**Convention on Long-range Transboundary Air Pollution** 

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Atmospheric Supply of Nitrogen, Lead, Cadmium, Mercury and Dioxines/Furans to the Baltic Sea in 2007

Jerzy Bartnicki Alexey Gusev Wenche Aas Semeena Valiyaveetil



# msc-w & msc-e & ccc

# **EMEP Centres Joint Report for HELCOM** EMEP/MSC-W TECHNICAL REPORT 2/2009

# Atmospheric Supply of Nitrogen, Lead, Cadmium, Mercury and Dioxines/Furanes to the Baltic Sea in 2007

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#### Summary

The results presented in this EMEP Centres Joint Report for HELCOM are based on the modelling and monitoring data presented to the 33th Session of the Steering Body of EMEP in Geneva in September 2009. It includes measurements, as well as emissions and depositions calculated by the EMEP models of nitrogen compounds, heavy metals and PCDD/F for the year 2007.

The measured monthly and annual 2007 concentrations in air and precipitation for nitrogen species and heavy metals are presented in the report. For all the components a significant south-east gradient can be noticed in the measured concentrations in 2007. The temporal patterns of monthly Cd and Pb concentrations in air show a strong winter maximum, and temporal pattern of Hg monthly concentrations weaker winter maximum. Reduced nitrogen in air has maximum both in spring and autumn, while oxidised nitrogen show a clear increase in spring. The different components show no seasonal variation in precipitation.

Annual emissions from the HELCOM Contractig Parties in 2007 are shown below for all pollutants considered in the report. The annual nitrogen oxides emission from the international ship traffic on the Baltic Sea in 2007 is107 kt N.

	POLLUTANT					
Country/ship	NO <sub>2</sub>	NH₃	Cd	Pb	Hg	PCDD/F
	kt N	kt N	tonnes	tonnes	tonnes	g TEQ
Denmark	51	62	0.7	6	1.1	28
Estonia	11	8	0.7	40	0.7	5
Finland	56	29	1.1	21	0.8	12
Germany	391	514	2.5	106	4.0	83
Latvia	13	13	0.6	18	0.0	13
Lithuania	21	30	0.4	7	0.4	11
Poland	269	240	39.6	573	15.9	442
Russia	1327	750	59.4	355	14.0	808
Sweden	50	41	0.6	16	0.6	36
HELCOM	2188	1687	106	1142	38	1438
Ship-Baltic	107					

Annual depositions of all considered pollutants in 2007 are shown in the Table below for 6 sub-basins of the Baltic Sea and for the entire Baltic Sea.

Basin	POLLUTANT							
	Ox-N	Red-N	Cd	Pb	Hg	PCDD/F		
	kt N	kt N	tonnes	tonnes	tonnes	g TEQ		
GUB	16,6	10,4	0.9	29	0.7	7		
BAP	7,2	4,4	4.3	128	1.9	24		
GUF	5,5	3,8	0.5	16	0.3	6		
GUR	61,0	50,1	0.4	11	0.2	4		
BES	8,8	14,2	0.5	16	0.2	10		
KAT	8,1	9,5	0.5	17	0.2	4		
BAS	107,1	92,4	7	217	3.4	55		

Oxidised nitrogen depositions in 2007 into the Baltic Sea were 3% lower in 2007 than in 2006, whereas reduced nitrogen depositions were 3% higher. Total nitrogen deposition remained on the same level in 2007 as in 2006.

Levels of cadmium and lead deposition to the entire Baltic Sea slightly decreased in 2007 comparing to 2006 by 6% and 9%, respectively. At the same time mercury deposition to the entire Baltic Sea for 2007 were 6% higher than that for 2006. In case of PCDD/Fs there is a decrease of deposition from 2006 to 2007 by 9%.

Anthropogenic emission sources of HELCOM countries contributed to the annual deposition over the Baltic Sea in 2007 about 20% for lead and mercury and about 40% for cadmium and PCDD/Fs. Essential contribution to total annual deposition belongs to other sources, in particular, natural emissions, re-suspension with dust, distant emissions, and re-emission.

The following sectors contributed most significantly to the annual anthropogenic emissions of HELCOM countries in 2007: Combustion in Power Plants and Industry (62 88 %), Commercial, Residential and other Stationary Combustion (5 22 %), and Industrial processes for Pb, Cd, And Hg (3 11 %), and Waste for PCDD/Fs (13%).

Most significant contribution to deposition of HMs and PCDD/Fs to the Baltic Sea was made by Poland followed by Estonia for Pb, Russia for Cd, and Denmark for Hg and PCDD/Fs.

Model results in comparison with available measurements for 2007 made around the Baltic Sea are within an accuracy of 60% for Pb and Cd, and 30% for Hg. Computed concentrations of PCDD/Fs are lower than measurements by a factor 2-3.

#### Preface

The Co-operative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) and the Baltic Marine Environment Protection Commission (HELCOM) are both conducting work on air monitoring, modelling and compilation of emission inventories. In 1995, HELCOM decided to rationalize its current programs by avoiding duplication of efforts with specialised international organizations. At the request of HELCOM, the steering Body of EMEP at its nineteenth session agreed to assume the management of atmospheric monitoring data, the preparation of air emission inventories and the modelling of air pollution in the Baltic region.

Following the coordination meeting held in Potsdam in Germany and the Pollution Load Input meeting held in Klajpeda-Joudkrante in Lithuania, both 1996, it was agreed that EMEP Centres should be responsible for regular evaluation of the state of the atmosphere in the Baltic Sea region and should produce an annual joint summary report which includes updated emissions of selected air pollution, modelled deposition fields, allocation budgets and measurement data.

This report was prepared for the HELCOM, based on model estimates and monitoring results presented to the thirtieth session of the Steering Body of EMEP. Following decision of the HELCOM /MONAS-11 Meeting, it presents the results for the year 2007.

#### Acknowledgements

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# 2. Observed Concentrations of Nitrogen, Cadmium, Lead and Mercury at HELCOM Stations in 2007

#### 2.1 HELCOM measurement stations

Eight countries have submitted data from all together twenty three HELCOM stations for 2007 (Fig. 2.1).

**Fig 2.1**. HELCOM sites with measurements of nitrogen, lead, cadmium and mercury in 2007



The stations are distributed in the six sub-basins (Fig. 2.1) as following: One in the Gulf of Riga (GUR), four in the Gulf of Bothnia (GUB) and five in Kattegat (KAT), three in the Belt Sea (BES), two in the Gulf of Finland (GUF), and eight in the Baltic proper (BAP). There is one station from: Germany, Lithuania, Poland, two stations from Latvia and Estonia, four stations from Finland, six stations from Denmark and Sweden. No stations have delivered data for all the components in air and precipitation. In this section we provide a broad view of the patterns and levels evident in monitoring data from 2007. Where possible regional average values are provided for the principal regions within the Baltic Sea. For actual monthly values on a component-by-component basis, the reader is referred to Appendix A. A description of sampling and analytical methods is given in Appendix B. Further statistical details are also found in the EMEP reports for 2007 data (Hjellbrekke and Fjæraa, 2009; Aas and Breivik, 2009) and the data are available form the web database at ebas.nilu.no The HELCOM laboratories have participated in different laboratory and field intercomparisons in 2007 (Uggerud and Hjelbrekke 2008a and 2008b). The laboratories generally have a good quality.

#### 2.2 Nitrogen concentrations in air

Altogether 13 stations have delivered data for total reduced nitrogen  $(NH_3+NH_4^+)$ , or total nitrate  $(HNO_3+NO_3^-)$ , and 14 for nitrogen dioxide  $(NO_2)$ . Stations from all the six sub-basins have delivered data of nitrogen concentration in air. Annual averages of the different nitrogen species are presented in Figure 2.2. Average air concentrations are arithmetic averages of the reported values. The lowest concentrations for all the three nitrogen species were reported at the northernmost Swedish site (SE05) in 2007: The concentrations were 0.16, 0.04 and 0.11 µg N/m<sup>3</sup> for respectively NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>, HNO<sub>3</sub>+NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub> at this site. Highest concentrations of nitrogen in aerosols were found at the German site DE09 and Danish sites DK03 and DK05 with about 2 µgN/m<sup>3</sup> of sum ammonium, and 0.8 µgN/m<sup>3</sup> for sum nitrate. The Estonian sites show highest level of NO<sub>2</sub> with about 3 µgN/m<sup>3</sup>.



**Figure 2.2.** Concentrations of left: NO<sub>2</sub> in air, middle: total reduced nitrogen (NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>), and right: total nitrate (HNO<sub>3</sub>+NO<sub>3</sub><sup>-</sup>) in 2007 Unit:  $\mu$ g N/m<sup>3</sup>.

There is a tendency of decreasing concentrations from south to north. A similar south north gradient can also be noticed in Figure 2.3-2.5 displaying the station averages of  $NH_3+NH_4^+$ ,  $HNO_3+NO_3^-$  and  $NO_2$  observations across six sub-basins

Observations of the total reduced nitrogen  $(NH_3+NH_4^+)$ , show a seasonal pattern similar for most the sub-basins with highest concentrations during March and April, and a peak is also common in August and October. Agricultural activities (natural fertilizer) are the main source for  $NH_3+NH_4^+$ . During the summer half year,  $NH_3$  is normally emitted from the ground due to higher temperatures.



Figure 2.3. Monthly total reduced nitrogen (NH<sub>3</sub>+NH<sub>4</sub>) concentrations in the air in 2007



Figure 2.4. Monthly total oxidized nitrate (HNO<sub>3</sub>+NO<sub>3</sub><sup>-</sup>) concentrations in the air in 2007



Figure 2.5. Monthly NO<sub>2</sub> concentrations in the air in 2007

Total nitrate (HNO<sub>3</sub>+NO<sub>3</sub>) concentration doesn t show that clear seasonal pattern, there are elevated levels for some months varying between the regions. NO<sub>2</sub> is reacting photochemically and the reaction product is total nitrate. This reaction is mostly dominating during spring and summer. However, total nitrate is dominated by particulate nitrate in the cold season, which has a higher residence time in the atmosphere than nitric acid. In the summer, more of total nitrate consists of nitric acid, which is dry deposited very fast. The overall effect is usually a less pronounced seasonal pattern, though spring gives the highest level in 2007. Concentrations of NO<sub>2</sub> show not unexpected temporal patterns with a winter maxima/summer minima. During winter the atmospheric residence time is longer due to high emissions, low photochemically activity and reduced vertical mixing.

#### 2.3 Nitrogen in precipitation

Altogether 18 stations have delivered data for ammonium and nitrate in precipitation. Stations from all the six sub-basins have delivered data for ammonium and nitrate in precipitation. Annual averages of the two nitrogen species are presented in Figure 2.6.



**Figure 2.6.** Concentrations of left: nitrate ( $NO_3^{-}$ )), and right: ammonium ( $NH_4^{+}$  in precipitation in 2007. Units: mg N/l.

The yearly mean concentrations in precipitation have been calculated from daily or weekly reported values as precipitation-weighted averages. A south-north gradient similar to air can also be seen for nitrogen in precipitation with higher concentrations in the south. But also a west-east gradient is seen. The concentration differences for ammonium are much higher than for nitrate, because stations can be affected by local agricultural activities. Lowest concentrations for both ammonium and nitrate were seen at SE05, annual concentration of 0.11 mg N/L for both compounds. The highest concentrations of ammonium were found at the EE11 and DK05 with about 1 mg N/L, and for nitrate highest level are seen at the two Danish sites DK05 and DK20 with about 0.5 mg N/L. Figure 2.7 displays the station average monthly depositions of oxidized and reduced nitrogen across the regions given.



**Figure 2.7**. Monthly nitrogen depositions in 2007 averaged for the sub-basins. Top: nitrate  $(NO_3^{-})$ , and bottom: reduced nitrogen  $(NH_4^{+})$ .

It is to be observed that seasonal patterns are not as strong as for airborne components. This is due to the presence of the precipitation effect. Though, it is very high deposition of ammonium in the BAP region in January. This is caused by relatively high precipitation amount at several of the sites in this region in January. The spatial pattern persists, however, with clearly decreasing depositions with progression northwards. For example, the northern regions typically receive half the deposition of reduced nitrogen supplied to southern areas.

#### 2.4 Heavy metals in the air

Altogether nine stations have delivered heavy metal data in air whereof six measuring cadmium, nine with lead and only two (SE12 and DE09) have delivered data for Hg in air. Annual averages of Cd and Pb are presented in Figure 2.8. The lowest concentrations for both Cd and Pb in aerosols were reported at SE14, with 0.07 and 2.0 ng/m<sup>3</sup>, respectively. The highest concentrations were found at EE09 with 0.2 and 6.3 ng/m<sup>3</sup> for Cd and Pb respectively.



**Figure 2.8**. Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2007. Units: ng/m<sup>3</sup>.

There are insufficient stations to reasonably represent regional patterns, hence the station data itself is presented here for some of the sites (Fig. 2.9).



Figure 2.9. Monthly concentrations in air in 2007 averaged for the sub-basins: Top: cadmium, bottom: lead

From this, it is to be observed that the temporal patterns for Cd and Pb show a winter maximum. During winter the atmospheric residence time is longer due to reduced vertical mixing. Hg concentrations at the two sites are similar and show a weak winter maxima for the two stations, Figure 2.10



Figure 2.10. Monthly concentrations of Hg in air in 2007 averaged for the sub-basins:

#### 2.5 Heavy metals in precipitation

In all twelve stations have delivered data for Cd and Pb in precipitation, and two have delivered data for Hg in precipitation. Stations from five of the six sub-basins have delivered data for Cd and Pb. Annual averages of Cd and Pb are presented in Figure 2.11. The yearly mean concentrations in precipitation have been calculated from weekly or monthly reported values as precipitation-weighted averages. The lowest concentration for Cd in precipitation was reported at the Swedish and sites in addition DK08 with less than 0.03  $\mu$ g/l. The lowest concentrations for Pb with 0.47 were observed at SE51. The highest concentration of Pb was measured at LV10 (2.5  $\mu$ g/l) while at FI17 for Cd (0.062  $\mu$ g/l.)



**Figure 2.11.** Concentrations of left: lead (Pb), right: cadmium (Cd) in precipitation. in 2007. Units:  $\mu g/l$ .

#### 2.6 Conclusions for Chapter 2

- Measurement data was reported from twenty three HELCOM stations in 2007, but few sites have a complete measurements program with measurements in both air and precipitation.
- There is a general tendency of decreasing concentrations from south to north for all relevant species.
- Total reduced nitrogen in air show a seasonal pattern with highest concentrations during spring and for some sub basins also peaks during autumn depending on the agricultural activates in the different regions.
- Oxidized nitrogen in air show winter maxima due to longer atmospheric residence time. Similar pattern is seen for cadmium and lead.
- The seasonal patterns for nitrogen species in precipitation are not as strong as for airborne components. This is due to the presence of the precipitation effect.

# 3. Atmospheric Supply of Nitrogen to the Baltic Sea in 2007

Nitrogen emission data, as well as the model results presented here have been approved by the 33<sup>rd</sup> Session of the Steering Body of EMEP in Geneva in September 2009. The EMEP Unified Eulerian model system has been used for all nitrogen computations presented in this Chapter.

It should be mentioned here that the model domain used for 2007 computations was different from this used for 2006. The 2007 domain covers the extended territory of the Russian Federation and therefore the Russian 2007 nitrogen emissions are higher than 2006 emissions. In addition, meteorological data used for deposition calculations for 2007 came from (HIRLAM) a slightly different numerical weather prediction model than the one used for 2006 (PARLAM).

Annual deposition of total nitrogen to the Baltic Sea basin in 2007 was 202 kt, approximately on the same level (1% higher) as in 2006. Deposition of oxidized nitrogen was 1% lower and deposition of reduced nitrogen was 5% higher in 2007 compared to 2006. Deposition of oxidized nitrogen accounted for 52% of total nitrogen deposition in 2007.

#### 3.1 Nitrogen emissions

**Table 3.1**. Annual total 2007 emissions of nitrogen oxides and ammonia from the HELCOM Contracting Parties and Baltic See ship traffic. Sum of HELCOM emissions is also included. Units: kt N per year.

Emission source	Pollutant			
	NO <sub>x</sub>	NH <sub>3</sub>		
Denmark	51	62		
Estonia	11	8		
Finland	56	29		
Germany	391	514		
Latvia	13	13		
Lithuania	21	30		
Poland	269	240		
Russian Federation	1 327	750		
Sweden	50	41		
HELCOM	2 188	1 687		
Baltic Sea	107	0		



**Figure 3.2.** Percent of annual emissions of total (oxidized + reduced) nitrogen from the HELCOM Parties and international ship traffic emissions on the Baltic Sea (Baltic Ship) deposited to the Baltic Sea basin in 2007.



Figure 3.3. Map of annual emission of oxidized nitrogen (including emissions from the ship traffic) in the Baltic Sea region in 2007. Units: Mg (tones) of NO<sub>2</sub> per year and per  $50 \times 50$  km grid cell.



**Figure 3.4.** Map of annual emission of ammonia in the Baltic Sea region in 2007. Units: Mg of  $NH_3$  per year and per 50×50 km grid cell.

Table 3.2.	The list	of 11	SNAP	emissions	sectors a	as specified	1 in th	ne EMEP-	-CORIN	JAIR
Emission I	Inventor	y Guid	lebook.							

•	
Sector 1	Combustion in energy and transformation industry
Sector 2	Non-industrial combustion plants
Sector 3	Combustion in manufacturing industry
Sector 4	Production processes
Sector 5	Extraction and distribution of fossil fuels and geothermal energy
Sector 6	Solvent and other product use
Sector 7	Road transport
Sector 8	Other mobile sources and machinery (including ship traffic)
Sector 9	Waste treatment and disposal
Sector 10	Agriculture
Sector 11	Other sources and sinks



**Figure 3.5.** Annual 2007 nitrogen oxides emissions from the HELCOM Parties split into the SNAP sectors. Sectors. Compared to 2006, the nitrogen oxides emissions from much larger part of the Russian Federation are taken into account for 2007.



**Figure 3.6.** Annual 2007 ammonia emissions from the HELCOM Parties split into the SNAP sectors. Compared to 2006, the ammonia emissions from much larger part of the Russian Federation are taken into account for 2007.



**Figure 3.7** Map of annual emissions of nitrogen oxides from the international ship traffic on the Baltic Sea in 2007 used in the EMEP model calculations. Units: Mg of NO<sub>2</sub> per year and per  $50 \times 50$  km grid cell. There are large uncertainties in the estimate for ship traffic emissions. The international ship emissions and their spatial distribution have been updated based on new emission estimates derived by ENTEC for the year 2000. Ship emissions for 2007, were deduced by applying an increase factor of 2.5 % per year on cargo vessel traffic and 3.9 % per year on passenger vessel traffic. The factors are the same as used by ENTEC for predicting emissions of nitrogen in 2010 based on the emission estimates for 2000.



# 3.2 Annual deposition of nitrogen

44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69

Figure 3.8. Map of annual deposition flux of oxidized nitrogen (dry + wet) in 2007. Units: mg N  $m^{-2}$  yr<sup>-1</sup>.



**Figure 3.9**. Map of annual deposition flux of reduced nitrogen (dry + wet) in 2007. Units: mg N  $m^{-2}$  yr<sup>-1</sup>.



**Figure 3.10.** Map of annual deposition flux of total (oxidized + reduced) nitrogen in 2007. Units: mg N m<sup>-2</sup> yr<sup>-1</sup>.



Figure 3.11. Map of annual precipitation in 2007. Units: mm yr<sup>-1</sup>.



# 3.3 Monthly depositions of nitrogen

**Figure 3.12.** Monthly depositions of oxidized, reduced and total (oxidized +reduced) nitrogen to the entire Baltic Sea basin in 2007. Units: ktonnes N month<sup>-1</sup>.

Month	Oxidized	Reduced	Total
January	3.0	5.1	8.1
February	9.3	8.5	17.8
March	7.8	9.9	17.8
April	4.3	4.9	9.2
May	12.2	13.3	25.5
June	9.9	7.3	17.2
July	11.6	7.6	19.2
August	10.8	8.9	19.7
September	10.5	8.6	19.1
October	8.5	7.2	15.7
November	6.6	6.8	13.4
December	9.0	6.8	15.8

**Table 3.3.** Values of monthly depositions of oxidized, reduced and total (oxidized +reduced) nitrogen to the entire Baltic Sea basin in 2007. Units: ktonnes N month<sup>-1</sup>.



#### 3.4 Source allocation of nitrogen deposition

**Figure 3.13**. Top ten countries with highest contributions of nitrogen emissions to annual deposition of oxidized nitrogen into the Baltic Sea basin in the year 2007. Units: 100 tonnes N year<sup>-1</sup>. BAS and NOS denote ship emissions form the Baltic Sea and from the North Sea, respectively. RUE denotes the contributions from emissions in extended Russian territory.



**Figure 3.14**. Top ten countries with highest contributions of nitrogen emissions to annual deposition of reduced nitrogen into the Baltic Sea basin in the year 2007. Units: 100 tonnes N year<sup>-1</sup>.



**Figure 3.15**. Top ten countries with highest contributions of nitrogen emissions to annual deposition of total (oxidized + reduced) nitrogen into the Baltic Sea basin in the year 2007. Units: 100 tonnes N year<sup>-1</sup>. BAS and NOS denote ship emissions form the Baltic Sea and from the North Sea, respectively. RUE denotes the contributions from emissions in extended Russian territory.

#### 3.5 Conclusions for Chapter 3

- The extension of the EMEP model domain with inclusion of larger part of the Russian territory resulted in larger 2007 emissions of nitrogen oxides and ammonia.
- In six out of nine HELCOM countries 2007 emissions of nitrogen oxides were lower compared to 2006 emissions and in three countries (Russia, Lithuania, Estonia) higher. Ship emissions from the Baltic Sea were also higher in 2007.
- Annual 2007 ammonia emissions were higher than annual 2006 ammonia emissions in six out of nine HELCOM countries. They were lower in Denmark, Finland and Sweden.
- Among the HELCOM Contracting Parties, the largest percent of 2007 nitrogen emissions deposited to the Baltic Sea basin can be noticed for Denmark (16.7) and the lowest for Russia (0.4%).
- Calculated annual deposition of total nitrogen to the Baltic Sea basin in 2007 was 202 kt N, 1% higher than in 2006.
- Compared to 2006, annual 2007 deposition of oxidized nitrogen to the Baltic Sea was 1% lower and deposition of reduced nitrogen 5% higher.
- No clear seasonal pattern can be found in monthly nitrogen depositions in 2007.
- Germany, ship traffic on the Baltic Sea and Poland are the main emissions sources contributing to oxidized nitrogen deposition into the Baltic Sea basin in 2007.
- Germany, Denmark and Poland are top three sources contributing to reduced nitrogen deposition into the Baltic Sea basin in 2007.
- Some distant sources, like United Kingdom, France and ship traffic on the North Sea contribute significantly to nitrogen deposition into the Baltic Sea basin in 2007.
## 4. Atmospheric Supply of Lead to the Baltic Sea in 2007

In this chapter the results of model evaluation of lead atmospheric input to the Baltic Sea and its sub-basins for 2007 is presented. Modelling of lead atmospheric transport and deposition was carried out using MSC-E Eulerian Heavy Metal transport model MSCE-HM (*Travnikov and Ilyin*, 2005). Latest available official information on lead emission from HELCOM countries and other European countries for 2007 was used in computations. Based on these data annual and monthly levels of lead deposition to the Baltic Sea region have been obtained and contributions of HELCOM countries emission sources to the deposition over the Baltic Sea are estimated. Model results were compared with observed levels of lead concentrations in air and precipitation measured at monitoring sites around the Baltic Sea in 2007.

### 4.1 Lead emissions



Figure 4.1. Annual total anthropogenic emissions of lead in the Baltic Sea region for 2007, kg/km<sup>2</sup>/y.



**Figure 4.2.** Annual lead emission from Combustion in Power Plants and Industry sector for 2007, t/y.



**Figure 4.4.** Annual lead emission from Commercial, Residential and Other Stationary Combustion sector for 2007, t/y.

**Figure 4.3.** Annual lead emission from Transport sector for 2007, t/y.



**Figure 4.5.** Annual lead emission from Industrial processes sector for 2007, t/y.





**Figure 4.6.** Annual lead emission from Solvent and Other Product Use sector in Finland for 2007, kg/y.

**Figure 4.7.** Annual lead emission from Waste sector for 2007, kg/y.

NFR										
emission	Sector name	Denmark	Estonia	Finland	Germany	Latvia	Lithuania	Poland	Russia	Sweden
sector										
1	Combustion in Power Plants and Industry	4.4	37.4	15.2	14.6	0.082	0.6	325.7	355	4
2a	Transport above 1000m	0	NA	< 0.01	NE	NA	NA	NA	NA	NE
2b	Transport below 1000m	1.5	1.6	< 0.01	82.9	1.586	6.1	17.2		5.3
3	Commercial, Residential and Other Stationary Combustion	0.2	0.9	2.5	7.2	0.053	0.1	130.3		0.9
4	Fugitive Emissions From Fuels		NA					2.2		0.05
5	Industrial Processes	0.1	< 0.01	2.9	1.7	16.2		96.4		5.3
6	Solvent and Other Product Use	NA	NA	0.01				NA		
7	Agriculture							NA		
8	Waste		0.2	0.01	> 0.01	0.031		1.4		
9	Other									
Total		6.2	40.2	20.6	106.4	17.9	6.8	573.4	355	15.7

**Table 4.1.** Annual total lead anthropogenic emissions of HELCOM countries from different sectors for 2007, in tonnes per year

NA not available

NE not estimated



**Figure 4.8.** Contributions of different sector to total annual lead emission of Denmark in 2007.



**Figure 4.9.** Contributions of different sector to total annual lead emission of Estonia in 2007.



**Figure 4.10.** Contributions of different sector to total annual lead emission of Finland in 2007.



**Figure 4.12.** Contributions of different sector to total annual lead emission of Latvia in 2007.



**Figure 4.14.** Contributions of different sector to total annual lead emission of Poland in 2007.



Figure 4.11. Contributions of different sector to total annual lead emission of Germany in 2007.



**Figure 4.13.** Contributions of different sector to total annual lead emission of Lithuania in 2007.



**Figure 4.15.** Contributions of different sector to total annual lead emission of Sweden in 2007.



**Figure 4.16**. Maps with the contributions of annual total anthropogenic lead emissions from HELCOM Parties to total lead deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).



**Figure 4.16**. (cont.) Maps with the contributions of annual total anthropogenic lead emissions from HELCOM Parties to total lead deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).



Sweden

**Figure 4.16**. (cont.) Maps with the contributions of annual total anthropogenic lead emissions from HELCOM Parties to total lead deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).

Table 4.2. Annual total anthropogenic emissions of lead of HELCOM countries and other EMEP
countries in period 1990-2007, tonnes (Expert estimates of emissions are shaded)

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Denmark	120	97	88	47	12	12	10	7.7	7.0	7.1	6.8	6.1	5.3	5.0	5.3	5.7	6.1	6.2
Estonia	201	185	121	101	124	84	65	52	46	44	37	34	34	39	38	37	34	40
Finland	327	248	175	99	58	56	35	18	21	29	36	38	40	34	28	24	25	21
Germany	1801	1055	761	606	405	331	221	95	93	94	101	104	105	105	104	104	106	106
Latvia	23	19	12	9.9	12	10	12	13	15	14	13	14	14	15	15	15	17	18
Lithuania	47	49	32	28	33	30	18	20	22	19	16	15	15	15	5.2	5.7	6.0	6.8
Poland	1372	1336	986	997	966	937	960	896	736	745	647	610	588	596	600	536	524	573
Russia	3591	3553	3095	3276	2643	2426	2304	2247	2262	2339	2352	2235	2118	2207	330	355	355	355
Sweden	361	317	296	144	51	36	33	33	32	29	26	23	20	19	18	15	14	16
HELCOM	7843	6858	5566	5307	4304	3922	3658	3381	3234	3321	3236	3080	2940	3035	1144	1096	1086	1142
Albania	33	34	35	36	37	38	39	40	41	42	43	39	35	32	28	24	20	16
Armenia	11	0.820	0.610	0.790	0.340	0.334	0.009	0.009	0.010	0.005	0.005	0.503	1.0	2.5	2.5	2.5	2.5	2.5
Austria	207	172	120	86	60	16	15	14	13	13	12	12	13	13	14	14	15	15
Azerbaijan	12	12	12	12	12	12	12	12	12	12	12	13	13	13	13	14	14	14
Belarus	794	519	450	377	348	147	46	42	41	38	46	41	44	43	45	50	57	59
Belgium	437	405	386	310	249	237	238	253	174	141	104	87	81	77	86	76	71	60
Bosnia and	97	97	97	97	97	97	97	97	97	97	97	91	85	79	72	66	60	54
Herzegovina	01	01	01	01	01	01	01	01	01	01	01	01	00	10		00	00	01
Bulgaria	436	408	381	353	325	297	279	231	251	224	213	177	105	148	143	115	124	263
Croatia	430	397	364	331	297	264	268	190	183	178	147	107	60	23	16	12	9.1	9.2
Cyprus	16	16	14	14	14	13	12	12	13	11	10	10	9	9	9.1	9.1	8.7	8.6
Czech Republic	269	240	247	232	202	180	165	180	169	157	108	47	47	39	37	47	43	40
France	4258	2852	2070	1813	1609	1434	1263	1112	995	758	239	203	197	144	127	123	115	108
Georgia	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9	6.9	7.0	7.2	7.3	7.5	7.6	7.8	8.0
Greece	505	499	493	488	482	476	470	470	470	470	470	470	470	470	470	470	470	470
Hungary	658	488	208	187	155	129	100	90	82	34	35	34	35	33	36	37	37	35
Iceland	6.4	5.8	5.1	4.5	3.9	3.3	2.7	2.1	1.4	0.816	0.197	0.197	0.197	0.197	0.197	0.197	0.197	0.197
Ireland	125	111	117	101	88	76	63	66	42	39	29	16	15	15	15	15	15	15
Italy	4372	3332	2460	2272	2096	1988	1874	1692	1548	1380	936	703	237	242	256	266	274	274
Luxembourg	77	71	65	59	53	30	26	18	6.8	2.3	1.8	2.0	1.9	1.9	1.9	1.9	1.9	1.9
Malta	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.9	0.8	0.8	0.8	0.8	0.8	0.8
Monaco	3.9	4.0	4.1	3.7	2.1	0.780	0.673	0.564	0.486	0.427	0.059	0.063	0.056	0.046	0.041	0.041	0.030	0.041
Netherlands	338	283	241	216	188	162	112	63	52	44	36	41	45	41	43	39	39	39
Norway	186	143	127	87	24	22	10	10	10	9	7.6	6.8	7.1	7.2	7.7	6.3	6.2	6.7
Portugal	572	589	632	612	583	561	542	521	509	342	144	160	162	166	167	158	153	149
Republic of Moldova	249	220	103	71	23	34	28	22	7.9	11	2.8	3.4	3.3	11	2.3	5.1	5.0	5.0
Romania	585	573	561	550	538	526	514	502	491	420	402	476	398	319	241	162	118	77
Serbia and Montenegro	597	567	538	508	478	448	419	389	359	329	300	275	250	225	200	176	151	126
Slovakia	150	149	148	116	84	71	73	73	70	58	67	68	69	64	70	71	73	65
Slovenia	325	290	286	305	304	193	79	69	53	46	40	24	14	14	14	13	14	14
Spain	2682	1810	1221	1116	1104	933	903	840	780	710	589	390	269	265	260	268	271	272
Switzerland	419	379	333	280	248	186	157	138	119	54	32	28	25	22	21	21	20	20
The FYR of Macedonia	210	198	185	173	161	148	136	124	112	99	87	83	79	74	70	66	62	58
Turkey	765	765	765	765	765	765	765	765	765	765	765	717	669	620	572	524	476	428
Ukraine	3878	3586	3293	3001	2709	2417	2124	1832	1540	1248	955	663	145	123	195	304	297	309
United Kinadom	2893	2639	2417	2143	1841	1531	1297	1134	832	478	150	142	131	116	118	109	82	70
EMEP	34447	28720	23952	22033	19493	17367	15797	14392	13080	11539	9325	8214	6661	6495	4506	4369	4198	4235

Expert estimates:

S Denier van der Gon, H.A.C., M. van het Bolscher A.J.H. Visschedijk P.Y.J. Zandveld [2006]



Figure 4.17. Time-series of total annual lead emissions of HELCOM countries in 1990-2007, tonnes/y.

# 4.2 Annual total deposition of lead



Figure 4.18. Annual total deposition fluxes of lead over the Baltic Sea region for 2007, kg/km<sup>2</sup>/year.



### 4.3 Monthly total deposition of lead

Figure 4.19. Monthly total deposition of lead to the Baltic Sea for 2007, tonnes/month.

Table 4.3. Monthly total deposition of lead to the Baltic Sea for 2007, tonnes/month.

Month	Deposition
Jan	11
Feb	26
Mar	23
Apr	9
May	16
Jun	9
Jul	9
Aug	12
Sep	22
Oct	23
Nov	19
Dec	38



#### 4.4 Source allocation of lead deposition

**Figure 4.20.** Top ten countries with the highest contribution to annual total deposition of lead into the Baltic Sea for 2007, tonnes/year.



**Figure 4.21.** Sorted contributions (in %) of HELCOM countries to total deposition to the Baltic Sea for 2007. HELCOM countries emissions of lead contributed about 18% to the total annual lead deposition over the Baltic Sea in 2007. Contribution of other EMEP countries accounted for 8%. Significant contribution was made by other emission sources, in particular, remote emissions sources, natural emissions and re-emission of lead (74%).

Table 4.4. Two most significant contributors to the annual total deposition of lead to the six Baltic Sea sub-basins for 2007.

Sub-basin	Country	%	Country	%	*, %
GUB	Poland	6	Finland	6	72
GUF	Estonia	16	Poland	5	62
GUR	Poland	8	Latvia	5	72
BAP	Poland	11	Germany	2	73
BES	Poland	6	Germany	3	80
KAT	Poland	4	Germany	2	83
BAS	Poland	9	Germany	2	74

\* - contribution of re-emission, natural and remote sources.

#### 4.5 Comparison of model results with measurements



DE9 Pb air concentrations, ng/m<sup>3</sup>

Figure 4.22. Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Zingst (DE9). Units: ng / m<sup>3</sup>.



**Figure 4.23.** Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Keldsnor (DK5). Units:  $ng / m^3$ .



Figure 4.24. Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Anholt (DK8). Units:  $ng / m^3$ .



**Figure 4.25**. Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Preila (LT15). Units:  $ng / m^3$ .



**Figure 4.26.** Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Rucava (LV10). Units:  $ng / m^3$ .



Figure 4.27. Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Zoseni (LV16). Units:  $ng / m^3$ .



**Figure 4.28.** Comparison of calculated mean monthly lead concentrations in air for 2007 with measurements of the station Räo (SE14). Units:  $ng / m^3$ .



**Figure 4.29.** Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Zingst (DE9). Units:  $\mu g / L$ .



DK8 Pb concentration in precipitation, µg/L

Figure 4.30. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Anholt (DK8). Units:  $\mu g / L$ .



Figure 4.31. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Pedersker (DK20). Units:  $\mu g / L$ .



EE9 Pb concentration in precipitation, µg/L

Figure 4.32. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Lahemaa (EE9). Units:  $\mu g / L$ .



**Figure 4.33.** Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Vilsandi (EE11). Units:  $\mu g / L$ .



#### FI17 Pb concentration in precipitation, µg/L

**Figure 4.34.** Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Virolahty II (FI17). Units:  $\mu g / L$ .



Figure 4.35. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Hailuoto (FI53). Units:  $\mu g / L$ .



LV10 Pb concentration in precipitation, µg/L

Figure 4.36. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Rucava (LV10). Units:  $\mu g / L$ .



Figure 4.37. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Zoseni (LV16). Units:  $\mu g / L$ .



PL4 Pb concentration in precipitation, µg/L

Figure 4.38. Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Leba (PL4). Units:  $\mu g / L$ .



Figure 4.39. Comparison of calculated mean monthly lead concentrations in precipitation with measured at station Arup (SE51). Units:  $\mu g / L$ .

It can be seen that in general, computed concentrations of lead in air and in precipitation obtained for the selected monitoring sites around the Baltic Sea reasonably agree with the measured concentrations. Some deviations between simulated and observed monthly mean concentrations of lead can be connected with the uncertainties in seasonal variation of lead emission used in modeling, differences between measured precipitation amount and the one used in the model, and difficulties in measurements of heavy metals.

#### 4.6 Conclusions for Chapter 4

- Emissions of lead from HELCOM countries have decreased from 1990 to 2007 by 85%. There is a slight increase of lead emission in HELCOM countries from 2006 to 2007 by 5%.
- Annual deposition of lead to the Baltic Sea has decreased from 1990 to 2007 by 69%. Level of lead deposition in 2007 was lower by 9% comparing to 2006.
- The contribution of anthropogenic sources of HELCOM countries to total lead deposition over the Baltic Sea was estimated to approximately 20%. Essential contribution belongs also to the anthropogenic sources of other EMEP countries, natural sources and resuspension.
- The most significant contribution to lead deposition over the Baltic Sea was made by Poland followed by Estonia.
- Modelling results for lead were within an accuracy of 60% in comparison with measurements made around the Baltic Sea in 2007.

### 5. Atmospheric Supply of Cadmium to the Baltic Sea in 2007

In this chapter the results of model evaluation of cadmium atmospheric input to the Baltic Sea and its sub-basins for 2007 is presented. Modelling of cadmium atmospheric transport and deposition was carried out using MSC-E Eulerian Heavy Metal transport model MSCE-HM (*Travnikov and Ilyin*, 2005). Latest available official information on cadmium emission from HELCOM countries and other European countries was used in computations. Based on these data annual and monthly levels of cadmium deposition to the Baltic Sea region have been obtained and contributions of HELCOM countries emission sources to the deposition over the Baltic Sea are estimated. Model results were compared with observed levels of cadmium concentrations in air and precipitation measured at monitoring sites around the Baltic Sea in 2007.

#### 5.1 Cadmium emissions



Figure 5.1. Annual total anthropogenic emissions of cadmium in the Baltic Sea region for 2007, g/km<sup>2</sup>/y.



**Figure 5.2.** Annual cadmium emission from Combustion in Power Plants and Industry sector for 2007, t/y.



**Figure 5.3.** Annual cadmium emission from Transport sources below 1000 m sector for 2007, t/y.



**Figure 5.4.** Annual cadmium emission from Commercial, Residential and Other Stationary Combustion sector for 2007, t/y.

**Figure 5.5.** Annual cadmium emission from Industrial Processes sector for 2007, t/y.



**Figure 5.6.** Annual cadmium emission from Solvent and Other Product Use sector for 2007, kg/y.

**Figure 5.7.** Annual cadmium emission from Waste sector for 2007, kg/y.

NFR emission sector	Sector name	Denmark	Estonia	Finland	Germany	Latvia	Lithuania	Poland	Russia	Sweden
1	Combustion in Power Plants and Industry	0.418	0.64	0.667	1.65	0.023	0.383	13.81	59.4	0.222
2a	Transport above 1000m	0.0002	NA	NA	NE	NA	NA	NA	NA	NE
2b	Transport below 1000m	0.045	0.01	< 0.001	0.30	0.012	0.018	0.313		0.004
3	Commercial, Residential and Other Stationary Combustion	0.279	0.03	0.249	0.5	0.001	0.003	22.54		0.176
4	Fugitive Emissions From Fuels		NA	NA				0.51		0.01
5	Industrial Processes	0.005	0	0.187	0.09	0.548		2.35		0.175
6	Solvent and Other Product Use	NA	NA	< 0.001				NA		
7	Agriculture							NA		
8	Waste		0	< 0.001	< 0.001	0.003		0.12		
9	Other									
Total		0.75	0.68	1.1	2.54	0.59	0.40	39.65	59.4	0.58

**Table 5.1.** Annual total anthropogenic emissions of cadmium of HELCOM countries from different sectors for 2007, in tonnes per year

NA not available

NE not estimated



**Figure 5.8.** Contributions of different sector to total annual cadmium emission of Denmark in 2007.



**Figure 5.10.** Contributions of different sector to total annual cadmium emission of Finland in 2007.



**Figure 5.11.** Contributions of different sector to total annual cadmium emission of Germany in 2007.

Cd emission, Estonia



**Figure 5.9.** Contributions of different sector to total annual cadmium emission of Estonia in 2007.



**Figure 5.12.** Contributions of different sector to total annual cadmium emission of Latvia in 2007.



**Figure 5.13.** Contributions of different sector to total annual cadmium emission of Lithuania in 2007.



**Figure 5.14.** Contributions of different sector to total annual cadmium emission of Poland in 2007.



**Figure 5.15.** Contributions of different sector to total annual cadmium emission of Sweden in 2007.



Finland

Germany

**Figure 5.16**. Maps with the contributions of annual total anthropogenic cadmium emissions from HELCOM Parties to total cadmium deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).





**Figure 5.16**. (cont.) Maps with the contributions of annual total anthropogenic cadmium emissions from HELCOM Parties to total cadmium deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).



Sweden

**Figure 5.16**. (cont.) Maps with the contributions of annual total anthropogenic cadmium emissions from HELCOM Parties to total cadmium deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Denmark	1.1	1.2	1.2	1.1	1.0	0.831	0.811	0.734	0.721	0.704	0.625	0.676	0.640	0.620	0.622	0.646	0.719	0.747
Estonia	4.4	4.2	3.0	2.2	2.9	2.0	1.0	1.1	1.0	0.945	0.605	0.560	0.560	0.620	0.586	0.576	0.548	0.680
Finland	6.3	3.5	2.9	2.8	2.2	1.6	1.5	0.9	1.3	1.3	1.3	1.6	1.3	1.2	1.5	1.3	1.3	1.1
Germany	12	8.0	5.1	3.6	2.5	2.3	2.2	2.4	2.2	2.6	2.3	2.5	2.6	2.7	2.4	2.5	2.5	2.5
Latvia	1.5	1.3	0.895	0.758	0.957	0.743	0.921	0.775	0.8	0.724	0.516	0.471	0.463	0.475	0.458	0.499	0.551	0.588
Lithuania	3.8	2.8	2.5	2.3	2.1	2.1	2.2	2.2	2.6	2.0	1.4	1.2	1.0	0.916	0.524	0.371	0.367	0.405
Poland	92	85	84	92	86	83	91	86	55	62	50	53	49	48	46	46	42	40
Russia	79	68	69	59	57	57	51	50	49	51	51	51	52	57	55	59	59	59
Sweden	2.3	1.7	1.4	1.1	0.752	0.729	0.698	0.693	0.612	0.527	0.510	0.591	0.515	0.508	0.528	0.530	0.545	0.578
HELCOM	202	176	170	165	155	150	152	145	114	121	108	111	107	113	108	112	108	106
Albania	0.647	0.602	0.557	0.513	0.468	0.423	0.378	0.333	0.289	0.244	0.199	0.199	0.198	0.198	0.198	0.197	0.197	0.197
Armenia	0.129	0.129	0.129	0.129	0.129	0.129	0.129	0.129	0.129	0.129	0.129	0.132	0.135	0.137	0.140	0.143	0.146	0.148
Austria	1.6	1.5	1.2	1.2	1.1	0.975	0.996	0.970	0.901	0.977	0.948	1.0	1.0	1.1	1.1	1.2	1.2	1.2
Azerbaijan	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.4	2.4	2.5	2.5	2.6	2.6
Belarus	2.1	2.2	2.0	1.7	1.3	1.1	1.2	1.3	1.5	1.4	1.4	1.8	1.9	1.8	1.8	2.1	2.5	2.6
Belaium	7.2	6.9	7.5	6.4	4.9	5.1	4.2	4.3	2.8	2.4	2.2	2.1	2.0	1.9	2.3	1.7	1.8	1.6
Bosnia and																		
Herzegovina	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.7	1.6	1.6	1.6	1.6	1.6
Bulgaria	28	25	22	19	16	13	14	14	15	14	11	10	12	15	15	12	12	3
Croatia	1.3	1.2	1.1	1.1	1.0	0.950	1.0	1.0	1.1	1.1	1.0	0.874	0.929	0.948	0.877	0.826	0.836	0.790
Cyprus	0.558	0.578	0.663	0.713	0.745	0.680	0.721	0.761	0.680	0.877	0.925	0.917	1.0	1.0	1.1	1.1	1.2	1.2
Czech																		
Republic	4.3	3.9	3.6	3.5	3.5	3.6	2.9	3.0	2.7	2.7	2.9	2.6	2.7	2.2	2.4	3.1	3.2	6.0
France	20	20	19	18	18	17	17	16	15	13	13	12	12	8.3	5.8	5.5	4.0	3.6
Georgia	0.210	0.210	0.210	0.210	0.210	0.210	0.210	0.210	0.210	0.210	0.210	0.215	0.221	0.226	0.232	0.237	0.243	0.248
Greece	4.5	4.2	4.0	3.7	3.5	3.2	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Hungary	5.5	4.7	4.0	4.1	4.1	3.9	3.4	3.3	3.1	3.3	3.2	3.2	3.0	3.0	3.0	3.5	3.4	1.5
Iceland	0 166	0 158	0 149	0 141	0 132	0 124	0 115	0 107	0.098	0.090	0.081	0.082	0.082	0.082	0.083	0.083	0.083	0.084
Ireland	0.839	0.862	0.869	0.855	0.947	0.948	0.905	0.994	1 020	1 016	1 066	0.948	0.750	0.697	0.710	0.722	0.635	0.626
Italy	10	11	10	10.0	9.6	9.6	9.3	9.001	89	8.8	9.1	9.0	7.3	7.5	82	8.5	8.6	8.6
Luxemboura	0.600	0.575	0.550	0.525	0.500	0 400	0 400	0.300	0 200	0.054	0.051	0.054	0.047	0.047	0.047	0.047	0.047	0.047
Malta	0.480	0.480	0.480	0.480	0.480	0.480	0.480	0.480	0.480	0.480	0.480	0.618	0.526	0.573	0.573	0.593	0.593	0.617
Monaco	0.056	0.058	0.063	0.060	0.006	0.006	0.007	0.008	0.007	0.007	0.008	0.008	0.020	0.006	0.005	0.005	0.000	0.005
Netherlands	2.1	1.8	1.6	1.003	1.3	1 1	1 1	1 1	1.2	1.0	1.0	1.6	2.007	2.4	1.8	0.003	1 0	1.005
Nonway	2.1	1.0	1.0	1.4	1.0	0.083	1.1	1.1	1.2	1.0	0.688	0.683	0.681	0.658	0.601	0.544	0 500	0.556
Portugal	5.3	5.8	5.9	5.2	5.5	5.7	1.1	5.4	6.1	6.0	5.5	5.4	6.1	5.4	5.3	6.2	5.2	5.4
Penublic of	0.0	5.0	5.5	5.2	5.5	5.7	4.5	5.4	0.1	0.0	5.5	5.4	0.1	5.4	5.5	0.2	5.2	5.4
Moldova	2.4	3.5	1.7	1.4	0.819	0.594	0.659	0.364	0.328	0.148	0.173	0.114	0.226	0.122	0.114	0.145	0.158	0.158
Romania	22	20	19	18	17	15	14	13	12	12	87	74	81	87	94	10	6.5	25
Serbia and	~~~	20	15	10	17	10	14	10	12	12	0.7	1.4	0.1	0.7	0.4	10	0.0	2.0
Montenearo	5.3	5.8	5.9	5.2	5.5	5.7	4.9	5.4	6.1	6.0	5.5	5.4	6.1	5.4	5.3	6.2	5.2	5.4
Slovakia	24	35	17	14	0.819	0 594	0.659	0 364	0 328	0 148	0 173	0 1 1 4	0.226	0 122	0 1 1 4	0 145	0 158	0 158
Slovenia	2.4	20	10	1.4	17	15	14	13	12	12	87	7.4	8.1	8.7	9.114	10	6.5	2.5
Spain	53	5.8	59	5.2	5.5	57	49	54	61	60	5.5	5.4	6.1	5.4	53	6.2	5.2	5.4
Switzerland	2.4	3.5	1.7	1.4	0.819	0.594	0.659	0.4	0.1	0.0	0.0	0.4	0.1	0.122	0.114	0.145	0.158	0.158
The EVR of	2.4	0.0	1.7	1.4	0.010	0.004	0.000	0.004	0.020	0.140	0.175	0.114	0.220	0.122	0.114	0.140	0.100	0.100
Macedonia	9.1	9.2	9.3	9.3	9.4	9.4	9.5	9.6	9.6	9.7	9.8	9.8	9.7	9.7	9.7	9.7	9.7	9.7
Turkey	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	17	18
l Ikraine	54	50	46	12	39	3/	30	26	22	19	1/	10	20	28	31	6.8	5.1	9.0
United	- 54	- 50	-10	72		- 54		20	- 22	10	14	10	2.0	20	0.1	0.0	5.1	3.0
Kinadom	23	23	22	14	13	11	9.4	8.6	6.3	6.0	5.9	4.6	4.5	3.2	3.4	3.5	3.5	2.9
FMFP	477	441	422	391	368	354	343	330	287	287	262	257	245	273	240	250	239	230
							0-0										200	

**Table 5.2.** Annual total anthropogenic emissions of cadmium of HELCOM countries and other EMEP countries in period 1990-2007, tonnes (Expert estimates of emissions are shaded).

Expert estimates:

S Denier van der Gon, H.A.C., M. van het Bolscher A.J.H. Visschedijk P.Y.J. Zandveld [2006]



Figure 5.17. Time-series of annual cadmium emissions of HELCOM countries in 1990-2007, tonnes/y.



### 5.2 Annual total deposition of cadmium

Figure 5.18. Annual total deposition fluxes of cadmium over the Baltic Sea region for 2007, g/km<sup>2</sup>/year.


# 5.3 Monthly total deposition of cadmium

Figure 5.19. Monthly total deposition of cadmium to the Baltic Sea for 2007, tonnes/month.

Table 5.2. Monthly total deposition of cadmium to the Baltic Sea for 2007, tonnes/month.

Month	Cd
Jan	0.38
Feb	0.73
Mar	0.97
Apr	0.28
May	0.62
Jun	0.35
Jul	0.36
Aug	0.49
Sep	0.64
Oct	0.66
Nov	0.58
Dec	0.98



### 5.4 Source allocation of cadmium deposition

**Figure 5.20.** Top ten countries with the highest contribution to annual total deposition of cadmium over the Baltic Sea for 2007, tonnes/year.



**Figure 5.21.** Sorted contributions (in %) of HELCOM countries to total deposition over the Baltic Sea for 2007. HELCOM countries emissions of cadmium contributed about 38% to the total annual cadmium deposition over the Baltic Sea in 2007. Contribution of other EMEP countries accounted for 11%. Significant contribution was made by other emission sources, in particular, remote emissions sources, natural emissions and re-emission of cadmium (51%).

Sub-basin	Country	%	Country	%	*, %
GUB	Poland	15	Finland	11	51
GUF	Russia	17	Poland	12	46
GUR	Poland	20	Russia	6	50
BAP	Poland	28	Russia	4	49
BES	Poland	14	Denmark	6	62
KAT	Poland	11	Denmark	7	65
BAS	Poland	23	Russia	5	51

**Table 5.3.** Two most significant contributors to the annual total deposition of cadmium to the six Baltic Sea sub-basins for 2007.

\* - contribution of re-emission, natural and remote sources.

### 5.5 Comparison of model results with measurements



**Figure 5.22.** Comparison of calculated mean monthly cadmium concentrations in air for 2007 with measurements of the station Zingst (DE9). Units:  $ng / m^3$ .



**Figure 5.23.** Comparison of calculated mean monthly cadmium concentrations in air for 2007 with measurements of the station Rucava (LV10). Units:  $ng / m^3$ .



**Figure 5.24**. Comparison of calculated mean monthly cadmium concentrations in air for 2007 with measurements of the station Zoseni (LV16). Units:  $ng / m^3$ .



**Figure 5.25.** Comparison of calculated mean monthly cadmium concentrations in air for 2007 with measurements of the station Preila (LT15). Units:  $ng / m^3$ .



**Figure 5.26.** Comparison of calculated mean monthly cadmium concentrations in air for 2007 with measurements of the station Räö (SE14). Units:  $ng / m^3$ .



Figure 5.27. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Zingst (DE09). Units:  $\mu g / L$ .



Figure 5.28. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Anholt (DK8). Units:  $\mu g / L$ .



Figure 5.29. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Pedersker (DK20). Units:  $\mu g / L$ .



Figure 5.30. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Lahemaa (EE9). Units:  $\mu g / L$ .



Figure 5.31. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Vilsandi (EE11). Units:  $\mu g / L$ .



**Figure 5.32**. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Virolahty II (FI17). Units:  $\mu g / L$ .



Figure 5.33. Comparison of calculated mean monthly cadmium concentrations in precipitation 2007 with measurements of the station Hailuoto (FI53). Units:  $\mu g / L$ .



Figure 5.34. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Rucava (LV10). Units:  $\mu g / L$ .



Figure 5.35. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Zoseni (LV16). Units:  $\mu$ g / L.



Figure 5.36. Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Leba (PL4). Units:  $\mu g / L$ .



**Figure 5.37.** Comparison of calculated mean monthly cadmium concentrations in precipitation for 2007 with measurements of the station Arup (SE51). Units:  $\mu g / L$ .

In general, reasonable level of agreement between the computed concentrations of cadmium in air and in precipitation is obtained for the selected monitoring sites around the Baltic Sea. Comparing to lead more significant deviations between simulated and observed monthly mean concentrations of cadmium can be mentioned. The reason of deviations is connected with the uncertainties in seasonal variation of cadmium emission, differences between measured precipitation amount and the one used in the model, and difficulties in measurements of heavy metals.

### 5.6 Conclusions for Chapter 5

- Emissions of cadmium from HELCOM countries have decreased from 1990 to 2007 by 48%. Decrease of cadmium emission from 2006 to 2007 is accounted for 2%.
- Annual deposition of cadmium to the Baltic Sea has decreased from 1990 to 2007 by 46%. Level of cadmium deposition in 2007 was lower 6% comparing to 2006.
- The contribution of anthropogenic sources of HELCOM countries to total cadmium deposition over the Baltic Sea was estimated to approximately 40%. Essential contribution belongs to the anthropogenic sources of other EMEP countries, natural sources and resuspension.
- The most significant contribution to cadmium deposition over the Baltic Sea was made by Poland and Russia.
- Modelling results for cadmium were within an accuracy of 60% in comparison with measurements made around the Baltic Sea in 2007.

## 6. Atmospheric Supply of Mercury to the Baltic Sea in 2007

In this chapter the results of model evaluation of mercury atmospheric input to the Baltic Sea and its sub-basins for 2007 is presented. Modelling of mercury atmospheric transport and deposition was carried out using MSC-E Eulerian Heavy Metal transport model MSCE-HM (*Travnikov and Ilyin*, 2005). Latest available official information on mercury emission from HELCOM countries and other European countries was used in computations. Based on these data annual and monthly levels of mercury deposition to the Baltic Sea region have been obtained and contributions of HELCOM countries emission sources to the deposition over the Baltic Sea are estimated. Model results were compared with observed levels of mercury concentrations in air and precipitation measured at monitoring sites around the Baltic Sea in 2007.

### 6.1 Mercury emissions



Figure 6.1. Annual total anthropogenic emissions of mercury in the Baltic Sea region for 2007, g/km<sup>2</sup>/yy.



**Figure 6.2**. Annual mercury emission of HELCOM countries from Combustion in Power Plants and Industry sector for 2007, t/y.



**Figure 6.4.** Annual mercury emission of HELCOM countries from Transport sources below 1000 m sector for 2007, t/y.



**Figure 6.3.** Annual mercury emission of HELCOM countries from Commercial, Residential and Other Stationary Combustion sector for 2007, t/y.



**Figure 6.5**. Annual mercury emission of HELCOM countries from Industrial Processes sector for 2007, t/y.



**Figure 6.6.** Annual mercury emission of Finland from Solvent and Other Product Use sector for 2007, kg/y.



**Figure 6.7**. Annual mercury emission of HELCOM countries from Waste sector for 2007, kg/y.



**Figure 6.8.** Annual mercury emission of HELCOM countries from Fugitive Emissions From Fuels sector for 2007, t/y.

NFR emission sector	Sector name	Denmark	Estonia	Finland	Germany	Latvia	Lithuania	Poland	Russia	Sweden
1	Combustion in Power Plants and Industry	0.74	0.63	0.389	2.664	0.012	0.407	13.51	14	0.264
2a	Transport above 1000m	0	NA	NA	NE	NA	NA	NA	NA	NE
2b	Transport below 1000m	0.005	0	< 0.001	0.107	NA	0.0004	0		< 0.001
3	Commercial, Residential and Other Stationary Combustion	0.327	0.02	0.028	0.329	0.003	0.021	1.29		0.031
4	Fugitive Emissions From Fuels		NA	NA				0.305		0.01
5	Industrial Processes	0	0	0.391	0.946	0.008		0.727		0.21
6	Solvent and Other Product Use	NA	NA	< 0.001				NA		
7	Agriculture							NA		
8	Waste		0	0.002	< 0.001	0.003		0.045		0.119
9	Other									
Total		1.07	0.65	0.81	4.05	0.03	0.43	15.88	14	0.63

**Table 6.1.** Annual total mercury anthropogenic emissions of HELCOM countries from different sectors for 2007, in tonnes per year

NA not available NE not estimated



**Figure 6.8.** Contributions of different sector to total annual mercury emission of Denmark in 2007



**Figure 6.9.** Contributions of different sector to total annual mercury emission of Estonia in 2007



**Figure 6.10.** Contributions of different sector to total annual mercury emission of Finland in 2007



**Figure 6.11.** Contributions of different sector to total annual mercury emission of Germany in 2007



Figure 6.12. Contributions of different sector to total annual mercury emission of Latvia in 2007



**Figure 6.13.** Contributions of different sector to total annual mercury emission of Lithuania in 2007



Figure 6.14. Contributions of different sector to total annual mercury emission of Poland in 2007



**Figure 6.15.** Contributions of different sector to total annual mercury emission of Sweden in 2007



**Figure 6.16.** Maps with the contributions of annual total anthropogenic mercury emissions from HELCOM Parties to total mercury deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).



**Figure 6.16. (cont.)** Maps with the contributions of annual total anthropogenic mercury emissions from HELCOM Parties to total mercury deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).



Sweden

**Figure 6.16. (cont.)** Maps with the contributions of annual total anthropogenic mercury emissions from HELCOM Parties to total mercury deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Denmark	3.3	3.5	3.4	3.4	2.5	2.4	2.5	2.1	1.9	2.0	1.2	1.3	1.2	1.3	1.2	1.4	1.3	1.1
Estonia	1.1	1.0	0.830	0.640	0.640	0.600	0.600	0.600	0.530	0.510	0.550	0.500	0.500	0.580	0.540	0.520	0.520	0.650
Finland	1.1	0.865	0.800	0.609	0.656	0.713	0.726	0.570	0.548	0.561	0.574	0.731	0.659	0.778	0.744	0.851	0.981	0.812
Germany	20	14	9.2	6.1	3.6	3.3	3.3	3.3	3.4	3.3	3.6	3.5	3.5	3.6	3.6	3.8	3.9	4.0
Latvia	0.311	0.241	0.209	0.200	0.229	0.171	0.202	0.150	0.141	0.120	0.063	0.049	0.041	0.033	0.028	0.027	0.026	0.025
Lithuania	0.018	0.016	0.011	0.014	0.013	0.153	0.159	0.232	0.245	0.253	0.252	0.516	0.314	0.352	0.417	0.413	0.418	0.428
Poland	33	33	32	33	32	32	34	33	30	27	26	23	20	20	20	20	21	16
Russia	16	13	11	12	10	10	10	9.6	9.4	9.9	10	10	10	11	12	14	14	23
Sweden	1.6	1.3	1.3	1.1	1.1	1.1	1.1	0.970	0.943	0.927	0.770	0.653	0.673	0.758	0.781	0.726	0.591	0.633
HELCOM	76	67	59	56	52	51	52	50	47	45	43	41	37	39	39	42	43	46
Albania	0.511	0.480	0.449	0.419	0.388	0.357	0.326	0.296	0.265	0.234	0.203	0.202	0.202	0.201	0.200	0.199	0.199	0.198
Armenia	0.164	0.164	0.164	0.164	0.164	0.164	0.164	0.164	0.164	0.164	0.164	0.167	0.170	0.174	0.177	0.180	0.184	0.187
Austria	2.1	2.0	1.6	1.4	1.2	1.2	1.2	1.1	0.949	0.937	0.897	0.967	0.954	1.0	0.975	1.0	1.1	1.1
Azerbaijan	0.984	0.984	0.984	0.984	0.984	0.984	0.984	0.984	0.984	0.984	0.984	1.0	1.0	1.0	1.1	1.1	1.1	1.1
Belarus	1.1	1.1	0.879	0.721	0.602	0.511	0.297	0.310	0.392	0.380	0.358	0.522	0.565	0.603	0.632	0.649	0.716	0.741
Belgium	6.9	5.5	5.6	3.7	4.0	3.6	3.7	3.5	2.9	3.0	2.7	2.3	3.3	3.1	3.0	1.8	1.6	2.7
Bosnia and Herzegovina	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.9	1.9	1.9	1.9	1.9
Bulgaria	13	12	11	9.4	8.1	6.9	4.7	4.3	4.7	4.1	4.2	4.0	3.9	5.0	4.7	3.4	3.7	1.6
Croatia	1.4	1.146	0.931	0.717	0.502	0.287	0.297	0.318	0.320	0.307	0.410	0.405	0.449	0.563	0.710	0.693	0.588	0.624
Cyprus	0.655	0.674	0.8	0.8	0.8	0.8	0.8	0.8	0.8	1.0	1.0	1.0	1.1	1.2	1.2	1.3	1.3	1.4
Czech Republic	7.5	7.4	7.3	7.5	7.2	7.4	5.9	5.5	5.2	3.7	3.8	3.3	2.8	1.8	2.1	3.8	3.8	3.9
France	27	27	26	24	23	22	21	16	16	14	13	11	11	8.5	8.2	8.6	8.2	6.7
Georgia	0.253	0.253	0.253	0.253	0.253	0.253	0.253	0.253	0.253	0.253	0.253	0.258	0.264	0.269	0.274	0.279	0.284	0.290
Greece	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13
Hungarv	6.8	5.8	5.0	5.0	4.7	4.2	4.7	4.5	4.3	3.6	3.6	3.5	3.2	3.1	3.0	3.0	3.2	2.8
Iceland	0.048	0.054	0.060	0.066	0.072	0.078	0.084	0.091	0.097	0.103	0.109	0.108	0.108	0.108	0.108	0.107	0.107	0.107
Ireland	0.875	0.939	0.791	0.782	0.771	0.791	0.740	0.854	0.609	0.584	0.752	0.894	0.810	0.849	0.810	0.849	0.772	0.858
Italy	12	11	11	10	10	11	10	10	9.8	9.2	9.6	9.8	9.6	9.5	10	10	11	11
Luxemboura	0.300	0.275	0.250	0.225	0.200	0.100	0.100	0.100	0.100	0.286	0.275	0.293	0.288	0.288	0.288	0.288	0.288	0.288
Malta	0.489	0.489	0.489	0.489	0.489	0.489	0.489	0.489	0.489	0.489	0.489	0.627	0.535	0.582	0.582	0.602	0.602	0.626
Monaco	0.108	0.110	0.121	0.132	0.069	0.069	0.073	0.083	0.078	0.079	0.081	0.086	0.077	0.064	0.057	0.057	0.041	0.056
Netherlands	3.5	2.8	2.4	2.0	1.6	1.2	0.974	0.713	0.633	0.700	0.874	0.742	0.715	0.663	1.0	0.813	0.769	0.655
Norway	1.5	1.4	1.2	0.925	0.958	0.873	0.900	0.900	0.863	0.905	0.751	0.699	0.671	0.673	0.702	0.694	0.644	0.687
Portugal	3.8	3.9	4.3	3.9	3.7	4.0	3.6	3.9	4.1	4.2	3.7	3.6	3.8	3.1	3.1	3.4	2.9	2.8
Republic of Moldova	3.4	3.8	3.3	1.8	1.3	0.894	0.954	0.571	0.406	0.180	0.259	0.226	0.392	0.340	0.323	0.244	0.217	0.217
Romania	7.5	7.5	7.4	7.4	7.3	7.3	7.2	7.2	7.2	6.3	6.7	7.3	8.3	9.4	10	11	8.3	4.1
Serbia and Montenegro	3.9	4.0	4.2	4.3	4.5	4.7	4.8	5.0	5.2	5.3	5.5	5.5	5.5	5.4	5.4	5.4	5.4	5.4
Slovakia	12	9.3	6.2	5.0	3.9	3.9	3.4	3.7	4.1	3.7	4.3	3.8	3.6	2.9	3.2	2.9	3.4	2.7
Slovenia	1.2	1.1	1.1	1.1	1.0	1.0	1.0	1.1	1.1	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.2
Spain	13	14	15	14	13	13	12	10	11	11	11	11	12	10	10	10	9.5	9.0
Switzerland	6.6	6.1	5.8	5.4	4.9	4.1	3.8	3.5	3.3	2.4	2.1	1.8	1.4	1.0	1.1	1.1	1.1	1.1
The FYR of	1.5	4.5	10	10	1.0	47	4 7	4 7	1.0	1.0	1.0	1.0	10	10	10	1.0	1.0	10
Macedonia	1.5	1.5	1.6	1.6	1.6	1.7	1.7	1.7	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Turkey	18	18	18	18	18	18	18	18	18	18	18	19	19	19	20	20	21	21
Ukraine	36	35	34	33	32	31	30	29	28	27	26	25	5.9	30	6.6	6.0	15.7	7.6
United Kingdom	38	38	36	22	21	20	15	12	10	8.1	8.1	7.8	6.9	7.4	6.4	7.1	7.4	7.2
EMEP	324	307	289	259	246	239	226	213	205	194	191	185	163	186	164	167	175	162

**Table 6.2.** Annual total anthropogenic emissions of mercury of HELCOM countries and other EMEP countries in period 1990-2007, tonnes (Expert estimates of emissions are shaded).

Expert estimates: Denier van der Gon, H.A.C., M. van het Bolscher A.J.H. Visschedijk P.Y.J. Zandveld [2006]



**Figure 6.17**. Time-series of total annual mercury emissions of HELCOM countries in 1990-2007, tonnes/y.

### 5.2 Annual total deposition of mercury



Figure 6.18. Annual total deposition fluxes of mercury over the Baltic Sea region for 2007, g/km<sup>2</sup>/y.



# 5.3 Monthly total deposition of mercury

Figure 6.19. Monthly total deposition of mercury to the Baltic Sea for 2007, tonnes/month.

<b>Table 6.2.</b> Monthly total	deposition	of mercury to	the Baltic Sea	for 2007,	tonnes/month.
---------------------------------	------------	---------------	----------------	-----------	---------------

Month	Hg
Jan	0.24
Feb	0.22
Mar	0.30
Apr	0.16
May	0.35
Jun	0.34
Jul	0.41
Aug	0.33
Sep	0.35
Oct	0.28
Nov	0.23
Dec	0.22



### 5.4 Source allocation of mercury deposition

**Figure 6.20.** Top ten countries with the highest contribution to annual deposition of mercury over the Baltic Sea for 2007, tonnes/year.



**Figure 6.21.** Sorted contributions (in %) of HELCOM countries to total deposition over the Baltic Sea for 2007. HELCOM countries emissions of mercury contributed 16% to the total annual mercury deposition over the Baltic Sea in 2007. Contribution of other EMEP countries accounted for 8%. Significant contribution was made by other emission sources, in particular, remote emissions sources, natural emissions and re-emission of mercury (76%).

**Table 6.3.** Two most significant contributors to the annual total deposition of mercury to the six Baltic Sea sub-basins for 2007.

Sub-basin	Country	%	Country	%	*, %
GUB	Finland	3	Sweden	2	86
GUF	Estonia	11	Russia	3	74
GUR	Poland	5	Lithuania	3	80
BAP	Poland	9	Denmark	3	75
BES	Denmark	20	Poland	4	61
KAT	Denmark	13	United Kingdom	3	71
BAS	Poland	6	Denmark	4	76

\* - contribution of re-emission, natural and remote sources.

### 5.5 Comparison of model results with measurements



**Figure 6.22.** Comparison of calculated monthly mean Hg concentrations in air for 2007 with measurements of the station Zingst (DE9). Units:  $ng / m^3$ .



Figure 6.23. Comparison of calculated monthly mean Hg concentrations in air for 2007 with measurements of the station Råö (SE14). Units:  $ng / m^3$ .



**Figure 6.24.** Comparison of calculated monthly mean Hg concentrations in precipitation for 2007 with measurements of the station Zingst (DE9). Units: ng/L.



SE14 Hg concentration in precipitation, ng/L

**Figure 6.25.** Comparison of calculated monthly mean Hg concentrations in precipitation for 2007 with measurements of the station Råö (SE14). Units: ng/L.

Computed concentrations of mercury in air and in precipitation were compared with the measurement data of four monitoring sites around the Baltic Sea. It can be seen that that the model values reasonably agree with the measured concentrations. Some deviations between simulated and observed monthly mean concentrations of mercury can be connected with the uncertainties in seasonal variation of mercury emission used in modeling, differences between measured precipitation amount and the one used in the model, and difficulties in measurements of mercury.

### 6.6 Conclusions for Chapter 6

- Mercury emissions from HELCOM countries have decreased from 1990 to 2007 by 51%. At the same time there is some increase of mercury emission from 2006 to 2007 amounted to approximately 7%.
- Annual deposition of mercury to the Baltic Sea has decreased from 1990 to 2007 by 23%. Level of mercury deposition in 2007 was higher comparing to 2006 by 6%.
- The contribution of anthropogenic sources of HELCOM countries to total mercury deposition over the Baltic Sea was estimated to approximately 40%. Essential contribution belongs to the global and natural sources and anthropogenic sources of other EMEP countries.
- The most significant contribution to mercury deposition over the Baltic Sea was made by Poland and Denmark.
- Modelling results for mercury were within an accuracy of 30% in comparison with measurements made around the Baltic Sea in 2007.

### 7. Atmospheric Supply of PCDD/Fs to the Baltic Sea in 2007

In this chapter the results of model evaluation of dioxins and furans (PCDD/Fs) atmospheric input to the Baltic Sea and its sub-basins for 2007 is presented. Modelling of PCDD/F atmospheric transport and deposition was carried out using MSC-E Eulerian Persistent Organic Pollutant transport model MSCE-POP (*Gusev et al.*, 2005). Latest available official information on PCDD/F emission from HELCOM countries and other European countries was used in computations. Based on these data annual and monthly levels of PCDD/F deposition to the Baltic Sea region have been obtained and contributions of HELCOM countries emission sources to the deposition over the Baltic Sea are estimated.

### 7.1 PCDD/Fs emissions



Figure 7.1. Annual total anthropogenic emissions of PCDD/F in the Baltic Sea region for 2007, ng  $TEQ/m^2/y$ .



**Figure 7.2.** Annual PCDD/F emission of HELCOM countries from Combustion in Power Plants and Industry sector for 2007, g TEQ/y.



**Figure 7.4.** Annual PCDD/F emission of HELCOM countries from Commercial, Residential and Other Stationary Combustion sector for 2007, g TEQ/y.



**Figure 7.3.** Annual PCDD/F emission of HELCOM countries from Transport sources below 1000 m sector for 2007, g TEQ/y.



**Figure 7.5.** Annual PCDD/F emission of HELCOM countries from Fugitive Emissions From Fuels sector for 2007, g TEQ/y.



**Figure 7.6.** Annual PCDD/F emission of HELCOM countries from Industrial Processes sector for 2007, g TEQ/y.



**Figure 7.8.** Annual PCDD/F emission of HELCOM countries from Agriculture sector for 2007, g TEQ/y.

**Figure 7.7.** Annual PCDD/F emission of HELCOM countries from Solvent and Other Product Use sector for 2007, g TEQ/y.

Finland



**Figure 7.9.** Annual PCDD/F emission of HELCOM countries from Waste sector for 2007, g TEQ/y.

Russia

Estonia

Germany

🔨 Latvia

Lithuania

Poland

NFR emission sector	Sector name	DK	EE	FI	DE	LV	LT	PL	RU	SE
1	Combustion in Power Plants and Industry	1.5	2.8	4.8	7.1	5.35	1.5	50.6	808	26.9
2	Transport	0.2	0.05	2.8	3.16	0.02	0.3	0.7		0.6
3	Commercial, Residential and Other Stationary Combustion	20	1.6	1.1	21.04	6.7	9.1	188.4		4.01
4	Fugitive Emissions From Fuels	< 0.001	NA	0	1.72			3.1		0.19
5	Industrial Processes	6.1	0	3.0	50.206	1.2		15.5		3.8
6	Solvent and Other Product Use	0	0	0.002	NA			NA		NA
7	Agriculture	0		0	NA	0.02		0.3		NA
8	Waste	0.04	0.3	0.1	0.13	0.07		183.01		1
9	Other				NA					
Total		27.8	4.8	11.8	83.4	13.3	10.9	441.6	808	36.5

**Table 7.1.** Annual total PCDD/F anthropogenic emissions of HELCOM countries from different sectors for 2007, in g TEQ/year

NA not available

NO not observed



**Figure 7.10.** Contributions of different sector to total annual PCDD/F emission of Denmark in 2007



**Figure 7.11.** Contributions of different sector to total annual PCDD/F emission of Estonia in 2007



**Figure 7.12.** Contributions of different sector to total annual PCDD/F emission of Finland in 2007



**Figure 7.14.** Contributions of different sector to total annual PCDD/F emission of Latvia in 2007



Figure 7.16. Contributions of different sector to total annual PCDD/F emission of Poland in 2007



**Figure 7.13.** Contributions of different sector to total annual PCDD/F emission of Germany in 2007



**Figure 7.15.** Contributions of different sector to total annual PCDD/F emission of Lithuania in 2007



**Figure 7.17.** Contributions of different sector to total annual PCDD/F emission of Sweden in 2007



**Figure 7.18.** Maps with the contributions of annual total anthropogenic PCDD/F emissions from HELCOM Parties to total PCDD/F deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).


**Figure 7.18. (cont.)** Maps with the contributions of annual total anthropogenic PCDD/F emissions from HELCOM Parties to total PCDD/F deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).



Sweden

**Figure 7.18. (cont.)** Maps with the contributions of annual total anthropogenic PCDD/F emissions from HELCOM Parties to total PCDD/F deposition over the Baltic Sea in 2007 (fraction of total deposition in % over the 50x50 km grid cell).

**Table 7.2.** Annual total anthropogenic emissions of PCDD/Fs of HELCOM countries and other EMEP countries in period 1990-2007, g TEQ/year (Unofficial emissions are shaded).

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007
Denmark	67	64	59	54	51	49	47	44	37	31	32	30	27	29	24	25	26	28
Estonia	6	5	4	4	4	5	5	5	4	3	3	3	4	4	4	3	3	5
Finland	36	35	33	35	41	41	40	39	40	41	32	31	32	32	32	26	14	12
Germany	114	105	86	82	80	89	85	89	83	80	82	81	80	80	82	80	82	83
Latvia	7	8	7	8	9	10	11	12	11	12	10	11	11	12	13	13	14	13
Lithuania	20	18	16	14	12	10	8	6	6	5	4	13	12	12	11	11	11	11
Poland	529	535	517	592	520	515	484	440	381	381	333	447	433	482	387	416	449	442
Russia	991	947	901	878	825	769	637	614	606	625	631	643	655	686	716	747	778	808
Sweden	60	56	50	47	44	40	38	37	35	34	33	34	34	33	36	39	38	36
HELCOM	1829	1773	1673	1713	1585	1527	1355	1284	1203	1212	1162	1293	1288	1371	1305	1361	1414	1438
Albania	43	43	43	43	43	43	43	43	43	43	43	43	44	44	44	44	44	44
Armenia	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	47	48
Austria	160	135	77	67	56	58	60	59	56	54	52	57	48	51	52	53	53	48
Azerbaijan	98	98	98	98	98	98	98	98	98	98	98	99	100	101	102	102	103	104
Belarus	16	16	16	16	16	16	16	16	16	15	18	23	25	26	25	24	27	27
Belgium	592	552	520	455	481	445	359	374	245	135	116	80	58	60	62	61	57	58
Bosnia and Herzegovina	67	67	67	67	67	67	67	67	67	67	67	65	63	61	59	57	56	54
Bulgaria	554	535	515	495	476	456	341	310	288	245	233	201	219	255	239	230	247	58
Croatia	160	150	139	129	118	108	97	95	111	98	109	76	75	97	93	91	93	79
Cyprus	8	7	8	8	8	8	7	7	8	7	7	7	7	6	6	6	6	3
Czech Republic	1252	1220	1220	1140	1135	1135	922	830	767	643	744	620	177	114	187	179	175	148
France	1763	1814	1836	1893	1893	1694	1478	1043	938	611	520	384	357	235	315	194	121	117
Georgia	122	122	122	122	122	122	122	122	122	122	122	122	111	98	85	85	85	85
Greece	279	279	279	279	279	279	279	279	279	279	279	255	231	207	183	159	135	111
Hungary	196	175	132	129	124	116	113	109	98	99	97	98	98	99	97	95	92	85
Iceland	9	9	9	8	7	6	5	5	4	3	3	3	3	2	1	1	1	1
Ireland	27	27	26	26	25	25	25	24	21	21	22	22	30	34	26	22	22	15
Italy	472	495	475	451	441	460	419	426	413	388	369	293	283	282	289	294	302	318
Kazakhstan	40	40	40	40	40	40	40	40	40	40	40	40	41	41	41	42	42	42
Luxembourg	45	40	34	29	23	24	16	16	8	7	5	4	3	2	2	2	2	2
Malta	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4
Monaco	2	2	3	3	3	3	3	4	4	4	4	4	4	3	3	3	2	3
Netherlands	742	548	427	306	185	66	54	50	43	33	31	30	29	26	28	36	26	25
Norway	129	97	95	95	93	70	49	40	34	38	34	33	32	29	32	24	24	23
Portugal	18	18	18	18	18	18	19	21	18	17	15	11	11	11	10	9	9	9
Republic of Moldova	14	11	7	6	5	3	3	3	6	2	2	2	3	4	5	5	6	6
Romania	1537	1444	1352	1260	1168	1075	983	891	799	706	614	522	430	338	245	297	268	216
Serbia and Montenegro	172	172	172	172	172	172	172	172	172	172	172	170	169	167	166	164	162	161
Slovakia	136	132	128	124	120	116	106	96	109	98	90	87	91	70	65	86	67	66
Slovenia	16	17	15	14	13	12	12	12	11	11	11	10	10	10	9	9	8	8
Spain	181	187	195	192	186	161	160	133	134	140	147	141	142	147	150	149	157	160
Switzerland	175	159	148	135	122	105	96	88	81	63	54	42	29	17	16	16	16	15
The FYR of Macedonia	166	166	166	166	166	166	166	166	166	166	166	166	166	163	163	163	163	163
Turkey	1012	1012	1012	1012	1012	1012	1012	1012	1012	1012	1012	1018	1024	1029	1035	1041	1047	1053
Ukraine	1022	1022	1022	1022	1022	1022	1022	1022	1022	1022	1022	1024	1026	1027	1029	1030	1032	1033
United Kingdom	1143	1121	1093	886	686	733	470	374	280	254	226	216	199	197	227	198	197	190
EMEP, kg TEQ/ year	14	14	13	13	12	12	10	9.4	8.8	8.0	7.8	7.3	6.7	6.5	6.4	6.4	6.3	6.0

#### Expert estimates:

§ Denier van der Gon, H.A.C., M. van het Bolscher A.J.H. Visschedijk P.Y.J. Zandveld [2006]



**Figure 7.19**. Time-series of total annual PCDD/F emissions of HELCOM countries in 1990-2007, g TEQ/year.



## 7.2 Annual total deposition of PCDD/F

Figure 7.20. Annual total deposition fluxes of PCDD/Fs over the Baltic Sea region for 2007, ng  $TEQ/m^2/year$ .



## 7.3 Monthly total deposition of PCDD/F

Figure 7.21. Monthly total deposition of PCDD/Fs over the Baltic Sea for 2007, g TEQ/month.

Table 7.3. Monthly total de	position of PCDD/Fs over	the Baltic Sea for 2007,	g TEQ/month
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Month	PCDD/Fs
Jan	3.19
Feb	4.05
Mar	3.29
Apr	2.71
May	4.62
Jun	6.83
Jul	9.00
Aug	7.02
Sep	3.81
Oct	3.58
Nov	3.63
Dec	3.71



#### 7.4 Source allocation of PCDD/F deposition

**Figure 7.22.** Top ten countries with the highest contribution to annual total deposition of PCDD/Fs over the Baltic Sea for 2007, g TEQ/y.



**Figure 7.23.** Contributions (in %) of HELCOM countries to annual total PCDD/F deposition to the Baltic Sea for 2007. HELCOM countries emissions of PCDD/Fs contributed 30% to total PCDD/F deposition over the Baltic Sea in 2007. Contribution of other EMEP countries accounted for 8%. Significant contribution was made by other emission sources, in particular, remote emissions sources and re-emission of PCDD/Fs (62%).

Sub-basin	Country (1)	%	Country (2)	%	*, %
GUB	Sweden	15	Finland	8	61
GUF	Russia	35	Estonia	4	47
GUR	Latvia	13	Poland	6	63
BAP	Poland	15	Sweden	6	62
BES	Denmark	19	Poland	3	70
KAT	Denmark	20	Sweden	4	64
BAS	Poland	8	Denmark	7	62

**Table 7.4**. Two most significant contributors to annual total deposition of PCDD/Fs to the six Baltic Sea sub-basins for 2007.

\* - contribution of re-emission and remote sources.

#### 7.5 Comparison of model results with measurements

PCDD/Fs are not currently included into the EMEP measurement programme. For this reason verification of the MSCE-POP model results for PCDD/Fs was based on the comparison with the data of various measurement campaigns. Due to the limited information on measured atmospheric levels of PCDD/Fs and their temporal variations the comparison with the model results for this contaminant is of a preliminary character.

The performance of MSCE-POP model for computation of PCDD/F pollution levels within the European region was evaluated during the model review carried out in the framework of EMEP Task Force on Monitoring and Measurements. In particular, MSCE-POP model results on long-range transport of one of the toxic PCDD/F congeners 2,3,4,7,8-PeCDF for the EMEP region and the period 1990-2003 were compared with measurements of EMEP monitoring network and observations of other studies within the European region (*Shatalov et al.*, 2005). One of the main conclusions of the TFMM Workshop on the Review of the EMEP Models on Heavy Metals and Persistent Organic Pollutants in Moscow in 2007 was that the MSCE-POP model represents the state-of-the-science and fits to the purpose of evaluating the contributions of long-range transport to the environment impacts caused by POPs . It was recognized that the MSCE-POP model air concentrations and deposition of POPs across Europe. The model provided reasonable agreement with long-term

temporal trends of air pollution at most EMEP monitoring sites.

Additional comparison of PCDD/Fs modelling results obtained for 2004 was carried out with the measurement data of monitoring campaign carried out in Denmark. The results of the comparison are presented in the Joint report of EMEP Centres for HELCOM (*Bartnicki et al.*, 2006).

In this report no results of comparison of modeling results with measurement is presented since there was no available measurements of dioxins and furans within the European region for 2007 were found.

### 7.6 Conclusions for Chapter 7

- PCDD/F emissions from HELCOM countries have decreased from 1990 to 2007 by 21%. At the same time there is some increase of dioxins and furans emission from 2006 to 2007 amounted to approximately 2%.
- Annual PCDD/F deposition to the Baltic Sea has decreased from 1990 to 2007 by 62%. Level of PCDD/F deposition in 2007 has decreased comparing to 2006 by 9%.
- The contribution of anthropogenic sources of HELCOM countries to total PCDD/F deposition over the Baltic Sea was estimated to approximately 40%. Essential contribution belongs to the anthropogenic sources of other EMEP countries and global emission sources.
- The most significant contribution to dioxins and furans deposition over the Baltic Sea was made by Poland and Denmark.

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Appendix A: Tables with measurements available at HELCOM stations for 2007

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		Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Year
DE0009R	nitrogen_dioxide	µg N/m <sup>3</sup>	1.42	2.14	2.98	1.40	1.46	1.76	1.07	1.58	1.42	1.54	2.76	3.08	1.85
DK0005R	nitrogen_dioxide	µg N/m³	1.91	3.34	3.66	3.35	2.66	2.57	1.40	1.97	1.60	2.53	3.15	3.71	2.67
DK0009R	nitrogen_dioxide	µg N/m³	0.97	0.99	1.43	2.90	2.27	2.08	1.41	1.98	1.73	1.11	0.94	1.46	1.61
DK0041R	nitrogen_dioxide	µg N/m³	2.53	2.90	2.88	2.59	2.52	2.30	1.62	3.05	2.70	2.69	1.55	3.28	2.56
EE0009R	nitrogen_dioxide	µg N/m³	2.22	5.60	4.23	3.06	3.24	2.90	2.58	1.93	1.82	2.66	2.96	3.79	3.07
EE0011R	nitrogen_dioxide	µg N/m <sup>3</sup>	1.83	3.05	5.01	4.26	3.01	2.47	1.46	1.46	1.83	2.24	2.54	3.76	2.72
FI0009R	nitrogen_dioxide	µg N/m³	0.83	-	2.91	1.33	2.00	1.48	0.67	1.07	0.91	1.01	0.96	1.55	1.30
FI0017R	nitrogen_dioxide	µg N/m³	1.48	2.85	2.33	1.34	1.51	0.98	0.83	0.98	0.87	1.20	1.26	1.53	1.42
LT0015R	nitrogen_dioxide	µg N/m³	1.08	1.22	1.54	1.09	0.96	0.96	0.79	0.89	1.10	1.00	1.32	2.19	1.17
LV0016R	nitrogen_dioxide	µg N/m³	0.60	0.90	0.60	0.42	0.42	0.40	0.34	0.41	0.41	0.51	1.52	1.69	0.65
PL0004R	nitrogen_dioxide	µg N/m³	1.43	2.10	2.24	1.53	1.22	1.12	1.18	1.65	1.23	1.34	1.80	2.34	1.60
SE0005R	nitrogen_dioxide	µg N/m³	0.13	0.26	0.12	0.05	0.06	0.05	0.08	0.08	0.07	0.13	0.11	0.25	0.11
SE0011R	nitrogen_dioxide	µg N/m <sup>3</sup>	1.21	1.20	1.51	1.10	1.10	0.89	0.90	0.89	1.24	1.44	1.88	2.04	1.28
SE0014R	nitrogen_dioxide	µg N/m <sup>3</sup>	1.13	1.16	1.77	1.67	1.21	1.19	0.87	0.99	1.03	1.70	1.83	2.09	1.39
DE0009R	sum_ammonia_and_ammonium	µg N/m³	0.80	1.78	2.83	2.53	1.87	1.19	1.49	1.86	1.54	2.10	1.57	1.52	1.76
DK0003R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.91	1.93	2.73	4.61	2.60	2.18	1.61	2.26	1.27	1.79	1.65	1.79	2.10
DK0005R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.83	1.75	2.64	3.35	1.91	1.43	1.27	1.84	1.29	3.96	1.38	1.78	1.92
DK0008R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.35	0.92	1.44	1.71	1.17	0.84	0.65	1.02	0.65	1.15	0.84	1.23	1.00
FI0009R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.09	0.28	0.35	0.15	0.28	0.19	0.21	0.32	0.22	0.22	0.30	0.31	0.24
FI0017R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.16	0.41	0.51	0.25	0.52	0.31	0.44	0.61	0.37	0.52	0.28	0.45	0.40
LT0015R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.77	2.01	2.24	0.95	2.43	1.57	1.19	1.35	1.36	1.65	1.69	2.80	1.66
LV0010R	sum_ammonia_and_ammonium	µg N/m³	0.66	1.01	1.30	0.78	1.36	0.99	0.75	1.10	0.86	1.06	1.30	1.29	1.04
LV0016R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.46	0.67	1.21	0.82	1.00	1.14	0.77	1.16	1.09	1.35	0.87	0.88	0.95
PL0004R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.57	1.44	2.19	1.30	1.49	1.37	1.02	1.41	1.03	1.34	1.04	1.24	1.29
SE0005R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.04	0.28	0.15	0.09	0.17	0.21	0.33	0.23	0.13	0.15	0.06	0.07	0.16
SE0011R	sum_ammonia_and_ammonium	µg N/m <sup>3</sup>	0.40	0.85	1.40	1.84	1.49	1.23	0.64	0.85	0.65	1.06	0.75	0.81	0.98
SE0014R	sum_ammonia_and_ammonium	µg N/m³	0.20	0.71	0.96	1.17	0.87	0.73	0.46	0.79	0.46	0.81	0.54	0.73	0.70
DE0009R	sum_nitric_acid_and_nitrate	µg N/m³	0.61	1.17	1.50	1.00	0.91	0.58	0.56	0.55	0.57	0.93	0.88	1.03	0.85
DK0003R	sum_nitric_acid_and_nitrate	µg N/m³	0.29	0.85	1.17	0.93	0.74	0.47	0.43	0.61	0.38	0.75	0.55	0.86	0.67
DK0005R	sum_nitric_acid_and_nitrate	µg N/m³	0.51	1.09	1.54	1.62	1.05	0.74	0.66	0.81	0.64	0.98	0.68	0.82	0.91
DK0008R	sum_nitric_acid_and_nitrate	µg N/m³	0.30	0.55	1.00	1.07	0.76	0.56	0.42	0.57	0.45	0.68	0.56	0.97	0.66
FI0009R	sum_nitric_acid_and_nitrate	µg N/m³	0.11	0.25	0.27	0.14	0.26	0.15	0.15	0.23	0.18	0.16	0.24	0.35	0.21
FI0017R	sum_nitric_acid_and_nitrate	µg N/m³	0.15	0.27	0.31	0.18	0.30	0.16	0.19	0.20	0.18	0.17	0.17	0.27	0.22
LT0015R	sum_nitric_acid_and_nitrate	µg N/m³	0.46	0.68	0.98	0.54	0.56	0.39	0.49	0.41	0.47	0.62	0.50	0.97	0.59
LV0010R	sum_nitric_acid_and_nitrate	µg N/m°	0.33	0.44	0.68	0.24	0.37	0.27	0.35	0.26	0.27	0.42	0.38	0.58	0.38
LV0016R	sum_nitric_acid_and_nitrate	µg N/m³	0.22	0.34	0.43	0.25	0.32	0.28	0.15	0.29	0.38	0.42	0.25	0.34	0.30
PL0004R	sum_nitric_acid_and_nitrate	µg N/m <sup>3</sup>	0.35	0.74	1.10	0.58	0.52	0.29	0.37	0.37	0.39	0.58	0.53	0.67	0.54
SE0005R	sum_nitric_acid_and_nitrate	µg N/m <sup>3</sup>	0.03	0.06	0.06	0.04	0.03	0.03	0.04	0.05	0.04	0.03	0.04	0.05	0.04
SE0011R	sum_nitric_acid_and_nitrate	µg N/m <sup>3</sup>	0.38	0.45	0.90	0.74	0.49	0.30	0.30	0.32	0.40	0.53	0.45	0.63	0.49
SE0014R	sum_nitric_acid_and_nitrate	µg N/m³	0.29	0.31	0.62	0.79	0.66	0.40	0.32	0.40	0.43	0.58	0.44	0.76	0.50

		Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
DE0009R	cadmium	ng Cd/m <sup>3</sup>	0.08	0.25	0.24	0.30	0.13	0.14	0.05	0.08	0.06	0.11	0.17	0.14	0.15
EE0009R	cadmium	ng Cd/m <sup>3</sup>	0.12	0.25	0.49	0.17	0.14	0.16	0.10	0.12	0.14	0.16	0.11	0.13	0.17
FI0017R	cadmium	ng Cd/m <sup>3</sup>	-	-	0.19	0.06	0.07	0.05	0.05	0.10	0.18	0.24	0.12	0.10	0.11
LV0010R	cadmium	ng Cd/m <sup>3</sup>	0.07	0.07	0.40	0.19	0.04	0.14	0.12	0.22	0.05	0.03	0.04	0.03	0.12
LV0016R	cadmium	ng Cd/m <sup>3</sup>	0.05	0.19	0.32	0.08	0.06	0.04	0.04	0.09	0.08	0.14	0.17	0.10	0.11
SE0014R	cadmium	ng Cd/m <sup>3</sup>	0.03	0.12	0.19	0.10	0.04	0.08	0.03	0.06	0.04	0.07	0.03	0.05	0.07
DE0009R	lead	ng Pb/m <sup>3</sup>	3.25	9.83	7.53	7.34	3.36	3.45	2.53	3.27	2.16	3.69	5.21	4.31	4.62
DK0003R	lead	ng Pb/m <sup>3</sup>	0.87	3.86	4.13	2.42	1.21	1.92	1.27	2.78	1.79	4.16	3.56	3.76	2.66
DK0005R	lead	ng Pb/m <sup>3</sup>	1.23	5.41	4.51	2.97	1.45	2.49	1.23	3.27	2.40	4.06	3.98	4.18	3.08
DK0008R	lead	ng Pb/m <sup>3</sup>	0.43	3.51	3.60	1.69	1.09	1.64	1.03	2.75	1.47	3.43	2.71	2.66	2.15
EE0009R	lead	ng Pb/m <sup>3</sup>	2.86	7.64	7.35	3.40	3.22	3.49	3.15	5.20	5.93	13.19	6.80	13.79	6.32
FI0017R	lead	ng Pb/m <sup>3</sup>	-	-	5.12	2.15	3.08	1.83	1.79	4.35	5.42	7.02	3.72	3.46	3.51
LV0010R	lead	ng Pb/m <sup>3</sup>	1.60	2.91	8.92	2.57	5.90	10.35	3.31	4.72	1.59	1.47	1.25	1.27	3.85
LV0016R	lead	ng Pb/m <sup>3</sup>	1.37	5.94	6.52	1.76	2.30	1.54	1.81	2.82	3.47	5.30	7.77	3.23	3.55
SE0014R	lead	ng Pb/m <sup>3</sup>	1.00	4.02	4.34	2.54	1.54	1.90	0.98	2.37	1.47	2.01	1.03	1.51	2.05
DE0009R	mercury (TGM)	ng Hg/m <sup>3</sup>	1.86	1.81	1.79	1.68	1.65	1.45	1.50	1.42	1.47	1.74	1.67	1.77	1.65
SE0014R	mercury (TGM)	ng Hg/m <sup>3</sup>	1.44	1.73	1.59	1.56	1.52	1.49	1.63	1.53	1.59	1.54	1.55	1.42	1.55
SE0014R	mercury (aerosol)	) ng Hg/m <sup>3</sup>	3.28	9.89	10.66	4.81	6.08	5.84	5.83	5.71	4.16	8.09	6.29	5.43	6.36

Table A.2 Monthly and annual mean concentrations of heavy metals in air.

Table A.3 Monthly and annual mean concentrations of ammonium and nitrate in precipitation.

Site	Comp	Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
DE0009R	ammonium	mg N m/L	0.26	0.62	1.01	1.99	0.63	0.29	0.32	0.53	0.41	0.85	0.34	0.16	0.44
DK0005R	ammonium	mg N m/L	0.41	1.01	1.00	1.36	0.86	0.28	0.39	0.82	0.34	0.35	0.48	0.36	0.56
DK0008R	ammonium	mg N m/L	0.14	0.41	0.30	0.51	0.23	0.13	0.10	0.31	0.06	0.28	0.37	0.30	0.19
DK0020R	ammonium	mg N m/L	2.72	0.68	0.95	1.20	1.31	0.31	0.31	0.79	1.31	4.25	0.29	0.20	0.96
EE0009R	ammonium	mg N m/L	0.07	0.08	0.30	0.23	0.21	0.08	0.08	0.29	0.14	0.20	0.15	0.29	0.16
EE0011R	ammonium	mg N m/L	4.83	3.29	0.06	0.39	0.03	0.01	0.01	1.30	1.38	0.44	0.16	0.23	1.08
FI0004R	ammonium	mg N m/L	0.06	0.18	0.19	0.11	0.24	0.11	0.14	0.11	0.12	0.15	0.15	0.17	0.13
FI0009R	ammonium	mg N m/L	0.19	0.20	0.48	0.25	0.69	0.21	0.18	0.26	0.11	0.24	0.30	0.46	0.26
FI0017R	ammonium	mg N m/L	0.16	0.27	0.54	0.32	0.45	0.18	0.15	0.21	0.22	0.32	0.48	0.48	0.29
FI0053R	ammonium	mg N m/L	0.16	0.46	0.23	0.15	0.23	0.05	0.09	0.15	0.20	0.40	0.26	0.22	0.19
LT0015R	ammonium	mg N m/L	0.46	0.37	0.76	0.56	0.50	0.49	0.29	0.44	0.30	0.86	0.14	0.22	0.38
LV0010R	ammonium	mg N m/L	0.22	0.28	1.05	0.31	0.75	0.23	0.16	0.26	0.34	0.28	0.27	0.41	0.32
LV0016R	ammonium	mg N m/L	0.36	0.81	0.55	0.30	0.56	0.26	0.19	0.31	0.20	0.33	0.28	0.43	0.34
PL0004R	ammonium	mg N m/L	0.22	0.49	0.67	0.59	0.72	0.31	0.44	0.38	0.32	0.54	0.24	0.30	0.39
SE0005R	ammonium	mg N m/L	0.02	0.01	0.11	0.04	0.13	0.06	0.17	0.26	0.16	0.13	0.03	0.03	0.11
SE0011R	ammonium	mg N m/L	0.26	0.67	0.56	0.77	0.59	0.30	0.16	0.43	0.41	0.59	0.42	0.37	0.38
SE0014R	ammonium	mg N m/L	0.19	0.66	0.33	0.40	0.60	0.39	0.22	0.53	0.18	0.99	0.44	0.48	0.37
SE0053R	ammonium	mg N m/L	0.08	0.13	0.20	0.16	0.42	0.16	0.06	0.54	0.20	0.38	0.19	0.11	0.22
DE0009R	nitrate	mg N m/L	0.26	0.61	0.73	1.33	0.57	0.30	0.31	0.36	0.31	0.59	0.33	0.26	0.39
DK0005R	nitrate	mg N m/L	0.38	1.11	0.67	1.41	0.80	0.28	0.33	0.48	0.23	0.24	0.48	0.50	0.50
DK0008R	nitrate	mg N m/L	0.25	0.68	0.65	0.57	0.53	0.25	0.19	0.37	0.24	0.58	0.73	0.67	0.36
DK0020R	nitrate	mg N m/L	0.40	0.91	0.78	0.82	0.55	0.33	0.26	0.44	0.47	1.13	0.49	0.38	0.48
EE0009R	nitrate	mg N m/L	0.23	0.41	0.58	0.26	0.23	0.13	0.15	0.18	0.17	0.25	0.33	0.56	0.25
EE0011R	nitrate	mg N m/L	0.33	0.32	0.34	0.50	0.09	0.02	0.01	0.07	0.05	0.20	0.33	0.49	0.19
FI0004R	nitrate	mg N m/L	0.19	0.45	0.39	0.18	0.24	0.14	0.16	0.13	0.15	0.22	0.29	0.37	0.22
FI0009R	nitrate	mg N m/L	0.52	0.76	0.89	0.29	0.70	0.27	0.22	0.25	0.25	0.39	0.59	1.07	0.42
FI0017R	nitrate	mg N m/L	0.36	0.59	0.76	0.31	0.40	0.22	0.17	0.19	0.19	0.44	0.64	0.70	0.35
FI0053R	nitrate	mg N m/L	0.22	0.62	0.28	0.14	0.18	0.10	0.11	0.12	0.14	0.37	0.29	0.34	0.20
LT0015R	nitrate	mg N m/L	0.53	0.47	0.50	0.40	0.31	0.37	0.20	0.39	0.38	1.03	0.34	0.39	0.35
LV0010R	nitrate	mg N m/L	0.38	0.43	0.79	0.27	0.53	0.27	0.12	0.22	0.37	0.39	0.39	0.49	0.34
LV0016R	nitrate	mg N m/L	0.28	0.19	0.35	0.19	0.32	0.18	0.15	0.17	0.19	0.33	0.31	0.34	0.23
PL0004R	nitrate	mg N m/L	0.36	0.79	0.56	0.39	0.52	0.33	0.34	0.30	0.31	0.54	0.30	0.40	0.39
SE0005R	nitrate	mg N m/L	0.07	0.12	0.20	0.06	0.14	0.09	0.08	0.16	0.13	0.16	0.08	0.15	0.11
SE0011R	nitrate	mg N m/L	0.28	0.69	0.52	0.41	0.50	0.20	0.18	0.24	0.37	0.46	0.42	0.52	0.34
SE0014R	nitrate	mg N m/L	0.29	0.82	0.55	0.24	0.43	0.20	0.19	0.33	0.21	0.93	0.73	0.72	0.35
SE0053R	nitrate	mg N m/L	0.22	0.34	0.31	0.34	0.29	0.05	0.12	0.17	0.20	0.35	0.22	0.35	0.24

Site	Comp	Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
DE0009R	cadmium	μg/L	0.014	0.054	0.086	-	0.040	0.024	0.018	0.035	0.027	0.045	0.028	0.011	0.030
DK0008R	cadmium	μg/L	0.019	0.071	0.024	0.058	0.033	0.018	0.016	0.036	0.014	0.027	0.041	0.011	0.023
DK0020R	cadmium	μg/L	0.023	0.061	0.055	0.055	0.055	0.036	0.034	0.033	0.075	0.287	0.047	0.019	0.051
EE0009R	cadmium	μg/L	0.065	0.076	0.052	0.062	0.030	0.026	0.051	0.010	0.071	0.042	0.135	0.110	0.057
EE0011R	cadmium	μg/L	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.300</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.300</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.300</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.300	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<></td></dl<>	<dl< td=""><td>0.100</td><td><dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<></td></dl<>	0.100	<dl< td=""><td>0.100</td><td>0.100</td><td>0.035</td></dl<>	0.100	0.100	0.035
FI0017R	cadmium	μg/L	0.030	0.146	0.200	0.045	0.051	0.029	0.037	0.118	0.031	0.090	0.104	0.103	0.062
FI0053R	cadmium	μg/L	0.017	0.154	0.031	0.021	0.020	0.014	0.031	0.040	0.011	0.063	0.029	0.018	0.030
LV0010R	cadmium	μg/L	0.096	0.067	0.096	0.190	0.057	0.034	0.048	0.062	0.048	0.039	0.044	0.040	0.056
LV0016R	cadmium	μg/L	0.077	0.061	0.047	0.015	0.042	0.061	0.048	0.029	0.050	0.034	0.082	0.046	0.051
PL0004R	cadmium	μg/L	0.050	0.041	0.046	0.057	0.049	0.024	0.040	0.034	0.038	0.041	0.022	0.033	0.039
SE0051R	cadmium	μg/L	0.010	-	0.040	0.040	0.050	0.010	0.010	0.040	0.040	0.040	0.070	0.040	0.027
SE0097R	cadmium	μg/L	0.090	0.086	0.039	0.020	0.030	0.027	0.012	0.020	0.020	0.040	0.037	0.020	0.027
DE0009R	lead	μg/L	0.44	1.83	2.39	-	0.94	0.65	0.46	0.92	0.67	1.21	0.75	0.24	0.81
DK0008R	lead	uq/L	0.44	1.60	0.94	1.82	1.20	0.59	0.33	1.03	0.48	0.75	1.30	0.54	0.67
DK0020R	lead	ua/L	0.62	2.03	1.26	2.01	2.01	0.92	0.90	0.87	0.81	1.30	0.64	0.45	0.99
EE0009R	lead	ug/L	0.50	0.50	1.20	0.50	0.50	0.50	0.50	0.50	0.50	0.50	1.20	1.50	0.62
EE0011R	lead	uq/L	0.50	0.50	0.50	2.20	1.20	0.50	1.30	0.50	0.50	0.50	0.50	0.50	0.69
FI0017R	lead	uq/L	1.52	4.42	4.28	1.00	1.40	0.64	0.86	2.04	0.93	2.17	3.84	4.09	1.76
FI0053R	lead	uq/L	0.48	3.80	1.35	0.61	0.47	0.31	0.33	0.66	0.24	1.09	1.33	0.81	0.66
LV0010R	lead	uq/L	5.83	6.45	8.76	0.75	1.14	1.72	0.69	1.34	0.54	1.63	2.30	7.06	2.51
LV0016R	lead	uq/L	0.93	1.79	1.90	0.42	1.19	1.18	1.00	0.38	0.73	1.19	2.16	1.80	1.11
PI_0004R	lead	uq/L	0.11	1.61	0.85	1.45	1.02	0.55	0.83	0.53	0.61	0.64	0.54	0.63	0.65
SE0051R	lead	uq/L	0.36	-	0.67	0.25	0.77	0.41	0.35	0.73	0.54	0.45	0.82	0.45	0.47
SE0097R	lead	ug/L	1.30	1.27	0.84	0.18	0.71	0.31	0.36	0.44	0.35	0.73	1.04	0.69	0.59
02	loud	P0					••••								
DE0009R	mercury	ng/L	5.4	9.2	9.3	11.8	11.9	7.4	8.1	8.7	7.7	7.6	5.6	4.2	7.9
LV0010R	mercury	ng/L	-		24.3	12.2	27.0	30.0	30.0	26.5	30.0	26.5	26.6	10.0	25.8
LV0016R	mercury	ng/L	- 1	-		30.0	25.0	36.5	36.8	27.8	30.0	26.0	22.3	10.0	28.8
SE0014R	mercury	ng/L	8.2	15.3	10.0	9.6	11.1	5.9	21.1	10.5	8.8	13.9	6.9	12.6	11.0
02	morou.,	Ŭ													
DE0009R	precipitation_amount	mm	86	44	44	3	74	153	132	51	65	34	44	41	771
DE0009R	precipitation_amount (Hg)	mm	90	25	61	20	91	157	124	57	64	34	42	48	814
DK0008R	precipitation_amount	mm	83	28	32	12	38	108	150	47	75	22	12	32	639
DK0020R	precipitation_amount	mm	63	17	40	16	53	56	150	59	38	18	55	50	615
EE0009R	precipitation_amount	mm	67	20	28	25	63	47	47	66	116	74	49	23	624
EE0011R	precipitation_amount	mm	114	19	43	21	15	74	110	79	57	38	76	44	689
FI0017R	precipitation_amount	mm	51	12	17	34	70	47	92	51	121	30	45	44	613
FI0053R	precipitation_amount	mm	29	6	25	20	40	25	87	72	53	35	25	37	452
LV0010R	precipitation_amount	mm	75	43	30	24	69	78	233	51	83	39	142	78	947
LV0016R	precipitation_amount	mm	112	22	29	33	80	75	115	88	61	63	62	35	777
PL0004R	precipitation_amount	mm	131	30	37	29	49	67	104	80	69	42	83	55	775
SE0014R	precipitation_amount	mm	46	15	21	23	79	97	98	63	108	16	47	19	632
SE0051R	precipitation_amount	mm	177	47	43	44	71	130	208	65	94	59	43	69	1049
SE0097R	precipitation_amount	mm	1	43	103	39	80	143	160	83	150	48	93	225	1166

Table A.4 Monthly and annual mean concentrations of heavy metals in precipitation.

Site	Comp	Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year	Total n
DE0009R	ammonium	mg N/m <sup>2</sup>	20	27	44	8	45	45	42	26	26	28	16	7	334	
DE0009R	nitrate	mg N/m <sup>2</sup>	20	26	32	6	41	46	40	18	19	20	15	12	293	627
DE0009R	precipitation amount	mm	77	43	43	4	72	153	130	49	63	33	47	45	758	
DK0005R	ammonium	mg N/m <sup>2</sup>	35	62	31	3	50	27	47	45	11	0	8	14	337	
DK0005R	nitrate	mg N/m <sup>2</sup>	32	68	21	3	47	27	40	26	7	0	8	19	303	639
DK0005R	precipitation amount	mm	84	62	31	2	59	98	122	55	32	1	17	38	601	
DK0008R	ammonium	mg N/m <sup>2</sup>	8	20	7	5	8	14	14	14	4	5	6	9	115	
DK0008R	nitrate	mg N/m <sup>2</sup>	15	33	16	6	18	27	28	16	15	10	11	21	217	331
DK0008R	precipitation amount	mm	60	49	24	10	35	107	142	44	61	18	15	32	598	
DK0020R	ammonium	mg N/m <sup>2</sup>	180	30	35	15	81	22	37	35	62	74	15	9	595	
DK0020R	nitrate	mg N/m <sup>2</sup>	27	41	29	10	34	23	31	19	22	20	25	17	298	892
DK0020R	precipitation_amount	mm	66	45	37	12	62	70	120	44	47	18	50	46	618	
		0														
EE0009R	ammonium	mg N/m <sup>2</sup>	5	2	8	6	13	4	4	19	16	15	7	7	99	
EE0009R	nitrate	mg N/m <sup>2</sup>	15	8	16	7	15	6	7	12	19	19	16	13	157	256
EE0009R	precipitation_amount	mm	67	20	28	25	63	47	47	66	116	74	49	23	624	
		0														
EE0011R	ammonium	mg N/m <sup>2</sup>	500	139	3	3	1	2	1	77	73	28	9	16	883	
EE0011R	nitrate	mg N/m <sup>2</sup>	34	13	19	4	4	2	1	4	3	13	18	34	155	1038
EE0011R	precipitation_amount	mm	104	42	56	9	50	137	120	59	53	63	54	69	817	
FI0004R	ammonium	mg N/m <sup>2</sup>	4	3	4	2	9	7	10	5	9	7	9	9	81	
FI0004R	nitrate	mg N/m²	14	9	9	4	8	9	12	7	12	10	19	20	131	212
FI0004R	precipitation_amount	mm	76	19	22	21	35	64	74	50	76	48	63	54	603	
FI0009R	ammonium	mg N/m <sup>2</sup>	5	1	5	3	7	9	9	16	4	5	15	11	89	
FI0009R	nitrate	mg N/m²	14	2	9	4	7	11	11	14	10	8	29	26	145	234
FI0009R	precipitation_amount	mm	27	3	10	12	10	43	51	59	38	20	50	24	346	
			-	-				-	-			-				
F10017R	ammonium	mg N/m <sup>2</sup>	8	3	15	11	26	9	9	19	24	8	25	19	177	
F10017R	nitrate	mg N/m <sup>2</sup>	19	8	22	10	23	11	10	17	20	11	33	28	215	391
F10017R	precipitation_amount	mm	54	13	29	33	58	51	61	93	107	25	51	40	615	
			-		_											
F10053R	ammonium	mg N/m	5	4		3	10	1	8	11	8	12	8	9	85	475
F10053R	nitrate	mg N/m⁻		5	9	3	8	3	9	-9	6	11	9	14	90	175
F10053R	precipitation_amount	mm	30	8	32	19	42	25	88	/1	41	30	30	41	456	
		mag. N1/mg <sup>2</sup>	20		4.4	~	40	05		24	27	4.4	4.4		200	
	ammonium	mg N/m <sup>2</sup>	20	4	14	0	42	40	22	31	21	14	14	0	300	500
L10015R	nitrate	mg N/m	29	5	9	4	26	49	38	2/	34	17	34	14	286	592
L10015R	precipitation_amount	mm	50	11	19	11	85	131	193	70	89	17	100	35	815	
	ommonium	$ma N l/m^2$	25	11	20	0	57	10	26	14	27	10	26	27	214	
	annonum	mg N/m <sup>2</sup>	20	16	29	0	37	19	20	14	27	10	50	37	224	645
	nuale	mm	44	20	22	24	40	22	20	12	29	26	127	44	006	045
LVUUTUR	precipitation_amount		110	30	20	24	70	03	222	50	79	30	137	91	960	
LV0016P	ammonium	$ma N / m^2$	13	10	15	10	46	20	21	31	0	21	17	16	267	
LV0016R	nitrato	mg N/m <sup>2</sup>	40	19	10	6	27	20	16	17	9	21	10	10	192	440
LV0016R	precipitation amount	mm	110	23	28	34	27	79	100	101	47	65	62	36	793	443
LV0010K	precipitation_amount		119	25	20	54	02	70	109	101	47	05	02	50	705	
PI 0004P	ammonium	ma N/m <sup>2</sup>	28	15	24	17	35	21	46	30	22	23	20	17	208	
PL0004R	nitrato	mg N/m <sup>2</sup>	47	24	24	11	25	21	40	24	22	23	20	22	200	600
PL0004R	nicale	mm	131	30	37	29	20	67	104	80	69	42	83	55	775	000
1 2000410	precipitation_amount		101	00	01	20	40	01	104	00	00	-12	00	00	110	
SE0005R	ammonium	ma N/m <sup>2</sup>	0	0	0	0	2	1	5	4	2	1	0	0	16	
SE0005R	nitrate	ma N/m <sup>2</sup>	1	Ő	1	1	2	1	2	3	1	1	1	2	16	32
SE0005R	precipitation amount	mm	10	2	3	9	15	10	27	16	11	9	18	15	144	02
0200000	prooplation_amount			-	Ũ	Ũ						Ũ				
SE0011R	ammonium	ma N/m <sup>2</sup>	33	21	35	19	31	35	22	42	40	17	25	21	339	
SE0011R	nitrate	ma N/m <sup>2</sup>	35	21	32	10	26	23	24	24	36	13	25	29	299	639
SE0011R	precipitation amount	mm	126	31	62	25	52	116	138	99	99	29	59	56	890	
02001111	prooplation_amount		.20		02					00		20	00	00	000	
SE0014R	ammonium	ma N/m <sup>2</sup>	14	8	14	14	44	50	37	44	21	24	16	31	320	
SE0014R	nitrate	ma N/m <sup>2</sup>	21	10	23		32	26	32	27	25	22	26	47	305	625
SE0014R	precipitation amount	mm	74	13	43	34	74	126	170	83	119	24	36	65	860	020
	, <u>_</u> ount											= -				
SE0053R	ammonium	mg N/m <sup>2</sup>	5	3	7	1	18	4	4	39	11	14	12	11	129	
SE0053R	nitrate	mg N/m <sup>2</sup>	14	8	11	3	12	1	8	12	11	13	14	36	141	270
SE0053R	precipitation amount	mm	62	22	35	7	42	27	69	73	53	36	63	102	591	-

Table A.5 Monthly and annual deposition of ammonium and nitrate in precipitation.

Site	Comp	Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
DE0009R	cadmium	µg Cd/m <sup>2</sup>	1.2	2.4	3.7	-	2.9	3.7	2.4	1.8	1.8	1.5	1.2	0.5	23.2
DK0008R	cadmium	µg Cd/m <sup>2</sup>	1.6	2.0	0.8	0.7	1.2	1.9	2.4	1.7	1.1	0.6	0.5	0.3	14.8
DK0020R	cadmium	µg Cd/m <sup>2</sup>	1.5	1.1	2.2	0.9	2.9	2.0	5.1	2.0	2.8	5.2	2.6	1.0	31.5
EE0009R	cadmium	µg Cd/m <sup>2</sup>	4.3	1.5	1.4	1.5	1.9	1.2	2.4	0.7	8.3	3.1	6.6	2.5	35.4
EE0011R	cadmium	µg Cd/m <sup>2</sup>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>6.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>6.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td>6.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	6.2	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<></td></dl<>	<dl< td=""><td>5.7</td><td><dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<></td></dl<>	5.7	<dl< td=""><td>7.6</td><td>4.4</td><td>23.8</td></dl<>	7.6	4.4	23.8
FI0017R	cadmium	µg Cd/m <sup>2</sup>	1.5	1.8	3.4	1.5	3.5	1.4	3.4	6.1	3.7	2.7	4.7	4.5	38.2
FI0053R	cadmium	µg Cd/m <sup>2</sup>	0.5	0.9	0.8	0.4	0.8	0.4	2.7	2.9	0.6	2.2	0.7	0.7	13.4
LV0010R	cadmium	µg Cd/m <sup>2</sup>	7.2	2.9	2.9	4.6	3.9	2.6	11.1	3.1	4.0	1.5	6.2	3.2	53.4
LV0016R	cadmium	µg Cd/m <sup>2</sup>	8.6	1.4	1.4	0.5	3.4	4.6	5.6	2.6	3.1	2.1	5.1	1.6	39.9
PL0004R	cadmium	µg Cd/m <sup>2</sup>	6.5	1.2	1.7	1.7	2.4	1.6	4.2	2.7	2.6	1.7	1.8	1.8	30.0
SE0051R	cadmium	µg Cd/m <sup>2</sup>	1.8	-	1.7	1.8	3.6	1.3	2.1	2.6	3.8	2.4	3.0	2.8	27.9
SE0097R	cadmium	µg Cd/m <sup>2</sup>	0.1	3.7	4.1	0.8	2.4	3.9	1.9	1.7	3.0	1.9	3.4	4.5	31.3
DE0009R	lead	µg Pb/m <sup>2</sup>	38	81	104	-	69	99	60	47	44	41	33	10	627
DK0008R	lead	µg Pb/m <sup>2</sup>	37	45	30	23	46	63	50	49	36	17	15	17	426
DK0020R	lead	µg Pb/m²	39	35	50	32	106	51	134	51	30	23	35	22	611
EE0009R	lead	µg Pb/m <sup>2</sup>	33	10	33	12	32	24	23	33	58	37	58	35	388
EE0011R	lead	µg Pb/m <sup>2</sup>	57	9	22	45	18	37	143	40	28	19	38	22	478
FI0017R	lead	µg Pb/m <sup>2</sup>	78	54	72	34	97	30	79	105	112	65	174	180	1078
FI0053R	lead	µg Pb/m <sup>2</sup>	14	22	33	12	19	8	29	48	13	38	33	30	297
LV0010R	lead	µg Pb/m <sup>2</sup>	436	279	266	18	79	133	160	68	44	64	327	554	2374
LV0016R	lead	µg Pb/m <sup>2</sup>	103	40	54	14	96	88	115	33	45	75	135	63	862
PL0004R	lead	µg Pb/m <sup>2</sup>	14	49	31	42	50	37	86	42	42	27	45	35	500
SE0051R	lead	µg Pb/m²	64	-	29	11	55	53	73	47	51	27	35	31	497
SE0097R	lead	µg Pb/m²	2	54	87	7	56	45	57	36	53	35	96	155	682
DE0009R	mercury	ng Hg/m <sup>2</sup>	486	229	566	232	1084	1165	1001	498	491	258	236	202	6446
LV0010R	mercury	ng Hg/m <sup>2</sup>	-	-	737	293	1858	2332	7004	1351	2496	1045	3784	785	24402
LV0016R	mercury	ng Hg/m <sup>2</sup>	-	-	-	999	2002	2742	4237	2457	1843	1640	1387	350	22393
SE0014R	mercury	ng Hg/m <sup>2</sup>	377	230	210	221	877	572	2068	662	950	222	324	239	6953

Table A.6 Monthly and annual deposition of heavy metals in precipitation.

# **Appendix B: Monitoring methods**

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 2007.

		Sampling	S	ampler	Analytical
Country		period	Wet only	Bulk	methods
Denmark	Nitrate ammonium	Biweekly	x		IC Spect. (CFA)
Estonia	Nitrate Ammonium	Weekly		х	IC Spect (indophenol)
Finland	Nitrate Ammonium	Weekly		х	
Germany	Nitrate Ammonium	Weekly	Х		IC IC
Latvia	Nitrate Ammonium	Daily	X (LV10)	X (LV16 ⊡until 04.2007)	IC Spect (indophenol)
Lithuania	Nitrate Ammonium	Daily	Х		IC Spect (indophenol)
Poland	Nitrate Ammonium	Daily		x	IC Spect (chloramin T)
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 2007.

Country		Sampl period	Sampler	Analytical methods
Denmark	NO <sub>2</sub>	Hourly	Chemiluminisence	
	Sum of nitric acid and nitrate Sum of ammonia and	Daily Daily	Millipore RAWP, 1.2 $\mu$ m + KOH-impregnated Whatman 41, 58 m <sup>3</sup> /day	IC
	ammonium		Millipore RAWP, 1.2 μm + Oxalic acid impregnated Whatman 41, 58 m³/day	Spect (CFA)
Estonia	NO <sub>2</sub>	Hourly	Chemiluscence	
Finland	NO <sub>2</sub>	Hourly	Chemiluscence	
	Sum of nitric acid and nitrate	Daily	Whatman 40 + NaOH impregnated Whatman 40 filter, 24 m <sup>3</sup> /day	IC
	Sum of ammonia and ammonium	Daily	Oxalic acid impregnated Whatman 40 filter, 24 m <sup>3</sup> /day	IC
Germany	NO <sub>2</sub>	Daily	Nal imp. Glass filters, 0.7m <sup>3</sup> /day	FIA
	Sum of nitric acid and nitrate	Daily	Teflon filter + KOH impr W40 filter, 22 m <sup>3</sup> /day	IC
	Sum of ammonia and ammonium	Daily	Teflon filter + Oxalic acid impr W40 filter	FIA
Latvia	NO <sub>2</sub>	Daily	KI method 0.2-0.4 m <sup>3</sup> /day	Spect. Griess
	Sum of nitric acid and nitrate	Daily		IC
	Sum of ammonia and		KOH-impregnated Whatman 41 filter, 14-20	
		Daily	m³/day	Spect
	ammonium		Oxalic acid impregnated Whatman 41 filter, 14-20 m <sup>3</sup> /day	(indophenol)
Lithuania	NO <sub>2</sub> ,	Daily	KI method 0.4-0.7 m <sup>3</sup> /day	Spect. Griess
	Sum of nitric acid and nitrate	Daily	KOH impregnated Whatman 40 filter, 16-17 m³/day	IC
	Sum of ammonia and ammonium	Daily	Oxalic acid impregnated Whatman 40 filter, 16-17 m³/day	Spect (indophenol)
Poland	NO <sub>2</sub>	Daily	Abs.sol. TGS 0.73 <sup>3</sup> /day	Spect. Griess
	Sum of nitric acid and nitrate	Daily	NaF impregnated Whatman 40 filter, 3.5-4 m³/day	Spect. Griess
	Sum of ammonia and ammonium	Daily	Oxalic acid impregnated Whatman 40 filter, 3.5-4 m <sup>3</sup> /day	Spect. Chloramin T)
Sweden	NO <sub>2</sub>	Daily	Nal imp. glass sinters 0.7 m <sup>3</sup> /day	Spect, FIA
	Sum of nitric acid and nitrate		Aerosol filter as for sulphate + KOH- impregnated Whatman 40 filter, 20 m <sup>3</sup> /day	IC
	Sum of ammonia and ammonium		Aerosol filter as for sulphate + Oxalic acid impregnated Whatman 40 filter, 20 m³/day	FIA

GF-AAS: ICP-MS: CV-AFS:

Graphite furnace atomic absorption spectroscopy Inductively coupled plasma - mass spectrometry Cold vapour atomic fluorescence spectroscopy

Table B.3. General information about sampling and analysis of heavy metals in 2007.

Country	Precipitation		Air and aeros	Laboratory mathed		
Country	Field method	Frequency	Field method	Frequency	Laboratory method	
Germany	wet only	Weekly	Low volume sampler	Weekly	ICP-MS	
Hg	wet only	vveekiy	I GIVI:gold trap	Dally	CV-AFS	
Denmark	Bulk	Monthly	Low volume sampler, Millipore RAWP 1.2 mm, 58 m <sup>3</sup> /day	Daily	Precip: GF-AAS , Aerosols: PIXE	
Estonia	Bulk	Monthly	PM <sub>10</sub> , low volume sampler	Weekly	F-AAS	
Finland	Bulk	Monthly	PM <sub>10</sub> . Teflon, Millipore, Fluoropore, 3 µm, 20 I/min	2+2+3	ICP-MS	
Hg	Bulk (Hg)	Monthly	Hg: gold traps (TGM) Hg: mini traps (TPM)	2 X 24 h a week weekly	CV-AFS CV-AFS	
Poland, PL05	Wet-only	Weekly	PM <sub>10</sub> High vol, quartz filter	weekly (bulked 24h)	Precip: GF-AAS, Air: ICP	
Hg	Bulk (Hg)	Weekly	Hg: gold traps (TGM)	24h a week	AAS-AMAanalyzer	
Sweden	Bulk	Monthly	Low volume sampler, teflon filter	monthly	ICP-MS	
Hg	Bulk (Hg)	Monthly	Hg: gold traps (TGM)	2 X 24 h a week	CV-AFS	
			Hg: mini traps (TPM)	2 X 24 h a week	CV-AFS	

GF-AAS: Graphic Furnace Atomic Absorption Spectroscopy ICP-MS: Inductively Coupled Plasma - Mass Spectrometry CV-AFS: Cold Vapour Atomic Fluorescence Spectroscopy

## **Appendix C: Indicator Fact Sheets on nitrogen emissions**

Here we give the links to Indicator Fact Sheets available on HELCOM web pages:

1. Nitrogen emissions: http://www.helcom.fi/environment2/ifs/ifs2009/en\_GB/NitrogenEmissionsAir/

2. Nitrogen depositions: http://www.helcom.fi/environment2/ifs/ifs2009/en\_GB/n\_deposition/

3. Heavy metals emissions: http://www.helcom.fi/environment2/ifs/ifs2009/en\_GB/hmemissions/

4. Heavy metals depositions: http://www.helcom.fi/environment2/ifs/ifs2009/en\_GB/hmdeposition/

5. PCDDFs emissions: http://www.helcom.fi/environment2/ifs/ifs2009/en\_GB/pcddfemissions/

6. PCDDFs depositions: http://www.helcom.fi/environment2/ifs/ifs2009/en\_GB/pcddfdeposition/