

# WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



**No. 136**

## **WMO/EMEP/UNEP WORKSHOP ON MODELLING OF ATMOSPHERIC TRANSPORT AND DEPOSITION OF PERSISTENT ORGANIC POLLUTANTS AND HEAVY METALS**

**(Volume I)**

**organized and sponsored by**

**Meteorological Synthesizing Centre East of EMEP and  
World Meteorological Organization  
in co-operation with the United Nations Environment Programme**

**(Geneva, Switzerland, 16-19 November 1999)**



**A contribution to the Convention on Long-range Transboundary Air Pollution**

## 1. INTRODUCTION

The Workshop on Modelling of Atmospheric Transport and Deposition of Persistent Organic Pollutants and Heavy Metals held in Geneva from 16 to 19 November 1999 was convened in accordance with the decision of the Executive Body for the Convention on the Long-Range Transboundary Air Pollution (ECE/EB.AIR/59).

Workshop was organized and sponsored by the World Meteorological Organization (WMO) and the Meteorological Synthesizing Centre East (MSC-E) of EMEP in cooperation with the United Nations Environment Programme (UNEP).

The main objectives of the Workshop were to evaluate the state of knowledge and the status of work with regard to emissions, measurements and modelling of heavy metals (HMs) and persistent organic pollutants (POPs); to promote the development of models of long-range atmospheric transport and deposition, parametrization of physical-chemical transformation processes, evaluation of exchange between various environmental compartments and of risk assessment; to identify the most essential issues in these fields accounting for the decisions of the WMO/EMEP Workshop on the assessment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development held in September 1996 in Moscow, Russia (see EB.AIR/GE.1/1997/6 and WMO/TD No. 806); to make recommendations on concrete actions in order to promote the implementation and compliance with the obligations of new Protocols on HMs and POPs to the Convention on Long-Range Transboundary Air Pollution of the UN Economic Commission for Europe as well as to contribute to international efforts in developing an international legally binding instrument on POPs initiated by UNEP.

The workshop in Geneva was attended by 68 experts from Austria, Republic of Belarus, Bulgaria, Canada, Chilli, Czech Republic, Estonia, Finland, France, Germany, Hungary, Italy, Republic of Korea, Latvia, Lithuania, Malaysia, the Netherlands, Norway, Russia, Slovak Republic, Spain, Sweden, Switzerland, United Kingdom, USA, CCC, MSC-E and MSC-W of EMEP and by representatives of WMO, UNEP, HELCOM, AMAP, EUROTRAC, EMEP, UN ECE Secretariat and Working Group on Effects. The list of participants is given in Annex A.

The Workshop programme (see Annex B) was prepared by the scientific committee involving: Dr. Sergey Dutchak (EMEP/MSC-E, Russia), Dr. John Munthe (IVL, Sweden), Prof. Jozef Pacyna (NILU, Norway), Prof. Gerhard Petersen (GKSS, Germany), Dr. Addo van Pul (RIVM, the Netherlands), Dr. Alexey Ryaboshapko (EMEP/MSC- E, Russia), Prof. Victor Shatalov (EMEP/MSC-E, Russia).

On the request of the Scientific Committee background documents were prepared by:

*Josef Pacyna and Knut Breivik* (NILU, Norway) on assessment of HM and POP emission;

*John Munthe, Eva Brorstrom-Lunden* (IVL, Sweden) and *Torunn Berg* (NILU, Norway) on HM and POP measurements;

*Alexey Ryaboshapko* (EMEP/MSC-E, Russia), *Gerhard Petersen* (GKSS, Germany), *John Munthe* (IVL, Sweden) and *Ilya Ilyin* (EMEP/MAC-E, Russia) on HM modelling; *Victor Shatalov, Alexey Gusev* (EMEP/MSC-E, Russia) and *Frank Wania* (University of Toronto, Canada) on POP modelling and by *Alexey Gusev* (EMEP/MSC-E) on HM model intercomparison.

Papers were presented in plenary and poster sessions and working groups were formed to discuss the following topics:

- Emissions - the state of the methodological base - EMEP/CORINAIR Emission Inventory Guidebook, official emission data, expert estimates, particle size spectrum, gas-aerosol partitioning, spatial distribution, seasonal variations, historical trends, verification procedures and uncertainties;
- Measurements - review of available measurement data, geographical scope, sampling protocols, concentration in air and precipitation, estimates of gas-aerosol partitioning, concentrations in sea, soil and vegetation; national and international programmes of POPs and HMs measurements in the Northern Hemisphere, background concentrations and historical trends, quality assurance and uncertainties;
- Modelling - progress and problems in multicompartiment approach to modelling of transport of POPs (lindane, benzo(a)pyrene, polychlorinated biphenyls, hexachlorobenzene, dioxins/furans) and HMs (cadmium, lead and mercury) in the EMEP region, physical-chemical processes determining POPs and HMs long-range transport, exchange processes between different environmental compartments, peculiarity of physical-chemical properties of selected POPs, regional, hemispheric and global modelling, intercomparison procedures, uncertainties, future priorities;
- Cooperation - strengthening of scientific collaboration between EMEP and various international organizations and conventions (WMO, UNEP, HELCOM, OSPAR, AMAP, EUROTRAC, etc), sharing of information so as to avoid unnecessary duplication of their efforts.

There were made thirty poster presentations at the Workshop which are included in Volume II.

## **2. OPENING OF THE MEETING, NOMINATION OF THE WORKSHOP OFFICERS, ADOPTION OF THE AGENDA**

The Workshop was opened by Mr M. Jarraud, Deputy Secretary-General of the World Meteorological Organization (WMO) who welcomed the workshop participants and briefed them on the WMO activities relevant to the workshop subject and implemented under the WMO Global Atmosphere Watch programme. He also noted the active role of WMO in initiation and implementation of EMEP in particular as related to modelling of long-range atmospheric transport and deposition of pollutants, and close nowadays co-operation between WMO and EMEP both in modelling and measurements including quality assurance and data management. Finally, he expressed hope that modern facilities available for the meeting in the new WMO building would further the workshop fruitful work and success. On behalf of the Workshop Organizing Committee Mr. A. Soudine (WMO) proposed that Mr. S. Dutchak (EMEP/MSC-E), Mr. G. Petersen (GKSS, Germany) and Mr. J. Schneider (EMEP Bureau) be nominated the chairmen for the plenary sessions of the Workshop. This proposal was adopted by the participants of the meeting. It was agreed that working groups sessions on emissions, measurements, HM modelling, POP modelling and on international cooperation held in parallel be chaired respectively by Heidi Fiedler (UNEP Chemical, Switzerland), John Munthe (IVL, Sweden), Gerhard Petersen (GKSS, Germany), Frank Wania (University, Canada) and Alexandre Soudine (WMO, Switzerland). Workshop also nominated Knut Breivik (NILU, Norway), Eva Brorstrom-Lunden (IVL, Sweden), Torunn Berg (NILU, Norway), Russ Bullock (NOAA, USA) and Martin Scheringer (SFIT, Switzerland) as rapporteurs of the above mentioned Working Groups.

Mr. S. Dutchak, co-Chairman of the Workshop, thanked the participants for his nomination and the hosts for provision of excellent facilities. He presented the main objectives of the meeting and introduced a draft programme of the Workshop, which was adopted and is reproduced in Annex B.

## **3. INTRODUCTORY PRESENTATIONS**

Review reports on the current activities of various international organizations and conventions related to HMs and POPs were presented by: Sergey Dutchak (EMEP/MSC-E), Alexandre Soudine (WMO), Bo Wahlstrom (UNEP), Vitaly Kimstach (AMAP), John Munthe (EUROTRAC), Keith Bull (UNECE/WGE), Keith Puckett (AES) and Peringe Grennfelt (EMEP).

### **3.1. EMEP Activity in the Field of the Long-range Transport of HMs and POPs**

Sergey Dutchak, Meteorological Synthesizing Centre of EMEP (Russia)

Environmental pollution by heavy metals (HM) and persistent organic pollutants (POP) more and more attracts attention on national and international levels. A range of projects related to the long-range atmospheric transport of these substances are being carried out by several international organizations and programmes such as WMO, UNEP, HELCOM, OSPAR, WHO, EUROTRAC, MEDPOL, EEA, AMAP.

An essential progress in the field of HM and POP air pollution was achieved within the framework of the UN ECE Convention on Long-Range Transboundary Air Pollution (LRTAP). In June 1998 in Arhus (Denmark) 36 Parties to the Convention signed the Protocols on POPs and HMs. In addition to the fulfilment of the basic obligations on the control of emissions, production and use Parties to the Protocols shall encourage research, monitoring and co-operation, in particular, in the fields of emissions, long-range transport, deposition levels, etc.

In accordance with the Protocols EMEP shall provide Executive Body with information on the long-range transport and deposition of HMs and POPs. EMEP results should promote further evaluating international abatement strategies and reviewing the implementation of the Protocols and compliance with Parties obligations.

At the first stage EMEP plans to concentrate its efforts on emission inventory, monitoring and modelling of the following substances: cadmium, lead, mercury and selected POPs (PAH, PCB, HCB, chlordane, HCH, DDT/DDE, dioxins/furans). Data on measurements and emissions and their geographical distribution is prerequisite for a successfully long-range transport modelling.

#### **Emissions**

Meteorological Synthesizing Centre West (MSC-W) is a responsible centre for EMEP emission database. Evaluating emission data available for HM and POP modelling it can be mentioned that compared to the previous years the situation is becoming better. The number of countries, which submitted data to MSC-W emission database increased. It is possible to distinguish a group of countries: Bulgaria, Great Britain, Hungary, Germany, the Netherlands, Poland, Slovakia, Finland, which contributed more actively. At the same time it can be mentioned that data on spatial distribution, source heights, temporal variations and uncertainty values are very limited. For the majority of countries total annual emissions and spatial distribution are based on expert estimates.

Another important objective is updating and complementing EMEP/CORINAIR Atmospheric Emission Inventory Guidebook providing countries with a unified methodology for HM and POP emission inventories. This activity is carried out by the UN ECE Task Force on Emission Inventories and Projects (TFEIP) with the support of countries and EMEP Centres.

### **Measurements**

Chemical Coordinating Centre (CCC) coordinates and develops measurements and their quality assurance, data reporting and the monitoring database, and processes, evaluates and reports data. Taking into account that HMs and POPs have not been a part of the EMEP monitoring programme before 1999, the Steering Body of EMEP requested CCC to collect already available data on these pollutants from national and international programmes (HELCOM, AMAP, OSPAR, MEDPOL). In 1999 measurement data on PCBs and B[a]P were collected from seventh stations located in the following countries: Germany, Ireland, Iceland, Norway, Finland, the Czech Republic, and Sweden. HM data base were gathered from seventieth stations located in Belgium, Czech Republic, Denmark, Estonia, Finland, Germany, Ireland, Iceland, Latvia, Lithuania, the Netherlands, Norway, Poland, Portugal, Slovakia, Sweden, Turkey, United Kingdom and Yugoslavia. The analysis of the network geographical location indicates that the majority of stations are located in central and northern Europe therefore the pattern of pollution distribution is far from being complete. A small number of stations have sufficiently long series of observations. It should be mentioned as well that the majority of stations do not carry out simultaneous measurements of concentrations in air and precipitation.

### **Modelling**

Meteorological Synthesizing Centre East (MSC-E) is responsible for the evaluation and modelling of POP and HM transport. At this stage of POP modelling a special attention is paid to the refinement of physical-chemical properties of selected PCBs, selected PAHs, lindane, selected PCDD/Fs. The next important point is the investigations of exchange processes between environmental compartments. The main attention is concentrated on the study of atmosphere/vegetation and atmosphere/sea exchange processes with emphases on the effect of sea currents on POP transboundary transport. Results of POP modelling were presented at the EUROTRAC/MEPOP workshop (February 1999) and AMAP workshop (June 1999). In parallel with the development of the regional model a preparatory work for hemispherical modelling is going on. This activity is aimed at the evaluation of POP transport between Europe and other continents (North America, Asia, Africa, the Arctic).

Transport modelling of heavy metals requires detailed knowledge of mechanisms of HM input to the atmosphere, transport processes, scavenging and accumulation in different

environmental compartments. Among heavy metals mercury represented by different physical-chemical forms takes a special place. For evaluation of Hg transport a multi-compartment approach (air, water, soil, and vegetation) should be used. In general HM models should provide the evaluation of regional, hemispheric and global airborne transport.

The operational model for HMs metals is being developed by the EMEP/MSC-E in collaboration with the Advisory Group of experts on HMs and POPs and in close co-operation with national experts from Sweden, Germany, Bulgaria, Belarus, and the USA, CANADA. The progress in investigations of physical-chemical properties of mercury and its behaviour in different compartments to a great extent are achieved due to the joint research within the framework of MEPOP/EUROTRAC project.

Special attention is given to the quality of modelling results. Two numerical experiments concerned with the intercomparison studies of lead and cadmium models developed by leading scientific groups in Europe have been carried out. Intercomparison of mercury models has been started.

The main tasks of EMEP in its seventh phase are:

- To determine the state and trends of air pollution in Europe for assessment of effects.
- To quantify transboundary fluxes and allocate the sources of the estimated deposition.
- To survey the compliance of the Parties with protocol commitments by analysing the progress towards reduction of deposition fluxes, in particular as they concern exceedance to critical loads.
- To provide guidance for the development of cost-effective abatement strategies at national and international level.

To fulfil these tasks EMEP should further develop interaction with national and international research programmes in relevant scientific fields, and utilize results of these programmes to improve the scientific quality of the work within EMEP.

It is expected that this workshop will contribute significantly for better understanding of many scientific issues. Its recommendations will be used for the development of EMEP strategy in the field of HM and POP long-range transport.

### **3.2 WMO Activities Related to Heavy Metals and POPS**

Alexandre Soudine, WMO (Switzerland)

The World Meteorological Organization was one of the first international organizations which started dealing with the protection of the environment and, in particular, with the atmospheric environment. The WMO Global Atmosphere Watch (GAW) system established in 1989 has integrated a number of WMO's research and monitoring activities in the field of the atmospheric environment including the WMO Background Air Pollution Monitoring Network (BAPMoN) and the WMO Global Ozone Observing System, established respectively in the 1960s and the 1950s. That was well before the historic Stockholm Conference of 1972 which led to the creation of the United Nations Environment Programme with which WMO has fruitfully co-operated for many years in many fields related to the environment including such problems as climate change, ozone layer depletion and others.

At the end of 1970's the WMO played an active role in preparing the Convention on Long-range Transboundary Air Pollution in Europe adopted in 1979 and in establishing its EMEP programme. Many WMO monitoring stations in Europe became EMEP stations and WMO closely collaborates with the EMEP modelling activities through two EMEP Meteorological Synthesizing Centres in Oslo and in Moscow established with the help of WMO. The co-operation between EMEP and WMO has especially strengthened in the last years in all aspects related to the long-range transport and deposition of pollutants including modelling, measurements and quality assurance. The present meeting co-sponsored by WMO, EMEP and UNEP is one more example of such a close co-operation in dealing with the most urgent environmental problems.

The theme of the present workshop is the modelling of atmospheric transport and deposition of persistent organic pollutants (POPs) and heavy metals. Pollution of the environment by POPs and heavy metals has been recognized as one of the most urgent environmental problems of nowadays. In this respect it should be noted that ten years ago, in 1989 WMO



prepared and published one of the first global assessments of the atmospheric input of POPs and heavy metals to the World Ocean. This assessment showed that for many heavy metals and for most of POPs their atmospheric inputs constitute from 70 to 98% of the total inputs of these toxic substances to the World Ocean. During the last decade these findings have been confirmed by many studies dealing with some specific seas such as North, Baltic and Mediterranean, as well as marine coastal areas and the Arctic.

On the basis of the existing scientific knowledge it is possible to state that many POPs and heavy metals are of anthropogenic origin. They have been or are heavily used and released to the environment in large quantities. They have long environmental half-lives. Many POPs and some heavy metals exist as semi-volatile compounds and this enables them to cycle through eco-systems and travel distances, on a local to global scale, with the atmosphere being the primary transport medium. A very important property of POPs and some heavy metals is their ability to bioaccumulate and biomagnify through the food-chain and thus to cause harmful health effects to humans.

It is clear that effective action to control the accumulation of POPs and some heavy metals in the environment is urgently needed and that it can be successful only if undertaken on an international and even global scale taking into account the long-range transport of these substances.

At the same time it has to be admitted that there are some gaps in our knowledge that hamper the development and implementation of cost-effective control measures. The most important uncertainties exist in the emission estimates, in parameterization of the processes of deposition, chemical transformations in the course of long-range transport, and exchange between the environmental media. There is also room for further improvement of models and for reduction of uncertainties introduced by the model concepts. Finally, more reliable

measurement data are needed to verify the model results and to improve the assessments of deposition.

The most urgent present task is to solve the uncertainty problems as related not only to modelling but also to the emission estimates and measurements. The first step in this direction was made in 1996 at the WMO/EMEP Workshop on the assessment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development, held in Moscow, Russia. The results of this workshop received cogent recognition and its report and proceedings were published by WMO (WMO/TD No.806).

The reason why WMO is involved in the activities related to POPs and heavy metals is rather evident. These toxic substances enter the environment mainly through the atmosphere and their long-range transport in the environment is mainly connected with the atmospheric transport. The main tool to estimate the atmospheric transport, transformations and deposition of airborne substances is the atmospheric transport numerical models which were originally developed and are widely used by atmospheric scientists and meteorologists. The basic input data for these models, such as wind speed fields, precipitation and evaporation intensity, air temperature, vertical and horizontal diffusion coefficients, boundary layer heights, etc., are also provided by meteorologists. Support to further development and application of the atmospheric transport modelling is one of the activities of the WMO Global Atmosphere Watch programme in which many meteorological services participate.

Furthermore, the WMO through its Global Atmosphere Watch system co-ordinates the work of the global network of monitoring stations which provide data on chemical composition and related physical characteristics of the atmosphere and their trends required to improve our understanding of the climate change, the long-range atmospheric transport and deposition of potentially harmful substances, and the natural cycling of chemical elements. At present the GAW system includes about 300 regional stations focused on specific regional

environmental problems, and 22 global stations which carry out a complete range of measurements relevant to climate change, depletion of the ozone layer and to other global-scale environmental issues. In addition to the monitoring stations the GAW system includes also Quality Assurance Centres, world calibration centres for selected parameters and six World Data Centres. A number of GAW stations already participate in monitoring of POPs and heavy metals and some more stations may wish to join this activity.

Another WMO activity related to heavy metals and POPs is connected with implementation of the Programme for the Assessment and Control of Pollution in the Mediterranean Region (presently MED POL – Phase III) initiated by UNEP and Mediterranean countries in 1975 as a component of the Mediterranean Action Plan (MAP) adopted in line with the Convention for the Protection of the Mediterranean Sea against Pollution (Barcelona Convention). The WMO is a co-operating agency for MED POL being responsible for monitoring, modelling and assessment of pollution of the Mediterranean Sea through the atmosphere. With the help of WMO several monitoring stations in the Mediterranean were established and equipped, a number of expert meetings and a training course were held, more than 30 national research projects were initiated and supported, and the following reports were prepared in co-operation with MSC-E of EMEP and Mediterranean experts:

- Meteorological and climatological data from surface and upper measurements for the assessment of atmospheric transport of pollutants in the Mediterranean basin.
- Assessment of airborne pollution of the Mediterranean Sea by sulphur and nitrogen compounds and heavy metals.
- Atmospheric input of mercury to the Mediterranean Sea.
- MED POL manual on sampling and analysis of aerosols and precipitation for major ions and trace elements.
- Atmospheric input of persistent organic pollutants to the Mediterranean Sea.

All the available GAW facilities and activities could make valuable contributions to the concerted international efforts aimed at providing a scientific basis for more precise estimates of POP and heavy metal emissions, for better understanding of their environmental fate and source-receptor relationships. The results of this work are urgently needed for the development of cost-effective control measures to protect our environment and people living in it against adverse effects of substances which are on the agenda of this meeting.

### **3.3 POP Related Activities in UNEP**

Bo Wahlstrom, UNEP Chemicals (Switzerland)

#### **Development of POPs treaty**

##### ***The negotiating process***

Based on a mandate given at UNEP GC 18/32, Nairobi, May 1995 and at UNEP GC 19/13C, Nairobi, Jan-Feb. 1997, UNEP has convened an Intergovernmental Negotiating Committee (INC) to develop an international legally binding instrument for implementing international action on certain persistent organic pollutants (POPs). Other important activities preceding the negotiations were the UNEP meeting in Washington in October 1995, which initiated a Global Programme of Action for the Protection of the Marine Environment from Land-Based Activities and the meeting of the Intergovernmental Forum on Chemical Safety (IFCS) *ad hoc* Working Group on Persistent Organic Pollutants in Manila in June 1996.

The 1<sup>st</sup> session of the INC (INC-1) was held in Montreal, June-July 1998, the 2<sup>nd</sup> session, INC-2 in Nairobi, January 1999 and the 3<sup>rd</sup> session, INC-3 in Geneva, September 1999. The 4<sup>th</sup> and 5<sup>th</sup> sessions are scheduled to be held, INC-4, 20-25 March 2000 in Bonn and INC-5, early December 2000 in South Africa. The Conference of the Plenipotentiaries (DIPCON) on the POPs convention is scheduled to take place in Stockholm in May 2001. It has been estimated that the treaty might enter into force two to three years after the diplomatic conference.

##### ***Criteria development***

The INC-1 established in accordance with its mandate a subsidiary body, the Criteria Expert Group for POPs with the task to develop criteria and procedure for identifying additional POPs as candidates for future international action. The 1<sup>st</sup> session of the Criteria Expert Group, CEG-1, was held in Bangkok in October 1998. The 2<sup>nd</sup> session, CEG-2, was held in Vienna in June 1999. The CEG-2 concluded that the mandate had been fulfilled at the 2<sup>nd</sup>

meeting and that its proposals for criteria and a procedure for identifying additional POPs as candidates for future international action should be submitted to the INC at its 3<sup>rd</sup> session.

The CEG proposed a number of screening criteria as follows:

- Persistence;
- Bio-accumulation;
- Potential for long-range transport;
- Reasons for concern/adverse effects.

For the first three the details are given below:

Persistence criteria:

- Water;  $t_{1/2} > [2][6]$  months;
- Soil,  $t_{1/2} > 6$  months;
- Sediment,  $t_{1/2} > 6$  months;
- or other evidence of persistence.

Bio-accumulation:

- $\text{Log}K_{ow} > [4][5]$ ;
- $\text{BCF}/\text{BAF} > 5,000$ ;
- or other evidence of bio-accumulation.

Potential for long-range transport:

- Measured levels of potential concern in distant locations;
- Monitoring data showing transport may have occurred;
- Fate properties or modeling showing potential for long-range transport;
- Substances that migrate via air;  $t_{1/2} > 2$  days.

### ***Procedure for new POPs***

The overall procedure to be followed in identifying possible candidate substances for future international action has the following characteristics:

- Nominations by Parties to treaty;
- Subsidiary body to review nominations at initial and later steps;
- Stepwise procedure;
- Check criteria fulfilled;
- Openness and transparency throughout;
- Possibilities for input at several stages;
- In depth assessment;

- Risk profile with risk management options;
- Recommendation to COP.

## **GEF projects**

### ***Regionally Based Assessment of Persistent Toxic Substances***

UNEP Chemicals has recently taken steps towards consolidating and expanding its activities in the field of chemicals assessment, with a strong emphasis on water related effects and impacts. Starting in late Spring 2000 UNEP Chemicals will execute a two-year US\$5 million global project on Regionally Based Assessment of Persistent Toxic Substances. The project will address Persistent Toxic Substances, which is a broader group than the POPs in the negotiations. The project will focus on the aquatic environment and will be executed in twelve regions around the globe.

Criteria for including substances in the project were suggested at the 1<sup>st</sup> technical expert workshop of the PDF-B phase as follows:

- persistence, including continuous release of moderately persistent substances;
- bio-accumulation;
- toxicity;
- organometallic substances should be included;
- regional and sub-regional transport scales.

Expected outputs of the project are:

- Overall global assessment of the issues and problems with PTS.
- Assessment of priorities in regions.
- Priorities for future GEF intervention.

### ***Other related GEF activities***

UNEP Chemicals is also executing a GEF PDF-B phase project on Assessing National Management Needs for Persistent Toxic Substances. The project brief for the full project will be submitted to the GEF Council for consideration and possible approval early 2001.

### **Immediate actions; capacity building**

UNEP Chemicals is executing a large number of immediate actions, in response to Decision 19/13C of the 20<sup>th</sup> UNEP Governing Council. During 2000 and 2001 a series of regional and sub-regional workshops will be held on i.a. the following issues:

- Controlling releases of dioxins and furans;
- Managing of stockpiles;

- Identification of PCB containing equipment;
- Source inventories; PCB, dioxins and furans;
- Integrated vector control, including alternatives to DDT;
- Chemicals legislation, infrastructure.

In addition to the workshops, UNEP Chemicals is preparing training material and guidance documents to assist countries in managing POPs.

### **3.4. AMAP Activities on Assessment of Persistent Toxic Substances**

Vitaly Kimstach, AMAP Secretariat (Norway)

Arctic Monitoring and Assessment Programme (AMAP) was established in 1991 as an inter-governmental environmental programme of the eight Arctic countries (Canada, Denmark, Finland, Iceland, Norway, Russia, Sweden and USA) within the framework of the Arctic Environmental Protection Strategy. Since 1996, this programme operates under the Arctic Council. The main objective of the programme is to monitor levels and trends of pollutants, and assess their effects on the Arctic environment and human health. Based on the request of the Ministers, persistent organic pollutants (POPs) and some heavy metals have received, together with radionuclides, special priority in this work.

To meet the ministerial request, special monitoring programme has been established and implemented based on national activities of the participating countries. In particular, a circumpolar network of atmospheric monitoring stations has been established to verify modelling results of long-range atmospheric transport of POPs.

The results of the 1<sup>st</sup> phase of AMAP have been presented in 1997 as the “Arctic Pollution Issues: State of the Arctic Environment Report”. It was supported by scientifically more comprehensive and fully referenced “AMAP Assessment Report: Arctic Pollution Issues”, which was published in 1998.

AMAP assessment has documented that, due to a number of factors, among which cold Arctic climate, physico-chemical characteristics of POPs, and lifestyle of the Arctic indigenous peoples, some indigenous communities can be considered among the most exposed to PTS groups of populations on the Earth. Taking into account that more or less significant sources of PTS are not found out in the Arctic, these effects are caused by long-range transport of these contaminants by atmospheric and aquatic pathways. Significant role in exposure of the Arctic indigenous population to PTS plays their biomagnification in lipid-rich Arctic food chains, and traditional diet based on biota of higher trophic levels.

During its 2<sup>nd</sup> phase, AMAP will continue, among other priority pollution issues, study of levels and trends of global contaminants in the Arctic and source-receptor assessment, with special focus on their biological and combined effects, particularly on human health. Taking into account difficult conditions for implementation of monitoring activities in this region, particular attention will be paid to modelling.

To improve AMAP modelling capacity a special workshop "Modelling and Sources: A Workshop on Techniques and Associated Uncertainties in Quantifying the Origin and Long-Range Transport of Contaminants to the Arctic" has been arranged in Bergen in June 1999. The Workshop emphasized that there is a large potential for cooperation between AMAP and UN ECE (EMEP) in relation to both modelling and assessment activities.

The conclusions and recommendations of the AMAP Assessment Report raised great concern of the Arctic Indigenous Peoples Organizations (IPOs) – Permanent Participants of the Arctic Council on PTS impact on health of their peoples. Situation in the Russian Federation, due to current economical conditions in this country, is of particular importance. Due to this, IPOs in collaboration with the AMAP Secretariat, have developed the Project Proposal "Persistent Toxic Substances, Food Security and Indigenous Peoples of the Russian Arctic", which will be financed with involvement of the Global Environmental Facilities (GEF). At present, besides GEF, this project has received financial support from the Nordic Council of Ministers, Norway, Denmark and some other sources.

Assessment of long-range atmospheric transport of PTS to the areas populated by indigenous population is one of important components of the project. It is agreed that MSC-E will take part in this work, and UN-ECE will provide an information on long-range atmospheric transport of PTS in the European part of Russia as its voluntary contribution to the project. However, the Asian part of the Russian North has not been studied so far, and will be included into the project programme.

This project, in combination with direct activities under the 2<sup>nd</sup> phase of AMAP, will provide valuable data, also needed for information support of the negotiation process on the UNEP's Global POPs Protocol, and will further strengthen collaboration between AMAP and UN-ECE.



### **3.5. Atmospheric cycling of mercury and persistent organic pollutants (MEPOP). Overview and highlights of scientific activities**

John Munthe  
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Sweden

The EUROTRAC-2 subproject MEPOP is focused on atmospheric transport, transformations and deposition of mercury (Hg) and Persistent Organic Pollutants (POPs).

The overall aim is:

- To quantify the regional atmospheric cycling of semivolatile species such as Hg and POPs.

A total of ca 25 Principal Investigators are active in the project in areas covering emissions, atmospheric measurements, process studies and modelling.

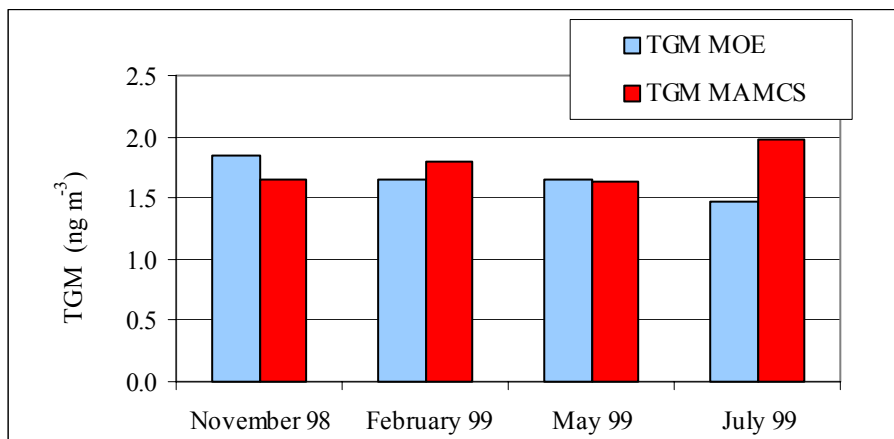
Main activities during the first years of MEPOP have included a broad range of activities such as:

- Modelling of Hg deposition to the Baltic Sea
- EMEP model development for Hg and POPs
- Development of hemispherical and global models for Hg
- Air-surface interactions of Hg
- Deposition processes of POPs
- Atmospheric measurements of Hg species and POPs
- PAH emissions in Russia
- Dynamical modelling of Hg in Mediterranean atmosphere
- Model of POPs in UK and Europe
- Hg dynamics in the Arctic atmosphere

The MOE and MAMCS projects

During 1998 and 1999, the mercury research activities within MEPOP have mainly been funded by the European Commissions Fourth Framework Programme. Two research projects focussing on the atmospheric cycling of mercury in Europe have been the core of the MEPOP activities: MOE (Mercury Over Europe) and MAMCS (Mediterranean Atmospheric Mercury Cycle System). The field measurement activities of the projects are co-ordinated with a total of 10 measurement stations in Europe operated in 5 campaigns. The MAMCS project is focussed on the Mediterranean region whereas measurements in the MOE project are focussed on northern Europe.

In Figure 1, average concentrations of Total Gaseous Mercury (TGM) from the MOE and MAMCS projects are presented. TGM mainly consists of elemental mercury vapour, which is relatively stable with an atmospheric lifetime of at least several months.



**Figure 1.** Average total gaseous mercury from the Mediterranean area (MAMCS) and northern Europe (MOE).

The measurement activities also include mercury species such as Total Particulate Mercury (TPM) and Reactive Gaseous Mercury (RGM). The RGM species mainly consists of gaseous divalent compounds such as  $\text{HgCl}_2$ . TPM and RGM typically make up a few percent of the atmospheric mercury but are still of importance for the overall deposition of mercury due to their higher dry deposition velocities and wash-out ratios.

In Figure 2, TPM measured at the MOE stations during a campaign in November 1998 are shown. A clear gradient from the expected source areas in central and Eastern Europe can be seen with decreasing concentrations at the more northerly stations.

#### Remaining questions in MEPOP

A number of scientific issues need to be resolved before scientifically based emission reduction strategies can be developed. For mercury, these include:

- Processes converting gaseous mercury to particulate forms
- The role of air-water exchange processes in the regional and global cycling of POPs and mercury
- Natural emissions of mercury and re-emissions from land and vegetation of POPs and mercury.

For mercury, the scientific activities on mercury within MEPOP have been satisfactory, mainly via two projects funded by the EC fifth framework programme. For POPs, similar co-

ordinated activities are necessary and will hopefully be a part of MEPOP in the coming years.

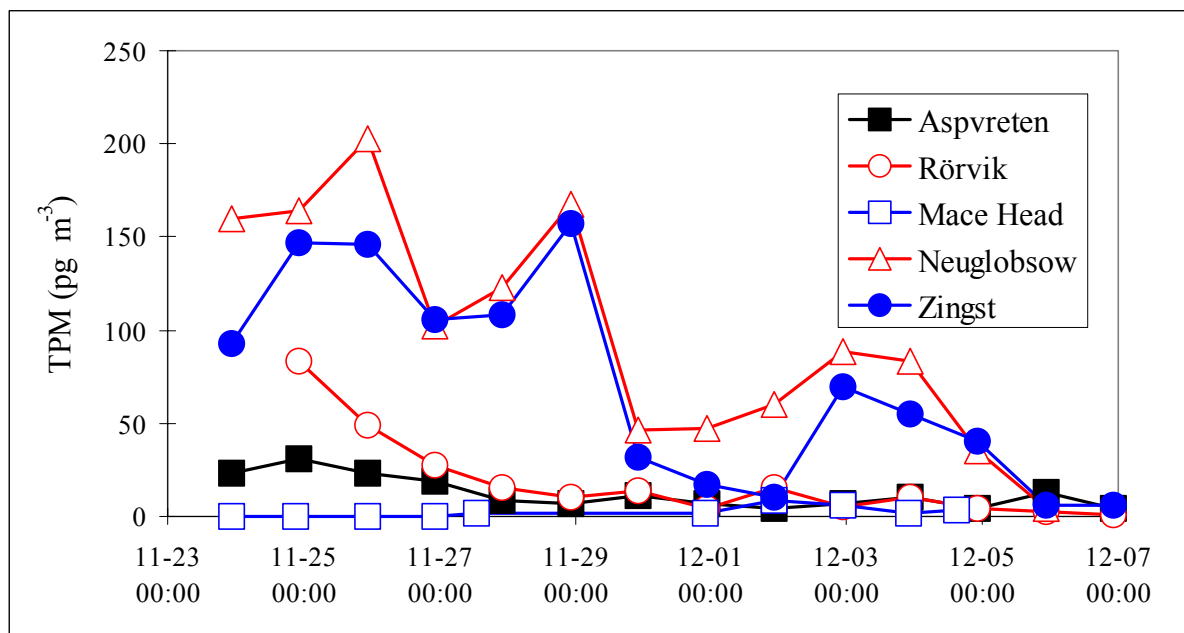


Figure 2 . TPM concentrations at 5 MOE stations in November, 1998.

### 3.6. Information on Effects, Progress in the Evaluation of Critical Loads and Risk Assessment

Keith Bull, Chairman of the Working Group on Effects (United Kingdom)

While the LRTAP Convention's Aarhus Protocols on heavy metals and POPs were not effect-based (i.e. using effects on specific regions and receptors to target the reductions of specific emissions) they were justified in terms of the effects of the pollutants proposed for control. This is in keeping with first protocols for other substances that have been simple "flat rate" or "technology based" protocols. Second step protocols have looked towards an effect-based mechanism. For sulphur and nitrogen this has been based on critical loads.

An Article in each of the POPs and heavy metals Protocols refers to collaboration between Parties on research, development and monitoring. Particularly important for a possible second step protocol is the suggestion that Parties work towards "an effects-based approach ...integrating information ...for formulating future control strategies which also take into account economic and technological factors." In the heavy metals Protocol the control strategies are described as "optimized". The two Articles suggest at the very least some form

of effects-based risk assessment and, in the case of heavy metals the use of optimization suggests a possible critical loads approach, for second step protocols.

The critical loads approach has already been successfully applied to the second step protocol for sulphur and is being applied to the new multi-pollutant, multi-effect protocol for sulphur, nitrogen and VOCs. For these, integrated assessment models have been used to optimize benefits, in terms of environmental protection derived from critical loads maps, through least cost scenarios. Scenarios are developed using information on national emissions, control technology costs and source receptor relationships defined by the EMEP model.

Consideration of effects-based approaches for POPs and heavy metals began, under the Mapping Programme of the Working Group on Effects, just prior to the Aarhus Protocols. A workshop in Bad Harzburg, Germany (November 1997) discussed the feasibility of such approaches taking into account two draft manuals prepared for the Dutch government following the ESQUAD project. Subsequent discussions took place at workshops held by the Coordination Center for Effects and the Task Force of the Mapping Programme. Recently a workshop to discuss effects-based approaches for heavy metals was held in Schwerin, Germany (October 1999). The main conclusions of the Bad Harzburg and Schwerin workshops are summarised below.

The Bad Harzburg workshop drew a clear distinction between risk assessment procedures, that did not involve mapping, and critical loads approaches that involved mapping aspects. In general the workshop did not believe that mapping critical loads for POPs was feasible at the time, and concluded that risk assessment approaches for POPs were more appropriate. Source receptor links for POPs were not thought credible, and although it was agreed that a critical loads approach might be possible for some pollutants (e.g. PAHs) and at local scales, there was a general belief that a critical loads approach was not needed for such pollutants.

For heavy metals, the Bad Harzburg workshop recommended a critical loads approach for lead and cadmium, and also for heavy metals that might be proposed for subsequent addition to the Protocol. There was less certainty about mercury for which both critical loads and risk assessment approaches were recommended for investigation. The use of steady state and dynamic models for calculating critical loads was discussed. For freshwaters it was recommended that steady state models were tested using dynamic approaches, and that methods for mercury should be developed. The workshop concluded that existing critical limits were inadequate though some available could serve as a starting point for further deliberations; terrestrial information in particular was lacking or of varying quality.

The Bad Harzburg workshop concluded that a methodology for the derivation of deposition rates for lead and cadmium were already available but that further development was required for mercury and POPs.

In Schwerin, the workshop believed that critical loads for heavy metals should be based upon effect-based critical limits, but noted that, even 2 years after the Bad Harzburg workshop, current limits were still not adequate. It was felt that there was now sufficient data and scientific understanding available. A re-evaluation of data in the near future, especially for soil systems, was recommended.

For terrestrial systems the workshop identified the need for both steady state and dynamic approaches. The steady state mass balance models should use reactive pools of metals for their calculations, but transfer functions were needed to estimate these from soil solution concentrations. For aquatic systems, the workshop felt that good progress had been made since Bad Harzburg. Feasible models were now available for mercury in addition to those for lead and cadmium. These models should be used for testing their suitability and for validating critical loads estimates. The workshop urged countries to proceed with mapping critical loads for heavy metals using the models.

With regard to deposition, the workshop felt that a better knowledge of mercury deposition was required for comparison with critical loads estimates. It also noted that there was a need to make comparisons of local deposition measurements with EMEP model estimates to provide a sound basis for calculating critical loads exceedances.

Overall the Schwerin workshop identified the progress made in recent years but also the significant amount of work needed by national experts to apply available models to national data to provide the testing and validation needed for effective mapping of critical loads for heavy metals.

The activities under the Working Group on Effects described above demonstrate the feasibility of effects-based approaches and the need for developing better models for defining deposition patterns for heavy metals and POPs.

### 3.7. Long-range Transport Models of Persistent Organic Pollutants and Heavy Metals in North America

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#### CONTENTS

1. INTRODUCTION	21
1.1. General Components for LRT Modelling of POPs and HM	22
1.2. Additional Challenges	24
2. DESCRIPTION OF NORTH AMERICAN MODELS USED IN THE LRT OF POPs AND HM	26
2.1. Local-to-Regional Scale Models	26
2.1.1. Back Trajectory Models	26
2.1.1.1. Potential Source Contribution Function (PSCF)	27
2.1.2. Lagrangian Models	28
2.1.2.1. RELMAP	28
2.1.2.2. ASTRAP	29
2.1.2.3. HYSPLIT	31
2.1.2.4. Hybrid-Receptor Modelling Approach	32
2.1.3. Eulerian Models	33
2.1.3.1. REMSAD	33
2.1.3.2. Regional Discrete Ordinate Model	34
2.1.3.3. ADOM	35
2.1.3.4. TEAM	36
2.1.3.5. MODELS-3	37
2.2. Global Scale Models	38
2.2.1. Global Chemical Transport Model	38
2.2.2. The Global/Regional Atmospheric Heavy Metals Model (GRAHM)	39
2.2.3. Global Multimedia Distribution Model	40
3. FUTURE TRENDS OF MODELLING	41
4. CONCLUSION	42
5. REFERENCES	44

#### 1. INTRODUCTION

The objective of this report is to inform the community of European modelers of the work being done in North America with respect to modelling the Long Range Transport (LRT) of Persistent Organic Pollutants (POPs) and Heavy Metals (HM) in the atmosphere. The approaches to model the atmospheric fate and transport of air pollutants have been diverse, but the most common for POPs and HM are Lagrangian, Eulerian or a combination of both. The description includes the type of approach and level of success, validation techniques are specified when ever possible. Finally, new trends observed in the different approaches are briefly addressed.

A large number of the models developed in North America came about because of the need to develop a response to national or international environmental agreements and policies. In Canada and the United States national air quality programs both research and regulatory in nature have motivated the development of diverse models by groups such as the government, industry, the academic community, and other interested parties. Some international agreements have also included obligations to model the LRT of POPs and HM. Specifically the Great Lakes Water Quality Agreement under Annex 15 stipulates the development of models to quantify the intermediate and long-range movement and transformation of toxic substances. In addition, the Bilateral Great Lakes Toxics Strategy (USEPA and Environment Canada, 1997) calls for Canada and the United States to assess the atmospheric inputs of persistent toxic substances by evaluating the impact of the LRT of such substances from world wide sources.

### 1.1. General components for LRT modelling of POPs and HM

Any modelling framework for the LRT of POPs and HM must address some general considerations. For persistent toxic substances, M.Cohen (1997) summarizes six considerations:

#### 1. Emissions inventory:

- The inventory must be geographically and temporally resolved.
- Information on the speciation and physical characteristics of pollutants is often necessary (e.g. elemental mercury vs.  $\text{HgCl}_2$ ; vapor vs. particle, size distribution etc.).
- Emissions conditions are needed (height, temperature, velocity, etc.) as well as re-emissions of previously deposited pollutants.

#### 2. Characterization of the Dynamic Meteorological Environment:

- Details of three-dimensional wind movement at different scales can be important (large scale motions, mesoscale dynamics, short-range phenomena, small-scale turbulent mixing);
- The dispersion and diffusion of the emitted pollutant in the atmosphere must be characterized over all relevant length scales.

**Table 1.** Toxic Compounds Considered for Modelling (Source: Cohen, 1997)

<b>Metals / organometallics</b>	<b>Polychlorinated Dibenso-P-Dioxins and Dibenzofurans</b>
<p><b>Alkylated Lead</b> Including, but not necessary limited to: Tetra-, tri- and di-ethyl lead, Tetra-, tri- and di-methyl lead</p> <p><b>Cadmium and Cadmium Compounds</b> Including, but not necessary limited to: Cadmium, cadmium oxide, cadmium dichloride, cadmium sulfide</p> <p><b>Mercury and Mercury Compounds</b> Including, but not necessary limited to: Elemental mercury, mercury dichloride, monomethyl mercury and particulate mercury</p> <p><b>Tributyltin Compounds (atmospheric transport is not known)</b></p>	<p>2,3,7,8-TCDD and 2,3,7,8-TCDF 1,2,3,7,8-PeCDD 1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,6,7,8-HpCDD OCDD 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF 1,2,3,4,6,7,8-HpCDF 1,2,3,4,7,8,9-HpCDF OCDF</p>
<b>Organochlorine Biocides</b>	<b>Polychlorinated Biphenyls (PCB's)</b>
<p>Aldrin / Dieldrin Atrazine DDT / DDD / DDE Mirex Toxaphene Endrin Heptachlor / Heptachlor Epoxide Hexachlorocyclohexanes (<math>\alpha</math>, <math>\beta</math>, <math>\delta</math> and <math>\gamma</math>) Methoxychlor Pentachlorophenol Chlordane</p>	<p>PCB's [an attempt is being made to do the analysis on a congener specific basis; there are more than 200 PCB congeners]</p>
<b>Industrial / Miscellaneous</b>	<b>Polycyclic Aromatic Hydrocarbons</b>
<p>Octachlorostyrene 3,3'-Dichlorobenzidene 4,4'-Methylene bis (2-Chloroaniline) 4-Bromophenyl Phenyl Ether Hexachloro-1,3-Butadiene</p>	<p>Dinitropyrenes (several congeners) Benzo[a]Pyrene  Plus PAH's: Phenanthrene, Anthracene, Benz[a]Anthracene, Perylene, Benzo[g,h,i]Perylene, Naphthalene, Acenaphthene, Acenaphthylene, Fluorene, Pyrene, Fluoranthene, Chrysene, Benzo[b]Fluoranthene, Benzo[j]Fluoranthene, Benzo[k]Fluoranthene, Benzo[e]Pyrene, Dibenz[a,h]Anthracene, Indeno[1,2,3-c,d]Pyrene</p>
<b>Chlorobenzenes</b>	
<p>1,4-dichlorobenzene Tetrachlorobenzenes (several congeners) Pentachlorobenzene Hexachlorobenzene</p>	

3. Characterization of the Spatially and Temporally Varying Micro-physical and Micro-chemical Environment

- Temperature; humidity, clouds; precipitation



- Physical and chemical nature of the ambient atmospheric aerosol
  - Concentration of the hydroxyl radical and other reactants
  - Intensity and spatial distribution of electromagnetic radiation
  - Detail characteristics of the earth's surface.
4. Characterization of the Interaction of the Pollutant Being Modeled with the Micro-physical and Micro-chemical Environment
- Vapor/particle partitioning
  - Partitioning of cloud water; precipitation
  - Reaction rates with hydroxyl radical and other reactants in vapor phase or particle phase
  - Reactions with atmospheric aerosols
  - Rates of droplet phase reactions
  - Rate of photolytic transformation
  - Deposition and re-emission phenomenon
5. Model Output
- Predicted atmospheric concentration and deposition (from all sources) at a given location at given times
  - Source-receptor relationships e.g. the amount of deposition at a given receptor at a given time attributable to the contribution of a given source's emissions
6. Model Evaluation
- Comparison of predicted concentrations and deposition with measured values

### 1.2. Additional challenges

There are at least four major challenges faced by these models beyond those faced by traditional air pollution models. These are: (1) the tremendous range of life-times and scales and species variations (congeners), (2) the unstable or semi-volatile nature of pollutants while in transit, (3) the possibility of re-emission at the surface or "hopping", and (4) basic lack of information on emissions, transformation pathways and rates, and species measurements.

Among the factors influencing the LRT of a compound, the lifetime in the atmosphere is the most important. For example hexachlorobenzene, which has an estimated atmospheric life measured in years, can be distributed globally. In some cases, the lifetime is linked to climatic zone. For example, a chemical that is considered not very persistent in temperate or

tropical environments can be very persistent in the Arctic (Wania and MacKay, 1999). In contrast, a substance very susceptible to photolytic degradation (e.g., 4,4'-methylene bis (2-chloroaniline) while airborne, may have a lifetime measured in minutes and thus very a limited atmospheric mobility (Cohen, 1997).

Based on this lifetime approach, persistent toxic substances have been classified into four qualitative categories of atmospheric long-range transport (LRT) potential (Cohen, 1997):

LRT rating 1: **Global**: Atmospheric half-life: one year or more

Geographic distribution from sources: global

LRT rating 2: **Continental**: Atmospheric half-life: one week to a few months

Geographic distribution from sources: 1,000-10,000 km

LRT rating 3: **Regional**: Atmospheric half-life: a few hours to a few days

Geographic distribution from sources: 100-1,000 km

LRT rating 4: **Local**: Atmospheric half-life: seconds to minutes

Geographic distribution from sources: local

These lifetime estimates contain significant uncertainties for practically all compounds.

As indicated, the scales the models must address range from local/regional to hemispheric. Either a different model gets built for each major scale, which is to some degree inefficient, or a model must be able to cover these scales consistently and with aplomb. This includes the meteorological models as well as the chemical transport models. This is not trivial, and we are only now beginning to gain experience in crossing scales with the same model. The species variations are too many to handle simultaneously, so, like the photochemical models, means of adequately collapsing variations into systematic classes are needed. Unlike the photochemical models, the collapsing cannot be based on a "stable" reaction attribute such as the OH rate constant. For example, the higher chlorinated congeners of dioxins and furans undergo photolytic dechlorination, whereas the lower chlorinated congeners react with the OH radical.

The semi-volatile nature of these pollutants, depending on the departure from equilibrium, makes them difficult to model. The partitioning of the POP's depends on the short-term micro-physical and micro-chemical environment, including properties such as type (organic or inorganic) and surface area of the local aerosol mass. This is a dynamic process that requires information on and influences the history of the pollutants. At this time, little is known about the details of the partitioning and the aerosol properties influencing the POP's. This is a key characteristic that makes modelling of POP's unique.

The transfer between the atmosphere and the surface can be bi-directional, i.e., re-emissions. Establishing the dynamic interaction with regard to vapor-phase, dry deposition, and re-emissions processes challenges existing models. The net direction of transfer will depend on the degree of thermodynamic imbalance and the motion, diffusion and mixing processes in each of the two phases. The degree of departure from equilibrium is dependent on the total concentrations of the pollutant in the local atmosphere and the total concentration of the pollutant in or on the materials at the earth's surface. This characteristic of re-emission, or the grasshopper effect, is also a key feature that makes modelling of POP's unique.

The lack of information on the interactions, chemical speciation and emissions is similar to issues faced 20 to 30 years ago in what are now the more mature modelling arenas. Of particular difficulty for mercury is that until very recently measurements of ambient concentrations of many of the key species involved could not be made. Many of the formulations of reaction sets and mechanisms in these models are based on very sparse information and heavy doses of judgment rather than well-understood, well-tested mechanisms. The emission inventories on which these models rely have significant uncertainties and in some cases no information about emissions appear to be available or it appears to be confidential and unavailable to the public and research community, including government researchers. The geographic coverage or geographic resolution and temporal resolution of the emissions tend to be woefully inadequate. The species differentiation is inadequate and even the means of stack testing may be providing the wrong information regarding the state of the specie beyond the high-temperature environment of a stack. For dioxins, the emissions are expressed in TEQ (toxicity equivalents), which is a weighted average total dioxin measure that relates to toxicity, but not actual mass units. This makes it almost impossible to actually model the emissions and provide the actual mass input required by the air quality models.

## 2. DESCRIPTION OF NORTH AMERICAN MODELS USED IN THE LRT OF POPs AND HM

### 2.1. Local-to-regional scale models

#### 2.1.1. Back trajectory models

In estimating a source-receptor relationship, back trajectory calculations have been used in attempts to estimate the relative importance of sources and/or source regions to the concentration and/or deposition at a give receptor. These back trajectories are in the form of pairs of endpoint co-ordinates describing where the air has been over a sequence of fixed

time intervals backwards in time. High-concentration events are assumed to result when air parcels arrive at the measurement site from regions with significant sources of the given pollutant. The distance between the source location and the measurement site obviously influences the concentration, dispersion, deposition, and chemical transformation of the pollutant (Blanchard *et al.*, 1997; Hopke *et al.*, 1999; Hoff *et al.*, 1992).

#### *Transport and fate of mercury*

A back trajectory analysis used to assess the sources of mercury in Michigan found that the highest mercury concentrations in precipitation were generally associated with air parcels that arrive from the west, southwest, south, and southeast. There were, however, some exceptions, occasionally, there were high concentrations from air parcels coming from the north and east sites (Hoyer *et al.*, 1995).

#### *Transport and fate of trace elements*

Another analysis of trace elements, including cadmium, on the north shore of Lake Ontario (Point Petre an Integrated Atmospheric Deposition Network (IADN) sampling site) associated highest levels to air trajectories that passed over heavily populated regions to the south and west of Point Petre. Cadmium and arsenic were related to trajectories coming from the north, which corresponded to smelters located in that area. Dorset, Ontario is another site where back trajectory analysis was performed. Due to lack of emissions inventory data, it is difficult to verify whether the source locations suggested by the analysis did indeed correspond to the large known sources (Blanchard *et al.*, 1997; Hopke *et al.*, 1999).

#### *Transport and fate of PCB's and pesticides*

Back trajectory analysis was also used in conjunction with measurements at Egbert, Ontario to estimate source regions of PCB's and several organohalogen pesticides such as toxaphene and DDT. It was found that high concentrations of pesticides corresponded to air flowing from the south, especially the southern US and the Caribbean. The concentrations of PCB's appeared to be only weakly dependent on source regions, and more dependent on ambient temperature. This is evident of significant emissions and re-emissions (grasshopper effect) occurring over widely dispersed areas (Hoff *et al.*, 1992).

##### 2.1.1.1. Potential source contribution function (PSCF)

In this receptor model meteorological information of back trajectories are combined with on the atmospheric constituent concentration data to produce conditional probability fields pointing to areas that are likely to have made significant contributions to samples with higher

than average concentrations. The movement of the air backwards in time is calculated with a deterministic atmospheric dynamic model. The model assumes that the air either follows lines of constant air pressure or constant entropy (Hopke *et al.*, 1999).

With this model maps were produced that have a good correspondence with areas of known high emissions. The tests included a variety of spatial scales from large urban centres such as Los Angeles, CA, regional transport of hazardous pollutants to southern Ontario and semi-global scale transport to several sites in the high Arctic. The use of 'bootstrapping' improves the quality of conditional probability (PSCF) values that relate the emissions and transport of pollutants to the presence of high concentration at a particular sampling site (Hopke *et al.*, 1999).

The use of PSCF in source-receptor relationships for total gaseous mercury in the St, Lawrence River Valley, Quebec points at the Gulf of Mexico as the strongest potential source. Long range transport from Eurasia or potential source areas over oceans due to possible water-air exchange are also suggested. Both sources seem to predominate in the winter (Poissant, 1999).

#### 2.1.2. Lagrangian models

In a Lagrangian model, the pollutant and transport are mathematically characterized relative to the trajectory of air parcels. They are mainly used to estimate the impact of a given source on downwind receptors. When multiple sources are involved, calculations can be made for one source at a time or, for all sources together. One drawback is that in situations with complex atmospheric chemistry and when the interaction of emissions from different sources is important, it presents difficulties. Keeping track of source-receptor relationship becomes numerically difficult (Moussiopoulos *et al.*, 1996; Cohen, 1997).

##### 2.1.2.1. RELMAP

The Regional Lagrangian Model of Air Pollution (RELMAP) conceived in the Federal Republic of Germany, was later refined by EPA to be used in North America in the late 1970s and 1980s. In recent years, its domain has been extended and its grid size made smaller. The model has four vertical layers, from the surface up to the top of the planetary boundary layer (typically about 700-1500 meters). It has been used to predict the transport of several heavy metals (arsenic, cadmium, chromium, lead and nickel). Air emissions inventories from US and Canadian sources were used to run this model. RELMAP is capable of producing results for source-receptor relationships (Cohen, 1997).

### *Transport of mercury*

RELMAP has been used to model the fate and transport of mercury emitted in the continental US (Bullock *et al.*, 1998). The modifications to simulate mercury were primarily based on Lagrangian models of atmospheric mercury used in Europe. The grid resolution was set to  $\frac{1}{2} \times \frac{1}{2}$  degree, approximately a 40-km square. The model domain encompasses the entire continental US, southern Canada and northern Mexico. The model takes into account the background concentrations of elemental mercury vapor of 1.6 ng/m<sup>3</sup> and estimates a total deposition of 111 metric tons of mercury per year (Cohen, 1997). Annual totals are within a factor of two of observed annual wet deposition (Bullock *et al.*, 1996). There is a general trend towards over-estimating wet deposition. Bullock *et al.* (1998) believe that emissions speciation is required to improve the model estimates.

### *Transport of dioxin*

This model was also used to simulate the fate and transport of dioxin air emissions in the US. Vapor/particle partitioning of individual PCDD/F congeners was treated using the approach of Junge (1978) and supercooled liquid vapor pressures, as suggested by Bidleman (1988). A constant aerosol surface area of  $3.5 \times 10^{-6}$  cm<sup>2</sup>/cm<sup>3</sup> was used, believed to be typical of "background + local sources." Average ambient temperatures were calculated for the vapor/particle partitioning calculation based on latitude and season. For this exercise, dioxins and furans are treated as chemically inert species (Cohen, 1997).

The results obtained from this model for 1997 were used in developing the "Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units- Final Report to Congress." It incorporates the latest scientific evidence of dry gaseous deposition of dioxins and furans to vegetated surfaces. It has been possible to assess the average concentration and total wet- and dry-deposition patterns of PCDD and PCDF congeners over the lower 48 States from hazardous waste incineration (Poole-Kober and Viebrock, 1999).

### *Transport of metals*

RELMAP has been used to simulate the transport and deposition of nickel and chromium compounds. It has also been used for arsenic, cadmium, and lead. Using expanded and updated air emissions inventories RELMAP was applied to estimate average concentrations from power generating utilities (Poole-Kober and Viebrock, 1999).

#### 2.1.2.2. ASTRAP

The Advanced Statistical Trajectory Regional Air Pollution model (ASTRAP) was initially developed in 1981 at the Argonne National Laboratory, and it has undergone further

development and application there and at Environmental Canada's Atmospheric Environment Service. It is a long-term statistical Lagrangian model that attempts to predict ambient concentrations of wet and dry deposition for specific receptors (Shannon and Voldner, 1995).

Horizontal dispersion is estimated by computing the statistical variability of the trajectory centerlines of a series of puffs emitted from each of the series of virtual sources. Wet deposition for each trajectory is calculated to be the half-power of the 6 hour precipitation rate encountered by the puff's centerline. Dry deposition, vertical dispersion, and loss to the free troposphere are calculated from the puff's age using time- and location-dependent parameterizations. The model can generate source-receptor relationship for the grid of virtual sources, which are combined with geographically resolved emissions inventory to calculate the concentration and deposition of specified receptors (Shannon and Voldner, 1995; Cohen, 1997).

#### *Transport of toxaphene*

This model was used to simulate atmospheric transport of toxaphene from sources in the US to the Great Lakes. The simulations were based in 1980 meteorological data from the Canadian Meteorological Centre for 1000 and 850 mb. According to the model, 60% of the emitted toxaphene was deposited in the US and Canada, and remaining 40% left the continent. Lack of ambient measurements and uncertainties on the emissions and in the physical/chemical properties of toxaphene make validation of the model very difficult. Nevertheless, a reasonable agreement between predicted and measured ambient air and rain concentrations was reported (Voldner and Schroeder, 1989).

#### *Transport of mercury*

The model was also used to simulate atmospheric transport of mercury from sources in the US and Canada east from about 95 °W. Meteorological data from the Canadian Meteorological Centre for 1000 and 850 mb was also used, as was 1985 emissions inventory. Anthropogenic and 'natural' emission sources were included. The simulation revealed that 78% of the mercury deposited in the Great Lakes was Hg(II) (e.g. mercury dichloride, HgCl<sub>2</sub>). Again, a reasonable agreement between predicted and observed ambient air and rain concentrations and independently estimated loadings to the Great Lakes was found (Shannon and Voldner, 1995).

#### *Transport of lead*

ASTRAP was also used for the atmospheric transport of lead to the Great Lakes. However, only total lead was modelled. Source-receptor relationships were not described. Wet and dry

deposition of total lead was estimated for the years from 1970-1990. The simulations reflect the dramatic decline over that time period, which coincides with the decrease of lead emissions as a result of the lead-free gasoline. The model predicted direct deposition to the Great Lakes decreased from 5200 metric tons/year in 1970 to only 250 tons/year in 1990 (Voldner *et al.*, 1993).

#### 2.1.2.3. HYSPLIT

The Hybrid Single Particle Lagrangian Integrated Trajectory model was developed at the National Oceanic and Atmospheric Administration (NOAA) United States for operational medium and long-range transport modelling of accidental releases of radioactive materials. It was lately refined to model dioxins, furans, hexachlorobenzenes, atrazine and cadmium (Cohen and Mathewson, 1999). This model has been used extensively to estimate the transport and deposition of dioxins, furans and hexachlorobenzenes from sources in the US and Canada to the Great Lakes as well as to dairy farms in Wisconsin and Vermont.

##### *Transport and fate of dioxin*

A recent use of the model for dioxin was simulating the air transfer coefficient of 2,3,7,8-TCDD from 28 “standard source locations” into Lake Ontario. The highest transport to the lake come from nearby sources and from sources to the west as would be expected from the prevailing winds across the continent (Cohen and Mathewson, 1999).

The latest version still under development, HYSPLIT-3/TRANSCO (Commer, 1999), covers a domain from southern Mexico to the Canadian Arctic. The motivation for this project is determining the source of dioxins found in Inuit mothers’ milk, which are twice the levels observed in southern Quebec, the geographical and seasonal variation in the rate of dioxin deposition. The model includes algorithms that calculate the rates of degradation of PCDD/PCDF congeners through photochemical reactions and reaction with OH radicals, as affected by latitude, cloud cover and season.

This model incorporates meteorological data tabulated at 6-hour intervals into a 3-dimensional grid of points 182.9 km apart horizontally, with six atmospheric layers vertically (up to 3000 m). The model computes the transport, degradation and deposition of material emitted by a source at a given geographical location, by estimating the atmospheric behavior of the emitted material in the form of 7 gram ‘puffs’ injected into the air at seven hour intervals.



The 1996 inventory for Canadian and US sources will be used together with an inventory of Mexican sources being developed by CBNS<sup>1</sup>. Apart from very few facilities for which actual measurement of dioxins are available, emissions are estimated from the capacity or throughput and an appropriate emission factor. The uncertainty on the emissions ranges over an order of magnitude. Emissions estimates for Mexico are even less certain. Validation of the model will be done with data from two rural sites 1200 km southeast of the closest receptor area. These sites are Kejimkujik and St. Andrews where single-day measurements were done during the period of interest (Commer, 1999).

#### 2.1.2.4. Hybrid-Receptor modelling approach

This modelling approach combines measured atmospheric concentrations and meteorological observations in a Lagrangian model. Measurement sites are treated as source regions and the impact on downwind receptors is simulated. From the meteorological measurements, forward trajectories for air parcels are constructed. The air parcels are assumed to be a certain size when over the measurement site. A virtual point source is constructed upwind of the measurement site and its emission rate is adjusted until the predicted concentration of the air parcel over the measurement site matches the measured concentration. The concentration or impact at a downwind receptor is estimated by simulating the fate and transport of material emitted from the virtual source along the entire trajectory (Cohen, 1997).

This model has been used to estimate the dry deposition flux of a range of semivolatile organic compounds to Lake Michigan. Estimates for the following compounds were reported: hexachlorobenzene,  $\gamma$ -HCH, dieldrin, a range of PCB's (including monochloro-PCB's, dichloro-PCB's, etc) and the following 11 PAH's: Benzo[a]Pyrene, Benzo[e]Pyrene, Fluorene, Pyrene, Fluoranthene, Chrysene, Dibenz[a,h]Anthracene, Indeno[1,2,3-c,d]Pyrene, Anthracene, Benzo[a,h]Anthracene, and Benzo[g,h,i]Pyrene.

Among the organic compounds it was used to estimate the following: Trans-nonachlor, Mirex, Aldrin, DDT, 1,4-dichlorobenzene, Hexachloro-1,3-butadiene, Naphthalene, Acenaphthylene, Phenanthrene, and Bensofluoranthenes.

The Hybrid-Receptor model was modified to account for vapor/particle partitioning of semivolatile organic compounds in the atmosphere. As might be expected, ambient concentrations and deposition flux decreased with distance from a hypothetical or virtual source as air parcel moves across the lake Michigan. The analysis found that the largest

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part of the decrease is due to atmospheric dispersion and not due to loss of material due to deposition to the lake.

Similar studies were performed for trace elements mainly for the Great Lakes and the Rouge River Watershed for the following elements: Cd, Cr, Mn, Ni, Hg, V, As, Se, and Pb. Particle size distribution for each element was used to estimate deposition velocities. The model suggests that deposition accounted for 5-20% of the overall decrease during over-water transport. Trend studies done for the Rouge River watershed suggest that emissions and deposition of cadmium, chromium, and nickel vary from year to year, but show an upward trend from 1982-1992. Lead shows a downward trend in response to the phasing out of leaded gasoline. Mercury shows an increase from 1988-1992.

### 2.1.3. Eulerian models

Eulerian approach estimates the pollutant fate and transport everywhere in the modelling domain relative to a fixed coordinate system. It is a 3-D model where all sources considered are mixed together into a grid cell. At each time step, which in some cases could be as short as 5 minutes, the model estimates the behavior of the pollutant within a given grid cell and estimates the movement of pollution from each cell to adjoining cells. It is ideal for complex chemistry interactions from different emissions sources (Cohen, 1997).

In some instances the mathematical formulations of deposition processes used in Lagrangian and Eulerian models are very similar, and in some cases are essentially identical. In fact, models such as HYSPLIT/TRANSCO used in the LRT of dioxins into Polar Regions of North America are a combination of both approaches (Bartlett, 1999).

#### 2.1.3.1. REMSAD

The Regulatory Modelling System for Aerosols and Deposition (REMSAD) is an Eulerian model based on the Urban Airshed Model (UAM), a regional air quality model. It is designed to be a flexible analytical system to support regulatory decisions, by allowing the deposition toxic pollutants to selected receptors under current conditions and under different regulatory scenarios.

The REMSAD aerosol and toxics deposition model (ATDM) is capable of “nesting” a finer-scale subgrid within a coarser overall grid, which permits high resolution over receptor regions without an intolerable computing burden. To deal with toxic substances the model uses a pre-computed hydroxyl chemistry package based on a multidimensional lookup table.

The REMSAD system consists of a meteorological data processor, the core aerosol and toxic deposition model (ATDM), and post processing programs (SAI Inc., 1998).

In the ATDM module the atmospheric chemistry and physics (gas/particulate partitioning) are estimated based on the parameters available from the core chemistry module: O<sub>3</sub>, OH, and particulate matter. In the case of cadmium, which is not volatile and therefore associates with particulates, the process involves simply emission, transport and deposition of Cd attached to particulate matter (SAI Inc., 1998).

Mercury, cadmium, and dioxin emissions are basically derived from particulate matter species, while naphthalene and Polycyclic Organic Matter (POM) emissions are derived from VOC. Therefore, distinct chemical speciation schemes from particulate matter and VOC speciations are applied. The model was run on US annual average emissions for coal fired ICI Boilers and utility boilers, ICI incineration, municipal waste combustion, medical waste incineration, non-road engines and motor vehicles (Guthrie *et al.*, 1998).

Because of the complexity of dealing with dioxins, this model uses a single dioxin species with physical/chemical properties half way between those of the tetrachloro and pentachloro congeners. These compounds are the least reactive to OH radical and not as sensitive to photolytic dechlorination (SAI Inc., 1998). Guthrie *et al.* (1998) make no reference to how well this model performs with respect to toxic substances.

#### 2.1.3.2. Regional discrete ordinate model

This Eulerian regional model is based on a discrete ordinate / pseudospectral method for the modelling of the atmospheric dispersion of heavy metals over regions of NE US and Canada. The grid resolution is 35 km over domain of 3000 km x 3000 km (Daggupaty and Ma, 1998). In the vertical, the model has 10 non-uniformly spaced levels at 0, 1.5, 3.9, 10, 100, 350, 700, 1200, 2000 and 3000 m (Ma, 1999). The meteorological data used was 6 hourly data set for July 1994 from the Canadian CMC' NWP model known as GEM (Global Environmental Multi-scale Model). Since dry deposition is susceptible to underlying surface properties and surface boundary layer processes, the introduction of flux parameterizations of surface boundary layer provided accuracy to the estimation of deposition fluxes.

#### *Transport of lead*

This model was used to estimate lead contribution of industrial emission sources from the US and Canada to the Great Lakes. The model used the North America lead Emissions data set (NAMEER89, USEPA) for 1989, which is an annual average that covers the US and Canada. A time dependent emission rate was deduced from that data set covering 1° x 1°

grid boxes. The model produced reasonable estimates of lead concentrations and deposition, which were similar to the observed concentrations measured around the Great Lakes (Daggupaty and Ma, 1999).

#### 2.1.3.3. ADOM

The Acid Deposition and Oxidant Model (ADOM) is an Eulerian model which considers meteorology, cloud physics, aqueous and gas phase chemistry, and wet and dry deposition processes. It was initially developed by the Ontario Ministry of Environment, Environment Canada's Atmospheric Environment Service, the Umweltbundesamt of the (then) Federal Republic of Germany, and the Electric Power Research Institute in the early 1980s to simulate acid deposition. A latest version of this model includes the Tropospheric Chemistry Module (TCM), which is a joint effort of Germany, Sweden, Canada, and India (Petersen *et al.*, 1998).

##### *Transport of mercury*

This version of ADOM focuses on the regional transport of atmospheric mercury species. It has been adapted to simulate the three forms of mercury in the atmosphere. Its grid sizes have been in the order of 127 km in the horizontal and 12 layers from the ground up to a height of 10 km. It was developed by systematic simplification of the Chemistry of Atmospheric Mercury (CAM) process model. Typically, this model contains modules designed to calculate explicitly the chemical interactions that move the gas phase mercury into and among the various aqueous phases within clouds as well as calculates the aqueous phase chemical transformations that occur within cloud and precipitation droplets. In a practical note, it is computationally simple enough to be readily incorporated into comprehensive Eulerian models for atmospheric mercury species without significant increase of total computational time (Petersen *et al.*, 1998). "Natural sources" were added to the emissions inventory for the US and Canada used as input to this model. The rate of "natural" emissions of mercury from soils or vegetation was assumed to be a function of temperature. The model included the oxidation of Hg(0) by O<sub>3</sub> to give HgO, known to occur in the aqueous phase. Dry deposition was modelled using deposition velocities, with Hg(II) assumed to deposit at similar rates to HNO<sub>3</sub> and particulate Hg assumed to deposit at rates similar to sulfate. Elemental Hg was only assumed to deposit on forest surfaces.

Predictions of mercury concentration in rainwater compare satisfactorily with observations at 4 European sites (Petersen *et al.*, 1998). However, due to lack of analytical methods capable of identifying individual oxidised mercury species, the impact of HgCl<sub>2</sub> and HgO on the atmospheric cycling of mercury cannot be evaluated at present. This model has shown

that the absorption of mercury species to particulate matter is very important in determining the atmospheric fate of mercury (Petersen *et al.*, 1998).

#### 2.1.3.4. TEAM

The Trace Element Analysis Model (TEAM) is based on a comprehensive, Eulerian, 3-dimensional grid model that was first developed to model acid deposition and subsequently adapted to model ozone at an urban sub-regional scale, visibility, and now hazardous air pollutants.

##### *Transport of mercury*

In modelling mercury Pai *et al.* (1997) incorporated specific modules that would handle dry and wet deposition as well as chemical transformations. When considering dry deposition of all mercury states: Hg(0), Hg(II) and Hg(p), the model calculates hourly dry deposition velocities for eight land-use categories. In a grid cell that may contain more than one category, a weighted average of the individual deposition velocities is used (Pai *et al.*, 1997).

Pai *et al.* (1997) explain the gas-phase reactions that are currently included in the chemistry module, which are the reaction of Hg(0) with O<sub>3</sub>, Cl<sub>2</sub>, HCl and H<sub>2</sub>O<sub>2</sub>. For typical atmospheric conditions, the rate of oxidation of Hg(0) to Hg(II) is small. Under moderate levels of SO<sub>2</sub> concentrations (01.-10 ppb) and liquid water content (0.02 g m<sup>-3</sup>) Hg(II) favours the formation of HgSO<sub>3</sub>. However, when HCl is present it acts as scavenger of Hg(II) from the gas-phase when precipitation occurs. Because Hg(0) has a low solubility and Hg(II) is highly soluble, wet deposition of gaseous mercury is dominated by Hg(II). For the wet deposition module, this model uses the cloud parameters and precipitation from the National Weather Service to determine the volume of the aqueous-phase reactor for the chemistry calculations. The wet deposition flux is the product of the cloud water concentration of the species and the precipitation amount.

This regional model was applied to the Continental US but estimated deposition for some States was larger than the observed. Improvements in the grid resolution will be necessary, but more importantly understanding the speciation and chemistry of mercury. For instance, wet deposition of mercury is twice the annual dry deposition and both wet and dry deposition are dominated by deposition of the divalent form of gaseous mercury Hg(II). Understanding the chemical reactions of the Hg(0)/Hg(II) system will improve the model results (Pai *et al.*, 1997). In a later work, Pai *et al.* (1999) identify five input parameters that significantly influence the model results. These are: emission speciation, Hg(II) dry deposition velocity, concentration of redox species, Hg(II) boundary conditions and precipitation amounts. Among these, the speciation of mercury emissions has a larger influence on the model

results near high deposition regions than in low-deposition regions. Chemistry, on the other hand, has a larger influence on mercury wet deposition in low-deposition regions than in high-deposition regions. This non-linear response clearly suggests that it is critical to know the speciation of mercury emissions. Furthermore, Pai *et al.* (1999) points out that very little is known about other issues such as the role of dimethyl mercury or the influence of size distribution of Hg(p) on observed mercury concentration and deposition.

#### 2.1.3.5. MODELS-3

Models-3 is a “third generation” air pollution modelling system developed by the US-EPA, which uses at least the following models as a base: (a) RADM; (b) The Regional Oxidant Model (ROM); and (c) The Urban Airshed model (UAM) (Cohen, 1997). Meteorological Processes are obtained using the Meteorological Mesoscale Model Version 5 (MM5), developed by researchers at the Pennsylvania State University and the National Centre for Atmospheric Research (NCAR). The initial release of the Models-3 include (1) Community Multiscale Air Quality (CMAQ) system for urban and regional scale; (2) the MEPPS emission modelling system. It is being developed as a highly flexible system and a powerful policy decision support tool capable of dealing with a range of pollutants over various grid scales. The first version was released in June 1998 (Poole-Kober and Viebrock, 1999).

#### *Transport and fate of atrazine*

The modelling of atrazine has three essential components - the emission of atrazine following application, transport by and chemical transformation in the atmosphere, and wet and dry removal from the atmosphere. For this purpose, NOAA contracted Canadian ORTECH Environmental to generate an hourly atrazine emissions data set for the period April 1, 1995-July 16, 1995 using their own Pesticide Emission Model (PEM). PEM was driven by MM5, coupled to a land-surface model (MM5-PX). The episodic atrazine inventory generated by PEM will be input to the U.S. EPA Community Multiscale Air Quality (CMAQ) model of atmospheric transportation, transformation and deposition which is being modified to address trace species issues (Cooter, 1999).

The domain of the present model is 36 km x 36 km rectangular grid extending eastward, from the Rocky Mountains to the Atlantic Ocean and from the Gulf of Mexico through southern Canada. A much smaller 12 km rectangular grid domain will be nested over the immediate Lake Michigan region. This is being done to better resolve important transport features such as lake-breeze effects. Capabilities exist to nest further to a 4 km resolution, but this will be done only if it is determined that significant transport and deposition features are not adequately represented by the 12 km domain. Verification of model estimates of wet

deposition of atrazine will be performed using field samples collected at several lakeshore sites. Although dry deposition measurements were also collected during the study period, very few samples were above detection limits and so we anticipate only limited dry deposition model verification will be possible. It is anticipated that data sets collected through IADN and the USGS (US Geological Survey) during 1995 will be used for model verification outside the immediate lake vicinity (Cooter, 1999).

### *Transport and fate of mercury*

A section of this model is under development for the transport and deposition of elemental mercury and various mercury compounds, and is expected to be tested during 2000 and 2001. At this stage of model development, only the elemental and divalent forms will be treated since known sources of methylated mercury have not been identified and concentrations are small. Certain limited evidence suggests that dimethylmercury may be produced under special biological conditions in water bodies and landfills, which may evade into the atmosphere and rapidly transform into methylmercury compounds. As Bullock (1999) suggests multi-media modelling approaches are necessary to deal with this potential source of methyl mercury. He adds that the partitioning of high-vapor-pressure mercury compounds to the particulate phase is not well understood at this time, and neither are the many gas- and aqueous-phase chemical reactions that are believed to govern oxidation and subsequent deposition of mercury in air and cloud water.

## 2.2. Global scale models

Global scale models that deal with the LRT of POPs and HM study the changes in the chemical composition of these pollutants in the global atmosphere. Their main objective is to describe or predict the evolution of the chemical composition and to provide boundary conditions to regional models. Their role in the assessment of local pollution levels is not as significant as the assessment of regional pollution levels (Moussiopoulos *et al.*, 1996). In the case of organic pollutants, it is necessary that a global model include different components of the global environment such as atmosphere, hydrosphere, cryosphere and soil system (Koziol and Pudykiewicz, 1999). In fact, these models would have modules on each of these components. A brief description of the models used in North America follows.

### 2.2.1. Global chemical transport model

The model was developed to simulate global long term transport of pesticides (hexachlorocyclohexanes in particular) (Koziol and Pudykiewicz, 1999). It mainly deals with alpha and gamma HCH (but it could be extended to include any other compound). The four

model components, i.e. atmosphere, soil, hydrosphere and cryosphere are driven by a Global Reanalysis data set or alternatively the meteorological data, which is the output from Numerical Weather Prediction Models at CMC, and information about usage of HCH. The inventory used was estimated from the amount of application of  $\alpha$ -HCH and  $\gamma$ -HCH during the years 1993 and 1994 (Li, 1999). The model outputs concentration fields of HCH in air, water, soil, and ice.

The atmospheric part of the model is based on equations in the general contravariant form that permit easy changes of the coordinate system. Considering the need to include explicitly the terrain effects, the model uses the terrain-following spherical coordinate system. This particular system is a combination of the Gal-Chen coordinates, commonly employed in mesoscale meteorological models, and the spherical coordinates, typical for global atmospheric models (Koziol and Pudykiewicz, 1999).

In addition to LRT transport, this model also simulates the exchange between air and different types of surfaces such as water, soil, snow, and ice. With this approach, absorption and delayed re-emission of pollutants from the surface to the atmosphere is well represented. In fact, the most comprehensive numerical representation of the exchange is for soil. This realistic soil module simulates both the tracer diffusion and the tracer advection driven by evaporation from the soil, precipitation, and gravity. The LRT was based on two-year meteorological data between January 1993 to December 1994 (Koziol and Pudykiewicz, 1999).

The model validation was done using High Arctic measurements. The agreement between the modelled and measured time series is reasonable and in some cases excellent, e.g. Ny-Ålesund. The model produces concentrations and temporal trends of the order of those measured. Increased resolution from  $2^\circ \times 2^\circ$  to  $0.25^\circ \times 0.25^\circ$  assures a more formal evaluation of source-receptor relationship (Koziol and Pudykiewicz, 1999).

### 2.2.2. The Global/Regional Atmospheric Heavy Metals Model (GRAHM)

The Global/Regional Atmospheric Heavy Metals Model (*GRAHM*) is an Eulerian Multiscale model. It deals with the four gas-phase species of mercury - Hg elemental, HgO, HgCl<sub>2</sub> and Hg particulate and the 10 aqueous phase species.

*GRAHM* has been developed starting from the operational weather forecasting model, the Global Environmental Model (GEM) at CMC (Dastoor, 1999). At present the model solves/integrates dynamic equations for all meteorological processes and physio-chemical processes for mercury species in the atmosphere. The model has variable resolution in



vertical as well as horizontal and uses hybrid vertical levels with 3-D finite element spatial discretization. The time discretization is a two-time-level semi-Lagrangian scheme. The transport scheme for the tracers employs a mass conserving 3-D quasi-monotonic semi-Lagrangian scheme. By making use of the variable resolution grid in the horizontal, the model could be used for simulations on scales from global to urban. Gas and aqueous phase chemistry parameterizations for mercury in the model are adapted from Petersen *et al.* (1998) (Tropospheric Chemistry Module).

Global emissions data for 1990 for anthropogenic sources of mercury available under 'Global Emissions Inventory Activity' program have been used for development of the model. This inventory has limitations because it does not contain information on the speciation of mercury. Furthermore, it provides no information about stack heights, neither point sources, and has insufficient resolution ( $1^\circ \times 1^\circ$ ) (Dastoor, 1999).

This model, which is under development, has as its first goal to produce reliable 3-dimensional concentrations of mercury in the global atmosphere. These 3-D fields will be used to produce high-resolution runs at global, regional or urban scales. Prediction of mercury concentrations will depend on the availability of detailed, accurate and recent emissions data (Dastoor, 1999).

Since the model domain is global and a high-resolution window could be located anywhere on the globe, the model is then capable of simulating Hg transport and transformation globally and for any region of the globe provided emissions data are available.

### 2.2.3. Global multimedia distribution model

This model was developed to determine the global distribution of persistent organic chemicals in Canada. This is a fugacity-based mass balance model that describes the global environment through 10 latitudinal bands (or climatic zones), each of which is divided into a set of well-mixed compartments, representing environmental phases such as the atmosphere, the terrestrial, the freshwater and the marine environments (Wania *et al.*, 1999). Using historical emission estimates on a global scale, it calculates fugacity amounts and concentrations in each of these compartments and chemical fluxes between them. It was recently refined to incorporate an additional climatic zone and a vertically layered atmosphere (Wania and Mackay, 1999).

#### *Transport of pesticides*

The model simulates transport and deposition amounts of  $\alpha$ -HCH into the High Arctic. The temporal trends and magnitude of both atmospheric and seawater concentrations as well as

seawater fluxes in the northern hemisphere are reproduced within an order of magnitude. The deviations are probably based on insufficient knowledge of the influence of climate on the degradation rate of  $\alpha$ -HCH in the aquatic and soil environments, and to the zonal averaging inherent in a two-dimensional model.

#### *Transport of PCBs*

The model includes a forest compartment, which was observed to decrease PCB concentrations in air and water by more than a factor of two. Wania and MacLachlan (1999) are preparing a manuscript on the role of forests in the overall chemical fate of POPs. To model PCBs the model has been modified to include a time-variable function of the soil-air partition coefficient and a two-dimensional distribution of the atmospheric hydroxyl radical. A further modification includes a reduction of the particle-settling rate on the ocean by an order of magnitude (Wania *et al.*, 1999).

### 3. FUTURE TRENDS OF MODELLING

Process understanding will continue to evolve and significantly improved modules for use in POP and HM models. The pace of improvements will depend on having adequate resources, because this modelling is at a relatively early stage of development. For mercury, the full set of aqueous chemistry reactions will need to be elucidated, described in a chemical mechanism, and then incorporated in the models. This development is expected to have a high priority and, progress in this area is very likely to occur. In support of mercury model development, methods for measuring speciated mercury will need to continue to advance, be field-tested and then applied in field campaigns and monitoring programs. In addition, emissions of mercury will need to be fully speciated and a more accurate spatial accounting of the emissions will be required to support advances in modelling and support sensible guidance for policy implementation. Advancement for the semi-volatile pollutants will improve as the fine particulate modules depend on increase in sophistication to provide a more complete set of basic parameters needed to describe the physics of semi-volatiles. Emissions models of the air-surface exchange of POP's will need to continue to be developed and improved to support future modelling.

Three-dimensional models (Eulerian) are likely to predominate over time. This is, in part, because they are able to incorporate increasingly sophisticated process-level understanding and description, and, in part, because they more accurately describe the complex interactions of different air parcels with differing histories and the full context of *in situ* interactions at a given location in space. The improvement in physical and chemical representation is at the cost of a high demand on computer resources. However, it is

expected that the more advanced model codes will be able to take advantage of a variety of computational avenues to meet the demand as the compute power available continues to expand. A shift to more advanced Eulerian models will also require a significant increase in input data requirements, often generated by other models. More importantly, there will be an increased linkage required between the meteorological models, soil models and the chemistry transport model.

An aspect that will likely increase in importance as more experience is gained, a focus on source-receptor relationships. At present, most model applications focus on estimating total impacts from all sources combined. In the future, more emphasis is expected on elucidation of source-relationships because this is a key application question.

As a final note, advances in modelling will not occur alone, but also will be tied to advances in measurement techniques and the uses of models and data together to better understand the important attributes of the system.

#### 4. CONCLUSION

This report, while not attempting to be a comprehensive summary of the models on LRT of POPs and HM used in North America, presents a good cross section of the type of models being developed in this area. Without doubt there are innumerable obstacles to be overcome in terms of speciation of compounds, knowledge gaps on the micro-chemical and micro-physical processes, deposition and re-emission processes, and emission inventories before good agreements between the simulated and the observed data may occur.

It is only fair to accept that this field of modelling is just beginning. There are a great deal of uncertainties that limit the accuracy of the use of any of the models discussed here to predict the long-range transport of persistent organic pollutants and heavy metals in contrast to the more mature models such as weather prediction models or acid deposition models.

Table 2. Summary table of all models

#	Model	Compounds Considered	Source Regions	Receptor Regions	Results Available
1	Back Trajectories	Mercury, Cadmium, PCB's and organochlorine biocides	US and Canada	Michigan, Lake Ontario, Dorset Ontario, Illinois, Egbert Ontario.	Information of the source regions contributing the observed concentrations at the receptor location
2	PSCF	Mercury	Eastern North America	Southern Ontario LA, CA	Good correspondence
3	RELMAP	Mercury	US	US	Over-estimating wet deposition
		Dioxin & furans	US	US	Needs further work
		Arsenic, cadmium, chromium, lead and nickel	US, Canada	Lake Michigan	Deposition to Lake Michigan
4	ASTRAP	Mercury	Eastern US and Canada	Great Lakes	Total deposition
		Toxaphene	US	Great Lakes	Total predicted deposition, few source-receptor relationships established
		Lead	US and Canada	Great Lakes	Total predicted deposition
5	HYSPLIT	PCDD/F, HCB, Endocrine-disrupting Biocides	US and Canada	Great Lakes, Canadian Arctic, Dairy Farms in Wisconsin and Vermont, Drinking Water Reservoirs in midwest and northeast	Atmospheric concentrations and predicted deposition; source-receptor relationships
6	Hybrid-Receptor Modelling Approach	Semivolatile Organic Compounds	Great Lakes	Lakes Michigan, Erie and Rouge River Watershed	Deposition from hypothetical "virtual" sources that could explain observed atmospheric concentrations at the particular locations.
		Trace Elements, Cadmium, Mercury			
7	REMSAD	PCDD/F, Mercury, Cadmium, Polycyclic Organic Matter, Atrazine	US	US	?

#	Model	Compounds Considered	Source Regions	Receptor Regions	Results Available
8	Regional Discrete Ordinate Model	Lead	US and Canada	Great Lakes	Total predicted deposition; plans to use it with other heavy metals
9	ADOM	Mercury	Eastern US and Canada	Eastern US and Canada	Hg(0) and predicted wet deposition had good agreement
10	TEAM	Mercury	US	US	Over-estimating
11	MODELS-3	Atrazine	US	Great Lakes	IADN data for 1995 will be used to estimate deposition
12	Global Chemical Transport Model	$\alpha$ -HCH, $\gamma$ -HCH	Global	Global soils, water, snow and ice	Long-term pesticide deposition
13	GRAHM	Mercury	Global	Global, regional and urban	Aiming for a 3-D concentration of mercury in the global atmosphere
14	Global Multimedia Distribution Model	$\alpha$ -HCH Pesticides	Global	Global	Global concentrations and fluxes

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## 4. PRESENTATION OF BACKGROUND DOCUMENTS

### 4.1. Status of Current Activities on Emissions Inventories for Organic and Inorganic Toxic Compounds in Europe

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#### 1. INTRODUCTION

*Why are emission inventories needed?*

Detailed and accurate emission inventories for organic and inorganic toxic compounds are needed for several reasons. First, one of the key users of emission inventories are dispersion modellers that use these data to address source-receptor relationships at various scales. Further, emission inventories are also needed as useful documentation between states that have agreed to reduce the emissions of these toxic compounds. While strong efforts have been made to improve inventories needed for research on ozone depletion (CFCs), climate change (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) and acid deposition (SO<sub>2</sub>, NO<sub>x</sub>), inventories for inorganic and organic toxic compounds are still unreliable and inaccurate (e.g. Graedel et al. 1993, Pacyna & Graedel, 1995).

The relative poor quality of the current data on toxic compounds is obviously mitigating the confidence in model outputs, e.g. the reliability concerning impact of current or altered emissions on environmental levels. However, improvements have been made in recent years, and the objective of this document is to highlight the status of current data related to emission inventories for inorganic and organic toxic compounds in Europe.

*National reported data versus so-called expert estimates*

When establishing atmospheric emission inventories, national reported emissions are preferably used, as national experts are expected to know detailed characteristics in their respective countries concerning fuel types, industrial processes and abatement technologies. The Task Force on Emission Inventories (TFEI) of the UN-ECE was established to harmonise methodologies and assist Parties to report their national emissions to EMEP (*the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe*). An important tool developed for this purpose is the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook. Unfortunately, the emission data that are received at EMEP do not have a complete temporal/spatial coverage. There might be several reasons for this, one being the fact that still, the guidebook is far from complete concerning the coverage of potential sources of POPs and Heavy Metals and needs an update of several chapters. This fact was highlighted in the Progress report by the



Co-Chairmen of the Task Force on Emission Inventories (TFEI) to the Steering Body to EMEP, following the annual meeting of TFEI in Denmark, this summer (UN/ECE, 1999). At his meeting which was attended by 120 experts representing 38 countries, it was further recognised that a stronger effort was needed to make the reporting guidelines, including associated templates and forms, clearer. Also, member states were asked to report emissions at a greater level of source detail, i.e. from SNAP level 1 to SNAP level 2 (UN/ECE, 1999). Other items of particular interest that were raised at this meeting included likely future need for integrated inventories (UN/ECE, 1999), i.e. covering emissions and discharges to all relevant receiving media. This issue is considered of high relevance for studies aiming at quantification of source-receptor relationships for POPs.

So-called expert estimates should not substitute national reported data. However, as long as the proper national bodies are not able to fulfil their obligations to report the national emissions to EMEP, expert estimates may play an important role for source-receptor modellers and for other research purposes. However, many of the sources of heavy metals and particular selected POPs are not yet well characterised (UNEP, 1999; Brzuzy & Hites, 1996). Emission inventories established by various research institutes (e.g. AEAT, TNO, NILU) are therefore still uncertain. Therefore, further source studies seem to be needed.

### *Basic Methodology*

The approach on how emission inventories are being established varies dependent on the compound of interest. However, there are a few general aspects of the methodology. The ideal approach for estimating the actual emissions from a given plant is through monitoring and measurements of the chemical composition of the exhaust gas and the accompanying flow. If such site-specific data are not available, preferably emission data reported from national experts are used as indicated previously. In other cases, emissions of a given pollutant are usually estimated by the use of activity data and emission factors. Activity data are usually found in national and international statistical yearbooks, and emission factors can be found in emission inventory guidebooks (e.g. Parma et al. 1995; UN/ECE, 1996). During the emission inventorying, numerous question arise which are typically due to:

- 1) Lack of proper activity data (*often problem when trying to calculate historical emissions or to obtain activity data from some countries*)
- 2) Unknown or minor sources that are excluded (*no information on activity or emission factors*)
- 3) If there is consistency between the activity data and the emission factor. (*That is a concern whether the emission factors is applicable for a reported statistical activity*)

- 4) Further, a shift in various emission factors are expected over time and from country to country due to potential control measures, type and technical standard of the production processes and the control devices. This information, if available, is taken into account to the extent possible.

The uncertainties, whether due to a general lack of proper data or methodological errors, result in varying quality of the emission data. In inventories, each estimate is therefore often accompanied by a simple quality code based on the assessment of the quality of the collected or generated emission data. These codes could then be transferred to quantify the uncertainty, e.g. of the total emissions in a country.

## 2. COMPLETED INVENTORIES WITH EUROPEAN DIMENSION

Overview tables of some completed and ongoing activities on European emission inventories, along with their major characteristics are listed in the Appendix. A brief historical overview of selected European inventories is given in the following sections. The emphasis here is on inventories that have been a part of research projects studying regional (European) source-receptor relationships. Obviously, there are several other inventories available, broadly categorised as;

- Various national inventories (by category, or by compounds(s)),
- National reported emission data at the EMEP-MSC/W in Oslo (EMEP/MSC-W, 1999).

However, a discussion about these inventories is considered to be out of the scope here.

### 2.1. Heavy Metals

A first European inventory of heavy metals emissions was prepared by Pacyna in 1983, and covered 16 trace elements from 12 source categories (Pacyna, 1993). This inventory was later updated and improved by Axenfeld et al. (1989)<sup>2</sup> and then used by modellers from GKSS. Transport and deposition of several metals to the North Sea and the Baltic Sea was estimated using the GKSS model. The emission inventory included As, Cd, Zn, Pb and Hg emitted at the beginning of the 1980s, and the emission maps were prepared within the grid system of 150 by 150 km. The Hg inventory was later updated by Axenfeld et al. (1991), covering both natural and anthropogenic sources, with the 1987 as a reference year. It included 868 point sources. Emission data was spatially distributed within the EMEP grid system (150 x 150 km) as well as ( $\frac{1}{2}^{\circ}$ Long. x  $\frac{1}{4}^{\circ}$ Lat.).

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<sup>2</sup> The so-called Dornier report

Further development of European emission inventory for Cd, Cu and Pb, was one of the main tasks within the ESQUAD-study (European Soil & sea Quality due to Atmospheric Deposition) (Berdowski et al. 1994). This study presented European anthropogenic emissions of these elements for the year 1990 ( $1^{\circ}\text{Long.} * \frac{1}{2}^{\circ}\text{Lat.}$ ). Later on, IIASA has carried out a project aiming at the estimation of historic cumulative deposition of Cd, Pb and Zn in Europe (Olendrzynski et al. 1995; Olendrzynski et al. 1996). For this study, historical emission data were estimated for thirteen major European countries for the years 1955, 1960, 1965, 1970, 1975, 1982 and 1987. These data were later updated by Pacyna for other projects at both IIASA and GKSS to cover the whole of Europe. In addition to three metals Cd, Pb and Zn, As was included, as well as emissions for 1990 and scenarios for year 2000, 2005 and 2010 (Pacyna, *personal communication*).

Further step in the development of European inventories for heavy metals was the estimate presented by TNO for the Umweltbundesamt (Berdowski et al. 1997). This study, which also included POPs, was presenting data for 1990 and included maps ( $50 * 50\text{km}$ ), figures and tables. The substances were those identified as priority substances by OSPARCOM and HELCOM. In the case of missing data from the national authorities in the UN ECE countries, Berdowski et al. (1997) performed their own estimates, based on default methodologies emission factors (Berdowski et al. 1995). In the national overview tables, presented on a category-by-category basis according to the SNAP nomenclature, data are classified as:

- Data submitted by the country.
- Data estimated by TNO, not approved by the country.
- Subdivision of country (sub)total based on TNO estimates, not approved by the country, and
- Summation of country data and TNO data not approved by the country.

## 2.2. Persistent Organic Pollutants

One of the first European inventories for POPs was presented by Duiser and Veldt (1989) for the Dornier-report (Axenfeld et al. 1989). It covered emissions of selected PAHs, PCBs,  $\gamma$ -HCH (Lindane) and HCB in Europe for the reference year 1982. European emissions of Lindane ( $\gamma$ -HCH) and Benzo[a]Pyrene (B[a]P) for the year 1990 were later included as a part of the previously mentioned ESQUAD-study (Berdowski et al. 1994).

Recently however, the study by Berdowski et al. (1997) has gained most interest. This study for 1990 cover several POPs, namely:

- Polycyclic Aromatic Hydrocarbons (PAHs)

- Polychlorinated Biphenyls (PCBs)
- Endosulfan
- Fenthione
- Quintozene
- Lindane ( $\gamma$ -HCH)
- Hexachlorobenzene (HCB)
- Pentachlorophenol (PCP)
- Dioxins and Furans (PCDD/Fs) [In g I-TEQ/year]
- Tetrachloroethene ( $C_2Cl_4$ )
- Trichloroethene( $C_2Cl_3H$ )
- Trichlorobenzene
- 1,1,1-Trichloroethane
- Tetrachloromethane, and
- Xylene

One of the major strengths of this study is thus the wide coverage of different POPs, both in terms of chemical compositions and sources (e.g. solvents, unwanted combustion by-products, intentional produced POPs and pesticides).

Very recently, a new inventory for POPs in Europe was completed (Pacyna et al. 1999). Selected details from this inventory are presented in section 3.2.

In addition to these European inventories, there have also been studies conducted with global resolution for selected pesticides as HCHs (e.g. Li, 1999), Toxaphene and DDT (Voldner and Li, 1995). Many of these data are available on  $1^\circ \times 1^\circ$  resolution on request from GEIA (the IGBP Global Emission Inventory Activities programme). A simple global inventory for PCDD/Fs was presented by Brzuzy & Hites (1996). Very recently an inventory of national and regional PCDD/Fs data became available from the UN Environment Programme (UNEP, 1999).

### 3. CURRENT ACTIVITIES AT NILU

#### 3.1. Heavy Metals

##### *Global emission inventory activities*

A global emission inventory for Hg from anthropogenic sources world-wide is now carried out for the Arctic Monitoring and Assessment Programme (AMAP). This inventory will result in the information on various chemical forms of Hg emitted from major anthropogenic source

categories, country by country estimates for 1995 from major source categories and emission gaps with data distribution using the 1° by 1° grid system.

A global emission inventory for 15 other (than Hg) trace metals from anthropogenic sources in 1995 is carried out for the International Lead and Zinc Research Organization (ILZRO). These estimates are carried out for major source categories in the countries world-wide.

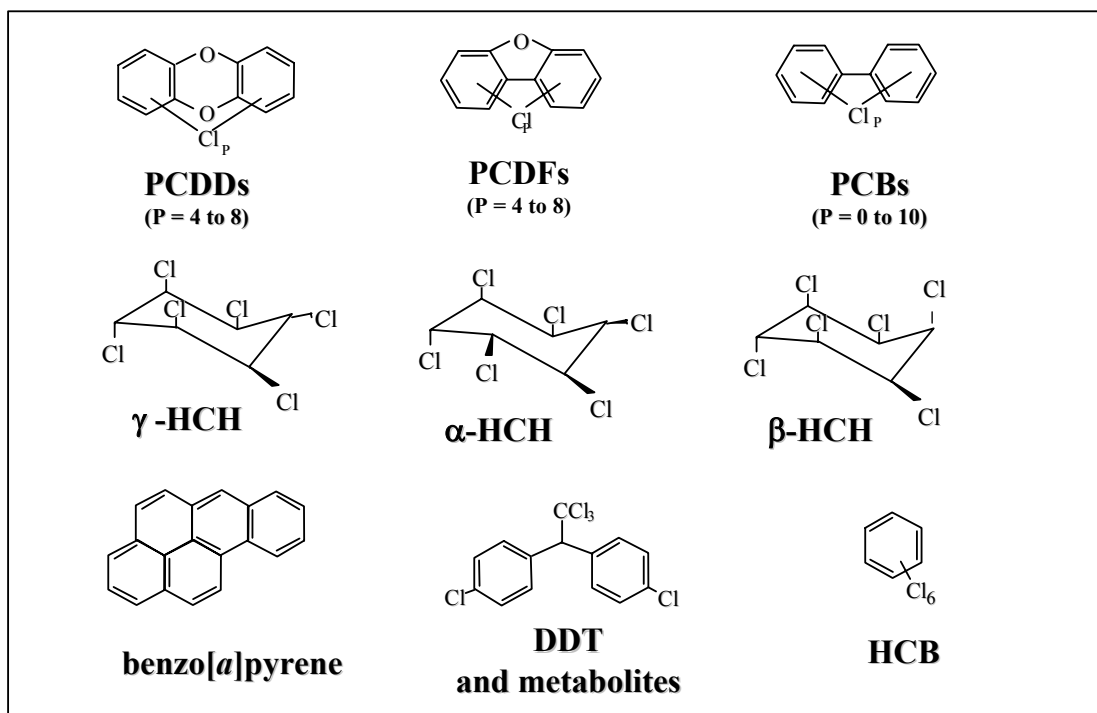
#### *European inventory for mercury (MAMCS/MOE)*

Currently, there are two ongoing projects within EU DG XII on Mercury. One is focusing on the environmental “multi-media” cycling of Mercury (MAMCS) in the Mediterranean Sea region. The other project is the Mercury Over Europe (MOE) project. Within these two projects, a joint emission inventory is now being prepared at NILU. The final inventory will include current speciated emissions ( $\text{Hg}^{2+}$ ,  $\text{Hg}(\text{p})$  and  $\text{Hg}^0$ ) from area sources, point sources (*e.g. including geographical co-ordinates, stack heights and diameters, as well as exhaust gas velocities and temperature*) and natural sources (*e.g. soil emissions, aqueous emissions and volcanoes*). Most likely, this inventory shall be of great interest for regional atmospheric modellers.

### 3.2. Persistent Organic Pollutants

POPs form a diverse class of compounds to be inventoried with respect to their sources, congener/isomer composition and physical-chemical properties, influencing their fate in the environment. This was clearly recognised during the development of a European emission inventory for selected POPs during the project “Popcycling-Baltic” (Pacyna et al. 1999).

Figure 1 shows the POPs that were selected within the “Popcycling-Baltic” project. Within this project, emphasis was on the emissions of individual congeners or isomers as depicted for HCH in Fig. 1. The reason for this was that we needed to produce an inventory intended for models that utilised information on physical-chemical properties at congener or isomer resolution. Obviously, this was a difficult task with respect to the lack of data from the literature. This is discussed with some examples given beneath on how we approached the issue. Next, we also had to determine the current (1995/1996) as well as historic emissions, going back to the 1970’s. This was done principally for modelling purposes. There was a need, not only to address the current spatial distribution of deposition over Europe due to current emissions, but also to address historical contamination levels of various compartments and the current re-emissions from natural surfaces in parallel.



**Figure 1.** Selected POPs within the Popcycling-Baltic project

#### *Example of pesticide POPs - HCHs*

HCHs (Hexachlorocyclohexanes – Fig.1) is an insecticide that was heavily used within Europe (Breivik et al. 1999) and other parts of the world (Li, 1999). Principally, two formulations have been made for the use as an insecticide. One is technical HCH that is the unpurified technical mixture of various isomers (about 55-80%  $\gamma$ -HCH, 5-14%  $\gamma$ -HCH, 8-15%  $\gamma$ -HCH as well as minor quantities of  $\gamma$ -HCH and  $\gamma$ -HCH). Within this “raw” product, only  $\gamma$ -HCH has any significant insecticidal properties. The other HCH-insecticide is lindane or essentially pure  $\gamma$ -HCH.

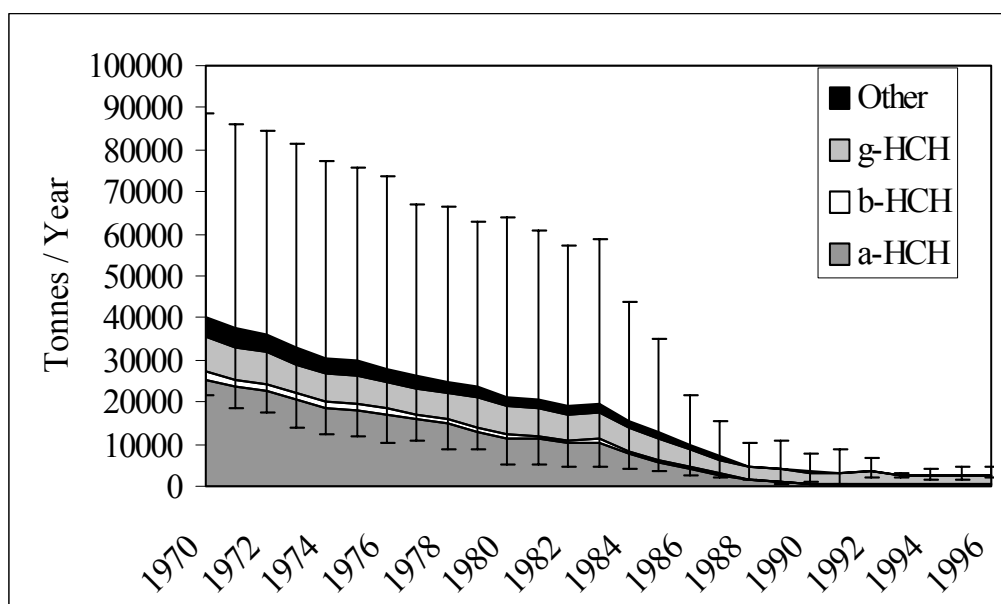
Unfortunately, only a few countries report their annual usage of each of these formulations based on active ingredient with isomeric resolution. Thus, we first collected all data that could be found on national annual consumption of lindane or technical HCH. Next, we collected data on insecticide usage in various countries, or data on usage of chlorinated hydrocarbons (*which is a subgroup of the insecticides*). In order to fill out both temporal and spatial gaps, we developed regional ratios (West, former Eastern, Mediterranean and Nordic regions) as well as grouping the ratios from 1970-1979, 1980-1985, 1986-1990 and 1991-1996. Finally we estimated the consumption of various isomers based on information on the relative consumption of technical HCH versus lindane as well as regional/national measures

against the usage of each of the two principal HCH-formulations. The intention was to assess the level and trend of the consumption over Europe. The result is given in Fig. 2.

With this extrapolation method, the risk of significantly over- or underestimating the consumption at the national level for a given year is high. As can be seen the uncertainty bands that are depicted do also indicate a high uncertainty in the estimated historical consumption of total HCH. A more detailed description of these estimates can be found in Breivik et al. (1999).

The uncertainties in the usage estimates are further amplified when we utilise these data to estimate the interannual emissions of HCHs to the air, e.g. for use in regional atmospheric transport models. To estimate the actual losses of HCHs to air within a year, based on the annual consumption is difficult for several reasons, e.g:

- 1) When is the insecticide used?
- 2) How is the insecticide applied?
- 3) Where is the insecticide used in a country?



**Figure 2.** Estimated annual usage of various isomers in Europe, 1970-1996

A rigorous treatment would require that each individual farmer using the insecticide would need to be localised and answer how he used HCHs (direct incorporation into the soil, seed treatment, spray application?) as well as the amounts that were applied at a given point of time. Further, the losses to air e.g. from spray application would be significantly influenced by e.g. the wind speed, the humidity as well as the temperature at the time of application. This

would need consideration as well. Obviously this information is impossible to obtain at a European scale for a 25 years period, and we have problems with parameterisation similar as modellers. Therefore, all we can do is to give some estimates on losses to air and/or other compartments and document our assumptions in hope that the estimates can be improved in the future as knowledge and methods is improved.

If we simply neglect losses/emissions of HCHs during the actual production and manufacturing process as well as any potential losses to the environment from handling, storage and disposal, the major loss process to air will be from application in the field. Our principal tasks within the project concerning HCH emissions were to:

- a) Estimate fractions of annual national consumption used for various applications (*soil, seed and other treatment*)
- b) Estimate losses to air and other compartments from these applications, based on literature research on field and chamber studies (e.g. Boehncke et al. 1990, Rüdell, 1997)
- c) Estimate spatial distribution of consumption / emissions by using crop area distribution as surrogate parameter for national usage/emissions (50x50 km resolution)
- d) Estimate time of application by including an annual distribution function for annual emissions.

#### *Example of unwanted by-products of combustion: Dioxins and Furans*

An emission inventory for dioxins and furans was also included within the Popcycling-Baltic project. This example is trying to highlight how emission inventories might be developed and aimed for various users with PCDD/Fs as an example.

For dioxins and furans, there are several sources, and many are not well characterised. For instance, a global mass balance study by Brzuzy & Hites (1996) indicated that the deposition of these compounds were about four times greater than the sum of known major sources accounted for in that study. This study focused on emissions to air only. Recently, two integrated inventories were established for dioxins and furans (AEAT, 1999; Environment Canada, 1999).

From previous inventories, the outcome are generally presented in international toxicity equivalents (UNEP, 1999). This is because these compounds are often found in complex mixtures. For risk assessment, a toxicity equivalence scheme was developed to describe the cumulative toxicity.



Although a good indicator of toxicity, the individual compounds does not behave in an I-TEQ manner in the environment. Therefore, for modeling purposes within the popcycling project, we also attempted to quantify the emissions of the individual dioxins and furans of particular interest. That is the 2,3,7,8 substituted ones by the use of “isomer group emission profiles” referring to tetras (TeCDD) pentas (PeCDD) etc, and “individual congener profiles” like the 2,3,7,8, TeCDD congener (*Emission profiles by congener weight*).

The group profiles tend to vary from source to source, but in general for combustion processes, the individual congener profiles for a given group are often very similar (Rappe, 1994).

Emission factors in I-TEQ are more readily available in the literature than emission factors for individual isomers and congeners. Partly, this might be explained that most inventories for dioxins and furans are aimed for governments as well as industries for risk assessment purposes. However, for the atmospheric modelling community, this is insufficient information. An emission value given in I-TEQ should provide no useful information to modellers, and unfortunately it is not possible to back calculate the emissions from I-TEQ over to weight unit. Thus future inventories for PCDD/Fs should ideally always report both emissions in weight as well as I-TEQ for multiple use purposes.

By selecting both methods (*directly applied I-TEQ factors as well as isomer/congener weight profiles*) in the “Popcycling-Baltic project” with factors from numerous sources we could estimate the I-TEQ emissions with two different set of factors. In spite of fewer activities included in the emission inventory based on emission profiles by congener weight, we obtained higher emissions in I-TEQ with this method than by calculating I-TEQ emissions directly.

We compared our directly-derived I-TEQ estimated emissions of PCDD/Fs for the year 1990 with a similar inventory by Berdowski et al. (1997). While the estimated total emissions for Europe were only deviating with 2.5% for Europe total, the discrepancy between estimates for individual countries could be substantial. For five European countries, the discrepancy was more than 100 %. The potential implication on model results seems obvious if these inventories were in weight units. In most cases, the discrepancies for the estimated national emissions are most likely due to discrepancies between emission factors used for single source categories.

#### *Example of intentionally produced POPs: PCBs*

As a result of the reduction or termination of production and the ending of open-system applications, the major sources of PCB emissions to various compartments have shifted from

open applications to unintentional releases from closed systems (Annema et al. 1995). Nowadays, the most important emission sources of PCBs to air are in general most likely:

- secondary re-emissions from terrestrial and aquatic compartments including landfills,
- evaporation from PCB-containing equipment still in use, storage or destroyed (i.e. fires) as well as
- unintentional by-products of various combustion processes.

The first source category should in principle be attributed to historical emissions from the second and the latter group. The study by Berdowski et al. (1997) suggest that for the early 1990s, electrical equipment was the overall source of PCBs to the air with more than 90% of the total emissions in Europe. Further, that emissions from various combustion processes as well as re-emissions are of less quantitative significance. In terms of total PCB emissions this could very well be the case. Within the Popcycling-Baltic project we utilised data on the chemical composition of various technical mixtures of PCBs (e.g. Schulz et al. 1989) to estimate congener emissions. However, combustion sources could e.g. be enriched in selected PCB-congeners, relatively to congeners originating from electrical equipment (e.g. Brown et al. 1995).

Historical data on production, usage and releases of PCBs seems therefore needed for the interpretation of present and future contamination levels in remote areas (Voldner & Li, 1995; Wania & Mackay, 1996; Vallack et al. 1998). Recent national and regional studies on atmospheric sources and emissions of PCBs in Europe have so far principally focused on total PCBs (Duiser & Veldt, 1989; Annema et al. 1995; Berdowski et al. 1997; Pacyna et al. 1999).

Currently, NILU is involved in the establishment of a dynamic global PCB emission inventory with congener resolution. This will be an inventory that couples information on congener production and emissions from both historically produced PCBs as well as emissions from various combustion processes. This inventory shall be completed within the next year, and data will be available on a 1°x1° latitude-longitude resolution.

#### 4. DISCUSSION

During the last decade, emission inventories for selected heavy metals and POPs for the European region have become available and improvements have been made. Emission data for these compounds seem to be more frequently reported by national authorities to EMEP (EMEP/MSW, 1999) and other international programs and organisations, and are also

available from various national inventories. However, there is still a lack of comparability between various inventories, e.g among:

- Data that are reported by national authorities (e.g. SNAP-level),
- Inventories by various research institutes,
- Compound specific inventory approaches, and
- National inventories

This clearly reduces the transparency when comparing or compiling emission inventories. Some of the causes for this weakness can be related to the fact that emission data are requested and aimed at various users, e.g:

- Policy makers (*requesting category based emission data*)
- Modellers (*need various temporal and spatial distribution of data*)
- Verification of implementation of environmental strategies (*e.g. requesting temporal trends in data*)
- Risk-assessment community (*need other units, e.g. I-TEQ*)

*When comparing inventories, significant discrepancies for given source categories are likely to be found. These discrepancies are in many cases due to the use of inaccurate emission factors that results in incorrect emissions for a given category. At a later stage this could influence the total emission for a given country that have this activity as a principal source.*

*Emission inventories supplied by various research institutes (e.g. TNO, AEA, NILU) may serve as an important aid, e.g. for modelling activities by filling out temporal and spatial gaps in national reported data. However for the pollutants considered, there is still an insufficient characterisation of sources as well as accompanying emission factors that results in high uncertainties of the estimates. For known sources, variations in technologies within Europe and over time make emission inventories uncertain due to the applicability of available factors. However, recent efforts are likely to improve the situation for heavy metals. For example, a guidebook on heavy metal emissions from the CIS countries has recently become available (Kakareka et al. 1998). Such regional specific factors are not readily available for POPs.*

*Improved emission data for POPs have become of increasing importance as emission- or source driven fate models for with regional and global resolution are being developed (Wania & Mackay, 1995; Cowan et al. 1995; Strand & Hov, 1996). Many of these models are focusing on temperature-dependent cycling processes between various media, and thus are using physical-chemical properties of isomers/congeners as input, due to the highly variable behaviour of individual compounds in the environment (Wania & Mackay, 1996). Thus, there*

*seems to be a need to strengthen the efforts on developing integrated inventories (for the atmospheric, terrestrial and aquatic compartments) with congener resolution. These models also address current and future contamination levels, so there is also a need to obtain historical emission data, reflecting the potential lifetime of these pollutants in the environment.*

Inventories are also developed to serve as useful information for decision makers in order to reduce the impact of these pollutants on the environment, but we are aware that some of the data are too uncertain at present to address issues as cost-effective control options. In order to achieve this, more work is clearly needed. A good starting point may be to start by comparing the existing European inventories to identify source discrepancies and the needs for further source investigations. This could perhaps be approached much in a similar manner as intercomparison studies of models (e.g. EMEP/MSC-East, 1999).

The following are subjective suggestions and potential items for discussion on how improvements may be achieved on the reliability of European emission inventories for heavy metals and POPs and thus in the estimated source-receptor relationships:

- 1) At present, emission inventories seem to be less prioritised on the research agenda. However, the quality of model results depends heavily on the accuracy and completeness of emission data. Therefore, the emission data should be in focus as much as modelling activities in order to obtain acceptable model estimates.
- 2) The efforts in various countries to report emissions of POPs and heavy metals should be encouraged. In addition, national authorities should give high priority for reporting emission data in compliance with international agreements on emission reductions. This could be facilitated by:
  - a) Improvement and extension of existing guidelines (Joint EMEP/CORINAIR Atmospheric Emission Inventory Guidebook).
  - b) Enhancing the contact with the national and international industries and other sectors and request them to report their releases to the environment.
  - c) Stronger support for research projects on emissions.
- 3) Stronger scientific co-operation between the modelling and emission inventory community may improve our understanding of links between sources and transport. For example, more work on natural emissions of Hg and temperature driven re-evaporation processes of POPs as well as emission processes for POPs that are released from

diffusive processes other than industrial combustion shall be attempted (e.g. pesticides from field application, and PCBs in products during use or after disposal).

- 4) Further harmonisation / standardisation of reporting, categorisation and estimation methods should be approached to facilitate transparency, cross-checks and integration of national inventories to a European scale.
- 5) Integrated inventories for “Multi-hop” pollutants (e.g. selected POPs and Hg-species) should be approached to improve source-receptor relationships.
- 6) Intercomparison studies of emission inventories should be undertaken to identify source discrepancies and needs for further source investigations.

Finally, emission inventories need frequent updating to resemble the current situation in pollution levels. In particular, this should be the case for those toxics for which various measures are strongly influencing the overall emissions, such as Pb, PCDD/Fs and selected pesticides.

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## Appendix: Selected inventories for POPs and HMs

<i>Brief description of inventory:</i>	<b>Congener specific emissions of POPs</b> - prepared by Pacyna et al. (NILU/Norway)
<i>Contaminants or issues that have (or can be) addressed:</i>	POPs (B[a]P; $\alpha$ -, $\beta$ -, and $\gamma$ -HCH; PCB; HCB; DDT; 2,3,7,8-substituted PCDD/F congeners; PCDD/Fs (I-TEQ))
<i>Geographical extent or areas covered:</i>	Regional (Europe)
<i>Geographical resolution:</i>	50 x 50 km
<i>Temporal resolution:</i>	Emissions calculated for every fifth year; annual for HCHs
<i>Periods covered by inventories:</i>	1970 – 1996
<i>Input data sets:</i>	National reported data or data calculated by activity using emission factors
<i>Notes (limitations, sources of uncertainty, future developments, etc.):</i>	Data emphasising regional and temporal trends for modelling; high uncertainty at the congener level.

<i>Brief description of inventory:</i>	<b>Emissions inventories for Hg</b> (a) prepared by Axenfeld et al. 1992 (b) prepared by Pacyna (NILU, Norway) (c) prepared by Pacyna et al. (joint MAMCS/MOE)
<i>Contaminants or issues that have (or can be) addressed:</i>	Hg
<i>Geographical extent or areas covered:</i>	(a) Regional (Europe); (b) Global; (c) Regional (Europe)
<i>Geographical resolution:</i>	(a) 150 x 150 km; (b) 1° x 1°; (c) 50 x 50 km
<i>Temporal resolution:</i>	Annual (various)
<i>Periods covered by inventories:</i>	(a) 1987; (b) 1990; (c) 1995
<i>Input data sets:</i>	National reported emissions, activity data, emission factors
<i>Notes (limitations, sources of uncertainty, future developments, etc.):</i>	(a) Speciated Hg inventory Hg <sup>0</sup> , Hg <sup>2+</sup> , Hg(p)), 7 major source categories (b) Total Hg only, 7 major source categories (c) Detailed speciated inventory (Hg <sup>0</sup> , Hg <sup>2+</sup> , Hg(p)), including point, area and natural sources; not yet completed

<i>Brief description of inventory:</i>	<b>Emissions inventories for metals other than Hg</b> (a) prepared by Olendzynski et al. 1995 (IIASA) (b) prepared by Pacyna for IIASA/GKSS (update of (a))
<i>Contaminants or issues that have (or can be) addressed:</i>	(a) Cd, Pb, Zn (b) As, Cd, Pb, Zn
<i>Geographical extent or areas covered:</i>	(a) and (b) Regional (European)
<i>Geographical resolution:</i>	(a) 150 x 150 km
<i>Temporal resolution:</i>	(a) Emissions calculated for every fifth year
<i>Periods covered by inventories:</i>	(a) 1955 -1987 (every fifth year); (b) 1990, 2000, 2005, 2010
<i>Input data sets:</i>	National reported emissions, activity data, emission factors
<i>Notes (limitations, sources of uncertainty, future developments, etc.):</i>	



<i>Brief description of inventory:</i>	Emissions inventories - prepared by <b>Berdowski et al. 1997</b> , (TNO, Netherlands) for UBA, Germany
<i>Contaminants or issues that have (or can be) addressed:</i>	<b>POPs, Hg and other heavy metals</b> , see text
<i>Geographical extent or areas covered:</i>	Regional (Europe)
<i>Geographical resolution:</i>	50 x 50 km
<i>Temporal resolution:</i>	Annual
<i>Periods covered by inventories:</i>	1990
<i>Input data sets:</i>	National reported data or data calculated by activity using emission factors
<i>Output data sets:</i>	Gridded emission inventories
<i>Notes (limitations, sources of uncertainty, future developments, etc.):</i>	Documentation (report) includes both national reported and estimated data

<i>Brief description of inventory:</i>	<b>National emissions reported to EMEP</b>
<i>Contaminants or issues that have (or can be) addressed:</i>	Priority heavy metals and POPs
<i>Geographical extent or areas covered:</i>	Regional (Europe)
<i>Geographical resolution:</i>	National (various, but not all, European countries)
<i>Temporal resolution:</i>	Annual
<i>Periods covered by inventories:</i>	Various, mainly from 1990 and onward
<i>Input data sets:</i>	
<i>Output data sets:</i>	National emissions data
<i>Notes (limitations, sources of uncertainty, future developments, etc.):</i>	Reported by national experts to EMEP; reasonably reliable as the experts involved know the relevant technologies in their respective countries

<i>Brief description of inventory:</i>	Emissions inventory – in prep. by Pacyna, Breivik (NILU, Norway)
<i>Contaminants or issues that have (or can be) addressed:</i>	<b>PCBs (22 congeners)</b>
<i>Geographical extent or areas covered:</i>	Global
<i>Geographical resolution:</i>	1° x 1° (most likely with assistance from dr. T. Scholtz, CGEIC, ORTECH)
<i>Temporal resolution:</i>	Annual
<i>Periods covered by inventories:</i>	Latest possible
<i>Input data sets:</i>	Production data with congener resolution, national reported emissions, activity data and emission factors
<i>Output data sets:</i>	
<i>Notes (limitations, sources of uncertainty, future developments, etc.):</i>	Not yet completed; inventory aimed for global modelling purposes at congener resolution

## **4.2. Measurement Programme for Heavy Metals and Persistent Organic Pollutants in Air and Deposition in Europe**

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### **1. GENERAL INTRODUCTION**

Measurements of Persistent Organic Pollutants (POPs) and Heavy Metals (HM) in air and deposition have previously been discussed in background documents prepared for EMEP workshops. The results from the workshops held in Durham, USA, and in Beekbergen, the Netherlands, have been well documented and the major conclusions are still valid (Pacyna et al., 1993; de Leeuw et al., 1996). For the Beekbergen workshop, a chapter of the background document was dedicated to ongoing measurement programs for heavy metals and persistent organic pollutants, but the focus was mostly on heavy metals (Iverfeldt, Chapter 5 in de Leeuw et al., 1996). Available results and especially the uncertainties were also considered, from which recommendations were derived. A general impression was that the ongoing measurement activity on heavy metals related to atmospheric emissions and long-range transport was large, but the data comparability was low. For POPs, the situation was that only a few species were measured at a very limited number of locations.

The background document on "Measurement Program for Heavy metals and Persistent Organic Pollutants in Air and Deposition in Europe" prepared for the third EMEP workshop on Heavy Metals and Persistent Organic Pollutants, which was held in Moscow, Russia September 1996, has been published in the Report and Proceedings of the Workshop on the Assessment of EMEP Activities concerning Heavy Metals and Persistent Organic Pollutants and their further Development (Varygina and Soudine EMEP/MSC-E report 1/97).

The general conclusions from the EMEP meeting in Moscow, Russia September 1996 were:

1. The major conclusions from the EMEP Workshops in Durham and Beekbergen on measurements of heavy metals and persistent organic pollutants (POPs) are still valid. The ongoing measurement activities on heavy metals related to atmospheric emission and long-range transport are considerable, but the data comparability is low. For POPs only a few species are measured at a very limited number of locations.
2. Harmonised and standardised measurements of HM and POPs are needed for evaluation of emission inventories, validation of models, and trend analysis.

Here, we add new information relevant for the future EMEP measurement activities for heavy metals and for persistent organic pollutants.

## 2. MEASUREMENT PROGRAMME FOR HEAVY METALS

### 2.1 Measurement sites and compounds

#### *Introduction*

As a basis for the discussion of heavy metals in this document, previous work of the EMEP Task Force on Heavy Metals, the EMEP/CCC-Note 2/93 on the EMEP long-term plans, the outcome from the two previous EMEP workshops on heavy metals and persistent organic pollutants (Pacyna et al., 1993; de Leeuw et al., 1996), and the ongoing activity related to AMAP, OSPARCOM, and HELCOM, have been taken into account.

#### *Selection of compounds*

Mercury (Hg), Cadmium (Cd), Lead (Pb), Copper (Cu), Zinc (Zn), Arsenic (As), Chromium (Cr), and Nickel (Ni) are considered to be of high priority for an EMEP measurement program to assess atmospheric concentration and deposition values of heavy metals. It should be noted that Selenium (Se) is not included in this list, which was the case in the Beekbergen document (de Leeuw et. al., 1996).

#### **Recommendations**

First priority compounds: Hg, Cd, and Pb are assigned to be of highest priority. A protocol has recently been signed under the UN-ECE LRTAP convention addressing emission reductions of these three heavy metals.

Second priority compounds: Cu, Zn, As, Cr, and Ni are of second priority, but the emissions of these five heavy metals will also be positively affected by a finalised and implemented protocol for Hg, Cd, and Pb.

#### *Measurement sites*

In the EMEP/CCC-Note 2/93, a change of measuring strategy, using a limited number of stations but with an adequate coverage and good geographical representation, was suggested for a future heavy metal monitoring program. High quality data would ensure comparability and known uncertainty, which is necessary for model validation. As far as possible the sampling sites should be based on the existing station network. The possibility of co-location with other monitoring programs should be investigated, especially activities in the framework of OSPARCOM, HELCOM, and AMAP.

## Recommendations

- For modelling purposes, an adequate coverage of Europe will be ensured by operating eight evenly distributed heavy metal "super-stations". In addition, two or three stations have to be included to resolve concentration and deposition gradients and to be used in supplementary campaigns. This type of measurement data is necessary for model validation, dry deposition estimates, trend analysis, and validation of emission estimates. During 2000, the Parties, in co-operation with CCC, will establish an EMEP network for trace metals, with first priority elements Hg, Cd and Pb and second priority elements Cu, Zn, As, Cr and Ni. in the following areas: northern and southern Scandinavia, western Russia/Belarus, southern Finland/Baltic, Baltic/Poland, central Europe/Czech Republic/Slovakia/Hungary, Balkan, Ireland/United Kingdom, Portugal/Spain, southern France/Italy, and Germany/Netherlands.
- At least five stations are necessary for validation of atmospheric mercury chemistry used in modelling. The siting must also adequately represent the observed concentration gradients.
- Strict criteria of acceptance of "super stations" should for example include adaptation of a manual for sampling and analysis and use of high level QA/QC programs.
- The following countries are suggested to be invited as hosts for a heavy metal "super-station": Spain, France, Italy, The Czech Republic, Germany, Lithuania, Russia, Norway, Sweden, Finland, United Kingdom, the Netherlands, Poland, Austria, and probably Switzerland, Latvia, Ireland, and Slovenia.
- A more widespread network designed to measure heavy metal deposition may support the small network of "super-stations" with high measurement resolution. CCC will, in co-operation with the relevant universities in Norway and Sweden, convert the moss surveys from 1995 to deposition maps.

### 2.2 Measuring techniques

#### *General*

The Joint Research Centre at Ispra (Italy) and CCC, in co-operation with other organisations, will organise a technical workshop in spring 2000 to share experience and consider the details of HM sampling and analytical procedures, quality assurance and laboratory comparisons.

CCC will continue the work on the HM standard operating procedures and quality control routines for the EMEP manual for sampling and chemical analysis.

CCC and Swedish Environmental Research Institute (IVL) will organise a training course on Hg measurements during 2000.

Guidelines for the sampling and analysis of atmospheric mercury species have been developed within OSPARCOM.

#### *Air*

In the EMEP/CCC-Note 2/93 (NILU and IVL, 1993), some suitable sampling and analytical techniques for air have been identified. Also, a compilation of the techniques presently used for heavy metals in air in Europe has been made (NILU and IVL, 1993; Iverfeldt, Chapter 5 in de Leeuw et. al., 1996).

Reference and standard methods for sampling and analysis must be used to ensure high quality and comparable results. For the specific heavy metal, only one reference method should be acceptable. To be able to use a well-accepted standard method, if different from the reference method, it is up to the responsible laboratory to demonstrate a high comparability with the stated reference method before acceptance.

#### *Mercury field intercomparison*

In 1995, methods for measurements of total gaseous mercury in air were intercompared at the Mace Head station, Ireland (Ebinghaus et al., 1996). 10 laboratories participated in the exercise, of which 7 used 5 different manual methods and 4 laboratories used 2 different automated analysers. Generally, the results show good agreement between the participants. Further, the manual and automated methods seem to generate comparable results.

#### **Recommendations**

- Reference sampling methods for heavy metals on particulates and total gaseous Hg, respectively, should be assigned.
- Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) should be adapted as the analytical reference method for Pb, Cd, Cu, Zn, As, Cr, and Ni in air.
- Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) should be adapted as the analytical reference method for Hg in air.

- A HELCOM-EMEP-OSPARCOM-AMAP intercomparison exercise for Hg in air should be arranged, involving laboratories responsible for the Hg measurements in the framework of the international monitoring programs.
- A HELCOM-EMEP-OSPARCOM-AMAP intercomparison exercise for heavy metals associated with particles should also be arranged.

### 2.3 New developments

A number of new methods for speciation of atmospheric mercury have recently been developed. This includes KCl-coated denuders (annular and tubular) (Sommar et al., 1996; Tekran 1999) and Mist Chambers (Stratton and Lindberg, 1995) for sampling of RGM (Reactive Gaseous Mercury, mainly divalent water-soluble mercury compounds). Despite accounting for only a few percent of the total gaseous mercury in air, RGM is important due to its high deposition velocity and high water-solubility. Furthermore, an inexpensive and simple sampling device for particulate-phase mercury has recently been developed (Lu *et al.*, 1998). This device consists of a quartz-fibre filter disc mounted in a quartz glass tube allowing direct analysis after thermal desorption and without acid digestion.

#### *Deposition*

In the EMEP/CCC-Note 2/93 (NILU and IVL, 1993), some suitable sampling and analytical techniques for precipitation have been identified. As for air measurements, a compilation of the techniques presently used for heavy metals in precipitation in Europe has been made (NILU and IVL, 1993; Iverfeldt, Chapter 5 in de Leeuw et al., 1996).

The same analytical reference methods should be adapted for heavy metals in deposition as in air. The bulk collector technique is preferred, compared to the wet-only collector, as the reference method for deposition sampling. Further, the same type of bulk collector should be used at all stations.

### 2.4 Intercomparison of heavy metals in precipitation

To increase the reliability in the measurements of heavy metals in precipitation collected as part of international monitoring, HELCOM, EMEP, PARCOM, and AMAP, recently established an *ad hoc* working group to arrange and carry out an intercomparison exercise among the laboratories involved in the respective monitoring program. Previously, similar intercomparisons have been carried out by HELCOM/PARCOM (SNV, 1989; Sjöberg, 1992; Ross and Areskoug, 1993). A comparison of methods for the determination of heavy metals

in precipitation was run as an initial analytical intercomparison carried out in 1994 (Berg and Semb, 1995), followed by a field intercomparison in 1995.

#### *Analytical intercomparison of heavy metals in precipitation*

Four synthetic precipitation samples containing Pb, Cd, Cu, Zn, As, Cr, Ni, and Sb were analysed in the HELCOM-EMEP-PARCOM-AMAP analytical intercomparison 1994 (Berg and Semb, 1995). Hg was not part of the intercomparison exercise. The samples were distributed to 25 laboratories. Between 17 and 23 laboratories submitted results for a high and low level sample of the respective heavy metal, with the exception of Sb, which was analysed by very few participants. For each heavy metal, the relative percentage deviation of the result reported by the various participants from the theoretical value can be taken as a measure of quality and comparability. In short, a majority of the laboratories reported deviation values within 25% from the theoretical values for both concentration levels of all heavy metals considered. Generally, the performance was better for the higher level sample. Of the individual heavy metals, the intercomparison result for Pb was the best.

#### *Field intercomparison of heavy metals in precipitation*

The field intercomparison part of the HELCOM-EMEP-PARCOM-AMAP exercise, was carried out at the German EMEP station Deuselbach (DE 04), March to October 1995. Weekly sampling using duplicate bulk samplers was used as the basis for collection. For comparison, additional measurements by wet-only sampling were carried out by the host institution. Seven heavy metals were considered in this field intercomparison: Pb, Cd, Cu, Zn, As, Cr, and Ni, but not Hg. The results are presently being reported, but were also extensively discussed at a workshop in Germany, September 16-17 1996. Generally, the outcome of the intercomparison is much more positive than in the case of previous exercises. For example, the agreement between the collectors regarding precipitation amount seems to be satisfactory. Further, the results for Pb, Cd and possibly Zn seem to be acceptable, but problems still remain to be solved for the other heavy metals considered. A new analytical intercomparison on heavy metals in precipitation is being carried out under the framework of EMEP during fall 1999.

#### *Field intercomparison of mercury in precipitation*

As a small part of the international field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland, 1995, the mercury levels derived from ground- and tower based bulk samplers were intercompared (Ebinghaus et. al., 1996). Five laboratories participated in this exercise and the result of the intercomparison was fairly good.

## **Recommendations**

- Separate sets of duplicate reference bulk samplers should be used for Hg and the other seven heavy metals, respectively. Preferably, reference bulk samplers should be manufactured and distributed free of costs to all participating stations.
- For comparison, the host countries may use their own collectors in parallel to the pair of reference collectors.
- Intercomparison exercises, both analytical and field studies, should continue to improve the quality of other heavy metals than Pb and Cd.
- A new analytical/field intercomparison for Hg in precipitation must be performed, involving the laboratories responsible for the measurement within the EMEP framework.
- Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) should be adapted as the analytical reference method for Pb, Cd, Cu, Zn, As, Cr, and Ni in precipitation.
- Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) should be adapted as the analytical reference method for Hg in precipitation.

### 2.5 Sampling frequency

In the EMEP/CCC-Note 2/93 and in the background document from the EMEP Beekbergen Workshop, suitable sampling frequencies have been discussed. The temporal resolution of heavy metals in air and precipitation should be at least on monthly basis, to assess annual trends and changes in atmospheric concentration levels. For model validation, measurements of a daily resolution are necessary, but should be run in campaigns.

## **Recommendations**

- Heavy metals on particulates in air should be run as 24 hours measurements during 3-4 week campaigns, twice per year every second year.
- For each station, test runs should be made to discover limitations of the regular campaign program. The detection limit of Pb/Cd will determine if it is possible to measure on a daily basis at a specific site.
- Hg in air should also be run as 24 hours measurements in campaigns. In addition, promising automated methods may increase the possibility of even better time resolution on a long-term basis.



## 2.6 Quality assurance and quality control

The importance of well-developed QA/QC procedures in determining heavy metals in air and precipitation, must not be underestimated. This was also stressed in the EMEP/CCC-Note 2/93.

### **Recommendations**

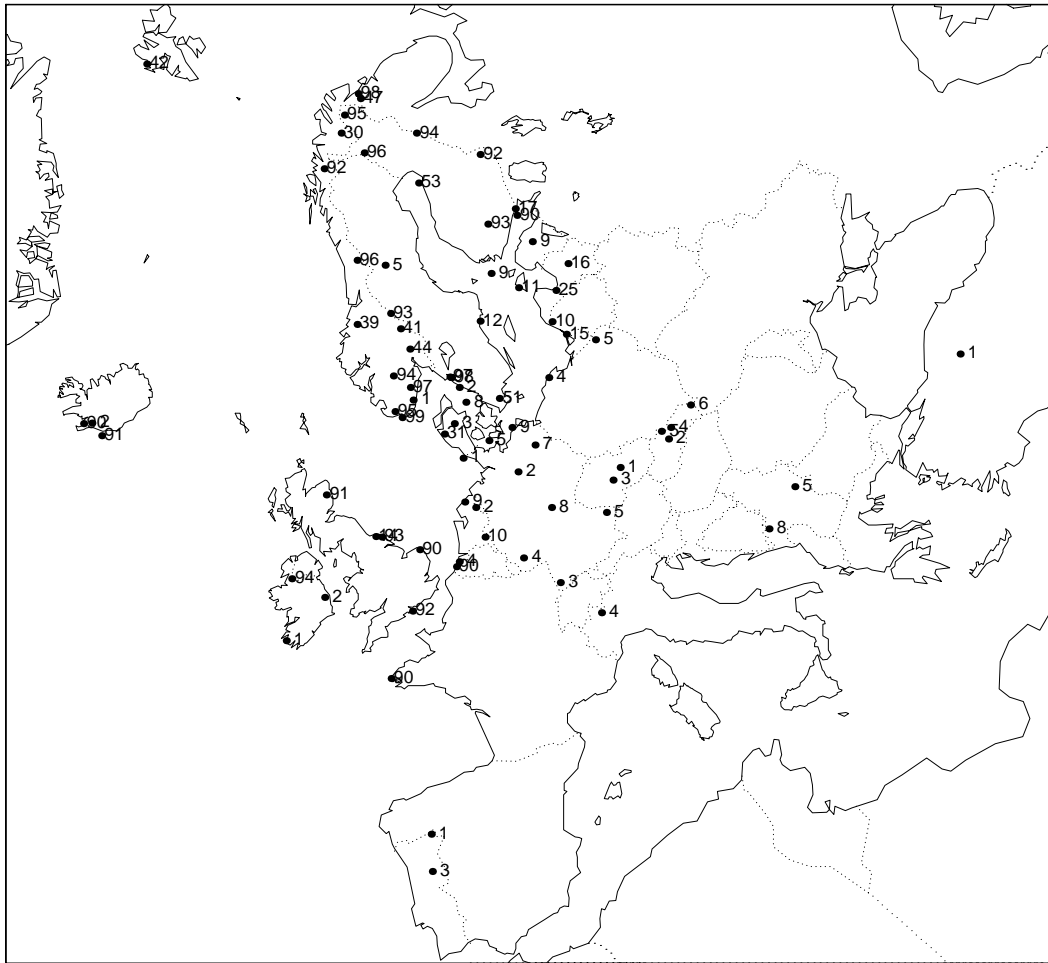
- Intercomparison exercises should regularly be run as an integrated part of the EMEP heavy metal measurement program and should be co-ordinated from the EMEP/CCC.
- Sampling and analysis guidelines for heavy metals should be developed and integrated in the normal laboratory QA/QC routines of all participating laboratories.
- Laboratories involved in the measurement of heavy metals should use QA/QC routines that include quantification of specific detection limit, frequent use of field and laboratory procedural blanks and sample duplicates, determination of chemical blanks, trace metal cleaning procedures, and regular participation in intercomparison exercises.

## 2.7 Reported data for mercury and heavy metals

The measurement stations for which data on mercury and heavy metals are reported to EMEP-CCC are presented in Figures 1 and 2. Further details on sampling frequency and measured mercury species are given in Tables 1 and 2.



**Figure 1.** Measurement stations reporting mercury data to EMEP-CCC-



**Figure 2.** Measurement stations reporting data for heavy metals to EMEP-CCC

**Table 1.** Mercury in precipitation

Country	Sites	Hg species	Resol. of reported data	Data received For the following years
Belgium	BE4	Hg (tot)	4 weekly	1997
Denmark	DK31	Hg (tot)	Monthly	1990-91
Finland	FI96	Hg (tot)	Monthly	1996-97
Germany	DE1	Hg (tot)	Monthly	1990-93+95-97
	DE9	Hg (tot)	Monthly	1995-97
Norway	NO99	Hg (tot)	Monthly	1991-97
Sweden	SE2	Hg (tot)	Monthly	1989-94+97
	SE2	CH3Hg	Monthly	1997
	SE5	Hg (tot), CH3Hg	Monthly	1995-97
	SE11	Hg (tot), CH3Hg	Monthly	1995-97
	SE12	Hg (tot), CH3Hg	Monthly	1995-97
	SE97	Hg(tot)	Monthly	1993-94
United Kingdom	GB90, 91	Hg (tot)	Monthly	1989-91
	GB93	Hg (tot)	Monthly	1989-92

**Table 2. Hg in air**

Country	Sites	Hg species	Resol. of reported data	Data received for the following years
Finland	FI96	TGM	1 day a week	1997
Ireland	IE31	TGM	Daily	1995-97
Norway	NO42	TGM	1 day a week	1991-97
	NO99	TGM	1 day a week	1994-97
Sweden	SE2	TGM	1 day a week	1997

In Tables 3-5, information on EMEP measurement stations for heavy metals in air and precipitation are given.

**Table 3. List of monitoring stations included in the heavy metal data base**

Country	Station codes		Station name	Location		Height above sea (m)
	Old code			Lat.	Long.	
Belgium	BE4		Knokke	51°21'N	3°20'E	0
	BE90		Bredenee	51°14'N	2°59'E	0
Czech Rep.	CS1		Svratouch	49°44'N	16°02'E	737
	CS3		Kosetice	49°35'N	15°05'E	633
Denmark	DK3		Tange	56°21'N	9°36'E	13
	DK5		Keldsnor	54°44'N	10°44'E	9
	DK8		Anholt	56°43'N	11°31'E	40
	DK31		Ulborg	56°17'N	8°26'E	10
Estonia	EE9		Lahemaa	59°03'N	25°54'E	32
	EE11		Vilsandi	58°23'N	21°49'E	6
Finland	FI9		Utö	59°47'N	21°23'E	7
	FI17		Virolahti II	60°31'N	27°41'E	4
	FI53	FI91	Hailuoto	65°00'N	24°41'E	4
	FI90		Haapasaari	60°17'N	27°12'E	15
	FI92		Hietajarvi	63°10'N	30°43'E	173
	FI93		Kotinen	61°14'N	25°04'E	158
	FI94		Pesosjarvi	66°18'N	29°30'E	257
	FI95		Vuoskojarvi	69°44'N	26°57'E	147
	FI96		Pallas	67°58'N	24°07'E	566
France	FR90		Porspoder	48°31'N	4°45'W	50
Germany	DE1		Westerland	54°55'N	8°18'E	12
	DE2		Langenbrügge	52°48'N	10°45'E	74
	DE3		Schauinsland	47°55'N	7°54'E	1205
	DE4		Deuselbach	49°46'N	7°03'E	480
	DE5		Brotjacklriegel	48°49'N	13°13'E	1016
	DE7		Neuglobsow	53°09'N	13°02'E	62
	DE8		Schmücke	50°39'N	10°46'E	937
	DE9		Zingst	54°26'N	12°44'E	1
Iceland	IS2		Irafoss	64°05'N	21°01'W	61
	IS90		Reykjavik	64°08'N	21°54'W	61
	IS91		Stórhöfði	63°24'N	20°17'W	118

Ireland	IE1	Valentia Observatory	51°56'N	10°15'W	9
	IE2	Turlough Hill	53°02'N	6°24'W	420
	IE31	Mace Head	53°19'N	9°54'W	5
Italy	IT4	Ispra	45°48'N	8°38'E	209
Latvia	LV10	Rucava	56°13'N	21°13'E	18
	LV16	Zoseni	57°08'N	25°55'E	183
	LV25	Kemeri	56°55'N	23°28'E	
Lithuania	LT15	Preila	55°21'N	21°04'E	5
Netherlands	NL2	Witteveen	52°49'N	6°40'E	18
Norway	NL9	Kollumerwaard	53°20'N	6°17'E	0
	NL10	Vreededepeel	51°32'N	5°51'E	-
	NO1	Birkenes	58°23'N	8°15'E	190
	NO30	Jergul	69°24'N	24°36'E	255
	NO39	Kårvatn	62°47'N	8°53'E	210
	NO41	Osen	61°15'N	11°47'E	440
	NO42	Spitsbergen, Zeppelinfjell	78°54'N	11°53'E	474
	NO44	Nordmoen	60°16'N	11°06'E	440
	NO47	Svanvik	69°27'N	30°02'E	474
	NO92	Øverbygd	69°03'N	19°22'E	90

**Table 4.** Reported data for heavy metals in precipitation

Country	Sites	Heavy metals	Resol. of reported data	Data received for the following years
Czech Republic	CS1, 3	Mn, Ni, Cd, Pb	Weekly	1994-97
Denmark	DK31	Cr, Ni, Cu, Zn, Cd, Pb	Monthly	1989-93+97
Estonia	EE9, 11	Cr, Ni, Cu, Zn, As, Cd, Pb	24h	1996-97
Finland	FI9, 96	V,Cr,Mn,Fe,Ni,Cu,Zn,As,Cd,Pb	Monthly	1996-97
	FI17	V,Cr,Mn,Fe,Ni,Cu,Zn,As,Cd,Pb		1995-97
	FI53	V,Cr,Mn,Fe,Ni,Cu,Zn,As,Cd,Pb		1989-97
	FI90	V,Cr,Mn,Fe,Ni,Cu,Zn,As,Cd,Pb		1989-95
	FI92-95	V,Cr,Mn,Fe,Ni,Cu,Zn,As,Cd,Pb		1990-97
France	FR90	Cr, Cu, Ni, Zn, As, Cd, Pb,	Monthly	1989-93
Germany	DE1	Al, Cr, Ni, Cu, Zn, As, Cd, Pb	Monthly	1989-90, 92+93, 95-97
	DE2	V, Cr, Mn, Ni, Cu, Zn, As, Cd, Pb	24h	
	DE4	Cr, Mn, Ni, Cu, Zn, As, Cd, Pb	weekly	1994-97
	DE9	Al, Cr, Ni, Cu, Zn, As, Cd, Pb	monthly	1989+91-97 1995-97
Iceland	IS2, 90	Cr, Ni, Cu, Zn, As, Cd, Pb	Monthly	1992-97
Ireland	IE1	Cr, Ni, Cu, Zn, As, Cd, Pb	Monthly	1991-97
	IE2	Cr, Ni, Cu, Zn, As, Cd, Pb		1992-97
Latvia	LV10	Cu, Zn, Cd, Pb	Monthly	1993-94+96-97
	LV16	Cu, Zn, Cd, Pb		1994+97
	LV25	Cu, Zn, Cd, Pb		1993-94
Lithuania	LT15	V, Mn, Cu, Zn, Cd, Pb	Monthly	1993-97

Netherlands	NL2	V, Mn, Fe, Ni, Cu, Cd, Pb	4weekly	1987-94
	NL9	Fe, Cu, Zn, Cd, Pb	4weekly	1990-94+97
	NL10	V, Mn, Fe, Ni, Cu, Cd, Pb	4weekly	1988-94
Norway	NO1,39,41,44	Zn, Cd, Pb	Weekly	1992-97
	NO30	Zn, Cd, Pb	Weekly	1992-96
	NO47	Cr, Co, Ni, Cu, Zn, As, Cd, Pb	Weekly	1992-97
	NO92	Cr, Co, Ni, Cu, Zn, As, Cd, Pb	Monthly	1996
	NO93, 99	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb	Monthly	1993-97
	NO94, 95	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb	Monthly	1992-97
	NO96, 97	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb	Monthly	1992-96
NO98	Cr, Co, Ni, Cu, Zn, As, Cd, Pb	Monthly	1993-95	
Poland	PL4	Zn, Cu, Cd, Pb	Monthly	1996
	PL5	Mn, Cr, Ni, Cu, Zn, Cd, Pb	Monthly	1992-96
Portugal	PT1, 3	Mn, Ni, Cu, Zn, Cd, Pb	Daily	1987-97
	PT4	Mn, Ni, Cu, Zn, Cd, Pb	Daily	1997
Slovakia	SK2	Al, Mn, Fe, Zn	Monthly	1987-96
	SK4-6	Al, Mn, Fe, Zn	Monthly	1994-96
Sweden	SE5,12,51,98	V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Pb	Monthly	1987-97
	SE97	Cd, Pb	Monthly	1995-97
United Kingdom	GB14	Cr, Ni, Cu, Zn, As Cd, Ti, Pb	1-4 months	1993-97
	GB90-91	Cr, Ni, Cu, Zn, As Cd, Pb	1-4 months	1989-91-97
	GB92	Cr, Ni, Cu, Zn, As Cd, Pb	Monthly	1993-95
	GB93	Cr, Ni, Cu, Zn, As Cd, Pb	Monthly	1989-92
	GB94	Cr, Ni, Cu, Zn, As Cd, Pb	Monthly	1989-93
Yugoslavia	YU5	Cd, Pb	Monthly	1991-96
	YU 8	Cd, Pb	Monthly	1993-96

**Table 5.** Reported data for heavy metals in air

Country	Sites	Heavy metals	Resol. of reported data	Data received for the following years
Belgium	BE4	Ni, Cu, Zn, Pb	Monthly	1997
	BE90	Cr, Ni, Cu, Zn, Pb		
Denmark	DK5, 8	Ni, Cu, Zn, Pb	Daily	1997
	DK31	Cr, Ni, Cu, Zn, As, Cd, Pb		
Finland	FI96	Hg	24h	1997
Germany	DE1, 3-5, 7-9	Mn, Fe, Ni, Cu, Cd, Pb	24h	1997
Iceland	IS91	Cr, Ni, Cu, Zn, As, Se, Cd, Pb	15d	1997
Ireland	IE31	Hg	24h	1997
Latvia	LV10, 16	Cu, Zn, Cd, Pb	Weekly	1997
Lithuania	LT15	Cu, Zn, Cd, Pb	24 h <sup>2</sup> )	1997
Netherlands	NL9	Zn, As, Cd, Pb	24h	1997
Norway	NO42, 99	Mn, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb,	48 h <sup>2</sup> )	1997
	NO42,99	Hg	12-24h	
United Kingdom	GB14, 90, 91	Cr, Ni, Cu, Zn, As Cd, Pb	Monthly	1997

- AAS: Atomic absorption spectroscopy  
GF-AAS: Graphite furnace atomic absorption spectroscopy  
ICP-MS: Inductively coupled plasma - mass spectrometry  
CV-AFS: Cold vapour atomic fluorescence spectroscopy  
Hg-monitor: For measurements of gaseous mercury

### 3. MEASUREMENT PROGRAM FOR PERSISTENT ORGANIC POLLUTANTS

#### 3.1 Introduction

Ambient air contains a number of POPs with different chemical and physical properties, and of different source origin. Many POPs are considered as semivolatile organic compounds (SOCs,) and have vapour pressures between  $10^{-4}$  and  $10^{-11}$  atm at ambient air temperature levels, which means that they are transported in the atmosphere both in the gas and particle phases (Bidleman, 1988). The major removal mechanism of POPs from air is through deposition. The partitioning between the phases will affect the removal mechanism (deposition, photo-decomposition, chemical degradation) of POPs from the atmosphere. The deposition of POPs takes place either as wet or dry deposition. Wet deposition includes scavenging of compounds in both the gas- and particle phases and dry deposition processes include removal of both particles and gases. For POPs, the gas exchange process has also to be considered. Unlike wet and dry deposition via particles, gas exchange takes place in two directions. Thus, POPs will undergo atmospheric transport and deposition to both aquatic and terrestrial ecosystems, but they may also be re-emitted back to the atmosphere.

A large number of compounds have to be considered in a POP measurement program. Furthermore POPs are present in different concentration levels. The distribution of POPs between different phases as well as the atmospheric processes must be taken into account in the choice of sampling method both for air and deposition.

Priority lists of POPs to be measured in a monitoring network must include compounds, which originate from different sources. The determination of POPs must also be compound specific and compounds, which differ in volatility, and reactivity must be chosen.

For model validation, as well as for studies of atmospheric processes and deposition/re-emission fluxes, the determination of the partitioning of POPs between the gas and particle phases in the atmosphere and between water and particle phases in precipitation, must be taken into consideration.

Here we focus on measurements of POPs in air and deposition. However, studies of gas exchange processes etc., include measurements of POPs also in compartments such as water, vegetation, and soil. Clearly, measurement techniques of POPs in other media than air and deposition have to be taken into account in future. This type of data is necessary for model validation.

Initiated and sponsored by the Nordic Council of Ministers (NMR) an expert workshop on “Assessments of the Sources, Atmospheric Fluxes, Environmental Cycling, Effects and Sinks

of Persistent Organic Pollutants, POPs” was held Preston UK, April 30 - May 1, 1998 (NMR-report in press). The overall aim of the workshop was to bring policy makers and scientists in the field of POPs together in order to summarise and evaluate the current knowledge on emissions, pathways and reservoirs as well as effects of POPs, and to identify knowledge gaps.

The workshop pointed out the need for monitoring programs of POPs. Long term monitoring is essential to follow predicted trends. Intensive studies of critical environmental compartments/processes should track the response of concentrations when restrictions or bans are placed on chemicals. It was also stressed that current (and planned) monitoring programs with their focus on precipitation monitoring do not address gas exchange to soil, vegetation, water, and snow. This exchange process is often very important, if not dominating.

#### *Selection of POPs*

Due to the time consuming and costly analyses of POPs as well as the low concentrations of some POPs in the atmosphere, the sampling and analysis techniques must be taken into account in the selection of relevant compounds. A selection of compounds has to be made based on priority. The choice of the compounds listed below follow the recommendation in the EMEP/CCC-Note 2/93.

1. Determination of compounds most frequently found in air and deposition samples and which are easy to detect:
  - Hexachlorobenzene (HCB)
  - Hexachlorocyclohexanes (HCH), *alpha- and gamma-HCH*
  - Polychlorinated biphenyls (PCB), *IUPAC-28,52,101,118,153,138, 180*
  - Polyaromatic hydrocarbons (PAH), where the choice will depend on method of analysis
  - Chlordanes, *gamma chlordane and alpha chlordane*
2. POPs which are present in low atmospheric concentrations and consequently require more specialised analytical methods, but are of great environmental importance (groups of compounds):
  - Current used pesticides, (*endosulfan, atrazine etc.*)
  - DDTs
  - Chlordanes, (*other than mentioned above*)

- Toxaphene
- Dioxins/furans
- PCB, coplanar
- Brominated flame retardants
- Chlorophenols
- Polychloronaphthalenes (PCNs)
- Polychlorinated diphenyl ethers (PCDEs)

*Ongoing measurements of POPs in air and deposition*

Today, the POP sampling stations operating in Europe are few and mostly found around the North Sea and the Baltic Sea. Monitoring stations for POPs are also operated within AMAP, Ny Ålesund in the Arctic and Pallas located in the northern part of Finland.

POP data from sampling sites operated within OSPARCOM and HELCOM are reported to EMEP/CCC at NILU. The location of the sampling sites which report POP-data in air and precipitation are shown in figure and the data reported to the database are summarised in tables below. The table also gives the sampling frequencies and show the POPs included in the measurements



**Figure 3.** Measurement stations reporting data on POPs to EMEP-CCC



**Table 6.** Reported data for POPs in precipitation

Country	Sites	POPs	Resolution of reported data	Data received for the following years
Belgium	BE4	Pesticides	Monthly	1997
Denmark	DK31	HCHs	Monthly	1990-92
Finland	FI96	PCBs, PAHs, HCHs	1 week each month	1996
Germany	DE1	(PAH, pesticides and HCB)	Monthly	1990+92-93+95-97
	DE9	PAH, pesticides and HCB	Monthly	1995-97
Iceland	IS91	PAH, pesticides and HCB	15d	1995-97
Ireland	IE2	Pesticides	Monthly	1994-97
Norway	NO99	HCHs, HCB	Monthly	1991-97
Sweden	SE2	PCBs, PAHs, HCHs	1 week each month	1996

**Table 7.** Reported data for POPs in air

Country	Sites	POPs	Sampling period	Data received for the following years
Czech. Rep	CZ3	PAH, PCB, HCHs	1-5days	1990-97
Finland	FI96	PCBs, PAHs, pesticides	1 week each month	1996
Iceland	IS91	PCBs, pesticides, HCB	15d	1995-97
Norway	NO42	(PAH), pesticides, HCB and PCBs	48h each week	1993-97
	NO99	HCB, pesticides, (PCBs)	48h each week	1992-97
Sweden	SE2	PCBs, PAHs, HCHs,	1 week each month	1994-96

The measurement programs are not harmonised among the countries and sampling sites, with differences in sampling techniques, the sampling frequency and selection of POPs. Most stations use adsorbents and filters and most common are polyurethane foam and glass fibre filters for air sampling, while a variety of different types of samplers is used for sampling of POPs in deposition.

### 3.2 Summary of measuring techniques – Air

Due to the low concentrations of POPs in ambient air, large air volumes must be collected, which require long sampling times and/or a sampler with a large flow capacity. These prerequisites create risks for changes in both the qualitative and the quantitative content of POPs in the sample compared within the original air mass. The methods used for sampling these compounds must be evaluated with regard to collection efficiency, reproducibility and recovery. Determination of the true partitioning of the compounds between the vapour and particle phases is important in the understanding of atmospheric processes. Some POPs are also reactive and may be chemically transformed during sampling.

A high volume air sampler (HVS) equipped with a filter for trapping the particles from the air and a solid adsorbent for collecting substances in the vapour phase, is the most frequently used technique for the sampling of SOCs (Oehme and Stay, 1982; Foreman and Bidleman, 1990; Hart et al., 1992).

Glassfibre filters are frequently used for trapping organic compounds in the particle phase. Other common filter materials are quartz fibre and Teflon coated filters. Intercomparisons of different sampling systems for collection of PAH on ambient particles have shown that the different samplers appeared to be in agreement when comparing the concentrations of total PAH. However, there were greater variations in the concentrations among individual PAHs. No differences in collection efficiency of PAH between different filter media have been found (Ligocki and Pankow, 1989; Alfheim and Lindskog, 1984).

The adsorbents commonly used for sampling POPs in the gas phase are polyurethane foam (PUF) and an amberlite polymer XAD-2. The sampling recovery of POPs may differ due to the different characteristics of the adsorbents, such as specific surface area and chemical properties. For example XAD-2 has been found to be more effective for trapping more volatile semivolatile organic compounds than the polyurethane foam (Chuang et al., 1987). However, polyurethane foam is easy to handle in the field and has good air flow characteristics and a low pressure drop (You and Bidleman, 1984). In order to enhance the collection efficiencies of the more volatile compounds, cartridges containing both Tenax or XAD-2 and polyurethane foam can be used (Zaranski et al., 1991).

Saturation of the adsorbent is not a problem, due to the often low concentrations of POPs in the atmosphere, while the breakthrough point of a polyurethane foam plug is related to the air volume and the subcooled liquid vapour pressure of the compound (You and Bidleman, 1984; Bidleman et al., 1984). The sampling temperature is also an important parameter influencing the collection efficiency. Hart et al. (1992) developed a high volume air sampler, equipped with polyurethane foam sheets instead of plugs, which permits higher flow rates with a minimal pressure drop. This design increases the number of theoretical plates.

A low volume air sampler for collection of low weight compounds such as 2-3 ring PAHs, chlorobensens and PCBs containing fewer than three chlorine must be used as a complement. Recently, Wallace and Hites (1995) used a computer controlled low volume air sampler for POPs in the gas phase coupled with a rapid sample preparation scheme. The advantage of this type of sampler is the high sample capacity and possible high sample resolution. However, this type of sampler has not yet been used in a monitoring network.

### 3.3 Partitioning of POPs between the gas-and particle phases

In aerosol sampling a possible error source is that some of the compounds bound to particles may volatilise and then adsorb onto the adsorbent, so-called "blow off ". On the other hand, organic compounds in the gas phase may be adsorbed onto the filter surface. As a consequence, the distribution of the compounds between the adsorbent and the filter will differ from the true distribution between the vapour and the particle phases.

There are several factors that may affect the distribution of POPs during sampling. Factors that may affect the degree of artefact formation include the length of sampling time, the ambient temperature, the vapour pressure of the compounds and the pressure drop behind the filter, as well as the surface of the carrier particles.

As the partitioning of POPs between the gas and particle phases may be affected by the sampling time duration, the total atmospheric concentrations of the compound, sum of filter and adsorbent retained compounds, have to be reported. The use of a high volume sampler with a short sampling time will reduce the risk for erroneous distribution between the phases. However, this will give a detection problem for the POPs that are present in low atmospheric concentrations.

#### *Chemical degradation of POPs during sampling*

The occurrence of chemical reactions during sampling of POPs may also be a source of error, which can give an underestimate of the atmospheric concentration of these compounds, as well as an erroneous distribution among different components.

During sampling, retrained compounds are exposed to the reactive gases during a relatively long time period. PAH, for example, may undergo chemical transformations in the atmosphere in presence of other air pollutants such as NO<sub>2</sub> and O<sub>3</sub>. A study of the decomposition of particle associated PAH has shown that the NO<sub>2</sub> levels found in urban air cause degradation of some reactive PAH. Further, acid particles seem to enhance the reactivity, while the filter media has no effect on the reactivity (Lindskog et al., 1987).

In the determination of the total PAH concentration in the atmosphere, losses of particle bound PAH due to chemical degradation during sampling may not be of quantitative great importance. However, chemical artefacts may be much more significant in studies of source-receptor relationships, which usually are based on the "PAH profiles", the relative distribution among different PAH as well as a comparison with the relative PAH content in air and deposition samples.

However, while the choice of the filter media did not seem to affect the formation of chemical artefacts during sampling, the opposite can be true for the adsorbent media. In a study of chemical artefacts formed on adsorbent media (XAD-2 and polyurethane foam) during sampling of gas phase PAH, a clear degradation of PAH components was observed in the case of XAD-2. On the other hand, PAH adsorbed onto the polyurethane foam were only marginally affected by the exposure to NO<sub>2</sub> (Brorström-Lundén, 1995). Taking PAHs as priority compounds in a measuring program, XAD-2 can not be recommended as an adsorbent for air sampling of POPs even when low concentrations of NO<sub>2</sub> are present. In the future, this may be even more important if other more reactive compounds are included in the monitoring program. From the chemical artefact point of view, polyurethane foam is a better choice even if there is a risk of breakthrough.

A high volume air sampler (HVS) equipped with a filter/PUF combination is mostly used for collecting POPs in ambient air. This type of equipment was previously recommended in EMEP/CCC-Note 2/93 and is used in the monitoring programs in Sweden and Norway. The HVS is operating with an air flow rate of 20-25 m<sup>3</sup> /hour and a volume of 1000-2000 m<sup>3</sup> is normally used for collecting POPs in background air.

#### 3.4 Summary of measuring techniques – Deposition

The deposition samplers consist of various types of surrogate surfaces, which will affect the deposition in a different way to that occurring in the environment. The sampling methods and their relevance are currently subjected to much discussion.

Deposition sampling involves measurements of both wet and dry deposition. To be able to specify the proportion of POPs in rain, an active sampler such as a "wet-only" collector, must be used. Passive collectors or bulk samplers are open to the atmosphere all the time. A bulk sampler will give an idea of both wet and dry deposition. Passive samplers are often easy to handle and relatively cheap.

Deposition samplers may vary in shape and surface characteristics. The material of the collection surface of the sampler must be non-contaminating and inert. Materials used are e.g. glass, stainless steel and Teflon (Kawamura and Kaplan, 1986; Famer and Wade, 1986; Mazurek et al., 1987; McVeety and Hites, 1988; Stachan and Huneault, 1984). Due to the often low concentrations of POPs in rain water it is an advantage to use a sampler with a surface of 1 m<sup>2</sup> (Murray and Andren, 1992; Leister and Baker, 1994; Brorström-Lundén, 1995).

Generally, the sampling characteristics are influenced by size and depth of the sampler. The wind flow over the opening of the collector is affected by the ratio between the depth to the bottom of collector and the size of the opening. However the depth of the sampler must be high enough to prevent the raindrops to be re-ejected. To avoid contamination by wind-raised material from the ground, the sampler must be placed at least 1 meter above the ground level, which will increase the wind flow over the opening. Thus, the sampling efficiency may be affected by meteorological factors such as wind speed and rain intensity.

Wet deposition samples includes POPs in both the dissolved and particle phases. The partitioning of the compounds between the two phases is important in understanding atmospheric removal processes. To be able to specify the proportions of the organic compounds in rain, an active sampler such as a "wet-only" collector including in-situ filtration of particles and collection of the dissolved phase on an adsorbent can be used (Leister and Baker, 1994). However, artefacts may arise due to adsorption of dissolved compounds onto the filter surface, or an overestimation of the dissolved phase because of small particles breaking through the filter.

By using an active or passive sampler, compounds in the water phase may be collected onto an adsorbent such as polyurethane foam, PUF, XAD-2 and Tenax. The advantage in using an adsorbent is that large amounts of precipitation may be concentrated. Adsorption onto an adsorbent may also prevent biological degradation in the sample. The disadvantages are that "breakthrough" may occur and that various compounds can have different affinities to the adsorbent.

### 3.5 Current use of samplers

There is a variety of deposition samplers used today which differ in size, shape, surface and collection principle, such as bulk/wet-only (Egebäck and Widequist 1992). In the counties reporting deposition data to OSPARCOM and/or EMEP different types samples are used such as wet-only samplers where funnel and collection bottle are either Teflon-coated or made from glass or stainless steel equipped with glass bottles and bulk samplers with glass or Teflon coated funnels equipped with glass bottles or with PUF plugs for collection of POPs in rain water (de Leeuw and Brorström-Lundén 1997 , EMEP/CCC report 8/98).

An intercomparison of methods for deposition sampling of selected POPs has been carried out in the Nordic countries. Five samplers with different sizes, shapes, surfaces and collection principles, such as bulk/wet-only and adsorbent/non-adsorbent, were compared

(Brorström-Lundén et al., 1994; Widequist et al., 1998). The selection of samplers was based on their actual use in the Nordic countries today.

The results from this study showed that there was a great variation among the different samplers in the collection of POPs in deposition. No single parameter such as collection principle, isolation mode, collection area or surface material explained the differences between the samplers.

The isolation mode, adsorbent versus non-adsorbent seemed to have a greater impact on the result than the collection principle, bulk versus wet-only. However, the whole sampling campaign was characterised by heavy rainfalls evenly distributed over time, which probably resulted in less difference between bulk and wet-only samplers. The results further indicated that the polarity of a compound would affect the collection more than the volatility.

The major conclusions of the deposition sampler intercomparison were:

- Due to the variation in the sampling efficiency among different types of samplers it is essential that all stations in a monitoring net use the same type of sampler
- The choice of the type of deposition sampler must depend on the purpose of the measurements and the results must be discussed with regards to potential sampling artefacts.
- It is necessary to clean the collection surface and include the rinse in the deposition sample. This must be done both using a wet only or bulk sampler.

### 3.6 Measurements of POPs—recommendation and conclusions from previous workshops

As a basis for the discussion of POPs in this document, previous work of the EMEP Task Force on Persistent Organic Pollutants, the EMEP/CCC-Note 2/93 on the EMEP long-term plans, the outcome from the previous EMEP workshops on heavy metals and persistent organic pollutants (Pacyna et al., 1993; de Leeuw et al., 1996; Varygina and Soudine EMEP/MSC-E report 1/97). The ongoing activity related to AMAP, OSPARCOM, and HELCOM, have also been taken into account

#### 3.6.1 EMEP/MSC-E workshop in Moscow, Russia, September 1996

The major conclusions from of workshop concerning POPs were:

- The major conclusions from the EMEP Workshops in Durham and Beekbergen on measurements of persistent organic pollutants (POPs) are still valid. Only a few POPs are measured at a very limited number of locations.
- Harmonised and standardised measurements of POPs are needed for evaluation of emission inventories, validation of models and trend analysis.
- In a first step five sampling sites for POPs measurements would be sufficient. Due to the importance of the air/water exchange of POPs, these first sites should preferably be located near the coast or at lakes. The preferred locations are:

Scandinavia/Baltic States  
 Northern Atlantic region  
 Continental Europe  
 Mediterranean region  
 South Atlantic region

If required, this concept could be expanded to a more widespread network in future. However, due to the limited number of stations in the location of the stations is very critical.

- It was recommended to restrict the measurements in the start-up phase to high volume sampling of air. Deposition measurements should be included in a second step.
- The sampling period recommended for air samples in the start-up phase is one 24 (48) hours sample every week. In a second step campaigns are recommended which should include more frequent air sampling, deposition sampling, and possible surface water sampling.
- In the first step the following compounds were recommended to be included in the measurement program:

PAH  
 PCB/HCB  
 Chlordane  
 Lindane  
 a-HCH  
 DDT/DDE

These components can all be determined in one series of chemical operations. The costs for one analysis of the components above is estimated to about 800 ECU.

- It was recommended to have standard operation procedures and quality assurance procedures for POPs worked out by the CCC and included in EMEP's manual for sampling and analysis.
- It was also recommended that the CCC collects POP results from soil and water measurements. The Workshop recommends the Steering Body of EMEP to consider to encourage the Parties to provide CCC with these data.
- The EMEP Workshop in Moscow recognised a strong need for a separate workshop to discuss sampling methods, particularly for deposition measurements of POPs.

### 3.6.2 EMEP-Expert meeting on "Measurements of Persistent Organic Pollutants in Air and Precipitation" Lillehammer, November 1997

An EMEP-Expert meeting on "measurements of POPs in air and precipitation was organised by the CCC at the Norwegian Institute for Air Research (NILU) in co-operation with the Swedish Environmental Research Institute (IVL). The meeting was held in Lillehammer, Norway 11-14 November 1997. EMEP/CCC report 8/98- O92016

The expert Meeting gave technical recommendations on measurements of POP in air and precipitation, and on the quality assurance of POP measurements.

The list of compounds compiled for the report of the Moscow meeting is in general still valid. All components should be reported individually. The method fails in sampling the most volatile compounds on the list (e.g. Naphthalene, other volatile PAHs and PCBs). It is not possible to detect all the listed compounds in one analysis.

The major conclusions and recommendations were:

#### *Air sampling*

- It is recommended that one type of high volume air sampler (HVS) be used at all sites. If different sampler types are used, an inter-comparison is required.
- A commercially available or easy to make HVS with glass or quartz fibre filter and polyurethane foam (PUF) is recommended. The distribution of POPs on filter and adsorbent should be reported. More research on methods measuring particle/vapour distribution is suggested.
- A sampling time of 24 - 48 h once every week was recommended. If shorter periods are chosen detection becomes difficult. In the case of longer sampling periods it is difficult to correlate the measurement results to air mass trajectories.



In addition to the EMEP recommendations, needs and goals of comparable programs, such as OSPARCOM, HELCOM and AMAP should be considered, e.g. high volume sampling equipment for 24 - 48 hours sampling has been recommended in EMEP while a lower volume air sampling equipment is used for monthly sampling in OSPARCOM.

#### *Deposition sampling*

- According to the EMEP Guideline a simple and easy-to-handle deposition sampler for precipitation monitoring is preferred.
- It is recommended for the initial measuring phase to use bulk deposition samplers at all sites. Bulk samplers are easy to use and give representative results on the regional scale.
- At least at two sites wet-only samplers should be used. Wet-only sampling provides valuable information to the modelling community. Results of the two sampler types should be evaluated at the end of one year, in order to make appropriate recommendations.
- The same sampler design should be used at the initial sampling stations. It is suggested that, on a voluntary basis, other EMEP stations also use the recommended sampling design.
- For precipitation sampling a glass funnel (approx. 30 cm i.d. and a rim height of 20 cm) is recommended.
- The sampling system should operate in all weather conditions. Necessary modifications should be made at some stations where snowfall is expected (e.g. thermostatic devices).
- Adsorbent (e.g., polyurethane foam, PUF) as a sample carrier is recommended. The same type of adsorbent should be used for wet-only and the bulk samplers. It is suggested that the CCC tests different adsorbents and recommends the most suitable one.
- After sampling the surface of the glass funnel it should be rinsed with methanol. The rinse should be added to the sample.
- The precipitation amount should be measured separately.
- The deposition sampling period should be one month, and the sampling time should be synchronised with WMO. The deposition group is aware of the fact that POP sampling artefacts such as re-volatilisation, degradation and adsorption may occur.

### *Chemical work and analysis*

- No recommendations on any specific analysis method are made, but a comprehensive method validation is necessary.

### *Quality control*

- A quality assurance protocol should follow the sampling and analytical procedure. QA/QC criteria shall generally be based on the AMAP protocol (“Method performance criteria and quality control measures for the determination of POPs in ambient air, precipitation and water”)
- Before the network is put in operation an analytical inter-comparison for laboratories involved in the analyses is essential, and an inter-comparison program should be arranged.

Research on processes and physical properties of POPs will be carried out in EUROTRAC and other research programs. The results should be used within EMEP.

### 3.7 Pilot Study and Intercomparison Exercise on Atmospheric Inputs of PAH-OSPARCOM

An intercomparison on sampling and analyses of PAHs in air and precipitation has recently been organized by INPUT/ OSPAR. The German Federal Environmental Agency (FEA) is the project leader for this study. The experimental part was carried out during 1998 and a “Workshop on Development of Guidelines for sampling and analyses of PAHs in air and precipitation based on the results of the field experiments was held at NORDUM GmbH&Co.KG (Institute for Environment and Analyses ) in June 1999 Rostock Germany. The pilot study was initiated with the aim to establish a manual for sampling and analysis of PAHs in air and precipitation. A draft manual is distributed to the Contracting Parties of OSPAR in November 1999, and will likely be adopted by the OSPAR groups INPUT and ASMO later that year. After this, the manual will be made available to other monitoring programmes in Europe.

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