

3.2 Nitrogen concentrations in air

Altogether 16 stations have delivered data for one or more nitrogen species in air: 12 for respectively total reduced nitrogen ($\text{NH}_3+\text{NH}_4^+$) and total nitrate ($\text{HNO}_3+\text{NO}_3^-$), and 13 for nitrogen dioxide (NO_2). Stations from all the six sub-basins have delivered data for the three nitrogen species. 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 2002: The concentrations were approximately 0.19, 0.06, 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 2.5 and 1.1 $\mu\text{g N/m}^3$ for respectively $\text{NH}_3+\text{NH}_4^+$ and $\text{HNO}_3+\text{NO}_3^-$, at DK5 and 2.2 $\mu\text{g N/m}^3$ for NO_2 at DE9.

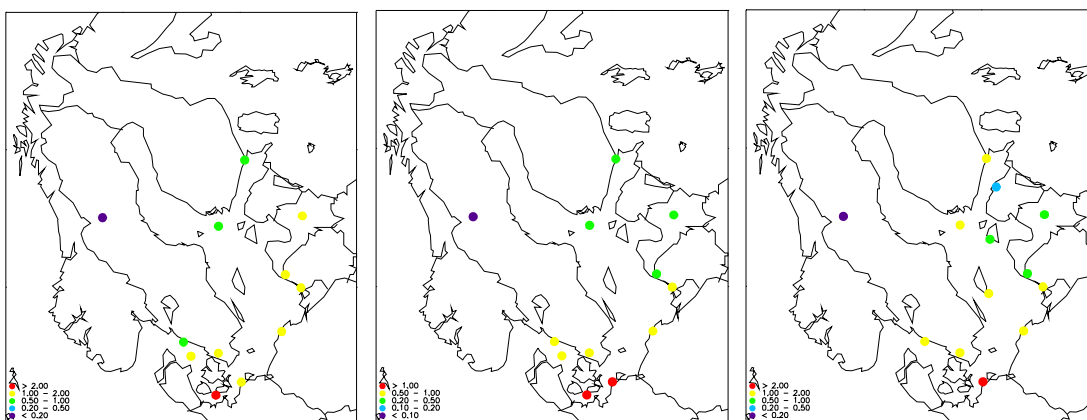


Figure 3.2. Concentrations of left: total reduced nitrogen ($\text{NH}_3+\text{NH}_4^+$), middle: total nitrate ($\text{HNO}_3+\text{NO}_3^-$), and right: NO_2 in air in 2002. Unit: $\mu\text{g N/m}^3$

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 –September. However they are not that high during May–July as the first and last parts of the summer half year. Agricultural activities (natural fertilizer) are the main source for $\text{NH}_3+\text{NH}_4^+$. During the summer half year NH_3 is emitted from the ground due to higher temperatures.

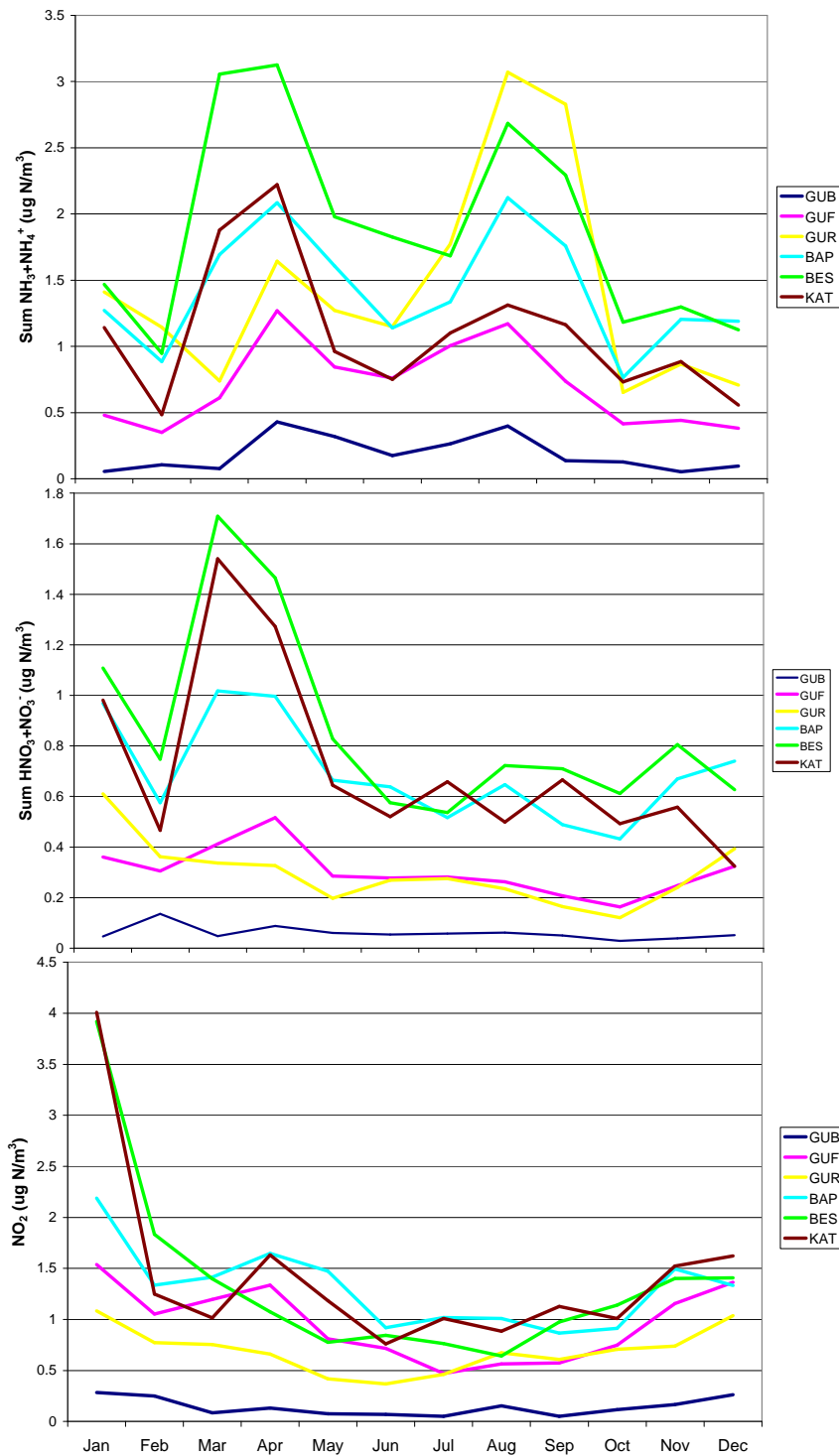


Figure 3.3. Monthly nitrogen concentrations in the air in 2002 averaged for the sub-basins: Top: total reduced nitrogen (NH_3+NH_4), middle: total nitrate ($\text{HNO}_3+\text{NO}_3^-$), bottom: NO_2 .

There is no clear seasonal pattern observed in the measurements for total nitrate ($\text{HNO}_3 + \text{NO}_3^-$), although there is a tendency that total nitrate concentrations are higher in spring. 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.

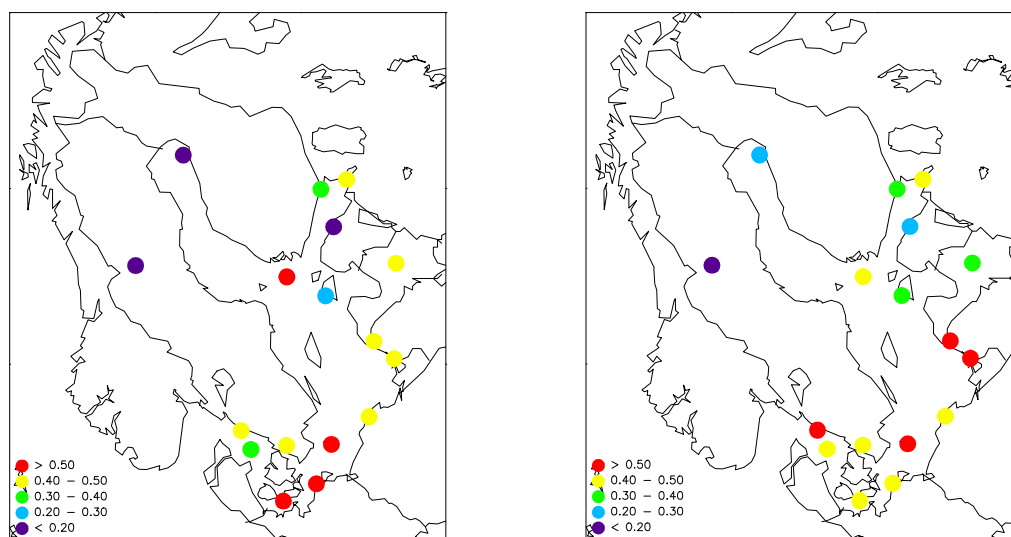


Figure 3.5. Concentrations of left: ammonium (NH_4^+), and right: nitrate (NO_3^-) in precipitation in 2002. Units: mg N/l.

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 (0.13-0.19 mg N/l) and nitrate (0.16-0.265 mg N/l) were reported at SE5, EE9 and FI53 in 2002. For ammonium highest concentrations was found at the southernmost Danish station (DK5) (0.9 mg N/l). The highest concentrations of nitrate (between 0.5 and 0.6 mg N/l) were measured at DK20, LT15, LV10 and SE14.

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

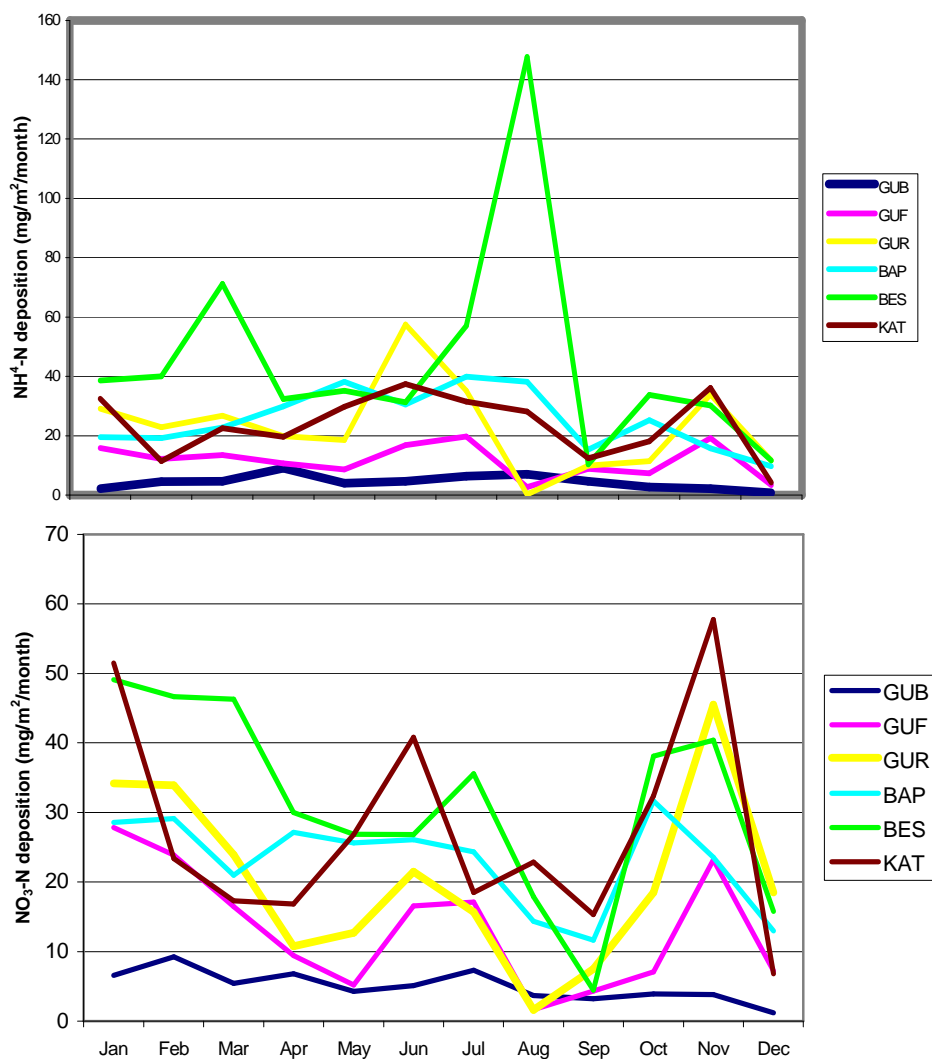


Figure 3.6. Monthly nitrogen depositions in 2002 averaged for the sub-basins: Top: reduced nitrogen (NH_4^+), and bottom: nitrate (NO_3^-).

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 8 stations have delivered data for Cd and Pb in aerosols in the HELCOM area, whereas only one has 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 and Pb in aerosols were reported at the northernmost Swedish site (SE5) in 2002: respectively 0.023 and 0.601 ng/m³. The highest concentrations were found at LV16 for Cd (0.3 ng/m³) and at DK5, DE9 and at LT15 for Pb (0.6 ng/m³). The high concentration seen for Cd at LV16 is due to one sample month with very high concentration. This sample may have been contaminated and should be handled with care. The annual average when excluding this month is 0.15 ng/m³. The concentrations differences between the stations with lowest and highest concentrations were about a factor of 10 for both Cd and Pb.

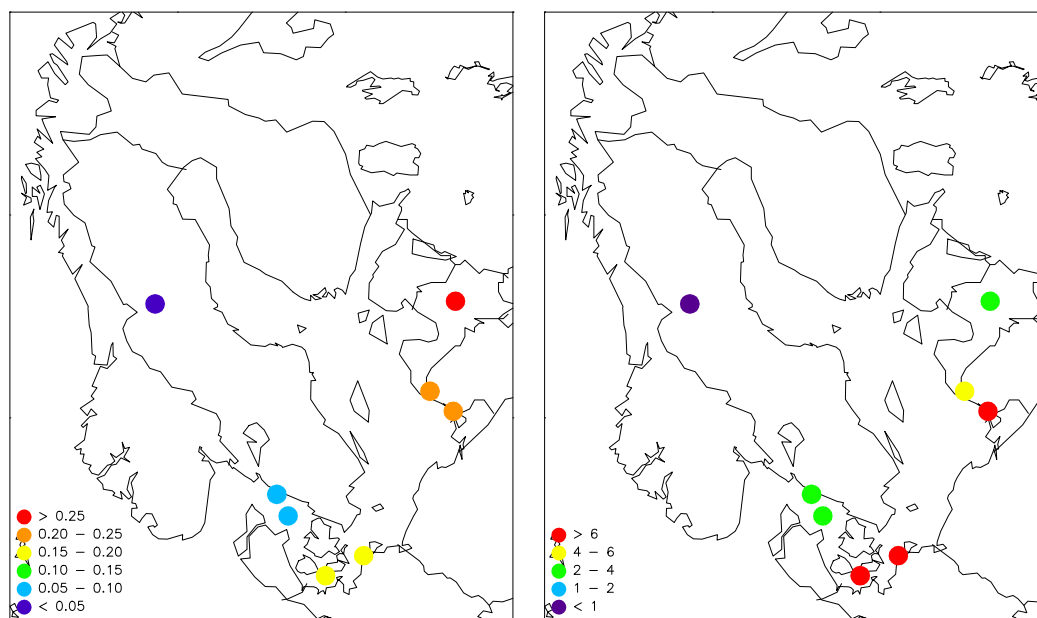


Figure 3.7. Concentrations of left: cadmium (Cd), and right: lead (Pb) in aerosol in 2002. Units:

ng/m³.

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).

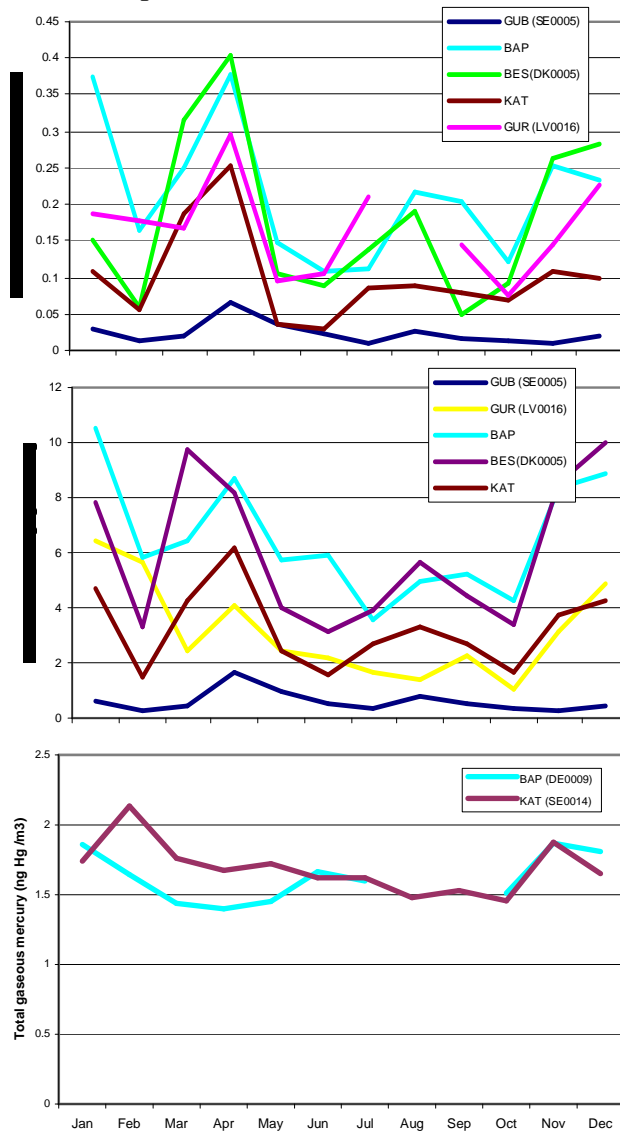


Figure 3.8. Monthly concentrations in air in 2002 averaged for two stations: Top: cadmium (LV16 deleted for August), middle: lead and bottom: mercury.

From this, it is to be observed that with the exception of one station the temporal patterns for Cd and Pb indicate a weak 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 14 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 northernmost Swedish site (SE5) in 2002: 0.03 $\mu\text{g/l}$. The lowest concentrations for Pb were measured at SE5 and the Estonian stations 0.50 and 0.45 $\mu\text{g/l}$. The highest concentrations of Cd and Pb were measured at LT15, respectively 0.5 and 3.4 $\mu\text{g/l}$.

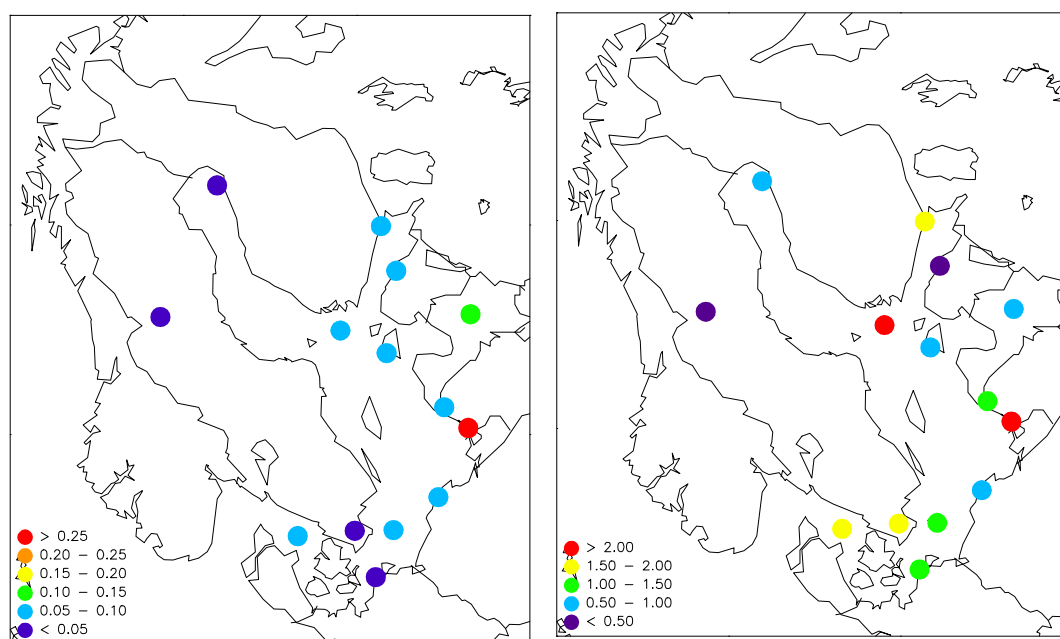


Figure 3.9. Concentrations of left: cadmium (Cd), and right: lead (Pb) in precipitation in 2002. Units: $\mu\text{g/l}$.

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 summer maximum.

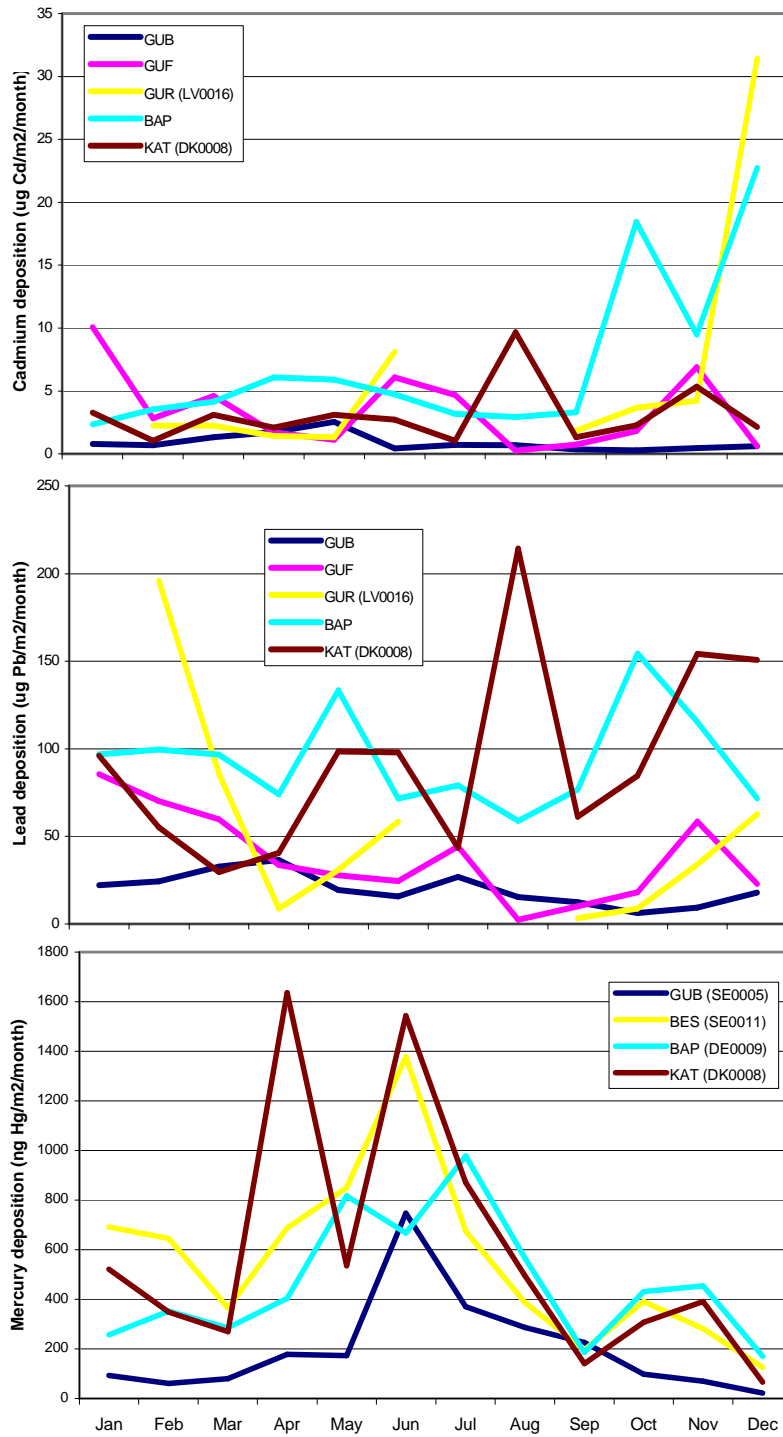
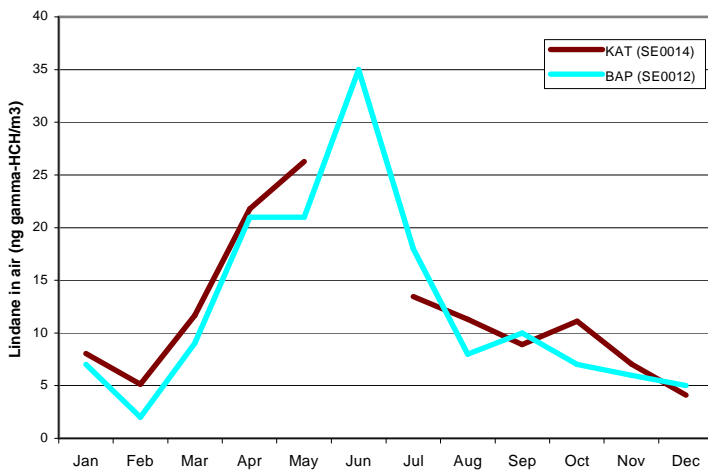


Figure 3.10. Monthly depositions in 2002: Top: cadmium, middle: lead and bottom: mercury.

3.6. Lindane (γ -HCH)

Two stations have delivered data for γ -HCH in air, and three 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 two stations, whereas Fig. 3.12 shows the same component in deposition for three stations. The two BAP stations are showed separately because they 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 2002 for two stations

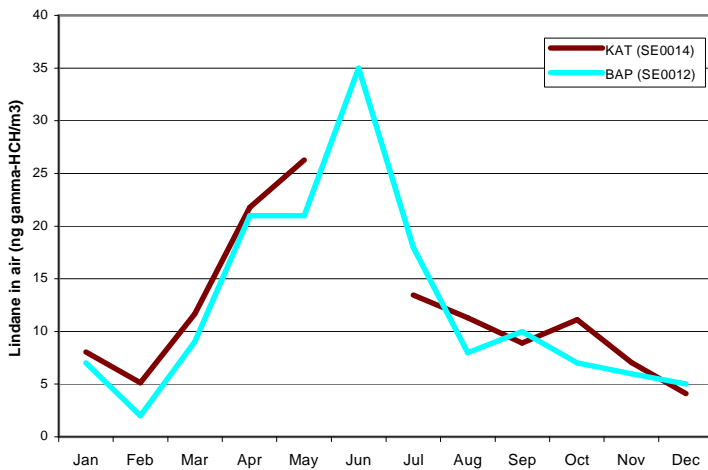


Figure 3.12. Monthly depositions of gamma-HCH for three stations.

3.7. Laboratory and field intercomparisons

The HELCOM laboratories have participated in different laboratory and field intercomparisons in 2002 which have been presented in Aas *et al.* (2004). The results are given below:



3.7.1. Nitrogen

EMEP field comparisons on main components in air were carried out in Estonia, Latvia and Lithuania in 2002. The results from Preila (LT15) were very satisfactory, except for NO₂. NO₂ was overestimated at LT15 and the spread is large. The results from the comparison in Rucava (LV0010) on both the sum of nitrate and nitric acid, and the sum of ammonia and ammonium were very good. The NO₂ measurements were also very good, the precision was not so very high but the correlation was perfect. The results from the Lahemaa (EE0009R) intercomparison were not satisfactory. The NO₂ measurements were uncertain. The manual method was almost half of the reference concentration and the precision was also quite low. It was highly recommended that Estonia change their methodology, i.e. using a filterpack with higher flow.

The results from the EMEP laboratory intercomparisons on main components in air and precipitation (Table 2.2) showed that the Russian laboratory had a -24 % bias for HNO₂ in air.

Table 2.2. Systematic error (RB%) in the 20th laboratory intercomparison for precipitation and air.

	Precip		Air	
	NO ₃ -N	NH ₄ -N	NO ₂	HNO ₃
DK	3 P	-3 N	2	1
FI	2 P	-1		3 P
DE(Leip.)	1 P	-1		
DE(Shau.)	-2 N	3	-5 N	0
PL	-3 N	-5 N	-2	-3
SE	1 P	-3 N	-1	0
RU	-6 N	-5 N	6 P	-24 N
LT	1 P	5	1 P	1
LV	2	7 P	3 P	-3
EE	-7 N	-5 N	-1	

P systematic positiv bias	N systematic negative bias
 more than 20 % or less than -20% bias	 between 10 and 20 % or between -10 and -20 % bias

3.7.2. Heavy metals

A national organized field comparison of heavy metals in precipitation has been performed in Germany (Langenbrügge DE02) comparing wet only and bulk collector. Large deviations were found for some elements, especially Cd indicating influence of dry deposition of coarse particles in the bulk collector.

The data quality objectives (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 2002 (Table 2.3) showed good results for Pb. The Lithuanian laboratory was more than 2 times outside DQO for Cd in low concentrations and between ½ and 1 for high concentrations. Estonia was outside ½ and 1 for both low and high concentrations, whereas Finland was ½-1 times outside DQO for Cd in high concentrations.

Table 2.3. Average per cent error (absolute) in low and high concentration samples, results from the heavy metal laboratory intercomparison in 2002.

	Cd		Pb	
	low	high	low	high
DE	3	1	3	2
EE	13	12		2
FI	7	8	7	7
LT	59	13	7	2
LV	10	3	11	2
NO for SE*	9	7	1	2
PL	0	0	0	7

1/2 - 1 DQO	1 - 2 DQO	> 2 DQO
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* measurement programme carried out by Norwegian Institute for Air Research

3.7.3. Lindane (γ -HCH)

The German laboratory has participated in the EMEP laboratory intercomparison on POPs (Aas *et al.* 2004). Their result for γ -HCH was 18% from the average deviation from the median. The Swedish laboratory did not participate in the intercomparison.

