Reduction of Atmospheric Transboundary Fluxes of Heavy Metals in Europe: Scientific Support for European Environmental Protection Conventions

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ABSTRACT

This study summarizes more than 15 years of scientific support for the United Nations-Economic Commission Europe (UN-ECE) Convention on Long Range Transboundary Air Pollution (LRTAP) and other European environmental protection conventions such as the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) and the Baltic Marine Environment Protection Commission (HELCOM) by means of development and application of numerical simulation models for the atmospheric long-range transport of heavy metals. The work is mainly based on results and conclusions described in the nine papers of the appendix but some more recent investigations which have not yet been published in the scientific literature are also presented.

An introductory overview and synthesis of current knowledge and understanding pertaining to all major aspects of heavy metals in the atmosphere is presented from a viewpoint that numerical modelling of their atmospheric processes is necessary and feasible to support the conventions mentioned above. The models discussed in this study have capabilities to quantify transboundary fluxes of lead, cadmium and mercury as the priority metals of concern and have a potential to identify sources as well as to predict the impact of emission reductions on the load of terrestrial and aquatic ecosystems in Europe. Advantages and limitations of relatively simple Lagrangian models are outlined within the context of issues currently facing the environmental scientific and policy making communities. However, a focus of this study is a comprehensive model system for atmospheric mercury species using a fully three-dimensional Eulerian reference frame and incorporating a state-of-science mercury chemistry scheme, which has been adopted by various scientific institutions for their modelling purposes. The model system, which has an established record of published investigations including the development and testing of the mercury chemistry scheme and comparison of model results against field observation in Europe, has been selected to be one of the reference models within the upcoming Air Quality Directive of the European Union and is currently participating into an international model intercomparison study in the framework of the UN-ECE LRTAP convention.

Overall, the present development level of the advanced models and their components presented in this study is such, that they can provide key information needed to quantify the relationship between anthropogenic emissions and deposition fluxes of heavy metals to remote ecosystems in Europe and that their application within the environmental protection conventions mentioned above is fully justified. The model will be extended and developed further with respect to air pollutants of future relevance (e.g. particulate matter, persistent organic pollutants) according to advancements in the knowledge of their atmospheric processes to ensure that the model maintains its capabilities to address effectively the scientific and political questions that may arise over the next decade.

ZUSAMMENFASSUNG

In dieser Arbeit wird die wissenschaftliche Unterstützung beschrieben, die während der vergangenen 15 Jahre auf dem Gebiet der Entwicklung und Anwendung von numerischen Simulationsmodellen zum grossräumigen atmosphärischen Transport von Schwermetallen für die Wirtschaftskommission der Vereinten Nationen für Europa (United Nations-Economic Commission Europe UN-ECE) über weiträumige, grenzüberschreitende Luftverschmutzung (LRTAP) sowie anderer europäischer Umweltschutzkonventionen wie die Kommission zum Schutz der marinen Umwelt des Nordost-Atlantiks (OSPAR) und der Ostsee (HELCOM) durchgeführt wurde. Die Arbeit basiert hauptsächlich auf den Ergebnissen und Schlussfolgerungen der 9 Publikationen im Anhang. Darüber hinaus werden neuere Forschungsergebnisse diskutiert, die noch nicht in der wissenschaftlichen Literatur veröffentlicht sind.

Einleitend wird der Stand des Wissens über atmosphärische Prozesse von Schwermetallen unter der Annahme dargestellt, dass diese Prozesse in einer für Zwecke der zuvor genannten Umweltschutzkonventionen geeigneten Weise in Modellen parameterisiert werden können. Mit diesen Modellen können grenzüberschreitende Flüsse der drei prioritären Schwermetalle Blei, Cadmium und Quecksilber quantifiziert werden sowie Aussagen über die Herkunft der gemessenen Schwermetallkonzentrationen gemacht werden und die Auswirkung von Emissionsminderungen auf terrestrische und aquatische Ökosysteme in Europa prognostisch abgeschätzt werden. Relativ einfache Lagrange Modelle werden im Kontext mit aktuellen umweltwissenschaftlichen und umweltpolitischen Fragen diskutiert. Schwerpunkt dieser Arbeit ist ein komplexes dreidimensionales Eulersches Modellsysten zum atmosphärischen Transport und chemischen Transformationen von Quecksilberspezies. Dieses Modellsystem representiert weltweit den aktuellen Stand der Wissenschaft und ist in seinen Kernstücken von anderen Umweltforschungsinstituten übernommen worden. Es ist als eines der drei Referenzmodelle für die derzeit erstellte ‘EU Air Quality Directive‘ für Quecksilber ausgewählt worden und nimmt an einem internationalen Modellvergleich im Rahmen der UN-ECE Konvention teil.

Der derzeitige Entwicklungsstand der in dieser Arbeit vorgestellten Modellsysteme erlaubt deren weiteren Einsatz für umweltpolitische Zwecke im Rahmen der obengenannten Konventionen. Dabei werden sowohl die Quantifizierung der grenzüberschreitenden atmosphärischen Schwermetalltransporte und deren Bewertung hinsichtlich ihrer Auswirkungen auf terrestrische und aquatische Ökosysteme als auch die Erweiterung der Modelle bezüglich umweltrelevanter Stoffe der Zukunft (Feinstaub, persistente organische Verbindungen) von besonderer Bedeutung sein.

PREFACE

A main purpose of the present work is to demonstrate the need for advanced numerical simulation models for the quantification of long-range atmospheric transboundary fluxes of heavy metals and their impacts on sensitive ecosystems in Europe. The work therefore deals with the identification of the transport of heavy metals from European anthropogenic sources in connection with physico-chemical transformations and deposition estimates with emphasis on source receptor relationships in the framework of the UN-ECE Convention and other European environmental protection agreements.

This work is based on the results and conclusions presented in the following papers, referred to by bold Roman numerals in the text:

I. G. Petersen, A. Iverfeldt, J. Munthe (1995):
Atmospheric Mercury Species over Central and Northern Europe. Model Calculations and Comparison with Observations from the Nordic Air and Precipitation Network for 1987 and 1988.
ATMOSPHERIC ENVIRONMENT, Vol 29, No.1, pp. 47-67.

II. G. Petersen, J. Munthe, R. Bloxam (1996):
Numerical Modelling of Regional Transport, Chemical Transformations and Deposition Fluxes of Airborne Mercury Species.
In: W. Baeyens, R. Ebinghaus and O. Vasiliev (eds.): Regional and Global Mercury Cycles: Sources, Fluxes and Mass Balances .NATO-Advanced Science Institute Series, Partnership Sub-Series 2: Environment - Vol. 21, pp. 191-217.
Kluwer Academic Publishers, 3300 AA Dordrecht, the Netherlands.
ISBN 0-7923-4314-X

III. G. Petersen, J. Munthe, R. Bloxam, A. Vinod Kumar (1998):
A Comprehensive Eulerian Modelling Framework for Airborne Mercury Species: Development and Testing of the Tropospheric Chemistry Module (TCM).
ATMOSPHERIC ENVIRONMENT - Special Issue on Atmospheric Transport, Chemistry, and Deposition of Mercury (edited by S. E. Lindberg, G. Petersen and G. Keeler), Vol. 32, No. 5, pp. 829-843.

IV. G. Petersen (1998):
Numerical Simulation Models for Airborne Heavy Metals in Europe: A Review.
In: I. Linkov and R. Wilson (eds.): Air Pollution in the Ural Mountains. Environmental, Health and Policy Aspects. NATO-Advanced Science Institute Series, Partnership Sub-Series 2: Environment - Vol. 40, pp. 81 -97.
Kluwer Academic Publishers, 3300 AA Dordrecht, the Netherlands.
ISBN 0-7923-4967-9

V. G. Petersen (1999):
Airborne Heavy Metals over Europe: Emissions, Long-range Transport and Deposition Fluxes to Natural Ecosystems.
In : I. Linkov and W. R. Schell (eds): Contaminated Forests, NATO SCIENCE Series, 2. Environmental Security, Vol. 58, pp. 123-132.
Kluwer Academic Publishers, 3300 AA Dordrecht, the Netherlands.
ISBN 0-7923-5739-6

VI. B. Schneider, D. Ceburnis, R. Marks, J. Munthe, G. Petersen, M. Sofiev (2000):
Atmospheric Pb and Cd input into the Baltic Sea: A new estimate based on measurements.
MARINE CHEMISTRY 71, pp. 297-307.

VII. M. Sofiev, G. Petersen, O. Krüger, B. Schneider, M. Hongisto, K. Jylhä (2001):
Model Simulations of the Atmospheric Trace Metal Concentrations and Depositions over the Baltic Sea.
ATMOSPHERIC ENVIRONMENT Vol. 35. No.8, pp. 1395-1409.

VIII. G. Petersen, R. Bloxam, S. Wong, J. Munthe, O. Krüger, S. R. Schmolke, A. Vinod Kumar (2001):
A Comprehensive Eulerian Modelling Framework for Airborne Mercury Species: Model Development and Applications in Europe.
ATMOSPHERIC ENVIRONMENT - Special ELOISE Issue, Vol. 35. No. 17, pp. 3063-3074.

IX. J. Munthe, K. Kindbom, O. Krüger, G. Petersen, J. Pacyna , A. Iverfeldt (2001):
Examining Source-Receptor Relationships for Mercury in Scandinavia - Modelled and Emperical Evidence.
WATER, AIR, AND SOIL POLLUTION: Focus 1: pp. 299-310.

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1. INTRODUCTION

The United Nations-Economic Commission Europe (UN-ECE) Convention on Long Range Transboundary Air Pollution (LRTAP) and other European environmental protection conventions such as the Commission for the Protection of the Marine Environment of the North-East Atlantic (OSPAR) and the Baltic Marine Environment Protection Commission (HELCOM) provide frameworks for international action to reduce the impact of air pollution in Europe and its marginal seas. The work under these conventions has established a sound process for negotiating concrete measures to control emissions of air pollutants through legally binding protocols. In this process, the main objective of the Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP) program is to regularly provide with qualified scientific information to support the review and further extension of the international protocols negotiated with the conventions mentioned above.

The main task of EMEP, whose organisational structure is schematically depicted in FIGURE 1, has been to provide the UN-ECE LRTAP, OSPAR, HELCOM and governments in Europe with regular information on past and predicted emissions, concentrations and/or depositions of air

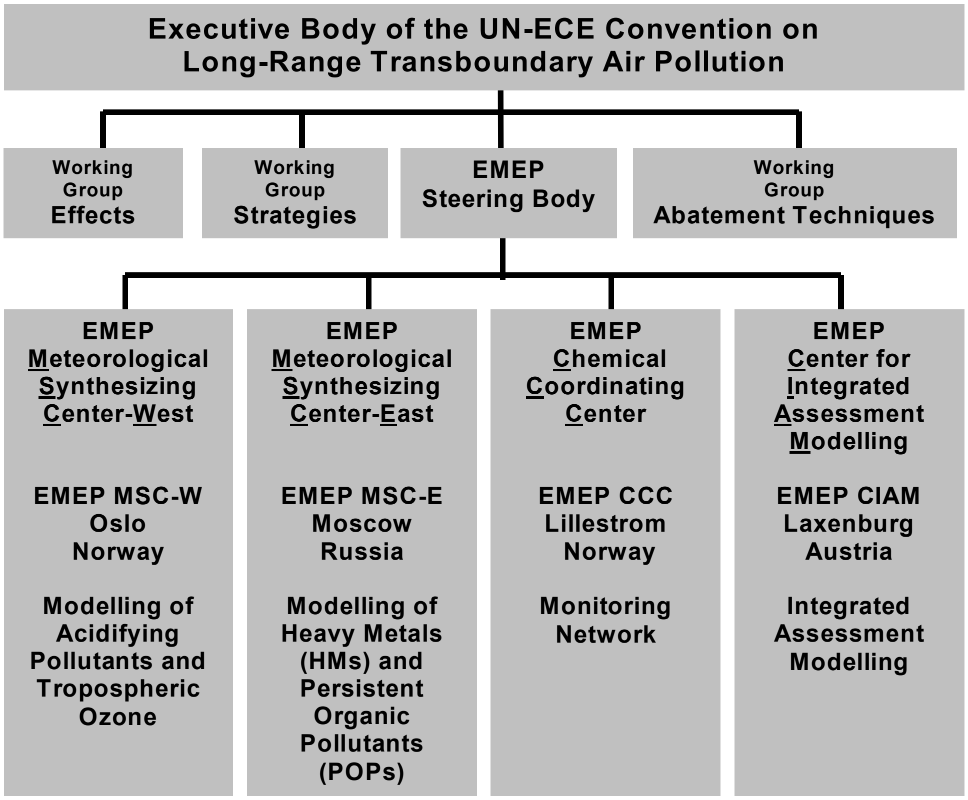

FIGURE 1. Organisational structure of the co-operative programme for monitoring and evaluation of the long range transmission of air pollutants in Europe (EMEP).

pollutants in Europe and, in particular, on the quantity and significance of their long-range transboundary transport. As the work of the conventions has advanced, the requirements on the information provided by EMEP have also evolved. On the seventh phase of the programme, EMEP has been requested to focus further in the evaluation of international abatement strategies and review the success or failure of the existing protocols. To satisfy these needs, the work of EMEP has been formulated in five thematic areas:

- Acid deposition and eutrophication
- Photochemical oxidants
- Heavy metals
- Persistent organic pollutants
- Aerosols

This study focuses on the third of these areas heavy metals, for which the Executive Body of the UN-ECE Convention adopted the „Protocol on Heavy Metals“ on 24 June 1998 in Aarhus (Denmark). It targets three particularly harmful metals: cadmium, lead and mercury. According to one of the basic obligations, Parties will have to reduce their emissions for these three metals below their levels in 1990 (or an alternative year between 1985 and 1995). The protocol aims to cut emissions from industrial sources (iron and steel industry, non-ferrous metal industry) combustion processes (power generation, road transport) and waste incineration. It lays down stringent limit values for emissions from stationery sources and suggests best available techniques (BAT) for these sources, such as special filters or scrubbers for combustion sources or mercury-free processes. The Protocol requires Parties to phase out leaded petrol. It also introduces measures to lower heavy metal emissions from other products, such as mercury in batteries, and proposes the introduction of management measures for other mercury containing products, such as electrical switches and thermostats, fluorescent lamps, dental amalgam, pesticides and paint.

The main task of EMEP within the Heavy Metals Protocol is the above mentioned assessment of the quantity and significance of their long-range transboundary transport in Europe by means of monitoring networks and numerical simulation models. The overall objective of the work described in the subsequent chapters is to give EMEP scientific support in fulfilling its tasks concerning modelling the long-range transport of the priority metals lead, cadmium an mercury over Europe. The support was initiated by the German Federal Environmental Agency (Umweltbundesamt) and is partly embedded into a formal co-operation agreement between the GKSS Research Center Geesthacht and the EMEP institution responsible for heavy metals modelling, namely the EMEP Meteorological Synthesizing Center East (MSC-E) (see FIGURE 1).

The work on which the scientific support is based, was carried out over the last 15 years and is still ongoing with a broad network of scientists from European countries, Canada and the United States that contribute with the systematic collection, analysis and reporting of emission inventories, measurements from monitoring networks inside and outside the EMEP area and results from modelling studies. Special emphasis is placed on the development and application of advanced numerical simulation models that incorporate detailed physical and chemical processes of heavy metals in the atmosphere.

This study consists of three parts and an appendix. The first part (chapter 2) briefly reviews the current state-of knowledge on the three heavy metals of concern with respect to atmospheric levels and species together with emissions and removal processes.

In the second part (chapters 3 and 4) regional cycles and budgets are introduced in the context of results, which have not yet been published in the scientific literature and are hence not included in the annex, are presented:

- A state-of-the-science chemistry and transport model for mercury species is discussed in the framework of an international model intercomparison study initiated by the UN-ECE Convention and organised by EMEP MSC-E.
- The performance of a comprehensive model system for mercury species is evaluated by comparing model results against field observations in Europe
- Model derived estimates of the atmospheric input of mercury to the Baltic Sea in support of HELCOM.

The third part (chapter 5) presents conclusions and a summary of major achievements with respect to introduction of models for the UN-ECE Convention, PARCOM and HELCOM and some suggestions for further model improvements and extensions are provided.

The appendix contains the reprints from publications in books and peer reviewed journals, on which this study is based.

1. EINLEITUNG

Mit der Konvention der Wirtschaftskommission der Vereinten Nationen (United Nations – Economic Commission Europe UN-ECE) über weiträumige, grenzüberschreitende Luftverschmutzung (Long-Range Transboundary Air Pollution LRTAP) sowie anderer Umweltschutzkonventionen wie die Kommissionen zum Schutz der marinen Umwelt des Nord-Ost Atlantiks (OSPAR) und der Ostsee (HELCOM) wurden internationale Vereinbarungen zur Reduzierung der Luftverschmutzung über Europa und seinen Randmeeren geschaffen. Die im Rahmen dieser Konventionen ausgehandelten rechtlich verbindlichen Protokolle beinhalten konkrete Ziele zur Emissionsminderung von Luftschadstoffen auf der Grundlage von regulärer und kontinuierlicher wissenschaftlicher Unterstützung durch das ‚Kooperative Programm zur Erfassung und Bewertung des grossräumigen Transports von Luftschadstoffen über Europa' (EMEP).

Die für die UN-ECE LRTAP, OSPAR und HELCOM hauptsächlich zu erbringenden Leistungen von EMEP, dessen Organisationsstruktur in Abbildung 1 schematisch dargestellt ist, umfassen die Bereitstellung von früheren und zukünftigen Emissionsdaten sowie der Konzentrations- und

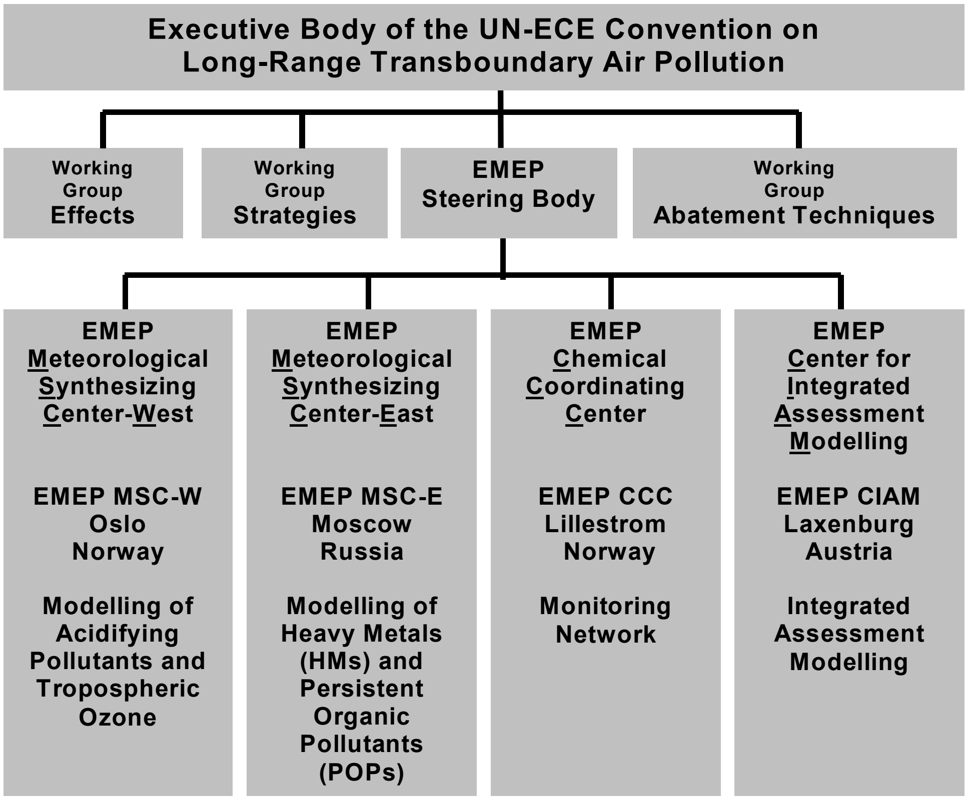

ABBILDUNG 1. Organigramm des Kooperativen Programms zur Erfassung und Bewertung des grossräumigen Transports von Luftschadstoffen in Europa (EMEP).

Depositionsfeldern von Luftschadstoffen über Europa mit besonderem Augenmerk auf die Quantifizierung von deren weiträumigen, grenzüberschreitenden Transporten. Im Zuge der von den Arbeitsprogrammen der Konventionen erzielten Fortschritte sind auch deren Anforderungen an EMEP erhöht worden und im Rahmen der derzeit laufenden siebenten Phase des Programms ist EMEP aufgefordert worden, sich zusätzlich auf die Bewertung von internationalen Emissionsminderungsstrategien hinsichtlich ihres Erfolges oder Misserfolges mit folgender thematischer Gliederung zu konzentrieren:

- Saure Deposition und Eutrophierung

- Photochemische Oxidantien

- Schwermetalle

- Persistente Organische Verbindungen

- Aerosole

Die vorliegende Arbeit ist auf das Themenfeld Schwermetalle konzentriert, für die das ‚Executive Body' der UN-ECE Konvention am 24. Juni in Aarhus, Dänemark, ein ‚Schwermetall-Protokoll' geschaffen hat, in welchem Blei, Cadmium und Quecksilber als die drei prioritären Schwermetalle genannt sind und in welchem sich die Teilnehmerländer grundsätzlich verpflichten, die Emissionen der zuvor genannten Metalle auf einen Stand von unterhalb der Emissionen des Jahres 1990 (oder eines alternativen Jahres zwischen 1985 und 1995) zu reduzieren. Das Protokoll zielt auf eine Minderung der Emissionen aus Industrieanlagen (Eisen- und Stahlindustrie, Verhüttung von Nichteisenmetallen), Verbrennungsprozesse (Kraftwerke, Strassenverkehr) und Müllverbrennung durch Einführung von stringenten Grenzwerten für Emissionen aus stationären Quellen. Dabei wird die Einführung der besten verfügbaren Technologien wie spezielle Filter und Reinigungsanlagen für Verbrennungsprozesse, die Nutzung quecksilberfreier Produktionsprozesse und die Herstellung quecksilberfreier Produkte (z.B. elektrische Schalter, Thermostate, Leuchtstoffröhren, Amalgam-Zahnfüllungen, Pestizide, Farbe) sowie die ausschliessliche Verwendung von bleifreiem Benzin im Strassenverkehr dringend empfohlen.

Die Hauptaufgabe von EMEP im Rahmen des Schwermetall-Protokolls besteht in der Quantifizierung der grenzüberschreitenden atmosphärischen Transporte von Schwermetallen durch ein europaweites Messnetz und durch die Entwicklung und Anwendung von numerischen Simulationsmodellen. In der vorliegenden Arbeit wird die wissenschaftliche Unterstützung beschrieben, die EMEP bei seinen Modellierungs-Aktivitäten zum Transport und Deposition der drei prioritären Schwermetalle Blei, Cadmium und Quecksilber zuteil wurde. Die Unterstützung wurde durch das Umweltbundesamt als der für die deutschen Belange bei der UN-ECE LRTAP zuständigen Fachbehörde initiiert und ist Gegenstand eines Kooperationsvertrages zwischen dem GKSS Forschungszentrum und dem EMEP Meteorologischen Synthesezentrum Ost, welches die Modellierung der Schwermetalltransporte im Auftrage der UN-ECE LRTAP durchführt (siehe Abbildung 1). Schwerpunkt der Unterstützung ist die Entwicklung und Anwendung von Simulationsmodellen mit detaillierten, dem aktuellen Stand der Wissenschaft entsprechenden

Parameterisierungen der physikalischen und chemischen Prozesse von Schwermetallen in der Atmosphäre.

Die vorliegende Arbeit besteht aus einem dreiteiligen Überbau und einem Anhang mit Sonderdrucken aus Fachzeitschriften und Büchern. Im ersten Teil des Überbaus (Kapitel 2) wird der aktuelle Stand des Wissens über die drei zuvor genannten prioritären Schwermetalle bezüglich ihrer physiko-chemischen Prozesse in der Atmosphäre zusammengefasst. Der zweite Teil (Kapitel 3 und 4) beinhaltet eine Beschreibung der historischen Entwicklung und des aktuellen Standes von numerischen Simulationsmodellen zum atmosphärischen Transport von Schwermetallen. Das für Schwermetalle modifizierte komplexe Euler'sche Modellsystem Acid Deposition and Oxidants Model (ADOM) bildet das Kernstück dieser Arbeit und wird im Überbau im Hinblick auf folgende neuere, bisher nicht veröffentlichten Modellanwendungen beschrieben:

- Entwicklung und Test eines den Stand der Wissenschaft repräsentierenden Chemie-Moduls für Quecksilberspezies im Rahmen eins internationalen Modellvergleichs, der von der UN-ECE intiiert wurde und vom EMEP MSC-E organisiert wird.

- Evaluation des Modellsystems mit Hilfe von europäischen Feldmessungen.

- Abschätzung der atmosphärischen Quecksilbereinträge in die Ostsee für HELCOM

Der dritte Teil (Kapitel 5) enthält Schlussfolgerungen aus der vorliegenden Arbeit. Die Ergebnisse bezüglich der Anwendung von numerischen Simulationsmodellen für die UN-ECE Konvention, PARCOM und HELCOM sowie Vorschläge für weitere Modellverbesserungen werden zusammenfassend dargestellt.

Der Anhang besteht aus 10 Sonderdrucken aus Büchern und Zeitschriften mit detaillierten Beschreibungen von Modellentwicklungen und –anwendungen zur wissenschaftlichen Unterstützung der zuvor genannten Umweltschutzkonventionen.

2. HEAVY METALS IN THE ATMOSPHERE

It is increasingly evident that human activities have modified the global atmospheric cycles of the heavy metals. In many instances, the emissions from anthropogenic sources exceed the contributions from natural sources by severalfold. Such massive redistribution caused by mankind has apparently overwhelmed the natural reservoirs and mass fluxes for some of the heavy metals in many ecosystems. In view of the close linkage of the metal cycles to biological processes, there is growing evidence which shows a general elevation of heavy metal burdens in many marine and land biota.

In absolute terms, the mass flux of heavy metals from the atmosphere into soils, forests and lakes in Europe is rather low compared to the flux of acidifying substances such as sulfur and nitrogen oxides [Georgii et al., 1983]. Nevertheless, heavy metals are mobile in the environment, sometimes bioaccumulate in fauna and flora, and can lead to a variety of soil, forest, aquatic and public health impacts [Nriagu, 1990]. The atmospheric deposition of heavy metals is also a major source of these substances in European marginal seas such as the North Sea and the Baltic Sea [**VI**; **VII**; Petersen, 1992b; Petersen and Krüger, 1993; Krüger, 1996; Bartnicki et al., 1998]. Circumstantial evidence and model calculations suggest that much of the deposition of heavy metals in rural areas of Europe is due to the transport of metals from distant (greater than 100 km) sources [Schroeder and Lane, 1988; Duce et al., 1991; Ryaboshapko et al., 1999].

It has been found that several heavy metals, including lead, cadmium and a part of atmospheric mercury species are associated with the fine particulate matter size ranges in the ambient air. This is important not only from a health viewpoint since fine particles (aerodynamic diameter < 2.5 μm) are respirable, but also because fine particles tend to persist in the atmosphere where they can undergo chemical reaction and be transported from their sources over long distances to pristine areas in the environment. This study is focusing on the three metals mentioned above, which have been defined by the UN-ECE LRTAP Convention, OSPAR and HELCOM to be the priority metals of concern. Special attention is being given to mercury occurring in the atmosphere in various chemical forms with typical concentration ranges in Central and Northern Europe summarised in TABLE 1. Unlike other heavy metals, mercury exists in ambient air predominantly in gaseous elemental form with an estimated global atmospheric residence time of about one year making it subject to long-range transport over spatial scales from about 100 km to continental and global. Hence, mercury is a pollutant of concern in remote areas far away from anthropogenic sources, such as polar regions, coastal seas and remote inland lakes in North America and Scandinavia. Sources of mercury are ubiquitous. According to the U.S. Environmental Protection Agency [EPA, 1996] the type of mercury emissions is defined as either

- anthropogenic mercury emissions: the mobilization or release of geologically bound mercury by human activities, with mass transfer of mercury to the atmosphere.
- natural mercury emissions: the mobilization or release of geologically bound mercury by natural processes, with mass transfer of mercury to the atmosphere

or

- re-emitted mercury: the mass transfer of mercury to the atmosphere by biologic and geologic processes drawing on a pool of mercury that was deposited to the earth´s surface after initial mobilization by either anthropogenic or natural activities.

TABLE 1: Mercury species in ambient air in Central and Northern Europe.
(typical concentration ranges and Henry's law coefficients)

species	**concentration range** [ng m^{-3}]	**Henry's law coefficient** [-]	**reference**
Hg^0	1-4	0.3	Ebinghaus et al., 1995 Schmolke et al., 1999
$HgCl_2$	0.005-0.050	$3x10^{-8}$	Munthe, 2001 Pirrone, 1998
MeHg	0.0005-0.010	0.3 $(CH_3)_2Hg$ $2x10^{-5}$ CH_3HgCl	Munthe, 2001
Hg(part.)	0.010-0.100		Pirrone, 1998 Munthe, 2001

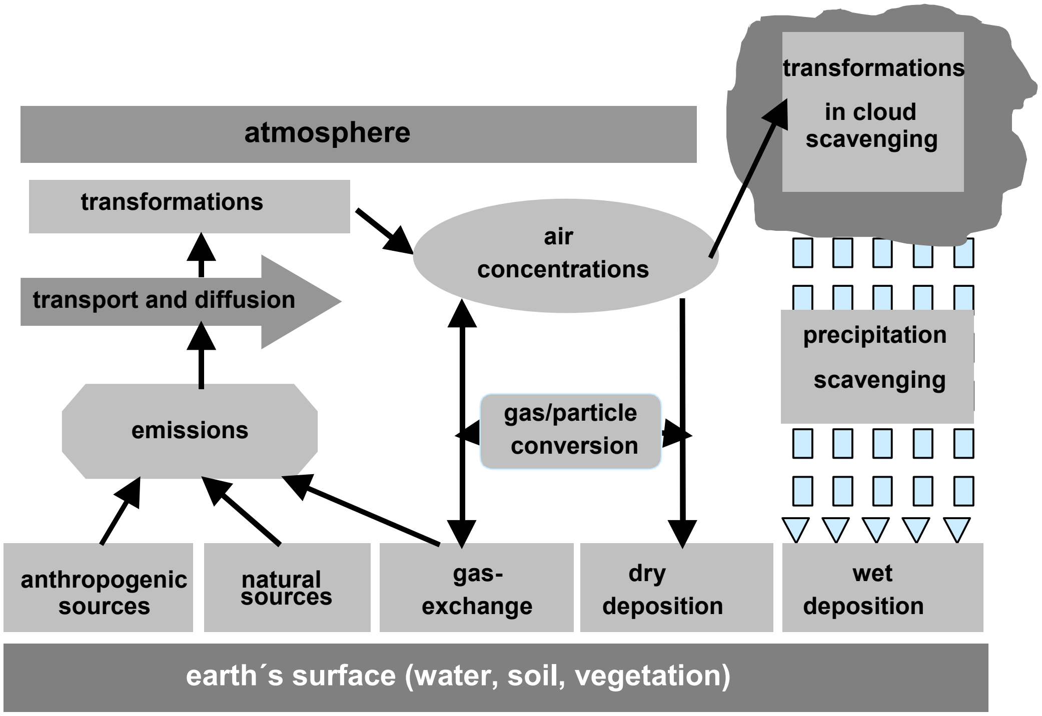

FIGURE 2. Conceptual framework of the atmospheric emissions-to-deposition cycle for heavy metals. (Adopted from Schroeder and Munthe (1998)).

Anthropogenic emissions of mercury (and other heavy metals) can be further divided into area and point sources. Anthropogenic area sources are typically small and numerous and usually cannot be readily located geographically. Point sources are those anthropogenic sources that are associated with a fixed geographic location.

Determinations of heavy metals in the atmosphere have, for the most part, been concerned with regions of high population density and with emissions from specific sources. However, a considerable amount of attention also has been recently focused on determining heavy metals in rural and remote areas in order to estimate the regional and global effects of man´s activities. A review of the processes by which airborne of heavy metals are transported from the main emission areas in Europe and become subject to deposition and absorption into terrestrial and aquatic ecosystems is given in **[V]** and references cited therein. Additionally, a broad overview and synthesis of current knowledge and understanding pertaining to all major aspects of mercury in the atmosphere is presented in Schroeder and Munthe (1998).

This study will build on the conceptual framework of atmospheric pathways and processes schematically depicted in FIGURE 2 and described in detail in **[V]**.

3. CURRENT STATE OF ATMOSPHERIC CHEMISTRY/TRANSPORT MODELS

Atmospheric phenomena such as increasing green house gas concentrations, stratospheric ozone depletion, acid deposition, increasing tropospheric ozone concentrations and higher levels of toxic trace substances such as persistent organic pollutants and heavy metals have been the focus of large national research programmes. Over the next 10-20 years, many difficult decisions will have to be made by policy makers world-wide to deal with these and other problems and the atmospheric science community must continue its efforts to lay a firm scientific foundation on which these policy decisions can be based. However, the complexity of physical and chemical atmospheric processes makes results from comprehensive air pollutants measurement programmes difficult to interpret without a clear conceptual model of the workings of the atmosphere. A single measurement campaign gives investigators only a snapshot of prevailing atmospheric conditions at a particular time and location, while most issues involving human-induced environmental impacts are concerned with the temporal change of these conditions over local, regional and global or near-global areas. Further, measurements alone cannot be used directly by policy-makers to form balanced and cost-effective strategies for dealing with these problems: an understanding of individual processes within the atmosphere does not automatically imply an understanding of the system as a whole. Only with detailed numerical models, based on best available conceptual and technological formulations, can a thorough understanding of individual processes and the atmospheric system as a whole be obtained.

A variety of modelling techniques have been developed for exploration of atmospheric processes of heavy metals. These include relative simple mass balance models that examine the pooling and exchange of heavy metals between various environmental compartments as well as complex deterministic atmospheric dispersion models attempting to simulate the transport and deposition of heavy metals over domains of hundreds to thousands of kilometers, while detailed chemical transformation models incorporate the most sophisticated treatment of atmospheric mercury chemical processes. An extensive review of models for the long-range transport of heavy metals over Europe and hence of particular relevance for potential application within the UN-ECE protocol on heavy metals, but also for OSPAR and HELCOM is given in **[IV]** and references cited therein.

The review presented in **[IV]** and other background documents for EMEP preparatory workshops for the UN-ECE Heavy Metals Protocol [Petersen, 1993; Petersen and Iverfeldt, 1994] comprises model developments until 1996. A typical example for model applications in the framework of the OSPAR and HELCOM Conventions in the time period from 1989 to 1995 for mercury is described in detail in **[I]**. Also, this model system has been used to assess the atmospheric input of heavy metals to the North Sea and the Baltic Sea for purposes of UBA policy issues concerning the protection of these sea areas from pollution from land-based sources [Petersen, 1991; Petersen, 1992a, 1992b; Petersen and Krüger, 1993] and to calculate annual concentration and deposition pattern of acidifying pollutants and heavy metals in Europe in support of the scientific advisory board „Global Environmental Changes" of the German Federal Government [Krüger and Petersen, 1993]. Moreover, the mercury model system has been used to examine the source-receptor relationship for mercury in Scandinavia and in particular the effects of mercury emission reductions in Central Europe on the mercury deposition fluxes in Sweden **[IX]**. The transport and deposition of heavy metals in the studies mentioned above have been analyzed through Lagrangian approaches. These types of models, which have also been extensively used to calculate transboundary fluxes of acidifying pollutants [Iversen, 1993; Tuovinen et al., 1994] and photo-chemical oxidants in Europe [Simpson et al. 1998], are variants of the so-called trajectory models formulated under assumptions of simplified turbulent diffusion, no convergent or divergent flows and no wind shear. In these models, parcels of air containing emissions from each source are advected with the mean wind, with a parcels location computed at equal time intervals.

A Lagrangian approach does offer advantages relative to a Eulerian approach (which is the main topic of discussion in this work). In particular, the Lagrangian approach avoids many of the computational complexities associated with the simultaneous solution of many differential equations; this generally results in requiring significantly less computational resources and can facilitate an understanding of problems that do not require interactive non-linear processes. However, with the Lagrangian approach, only first-order chemical reactions can be treated rigorously. For higher order reactions (which is the case for the majority of atmospheric chemical reactions of mercury species), a simple superposition of Lagrangian parcels is not strictly valid. Hence, for direct modelling of the complex non-linear chemistry of the atmosphere and to obtain three dimensional air pollutant distributions which are desirable from the standpoint of policy applications of the UN-ECE Protocols and the other agreements mentioned above, the Eulerian modelling approach seems to offer the most appropriate basis for current and future atmospheric chemistry and transport models.

Besides basic differences in their mathematical formulation, the distinction between Lagrangian and Eulerian models lies mainly in their treatment of gas- and aqueous phase chemistry, and cloud and precipitation scavenging processes. Lagrangian models typically use highly parameterized formulations for chemical transformation, usually with both gas and aqueous phase reactions lumped into one overall transformation rate. Further, Lagrangian models either ignore cloud and precipitation scavenging processes or use highly parameterized treatments (e. g. scavenging coefficients). On the other hand, Eulerian models employ extensive gas- and aqueous phase chemical mechanisms and explicitly track numerous pollutants concentrations. Also, Eulerian models include a more detailed numerical formulation for physical and chemical processes occurring within and below precipitating clouds. Typically, these models contain modules designed to calculate explicitly the chemical interactions that move gas-phase material into and among the various aqueous phases within clouds, as well as calculate the aqueous-phase chemical transformations that occur within cloud and precipitation droplets.

Since 1996, in view of the upcoming UN-ECE heavy metals protocol and other environmental protection agreements such as the U.S/Canada Great Lakes Water Quality Agreement (GLWQA), an intensified scientific and political interest in comprehensive Eulerian model developments to derive estimates of ambient concentrations and dry and wet deposition fluxes of heavy metals over Europe [Bartnicki, 1998; Pirrone, 1998; Ryaboshapko et al., 1999; Lee et al., 2001] and North America [Pai et al., 1997, Pai et al., 1999, Bullock, 2000; Seigneur et al., 2001] has been observed. These models are typical of the state-of-science models over the past several years and their main features show a couple of similarities. This is not surprising since these models were all developed in similar time periods and were all focused on the simulation of continental scale transport and deposition of heavy metals. Since these types of continental-scale models have been under intense development for several years, they are more comprehensive in many respects than current global-scale models [Bergan et al., 1999; Shia et al., 1999, Seigneur et al., 2001], particularly in their treatment of gas- and aqueous-phase chemistry. However, the next generation of global-scale models will likely be more comprehensive than even the most sophisticated of the current continental-scale models.

A relatively long-term effort beginning in the early 1990s and involving a large team of atmospheric scientists is the Models-3 Community Multiscale Air Quality (CMAQ) system of the U.S. EPA [Dennis et al., 1996; U.S. EPA, 1999]. Models-3 represents the next generation of urban and regional scale air quality models in terms of a flexible software system, that provides a user-interface for CMAQ air quality modelling applications and tools for analysis, management of model input/output, and visualization of data. The Models-3 framework relies on two modelling systems to provide the meteorological and emissions data needed for air quality modelling. With this data, the Models-3 CMAQ Modelling system can be used for air quality simulation of tropospheric ozone, acid deposition, visibility and particulate matter ($PM_{2.5}$ and PM_{10}). The model framework is designed as an open system where alternative models such as the heavy metals version of ADOM described in the next chapter can be used to generate the data.

4. A COMPREHENSIVE EULERIAN MODELLING FRAMEWORK FOR AIRBORNE HEAVY METALS

The methodology and basic structure of current Eulerian atmospheric chemistry and transport models are a decade old and were based on computer architectures and numerical schemes that were leading-edge at that time. Many of the models have been improved and enhanced, especially during the early to mid 1990s, and more than a single version of most models exists. Representative examples for these model developments are the chemical transport models RADM [Chang et al., 1987] and ADOM [Venkatram et al., 1988] and their recent updates, extensions and modifications which are still representative and state-of-science models for continental scale applications for acid rain and photochemical oxidants studies in North America [Binkowski et al., 1991; Karamchandani and Venkatram, 1992; Venkatram et al., 1994] and Europe [Stern et al., 1990; Memmesheimer et al., 1995; Ebel et al., 1997]. A detailed comparison of the features and applications of the basic version of these models (and others) is contained in Seigneur and Saxena, 1990) and is not repeated here. In order to test the performance of RADM and ADOM, and to establish its usefulness as a tool for making acid rain policy decisions, a comprehensive two-year field study, called the Eulerian Model Evaluation and Field Study (EMEFS) was undertaken providing a unique data base for model evaluation [NTIS, 1991]. One finding of EMEFS was that RADM and ADOM type models can realistically simulate the transport and deposition of sulphur and other compounds related to acid rain and that future efforts should include adapting the models for other air quality issues, such as particulate matter and air toxics. In this context the basic version of ADOM has been fundamentally restructured in this work to

- address current understanding of atmospheric processes of heavy metals
- utilize an up-to-date understanding of the complex physico-chemical transformations of atmospheric mercury species
- handle cloud physics and precipitation chemistry more effectively.

This model, which has an established record of published investigations [**II, III, VII, VIII**], represents the state-of-science in continental scale heavy metals modelling over the past several years. It exists in two basic versions: one for metals associated with airborne particles assumed to be chemically inert such as lead and cadmium, the other for a variety of mercury species in gaseous and particulate form including their chemical transformation reactions.

In the following paragraphs, the main features of the comprehensive model system for heavy metals using the Eulerian reference frame of the ADOM model are summarized. A number of key processes incorporated into the chemistry module of the mercury version are discussed in the context of an international inter-comparison study of mercury chemistry schemes. Comparisons of model results with field observations additional to those presented in [**VII**] and **[VIII]** are presented. Finally, model results concerning the atmospheric input of lead and cadmium into the Baltic Sea are evaluated against previous estimates based on model calculations and extrapolations from measurements at coastal sites and atmospheric fluxes of mercury species into the Baltic Sea are estimated using the latest mercury version of the ADOM model.

4.1 Approaches to the ADOM model for heavy metals

The starting point for the heavy metals version of ADOM was the existing Eulerian modelling framework that included the governing processes relevant to long range transport of atmospheric pollutants. These processes include transport by three dimensional flows over a domain with horizontal scales of a few thousand kilometers and vertical scales of a few kilometers, transformation by gas- and aqueous phase chemistry, scavenging by cloud processes and interactions of gaseous and particulate species with the ground.

FIGURE 3 shows schematically the various components of the ADOM model modified for transport, transformations and deposition of heavy metals. Two different versions of the model exist: a European 76 by 76 grid domain (FIGURE 4a) and a North American 33 by 33 grid domain (FIGURE 4b) version with a grid cell size of approximately 55x55 km^2 and 127x127 km^2, respectively. The vertical grid, with 12 unevenly spaced levels between 0 and 10 km, is identical for both versions and is designed to resolve the higher concentration gradients in the boundary layer.

The basic model time step is one hour. Horizontal and vertical wind fields along with the eddy diffusivity, temperature, humidity, surface precipitation, and information about the distribution of clouds make up the meteorological input data set. The data set is derived diagnostically using the weather prediction model HIRLAM for Europe and the Canadian Meteorological Center's model for a North American version of the model. Other than meteorological data, the input and data requirements for ADOM are emissions, initial and boundary conditions, geophysical data and fields of other air pollutants relevant for chemical reactions with mercury species such as ozone and elemental black carbon (soot).

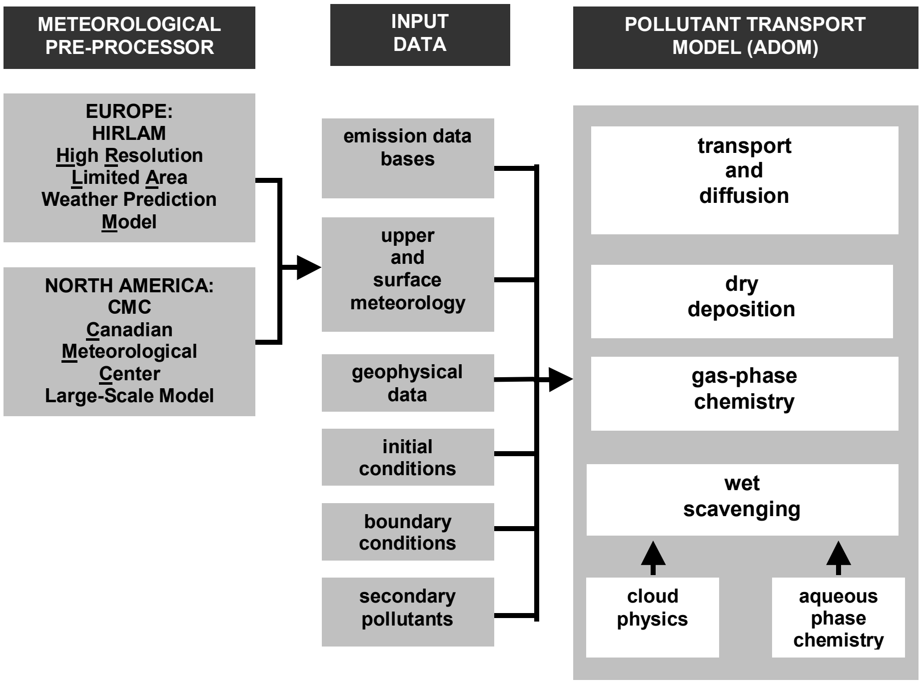

FIGURE 3. The ADOM model system for heavy metals.

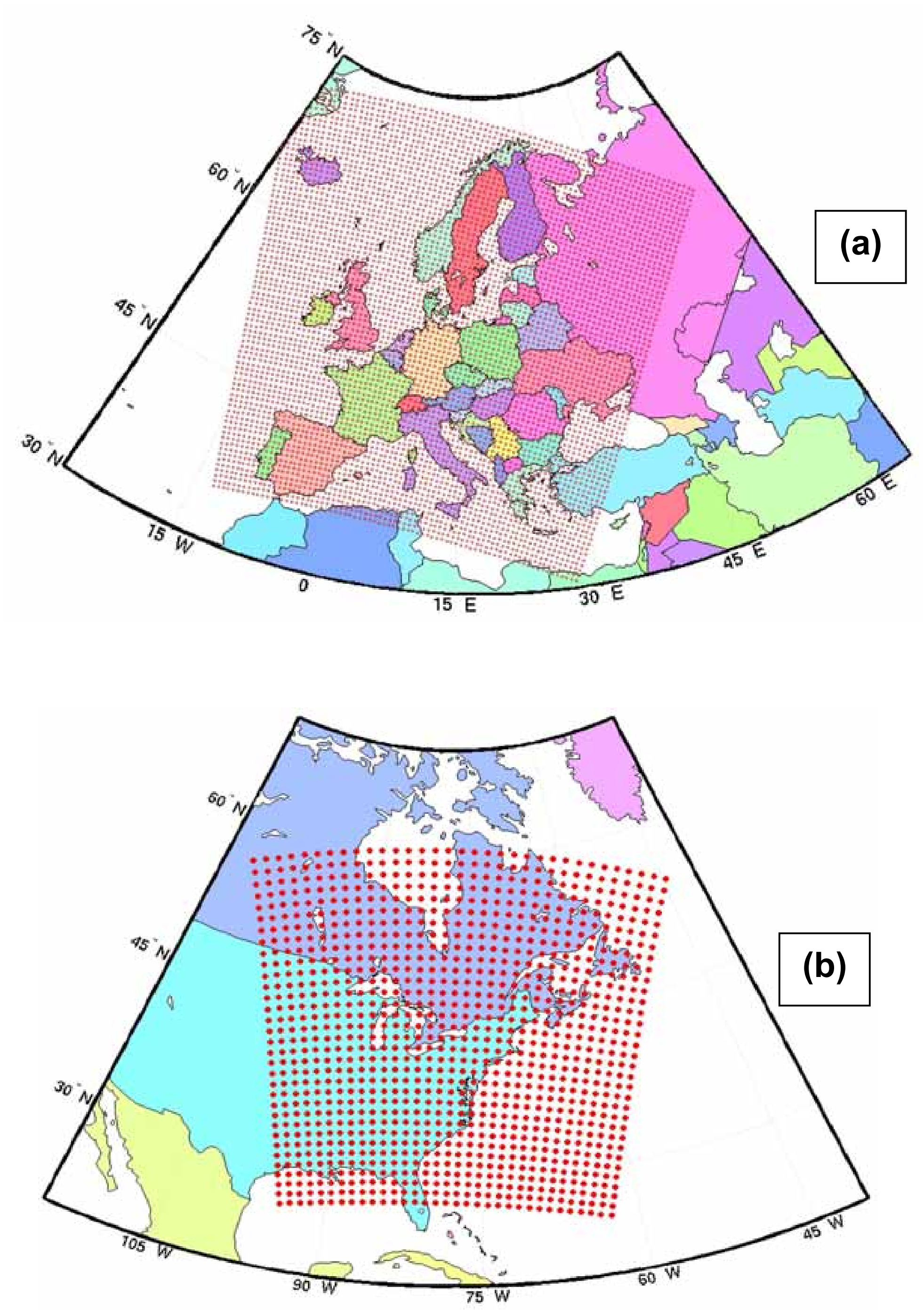

FIGURE 4. The ADOM model domain for
(a) Europe (76 by 76 grid cells, 55x55 km^2 grid cell size)
(b) North America (33 by 33 grid cells, 127x127 km^2 grid cell size)

European emission data for lead, cadmium and mercury were derived from the UBA/TNO inventory for toxic substances in Europe [Berdowski et al., 1997]. These inventories were compiled for the reference year 1990, which results in uncertainties connected with emission trends between 1990 and 1998. For mercury, an emission update for 1995 including mercury speciation and emission heights for various source categories has become available now [Pacyna et al., 2001] and comparative model runs using the inventories for 1990 an 1995 are now underway [Petersen et al., 2002].

Wet scavenging involves modules for handling cloud physics and aqueous phase chemistry. Clouds are classified as stratus (layer clouds) or cumulus (convective clouds) according to the diagnostic output from the weather prediction model. Observations of the fractional coverage and the vertical extent of clouds are combined with output from the diagnostic model to yield the input fields used in this module.

A detailed description of the entire ADOM modelling framework can be found in ERT (1984). The development and testing of the cloud physics and mercury chemistry module considered to be the core part of the ADOM model system for heavy metals is discussed in the subsequent chapter.

4.2 The tropospheric chemistry module for mercury

In the framework of restructuring the ADOM model system for heavy metals a stand-alone version of the cloud mixing, scavenging, chemistry and wet deposition model components referred to as the Tropospheric Chemistry Module (TCM) has been developed and tested **[II, III]**. This module schematically depicted in FIGURE 5 can be used to test the sensitivity of heavy metals wet deposition to various assumptions about the chemical reactions illustrated in FIGURE 6 including the rate constants and the scavenging of mercury species by water droplets. The sensitivity of the of the model to various cloud parameters such as the cloud depth, vertical temperature and moisture profiles, the lifetime of cumulus clouds, cloud fractional coverage and the precipitation rate can also be examined.

Besides initial tests described in **[II, III]** the TCM took part in an international model intercomparison study for mercury chemistry modules [Ryaboshapko et al., 2001]. The study was organised by the EMEP MSC-E in the framework of the UN-ECE Heavy Metals Protocol involving four other advanced chemistry modules, namely the

- Single volume version of the Community Multi-Scale Air Quality Model (CMAQ) of the U.S. Environmental Protection Agency (U.S.A.)
- Mercury chemistry module of the Atmospheric Environment Research/Electric Power Research Institute (AER/EPRI) (U.S.A.)
- Chemistry of Atmospheric Mercury (CAM) process model of the Swedish Environmental Research Institute (IVL) (Sweden)
- Chemical module of MSC-E Heavy Metal Model (MSCE-HM) of the EMEP Meteorological Synthesizing Centre-East (Russia)

The objective of the intercomparison was a comparative evaluation of the chemistry module performances by running them in a cloud environment with identical initial vertical concentration profiles of elemental mercury (Hg^0), mercury chloride ($HgCl_2$) and particulate mercury

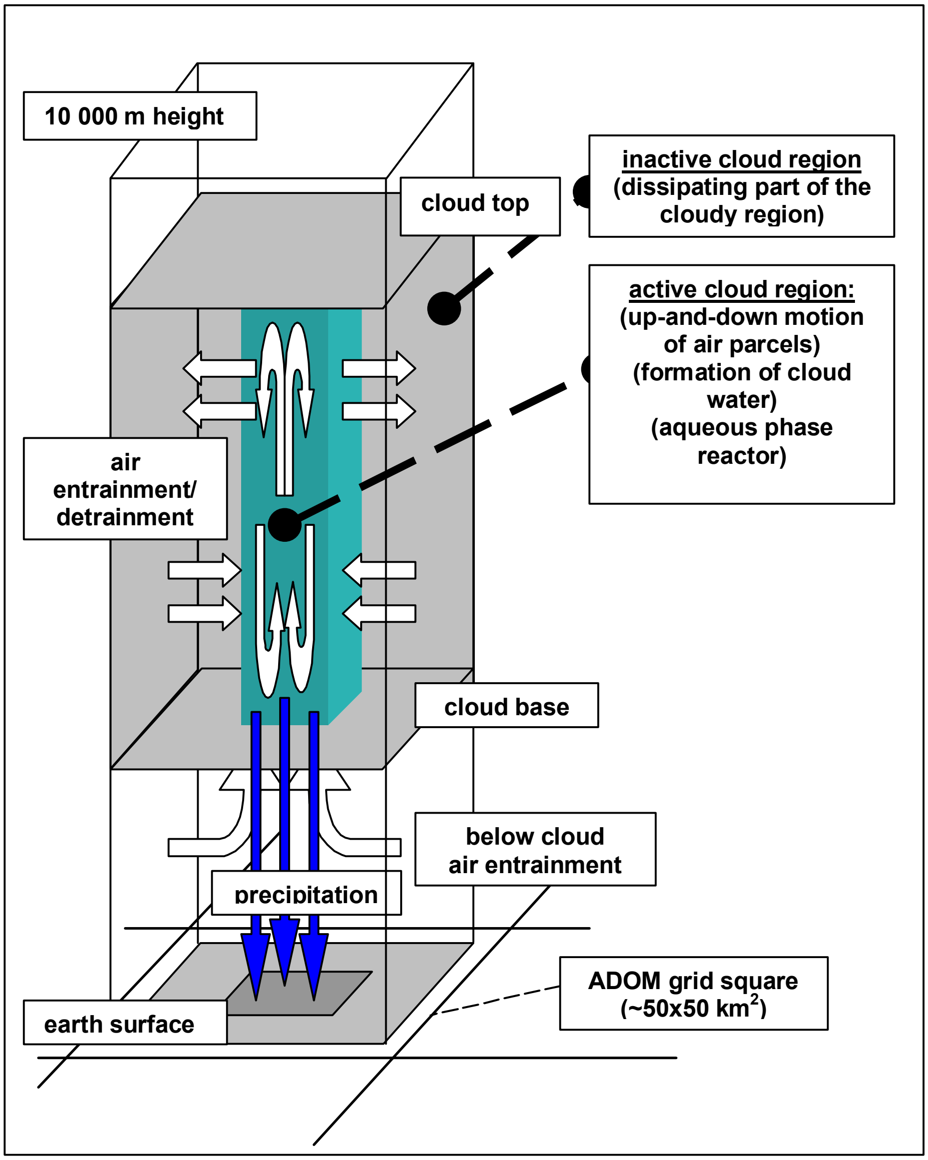

FIGURE 5: Schematic view of the Tropospheric Chemistry Module (TCM) for cumulus clouds.

(Hg(part.)) and other trace constituents affecting the mercury chemistry such as soot, ozone and sulfur dioxide. The TCM has been run over the agreed time period of 48 hours using the closest possible approximation to the common input parameters for the cloud environment, i.e. a non-precipitating cumulus cloud with a cloud base and top height of about 400 m and 4700 m, respectively. The input vertical profiles of temperature, pressure and relative humidity have been adjusted to generate a cloud with an average liquid water content of 0.5 g m^{-3}. The initial mercury concentration profiles in the cloud region and above are identical with the concentrations from the input parameter list, whereas the below-cloud initial concentrations are two orders of magnitude lower to avoid any substantial mercury inflow into the cloud from the below-cloud region.

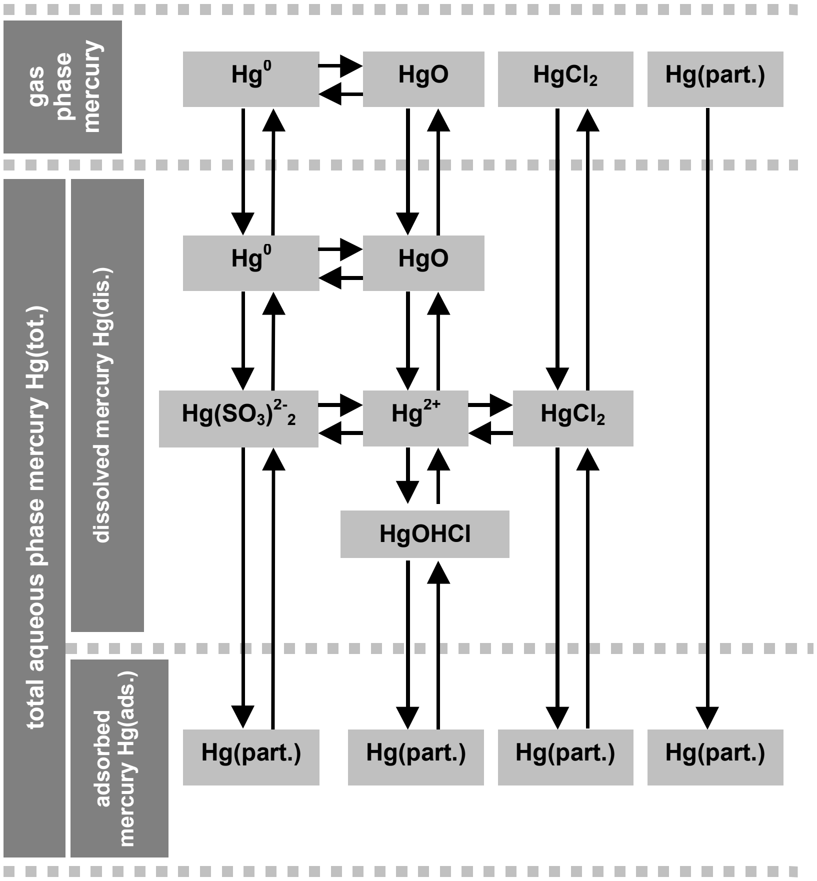

FIGURE 6. The mercury chemistry scheme used with the Tropospheric Chemistry Module (TCM).

Since the TCM is a system which incorporates atmospheric mercury chemistry together with cloud mixing, the results are affected by cloud formation and dissipation processes and by vertical up-and-down motion of air parcels resulting in pronounced vertical Hg^0, $HgCl_2$ and Hg(part.) concentration profiles after cloud evaporation at the end of each time step (FIGURES 7a-7c). These profiles are generated over the entire troposphere assuming a soot concentration in air of 0.5 $\mu g\ m^{-3}$ including the regions below and above cloud base and cloud top, respectively. For all three species, changes in vertical profiles in the cloud area are due to vertical mixing together with aqueous phase chemistry, scavenging and back evaporation of the aqueous species at the end of each time step. Due to vertical redistribution after cloud dissipation below cloud concentrations of all three species are adjusting with time to cloud area concentrations, i. e. initial below cloud concentrations are increasing with time until they have reached the concentration level in the cloud and then closely follow in-cloud concentration changes.

FIGURE 7a shows a relative small Hg^0 depletion in the cloudy area caused by mass transfer of this species into the aqueous phase. The $HgCl_2$ depletion in FIGURE 7b is far more pronounced since this species is readily scavenged and subsequently adsorbed on soot particles. At the end of each time step, adsorbed $HgCl_2$ is evaporated back to Hg(part.) in air and hence contributing to the increase of Hg(part.) concentration as a function of time (FIGURE 7c).

Concentration profiles generated by the TCM for a no-soot scenario are depicted in FIGURE 8a, 8b and 8c. A comparison of profiles in FIGURE 7a and 8a reveals their similarities. Due to its low water solubility changes in Hg^0 concentrations are mainly determined by mass transfer processes into the aqueous phase and only to a minor extent by subsequent adsorption on soot particles. In the absence of soot $HgCl_2$ depletion is considerably smaller (FIGURE 8b), because mass transfer of $HgCl_2$ from the gas phase into the aqueous phase is slowed down if a subsequent adsorption on soot particles is missing. This also effects the time evolution of Hg(part.), i.e. a smaller amount of adsorbed $HgCl_2$ is evaporated back thus changing the Hg(part.) build up into a slight Hg(part.) depletion.

FIGURES 9 and 10 show time dependent average gas-phase and aqueous-phase concentrations for the 0.5 $\mu g\ m^{-3}$ soot and the no-soot scenario, respectively, in the cloudy area after chemistry has taken place but before cloud dissipation and vertical redistribution of mercury species. It should be noted, that concentrations of all species undergo a spin-up period of about 6 hours according to the adjustments in the cloudy area as illustrated in FIGURES 8 and 9.

The low solubility of Hg^0 causes the majority of Hg^0 to be present in the gas phase in both the 0.5 $\mu g\ m^{-3}$ soot and the no-soot scenario (FIGURES 9a and 9b). However, $HgCl_2$ and Hg(part.) gas phase concentrations behave significantly different in both scenarios: In case of the 0.5 $\mu g\ m^{-3}$ soot scenario Hg(part.) concentrations are slightly increasing with time after the spin-up period, whereas $HgCl_2$ shows the opposite trend (FIGURE 9a). This can be explained by an increasing ratio of adsorbed and dissolved species in the aqueous phase as a function of time and hence, after back evaporation at the end of the cloud life cycle, an increasing ratio of Hg(part.) and $HgCl_2$ gas phase concentrations. At the end of the 48 hours simulation the Hg(part.) concentrations are a factor of about 8 higher than $HgCl_2$ concentrations. If no soot is involved (FIGURE 9b) less aqueous Hg is present in the adsorbed phase resulting in less back evaporation of Hg(part.) and, at he end of the simulation period, in $HgCl_2$ concentrations slightly higher than Hg(part.) (FIGURE 9b)

The $Hg(dis.)_{aq}$ and the $Hg(ad.)_{aq}$ lines in FIGURES 10a and 10b represent the sum of all dissolved and adsorbed species, respectively, in the aqueous phase and the $Hg(tot.)_{aq}$ line is the sum of $Hg(dis.)_{aq}$ and $Hg(ad.)_{aq}$ (see FIGURE 5). For both scenarios the curves for $Hg(dis.)_{aq}$ and $Hg(ad.)_{aq}$ show a shape very similar to $HgCl_2$ and Hg(part.) gas phase concentrations in FIGURES 9a and 9b. because the mercury species in the cloud are not depleted by precipitation after aqeous phase chemistry has taken place and no gas phase species are added the beginning of the next time step. Hence, the cloud is governed by back evaporation i.e. most of the aqueous species are converted back to gaseous $HgCl_2$ and Hg(part.) at the end of each time step reaching almost steady state conditions at the end of the simulation period with $Hg(tot.)_{aq}$ concentrations of about 110 ng l^{-1} for both scenarios. In case of the 0.5 $\mu g\ m^{-3}$ soot scenario about 95% of the aqueous species are associated with particles at the end of the simulation period, whereas for the no-soot scenario the major fraction (about 54%) is in the dissolved phase, but a relative large $Hg(ad.)_{aq}$ fraction of about 46% is also present due to a certain amount of initial Hg(part.) in air, which is chemically inert and therefore just scavenged and evaporated back during the simulation period.

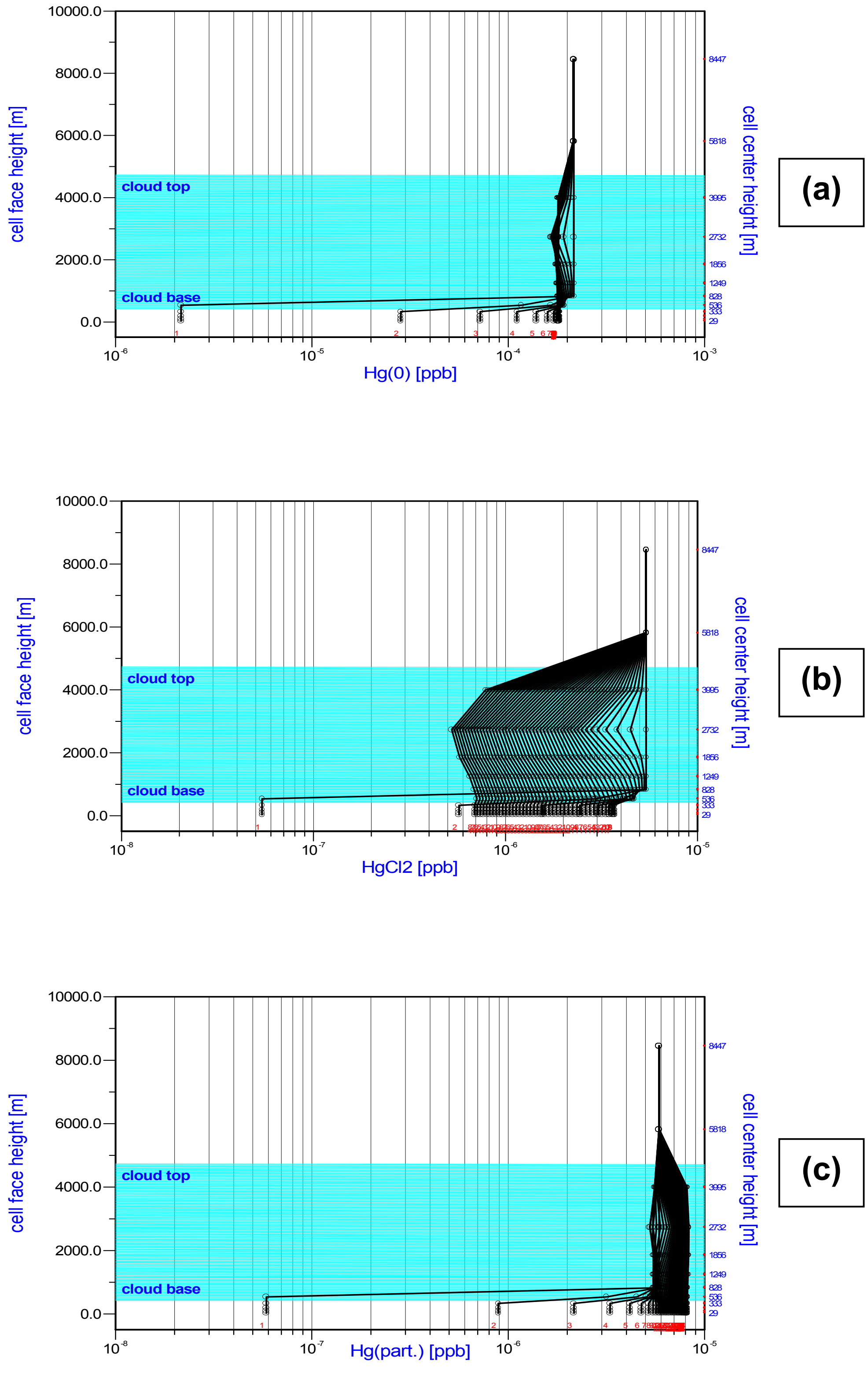

FIGURE 7. 48 hour time evolution of (a) Hg^0 (b) $HgCl_2$ (c) Hg(part.) concentration profiles at the end of each 1 hour time step after cloud evaporation. (0.5 μg m^{-3} soot)

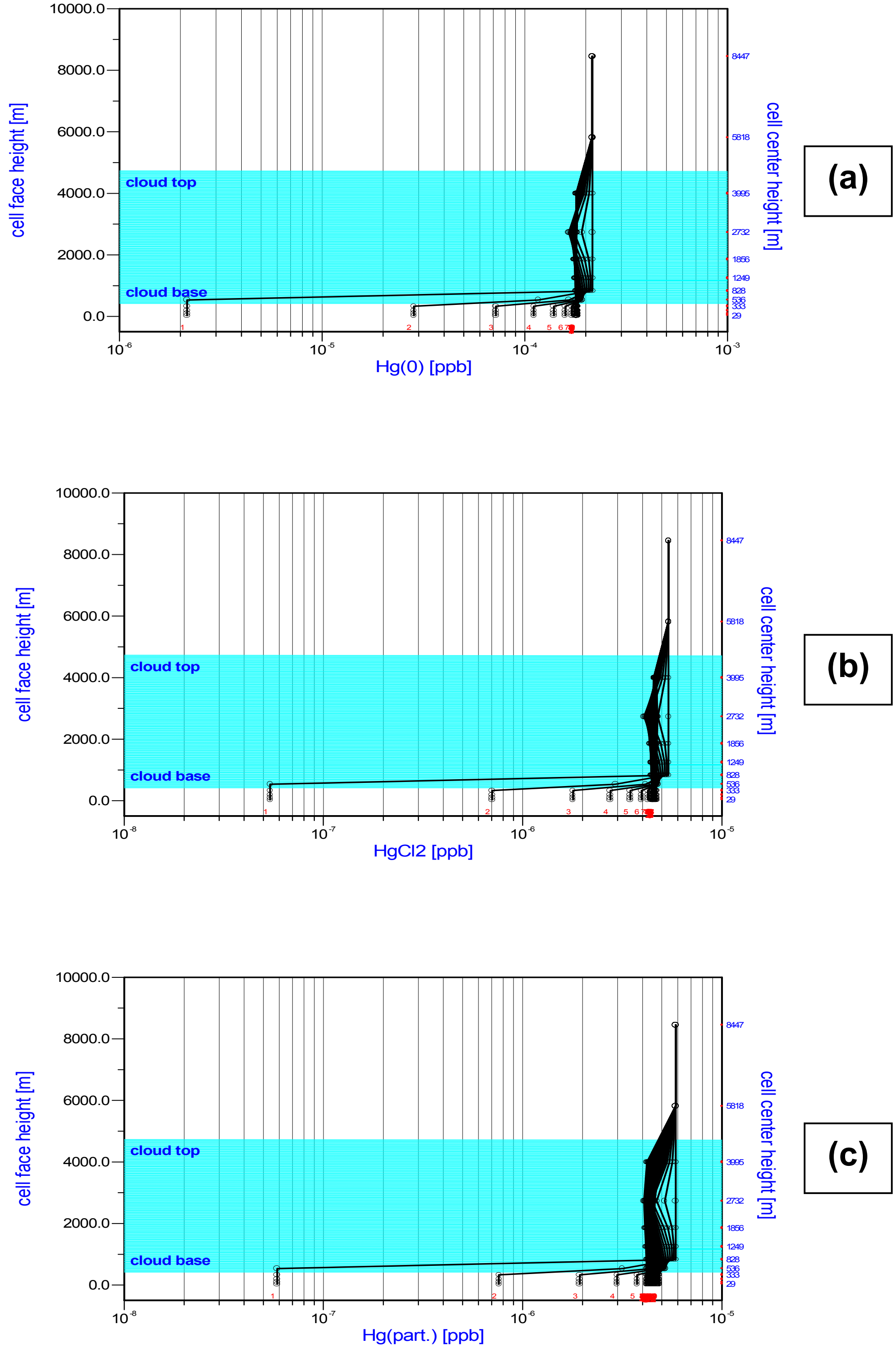

FIGURE 8. 48 hour time evolution of (a) Hg^0 (b) $HgCl_2$ (c) Hg(part.) concentration profiles at the end of each 1 hour time step after cloud evaporation. (no soot)

TABLE 2. Input parameters for the intercomparison study of atmospheric mercury chemistry schemes.

	Hg^0 [ng m^{-3}]	**$HgCl_2$** [ng m^{-3}]	**Hg(part.)** [ng m^{-3}]	**soot** [µg m^{-3}]	**precip. rate** [mm (48 h)$^{-1}$]
case 1	1.600	0.000	0.000	0.0	0.00
case 2	1.600	0.000	0.000	0.5	0.00
case 3	1.600	0.000	0.040	0.0	0.00
case 4	1.600	0.005	0.000	0.5	0.00
case 5	1.600	0.005	0.040	0.5	0.00
case 6	1.600	0.005	0.040	0.5	3.50
case 7	1.600	0.005	0.040	0.5	7.00
case 8	1.600	0.005	0.040	0.5	10.50

Additional runs have been performed to compare TCM results against field observations using data from simultaneous measurements of mercury species in ambient air and in precipitation at a site at the GKSS Research Center Geesthacht. These data form the basis for eight different cases defined in TABLE 2. Results in terms of $Hg(tot.)_{aq}$ concentrations as a function of time and soot concentrations are summarized in FIGURES 11a and 11b. To demonstrate the impact of TCM depletion by precipitation in more detail, $Hg(tot.)_{aq}$ concentrations in these two figures have been generated without spin up during the first six hours as mentioned above and as shown in FIGURES 7-8.

FIGURE 11a illustrates the impact of $HgCl_2$ and Hg(part.) concentrations on $Hg(tot.)_{aq}$ at a constant Hg^0 level of 1.6 ng m^{-3}. As expected, $Hg(tot.)_{aq}$ shows minimum values for both with and without soot when $HgCl_2$ and Hg(part.) are set to zero (case 1 and 2). Adding 0.04 ng m^{-3} Hg(part.) results in an about fourfold increase of $Hg(tot.)_{aq}$ (case 3), whereas additional 0.005 ng m^{-3} $HgCl_2$ only contributes to about 10-15% to $Hg(tot.)_{aq}$ (case 4). The input data of case 5 represent the observed average Hg concentrations in air but with the precipitation rate set to zero yielding a $Hg(tot.)_{aq}$ concentration of about 80 ng l^{-1} (FIGURE 11a and 11b). If the TCM is depleted with the observed average precipitation rate of 3.5 mm during 48 hours, $Hg(tot.)_{aq}$ is decreasing to about 30 ng l^{-1} (case 6 in FIGURE 11b). The observed precipitation rate represents an average value during a ten days sampling period, and is therefore most probably underestimated for events of heavier rainfalls during a 48 hour period. Increasing the precipitation by factors of 2 and 3 (case 7 and 8, respectively) gives $Hg(tot.)_{aq}$ concentrations of about 10 ng l^{-1} or less. If one allows for potential uncertainties in the observed precipitation rate during the 48 hours of simulation, agreement with the observed average $Hg(tot.)_{aq}$ concentration of 7.2 ng l^{-1} is fairly good and the TCM has demonstrated its capabilities to reproduce observed field data in terms of concentrations in precipitation as a function of both cloud mixing and mercury chemistry reasonably well.

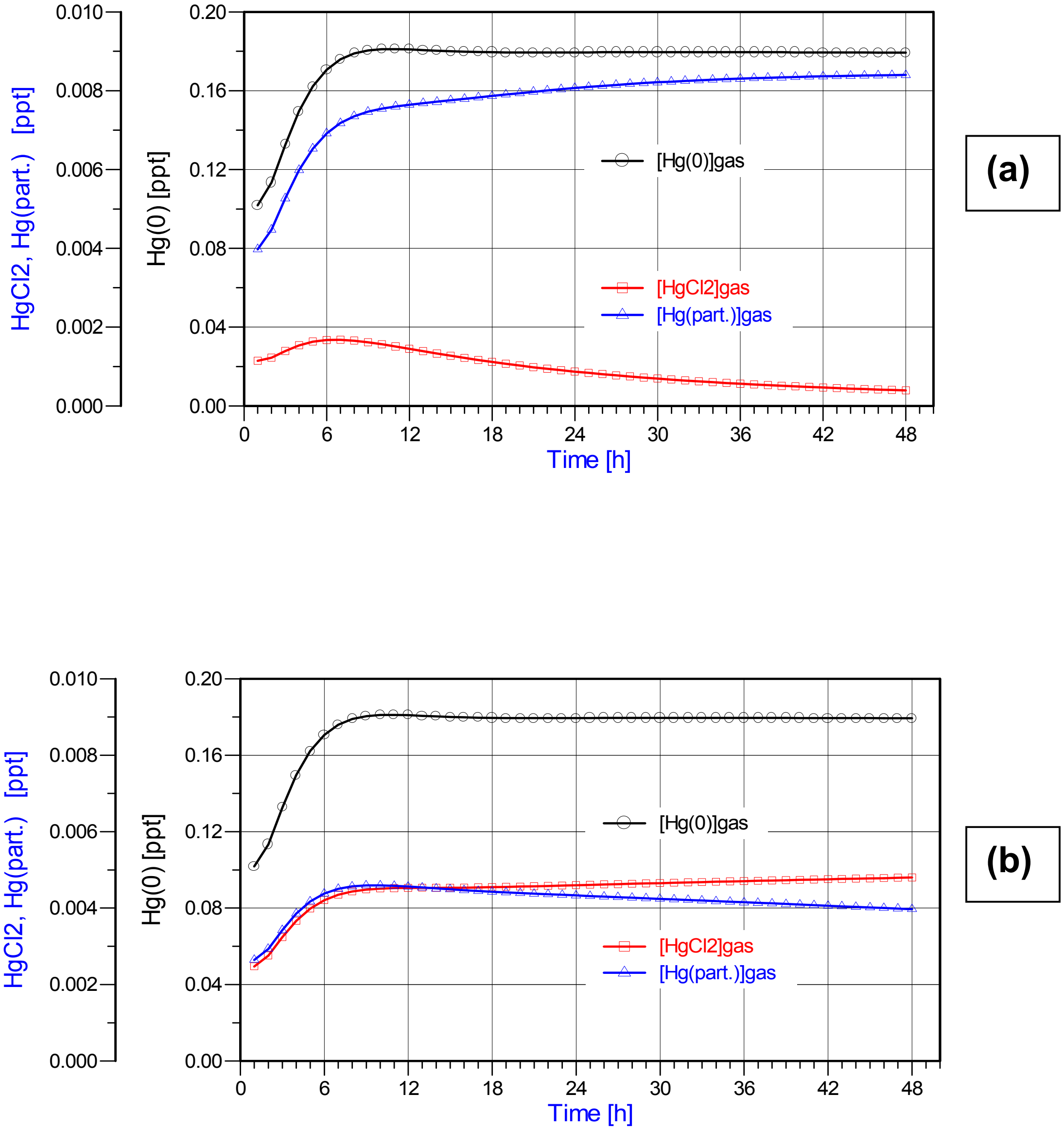

FIGURE 9. 48 hour time evolution of
(a) average gas phase concentration in the cloud area after aqueous phase chemistry (0.5 µg m^{-3} soot)
(b) average gas phase concentration in the cloud area after aqueous phase chemistry (no soot)

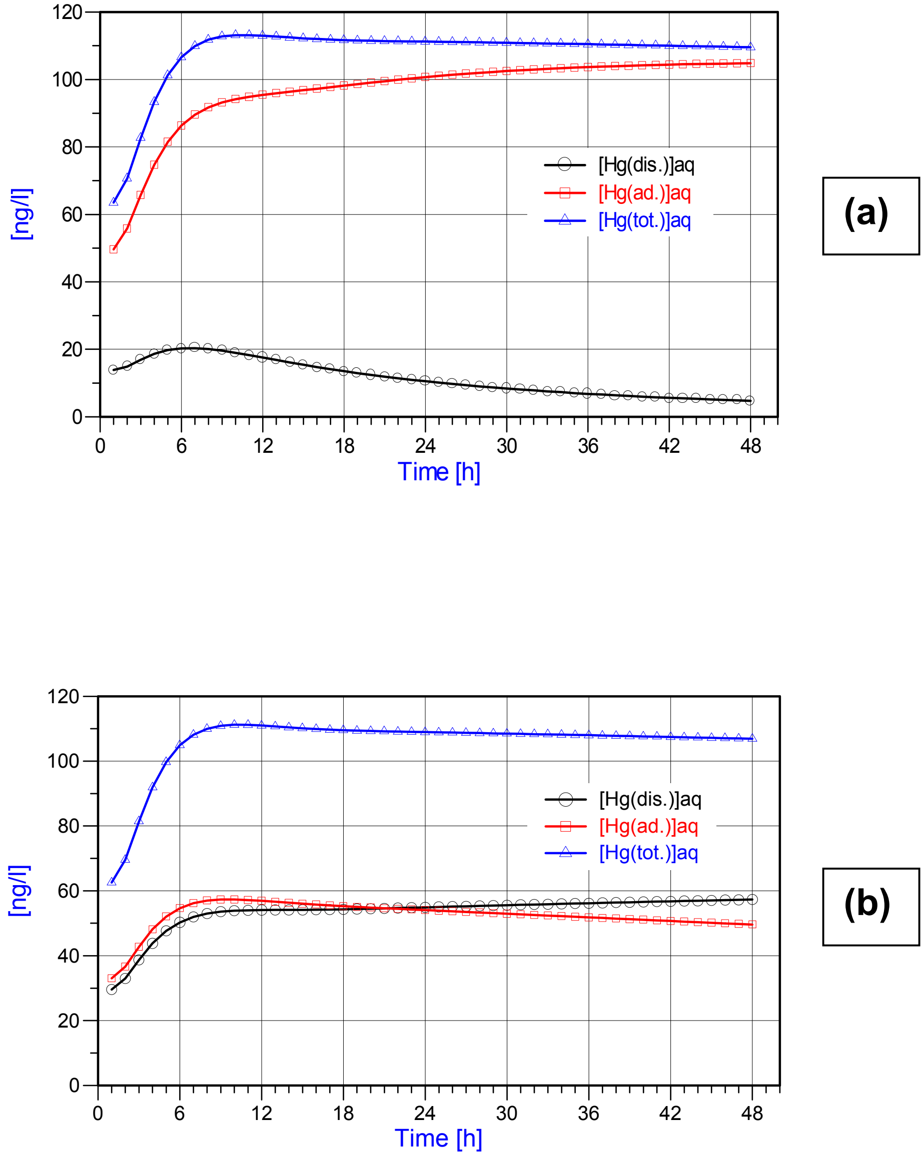

FIGURE 10. 48 hour time evolution of
(a) average aqueous phase concentration in the cloud area after aqueous phase chemistry (0.5 µg m^{-3} soot)
(b) average aqueous phase concentration in the cloud area after aqueous phase chemistry (no soot)

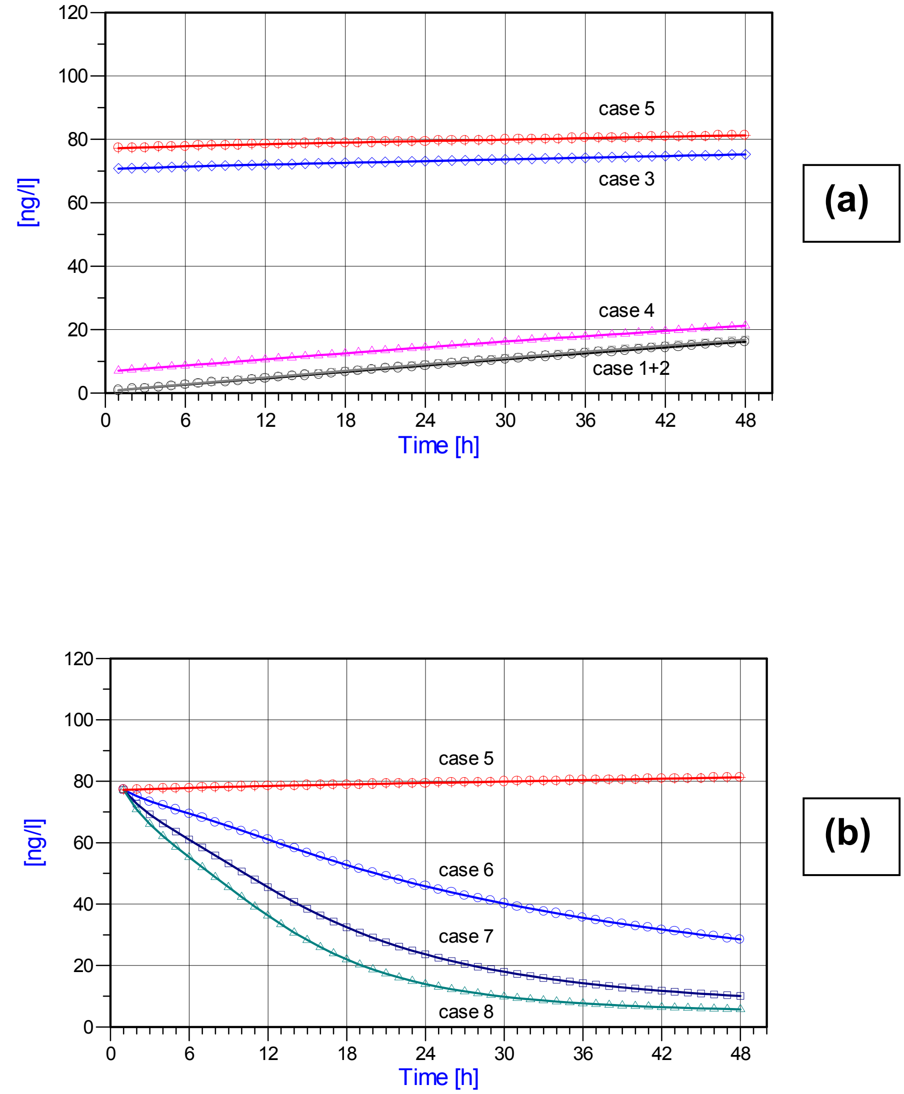

FIGURE 11. 48 hour time evolution of
(a) average aqueous phase concentration in the cloud area after aqueous phase chemistry for 5 cases defined in TABLE 2.
(b) average aqueous phase concentration in the cloud area after aqueous phase chemistry for 4 cases defined in TABLE 2.

4.3 Evaluation of model performance

Model evaluation is a key consideration when developing new and advanced comprehensive models. Since the ADOM for heavy metals, in particular the mercury version, was intended to be applied to simulations with policy implications, thorough validation and verification of the model and its components (such as the TCM discussed in the previous chapter) is a requirement. A model developed or utilized without continual comparison against actual data is less than worthless: it is dangerous. Such a model is nothing more than a collection of mathematical formulae, no matter how elegant its formulation or how efficient its coding. Only with the close integration of state-of-science models and state-of-science experimental measurements can real progress be made towards the solution of the complex problems that are currently faced, i. e. the continual interplay between conceptual understanding and experimental evidence.

4.3.1 Applications of the model to episodes of high mercury concentrations in Central Europe

High quality monitoring data for mercury air concentrations and deposition in Europe are still limited, although several recent investigations have improved the database [Ebinghaus et al., 1995, Lee et al., 1998; Munthe, 2001; Pirrone et al. 2000; Berg et al., 1996; Berg et al., 1997, Berg and Hjellbrekke, 1998; Schmolke et al., 1999]. Fortunately, a few studies of air concentrations measured simultaneously in Germany and in Sweden are available now for evaluation of model performance. These data, although restricted to four sites (FIGURE 12) and

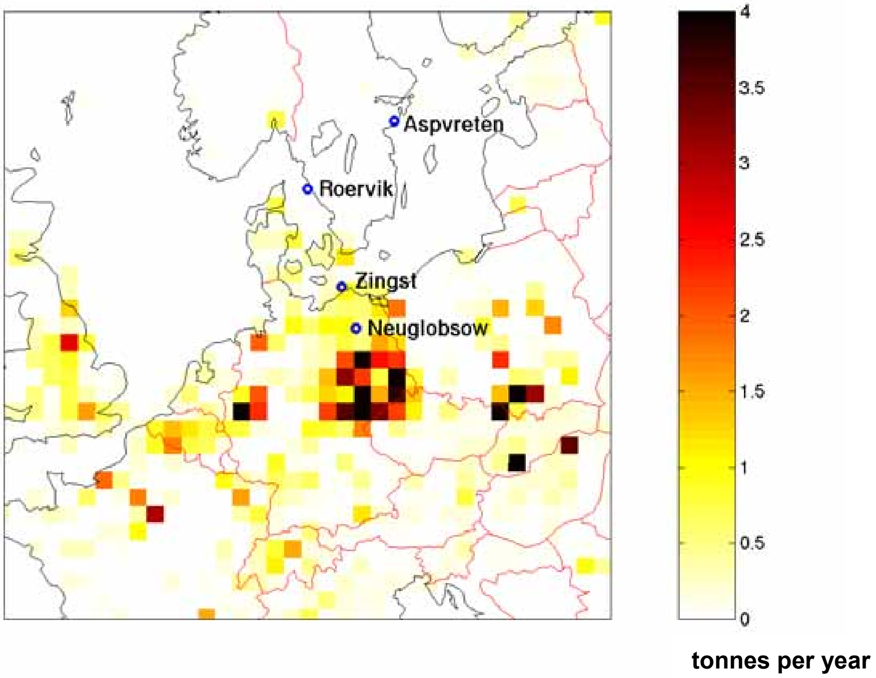

FIGURE 12. Location of sites involved in the evaluation of the model performance and mercury emissions in individual grid cells.

to a few 1-2 months measurement periods provide an opportunity for comparison with model predicted concentrations. A detailed description and a full documentation of the comparison of model results against observations is provided in [Schmolke and Petersen, 2002], and in the final report of the project "Mercury Species over Europe" funded by the EC [Munthe, 2001], respectively. This chapter is restricted to some illustrative examples concerning episodes of high mercury concentrations in Europe.

FIGURE 13 shows hourly averages (Neuglobsow, Zingst and Aspvreten) and three or one day averages (Roervik) of TGM observations together with model predicted hourly Hg^0 concentrations for November/December 1998. Measurements at Zingst cover the entire two months, whereas the other three sites are limited to a two weeks period of measurements. One should note the episodic nature of the observed and model predicted values at the two German sites spanning more than a threefold range of concentrations from 1.5 to approximately 5 ng m^{-3}. The lower end of the range is representative of hemispheric background concentrations of about 1.5 ng m^{-3} [Ebinghaus et al., 1995; Lee et al. 1998], whereas the concentrations at the upper end of the range are most probably due to long-range transport from anthropogenic sources in Central Europe. Of particular interest are November 25 and December 4-5 of 1998 when the model predictions show coinciding peaks at all four sites ranging from about 2.5 to 5.5 ng m^{-3}. Observed levels are on a similar elevated level, except Aspvreten on November 25. This day has been examined with reference to 72 hours back trajectories, which have been derived from the horizontal wind field at the third ADOM vertical level at approximately 250 meters height. These trajectories describe the route taken during the previous three days by the air masses arriving at the four sites (FIGURE 14). Originating in Romania and the Ukraine air masses move along the trajectories into the main emission areas in southern Poland and eastern Germany, where they change their directions and move northwards arriving at the four sites. The good agreement between observed and model predicted peak concentrations during episodes when trajectories exhibit the above described travel pattern is an indication that the model has capabilities to simulate atmospheric transport over distances of several hundred kilometers and that the emission inventory used with the model is based on realistic emission estimates for central Europe in 1998.

Another example for coinciding peaks of observed and model predicted mercury concentrations is depicted in FIGURE 15. The elevated levels during March 26 of 1997 are quite well reproduced by the model at all 4 sites. Maximum concentrations have been observed and calculated around noon of March 26 at Neuglobsow, Zingst and Roervik with second smaller peaks predicted by the model (and observed at Neuglobsow and Roervik as well) in the evening. The Aspvreten maximum is occurring a couple of hours later and the slight evening peak is missing at this site. These phenomena are supported by the routes of the trajectories on March 26 (FIGURE 16): During the first half of the day air masses start over Poland and adjacent areas, traverse East Germany picking up high emission rates and eventually arrive at the four sites. In the afternoon trajectories arriving at all sites except Aspvreten are changing their routes significantly: They originate over the Western Atlantic and subsequently pass over emission areas in Britain and West Germany. Evidently, the routes of these trajectories cause the smaller concentration peaks mentioned above.

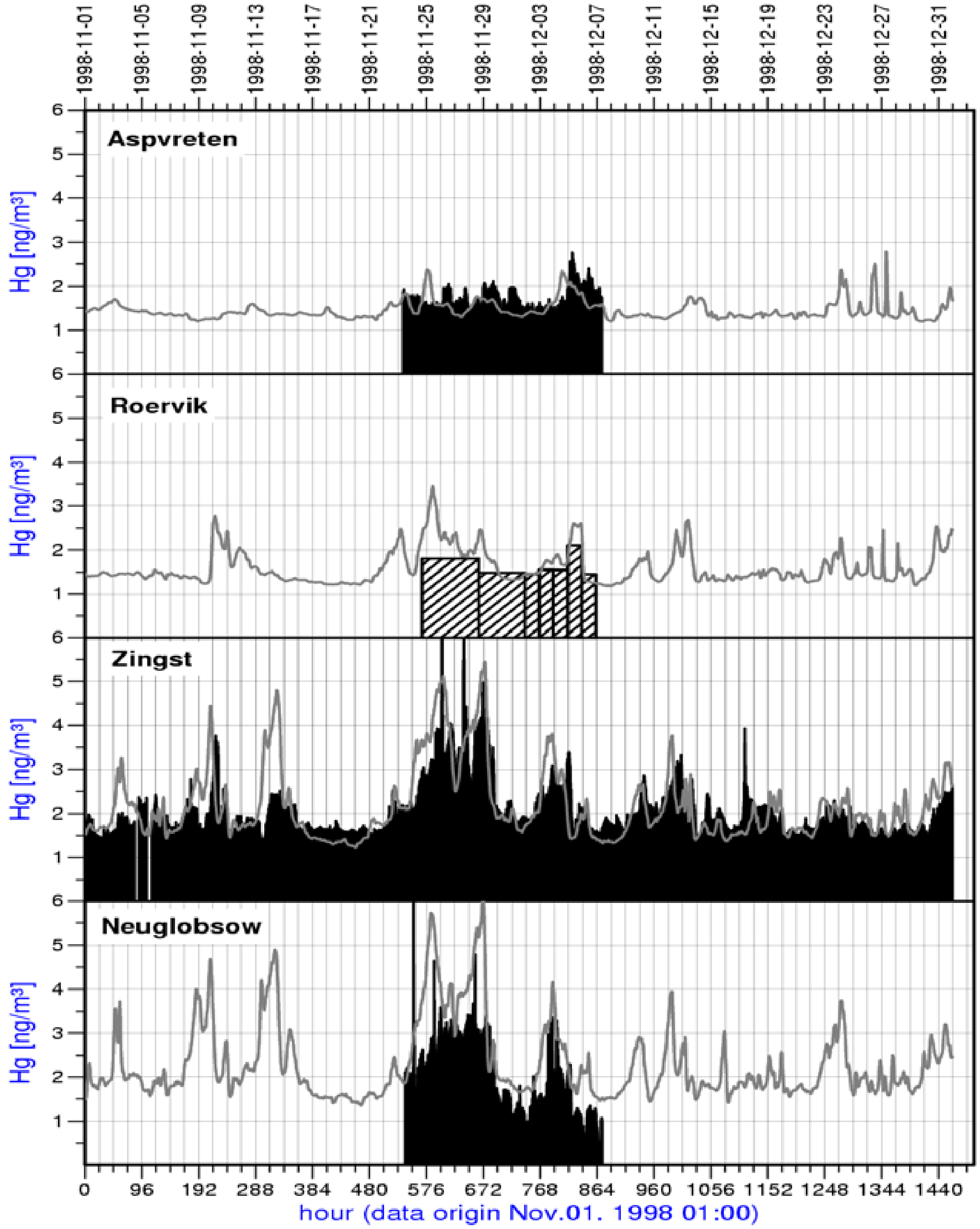

FIGURE 13: Time series of hourly averages of observed TGM concentrations (black area) and model predicted Hg^0 concentrations in air (grey line) at two Swedish sites (Aspvreten, Roervik) and two German sites (Zingst, Neuglobsow), November/December 1998.
(The observations at Roervik are daily and multi-day averages)

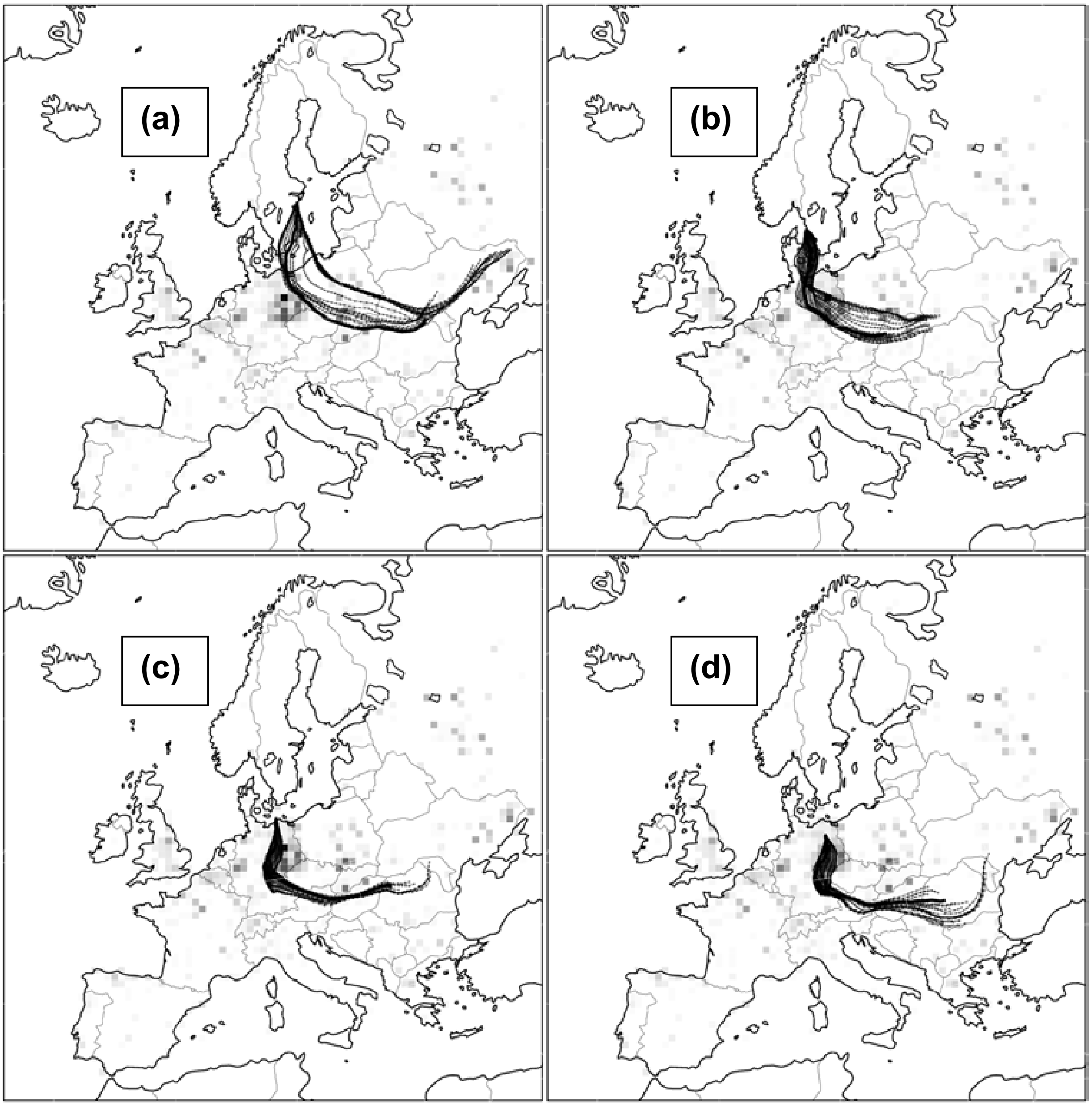

FIGURE 14: 72 hours backward trajectories November 25, 1998 for
(a) Aspvreten
(b) Roervik
(c) Zingst
(d) Neuglobsow

4.3.2 Applications of the model to episodes of low mercury concentrations in Northern Europe

In terms of comparing measurements made at the two Swedish sites with model output there is evidence that the model has a tendency to underestimate observations probably due to missing natural and re-emission processes in the model at present. Both observed and model predicted time series are characterized by low temporal variability except the high concentration episode described in the previous section and except some low concentration episodes typically occurring over a time period of 12 hours or less.

Of particular interest in FIGURE 15 are the four events of observed low concentration at the northern most site Aspvreten on 22, 23, 24 and 28 of March 1997, which are not reproduced by the model. The trajectories in FIGURE 17 are either originating from Finland and Northern Russia or they are pointing towards ice-covered regions of the Arctic Ocean as a potential source of mercury depleted air masses during that time of the year. Indeed, mercury depletion phenomenon have been observed during the three months period following polar sunrise in March [Schroeder et al., 1998; Schroeder and Barrie, 1998, Lu et al., 2001] and the observed episodic minimum concentrations in the Aspvreten time series may be an indication for transport of air masses from polar regions. However, the database is too scarce to draw any firm conclusions and more work in terms of using a model approach that can take into account the global cycling of mercury is required to identify this phenomenon with more confidence [Seigneur et al., 2001]. Because of the coarse resolution necessarily used in global simulations, such simulations cannot be used to assess the mercury deposition fluxes in specific regions such as the Baltic Sea which are discussed in the next chapter. On the other hand, these regional simulations must rely on boundary conditions that may influence the model results. It is necessary therefore to develop a multiscale modelling approach, that consists of the existing regional scale ADOM model for mercury and a global chemical transport model, which provides the time dependent boundary concentrations for the ADOM model.

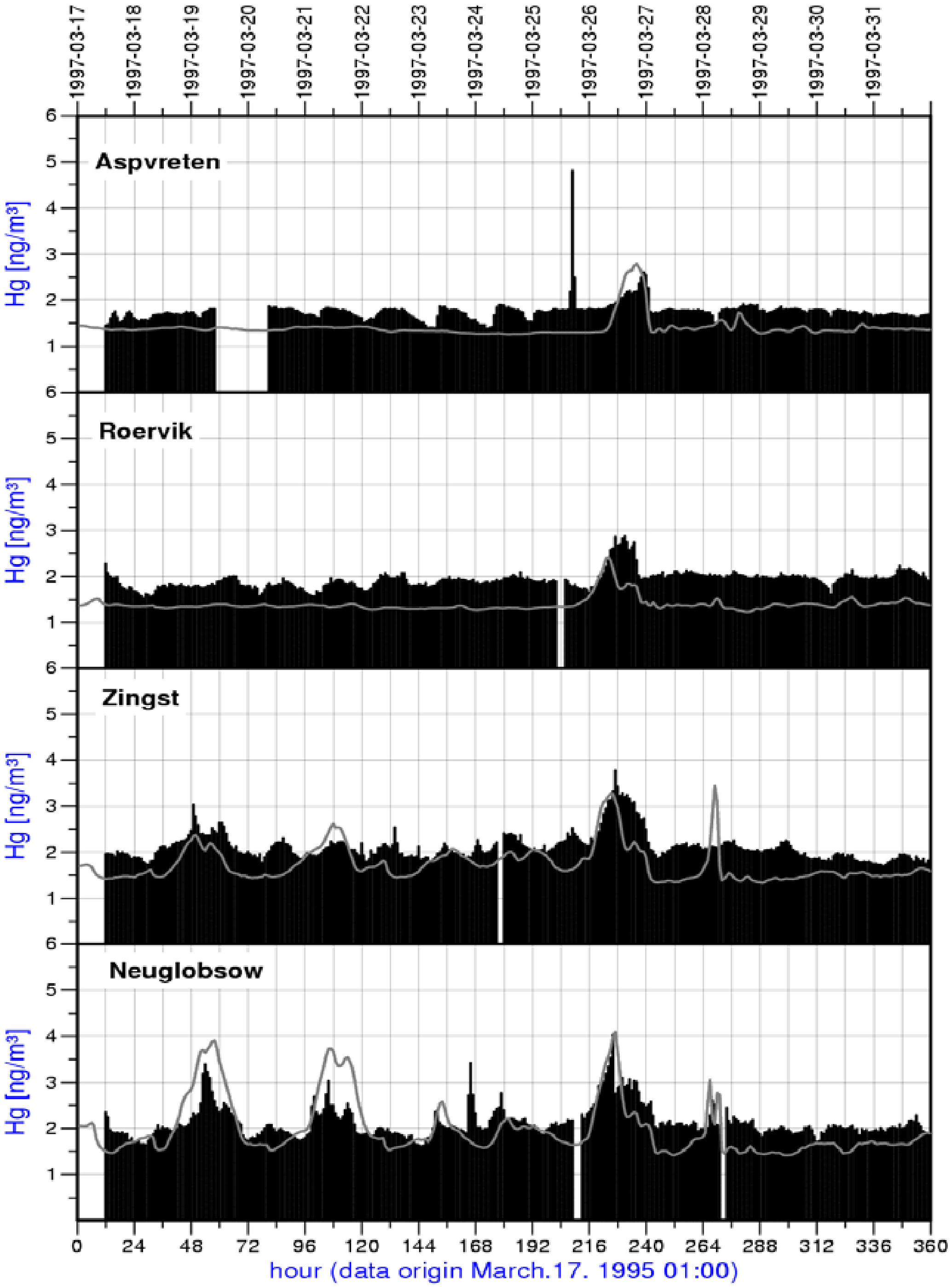

FIGURE 15: Time series of hourly averages of observed TGM concentrations (black area) and model predicted Hg^0 concentrations in air (grey line) at two Swedish sites (Aspvreten, Roervik) and two German sites (Zingst, Neuglobsow), March, 1997.

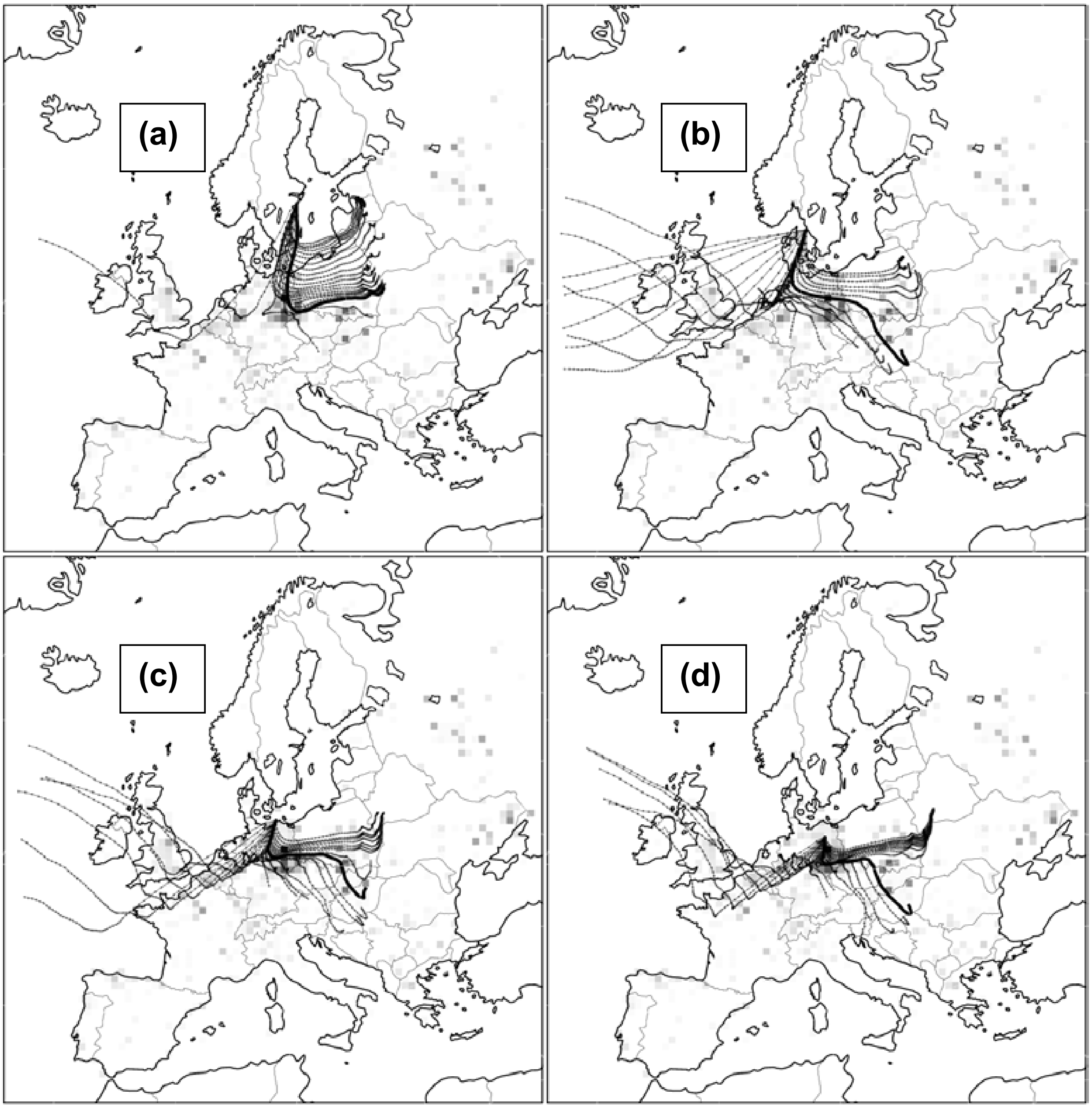

FIGURE 16: 72 hours backward trajectories March 26, 1997 for
(a) Aspvreten
(b) Roervik
(c) Zingst
(d) Neuglobsow

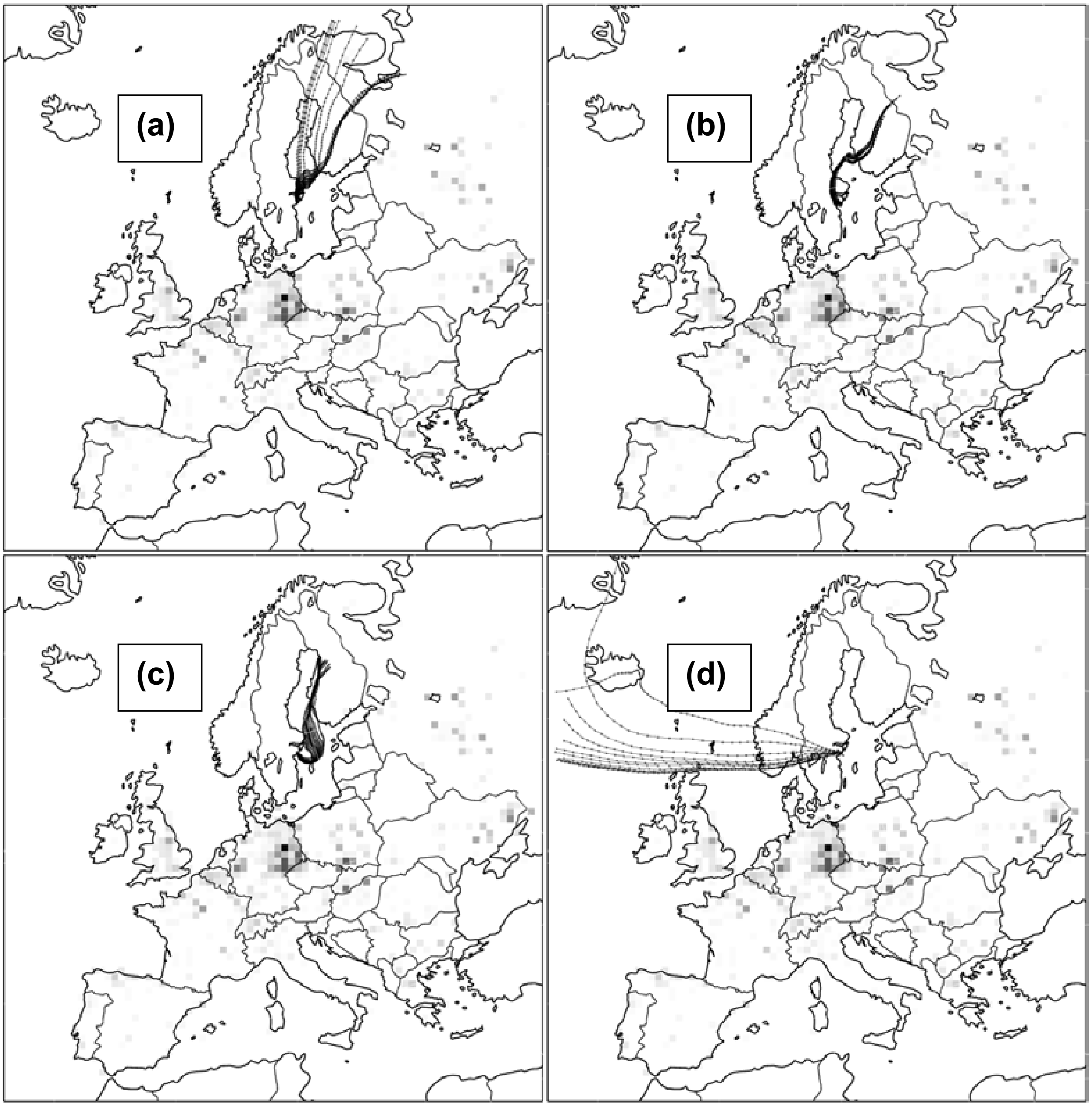

FIGURE 17: 72 hours backward trajectories Aspvreten
(a) March 22 1997
(b) March 23 1997
(c) March 24 1997
(d) March 28 1997

4.4 Atmospheric Input of Heavy Metals to the Baltic Sea

Concern over the quality of marine waters and biota has highlighted the numerous geochemical pathways for the transfer of terrestrial and anthropogenically derived heavy metals from their sources to the marine environment. Traditionally these pathways have been assumed to be riverine, but there is much evidence that atmospheric inputs contribute significantly to marine areas [Duce et al., 1991] and may be comparable to those of riverine inputs for the Baltic Sea as an almost totally enclosed water body [HELCOM, 1996; HELCOM, 1998].

Despite the fact that the metals in question exist almost solely in particulate form (with the exception of mercury) there are still massive problems in making reliable estimates of atmospheric input. These problems include uncertainties in both wet and dry deposition flux contributions to the overall atmospheric input due substantially to inadequate knowledge of pollutant concentration fields over the sea area, together with a poorly defined precipitation field, and in quantification of the dry deposition velocity for particulate material to the sea surface.

Estimates of atmospheric input of heavy metals to the Baltic Sea are either based on extrapolations from measurements made on the edges of the surrounding landmasses or on applications of numerical simulation models. Most recent results for lead and cadmium achieved in the framework of the EU MAST III Baltic Sea System Study (BASYS) do suggest that the atmospheric input for both metals has significantly decreased during the past 10-15 years but that the atmospheric input still exceeds the riverine input by about 50% [**VI**]. Compared to extrapolated measurements model results show a tendency for underprediction of annual inputs, which may be due to inaccurate emission data bases used with the model calculations [**VII**].

Recent progress in understanding physico-chemical processes of atmospheric mercury and the availability of European emission data bases for different mercury species has permitted to investigate mercury input to the Baltic Sea by means of the comprehensive Eulerian model ADOM described in the previous chapters. Model runs were performed for two episodes i.e. for a BASYS summer network study during June-August 1997 and for a winter network study during February-March 1998. Typical results in terms of monthly average concentrations and deposition fluxes inside and around the Baltic Sea receptor area used with the model are depicted in FIGURE 18. The area within the irregular frame consists of grid cells which cover the Baltic Sea and for which sea area weighted average concentrations and deposition fluxes have been calculated for two scenarios:

1. Using the UBA-TNO inventory for anthropogenic mercury emissions in Europe compiled for the reference year 1990 [Berdowski et al., 1997].

2. Cutting off the European anthropogenic emissions and calculating deposition fluxes to the Baltic Sea caused by global mercury background concentrations by using a typical European background concentration of 1.5 ng m^{-3} for Hg^0 as a boundary condition for the model runs.

TABLE 3 and 4 summarize the results in terms of deposition fluxes of individual mercury species and the total input rates for both episodes and both scenarios. Deposition fluxes and hence input rates to the Baltic Sea are higher in winter due to more intense transport from the main emission areas and from the western inflow boundary of the model domain as well as lower mixing layer

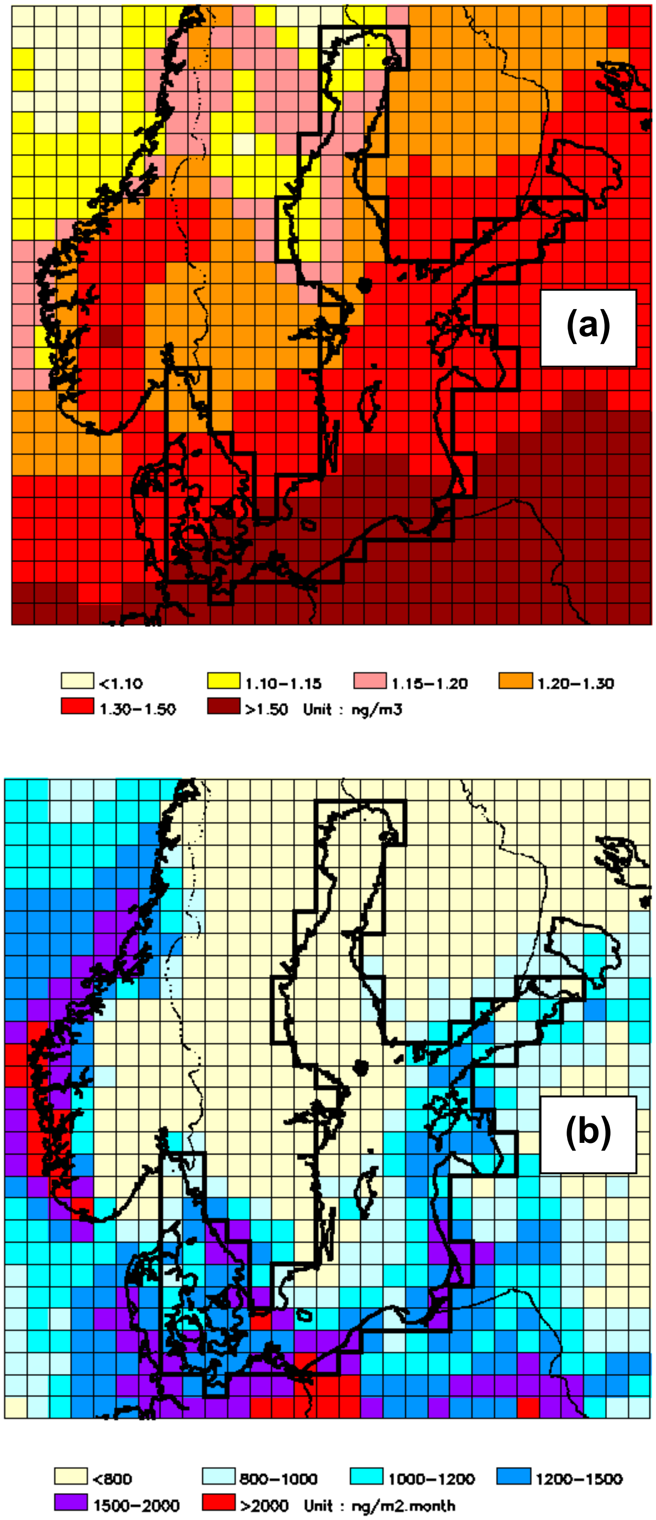

FIGURE 18. Model predicted
(a) monthly average concentrations of elemental mercury (Hg^0) in air
(b) monthly total deposition flux (dry + wet) of mercury.
Baltic Sea-February 1998

TABLE 3. Model predicted deposition fluxes of mercury species to the Baltic Sea.

Daily dry and wet deposition fluxes with anthropogenic emissions in Europe

	summer network study 1997		winter network study 1998	
	ng m^{-2} d^{-1}	kg d^{-1}	ng m^{-2} d^{-1}	kg d^{-1}
dry Hg^0	0.00	0.00	0.00	0.00
dry $HgCl_2$	1.16	0.48	1.05	0.43
dry Hg(part.)	1.78	0.74	0.41	0.17
dry HgO	1.82	0.76	1.39	0.58
dry total	4.76	1.98	2.85	1.18
wet Hg (diss.)	4.24	1.76	7.05	2.92
wet Hg (part.)	7.82	3.24	15.80	6.54
wet total	12.06	5.00	22.85	9.46
dry + wet total	16.82	6.98	25.70	10.64

Daily dry and wet deposition fluxes without anthropogenic emissions in Europe
(contribution from global background)

	summer network study 1997		winter network study 1998	
	ng m^{-2} d^{-1}	kg d^{-1}	ng m^{-2} d^{-1}	kg d^{-1}
dry Hg^0	0.00	0.00	0.00	0.00
dry $HgCl_2$	0.07	0.03	0.00	0.00
dry Hg(part.)	0.10	0.04	0.36	0.15
dry HgO	1.07	0.44	0.90	0.37
dry total	1.24	0.51	1.26	0.52
wet Hg (diss.)	1.85	0.77	3.45	1.43
wet Hg (part.)	4.61	1.91	5.13	2.13
wet total	6.46	2.68	8.58	3.56
dry + wet total	7.60	3.19	9.84	4.08

TABLE 4. Model predicted atmospheric input rates of mercury to the Baltic Sea.

Monthly and annual input rates with anthropogenic emissions in Europe

	summer network study 1997	winter network study 1998
extrapolated monthly input rates	212 kg / month	324 kg / month
extrapolated annual input rate (average of 1997 and 1998)	**3216 kg / year**	

Monthly and annual input rates without anthropogenic emissions in Europe (contribution from global background)

	summer network study 1997	winter network study 1998
extrapolated monthly input rates	97 kg / month (46%)	124 kg / month (38%)
extrapolated annual input rate (average of 1997 and 1998)	**1326 kg / year (41%)**	

heights and more precipitation. In all cases wet deposition is the main contributor to to the total input. The reason for the relatively low dry deposition is twofold: Firstly, there is no experimental evidence for dry deposition of Hg^0 over sea surfaces and is hence assumed to be zero in the model and secondly, the dry deposition of the other species is minor over the sea, because they are already effectively dry deposited over land close to the land-based sources of those species.

An interesting feature in TABLE 4 is the relative high contribution from global mercury background concentrations to the total input to the Baltic Sea in the range of 38-46%. Conversely, current anthropogenic emissions in Europe only account for about 60% of atmospheric mercury load of the Baltic Sea with a decreasing portion towards the northern parts of that sea area, since the density of anthropogenic emissions is greater around the southern Baltic Sea. This indicates that emission reductions of land-based mercury sources in Europe, which is the main target of the UN-ECE CLRTAP Convention and HELCOM, would only have a

TABLE 5: Estimates of annual atmospheric mercury input rates to the Baltic Sea.

annual input rate [tonnes per year]	**reference year(s)**	**method**	**reference**
6	1980	extrapolation from observations at coastal sites	GESAMP, 1989
11.3	1980	extrapolation from observations at coastal sites	Lithner et al., 1990
6-13	1987-1988	model calculation	Petersen et al., 1995 [**I**]
5.5	1994-1996	model calculation	Bartnicki et al., 1998
5	1997-1998	model calculation	Ilyin et al., 2000
3.2	1997-1998	model calculation	this study

limited effect on the atmospheric load of the Baltic Sea particularly its the northern parts. Knowledge of global or at least hemispherical emissions and their effects on boundary conditions (i. e. upwind time dependent vertical concentration profiles) is of similar importance. Since measurements, particularly aloft, are scarce, uncertainties are believed to be associated with the boundary conditions mentioned above and a multiscale modelling approach consisting of a global and a continental scale model is needed to reduce those uncertainties.

In TABLE 5 estimates of integrated mercury loading to the Baltic Sea from other investigators are compared with results from this study. Overall, annual input rates span more than a fourfold range from about 3 to 13 tonnes per year most probably due to uncertainties in the estimated input rates and to changes in European mercury emissions during the last two decades. The discrepancy in the two 1980 estimates based on extrapolated measurements at coastal sites is rather large and may be attributed to both uncertainties in the quality of measurement data at that time and to insufficient extrapolation methods. The model predicted results in TABLE 5 show some evidence of decreasing inputs after the political changes of the 1990s in Central and Eastern Europe, which brought a sharp decline of industrial activities, followed by significant restructuring of the economy and industry. The resulting mercury emission reductions from 730 tonnes per year in the late 80s [Axenfeld et al., 1991] to 460 tonnes per year in the early 90s [Berdowski et al., 1997] are clearly reflected in the corresponding input rates of Petersen et al., 1995 and of this study. The relative wide range of the 1987-1988 estimate was caused by a certain range of speciation percentages of emissions, which had to be assumed in the model since knowledge of mercury speciation was more limited at that time. The results from model simulations performed by Bartnicki et al., 1998, and by Ilyin et al., 2001, are similar, which is not surprising since they are based on the same model approach. Comparing these results with the result of this study, the difference is rather large and requires resolution. The anthropogenic emission inventory and the chemistry schemes used in the models is either identical or very similar and cannot account for the differences. However, the different results are explicable by the treatment of natural emissions and reemissions, which are implemented into the model approach of Bartnicki and Ilyin in a simple and uncertain way. In this study, these processes are not incorporated in the current version of the model since surface/atmosphere exchange terms for mercury over land and seawater are not well characterized for Central and Northern Europe and this requires more work so that models can be parameterized with more confidence.

5. SUMMARY AND CONCLUSIONS

The main objective of activities described in this work was to develop and test numerical simulation models with capabilities to quantify atmospheric transboundary fluxes of heavy metals over Europe in order to provide scientific support for European environmental protection conventions by either

- applying models to assess long-range transport of heavy metals over Europe with subsequent deposition into aquatic and terrestrial ecosystems

or

- transferring advanced models or parts of them to institutions directly involved in the scientific work of the conventions (e.g. the EMEP Meteorological Synthesizing Centers in the framework of the UN-ECE Protocol on Heavy Metals and the Arctic Monitoring and Assessment Programme AMAP) for direct use or for implementation into their existing operational models.

Examples for both model applications and model transfers discussed in the previous chapters and in some of the ten annex papers are:

- Lagrangian model applications for the European marine environment protection conventions OSPAR (North Sea, North East Atlantic) and HELCOM (Baltic Sea) to assess the atmospheric input of mercury [Petersen, 1992b] and of lead, cadmium zinc and arsenic [Petersen and Krueger, 1993] into the Convention Waters.

- Lagrangian model applications for the Scientific Council "Global Environmental Changes" of the German Federal Government to calculate concentration and deposition patterns of acidifying pollutants and heavy metals over Europe [Krueger and Petersen, 1993].

- Eulerian model applications for the EU E&C and ELOISE Study MOE to calculate concentration and deposition patterns of mercury species over Europe [Munthe, 2001, **III, VIII**].

- Eulerian model applications for the EU MAST III Regional Seas Study BASYS to simulate atmospheric deposition fluxes of lead, cadmium and zinc into the Baltic Sea ecosystem by one-way nesting with the mesoscale model HILATAR of the Finnish Meteorological Institute (FMI) [**VII**] and by comparing model results with measurement based estimates of the Baltic Sea Research Institute Warnemünde (IOW) **[VI]**.

- Selection of the mercury version of the Eulerian model as one of the reference models in the upcoming EU Air Quality Directive for mercury [European Commission, 2001].

- Transfer of relative simple mercury chemistry schemes adequate for Lagrangian models to the US-EPA [Bullock et al., 1997] and AMAP [Bartnicki et al., 1998]

- Transfer of complex state-of-science mercury chemistry schemes adequate for comprehensive Eulerian models to the EMEP MSC-E for use in their operational model [Ryaboshapko et al., 1999], the Meteorological Service of Canada [MSC] for use in their global mercury model [Dastoor and Larocque, 2002] and the Danish National Environmental Research Institute (NERI) for their mercury model of the Northern hemisphere [Christensen, 2001].

- Participation into international model intercomparison studies for lead [Sofiev et al., 1996], cadmium [Gusev et al., 1998] and mercury [Ryaboshapko et al., 2001] initiated by the UN-ECE Convention and organised by the EMEP Meteorological Synthesizing Centre East.

These model developments and applications comprise both relatively simple Lagrangian and comprehensive Eulerian approaches with an established record of published investigations, which are either listed in the annex or mentioned in the reference list. This study is focusing on the most recent heavy metals version of the Eulerian model system ADOM with the Tropospheric Chemistry Module (TCM) as its major component, which is considered to be a state-of-the-science model over the past several years. The evaluation of the model performance led to four main issues provided below:

1. In general, the model system has capabilities to describe the atmospheric pathways of transport, transformations and deposition of heavy metals from their way from emissions to deposition over spatial scales from about hundred kilometer to continental with a basic time step of one hour. These capabilities can be used (and are used now) for making future predictions of heavy metals deposition patterns as well as for optimizing control measures and for estimating how a specific region is affected by heavy metals emissions in other areas.

2. Sensitivity studies conducted with the Tropospheric Chemistry Module (TCM) allowed for gaining scientific insights into mercury transport, chemical transformations and deposition processes which cannot be obtained through field measurements or experiments in the laboratory. TCM predictions of mercury concentrations in rainwater compare satisfactorily with observations thus indicating that the TCM is based on an adequate parameterization of atmospheric mercury processes.

3. Modelled hourly average concentrations of elemental mercury in air were shown to compare satisfactorily with observations from stations in Germany and Sweden. Coinciding peaks of observed and calculated concentrations at the two German stations indicate, that the emission data base used with the model calculations is based on realistic estimates of emission peaks in the main source areas of Central Europe. However, the model tends to underestimate observations at the two Swedish stations, most probably due to exclusions of processes e.g. air-soil and air-water exchange that may influence the atmospheric concentration level of mercury. These processes have not been explicitly treated in the model due to significant gaps in our current understanding and knowledge.

4. Results from measurements and model simulations to quantify the cumulative deposition of heavy metals to the Baltic Sea do suggest that the atmospheric input has significantly decreased during the last 10-15 years, but the atmosphere is still the dominating pathway for the heavy metals loading of the Baltic Sea. Model simulations for mercury performed in this study show a contribution from global background concentrations in the order of 40% of the total atmospheric input. This indicates that emission reductions in Europe would only have a limited effect on the reduction of the total mercury load of the Baltic Sea, and global scale models are clearly needed to quantify the contribution from global background concentrations

more accurately. The results from this study are believed to be the best estimates currently available when only emissions from European land based sources are taken into account but as already indicated above, contributions from natural emissions and re-emissions are still missing and have to be implemented into the model when better knowledge on these processes becomes available.

Overall, the present development level of the ADOM model for heavy metals is such, that it can provide key information needed to quantify the relationship between anthropogenic emissions and deposition fluxes of heavy metals to remote ecosystems and that its application within environmental protection conventions mentioned above is fully justified. The model will be extended and developed further according to advancements in the knowledge of atmospheric processes of heavy metals and persistent organic pollutants (POPs) to ensure that it maintains its capabilities to address effectively the scientific and political questions that may arise over the next decade. Some suggestions for model improvements and extensions are provided below, but certainly not limited to:

- Emission data bases: Emissions are always a potential source of uncertainty in the modelling of atmospheric pollution, but in case of mercury the uncertainties in the total amount and spatial and temporal distribution of emissions are further complicated by the importance of mercury speciation that arises from the vastly different removal rates for the principal emitted species Hg^0, $HgCl_2$ and Hg(part.). Because $HgCl_2$ and Hg(part.) are deposited so efficiently, knowledge of the effective emission heights of these species is also important, as the dry deposition pattern for a surface source is greater in magnitude and shorter in distance than that of an elevated source, which may be decoupled from surface removal processes during stable nocturnal conditions.

- Up and downscale links to global scale models: New links with other areas of modelling, including scale and media, are envisioned. It is planned that information from ADOM applications and from global and hemispheric modelling applications will be bridged. Because ADOM and in particular the mercury version offers the state of science to simulate atmospheric processes of mercury species as realistic as possible, ADOM output can be used to benchmark or examine the parametric basis of process formulation in global and hemispheric models. From a downscale perspective, global model output can be used to improve or enhance the initial and boundary concentrations in ADOM simulations.

- Ecosystem modelling: Efforts to combine environmental modelling techniques to encompass an entire ecosystem is needed to address heavy metals and POPs cycle modelling, which includes pathways through the atmosphere, water bodies and soil. With this ecosystem approach, air quality issues can be studied in combination with other aspects of environmental health such as adverse indirect human exposure from bioaccumulation through the food chain.

Maintaining the extended model system to use emerging computing capabilities and transferring that capabilities to the scientific community and environmental decision makers will continue to be the focus of the efforts described in this study.

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8. LIST OF SYMBOLS, UNITS AND ACRONYMS

ADOM	Acid Deposition and Oxidants Model
AER	Atmospheric and Environmental Research Inc., San Ramon, CA, U.S.A.
AMAP	Arctic Monitoring and Assessment Programme
BASYS	Baltic Sea System Study
BAT	Best Available Technology
CAM	Chemistry of Atmospheric Mercury
CCC	Chemical Co-ordinating Centre of EMEP
CMAQ	Community Multi-Scale Air Quality Model
CMC	Canadian Meteorological Center
CIAM	Centre for Integrated Assessment Modelling of EMEP
DNMI	Det Norske Meteorologiske Institutt (The Norwegian Meteorological Institute)
EC	European Commission
E&C	Environment and Climate
ECE	Economic Commission for Europe
EEM	EURAD Emission Model
ELOISE	European Land Ocean Interaction Studies
EMEFS	Eulerian Model Evaluation and Field Study
EMEP	Co-operative Programme for Monitoring and Evaluation of the long-range Transmission of Air Pollutants in Europe
EPRI	Electric Power Research Institute
ERT	Environmental Research and Technlogy
EU	European Union
EURAD	European Air Pollution Dispersion Model System

EUROTRAC	The Eureka Project on the Transport and Chemical Transformation of Environmentally Relevant Trace Constituents in th Troposphere over Europe
FAO	Food and Agricultural Organisation
FMI	Finnish Meteorological Institur
GASPAR	Gas-Particle Partitioning Model
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Pollution
GLWQA	U.S./Canada Great Lakes Water Quality Agreement
HELCOM	Baltic Marine Environment Protection Commission (Helsinki Commission)
Hg^0	elemental mercury
$HgCl_2$	mercury chloride
Hg(part.)	mercury associated with particles
HgO	mercury oxide
$Hg(dis.)_{aq}$	dissolved mercury species in the aqueous phase
$Hg(ads.)_{aq}$	mercury species in the aqueous phase adsorbed on particles
$Hg(tot.)_{aq}$	total mercury species in the aqueous phase ($Hg(dis.)_{aq}$+ $Hg(ads.)_{aq}$)
HILATAR	High Resolution Limited Area Transport And Removal Model
HIRLAM	High Resolution Limited Area Weather Prediction Model
HMET	Heavy Metals Model
IAEA	International Atomic Energy Organisation
IGAC	International Global Atmospheric Chemistry
IOW	Institut für Ostseeforschung Warnemünde
IVL	Institutet för Vatten- och Luftvardsforskning (Swedish Environmental Research Institute)
LRTAP	Long Range Transboundary Air Pollution
MAMCS	Mediterranean Atmospheric Mercury Cycling Study

MAST	Marine Science and Technology
MeHg	methyl mercury
MEPOP	Mercury and Persistent Organic Pollutants (EUROTRAC-2 subproject)
MSC	Meteorological Service of Canada
MSC-E	Meteorological Synthesizing Centre-East of EMEP
MSC-W	Meteorological Synthesizing Centre-West of EMEP
NERI	National Environmental Research Institute (Denmark)
NILU	Norsk Institutt for Luftforskning (Norwegian Institute for Air Research).
NMR	Nordisk Minister Rat
NTIS	National Technical Information Service
OSPAR	The Convention for the Protection of the Marine Environment of the North-East Atlantic (Oslo-Paris-Commission)
$PM_{2.5}$	Particulate matter less than 2.5 µm in diameter
PM_{10}	Particulate matter less than 10 µm in diameter
POPs	Persistent organic pollutants
RADM	Regional Acid Deposition Model
RELMAP	Regional Lagrangian Model of Air Pollution
RGM	Reactive Gaseous Mercury
SOMS	Simplified Ozone Modelling System
TADAP	Transport and Deposition of Acidifying Pollutants
TCM	Tropospheric Chemistry Module
TGM	Total Gaseous Mercury
TNO	Togepasste Naturwetenschapplike Ondersuchtungen (The Netherlands Institute for Applied Research
UBA	Umweltbundesamt (German Federal Environmental Agency)

UN-ECE	United Nations - Economic Commission for Europe
US-EPA	United States Environmental Protection Agency
WMO	World Meteorological Organisation

9. LIST OF FIGURES

FIGURE 13. time series of hourly averages of observed TGM concentrations (black area) and model predicted Hg^0 concentrations (grey line) in air at two Swedish sites (Aspvreten, Roervik) and two German sites (Zingst, Neuglobsow).
November/December, 1998
(The observations at Roervik are multi-day and daily averages)

FIGURE 14. 72 hours backward trajectories November 25, 1998 for
(a) Aspvreten
(b) Roervik
(c) Zingst
(d) Neuglobsow

FIGURE 15. Time series of hourly averages of observed TGM concentrations (black area) and model predicted Hg^0 concentrations (grey line) in air at two Swedish sites (Aspvreten, Roervik) and two German sites (Zingst, Neuglobsow).
March, 1997.

FIGURE 16. 72 hours backward trajectories March 26, 1997 for
(a) Aspvreten
(b) Roervik
(c) Zingst
(d) Neuglobsow

FIGURE 17. 72 hours backward trajectories Aspvreten
(a) Aspvreten
(b) Roervik
(c) Zingst
(d) Neuglobsow

FIGURE 18. Model predicted
(a) Monthly average concentrations of elemental mercury (Hg^0) in air
(b) Monthly total deposition flux (dry+wet) of mercury
Baltic Sea-February 1998.

10. LIST OF TABLES

APPENDIX

This study is based on the following ten papers presented in chronological order of their publication and referred to by bold Roman numerals in the text.

Paper I

Paper II

Paper III

Paper IV

Paper V

Paper VI

Paper VII

Paper VIII

Paper IX