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

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# 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.



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.



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  $(HNO<sub>3</sub>+NO<sub>3</sub>)$ , and 14 for nitrogen dioxide  $(NO<sub>2</sub>)$ . 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  $\mu$ g N/m<sup>3</sup> for respectively NH<sub>3</sub>+NH<sub>4</sub><sup>+</sup>,  $HNO<sub>3</sub>+NO<sub>3</sub>$  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  $\mu$ gN/m<sup>3</sup> of sum ammonium, and 0.8  $\mu$ gN/m<sup>3</sup> for sum nitrate. The Estonian sites show highest level of NO<sub>2</sub> with about 3  $\mu$ gN/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  $(HNO_3+NO_3)$  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<sub>3</sub> 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  $(HNO<sub>3</sub>+NO<sub>3</sub>)$  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  $(NO<sub>3</sub>))$ , and right: ammonium  $(NH<sub>4</sub><sup>+</sup>$  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  $(NO<sub>3</sub>$ <sup>'</sup>), and bottom: reduced nitrogen  $(NH<sub>4</sub><sup>+</sup>)$ .

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 µg/l. The lowest concentrations for Pb with 0.47 were observed at SE51. The highest concentration of Pb was measured at LV10 (2.5 µg/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 33rd 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.





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 50×50 km grid cell.



**Figure 3.4.** Map of annual emission of ammonia in the Baltic Sea region in 2007. Units: Mg of  $N_{13}$  per year and per 50×50 km grid cell.







**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  $50\times50$  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**

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



**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>.



**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-1. 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-1 .



**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.



**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).



Poland Russia

**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).





*Expert estimates:* 

§ *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.

<b>Month</b>	<b>Deposition</b>
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.



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

#### **4.5 Comparison of model results with measurements**



**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: µg / L.



**DK8 Pb concentration in precipitation,** µ**g/L**

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



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



**EE9 Pb concentration in precipitation,** µ**g/L**

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



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



#### **FI17 Pb concentration in precipitation,** µ**g/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: µg / L.



**LV10 Pb concentration in precipitation,** µ**g/L**

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



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



#### **PL4 Pb concentration in precipitation,** µ**g/L**

**Figure 4.38.** Comparison of calculated mean monthly lead concentrations in precipitation for 2007 with measurements of the station Leba (PL4). Units: µg / 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,  $g/km^2/y$ .



**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.



**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.

**Cd emission, Germany 03 20% 08 < 0.01% 01 64% 05 4% 02b 12%**

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



**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.





**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).



**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:* 

§ *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.





#### **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%).



**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  $/m<sup>3</sup>$ .



**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: µg / 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: µg / 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: µg / L.



**Figure 5.33.** Comparison of calculated mean monthly cadmium concentrations in precipitation 2007 with measurements of the station Hailuoto (FI53). Units: µg / 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: µg / 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.



**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).



**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,  $g/km^2/y$ .



# **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.		





## **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.



\* - 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.



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



**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).



#### *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.

<b>Table 7.3.</b> Monthly total deposition of PCDD/Fs over the Baltic Sea for 2007, g TEQ/month.								
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### **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 $(1)$	$\frac{0}{0}$	Country $(2)$	$\%$	$*, \frac{9}{6}$
<b>GUB</b>	Sweden	15	Finland	δ	0 l
<b>GUF</b>	Russia	35	Estonia		47
<b>GUR</b>	Latvia	13	Poland	o	63
<b>BAP</b>	Poland	15	Sweden	o	62
<b>BES</b>	Denmark	19	Poland		70
<b>KAT</b>	Denmark	20	Sweden		64
<b>BAS</b>	Poland		Denmark		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 longrange 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 results demonstrated its ability to provide spatially and temporally resolved 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**





		Unit	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Year
<b>DE0009R</b>	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
<b>EE0009R</b>	cadmium	ng Cd/ $m3$	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
<b>SE0014R</b>	cadmium	ng Cd/ $m3$	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
<b>DE0009R</b>	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
<b>DK0003R</b>	lead	nq 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
<b>DK0005R</b>	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
<b>DK0008R</b>	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
<b>EE0009R</b>	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	nq 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
<b>LV0010R</b>	lead	ng $Pb/m3$	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	nq 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
<b>DE0009R</b>	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
<b>SE0014R</b>	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
<b>SE0014R</b>	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
<b>DE0009R</b>	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
<b>DK0005R</b>	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
<b>DK0008R</b>	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
<b>DK0020R</b>	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
F10004R	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
F10009R	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
<b>LV0016R</b>	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
<b>PL0004R</b>	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
<b>SE0005R</b>	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
<b>SE0053R</b>	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
<b>DE0009R</b>	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
<b>DK0005R</b>	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
<b>DK0008R</b>	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
<b>DK0020R</b>	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
<b>EE0009R</b>	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
<b>LV0010R</b>	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
<b>PL0004R</b>	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
<b>SE0005R</b>	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
<b>SE0014R</b>	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



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



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



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  $\overline{B.5}$ :

**Table B.1**. General information about sampling and analysis of nitrogen compounds in precipitation in 2007.



\*IC: Ion chromatograpy

\*\*Spect Spectrofotometric detection

**Table B.2**. General information about sampling and analysis of nitrogen compounds in air in 2007.



GF-AAS: Graphite furnace atomic absorption spectroscopy

ICP-MS: Inductively coupled plasma - mass spectrometry

CV-AFS: Cold vapour atomic fluorescence spectroscopy

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



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/