IVL report
IVL Swedish Environmental Research Institute

Atmospheric deposition of mercury in the Nordic countries at different scenarios of reduced anthropogenic emissions in Europe

Report to the Nordic Council of Ministers

John Munthe, Karin Pleijel and Åke Iverfeldt, IVL

Olaf Kruger and Gerhard Petersen
GKSS-Research Centre, Institute of Hydrophysics, Model Systems Unit (GMS),
Max-Planck-Strasse 1, D-21502 Geesthacht, Germany

B 1292
Göteborg, March 1998

1. SUMMARY

A model evaluation of the effects of reducing emissions of mercury in Europe has been made. Wet deposition fluxes of mercury at 6 Nordic sites have been calculated at different emission scenarios. The model simulations of transboundary transport was performed using the EMEP-Hg model (Petersen *et al.*, 1995) and assumed reductions of mercury emissions in Europe. The effects of reductions of 50 and 75% of the 1987/88 emissions of mercury have been evaluated. The EMEP-Hg model has also been used for investigating the effect of removing gaseous oxidised forms of mercury from the emissions. The major conclusions from this study are:

- Model simulations using the EMEP - Hg model suggest that reductions of mercury emissions in Europe by 50% will lead to decreases in wet deposition of around 35% in the southern regions of the Nordic countries and by 7 to 15% in the northern and eastern regions.
- If European mercury emissions are reduced by 75% the corresponding reduction of wet deposition for the southern parts of the Nordic countries will be 50%. The wet deposition of mercury in the northern and eastern regions will be reduced by an additional 2 to 5% in comparison to the 50% reduction scenario.
- The atmospheric deposition of mercury over the Nordic countries will significantly decrease (up to 60%) if measures are taken to remove Hg(II) species from point sources in Europe.

In addition to the EMEP-Hg model simulations, the IVL-Hg process model has been used to simulated the episodic transport of mercury over a 48 h period roughly corresponding to a typical air parcel transport time from Europe to the Nordic countries. These investigations lead to the conclusions:

- Episodic deposition of mercury in southern Scandinavia can be reduced by up to an order of magnitude if measures are taken to reduce emissions.

The conclusions from the modelling described above are supported by an observed decrease in mercury concentrations in air as well as wet deposition caused by decreased emissions in industrialised areas of Europe.

2. INTRODUCTION

Atmospheric regional transport of mercury (Hg) has been shown to be an important source of Hg in remote ecosystems in Scandinavia (Brosset, 1987; Lindqvist *et al..*, 1991; Iverfeldt, 1991; Petersen *et al.*, 1995). Most studies have, however, recognised the difficulty in quantitatively describing the relations between emissions and effects and between sources and receptors. This is mainly due to the complex atmospheric behaviour of Hg and the existence of a regional/global background of mercury in air (partly of natural origin) which makes interpretation of source-receptor relationships difficult.

The aim of this report is to describe the effects of reducing anthropogenic emissions of mercury in Europe. Different approaches have been used to evaluate and quantify the effects:

. Simulations of transboundary transport with different European emission scenarios for mercury using the EMEP-Hg model

. Simulation of deposition rates using the IVL-Hg atmospheric process model in order to verify and quantify the effects of changing atmospheric concentrations of different mercury species

The model simulations and data evaluation in approach 1 is focused on transport of mercury from European sources to the region of the Nordic countries (S, DK, FI, N) for which the EMEP-Hg model has been validated.

In approach 2 the IVL-Hg model was used to simulate different concentration scenarios. The input concentration values of different mercury species are taken to represent different emissions scenarios and the results of these calculations can be used as a quantitative estimate of the effectiveness of different levels of emissions reduction.

In additions to the modelling exercises this report also contains a summary of recent findings from investigations of time trends of mercury in air and precipitation.

3. MODEL DESCRIPTIONS

3.1 The EMEP - Hg model

The EMEP-Hg model is extensively described in Petersen *et al.* (1995) and only a short description is given here.

3.1.1 General

The model is based on the long-period sulphur model used in the European Monitoring and Evaluation Programme (EMEP) (Eliassen and Saltbones, 1983) modified for simulation of transport, chemical transformation and deposition of mercury species. The model uses a Langragian approach which means that a column of air is followed along a trajectory. Within the column, chemical transformations, dry and wet deposition are simulated. Meteorological input is taken from the Norwegian Numerical Weather Prediction model (NWP).

3.1.2 Mercury parameterisation

The Hg deposition parameterisation is based on the occurrence of different species;

elemental mercury	Hg^0
gaseous divalent mercury	Hg(II)
particulate mercury	Hg(p).

For each of these species, a wash-out ratio was used to calculate the wet deposition. The wash-out ratio for elemental mercury was calculated from both field and laboratory measurements and is a function of the concentration of ozone and soot particles in the airmass.

Gaseous divalent mercury (Hg(II)) was not included in the base case due to lack of reliable emission inventories and field data for this species. The EMEP-Hg model was originally validated using only the results of the Hg^0 and Hg(p) simulation results. Owing to the potential importance of the Hg(II) species for actual deposition fluxes it was included in some of the scenario calculations presented below.

3.1.3 Emissions inventory

The emissions inventory was taken from Axenfeldt *et al.* (1992), see Table 1.

Table 1. Emissions inventory for 1987/88 used in the EMEP - Hg simulations.

Country	**Hg emission (ton/year)**
Albania	0.8
Belgium	8.9
Germany	65
Bulgaria	8.7
Checkoslovakia	15
Denmark	4.8
Finland	4.1
France	29.9
GDR	330
Great Britain	40.6
Greece	2.1
Ireland	8.8
Italy	13.1
Yugoslavia	7.2
The Netherlands	8.3
Norway	2.1
Austria	1.1
Poland	44.8
Portugal	5.5
Romania	16
Sweden	7.5
Switzerland	0.2
Spain	10.8
Soviet Union	87.8
Hungary	2.8
Total	**726.4**

Present day emissions are most likely to be lower than the values cited in Table 1 but more recent emission inventories are not presently available. In this emission inventory, GDR emissions amount to more than 40% of the total European mercury

emissions. The GDR emissions have most likely been drastically reduced after the re-unification of Germany (Petersen *et al.*, 1995).

3.1.4 Scenarios

The different scenarios used in the EMEP - Hg calculations are based on the emission of different mercury species with different atmospheric fate and lifetimes. Three different species are simulated in the EMEP - Hg model; elemental mercury Hg^0, particulate bound mercury Hg(p) and gaseous divalent mercury, Hg(II). The main difference between these three species are the different atmospheric lifetimes. While Hg^0 is relatively stable and can be transported over long distances, Hg(p) and Hg(II) are more readily washed out from the air and deposited on a local or regional scale. From an emissions point of view, Hg^0 is a volatile species and thus less likely to be trapped in conventional flue gas cleaning facilities in comparison to Hg(p) and Hg(II).

The first modelled scenario is an overall reduction of the 1988 emissions by 50%. Monthly averages of air concentrations of Hg^0 as well as wet deposition fluxes were calculated using the modelled results. In this scenario, all emissions were assumed to be in the form of Hg^0. The results of the 50% reduction modelling scenario are also used to estimate the effects of a further reduction of emissions down to 25% of the 1988 values. Hg(p) was not included in this scenario.

The second scenario is a comparison of modelled wet deposition fluxes with and without the presence of Hg(II) in the emissions. The removal of Hg(II) is a feasible first step in a future strategy to reduce Hg emissions since it is considerably more easily removed from flue gases than Hg^0.

3.2 IVL model description

The atmospheric model used at IVL simulates the chemical fate of mercury in a 48-hour trajectory framework, including a rain event. Mercury species in the gas and aqueous phase as well as adsorbed onto particles are treated. This model is a development of the earlier described mercury fog model which was used for process modelling and sensitivity analysis (Pleijel and Munthe, 1995a). Gas-phase reactions are described by the EMEP chemical scheme (Simpson *et al.*, 1993), including 72 species interacting in 142 kinetic and photochemical reactions. Mercury gas-phase chemistry is restricted to the oxidation of elemental mercury by ozone. During one half-hour of the 48 hour simulation, the 600 meter deep trajectory air parcel is assumed to leave the ground level and rise up to 1800 meters altitude at 1 m s^{-1} vertical velocity. The initial temperature is chosen to 283 K, and the air parcels vertical movements leads to an adiabatic cooling of 9 K km^{-1} inducing the condensation of cloud droplets and subsequently formation of rain droplets. The processes of condensation of cloud droplets, condensation of rain droplets, accretion and autoconversion of cloud droplets into rain droplets, are simulated using the parameterisation framework described by Lee (1992). The cloud and rain droplets are represented by one size each, the cloud droplet radius is set to 20 μm and rain droplet radius is 1 mm. The increase in mixing ratio of cloud and rain water content causes a higher liquid water content, not increased droplet sizes.

As soon as the cloud simulation starts, the air parcel is rising and condensation takes place. All species soluble in water will dissolve into the water droplets, using the gas to liquid transport parameterization also described in Pleijel and Munthe (1995).

Particulate mercury is assumed to be washed out at the rain event, and is in the model treated as a soluble species using the Henry's law coefficient of $5 \cdot 10^5$. The Henry's law coefficient for gaseous divalent mercury species, i.e. HgO(g) and Hg(II)(g) is assumed to be $1.41 \cdot 10^6$.

As the trajectory moves across the landscape, dry deposition of 8 species will take place, including 3 mercury species, i.e. Hg^0, Hg(II) and Hg(p). The deposition velocities are assumed to follow the diurnal solar cycle for all species except HNO_3 (Shannon and Voldner, 1995), where the maximum daytime value and the minimum night-time values for the mercury species are shown in Table 2. The deposition values are chosen to be representative for a forested landscape.

Table 2. Dry deposition rates for mercury species used in the model calculations.

Species	Night-time value [cm s^{-1}]	Max. daytime [cm s^{-1}]
Hg^0	0.0005	0.03
Hg(II)	0.15	3.2
Hg(p)	0.05	0.5

3.2.1 Scenarios

In this work a simple simulation set-up was used in order to make an estimation of wet and dry deposition in the Nordic countries caused by transport of an air mass from Europe. Only three cases were studied, representing situations of normal, high and low concentrations of mercury species, as specified in Table 3.

Table 3. Initial concentrations of mercury species and soot used in the IVL model simulation.

	Hg^0 [ng m^{-3}]	$HgCl_2$ [ng m^{-3}]	Hg(p) [ng m^{-3}]	Soot [µg m^{-3}]
Reference case	2	0.01	0.01	1
High	5	0.1	0.1	10
Low	1.5	0.005	0.005	0.1

These scenarios represent different episodic conditions typical for the transport of air masses from the European continent to the southern areas of the Nordic countries. The reference case represents a "normal" situation were a moderately polluted air mass is transported to Scandinavia. The "low" case simulates a situation where the selected concentrations represent typical regional background concentrations. The "high" case describes an extreme episode of pollutant transport from central and northern Europe. The concentrations used in this extreme case are considerably elevated but well within the range of measurement results obtained during the late eighties.

4. RESULTS OF THE EMEP - HG MODELLING

4.1 Model validation

A detailed evaluation of the EMEP - Hg model has been presented in Petersen *et al.* (1995) including a comparison of modelled and measured air and precipitation concentrations of mercury. In Table 4, a summary of measured and modelled mercury wet deposition fluxes are given.

Table 4. Comparison of modelled and measured annual wet deposition fluxes at stations in the Nordic mercury network (Petersen *et al.*, 1995). The measurements were performed during 1988-89 and the modelling was made using the 1988 emission database.

Station	**Annual Hg wet deposition, μg/m^2**	
	Measured (1988-90)	**Modelled**
Rörvik	27	15.4
Aspvreten	10.1	10.2
Vindeln	7.3	4.9
Överbygd	5.0	2.1

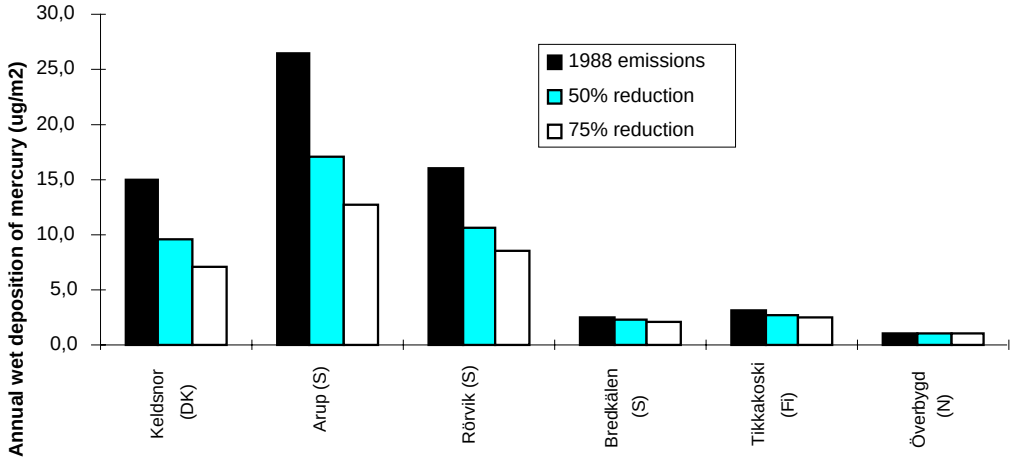
The agreement between measured and modelled deposition fluxes are reasonable considering the relative simplicity of the EMEP - Hg model. The measured deposition fluxes decline after a steeper south-to-north gradient than does the modelled fluxes. However, the fluxes are within a factor of 2 except for the northernmost station which is reasonable for this type of exercise.

4.2 Effects of reducing Hg^0 emissions

The EMEP-Hg model was run using the emission inventory presented in Table 1 and with the emissions reduced by 50% for all European countries. The simulated results for Hg^0 concentrations was then used to calculate the resulting wet deposition flux at the different sites using the parameterisation described in Petersen *et al* (1995). Monthly averages of ozone and soot particles and precipitation amounts were taken from monitoring reports from EMEP and the Swedish National Monitoring Program (PMK).

The effects of a further reduction of the 1987/88 emissions was estimated by assuming that the relative change in Hg^0 concentrations was the same for the first scenario (*i.e.* from 0% to 50%) as for a further reduction by 50% (*i.e.* from 50% to 75%). The ratio between the modelled concentrations with no reduction and the 50% reduction was applied to the 50% reduction simulation results in order to obtain an estimate of a total reduction by 75%.

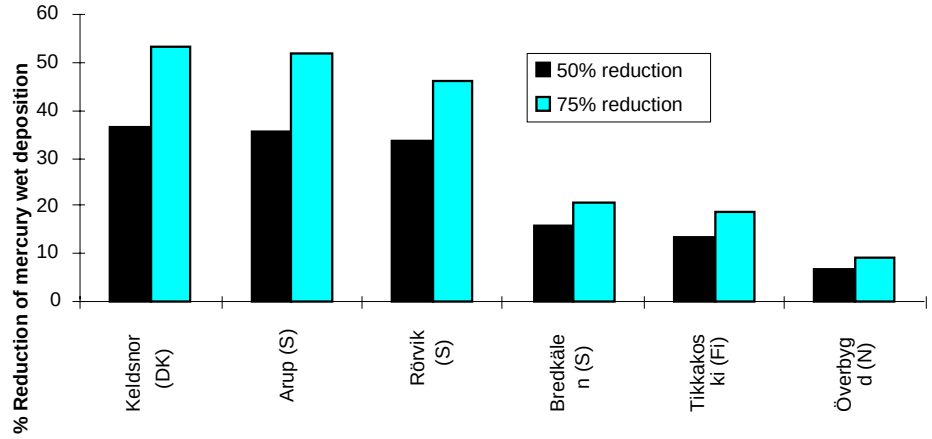
The results of these scenario calculations are presented in Figure 1.



0

Figure 1. Modelled wet deposition fluxes of mercury at 6 Nordic sites. The columns represent the 3 scenarios; emissions according to the 1987/88 emissions inventory, 50% reduction of the emissions and 75% reduction of emissions.

The model results clearly show that reducing emissions of Hg^0 will lead to significant decreases in wet deposition fluxes in the southern regions of the Nordic countries. At the northern and eastern sites Bredkälen, Tikkakoski and Överbygd the effects are small. The relative decreases are presented in Figure 2.



0

Figure 2. Relative decrease of wet deposition of mercury at 6 Nordic sites at 50% and 75%, of the 1987/88 emissions.

The relative decreased for a 50% reduction in emissions range from about 35% at the southern sites to less than 10% at the northernmost site. For the 75% reductions scenario the estimated decrease ranges from over 50% in the south to about 10% in the north.

4.3 The effects of reducing Hg(II) emissions

Since no reliable emission inventory for Hg(II) species is available and model validation is not possible due to lack of data on ambient air concentrations of Hg(II), this species was not included in the scenario calculations discussed above. Despite the

lack of knowledge in this area it is possible to estimate the influence of wet deposition fluxes if this species is included in the simulations. The results can then be used as a guideline for judging the importance of reducing the emissions of this species from point sources.

In Petersen (1992a,b) the EMEP-Hg model was used to simulate wet deposition fluxes over Scandinavia with and without Hg(II) species included in the emissions inventory. In Table 5, the calculated deposition fluxes for mercury and the resulting reduction in wet deposition are presented. When Hg(II) is not included in the model, the calculated deposition fluxes are at least 40% (range 68 to 41%) lower than in the presence of Hg(II). The effect is largest in Denmark being closest to the source regions in northern and central Europe.

Table 5. Modelled deposition fluxes of mercury in the Nordic countries with and without Hg(II) species included in the emissions inventory.

	Deposition (kg/yr.)			
	Denmark	**Sweden**	**Norway**	**Finland**
With Hg(II)	3872	7484	4349	3093
With all Hg(II) removed	1223	3666	2381	1817
Reduction (%)	68	51	45	41

These model simulations show that considerable reductions in deposition of atmospheric mercury can be obtained by changing the chemical form of the emitted mercury.

5. RESULTS OF THE IVL - HG MODELLING

The results of the IVL - Hg model simulations are presented in Table 6. Relative values of the episodic wet and dry deposition have been calculated using the wet deposition in the reference case as the value for comparison.

Table 6. Relative deposition of mercury based on simulations using the IVL - Hg model in three different episode scenarios (see Table 3). Wet deposition in reference case is set equal to 1.

	Wet deposition	Dry deposition	Dry deposition (no rain event)
Reference case	1	0.15	0.16
High	10	0.42	0.63
Low	0.5	0.11	0.12

The results clearly show the effects of reducing mercury emissions on the wet and dry deposition of mercury in the Nordic region. The simulation results are greatly influenced by the choice of mercury speciation *i.e.* the concentrations of $HgCl_2$ and Hg(p); the two mercury species with the shortest atmospheric lifetime.

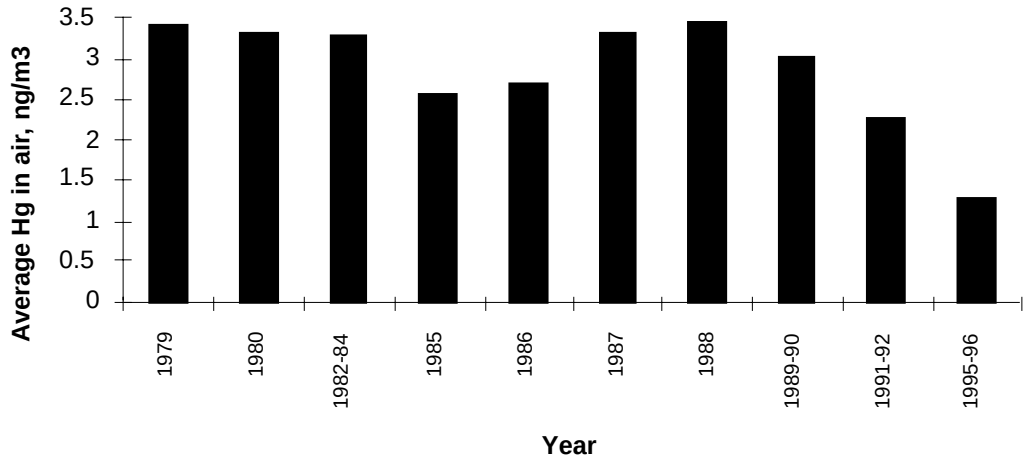
The IVL model simulations suggests that a decrease in the Hg(II) emissions will lead to a near linear decrease in mercury wet deposition. This is the case for episodic transport of polluted air masses over limited distances *i.e.* transport from the northern parts of the European continent to southern Sweden. For more remote sites, a more complex relationship between the emissions and deposition exists.

6. RESULTS FROM FIELD MEASUREMENTS OF MERCURY

Mercury in the environment has been monitored in Sweden for more than 15 years. This data can be used to evaluate time trends in concentrations which can be related to known changes in emissions of mercury in Europe. Thus, a quantitative estimate of the effects of emission reductions can be made.

6.1 Air concentrations

Air concentrations of mercury have been measured intermittently since 1979 at the Swedish west coast. An earlier evaluation of these data has shown that the overall background concentrations of mercury in air have decreased since 1990 and that the number of episodes with extreme concentrations of mercury have practically disappeared (Iverfeldt *et al*., 1995). The decrease in air concentrations is difficult to statistically prove and quantify since the measurements have not been made systematically and not always with monitoring long term trends as the primary focus. In Figure 1, annual average air concentration of mercury at the Swedish west coast are presented. For years where only few data were available, averages were calculated using data from 2 to 3 years.



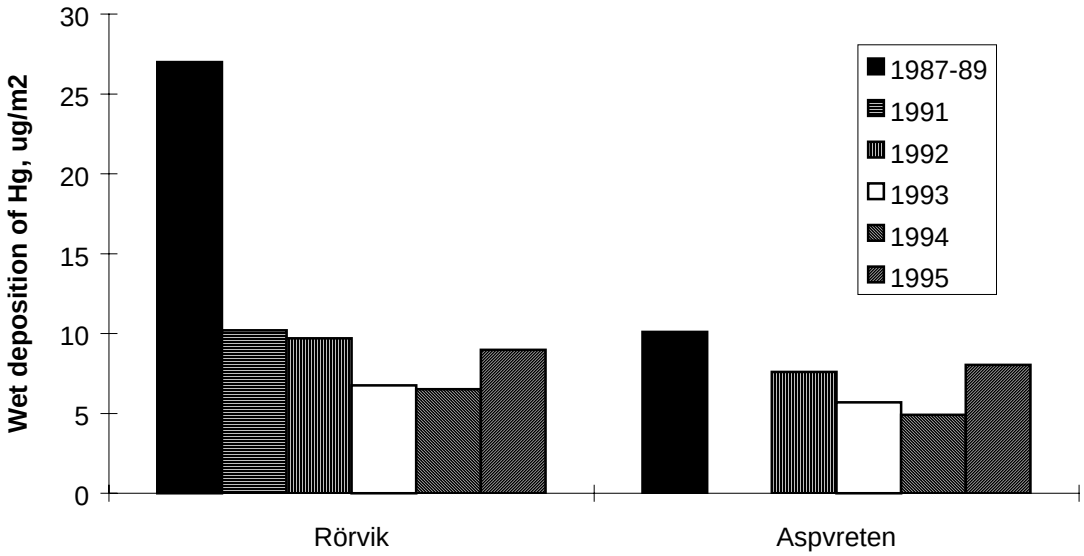
0

Figure 3. Annual average air concentrations at the Swedish west coast 1979 to 1996.

The decrease of mercury in air cannot be quantified due to the incompleteness of the data. However, using the average values for the years 1987 to 1990 and 1994 to 1996, the decrease seems to be at least 30%.

6.2 Wet deposition

Wet deposition has been monitored in Sweden since 1988/1989. A decrease in wet deposition fluxes similar to the decrease in air concentrations has been found for the years after 1990. The decrease is most striking in SW Sweden but can also be seen at the Swedish Baltic coast. Data from 2 monitoring stations are presented in Figure 4.



0 Figure 4. Wet deposition of mercury at Rörvik (west coast) and Aspvreten (East coast) during 19987/89 to 1995.

The wet deposition of mercury increased in 1995 at both the Rörvik and Aspvreten sites. Further monitoring is necessary in order to assess if this is a permanent change in the decreasing trend.

7. **CONCLUSIONS**

- Model simulations using the EMEP - Hg model suggest that reductions of mercury emissions in Europe by 50% will lead to decreases in wet deposition of around 35% in the southern regions and by 7 to 15% in the northern and eastern regions.
- If European mercury emissions are reduced by 75% the corresponding reduction of wet deposition for the southern region will be 50%. The wet deposition of mercury in the northern and eastern regions will be reduced by an additional 2 to 5% compared to the 50% reduction scenario.
- The atmospheric deposition of mercury over the Nordic countries will significantly decrease (up to 60%) if measures are taken to remove Hg(II) species from point sources in Europe.
- Model simulations focusing on episodic transport of mercury from Europe to Scandinavia suggests that episodic deposition of mercury can be reduced by an order of magnitude if measures are taken to reduce emissions.
- Evaluation of results from field measurement in SW Sweden suggests that a decrease in air concentrations (30 to 50 %) and wet deposition of mercury has occurred.

8. REFERENCES

Axenfeldt, F., Munch, J. and Pacyna, J. 1991. Europeische Test-Emissionsdatenbasis von Quecksilbermomponenten fur Modellrechnungen. Umweltforschungsplan des Bundesministers fur Umwelt, Naturschutz und Reaktorsicherheit . Luftreinhaltung-104 02 726.

Brosset, C. (1987) The behaviour of mercury in the physical environment. *Water, Air, and Soil Pollution* **34,** 145-166..

Eliassen, A. and Saltbones, J. 1983. Modelling of long-range transport of sulphur over Europe: a two-year model run and some model experiments. *Atmospheric Environment* **17**, 1457-1473.

Iverfeldt Å. (1991) Occurrence and turnover of atmospheric mercury over the Nordic Countries. *Water, Air, and Soil Pollution* **56,** 251-265.

Iversen, T., Halvorsen, N.E., Mylona, S. and Sandnes, H. (1991). Calculated budgets for airborne acidifying components in Europe 1985, 1987, 1988, 1989 and 1990. EMEP/MSC-W, Report 1/91.

Lee, I.Y. (1992). Comparison of cloud microphysics parameterizations for simulation of mesoscale clouds and precipitation. Atmos. Environment Vol. 26A: 2699-2712.

Lindqvist O., Johansson K., Aastrup M, Andersson A., Bringmark L., Hovsenius G., Håkanson L., Iverfeldt Å., Meili M. and Timm B. (1991) Mercury in the Swedish environment -Recent research on causes, consequences and corrective methods. *Wat. Air Soil Poll.* **55**, 261.

Petersen, G., Iverfeldt, Å. and Munthe, J. (1995) Atmospheric mercury species over central and northern Europe. Model calculations and comparison with observations from the Nordic air and precipitation network for 1987 and 1988. *Atmospheric Environment.* **29**, 47-67.

Petersen,G. Numerische moldellierung des transports und der chemisches umwandlung von quecksilber über Europa. (1992a) Ph.D: Thesis, University of Hamburg, Germany.GKSS 92/E/51 External Report GKSS Research Centre, D-21502 Geestacht ,Germany.

Petersen,G. (1992b). Belastung von Nord- und Ostsee durch ökologisk gefärliche stoffe am bespiel atmosphärischer quecksilberbindungen. Umweltforsschungsplan des Bundesministers für Umwelt, Naturschutz und Reaktorsicherheit-Luftreinhaltung-10402726. GKSS 92/E/111 External Report GKSS Research Centre, D-21502 Geestacht ,Germany.

Pleijel K. and Munthe J. (1995a) Modelling the atmospheric mercury cycle - chemistry in fog droplets. *Atmos. Environ.*, **29,** 1441-1457.

Pleijel K. and Munthe J. (1995b) Modelling the atmospheric chemistry of mercury - The importance of a detailed description of the chemistry of cloud water *Water, Air and Soil Pollution* **80,** 317-324.

Shannon J. D. and Voldner E. C. (1995) Modeling atmospheric concentrations of mercury and deposition to the Great Lakes. Atmospheric Environment 29, 1649-1661.

Simpson, D., Andersson-Sköld, Y. and Jenkin, M.E. (1993) Updating the chemical scheme for the EMEP MSC-W oxidant model: current status, EMEP MSC-W Note 2/93.

IVL Svenska Miljöinstitutet AB

Box 210 60, SE-100 31 Stockholm
Hälsingegatan 43, Stockholm
Tel: +46 8 598 563 00
Fax: +46 8 598 563 90

IVL Swedish Environmental Research Institute Ltd

Box 470 86, SE-402 58 Göteborg
Dagjämningsgatan 1, Göteborg
Tel: +46 31 725 62 00
Fax: +46 31 725 62 90

Aneboda, SE-360 30 Lammhult
Aneboda, Lammhult
Tel: +46 472 26 20 75
Fax: +46 472 26 20 04

www.ivl.se