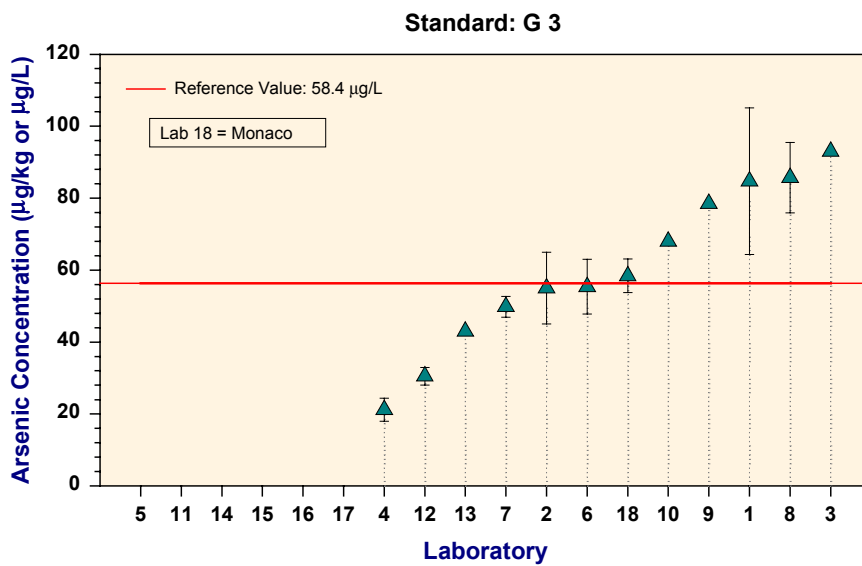
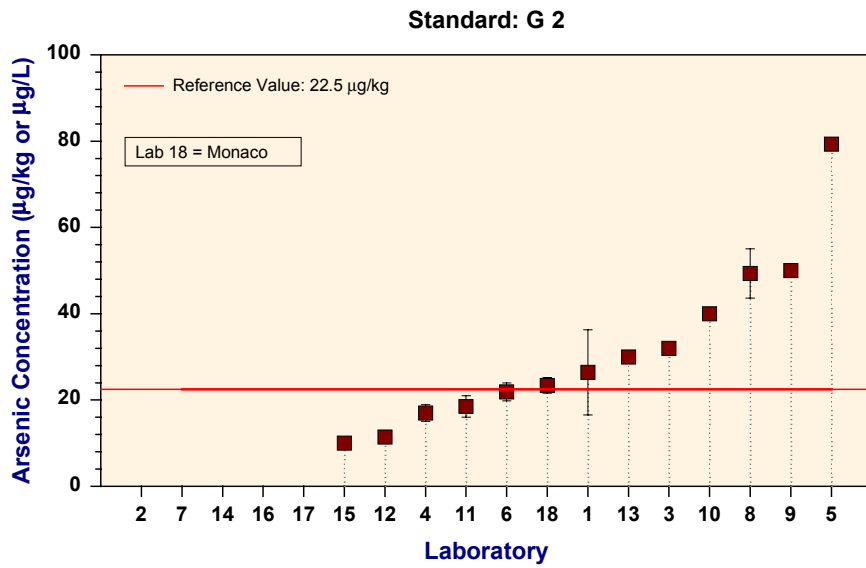


Figure 6. Comparison of analytical results for synthetic arsenic standard G-1 in simulated groundwater. The reference value for the standard is shown by the solid line.



Figures 7-8. Comparison of analytical results for synthetic arsenic standard G-2 and G-3 in simulated groundwater. The reference value for the standard is shown by the solid line.



Figures 9-10. Comparison of analytical results for synthetic arsenic standards G-4 and G-5 in simulated groundwater. The reference value for the standard is shown by the solid line.

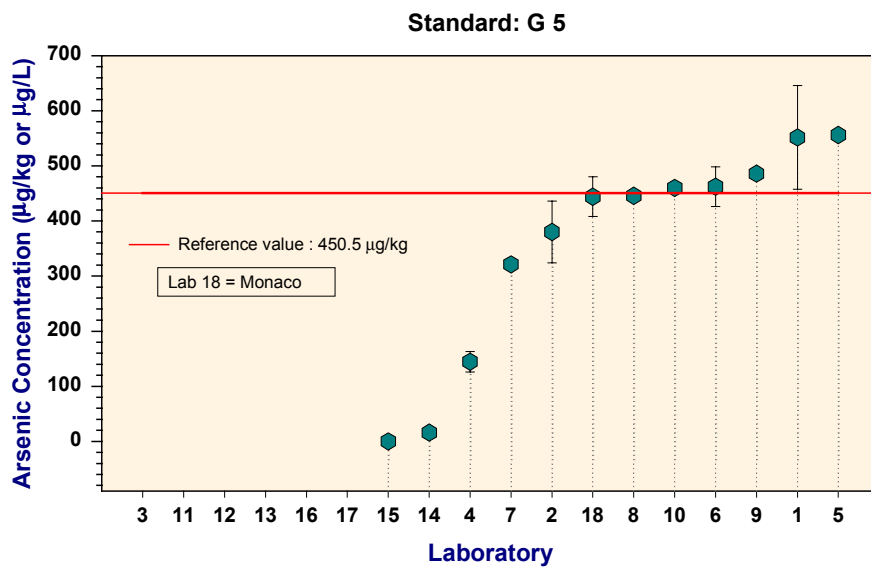
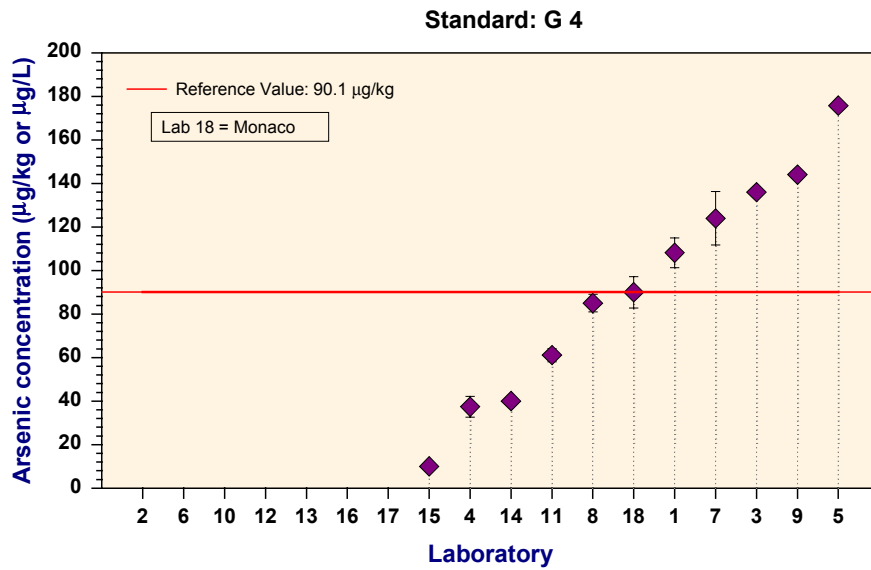


Figure 11. Comparison of analytical results for groundwater sample PW-1 collected from a well near Dhaka, Bangladesh. The sample had significant chloride concentration (perhaps because of acidification with HCl), and the value determined by the University of Rochester may have an uncertainty of as much as 10%.

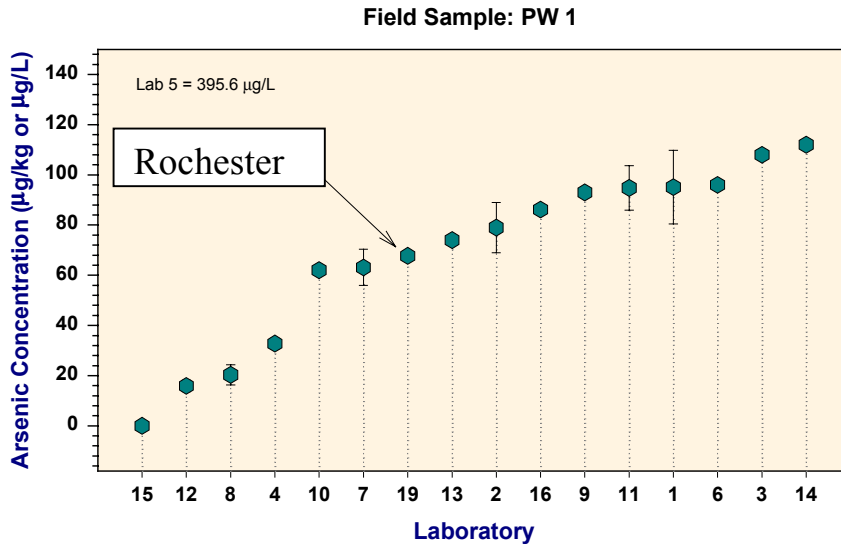
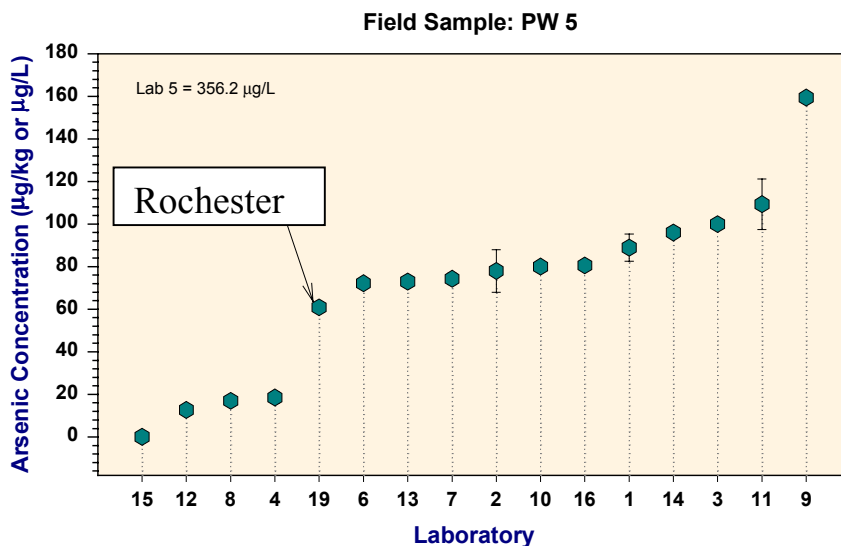


Figure 12. Comparison of analytical results for groundwater sample PW-5 collected from a well near Dhaka, Bangladesh. The sample had significant chloride concentration (perhaps because of acidification with HCl), and the value determined by the University of Rochester may have an uncertainty of as much as 10%.



APPENDIX A

Preparation of synthetic arsenic standards

Synthetic arsenic standards were prepared by spiking de-ionized water and simulated groundwater with appropriate quantities of a NIST Standard Reference Material 3103a to obtain different concentrations in the range of 20, 50, 100 and 500 µg/kg. The high purity NIST standard solution contained 8.44 ± 0.03 µg/g of arsenic in an approximate nitric acid volume fraction of 10%. The preparation was based on gravimetric dilution procedure involving the transfer of the required amount of NIST arsenic standard solution and de-ionized or simulated groundwater to acid cleaned, dry, pre-weighed, 20 L polyethylene containers. In the preparation, pre-weighed polyethylene containers were first filled with some acidified (approx. 2% supra-pure nitric acid), de-ionized or simulated groundwater and re-weighed. Then the required amount of NIST arsenic standard solution was added by mass and the containers filled with acidified stock solution of de-ionized or simulated groundwater and weighed, until the final dilution was obtained.

Preparation of Simulated Groundwater

The simulated groundwater was prepared by using water from a domestic well in Marchfeld, near Vienna, Austria. This water was first analysed to determine naturally present concentrations of major ions, and then spiked with required amount of sodium nitrate and sodium chloride salts (supra pure - Merck) in order to obtain the final concentration of approx. 1000 mg/L Cl and 160 mg/l NO₃. The addition of given anions also increased sodium concentration to 595 mg/L. The concentrations of major ions present in the ground water before and after spiking are given in Table A1.

Preparation of synthetic standards:

De-ionized Water

Standard DI-5

0.9 g of NIST standard solution was transferred to a 20 L container and filled with de-ionized water until a weight of 15 kg was obtained.

According to the calculation:

$$\begin{aligned} 1 \text{ g standard} &= 8.44 \text{ mg As (standard certified value)} \\ 0.9 \text{ g} &= 7.596 \text{ mg} / 15 \text{ kg} = 0.5064 \text{ mg/kg} = 506.4 \text{ µg/kg of arsenic} \end{aligned}$$

Standard DI-4

2 kg of water sample DI-5 was transferred to a 20 L container and 8 kg of acidified de-ionized water added.

According to the calculation:

$$2 \text{ kg} = 2 \times 506.4 \text{ µg} = 1012.8 \text{ µg} / 10 \text{ kg} = 101.28 \text{ µg/kg of arsenic}$$

Standard DI-3

1.25 kg of water sample DI-5 was transferred to a 20 l container and 8.75 kg of acidified de-ionized water added.

According to the calculation:

$$1.25 \text{ kg} = 1.25 \times 506.4 \text{ µg} = 633 \text{ µg} / 10 \text{ kg} = 63.3 \text{ µg/kg of arsenic}$$

Standard DI-2

0.35 kg of water sample DI-5 was transferred to a 20 l container and 9.65 kg of acidified de-ionized water was added.

According to the calculation:

$$0.35 \text{ kg} = 0.35 \times 506.4 \text{ } \mu\text{g} = 177.24 \text{ } \mu\text{g} / 10 \text{ kg} = 17.724 \text{ } \mu\text{g/kg of arsenic.}$$

Simulated Groundwater

Standard G-5

0.881g of NIST standard solution was transferred to a 2 l calibration flask and filled with a ground water until exact 2kg were obtained. Then an aliquot of 70g was taken for check up, and the residue of exact 1930.44g was used for further dilution with ground water until the weight of 15.930 kg was obtained.

1g = 8.44 mg As (standard certified value)

0.881g = 7.43564 mg As in 2 kg of ground water, and after taking 70g of solution 7.177mg of arsenic is left in 1.93044g of solution.

This is further diluted to 15.930 kg, and according to the calculation:

$$7.177\text{mg}/15.930 \text{ kg}=450.5\mu\text{g/kg of arsenic is obtained.}$$

Standard G-4

2 kg of water sample G-5 was transferred to a 20 l container, and 8 kg of acidified ground water was added.

According to the calculation:

$$2 \text{ kg} = 2 \times 450.5 \text{ } \mu\text{g} = 901 \text{ } \mu\text{g} / 10 \text{ kg} = 90.1 \text{ } \mu\text{g} / \text{kg of arsenic.}$$

Standard G-3

1.25 kg of water sample G-5 was transferred to a 20 l container, and 8.75 kg of acidified ground water was added.

According to the calculation:

$$1.25 \text{ kg} = 1.25 \times 450.5\mu\text{g} = 563.1 \text{ } \mu\text{g} / 10 \text{ kg} = 56.31 \text{ } \mu\text{g/kg of arsenic}$$

Standard G-2

0.5 kg of water sample G-5 was transferred to a 20 l container, and 9.5 kg of acidified ground water was added.

According to the calculation:

$$0.5 \text{ kg} = 0.5 \times 450.5 \text{ } \mu\text{g} = 225.2 \text{ } \mu\text{g} / 10 \text{ kg} = 22.52 \text{ } \mu\text{g/kg of arsenic.}$$

Table A1. Concentrations of major ions in simulated groundwater

Component	Natural conc. (mg/L)	Final conc. (mg/L)
Ca	145	145
Mg	95	95
Na	45	595
K	7	7
Cl	180	1000
SO ₄	210	210
HCO ₃	365	365
NO ₃	76	160

APPENDIX B

Uncertainty in arsenic concentrations in synthetic standards

The major components of the combined uncertainty for the prepared solutions are as follows (relative uncertainties):

1. Relative uncertainty of the NIST standard: $u_{\text{NIST}}=3.55\times 10^{-3}$
2. Weighing with High Precision balance Mettler PM460 Delta range:
four uncertainty components:
 - a) calibration: $\pm 0.001\text{g}$
 - b) display: $\pm 0.001\text{g}$
 - c) drift: $\pm 0.001\text{g}$
 - d) reproducibility: $\pm 0.002\text{g}$ (for masses of 0.8g)

Weighing uncertainty for mass at 0.8g range: $u_{\text{PM460-0.8g}}=3.31\times 10^{-4}$

3. Weighing with Precision balance Mettler PM4000:
four uncertainty components:
 - a) calibration: $\pm 0.052\text{g}$
 - b) display: $\pm 0.01\text{g}$
 - c) drift: $\pm 0.01\text{g}$
 - d) reproducibility: $\pm 0.09\text{g}$ (for masses of 2000g)

Weighing uncertainty for mass at 2kg range: $u_{\text{PM4000-2kg}}=5.24\times 10^{-5}$

Weighing uncertainty for mass at 350g range: $u_{\text{PM4000-350g}}=2.94\times 10^{-5}$

The three uncertainty components can be added according to the law of uncertainty propagation taking into account the number of weighings for the total water mass according to step three (between one and nine times). The solutions A and B were used to prepare the dilutions A1-A3 and B1-B3.

4. Contribution of possible Arsenic background in added water:

No detectable Arsenic was found in the distilled and in the groundwater sample. The upper limit is given by the detection limit ($2\mu\text{g}/\text{kg}$):

$$u_{\text{detect-limit}}=4.46\times 10^{-3}$$

This last component from step 4. should be added directly to the uncertainty derived from steps 1.-3. to calculate the combined uncertainty for each of the samples.

The combined relative standard uncertainty for all eight solutions prepared for this exercise is therefore $\pm 0.8\%$ of the stated concentration.

APPENDIX C. List of participating laboratories.

Intronics Technology Center
971, Beum Rokeya Sarani
Mirpur, Dhaka-1216, Bangladesh

DPHE-Danida Laboratory
PMU, Noakhali, Bangladesh

Tetrahedron, Inc.
Dhaka, Bangladesh

Analytical Research Laboratory
Department of Chemistry
University of Dhaka, Dhaka-1000

AFTAB BIOTECH Jalam Group
Dhaka, Bangladesh

Analytical Research Division
BCSIR Laboratories, Dhanmondi
Dhaka-1205

Nuclear and Radiation
Chemistry Division
Institute of Nuclear Science
and Technology,
Ganakbary, Savar, Dhaka

Chemistry Division
Atomic Energy Centre, Dhaka

Department of Public Health
Engineering DPHE, Khulna

Office of the Senior Chemist
DPHE, Zonal Laboratory
Rajshahi, Bangladesh

SDC Environment Initiative,
College More, Courtpara, Kusthia
Bangladesh

Environmental Engineering
Laboratory, Department
of Civil Engineering, BUET
Dhaka-1000, Bangladesh

Water Quality Testing Lab.
NGO Forum for Drinking water.

Department of Environment,
Dhaka Division E-16
Dhaka 1207, Bangladesh

Geological Survey of Bangladesh
153 Pioneer Road, Dhaka-1000

Environmental Research Lab.
School of Environmental
Science and Management,
Independent University,
Bangladesh

DPHE Zonal Laboratory,
Comilla, Bangladesh

APPENDIX D. Analytical results reported to the IAEA

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
<u>Laboratory 1</u>								
	69	D11	µg/l	0	11	-		5 AAHG
	81	D12	µg/l	17.7	29.3	4.7		5 AAHG
	179	D13	µg/l	63.3	69.1	12.6		5 AAHG
	30	D15	µg/l	506.4	528.1	32.3		5 AAHG
	84	G2	µg/l	22.5	26.4	9.9		5 AAHG
	55	G3	µg/l	56.3	84.7	20.4		5 AAHG
	164	G4	µg/l	90.1	108.1	6.8		5 AAHG
	96	G5	µg/l	450.5	551.6	93.8		5 AAHG
	PW-1		µg/l	67.7	95.1	14.7		5 AAHG
	PW-5		µg/l	60.9	88.9	6.4		5 AAHG
<u>LABORATORY 2</u>								
	170	D11	µg/l	0	<10	-		3 Spectrom.
	29	D14	µg/l	101.3	96.6	(8.5)		3 520 nm
	146	D15	µg/l	506.4	495.52	(73.5)		3
	147	D15	µg/l	506.4	489.66	(93.3)		3
	36	G1	µg/l	0	<10	-		3
	93	G1	µg/l	0	<10	-		3
	158	G3	µg/l	56.3	55.10	(14)		3
	200	G5	µg/l	450.5	380.56	(79)		3
	PW-1		µg/l	67.7	79	10		1
	PW-5		µg/l	60.9	78	10		1

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
LABORATORY 3								
	88	D11	µg/l	0	4	-	-	
	48	D12	µg/l	17.7	47	-	-	
	181	D13	µg/l	63.3	100	-	-	
	57	D14	µg/l	101.3	158	-	-	
	68	G1	µg/l	0	7	-	-	
	67	G2	µg/l	22.5	32	-	-	
	123	G3	µg/l	56.3	93	-	-	
	173	G4	µg/l	90.1	136	-	-	
	PW-1		µg/l	67.7	108	-	-	
	PW-5		µg/l	60.9	100	-	-	
LABORATORY 4								
	154	D11	µg/l	0	4.91	1.85 (4.59)		6 AAS-GF
	89	D13	µg/l	63.3	33.66	2.36 (5.86)		6 AAS-GF
	135	D14	µg/l	101.3	41.64	6.18 (15.34)		6 AAS-GF
	197	G1	µg/l	0	15.48	2.46 (15.48)		6 AAS-GF
	22	G2	µg/l	22.5	16.97	1.94 (4.81)		6 AAS-GF
	33	G3	µg/l	56.3	21.19	3.23 (8.02)		6 AAS-GF
	192	G4	µg/l	90.1	37.422	4.80 (11.91)		6 AAS-GF
	145	G5	µg/l	450.5	144.53	18.61 (10.74)		6 AAS-GF
	PW-1		µg/l	67.7	32.75	2.19 (5.45)		6 AAS-GF
	PW-5		µg/l	60.9	18.54	2.71 (6.72)		6 AAS-GF

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
LABORATORY 5								
	137	D11	µg/l	0	4.18	-		3 AAHG
	102	D12	µg/l	17.7	65.9	-		3 AAHG
	43	D13	µg/l	63.3	79.01	-		3 AAHG
	109	D14	µg/l	101.3	350.3	-		3 AAHG
	21	G1	µg/l	0	3.42	-		3 AAHG
	92	G2	µg/l	22.5	79.3	-		3 AAHG
	53	G4	µg/l	90.1	175.7	-		3 AAHG
	54	G5	µg/l	450.5	556.1	-		3 AAHG
	PW-1		µg/l	67.7	395.6	-		3 AAHG
	PW-2		µg/l	60.9	356.2	-		3 AAHG
LABORATORY 6								
	182	D11	µg/l	0	BDL	BDL		6 AAHG
	19	D12	µg/l	17.7	18.2		3	6 AAHG
	101	D13	µg/l	63.3	60.9		2.2	6 AAHG
	87	D14	µg/l	101.3	103.1		12.3	6 AAHG
	111	D15	µg/l	506.4	490.1		30.1	6 AAHG
	20	G2	µg/l	22.5	21.9		2.1	6 AAHG
	31	G3	µg/l	56.3	55.4		7.6	6 AAHG
	11	G5	µg/l	450.5	462.2		35.9	6 AAHG
	PW-1		µg/l	67.7	96			6 AAHG
	PW-5		µg/l	60.9	72.2			6 AAHG

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD	
Laboratory 7	183	DI2	µg/l	17.7	5.9	0.7 (4)	10	AAHG	
	24	DI3	µg/l	63.3	88.9	2.2 (7)	8	AAHG	
	65	DI4	µg/l	101.3	103.4	4 (5)	8	AAHG	
	25	DI5	µg/l	506.4	308.8	4.9 (21)	8	AAHG	
	190	G1	µg/l	0	BDL	-	6	AAHG	
	60	G3	µg/l	56.3	49.8	2.9 (7)	8	AAHG	
	157	G4	µg/l	90.1	123.9	12.3 (20)	8	AAHG	
	132	G5	µg/l	450.5	321.1	9.3 (12)	8	AAHG	
	PW-1		µg/l	67.7	63.1	7.2(14)	8	AAHG	
	PW-5		µg/l	60.9	74.3	2.7(10)	8	AAHG	
Laboratory 8									
		116	DI1	µg/l	0	0		3	TXRF
		115	DI2	µg/l	17.7	25	1.7	3	TXRF
		162	DI4	µg/l	101.3	84.7	7.4	3	TXRF
		151	DI5	µg/l	506.4	431	23.9	3	TXRF
		198	G2	µg/l	22.5	49.3	5.7	3	TXRF
		74	G3	µg/l	56.3	85.7	9.8	3	TXRF
		50	G4	µg/l	90.1	85	4	3	TXRF
		187	G5	µg/l	450.5	445.7	7.6	3	TXRF
		PW1		µg/l	67.7	20.3	4	3	TXRF
	PW5		µg/l	60.9	17	2	3	TXRF	

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
Laboratory 9								
	13	D13	µg/l	63.3	37.4	-	3	-
	127	D14	µg/l	101.3	112	-	3	-
	72	D15	µg/l	506.4	368.58	-	3	-
	42	G1	µg/l	0	25.5	-	3	-
	121	G2	µg/l	22.5	50	-	3	-
	176	G3	µg/l	56.3	78.45	-	3	-
	83	G4	µg/l	90.1	144	-	3	-
	149	G5	µg/l	450.5	485.9	-	3	-
	PW1		µg/l	67.7	93	-	3	-
	PW5		µg/l	60.9	159.4		3	
Laboratory 10								
	37	D11	µg/l	0 <10				SDDC
	90	D13	µg/l	63.3	64	-		SDDC
	185	D14	µg/l	101.3	90	-		SDDC
	4	D15	µg/l	506.4	545	-		SDDC
	117	G1	µg/l	0 <10				SDDC
	113	G2	µg/l	22.5	40	-		SDDC
	9	G3	µg/l	56.3	68	-		SDDC
	131	G5	µg/l	450.5	460	-		SDDC
	PW1		µg/l	67.7	62	-		SDDC
	PW5		µg/l	60.9	80			SDDC

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
Laboratory 11								
	139	D11	µg/l	0	BDL	-		3 ASV
	189	D12	µg/l	17.7	11.4	1.4		3 ASV
	2	D13	µg/l	63.3	60.4	6.2		3 ASV
	150	D14	µg/l	101.3	111	9		3 ASV
	124	D15	µg/l	506.4	499.8	11.2		3 ASV
	28	G1	µg/l	0	BDL	-		3 ASV
	85	G2	µg/l	22.5	18.5	2.5		3 ASV
	114	G4	µg/l	90.1	61.1	3		3 ASV
	PW1		µg/l	67.7	94.8	8.84		3 ASV
	PW5		µg/l	60.9	109.3	11.9		3 ASV
Laboratory 12								
	41	D11	µg/l	0	<0.1	-		3 AAS-GF
	64	D12	µg/l	17.7	18.6	0.28		3 AAS-GF
	156	D13	µg/l	63.3	51	1.57		3 AAS-GF
	63	D14	µg/l	101.3	95.1	6.79		3 AAS-GF
	98	D15	µg/l	506.4	426	15.45		3 AAS-GF
	142	G1	µg/l	0	2.3	0.76		3 AAS-GF
	61	G2	µg/l	22.5	11.4	1.27		3 AAS-GF
	70	G3	µg/l	56.3	30.5	2.47		3 AAS-GF
	PW1		µg/l	67.7	15.92	2.28		3 AAS-GF
	PW5		µg/l	60.9	12.7	0.58		3 AAS-GF

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
Laboratory 13								
	1	D11	µg/l	0	<30		3	Spectrom.
	71	D11	µg/l	0	<30		3	520 nm
	122	D12	µg/l	17.7	<30		3	
	3	D13	µg/l	63.3			3	
	107	D15	µg/l	506.4			3	
	166	G1	µg/l	0	<30		3	
	16	G2	µg/l	22.5	<30		3	
	186	G3	µg/l	56.3			3	
	PW1		µg/l	67.7			3	
	PW5		µg/l	60.9			3	
Laboratory 14								
	58	D11	µg/l	0			9.1	Spectrom.
	99	D11	µg/l	0			40	520 nm
	178	D12	µg/l	17.7			15	
	133	D14	µg/l	101.3			176	
	171	G1	µg/l	0			16	
	119	G1	µg/l	0			12.8	
	45	G4	µg/l	90.1			40	
	95	G5	µg/l	450.5			16	
	PW1		µg/l	67.7			112	
	PW5		µg/l	60.9			96	

	SAMPLE ID NO.	STANDARD	UNITS	REFERENCE	ANALYZED	UNCERTAINTY	# OF DETM.	METHOD
Laboratory 15								
	165	D11	µg/l	0	0			
	134	D12	µg/l	17.7	0			
	32	D13	µg/l	63.3	<DL			
	125	D15	µg/l	506.4	0.01			
	110	G1	µg/l	0	<DL			
	194	G2	µg/l	22.5	<DL			
	105	G4	µg/l	90.1	<DL			
	199	G5	µg/l	450.5	0			
	PW1		µg/l	67.7	0/08			
	PW5		µg/l	60.9	0.1			
Laboratory 16								
	PW1		µg/l	-	86.2	1.85		3 ASV
	PW5		µg/l	-	80.57	1.7		3 ASV
Laboratory 17								
	148	D12	µg/l	17.7	24	1		3 CO
	40	D13	µg/l	63.3	67	1		3 CO
	106	D14	µg/l	101.3	104	1		3 CO
	15	D15	µg/l	506.4	440	1		3 CO
	144	G2	µg/l	22.5	30	1		3 CO
	174	G3	µg/l	56.3	61	1		3 CO
	94	G4	µg/l	90.1	96	1		3 CO
	140	G5	µg/l	450.5	391	1		3 CO
	PW1		µg/l	67.7	81	1		3 CO
	PW5		µg/l	60.9	80	1		3 CO