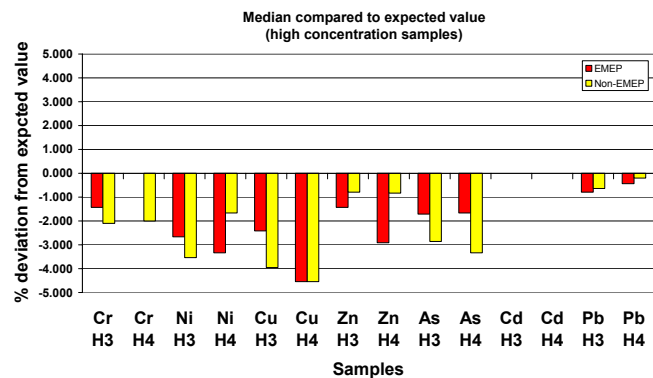
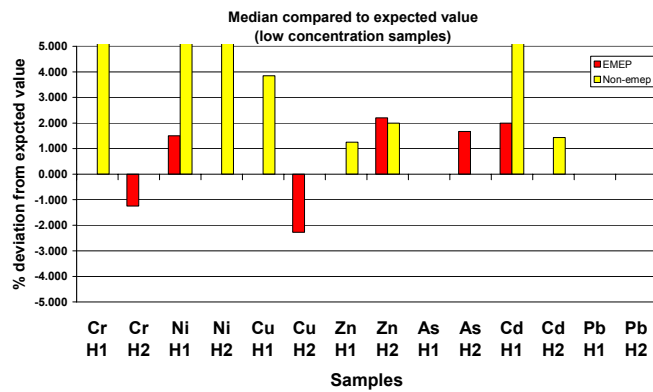


# Analytical intercomparison of heavy metals in precipitation 2002

Hilde Thelle Uggerud and Jan Erik Skjelmoen



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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 2002**

**Hilde Thelle Uggerud and Jan Erik Skjelmoen**



**Norwegian Institute for Air Research**  
P.O. Box 100, N-2027 Kjeller, Norway

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# Analytical intercomparison of heavy metals in precipitation 2002

## 1. Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. In 2001, 17 countries reported 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 four intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 1999; Uggerud and Skjelmoen, 2000; Uggerud and Skjelmoen, 2001).

This report presents results from the fifth analytical intercomparison of heavy metals in precipitation, which was carried out during 2002. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

## 2. Organization of the intercomparison

The samples for the fifth intercomparison were prepared and distributed to 41 laboratories. In addition to 17 EMEP laboratories, 13 laboratories connected to the ICP-forest measurement programme, 5 laboratories connected to WMO and 6 other laboratories also received samples. 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. Tables A.1.1a and A.1.1b give the names of the participating laboratories together with the number used when presenting the results in tables and figures.

## 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<sub>3</sub>. The distributed synthetic precipitation samples contained Pb, Cd, Cu, Zn, As, Cr, and Ni in 0.5% HNO<sub>3</sub>. 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 equipment in contact with the samples were soaked in 3% HNO<sub>3</sub> for at least 4 days. Preparation of the intercomparison samples was carried out in a clean room area.

## 4. Presentation of data

Tables A1.2-A1.8 present the reported results in decreasing order together with the laboratory numbers. The theoretical value, the number of results, the arithmetic mean value, the median, the standard deviation and the relative standard deviation are also given. In the first statistic run only values below detection limit were excluded. In the second run also outliers were excluded. The outliers were defined as values more than two standard deviations from the mean value in the first run.

In Figures A2.1-A2.7 the results are presented in plots showing the relative percentage deviation from expected value for each participating laboratory. There is one plot for every single sample.

The median calculated from the results reported from EMEP laboratories and other participating laboratories respectively, are compared to expected value in Figure A2.8.

A summary of the results is presented in Table A1.9. The results reported from each laboratory are divided in four percent intervals. The number of results reported by the laboratories in each per cent interval is also shown.

Table A1.10 gives information of the analytical techniques used by each laboratory.

## 5. Results

The analytical results from the intercomparison are presented in Figures A2.1-A2.8, Tables A1.2-A1.8 and Table A1.9. The results that were reported by the participating laboratories were generally in accordance with the theoretical values, with good agreement between the median from the second runs and the expected values.

### 5.1 Chromium (Cr)

A total of 31 laboratories reported values for chromium. Five laboratories reported values below detection limit for the low concentration samples. Six laboratories reported values from the low concentration samples that deviated more than 25% from expected value, whereas three laboratories reported values more than 15% from expected value for the high concentration samples. The relative standard deviations for the low concentration samples are 19.2% and 42.4%, when outliers are excluded. This is not as good as last year's result. For the high concentration samples, the standard deviations are 8.7% and 7.6%, when outliers are excluded. This is slightly better than last year's result.

### 5.2 Nickel (Ni)

Results from determination of nickel were obtained from 31 laboratories. Ten laboratories reported values below detection limit for the low concentration samples. Ten laboratories reported values for the low concentration samples that deviated more than 25% from expected value. For the high concentration samples,

five laboratories reported values that deviated more than 15% from expected value. The relative standard deviations for the low concentration samples are 49.6% and 49.0%, when outliers are excluded. This is about the same as in earlier intercomparisons. The relative standard deviations for the high concentration samples are 7.6% and 6.6%, when outliers are excluded. This is a slightly improvement compared to last year's results.

### **5.3 Copper (Cu)**

A total of 31 laboratories reported values for copper. Three laboratories reported results from analysis of low concentration samples to be below detection limit. No such results were reported for the high concentration samples. Four laboratories reported values for the low concentration samples that deviated more than 25% from expected value. For high concentration samples, three laboratories reported values that deviated more than 15% from expected value. The relative standard deviations for the low concentration samples were 38.5% and 48.8% when outliers were excluded. This is not as good as last year's results. For the high concentration samples the relative standard deviation were 6.6% and 5.8%, which is slightly better than last year.

### **5.4 Zinc (Zn)**

Results from determination of zinc were obtained from 31 laboratories. Five laboratories reported results from analysis of low concentration samples to be below detection limit. No such results were reported for the high concentration samples. Eight laboratories reported values for low concentration samples that deviated more than 25% from expected value, whereas two laboratories reported values more than 15% from expected value for the high concentration samples. The relative standard deviations for the low concentration samples are 17.0% and 28.0%, which is about the same result as last year. For the high concentration samples the relative standard deviation are 5.9% and 4.6%, which is a marked improvement compared to last year's results.

### **5.5 Arsenic (As)**

Results from determination of arsenic were obtained from 23 laboratories. Five laboratories reported altogether eight values below detection limits for the two low concentration samples. All the reported values for the low concentration samples were within 25% deviation from expected value. For high concentration samples, six laboratories reported values that deviated more than 15% from expected value. The relative standard deviations for low concentration samples are 12.8% and 9.7%, when outliers are excluded. For the high concentration samples the relative standard deviations are 10.7% and 7.0%, when outliers are excluded. This is about the same as last year's results.

### **5.6 Cadmium (Cd)**

Results from determination of cadmium were obtained from 31 laboratories. Eleven laboratories reported values for the low concentration samples to be below detection limit. Eight laboratories reported values for low concentration samples that deviated more than 25% from expected value, whereas only one laboratory reported values more than 15% from expected value for the high concentration

samples. The relative standard deviations for the low concentration samples are 24.6% and 24.5%, when outliers are excluded. This is slightly better than last years' results. For high concentration samples the relative standard deviations are 6.9% and 7.0%, which is about the same as reported last year.

### **5.7 Lead (Pb)**

A total of 31 laboratories reported values for determination of lead. Five laboratories reported values for the low concentration samples to be below detection limit. Three laboratories reported values for the low concentration samples that deviated more than 25% from expected value. For high concentration samples, four laboratories reported values that deviated more than 15% from expected value. For the low concentration samples the relative standard deviation are 13.2% and 9.9%, when outliers are excluded. This is comparable to the results reported last year. For the high concentration samples, the relative standard deviations are 6.5% and 5.3%, which is slightly better than last year's results.

## **6. Conclusions**

For all the samples analysed the deviation from theoretical values were calculated. The median deviations for the EMEP laboratories are lower than 2.3% and 5.0% for the low- and high concentration samples, respectively. This is the best result since laboratory intercomparisons on heavy metal started. Except for nickel, the median deviations for the other participating laboratories are below 18% for the low concentration samples. For the high concentration samples the median deviations are below 5%. This is an improvement compared to last year.

Figures that show the EMEP laboratories performance on determination of lead and cadmium from 1995 to 2002 can be seen in Aas et al. (2003).

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# **Appendix 1**

## **Tables**

*Table A1.1a: Participating laboratories in the EMEP network. The numbers in front are used in tables.*

<b>No.</b>	<b>Laboratory identification</b>
1	Federal Environmental Agency, Austria
3	Czech Hydrometeorological Institute, Czech Republic
5	Finnish Meteorological Institute, Finland
6	Laboratories Wolf, France
7	IfE-Analytik GmbH, Germany
8	Umweltbundesamt, Germany
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
26	Ontario Ministry of Environment, Canada
31	Slovak Hydrometeorological Institute, Slovakia
32	Atmospheric Pollution Research Laboratory, Lithuania
33	Latvian Hydrometeorological Agency, Latvia
34	Ministry of Health, Refit Saydam Hygiene Center, Turkey
38	Estonian Environmental Research Centre, Estonia
39	Institute of Environmental Protection, Poland

*Table A1.1b: Participating laboratories outside the EMEP network. The number in front of the names is used in tables and figures.*

<b>No.</b>	<b>Laboratory identification</b>
105	Universität des Saarlandes Umweltforschungszentrum, Germany
109	Institut f. Bondenkunde und Waldernährung der Universität, Germany
110	Thüringer Landesanstalt für Landwirtschaft (TLL), Germany
112	Niedersächsische Forstliche Versuchsanstalt (NVF), Germany
118	Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany
119	Landesumweltamt (LUA)
121	Landesamt für Natur und Umwelt, Germany
125	Bayerisches Landesamt für Umweltschutz, Germany
127	Department of Chemistry, Jalan Sultan, Malaysia
129	Ecole Nationale d'Ingenieurs de Sfax, Tunisie
132	Comision Chilena De Energia Nuclear, Chile
137	UST Umwelt-Systemtechnik GmbH, Germany
141	Pollutants Chemical Analysis Center, Japan
142	EPLD, Centre de Lagor, France

Table A1.2: Analytical results for Cr in synthetic precipitation samples.

<p>Cr SAMPLE NO.: H1 THEORETICAL VALUE 0.600 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.687 MEDIAN: 0.600 STANDARD DEVIATION: 0.362 REL. ST. DEVIATION (%): 52.700</p> <p>RUN 2: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 0.590 MEDIAN: 0.600 STANDARD DEVIATION: 0.114 REL. ST. DEVIATION (%): 19.266</p> <p>RESULTS IN DECREASING ORDER: 129 2.000 UNUSED 14 0.600 142 &lt; 2 105 1.700 UNUSED 40 0.600 112 &lt; 1.5 132 &lt; 1.4 137 &lt; 1 38 &lt; 1 121 0.760 110 0.600 26 0.740 31 0.590 125 0.726 15 0.580 3 0.700 23 0.580 39 0.700 109 0.570 118 0.700 1 0.540 32 0.640 16 0.500 119 0.640 5 0.461 8 0.620 33 0.400 7 0.607 127 0.400 6 0.600 34 0.300</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Cr SAMPLE NO.: H2 THEORETICAL VALUE 0.800 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.975 MEDIAN: 0.790 STANDARD DEVIATION: 0.712 REL. ST. DEVIATION (%): 73.016</p> <p>RUN 2: NUMBER OF LABORATORIES: 25 ARITHMETIC MEAN VALUE: 0.854 MEDIAN: 0.790 STANDARD DEVIATION: 0.362 REL. ST. DEVIATION (%): 42.421</p> <p>RESULTS IN DECREASING ORDER: 129 4.000 UNUSED 15 0.790 105 2.300 26 0.790 142 &lt; 2 33 1.620 31 0.790 112 &lt; 1.5 132 &lt; 1.4 137 &lt; 1 38 &lt; 1 14 1.000 32 0.790 125 0.847 8 0.770 119 0.840 1 0.750 23 0.830 16 0.700 3 0.820 39 0.700 6 0.800 110 0.700 40 0.800 5 0.669 109 0.800 121 0.600 118 0.800 127 0.600 7 0.790 34 0.450</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>
<p>Cr SAMPLE NO.: H3 THEORETICAL VALUE 9.500 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 8.967 MEDIAN: 9.300 STANDARD DEVIATION: 1.514 REL. ST. DEVIATION (%): 16.888</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 9.199 MEDIAN: 9.300 STANDARD DEVIATION: 0.802 REL. ST. DEVIATION (%): 8.716</p> <p>RESULTS IN DECREASING ORDER: 105 10.900 110 9.300 3 10.310 118 9.300 6 9.900 1 9.290 125 9.670 40 9.200 31 9.660 127 9.100 119 9.570 15 9.000 14 9.500 102 9.000 16 9.500 5 8.970 34 9.500 7 8.910 38 9.500 121 8.700 26 9.420 137 8.400 32 9.400 132 8.330 112 9.400 33 8.310 8 9.330 23 6.000 39A 9.300 129 2.000 UNUSED 109 9.300</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Cr SAMPLE NO.: H4 THEORETICAL VALUE 5.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 4.846 MEDIAN: 4.960 STANDARD DEVIATION: 0.647 REL. ST. DEVIATION (%): 13.346</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 4.941 MEDIAN: 4.980 STANDARD DEVIATION: 0.380 REL. ST. DEVIATION (%): 7.682</p> <p>RESULTS IN DECREASING ORDER: 105 6.100 109 4.930 32 5.600 1 4.900 125 5.330 14 4.900 6 5.300 118 4.900 119 5.280 142 4.900 3 5.110 7 4.850 40 5.100 110 4.800 38 5.060 121 4.700 31 5.040 127 4.600 15 5.000 132 4.590 16 5.000 5 4.410 26 5.000 137 4.400 34 5.000 33 4.270 39A 5.000 23 4.200 112 5.000 129 2.000 UNUSED 8 4.960</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>

Table A1.3: Analytical results for Ni in synthetic precipitation samples.

<p>Ni SAMPLE NO.: H1 THEORETICAL VALUE 0.400 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.586 MEDIAN: 0.430 STANDARD DEVIATION: 0.409 REL. ST. DEVIATION (%): 69.726</p> <p>RUN 2: NUMBER OF LABORATORIES: 20 ARITHMETIC MEAN VALUE: 0.515 MEDIAN: 0.430 STANDARD DEVIATION: 0.256 REL. ST. DEVIATION (%): 49.595</p> <p>RESULTS IN DECREASING ORDER:</p> <table> <tbody> <tr><td>142</td><td>&lt;</td><td>5</td><td></td><td></td></tr> <tr><td>137</td><td>&lt;</td><td>2</td><td></td><td></td></tr> <tr><td>129</td><td>2.000</td><td>UNUSED</td><td>23</td><td>0.430</td></tr> <tr><td>127</td><td>&lt;</td><td>2</td><td></td><td></td></tr> <tr><td>112</td><td>&lt;</td><td>1.7</td><td></td><td></td></tr> <tr><td>105</td><td>1.400</td><td></td><td>7</td><td>0.406</td></tr> <tr><td>132</td><td>&lt;</td><td>1.14</td><td></td><td></td></tr> <tr><td>38</td><td>&lt;</td><td>1</td><td></td><td></td></tr> <tr><td>39A</td><td>&lt;</td><td>1</td><td></td><td></td></tr> <tr><td>119</td><td>&lt;</td><td>0.9</td><td></td><td></td></tr> <tr><td>33</td><td>0.820</td><td></td><td>14</td><td>0.400</td></tr> <tr><td>109</td><td>0.770</td><td></td><td>16</td><td>0.400</td></tr> <tr><td>121</td><td>0.700</td><td></td><td>40</td><td>0.400</td></tr> <tr><td>32</td><td>0.570</td><td></td><td>8</td><td>0.380</td></tr> <tr><td>31</td><td>0.530</td><td></td><td>15</td><td>0.360</td></tr> <tr><td>3</td><td>0.500</td><td></td><td>34</td><td>0.300</td></tr> <tr><td>6</td><td>&lt;</td><td>0.5</td><td></td><td></td></tr> <tr><td>110</td><td>&lt;</td><td>0.5</td><td></td><td></td></tr> <tr><td>118</td><td>0.500</td><td></td><td>26</td><td>0.290</td></tr> <tr><td>5</td><td>0.433</td><td></td><td>125</td><td>0.290</td></tr> <tr><td>1</td><td>0.430</td><td></td><td></td><td></td></tr> </tbody> </table> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	142	<	5			137	<	2			129	2.000	UNUSED	23	0.430	127	<	2			112	<	1.7			105	1.400		7	0.406	132	<	1.14			38	<	1			39A	<	1			119	<	0.9			33	0.820		14	0.400	109	0.770		16	0.400	121	0.700		40	0.400	32	0.570		8	0.380	31	0.530		15	0.360	3	0.500		34	0.300	6	<	0.5			110	<	0.5			118	0.500		26	0.290	5	0.433		125	0.290	1	0.430				<p>Ni SAMPLE NO.: H2 THEORETICAL VALUE 0.600 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.808 MEDIAN: 0.600 STANDARD DEVIATION: 0.445 REL. ST. DEVIATION (%): 55.056</p> <p>RUN 2: NUMBER OF LABORATORIES: 22 ARITHMETIC MEAN VALUE: 0.754 MEDIAN: 0.600 STANDARD DEVIATION: 0.369 REL. ST. DEVIATION (%): 49.023</p> <p>RESULTS IN DECREASING ORDER:</p> <table> <tbody> <tr><td>142</td><td>&lt;</td><td>5</td><td></td><td></td></tr> <tr><td>137</td><td>&lt;</td><td>2</td><td></td><td></td></tr> <tr><td>129</td><td>2.000</td><td>UNUSED</td><td>16</td><td>0.600</td></tr> <tr><td>127</td><td>&lt;</td><td>2</td><td></td><td></td></tr> <tr><td>112</td><td>&lt;</td><td>1.7</td><td></td><td></td></tr> <tr><td>125</td><td>1.630</td><td></td><td>33</td><td>0.600</td></tr> <tr><td>105</td><td>1.600</td><td></td><td>40</td><td>0.600</td></tr> <tr><td>38</td><td>1.460</td><td></td><td>110</td><td>0.600</td></tr> <tr><td>23</td><td>1.200</td><td></td><td>118</td><td>0.600</td></tr> <tr><td>132</td><td>&lt;</td><td>1.14</td><td></td><td></td></tr> <tr><td>39A</td><td>&lt;</td><td>1</td><td></td><td></td></tr> <tr><td>119</td><td>&lt;</td><td>0.9</td><td></td><td></td></tr> <tr><td>32</td><td>0.820</td><td></td><td>7</td><td>0.596</td></tr> <tr><td>121</td><td>0.820</td><td></td><td>8</td><td>0.570</td></tr> <tr><td>31</td><td>0.670</td><td></td><td>26</td><td>0.540</td></tr> <tr><td>1</td><td>0.620</td><td></td><td>6</td><td>&lt; 0.5</td></tr> <tr><td></td><td></td><td></td><td>5</td><td>0.486</td></tr> <tr><td>3</td><td>0.600</td><td></td><td>34</td><td>0.470</td></tr> <tr><td>14</td><td>0.600</td><td></td><td>109</td><td>0.300</td></tr> <tr><td>15</td><td>0.600</td><td></td><td></td><td></td></tr> </tbody> </table> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	142	<	5			137	<	2			129	2.000	UNUSED	16	0.600	127	<	2			112	<	1.7			125	1.630		33	0.600	105	1.600		40	0.600	38	1.460		110	0.600	23	1.200		118	0.600	132	<	1.14			39A	<	1			119	<	0.9			32	0.820		7	0.596	121	0.820		8	0.570	31	0.670		26	0.540	1	0.620		6	< 0.5				5	0.486	3	0.600		34	0.470	14	0.600		109	0.300	15	0.600			
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132	<	1.14																																																																																																																																																																																																												
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32	0.820		7	0.596																																																																																																																																																																																																										
121	0.820		8	0.570																																																																																																																																																																																																										
31	0.670		26	0.540																																																																																																																																																																																																										
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15	0.600																																																																																																																																																																																																													
<p>Ni SAMPLE NO.: H3 THEORETICAL VALUE 7.500 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 7.173 MEDIAN: 7.270 STANDARD DEVIATION: 0.651 REL. ST. DEVIATION (%): 9.078</p> <p>RUN 2: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 7.174 MEDIAN: 7.270 STANDARD DEVIATION: 0.551 REL. ST. DEVIATION (%): 7.686</p> <p>RESULTS IN DECREASING ORDER:</p> <table> <tbody> <tr><td>121</td><td>8.600</td><td>UNUSED</td><td>1</td><td>7.200</td></tr> <tr><td>3</td><td>8.000</td><td></td><td>26</td><td>7.200</td></tr> <tr><td>39A</td><td>8.000</td><td></td><td>40</td><td>7.200</td></tr> <tr><td>15</td><td>7.800</td><td></td><td>110</td><td>7.200</td></tr> <tr><td>31</td><td>7.800</td><td></td><td>118</td><td>7.200</td></tr> <tr><td>109</td><td>7.800</td><td></td><td>127</td><td>7.000</td></tr> <tr><td>119</td><td>7.640</td><td></td><td>33</td><td>6.880</td></tr> <tr><td>7</td><td>7.530</td><td></td><td>32</td><td>6.700</td></tr> <tr><td>6</td><td>7.500</td><td></td><td>142</td><td>6.600</td></tr> <tr><td>16</td><td>7.500</td><td></td><td>5</td><td>6.510</td></tr> <tr><td>112</td><td>7.500</td><td></td><td>137</td><td>6.400</td></tr> <tr><td>8</td><td>7.410</td><td></td><td>38</td><td>6.320</td></tr> <tr><td>14</td><td>7.300</td><td></td><td>105</td><td>6.000</td></tr> <tr><td>23</td><td>7.300</td><td></td><td>129</td><td>6.000</td></tr> <tr><td>132</td><td>7.290</td><td></td><td>34</td><td>5.700</td></tr> <tr><td>125</td><td>7.270</td><td></td><td></td><td>UNUSED</td></tr> </tbody> </table> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	121	8.600	UNUSED	1	7.200	3	8.000		26	7.200	39A	8.000		40	7.200	15	7.800		110	7.200	31	7.800		118	7.200	109	7.800		127	7.000	119	7.640		33	6.880	7	7.530		32	6.700	6	7.500		142	6.600	16	7.500		5	6.510	112	7.500		137	6.400	8	7.410		38	6.320	14	7.300		105	6.000	23	7.300		129	6.000	132	7.290		34	5.700	125	7.270			UNUSED	<p>Ni SAMPLE NO.: H4 THEORETICAL VALUE 9.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 8.661 MEDIAN: 8.700 STANDARD DEVIATION: 1.039 REL. ST. DEVIATION (%): 11.993</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 8.817 MEDIAN: 8.700 STANDARD DEVIATION: 0.585 REL. ST. DEVIATION (%): 6.633</p> <p>RESULTS IN DECREASING ORDER:</p> <table> <tbody> <tr><td>11</td><td>10.400</td><td></td><td>23</td><td>8.700</td></tr> <tr><td>3</td><td>9.800</td><td></td><td>142</td><td>8.700</td></tr> <tr><td>39A</td><td>9.600</td><td></td><td>125</td><td>8.680</td></tr> <tr><td>15</td><td>9.300</td><td></td><td>33</td><td>8.670</td></tr> <tr><td>105</td><td>9.300</td><td></td><td>1</td><td>8.630</td></tr> <tr><td>119</td><td>9.290</td><td></td><td>110</td><td>8.600</td></tr> <tr><td>109</td><td>9.200</td><td></td><td>5</td><td>8.510</td></tr> <tr><td>31</td><td>9.190</td><td></td><td>118</td><td>8.500</td></tr> <tr><td>112</td><td>9.000</td><td></td><td>132</td><td>8.480</td></tr> <tr><td>127</td><td>9.000</td><td></td><td>6</td><td>8.400</td></tr> <tr><td>7</td><td>8.960</td><td></td><td>38</td><td>8.230</td></tr> <tr><td>8</td><td>8.960</td><td></td><td>32</td><td>8.100</td></tr> <tr><td>26</td><td>8.900</td><td></td><td>34</td><td>7.600</td></tr> <tr><td>40</td><td>8.900</td><td></td><td>137</td><td>7.500</td></tr> <tr><td>14</td><td>8.700</td><td></td><td>129</td><td>4.000</td></tr> <tr><td>16</td><td>8.700</td><td></td><td></td><td>UNUSED</td></tr> </tbody> </table> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	11	10.400		23	8.700	3	9.800		142	8.700	39A	9.600		125	8.680	15	9.300		33	8.670	105	9.300		1	8.630	119	9.290		110	8.600	109	9.200		5	8.510	31	9.190		118	8.500	112	9.000		132	8.480	127	9.000		6	8.400	7	8.960		38	8.230	8	8.960		32	8.100	26	8.900		34	7.600	40	8.900		137	7.500	14	8.700		129	4.000	16	8.700			UNUSED																																													
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Table A1.4: Analytical results for Cu in synthetic precipitation samples.

<p>Cu SAMPLE NO.: H1 THEORETICAL VALUE 1.300 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 2.433 MEDIAN: 1.300 STANDARD DEVIATION: 5.672 REL. ST. DEVIATION (%): 233.165</p> <p>RUN 2: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 1.384 MEDIAN: 1.300 STANDARD DEVIATION: 0.533 REL. ST. DEVIATION (%): 38.539</p> <p>RESULTS IN DECREASING ORDER: 05 31.800 UNUSED 15 1.300 29 4.000 39A 1.300 37 &lt; 2 40 1.700 110 1.300 19 &lt; 1.68 18 1.500 6 1.260 25 1.430 5 1.230 32 1.420 33 1.230 14 1.400 23 1.200 34 1.400 127 1.200 21 1.400 32 1.130 31 1.380 16 1.100 38 1.360 142 1.100 8 1.330 112 1.100 1 1.300 26 1.050 3 1.300 109 1.030 7 1.300</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Cu SAMPLE NO.: H2 THEORETICAL VALUE 1.100 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 6.390 MEDIAN: 1.090 STANDARD DEVIATION: 27.563 REL. ST. DEVIATION (%): 431.317</p> <p>RUN 2: NUMBER OF LABORATORIES: 27 ARITHMETIC MEAN VALUE: 1.183 MEDIAN: 1.090 STANDARD DEVIATION: 0.577 REL. ST. DEVIATION (%): 48.792</p> <p>RESULTS IN DECREASING ORDER: 105 147.000 UNUSED 31 1.090 129 4.000 8 1.080 137 &lt; 2 119 &lt; 1.68 118 1.300 6 1.070 125 1.300 7 1.060 3 1.200 5 1.010 14 1.200 142 &lt; 1 23 1.000 16 1.200 40 1.000 34 1.200 112 1.000 38 1.200 127 1.000 132 1.150 32 0.970 15 1.100 33 0.970 110 1.100 26 0.910 121 1.100 39A 0.900 1 1.090 109 0.730</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>
<p>Cu SAMPLE NO.: H3 THEORETICAL VALUE 6.200 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 7.295 MEDIAN: 6.000 STANDARD DEVIATION: 7.713 REL. ST. DEVIATION (%): 105.717</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 5.912 MEDIAN: 5.965 STANDARD DEVIATION: 0.392 REL. ST. DEVIATION (%): 6.638</p> <p>RESULTS IN DECREASING ORDER: 105 48.800 UNUSED 1 5.930 14 6.400 109 5.910 6 6.370 23 5.900 125 6.330 34 5.900 31 6.210 40 5.900 3 6.200 142 5.900 8 6.200 118 5.900 15 6.200 38 5.860 26 6.200 5 5.790 110 6.200 109 5.670 127 6.200 132 5.360 7 6.140 112 5.300 32 6.100 33 5.290 121 6.100 39A 5.200 16 6.000 137 4.700 129 6.000</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Cu SAMPLE NO.: H4 THEORETICAL VALUE 11.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 11.998 MEDIAN: 10.500 STANDARD DEVIATION: 9.114 REL. ST. DEVIATION (%): 75.964</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 10.364 MEDIAN: 10.500 STANDARD DEVIATION: 0.607 REL. ST. DEVIATION (%): 5.861</p> <p>RESULTS IN DECREASING ORDER: 105 61.000 UNUSED 109 10.500 5 11.200 121 10.500 125 11.200 26 10.300 31 11.120 118 10.300 8 11.100 40 10.200 14 11.000 132 10.100 16 11.000 129 10.000 15 10.900 23 9.900 110 10.800 102 9.900 119 10.740 6 9.890 32 10.700 33 9.780 3 10.600 142 9.600 127 10.600 34 9.400 1 10.500 39A 9.400 7 10.500 137 8.700 38 10.500</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>

Table A1.5: Analytical results for Zn in synthetic precipitation samples.

<p>Zn SAMPLE NO.: H1 THEORETICAL VALUE 8.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 10.921 MEDIAN: 8.000 STANDARD DEVIATION: 10.975 REL. ST. DEVIATION (%): 100.493</p> <p>RUN 2: NUMBER OF LABORATORIES: 25 ARITHMETIC MEAN VALUE: 7.935 MEDIAN: 8.000 STANDARD DEVIATION: 1.350 REL. ST. DEVIATION (%): 17.015</p> <p>RESULTS IN DECREASING ORDER: 105 54.500 UNUSED 31 8.000 129 42.000 UNUSED 32 8.000 119 &lt; 30 118 10.900 5 7.750 142 &lt; 10 137 &lt; 10 109 10.000 132 7.750 38 &lt; 10 125 9.970 1 7.660 6 9.230 33 7.500 8 8.800 110 7.400 23 8.500 127 7.400 26 8.260 15 7.200 7 8.250 34 7.000 40 8.200 39A 6.800 121 8.100 16 5.500 3 8.000 112 4.200 14 8.000</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Zn SAMPLE NO.: H2 THEORETICAL VALUE 5.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 8.526 MEDIAN: 5.155 STANDARD DEVIATION: 11.833 REL. ST. DEVIATION (%): 138.781</p> <p>RUN 2: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 5.320 MEDIAN: 5.055 STANDARD DEVIATION: 1.491 REL. ST. DEVIATION (%): 28.021</p> <p>RESULTS IN DECREASING ORDER: 105 58.000 UNUSED 33 5.110 129 36.000 UNUSED 14 5.000 119 &lt; 30 142 &lt; 10 137 &lt; 10 109 &lt; 10 38 &lt; 10 34 9.200 16 5.000 125 8.210 31 5.000 118 7.500 40 5.000 6 6.290 15 4.900 8 5.900 1 4.780 23 5.800 5 4.680 26 5.620 39A 4.400 3 5.500 132 4.310 32 5.300 127 4.200 7 5.280 110 4.100 121 5.200 112 1.400</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>
<p>Zn SAMPLE NO.: H3 THEORETICAL VALUE 105.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 108.785 MEDIAN: 103.330 STANDARD DEVIATION: 30.534 REL. ST. DEVIATION (%): 28.068</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 103.411 MEDIAN: 103.165 STANDARD DEVIATION: 6.196 REL. ST. DEVIATION (%): 5.992</p> <p>RESULTS IN DECREASING ORDER: 105 270.000 UNUSED 31 103.000 26 112.000 119 103.000 129 112.000 118 102.400 8 111.100 5 102.000 127 110.500 34 101.500 6 109.700 33 101.000 3 109.000 39A 101.000 14 109.000 112 100.300 125 109.000 16 100.000 7 108.000 142 99.200 121 108.000 137 98.000 110 106.000 1 97.800 15 105.000 23 97.000 32 104.000 38 91.000 40 104.000 132 84.500 109 103.33</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Zn SAMPLE NO.: H4 THEORETICAL VALUE 120.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 136.661 MEDIAN: 117.000 STANDARD DEVIATION: 109.321 REL. ST. DEVIATION (%): 79.994</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 117.050 MEDIAN: 116.750 STANDARD DEVIATION: 5.419 REL. ST. DEVIATION (%): 4.630</p> <p>RESULTS IN DECREASING ORDER: 105 725.000 UNUSED 118 116.500 8 128.200 3 116.000 125 126.000 33 116.000 127 124.500 39A 116.000 7 123.000 112 116.000 26 123.000 6 115.400 14 120.000 5 115.000 15 120.000 142 113.400 16 120.000 129 112.000 32 120.000 34 111.500 40 120.000 1 111.000 109 120.000 137 111.000 110 120.000 23 110.000 121 120.000 132 107.000 119 118.000 38 105.000 31 117.000</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>

Table A1.6: Analytical results for As in synthetic precipitation samples.

<p>As SAMPLE NO.: H1 THEORETICAL VALUE 0.400 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 23 ARITHMETIC MEAN VALUE: 0.402 MEDIAN: 0.400 STANDARD DEVIATION: 0.052 REL. ST. DEVIATION (%): 12.879</p> <p>RUN 2: NUMBER OF LABORATORIES: 18 ARITHMETIC MEAN VALUE: 0.402 MEDIAN: 0.400 STANDARD DEVIATION: 0.052 REL. ST. DEVIATION (%): 12.879</p> <p>RESULTS IN DECREASING ORDER: 142 &lt; 2 119 &lt; 1.05 38 &lt; 1 137 &lt; 0.5 118 0.500 127 0.400 110 &lt; 0.5 7 0.499 26 0.390 33 0.460 125 0.381 132 0.449 23 0.380 14 0.430 15 0.370 8 0.423 32 0.370 1 0.400 31 0.330 3 0.400 121 0.330 6 0.400 5 0.323</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>As SAMPLE NO.: H2 THEORETICAL VALUE 0.600 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 23 ARITHMETIC MEAN VALUE: 0.597 MEDIAN: 0.605 STANDARD DEVIATION: 0.067 REL. ST. DEVIATION (%): 11.202</p> <p>RUN 2: NUMBER OF LABORATORIES: 19 ARITHMETIC MEAN VALUE: 0.605 MEDIAN: 0.610 STANDARD DEVIATION: 0.059 REL. ST. DEVIATION (%): 9.725</p> <p>RESULTS IN DECREASING ORDER: 42 &lt; 2 19 &lt; 1.05 38 &lt; 1 18 0.700 1 0.600 7 0.696 6 0.600 32 0.690 110 0.600 132 0.635 14 0.590 31 0.630 125 0.588 137 0.630 15 0.560 3 0.620 121 0.520 26 0.620 127 0.500 8 0.612 5 0.486 23 0.610 33 0.450 UNUSED</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>
<p>As SAMPLE NO.: H3 THEORETICAL VALUE 3.500 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 23 ARITHMETIC MEAN VALUE: 3.392 MEDIAN: 3.400 STANDARD DEVIATION: 0.576 REL. ST. DEVIATION (%): 16.993</p> <p>RUN 2: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 3.420 MEDIAN: 3.400 STANDARD DEVIATION: 0.365 REL. ST. DEVIATION (%): 10.664</p> <p>RESULTS IN DECREASING ORDER: 32 4.600 UNUSED 118 3.400 6 4.400 121 3.400 7 3.810 137 3.400 33 3.670 125 3.390 8 3.610 26 3.340 3 3.570 1 3.330 10 3.500 119 3.320 27 3.500 31 3.300 14 3.480 5 2.650 15 3.400 132 2.540 23 3.400 38 1.610 UNUSED 42 3.400</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>As SAMPLE NO.: H4 THEORETICAL VALUE 6.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 23 ARITHMETIC MEAN VALUE: 5.840 MEDIAN: 5.800 STANDARD DEVIATION: 0.589 REL. ST. DEVIATION (%): 10.093</p> <p>RUN 2: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 5.840 MEDIAN: 5.800 STANDARD DEVIATION: 0.413 REL. ST. DEVIATION (%): 7.072</p> <p>RESULTS IN DECREASING ORDER: 6 7.300 UNUSED 23 5.800 7 6.570 110 5.800 142 6.500 121 5.800 8 6.280 119 5.790 127 6.200 1 5.690 3 6.110 5 5.620 31 6.080 137 5.600 32 6.000 118 5.500 14 5.900 33 4.990 26 5.900 132 4.850 125 5.860 38 4.390 UNUSED 15 5.800</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>

Table A1.7: Analytical results for Cd in synthetic precipitation samples.

<p>Cd SAMPLE NO.: H1 THEORETICAL VALUE 0.050 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.068 MEDIAN: 0.052 STANDARD DEVIATION: 0.055 REL. ST. DEVIATION (%): 81.243</p> <p>RUN 2: NUMBER OF LABORATORIES: 20 ARITHMETIC MEAN VALUE: 0.056 MEDIAN: 0.052 STANDARD DEVIATION: 0.014 REL. ST. DEVIATION (%): 24.675</p> <p>RESULTS IN DECREASING ORDER: 129 &lt; 4 142 &lt; 1 39A 0.300 UNUSED 1 0.051 105 0.100 14 0.051 112 &lt; 0.5 137 &lt; 0.2 132 &lt; 0.2 127 &lt; 0.2 110 &lt; 0.1 109 &lt; 0.1 6 &lt; 0.1 119 &lt; 0.08 32 0.080 16 0.050 141 0.071 31 0.050 33 0.060 121 0.049 118 0.060 38 0.048 8 0.056 5 0.048 23 0.055 3 0.047 26 0.055 15 0.042 125 0.055 34 0.040 7 0.052</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Cd SAMPLE NO.: H2 THEORETICAL VALUE 0.070 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.077 MEDIAN: 0.070 STANDARD DEVIATION: 0.024 REL. ST. DEVIATION (%): 31.540</p> <p>RUN 2: NUMBER OF LABORATORIES: 20 ARITHMETIC MEAN VALUE: 0.073 MEDIAN: 0.070 STANDARD DEVIATION: 0.018 REL. ST. DEVIATION (%): 24.501</p> <p>RESULTS IN DECREASING ORDER: 129 &lt; 4 142 &lt; 1 112 &lt; 0.5 39A &lt; 0.3 137 &lt; 0.2 132 &lt; 0.2 127 &lt; 0.2 110 &lt; 0.1 6 &lt; 0.1 105 0.150 UNUSED 16 0.070 32 0.110 33 0.070 31 0.100 7 0.069 109 0.100 26 0.068 141 0.091 5 0.064 3 0.090 1 0.064 119 &lt; 0.08 14 0.073 121 0.064 15 0.072 34 0.060 23 0.071 38 0.055 125 0.071 118 0.030 8 0.070</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>
<p>Cd SAMPLE NO.: H3 THEORETICAL VALUE 0.700 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.699 MEDIAN: 0.700 STANDARD DEVIATION: 0.061 REL. ST. DEVIATION (%): 8.684</p> <p>RUN 2: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 0.692 MEDIAN: 0.700 STANDARD DEVIATION: 0.048 REL. ST. DEVIATION (%): 6.900</p> <p>RESULTS IN DECREASING ORDER: 129 &lt; 4 142 &lt; 1 105 0.900 UNUSED 39A 0.700 32 0.800 110 0.700 109 0.770 118 0.700 141 0.735 127 0.700 3 0.730 125 0.693 119 0.730 34 0.680 121 0.730 1 0.670 33 0.720 23 0.660 8 0.713 5 0.642 14 0.712 15 0.640 6 0.710 38 0.617 31 0.710 137 0.610 7 0.703 132 0.607 16 0.700 112 0.600 26 0.700</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Cd SAMPLE NO.: H4 THEORETICAL VALUE 0.800 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 0.790 MEDIAN: 0.800 STANDARD DEVIATION: 0.055 REL. ST. DEVIATION (%): 7.011</p> <p>RUN 2: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 0.790 MEDIAN: 0.800 STANDARD DEVIATION: 0.055 REL. ST. DEVIATION (%): 7.011</p> <p>RESULTS IN DECREASING ORDER: 129 &lt; 4 142 &lt; 1 32 0.900 110 0.800 105 0.900 118 0.800 109 0.870 127 0.800 141 0.831 125 0.794 8 0.825 26 0.780 3 0.820 1 0.770 33 0.820 15 0.760 119 0.820 23 0.760 121 0.820 5 0.732 14 0.816 137 0.720 7 0.806 39A 0.700 6 0.800 112 0.700 16 0.800 38 0.695 31 0.800 132 0.683 34 0.800</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>



Table A1.8: Analytical results for Pb in synthetic precipitation samples.

<p>Pb SAMPLE NO.: H1 THEORETICAL VALUE 1.400 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 1.463 MEDIAN: 1.400 STANDARD DEVIATION: 0.362 REL. ST. DEVIATION (%): 24.731</p> <p>RUN 2: NUMBER OF LABORATORIES: 25 ARITHMETIC MEAN VALUE: 1.402 MEDIAN: 1.400 STANDARD DEVIATION: 0.185 REL. ST. DEVIATION (%): 13.179</p> <p>RESULTS IN DECREASING ORDER: 137 &lt; 5 132 &lt; 5 39A &lt; 5 105 3.000 UNUSED 16 1.400 129 2.000 23 1.400 112 1.600 40 1.400 125 1.560 110 1.400 14 1.500 127 1.400 32 1.500 26 1.360 118 1.500 5 1.310 7 1.470 33 1.280 31 1.460 119 1.260 1 1.440 6 1.200 8 1.440 34 1.200 15 1.430 121 1.140 3 1.400 142 &lt; 1 38 &lt; 1 109 1.000</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Pb SAMPLE NO.: H2 THEORETICAL VALUE 1.600 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 1.778 MEDIAN: 1.600 STANDARD DEVIATION: 0.686 REL. ST. DEVIATION (%): 38.593</p> <p>RUN 2: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 1.588 MEDIAN: 1.600 STANDARD DEVIATION: 0.158 REL. ST. DEVIATION (%): 9.952</p> <p>RESULTS IN DECREASING ORDER: 137 &lt; 5 132 &lt; 5 39A &lt; 5 105 4.100 UNUSED 16 1.600 129 4.000 UNUSED 26 1.600 109 2.000 50 1.600 125 1.960 8 1.580 32 1.700 121 1.580 40 1.700 23 1.500 112 1.700 34 1.500 7 1.620 127 1.500 31 1.610 5 1.470 1 1.600 119 1.410 3 1.600 6 1.400 14 1.600 33 1.390 15 1.600 118 1.300 142 &lt; 1 38 &lt; 1</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>
<p>Pb SAMPLE NO.: H3 THEORETICAL VALUE 47.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 45.994 MEDIAN: 46.500 STANDARD DEVIATION: 4.196 REL. ST. DEVIATION (%): 9.124</p> <p>RUN 2: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 46.052 MEDIAN: 46.500 STANDARD DEVIATION: 3.020 REL. ST. DEVIATION (%): 6.557</p> <p>RESULTS IN DECREASING ORDER: 132 56.800 UNUSED 125 46.400 109 50.330 31 46.380 14 49.900 38 46.200 119 49.600 129 46.000 3 49.400 1 45.900 118 49.300 110 45.000 32 49.000 39A 44.000 7 48.500 5 43.900 40 48.000 121 43.900 34 47.500 6 43.800 112 47.200 23 42.000 127 47.100 137 40.500 15 47.000 16 40.000 26 47.000 142 38.400 8 46.800 105 33.500 UNUSED 33 46.500</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>	<p>Pb SAMPLE NO.: H4 THEORETICAL VALUE 25.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 31 ARITHMETIC MEAN VALUE: 24.345 MEDIAN: 24.900 STANDARD DEVIATION: 1.517 REL. ST. DEVIATION (%): 6.230</p> <p>RUN 2: NUMBER OF LABORATORIES: 30 ARITHMETIC MEAN VALUE: 24.490 MEDIAN: 24.950 STANDARD DEVIATION: 1.307 REL. ST. DEVIATION (%): 5.335</p> <p>RESULTS IN DECREASING ORDER: 119 26.500 127 24.900 132 26.300 31 24.780 14 25.800 1 24.500 38 25.800 6 24.400 118 25.500 33 24.300 7 25.400 110 24.100 109 25.330 15 24.000 112 25.300 121 24.000 3 25.200 5 23.000 26 25.200 137 22.800 8 25.100 23 22.000 16 25.000 34 22.000 32 25.000 129 22.000 40 25.000 142 21.600 105 25.000 39A 20.000 UNUSED 125 24.900</p> <p>"UNUSED": DATA UNUSED IN RUN 2</p>

Table A1.9: Percentage deviation from theoretical concentration value.

Element and percent interval	Lab. Identification		
	The number in brackets are number of results reported in the particular percent interval by the laboratory		
	EMEP	Other	
<b>Cr</b>			
0-5%			1(2), 3(2), 6(3), 7(3), 8(4), 14(3), 15(2), 16(2), 23(2), 26(3), 31(4), 32(2), 34(2), 39A(2), 39B(4), 109(4), 110(3), 118(3), 119(2), 125(1), 127(1)
5-15%			1(2), 3(2), 5(2), 6(1), 7(1), 15(2), 16(1), 32(2), 33(2), 39A(1), 105(1), 110(1), 119(2), 121(2), 125(2), 127(1), 132(2), 137(2)
15-25%			5(2), 14(1), 16(1), 23(1), 26(1), 39A(1), 105(1), 118(1), 121(1), 125(1), 127(1)
>25%			23(1), 33(2), 34(2), 105(2), 121(1), 127(1), 129(4)
<b>Ni</b>			
0-5%			1(3), 3(1), 7(4), 8(3), 14(4), 15(3), 16(4), 23(2), 26(2), 31(2), 33(2), 39B(4), 105(1), 109(2), 110(2), 112(2), 118(2), 119(2), 125(2), 127(1), 132(1), 142(1)
5-15%			1(1), 3(2), 5(3), 8(1), 15(1), 23(1), 26(1), 31(1), 32(2), 33(1), 39A(2), 118(1), 127(1), 132(1), 137(1), 142(1)
15-25%			3(1), 5(1), 34(4), 38(1), 105(1), 118(1), 121(2), 129(1), 137(1)
>25%			23(1), 26(1), 31(1), 32(2), 33(1), 105(2), 109(2), 121(2), 125(2), 129(3)
<b>Cu</b>			
0-5%			1(4), 3(3), 5(1), 6(3), 7(4), 8(4), 14(2), 15(4), 16(2), 23(1), 26(1), 31(3), 32(2), 34(1), 38(2), 39A(1), 39B(1), 109(1), 110(4), 118(1), 121(3), 125(1), 127(2), 129(1), 132(1), 142(1)
5-15%			3(19), 5(3), 6(1), 14(2), 16(1), 23(3), 26(1), 31(1), 32(2), 33(4), 34(3), 38(2), 39A(1), 39B(2), 109(1), 112(3), 118(1), 121(1), 125(1), 127(2), 129(1), 132(3), 142(1)
15-25%			16(1), 26(2), 39A(2), 109(1), 112(1), 118(2), 125(1), 142(1)
>25%			39B(1), 105(4), 109(1), 129(2)
<b>Zn</b>			
0-5%			1(2), 3(3), 5(3), 6(2), 7(3), 14(4), 15(3), 16(3), 26(2), 31(4), 32(3), 33(3), 34(1), 39A(2), 39B(4), 109(2), 110(2), 112(2), 118(2), 119(2), 121(4), 125(1), 127(1), 132(1)
5-15%			1(2), 3(1), 5(1), 7(1), 8(3), 15(1), 23(3), 26(2), 31(4), 32(3), 33(1), 34(2), 38(2), 39A(2), 110(1), 129(2), 137(2), 142(2)
15-25%			6(1), 8(1), 23(1), 110(1), 125(1), 127(1), 132(1)
>25%			6(1), 16(1), 34(1), 105(4), 109(1), 112(2), 118(2), 125(1), 129(2)
<b>As</b>			
0-5%	11	7	1(3), 3(4), 6(2), 8(3), 14(3), 15(2), 23(3), 26(4), 31(1), 32(1), 33(1), 110(3), 118(1), 119(1), 121(2), 127(3), 137(1), 142(1)
5-15%	9	6	1(1), 5(1), 7(2), 8(1), 14(1), 15(2), 23(1), 31(2), 32(1), 118(1), 119(1), 121(1), 132(2), 137(2), 142(1)
15-25%	7	4	5(3), 6(1), 7(1), 16(1), 31(1), 32(1), 33(3), 118(2), 121(1), 127(1), 132(1)
>25%	3	1	6(1), 32(1), 38(1), 132(1)
<b>Cd</b>			
0-5%	16	7	1(3), 3(2), 5(1), 6(2), 7(4), 8(3), 16(4), 14(4), 15(1), 23(1), 26(3), 31(3), 33(3), 34(2), 38(1), 39A(1), 110(2), 118(2), 119(2), 121(3), 125(3), 127(2), 141(1)
5-15%	11	8	1(1), 3(1), 5(4), 8(1), 15(2), 23(3), 26(1), 32(2), 34(1), 38(2), 39A(1), 105(1), 109(2), 112(2), 121(1), 125(1), 132(2), 137(2), 141(1)
15-25%	4	1	15(1) 33(1), 34(1), 38(1), 118(1)
>25%	4	4	3(1), 31(1), 32(2), 39A(1), 105(3), 109(1), 118(1), 141(2)

Table A1.9, cont.

Element and percent interval	Lab. Identification		
	<i>The number in brackets are number of results reported in the particular percent interval by the laboratory</i>		
	EMEP	Other	
<b>Pb</b>			
0-5%	16	8	1(4), 3(3), 6(1), 7(3), 8(4), 14(2), 15(4), 16(3), 23(1), 26(4), 31(4), 32(2), 33(2), 34(1), 38(2), 39B(3), 105(1), 109(1), 110(4), 112(2), 118(2), 121(2), 125(2), 129(1)
5-15%	11	11	5(4), 3(1), 6(3), 7(1), 14(2), 16(1), 23(3), 32(2), 33(2), 34(3), 39A(1), 109(1), 112(2), 118(1), 119(4), 121(1), 125(1), 127(1), 129(1), 132(1), 137(2), 142(1)
15-25%	1	6	39A(1), 109(1), 118(1), 121(1), 125(1), 132(1), 142(1)
>25%	0	3	105(3), 109(1), 129(2)

Table A1.10: Analytical techniques used at the participating laboratories for the different elements.

Lab. no.	Elements	Technique
1	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
3	Ni, Cd, Cu, Pb, Cr, As Zn	GF-AAS ICP-MS F-AAS
5	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
6	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
7	Cr, Ni, Cu, Zn, As, Cd, Pb Zn	GF-AAS F-AAS
8	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
14	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
15	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
16	Cr, Ni, Cu, Cd, Pb Zn	GF-AAS F-AAS
23	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
26	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
31	Cr, Ni, Cu, Cd, Pb, As Zn	GF-AAS F-AAS
32	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
33	Cu, Cd, Pb Zn As	GF-AAS F-AAS HG-AAS
34	Ni, Cu	AAS
36	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
38	Cr, Ni, Cu, , Cd, Pb Zn	GF-AAS F-AAS
39A	Cr, Ni, Cu, Zn, Cd, Pb	UN-ICP-AES
39B	Cr, Ni, Cu, Zn, Pb	GF-AAS
105	Cr, Ni, Cu, Zn, Cd, Pb	GF-AAS
109	Cr, Ni, Cu, Zn, Cd, Pb	GF-AAS
110	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
112	Cr, Ni, Cu, Zn, As, Cd, Pb	USN-ICP-MS
115	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
117	Cr, Ni, Cu , Zn As, Cd, Pb	USN-ICP-OES GF-AAS
118	Cu, Cd, Pb As ,Zn Cr, Ni	GF-AAS ICP-OES
119	Cr, Ni, Cu, As, Cd, Pb Zn	GF-AAS F-AAS
121	Cr, Ni, Cu, Cd, Pb Zn As	GF-AAS Voltametry HG-AAS
125	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS

Table A1.10, cont.

Lab. no.	Elements	Technique
127	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
128	Cu, Cd, Pb As Zn	GF-AAS HG-AAS F-AAS
129	Cr, Ni, Cu, Zn, Cd, Pb	F-AAS (Polarized Zeeman)
132	Cr, Ni, Cu, Zn, Cd Pb As	USN-ICP-OES GF-AAS HG-AAS
134	Zn	ICP-OES
137	Cr, Cd, Pb Ni, Cu, Zn As	GF-AAS F-AAS HG-AAS
141	Cd	GF-AAS
142	Cr, Ni, Cu, As, Cd, Pb Zn	ICP-MS ICP-AES

## **Appendix 2**

### **Figures**

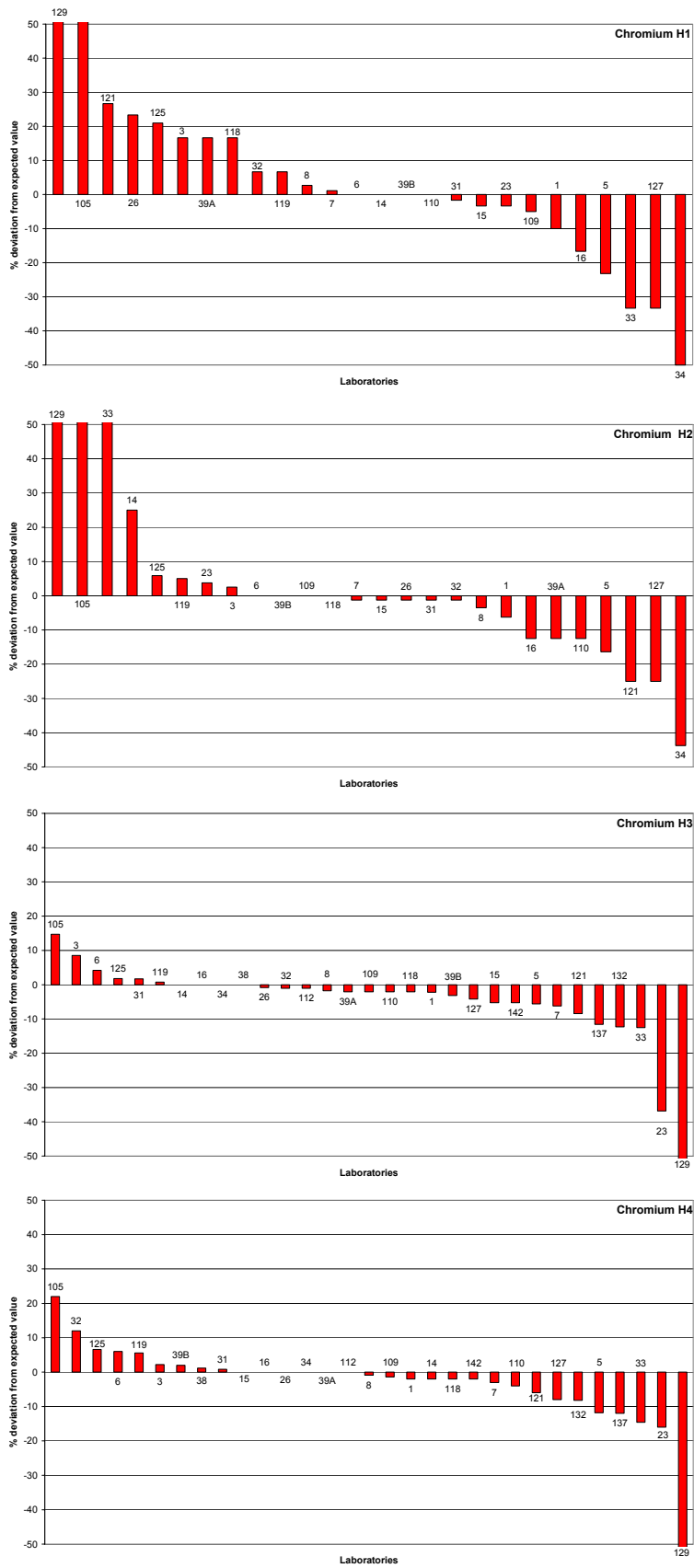


Figure A2.1: Results from determination of Cr.

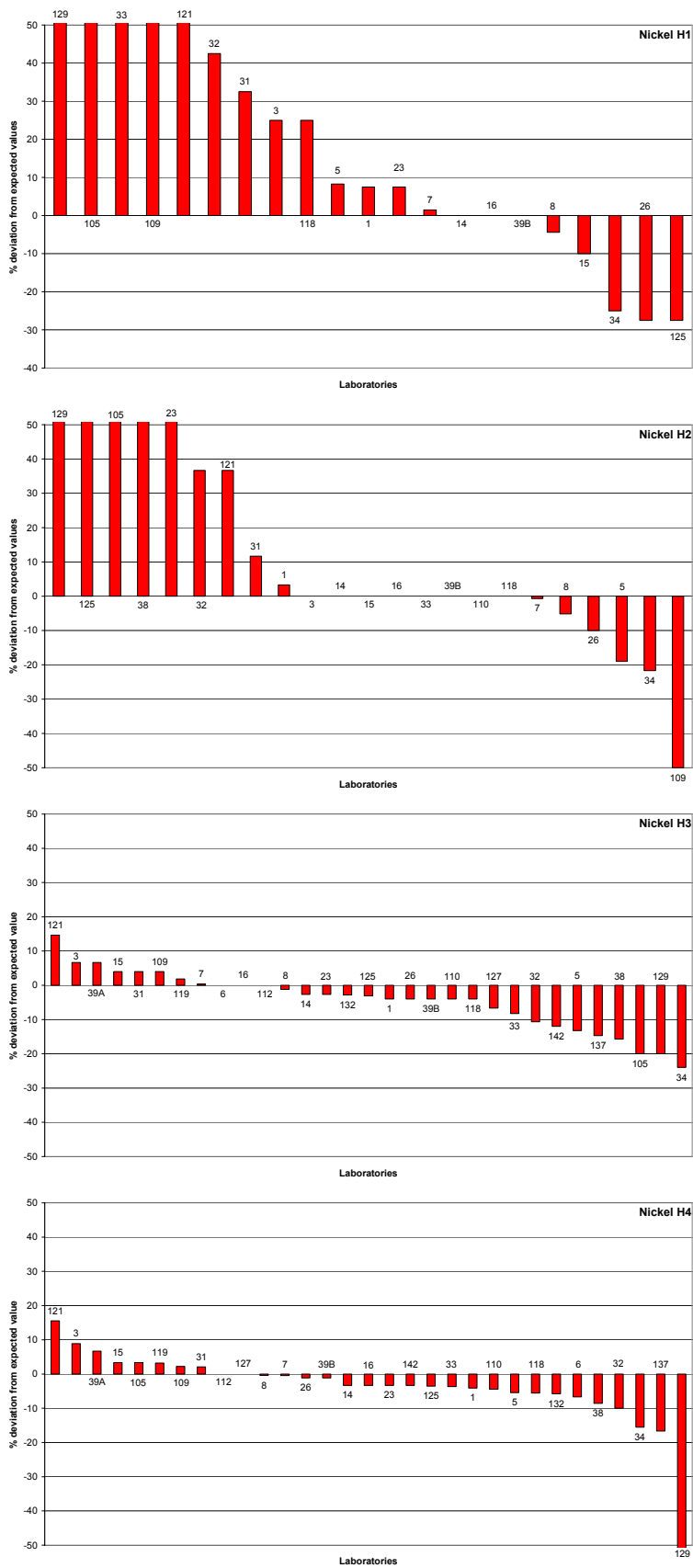


Figure A2.2: Results from determination of Ni.



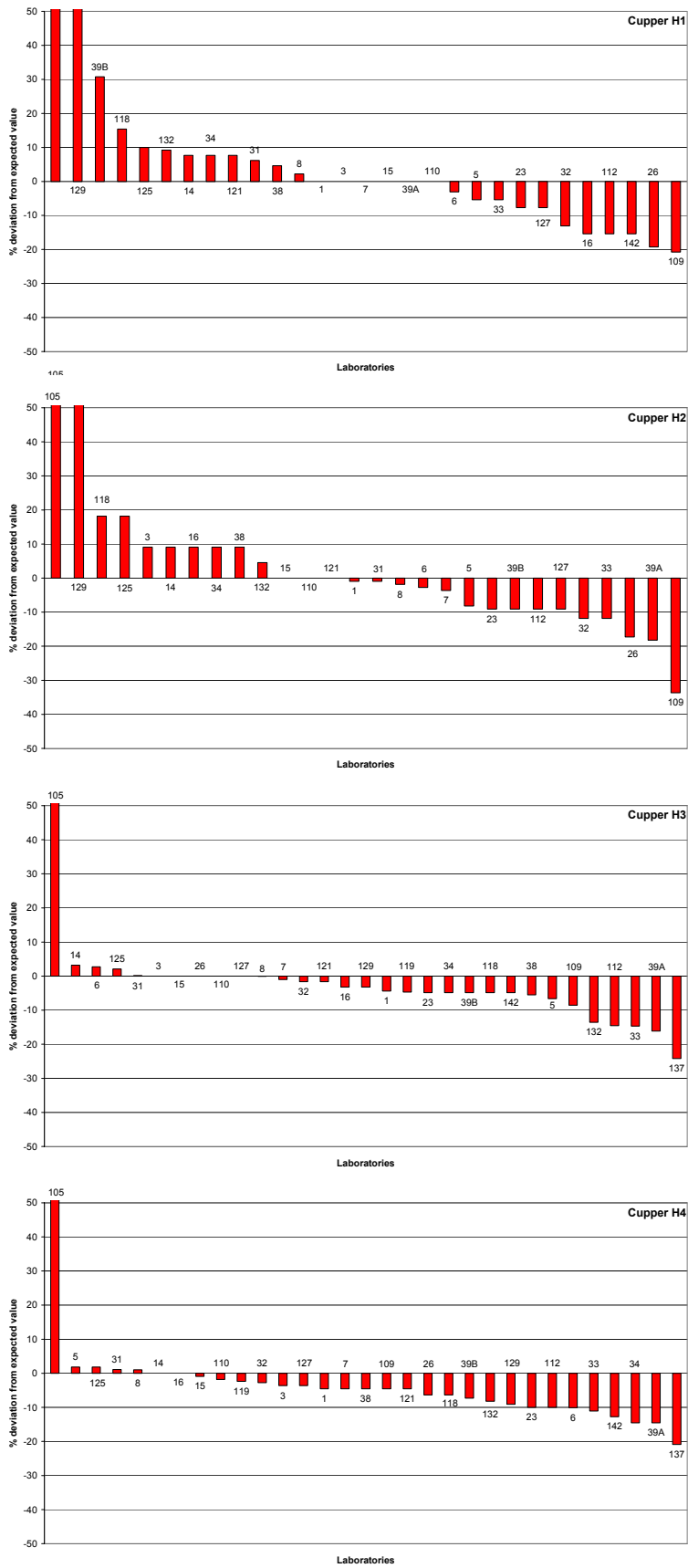


Figure A2.3: Results from determination of Cu.

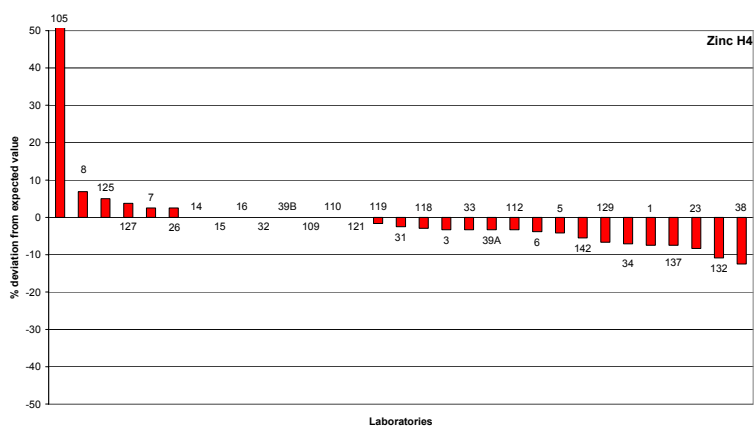
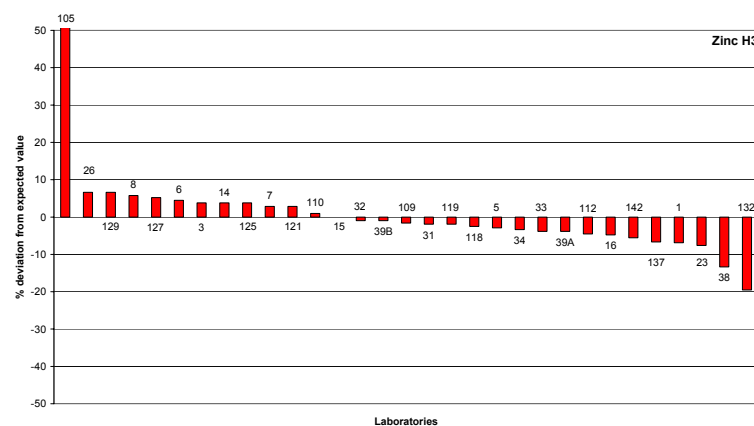
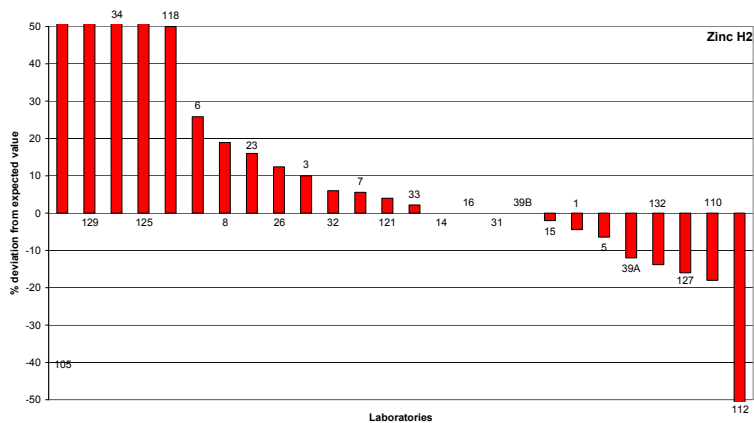
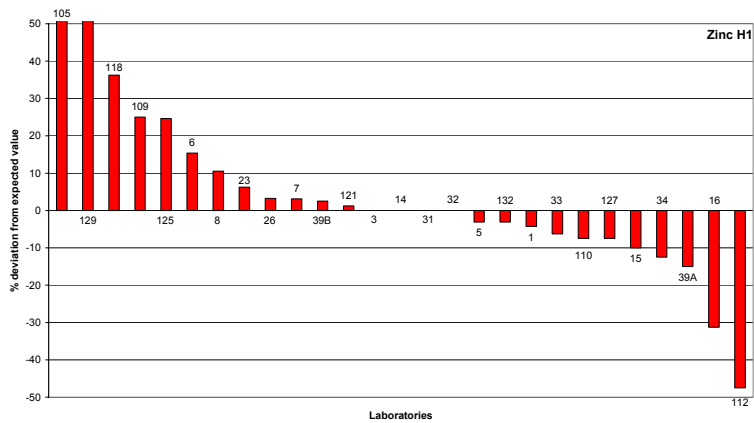


Figure A2.4: Results from determination of Zn.

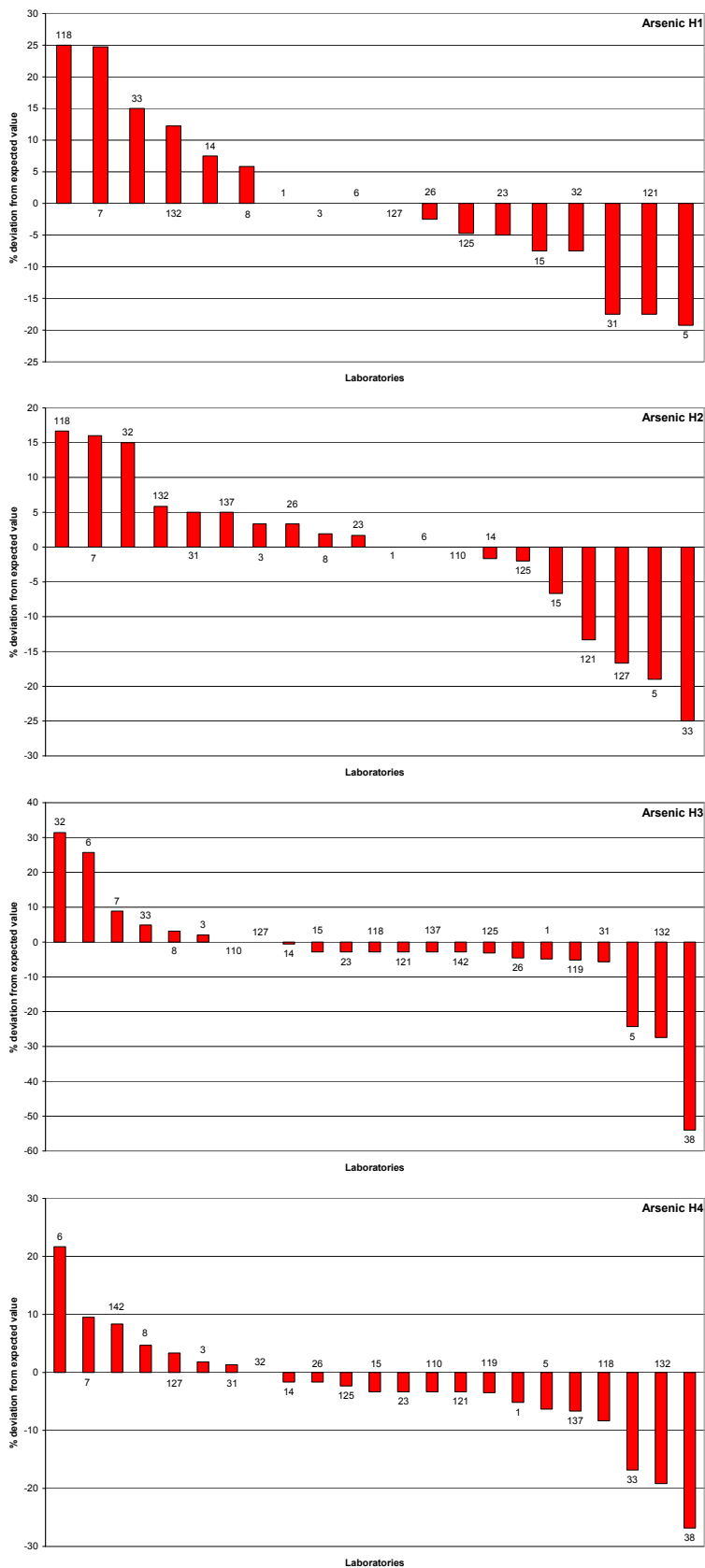


Figure A2.5: Results from determination of As.

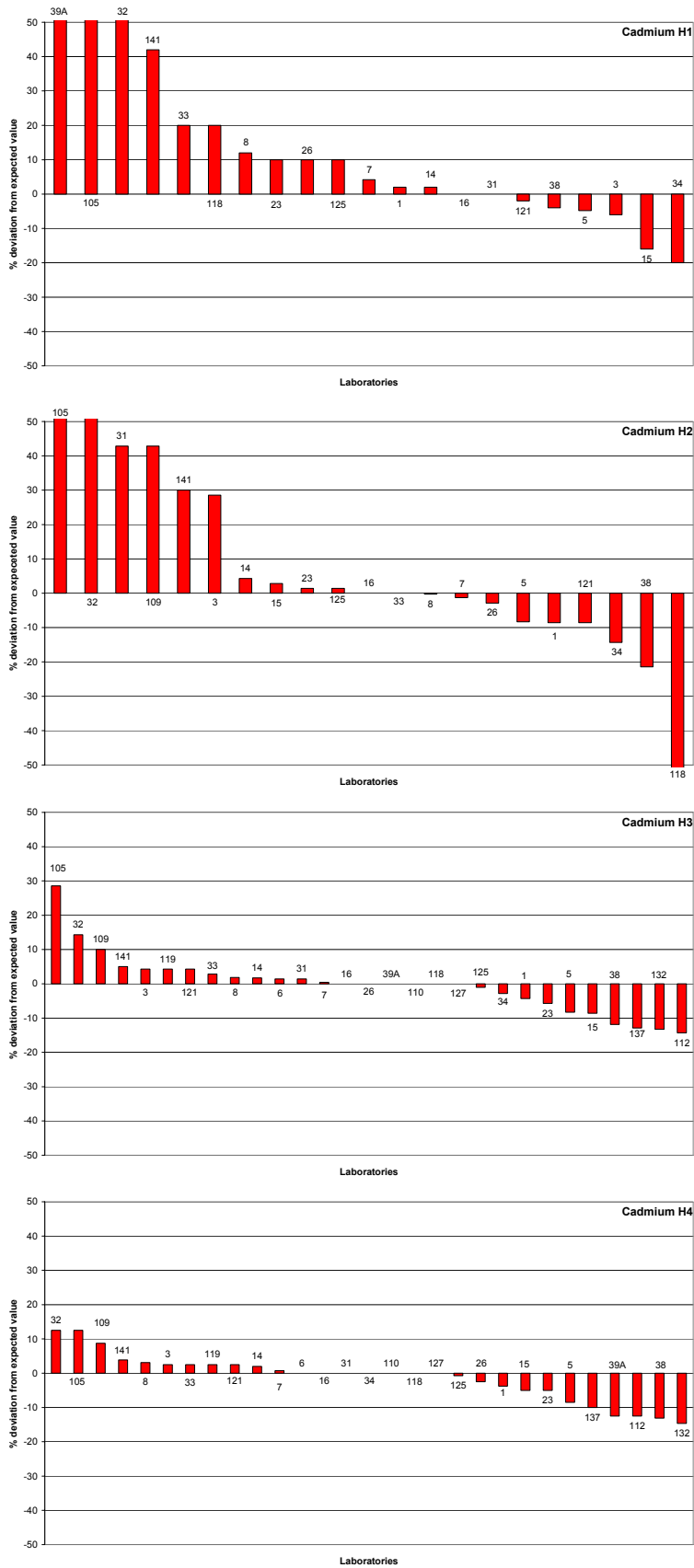


Figure A2.6: Results from determination of Cd.

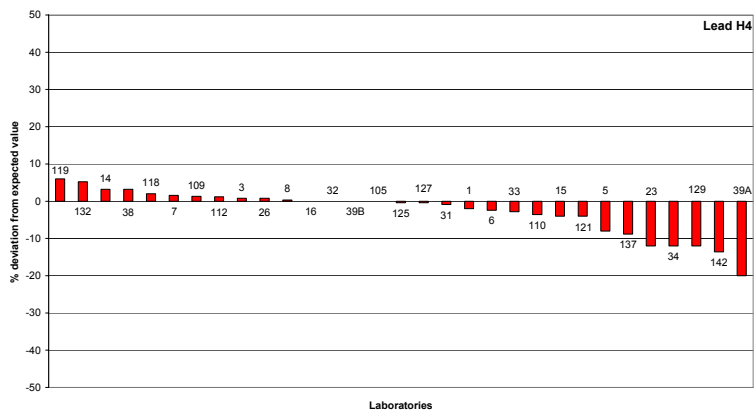
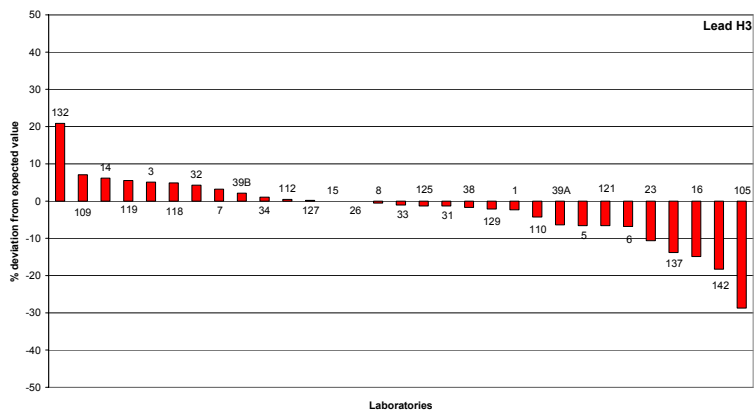
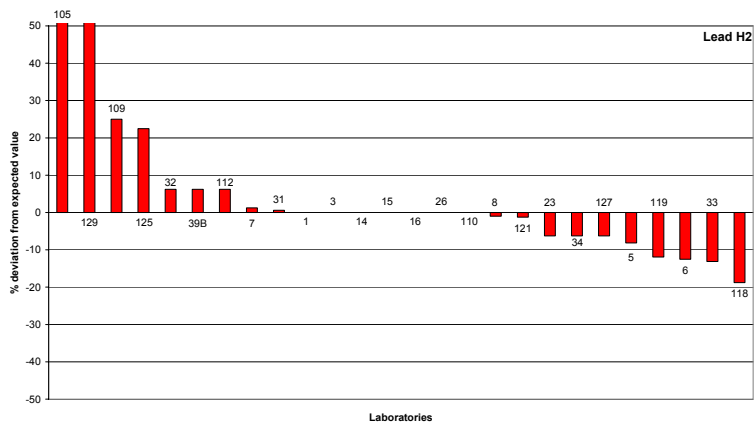
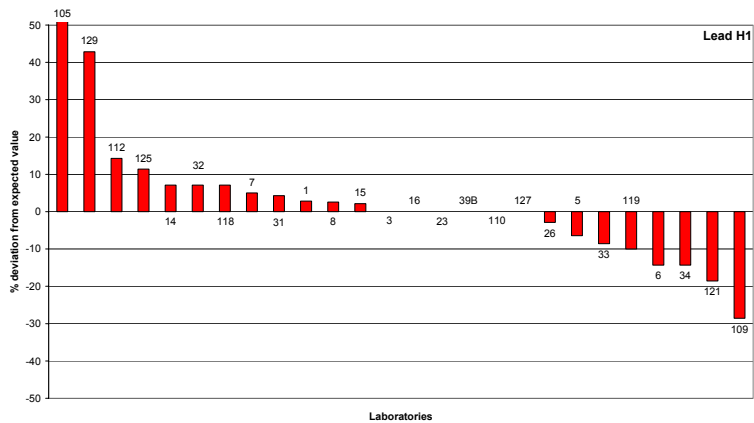


Figure A2.7: Results from determination of Pb.

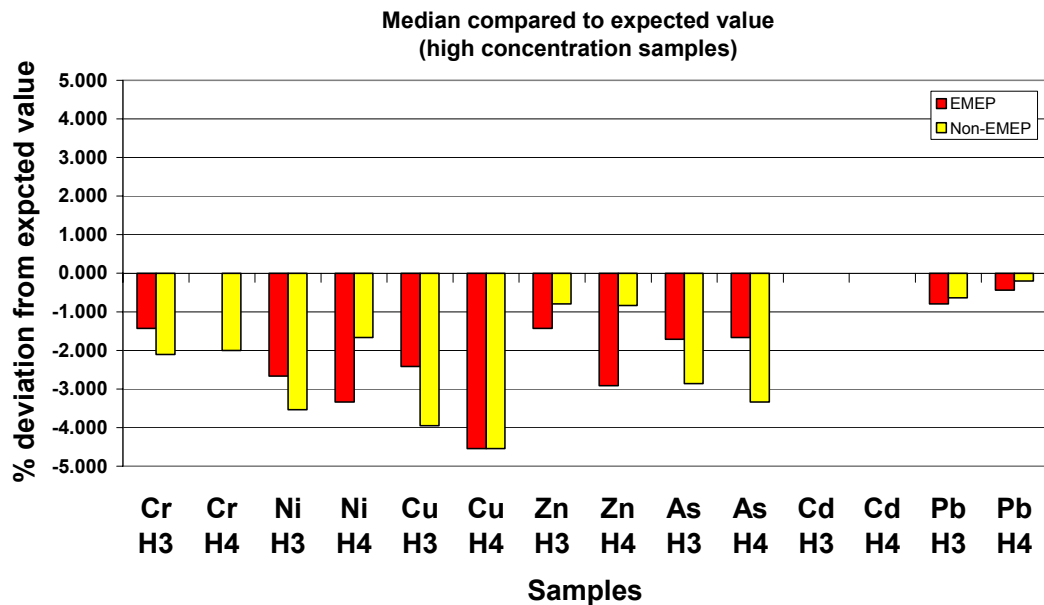
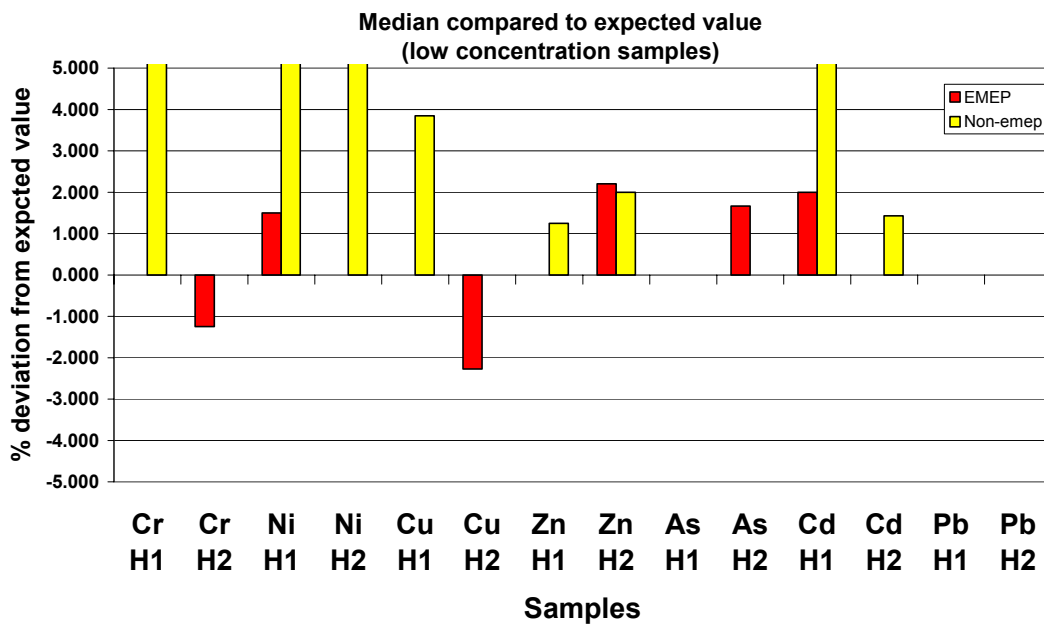


Figure A2.8: The median compared to theoretical value for low and high concentration samples, respectively.