

Figure 3.1. Geographical locations of the HELCOM stations with available measurements for the year 2003.

3.2 Nitrogen concentrations in air

Altogether 16 stations have delivered data for one or more nitrogen species in air: 10 for respectively total reduced nitrogen ($\text{NH}_3+\text{NH}_4^+$) and total nitrate ($\text{HNO}_3+\text{NO}_3^-$), and 14 for nitrogen dioxide (NO_2). Stations from five of the six sub-basins have delivered data for total reduced nitrogen and total nitrate, whereas stations from all the sub-basins have delivered data for total nitrate. Annual averages of the different nitrogen species are presented in Figure 3.2. 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 (SE5) in 2003: The concentrations were approximately 0.25, 0.12, 0.14 $\mu\text{g N/m}^3$ for respectively $\text{NH}_3+\text{NH}_4^+$, $\text{HNO}_3+\text{NO}_3^-$ and NO_2 at this site. Highest concentrations were found at the German station (DE9) and the southernmost Danish station (DK5) close by: The concentrations were approximately 2.9 $\mu\text{g N/m}^3$ for $\text{NH}_3+\text{NH}_4^+$ at DK5, and 1.4 and 2.5 $\mu\text{g N/m}^3$ for $\text{HNO}_3+\text{NO}_3^-$ and NO_2 , respectively at DE9.

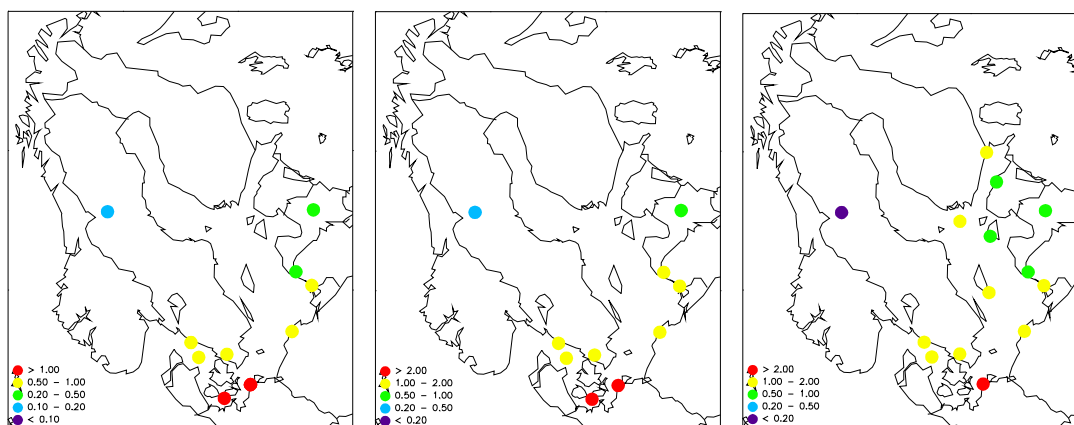


Figure 3.2. Concentrations of left: total reduced nitrogen ($\text{NH}_3+\text{NH}_4^+$), middle: total nitrate ($\text{HNO}_3+\text{NO}_3^-$), and right: NO_2 in air in 2003 Unit: $\mu\text{g N/m}^3$

A similar south north gradient can also be noticed in Figure 3.3 displaying the station averages of $\text{NH}_3+\text{NH}_4^+$, $\text{HNO}_3+\text{NO}_3^-$ and NO_2 observations across six sub-basins. There is a clear decrease in concentrations from south to north. As mentioned earlier some of the sub-basins have only one station whereas others have more.

Observations of the total reduced nitrogen ($\text{NH}_3+\text{NH}_4^+$), show a seasonal pattern similar for all the sub-basins with highest concentrations during March. Agricultural activities (natural fertilizer) are the main source for $\text{NH}_3+\text{NH}_4^+$. During the summer half year NH_3 is normally emitted from the ground due to higher temperatures. Quite surprisingly, no summer maxima is seen for 2003.

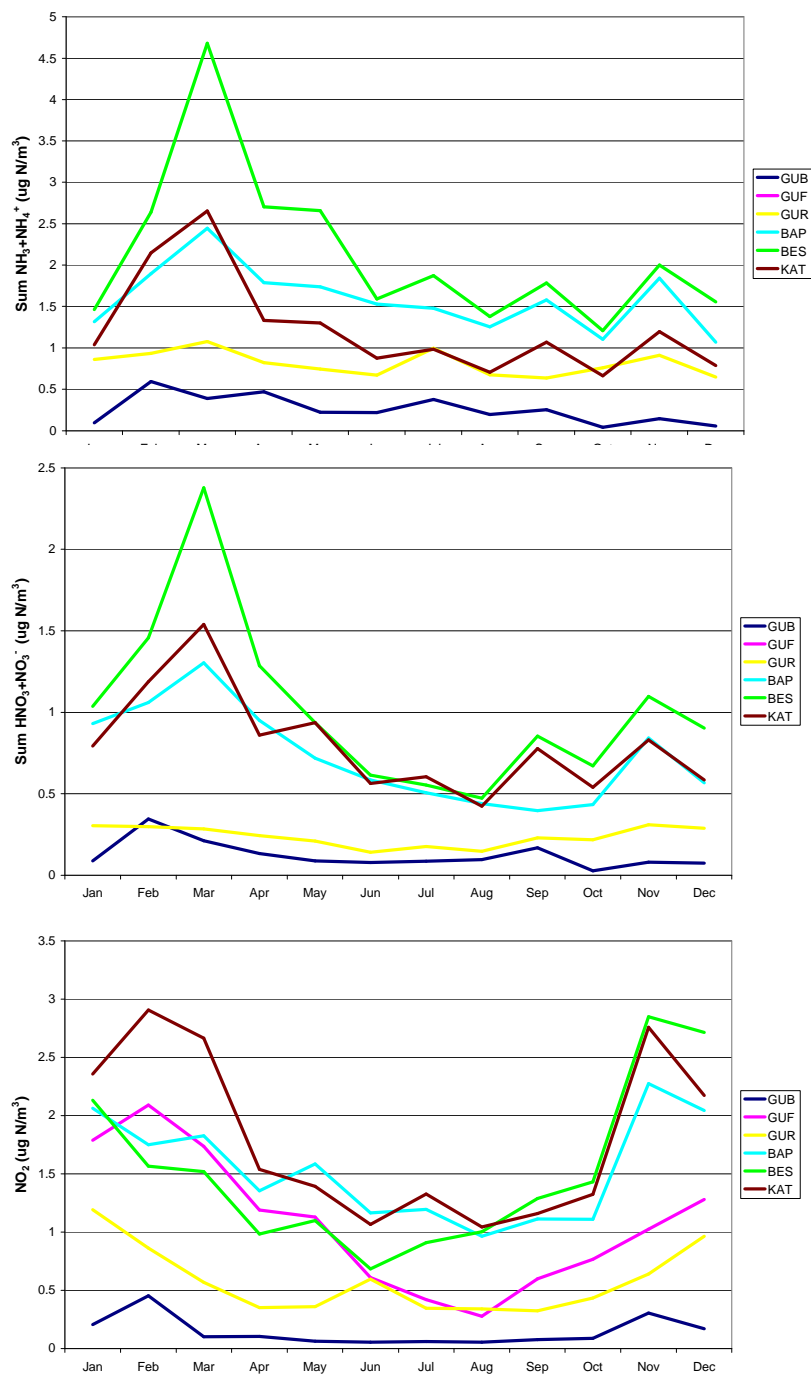


Figure 3.3. Monthly nitrogen concentrations in the air in 2003 averaged for the sub-basins: Top: total reduced nitrogen (NH_3+NH_4), middle: total nitrate ($\text{HNO}_3+\text{NO}_3^-$), bottom: NO_2 .

Total nitrate ($\text{HNO}_3 + \text{NO}_3^-$) concentrations shows a clear seasonal pattern with highest concentrations in March. NO_2 is reacting photochemically and the reaction product is total nitrate. This reaction is mostly dominating during spring. 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 a less pronounced seasonal pattern. Concentrations of NO_2 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.

3.3 Nitrogen in precipitation

Altogether 17 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 3.3.

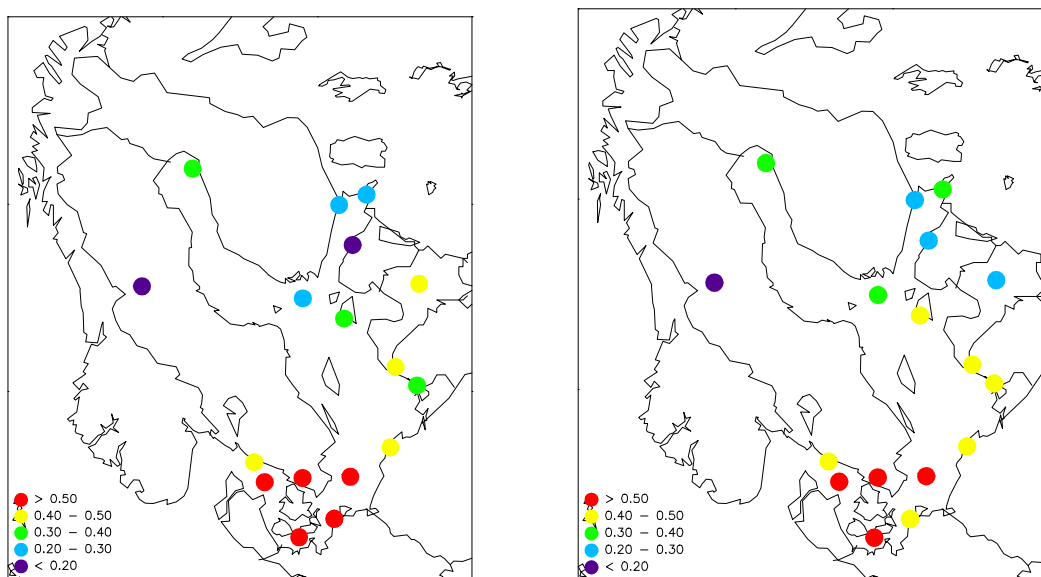


Figure 3.5. Concentrations of left: ammonium (NH_4^+), and right: nitrate (NO_3^-) in precipitation in 2003. Units: mg N/l.

The yearly mean concentrations in precipitation have been calculated from daily, weekly or monthly 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. The concentration differences for ammonium are much higher than for nitrate, because stations can be affected by local agricultural activities. Lowest concentration for ammonium (0.13 mg N/l) were reported at SE5 and EE9. Lowest concentrations of nitrate (0.17 mg N/l) were reported at SE5. For ammonium highest concentrations were found at the DK20 (1.5 mg N/l) and PL4 (1.1 mg N/l). The highest concentrations of

nitrate (0.9 mg N/l) were measured at DK20.

Figure 3.6 displays the station average deposition of oxidized and reduced nitrogen across the regions given.

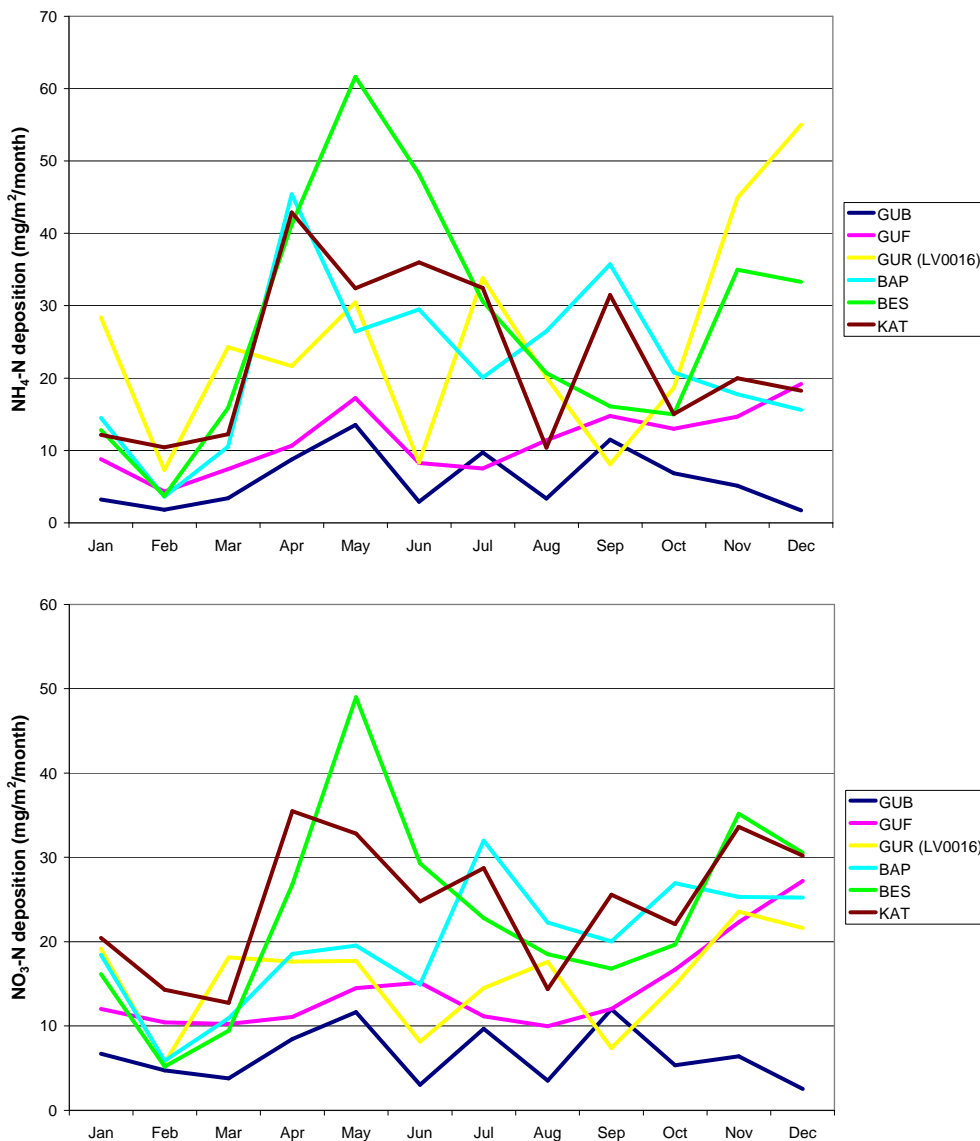


Figure 3.6. Monthly nitrogen depositions in 2003 averaged for the sub-basins: Top: reduced nitrogen (NH_4^+), and bottom: nitrate (NO_3^-).

It is to be observed that seasonal patterns are not so strong as for airborne components. This is due to the presence of the precipitation effect. Airborne nitrogen species will be

washed out at precipitation events during transport. The spatial pattern persists, however, with clearly decreasing depositions with progression northwards. For example, the northern regions receive typically half the deposition of reduced nitrogen supplied to southern areas.

3.4 Heavy metals in the air

Altogether 7 stations have delivered data for Cd and Pb in aerosols in the HELCOM area, whereas two have delivered data for Hg in air. 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 3.7. Average air concentrations are arithmetic averages of the reported values. The lowest concentrations for Cd in aerosols were reported at SE14 and DK8 in 2002: respectively 0.09 and 0.10 ng/m^3 . The lowest concentrations (3 ng/m^3) for Pb in aerosols were reported at SE14 and LV16. The highest concentrations were found at LV16 for Cd (0.3 ng/m^3) and at DK5, DE9 and at LT15 for Pb (7 ng/m^3). The concentrations differences between the stations with lowest and highest concentrations were a factor of 2.5-3 for Pb and Cd respectively. For Hg, the annual mean concentrations are 1.66 and 1.78 ng/m^3 at DE9 and SE14.

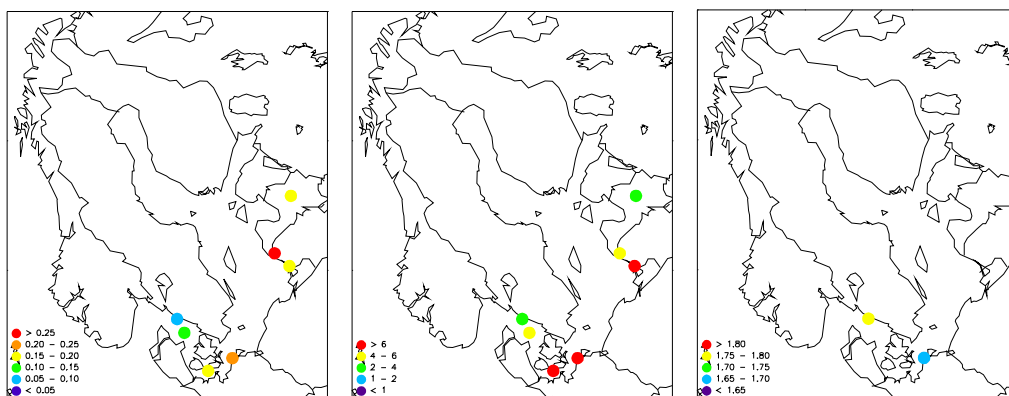


Figure 3.7. Concentrations of left: cadmium (Cd), middle: lead (Pb) in aerosol and right: mercury in air+aerosol in 2003. Units: ng/m^3 .

There are insufficient stations to reasonably represent regional patterns, hence the station data itself is presented here for some of the sites (Fig. 3.8).

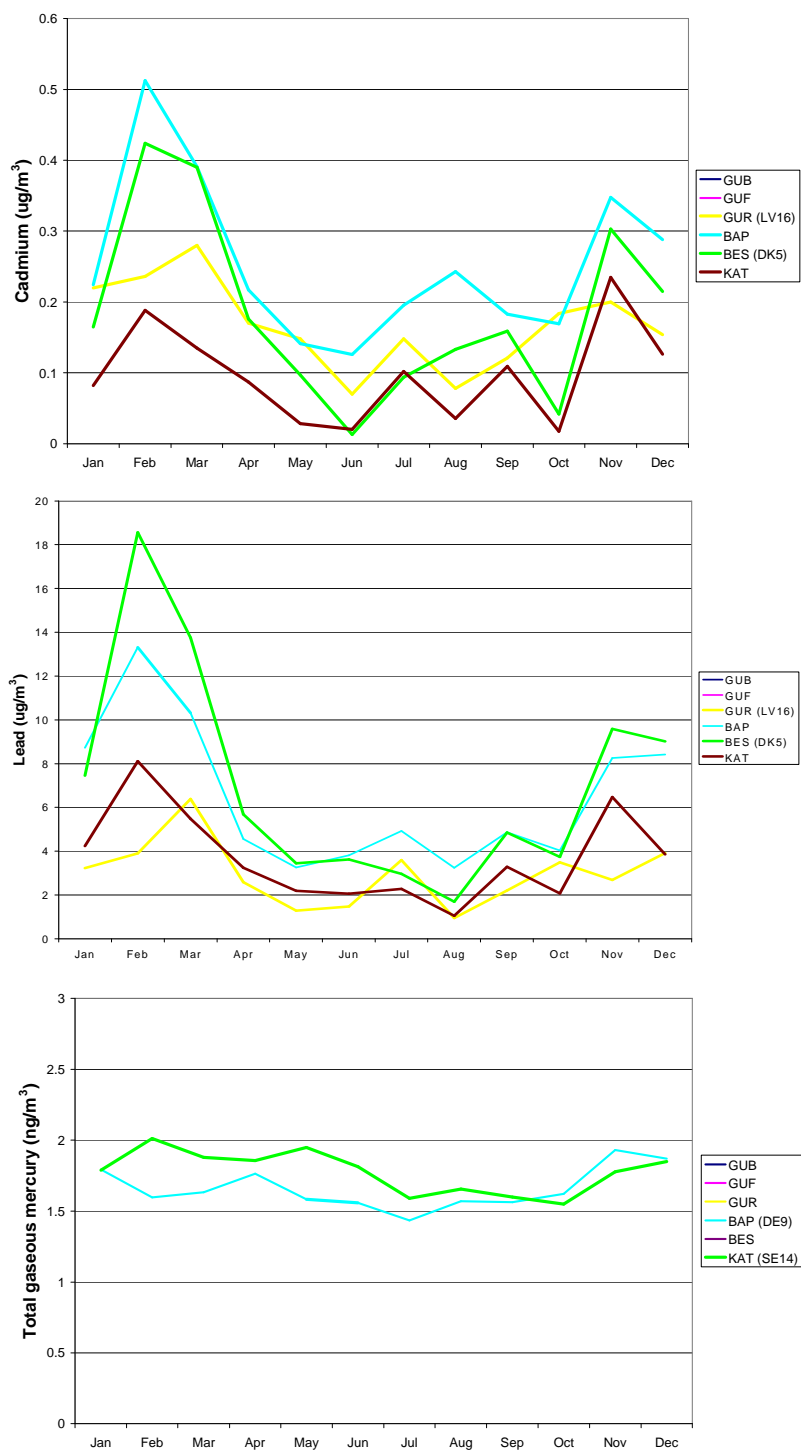


Figure 3.8. Monthly concentrations in air in 2003 averaged for the sub-basins: Top: cadmium, middle: lead and bottom: mercury.

From this, it is to be observed that the temporal patterns for Cd and Pb show a strong 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.

3.5 Heavy metals in precipitation

In all 13 stations have delivered data for Cd and Pb in precipitation, and four 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 3.9. The yearly mean concentrations in precipitation have been calculated from daily, weekly or monthly reported values as precipitation-weighted averages. The lowest concentration for Cd in precipitation was reported at the Polish station (PL4) in 2003: 0.046 $\mu\text{g/l}$. The lowest concentrations for Pb (0.6-0.7 $\mu\text{g/l}$) were measured at the two Estonian sites. The highest concentrations of Cd and Pb were measured at LT15, respectively 0.2 and 3.6 $\mu\text{g/l}$. For Hg, the lowest annual mean concentrations were 7.6 ng/l (SE5) and the highest 11.6 ng/l (SE11).

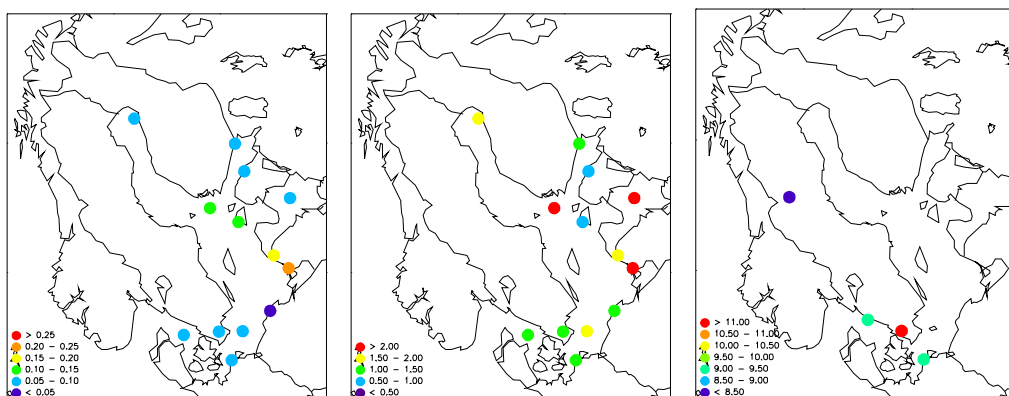


Figure 3.9. Concentrations of left: cadmium (Cd), middle: lead (Pb) in precipitation. Units: $\mu\text{g/l}$, and right: mercury (Hg) in precipitation in 2003. Units: ng/l. All 2003.

Also for heavy metals in precipitation there are insufficient stations to reasonably represent regional patterns, and the station data itself is presented for some of the sites (Fig. 3.10). Examination of the precipitation quality with respect to Cd and Pb does not reveal clear patterns. The rather variable data suggests notable local meteorological effects in the absence of quality control issues. For Hg there is a minimum from August to January.

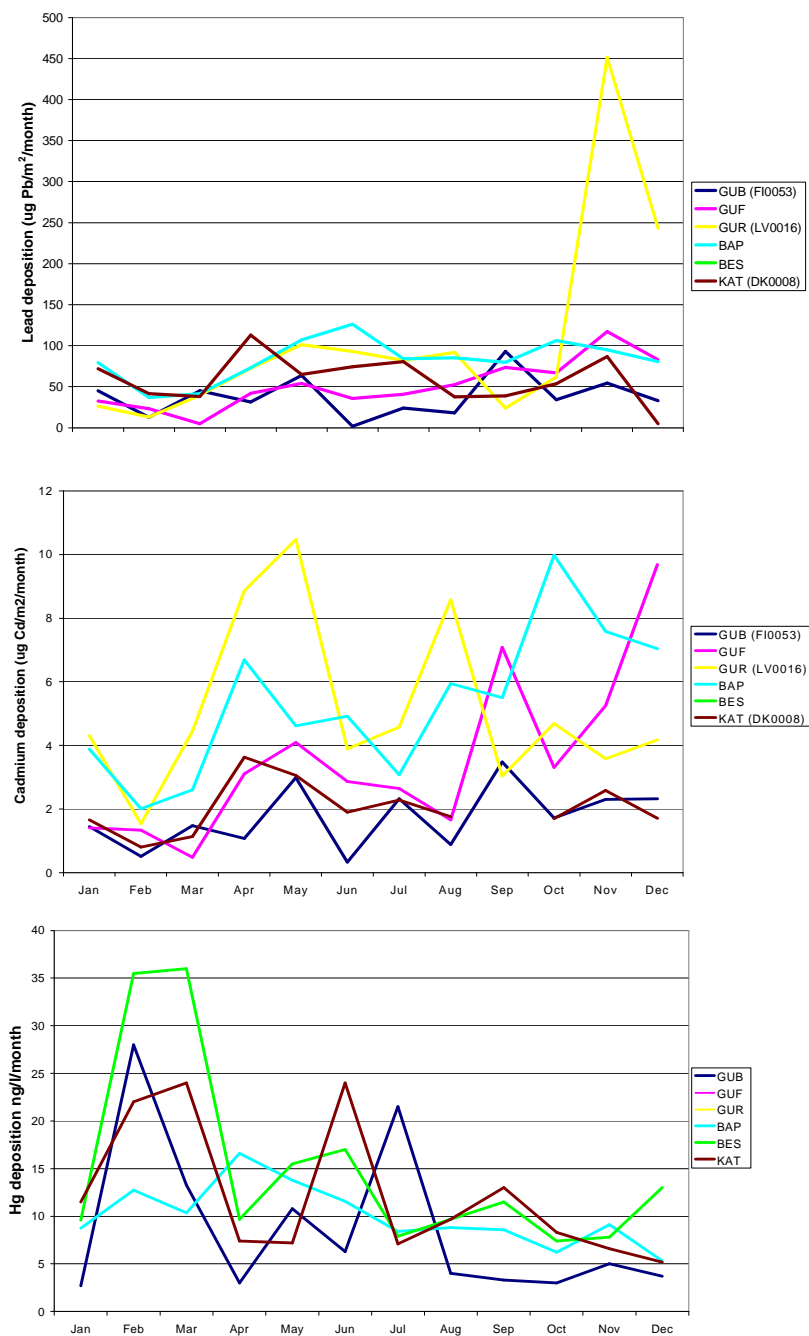


Figure 3.10. Monthly depositions in 2003: Top: cadmium, middle: lead and bottom: mercury.

3.6. Lindane (γ -HCH)

Only one station has delivered data for γ -HCH in air, and two have delivered data for γ -HCH in deposition. Stations from two of the six sub-basins have delivered data for γ -HCH.

Fig. 3.11 displays monthly averages of γ -HCH in air for one station, whereas Fig. 3.12 shows the same component in deposition for two stations. The two BAP stations are sampled in very different ways.. From this, it is to be observed that the temporal patterns for γ -HCH shows a summer maximum. In western countries the use of lindane (containing >95% γ -HCH) in agricultural application is still allowed, explaining the summer maximum.



3.11. Monthly concentrations of gamma-HCH in air in 2003 for one station

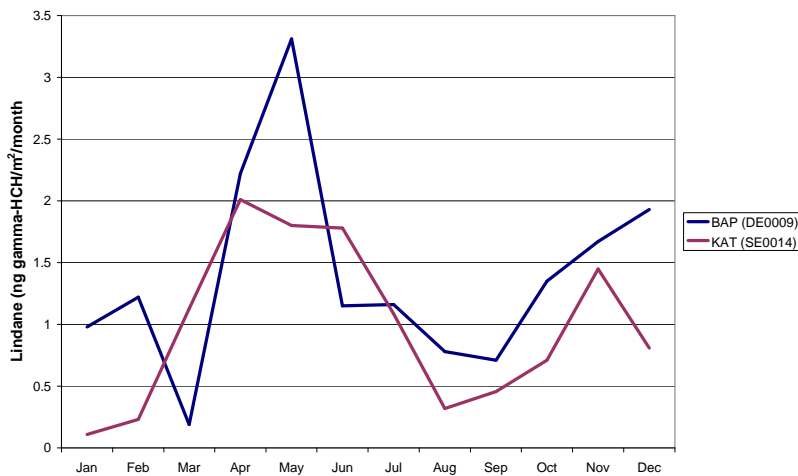


Figure 3.12. Monthly depositions of gamma-HCH for two stations.

3.7. Laboratory and field intercomparisons

The HELCOM laboratories have participated in different laboratory and field intercomparisons in 2003 which have been presented in Aas *et al.* (2004). The results are given below:

3.7.1. Nitrogen

Measurements of airborne nitrate are expected to have a rather large uncertainty due to the very different physical characteristics of the compounds making up total nitrate. Whilst nitric acid is a spatially variable volatile gas with fast dry deposition, particulate nitrate dry deposits only slowly and hence concentrations are more determined by long range transport.

The results from the EMEP laboratory intercomparisons on main components in air and precipitation (Table 2.2) showed that the Swedish laboratory had a -10 % bias for NH₃-N in air.

Table 2.2. Systematic error (RB%) in the 21th laboratory intercomparison for precipitation and air.

	Precipitation		Air and aerosols		
	NO ₃ -N	NH ₄ -N	HNO ₃ -N	NO ₂ -N	NH ₃ -N
8 DE	1	-2	2	0	9
7 DE (Leip)	-1	0			
4 DK	-1	-1	1	3	-4
38 EE	4	0		-2	
5 FI	1	-1	1		-8
32 LT	0	-4		6	-1
33 LV	3	8	4	8	9
16 PL	-5	-3	2	1	
22 RU	-8	4	6	-2	
20 SE	1	3	4	1	-10

 systematic bias
 more than 20 % or less than -20% bias
 between 10 and 20 % or between -10 and -20 % bias

3.7.2. Heavy metals

The data quality objective (DQO) in EMEP states that the accuracy in the laboratory should be better than 15% and 25% for high and low concentrations of heavy metals, respectively. Results from the EMEP laboratory intercomparisons in 2003 (Table 2.3) showed quite good results for Pb. The Danish laboratory was more than 2 times outside DQO for Cd in low concentrations, between ½-1 times outside DQO for Cd in high

concentrations, and between 1-2 for Pb in high concentrations. Finland was between ½-1 times outside DQO for Pb in high concentrations. Poland was between ½-1 times outside DQO for Cd in high concentrations. Lithuania was ½-1 times outside DQO for Cd in low concentrations, whereas Estonia was 1-2 times outside DQO for Cd in low concentrations.

Table 2.3. Average per cent error (absolute) in low and high concentration samples, results from the heavy metal laboratory intercomparison in 2003.

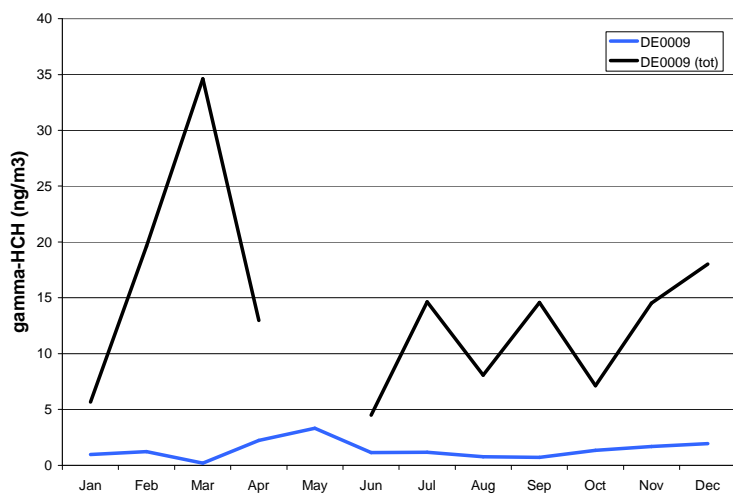
	Cd		Pb	
	low	high	low	high
DK	252	9	28	2
FI	8	7	8	14
DE	2	1	3	3
NO for SE*	4	0	1	1
PL	7	13	5	5
LT	13	2	10	3
LV	0	3	4	3
EE	30	7	3	4

1/2 - 1 DQO
 1 - 2 DQO
 > 2 DQO

* measurement programme carried out by Norwegian Institute for Air Research

3.7.3. Lindane (γ -HCH)

Since 1999, Germany has two dataset for γ -HCH in precipitation. One set with precipitation measurements only, and one that includes rinsing solution from the wet-only funnel. This latter will then include γ -HCH that is retained on the funnel surface. Figure 3.13 shows the results for 2003.



3.13. Monthly concentrations of gamma-HCH in air in 2003 for DE9 in precipitation sample only (blue) and in precipitation sample including rinsing solution (black).