2. Observed Concentrations of Nitrogen, Cadmium, Lead, Mercury and Lindane at HELCOM Stations in 2006

2.1 HELCOM measurement stations

Nine countries have submitted data from all together twenty HELCOM stations for 2006 (Table 2.1. and Fig. 2.1).

Table 2.1. Available measurements of nitrogen, lead, cadmium, mercury and lindane from HELCOM stations for 2006.

Sites			In precipitation						In air						
region	Site	Name	NO3	NH4	Cd	Pb	Hg	γ HCH	NO2	sNO3	sNH4	Cd	Pb	Hg	γ HCH
BAP	DE0009R	Zingst	■	■	■	■	■	■	■	■	■	■	■	■	
BAP	DK0020R	Pedersker	■	■	■	■									
BAP	EE0011R	Vilsandi	■	■		■			■						
BAP	FI0009R	Utö	■	■					■	■	■				
BAP	LT0015R	Preila	■	■	■	■			■	■	■	■	■		
BAP	LV0010R	Rucava	■	■	■	■			■	■	■	■	■		
BAP	PL0004R	Leba	■	■	■	■			■	■	■				
BAP	SE0012R	Aspvreten						■							
BAP	SE0051R	Arup			■	■									
BES	DK0005R	Keldsnor	■	■					■	■	■		■		
BES	SE0011R	Vavihill													
KAT	DK0003R	Tange								■	■		■		
KAT	DK0008R	Anholt	■	■	■	■			■	■	■		■		
KAT	SE0014R	Råö	■	■			■	■	■	■	■	■	■	■	■
KAT	SE0097R	Gårdsjön			■	■									
GUF	EE0009R	Lahemaa	■	■	■				■						
GUF	FI0017R	Virolahti II	■	■	■	■			■	■	■				
GUF	RU0016R	Shepeljovo	■	■											
GUB	FI0004R	Åhtari	■	■											
GUB	SE0005R	Hailuoto II	■	■					■	■	■				
GUB	SE0053R	Bredkälen	■	■											
GUB	FI0053R	Rickleå			■	■									
GUR	LV0016R	Zoseni	■	■	■	■			■	■	■	■	■		

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 in Kattegat (KAT), three in the Belt Sea (BES) and in the Gulf of Finland (GUF), and nine in the Baltic proper (BAP). There is one station from: Germany, Lithuania, Poland and Russia, two stations from Latvia and Estonia, four 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 2006. 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.

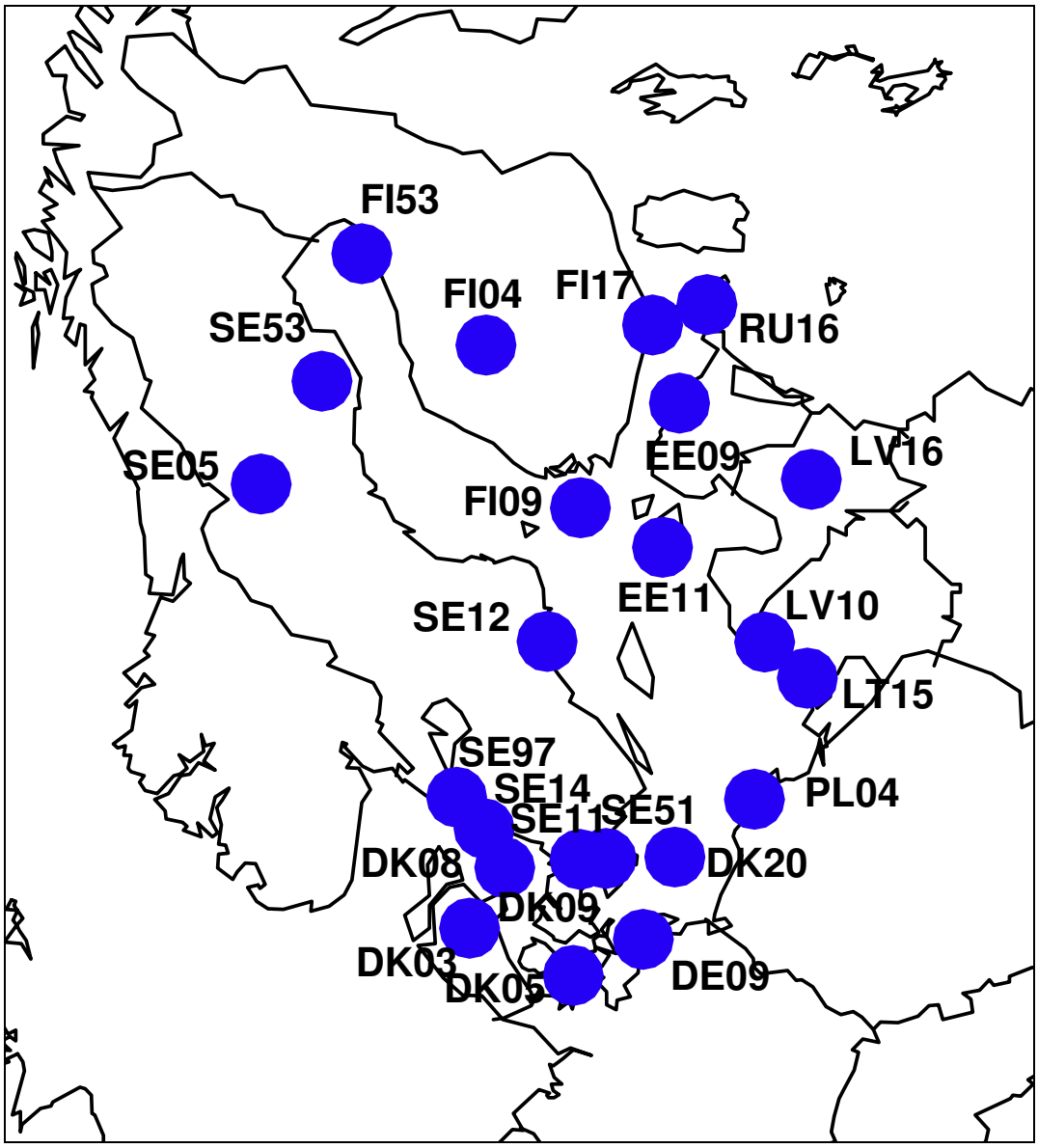

Figure 2.1. Geographical locations of the HELCOM stations with available measurements for the year 2006.

2.2 Nitrogen concentrations in air

Altogether 15 stations have delivered data for one or more nitrogen species in air: 13 for respectively total reduced nitrogen (NH_3+NH_4^+), or total nitrate (HNO_3+NO_3^-), and 14 for nitrogen dioxide (NO_2). Stations from all the six sub-basins have delivered data of nitrogen concentration in air. Annual averages of the different nitrogen species are presented in Figure 2.2. Average air concentrations are arithmetic averages of the reported values. The lowest concentrations for all the three nitrogen species were reported at the northernmost Swedish site (SE05) in 2006: The concentrations were 0.23, 0.08, 0.14 µg N/m^3 for respectively NH_3+NH_4^+, HNO_3+NO_3^- and NO_2 at this site. Highest concentrations of nitrogen in aerosols were found at the German site DE09, more than 2 µgN/m^3 of sum ammonium, and 1 µgN/m^3 for sum nitrate. The Estonian sites show highest level of NO_2 with more than 3 µgN/m^3

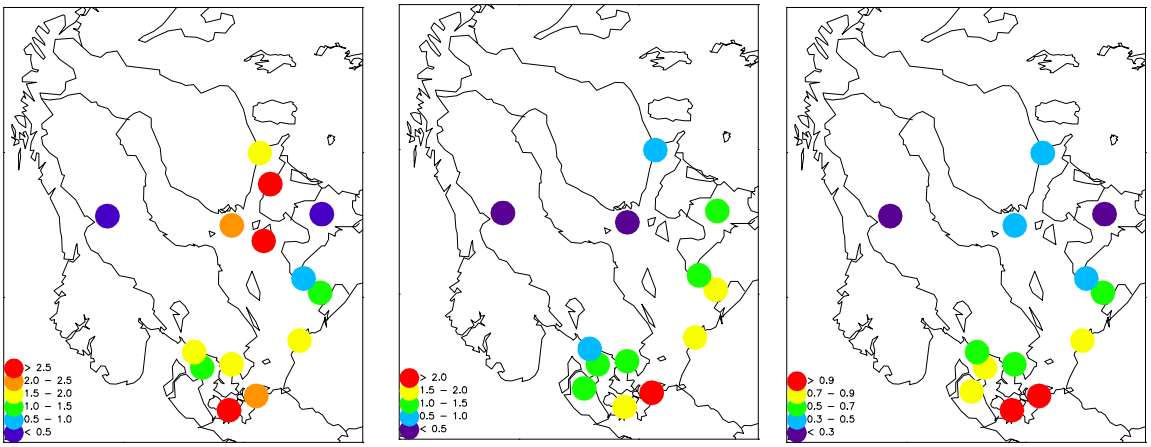

Figure 2.2. Concentrations of left: NO_2 in air, middle: total reduced nitrogen (NH_3+NH_4^+), and right: total nitrate (HNO_3+NO_3^-) in 2005 Unit: µg N/m^3.

. 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 April, and a peak is also common in august. Agricultural activities (natural fertilizer) are the main source for NH_3+NH_4^+. During the summer half year, NH_3 is normally emitted from the ground due to higher temperatures.

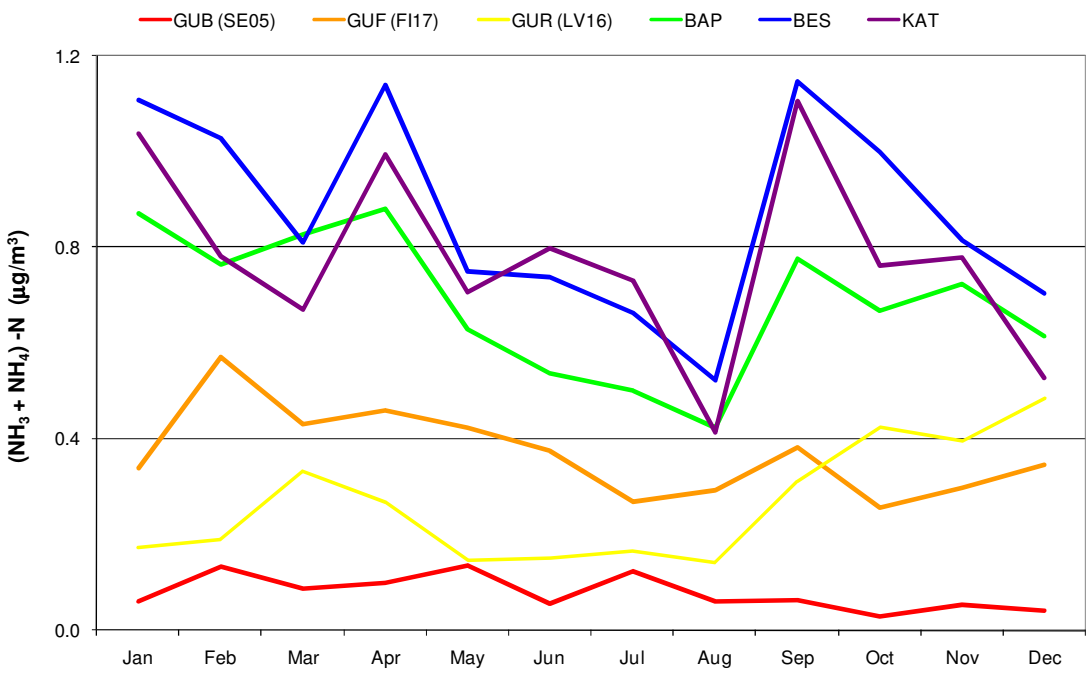

Figure 2.3. Monthly total reduced nitrogen (NH_3+NH_4) concentrations in the air in 2006

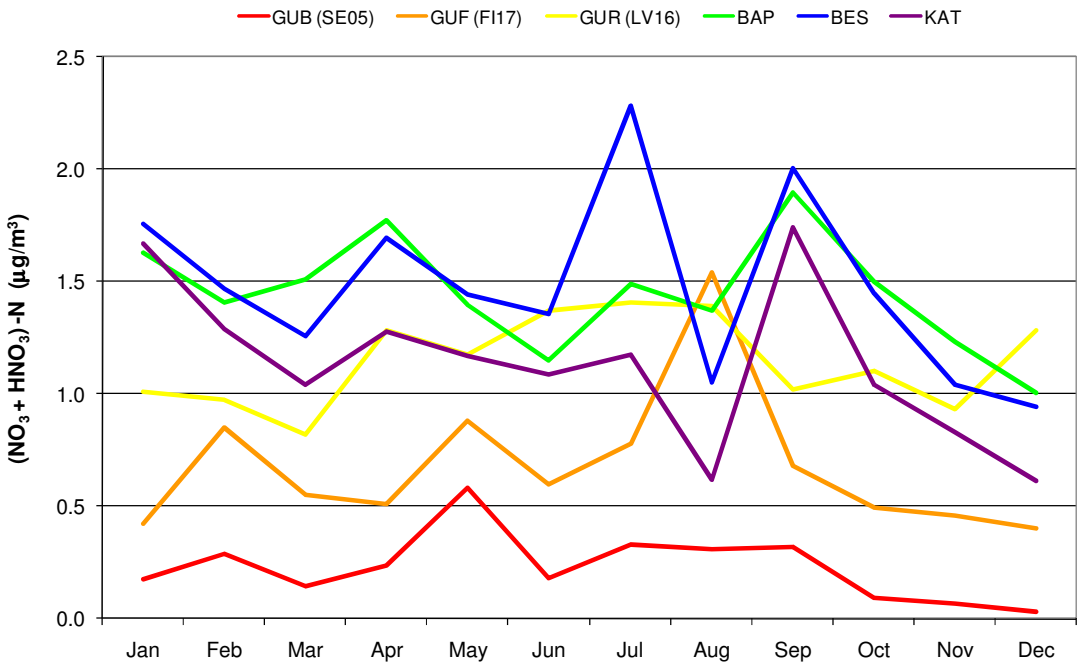

Figure 2.4. Monthly total oxidized nitrate (HNO_3+NO_3^-) concentrations in the air in 2006

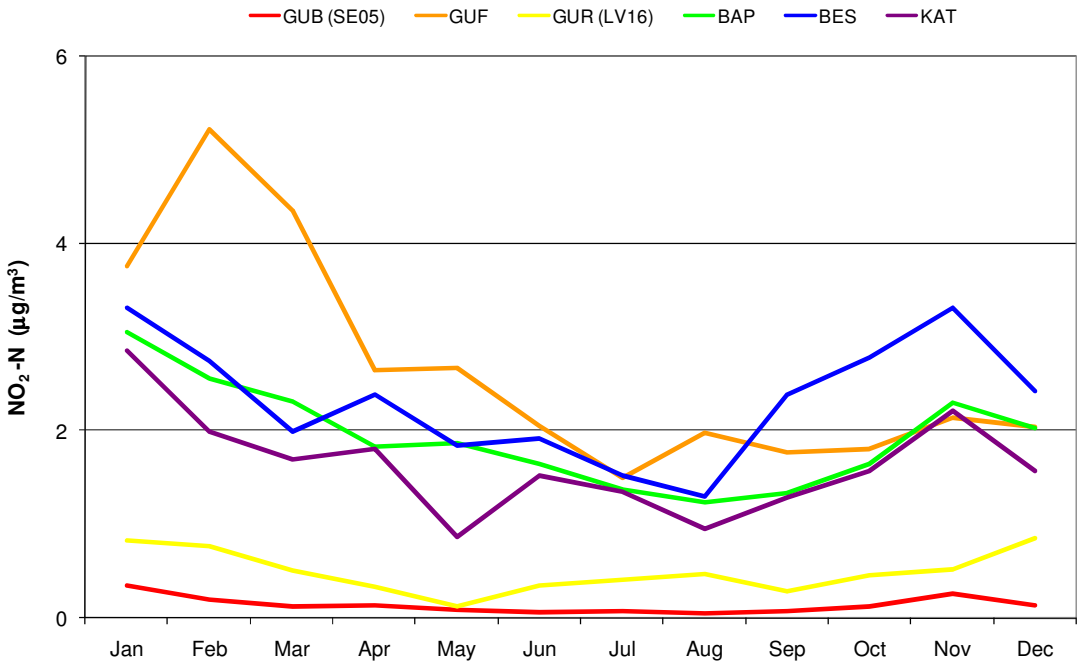

Figure 2.5. Monthly NO_2 concentrations in the air in 2006

Total nitrate (HNO_3+NO_3^-) concentration doesn't show any clear seasonal pattern, there are elevated levels for some months varying between the regions. NO_2 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 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 18 stations have delivered data for ammonium and nitrate in precipitation. Stations from all the six sub-basins have delivered data for ammonium and nitrate in precipitation. Annual averages of the two nitrogen species are presented in Figure 2.6.

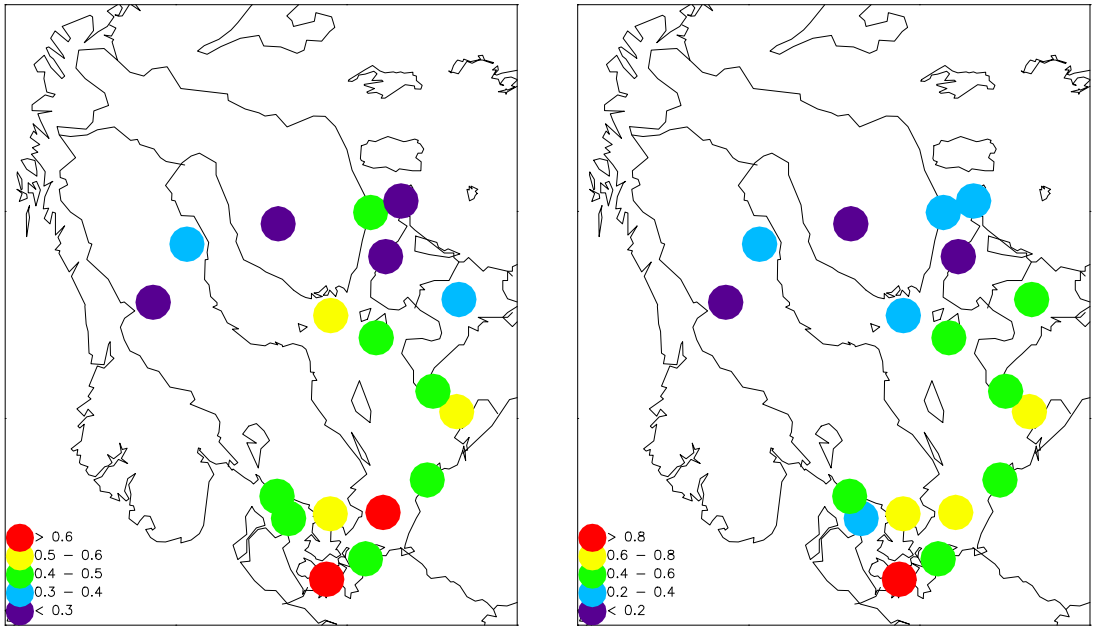

Figure 2.6. Concentrations of left: nitrate (NO_3^-)), and right: ammonium (NH_4^+ in precipitation in 2006. Units: mg N/l.

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. 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 for ammonium and nitrate were seen at SE05, annual concentration of 0.11 and 0.13 mg N/L respectively. The highest concentrations were found at the DK05, 0.95 mg N/l and 0.65 mg N/l for ammonium and nitrate respectively. Figure 2.7 displays the station average deposition of oxidized and reduced nitrogen across the regions given.

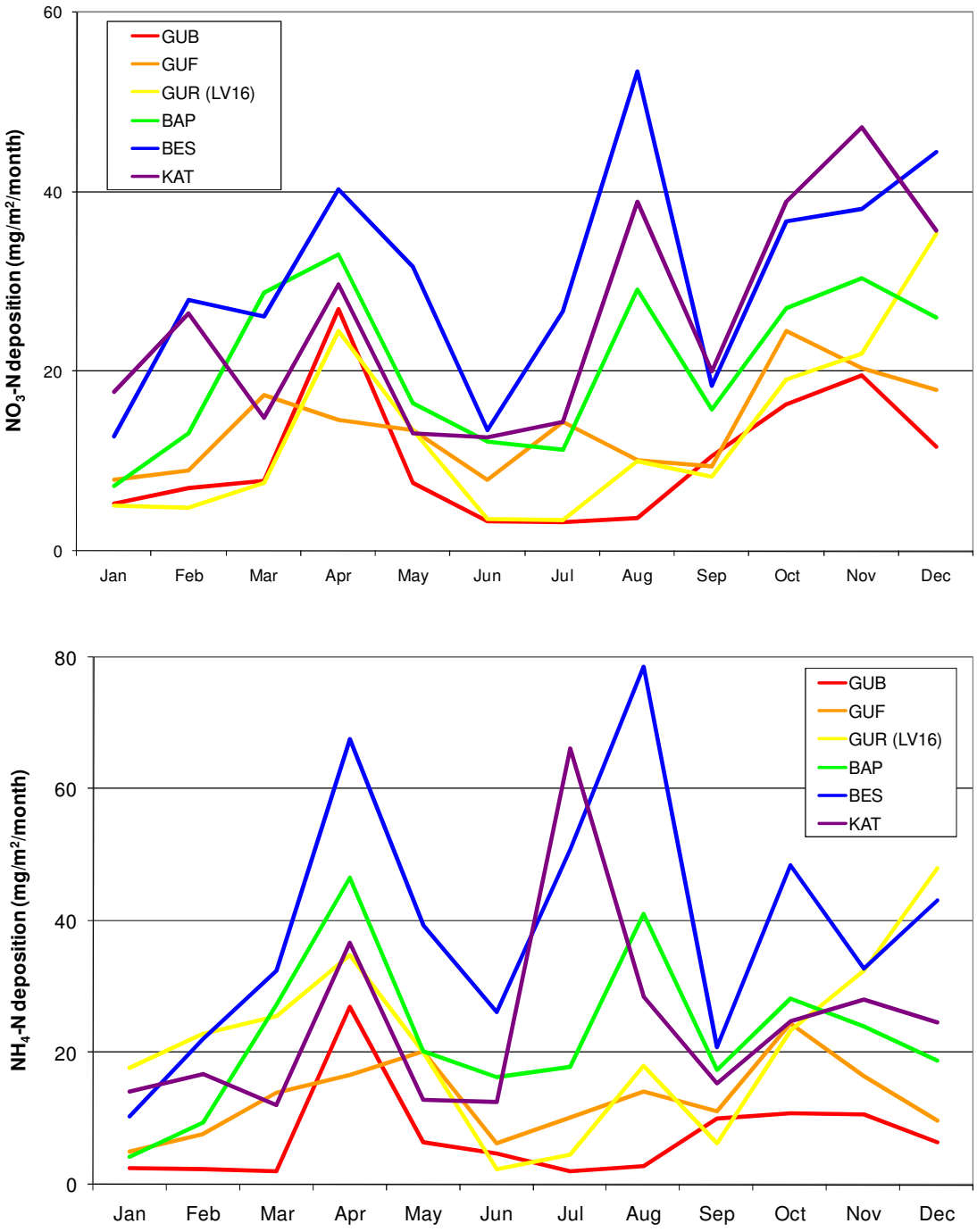

Figure 2.7. Monthly nitrogen depositions in 2006 averaged for the sub-basins. Top: nitrate (NO_3^-), and bottom: reduced nitrogen (NH_4^+).

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

2.4 Heavy metals in the air

Altogether eight stations have delivered heavy metal data in air whereof five measuring cadmium, eight 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. Average air concentrations are arithmetic averages of the reported values. The lowest concentrations for Cd in aerosols were reported at SE14, 0.15 ng/m^3. The lowest concentration (3.1 ng/m^3) for Pb in aerosols was reported at LV16. The highest concentrations were found at LV10 for cadmium (0.22 ng/m^3) and LT15 (6.9 ng/m^3) for lead

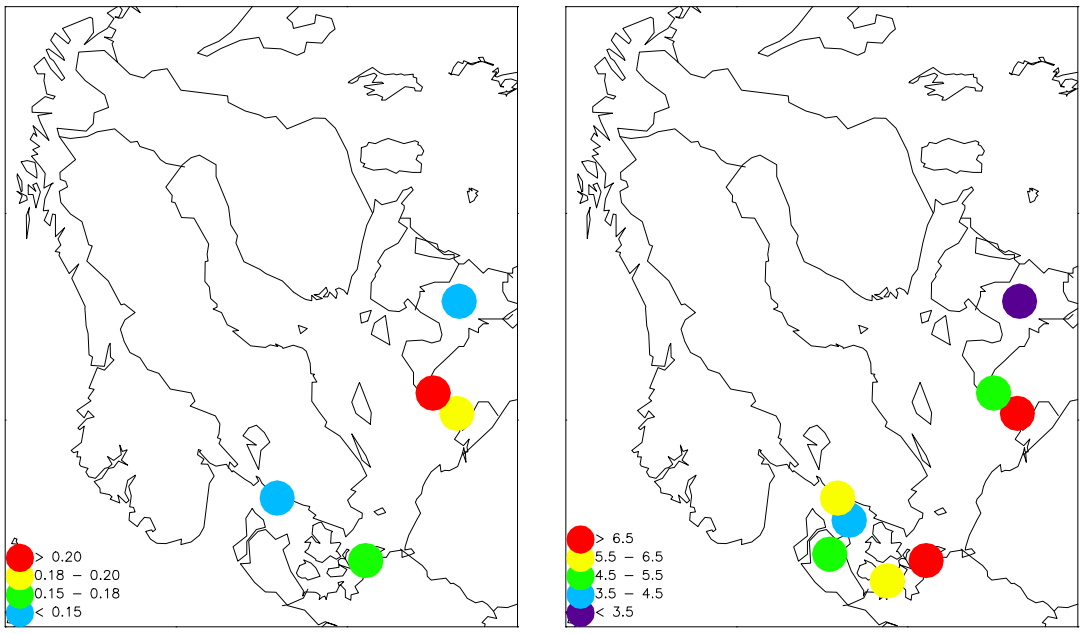

Figure 2.8. Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2006. Units: ng/m^3.

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

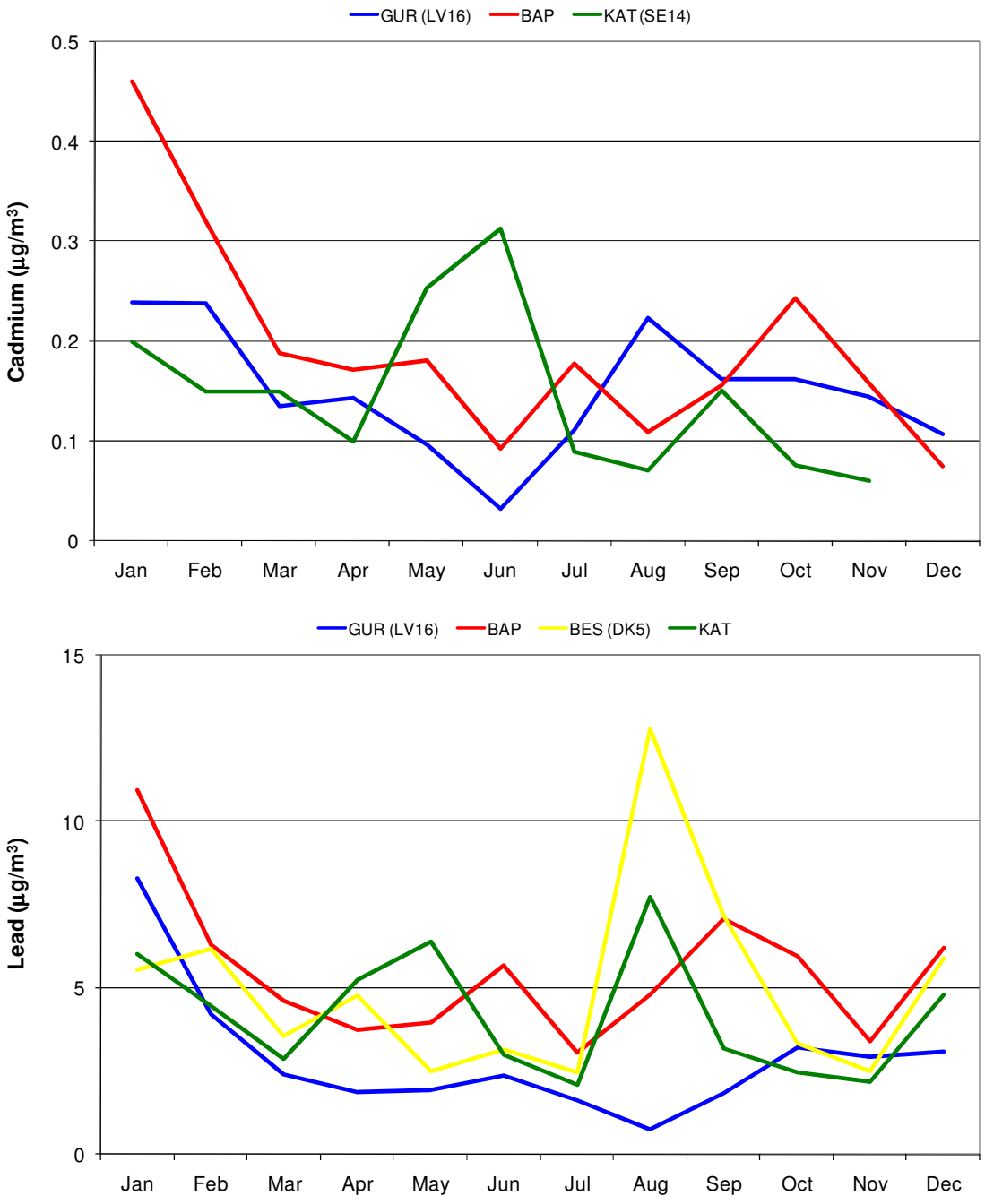

Figure 2.9. Monthly concentrations in air in 2006 averaged for the sub-basins: Top: cadmium, bottom: lead

From this, it is to be observed that the temporal patterns for Cd and Pb show a winter maximum. In addition there is elevated level of Pb at several sites in august. 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

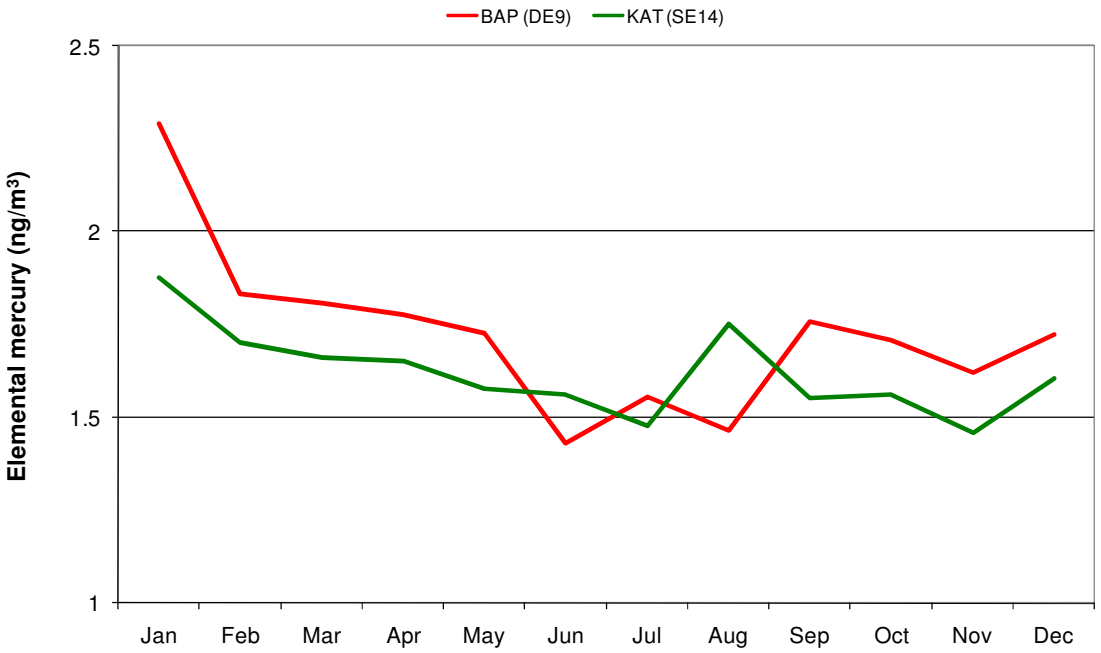

Figure 2.10. Monthly concentrations of Hg in air in 2006 averaged for the sub-basins:

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 daily, weekly or monthly reported values as precipitation-weighted averages. The lowest concentration for Cd in precipitation was reported at the the sites SE97 and FI53 with about 0.03 µg/l. The lowest concentrations for Pb with 0.55 were observed at EE11. The highest concentration of Pb was measured at LT15 (4.1 µg/l) while at PL04 for Cd (0.10 µg/l.)

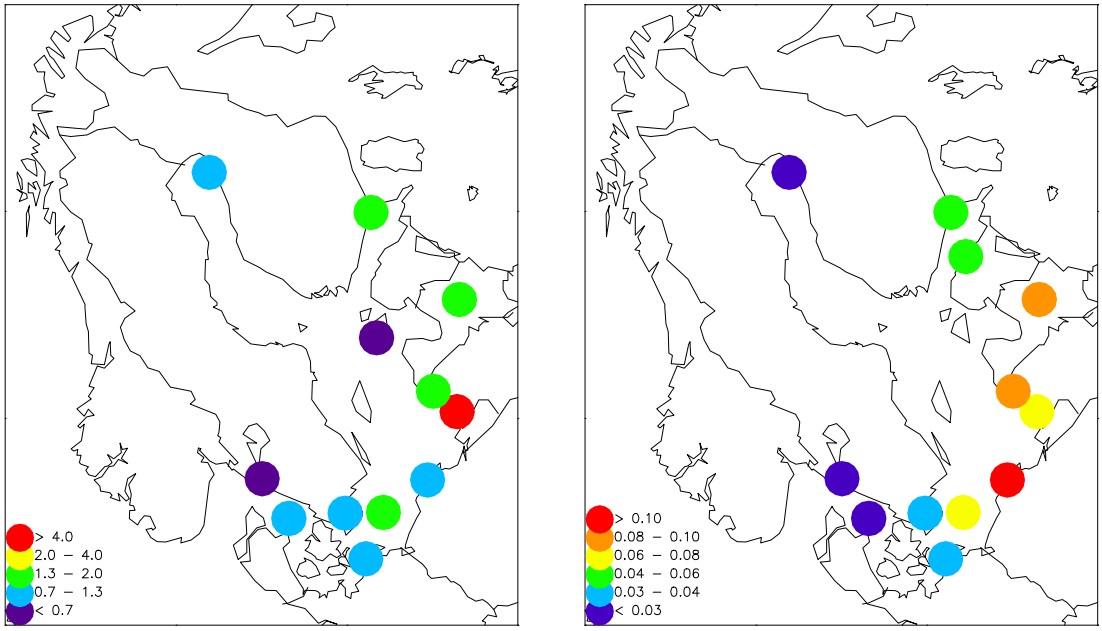

Figure 2.11. Concentrations of left: lead (Pb), right: cadmium (Cd) in precipitation. in precipitation in 2006. Units: µg/l.

2.6. Lindane (γ-HCH)

Only Sweden delivered data for γ-HCH in air, while Germany in addition delivered data for γ-HCH in precipitation. Fig. 2.12 displays monthly averages of γ-HCH in air at SE14.

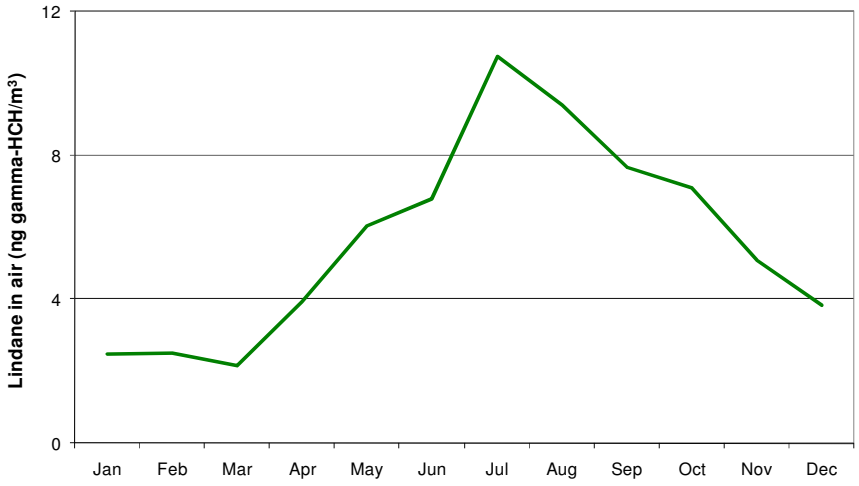

Figure 2.11 Monthly concentrations of γ-HCH in air at SE14 in 2006

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. The deposition data are not shown, because of where different sampling methods make the this difficult to compare. The data are found in appendix A.

2.7. Laboratory intercomparisons

The HELCOM laboratories have participated in different laboratory and field intercomparisons in 2006 which have been presented in EMEP's QA/QC report (EMEP/CCC 3/2008). The laboratory uncertainty is one source to the total uncertainty and the performance of the different labs are testes in the annual EMEP laboratory intercomparison. The results from the intercomparison on main components in air and precipitation (Table 2.2) representative for the 2006 data showed that the laboratories generally have a good quality.

	Precip		Air		
Lab	NH4	NO3	HNO3	NH3	NO2
DE	1.5	1.4			
DK	0.5	1.6	1.9	2.8	0.7
EE	1.0	1.6	3.8	2.1	0.5
FI	0.9	1.5	3.8	2.2	
LT	3.5	3.3	3.8	8.4	1.8
LV	1.2	1.4	1.9	5.1	0.9
PL	3.9	1.1	1.9		1.4
RU	16.2	5.7	5.7		55.2
SE	0.7	1.3	3.8	1.0	0.9

between 10 and 25 % RSD

> 25% RSD

Table 2.2. Relativ standard deviation (RSD) in nitrogen species in the EMEP's 25th laboratory intercomparison for precipitation and air.

Results from the EMEP laboratory intercomparison of heavy metals in 2006 is shown in table 2.3, and it is quite good quality for Pb, and somewhat higher uncertainty for the cadmium measurements.

	Cd		Pb	
	low	high	low	high
DK	146	11	15	21
FI	13	12	9	11
DE	2	2	3	6
PL	0	0	9	3
LT	23	5	19	4
LV	15	1	4	6
EE	<DL	12	21	3

between 10 and 25% RSD

Between 25 and 50% RSD

> 50% RSD

Table 2.3. Average per cent error (absolute) in low and high concentration samples, results from the heavy metal laboratory intercomparison in EMEP, 2006.