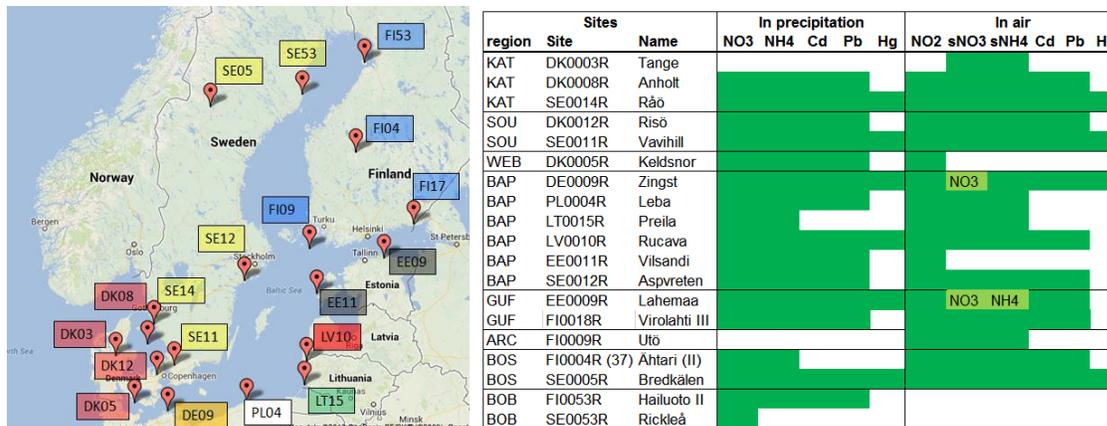


## 2. Observed Concentrations of Nitrogen, Cadmium, Lead and Mercury at HELCOM Stations in 2015

### 2.1 HELCOM measurement stations

Eight countries have submitted data from all together nineteen HELCOM stations for 2015 (Fig. 2.1), which is the same number as last years. 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, Bredkälen and Vavihill in Sweden are the only ones with data for all the components in air and precipitation for 2015. In addition, the German site Zingst almost fulfils the requirements, but lack measurements of nitric acid in air. Furthermore, four sites (DE09, LV10, SE12 and SE14) report data on various compounds of persistent organic pollutants (POPs). The POP data are only given in Annex A, and not discusses in this chapter, due to few sites with comparable methods and components.

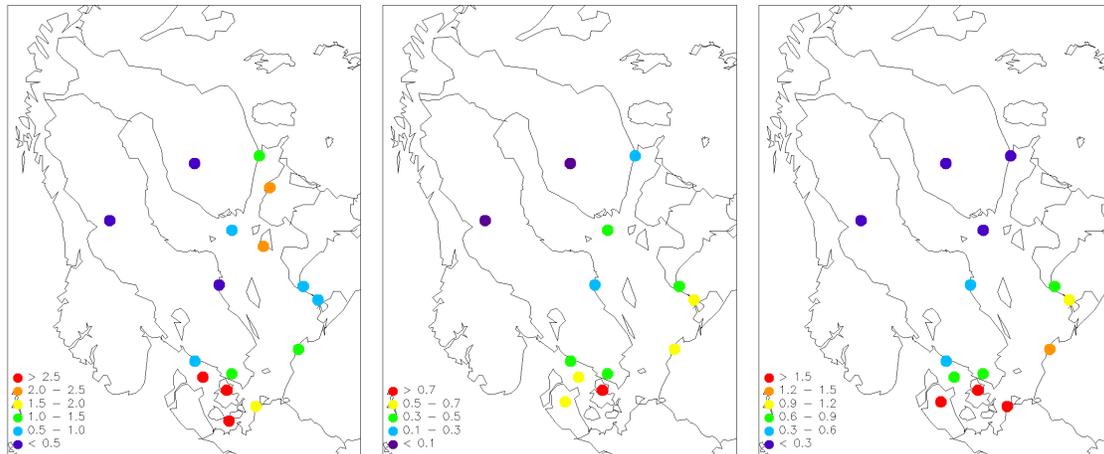
**Fig 2.1.** HELCOM sites with measurements of nitrogen, lead, cadmium and mercury in 2015



In this section, we provide a broad view of the patterns and levels evident in monitoring data from 2015. 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 2015 data (Hjellbrekke, 2017; Aas and Nizzetto, 2017), 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 sixteen stations have delivered data for nitrogen dioxide ( $\text{NO}_2$ ) while fifteen for oxidized nitrogen ( $\text{HNO}_3+\text{NO}_3^-$ ) and reduced nitrogen ( $\text{NH}_3+\text{NH}_4^+$ ). 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 2015. The concentrations were  $0.10$ ,  $0.03$  and  $0.09 \mu\text{g N/m}^3$  for respectively  $\text{NH}_3+\text{NH}_4^+$ ,  $\text{HNO}_3+\text{NO}_3^-$  and  $\text{NO}_2$  at this site. Highest concentrations of oxidized nitrogen,  $\text{NO}_2$  and  $\text{HNO}_3+\text{NO}_3^-$ , were found at Risö (DK12) with an annual concentration mean of  $7.6 \mu\text{gN/m}^3$  and  $0.84 \mu\text{gN/m}^3$ , respectively. While highest concentration of reduced nitrogen ( $\text{NH}_3+\text{NH}_4^+$ ) was seen at Zingst (DE09) with  $1.8 \mu\text{gN/m}^3$ . Note that the sum of nitrate and sum of ammonium are not measured at the Estonian sites, and at DE09, nitric acid is not included in the measurement programme. Details for monthly and annual concentrations for all the sites are found in the annex, table A.1.



**Figure 2.2.** Concentrations of left:  $\text{NO}_2$  in air, middle: total nitrate ( $\text{HNO}_3+\text{NO}_3^-$ ) and right: total reduced nitrogen ( $\text{NH}_3+\text{NH}_4^+$ ) in 2015 Unit:  $\mu\text{g N/m}^3$ .

There is a tendency of increasing concentrations from north to south and towards west. These 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  $\text{NH}_3+\text{NH}_4^+$ ,  $\text{HNO}_3+\text{NO}_3^-$  and  $\text{NO}_2$  observations across the different sub-basins

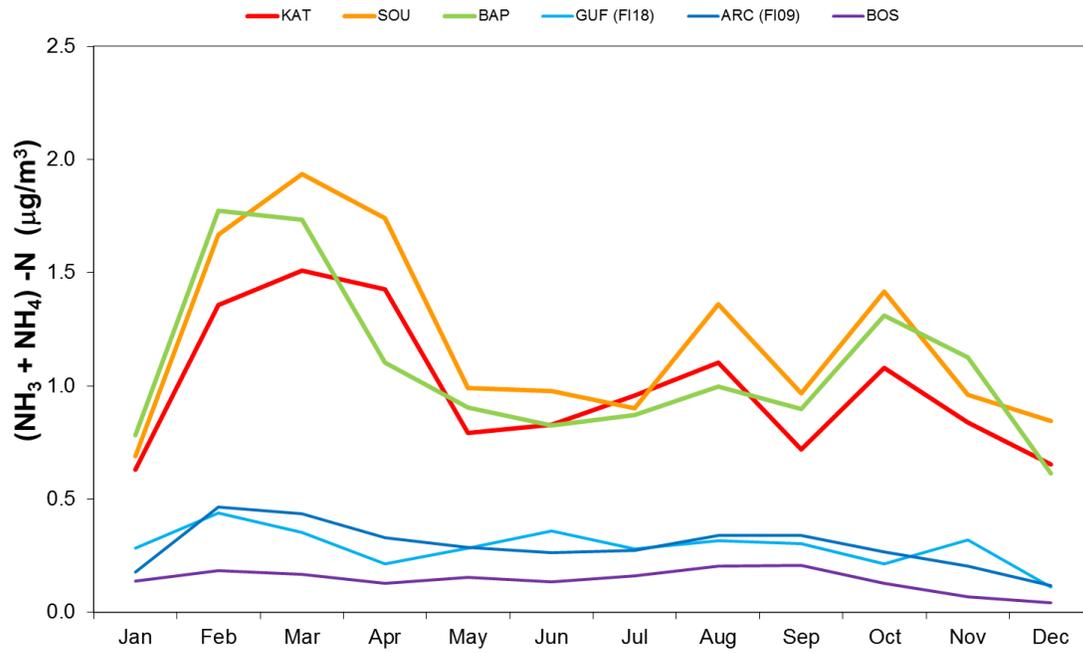


Figure 2.3. Monthly total reduced nitrogen ( $\text{NH}_3 + \text{NH}_4$ ) concentrations in the air in 2015.

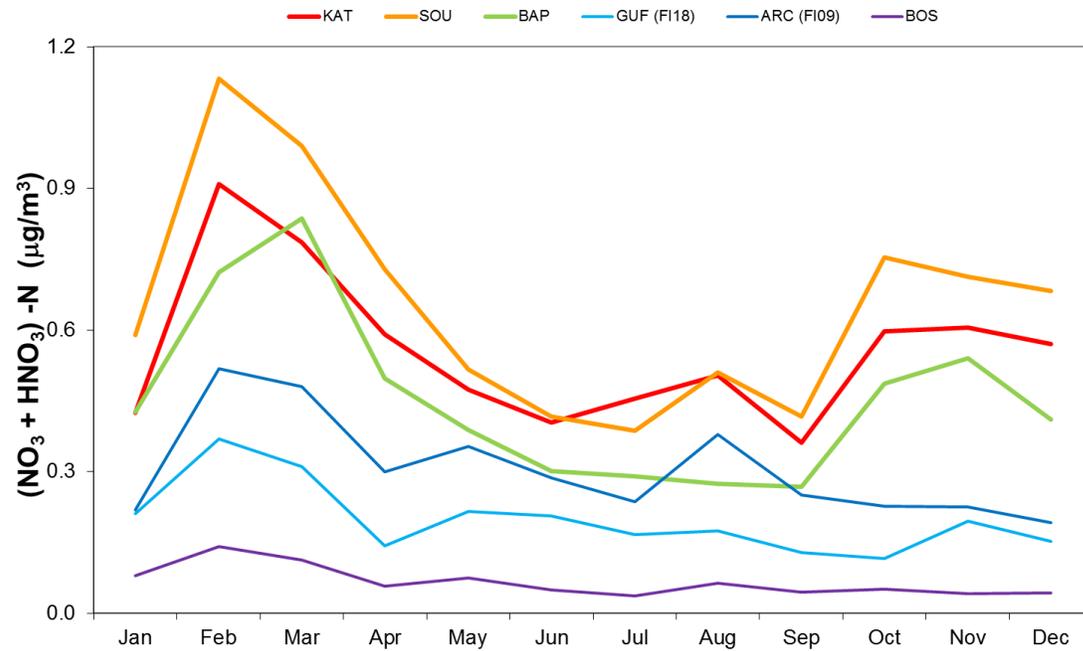
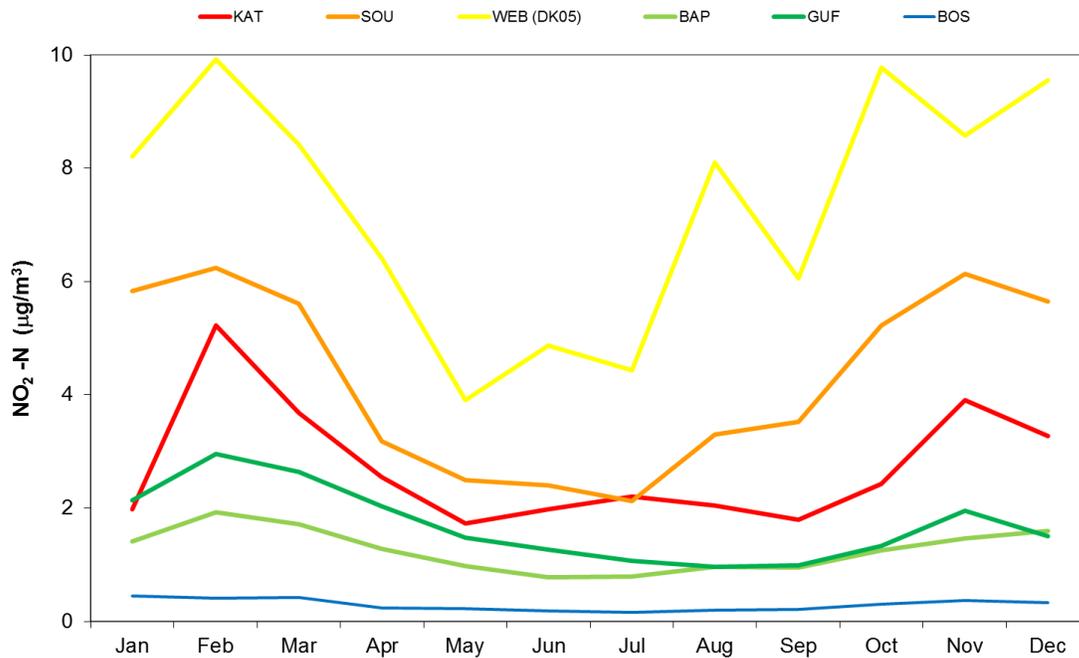


Figure 2.4. Monthly total oxidized nitrate ( $\text{HNO}_3 + \text{NO}_3^-$ ) concentrations in the air in 2015.



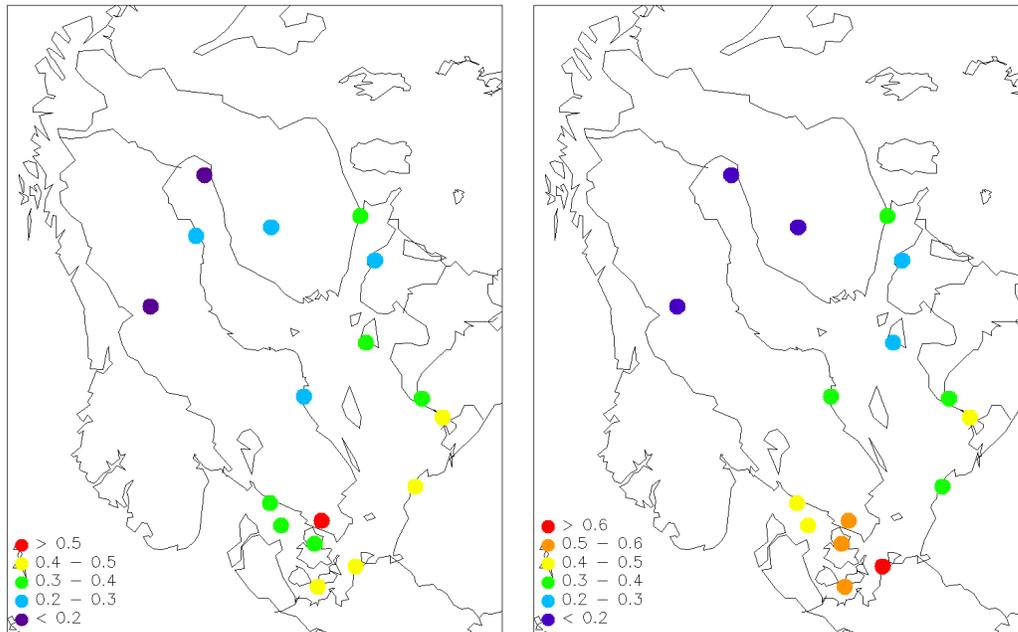
**Figure 2.5.** Monthly  $\text{NO}_2$  concentrations in the air in 2015.

Observations of the total reduced nitrogen ( $\text{NH}_3+\text{NH}_4^+$ ), show a seasonal pattern similar for most the sub-basins with highest concentrations in March when the fertilizing is most important. Agricultural activities (natural fertilizer) are the main source for  $\text{NH}_3+\text{NH}_4^+$ . But also high concentrations are seen in late autumn, maybe due to some fall fertilization, but more likely due to longer residence time of  $\text{NH}_4\text{NO}_3$  in the atmosphere (see below).

Total nitrate ( $\text{HNO}_3+\text{NO}_3^-$ ) concentration show elevated levels in the spring late autumn; and generally somewhat higher concentrations in winter than summer.  $\text{NO}_2$  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  $\text{NO}_2$  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

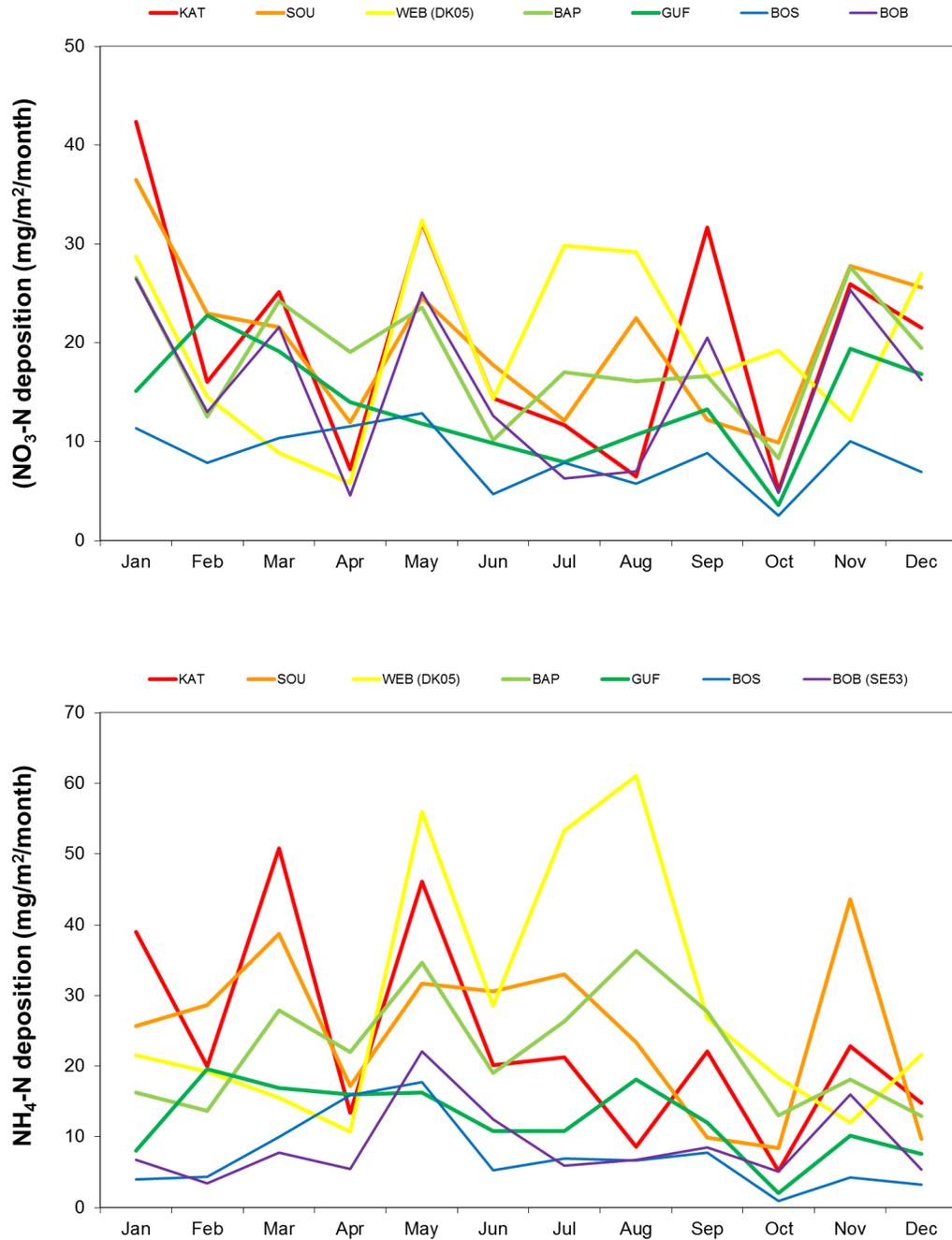
Altogether seventeen stations have delivered data for nitrate and sixteen for ammonium in precipitation. Stations from seven sub-basins have delivered data for ammonium and nitrate in precipitation. Annual averages of the two nitrogen species are presented in Figure 2.6.



**Figure 2.6.** Concentrations of left: nitrate ( $\text{NO}_3^-$ ), and right: ammonium ( $\text{NH}_4^+$ ) in precipitation in 2015. 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 SE05 with 0.10 and 0.12 mg N/L for nitrate and ammonium respectively. The highest levels of ammonium are found at DE09 with 0.99 mg N/L, and at SE11 for nitrate (0.56 mg N/L). Figure 2.7 displays the station average monthly depositions of oxidized and reduced nitrogen across the regions given.

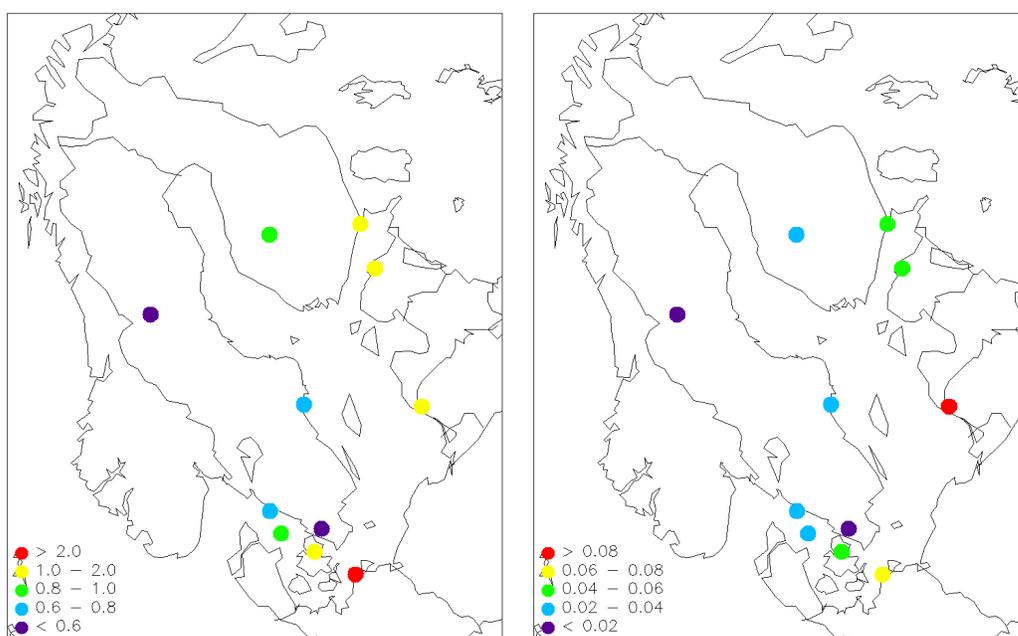
There is no clear seasonal patterns for the nitrogen wet deposition as for airborne components. The spatial pattern persists, however, with clearly decreasing depositions with progression northwards. For example, the northern regions typically receive half the deposition of reduced nitrogen supplied to southern areas.



**Figure 2.7.** Monthly nitrogen depositions in 2015 averaged for the sub-basins. Top: nitrate ( $\text{NO}_3^-$ ), and bottom: reduced nitrogen ( $\text{NH}_4^+$ ).

## 2.4 Heavy metals in the air

Altogether eleven stations have delivered heavy metal data 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 cadmium and lead were seen at the Swedish sites SE05 (0.009 and 0.27  $\text{ng}/\text{m}^3$  respectively) while the highest concentration of cadmium was seen at LV10 with 0.12  $\text{ng}/\text{m}^3$ . For lead, the highest concentration was observed at DE09 with 2.51  $\text{ng}/\text{m}^3$ . For elemental mercury the concentrations ranged from 1.36 (SE05) to 1.64 (DE09).



**Figure 2.8.** Concentrations of left: lead (Pb) and right: cadmium (Cd) in aerosol in air in 2015. Units:  $\text{ng}/\text{m}^3$ .

There are insufficient stations to reasonably represent regional patterns; hence, the station data itself is used here for some of the regions (Fig. 2.9) and showing the regional pattern similar to the maps (Figure 2.8). Most of the sites show a winter maximum for Cd and Pb. This is probably due longer atmospheric residence time in winter and reduced vertical mixing.

Hg concentrations at the four sites have no clear seasonal pattern, though a tendency for a weak winter maxima, Figure 2.10.

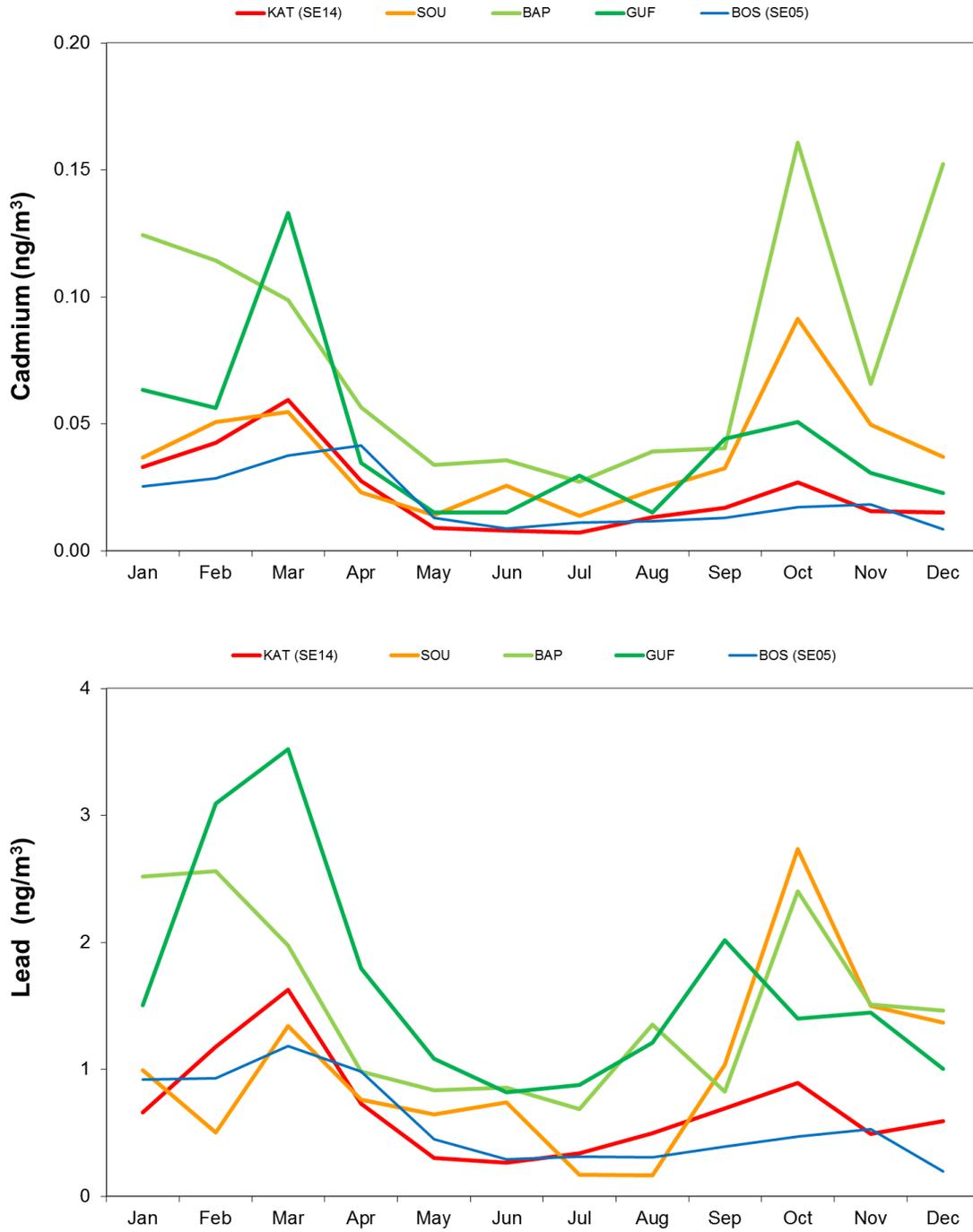
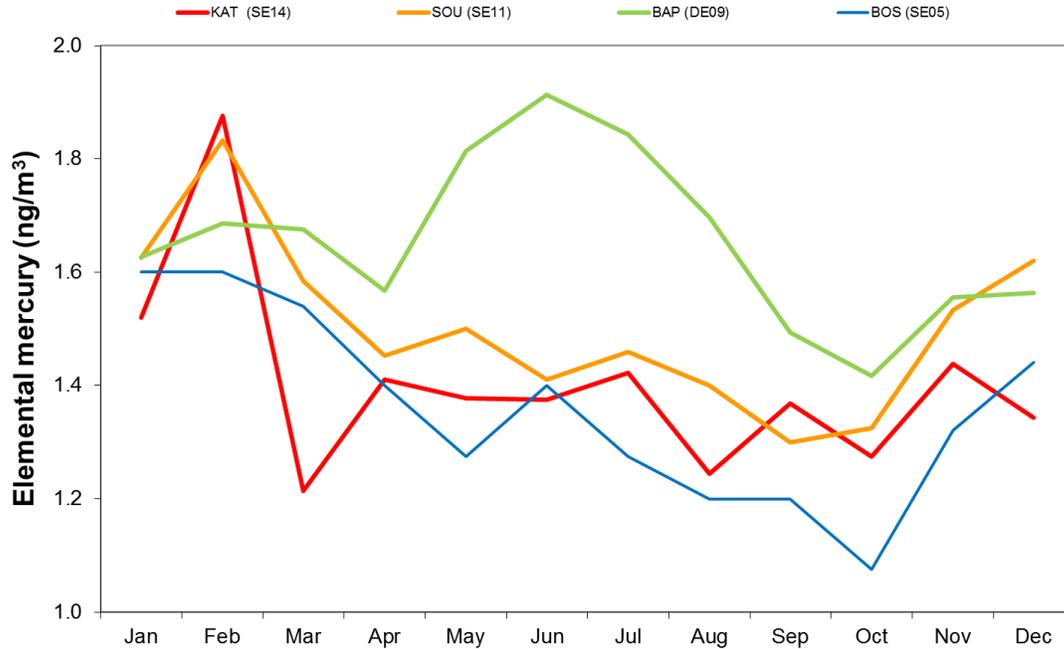


Figure 2.9. Monthly concentrations in air in 2015 averaged for the sub-basins: Top: cadmium,

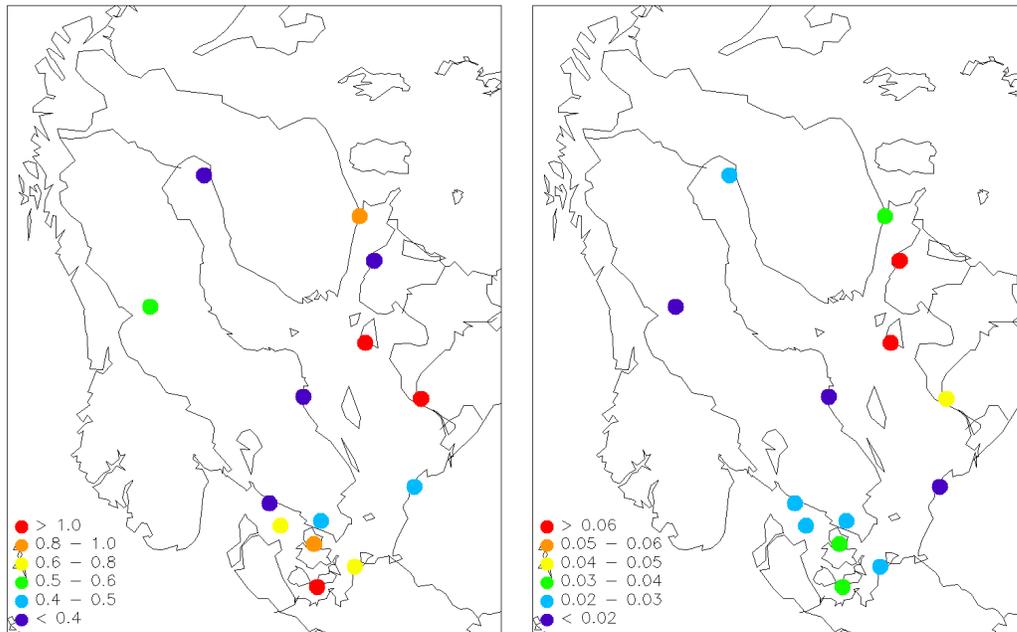
bottom: lead.



**Figure 2.10.** Monthly concentrations of Hg in air in 2015 for the four sites representing different the sub-basins.

## 2.5 Heavy metals in precipitation

Fourteen 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 in cadmium were seen at PL04 and SE05 with 0.019  $\mu\text{g/l}$ . The highest concentration was seen at EE011 with 0.10  $\mu\text{g/l}$ . The highest concentration of lead was measured at DK05 with 2.5  $\mu\text{g/l}$ , while SE12 and FI53 show the lowest level with 0.3  $\mu\text{g/l}$ . For mercury in precipitation, the highest levels are seen LV10 with 10.6 ng/L and the lowest at SE05 with 4.9 ng/L.



**Figure 2.11.** Concentrations of left: lead (Pb), right: cadmium (Cd) in precipitation in 2015. Units: µg/l.

## 2.6 Conclusions for Chapter 2

- Measurement data was reported from nineteen HELCOM stations in 2015, 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