

Appendix B: Monitoring methods, accuracy, detection limits and precision

All stations reporting to HELCOM conduct daily sampling of nitrogen compounds in air and in precipitation. The monitoring regime for metals and lindane is more specific to each country, and is summarised in tables B.1 to B.3:

Table B.1. General information about sampling and analysis of heavy metals in precipitation in 2002.

| Country | Sites | metals | Sampling period | Sampler | | Analytical methods |
|-----------|------------------------------------|------------|-----------------|----------|--------|----------------------------|
| | | | | Wet only | Bulk | |
| Denmark | DK0008R, DK0020R | Cd, Pb | Monthly | | X | ICP-MS |
| Estonia | EE0009R, EE0011R | Cd, Pb | Monthly | | X | |
| Finland | FI0009R, FI0017R, FI0053R | Cd, Pb | Monthly | | X | ICP-MS |
| Germany | DE0009R | Cd, Pb, Hg | Weekly | X | | CV-AAS Hg ICP-MS Cd, Pb |
| Lithuania | LT0015R | Cd, Pb | Weekly | | X | GF-AAS |
| Latvia | LV0010R, LV0016R | Cd, Pb | Monthly | | X | GF-AAS |
| Sweden | SE0005R, SE0011R, SE0012R, SE0014R | Cd, Pb, Hg | Monthly | | X X | CV-AFS Hg ICP-MS Cd, Pb |

GF-AAS: Graphite furnace atomic absorption spectroscopy

ICP-MS: Inductively coupled plasma - mass spectrometry

CV-AFS: Cold vapour - atomic fluorescence spectroscopy

Table B.2. General information about sampling and analysis of heavy metals in air in 2002.

| Country | Sites | metals | Sampling period | Sampler | Analytical methods |
|-----------|----------------------------|--------------|-----------------|----------------------------|--------------------|
| Denmark | DK0005R, DK0008R, DK0031R | Cd, Pb | 24h | Filter-3pack | Pixe |
| Germany | DE0009R | Cd, Pb | 10d | High vol. | ICP-MS |
| Latvia | LV0010R, LV0016R | Cd, Pb | Weekly | Filter-1pack | GF-AAS |
| Lithuania | LT0015R | Cd, Pb | Weekly | Filter-1pack | GF-AAS |
| Sweden | SE0002R SE0005, SE00014 | Hg Cd, Pb | 12 h Weekly | Gold traps Filter-1pack | CV-AFS ICP-MS |

GF-AAS: Graphite furnace atomic absorption spectroscopy

ICP-MS: Inductively coupled plasma - mass spectrometry

CV-AFS: Cold vapour atomic fluorescence spectroscopy

Table B.3. General information about sampling and analysis of γ -HCH.

| Country | Sites | Sampling period | Sampler | Analytical methods |
|----------------------|------------------|-----------------|-----------|--------------------|
| <i>Precipitation</i> | | | | |
| Germany | DE0001R | Monthly | Wet-only | GC/ECD |
| Sweden | SE0012R,SE0014R | 1 w a month | Bulk | HPLC |
| <i>Airborne</i> | | | | |
| Sweden | SE0012R, SE0014R | 1 w a month | High vol. | HPLC |

GC-MS: Gas chromatography with mass spectrometry

ECD: Electron capture detector

There are various ways of defining the measurement and laboratory precision and detection limit. The methods for calculating these data are defined in the EMEP Manual (EMEP, 1996). To quantify the precision in the measurements, parallel sampling is necessary and the precision should be given as M.MAD and CoV, relative standard deviation (RSD) is also an informative parameter. M.MAD expresses the spread of the data and equals the standard deviation if the population has a normal distribution. CoV expresses the relative spread of the data, and, similar to the M.MAD, approaches the relative standard deviation for a normal distributed population. Both parameters are non-parametric statistics, which make them particularly useful for measurements with spikes in the data. The definitions of M.MAD and CoV are (Sirois and Vet, 1994):

$$M.MAD = \frac{1}{0.6754} \text{median} (|e_i - \text{median}(e_i)|)$$

where e_i is the error in the two measurements

$$CoV = \frac{M.MAD}{\text{median}(\bar{C})} * 100\%$$

where \bar{C} is the average of the two corresponding results. If a reference method is used to evaluate the national/local measurements, the median of the reference measurements is used.

The detection limit is calculated using three times the standard deviation of the field blanks and given in the same unit as the measurement data. By using split samples and laboratory blank samples, laboratory precisions and detection limits can be assessed in a similar way.

Not all countries have reported such data. The following tables give the information that has been received for nitrogen and metals monitored in precipitation and in air.

Reported detection limits and precision for airborne components – nitrogen**Table B.4.** Detection limits and precision of nitrogen dioxide.

| Country | Measurements | | Laboratory | |
|-----------|------------------------------------|--------------------------------------|---|--------------------------|
| | Precision | Detection limit, $\mu\text{g N/m}^3$ | Precision | Detection limit |
| Denmark | | DK08: 0.07 | M.MAD: 0.01 $\mu\text{g N/m}^3$; CoV: 1.04% | 0.01 $\mu\text{g N/m}^3$ |
| Estonia* | | 0.07 | | |
| Finland** | 0.3 $\mu\text{g N/m}^3$ | 0.3 | | |
| Latvia | | 0.16 | RSD: 2.8% | 0.005 mg N/l |
| Lithuania | | 0.08 | at $c < 2.0 \mu\text{g N/m}^3$: 3.75-6.9% RSD | 0.03 mg N/l |
| Poland | | 0.2 | RSD: 1.0% at 0.304 mgN/l RSD: 5.9 % at 0.015 mgN/l | 0.008 mg N/l |
| | PL05 | M.MAD: 0.37; CoV: 24.5% | RSD: 3.17% | 0.02 mg N/l |
| Sweden | uncertainty (95% conf.int.): 6% | 0.3 | R: 2% | 0.02 mg N/l |

* Data from EE is taken from earlier years.

** FI: Monitor, Thermo Environment 42TCL

Table B.5. Detection limits and precision of nitrate and nitric acid in air.

| Country | Measurements | | Laboratory | |
|-----------|--|---|--|---|
| | Precision | Detection limit, $\mu\text{g N/m}^3$ | Precision | Detection limit |
| Denmark | M.MAD: 0.04 $\mu\text{g N/m}^3$ CoV: 7,3% | DK05,08: 0.05 DK03: 0.04 | M.MAD: 0,01 $\mu\text{g N/m}^3$ CoV: 1.0% | 0.01 $\mu\text{g N/m}^3$ |
| Finland | | 0.02 | M.MAD: 0.001 $\mu\text{g N/m}^3$ CoV: $\text{HNO}_3 = 5.0\%$ and $\text{NO}_3 = 0.9\%$ | 0.005 $\mu\text{g N/m}^3$ |
| Germany | < 0.02 $\mu\text{g/m}^3$ M.MAD | | | 0.01 $\mu\text{g/m}^3$ |
| Latvia | | $\text{HNO}_3, \text{NO}_3$: 0.01 | RSD: 2.6% | 0.011 mg N/l |
| Lithuania | | 0.014 | $c=0.3-1.0 \mu\text{g N/m}^3$; 0.5-1.2% RSD | 0.013 mg N/l |
| Poland | | 0.02 | | 0.01 mg N/l |
| | PL05 | M.MAD: 0.11; CoV: 16.9% | RSD: 2% | 0.05 mg N/l |
| Sweden | uncertainty (95% conf. int.): 12% | $\text{NO}_3\text{-N}$: 0.005; $\text{HNO}_3\text{-N}$: 0.01 | R: 2% | $\text{NO}_3\text{-N}$: 0.005; $\text{HNO}_3\text{-N}$: 0.01 mg N/l |

Table B.6. Detection limits and precision of ammonia and ammonium in air.

| Country | Measurements | | Laboratory | |
|-----------|--|---|--|---|
| | Precision | Detection limit, $\mu\text{g N/m}^3$ | Precision | Detection limit |
| Denmark | M.MAD: 0.13 $\mu\text{g N/m}^3$ CoV: 6.6% | DK08: 0.04 DK03,05: 0.05 | NH ₄ : M.MAD: 0.02 $\mu\text{g N/m}^3$; CoV: 1.3% NH ₃ : M.MAD: 0.01 $\mu\text{g N/m}^3$; CoV: 1.0% | NH ₄ ⁺ : 0.01 $\mu\text{g N/m}^3$ NH ₃ : 0.02 $\mu\text{g N/m}^3$ |
| Finland | | 0.04 | M.MAD: 0.004 $\mu\text{g N/m}^3$, CoV: 1.5% | 0.01 $\mu\text{g/m}^3$ |
| Germany | M.MAD < 0.02 $\mu\text{g/m}^3$ | | | 0.01 $\mu\text{g/m}^3$ |
| Latvia | | NH ₃ : 0.43, NH ₄ : 2.58 | RSD: NH ₄ : 4%; NH ₃ : 2% | NH ₄ : 0.03 mg N/l NH ₃ : 0.02 mg N/l |
| Lithuania | | 0.027 | at c<1.0 $\mu\text{g N/m}^3$: 4.0% RSD at c>1.0 mg N/m ³ : 0.6-1.8% RSD | 0.04 mgN/l |
| Poland | | 0.06 | | 0.03 mg N/l |
| PL05 | M.MAD: 0.24; CoV: 20.8% | 0.03 | RSD: 1.64% | 0.01 mg N/l |
| Sweden | uncertainty (95% conf. int.): 13% | NH ₃ -N: 0.03; NH ₄ -N: 0.02 | R: 3% | NH ₄ : 0.017; NH ₃ : 0.03 (N mg/l) |

Reported detection limits and precision for components in precipitation- nitrogen**Table B.7.** Detection limits and precision of nitrate in precipitation.

| Country | Measurements | | Laboratory | |
|--------------|--|------------------------|---|------------------------|
| | Precision | Detection limit mg N/l | Precision | Detection limit mg N/l |
| Denmark | | | M.MAD: 0.02 mg N/l; CoV: 2.6% | 0.02 |
| Estonia* | | 0.302 | | 0.167 |
| Finland | | | M.MAD: 0.003 mg N/l; CoV: 1.5% | 0.01 |
| Germany | | | | 0.01 |
| Latvia | | | CoV: 0.2% | 0.001 |
| Lithuania | | | c<0.5 mg N/l: 5.1% RSD c>0.5 mg N/l: 1.8% RSD | 0.013 |
| Poland | | | RSD: 1.7% at 4.5 mg N/l RSD: 1.9% at 0.45 mg N/l RSD: 2.0% at 0.23 mg N/l | 0.015 |
| PL05 | M.MAD: 0.03; CoV: 7.1% | 0.1 | M.MAD: 0.02; CoV: 5.2% | 0.1 |
| Russia | | | | 0.01 |
| Sweden Water | uncertainty (95% conf. int.): 5% (0.002-1 mg/l) uncertainty (95% conf. int.): 1% (1-6 mg/l) | 0.002 | R: 2% | 0.002 |

Table B.8. Detection limits and precision of ammonium in precipitation.

| Country | Measurements | | Laboratory | |
|--------------|--|-------------------------|--|-------------------------|
| | Precision | Detection limit, mg N/l | Precision | Detection limit, mg N/l |
| Denmark | | | M.MAD: 0.01 mg N/l; CoV: 1.7% | 0.01 |
| Estonia* | | 0.064 | | 0.077 |
| Finland | | | M.MAD: 0.001 mg N/l; CoV: 0.5% | 0.002 |
| Germany | | | | 0.01 |
| Latvia | | | CoV: 2.9% | 0.015 |
| Lithuania | | | c<1.0 mg N/l: 3.3% RSD | 0.04 |
| Poland | | | RSD: 2.7% at 1 mg/l RSD: 4.6% at 0.1 mg/l | 0.03 |
| PL05 | M.MAD: 0.05; CoV: 8.9% | 0.01 | M.MAD: 0.02; CoV: 3.4% | 0.01 |
| Russia | | | CoV: 2.24%; M.MAD: 0.02 | 0.02 |
| Sweden Water | uncertainty (95% conf. int.): 5% (0.01-1 mg/l) uncertainty (95% conf. int.): 2% (1-10 mg/l) | 0.01 | R: 3% | 0.02 |

* Data from EE is taken from earlier years.

Reported detection limits and precision for components in precipitation- metals

Table B.9. Detection limits and precision of cadmium in precipitation.

| Country | Measurements | | Laboratory | |
|----------|--------------|-----------------------|--------------------------------|-----------------------|
| | Precision | Detection limit, µg/l | Precision | Detection limit, µg/l |
| Estonia* | | 0.01 | | |
| Finland | | | M.MAD: 0.002 µg/l CoV: 3.0% | 0.002 |
| Germany | | | | 0.003 |
| Latvia | | | CoV: 8.1% | 0.03 |
| Sweden | | | | 0.005 |

* Data from EE is taken from earlier years.

Table B.10. Detection limits and precision of lead in precipitation.

| Country | Measurements | | Laboratory | |
|----------|--------------|-----------------------|--------------------------------|-----------------------|
| | Precision | Detection limit, µg/l | Precision | Detection limit, µg/l |
| Estonia* | | 0.6 | | |
| Finland | | | M.MAD: 0.049 µg/l CoV: 3.7% | 0.03 |
| Germany | | | | 0.002 |
| Latvia | | | CoV: 4.7% | 0.4 |
| Sweden | | | | 0.01 |

* Data from EE is taken from earlier years.

Table B.11. Detection limits and precision of cadmium in air.

| Country | Measurements | | Laboratory | |
|---------|--------------|------------------------------------|------------|-------------------------|
| | Precision | Detection limit, ng/m ³ | Precision | Detection limit |
| Germany | | | | 0.003 µg/l |
| Latvia | | 0.005 | CoV: 1.9% | 0.13 µg/l |
| Sweden | | | | 0.002 ng/m ³ |

Table B.12: Detection limits and precision of lead in air.

| Country | Measurements | | Laboratory | |
|---------|--------------|------------------------------------|------------|-----------------|
| | Precision | Detection limit, ng/m ³ | Precision | Detection limit |
| Germany | | | | 0.002 µg/l |
| Latvia | | 0.05 | CoV: 1.1% | 1.8 µg/l |
| Sweden | | | | 0.008 µg/l |