MERCURY MODEL DEVELOPMENTS FOR REGULATORY PURPOSES

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ABSTRACT

In the recent years there has been a remarkable interest in mercury as an atmospheric pollutant due to its impacts on human health and the environment. Two large European research projects initially MAMCS and recently MERCYMS have been focused on investigating the mercury cycle in the atmosphere, understanding its physical and chemical properties and developing integrated atmospheric modelling systems for the description of the individual mercury processes and their interactions with the atmospheric and marine systems. This presentation deals with the latest developments of such modelling systems performed within the framework of MERCYMS project. In particular, RAMS atmospheric modelling system was used to perform sensitivity analysis on the factors that affect transport, transformation, deposition of atmospheric mercury and re-emission of mercury from natural sources, namely water and soil surfaces. Some preliminary results for the 24 July to 4 August 1999 evaluation period are presented.

INTRODUCTION

Mercury is a pollutant emitted to the atmosphere through various anthropogenic and natural sources. A remarkable interest has been raised over the last decades on investigating the mercury cycle in the atmosphere due to its harmful effects on human health and the environment. During the last years two large research projects, MAMCS and MERCYMS [1,2] funded by the European Union, focused on understanding its physical and chemical properties and developing integrated atmospheric modelling systems for the description of the individual mercury processes and their interactions with the atmospheric and marine systems.
A number of modelling studies on atmospheric mercury have been performed during the last years [3,4]. In this study latest model developments on atmospheric mercury cycle have been adapted in RAMS atmospheric modelling system. Modelling efforts where focused on implementing bi-directional atmosphere-surface exchange formulas describing the emissions from natural sources of mercury and reemissions proposed by Mackay and Yeun [5], Shannon and Voldner [6], Capri et al.,[7], and Xu et al. [8]. An attempt was also made to improve the wet and dry deposition schemes initially formulated at the framework of MAMCS project. Emphasis is given on the development of mechanisms describing the wet and dry deposition processes of mercury in the forms of particulate and divalent mercury. The area under consideration is Europe and the Mediterranean Sea Region. Simulations were performed using a wet deposition scheme based on the scavenging coefficient approach. In addition new dry deposition schemes for reactive mercury and mercury particles have been tested. The total deposition of all mercury species has been also calculated for the simulation period.

THEORETICAL CONCIDERATIONS

The various atmospheric and surface processes of mercury species implemented in RAMS model are briefly described below:

***a. Anthopogenic Emissions*:** The atmospheric emissions of mercury from anthropogenic sources in Europe [9] had been collected during MAMCS project [2] and updated at the framework of MERCYMS in the Mercury Emission Inventory (MEI).

***b. Natural Emissions-Reemissions-Atmosphere-surface exchange*:** Natural emissions and re-emissions were considered in the developed model and treated accordingly. Fluxes of mercury from soil and water have been considered constant at the previous version of the model. Mercury fluxes from soil are calculated at the presented version as a function of soil temperature [7,8] while for air-water exchange of mercury wind speed at 10m above surface, whitecap coverage, friction velocity and Hg^0 concentration in air and water were considered [5,6,8].

***c. Chemistry module*:** The modified chemistry module deals not only with the gas and aqueous phase chemistry reactions of mercury species with other reactants but also with photochemical, bimolecular and termolecular reactions that form these reactants. The photochemical reactions of O_3 and H_2O_2 both in aqueous and gaseous phase are treated within the chemistry module using the Fast-J scheme proposed by Wild et al. [10]. Other reactions include the bimolecular reactions of SO_x, CO and CO_2 with O_2, H_2O, OH and H_2O_2. The gas and liquid phase reactions of mercury considered in the chemistry module are those with ozone, hydrogen peroxide, chlorines and sulphite [11,12].

***c. Dry Deposition module*:** In most deposition models [13] the deposited quantity over a given surface is the product of the pollutant's concentration, at the first model layer and the deposition velocity. In the dry deposition process the velocity is calculated using the resistance method. The deposition velocity of Hg associated with particles, (Hg^p), was calculated by distributing its mass according to a lognormal particle size distribution. The geometric mass mean diameter and the geometric standard deviation were chosen to be 0.4 μm and 1.5 μm. The whole particle size distribution is subdivided into 15 size intervals and the deposition velocity is calculated for each one. Thus the deposition velocity of Hg^p is obtained as a weighted average of the previous velocities.

***d. Wet Deposition module*:** The wet removal process concerns the soluble chemical species (Hg^2 and its compounds), and also particulate matter scavenged only from below the precipitating clouds. Wet scavenging of the divalent mercury (Hg^2) is assumed to occur in and below clouds. As Hg^2 has similar aqueous solubility with HNO_3 [4] is assumed to be an irreversibly soluble gas and its scavenging coefficient is calculated accordingly [14]. In cloud Hg^2 can be removed from interstitial cloud air by dissolution into cloud drops.

PRELIMINARY VALIDATION

Several sensitivity experiments have been performed during the summer period 24 July to 3 August 1999 using the modified version of RAMS atmospheric model with all mercury processes included. Sensitivity tests performed to examine the influence of the atmosphere-surface exchange processes and the O_3 background concentrations implemented into the model are presented at the following section.

1. Sensitivity tests on atmosphere-surface processes

The air-soil exchange of elemental mercury has been investigated using the empirical functions proposed by Capri and Lindberg [7] also adopted by Xu et al. [8]. According to this proposed formula the net exchange rate of Hg^0 is linearly related with soil temperature. However the regression constants used are a=0.057 and b=-1.7 (case 1) for Capri and Lindberg [7] and a=0.064 and b=-2.03 (case 2) for Xu et al.[8] Both approaches have been implemented in RAMS and the differences are presented in Fig. 1. The mercury flux is negligible for soil temperature below 20^{o}C , while for higher soil temperatures mercury fluxes (ng/m^{2}h) in case 1 can be twice the fluxes estimated in case 2 as shown in Fig. 1a. These differences attributed to the mercury emitted from soil are also illustrated on the Hg^0 concentrations (Fig. 1b) calculated over several soil grid points. The calculated Hg^0 is approximately 0.1 ng/m^3 higher in case 1, indicating the influence of the regression constants used in the empirical functions. The approach finally adapted was the case 2 one as the known seasonally averaged concentrations of Hg^0 do not exceed 1.8 ng/m^3 [15].

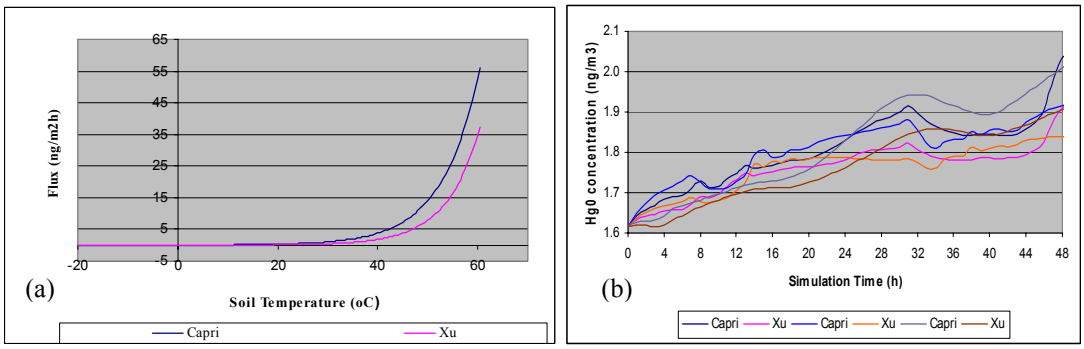

Fig. 1 : (a) Mercury flux (in ng/m^{2}h) dependence on temperature (^{o}C) using Capri et al, and Xu et al. empirical functions and (b) Modelled Hg^0 concentration (in ng/m^3) after 48h using Capri et aland Xu et al. (blue and purple lines respectively).

The air-water exchange of Hg^0 has been calculated by implementing either the formula proposed by Shannon et al. [6] (1st approach), or a combination of the Mackay and Yeun [5] and Xu et al. [8] expression (2nd approach). Following Shannon et al., [6] the air-water exchange rate is a function of sea surface temperature only. Mackay and Yeun [5] and Xu et al. [8] proposed a function where the liquid phase transfer coefficient depends also on the friction velocity and wind speed at 10m above the surface. Figure 2 illustrates the variations of the Hg^0 concentration following both expressions at specific grid points over soil and over sea. The calculated values of Hg^0 (Figs 2a,b) are much higher in both cases, almost twice over sea (Fig. 2b), using 1st approach, indicating the effect of air-surface exchange fluxes when calculating the Hg^0 concentration. The effect of wind at 10m above surface on Hg^0 concentration using the 2nd approach is pronounced in Fig. 2c.

Fig. 3 illustrates also this effect of wind speed at 10m above surface on mercury fluxes over sea calculated using the 2nd approach over the whole domain. A large amount of mercury is re-emitted over the eastern Mediterranean Sea Region (Fig. 3b) and southern Italy where strong winds prevail (Fig. 3a). The re-emitted amount during the simulation period is greater over the eastern Mediterranean Sea Region in both scenarios than the one re-emitted from western part. This path follows the general pattern of transport where the atmospheric circulation is persistent to the North to South transport.

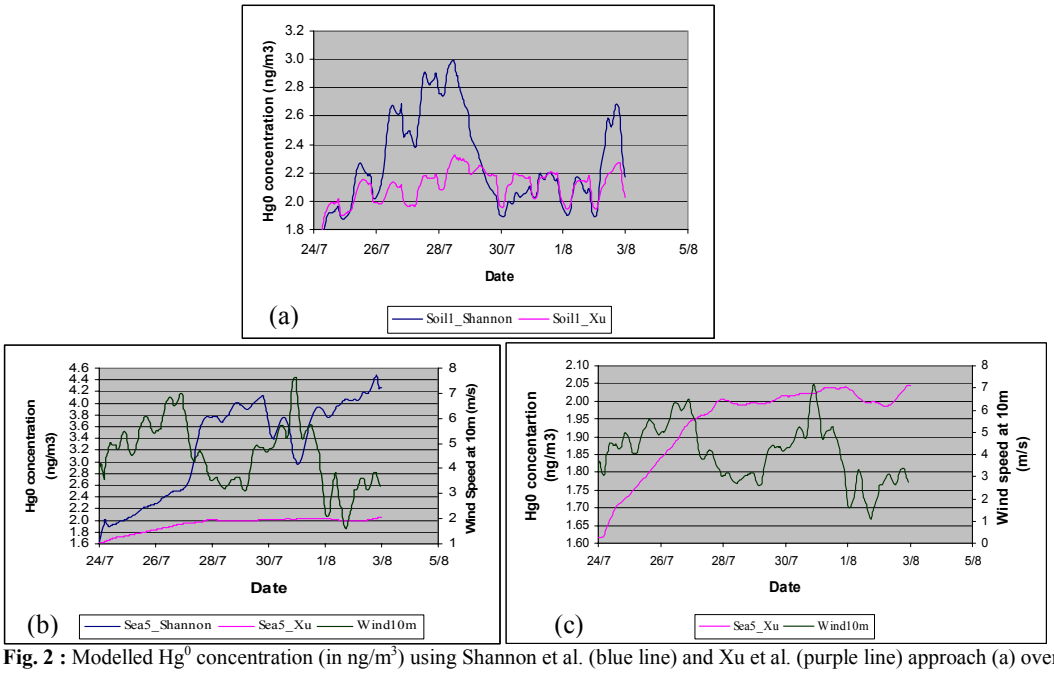

Fig. 2 : Modelled Hg^0 concentration (in ng/m^3) using Shannon et al. (blue line) and Xu et al. (purple line) approach (a) over land (b) over water, 10m wind speed (in m/s, green line) is also indicated (c) over water using Xu et al. and 10m wind speed (in m/s, green line).

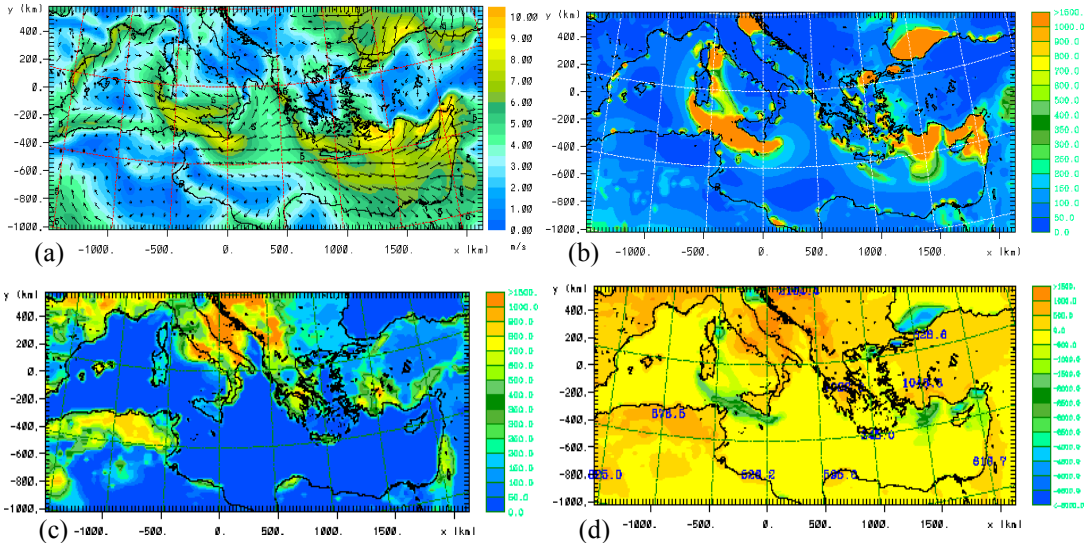

Fig. 3: (a) Wind speed at 10m over surface (in m/s) and (b) accumulated reemission of Hg^0 (in ng/m^2) using Xu et al. approach (c) Total deposited mercury (in ng/m^2) (d) Mercury Budget (Deposited-Emitted) (in ng/m^2) for the simulation time period 24 Jul-3 Aug. 1999. From the RAMS model.

On the contrary the deposited amount of mercury, mainly affected by wet deposition, is much higher over land (Fig. 3c) than over sea, where higher amounts of precipitation are predicted during the simulation period. This leads to a 'negative' mercury budget (blue to yellow colour in Fig. 3d) extracted out from differences on deposited-emitted mercury over the Mediterranean Sea region and a positive mercury budget over land (orange colour in Fig. 3d). This pattern may vary with the prevailing synoptic weather conditions. However an attempt was made to calculate the mercury budget in order to evaluate the model performance. Longer period simulations are required for deriving reliable conclusions on the net budget.

2. Sensitivity tests on O_3 background concentrations

The sensitivity of the model results to the variability of tropospheric O_3 is investigated here. Experiments showed that the predicted concentrations of Hg^0 and Hg^P are relatively sensitive to the predefined value of lower tropospheric O_3. Reduction of O_3 (occurs during winter), results in increasing Hg^0 and decreasing Hg^P as illustrated in Fig. 4. The opposite occurs when O_3 increases (e.g. during summer). The control experiment has been performed with 20 ppb O_3 background concentration while the background value of 60 ppb has also been examined. These results are consistent with the known photochemistry of mercury as Hg^0 is known to react with O_3 both in gas [16] and aqueous phase [12]. The products in each reaction are Hg^P and Hg^2 respectively (Figs 4b and 4c).

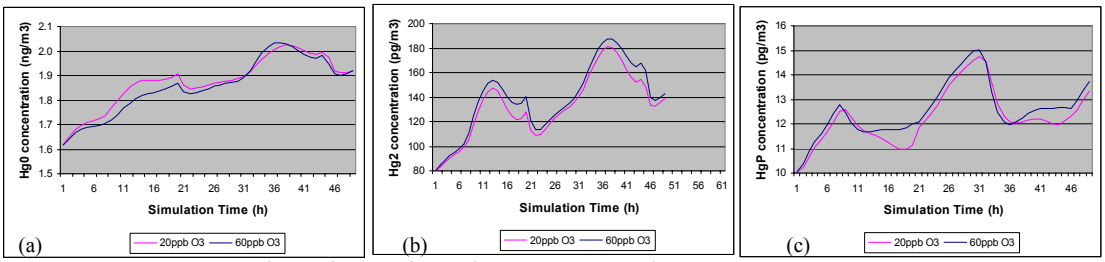

Fig. 4 (a) Concentration of Hg^0 (ng/m^3) (b) Hg^2 (pg/m^3) and (c) Hg^p (pg/m^3) in July 1999. The blue line represents background ozone 60 ppb and purple line ozone 20 ppb.

These preliminary results indicate a good performance of the implemented chemistry module. Further sensitivity tests are required in order to investigate the effect of the background concentrations of other reactants such as hydrogen peroxide, sulphites and chlorines on mercury concentration.

CONCLUSIONS

Sensitivity experiments have been performed using the modified version of RAMS atmospheric model with all mercury processes included. The developed model is able to describe adequately the transport, transformation and deposition of mercury due to the coupling of the atmospheric model with the chemistry, photolytic and bi-directional formulas. The use of detailed meteorological variables such as temperature, wind speed, sea surface temperature can lead to more reliable calculations of the re-emitted quantities. Furthermore estimating Hg^0 emissions from natural sources and re-emissions using atmospheric models, in addition to the wet and dry deposition calculations also implemented, can be useful in Hg budget calculations. The experience gained so far showed that these calculations are more sensitive to the physical rather than the chemical processes.
However further model testing is required for the chemical processes induced to this version, as elemental mercury is converted through this mechanism to divalent and mercury in the particulate phase. Divalent mercury and mercury in the particulate phase are subsequently removed by wet and dry deposition leading to the increase/decrease of total mercury budget calculations.

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