

METHYLMERCURY IN THE BLACK SEA: NEW OBSERVATIONS COMPARED WITH A 1D NUMERICAL MODEL

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Abstract

Here we present the results of a 1D mercury (Hg) model implemented to the Black Sea based on the results of the 2013 GEOTRACES MEDBlack cruise. We discuss the observed vertical profiles of Hg and methylmercury (MeHg) in the water column as well as preliminary model results, providing interesting insights into the Hg dynamics and Hg methylation process along the redox gradient.

Keywords: Models, Black Sea, Mercury, Vertical profile, Anoxic basin

Concern has been raised about possible implications for ecosystems and human health from anthropogenic Hg emissions, that may enhance the production of the toxic and bioaccumulating MeHg species. MeHg production is thought to be a microbially mediated process, related to the remineralization of organic matter (OM) in marine sediments and the water column [1]. In addition to initial HgII concentrations [2], microbial and redox conditions as well as OM quantity and quality, may determine MeHg production. Sedimentary MeHg data and equilibrium modeling suggest that at high sulfide levels (<10 μM) methylation is hindered due to reduced Hg availability to microbes [3] but this theory has been debated [4]. The Black Sea water column is permanently stratified, with anoxic sulfidic deep waters and a large suboxic layer. Thus, it is an ideal site to investigate on the relations among OM oxidation and Hg dynamics under changing redox conditions. We collected vertical profiles of Hg and MeHg, nutrients and other dissolved metals along an E to W transect in the southern Black Sea. Analysis of MeHg and Hg samples were performed according to [5]. Our new data were integrated with literature data to implement a fate and transport 1D-model for Hg and MeHg [6]. We compiled the Hg budget and simulated present day conditions. To investigate the vertical profile of MeHg, we performed scenario analysis, imposing the occurrence of methylation at different depths in each scenario and comparing modeled MeHg profiles with observations. Methylation rates in oxic, suboxic and anoxic environment were taken from the literature. For both Hg and MeHg, we observe peak concentrations in the upper part of the anoxic zone, tightly coupled to Mn and Fe peaks (Fig. 1).

Observed vertical profiles hint that most of the Hg is scavenged by OM and Mn oxides and transported to deeper waters, where it is released during the concomitant reduction of Mn and OM oxidation. MeHg may be either regulated by mechanisms similar to Hg or be produced *in situ* in the anoxic layer. A previous study in the Black Sea [7] found a maximum of MeHg in the suboxic layer, likely due to the different analytical method. On the other hand, high MeHg levels in sulfidic water were observed by others [8],[9]. Preliminary model results show that input of MeHg from watershed and system boundaries cannot explain the observed MeHg levels. The best fit between modeled and measured MeHg is achieved when methylation is set either in the whole water column with variable rates or only in the anoxic zone.

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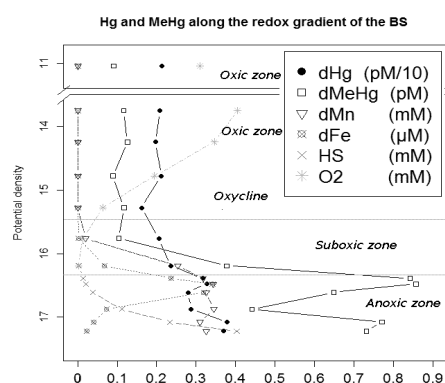


Fig. 1. Horizontally averaged ($n=10$) vertical profiles of dissolved Hg, MeHg, Mn and Fe in relation to redox conditions in the Black Sea, as detected during the GEOTRACES MEDBlack cruise (July 2013). Data show concentrations in the whole water column up to 2200 m depth. Potential density is used as y-axis (note the break in the axis).