

CHAPTER-3. MODELLING THE CYCLE OF ATMOSPHERIC MERCURY

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3.1 INTRODUCTION

It is well known that since the industrial revolution, due to its unique physico-chemical properties (i.e., high specific gravity, low electrical resistance, constant volume of expansion), mercury has been employed in a wide variety of applications (i.e., manufacturing, dentistry, metallurgy). As a result of its use the amount of mercury mobilised and released into the atmosphere has increased compared to the pre-industrial levels. Several advances in theoretical and experimental techniques have been made in recent years to assess spatial and temporal distributions of ambient concentrations and deposition fluxes of mercury and its compounds in Europe. Temporal and spatial scales of mercury transport in the European atmosphere and its transfer to aquatic and terrestrial receptors were found to depend primarily on the chemical and physical characteristics of the three main forms of atmospheric mercury (Munthe, 1992; Petersen, *et al.*, 1998; Pirrone *et al.*, 2000; Petersen *et al.* 2001; Hedgecock and Pirrone, 2001). Therefore the outcome of experimental and theoretical research indicates that natural and human (anthropogenic) activities can redistribute this element in the atmospheric, soil and water ecosystems through a complex combination of chemical, physical and biological mechanisms.

Regional scale modeling of major atmospheric transport and removal mechanisms of Hg(0), Hg(II) and Hg-bound to particulate have been performed within the framework of MOE and MAMCS projects. Model results suggest that up to 75% of mercury in cloud and rain droplets is associated with particles in polluted areas of Europe due to adsorption on to soot particles (Petersen *et al.*, 2001), and that the sea salt aerosol and spray droplets play an important role in the production of Hg(II) in the Marine Boundary Layer (MBL), possibly accounting for up to 20% of the total Hg(II) observed in coastal areas, with higher values expected in open sea (Forlano *et al.*, 2000; Hedgecock and Pirrone, 2001). Preliminary assessments of spatial distributions of atmospheric deposition fluxes of Hg(0), Hg(II) and particulate Hg over Europe have been based on the up-to-date Mercury Emission Inventory (MEI) (Pacyna *et al.*, 2001) developed for Europe, North Africa and the Middle East and executed for different seasons as discussed in Petersen *et al.* (2001) and Pirrone *et al.* (2000a).

Different modeling techniques are currently used to assess the emission source areas (receptor models) as well as spatial and temporal distribution of mercury transported for long distances from the emission sources (Lagrangian and Eulerian modeling approaches). In this chapter, an overview on major chemical and physical processes affecting the dynamics of mercury in the atmosphere and its cycle between air, water and terrestrial ecosystems is provided. In particular, major modeling techniques currently used in Europe to assess spatial and temporal distributions of ambient concentrations and deposition fluxes with changing meteorological conditions are briefly highlighted and recommendations on future research needs for implementing the New European Directive on Mercury will be discussed.

3.2 ATMOSPHERIC PROCESSES

3.2.1 The Chemistry of Mercury

Gas phase elemental mercury makes up the bulk of mercury emitted from industrial and natural sources and is also the most common form of mercury in the gas phase. The reason for this is that elemental Hg reacts slowly with atmospheric oxidants. The most important gas phase oxidation pathway is the reaction with ozone. This reaction is slower than some other gas phase reactions, but the relatively high concentrations of ozone found in the troposphere with respect to other oxidant compounds makes it the most important. Oxidation of Hg(0) leads to Hg(II) species which are notably less volatile than Hg(0) and will tend to condense onto atmospheric particulate matter or be deposited to marine or terrestrial surfaces.

The partitioning of Hg(0) between the gaseous, dissolved and adsorbed states generally provides a sink for a part of the Hg(0) present in the gas phase. Hg(0) may dissolve into rain water or adsorb onto the atmospheric aerosol and subsequently be precipitated or deposited. These deposition processes provide the major removal pathways for atmospheric mercury.

Elemental mercury is present in atmospheric water, whether it be fog or cloud water or the water associated with deliquesced aerosol particles. The Henry's Law constant for mercury is low so the elemental mercury concentration in atmospheric water should reach equilibrium with the gas phase concentration rapidly, if no particularly rapid reactions of elemental mercury occur in the aqueous phase. In fact this is the case for mercury because even though the oxidation of mercury in the aqueous phase is significantly more rapid in the aqueous phase than the gas phase, the mass transfer of Hg(0) from the gas phase is faster for the droplet radius range found in fogs and clouds.

Oxidised Hg in atmospheric water is usually found complexed with SO_3^{2-} , OH^- or Cl^- ions, the concentrations of the various complexes depending on the origin of the aqueous phases. In most cases, apart from sea-salt aerosol, the concentration of chloride ions is low and OH^- and SO_3^{2-} complexes are predominant. The greater solubility and lower volatility of Hg(II) with respect to Hg(0) means that Hg(II) does not generally outgas from the aqueous phase in any significant fashion, although recent research suggests that HgCl_2 outgassing from the marine aerosol may be an important process in the marine boundary layer (Hedgecock and Pirrone, 2001).

Hg(II) in fog and raindrops may adsorb to particulate matter scavenged by the droplets. This is particularly likely if the particulate matter is rich in elemental carbon (soot) as the adsorption coefficient for Hg on soot is high (Petersen et al., 1998, Pirrone et al., 2000)

Mercury associated with particulate matter in the atmosphere may be the result of direct emissions from industry where the small amount of Hg present in fossil fuels is emitted bound to particulate matter, usually soot. This mercury is unlikely to be released or react in the atmosphere and is deposited together with the particulate. The other possibility for Hg association with particulate matter is the adsorption of elemental Hg present in the atmosphere, the amount of Hg adsorbed will depend on the composition of the aerosol and the gas phase concentration of Hg. There is also the possibility that particulates which undergo cycling through droplets or periods of deliquescence contain Hg(II) compounds which remain after the evaporation of the water.

3.2.2 Gas-Particle Partitioning

The modeling of the atmospheric aerosol is fundamental for many questions involving the quality of the environment in which we live. Aerosols directly affect health when inhaled, they reduce visibility [see Seinfeld, 1986, and references therein] and provide surfaces for the heterogeneous production of gaseous pollutants [Dentener and Crutzen, 1993]. Aerosols are also intimately involved in the transport of pollutant species and in the chemical and physical transformation of hazardous atmospheric pollutants (HAPs). The transport and dispersion of pollutants via the particulate matter emitted in industrial plumes has been studied and modeled [Shannon and Voldner, 1995; Constantinou et al., 1995, Pirrone et al., 1995ab]. The ambient aerosol population is not a very well defined entity, and is constantly changing, adsorption isotherms of Hg for the various types of aerosol are unavailable and the interaction of gaseous pollutants with aerosol particles is dependent on the chemical composition of the particle. Although the composition is at least partially known in some instances or can be modeled, in others it remains nevertheless an obstacle to the rigorous treatment of adsorption processes.

3.2.3 Dry deposition to Terrestrial and Aquatic Receptors

Dry deposition of Hg may occur via two processes. One is the direct deposition of elemental gas phase Hg, the other is the deposition of atmospheric particulate matter to which Hg is reversibly or irreversibly adsorbed. The first process is extremely difficult to quantify depending as it does on meteorological phenomena such as temperature and wind speed, but also on the type and geomorphology of the surface in consideration. Most regional scale studies have assumed that the gaseous flux of Hg(0) the land/water surface is zero, (Pai et al., 1997). Recently a number of flux chamber experiments, especially on water surfaces have been performed to test the validity of this assumption and to determine whether it is possible to parameterise net fluxes as a function of air and sea temperature and solar irradiation (Atmos. Env. special issue 2001).

The second process, that of Hg deposition together with particulate matter has until recently only been considered in terms of Hg irreversibly bound to particulate matter emitted with flue gases from industrial installations. The role of the atmospheric aerosol as a vehicle for Hg deposition was recently investigated by Pirrone et al., (2000). This preliminary investigation sought to consider the various possible aerosol sources, urban, continental, marine and desert individually and also to take into account the possible deliquescence of the particles during periods of high humidity with the consequent aqueous phase chemistry and altered deposition velocity due to the increase in mass and diameter resulting from the adsorption of water vapour. Their results suggest that where rainfall is relatively frequent this process is secondary to wet deposition. However in regions with prolonged periods of dry weather it could be the major deposition process for part of the year. This would be particularly true of coastal areas where the sea is a constant source of deliquesced aerosol particles capable of adsorbing Hg(0), which undergoing oxidation to Hg(II) in the aqueous phase would result in continuing adsorption of Hg(0).

3.2.4 Wet Scavenging by Precipitation Events

Wet removal processes concern soluble chemical species (Hg(II) and its compounds, and some Hg(0)), and also particulate matter scavenged from below the precipitating clouds.

The total wet deposition flux is made up of two contributory factors. The first derives from the continuous transfer of mercury to cloud water, described by chemistry models. There are two limiting factors here, the rate of uptake of gas phase elemental mercury, which is regulated by Henry's constant, and the subsequent oxidation of Hg(0) to Hg(II) which is governed by reaction rate constants and the initial concentrations of the oxidant species. The total flux depends upon the liquid water content of the cloud and the percentage of the droplets in the cloud which reach the earth's surface.

The second contribution to the total mercury flux is the physical removal of particulate matter during precipitation events. The latter case is modelled by specifying a scavenging coefficient.

3.2.5 Exchange of Mercury Between Atmospheric, Aquatic and Terrestrial Compartments

The exchange of pollutants between different environmental media is a phenomenon that involves chemical and physical processes which operate on different temporal and spatial scales. It plays an important role in the cycle of all semi-volatile contaminants due to the propensity of these contaminants to be partitioned between the gas, aqueous and solid phases depending on the Henry's Law constant and ambient conditions. Although the exchange of contaminants between the atmospheric, water and terrestrial compartments is considered a critical mechanism in the overall biogeochemical cycle for a wide array of semi-volatile contaminants including mercury and several organic compounds (i.e., PAHs, PCBs, pesticides) in the last two decades not very much progress has been made in understanding its magnitude, its possible variation over time and space, of the different processes/mechanisms involved (Cossa et al. 1996; Rasmussen 1994; Schroeder et al. 1989; Xiao et al. 1991; Ferrara, et al. 2000). Recently attempts have been made to develop a comprehensive model to assess the role of sea spray aerosol in the overall cycling of atmospheric mercury over the Mediterranean Sea. The relative contribution of sea spray at different wind speeds with respect to the exchange of gas phase Hg at low wind speeds has been investigated. The latter phenomena is driven primarily by the concentration gradient between the top-water micro-layer and lower atmosphere (Pirrone 1998; Trombino *et al.* 2000) and solar irradiation (Hedgecock and Pirrone, 2001).

There are not many models that describe the air-water exchange mechanisms and those that exist are mostly used to estimate the rate of air-water exchange of Persistent Organic Pollutants (POPs) (Deacon, 1977; Liss and Slater, 1974; Kerman, 1984; Schwartzbach *et al.*, 1993). The two-film model (Liss and Slater, 1974; Schwartzbach et al., 1993) is the most commonly used to describe air-water exchange, although surface renewal (Daenkwerfs, 1951; Asher and Pankow, 1991) and boundary layer (Deacon, 1977; Kerman, 1984) models are sometimes employed. The model is used to assess the dynamics of gaseous mercury via sea spray formation in the Marine Boundary Layer (MBL) and its magnitude compared to other mechanisms. Wind stress at the sea surface generates droplets in the size range 37.5 to 400 μm . The droplet radius is of great importance as it determines whether gas phase

elemental mercury is removed from or released to the atmosphere. When the sea water top micro-layer Hg concentration is high ($C_0=0.1 \text{ ng L}^{-1}$) the aerosol which is eventually re-deposited on the sea surface releases mercury whilst it remains in the air. Conversely when the Hg concentration in the sea top micro-layer is low ($C_0=0.001 \text{ ng L}^{-1}$) the trend is inverted and the aerosol absorbs Hg before re-deposition.

3.3 TIME SCALE AND UNCERTAINTY ANALYSIS

3.3.1 Introduction

Atmospheric processes occur over a very wide range of time scales, varying from almost instantaneous in the case of chemical reactions involving radicals, to the hours sometimes required to establish gas-aqueous phase equilibria and the days or even weeks required for atmospheric transport. The impact of any one equilibria or a particular reaction on the speciation, deposition or transport of mercury therefore requires an in depth analysis of the result of variations of the parameters that determine the time scale of the equilibrium or reaction. The parameters involved could be many, meteorological factors such as temperature, pressure, relative humidity and atmospheric liquid water content are clearly important, as are the concentrations of atmospheric chemical species which react with mercury itself or compete with mercury to react with complexing ligands or oxidants. The most common method used to assess the importance of specific reactions and equilibria or initial model concentrations is to run the model a large number of times, varying initial concentrations or reaction and equilibrium constants to obtain an idea of the sensitivity of the model's output to these parameters.

A more rigorous and quantitative approach to the analysis of a model's sensibility to initial concentrations, reaction rate constants and equilibrium constants is to obtain the derivative of a species' concentration with respect to initial concentrations and individual rate constants. This is less easy to achieve but once performed may save time and produce less ambiguous results than the empirical approach of varying individual concentrations and rate parameters. The other advantage is that the sensitivity of a given species concentration to an initial concentration or rate constant may change over time, and this is easily seen in a plot of sensitivity against time.

3.3.2 Initial Results with a Condensed Chemical Reaction Scheme

A condensed gas and aqueous phase chemistry scheme for mercury was prepared for use with a model describing the interactions of gas phase mercury with the ambient aerosol based on the condensed scheme used by Petersen et al., (1998), which in turn had been derived from the much more comprehensive reaction set used by Pleijel and Munthe (1995). The aqueous phase chemistry was included originally to account for mercury chemistry fog and rain droplets and then in gas-particle interaction model to describe the chemistry in deliquesced aerosols. Sensitivity analysis was performed on this condensed mercury chemistry scheme using the Direct Decoupled Method (DDM) devised by Dunker (1984), and incorporated in the freely available Fortran programme ODESSA which uses a Gear based integration

routine to solve the system of Ordinary Differential Equations (ODEs) which mathematically represents the ensemble of reactions in the chemistry scheme.

The sensitivity to initial concentrations revealed that the mercury compound concentrations which are initially dependent on the concentration of aqueous phase elemental mercury become entirely dependent on the gas phase elemental mercury concentration after 100s. The concentration of elemental mercury itself establishes its gas-aqueous phase equilibrium in approximately a microsecond. Thus the gas phase concentration is by far the most important parameter in the determination of final mercury compound concentrations in the atmospheric aqueous phase, and the quantity of mercury adsorbed on particles which deliquesce or are scavenged has little impact on the final steady state concentration of the mercury compounds. The most important factor in determining the eventual steady state mercury compound concentrations proved to be the initial concentration of chloride ions. Mercury is oxidised rapidly in the aqueous phase by dissolved ozone and also by OH and HOCl, but the total concentration of mercury in the aqueous phase is determined by the concentration of ions present which may form complexes with mercury. The most important are OH⁻, SO₃²⁻ and Cl⁻. The sensitivity analysis showed clearly that the initial concentration of chloride ion was fundamental in determining the eventual total mercury content of the aqueous phase. In the presence of high chloride concentrations the total concentration of dissolved mercury compounds could be 100 times that in conditions with low chloride ion concentration. This fact illustrated the difference between sea-salt and other types of aerosol, where the chloride concentration is very high in the former and thus is able to have high concentrations of dissolved mercury compounds, and other particles where the chloride concentration is determined by the gas phase HCl concentration, which is generally low. In the low chloride concentration case the major mercury containing complexes are Hg(SO₃)₂²⁻ and Hg(OH)₂, both of which are dependent on pH so that their concentration is sensitive to the concentration of acidic species in the gas phase and aqueous phases. The sensitivity of the mercury compound concentrations to individual reaction rates was shown to be dependent on gas and aqueous phase oxidation rates as would be expected, because of the necessity of this first step to provide Hg²⁺ for complexation by Cl⁻, OH⁻ and SO₃²⁻.

3.3.3 Recent Advances

The importance of the role of the sea-salt aerosol as a possible carrier of oxidised mercury due to its ability to complex relatively large quantities of oxidised mercury due to its high chloride concentration, prompted more detailed studies of the role of the sea-salt aerosol in mercury chemistry in the marine boundary layer. Preliminary results show that the most important oxidation pathway is gas phase oxidation of elemental mercury by ozone. It had been suggested that in low ozone regimes, typically regions where there is little anthropogenic production of nitrogen oxides, such as those prevailing in the remote marine boundary layer that a two-step oxidation of mercury by OH radical in the aqueous phase would also become a major pathway, Lin and Pekhonen (1997). This has been shown not to be the case, and it is the gas phase oxidation of elemental mercury by ozone and the subsequent scavenging of HgO by deliquesced aerosol which makes the largest contribution overall to the oxidation process in the marine boundary layer in non-cloudy conditions. Current work is focussing on the sensitivity of mercury oxidation and speciation to atmospheric liquid water content and photolysis rate constants which are behind the diurnal photooxidant concentration variations in the atmosphere.

3.4 MODELLING FRAMEWORKS

A variety of modelling techniques have been developed for exploration of atmospheric mercury processes. These include relative simple mass balance models that examine the pooling and exchange of mercury species between various environmental compartments as well as complex deterministic atmospheric dispersion models attempting to simulate the transport and transformation of mercury over domains of hundreds to thousands of kilometers, while detailed chemical transformation models incorporate the most sophisticated treatment of atmospheric mercury chemical processes. In addition to source-based models, receptor models show promise for explaining source-receptor relationships. It is expected that improved modelling techniques and increasing monitoring data bases will enable detailed source attribution determination for the EU region within the next several years.

3.4.1 Modelling Local Scale and Near Source Transport

Local scale models for mercury are used to predict concentrations and deposition fluxes downwind of point sources over a few hours or days in an array of grid cells which range in horizontal size from about 1 to 2000 km². They require detailed understanding of chemical reactions and atmospheric processes on the order of minutes or hours. Such models can be employed to predict worst-case episode conditions and are typically used by regulatory agencies as a basis for control strategies. Local scale models can be described as simple or advanced based on the assumptions with which the important variables are treated. Relative simple models based on Gaussian diffusion assume that concentrations of pollutants will be normally distributed and do not undergo significant chemical reaction and removal as they travel away from the source. In extended versions of the elementary Gaussian model transport equations are solved numerically using a momentum reduction in cross-wind direction in order to reduce the three-dimensional problem to a two-dimensional one. This procedure preserves a high resolution of the plume structure even far from sources. As the vertical grid is oriented vertically in the mean wind direction, a high cross-wind resolution can be used over the entire model domain.

3.4.2 Modelling Long-Range Transport

The major European marine environment protection conventions (OSPAR, HELCOM and MEDPOL), the Arctic Monitoring and Assessment Program (AMAP), and the recently signed UN-ECE protocol on reducing the atmospheric transboundary transport of mercury in Europe have intensified the scientific interest in relating the spatial and temporal information on the release of mercury into the atmosphere to the pattern of atmospheric deposition fluxes to various ecosystems by means of long-range transport modelling on regional European scales. In this context, efforts have been made to simulate the atmospheric transport and fate of mercury and to derive estimates of ambient concentrations and dry and wet deposition fluxes of mercury over Europe (Petersen et al., 1995; Ryaboshapko, 1998) through either relative simple Lagrangian formulations or Eulerian approaches employing extensive gas- and aqueous phase chemical mechanisms and explicitly tracking numerous species concentrations. Results from regional scale models reveal that mercury transport over Europe is significantly affected by the temporal and spatial variability of global background concentrations of

elemental mercury suggesting a need for hemispheric and global scale models to calculate time dependent boundary concentration fields as input data for European scale models.

3.4.2.1 Lagrangian Modeling

Lagrangian models developed for mercury and currently in use are variants of the so-called trajectory models. These models are usually formulated under assumptions of simplified turbulent diffusion, no convergent flows and no wind shear. In these approaches only first-order chemical reactions can be treated rigorously. However, 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 descriptions of interactive non-linear processes.

3.4.2.2 Eulerian Modeling

Further progress in understanding the atmospheric cycling of mercury has emphasised the need for direct modelling of the complex physico-chemical transformations of atmospheric mercury species by comprehensive Eulerian models. These approaches employ extensive gas- and aqueous phase chemical mechanisms and explicitly track numerous species concentrations. Also, a more detailed numerical formulation of physical and chemical processes occurring within and below precipitating and non-precipitating clouds is included. Typically, these models contain modules designed to calculate explicitly the chemical interactions that move gas-phase species 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.

3.4.2.3 Mass Balance

Multimedia mass balance models are relatively simple mathematical descriptions of the environment designed to gain a qualitative and quantitative understanding of the behaviour of mercury species, which are likely to be found in more than one environmental medium. Such models subdivide the environment into a number of well mixed boxes which are assumed to have homogenous environmental characteristics and concentrations. The model then calculates how mercury species are distributed within that simplified system. The distribution, and thus the concentration that is established in each medium, is influenced both by the intrinsic mercury properties and emission pattern and by the characteristics of the environment into which the mercury species are released. The models thus integrate information on multiple and interacting processes of partitioning, transport and transformation into a comprehensive picture of mercury in the environment.

Compartmental box models may serve as test modules for more complex atmospheric dispersion models which can be overwhelming in their complexity and in the amount of data they require and produce. For example, the incorporation of soil, vegetation and marine

environments into an atmospheric dispersion model can make them completely impractical and non-transparent. It was therefore suggested that box models can play an important role in:

- testing which fate processes are important and thus need to be included in the atmospheric dispersion models
- attempts to understand model behaviour
- testing expressions and parameter values for air-surface exchange
- conducting sensitivity and uncertainty analysis

3.4.2.4 Receptor Modeling

In the last two decades a number of receptor models were developed and applied for different regions and for a number of trace elements and organic compounds in order to evaluate the emission source profiles in relation to ambient concentrations. There are different type of receptor models. Multivariate statistical techniques (i.e., FA, PCA) combined with backward trajectory analysis were the first to be applied to trace elements and provide the emission source profiles of emission sources from which the observed ambient concentrations at a give location originate from. Alternatively, hybrid receptor-deposition modeling techniques combine Lagrangian model with physical or/and empirical process models (Pirrone et al. 1995a; 1995b) in order to assess the relative contribution of anthropogenic emission sources to air masses crossing the monitoring site. These techniques have been used for trace elements (Pirrone et al. 1995a) including mercury (Pirrone and Keeler, 1995) and semi-volatile organic compounds (Pirrone et al. 1995b; Pirrone and Keeler 1997). However, regardless of the technique employed, the application of receptor models require continuous observations, preferably with high temporal resolution, of ambient concentrations of trace elements. It is particularly suitable for regulatory purposes when continuous and dense (spatially) monitoring network data are available.

3.4.3 Integrated Mercury Modeling Frameworks used in EU

Hemispheric and global model developments are now underway based on national research efforts in Scandinavia and Canada but results are still in a preliminary stage. The major European scale mercury model developments and applications have been performed under the Heavy Metals Protocol of the UN-ECE LRTAP Convention and in the framework of two European projects, namely the Mercury Over Europe (MOE) and the Mediterranean Atmospheric Mercury Cycle System (MAMCS) funded by the European Commission-Environment and Climate Programme. In the following three subsections, the basic features of these three modeling frameworks are briefly outlined and main results in terms of model predicted concentrations and deposition fields are summarised.

3.4.3.1 Integrated Modeling System developed at MSC-E, Russia

The MSC-E model for mercury transport and deposition includes basic chemical and physical processes such as emission, advective transport, turbulent diffusion, chemical transformations, and dry and wet deposition. The MSC-E model operates within the EMEP

grid region (135×111 cells) with a grid cell size of 50×50 km² and a time step of 20 min. The basis of this version are models described by Pekar (1996) and Ryaboshapko et al. (1998; 1999). In the last model version the most essential changes concern the description of mercury gas-phase chemistry and boundary concentrations.

A detailed description of the model is given in MSC-E report for 1999 (Ryaboshapko *et al.*, 1999). The schematic representation of the model is given in Figure 3.1. The model operates with five vertical layers of 100, 300, 700, 1000 and 1800 m depth. Thus, the calculation domain covers the whole boundary layer and an essential part of the free troposphere. Emissions enter either the first or the second model layer according to the source height. Interlayer exchange is realised by vertical turbulent diffusion and ordered vertical fluxes. The latter are calculated at each time step in each cell reasoning from the condition of air mass balance. The upper boundary of the model reservoir is open for the exchange with the above atmospheric layers. The lateral margins of the model reservoir are also open for the exchange with the ambient atmosphere. Mercury and its compounds can undergo chemical reactions both in the gaseous phase and in the liquid phase of clouds. It is assumed that clouds can be present in the third, fourth and fifth model layers. The model describes heavy metal scavenging from the atmosphere due to dry uptake by the underlying surface as well as due to wet removal.

The advection scheme has been developed by Pekar (1996). Horizontal diffusion is described according to the approach suggested by Izrael et al. (1980). The model description of turbulent diffusion is based on the assumption that substance flux is proportional to the concentration gradient. The proportionality factor is the coefficient of turbulent diffusion calculated by the boundary layer parameterisation described in Pekar (1996). Vertical diffusion is described by an implicit scheme in which stability does not depend on the ratio of time-step and diffusion coefficient (Samarsky, 1977). The diffusion equation is solved by the sweep method.

Petersen et al. (1998) developed a chemical module containing only basic reactions. On the basis of this module Ryaboshapko et al. (1999) have developed a simplified scheme which does not require much computer time and can be used in operational calculations (Figure 3.2). In this scheme gaseous elemental mercury is dissolved in the liquid phase of cloud (fog) drops according to Henry's Law (equilibrium E1). In the liquid phase the process of mercury oxidation by ozone takes place (reaction R6). Products of the liquid phase oxidation react with dissolved species (reactions R13, equilibrium E2) and are absorbed by solid insoluble particles, for example, soot particles (equilibrium E3, E4). The reaction of divalent mercury with sulfite ions produces unstable mercury-sulfite complexes (reaction R13). Their decay (reaction R9) results in mercury reduction to the elemental state and in the elevation of the elemental mercury concentration in the solution. Therefore this scheme presumes a negative feedback controlling the rapidity of gaseous elemental mercury dissolution process in the liquid phase. It is possible to group mercury compounds which are in equilibrium. The first group - elemental mercury in the air and water, the second one - mercury of the mercury-sulfite complexes in the aqueous phase and on soot particles, the third - free mercury ions and mercury-chloride complexes in solution and on particles. These groups are denoted as A, B, and C respectively: A, B and C can be considered as individual "substances" and the distribution inside A, B or C can be established by equilibrium coefficients. For example, the distribution between Hg(0)(liquid) and Hg(0)(gas) within A is defined by Henry's law. Mean monthly concentration fields of sulphur dioxide were calculated by Meteorological Synthesizing Centre - West using a Eulerian model for acidifying species with spatial

resolution of 50x50 km (Olendrzynski, 1999). The equilibrium ratio between sulfite and chloride complexes in a solution drop and associated with soot particles is assumed to be 1/6 (Petersen *et al.*, 1998). Henry's law constants for ozone H_{O_3} and elemental mercury H_{Hg} depend on temperature. For temperatures below 273⁰K it was assumed that cloud water is partially in the super-cooled liquid state. For the liquid phase appropriate Henry's law constants both for mercury and ozone were calculated by extrapolation of known temperature dependencies into the negative temperature range. In addition to the liquid phase reactions, the gas-phase reactions of mercury and its compounds can also take place. Gas-phase elemental mercury is oxidised by ozone with a second order rate constant of 0.74E-9 ppb⁻¹s⁻¹ (Petersen *et al.*, 1998). Since ozone is present in large excess relative to mercury the reaction may be considered as a quasi-first order process. In our calculations mean monthly ozone concentrations calculated for the boundary layer with spatial resolution 50x50 km in Meteorological Centre-West (Simpson *et al.*, 1997) are used.

It is assumed that mercury associated with particles behaves like sulfate with an equilibrium washout ratio of 7×10^5 . Washout of inorganic gaseous oxidised mercury by the cloud liquid phase is set equal to the equilibrium washout ratio characteristic for nitric acid: 1.4×10^6 (Petersen *et al.*, 1995).

Dry deposition of elemental mercury is taken into account by assuming a dry deposition velocity of 0.03 cm/s over land during May-October and 0.01 cm/s during the other months. On the sea surface the dry deposition velocity of Hg^0 is always zero. For gaseous oxidised inorganic mercury the dry deposition velocity is always 0.5 cm s⁻¹ regardless of season and the underlying surface type.

Results from model simulations in terms of mean annual surface air TGM concentration fields for 1998 are shown in Figure 3.3. As can be seen from the figure the highest concentrations occur in central Europe with maximum values up to 7 ng m⁻³. The regions of northern Scandinavia however show concentrations close to the global background level. The spatial distribution of mean annual mercury concentrations in precipitation for 1998 depicted in Figure 3.4 shows pronounced peak values close to the main European emission areas with relatively high contributions from divalent mercury, which is readily transferred into the aqueous phase. The total deposition flux (Figure 3.5) consists of contributions from all mercury species in ambient air and precipitation. Maximum values in main emission areas with high concentrations and precipitation rates are in the range of 600 g m⁻² a⁻¹ with a pronounced decreasing gradient towards the remote European areas.

For comparison purposes model results were compared with observations of mercury concentrations in air and precipitation carried out in the framework of EMEP programme. Only a small number of EMEP stations have in the past measured mercury concentrations in air and precipitation: 5 stations in 1997 and 3 in 1998 (Figure 3.6). The situation with mercury in precipitation is somewhat better – the measurements were carried out at 8 and 6 stations (Figure 3.7). The model slightly overestimates mercury concentrations in air. This difference is quite understandable because the model is very sensitive to background concentrations of elemental mercury. The model will be able to provide a high level of agreement between measured and calculated values if reliable information on mercury background concentrations outside the modelling domain were available. However, observed and model predicted mercury concentrations in precipitation agree satisfactorily within a factor of 1.2.

3.4.3.2 Integrated Modeling System Developed at CNR-IIA, Italy

The mercury modeling system was developed within the framework of the Mediterranean Atmospheric Mercury Cycling System (MAMCS) project funded by the EU-Environment and Climate Program (Contr. No. ENV4-CT97-0593) in which major research and university institutions were involved (see Final MAMCS Report, Pirrone et al. 2000a). The major goal of MAMCS was to examine the cycling of atmospheric mercury in order to characterise and quantify the emission, ambient concentration and deposition flux patterns in the Mediterranean region. The climatic conditions in the Mediterranean region are such that one of the major foci of the project was the investigation and modelling of the interaction between gas phase mercury species and the ambient aerosol. The reason for this is that for relatively long periods during the year there is very little, if any, rainfall in the area. Under such conditions the major mercury deposition pathway, precipitation is unavailable, and the major deposition process will be via the ambient aerosol. This fact has important implications, particularly in the marine environment where deliquesced sea salt aerosol is present, providing both a means of deposition and of oxidation of elemental mercury.

The MAMCS integrated modelling system (see Figures 3.8-3.10) is based on two well known meteorological-dispersion models, the Regional Atmospheric Modelling System (RAMS) and the SKIRON/Eta meteorological system (Figure 3.8). RAMS is a highly versatile Eulerian model developed jointly by Colorado State University and Mission Research Inc/ASTeR Division. It is a merger of a non-hydrostatic cloud model and a hydrostatic mesoscale model. There is no lower limit to the domain size or to the mesh cell size of the model finite difference grid. The large number of RAMS applications worldwide has given valuable information about the model behaviour under different climatic conditions. RAMS has a number of features which make it extremely useful for air quality studies on various scales. It has two-way interactive nesting capabilities with any number of either telescoping or parallel fine nest grids, terrain following coordinate surfaces with Cartesian or polar stereographic horizontal coordinates and non-hydrostatic time-split time differencing. The cloud microphysics parameterization works at various levels of complexity, there are various turbulence parameterization schemes, radiative transfer parameterizations (short and long wave) through clear and cloudy atmospheres, options for upper and lateral boundary conditions and for finite operators. The surface-layer parameterization (soil, vegetation type, lakes and seas, etc) may be used with with different levels of complexity depending on the users requirements. RAMS is therefore a highly versatile tool and is used in air quality studies and to study a wide variety of other atmospheric phenomena. This model is the backbone of the modeling system.

A second meteorological model (SKIRON system) can also be used, it is less time consuming with respect to RAMS because the treatment of cloud microphysics is simplified. The SKIRON system was developed at the University of Athens and is in use in several Mediterranean countries as operational weather forecast model. It is based on the Eta/NMC model originally developed at the University of Belgrade, with the specific objective of being applicable to regions with steep mountains. It therefore uses a unique "step-mountain" vertical coordinate rather than the customary pressure or sigma (or hybrid) coordinate. This model is the fully operational weather forecasting model in use in the United States and several other countries. SKIRON has several capabilities which make it appropriate for regional/mesoscale simulations. One of the more important features of this model is the use of Eta as the vertical coordinate which is a generalisation of sigma-coordinates to give a better parameterization of step-like terrain. The model uses a split-explicit time differencing scheme, a 2.5 order closure

scheme for parameterization of the boundary and surface layer, a viscous sub-layer scheme, a parameterization of surface processes, a 4th diffusion scheme in the field boundaries with diffusion coefficients dependent on deformation and turbulent kinetic energy. It also uses mass convergence and convection for the small, medium and large scale precipitation parameterization scheme, the GFDL radiation scheme with random interaction of clouds at various levels, and importantly includes a dust uptake-transport-deposition module.

The links (see Figure 3.8) between the input required by RAMS (or SKIRON), the mercury emission database, mercury boundary conditions and vertical profiles and the chemical-physical process modules are described below.

The gas and aqueous phase chemistry of mercury is modelled using a reaction scheme based on that of Pleijel and Munthe (1995), and updated to include the radical reactions in the gas and aqueous phases for which rate constants have been published in the last six years. These include the gas and aqueous phase oxidation of elemental mercury by the hydroxyl radical (Sommar et al. (2001), the aqueous phase oxidation of elemental mercury by HOCl and the aqueous phase reduction of oxidised mercury by HO₂ (Lin and Pehkonen, (1998)). A number of versions of the chemistry model exist, all of which may be linked to RAMS, but obviously the more complex the reaction scheme is in the model the more time consuming become the simulations. The most complex schemes treat atmospheric photochemistry in urban areas (complex volatile organic compound chemistry) and marine environments (complex halogen chemistry), both are used predominantly as box models. The advantage of these complex schemes is that by using sensitivity analysis techniques i.e., the Direct Decoupled Method (Pirrone et al. 2000), it is possible to derive a slim-line reaction scheme for mercury and its compounds whilst ensuring that no important reactions are overlooked. This has proved to be particularly important in the marine environment where the omnipresent sea salt aerosol not only provides a reservoir of complexing ligands in the form of high concentrations of halide ions (including bromide and iodide), but also provides a means by which oxidised mercury may be returned to the gas phase (Hedgecock and Pirrone, 2001). The chemistry model normally used with RAMS includes gas phase and aqueous phase oxidation pathways, and in the aqueous phase the complexation equilibria which determine the speciation and concentration of oxidised mercury compounds, this is shown schematically in Figure 3.9. In this version of the model the concentrations of the important oxidants produced by photolytic processes is calculated using a minimum and maximum value for each grid cell and varying the concentration sinusoidally with a maximum when the sun reaches its zenith.

The study of the interaction between mercury and the ambient aerosol, mentioned above, resulted in the development of the gas-particle partitioning (GASPAR) model (Pirrone et al. 2000; Hedgecock and Pirrone, 2001). GASPAR represents the ambient aerosol in a parameterised fashion, and describes the particulate in terms of its source (urban, continental, marine or desert), a maximum of three modal diameters for each source, its hygroscopicity and its soot and chloride ion content. The model calculates the diffusion of mercury into the particles and using empirically derived adsorption enthalpies from experimental data the concentration of mercury associated with particulate matter is obtained. This is not all however, one of the most important characteristics of an aerosol particle is its hygroscopicity, which determines whether or not the particle, or some of the particle, adsorbs enough water vapour to deliquesce. If deliquescence occurs there is an atmospheric aqueous phase present, providing the possibility for all the aqueous phase chemistry of mercury to take place even in the absence of fog and clouds. Deliquescence obviously depends on relative humidity, which is a fundamental parameter for any meteorological model and is therefore known for each grid

cell. The eventual fate of the ambient aerosol is either dry deposition to aquatic or terrestrial surfaces, or scavenging by fog or cloud droplets. Dry deposition velocities are calculated using the resistance method and scavenging is modelled using below and in cloud scavenging ratios. The interaction between the meteorological, chemistry and gas-particle partitioning models is shown in Figure 3.10.

Another important process in the global mercury cycle is the exchange of gaseous mercury at the air-water interface, as indicated in Figure 3.8. This may occur by gas phase diffusion to water surfaces and evasion from the top water micro-layer, or it may be provoked by the mechanical action of the wind on the water surface producing waves and thereby mechanically generating sea-water droplets which may either release or take up elemental mercury. These processes are not as yet thoroughly understood but empirical models capable of reproducing experimental data from flux chamber measurements exist, as do models to predict the size distribution of droplets produced by the action of the wind on the water surface as a function of wind speed (Pirrone et al. 2000a; Trombino et al. 2000).

The integrated MAMCS modelling system has been tested using the results of four intensive measurement campaigns carried out at five sites during the MAMCS project. As an example of MAMCS modeling system application hereafter is reported the results obtained for the fourth MAMCS intensive measurement campaigns carried out from 17 July to 3 August, 1999.

In order to understand the dynamic processes of pollutants during atmospheric transport it is important to characterise the meteorological conditions. The meteorological conditions predicted for the summer period of simulation varied between a high pressures system over the Central and West Mediterranean Regions (17 July) and weak pressure gradients over the North-East Mediterranean at the same time followed by a high-pressure system extending over the Aegean Sea and the Mediterranean Sea region (July 21). On 23 July, weak pressure gradients prevailed over the eastern Mediterranean as a result of the extension of the thermal flow of the Anatolian Plateau, while high pressures over the Northern Africa and strong northerlies and north-westerlies were predicted over the sea on the west side of Italy (23 July). These conditions could promote the long-range transport of mercury from the Central Europe towards the Central Mediterranean. As an example Figure 3.11-a shows a trough that covered the Central Mediterranean and the Balkans on 25 July while it moved towards the Anatolian Plateau on 27 July, followed by strong north-westerly winds predicted over the southeastern Mediterranean on 31 July (Figure 3.11-b). The combination of the low and high-pressure systems over northern Europe induced strong northeastern winds. During the last two days of the simulation a weak synoptic circulation was observed over the Balkans.

Examples of spatial distributions of ambient concentrations (in the first model layer) and deposition fluxes (wet and dry) of Hg^0 , Hg(II) and Hg(part) predicted with MAMCS modeling framework during the simulation period are shown in Figures 3.11-3.12. During the initial days of the simulation the weak flow towards the Mediterranean Sea region did not favour the transport of gaseous mercury. The concentration of mercury species is a function of many factors that affect chemical and physical processes, such as atmospheric reactions and deposition, but it also depends strongly on flow conditions and source locations. Therefore the Hg^0 concentrations were high only around the sources during the first days of the simulation, while there is a weak mercury concentration gradient over the Mediterranean Sea region. The strengthening of the northerlies west of Italy during the next days (i.e around 23 July), led to the increase in Hg^0 concentration to 2.4-2.5 ng m^{-3} in the Central and Western Mediterranean

(Figures 3.11-c) from sources located in those areas. The low-pressure system that covered the Central Mediterranean and the Balkans on 25 July favoured a further increase in Hg^0 concentration over the above region and over southern Greece. As the cyclone moved towards the Anatolian Plateau, followed by strong northerlies, high values (approximately 2.3 ng m^{-3}) of Hg^0 were observed over the sea and reaching the eastern Mediterranean (Figure 3.11-d). The concentration of gaseous mercury increased above the usually observed value (background value) over Europe, where most of the sources (e.g. factories, power plants etc.) are located. The opposite is observed over northern Africa and the Middle East where Hg^0 concentration values are either close to, or just below background levels. The relatively high concentrations observed over the sea, are mainly due to advection of mercury from Europe, while air water exchange processes also make a small contribution.

Similar patterns were followed by the spatial and temporal distributions of Hg^{II} concentrations as illustrated in Figures 3.11-e (on 20 July 1999) during the summer experimental period. High concentrations of Hg^{II} are observed in the vicinity of sources due to its short residence time in the atmosphere, however higher concentrations events were observed on 22 July (Figure 3.11-f) far from the emission sources and over the sea. These patterns are primarily due to a combination of two synergetic factors (1) regional scale transport due to strong horizontal advection, and (2) Hg^{II} formation in the marine boundary layer as also suggested previously in Forlano et al. (2000) and Hedgecock and Pirrone (2001).

Hg^{P} is usually deposited at intermediate distances from its source, therefore high concentrations are naturally observed near the sources. However, the removal of Hg^{P} from the atmosphere is mainly dependent on wash-out mechanisms. During the summer and spring experimental periods precipitation amounts were much lower than during the wet period of the year. The concentrations of Hg^{P} modelled on 28 July (as example) are higher near the sources as illustrated in Figure 3.11-g.

The wet and dry deposition of mercury over land or water is a very important issue for human activities and health. Figure 3.12 shows the wet and dry deposition patterns of Hg^{P} , Hg^{II} and Hg^0 -adsorbed modelled for the summer MAMCS experimental period, whereas Figure 3.13 shows the total annual deposition fluxes of the three Hg species which were obtained by integrating that related to the four simulation periods (winter, spring, summer and autumn) assuming that each simulation was representative of each season.

The deposition patterns (see Figure 3.13) show that the greatest amounts of mercury are deposited in eastern Europe and in the Mediterranean region, especially in its eastern part. Taking into account the fact that the vast majority of mercury sources are located over central and northwest Europe, two main transport paths are indicated. One is from central to eastern Europe and the other is from Europe towards the Mediterranean sea, namely from north to south.

On a yearly basis the accumulated (within the 17 days of the simulation) amounts of Hg^{P} that is dry deposited are greater over the sea than over land. The deposition velocity of Hg^{P} is a weighted average of 15 deposition velocities, corresponding to the 15 size intervals over which particle radii are distributed. Over regions with high humidity (e.g. over the sea surface) greater deposition velocities are observed due to water uptake and the dependence of the deposition velocity with the size of the particles. The simulated values of Hg^{P} dry deposited, reached 180 ng/m^2 over the waters surfaces of the South and East Mediterranean Sea during the summer simulation period. On the contrary, higher wet deposition of Hg^{P} is

predicted, over mountainous areas, as expected due to the higher precipitation usually occurring there.

The wet deposition pattern of Hg^0 -adsorbed is similar to that of Hg^{P} , as the total amount of precipitation is higher over the Alps and the Mountains of Greece and East Turkey. The dry deposition pattern of Hg^0 -adsorbed in Total Suspended Particulate (TSP) shows a seasonal variation. The dry deposition patterns also vary over the sea and over land. Higher values are observed over the sea during the cold simulated periods (13 February to 2 March and 21 November to 7 December). This dry deposition pattern can be attributed firstly to the prevailing flow and turbulence conditions in the region, and secondly to the size of the particles. Relatively strong northwesterly and northerly winds were evident over Central and Northern Europe during the winter and fall simulation periods. The above-described atmospheric circulation favoured the increase of mercury concentration over the Mediterranean region. Therefore higher amounts of the pollutant were dry deposited over water surfaces, during the cold simulation period.

During the warm periods (1 to 18 May and 17 July to 3 August) the dry deposition values of Hg^0 -adsorbed, are higher over land as the total amount of aerosol is larger. The dry deposition patterns of Hg^{P} and Hg^0 -adsorbed also depend on the pollutant concentration and the deposition velocity. The transport of mercury species is dependent on advective transport by wind and transport by turbulent dispersion. The wet and dry deposition patterns of Hg^{II} are highest near the sources. Hg^{II} is also highly soluble so it dominates the wet deposition pattern of gaseous mercury. The wet deposition pattern of Hg^{II} has several similarities with the wet deposition pattern of Hg^0 -adsorbed, but that of Hg^{II} are four orders of magnitude greater than those of Hg^0 -adsorbed.

The total annual depositions (Figure 3.13) were calculated using weighted values of the four seasonal runs. It should be remembered that Hg^0 is deposited only as Hg^0 -adsorbed. It can be adsorbed either on particulates (see Pirrone et al. 2001) when it is dry deposited or dissolved in raindrops during wet deposition events. Two main reasons allow the inference of seasonal and annual values of deposition from the four model runs. Firstly the four model integration for the different scenarios lasted several days (~17 days each) and secondly there were a representative of the inter-synoptic variability in them. Various synoptic patterns were present in these simulations and thus the deposition patterns and amounts can be considered as representative of their “annual” and seasonal values.

The annual wet deposition patterns of the three mercury species are illustrated in Figures 3.13-b, 3.13-d, 3.13-f. The wet deposition patterns follow the rain pattern simulated by the atmospheric model. For example, this can be understood from the fact that the highest wet deposition amounts are estimated in the vicinity of mountainous regions (e.g. Alps, Atlas mountains). The dominance of the wet processes in mountainous regions was also associated with a well-defined minima of dry deposition of Hg^{P} in these regions.

In conclusion, the wet deposition of Hg^{II} and Hg^{P} were found in general to be one order of magnitude larger than for dry deposition, and the domain-averaged “annual” wet deposition of total mercury was found to be of the same order of magnitude as that measured by Iverfeldt (1991) in northern Europe. The “annual” wet and dry deposition of Hg^{P} are within the range simulated by Petersen et al. (1995) for selected stations in northern Europe. This agreement between our study and the literature gives confidence in the results, although further development is certainly needed. Finally, the total domain-averaged seasonal deposition

exhibited higher values during the wet season (winter, autumn) than during the dry season (summer, spring) of the year (Pirrone et al. 2000a). This is due to the fact that the total deposition is dominated by wet deposition, which is obviously greater during rainy periods. On the other hand, the highest domain-averaged dry depositions of Hg^{II} and Hg^{P} were observed during summer. In conclusion the deposition patterns modelled in MAMCS for the Mediterranean region show that large amounts of mercury are deposited in the Mediterranean region which should be considered in the future development of the European policy for regulating the emissions and controlling the amount of mercury (and its compounds) transferred from the emission sources to terrestrial and aquatic receptors.

Figure 3.14 shows a preliminary comparison of modelled concentrations of Hg^0 , Hg^{P} and Hg^{II} with that observed at some of the MAMCS stations during the spring period. Hg^0 concentrations observed in Sicily and Neve Yam were compared with those modelled with the SKIRON MAMCS based framework (Figures 3.14-a, 3.14-b). The bold line represents the 6-hour moving average. In Figure 3.14-c the Hg^{P} concentrations measured in Fuscaldo for the spring simulation period (1-18 May) are also illustrated. The thin line indicates the modelled concentrations (in 6-hour increments) in the lowest model layer (~62m above the ground) with both the background and lateral boundary concentration of Hg^0 (in the lowest 2 km) equal to 1.6 ng/m^3 . The model follows the trends of Hg^0 in Porte Palo and Neve Yam quite satisfactorily. Hg^{P} trends in Calabria are also represented satisfactorily by model outputs. Significant differences between the model forecasts and the observations seem to appear in some relatively short periods of the simulation. Although models can simulate several phenomena effectively, it is difficult to observe or predict any peaks that might occur over short time scales. Figure 3.14-d represents the Hg^{II} concentrations, observations and model simulation, in Antalya for the same period. The measured values used are limited, however it can be assumed, that the modeled Hg^{II} concentrations are in satisfactory agreement with the observations.

Major details on the MAMCS modeling results for the period of 1998-1999 can be found in the MAMCS Final Technical Report (Pirrone et al. 2000a). It would be unrealistic to say that the cycling of mercury, its emission, transformation and deposition is perfectly reproduced by the model, there are still processes which need to be better understood, among them, the role of the ambient aerosol and air-water exchange would head the list; however it is clear that even when empirical or parameterised approaches have had to be used due to a lack of theoretical studies, the model does reproduce the trends in mercury concentration.

3.4.5.3 Integrated Modelling System Developed at GKSS, Germany

A comprehensive mercury modelling system using the Eulerian reference frame of the Acid Deposition and Oxidant Model (ADOM) has been developed under the Canada-Germany Science & Technology Co-operation Agreement and applied within the European Union Marine Science and Technology – Baltic Sea System Study (MAST-III-BASYS) and the Environment & Climate project Mercury Species over Europe (MOE), to study the regional transport and deposition fluxes of atmospheric mercury species. The cloud mixing, scavenging, chemistry and wet deposition modules of the Acid Deposition and Oxidants Model (ADOM), originally designed for regional-scale acid precipitation and photochemical oxidants studies (Venkatram et al., 1988; Misra et al., 1988) have been restructured to accommodate recent developments in atmospheric mercury chemistry. A stand-alone version of these modules referred to as the Tropospheric Chemistry Module (TCM) was designed to simulate the meteorology and chemistry of the entire depth of the troposphere to study cloud mixing, scavenging and chemical reactions associated with precipitation systems that generate wet deposition fluxes (Petersen et al., 1998). The TCM chemistry scheme was developed by systematic simplification of the detailed Chemistry of Atmospheric Mercury (CAM) process model, which is based on current knowledge of physico-chemical forms and transformation reactions of atmospheric mercury species (Pleijel and Munthe, 1995).

After comprehensive testing under different environmental conditions the TCM has been implemented into the full ADOM model. Within the constraints of the available computer resources and input data, these models incorporate an up-to-date understanding of the detailed physical and chemical processes in the atmosphere. The vertical grid consists of 12 unequally spaced levels between the surface and the top of the model domain at 10 km. The model is run for a grid cell size 55 by 55 km (High Resolution Limited Area Model (HIRLAM) grid) over a 76 by 76 domain.

The major modules making up the mercury version of ADOM together with the model input data sets are schematically depicted in Figure 3.15. The transport and diffusion module uses a sophisticated cell-centered flux formulation solver for the 3-dimensional advection-diffusion equation. Dry deposition is modelled in terms of a deposition velocity for gaseous and particle associated mercury species, which is calculated as the inverse of the sum of the aerodynamic, deposition layer and surface canopy resistance. The mass transfer, chemistry and adsorption component of the model is illustrated in Figure 3.16. It incorporates 14 mercury species and 21 reactions including mass transfer (R1-R5), aqueous phase (R6-R17) and gas phase (R20-R21) chemical reactions and adsorption processes on particles (R18-R19). The reaction rates are derived from published data and from assumption of the rates of complex formation. The cloud physics module simulates the vertical distribution of mercury species in clouds. Two different modules are incorporated: one describes stratus (layer) clouds and the other simulates cumulus (convective) type clouds. One or the other or a combination (cumulus deck embedded in a stratus cloud) is used in the calculation depending on the characteristics of the precipitation observed.

The details of each module comprising the original ADOM version for acid rain studies are given in ERT (1984). The development and testing of the mercury wet scavenging module consisting of cloud physics and mercury gas and aqueous phase chemistry sub-modules is described in detail in Petersen et al. (1998).

The database for anthropogenic mercury emissions in Europe employed in the model calculations has been compiled for 1995 (Pacyna et al. 2001). The emission rates and their spatial distribution in the model grid depicted in Figure 2.5 of Chapter 2 and are based on location and capacity of their dominating source categories such as combustion of fossil fuels in power plants, non-ferrous metal smelters, waste incinerators, chlor-alkaline factories and other industrial installations.

The meteorological input data needed by ADOM are three-dimensional fields of wind speed, wind direction, pressure, temperature, relative humidity, vertical velocity and vertical diffusivity, and two-dimensional fields of surface winds, surface pressure, surface air temperature, friction velocity, Monin-Obukhov length, mixing height, cloud base and top height, amount of cloud cover and the amount of precipitation at every one hour model time step. These data sets are derived diagnostically using the weather prediction model HIRLAM. The geophysical data include files for 8 land use categories (i. e. deciduous forest, coniferous forest, grassland, cropland, urban, desert, water and swamp) and 12 soil categories. The database also includes information on terrain height and the growing season. This geophysical data affects meteorology, dry deposition processes and air-surface exchange of gaseous mercury species.

Initial and boundary conditions are needed for all advected species in the model. This includes the emitted compounds and mercuric oxide (HgO) formed by gas phase oxidation of Hg⁰. A typical European background mixing ratio of 0.18 ppt corresponding to a mass per unit volume concentration of about 1.5 ng m⁻³ is used for Hg⁰ in the atmospheric boundary layer (layers 1-4 in the vertical model grid) with a slight vertical mixing ratio decrease of approximately 80% of the boundary layer value at the top of the modelling domain. Observations for mercury species other than Hg⁰ are still scarce in Europe and vertical profiles are not available at all. Therefore, initial and boundary concentrations of 2 pg m⁻³, and 20 pg m⁻³ estimated to be average values from a limited number of observations in Europe are used for HgCl₂ and Hg(part.) in the boundary layer. Due their relative short atmospheric residence time and due to anthropogenic emissions occurring near the ground concentrations of HgCl₂ and Hg(part.) are allowed to decrease with height to a value of about 10 % of the boundary value at the model top. In addition to HgCl₂, boundary concentrations for HgO are also given. HgO is believed to be the initial product from the gas phase reaction with Hg⁰ and O₃ and is included in the chemistry scheme employed in the model. No information on ambient air concentrations of HgO or its physical/chemical properties such as Henry's law constant are available. For this reason, HgO is treated using the same parameterisation as for HgCl₂, believed to be the main gaseous divalent species in the atmosphere. In the absence of reliable measurement data, a very low initial value of 0.7*10⁻⁶ pg m⁻³ constant with height is used for HgO. The more realistic initial value for HgCl₂ (2 pg m⁻³) is thus assumed to represent all divalent mercury compounds in the boundary air masses. The mercury chemistry in ADOM, described in Petersen et al. 1998, requires the specification of O₃, SO₂, and soot carbon concentrations in ambient air as well as Cl⁻ concentrations in cloud water and cloud water pH. For the results with the European version of ADOM, the concentrations of O₃, SO₂, and soot carbon were fixed at 35 ppb, 1 ppb and 1 microgram per m³. The cloudwater concentration of Cl⁻ and the cloudwater pH were specified as 2*10⁻⁶ mol l⁻¹ and 4.5, respectively.

As an example for model applications in Europe, Figures 3.17, 3.18 and 3.19 show calculated Hg⁰, HgCl₂ and Hg(part.) air concentration patterns study averaged over the entire month of November 1998. As expected the maximum concentrations of all three species are closely

related to the source areas. Concentration values of Hg^0 generally range from about 1.2 ng m^{-3} in remote locations to 2.2 ng m^{-3} in the main emission area in Central Europe. The concentration pattern of Hg^0 is substantially elongated towards Eastern Europe, i. e. in the direction of the mean wind during that month. In the main emission areas, concentrations of HgCl_2 and $\text{Hg}(\text{part.})$ are about two orders of magnitude lower than Hg^0 concentrations due to lower emission rates of these species. Due to rapid dry and wet deposition close to sources the HgCl_2 concentration pattern (Figure 3.17-a) clearly reflects the spatial emission distribution of that species. The $\text{Hg}(\text{part.})$ concentration pattern (Figure 3.17-c) is influenced by both $\text{Hg}(\text{part.})$ emissions and secondary formation of $\text{Hg}(\text{part.})$ at the end of the life cycle of non-precipitating clouds when dissolved mercury species are evaporated back to particulate mercury.

The dry deposition fluxes shown in Figure 3.17-d denote the sum of Hg^0 , HgCl_2 and $\text{Hg}(\text{part.})$ deposition across the entire model domain. As can be seen, dry mercury deposition fluxes mainly occur over land surfaces with elevated levels in the major emission areas. The reason for that is twofold: First, due to its very low solubility the dry deposition rate of Hg^0 to all surfaces was set to zero except forests where dry deposition velocities in the range of 0.001 to 0.03 cm s^{-1} have been determined from experimental studies (Iverfeldt, 1991b, Lindberg et al., 1991). Second, HgCl_2 and $\text{Hg}(\text{part.})$ are readily dry deposited in the vicinity of sources resulting in very minor dry deposition over sea areas.

For precipitating clouds, the total monthly wet deposition flux depicted in Figure 3.18-a is derived by summing up the product of the hourly average cloud water concentration of all aqueous species (AQ(1) – AQ(10) in Figure 3.18-c) and the hourly precipitation amount over the entire month. As expected, wet deposition is determined by the precipitation distribution (Figure 3.18-b) and to a certain extent by the concentrations of mercury species in ambient air (see Figure 3.18) yielding a deposition pattern that comprises areas of high precipitation amounts as well as areas of elevated levels of Hg^0 , HgCl_2 and $\text{Hg}(\text{part.})$ concentrations in ambient air.

Concerning the physicochemical composition of mercury in cloudwater and precipitation, the scheme shown in Figure 3.16 is based on the assumption, that the total wet deposition flux $\text{Hg}(\text{tot.})$ can be divided into a dissolved fraction $\text{Hg}(\text{diss.})$ and a fraction adsorbed on particles $\text{Hg}(\text{ads.})$ depicted in Figure 3.18-c and Figure 3.18-d, respectively. The very distinct pattern in these two figures clearly reflect the design of two important and sensitive parts of the scheme:

In general, $\text{Hg}(\text{diss.})$ and $\text{Hg}(\text{ads.})$ are based on an equilibrium relation depending on gaseous and aqueous species concentration and rate expressions (R1-R21). However, in areas of relative high HgCl_2 (G(2)) concentrations in ambient air (i.e. close to major sources) the equilibrium is shifted towards a higher $\text{Hg}(\text{diss.})$ fraction and hence a relative high $\text{Hg}(\text{diss.})$ deposition flux as shown in Figure 3.18-d, since HgCl_2 is very water soluble and the mass transfer rate of this species into the aqueous phase is much higher than the adsorption rate of aqueous HgCl_2 on particles. In areas of low HgCl_2 concentrations in ambient air (i. e. far from sources) the $\text{Hg}(\text{diss.})$ and $\text{Hg}(\text{ads.})$ equilibrium relation is more determined by Hg^0 (AQ(1)) and its oxidation products and by aqueous phase reactions of Hg^{2+} (AQ(8)) leading to the formation of complexes, namely HgCl_2 (AQ(2)), HgOHCl (AQ(9)) and $\text{Hg}(\text{SO}_3)^{2-}_2$ (AQ(7)). Compared to HgCl_2 the concentration level of Hg^0 in ambient air is almost uniform in areas far from sources and hence the deposition pattern in these areas is mainly governed by

precipitation, but elevated Hg^0 concentrations in source areas are also reflected to a certain extent (see Figure 3.17-a).

A comparison of Figure 3.17 and Figure 3.18 shows, that the total mercury deposition over Central Europe is dominated by wet deposition. The dry deposition of all mercury species, shown in Figure 3.17-d, indicates that over most of the main source areas in Central Europe the model estimated monthly dry deposition is in the range of 100 to 500 ng m^{-2} , whereas the wet deposition flux (Figure 3.18-a) exceeds 1000 ng m^{-2} despite relatively low precipitation amounts (less than 50 mm per month) in that area.

As an illustrative example for comparisons between model predicted and observed mercury concentrations in air, Figure 3.19 shows Hg^0 , HgCl_2 and $\text{Hg}(\text{part.})$ concentrations at the German monitoring stations of Zingst and Neuglobsow, respectively. The Hg^0 time series at Zingst are consistent with respect to time intervals, i.e. model predicted and observed hourly averages are compared. Observations and model predictions are in reasonable agreement. However, the model predicted time series shows some peak events with calculated hourly concentrations exceeding 3.0 ng m^{-3} . Almost coinciding peaks have also been observed but on a lower level, indicating that the model is capable to simulate elevated concentrations with a tendency of over-prediction most probably due to both overestimated emissions near the measurement site and underestimated vertical exchange of air masses in the grid cell in which the measurement site is located. Calculated $\text{Hg}(\text{part.})$ and HgCl_2 concentrations at Neuglobsow are also hourly averages, whereas the observed numbers are daily and 7 hours averages, respectively, due to the constraints in current measurement techniques. The agreement between model predictions and observations is fair for $\text{Hg}(\text{part.})$ but rather poor for HgCl_2 . However, the limited data material does not allow to draw any firm conclusions at present and a larger data set comprising additional time series from other measurement sites would be needed.

3.5 RECOMMENDATIONS

Therefore, in order to support the implementation of the new Mercury Directive in Europe there is a great need to improve our knowledge of certain specific aspects involved in the cycling of mercury on local and regional scales, these include:

- There is a strong need to promote measurement programs to assess the level of mercury and its compounds (Hg(0), Hg(II) and particulate Hg on a European scale and at major urban, industrial and remote sites.
- An improved mercury emission inventory for major anthropogenic sources, possibly on a 0.5 x 0.5 degree spatially resolved grid including North Africa and the Middle East regions.
- The role played by sea salt aerosol and sea spray formation in the cycling of mercury and its compounds in the MBL.
- Gas phase mercury and halogen containing radical kinetic studies.
- Exchange fluxes of gaseous mercury at the air-water, air-soil and air-vegetation interfaces with changing meteorological conditions and geophysical parameters.
- A better knowledge of the time-dependent vertical profile of Hg(0) concentrations at the model inflow boundaries in order to improve the modeling capability.
- To assess the relationship between the atmospheric input of mercury and its compounds to surface waters and the formation/production of the most toxic organic forms of mercury i.e., methylmercury, which have a significant impact on human health and the quality of the environment.
- There is a strong need to develop hemispherical/global models for a better assessment of the boundary conditions on regional scale.
- Intercomparison of the three modeling techniques currently used in Europe for assessing the spatial and temporal distribution of mercury and its compounds and to evaluate the relative contribution of each emission source category to the ambient level and deposition flux of mercury to terrestrial and aquatic receptors.

3.6 REFERENCES

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