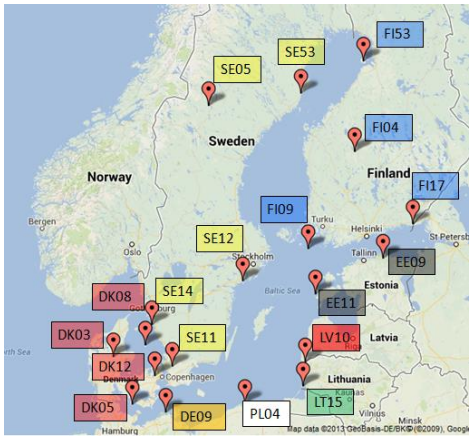
2. Observed Concentrations of Nitrogen, Cadmium, Lead and Mercury at HELCOM Stations in 2012

2.1 HELCOM measurement stations

Eight countries have submitted data from all together nineteen HELCOM stations for 2012 (Fig. 2.1), which is the same number as in 2011. 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 2012. In addition, the German site Zingst almost fulfil the requirements, but lack measurements of ammonia and nitric acid in air.

Fig 2.1. HELCOM sites with measurements of nitrogen, lead, cadmium and mercury in 2012



Sites			In precipitation					In air					
region	Site	Name	NO3	NH4	Cd	Pb	Hg	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	NH4	■	■	■
BAP	PL0004R	Leba	■	■	■	■		■	■	■	■		
BAP	LT0015R	Preila	■		■	■	■	■	■	■	■		
BAP	LV0010R	Rucava	■	■	■	■	■		NO3	NH4	■	■	
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 2012. 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 2012 data (Hjellbrekke, 2014; Aas and Nizzetto, 2014), and all 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 2012: The concentrations were 0.14, 0.03 and 0.12 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 Danish site Risö (DK12) with annual concentration means of 2.8 µgN/m^3 for NO_2), 1.86 µgN/m^3 for sum ammonium and 0.86 µgN/m^3 for sum nitrate. Data for particulate nitrate and ammonium from the German site (DE09) is not included in the figures below, because it is not comparable with the sums shown there, though the data are given in the annex. Details for monthly and annual concentrations for all the sites are found in the annex, table A.1.

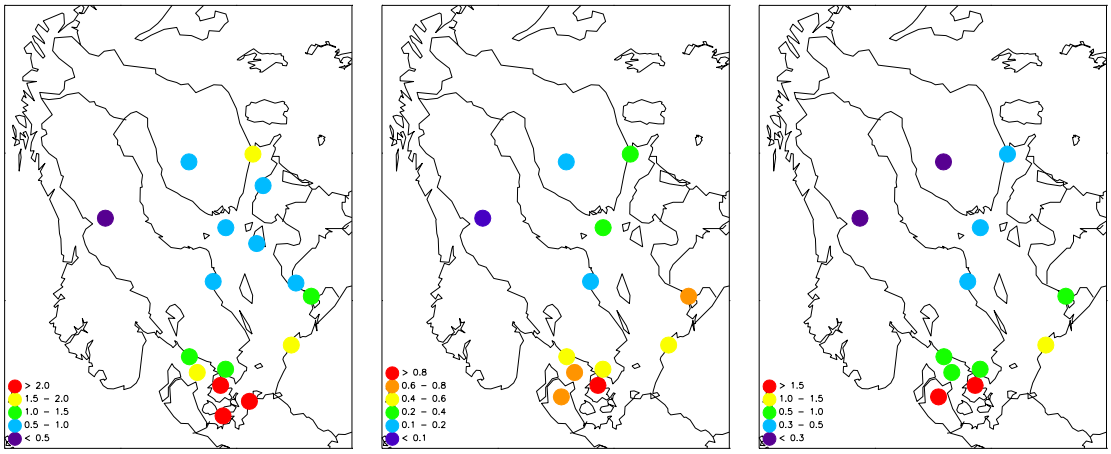


Figure 2.2. Concentrations of left: NO_2 in air, middle: total nitrate ($HNO_3+NO_3^-$) and right: total reduced nitrogen ($NH_3+NH_4^+$) in 2012 Unit: µg N/m^3.

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

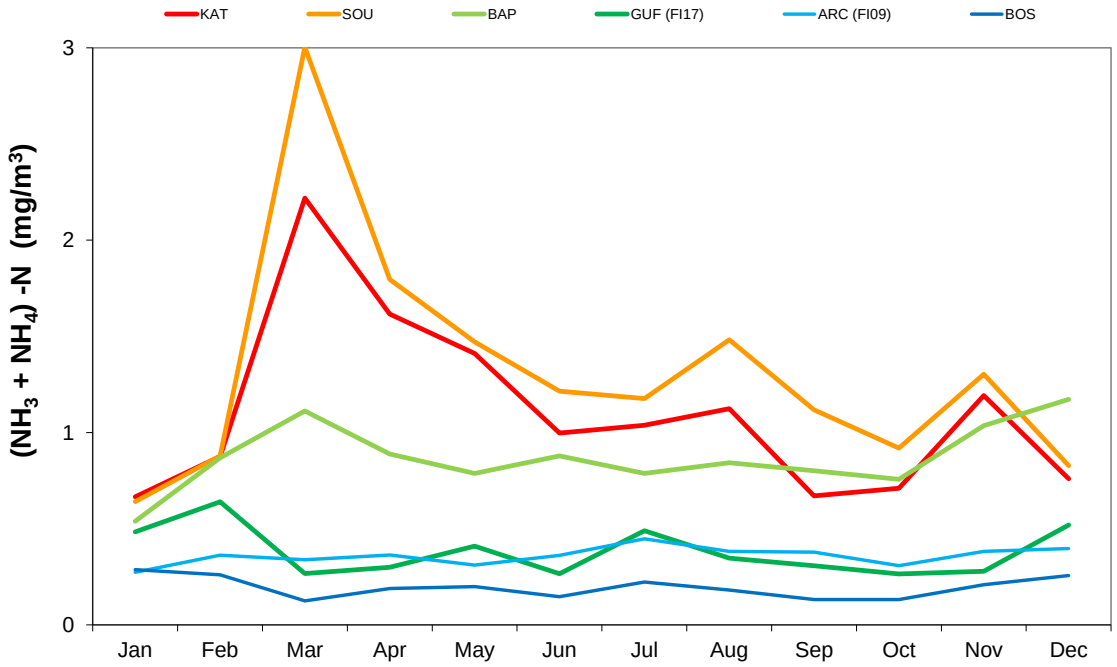


Figure 2.3. Monthly total reduced nitrogen (NH_3+NH_4) concentrations in the air in 2012

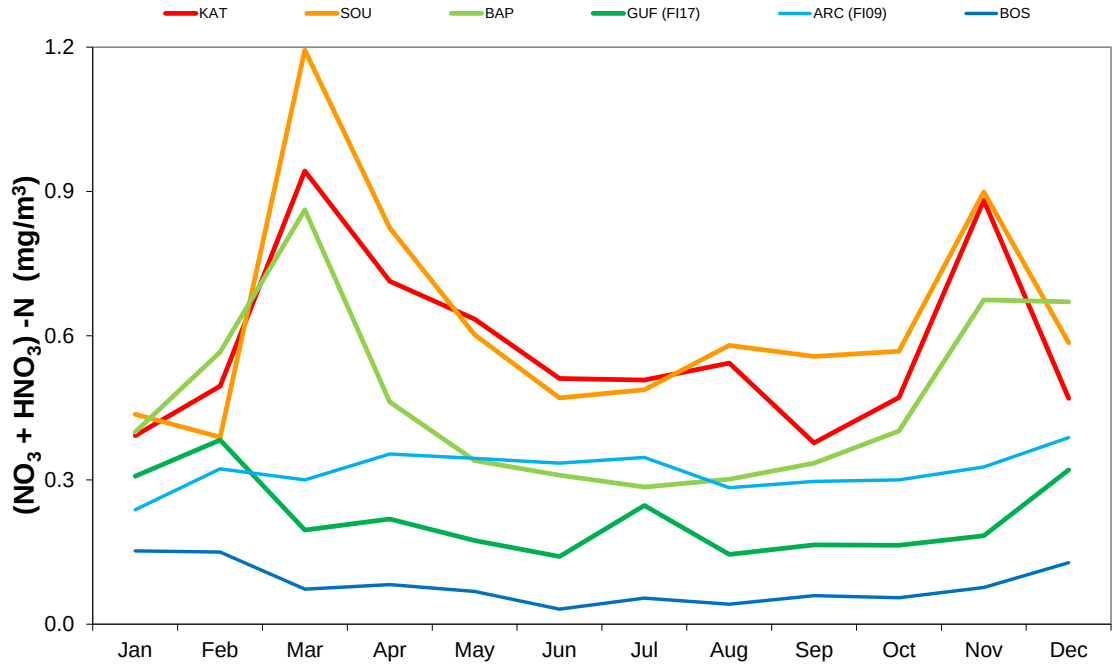


Figure 2.4. Monthly total oxidized nitrate (HNO_3+NO_3^-) concentrations in the air in 2012.

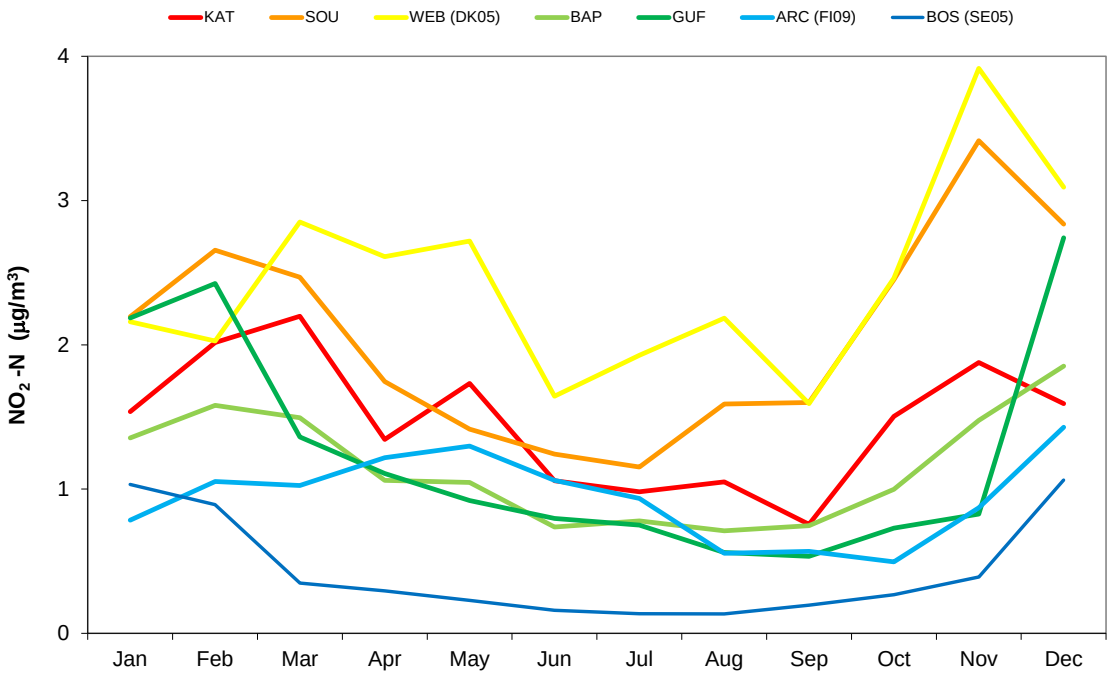


Figure 2.5. Monthly NO_2 concentrations in the air in 2012

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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.

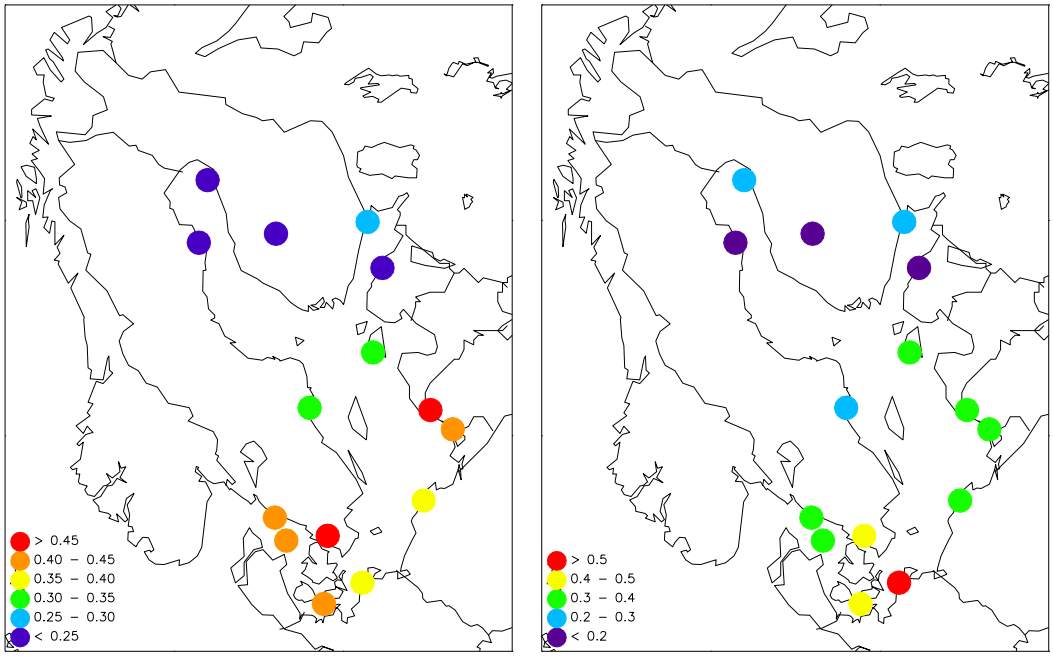

Figure 2.6. Concentrations of left: nitrate (NO_3^-), and right: ammonium (NH_4^+) in precipitation in 2012. Units: mg N/l.

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 for both nitrogen species were seen at FI04 and SE53 with (0.11 and 0.16 mg N/L) and (0.20 – 0.21 mg N/L) for nitrate and ammonium respectively. The highest levels are found at DE09 and DK05,SE11 for ammonium (0.61 and 0.49 mg N/L) and SE11 and LV10 for nitrate (0.50 and 0.48 mg N/L). Figure 2.7 displays the station average monthly depositions of oxidized and reduced nitrogen across the regions given.

There is no clear seasonal patterns for the nitrogen wet deposition as for airborne components. 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.

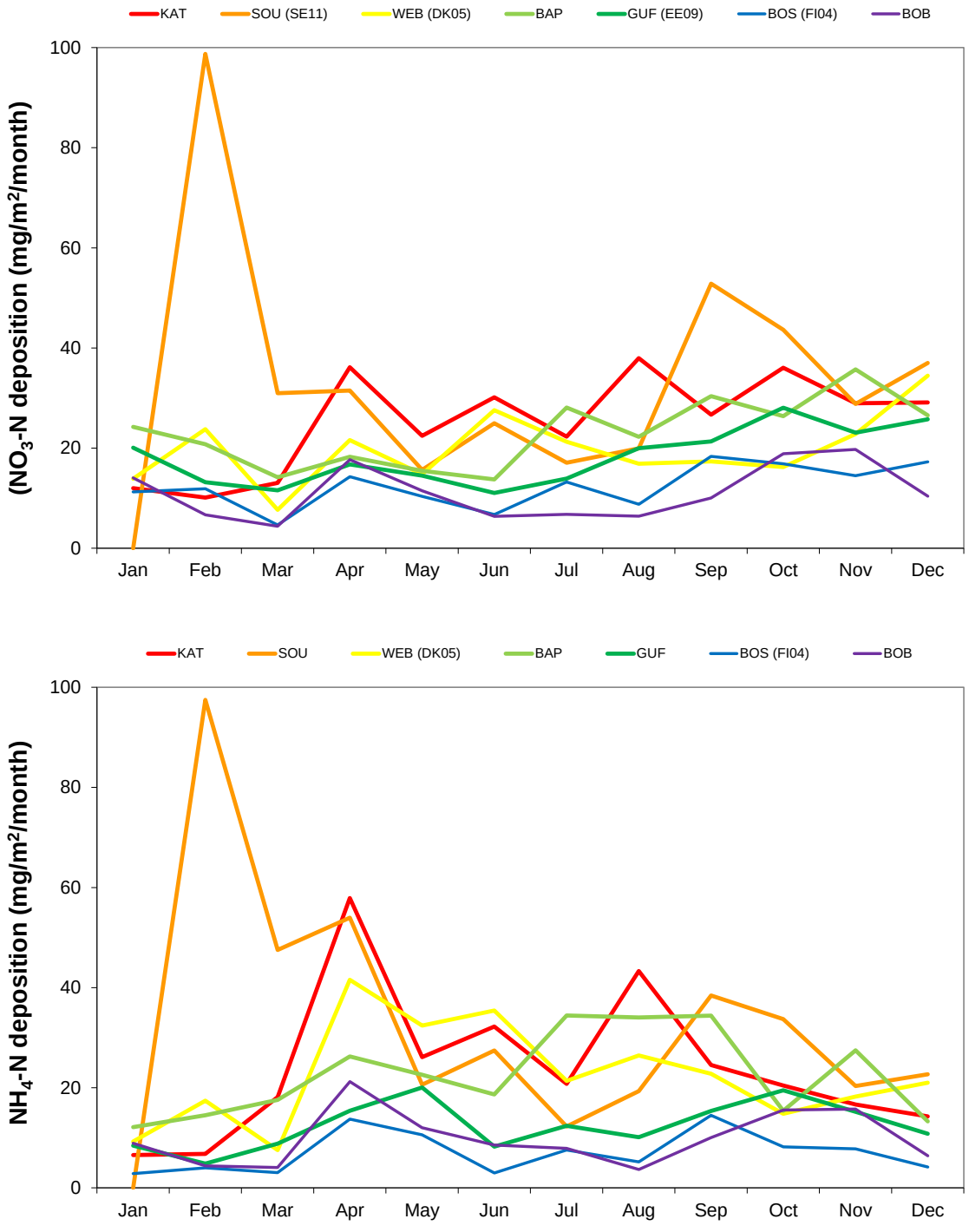

Figure 2.7. Monthly nitrogen depositions in 2012 averaged for the sub-basins. Top: nitrate (NO_3^-), and bottom: reduced nitrogen (NH_4^+).

2.4 Heavy metals in the air

Altogether twelve stations have delivered heavy metal data. 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 (0.009 ng/m^3) while the highest concentration was seen at FI17 with 0.11 ng/m^3. For lead, the highest concentrations were observed at DE09 and FI17 with 3.3 ng/m^3; while the lowest level was at SE05 with 0.28 ng/m^3. At the Latvian site LV10 there were only measurements seven of the months in 2012, so these data are not included in the maps below. However the pollution level are one of the the highest in this regions with 0.14 and 4.4 ng/m^3 respectively for cadmium and lead for the seven month with measurements. For elemental mercury the concentrations ranged from 1.25 (SE05) to 1.66 (DE09).

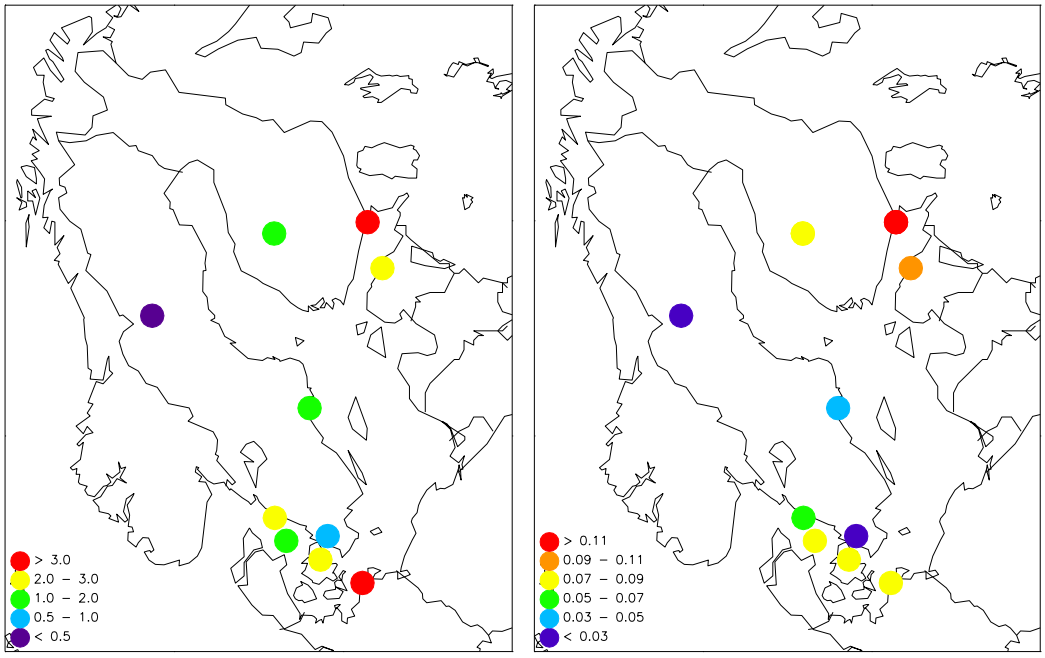

Figure 2.8. Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2012. Units: ng/m^3.

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.

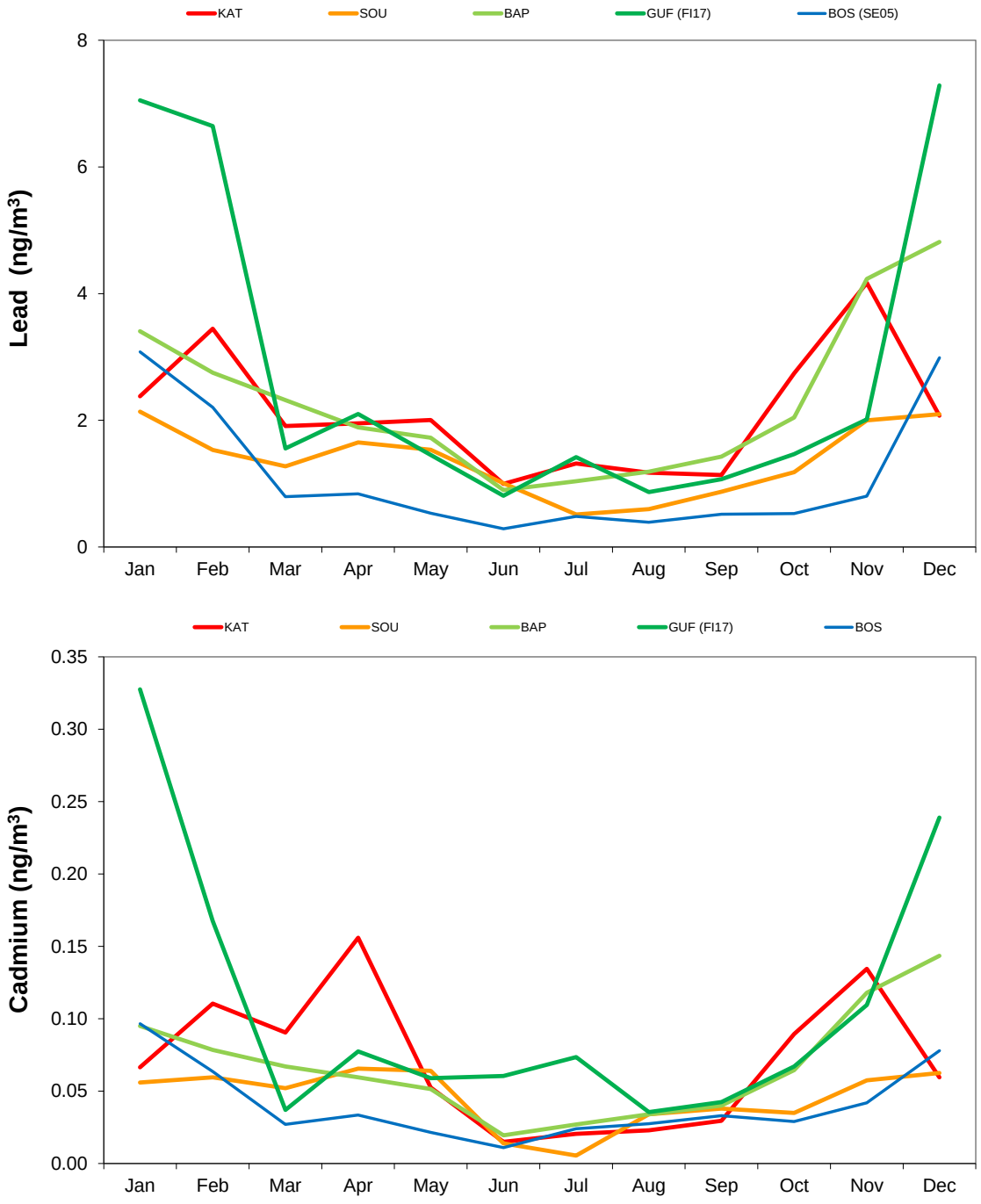

Figure 2.9. Monthly concentrations in air in 2012 averaged for the sub-basins: Top: cadmium, bottom: lead.

Hg concentrations at the four sites also show a weak winter maxima. September-October seems to be relatively low for several of the sites. Figure 2.10.

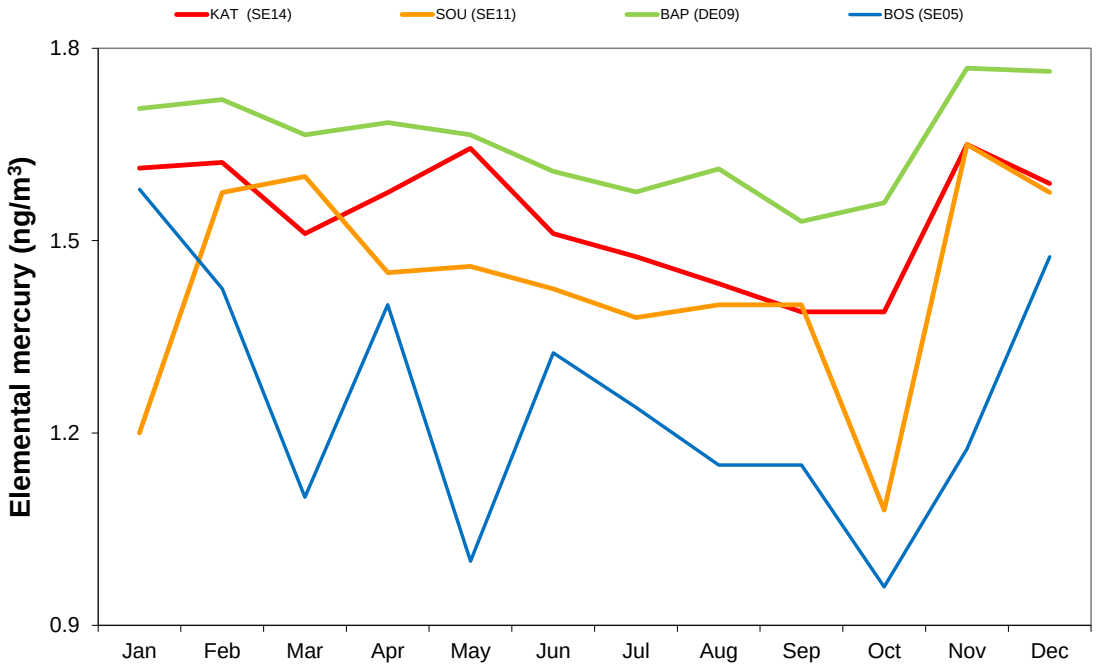

Figure 2.10. Monthly concentrations of Hg in air in 2012 for the four sites representing different the sub-basins.

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. The lowest concentrations were seen at the Estonian site, but here there are problems with the detection limit especially for Cd. Besides EE09, the lowest concentrations for both Cd and Pb in precipitation were reported for the Swedish site SE05 with 0.02 and 0.4 µg/l, respectively. For lead, similar low concentrations were seen at DE09, and for cadmium at LV10 and SE15. 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 5.2 µg/l. This is much higher concentration than the second highest level, which was observed at DK08 with 1.4 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 and SE14 with 11 ng/L and the lowest at FI17 with 4 ng/L.

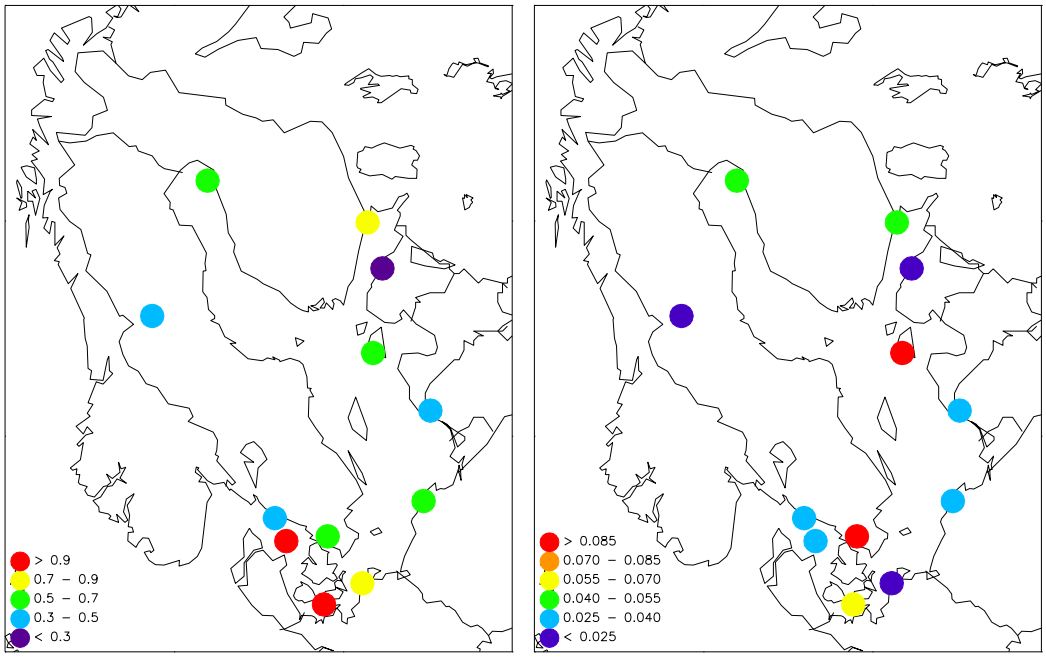

Figure 2.11. Concentrations of left: lead (Pb), right: cadmium (Cd) in precipitation in 2012. Units: µg/l.

2.6 Conclusions for Chapter 2

- Measurement data was reported from eighteen HELCOM stations in 2012, 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