

MEPOP – NMR - AMAP

**Mercury and POP Workshop – Sept 10-12,
2001, Roskilde, Denmark**

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Workshop summary, abstracts and conclusions

1 Preface

This workshop was a joint arrangement of the Nordic Council of Ministers (NMR) (Hav- och luftgruppen), the EUROTRAC2 subproject MEPOP and the Danish AMAP Programme. The three organisations had the mutual aim of summarising the current status of atmospheric research on mercury. In addition to this, the three organisers had specific aims:

- EUROTRAC2: To report progress of research projects on atmospheric mercury and POPs within MEPOP.
- NMR: To identify research priorities for mercury in the environment relevant to Nordic strategies on mercury.
- AMAP: To assess the status of Nordic mercury research in the Arctic.

The workshop was organised by John Munthe, IVL (NMR, MEPOP) and Gary Geernaert, NERI (AMAP). The workshop was supported financially by NMR (hav- och luftgruppen), the Swedish Environmental Protection Agency and the Danish AMAP Programme.

The workshop steering committee sincerely thanks the presenters for their keen insights on the state of the science and recommendations for future priorities. All participants are also acknowledged for their active engagement in the discussions and working groups. NMR and AMAP are sincerely acknowledged for their support.

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2 Workshop summary

2.1 Background

Both the transport pathways and effects of environmental contaminants are recognised as among the more serious challenges for the scientific, monitoring, and policy communities. From the policy side, challenges involve the development of science-based policy frameworks, which include possible remediation strategies for the most affected regions. Scientific challenges involve transport and transformation processes in the atmosphere, terrestrial, freshwater and marine compartments, with a special view towards accumulation in various ecosystems and food chains. Progress in these fields will benefit from a strengthening of collaboration between scientific research, monitoring, and policy analysis communities.

Mercury and POPs are recent additions to the UN ECE protocol on long range transboundary air pollution (CLRTAP). This protocol has already been successful in reducing sulphur emissions across Europe, and there has also been progress in reducing emissions of nitrogen oxides and volatile organic compounds. Because the successes of CLRTAP on sulphur can be attributed in part to the sustained interaction of science and policy during last few decades, for example with use of critical load concepts, legislation under CLRTAP for mercury and POPs is expected to build from the same means of linking science with policy. Mercury and POP's, however, face additional challenges which go beyond the scientific problems necessary for constructing the sulphur protocol. Although there is some basic knowledge on emissions, transport, transformations and effects of mercury and POPs, there is much more to be learned on the processes governing compartment fluxes and accumulation pathways in ecosystems and food chains, and special attention needs to be given to the long time scales associated with processes governing these compounds. For these reasons, there are ambitious plans within the UN ECE framework to make significant progress on atmospheric modelling of both mercury and POPs (e.g., carried out by MSC-E, Moscow) and work with the development of critical limits and critical loads for mercury will require integrated multidisciplinary modelling. Global efforts to develop strategies for limitations of toxic compounds are also made within UNEP for both POPs (on-going) and mercury (planned).

For several years, a European scientific network, EUROTRAC2 subproject MEPOP (Atmospheric Cycling of MErcury and POP's), has been exploring various scientific aspects of atmospheric mercury and POP's, involving laboratory studies, field measurements, and modelling. The general aim of the EUROTRAC2 program is to provide scientific support on emissions, transport, transportation and deposition to policy makers within the UN-ECE program, the EU and national authorities. For MEPOP, the overall aim is to quantify the regional cycling of mercury and POP's. The MEPOP network consists of around 20 scientists from Europe and North America.

The Arctic Monitoring and Assessment Programme (AMAP) has the responsibility to measure the levels, and assess the effects of anthropogenic pollutants in all compartments of the Arctic environment, including humans. AMAP scientists also document trends and impacts of pollution on Arctic flora and fauna, and they produce models and other tools which examine sources and pathways of pollutants, using extensive data bases carried out under its Arctic monitoring programs. The tools produced under AMAP are expected to lead to remediation strategies in the near future.

The Nordic Council of Ministers (NMR) supports, among other subjects, environmental policy development, by leveraging against the existing scientific and technical capacity within Nordic research and development institutes. Among NMR's strategic interests is the co-ordination and funding of policy related environmental research, which has a direct benefit to Europe's northern countries.

During the past year, the AMAP community began an intensive planning process to identify priorities for its next phase of monitoring and policy related activities. For the Nordic countries, in particular, there is heightened concern on mercury and POP's, in most part due to the high levels which have been observed in Arctic ecosystems, namely west and east Greenland, Faroe Islands, Svalbard, Lapland and northwest Russia, and parts of northern Canada (particularly Hudson Bay). Data sets gathered in recent years suggest that it is time to reformulate a strategy, by building in a combination of measurement and modelling approaches, in order to explore remediation strategies based on intervention in numerous emission sectors. The Nordic Council of Ministers faces similar concerns as AMAP, yet the focus is more on identifying the best strategies which link Nordic needs within the frameworks of both CLRTAP and AMAP, in order to identify the Nordic niche.

The Mercury and POP Workshop, which was carried out during September 10-12, 2001, served to provide a status of the European science base in mercury and POP's research, and to explore the challenges for monitoring and policy development with a focus on mercury in northern Europe and the Arctic as well as POP's in Europe.

The workshop was organised jointly between NMR, Danish AMAP and MEPOP. John Munthe was chairman of the NMR and MEPOP activities whereas Gary Geernaert chaired the AMAP sessions. NERI hosted the workshop at the Niels Bohr Auditorium, Risø Laboratory, Roskilde. Gary Geernaert (NERI) was the local host, and Christel Ege-Johansen (NERI) served as the workshop secretary. Because of support provided by NMR and AMAP, there were no registration fees.

2.2 Aims of the workshop

The aims of the workshop were to:

- summarise the state of the science on mercury and POP's in Europe, Scandinavia, and the Arctic, with a special focus on emission, transport, transformation, and effects.
- identify scientific challenges and future needs for POP research in Europe.
- document the scientific challenges which must be addressed, in order to improve the quality of mercury monitoring programs and accuracy of mercury modelling systems, for use in both Scandinavia and the Arctic.
- to produce a list of priorities for mercury research which directly supports the policy objectives of NMR and AMAP.

2.3 Workshop structure

The agenda of the workshop is shown in Appendix 2. During the two first days results from recent POP and mercury research were presented. The third day was exclusively focussed on mercury research and policy. The third day also included two working groups dedicated to identifying priorities for mercury research and monitoring, relevant to NMR and AMAP.

2.4 Summary of workshop conclusions of research priorities for mercury

The Nordic countries have a long tradition in research on the environmental transport, transformations and fate of mercury. Nordic scientists have made significant contributions to the international knowledge-base and have thus played an important role in the development of control strategies and agreements on emission control and limitations in use of mercury in industry and consumer goods. During the most recent 5 - 10 years, funding for basic and applied environmental

research on mercury in the Nordic countries have decreased in significance. Today, USA and Canada dominate the basic research and several other European countries are making significant contributions. While this has led to a most welcome broadening of the research community, the applied research is no longer focussed on the environmental conditions relevant to the Nordic countries. One of the major conclusions of the workshop was that the Nordic countries need to strengthen their efforts on applied research on mercury. At the same time, it is becoming more and more evident that mercury is a global pollutant and research into the global cycling of mercury is needed in support of global agreements on emission control and limitations of use.

At the workshop, a number of research priorities were discussed (see detailed reports from Working groups). In the following section we have summarised the main research priorities and also tried to group after the size of the necessary scientific effort and funding. While the "small-scale" and to some extent the "medium-scale" efforts only require limited funding and are thus suitable for national funding sources or NMR, the "large-scale" efforts should be made in international co-operation within the European Union or with North American scientists. On a policy level, Nordic representatives should strive to provide support for initiatives within the Sixth Framework Programme of the European Commission.

It should be noted that the focus of the workshop was the environmental cycling of mercury. Thus research into human health effects, technical development of substitution materials for mercury in industry and consumer goods, and other equally important research areas were not discussed.

2.4.1 Large-scale efforts - International co-operation

Topic 1: Development of integrated modelling tools for mercury.

Motivation: The couplings between use of mercury in industry and consumer goods and environmental impact, or, between emissions from energy production and human exposure to methylmercury in fish are complex and to a large extent associated with high degrees of uncertainty. The development of an integrated modelling tool would greatly increase the possibilities of visualisation and quantification of the problems associated with mercury as well as the benefit of abatement strategies.

Scientific effort: Coupling of socio-economic models describing use and emissions of mercury (as well as control technology options) to global/regional atmospheric models and terrestrial/aquatic fate models and, finally, human exposure models.

Topic 2: Export of mercury from terrestrial to aquatic ecosystems

Motivation: Substantial amounts of mercury have accumulated in forest soils in the Boreal forest belt due to increased levels of atmospheric deposition during the last century. Our current understanding of what controls the long-term mobility of this mercury and how it is affected by current deposition levels, land-use (forestry) and climate change is not sufficient and constitutes a serious limitation on our possibilities to predict effects of emission reductions on aquatic levels of methylmercury.

Scientific efforts: Field measurements in natural and manipulated (land-use, climate change etc) forest ecosystems. Process studies of forest soil mobility and mechanisms. Development of models for mercury mobility in Boreal forest ecosystems.

Topic 3: Determination of net input and subsequent ecological impact of atmospheric mercury during Mercury Depletion Events (MDE) in the Arctic.

Motivation: The population of the Arctic may be exposed to harmful levels of methylmercury from consumption of fish, seafood and marine mammals. Tracing the origin of this mercury/methylmercury is a necessary step towards abatement and control measures.

Scientific effort: This includes measurements of atmospheric mercury species during MDE, re-emissions during snowmelt, input to seawater via runoff and uptake in food-chain. For assessment of fluxes and transformations, atmospheric as well as ecosystem models need to be applied. A broad scientific expertise is necessary.

Topic 4: Global air-surface exchange processes of mercury.

Motivation: Air-surface exchange processes control the environmental life-time of mercury in a global perspective. Without a deeper knowledge of the role of re-emissions from world oceans and the ocean as a reservoir for mercury as well as exchange processes over vegetation (forests) we cannot predict the results of control measures or global agreements on restrictions in mercury use and emissions.

Scientific effort: Field measurements of natural emissions, re-emissions from land (vegetation) and oceans, dry and wet deposition. Includes measurements of governing processes such as photochemistry in surface waters and atmospheric speciation.

2.4.2 Medium scale efforts - Nordic/international co-operation

Topic 5: Mercury in Nordic ecosystems. Assessment and visualisation of concentrations, time trends, variability, critical loads and possible health impacts in the Nordic countries.

Motivation: Provide a status report on mercury pollution in the Nordic countries aimed at national and international policy makers.

Scientific effort: Data compilation, statistical evaluation and mapping. Evaluation of variability in fish levels and links to changing atmospheric input.

Topic 6: Assessment of land-use impact on mercury fluxes from terrestrial to aquatic ecosystems at selected site(s) in the Nordic countries

Motivation: Recent data from Finland and Sweden show that forestry (clear-cutting, destruction of forest soil by heavy machinery) can greatly increase mercury and methylmercury output from soil to water. Assessment of the overall impact is needed but may prove to be a significant source of methylmercury to aquatic ecosystems. Impacts of wetland restoration unknown.

Scientific effort: Field measurements (run-off and soilwater chemistry) in a variety of catchments where different forestry methods have been used. Measurements of fish mercury in lakes where different forestry methods have been used in catchments.

Topic 7: Reactive Gaseous Mercury (RGM) and methylmercury dynamics and fluxes during MDEs in the Arctic

Motivation: Develop an understanding of mechanisms and net input of mercury species to the Arctic during polar sunrise. Provide basic knowledge for model developers.

Scientific efforts: Field measurements and laboratory process studies of RGM and methylmercury formation and deposition. Field measurements of re-emissions during snow-melt.

Topic 8: RGM and methylmercury dynamics and fluxes non-arctic

Motivation: Increase knowledge on emission sources and formation of RGM and methylmercury in boundary layer and free troposphere. Input to regional and hemispherical/global models.

Scientific effort: Field measurements and laboratory process studies of RGM and methylmercury formation and deposition. Measurements of RGM and methylmercury emissions from point and area sources.

Topic 9: Refinement and application of global/hemispherical model

Motivation: Develop tools for global emission scenarios and impact on *e.g.* deposition in the Nordic countries or in the Arctic.

Scientific effort: Refinement of model parameterisation in terms of chemistry and meteorology. Update and improvement of global emission inventories.

Topic 10: Variability of soil microbe effects

Motivation: Current scientific evidence has shown a potential risk for large scale impacts in forest soils. Further research is needed to assess the geographical variability and the dependence on soil status etc.

Scientific effort: Laboratory and field investigations of soil respiration in different soil types with different mercury levels.

Topic 11: Refinement and further development of critical load model for Hg

Motivation: Empirical critical load models are useful and required tools in the policy making process within the UN ECE convention on transboundary air pollution.

Scientific effort: Data assimilation, model parameterisation and testing.

Topic 12: Monitoring of net-deposition in geographically representative forested site (litterfall, throughfall)

Motivation: Our current understanding of the mechanisms of mercury deposition in forested areas is not sufficient to explain the high variability found in litterfall deposition in the Nordic countries (Sweden and Finland).

Scientific effort: Field measurements of deposition in open field, throughfall and litterfall as well as air measurements of mercury species. Development of deposition and vegetation uptake models.

2.4.3 Small scale efforts - Nordic/national projects

In general, small-scale efforts can be made within any of the above general topics. With limited resources, investigations will necessarily be smaller and in the form of campaigns or case studies. In some cases, monitoring activities (complementary to national programs) can provide useful information on specific processes. Some prioritised areas are:

- 1. Assessment of geographical and temporal trends of mercury in freshwater fish in the Nordic countries.**
- 2. Assessment of variability of mercury levels in Nordic ecosystem and their response to changing atmospheric deposition.**
- 3. Measurements of mercury species in the atmosphere (Arctic and non arctic).**
- 4. Measurements of net-deposition in selected forested sites (litterfall, throughfall).**
- 5. Measurements of catchment output of mercury and methylmercury in relation to landscape characteristics (forest type, wetlands etc) and land-use (forestry).**
- 6. Quantification of soil microbe impact at selected locations.**

2.5 Detailed Report from Working Group 1

Rapporteur: Gary Geenaert.

1. Terms of Reference: Group 1

The group was tasked to prioritise the most important policy oriented mercury research tasks, which in turn are necessary to improve the performance of modelling, assessment, and monitoring tools for the Nordic countries and the Arctic.

2. Overview of the policy modelling process

As a starting point, the group summarised "endpoints" which have demonstrated that a problem needs to be solved with policy action. Endpoints included monitoring data which demonstrate unacceptably high levels of mercury in soils, water, fish, sea birds, and humans. Contaminated soils particularly in Sweden and Finland were pointed out, and human health concerns due to consumption of traditional foods were noted for the Faroe Islands, Greenland, Canada, and northeast Scandinavia.

In order to reduce concentrations to "acceptable levels", there was unanimous agreement that a policy tool must be constructed, which contains a series of major processes which link anthropogenic emissions to measurable endpoints. This involves the development of process submodels based on dynamical and/or statistical mathematical relationships.

The series of submodels must include:

- (a) Emissions from both anthropogenic and natural sources (note that remissions are covered under (d) below);
- (b) Atmospheric transport and chemical transformations in advecting air masses;
- (c) Mercury flux from the atmosphere into both marine and terrestrial surfaces, including estimates of net mercury fluxes to or from oceans, lakes, vegetation, and soils;
- (d) Mercury fluxes within the surface compartment, i.e., mercury budgets based on immediate biomass uptake, flux into soils and surface water, and re-emission to the atmosphere;
- (e) Mercury flux up the food chains, i.e., mercury transport pathways from bacteria and/or phytoplankton up the food chains up to, and including, humans.
- (f) Monitoring endpoints, i.e., mercury concentrations in soils, plants, and tissues of birds, fish, polar bears, marine mammals, and humans.

Fundamental questions in policy research:

- What is the relative contribution of anthropogenic and natural emission sources as causes of observed monitoring endpoints: locally, regionally, and globally? Are the differences spatially variable, i.e., in the Nordic countries and in the Arctic?
- What is the efficiency of emission reductions in producing a desired outcome in monitoring endpoints? Will receptor modelling give insight on the potential benefits of mitigation strategies, and will there be strong spatial variation of such efficiencies?
- Is the timing of severe mercury deposition events (such as the Arctic sunrise) correlated with ecosystem events (such as phytoplankton blooms, terrestrial bacterial growth) to such a degree that most mercury deposited will be taken up in the food chain? Is there large spatial variability of this phenomenon, in both the Nordic countries and in the Arctic?

4. Relevant findings of the workshop to the discussion of priorities

mercury concentrations found in Nordic and Arctic ecosystems are most likely due to atmospheric deposition. Riverine pathways as well as ocean currents are generally of minor importance.

Natural mercury emissions are probably about 1/3 of the total global emissions. While emission inventories are available as annual averages and on global grids of order 100X100 km², the uncertainty in the inventories is unacceptably large. Natural emissions exhibit much more uncertainty than anthropogenic emissions, and natural emissions are more episodic. It was the group's opinion that annual averages are probably sufficient for modelling in support of the assessment and policy process, and there is no need to go to finer temporal resolution.

The present state of the art for atmospheric mercury modelling shows that model estimates are typically uncertain with a factor of two, based on comparisons with measurements of elemental mercury. For RGM, there are uncertainties reaching a factor of 10 in some places of Europe and the Arctic. In the Arctic, models of the Arctic sunrise depletion events can show uncertainties exceeding a factor of 10, depending on location. Model uncertainty in Europe is dominated by uncertainty in emission inventories and re-emissions from land surfaces. Model uncertainty in the Arctic is dominated by missing chemical mechanisms associated with the Arctic sunrise event, and large uncertainties in re-emissions from both sea and land surfaces.

For policy analysis, the relative benefits of reduced emissions can be estimated in spite of large uncertainties in mercury emissions. However, the regional variations around the Arctic associated with sunrise depletion events will complicate present policy studies, since the Svalbard events are not well modelled (see below).

The mercury depletion event of the Arctic sunrise, of perhaps one month duration, is most likely responsible for between 40% to 90% of the total annual deposition to the Arctic. During most years, the monitoring stations at Barrow, Alert, St. Nord, and Svalbard all showed mercury depletion events. There was one year, i.e., in 1999, where Svalbard did not experience an arctic sunrise mercury depletion event, while all others did. One hypothesis which has been put forward to explain the lack of a depletion event at Svalbard is that the depletion events may be based on chemistry which is unique to the atmospheric boundary layer, since the halogens involved in the reactions are emitted from the sea surface. Note that the monitoring at Svalbard takes place on top of a mountain, while all other Arctic stations are located near sea level.

It is likely that minor mercury depletion events could also occur in midlatitudes of Europe, i.e., in areas where halogen reactions could take place, and using the same chemistry of the Arctic sunrise event. No such depletion events have yet been observed in Europe.

The Arctic sunrise event is most likely driven by atmospheric photochemical processes which are presently known to trigger reactions between elemental mercury and either chlorine and/or bromine halogens, thus producing the more volatile and rapidly depositing RGM. The beginning of the arctic mercury depletion event is thought to be triggered by photochemistry in the top film of snow, where sea salt halogens are released. There have been only a few laboratory studies of the halogen chemistry of mercury, and there are no Arctic research projects yet carried out which contain all the necessary measurements. Modelling (in Denmark and Canada) is now based on different assumptions of the possible chemistry. The Arctic sunrise depletion event which was missing at Svalbard but observed at other stations in 1999, presently cannot be modelled.

There are no monitoring programs which measure the concentrations of all relevant mercury components simultaneously, i.e., elemental mercury, RGM, and particulate mercury. Each has different deposition rates, and the rapid conversion of elemental to RGM is primary feature of the Arctic sunrise event. On the other hand, the US EPA has funded two small technology intercomparison studies related to air chemistry of the Arctic sunrise, to be carried out in Barrow and Svalbard.

Mercury depletion events of the Arctic spring have only been observed at central Arctic stations: Barrow, Alert, St. Nord, and Svalbard. A new station will be installed by NOAA in eastern Arctic Siberia, thus adding to geographic coverage. The event observed at more southern stations, i.e., Nuuk, Faroe Islands, central Canada, and Europe.

Air mercury measurements on the Faroe Islands showed very elevated concentrations during a short period in 2000. The elevated concentrations have been shown to be most likely due to long range transport from Hekla Volcano on Iceland, in one period, and long range transport from Europe during another.

Unlike the central Arctic, mercury deposition to the Faroe Islands and south Greenland is most likely dominated by wet deposition. Monitoring programs in these southern regions presently do not include wet deposition. In the Faroe Islands, a time-limited project has recently been initiated by the Food and Environment Agency, Tórshavn, to analyze rain for mercury concentrations.

Measurements of RGM flux using "relaxed eddy accumulation" and a TEKRAN was demonstrated in Barrow, Alaska, in April 2001. This study will be repeated by NOAA and NERI in 2002.

Atmospheric transport mechanisms are considered to be adequately treated in models, in particular in the European latitudes.

Re-emission is considered to be a major source of mercury over the open ocean. The biological and thermodynamic controls over re-emissions has not yet been investigated. There are, however, some simple parameterizations available. Re-emission from land is more problematic. It has been suggested that the new REA Hg flux technology should be employed to measure such upward fluxes, with particular reference to terrestrial regions of Europe, and coastal areas of the Arctic.

There is little known about the rates and mechanisms governing the transport of mercury up the food chains, i.e., from bacteria and phytoplankton up to marine and terrestrial mammals (including humans). Migration and foraging patterns are important in describing the mercury accumulation rates in different trophic levels.

There are various scientific investigations and even fewer monitoring programs, which have documented a time series of mercury endpoints which can easily be used in policy modelling. The massive data sets available on contaminated soils and arctic mammals, for example, have not been collected with consideration for use in the development of end to end models in support of policy analysis. The connection has to be made more apparent and monitoring programs need to be adjusted to consider policy modelling needs.

While peat cores from the Faroe Islands show that atmospheric mercury deposition is around three times higher than pre-industrial levels, the core data show that the mercury deposition has most likely been decreasing during the past 15 years. This implies that Faroe Islands and Arctic ecosystems will slowly approach more healthy conditions. However, without system modelling, it is not clear how quickly ecosystems will recover.

5. Priorities

5.1 Emissions

- * Improved global emission inventories is needed, where speciation is provided. In particular, inventories need to include Hg(0), RGM, and particle emissions.
- * Natural emissions need to be improved, on both regional and global scales.

5.2 Atmospheric chemistry

- * Initiate controlled laboratory studies which simulate the atmospheric and surface conditions associated with the Arctic sunrise mercury depletion events. Such studies should be dedicated to describing the chemistry responsible for production of RGM from elemental mercury.
- * Establish a few monitoring stations in both Europe and the Arctic, which contain all three relevant mercury species (elemental, RGM, and particulate). Adding a mercury flux package on a periodic basis to each of these stations would be advantageous, in particular for the Arctic sunrise event. Candidate sites must be flat, easily accessible, and with good support infrastructure, thus Alert, St. Nord, and Barrow are ideal. Zackenberg is a potential future site, only if infrastructure is provided.

5.3 Regional models of surface mercury budgets (biomass uptake, flux into soils, re-emissions, etc.)

- * Develop a regional scale model of mercury flux between different components of the terrestrial and marine surface environments. One model for the Nordic countries, and another for the Arctic. Based on atmospheric Hg deposition, the model should predict Hg flux into surface biomass, into water and soils, and re-emitted flux to the atmosphere. Existing data bases should be used, as much as possible.
- * Develop and apply the new REA mercury flux technology over selected terrestrial sites of Europe and selected sites of the Arctic, to measure deposition and re-emissions, i.e., in areas where re-emissions are anticipated. Flat areas only, no mountainous terrain nearby.

5.4 Mercury transport up the food chains

- * Develop a food chain flux model for mercury, which describes transport of Hg up the food chain. The model needs to be regional scale, and contain migration patterns of species at different trophic levels. This will also require coupling with the atmospheric transport and deposition model.

5.5 Data bases and accessibility

- * Assemble existing data bases from all components of the policy model system as described in Section 2. It should include atmospheric, marine, terrestrial, and ecosystem information, as well as endpoint indicators. The data bases should be labelled with temporal and spatial information, including such detail as migration patterns of trophic level species.

6. Highest priorities for NMR

- * Develop a regional scale model of mercury flux between different components of the terrestrial and marine surface environments. Based on atmospheric Hg deposition, the model should predict

Hg flux into surface biomass, into water and soils, and re-emitted flux to the atmosphere. Existing data bases should be used, as much as possible.

* Develop and apply the new REA mercury flux technology over selected terrestrial sites of Europe and selected sites of the Arctic, to measure re-emissions, i.e., in areas where re-emissions are anticipated. Flat areas only, no mountainous terrain nearby.

7. Highest priorities for AMAP

* Assemble existing data bases from all components of the policy model system as described in Section 2. It should include atmospheric, marine, terrestrial, and ecosystem information, as well as endpoint indicators. The data bases should be labelled with temporal and spatial information, including such detail as migration patterns of trophic level species.

* Develop a regional scale model of mercury flux between different components of the terrestrial and marine surface environments. Based on atmospheric Hg deposition, the model should predict Hg flux into surface biomass, into water and soils, and re-emitted flux to the atmosphere. Existing data bases should be used, as much as possible.

* Develop and apply the new REA mercury flux technology over selected flat coastal sites of the Arctic, to measure deposition and re-emissions, i.e., in areas where re-emissions are anticipated. Note flat areas only, no mountainous terrain nearby.

* Initiate controlled laboratory studies which simulate the atmospheric and surface conditions associated with the Arctic sunrise mercury depletion events. Such studies should be dedicated to describing the chemistry responsible for production of RGM from elemental mercury.

* Establish a monitoring station in the Arctic, which contains all three relevant mercury species (elemental, RGM, and particulate). The objective of such a station would be to parameterise the chemical mechanisms responsible for conversion of elemental mercury to RGM, transformation of RGM to TPM, and deposition of RGM and TPM. Adding a mercury flux package on a periodic basis to each of these stations would be advantageous, at the least to quantitatively document the Arctic sunrise event. Ideally, it would be St. Nord, Alert, or Barrow. Secondary stations which focus on geographic variability of the halogen chemistry associated with sunrise events. As the only mountainous site, Svalbard should be the focus on a study to explore whether the arctic sunrise is confined to the atmospheric boundary layer or if it is a prevailing phenomenon throughout the troposphere.

2.6 Detailed Report from Working Group 2

Rapporteur: John Munthe

1. Air surface exchange/re-emissions/natural emissions

The oceans play a major role in the global cycling of mercury. Oxidised mercury in seawater can act as a reservoir which may be re-emitted to the atmosphere after reduction to Hg^0 . The current knowledge of these processes indicates that re-emissions are of the same order of magnitude as wet deposition on the ocean surfaces. Since mercury is a pollutant with hemispherical and global distribution, the oceanic deposition/re-emission cycle may significantly influence the results of emission reductions on global or regional scales by a continuous release of mercury. An accurate assessment of the role of oceanic emissions can only be made using hemispherical or global models. At present, the global estimates of oceanic (re-) emissions are highly uncertain.

Increasing the understanding of oceanic re-emission/deposition processes and the role of the world's oceans as a reservoir of mercury would require very large research efforts. The Nordic countries cannot act alone in this but should actively seek international co-operation in scientific networks or collaborative programs within the European Union.

2. Terrestrial transfer to aquatic

One of the most important processes for the long-term reduction of mercury contamination in freshwater fish in the Nordic countries is the export of mercury and methylmercury from forest soils and wetlands. Large quantities of mercury have accumulated in forest soils due to atmospheric deposition. A significant fraction of the mercury is probably of natural origin but clear increases in topsoil levels clearly show the impact of anthropogenic emissions over the last century.

Catchment export to lakes is a significant source of mercury in aquatic ecosystems. The transport of mercury and methylmercury from catchment to lake is linked to the transport of dissolved organic matter. The mechanisms and thus our capability to model and predict future export is limited.

Wetlands differ from forest soils in that the export of mercury and specifically methylmercury is significantly higher. The driving force behind this is not known.

Recent results from Finland and Sweden have shown that forestry practices may play an important role in the transfer of mercury and methylmercury from forest soils to the aquatic ecosystem. The main impact of forestry (clear-cutting or other activities) is probably the damaging of the forest soil and disturbance of the humic layer as well as the hydrology which leads to increased output of mercury as well as methylmercury.

Based on the above findings, on-going discussions and activities on restoration of wetlands and drained forest soils should be followed. If disturbance of hydrological pathways in forest soils leads to enhanced export of methylmercury then restoration of forest soils may lead to increased methylmercury levels in the aquatic ecosystems.

The role of sulphate deposition in the methylation of mercury in forest soils is to a large extent unknown. A feasible hypothesis is that sulphate in soil water stimulates sulphate reducing bacteria which in turn can methylate inorganic mercury.

Mercury has been shown to have negative effects on soil microbes. These findings indicate that mercury accumulation in forest soils may impact the forest ecosystem by affecting degradation of organic matter and thus release of nutrients etc. At present, only limited field and laboratory studies

have been made. Experimental techniques have been developed which makes further studies of geographical variation and impact of external parameters such as organic matter characteristics and soil status feasible.

Mercury research on freshwater ecosystems has been almost non-existent during the last decade in the Nordic countries. Despite significant efforts during the seventies and eighties, several key questions remain unanswered. One major issue is the question of methylation: where it occurs and at which rate. Bioavailability of inorganic mercury and its variability with dissolved organic carbon characteristics is also an important issue.

In Arctic ecosystems, there is very little information on the pathways of mercury and methylmercury. With the discovery of the Mercury Depletion Events (MDE), a possible channel for mercury input to the food chain has been identified. Further research is, however, needed before the net input of mercury and its impact on Arctic ecosystems can be quantified.

3. Emissions, atmospheric speciation and dispersion

Anthropogenic emission inventories are today available for mercury for Europe and globally. Uncertainties are relatively large especially for speciation and emissions from diffuse sources such as contaminated soils and small scale use of mercury. For natural emissions the uncertainties in current estimates are significant. Further research into these areas is a high priority.

Atmospheric models capable of simulating transport and transformation of mercury on local, regional and global scales are today available. The development of large-scale models (global/hemispherical) is promising. Accuracy of models are dependent on accuracy of emission inventories, description of chemical transformations and deposition processes. Areas where more basic research is needed to provide model input are:

- Chemistry and deposition in the Arctic atmosphere
- Oxidation of elemental mercury in the free troposphere and the marine boundary layer
- Dry deposition of mercury species to vegetation (forests)

3 Abstracts and extended abstracts

3.1 Theme 1 POP's and transport and uptake processes

The influence of air temperature, solar radiation and ozone on benzo(a)pyrene changes in atmosphere

A. Milukaite, A. Girgzdiene, A. Mikelinskiene (Institute of Physics, Vilnius)

According to EMEP data a great amount of carcinogenic polycyclic aromatic hydrocarbons (PAHs) is emitted to the atmosphere every year in the various European countries. Laboratory experiments have shown, that UV radiation and ozone in the concentrations 10 or 100 times exceeding natural concentrations have a destructive influence on PAHs. The behavior of these pollutants under natural conditions was studied scantily in the polluted atmosphere, while this process in rural atmospheric air is still unknown. The purpose of this study was to evaluate the influence of ozone, air temperature and solar radiation on benzo(a)pyrene (BP) concentration in atmospheric air of rural site.

The concentration of benzo(a)pyrene was determined and meteorological parameters were recorded at the background station Preila since 1980. To fulfill purpose of study the monthly averaged data of investigation and data of separate periods of investigation, including ozone measurements, were used. The results of investigation showed a confidence anti-correlation between the atmospheric air temperature, intensity of solar radiation, ozone and concentration of benzo(a)pyrene in warm seasons of the years. Furthermore, the data of investigation showed that day-time temperatures higher than 25°C, solar radiation duration of 12-15 h·day⁻¹ and the concentration of ozone higher than 100 µg·m⁻³ may change the concentration of benzo(a)pyrene in the atmospheric air by one order of magnitude.

OH-Exposure of POPs - Employing Filter Samples of Coated Aerosol

Heinz-Ulrich Krüger and Cornelius Zetzsch (Fraunhofer-Institut für Toxikologie und Aerosolforschung)

Environmental transformation and degradation of POPs and other semivolatile organic compounds is known to be largely governed by atmospheric chemistry involving OH radicals. Although the majority of current pesticides and the vast majority of existing chemicals belong to this class with vapour pressures below 1 mPa, there are only very few laboratory studies about their atmospheric transformation, in contrast to the ubiquitous occurrence in the environment. The reason is that the handling of such vapours in small vessels may be more tedious than the environmental analytics. We investigated the behaviour of sub-monolayer coatings of POPs and other pesticides on inert aerosol particles, deposited on Teflon filters during exposure to OH radicals in a small smog chamber. Using di-(2-ethylhexyl)-phthalate and terbuthylazine as reference compounds, the dependence of the consumption rate on OH exposure was investigated to explore a simplification of the aerosol-borne technique by introducing a relative rate technique. Evaporation was observed to compete with OH reaction, as demonstrated for Lindane and DDT.

Uptake of Airborne Persistent Organic Pollutants in Pine Needles: A Reversal of Global Fractionation?

Henrik Kylin, Anna Hellström (Swedish University of Agricultural Sciences)

Understanding the uptake mechanisms of airborne persistent organic pollutants (POPs) in vegetation is important to understand how plants affect the entry of POPs into terrestrial ecosystems and how the vegetation affects the long range transport and global fractionation of POPs. In a long-term study the uptake of some POPs in pine needles was studied. Contrary to what was hypothesised, POPs in the gas phase accumulate in the pine needles during the hot summer season while very little accumulation takes place during the cold winter season. Accumulation continues for the entire life of the pine needles except for the last needle year-class, irrespective of how old the needles grow. Particle bound compounds on the other hand seem to be deposited on the needles during winter and then washed off during spring. The result of these two processes seems to contradict the chemical-physical models of plant uptake of airborne POPs. Combining the above observations with data on the distribution of POPs in pine needles throughout Europe shows that the uptake rate of POPs in the gas phase is highest in a cold climate, but that the total deposition to the terrestrial ecosystem is higher in the south than in the north. Thus it seems that the importance of air-plant gas exchange is underestimated in warm climates and that the boreal coniferous forest is a much more effective scavenger of volatile POPs than has been presumed. Judging from our data, grasshopping of POPs is not an important phenomenon in terrestrial environments.

3.2 Theme 2 POP's in the European atmosphere

Monitoring of POP concentrations and depositions in the Netherlands

Jan Duyzer (TNO MEP, Netherlands)

Estimates have shown that atmospheric deposition may be an important source of persistent organic compounds for the Dutch coastal and inland waters. These estimates of the input have been made using atmospheric dispersion models. The uncertainty is however large.

A multi-disciplinary project was defined with the aim to improve the quality of estimates of the atmospheric deposition of POP to Dutch waters and to assess the relative contribution of different sources and source categories to the deposition. The project consists of a comprehensive monitoring programme and a modelling study. A detailed emission inventory will be made for the Netherlands. This inventory will form the basis of model calculations using models operated by RIVM such as EUROS and TREND. For a period of two years (1999-2001) a monitoring network will be operated. The network consists of three core stations and fifteen regional stations. At the core stations, located in remote areas the concentrations of pesticides, PCB's and PAH's in air and precipitation will be determined on a weekly basis. On the regional stations the concentrations of pesticides in air and precipitation will be determined on a monthly basis.

The results of the monitoring programme will be presented. These will include the average levels and regional patterns of concentrations and depositions of pesticides, PAH and PCB's. The results will be discussed with respect to emissions, long range transport etc.

Modelling the Environmental Distribution and Fate of Persistent Organic Pollutants on a European Scale

Andy Sweetman (Lancaster University)

Persistent organic pollutants have been the subject of Internationally agreed protocols to ensure that their impact on humans and the environment are minimised. Currently there are twelve POPs (or chemical groups) which have been targeted for elimination or reduction. They have been selected because of concerns over their persistence in the environment, their ability to undergo long range transport (LRT) and their ability to bioaccumulate through food chains. As a result of these properties and their potential to exert toxic effects, efforts are being made to reduce environmental and human exposure. However, there are many chemicals are being produced that may have similar properties and hence may be considered POPs.

As a result of their ability to undergo LRT there is a need to develop predictive models which can cope with a range of geographical scales. At Lancaster we are developing a multimedia model designed to investigate POP fate and transport on a European scale. This project is being carried out in collaboration with the Canadian Environmental Modelling Centre at Trent University. They have developed a North American Contaminant Fate Model in conjunction with Lawrence Berkeley National Laboratory, USA, which we are currently modifying for Europe. This involves re-parameterisation of the air and water mass balances, compartment description and inter-compartmental transfer. The Berkeley-Trent North American Contaminant Fate Model (BETR North America) is a linked multi-compartment regional mass balance chemical fate model. The model calculates steady state or non-steady state (dynamic) mass balances of chemical contaminants on regional and continental scales from inputs describing the environmental characteristics of North America, the physico-chemical properties of the contaminant of interest, and contaminant emission rates. The focus is on describing contaminant fate and transport over the entire continent, including transfer, transport and cycling in and between air, vegetation, soil, surface water, sediments and near-shore coastal water. The BETR North America model is built on a general framework that links contaminant fate models of individual regions to create a model that encompasses a larger, spatially heterogeneous area.

Assessing the environmental fate of chemicals of emerging concern: a case-study of the polybrominated diphenyl ethers

Anna Palm (IVL), Ian Cousins (Trent Univ., Canada), Donald Mackay (Trent Univ, Canada)

1. Introduction

In a paper soon to be published (Palm et al., [1]), the physical-chemical properties for 20 PBDE congeners of various bromination levels (including the non-brominated diphenyl ether) were reviewed and analysed using a structure-property approach known as the “three solubility” approach [2]. The physical-chemical properties were used as inputs to evaluative fate models, specifically the well-known EQC model [3] and the TaPL3 model [4], which has been designed specifically to evaluate environmental persistence and characteristic travel distances in air and water. A local-scale urban model, called “CeStoc” has also been developed to evaluate the fate of these compounds in an urban area [5]. In this presentation some of the results from the paper of Palm et al. will be reviewed with particular emphasis on the analysis of the physical-chemical properties and evaluative fate modelling. The CeStoc model will also briefly be presented to exemplify how multimedia models can be applied to POPs in local areas.

2. Methods

The “three solubility approach”

Available experimental data on physical-chemical properties were compiled and used to derive solubilities or “apparent-solubilities” of liquid state substances in air, octanol and water. The logarithms of these solubilities were then plotted against Le Bas Molar Volume [6]. Correlating solubilities against a molecular descriptor such as Le Bas molar volume in this way is beneficial for homogenous chemical groups such as PBDEs since structure-activity relationships are often found. Experimental data gaps were filled with estimated values. The solubility equations were then used to derive input properties for the environmental fate models used. Experimental values for degradation half-lives were not available, thus they had to be estimated using the EPIWIN estimation software [7].

EQC model

The EQC model was originally developed to evaluate the generic fate of chemicals in the environment. Performing this kind of generic modelling gives initial insight to likely partitioning media of the chemical, dominant transport and loss processes, tendency to bioaccumulate and undergo long-range transport and environmental persistence. In the current study, the model was used to evaluate the chemical behaviour of the PBDEs by running various hypothetical releases to the model environment, 1000 kg/h to air, water and soil, one at a time, and then 1000 kg/h to all three media simultaneously. These hypothetical scenarios allow comparison with other chemicals on an equal basis, which is useful since release information is often not available.

TaPL3 model

The TaPL3 model is a long-range transport model based on the EQC model described above, and is used to calculate characteristic travel distances of chemicals in air and water.

CeStoc model

The CeStoc model was also based on the principles and equations of the EQC model, but one extra compartment was added, namely an organic film that covers all the hard surfaces in a city. The model was parameterised to the centre of Stockholm and run for selected PBDE congeners with

emission estimates that were based on a Danish study [8] and scaled to the Stockholm conditions on a population basis.

3. Results and Discussion

Three Solubility Approach

Obtained relationships between the three solubilities and Le Bas Molar Volume are shown in Fig 1 a-c. Solubilities of PCBs [9] and chlorobenzenes [2] have also been included for comparative reasons. Fig 1a shows that the solubility in air decreases with molar volume, as does the solubility in water (Fig 1b) and octanol (Fig 1c). The solubility in air falls by a factor of 6.5 per bromine added (0.82 log units). The slope is similar to PCBs and chlorobenzenes, with absolute values being a factor of 10^3 to 10^5 lower at the same molar volume. The water solubility decreases much more per bromine added than the solubility in octanol, which accounts for an increasing octanol-water partition coefficient with molar volume. Deducing key partition coefficients (K_{OW} , K_{AW} , K_{OA}) showed increasing trends with increasing molar volume. Generally, estimated values for physical-chemical properties differed considerably from measured values, which emphasises the importance of experimental determination of properties.

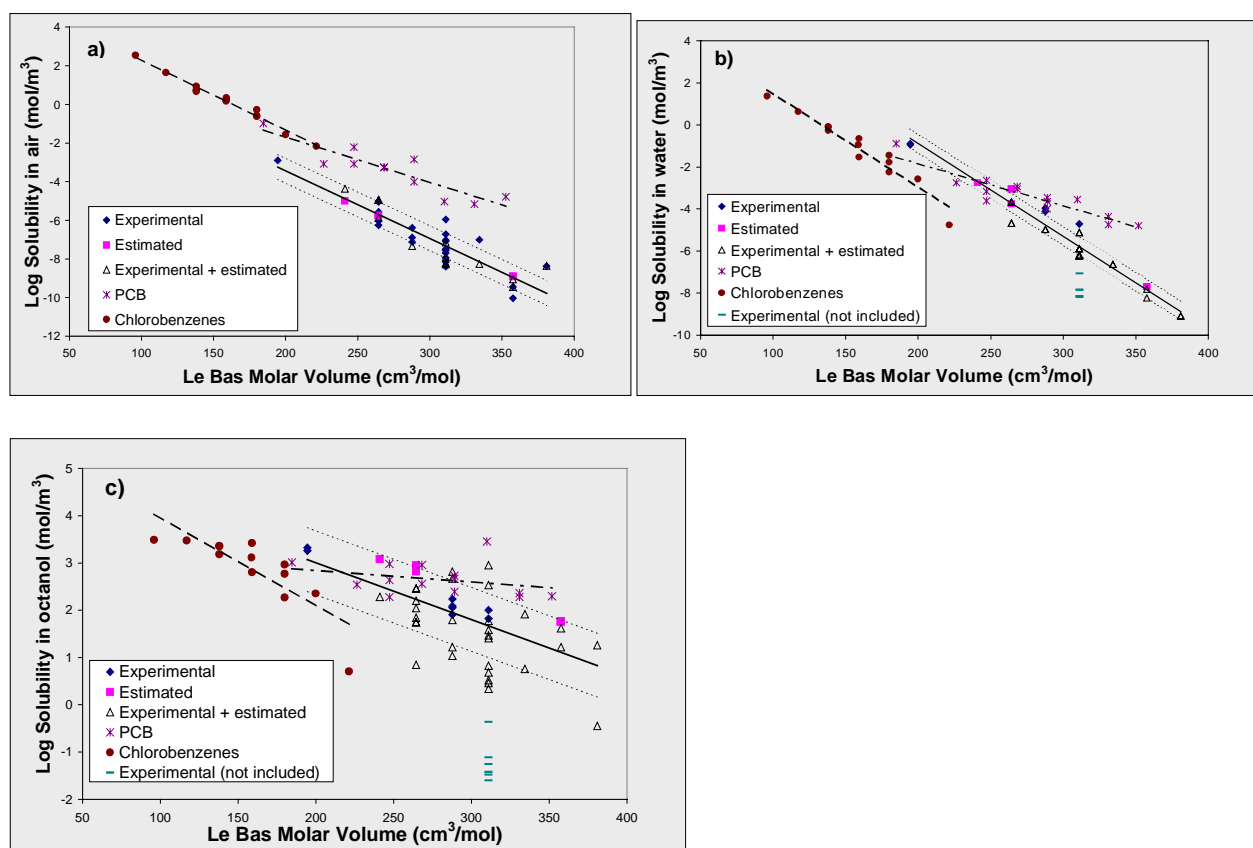


Figure 1. Plots of log solubility in air (i.e. vapour pressure/RT), water and octanol (i.e. $K_{OW} \times S_w$) (mol/m^3) for the liquid state at 25°C for PBDEs, chlorobenzenes and PCBs.

EQC model

Evaluative modelling was carried out for three brominated compounds (BDE 47, 99 and 209) and the non-brominated diphenyl ether for comparative reasons. When releasing the chemical individually to air, water and soil the non-brominated compound tends to stay in the release medium. Brominated compounds are more likely to be transported to soil and sediment when emitted to air, with transport to sediment slightly decreasing with increasing molar volume, which is likely to be due to decreasing water solubility of higher brominated compounds and thus preferential partitioning to soil when deposited. Emission to water results in predicted transport to

sediment, increasingly as molar volume increases, and if soil is the receiving medium the chemicals are predicted to remain there. Simultaneous emission to all three media results in dominant partitioning to soil and sediment, with an increasing proportion in soil as the degree of bromination increases. The major net transport process is transport from air to soil, followed by water to sediment. Reaction in soil is the dominant removal process for all modelled congeners. An example of the output is shown in Fig 2 a-b with BDE 47 and BDE 209 as representative compounds.

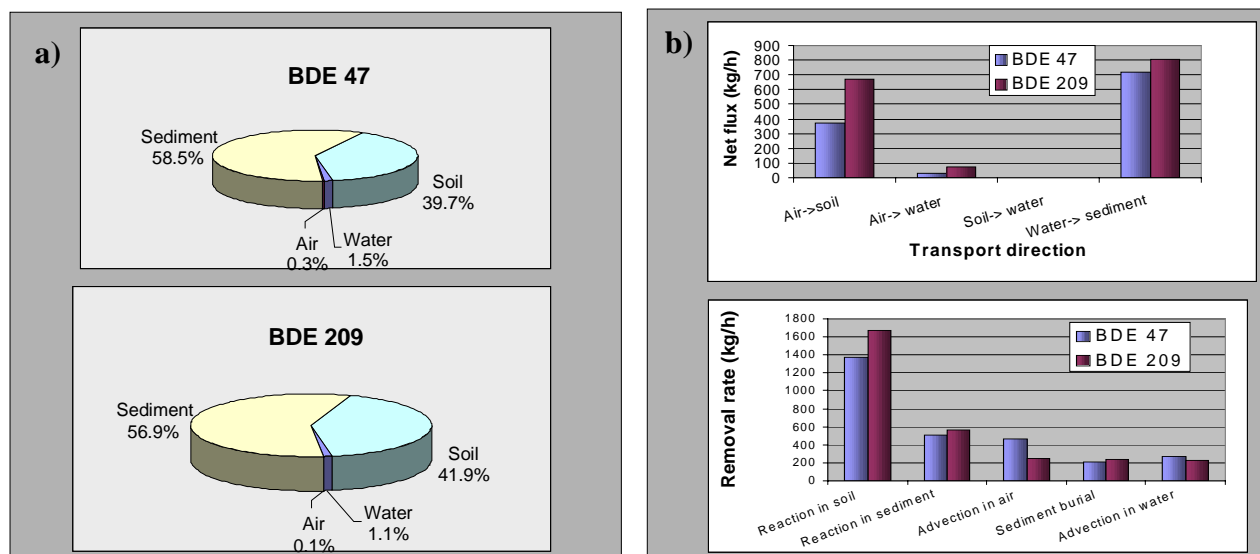


Figure 2. Partitioning percentages in the EQC environment (level III), dominant intermedia transport processes and major removal pathways predicted by the EQC model for BDE 47 and 209.

TaPL3 model

The two main factors that determine a chemical's potential to be transported long distances are a) persistence in the atmosphere and b) 'stickiness' i.e. tendency to partition to terrestrial surfaces while transported in air or water. The TaPL3 estimates the atmospheric travel distances for PBDE congeners to be less than 1,200 km which can be compared to calculated distances of 130,000 km for hexachlorobenzene, 13,000 km for lindane and 750 km for 2,3,7,8-TCDD [4]. PBDEs are "stickier" and less persistent than some other well-known pollutants and might be transported shorter distances in air and water. However, due to the wide use of flame-retarded products and the large amount of usage of e.g. deca-BDE, polybrominated diphenyl ethers might still be found in samples from remote sites.

CeStoc model

Under the given emission estimates, CeStoc predicts the majority of the chemical to be advected out of the region in air, regardless of degree of bromination. Soil is predicted to be the major sink for the remainder, followed by sediment. The CeStoc results also indicate that physical-chemical properties are of less importance in a small area such as Stockholm than environmental parameters. Emission medium is also crucial and ultimately determines the fate of the chemical.

Conclusions

This study has helped us to get a first overview of the likely environmental fate of PBDEs. It indicates that they are persistent chemicals which may be subject to long-range transport, even if this potential is slightly less than for other well-known pollutants. The study also points out that there is a strong need for experimental determination of physical-chemical properties, for more environmental monitoring of a larger number of congeners, particularly in background areas. Other recommended research topics are environmental emission estimates and determination of

degradation rates. When this has been done, the multi-stage assessment can be reapplied and yield a more complete picture of the environmental fate of PBDEs.

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POP modelling within UN ECE CLRTAP

Victor Shatalov, Alexandr Malanichev, and Nadezhda Vulykh (MSC-East, Moscow)

In the talk, the information on the modelling work in the field of POPs undertaken under EMEP during the recent time is presented. This work includes the refinement of MCSE-POP multicompartment model (refinement of atmosphere/sea exchange module taking into account transport of pollutants by sea currents, refinement of the model description of dry deposition to a forest, modification for calculations of country-to-country matrices for B[a]P, and development of the multicompartment POP model on the hemispheric scale), preparatory work for model assessment (refinement of model parameterizations for dioxins/furans, HCB, and γ -HCH, examination of PCDD/Fs congener composition in emissions and environmental media, collecting emission data and measurement data of air concentrations for the listed POPs on the EMEP grid boundaries), and the following model runs:

- Evaluation of transboundary transport of B[a]P by source-receptor scheme for 1998.
- Evaluation of HCB and PCDD/F transport and accumulation from 1970 to 1998.
- Assessment of transport and accumulation of PCBs from 1970 to 1998. Evaluation of media response to emission reduction up to 2010.

Particulate attention was given to the following questions:

Examination of the congener composition of dioxins/furans in emissions and environmental compartments. On this way the list of congeners for primary modelling was elaborated (1,2,3,7,8-PeCDD, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, and 1,2,3,6,7,8-HxCDF). It was shown that usage physical-chemical properties of 2,3,4,7,8-PeCDF congener for modelling of the dioxins/furans mixture leads to the discrepancies in the spatial distribution of about 30%. Hence, this congener can be viewed at this stage of investigation as “indicator one”.

Evaluation of B[a]P transboundary transport. The first attempt of calculations of B[a]P country-to-country matrices in 50x50 km grid was performed. These matrices were calculated both for depositions and for air concentrations.

Model validation including model sensitivity study as well as comparison with measurement data and results of other models was performed for all listed pollutants. The comparison showed the agreement between measurement and modelling data within an order of magnitude for all the pollutants and somewhat best results (on the average within a factor of 3) for B[a]P and PCB. The comparison was performed for concentration levels in various environmental compartments (atmosphere, soil, seawater, vegetation) and deposition fluxes.

The results of the recent work are described in:

V. Shatalov, A. Malanichev, N. Vulykh, T. Berg, and S. Manø, Assessment of POP transport and accumulation in the environment, EMEP report 4/2001 and the references therein (see www.msceast.org for details).

3.3 Theme 3: Arctic research on Hg and POPs

Overview of AMAP monitoring studies of mercury and POP's in Greenland biota

Møller, Per (NERI)

In september 1989 the 'Rovaniemi process' was initiated which led to the Rovaniemi Declaration and the adoption of the Arctic Environmental Protection Strategy (AEPS). To implement certain components of the AEPS the Arctic Monitoring and Assessment Programme (AMAP) was established in 1991.

The presentation includes a brief introduction to AEPS and AMAP and an overview of AMAP monitoring studies of mercury and POP's in Greenland biota. Examples of spatial and temporal trends are given for representatives of the marine, freshwater and terrestrial environment with references to circumpolar trends. The present status and future strategies are presented.

Human exposure to mercury and POPs from the Greenland diet.

Johansen, Poul (NERI)

Humans in Greenland are exposed to higher intakes of some contaminants from their diet than humans in most of Europe and North America. The explanation is that people in Greenland to a much larger extent eat marine mammals and birds, often representing high trophic levels with high contaminant concentrations.

The presentation includes results from a new study in which the most important diet items in West Greenland systematically are analysed for mercury, selenium, cadmium and a large suite of organochlorines. Significant differences in contaminant levels among ecosystems, species and tissues are found. For example, in general low mercury and POP levels are found in terrestrial species, whereas levels may be high in marine species.

Contaminants in the Greenland Sea polar bear. Anatomical studies regarding contaminant induced pathological and histopatological/immunohistochemical changes in skulls and gonads/adrenals

Sogne-Hansen, Christian (NERI)

An overview is given of a current study of the effect of POPs (Persistent Organic Pollutants) on polar bears in eastern Greenland.

More than 300 skulls from East Greenland polar bears collected between 1892 and 2001 were examined morphologically to detect the degree of fluctuating asymmetry over time. Fluctuating asymmetry was estimated from 17 foramina and 16 length measurements on each skull. Results will be provided if possible.

Furthermore, macroscopic pathological changes were examined and 12 types (adonti, caries, osseous proliferation etc.) of pathological changes were detected. Of these, only parodontosis was found in frequencies high enough to detect changes over time. Osteopenia (osteoporosis and osteomalacia) was examined by DXA-scanning (Dual X-ray Absorptiometry) to detect the bone mass density (calcium phosphate level). Information on changes in bone mass density by sex and age over time will be provided if possible.

In order to detect potential POP-induced pathological changes in target organs and tissues (especially adrenal glands and gonads), samples were collected from more than 100 polar bears that had been shot by East Greenland hunters between 1999 and 2001. One pseudo-hermaphroditic female (June 1999) was found among the sampled polar bears. A macroscopical examination indicated that the internal sexual organs of this aberrant female were functional.

To detect temporal trends, 20 polar bears were analysed for POPs (chlorinated pesticides and PCBs). Ten of the 20 bears. A sub-set of 10 individuals were also analysed for new contaminants such as MeSO₂-PCBs, HO-PCBs, chlorinated paraffins, Polybrominated Diphenyl Ethers (PBDEs) and Co-planar PCBs/PCDDs/ PCDFs.

Mercury was analysed in hair as part of a temporal trend survey extending back to the early 1970's. Analyses of heavy metals such as Hg, Se, Cd, Zn were examined in soft tissues (muscle, liver and kidney). The results of these analyses will be compared with the previous published results from the same area.

The Post-Industrial Increase In The Atmospheric Background Level of Mercury,As Seen in an Ombrogenic Peat Core from the Faroe Islands

Goodsite, Michael (NERI), Shotyk, William(Univ Berne), Knudsen, Kristina (Univ Southern Denmark), Roos, Fiona (Univ of Berne)*

*since 1. October 2000, Institute of Environmental Geochemistry,
University of Heidelberg, INF 236, D-69120 Heidelberg, Germany)

A peat core from the Faroe Islands was obtained and geochemically analysed producing a long-term record of atmospheric deposition of Hg, Pb and As in the Faroe Islands. The goal of the study is to better understand the true natural background values of various contaminants deposited to the Faroe Islands via long range atmospheric transport; as well as to test the hypothesis that Icelandic emissions may be responsible for the elevated Hg inventories and long term rates of atmospheric Hg accumulation in Scotland and Shetland, compared to Switzerland. The landmark cohort study of Hg on the Faroe Islands (Grandjean et al.,) increased the scientific need for a temporal record of (especially) mercury. The peat profile appears to be ombrogenic and continuous through the industrial age, as determined by ^{210}Pb and ^{241}Am dating, though the basal date at 70 cm (determined by ^{14}C dating) of approximately 5400 BP suggests peat cutting event(s) between the loss of the ^{210}Pb signal and the basal layer. Ti and Zr as well as Y, Rb and Sn indicate an important source of mineral matter in the profile; which is most likely volcanic, since elevated levels are found in discreet depths. The core is presently undergoing further analysis and ^{14}C dating to determine if these depths coincide with known volcanic eruptions on Iceland, as well as to pinpoint the peat cutting event(s). High Br and Cl levels indicate the influence of sea salt spray on the profiles. The chronologies never the less appear to be well preserved. Preliminary analysis of the core shows a five-fold increase in the net accumulation of Hg, culminating in the early 1970's, and falling since. To account for the influence of sea salt spray in order to look at anthropogenic input, we also normalized [Hg] to [Se]. The [Hg]/[Se] ratio gives a very clear profile, with a nearly constant low ratio ($[\text{Hg}]/[\text{Se}] = 0.01 \pm 0.002$ ($n=54$), over what is probably the past thousands of years. Then the ratio rapidly increases from the start of the industrial age to approximately the 1940's ($[\text{Hg}]/[\text{Se}] = 0.22$), the ratio then falls with a rapid rate and appears to become nearly constant since approximately 1960 at ($[\text{Hg}]/[\text{Se}] = 0.07$). The profile suggests that atmospheric Hg levels were consistently low until the start of the industrial age where they greatly increased. At some point, (control/change of coal fired power?) the amount of mercury tapered to an increased (relative to pre-industrial) background level. Further analysis and high resolution dating of the profile continues. In addition the project work with peat taken this summer from the Cary Islands, Northwest Greenland will be described.

Long-term record of atmospheric Hg accumulation in the high arctic from peat deposits on Bathurst Island Nunavut, Canada

Givelet, N. (Univ of Berne); Ross, F (Univ of Berne); Goodsite, M (NER); and Shoty, W (Univ of Heidelberg)

On Bathurst Island (75°N) in Nunavut, Canada, a deposit of peat has been continuously accumulating organic matter for the past 9000 years. Four types of peat cores were collected and used to reconstruct a complete long-term historical record of atmospheric deposition of Hg for the High Arctic. At a hummock, the non-frozen layer was cut away as blocks. The underlying frozen layer was collected using a drilling machine. Both of these sections are thought to represent ancient peat formation. A miniature peat core of actively growing plant material was collected from a surface pool. The fourth core was collected in a nearby fen which also has active peat formation. All samples were frozen. In the lab, the cores were cut into 1cm slices. Four plugs were subsampled in the middle of the core. One of them was used to determine the dry bulk density. The others were used for Hg measurements after being air-dried in a Class 100 laminar flow clean cabinet. Mercury concentrations were measured in solid peat samples using a LECO AMA 254. In the hummock block, total Hg ranges from 25 to 75ng/g with the largest increase in Hg beginning at 10cm. In the underlying, frozen peat, Hg concentrations are relatively uniform ($28 \pm 4\text{ng/g}$). While there is an increase in bulk density at the top of the hummock (ca. 27%), this cannot explain the increase in Hg concentrations (ca. 3x). In the core from the pool, Hg concentrations decrease from 78ng/g at 7cm to 40ng/g at the surface. In the fen, total Hg ranges from 42 to 124ng/g. Mercury concentrations increase from 17cm to 10cm, but then decrease from 6cm to the top. From 17 cm to the top profile, bulk density decreases from 0,3 to 0,1g/cm³. In the fen, the Hg concentrations show more variability within a given sample, probably because of the diversity in peat-forming vegetation. Future studies will include Hg concentration measurements of individual plant macrofossils removed from the fen peat core. Elevated Hg concentrations are seen both in the top of the block from the hummock, and in the subsurface layers in the core recovered from the fen. Age dating of the profiles (²¹⁰Pb and ¹⁴C) is now needed to determine the changing rates of atmospheric Hg deposition. Once this has been accomplished, we hope to be able to distinguish between the increase in Hg fluxes due to anthropogenic emissions, and changes due to natural processes.

Complete 15,000 year record of mercury accumulation in a peat core from the Swiss Jura Mountains: natural variation and anthropogenic influences

Roos-Barraclough, F (Univ of Berne). Martinez-Cortizas, A (Depart. De Edafologia, Spain) Shotyk, W (Univ of Berne)

In order to be able to quantify the effect of anthropogenic emissions on global atmospheric mercury concentrations and fluxes, knowledge of the background concentration and its natural variations is required. Peat bogs can be used as archives of atmospheric mercury deposition. We have measured total mercury in a 6.5m long peat core from the ombrotrophic Etang de la Gruère bog in the Swiss Jura mountains, which was collected in 1991. The profile dates back ca 15,000 years and has therefore recorded mercury accumulation throughout much of the Late Glacial and the entire Holocene. The core was sliced frozen every centimetre from 0-67cm and every second centimetre thereafter. Mercury was measured in air-dried samples using the Leco AMA 254, an AAS-based Hg analyser. Inter-laboratory comparisons were in good agreement. ¹⁴C AMS dating of macrofossils was employed to date forty samples from deeper parts of the core. ²¹⁰Pb was determined by gamma decay counting and used to date the past 200 years of the profile. Trace elements including Br, Ti and Zr were determined by X-ray fluorescence spectroscopy. The natural background concentrations of mercury were found to be highly variable, and the effects of climate change and volcanism can clearly be seen in the deeper parts of the profile. The highest concentrations in the older (pre-anthropogenic) part of the core are even comparable to concentrations seen in the modern period. During the Younger Dryas cold period (10,000-11,000 ¹⁴C yr BP), Hg concentrations are seen to increase by a factor of three. During the Holocene, volcanic eruptions caused peaks of up to six times the background concentration. A large peak corresponding to the Little Ice Age occurs in the upper part of the core, followed by the highest concentrations of the entire profile -over ten times the natural background value- during and after the industrial revolution. Concentrations decrease considerably thereafter. Two smaller peaks, probably due to emissions from chlor-alkali plants and rubbish incinerators, are centred ca 1960 and 1979. Concentrations decrease sharply thereafter and continue to decrease steadily up to the surface of the core. Correlations between Hg, Ti and Br have been investigated to reveal a relationship between Hg and dust deposition and precipitation plus another relationship between Br and Hg deposition.

Arctic springtime depletion of mercury at Zeppelin, Svalbard

Berg, T (NILU), Sekkeseter, S (NILU, Univ of Sci and Tech, Norway), Steinnes, E (Univ of Sci and Tech., Norway), Valdal, A (Univ of Oslo) and Wibetoe, G (Univ of Oslo)

Different species of mercury (total gaseous mercury (TGM), particulate mercury (TPM), reactive gaseous mercury (RGM) and total mercury in surface snow) have been measured at the new research station at the Zeppelin mountain, Svalbard, during 2000-2001. TGM has been measured with a high time resolution automatic monitor (Tekran 2537A), particulate mercury with high volume samplers and RGM with annual denuders. During spring of 2000 there were several episodic depletions in mercury vapour concentrations correlating well with the depletions of surface ozone, during the three-month period following polar sunrise. Highly variable concentrations of the mercury vapour and ozone concentrations are seen following polar sunrise, with a pronounced tendency towards unusually low concentrations. This phenomenon was first seen at Alert in the Canadian Arctic in 1995 (Schroeder et al. 1998). Measurements of reactive gaseous mercury and particulate mercury show higher concentrations of these mercury species during the depletion period than the rest of the year. This is caused by the specific chemical and physical conditions that occur in the Arctic during the spring. Elemental mercury vapour may be oxidised and converted to more reactive forms, which have a considerably higher deposition velocity than the vapour phase species, which leads to an overall enhanced deposition flux of mercury. A new polar sunrise campaign will be carried out in 2001, measuring total gaseous mercury, reactive gaseous mercury, particulate mercury and total mercury in surface snow. A summer campaign including flux measurements of TGM (soil-air) will also be carried out during the summer of 2001. The results from these campaigns will also be presented. Acknowledgements: The staff at the Norwegian Polar Research Institute, Ny-Ålesund are gratefully acknowledged.

Springtime depletion of atmospheric mercury in Antarctica

R. Ebinghaus, H.H. Kock, Ch. Temme, A. G. Löwe, W.H. Schroeder

Unlike other heavy metals that are associated with atmospheric aerosols, mercury in ambient air predominantly exists in the gaseous elemental form. Due to its prolonged atmospheric residence time, elemental mercury vapour is distributed on a global scale. Recently, Canadian researchers have discovered that lower tropospheric total gaseous mercury levels in the Canadian Arctic are significantly depleted during the months after polar sunrise. A possible explanation may involve oxidation of elemental mercury followed by an adsorption and deposition of the oxidized form leading to an increased input of atmospheric mercury into the Arctic ecosystem. Here we present the first continuous high-time resolution measurements of total gaseous mercury in the Antarctic covering a 13 months period. We report that mercury depletion events do also occur in the Antarctic after polar sunrise. We also show that BrO radicals and ozone play a key role in the boundary layer chemistry during springtime mercury depletion events in the Antarctic troposphere.

3.4 Theme 4: Atmospheric mercury

Dry Deposition Flux Measurements of Reactive Gaseous Mercury by Relaxed Eddy Accumulation using KCl Coated Annular Denuders as Reservoirs: Experience and Results from the Arctic (Barrow, Alaska)

Michael E. Goodsite (NERI), Henrik Skov (NERI), Glen McConville (NOAA/CMDL) Steve Brooks (NOAA/ATDD) Tilden Meyers (NOAA/ATDD) Steve Lindberg (4) Matthew Landis (5) Robert K. Stevens (EPA/FLA)

Until recently it has not been possible to directly measure the flux of RGM, but in a co-operative project between National Environmental Research Institute (Denmark), US-Oak Ridge National Laboratory, the US-National Oceanic and Atmospheric Administration and the US EPA, as well as the Florida Department of Environmental Protection, a new system has been developed to measure directly the fluxes of reactive gaseous mercury (RGM). The method is based on the US-EPA method for sampling and analysis of RGM (Landis 2001, to be published) combined with conditional sampling, also called relaxed eddy accumulation (REA) (Businger and Oncley 1990). REA is a micrometeorological method designed to measure fluxes of chemical species at low time resolution on the order of a few hours (Christensen, Hummelshøj et al. 2000). The flux measurements are made by coupling a sonic anemometer to three KCl coated annular denuder tubes through a fast shifting valve. The system is optimized with respect to both micrometeorology and sampling. The flux, F is calculated with data from the sonic anemometer and RGM concentrations from two denuders:

$$F = k \cdot \sigma_V (C_{up} - C_{down})$$

where F is the flux; k is an empirical constant, σ_V is the standard deviation on the vertical wind velocity (given by the sonic anemometer integrated with the REA system) and C_{up} and C_{down} are the concentrations in the upward and downward channels respectively. It is thus very important that the concentration differences seen in the two denuders are true, and not artifacts. Therefore extreme care is taken in handling, coating, collecting on and analyzing the denuders. The average of the concentrations for upward, downward and dead band should be equal to the ambient concentration of RGM during the sampling period, so the average of these concentrations is validated by comparison with ambient concentration measurements. The flux data, with the concentration data are used to calculate the depositional velocity: The preliminary results from flux measurements made with the REA RGM flux system at Barrow, Alaska during the 2001 Arctic spring until snowmelt, indicate that the species has a deposition velocity of about $V_d = 0.5$ to 2 cm/sec during the day, very similar to the deposition velocity of HNO_3 (Seinfeld and Pandis 1998). During the night the deposition was zero. This indicates a strong connection between photochemical activity and deposition of atmospheric mercury. A second generation of the system is now developed and tested and will be used for arctic campaigns in the 2002 season.

Some transformation processes of mercury in natural waters

Katarina Gårdfeldt, Jonas Sommar, Dan Strömberg and Oliver Lindqvist (Göteborg University)

The relative importance of some aqueous phase transformation processes due to the biogeochemical cycling of mercury has been under investigation in recent and on-going studies. The reemission of mercury from water surfaces has been estimated at one fresh-water site in Sweden and three seawater sites in Europe; Skagerrak at the fjord Gullmaren, the Atlantic Ocean at the Irish west coast and the open basin of the Mediterranean Sea. Field observations indicate that dissolved gaseous mercury is formed from photolytically induced processes.

In the laboratory we have performed reaction studies on several transformation processes relevant to hydro meteors, sea- and terrestrial-waters. These include the oxidation of elemental mercury (Hg^0) and monomethylmercury (CH_3Hg^+) by OH radicals, photolytical degradation of CH_3Hg^+ , and abiotic formation of CH_3Hg^+ . The temperature dependence of the partition coefficient for Hg^0 between air and water has also been under investigation.

Field and laboratory studies on the formation and behaviour of oxidised gaseous mercury in air

Jonas Sommar, Katarina Gårdfeldt, Dan Strömberg, and Oliver Lindqvist (Göteborg University)

The atmospheric elemental state of mercury is unique to entirely (>95%) the atmospheric composition of a metal. It is influenced by a complex source distribution including recycling of anthropogenically mobilised mercury and multiple simultaneous removal processes. The presence of gas-to-particle phase conversion in ambient air preceded by gas-phase oxidation has been inferred. Oxidised and particulate-phase mercury is readily deposited. In the wet aerosol, a reversible redox-balance appears to be present making it a possible source of Hg^0 . Phenomenologically, the depletion of the reduced gaseous form in the Arctic boundary layer during spring events and in the tropopause has been attributed to oxidation by oxygenated species. Being slow at mid-latitudes, such processes may potentially be traced by following the transient fractions formed rather than the bulk of airborne mercury.

In this contribution, the general features (mixing ratios, seasonal variations, spatial and temporal variations etc.) of ~280 field observations of oxidised gaseous mercury (“RGM”) in ambient, urban and industrialised air will be presented. Plausible sources and sinks of RGM in ambient air will be discussed. In addition, some quantitative and qualitative results from laboratory studies of relevant chemical kinetics will be given.

Distribution of TPM in Northern Europe

Wängberg, I (IVL); Munthe, J (IVL); Gårdfeldt, K (Göteborg Univ); Sommar, J(Göteborg Univ); Iverfeldt, Å (IVL); and Ebinghaus, R (GKSS)

A new sampling technique for measuring Total Particulate Mercury (TPM) has been tested and utilised in field campaigns within the MOE project (Mercury over Europe). The new sampling method is presented and measurement results are reported. The particle sampler, originally developed by Julia Lu at al., 1998, consist of quartz glass filter housed in a quartz glass tube. The traps are analysed by pyrolysis and CVAFS detection in a similar manner as Au-traps. The new technique gives excellent results in comparison to sampling on Teflon filters and allows low detection limit and high reproducibility. Mercury species in air were measured at five sites in Northwest Europe during five measurements campaigns each of two weeks duration. Trajectory analysis of events where high concentrations of TPM simultaneously were observed at sites in North Europe indicate source areas in Central Europe and provide evidence of transport of mercury on particles on a regional scale. Lu, J. Y., Schroeder, W. H., Berg, T. Munthe, J., Schneeberger, D., Schaedlich, F., 1998., Analytical Chemistry 70, 2403-2408.

Reactive Gaseous Mercury (RGM). Measurements in Denmark

Michael Roar Bo Larsen, Catherine Laurent, Henrik Skov and Michael E. Goodsite (NERI)

Reactive Gaseous Mercury (RGM), is of unknown composition. However it is currently accepted that RGM dominate the total Hg depositional flux, due to its higher surface reactivity and water solubility than gaseous elemental mercury (GEM). The aim of this presentation is to find and determine the concentration of RGM in the atmosphere at different locations (DK, USA and Arctic). Furthermore RGM measurements will be carried out together with a Relaxed eddy Accumulation (REA) system –so that flux measurements can be performed. RGM was sampled on Annular Quartz Denuders (from URG) coated with KCl and analysed by a Tekran Model 2537A Mercury Vapour Analyser. The method used is an US-EPA method kindly provided by Dr. Matthew Landis.

In the 2 months since launch of the project, a few measurements have been obtained. The measurements are 2-hour average concentrations from 26 July to 6 September 2001, of RGM. A detection Limit of 2.18 pg/m^3 has been determined ($3 \cdot \text{std. dev. of field-blanks}$). The measurements were in the range $7\text{-}13 \text{ pg/m}^3$ in July in warm ($\sim 25^\circ\text{C}$) and Sunny weather and below detection limit in September at colder weather (~ 15 degree) with clouds and showers. 2 measured nighttime concentrations were also below detection limit.

Our provisionally results are comparable with data from Canada Pristine area at ELA, where mean daytime concentrations of 2 pg/m^3 (4-hour average concentrations) during the day and zero during the night (Lindberg Private communication 2001) were measured.

In the future we will determine our precision (measurements done by Michael E. Goodsite in Walker Branch Watershed indicate a precision around 20 % as 2 times standard deviation on replicates). Work will be carried out in order to lower the blank values in order to improve the detection limit. The time average of future measurements will be increased from 2-hour to at least 4-hour average concentrations. A continuation of the measurements of RGM concentration will be done at NERI, further to seek out a seasonal and daily variation. Flux measurements will be carried out at Lille Valby Station, Barrow Alaska and at Station Nord, Northeast Greenland. Interpretation of data will be performed and for example they will be analysed by comparison with meteorology, concentrations of other pollutants as e.g. O_3 , SO_2 and with results from the Danish Eulerian hemispheric model (DEHM).

Measurements and source-receptor analysis of elemental mercury in the Faroe Islands

Maria C. Petersen (NERI), H.Skov (NERI), M.E.Goodsite (NERI), J.Christensen (NERI), C.A.Skjøth (NERI), G.Geernaert (NERI), P.Løfstrøm (NERI), Ole Hertel (NERI), and J.Olsen (Food and Environmental Agency, Faroe Islands)

Gaseous Elemental Mercury Hg⁰, has been measured on the Faroe Islands from May, 2000 through March, 2001. The measured data have been analysed together with basic meteorology, and the Schoeberl's isentropic trajectory model and the DEHM model were subsequently used to determine the most likely source regions which are associated with the measured concentrations. In the air concentration time series collected on the Faroe Islands, there were several periods of unexpectedly high mercury concentrations. The high concentrations were attributed to several potential causes: local sources; and long range transport. After a detailed analysis, it was determined that local sources were not responsible for the elevated levels. On the other hand, use of the trajectory models gave good evidence that the high levels in the mercury concentration time series were caused by long-range transport, in particular transport from Iceland with peaking seen after the volcanic eruption of Hekla in February-March 2000, and also transport from Europe during other periods.

Modelling of Mercury with the Danish Eulerian Hemispheric Model

Jesper Christensen (NERI)

A 3-d mercury model is in the progress of development. Currently the model is a preliminary model based on the Danish Eulerian Hemispheric model, which in the original version have been used to study the transport of SO₂, SO₄²⁻ and Pb into the Arctic (see Christensen, 1997). The horizontal space of the model is defined on a regular 96x96 grid that covers most of the Northern Hemisphere with a grid-resolution of 150 km at 60°N. Meteorological data are obtained from the European Centre for Medium-range Weather Forecasts (ECMWF) on a 2.5°x2.5° grid with a time resolution of 12 hours, which are used as input to the MM5 mesoscale modelling system, which produce the final meteorological input for the DEHM model. The whole system includes also 2-way nesting capabilities, so it is possible to do finer (150 km → 50 km → 16.67 km, etc) model calculations over e.g. the Arctic Ocean or Greenland. In the current version the emissions of anthropogenic Mercury are based on the global GEIA inventory of Mercury emissions for 1990 on a 1°x1° grid (Pacyna, CGEIC). The chemistry is based on the scheme from the GKSS model (see Petersen et al, 1998). Some results from the model system will be presented with emphasizing on the simulation of the mercury depletion in the Arctic during the Polar Sunrise.

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Mercury Modelling: Progress and Problems.

Gerhard Petersen (GKSS Research Center)

A variety of modelling techniques have been developed for exploration of atmospheric mercury processes. These include relative simple mass balance models that examine the pooling and exchange of mercury species between various environmental compartments as well as complex deterministic atmospheric dispersion models attempting to simulate the transport and transformation of mercury over domains of hundreds to thousands of kilometers.

The recently signed UN-ECE protocol on reducing the atmospheric transboundary transport of mercury in Europe have intensified the scientific interest in relating the spatial and temporal information on the release of mercury into the atmosphere to the pattern of atmospheric deposition fluxes to various ecosystems by means of long-range transport modelling on regional European scales. In this context, efforts have been made to simulate the atmospheric transport and fate of mercury and to derive estimates of ambient concentrations and dry and wet deposition fluxes of mercury over Europe through either relative simple Lagrangian formulations or Eulerian approaches employing extensive gas- and aqueous phase chemical mechanisms and explicitly tracking numerous species concentrations.

Overall, the development level of mercury models is such, that they can be considered as an essential step towards decisive assessments of the sources or source types most responsible for mercury contamination in Europe through the atmospheric pathway. Although the model incorporates significant progress in the understanding of mercury atmospheric processes our knowledge is far from complete. Models have to be developed further as additional information on emission speciation, atmospheric chemistry, air-soil exchange and vertical profiles of time dependent boundary conditions becomes available. Similarly, very little is known about other issues such as the role of methyl mercury compounds on observed deposition pattern. As research on these issues matures and more data exist, an explicit treatment of methyl mercury processes in European scale models is one of the most important next logical steps.

3.5 Theme 5: Mercury in the Nordic countries: current status and future research needs

Modelling and mapping ecosystem susceptibility to atmospheric mercury pollution: increasing effects on soils and lakes?

Markus Meili (Stockholm University)

Atmospheric Hg deposition is considered a threat to lake fish consumers and soil microflora in the boreal forest zone. Hg deposition has increased 2- to >20-fold over the last centuries due to anthropogenic emissions and subsequent dispersal on different scales. Based on recent atmospheric modelling (EMEP), the deposition of Hg from local, regional, and global sources can now be quantified for >100 regions in Sweden, where Hg levels in fish exceed health advisory guidelines in tens of thousands of lakes. The issue is accentuated by the fact that present Hg levels in most soils and lakes are still far from equilibrium with atmospheric Hg pollution. This is evident not only from mass balance calculations, but also from the delayed response of surface waters to the pollution pulse of the past decades. Hg concentrations in fish are therefore likely to increase further during several centuries and to reach levels much higher than the current ones. The increase will be particularly pronounced in humic lakes, where Hg concentrations already today are most elevated, and where most Hg is supplied by soil runoff in highly bioavailable form but substantially delayed. In many humic lakes, even the natural Hg levels in predatory fish are estimated to touch the common limit of 0.5 mg/kg fresh weight. In clearwater lakes on the other hand, which respond to environmental changes more rapidly (years or decades) and which today show a similar degree of contamination as the humic lakes, natural Hg levels are estimated to be often less than 0.1 mg/kg. The maximum tolerable Hg concentration in precipitation to (1) avoid a further increase of Hg in Swedish soils and (2) to keep future Hg levels in predatory fish below 0.5 mg/kg in most lakes is estimated to be similar to the pre-industrial level. Present efforts to produce maps of lake susceptibility to Hg pollution based on readily available information show substantial regional differences and also suggest that high Hg levels in fish previously attributed to local Hg emissions may instead represent an issue of susceptibility to global Hg emissions.

Microbial effects of Hg in forest soils

Lage Bringmark (Swedish University of Agricultural Sciences)

The humus layer. Upper organic soil layers are the prime location where adverse effects of Hg and other metals on forest biota can be expected. This is due to very effective retention of deposited airborne Hg in the organic material combined with an abundance of important fungi, bacteria and other organisms in the very same layers. Hg contents in forest humus layers are about 0.2 mg/kg in Northern Sweden, 0.3 in Southern Sweden and can be up to 0.8 mg/kg in Central Europe. The gradient is the result of long-range air pollution. However, apart from the Nordic countries European data on soil Hg contents are scarce.

Studies of field situations. We have asked the question whether biological effects can be detected at the rather low levels of Hg found in field situations affected by long-range pollution. In a recently terminated Swedish EPA project we followed two lines of investigating low-level effects; one analysis of spatial patterns in field plots and another with added Hg in long-term laboratory experiments. Our biological variable in both cases was a very simple respiration measurement at standard temperature (20°C) and water content. In the field approach we made use of the fact that Hg as well as other metals are very unevenly intercepted in tree crowns. The deposition on the soil surface by throughfall or litterfall is accordingly uneven. This offers possibility to look for spatial relationships (negative) between metal contents and biological activity in the humus layer. Indeed,

such relations between Hg and base respiration were found regionally in South Sweden in sites situated towards south-west (relatively high pollution), while they were absent in north-eastern sites (low pollution). However, as Pb and Hg are also correlated internally within sites observed effects were attributed to a combination of Hg and Pb. In fact, regionally in South Sweden the gradient of lead is more pronounced than that for Hg. The sites showing significant correlations between Hg and respiration had >0.25 mg/kg of Hg.

Long-term experiments. Due to the co-occurrence of many factors, man-made as well as natural, in field situations we had to rely on experiments to isolate Hg effects. We found that low doses of Hg added to humus layer samples did not result in negative effects on respiration in the beginning. Even stimulation occurred. Two months had to elapse before negative effects of Hg developed and a year was needed for a full development. This is contrary to the common notion that metals are becoming less dangerous with time due to developing tolerance and immobilisation, but effects faded away after fifteen months even in our experiment. Added Hg doses were very small; 0.11, 0.26 and 1.0 mg/kg on top of an original content of 0.36 mg/kg. Fresh plant litter was added a few times during the long experiment time to keep the microbes going. 10% reduction of cumulated decomposer activity during the whole experiment was estimated for 2-3 mg/kg of Hg (added+original) while a 5% effect can be calculated for 0.6 mg/kg. Considering that the South Swedish humus sample used for the experiment already was polluted to some degree, effect levels could probably be pushed down even further using a less polluted sample. At least the recorded 5% effect level is rather close to South Swedish concentrations and indeed within ranges found in humus layers of Central Europe.

Comparison with other investigations. Among the few investigations of soil microbial effects of Hg found in literature there are four reporting effects at 0.07-0.13 mg Hg/kg. Our effect levels are higher but they are the only ones reported for humus layers. Humus layers with 90 % organic content cannot be directly compared with soils having only 2-4% organic content. Expressing Hg per gram of carbon our effect levels are considerably lower than the others reported. But different types of organic material have different sensitivity for biological effects making comparisons difficult. Research on the influence of age and properties of the organic material is needed.

Critical levels. A task of mapping critical loads of Pb, Cd and Hg in Europe has been instigated under the Convention on Long-range Transboundary Air Pollution, CLRTAP. Critical limits for soils are to be defined as starting points for mass balance calculations. An expert group on critical limits has been formed after a UN-ECE workshop in Bratislava in 2000, lead by the German EPA. It was decided to assess bioavailable metal fractions to relate them to biological effects. This is considered to be more sensitive and generally valid for different soil types than total metal contents. The expert group considers Hg to be a especially great scientific problem to be postponed, but according to Swedish opinion it is quite feasible and urgent to conduct the critical loads exercise for Hg as well.

Bringmark, L., and Bringmark, E. (in publ). Soil respiration in relation to small-scale patterns of lead and

mercury in moor layers of Southern Swedish forest sites. *Water Air and Soil Pollution*.

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Impact of forestry practices on mercury and methylmercury output in boreal forests

Porvari P.*, Verta M.*, Munthe J.† & Haapanen, M.*

* SYKE Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland

† IVL Swedish Environmental Research Institute, P.O. Box 47086, SE 402 58, Gothenburg, Sweden

We observed a significant increase in the export of total mercury (TotHg) and methyl mercury (MeHg) from a spruce forest catchment in the boreal zone after clear cutting. Here we show that the mercury load due to clear cutting, combined with site preparation prior to planting, may act as a significant source of mercury for forest lakes.

We studied the effects of clear cutting, combined with site preparation (scarification) and regeneration, on the total and methyl mercury concentrations in the outflow stream and on the output fluxes in a small Norway spruce forest catchment (0.071 km²) situated in southern Finland (61°01'N, 24°45'E). The TotHg and MeHg concentrations and fluxes were measured during a six-year period (1995 – 2000). The catchment was clear cut in 1997. During the three years after clear cutting, the annual TotHg load (2.0-5.3 g km⁻² a⁻¹) and MeHg load (0.11-0.16 g km⁻² a⁻¹) were significantly higher than during the preceding two-year calibration period (0.80-0.97 and 0.011-0.036 g km⁻² a⁻¹, respectively). The monthly TotHg and MeHg loads were also significantly (Wilcoxon test, p<0.005) higher after clear cutting (Fig. 1).

The TotHg (8.0±4.0 ng l⁻¹) and MeHg (0.22±0.37 ng l⁻¹) concentrations and the output fluxes before silvicultural treatment were of the same level as in studies carried out in forest catchments with upland and wetland sites in Sweden^{1,2}, Canada³ and the USA^{4,5}. The changed hydrological conditions, i.e. decreased canopy water retention capacity and evapotranspiration and increased water discharge, had a major impact on the TotHg and MeHg output, especially during the first year after clear cutting. In addition to the elevated mercury loads, the TotHg (14±6.2 ng l⁻¹) and MeHg (0.61±0.70 ng l⁻¹) concentrations also increased. The MeHg concentrations rose significantly only during the second and third year after clear cutting. This is a strong indication not only of increased MeHg leaching, but also of higher Hg methylation activity in the catchment. Total organic carbon (TOC) increased significantly only during the first year, and then returned to the same level as during the calibration period. As a result, TOC cannot explain the increased outflow of MeHg.

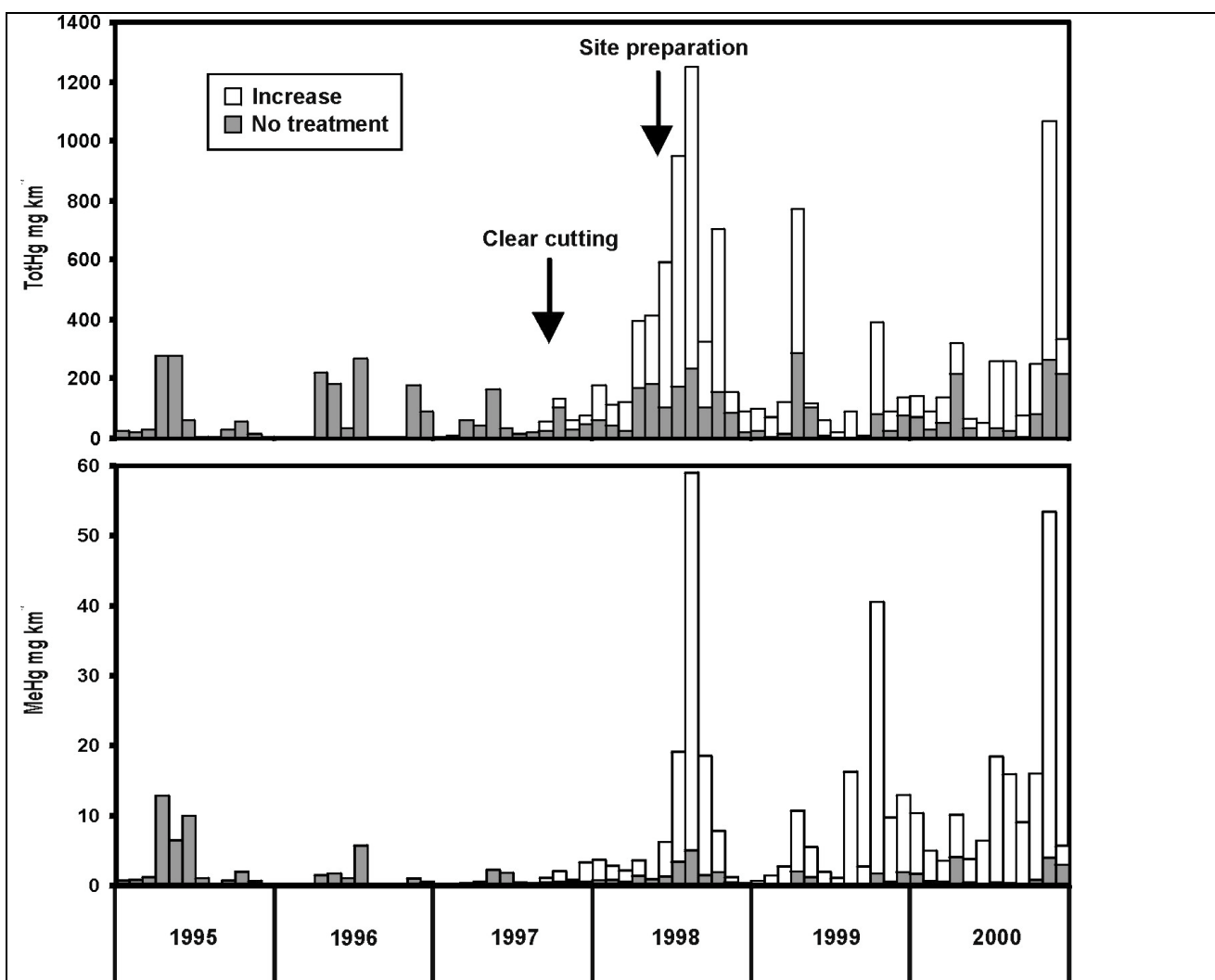


Figure 1. The monthly total mercury (TotHg) and methyl mercury (MeHg) loads (mg km^{-2}) from the spruce forest catchment. Closed bars represent the calculated Hg load without silvicultural treatment and open bars indicate the measured increase in the Hg load. Regression was calculated for the pre-treatment period using simultaneous monthly load values from the silvicultural treatment and control area. The regression equations were used to calculate the predicted load values without the silvicultural measures for the post-treatment period. The difference between the measured and predicted values was used to indicate the change caused by the silvicultural treatment.

In boreal forests, timber harvesting is usually carried out as regeneration felling or thinnings. Regeneration felling in boreal spruce stand normally takes the form of clear cutting. The store of Hg in the soil and vegetation has increased due to increased anthropogenic emissions of Hg into the atmosphere and the subsequent deposition of Hg in northern hemisphere during the late 1900s^{6,7}. The leaching of Hg from logged boreal forests may therefore result in a significant increase in the TotHg and MeHg load from catchments to lakes for a number of years, subsequently leading to elevated MeHg concentrations in fish. It is interesting to note that the maximum MeHg concentrations were recorded in the second and third year after logging, thus suggesting that this silvicultural measure has a longer lasting effect on the output of MeHg than on TotHg. Boreal forests cover about a land area of 1400 Mha, or 10%, of the earth's terrestrial surface^{8,9}. The significance of Hg leaching from watershed to lakes, as well as the time scale of increased Hg exports from logged forest catchments, should be studied in more detail in all the boreal forest regions.

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3.6 Appendix 1 List of participants

List of participants in the MEPOP/NMR/AMAP Workshop

	Deltagere	Institution	e-mail	Country
1.	Asman, Willem	NERI, Department of Atmospheric Environment	wa@dmu.dk	Denmark
2.	Bartnicki, Jerzy	Norwegian Meteorological Institute (DNMI)	fajb@dnmi.no	Norway
3.	Berg, Torunn	Norwegian Institute for Air Research (NILU)	torunn.berg@nilu.no	Norway
4.	Breivik, Knut	Norwegian Institute for Air Research (NILU)	kbr@nilu.no	Norway
5.	Bringmark, Lage	Sveriges Lantbruksuniversitet	lage.bringmark@ma.slu.se	Sweden
6.	Brorström-Lundén, Eva	IVL, Swedish Environmental Research Institute	eva.bl@ivl.se	Sweden
7.	Christensen, Jesper	NERI, Department of Atmospheric Environment	jc@dmu.dk	Denmark
8.	Duyzer, J.H.	TNO	j.h.duyzer@mep.tno.nl	Netherlands
9.	Ebinghaus, Ralf	GKSS Research Centre	ralf.ebinghaus@gkss.de	Germany
10.	Fjeld, Erik	Norwegian Institute for Water Research (NIVA)	eirik.fjeld@niva.no	Norway
11.	Geernaert, Gerald L.	NERI, Department of Atmospheric Environment	glg@dmu.dk	Denmark
12.	Givelet, Nicolas	University of Bern	fiona.roos@geo.unibe.ch	Switzerland
13.	Glasius, Marianne	NERI, Department of Environmental Chemistry	mag@dmu.dk	Denmark
14.	Goodsite, Michael E.	NERI, Department of Atmospheric Environment	mgo@dmu.dk	Denmark
15.	Gårdfeldt, Katarina	Göteborg Universitet	sommar@inoc.chalmers.se	Sweden
16.	Havnø, Herdis Palsdottir	Miljøstyrelsen (Danish EPA)	hpa@mst.dk	Denmark
17.	Heidam, Niels Zeuthen	NERI, Department of Atmospheric Environment	nzh@dmu.dk	Denmark

18.	Hjæresen, Christina	NERI, Department of Environmental Chemistry	chj@dmu.dk	Denmark
19.	Holoubek, Ivan	RECETOX TOCOEN & Associates	holoubek@chemi.mu.cz	Czech Republic
20.	Hoydal, Katrin	Miljø- og Levnedsmiddelstyrelsen (Food and Environ. Agency)	katrinh@hfs.fo	Faroe Islands
21.	Johansen, Kurt	Univ of Southern Denmark	kkj@chem.sdu.dk	Denmark
22.	Johansen, Poul	NERI, Department of Arctic Environment	poj@dmu.dk	Denmark
23.	Johansson, Kjell	Swedish EPA	kjell.johansson@ma.slu.se	Sweden
24.	Knudsen, Kristina	University of Odense	kkn@chem.sdu.dk	Denmark
25.	Kvietkus, Kestutis	Institute of Physics, Atmospheric Pollution Research Lab.	kvietkus@ktl.mii.lt	Lithuania
26.	Larsen, Michael Roar Bo	NERI, Department of Atmospheric Environment	mrl@dmu.dk	Denmark
27.	Laurent, Catherine	NERI, Department of Atmospheric Environment	cla@dmu.dk	Denmark
28.	Leppänen, Sirkka	Finnish Meteorological Institute (FMI)	sirkka.leppanen@fmi.fi	Finland
29.	Lerche, Dorte	National Environmental Research Institute, Department of Environmental Chemistry	dortelerche@hotmail.com	Denmark
30.	Lohse, Christian	Univ. of Southern Denmark	lohdr@chem.sdu.dk	Denmark
31.	McLachlan, Michael	Baltic Sea Research Institute	michael.mclachlan@io-warnemuende.de	Germany
32.	Meili, Markus	University of Stockholm	markus.meili@it.m.su.se	Sweden
33.	Milukaite, Audrone-Regina		ulevicv@ktl.mii.lt	Lithuania
34.	Munthe, John	IVL, Swedish Environmental Research Institute	john.munthe@ivl.se	Sweden
35.	Møller, Per	NERI, Department of Arctic Environment	pem@dmu.dk	Denmark
36.	Nielsen, Ole John	University of Copenhagen	ojn@kiku.dk	Denmark
37.	Palm, Anna	IVL, Swedish Environmental		Sweden

		Research Institute		
38.	Petersen, Gerhard	GKKS – Research Centre Institute for Coastal Research System Analysis and Modelling	gerhard.petersen@gkss.de	Germany
39.	Petersen, Maria C.	NERI, Department of Atmospheric Environment	mcp@dmu.dk	Denmark
40.	Porvari, Petri	Finnish Environment Institute		Finland
41.	Prevedouros, Costas	University of Lancaster	a.sweetman@lancaster.ac.uk	United Kingdom
42.	Riget, Frank F.	NERI, Dept. of Arctic Environment	ffr@dmu.dk	Denmark
43.	Rognerud, Sigurd	Norwegian Institute for Water Research (NIVA)		Norway
44.	Roos, Fiona	University of Bern	fiona.roos@geo.unibe.ch	Switzerland
45.	Shatalov, Victor	MSC East	viktor.shatalov@msceast.org	Russia
46.	Skjøth, Carsten A.	NERI, Department of Atmospheric Environment	cas@dmu.dk	Denmark
47.	Skov, Henrik	NERI, Department of Atmospheric Environment	hsk@dmu.dk	Denmark
48.	Skaarup, Jesper	COWI	jss@cowi.dk	Denmark
49.	Sommar, Jonas	Göteborg University	sommar@inoc.chalmers.se	Sweden
50.	Sonne-Hansen, Christian	NERI, Dept. of Arctic Environment	csh@dmu.dk	Denmark
51.	Svensson, Margareta	Sydkraft Sabak AB	margareta.svensson@nat.oru.se	Sweden
52.	Sweetman, Andrew	Lancaster University	a.sweetman@lancaster.ac.uk	United Kingdom
53.	Sørensen, Tina	Univ of Southern Denmark, Chem Inst.	tso@chem.sdu.dk	Denmark
54.	Verta, Matti	Finnish Environment Institute	matti.verta@vyh.fi	Finland
55.	Wängberg, I	IVL, Swedish Environmental Research Institute	ingvar.wangberg@ivl.se	Sweden
56.	Zetsch, Cornelius	Fraunhofer Institut für Toxikologie und Aerosolforschung	zetsch@ita.fhg.de	Germany
57.	Aagaard, Alf	Danish EPA	aaa@mst.dk	Denmark

3.7 APPENDIX 2 Workshop programme

MEPOP – NMR – AMAP Mercury and POP Workshop – Sept 10-12, 2001, Roskilde, Denmark

Location: The Niels Bohr Auditorium, Risø National Laboratory, Roskilde, Denmark

Program

Monday September 10		
09.00	Registration and coffe	
10.00	Welcome and John Munthe/Gary Geernaert Workshop Introduction	
Theme 1: POPs and transport and uptake processes, Chairman: J.H. Duyzer		
10.30	Duyzer/Brorström- Lundén/Holoubek	POP overview
10.50	Audrone Milukaite	The Influence of Air Temperature, Solar Radiation and Ozone on Benzo(a)pyrene Changes in Atmosphere
11.10	Cornelius Zetzsch	OH-Exposure of POPs – Employing Filter Samples of Coated Aerosol
11.30	Henrik Kylin, Anna Hellström	Uptake of Airborne Persistent Organic Pollutants in Pine Needles: A Reversal of Global Fractionation ?
11.50	Lunch	
3.7.1.1 Theme 2: POPs in the European atmosphere, Chairman: Ivan Holoubek		
13.00	Eva Brorström- Lundén	Atmospheric Concentrations and Deposition Fluxes of Persistent Organic Pollutants (POPs) at the Swedish West Coast and in northern Fennoscandia: 1989-1999
13.20	J.H. Duyzer	Monitoring of POP concentrations and depositions in the Netherlands
13.40	Michael McLachlan	Quantifying air/sea gas exchange of POPs
14.00	Andrew Sweetman	Modelling the Enviromental Distribution and Fate of Persistent Organic Pollutants on a European Scale
14.20-14.40	Anna Palm	Assessing the environmental fate of chemicals of emerging concern: a case study of the polybrominated diphenyl ethers.
14.40	Coffe break	
15.00	Viktor Shatalov	POP modelling within UN ECE CLRTAP
15.20	J.H. Duyzer	Eurotrac synthesis and future
15.40	Ivan Holoubek	POPs in UNEP

16.00		Discussion
17.30		Close
19.00 - ?		Workshop Dinner
Tuesday September 11		
Theme 3: Arctic research on Hg and POPs, Chair: Gary Geernaert		
09.00	Knut Breivik	Current status of global emission inventories for Hg and PCB
09.20	Frank F. Riget, and Per Møller	Overview of AMAP monitoring Studies of Mercury and POP's in Greenland Biota
09.40	Poul Johansen	Human Exposure to Mercury and POP's from the Greenland Diet
10.00	Christian Sonne-Hansen	Contaminants in the Greenland Sea Polar Bear. Anatomical Studies regarding contaminant induced pathological and histopathological/immunohistochemical Changes in Skulls and Gonads/Adrenals
10.20	Michael Evan Goodsite	The Post-Industrial Increase in the Atmospheric Background Level of Mercury, As Seen in an Ombrogenic Peat Core from the Faroe Islands
10.40	Coffe break	
11.00	Nicolas Givelet	Long-term Record of Atmospheric Hg Accumulation in the high Arctic from Peat Deposits on Bathurst Island, Nunavut, Canada
11.20	Fiona Roos	Complete 15,000-Year Record of Mercury accumulation in a Peat Core from the Swiss Jura Mountains: Natural Variation and Anthropogenic Influences
11.40	Torunn Berg	Arctic Springtime Depletion of Mercury at Zeppelin, Svalbard
12.00	Ralf Ebinghaus	Springtime Depletion of Atmospheric Mercury in Antarctica
12.20-13.30	Lunch	
Theme 4: Atmospheric Hg. Chairman; John Munthe *		
13.30	Michael Evan Goodsite	Dry Deposition Flux Measurements of Reactive Gaseous Mercury by relaxed Eddy Accumulation using KCI Coated Annular Denuders as Reservoirs: Experience and Results from the Arctic(Barrow, Alaska)
13.50	Katarina Gårdfeldt	Some Transformation Processes of Mercury in Natural Waters
14.10	Jonas Sommar	Some tranformation processes of mercury in the gas phase
14.30	Ingvar Wängberg	Distribution of TPM in Northern Europe
14.50	Michael Larsen	RGM measurements in Denmark
15.10	Coffe break	
15.30	Maria Petersen	Measurements and source-receptor analysis of elemental mercury in the Faroe Islands
15.50	Jesper Christensen	Modelling of Mercury with the Danish Eulerian Hemispheric Model

16.10	Gerhard Petersen	Mercury Modelling: Progress and Problems
16.30	Discussion	
17.30	Close	

***A parallel discussion on POPs research will be organised tuesday afternoon**

Wednesday September 12		
<i>Theme 5: Mercury in the Nordic countries: current status and future research needs, Chairman: Matti Verta</i>		
09.00	Matti Vertta	Overview - mercury in terrestrial and aquatic ecosystems
09.20	John Munthe	Overview - atmospheric mercury
09.40	Kjell Johansson	CLRTAP on Hg - Current status
10.00	John Munthe	EU Air Quality Directive on Hg/UNEP activities
10.20	Markus Meili	Modelling and Mapping Ecosystem Susceptibility to Atmospheric Mercury Pollution: increasing Effects on Soils and Lakes
10.40	Lage Bringmark	Biological effects of mercury in forest soils
11.00	Coffe break	
11.20	Discussions on research needs and priorities	
	<i>Topics</i>	
	1. What are the main limitations of models for assessment and policy support?	
	2. Research needs: Emissions, speciation, fluxes and effects	
12.20	Lunch	
13.30	Continued discussions	
15.00	Report from discussions	
15.40	Summing up	
16.00	Closing of workshop	