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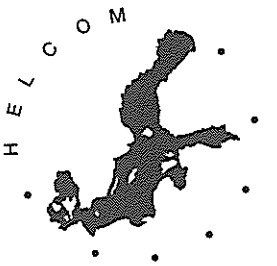
Atmospheric Supply of Nitrogen, Lead, Cadmium, Mercury and Lindane to the Baltic Sea over the period 1996–2000



Helsinki Commission
Baltic Marine Environment Protection Commission

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Contents

Introduction

This report was prepared for the Helsinki Commission (HELCOM), Baltic Marine Environment Protection Commission, and is based on modeling estimates and monitoring results presented to the twenty-sixth session of the Steering Body of EMEP (Co-operative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe).

The fifth joint summary report for HELCOM follows guidelines arising from the third MONAS Meeting conducted in Ispra, Italy during 2001 and uses direct measurements as well as the results of modelling analyses to determine the levels of oxidized nitrogen, reduced nitrogen, lead, cadmium, mercury and lindane depositions in the Baltic Sea region over the five year period 1996 - 2000. The report was developed in a framework of close collaboration among three EMEP centres: Meteorological Synthesizing Centre –West (MSC-W), Meteorological Synthesizing Centre – East (MSC-E) and Chemical Coordinating Centre (CCC), and is available online, on the main EMEP website and also on the HELCOM website. The report was presented in draft form and discussed at the fourth MONAS Meeting in Warnemünde (21-25/10/2002). Participants of this meeting were asked to contribute comments and amendments, which are included in the final version.

Acknowledgements

The authors are indebted to the scientific teams at MSC-E, MSC-W and CCC for providing the results which form the basis of this report and are especially grateful to Heiko Klein for his help with the Internet-related tasks, Hilde Fagerli for stimulating discussions and deposition maps, and Vigdis Vestreng for the emissions data and related comments. We are indebted to Ms. Marina Varygina, Dr. Ilia Iliyn, Prof. Victor Shatalov and Dr. Alexander Malanichev for their contribution to this work, as well as their valuable remarks and comments.

1 Executive summary

Following decisions arising out of the third HELCOM-MONAS Meeting in Ispra, Italy the 2002 Joint EMEP Report for HELCOM is based on two main goals. The first is to provide the data required for the Pollution Load Compilation (PLC) task of considering atmospheric input. The second is to provide the input data for the draft indicator report. Because of this dual purpose, the monitoring data, model results and analysis presented here, cover the five-year period 1996 – 2000.

Summary findings for each compound

Nitrogen

A new unified model was used for nitrogen computations over the period 1996-2000. Tests performed using this model to date, indicate that it provides improved and more reliable results than the previous method. However, because by the time calculations were performed the model was not operational, we recommend that the results presented here for nitrogen be considered only preliminary.

In the cases of nitrogen oxides and ammonia, the emission data used in the model computations were observed to have declined from 1996 to 2000. Additionally annual emissions of nitrogen oxides from HELCOM countries declined by 13.5%, while emissions of ammonia and total nitrogen fell by 11% and 9% respectively. Annual nitrogen oxides emissions from the international shipping traffic on the Baltic Sea available for 1990 were used for the period under review. Nitrogen emission reduction was observed to be more effective in HELCOM countries than in the entire EMEP domain, where nitrogen and ammonia decreased by 9% and 4% respectively.

In spite of these positive developments, recorded air concentrations of nitrogen compounds over the period 1996-2000 have shown an irregular pattern. There is some suggestion of decline in concentrations on the southern Baltic shore, but otherwise the temporal pattern is somewhat erratic. In addition to this, the observed concentrations of nitrate and ammonium in precipitation do not themselves reveal clear temporal patterns during the period under consideration.

Consistent with the recorded data, the time series analysis of computed annual depositions for the period 1996 – 2000 also deviate from the reported emission changes. It should be noted however, that when an uncertainty level of approximately 30% is factored into the model results, there is no significant difference between measured and computed values for annual depositions. Alternatively, the overriding impact of meteorology during the short period under consideration may possibly explain why the effects of the modest emission changes are not reflected in the computed deposition values.

A second and more significant reason for the slight variation between the patterns of emission on the one hand and the measurements and computed depositions on the other, is the lack of updated information on nitrogen emissions from the ship traffic. Other than for the year 1990, there is no data available on international shipping traffic on the Baltic Sea, and this difficulty is compounded by the inevitable uncertainty in the reported terrestrial emissions. Shipping emissions are a major contributor to nitrogen deposition in the Baltic Sea and if unreported or underestimated can result in significant errors in computed depositions. Not to be forgotten, are the impact of distant emission sources from countries beyond the HELCOM region, and the fact that some nitrogen components can be long-lived in the atmosphere.

Heavy metals

Based on available official data and expert estimates, the emissions of heavy metals from the HELCOM countries decreased during 1996-2000 by 26% in the case of Cd, by 15% for Hg, and by 10% for Pb. Across the entire EMEP region, the decrease of heavy metal emissions was more significant: in 2000 emissions of lead, cadmium and mercury were 31%, 22%, and 17% lower than those in 1996, respectively.

As for nitrogen, measured air concentrations of heavy metals do not reflect a consistent regional pattern between 1996 and 2000. In Germany and Denmark some decline was observed in heavy metals concentrations in air, but elsewhere there was no discernible pattern.

Temporal patterns are equally unclear. In order to maintain a reasonable level of comparability among the stations on the basis of the available data, analysis began only from 1990. In spite of this, the degree of inter-annual variability appears quite large, and as a result, the approach does not reveal any recognizable patterns. It should also be noted that the stations observed varied from year-to-year. Even so, narrowing the analysis to review the recorded concentrations at individual stations also does not highlight any consistent regional patterns. For example, in the case of lead concentrations, there appear to be declines observed at Zingst and Vilsandy in Germany and Estonia respectively, while between these two stations there appears to be no clear pattern of concentrations.

According to modelling results for the period 1996-2000, atmospheric depositions of lead and cadmium into the Baltic Sea region decreased by approximately 4%, while atmospheric depositions of mercury increased by 14% during the same interval.

As in the case of nitrogen, computed depositions of heavy metals do not closely reflect the observed emission patterns between 1996 and 2000. In this case also, the sensitivity of the heavy metals model to meteorological conditions could explain such findings. Moreover information about heavy metals emissions from international shipping traffic on the Baltic Sea does not exist. If taken into account, this important emission source could significantly alter the emissions pattern for the period 1996 – 2000.

Source allocation budgets of heavy metals depositions into the Baltic Sea were computed for the entire period 1996 – 2000. The results revealed that the input of anthropogenic sources to atmospheric depositions in 2000 decreased in comparison with 1996. A significant proportion of these inputs was due to natural, previous and remote anthropogenic sources.

In the case of cadmium, the proportion contributed by HELCOM countries to total deposition into the Baltic Sea decreased from 50% to 39% during the period 1996-2000. Of all these countries, anthropogenic emission sources from Poland accounted for the most significant inputs – 34% in 1996 and 24% in 2000. Other EMEP countries contributed 7% in 1996 and 11% in 2000.

HELCOM countries' total deposition of lead into the Baltic Sea declined from 39% to 31%. Sources from Poland represented the most significant contribution – 14% in 1996 and 11% in 2000. Other EMEP countries accounted for roughly 20%.

With respect to mercury, HELCOM territories and other EMEP countries' total depositions into the Baltic Sea remained at practically the same level during the period 1996- 2000. The most significant contributions from HELCOM countries in 1996 came from Poland (15%) and from Germany in 2000 (19%). Other EMEP countries were accounted for 5-6% of the total.

Lindane (γ-HCH)

According to available official information and expert estimates, most of the changes in lindane (γ-HCH) emissions occurred during the 1970s and 1980s as a result of restrictions or prohibitions on of the use of lindane. Over the period 1990-1998, emissions of lindane (γ-HCH) in the Baltic Sea region decreased by almost two orders of magnitude. At the same time lindane emissions in the entire European region decreased by only 20% during the same period.

In spite of the significant decrease in lindane emissions in HELCOM countries during the period 1990-1998, the level of lindane (γ-HCH) depositions into the Baltic Sea decreased by only 14%. This phenomenon can be accounted for by the impact of sources of lindane emissions outside the Baltic Sea region.

Recommendations to HELCOM

Lack of, or inaccurate emission data for international shipping traffic on the Baltic Sea is one possible explanation for the differences between the pattern of computed depositions and the pattern of emissions during the period 1996 – 2000. It is consequently recommended that the nitrogen emission data from shipping traffic on the Baltic Sea be brought up to date for the entire five-year period under review, or at least for the beginning and end of the considered period.

Corresponding emission data do not exist for heavy metals at all. In the case of lead and cadmium at least, emissions from shipping can be an important source in the deposition of these metals into the Baltic Sea. It is therefore proposed that emission inventories covering at minimum the latter part of

the survey period should be developed at least for the two mentioned metals.

Regional patterns of atmospheric deposition into the Baltic Sea vary significantly, depending on the component in question. As a result, both measurements and model results are needed for accurate estimation of the atmospheric load of pollution. A long term series of measurements from the stations close to the coast or located on the islands would be especially useful for this purpose.

2 State of the airborne load during the period 1996 – 2000

2.1 Measured concentrations in air and precipitation

This chapter outlines the state of the airborne load into the Baltic Sea during the period 1996 – 2000, as recorded by observation.

2.1.1 Overview of HELCOM stations and available measurements

The HELCOM measurement database for nitrogen compounds, heavy metals and persistent organic pollutants is located at the Norwegian Institute for Air Research (NILU) in Kjeler, Norway. During the period 1996 – 2000, a total of 17 HELCOM stations reported measurements of concentrations in air as well as precipitation. The list of available measurements at the HELCOM stations for nitrogen, heavy metals and POPs is given in Tables 2.1, 2.2 and 2.3, respectively. All stations reported measurements for nitrogen, 13 stations reported for heavy metals and results for lindane were available from only 3 stations. Shading in Tables 2.1 – 2.3 indicates data available for at least one compound.

A map detailing the geographical locations of the HELCOM stations is shown in Figure 2.1. Most of these stations are located in the southern sub-basins of the Baltic Sea.

2.1.2 Measured concentrations in air

Measurements of nitrogen concentrations in the air were available from 15 HELCOM stations for the entire period 1996 – 2000. In the case of heavy metals, 11 stations reported data but only 7 submitted observations for the entire 5-year period. With respect to lindane, measurements were available from only 2 Swedish stations, 1 of which reported for the entire 5-year period, and the other for 4 years.

The pattern of nitrogen compound concentrations in air during the 1996-2000 period has been uncertain. There is some suggestion of a decline in concentrations on the southern Baltic shore, but the temporal pattern is otherwise erratic. This is consistent with the emerging picture concerning nitrogen present in precipitation.

Similarly, concentrations of heavy metals in air do not indicate a consistent regional pattern for the period. As with precipitation, concentrations in Germany and Denmark indicate some decline, but patterns elsewhere are variable.

Because lindane (γ-HCH) concentrations in air were reported by only 2 Swedish stations, it is not possible to draw any general conclusions about this compound. However, available measurements suggest large inter-annual variations of lindane (γ-HCH) concentrations in the air and a general absence of any significant trends during the 5-year period of the study.

2.1.3 Measured concentrations in precipitation

Measurements of nitrate and ammonium in precipitation were performed at 16 HELCOM stations, but only 11 stations reported observations for the entire period 1996 – 2000. In the case of heavy metals, 13 stations reported concentrations in precipitation, but only 8 of them for the entire 5-year period. Data on lindane (γ-HCH) concentrations in precipitation are available only from 1 station located in Germany - Zingst - and only for 2 years: 1996 and 1997.
The observed concentrations of nitrate and ammonium in precipitation do not themselves reveal clear temporal patterns during the 5-year period. Analysis has therefore focused on the annual average rates of deposition of nitrogen in precipitation (i.e. concentration multiplied by total precipitation) into coastal waters. The analysis considered the data submitted by all the monitoring stations, for any year, with values precipitation-weighted to generate a single indicative vaiue. This study covered the period 1990-2000, and even this approach yielded no clear trend between 1996 and 2000. The early years of the decade indicate an apparent decline of 30% or more in the annual rates of nitrogen deposition, while during the latter years the picture reveals relatively little change.

Temporal patterns of metals concentrations are equally unclear. In order to maintain a reasonable degree of comparability among the stations with available data, the analysis commenced only from 1990. However, because of a high degree of inter-annual variability even this approach did not reveal any apparent patterns. However these results should be treated with caution as there was some variation in the stations considered from year-to-year. At same time, it must be remembered that a review of the observed concentrations at individual stations

does not suggest consistent regional patterns. For example, in the case of lead there appeared to be decreased concentrations at Zingst and Vilsandy in Germany and Estonia respectively, while between these 2 stations there is a very variable pattern. The same observations hold for other compounds.

Where lindane (γ-HCH) is concerned there are not enough available measurements to draw any conclusions for the Baltic Sea region.

2.1.4 Quality of observations: the observation metadata

The accompanying metadata or "information about the data" assists with interpretation of the recorded observations. Details relating to the quality and availability of the data in time and space are provided in Chapter 5. Precise information on the accuracy, detection limits and precision of the reported observations has been provided in the Annex.

Station		Nitrogen in air					Nitrogen in precipitation				
Code	Name	1996	1997	1998	1999	2000	1996	1997	1998	1999	2000
FI53	Hailuoto										
FI9	Uto										
FI17	Virolahti										
EE09	Lahemaa										
LV16	Zoseni										
EE11	Vilsandy										
LV10	Rucava										
LT15	Preila										
PL04	Leba										
DE09	Zingst										
SE05	Bredkalen										
SE08	Hoburg										
SE12	Aspvreten										
SE02	Roervik										
SE11	Vavihill										
DK05	Keldsnor										
DK08	Anholt										

Table 2.1.
Nitrogen measurements from HELCOM stations for the period 1996 - 2000. The colour green indicates data available for at least one component.

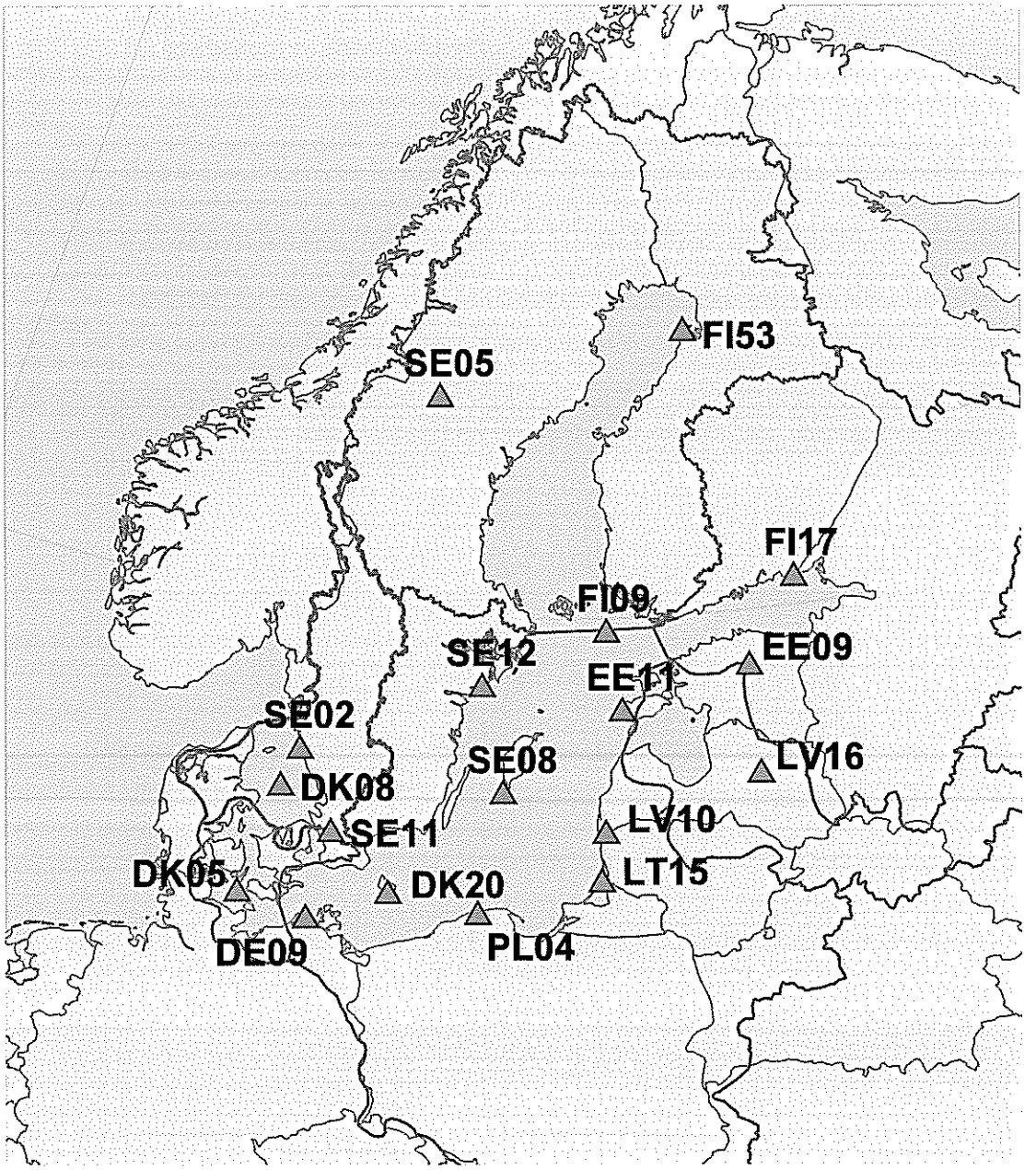
Station		Metals in air					Metals in precipitation				
Code	Name	1996	1997	1998	1999	2000	1996	1997	1998	1999	2000
FI53	Hailuoto										
FI9	Uto										
FI17	Virolahti										
EE09	Lahemaa										
LV16	Zoseni										
EE11	Vilsandy										
LV10	Rucava										
LT15	Preila										
PL04	Leba										
DE09	Zingst										
DK20	Bornholm										
SE12											
DK05	Keldsnor										
DK08	Anholt										

Table 2.2.
Heavy metals measurements from HELCOM stations for the period 1996 - 2000. The colour green indicates data available for at least one component.

Station		γ-HCH in air					γ-HCH in precipitation				
Code	Name	1996	1997	1998	1999	2000	1996	1997	1998	1999	2000
DE09	Zingst										
SE02	Roervik										
SE12	Aspvreten										

Table 2.3.
Lindane (γ-HCH) measurements from HELCOM stations for the period 1996 - 2000. The colour green indicates data available for at least one component.

Figure 2.1
Geographical locations of HELCOM stations with available measurements for the period 1996 - 2000.



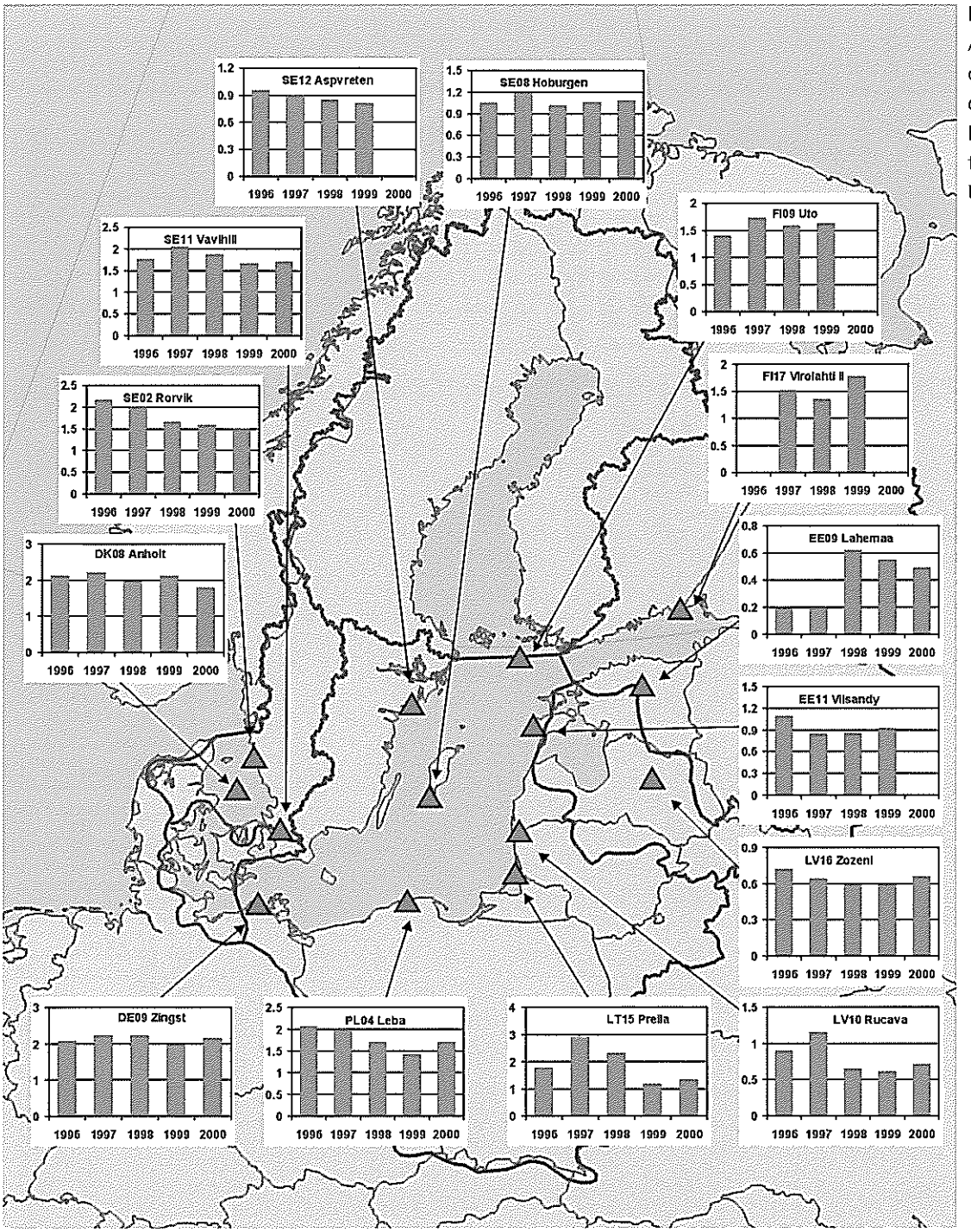
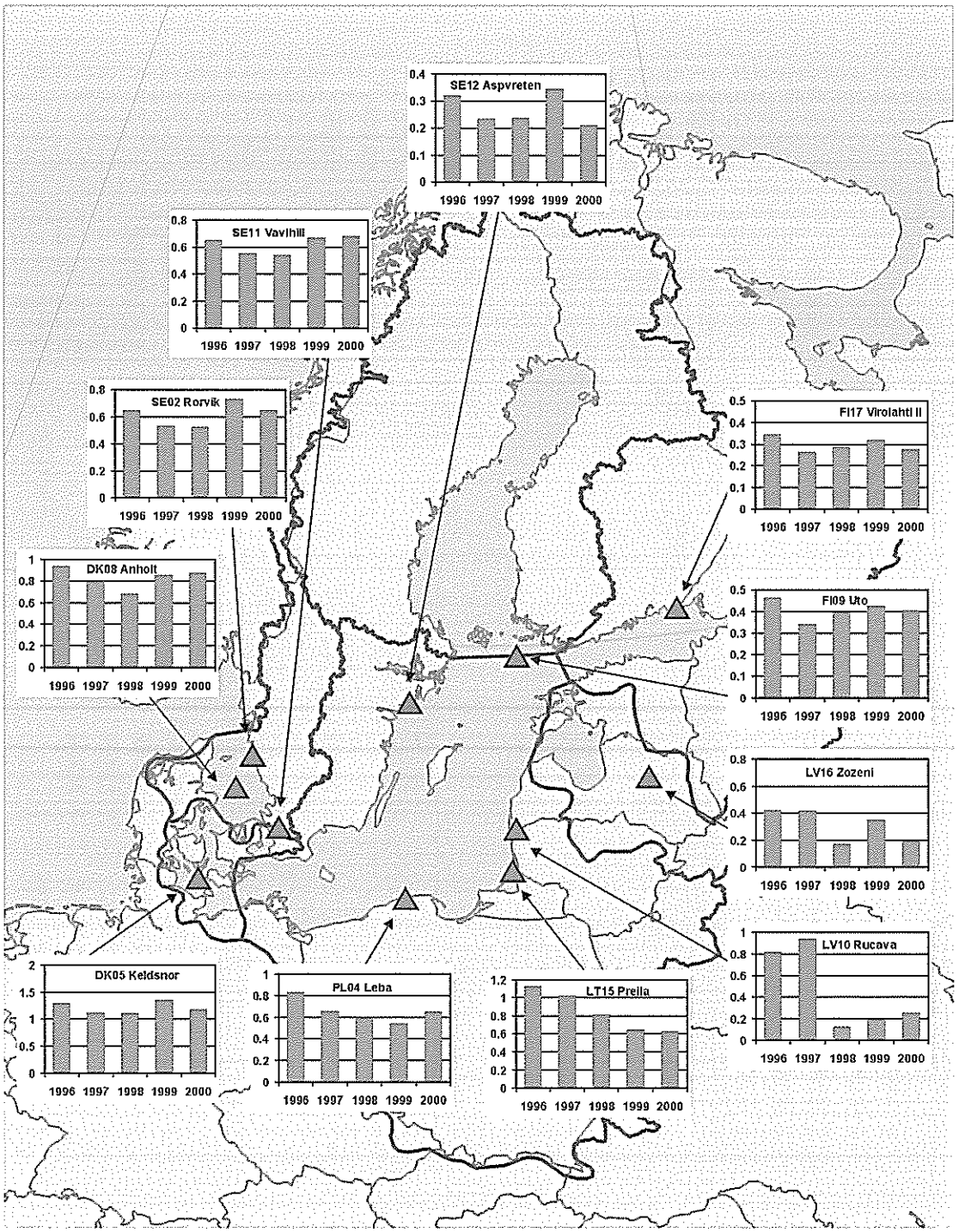


Figure 2.2
Annual average concentrations of nitrogen oxide in air measured, at HELCOM stations, over the period 1996-2000. Units: µg N/m³.

Figure 2.3
Annual average concentrations of total nitrate (HNO_3+NO_3-N) in the air measured at HELCOM stations over the period 1996-2000.
Units: µg N/m³.



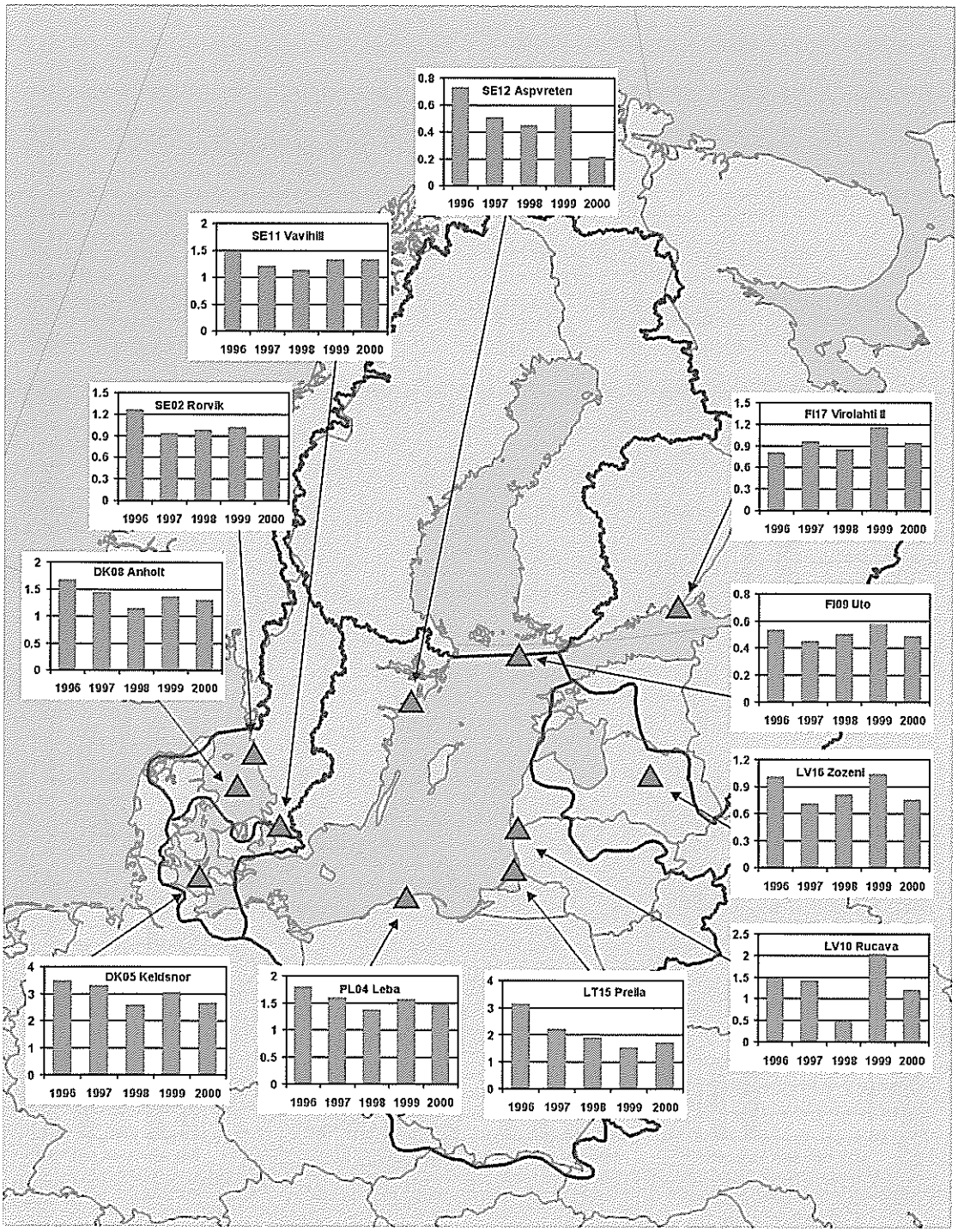
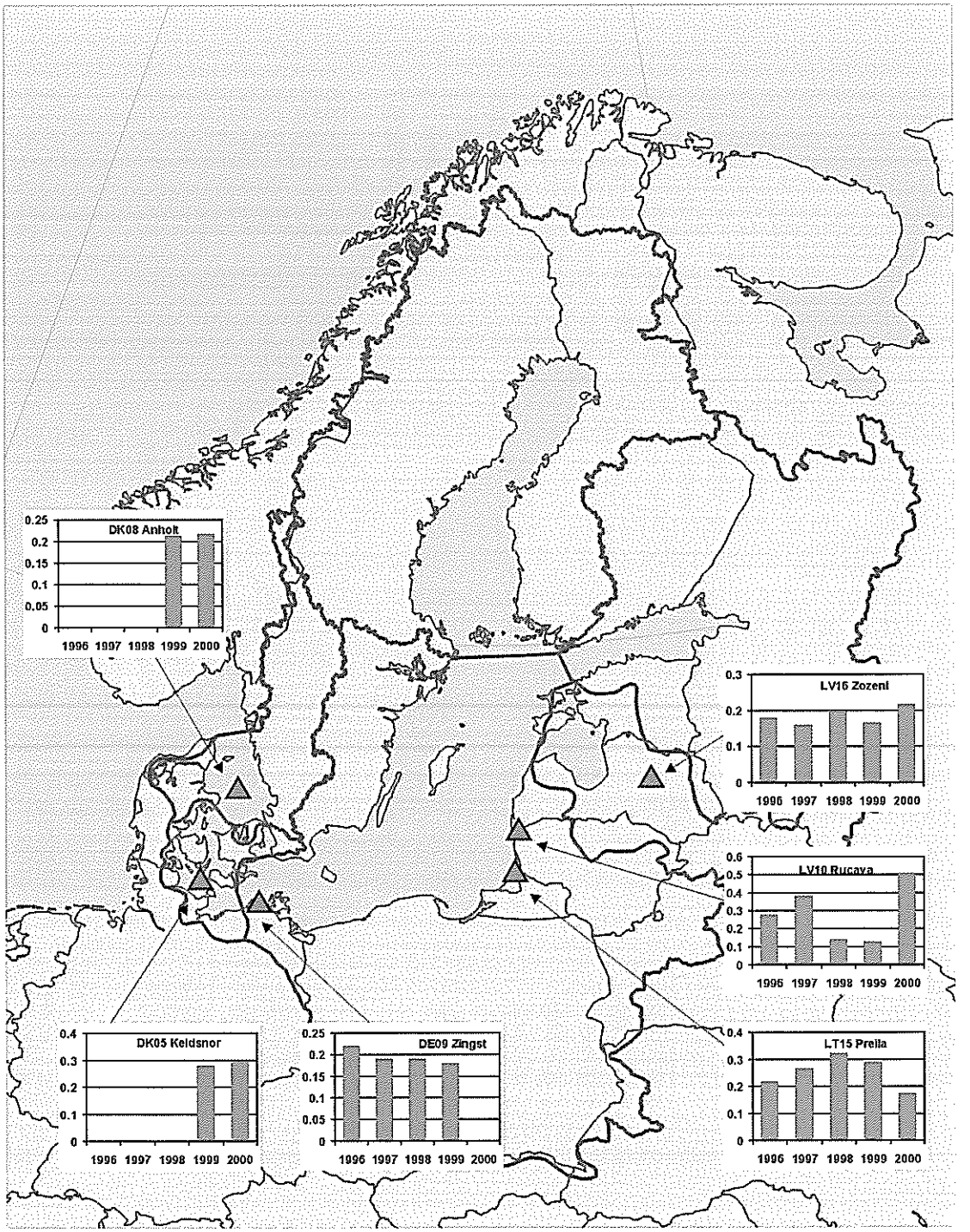


Figure 2.4
Annual average concentrations of reduced nitrogen (NH_3+NH_4^+-N) in the air measured at HELCOM stations over the period 1996-2000.
Units: µg N/m^3.

Figure 2.5
Annual average concentrations of cadmium in the air measured at HELCOM stations over the period 1996-2000. Units: ng/m³.



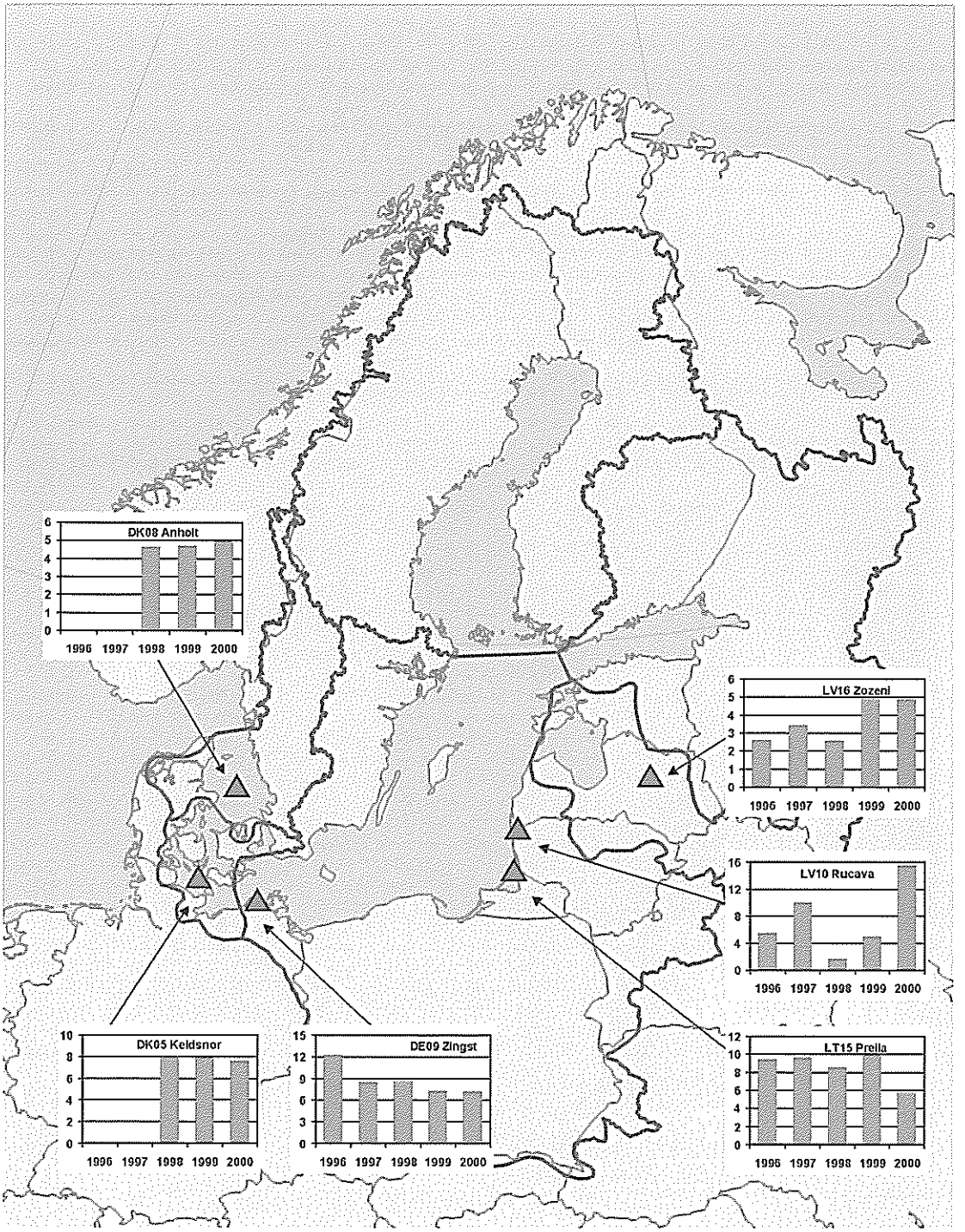
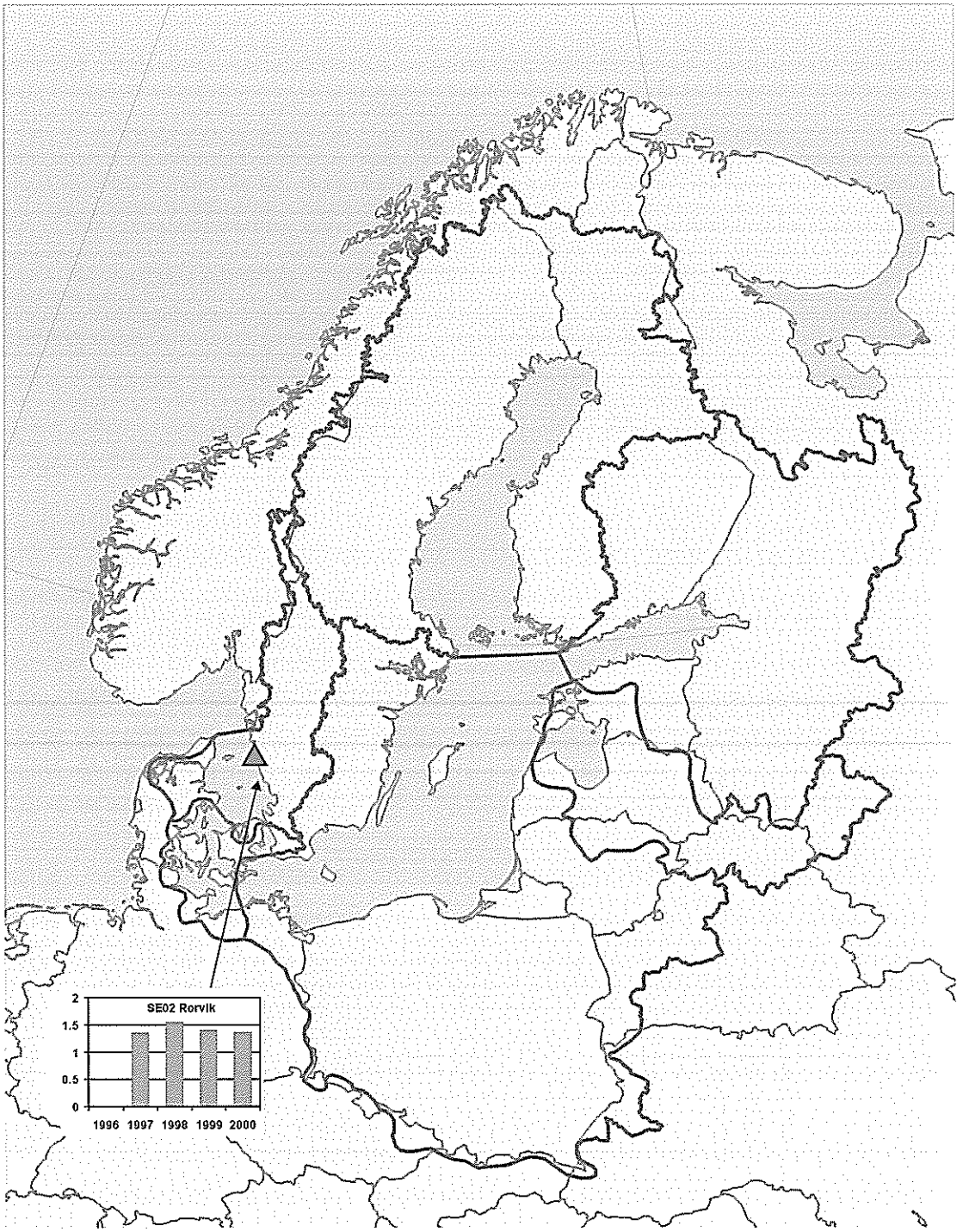


Figure 2.6
Annual average concentrations of lead in the air measured at HELCOM stations over the period 1996-2000.
Units: ng/m^3.

Figure 2.7
Annual average concentrations of mercury in the air measured at HELCOM stations over the period 1996-2000. Units: ng/m^3.



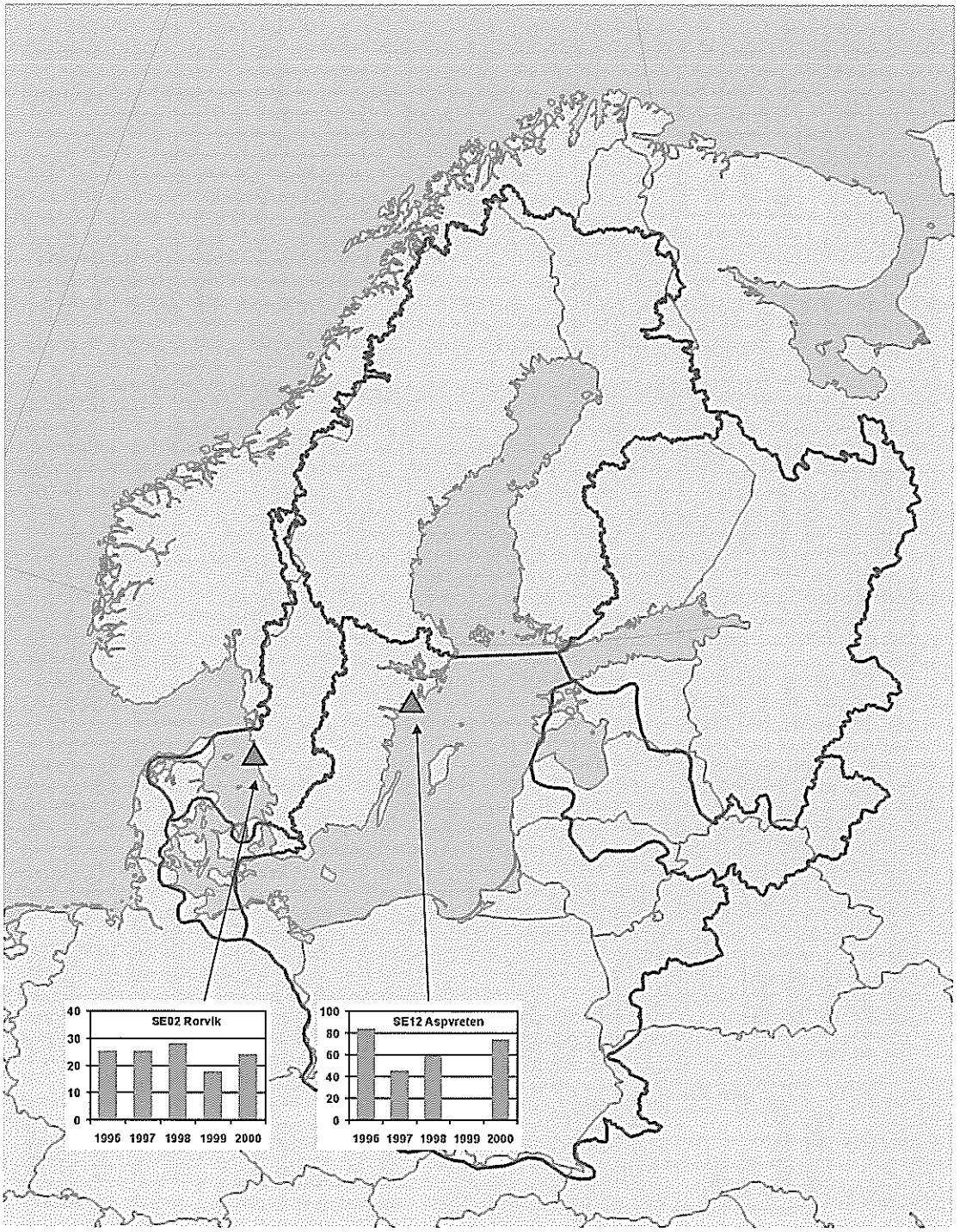
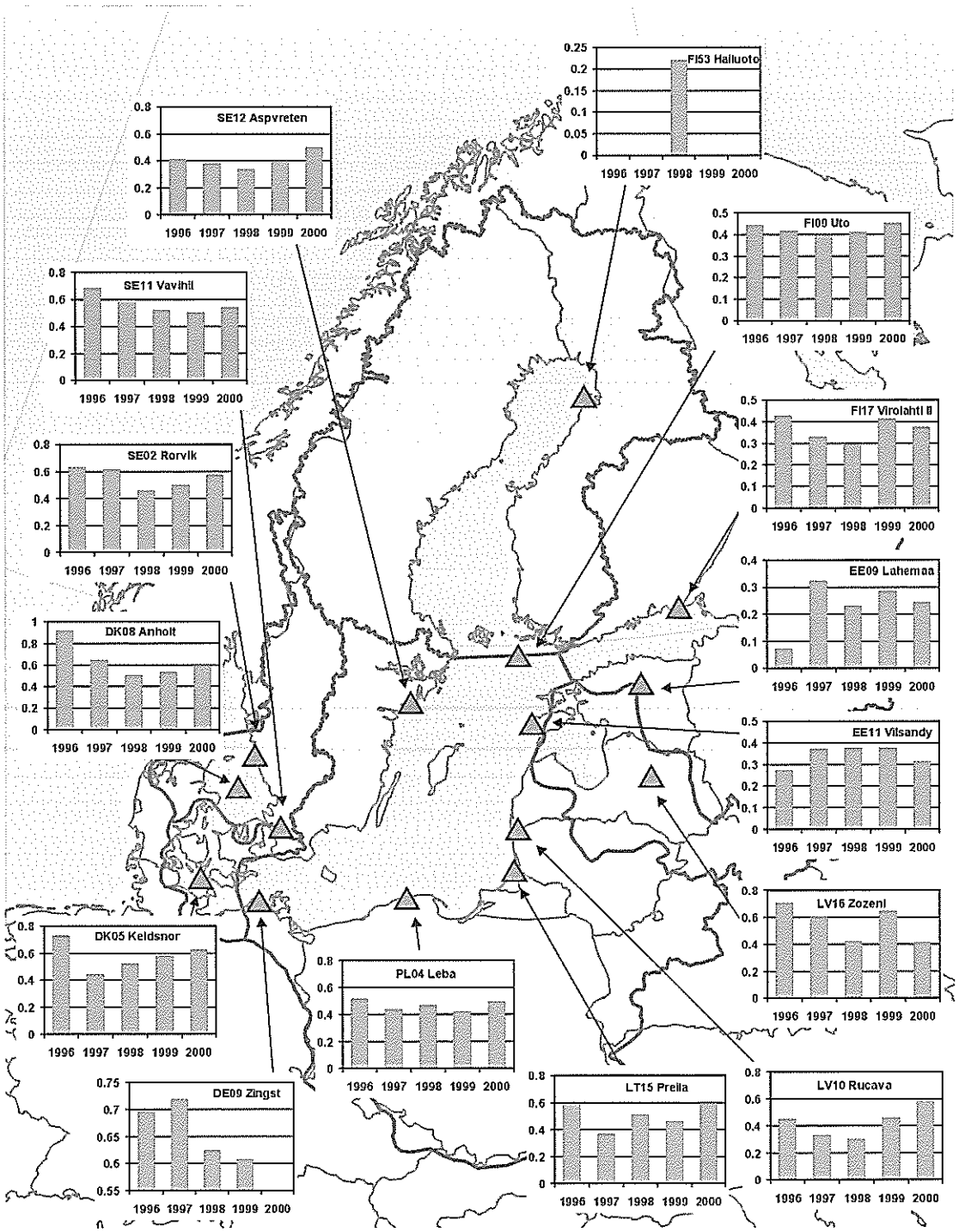


Figure 2.8
Annual average concentrations of lindane in the air measured at HELCOM stations over the period 1996-2000.
Units: pg/m^3.

Figure 2.9
Annual average concentrations of nitrate in precipitation measured at HELCOM stations over the period 1996-2000. Units: mg N/l.



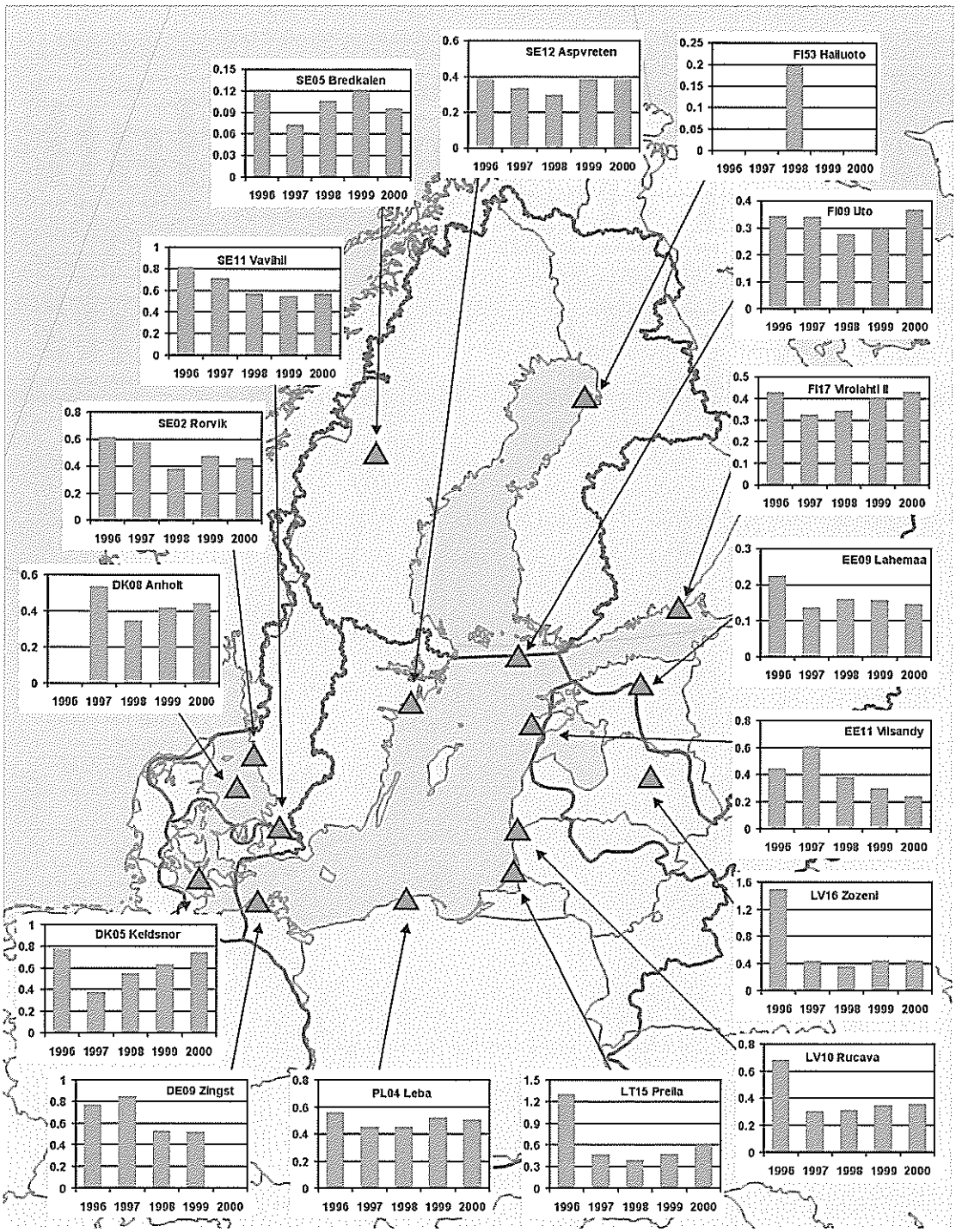
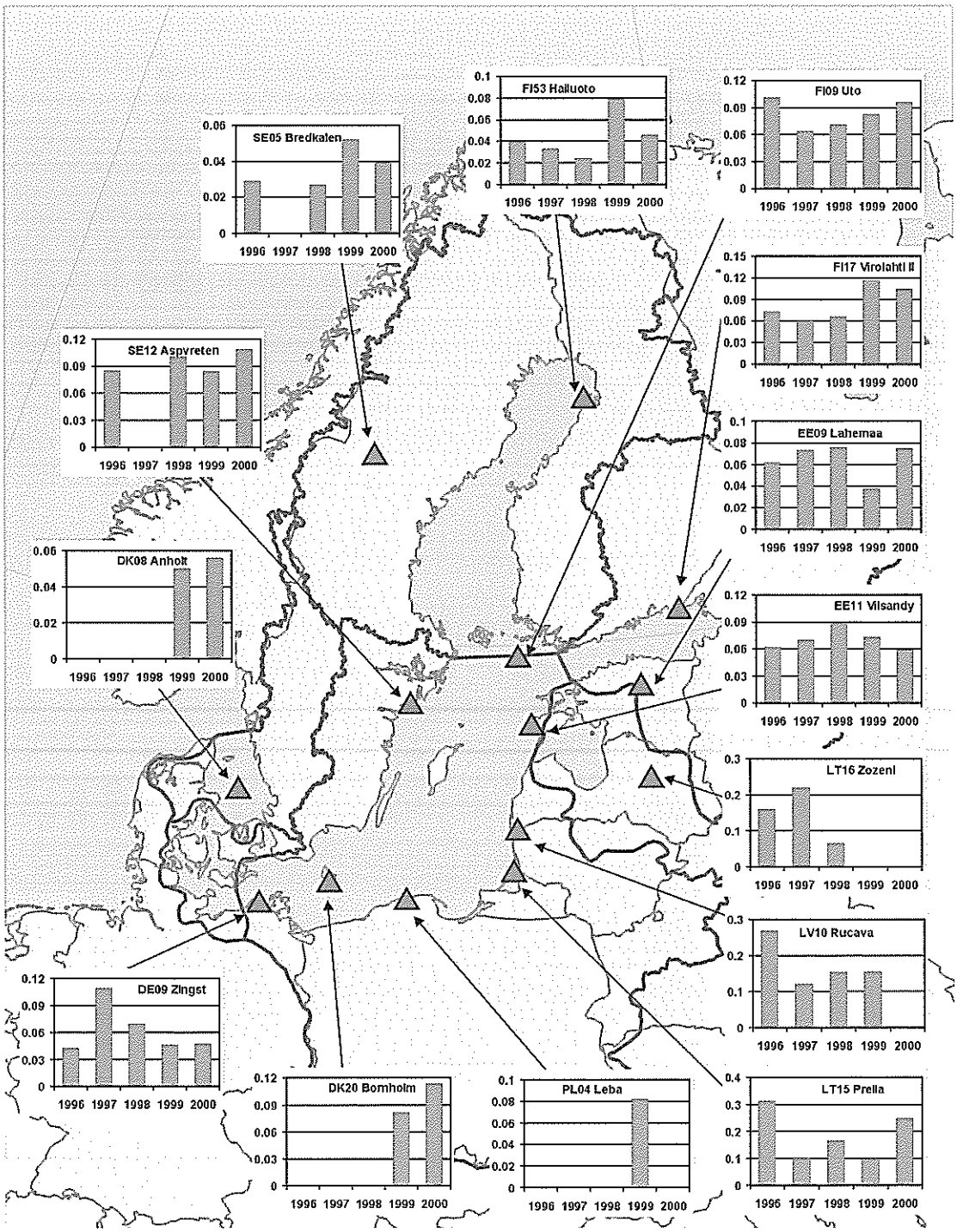


Figure 2.10
Annual average concentrations of NH_4 in precipitation measured at HELCOM stations over the period 1996-2000. Units: mg N/l.

Figure 2.11
Annual average concentrations of cadmium in precipitation measured at HELCOM stations over the period 1996-2000. Units: µg/l.



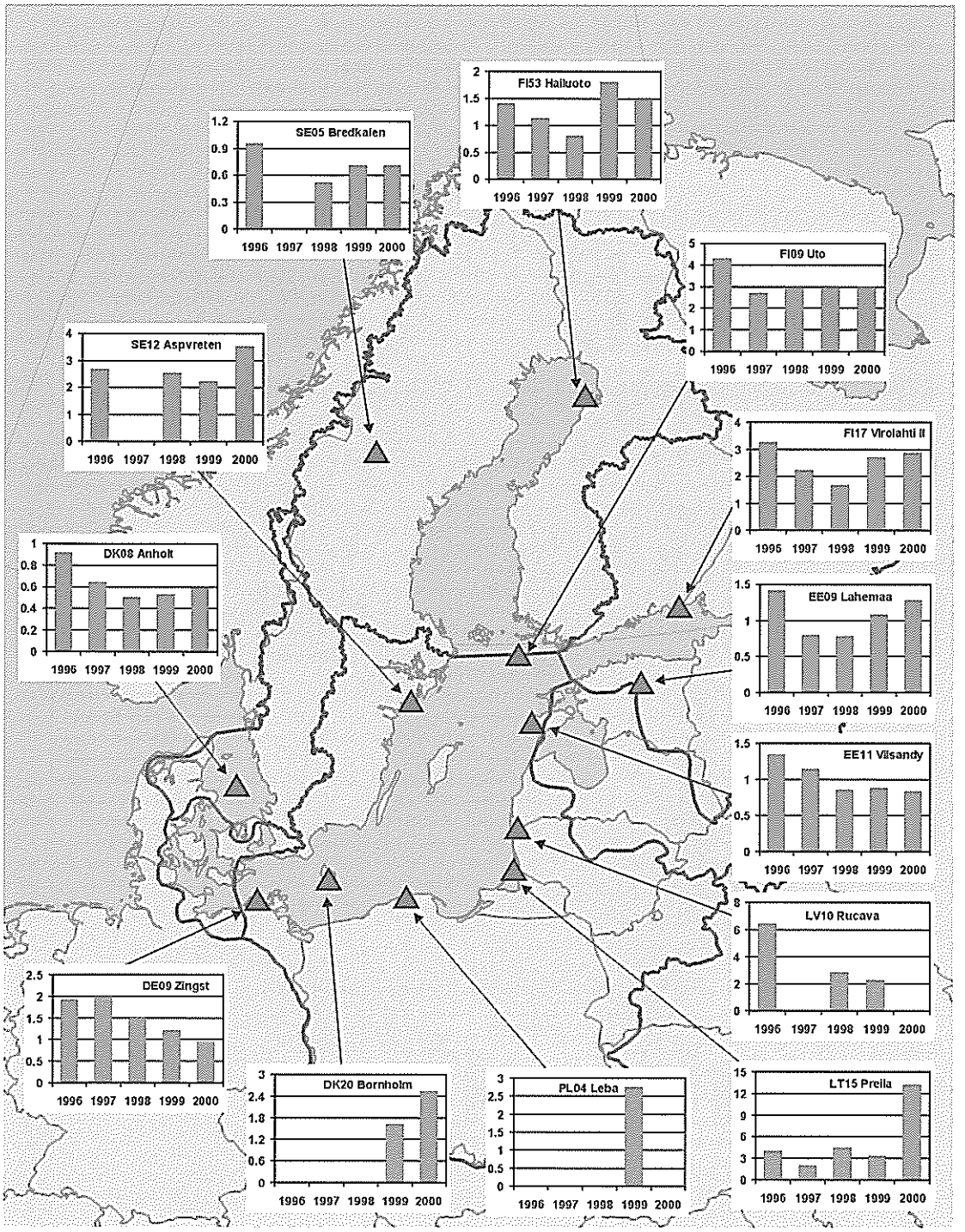
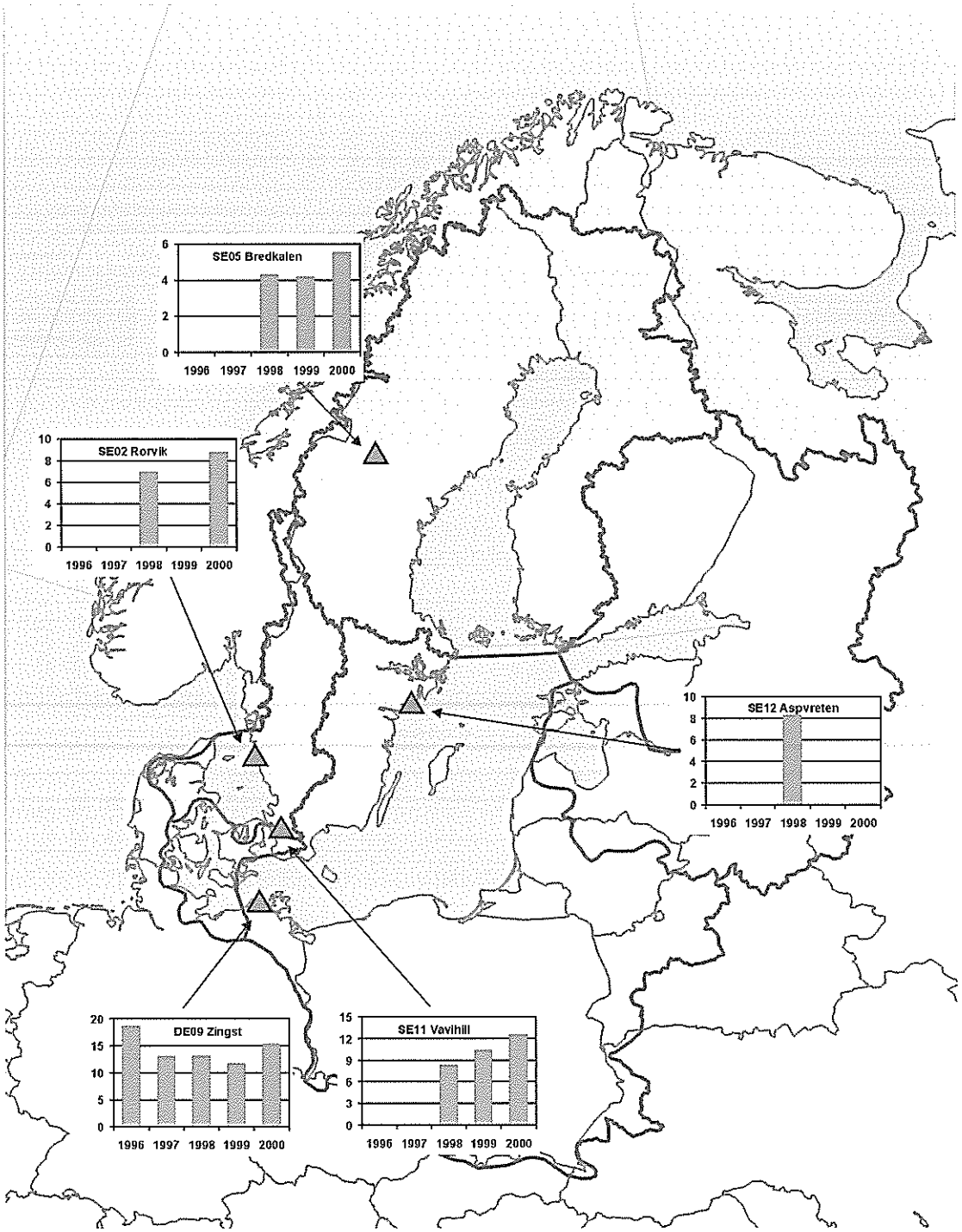


Figure 2.12
Annual average concentrations of lead in precipitation measured at HELCOM stations over the period 1996-2000. Units: µg/l.

Figure 2.13
Annual average concentrations of mercury in precipitation measured at HELCOM stations over the period 1996-2000. Units: ng/l.



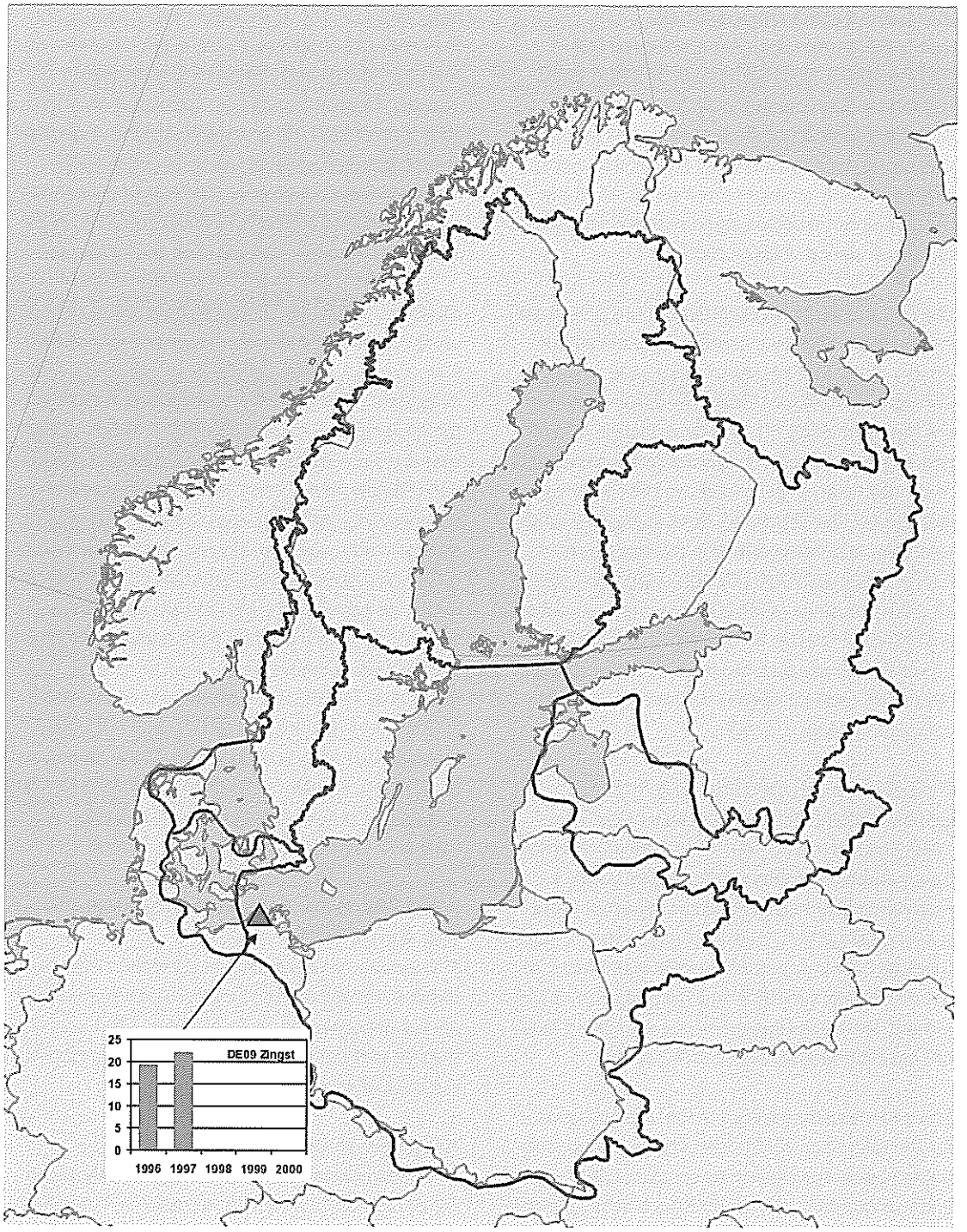


Figure 2.14
Annual average concentrations of lindane in precipitation measured at HELCOM stations over the period 1996-2000. Units: ng/l.

2.2 Calculated depositions

Four EMEP Centres Joint Reports for HELCOM (Tarrason *et al.* 1997; Bartnicki *et al.* 1998, 2000, 2001) have been published before the present one. With the exception of the first report, all focused analysis on the annual results. The present report bears a closer resemblance to the first, as all the computations presented and discussed in it relate to the 5-year period: 1996 – 2000.

The calculations of nitrogen depositions presented in this report have been performed using a new version of the EMEP Eulerian model, the so-called Unified model (EMEP, 2002). The latest version of this model (revision rv1.2) permits precise calculation of the stomatal and non-stomatal components of surface fluxes to each land-use class within a grid square. The deposition module was previously examined and tested mainly in relation to ozone (Emberson et al., 2000a, 2000b, 2001; Simpson *et al.*, 2001, Tuovinen *et al.*, 2001), but usage has been extended to measure other EMEP gases. It should be noted that this new model gives rather different deposition rates for species such as NO_2 and NH_3 compared to earlier versions.

The calculation of sub-fluxes has in fact been included in the EMEP acidification models (Tsyro 1998, Olendrzynski 1999), albeit with much simpler treatments of vegetation and seasonal patterns. However, in previous versions the results of these sub-grid calculations were aggregated to grid-square averages before output of deposition estimates. In the new model version, no such aggregation is performed, and deposition rates for each type of land use are exported directly from the model.

This new procedure has a number of implications for the estimation of Nitrogen deposition into sea areas, at least for those grids containing both land and marine zones. Compounds such as NO_2, which are relatively insoluble, will exhibit negligible deposition into sea areas, but deposition over land can be considerable. On the other hand, NH_3 is a relatively soluble gas and deposition into the sea may be significant compared to land areas.

The Eulerian three-dimensional operational MSCE-HM model was used as the basis for computation of airborne transport and depositions as well as source allocation forecasts of cadmium, lead, and mercury within the EMEP domain. The model's vertical structure consists of five non-uniform layers, ranging from the entire planetary boundary layer and a part of the free troposphere, where the horizontal resolution is 50x50 km. The model takes into account the processes of advection, turbulent diffusion, wet and dry removal and chemical transformations of mercury. Deposition rates are calculated explicitly for each type of land use and water surface. A detailed description of the model can be found in EMEP reports (Ryaboshapko *et al.*, 1999; Ilyin *et al.*, 2001) on the EMEP website (http://www.emep.int) in the section relating to information on Heavy Metals.

Modelling results for lindane (γ-HCH) were obtained using the three-dimensional Eulerian multimedia POP transport model (MSCE-POP), which is being developed at MSC-E. The model functions within the geographical scope of the EMEP region using spatial resolutions of 50×50 km (135×111 cells) and 150x150 km (45x37 cells). It makes provision for the following basic processes: advective transport, turbulent diffusion, dry and wet deposition, gas/particle partitioning, degradation, and gaseous exchange between the atmosphere and different types of underlying surface (soil, seawater, vegetation). It also examines air, soil, sea, vegetation and forest litter fall. Detailed descriptions of the MSCE-POP long-range transport model can be found in several EMEP reports (Pekar *et al.*, 1999; Shatalov *et al.*, 2000; Shatalov et al., 2001) and on the EMEP website (http://www.emep.int) in the section on Persistent Organic Pollutants.

2.2.1 Maps of annual depositions to the Baltic Sea

This section compares annual deposition maps for the year 1996 (beginning of the 5-year period) with annual deposition maps for the year 2000 (end of the five year period). All components are included in the comparison.

Annual deposition maps (1996 *vs.* 2000) for oxidized, reduced and total nitrogen are shown in Figures 2.15, 2.16 and 2.17, respectively. The same scale is used for all three figures. The year 2000 shows an increase in the deposition of reduced nitrogen compared to 1996, particularly in the South-West Baltic, but also to a lesser extent in the Northern Baltic. The same observation applies to the deposition of total nitrogen.

Annual deposition maps for cadmium, lead, and mercury are presented in Figures 2.18, 2.19, and 2.20, respectively. Fluctuations in computed cadmium deposition into the Baltic Sea for 1996 and 2000 do not differ significantly (Figure 2.18). Some decrease was observed across the north-western part and south-eastern coast of Baltic Proper, while

lower values for deposition fluxes in the Gulf of Bothnia can be seen in 2000. At the same time cadmium deposition fluxes in the Belt Sea in 2000 were higher than in 1996. Similarly, there were no significant changes in lead deposition fluxes in the Baltic Sea for the period under consideration (Figure 2.19). In 2000 a slight decrease in lead deposition fluxes was noted over the north-western part of the Baltic Proper and over the Gulf of Bothnia. Mercury deposition fluxes over the Gulf of Bothnia, Gulf of Finland, and Gulf of Riga remained practically unchanged between 1996 and 2000. Over the southern part of the Baltic Proper, Belt Sea, and Kattegat an increase of mercury deposition fluxes was observed in 2000 (Figure 2.20). Modelling results for lindane (γ-HCH) cover only part of the considered 5-year period, specifically 1996-1998. During these three years computed annual lindane (γ-HCH) net deposition fluxes into the Baltic Sea did not change significantly. Therefore, to describe the level of lindane depositions into the Baltic Sea a spatial distribution of net depositions was given for 1998 (Figure 2.21). The most significant values of lindane deposition fluxes were seen in the south-western part of the Baltic Sea – the Belt Sea and Kattegat sub-basins.

2.2.2 Time series of annual depositions to sub-basins

This part of the report presents the time series of annual depositions for all components into the six main sub-basins of the Baltic Sea over the period 1996 – 2000.

Time series for total, oxidized and reduced nitrogen are shown in Figures 2.22, 2.23 and 2.24, respectively. In the case of total nitrogen there was increased deposition in 2000 compared to 1996 in four sub-basins: the Gulf of Bothnia, the Baltic Proper, the Belt Sea and Kattegat. Larger values of annual deposition into these four sub-basins in 2000 were mainly the result of increased deposition of reduced nitrogen (Figure 2.24) in these areas during the same period. Annual depositions of oxidized nitrogen (Figure 2.23) were not seen to fluctuate notably during the 5-year period.

Over the 5-year period all types of nitrogen depositions appeared scattered, probably due to variable annual meteorological activity. As a result, no significant trend can be observed in any type of annual nitrogen deposition.

Time series analyses of cadmium, lead, mercury, and lindane annual depositions are presented in Figures 2.25, 2.26, 2.27, and 2.28, respectively. As in the case of nitrogen compounds, no significant trend can be extracted in the computed depositions of heavy metals into the Baltic Sea sub-basins during 1996-2000. Changes in annual depositions of heavy metals into the Baltic Sea were most likely caused by variations in meteorological conditions during the 5-year period. Maximum deposition values in most of sub-basins of the Baltic Sea were recorded for cadmium in 1997, for lead in 1998, and for mercury in 2000. According to modeling results, atmospheric depositions of lead and cadmium into the Baltic Sea during the 5-year period under review decreased by approximately 4%, whereas atmospheric depositions of mercury increased by 14%.

Time-series analyses of lindane (γ-HCH) depositions indicate a substantial decline in annual depositions into the Baltic Sea sub-basins between 1970 and 1998, with the most significant changes in depositions taking place during the 70s and 80s, in particular. During 1996-1998 annual depositions in the sub-basins of the Gulfs of Bothnia, Finland, and Riga were not seen to change significantly. In the south-western part of the Baltic Sea however, (the Baltic Proper, Kattegat, and the Belt Sea sub-basins) some increase in lindane (γ-HCH) depositions within this period can be observed. The level of annual volatilisation of lindane from the Baltic Sea was generally lower for all sub-basins during the review period.

2.2.3 Seasonal variability of computed depositions

Seasonal variation of computed monthly depositions into the Baltic Sea is presented in the form of five separate lines, one for each year of the 1996 – 2000 period.

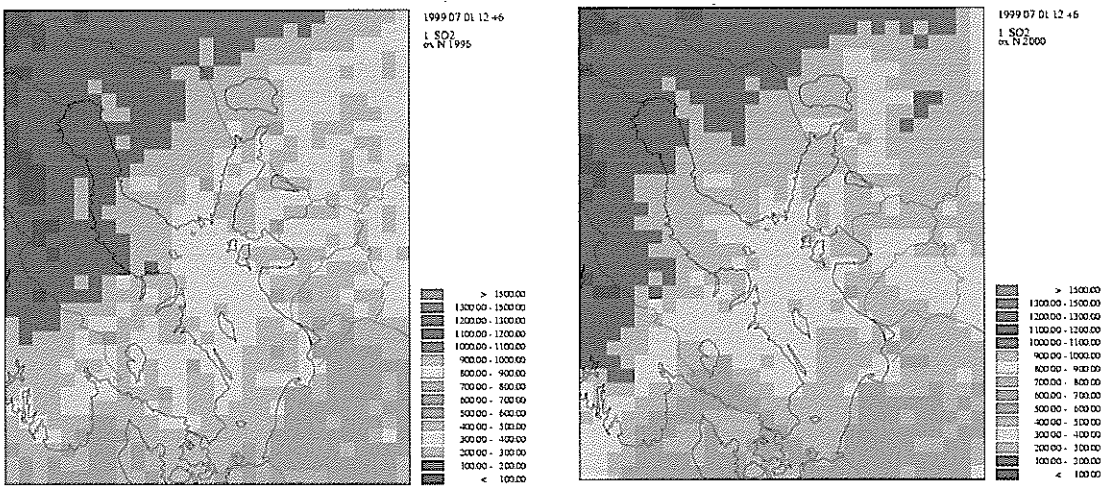
In the case of monthly depositions of total nitrogen (Figure 2.29), two local peaks can be observed, one in June and the other from October – November. The first is more significant, as it occurs in four years of the 5-year review period, while the second occurs only in 2-3 years of the 5-year period.

Variations of computed lead, cadmium, and mercury depositions are presented in Figures 2.30, 2.31, and 2.32. The figures indicate a similarity in the seasonal changes of depositions of these heavy metals, with higher deposition values observable during the

winter period. In the case of mercury, higher deposition values also occur during the summer.

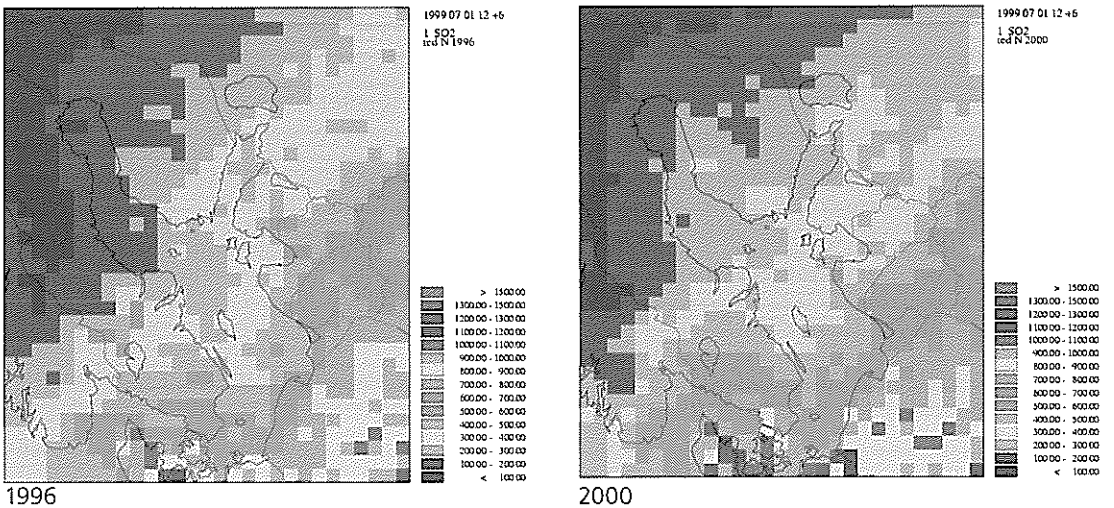
Figure 2.33 shows the seasonal pattern of net depositions of lindane into the Baltic Sea between 1996 and 1998. Due to pronounced temporal variations in emissions and the influence of meteorological conditions, monthly net deposition fluxes of lindane vary significantly during each year and also from year to year. It is assumed that emissions peaked during the spring time, and therefore maximum values for deposition fluxes are obtained for the spring months. During the second part of the year when emissions are absent, the re-emission process prevails.

Figure 2.15
Maps of calculated, annual average depositions of oxidized nitrogen for the years 1996 and 2000.
Units: mg N/m²/yr.



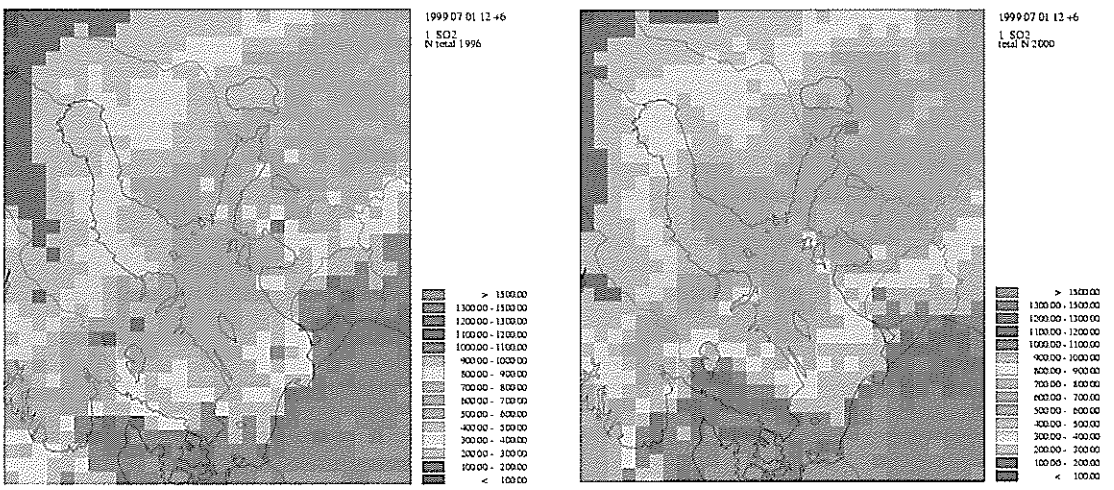
1996 2000

Figure 2.16
Maps of calculated, annual average depositions of reduced nitrogen for the years 1996 and 2000.
Units: mg N/m²/yr.

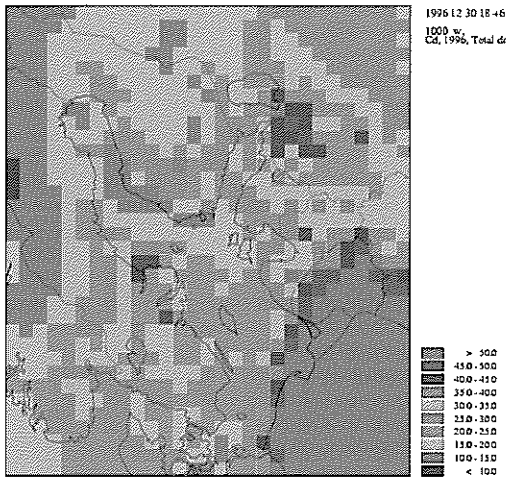


1996 2000

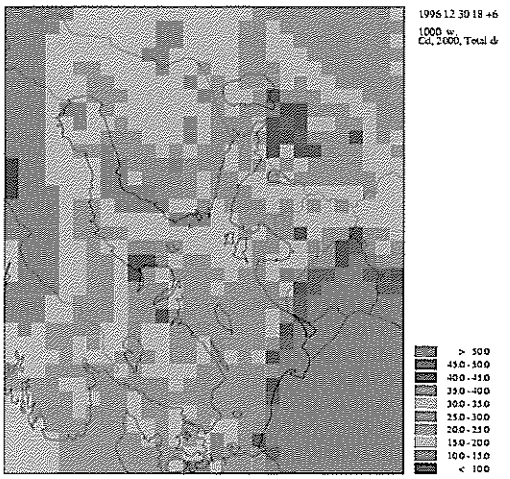
Figure 2.17
Maps of calculated, annual average depositions of total (oxidized plus reduced) nitrogen for the years 1996 and 2000.
Units: mg N/m²/yr.



1996 2000

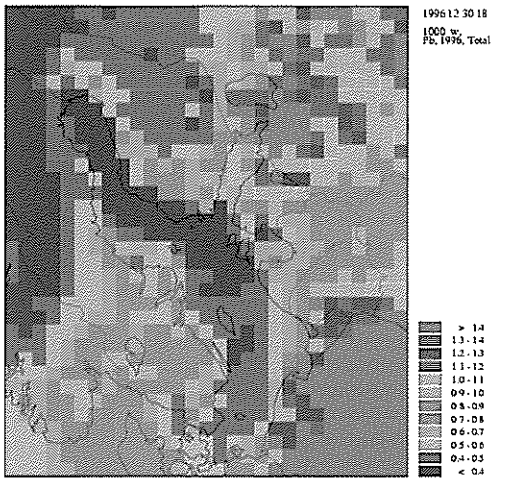


1996

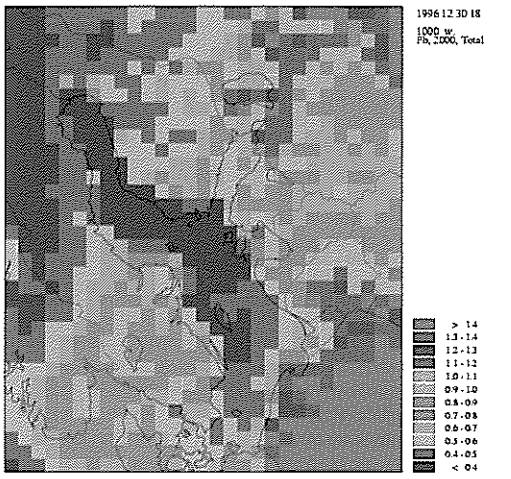


2000

Figure 2.18
Maps of calculated, annual average depositions of cadmium for the years 1996 and 2000. Units: g/km^2/yr.

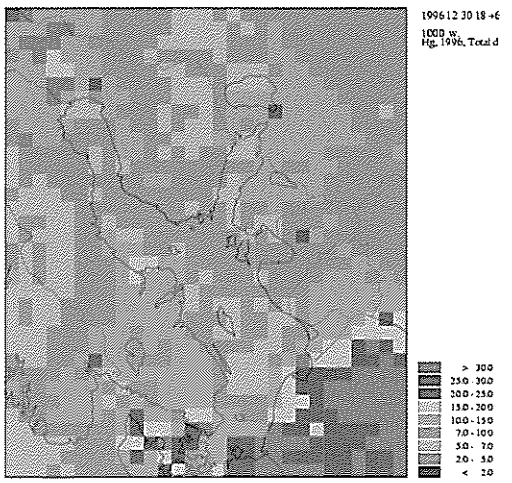


1996

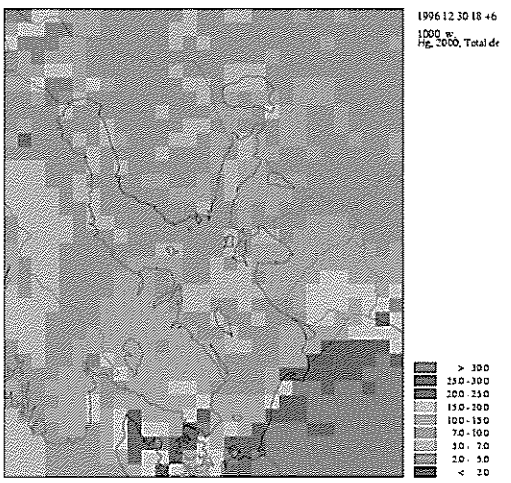


2000

Figure 2.19
Maps of calculated, annual average depositions of lead for the years 1996 and 2000. Units: kg/km^2/yr.



1996



2000

Figure 2.20
Maps of calculated, annual average depositions of mercury for the years 1996 and 2000. Units: g/km^2/yr.

Figure 2.21.
Map of calculated annual depositions of g-HCH in 1998.
Units: g/km²/yr.

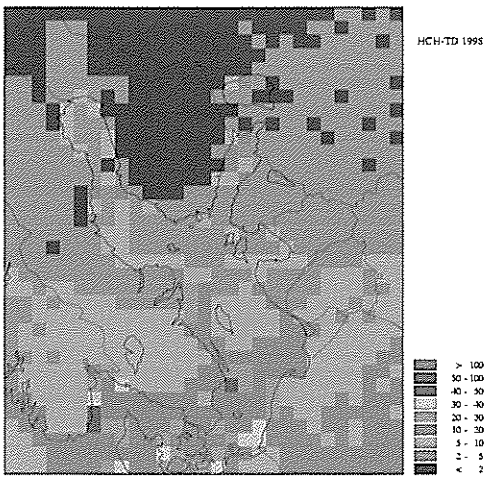
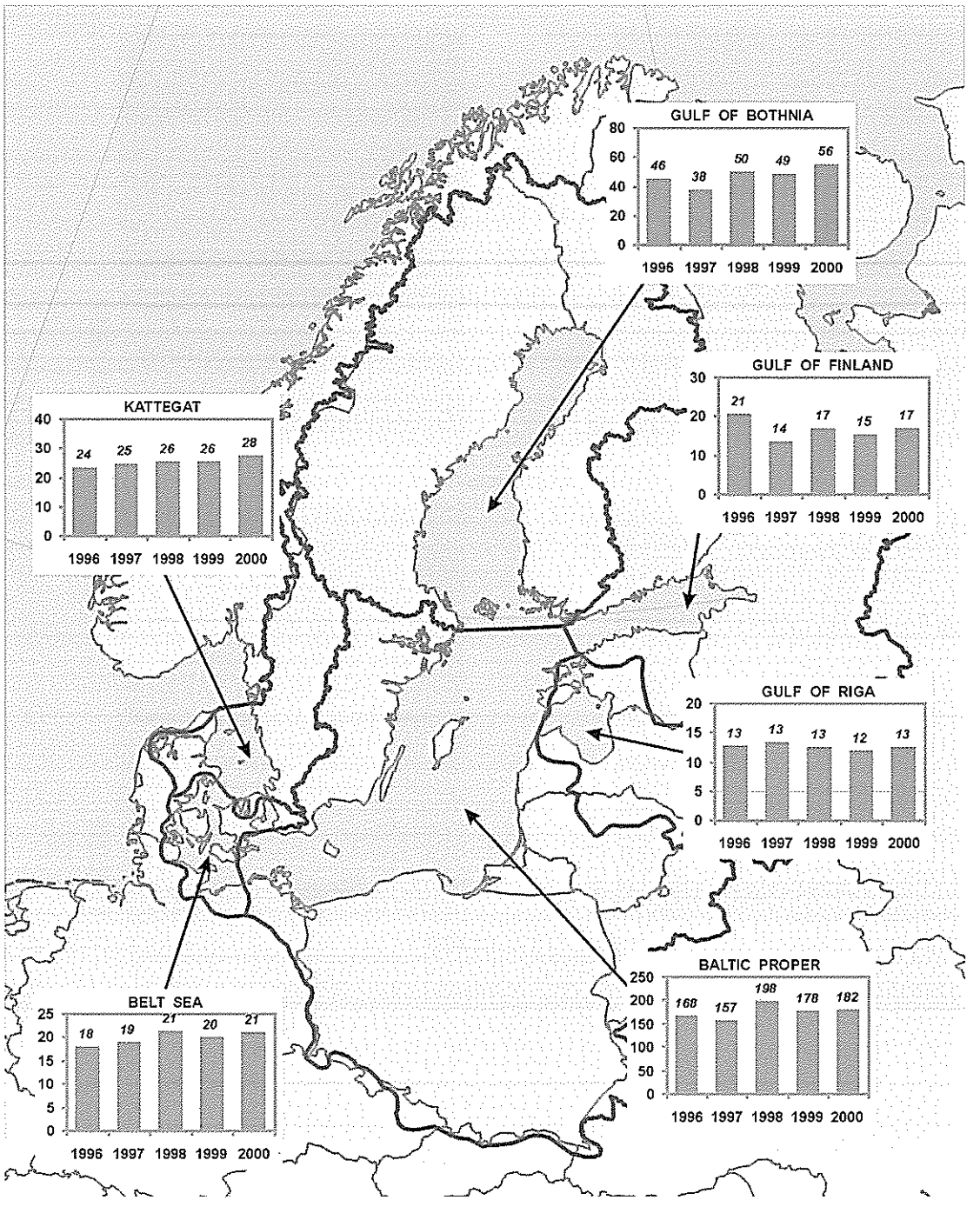


Figure 2.22
Time series analysis of total nitrogen deposition into six main sub-basins of the Baltic Sea for the period 1996-2000.
Units: ktonnes N/yr.



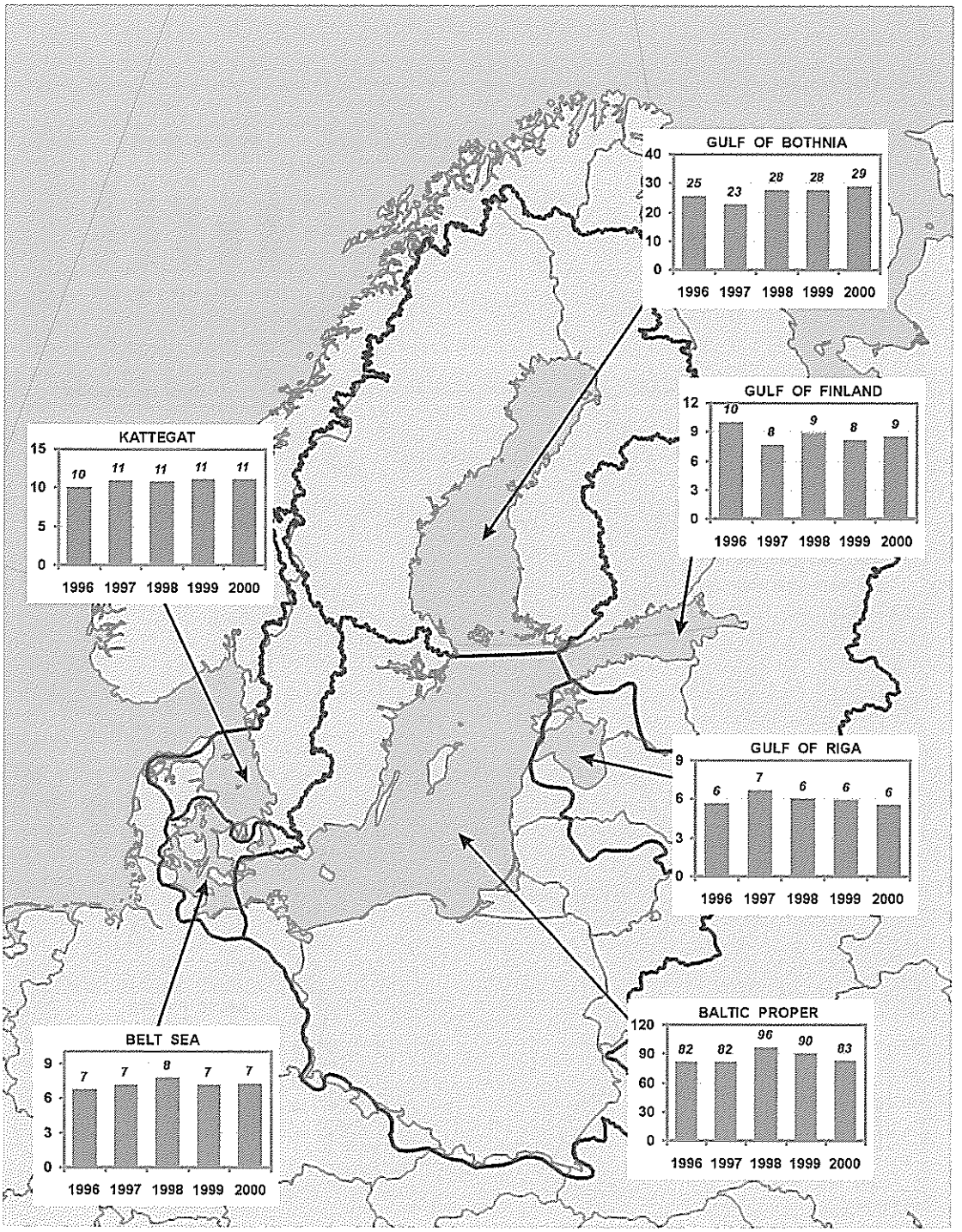
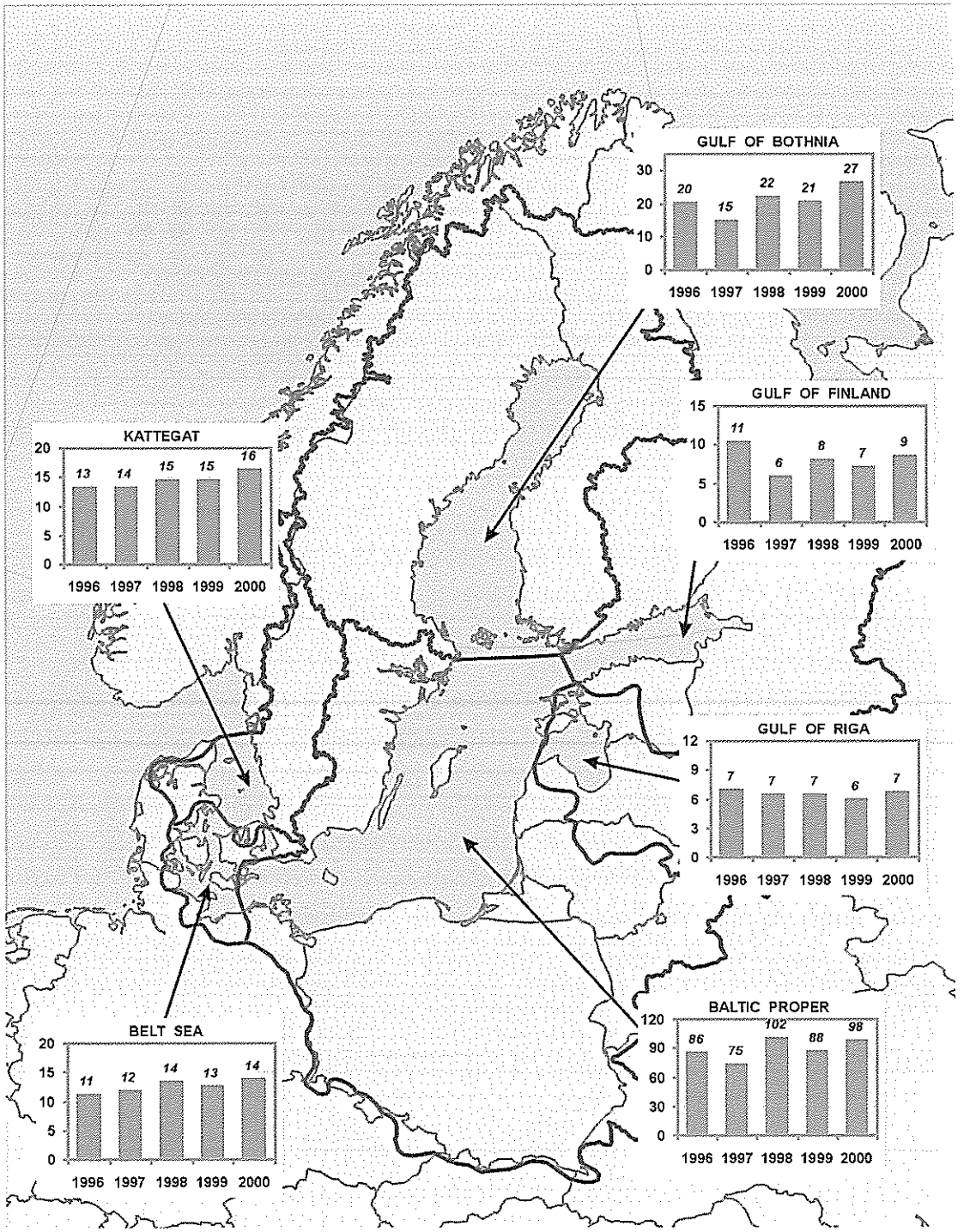


Figure 2.23
Time series analysis of oxidized nitrogen deposition into six main sub-basins of the Baltic Sea for the period 1996-2000.
Units: ktonnes N/yr.

Figure 2.24
Time series analysis of reduced nitrogen deposition into six main sub-basins of the Baltic Sea for the period 1996-2000.
Units: ktonnes N/yr.



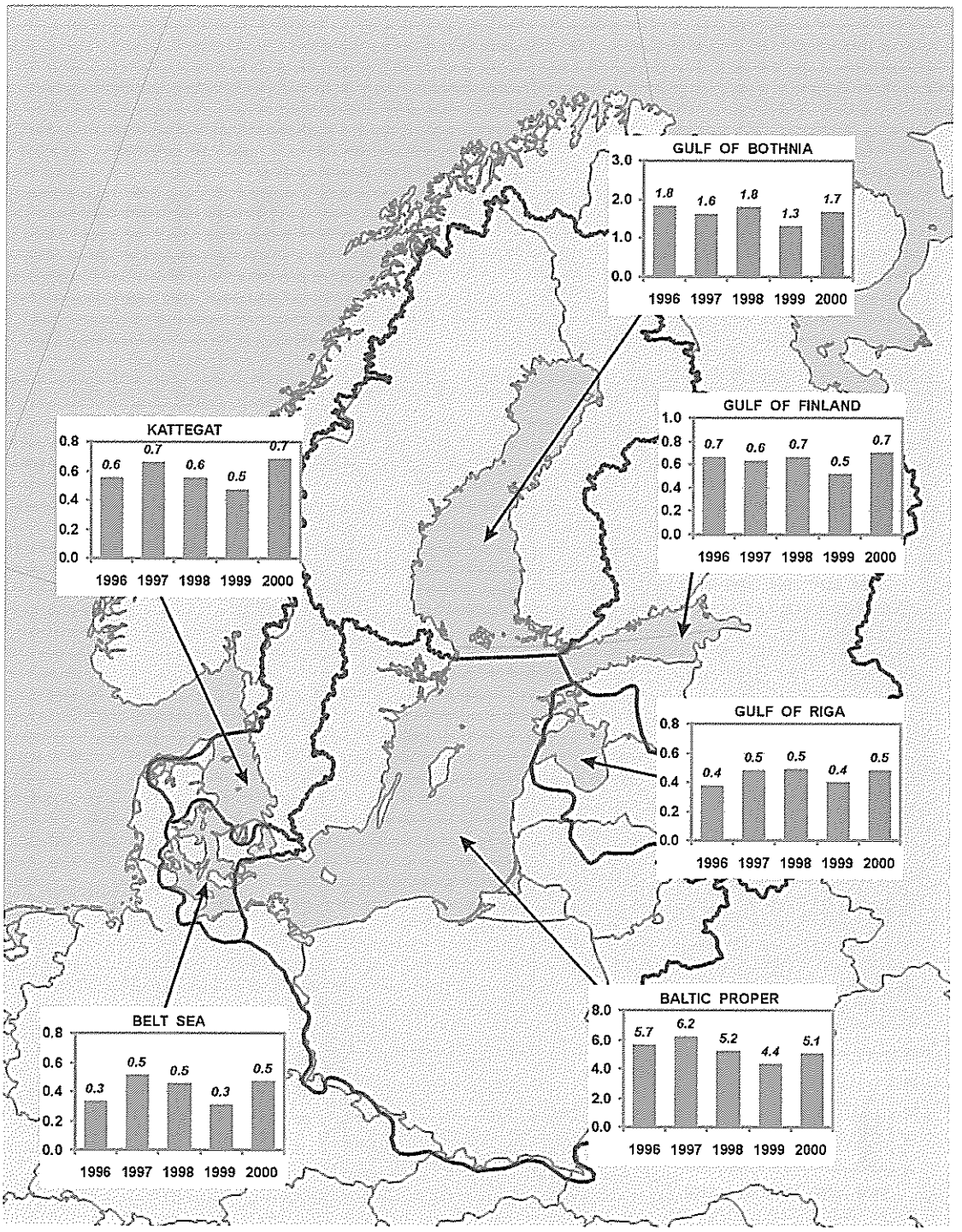
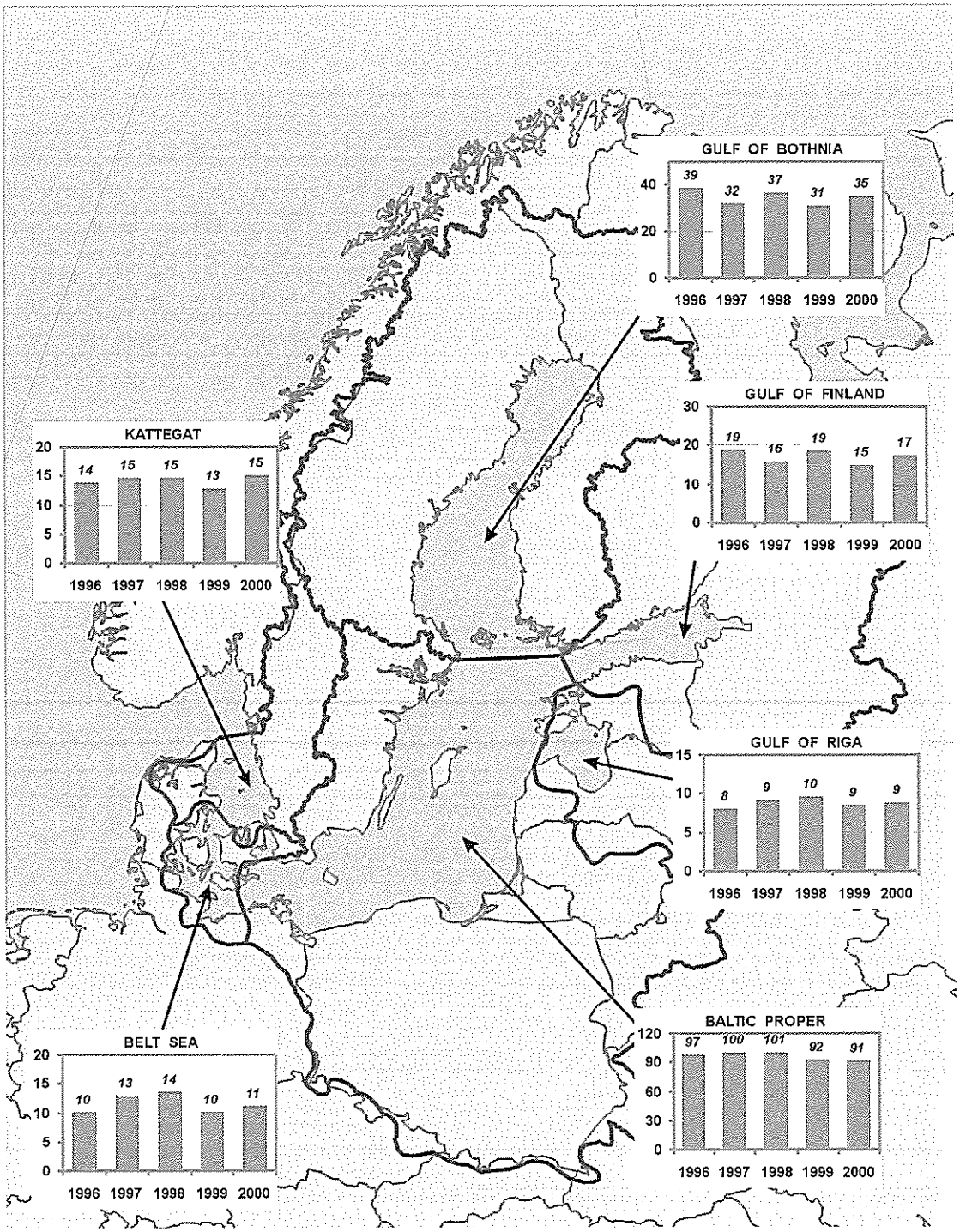


Figure 2.25
Time series analysis of cadmium deposition into six main sub-basins of the Baltic Sea for the period 1996-2000. Units: tonnes/yr.

Figure 2.26
Time series analysis of lead deposition into six main sub-basins of the Baltic Sea for the period 1996-2000.
Units: tonnes/yr.



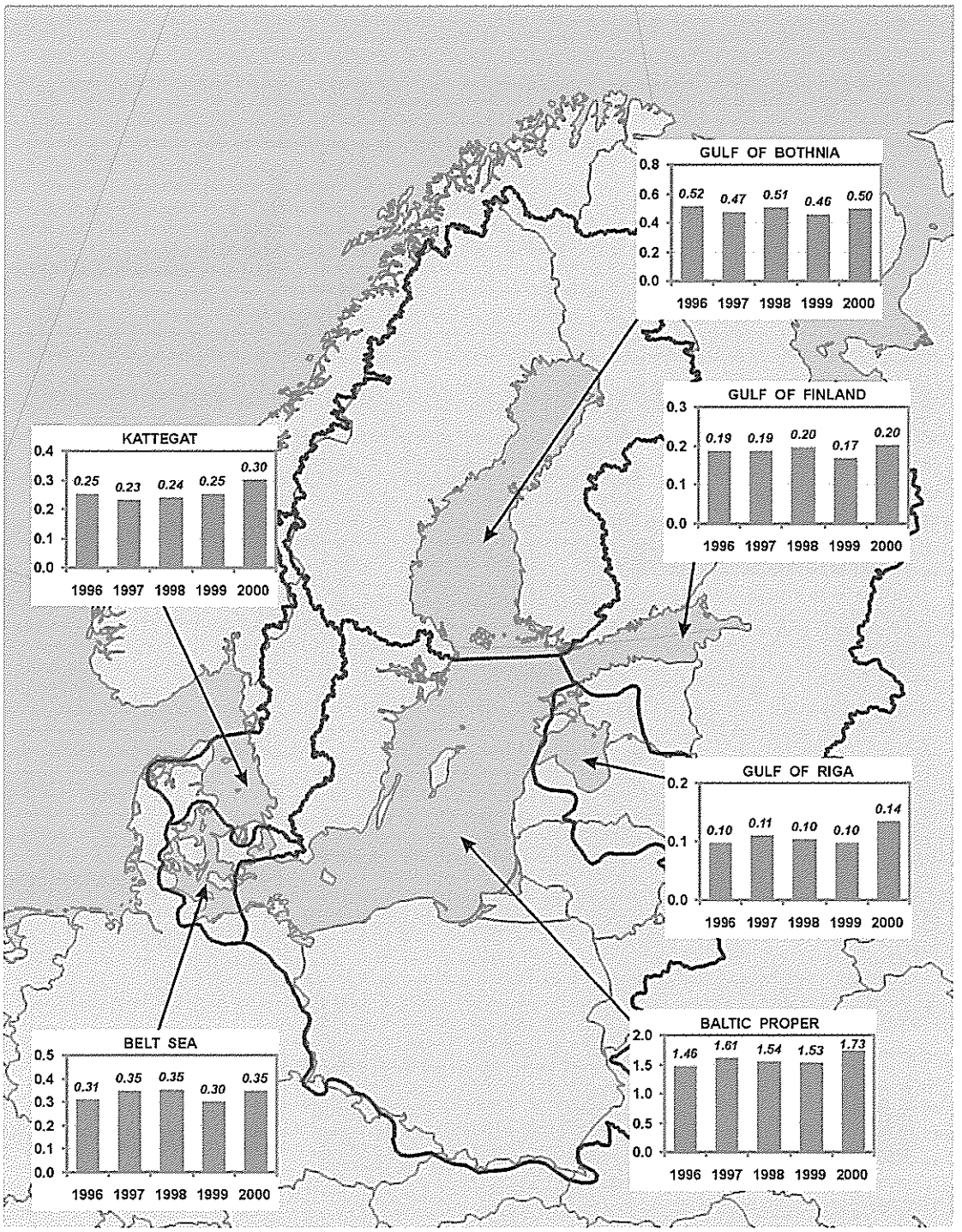
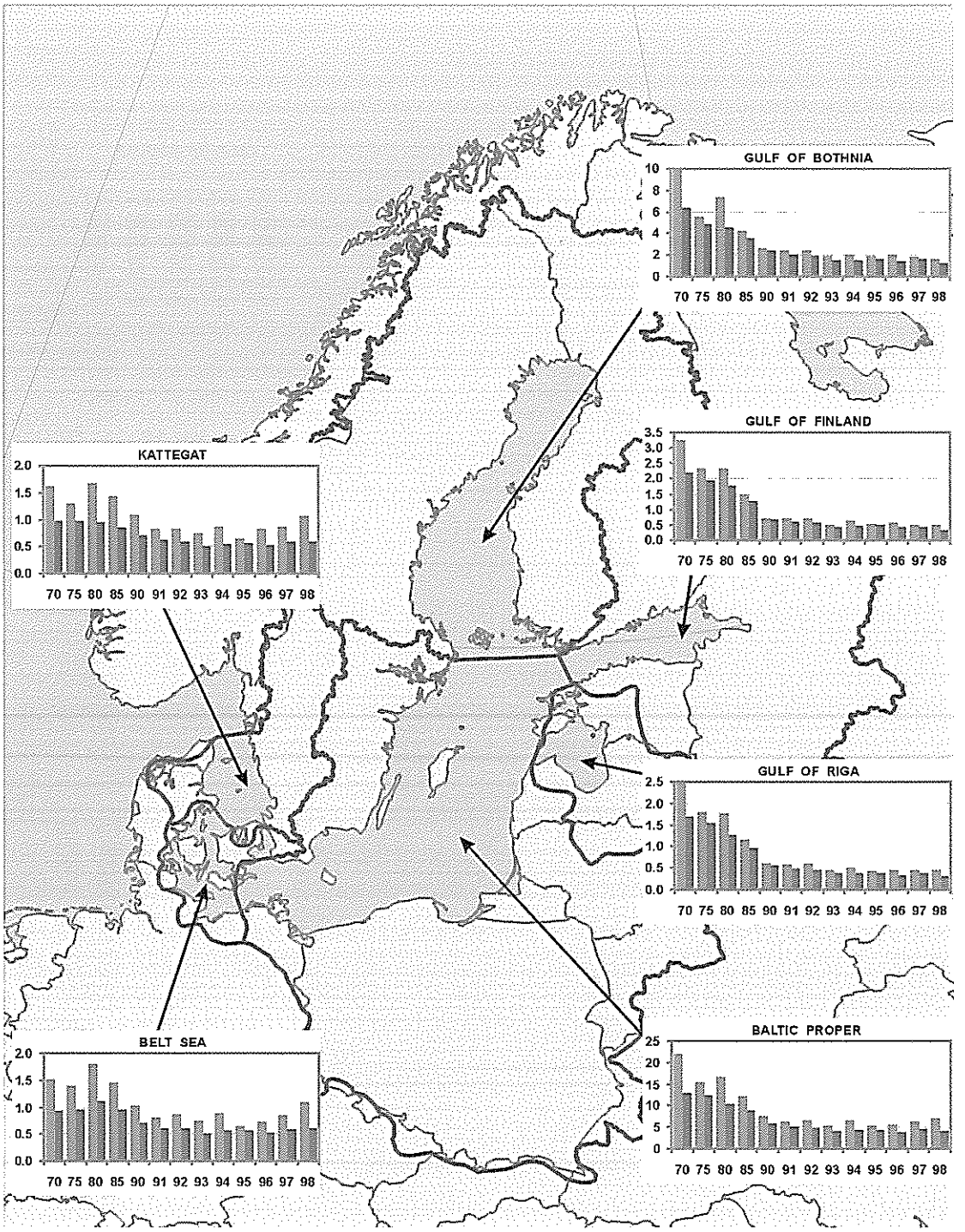


Figure 2.27
Time series analysis of mercury deposition into six main sub-basins of the Baltic Sea for the period 1996-2000. Units: tonnes/yr.

Figure 2.28
Time series analysis of lindane deposition into and volatilization from the six sub-basins of the Baltic Sea for the period 1970-1998.
Units: in tonnes/yr.



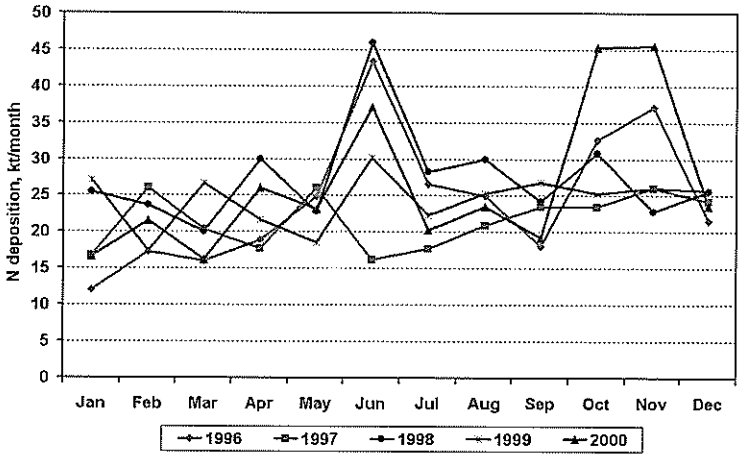


Figure 2.29
Seasonal variation of computed total nitrogen depositions into the Baltic Sea for the period 1996-2000 in ktonnes/month.

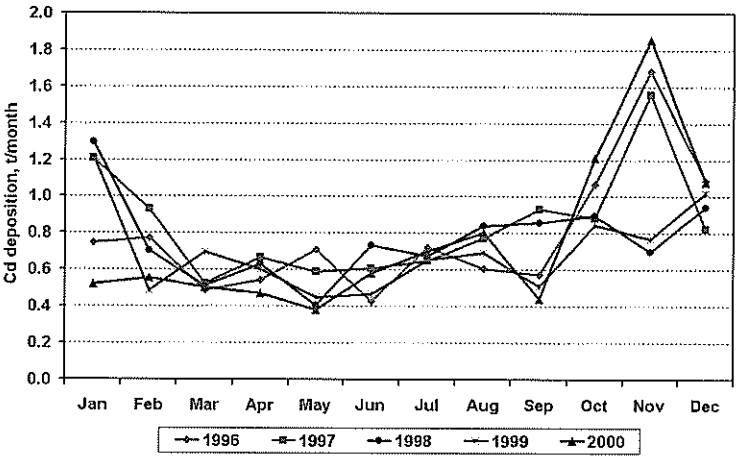


Figure 2.30
Seasonal variation of computed cadmium depositions into the Baltic Sea for the period 1996-2000 in tonnes/month.

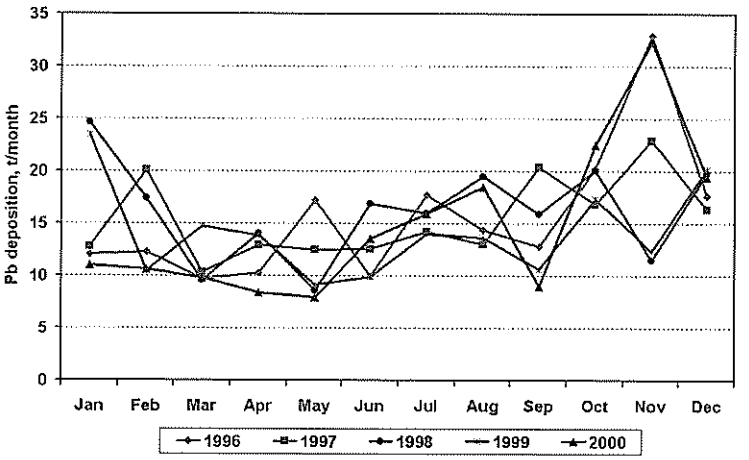


Figure 2.31
Seasonal variation of computed lead depositions into the Baltic Sea for the period 1996-2000 in tonnes/month.

Figure 2.32
Seasonal variation of computed mercury depositions into the Baltic Sea for the period 1996-2000 in tonnes/month.

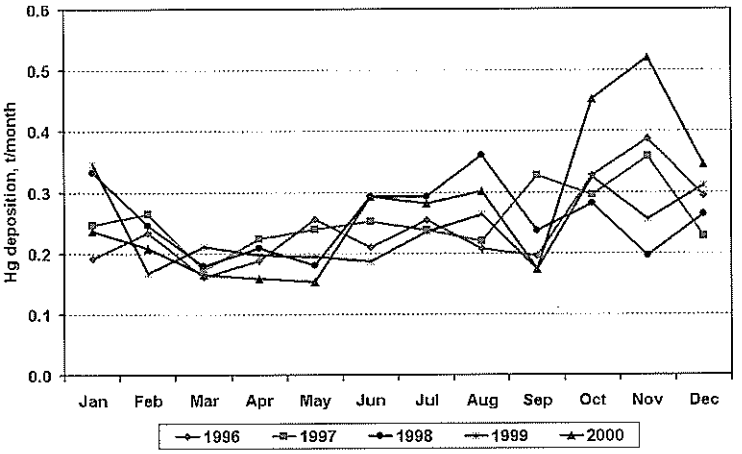
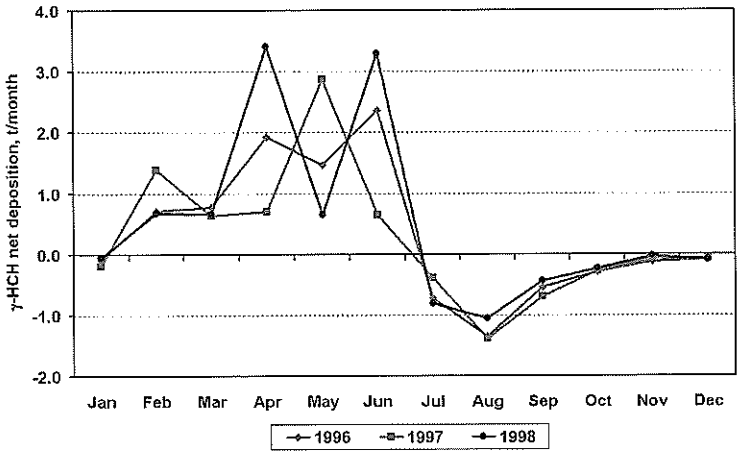


Figure 2.33
Seasonal variation of computed lindane depositions into the Baltic Sea for the period 1996-2000 in tonnes/month.



3 Deposition trends

This chapter compares depositions during the previous period (1991 – 1995) with data for the present period (1996 – 2000), then contrasts changes in depositions and emissions during the years 1996 – 2000.

3.1 Comparison of depositions in the present and previous five year period

In order to compare depositions for two different 5-year periods, mean deposition over the period 1991 – 1995 has been assigned a value of 100% and depositions for the period under review (1996 – 2000) are expressed as a percentage of the previous period.

In Figure 3.1, total nitrogen depositions into the Gulf of Bothnia, the Baltic Proper and the Gulf of Riga were 25%, 24% and 4% higher respectively in the review period than in the previous 5-year period. In the remaining three sub-basins depositions in the present 5-year period were lower than the base period.

In the case of heavy metals, computations of atmospheric depositions of lead and cadmium into the Baltic Sea during the period 1991-1995 are available. These computations were carried out by MSC-E as part of an evaluation of trends in concentrations and depositions of lead and cadmium within the EMEP region for the period 1990-1998 (Ilyin *et al.*, 2001). However, it should be mentioned that the evaluation of depositions for the 1990-1998 period was made on the basis of a slightly different set of emissions data.

By and large, during the 5-year period average cadmium depositions in all sub-basins of the Baltic Sea were 30% lower in comparison with the previous period (Figure 3.2). The most significant changes can be observed in two sub-basins, the Gulf of Finland (62%) and the Belt Sea (61%).

The picture for lead shows a more significant decrease in depositions. Typically, mean depositions of lead in all sub-basins of the Baltic Sea during the review period were 60% lower than in the previous period (Figure 3.3). With respect to cadmium the most significant changes can be seen in the Belt Sea (34%).

No comparison of mercury depositions over the two review periods is presented in this report because modelling results for the 1991-1995 period are not currently available. Once these calculations are performed the comparison will be included in this section.

A similar comparison was also performed for lindane (γ-HCH) depositions (Figure 3.4). The analysis showed that mean depositions of lindane (γ-HCH) for the period 1991-1995 were by and large, practically the same during the period 1996-1998. However, at the level of the individual sub-basins, changes in depositions varied in different parts of the Baltic Sea. As a result, some increases in mean depositions can be seen in the Kattegat, Belt Sea, and Baltic Proper whereas decreases in depositions were observed in the Gulf of Riga, the Gulf of Finland, and the Gulf of Bothnia.

3.2 Annual depositions compared to annual emissions during 1996 - 2000

As a basis for comparing emissions and depositions during the period under consideration, this report assumes that both the sum of annual emissions from all sources into the Baltic Sea and annual total depositions into the entire Baltic Sea are equal to 100% in 1996. Emissions and depositions occurring during the years following 1996 are then expressed as percentages of their baseline 1996 values.

Annual emissions of total nitrogen (Figure 3.5) declined steadily over the entire period with annual emissions in 2000 recorded at 11% lower than annual emissions in 1996. It should be noted however, that this level of decline in nitrogen emissions occurs well within the uncertainty range for emissions and therefore should not be considered significant. During the 1996 - 2000 period, annual depositions of total nitrogen (oxidized and reduced, wet and dry) did not closely follow the emission pattern, reflecting the impact of meteorological conditions. In general, the annual deposition values for different years fall on either side of the 1996 baseline value, with maximum levels recorded in 1998.

The comparison of heavy metal emissions and depositions is presented in Figures 3.6-3.8. In terms of the nitrogen compounds, the emissions for cadmium, lead, and mercury were seen to gradually decrease during the period 1996-2000. Nevertheless, annual

depositions do not closely correspond to variations in the levels of emissions. Maximum annual depositions of cadmium were recorded in 1997, and of lead in 1998. Annual depositions of mercury into the Baltic Sea were seen to increase during the period 1996-2000, reaching a maximum in 2000. Modelling results for lindane (γ-HCH) do not cover the entire duration of the study. As a result, the comparison of lindane emissions and depositions is presented for the three-year period from 1996-1998 (Figure 3.9). Overall, some increase in depositions of lindane into the Baltic Sea was observed from 1996 to 1998.

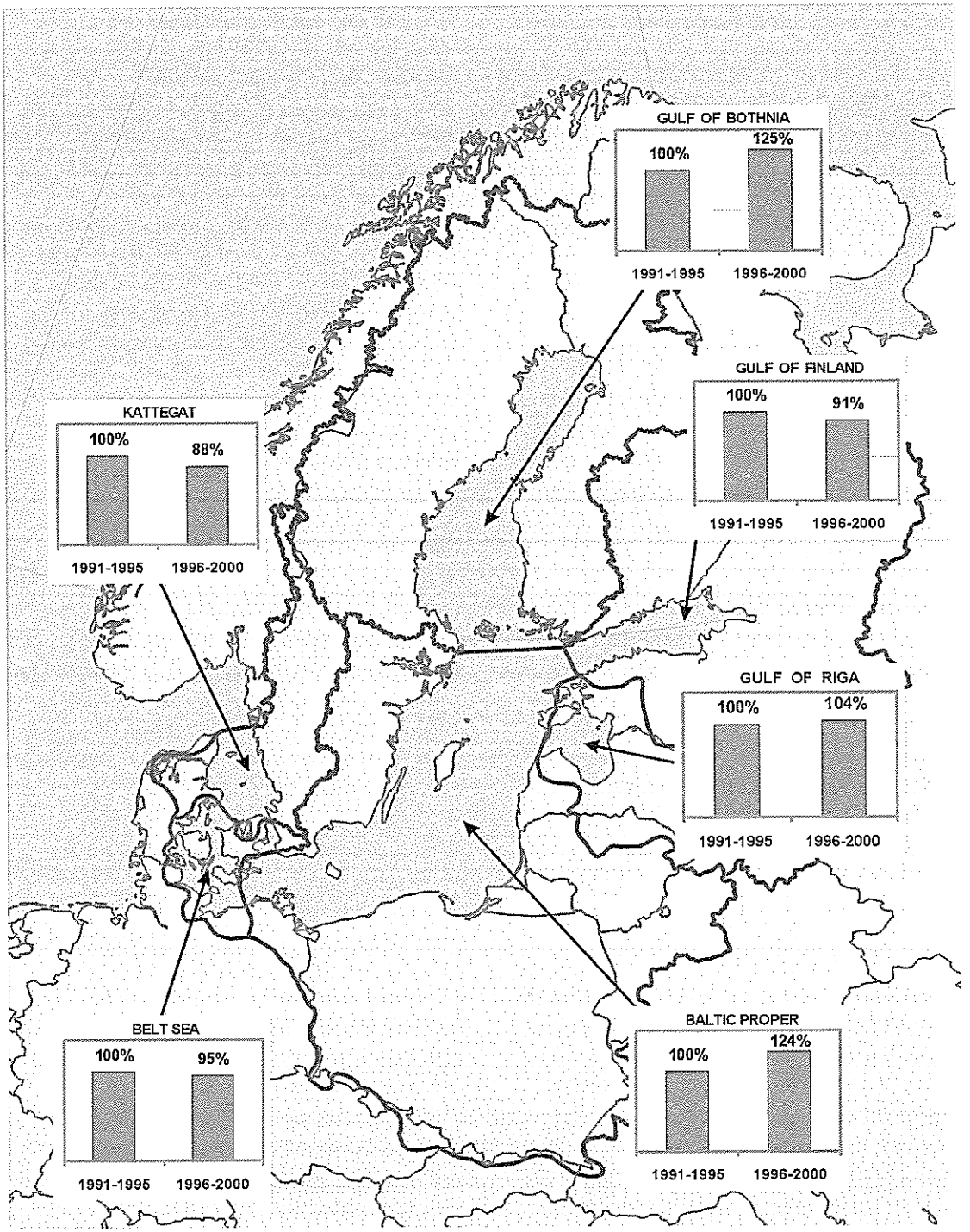


Figure 3.1
Comparison of percentage changes in average total annual nitrogen depositions between the 5-year periods 1991-1995 and 1996-2000.

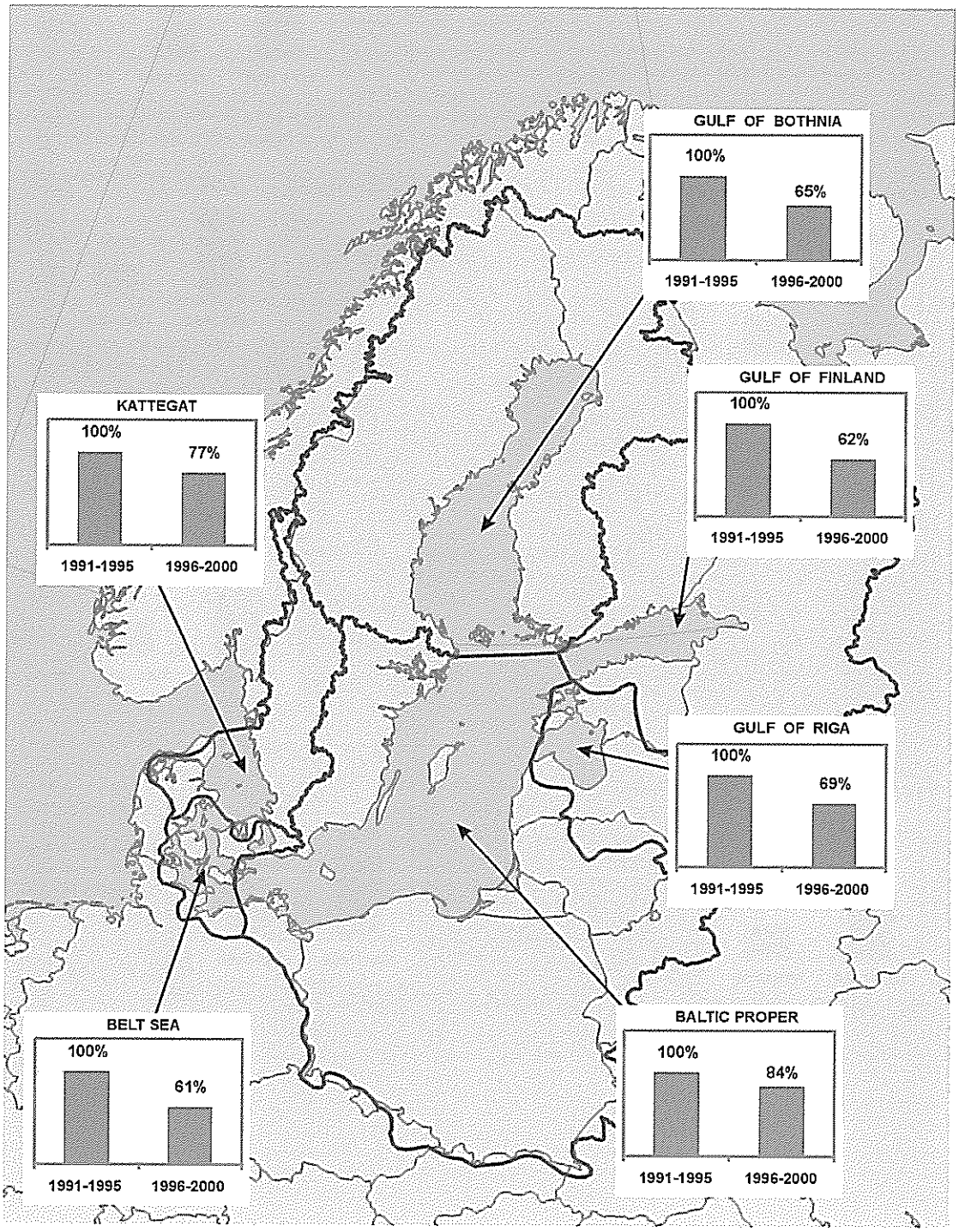
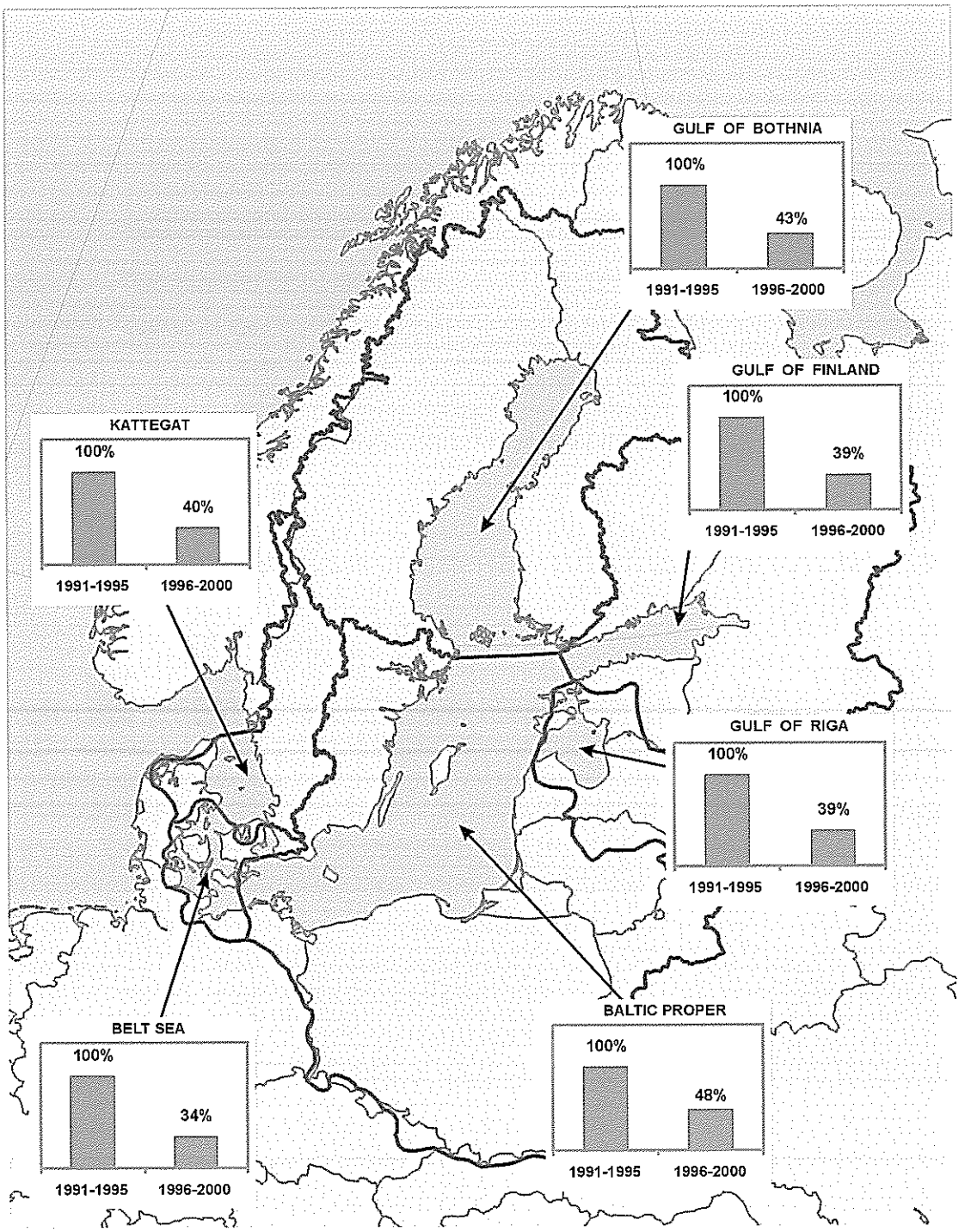


Figure 3.2
Comparison of percentage changes in average annual cadmium depositions between the 5-year periods 1991-1995 and 1996-2000.

Figure 3.3
Comparison of percentage changes in average annual lead depositions between the 5-year periods 1991-1995 and 1996-2000.



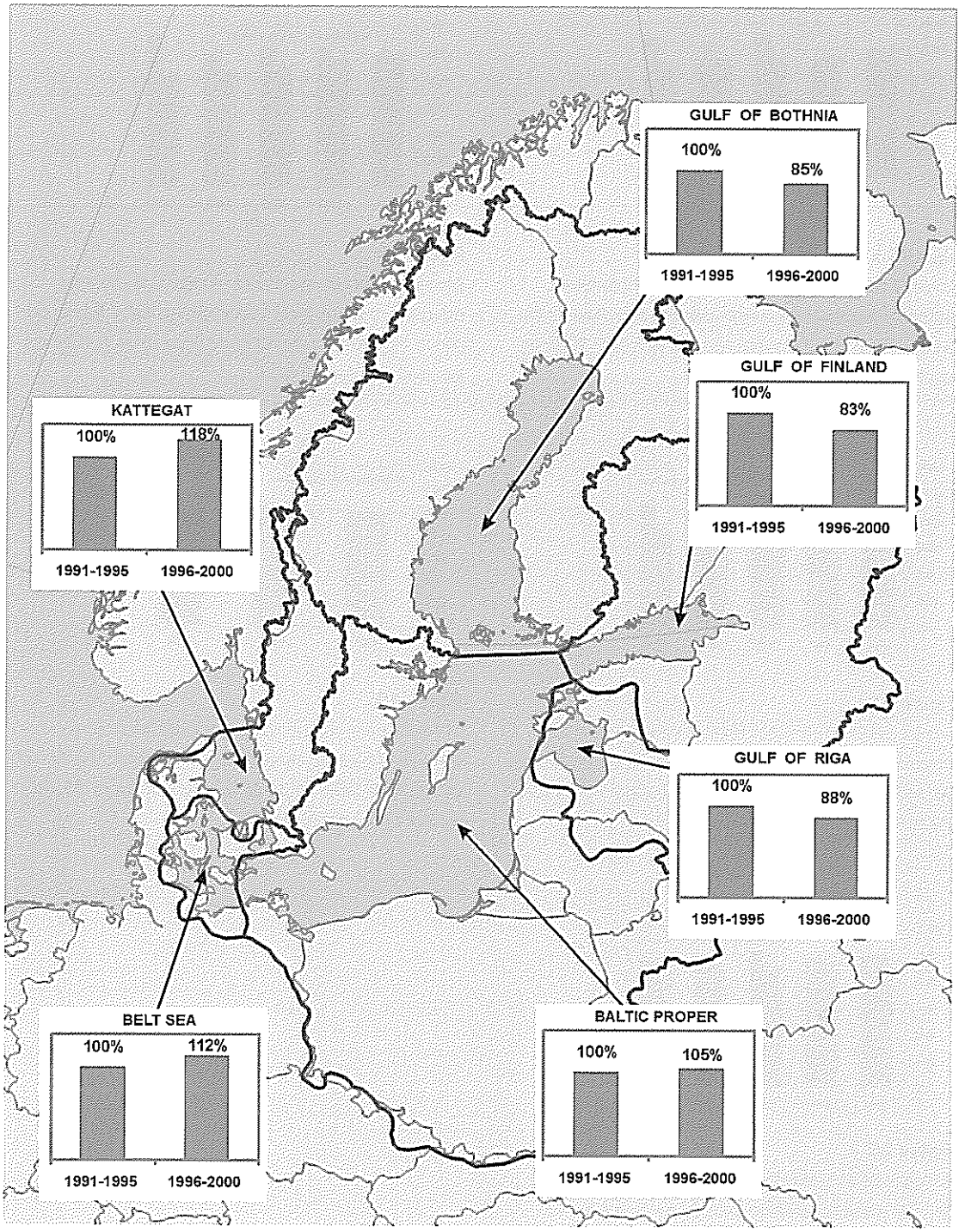


Figure 3.4
Comparison of percentage changes in average annual lindane (γ-HCH) depositions between the 5-year periods 1991-1995 and 1996-2000.

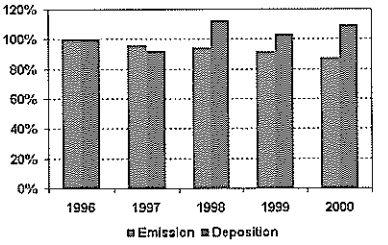


Figure 3.5
Annual nitrogen emissions from all HELCOM countries compared to annual depositions into the Baltic Sea for the period 1996-2000. Emissions and depositions in 1996 are assumed at a level of 100%.

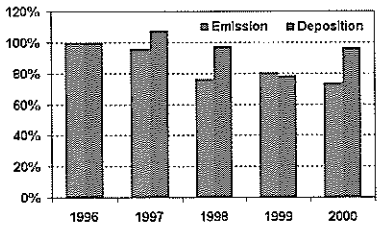


Figure 3.6
Annual cadmium emissions from all HELCOM countries compared to annual depositions into the Baltic Sea for the period 1996-2000. Emissions and depositions in 1996 are assumed at a level of 100%.

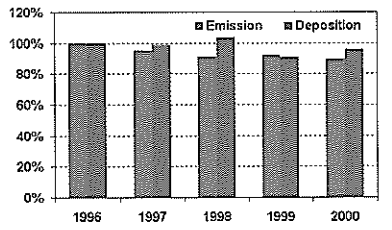


Figure 3.7
Annual lead emissions from all HELCOM countries compared to annual depositions into the Baltic Sea for the period 1996-2000. Emissions and depositions in 1996 are assumed at a level of 100%.

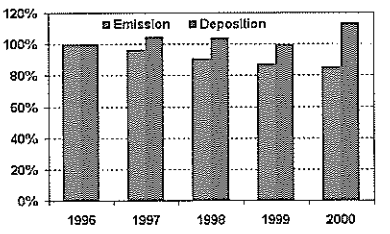


Figure 3.8
Annual mercury emissions from all HELCOM countries compared to annual depositions into the Baltic Sea for the period 1996-2000. Emissions and depositions in 1996 are assumed at a level of 100%.

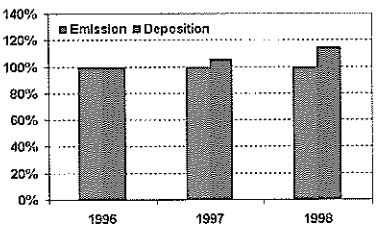


Figure 3.9
Annual lindane emissions from all HELCOM countries compared to annual depositions into the Baltic Sea for the period 1996-1998. Emissions and depositions in 1996 are assumed at a level of 100%.

4 Emissions and source allocation budgets

Emissions from the HELCOM countries and international shipping traffic on the Baltic Sea are the major sources of pollution in the Baltic Sea. It should be noted however that in some cases emissions from other parts of the entire EMEP region also contribute significantly to such harmful depositions. Consequently this report first considers emissions from the entire EMEP domain.

4.1 Emissions from the EMEP region during the period 1996 - 2000

Annual emissions of nitrogen oxides, ammonia and total nitrogen (nitrogen oxides plus ammonia) over the period 1996 - 2000 are shown in Figure 4.1.

Emissions of both nitrogen oxides and ammonia were slightly lower in 2000 than in 1996, but the difference is not significant, particularly with respect to ammonia. Over the 5-year period, the reduction of oxidized nitrogen oxides emissions was seen to be more notable than the reduction of ammonia emissions, falling by approximately 9% in relation to ammonia emissions, which fell by roughly 4%.

In comparison with the emissions of nitrogen oxides and ammonia, the reduction of anthropogenic emissions of lead was more significant during the same period (Figure 4.2). Emissions of lead, cadmium and mercury in 2000 were 31%, 22% and 17% lower than in 1996, respectively.

Available official information and expert estimates indicate that lindane emissions remained more or less constant between 1996 and 1998 (Figure 4.3). More significant changes took place earlier on from 1970 to 1990, when the emissions within the EMEP region declined by more than three times.

4.2 Map with ship emissions in the Baltic Sea

Data on emissions from the international shipping traffic on the Baltic Sea are only available for nitrogen oxides at present, and solely for the year 1990. The total annual emissions of nitrogen oxides from international shipping operations on the Baltic Sea are relatively high, amounting to 353 ktonnes (NO_2). In comparison to annual emissions from the individual HELCOM countries during the same year, only emissions from the Russian Federation, Germany and Poland are higher than emissions from shipping traffic. Ship emissions therefore have to be considered as a very important source of depositions into the Baltic Sea. A map illustrating annual nitrogen oxides emissions issuing from ship traffic on the Baltic Sea in 1990 is shown in Figure 4.4.

4.3 Nitrogen emissions from HELCOM countries during the period 1996 - 2000

A map showing annual emissions of nitrogen oxides from all HELCOM countries between 1996 and 2000 is shown in Figure 4.5. Emissions from all these countries are lower in 2000 than in 1996 with the most significant drop in nitrogen oxides emissions occurring in Denmark – 32%. During the considered period constant reductions were observed in Finland, Sweden, Denmark, Germany and Poland, whereas variable emissions could be seen coming from the Russian Federation, Estonia, Latvia and Lithuania.

A similar map illustrating annual emissions of ammonia from all HELCOM countries during the period 1996 – 2000 is shown in Figure 4.6. In the case of ammonia also, emissions from all HELCOM countries were found to be lower in 1996 than in 2000, however, differences were smaller than in the case of nitrogen oxides. No clear pattern in annual emissions of ammonia from the HELCOM countries can be discerned over the considered period.

Annual emissions of nitrogen oxides, ammonia and total nitrogen (nitrogen oxides plus ammonia), from all HELCOM countries during the review period 1996 - 2000 are shown in Figure 4.7. Nitrogen oxides emissions from international shipping traffic on the Baltic Sea are not taken into account in Figure 4.7 because of the lack of data for the considered period. Emissions of nitrogen oxides and ammonia from HELCOM countries were lower in 2000 than in 1996. Over the 5-year period, emissions of nitrogen oxides declined by 13.5%, compared to a 9% decrease in ammonia emissions. Total nitrogen emissions (nitrogen oxides + ammonia) were 11% lower in 2000 than in 1996. These findings indicate that nitrogen emission reduction was more effective in HELCOM countries than in the entire EMEP domain.

4.4 Heavy metal emissions from HELCOM countries during the period 1996 - 2000

Maps describing annual emissions of cadmium, mercury, and lead from all HELCOM countries over the period 1996–2000 are shown in Figures 4.8 - 4.10. Most of these values are based on official information submitted by countries. However in cases where there was no information on emissions, values for the previous years were used. The tables with the emissions data used in the modelling analysis can be found in the Annex.

Total emissions of lead into the Baltic Sea region decreased from 4051 t in 1996 to 3632 t in 2000, with the most significant decline coming from Latvia (more than 90%). Cadmium emissions in this region decreased from 160 t in 1996 to 117 t in 2000 with the largest decrease of approximately 90% observed in Sweden. Emissions of mercury fell from 80 t in 1996 to 68 t in 2000, and in the case of lead the greatest reduction was recorded in Latvia (76%).

Based on the available official data and expert estimates, emissions of heavy metals from the HELCOM Contracting Parties decreased between 1996 and 2000 - by 26% for Cd, 15% for Hg, and 10% for Pb (Figure 4.11). The data show that compared to changes in total emissions within the EMEP region there has been a smaller decrease in the heavy metals emissions from the HELCOM Contracting Parties.

4.5 Lindane emissions from HELCOM countries during the period 1996 - 1998

Observations of lindane depositions into the Baltic Sea were conducted over a longer period than for heavy metals and nitrogen compounds. These extended observations were designed to take into account accumulation in and subsequent re-emission from soil and seawater compartments. Modelling results were obtained using available expert estimates from the POPCYCLING Baltic project (Pacyna, 1999b) for 1970-1996 and the available official data on lindane emissions from HELCOM Contracting Parties between 1990 and1998. According to official information submitted by HELCOM countries there were no emissions of lindane from Finland and Sweden after 1990. In the case of Germany and Russia, official emissions data are available for 1994 and 1990, respectively. Due to the absence of official information it was assumed that there were no emissions of lindane in the Russian Federation from 1991.

A map showing annual emissions of lindane from all HELCOM countries for the period 1970–1998 is shown in Figure 4.12. Most changes in emissions patterns occurred in the 70s and 80s as a result of restrictions or prohibitions on the use of lindane in these countries. Since 1990 the level of lindane (γ-HCH) emissions in this region has decreased by more than an order of magnitude compared to 1970 (Figure 4.13). According to available data lindane emissions of HELCOM countries during the period 1996-1998 remained practically on the same level.

4.6 Source allocation budgets for nitrogen

Source allocation budgets for nitrogen compounds were not available for the entire period 1996 – 2000. Therefore as a model, Figure 4.14 shows the source allocation estimates for nitrogen for 1997. The assumption is that with some uncertainty, Figure 4.13 can represent a typical pattern for the entire period 1996 – 2000. Once the remaining model data become available, source allocation budgets for 1997 will be replaced by the nitrogen source allocation estimates for the period 1996 – 2000.

4.7 Source allocation budgets for heavy metals

Source allocation budgets for depositions of heavy metals into the Baltic Sea were computed for the entire period 1996 – 2000. Figures 4.15 - 4.17 present the source allocation budgets for cadmium, lead, and mercury, respectively for 1996 and 2000. It can be seen that compared to depositions occurring in 1996 the input from anthropogenic sources in 2000 has decreased. Inputs from natural, previous and remote anthropogenic sources have played an important role in this process.

The contribution of HELCOM Contracting Parties to the total deposition of cadmium into the Baltic Sea decreased from 50% to 39% during the review period. Of these countries the most significant proportion came from anthropogenic emission sources from Poland – 34% in 1996 and 24% in 2000. Other EMEP countries contributed 7% in 1996 and 11% in 2000.

Total lead total deposition into the Baltic Sea by HELCOM Contracting Parties decreased from 39% to 31%. The proportion of depositions from other

EMEP countries is more significant in relation to cadmium – roughly 20%. Of all the HELCOM Contracting Parties, the most significant input also emanated from anthropogenic sources in Poland – 14% in 1996 and 11% in 2000.

Total deposition of mercury from HELCOM Contracting Parties into the Baltic Sea decreased less significantly – from 46% in 1996 to 43% in 2000.

According to modelling results the contribution of emissions from HELCOM and other EMEP countries remained on practically the same level from 1996 to 2000. Emissions of mercury from HELCOM countries were contributing more significantly (46% in 1996 and 43% in 2000) than from other EMEP countries, which amounted to 5-6%. The most significant inputs from HELCOM countries came from Poland in 1996 (15%) and Germany in 2000 (19%).

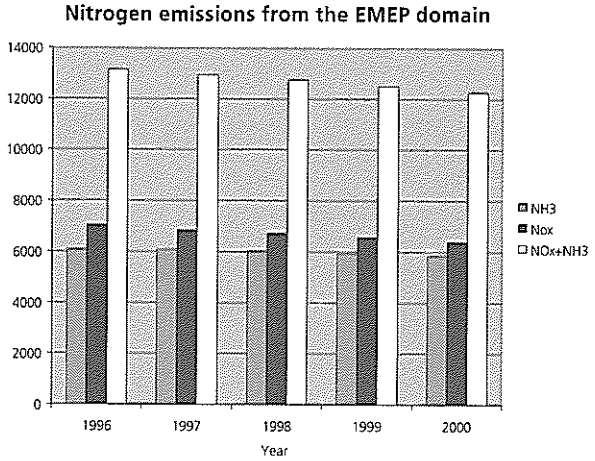


Figure 4.1
Annual emissions of nitrogen oxides, ammonia and total nitrogen (nitrogen oxides + ammonia) from the EMEP domain for the period 1996 - 2000. Units: ktonnes N/yr.

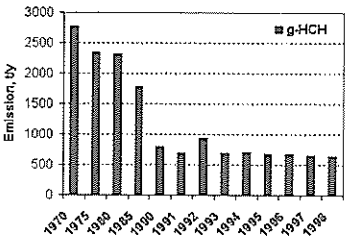


Figure 4.3
Annual emissions of lindane (γ-HCH) from the EMEP domain for the period 1996 - 2000. Units: tonnes/yr.

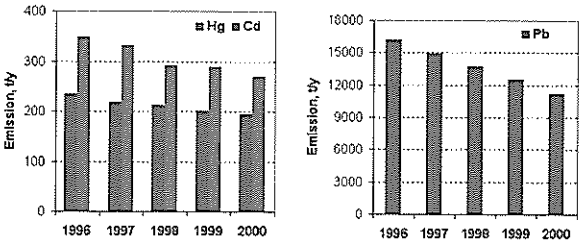


Figure 4.2
Annual emissions of cadmium, mercury and lead form the EMEP domain for the period 1996 - 2000. Units: tonnes/yr.

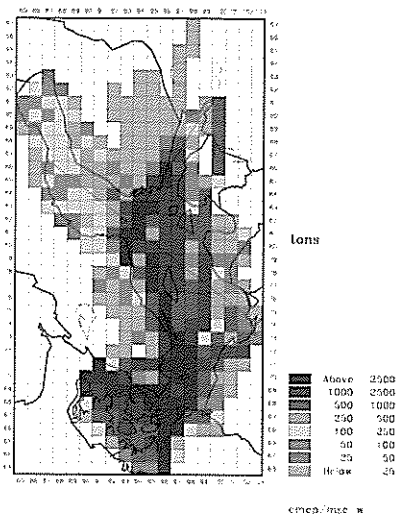
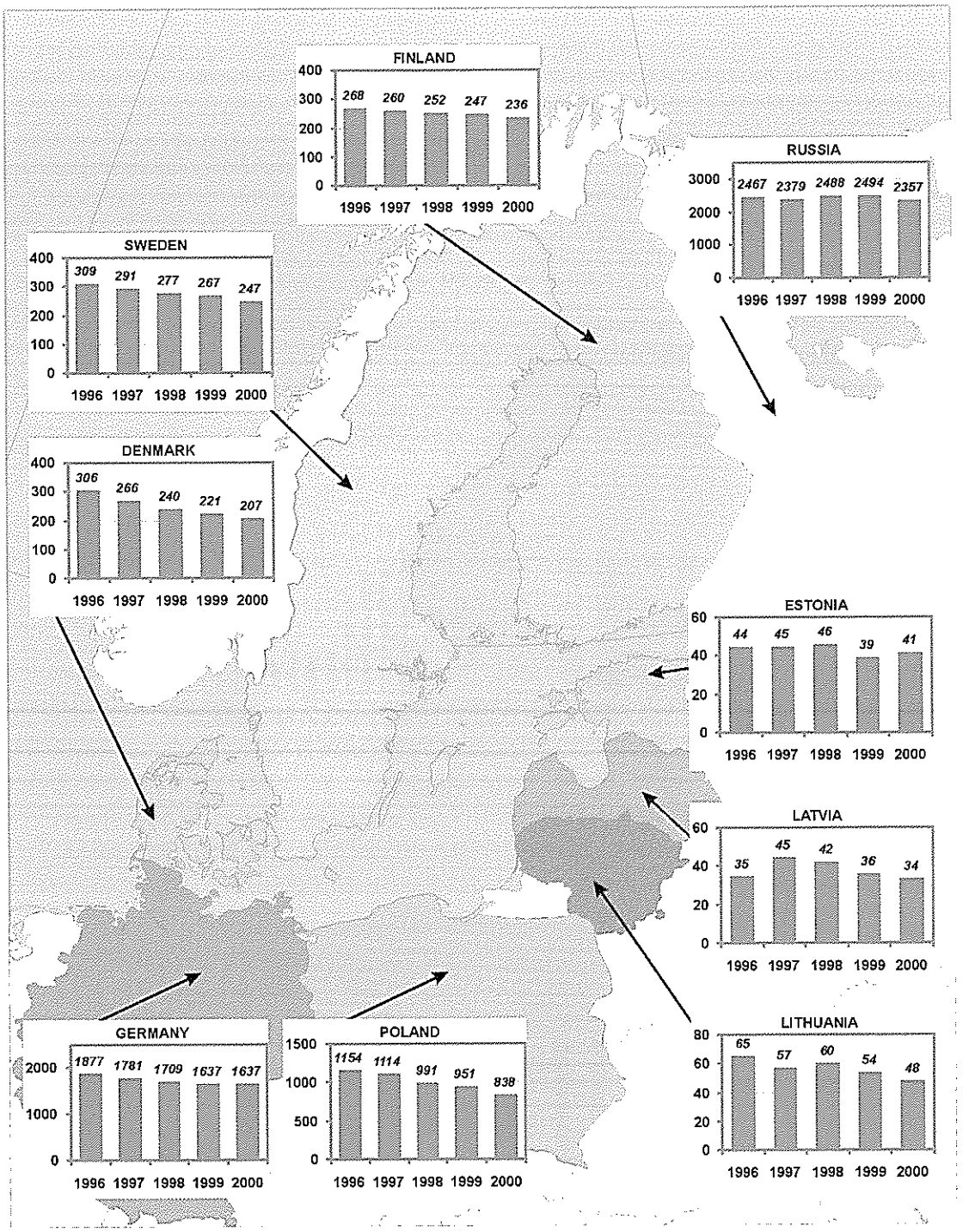


Figure 4.4
Map showing annual emissions of nitrogen oxides from international shipping traffic on the Baltic Sea in 1990. Units: tonnes/yr/50×50km grid.

Figure 4.5
Map showing annual emissions of nitrogen oxides from individual HELCOM countries for the period 1996 – 2000. Units: ktonnes/yr.



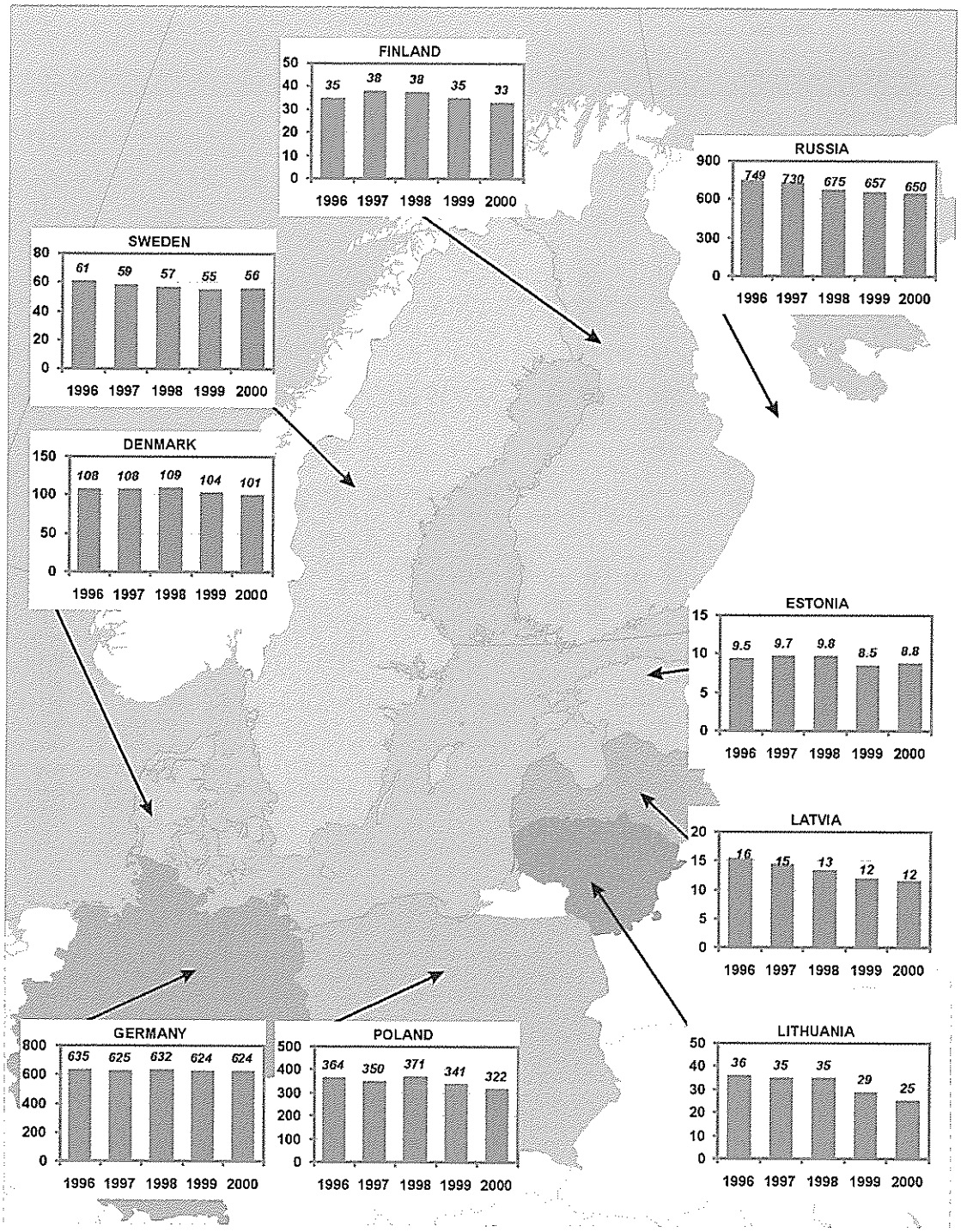


Figure 4.6
Map showing annual emissions of ammonia from HELCOM countries for the period 1996 – 2000. Units: ktonnes/yr.

Figure 4.7
Annual emissions of nitrogen oxides, ammonia and total nitrogen (nitrogen oxides plus ammonia) from all HELCOM countries for the period 1996 – 2000.
Units: ktonnes N/yr.

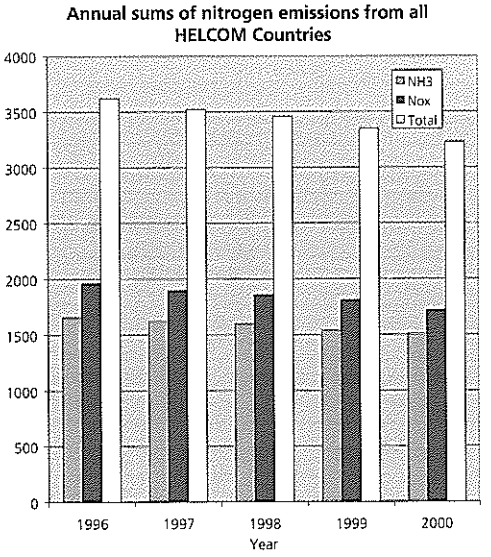
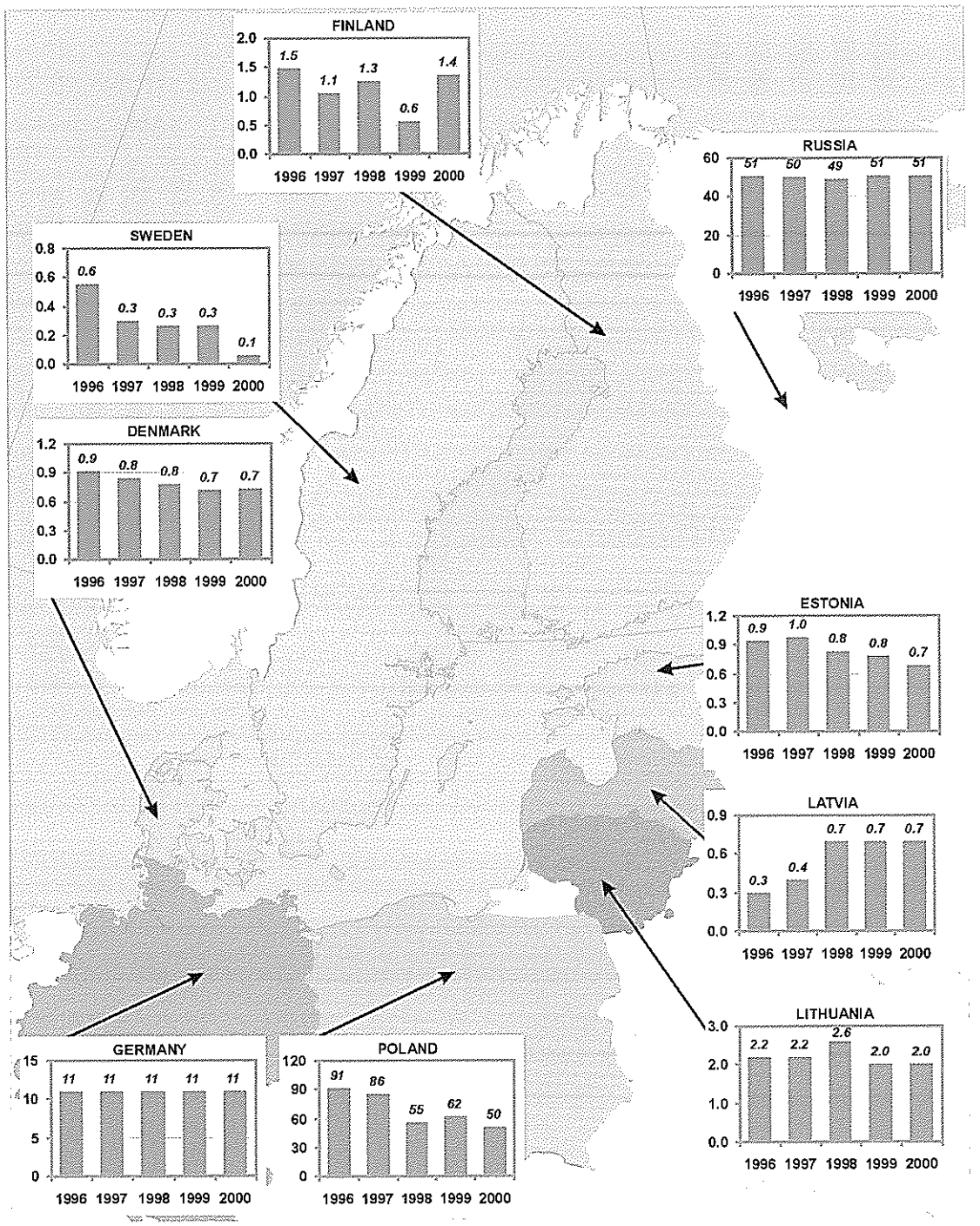


Figure 4.8
Map showing annual emissions of cadmium from individual HELCOM countries for the period 1996 – 2000.
Units: tonnes/yr.



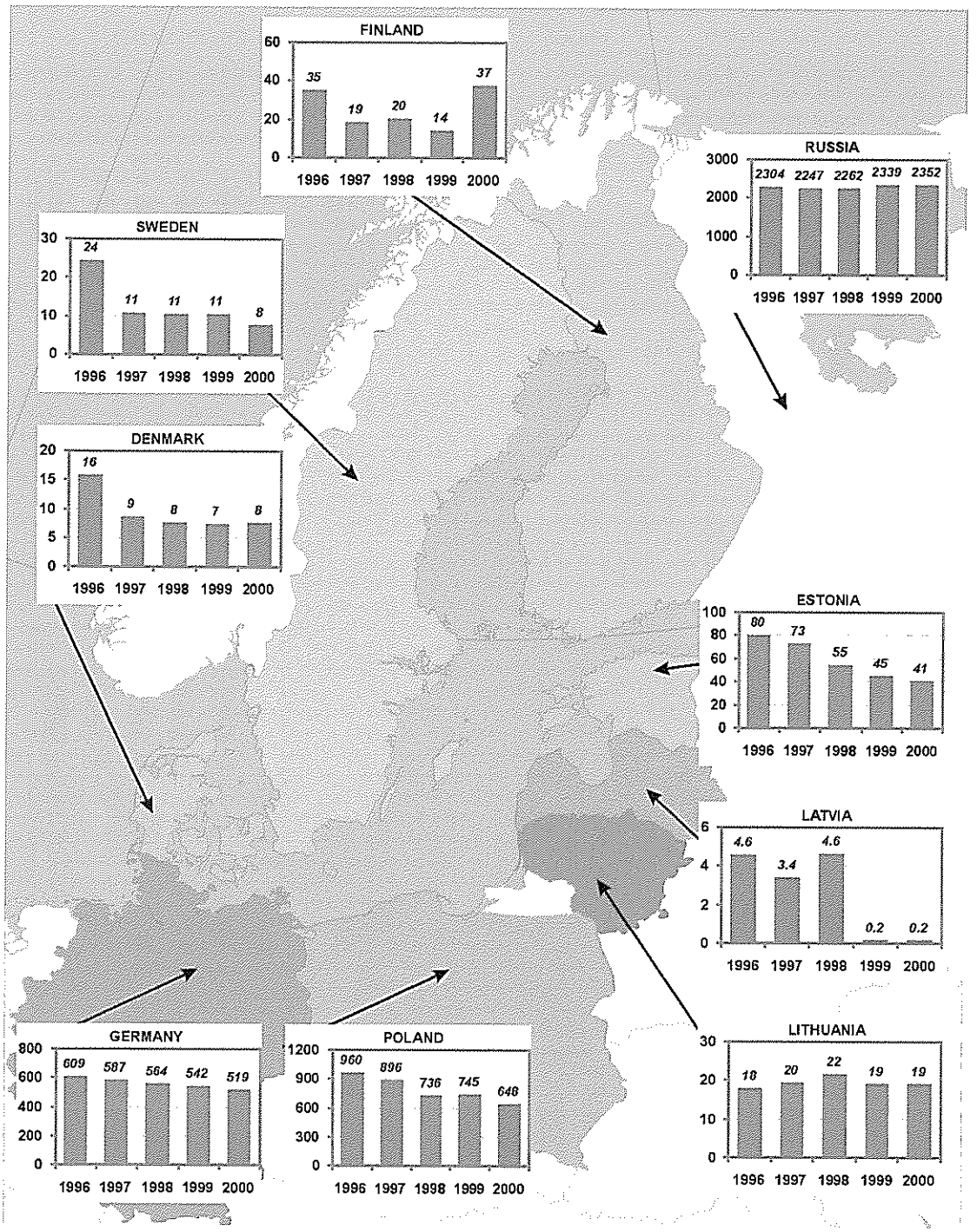
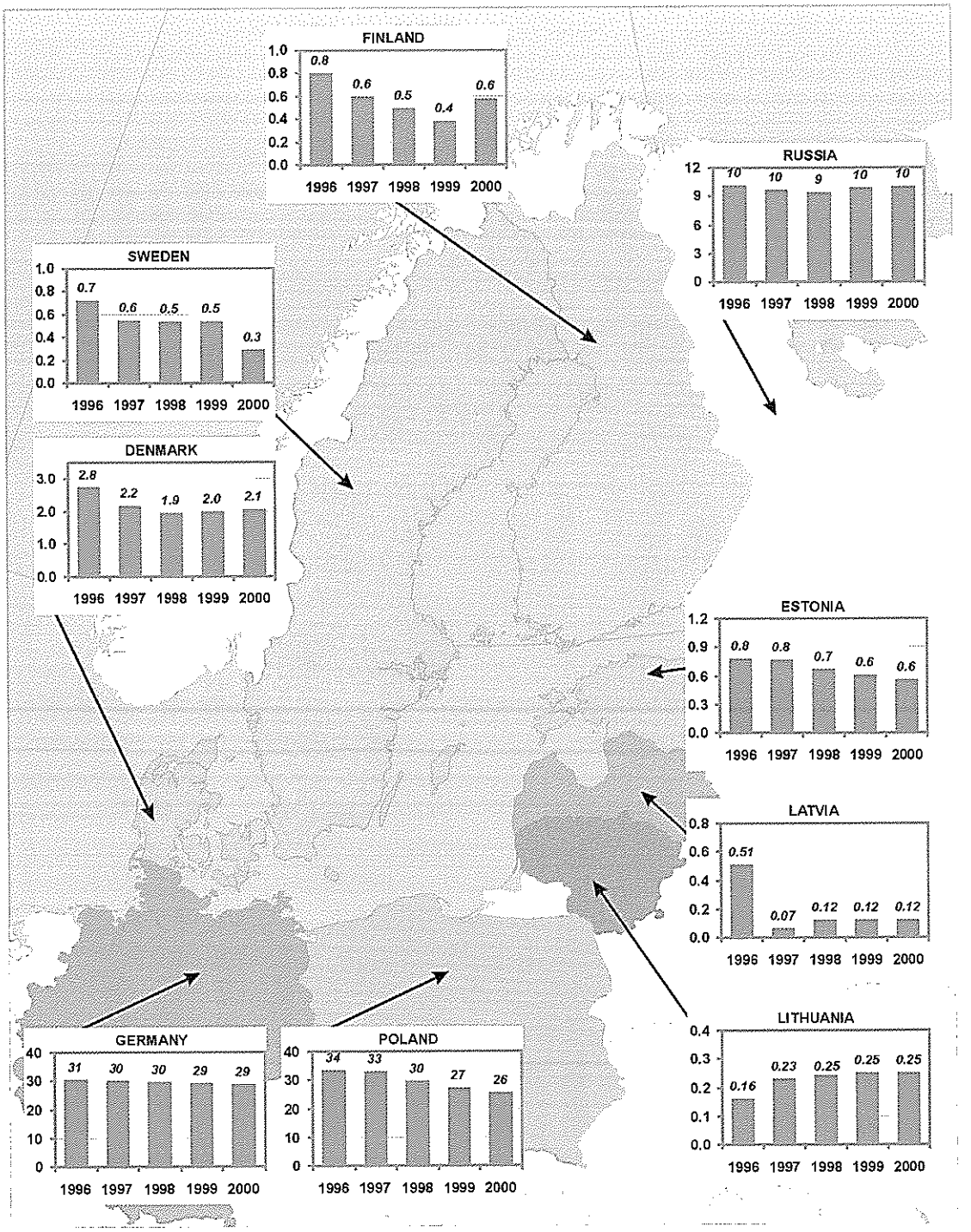
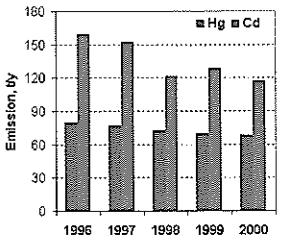


Figure 4.9
Map showing annual total emissions of lead from individual HELCOM countries for the period 1996 – 2000. Units: tonnes/yr.

Figure 4.10
Map showing annual total emissions of mercury from individual HELCOM countries for the period 1996 – 2000. Units: tonnes/yr.





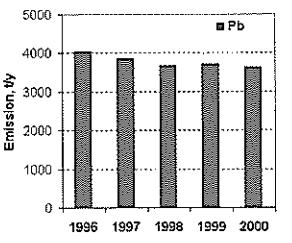


Figure 4.11
Annual emissions of cadmium, mercury and lead from all HELCOM countries for the period 1996 - 2000.
Units: tonnes/yr.

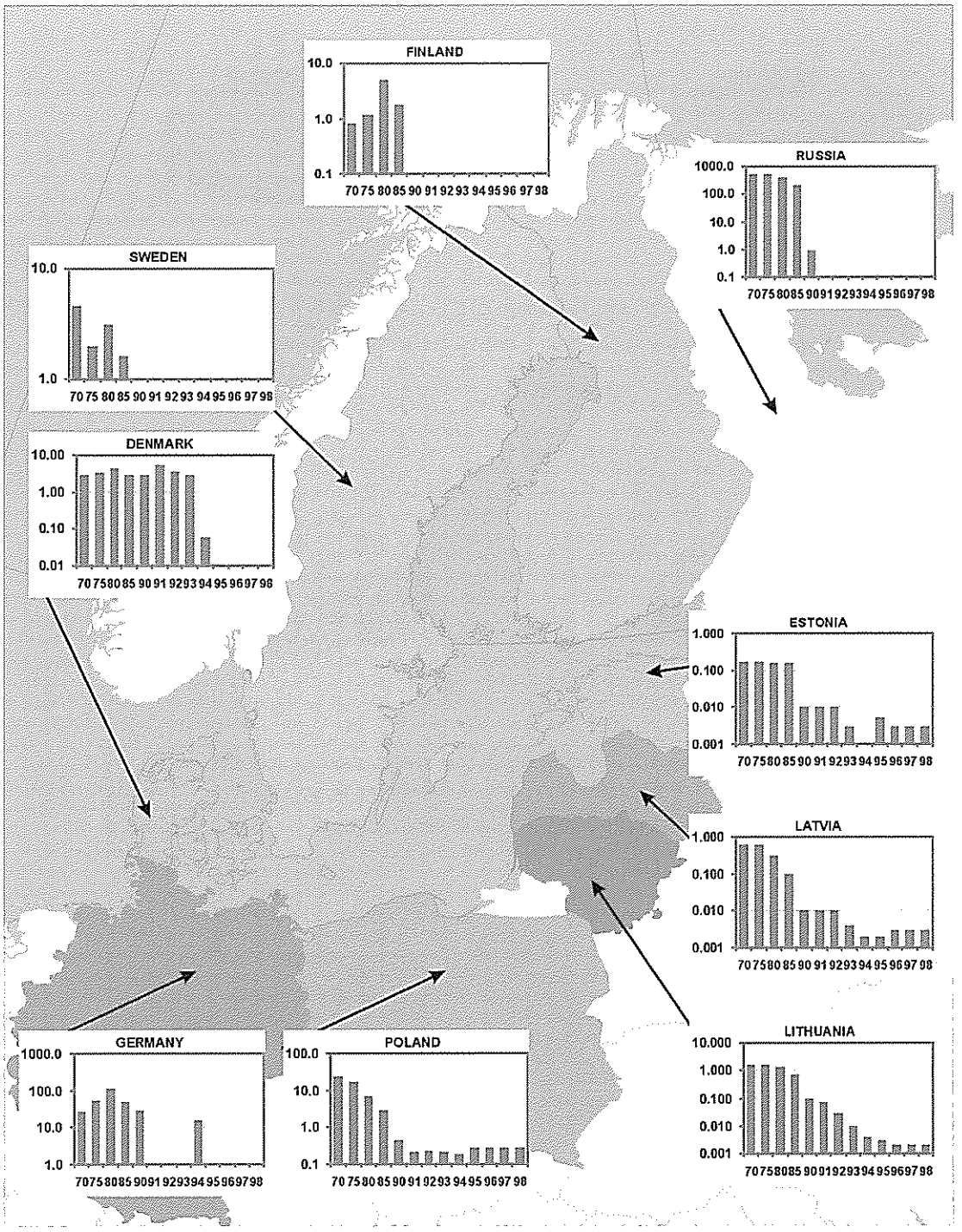


Figure 4.12
Map showing annual total emissions of lindane from individual HELCOM countries for the period 1970 – 1998. Emissions values are presented on the logarithmic scale. Missing bars correspond to an absence of lindane emissions in the particular year. Units: tonnes/yr.

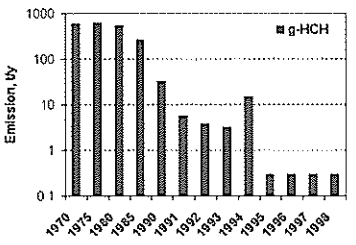


Figure 4.13
Annual total emissions of lindane from all HELCOM countries for the period 1970 – 1998. Emission values are presented on the logarithmic scale. Units: tonnes/yr.

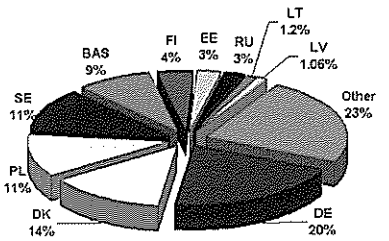
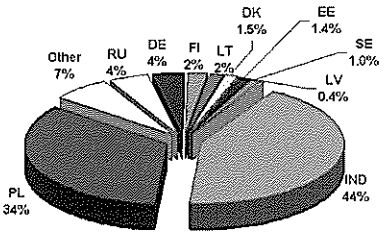
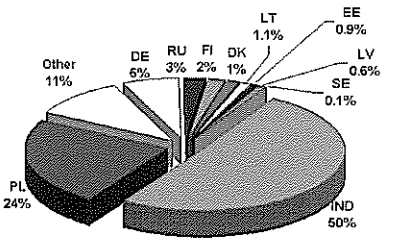


Figure 4.14
Main emissions sources of nitrogen contributing to its annual deposition over the entire Baltic Sea Basin in 1997.



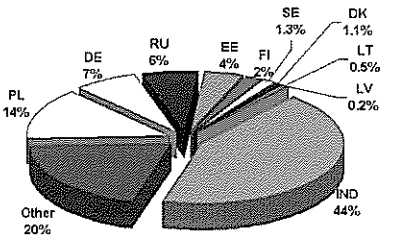
(a)



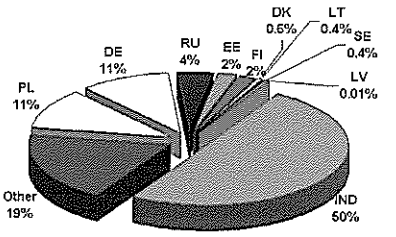
(b)

Figure 4.15

Comparison of main emissions sources of cadmium contributing to its annual deposition over the entire Baltic Sea Basin in 1996 (a) and 2000 (b). Other – means other European countries in total; IND – means indeterminate sources: natural, previous and remote anthropogenic sources.



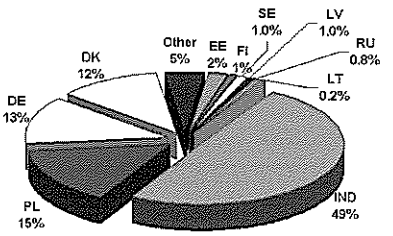
(a)



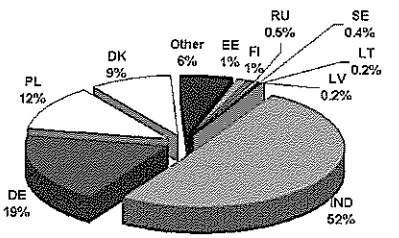
(b)

Figure 4.16

Comparison of main emissions sources of lead contributing to its annual deposition over the entire Baltic Sea Basin in 1996 (a) and 2000 (b) Other – means other European countries in total; IND – means indeterminate sources: natural, previous and remote anthropogenic sources.



(a)



(b)

Figure 4.17

Comparison of main emissions sources of mercury contributing to its annual deposition over the entire Baltic Sea Basin in 1996 (a) and 2000 (b). Other – means other European countries in total; IND – means indeterminate sources: natural, previous and remote anthropogenic sources.

5 Remarks about uncertainties

Precise estimation of uncertainty concerning measurements, emission data and model results is always very difficult and in some cases (e.g. source-receptor matrices) not possible at all. This chapter consequently considers only uncertainties related to the data presented in the report.

5.1 Quality, detection limits and accuracy of measurements

This section addresses the expected quality of the data used in this report. Precise information on accuracy, detection limits and reliability of the reported observations is found in the Annex.

5.1.1 Evaluation of monitoring quality

Matters of quality control generally are the responsibility of the individual monitoring stations and analytical laboratories. As a data monitoring centre, NILU cannot calculate criteria such as detection limits but is able to provide advice, present data for inter-comparison, and offer a forum for cross-comparison. Data evaluation work such as this is necessarily conducted in association with other international programmes, such as the Arctic Monitoring and Assessment Programme (AMAP), and the European Monitoring and Evaluation Programme (EMEP) of the UN ECE (United Nations Economic Commission for Europe).

In order to provide a summary of different statistical assessments of quality, the results of various audits have been combined. Focusing on nitrogen components, the collected results of the monitoring quality relating to nitrogen components have been evaluated during the latter years of the 1996-2000 period. The resulting classification is intended to provide such an analysis. Results presented here are taken from the EMEP data quality report (Aas *et al.* 2001), and are intended to provide an assessment of expected data quality on the basis of examinations conducted over a period. The sources used in the estimates were:

1) EMEP laboratory inter-comparisons for 1999 and 2000 (Hanssen and Skjelmoen, 2001 and Uggerud *et al.*, 2001)
2) Field inter-comparison results (Schaug *et al.* 1998, Aas *et al.* 1999)
3) Ion balance calculations.

It should be noted that the intention of Table 5.1 below is not to give precise values, but to assemble available data and provide a reliable judgment about the expected quality of the data used throughout the period. As stated, more precise information on accuracy, detection limits and reliability is contained in the Annex, where the information assembled from a request for quality assurance data made earlier this year is also presented. Data requested included

	NH_4 prec	NO_3 prec	NO_2 Air	NO_3 Air	NH_4 Air	HNO_3+NO_3 Air	NH_3+NH_4 Air
DE9 Zingst	A	A	D				
DK5 Keldsnor	A	A	A				
DK8 Anholt	A	A	A				
EE9 Lahemaa	A	A	C				
EE11 Vilsandy	A	A	U				
FI9 Utoe	A	A	C			A	A
FI17 Virolahti	A	A	C			A	A
LT15 Preila	A	A	A	U	U	A	A
LV10 Rucava	A	A	A	U	U	A	A
LV16 Zoseni	A	A	A	U	U	A	A
PL4 Leba	A	A	B	U	U	A	A
SE2 Roervik	A	A	A			A	A
SE5 Bredkaelen	A	A	A			A	A
SE8 Hoburg	A	A	A				
SE11 Vavihill	A	A	A			A	A
SE12 Aspvreten	A	A	A			A	A

Table 5.1
Classified summary of data quality for nitrogen components.

Table 5.1 gives a summary of the expected quality of nitrogen monitoring data expressed in four classes:

- Class **A**: expected error 10% or better
- Class **B**: expected error 25% or better
- Class **C**: expected error 30% or better
- Class **D/U**: expected error worse than 30% (D), or unknown quality (U)

Table 5.2
Laboratory inter-calibration of components in air and precipitation; average percentage error compared with expected value (in high and low concentrations samples for metals).

Country	AIR			PRECIPITATION					
	HNO_3	NH_3	NO_2	NO_3-N	NH_4-N	Cd		Pb	
						low	high	low	high
DK	3.7	6.4	4.4	1.0	0.9				
FI	0.8	3.1		1.2	1.4	18	13	13	9
DE	0.7			3.7	3.1	5	4	5	1
PL	4.4	15	2.7	4.2	4.2	5		10	5
SE	4.4	2.7	1.4	1.0	0.4				
LV	30	43	6.7	0.8	2.2	10	12	10	1
EE			2.0	15	3.5		4		17

<5% 5-10% 10-20% >20%

measurement and laboratory lower detection limits and precision results from control samples, as well as detection limits and precision data for monitors.

The quality of laboratory analysis of components can also be summarised. Recent laboratory inter-comparisons have been conducted by EMEP in which the participating national laboratories were provided with manufactured samples, and the results of their analysis compared with the actual concentrations. Results are available for both nitrogen and metal components. Table 5.2 provides the summarised results.

5.2 Emissions, computed concentrations and depositions

Uncertainties for national nitrogen oxides and ammonia emissions varied significantly from one country to another. In addition, for some countries there was no information at all about the uncertainty of emissions. The preceding remarks refer to total annual emissions from the countries in question. With regard to the individual grid cells, the uncertainties were larger and there was practically no information available about the uncertainties of nitrogen emissions. Furthermore, the typical uncertainty level for annual total emissions from the HELCOM countries was approximately 20% (EMEP, 2002).

Official data on heavy metal emissions can be underestimated to some extent since it is impossible to take into account the total diversity of possible sources when emissions data are compiled at unit levels (Ilyin *et al.*, 2002). According to data gathered from the UBA/TNO project (Berdowski *et al.*, 1997) the uncertainty can vary between factors of 1.5 and 3.5. The real emissions values of north-western Europe countries can differ from estimates by 20-50% and the uncertainty level can be even higher for countries in central and eastern Europe.

There are gaps in time coverage in the official data for lindane, and furthermore this information is not available for all European countries. As a result expert estimates on omissions on the relevant pollutants were used to fill gaps in official information. Pacyna *et al.* (1999), show that the accuracy of data increases from the 1970s to the 1990s, reflecting the availability of more reliable information.

With respect to computed concentrations and depositions of nitrogen, uncertainty levels typically lie at 30% (EMEP, 2002), but in some cases differences between measured and computed values can be much larger. A comparison of computed and measured wet depositions of nitrogen compounds is laid out in the next section. However the issue of uncertainty is more difficult when it must be estimated for source-receptor relations. In the case of nitrogen such an analysis has not been done. Moreover, computed source receptor relationships cannot be compared with measurements, because such measurements do not exist.

The MSCE-HM model has been verified in a number of inter-comparison campaigns with other regional standards (*Sofiev et al.*, 1996; *Gusev et al.*, 2000; *Ryaboshapko et al.*, 2001) and has been proven by means of sensitivity and uncertainty studies (*Travnikov*, 2000). It has been satisfactorily proven that modelling analysis performed in relation to the airborne transportation of heavy metals conform to the available measured data, and that any discrepancies do not exceed a factor of two. This comparison of calculated results against the measured data indicates that the model can predict the observed air concentrations of lead and cadmium with an accuracy level of 30%. Calculated values for concentrations in precipitation may be twice as much as measured values, or vice versa. Computed mercury concentrations deviate from measured values by a factor of two. Discrepancies between

measured and calculated concentrations of γ-HCH in the MSCE-POP model lie between the factors of 3-4 (Shatalov *et al.*, 2000).

5.3 Comparison of measured and computed concentrations

A comparison of measured and computed values for annual wet depositions of oxidized and reduced nitrogen is shown in Figures 5.1 and 5.2 respectively.

In the case of both oxidized and reduced nitrogen, agreement between measured and computed wet depositions values was satisfactory, when all uncertainties were considered. In terms of oxidized nitrogen, the best level of agreement was apparent at the Danish station Anholt, Swedish stations Brodkalen and Vavihill and the Polish station Leba. The best level of agreement between the measured and computed values of reduced nitrogen was evident at these same locations, and also at the Finish station Virolahti II.

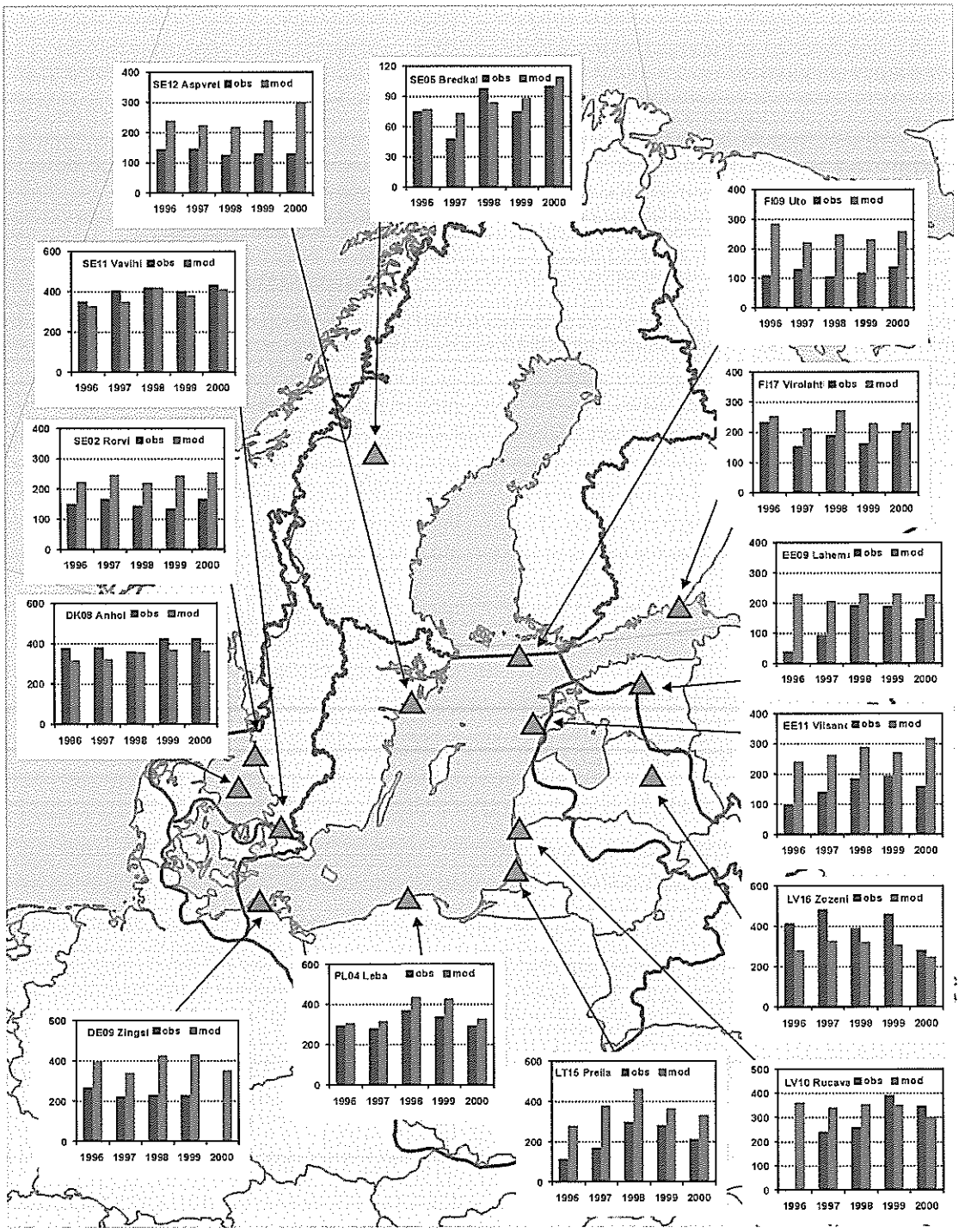
At some stations, mainly those in the Baltic Proper sub-basin, computed wet depositions of oxidized and reduced nitrogen slightly overestimated measured wet depositions.

Comparison of measured and computed mean annual concentrations of cadmium, lead, mercury, and lindane (γ-HCH) in precipitation is shown in Figures 5.3-5.6. Computed concentrations in precipitation were compared with observations at selected sites. Data were not included from sites for which values of total measured and estimated annual precipitation differed by more than 1.5 times. Additionally, the mean annual concentrations were not included for years in which there were no monthly mean data for three or more months. Concentrations of lead and cadmium in precipitation computed with the MSCE-HM model were on average lower than observed; 3 times in the case of lead and in the case of cadmium, twice (Figures 5.3 and 5.4). The most probable reason for underestimations in observed concentrations of lead and cadmium was the underestimated emissions data. This meant that the actual atmospheric load of these compounds entering the Baltic Sea was probably higher than the estimated depositions values.

Comparison of computed concentrations of mercury and lindane (γ-HCH) in precipitation were complicated by the unavailability of measurement data. Computed concentrations for mercury were slightly higher than measurements recorded at the Swedish stations Rorvik (SE02), Bredkalen (SE05), Aspvreten (SE12), and Vavihill (SE11). More significant discrepancies were observed at Zingst (DE09) (Figure 5.5). On the other hand, computed concentrations of lindane (γ-HCH) in precipitation were consistent with measurements recorded at Zingst (DE09) for 1996 and 1997 (Figure 5.6).

Comparison of measured and computed mean annual concentrations of cadmium, lead, mercury, and lindane (γ-HCH) in air is shown in Figures 5.7-5.10. In general computed air concentrations for lead and cadmium were slightly lower than the measured data (Figures 5.7 and 5.8), variations between the two values falling in the 30% range. Fewer observations were available for mercury and lindane (γ-HCH) air concentrations. Computed mercury concentrations were 1.5 times higher than measured data at Rorvik (SE2) for the period under review (Figure 5.9). Findings relating to lindane (γ-HCH) showed that computed air concentrations were significantly higher at Rorvik (SE2) and closer to observed values at Aspvreten (SE12) (Figure 5.10).

Figure 5.1
Comparison of measured and calculated annual wet depositions of oxidized nitrogen for the period 1996 - 2000. Units: mg m^{-2} yr^{-1}.



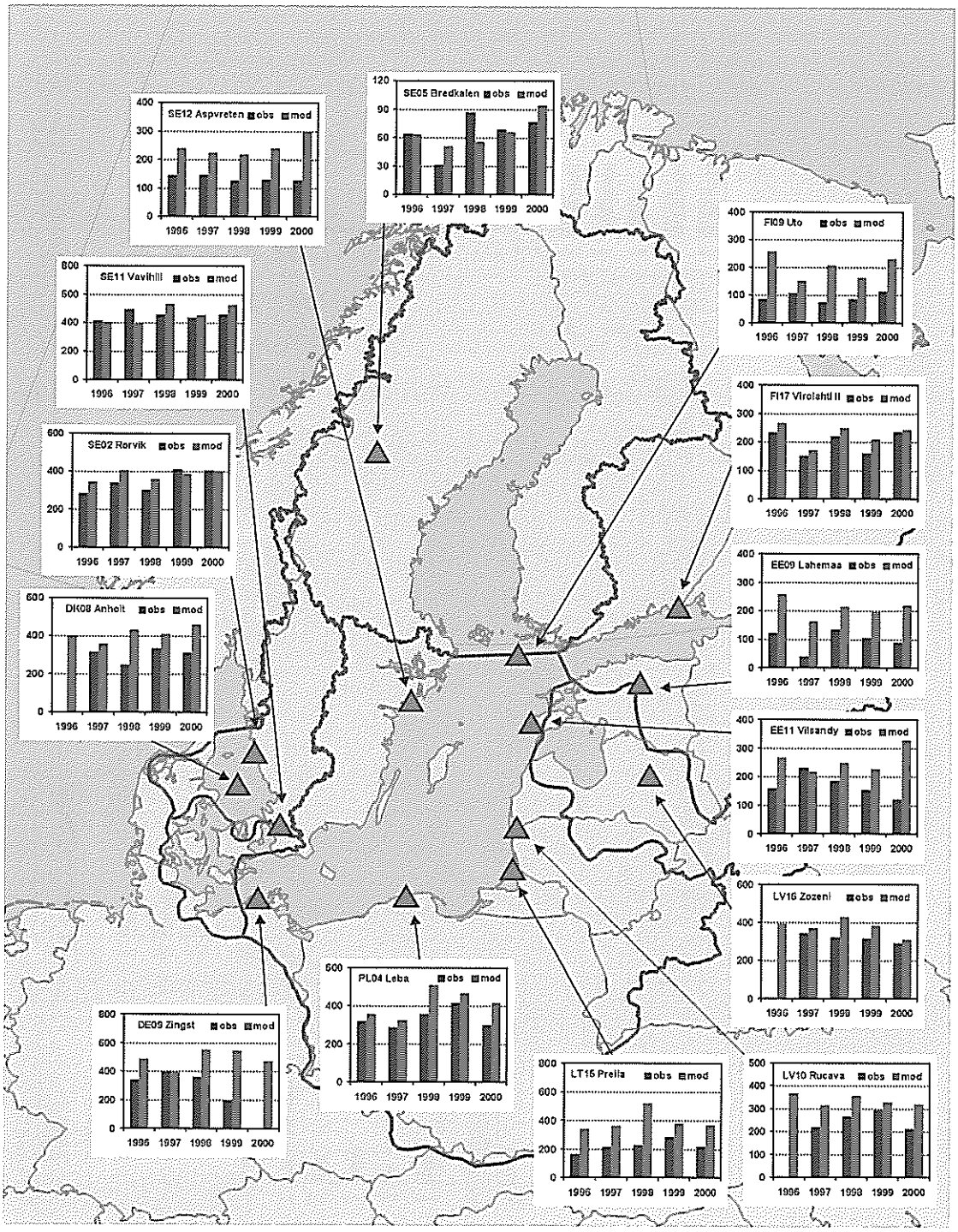
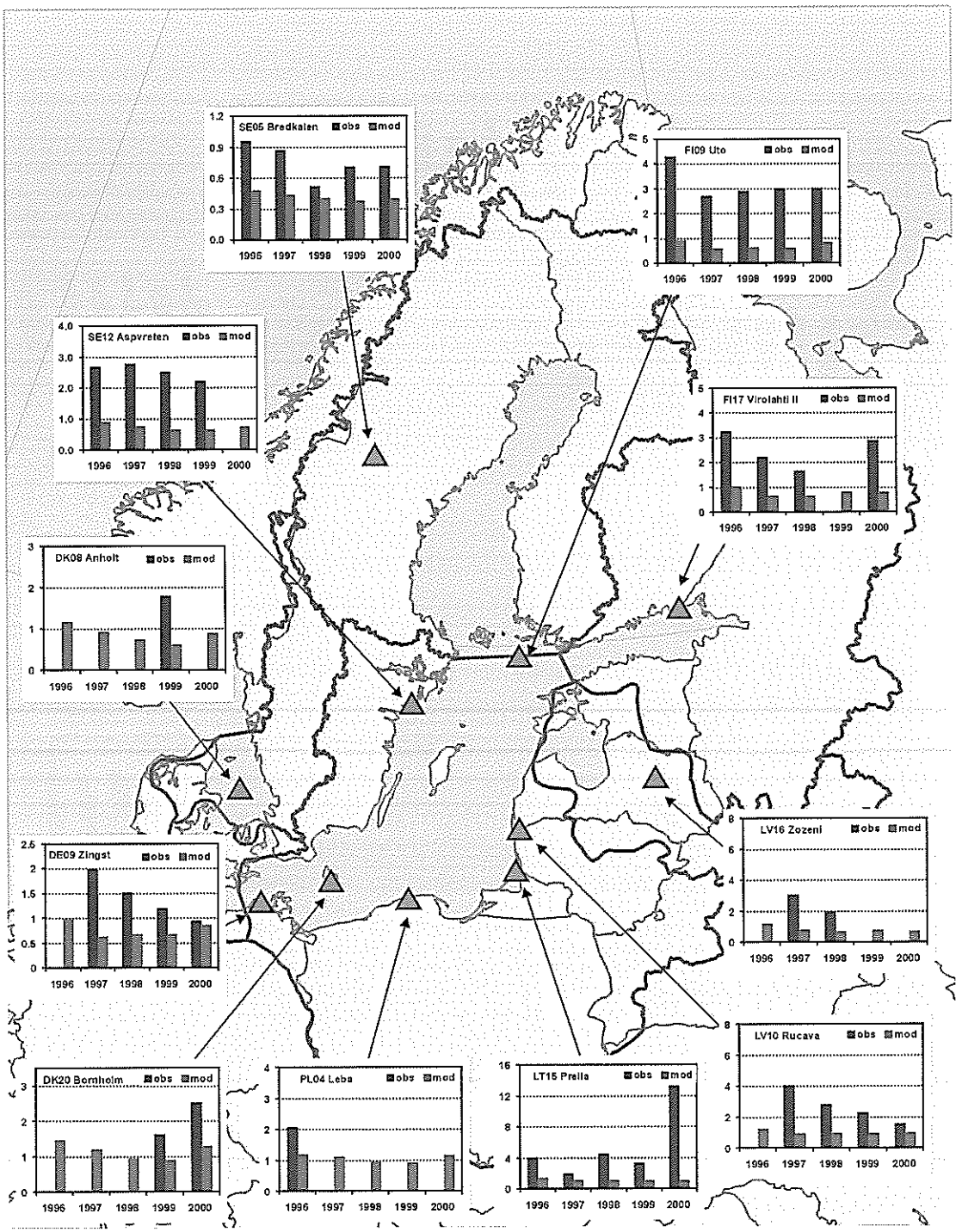


Figure 5.2
Comparison of measured and calculated annual wet depositions of oxidized nitrogen for the period 1996 - 2000.
Units: mg m^{-2} yr^{-1}.

Figure 5.3
Comparison of measured and calculated annual average concentrations of lead in precipitation for the period 1996 - 2000. Units: µg/l.



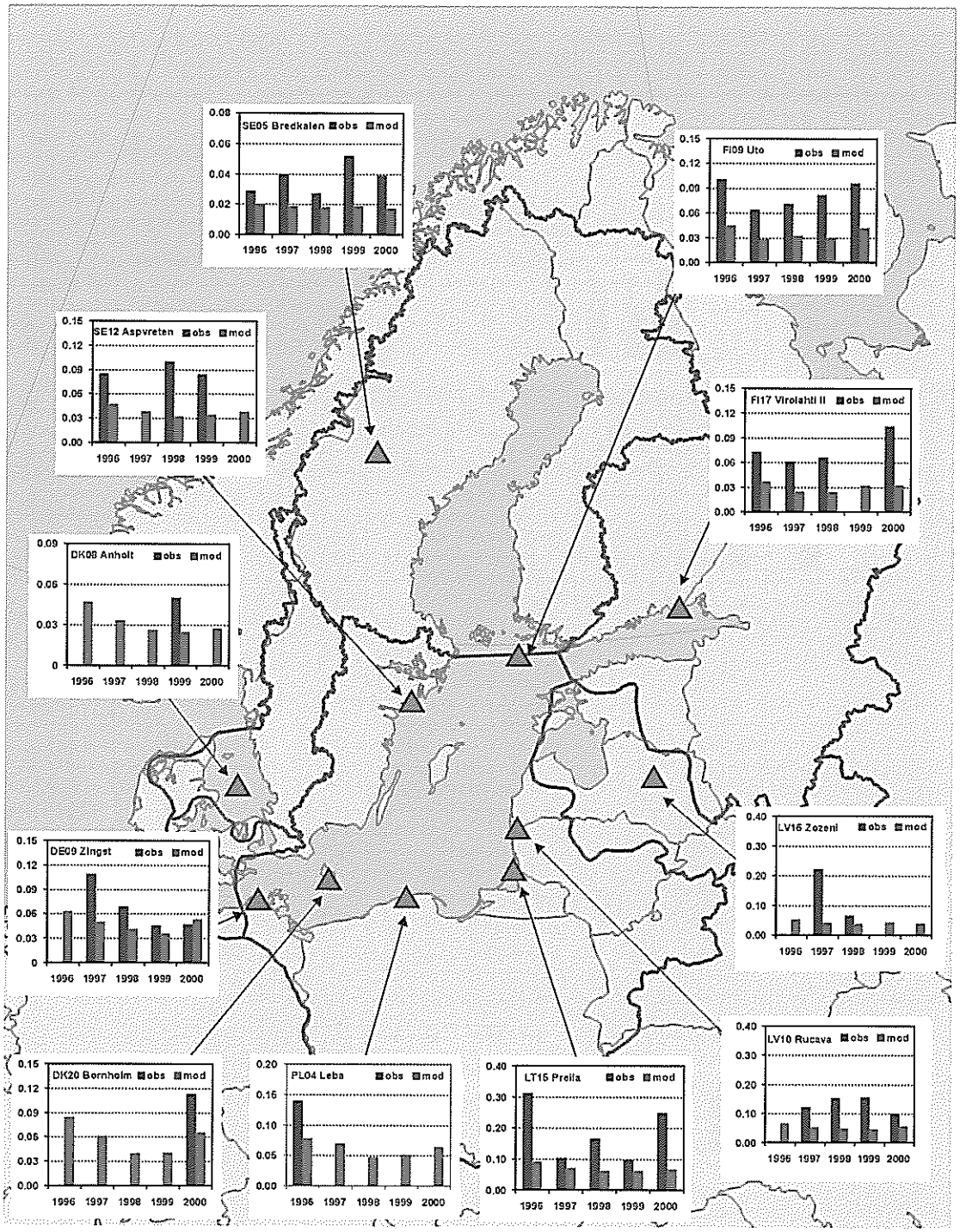
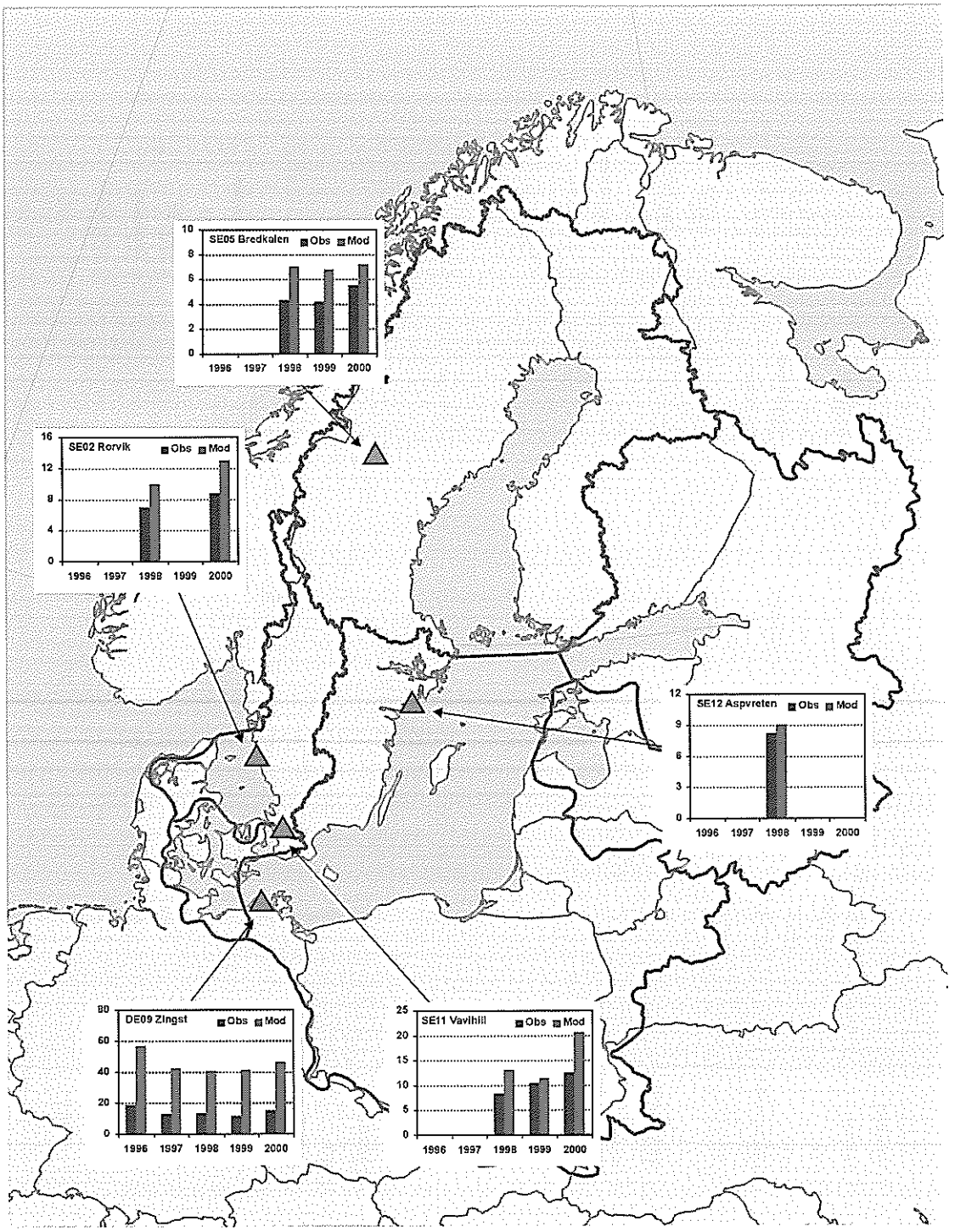


Figure 5.4
Comparison of measured and calculated annual average concentrations of cadmium in precipitation for the period 1996 - 2000. Units: pg/l.

Figure 5.5
Comparison of measured and calculated annual average concentrations of mercury in precipitation for the period 1996 - 2000. Units: ng/l.



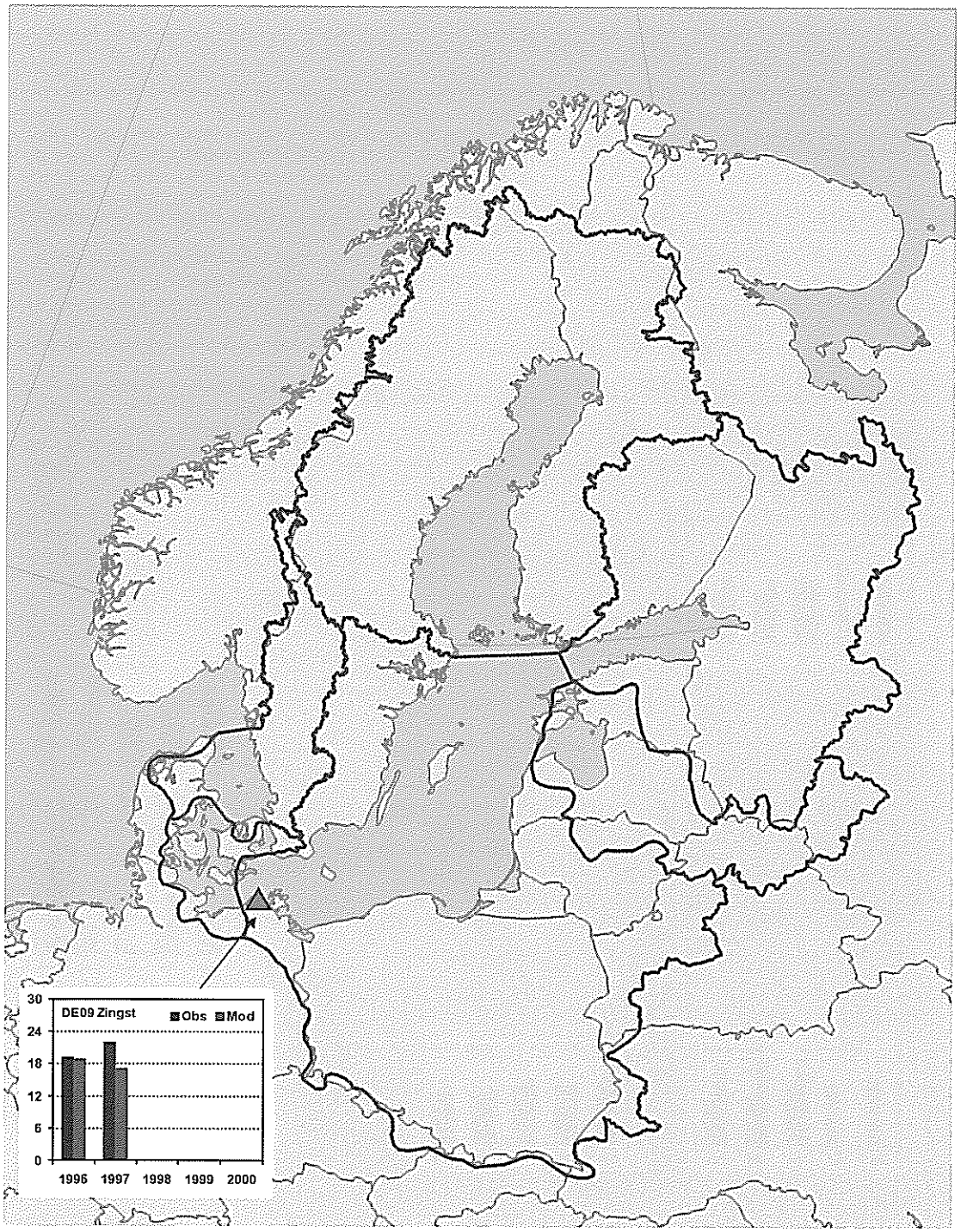
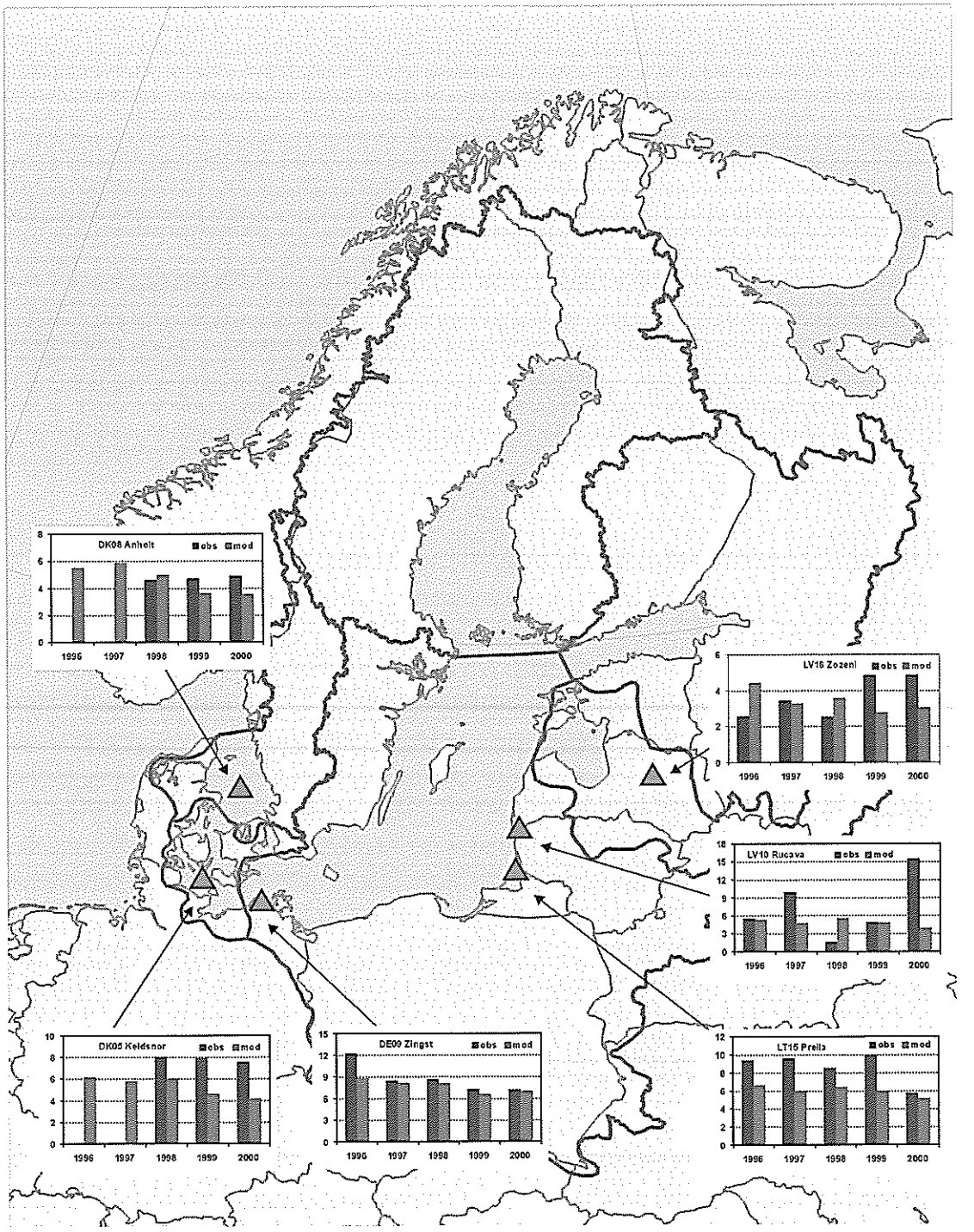


Figure 5.6
Comparison of measured and calculated average concentrations of γ-HCH in precipitation for the period 1996 - 2000. Units: ng/l.

Figure 5.7
Comparison of measured and calculated annual lead concentrations in air.
Units: ng/m^3.



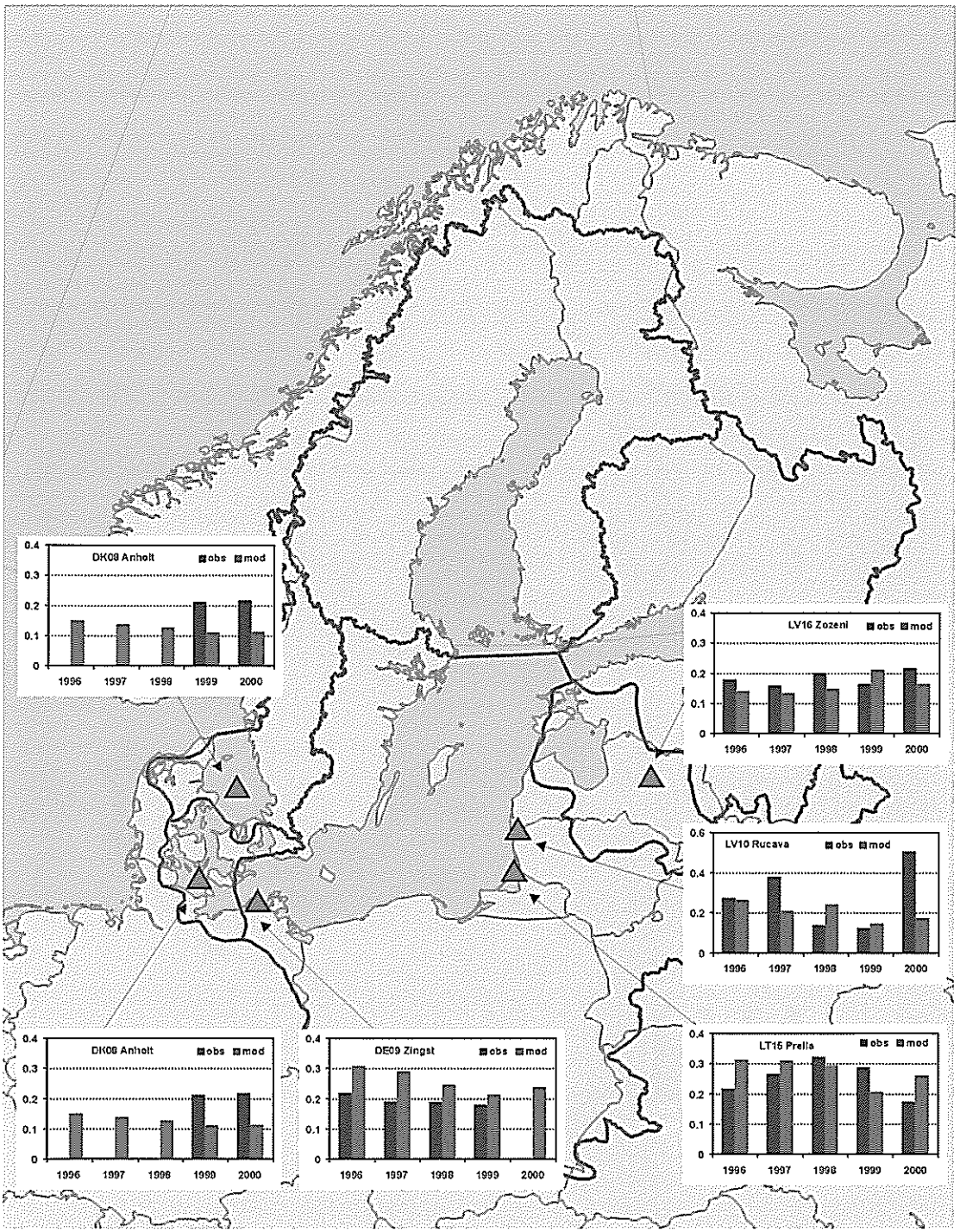
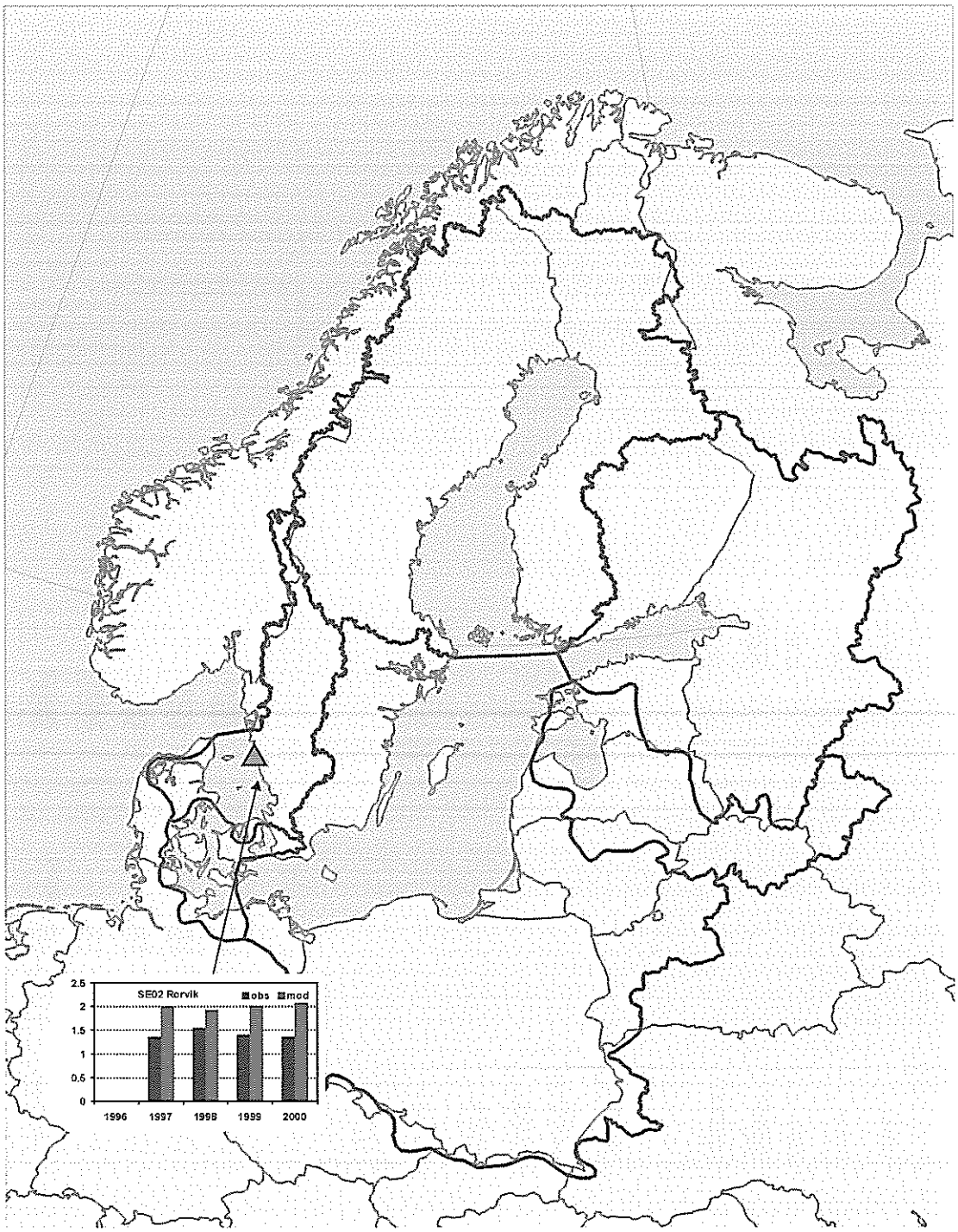


Figure 5.8
Comparison of measured and calculated annual cadmium concentrations in air.
Units: ng/m^3.

Figure 5.9
Comparison of measured and calculated annual mercury concentrations in air. Units: ng/m^3.



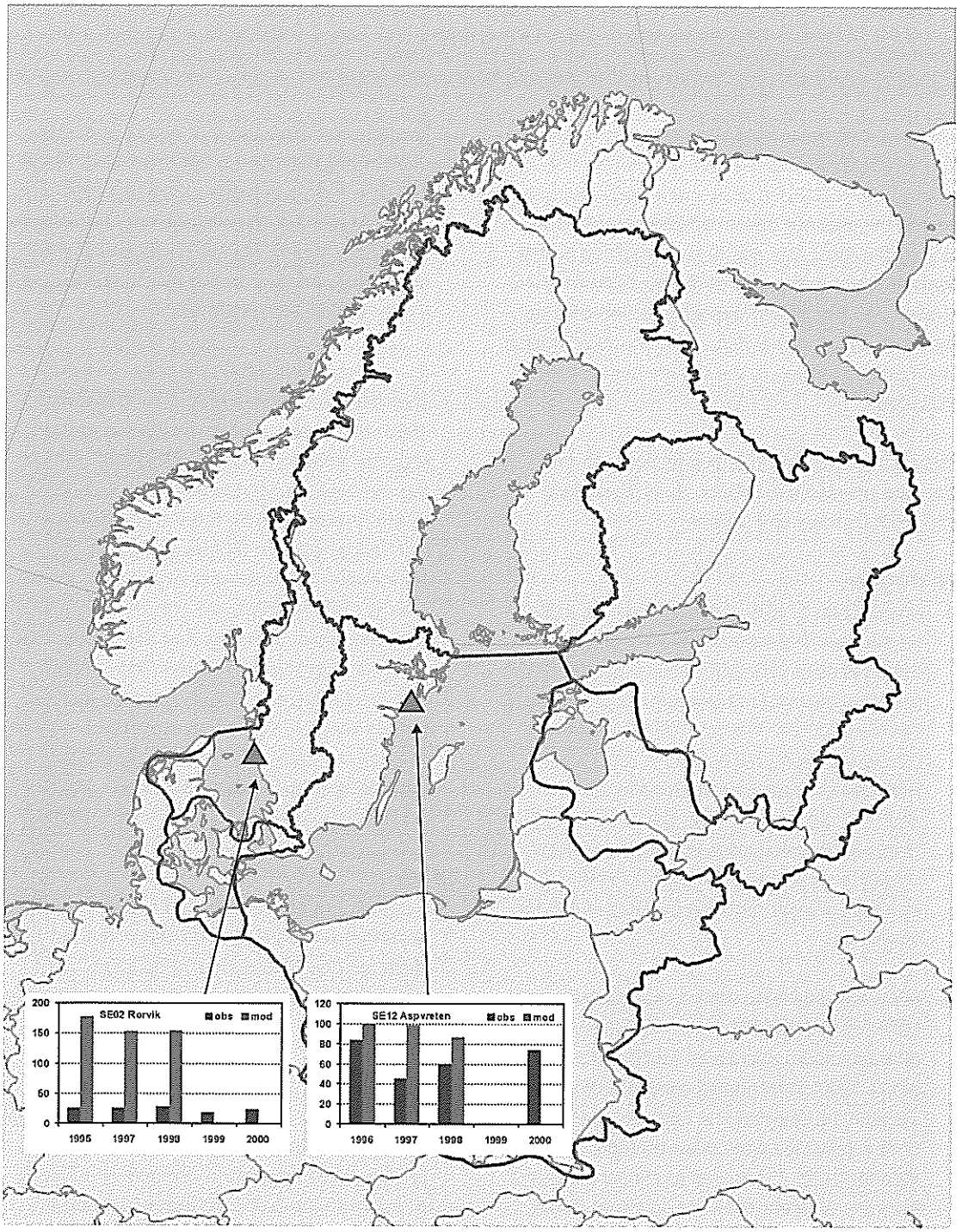


Figure 5.10
Comparison of measured and calculated annual γ-HCH concentrations in air. Units: ng/m^3.

6 Conclusions

The main difference between the present report and its predecessor is the period covered - five years (1996 – 2000) in the current study and one year in the previous one. In addition to this, division of the Baltic Sea was further modified on the basis of the requirements of the HELCOM MONAS 3 meeting. The present report considers only six main sub-basins of the Baltic Sea. This new division was made according to the requirements of the PLC report.

These conclusions include five sections, covering the data presented in relation to nitrogen, lead, cadmium mercury and lindane.

Nitrogen

1. A reduction of annual nitrogen oxides and ammonia emissions from all HELCOM countries was observed, with the most significant decrease ocurring in Denmark (32% between 1996 and 2000). The total of all nitrogen oxides and ammonia emissions from the HELCOM countries, decreaseed by 13.5% and 9%, respectively, over the same period. The sum of emissions from the entire EMEP domain was also slightly lower in 2000 than in 1996, 9% for nitrogen oxides and 4% for ammonia.

2. Emissions data from the international shipping traffic on the Baltic Sea are only available for nitrogen oxides at present, and only for one year – 1990. Total annual emissions of nitrogen oxides from international shipping operations on the Baltic Sea were relatively high, 353 ktonnes (NO_x). Compared to annual emissions from the different HELCOM countries during the same year, only emissions from the Russian Federation, Germany and Poland were higher than emissions from shipping. Ship emissions should therefore be recognized as a very important source of depositions into the Baltic Sea which warrants further investigation.

3. The pattern of measured air concentrations of nitrogen compounds ocurring during the period 1996 – 2000 has been uncertain. There is some suggestion of a decline in concentrations along the southern Baltic shore, but otherwise the temporal pattern appears to be somewhat erratic.

4. Recorded concentrations of nitrate and ammonium in precipitation do not themselves reveal any clear temporal pattern between 1996 and 2000. As a result, the average rates of nitrogen deposition in precipitation have been analysed, but even so no clear trends for the considered 5-year period have emerged.

5. As with observed data, time series analyses of computed annual depositions for the period 1996 – 2000 also do not correspond to the reported emission changes. However, considering the level of uncertainty in the model results, which is roughly 30%, there is no significant difference between the measured and computed values. One possible explanation for the effects of the modest emission changes that is not reflected in the computed depositions may be the strong effect of meteorology during this short time period 1996 – 2000. Another potentially more significant explanation may be the lack of information on nitrogen emissions emanating from international shipping traffic on the Baltic Sea for years other than 1990.

Lead

1. According to official data and expert estimates, emissions of lead from HELCOM countries decreased by 10% during 1996-2000. In the entire EMEP region the decrease is more significant (31%).

2. Measured lead concentrations in air do not demonstrate a consistent regional and temporal pattern for the period 1996-2000. Time series analysis of computed atmospheric depositions of lead into the Baltic Sea indicates a small decrease of approximately 4%. As in the case of nitrogen compounds, computed lead depositions do not closely reflect the emission patterns for the years 1996 – 2000.

3. In comparison with 1996 the level of anthropogenic lead emission sources in 2000 declined. It should be noted that one important origin of total lead depositions was the input of natural, previous and remote anthropogenic sources.

4. The total lead deposition from HELCOM countries into the Baltic Sea decreased from 39% to 31%. Other EMEP countries accounted for

20% of the total. Of all the HELCOM countries, the most significant factor was emissions sources in Poland – 14% in 1996 and 11% in 2000.

Cadmium

1. According to official data and expert estimates, cadmium emissions from HELCOM countries decreased by 26% between 1996 and 2000, while emissions in the entire EMEP region decreased by 22%.

2. Measured concentrations of cadmium in air do not indicate consistent regional or temporal patterns for the period 1996-2000. Time-series analyses of computed depositions of cadmium from the atmosphere into the Baltic Sea indicate a moderate decrease of roughly 4%. Like nitrogen compounds, computed cadmium depositions also did not correspond to the emissions patterns for the years 1996 – 2000.

3. In comparison with 1996 the impact of anthropogenic cadmium emission sources decreased in 2000. One important contribution to total cadmium depositions came from natural, previous and remote anthropogenic sources.

4. Total lead depositions from HELCOM countries into the Baltic Sea decreased from 50% to 39% during the period 1996-2000. Other EMEP countries accounted for 7% of total depositions in 1996 and 11% in 2000. Of all HELCOM countries, anthropogenic lead emissions from Poland accounted for the most significant contributions – 34% in 1996 and 24% in 2000.

Mercury

1. According to official data and expert estimates, emissions of mercury from HELCOM countries decreased by 15% during 1996-2000, whereas decreases in mercury emissions for the entire EMEP region amounted 17%.

2. Time-series analyses of computed atmospheric depositions of mercury into the Baltic Sea region indicate an increase of some 14% for the period 1996-2000.

3. Inputs of mercury depositions into the Baltic Sea from HELCOM countries, EMEP countries and other sources including from natural, previous and remote anthropogenic sources remained at more or less the same level during the period 1996-2000. Among the HELCOM countries the most significant inputs came from Poland in 1996 (15%) and from Germany in 2000 (19%). Other EMEP countries accounted for roughly 5-6% of the total. One important input to total depositions of mercury was natural, previous and remote anthropogenic sources (about 50%).

Lindane

1. According to available official information and expert estimates from the POPCYCLING-Baltic project, during the period 1990-1998 emissions of lindane (γ-HCH) into the Baltic Sea region decreased by almost two orders of magnitude. On the other hand, lindane emissions from the entire European region decreased by only 20% during the same period.

2. By using POPCYCLING-Baltic project emission estimates it is possible to evaluate long-term trends in lindane (γ-HCH) concentrations and deposition fluxes for the Baltic Sea region.

3. In spite of significant declines in emissions from HELCOM countries during the period 1990-1998 the overall level of lindane (γ-HCH) depositions into the Baltic Sea decreased by only 14%. This result is no doubt due to the impact of sources of lindane emissions, which lie outside the Baltic Sea region.

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Annex: Monitoring methods, accuracy, detection limits and precision

All stations reporting to HELCOM conduct daily sampling of nitrogen compounds in air and in precipitation. The monitoring regime for metals and lindane is more specific to each country, and is summarised in tables A.1 to A.3:

Table A.1
General information about sampling and analysis of heavy metals in precipitation in 2000.

Country	Sites	metals	Sampling period	Sampler		Analytical methods
				Wet only	Bulk	
Denmark	DK0008R, DK0020R	Cd, Pb	Monthly		X	ICP-MS
Estonia	EE0009R, EE0011R	Cd, Pb	Monthly		X	
Finland	FI0009R, FI0017R, FI0053R	Cd, Pb	Monthly		X	ICP-MS
Germany	DE0009R	Cd, Pb, Hg	Monthly	X		CV-AAS HgICP-MS Cd, Pb
Lithuania	LT0015R	Cd, Pb	Monthly		X	AAS
Latvia	LV0010R, LV0016R	Cd, Pb	Monthly		X	GF-AAS
Sweden	SE0002R, SE0005R, SE0011R, SE0012R	Cd, Pb, Hg	Monthly		XX	CV-AFS HgICP-MS Cd, Pb

AAS: Atomic absorption spectroscopy
GF-AAS: Graphite furnace atomic absorption spectroscopy
ICP-MS: Inductively coupled plasma - mass spectrometry
CV-AFS: Cold vapour - atomic fluorescence spectroscopy

Table A.2
General information about sampling and analysis of heavy metals in air in 2000.

Country	Sites	metals	Sampling period	Sampler	Analytical methods
Denmark	DK0005R, DK0008R, DK0031R	Cd, Pb	24h	Filter-3pack	Pixe
Germany	DE0009R	Pb	24h	High vol.	ICP-MS
Latvia	LV0010R, LV0016R	Cu, Zn, Cd, Pb	Weekly	Filter-1pack	AAS/GF-AAS
Lithuania	LT0015R	Cu, Zn, Cd, Pb	24h[2)]	Filter-1pack	AAS
Sweden	SE0002R	Hg	12 h	Gold traps	CV-AFS

AAS: Atomic absorption spectroscopy
GF-AAS: Graphite furnace atomic absorption spectroscopy
ICP-MS: Inductively coupled plasma - mass spectrometry
CV-AFS: Cold vapour atomic fluorescence spectroscopy

Table A.3
General information about sampling and analysis of γ-HCH.

Country	Sites	Sampling period	Sampler	Analytical methods
Precipitation				
Germany	DE0001R	Monthly	Wet-only	GC/ECD
Airborne				
Sweden	SE0002R, SE0012R	1 w a month	High vol.	GC/MS

GC-MS: Gas chromatography with mass spectrometry
ECD: Electron capture detector

There are various ways of defining measurement and laboratory precision and detection limits. Methods for calculating these are given in the EMEP Manual (EMEP, 1996). To quantify the degree of precision in the measurements, parallel sampling is necessary. The precision can be defined as the modified median absolute deviation (M.MAD), a non-parametric measure of the spread difference between corresponding daily results from two samplers. This equals the standard deviation when the differences have a normal distribution. The coefficient of variation, CoV, is also an informative non-parametric parameter, expressing the ratio between the mean and the standard deviation as a percentage. As non-parametric statistics, they are particularly useful for measurements with spikes in the data. The relative standard deviation (RSD) is also sometimes reported. The M.MAD and CoV may be defined as:

$$M.MAD = \frac{1}{0.6754}\, median\left(\left|e_i - median(e_i)\right|\right)$$

where e_i is the error in the two measurements

$$CoV\ \frac{M.MAD}{median\left(\overline{C}\right)} \quad *100\%$$

where $\overline{C}$ is the average of the two corresponding results (Sirois and Vet, 1994). If a reference method is used to evaluate the national/local measurements, the median of the reference measurements is used.

The laboratory detection limit is estimated at three times the standard deviation of the field blanks, and is given in the same unit as the measurement data. By using split samples and laboratory blank samples, laboratory precisions and detection limits can be assessed in a similar way.
Not all countries have reported such data. The following tables give the information that has been received for nitrogen and metals monitored in precipitation and in air.

Reported detection limits and precision levels for airborne components – nitrogen

Country	Measurements		Laboratory	
	Precision	Detection limit, µgN/m³	Precision	Detection limit
Denmark		0.06	M.MAD: 0.03; CoV: 2.6%	0.06 µgN/m³
Estonia		0.01		
Finland	0.3 µgN/m³	0.3		
Latvia		0.1	CoV: 1.3%	0.04
Lithuania		0.17	c<2.0 µgN/m³: 4-7% RSD;	0.03 mgN/l
Poland		0.2	RSD: 1.0% at 0.3 mgN/l	0.008 mgN/l
			RSD: 5.9 % at 0.015 mgN/l	
Sweden	RSD: 12%	0.2	2%	0.05

Table A.4
Detection limits and precision levels for nitrogen dioxide.

Country	Measurements		Laboratory	
	Precision	Detection limit, µgN/m³	Precision	Detection limit
Denmark	M.MAD: 0,04 µgN/m³CoV: 7,3%	DK03,08: 0.05	M.MAD: 0,01 µgN/m³	0.01 µgN/m³
		DK05: 0.07	CoV: 0.9%	
Finland			NO3: c=0.35 mgN/l; 5% RSD	NO3: 0.01 mgN/l
			c=0.9 mgN/l; 3.0% RSD	HNO3: 0.01 mgN/l
			HNO3:c=0.35 mgN/l; 4% RSD	
			c=0.9 mg N/l; 2.6% RSD	
Latvia		NO3: 0.01-0.02	NO3: CoV: 2.1%	NO3: 0.05 mg/l
Lithuania		0.014	c=0.3-1.0 mgN/m³ 0.5-1.2% RSD;	0.013 mgN/l
Poland		0.02		NO3: 0.01 mgN/l
Sweden	RSD: 12%	NO3: 0.002; HNO3: 0.004	2%	NO3: 0.002; HNO3 0.005

Table A.5
Detection limits and precision levels for nitrate and nitric acid in air.

Table A.6
Detection limits and precision levels for ammonia and ammonium in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, µgN/m³	Precision	Detection limit
Denmark	M.MAD: 0.13	DK03: 0.05	NH4: M.MAD: 0.02; CoV: 1.8%	0,01 µgN/m³
	CoV: 6.6%	DK05: 8: 0.04	NH3: M.MAD: 0.01; CoV: 1.6%	
Finland			c=0.22 mg N/l; 7.3% RSD	0.02 mgN/l
			c=0.72 mg N/l; 2.7% RSD	
			c=1.42 mg N/l; 2.8% RSD	
Latvia		NH4: 0.15-0.02	NH4: CoV: 2.1%	NH4: 0.06 mgN/l
Lithuania		0.027	c<1.0 mgN/m³: 4.0 % RSD	0.04 mgN/l
			c>1.0 mgN/m³: 0.6-1.8 % RSD	
Poland		0.08		NH4: 0.03 mgN/l
Sweden	RSD: 13%	0.03	3%	NH4: 0.017NH3: 0.03

Reported detection limits and precision levels for components in precipitation- nitrogen

Table A.7
Detection limits and precision levels for nitrate in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit mgN/l	Precision	Detection limit mgN/l
Denmark			M.MAD: 0.02; CoV: 1.6%	0.03
Estonia		0.5		
Finland			c=0.35 mg N/l; 3.1% RSD	0.01
			c=0.9 mg N/l; 2.5% RSD	
Germany				0.01
Latvia			CoV: 2.7%	0.01
Lithuania			c<0.5 mgN/l: 5.1% RSD	0.013
			c>0.5 mgN/l: 1.8% RSD	
			SD: 0.016 at c=0.39 mgN/ml	
Poland			RSD: 0.4% at 4.5 mgN/l	0.015
			RSD: 1.7% at 0.45 mgN/l	
			RSD: 2.1% at 0.23 mgN/l	
Sweden	RSD: 5%	0.002	2%	0.002

Table A.8
Detection limits and precision levels for ammonium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, mgN/l	Precision	Detection limit, mgN/l
Denmark			M.MAD: 0.01 CoV: 1.7%	0.02
Estonia		0.1		
Finland			c=0.23 mg N/l; 2.6% RSD	0.002
			c=0.70 mg N/l; 2.8% RSD	
Germany				0.01
Latvia			CoV: 1%	0.008
Lithuania			c<1.0 mgN/l: 3.3% RSD	0.04
			c>1.0 mgN/l: 1.0% RSD	
Poland			RSD: 2.7 % at 1 mg/l	0.03
			RSD: 4.6 % at 0.1 mg/l	
Sweden	RSD: 5%	0.02	3%	0.02

Reported detection limits and precision levels for components in precipitation- metals

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, µg/l
Estonia		0.01		
Finland			RSD: 3.5% at c=1 µg /l	0.002
Latvia			CoV: 6.8%	0.05

Table A.9
Detection limits and precision levels for cadmium in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, mg/l
Estonia		26		
Finland			RSD: 6.2% at c=1 µg/l	0.05
Latvia			CoV: 9.1%	0.14

Table A.10
Detection limits and precision levels for copper in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, µg/l	Precision	Detection limit, mg/l
Estonia		0.6		
Finland			RSD: 4.7% at c=1 µg/l	0.03
Latvia			CoV: 0.7%	0.6

Table A.11
Detection limits and precision levels for lead in precipitation.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m³	Precision	Detection limit
Latvia		0.02	CoV: 2.9%	1.5 µg/l

Table A.12
Detection limits and precision levels for cadmium in air.

Country	Measurements		Laboratory	
	Precision	Detection limit, ng/m³	Precision	Detection limit
Latvia		2.39	CoV: 6.8%	0.6 µg/l

Table A.13
Detection limits and precision levels for lead in air.