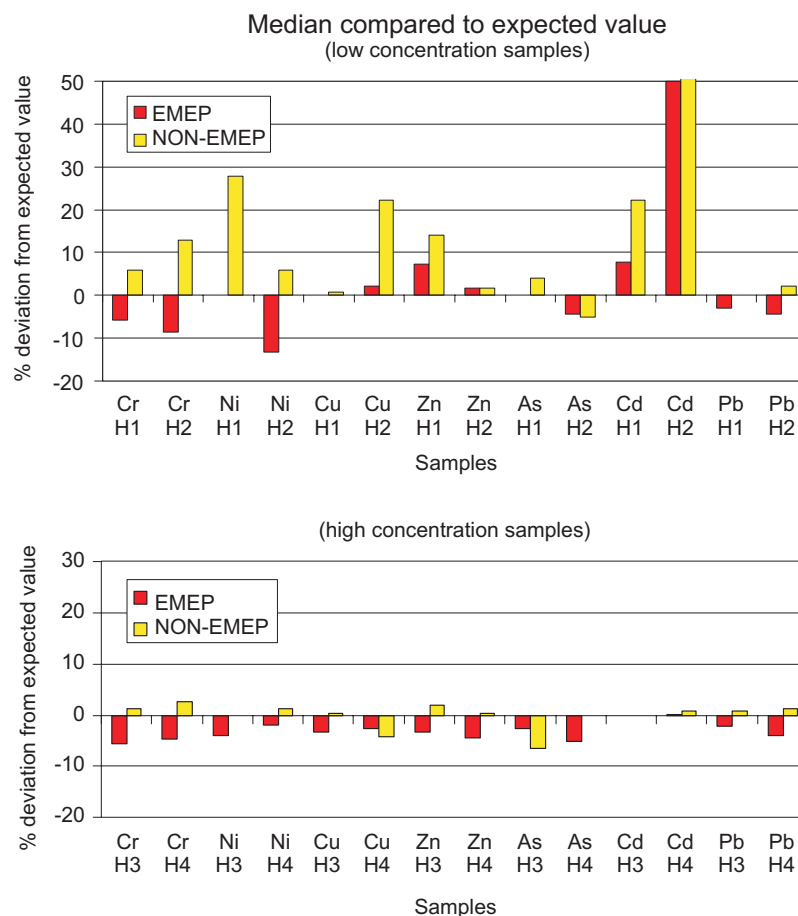


Analytical intercomparison of heavy metals in precipitation 2000

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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 2000**

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Analytical intercomparison of heavy metals in precipitation 2000

1. Introduction

Heavy metals were included in the EMEP's monitoring programme in 1999. 21 laboratories are reporting data to the heavy metal data base. 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 two intercomparisons have been arranged (Berg and Semb, 1995; Berg and Aas, 1999).

This report presents results from the third analytical intercomparison of heavy metals in precipitation which was carried out during 2000. Seven heavy metals were included: Pb, Cd, Cu, Zn, As, Cr, and Ni.

2. Organization of the intercomparison

The samples for the third intercomparison were prepared and distributed to 37 laboratories. In addition to the 21 EMEP laboratories, 16 other laboratories, most of them connected to the ICP-forest measurement programme, also received samples. A total of 29 laboratories, 18 from the EMEP network and 11 from other measurement programmes, reported within the end of October. 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 A1.1b 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% HNO₃. The distributed synthetic precipitation samples contained Pb, Cd, Cu, Zn, As, Cr, and Ni in 0.5% HNO₃. 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% HNO₃ for 4 days. Preparation of the intercomparison samples was carried out in a clean room area.

4. Presentation of data

Tables A.1.2-A.1.8 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 A.2.8.

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

Table A.1.10 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 A.1.9. The results reported from the participating laboratories were generally in accordance with the theoretical values, with a good agreement between the median from the second runs and the expected values.

5.1 Chromium (Cr)

A total of 26 laboratories have reported results for Cr, which included 5 values below detection limits for the low concentration samples and two for the high concentration samples. Six laboratories reported results from the low concentration samples that were more than 25% from expected value, whereas one laboratory reported results that deviated more than 25% from expected value for the high concentration samples. The relative standard deviations were 11.5%–24.8% for the low concentration samples, when outliers were excluded. This was higher than in the last intercomparison. For the high concentration samples the relative standard deviation was 9.4%–11.9% when outliers were excluded, which was slightly better than in the last intercomparison.

5.2 Nickel (Ni)

26 laboratories have reported results for Ni. This included 7 values below limits of detection for the low concentration samples and 2 values below limit of detection for high concentration samples. 8 laboratories reported values that deviate more

than 25% from expected value. The relative standard deviations for the low concentration samples were 18.3%–29.5%. The relative standard deviations for the high concentration samples were 15.8%–12.4%. For both high and low concentrations this was about the same as reported in the last intercomparison.

5.3 Copper (Cu)

Results are obtained from 28 laboratories. This included 8 values below detection limit for the low concentration samples. Six laboratories reported values that deviate more than 25% from expected value. The relative standard deviation for the low concentration samples H1 and H2 were 15.9% and 51.9%, respectively. The relative standard deviation for the high concentration samples H3 and H4 were 10.2% and 9.7%, respectively. With the exception of H2, this was an improvement compared to the results obtained last year.

5.4 Zinc (Zn)

27 laboratories reported results for Zn. This included 8 values below detection limit for the low concentration samples. Seven laboratories reported values that deviate more than 25% from expected value. The relative standard deviation for the low concentration samples was 17.6%–25.4%. This was higher than last year's results. For the high concentration samples, the relative standard deviation was 8.5%–10.0%. This was an improvement compared to the results reported last year.

5.5 Arsenic (As)

A total of 21 laboratories reported results for As. This included 10 values below detection limit for the low concentration samples. Four laboratories report values that deviate more than 25% from expected value. The relative standard deviation for the low concentration samples was 19.0%–21.2%. This was higher than reported in the last intercomparison. The relative standard deviation for the high concentration samples was 7.9%–16.1%. This was about the same as reported last year.

5.6 Cadmium (Cd)

A total of 29 laboratories reported results for Cd. This included 18 values below detection limit for the low concentration samples. It should be noted that the Cd concentration given in sample H2 was extremely low and that 16 of the results below detection limit were reported for this sample. The relative standard deviation for the low concentration samples was 18.5%–66.2%. The relative standard deviation for the high concentration samples was 19.8%–20.9%. This was better than in the last intercomparison.

5.7 Lead (Pb)

29 laboratories reported results for Pb. This included 5 values below detection limit. 7 laboratories report results that deviate more than 25% from expected value. The relative standard deviation is 23.2%–17.2% for the low concentration samples when outliers are excluded. This was slightly higher than last year's result. The relative standard deviation for the high concentration samples was 6.8%–6.6% when outliers were excluded. This was better than in the last intercomparison.

6. Conclusions and further work

A total of 30 laboratories participated in the intercomparison on heavy metals.

The elements showed the following order of success: Pb>Cr>Zn>As>Ni>Cu>Cd. This is a different order than last years results which showed Zn as the least and Cr as the most successful element. For all the samples analysed the deviations from the theoretical values were calculated. The median deviations for the EMEP laboratories were below 13.3% (exclusive the median value for Cd in sample H2) and below 5.7% for the low- and high concentration samples, respectively. This is a marked improvement from last year's results. The median deviations for the rest of the participating laboratories were below 27.8% (exclusive the median value for Cd in sample H2) and below 6.5% for the low- and high concentration samples, respectively.

In 2001 the non-European laboratories within WMO/GAW will also participate in the intercomparison of heavy metals in precipitation.

It is in course of preparation to arrange a field intercomparison on Hg in precipitation and air during 2002. Germany has offered to be the host country.

7. References

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- Berg, T. and Semb, A. (1995) Preliminary results from HELCOM-EMEP-PARCOM-AMAP analytical intercomparison of heavy metals in precipitation. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Note 1/95).
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Appendix 1

Tables

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

No	Laboratory identification
1	Federal Environmental Agency, Austria
3	Czech Hydrometeorological Institute, Czech Republic
5	Finnish Meteorological Institute, Finland
6	Laboratories Wolf, France
7	IfE Leipzig GmbH, Umweltlaborator., 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
19	Instituto de Salud Carlos III, Centro Nacional de Sanidad Ambiental Area de Contaminacion Atmosferica, Spain
23	AEA Technology, National Environmental Techn. Centre, United Kingdom
24	Federal Hydrometeorological Institute, Yugoslavia
26	Ontario Ministry of Environment, Canada
31	Slovak Hydrometeorological Institute, Slovakia
32	Institute of physics, Aerosol research laboratory, Lithuania
33	Latvian Hydrometeorological Agency, Latvia
36	Hydrometeorological Institute of Slovenia, Slovenia
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.

No	Laboratory identification
108	Institut f. Bodenkunde und Standortlehre, Germany
110	Thüringer Landesanstalt für Landwirtschaft (TTL), Germany
112	Niedersächsische Forstliche Versuchsanstalt (NVF), Germany
115	Bayerische Landesanstalt f. Wald- und Forstwirtschaft, Germany
117	Sächsische Landesanstalt für Forsten, Germany
118	Forstliche Versuchs- und Forschungsanstalt Baden-Württemberg, Germany
119	Landesumweltamt (LUA)
120	Landwirtschaftliche Untersuchungs- und Forschungsanstalt (LUFA), Germany
121	Landesamt für Natur und Umwelt, Germany
123	Limnological Institute, Russia

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

<p>Cr SAMPLE NO.: H1 THEORETICAL VALUE 1.700 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 25 ARITHMETIC MEAN VALUE: 1.758 MEDIAN: 1.720 STANDARD DEVIATION: 0.295 REL. ST. DEVIATION (%): 16.773</p> <p>RUN 2: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 1.690 MEDIAN: 1.700 STANDARD DEVIATION: 0.194 REL. ST. DEVIATION (%): 11.512</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 118 < 3 3 2.500 * 1 1.720 31 2.470 * 5 1.700 123 2.150 14 1.700 110 1.900 23 1.700 38 1.860 16 1.600 119 1.840 32 1.600 112 1.800 120 1.600 117 1.800 15 1.500 121 1.800 39 1.500 8 1.790 26 1.440 115 1.770 7 1.400 36 1.300</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Cr SAMPLE NO.: H2 THEORETICAL VALUE 0.700 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 0.752 MEDIAN: 0.700 STANDARD DEVIATION: 0.229 REL. ST. DEVIATION (%): 30.380</p> <p>RUN 2: NUMBER OF LABORATORIES: 20 ARITHMETIC MEAN VALUE: 0.721 MEDIAN: 0.700 STANDARD DEVIATION: 0.179 REL. ST. DEVIATION (%): 24.797</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 38 < 1 39 < 1 3 1.400 * 5 0.700 31 1.130 14 0.700 123 1.080 120 0.700 115 0.910 1 0.680 110 0.800 23 0.640 117 0.800 32 0.640 121 0.780 26 0.610 112 0.760 16 0.600 8 0.730 15 0.580 119 0.730 36 0.500 7 0.340</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>
<p>Cr SAMPLE NO.: H3 THEORETICAL VALUE 5.300 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 26 ARITHMETIC MEAN VALUE: 5.310 MEDIAN: 5.300 STANDARD DEVIATION: 0.897 REL. ST. DEVIATION (%): 16.902</p> <p>RUN 2: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 5.177 MEDIAN: 5.250 STANDARD DEVIATION: 0.616 REL. ST. DEVIATION (%): 11.899</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 108 8.500 * 110 5.300 38 6.520 120 5.200 3 6.000 1 5.190 31 5.950 39 5.100 5 5.000 117 5.800 16 5.000 115 5.530 32 4.900 112 5.470 15 4.800 8 5.440 26 4.790 7 4.710 121 5.400 36 4.400 119 5.370 118 4.000 123 5.370 23 3.700 14 5.300</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Cr SAMPLE NO.: H4 THEORETICAL VALUE 4.200 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 26 ARITHMETIC MEAN VALUE: 4.195 MEDIAN: 4.200 STANDARD DEVIATION: 0.524 REL. ST. DEVIATION (%): 12.481</p> <p>RUN 2: NUMBER OF LABORATORIES: 23 ARITHMETIC MEAN VALUE: 4.191 MEDIAN: 4.200 STANDARD DEVIATION: 0.397 REL. ST. DEVIATION (%): 9.483</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 38 5.490 * 108 4.200 31 5.050 120 4.100 3 4.900 1 4.080 115 4.840 16 4.000 123 4.580 23 4.000 32 4.000 117 4.400 5 3.900 121 4.400 39 3.900 15 3.800 8 4.360 26 3.780 112 4.310 7 3.670 110 4.300 36 3.400 119 4.220 118 3.000 * 14 4.200</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>

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

<p>Ni SAMPLE NO.: H1 THEORETICAL VALUE 0.700 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 21 ARITHMETIC MEAN VALUE: 0.728 MEDIAN: 0.700 STANDARD DEVIATION: 0.237 REL. ST. DEVIATION (%): 32.501</p> <p>RUN 2: NUMBER OF LABORATORIES: 17 ARITHMETIC MEAN VALUE: 0.720 MEDIAN: 0.700 STANDARD DEVIATION: 0.132 REL. ST. DEVIATION (%): 18.277</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 117 1.400 * 1 0.700 39 < 1.000 121 1.000 5 0.700 123 0.990 14 0.700 16 0.630 3 0.800 15 0.620 110 0.800 26 0.620 112 0.780 23 0.600 31 0.750 36 0.600 32 0.740 7 0.497 8 0.710 120 0.200 *</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Ni SAMPLE NO.: H2 THEORETICAL VALUE 0.600 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 0.592 MEDIAN: 0.570 STANDARD DEVIATION: 0.218 REL. ST. DEVIATION (%): 36.800</p> <p>RUN 2: NUMBER OF LABORATORIES: 16 ARITHMETIC MEAN VALUE: 0.556 MEDIAN: 0.550 STANDARD DEVIATION: 0.164 REL. ST. DEVIATION (%): 29.568</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 118 < 2 115 < 1.35 8 0.580 123 1.170* 112 0.570 39 < 1.000 117 1.000 26 0.530 119 < 0.9 15 0.510 110 0.700 121 < 0.5 32 0.650 3 0.500 1 0.600 23 0.500 5 0.600 36 0.500 14 0.600 16 0.460 7 < 0.4 31 0.400 120 0.200</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>
<p>Ni SAMPLE NO.: H3 THEORETICAL VALUE 7.700 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 26 ARITHMETIC MEAN VALUE: 7.186 MEDIAN: 7.410 STANDARD DEVIATION: 1.351 REL. ST. DEVIATION (%): 18.797</p> <p>RUN 2: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 7.333 MEDIAN: 7.480 STANDARD DEVIATION: 1.159 REL. ST. DEVIATION (%): 15.810</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 108 9.800 5 7.400 117 9.400 16 7.400 115 8.130 39 7.400 32 7.100 119 7.950 120 7.100 14 7.900 38 7.840 26 6.980 8 7.830 15 6.600 110 7.700 36 6.500 112 7.700 7 5.300 121 7.700 23 5.200 3 7.600 118 4.500 1 7.550 123 3.670 * 31 7.410</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Ni SAMPLE NO.: H4 THEORETICAL VALUE 9.800 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 26 ARITHMETIC MEAN VALUE: 9.149 MEDIAN: 9.620 STANDARD DEVIATION: 1.463 REL. ST. DEVIATION (%): 15.990</p> <p>RUN 2: NUMBER OF LABORATORIES: 24 ARITHMETIC MEAN VALUE: 9.333 MEDIAN: 9.660 STANDARD DEVIATION: 1.160 REL. ST. DEVIATION (%): 12.425</p> <p>RESULTS IN DECREASING ORDER: 108 11.700 5 9.400 121 11.000 32 9.200 115 10.450 8 10.200 120 9.000 119 10.100 26 8.810 6 < 10 112 9.930 15 8.300 14 9.900 23 8.300 38 9.890 36 8.300 31 9.790 118 7.400 16 9.700 7 7.110 110 9.700 117 6.900 39 9.700 1 9.620 123 4.720 * 3 9.600</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>

Table A1.4: Analytical results for Cu in synthetic precipitation samples.

<p>Cu SAMPLE NO.: H1 THEORETICAL VALUE 1.400 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 27 ARITHMETIC MEAN VALUE: 1.668 MEDIAN: 1.400 STANDARD DEVIATION: 1.290 REL. ST. DEVIATION (%): 77.316</p> <p>RUN 2: NUMBER OF LABORATORIES: 22 ARITHMETIC MEAN VALUE: 1.403 MEDIAN: 1.400 STANDARD DEVIATION: 0.223 REL. ST. DEVIATION (%): 15.906</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 24 7.500 * 14 1.400 33 2.030 16 1.350 118 < 2 121 1.340 73 1.690 15 1.300 119 < 1.68 23 1.300 3 1.600 117 1.300 39 1.600 26 1.230 110 1.600 120 1.200 31 1.580 32 1.100 8 1.470 36 1.100 115 1.420 38 < 1 112 1.410 7 1.050 1 1.400 5 1.400</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Cu SAMPLE NO.: H2 THEORETICAL VALUE 0.900 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 27 ARITHMETIC MEAN VALUE: 1.224 MEDIAN: 0.970 STANDARD DEVIATION: 1.087 REL. ST. DEVIATION (%): 88.763</p> <p>RUN 2: NUMBER OF LABORATORIES: 22 ARITHMETIC MEAN VALUE: 1.025 MEDIAN: 0.960 STANDARD DEVIATION: 0.533 REL. ST. DEVIATION (%): 51.981</p> <p>RESULTS IN DECREASING ORDER: 6 < 10 118 < 2 24 5.600* 1 0.970 120 3.100 16 0.950 119 < 1.68 121 0.950 8 1.360 23 0.920 123 1.350 14 0.900 5 1.100 15 0.900 110 1.100 26 0.900 117 1.100 112 0.820 31 1.030 36 0.800 115 1.010 7 0.640 38 < 1 39 0.600 3 1.000 33 0.060 32 1.000</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>
<p>Cu SAMPLE NO.: H3 THEORETICAL VALUE 15.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 14.697 MEDIAN: 14.650 STANDARD DEVIATION: 2.178 REL. ST. DEVIATION (%): 14.816</p> <p>RUN 2: NUMBER OF LABORATORIES: 25 ARITHMETIC MEAN VALUE: 14.861 MEDIAN: 14.800 STANDARD DEVIATION: 1.515 REL. ST. DEVIATION (%): 10.197</p> <p>RESULTS IN DECREASING ORDER: 24 20.000 * 16 14.500 123 19.000 118 14.500 38 17.800 32 14.200 108 17.500 119 14.100 117 16.300 112 14.070 8 15.600 26 14.040 14 15.300 7 14.000 115 15.140 110 13.900 3 15.100 6 13.300 110 15.100 15 13.000 31 15.020 39 12.900 121 15.000 33 12.550 1 14.800 6 10.000* 5 14.800 23 10.000*</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Cu SAMPLE NO.: H4 THEORETICAL VALUE 12.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 11.537 MEDIAN: 11.600 STANDARD DEVIATION: 1.595 REL. ST. DEVIATION (%): 13.824</p> <p>RUN 2: NUMBER OF LABORATORIES: 26 ARITHMETIC MEAN VALUE: 11.563 MEDIAN: 11.600 STANDARD DEVIATION: 1.122 REL. ST. DEVIATION (%): 9.700</p> <p>RESULTS IN DECREASING ORDER: 123 15.500 * 16 11.700 38 13.600 7 11.500 108 13.300 118 11.500 117 12.800 119 11.500 8 12.700 121 11.500 14 12.500 26 11.280 32 12.300 62 11.230 31 12.280 15 11.000 115 12.210 36 10.700 3 12.200 39 10.300 1 12.000 33 10.040 110 12.000 6 10.000 5 11.900 23 9.700 120 8.900 24 6.900 *</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>

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

<p>Cd SAMPLE NO.: H1 THEORETICAL VALUE 0.090 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 0.127 MEDIAN: 0.100 STANDARD DEVIATION: 0.140 REL. ST. DEVIATION (%): 110.001</p> <p>RUN 2: NUMBER OF LABORATORIES: 23 ARITHMETIC MEAN VALUE: 0.099 MEDIAN: 0.100 STANDARD DEVIATION: 0.018 REL. ST. DEVIATION (%): 18.581</p> <p>RESULTS IN DECREASING ORDER: 6 < 2 24 0.780 * 39 < 0.3 15 0.099 19 < 0.2 31 0.098 115 0.140 3 0.097 118 0.140 5 0.090 119 0.117 26 0.090 14 0.110 36 0.090 112 0.110 123 0.086 117 0.110 33 0.081 7 0.105 23 0.075 8 0.104 32 0.075 110 < 0.1 16 0.061 1 0.100 38 0.100 120 0.100 121 0.100</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Cd SAMPLE NO.: H2 THEORETICAL VALUE 0.007 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 0.035 MEDIAN: 0.014 STANDARD DEVIATION: 0.068 REL. ST. DEVIATION (%): 193.915</p> <p>RUN 2: NUMBER OF LABORATORIES: 11 ARITHMETIC MEAN VALUE: 0.016 MEDIAN: 0.011 STANDARD DEVIATION: 0.010 REL. ST. DEVIATION (%): 66.267</p> <p>RESULTS IN DECREASING ORDER: 6 < 2 39 < 0.3 24 0.250 * 36 < 0.02 19 < 0.2 121 < 0.02 110 < 0.1 8 0.006 112 < 0.1 33 0.020 118 < 0.1 31 0.019 120 < 0.1 7 0.016 115 < 0.06 15 0.011 117 < 0.05 5 0.010 26 < 0.05 14 0.010 3 < 0.04 16 0.008 1 < 0.04 23 0.005 73 0.038 119 < 0.03 32 < 0.03 38 0.03</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>
<p>Cd SAMPLE NO.: H3 THEORETICAL VALUE 1.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 1.207 MEDIAN: 1.000 STANDARD DEVIATION: 1.441 REL. ST. DEVIATION (%): 119.418</p> <p>RUN 2: NUMBER OF LABORATORIES: 27 ARITHMETIC MEAN VALUE: 0.937 MEDIAN: 1.000 STANDARD DEVIATION: 0.186 REL. ST. DEVIATION (%): 19.847</p> <p>RESULTS IN DECREASING ORDER: 24 8.500 * 39 1.000 6 < 2 108 1.000 19 1.150 70 1.000 112 1.090 26 0.980 31 1.062 1 0.970 115 1.060 33 0.957 16 1.030 38 0.920 118 1.020 36 0.900 119 1.020 110 0.900 7 1.017 121 0.900 8 1.010 32 0.850 3 1.000 23 0.620 5 1.000 123 0.610 14 1.000 117 0.220 15 1.000</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Cd SAMPLE NO.: H4 THEORETICAL VALUE 1.400 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 1.478 MEDIAN: 1.407 STANDARD DEVIATION: 0.852 REL. ST. DEVIATION (%): 57.669</p> <p>RUN 2: NUMBER OF LABORATORIES: 27 ARITHMETIC MEAN VALUE: 1.325 MEDIAN: 1.403 STANDARD DEVIATION: 0.277 REL. ST. DEVIATION (%): 20.873</p> <p>RESULTS IN DECREASING ORDER: 24 5.600 * 15 1.400 6 < 2 120 1.400 108 1.600 1 1.360 16 1.540 26 1.350 19 1.500 5 1.300 39 1.500 36 1.300 31 1.486 110 1.300 118 1.470 121 1.300 3 1.450 32 1.260 14 1.450 38 1.240 115 1.450 23 1.000 7 1.440 123 0.810 112 1.440 117 0.200 119 1.420 8 1.410 8 1.410 33 1.403</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>

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

<p>Pb SAMPLE NO.: H1 THEORETICAL VALUE 2.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 2.397 MEDIAN: 2.000 STANDARD DEVIATION: 2.746 REL. ST. DEVIATION (%): 114.579</p> <p>RUN 2: NUMBER OF LABORATORIES: 25 ARITHMETIC MEAN VALUE: 1.865 MEDIAN: 2.000 STANDARD DEVIATION: 0.434 REL. ST. DEVIATION (%): 23.251</p> <p>RESULTS IN DECREASING ORDER: 24 15.700 * 6 < 10 39 < 3 118 2.400 120 2.000 119 2.320 38 1.980 3 2.200 115 1.940 8 2.170 15 1.900 31 2.110 123 1.900 5 2.100 26 1.700 14 2.100 36 1.700 112 2.100 32 1.600 117 2.100 23 1.500 1 2.050 7 1.420 16 2.000 108 < 1.4 110 2.000 19 0.850 33 0.480</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Pb SAMPLE NO.: H2 THEORETICAL VALUE 4.500 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 4.857 MEDIAN: 4.500 STANDARD DEVIATION: 2.494 REL. ST. DEVIATION (%): 51.346</p> <p>RUN 2: NUMBER OF LABORATORIES: 26 ARITHMETIC MEAN VALUE: 4.398 MEDIAN: 4.470 STANDARD DEVIATION: 0.756 REL. ST. DEVIATION (%): 17.193</p> <p>RESULTS IN DECREASING ORDER: 24 16.770 * 6 < 10 39 7.000 38 4.440 120 5.000 31 4.420 23 4.930 3 4.400 119 4.890 15 4.300 5 4.800 118 4.200 8 4.750 16 4.100 122 4.740 32 4.100 14 4.700 26 3.850 110 4.600 7 3.740 117 4.600 36 3.600 115 4.550 33 3.580 1 4.500 19 3.170 121 4.500 23 2.900 108 < 1.4</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>
<p>Pb SAMPLE NO.: H3 THEORETICAL VALUE 58.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 57.013 MEDIAN: 57.600 STANDARD DEVIATION: 6.292 REL. ST. DEVIATION (%): 11.036</p> <p>RUN 2: NUMBER OF LABORATORIES: 27 ARITHMETIC MEAN VALUE: 57.274 MEDIAN: 57.600 STANDARD DEVIATION: 3.910 REL. ST. DEVIATION (%): 6.826</p> <p>RESULTS IN DECREASING ORDER: 117 72.000 * 33 57.560 123 68.000 1 57.000 14 64.000 120 57.000 5 61.000 7 56.600 8 60.800 19 56.150 3 59.900 32 55.000 118 59.800 26 54.700 119 59.300 15 54.000 112 58.670 108 53.900 110 58.500 38 53.700 16 58.000 24 51.630 121 58.000 39 51.000 115 57.810 36 49.000 31 57.770 23 35.000 * 6 57.600</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>	<p>Pb SAMPLE NO.: H4 THEORETICAL VALUE 45.000 UNIT: ng/ml</p> <p>RUN 1: NUMBER OF LABORATORIES: 29 ARITHMETIC MEAN VALUE: 43.794 MEDIAN: 45.000 STANDARD DEVIATION: 3.782 REL. ST. DEVIATION (%): 8.635</p> <p>RUN 2: NUMBER OF LABORATORIES: 28 ARITHMETIC MEAN VALUE: 44.251 MEDIAN: 45.000 STANDARD DEVIATION: 2.924 REL. ST. DEVIATION (%): 6.608</p> <p>RESULTS IN DECREASING ORDER: 123 50.500 121 45.000 117 48.600 1 44.400 8 47.800 120 44.000 14 47.200 33 43.410 5 47.000 15 43.000 31 46.540 32 42.600 3 45.800 7 42.500 112 45.800 26 42.300 115 45.620 19 42.100 110 45.600 24 41.750 119 45.500 108 39.400 38 45.200 6 39.300 118 45.100 36 39.000 16 45.000 39 39.000 23 31.000 *</p> <p>< : DATA UNUSED IN RUN 1 AND 2 * : DATA UNUSED IN RUN 2</p>

Table A1.9 Percentage deviation from theoretical concentration value.

Element and percent interval	No. of laboratories			Lab. Identification <i>The number in brackets are number of results reported in the particular percent interval by the laboratory</i>
	EMEP	Other	Total	
Cr				
0-10%	9	9	18	1(4), 5(4), 8(4), 14(4), 15(2), 16(3), 23(3), 26(2), 32(2), 39(2), 110(29), 112(4), 115(2), 117(39), 119(4), 120(4), 121(3), 123(2)
10-25%	8	6	14	3(2), 7(3), 15(2), 16(1), 26(2), 31(1), 36(2), 38(2), 39(1), 110(2), 115(1), 117(1), 118(1), 121(1)
>25%	6	4	10	3(2), 7(1), 23(1), 31(3), 36(2), 38(1), 108(1), 115(1), 118(1), 123(2)
Ni				
0-10%	11	7	18	1(4), 3(2), 5(4), 8(3), 14(3), 15(1), 16(3), 26(2), 31(3), 32(4), 38(2), 39(2), 110(2), 112(3), 115(2), 119(2), 120(2)
10-25%	5	5	10	3(2), 15(3), 16(1), 23(3), 26(2), 36(4), 108(1), 110(2), 112(1), 121(1)
>25%				7(3), 23(1), 31(3), 108(1), 117(4), 118(2), 120(2), 121(1), 123(4)
Cu				
0-10%	11	10	20	1(4), 3(2), 5(3), 7(2), 8(3), 14(4), 15(3), 16(4), 23(2), 26(3), 31(2), 32(2), 110(2), 112(4), 115(3), 117(3), 118(2), 119(2), 120(1), 121(4)
10-25%	11	7	18	3(2), 5(1), 6(1), 15(1), 23(1), 26(1), 31(2), 32(2), 33(2), 36(4), 38(2), 39(3), 108(2), 115(1), 110(2), 117(1), 120(1), 123(1)
>25%	7	2	9	6(1), 7(2), 8(1), 23(1), 24(4), 33(2), 39(1), 120(2), 123(3)
Zn				
0-10%	13	10	23	1(4), 3(2), 5(3), 7(1), 14(2), 15(4), 16(3), 23(2), 26(4), 31(2), 32(1), 36(1), 38(2), 39(3), 108(2), 110(3), 112(2), 115(2), 118(2), 119(2), 120(3), 121(4), 123(1)
10-25%	12	6	18	3(1), 6(1), 7(1), 8(4), 14(2), 16(1), 24(2), 31(2), 32(1), 36(2), 39(1), 110(1), 112(1), 115(1), 117(4), 120(1), 123(1)
>25%	6	3	9	3(1), 6(1), 7(1), 23(1), 24(2), 32(1), 112(1), 115(1), 123(2)
Cd				
0-10%	14	10	24	1(2), 3(3), 5(3), 8(2), 14(2), 15(2), 16(1), 19(1), 26(3), 31(3), 33(3), 36(2), 38(1), 39(2), 108(1), 110(1), 112(2), 115(2), 118(2), 119(2), 120(2), 121(1)
10-25%	11	5	16	1(1), 8(2), 14(1), 15(1), 16(2), 19(1), 23(1), 108(1), 32(3), 36(1), 38(2), 110(1), 112(1), 117(1), 120(1), 121(2)
>25%	10	5	15	5(1), 7(1), 14(1), 15(1), 16(1), 23(3), 24(4), 31(1), 33(1), 38(1), 115(1), 117(2), 118(1), 119(1), 123(3)
Pb				
0-10%	15	11	26	1(4), 3(3), 5(4), 6(1), 7(2), 8(4), 14(3), 15(4), 16(4), 19(2), 24(2), 26(2), 31(4), 32(4), 33(2), 38(4), 108(1), 110(4), 112(4), 115(4), 117(3), 118(3), 119(3), 120(3), 121(4), 123(2)
10-25%	9	6	15	3(1), 6(1), 7(1), 14(1), 24(1), 26(2), 32(1), 36(3), 39(2), 108(1), 117(1), 118(1), 119(1), 120(1), 123(2)
>25%	6	0	6	7(1), 19(2), 23(4), 24(2), 33(2), 39(1)

Table A1.10: Analytical technique 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, Cd, Pb As	USN-ICP-OES ICP-MS
7	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-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, Zn, Cd, Pb	GF-AAS
19	Cd, Pb	GF-AAS
23	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
24	Cu, Zn, Cd As, Pb	F-AAS HG-F-AAS
26	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
31	Cr, Ni, Cu, Cd, Pb Zn	GF-AAS F-AAS
32	Cr, Ni, Cu, Zn, As, Cd, Pb	GF-AAS
33	Cu, Cd, Pb	GF-AAS
36	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
38	Cr, Ni, Cu, As, Cd, Pb Zn	GF-AAS F-AAS
39	Cr, Ni, Cu, Zn, Cd, Pb	USN-ICP-OES
108	Cr, Ni, Cu, Zn, Cd, Pb	GF-AAS
110	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
112	Cr, Ni, Cu, Zn, Cd, Pb	USN-ICP-MS
115	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS
117	Cr, Ni, Cu, As, Cd, Pb Zn	GF-AAS USN-ICP-OES
118	Cr, Ni, Cu, Cd, Pb Zn	GF-AAS ICP-OES
119	Cr, Ni, Cu, As, Cd, Pb Zn	GF-AAS F-AAS
120	Cr, Ni, Cu, Cd, Pb Zn As	GF-AAS ICP-OES HG-AAS
121	Cr, Ni, Cu, Cd, Pb As Zn	GF-AAS FIA-AAS Voltammetry
123	Cr, Ni, Cu, Zn, As, Cd, Pb	ICP-MS

Appendix 2

Figures

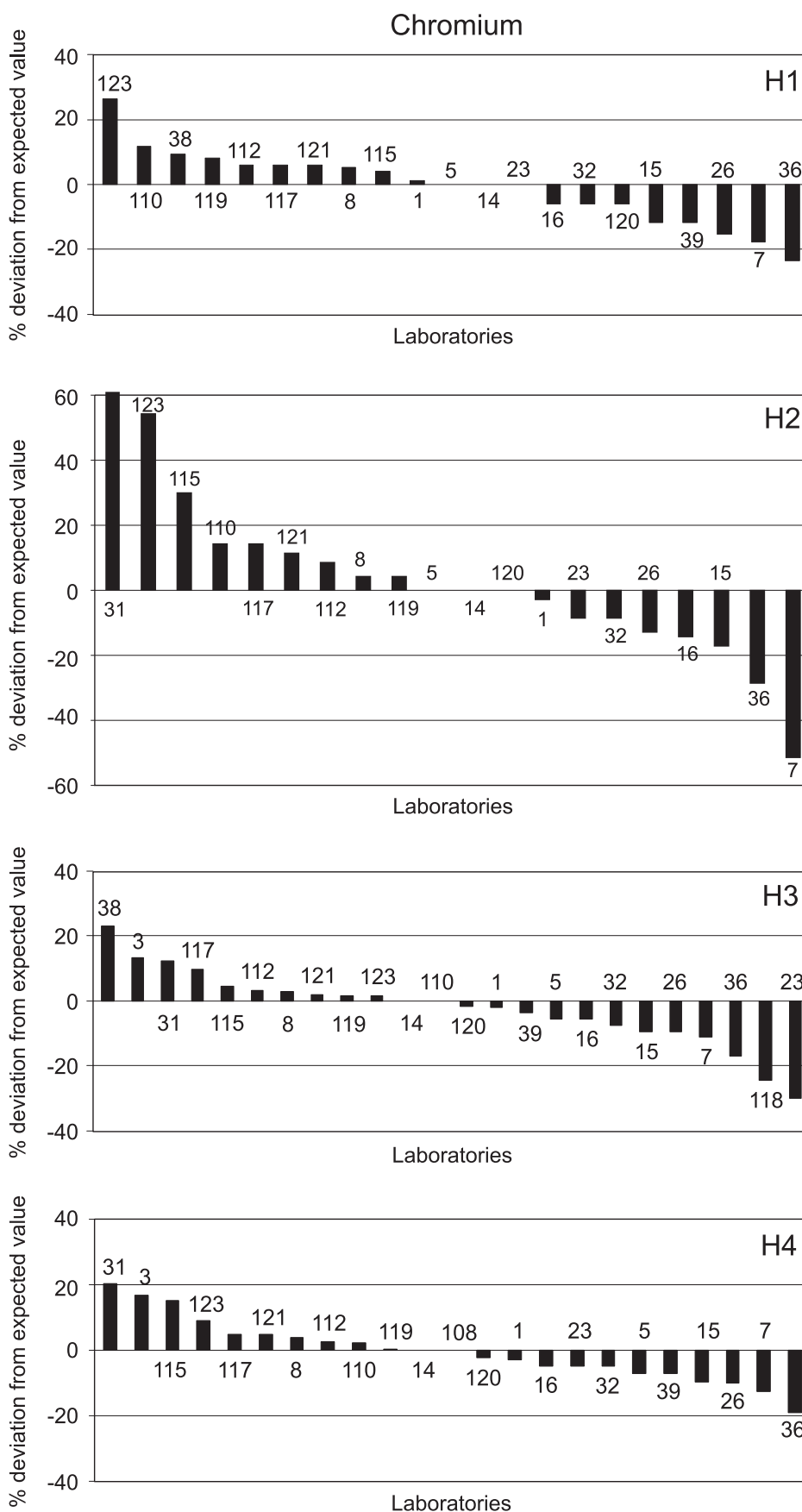


Figure A2.1: Results from determination of Cr.

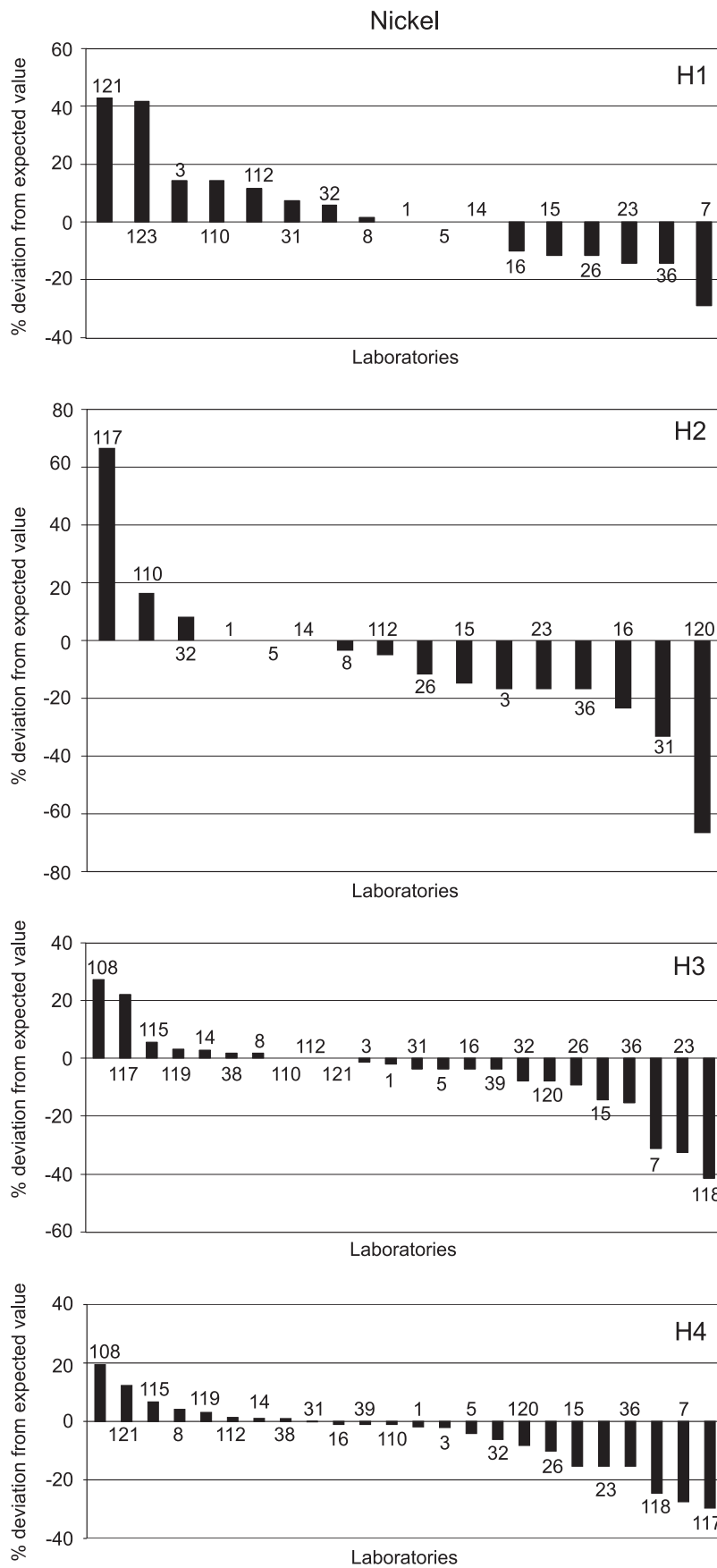


Figure A2.2: Results from determination of Ni.

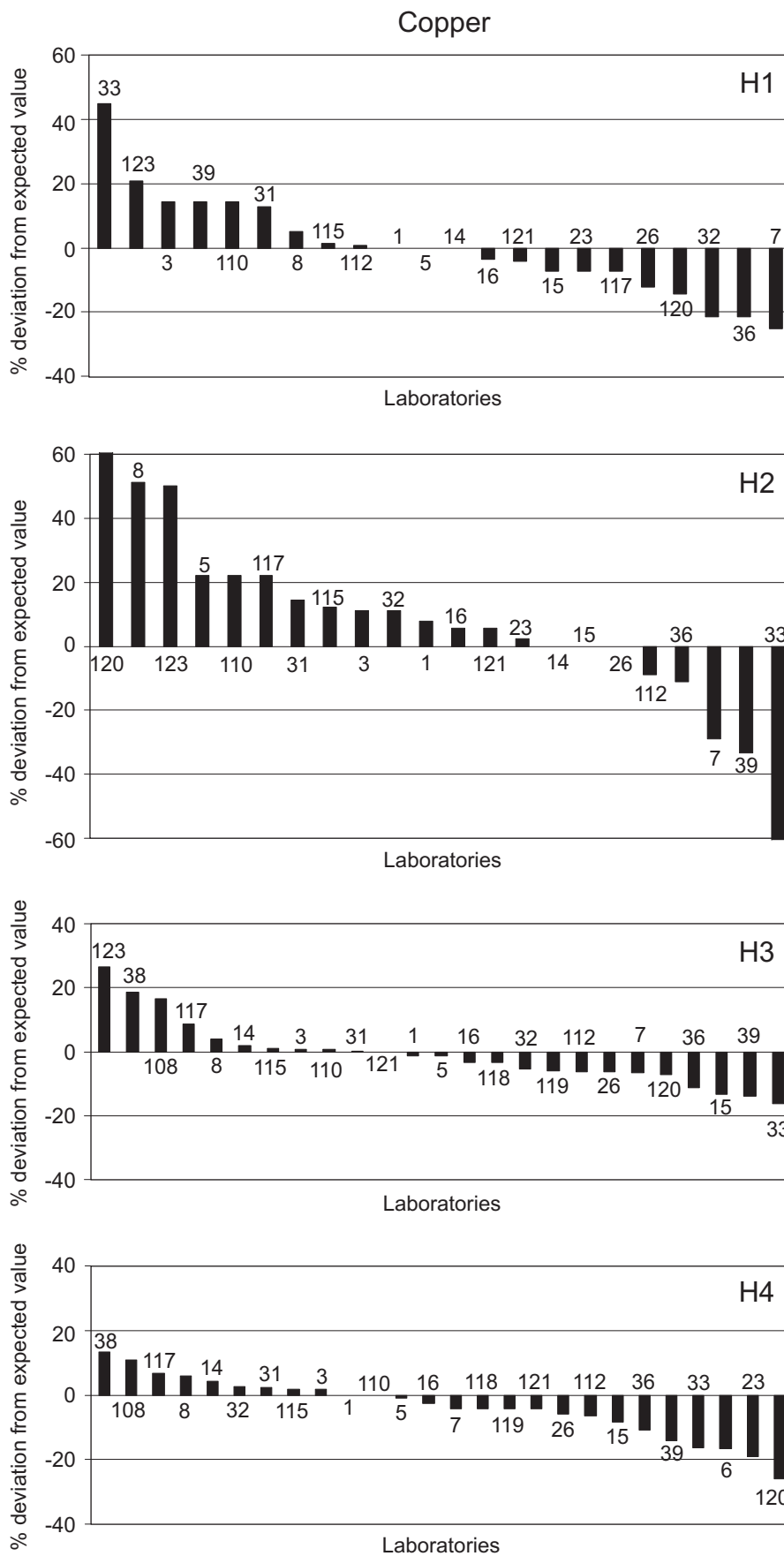


Figure A2.3: Results from determination of Cu.

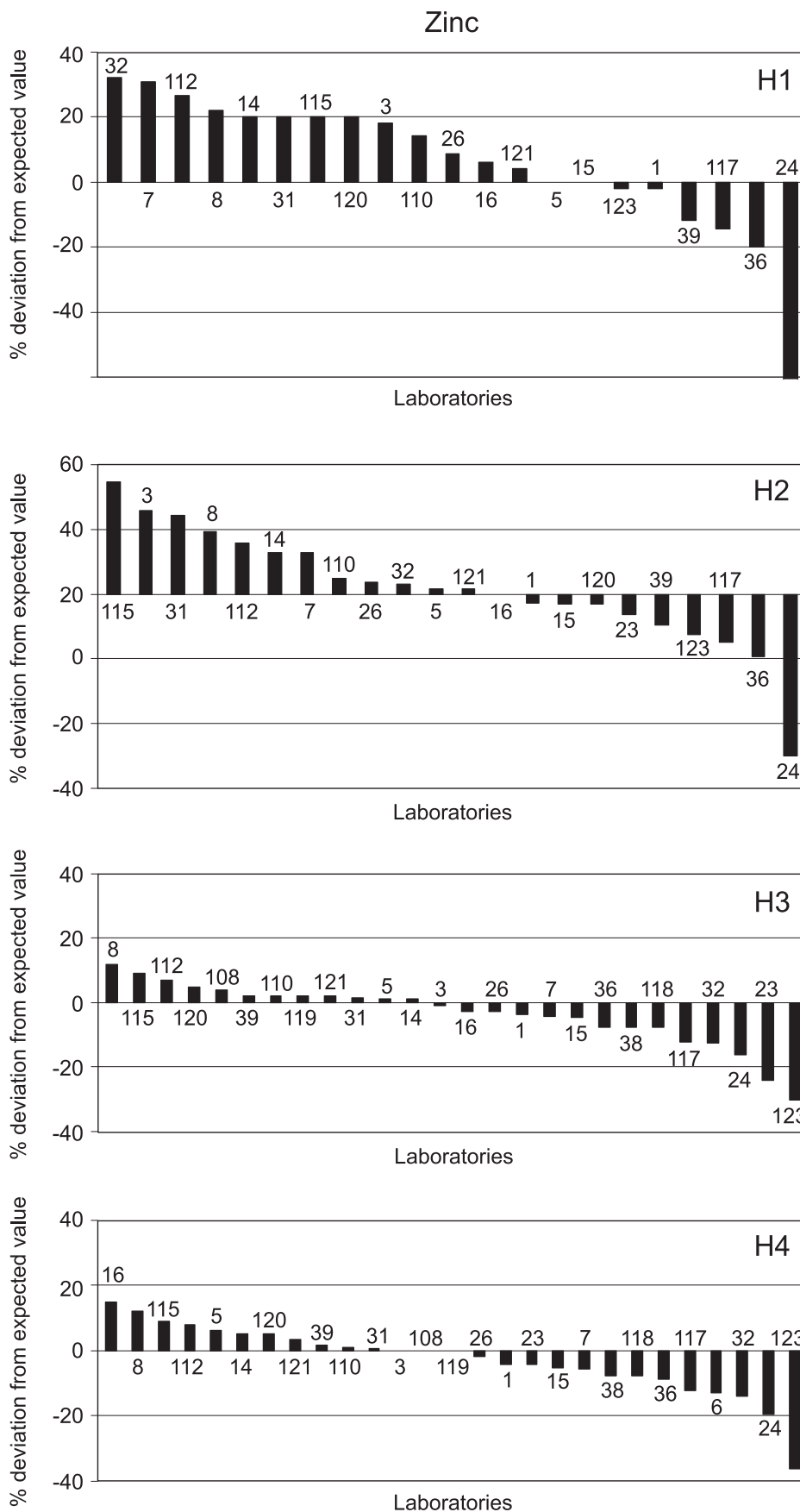


Figure A2.4: Results from determination of Zn.

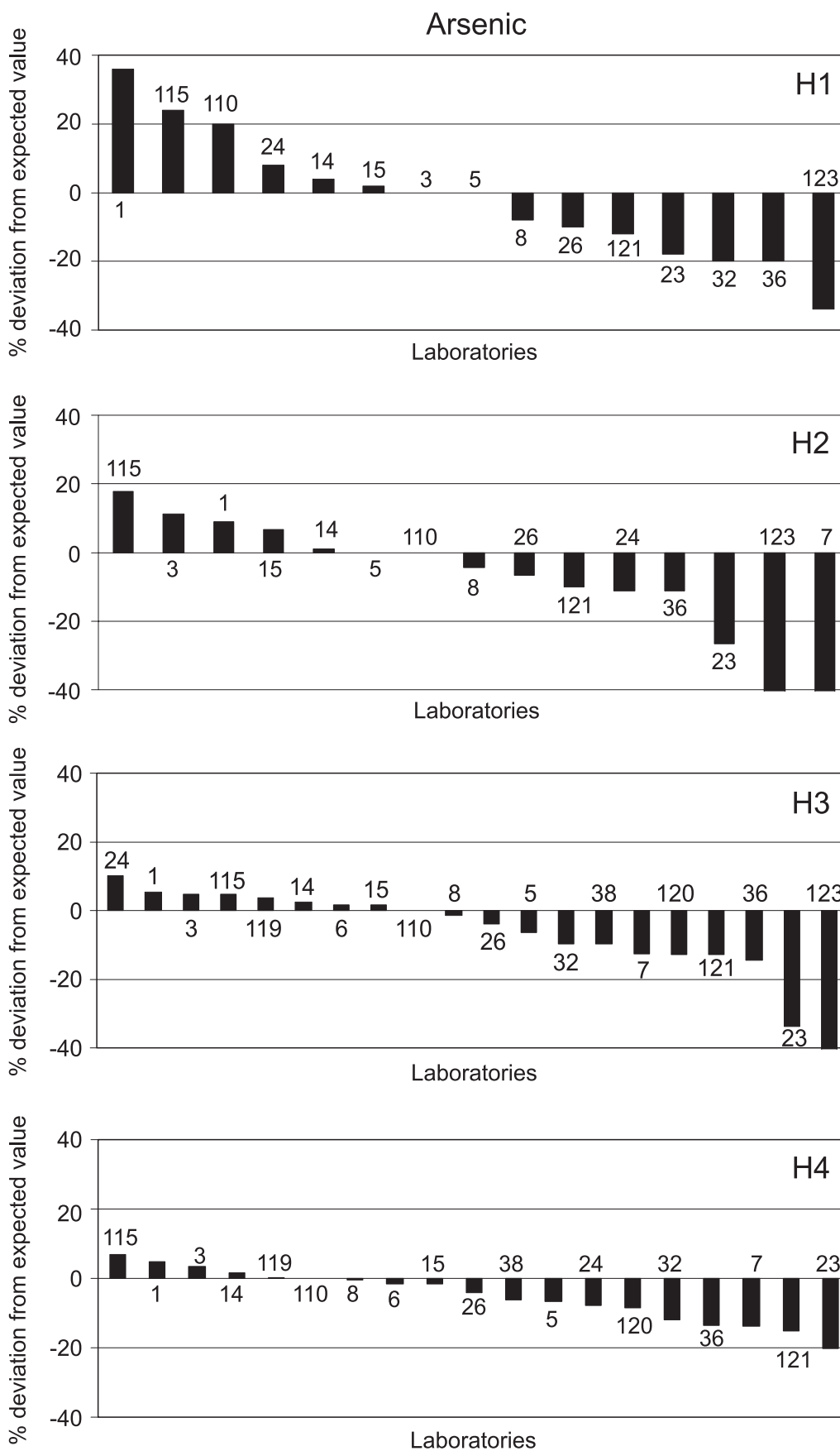


Figure A2.5: Results from determination of As.

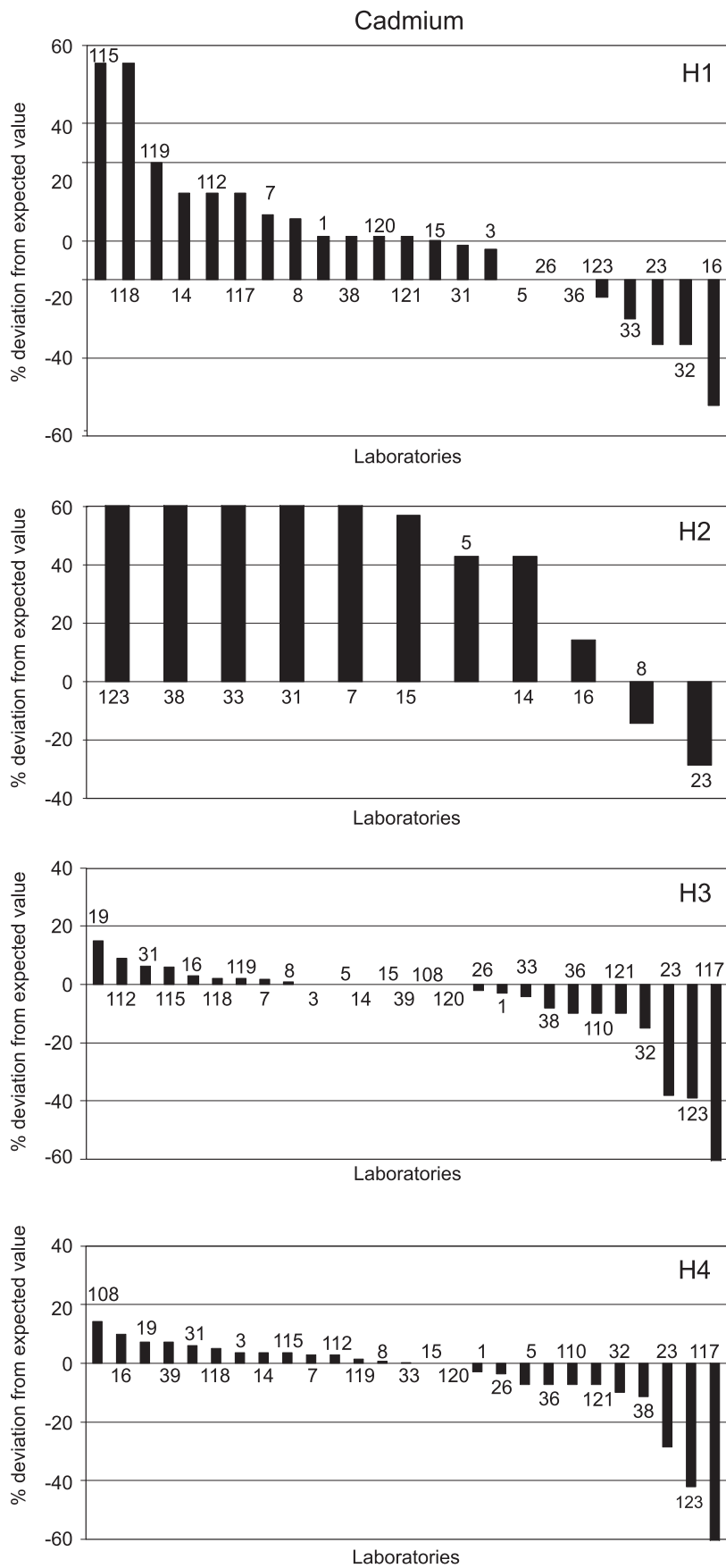


Figure A2.6: Results from determination of Cd.

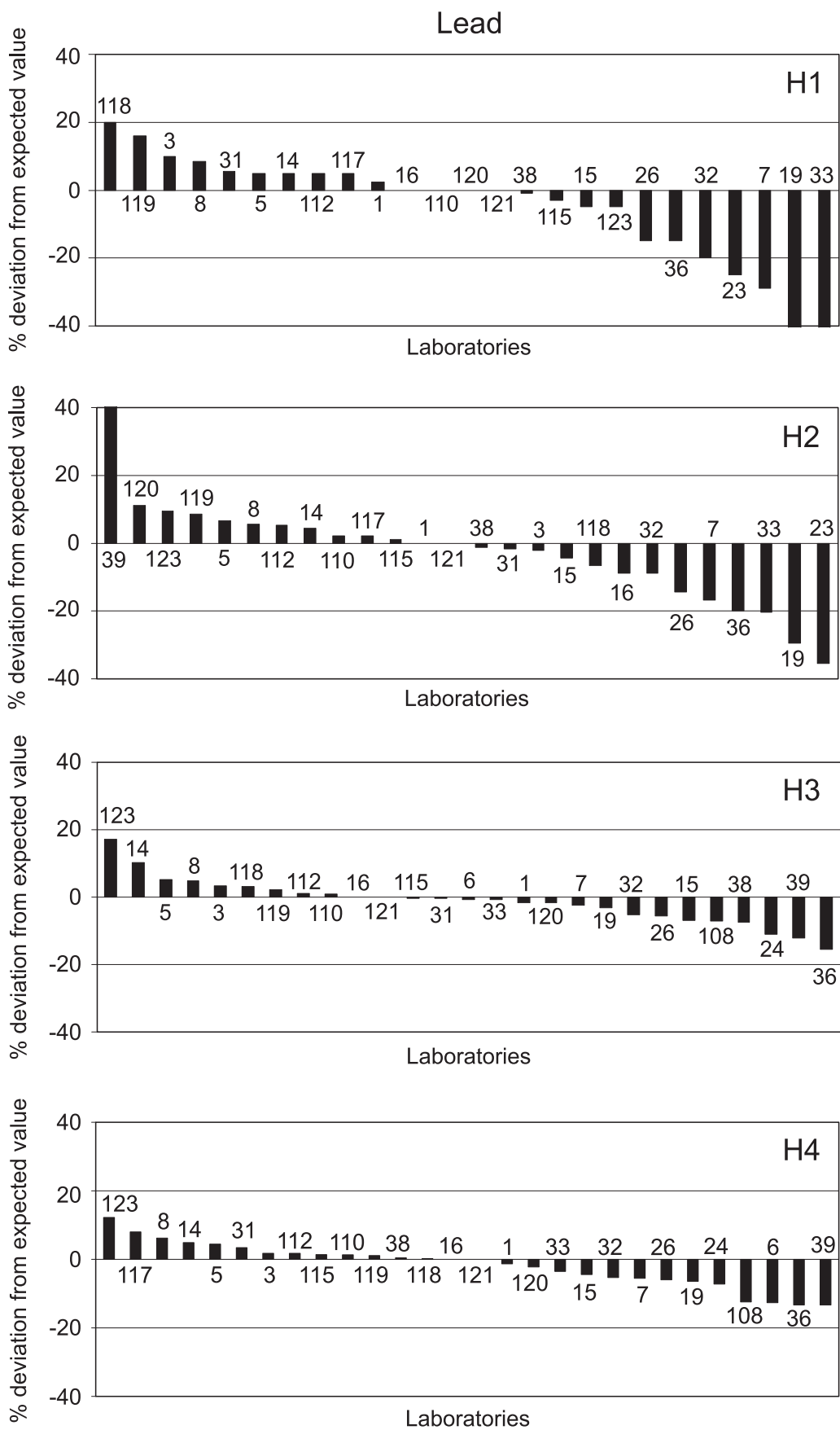


Figure A2.7: Results from determination of Pb.

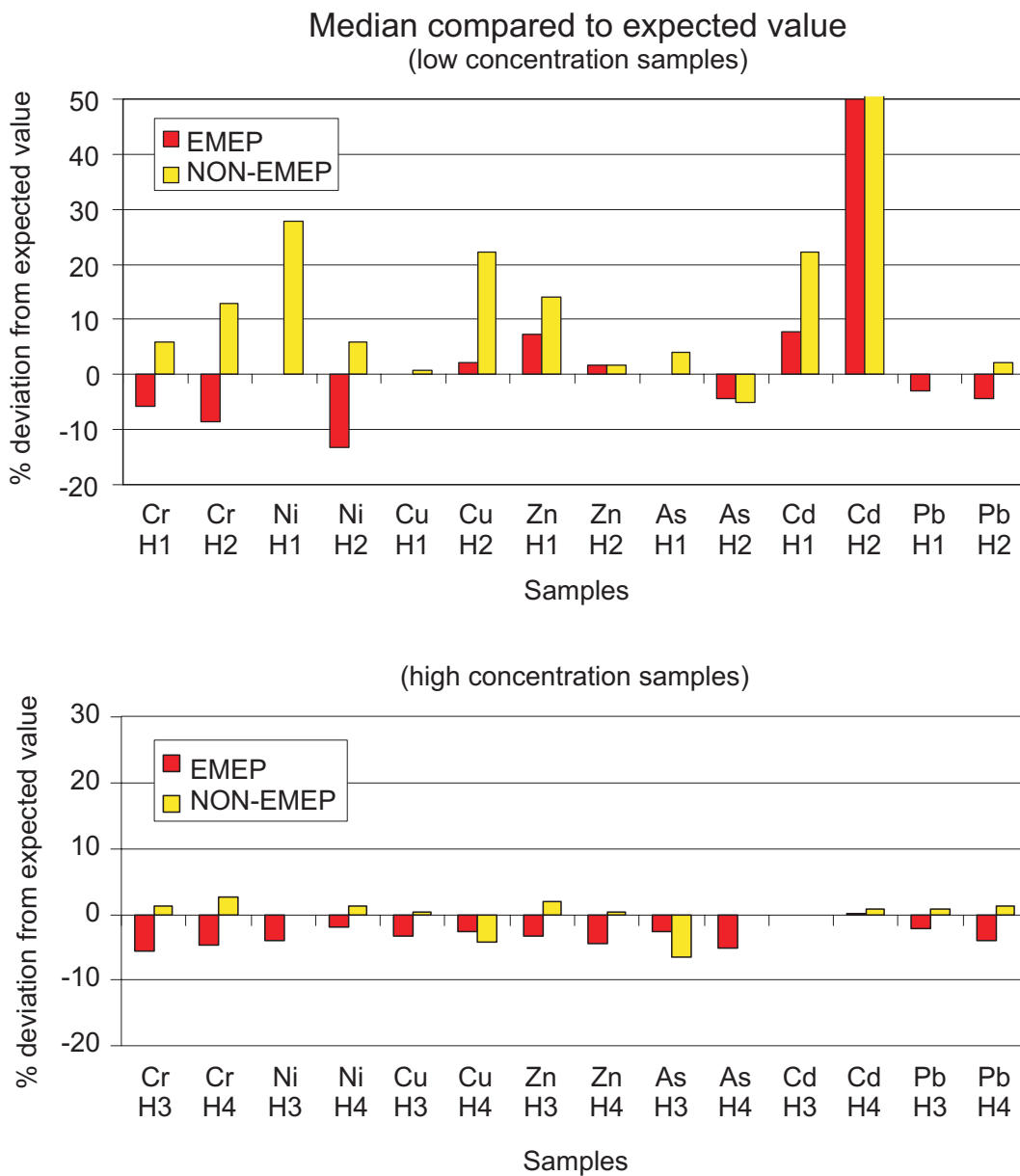


Figure A2.8: The median compared to theoretical value for low- and high concentration samples, respectively.