

BALTIC SEA ENVIRONMENT PROCEEDINGS

No. 32

DEPOSITION OF AIRBORNE POLLUTANTS TO THE BALTIC SEA AREA 1983-1985 AND 1986



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DEPOSITION OF AIRBORNE POLLUTANTS TO THE BALTIC SEA AREA
1983-1985 AND 1986

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PREFACE

Within the framework of the Baltic Marine Environment Protection Commission - Helsinki Commission, monitoring data on airborne pollution are collected according to the programme adopted by the Commission. Sweden has acted as Lead Country for the preparation of evaluation reports based on data for 1983-1986 provided by all Baltic Sea States (Denmark, Finland, German Democratic Republic, Federal Republic of Germany, Poland, Sweden and Union of Soviet Socialist Republics). The first report, **containig** the evaluation of data for 1983-1985 has been available since 1988 as a preprint copy suitable for citing. The draft reports have been considered by the meetings of the Group of Experts on Airborne Pollution of the Baltic Sea Area (EGAP) of the Baltic Marine Environment Protection Commission - Helsinki Commission and they have been finally edited by Swedish experts for the purpose of the Helsinki Commission.

SUMMARY

The annual deposition of airborne nitrogen and heavy metals on the Baltic Sea Area has been estimated.

Two deposition estimates are presented, one for the period 1983 - 1985 and one for 1986.

The estimates are based on data on concentrations of pollutants in air and precipitation reported to the HELCOM database from approximately 25 coastal stations situated in the Baltic Sea Area.

Wet deposition estimates are based on reported concentrations and the climatological precipitation amount.

Dry deposition is estimated from data on concentrations in air using the concept of dry deposition velocity.

The two estimates presented here have to be treated as fairly crude, as they are based on data series with large gaps. The deposition estimate for 1986 is slightly more reliable than the one for 1983 - 1985 since it is based on a more complete data set.

The deposition of nitrogen 1986 has been estimated at 270,000 - 630,000 tonnes. The deposition rate in the southern part of the Baltic was substantially higher than the rate in the northern part (Belt Sea & Kattegatt $\approx 1.5 \text{ g N/m}^2, \text{yr}$; Bothnian Bay $\approx 0.6 \text{ g N/m}^2, \text{yr}$).

The annual deposition of nitrogen to the Baltic Sea Area estimated for 1983 -1985 is within the range given for 1986.

The annual deposition of heavy metals was 1986 estimated at : cadmium 35 tonnes, copper 470 tonnes, lead 1560 tonnes and zinc 3400 tonnes.

The annual deposition of heavy metals estimated for 1986 is a bit lower than the estimate for 1983 - 1985. The lower deposition values for zinc, cadmium and copper are probably explained by a somewhat different estimation method. However, the decrease of lead deposition (1985 2300, 1986 1560 tonnes) could also reflect the reduced use of lead additives in petrol in Europe.

These estimates should be used with great caution, because there are differences in the reliability in the data used. Additionally, a better understanding of the exchange processes between the sea and the atmosphere, is needed to give a greater degree of certainty. However, there has been an obvious need for an evaluation of the load of airborne pollutants to the Baltic Sea. Therefore, this estimation, however rough it is, should be seen as a first step towards further, more reliable evaluations.

COMMENTS ON METHODOLOGY

Two independent approaches to **evaluate** the deposition of airborne pollutants to the open sea are measurements and modeling. The two methods have both their merits and shortcomings.

The accuracy of the deposition estimates based on modeling, depends very much on the quality of emission inventories. The models ability to correctly calculate the long-range transport (meteorology, **chemical transformations** and deposition processes) are also **crucial**. An advantage is that a monitoring network for measurements of concentrations in air and precipitation normally not is needed.

Deposition estimates based on measurements of airborne pollutants and precipitation amount at coastal and island stations, assumes that the observations from the landbased stations are representative for the situation at the open sea. At present, little information is available to justify or discard this assumption. Additionally, the accuracy of the data generally is not known. An obvious advantage is that no special knowledge about emissions and long-range transport is required.

The different methods to estimate the deposition can both give valuable information. They shall not be regarded as competitors, but as complements. Further developments of the two independent approaches, will make it possible to get more precise estimates of the **load** of airborne pollutants to the Baltic Sea Area.

DEPOSITION ESTIMATES TO THE BALTIC SEA AREA BASED ON REPORTED DATA FOR 1983 - 85.

By: Rolf Soderlund and Hans Areskoug

ABSTRACT

The deposition to the Baltic Sea area of nitrogen, phosphorous and heavy **metals is estimated.**

The estimates are based on data on atmospheric abundance of air pollutants and concentration in precipitation, submitted to the HELCOM secretariat **for** the years 1983-1985.

Precipitation data were when possible analysed for a regional pattern and a typical concentration value was assigned for each of the sub-basins of the Baltic Sea area. Deposition calculations were based on these concentrations and the climatological precipitation amounts.

Dry deposition was estimated from data on gaseous compounds and atmospheric aerosols using the concept of dry deposition velocity.

The annual deposition of nitrogen was estimated to approximately 400.000 tons. Substantially higher deposition levels were estimated in the southern part of the region (Belt Sea 1.2 **gN/m²,yr**) than in the northern parts (Bothnian Bay 0.4 **gN/m²,yr**).

The annual deposition of phosphorous was estimated to 6 000 tons.

The annual deposition of heavy metals was tentatively estimated to : cadmium 60 tons, copper 500 tons, lead 2300 tons and zinc 5200 tons.

These estimates have to be considered as fairly crude, because the reported data are insufficient to be used for a detailed analysis of the deposition pattern over the Baltic. More data on precipitation amount, chemical composition of air and precipitation, as well as better understanding of the exchange processes between the atmosphere and the sea, are needed to decrease the uncertainty.

The estimates presented here are comparable to previous estimates, mainly because the same methods have been used when calculating the deposition. The deposition estimates in this report could be considered slightly more reliable than previous ones since they are based on data from more sites around the Baltic than before.

INTRODUCTION

The purpose of this report is to use the data reported to HELCOM to estimate the deposition of airborne pollutants to the Baltic.

The report is by no means a complete review of all information available with respect to deposition.

The data have been used to tentatively estimate the annual deposition of nitrogen, phosphorous and heavy metals to the Baltic. The original intention **was** also to evaluate the temporal and spatial correlation in this region using the data reported to the HELCOM secretariat. Due to lack of data and data series with large gaps, this was not possible.

THE DATA

Data on precipitation and/or air are reported from 5 sites 1983, 20 1984 and 25 1985.

The location of the sites are shown in figure 1.

The parameters and number of data reported from each station are given in annex 1.

Most of the reported data are data on concentration of **macroconstituents** in precipitation. Data on heavy metals in precipitation are very few; 1983 from 2 sites (a few monthly averages); 1984 from 5 sites and 1985 from 6 sites.

Data on nitrogen **compounds** in gases and aerosols are reported from 3 sites 1983, 5 sites 1984 and 8 sites 1985.

The quality assurance for the reported data with respect to laboratory performance are considered to be taken care of within the EMEP and/or WMO framework.

In some cases the relation of the reported data to sulphur was used as a primitive quality control test.

All reported data on nitrogen compounds and heavy metals were used in the estimation of the deposition with the exception of the dry fallout data reported from Finland.

DEPOSITION OF NITROGEN COMPOUNDS

Wet deposition

The major amount of the reported data refer to nitrogen compounds. The western and northern parts of the region are better covered than the others (see table 1 and figure 1). At each station the monthly mean concentration for the period 1983 - 85 (precipitation weighted mean) of nitrate and ammonium was calculated. The average concentration of nitrogen in precipitation was then calculated as the sum of the monthly mean concentrations of nitrate and ammonium. The averages obtained in this way are shown in figure 2. Since not all stations have reported data for the whole period these averages are uncertain for some stations.

Data on total nitrogen (organic and inorganic forms of nitrogen), are reported from some Finnish stations for 1984. **Söderlund** (1983) found from measurements in Sweden that the total nitrogen content in precipitation was approximately 1.5 times the inorganic content. No such systematic difference was obvious from the data reported from Finland, which reports on both inorganic and total nitrogen at nearby sites. The concentration of total nitrogen is slightly higher than the concentration of inorganic forms at comparable latitudes, but the difference is by no means as large as in the findings by **Söderlund (loc. cit.)**. Hence, no correction was made for organic nitrogen, when the deposition was calculated.

Each sub-basin of the Baltic Sea area was assigned a typical con-

centration value based on data from stations surrounding the sub-basin. The averages for the stations SF Ylimarkku, SF Jomala, SU Lahemaa and SE **Hoburg** differ markedly compared with averages from nearby stations and have not been used when assigning the concentration values.

Deposition was then calculated by using the climatological precipitation amount (Rohde et al,1980) for each sub-basin. The deposition values are given in table 2.

Nitrogen is the only constituent for which we have enough information to be able to point out systematic geographical differences. The concentration in precipitation is higher to the south and since the annual precipitation also is higher to the south the deposition is substantially higher there.

The deposition data in table 2 are based on the assumption that observations on the amount and chemical content of precipitation at the landbased stations are representative for the situation over the Baltic. No information was available to either justify or discard this assumption.

Dry deposition of gases

The dry deposition of ammonia was considered insignificant as only a very small amount of the total ammonium content is present in the gaseous forms (**Ferm,1986**) which likely is in equilibrium with the sea water according to Henry's law. The remainder of the ammonia is in particulate form. (Ayers et. al,1984).

For nitrogen dioxide the seasonal variation (figure 3) could reflect a low affinity to the sea water. We observe the highest concentrations in the cold periods, when we expect high instability of the air layers near the sea surface. If nitrogen dioxide has a high affinity to sea water, we will find the lowest concentrations during these periods. As this is not the case we

belive that only minor amounts of nitrogen dioxide are deposited to the Baltic.

Gaseous nitric acid, on the other hand, has a very high affinity to water and thus is expected to be readily absorbed. The available information on the abundance of nitric acid in the air in the Baltic region is meager. According to Ferm (1984, a) the annual mean concentration at the **Rörvik** station is $0.35 \mu\text{gN}/\text{m}^3$ for nitric acid and $0.94 \mu\text{gN}/\text{m}^3$ for total nitrates. This indicates that approximately 40% of the combined nitrates are in gaseous form. A total nitrate concentration of $0.4 \mu\text{gN}/\text{m}^3$ is reported for the period **1984/85** from Aspvreten (see table 3), indicating lower concentrations in the air in this part of the Baltic.

The deposition of gaseous nitric acid is calculated by assuming that 40% of the total nitrates are gaseous nitric acid and that data reported from Aspvreten are applicable over most of the Baltic. For the Belt Sea and Kattegatt data reported by Ferm are used. The deposition velocities used are 1.0 cm/s for the winter period (**oct.-apr.**) and 0.5 cm/s for the rest of the year. The dry deposition estimates for nitrates reported in table 4 include the contribution from particulate nitrate, see below.

The calculated deposition for nitrate would increase if there was a rapid transfer of nitric acid from the aerosol phase to the gaseous phase or if the deposition velocities are higher. The deposition would decrease if a larger fraction of the total nitrates was in the particulate form. This follows from the higher deposition velocities for gaseous forms compared with particulate forms. At present, little is known about air-sea exchange processes.

Dry deposition of aerosols

Particulate ammonium and nitrates can be trapped at the sea surface. From the work of Slinn & Slinn (1981), we selected a dry deposition velocity for the particulate ammonium and nitrate of

1 mm/s. By using reported data (table 3) and assuming that 60% of the total nitrates are in the particulate form and that data reported from Rorvik are applicable for the Belt Sea and Kattegatt and data from Aspvreten for the rest of the Baltic, we can roughly estimate the dry deposition of nitrate. Particulate ammonium concentrations are assigned to the different sub-basins by using data from table 3.

The total dry deposition (gases and aerosols) for the different sub-basins of the Baltic are given in table 4.

A summary of wet and dry deposition are given in table 5.

DEPOSITION OF PHOSPHOROUS COMPOUNDS

Total phosphorous in precipitation was reported from 10 stations and only for 1984. The coverage of the stations was fairly uneven, see table 6 and figure 1.

It seems as if the data reported from Sweden are considerably lower than those reported from Finland. No explanation is offered for this.

A tentative estimate of wet deposition can be made by assigning the mean concentration reported to the mean annual climatological precipitation for the Baltic (616 mm). This estimate gives an annual deposition of 5 900 tons of phosphorous for the Baltic Sea area.

The wet deposition can also be estimated by scaling the mean deposition rates from these 10 stations (table 6) to an area the size of the Baltic. This estimate gives an annual deposition of 5 800 tons.

It is impossible to assign these estimates any certainty, due to the incomplete data reported and also because of incomplete understanding of the sources and sinks for atmospheric phosphorous.

DEPOSITION OF METALS

Wet deposition

It's a simple but not necessary meaningful excercise to extrapolate the very limited data on metal content in precipitation (figure 4-7 and table 7) to estimate the wet deposition. Nevertheless this was done. The results given in table 10 are based on the mean concentrations given in table 7 and the mean **climato-**logical precipitation amount for the Baltic (616 **mm/yr**). Similar figures are obtained if we use the mean annual depositions given in table 8 and apply them to an area of the size of the Baltic. This is because we observe similar precipitation amounts at the stations reporting on precipitation chemistry as the precipitation amounts over the Baltic.

The data for copper reported from the Finnish station **Vanhankylänmaa** is considered an outlier. The yearly mean is about 15 times higher than the mean reported from the Swedish station Aspvreten (at comparable latitude) and is also about 2 times the value reported from DE Kiel, where the highest concentration is expected, because of the vicinity to the European continent.

The intercalibration of analytical methods for metals in precipitation in which institutes reporting to HELCOM participated, (Baltic Marine ..,1987) showed that the methods used are by no means satisfactory. Because of both this and the small quantity of reported data, the figures given in table 10 are highly uncertain.

Dry deposition

Very few data on the metal content of aerosols over the Baltic are reported. No station reporting to HELCOM has reported any data for the period 1983-85.

The metal content of fine particles (aerodynamic diameter < 2 microns) were studied at three lighthouses situated along the southern Baltic coast of Sweden (Swietlicki 1988). The monitoring program was performed on an event basis during 1985 - 1986. The mean concentrations of copper, lead and zinc are given in table 9.

The dry deposition of metals was calculated by assuming that the means given in table 9 are applicable over the Baltic. A dry deposition velocity of 1 mm/s, in accordance with Slinn & Slinn (1983) is used. The dry deposition of metals in coarse particles was considered insignificant as most of the metal-containing particles are in the sub-micrometer range. (Lannefors et al. 1983). The dry deposition of cadmium is estimated using data from Bikenes, a remote site in south Norway. Pacyna et al. (1984) report a mean **concentration** of 0.3 ng/m³. The dry deposition estimates are given in table 10.

DISCUSSION

The deposition estimates given above could be compared with previous estimates for the Baltic (table 11). We note that the deposition figures agree well (within 30%) for nitrogen, cadmium, zinc and lead, most likely due to that the same method and assumptions are used for obtaining the estimates. The higher deposition for copper reported by Ferm (1984:33) is probably due to that Ferm estimated wet deposition from data on aerosol content and scavenging ratios, not from data on concentrations in precipitation. The substantially higher estimate for phosphorus in this report should be treated with great caution. We observe large differences in data on concentrations in precipitation from near-by stations, eg. SE **Rickleå** 8 µgP/l and SF **Sulva** 43 µgP/l, situated approximately 120 km from each other across the southern part of the Bothnian Bay. Investigations looking at the phosphorous content of air and precipitation could resolve this unexpectedly high variation and also allow us to draw some firmer conclusions with respect to deposition patterns over the

Baltic.

All estimates given in this report should be considered as fairly crude as they are based on data series with large gaps. Additionally, too little is known about the reliability and comparability of the reported data. The analytical methods used for determining components in precipitation have been compared, (Baltic Marine .., 1987) and show satisfactory results for nitrate and ammonium, but unsatisfactory for the metals.

Presently nothing is known about the comparability of the sampling methods used. The planned intercomparisons within HELCOM will increase our knowledge and make it possible to make more precise deposition estimates.

A better understanding of the exchange processes between the atmosphere and the sea is also needed to increase the accuracy of deposition estimates.

It is interesting to compare the transport of material from the atmosphere with the biological turnover. If we for instance compare the atmospheric supply of fixed nitrogen with the annual biomass production of 55 - 80 g carbon/m² (Fonselius, 1972), we find, by using a carbon to nitrogen ratio of 6, that the annual atmospheric nitrogen load can supply at least 10% of the annual need for fixed nitrogen. This contribution could be larger if we have a rapid turnover of biomass and a **efficient** use of the nutrients in the degraded material. The mean lifetime (or turnover time) of living organic matter needs only to be 1/10 of a year in order for the atmospheric supply to account for all nitrogen needed in the annual primary production.

The atmospheric input could be of greater ecological importance than first thought since this nitrogen is being added in amounts far in excess of what we expect to find in a supposed pristine situation and this would also allow a larger standing biomass to be formed. Disturbances of this kind could propagate

in the Baltic ecosystems and cause serious effects on the oxygen status of the bottom waters. On the other hand the input **of** metals could work in opposite direction, because metals in excess are harmful to living matter, and could decrease biological activity and thus decrease the eutrophication of the Baltic. A man induced balance like this is unstable as it is based on activities which are likely to be changed in the future.

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Table 1. Yearly mean concentration of nitrogen compounds in precipitation. Stations around the Baltic 1983-85.

Station	Year	NO ₃ -N mg/l	NH ₄ -N mg/l	Tot.N mg/l
DD KapÅ	85	0.80(12)	0.91(12)	
DE Kiel	85	2.62(05)		
DK Keld	83	0.85(12)	0.79(12)	
DK Keld	84	0.98(12)	0.91(12)	
DK Keld	85	0.64(12)	0.94(12)	
SE Arup	83	0.59(10)	0.73(10)	
SE Arup	84	0.72(12)	0.81(12)	
SE Arup	85	0.67(11)	0.81(11)	
SE Vavi	85	0.74(12)	0.84(12)	
SE Rörv	83	0.62(12)	0.63(12)	
SE Rörv	84	0.68(12)	0.75(12)	
SE Rörv	85	0.82(12)	0.82(12)	
SE Hobu	84	0.78(12)	1.09(12)	
SE Hobu	a5	1.34(12)	1.58(12)	
SE Asp	a4	0.56(10)	0.62(10)	
SE Asp	85	0.59(11)	0.57(11)	
SE Rick	83	0.28(10)	0.33(10)	
SE Rick	84	0.36(11)	0.44(11)	
SE Rick	85	0.30(09)	0.31(09)	
SU Nida	84	0.81(02)	0.56(10)	
SU Nida	85	0.96(12)	0.87(12)	
SU Ruts	85		0.57(07)	
su syr	84	1.10(02)	0.82(10)	
su syr	85	0.70(06)	0.82(06)	
SU Lahe	85	0.20(01)	0.49(12)	
SF Utö	84	0.49(12)	0.44(12)	
SF Utö	85	0.95(12)	0.81(12)	
SF Tvär	84			1.36(12)
SF Tvär	85	0.93(12)	0.56(12)	
SF Joma	84			1.68(12)
SF Joma	85	0.96(12)	1.11(12)	
SF Korp	84			1.00(10)
SF Korp	85	0.65(12)	0.46(12)	
SF Vanh	85	0.68(12)		
SF Haap	85	0.93(05)		
SF Sipo	84			1.24(11)
SF Sipo	85	0.60(12)	0.44(12)	
SF Virol	85	0.56(12)	0.60(12)	
SF Viro2	85	0.68(12)	0.93(12)	
SF Ylim	84			1.66(12)

Table 1, continued

Station	Year	NO ₃ -N mg/l	NH ₄ -N mg/l	Tot.N mg/l
SF Ylim	85	0.47 (12)	1.16 (12)	1.16 (12)
SF Sulv	84			
SF Sulv	85	0.47 (11)	0.52 (10)	
SF Kala	85	0.35 (11)	0.32 (11)	
SF Hail1	85	0.45 (10)		
SF Hail2	85	0.44 (10)	0.46 (09)	

The numbers within brackets are the number of months for which data are reported.

Tot.N = Total nitrogen. The sum of organic and inorganic nitrogen.

Some stations appear more than once, due to data reported by more than one institute.

Table 2. Yearly wet deposition of nitrogen. Estimates for the sub-basins of the Baltic Sea area. Based on climatological precipitation amount and average concentrations in precipitation for 1983-85.

Sub-basin	Area km ²	Precip. mm	Sum-N mgN/l	Dep./m ² gN	Dep. ton
Bothnian Bay	36 260	510	0.83	0.42	15 000
Bothnian Sea	79 256	570	1.23	0.70	55 000
Gulf of Finland	29 498	655	1.32	0.86	25 000
Gulf of Riga	17 933	648	1.62	1.05	19 000
Baltic Proper	211 096	638	1.50	0.96	203 000
Belt Sea	18 955	685	1.70	1.16	22 000
Kattegatt	22 287	676	1.50	1.01	23 000
Summ/mean	415 265	616	1.42	0.86	362 000

Note : Sum-N is NO₃⁻ + NH₄⁺ or Tot.N

Table 3. Mean air concentrations of total nitrates, ammonium and nitrogen dioxide. Stations around the Baltic 1983-85.

Station	Year	TNO ₃ μgN/m ³	μNH ₄ μgN/m ³	NO ₂ μgN/m ³
DK Keld	83		2.9 (12)	
DK Keld	84		3.5 (12)	
DK Keld	85	1.6 (02)	3.4 (09)	
SE Arup	84		1.2 (11)	
SE Rick	84		0.6 (11)	
SE Rörv	83			1.8 (12)
SE Rörv	84			1.7 (12)
SE Rörv	85	1.2 (03)		1.9 (12)
SE Hobu	83			0.8 (12)
SE Hobu	84			0.7 (12)
SE Hobu	85			0.7 (12)
SE Asp v	84	0.4 (06)	0.7 (07)	
SE Asp v	85	0.4 (07)	0.9 (03)	0.7 (03)
SE Vavi	85			1.7 (12)
SU Syrv	84		1.0 (09)	
su syrv	85		0.6 (01)	
SU Nida	84		0.7 (12)	
SU Nida	85		1.1 (01)	
SU Lahe	85		3.0 (03)	1.2 (01)

The numbers within brackets are the number of months for which data are reported

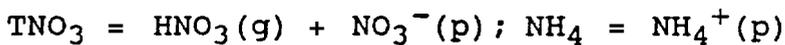


Table 4. Mean concentrations in air of nitrogen compounds and annual dry deposition of nitrogen. Estimates for the sub-basins of the Baltic Sea area. Based on data for 1983 - 85.

Sub-basin	Area km ²	μNH ₄ μgN/m ³	HNO ₃ μgN/m ³	NO ₃ μgN/m ³	Dep. ton N
Bothnian Bay	36 260	0.6	0.16	0.24	2 200
Bothnian Sea	79 256	0.6	0.16	0.24	4 800
Gulf of Finland	29 498	1.0	0.16	0.24	2 100
Gulf of Riga	17 933	1.0	0.16	0.24	1 300
Baltic Proper	211 096	1.1	0.16	0.24	15 800
Belt Sea	18 955	3.5	0.35	0.59	3 800
Kattegatt	22 287	2.0	0.35	0.59	3 300
Summ/mean	415 265	1.1	0.18	0.27	33 300

Table 5. Yearly deposition of nitrogen. Estimates for the sub-basins of the Baltic Sea area.

Sub-basin	Deposition tons N/year		
	Wet	Dry	Total
Bothnian Bay	15 000	2 200	17 000
Bothnian Sea	55 000	4 800	60 000
Gulf of Finland	25 000	2 100	27 000
Gulf of Riga	19 000	1 300	20 000
Baltic Proper	203 000	15 800	219 000
Belt Sea	22 000	3 800	26 000
Kattegatt	23 000	3 300	26 000
Total	362 000	33 300	395 000

Table 6. Yearly mean concentration and deposition of total phosphorous in precipitation. Stations around the Baltic.

Station	Year	Precip. mm	Conc. µg/l	Dep. mg/m ²
SE Arup	84	588	9 (11)	5
SE Asp v	84	482	8 (09)	4
SE Rick	84	377	8 (05)	3
SF Ylim	84	643	55 (11)	35
SF Joma	84	780	12 (12)	9
SF Kala	84	459	37 (07)	17
SF Korp	84	623	15 (11)	9
SF Sipo	84	805	21 (11)	17
SF Sulv	84	474	43 (11)	20
SF Tvär	84	764	25 (12)	19
Mean			23	14

The numbers within brackets are the number of months for which data are reported.

Table 7. Yearly mean concentration of heavy metals in precipitation. Stations around the Baltic 1983-85.

Station	Year	Pb μg/l	Cd μg/l	cu μg/l	Zn μg/l
DE Kiel	85	18.5(04)		8.7(04)	29.9(04)
SE Arup	83	9.2(03)	0.16(03)	1.2(03)	
SE Arup	84	8.5(11)	0.13(11)	1.2(11)	
SE Arup	85	7.5(10)	0.13(10)	1.3(10)	17.0(10)
SE Aspvt	83	7.3(03)	0.14(03)	0.9(03)	
SE Aspvt	84	7.3(11)	0.12(11)	1.0(11)	
SE Aspvt	85	10.2(11)	0.17(11)	2.0(11)	18.6(11)
SF Haap	84	10.8(11)	0.46(11)		
SF Haap	85	6.4(05)	0.30(05)		27.8(02)
SF Hail	84	6.3(12)	0.23(12)		
SF Hail	85	4.3(10)	0.10(10)		19.0(05)
SF Vanh	84	8.7(11)	0.40(11)		
SF Vanh	85	5.4(12)	0.13(12)	[19.1(12)]	12.7(06)
Mean		8.0	0.21	1.9	19.2

The numbers within brackets are the number of months for which data are reported.

The means are weighed in relation to the number of monthly means reported per station and **year**. The **concentration** of Cu for SF Vanh is considered an outlier (see text) and is not used when calculating the mean.

Table 8. Yearly wet deposition of heavy metals. Based on reported precipitation amount and concentrations. Stations around the Baltic 1983 - 85.

Station	Year	Pb mg/m ²	Cd mg/m ²	cu mg/m ²	Zn mg/m ²
DE Kiel	85	6.6		3.11	10.7
SE Arup	83	6.5	0.11	0.83	
SE Arup	84	5.5	0.08	0.79	
SE Arup	85	5.8	0.10	0.99	13.1
SE Aspvt	83	3.0	0.06	0.34	
SE Aspvt	84	3.8	0.06	0.54	
SE Aspvt	85	5.0	0.08	0.94	9.0
SF Haap	84	6.5	0.28		
SF Haap	85	1.6	0.05		12.9
SF Hail	84	2.7	0.10		
SF Hail	85	1.2	0.03		8.9
SF Vanh	84	5.9	0.27		
SF Vanh	85	2.6	0.06		7.6
Mean		4.4	0.11	1.08	10.4

Table 9. Metal content of fine particles (< 2 µm). Mean values from Swedish lighthouses 1985 - 1986. Swietlicki (1988).

Station	Lat. °N	n	Pb ng/m ³	cu ng/m ³	Zn ng/m ³
Utlången	56.0	127	21.3	1.7	25.6
Landsort	58.8	64	18.0	1.4	23.5
Sv. Hög.	59.5	51	17.0	1.2	19.5
Summ/mean		242	19.5	1.5	23.6

n = Number of samples (12 hours sampling time).

Table 10. Estimates of metal deposition to the Baltic Sea area. Based on data for 1983-85 on aerosol concentrations and composition of precipitation.

Metal	Deposition, tons/yr		
	Wet	Dry	Total
Pb	2 050	255	2 305
Cd	55	4	59
cu	490	20	510
Zn	4900	310	5 210

Table 11. Some estimates for the atmospheric load to the Baltic/Baltic Sea area. Unit : Tons/year.

Nitrogen	Phosph	Cd	Cu	Pb	Zn	Ref.
400 000	1 400	80	1 400	2 400	6 000	Rohde et al. 1981
500 000	-	80	600	3 000	8 000	Ferm 1984b
400 000	6 000	60	500	2 300	5 200	This report

Figure 1. Location of stations reporting to HELCOM



Figure 2. Mean concentration of nitrogen in precipitation.
Based on data reported for 1983-1985.

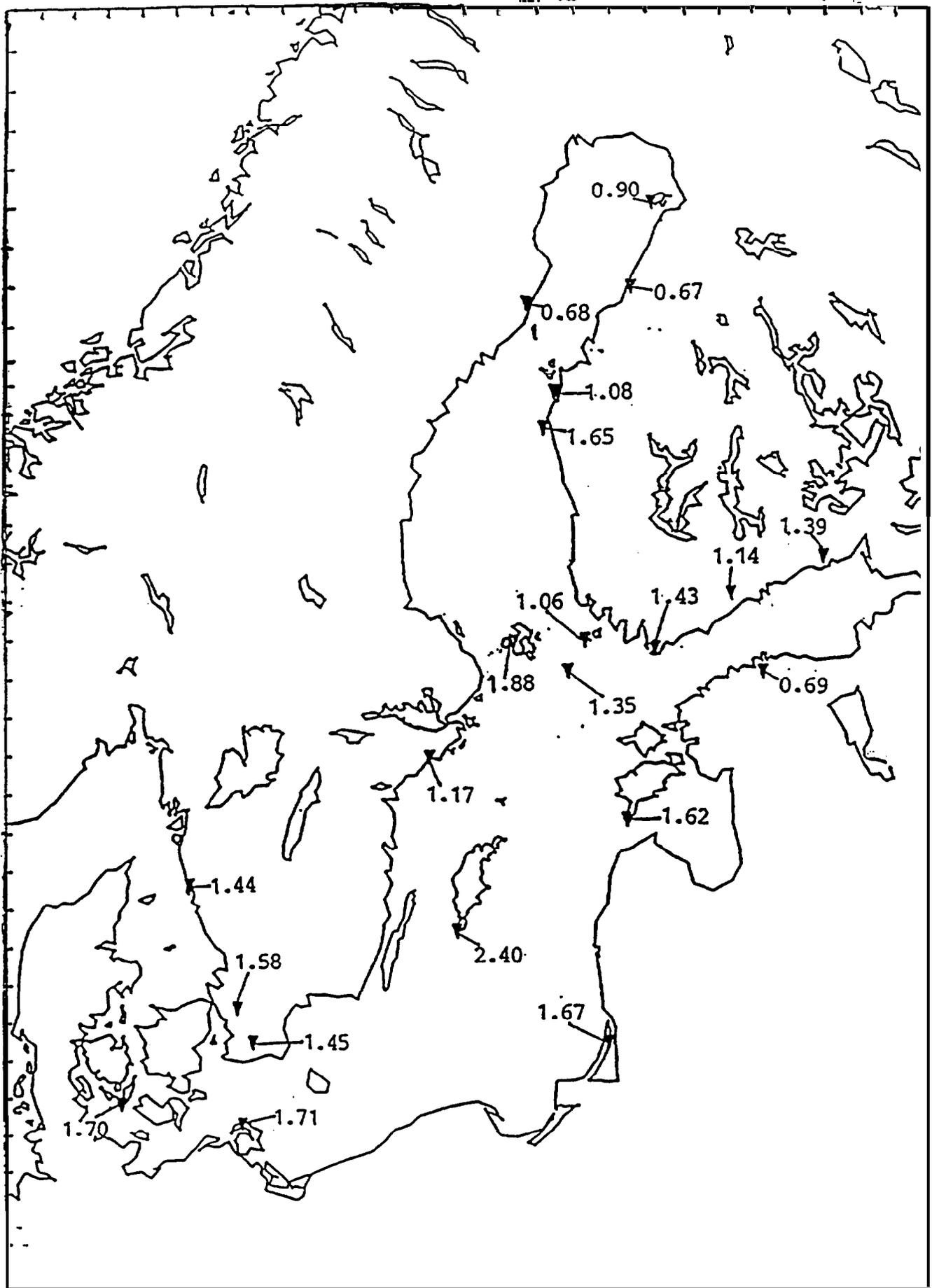


Figure 3. Seasonal variation of nitrogen dioxide concentrations at stations around the Baltic.

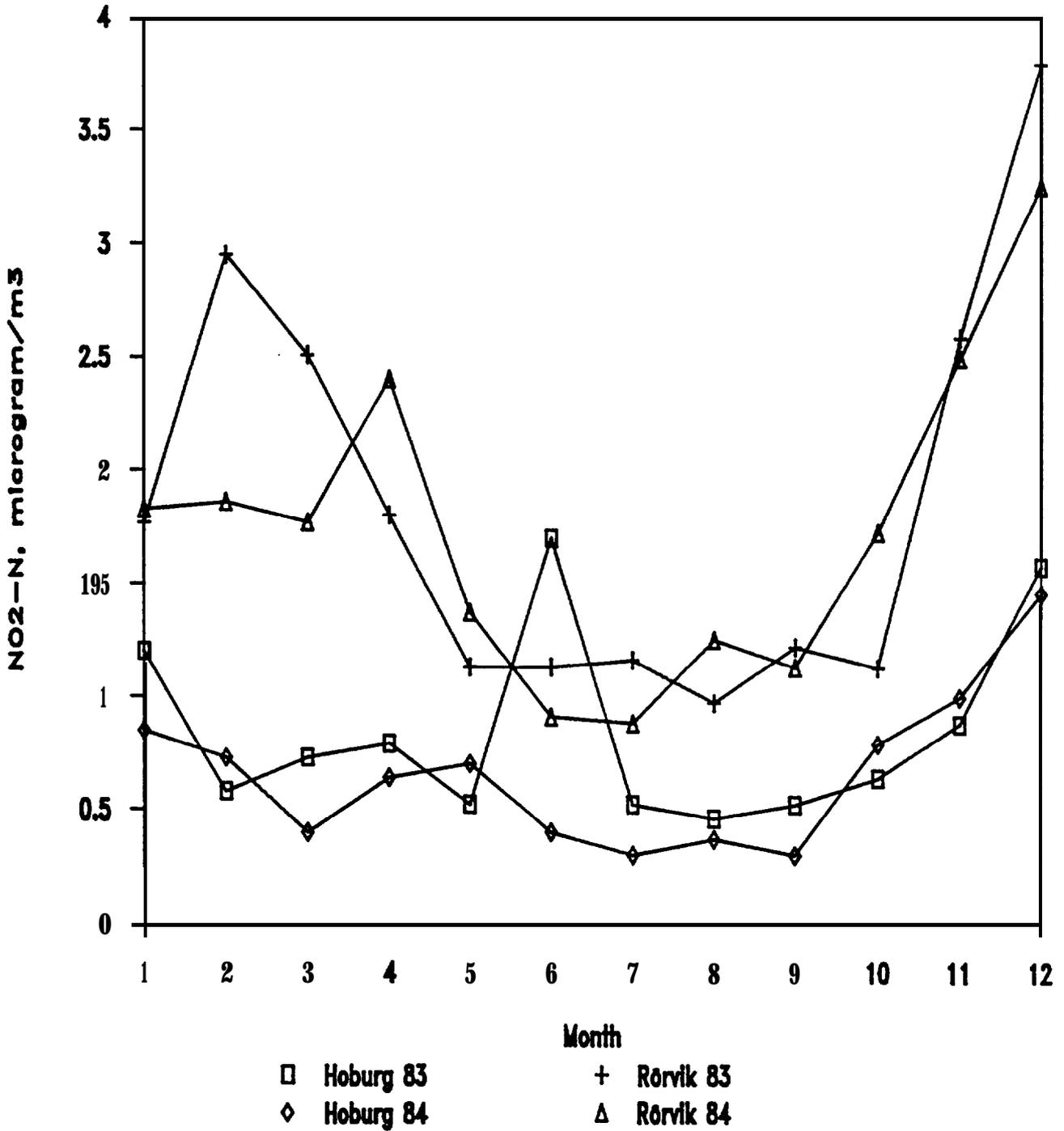


Figure 4. Mean concentration of Cu in precipitation.
Based on data reported for 1983-1985.

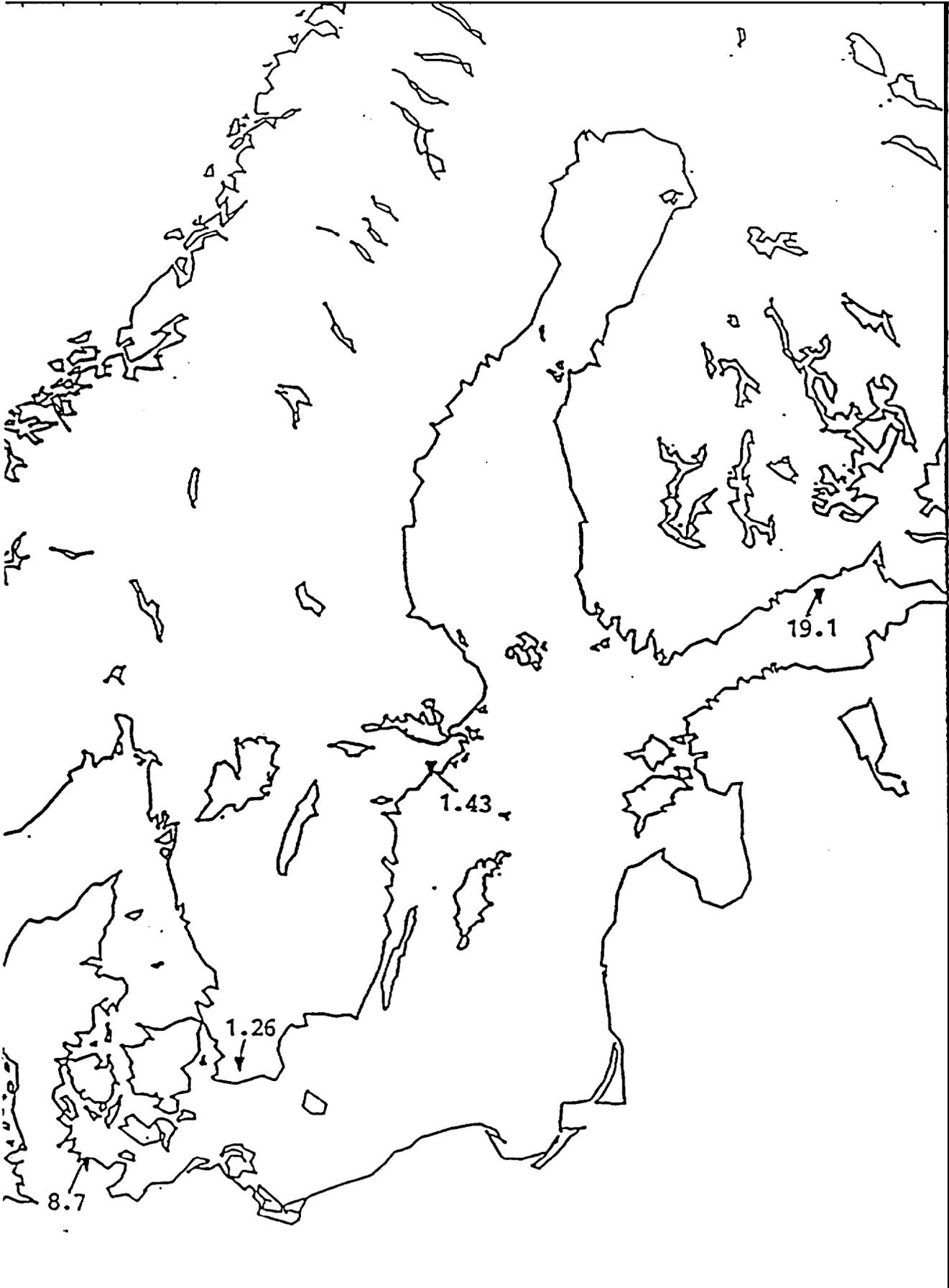


Figure 5. Mean concentration of Cd in precipitation.
Based on data reported for 1983-1985.

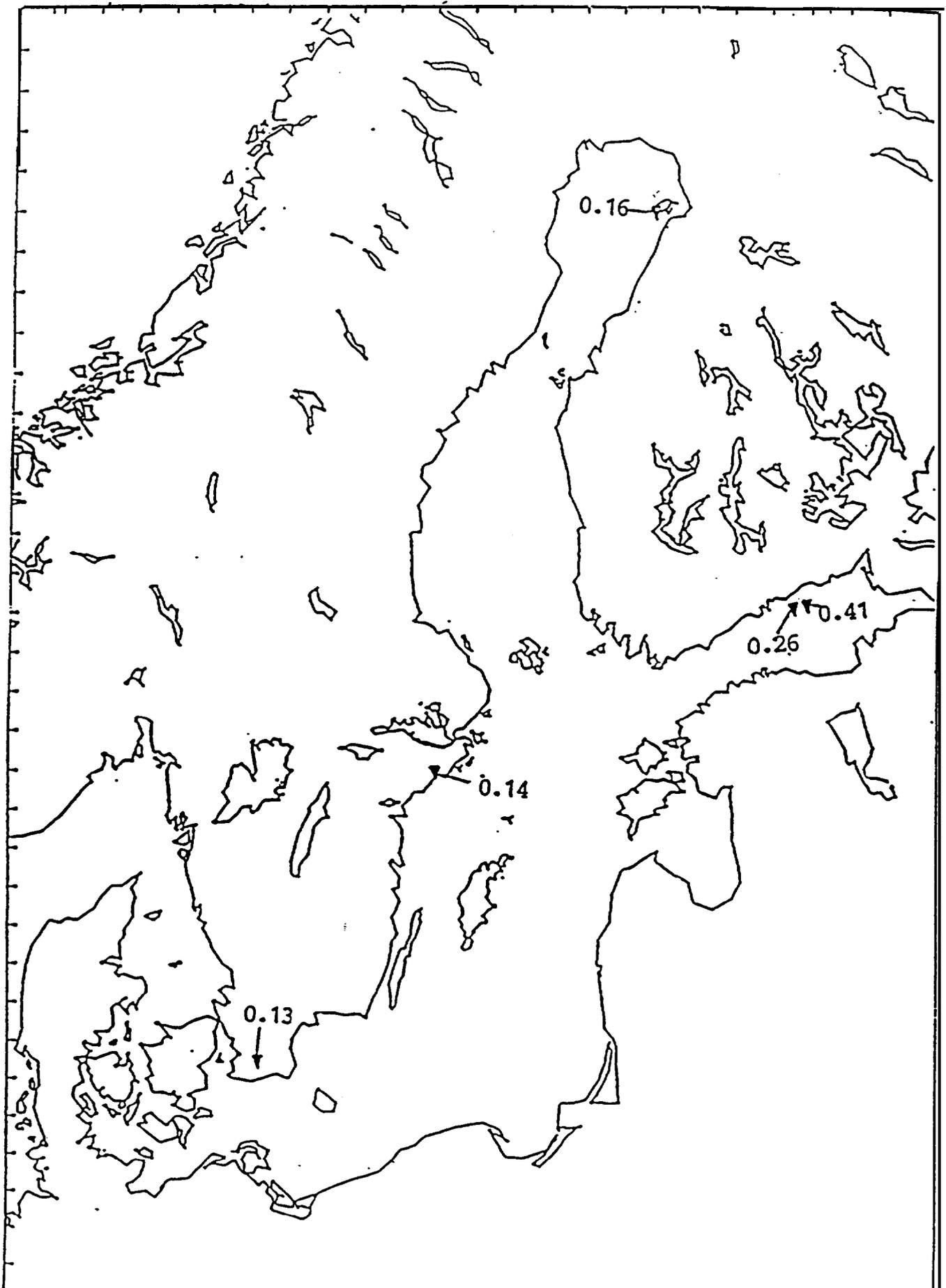


Figure 6. Mean concentration of Zn in precipitation.
Based on data reported for 1983-1985.

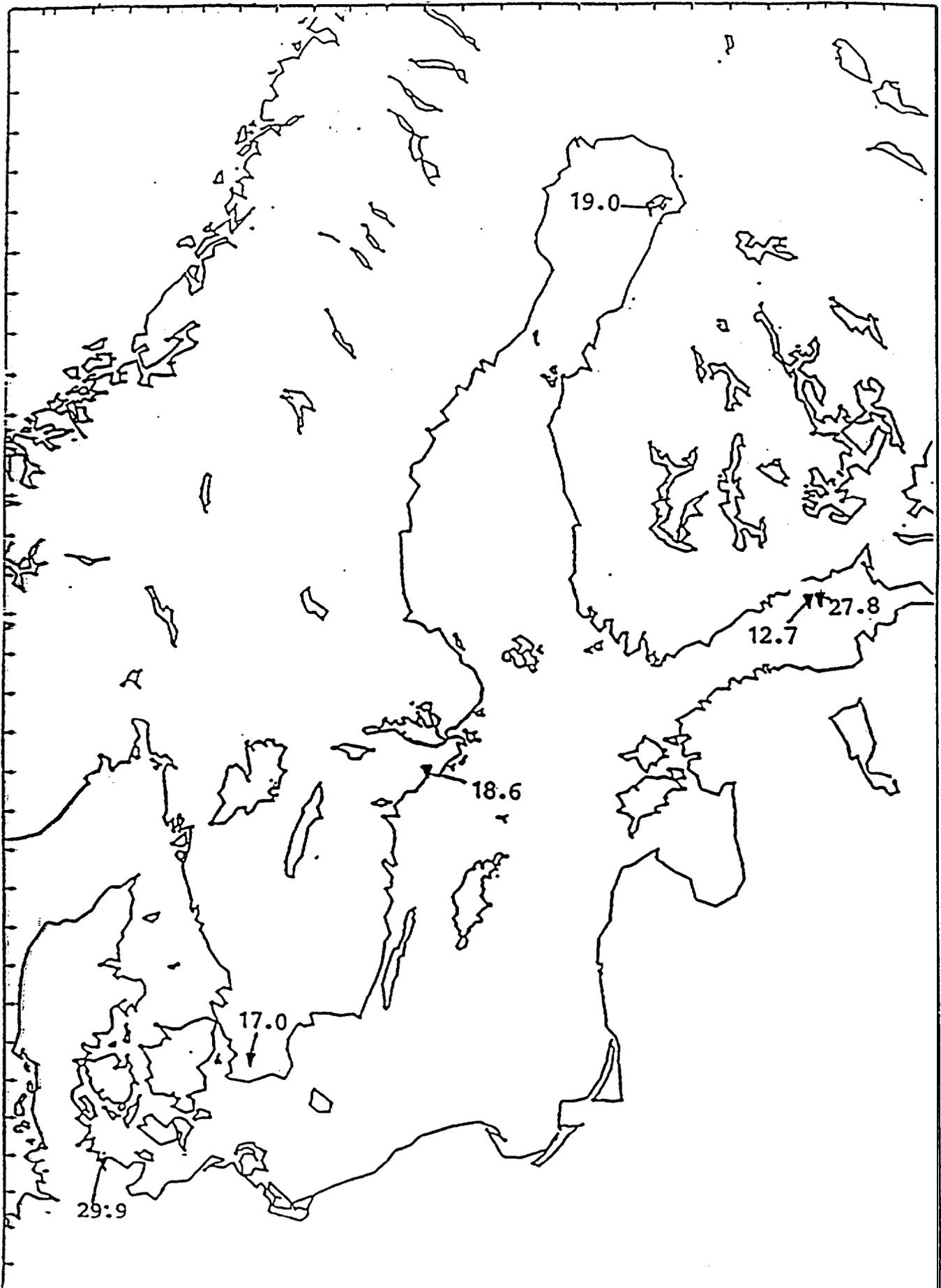
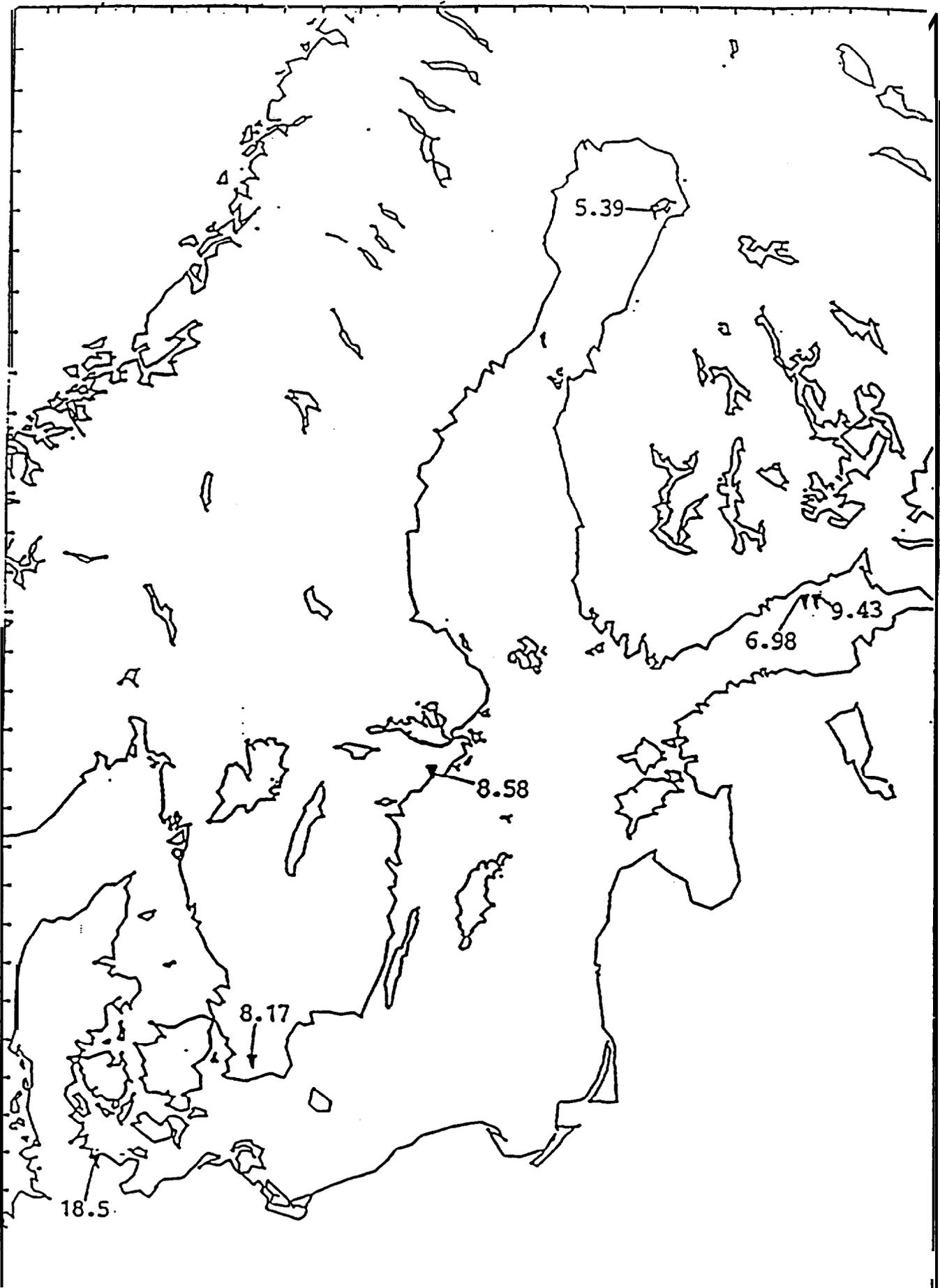


Figure 7. Mean concentration of Pb in precipitation.
Based on data reported for 1983-1985.



ANNEX 1

Number of monthly averages
reported per station, compound and year

Air and precipitation data reported to HELCOM

Year: 1983

Number of monthly averages reported per station

Station	Precipitation											Air				
	mm	NO ₃ ⁻	NH ₄ ⁺	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Pb	Cd	Cu	Zn	Cl ⁻	SO ₂	SO ₄	NO ₂	TNO ₃ ⁺	TNH ₄ ⁺
FI Yliina															-	-
FI Hailu															-	-
FI Vanha															-	-
FI Virol															-	-
FI Utö															-	-
FI Haapa															-	-
FI Jomal															-	-
FI Korpp															-	-
FI Tvärm															-	-
FI Sipoo															-	-
FI Kalaj															-	-
FI Sulva															-	-
SE Vavih															-	-
SE Rörvi	12	12	12	12								12	12	12	-	-
SE Hobur	12	12	12	12								12	12	12	-	-
SE Arup	10	10	10	10	10	10	3	3	3	3		-		-	-	-
SE Aspvr							3	3	3	3				-	-	-
SE Rickl	10	10	9	10	10	10									-	-
DK Kelds	12	12	12	12								12	12		-	12 ^a
DE KielB															-	-
SU Lahem															-	-
SU Syrve															-	-
SU Rutsa															-	-
SU Nida															-	-
DD KapAr															-	-

TNO₃ = HNO₃ + NO;

TNH₄ = NH₃ + NH;

a. Reporting NH₄⁺ (p)

Number of monthly averages reported per station

Station	Precipitation											Air				
	mm	NO ₃ ⁻	NH ₄ ⁺	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Pb	Cd	Cu	Zn	Cl ⁻	SO ₂	SO ₄	NO ₂	TNO ₃ ⁺	TNH ₄ ⁺
FI Yläna a.	12	12	12	12		11										
FI Hailu	12			12		12	12	12								
FI Vanha	12			11		11	11	11								
FI Virol	12	12	12	12		12						12	12			
FI Utö	12	12	12	12		12						10	10			
FI Haapa a.	12	11	11	11		11	11									
FI Jomal a.	12	12	12	12		11				-						
FI Korpp a.	12	10	10	11		10										
FI Tvärn a,	12	12	12	12		11										
FI Sipoo a.	12	11	11	11		11										
FI Kalaj a.	12	7	7	7		6										
FI Sulva a.	12	12	12	12		11										
SE Vavih																
SE Rörvi	12	12	12	12								12	12	12		
SE Hobur	12	12	12	12								12	12	12		
SE Arup	12	12	12	12	12	12	11	11	11	11	-					
SE Aspvr	11	11	11	10	11	11	11	11	11	11	-					
SE Rickl	11	11	11	11	11	11										
DK Kelds	12	12	12	12								12	12			12 ^{b.}
DE KielB																-
SU Lahem																-
SU Syrve	10	2	10	10	10								9			9 ^{b.}
SU Rutsa																-
SU Nida	10	2	10	10	10								12			12 ^{b.}
DD KapAr																

$TNO_3 = HNO_3 + NO_3^-$, $TNH_4 = NH_3 + NH_4^+$

a. Reporting total nitrogen b

Reporting NH₄⁺ (p)

Number of monthly averages reported per station

Station	Precipitation											Air				
	mm	NO ₃ ⁻	NH ₄ ⁺	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Pb	Cd	Cu	Zn	Cl ⁻	SO ₂	SO ₄	NO ₂	TNO ₃ ⁺	TNH ₄ ⁺
FI Yliuva	12	12	11	12	12	12		-	-		12					
FI Hailu	10	10	9	10	8	8	10	10	-	5	11					
FI Vanha	12	12		12		12	12	12	12	6						
FI Virol	12	11	11	11	12	12		-	-		11	12	12	-	-	
FI Utö	12	12	12	12		12		-	-		12	12	12	-	-	
FI Haapa	5	5		5		5	5	5	-	2						
FI Jomal	12	12	12	11	10	10					11					
FI Korpp	12	12	12	12	12	12					12					
FI Tvärm	12	12	12	12	11	12					12					
FI Sipoo	12	12	12	12	12	12					12					
FI Kalaj	12	11	11	10	11	11					11					
FI Sulva	12	11	10	11	11	11					11					
SE Vavih	12	12	12	12							12	12	12	12	-	
SE P&vi	12	12	12	12							12	12	12	12	-	
SE Hobur	12	12	12	12							12	12	12	12	3	3
SE Arup	11	11	12	11	11	11	10	10	10	10	11					
SE Aspvr	11	11	11	11	11	11	11	11	11	11	11	12	12	4	3	3
SE Rickl	9	9	9	9	9	9					9					
DK Kelds	12	12	12	12							12	11	11	-	2	11 ^{a.}
DE KielB	7	5		5			4		4	4	5					
SU Lahem	12	1	12	12	12							2	3	1	-	3 ^{b.}
SU Syrve	6	6	6	6	6							4	1	-	-	1 ^{b.}
SU Rutsa	7		7	7	7							6	-	-	-	-
SU Nida	12	12	12	12	12							9	1	-	-	1 ^{b.}
DD KapAr	12	12	12	12	12	12					12	12	12	-	-	-

TN03 = HNO₃ + NO₂; , TNH₄ = NH₃ + NH₄⁺

a. Reporting NH₄⁺ (p) for 9 months

b. Reporting NH₄⁺ (p)

DEPOSITION ESTIMATES TO THE BALTIC SEA AREA BASED ON REPORTED
DATA FOR 1986.

By: Hans Areskoug
National Environmental Protection Board
Air Research Laboratory
Nyköping, Sweden

ABSTRACT

The deposition to the Baltic Sea Area of nitrogen and heavy metals has been estimated.

The estimates are based on data on atmospheric abundance of air pollutants and concentration in precipitation, submitted to the HELCOM secretariat for 1986.

Precipitation data was when possible analysed for a regional pattern and a typical concentration value was assigned for each of the sub-basins of the Baltic Sea Area. Deposition calculations were based on **these** concentrations and the climatological precipitation amounts.

Dry deposition was estimated from data on gaseous compounds and atmospheric aerosols using the concept of dry deposition velocity.

The annual deposition of nitrogen to the Baltic Sea Area was estimated at 270,000 - 630,000 tonnes. The deposition level in the the southern part of the region (Belt Sea and Kattegat) was about 2.5 times the deposition levels in the northern part (Bothnian Bay).

The annual deposition of heavy metals was tentatively estimated at: cadmium 35 tonnes, copper 470 tonnes, lead 1560 tonnes and zinc 3400 tonnes.

These estimates have to be treated as fairly crude, because the reported data is insufficient to be used for a detailed analysis of the deposition pattern over the Baltic. More data on precipitation quantities, chemical composition of air and precipitation, as well as better understanding of the exchange processes between the atmosphere and the sea, is needed to give a greater degree of certainty.

The estimates presented here are comparable to previous estimates, mainly because the same methods have been used when calculating the deposition. The deposition estimates in this report may be considered to be slightly more reliable than previous ones since they are based on data from more sites around the Baltic than earlier.

INTRODUCTION

The purpose of this report is to use the data reported to HELCOM to estimate the deposition of airborne pollutants to the Baltic.

The report is by no means a complete review of all information available with respect to deposition.

The data has been used to estimate tentatively the annual deposition of nitrogen and heavy metals to the Baltic. The original intention was also to evaluate the temporal and spatial correlation in this region using the data reported to the HELCOM secretariat. Due to lack of data and data series with large gaps, this was only possible for wet deposition of nitrogen.

THE DATA

Data on precipitation and/or air is reported from 25 sites for 1986. Two institutes report data from the Finnish sites Hailuoto and Virolahti.

The location of the sites is shown in Figure 1.

Most of the reported data is on concentration of macroconstituents in precipitation. Data on heavy metals in precipitation is only reported from 6 sites. Data on nitrogen dioxide is reported from 8 sites and on nitrogen in particles from 5 sites.

The parameters and number of monthly averages reported from each station are given in Appendix 1.

DEPOSITION OF NITROGEN COMPOUNDS

Wet deposition

Data on nitrate and ammonium in precipitation is reported from 25 stations as monthly values. Since the data series does not contain

any large gaps and the coverage of the stations around the Baltic is fairly uniform, an evaluation of the temporal and spatial distribution of nitrogen in precipitation has been possible.

To evaluate the spatial distribution, six sub-basins have been considered (Fig. 2). Each sub-basin was assigned a typical monthly nitrate and ammonium concentration value and a monthly precipitation **amount value**, based on reported data from stations surrounding the sub-basin. Reported data which differs markedly compared with data from **nearby** stations has not been used when assigning the concentration and precipitation amount values. The evaluation method is further described in Appendix 2. The concentration and precipitation amount values obtained in this way are given in Tables 1, 2 and 3.

Table 1. Monthly concentrations of nitrate in precipitation for 1986. Estimates for the sub-basins of the Baltic. Based on data reported to the HELCOM database. Sort : mg N/l.

	Bothnian Bay	Bothnian Sea	Gulf of Finland	Baltic Proper,N	Baltic Proper,S	Belt Sea& Kattegat
Jan	0.60	0.70	0.90	1.06	0.86	0.61
Feb	0.39	1.70	0.50	1.07	1.07	1.60
Mar	1.25	1.37	1.07	1.40	1.31	1.07
Apr	0.40	0.55	0.82	0.56	0.98	1.20
May	0.34	0.77	1.15	0.95	1.13	1.10
Jun	0.01	0.16	0.30	0.37	0.61	0.70
Jul	0.30	0.30	0.20	0.41	0.53	0.69
Aug	0.15	0.20	0.21	0.29	0.56	0.70
Sep	0.10	0.20	0.20	0.27	0.38	0.38
Oct	0.47	0.58	0.70	0.60	0.62	0.60
Nov	0.46	0.68	0.90	0.81	0.75	0.70
Dec	0.53	0.64	0.65	0.76	0.76	0.70
1986	0.41	0.54	0.58	0.63	0.74	0.75

Table 2. Monthly concentrations of ammonium in precipitation for 1986
Estimates for the sub-basins of the Baltic.
Based on data reported to the HELCOM database.
Sort : mg N/l.

	Bothnian Bay	Bothnian Sea	Gulf of Finland	Baltic Proper,N	Baltic Proper,S	Belt Sea& Kattegat
Jan	0.53	0.78	0.62	0.67	0.52	0.43
Feb	0.31	0.76	0.42	0.79	0.64	0.63
Mar	1.25	1.46	1.34	1.23	1.51	1.48
Apr	1.69	1.42	1.50	1.01	1.37	1.39
May	0.99	1.07	2.13	0.86	1.03	1.26
Jun	0.36	0.51	0.19	0.94	0.99	0.99
Jul	0.20	0.34	0.21	0.51	0.64	1.15
Aug	0.35	0.34	0.35	0.45	0.75	1.08
Sep	0.07	0.11	0.15	0.17	0.33	0.46
Oct	0.42	0.49	1.08	0.31	0.51	0.61
Nov	0.40	0.55	1.06	0.54	0.67	0.64
Dec	0.10	0.33	0.50	0.52	0.63	0.58
1986	0.54	0.62	0.72	0.59	0.75	0.88

The annual mean concentration (precipitation weighted mean) of nitrate and ammonium for each sub-basin was then calculated using the obtained monthly values. The annual mean values are shown in Tables 1 and 2.

Table 3. Monthly precipitation amount for 1986
Estimates for the sub-basins of the Baltic.
Based on data reported to the HELCOM database.
Sort :mm.

	Bothnian Bay	Bothnian Sea	Gulf of Finland	Baltic Proper,N	Baltic Proper,S	Belt Sea& Kattegat
Jan	41	50	64	47	60	60
Feb	3	3	11	5	9	5
Mar	60	44	32	32	43	47
Apr	26	42	49	50	42	36
May	52	52	27	47	47	49
Jun	11	16	22	34	31	29
Jul	49	40	63	52	71	66
Aug	128	114	95	94	75	53
Sep	59	65	68	72	68	47
Oct	65	61	59	50	75	71
Nov	59	63	58	71	67	62
Dec	19	32	54	51	53	56
1986	572	581	600	605	641	581

The annual deposition of nitrogen was then calculated as the sum of deposition of nitrate and ammonium by using the climatological precipitation amount (Rohde et al, 1980) for each sub-basin. The deposition values are given in Table 4.

Table 4. Wet deposition of nitrogen for 1986. Estimates for the sub basins of the Baltic. Based on climatological precipitation amount and calculated concentrations.

Sub-basin	Area km ²	Precip. mm	Sum-N mgN/l	Dep./m ² gN	Dep. tonnes N
Bothnian Bay	36 500	510	0.95	0.48	18 000
Bothnian Sea	79 500	570	1.08	0.62	49 000
Gulf of Finland	29 500	655	1.30	0.85	25 000
Baltic Proper,North	168 000	638	1.22	0.78	131 000
Baltic Proper,South	61 000	638	1.49	0.95	58 000
Belt Sea & Kattegat	41 000	680	1.63	1.11	45 000
Baltic Sea Area	415 500	616	1.28	0.79	326 000

Note : Sum-N is $\text{NO}_3^- \text{-N} + \text{NH}_4^+ \text{-N}$

Substantially higher deposition levels are estimated in the southern part (Belt Sea and Kattegat 1.1 gN/m²,yr) than in the northern part (Bothnian Bay 0.5 gN/m²,yr). This is explained by the higher concentration and the higher annual precipitation amount in the southern part.

The annual deposition to the Baltic Sea Area estimated in this way is approximately 330,000 tonnes.

The deposition data in Table 4 is fairly crude, **since** it is based on a **number of assumptions :**

1. **Observations** on the amount and chemical content of precipitation at the land-based stations are representative for the situation throughout the Baltic.

Granat (1988) studied the precipitation chemistry at island, coastal and inland sites on both sides of the water in the Bothnian

Bay area over one year (1986). The concentration of NO, at the island site was about equal and NH, about 10% less than the value obtained by linear interpolation between coastal sites. The amount of precipitation was about 30% less at the island site. The deposition was thus estimated to be 30 to 40% lower than the values measured at coastal sites. He concluded that estimates of wet deposition to the open water should be made from a combination of concentration data obtained from many measurements around the water body and estimated amount of precipitation over the water.

2. No correction for organic nitrogen is made.

Soderlund (1983) found from measurements in Sweden that the total nitrogen content (organic and inorganic forms) in precipitation was approximately 1.5 times the inorganic content. No such systematic difference was obvious from data reported from Finland 1984, which reported on both inorganic and total nitrogen at nearby sites.

3. The data reported is assumed to be comparable and not to contain any systematic difference because of sampling and analytical incomparability between the results reported from different stations.

An intercomparison of precipitation collectors, arranged between most of the institutes reporting to HELCOM has been performed. It was performed during three winter and three summer months. 17 samplers/11 institutes participated.

The precipitation weighted mean concentrations of nitrogen (sum of ammonium and nitrate) calculated for the samplers for the whole test period varied from 1.16 - 1.60 mgN/l. The average value was 1.35 and the relative standard deviation 10%. (Granat et al, 1989).

A rough estimate of the annual wet deposition of nitrogen to the Baltic Sea Area based on the uncertainties in the assumptions made, gives a range of 230,000 - 490,000 tonnes nitrogen, see Table 5. The lower limit is based on the assumption that the precipitation amount on the open water is about 30% lower than the climatological values

used in the calculations above. The upper limit is based on the assumption that the content of total nitrogen (inorganic and organic forms) is about 1.5 times the inorganic content.

Table 5. Wet deposition of nitrogen. Estimates for the sub-basins of the Baltic Sea Area for 1986

Sub-basin	Area km ²	Deposition gN/m ² , yr	tonnes N
Bothnian Bay	36 500	0.34 - 0.72	12 500 - 26 000
Bothnian Sea	79 500	0.44 - 0.93	35 000 - 74 000
Gulf of Finland	29 500	0.60 - 1.28	18 000 - 38 000
Baltic Proper,N	168 000	0.55 - 1.17	92 500 - 197 000
Baltic Proper,S	61 000	0.67 - 1.43	41 000 - 87 000
Belt Sea & Katt.	41 000	0.78 - 1.67	32 000 - 68 500
Baltic Sea Area	415 500	0.56 - 1.18	231 000 - 490 500

To obtain a better estimate of the wet deposition the following improvements and investigations should be made :

- More measurement **sites**, especially around the southern part of the Baltic Proper, around Kattegat and along the Swedish Baltic coast.
- Better understanding of the spatial and temporal distribution of precipitation over the Baltic.
- Further investigations on the content of organic nitrogen in precipitation.

The uncertainty in the deposition estimates because of sampling and analytical incomparability seems to be of minor importance.

Dry deposition of gases and aerosols

The dry deposition of nitrogen was estimated from reported data on gaseous and particulate nitrogen using the concept of dry deposition velocity.

The dry deposition of ammonia was considered to be insignificant as only a very small amount of the total ammonium content is present in the gaseous forms. Ferm (1988) reports that on average only 5% of the total ammonium content in air was gaseous. The ammonia is also likely to be in equilibrium with the **sea** water according to Henry's law. The remainder of the ammonia is in particulate form. (Ayers et. al,1984).

The dry deposition of nitrogen dioxide is considered to be very low, because of its low solubility in water. The seasonal variation of nitrogen dioxide (Baltic Marine1988) justifies this assumption.

Gaseous nitric acid, on the other hand, has a very high affinity to water and is thus expected to be readily absorbed. The available information on the abundance of nitric acid in the air in the Baltic region is meagre. According to Granat (1988), approximately 40% of the total nitrates (nitric acid and particulate nitrate) is in gaseous form at the Asvreten station.

Data on total nitrates is reported from three Swedish sites, Vavihill, Rorvik and Aspvreten, see Table 6.

Table 6. Mean air concentrations of total nitrates, total ammonium and particulate ammonium. Stations around the Baltic 1986.

Station	TNO ₃ μgN/m ³		TNH ₄ μgN/m ³	NH ₄ ⁺ μgN/m ³
	Summer	Winter		
Vavihill	0.68	1.32	2.01	
Rorvik	0.73	0.98	1.68	
Aspvreten	0.34	0.48	1.09	
Keldsnor				2.48

Summer = May - Sept; Winter = Oct - Apr
 TNO₃ = HNO₃ (g) + NO₃⁻(p); TNH₄ = HNO₃(g) + NH₄⁺(p)

The deposition of nitrate is therefore calculated by assuming that 40% of the total nitrates is gaseous nitric acid, the remainder in particulate form. Data on particulate nitrate reported from the Soviet stations Lahemaa, Syrve, Nida and Rutsava has not been used,

because only 4-5 monthly averages are reported.

The deposition of particulate ammonium is calculated by using the data on particulate ammonium reported from the Danish station Keldsnor and the data on total ammonium from Vavihill, Rorvik and Aspvreten assuming that 95% of the total ammonium is in the particulate form (see Table 6). The data reported from the Soviet stations has not been **used, because** of the same reasons as for particulate nitrate.

Dry deposition has been calculated using the deposition velocity values given in Table 7.

Table 7. Values of the deposition velocity parameter used to estimate the dry deposition to the Baltic Sea Area.

Compound	Deposition velocity (cm/s)
NH_4^+ (P)	0.1 ^a - 0.4 ^b
NO_3^- (P)	0.1 ^a - 0.5 ^c summer 0.1 ^a - 1.0 ^c winter
HNO_3 (g)	0.5 ^d summer 1.0 ^d winter

a. Slinn & Slinn (1981) ; b. Prahm et al. (1976)
c. Ferm (1984) ; d. Williams (1982)

It is also assumed that data reported from Aspvreten is applicable over most of the Baltic. For the Belt Sea, Kattegat and the southern part of the Baltic Proper, data reported from Rorvik, Keldsnor and Vavihill is used.

The total **dry deposition (gases and aerosols) obtained for the different sub-basins of the Baltic is given in Table 8.**

Table 8. Dry deposition of nitrogen. Estimates for the sub-basins of the Baltic Sea Area for 1986

Sub-basin	Area km ²	Deposition gN/m ² , yr	tonnes N
Bothnian Bay	36 500	0.07 - 0.25	2 500 - 9 000
Bothnian Sea	79 500	0.07 - 0.25	5 500 - 20 000
Gulf of Finland	29 500	0.07 - 0.25	2 000 - 7 500
Baltic Proper,N	168 000	0.07 - 0.25	12 000 - 42 000
Baltic Proper,S	61 000	0.16 - 0.50	10 000 - 31 000
Belt Sea & Katt.	41 000	0.16 - 0.50	6 500 - 20 500
Baltic Sea Area	415 500	0.09 - 0.31	38 500 - 130 000

More data on particulate and gaseous nitrogen compounds in air, as well as a better understanding of the exchange processes between the atmosphere and the sea, is needed to give a greater degree of certainty for the estimated dry deposition.

The total annual deposition (dry + wet) of nitrogen to the Baltic Sea Area is thus estimated to 270,000 - 630,000 tonnes. A summary of wet and dry deposition is given in Table 9.

The deposition level in the southern part of the Baltic (Belt Sea and Kattegat) is about 2.5 times the level in the northern part (Bothnian Bay).

Table 9. Total deposition of nitrogen. Estimates for the sub-basins of the Baltic Sea Area for 1986

Sub-basin	gN/m ² , yr	Deposition tonnes N, yr
Bothnian Bay	0.41 - 0.97	15 000 - 35 000
Bothnian Sea	0.51 - 1.18	40 500 - 94 000
Gulf of Finland	0.67 - 1.53	20 000 - 45 500
Baltic Proper,N	0.62 - 1.42	104 500 - 237 000
Baltic Proper,S	0.83 - 1.93	51 000 - 128 000
Belt Sea & Katt.	0.94 - 2.17	38 500 - 89 000
Baltic Sea Area	0.65 - 1.51	269 500 - 628 500

DEPOSITION OF METALS

Data on trace metals in precipitation has been reported from 6 stations. The annual precipitation weighted mean concentrations are given in Table 10.

Table 10. Annual precipitation weighted mean concentrations of trace metals in precipitation. Stations around the Baltic 1986.

Station	Pb $\mu\text{g/l}$	Cd $\mu\text{g/l}$	cu $\mu\text{g/l}$	Zn $\mu\text{g/l}$
Kiel Bight ^a	9.8		14.3	56.8
Arup	6.8	0.13	1.3	14.9
Aspvreten	4.8	0.10	0.9	10.4
Hapasaari	5.3	0.30	a.9	15.7
Vanhankyl.	5.3	0.30	9.7	21.1
Hailuoto ^b	1.7	0.14	2.7	33.2

a. Based on 4 monthly averages

b. Based on 5 monthly averages

The concentrations of lead show a gradient with higher values in the southern part than in the northern part of the Baltic Sea Area. The concentrations of the other metals do not have any obvious south-north gradient. The relatively high values for copper reported from the stations in the Gulf of Finland (Hapasaari and Vanhankylanmaa) possibly reflect a local/regional influence. The values reported from Kiel Bight and Hailuoto should be treated with caution as they are based on a limited data set.

The data in Table 10 is used to assign the sub-basins of the Baltic Sea Area a typical annual precipitation weighted mean concentration. The data from Kiel Bight and Hailuoto has not been used. Concentration data from the Swedish station Liehittaja (Ross, 1987) from 1985 is used for assigning a typical concentration to the Bothnian Bay. The station is situated along the border between Sweden and

Finland, approximately 100 km from the Baltic coast. The reported concentrations were : Pb 4.1, Cd 0.09, Cu 1.5 and Zn 13 $\mu\text{g}/\text{l}$. The fact that the concentrations of Cu, Zn and Cd in precipitation in the Baltic Sea Area do not show any trend from 1984 to 1987 (Schneider 1988), justifies the use of data from 1985. However, the concentrations of lead show a **significant trend** towards lower values. Thus, the use of data from 1985 possibly results in an overestimation of the concentration in the Bothnian Bay area.

Data from Arup is used for the Belt Sea, Kattegat and the southern part of the Baltic Proper, data from Aspvreten for the northern part of the Baltic Proper, data from Vanhankylanmaa and Hapasaari for the Gulf of Finland and data from Liehittaja for the Bothnian Bay. The values for the Bothnian Sea are calculated as the average of the values from Aspvreten and Liehittaja. The assigned concentration values and the climatological precipitation amount are used to calculate the deposition values given in Tables 11 - 14.

The annual deposition to the Baltic sea area of copper has been estimated at 450 tonnes, of lead at 1300 tonnes, of zinc at 3100 tonnes and of cadmium at 30 tonnes.

Table 11. Annual wet deposition of lead. Estimates for the **sub-basins** of the Baltic Sea Area for 1986.

Sub-basin	Area km^2	Precip. mm	Conc. $\mu\text{g}/\text{l}$	Deposition mg/m^2	tonnes
Bothnian Bay	36 500	510	3.4	1.7	63
Bothnian Sea	79 500	570	4.1	2.3	185
Gulf of Finland	29 500	655	5.3	3.5	102
Baltic Proper,N	168 000	638	4.8	3.1	514
Baltic Proper,S	61 000	638	6.8	4.3	264
Belt Sea, Katteg.	41 000	638	6.8	4.3	177
Baltic Sea Area	415 500	616	5.0	3.1	1305

Table 12. Annual wet deposition of cadmium. Estimates for the **sub-**basins of the Baltic Sea Area for 1986.

Sub-basin	Area km ²	Precip. mm	Conc. µg/l	Deposition mg/m ²	tonnes
Bothnian Bay	36 500	510	0.08	0.04	1.5
Bothnian Sea	79 500	570	0.09	0.05	4.1
Gulf of Finland	29 500	655	0.30	0.20	5.8
Baltic Proper,N	168 000	638	0.10	0.06	10.7
Baltic Proper,S	61 000	638	0.13	0.08	5.1
Belt Sea, Katteg.	41 000	638	0.13	0.08	3.4
Baltic Sea Area	415 500	616	0.12	0.07	30.6

Table 13. Annual wet deposition of copper. Estimates for the **sub-**basins of the Baltic Sea Area for 1986.

Sub-basin	Area km ²	Precip. mm	Conc. µg/l	Deposition mg/m ²	tonnes
Bothnian Bay	36 500	510	1.5	0.77	28
Bothnian Sea	79 500	570	1.2	0.68	54
Gulf of Finland	29 500	655	9.4	6.20	182
Baltic Proper,N	168 000	638	0.9	0.57	96
Baltic Proper,S	61 000	638	1.3	0.83	51
Belt Sea, Katteg.	41 000	638	1.3	0.83	34
Baltic Sea Area	415 500	616	1.7	1.07	445

Table 14. Annual wet deposition of zinc. Estimates for the **sub-**basins of the Baltic Sea Area for 1986.

Sub-basin	Area km ²	Precip. mm	Conc. µg/l	Deposition mg/m ²	tonnes
Bothnian Bay	36 500	510	10.0	5.1	186
Bothnian Sea	79 500	570	10.2	5.8	462
Gulf of Finland	29 500	655	18.5	12.1	357
Baltic Proper,N	168 000	638	10.4	6.6	1115
Baltic Proper,S	61 000	638	14.9	9.5	580
Belt Sea, Katteg.	41 000	638	14.9	9.5	390
Baltic Sea Area	415 500	616	12.1	7.4	3090

The deposition calculation for lead is probably the most reliable, because it is based on a more comprehensive data set than the other ones. The high deposition values for copper to the Gulf of Finland should, as explained above be, treated with caution. The limited data set from Kiel Bight indicates higher concentrations of lead, copper and zinc in the southern part of the Baltic than the ones used in the deposition estimates. Cadmium is not reported from Kiel Bight, but since the correlation between concentrations of cadmium and copper and between cadmium and zinc is high (Ross 1988), the cadmium concentrations used also probably results in an underestimation of the deposition to the southern part of the Baltic.

The intercalibration of analytical methods for trace metals in precipitation in which institutes reporting to HELCOM participated, (Baltic Marine ..,1987) showed that the methods used are by no means satisfactory. Because of both this and the small quantity of reported data, the figures given in Tables 11 - 14 are highly uncertain.

The dry deposition of trace metals was estimated in the evaluation of the data reported to HELCOM 1983-1985 (Baltic Marine1988). Since no further information was available, the previous estimates are used.

A summary of the total deposition (dry + wet) of trace metals to the Baltic Sea Area is given in Table 15.

Table 15. Estimates of metal deposition to the Baltic Sea Area for 1986.

Metal	Deposition, tonnes/yr		
	Wet	Dry	Total
Pb	1 305	255	1 560
Cd	31	4	35
cu	445	20	465
Zn	3 090	310	3 400

DISCUSSION

The deposition estimates given above could be compared with previous estimates for the **Baltic (Table 16)**.

All previous estimates for nitrogen agree well with the broad range that is given in this report. The deposition estimates for lead reported here and in the estimates by Schneider are lower by a factor of 1.5 - 3 than the previous ones. This reflects the reduced use of lead additives in petrol in Europe. The deposition values for cadmium, copper and zinc presented here, which are lower compared to other estimates, can possibly be explained by the lack of complete data sets from the southern part of the Baltic. They can also be explained by the inconsistency in the data reported to the HELCOM database.

Table 16. Some estimates for the atmospheric load to the Baltic/Baltic Sea Area. Unit : Tonnes/year.

Nitrogen	Cd	cu	Pb	Zn	Ref.
400 000	80	1 400	2 400	6 000	Rohde, 1981
500 000	80	600	3 000	8 000	Ferm, 1984
400 000	60	500	2 300	5 200	Balt. Marine, 1988
	57	1 210	1 030	4 740	Schneider, 1988
266 000					Eliassen, 1988
	20		1 150		Petersen, 1988
270 - 630 000	35	470	1 560	3 400	This report

The deposition values given by Rohde, Ferm and in Balt. Marine are based on data on concentrations in air and precipitation; Petersen and Eliassen have used model **calculations**, based on the EMEP-model and emission data, and Schneider has used a combination of the two methods.

All estimates given in this report should be considered to be fairly crude, as they are based on data series with large gaps. Additionally, too little is known about the reliability and comparability of the reported data, especially about the reported data on trace metals. The analytical methods used for determining

components in precipitation have been compared, (Baltic Marine .., 1987) and show satisfactory results for nitrate and ammonium, but unsatisfactory ones for the metals.

The intercomparison of sampling equipment for macroconstituents showed satisfactory results for ammonium and nitrate. The planned intercomparison of samplers for trace metals within PARCOM, where many of the HELCOM members will probably participate, will increase our knowledge and make it possible to make more precise deposition estimates.

A better understanding of the exchange processes between the atmosphere and the sea is also needed to increase the accuracy of deposition estimates.

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Figure 1. Location of stations reporting to HELCOM

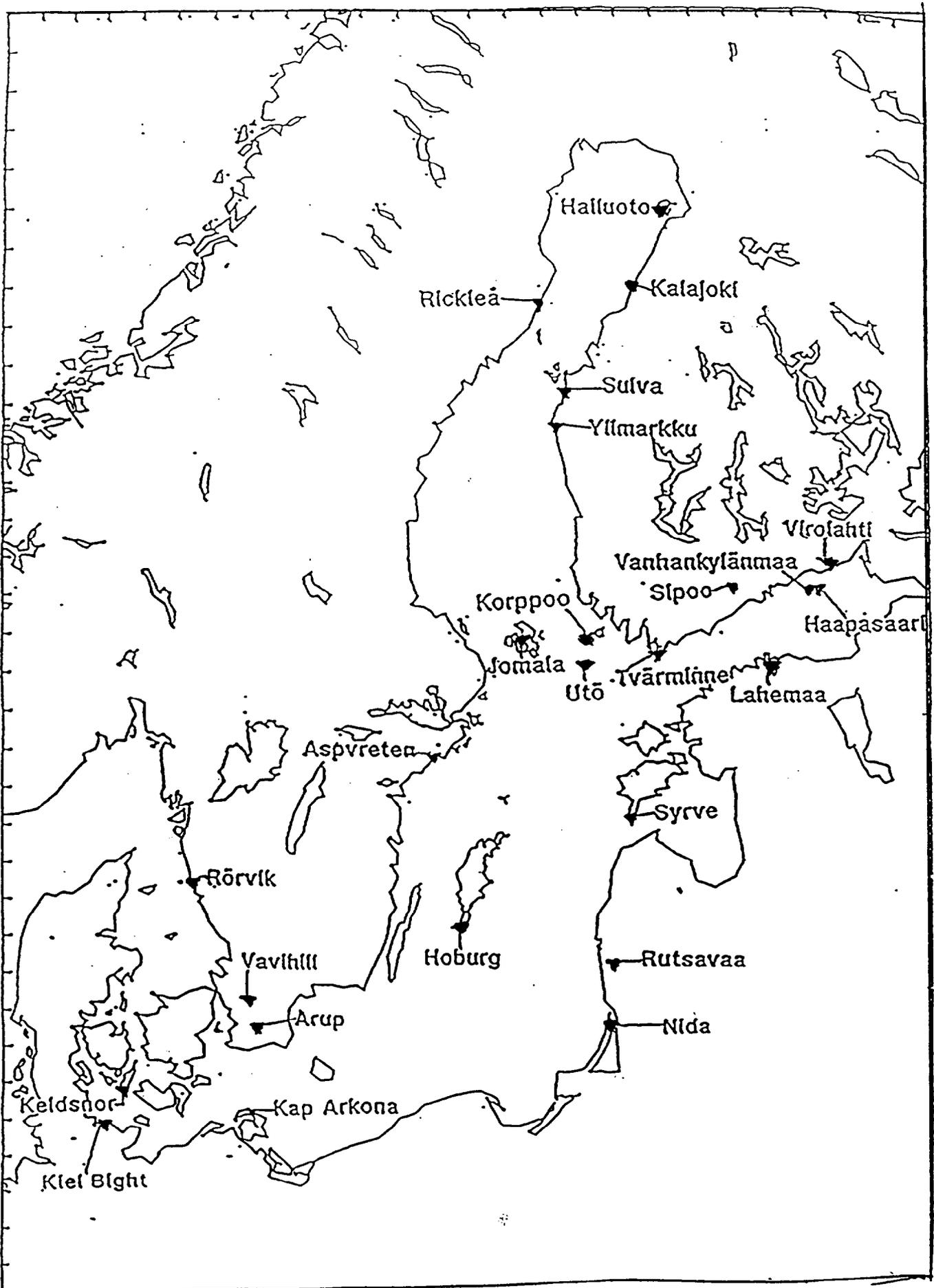
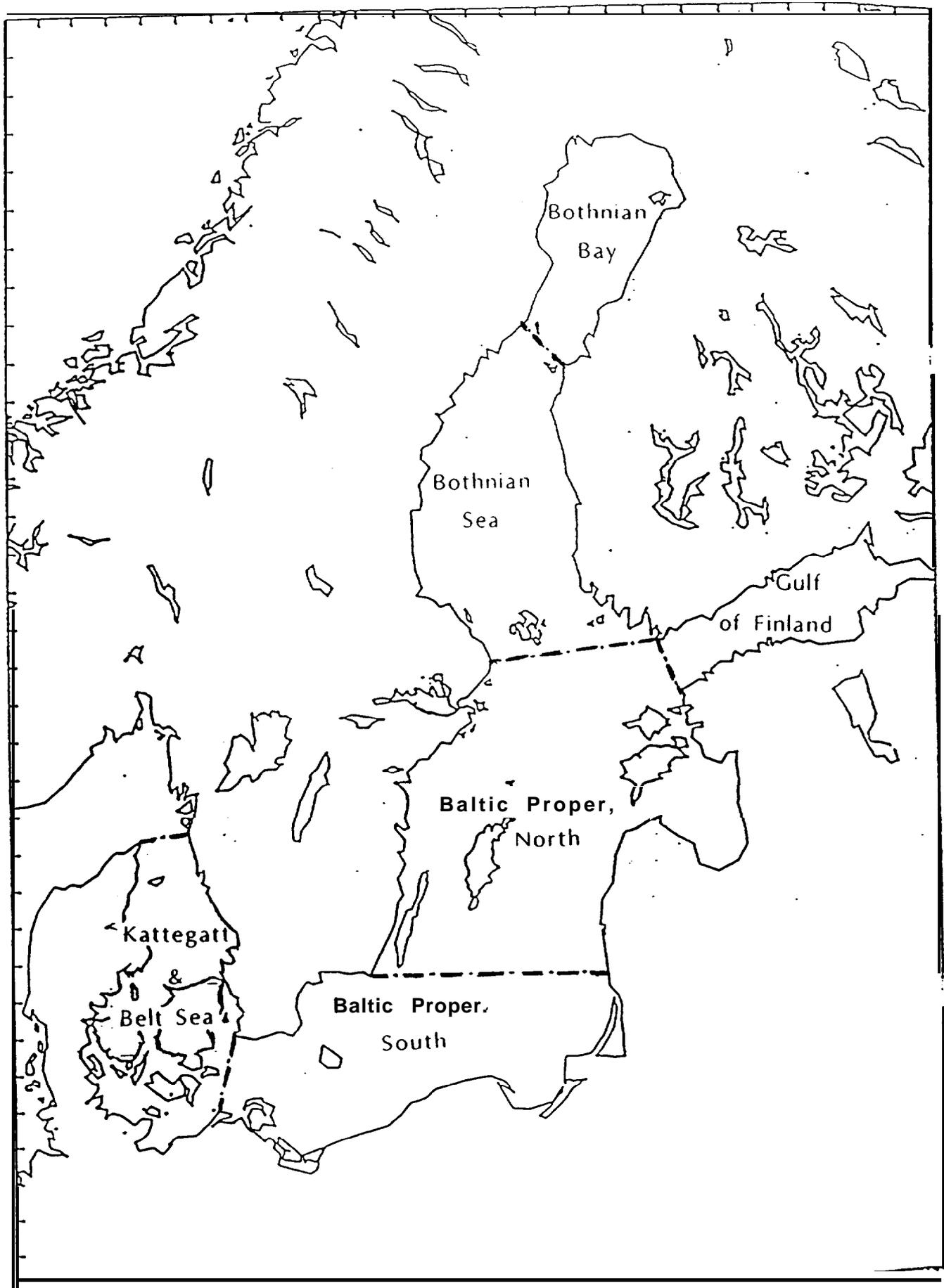


Figure 2. Sub-basins of the Baltic Sea area used for evaluation of spatial distribution.



APPENDIX 1

Air and Precipitation Data for 1986 Reported to HELCOM

Number of monthly values reported per station

Station	Precipitation											Air				
	mm	NO ₃ ⁻	NH ₄ ⁺	SO ₄ ²⁻	Na ⁺	Mg ²⁺	Pb	Cd	Cu	Zn	Cl	SO ₂	SO ₄ ²⁻	NO ₂	TNO ₃	TNH ₄
SF Ylimark		8	10	9	8	8										
SF Hailuot	5	12	11	11	10	10	5	5	5	11						
SF Vanhank	2	12	12	12	12	12	12	2	2							
SF Virolah	2	12	12	12	9	12				2			12			
SF Utö	2	12	12	12	11	11				2			12	4		
SF Haapasa	8	8	8	8	8	8	7	8	8	7						
SF Jomala		10	10	10	9	9				10						
SF Korpoo		10	10	10	9	9				10						
SF Tvärmi		10	10	10	9	9				10						
SF Sipoo		10	10	10	0	0				10						
SF Kalajok		9	10	10	9	9				10						
SF Sulva		10	10	10	9	9				10						
SE Vavihil	11	11	11	11	11	11				11			9	12	11	11
SE Rörvik	11	11	11	11	11	11				11			9	12	12	11
SE Hoburg	12	12	12	12	12	12				12			9	12		
SE Arup	12	12	12	12	12	12	12	2	12	12	12					
SE Aspvre	12	12	12	12	12	12	11	1	11	11	12		2	12	9	11
SE Rickle	12	12	12	12	12	12				12			1			
DK Keldsn	12	12	12	12						12			12	12		12 ^a
DE Kiel B	12	12	8	12			4		4	4	12					
SU Lahema	8	8	8	8	8	8							8	5	8	5 ^b
SU Syrve	11	11	11	11	11								12	5	11	5 ^b
SU Rutsav	12	12	12	12	12								10	4	10	4 ^b
SU Nida	10	10	10	10	10								10	4	9	4 ^b
DD Kap Ar	12	12	12	12	12	12				2			12	11		

b. Reporting NO₃(p)

a. Reporting NH₄(p)

TNH₄ : NH₃(g) + NH₄(p) ; TNO₃ : HNO₃(g) + NO₃(p)

APPENDIX 2

Description of method used for assigning typical monthly concentration and precipitation amount values to the sub-basins of the Baltic Sea Area.

1. Nomination of stations representative for the sub-basins.

Bothnian Bay :	Hailuoto 1 ^a , Hailuoto 2 ^a , Kalajoki, Rickleå, Ylimarku and Sulva.
Gulf of Finland :	Sipoo, Vanhankylanmaa, Hapasaari, Virolahti 1 ^a , Virolahti 2 ^a and Lahemaa.
Baltic proper, North :	Utö, Syrve, Rutsava, Nida, Hoburg and Aspvreten.
Baltic proper, South :	Hoburg, Rutsava, Nida, Kap Arkona Vavihill and Arup.
Belt Sea & Kattegat :	Rorvik, Arup, Vavihill, Keldsnor, Kap Arkona and Kiel Bight.

The Bothnian Sea is treated in another manner. The typical monthly precipitation concentration and amount values are assumed to be an average of the values assigned for the Bothnian Bay and the Archipelago Sea. The stations nominated for the Archipelago Sea are given below.

Archipelago Sea : Jomala, Korpoo, Utö and Tvarminne.

2. Detection of **outliers**.

All monthly values (nitrate, ammonium and precipitation amount) for 1986 from all stations nominated for a sub-basin are plotted. An example is given in figure 2:1. Outliers are detected by visual inspection.

^a Two institutes reports from Hailuoto and Virolahti

The following values are regarded as outliers and are not included when assigning the typical monthly values :

<u>Nitrate</u>		<u>Ammonium</u>		<u>Amount</u>	
Sulva	March	Hail VMS	March	Nida	Jan
Sulva	Dec	Sulva	March	Nida	Apr
Hail VMS	Dec	Ylima	Sept	Nida	May
Utö	Dec	Hail VMS	Dec		
Vanh	Oct	Kala	Dec		
Hapa	Dec	Ylim	Dec		
Vanh	Dec	Sulv	Dec		
Hobu	Feb	Ylim	Jul		
KapA	Aug	Sulv	Jul		
Nida	Dec	Korp	Sep		
KielB	Jan	Sipo	Nov		
KielB	Mar	Lahe	May		
KielB	Apr	Hapa	Nov		
KielB	Oct	Hobu	Jun		
KielB	Nov	Vavi	Mar		
KielB	Dec	KielB	Oct		
		KielB	Nov		
		KielB	Dec		
		Hapa	Dec		

VMS and **FMI** are the notations for the two institutes reporting from Virolahti and Hailuoto.

3. **Calculation of typical monthly precip. amount and concentration values.**

The average of the remaining values from stations nominated as representative for a sub-basin is calculated for each month. The average of the data reported from the Finnish sites with two reporting institutes is used in the calculation.

Nitrate in precipitation 1986

Outlier detection - Baltic Proper, south

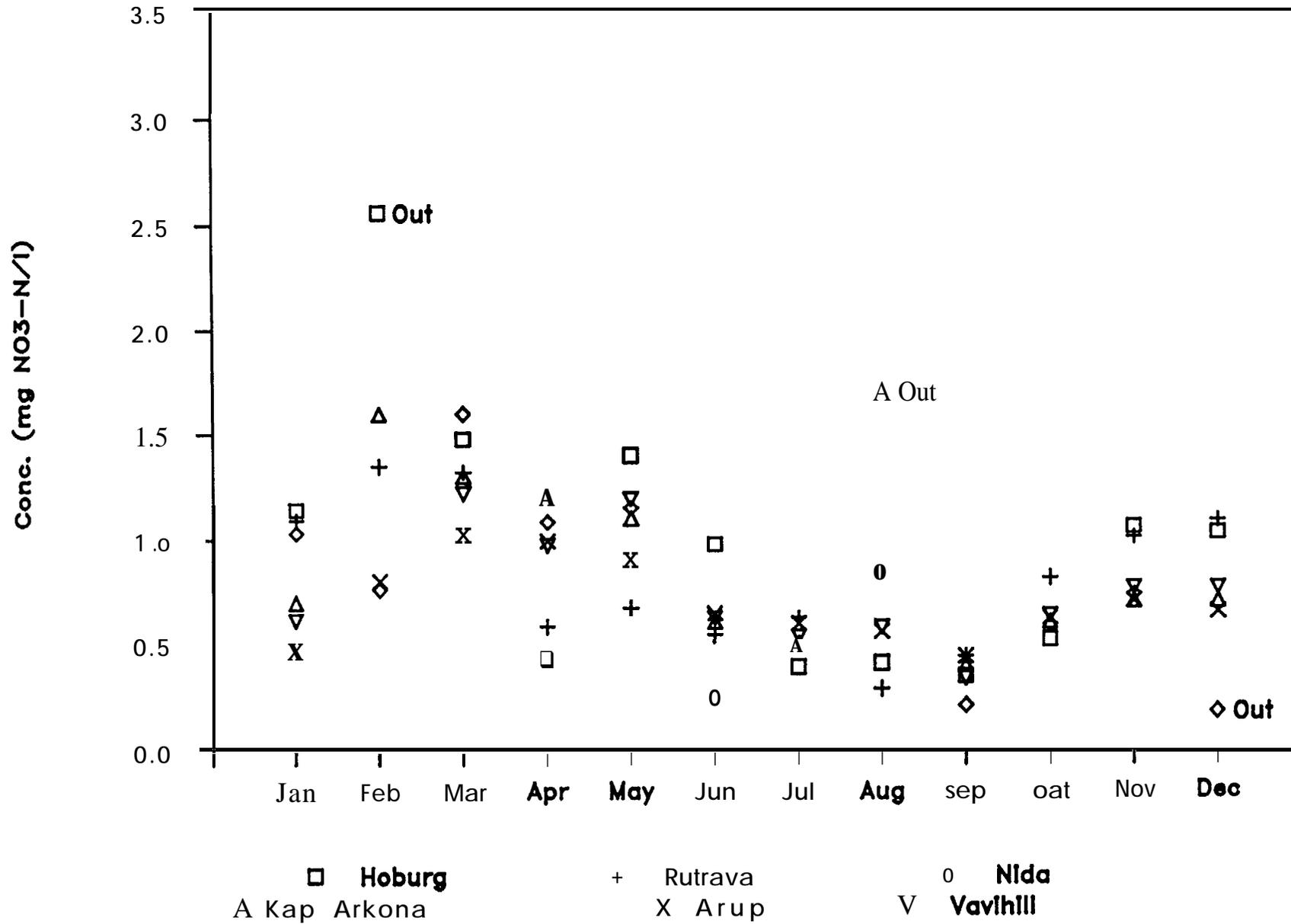


Figure 2:1

BALTIC SEA **ENVIRONMENT** PROCEEDINGS

- No. 1 JOINT ACTIVITIES OF THE BALTIC SEA STATES WITHIN THE FRAMEWORK OF THE CONVENTION ON THE PROTECTION OF THE MARINE ENVIRONMENT OF THE BALTIC SEA AREA 1974-1978
(1979)*
- No. 2 REPORT OF THE INTERIM COMMISSION (**IC**) TO THE BALTIC MARINE ENVIRONMENT PROTECTION COMMISSION
(1981)
- No. 3 ACTIVITIES OF THE COMMISSION 1980
- Report on the activities of the Baltic Marine Environment Protection Commission during 1980
- HELCOM Recommendations passed during 1980
(1981)
- No. 4 BALTIC MARINE ENVIRONMENT BIBLIOGRAPHY 1970-1979
(1981)
- No. 5A ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980
PART A-1: OVERALL CONCLUSIONS
(1981)*
- No. 5B ASSESSMENT OF THE EFFECTS OF POLLUTION ON THE NATURAL RESOURCES OF THE BALTIC SEA, 1980
PART A-1: OVERALL CONCLUSIONS
PART A-2: SUMMARY OF RESULTS
PART B: SCIENTIFIC MATERIAL
(1981)
- No. 6 WORKSHOP ON THE ANALYSIS OF HYDROCARBONS IN SEAWATER
Institut **für** Meereskunde an der **Universität** Kiel, Department of Marine Chemistry, March 23 - April 3, 1981
(1982)
- No. 7 ACTIVITIES OF THE COMMISSION 1981
- Report of the activities of the Baltic Marine Environment Protection Commission during 1981 including the Third Meeting of the Commission held in Helsinki 16-19 February 1982
- HELCOM Recommendations passed during 1981 and 1982
(1982)
- No. 8 ACTIVITIES OF THE COMMISSION 1982
- Report of the activities of the Baltic Marine Environment Protection Commission during 1982 including the Fourth Meeting of the Commission held in Helsinki 1-3 February 1983
- HELCOM Recommendations passed during 1982 and 1983
(1983)
- No. 9 SECOND BIOLOGICAL INTERCALIBRATION WORKSHOP
Marine Pollution Laboratory and Marine Division of the National Agency of Environmental Protection, Denmark, August 17-20, 1982, **Rønne**, Denmark
(1983)

* out of print

- No. 10** TEN YEARS AFTER THE SIGNING OF THE HELSINKI CONVENTION
National Statements by the Contracting Parties on the
Achievements in Implementing the Goals of the Convention on the
Protection of the Marine Environment of the Baltic Sea Area
(1984)
- No. 11** STUDIES ON SHIP CASUALTIES IN THE BALTIC SEA 1979-1981
Helsinki University of Technology, Ship Hydrodynamics Labora-
tory, Otaniemi, Finland
P. Tuovinen, V. Kostilainen and A. **Hämäläinen**
(1984)
- No. 12 GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE SECOND
STAGE
(1984)
- No. 13 ACTIVITIES OF THE COMMISSION 1983
- Report of the activities of the Baltic Marine Environment
Protection Commission during 1983 including the Fifth Meeting
of the Commission held in Helsinki 13-16 March 1984
- HELCOM Recommendations passed during 1983 and 1984
(1984)
- No. 14 SEMINAR ON REVIEW OF PROGRESS MADE IN WATER PROTECTION MEASURES
17-21 October 1983, **Espoo**, Finland
(1985)
- No. 15 ACTIVITIES OF THE COMMISSION 1984
- Report on the activities of the Baltic Marine Environment
Protection Commission during 1984 including the Sixth Meeting
of the Commission held in Helsinki 12-15 March 1985
- HELCOM Recommendations passed during 1984 and 1985
(1985)
- No. 16 WATER BALANCE OF THE BALTIC SEA
A Regional Cooperation Project of the Baltic Sea States;
International Summary Report
(1986)
- No. 17A FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT
OF THE BALTIC SEA AREA, 1980-1985; GENERAL CONCLUSIONS
(1986)
- No. 17B FIRST PERIODIC ASSESSMENT OF THE STATE OF THE MARINE ENVIRONMENT
OF THE BALTIC SEA AREA, 1980-1985; BACKGROUND DOCUMENT
(1987)
- No. 18 ACTIVITIES OF THE COMMISSION 1985
- Report on the activities of the Baltic Marine Environment
Protection Commission during 1985 including the Seventh Meeting
of the Commission held in Helsinki 11-14 February 1986
- HELCOM Recommendations passed during 1986
(1986)*
- No. 19 BALTIC SEA MONITORING SYMPOSIUM
Tallinn, USSR, 10-15 March 1986
(1986)

- No. 20 FIRST BALTIC SEA POLLUTION LOAD COMPILATION
(1987)*
- No. 21 SEMINAR ON REGULATIONS CONTAINED IN ANNEX II OF MARPOL 73/78 AND
REGULATION 5 OF ANNEX IV OF THE HELSINKI CONVENTION
National Swedish Administration of Shipping
and Navigation; 17-18 November 1986, Norrköping,
Sweden
(1987)
- No. 22 SEMINAR ON OIL POLLUTION QUESTIONS
19-20 November 1986, Norrköping, Sweden
(1987)
- No. 23 ACTIVITIES OF THE COMMISSION 1986
- Report on the activities of the Baltic Marine Environment
Protection Commission during 1986 including the Eighth Meeting
of the Commission held in Helsinki 24-27 February 1987
- HELCOM Recommendations passed during 1987
(1987)*
- No. 24 PROGRESS REPORTS ON CADMIUM, MERCURY, COPPER AND ZINC
(1987)
- No. 25 SEMINAR ON WASTEWATER TREATMENT IN URBAN AREAS
7-9 September 1986, Visby, Sweden
(1987)
- No. 26 ACTIVITIES OF THE COMMISSION 1987
- Report on the activities of the Baltic Marine Environment
Protection Commission during 1987 including the Ninth Meeting
of the Commission held in Helsinki 15-19 February 1988
- HELCOM Recommendations passed during 1988
(1988)
- No. 27A GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE THIRD
STAGE; PART A. INTRODUCTORY CHAPTERS
(1988)
- No. 27B GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE THIRD
STAGE; PART B. PHYSICAL AND CHEMICAL DETERMINANDS IN SEA WATER
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- No. 27C GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE THIRD
STAGE; PART C. HARMFUL SUBSTANCES IN BIOTA AND SEDIMENTS
(1988)
- No. 27D GUIDELINES FOR THE BALTIC MONITORING PROGRAMME FOR THE THIRD
STAGE; PART D. BIOLOGICAL DETERMINANDS
(1988)
- No. 28 RECEPTION OF WASTES FROM SHIPS IN THE BALTIC SEA AREA
- A MARPOL 73/78 SPECIAL AREA
(1989)

- No. 29 ACTIVITIES OF THE COMMISSION 1988
- Report on the activities of the Baltic Marine Environment
 Protection Commission during 1988 including the Tenth Meeting
 of the Commission held in Helsinki 14-17 February 1989
- HELCOM Recommendations passed during 1989
(1989)
- No. 30 SECOND SEMINAR ON WASTEWATER TREATMENT IN URBAN AREAS
6-8 September 1987, Visby, Sweden
(1989)
- No. 31 THREE YEARS OBSERVATIONS OF THE LEVELS OF SOME RADIONUCLIDES IN
THE BALTIC SEA AFTER THE CHERNOBYL ACCIDENT
Seminar on Radionuclides in the Baltic Sea
29 May 1989, Rostock-Warnemünde, German Democratic Republic
(1989)

**Baltic Marine Environment
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— Helsinki Commission —
Mannerheimintie 12 A
SF-00100 Helsinki

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