Annex 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 2001.

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	Monthly	X		CV-AAS Hg ICP-MS Cd, Pb
Lithuania	LT0015R	Cd, Pb	Monthly		X	AAS
Latvia	LV0010R, LV0016R	Cd, Pb	Monthly		X	GF-AAS
Sweden	SE0002R, SE0005R, SE0011R, SE0012R	Cd, Pb, Hg	Monthly		X X	CV-AFS Hg ICP-MS Cd, Pb

AAS: Atomic absorption spectroscopy
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 2001.

Country	Sites	metals	Sampling period	Sampler	Analytical methods
Denmark	DK0005R, DK0008R, DK0031R	Cd, Pb	24h	Filter-3pack	Pixe
Germany	DE0009R	Pb	24h	High vol.	ICP-MS
Latvia	LV0010R, LV0016R	Cu, Zn, Cd, Pb	Weekly	Filter-1pack	AAS/GF-AAS
Lithuania	LT0015R	Cu, Zn, Cd, Pb	24h[2)]	Filter-1pack	AAS
Sweden	SE0002R	Hg	12 h	Gold traps	CV-AFS

AAS: Atomic absorption spectroscopy
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
Precipitation				
Germany	DE0001R	Monthly	Wet-only	GC/ECD
Airborne				
Sweden	SE0002R, SE0012R	1 w a month	High vol.	GC/MS

GC-MS: Gas chromatography with mass spectrometry
ECD: Electron capture detector

There are various ways of defining measurement and laboratory precision and detection limits. Methods for calculating these are given in the EMEP Manual (EMEP, 1996). To quantify the precision in the measurements, parallel sampling is necessary. The precision can be given as the modified median absolute deviation (M.MAD), a non-parametric measure of the spread difference between corresponding daily results from two samplers. This equals the standard deviation when the differences have a normal distribution. The coefficient of variation, CoV, is also an informative non-parametric parameter, expressing the ratio between the mean and the standard deviation as a percentage. Being non-parametric statistics, they are particularly useful for measurements with spikes in the data. The relative standard deviation (RSD) is also sometimes reported. The M.MAD and CoV may be defined as (Sirois and Vet, 1994):

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

where e_i is the error in the two measurements

$$CoV\ \frac{M.MAD}{median\left(\overline{C}\right)} * 100\%$$

where $\overline{C}$ 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 laboratory detection limit is estimated at three times the standard deviation of the field blanks, and is 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.

	Measurements		Laboratory	
Country	**Precision**	**Detection limit, µgN/m^3**	**Precision**	**Detection limit**
Denmark		0.06	M.MAD: 0.03; CoV: 2.6%	0.06 µgN/m^3
Estonia		0.01		
Finland	0.3 µgN/m^3	0.3		
Latvia		0.1	CoV: 1.3%	0.04
Lithuania		0.17	c<2.0 µgN/m^3: 4-7% RSD;	0.03 mgN/l
Poland		0.2	RSD: 1.0% at 0.3 mgN/l RSD: 5.9 % at 0.015 mgN/l	0.008 mgN/l
Sweden	RSD: 12%	0.2	2%	0.05

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

	Measurements		Laboratory	
Country	**Precision**	**Detection limit, µgN/m3**	**Precision**	**Detection limit**
Denmark	M.MAD: 0,04 µgN/m^3 CoV: 7,3%	DK03,08: 0.05 DK05: 0.07	M.MAD: 0,01 µgN/m^3 CoV: 0.9%	0.01 µgN/m^3
Finland			NO3: c=0.35 mgN/l; 5% RSD c=0.9 mgN/l; 3.0% RSD HNO3:c=0.35 mgN/l; 4% RSD c=0.9 mg N/l; 2.6% RSD	NO3: 0.01 mgN/l HNO3: 0.01 mgN/l
Latvia		NO3: 0.01-0.02	NO3: CoV: 2.1%	NO3: 0.05 mg/l
Lithuania		0.014	c=0.3-1.0 µgN/m^3 0.5-1.2% RSD;	0.013 mgN/l
Poland		0.02		NO3: 0.01 mgN/l
Sweden	RSD: 12%	NO3: 0.002; HNO3: 0.004	2%	NO3: 0.002; HNO3 0.005

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

Country	Measurements		Laboratory	
	Precision	Detection limit, µgN/m^3	Precision	Detection limit
Denmark	M.MAD: 0.13 CoV: 6.6%	DK03: 0.05 DK05: 8: 0.04	NH4: M.MAD: 0.02; CoV: 1.8% NH3: M.MAD: 0.01; CoV: 1.6%	0,01 µgN/m^3
Finland			c=0.22 mg N/l; 7.3% RSD c=0.72 mg N/l; 2.7% RSD c=1.42 mg N/l; 2.8% RSD	0.02 mgN/l
Latvia		NH4: 0.15-0.02	NH4: CoV: 2.1%	NH4: 0.06 mgN/l
Lithuania		0.027	c<1.0 mgN/m^3: 4.0 % RSD c>1.0 mgN/m^3: 0.6-1.8 % RSD	0.04 mgN/l
Poland		0.08		NH4: 0.03 mgN/l
Sweden	RSD: 13%	0.03	3%	NH4: 0.017 NH3: 0.03

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 mgN/l	Precision	Detection limit mgN/l
Denmark			M.MAD: 0.02; CoV: 1.6%	0.03
Estonia		0.5		
Finland			c=0.35 mg N/l; 3.1% RSD c=0.9 mg N/l; 2.5% RSD	0.01
Germany				0.01
Latvia			CoV: 2.7%	0.01
Lithuania			c<0.5 mgN/l: 5.1% RSD c>0.5 mgN/l: 1.8% RSD	0.013
			SD: 0.016 at c=0.39 mgN/ml	
Poland			RSD: 0.4% at 4.5 mgN/l RSD: 1.7% at 0.45 mgN/l RSD: 2.1% at 0.23 mgN/l	0.015
Sweden	RSD: 5%	0.002	2%	0.002

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

Country	Measurements		Laboratory	
	Precision	Detection limit, mgN/l	Precision	Detection limit, mgN/l
Denmark			M.MAD: 0.01 CoV: 1.7%	0.02
Estonia		0.1		
Finland			c=0.23 mg N/l; 2.6% RSD c=0.70 mg N/l; 2.8% RSD	0.002
Germany				0.01
Latvia			CoV: 1%	0.008
Lithuania			c<1.0 mgN/l: 3.3% RSD c>1.0 mgN/l: 1.0% RSD	0.04
Poland			RSD: 2.7 % at 1 mg/l RSD: 4.6 % at 0.1 mg/l	0.03
Sweden	RSD: 5%	0.02	3%	0.02

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			RSD: 3.5% at c=1 ug /l	0.002
Latvia			CoV: 6.8%	0.05

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			RSD: 4.7% at c=1 µg/l	0.03
Latvia			CoV: 0.7%	0.6

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

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Latvia		0.02	CoV: 2.9%	1.5 µg/l

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

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m^3	Precision	Detection limit
Latvia		2.39	CoV: 6.8%	0.6 µg/l