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Mercury in the Black Sea: new insights from measurements and numerical modeling

Ginevra Rosati (1), Lars-Eric Heimbürger (2), Donata Melaku Canu (1), Christine Lagane (3), Laure Laffont (3), Micha J. A. Rijkenberg (4), Loes J. A. Gerringa (4), Cosimo Solidoro (1,5), Christian N. Gencarelli (6), Ian M. Hedgecock (6), Hein J. W. De Baar (4), and Jeroen E. Sonke (3)

(1) OGS, National Institute of Oceanography and Experimental Geophysics, OCE Research Section, ECHO group, Trieste, Italy (grosati@ogs.trieste.it), (2) Aix Marseille Université, CNRS/INSU, Université de Toulon, IRD, Mediterranean Institute of Oceanography (MIO) UM 110, 13288, Marseille, France, (3) Observatoire Midi-Pyrénées, Laboratoire Géosciences Environnement Toulouse, CNRS/IRD/Université Paul-Sabatier, Toulouse, France, (4) NIOZ, Royal Institute for Sea Research, department of GCO, and Utrecht University, Den Burg, the Netherlands, (5) ICTP, The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, (6) CNR, Institute of Atmospheric Pollution Research, Division of Rende, UNICAL-Polifunzionale, Rende, Italy

The conversion of inorganic mercury (Hg^{II}) to neurotoxic methylmercury (MeHg) is related to organic matter remineralization in water and sediment. Major biogeochemical controls on Hg methylation are the bioavailability of inorganic Hg and the composition and activity of the microbial community, which are in turn dependent on redox conditions and organic matter abundance and quality. The Black Sea, which is the largest and deepest anoxic basin in the world, is an ideal site to study metals speciation along the extended redox gradient. We sampled high resolution full water profiles during the 2013 GEOTRACES MEDBlack cruise (GN04_leg2). In contrast with a previous study, we detected the highest MeHg concentrations in the permanently anoxic waters. Remarkably, MeHg in the anoxic waters of the Black Sea is on average 22% of total Hg (range 9 – 57%), which is comparable to other subsurface maxima detected in oxic open-ocean waters. Hg species data together with literature information were integrated into a 1D numerical model, to track the fate and dynamics of Hg and MeHg. Sensitivity analysis was performed to deal with the most uncertain processes (i.e. partition coefficients and riverine load). Different model scenarios were explored, by varying the configuration of Hg methylation and demethylation processes along the redox gradient. We simulated dynamic temporal evolution (1850 – 2050) of Hg and MeHg concentrations and fluxes. In spite of a reduction in anthropogenic Hg input since the 1970s, both Hg and MeHg concentrations in the anoxic waters do not recover, and they rather show a slightly increasing trend. The increase of concentrations in the anoxic waters is triggered by the biogeochemical barrier created by precipitation of Mn oxides in the suboxic waters, which prevent upward diffusion of dissolved Hg species through adsorption. Moreover, according to our budget, Hg_T inputs to the Black Sea (32 ± 2.5) exceeds the output (21 ± 2.8) and thus the system is not expected to recover, unless input from the watershed are substantially reduced. Model results allowed us to quantify the extent of net MeHg demethylation occurring in oxic and suboxic waters ($\sim$5 kmol/y), as well as net Hg methylation in the anoxic waters of the Black Sea ($\sim$8 kmol/y). Another simulation was setup to model the natural pre-anthropogenic cycle of Hg, and estimate the amount of natural (7% - 15%) versus anthropogenic (85 – 93%) Hg in the Black Sea.