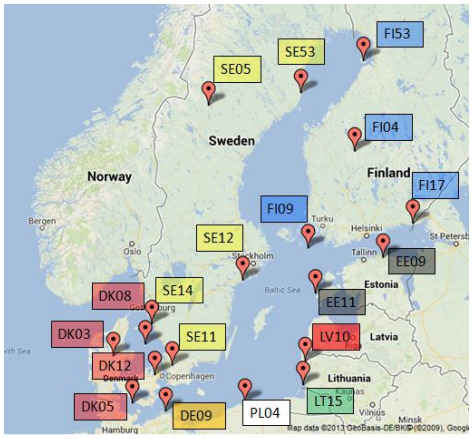
2. Observed Concentrations of Nitrogen, Cadmium, Lead and Mercury at HELCOM Stations in 2011

2.1 HELCOM measurement stations

Eight countries have submitted data from all together nineteen HELCOM stations for 2011 (Fig. 2.1). This is one more than for 2010. The stations are distributed in eight of the nine sub-basins (Fig. 2.1) as following: Three in Kattegat (KAT), two in The Sound (SOU), one in Western Baltic (WEB), six in the Baltic proper (BAP), two in Gulf of Finland (GUF), one in Archipelago Sea (ARC), two in Bothnian Sea (BOS) and two in Bothnian Bay (BOB). There is one station from Germany, Lithuania, Latvia, Poland; two stations from Estonia; four in Denmark and Finland; and five stations from Sweden. Råö and Vavihill in Sweden are the only ones with data for all the components in air and precipitation for 2011.

Fig 2.1. HELCOM sites with measurements of nitrogen, lead, cadmium and mercury in 2011



region	Site	Name	In precipitation NO3	NH4	Cd	Pb	Hg	In air NO2	sNO3	sNH4	Cd	Pb	Hg
KAT	DK0003R	Tange											
KAT	DK0008R	Anholt											
KAT	SE0014R	Råö											
SOU	DK0012R	Risö											
SOU	SE0011R	Vavihill											
WEB	DK0005R	Keldsnor											
BAP	DE0009R	Zingst						NO3					
BAP	PL0004R	Leba											
BAP	LT0015R	Preila											
BAP	LV0010R	Rucava											
BAP	EE0011R	Vilsandi											
BAP	SE0012R	Aspvreten											
GUF	EE0009R	Lahemaa											
GUF	FI0017R	Virolahti II											
ARC	FI0009R	Utö											
BOS	FI0004R (37)	Ähtari (II)											
BOS	SE0005R	Bredkälen											
BOB	FI0053R	Hailuoto II											
BOB	SE0053R	Rickleå											

In this section, we provide a broad view of the patterns and levels evident in monitoring data from 2011. 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 2011 data (Hjellbrekke and Fjæraa, 2013; Aas and Breivik, 2013) and the data are available from the web database at http://ebas.nilu.no/. The HELCOM laboratories have participated in the EMEP and laboratory intercomparison and the laboratories generally have a satisfactory quality.

2.2 Nitrogen concentrations in air

Altogether thirteen stations have delivered data for total reduced nitrogen ($NH_3+NH_4^+$) and total nitrate ($HNO_3+NO_3^-$), and thirteen for nitrogen dioxide (NO_2). Annual averages of the different nitrogen species are presented in Figure 2.2. The lowest concentrations for all the three nitrogen species were reported at the northernmost Swedish site (SE05) in 2011: The concentrations were 0.16, 0.04 and 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 air were found in Denmark, with annual concentration means of 3.1 µgN/m^3 for NO_2 (at DK05), 2.5 µgN/m^3 for sum ammonium (at DK03), and 1.1 µgN/m^3 for sum nitrate (at DK12). Data for nitrate and ammonium from the German site (DE09) is not included in the figures below, because of change of method during the year, but the annual concentration of ammonium can be estimated to be somewhat lower than the Danish sites (se details for monthly concentrations in the annex, table A.1.

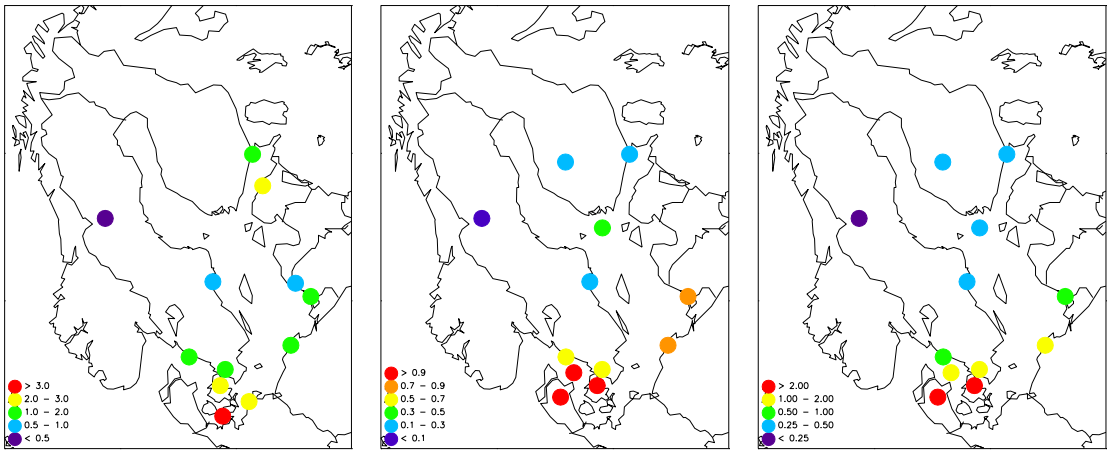


Figure 2.2. Concentrations of left: NO_2 in air, middle: total nitrate ($HNO_3+NO_3^-$) and right: total reduced nitrogen ($NH_3+NH_4^+$) in 2011 Unit: µg N/m^3.

There is a tendency of increasing concentrations from north to south and towards west. This concentration gradients reflect the varied influence of traffic (ship as well as cars) and agricultural activities. A similar 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

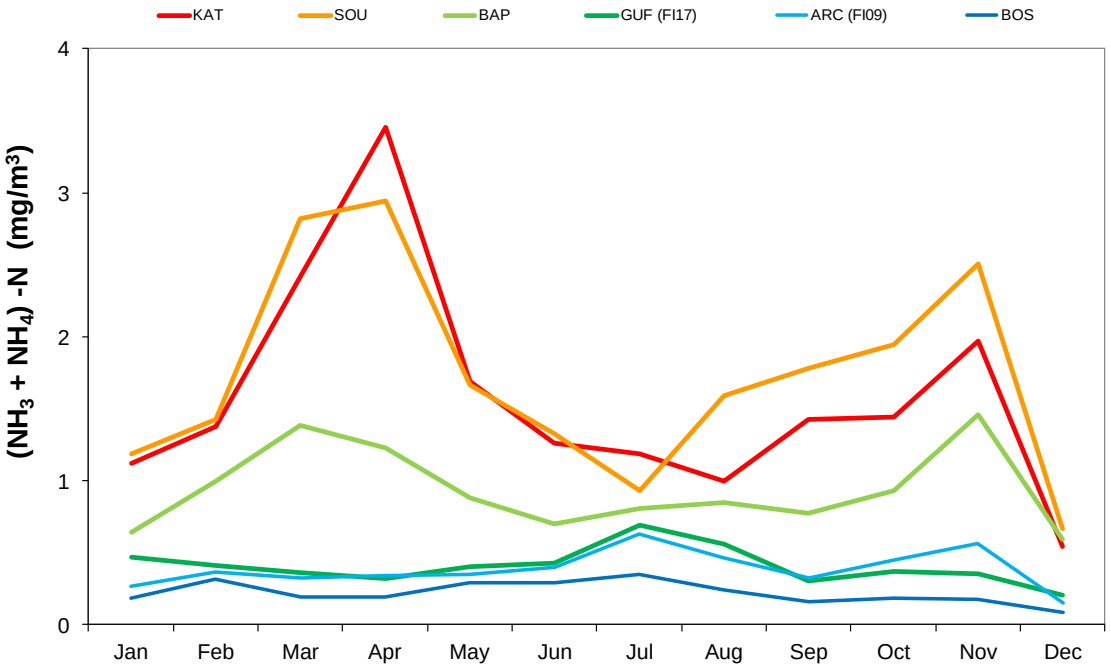


Figure 2.3. Monthly total reduced nitrogen (NH_3+NH_4) concentrations in the air in 2011

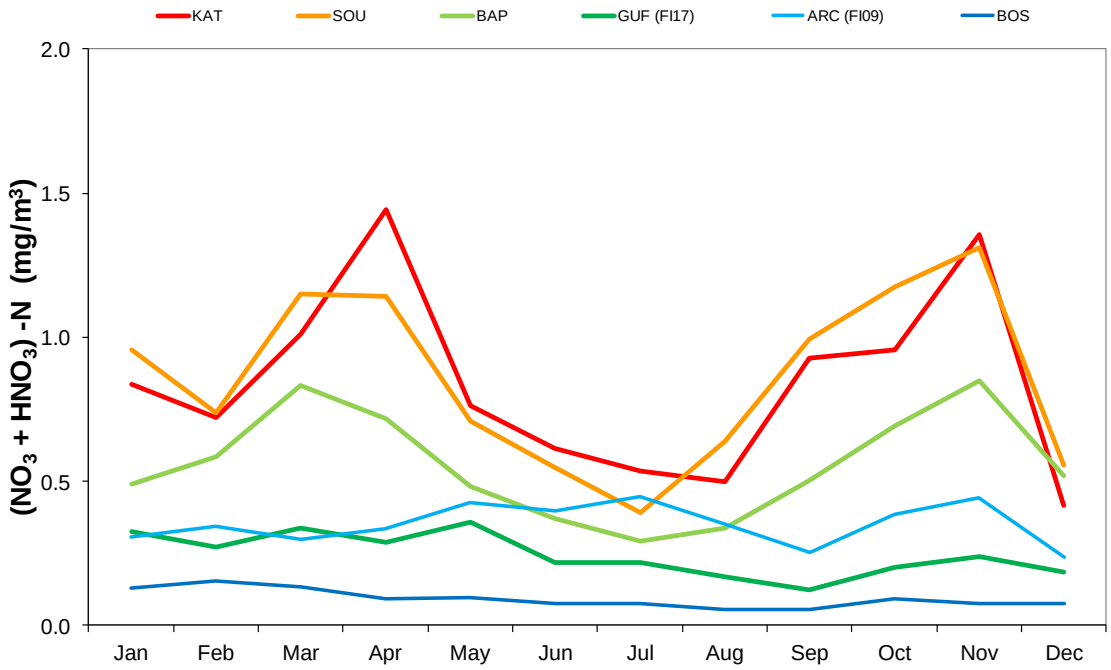


Figure 2.4. Monthly total oxidized nitrate (HNO_3+NO_3^-) concentrations in the air in 2011.

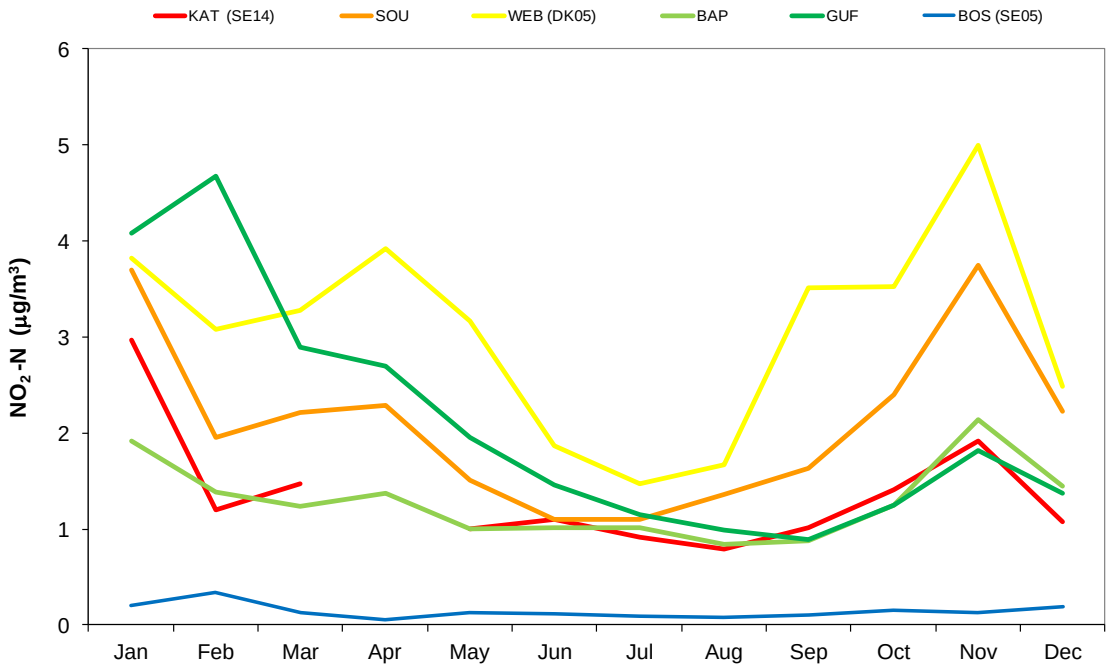


Figure 2.5. Monthly NO_2 concentrations in the air in 2011.

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 when the fertilizing is most important. Agricultural activities (natural fertilizer) are the main source for NH_3+NH_4^+. But also high concentrations are seen in late autumn, maybe due to some fall fertilization, but more likely due to longer resistance time of NH_4NO_3 in the atmosphere (see below).

Total nitrate (HNO_3+NO_3^-) concentration show elevated levels in the spring late autumn; and generally somewhat higher concentrations in winter than summer. NO_2 is reacting photo-chemically 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. This effect of fast removal of sum nitrate seems to be relatively more important than higher production in summer, causing summer minima. Concentrations of NO_2 also show, not unexpectedly, a temporal pattern with a winter maxima/summer minima. During winter the atmospheric residence time is longer due to low photo-chemically activity and reduced vertical mixing.

2.3 Nitrogen in precipitation

Altogether fifteen stations have delivered data for ammonium and nitrate in precipitation. Stations from eight sub-basins have delivered data for ammonium and nitrate in precipitation. Annual averages of the two nitrogen species are presented in Figure 2.6.

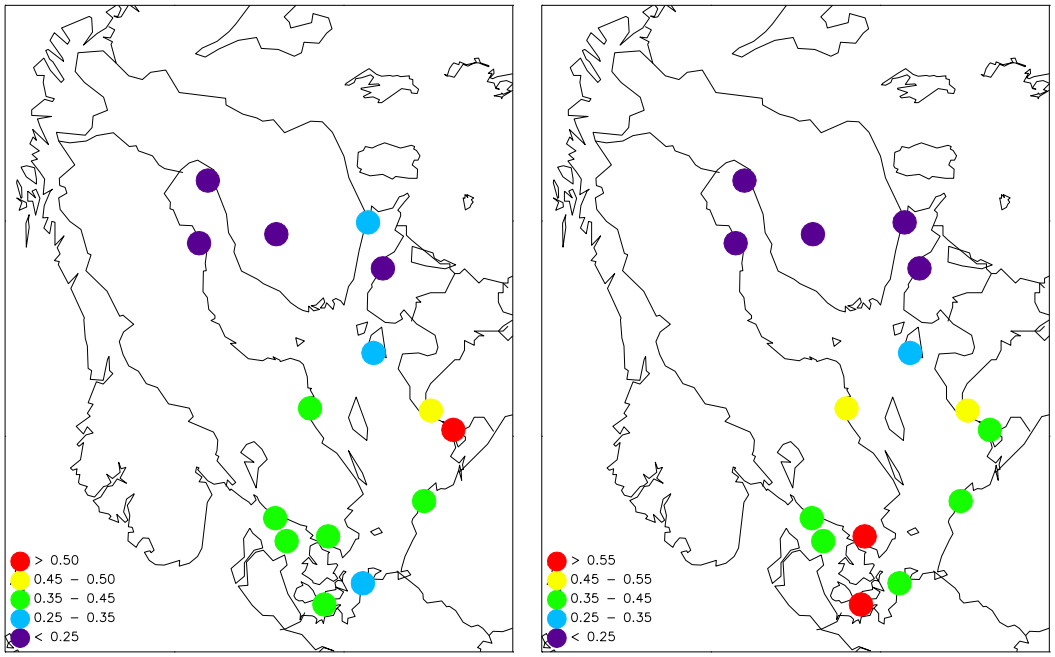


Figure 2.6. Concentrations of left: nitrate (NO_3^-), and right: ammonium (NH_4^+) in precipitation in 2011. Units: mg N/l.

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, and also a west-east gradient is seen. Lowest concentrations of ammonium were seen at EE09 and FI04 (0.12 and 0.14 mg N/L) and for nitrate at FI04, FI53 and SE53 and (0.20 – 0.23 mg N/L). The highest levels are found at DK05 and SE11 for ammonium (0.61 and 0.56 mg N/L) and LT15 and LV10 for nitrate (0.51 and 0.48 mg N/L). Figure 2.7 displays the station average monthly depositions of oxidized and reduced nitrogen across the regions given.

The seasonal patterns for the nitrogen components in precipitation are not as strong as for airborne components. This is due to the presence of the precipitation effect. However, it is higher deposition of ammonium in summer than winter, which is seen also for ammonium in air. 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.

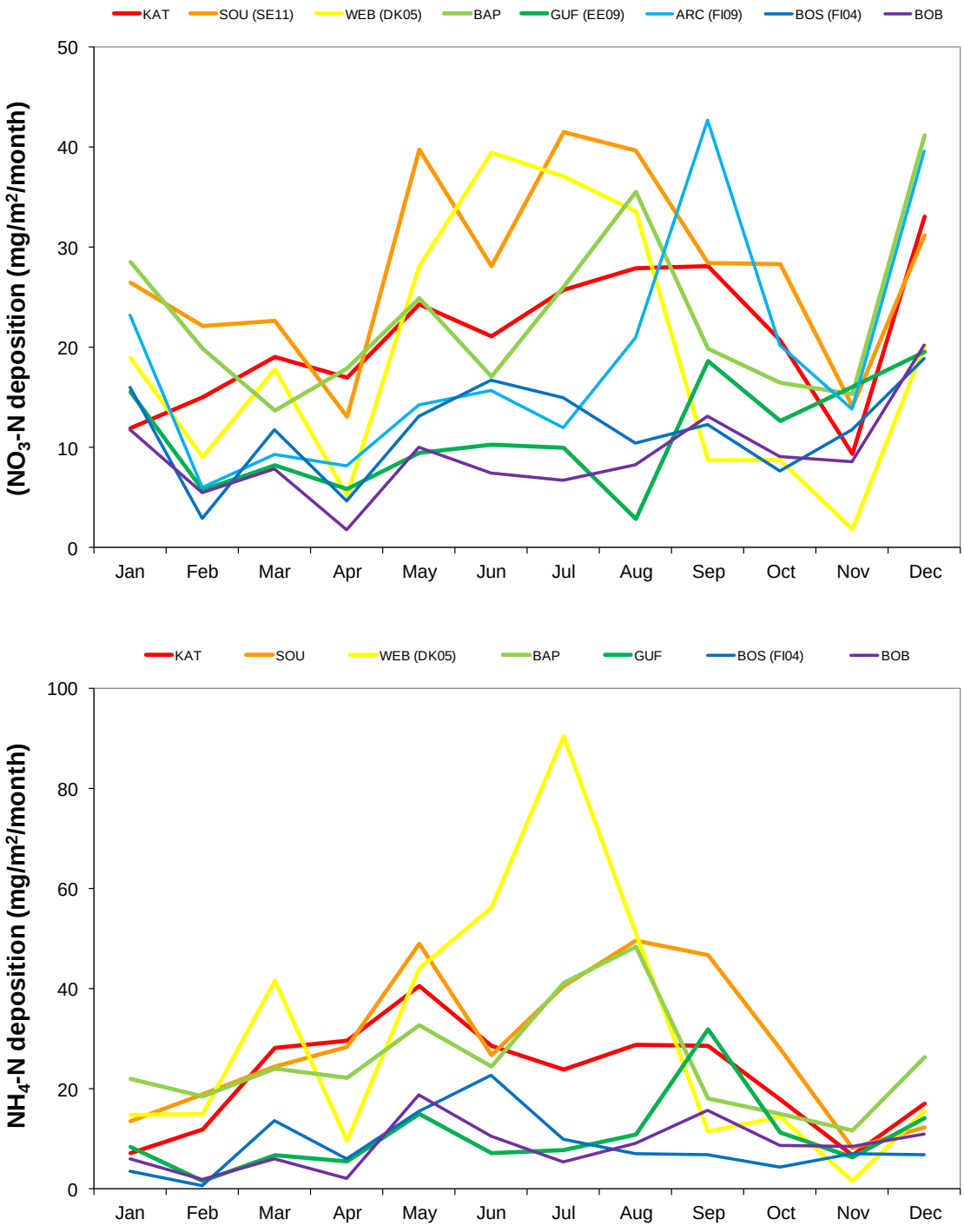


Figure 2.7. Monthly nitrogen depositions in 2011 averaged for the sub-basins. Top: nitrate (NO_3^-), and bottom: reduced nitrogen (NH_4^+).

2.4 Heavy metals in the air

Altogether twelve stations have delivered heavy metal data (cadmium, one less site for lead) in air. Only four sites have reported data for elemental Hg in air, and three of these sites were Swedish. Annual averages of Cd and Pb are presented in Figure 2.8. The lowest concentrations of Cd is seen at the Swedish site SE05 (0.008 ng/m^3) while the highest concentration was seen DK12 with 0.14 ng/m^3. For lead, the highest concentration was observed at DE09 with 4.5 ng/m^3; while the lowest level was at SE05 with 0.44 ng/m^3. For elemental mercury the concentrations ranged from 1.39 (SE05) to 1.64 (DE09) ng/m^3.

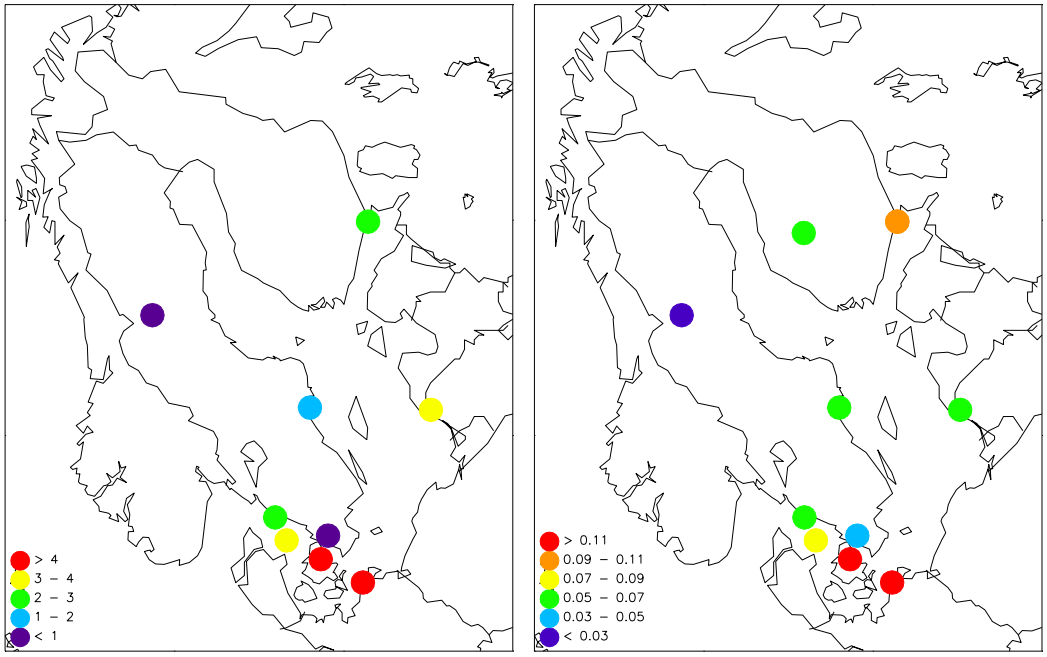


Figure 2.8. Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2011. Units: ng/m^3.

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). From this, it is to be observed that the temporal patterns for Cd and Pb show a winter maximum. This is probably due longer atmospheric residence time in winter and reduced vertical mixing.

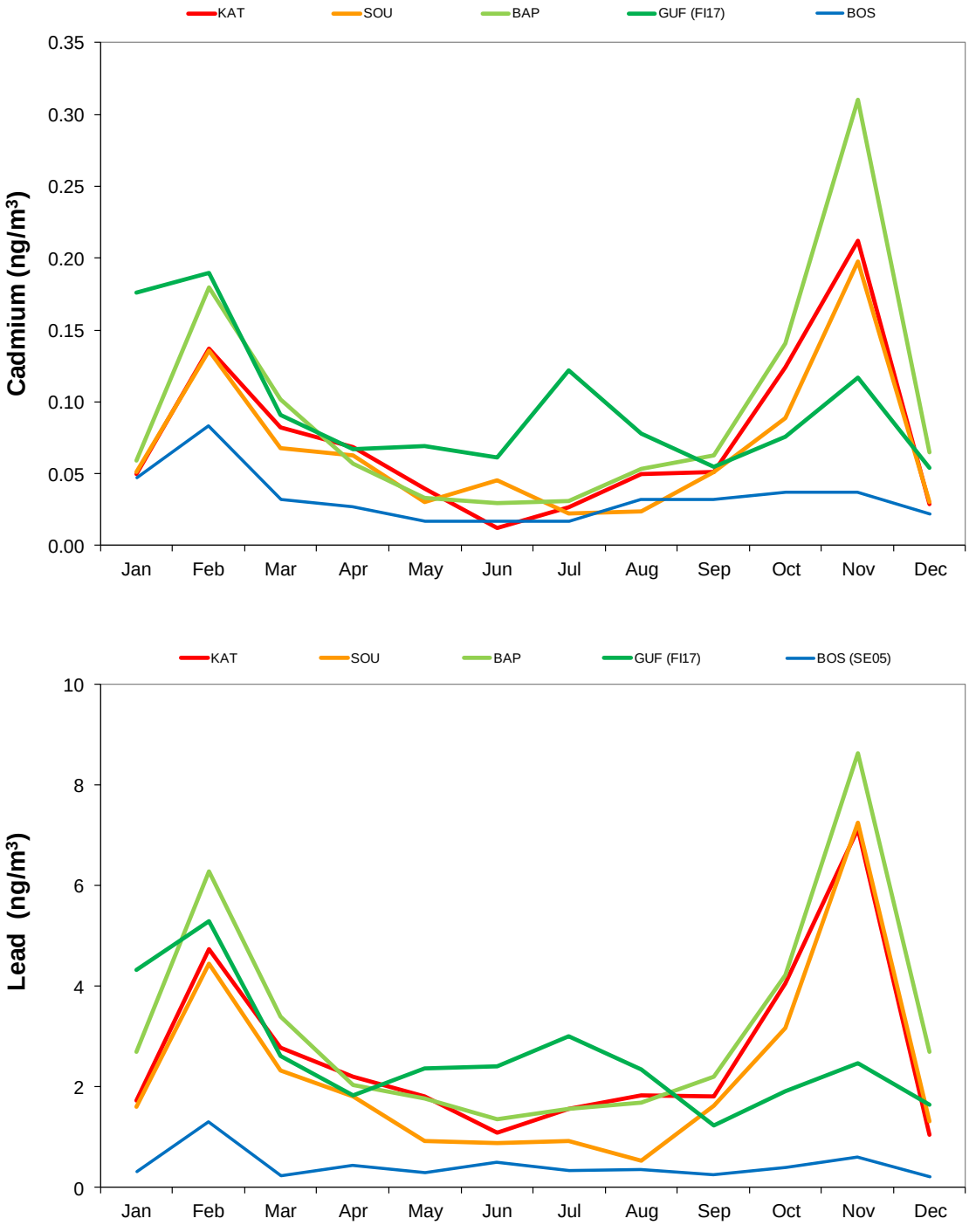


Figure 2.9. Monthly concentrations in air in 2011 averaged for the sub-basins: Top: cadmium, bottom: lead.

Hg concentrations at the four sites also show a weak winter maxima. August-October seems to be relatively low at the northern Swedish sites compared to the German site at Zingst. Figure 2.10.

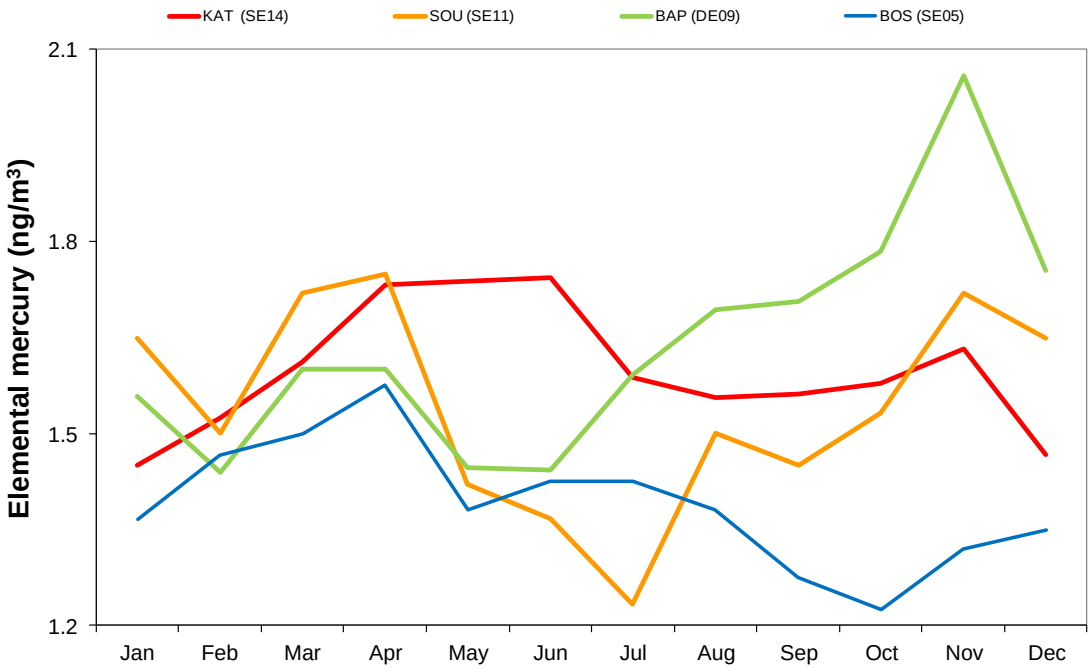


Figure 2.10. Monthly concentrations of Hg in air in 2011 for the four sites representing different the sub-basins.

2.5 Heavy metals in precipitation

Twelve stations have delivered data for Cd and Pb in precipitation, and six have delivered data for Hg in precipitation. 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. If we neglect the Estonian data where there are problems with the detection limit of the heavy metal measurements in precipitation, the lowest concentrations for both Cd and Pb in precipitation were reported for the Swedish site SE05 with 0.02 and 0.3 μg/l, respectively. The highest concentration of Cd was measured at SE11 with 0.13 μg/l, while the highest level of lead was seen at DK05 with 5.5 μg/l. For mercury in precipitation, the highest levels are seen in Latvia, but the detection limit for their analysis is very high and the highest level of the remaining sites is seen at SE11 with 9 ng/L and the lowest at FI17 with 5 ng/L

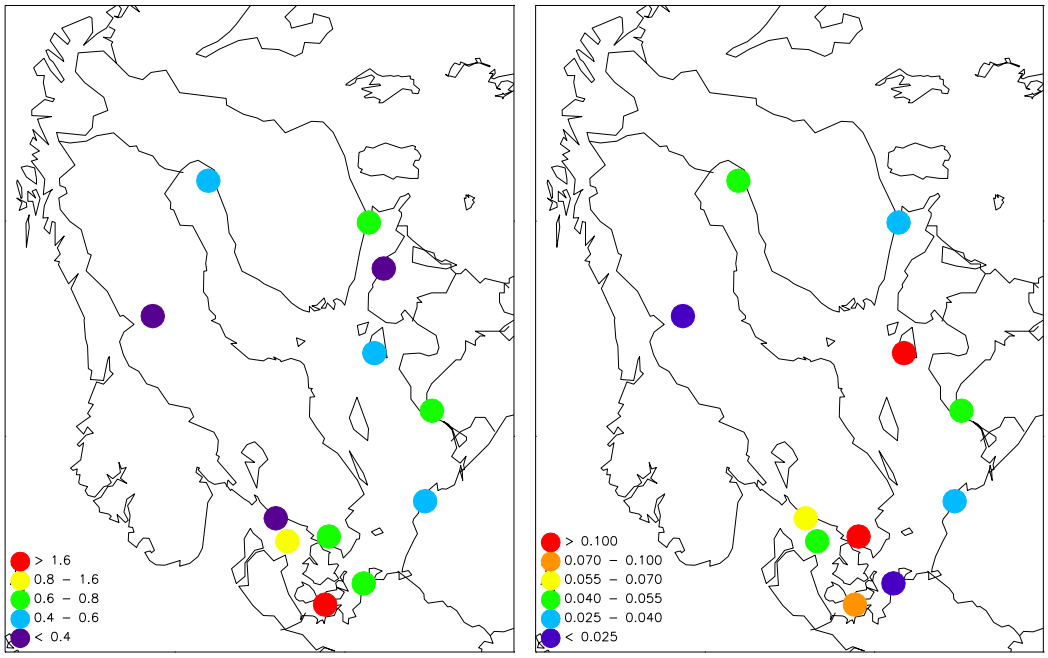


Figure 2.11. Concentrations of left: lead (Pb), right: cadmium (Cd) in precipitation in 2011. Units: µg/l.

2.6 Conclusions for Chapter 2

- Measurement data was reported from eighteen HELCOM stations in 2011, 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; and for many species an east west gradient.
- Many of the components measured in air show a winter maxima due to longer atmospheric residence time.
- The seasonal patterns in precipitation are not as strong as for airborne components. This is due to the presence of the precipitation effect. Though the highest deposition of reduced nitrogen is seen in summer due to enhanced agricultural activity