

## 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. Therefore, in this chapter, we will only make some remarks about 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 that data. Precise information on accuracy, detection limits and precision of the reported observations is found in the Annex.

#### 5.1.1 Evaluation of monitoring quality

Matters of quality control in practice lie with the individual monitoring stations and analytical laboratories. As monitoring data centre, NILU cannot calculate such criteria as detection limits etc, but is able to provide advice, present data for intercomparison, 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.

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

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

It is to be stressed that the intention of table 5.1 below is not to give a precise evaluation, but to assemble available data and provide a best judgment of expected quality throughout the period. As stated, more precise information on accuracy, detection limits and precision is contained in the Annex, where the information assembled from a request

for quality assurance data made earlier this year is presented. Data requested included measurement and laboratory lower detection limits and precision results from control samples, and detection limits and precision for monitors.

Table 5.1 gives the summary of 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 5.1 Classified summary of data quality for nitrogen components.

	NH <sub>4</sub> prec	NO <sub>3</sub> prec	NO <sub>2</sub> Air	NO <sub>3</sub> Air	NH <sub>4</sub> Air	HNO <sub>3</sub> +NO <sub>3</sub> Air	NH <sub>3</sub> +NH <sub>4</sub> 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
FI37 Ahtari	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

<sup>1</sup>. Data is for 1999

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

Table 5.2 Laboratory intercalibration of components in air and precipitation, average percent error compared with expected value (in high and low concentrations samples for metals).

Country	AIR			PRECIPITATION					
	HNO <sub>3</sub>	NH <sub>3</sub>	NO <sub>2</sub>	NO <sub>3</sub> -N	NH <sub>4</sub> -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%

## 5.2 Emissions, computed concentrations and depositions

Uncertainties of national nitrogen oxides and ammonia emissions vary significantly from one country to another. In addition, for some countries there is no information at all about the uncertainty of emissions. The above remarks refer to total annual emissions from the countries. Uncertainties are larger and there is practically no information available about the uncertainties of nitrogen emissions from individual grid cells. A typical uncertainty in annual total emissions from the HELCOM countries is approximately 20% (EMEP, 2002).

Official data on heavy metal emissions can be underestimated to some extent since at any minuteness of inventorization of emission it is impossible to take into account the total diversity of possible sources (Ilyin et al., 2002). According to the data of UBA/TNO project (Berdowski et al., 1997) the uncertainty can vary within a factor of 1.5 - 3.5. For countries of north-western Europe real emission values can differ from estimates by 20-50% and for countries of central and eastern Europe the uncertainty can be essentially higher.

The official information on lindane emissions have gaps in time coverage and are available not for all European countries. Therefore emission expert estimates for the above mentioned pollutants are used in order to fill gaps in official information. As it was mentioned in [Pacyna et al., 1999], the accuracy of data increases from the 1970s to the

1990s reflecting the availability of more reliable information.

Concerning computed concentrations and depositions of nitrogen, a typical value of uncertainty is 30% (EMEP, 2002), but in some cases differences between measured and computed values can be much larger. Such a comparison for computed and measured wet depositions of nitrogen compounds can be found in the next section. Problem is more difficult when uncertainty of the source-receptor relations is to be estimated. In case of nitrogen such an analysis has not been done. In addition, 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 intercomparison campaigns with other regional models [*Sofiev et al.*, 1996; *Gusev et al.*, 2000; *Ryaboshapko et al.*, 2001] and has been qualified by means of sensitivity and uncertainty studies [*Travnikov*, 2000]. It was concluded that the results of heavy metal airborne transport modeling are in satisfactory agreement with available measurements and discrepancy does not exceed on average a factor of two. The comparison of calculated versus measured data indicates that the model predicts the observed air concentrations of lead and cadmium within the accuracy of 30%. For concentrations in precipitation the difference between calculated and measured values may reach two times. Computed mercury concentrations deviate from measured values within a factor of two. For MSCE-POP model the discrepancies between measured and calculated concentrations of  $\gamma$ -HCH are within the factor of 3-4 (*Shatalov et al.*, 2000).

### **5.3 Comparison of measured and computed concentrations**

Comparison of measured and computed annual wet depositions of oxidized and reduced nitrogen is shown in Figures 5.1 and 5.2 respectively.

Both for oxidized and reduced nitrogen, agreement between measured and computed wet depositions is, taking into account all uncertainties good. For oxidized nitrogen, the best agreement can be noticed for the Danish station Anholt, Swedish stations Brodkalen, Vavihill and for Polish station Leba. In case of reduced nitrogen, best agreement can be seen for the same stations as for oxidized nitrogen and for the Finish station Virolahti II, in addition.

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

Comparison of measured and computed mean annual concentrations of cadmium, lead, mercury, and lindane ( $\gamma$ -HCH) in precipitation is shown in figures 5.3-5.6. Computed concentrations in precipitation were compared with observations of the selected sites.

Data of sites for which total measured and model annual precipitation amount differ more than 1.5 times were not included in the comparison. Additionally, if for some year there were no monthly mean data for three or more months, the mean annual concentration for this year was not used. Concentrations of lead and cadmium in precipitation computed with MSCE-HM model are on average lower than observed 3 times for lead and 2 times for cadmium (Figures 5.3 and 5.4). The most likely reason of the underestimation of observed lead and cadmium concentrations can be connected with the underestimated emission data. It means that actual atmospheric load of these compounds to the Baltic Sea is most likely higher than estimated values of depositions.

Comparison of computed concentrations of mercury and lindane ( $\gamma$ -HCH) in precipitation was complicated by the lack of available measurement data. Computed concentrations for mercury are slightly higher than measured at Swedish stations Rorvik (SE02), Bredkalen (SE05), Aspvreten (SE12), and Vavihill (SE11). More significant discrepancies can be indicated for Zingst (DE09) (Figure 5.5). Computed concentrations of lindane ( $\gamma$ -HCH) in precipitation are in good agreement with measured at Zingst (DE09) for 1996 and 1997 (Figure 5.6).

Comparison of measured and computed mean annual concentrations of cadmium, lead, mercury, and lindane ( $\gamma$ -HCH) in air is shown in figures 5.7-5.10. On average computed air concentrations for lead and cadmium are slightly lower than measured ones (Figures 5.7 and 5.8). The discrepancies are within the 30% range comparing to observed values. Fewer observations were available for mercury and lindane ( $\gamma$ -HCH) air concentrations. Computed mercury concentrations are 1.5 times higher than measured ones at Rorvik (SE2) for the considered period (Figure 5.9). For lindane ( $\gamma$ -HCH) computed air concentrations are significantly higher for Rorvik (SE2) and rather close to observed values for Aspvreten (SE12) (Figure 5.10).

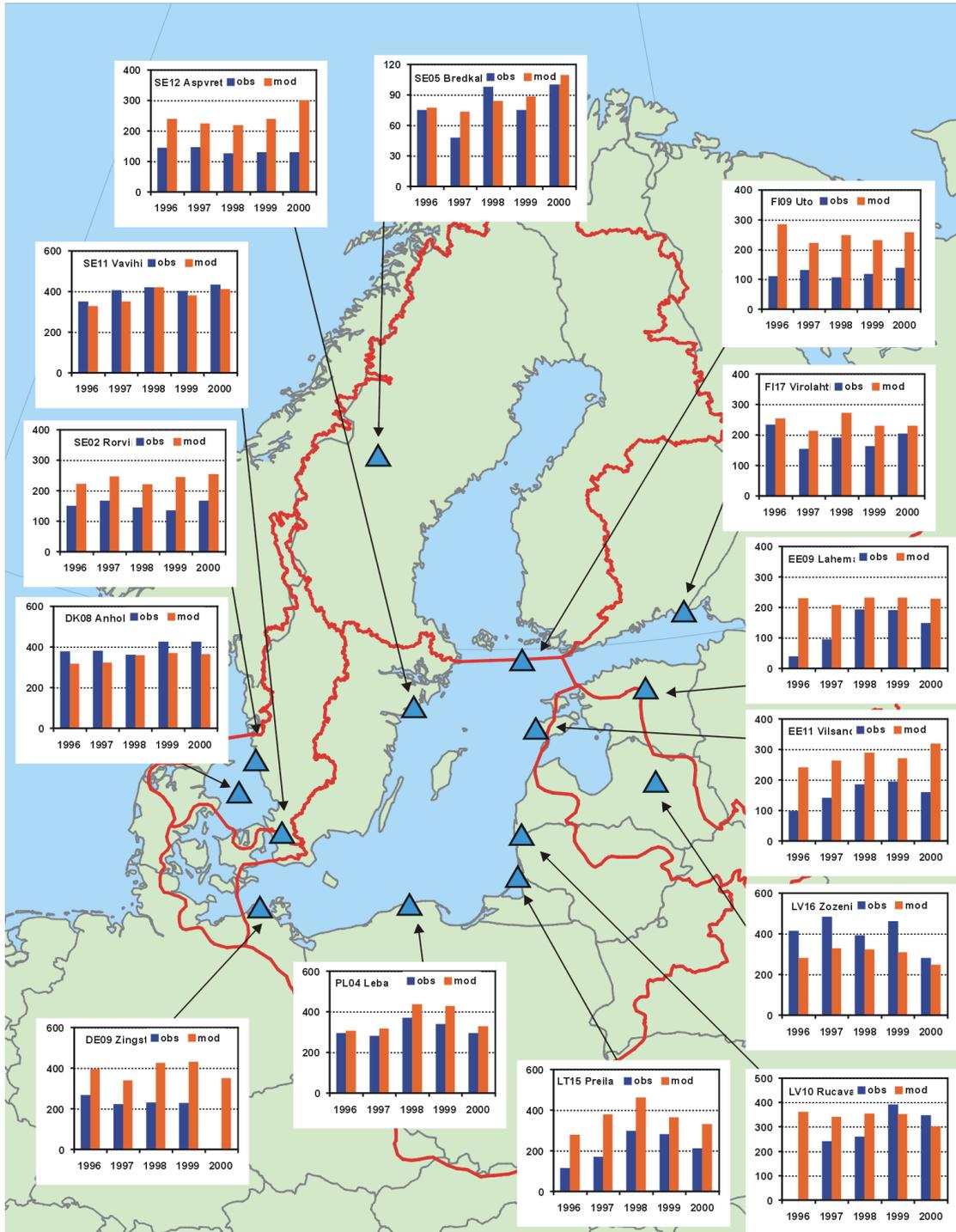


Figure 5.1. Comparison of measured and calculated annual wet depositions of oxidized nitrogen in the period 1996 - 2000. Units:  $\text{mg m}^{-2} \text{yr}^{-1}$ .

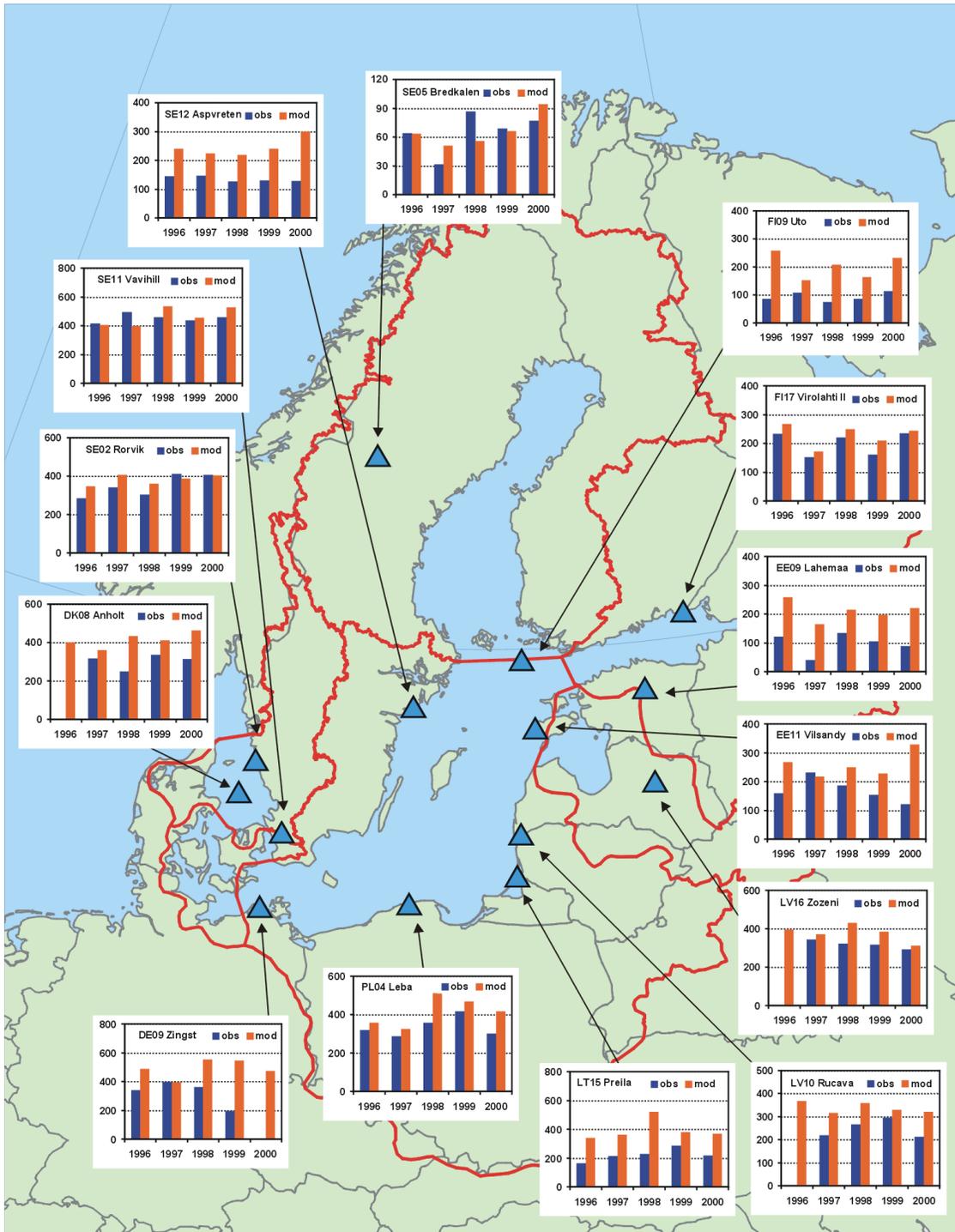


Figure 5.2. Comparison of measured and calculated annual wet depositions of reduced nitrogen in the period 1996 - 2000. Units: mg m<sup>-2</sup> yr<sup>-1</sup>.

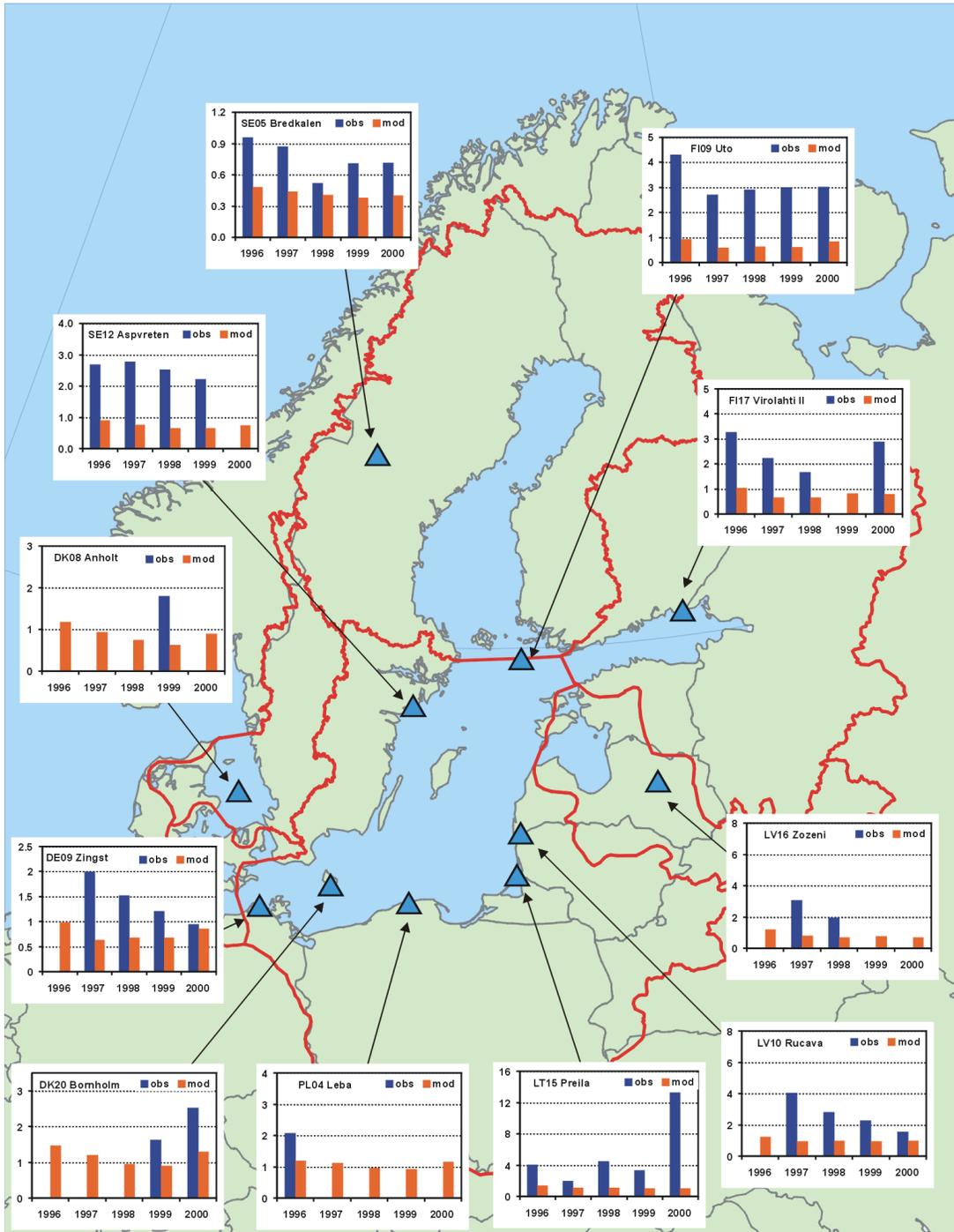


Figure 5.3. Comparison of measured and calculated annual average concentrations of lead in precipitation in the period 1996 - 2000. Units:  $\mu\text{g/l}$ .

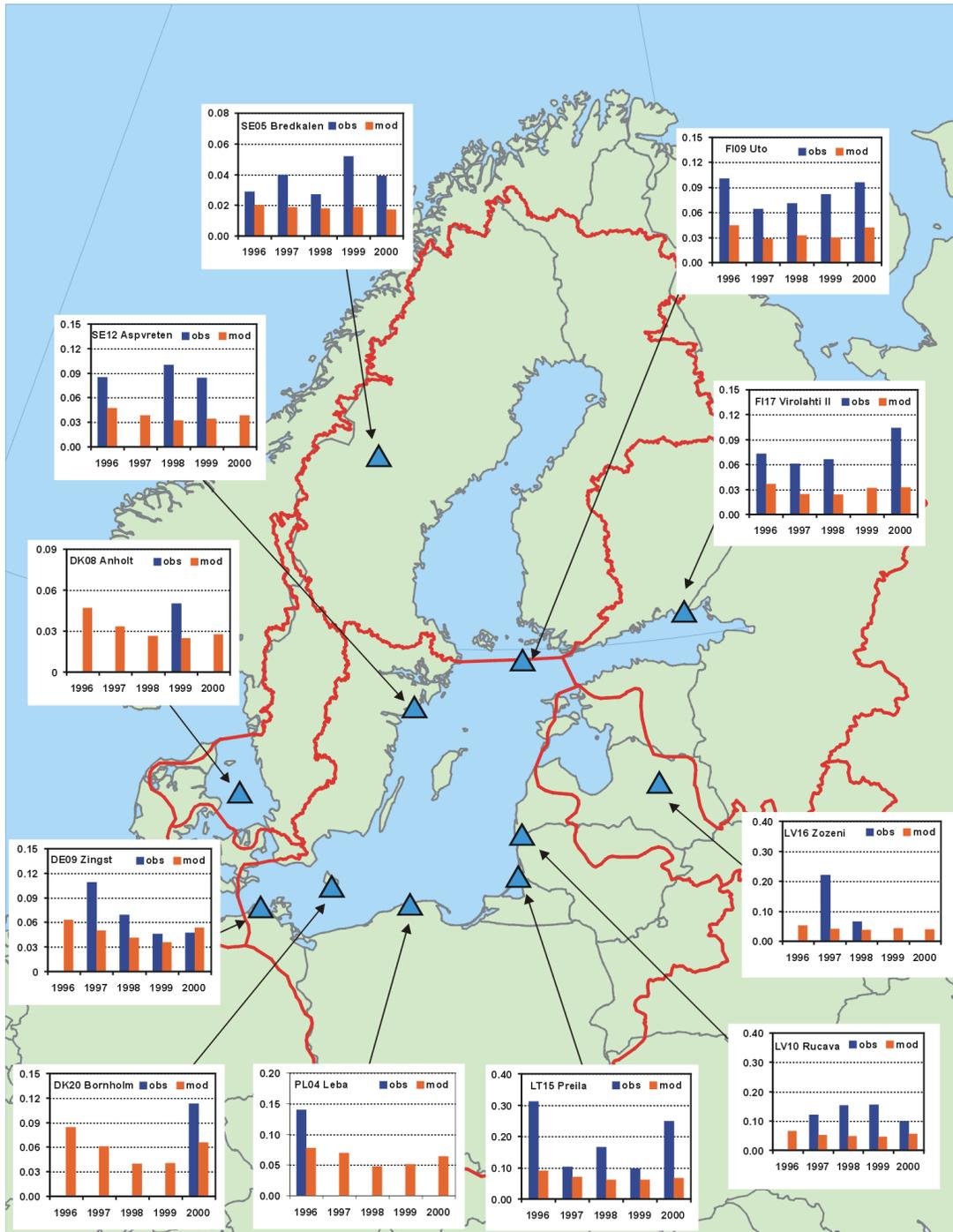


Figure 5.4. Comparison of measured and calculated annual average concentrations of cadmium in precipitation in the period 1996 - 2000. Units:  $\mu\text{g/l}$ .

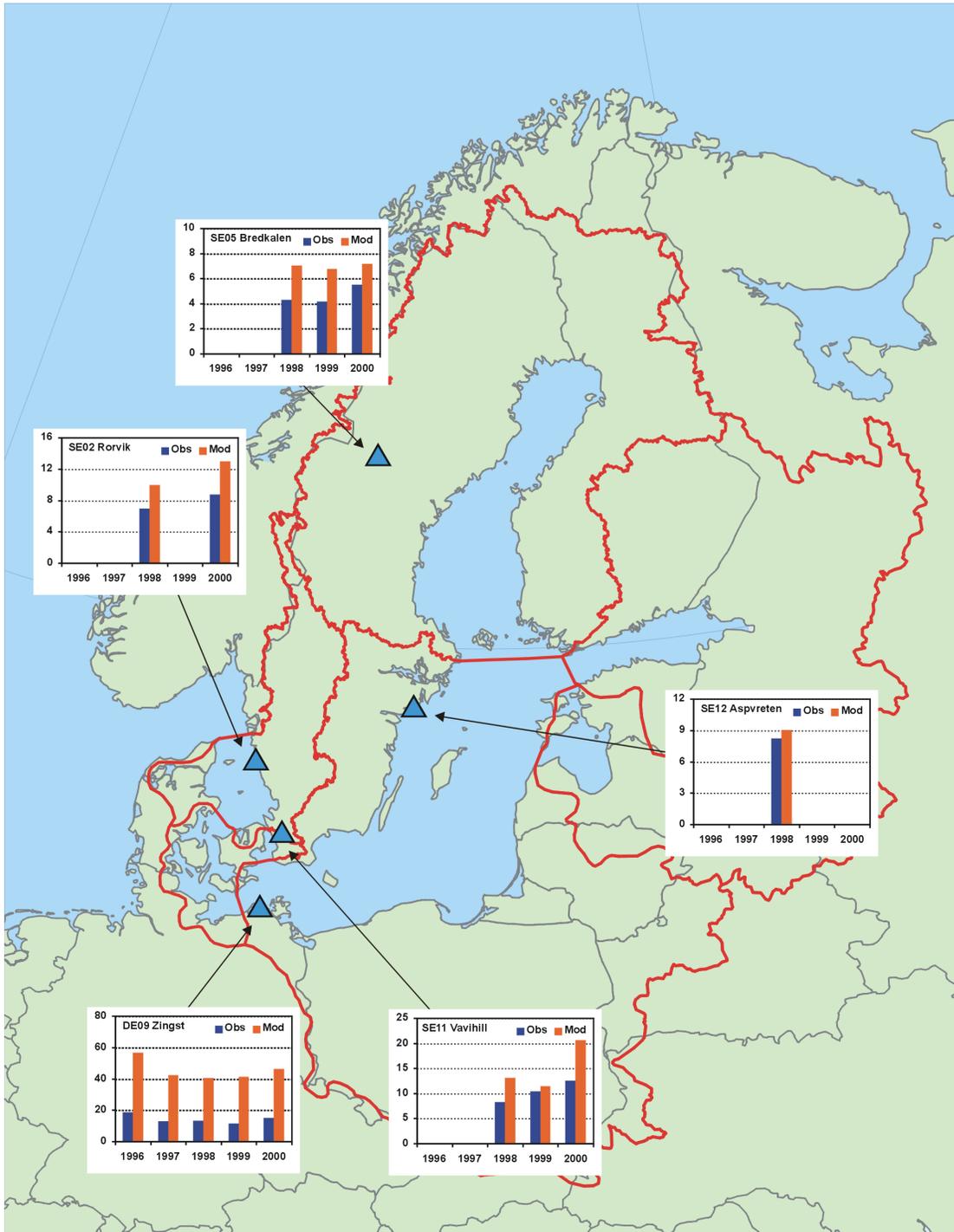


Figure 5.5. Comparison of measured and calculated annual average concentrations of mercury in precipitation in the period 1996 - 2000. Units: ng/l.



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

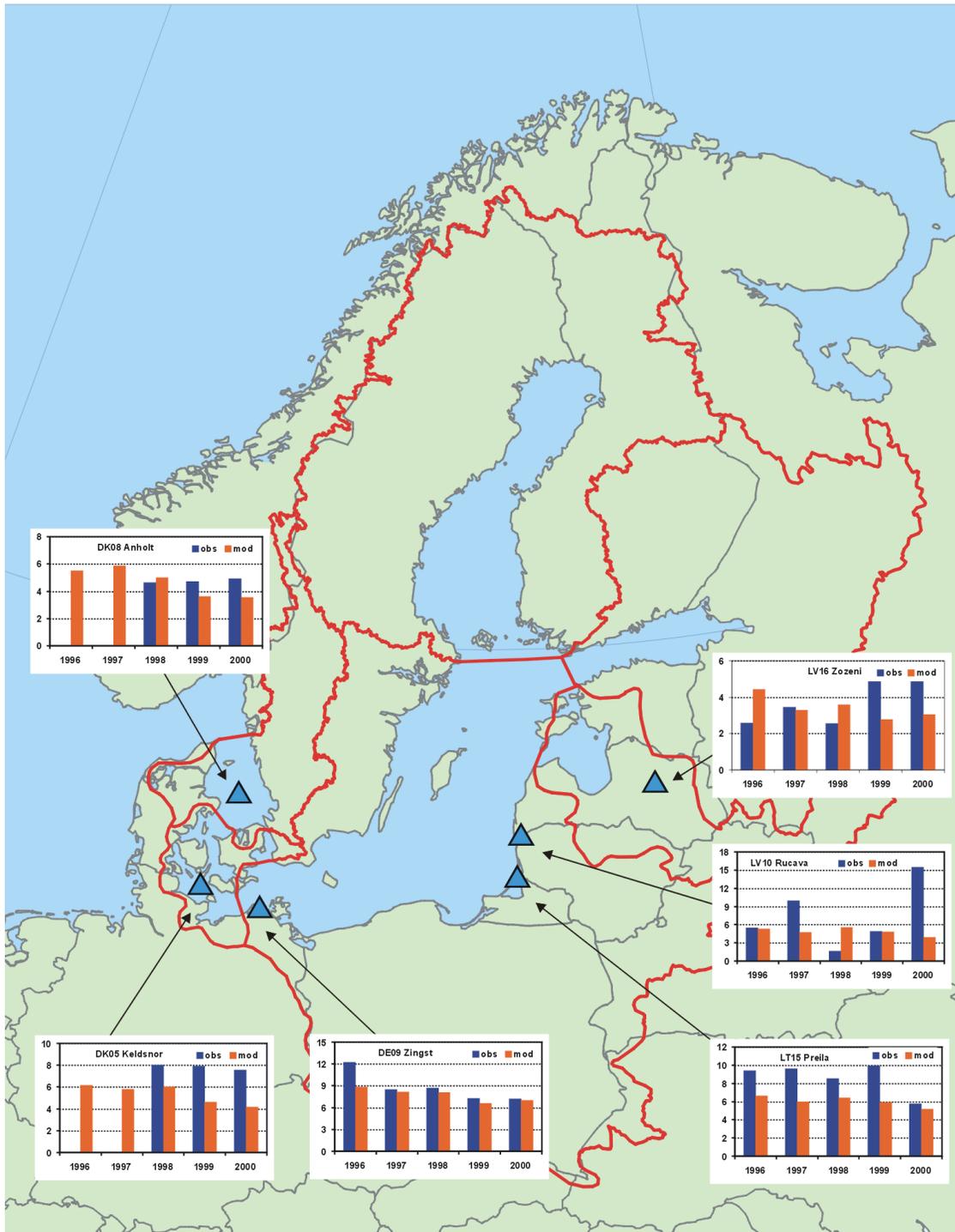


Figure 5.7. Comparison of measured and calculated annual lead concentrations in air. Units:  $\text{ng}/\text{m}^3$ .

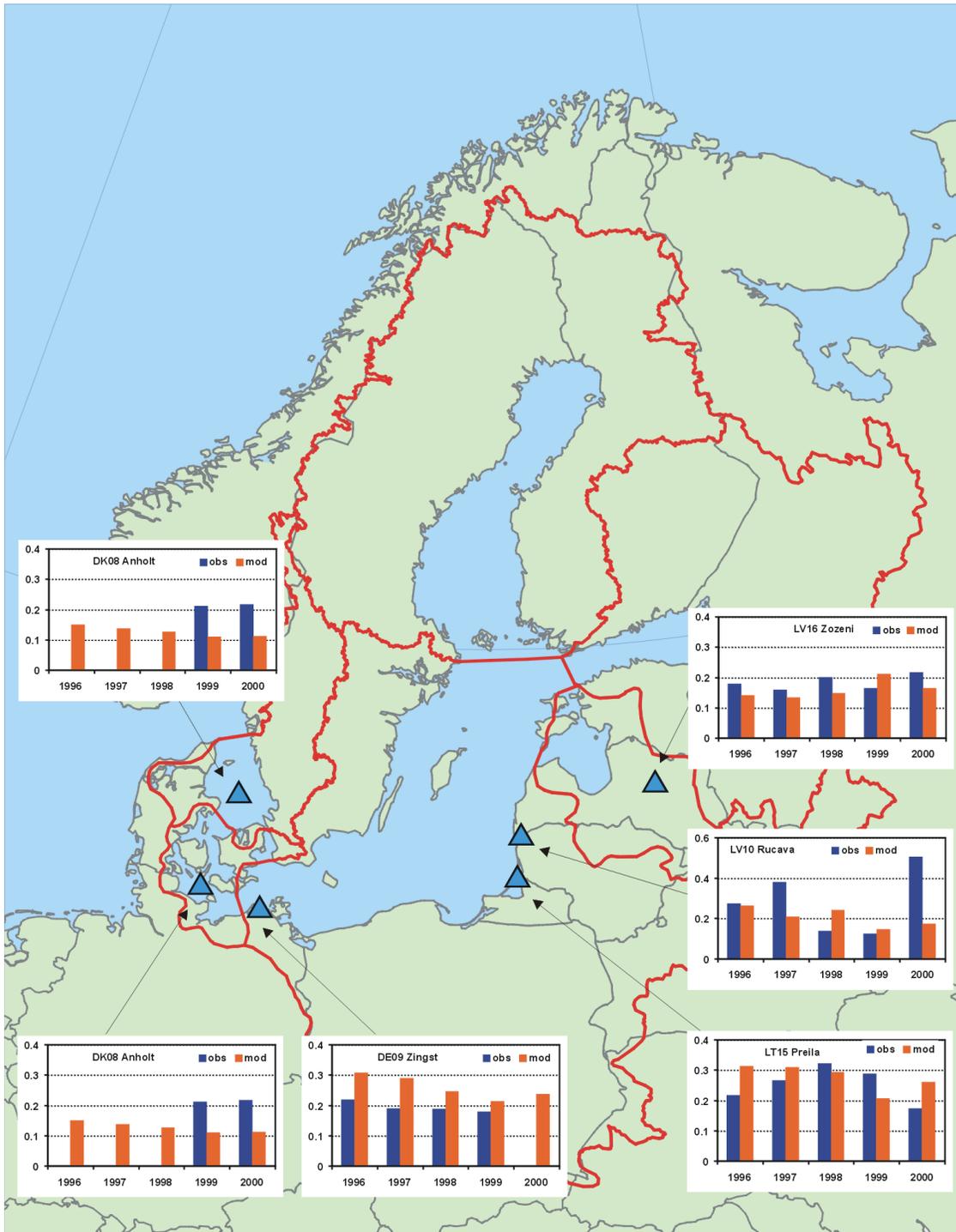


Figure 5.8. Comparison of measured and calculated annual cadmium concentrations in air. Units: ng/m<sup>3</sup>.

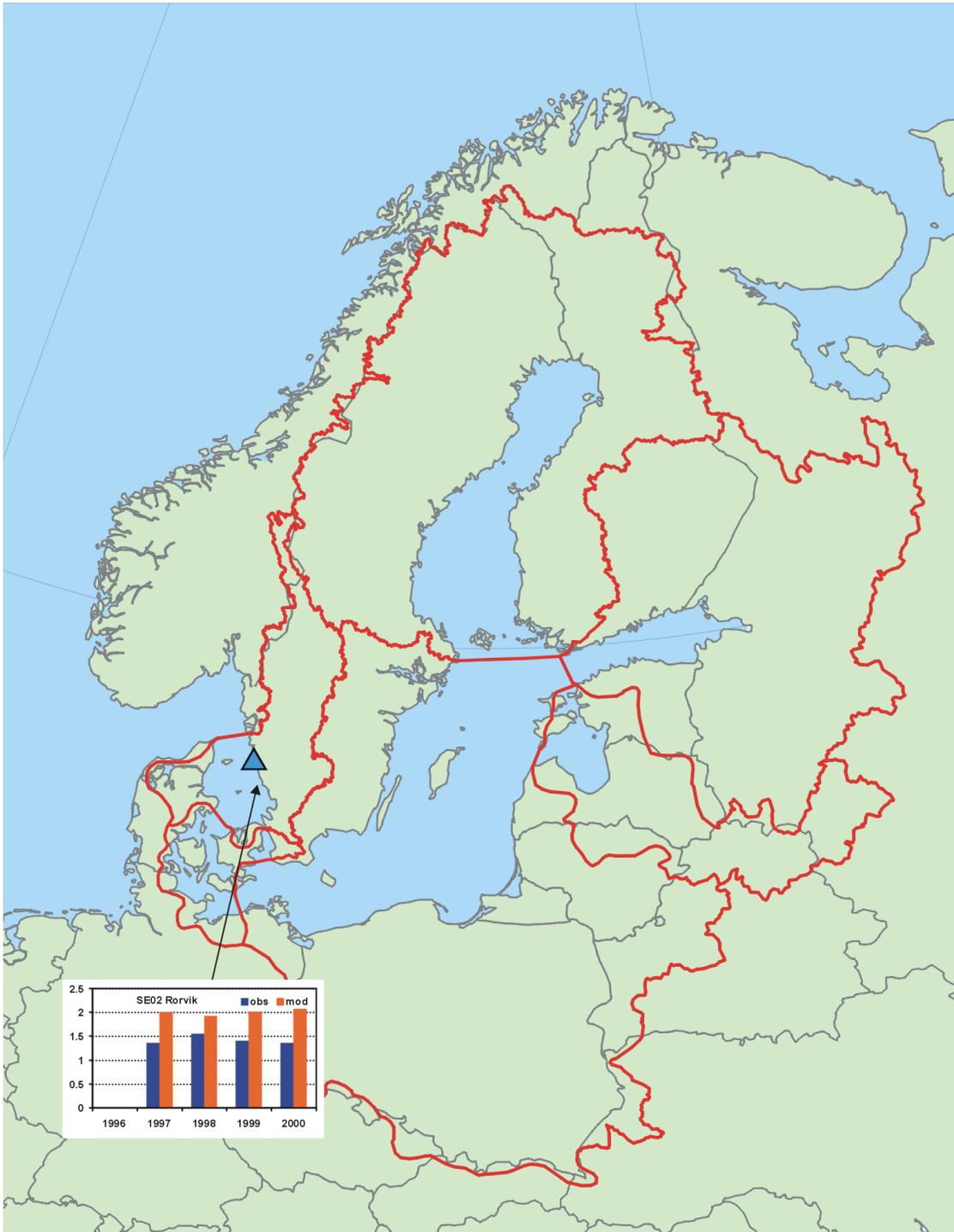


Figure 5.9. Comparison of measured and calculated annual mercury concentrations in air.  
Units: ng/m<sup>3</sup>.

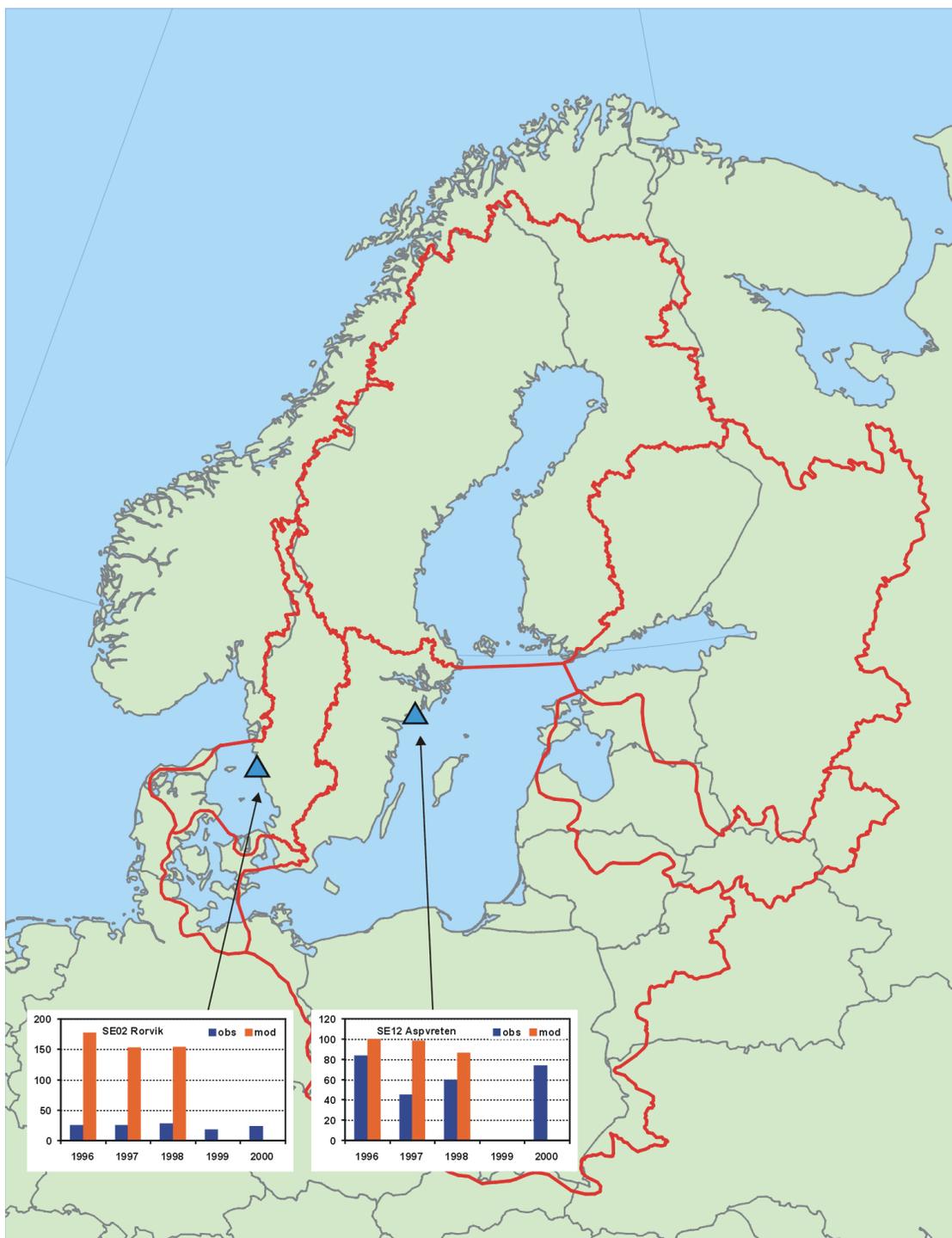


Figure 5.10. Comparison of measured and calculated annual  $\gamma$ -HCH concentrations in air. Units:  $\text{ng}/\text{m}^3$ .