

2. Observed Concentrations of Nitrogen, Cadmium, Lead, Mercury and Lindane at HELCOM Stations in 2004

2.1 HELCOM measurement stations

Nine countries have submitted data from all together twenty HELCOM stations for 2004 (Table 2.1. and Fig. 2.1).

Table 2.1. Available measurements of nitrogen, lead, cadmium, mercury and lindane from HELCOM stations for 2004. Region shows HELCOM sub-basins, Green colour indicates data for at least one component.

Station			Concentrations in air					Concentrations in precipitation				
Region	Code	Name	N	Pb	Cd	Hg	HCH	N	Pb	Cd	Hg	HCH
GUB	FI053	Hailuoto										
GUB	SE05	Bredkälen										
GUF	EE09	Lahemaa										
GUF	FI07	Virolahti										
GUF	RU16	Shepeljovo										
GUR	LV16	Zoseni										
BAP	DE09	Zingst										
BAP	DK20	Pedersker										
BAP	EE11	Vilsandy										
BAP	FI09	Uto										
BAP	LT15	Preila										
BAP	LV10	Rucava										
BAP	PL04	Leba										
BAP	SE51	Arup										
BAP	SE08	Hoburg										
BAP	SE12	Aspvreten										
BES	DK05	Keldsnor										
BES	SE11	Vavihill										
KAT	DK08	Anholt										
KAT	SE14	Råö										

The stations are distributed in the six sub-basins (Fig. 2.1) as following: One in the Gulf of Riga (GUR), two in the Gulf of Bothnia (GUB), Belt Sea (BES) and Kattegat (KAT), three in the Gulf of Finland (GUF) and ten in the Baltic proper (BAP). There is one station from: Germany, Lithuania, Poland and Russia, two stations from Latvia and Estonia, three stations from Denmark and Finland, and six stations from 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 2004. 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.

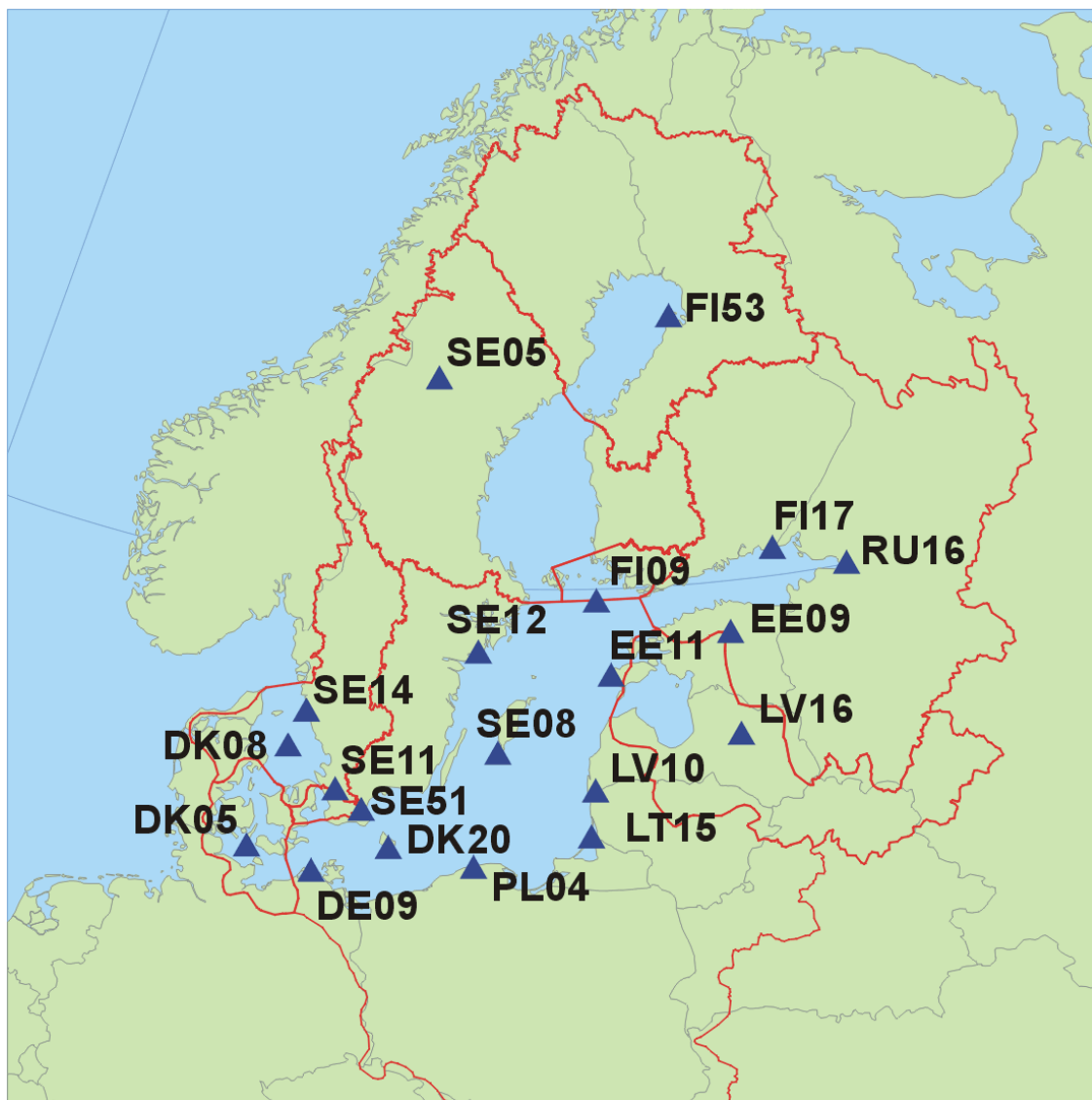


Figure 2.1. Geographical locations of the HELCOM stations with available measurements for the year 2004.

2.2 Nitrogen concentrations in air

Altogether 17 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 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 (SE5) in 2004: The concentrations were approximately 0.19, 0.06, 0.13 $\mu\text{g N}/\text{m}^3$ 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 and one of the Latvian stations (DE9 and LT15). But for DE09, data on sum of ammonium is missing for several months so the annual average value is uncertain. For NO_2 , DK05 and the Estonian sites also show high levels.

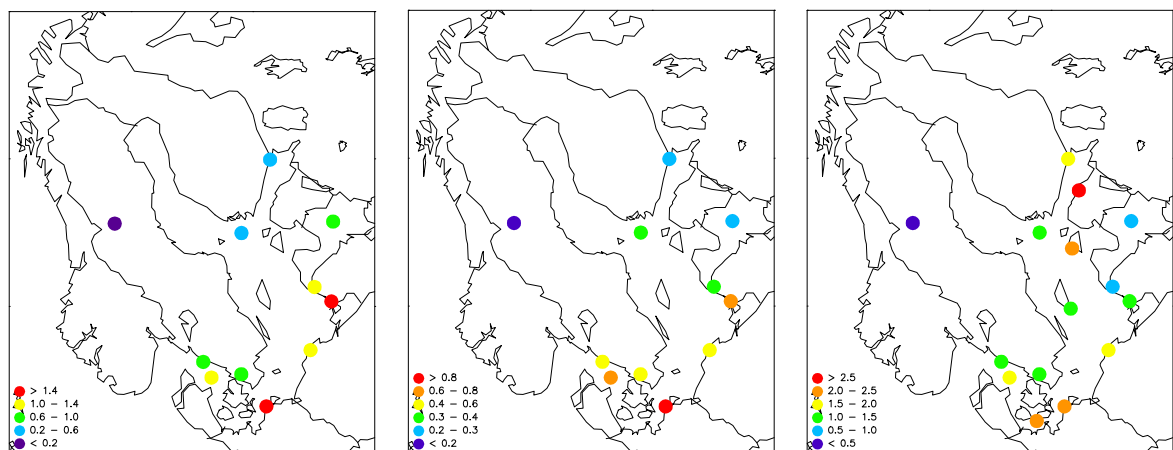


Figure 2.2. Concentrations of left: total reduced nitrogen ($\text{NH}_3+\text{NH}_4^+$), middle: total nitrate ($\text{HNO}_3+\text{NO}_3^-$), and right: NO_2 in air in 2004 Unit: $\mu\text{g N}/\text{m}^3$.

A similar south north gradient can also be noticed in Figure 2.3 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 April, and a peak is also common in August. 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.

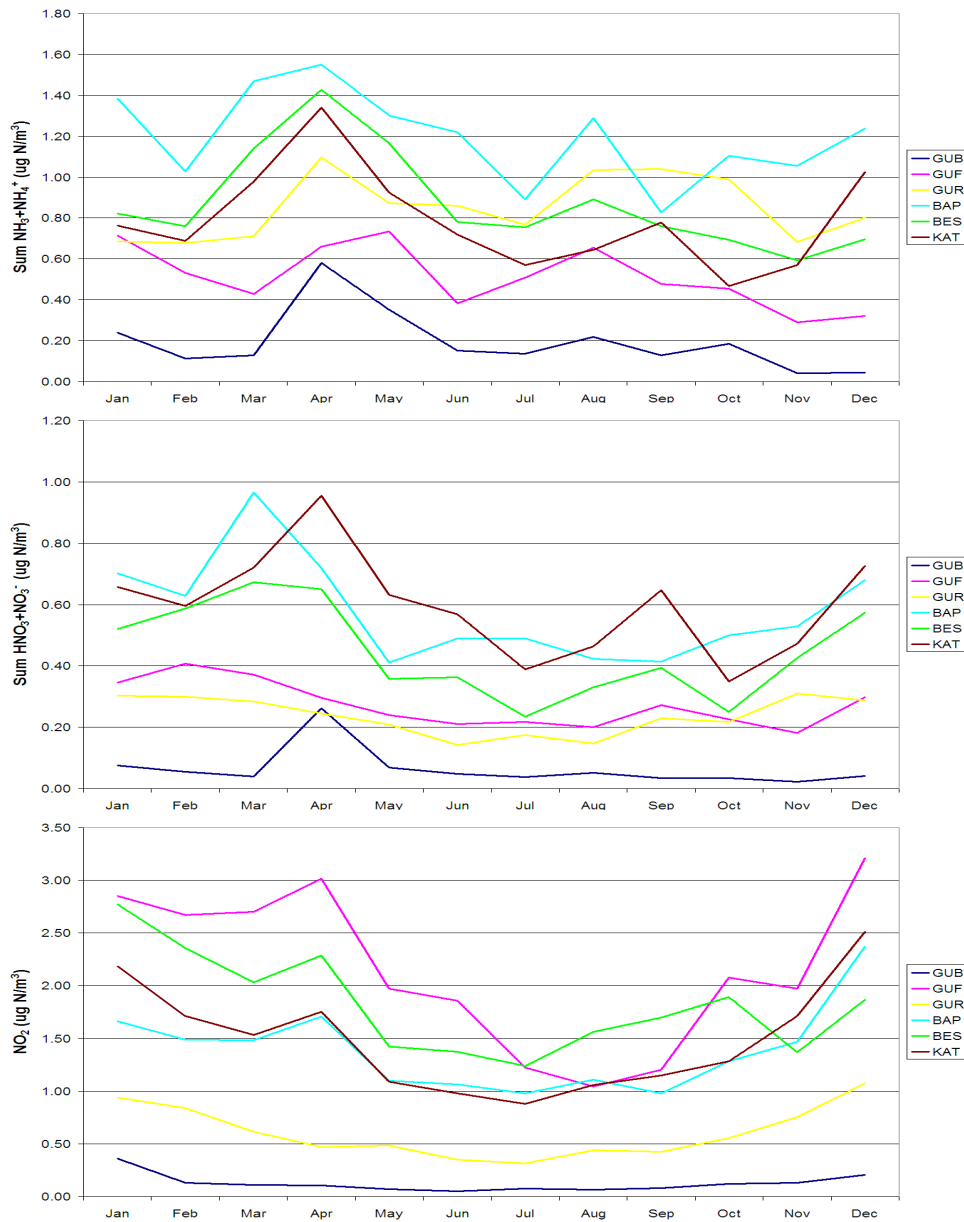


Figure 2.3. Monthly nitrogen concentrations in the air in 2004 averaged for the sub-basins: Top: total reduced nitrogen (NH_3+NH_4), middle: total nitrate ($\text{HNO}_3+\text{NO}_3^-$), bottom: NO_2 .

Total nitrate ($\text{HNO}_3+\text{NO}_3^-$) concentrations shows a clear seasonal pattern with highest concentrations in March and April. 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.

2.3 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 2.4.

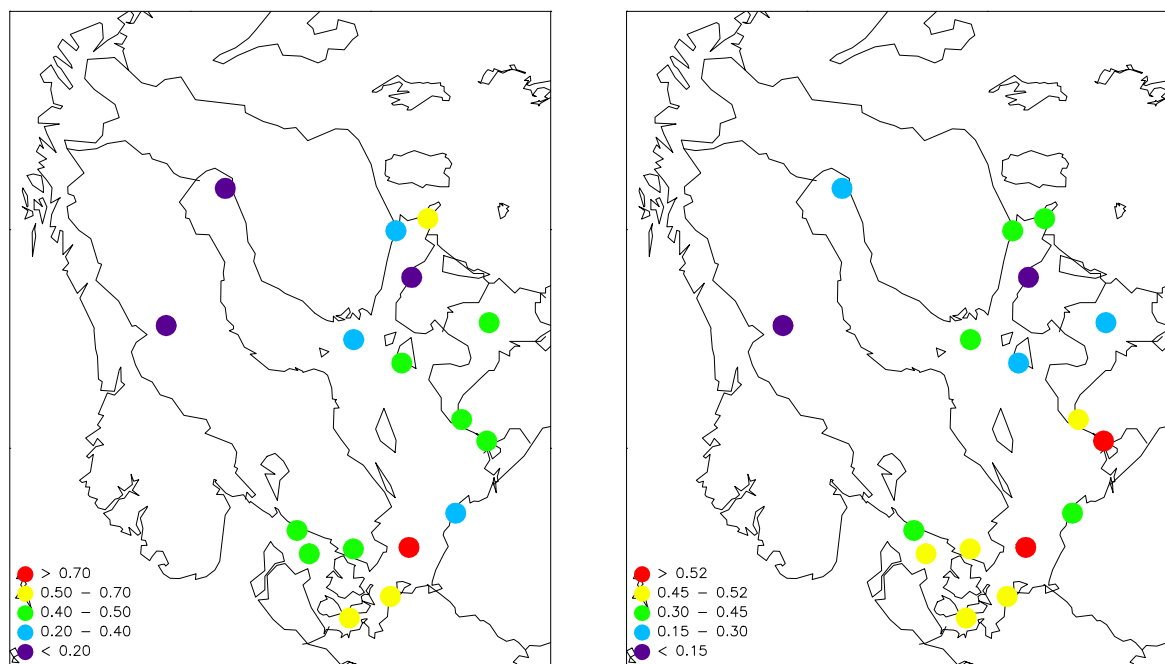


Figure 2.4. Concentrations of left: ammonium (NH_4^+), and right: nitrate (NO_3^-) in precipitation in 2004. Units: mg N/l.

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 (0.1 mg N/l) were reported at SE5 and EE9. Lowest concentrations of nitrate were also seen at these sites with 0.10 and 0.13 mg N/l for SE5 and EE9 respectively. For ammonium highest concentrations were found at the DK20 (0.99 mg N/l). The highest concentrations of nitrate (0.58 and 0.51 mg N/l) were measured at DK20 and LV10 respectively. Figure 2.5 displays the station average deposition of oxidized and reduced nitrogen across the regions given.



Figure 2.5. Monthly nitrogen depositions in 2004 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 as 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 typically receive half the deposition of reduced nitrogen supplied to southern areas.

3.4 Heavy metals in the air

Altogether 6 stations have delivered data for Cd and Pb in aerosols in the HELCOM area, whereas only one (SE12) has delivered data for Hg in air. Annual averages of Cd and Pb are presented in Figure 2.6. Average air concentrations are arithmetic averages of the reported values. The lowest concentrations for Cd in aerosols were reported at SE14 and DK8 in 2004: respectively 0.11 and 0.12 ng/m^3 . The lowest concentration (2.7 ng/m^3) for Pb in aerosols was reported at LV16. The highest concentrations were found at LT15 and DE09 for both Cd (0.19 ng/m^3) and Pb (5.9 and 5.4 ng/m^3 , respectively).

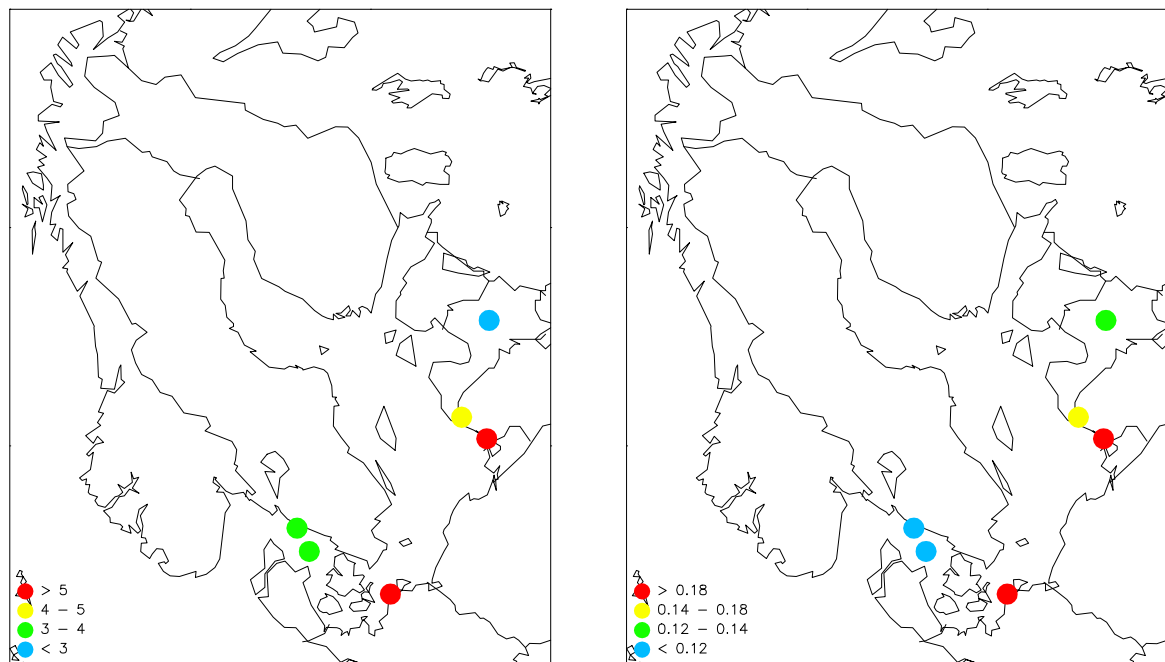


Figure 2.6. Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2004. Units: ng/m^3 .

There are insufficient stations to reasonably represent regional patterns, hence the station data itself is presented here for some of the sites (Fig. 2.7).

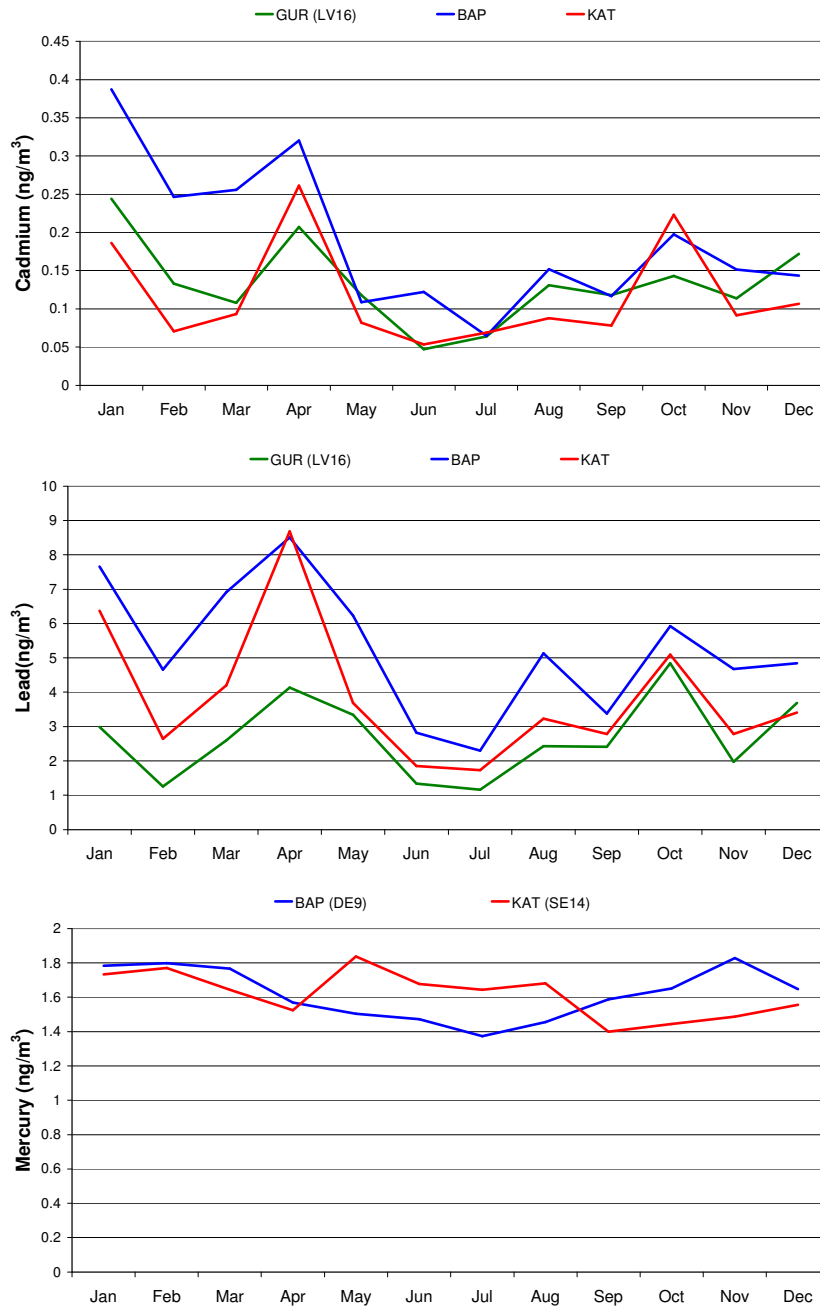


Figure 2.7. Monthly concentrations in air in 2004 averaged for the sub-basins: Top: cadmium, middle: lead and bottom: mercury.

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.

2.5 Heavy metals in precipitation

In all 12 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 2.8. 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 and a Finnish site: 0.03 $\mu\text{g/l}$. These sites also reported the lowest concentrations for Pb with 0.71 and 0.96 $\mu\text{g/l}$ at FI53 and PL04 respectively. The highest concentrations of Cd and Pb were measured at LT15, but the levels are very high in some months so it might be some local influence/contamination at this site.

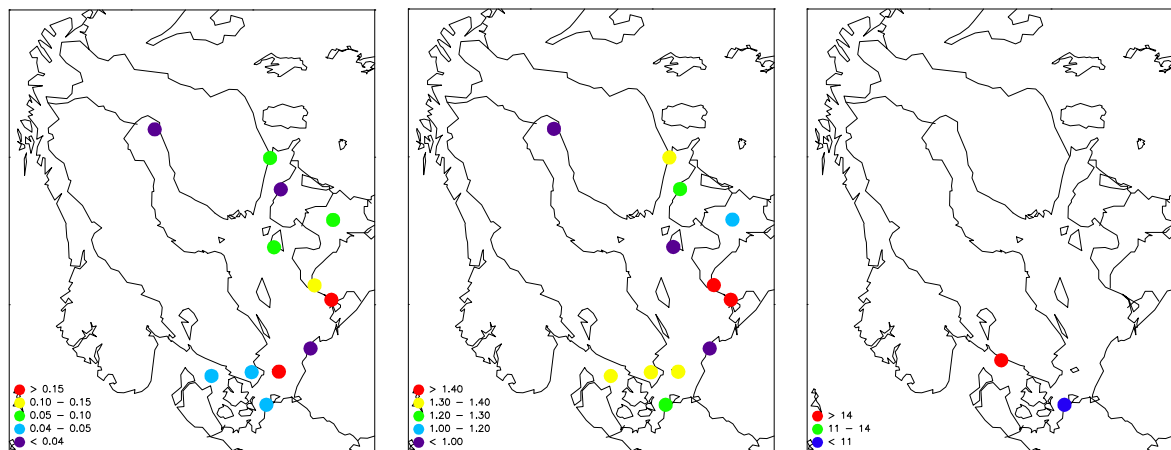


Figure 2.8. Concentrations of left: cadmium (Cd), middle: lead (Pb) in precipitation. Units: $\mu\text{g/l}$, and right: mercury (Hg) in precipitation in 2004. Units: ng/l .

2.6. Lindane ($\gamma\text{-HCH}$)

2 stations from 2 sub basins delivered data for $\gamma\text{-HCH}$ in air, and three have delivered data for $\gamma\text{-HCH}$ in deposition.

Fig. 2.9 displays monthly averages of $\gamma\text{-HCH}$ in air. From this, it is to be observed that the temporal patterns for $\gamma\text{-HCH}$ 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. The deposition data are not shown, because of where different sampling methods make the data difficult to compare. The data are found in appendix A.

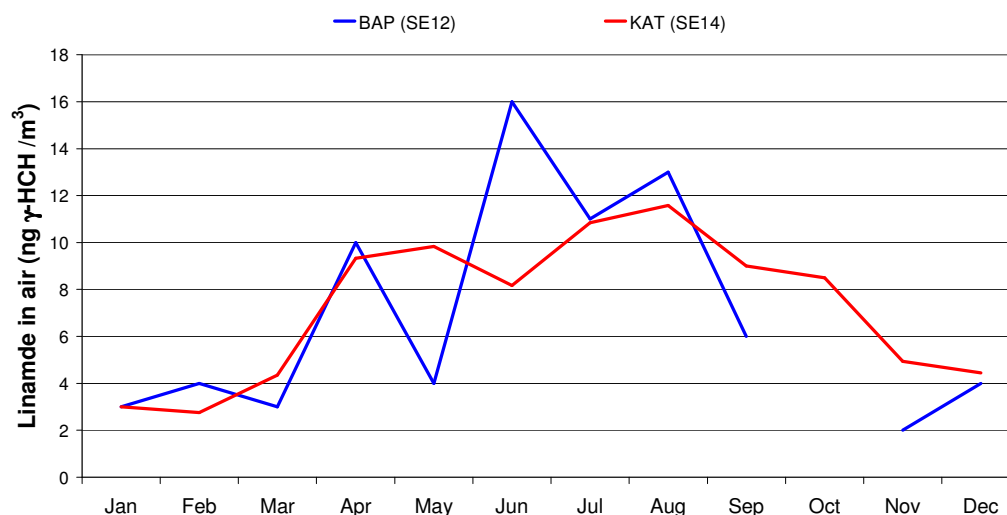


Figure 2.9 Monthly concentrations of γ -HCH in air in 2004

2.7. Laboratory and field intercomparisons

The HELCOM laboratories have participated in different laboratory and field intercomparisons in 2004 which have been presented in EMEP's QA/QC report (EMEP/CCC 3/2006). The results are given below:

2.7.1. 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 there are some measurements with relatively high bias, but in general the results are quite satisfactory

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

	Precipitation			Air	
	NO ₃ -N	NH ₄ -N	NH ₃ -N	NO ₂ -N	HNO ₃ -N
8 DE	1	-3	11	1	1
4 DK	-5	-1	2	-3	-2
38 EE	-2	1		9	
5 FI	2	-1	0		2
16 PL	-2	3	4	-17	-2
22 RU	-3	16		4	-15
20 SE	0	-1	-3	8	-1

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

2.7.2. Heavy metals

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 2004 (Table 2.3) showed quite good results for Pb. Especially Poland and Denmark need to look into their QA/QC routines for heavy metals. The large errors may be due to incorrect reporting of the intercalibration results, but this is also part of the QA/QC routines. The Danish laboratory was more than 2 times outside DQO for Cd, and between 1-2 for Pb in high concentrations. Poland was 2 times outside DQO for Cd and Pb in high concentrations, but better in low concentrations, which is somewhat strange.

Table 2.3. Average per cent error (absolute) in low and high concentration samples, results from the heavy metal laboratory intercomparison in 2004.

	Cd		Pb	
	low	high	low	high
DK	860	829	46	3
FI	5	1	2	4
DE	0	0	5	0
NO for SE*	8	2	2	5
PL	22	61	37	78
GB	18	10	0	1
LT	25	17	3	4
EE		11	22	23

■ 1/2 - 1 DQO
■ 1 - 2 DQO
■ > 2 DQO

- measurement programme carried out by NILU

