MODELLING OF MERCURY CYCLING IN THE MEDITERRANEAN SEA

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Abstract

The 3D hydrodynamic and transport model PCFLOW3D was upgraded with a biogoechemical module and linked to the atmospheric model RAMS-Hg to simulate mercury cycling in the Mediterranean Basin. Transport, transformations and fluxes of three mercury species in the water compartment were simulated: elemental mercury (Hg^0), divalent mercury (Hg^{2+}) and monomethyl-mercury (MMHg). The model results show acceptable agreement with measurements for elemental and total Hg. Further improvements of the model and additional measurements are needed to improve the agreement of monomethyl-mercury behaviour. On the basis of measurements and modelling a mass balance of mercury for the Mediterranean Sea was calculated.

Keywords : Air-sea Interactions, Circulation Models, Geochemical Cycles, Pollution, Mercury.

During the last decades several studies have been conducted in the Mediterranean area in order to assess the state of Hg pollution. The atmospheric processes and fluxes between the air and the sea were mostly studied [1, 2]. Among many different Hg species, the mono-methylmercury is the most dangerous. It can be bioaccumulated and biomagnified and as such it is harmful to the entire food-web. The problem is assessed by measurements and modelling. In the frame of the EU project MERCYMS (Contr.No. EVK3-CT-2002-00070) several coastal and deep-sea measurement campaigns were performed to gather the data needed for the modelling purpose. Measurements from previous campaigns [3] were also used. The appropriate approach for simulating Hg processes in the water compartment requires the use of a hydrodynamic model with additional modules for transport-dispersion and biogeochemistry. The model PCFLOW3D [4, 5] has been upgraded with a biogeochemical module and used for simulations of Hg transport and transformation processes. The circulation for the four seasons due to wind, thermohaline forcing and inflow momentum of the main rivers and through the straits has been calculated. The results were compared with the measurements and the results of another model (POM - Princeton Ocean Model). An acceptable agreement has been achieved. The obtained seasonally averaged velocity fields were used to simulate transport and dispersion of mercury.

The new biogeochemical module deals with three mercury species: elemental (Hg^0), divalent (Hg^{2+}), and mono-methylmercury (MMHg) in dissolved and particulate form. Exchange of Hg at the boundaries (sediment/water and water/atmosphere) and transformation processes (methylation, demethylation, reduction and oxidation) were simulated. The transformation rates between the mercury species are described using simple equations, thus the time and space variable reaction coefficients should be determined from in-situ measurements. Instead, machine learning tools were used to connect the measured sets of geophysical / environmental parameters and the concentrations of Hg species. The established provisional annual Hg mass balance for the Mediterranean showed that the exchange with atmosphere is the most important source / sink of mercury for the water compartment. The model has been further upgraded with a gas exchange module for Hg^0. To improve the results of simulations the PCFLOW3D model was linked to the RAMS-Hg atmospheric model [6] which provided real-time meteorological data, deposition and concentrations of mercury in the atmosphere.

The results of the integrated air-water model simulations were compared to the measurements. An acceptable agreement of the average concentrations along the water column for both total mercury (HgT) and elemental mercury (Hg^0) was achieved. Agreement of Hg^0 concentrations near the surface was good, thus, exchange with the atmosphere can be simulated with relatively high reliability. Agreement of simulated MMHg concentrations with measurements was not satisfactory, which is probably due to poor understanding of processes for MMHg formation and its dependence on environmental factors, which have, so far, not been taken into account in the modelling.

Due to acceptable modelling results obtained for HgT, simulation of management scenarios, particularly the policy target scenarios for 2010 and 2020 was performed. These results were used to determine the mass balance of Hg in the Mediterranean Sea and to simulate future trends of mercury contamination in the area. The following terms were taken into account: sources of mercury from major rivers and from point sources, exchange with the Atlantic Ocean and the Black Sea, estimated natural sources from geotectonic active areas in the sea, exchange with bottom sediments, and evasion to and deposition from the atmosphere.

The main conclusions are summarized as follows:

(a) Based on the measurements, HgT concentrations in the Mediterranean Sea in 2005 was about 1.5 pM. Thus the total mass of HgT in the Sea was about 5400 kmol (1080 tons).

(b) The outflow of HgT exceeds the inflow for about 46 kmol/yr. This indicates that the Mediterranean Sea is slowly recovering from mercury pollution. However, this also shows that the Mediterranean is a net source of HgT for the atmosphere and the connecting seas.

(c) The main sources are (in kmol/yr): atmospheric deposition (115), river inflow (68.5), and the bottom sediment (75, includes estimated contribution of underwater geotectonic sources), while point sources of mercury are estimated to 12.5 kmol/yr. The main outputs are: evasion to atmosphere (249), and burial in the bottom sediments (55). The net outflow through Gibraltar is about 8.5 kmol/yr, while the Black Sea seems to be a very small source of HgT to the Mediterranean.

(d) Some of the important terms in the mass balance equation were obtained by rough estimates. For this reason the prediction for 2020, based on policy target scenarios, can only be given in a wide range. It is expected that HgT concentration will decrease for about 3 to 12 % compared to 2005.

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