Appendix B: Monitoring methods, accuracy, detection limits and precision (updated for 2004)

The monitoring regime for nitrogen compounds, metals and lindane are summarised in tables B.1 to B.5:

Table B.1. General information about sampling and analysis of nitrogen compounds in precipitation in 2004.

Country		Sampling period	Sampler		Analytical methods
			Wet only	Bulk	
Denmark	Nitrate ammonium	Biweekly	x		IC Spect (CFA)
Estonia	Nitrate Ammonium	Weekly		X	IC Spect (indophenol)
Finland	Weekly	Daily		X	IC
Germany	Nitrate Ammonium	Weekly	X		IC Spect (FIA)
Latvia	Nitrate Ammonium	Daily	X (LV10)	X (LV16)	IC Spect (indophenol)
Lithuania	Nitrate Ammonium	Daily	X		IC Spect (indophenol)
Poland	Nitrate Ammonium	Daily		x	IC Spect (chloramin T)
Russia	Nitrate Ammonium	Daily		x	IC
Sweden	Nitrate Ammonium	Weekly	X		IC Spect (FIA)

*IC: Ion chromatograpy

**Spect Spectrofotometric detection

Table B.2. General information about sampling and analysis of nitrogen compounds in air in 2004.

Country		Sampl period	Sampler	Analytical methods
Denmark	NO_2 Sum of nitric acid and nitrate Sum of ammonia and ammonium	Daily Daily Daily	KI method 0.73m^3/day Aerosol filter as for sulphate + KOH-impregnated Whatman 41, 58 m^3/day + Oxalic acid impregnated Whatman 41, 58 m^3/day	Spect IC Spect (CFA)
Estonia	NO_2	Daily	Instr: Chemiluscence	
Finland	NO_2 Sum of nitric acid and nitrate Sum of ammonia and ammonium	Hourly Daily Daily	Instr: Chemiluscence Whatman 40 + NaOH impregnated Whatman 40 filter, 24 m^3/day Oxalic acid impregnated Whatman 40 filter, 24 m^3/day	 IC IC
Germany	NO_2 Sum of nitric acid and nitrate Sum of ammonia and ammonium	Daily Daily	NaI imp. Glass filters, 0.7m^3/day Aerosol filter as for sulphate + KOH impregnated filter as for SO_2, 25 m^3/day (Filterpack)	FIA IC FIA
Latvia	NO_2 Sum of nitric acid and nitrate Sum of ammonia and ammonium	Daily Daily Daily	KI method 0.2-0.4 m^3/day KOH-impregnated Whatman 41 filter, 14-20 m^3/day Oxalic acid impregnated Whatman 41 filter, 14-20 m^3/day	Spect. Griess IC Spect (indophenol)
Lithuania	NO_2, Sum of nitric acid and nitrate Sum of ammonia and ammonium	Daily Daily Daily	KI method 0.4-0.7 m^3/day KOH impregnated Whatman 40 filter, 16-17 m^3/day Oxalic acid impregnated Whatman 40 filter, 16-17 m^3/day	Spect. Griess IC Spect (indophenol)
Poland	NO_2 Sum of nitric acid and nitrate Sum of ammonia and ammonium	Daily Daily Daily	Abs.sol. TGS 0.73^3/day NaF impregnated Whatman 40 filter, 3.5-4 m^3/day Oxalic acid impregnated Whatman 40 filter, 3.5-4 m^3/day	Spect. Griess Spect. Griess Spect. Chloramin T)
Russia	Ammonium, Nitrate	Daily	Whatman 40 filter, 10-15 m^3/day	IC
Sweden	NO_2 Sum of nitric acid and nitrate Sum of ammonia and ammonium	Daily	NaI imp. glass sinters 0.7 m^3/day Aerosol filter as for sulphate + KOH-impregnated Whatman 40 filter, 20 m^3/day Aerosol filter as for sulphate + Oxalic acid impregnated Whatman 40 filter, 20 m^3/day	Spect IC FIA

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 heavy metals in precipitation in 2004.

Country	Sites	metals	Sampling period	Sampler		Analytical methods
				Wet only	Bulk	
Denmark	DK0008R, DK0020R	Cd, Pb	Monthly		X	GF-AAS
Estonia	EE0009R, EE0011R	Cd, Pb	Monthly		X	GF-AAS
Finland	FI0009R, FI0017R, FI0053R	Cd, Pb	Monthly		X	ICP-MS
Germany	DE0009R	Cd, Pb, Hg	Weekly	X		CV-AFS Hg ICP-MS Cd, Pb
Lithuania	LT0015R	Cd, Pb	Weekly		X	GF-AAS
Latvia	LV0010R, LV0016R	Cd, Pb	Weekly		X	GF-AAS
Poland	PL0004	Cd, Pb	Biweekly	X		GF-AAS
Sweden	SE0005R, SE0011R, SE0014R	Hg Cd, Pb, Hg	Monthly X		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.4. General information about sampling and analysis of heavy metals in air in 2004.

Country	Sites	metals	Sampling period	Sampler	Analytical methods
Denmark	DK0005R, DK0008R, DK0031R	Cd, Pb	24h	Filter-3pack	Pixe
Germany	DE0009R	Cd, Pb Hg	10d Continuously	High vol. Monitor	ICP-MS CV-AFS
Latvia	LV0010R, LV0016R	Cd, Pb	Weekly	Filter-1pack	GF-AAS
Lithuania	LT0015R	Cd, Pb	Weekly	Filter-1pack	GF-AAS
Sweden	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.5. General information about sampling and analysis of γ-HCH.

Country	Sites	Sampling period	Sampler	Analytical methods
Precipitation				
Germany	DE0001R	Monthly	Wet-only	GC MS
Sweden	SE0014R	1 w a month	Bulk	HPLC
Airborne				
Sweden	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):

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

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 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 2003.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg N/m^3	Precision	Detection limit
Denmark		DK08: 0.07	M.MAD: 0.01 µg N/m^3; CoV: 3.45%	0.07 µg N/m^3
Estonia		0.07		
Finland*	0.3 µg N/m^3	0.3		
Latvia		0.13	RSD: 2.8%	0.005 mg N/l
Lithuania		0.08	RSD 3.75-6.9% at c<2.0 µg N/m^3	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
Sweden	uncertainty (95% conf.int.): 6%	0.3	R: 2%	0.02 mg N/l

* 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, µg N/m3	Precision	Detection limit
Denmark	M.MAD: 0.04 µg N/m^3, CoV: 7,3%	DK03: 0.04 DK05: 0.06 DK08: 0.03	NO_3; M.MAD: 0,01 µg N/m^3, CoV: 1.2%	NO_3: 0.01 µg N/m^3
Finland		0.02	M.MAD: 0.001 µg N/m^3 CoV: HNO_3 = 5.0% and NO_3 = 0.9%	0.005 µg N/m^3
Germany	< 0.02 µg/m^3 M.MAD			0.01 µg/m^3
Latvia		HNO_3, NO_3: 0.01	RSD: HNO_3 1.2%, NO_3 2.9%	HNO_3: 0.006 mg N/l NO_3: 0.015 mg N/l
Lithuania		0.014	RSD 0.5-1.2% at c=0.3-1.0 µg N/m^3	0.013 mg N/l
Poland		0.02		0.01 mg N/l
Russia	NO_3: M.MAD 0.01			0.01 mg/l
Sweden	uncertainty (95% conf. int.): 12%	NO_3-N: 0.005; HNO_3-N: 0.01	R: 2%	NO_3-N: 0.005; HNO_3-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, µg N/m^3**	**Precision**	**Detection limit**
Denmark	M.MAD: 0.13 µg N/m^3 CoV: 6.6%	DK03: 0.05 DK05: 0.06 DK08: 0.03	NH_4: M.MAD: 0.01 µg N/m^3; CoV: 1.3% NH_3: M.MAD: 0.01 µg N/m^3; CoV: 1.0%	NH_4^+: 0.02 µg N/m^3 NH_3: 0.02 µg N/m^3
Finland		0.04	M.MAD: 0.004 µg N/m^3; CoV: 1.5%	0.01 µg/m^3
Germany	M.MAD < 0.02 µg/m^3			0.01 µg/m^3
Latvia		NH_3: 0.09 NH_4: 0.08	RSD: NH_4: 4%; NH_3: 2%	NH_4; 0.03 mg N/l NH_3: 0.02 mg N/l
Lithuania		0.027	RSD: 4.0% at c<1.0 µg N/m^3 RSD 0.6-1.8% at c>1.0 µg N/m^3	0.04 mg N/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
Russia	NH_4: RU01: M.MAD 0.05; CoV=5.37% NH_4: RU16: M.MAD 0.03; CoV=5.13% NH_4: RU18: M.MAD 0.01; CoV=0.84%		NH_4: M.MAD: 0.01 µg/m^3 CoV: 3.39 µg/m^3	NH_4: 0.02 mg/l
Sweden	uncertainty (95% conf. int.): 13%	NH_3-N: 0.03; NH_4-N: 0.02	R: 3%	0.02 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: 0.01 mg N/l; CoV: 2.7%	0.02
Estonia		0.302		0.167
Finland			M.MAD: 0.003 mg N/l; CoV: 1.5%	0.01
Germany				0.01
Latvia		0.04	CoV: 1.9%	0.0052
Lithuania			RSD: 5.1% at c<0.5 mg N/l RSD: 1.8% at c>0.5 mg N/l	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
Russia	RU16: M.MAD: 0.01			0.01
Sweden	uncertainty (95% conf. int.): 5% (0.006-1 mg/l) uncertainty (95% conf. int.): 1% (1-6 mg/l)	0.006	R: 2%	0.006

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:3.1%	0.02
Estonia		0.064		0.077
Finland			M.MAD: 0.001 mg N/l; CoV: 0.5%	0.002
Germany				0.01
Latvia		0.06	CoV: 3.7%	0.015
Lithuania			RSD: 3.3% at c<1.0 mg N/l RSD: 1.0% at c>1.0 mg N/l	0.04
Poland			RSD: 2.7% at 1 mg/l RSD: 4.6% at 0.1 mg/l	0.03
Russia	RU18: M.MAD: 0.01; CoV: 0.85%		CoV: 2.24%; M.MAD: 0.02	0.02
Sweden	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

Reported detection limits and precision for airborne components – heavy metals

Table B.9. 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		0.01	CoV: 3.5%	0.20 µg/l

Table B.10. 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: 2.0%	2.0 µg/l

Reported detection limits and precision for components in precipitation- heavy metals

Table B.11. 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: 5.7%	0.04
Norway				0.002

Table B.12. 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: 4.0%	0.4
Norway				0.01