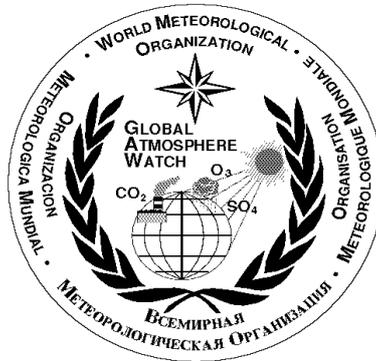


# WORLD METEOROLOGICAL ORGANIZATION GLOBAL ATMOSPHERE WATCH



**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  
Swedish Environmental Research Institute (IVL), P.O. Box 47086, S-402 58 Göteborg  
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.

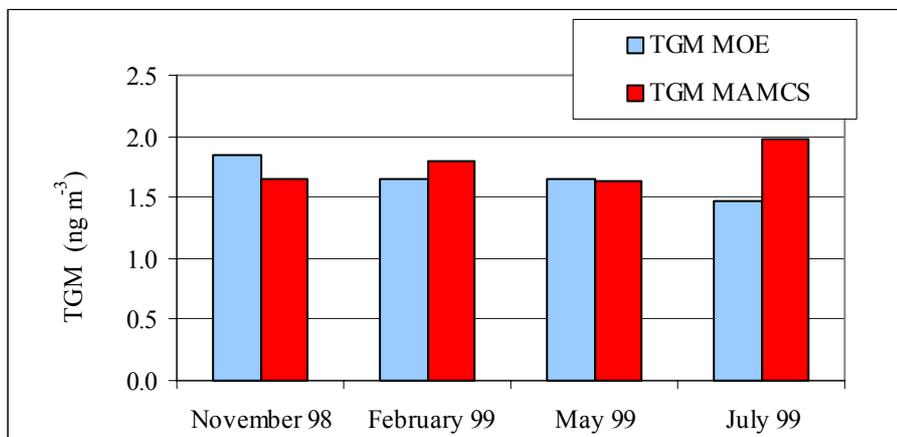
Main activities during the first years of MEPOP have included a broad range of activities such as:

- 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.

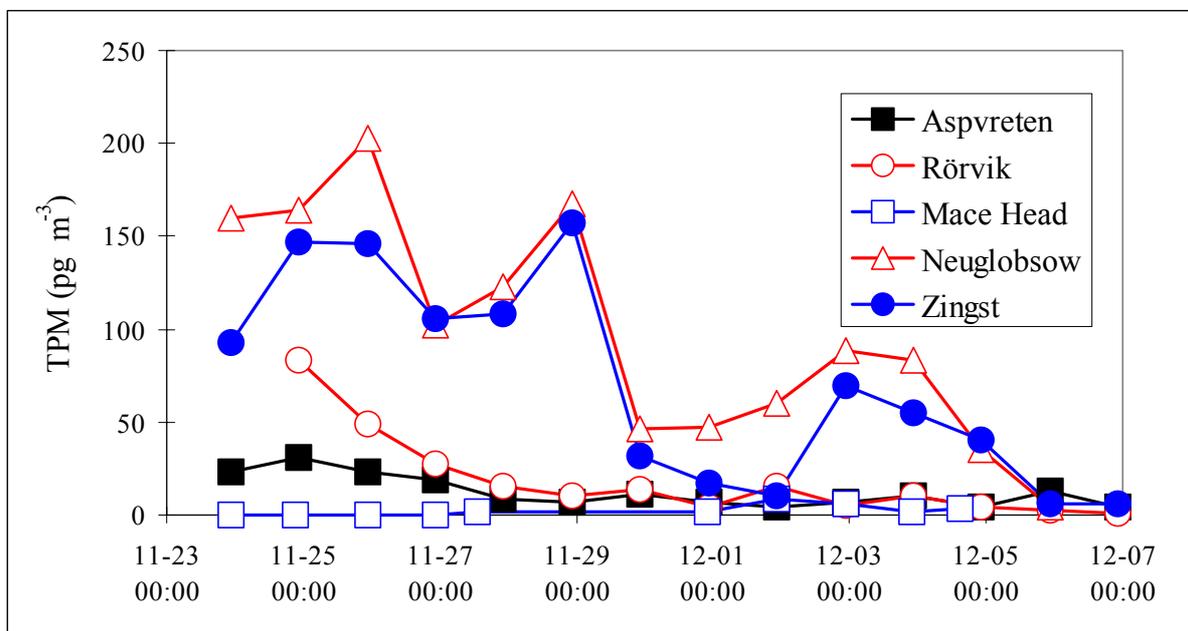


Figure 2 . TPM concentrations at 5 MOE stations in November, 1998.

### 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

K.J.Puckett, AES, Environment Canada (Canada)

N.Urquizo, Rainmakers Environmental Group, Niagara on the Lake (Canada)

R.L. Dennis, US-EPA, Raleigh, NC (USA)

#### 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  $3.5 \times 10^{-6} \text{ cm}^2/\text{cm}^3$  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

---

<sup>1</sup> Centre for the Biology of Natural Systems, Queens College, City University New York.

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 (Daggupati 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

## 5. REFERENCES

- Bartlett, P. 1999. Pers. Comm. Principal analyst for the arctic project on assessing the efficacy of the HYSPLIT/TRANSCO air transport model, as means of ranking the North American source of airborne dioxins. Queens College, CUNY, New York. (Sep 21, 1999).
- Bidleman, T. F. 1988. Atmospheric Processes – Wet and Dry Deposition of Organic Compounds Are Controlled by their Vapor Particle Partitioning. *Environmental Science & Technology*, Vol. 22(4): 361-367 pp.
- Blanchard, P.; J.F. Hopper and R. M. Hoff. 1997. Principal Component Analysis of IADN Elemental Data from a Site in Ontario. Proceedings of the 90<sup>th</sup> Annual Meeting & Exhibition on Air and Waste Management Association. Jun 8-13.
- Bullock, O. R. Jr. 1999. Per. Comm. Meteorologist, NOAA Air Resources Laboratory on assignment to USEPA, National Exposure Research Laboratory Atmospheric Modelling Division., Research Triangle Park, North Carolina.
- Bullock, O. R. Jr.; K. A. Brehme; G. R. Mapp. 1998. Lagrangian modelling of mercury air emission, transport and deposition: An analysis of model sensitivity to emissions uncertainty. *The Science of the Total Environment*, Vol. 213:1-12pp.
- Bullock, O. R. Jr.; W.G. Benjey and M.H. Keating. 1996. The modelling of regional-scale atmospheric mercury transport and deposition using RELMAP. *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*. Ed. Joel E. Baker, SETAC Press, 323-347pp.
- USEPA and Environment Canada. 1997. The Great Lakes Binational Toxics Strategy - Canada-United States Strategy for the Virtual Elimination of Persistent Toxic Substances in the Great Lakes. <http://www.epa.gov/glnpo/p2/bns.html>.
- Cohen, M. and L. Mathewson. 1999. Sources and Source Regions Contributing to Atmospheric Deposition of Toxic Pollutants to the Great Lakes. International Joint Commission, Great lakes Water Quality Forum. Sep 24-26, Milwaukee, WI.

- Cohen, M. 1997. The transport and Deposition of Persistent Toxic Substances to the Great Lakes. III Modelling the Atmospheric Transport and Deposition of Persistent Toxic Substances to the Great Lakes. International Joint Commission, 66 pg.
- Cohen, M; P. Cooney and B. Commoner. 1997. The Transport and Deposition of Persistent Toxic Substances to The Great Lakes, V. Summary. International Joint Commission, 46 pg.
- Commer, B. 1999. Protocol – The Efficiency of the HYSPLIT/TRANSCO Air Transport Model as a Means of Ranking the North American Sources that Contribute to the Deposition of Dioxin in Polar Regions of North America. Report for the Commission of Environmental Cooperation. *Centre for the Biology of Natural Systems*, Queens College, CUNY, NY. 9 pp.
- Cooter, E. 1999. Per. Comm. Meteorologist NOAA/ERL/ARL/ASMD on assignment to USEPA ORD/NERL/AMD, Research Triangle Park, North Carolina.
- Daggupaty, S. M. and J. Ma. 1998. Discrete Ordinate / Pseudospectral Simulations of Transport of Heavy Metals over Regions of North America. Proceedings of the 10<sup>th</sup> Joint Conference on the Application of Air Pollution Meteorology with the A&WMA, American Meteorological Society. Phoenix, Arizona 11-16 January. 410-413 pp.
- Daggupaty, S. M. and J. Ma. 1999. Lead Deposition to the Great Lakes Simulated Using Sources from Canada and United States. Paper to be presented at the 11<sup>th</sup> Joint Conference on the Application of Air Pollution Meteorology with the A&WMA, American Meteorological Society in January 2000.
- Dastoor, Ashu. 1999. Pers. Comm. Research Scientist, Modelling and Integration Research Division, Air Quality Research Branch, Atmospheric Environment Service, September, 1999.
- Guthrie, P.D.; D. Gao and G.E. Mansell. 1998. Evaluation of the Performance of the REMSAD Modelling System for Fine Particles and Deposition. SAI SYSAPP-98/24, June. Report prepared for the Air Quality Planning and Standards USEPA.
- Hoff, R. M.; D. C.G. Muir and N. P. Grift. 1992. Annual Cycle of Polychlorinated Biphenyls and Organohalogen Pesticides in Air in Southern Ontario. 2. Atmospheric Transport and Sources. *Environmental Science and Technology*, Vol. 26(2): 276-283.
- Hopke, P.K.; C.L. Li; W. Cizek and S. Landsberger. 1999. The Use of Bootstrapping to Estimate Conditional Probability Fields for Source Locations of Airborne Pollutants. <http://lancair.emsl.pnl.gov:2080/docs/incinc/general/PKHdoc.html>.
- Hoyer, M.; J. Burke and G. Keeler. 1995. Atmospheric Sources, Transport and Deposition of Mercury in Michigan: Two year of Event Precipitation. *Water, Air, and Soil Pollution* Vol. 80(1-4):199-208.
- Junge, C.E. 1977. Basic Considerations About Trace Constituents in the Atmosphere as Related to the Fate of Global Pollutants. Fate of Pollutants in the Air and Water Environments. I.H. Suffet. New York, Wiley: 7-22 pp.
- Koziol, A.S. and J. A. Pudykiewicz. 1999. Numerical Simulation of the Global Atmospheric Transport of Organic Pollutants. *Internal Report*, Environment Canada, Dorval. 34 pg.
- Li, Y.F. 1999. Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. *The Science of the Total Environment*, Vol. 232(1999): 121-158.
- Ma, J. 1999. Modelling of Heavy Metal Deposition over the Great Lakes – Model description. Internal Report AES, Environment Canada. 9 pg.
- Moussiopoulos, N.; E. Berge; T. Bøhler; F. de Leeuw; K. Grønseki; S. Mylona and M. Tombrou. 1996. Ambient Air Quality, Pollutant Dispersion and Transport Models. *European Environment Agency*, Topic Report 19, 94 pp.
- Pai, P.; P. Karamchandani; and Christian Seigneur. 1997. Simulation of the Regional Atmospheric Transport and Fate of Mercury Using a Comprehensive Eulerian Model. *Atmospheric Environment* Vol. 31(17): 2717-2732 pp.

- Pai, P.; P. Karamchandani; and Christian Seigner. 1999. Sensitivity of Simulated Atmospheric Mercury Concentrations and Deposition to Model Input Parameters. *Journal of Geophysical Research* Vol. 104(D11): 13,855-13,868 pp.
- Petersen, G. ; J.Munthe; K. Pleijel; R. Bloxam; and A. Vinod Kumar. 1998. A Comprehensive Eulerian Modeling Framework for Airborne Mercury Species: Development and Testing of the Tropospheric Chemistry Module (TCM). *Atmospheric Environment* Vol. 32(5): 829-843 pp.
- Poissant, L.1999. Potential Sources of Atmospheric Total Gaseous Mercury in the St. Lawrence River Valley. *Atmospheric Environment*, Vol. 33(1999): 2537-2547.
- Poole-Kober, E.M. and H. J. Viebrock. 1999. Fiscal Year 1998 Summary Report of the NOAA Atmospheric Science Modelling Division to the U.S. Environmental Protection Agency. NOAA Technical Memorandum ERL ARL-231.91 pp.
- SAI Inc. 1998. User's Guide to the Regulatory Modeling System for Aerosols and Deposition (REMSAD). Systems Application International, Inc.
- Seigneur, C.; P. Pai; P.K. Hopke; and D. Grosjean. 1999. Modelling Atmospheric Particulate Matter. *Environmental Science & Technology / News*. Feb. 1<sup>st</sup>.
- Shannon, J.D. and E. C. Voldner. 1995. Modelling atmospheric concentrations of mercury and deposition to the Great Lakes. *Atmospheric Environment*, Vol. 29: 1649-1661 pp.
- Voldner, E.C. J.D. Shannon and D. Mackay. 1993. Modeled Trends in Atmospheric Deposition of Lead to the Great Lakes and Resulting Lake Mass Balance. Proceedings of the 9<sup>th</sup> International Conference on Heavy Metals in the Environment. CEP Consultants Ltd., Heavy Metals Secretariat, Edinburgh, U.K. 275 pp.
- Voldner, E.C. and W.H. Schroeder. 1989. Modelling of Atmospheric Transport and Deposition of Toxaphene into the Great Lakes Ecosystem. *Atmospheric Environment* Vol. 23(9):1949-1961pp.
- Wania F. and D. MacKay. 1999. Global Chemical Fate of  $\alpha$ -Hexachlorocyclohexane. 2. Use of a Global Distribution Model for Mass Balancing, Source Apportionment, and Trend Prediction. *Environmental Toxicology and Chemistry*, vol. 18(7): 1400-1407 pp.
- Wania, F.; D. Mackay; M. McLachian; A. Sweetman and K. Jones. 1999. Global Modelling of Polychlorinated Biphenyls. Synopsis of Research Conducted under the 1998/99 Northern Contaminants Program. Indian and Northern Affairs, Canada. 61-70 pp.

## 4. PRESENTATION OF BACKGROUND DOCUMENTS

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

Knut Breivik and Jozef M. Pacyna, Norwegian Institute for Air Research (Norway)

#### 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.).

---

<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:

- Polyaromatic 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.

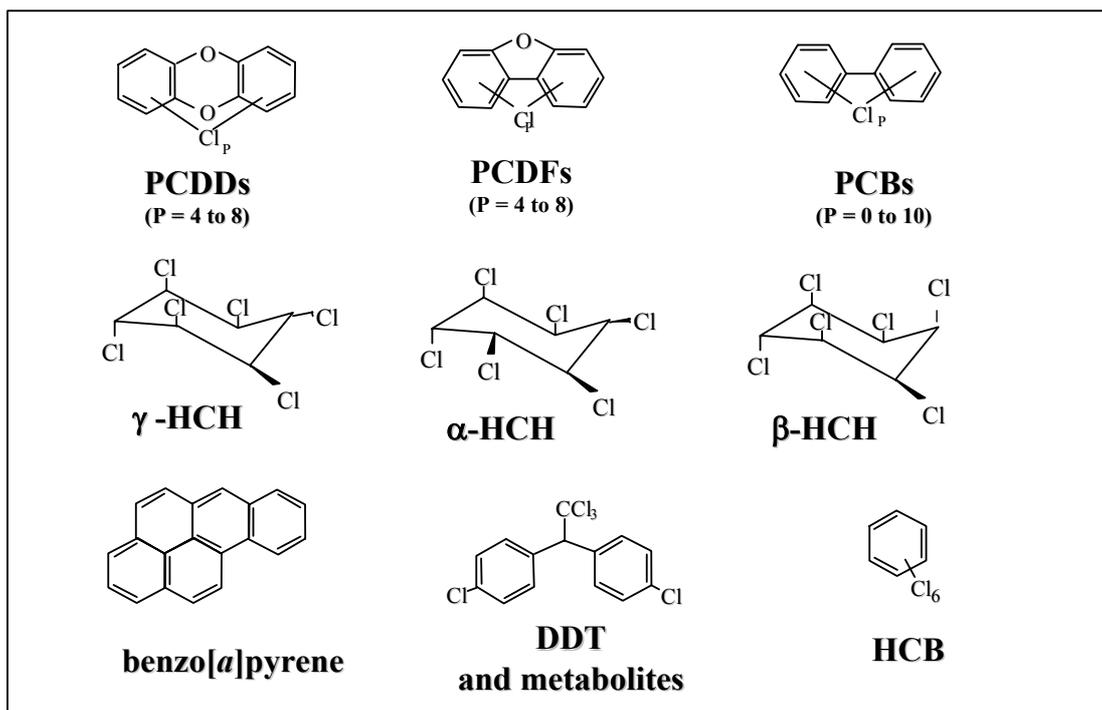
#### *European inventory for mercury (MAMCS/MOE)*

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.

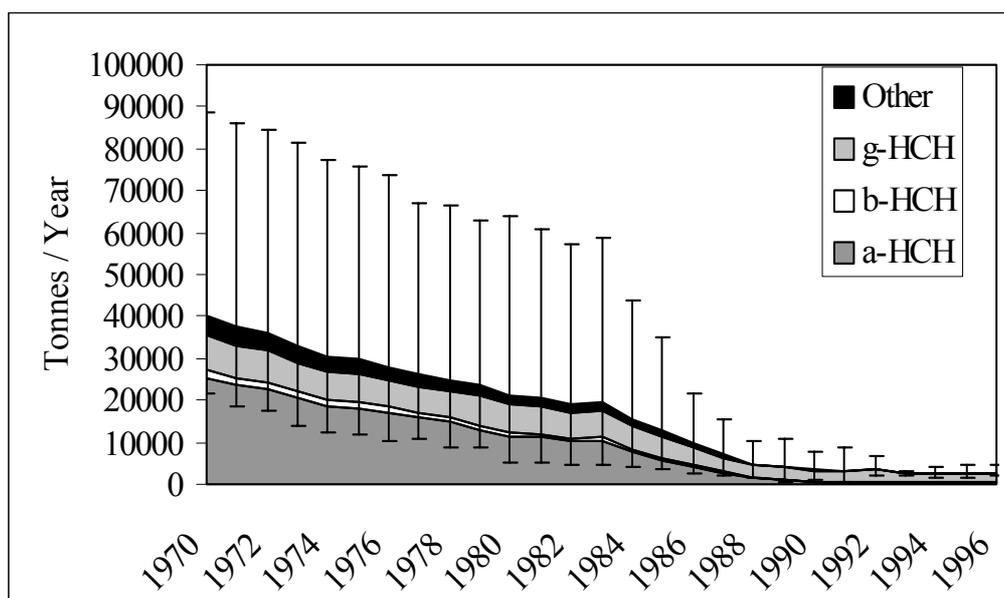
Unfortunately, only a few countries report their annual usage of each of these formulations based on active ingredient with isomeric resolution. Thus, we first collected all data that could be found on national annual consumption of lindane or technical HCH. Next, we collected data on insecticide usage 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.

## 5. REFERENCES

- AEAT, 1999: Identification of Relevant Sources of Releases of Dioxins and Furans to Land and Water in Europe. Draft for Comment. Restricted. AEAT-4703/20591001.
- Annema, J.A., J.E.M. Beurskens and C.W.M. Bodar (eds.), 1995: Evaluation of PCB fluxes in the environment. Report No. 601014011. National Institute of Public Health and Environmental Protection. Bilthoven, The Netherlands.
- Axenfeld, F., J. Münch, J.M. Pacyna, J.A. Duiser and C. Veldt, 1989: Emissionsdatenbasis für die Spurenelemente As, Cd, Hg, Pb, Zn und für Spezielle Organische Verbindungen □-HCH (Lindan), HCB, PCB und PAK. Umweltforschungsplan des Bundesministers für Umwelt Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungsbericht 104 02 588. Dornier, Juli 1989.
- Axenfeld, F., J. Münch, J.M. Pacyna, 1991: Belastung von Nord- und Ostsee durch ökologisch gefährliche Stoffe am Beispiel atmosphärischer Quecksilberkomponenten. Teilprojekt: “Europäische Test-emissionsdatenbasis von Quecksilber-komponenten für Modellrechnungen”. Umweltforschungsplan des Bundesministers für Umwelt Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungsbericht 104 02 726. Erstellt im Auftrag von: GKSS Forschungszentrum Geesthacht GmbH, November 1991.
- Berdowski, J.J.M., J.M. Pacyna and C.Veldt, 1994: Chapter 3: Emissions. *In*: Van den Hout, K.D. (ed.), 1994: The Impact of Atmospheric Deposition of Non-Acidifying Pollutants on the Quality of European Forest Soils and the North Sea. Main report of the ESQUAD project. Air and Energy Directorate of the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM).
- Berdowski, J.J.M., C. Veldt, J. Baas and A.E. Klein, 1995: Technical paper to the OSPARCOM-HELCOM-UNECE emission inventory of heavy metals and persistent organic pollutants. TNO-report. TNO\_MEP-R95/247. Delft, the Netherlands.
- Berdowski, J.J.M., J. Baas, JP.J. Bloos, A.J.H. Visschedijk and P.Y.J. Zandveld, 1997: The European Emission Inventory of Heavy Metals and Persistent Organic Pollutants. Umweltforschungsplan des Bundesministers

- für Umwelt, Naturschutz und Reaktorsicherheit. Luftreinhaltung. Forschungsbericht 104 02 672/03. TNO, Apeldoorn, The Netherlands.
- Boehncke, A., J. Siebers and H.G. Nolting, 1990: Investigations of selected pesticides from natural and model surfaces. *Chemosphere*, Vol. 21: 1109-1124.
- Breivik, K., J.M. Pacyna, J. Münch, 1999: Use of  $\alpha$ -,  $\beta$ - and  $\gamma$ -hexachlorocyclohexane in Europe, 1970-1996. *The Science of the Total Environment*, Vol. 239, No. 1-3: 151-163.
- Brown, J.F. jr., G.M. Frame II, D.R. Olson and J.L. Webb, 1995: The Sources of the Coplanar PCBs. *Organohalogen Compounds*, Vol.26: 427-430.
- Brzuzy, L.P. and R.A. Hites, 1996: Global Mass Balance for Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans. *Environmental Science & Technology*, Vol. 30: No. 6: 1797-1804.
- Cowan, C.E., D. Mackay, T.C.J. Feitel, D. van de Meent, A. Di Guardo, J. Davies, N. Mackay (eds.), 1995: The Multi-Media Fate Model: A vital tool for predicting the fate of chemicals. Proceedings of workshop organised by the Society of Environmental Toxicology and Chemistry (SETAC). Setac Press.
- Duiser, J.A., and C. Veldt, 1989: Emissions into the atmosphere of polyaromatic hydrocarbons, polychlorinated hydrocarbons, polychlorinated biphenyls, lindane and hexachlorbenzene in Europe. TNO-Report 89-036. Apeldoorn, The Netherlands.
- EMEP/MSC-East, 1999: Long-Range Transport Model Intercomparison Study for Cadmium. Co-operative programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP). Prepared by Meteorological Synthesizing Centre-East/EMEP in co-operation with Advisory Expert Group. February, 1999, Moscow. Draft Report.
- EMEP/MSC-W, 1999: EMEP Emission data. Status Report 1999. EMEP/MSC-W Report, 1999. Report 1 / 99. Meteorological Synthesizing Centre – West, Norwegian Meteorological Institute. Oslo, Norway.
- Environment Canada, 1999: Dioxins and Furans and Hexachlorobenzene. Inventory of releases. Prepared by Environment Canada and the Federal/Provincial Task Force on Dioxins and Furans for the Federal-Provincial Advisory Committee for the Canadian Environmental Protection Act (CEPA-FPAC).
- Graedel, T.E., T.S. Bates, A.F. Bouwman, D. Cunnold, J. Dignon, I. Fung, D.J. Jacob, B.K. Lamb, J.A. Logan, G. Marland, P. Middleton, J.M. Pacyna, M. Placet and C. Veldt, 1993: A Compilation of Inventories of Emissions to the Atmosphere. *Global Biogeochemical Cycles*, Vol.7, No.1: 1-26.
- Kakareka, S., V. Khomich, T. Kukharchyk, V. Loginov, 1998: Heavy Metals Emission Factors Assessment for the CIS countries. Institute for Problems of Natural Resources Use and Ecology of the National Academy of Sciences of Belarus. Minsk, 1998.
- Li Y.-F. 1999: Global technical hexachlorocyclohexane usage and its contamination consequences in the Environment: From 1948 to 1997. *Science of the Total Environment*, Vol. 232: No. 3: 121-158.
- Olendrzynski, K., S. Anderberg, J. Bartnicki, J. Pacyna and W. Stigliani, 1995: Atmospheric Emissions and Depositions of Cadmium, Lead and Zinc in Europe During the Period 1955-1987. IIASA WP-95-35. International Institute for Applied Systems Analysis. Laxenbourg, Austria.
- Olendrzynski, K., S. Anderberg, J. Bartnicki, J. Pacyna and W. Stigliani, 1996: Atmospheric Emissions and Depositions of Cadmium, Lead and Zinc in Europe During the Period 1955-1987. *Environmental Reviews*, Vol. 4: 300-320.
- Pacyna, J.M., 1983: Trace Element Emission from Anthropogenic Sources in Europe. Norwegian Institute for Air Research, NILU Technical Report No. 10/82. Lillestrøm, Norway.
- Pacyna, J.M. and T.E.Graedel, 1995: Atmospheric emission inventories: Status and Prospects. *Ann. Rev. Energy Environ.* Vol. 20: 265-300.

- Pacyna, J.M. et al. 1999: Technical Report. Appendix 1 to the Executive Final Summary Report. Environmental Cycling of Selected Persistent Organic Pollutants (POPs) in the Baltic Region (Popcycling-Baltic project) Contract No. ENV4-CT96-0214. CD-Rom.
- Parma, Z., J. Vosta, J. Horejs, J.M. Pacyna and D. Thomas, 1995: Atmospheric emission inventory for persistent organic pollutants (POPs). A report prepared for External Affairs, Canada. Prague, The Czech Republic.
- Rappe, C., 1994: Dioxin, patterns and source identification. *Fresenius Journal of Analytical Chemistry*. Vol. 348: 63-75.
- Rüdel, H., 1997: Volatilisation of pesticides from soil and plant surfaces. *Chemosphere*, Vol. 35: 143-152.
- Schulz, D.E., G. Petrick and J.C. Duinker, 1989: Complete Characterization of Polychlorinated Biphenyl Congeners in Commercial Aroclor and Clophen Mixtures by Multidimensional Gas Chromatography – Electron Capture Detection. *Environmental Science and Technology*, Vol. 23: No. 7: 852-859.
- Strand, A., and Ø. Hov, 1996: A Model Strategy for the Simulation of Chlorinated Hydrocarbon Distributions in the Global Environment. *Water, Air and Soil Pollution*, Vol. 86: 283-316.
- UN/ECE, 1996: Joint EMEP/CORINAIR Atmospheric emission inventory guidebook. Prepared by the Task Force on Emission Inventories. European Environment Agency, Kongens Nytorv 6, DK 1050 Copenhagen, Denmark.
- UN/ECE, 1999: Progress report by the Chairman of the Task Force on Emission Inventories. EB.AIR/GE.1/1999/7.
- UNEP, 1999: Dioxin and Furan Inventories. National and regional emissions of PCDD/PCDF. United Nations Environment Programme. Prepared by UNEP Chemicals, Geneva, Switzerland. May, 1999.
- Vallack, H.W., D.J. Bakker, I. Brandt, E. Brorström-Lunden, A. Brouwer, K.R. Bull, C. Gough, R. Guardans, I. Holoubek, B. Jansson, R. Koch, J. Kuylenstierna, A. Lecloux, D. Mackay, P. McCutcheon, P. Mocarelli, R.D.F. Taalman, 1998: Controlling persistent organic pollutants – what next? *Environmental Toxicology and Pharmacology*, Vol. 6: 143-175.
- Van den Hout, K.D. (ed.), 1994: The Impact of Atmospheric Deposition of Non-Acidifying Pollutants on the Quality of European Forest Soils and the North Sea. Main report of the ESQUAD project. Air and Energy Directorate of the Dutch Ministry of Housing, Spatial Planning and the Environment (VROM).
- Voldner, E.C. and Y.-F. Li, 1995: Global usage of selected persistent organochlorines. *Science of the Total Environment*. Vol. 160/161: 201-210.
- Wania, F. and D. Mackay, 1995: A global distribution model for persistent organic pollutants. *Science of the Total Environment*, Vol. 160/161: 211-232.
- Wania, F. and D. Mackay, 1996: Tracking the Distribution of Persistent Organic Pollutants. *Environmental Science and Technology*, Vol. 30, No.9: 390A-396A.

## 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**

Eva Brorström-Lundén, Swedish Environmental Research Institute (IVL), (Sweden)

Torunn Berg, Norwegian Institute for Air Research (NILU), (Norway)

John Munthe, Swedish Environmental Research Institute (IVL), (Sweden)

### **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**

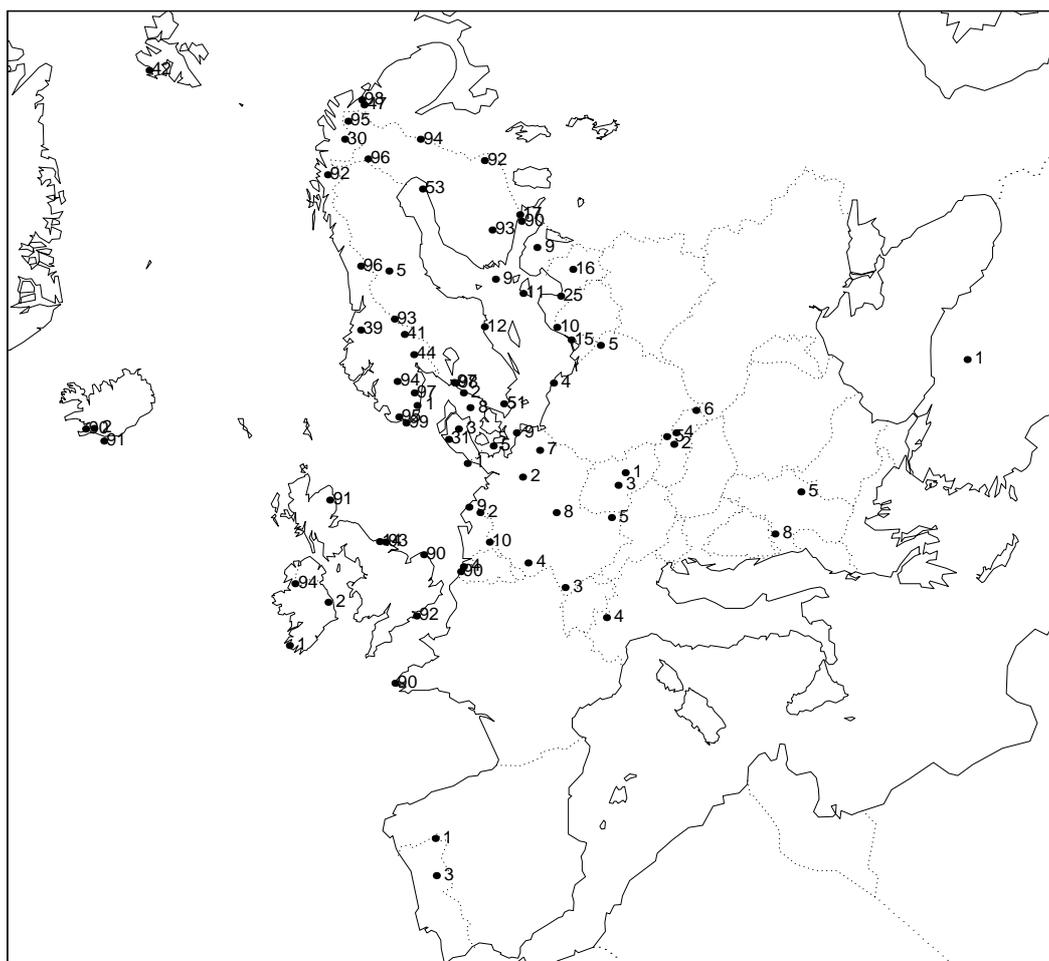
- Intercomparison exercises should regularly be run as an integrated part of the EMEP heavy metal measurement program and should be co-ordinated from the EMEP/CCC.
- Sampling and analysis guidelines for heavy metals should be developed and integrated in the normal laboratory QA/QC routines of all participating 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
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.

## 4. REFERENCES

- Alfheim, I. and Lindskog, A. (1984) A Comparison between Different High Volume Sampling for Collecting Ambient Airborne Particles for Mutagenicity Testing and for Analyses of Organic Compounds. *The Science of the Total Environ.*, 34, 203-222.
- Berg, T. and Semb, A. (1995) Preliminary Results from the HELCOM-EMEP-PARCOM-AMAP Analytical Intercomparison of Heavy Metals in Precipitation. EMEP/CCC-Note 1/95, Norwegian Institute for Air Research (NILU), P.O.Box 100, N-2007 Kjeller, Norway.

- Bidleman, T.F. (1988) Atmospheric processes. *Environ. Sci. Technol.*, 22, 361-367.
- Brorström-Lundén, E., Hilbert, G., Erecius-Poulsen, M., Kiviranta, A. Sandell, E., Braathen, O:A., Oehme, M., Larsson, P., Bakke, C., Alsberg, T., Egebäck, A-L. and Widequist, U. (1994) Intercomparison of Sampling Methods for Deposition Measurements of POPs. In proceedings from "Workshop on Techniques of Persistent Organic Pollutant Measurements in Northern Environments", Waterloo, Ontario ,Canada June, 1994.
- Brorström-Lundén E. (1995) Measurements of Semivolatile Organic Compounds in Air and Deposition. Ph.D thesis April 1995 Department of Analytical and Marine Chemistry, University of Göteborg.
- Chuang, J., Hannan, S. and Wilson, N. (1987) Field Comparison of Polyurethane Foam and XAD-2 for Air Sampling of Polynuclear Aromatic Hydrocarbons. *Environ. Sci. Technol.*, 21, 798-804.
- Cotham, W. and Bidleman, T. (1992) Laboratory Investigations of Partitioning of Organochlorine Compounds between the Gas phase and Atmospheric Aerosols on Glass Fiber Filter. *Environ. Sci. Technol.*, 26, 469-478.
- De Leeuw, F.A.A.M. et al., (1996) Proceedings of the EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants. RIVM Report 722401013, in press.
- Ebinghaus, R., S.G. Jennings, W.H. Schroeder, T. Berg, T. Donaghy, J. Guentzel, C. Kenny, H.H. Kock, K. Kvietkus, W. Landing, J. Munthe, E.M. Prestbo, D. Schneeberger, F. Slemr, J. Sommar, A. Urba, D. Wallschläger, Z. Xiao (1999): International field intercomparison measurements of atmospheric mercury species at Mace Head, Ireland, *Atmospheric Environment* **33** , 3063-3073
- Farmer, C. and Wade, T. (1986) Relationship of Ambient Atmospheric Hydrocarbon (C12-C32) Concentrations to Deposition. *Water Air and Soil Pollution*, 29,439-452.
- Foreman, W.T. and Bidleman, T.F. (1990). Semivolatile Organic Compounds in the Ambient air of Denver, Colorado. *Atmos. Environ.*, 24 A, 2405-2416.
- Franz, T. Eisenreich, S. and Swanson, M. (1991) Evaluation of Precipitation Samplers for Assessing Atmospheric Fluxes of Trace Organic Contaminants. *Chemosphere*, 23, 343-361.
- Hart, K., Loran, I. and Pankow, J. (1992) High-Volume Air Sampler for Particle and Gas Sampling Performance. *Environ. Sci. Technol.*, 26, 1048-1052.
- Kawamura, K. and Kaplan, I.R. (1986) Biogenic and Anthropogenic Organic Compounds in Rain and Snow Samples Collected in Southern California. *Atmos. Environ.*, 20,115-124.
- Leister, D and Baker, J. (1994) Atmospheric deposition of Organic Contaminants to the Chesapeake Bay. *Atmos. Environ.*, 28, 1499-1520.
- Ligocki, M.P. and Pankow, J.F. (1989) Measurements of the Gas/Particle Distributions of Atmospheric Organic Compounds. *Environ. Sci. Technol.*, 23, 75-83.
- Lindskog, A., Brorström-Lundén E., Alfheim, I. and Hagen, I.(1987) Chemical Transformation of PAH on Airborne Particles by Exposure to NO<sub>2</sub> during Sampling: Comparison between Two Filter Media. *Science Total Environ.*, 61, 51-57.
- McVeety, B. and Hites, R. (1988) Atmospheric Deposition of Polycyclic Aromatic Hydrocarbons to Water Surfaces: a Mass Balance Approach. *Atmos. Environ.*, 22, 511-536.
- Mazurek, M., Simoneit, B. R. T., Standley, L, Friedeman, D. and Beeman, C. (1987) Design an Use of a Collector for In Situ Isolation of Particulate Trace Organic Species in Precipitation. *Water Air and Soil Pollution*, 36, 193-206.
- Murray, M. and Andren, A. (1992) Precipitation Scavenging of Polychlorinated Biphenyl Congeners in the Great Lakes Region. *Atmos.Environ.*, 26 A, 883-897.

- NILU and IVL (1993) EMEP - Long term plans, Annex 1: Measurement Programme For Heavy Metals (Toxic Trace Elements). EMEP/CCC-note 2/93, Norwegian Institute for Air Research (NILU), P.O. Box 100, N-2007 Kjeller, Norway.
- Oehme, M. and Stray, H. (1982) Quantitative Determination of Ultra-Traces of Chlorinated Compounds in High-Volume Air Samples from the Arctic Using Polyurethane Foam as Collection Medium. *Z. Anal. Chem.*, 311, 665-673.
- Pacyna, J.M., Voldner, E., Keeler, G.J., and Evans, G. (1993) Proceedings of the First Workshop on Emissions and Modelling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals, EMEP/CCC-report 7/93, Norwegian Institute for Air Research (NILU), P.O. Box 100, N-2007 Kjeller, Norway.
- Ross, H.B. and Areskoug, H. (1993) Intercomparison of collection methods for the determination of trace metal deposition to European marginal seas. Institute of Environmental Research, Sweden, ITM Report 14.
- Sjöberg, K. (1992) Workshop on the collection and analysis of trace metals in precipitation. Swedish Environmental Research Institute, Sweden, IVL Report B 1081.
- SNV (1989) Atmospheric Trace Metals: Workshop on Their Collection and Analysis. Örsundsbro, Sweden, 1989, Swedish Environmental Protection Agency, SNV Report 3597.
- Wallace, J. and Hites, R. (1995) Computer Controlled Low Volume Air Sampler for the Measurements of Semivolatile Organic Compounds *Environ. Sci. Technol.*, 29, 2099-2106.
- Widequist, U., Alsberg, T., Egebäck, A-L Brorström-Lundén, E., Hilbert, Erecius-Poulsen, M., Kiviranta, A. Sandell, E., Braathen, O.A., Oehme, M., Larsson, P., and Bakke, C. (1996) Intercomparison of Sampling Methods for Deposition Measurements of POP. To be published.
- You, F. and Bidleman, F. (1984) Influence of Volatility on the Collection of Polycyclic Aromatic Hydrocarbon with Polyurethane Foam. *Environ. Sci. Technol.*, 18, 330-333.
- Zaranski, M., Patton, G., McConnell, L., Bidleman, T. and Mulik, J. (1991) Collection of Nonpolar Organic Compounds from Ambient Air Using Polyurethane Foam-Granular Adsorbent Sandwich Cartridges. *Anal. Chem.*, 63, 1228-1232.

### **4.3. Numerical Models of Long-range Atmospheric Transport of Heavy Metals: Current State, and Direction of Further Development**

I.Ilyin, Meteorological Synthesizing Center EAST (Russia)

J.Munthe, Swedish Environmental Research Institute (Sweden)

G.Petersen, GKSS Research Centre, Institute of Hydrophysics, (Germany)

A.Ryaboshapko, Meteorological Synthesizing Center EAST (Russia)

#### **1. INTRODUCTION**

During the last 2-3 decades considerable attention has been given to problems concerning negative effects of heavy metals (HMs) on various ecosystems in different environmental media. Numerous field observations indicate a significant increase of HM concentrations in agricultural and forest soils as well as in marine and inland water sediments. This increase is frequently observed in remote areas thousands of kilometers away from major anthropogenic sources and can be explained by transboundary atmospheric long-range transport only. An assessment of the potential ecological and health risks associated with atmospheric fluxes of heavy metals requires an understanding of the relationships between sources of emission to the atmosphere and the levels of concentrations measured in ambient air and precipitation. However, the complexity of the atmospheric processes of heavy metals makes results from measurement programs difficult to interpret without a clear conceptual model of the workings of the atmosphere. Further, measurements alone cannot be used directly by policy-makers to form balanced and cost-effective strategies for dealing with this problem; an understanding of individual processes within the atmosphere does not automatically imply an understanding of the entire system. A complete picture of individual heavy metal processes and their interactions with the atmospheric system as a whole can only be obtained by means of numerical modeling.

A detailed review of existing models of HM regional atmospheric transport was presented at each of the three previous WMO/EMEP workshops on POPs and HMs [Petersen 1993, 1994, 1996]. Since then, new and existing models for long-range transport of HMs have been developed and improved, respectively, with special emphasis on mercury, lead and cadmium, which have been defined by the recently ratified UN-ECE protocol on HMs and POPs to be the priority HMs of concern. The main focus of this paper is on basic features of new model developments since 1996 and on improvements that are still needed to address effectively the issues facing the above mentioned protocol.

## 2. PROGRESS IN HM MODEL DEVELOPMENT SINCE 1996

Basic features of HM atmospheric transport models together with input data requirements and output characteristics are summarised in the appendix in terms of an updated table from the background document of the previous workshop in Moscow [Petersen, 1996]. Model developments and applications since 1996 are discussed below in some more detail.

A numerical experiment for conjunction of models of regional and local scales was described by *M.Uliaz and K.Olendrzynski* [1996]. The goal of the work was to calculate concentrations of As, Cd, Pb and Zn in Polish province with rather fine (5 km) resolution. The calculation domain was presented by only one 150x150 km<sup>2</sup> EMEP grid cell, which covered the province. For estimation of deposition from other European sources the HMET model [Bartnicki *et al*, 1993] was applied. Detailed computations of concentrations and depositions within the grid cell were fulfilled by a mesoscale LPDD (Lagrangian Particle Dispersion and Deposition) model. Parameterisation of dry and wet deposition was adopted from the HMET [Bartnicki *et al*, 1993] model. Meteorological pre-processing for the LPDD was accomplished by a mesoscale meteorological model, which assimilated the data from six Polish meteorological observation stations. The LPDD also adopted detailed information about underlying surface types and about both point and area emission sources [Hawicka *et al*, 1996].

The LPDD could operate in the mode of forward trajectories resulting to fields of concentrations and depositions, and in the mode of backward trajectories. In latter case so-called influence functions could be calculated. The authors defined it as a value which, being multiplied by emission magnitude, could give a contribution of a certain source to pollution of a given receptor.

When comparing with the only measurement station, located not far from a zinc smelter, it was found out that the model underestimated Cd deposition about 2 orders of magnitude. The authors noted that the discrepancy could be connected both with possible analytical errors and with unreliable emission estimate for this zinc smelter.

*P.Pai et al.* [1997] undertook calculations of mercury concentrations and deposition fluxes over the USA by TEAM (Trace Element Analysis Model) model. Spatial resolution of the model was 100 km and time step was 1 hour. The model consisted of 6 layers along the vertical using terrain-following vertical co-ordinate and extended along the vertical up to 6 km. The model operated with three mercury forms – elemental mercury (Hg<sup>0</sup>), gaseous divalent mercury (Hg(II)<sub>gas</sub>) and particulate mercury (Hg<sub>part</sub>).

Three-dimensional meteorological fields of wind, temperature and humidity as well as two-dimensional fields of micrometeorological parameters used in the model were obtained using a diagnostic NGM (Nested Grid Model) model [Hoke *et al.*, 1989; Pai *et al.*, 1994]. The NGM assimilated the input meteorological data in a grid with rough resolution and then transformed them into fields with finer resolution.

Parameterisation of mercury chemistry was based on the approach suggested by C.Seigneur *et al.* [1994]. C.Seigneur *et al.* [1994, 1998, 1999] cast doubt on the key role of soot particles and relative importance of gas-phase and liquid-phase reactions. The authors believed that gas-phase reactions led mainly to mercury oxidation while in the liquid-phase reduction reactions prevailed.

Dry deposition of elemental mercury was neglected in the model. Dry deposition velocities of gaseous divalent and particulate mercury were calculated using electric resistance analogy approach [Pleim *et al.*, 1984]. For gaseous divalent mercury it was suggested to use the analogy to SO<sub>2</sub> and then to scale obtained value according to their solubilities. Wet deposition of elemental and gaseous divalent mercury was described using the chemical module. Wet scavenging of particulate form was computed using washout efficiency approach.

Emission fields used in the model were prepared by P.Pai *et al.* [1996]. Different source categories and heights were considered. Seasonal variations of the emissions were not included in the model. The model did not handle natural sources or re-emission but background concentrations of the three mercury forms were introduced instead.

Calculated and measured total gaseous mercury concentrations and wet depositions were within a factor of 2. It should be mentioned that the stations engaged into the comparison provided the data for different years. It was shown that wet deposition dominated over dry one. Uncertainties affected model results to the greatest degree were the emission data, cloudiness and precipitation, removal parameters and concentrations of oxidants used in the chemical module.

G.Petersen *et al.* [1998] presented a comprehensive Eulerian modeling framework for airborne mercury species. They suggested a condensed chemical tropospheric module to describe mercury transformations and wet removal. The module showed that adsorption of mercury species is very important for mercury fate. The framework included an explicit treatment of cloud processes. Two types of cloudiness – stratus and cumulus – were considered.

In 1998 *J. Bartnicki* presented a new version of the HMET model [*Bartnicki*, 1998]. Copper and three forms of mercury - elemental, gaseous divalent and particulate - were added to the previously calculated elements – Zn, As, Pb, and Cd [*Bartnicki et al*, 1993]. In contrast to the previous version, the model became two-layered one: a residence layer with a fixed top height of 3000 m was added and an exchange mechanism between the two layers was introduced. Seasonal and diurnal variations of emissions were included as well. Mercury related process parameterisation was based on ideas proposed by *G. Petersen et al.* [1995].

The calculations of Cu and Hg were carried out for one year and of the other metals for 11-year period from 1985 to 1995. The emission data used in the model were prepared in IIASA [*Olendrzynski et al.*, 1995]. A meteorological data set was prepared by LAM50E model (Limited Area Model, 50 km grid, EMEP version).

The comparison with measurements was based on the CCC (Chemical Coordinating Centre) database [*Berg et al*, 1996]. The comparison demonstrated that the best agreement between measured and modelled values was for network-averaged values of Pb and Cd concentrations. The correlation coefficients were also rather high (up to 0.75). On the other hand, the data for As and Zn differed from 3 to 7 times.

It was found out that the modelled deposition values were the most sensitive to introduction of the second layer and to parameterisation of wet depositions. The model was less sensitive to parameterisation of dry deposition and of assumed local deposition within a grid cell. The temporal emission variations practically did not affect the final results.

In the MSC-E on the base of the ASIMD model [*Pekar*, 1996] an operational model of HM transport, deposition and transformation was developed [*Ryaboshapko et al*, 1999]. The present version of the model took into account pollutant transport by large-scale vertical fluxes up to four-km height. The model was focussed on calculations of fields of concentrations, depositions and budget (country-by-country) matrices for Pb, Cd and Hg on annual basis in accordance with EMEP requirements. It operated four mercury forms since an organic form – dimethyl mercury – was added to traditionally used  $\text{Hg}^0$ ,  $\text{Hg(II)}$ , and  $\text{Hg}_{\text{part}}$ .

A chemical scheme used in the model was based on the Tropospheric Chemical Module (TCM) [*Petersen et al.*, 1998]. The authors significantly simplified the physical-chemical scheme by consideration of the most important processes only. They were able to find an analytical solution for the simplified scheme. In addition to the TCM decay reaction of dimethyl mercury was introduced.

Dry deposition velocity of elemental mercury was assumed to depend on seasons and a type of the underlying surface. Dry deposition for particulate form was calculated as for lead [Pekar, 1996] because of similarity of mass median diameters of particles-carriers. For divalent mercury dry deposition velocity was assumed to be constant. Dry deposition parameterisation for Pb and Cd was adopted from the ASIMD [Pekar, 1996].

Wet removal of elemental mercury was described by the chemical scheme. Wet deposition parameters of gaseous divalent mercury were taken as for nitric acid, and of particulate mercury – as for sulfate particles. For Pb and Cd a seasonal dependence of washout ratio was introduced.

The model used 50x50-km resolution fields of anthropogenic and natural emissions of the three metals and re-emission of mercury. Mercury re-emission field in Europe was assessed by *A.Ryaboshapko et al.* [1998]. Natural emission estimates were based on the works of *J.Nriagu* [1989], *F.Axenfeld et al.* [1991], *W.Fitzgerald and R.Mason* [1996], *B.Moiseev* [1997] and described in detail by *A.Ryaboshapko et al.* [1998].

The modelling results for Pb and Cd were verified on the base of some tens of measurement stations. The agreement was better than  $\pm 40\%$  for air concentrations and about factor of 2 for wet depositions. Wet deposition values were somewhat underestimated by the model. Only four stations measured air concentrations of total gaseous mercury and eight stations measured wet deposition were involved the verification procedure. For total gaseous mercury the compliance of measured and modelled concentrations was within  $\pm 30\%$ . Wet deposition values agreed within a factor of 2 for most of the stations. The measurements of all metals were referred to 1996 [Berg et al., 1996, 1997; Berg and Hjellbrekke, 1998].

*M.Sofiev* [1999] has developed three-dimensional hemispheric-scale model of transport and deposition of two mercury forms - elemental mercury and particulate mercury. The model includes simplified parameterisations of dry and wet deposition, sedimentation in oceanic water, soil fixation, chemical transformation and re-emission of the elemental form.

The model was run for a period of several years with anthropogenic emissions of America and Europe [Pacyna et al., 1993] starting with zero initial concentrations in air. It was shown that for the first 2 years concentrations of mercury in the atmosphere rapidly increased and then the increase had continued but much slower. The similar trend was indicated for deposition and re-emission fluxes.

*T. Bergan et al.* [1999] computed mercury concentrations and depositions on the global level. Climatological MOGUNTIA model [Zimmermann, 1987] was used to calculate two

mercury forms - Hg<sup>0</sup> and Hg(II) with spatial resolution of 10°x10° and 10 isobaric levels up to 100 hPa along the vertical.

The authors applied global anthropogenic mercury emission prepared in the framework of a GEIA project [*Pacyna*, 1998]. As to natural emission, it was assumed to be proportional to soil mercury content in the case of land and depended on latitude in the case of the Ocean. Re-emission was assumed to be proportional to the amount of current anthropogenic deposition.

The model did not consider detailed mercury chemistry. Only net conversion of Hg<sup>0</sup> to Hg(II) was described with the lifetime regarding this process equal to 1 yr. Dry deposition of gaseous divalent mercury was assumed to depend on the time of a day. For wet deposition gaseous divalent mercury lifetime of 2 weeks with regard to in-cloud scavenging was assumed. For elemental mercury dry deposition and wet scavenging were neglected.

The model results for 1990 demonstrated rather good agreement with measurements since concentrations and wet depositions fell within a factor of 2. However, the measurement data were taken for different years and some of them had an episodic character.

As mercury modelling comprises much more processes and compounds than modelling of other metals, extensive sensitivity studies are needed. *P.Pai et al.* [1999] carried out a sensitivity study of the TEAM model results (wet deposition, dry deposition and total gaseous mercury concentration) to different input parameters. The following parameters were considered: speciation of mercury emissions, dry deposition velocity of gaseous divalent mercury Hg(II), air concentrations of different reactants (chemistry), Hg(II) concentrations at the domain boundaries, and precipitation rate.

Results of the sensitivity study for the TEAM indicated that emission speciation had non-linear influence on the results and affected both the concentrations and depositions in the high-deposition regions to greater extent than in low-deposition regions. Chemistry had larger effect on the wet deposition for low-deposition than for high-deposition regions. Chemistry showed up a small effect on air concentrations and dry deposition. The effect of boundary Hg(II) concentrations was proved to be negligible for all investigated results. The effect of precipitation rate was more pronounced for wet deposition and nearly negligible for air concentrations and dry deposition. The authors showed that influence of change in dry deposition velocity of Hg(II) on wet and dry deposition had opposite signs, assuming nearly constant total deposition flux.

A more detailed hybrid kinetic and equilibrium modelling scheme (in comparison to *K.Pleijel and J.Munte's* one [1995]) was considered by *C.-J.Lin and S.O.Pehkonen* [1998]. They examined both liquid-phase and gas-phase reactions. Significant attention was paid to radical reactions in redox processes. The authors have showed that under atmospheric conditions OH<sup>·</sup> radical can act as a stronger oxidant than ozone, traditionally considered in the models. Reduction of divalent mercury in clouds is induced not only by sulfite complex but HO<sub>2</sub><sup>·</sup> radical also, at that the role of the radical is especially high in the oceanic atmosphere [*Lin and Pehkonen*, 1997]. A very important conclusion derived from Lin and Pehkonen's modelling study is that in 15- 20 hours divalent mercury concentration in a drop reaches its equilibrium even if concentrations of other reactants vary in wide ranges. When using typical for polluted atmosphere values of input parameters and concentrations of various reactants, the mercury concentrations calculated by the chemical model were similar to observed ones under real conditions.

### 3. EMISSION BASE

Any model of HM atmospheric transport rests first of all upon emission data. Obviously, accuracy of emission estimates directly affects accuracy of modelling results. Information on heavy metal emissions in Europe has been significantly improved for the recent years. As for 1997, 21 countries officially submitted information on emissions of lead, 16 - on cadmium, 15 - on mercury to the EMEP emission database. The accuracy of atmospheric emission data rose considerably. For example, in some countries the accuracy of lead emission data has risen up to 20%. It was favoured by widespread use of a common methodical guidebook developed in the framework of *EMEP/CORINAIR* [1996].

As a rule, emission sources are aggregated in spatial cells, which correspond to cells of a calculation domain and in their turn – to spatial resolution of calculated concentration and deposition fields. If earlier the information on emissions was available only with spatial resolution of 150 km, now the resolution on European scale has increased up to 50 km. In some cases [*Jaarsveld*, 1990; *Spasova and Todorov*, 1998] large point sources along with their specific characteristics such as co-ordinates, emission height, and emission amount are taken into account.

According to the UBA/TNO project [*Berdowski et al.*, 1997] the uncertainty of the emission data for Europe on the whole varies for different metals within the range of 1.5 - 3.5. At that, for countries of the north-western part of Europe real emission values can differ from corresponding estimates by 20-50%, and for countries of central and eastern Europe the uncertainty can be considerably higher. *J.Bartnicki* [1998] reported that the uncertainty for

lead emission in Europe is on the level of 25% and for cadmium - 50%. *J.Pacyna* [1999] believes that the accuracy of his latest estimates of cadmium and lead emissions is better than 25%.

#### 4. OBSERVATIONAL BASE

Model results can be considered as reliable if they are in a reasonable agreement with the measurement data. At the same time it should be kept in mind that measurement data have their own uncertainty. Considerable progress in improving of HM measurements within the EMEP region has been reached in the last three years [*Berg et al.*, 1996, 1997; *Berg and Hjellbrekke*, 1998]. At present the CCC/EMEP database comprises the measurement data of HM (mainly Pb and Cd) concentrations in air and precipitation from 70 stations in 20 European countries for the last decade. Accuracy of Pb measurements for the whole totality of data is about 25%. Total gaseous mercury concentration in air is measured with the accuracy of about 10%. Uncertainty in measurements of other metals can amount up to 50%.

In North America a programme of monitoring and assessment of mercury atmospheric transport has been launched. The programme joins efforts of Canada, the USA and Mexico. A great amount of published measurement data on concentrations of heavy metals over Great Lakes region is available.

#### 5. METEOROLOGICAL DATA

Meteorological information is certainly a very important input for any HM transport and deposition model. Selection of meteorological parameter fields, their spatial extent and detailisation is determined by purpose of calculations. Usually these parameters are wind direction and velocity, precipitation rate and temperature. As not all meteorological parameters can be obtained from observations or objective analysis data, some of them have to be calculated using meteorological pre-processing. For the analysis of atmospheric stability, calculations of mixing layer height, diffusion coefficients, etc., derivative parameters such as friction velocity, Monin-Obuckhov length, roughness length are needed.

First transport models applied to HMs [*Pacyna et al*, 1985, 1988; *Petersen et al.*, 1988] used the data from routine meteorological observations. Later versions [e.g., *Pekar*, 1996; *Barnicki*, 1998] began to assimilate data processed by objective analysis procedure. In this case the calculated parameters are distributed within a regular grid. In climatic models, for

example, in TRACE [*Alcamo et al*, 1992] the long-term (season-year) averaged meteorological data are used.

One of the most serious problems connected with the meteorological data assimilation is the problem of application of precipitation fields. The key parameters are precipitation rate, duration of events and frequency of precipitation. As a rule, the data prepared by meteorological models are used, since real precipitation is characterised by high patchiness and correct interpolation of them is hardly possible. At present, most of the transport models deal with 6-hour precipitation amounts and operate with 6-hour averaged precipitation rate. Modelled precipitation at some individual points can often differ significantly from the observed ones at monitoring stations, even if precipitation fields themselves are well correlated. It leads to the necessity of a critical analysis when comparing measured and calculated data on wet deposition. This was shown by *A.Ryaboshapko et al.* [1999].

It appears that in mercury modelling a problem of liquid water content in clouds can be important. Mercury in its different forms can be dissolved in cloud droplets, transported on long distances, and then wet deposited with precipitation. Besides, droplets can evaporate releasing mercury compounds back to air. It is noticeable that mercury properties “before dissolution” can differ considerably from those “after evaporation”. However, importance of these processes for long-range transport is not studied yet.

## 6. TRANSPORT SCHEMES

According to mathematical description of transport (advection) models can be divided into two large groups – Eulerian-type models and Lagrangian-type models. In Lagrangian-type models [e.g., *Pacyna et al.*, 1985, 1988; *Petersen et al.*, 1988; *Krell and Roeckner*, 1988; *Jaarsveld*, 1990; *Shannon and Voldner*, 1995; *Bullock et al.*, 1997] frame of reference is bound with air parcel moving along a trajectory. Usually such models use simplified descriptions of diffusion and removal processes. In climatological transport models wind roses or wind sector analyses are usually implemented. Concentrations of a pollutant at a receptor point formed by contributions of all sources are determined by probability of transport from different wind sectors. Eulerian-type models operate on fixed grid and deal with fluxes from one grid cell to another [e.g., *Petersen et al.*, 1990; *Pekar*, 1996; *Pai et al.*, 1997; *Bartnicki et al.*, 1993; *Bartnicki*, 1998]. Eulerian-type models can adopt more complicated description of diffusion and chemical transformation. On the other hand, there is a problem of artificial diffusion and these models usually consume more computer resources.

## 7. DRY DEPOSITION DESCRIPTIONS

Dry deposition of HM is usually defined by dry deposition velocity, which depends on a large number of parameters. They include atmospheric conditions, characteristics of the underlying surface, sizes of particles in case of aerosols. In some models [Syrakov and Galperin, 1998, Pai et al., 1997] gravitational settling is also considered.

In the first models of HM transport and deposition relatively simple formulations of dry deposition were used. In the works by *J.Pacyna et al.* [1985]; *U.Krell and E.Roeckner* [1988]; *G.Petersen et al.* [1988] dry deposition velocity of HMs was taken as a constant in time and space. Some models [e.g., *Pekar*, 1996; *Bartnicki*, 1998] calculated dry deposition velocity on the assumption of monodisperse aerosol. Presently just a few models take into account particle size distribution. In the EUTREND model [*Jaarsveld*, 1990, *Baart and Diederer*, 1991] five classes of particle sizes were introduced. The TRACE model [*Alcamo et al.*, 1992, 1994] used data on size distribution based on field measurements by *F.Dulac et al.* [1989]. Two important circumstances connected with particle size distribution should be mentioned. First, particle size spectrum is known rather poorly and a scatter of experimental data is quite broad [*Milford and Davidson*, 1985]. Second, it is not well known how this spectrum changes in the course of the atmospheric transport.

In mercury transport/deposition models dry deposition velocity is found for every mercury form separately. *J.Shannon and E.Voldner* [1995] in calculations of dry deposition flux of three mercury forms ( $\text{Hg}^0$ ,  $\text{Hg(II)}$  and  $\text{Hg}_{\text{part}}$ ) used tabulated dry deposition velocities, which were calculated on the base of field investigations and ideas on global mercury cycling. These dry deposition velocities depended on seasons and time of the day. Both earlier and now in the majority of mercury models [*Bloxam et al.*, 1991, *Petersen et al.*, 1995, *Bullock et al.*, 1997; *Pai et al.*, 1997, *Bergan et al.*, 1999] dry deposition of elemental mercury is firmly neglected or described using an extremely small value of dry deposition velocity [*Bartnicki*, 1998]. In some models [*Ryaboshapko et al.*, 1999] a value of dry deposition velocity, estimated on the base of field investigations and ideas of global cycle, was set. It depended on seasons (temperature) and the underlying surface type. *C.-J.Lin and S.O.Pehkonen* [1999] believe that elemental mercury is transported back to the earth mainly through dry deposition. Most probably that in real nature gaseous exchange between the atmosphere and underlying surface (water, soil, vegetation) occurs. A correct description of these exchange processes seems to be an important problem for further research.

*R.Bloxam et al.* [1991] adopted a sulfate particle analogy to describe dry deposition of particulate mercury. *G.Petersen et al.* [1995], *R. Bullock et al.* [1997], *A.Ryaboshapko et al.*,

[1999] and *J.Bartnicki* [1998] assumed that  $Hg_{part}$  behaviour was similar to that of lead-carrying particles. *P.Pai et al.* [1997] accepted log-normal distribution of mercury-bearing particles and obtained spectrum split into 15 intervals, taking into account gravitational settling as well. For every interval dry deposition velocity was calculated using resistance-analogy scheme [*Pleim et al.*, 1984]. However, the question about size spectrum of mercury containing particles is still open.

When describing dry deposition of gaseous divalent mercury *R.Bloxam et al.* [1991] assumed an analogy to nitric acid. This assumption was adopted in many models [*Petersen et al.*, 1995; *Bullock et al.*, 1997; *Bartnicki*, 1998; *Ryaboshapko et al.*, 1999]. The proposed reason for that is similar solubilities of  $HNO_3$  and  $Hg(II)$ . To compute surface resistance of  $Hg(II)$  *P.Pai et al.* [1997] suggested to use the analogy to  $SO_2$  and then to scale obtained value according to their solubilities. Anyway, it is not clear, how appropriate is the approach of the analogy to nitric acid or to sulfur dioxide, because neither field nor laboratory data on dry deposition velocity of  $Hg(II)$  are available. This mercury form can substantially contribute to depositions, especially in the vicinity of anthropogenic sources, that is why both theoretical and experimental researches seem to be necessary.

## 8. WET DEPOSITION DESCRIPTIONS

Wet deposition of “aerosol” heavy metals (Pb, Cd, Zn, Cu, etc) and readily soluble mercury forms ( $Hg(II)$  and  $Hg_{part}$ ) is considered in most of the models nearly in the same way. As a rule, washout ratio (equilibrium ratio of metal concentration in precipitation and in air) approach is applied. Sometimes a modification of the approach based on scavenging efficiency (ratio of dissolved mass of metal to total mass of metal within a selected volume) is implemented. Processes of in-cloud and sub-cloud scavenging are not subdivided in most of the models. Hence, it makes sense not to describe all the models, but just mention some peculiarities.

When describing wet scavenging on local (up to 10 km) scale, the TREND model considered in-cloud and sub-cloud scavenging separately. On the local scale wet scavenging is simulated in more detail because raindrop size spectrum and collision coefficients are taken into account. On larger scales wet scavenging is described in a simpler way. Another feature of the TREND is that not only precipitation rate, but also its duration is considered. *J.Bartnicki* [1998] in the HMET assumed that in the case of rainout, washout ratio is 50% greater than in the case of washout. Another remarkable feature of the HMET is that a portion of a grid cell occupied by precipitation is considered. *A.Ryaboshapko et al.* [1999] on the base of analysis of the data on HM concentrations in air and precipitation made an

attempt to trace seasonal variations of washout ratio for Pb and Cd. Derived seasonal dependence was applied to the model calculations. In mercury transport and deposition model ASTRAP [Shannon and Voldner, 1995] wet deposition process of particulate and gaseous divalent as well as elemental mercury was assumed as a power function of precipitation rate. For divalent mercury, loss to the free troposphere due to convective mixing was considered. Elemental mercury scavenging is usually described by a scheme of mercury chemical transformations in the aqueous phase [Petersen et al, 1995; Bullock et al., 1997; Pai et al, 1997; Bartnicki, 1998; Ryaboshapko et al, 1999].

## 9. DESCRIPTIONS OF MERCURY CHEMISTRY

In recent years range of investigations in the field of atmospheric chemistry of mercury and its compounds has extended dramatically. Studies of European school on atmospheric mercury behaviour modelling [Pleijel and Munte, 1995; Petersen et al., 1998] assume that aqueous-phase reactions in cloud drops lead presumably to oxidation of elemental mercury and eventual scavenging from the atmosphere by precipitation. On the other hand, C.Seigneur et al. [1998, 1999] have offered a fundamentally different scheme of mercury atmospheric behaviour: in cloud aqueous phase predominantly reduction of mercury to elemental form is supposed to occur. It implies that the presence of cloud aqueous phase increases mercury atmospheric lifetime.

In first mercury models, the rate of gas-phase oxidation of elemental mercury was assumed to be quite low. In many models this process have been just ignored. Recent studies showed that, besides ozone, a large number of other oxidants could take part in this process. Oxidation rate under specific conditions can be very fast. That can lead to sharp gradients of total gaseous mercury concentration [Schroeder et al., 1999].

## 10. MODEL RESULTS AND UNCERTAINTIES

The output from most of the HM transport models is provided in terms of annual averages of concentrations in air and precipitation and annual dry and wet deposition fluxes. Due to the scarcity of long-term HM field observations until the mid 90-s model predicted annual averages had to be compared against short term observed averages and/or observations from different years in most of the cases. Since 1995, several data sets of long-term measurements have become available for Pb and Cd allowing comparisons of model results against observations in a more consistent way for these two metals. Modelling and measurement results for Pb concentrations in air and precipitation agree within a factor of 2 for the most of the stations. Cr, Cu, Ni, Zn and As model results compare less satisfactorily

with observations: Models tend to underpredict concentrations of these species by a factors in the range of 2-7.

Mercury model results are characterised by larger uncertainties due to both insufficient understanding of mercury-related processes and limited amount of measurement data. In most cases, model outputs are presented in terms of total gaseous mercury concentration in air and concentration in precipitation. Sometimes results on air concentration of particulate mercury are also presented [*Petersen et al.*, 1995; *Ryaboshapko et al.*, 1998]. The output of existing models and observations generally agree within +/- 30% for total gaseous mercury concentration in air and within a factor of 2 for wet deposition.

## 11. REMAINING PROBLEMS AND DIRECTIONS OF FURTHER INVESTIGATIONS

As mentioned above, considerable progress in understanding the key processes governing HM emission, transport, and deposition from the atmosphere has been made in recent years. For example, mercury modelling has progressed by implementing more detailed chemical schemes and by explicit treatment of cloud processes. Despite of significant advancements in the knowledge of HM properties and in the understanding of the processes which determine control and fate of HMs in the atmosphere, our knowledge is far from complete. Listed below are the main areas of uncertainties and required activities towards further development of atmospheric transport models for HMs:

1. First of all, further revision of HM atmospheric emission data should be continued. In a framework of the EMEP it is presumably referred to countries of eastern and south-eastern Europe. Use of information on large point sources can contribute to increase of reliability of modelling results. Revision of seasonal variability of anthropogenic emission seems to be important. Key problem of mercury anthropogenic emissions is its speciation.
2. As a rule, existing models do not take into account natural HM input to the atmosphere. Only in mercury modelling this process is considered. For mercury as well as for the other metals natural contribution on the level of large regions can be comparable with anthropogenic. Hence, detailed investigation of HM natural emissions and their inventory are needed.
3. So far only in one regional-scale model [*Ryaboshapko et al.*, 1999] and also global model [*Bergan et al.*, 1999] it was attempted to use field of the long-term mercury atmospheric re-emission. However, it is universally recognised, that this process can substantially contribute to atmospheric input on the level of individual countries or model

domains as a whole. A question about possible re-emission of the other metals is still unclear.

4. All heavy metals are permanently present in the atmosphere in certain amounts. Global levels are considerably lower than those in air of industrial regions are. However, on a periphery of model domains on the regional level importance of HM (especially, of mercury) inflow can be considerable. Hence, reliable data on global background concentrations of the heavy metals are necessary.
5. Since all heavy metals (or at least some of them) can migrate in natural environments and re-enter the atmosphere, multi-compartment models of regional and global scale should be developed. These models should include the atmosphere but also vegetation, soil, and water bodies. Correct description of the exchange processes seems to be important problem for the further research.
6. HM particles-carriers are characterised by broad range of sizes. Obviously, models should consider behaviour of separate particle fractions, since their ability to be removed by wet or dry scavenging is determined by aerodynamic size to great extent. This fact conditions the necessity to obtain additional information of particle size distribution at moment of emission.
7. At present regional-scale and global-scale models use a concept of constancy of particle-carrier properties in a course of long-range transport. In the real atmosphere the spectrum of particles-carries can vary depending on surrounding conditions and processes of particle interactions. It leads to change of removal parameters.
8. Washout ratio (or scavenging efficiency) depends on properties of particles such as size, hydrophilicity or hydrophobity, and properties of precipitation, such as raindrop size spectrum, phase state. Accuracy of washout ratio as integral parameter for wet removal description is still not very high. In-cloud and sub-cloud wet scavenging processes are controlled by different mechanisms, and, hence, should be considered separately.
9. The question about dry uptake of elemental mercury is still open. This process is neglected in a number of models [e.g., *Pai et al.*, 1997]. However, some authors [*Lin and Pehkonen*, 1999] assume that this process is dominating pathway of elemental mercury removal from the atmosphere.
10. Sea water is supersaturated by elemental mercury everywhere (if only Henry's law works in this case). It implies permanent net flux from water to air. However, possible magnitude of direct elemental mercury flux from the atmosphere to sea water is uncertain. In other words, if sea water can be sink of additional portions of elemental mercury from polluted air masses.

11. At present dry and wet deposition fluxes of mercury compounds are described using analogy to better-investigated substances such as nitric acid, sulfur dioxide, sulfate particles. However, it is not clear how appropriate is the approach of the analogy, because neither field nor laboratory data are available. Hence, both theoretical and experimental research seems to be necessary.
12. In first models of mercury atmospheric transport its gas-phase oxidation was flatly ignored. Recent studies have shown that, besides ozone, large number of the other oxidants can take part in this process. Taking those into account can substantially change a role of gas-phase reactions in model schemes.
13. When describing aqueous-phase processes it is assumed that significant part in mercury chemistry is played by cloud water composition. Information on this question is rather scarce. Only one station in Europe proceeds measurements of cloud water composition in operational mode.
14. Recent *C.Seigneur et al.* [1998, 1999] studies cast doubt on key role of sorption of mercury and its compounds by particles both in gas and aqueous phase. The question, if there is enough solid particles (including soot particles) in air and drops for mercury accumulation, appears. Besides, question about exchange rates of mercury between solid sorbent and gas or water is still unclear.
15. Presently two fundamentally viewpoints on aqueous-phase mercury chemistry are distinguished. According to [*Pleijel and Munthe, 1995; Petersen et al., 1998*] presence of clouds favours oxidation and removal of mercury from the atmosphere. On the other hand, *C.Seigneur et al.* [1998, 1999] believe that presence of cloud liquid phase leads mainly to reduction of elemental mercury and increases its lifetime in the atmosphere. In order to increase reliability of model schemes solution of this dilemma and revision of gas-phase and aqueous-phase reaction rates is needed.
16. Many model experiments indicated that characteristic times of establishment of chemical equilibrium in cloud droplets made up hours-tens of ours. On the other hand, lifetime of usual cloud system is much less. Thus, process of drop evaporation in case of cloud system destruction and mercury fate after drop evaporation could play important role in the model schemes.
17. Taking into account the complexity of heavy metal modelling, co-operation between EMEP and national, international programs is of great importance. A considerable role belongs to model intercomparison studies, which can reveal shortcomings of operational models and increase accuracy of environment state assessment.

Appendix  
Summary of HM transport models

Model name	Type	Typical period of calculations	Domain, grid size	Metals	Institution	Source of meteorological input	Reference
EMEP/MSC-W	Lagrangian, 1-layer	days - weeks	Europe, 150 km	As, Cd, Cr, Mn, Ni, Pb, Sd, Se, V, Zn	NILU	Routine 6-hour observations or NWP	<i>Pacyna et al., 1985, 1988</i>
GKSS EMEP/MSC-W	Lagrangian, 1-layer	months - years	Europe, 150 km	Pb	GKSS	Observations or HIRLAM	<i>Petersen et al., 1988</i>
HHLRT	3D, stochastic	months	Europe, 1.5°x1.5°	Pb, Cd	HMI	ECMWF and NILU	<i>Krell and Roeckner, 1988</i>
ADOM (Hg version)	3D, Eulerian	months - years	North America	Hg <sup>0</sup> , Hg <sup>2+</sup> (gas), Hg(part)	GKSS/AES		<i>Petersen et al., 1990, Bloxam et al., 1991</i>
TREND (EUTREND)	Statistical, Gaussian, trajectory	months - years	Europe, 1/2° lat, 1° long; or 50 km	Cd, Cr, Cu, Pb, Hg Ni, Zn	RIVM/TNO	KNMI and ECMWF	<i>Baart and Diederer, 1991, Jaarsveld, 1990</i>
TRACE	Climatological	years	Europe, 150 km	As, Cd, Pb, Zn	IIASA	Climatological	<i>Alcamo et al., 1992; Alcamo et al., 1994</i>
HMET	3D, Eulerian	months - years	Europe, 150 or 50 km	As, Cd, Cu, Pb, Zn Hg	DNMI	LAM50E	<i>Bartnicki, 1998</i>
LPDD	Lagrangian	months - years	Polish province, 5 km	Cd, As, Pb, Zn	IIASA	observations + mesoscale model	<i>Uliasz and Olendrzynski, 1996</i>
ASIMD	3D, Eulerian	months - years	Europe, 150 or 50 km	Cd, Pb	EMEP/MSC-E	SDA-RHMC	<i>Pekar, 1996</i>
LPMOD	3D Eulerian	months - years	Europe, 75 km.	Cd, Pb	EMEP/MSC-E	SDA-RHMC	<i>Pekar, 1996</i>
GKSS-EMEP	Lagrangian, 1-layer	months - years	Europe, 150 km.	Hg <sup>0</sup> , Hg <sup>2+</sup> (gas), Hg(part)	GKSS	NWP and observations	<i>Petersen et al., 1995</i>
ASTRAP	Lagrangian, statistical description of diffusion	seasons- years	Great Lakes Region, about 60 km	Hg <sup>0</sup> , Hg <sup>2+</sup> (gas), Hg(part)	ANL-USA and Environment Canada	CMC analyses	<i>Shannon and Voldner, 1995</i>
RELMAP	Lagrangian, 3D puff	months - years	USA, 1/3° lat, 1/2° long.	Hg <sup>0</sup> , Hg <sup>2+</sup> (gas), Hg(part)	NOAA and EPA USA	NGM and NCDC	<i>Bullock et al., 1997</i>
TEAM	Eulerian, 3D	months - years	USA, 100 km.	Hg <sup>0</sup> , Hg <sup>2+</sup> (gas), Hg(part)	ENSR	Interpolated NGM output	<i>Pai et al., 1997</i>
HM – MSC-E (Modified ASIMD)	Eulerian, 3D	months-years	Europe, 50 km	Pb, Cd, Hg <sup>0</sup> , Hg <sup>2+</sup> (gas), Hg(part), DMM	EMEP/MSC-E	SDA - RHMC	<i>Pekar, 1996 Ryaboshapko et al., 1999</i>
	Eulerian, 3D	years	Northern Hemisphere	Hg <sup>0</sup> and Hg <sup>2+</sup>		NCAR	<i>Sofiev, 1999</i>
MOGUNTIA	Eulerian, 3D	years	Global, 10°x10°	Hg <sup>0</sup> and Hg <sup>2+</sup>	Stockholm University	monthly averaged observations	<i>Bergan et al., 1999</i>

Abbreviations used in the Table

ADOM - Acid Deposition and Oxidation Model	KNMI - The Netherlands Meteorological Institute
ANL - Argonne National Laboratory	LAM50E - Limited Area Model, 50 km grid, EMEP version
ASIMD - asymmetric advection scheme	LPDD - Lagrangian Particle Dispersion and Deposition
ASTRAP - Advanced Statistical Trajectory Regional Air Pollution	LPMOD - Large Particle MODel
DMM - dimethyl mercury	MSC-E - Meteorological Synthesising Centre - East
DNMI - Norwegian Meteorological Institute	MSC-W - Meteorological Synthesising Centre – West
CCC - Chemical Coordinating Centre	NCAR – National Center for Atmospheric Research
CMC - Canadian Meteorological Centre	NCDC - National Climatic Data Center
ECMWF - European Centre for Medium-Range Weather Forecast	NGM - Nested Grid Model
EMEP - European Monitoring and Evaluation Programme	NOAA - National Ocean and Atmosphere Administration
ENSR - ?	NWP - Norwegian Numerical Weather Prediction model
EPA - Environmental Protection Agency	RELMAP - Regional Lagrangian Model of Air Pollution
GEIA - Global Emission Inventory Activity	RHMC - Russian HydroMeteorological Centre
GKSS - ?	RIVM - National Institute of Public Health and Environmental Protection
HHLRT - Hamburg Long-Range Transport Model	SDA - System for Diagnosis of state of the lower Atmosphere
HIRLAM - High Resolution Limited Area Model	TCM - Tropospheric Chemistry Module
HM - heavy metal	TEAM - Trace Element Analysis Model
HMI - Hamburg Meteorological Institute	TNO - Netherlands organisation for applied scientific research
HMET - Heavy Metal Eulerian Transport	TRACE - TRace toxic Air Concentrations in Europe
IIASA - International Institute for Applied Systems Analysis	

## References

- Alcamo J., Bartnicki J., Olendrzynski K. and Pacyna J. [1992] Computing heavy metals in Europe's atmosphere – I. Model development and testing. *Atmospheric Environment*, Vol. 26A, N18, pp. 3355 – 3369.
- Alcamo J., Bozo L. and Bartnicki J. [1994] Model simulations of the atmospheric input of trace metals into the North, Baltic, Mediterranean and Black Seas. In: *Air pollution modeling and its application X*. Ed: Sven-Erik Gryning and Millan M. Millan, NATO, Plenum Press.
- Axenfeld F., Münch J., and Pacyna J.M. [1991] Belastung von Nord- und Ostsee durch ökologisch gefährliche Stoffe am Beispiel atmosphärischer Quecksilberkomponenten. Teilprojekt: Europäische Test-Emissionensdatenbasis von Quecksilber-Komponenten für Modellrechnungen". Dornier, Report 104 02 726, 99 p.
- Baart A. C. and Diederer H. S. M. A. [1991] Calculation of the atmospheric deposition of 29 contaminants to the Rhine catchment area. TNO-rapport R 95/219. Instituut voor Milieuwetenschappen. TNO, 2600 JA Delft, The Netherlands.
- Bartnicki J., Modzelewski H., Szweczyk-Bartnicka H., Saltbones J., Berge E., Bott A. [1993] An Eulerian Model for Atmospheric Transport of Heavy Metals over Europe: Model Development and Testing. Technical report No 117, ISSN 0332-9879, OSLO, August.
- Bartnicki J. [1998] Heavy Metals Eulerian Transport Model – HMET. Model Description and Results. Norwegian Meteorological Institute (DNMI), Oslo, Norway, Research Report No. 65, 286 p.
- Berdowski J. J. M., Baas J., Bloos J. P. J., Visschedijk A. J. H. and Zandveld P. Y. J. [1997], The European Emission Inventory of Heavy Metals and Persistent Organic Pollutants for 1990, TNO Institute of Environmental Sciences, Energy Research and Process Innovation, UBA-FB report 104 02 672/03, Apeldoorn, The Netherlands, June 1997, 239 p.
- Berg T., Hjelmbrekke, A. G., Skjelmoen J. E. [1996] Heavy Metals and POPs within the ECE region. EMEP/CCC Report 8/96. Norwegian Institute for Air Research, Kjeller, Norway.
- Berg T. and Hjelmbrekke A.G. [1998] Heavy metals and POPs within the ECE region. Supplementary data for 1989-1996. Kjeller, Norwegian Institute for Air Research, NILU EMEP/CCC-Report 7/98, 105 p.
- Berg T., Hjelmbrekke A.-G., and Ritter N. [1997]. Heavy metals and POPs within the ECE region. Additional data. EMEP/CCC-Report 9/97, 79 p.
- Bergan T., Gallardo L. and Rodhe H. [1999] Mercury in the global troposphere: a three-dimensional study. *Atmospheric Environment* 33, pp 1575-1585.
- Bloxam R., Wong S., Misra P. K., Voldner E., Schroeder W. and Petersen G. [1991]. Modelling the long range transport, transformation and deposition of mercury in a comprehensive Eulerian framework. Proc. 8<sup>th</sup> Internat. Conf. Heavy Metals in the Environment. CEP Consultants Ltd., Heavy Metals Secretariat, Edinburgh, U.K.
- Bullock R. O, Benjey W. G., and Keating M. H. [1997] Modeling of regional scale atmospheric mercury transport and deposition using RELMAP. In: *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*. Ed. by Joel E. Baker. SETAC Press, Pensacola, 1997, pp.323-347.
- Fitzgerald W.F. and Mason R.P. [1996] The global mercury cycle: oceanic and anthropogenic aspects. In: *Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances*. Ed. By W.Baeyens, R.Ebinghaus and O.Vasiliev. NATO ASI Series, 2. Environment- Vol. 21. Kluwer Academic Publ., Dordrecht, pp. 85-108.
- EMEP/CORINAIR [1996] Atmospheric Emission Inventory Guidebook - First Edition (ed. by G.McInnes), European Environment Agency, Copenhagen.
- Hławicka S., Korcz, M., Cenowski, M., Bronder J., and Fudała J. [1996]. Atmospheric emission of selected heavy metals in the Katowice voivodship and high resolution land use data of the area. Technical report for the International Institute for Applied System Analysis, IIASA, Laxenburg, Austria
- Hoke, J. E., Phillips, N. A., DiMego, G. L., Tuccillo, J. I. and Sela, J. G. [1989]. The regional analysis and forecast system of a national meteorological center. *Weather and Forecasting* 4.
- Jaarsveld van, J. A. [1990]. An Operational atmospheric model for Priority Substances; specification and instructions for use. RIVM report No. 222501002, Bilthoven, The Netherlands.
- Krell U. and Roeckner E. [1988] Model simulation of the atmospheric input of lead and cadmium into the north sea. *Atmospheric Environment*, Vol. 22, N2, pp 357 – 381
- Lin C.-J. and Pehkonen S.O. [1997]. Aqueous free radical chemistry of mercury in the presence of iron oxides and ambient aerosol. *Atm. Envir.*, Vol. 31, pp. 4125-4137.

- Lin C.-J. and Pehkonen S.O. [1998]. Two-phase model of mercury chemistry in the atmosphere. *Atm. Envir.*, Vol. 32, No 14/15, pp. 2543-2558.
- Lin C.-J. and Pehkonen S.O. [1999]. The chemistry of atmospheric mercury: a review. *Atm. Envir.*, Vol. 33, pp. 2067-2079
- Moiseev B.N. [1997] Development of a model of mercury emission fluxes from soil and their mapping in Europe within the EMEP grid. EMEP/MSC-E Technical note 8/97.
- Nriagu J.O. [1989]. A global assessment of natural sources of atmospheric trace metals. *Nature*, 338, 47-49.
- Olendrzynski K., Anderberg S., Bartnicki J., Pacyna J. Stigliani W. [1995] Atmospheric emissions and depositions of cadmium, lead and zinc in Europe during the period 1955-1987 Working Paper WP-95-35. International Institute for Applied Systems Analysis, Laxenburg, Austria.
- Pacyna J., Ottar B., Tomza U., and Maenhaut W. [1985]. Long-Range Transport of Trace Elements to Ny Alesund, Spitsbergen. *Atmospheric Environment*, Vol 19, N6, pp857 – 865
- Pacyna J., Bartonova A., Cornille P., and Maenhaut W. [1988] Modelling of Long-Range Transport of Trace Elements. A Case Study. *Atmospheric Environment*, Vol 32, N1, pp107 –114
- Pacyna, J. M. [1984] Estimation of atmospheric emissions of trace elements from anthropogenic sources in Europe. *Atmospheric Environment.*, 18, pp.41-50., 1984
- Pacyna J. M. [1985]. Spatial distribution of the As, Cd, Cu, Pb, V and Zn emissions in Europe within 1.5° grid net. Report No. 60/85. The Norwegian Institute for Air Research, Lillestrøm, Norway
- Pacyna J. [1988] Atmospheric lead emission in Europe in 1985. The Norwegian Institute for Air Research, NILU OR: 19/88
- Pacyna J.M. [1999] Private communication with Prof. Jozef Pacyna.
- Pacyna J. M. [1998] Heavy Metals. Chapter 7 of the AMAP Assessment Report: Arctic Pollution Issues. The Arctic Monitoring and Assessment Programme, P.O. Box 8100, N-0037 Oslo, Norway.
- Pacyna J. M., Voldner E., Bidleman, T., Evans, G., Keeler G. J. [1993] Emission, atmospheric transport and deposition of heavy metals and persistent organic pollutants. Proceedings 1<sup>st</sup> Workshop on Emission and Modelling of the Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals, Durham, NC, USA, EMEP/CCC report 7/93, 1993, pp 45-138.
- Pai P., Karamchandani P. and Venkatram, A. [1994] Development of meteorological fields for an Eulerian visibility model. In: Proceedings of Aerosol and Visibility Conference, Snowbird, UT, pp. 1215-1222
- Pai P., Heisler, S. and Joshi, A. [1996]. An emission inventory for regional atmospheric modeling of mercury. *Water, Air and Soil Pollution*,
- Pai P., Karamchandani P. and Seigneur C. [1997]. Simulation of the Regional Atmospheric Transport and Fate of Mercury using a comprehensive Eulerian Model. *Atmospheric Environment*, Vol 31, N17, pp2717 – 2732, 1997
- Pai P., Karamchandani P. and Seigneur C. [1999]. Sensitivity of simulated atmospheric mercury concentrations and deposition to model input parameters. *Journal of Geophysical Research*, Vol. 104., pp. 13,855-13,868.
- Pekar M. [1996]. Regional model LPMOD and ASIMD. Algorithms, parameterization and results of application to Pb and Cd in Europe scale for 1990. EMEP/MSC-E Report 9/96, August, 1996
- Petersen G., Weber H., Graßl H. [1988]. Modelling the atmospheric transport of trace metals from Europe to the North Sea and the Baltic Sea. In: Control and fate of atmospheric trace metals. Edited by Pacyna J. M. and Ottar B. Kluwer, Dordrecht, 1988
- Petersen G., Schneider B., Eppel D., Grassl H., Iverfeldt A., Misra P.K., Bloxam R., Wong S., Schroeder W.H., Voldner E., and Pacyna J. [1990]. Numerical modelling of the atmospheric transport, chemical transformations and deposition of mercury. Report GKSS 90/E/24, GKSS Research Center, Geesthacht, Germany.
- Petersen G., Iverfeldt, A. and Munthe J. [1995]. Atmospheric mercury species over Central and Northern Europe. Model calculations and comparison with measurements from the Nordic air and precipitation network for 1987 and 1988. *Atmospheric Environment* 29, 47-67.
- Petersen G. [1993]. Modelling the Atmospheric Transport and Deposition of Heavy Metals—A Review from Results from Models Applied in Europe. First Workshop on Emissions and Modelling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals. U. S Environmental Protection Agency, Research Triangle Park, NC, U.S.A. , Mayy 6-7, 1993. In : J. M. Pacyna, E. Voldner, G. J. Keeler, G. Evans (eds) : Proceedings of the First Workshop on Emissions and Modelling of Atmospheric Transport of Persistent Organic Pollutants and Heavy Metals. EMEP-CCC Report 7/93, pp 261-279.

- Petersen G., Iverfeldt A. [1994]. Numerical Modelling of Atmospheric Transport and Deposition of Heavy Metals-A Review of Results from Models Applied in Europe. EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants. Beekbergen, the Netherlands, May 3-6, 1994. In: EMEP Workshop on European Monitoring, Modelling and Assessment of Heavy Metals and Persistent Organic Pollutants. Rijksinstituut voor Volksgezondheid en Milieuhygiene, P.O. Box 1, NL-3720 BA Bilthoven, the Netherlands, pp. 23-31.
- Petersen G., [1996]. The current state and future direction of numerical models in simulating atmospheric long-range transport of heavy metals over Europe: A Review. Report and proceedings of the assessment of EMEP activities concerning heavy metals and persistent organic pollutants and their further development. Vol. 1. World Meteorological Organization, Global Atmosphere Watch, No. 117, pp. 33-49.
- Petersen G., Munthe J., Pleijel K., Bloxam R., and Kumar A.V. [1998] A comprehensive Eulerian modeling framework for airborne mercury species: Development and testing of the tropospheric chemistry module (TCM). *Atm. Environ.*, Vol. 32, No. 5, pp. 829-843.
- Pleijel K., and Munte J. [1995]. Modeling the atmospheric mercury cycle - chemistry in fog droplets. *Atm. Environ.*, Vol. 29, No. 12, pp. 1441-1457.
- Pleim, J., Venkatram, A. and Yamartino, R. [1984]. ADOM/TRAP model development program, volume 4: the dry deposition module. ERT Document No. PB890-520, ENSR Consulting and Engineering, Acton, MA.
- Pul van W. A. J., Nijenhuis W. A. S., and de Leeuw F. A. A. M. [1998] Deposition of heavy metals to the Convention waters of OSPARCOM. March, 1998 RIVM, report 722401016, Bilthoven, The Netherlands.
- Ryaboshapko A., Ilyin I., Gusev A., and Afinogenova O., [1998]. Mercury in the Atmosphere of Europe: Concentrations, deposition patterns, transboundary fluxes. Meteorological Synthesizing Centre - East, EMEP/MSCE Report 7/98, June 1998, Moscow, 55 p.
- Ryaboshapko A., Ilyin I., Gusev A., Afinogenova O., Berg T., and A.G. Hjellbrekke [1999] Monitoring and modelling of lead, cadmium and mercury transboundary transport in the atmosphere of Europe. Joint report of EMEP centers MSCE and CCC. MSCE report No 1/99, 1999
- Schroeder W.H., Anlauf K.A., and Barrie L.A., [1999]. Depletion of elemental mercury vapour in the Arctic troposphere after polar sunrise. Proceedings of EUROTRAC Symposium'98. Volume 2. Eds: Patricia Borrell and Peter Borrell. WIT Press, Boston, Southampton, pp. 358-362.
- Shannon J. D., and Voldner E. C. [1995] Modeling atmospheric concentrations of mercury and depositions to the Great Lakes. *Atmospheric Environment* Vol. 29, No 14, pp. 1649-1661
- Seigneur, C., Wrobel, J. and Constantinou, E. [1994]. A chemical kinetic mechanism for atmospheric inorganic mercury. *Environmental Science and Technology* 28, 1589-1597.
- Seigneur C., Abeck H., Chia G., and Reinhard M., [1998]. Mercury adsorption to elemental carbon (SOOT) particles and atmospheric particulate matter. *Atm. Environ.*, Vol. 32, No. 14/15, pp. 2649-2657.
- Seigneur C., and Lohman K., [1999]. Comparison of several chemical mechanisms for atmospheric mercury concentrations. In: *Mercury as a Global Pollutant. 5<sup>th</sup> International Conference*, Rio de Janeiro, May 23-28, 1999. Book of abstracts, p. 90.
- Sofiev, M. [1999] A computer simulation of the anthropogenic mercury accumulation in the environment. Proceedings of EUROTRAC Symposium'98. Volume 2. Eds: Patricia M. Borrell and Peter Borrell. WIT press, Boston, Southampton, pp. 369-373.
- Spasova T., and Todorov T. [1998] Computation of the lead and benzo(a)pyrene concentrations and depositions over south-eastern Europe using the Bulgarian model EMAP. In: *Long-Range Air Pollution: from Models to Policies*. Eds. D.Syrakov, E.Batchvarova and B.Wiman. Proc. From the Swedish-Bulgarian Workshop, 19-23 October 1997, Sozopol, Bulgaria, Pensoft Publisher, pp. 85-93.
- Syrakov D., Galperin M. [1998]. Parameterization of aerosol specific properties in long-range air pollution transport. 3D realization and validation. In: *Long-Range Air Pollution: from Models to Policies*. Eds: Syrakov D., Batchvarova E. and Wiman B. Proceedings from the Swedish-Bulgarian Workshop 19-23 October 1997, Sozopol, Bulgaria.
- Uliasz M. and Olendrzynski K. [1996] Modeling of Atmospheric Transport and Deposition of Heavy Metals in the Katowice Province IASIA, Working Paper WP-96-123, November 1996
- Zimmermann, P., 1987. MOGUNTIA a handy global tracer model. XVI NATO/CCMS International Technical Meeting on air pollution modeling and application, 6-10 April Lindau, Lake Constance, FRG.

#### **4.4. Cadmium Model Intercomparison Study**

A. Gusev, Meteorological Synthesizing Centre - East (Russia)

The intercomparison of transport models for heavy metals (HM) was initiated by recommendations of the EMEP workshop held in Beekbergen in 1994 and the 18th session of the EMEP Steering Body. This study was aimed at the comparison of approaches used for evaluation of HM transport and deposition within the scope of European region. Beginning with the lead model intercomparison in 1996, this activity has been continued with cadmium study and is planned to be continued for mercury models. These intercomparisons form a sequence of studies which makes a valuable contribution to the development of modelling basis for HMs.

The intercomparison program for the first stage devoted to lead models was developed by a group of experts in the field of HM modelling representing DNMI (Norway), IVL (Sweden), RIVM (the Netherlands), IIASA (Austria), NILU (Norway), GKSS (Germany). MSC-E in collaboration with advisory expert group prepared a protocol, program and initial data for calculations. Seven regional HM transport models participated at the first stage. Results of the comparison were presented in the report submitted to the EMEP Steering Body [EMEP/MSC-E report 2/96, 1996].

The comparison of cadmium transport models for European region is the next stage of this activity. The same group of experts from different scientific organizations in cooperation with MSC-E has developed the program of the cadmium model intercomparison. The main objective of a given study, as well as of the previous one for lead, is the comparison of approaches used for HM transport modelling by different groups of scientists. The answer to the question - how close are modelling results of different models - is of particular interest. The set of data including meteorology, emission, and measurements was agreed by this advisory expert group. 1990 was selected as the reference year. The calculation domain covers the EMEP region.

Four regional HM transport models participated in this stage of model intercomparison: ASIMD, EMAP, GKSS, and TREND. These models are of different types - three-dimensional Eulerian and two-dimensional Lagrangian. Most of them use rather high spatial resolution 50x50 km<sup>2</sup>. Besides, independent of the type, there are some differences in approaches to the description of wet and dry deposition as well as different parameterization of particle size distribution.

The suggested methodology is similar to those used in other model evaluation studies, for example, ETEX. It should be noted that in distinction from ETEX project, in which the transport of a neutral pollutant was considered during a short episode, this study deals with transport of

trace metal, cadmium, and computations are made within the EMEP region for the whole year (1990). The comparison of model results with measurements makes the basis for the study. As at the previous stage for lead intercomparison procedure involves calculations of transboundary transport on example of three countries – Italy, Poland and United Kingdom.

As it was recommended by the advisory expert group, cadmium emission estimates of ESQUAD project for 1990 were used in calculations. Total emission for Europe accounted to 1,634 tonnes per year. Temporal variations of emissions were not considered. It was assumed that emissions are uniform round the year. Emission distribution with height was determined by each model separately.

Measurement data were obtained from the database of Chemical Coordinating Centre of EMEP (CCC). The following data were used for the comparison: air concentrations of Cd measured at 16 stations; Cd concentrations in precipitation measured at 26 stations. No data were available for the eastern and southern parts of the EMEP region.

Intercomparison procedure comprised two parts: the comparison of calculation results with observations and the assessment of cadmium transboundary transport. In view of the fact that practically the same models took part in this intercomparison study compared to the previous one, a general approach was kept but the methodology was modified. According to the procedure each model made four runs of calculations with different sets of emissions: one with cadmium emissions of all European countries (included in the inventory of ESQUAD project) and three runs with emissions of Italy, Poland, and United Kingdom.

The comparison with observed concentrations of cadmium was made on the basis of mean annual values. Calculated and measured cadmium concentrations in air and in precipitation and wet deposition for 1990 were compared. To quantitatively compare modelling results with measurements the following statistical parameters often used in other studies were calculated: fractional bias, fractional standard deviation, normalized mean square error, correlation coefficient, and "Factor of 2" parameter. Results of the comparison demonstrated that all models provided rather close results. All of them were within a factor of two with measurements. Moreover in almost all cases the deviation did not exceed 50%. With respect to correlation Lagrangian models demonstrated better results in comparison with Eulerian ones. Contrary to that Eulerian models were closer to observations.

The second part of the intercomparison procedure was devoted to the evaluation of cadmium transboundary transport for selected countries - Italy, Poland, and United Kingdom. The same countries were selected as at the previous stage for lead. On the basis of the total deposition two parameters were calculated: a fraction of the national emission transported outside selected country and a fraction of total deposition on selected country from all European sources located outside its borders. The differences between the models for the export values are relatively small being on the whole within a factor of two. Partly this can be explained by the fact that the removal processes on these short distances are relatively less important compared to other processes like dispersion and transport. In contrary to the export values, the import values are largely dependant on the parameterizations of the removal processes like the assumptions on particle distribution, deposition velocities per particle size etc.

On the whole, the intercomparison revealed that the models manifested rather close results testifying to similar approaches in modelling of cadmium transboundary transport. The comparison of measured and calculated values indicated that modelling results of participated models range within a factor of two with regard to measurements. At the same time it should be noted that available HM measurements are rather scarce and only about one third of the EMEP region is covered by measurements. The assessment of cadmium transboundary transport revealed similar results for the export values (within 20-30%) but some differences in the import ones (within a factor of 2). The differences obtained are connected with the different parameterizations of and assumptions in the emission, transport, dispersion, and removal processes used by the models.

As recommendations for the next stages of the model intercomparison it can be suggested to extend the measurement database and to use recent estimates of HM emissions in Europe. It could be feasible to repeat lead and cadmium model intercomparison studies at the next stages, as far as input data will be accumulated. Indicating the importance of model parameterization of emission, transport, dispersion, and removal processes sensitivity tests with the ASIMD model should be carried out. This could provide the information on the uncertainty of model im- and export estimates.

## 4.5. Differences, Similarities, and Complementarity of Various Approaches to Modelling Persistent Organic Pollutant Distribution in the Environment

Frank Wania, University of Toronto at Scarborough (Canada)

### CONTENT

1. Introduction	115
1.1. Definition of POPs	115
1.2. The rationale for transport models	116
2. The two approaches to modelling POPs	117
2.1. Multi-compartmental mass balance models for POPs	117
2.1.1. Characteristics of multimedia mass balance models	117
2.1.2. Types of multimedia mass balance models	119
2.1.3. An illustrative example: the POPCYCLING-Baltic Model	120
2.2. Adapting atmospheric dispersion models to POPs	123
2.3. The complementarity of the two approaches	124
2.3.1. Answering different questions	124
2.3.2. Simulating different groups of chemicals	125
2.4. The convergence of the two approaches	125
3. Using the complementarity and similarity of the two approaches	128
3.1. Exchanging information concerning phase equilibria	129
3.2. Exchanging information concerning transport processes	129
3.2.1. Identifying relevant transport pathways for POPs	129
3.2.2. Adopting kinetic parameter values	130
3.3. Using the simplicity of box models	131
3.3.1. Example 1: quantifying the role of forests on the fate of POPs	132
3.3.2. Example 2: modelling air-soil exchange of POPs	133
3.4. Using concepts from box models	135
4. Acknowledgements	137
5. References	137

### 1. INTRODUCTION

#### 1.1. Definition of POPs

Persistent organic pollutants (POPs) is a term that describes a rather diverse group of compounds, which includes the polychlorinated biphenyls (PCBs), the polychlorinated dibenzo-p-dioxins and -furans (PCDD/Fs), and organochlorinated pesticides such as DDT, toxaphene and dieldrin. Chemically, these substances have in common one or more cyclical ring structures of either aromatic or aliphatic nature, a lack of polar functional groups, and a variable amount of halogen substitutions, most commonly chlorine. These chemical similarities result in common features in the environmental fate and behaviour of POPs, notably that (1) they degrade only slowly or not at all in the environment («persistent»), (2) occur to a significant extent in both the

gas phase and condensed states (i.e. in the sorbed or dissolved state) at environmental temperatures («semi-volatile»), (3) tend to accumulate in the lipophilic tissues of organisms («bioaccumulative»), and (4) have the potential to harm wildlife and human populations exposed to trace amounts («toxic»). They are sometimes also referred to as persistent, bioaccumulative and toxic substances (PBTs). In a regulatory context, POPs are compounds that fulfill a set of criteria defined in the UN-ECE Protocol on the Long-Range Transport of Air Pollutants (LRTAP). These criteria are certain threshold values of persistence, toxicity, potential to bioaccumulate and potential for long-range transport (Rodan et al., 1999, Klecka and Mackay, 1999).

## 1.2. The rationale for transport models

The UN-ECE protocol on reducing the atmospheric transboundary transport of POPs in Europe mentioned above, as well as presently ongoing negotiations at the UNEP level to develop an agreement to limit the production and use of POPs on a global scale have spurred an interest in **relating spatial and temporal information on the release of POPs into the environment** (i.e. the emissions) **with the risk posed by their presence in particular environments**, which is most often correlated with environmental exposure concentrations. The rationale is that if such a quantitative relationship can be established, the most efficient means of reducing the risk by reducing emissions can be sought. This is essentially the approach adopted in response to earlier UN-ECE LRTAP agreements on air pollutants other than POPs, such as the acidifying pollutants and volatile organic chemical (VOCs). An important part of this approach is the atmospheric transport of POPs on a regional European and on a global scale.

Independent of the question of the availability of transport models that can credibly and reliably establish a relationship between emissions and atmospheric concentrations of POPs, it should be cautioned that this approach has its limitations when used for POPs for several reasons. In contrast to the classical air pollutants,

1. atmospheric concentrations and deposition rates are only very indirectly measures of the risk posed by POPs in an area. That is because the risk tends to be highest for organisms at the top of the food-chain, the exposure of which is as much controlled by the «processing» of the chemicals within the receiving ecosystem as it is by the atmospheric input rate (Wania, 1998). A case in point is the Arctic environment, which despite lower atmospheric concentrations and deposition rates of POPs is home to the human population with some of the highest exposure situation anywhere.

2. It is conceptually more difficult to derive critical loads for chemicals that undergo reversible atmospheric deposition (Wania, 1998).
3. Emission reductions are often not a feasible regulatory option for POPs because: (a) significant emission occurs from so-called secondary sources, i.e. environmental reservoirs originating from releases in the past, and in other cases (b) the sources are unknown, or at least poorly allocated.

Independent of these reservations, the task that the transport or distribution models of POPs are asked to address is to relate quantitatively emissions of POPs with exposure concentrations of relevance for organisms at the top of the food-chain. Independently, two different approaches to describing the environmental distribution of persistent organic pollutants (POPs) have evolved over the last ten years or so. The first approach involves the use of multi-compartmental mass balance models (or box models) to describe the overall fate of a chemical in a specified environment. A more recent, second approach is the adaptation of classical air pollution dispersion models to POPs. This paper aims to give a brief outline of the scope, advantages and disadvantages of the two approaches, and to discuss how they may complement and support each other.

## 2. THE TWO APPROACHES TO MODELLING POPs

### 2.1. Multi-compartmental mass balance models for POPs

#### 2.1.1. Characteristics of multimedia mass balance models

Multimedia mass balance models are relatively simple mathematical descriptions of the natural environment designed to gain a qualitative and quantitative understanding of the environmental behavior of chemicals, which are likely to be found in more than one environmental phase or medium. Such models subdivide the environment into a number of compartments – well mixed «boxes» which are assumed to have homogeneous environmental characteristics and chemical concentrations. The model then calculates how a chemical is distributed within that simplified system. The distribution, and thus the concentration that is established in each medium, is influenced both by the chemical's intrinsic properties and emission patterns and the characteristics of the environment into which it is released. The models thus integrate information on multiple and interacting processes of partitioning, transport and transformation into a comprehensive yet readily comprehensible picture of a chemical's fate in the environment (Mackay, 1991, Cowan et al., 1995).

These models are typically designed for non-ionic organic chemicals, but modifications have been presented that describe speciating (Diamond et al., 1992), and non-volatile chemicals (Mackay et al., 1996). Although not exclusively developed for the simulation of POPs, such models have been used extensively to describe the environmental behaviour of chemicals, which are classified as POPs as defined by the UN-ECE LRTAP protocol. As reviewed recently (Wania and Mackay, 1999b) such models tend to:

- involve multiple environmental compartments,
- have a low spatial resolution, and
- involve simplifying assumptions of equilibrium and steady-state.

If the models are dynamic, they usually allow simulation of chemical fate over long time scales, i.e. in the range of decades. It was argued that these attributes make multi-compartmental mass balance models well-suited for the task of describing the environmental behaviour of POPs, because such chemicals readily partitioning into and are transported between various media, and are by definition persistent and thus «have time» to establish relatively uniform environmental concentrations (Wania and Mackay, 1999b). On the other hand, these attributes also define the principal limitations of that approach in that the degree of spatial and temporal resolution that can be expected from box models is small.

It is important to note that this low spatial and temporal resolution often is a deliberate restriction rather than a regrettable shortcoming. This is based on the belief that the predictive capability of numerical models of environmental POP behaviour is not limited by the resolution of atmospheric transport processes, but rather by the uncertainties inherent in emission estimates, physical-chemical properties, degradation rates, and air-surface exchange descriptions of POPs. Adding complexity in the presence of such uncertainty does not improve a model.

This may be illustrated using the example of air-soil exchange of POPs. Soil is the major reservoir of many POPs in the environment and volatilisation from soil is likely controlling air concentrations of PCBs and OC pesticides over wide areas. The rates of volatilisation of POPs from soils are dependent on soil properties which are highly variable on either a spatial (e.g. concentration of POP in soil, soil depth, soil texture, organic carbon content) or temporal scale (e.g. soil temperature), or both (e.g. soil moisture). Predicting the short term fluctuation of air concentrations with a high spatial resolution would thus require to capture the spatial and temporal variability of these parameters **and** accurately predict how they in concert influence volatilisation rates – clearly a challenge subject to huge uncertainties. For the large areas of soil

compartments in box models and the long time scales being simulated, it can reasonably be argued that the use of parameter choices reflecting the average properties and conditions of soils in an area will in turn provide volatilisation rates that reflect the average for that area and time period. And whereas that average number will be quite uncertain, it is very likely less so than volatilisation rates estimated for a large number of individual grid cells. It is also more likely to be evaluated.

#### 2.1.2. Types of multimedia mass balance models

For a comprehensive overview of the range and scope of multi-compartmental mass balance models that have been used to describe POPs fate in the environment, the interested reader is referred to the recent review by Wania and Mackay (1999b). Briefly, multimedia mass balance models are used as:

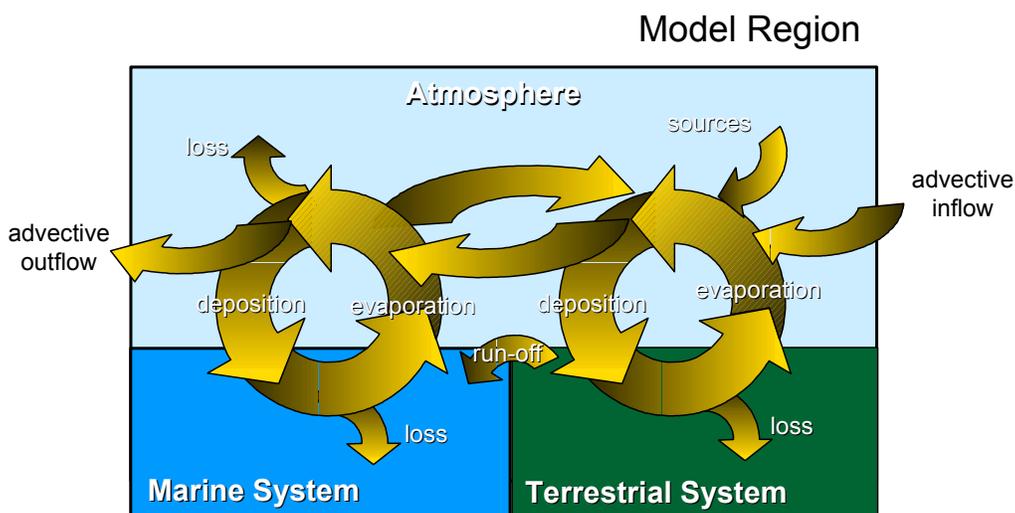
- evaluative models, that describe chemical fate in a hypothetical, or generic environment. The objective is not to describe a real situation, but to provide the likely picture of a chemical's fate in a generic environment for the purpose of assessment and evaluation. This is particularly useful within a regulatory context, e.g. in the registration process for new chemicals, or when the environmental behavior of several chemicals is to be compared. Examples for this mode of model use are the SimpleBox model (Brandes et al., 1996) and the EQC model (Mackay et al., 1996).
- evaluative models, that have been parameterised to describe a specific site or region, often a jurisdictional unit such as a country, without introducing spatial resolution. Examples of such models are the ChemCan model (Mackay et al., 1991) or a model developed to describe chemical behaviour in the Danish environment (Severinsen et al., 1996).
- models, that have been custom-designed to describe chemical behaviour at a very specific site or region, usually a aquatic systems with a specific POP contamination history. Examples are models describing the fate of PCBs in the Hudson River, NY (Thomann et al., 1991), or PAHs in the Saguenay Fjord, Canada (Lun et al., 1998)

The latter models usually focus on aquatic systems, because traditionally POPs have been perceived as being most cause for concern in aquatic organisms and food chains. As it is increasingly recognised that the concentration levels in aquatic systems can not be understood independently of what is happening in the surrounding terrestrial environment, drainage basins are becoming part of these site specific models (Thomann, 1998). This is additionally warranted by the fact that in many instances uptake of POPs through the agricultural food chain has been

identified of equal, if not greater importance for human exposure than the uptake through the marine or fresh water food chain (McLachlan, 1996).

### 2.1.3. An illustrative example: the POPCYCLING-Baltic model

The POPCYCLING-Baltic model is one of the most comprehensive multi-compartmental box models for POPs so far and may serve to illustrate this approach (Wania et al., 1999b). This model aims to distinguish and quantify the environmental pathways of selected POPs in the Baltic Sea environment. In particular, it aims to estimate the fractions of the POPs currently present in various parts of that environment, which are derived from (i) recent releases within the drainage basin, (ii) past emissions in the drainage basin and (iii) contaminated air masses being advected into the area. Within the model region, a main focus is on the relative importance of the riverine and atmospheric pathway for delivering POPs to the marine ecosystem of the Baltic Sea. Furthermore, the model is designed to address the question, what fraction of the riverine load is actually atmospherically derived vs. being emitted directly to the soils, plants and rivers of a drainage basin (Figure 1).



**Figure 1.** The POPCYCLING-Baltic model aims to quantify the pathways of POPs from the terrestrial environment to the marine environment via atmosphere and rivers

The compartmentalisation of the Baltic Sea region into boxes and the description of environmental chemical fate are based on a number of considerations:

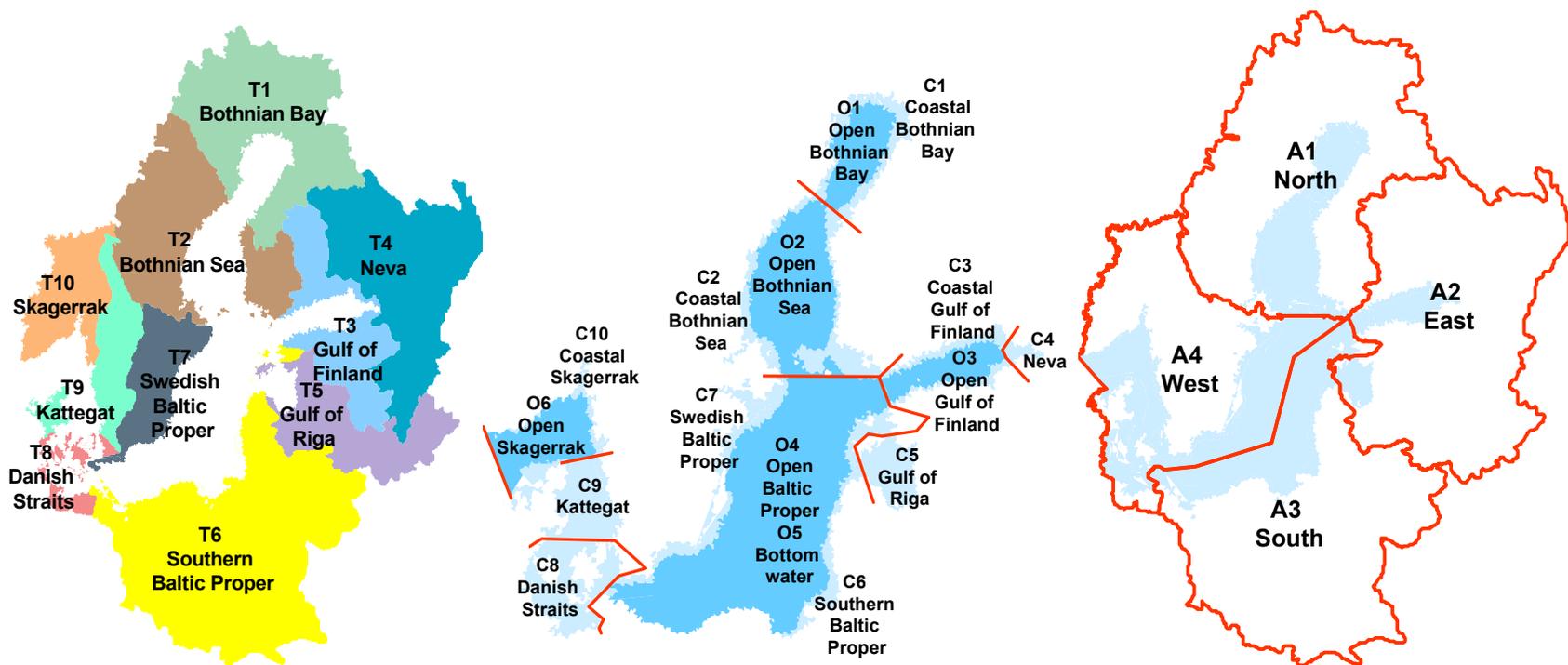
- The size of the compartments is based on what areas can reasonably be considered uniform and well mixed on the time scales relevant for POPs. Uniformity refers to both

environmental characteristics and contamination with POPs. This in turn is influenced by climatic and socio-economic factors. This area will be larger for rapidly mixed environmental media such as the atmosphere, than for stationary media such as vegetation.

- The number of boxes per environmental medium should be on the same order of magnitude as observed data sets for model evaluation could be expected to be available. Even though the Baltic Sea environment is worldwide one of the best studied with respect to POPs, there is usually only a handful of studies that quantified POPs in a particular environmental medium.
- Only compartments and processes which notably influence the long-term fate of the modelled chemicals and which are deemed important for the exposure of wildlife and humans are included. In particular, the description of the terrestrial part of the drainage basin of the Baltic Sea is restricted to those aspects, which influence the magnitude and the timing of POPs delivery to the Baltic Sea. This implies that the model aims to describe accurately the rates of release of POPs from the main terrestrial storage media for POPs, i.e. soil and vegetation, into the two transport media delivering POPs to the marine environment, i.e. atmosphere and fresh water.
- Key processes are the two-directional exchange of POPs between the atmosphere and aquatic and terrestrial surfaces, and the uni-directional run-off of chemical from soil to fresh water and further to the marine system. Important are further the processes that could lead to loss of chemical during the transport in atmosphere and river water.

As result, the Baltic Sea environment is described in the model by four atmospheric compartments, 16 marine water compartments, 15 marine sediment, and ten drainage basins, each of which is described by five compartments (forest canopy, forest soil, agricultural soil, fresh water, fresh water sediment) (Figure 2).

As this model is meant to calculate long term trends on the scale of decades, it employs long term averaged monthly values for atmospheric transport rates, temperatures, wind speeds and OH radical concentrations. Other environmental parameters, in particular those relating to the cycle of water and organic carbon in the Baltic sea environment are assumed fixed in time, i.e. are not even resolved on a seasonal scale. No processes or aspects of processes are considered that lead to concentration fluctuations on a time scale shorter than a month, which implies that atmospheric events or episodes such as weather situations favourable for long range transport into a particular region cannot be described by such a model.



**Figure 2.** Maps showing the compartmentalisation of the terrestrial (A), marine (B) and atmospheric (C) environment of the Baltic Sea drainage basin in the POPCYCLING-Baltic model. Each of the ten terrestrial units is represented by five compartments (agricultural soil, forest soil, forest canopy, fresh water, and fresh water sediment), each of the marine units by a water and a sediment compartment

## 2.2. Adapting atmospheric dispersion models to POPs

The second approach to quantitatively describing the distribution of POPs in the environment is the adaptation of classical air pollution dispersion models to POPs. These models tend to:

- be atmospheric models, where the Earth's surface constitutes a more or less complex boundary,
- have a high spatial resolution with often several hundred or thousand grid cells, and
- are often limited to simulating relatively short time periods on the scale of days to weeks, although with the increase in computing power even multi-year calculation have become possible.

It has been argued previously (Wania, 1997), that the use of highly resolved atmospheric dispersion models for POPs is hampered by the fact, that:

- the models need to be able to tackle the reversibility of air-surface exchange that most POPs undergo, which implies the need to calculate surface concentrations and thus to describe fairly complex fate processes in the surface media soil, water and possibly also vegetation (on the resolution of the atmospheric model).
- the emission inventories for POPs that are presently available, or are likely to come into existence, have such high intrinsic uncertainty that the high resolution of dispersion models is not warranted (and could actually be misleading).
- the number of concentration and deposition measurements available for POPs is limited and stands in no relationship to the degree of resolution of the dispersion models, frustrating any attempt at a sensible model evaluation.

However, such formidable challenges have not prevented such modelling studies from being conducted or at least being attempted quite the same. (Similarly, many scientists continue to work on models that aim to predict global warming, despite the overwhelming complexity involved, the highly uncertain emission inventories for climatically active gases, and the complete impossibility to evaluate the model results.) This presumably has many reasons, most notable among them the interest of the regulatory and scientific community to employ the same tools that have proven useful for other pollution issues in the past. One of the obvious dangers is that dispersion models support the perception of a degree of predictability of POP behaviour, which simply does not exist and is not likely to be achieved in the near future.

Various groups have been working on the adaptation of atmospheric dispersion models to POPs. Some of these studies are at the stage of developing and testing subroutines for gas-particle partitioning, air-water exchange, and air-soil exchange for inclusion into existing models (Jacobs and van Pul, 1996, Ching et al., 1998). For example, Sahsuvar (1999) developed expressions for adapting the Northern Aerosol Regional Climate Model (NARCM) for use with a variety of PCB congeners. Others studies are more progressed and have mostly focussed on HCHs (Pudykiewicz and Dastoor, 1996; Persson and Ullerstig, 1996; Van Jaarlsveld et al., 1997, Pekar et al., 1998). Such models have been used to calculate highly resolved maps of air concentrations and atmospheric deposition rates over a model region. They are able to resolve and simulate events and fluctuations that occur on a time scale smaller than one month. It should thus be feasible to describe specific long-range transport episodes.

### 2.3. The complementarity of the two approaches

#### 2.3.1. Answering different questions

It becomes clear from the above discussion that the two approaches to modelling POPs are complementary, in that they provide answers to quite different questions. The box models aim to describe the big picture of a chemical's fate in the environment. The focus is on large-scale spatial patterns and long term trends. The use of average conditions is possible and common. It is conceivable to simulate the entire lifetime of a persistent chemical substance in a region from initial release to final degradation, even if that time period spans several centuries. These models deliberately ignore the fine detail and have no capacity to resolve concentration differences on a small spatial or temporal scale. The dispersion models, on the other hand, aim to describe primarily the atmospheric transport, taking into account the highly variable nature of meteorological and transport conditions. Short-term fluctuations on the scale of days or even hours are resolved. Rather than aiming to describe long-term averaged conditions, dispersion modellers are often interested in describing events, such as particular long-range transport episodes. It is conceivable to simulate the time course of air concentrations at a location and seek to explain the variability observed in long term measurements campaigns such as those described for the IADN stations (Hillery et al., 1997), Lista, Norway (Haugen et al., 1998) or stations in the Canadian Arctic (Stern et al., 1998).

### 2.3.2. Simulating Different Groups of Chemicals

But there is also another aspect of complementarity. The term POPs comprises groups of compounds with widely variable source characteristics, properties and environmental behaviour. Specifically, the group of low volatility POPs, which include the more highly chlorinated dibenzo-p-dioxins and dibenzofurans, as well as the polycyclic aromatic hydrocarbons with more than four fused aromatic rings, are distinct, in that:

- they are present in the atmosphere essentially completely in the particle phase, and their atmospheric deposition is therefore dominated by particle-associated deposition processes,
- their potential for volatilisation from soils and vegetation is negligible,
- and, at least for the combustion-derived PAHs, the emission situation more closely resembles that of classical air pollutants (no secondary sources, emissions quantifiable by measurements of various combustion sources, etc.)

In many respects these chemicals thus resemble the heavy metals (with the exception of mercury) and other more classical air pollutants. The environmental fate of such compounds is controlled by the respective dispersion and deposition behaviour of the particles that they sorb to, which are usually the small particles of less than 1  $\mu\text{m}$  diameter. The Earth's surface can simply be described as a sink, and there is no need for calculations that cover time periods that are longer than the residence time of particles in the atmosphere. The task of describing the environmental behaviour of these POPs is thus much closer to classical air pollution problems than the task of describing the distribution of reversibly deposited POPs. Atmospheric models, that are capable of simulating the dispersion behaviour of such particles should be well suited for the simulation of low volatility POPs (Ching et al., 1998, Sahsuvar, 1999). Box models with limited spatial resolution, on the other hand, are poorly equipped to describe aerosol transport and deposition in the atmosphere.

### 2.4. The convergence of the two approaches

It should be worth pointing out, that the two approaches to modelling POPs are not intrinsically different and have in fact many similarities. They are both based on the principle of conservation of mass, and they often use similar, if not identical expressions for atmospheric partitioning, deposition, degradation and many other atmospheric fate processes. It is actually possible to perceive the atmospheric dispersion models as box models with a large number of air compartments. This becomes particularly obvious with one-dimensional column versions of

atmospheric transport models (e.g. Sahsuvar, 1999), which are in fact box models with fairly sophisticated descriptions of atmospheric fate processes.

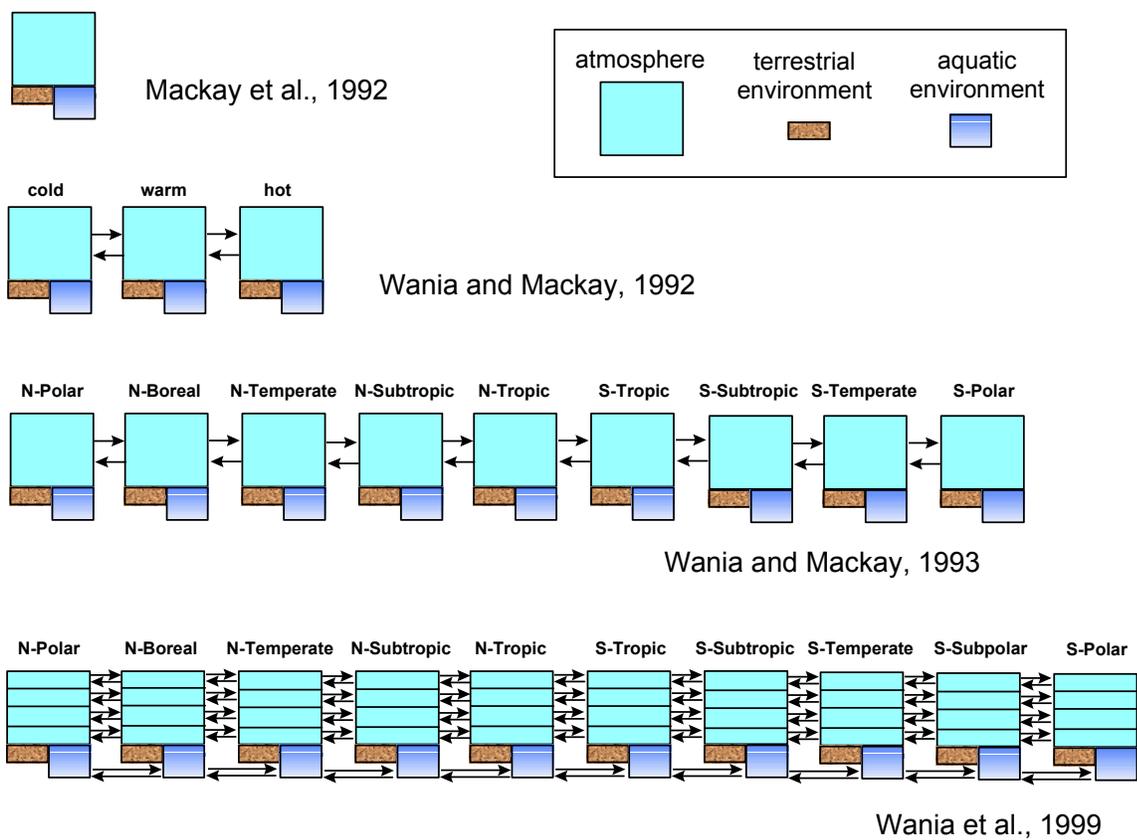
Indeed, it may even be justified to argue that the two approaches to modelling POPs are evolving in a fashion to become more and more similar. A case in point are two modelling studies of  $\alpha$ -hexachlorocyclohexane on a global scale, one conducted by box modellers (Wania and Mackay), the other by atmospheric dispersion modellers (Strand and Hov). Although starting from very different points of origin, the two studies eventually created very similar models.

The approach by Wania and Mackay took its origin in a classical evaluative multi-compartmental box model (Mackay et al., 1992), which was:

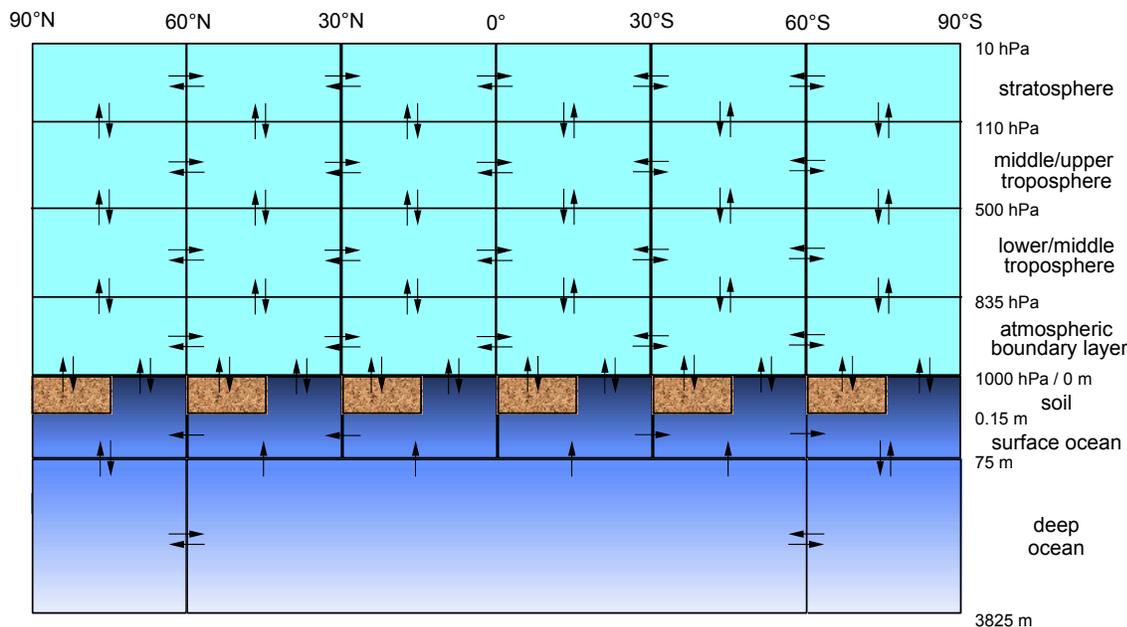
- initially triplicated to represent three interconnected environments at different temperatures (Wania and Mackay, 1992)
- then was increased in size by another factor of three to give a global scale model that describes each of nine climatic zones with the original multimedia building block (Wania and Mackay, 1993).
- Eventually, additional compartments were added (Wania and Mackay, 1995) and the atmospheric compartments were stratified into four vertical layers to yield a model with a two dimensional representation of the global atmosphere, that takes into account convective as well as diffusive atmospheric transport terms (Wania et al., 1999a, Wania and Mackay, 1999a) (Figure 3).

Quite different from this process of adding complexity and spatial resolution, the atmospheric description in the global HCH model by Strand and Hov (1996) evolved by simplification of more complex and more highly resolved atmospheric dispersion models. The model uses transport coefficients for zonally averaged transport (Plumb and Mahlmann, 1987), which were generated from the three-dimensional Geophysical Fluid Dynamics Laboratory general circulation/tracer model (Mahlmann and Moxim, 1978). An initially developed zonally averaged model with 75 equally spaced latitude points and 33 equally spaced pressure points (Strand and Hov, 1993) was further simplified to an atmosphere divided into six equally spaced latitude zones and four vertical layers (Strand and Hov, 1996) for the purpose of describing the fate of the HCHs. After adding a soil model (Jury et al., 1983) and a two dimensional description of the global surface ocean (Siegenthaler and Joos, 1987) to what originally has been an atmospheric model, the final model design (Figure 4) resembles very closely the model by Wania and Mackay. Although

this may be merely incidental, it may also suggest that for a specific POP modelling task there is an optimum spatial resolution, that reflects the uncertainty of the overall simulation (Håkanson, 1995).



**Figure 3.** Evolution of the global distribution model for persistent organic pollutants by Wania and Mackay from a simple box model to a zonally averaged, two-dimensional multimedia model.



**Figure 4.** Structure of the two-dimensional global multimedia model for HCHs by Strand and Hov (1996).

### 3. USING THE COMPLEMENTARITY AND SIMILARITY OF THE TWO APPROACHES

The fact that the two approaches are complementary and yet have many similarities, implies that there is great potential to enhance either approach by adopting tested or superior aspects from the other. For example, multimedia box modellers have gained some valuable experience in describing environmental fate processes of POPs, in particular those that relate to the transfer between phases. The expressions for phase equilibria and intermedia transport processes that they have developed may be of use to the atmospheric dispersion modeller. The description of diffusive air-water and air-soil exchange employed in dispersion models for POPs are indeed based on the same expressions that have been developed and employed in multimedia box models (Mackay and Leinonen, 1975; Jury et al., 1983). Vice versa, the expertise of the atmospheric modelling community on atmospheric transport processes can greatly benefit the multimedia box modeller. An example of the latter is the improvement of the description of the atmosphere in the global distribution model by Wania and Mackay (1995) with the help of Strand (Wania et al., 1999a).

### 3.1. Exchanging information concerning phase equilibria

Box modellers have established techniques for estimating partitioning equilibria between a variety of environmental phases, such as between gas phase and particle phase (e.g. Finizio et al., 1996), air and soil (e.g. McKone, 1996), air and vegetation (e.g. Hung and Mackay, 1997), or water and suspended solids (e.g. Seth et al., 1999) from more fundamental chemical properties such as vapour pressure, water solubility, octanol-water and octanol-air partition coefficients and Henry's law constant (e.g. Mackay, 1991). They have compiled both measured and calculated values for these properties (Mackay et al., 1999), and they have developed relationships that take into account the dependence of these phase equilibria on environmental properties such as temperature (e.g. Paasivirta et al., 1999), salinity (e.g. Xie et al., 1997), and phase composition. Many of these expressions can find direct application in atmospheric dispersion models.

### 3.2. Exchanging information concerning transport processes

#### 3.2.1. Identifying relevant transport pathways for POPs

The use of box model experience on POP transport processes may take the form of helping to decide which processes are important and which ones are not. Examples of such information are:

- Air-water exchange descriptions for most POPs needs to take into account transfer resistances on both the air and water side, as well as the partitioning of POPs between the dissolved phase and the phase bound to suspended solids within the water column (Wania et al., 1998).
- Diffusive gas exchange is often the dominant pathway of atmosphere-surface exchange for POPs. This implies that a deposition monitoring network based on wet and particle deposition, and a model evaluation based on such observed deposition rates (e.g. Persson and Ullerstig, 1996), may provide information of little relevance.
- Transport processes in the dissolved aqueous phase, such as vapour scavenging by rain or movement with water in soils, are very often negligible for POPs, except for the most water-soluble compounds (such as the HCHs). On the other hand, transport processes associated with organic carbon tend to be of great importance in both the terrestrial and aquatic environment.
- Uptake of POPs into vegetation occurs through the cuticle, and not the stomata.

### 3.2.2. Adopting kinetic parameter values

Sometimes it may also be possible to directly adopt parameter choices for mass transfer coefficients and deposition velocities that have been used in the different modelling approaches. There is however need for caution: As described above most box models do not have any vertical resolution of the atmosphere. The mass transfer coefficients for the air-side over soil and water in such models therefore lump all transfer resistances that may exist between the bulk of the troposphere and the air-water/soil interface. (Similarly, the mass transfer coefficients for the water side implicitly include the resistance to transfer from the bulk of the water body to the water-air interface.) The underlying assumption in these box models is, that the rate limiting step to mass transfer across the Earth's surface is the molecular diffusion through a stagnant air (and water) layer right next to the interface, and there is thus no need to include additional resistances that may exist in the bulk phases. (Without this assumption, the mass transfer coefficients would have to be functions of the height of the atmospheric compartment or the depth of the water compartment, which they are typically not.)

Atmospheric dispersion models, on the other hand do have vertical resolution and therefore explicitly account for the resistances that exist in the bulk atmosphere. Transport to and from the surface is more likely described by a series of resistances, e.g. between the bulk atmosphere and the atmospheric boundary layer, between the air above and below the vegetation canopy, and within the stagnant air film right next to the interface. Therefore, mass transfer coefficients and dry deposition velocities for air-surface exchange may not be readily adopted between modelling approaches.

This difference in approach is likely explained by the different time resolution of box and atmospheric dispersion models. On the time scale that the atmospheric dispersion models resolve, situations of high atmospheric stability are likely to occur that do present significant additional resistances to air-surface exchange within the bulk of the atmosphere, and thus need to be accounted for. These situations will often not be of great significance on the long-term averaged time scale adopted in box models. However, when box model are used to resolve POP concentrations on shorter time scales, e.g. for describing diurnal fluctuations of POP concentrations in air (Lee et al., 1998), consideration of atmospheric stability should influence the choice of mass transfer coefficients and dry deposition velocities. Also, when box models are used in regions of unusually high atmospheric stability, such as the Arctic, the parameter choices for air surface exchange have to be adjusted accordingly.

In the POPCYCLING-Baltic model described above a factor has been introduced into the description of air-surface exchange that allows accounting for seasonal differences in atmospheric stability. Mass transfer coefficients and dry particle deposition velocities applying to the exchange of POPs with terrestrial surfaces are scaled using that factor, being smaller during seasons of greater average atmospheric stability. In particular, the availability of less radiative energy during winter often results in prolonged thermal inversions.

Any attempt to assess the need to account for vertical atmospheric mixing processes when modelling POPs is currently compromised by the almost complete lack of measured vertical atmospheric concentration profiles (a notable exception is the study by Knap and Binkley, 1991). Without such measurements it is impossible to say whether significant concentration differences with altitude, and thus significant transfer resistances, exist. Presently, no height resolved data exist that would allow to judge whether a forest canopy is a significant resistance for the transport of POPs to forest soils.

### 3.3. Using the simplicity of box models

One of the most important ways box models may complement atmospheric dispersion models is by serving as test modules for more complex models. Wania and Mackay (1999b) compiled a number of reasons for keeping models simple and emphasised «that complexity does not equate with utility or reliability». Dispersion models can be overwhelming in their complexity and in the amount of data they require and produce. The result of subtle changes in model structure and parameterisation on model result is easily obscured by that complexity. The incorporation of soil, vegetation and marine environments into atmospheric dispersion models bears the risk of making them completely unwieldy, impractical and non-transparent.

It is thus suggested that box model can play an important role in

- testing which fate processes are important and thus need to be included in the atmospheric dispersion models. The answer to this question is often very sensitive to chemical properties and therefore needs to be answered differently for different POPs.
- attempts to understand model behaviour.
- testing expressions and parameter values for air-surface exchange.
- conducting sensitivity and uncertainty analyses.

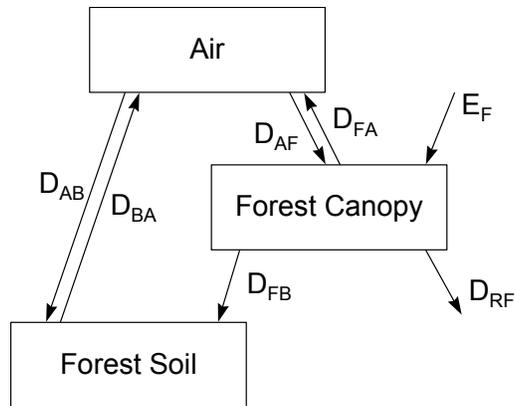
Two examples of recent improvements in air-surface exchange descriptions in multimedia models of POPs may serve to illustrate the potential use of box models in this respect:

### 3.3.1. Example 1: quantifying the role of forests on the fate of POPs

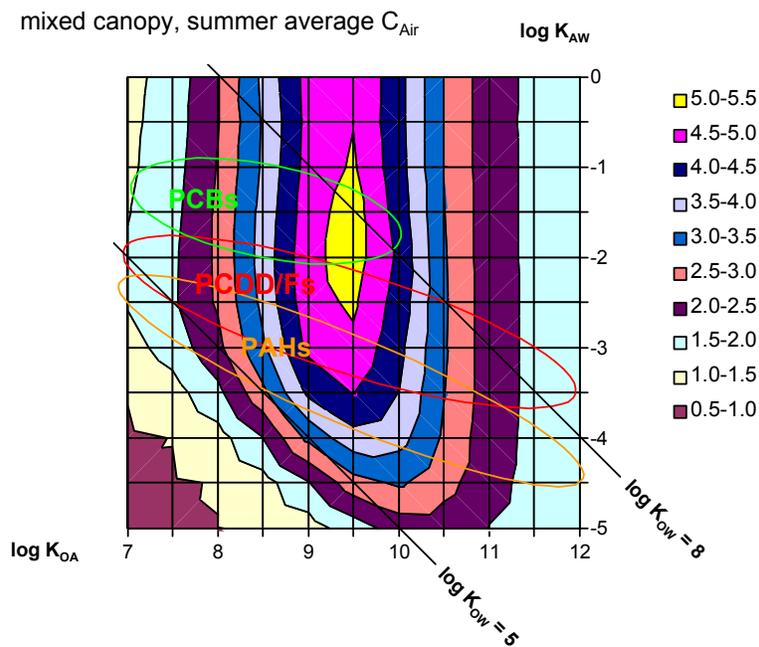
Recently, unusually high deposition velocities of POPs to two forest canopies have been observed in Germany (Horstmann and McLachlan, 1998). Most multi-compartmental box models and all existing atmospheric dispersion models adapted to POPs assume that the exchange between the atmosphere and vegetation can be subsumed in the exchange between the atmosphere and soil. Deposition velocities to forests which for some chemicals are up to one order of magnitude higher than those to bare soil (Schröder et al., 1997) question the validity of that assumption, and suggest that models of POPs need to incorporate descriptions of air-forest exchange.

We have incorporated a forest canopy compartment in a simple multi-compartmental box model (Figure 5) and tested, how it affects the predicted fate of a variety of chemicals (Wania and McLachlan, in prep.). Specifically, expressions were developed for fugacity capacities for a mixed coniferous and deciduous forest canopy, for three intermedia transport processes (namely between air and canopy, canopy and air, and canopy and soil), and for chemical degradation in the canopy. The air-canopy exchange takes into account diffusive gas exchange, dry particle and wet deposition processes. The exchange between canopy and soil includes a litterfall component, and the seasonality in the development of the canopies is taken into account. The model also accounts for the change in atmosphere-soil exchange under a canopy relative to an open surface.

Using the simple box model we tested the effect of a 50 % mixed forest cover on the calculated summer air concentrations of a variety of chemical-property combinations (Figure 6). We further tested the sensitivity of other parameter choices on the calculated reduction in air concentration caused by a forest cover. The results from these tests suggested that for a relatively small group of chemicals with a  $\log K_{OA}$  around 9.5 and a  $\log K_{OW} > 5$ , high deposition rates to forest canopies can lead to significant reductions in atmospheric concentrations. Because of the relative small storage capacity of a forest canopy, the efficiency of the forest to act as a filter depends strongly on the existence of a strong sink removing chemicals from the canopy compartment. This implies that the transfer of chemicals from canopy to forest soil and the degradation in the canopy needs to be described accurately.



**Figure 5.** Link of a new forest canopy compartment with compartments traditionally found in multimedia fate models.



**Figure 6.** Ratio of the concentrations in air calculated for a completely persistent chemical in a hypothetical environment without and with a forest cover, given for various combinations of  $\log K_{OW}$  and  $\log K_{AW}$  values. Highest forest-induced reduction of air concentration occurs for chemicals with a  $K_{OA}$  around 9.5.

### 3.3.2. Example 2: modelling air-soil exchange of POPs

Recently, long term simulations of PCB fate in a box model without spatial resolution (CoZMo-POP) indicated that the classical formulation for air-soil exchange, used in the large majority of POP models, seriously underestimates the rates of volatilisation from soil. This formulation

assumes that POPs diffuse from the bulk of the soil to the soil-air interface by molecular diffusion in the air-filled pore space. (Advection and diffusion in the water-filled pore space can safely be neglected because of the very low water solubility of most POPs.) The model suggested that the rate of diffusion within the soil is limiting air soil-exchange of PCBs, and predicted soil concentrations that remained at a high level for decades after peak emissions despite significantly reduced air concentrations. This was in contradiction to temporal trends of PCB concentrations observed in soil, which showed a significant reduction in the past twenty years (Alcock et al., 1993).

Further analysis revealed that diffusion from the bulk soil to the air-soil interface is not necessary for evaporation of PCBs from soils to occur: Namely, the capacity of the uppermost soil micro-layer for PCBs is so large that it can supply the atmosphere with PCB for a long time before being notably depleted. That implies that as long as resupply of PCBs to that micro-surface layer is sustained on the time scale of years, the air-side resistance, that is the resistance to evaporation posed by the atmospheric boundary layer, becomes the rate-controlling step for the evaporation from POPs to air. Such slow resupply is easily accomplished by physical soil mixing processes such as bioturbation and common agricultural practices. Determining the rate of volatilisation of highly sorptive POPs from soil are thus (1) the air side resistance over soil, (2) the rate of physical soil mixing processes, and (3) the characteristics of the surface micro-layer of soil. The routines that are presently used to describe air-soil exchange in POPs models fail to describe this accurately.

These two examples grew out of the work on the POCYCLING-Baltic model described above. However, the testing of these expressions was performed using CoZMo-POP, a one-basin version of the POCYCLING-Baltic model without any spatial resolution. Without the help of that simplified model, it would have been very difficult:

- to develop and test the expressions for incorporating a forest compartment into a POP model. Specifically, the calculations for a large variety of chemical property combinations (Figure 6) and the sensitivity calculations for the environmental parameters are very time consuming even using a simple non-steady state box model without spatial resolution.
- to explain why the model fails to reproduce the time course of soil concentrations observed in the environment. Often a large number of model runs are required to obtain even a rudimentary understanding of why the result of a very simple box model changes in a certain way in response to a specific input parameter change.

It is hard to imagine that either could be done using a full-scale three-dimensional atmospheric dispersion model.

#### 3.4. Using concepts from box models

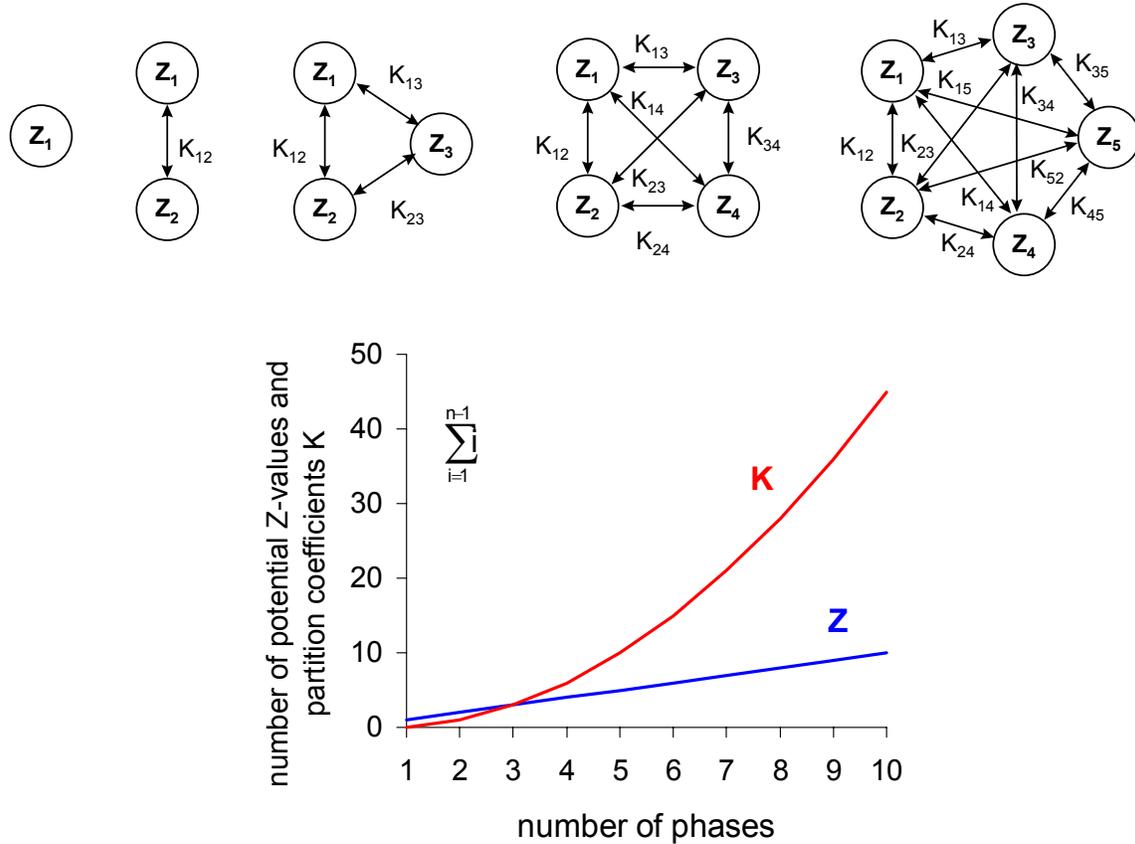
Many compartmental box models are written in fugacity notation (Mackay, 1991), which implies the use of:

- fugacities  $f$  in units of Pascal (Pa) instead of concentrations to describe the activity of a chemical in a phase.
- Z-values or fugacity capacities in units of  $\text{mol}/(\text{Pa}\cdot\text{m}^3)$  instead of partition coefficients to describe phase partition equilibria.
- D-values in units of  $\text{mol}/(\text{Pa}\cdot\text{h})$  instead of rate constants to describe intercompartmental transport and degradation processes.

The use of this notation is not a prerequisite for multi-compartmental box models, because it is always possible to write the model equations in terms of concentrations, partition coefficients and rate constants. However there are distinct advantages in using the concept of fugacity:

- The equilibrium status between two compartments becomes instantly obvious. Fugacity is a criterion of equilibrium, whereas concentration is not. That means that two phases in equilibrium have the same fugacity, but very often different concentrations. From the fugacity ratio it is possible to directly infer the direction of diffusive exchange across phase boundaries.
- The use of Z-values allows the calculation of chemical transfer rates between two phases of different temperature (e.g. a layer of cold air over a warm ocean or vice versa). When using partition coefficients, it is difficult to decide which temperature should apply to the partition coefficient between the two phases.
- If there are more than three phases in a model, consistency of partition data is more easily assured if Z-values are used instead of partition coefficients. If a model has  $n$  different compartments there are  $n$  independent Z-values, one for each compartment, but there are  $\sum_{i=1}^{N-1} i$  potential partition coefficients, which are not independent of each other. For example, for a model with five different media there are five Z-values, but potentially ten interrelated partition coefficients. This implies that the number of partition coefficients increases much more rapidly with increasing number of phases than the number of fugacity

capacities (Fig. 7). When we further note that partition coefficients are highly temperature dependent, which implies the need to additionally specify enthalpies of phase change, it is clear that the definition of consistent partition coefficients can constitute a significant challenge.



**Figure 7.** Relationship between the number of phases of a multi-compartment model and the need for partitioning data. The number of partition coefficients K increases much more rapidly with increasing phase number than the number of fugacity capacities Z.

- The use of D-values allows the instantaneous comparison of the relative importance of various fate processes, because diffusive and advective transport processes as well degradation rates are expressed in the same units.

It would obviously be possible to formulate the equations used in atmospheric dispersion models in fugacity notation. We have recently presented a fugacity model that includes a two-dimensional treatment of the global atmosphere (Wania et al., 1999a). For that model

expression were derived that allow the calculation of Z-values for atmospheric layers of variable density and of D-values for atmospheric advection and diffusion between such layers. There is thus no reason why it should not be possible to formulate a three-dimensional atmospheric dispersion model in terms of fugacity.

It probably is neither advisable nor worthwhile to rewrite existing, tested atmospheric dispersion models in terms of fugacity. But it may be worthwhile to adopt some of the concepts that make the fugacity concept so useful.

- Fugacity capacities could be employed prior to model use to derive sets of consistent partition coefficients and their temperature dependence.
- The calculation of D-values from the transport and degradation parameters used in the model can facilitate the comparison of the relative importance of various fate processes.
- The equilibrium status of various model compartments could be probed by converting concentrations calculated by the model into fugacities. Fugacity ratios then can provide information on the equilibrium status between the atmosphere and various surface compartments, and allow the estimation of the net direction of diffusive air-surface exchange.

#### 4. ACKNOWLEDGEMENTS

I have benefited greatly from discussions with Profs. Michael McLachlan (Baltic Sea Research Institute, Rostock-Warnemünde) and Donald Mackay (Trent University, Peterborough) on the subjects covered in this paper. The POPCYCLING-Baltic and CoZMo-POP models mentioned in the text have been developed in collaboration with Johan Persson (Stockholm University), Dr. Antonio Di Guardo (University of Insubria, Varese) and other participants in the POPCYCLING-Baltic project. The writing of this report has been supported by the World Meteorological Organization (WMO). All this is gratefully acknowledged.

#### 5. REFERENCES

- Alcock, R.E., Johnston A.E., McGrath S.P., Berrow K.L., Jones K.C. **1993**. Long-term changes in the polychlorinated biphenyl content of United Kingdom soils. *Environ. Sci. Technol.* **27**: 1918-1923.
- Brandes, L.J., den Hollander, H., van de Meent, D. **1996**. Simplebox 2.0: A Nested Multimedia Fate Model for Evaluating the Environmental Fate of Chemicals. RIVM Report No. 719101029, 155pp.
- Ching, J.K.S., Binkowski, F.S., Bullock, Jr. O.R. **1997**. Deposition of semivolatile toxic air pollutants to the Great Lakes: A regional modelling approach. In Baker, J.E. (Ed.) *Atmospheric Deposition of Contaminants to the Great Lakes and Coastal Waters*. SETAC Press, Pensacola, FL, 293-304.

- Cowan, C., Mackay D., Feijtel T., van de Meent D., Di Guardo A., Davies J., Mackay N. **1995**, *The multi-media model: A vital tool for predicting the fate of chemicals*. SETAC Press, Pensacola, FL, 78 pages.
- Diamond, M.L., Mackay, D., Welbourn, P.M. **1992**. Models of multimedia partitioning of multi-species chemicals: The fugacity/aquivalence approach. *Chemosphere* **25**: 1907-1921.
- Finizio, A., Mackay, D., Bidleman, T., Harner, T. **1997**. Octanol-air partition coefficient as a predictor of partitioning of semivolatile organic chemicals to aerosols. *Atmos. Environ.* **31**, 2289-2296.
- Haugen, J.-E., Wania, F., Ritter, N., Schlabach, M. **1998**. Hexachlorocyclohexanes in air in Southern Norway. Temporal variation, source allocation, and temperature dependence. *Environ. Sci. Technol.* **32**, 217-224.
- Hillery, B.R., Basu, I., Sweet, C.W., Hites, R.A. **1997**. Temporal and spatial trends in a long-term study of gas-phase PCB concentrations near the Great Lakes. *Environ. Sci. Technol.* **37**, 1811-1816.
- Horstmann, M., McLachlan, M.S. **1998**. Atmospheric deposition of semivolatile organic compounds to two forest canopies. *Atmos. Environ.*, **32**, 1799-1809.
- Hung, H., Mackay, D. **1997**. A novel and simple model of the uptake of organic chemicals by vegetation from air and soil. *Chemosphere* **35**, 959-977.
- Håkanson, L. 1995. Optimal size of predictive models. *Ecol. Model.* **78**, 195-204.
- Jacobs, C.M.J., van Pul, W.A.J. **1996**. Long-range atmospheric transport of persistent organic pollutants, I: Description of surface-atmosphere exchange modules and implementation in EUROS. RIVM (National Institute of Public Health and the Environment), Bilthoven, The Netherlands, Report 722401013.
- Jury, W.A., Spencer, W.F., Farmer, W.J. **1983**. Behaviour assessment model for trace organics in soil. I. Model description. *J. Environ. Qual.* **12**: 558-564.
- Knap, A.H., Binkley, K.S. **1991**. Chlorinated organic compounds in the troposphere over the Western North Atlantic Ocean measured by aircraft. *Atmos. Environ.* **25A**: 1507-1516.
- Klecka, G. M., Mackay, D. (Eds.) **1999**. Evaluation of persistence and long-range transport of organic chemicals in the environment: Summary of a SETAC Pellston workshop. SETAC Press, Pensacola, FL, 19 pages.
- Lee, R.G.M., Hung, H., Mackay, D., Jones, K.C. **1998**. Measurement and modeling of the diurnal cycling of atmospheric PCBs and PAHs. *Environ. Sci. Technol.* **32**, 2172-2179.
- Lun, R., Lee, K., De Marco, L., Nalewajko, C., Mackay, D. **1998**. A model of the fate of polycyclic aromatic hydrocarbons in the Saguenay Fjord, Canada. *Environ. Toxicol. Chem.* **17**, 333-341.
- Mackay D.; Leinonen, P. **1975**. The rate of evaporation of low solubility contaminants from water bodies. *Environ. Sci. Technol.* **9**, 1178-1180.
- Mackay, D. **1991**. *Multimedia Environmental Models: The Fugacity Approach*. Chelsea, MI: Lewis. 257 pp.
- Mackay, D., Paterson, S., Shiu, W.Y. **1992**. Generic models for evaluating the regional fate of chemicals. *Chemosphere* **24**, 695-717.
- Mackay, D., Di Guardo, A., Paterson, S., Cowan, C.E. **1996**. Evaluating the environmental fate of a variety of types of chemicals using the EQC model. *Environ. Toxicol. Chem.* **15**, 1627-1637.
- Mackay, D., Shiu, W.Y., Ma, K.C. **1999**. *Physical-chemical properties and environmental fate Handbook*. CRCnetBase 1999.
- Mahlmann, J.D.; Moxim, W.J. **1978**. Tracer simulations using a global general circulation model: results from a midlatitude instantaneous source experiment. *J. Atmos. Sci.* **35**, 1340-1374.
- McKone, T.E. **1996**. Alternative modeling approaches for contaminant fate in soils: uncertainty, variability, and reliability. *Reliability Engineering and Systems Safety* **54**, 165-181.
- McLachlan, M.S. **1996**. Bioaccumulation of hydrophobic chemicals in agricultural foodchains. *Environ. Sci. Technol.* **30**, 252-259.
- McLachlan, M.S., Wania, F. Modelling soil/air exchange of persistent organic pollutants. In prep..
- Paasivirta, J., S. Sinkkonen, P. Mikkelsen, T. Raantio, F. Wania. Estimation of vapor pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature. *Chemosphere* **39**, 811-832.

- Pekar, M., Pavlova, N., Erdman, L., Ilyin, I., Strukov, B., Gusev, A., Dutchak, S., van Pul, W.A.J. **1998**. Long range transport of selected persistent organic pollutants. Part I: Development of transport models for lindane, polychlorinated biphenyls, benzo(a)pyrene. EMEP/MSC-E Report 2/98, August 1998.
- Persson, C., Ullerstig A. **1996**. Model calculations of dispersion of lindane over Europe. SMHI RMK No. 68, Feb. 1996.
- Plumb, R.A., Mahlmann, J.D. **1987**. The zonally averaged transport characteristics of the GFDL General Circulation/Transport Model. *J. Atmos. Sci.* **44**, 298-327.
- Pudykiewicz, J., Dastoor, A.P. **1996**. Study of the global scale transport of sulphur and persistent organic pollutants with special emphasis on Arctic regions. In: J.L. Murray, R.G. Shearer, S.L. Han (Eds.), *Synopsis of Research Conducted under the 1994/95 Northern Contaminants Program*, Environmental Studies No. 73, Department of Indian and Northern Affairs, Ottawa, Canada.
- Rodan, B.D., Pennington, D.W., Eckley, N.; Boethling, R.S. **1999**. Screening for persistent organic pollutants: techniques to provide a scientific basis for POPs criteria in international negotiations. *Environ. Sci. Technol.* **33**, 3482-3488.
- Sahsuvar, L. **1999**. *Modelling physical chemical properties and pathways of polychlorinated biphenyls in the atmosphere*. M.Sc. Thesis, York University, Toronto, Ontario, Canada, April 1999, 141 pp. + Appendices.
- Schröder, J., Welsch-Paul K., McLachlan, M.S. **1997**. Measurement of atmospheric deposition of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) to a soil. *Atmos. Environ.* **31**, 2983-2989.
- Seth, R. Mackay, D., Muncke, J. **1999**. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ. Sci. Technol.* **33**, 2390-2394.
- Severinsen, M., Andersen, M.B., Chen, F., Nyholm, N. **1996**. A regional chemical fate and exposure model suitable for Denmark and its coastal sea. *Chemosphere* **32**, 2159-2175.
- Siegenthaler, U.; Joos, F. **1992**. Use of a simple model for studying oceanic tracer distribution and the global carbon cycle. *Tellus* **44B**, 186-207.
- Stern, G.A., Halsall, C.J., Barrie, L.A., Muir, D.C.G., Fellin P., Rosenberg, B., Rovinski, F., Konovov, E., and Postoukov, B. **1997**. Polychlorinated Biphenyls in Arctic Air. 1. Temporal and Spatial Trends: 1992-1994. *Environ. Sci. Technol.* **31**, 3619-3628.
- Strand, A., Hov, Ø. **1993**. A two-dimensional zonally averaged transport model including convective motions and a new strategy for the numerical solution. *J. Geophys. Res.* **98**, 9,023-9,037.
- Strand, A., Ø. Hov **1996**. A model strategy for the simulation of chlorinated hydrocarbon distribution in the global environment. *Water, Air and Soil Pollution* **86**: 283-316.
- Thomann, R.V., Mueller, J.A., Winfield, R.P., Huang, C.R. **1991**. Model of the fate and accumulation of PCB homologues in Hudson Estuary. *J. Environ. Eng.* **117**, 161-177.
- Thomann, R.V. **1998**. The future "golden age" of predictive models for surface water quality and ecosystem management. *J. Environ. Eng.* **124**, 94-103.
- Van Jaarsveld, J.A., van Pul, W.A.L., de Leeuw, F.A.A.M. **1997**. Modelling transport and deposition of persistent organic pollutants in the European region. *Atmos. Environ.* **37**, 1011-1024.
- Wania, F., D. Mackay **1992**. Temperature and the global distribution of low volatile organic compounds. In: A. Niimi, M. Taylor (Eds.), *Proceedings of the Eighteenth Annual Aquatic Toxicity Workshop: September 30-October 3, 1991, Ottawa, Ontario*. Can. Tech. Rep. Fish. Aquat. Sci. 1863, 245-252.
- Wania, F., D. Mackay **1993**. An approach to modelling the global distribution of toxaphene: A discussion of feasibility and desirability. *Chemosphere* **27**, 2079-2094.
- Wania, F., D. Mackay **1995**. A global distribution model for persistent organic chemicals. *Sci. Total Environ.* **160/161**, 211-232.
- Wania, F. **1997**. What is feasible with respect to atmospheric transport modelling of persistent organic pollutants? A call for caution. In: *Report and Proceedings of the Workshop on the Assessment of EMEP Activities Concerning Heavy Metals and Persistent Organic Pollutants and Their Further Development, Moscow, Russian Federation, September 24-26, 1996*, World Meteorological Organization, Global Atmospheric Watch No. 117, 261-265.

- Wania, F. **1998**. Obstacles to deriving critical loads for persistent organic pollutants. In: *Proceedings of the Workshop on Critical Limits and Effect-Based Approaches for Heavy Metals and Persistent Organic Pollutants, Bad Harzburg, Germany, Nov. 3-7, 1997*. Umweltbundesamt, Texte 5/98, Berlin 1998, pp. II-39-II-43.
- Wania, F., Axelman, J., Broman, D. **1998**. A review of processes involved in the exchange of persistent organic pollutants across the air-sea interface. *Environ. Pollut.* **102**, 3-24.
- Wania, F., D. Mackay, Y.-F. Li, T.F. Bidleman, A. Strand **1999a**. Global chemical fate of  $\alpha$ -hexachlorocyclohexane. Part 1: Evaluation of a global distribution model. *Environ. Toxicol. Chem.* **7**, 1390-1399.
- Wania, F., D. Mackay **1999a**. Global chemical fate of  $\alpha$ -hexachlorocyclohexane. Part 2: Use of a global distribution model for mass balancing, source apportionment, and trend predictions. *Environ. Toxicol. Chem.* **7**, 1400-1407.
- Wania, F., D. Mackay **1999b**. The evolution of mass balance models of persistent organic pollutant fate in the environment. *Environ. Pollut.* **100**, 223-240.
- Wania, F.; Persson, J.; McLachlan, M.S., Di Guardo, A., Paasivirta, J. et al. **1999b**. The POPCYCLING-Baltic Model. A non-steady state multicompartiment mass balance model of the fate of persistent organic pollutants in the Baltic Sea environment. In: Pacyna, J.M. et al., Final report to the European Commission on project POPCYCLING-Baltic. Environmental cycling of selected persistent organic pollutants (POPs) in the Baltic region, June 1999.
- Wania, F., McLachlan, M.S. Estimating the influence of forests on the overall fate of semivolatile organic compounds using a multimedia fate model. In preparation.
- Xie, W.H., Shiu, W.-Y., Mackay, D. **1997**. A review of the effect of salts on the solubility of organic compounds in seawater. *Mar. Environ. Res.* **44**, 429-444.

#### 4.6. Modelling of POP Transboundary Transport over Europe

V.Shatalov and A.Gusev, Meteorological Synthesizing Centre-East (Russia)

##### 1. INTRODUCTION

Problems of environment pollution by persistent organic pollutants (POPs) attract much attention on national and international levels. A number of international organizations such as AMAP, EMEP, EUROTRAC, HELCOM, OSPARCOM, UNEP, WMO and others have incorporated POPs to their working plans. Despite specific goals of these organizations their research programmes have much in common. Close cooperation on POP problems between agencies and national programmes is successfully expanding.

Significant progress in this field was achieved within the framework of the Convention on Long-Range Transboundary Air Pollution (Convention on LRTAP). In 1999 thirty-six Parties to the LRTAP Convention signed the Protocol on POPs. The Protocol contains basic obligations on control, reduction and elimination of emissions, discharges and losses of selected POPs. In accordance with the Protocol EMEP (Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe) shall provide Executive Body of the LRTAP Convention with information on the long-range transport and deposition of POPs on an annual basis. ***To fulfil these objectives the Parties to the Protocol shall encourage research, monitoring and cooperation in the field of emission inventories, long-range transport, deposition levels, etc.***

Research activities carried out under international programmes are usually based on recommendations of workshops. In particular, scientific recommendations of the UN ECE Workshop on Emissions and Modelling of Atmospheric Transport of POPs and HMs (Durham, USA, 1993), EMEP Workshop on European Monitoring, Modelling and Assessment of HMs and POPs (Beekbergen, the Netherlands, 1994), and Workshop on the Assessment of EMEP Activities concerning Heavy Metals and Persistent Organic Pollutants and Their Further Development (Moscow, Russian Federation, 1996) were included in the work programme of EMEP. The sixteenth session of the Executive Body to the Convention on LRTAP adopted the following EMEP work-plan element for 1999 "Increase the provision of monitoring and modelling data on transboundary fluxes, concentrations and depositions of selected POPs (PAH, PCB, HCB, clordane, lindane,  $\alpha$ -HCH, DDT/DDE) over Europe. Develop the modelling bases on selected POPs (PCBs, B[a]P, dioxines/furans) and verify the functioning of the models. Study further the physical-chemical processes of POPs in different environmental compartments,

taking also into account their global transport". Strategic and operational tasks in the field of research and evaluation of POP transport have been formulated in "Visions for the EMEP work by 2005/2010. Seven-phase programme (1999 – 2001)".

The main goal of the present workshop is to assess a progress in the development of POP modelling and to prepare concrete recommendations focused on further model development, improvement of monitoring and emission activity. These recommendations will contribute to the further development of strategy and policy of EMEP as well as other national and international programmes.

In this paper some materials of the background document of Moscow Workshop [*van Pul et al.*, 1996a] were used.

## 2. POP MODELLING AND ASSOCIATED PROBLEMS

### 2.1 POP modelling

During recent years several reviews on POP modelling has been published. In particular, the review [*Wania and Mackay*, 1999] contains a description of main concepts of POP modelling. The overview of the modelling work aimed at the evaluation of POP contamination in the Arctic region can be found in [*AMAP report*, 1999]. The detailed description of modelling work in North America will be presented by Keith Puckett at this Workshop. In this paper we concentrated on modelling activity connected with the EMEP region.

Among models developed for the evaluation the environmental contamination by POPs it is possible to outline two main types: box models and transport models. These two approaches have different objectives but they have much in common in the description and parameterization of main processes and can complement each other. The advantage of box models is their clearness and simplicity. These models describe the environmental fate of POPs on relatively large time scales (decades and more) and use relatively low spatial resolution. They calculate concentration values averaged over the whole box for the long-term period. On the other hand, transport models are oriented to obtaining more detailed information on spatial distribution of concentrations and depositions of pollutants and apply more detailed description of atmospheric processes. An analysis of differences, similarity and complementarity of these types of models will be made in the background document of Frank Wania.

Main features of transport models applied on European and sub-European scales are summarized in Table 1 (this is a modified version of Table 1 from [van Pul et al, 1996a]).

**Table 1.** Summary of POP models for the European and sub-European scales

Nr	Compounds	Media and processes	Receptor area	Model applied	Institution and references
1	Carbon tetrachloride, atrazine, benzene, chloroform, dichloro-propene, PAH, dichloroethane, endosulphan, PCB, trichloroethane, fentin compounds, tetrachloroethene, lindane, trichlorethene, parathion	Air; Gas/aerosol partitioning, dry and wet deposition, revolatilization, degradation	North sea	OPS (Operational Priority Substances Model)	TNO, [Warmenhoven et al., 1989]
2	Same as 1 plus: azinphosmethil, pentachlorophenol, bentazone, simazine, dichlorvos, trifluralin	Same as 1	River Rhine drainage area	OPS	TNO, [Baart and Diederer, 1991]
3	Dioxins and furans expressed as International Toxic Equivalents (I-TEQ)	Same as 1	NW-Europe	TREND	RIVM, [van Jaarsveld and Schutter, 1993]
4	Lindane, benzo[a]pyrene	Same as 1 but without aerosol/gas partitioning	Europe	EUTREND	RIVM, [van Jaarsveld et al, 1993], ESQUAD project
5	PAH (six of Borneff), 1,1,1-trichloroethane, PCBs, dioxins, 2,4-D, atrazine, azinphos-methyl, bentazon, dichlorvos, diuron, endosulfan, fentin-hydroxid, lindane, mecoprop (MCP), mevinphos, parathion, pentachlorophenol, simazine, trifluraline	Same as 1, dry deposition velocities are parameterized with the help of DEPASS model [van Jaarsveld, 1995]	Netherlands North Sea, Wadden Sea, Dutch coastal waters, some Dutch inland waters	EUTREND	TNO/RIVM, [Baart, Berdowski, and van Jaarsveld, 1995]
6	Lindane	Air, soil and sea; Wet deposition, revolatilization, degradation, air/soil and air/sea exchange	Europe	EUROS	RIVM, [van Pul et al., 1996b], [Jacobs and van Pul, 1996]
7	Lindane	Same as 5, except for gas/aerosol partitioning	Europe	MATCH	SMHI, [Persson and Ullrestig, 1996]
8	PCBs (PCB-28, 52, 101, 118, 138, 153, and 180), B[a]P, 2,3,4,7,8-PeCDF, lindane	Air, soil, sea, and vegetation; Gas/aerosol partitioning, wet deposition, revolatilization, degradation, air/soil, air/sea and air/vegetation exchange	Europe	ASIMD	EMEP/MSC-E, [Pekar et al, 1998]

EUROS model considers only the gaseous phase of the pollutant [Jacobs and van Pul, 1996]. EMEP/MSC-E model constructed on the basis of 3D transport model ASIMD ([Pekar, 1996]) considers gaseous and aerosol phases of POPs. In this model it is assumed that the equilibrium

between gas and aerosol phase is set up instantaneously in air as described by the *Junge* model [*Junge*, 1977; *Pankow*, 1987]. The process of the gas phase dry deposition is considered in both models as the process of POP exchange between the atmosphere and underlying surface. The corresponding sea and soil blocks are described in [*Jacobs and van Pul*, 1996].

The soil model based on the soil storage and transport theory by [*Jury et al.*, 1983] considers the soil surface layer of 15 cm split into 5 layers which thickness increases with depth. The routes of POP input to soil are wet deposition, dry deposition of the aerosol phase, and gaseous air/soil exchange. It is supposed that POPs are present in soil in three phases: gaseous, dissolved and sorbed on particles and the equilibrium between the phases is set up instantaneously. The processes of vertical diffusion, transport of POPs with convective water flows (both in upward and downward directions), volatilization (re-emission), and degradation in soil are included in the model.

The sea model based on [*Liss and Slatter*, 1974] considers the water surface layer of 25 m depth and includes volatilization (re-emission) and degradation processes. Mechanisms of POP input to water are the same as in soil: wet deposition of the gas and aerosol phase, dry deposition for the aerosol phase, and the gaseous exchange between the atmosphere and sea surface. Due to hydrophobic character of some POPs their volatilization fluxes from the sea and lake surfaces can be very high.

Atmosphere/vegetation exchange in the EMEP/MSC-E model is roughly described on the basis of one-chamber leaf model presented in [*Duyzer and van Oss*, 1997; *Hauk et al.*, 1994; *Paterson et al.*, 1994]. The uptake of a pollutant by vegetation is described by resistance analogy. The resistance is calculated for deciduous and coniferous forests and grass cover. The model considers the defoliation of vegetation. Further decay of plant material and its transfer to soil is studied insufficiently and is described in the model as a first-order process (preliminary hypothesis).

Box models are commonly used for the assessment of contamination of different environmental compartments. In models of this type the environment is split into several boxes (representing environmental compartments or their parts). These boxes are supposed to be well-mixed. Further these models use as a rule simplified description of processes governing the long-range atmospheric transport of pollutants and concentrations averaged over sufficiently large boxes. In order to describe spatial variability of contamination, recent box models divide environmental compartment into considerably small number of boxes; such process shifts box models into the direction of transport ones.

The most recent model of this type described in the literature is the POPCYCLING-Baltic model (see [Pacyna, 1999]). This is a fugacity-based box model of the contamination of the Baltic Sea and its drainage basin by POPs. Model developed was applied for the calculation of contamination by HCHs and PCBs (PCB-28, 52, 101, 118, 138, 153, and 180). The model includes 85 boxes (compartments) including different atmospheric compartments, soil compartments (both agricultural and forest), water compartments (fresh, coastal and open; open sea water is divided into surface and deep water boxes which allows to take into account the transport of the pollutant into deep water layers), sediment compartments (for fresh, coastal and sea water), and forest canopy compartments.

One can see that, in spite of their different aims, box and transport models have much in common. They consider various environmental compartments and use similar description of main processes. Some models combine box and transport model approaches. The 2D-model by [Strand and Hov, 1993] exemplifies such a combined approach. Hence it is clear that results obtained by models of the two types are comparable, and the descriptions of processes verified by a model of one type can be used in a model of the other type as well.

Though development of POP long-range transport multicompartment models is far from being completed at present, these models allow us to give a preliminary assessment of the relative importance of different processes for POP long-range transport and to make rough estimates of contamination levels for some pollutants. More reliable estimates of POP transport can be made for pollutants with high particle-bound fraction (PAH, heavy congeners of PCBs and of PCDD/Fs).

Further development of POP fate models depends on a progress in the understanding of main processes affecting POP long-range transport.

## 2.2 Processes affecting POP long-range transport

The complexity of investigations of persistent organic pollutants connected with a very wide spectrum of their physical-chemical properties determining large differences in their behavior in the environment. Some of processes affecting POP long-range transport will be considered below.

### 2.2.1 Gas/aerosol partitioning

Persistent organic pollutants are characterized by the ability to exist in the atmosphere both in gaseous and aerosol phases. From the viewpoint of gas/aerosol partitioning one can distinguish highly volatile POPs existing in the atmosphere mainly in the gaseous phase, semi-volatile

POPs which can exist in the atmosphere both in gaseous and particulate phase, and particle-bound POPs which are concentrated mainly on the particulate matter.

Due to high vapor pressure (0.245 Pa according to [Mackay *et al.*, 1992]) HCB is presented in the atmosphere mainly in the gaseous phase and belongs to a group of highly volatile POPs.

Table 2 shows PCB fractions absorbed on atmospheric aerosol particles at 10<sup>0</sup>C.

**Table 2.** PCB fractions sorbed on atmospheric aerosol particles at 10<sup>0</sup>C

IUPAC No	28	52	101	118	138	153	180
Aerosol fraction, %	0.4	1	5	13	26	21	61

Hence almost all PCBs considered (with exception for PCB-180) have a considerable fraction of the gaseous phase under typical atmospheric conditions and can be viewed as highly volatile or semi-volatile POPs.

The fraction of particle-bound phase of PCDD/Fs is presented in Table 3.

**Table 3.** Fractions of PCDD/Fs homologue groups sorbed on atmospheric aerosol particles ([Horstmann and McLachlan, 1998], warm season)

Homologue group	<b>PeCDF</b>	HxCDF	PeCDD
Aerosol fraction, %	36	64	38

As seen from this table, significant part of HxCDF congeners is concentrated on the aerosol whereas for PeCDFs and PeCDDs the gaseous phase of the pollutant prevails in the atmosphere.

Four indicator PAH compounds included into POP protocol (benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd pyrene]) are present in the atmosphere mainly in the aerosol phase except for B[a]P for which the fraction of the gaseous phase is about 10%. With this accuracy these PAHs can be considered as aerosol-bound POPs.

It should be emphasized that the partitioning coefficient between aerosol and gaseous phases of POPs is strongly temperature dependent, and the equilibrium is shifted towards the aerosol phase at low temperatures (e.g., in the Arctic regions).

Compounds with relatively high content of gaseous phase are characterized by the ability for revolatilization, which leads to strengthening their potential to long-range transport. For such

compounds the exchange processes between different environmental compartments (soil, sea water, vegetation) are central. On the opposite, modelling of POPs with large fraction of the aerosol phase does not differ in essence from that for other aerosol-bound pollutants (e.g., heavy metals).

The estimation of gas/aerosol partitioning was usually made with the well-known Junge-Pankow adsorption model [Junge, 1977], [Pankow, 1987] using the saturated vapor pressure  $p_L^0$  of overcooled liquid for the compound in question. According to this model the aerosol fraction  $\phi$  of the compound is expressed as:

$$\phi = \frac{c\theta}{p_L^0 + c\theta},$$

where  $c$  is a constant depending on thermodynamic parameters of the adsorption process and on properties of aerosol particle surface,  $c=0.17 \text{ Pa}\cdot\text{m}$  [Junge, 1977],

$\theta$  is the specific surface of aerosol particles,  $\theta=1.5\times 10^{-4} \text{ m}^2/\text{m}^3$  [Whitby, 1978].

The alternative approach is based on the absorption partitioning model (see [Finizio et al, 1997], [Pankow, 1998], [Harner and Bidleman, 1998]). This approach links gas/aerosol partitioning coefficient  $K_p$  with octanol/air partitioning coefficient  $K_{OA}$  and the fraction of organic content in the aerosol particles  $f_{OM}$ , namely:

$$\log K_p = \log K_{OA} + \log f_{OM} - 11.91,$$

where  $K_p = C_p / (C_G \times TSP)$ ,  $C_p$  and  $C_G$  are POP concentrations in aerosol and gaseous phases ( $\text{ng}/\text{m}^3$ ),

$TSP$  is the concentration of total suspended particulate matter in air,  $\mu\text{g}/\text{m}^3$ ,

$f_{OM}$  is the fraction of organic matter in aerosol particles (for urban aerosols  $f_{OM}=0.1 - 0.2$ ).

On the example of PCBs Harner and Bidleman have shown that  $K_{OA}$  is better predictor for  $K_p$  than  $p_L^0$  since it characterizes not only substance volatility but also its absorption by the organic matter of aerosol particles. However, for the applicability of this method one should have the correlation relations between  $K_{OA}$  and  $K_p$  obtained on the basis of sufficiently large number of measurements. This approach is used, in particular, in POPCYCLING-Baltic model (see [Pacyna, 1999]).

Note that temperature dependence of the parameters governing the gas/aerosol partitioning is essential especially for low temperatures.

Thus, at present there exist two approaches to the description of gas-aerosol partitioning. The advantage of the absorption model is that it takes into account the fraction of the organic content in the aerosol, which is an important factor for gas/aerosol partitioning.

### 2.2.2 Wet deposition

Here we shall consider the processes of wet deposition of both gaseous and aerosol phase of the pollutant.

The wet deposition process is usually parameterized by washout ratio  $W_T$  that is, the ratio of pollutant concentrations in rain water (snow, fog) and in air:

$$W_T = W_P \times \phi + W_G \times (1 - \phi),$$

where  $\phi$  is the fraction of particle-bound phase of the pollutant,

and  $W_P$  and  $W_G$  are washout ratios for particulate and gaseous phases, respectively.

For the gaseous phase the washout ratio  $W_G$  (for washout by rain) is usually estimated as an inverse to the dimensionless Henry constant of the compound:

$$W_G = RT/H,$$

where  $R$  is the universal gas constant,  $\text{Pa} \times \text{m}^3 / \text{mol} / ^\circ\text{K}$ ,

$T$  is the absolute temperature  $^\circ\text{K}$ ,

$H$  is the Henry constant,  $\text{Pa} \times \text{m}^3 / \text{mol}$ .

It is assumed that the equilibrium between the gaseous phase of the pollutant and rain drops is established instantaneously. As indicated in the literature, *the parameters of wet deposition for different types of scavenging (in-cloud and sub-cloud washout, scavenging with rain or snow) are essentially different. It is therefore desirable to take into account different types of scavenging in POP transport models.*

In the majority of models wet deposition process for the aerosol phase is usually described as one bulk process by scavenging ratios.

There exist more sophisticated models describing wet deposition process for the aerosol phase (see, e.g., [Guelle et al., 1998], [Mircea and Stefan, 1998] and the bibliography therein). This process depend both on different characteristics of particles-carriers: their size distribution, chemical composition, and solubility, and on type of scavenging (with rain or snow, in-cloud or sub-cloud) and its intensity.

Hence, to parameterize the wet deposition process it is important, at the first stage, to study size distribution of pollutants and to take into account different types of scavenging (rain, snow).

### 2.2.3 Dry deposition

In some models dry deposition of POP gaseous phase is parameterized with an effective dry deposition velocity taking into account the saturation of the receptor surfaces and consequently re-volatilization. In more recent models (No 6 and 8 in Table 1) dry deposition process for the gaseous phase is described as the exchange process between the atmosphere and underlying surface (soil, sea, vegetation). In this approach dry deposition flux between air and soil is estimated on the basis of the resistance analogy. The total resistance for the exchange is represented as a sum of three resistances: resistance of the turbulent layer, quasi-laminar layer adjacent to the surface, and the internal resistance of the receiving surface. The description of exchange between the atmosphere and underlying surface is presented below in items devoted to air/surface exchange.

Dry deposition of the particle-bound phase is usually described by effective deposition velocity depending on particle size distribution of the compound in question, by type and characteristics of the underlying surface (in particular, forest canopies essentially affect the dry deposition process), and by the state of the atmospheric boundary layer. The approach based on effective deposition velocity is used, for example in EMEP/MSC-E model [Pekar, 1996]. Only few models take into account particle size distribution. For example, in the EUTREND model ([van Jaarsveld *et al.*, 1993], [Bart and Diederer, 1991]) five classes of particle sizes were used. At present there exist a lot of works devoted to the experimental determination of size distributions for different POPs (see [Holsen and Noll, 1992], [Kaupp *et al.*, 1994], [Poster *et al.*, 1995], [Doskey and Andren, 1981], [Caricchia *et al.*, 1999], [Kaupp and McLachlan, 1999], [Venkataraman *et al.*, 1999]). However, it is not well known how the size distribution of a pollutant changes in the process of its transport.

*At the present stage of model development a rough description of dry deposition process for aerosol phase by an effective velocity can be used. In future for the description and parameterization of this process the influence of the following factors should be evaluated: particle-size distribution of POPs, physical-chemical composition of the aerosol matter, various types of the underlying surface, etc.*

#### 2.2.4 Air/vegetation exchange

As it is mentioned in the literature (see, e.g. [Simonich and Hites, 1994], [Chrostowski and Foster, 1996], [MacCrady and Maggard, 1993]) vegetation can essentially affect the long-range transport of some POPs, being a sink for these compounds. As mentioned in [Trapp and Matthies, 1995], “uptake of chemical by vegetation is a major pathway for toxic substances into the food chain leading to human beings”. For the description of air/vegetation exchange one has to determine uptake, volatilization, and degradation rates for different types of vegetation (deciduous forests, coniferous forests, grass, etc.). Besides the information on spatial distribution of different types of vegetation is used.

There exist different models describing the atmosphere-vegetation exchange (see [Duyzer and van Oss, 1997], [Pacyna, 1999], [Pekar et al., 1999]). In EMEP/MSC-E model air/vegetation exchange is described by the approach suggested in [Bacci et al, 1990a,b, MacCrady and Maggard, 1993, Paterson et al, 1994, McLachlan et al, 1995]. In this approach each type of vegetation is represented as a single block (within each grid cell) and the POP atmosphere/leaf exchange is described as a reversible first-order process. As an alternative one can consider the so-called two-chamber approach ([Hauk et al, 1994], [McLachlan et al, 1995]) where vegetation is considered as some “internal reservoir” surrounded by a cuticle layer. Consequently, in such approach the exchange between the atmosphere and vegetation takes place into two steps: at the first step a pollutant penetrates from air to cuticle layer, and then from cuticle layer to the internal reservoir. In [Hauk et al, 1994] it was shown that the two-chamber approach is in a good agreement with observations indicating two characteristic time scales of the interaction (fast exchange with cuticle layer and slow penetration into the internal reservoir). At the same time it is indicated that the calculation schemes based on such approach appear to be unstable. Besides, in modelling of a sufficiently long processes (long-range transport, for instance) two characteristic time scales becomes insignificant since all processes can be correctly described by the choice of effective values of kinetic parameters.

For more soluble compounds the removal of POPs (e.g., HCH) from vegetation by floem transport and the root uptake processes are to be considered. A model taking into account these processes is described in [Trapp and Matthies, 1995].

The air/vegetation exchange process was applied in some POP fate model (e.g. POPCYCLING-Baltic and EMEP/MSC-E models). Preliminary calculations by EMEP/MSC-E model show that the uptake of PCBs by vegetation can constitute up to 20 –30% of the total emission. The results of calculations with the help of POPCYCLING-Baltic model show that the concentration

of PCBs (seven congeners) in the forest canopy is about 15 ng/g wet weight with atmospheric concentrations being about 150 pg/m<sup>3</sup>.

At present uncertainties in the determination of the parameters of air/vegetation exchange are rather high, and availability of experimental data is insufficient.

*Hence, at present the one-chamber approach seems to be reasonable for rough estimation of air/vegetation exchange. Parameterization of uptake, volatilization, and degradation rates need further refinement. Measurements of POP concentrations in vegetation (simultaneously with air concentrations) are required.*

#### 2.2.5. Air/soil exchange

The parameters of the gaseous exchange between the atmosphere and soil such as uptake, volatilization and degradation rates are affected by different factors: organic carbon content in soil, surface type (forests, grass, arable land), humidity and porosity of the soil, solubility of the compound in question, etc. These parameters determine in particular the characteristic time for accumulation and clearance processes.

There exist a number of models describing air/soil exchange process (DEPASS model [van Jaarsveld, 1995], PESTRAS model, [Tiktak et al, 1994], CHEMTRIS model, [Appels and Bakker, 1991]). The exchange description in these models is based on a soil model [Jury et al., 1983]; more detailed description of these models one can find in [Jacobs and van Pul, 1996], [van Oss and Duyzer, 1996] [Duyzer and van Oss, 1997]. For modelling of the long-range transport on European scale a model described in [Jacobs and van Pul, 1996] can be used. In this model, soil is split into several layers; soil properties are assumed to be constant along the vertical. The flux of the pollutant in soil is considered as a sum of diffusion fluxes of vapor and dissolved phases of the pollutant and the convective flux of the dissolved phase. It is assumed that the pollutant sorbed onto the solid material does not take part in the transport. *In this model no horizontal transport in soil is considered, soil properties are supposed to be homogeneous and to have no temporal variability.*

The preliminary estimate performed by EMEP/MSC-E model have shown that for some POPs (e.g., PCBs) this time can reach several decades.

*The refinement of the air/soil exchange description from the viewpoint of its parameterization for different types of underlying surfaces is required. The uptake and clearance time scales for*

*air/soil exchange process are to be evaluated. Further, for model verifications the availability of measurements of POP soil concentration is desirable.*

#### 2.2.6 Processes in the marine environment and air/sea exchange

It is well known that there are a lot of factors affecting the contamination of the marine environment. In particular, foaming and rough water effects influence the uptake and volatilization rates of the gaseous exchange. Sedimentation process in sea water can be an important mechanism of POPs removal from the marine environment (see, e.g., [Izrael and Tsyban, 1989], [Pacyna et al., 1997], [Pacyna, 1999], [Wania and Mackay, 1999]). The processes of transport of pollutants into deep water layers and sedimentation process as well as horizontal transport by sea currents are to be taken into account. The inclusion of these processes into transport models is in progress in the framework of EMEP.

Since only the dissolved phase of the pollutant is available for re-volatilization, the partitioning between dissolved and suspended phase of the pollutant is important for re-volatilization process modelling.

A simple description of the air/sea exchange used in some models is based on the work [Liss and Slatter, 1974]. In such a description the atmospheric concentration at air/water interface is supposed to be in the equilibrium with water concentration. The marine environment is represented by a single water layer.

At present, there exist a lot of models describing the transport of different pollutants in ocean (an overview of these models one can find, in particular, in [AMAP report, 1999]). Coupling of atmospheric and ocean transport models can be useful for developing multicompartiment POP models.

*Hence, in the description of processes in the marine environment it is important to refine the parameterization of air/sea exchange process and to include transport by sea currents. For verification of models the availability of measurements of POP concentration in sea water is desirable.*

#### 2.2.7 Degradation

One of the processes important for modelling of POP long-range transport is their chemical and physical degradation in various environmental compartments. Usually degradation process is described by first-order reaction mechanisms. In the atmosphere degradation rate can be

determined by different factors. It is assumed that reaction with OH radicals is the main degradation mechanism for pollutants in the gas-phase. Degradation of the particle-bound phase was considered as a process of minor importance. The photolysis process being also of importance for evaluation degradation rates for some pollutants (e.g., benzo[a]pyrene) is not at present well investigated.

The degradation rates in soil and sea water are determined by different processes such as biodegradation, hydrolysis, and photolysis. These rates are rather low. According to the estimates by [Mackay *et al*, 1992] half-lives of PAHs can vary from several weeks to several years in surface waters and from several months to several years in soil; for PCBs half-lives in sea surface waters and soil can vary between several months and several years. These rates can also depend both on temperature and chemical composition of the aerosol matter.

Degradation in vegetation can essentially affect the long-range transport of POPs and their accumulation in the environment. The degradation rates were experimentally determined by [MacCrady and Maggard, 1993] (see also [Chrostowski and Foster, 1996]) for PCDD/Fs. There is the lack of information available on experimental determination of degradation rates of other POPs. Nevertheless, it is possible to perform a rough estimates of degradation rates in vegetation by using measured ratios of POP concentrations in the atmosphere and vegetation (such data are available, for instance, in [Thomas *et al.*, 1998] for PCBs and in [Simonich and Hites, 1994] for PAHs). Such estimation is described in [Pekar *et al*, 1999]. On the basis of these estimates tentative calculations for PCBs were carried out by the EMEP/MSC-E model. The calculation results show that this process can not be ignored.

Note that the degradation process of some POPs can lead to the appearance of even more toxic chemicals than parent ones. Hence, the degradation products are to be taken into account in the modelling process.

*The description of the degradation process for selected POPs in all media is to be further investigated taking into account the degradation products.*

\* \* \*

The preliminary version of parameterizations of the above mentioned processes for selected POPs is presented in EMEP/MSC-E report 4/99 [Pekar *et al.*, 1999].

## 2.3 Other issues

### 2.3.1 Residence time and background concentrations

An important characteristic of POPs is their residence time in the atmosphere. The latter can be evaluated taking into account main removal processes such as degradation, wet and dry deposition (including the gaseous exchange with underlying surface and, consequently, re-volatilization). The residence time and characteristics of transport conditions determine the spatial scale required for the consideration of this or that chemical. For modelling of long-range transport of persistent organic pollutants the background concentrations in different environmental compartments and especially on the boundaries of the calculation grid can be of importance. Due to sufficiently large atmospheric residence time (according to [van Pul *et al.*, 1996a] it can vary from several days to several years) and persistence of the considered compounds in other compartments, these concentrations can essentially affect the contamination levels over Europe for such POPs as PCBs, HCH, HCB. These concentrations can be obtained from hemispheric transport modelling or box models, or from direct measurements. Consequently, *in studies of POP long-range transport the background concentration should be taken into account.*

### 2.3.2 Emission data

In the framework of EMEP emission data are based on the official information reported by countries participating in the Convention. This information is far from being complete. Therefore expert estimates are needed for preparing the emission data sets to be used in modelling work (total emissions, spatial and height distributions, temporal variability, size distribution, etc.). At present the situation with emission data becomes better. The number of countries submitting official data increases. There exist emission expert estimates (see, e.g., [Berdowski *et al.*, 1997], [Pacyna, 1999]). In particular, the emission inventory by [Pacyna, 1999] includes data on a long time period which allows to investigate concentration and deposition trends. The investigations of emissions on the hemispheric scale is now in progress (see [AMAP report, 1999]).

### 2.3.3 Comparison with measurements

Persistent organic pollutants have been included in the EMEP monitoring program since 1999. As a first step the Steering Body of EMEP requested EMEP/CCC to collect already available data on POPs. A number of stations have reported POPs within the EMEP area in connection

with different national and international programmes (HELCOM, AMAP, OSPARCOM) [Pekar et al., 1999].

At present in the framework of the EMEP monitoring network there exist seven stations reporting POPs. However, geographically the existing EMEP monitoring stations are located mainly in the north-west part of Europe. It is desirable to have three-four stations more with locations allowing to obtain the measurement data more uniformly distributed over the EMEP region.

The comparison of modelling results and measurement data is illustrated on the example of POPs (PCB, HCH, B(a)P, PCDD/F) transport calculations with the EMEP/MSC-E model (No.8 in Table 1). The results were compared with measurement data obtained at the EMEP monitoring network. On the average, the calculation results differ from observations within an order of magnitude.

*For model validation it is desirable to use any measurements obtained in the framework of national and international programmes both inside and outside Europe. Besides, it is desirable to have measurements of POP concentrations in other environmental compartments (soil, sea, and vegetation).*

#### 2.3.4 Uncertainties

The description of possible uncertainties in the modelling of POP long-range transport is presented in the background document [van Pul et al., 1996a] at Moscow workshop. Here we shall make some additional remarks. First, one of the main source of uncertainties for POP modeling is still emission data (official and expert estimates). For example, the range of uncertainty factor reported in [Berdowski et al, 1997] is 2 – 5 for  $\gamma$ -HCH and 2 – 4 for B[a]P. The same range of the uncertainty is reported in [Pacyna, 1999] for PCBs. As before, large uncertainty results from spatial and temporal distributions of emissions. Secondly, as shown by tentative calculations in [Pekar et al., 1999], uncertainties in the evaluation of concentration value in vegetation due to the degradation rate in vegetation can reach order of magnitude.

Clearly, large uncertainties in POP modelling arise due to description and parameterization of gaseous exchange processes between atmosphere and different environmental compartments. Hence, it seems that at present the uncertainties for less volatile POPs (e.g., PAHs and HxCDF) are lower than for POPs with essential fraction of gaseous phase (such as HCB, PCBs, and some dioxines/furans). In particular, for POPs existing in the atmosphere essentially completely

in the aerosol phase (e.g. for such PAHs as benzo[b]fluoranthene, benzo[k]fluoranthene, and indeno[1,2,3-cd pyrene]) the model uncertainties are of the same order as for heavy metal modelling.

### 3. CONCLUSION

#### 3.1 Main conclusions

- After the Moscow workshop (1996) a certain progress has been achieved in the description of physical-chemical properties and development of multicompartment approach for selected POP. At the same time, a great number of problems are to be solved to increase the reliability of POP modelling.
- At this stage transport models allow to give rough estimates of transport and contamination level at least for pollutants with high fraction of atmospheric aerosol phase.
- For POPs with large fraction of atmospheric gaseous phase the description and parameterization of atmosphere/soil/sea/vegetation exchange processes are to be further developed and improved.
- Further development of models with different scales (from regional to global) is needed to obtain more complete picture of POP transport and contamination in different environmental compartments.
- Model approaches of different types can supplement each other for better understanding of POP cycling in the environment.
- Taking into account the complexity of the POP modelling the co-operation between international and national programmes and institutions (EMEP, MEPOP, PARCOM, HELCOM, AMAP) is of importance.

#### 3.2 Topics for discussion

- a) Problems of complex chemical mixtures (PCBs, PCDD/Fs). Approaches to PAH and HCH modelling.
- b) Deposition processes. Particle-size distribution and organic carbon content of aerosols. Scavenging with snow. Influence of forest canopies on dry deposition.
- c) Air/vegetation exchange. Uptake, clearance, and degradation rates in vegetation.

- d) Air/soil exchange. Accumulation in and volatilization from soil of highly sorptive POPs.
- e) Air/sea exchange. Sedimentation transport in the marine environment.
- f) Background concentrations of POPs in different environmental compartments.
- g) Complementarity of various approaches to POP modelling.
- h) Requirements to emissions, monitoring and geophysical data (soil, vegetation, land use etc.).

*Any proposals on discussion topics and recommendations for future activities are welcome.*

#### 4. REFERENCES

- AMAP Report [1999] Modelling and Sources: A Workshop on Techniques and Associated Uncertainties in Quantifying the Origin and Long-Range Transport of Contaminants to the Arctic. Report and extended abstracts of the Workshop, AMAP Report 99:4, Bergen, 14-16 June.
- Appels G. and D.J.Bakker [1991] De modellering van de interactie tussen lucht en boden voor vluchtige organische stoffen, TNO rapport R91/191, TNO Institute of Environmental Sciences, Delft, The Netherlands.
- Baart A.C. and H.S.M.A.Diederer [1991] Calculation of the atmospheric deposition of 29 contaminants to the Rhine Catchment area. Report No R 91/219, TNO Division of Technology for Society, P.O. Box 217, 2600AE Delft, The Netherlands.
- Baart A.C., Berdowski J.J.M. and van J.A.Jaarsveld [1995] Calculation of atmospheric deposition of contaminants on the North Sea. TNO report R 95/138.
- Bacci E., Cerejeira M.J., Gaggi C., Chemello G., Calamari D. and M.Vihgi [1990a] Bioconcentration of organic chemical vapours in plant leaves: The Azalea model. *Chemosphere*, **21**, 525-535.
- Bacci E., Calamari D., Gaggi C. and M.Vihgi [1990b] Bioconcentration of organic chemical vapours in plant leaves: Experimental measurements and correlation. *Environ. Sci. Technol.*, **24**, 885-889.
- Berdowski J.J.M., J.Baas, J.P.J. Bloos, A.J.H. Visschedijk, and P.Y.J Zandveld [1997] The European Emission Inventory of Heavy Metals and Persistent Organic Pollutants, Umweltforschungsplan des Bundesministers für Umwelt, Naturschutz und Reaktorsicherheit. Forschungsbericht 104 02 672/03. TNO Institute of Environmental Sciences, Energy Research and Process Innovation.
- Chrostowski P.C. and S.A.Foster [1996] A methodology for assessing congener-specific partitioning and plant uptake of dioxins and dioxin-like compound. *Chemosphere*, **32**, 2285 - 2304.
- Caricchia A.M., S.Chiavarini and M.Pezza [1999] Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples (Italy). *Atmospheric Environment*, **33**, 3731-3738.
- Doskey P.V. and W.Andren [1981] Modelling the flux of atmospheric polychlorinated biphenyls across the air/water interface. *Environmental Science&Technology*, **15**, 6, 705-711.
- Duyzer J.H. and R.F.van Oss [1997] Determination of deposition parameters of a number of persistent organic pollutants by laboratory experiments. TNO-Report TNO-MEP-R97/150.
- Finizio A., Mackay D., Bidleman T. and T.Harner [1997] Octanol-air partition coefficient as a predictor of partitioning of semi-volatile organic chemicals to aerosols. *Atmos. Environ.*, **31**, 2289-2296.
- Guelle W., Y.J.Balkanski, J.E.Dibb, M.Shulz and F.Dulac [1998] Wet deposition in a global size-dependent aerosol transport model. 2. Influence of the scavenging scheme on <sup>210</sup>Pb vertical profiles, surface concentrations and depositions. *Geophysical Research*, **103**, D22, 28875-28891.
- Harner T.and T.F.Bidleman [1998] Octanol-Air Partition Coefficient for Describing Particle/Gas Partitioning of Aromatic Compounds in Urban Air. *Environ. Sci. Technol.*, **32**, 1494-1502.
- Hauk H., Umiauf G. and M.S.McLachlan [1994] Uptake of gaseous DDE in spruce needles. *Environ. Sci. Technol.*, **28**, 2372-2379.

- Holsen T. and K.E.Noll [1992] Dry deposition of atmospheric particles: application of current models to ambient data. *Environ. Sci. Technol.*, **26**, 9, 1807-1815.
- Horstmann M. and M.S.McLachlan [1998], Atmospheric deposition of semivolatile organic compounds to two forest canopies, *Atmos. Environ.*, **32** 1799-1809.
- van Jaarsveld J.A. [1995] Atmospheric deposition of cadmium, copper, lead,, benzo(a)pyrene, and lindane over Europe and its surrounding marine areas. Report 722401002, National Institute of Public Health and the Environment, Bilthoven.
- van Jaarsveld J.A. and M.A.A.Schutter [1993] Modelling the long-range transport and deposition of dioxins; first results for the North Sea and surrounding countries. *Chemosphere*, **27**, 131 – 139.
- van Jaarsveld J.A., van Pul W.A.J. and F.A.A.M. de Leeuw [1993] Modelling the long-range transport and deposition of persistent organic pollutants over Europe and its surrounding marine areas. Paper presented at the 20<sup>th</sup> ITM on Air Pollution Modelling and its Application, 29 Nov. – 3 Dec. 1993, Valencia, Spain.
- Jacobs C.M.J. and W.A.J. van Pul [1996] Long-range atmospheric transport of persistent organic pollutants, I: Description of surface-Atmosphere exchange modules and implementation in EUROS. National Institute of Public Health and the Environment, Bilthoven, The Netherlands. Report No.722401013.
- Junge C.E. [1977] Basic considerations about trace constituents in the atmosphere as related to the fate of global pollutants. In Fate of Pollutants in the Air and Water Environment. Part I (edited by Suffer I. H.) (*Advances in Environmental Science and Technology* **8**). Wiley-Interscience, New York.
- Jury W.A., Spencer W.F. and W.J.Farmer [1983] Behaviour assessment model for trace organics in soil. *Environ. Qual.*, **12**, 558-564.
- Izrael Yu.A. and A.V.Tsyban [1989] Anthropogenic Ecology of the ocean. Hydrometeoizdat, Leningrad, (in Russian).
- Kaupp H., Towara J. and M.S.McLachlan [1994] Distribution of polychlorinated dibenzo-p-dioxins and dibenzofurans in atmospheric particulate matter with respect to particle size, *Atmospheric Environment*, **28**, 4, 585-993.
- Kaupp H. and M.S.McLachlan [1999] Atmospheric particle size distributions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) and their implications for wet and dry deposition, *Atmospheric Environment*, **33**, 85-95.
- Liss P.S. and P.G.Slatyer [1974] Fluxes of gases across the air-sea interface. *Nature*, **247**, 181.
- MacCrady J.K. and S.P.Maggard [1993] Uptake and photodegradation of 2,3,7,8- tetrachlorodibenzo-p-dioxinsorbed to grass foliage. *Environ. Sci. Technol.*, **27**, 343 - 350.
- McLachlan M.S., Welsch-Pausch K. and J.Tolls [1995] Field validation of a model of uptake of gaseous SOC in Lolium multiflorum (Rye grass). *Environ. Sci. Technol.*, **29**, 1998-2004.
- Mackay D., Shiu W.Y. and K.C.Ma [1992] Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. CRC Press. Boca Raton, FL., vol. II.
- Mackay D. and F.Wania [1995] Transport of contaminants to the Arctic: partitioning processes and models. *The Science of the Total Environment* 160/161, 25 – 38.
- Mircea M. and S.Stefan [1998] A theoretical study of the microphysical parametrization of the scavenging coefficient as a function of precipitation type and rate, *Atmos.Environ.*, **32**, 17, 2931-2938.
- van Oss R.F. and J.H.Duyzer [1996] Deposition of persistent organic pollutants; a literature survey, TNO report, TNO-MEP – R 96/409.
- Pacyna J.M. (coordinator) [1999] Environmental cycling of selected persistent organic pollutants (POPs) in the Baltic region (POPCYCLING-Baltic). Technical report.
- Pacyna J.M., Broman D. and E.Lipiatou [1997] Sea-Air Exchange: Processes and Modelling. Scientific report of the workshop on sea-air exchange: Processes and modelling Kjeller, NILU, 11 to 13 June 1997.
- Pankow J.F. [1987] Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.*, **22**, 2275 - 2283.
- Pankow J.F. [1998] Further discussion of the octanol/air partition coefficient  $K_{oa}$  as a correlating parameter for gas/particle partitioning coefficients. *Atmos. Environ.*, **32**, 9, 1493 - 1497.
- Paterson S., Mackay D. and C.McFarlane [1994] A model of organic chemical uptake by plants from soil and the atmosphere. *Env. Sci. Technol.*, **28**, 13, 2259-2266.

- Pekar M. [1996] Regional models LPMOD and ASIMD. Algorithms, parameterization and results of application to Pb and Cd in Europe scale for 1990 MSC-E Report 9/96, September.
- Pekar M., Pavlova N., Erdman L., Ilyin I., Strukov B., Gusev A. and S.Dutchak [1998] Long-Range transport of persistent organic pollutants. Development of transport models for lindane, polychlorinated biphenyls, benzo(a)pirene. EMEP/MSC Report 2/98, Part I..
- Pekar M., Pavlova N., Gusev A., Shatalov V., Vulikh N., Ioannisian D., Dutchak S., Berg T. and A.-G.Hjellbrekke [1999] Long-range transport of selected persistent organic pollutants. Development of transport models for polychlorinated biphenyls, benzo[a]pyrene, dioxins/furans and lindane Joint report of EMEP Centres: MSC-E and CCC, EMEP/MSC Report 4/99.
- Persson C. and A.Ullrestig [1996] Model calculation of dispersion of lindane over Europe. SMHI Report No 68.
- Poster D.L., Hoff R.M. and J.E.Baker [1995] Measurement of particle-size distributions of semivolatile organic contaminants in the atmosphere. *Environ. Sci. Technol.*, **29**, 1990 – 1997.
- van Pul W.A.J., van Jaarsveld J.A. and F.A.A.M. de Leeuw [1996a] Modelling of the atmospheric long-range transport and deposition of POP over Europe. In: Report and Proceedings of the Workshop on the Assessment of EMEP Activities concerning Heavy Metals and Persistent Organic Pollutants and their Further Development (Moscow, Russian Federation, 24 – 26 September 1996), EMEP/MSC-E Report 1/97.
- van Pul W.A.J., Jacobs C.M.J. and J.A. van Jaarsveld [1996b] Deposition of Persistent Organic Pollutants over Europe. *Proceedings of 21<sup>th</sup> NATO/CCMS ITM on Air Pollution Modelling and Its Application*. Vol XI (Ed. S.-E. Gryning and Schiermeyer).
- Simonich S.L. and R.A.Hites [1994] Importance of vegetation in removing polycyclic aromatic hydrocarbons from the atmosphere. *Nature*, **370**, 49 - 51
- Strand A. and Ø.Hov [1993] A two-dimensional zonally averaged transport model including convective motions and a new strategy for the numerical solution. *Geophys. Res.*, **98**, 9023 – 9037.
- Tiktak A., A.M.A. van der Linden, and F.A.Swartjes [1994] A one-dimensional model for assessing leaching and accumulation of pesticides in soil. Report 715501003, National Institute of Public Health and the Environment, Bilthoven.
- Thomas G., Sweetman A.J., Ockenden W.A., Mackay D. and K.C.Jones [1998] Air-pasture transfer of PCBs. *Environ. Sci. Technol.*, **32**, 930 - 942.
- Trapp S. and M.Matthies [1995] Generic One-Compartment Model for Uptake of Organic Chemicals by Foliar Vegetation. *Environ.Sci.Technol.*, **29**, 2333-2338.
- Venkataraman C., Thomas S. and P.Kulkarni [1999] Size distribution of polycyclic aromatic hydrocarbons-gas/particle partitioning to urban aerosols, *Aerosol Sci.*, **30**, 6, 759-770.
- Wania F. and D.Mackay [1999] The evolution of mass balance models of persistent organic pollutant fate in the environment. *Environmental Pollution*, **100**, 223 – 240.
- Warmenhoven J.P., Duiser J.A., de Leu L.Th. and C.Veldt [1989] The contribution of the input from the atmosphere to the contamination of the North Sea and the Dutch Wadden Sea. Report No R 89/349A, TNO Division of Technology for Society, P.O.Box 217, 2600AE Delft, The Netherlands.
- Whitby K.T. [1978] The physical characteristics of sulphur aerosols. *Atm. Environ.*, **12**, 135-195.

## 5. CONCLUSIONS AND RECOMMENDATIONS OF THE WORKSHOP WORKING GROUPS

### 5.1. Working Group on Emission

*Chairman:* Heidi Fiedler

*Rapporteur:* Knut Breivik

#### 1. CONCLUSIONS

1. In recent years considerable improvements have been made in emission inventories for HMs and POPs, however, the available emission estimates is still uncertain.
2. Both reported national data and expert estimates can play an important role in making future emission inventories more reliable and more accurate.
3. There is an urgent need to reduce and quantify the uncertainty inherent in present emission estimates for HMs and POPs.
4. The EMEP/CORINAIR Atmospheric Emission Inventory Guidebook as it now stands is insufficient for individual countries to estimate emissions of individual congeners or isomers of selected POPs, such as PCBs, PCDD/Fs and PAHs. Substantial efforts are required to derive reliable emission factors of individual PCB congeners for the Guidebook.
5. Lack of emission data seriously impedes the modelling activities of EMEP/MSC-E that attempts to obtain reliable source-receptor relationships.
6. Certain POPs as well as some Hg species are volatile and have the potential to be re-emitted from environmental reservoirs. There are not established methods to quantify these releases. Further studies are required to improve the treatment for modelling of these atmospheric inputs.
7. There is a need to better characterize HM content in various fuel types to improve emission estimates.

#### 2. GENERAL RECOMMENDATIONS

8. Co-operation and exchange of information concerning emission inventory activities should be strengthened between various conventions, programmes and intergovernmental organizations (e.g. UNEP, EMEP, EEA, WMO, HELCOM, OSPAR, AMAP etc.) to improve the use of resources by avoiding duplication in inventory development.

9. National authorities should give high priority to reporting emission data of HMs and POPs in compliance with the international agreements on emission reductions, and these efforts should be further encouraged by the appropriate international bodies.
10. Countries should be further encouraged to report and make information, from major HM and POP research activities available to relevant international organizations, such as EMEP.
11. Current information and knowledge available within international programmes on emissions, such as EMEP, is insufficient to meet modellers' requirements. Countries should provide EMEP with information about the characteristics of point sources, such as stack heights, exhaust gas velocities as specified by modellers.
12. In many cases national authorities do have more detailed information about emissions from individual point sources than is reported to EMEP. Mechanisms that facilitate the availability of these data for international organizations and programmes should be promoted.
13. The Task Force on Emission Inventories and Projections (TFEIP) is encouraged to further strengthen its efforts on quality assurance/quality control procedures concerning emission inventories.
14. The Convention bodies should discuss a possible harmonization in the selection of various congeners-/isomers of POPs that are specified within their protocols. For example, OSPAR includes 7 individual PAHs, while 4 PAHs are included within the EMEP programme. Among these only 2 overlap.
15. The feasibility of conducting intercomparison studies for emission inventories and emission factors, as is done for models and sampling/analytical schemes, should be investigated.
16. Activities that may assist national experts in their work, such as training courses and quality assurance/quality control procedures, should be promoted.
17. Translation of the new editions of the Guidebook into Russian for CIS and other interested east European countries should be considered. In addition, the demand for translation into other languages should be assessed.
18. On the national level, contact with industries should be increased to obtain more reliable data.
19. The outcome of the system of Harmonised Quantification and Reporting Procedures for Hazardous Substances (HARP-HAZ), founded for the Preparation of the fifth North Sea Conference in 2002 and information included about sources, calculation methods and

emission factors should be taken into account. The activity under the North Sea Declaration and within the OSPAR framework is focused on the following hazardous substances (mercury, cadmium, lead, dioxins, HCH, pentachlorophenol...).

3. RECOMMENDATIONS RELATED TO THE EMEP/CORINAIR ATMOSPHERIC EMISSION INVENTORY GUIDEBOOK

20. Currently, temporal resolution of emission data is only feasible for a limited number of source categories, such as pesticide. The TFEI should be asked to present simple default temporal distribution functions of these emissions with at least monthly resolution.
21. Emission factors in the Guidebook should be better adapted to the range of technologies across the EMEP grid, taking into account regional differences. For example, emission factors for POPs applicable to the CIS countries are urgently needed. For this reason experts from eastern Europe should take a more active part in the activity of TFEI to speed up the acquisition of the information required.
22. The establishment of a database on the HM content of various fuel types and sources would be of great value to increase confidence in HM emission estimates from various combustion sources.
23. The source categories for the individual HMs and POPs should be prioritized in order of importance for future improvements of individual chapters of the Guidebook.
24. More background information on technologies for which individual emission factors are applicable, are needed in the Guidebook; both the description of the process on which the measurements were made and a description of other technologies for which the emission factor may be applicable.
25. Methodology of emission factors assessment should be included in the existing Guidebook to the extent possible. Harmonization in the elaboration procedures of emission factors is encouraged.

More data on particle emissions and size distributions are needed. Efforts to improve the Guidebook on this issue should take into consideration variations in particulate matter emissions as influenced by abatement technologies. The Task Force on Emission Inventories and Projections should consider establishing, as a minimum, default particle size distributions from important categories for modelling purposes. Current activities to determine of fine particulate emissions ( $PM_{10}$ ,  $PM_{2.5}$ ) should be taken into account.

## 5.2. Working Group on Measurements

*Chairman:* John Munthe

*Rapporteurs:* Torunn Berg, Stein Manö and Eva Brorström-Lundén

### Abbreviations:

HMs = Heavy metals other than mercury

Hg = Mercury

POPs = Persistent Organic Pollutants

PAHs = Polycyclic Aromatic Hydrocarbons

PCBs = Polychlorinated Biphenyls

TGM = Total Gaseous Mercury

CCC = EMEP Chemical Co-ordinating Center, Kjeller, Norway

JRC = Joint Research Center, Ispra, Italy

SOP = Standard Operating Procedure

IVL = Swedish Environmental Research Institute

MEPOP = EUROTRAC Subproject "Atmospheric Cycling of Mercury and Persistent Organic Pollutants"

AAS = Atomic Absorption Spectroscopy

AFS = Atomic Fluorescence Spectrometry

ICP-MS = Inductively Coupled Plasma – Mass Spectrometry

### 1. INTRODUCTION

The discussions in the measurements working group were based on recommendations made at previous workshops in Durham (1993), Beekbergen (1994), Moscow (1996) (mercury (Hg), heavy metals (HMs) and Persistent Organic Pollutants (POPs)) and Lillehammer (1997) (only POPs). Furthermore, the working group recognised that the initiation of a measurement programme for Hg, HMs and POPs within the EMEP monitoring network was included in the EMEP work plan for the year 2000. This work plan includes a number of tasks for the Chemical Co-ordination Center (CCC) aimed at increasing the number of measurement stations for Hg, HMs and POPs. These tasks include:

1. Arrangement of a technical workshop on measurement techniques for mercury and HMs (joint task JRC, Ispra and CCC).

2. Arrangement of a training course on measurement techniques for atmospheric Hg (joint task CCC and IVL).
3. Establish a network of 5 “super-stations” for Hg and POPs and 10 “super-stations” for HMs (in specified geographical regions).
4. Develop POPs and quality control routines for mercury, HMs and POPs for the EMEP manual for sampling and chemical analysis.

Based on these main tasks of CCC, the working group made the following general statements on the status of the current measurement activities within EMEP:

1. The number of current measurement stations for Hg and POPs are not sufficient for assessment of geographical patterns, trends or for model assessment.
2. The geographical distribution needs to be improved mainly by including monitoring stations for Hg and POPs in southern Europe.
3. For HMs, the number of current monitoring stations is larger but the geographical distribution is not satisfactory.
4. The activities of CCC should focus on establishing new monitoring stations in southern Europe and on the development of SOPs for measurements of Hg, HMs and POPs in air and precipitation.
5. CCC should work actively to ensure harmonisation of measurement techniques used in other international programmes and conventions (*e.g.* HELCOM, OSPAR, CEN)
6. CCC and EMEP should strengthen its co-operation with relevant research programmes and other institutions in this field (*i.e.* EUROTRAC/MEPOP, EU-funded projects, UNEP).
7. The successful implementation of the work plan will require that CCC and the EMEP Parties collaborate closely.

A major task for CCC and the Parties during the work plan is to establish measurement stations in specified regions and countries in southern Europe. The Working Group on Measurements did not discuss the exact location of the planned measurement sites or the management procedures (including technical and financial matters) since representatives of candidate regions/countries were not present at the workshop.

## 2. SPECIFIC RECOMMENDATIONS FOR HEAVY METALS

### 2.1 General

The following recommendations are based on the EMEP meeting in Moscow and have been updated during the meeting in Geneva, and will be discussed further at the coming EMEP meeting on measurements of heavy metals in Ispra.

### 2.2 Precipitation

1. CCC should assign a reference method for the sampling and analysis of HM in precipitation including standardised sampling equipment. In principal the applicability of bulk samplers could be shown during a field intercomparison in Germany in 1995. (Deviations between 10 and 20% for Pb and Cd and between 20 and 40% for the other elements). However the suitability of bulk samplers for the application in Southern Europe can not be derived from this intercomparison exercise. In drier climatic regions with low precipitation levels and higher dust particle fluxes (*i.e.* in southern Europe), the errors associated with bulk sampling may be larger and wet-only samplers may be required. This question will be discussed in detail at the planned CCC/JRC workshop in May 2000.
2. Inductively Coupled Plasma/Mass Spectrometry (ICP-MS) and/or Atomic Absorption Spectroscopy (AAS) should be adopted as the analytical reference method for heavy metals except Hg.
3. CCC should assign a reference method for the sampling and analysis of Hg in precipitation including a standard sampler. Bulk samplers for sampling of Hg in precipitation have been shown to be adequate in comparison to wet-only samplers, in northern Europe<sup>1</sup>. Information on the applicability of bulk vs. wet-only samplers in southern Europe is not available.
4. Cold vapour Atomic Fluorescence Spectrometry (AFS) and/or Atomic Absorption Spectroscopy (AAS) should be adopted as the analytical reference method for Hg in precipitation. The detection limit for AAS may not be sufficient.
5. The intercomparison of methods for collection of precipitation for HMs, held in 1995, revealed that significant amounts of HMs might remain in the collection funnel after the sampling period. The HMs thus adsorbed can be rinsed from the funnel but different

---

<sup>1</sup> Iverfeldt, Å. and Munthe, J. Determining the Wet Deposition of Mercury - A Comparison of Weekly, Biweekly, and Monthly Collection of Precipitation Samples. *Proceedings from USEPA/A&WMA Symposium on Measurement of Toxic and Related Air Pollutants, Durham, NC, May 3-7, 1993.*

principles are today used what to do with the rinsed material (adding it to the sample or discarding it). This has to be clarified and specified in the SOP.

6. CCC should take advantage of on-going activities on standardisation of methods for sampling and analysis of Hg and HMs in other international conventions and co-operations (e.g. HELCOM, OSPAR, CEN). Guidelines for sampling and analysis of Hg in air and precipitation have been prepared within OSPAR, which should be taken into account and used for the development of the EMEP manual.

### 2.3 Air

1. CCC should assign a reference method and develop SOPs for the sampling and analysis of total HMs and Hg in air including standardised sampling equipment. This request will also be enforced in connection with planned and existing daughter directives of the EU. Sampling techniques with capacity to separate the PM10 size fraction are available and should be considered initially. PM2.5 should follow as a second step.
2. It should be noted that fractionation into PM10 and PM2.5 size classes is not considered sufficient for model evaluation purposes. The EMEP parties are thus encouraged to establish measurements using impactor systems. SOPs for size fractionated HMs and Hg sampling should also be considered in future work plans of CCC.
3. CCC should arrange an analytical intercomparison on HMs in air. When the first study has been completed and evaluated, a field intercomparison should follow.
4. Inductively Coupled Plasma/Mass Spectrometry (ICP-MS) and/or Atomic Absorption Spectroscopy (AAS) should be adopted as the analytical reference method for HMs.
5. Total gaseous mercury (TGM) should be sampled on gold surfaces using the amalgamation technique. Particles should be removed from the sample air stream at the sample inlet. Analysis should be carried out using thermal desorption in manual or automatic modes. Cold vapour AFS and/or AAS should be used for the detection of Hg in air.
6. The training course arranged by CCC and IVL in 2000 should focus on TGM and total Hg in precipitation.
7. CCC should arrange a field intercomparison on Hg in air and precipitation approximately one year after the training course.
8. Oxidised Hg species are important for determining the atmospheric deposition of Hg and thus important parameters in models. Furthermore, organo-mercury species (e.g.

methylmercury) are also relevant due to the high toxicity and capacity for bioaccumulation. At present, directly applicable routine methods for these species are not available. Close co-operation between the Parties, CCC and relevant research programmes on this topic is encouraged for possible inclusion of these measurements in future work plans.

9. CCC should take advantage of ongoing activities on standardisation of methods in other international conventions and co-operations (e.g. HELCOM, OSPAR, CEN). Guidelines for sampling and analysis of Hg have been developed within OSPAR, which should be taken into account and used as a basis for the development of an EMEP manual.

### 3. SPECIFIC RECOMMENDATIONS FOR PERSISTENT ORGANIC POLLUTANTS

The background paper and the recommendations from Moscow and Lillehammer were reviewed and considered to be generally valid. However, the following additional recommendations are proposed:

1. The selection list of compounds to be monitored (specified in Lillehammer) has been governed by availability of analytical methods, instrumentation and economic feasibility:
  - For PAHs, determination of B[a]P is a mandatory requirement, but other PAH species with carcinogenic importance and various volatility range should also be considered by CCC for measurement<sup>2</sup>
  - For PCBs, a minimum list of "7 congeners" is assumed i.e. #28, 52, 101, 118, 138, 153, 180
2. Weekly air samples (particle and vapour-phase combined) are considered to be sufficient for EMEP objectives and will give continuous coverage. However, to give improved time resolution, intensive campaigns using 24 hours sampling (particle and vapour-phase independently determined) are advised;
3. For deposition sampling, the use of wet-only samplers is now recommended. Wet-only samplers will provide well defined wet deposition fluxes suitable for model validation and assessment. It is recognised that particle dry deposition may constitute an important deposition flux for less volatile POPs (e.g. PAHs). For more volatile POPs, measurements of gas exchange (i.e. dry deposition and re-emissions) would be needed for accurate

---

<sup>2</sup> In the POP Protocol, the reporting requirements for emission data include benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene)

determination of total fluxes. However, due to a lack of monitoring techniques for accurate measurements of dry deposition fluxes, wet-only samplers are recommended due to the well-defined nature of the flux. The use of wet-only samplers would also put EMEP in line with the approaches used in U.S./Canadian programmes and will harmonise with the OSPAR programme. Monthly samples should be collected, as previously suggested at Lillehammer. The selection of deposition sampler design should be made by CCC in co-operation with international experts.

4. The importance of harmonising sampling and analysis procedures within the various European measurement programmes should be stressed;
5. Data from all stations available (not only the five "super stations") should be reported to EMEP. This stresses the need for participation by all institutes contributing data providers in organised interlaboratory studies.
6. The recommended sampling approaches for air and wet deposition will allow for the inclusion of new compounds on the POP list in the future<sup>3</sup>. However, the analytical methods appropriate for the Lillehammer POP list may need to be modified for new compounds to be successfully determined;
7. In the next phase of EMEP, monitoring of POPs in other environmental compartments (e.g. seawater, soil) should be included. For some species, such data is needed for estimation of intermedia fluxes and for model assessment and validation. A co-operation with International Cooperative Programmes (ICPs) within the Working Group on Effects could be beneficial for both sides.
8. The monitoring programme of EMEP should maintain the links with relevant research programmes such as EUROTRAC.
9. A draft manual for sampling and analysis of PAHs in air and precipitation has been prepared within OSPAR and will become available for other existing programmes in 2000.

---

<sup>3</sup> E.g. dioxins and furans; they are included in the POP protocol, and the long range transport of these substances is modelled within the MSC-E, data for validation of the models are needed.

### 5.3. Working Group on HMs modelling

*Chairman:* Gerhard Petersen

*Rapporteur:* Russell Bullock

#### 1. OBJECTIVES

The HM working group identified four main goals for the purposes of the workshop. First, to review the state of the art of modelling heavy metals on regional scales as reported in the presentation of the background document and the plenary session. Second, to identify progress made since the last workshop in 1996 held in Moscow. Third, to identify remaining gaps in environmental data, emissions data, and the scientific understanding of atmospheric processes. And fourth, to make recommendations to the workshop organisers with respect to future model development and application.

For mercury and other heavy metals, we addressed atmospheric processes, emissions, and measurement data with regard to the needs of further model development.

#### 2. PROGRESS

Since the Moscow workshop in 1996 progress has been made in the following areas:

- Fully operational models for Cd and Pb are now available and successful model inter-comparisons have taken place.
- Improved mercury chemistry and wet deposition schemes have been implemented into atmospheric transport models.
- An increasing number of countries has made available national emissions inventories and, together with expert estimates of European emissions, it has been possible to prepare different scenarios of Cd, Pb and Hg deposition for 1997.
- More monitoring data for model assessment are available.
- Cooperation between national modelling initiatives and the EMEP MSC-E modelling programme has been intensified.

### 3. ATMOSPHERIC PROCESSES

#### 3.1 Mercury

There are indications from modelling results that the concentration and deposition patterns within regional model domains are influenced by the global mercury background. Therefore, there is a need for time dependent descriptions of boundary concentrations which could be derived from global mercury transport models supported by measurements.

Cloud chemistry and wet deposition of mercury are known to be strongly connected. Recent progress in understanding physico-chemical processes of atmospheric mercury has permitted development of more comprehensive chemical and wet removal schemes for the explicit treatment of chemical reactions in a three-dimensional Eulerian framework. Further extension of these schemes would require additional information on specific chemical reactions and adsorption to particles by means of field campaigns and laboratory studies. The products of gas-phase oxidation of elemental Hg need to be identified with respect to chemical speciation and physical forms. Due to their toxicity, organic Hg compounds should be implemented into the existing schemes, however additional information on sources and pathways of organic Hg is needed.

To describe air-surface exchange of gaseous mercury species, flux measurements as a function of surface characteristics and meteorological conditions are necessary.

#### 3.2 Other Heavy Metals

One of the most severe gaps in modelling particulate heavy metals relates to the particle size distribution at emission and its evolution during transport and removal from the atmosphere. Evolution of particle size distribution due to processes such as coagulation and cloud microphysics needs to be understood for inclusion in future model development.

Further efforts need to address major uncertainties concerning washout ratio. Transition to a mechanistic description of the washout process is highly recommended. Parameterizations of dry deposition velocities as a function of particle size and surface roughness need to be reassessed in the light of new measurement data.

## 4. EMISSIONS

### 4.1. General Issues

Emissions are recognised as the major source of uncertainty in model predicted concentrations and depositions. In order to improve model results, emissions should be reported:

- with minimum/maximum/best estimate
- as gridded area sources and a list of point sources with geographical reference and stack parameters
- broken down by source category

Our request is measurement of particle size distribution of each metal from the different source categories.

### 4.2. Issues specific to mercury

Emission inventories need to be broken down the most important mercury species in ambient air, i.e., elemental mercury, divalent inorganic gaseous mercury, and mercury associated with particles. Databases for natural emissions and re-emissions of gaseous mercury species are needed which include information about spatial and temporal variability.

## 5. MEASUREMENTS

### 5.1 General Issues

Spatial coverage of the monitoring network in Europe has improved in recent years. However, there are spatial gaps in southern and eastern Europe that need to be addressed to provide a means to test model results over the entire EMEP domain.

Parameters of accuracy should be reported for all data from the monitoring network.

Measurements of particle size distribution are needed for each of the metals at selected sites at various distances from source areas.

Campaign-based measurements of daily air concentrations and precipitation concentrations are needed at selected sites to support further model development.

Micrometeorological size-segregated dry deposition flux measurements for aerosol particles are needed over various surface types to improve model parameterization of dry deposition processes.

## 5.2 Issues specific to mercury

In contrast to the other metals, the mercury monitoring network is limited to four stations in central and northern Europe at present. The mercury monitoring network needs to be expanded by at least four or five stations in southern and eastern Europe. For further model development, we need measurements of particulate mercury and reactive gaseous mercury, in addition to measurements of total gaseous mercury. Event-based measurements of dissolved and total mercury in precipitation are needed at selected sites for validation of aqueous-phase chemistry and wet deposition parameterizations in the models. Methods for the measurement of dry deposition flux of gaseous mercury, especially reactive gaseous mercury, are needed and must be exercised in field campaigns to provide basic process information for model development.

## 6. FUTURE MODELLING ACTIVITIES

### 6.1 Model improvement

As future field studies provide more detailed atmospheric process definition, emissions data, and measurement data, models for all heavy metals should be expanded and improved commensurate to the findings of these field studies.

### 6.2. Model inter-comparison

Previously, an inter-comparison for cadmium and lead models in Europe was performed. This type of model inter-comparison is going to be repeated for mercury with the addition of model developed in North America. Future inter-comparison studies are needed for operational and scientific models to promote long-term development of operational models to be used in the framework of the Convention.

### 6.3. Source-receptor modelling

Modelling can provide more information than just the total concentration and deposition of heavy metals. Once it is known that they are accurate representations of real atmospheric processes, models can also be used to identify particular sources, or source categories, responsible for concentrations and depositions of heavy metals at receptor sites of particular interest. Due to the potential importance of this source-receptor modelling information to policy and evaluation of emission reduction, efforts should be made to include source-receptor analysis capabilities in models as they being further developed.

## 7. PRIORITY OF NEEDS

It was recognised by the heavy metals working group that the additional measurement data requested above are quite extensive and that some prioritisation of these needs would be helpful. In order to fulfill the programmatic needs of EMEP, it is believed that priority should be given to filling spatial gaps in the existing monitoring network. However, it should be understood that field campaigns using new measurement capabilities are required to advance the state of the art in the modelling of all heavy metals.

#### 5.4. Working Group on POPs Modelling

*Chairman:* Frank Wania

*Rapporteur:* Martin Scheringer

#### CONCLUSIONS AND RECOMMENDATIONS

1. After the Moscow workshop (1996) progress has been achieved in the description of physical-chemical properties and the development of multi-phase approaches for selected POPs. At the same time, a great number of problems remains to be solved to increase the reliability of POP modelling.
2. Model approaches of different types such as multi-compartmental box models and highly resolved transport models can supplement each other in gaining a better understanding of POP cycling in the environment. Presently, the highly resolved transport models are more suitable for POPs with a high fraction in the atmospheric particle phase. A better understanding of the exchange processes between the atmosphere and the Earth's surface (soil/sea/vegetation/snow and ice) has the potential to greatly improve their reliability for gaseous POPs. Box models are presently more suitable for describing the partitioning and transport of gaseous POPs on a long time scale. This is because requirements of these models for a detailed understanding of the intermedia exchange mechanisms and for spatially and temporally resolved data are much smaller. The emergency of efficient 3-dimensional models is definitely changing the traditional practices of prediction of the exposure to toxics in the environment. Such models should be used in line with box models for evaluation of long-range transport and deposition of POPs.
3. Further development of models with different scales (from regional to global) is needed to obtain a more complete picture of POP transport and contamination in different environmental compartments. Taking into account the complexity of the task of modelling POPs the co-operation between international and national programmes and institutions (EMEP, MEPOP, PARCOM, HELCOM, AMAP) is important. The exchange of information and knowledge between researchers is crucial for the progress in this field.
4. For all aspects of POPs assessment it is imperative to select a number of priority substances (e.g. individual PCB congeners or PAH compounds) which are the focus of substance specific emission estimates, physical-chemical property determination, modelling,

and measurements. The selection has to be a compromise between importance for exposure assessment (most toxic) and scientific suitability (wide range of properties).

5. For the preliminary evaluation of the transport of complex mixtures of substances it is feasible to use properties reflecting the average properties of the mixture or a rough interpolation between chosen representative constituents. Some model results such as mass budgets are relatively insensitive; others such as the spatial distribution pattern can be very sensitive to the use of congener specific data.
6. Every process description in the model may have an optimum degree of complexity minimising uncertainty of the outcome. The complexity of description of a process and its very inclusion in the model has to relate to what the model seeks to accomplish and should be tested.
7. The relationship of the uncertainty of the input information and the employed methods should be related to the uncertainty of the model results. Sensitivity analysis should therefore become routinely part of modelling studies.
8. Approaches of widely different complexity are possible and have their specific field of application. The rationale for modelling includes both the gaining of an understanding of POP behaviour in the environment and the quantitative description of transport processes and exposure situations. An example for the former is to decide the spatial scale of a POP problem (At which level (national regional, global) should regulatory action be taken?), an example for the latter is the establishment of source-receptor relationships.
9. On the policy level the credibility of a model rest on its transparency, i.e. it should be possible to gain insight in the main assumptions and uncertainties. This includes the need to be able to communicate information on model structure and results to those not involved in modelling.
10. Atmospheric transport models are only a step towards the assessment of environmental effects and dose-response modelling, and in the case of POPs play a different role than in the more classical air pollution issues such as NO<sub>x</sub> or SO<sub>2</sub>. It should be assured that the appropriate methods for these assessments are being developed, and that the results of the transport modelling are suitable for these effect assessments. In particular, the effect assessment needs to take into account the stochastic nature of POP effects and the possibility of effects without a lower threshold.

11. At different temporal and spatial scales, different processes are controlling chemical behaviour and fate. For example, in simulations of episodic atmospheric transport, the influence of degradation rates can be of less importance, whereas it is almost always of major significance in modelling studies of the long-term fate of POPs. The description of the degradation process for selected POPs in all media is to be further investigated taking into account the degradation products.
12. Whereas it was recognised that the use of size distributions is preferable for the description of particle-bound deposition processes of POPs, their use is presently restricted by the lack of sufficient measured distributions for POP chemicals other than PAHs. In the meantime descriptions based on effective deposition velocities may be used.
13. The implementation of the absorption model for the description of gas-particle partitioning is presently limited by the availability of temperature dependent octanol-air partition coefficients and information on the organic fraction of different aerosol types and size classes.
14. In light of the potentially high efficiency of snow in depositing POPs to the surface, improvement of present approaches at describing the scavenging of both particle-bound and gaseous POPs with snow is needed.
15. The dry particle deposition to vegetated surfaces and the diffusive gaseous exchange with plant surfaces may be very important for some POPs and should be the subject of further process-related measurements aiming at deriving the necessary partitioning data and kinetic parameters. Especially, degradation rates on plants need further refinement.
16. In order to realistically simulate both chemistry and transport of atmospheric organic pollutants, it is indispensable that the applied models explicitly include coupling between different components of the global environment such as atmosphere, hydrosphere, cryosphere and soil system. This coupling permits a realistic representation of absorption and delayed re-emission of pollutants from the surface to the atmosphere and, consequently, allows to capture hysteresis-like effects of the exchange between the atmosphere and the other components of the system.
17. The soil/air exchange of POPs is presently not sufficiently well understood (transport in soil, role of soil moisture, transfer resistances, physical soil mixing). There was a perception that a lot can be learnt from modelling the volatilisation of pesticide chemicals from soils. Measurements should focus on an understanding of the variety of processes involved in air-

soil exchange. Further, for model verifications the availability of more measured POP soil concentration is desirable.

18. With respect to the description of processes in the marine environment, paired measurements of concentrations in air and sea water and a better quantitative knowledge of the role of ocean currents and the settling of particulate matter on air-surface exchange is required.
19. Background concentrations in the atmosphere and in seawater, especially on model boundaries, are important for modelling of POP long-range transport. These concentrations can be obtained either by application of hemispheric/global models or by usage of available measurement data in remote areas such as the Arctic or over the oceans. For a better understanding of POP cycling in the environment modelling on hemispheric/global scale is required along with regional modelling.
20. There was a consensus that an intercomparison of POP fate models of different types and scales is to be encouraged. This would likely involve a step-wise progression:
  - discussion and comparison of process descriptions
  - decide on a common region, common time period and common input parameters
  - decide on what sort of output parameters can and should be compared between model approaches (e.g. mass balances and fluxes can be compared between otherwise widely different modelling approaches)
  - choose and conduct appropriate comparison procedures
21. Efforts should be taken to provide the resources required for such an international undertaking. Such an intercomparison would lend additional credibility and reliability to existing models.
22. Information of relevance to modellers of POP fate and transport should be shared and easily available. EMEP/MSC-East's website may serve as a platform for exchanging and posting relevant information (input data, description of models, algorithms, results, and links).
23. There is need to provide assistance to those who wish to start activities in the field of modelling POPs. Such capacity building could take the form of summaries of model experience (assumption, limitations, and requirements) or the sharing of existing models, which should thus be user-friendly. This includes information on how to display and communicate the results of modelling activities.

24. Emission data is the weakest link in our systems designed to trace toxic substances in the environment. On many occasions, various participants were suggesting the possible ways of improving emission inventories used in modelling, exposure studies, and various other policy related issues.
25. A lack or a very high uncertainty of emission estimates presently limits many modelling activities. Certain types of modelling studies, in particular those seeking an understanding of POP fate and transport, are worthwhile and can be conducted without or with partial, relative or entirely hypothetical emission information. In the long term, it may be a goal to include the estimation of emissions into the overall transport models. This may even include socio-economic factors with an impact on emission strength and distribution. This would also allow the simulation with predicted future emission scenarios.
- The development of emission inventories should use more advanced mathematical methods such as inverse modelling (this view was supported by numerous scientists who, during the working group sessions, were very interested in this prospect).
  - The traditional methods of collecting information about the emission should be supplemented by the emission generators based on econometric models and models simulating agriculture practices.
  - Evaluation of source-receptor relationships should use more advanced mathematical techniques based on the adjoint tracer transport model.
26. Geophysical data, which are presently not included in most models, but which are needed are data related to land use and type, soil properties (e.g. OC content in soil) snow and ice cover and vegetation-related information such as biomass density, leaf area index and forest composition. Such data should be accessible easily and without major expense.
27. Planning of the future measurement networks and establishing intensive measurement programs was very intensively discussed. It is clear however that the measurements are still not sufficient to support systematic model verifications. The collection of appropriate data is expensive and requires a significant international effort.
28. In response to a request from the WG on measurements on what temporal resolution atmospheric POP measurements should have, it was decided that both long term averaged data (e.g. on a monthly resolution) are required for long time periods, and highly resolved data series for short measurements campaigns (e.g. daily for 2 weeks) of specific purposes. With limited resources there has to be a compromise between the number of locations and

the degree of temporal resolution. The number and location of sites should be representative for a region. For modelling purposes sampling sites should be remote from sources, which sometimes conflicts with the requirements for exposure assessment. Measurements of toxic substances, chemical and other essential numbers required for the model development and verification should be posted on a web site to facilitate the collaboration between various groups involved with toxic substances in the environment.

## 5.5. Working Group on International Cooperation

*Chairman:* Alexandre Soudine

*Rapporteur:* Marina Varygina

Taking into account the great concern about pollution of the environment with POPs and heavy / metals, and that many international organizations and programmes are presently involved in various activities related to this urgent problem, including emission estimates, measurements, modelling, assessments and pollution control measures, a group of the representatives of a number of international organizations and programmes present at the Workshop (WMO, EMEP, UNEP, AMAP, OSPAR, EUROTRAC (MEPOP) and HELCOM) as well as a representative of the UN ECE Working Group on Effects met on 18 November to consider the needs as well as ways and means for strengthening cooperation and for improving coordination of their activities.

After a brief exchange of information about the current and planned relevant activities (both regional and global) and about on-going cooperation and coordination, the group agreed that such coordination meetings are very important and useful and should take place regularly (e.g. once a year) on an agreeable occasion preferably in conjunction with a relevant meeting jointly organized or attended by representatives of the organizations in question.

To strengthen coordination and cooperation between the organizations and programmes involved in POP and heavy metal issues the group recommended that the following should be implemented:

- to exchange information on existing and planned relevant publications;
- to promote easy access to and exchange of emission data available at various data bases of the cooperating parties;
- to exchange information on the planned meetings and other relevant events to better coordinate their conduct and to try to organize as far as possible joint meetings of the interested parties;
- to further participation of all interested groups in quality assurance activities and in measurement and modelling intercomparison exercises;
- to promote cooperation and collaboration activities (such as joint studies, projects, etc...) in the regions where the data on POPs and heavy metals are missing or scarce (e.g. the Asian part of the Arctic, North Pacific, South-East Asia);

- to exchange information on the existing web sites of the cooperating organizations and to ensure links in each web site to other relevant sites;
- to welcome participation of experts and representatives of relevant programmes in the meetings of the Advisory Group on heavy metals and POPs regularly hold by EMEP/MSC-E;
- to include interested organizations and programmes in the mailing lists.

The participants of the Working Group requested MSC-E to assist in implementation of the above recommendations.

## **6. CLOSING OF THE WORKSHOP**

Mr J. Schneider stressed the success of the workshop and the importance of arriving at useful proposals and recommendations, noting that the output of the workshop was expected to:

- develop conclusions and recommendations for further development of the long-term strategy of EMEP as related to HMs and POPs;
- strengthen scientific co-operation in HM and POP modelling between international organizations and programmes;
- prepare a report and proceedings of the Workshop and present them to the twenty fourth session of the Steering Body of EMEP.

On behalf of the Workshop participants Mr S. Dutchak thanked the WMO organizers for hosting the meeting and for providing excellent conference facilities. Mr A. Soudine thanked all the scientists for their participation and their significant contributions to the workshop.