# MATHEMATICAL MODELLING OF MERCURY TRANSPORT AND TRANSFORMATIONS IN THE MEDITERRANEAN

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Due to its toxicity and bioaccumulativity mercury, particularly in monomethylated form (MMHg) represents potential danger for the whole food-web and humans at its end. In the Mediterranean elevated concentrations of mono-methyl mercury in fish tissue have been measured during the last decades. The methylation of Hg mostly occurs in the aquatic environment. As the Mediterranean Basin is highly heterogeneous regarding its climate and oceanographic properties, the appropriate approach to simulate the transport and transformations of Hg requires the use of a hydrodynamic model with additional modules for transport-dispersion and biogeochemistry.

An existing non-steady state 3D model PCFLOW3D (Rajar et al., 2004) has been upgraded and used for simulations of mercury transport and transformation processes. The circulation for the four main seasons due to wind forcing, thermohaline forcing and inflow momentum of the main rivers and through the straits has been calculated and an acceptable agreement with the measured values (MODB – Mediteranean Oceanographic Database) and the results of the POM model (Zavatarelli and Mellor, 1995). Transport and dispersion of the total mercury has been simulated with seasonally averaged velocity fields. The results of a one-year season by season simulation of spreading of mercury from the four main Rivers (Po, Ebro, Rhone, Nile) and seven hot-spots showed that mercury concentrations still remain much higher near the pollution sources.

The new biogeochemical (BGC) module deals with three different mercury species: elemental ($Hg^0$), divalent ($Hg^{2+}$), and mono-methyl (MMHg) mercury, in dissolved, particulate, plankton and gaseous form (Fig. 1). Concentrations of each mercury species due to advection and dispersion are previously calculated by the hydrodynamic and the transport dispersion module, while the BGC module calculates some of the transformation processes. Exchange with the bottom sediment, exchange with the atmosphere, methylation, demethylation, reduction and oxidation can be taken into account. The transformation reactions are described by very simple equations; in each control volume the source term in advection-dispersion equation for each of the Hg species was calculated as

$$\Delta M_i = K_r * M_r,$$

where $\Delta M_i$ represents change in mass of reaction product ($Hg^0$, $Hg^{2+}$ and MMHg, respectively), $K_r$ are reaction coefficients (methylation, demethylation, oxidation and reduction, respectively) and $M_r$ is the mass of reactant. Due to complexity of the processes and simplicity of equations the time and space variable reaction coefficients ($K_r$) had to be determined from in-situ measurements. The calibration of the BGC module is still in progress; machine learning tools (regression trees) and classical statistical methods are being used to connect the environmental parameters and concentrations of different Hg species. However, the main relations between reaction rates and the most significant oceanographic parameters can be seen clearly.

The established annual Hg mass balance for the Mediterranean showed that exchange with the atmosphere is the main source / sink of mercury and the model has been further upgraded with a gas exchange module for $Hg^0$. Evasion of $Hg^0$ in gaseous form is calculated as described by Wanninkhof (1992), on the basis of known Hg concentrations in water and in the air, wind speed and surface water temperature.

Simulations for typical conditions during the three winter months with improved model were performed and high significance of the evasion process was confirmed. In order to improve the results of simulations the aquatic model used for mercury cycling simulations in the Mediterranean should be coupled to a reliable meteorological model, possibly equipped with a module for transport and transformations of different mercury species in the air compartment. The RAMS / SKIRON modelling tool, described by Kallos et al. (2001) meets all the above requirements and the two models are being linked. The PCFLOW3D model should provide Hg concentrations and water temperature of the surface layer of water, while the atmospheric model will give the concentrations of Hg in the bottom layer of the atmosphere, wind speed as well as wet and dry deposition of different mercury species.

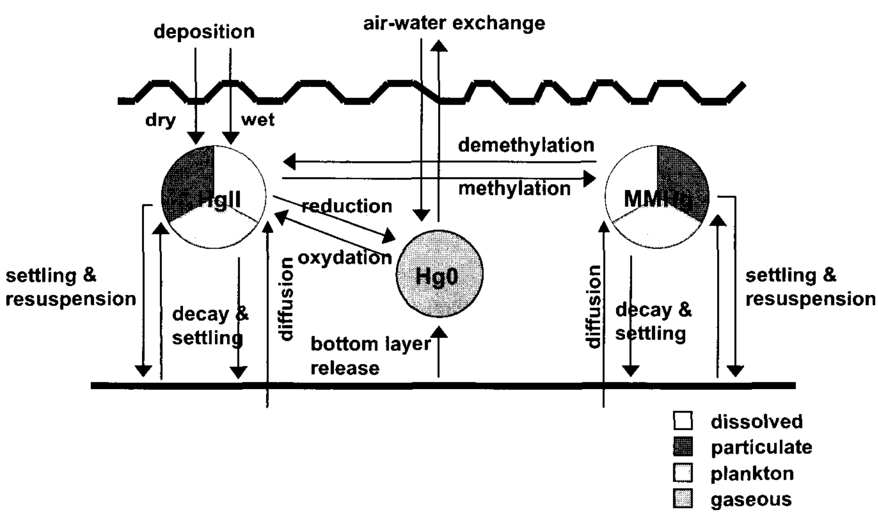


Fig. 1 Biogeochemical module of the PCFLOW3D model

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