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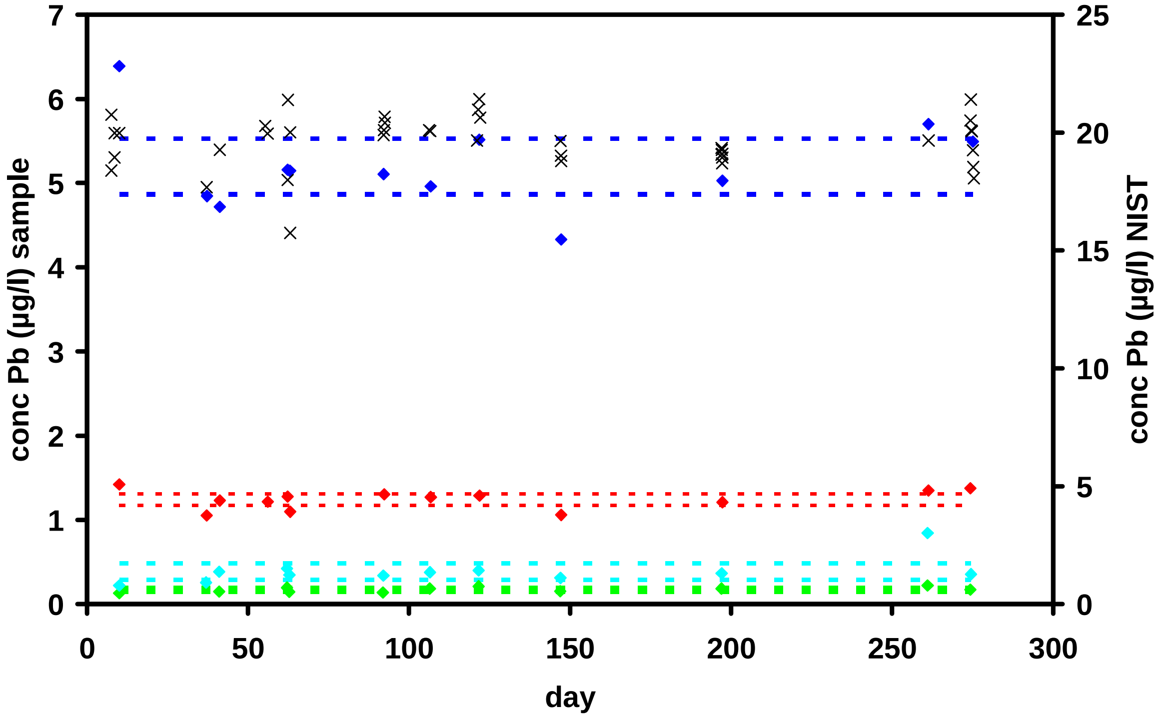
Elements in tap water

Part 2

Quality assurance of analysis

Eddo J. Hoekstra, Valerio Pedroni, Rosanna Passarella, Pier Renato Trincherini



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ABSTRACT

Due to the inclusion of the quality of the water distribution system in the DWD this new directive prescribes new parametric values and the performance characteristics. The trueness, precision and limit of detection are defined as percentage of the parametric value.

In the framework of our research on the effect of products on the quality of drinking water at the consumers' tap, we studied the quality of our data using certified reference water and four selected samples. Elements additional to the DWD, i.e. those evaluated by the WHO and those mentioned in national regulations concerning the acceptance of products that come in contact with drinking water, were included in our study.

Analysis of the certified standard revealed that K, Pb and Se might only suffer from a small systematic error whereas As and Ca might suffer a bigger systematic error (P=0.05). The trueness of As is out of range compared to what is defined in the DWD. The trueness of Cu and Pb is at the edge. The precision of As and Se are on the edge.

In general, the low concentrations in the samples compared to the parametric values in the DWD result in slightly or significantly lower precisions. The precision of Al, Ca, Fe, Mg and Zn for the samples is lower compared to that of the certified standard at a similar concentration level whereas U showed the opposite behaviour.

The certified values and their precision for certified standards are normally obtained by single element analysis and do not consider performance during time. Considering the fact that our method analyses 28 elements and that this might introduce additional variations both in trueness and precision compared to single element analysis and the fact that the results were obtained during ten month, our method is fit for our purpose to study release from materials. For legal purposes or for detailed studies on specific elements a single element analysis may be more appropriate. This is especially true for arsenic.

INTRODUCTION

The quality of the products that are used in the distribution system and come in contact with drinking water has become a key issue in the European Drinking Water Directive (DWD) [1], that is in force from 25 December 1998, compared to the “old” DWD [2]. Article 6.1 defines the point of compliance for parametric values set in Article 5 in the case of water supplied from a distribution network, at the point, within premises or an establishment, at which it emerges from the taps that are normally used for human consumption. And Article 10 states that:

> “Member States shall take all measures necessary to ensure that no substances or materials for new installations used in the preparation or distribution of water intended for human consumption or impurities associated with such substances or materials for new installations remain in water intended for human consumption in concentrations higher than is necessary for the purpose of their use and do not, either directly or indirectly, reduce the protection of human health provided for in this Directive; the interpretative document and technical specifications pursuant to Article 3 and Article 4 (1) of Council Directive 89/106/EEC of 21 December 1988 on the approximation of laws, regulations and administrative provisions of the Member States relating to construction products [3,4] shall respect the requirements of this Directive.”

Although the former DWD did not regulate the effect of the distribution system on the quality of drinking water, several EU Member States have a national acceptance system for these products in place. Due to the new DWD and the market barriers created by the national acceptance schemes, a European Acceptance Scheme (EAS) for products in contact with drinking water will be established [5]. The goal of the EAS is to assure a high-level of drinking water quality and consumers’ health by eliminating products that are not fit for the intended use, from the European market.

Due to the inclusion of the quality of the water distribution system in the DWD this new directive prescribes new parametric values and the performance characteristics. The trueness, precision and limit of detection are defined as percentage of the parametric value (Table 1). Additional elements are listed, for which the WHO has set guideline values [6]. The leaching of additional elements is also limited in some national regulations concerning the acceptance of products that come in contact with drinking water.

In the framework of our research on the effect of products on the quality of drinking water at the consumers’ tap [7], we studied the quality of our data, which is reflected in this report.

Table 1 Elements, which are regulated by the DWD and evaluated by the WHO

		Parametric value µg l^{-1}	Trueness[1] µg l^{-1}	Precision[2] µg l^{-1}	LoD[3] µg l^{-1}	Guideline WHO µg l^{-1}
DWD Annex 1B						
Antimony	Sb	5	1.25	1.25	1.25	20
Arsenic	As	10	1	1	1	10
Boron	B	1000	100	100	100	500
Cadmium	Cd	5	0.5	0.5	0.5	3
Chromium	Cr	50	5	5	5	50
Copper	Cu	2000	200	200	200	2000
Lead	Pb	10	1	1	1	10
Mercury	Hg	1	0.2	0.1	0.2	1
Nickel	Ni	20	2	2	2	20
Selenium	Se	10	1	1	1	10
DWD Annex 1C						
Aluminium	Al	200	20	20	20	100
Iron	Fe	200	20	20	20	-
Manganese	Mn	50	5	5	5	400
Sodium	Na	200000	20000	20000	20000	-
WHO						
Barium	Ba					700
Beryllium	Be					-
Molybdenum	Mo					70
Silver	Ag					-
Tin	Sn					-
Uranium	U					15
Zinc	Zn					-

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[1] The closeness of agreement between the average value obtained from a large series of test results and an accepted reference value (ISO 5725-1).

[2] The closeness of agreement between independent test results obtained under stipulated conditions (ISO 5725-1). The precision is computed as the standard deviation.

[3] LoD, Limit of Detection is either three times the within standard deviation of a natural sample containing a low concentration of the compound five times the within standard deviation of a blank sample

EXPERIMENTAL

Sample handling

Samples were taken in autoclavable polypropene bottles (Kartell) [8]. The sample bottles were pre-cleaned by shaking with 100 ml of a 1% nitric acid solution. The samples were acidified to 1% of nitric acid by 69 % nitric acid (BDH Aristar no. 450042N) and stored at 5°C. Prior to analysis samples were brought to the clean chemistry laboratory (<100 Class) and transferred into LDPE and fluoroethylenepropylene (FEP) containers which were pre-cleaned according to a consolidated internal procedure [9]. The samples were 100-fold diluted for the analysis of sodium, potassium, magnesium, calcium, iron and silicon, and also, depending on their concentration, for copper and zinc.

Acidified (NIST, HNO_3 1/100) multi-element synthetic standard solutions were prepared by successive dilutions of ICP-MS stock solutions (1000 mg/L Merck or SPEX) in Milli-Q water in the clean chemistry laboratory using LDPE and FEP containers. Ultra pure water was obtained by coupling Milli-RO and Milli-Q system.

The samples were transported out of the clean area immediately before analysis by ICP-HRMS (Thermo Finnigan, Axiom Plus). The elements were analysed with the masses as indicated in Table 2. This table also gives the concentration range of the standard solutions with which the ICP-MS was calibrated. Ca, Fe, Na, Mg and Si were analysed at a mass resolution of 6400, Potassium at 10740 and the remaining elements at 400. The results were automatically corrected for the blank of Milli-Q water containing ultra pure 1% HNO_3.

Sensitivity, blanks and detection limit

A very good reproducibility in terms of sensitivity for all the elements was generally obtained even when standard solutions were prepared and analysed at different times. Several different blank samples (1% HNO_3) were analysed in order to evaluate the mean elemental concentration. The limit of detection of detection for all elements is about <0.001 µg/l.

Accuracy and Uncertainty

In order to achieve statistically good results, the NIST certified reference material SRM 1643d, simulating elemental composition of freshwater, was used for checking the performance of the ICP-MS analysis. The standard was 20, 50 and 100-fold diluted and the dilutions were analysed randomly during the analysis of samples.

Table 2 Overview of the isotope mass, abundance and calibration range used for analysis

		Mass	Natural abundance	Calibration standards (µg l^{-1})						
		amu	%	0.1	1	5	10	50	100	500
DWD Annex 1B										
Antimony	Sb	121	57.3	X	X	X	X	X		
Arsenic	As	75	100	X	X	X	X	X		
Boron	B	11	80.1	X	X	X	X	X		
Cadmium	Cd	111	13	X	X	X	X	X		
Chromium	Cr	53	9.5	X	X	X	X	X		
Copper	Cu	63	69.2	X	X	X	X	X		
Lead	Pb	208	52.4	X	X	X	X	X		
Mercury	Hg	202	29.9	X	X	X	X	X		
Nickel	Ni	60	26.1	X	X	X	X	X		
Selenium	Se	82	8.7	X	X	X	X	X		
DWD Annex 1C										
Aluminium	Al	27	100	X	X	X	X	X		
Iron	Fe	56	91.7		X		X	X	X	X
Manganese	Mn	55	100	X	X	X	X	X		
Sodium	Na	23	100		X		X	X	X	X
WHO										
Barium	Ba	137	11.2	X	X	X	X	X		
Beryllium	Be	9	100	X	X	X	X	X		
Molybdenum	Mo	95	15.92	X	X	X	X	X		
Silver	Ag	107	51.84	X	X	X	X	X		
Tin	Sn	118	24.22	X	X	X	X	X		
Uranium	U	238	99.27	X	X	X	X	X		
Zinc	Zn	66	27.9	X	X	X	X	X		
OTHERS										
Calcium	Ca	44	2.1		X		X	X	X	X
Lithium	Li	7	92.5	X	X	X	X	X		
Magnesium	Mg	24	78.99		X		X	X	X	X
Potassium	K	39	93.3		X		X	X	X	X
Silicon	Si	28	92.2		X		X	X	X	X
Titanium	Ti	47	7.3	X	X	X	X	X		
Vanadium	V	51	99.75	X	X	X	X	X		

RESULTS

In a preliminary study to get information on the repeatability of the analytical method it was observed that the repeatability was rather low. The certified standard and four samples of the initial sampling programme [10] have been measured regularly to control the performance of the ICP-HRMS during 10 month [11]. Figure 1 shows an example of the certified standard for nickel. Most values fall within the 95% confidence interval of the target value. Annex 1 shows similar figures for the other elements. Al, Cd, Cu, K, Mg, Mn, Se show occasionally consistent deviations from the average. This may have influence on the evaluation of the trueness and precision as discussed below.

For potassium the Dixon's outlier test [12] shows that two values at day 218 are outliers (P=0.05). Visually, beryllium, sodium, molybdenum and zinc will have one or two outliers. The data in the following tables include the outliers, but the effect to exclude the outliers will be explained.

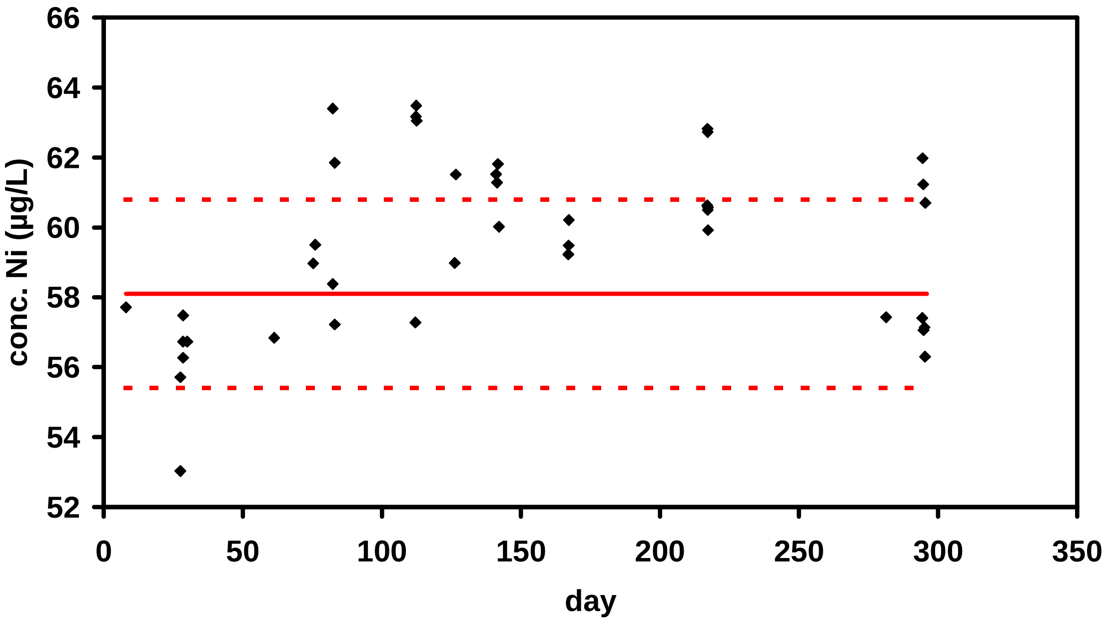

Figure 1 **The concentrations of nickel in the certified standard during 10 month. The red line indicates the target value and the red broken line the 95% confidence limits of the target value**

Systematic deviation from certified target value

The target values of the elements in standard SRM 1643d and its 95% confidence limit are given in Table 3 and can be compared with the average of the measured values and the two-sided 95% confidence limit of the average (CL) as calculated from

$$CL_{average} = \frac{t\,\sigma}{\sqrt{n}}$$

where t is the tabled value for the amount of samples, n, at the two-sided 95% confidence level and σ the standard deviation of the data set [13]. Unfortunately, SRM 1643d has not certified target values for Hg, Ba, Si, Sn, Ti and U. A non-certified value is given for silicon. In the case of As, Ca, Cr, K, Mg, Mo, Na, Se and Zn the 95% confidence limit of the average of the observed values is higher than that of the target value. By excluding outliers the 95% confidence limit of the average of molybdenum is similar to that of the target value.

Table 3 Results of SRM 1643d (n=33-42) during 10 month

		Target		Measured		Risk limit	Trueness (DWD)	Precision (DWD)
		average	95 % confidence limit	average	95 % confidence limit			
		µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	µg l^{-1}	%	%
DWD Annex 1B								
Antimony	Sb	54.1	1.1	55.3	0.9	1.8	2 (+)	5 (+)
Arsenic	As	56.02	0.73	63.67	2.21	2.57	14 (–)	11 (–)
Boron	B	144.8	5.2	144.4	1.8	6.7	0.2 (+)	4 (+)
Cadmium	Cd	6.47	0.37	6.82	0.12	0.47	5 (+)	5 (+)
Chromium	Cr	18.53	0.2	18.89	0.38	0.52	2 (+)	6 (+)
Copper	Cu	20.5	3.8	22.7	1.1	4.7	10 (+)	15 (+)
Lead	Pb	18.15	0.64	19.58	0.35	0.93	8 (+)	6 (+)
Mercury	Hg	-	-	1.5	0.6	-	-	115 (–)
Nickel	Ni	58.1	2.7	59.4	0.8	3.4	2 (+)	4 (+)
Selenium	Se	11.43	0.17	12.10	0.39	0.50	6 (+)	10 (+)
DWD Annex 1C								
Aluminium	Al	127.6	3.5	124.8	2.0	5.2	2 (+)	5 (+)
Iron	Fe	91.2	3.9	94.1	1.3	5.0	3 (+)	4 (+)
Manganese	Mn	37.66	0.83	38.97	0.75	1.46	3 (+)	6 (+)
Sodium	Na	22070	640	21342	1187	1627	3 (+)	16 (+)
WHO								
Barium	Ba	-	-	505	5	-	-	3
Beryllium	Be	12.53	0.28	12.65	0.20	0.45	1	5
Molybdenum	Mo	112.9	1.7	115.9	3.1	4.2	3	8
Silver	Ag	1.27	0.057	1.30	0.047	0.096	2	11
Tin	Sn	-	-	4.4	0.4	-	-	24
Uranium	U	-	-	0.23	0.12	-	-	152
Zinc	Zn	72.48	0.65	73.25	1.83	2.17	1	8
OTHERS								
Calcium	Ca	31040	50	31891	410	391	3	4
Lithium	Li	16.5	0.55	16.5	0.46	0.93	0.3	8
Magnesium	Mg	7989	35	7967	150	160	0.3	6
Potassium	K	2356	35	2501	125	139	6	16
Silicon	Si	2700	-	2800	56	-	3	6
Titanium	Ti	-	-	0.95	0.15	-	-	45
Vanadium	V	35.1	1.4	34.8	0.4	1.7	0.9	4

In order to know if systematic deviation of the average of the measured values and the target value exists, the null hypothesis, i.e. there is no difference other than random variation, was tested. The difference between the target value and the average of the observed values is significant for As, Ca, Cr, K, Mn, Mo, Na, Pb, Sb, Se and Zn (P=0.05). The average concentrations are outside the 95% confidence interval of the target value. This implicates that a systematic error might be present. It also means that there is a probability of 5% that the null hypothesis is rejected even though it is true (Type 1 error). By excluding the outliers for molybdenum, sodium and zinc the averages become 114.6 µg/l, 22009 µg/l and 73.9 µg/l, respectively. Only zinc remains outside the risk limit.

It is also possible that the null hypothesis is retained even tough it is false (Type 2 error). The probability of this type of error can be calculated by defining an alternative hypothesis, i.e. that the target is the average of the observed values. The one-sided 95% confidence limit of the average gives the probability of 5% that the alternative hypothesis is rejected even though it is true. The risk limit (RL) around the target value covering both Type1 and Type 2 errors is given by:

$$\mathrm{RL} = \mathrm{CL}_{\mathrm{target}} + \left(\frac{t\,\sigma}{\sqrt{n}}\right)_{\mathrm{average}}$$

where CL is the two-sided 95% confidence limit of the target, t the tabled value for the amount of samples, n, at the 95% confidence level (one-sided) and σ the standard deviation of the data set [13]. In the case of the results in Table 3 t=1.684 (n=40) was taken [14]. This calculation shows that that the average concentrations of As, Ca, K, Pb and Se are outside the risk limit and these elements might suffer from a systematic error (P=0.05). If the two outliers for potassium are excluded, the average (2422 µg/l) is similar to the target value plus the risk limit (64 µg/l).

Trueness for compliance parametric value in DWD

If one compares the trueness, i.e. the difference between the target and the average of the observed values, with the trueness as defined in the DWD, the trueness of arsenic is out of range. The trueness of arsenic is defined in the DWD as 10% of the parametric value, which is 10 µg/l.

The trueness for copper is found to be 10% and is at the limit as defined by the DWD, i.e. 10% of 2000 µg/l. This result is acceptable because the concentration in the certified standard is a 100-fold lower than that of the parametric value.

The trueness for lead is 8% at a 1.8 fold higher concentration compared to the parametric value in the DWD, i.e. 10 µg/l. This result is acceptable, but at the edge because the trueness is set at 10% of the parametric value in the DWD.

Precision for compliance parametric value in DWD

The precision of arsenic and selenium are on the edge. One may also doubt about the precision of copper and sodium. The observed relative precision is a little lower than that defined in the DWD. However, the target values for copper and sodium are a 10 and 100-fold lower, respectively, than the parametric value. The concentration of mercury in the certified standard, although it is not certified for mercury, was on average near the parametric value in the DWD. The certified standard seems not to be stable for mercury reflecting in its low precision of 115%.

The elements not mentioned in the DWD, but with a certified target value, have a precision below 10%, except silver (11%) and potassium (16%). By eliminating the two outliers the precision of potassium reduces to 4%. The elements that do not have a certified target value have low precision, tin (24%), titanium (45%) and uranium (152%). Barium is an exception with a precision of 3%.

Table 4 and Table 4 Concentrations and standard deviations of four samples analysed during 10 month

Sample		1		2		3		4	
n		9-13		8-11		8-12		8-12	
		average µg l^{-1}	sd µg l^{-1}	average µg l^{-1}	sd µg l^{-1}	average µg l^{-1}	sd µg l^{-1}	average µg l^{-1}	sd µg l^{-1}
DWD Annex 1B									
Antimony	Sb	0.085	0.014	0.085	0.013	0.080	0.016	0.108	0.013
Arsenic	As	1.90	0.24	1.53	0.22	1.89	0.29	1.58	0.25
Boron	B	10.0	0.7	9.36	0.67	9.09	0.72	9.71	0.79
Cadmium	Cd	0.082	0.016	0.027	0.011	0.035	0.013	1.91	0.13
Chromium	Cr	0.31	0.13	0.26	0.14	0.25	0.16	0.27	0.15
Copper	Cu	30.8	4.6	2.29	0.24	2.47	0.31	2.26	0.18
Lead	Pb	1.24	0.12	0.171	0.030	0.39	0.16	5.20	0.53
Mercury	Hg	0.079	0.139	0.039	0.035	0.036	0.031	0.035	0.033
Nickel	Ni	41.1	5.5	1.56	0.19	1.52	0.19	1.70	0.12
Selenium	Se	0.214	0.043	0.169	0.028	0.159	0.041	0.210	0.038
DWD Annex 1C									
Aluminium	Al	29	10	25.6	4.0	10.4	1.8	18.1	1.7
Iron	Fe	626	74	361	33	43	10	103	15
Manganese	Mn	7.15	0.77	4.43	0.40	1.33	0.16	9.6	1.2
Sodium	Na	3800	1200	3600	1200	3100	1000	3200	1100
WHO									
Barium	Ba	11.50	0.78	10.2	1.2	9.8	1.4	11.11	0.96
Beryllium	Be	0.004	0.006	0.009	0.012	0.009	0.012	0.004	0.006
Molybdenum	Mo	0.794	0.069	0.812	0.091	0.77	0.10	0.734	0.076
Silver	Ag	0.005	0.003	0.003	0.004	0.001	0.002	0.005	0.002
Tin	Sn	0.064	0.062	0.047	0.015	0.032	0.032	0.071	0.025
Uranium	U	0.376	0.045	0.387	0.049	0.340	0.057	0.257	0.043
Zinc	Zn	730	480	84	55	310	110	1100	300
OTHERS									
Calcium	Ca	23900	2400	24000	3500	20800	3900	21700	3000
Lithium	Li	0.47	0.10	0.45	0.11	0.43	0.10	0.44	0.14
Magnesium	Mg	4010	400	4080	480	3430	400	3640	540
Potassium	K	1500	130	1500	160	1580	450	1570	190
Silicon	Si	930	120	920	120	1187	99	1360	180
Titanium	Ti	1.37	0.33	1.27	0.34	0.63	0.25	0.71	0.31
Vanadium	V	0.331	0.065	0.303	0.058	0.385	0.070	0.289	0.066

Table 5 show the average concentration, standard deviation and precision of four different tap samples that were analysed during ten month at the same time as the certified standard. These samples were selected on the basis of the initial sampling programme [10]. In general, the elements are present in lower concentrations than in the certified standard.

Table 4 Concentrations and standard deviations of four samples analysed during 10 month

Sample		1		2		3		4	
n		9-13		8-11		8-12		8-12	
		average µg l^{-1}	sd µg l^{-1}	average µg l^{-1}	sd µg l^{-1}	average µg l^{-1}	sd µg l^{-1}	average µg l^{-1}	sd µg l^{-1}
DWD Annex 1B									
Antimony	Sb	0.085	0.014	0.085	0.013	0.080	0.016	0.108	0.013
Arsenic	As	1.90	0.24	1.53	0.22	1.89	0.29	1.58	0.25
Boron	B	10.0	0.7	9.36	0.67	9.09	0.72	9.71	0.79
Cadmium	Cd	0.082	0.016	0.027	0.011	0.035	0.013	1.91	0.13
Chromium	Cr	0.31	0.13	0.26	0.14	0.25	0.16	0.27	0.15
Copper	Cu	30.8	4.6	2.29	0.24	2.47	0.31	2.26	0.18
Lead	Pb	1.24	0.12	0.171	0.030	0.39	0.16	5.20	0.53
Mercury	Hg	0.079	0.139	0.039	0.035	0.036	0.031	0.035	0.033
Nickel	Ni	41.1	5.5	1.56	0.19	1.52	0.19	1.70	0.12
Selenium	Se	0.214	0.043	0.169	0.028	0.159	0.041	0.210	0.038
DWD Annex 1C									
Aluminium	Al	29	10	25.6	4.0	10.4	1.8	18.1	1.7
Iron	Fe	626	74	361	33	43	10	103	15
Manganese	Mn	7.15	0.77	4.43	0.40	1.33	0.16	9.6	1.2
Sodium	Na	3800	1200	3600	1200	3100	1000	3200	1100
WHO									
Barium	Ba	11.50	0.78	10.2	1.2	9.8	1.4	11.11	0.96
Beryllium	Be	0.004	0.006	0.009	0.012	0.009	0.012	0.004	0.006
Molybdenum	Mo	0.794	0.069	0.812	0.091	0.77	0.10	0.734	0.076
Silver	Ag	0.005	0.003	0.003	0.004	0.001	0.002	0.005	0.002
Tin	Sn	0.064	0.062	0.047	0.015	0.032	0.032	0.071	0.025
Uranium	U	0.376	0.045	0.387	0.049	0.340	0.057	0.257	0.043
Zinc	Zn	730	480	84	55	310	110	1100	300
OTHERS									
Calcium	Ca	23900	2400	24000	3500	20800	3900	21700	3000
Lithium	Li	0.47	0.10	0.45	0.11	0.43	0.10	0.44	0.14
Magnesium	Mg	4010	400	4080	480	3430	400	3640	540
Potassium	K	1500	130	1500	160	1580	450	1570	190
Silicon	Si	930	120	920	120	1187	99	1360	180
Titanium	Ti	1.37	0.33	1.27	0.34	0.63	0.25	0.71	0.31
Vanadium	V	0.331	0.065	0.303	0.058	0.385	0.070	0.289	0.066

Table 5 Results of the precision of four samples and certified standard analysed during 10 month. Values between brackets indicate precision after elimination of outliers.

		NIST %	Sample 1 %	Sample 2 %	Sample 3 %	Sample 4 %
DWD Annex 1B						
Antimony	Sb	5	17	15	20	12
Arsenic	As	11	13	14	15	16
Boron	B	4	8	7	8	8
Cadmium	Cd	5	20	42	39	7
Chromium	Cr	6	41	55	65	67
Copper	Cu	15	15	11	12	8
Lead	Pb	6	9	18	40 (18)	10
Mercury	Hg	115	180 (54)	89	85 (54)	93 (73)
Nickel	Ni	4	13 (7)	12	12	7
Selenium	Se	10	20	17	26	18
DWD Annex 1C						
Aluminium	Al	5	35 (16)	16	18	9
Iron	Fe	4	12	9	24	15
Manganese	Mn	6	11	9	12	12
Sodium	Na	16	31	35	33	34
WHO						
Barium	Ba	3	7	12	14	9
Beryllium	Be	5	140	140	130	160
Molybdenum	Mo	8	9	11	13	10
Silver	Ag	11	51	130	130	40
Tin	Sn	24	96 (40)	33	100	35
Uranium	U	152	12	13	17	17
Zinc	Zn	8	66 (34)	66	36	27
OTHERS						
Calcium	Ca	4	10	15	19	14
Lithium	Li	8	21	24	23	32
Magnesium	Mg	6	10	12	12	15
Potassium	K	16	9	11	28 (9)	12
Silicon	Si	6	13	12	8	13
Titanium	Ti	45	24	27	40 (24)	44 (16)
Vanadium	V	4	20	19	25	23

In general the low concentrations in the samples compared to the parametric values in the DWD result in slightly or significantly lower precisions. Cadmium is an example where it can be clearly shown that the relative higher concentration has a better precision (Figure 2). The precision of lead for sample no. 4 is at the edge of performance, as was also observed for the certified standard. Elimination of an outlier in sample no. 3 for lead gives a concentration of 0.34±0.06 µg/l. Mercury shows a low precision in the samples but the precision is not worse compared to that of the certified standard and better after elimination of outliers. The concentrations of mercury in the respective samples become 33±18 ng/l, 31±23 ng/l, 28±15 ng/l and 27±20 ng/l. Nickel is also at the edge of its DWD precision in sample no. 1, although this was not observed for the results of the certified standard. Elimination of an outlier gives an average concentration of 42.4±3.0 µg/l and shows that nickel performs according to the requirements in the DWD (Figure 3). The precision of Al, Ca, Fe, Mg and Zn for the samples is lower compared to that of the certified standard at the same concentration level. Uranium shows the opposite of the previous elements, i.e. a better precision in the samples compared to the certified standard at a similar concentration level. The precision of potassium and titanium between the samples become consistent after elimination of outliers. The average concentration of potassium in sample no. 3 becomes 1430±124 µg/l and that of titanium in sample no. 3 and 4 0.57±0.14 µg/l and 0.59±0.09 µg/l, respectively. The concentration of Al, Sn and Zn in sample no. 1 becomes 26±4 µg/l, 0.052±0.021 µg/l and 592±200 µg/l, respectively, by elimination of outliers.

The difference in precision of several elements between the certified standard and the samples might be due to the fact that the certified standard does not reflect the complete composition of a real sample. It was prepared from acidified distilled water to which the elements have been added and next filtered and sterilised.

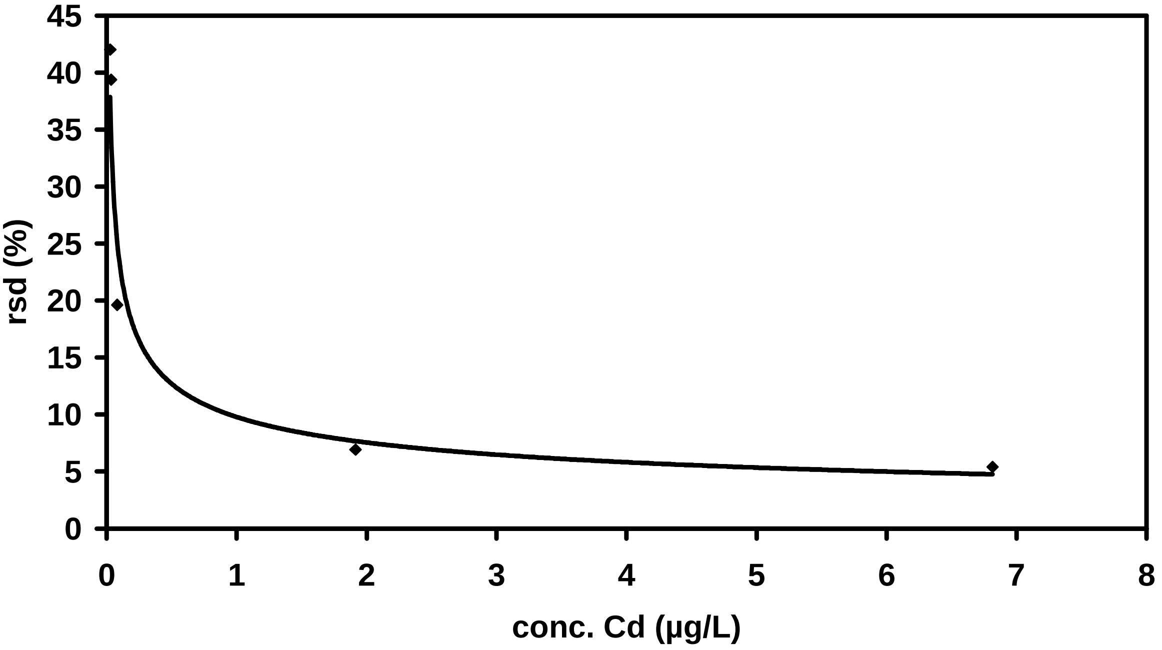

Figure 2 Relative precision of cadmium as function of the concentration

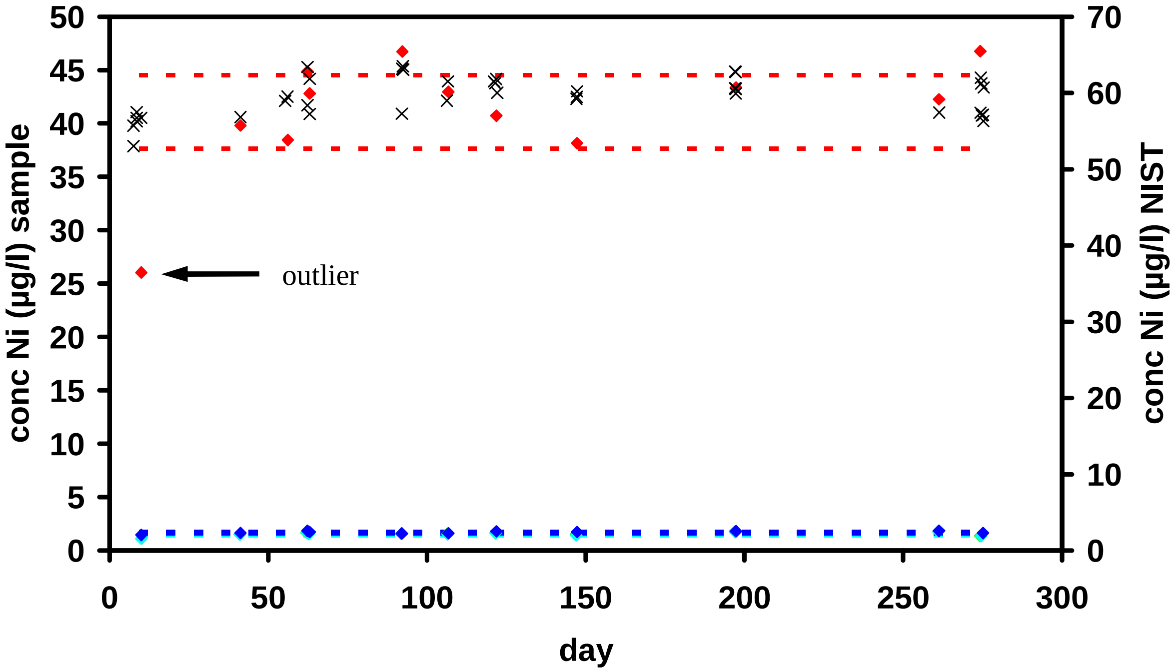

Figure 3 The concentrations of nickel in the samples during 10 month. The red broken line are the 95% confidence limits of the average concentration in one sample. The black crosses are the results of the certified standard for comparison.

CONCLUSION

The analysis of the certified standard over about one year showed that the average concentrations of As, Ca, Pb and Se are outside the risk limit around the target value. Lead and selenium suffer only from a small systematic error whereas arsenic and calcium suffer a bigger systematic error ($P=0.05$).

The trueness of arsenic, i.e. the difference between the target and the average of the observed values, is out of range compared to what is defined in the DWD. The trueness of copper and lead are at the edge.

The precision of arsenic and selenium are on the edge compared to the requirements in the DWD. The observed precision of copper and sodium is a little lower than that defined in the DWD. However, the target values for copper and sodium are a 10 and 100-fold lower than the parametric value. The elements not mentioned in the DWD, but with a certified target value, have a precision below 10%, except silver (11%). The elements that do not have a certified target value have low precision, mercury (115%), tin (24%), titanium (45%) and uranium (152%). Barium is an exception with a precision of 3%.

In general, the low concentrations in the samples compared to the parametric values in the DWD result in slightly or significantly lower precisions. Compared to the certified standard nickel appeared to be at the edge of its DWD precision in the samples, but after elimination of an outlier nickel fulfils the requirements. The precision of Al, Ca, Fe, Mg and Zn for the samples is lower compared to that of the certified standard at a similar concentration level whereas uranium showed the opposite behaviour.

Multi-element analysis ($n = 28$), implies the possible introduction of additional variations both in trueness and precision compared to single element analysis. The setting of certified values and their precision for Certified Reference Materials is normally performed on the single element and in a short timeframe. Considering the fact that many samples are analysed for 28 elements and during 10 month, the multi-element analysis is sufficient for its purpose. For legal purposes or for detailed studies on specific elements a single element analysis may be more appropriate. This is especially true for arsenic.

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4 COUNCIL DIRECTIVE 93/68/EEC of 22 July 1993 amending …, 89/106/EEC (construction products), …; Official Journal of the European Communities L220, 1-22 (1993)

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12 Rorabacher D.B.; Statistical Treatment for Rejection of Deviant Values: Critical Values of Dixon's "Q" Parameter and Related Subrange Ratios at the 95% Confidence Level; Anal. Chem. 63, 139-146 (1991)

13 Miller J.C., Miller J.N.; Statistics for analytical chemistry, 2nd Ed.; Ellis Horwood, Chichester (1988)

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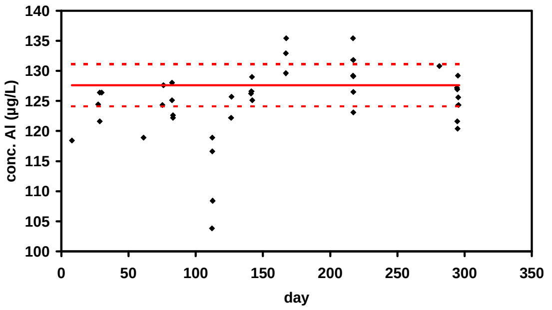
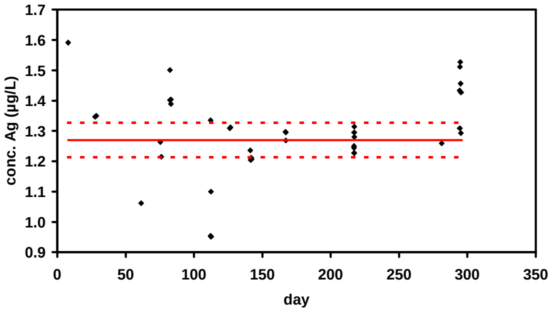
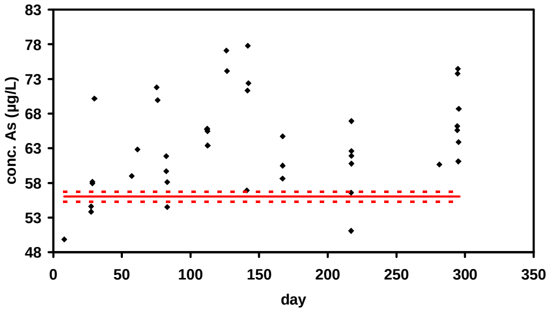
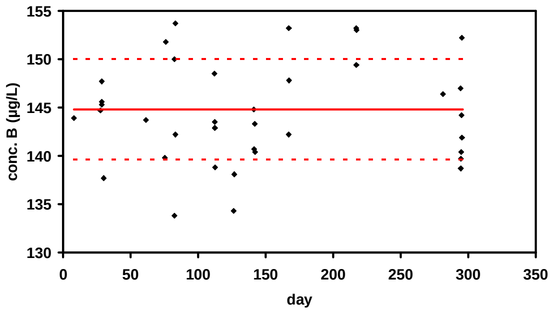
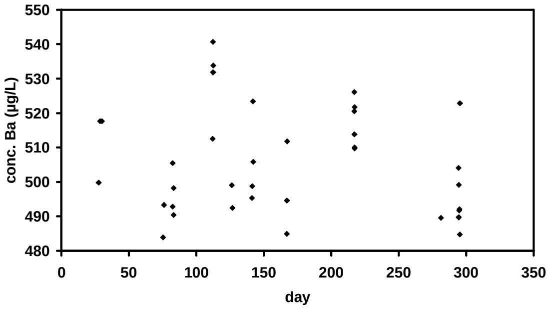
ANNEX 1 RESULTS OF NIST 1643D STANDARD

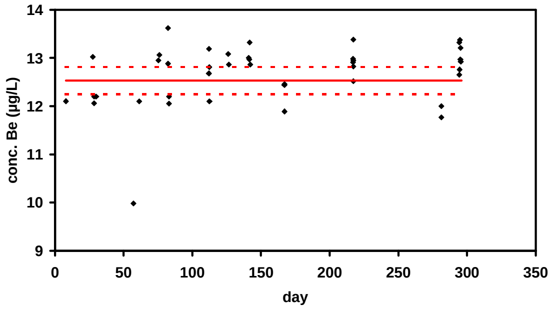


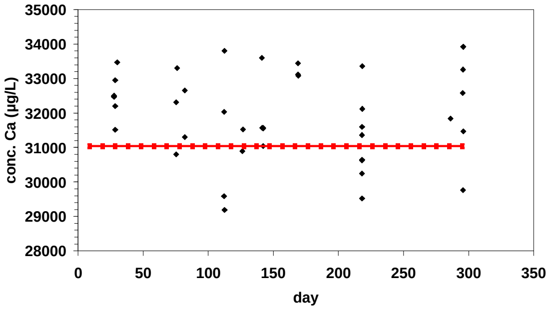


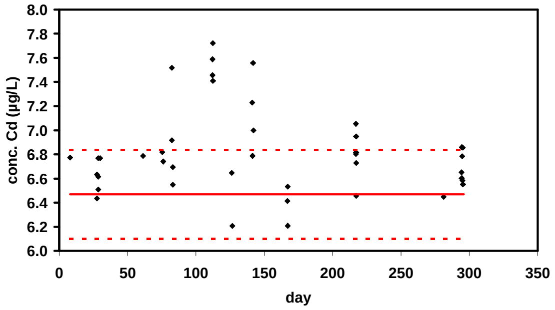


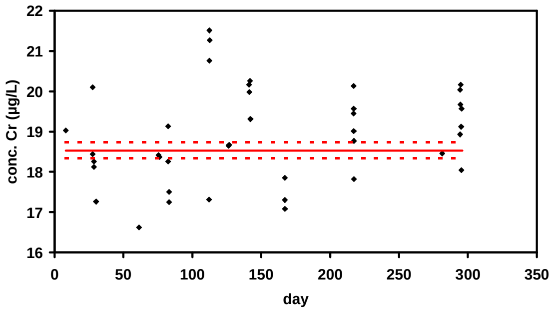


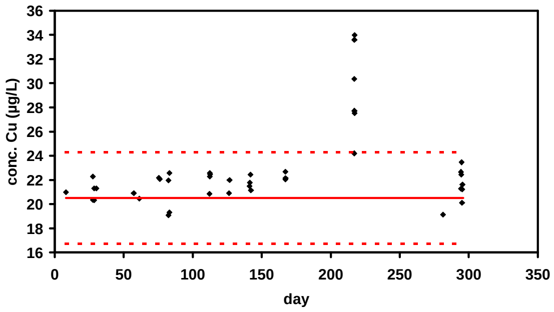


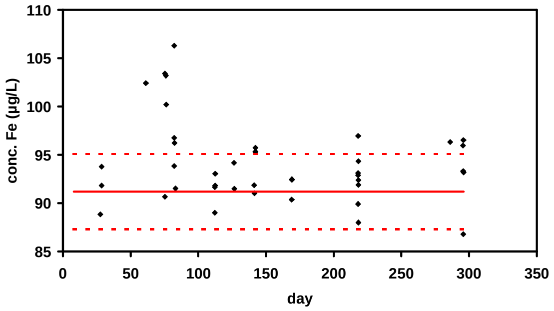


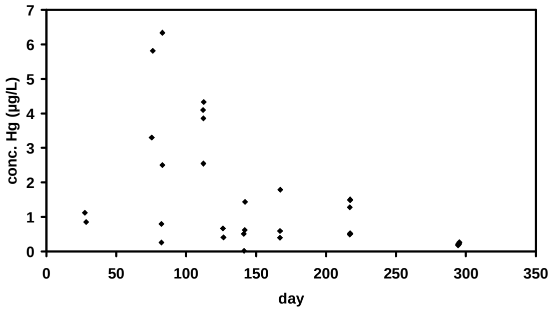


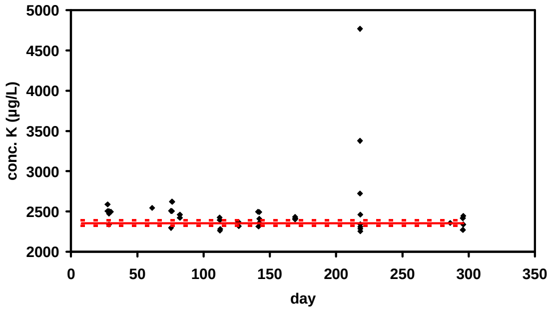


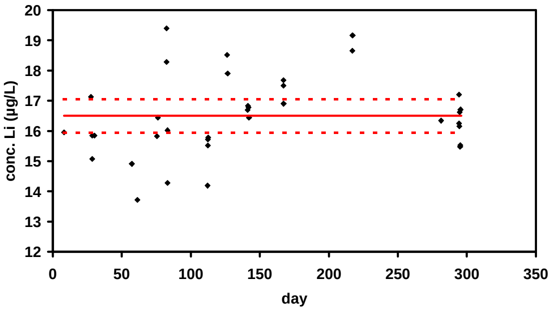

conc. Cr (µg/L)
16
17
18
19
20
21
22
0
50
100
150
200
250
300
350
day

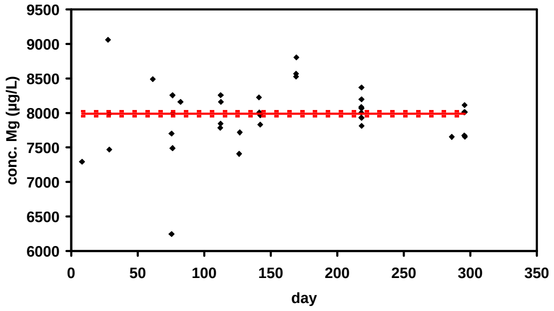

conc. Cu (µg/L)
16
18
20
22
24
26
28
30
32
34
36
0
50
100
150
200
250
300
350
day

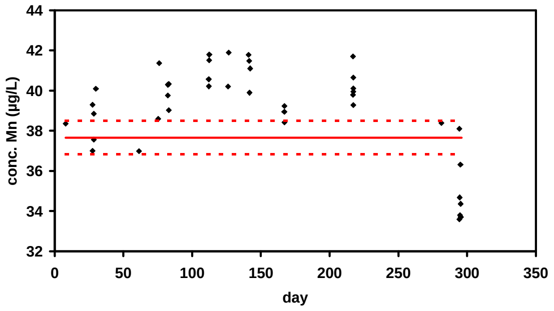

conc. Fe (µg/L)
85
90
95
100
105
110
0
50
100
150
200
250
300
350
day

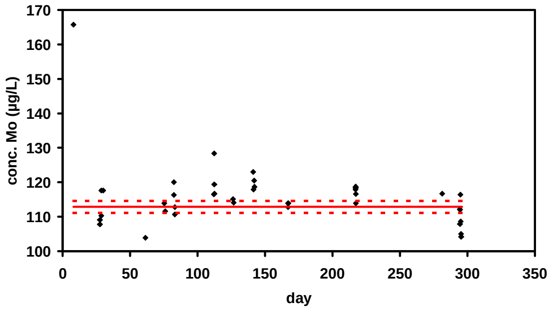

conc. Hg (µg/L)
0
1
2
3
4
5
6
7
0
50
100
150
200
250
300
350
day

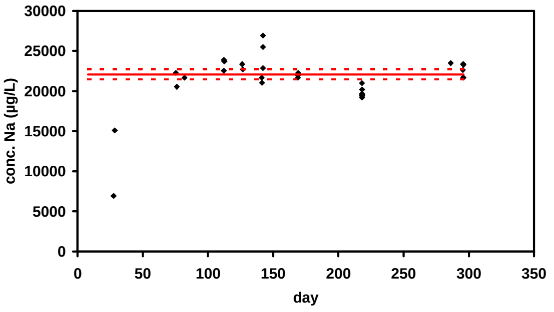

conc. K (µg/L)
2000
2500
3000
3500
4000
4500
5000
0
50
100
150
200
250
300
350
day

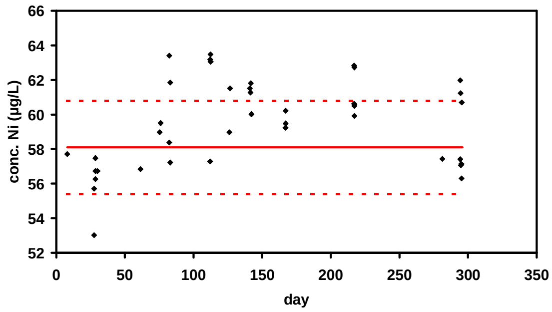

conc. Li (µg/L)
12
13
14
15
16
17
18
19
20
0
50
100
150
200
250
300
350
day

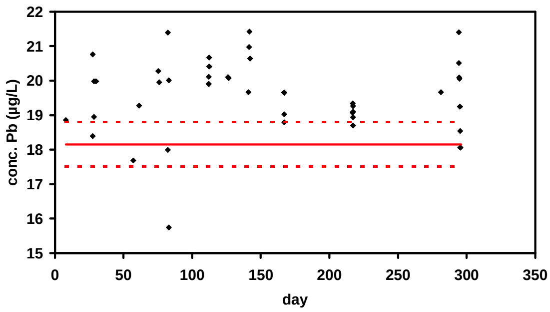

conc. Mg (µg/L)
6000
6500
7000
7500
8000
8500
9000
9500
0
50
100
150
200
250
300
350
day

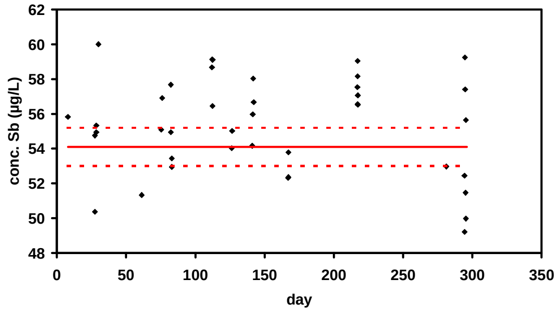

conc. Mn (µg/L)
32
34
36
38
40
42
44
0
50
100
150
200
250
300
350
day

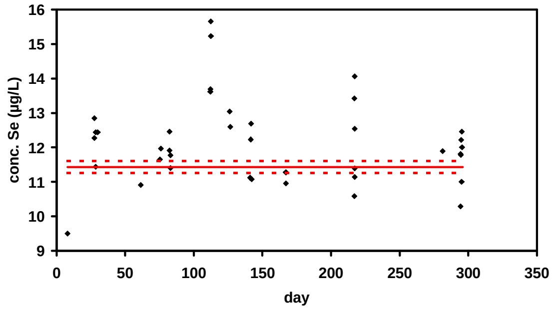

conc. Mo (µg/L)
100
110
120
130
140
150
160
170
0
50
100
150
200
250
300
350
day

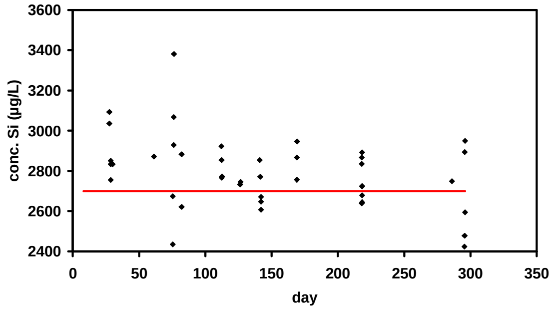

conc. Na (µg/L)
0
5000
10000
15000
20000
25000
30000
0
50
100
150
200
250
300
350
day

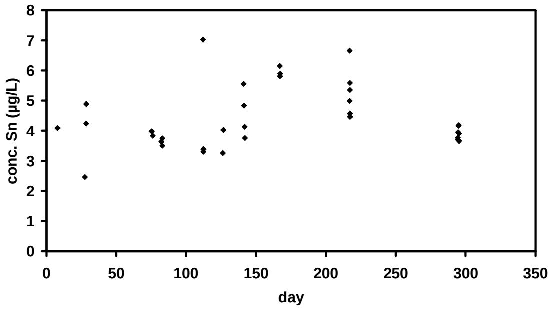

conc. Ni (µg/L)
66
64
62
60
58
56
54
52
0
50
100
150
200
250
300
350
day

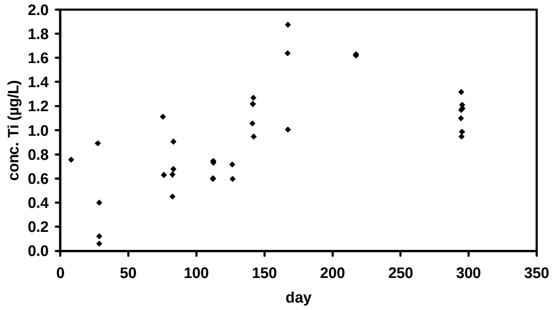

conc. Pb (µg/L)
22
21
20
19
18
17
16
15
0
50
100
150
200
250
300
350
day

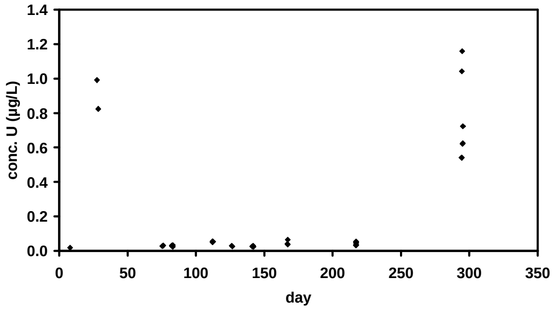

conc. Sb (µg/L)
62
60
58
56
54
52
50
48
0
50
100
150
200
250
300
350
day

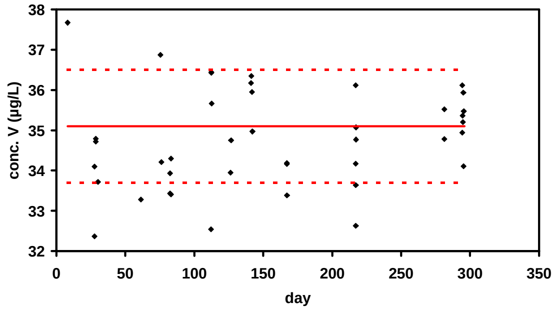

conc. Se (µg/L)
16
15
14
13
12
11
10
9
0
50
100
150
200
250
300
350
day

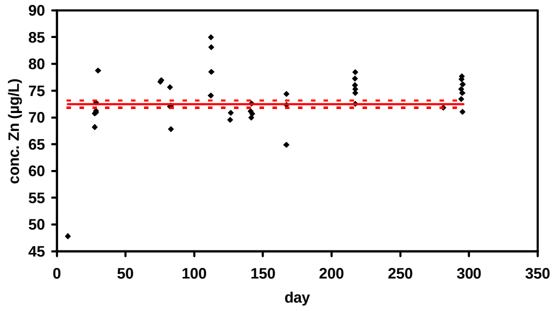

conc. Si (µg/L)
3600
3400
3200
3000
2800
2600
2400
0
50
100
150
200
250
300
350
day


conc. Sn (µg/L)
8
7
6
5
4
3
2
1
0
0
50
100
150
200
250
300
350
day

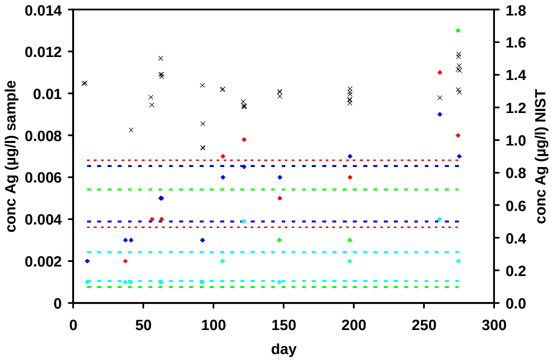

conc. Ti (µg/L)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
350
day

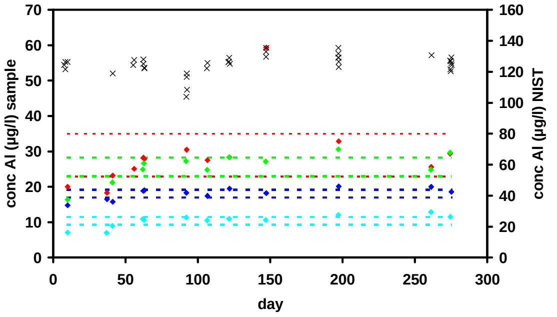

conc. U (µg/L)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
350
day

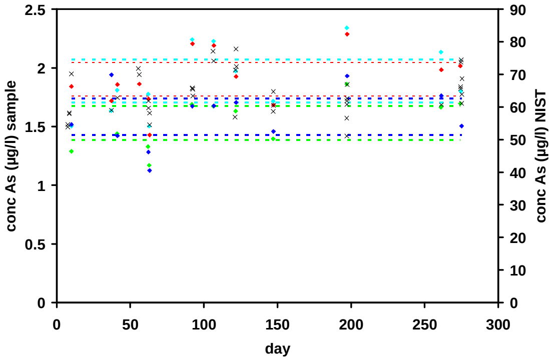

conc. V (µg/L)
38
37
36
35
34
33
32
0
50
100
150
200
250
300
350
day

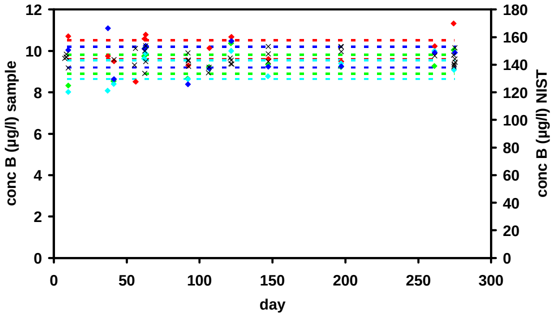

conc. Zn (µg/L)
90
85
80
75
70
65
60
55
50
45
0
50
100
150
200
250
300
350
day

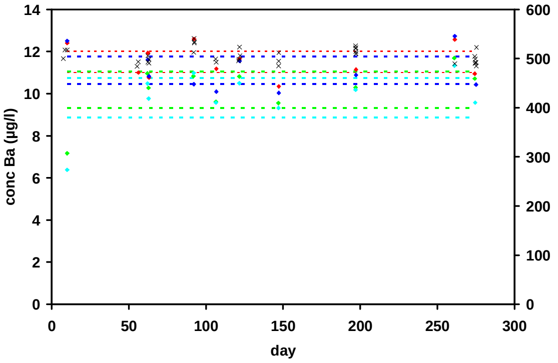
ANNEX 2 RESULTS OF FOUR SAMPLES

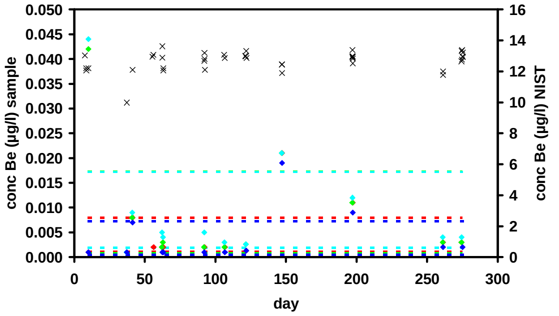


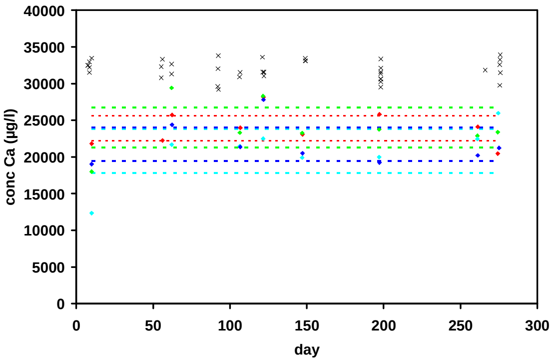


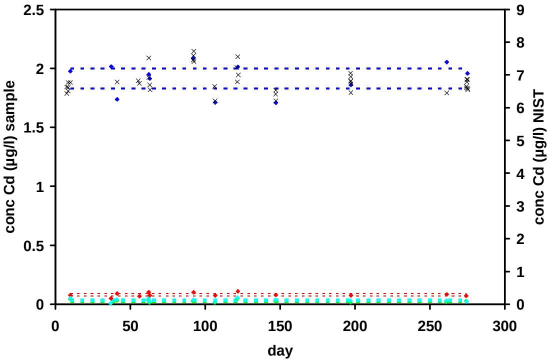


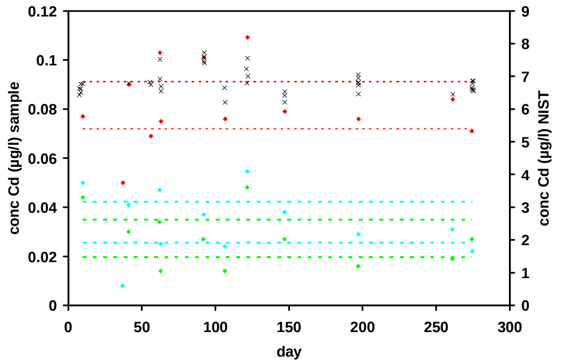


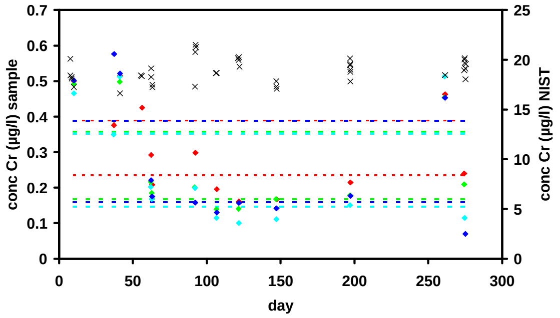


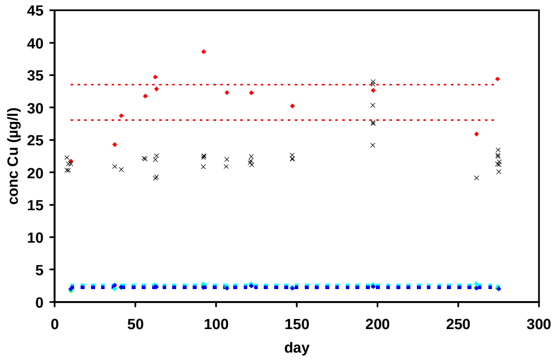


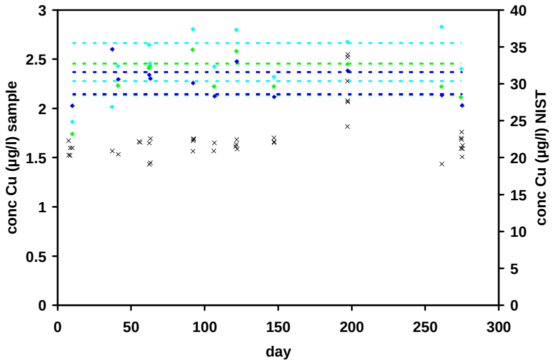


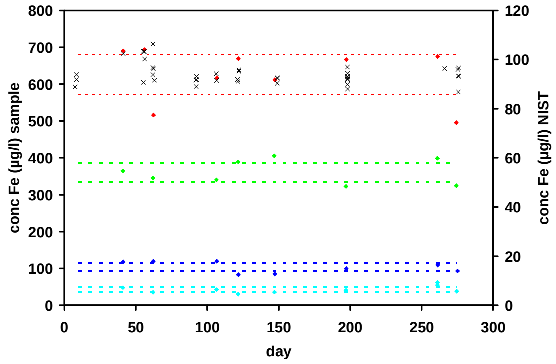


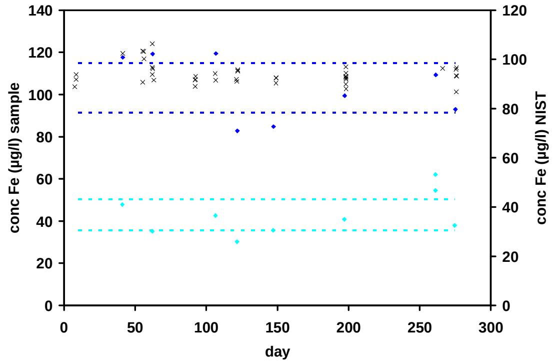

conc Cd (µg/l) sample
0.12
0.1
0.08
0.06
0.04
0.02
0
conc Cd (µg/l) NIST
9
8
7
6
5
4
3
2
1
0
0
50
100
150
200
250
300
day

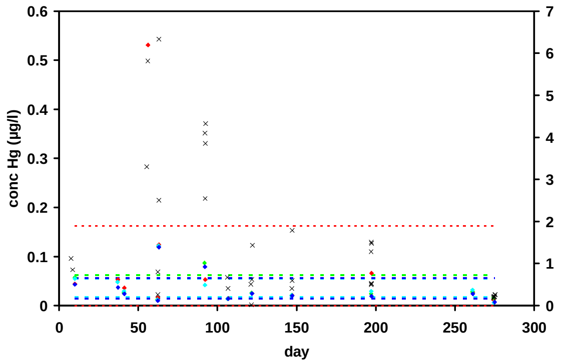

conc Cr (µg/l) sample
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
conc Cr (µg/l) NIST
25
20
15
10
5
0
0
50
100
150
200
250
300
day

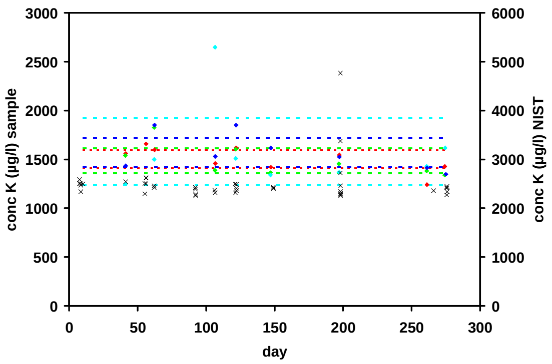

conc Cu (µg/l)
45
40
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
day

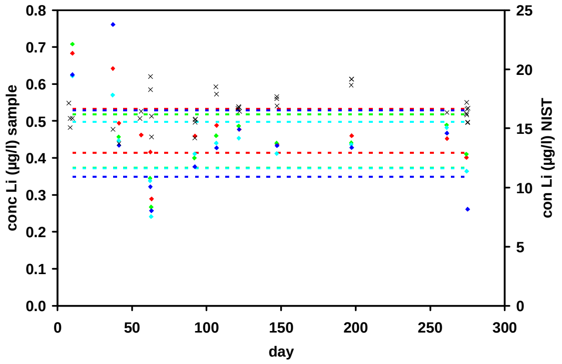

conc Cu (µg/l) sample
3
2.5
2
1.5
1
0.5
0
conc Cu (µg/l) NIST
40
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
day

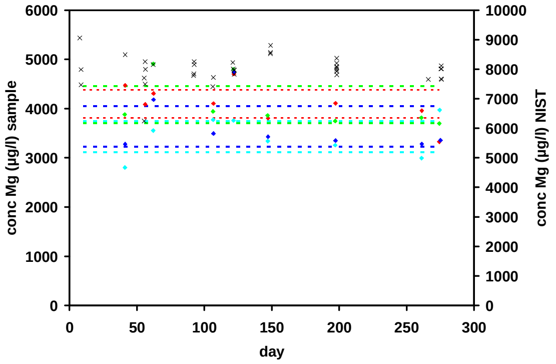

conc Fe (µg/l) sample
800
700
600
500
400
300
200
100
0
conc Fe (µg/l) NIST
120
100
80
60
40
20
0
0
50
100
150
200
250
300
day

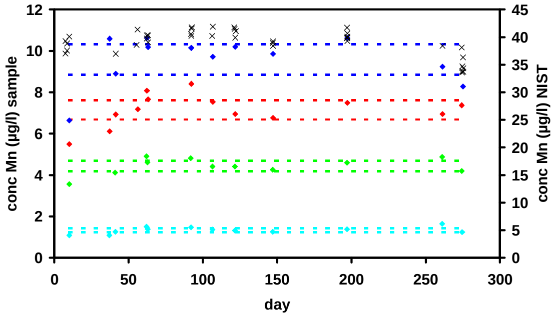

conc Fe (µg/l) sample
140
120
100
80
60
40
20
0
conc Fe (µg/l) NIST
120
100
80
60
40
20
0
0
50
100
150
200
250
300
day

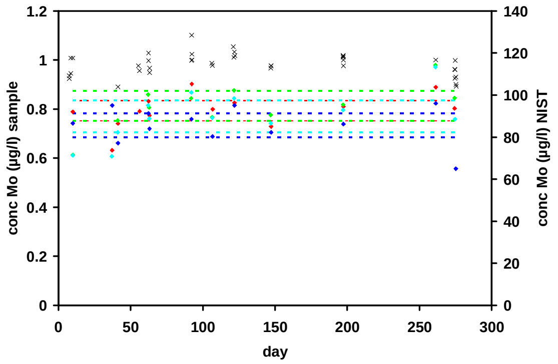

conc Hg (µg/l)
0.6
0.5
0.4
0.3
0.2
0.1
0
7
6
5
4
3
2
1
0
0
50
100
150
200
250
300
day

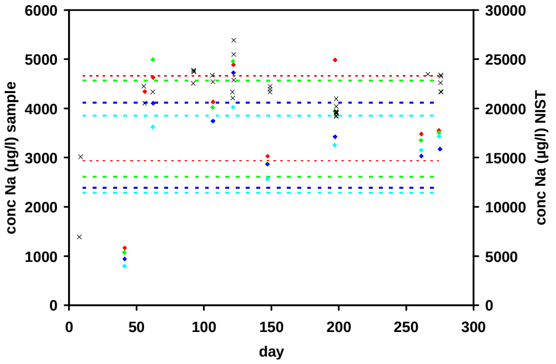

conc K (µg/l) sample
3000
2500
2000
1500
1000
500
0
conc K (µg/l) NIST
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
250
300
day

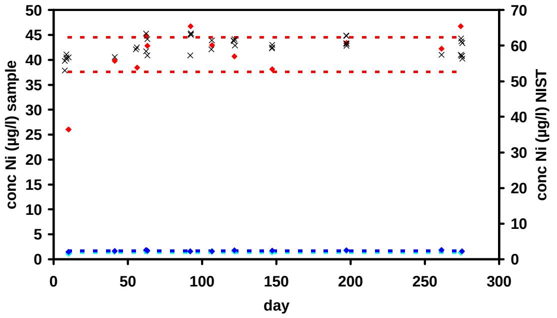

conc Li (µg/l) sample
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
con Li (µg/l) NIST
25
20
15
10
5
0
0
50
100
150
200
250
300
day

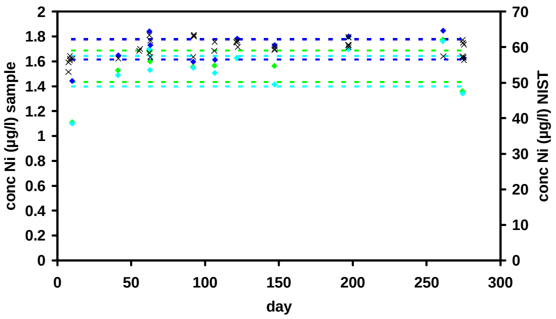

conc Mg (µg/l) sample
6000
5000
4000
3000
2000
1000
0
conc Mg (µg/l) NIST
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
50
100
150
200
250
300
day

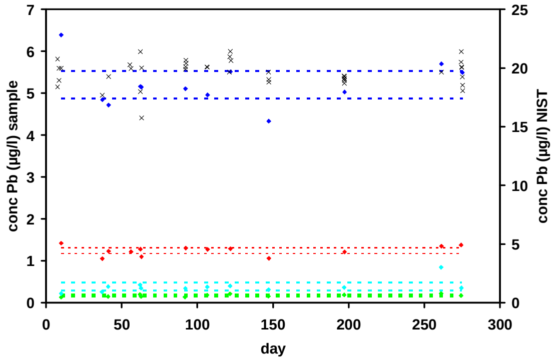

conc Mn (µg/l) sample
conc Mn (µg/l) NIST
day
0
2
4
6
8
10
12
0
5
10
15
20
25
30
35
40
45
0
50
100
150
200
250
300

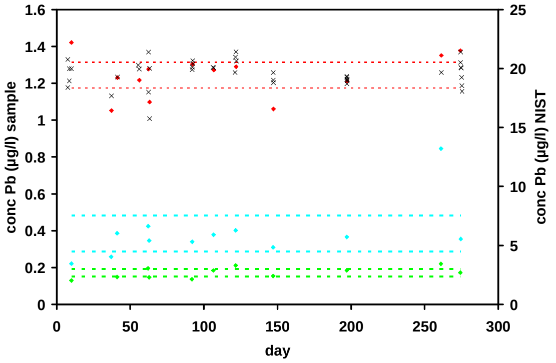

conc Mo (µg/l) sample
conc Mo (µg/l) NIST
day
0
0.2
0.4
0.6
0.8
1
1.2
0
20
40
60
80
100
120
140
0
50
100
150
200
250
300

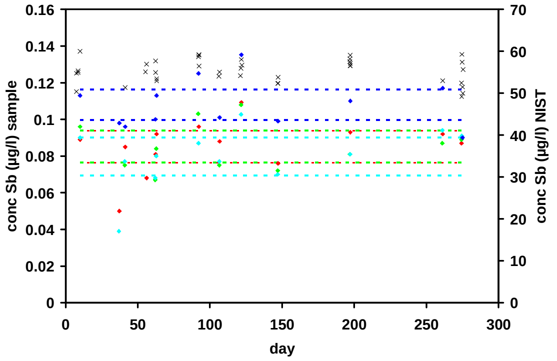

conc Na (µg/l) sample
conc Na (µg/l) NIST
day
0
1000
2000
3000
4000
5000
6000
0
5000
10000
15000
20000
25000
30000
0
50
100
150
200
250
300

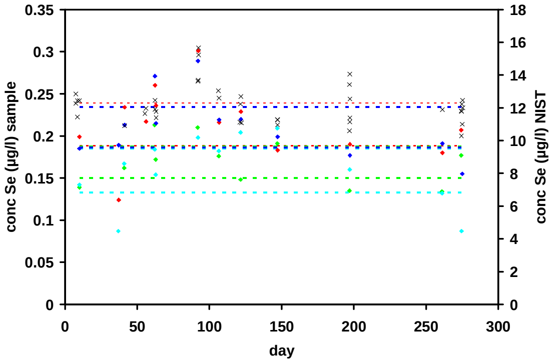

conc Ni (µg/l) sample
conc Ni (µg/l) NIST
day
0
5
10
15
20
25
30
35
40
45
50
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300

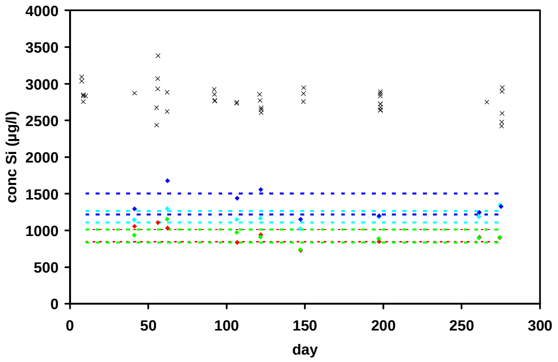

conc Ni (µg/l) sample
conc Ni (µg/l) NIST
day
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300

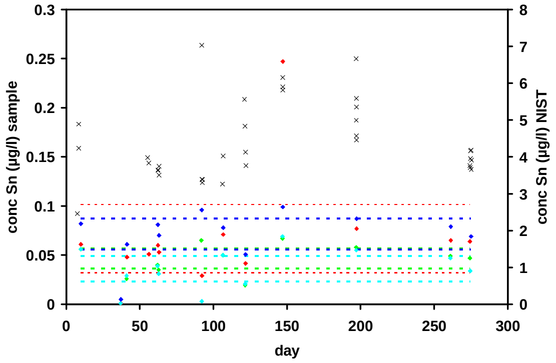

conc Pb (µg/l) sample
conc Pb (µg/l) NIST
day
0
1
2
3
4
5
6
7
0
5
10
15
20
25
0
50
100
150
200
250
300

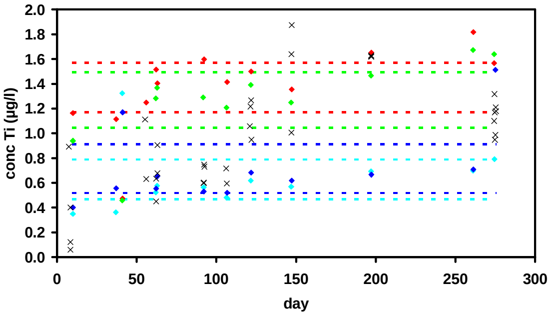

conc Pb (µg/l) sample
conc Pb (µg/l) NIST
day
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
0
5
10
15
20
25
0
50
100
150
200
250
300

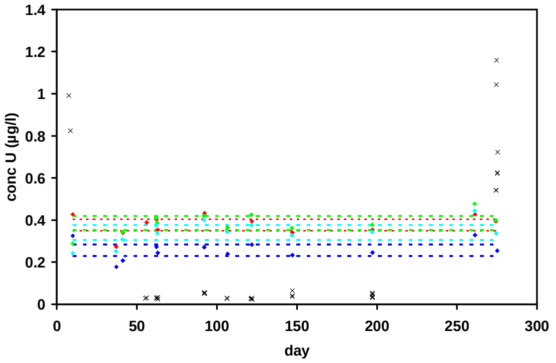

conc Sb (µg/l) sample
conc Sb (µg/l) NIST
day
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0
10
20
30
40
50
60
70
0
50
100
150
200
250
300

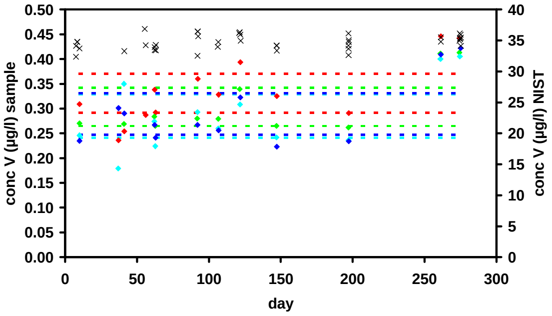

conc Se (µg/l) sample
conc Se (µg/l) NIST
day
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0
2
4
6
8
10
12
14
16
18
0
50
100
150
200
250
300

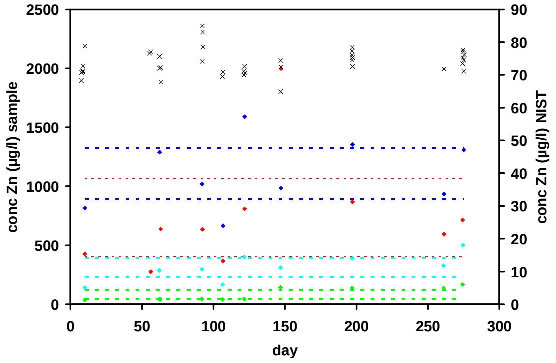

conc Si (µg/l)
day
0
500
1000
1500
2000
2500
3000
3500
4000
0
50
100
150
200
250
300

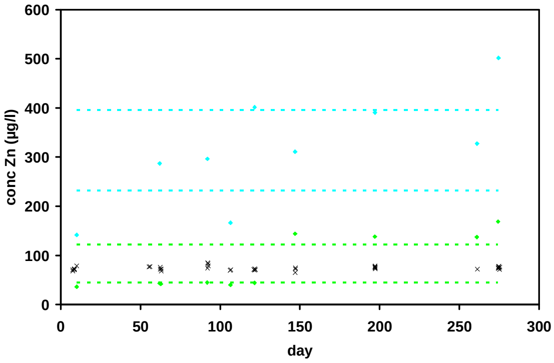

conc Sn (µg/l) sample
conc Sn (µg/l) NIST
0.3
0.25
0.2
0.15
0.1
0.05
0
8
7
6
5
4
3
2
1
0
0
50
100
150
200
250
300
day


conc Ti (µg/l)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
day


conc U (µg/l)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
50
100
150
200
250
300
day


conc V (µg/l) sample
conc V (µg/l) NIST
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
40
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
day


conc Zn (µg/l) sample
conc Zn (µg/l) NIST
2500
2000
1500
1000
500
0
90
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
day


conc Zn (µg/l)
600
500
400
300
200
100
0
0
50
100
150
200
250
300
day

Mission of the JRC

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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