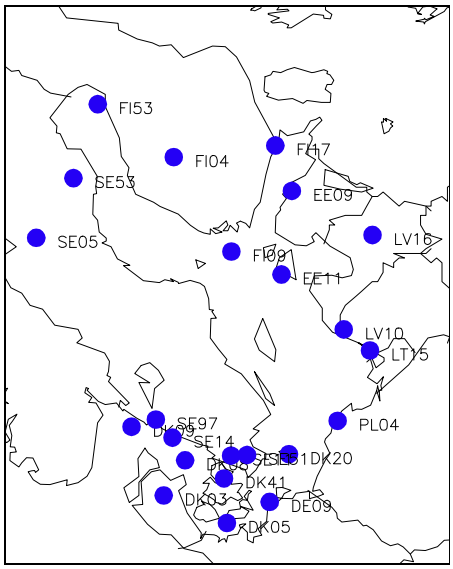
2. Observed Concentrations of Nitrogen, Cadmium, Lead and Mercury at HELCOM Stations in 2007

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

Sites			In precipitation					In air					
region	Site	Name	NO3	NH4	Cd	Pb	Hg	NO2	sNO3	sNH4	Cd	Pb	Hg
BAP	DE0009R	Zingst											
BAP	DK0020R	Pedersker											
BAP	EE0011R	Vilsandi											
BAP	FI0009R	Utö											
BAP	LT0015R	Preila											
BAP	LV0010R	Rucava											
BAP	PL0004R	Leba											
BAP	SE0051R	Arup											
BES	DK0005R	Keldsnor											
BES	DK0041R	Lille Valby											
BES	SE0011R	Vavihill											
KAT	DK0003R	Tange											
KAT	DK0008R	Anholt											
KAT	DK0009R	Storebaelt											
KAT	SE0014R	Råö											
KAT	SE0097R	Gårdsjön											
GUF	EE0009R	Lahemaa											
GUF	FI0017R	Virolahti II											
GUB	FI0004R	Ähtari											
GUB	SE0005R	Bredkälen											
GUB	SE0053R	Rickleå											
GUB	FI0053R	Hailuoto											
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 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 ($HNO_3+NO_3^-$), 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 2007: The concentrations were 0.16, 0.04 and 0.11 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 and Danish sites DK03 and DK05 with about 2 µgN/m^3 of sum ammonium, and 0.8 µgN/m^3 for sum nitrate. The Estonian sites show highest level of NO_2 with about 3 µgN/m^3.

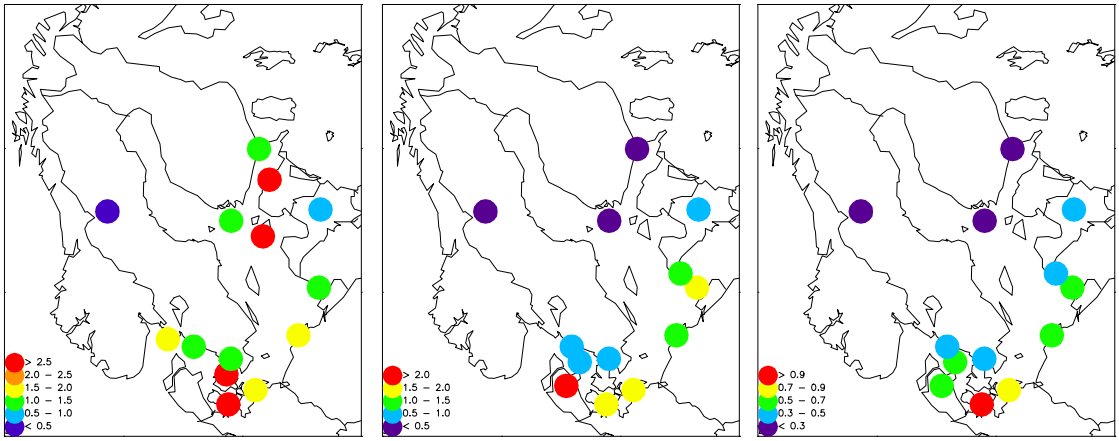


Figure 2.2. Concentrations of left: NO_2 in air, middle: total reduced nitrogen ($NH_3+NH_4^+$), and right: total nitrate ($HNO_3+NO_3^-$) in 2007 Unit: µg N/m^3.

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 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_3 is normally emitted from the ground due to higher temperatures.

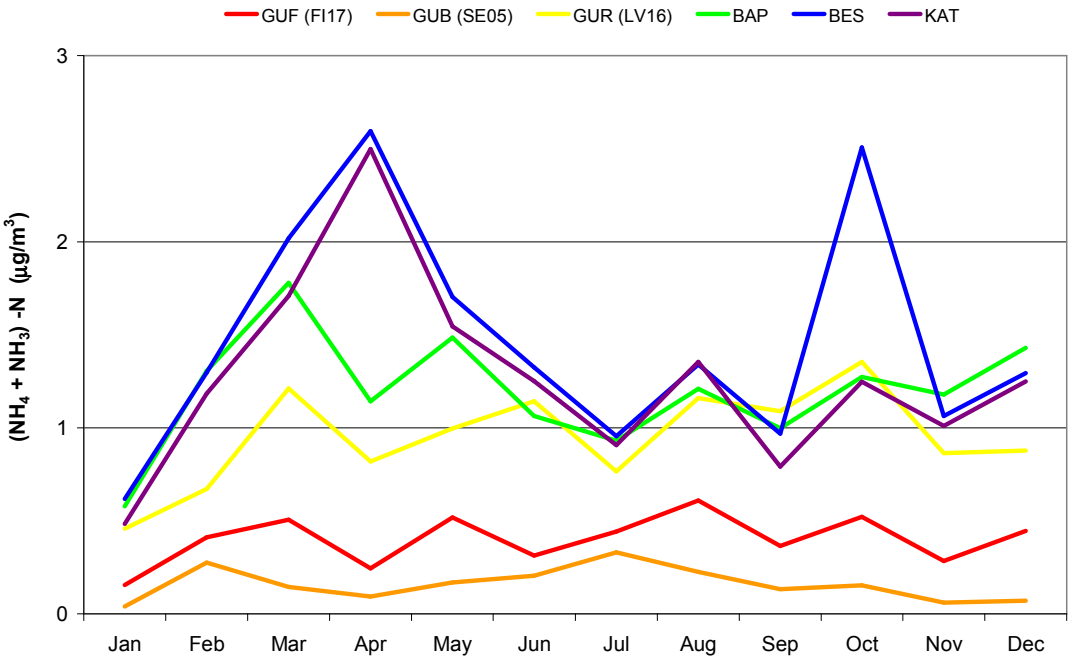


Figure 2.3. Monthly total reduced nitrogen (NH_3+NH_4) concentrations in the air in 2007

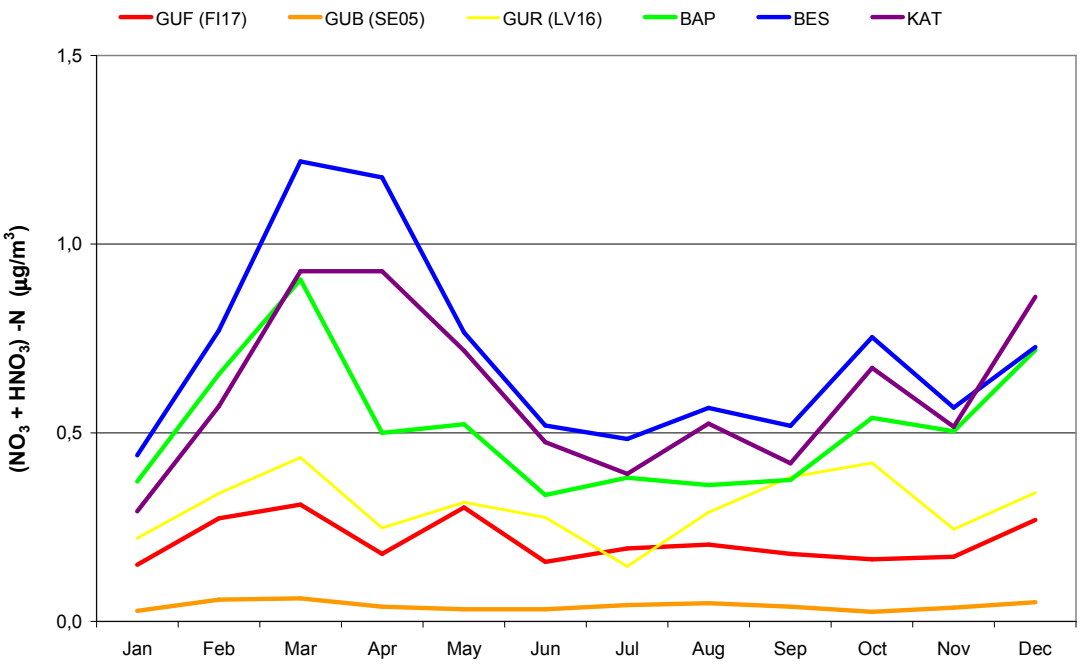


Figure 2.4. Monthly total oxidized nitrate (HNO_3+NO_3^-) concentrations in the air in 2007

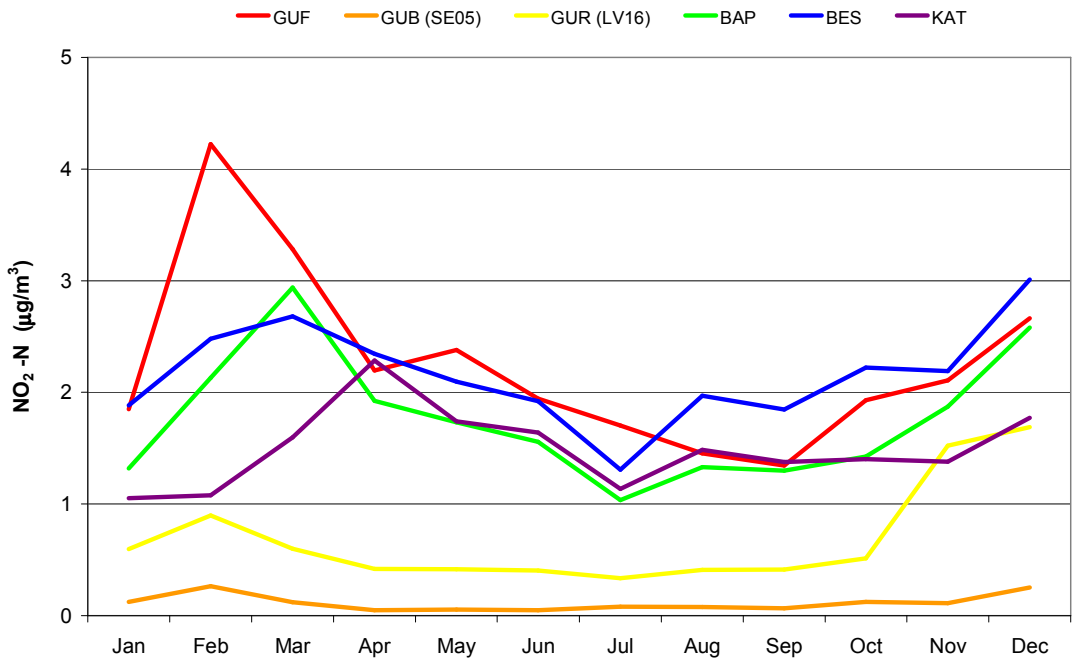


Figure 2.5. Monthly NO_2 concentrations in the air in 2007

Total nitrate (HNO_3+NO_3^-) concentration doesn't show that 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 usually a less pronounced seasonal pattern, though spring gives the highest level in 2007. 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.

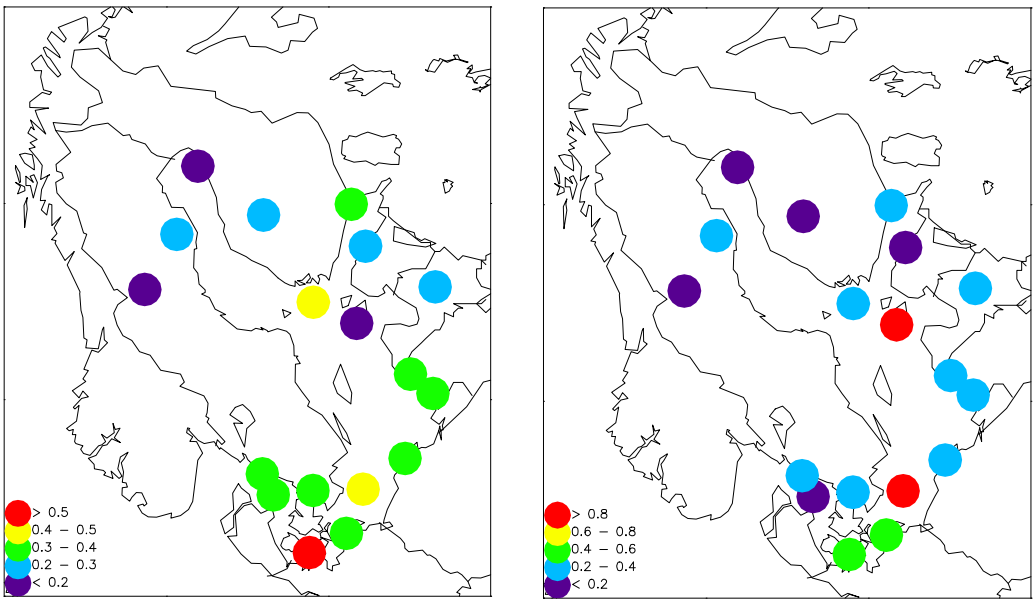


Figure 2.6. Concentrations of left: nitrate (NO_3^-)), and right: ammonium (NH_4^+ in precipitation in 2007. Units: mg N/l.

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.

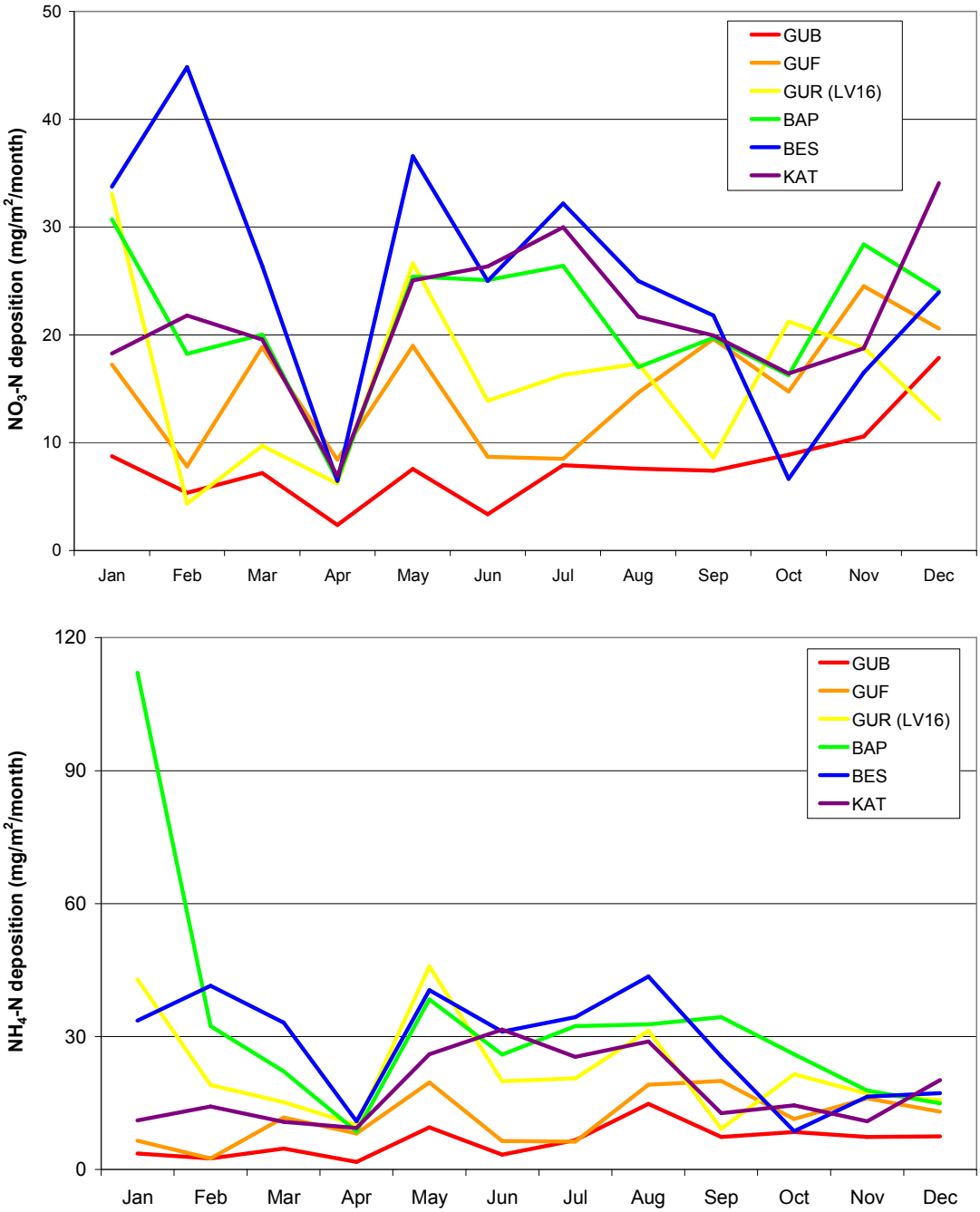


Figure 2.7. Monthly nitrogen depositions in 2007 averaged for the sub-basins. Top: nitrate (NO_3^-), and bottom: reduced nitrogen (NH_4^+).

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. 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^3, respectively. The highest concentrations were found at EE09 with 0.2 and 6.3 ng/m^3 for Cd and Pb respectively.

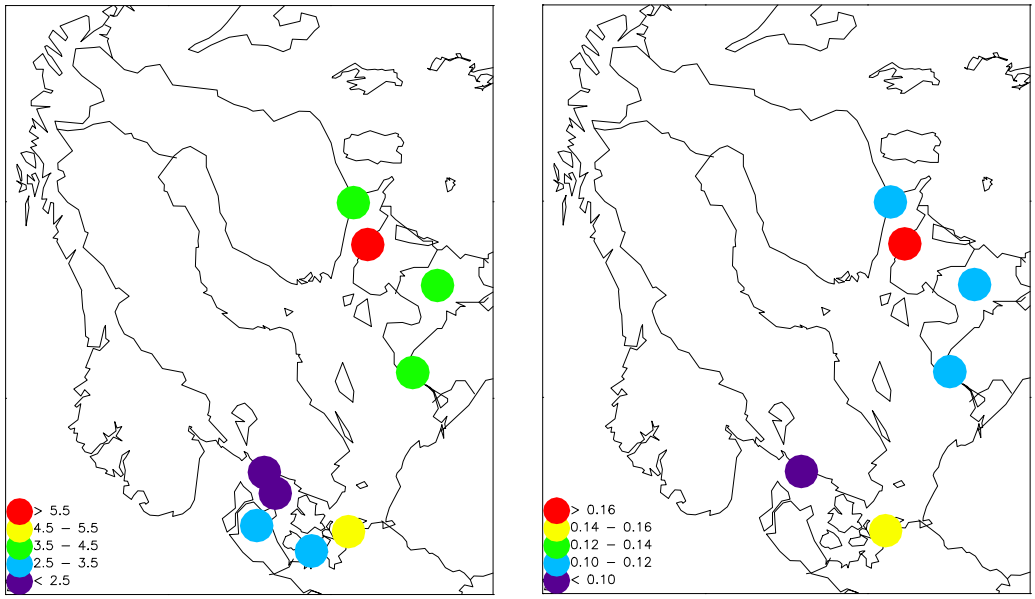


Figure 2.8. Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2007. Units: ng/m^3.

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).

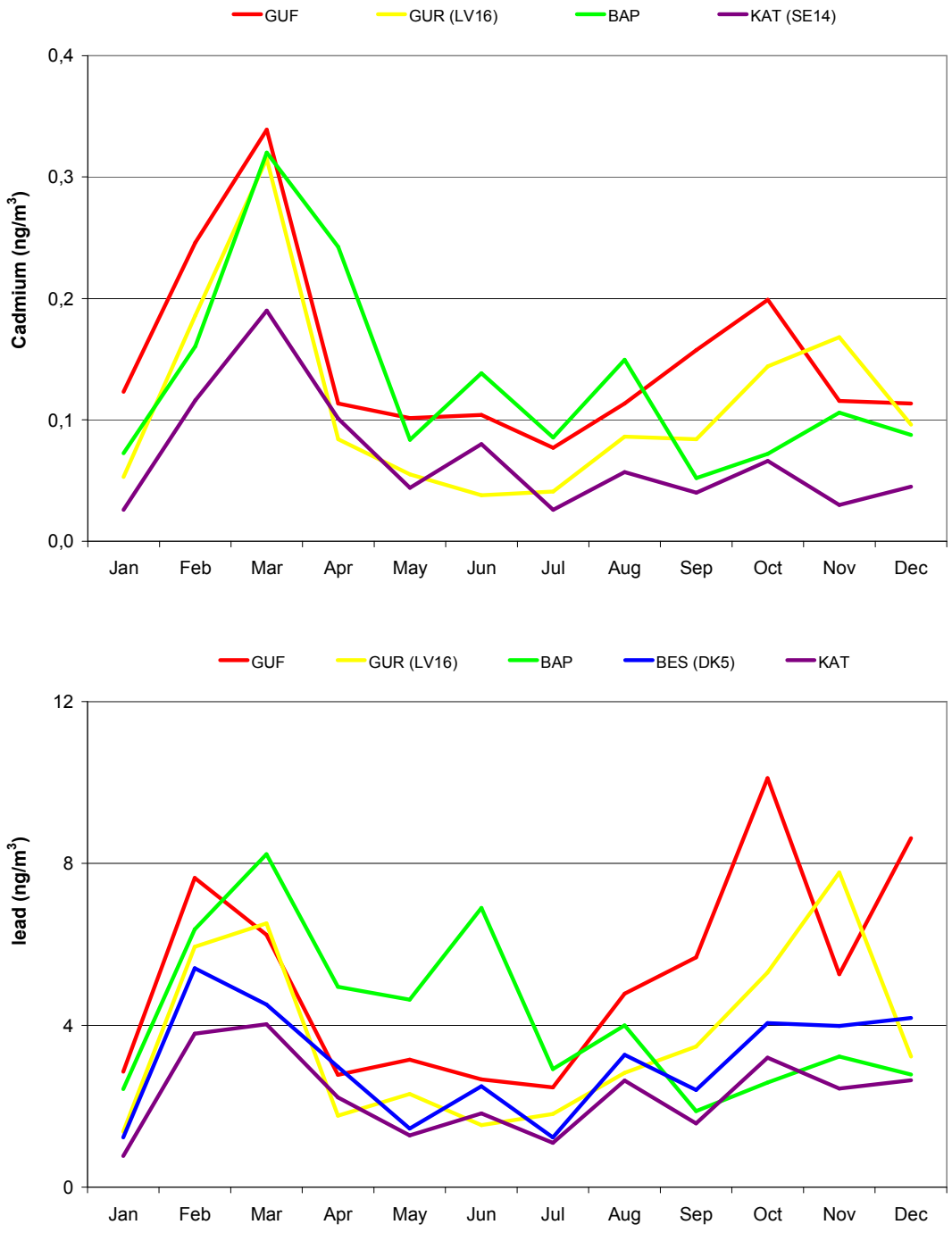


Figure 2.9. Monthly concentrations in air in 2007 averaged for the sub-basins: Top: cadmium, bottom: lead

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

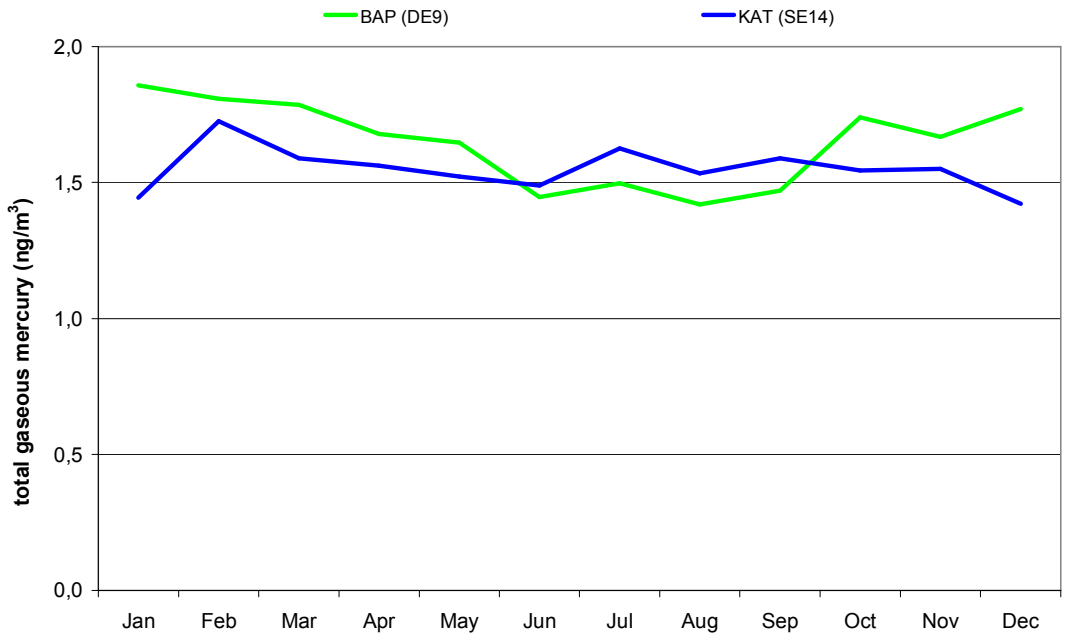


Figure 2.10. Monthly concentrations of Hg in air in 2007 averaged for the sub-basins:

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 µg/l.)

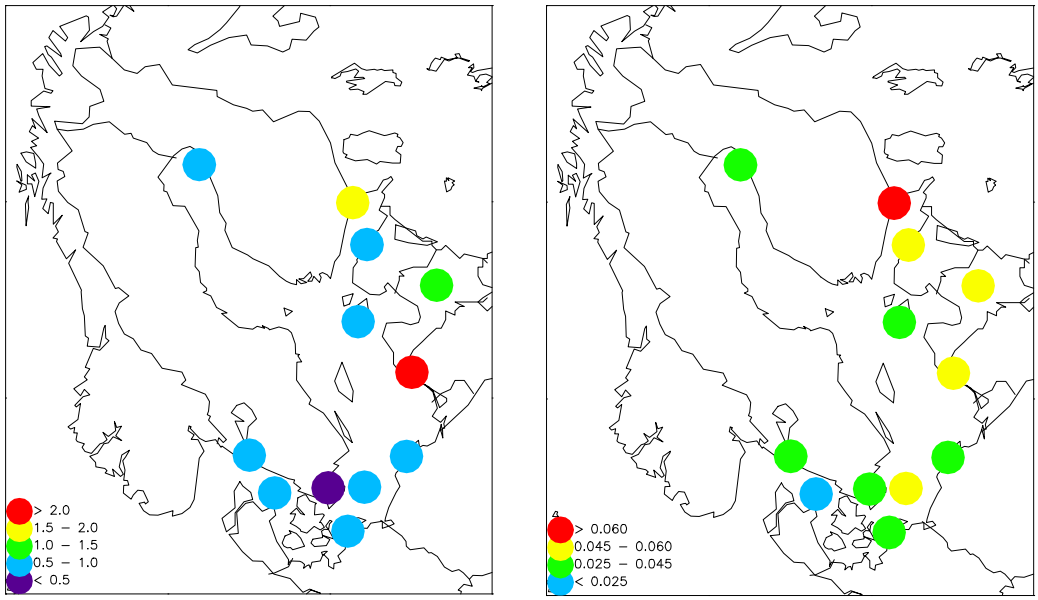


Figure 2.11. Concentrations of left: lead (Pb), right: cadmium (Cd) in precipitation. in 2007. Units: µg/l.

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.