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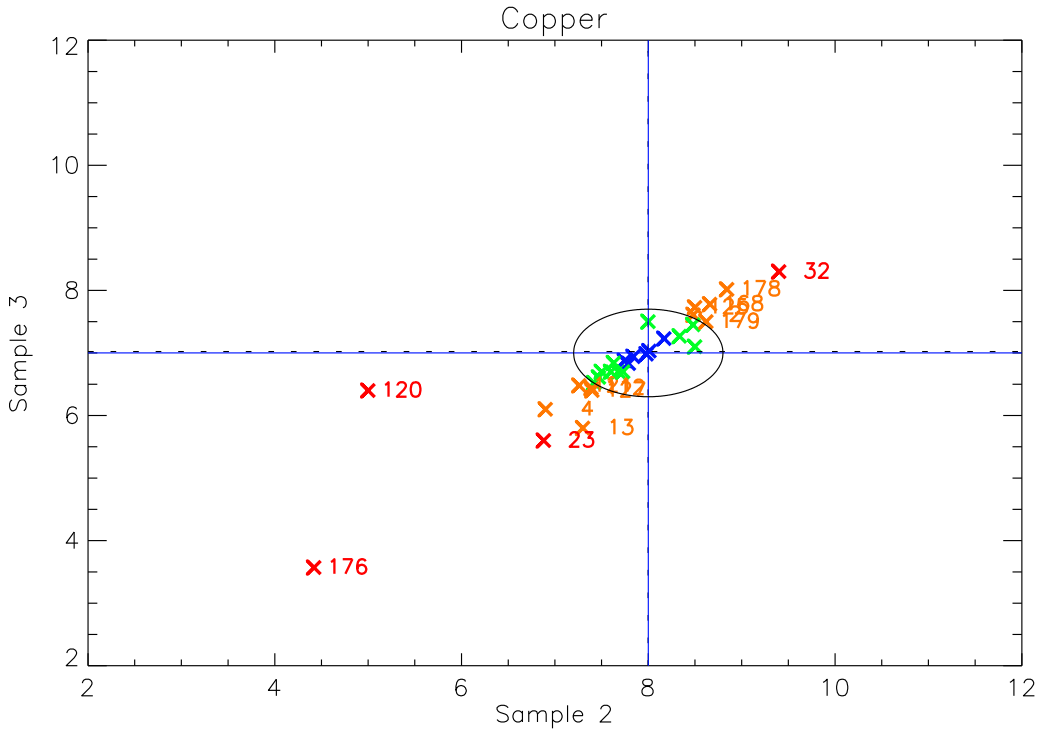
EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

Analytical intercomparison of heavy metals in precipitation, 2009 and 2010

Hilde Thelle Uggerud and Anne-Gunn Hjellbrekke



Youden plot of copper, 2010

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1. Analytical intercomparison of heavy metals in precipitation, 2009 and 2010

1.1 Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. 20 countries are reporting data to the heavy metal database. Since EMEP's measurement programme is based on individual national networks, different sampling and analytical methods are applied by the participating laboratories. In order to ensure data comparability, interlaboratory tests are organized by the Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research. So far 13 intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 2000; Uggerud and Skjelmoen, 2001, 2002, 2003; Uggerud and Hjellbrekke, 2005, 2007, 2008, 2009).

The present report presents results from the twelfth and thirteenth analytical intercomparison of heavy metals in precipitation, which was carried out in 2009 and 2010, respectively. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

1.2 Organization of the intercomparison

1.2.1 Organization of the twelfth intercomparison

The samples for the twelfth intercomparison were prepared and distributed to 50 laboratories in July 2009.

A total of 43 laboratories, 19 from the EMEP network, reported results within the end of December 2009. In accordance with the decision of the Steering Body of EMEP, the results are presented in such a way that the different laboratories are identified. All tables and figures are given in Appendix 1. Tables 2a and 2b give the names of the participating laboratories together with the number used when presenting the results in tables and figures.

Information received on the analytical methods used is given in Table 3.

1.2.2 Organization of the thirteenth intercomparison

The samples for the thirteenth intercomparison were prepared and distributed to 55 laboratories in July 2010.

A total of 37 laboratories, 17 from the EMEP network, reported results within the end of November 2010. In accordance with the decision of the Steering Body of EMEP, the results are presented in such a way that the different laboratories are identified. All tables and figures are given in Appendix 2. Tables 12a and 12b give the names of the participating laboratories together with the number used when presenting the results in tables and figures.

Information received on the analytical methods used is given in Table 13.

1.3 Intercomparison samples

The four synthetic precipitation samples distributed were made from multi-element standards traceable to NIST-standards. The multi-element standards were conserved with 2.5% HNO_3. The distributed synthetic precipitation samples contained Pb, Cd, Cu, Zn, As, Cr, and Ni in 0.5% HNO_3. Sample H1 and H2 contained concentrations similar to what is normally found in Southern Scandinavia. Sample H3 and H4 contained the elements in concentrations normally found in Central Europe.

All equipments in contact with the samples were soaked in 3% HNO_3 for 4 days. Preparation of the intercomparison samples was carried out in a clean room area.

1.4 Data handling

The data reported for the twelfth intercomparison from the participants are presented in Tables 5-11and Figures 1-7. An overview of all results is presented in Table 4.

The data reported for the thirteenth intercomparison from the participants are presented in Tables 15-21 and Figures 8-14. An overview of all results is presented in Table 14.

1.4.1 Data analysis

The reported values are presented in the tables in decreasing order together with the number of the laboratory. The expected (theoretical) value, the number of results, the arithmetic mean value, the median, the standard deviation and the relative standard deviation in percent are also given. After the first statistical run with all results included, the calculation was repeated with the outliers excluded. The outliers (unused) are defined as the results more than two standard deviations from the mean value in the first run.

In EMEP2010, all reported results for Ni in sample H1 showed a systematic error of 30%. This is highly unusual and most probably the theoretical value is wrong. Thus, the expected value for Ni in sample H1 is in all calculations replaced with the median value of the reported values.

1.4.2 Youden plot

Youden plot is a graphical technique, which allows for analysing interlaboratory data, where two samples of equal or similar concentrations have been analysed. The Youden plot visualises systematic errors as well as random errors.

The precipitation samples are made in pairs with similar concentrations and the reported value for one sample is plotted on the x-axis and the reported value of the other sample is plotted on the y-axis. Thus, each point in the plot is representing a pair of results from a single laboratory. Two fully drawn lines represent the expected values of the two samples. Two dotted lines represent the arithmetic mean values in the second statistical run. The lines divide the plot in four

quadrants. A 45º-reference line may be drawn through the intercept of the lines representing the expected values.

If the errors are due to random factors, the points will be evenly distributed around the mean value and be situated in all four quadrants of the chart.
If the errors are due to systematic factors, the results will be close to the 45º-reference line, but situated in the upper right or lower left quadrant.

Ellipses with radii corresponding to the data quality objectives within EMEP are drawn in each plot (see table 1). The data points are colour coded as given in Table 1. Drawn arrows indicate points outside the plot area.

Table 1: Youden-plot parameters.

Radii = DQO	**Concentration**
25% accuracy or better	Pb, Ni, Cr, As <1 μg/l, Cd <0.5 μg/l, Zn< 10 μg/l, Cu <2 μg/l
15% accuracy or better	Pb, Ni, Cr, As >1 μg/l, Cd >0.5 μg/l, Zn >10 μg/l, Cu >2 μg/l
Criteria	Colour
Within 0.5*DQO	Blue
Within DQO	Green
Within 2*DQO	Orange
> 2*DQO	Red

The length of the perpendicular from an individual point and to the reference line gives a measure of the random error. The perpendicular intercepts the 45º-reference line at a distance from the origin of the fully drawn lines. This distance is a measure of the systematic error.

Youden plots are presented in Figures 1-7 and Figures 8-14 for EMEP2009 and EMEP2010, respectively.

1.5 Summary

The data quality objectives (DQO) in EMEP, states that the accuracy in the laboratory should be better than 15% and 25% for high and low concentration samples, respectively. More than 94% of the results reported in 2009 lies within DQO. In 2010, 90% of the reported results were acceptable.

As in earlier intercomparisons, outliers are defined as values that deviates more than two standard deviations from the mean value. Outliers occur for all samples and all parameters in both intercomparisons. Out of a total of 972 single results reported to EMEP2009, 47 are defined as outliers. This is about 5% of the reported data, which is comparable to earlier intercomparisons. Out of a total of 930 single results reported to emep2010, 38 are defined as outliers. This is about 4% of the reported data, which is slightly better than earlier intercomparisons.

2. References

Berg, T., Aas, W. (2000) Analytical intercomparison of heavy metals in precipitation 1999. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 8/2000).

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Appendix 1

Tables and figures, 2009

Table 2a: Participating laboratories in the EMEP network, 2009. The numbers in front are used in tables.

No	Laboratory identification
1	Federal Environmental Agency, Austria
2	Flemish Environment Agency, Belgium
3	Czech Hydrometeorological Institute, Czech Republic
4	National Environmental Research Institute. Air Pollution Laboratory, Denmark
5	Finnish Meteorological Institute, Finland
6	SGS Multilab, France
8	Umweltbundesamt, Germany
10	Hungarian Meteorological Service, Hungary
13	C.N.R. Istituto Inquinamento Atmosferico, Italy
14	RIVM Laboratory of Inorganic Analytical Chemistry, The Netherlands
15	The Norwegian Institute for Air Research, Norway
16	Inst. Of Meteorology and Water Management, Poland
23	AEA Technology, National Environmental Techn. Centre, United Kingdom
31	Slovak Hydrometeorological Institute, Slovakia
33	Environmental Pollution Observ. Centre, Latvia
36	Hydrometeorological Institute of Slovenia, Slovenia
38	Estonian Environmental Research Centre, Estonia
39	Environmental Monitoring Laboratory, Institute of Environmental Protection, Poland
45	Environmental Impact Monitoring Center, Yerevan, Armenia

Table 2b: Participating laboratories outside the EMEP network, 2009. The number in front of the names is used in tables and figures.

No	Laboratory identification
108	Institut f. Bondenkunde und Standortlehre der TU Dresden, Germany
109	Institut f. Bondenkunde und Waldernährung der Universität, Germany
110	Thüringer Landesanstalt für Landwirtschaft (TTL), Germany
112	Niedersächsische Forstliche Versuchsanstalt (NVF), Germany
113	Fachhochschule Eberswalde, Germany
114	C.N.R. Istituto Italiano di Idrobiologia, Italy
115	Bayerishe Landesanstalt f. Wald- und Forstwirtschaft, Germany
118	Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany
120	Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA), Germany
121	Landesamt für Natur und Umwelt, Germany
125	Bayerisches Landesamt für Umweltschutz, Germany
127	Dept. Of Chemistry, Environmental Health Division, Malaysia
129	Ecole Nationale d'ingenieurs de Sfax, Tunisia
132	Comision Chilena De Energia Nuclear, Chile
141	Pollutants Chemical Analysis Centre, Marine Division, Japan
146	Cellule de Research en Environment et Biotechnologies Public Research Center-Gabriel Lippman, Luxembourg
159	CARSO, France
160	Coillte, Wicklow, Ireland
161	National Institute of Chemistry, Slovenia
168	Universite de Bretagne Occidentale, France
169	Lancaster Environment Centre, Centre for Ecology &Hydrology, UK
171	Ecole de Mines de Douai, Departement Chimie et Environment, France
174	Background Monitoring Department, Institute of Global Climate and Ecology(IGCE), Russian Federation
179	Murmansk Environmental Monitoring Center, Russian Federation

Table 3: Analytical techniques used at the participating laboratories for the different elements, 2009.

Lab no	Network	As	Cd	Cr	Cu	Pb	Ni	Zn
1	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
2	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
3	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
4	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	
5	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
6	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
8	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
10	EMEP		GF-AAS			GF-AAS		
13	EMEP		AS voltammetry		AS voltammetry	AS voltammetry		
14	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
15	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
16	EMEP	As methods	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
23	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
31	EMEP	HG-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
33	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
36	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
38	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
39	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
45	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
108	EMEP			ICP-AES	ICP-AES		ICP-AES	ICP-AES
109	EMEP		ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
110	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
112	ICP-Forest		ICP-AES	ICP-MS	ICP-AES	ICP-AES	ICP-AES	ICP-AES
113	Other	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
114	ICP-Forest	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
115	ICP-Forest	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
118	EMEP	ICP-AES	GF-AAS	ICP-AES	ICP-AES	GF-AAS	ICP-AES	ICP-AES
120	EMEP							ICP-AES
121	EMEP	Hydrid-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS ICP-OES (H3, H4)	GF-AAS	ICP-AES
125	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
127	EANET	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
129	EMEP		GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
132	EMEP		ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
141	WMO-GAW		GF-AAS					
146	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
159	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
160	EMEP	As methods	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
161	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
168	Other	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
169	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
171	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
174	WMO-GAW		GAAS (H1 & H2 done with pre-concentrating by evaporation)					
179	WMO-GAW	GAAS	GAAS	GAAS	GF-AAS	GF-AAS	GAAS	F-AAS

Table 4: Reported results for metal determination in precipitation samples, expressed as % deviation from expected value, 2009.

Lab no.	Arsenic				Cadmium				Chromium				Copper				Lead				Nickel				Zinc			
	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4
1	-3	-5	-7	-7	-7	-1	-4	-4	-5	-8	-5	-5	5	-3	-4	-5	0	1	0	1	6	4	-5	-7	7	2	0	1
2	1	1	4	-2	-4	0	3	-1	1	-3	8	7	-22	-10	8	5	-10	-7	-3	-5	-1	5	4	3	9	5	8	6
3	-4	-8	-4	-3	-6	-10	-4	-1	10	7	4	7	-5	-3	0	1	-5	-7	0	1	-11	-13	-2	-1	4	1	3	4
4	< 1.5	< 1.5	-2	-1	< 0.35	< 0.35	-13	-17	< 1.35	< 1.35	-8	-10	< 2.5	< 2.5	-3	-16	< 3.0	< 3.0	-4	-5	< 3.0	< 3.0	-9	-8				
5	-10	-13	-8	-8	-4	-7	-4	-4	-4	-10	-1	-2	4	2	2	3	2	3	1	2	-7	-8	1	1	6	0	-2	-3
6	4	4	4	2	<0.1	<0.1	-1	-3	-21	-27	-8	-9	-14	-9	-7	-8	-25	-28	3	3	-19	-16	-8	-8	23	19	10	10
8	-3	-4	-3	-5	4	2	-3	-3	-1	-3	-2	-3	-1	-5	-3	-5	-3	-4	-6	-7	-3	-4	-3	-4	3	0	-1	-3
10					-16	-33	-1	-2									35	5	-14	-19								
13					-14	17	-6	18					75	57	-15	6	20	10	-4	1					18	15	0	-2
14	-14	1	-9	-4	-1	13	-4	-4	1	2	-1	-1	-1	-7	-8	-9	-6	7	0	0	-15	1	-4	-3	70	5	-2	-1
15	-9	-10	0	2	0	-2	-6	0	-18	-17	-7	-3	-19	-24	1	-1	-7	0	0	0	-19	-15	-2	-7	1	-4	-5	-4
16					0	0	0	0	0	0	0	0	0	0	0	-6	0	0	0	0	-14	-13	0	0	8	-6	-3	-2
23	-57	20	-8	-1	329	< 0.08	-14	0	25	67	-33	-6	150	43	-9	-9	33	-10	-8	-5	186	-38	-4	-11	233	-13	-7	0
31	-3	-4	-6	-4	1	-2	-4	-7	15	12	3	3	-1	12	-1	-2	-1	2	0	-3	20	9	2	2	17	13	-1	0
33	-1	4	0	0	0	0	0	-2	1	-2	2	3	0	0	2	3	0	-10	0	0	14	0	1	1	33	0	3	3
36	-1	-8	0	0	-10	0	0	-2	1	-5	-4	-6	4	-5	-5	-5	2	-3	-6	-7	-11	-14	-4	-4	15	6	0	0
38	-4	-2	-3	-3	-14	867	-9	-5	6	7	5	6	7	7	6	6	-13	-8	-10	-6	-6	-4	-1	-1	-12	-11	-14	-10
39			0	0	0	0	0	0	0	0	0	0	-6	-14	-6	0	0	30	-8	-7			0	0	0	0	0	0
45	-21	-33	8	18	-66	-72	-9	2	-25	-32	4	10	-58	-28	0	10	-25	-24	-13	-8	-38	-30	2	10	11	15	20	26
108									< 1.35	< 1.35	-18	-7	575	300	55	56					< 2.35	< 2.35	-1	8	32	18	-1	1
109					< 0.1	< 0.1	-29	-67	-38	13	-6	-10	179	161	20	17	< 1.0	< 1.0	-13	-15	< 0.1	< 0.1	-15	-15	< 20	< 20	-4	-4
110	-23	-10	-18	-19	-14	0	-21	13	-35	-47	-26	-22	793	116	-8	-6	10	91	-11	11	-10	-15	-29	-8	29	7	10	9
112					10	12	1	2	4	3	3	2	-1	-4	-5	-6	-5	-1	-2	-3	-9	-5	2	1	5	2	0	-1
113	< 4	< 4	-4	15	< 0.4	< 0.4	11	13	199	306	49	44	< 4	< 4	-34	-20	< 7	< 7	-9	-4	< 1.5	< 1.5	-34	-30	< 5	-31	-9	-8
114			-17	-14	43	67	-14	-17	-13	-17	-15	-14	-13	-21	-15	-14	-13	-10	-18	-17	-14	-25	-17	-15	2	-11	-15	-16
115	27	47	9	5	4	-3	2	3	-6	-18	-9	-6	5	-2	-2	-2	3	2	2	2	-3	-4	-90	-4	12	7	5	6
118	71	200	3	-7	-71	-100	-4	-7	-25	-50	-8	-7	-13	-14	-6	-7	-60	-100	-1	1	29	38	1	-1	-33	-35	-3	-6
120																									3	-4	-3	-2
121	4	12	-5	-9	29	0	3	5	23	2	10	13	-25	-23	-9	-13	-3	5	2	1	-29	-25	-2	-5	2	5	4	4
125	10	9	8	10	3	3	3	5	7	5	-2	-2	6	1	-1	-1	3	6	-1	0	-2	-3	-2	1	15	8	9	9
127	0	0	3	1	< 0.2	< 0.2	14	0	0	0	2	-1	0	0	4	2	0	0	6	3	< 2	< 2	4	2	8	6	6	4
129					< 4	< 4	< 4	< 4	4250	5033	350	279	350	900	78	-33	433	< 41	-74	21	< 88	< 88	< 88	< 88	145	1450	16	-77
132					< 5	< 5	< 5	< 5	11	41	-1	1	< 1	< 1	-26	-27	< 5	< 5	5	9	< 5	< 5	7	-11	-13	-12	-3	-3
141					-11	-25	-15	-17																				
146	-18	-8	4	12	14	2	3	3	6	8	-3	0	5	-5	-5	-6	2	2	-2	0	10	6	1	3	5	-13	9	8
159	< 1	< 1	5	3	< 1	< 1	< 1	< 1	< 1	< 1	-28	-29	< 1	< 1	-26	-27	< 1	< 1	-8	-10	< 1	< 1	-24	-28	< 1	< 1	-46	-41
160															-4	-11	-14			3	5			-10	-10	39	31	15	45
161	-1	2	1	6	0	0	0	3	2	3	2	4	4	1	-1	-1	3	3	-2	2	-6	-6	-4	-4	7	4	-2	-2
168	-11	-10	-7	-10	-14	-17	0	0	-24	-20	-12	-10	-16	-23	-18	-17	-1	5	-6	-9	31	9	-7	-3	-3	-8	-3	-5
169	-11	-11	-5	-8	-9	-13	-8	-10	-6	-5	-6	-9	-5	-8	-8	-10	-7	-8	-8	-10	-9	-10	-8	-11	6	1	-3	-5
171	1	0	-4	-4	-1	-6	-3	-2	-2	-6	-5	-3	1	-3	-4	-4	-6	-7	-7	-7	-3	-5	-3	-3	8	5	-2	-2
174					34	12	-27	-22					69	-11	-20	-31	-70	-71	-54	-65								
179	10	-10	-6	-9	0	-17	-19	-17	-8	-12	-11	-12	-3	-24	-6	-4	10	15	-3	5	-14	-6	-25	-26	42	22	1	0

between ± 25–50%
more than ± 50%
for low theoretical values ((Pb, Ni, Cr, As <1 µg/l, Cd <0.5 µg/l, Cu <2 µg/l

between ±15–30%
more than ± 30%
for high theoretical values ((Pb, Ni, Cr, As >1 µg/l, Cd >0.5 µg/l, Cu >2 µg/l

Table 5: Analytical results for Cr in synthetic precipitation samples, 2009.

Chromium
Sample no.: H1
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 1.820
Median: 0.800
Standard deviation 5.835
Rel. st. deviation (%) 320.644

Run 2:
Number of laboratories: 33
Arithmetic mean value: 0.820
Median: 0.800
Standard deviation 0.305
Rel. st. deviation (%) 37.194

Results in decreasing order:

129	34.800 (*)	39	0.800
4	< 2.0		
108	1.35		
159	< 1		
113	2.391	127	0.800
23	1.000	8	0.790
121	0.980	171	0.783
31	0.920	5	0.771
132	0.887	1	0.760
3	0.877	115	0.755
125	0.857	169	0.754
38	0.850	179	0.740
146	0.845	114	0.700
112	0.833	15	0.660
161	0.820	6	0.630
14	0.811	168	0.610
33	0.810	45	0.603
36	0.810	118	0.600
2	0.807	110	0.520
16	0.800	109	0.500

Chromium
Sample no.: H2
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 1.523
Median: 0.595
Standard deviation 5.184
Rel. st. deviation (%) 340.493

Run 2:
Number of laboratories: 33
Arithmetic mean value: 0.635
Median: 0.590
Standard deviation 0.347
Rel. st. deviation (%) 54.578

Results in decreasing order:

129	30.800 (*)	33	0.590
4	< 2.0		
108	< 1.34		
159	< 1		
113	2.433	2	0.584
23	1.000	8	0.580
132	0.845	36	0.570
109	0.680	169	0.569
31	0.670	171	0.562
146	0.648	1	0.554
3	0.642	5	0.541
38	0.640	179	0.530
125	0.630	15	0.500
112	0.620	114	0.500
161	0.620	115	0.494
14	0.610	168	0.480
121	0.610	6	0.440
16	0.600	45	0.407
39	0.600	110	0.320
127	0.600	118	0.300

Chromium
Sample no.: H3
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 6.319
Median: 5.852
Standard deviation 3.532
Rel. st. deviation (%) 55.903

Run 2:
Number of laboratories: 37
Arithmetic mean value: 5.760
Median: 5.844
Standard deviation 0.789
Rel. st. deviation (%) 13.690

Results in decreasing order:

129	27.000 (*)	146	5.844
113	8.911	36	5.790
121	6.570	171	5.727
2	6.450	1	5.710
38	6.300	109	5.650
45	6.239	169	5.630
3	6.226	15	5.580
31	6.180	6	5.530
112	6.170	4	5.500
33	6.100	118	5.500
127	6.100	115	5.450
161	6.100	179	5.350
16	6.000	168	5.300
39	6.000	114	5.100
14	5.960	108	4.900
5	5.957	110	4.430
132	5.924	159	4.300
8	5.870	23	4.000
125	5.860		

Chromium
Sample no.: H4
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 7.364
Median: 6.838
Standard deviation 3.283
Rel. st. deviation (%) 44.581

Run 2:
Number of laboratories: 37
Arithmetic mean value: 6.847
Median: 6.791
Standard deviation 0.794
Rel. st. deviation (%) 11.595

Results in decreasing order:

129	26.500 (*)	171	6.791
113	10.106	8	6.790
121	7.940	15	6.790
45	7.727	1	6.670
3	7.496	36	6.610
2	7.461	115	6.610
38	7.400	23	6.600
161	7.300		
33	7.200	108	6.500
31	7.180	118	6.500
112	7.130	6	6.400
132	7.053	169	6.390
146	7.002	109	6.330
16	7.000	4	6.300
39	7.000	168	6.280
14	6.960	179	6.160
127	6.900	114	6.000
125	6.890	110	5.480
5	6.885	159	5.000

Table 6: Analytical results for Ni in synthetic precipitation samples, 2009.

Nickel
Sample no.: H1
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 0.714
Median: 0.655
Standard deviation 0.274
Rel. st. deviation (%) 38.371

Run 2:
Number of laboratories: 27
Arithmetic mean value: 0.666
Median: 0.651
Standard deviation 0.109
Rel. st. deviation (%) 16.393

Results in decreasing order:

129 <	88			
132 <	5			
4 <	3.0			
108 <	2.35			
127 <	2			
23	2.000 (*)	5	0.651	
113 <	1.5			
159 <	1.0			
168	0.920	112	0.640	
118	0.900	169	0.639	
31	0.840	110	0.630	
33	0.800	3	0.624	
146	0.773	36	0.620	
1	0.740	16	0.600	
2	0.696	114	0.600	
125	0.683	179	0.600	
115	0.682	14	0.595	
8	0.680	6	0.570	
171	0.678	15	0.570	
38	0.660	121	0.500	
161	0.660	45	0.436	

Nickel
Sample no.: H2
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 0.747
Median: 0.755
Standard deviation 0.114
Rel. st. deviation (%) 15.290

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.743
Median: 0.755
Standard deviation 0.081
Rel. st. deviation (%) 10.971

Results in decreasing order:

129 <	88			
132 <	5			
4 <	3.0			
108 <	2.35			
127 <	2			
113 <	1.5			
118	1.100 (*)	161	0.750	
159 <	1.0			
31	0.870	179	0.750	
168	0.870	5	0.735	
146	0.850	169	0.724	
2	0.840	3	0.700	
1	0.834	16	0.700	
14	0.804	36	0.690	
33	0.800	15	0.680	
125	0.775	110	0.680	
8	0.770	6	0.670	
38	0.770	114	0.600	
115	0.767	121	0.600	
171	0.762	45	0.562	
112	0.760	23	0.500 (*)	

Nickel
Sample no.: H3
Theoretical value: 9.000
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 8.310
Median: 8.769
Standard deviation 1.498
Rel. st. deviation (%) 18.031

Run 2:
Number of laboratories: 37
Arithmetic mean value: 8.511
Median: 8.783
Standard deviation 0.851
Rel. st. deviation (%) 9.998

Results in decreasing order:

129 <	88			
132	9.592	171	8.755	
127	9.400	8	8.730	
2	9.339	36	8.630	
45	9.220	14	8.600	
112	9.210	23	8.600	
31	9.140	161	8.600	
33	9.100	1	8.590	
118	9.100	168	8.330	
5	9.094	6	8.290	
146	9.093	169	8.250	
16	9.000	4	8.200	
39	9.000	160	8.120	
38	8.900	109	7.650	
108	8.900	114	7.500	
		159	6.800	
15	8.810	179	6.760	
121	8.800	110	6.410	
125	8.800	113	5.926	
3	8.783	115	0.860 (*)	

Nickel
Sample no.: H4
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 7.579
Median: 7.680
Standard deviation 0.695
Rel. st. deviation (%) 9.163

Run 2:
Number of laboratories: 35
Arithmetic mean value: 7.734
Median: 7.798
Standard deviation 0.460
Rel. st. deviation (%) 5.949

Results in decreasing order:

129 <	88			
45	8.773	36	7.660	
108	8.600	8	7.650	
146	8.248	115	7.650	
2	8.203	121	7.600	
127	8.200			
31	8.150	1	7.460	
112	8.120	15	7.460	
33	8.100	4	7.400	
125	8.070	6	7.380	
5	8.067	110	7.370	
16	8.000	160	7.220	
39	8.000	169	7.160	
3	7.917	132	7.141	
38	7.900	23	7.100	
118	7.900	114	6.800	
14	7.800	109	6.780	
168	7.800	179	5.960 (*)	
171	7.798	159	5.800 (*)	
161	7.700	113	5.572 (*)	

Table 7: Analytical results for Cu in synthetic precipitation samples, 2009.

Copper
Sample no.: H1
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 1.378
Median: 0.800
Standard deviation 1.538
Rel. st. deviation (%) 111.616

Run 2:
Number of laboratories: 33
Arithmetic mean value: 0.960
Median: 0.800
Standard deviation 0.600
Rel. st. deviation (%) 62.504

Results in decreasing order:

112	< 4		
3	< 2.5		
132	< 1		
159	< 1		
110	7.140 (*)	33	0.800
108	5.400 (*)	127	0.800
		8	0.790
129	3.600	14	0.790
109	2.230	31	0.790
23	2.000	112	0.790
13	1.400	179	0.780
174	1.350	169	0.762
38	0.860	3	0.759
125	0.848	39	0.750
115	0.843	114	0.700
1	0.839	118	0.700
146	0.839	6	0.690
36	0.830	168	0.670
161	0.830	15	0.650
5	0.829	2	0.621
171	0.806	121	0.600
16	0.800	45	0.335

Copper
Sample no.: H2
Theoretical value: 1.400
Unit: µg/l

Run 1:
Number of laboratories: 37
Arithmetic mean value: 2.024
Median: 1.353
Standard deviation 2.293
Rel. st. deviation (%) 113.287

Run 2:
Number of laboratories: 36
Arithmetic mean value: 1.691
Median: 1.351
Standard deviation 1.093
Rel. st. deviation (%) 64.637

Results in decreasing order:

112	< 4		
		3	< 2.5
132	< 1		
159	< 1		
129	14.000 (*)	112	1.350
108	5.600	160	1.340
		8	1.330
109	3.650	36	1.330
110	3.020	146	1.327
13	2.200	14	1.300
23	2.000	169	1.290
31	1.570	6	1.270
38	1.500	2	1.264
5	1.434	174	1.240
161	1.420	39	1.200
125	1.410	118	1.200
16	1.400	114	1.100
33	1.400	121	1.080
127	1.400	168	1.080
115	1.370	179	1.070
1	1.360	15	1.060
3	1.354	45	1.009
171	1.353		

Copper
Sample no.: H3
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 41
Arithmetic mean value: 7.930
Median: 7.650
Standard deviation 1.651
Rel. st. deviation (%) 20.826

Run 2:
Number of laboratories: 38
Arithmetic mean value: 7.529
Median: 7.577
Standard deviation 0.801
Rel. st. deviation (%) 10.634

Results in decreasing order:

129	14.200 (*)	36	7.580
108	12.400 (*)	146	7.574
		112	7.570
109	9.600	39	7.500
2	8.670	118	7.500
38	8.500	179	7.500
127	8.300	6	7.410
33	8.200	14	7.400
5	8.197	110	7.400
15	8.050	169	7.350
16	8.000	23	7.300
45	7.986	121	7.300
3	7.983	160	7.100
125	7.960	13	6.800
31	7.900	114	6.800
161	7.900	168	6.530
115	7.850	174	6.400
4	7.800	159	5.900
8	7.800	132	5.887
171	7.675	113	5.298
1	7.650		

Copper
Sample no.: H4
Theoretical value: 9.000
Unit: µg/l

Run 1:
Number of laboratories: 41
Arithmetic mean value: 8.680
Median: 8.520
Standard deviation 1.548
Rel. st. deviation (%) 17.834

Run 2:
Number of laboratories: 39
Arithmetic mean value: 8.407
Median: 8.510
Standard deviation 0.978
Rel. st. deviation (%) 11.635

Results in decreasing order:

108	14.000 (*)	36	8.510
		16	8.500
109	10.550	146	8.453
45	9.894	110	8.440
13	9.500	112	8.440
38	9.500	118	8.400
2	9.440	6	8.300
33	9.300	14	8.210
5	9.258	23	8.200
127	9.200	169	8.090
3	9.097	121	7.800
39	9.000	160	7.760
15	8.940	114	7.700
125	8.930	4	7.600
161	8.900	168	7.450
115	8.810	113	7.211
31	8.790	159	6.600
171	8.634	132	6.553
179	8.620	174	6.200
8	8.590	129	6.000
1	8.520		

Table 8: Analytical results for Zn in synthetic precipitation samples, 2009.

Zinc
Sample no.: H1
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 37
Arithmetic mean value: 7.280
Median: 6.500
Standard deviation 2.733
Rel. st. deviation (%) 37.537

Run 2:
Number of laboratories: 35
Arithmetic mean value: 6.704
Median: 6.459
Standard deviation 1.087
Rel. st. deviation (%) 16.217

Results in decreasing order:

109 < 20			
23	20.000 (*)	171	6.459
129	14.710 (*)	1	6.440
14	10.200	161	6.400
179	8.530	169	6.380
160	8.360	5	6.368
33	8.000	112	6.320
108	7.900	146	6.274
		3	6.241
110	7.730	8	6.200
6	7.380	120	6.200
13	7.100	114	6.100
31	7.000	121	6.100
36	6.880	15	6.030
125	6.880	39	6.000
115	6.740	168	5.800
45	6.639	38	5.300
2	6.543	132	5.240
16	6.500	118	4.000
127	6.500	159 <	1

Zinc
Sample no.: H2
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 38
Arithmetic mean value: 11.188
Median: 8.235
Standard deviation 18.824
Rel. st. deviation (%) 168.252

Run 2:
Number of laboratories: 37
Arithmetic mean value: 8.139
Median: 8.170
Standard deviation 1.056
Rel. st. deviation (%) 12.974

Results in decreasing order:

129	124.000 (*)	112	8.170
109 < 20			
160	10.440	1	8.130
179	9.790	169	8.060
6	9.530	3	8.049
108	9.400	8	8.000
		33	8.000
45	9.208	39	8.000
13	9.200	5	7.991
31	9.000	120	7.700
125	8.600	15	7.660
115	8.590	16	7.500
110	8.550	168	7.400
127	8.500	38	7.100
36	8.460	114	7.100
2	8.418	132	7.045
121	8.400	23	7.000
14	8.390	146	6.941
171	8.369	113	5.552
161	8.300	118	5.200
		159 <	1

Zinc
Sample no.: H3
Theoretical value: 100.000
Unit: µg/l

Run 1:
Number of laboratories: 40
Arithmetic mean value: 99.746
Median: 99.500
Standard deviation 10.324
Rel. st. deviation (%) 10.350

Run 2:
Number of laboratories: 39
Arithmetic mean value: 100.919
Median: 99.500
Standard deviation 7.273
Rel. st. deviation (%) 7.207

Results in decreasing order:

45	119.958			
129	116.000	8	99.000	
160	114.600	31	99.000	
110	110.000	161	98.400	
6	109.500	171	97.975	
146	109.300	5	97.864	
125	109.000	14	97.800	
2	108.140	118	97.500	
127	106.000	120	97.500	
115	105.300	132	97.120	
121	104.000	16	97.000	
33	103.000	168	97.000	
3	102.900	169	97.000	
179	100.800	109	95.780	
1	100.000	15	94.800	
13	100.000	23	93.000	
39	100.000	113	91.202	
36	99.600	38	86.200	
112	99.600	114	85.000	
108	99.500	159	54.000	(*)

Zinc
Sample no.: H4
Theoretical value: 110.000
Unit: µg/l

Run 1:
Number of laboratories: 40
Arithmetic mean value: 108.328
Median: 109.500
Standard deviation 18.697
Rel. st. deviation (%) 17.260

Run 2:
Number of laboratories: 37
Arithmetic mean value: 110.385
Median: 110.000
Standard deviation 7.581
Rel. st. deviation (%) 6.868

Results in decreasing order:

160	159.000 (*)	14	109.000	
45	138.292	112	108.900	
6	121.100	13	108.000	
110	120.000	16	108.000	
125	120.000	161	107.900	
146	118.400	171	107.636	
2	116.758	120	107.600	
115	116.700	132	107.150	
121	114.000	5	107.136	
127	114.000	8	107.000	
3	113.950	15	106.000	
33	113.000	109	105.580	
108	111.500	168	104.000	
		169	104.000	
1	111.000	118	103.900	
179	110.450	113	101.077	
23	110.000	38	98.700	
31	110.000	114	92.000	
36	110.000	159	65.000	(*)
39	110.000	129	24.880	(*)

Table 9: Analytical results for As in synthetic precipitation samples, 2009.

Arsenic
Sample no.: H1
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 26
Arithmetic mean value: 0.682
Median: 0.680
Standard deviation 0.148
Rel. st. deviation (%) 21.661

Run 2:
Number of laboratories: 24
Arithmetic mean value: 0.677
Median: 0.680
Standard deviation 0.076
Rel. st. deviation (%) 11.158

Results in decreasing order:

113	< 4.000			
4	< 1.500			
118	1.200 (*)	8	0.680	
159	< 1.000			
115	0.892	31	0.680	
179	0.770	3	0.671	
125	0.769	38	0.670	
6	0.730	15	0.640	
121	0.730	5	0.633	
2	0.705	169	0.626	
171	0.705	168	0.620	
127	0.700	14	0.602	
33	0.690	146	0.572	
36	0.690	45	0.555	
161	0.690	110	0.540	
1	0.680	23	0.300	(*)

Arsenic
Sample no.: H2
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 26
Arithmetic mean value: 0.532
Median: 0.485
Standard deviation 0.209
Rel. st. deviation (%) 39.386

Run 2:
Number of laboratories: 25
Arithmetic mean value: 0.493
Median: 0.480
Standard deviation 0.071
Rel. st. deviation (%) 14.385

Results in decreasing order:

113	< 4.000			
4	< 1.500			
118	1.500 (*)	8	0.480	
159	< 1.000			
115	0.735	31	0.480	
23	0.600	1	0.476	
121	0.560	146	0.461	
125	0.544	36	0.460	
6	0.520	3	0.458	
33	0.520	15	0.450	
161	0.510	110	0.450	
14	0.506	168	0.450	
2	0.504	179	0.450	
127	0.500	169	0.446	
171	0.500	5	0.434	
38	0.490	45	0.337	

Arsenic
Sample no.: H3
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 5.869
Median: 5.840
Standard deviation 0.393
Rel. st. deviation (%) 6.698

Run 2:
Number of laboratories: 29
Arithmetic mean value: 5.932
Median: 5.900
Standard deviation 0.318
Rel. st. deviation (%) 5.357

Results in decreasing order:

115	6.530	38	5.800	
125	6.500	113	5.758	
45	6.481	171	5.748	
159	6.300	3	5.740	
6	6.250	121	5.690	
2	6.240	169	5.690	
146	6.224	179	5.650	
118	6.200	31	5.630	
127	6.200	1	5.590	
161	6.040	168	5.560	
15	6.000	5	5.513	
33	6.000	23	5.500	
39	6.000	14	5.460	
36	5.990	114	5.000	(*)
4	5.900	110	4.900	(*)
8	5.840			

Arsenic
Sample no.: H4
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 6.901
Median: 6.895
Standard deviation 0.561
Rel. st. deviation (%) 8.133

Run 2:
Number of laboratories: 28
Arithmetic mean value: 6.855
Median: 6.857
Standard deviation 0.419
Rel. st. deviation (%) 6.111

Results in decreasing order:

45	8.279 (*)	3	6.820	
113	8.025 (*)	38	6.800	
146	7.808	31	6.750	
125	7.700	14	6.710	
161	7.400	171	6.691	
115	7.320	8	6.680	
159	7.200	118	6.500	
6	7.170	1	6.490	
15	7.150	169	6.470	
127	7.100	5	6.469	
33	7.000	121	6.380	
39	7.000	179	6.360	
36	6.990	168	6.290	
4	6.900	114	6.000	
23	6.900	110	5.680	(*)
2	6.895			

Table10: Analytical results for Cd in synthetic precipitation samples, 2009.

Cadmium
Sample no.: H1
Theoretical value: 0.070
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 0.075
Median: 0.070
Standard deviation 0.045
Rel. st. deviation (%) 59.525

Run 2:
Number of laboratories: 30
Arithmetic mean value: 0.067
Median: 0.070
Standard deviation 0.016
Rel. st. deviation (%) 23.335

Results in decreasing order:

132	< 5			
129	< 4			
159	< 1			
113	< 0.4			
4	< 0.35			
127	< 0.2			
23	0.300	(*)		
1	< 0.1			
6	< 0.1			
109	< 0.1	179	0.070	
114	0.100	14	0.069	
174	0.094	2	0.067	
121	0.090	5	0.067	
146	0.080	3	0.066	
112	0.077	169	0.064	
8	0.073	36	0.063	
115	0.073	141	0.062	
125	0.072	13	0.060	
31	0.071	38	0.060	
15	0.070	110	0.060	
16	0.070	168	0.060	
33	0.070	10	0.059	
39	0.070	45	0.024	
161	0.070	118	0.020	
171	0.070			

Cadmium
Sample no.: H2
Theoretical value: 0.060
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 0.056
Median: 0.059
Standard deviation 0.017
Rel. st. deviation (%) 29.705

Run 2:
Number of laboratories: 27
Arithmetic mean value: 0.058
Median: 0.060
Standard deviation 0.007
Rel. st. deviation (%) 12.304

Results in decreasing order:

132	< 5			
129	< 4			
159	< 1			
23	< 0.8			
113	< 0.4			
4	< 0.35			
127	< 0.2			
114	0.100	(*)		
1	< 0.1			
6	< 0.1			
109	< 0.1	15	0.059	
13	0.070	31	0.059	
14	0.068	38	0.058	
112	0.067	115	0.058	
174	0.067	171	0.057	
125	0.062	5	0.056	
8	0.061	3	0.054	
146	0.061	169	0.052	
2	0.060	168	0.050	
16	0.060	179	0.050	
33	0.060	36	0.045	
39	0.060	141	0.045	
110	0.060	10	0.040	
121	0.060	45	0.017	(*)
161	0.060	118	0.000	(*)

Cadmium
Sample no.: H3
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 37
Arithmetic mean value: 0.665
Median: 0.673
Standard deviation 0.064
Rel. st. deviation (%) 9.642

Run 2:

Number of laboratories: 34
Arithmetic mean value: 0.671
Median: 0.676
Standard deviation 0.048
Rel. st. deviation (%) 7.226

Results in decreasing order:

132	< 5			
129	< 4			
159	< 1			
127	0.800	(*)	1	0.672
113	0.774		31	0.670
125	0.723		118	0.670
2	0.721		5	0.669
121	0.720		14	0.669
146	0.719		13	0.660
115	0.713		15	0.660
112	0.710		169	0.643
16	0.700		38	0.640
33	0.700		45	0.636
36	0.700		4	0.610
39	0.700		23	0.600
161	0.700		114	0.600
168	0.700		141	0.594
6	0.690		179	0.570
10	0.690		110	0.550
171	0.681		174	0.510 (*)
8	0.679		109	0.500 (*)
3	0.673			

Cadmium
Sample no.: H4
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 37
Arithmetic mean value: 0.577
Median: 0.590
Standard deviation 0.081
Rel. st. deviation (%) 13.998

Run 2:

Number of laboratories: 36
Arithmetic mean value: 0.587
Median: 0.591
Standard deviation 0.050
Rel. st. deviation (%) 8.574

Results in decreasing order:

132	< 5			
129	< 4			
159	< 1			
13	0.710		36	0.590
110	0.680		171	0.588
113	0.675		10	0.587
125	0.631		8	0.581
121	0.630		6	0.580
161	0.620		5	0.579
146	0.619		14	0.579
115	0.618		1	0.576
112	0.613		38	0.570
45	0.612		31	0.560
15	0.600		118	0.560
16	0.600		169	0.541
23	0.600		141	0.501
39	0.600		4	0.500
127	0.600		114	0.500
168	0.600		179	0.500
3	0.594		174	0.470
2	0.593		109	0.200 (*)
33	0.590			

Table 11: Analytical results for Pb in synthetic precipitation samples, 2009.

Lead
Sample no.: H1
Theoretical value: 1.500
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 1.630
Median: 1.495
Standard deviation 1.164
Rel. st. deviation (%) 71.395

Run 2:
Number of laboratories: 33
Arithmetic mean value: 1.437
Median: 1.490
Standard deviation 0.301
Rel. st. deviation (%) 20.911

Results in decreasing order:

129	8.000 (*)	31	1.490	
113	< 7			
132	< 5			
10	2.027	168	1.480	
23	2.000	121	1.460	
13	1.800	8	1.450	
110	1.650	3	1.429	
179	1.650	112	1.420	
115	1.540	14	1.410	
125	1.540	171	1.403	
161	1.540	15	1.400	
146	1.534	169	1.390	
36	1.530	2	1.356	
5	1.524	38	1.300	
1	1.500	114	1.300	
16	1.500	6	1.130	
33	1.500	45	1.120	
39	1.500	4	< 1	
127	1.500	159	< 1	
		118	0.600	
		174	0.450	

Lead
Sample no.: H2
Theoretical value: 1.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 0.967
Median: 1.000
Standard deviation 0.287
Rel. st. deviation (%) 29.660

Run 2:
Number of laboratories: 30
Arithmetic mean value: 0.990
Median: 1.000
Standard deviation 0.107
Rel. st. deviation (%) 10.801

Results in decreasing order:

110	1.910 (*)	127	1.000	
113	< 7			
132	< 5			
39	1.300	112	0.990	
179	1.150	36	0.970	
13	1.100	8	0.960	
14	1.070	2	0.934	
125	1.060	171	0.934	
121	1.050	3	0.928	
168	1.050	169	0.923	
10	1.047	38	0.920	
161	1.030	23	0.900	
5	1.029	33	0.900	
31	1.020	114	0.900	
115	1.020	45	0.763	
146	1.018	6	0.720	
1	1.010	174	0.290	(*)
4	< 1	118	0.000	(*)
159	< 1			
15	1.000			
16	1.000			

Lead
Sample no.: H3
Theoretical value: 25.000
Unit: µg/l

Run 1:
Number of laboratories: 40
Arithmetic mean value: 23.290
Median: 24.301
Standard deviation 3.631
Rel. st. deviation (%) 15.591

Run 2:
Number of laboratories: 38
Arithmetic mean value: 24.042
Median: 24.385
Standard deviation 1.402
Rel. st. deviation (%) 5.833

Results in decreasing order:

127	26.400	2	24.232	
132	26.340	13	24.100	
160	25.730	4	24.000	
6	25.720	8	23.600	
115	25.600	36	23.400	
121	25.600	168	23.400	
5	25.279	171	23.260	
16	25.000	169	23.100	
33	25.000	23	23.000	
1	24.900	39	23.000	
14	24.900	159	23.000	
15	24.900	113	22.792	
3	24.890	38	22.500	
31	24.880	110	22.300	
118	24.800	45	21.808	
125	24.700	109	21.750	
146	24.620	10	21.380	
112	24.460	114	20.500	
161	24.400	174	11.400	(*)
179	24.370	129	6.600	(*)

Lead
Sample no.: H4
Theoretical value: 30.000
Unit: µg/l

Run 1:
Number of laboratories: 40
Arithmetic mean value: 28.942
Median: 29.930
Standard deviation 3.706
Rel. st. deviation (%) 12.807

Run 2:
Number of laboratories: 38
Arithmetic mean value: 29.228
Median: 29.930
Standard deviation 1.949
Rel. st. deviation (%) 6.670

Results in decreasing order:

129	36.400 (*)	146	29.860	
110	33.300	112	29.210	
132	32.640	31	29.160	
179	31.620	113	28.735	
160	31.540	23	28.500	
6	31.040	4	28.400	
127	30.900	2	28.380	
115	30.700	38	28.300	
161	30.700	8	28.000	
5	30.522	36	28.000	
121	30.400	39	28.000	
3	30.395	171	27.753	
118	30.300	45	27.570	
1	30.200	168	27.200	
13	30.200	169	27.100	
14	30.000	159	27.000	
15	30.000	109	25.650	
16	30.000	114	25.000	
33	30.000	10	24.400	
125	30.000	174	10.600	(*)

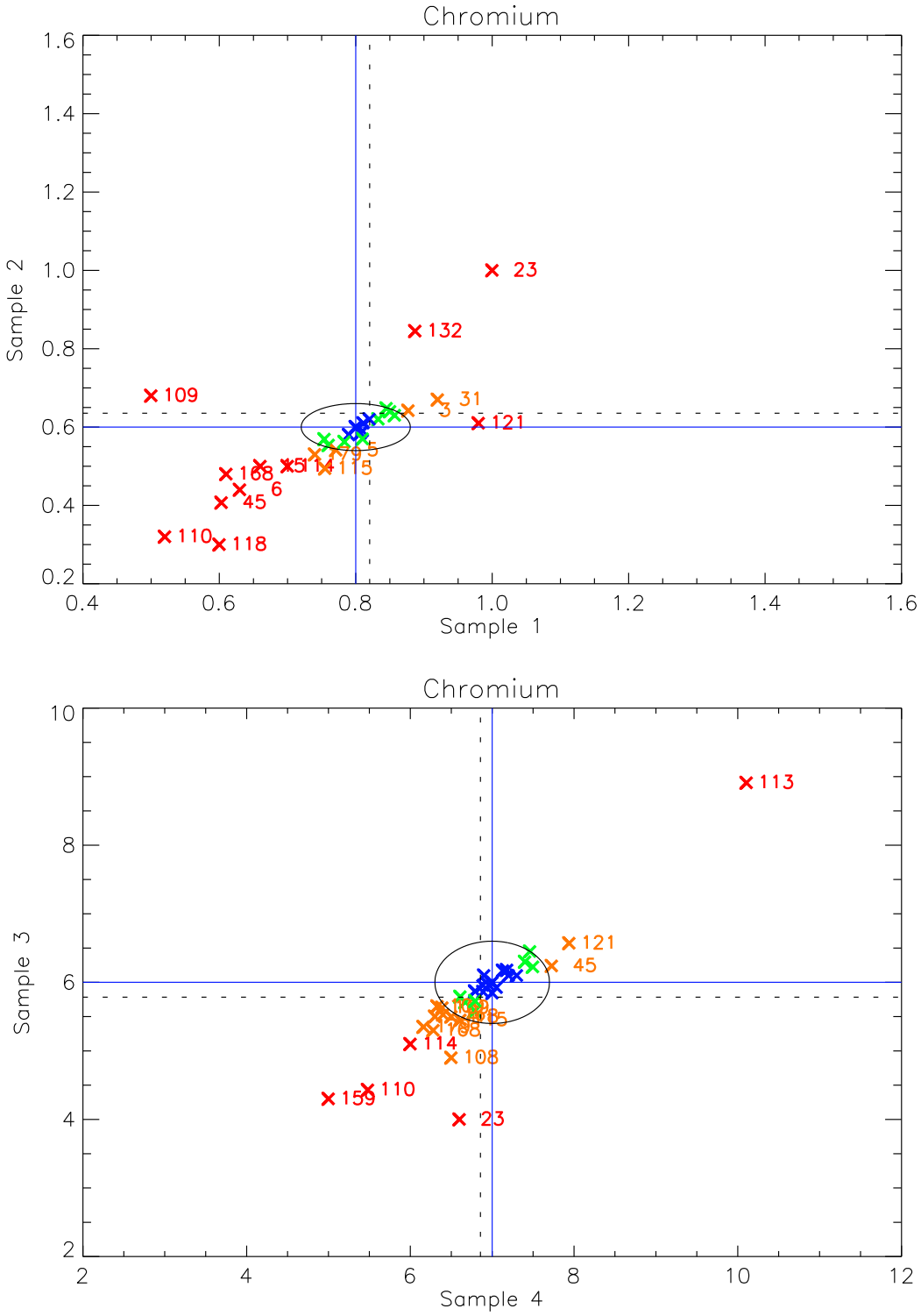

Figure 1: Youden plot of chromium, 2009.

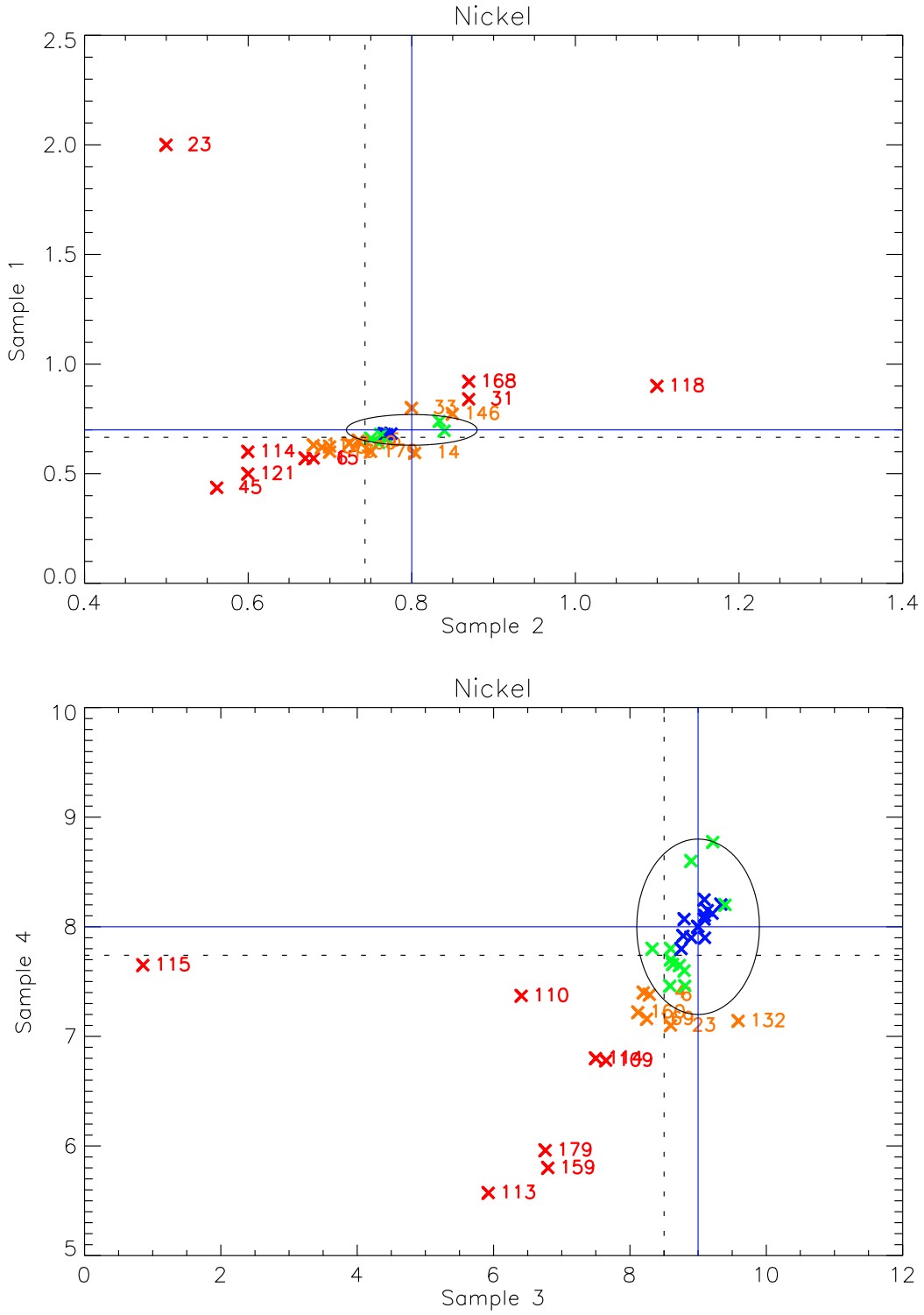

Figure.2: Youden plot of nickel, 2009.

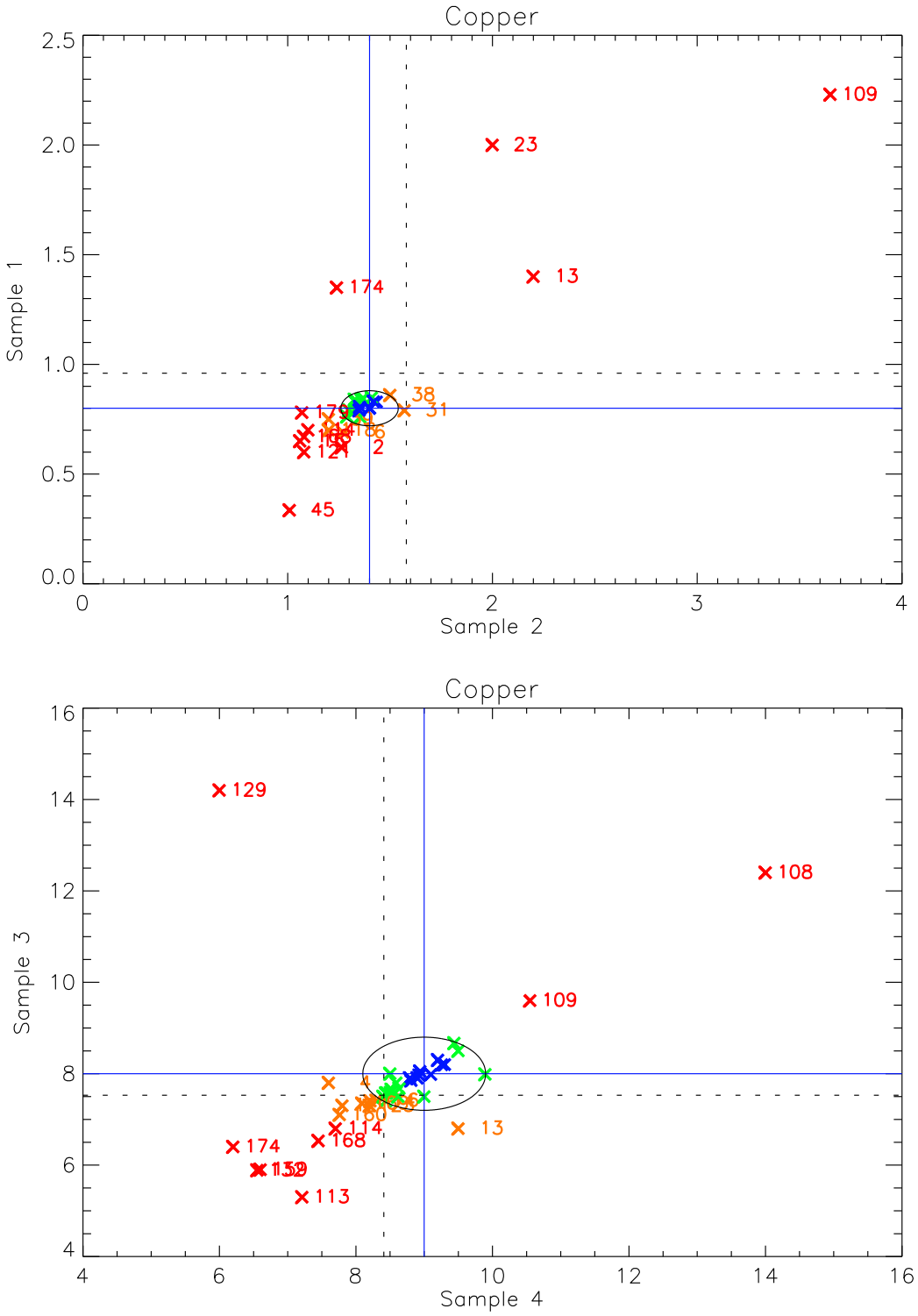

Figure.3: Youden plot of copper, 2009.

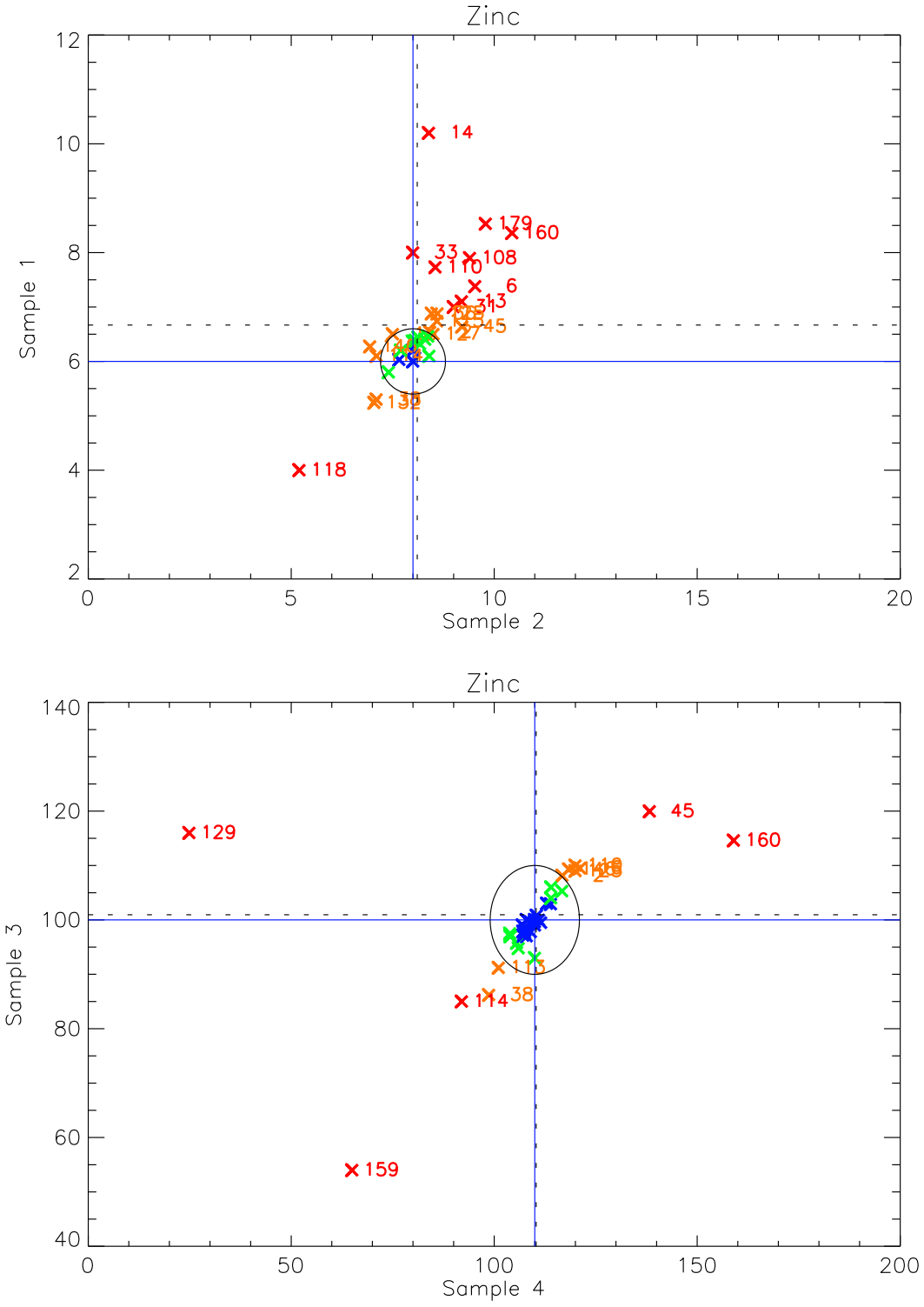

Figure.4: Youden plot of zinc, 2009.

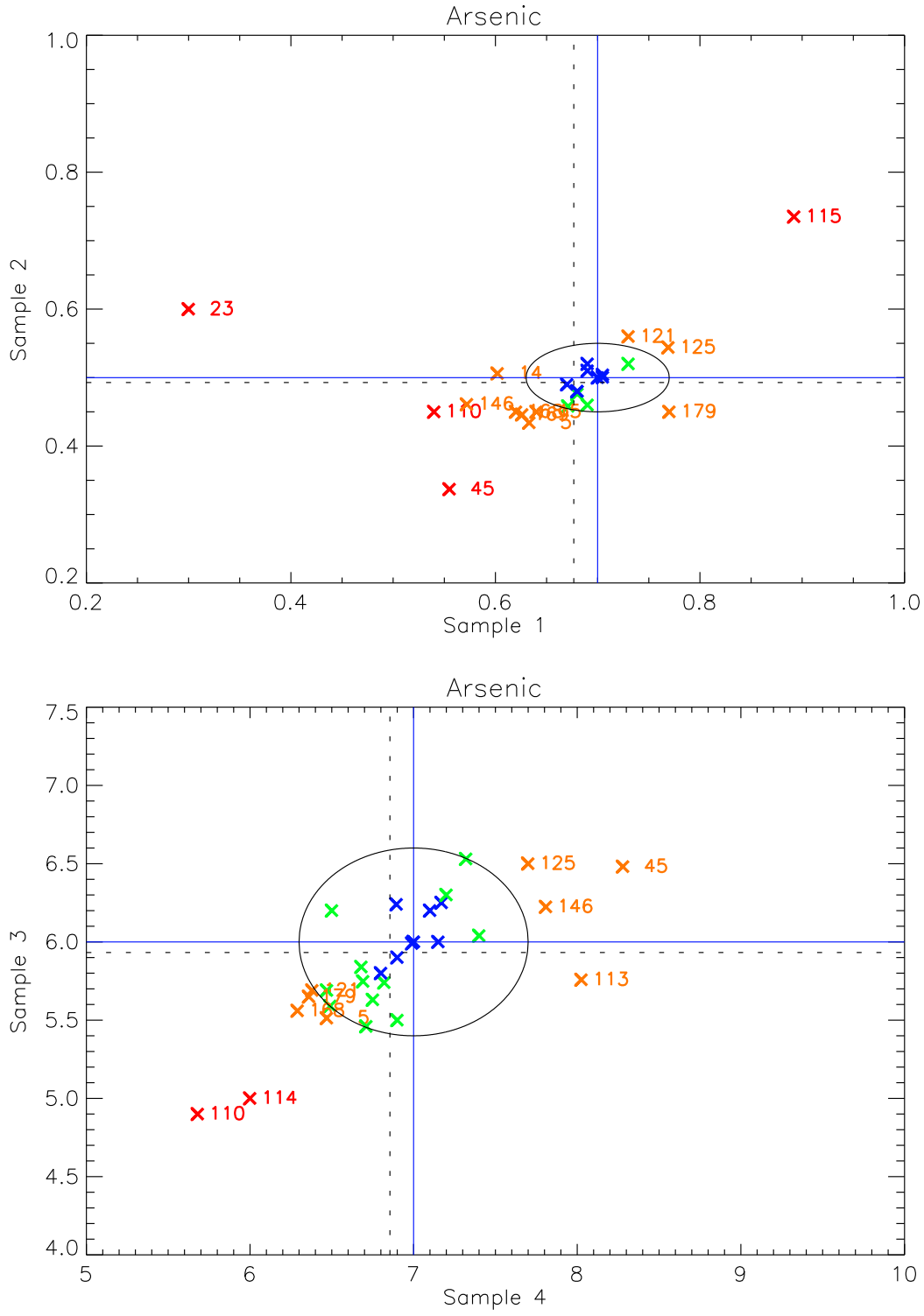

Figure.5: Youden plot of arsenic, 2009.

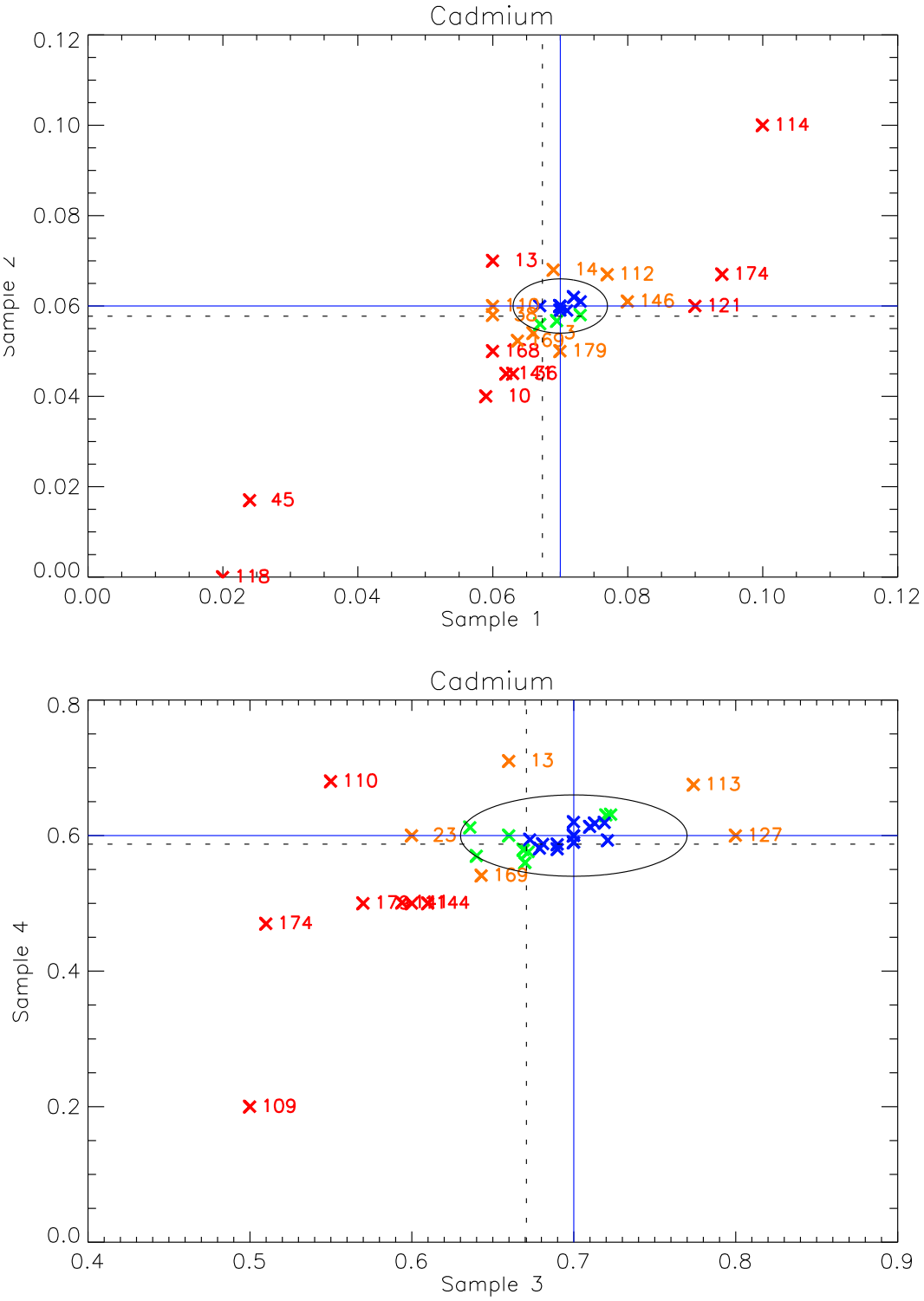

Figure 6: Youden plot of cadmium, 2009.

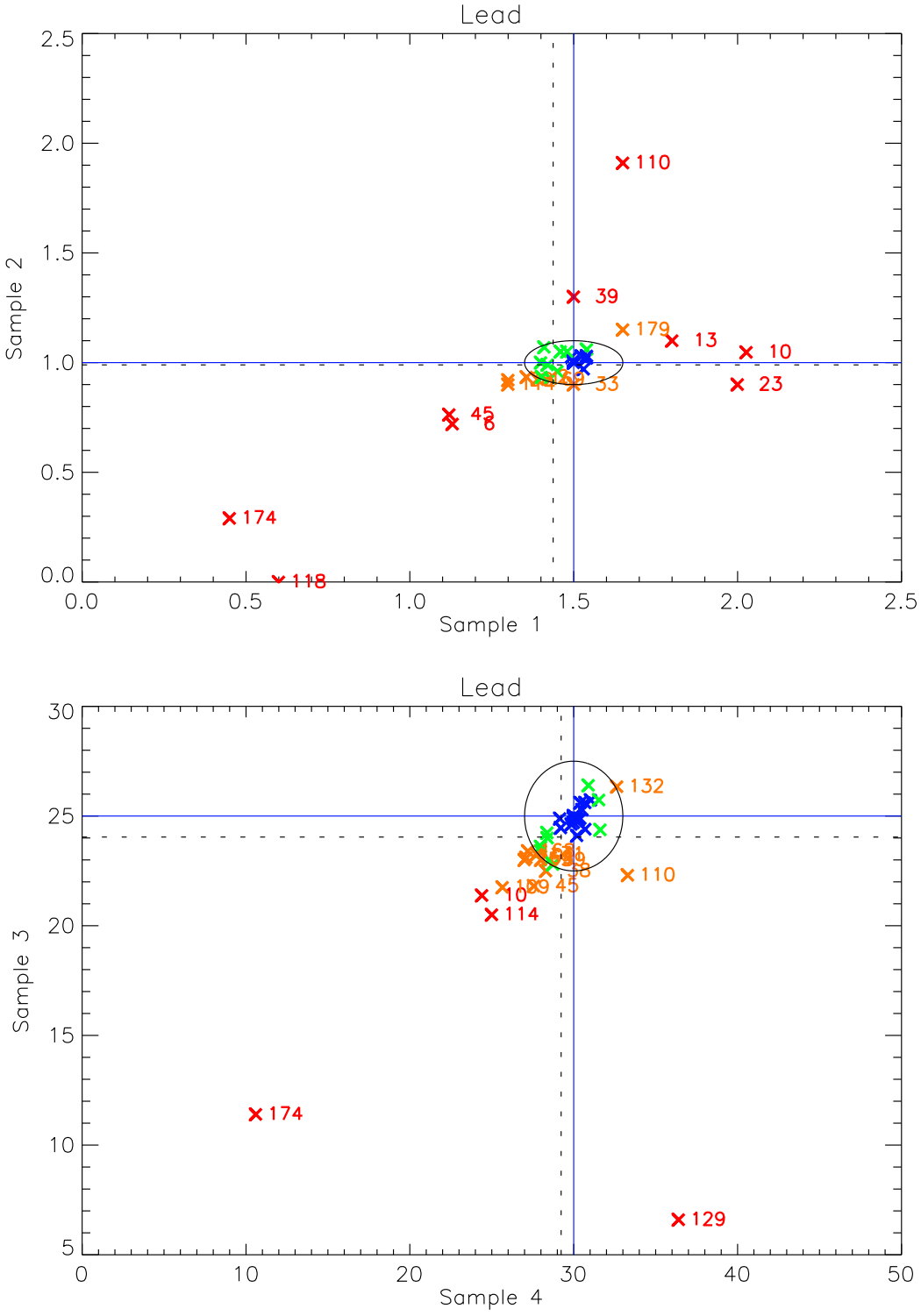

Figure 7: Youden plot of lead, 2009.

Appendix 2

Tables and figures, 2010

Table 12a: Participating laboratories in the EMEP network, 2010. The numbers in front are used in tables.

No	Laboratory identification
2	Flemish Environment Agency, Belgium
3	Czech Hydrometeorological Institute, Czech Republic
4	National Environmental Research Institute. Air Pollution Laboratory, Denmark
5	Finnish Meteorological Institute, Finland
8	Umweltbundesamt, Germany
10	Hungarian Meteorological Service, Hungary
13	C.N.R. Istituto Inquinamento Atmosferico, Italy
14	RIVM Laboratory of Inorganic Analytical Chemistry, The Netherlands
15	The Norwegian Institute for Air Research, Norway
16	Inst. Of Meteorology and Water Management, Poland
23	AEA Technology, National Environmental Techn. Centre, United Kingdom
24	Hydrometeorological Institute of Serbia, Serbia
31	Slovak Hydrometeorological Institute, Slovakia
32	Atmospheric Pollution Research Laboratory, Institute of Physics, Lithuania
33	Environmental Pollution Observ. Centre, Latvia
36	Hydrometeorological Institute of Slovenia, Slovenia
38	Estonian Environmental Research Centre, Estonia

Table 12b: Participating laboratories outside the EMEP network, 2010. The number in front of the names is used in tables and figures.

No	Laboratory identification
110	Thüringer Landesanstalt für Landwirtschaft (TTL), Germany
112	Niedersächsische Forstliche Versuchsanstalt (NVF), Germany
115	Bayerishe Landesanstalt f. Wald- und Forstwirtschaft, Germany
118	Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany
120	Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA), Germany
121	Landesamt für Natur und Umwelt, Germany
125	Bayerisches Landesamt für Umweltschutz, Germany
127	Dept. Of Chemistry, Environmental Health Division, Malaysia
129	Ecole Nationale d'ingenieurs de Sfax, Tunisia
132	Comision Chilena De Energia Nuclear, Chile
141	Pollutants Chemical Analysis Centre, Marine Division, Japan
159	CARSO, France
161	National Institute of Chemistry, Slovenia
168	Universite de Bretagne Occidentale, France
169	Lancaster Environment Centre, Centre for Ecology &Hydrology, UK
171	Ecole de Mines de Douai, Departement Chimie et Environment, France
174	Background Monitoring Department, Institute of Global Climate and Ecology(IGCE), Russian Federation
176	Main Geophysical Observatory, Russian Federation
178	Environmental Chemistry and EANET Monitoring Laboratory, Limnological Institute RAS/SB, Russian Federation
179	Murmansk Environmental Monitoring Center, Russian Federation

Table 13: Analytical techniques used at the participating laboratories for the different elements, 2010.

Lab no	Network	As	Cd	Cr	Cu	Pb	Ni	Zn
2	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
3	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
4	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
5	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
8	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
10	EMEP		GF-AAS			GF-AAS		
13	EMEP		GF-AAS		GF-AAS	GF-AAS		GF-AAS
14	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
15	EMEP	HR-ICP-MS	HR-ICP-MS	HR-ICP-MS	HR-ICP-MS	HR-ICP-MS	HR-ICP-MS	HR-ICP-MS
16	EMEP		GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS Higher conc F-AAS
23	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-AES
24	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
31	EMEP	HG-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS
32	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
33	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
36	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
38	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
110	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
112	ICP-Forest		ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
115	ICP-Forest	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
118	EMEP	ICP-AES	GF-AAS	ICP-AES	ICP-AES	GF-AAS	ICP-AES	ICP-AES
120	ICP-Forest	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	ICP-AES
121	EMEP	Hydrid-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	Voltammetry
125	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
127	EANET	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
129	EMEP	AAS	AAS	AAS	AAS	AAS	AAS	AAS
132	EMEP		ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES	ICP-AES
141	WMO-GAW		GF-AAS					
159	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
161	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
168	Other	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
169	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
171	EMEP	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
174	Other		GF-AAS	Cr methods	GF-AAS	GF-AAS	GF-AAS	GF-AAS
176	EMEP		GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS
178	EANET	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS
179	EMEP	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	GF-AAS	F-AAS

Table 14: Reported results for metal determination in precipitation samples, expressed as % deviation from expected value, 2010.

	Arsenic				Cadmium				Chromium				Copper				Lead				Nickel				Zinc			
Lab no	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4	H1	H2	H3	H4
2	6	7	7	9	17	5	3	6	1	3	4	5	9	6	9	11	0	0	-1	-3	-4	1	3	-10	12	6	6	10
3	4	0	1	0	57	7	8	12	3	3	4	1	11	6	6	9	-5	-6	-6	-3	1	3	4	-1	1	5	5	3
4	< 1.5	-5	-4	< 1.5	< 0.35	-14	-20	< 0.35	< 2.0	3	4	< 2.0	< 2.5	-14	-13	< 2.5	< 3.0	-3	-1	< 3.0		2	2	< 3.0				
5	-10	-7	-7	-10	-8	-7	-8	-16	-9	-7	-7	-10	-8	-7	-7	-9	-7	-7	-7	-8	-3	-6	-6	-4	-6	-7	-6	-4
8	-5	-5	-5	-5	-2	-6	-5	-6	-2	-7	-7	-2	0	-4	-4	-5	-2	-8	-9	-3	-2	-6	-6	-3	14	-1	-2	2
10					-25	4	4	-34									-1	12	14	17								
13					17	-31	-14	20					6	-9	-17	-7	0	-7	-11	-36					58	8	-3	50
14	-4	-2	-1	-4	8	0	5	-20	0	2	0	-9	-1	-3	-2	-5	4	-1	-1	0	-5	-1	-4	-8	9	0	-1	5
15	-3	4	1	8	0	-2	-3	0	-1	0	1	1	-3	0	0	2	-3	-2	-1	10	1	-1	1	6	-4	-4	0	0
16					0	0	0	0	0	0	0	0	-11	0	7	0	8	0	0	0	11	0	0	7	0	0	0	14
23	4	-1	-3	17	13	-5	-8	29	7	9	0	65	< 2	-14	-20	<2	41	-1	-2	81		-3	-3	< 0.9	-24	5	5	-43
24	33	2	-2	50	100	-1	-4	380	0	-7	-10	0	3311	281	330	1040	154	-4	-8	256	157	16	6	286	514	22	24	437
31	-8	-4	-3	-10	0	-6	-6	0	3	-1	0	4	2	-2	-1	0	-7	-8	-8	-9	1	-2	-1	-3	20	0	-3	14
32	33	-3	-12	-25	-33	13	0	20	14	3	2	0	33	18	19	20	23	8	9	11	1	2	3	0	12	-2	-2	-4
33	33	12	14	100	-33	-3	-16	-20	29	17	22	120	33	6	1	20	-42	4	9	-56	11	-2	-70	29	100	0	3	43
36	8	3	4	12	33	2	5	30	0	-2	0	2	-9	-5	-2	-6	-1	-5	-6	5	-7	-3	-1	0	6	3	0	19
38	16	-90	-1	23	3	-1	2	6	-9	-6	-4	< 0.5	< 1	2	3	2	0	-3	-1	4	3	-3	0	8	-7	3	2	-1
110	0	0	1	0	< 0.1	-6	-4	< 0.1	-14	-9	-10	-20	11	0	0	7	21	2	3	11	18	0	-1	19	23	1	1	0
112					0	2	2	0	-1	0	0	-8	-9	-8	-8	-9	2	-1	-1	-1	-32	0	1	-46	13	2	3	9
115	28	1	4	38	7	3	5	6	-11	-5	-4	-11	-29	-7	-6	-24	62	8	8	12	-1	-5	-4	-3	27	5	6	8
118		-8	-12		-33	-3	-2	-40	-29	-8	-10	-80	-11	-4	-1	-7	15	7	9	0	-9	-6	-5	-57	10	-4	-4	-11
120	-33	-13	-10	-75		0	0		-29	-7	-6	-40	-11	-38	-9	-13	54	-20	-17	122		0	40		22	0	0	9
121	7	-1	-1	5	0	11	4	-20	9	1	3	10	-20	-9	-7	-5	5	0	-2	3	9	-4	0	9	8	-1	4	2
125	7	9	13	13	2	3	7	6	-1	1	5	3	13	6	10	11	2	0	3	3	6	3	7	7	27	14	19	18
127	-17	-3	-4	0	< 0.2	-25	-20	< 0.2	0	-5	-4	0	-11	-8	-9	-13	-8	-6	-7	-11		-6	-5		-40	-6	-7	-20
129					2133	113	< 5	< 5	< 50	< 50	< 50	< 50	1256	113	86	407	-55	24	-19	-40	443	11	0	1343	< 8	-82	< 8	< 8
132					< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	0	9	< 10		< 10	10	< 10	< 10	-7	-7	< 10
141					-20	-8	-10	-24																				
159	30	5	6	55	< 0.1	< 0.1	-2	1480	-26	-8	-8	< 0.5	< 1	-5	-4	-13	-15	-4	-4	< 1		-12	-11	< 0.5	-10	10	11	-11
161	-8	0	-12	-18	0	-8	-10	0	-11	-4	-3	-14	-6	-3	-2	-5	41	-2	-3	-6	-14	-5	-4	-17	6	0	-1	3
168	-7	-1	-3	7	-8	3	6	2	-7	0	3	0	54	8	11	13	10	2	2	1	-12	-4	1	-10	6	-13	-7	1
169	-3	-2	-2	-2	-3	-2	-5	-3	-4	-4	-3	0	-2	-3	-4	-3	1	-2	-2	-1	-1	-4	-3	-1	11	4	5	9
171	7	4	4	5	13	9	10	6	-4	-3	-6	-10	6	4	4	6	6	-1	0	2	0	-1	-1	-1	31	15	15	30
174					25	-11	-4	36					-13	-6	-4	-33	38	8	4	67		10	-12			21	33	
176					-25	-36	-36	-32	-64	-68	-69	-70	219	-45	-49	295	-70	-79	-62	-51	619	927	84	2869	503	-21	-70	268
178	38	14	20	34	122	13	26	84	8	4	9	60	-12	11	15	-3	1	-4	-2	41	23	12	10	32	34	21	23	32
179	28	6	13	13	17	-38	14	0	6	3	7	6	-13	8	7	-29	27	26	6	28	-19	-34	-32	7	71	10	6	40

between ± 25–50%
more than ± 50%
for low theoretical values ((Pb, Ni, Cr, As <1 µg/l, Cd <0.5 µg/l, Cu <2 µg/l

between ±15–30%
more than ± 30%
for high theoretical values ((Pb, Ni, Cr, As >1 µg/l, Cd >0.5 µg/l, Cu >2 µg/l

Table 15: Analytical results for Cr in synthetic precipitation samples, 2010.

Chromium
Sample no.: H1
Theoretical value: 0.700
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 0.666
Median: 0.691
Standard deviation 0.114
Rel. st. deviation (%) 17.112

Run 2:
Number of laboratories: 28
Arithmetic mean value: 0.673
Median: 0.691
Standard deviation 0.074
Rel. st. deviation (%) 10.999

Results in decreasing order:

33	0.900	(*)	112	0.690
32	0.800		125	0.690
121	0.760		8	0.685
178	0.754		171	0.671
23	0.747		169	0.669
179	0.740		168	0.650
3	0.723		5	0.640
31	0.720		38	0.635
2	0.710		115	0.624
36	0.702		161	0.620
16	0.700		110	0.600
24	0.700		159	0.520
127	0.700		118	0.500
14	0.697		120	0.500
15	0.692		176	0.250 (*)
			129 <	50.000
			132 <	10.000
			4 <	2.000

Chromium
Sample no.: H2
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 5.805
Median: 5.960
Standard deviation 0.796
Rel. st. deviation (%) 13.718

Run 2:
Number of laboratories: 30
Arithmetic mean value: 5.935
Median: 5.980
Standard deviation 0.340
Rel. st. deviation (%) 5.725

Results in decreasing order:

33	7.000		36	5.890
23	6.530		171	5.804
178	6.216		169	5.790
2	6.201		161	5.750
4	6.200		127	5.700
32	6.200		115	5.680
3	6.190		38	5.640
179	6.160		8	5.600
14	6.148		24	5.600
125	6.060		120	5.600
121	6.040		5	5.570
112	6.020		118	5.500
168	6.020		159	5.500
15	6.015		110	5.460
16	6.000		176	1.910 (*)
31	5.960		129 <	50.000
			132 <	10.000

Chromium
Sample no.: H3
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 4.860
Median: 4.980
Standard deviation 0.694
Rel. st. deviation (%) 14.287

Run 2:
Number of laboratories: 30
Arithmetic mean value: 4.970
Median: 4.985
Standard deviation 0.333
Rel. st. deviation (%) 6.694

Results in decreasing order:

33	6.100		36	4.980
178	5.446		169	4.860
179	5.350		161	4.840
125	5.240		38	4.810
4	5.200		115	4.810
2	5.192		127	4.800
3	5.190		171	4.720
121	5.170		120	4.700
168	5.130		5	4.670
32	5.100		8	4.670
15	5.062		159	4.600
112	5.020		24	4.500
14	5.001		118	4.500
16	5.000		110	4.480
31	4.990		176	1.560 (*)
23	4.980		129 <	50.000
			132 <	10.000

Chromium
Sample no.: H4
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 0.501
Median: 0.500
Standard deviation 0.184
Rel. st. deviation (%) 36.683

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.493
Median: 0.500
Standard deviation 0.125
Rel. st. deviation (%) 25.329

Results in decreasing order:

33	1.100	(*)	32	0.500
23	0.827		127	0.500
178	0.801		168	0.500
121	0.550		8	0.492
179	0.530		112	0.460
2	0.523		14	0.456
31	0.520		5	0.450
125	0.516		171	0.450
36	0.512		115	0.445
3	0.506		161	0.430
15	0.504		110	0.400
169	0.501		120	0.300
16	0.500		176	0.150
24	0.500		118	0.100 (*)
			129 <	50.000
			132 <	10.000
			4 <	2.000
			38 <	0.500
			159 <	0.500

Table 16: Analytical results for Ni in synthetic precipitation samples, 2010.

Nickel
Sample no.: H1
Theoretical value: 0.791
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 1.244
Median: 0.800
Standard deviation 1.493
Rel. st. deviation (%) 120.033

Run 2:
Number of laboratories: 25
Arithmetic mean value: 0.846
Median: 0.791
Standard deviation 0.344
Rel. st. deviation (%) 40.644

Results in decreasing order:

176	7.120 (*)	171	0.791
129	5.320 (*)	169	0.785
24	2.400	115	0.782
178	1.022	8	0.773
110	0.970	5	0.760
16	0.900	2	0.752
33	0.900	14	0.744
121	0.880	36	0.723
125	0.850	118	0.700
38	0.819	168	0.670
15	0.805	161	0.650
3	0.804	179	0.600
31	0.800	112	0.460
32	0.800	132	< 10.000
		4	< 3.000
		127	< 2.000
		174	< 1.000
		23	< 0.900
		159	< 0.500

Nickel
Sample no.: H2
Theoretical value: 9.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 11.397
Median: 8.870
Standard deviation 14.567
Rel. st. deviation (%) 127.814

Run 2:
Number of laboratories: 32
Arithmetic mean value: 8.865
Median: 8.835
Standard deviation 0.748
Rel. st. deviation (%) 8.442

Results in decreasing order:

176	92.440 (*)	31	8.800
24	10.400	33	8.800
178	10.122	23	8.750
129	10.000	38	8.710
174	9.900	36	8.700
3	9.300	121	8.670
125	9.250	169	8.660
4	9.200	168	8.630
32	9.200	161	8.580
2	9.072	115	8.540
112	9.020	118	8.500
16	9.000	127	8.500
120	9.000	5	8.470
110	8.980	8	8.420
14	8.892	159	7.900
171	8.872	179	5.960
15	8.870	132	< 10

Nickel
Sample no.: 3
Theoretical value: 10.000
Unit: æg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 10.009
Median: 9.967
Standard deviation 2.158
Rel. st. deviation (%) 21.562

Run 2:
Number of laboratories: 32
Arithmetic mean value: 9.966
Median: 9.967
Standard deviation 1.051
Rel. st. deviation (%) 10.549

Results in decreasing order:

176	18.390 (*)	171	9.944
120	14.000	110	9.910
178	11.040	36	9.890
132	11.000	31	9.880
125	10.700	169	9.730
24	10.600	23	9.720
3	10.400	115	9.640
32	10.300	161	9.610
2	10.260	14	9.598
4	10.200	118	9.500
15	10.100	127	9.500
112	10.070	8	9.430
168	10.050	5	9.380
16	10.000	159	8.900
121	10.000	174	8.800
129	10.000	179	6.760
38	9.990	33	3.000 (*)

Nickel
Sample no.: 4
Theoretical value: 0.700
Unit: æg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 1.855
Median: 0.700
Standard deviation 4.206
Rel. st. deviation (%) 226.716

Run 2:
Number of laboratories: 26
Arithmetic mean value: 1.127
Median: 0.697
Standard deviation 1.876
Rel. st. deviation (%) 166.455

Results in decreasing order:

176	20.780 (*)	171	0.694
129	10.100	169	0.692
24	2.700	3	0.690
178	0.923	115	0.682
33	0.900	8	0.681
110	0.830	31	0.680
121	0.760	5	0.670
38	0.757	14	0.642
16	0.750	168	0.630
179	0.750	2	0.629
125	0.746	161	0.580
15	0.742	112	0.380
36	0.702	118	0.300
32	0.700	132	< 10.000
		4	< 3.000
		127	< 2.000
		174	< 1.000
		23	< 0.900
		159	< 0.500

Table 17: Analytical results for Cu in synthetic precipitation samples, 2010.

Copper
Sample no.: H1
Theoretical value: 0.900
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 2.338
Median: 0.885
Standard deviation 5.748
Rel. st. deviation (%) 245.829

Run 2:
Number of laboratories: 29
Arithmetic mean value: 1.360
Median: 0.878
Standard deviation 2.122
Rel. st. deviation (%) 156.005

Results in decreasing order:

24	30.700 (*)	169	0.878
129	12.200	15	0.871
176	2.870	161	0.850
168	1.390	5	0.830
32	1.200	112	0.820
33	1.200	36	0.815
125	1.020	16	0.800
3	1.000	118	0.800
110	1.000	120	0.800
2	0.983	127	0.800
171	0.955	178	0.789
13	0.950	174	0.780
31	0.920	179	0.780
8	0.900	121	0.720
14	0.892	115	0.636
		132 <	10.000
		4 <	2.500
		23 <	2.000
		38 <	1.000
		159 <	1.000

Copper
Sample no.: H2
Theoretical value: 8.000
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 8.651
Median: 7.768
Standard deviation 4.282
Rel. st. deviation (%) 49.496

Run 2:
Number of laboratories: 33
Arithmetic mean value: 7.989
Median: 7.747
Standard deviation 1.881
Rel. st. deviation (%) 23.543

Results in decreasing order:

24	30.500 (*)	14	7.747
129	17.000	169	7.730
32	9.400	118	7.700
178	8.842	8	7.680
168	8.660	36	7.630
179	8.620	159	7.600
33	8.500	174	7.500
125	8.500	115	7.470
2	8.483	5	7.420
3	8.480	127	7.400
171	8.335	112	7.390
38	8.170	13	7.300
15	8.010	121	7.260
16	8.000	4	6.900
110	7.980	23	6.880
31	7.840	120	5.000
161	7.790	176	4.420
		132 <	10.000

Copper
Sample no.: H3
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 7.697
Median: 6.888
Standard deviation 4.179
Rel. st. deviation (%) 54.291

Run 2:
Number of laboratories: 33
Arithmetic mean value: 7.018
Median: 6.875
Standard deviation 1.360
Rel. st. deviation (%) 19.376

Results in decreasing order:

24	30.100 (*)	14	6.875
129	13.000	36	6.840
32	8.300	161	6.830
178	8.017	8	6.700
168	7.780	159	6.700
125	7.730	169	6.700
2	7.611	174	6.700
16	7.500	115	6.610
179	7.500	5	6.520
3	7.450	121	6.480
171	7.268	112	6.440
38	7.230	120	6.400
33	7.100	127	6.400
15	7.031	4	6.100
110	6.980	13	5.800
31	6.940	23	5.600
118	6.900	176	3.570
		132 <	10.000

Copper
Sample no.: H4
Theoretical value: 1.500
Unit: µg/l

Run 1:
Number of laboratories: 32
Arithmetic mean value: 2.274
Median: 1.458
Standard deviation 3.017
Rel. st. deviation (%) 132.635

Run 2:
Number of laboratories: 31
Arithmetic mean value: 1.796
Median: 1.455
Standard deviation 1.356
Rel. st. deviation (%) 75.521

Results in decreasing order:

24	17.100 (*)	178	1.455
129	7.600	8	1.430
176	5.930	161	1.430
32	1.800	14	1.426
33	1.800	121	1.420
168	1.690	36	1.410
125	1.660	13	1.400
2	1.659	118	1.400
3	1.630	5	1.370
110	1.600	112	1.360
171	1.585	120	1.300
38	1.530	127	1.300
15	1.523	159	1.300
16	1.500	115	1.140
31	1.500	179	1.070
169	1.460	174	1.000
		132 <	10.000
		4 <	2.500
		23 <	2.000

Table 18: Analytical results for Zn in synthetic precipitation samples, 2010.

Zinc
Sample no.: H1
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 7.332
Median: 5.575
Standard deviation 6.299
Rel. st. deviation (%) 85.920

Run 2:
Number of laboratories: 29
Arithmetic mean value: 5.740
Median: 5.560
Standard deviation 1.351
Rel. st. deviation (%) 23.539

Results in decreasing order:

24	30.700 (*)	169	5.560
176	30.130 (*)	118	5.500
33	10.000	14	5.450
179	8.530	121	5.420
13	7.900	36	5.320
178	6.675	168	5.300
171	6.536	161	5.280
115	6.370	3	5.030
125	6.370	16	5.000
110	6.150	15	4.795
120	6.100	5	4.700
31	6.000	38	4.660
8	5.680	159	4.500
112	5.630	23	3.820
32	5.600	127	3.000
2	5.575	132	< 10.000
		129	< 8.000

Zinc
Sample no.: H2
Theoretical value: 100.000
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 100.219
Median: 100.550
Standard deviation 17.186
Rel. st. deviation (%) 17.149

Run 2:
Number of laboratories: 33
Arithmetic mean value: 102.717
Median: 101.000
Standard deviation 9.267
Rel. st. deviation (%) 9.022

Results in decreasing order:

24	122.300	14	100.100
174	121.000	16	100.000
178	120.690	31	100.000
171	115.400	33	100.000
125	114.000	120	99.800
179	110.450	161	99.710
159	110.000	8	98.900
13	108.000	121	98.700
2	106.400	32	98.000
3	105.000	15	96.350
23	105.000	118	95.600
115	104.900	127	93.800
169	104.000	5	93.400
36	103.000	132	92.700
38	103.000	168	87.500
112	101.800	176	79.150
110	101.000	129	17.800 (*)

Zinc
Sample no.: H3
Theoretical value: 95.000
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 96.735
Median: 96.200
Standard deviation 15.083
Rel. st. deviation (%) 15.592

Run 2:
Number of laboratories: 32
Arithmetic mean value: 98.855
Median: 96.600
Standard deviation 9.042
Rel. st. deviation (%) 9.147

Results in decreasing order:

174	126.000	120	95.400
24	117.700	36	95.200
178	117.260	16	95.000
125	113.000	15	94.630
171	109.210	161	94.440
159	105.000	14	94.130
179	100.800	8	93.300
2	100.700	32	93.000
115	100.700	13	92.000
3	100.000	31	92.000
169	99.900	118	91.600
23	99.700	5	89.200
121	99.200	168	88.800
33	98.000	127	88.300
112	97.900	132	88.100
38	97.000	176	28.900 (*)
110	96.200	129	< 8.000

Zinc
Sample no.: H4
Theoretical value: 7.000
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 9.103
Median: 7.580
Standard deviation 6.351
Rel. st. deviation (%) 69.769

Run 2:
Number of laboratories: 29
Arithmetic mean value: 7.545
Median: 7.383
Standard deviation 1.330
Rel. st. deviation (%) 17.633

Results in decreasing order:

24	37.600 (*)	14	7.383
176	25.780 (*)	3	7.200
13	10.500	161	7.190
33	10.000	121	7.150
179	9.790	8	7.120
178	9.229	168	7.100
171	9.066	15	7.022
36	8.350	110	7.000
125	8.270	38	6.940
16	8.000	5	6.700
31	8.000	32	6.700
2	7.668	118	6.200
112	7.630	159	6.200
169	7.610	127	5.600
120	7.600	23	4.020
115	7.580	132	< 10.000
		129	< 8.000

Table 19: Analytical results for As in synthetic precipitation samples, 2010.

Arsenic
Sample no.: H1
Theoretical value: 0.600
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 0.618
Median: 0.624
Standard deviation 0.163
Rel. st. deviation (%) 26.383

Run 2:
Number of laboratories: 26
Arithmetic mean value: 0.642
Median: 0.629
Standard deviation 0.109
Rel. st. deviation (%) 16.914

Results in decreasing order:

178	0.826	23	0.623	
24	0.800	110	0.600	
32	0.800	169	0.581	
33	0.800	15	0.580	
159	0.780	14	0.577	
179	0.770	8	0.568	
115	0.766	168	0.560	
38	0.697	31	0.550	
36	0.650	161	0.550	
171	0.641	5	0.541	
121	0.640	127	0.500	
125	0.640	120	0.400	
2	0.634	118	0.000	(*)
3	0.624	4	< 1.500	

Arsenic
Sample no.: H2
Theoretical value: 6.000
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 5.831
Median: 5.985
Standard deviation 1.092
Rel. st. deviation (%) 18.723

Run 2:
Number of laboratories: 27
Arithmetic mean value: 6.026
Median: 6.000
Standard deviation 0.366
Rel. st. deviation (%) 6.079

Results in decreasing order:

178	6.851	23	5.970	
33	6.700	121	5.970	
125	6.540	168	5.920	
2	6.397	14	5.904	
179	6.360	169	5.860	
159	6.300	32	5.800	
171	6.270	127	5.800	
15	6.219	31	5.770	
36	6.200	4	5.700	
24	6.100	8	5.690	
115	6.080	5	5.554	
3	6.020	118	5.500	
161	6.020	120	5.200	
110	6.000	38	0.571	(*)

Arsenic
Sample no.: H3
Theoretical value: 5.000
Unit: µg/l

Run 1:
Number of laboratories: 28
Arithmetic mean value: 5.009
Median: 4.930
Standard deviation 0.404
Rel. st. deviation (%) 8.063

Run 2:
Number of laboratories: 27
Arithmetic mean value: 4.972
Median: 4.930
Standard deviation 0.360
Rel. st. deviation (%) 7.237

Results in decreasing order:

178	6.010	(*) 121	4.930	
33	5.700	24	4.900	
125	5.650	169	4.900	
179	5.650	23	4.870	
2	5.355	31	4.840	
159	5.300	168	4.840	
171	5.216	4	4.800	
115	5.200	127	4.800	
36	5.190	8	4.760	
3	5.040	5	4.639	
110	5.040	120	4.500	
15	5.037	32	4.400	
14	4.971	118	4.400	
38	4.930	161	4.390	

Arsenic
Sample no.: H4
Theoretical value: 0.400
Unit: µg/l

Run 1:
Number of laboratories: 27
Arithmetic mean value: 0.421
Median: 0.422
Standard deviation 0.148
Rel. st. deviation (%) 35.194

Run 2:
Number of laboratories: 24
Arithmetic mean value: 0.436
Median: 0.426
Standard deviation 0.078
Rel. st. deviation (%) 17.968

Results in decreasing order:

33	0.800	(*) 121	0.420	
159	0.620	3	0.401	
24	0.600	110	0.400	
115	0.550	127	0.400	
178	0.534	169	0.392	
38	0.492	14	0.385	
23	0.469	8	0.381	
125	0.451	5	0.361	
179	0.450	31	0.360	
36	0.448	161	0.330	
2	0.435	32	0.300	
15	0.433	120	0.100	(*)
168	0.430	118	0.000	(*)
171	0.422	4	< 1.500	

Table 20: Analytical results for Cd in synthetic precipitation samples, 2010.

Cadmium
Sample no.: H1
Theoretical value: 0.060
Unit: µg/l

Run 1:
Number of laboratories: 31
Arithmetic mean value: 0.106
Median: 0.060
Standard deviation 0.230
Rel. st. deviation (%) 216.995

Run 2:
Number of laboratories: 30
Arithmetic mean value: 0.065
Median: 0.060
Standard deviation 0.021
Rel. st. deviation (%) 31.810

Results in decreasing order:

129	1.340 (*)	16	0.060
178	0.133	31	0.060
24	0.120	112	0.060
3	0.094	121	0.060
36	0.080	161	0.060
174	0.075	8	0.059
2	0.070	169	0.058
13	0.070	5	0.055
179	0.070	168	0.055
23	0.068	141	0.048
171	0.068	10	0.045
14	0.065	176	0.045
115	0.064	32	0.040
38	0.062	33	0.040
125	0.061	118	0.040
15	0.060	132	< 10.000
		4	< 0.350
		127	< 0.200
		110	< 0.100
		159	< 0.010

Cadmium
Sample no.: H2
Theoretical value: 0.800
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 0.795
Median: 0.790
Standard deviation 0.183
Rel. st. deviation (%) 22.997

Run 2:
Number of laboratories: 35
Arithmetic mean value: 0.769
Median: 0.790
Standard deviation 0.098
Rel. st. deviation (%) 12.749

Results in decreasing order:

129	1.700 (*)	159	0.790
178	0.904	169	0.788
32	0.900	15	0.786
121	0.890	33	0.780
171	0.874	118	0.780
3	0.857	23	0.757
2	0.843	8	0.756
10	0.830	31	0.750
125	0.828	110	0.750
168	0.828	5	0.745
115	0.821	141	0.740
36	0.820	161	0.740
112	0.820	174	0.710
16	0.800	4	0.690
120	0.800	127	0.600
14	0.797	13	0.550
38	0.791	176	0.510
24	0.790	179	0.500
		132	< 10.000

Cadmium
Sample no.: H3
Theoretical value: 0.500
Unit: µg/l

Run 1:
Number of laboratories: 35
Arithmetic mean value: 0.489
Median: 0.490
Standard deviation 0.055
Rel. st. deviation (%) 11.215

Run 2:
Number of laboratories: 33
Arithmetic mean value: 0.490
Median: 0.490
Standard deviation 0.041
Rel. st. deviation (%) 8.369

Results in decreasing order:

178	0.630 (*)	159	0.490	
179	0.570	15	0.486	
171	0.548	24	0.480	
3	0.538	110	0.480	
125	0.534	174	0.480	
168	0.529	169	0.476	
36	0.527	8	0.475	
14	0.526	31	0.470	
115	0.524	5	0.461	
121	0.520	23	0.459	
10	0.519	161	0.450	
2	0.515	141	0.448	
112	0.510	13	0.430	
38	0.509	33	0.420	
16	0.500	4	0.400	
32	0.500	127	0.400	
120	0.500	176	0.320	(*)
118	0.490	132	< 10.000	
		129	< 5.000	

Cadmium
Sample no.: H4
Theoretical value: 0.050
Unit: µg/l

Run 1:
Number of laboratories: 30
Arithmetic mean value: 0.057
Median: 0.050
Standard deviation 0.037
Rel. st. deviation (%) 64.065

Run 2:
Number of laboratories: 29
Arithmetic mean value: 0.051
Median: 0.050
Standard deviation 0.012
Rel. st. deviation (%) 24.250

Results in decreasing order:

24	0.240 (*)	16	0.050
178	0.092	31	0.050
174	0.068	112	0.050
23	0.065	161	0.050
36	0.065	179	0.050
13	0.060	169	0.048
32	0.060	8	0.047
3	0.056	5	0.042
2	0.053	14	0.040
38	0.053	33	0.040
115	0.053	121	0.040
125	0.053	141	0.038
171	0.053	176	0.034
168	0.051	10	0.033
15	0.050	118	0.030
		132	< 10.000
		129	< 5.000
		4	< 0.350
		127	< 0.200
		110	< 0.100
		159	< 0.010

Table 21: Analytical results for Pb in synthetic precipitation samples, 2010.

Lead
Sample no.: H1
Theoretical value: 1.300
Unit: µg/l

Run 1:
Number of laboratories: 34
Arithmetic mean value: 1.415
Median: 1.317
Standard deviation 0.479
Rel. st. deviation (%) 33.866

Run 2:
Number of laboratories: 32
Arithmetic mean value: 1.388
Median: 1.317
Standard deviation 0.308
Rel. st. deviation (%) 22.217

Results in decreasing order:

24	3.300 (*)	178	1.315	
115	2.100	169	1.310	
120	2.000	2	1.305	
23	1.830	13	1.300	
161	1.830	38	1.300	
174	1.800	10	1.293	
179	1.650	36	1.290	
32	1.600	8	1.280	
110	1.570	15	1.260	
118	1.500	3	1.230	
168	1.430	5	1.210	
16	1.400	31	1.210	
171	1.384	127	1.200	
121	1.370	159	1.100	
14	1.353	33	0.750	
112	1.330	129	0.588	
125	1.320	176	0.390	(*)
		132 <	10.000	
		4 <	3.000	

Lead
Sample no.: H2
Theoretical value: 25.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 24.493
Median: 24.705
Standard deviation 3.896
Rel. st. deviation (%) 15.905

Run 2:
Number of laboratories: 35
Arithmetic mean value: 25.039
Median: 24.730
Standard deviation 2.135
Rel. st. deviation (%) 8.528

Results in decreasing order:

179	31.620	112	24.680	
129	30.900	161	24.580	
10	27.970	15	24.570	
115	27.100	169	24.400	
32	27.000	38	24.300	
174	27.000	4	24.200	
118	26.700	24	24.000	
33	26.000	159	24.000	
110	25.500	178	23.927	
168	25.400	36	23.800	
2	25.110	3	23.500	
121	25.100	127	23.400	
16	25.000	13	23.300	
132	25.000	5	23.253	
125	24.900	31	23.000	
23	24.800	8	22.900	
171	24.739	120	20.000	
14	24.730	176	5.370	(*)

Lead
Sample no.: H3
Theoretical value: 23.000
Unit: µg/l

Run 1:
Number of laboratories: 36
Arithmetic mean value: 22.319
Median: 22.665
Standard deviation 2.868
Rel. st. deviation (%) 12.850

Run 2:
Number of laboratories: 35
Arithmetic mean value: 22.710
Median: 22.670
Standard deviation 1.678
Rel. st. deviation (%) 7.388

Results in decreasing order:

10	26.180	112	22.660	
132	25.100	169	22.600	
32	25.000	178	22.511	
33	25.000	23	22.500	
118	25.000	121	22.500	
115	24.900	161	22.280	
179	24.370	159	22.000	
174	24.000	3	21.700	
125	23.800	36	21.600	
110	23.700	127	21.400	
168	23.500	5	21.286	
16	23.000	24	21.200	
171	22.986	31	21.100	
14	22.880	8	21.000	
4	22.800	13	20.500	
38	22.800	120	19.000	
2	22.690	129	18.620	
15	22.670	176	8.650	(*)

Lead
Sample no.: H4
Theoretical value: 0.900
Unit: µg/l

Run 1:
Number of laboratories: 33
Arithmetic mean value: 1.021
Median: 0.910
Standard deviation 0.497
Rel. st. deviation (%) 48.618

Run 2:
Number of laboratories: 32
Arithmetic mean value: 0.953
Median: 0.905
Standard deviation 0.311
Rel. st. deviation (%) 32.618

Results in decreasing order:

24	3.200 (*)	16	0.900	
120	2.000	118	0.900	
23	1.630	14	0.898	
174	1.500	112	0.890	
178	1.268	169	0.888	
179	1.150	3	0.877	
10	1.053	2	0.871	
115	1.010	8	0.870	
32	1.000	161	0.850	
110	1.000	5	0.827	
15	0.988	31	0.820	
36	0.944	127	0.800	
38	0.932	13	0.580	
121	0.930	129	0.540	
125	0.925	176	0.440	
171	0.918	33	0.400	
168	0.910	132 <	10.000	
		4 <	3.000	
		159 <	1.000	

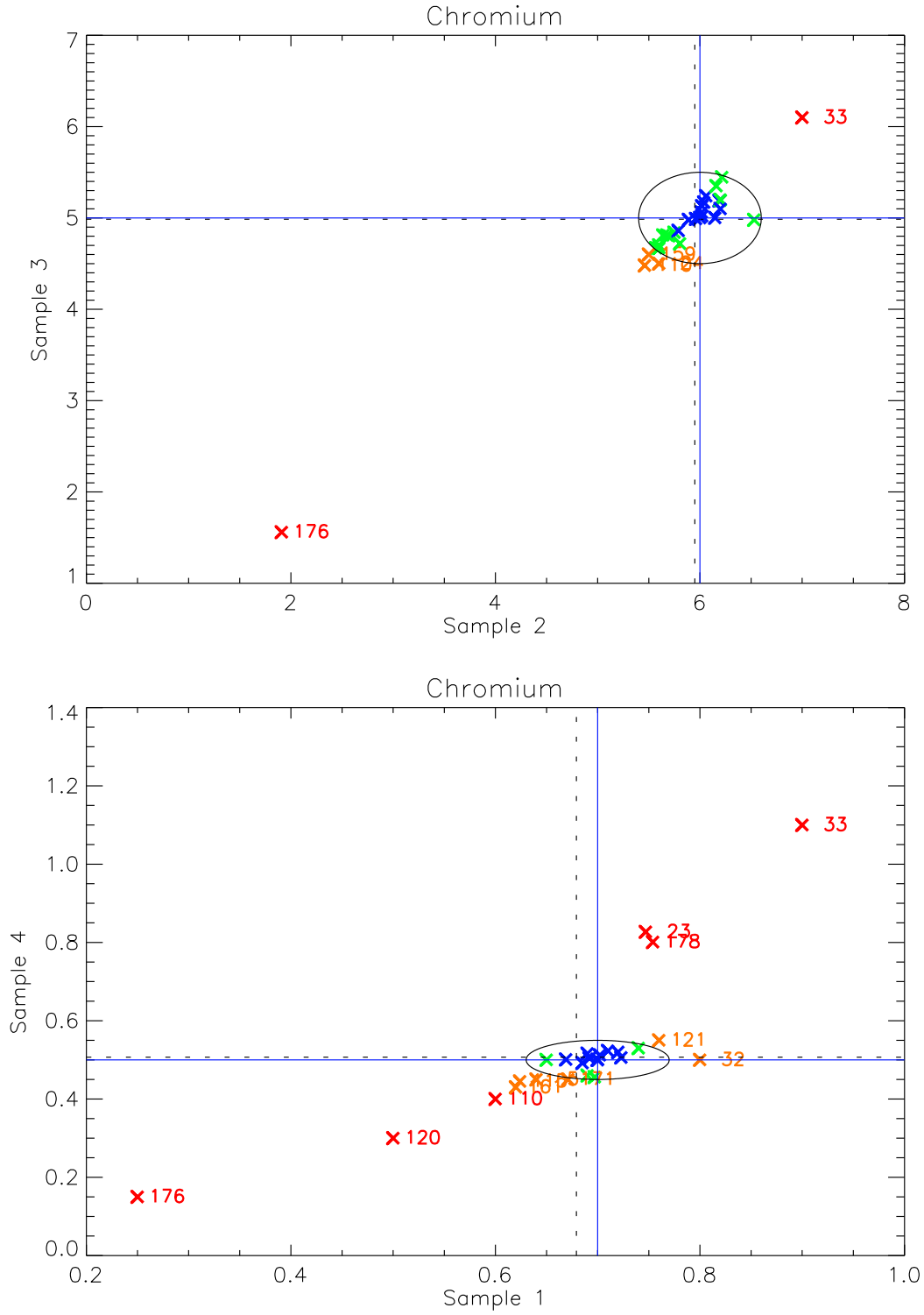

Figure 8: Youden plot of chromium, 2010.

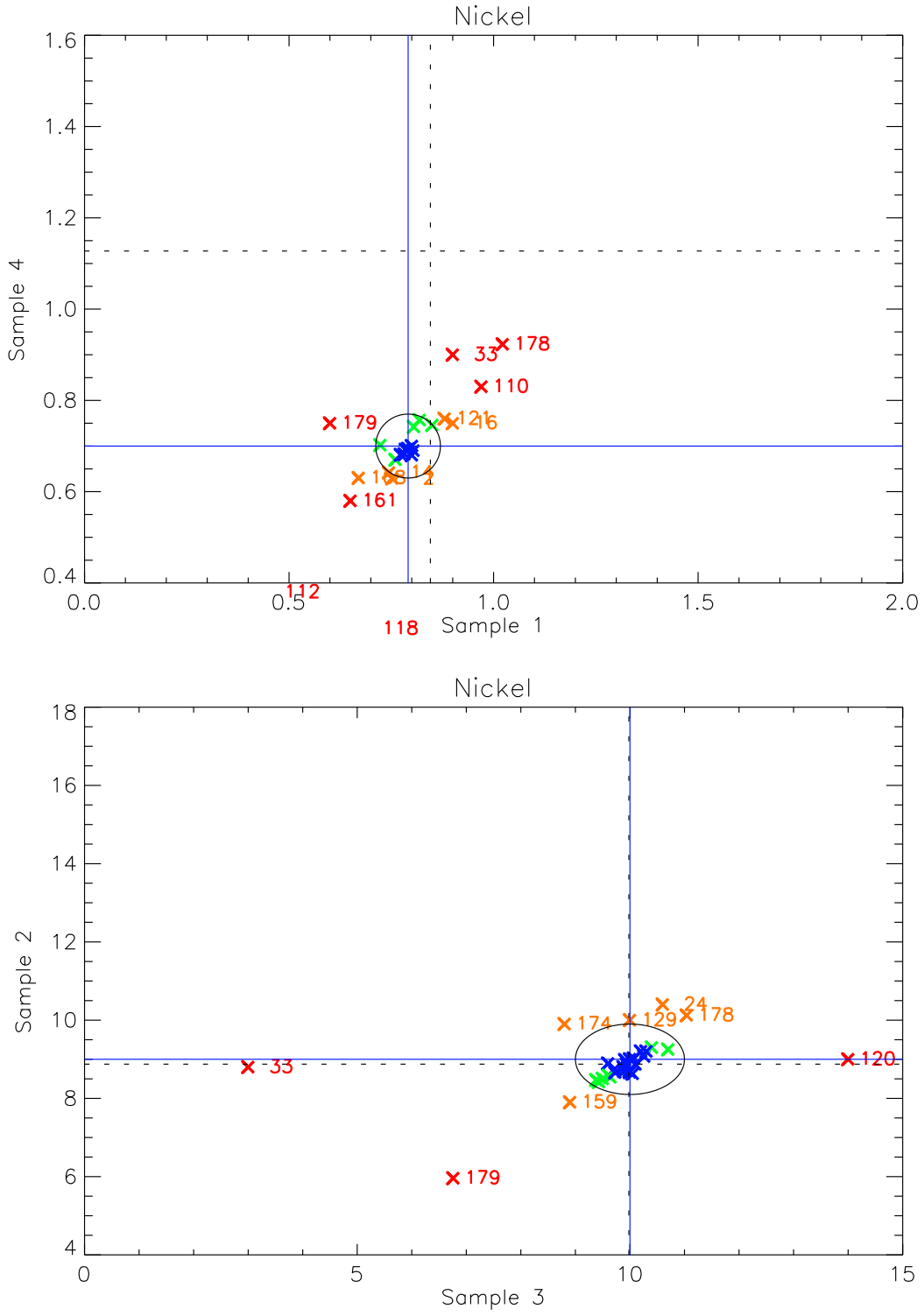

Figure.9: Youden plot of nickel, 2010.

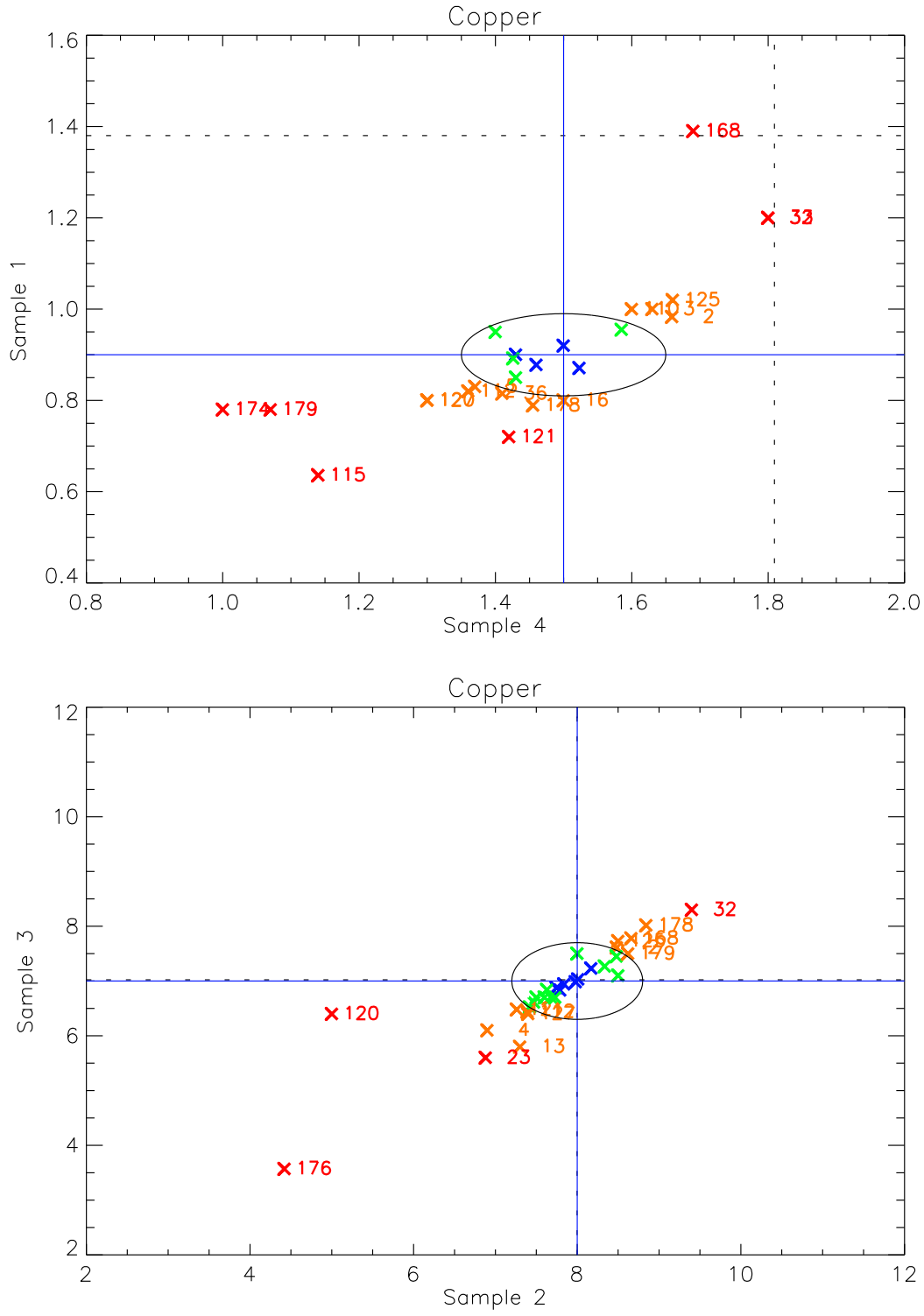

Figure.10: Youden plot of copper, 2010.

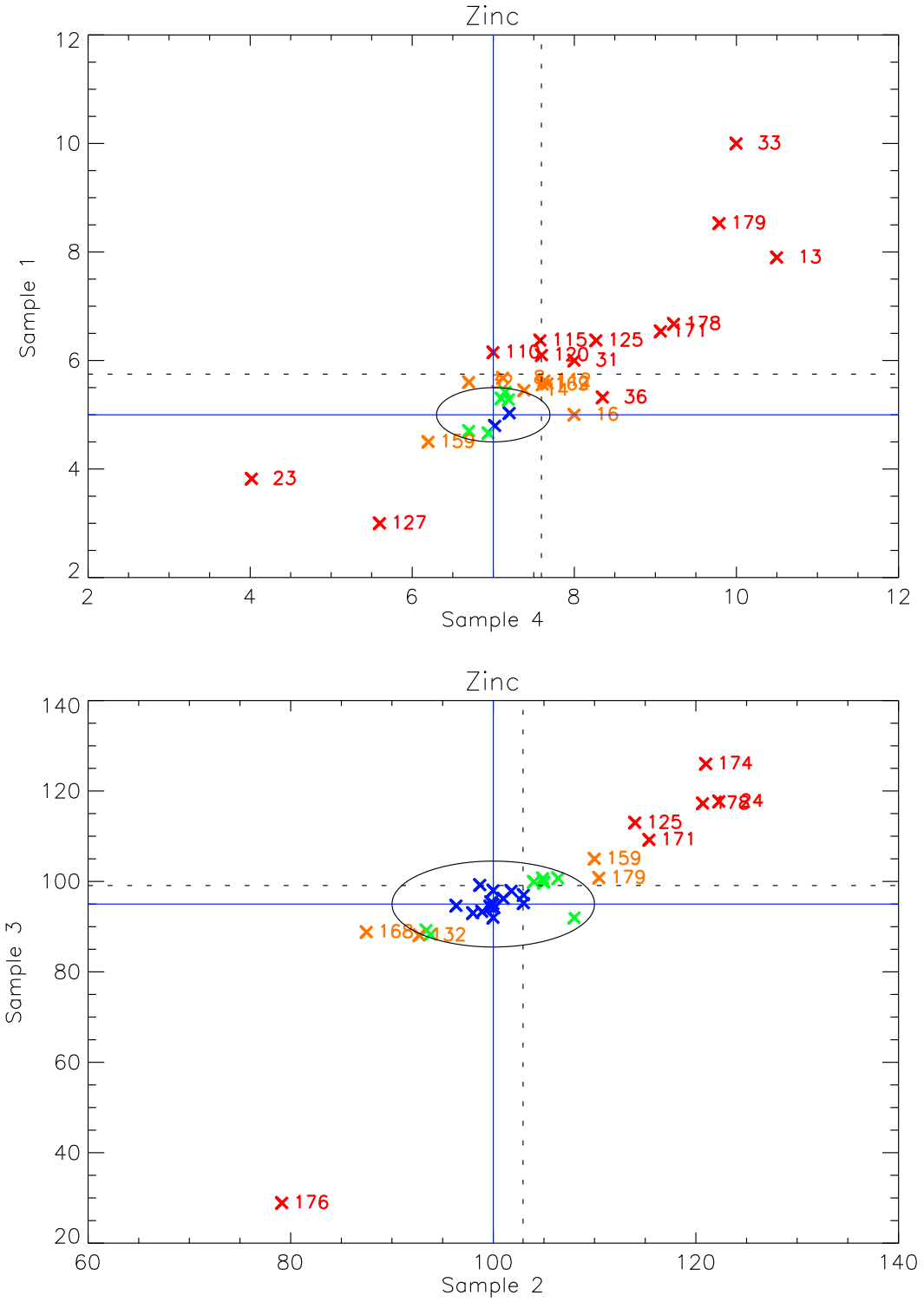

Figure.11: Youden plot of zinc, 2010.

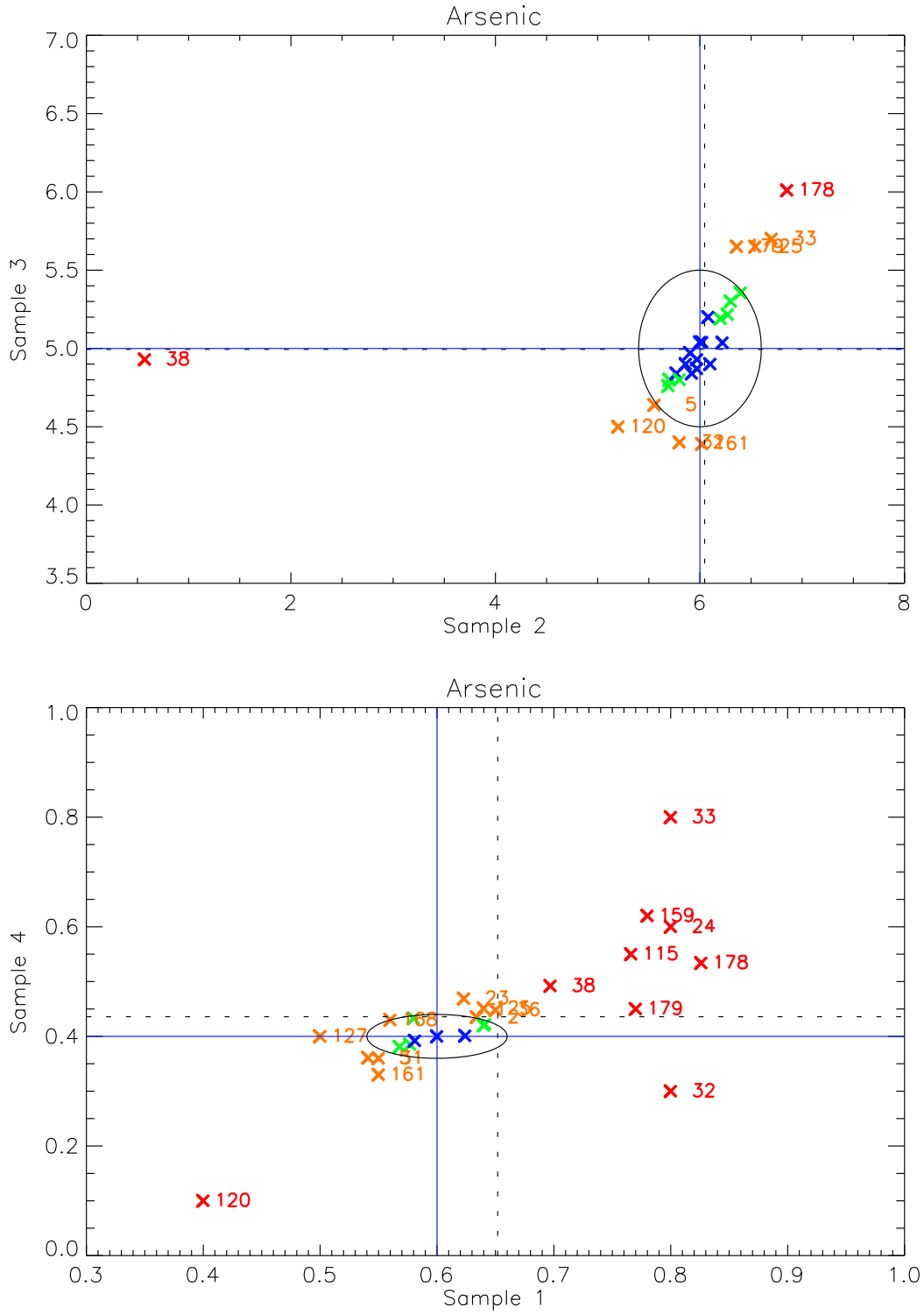

Figure.12: Youden plot of arsenic, 2010.

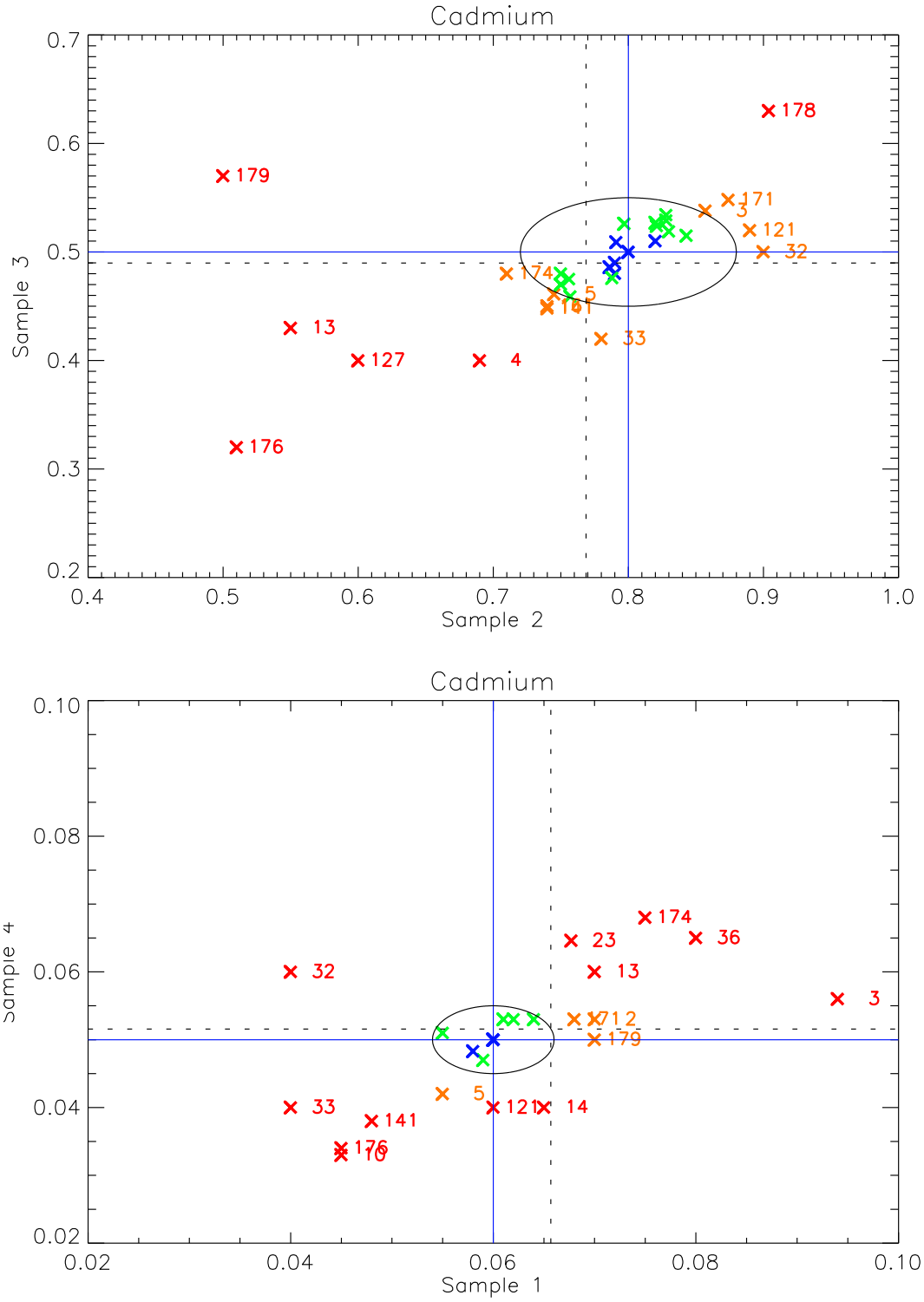

Figure13: Youden plot of cadmium, 2010.

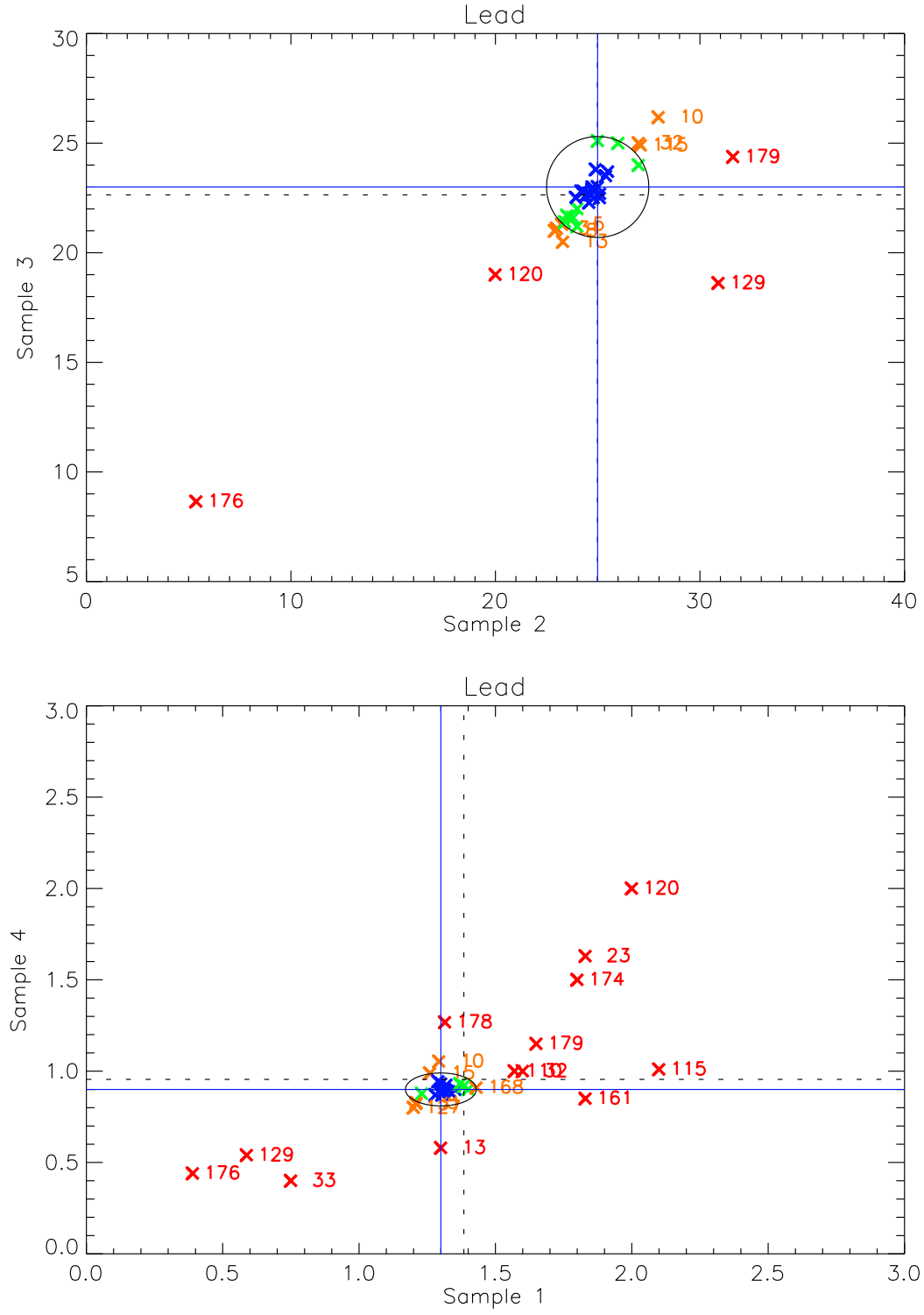

Figure14: Youden plot of lead, 2010.