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Numerical modelling of mercury evasion in a two-layered Adriatic Sea using a coupled atmosphere-ocean model

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ABSTRACT

A new mercury (Hg) evasion model for the Adriatic Sea was developed accounting for the ocean mixed layer depth in order to decrease Hg depletion at the surface. Previously modelled airborne Hg species and measured Hg in the ocean were used. Simulations were run using one- and two-way coupled atmosphere-ocean models. Discrepancies in evasion between the applied coupling schemes were shown to be insignificant. The model was evaluated by applying various wind parameterisations and diffusive coefficient formulae. Relatively high discrepancies among the applied methods were observed. The results of a shorter simulation were extrapolated over a one-year period by applying a measurement-based adaptation. We obtained good agreement with previously published data on Hg evasion in the entire Mediterranean area, thus confirming the suitability of the new model for Hg evasion simulations. Model computations performed for the Adriatic Sea resulted in levels of evasion approximately two times lower than previously estimated.

1. Introduction

Due to its toxicity and increased concentrations in all environmental compartments mercury (Hg) is a potent problem in the Mediterranean area. From its reactive form Hg can transform into a gaseous elemental form (*DGM*) or monomethyl mercury (*MMHg*). The former is partially subject to volatilisation and evasion from the water compartment, while the latter can enter the food chain. Levels of *MMHg* in fish in the Mediterranean are severely increased, affecting marine organisms and human health (Cinnirella et al., 2013a; Cinnirella et al., 2013b; Llull et al., 2017; Spada et al., 2012; Žagar et al., 2014). In recent decades numerous research projects have been dedicated to Hg speciation in the ocean and in the atmosphere in this region. As reported by Kotnik et al. (2017) and the references therein, nine oceanographic cruises were made in the last 15 years as part of MEDOCEANOR, MERCYMS, GMOS, and other research projects dedicated to Hg pollution in the Mediterranean Sea. Predictions of future Hg emissions from anthropogenic and natural sources were established based on various policy-driven scenarios (Pacyna et al., 2010; Streets et al., 2009). Furthermore, several numerical models were developed and used to assess the temporal and spatial variability of Hg species in different environmental compartments (Hedgecock et al., 2005; Holmes et al., 2010; Rajar et al., 1997; Rajar et al., 2000; Ramšak et al., 2013; Žagar et al., 2007; Žagar et al., 2014). Based on measurements and model results the annual Hg mass balances of the entire Mediterranean as well as of the Adriatic Sea and the Gulf of Trieste were computed in order to quantify the most important sources and sinks of Hg for the ocean (Kotnik et al., 2015; Rajar et al., 2007; Širca et al., 1999; Žagar et al., 2014). The established Hg mass balances of the Adriatic Sea (Kotnik et al., 2015) and of the Mediterranean (Rajar et al., 2007; Žagar et al., 2014) depicted the ocean–atmosphere flux as the largest sink term for the ocean. Therefore, it is of utmost importance to quantify, as correctly as possible, the exchange processes in order to assess the quantity of Hg available for transport and transformations within the Mediterranean Sea and/or its parts. Hg deposition was modelled throughout the entire oceanic area and measured at numerous coastal sites (De Simone et al., 2016; Gencarelli et al., 2015; Hedgecock et al., 2006; Hedgecock et al., 2005; Žagar et al., 2007), while the evasion was measured by flux chambers during the cruises and coastal campaigns (Bratkič et al., 2013; Mastromonaco et al., 2017 and the references therein). Gas exchange models (GEM) were introduced to better understand the exchange processes and to extrapolate the measured evasion over the entire area (Andersson et al., 2007; Andersson et al., 2008; Fantozzi et al., 2007; Gårdfeldt et al., 2003; Mastromonaco et al., 2017). Furthermore, both the GEMs and the sampling results were used in various numerical models, either as the input data or for calibration and validation of the models (De Simone et al., 2014; Gencarelli et al., 2014; Hedgecock et al., 2006; Žagar et al., 2007; Žagar et al., 2014). Comparable results

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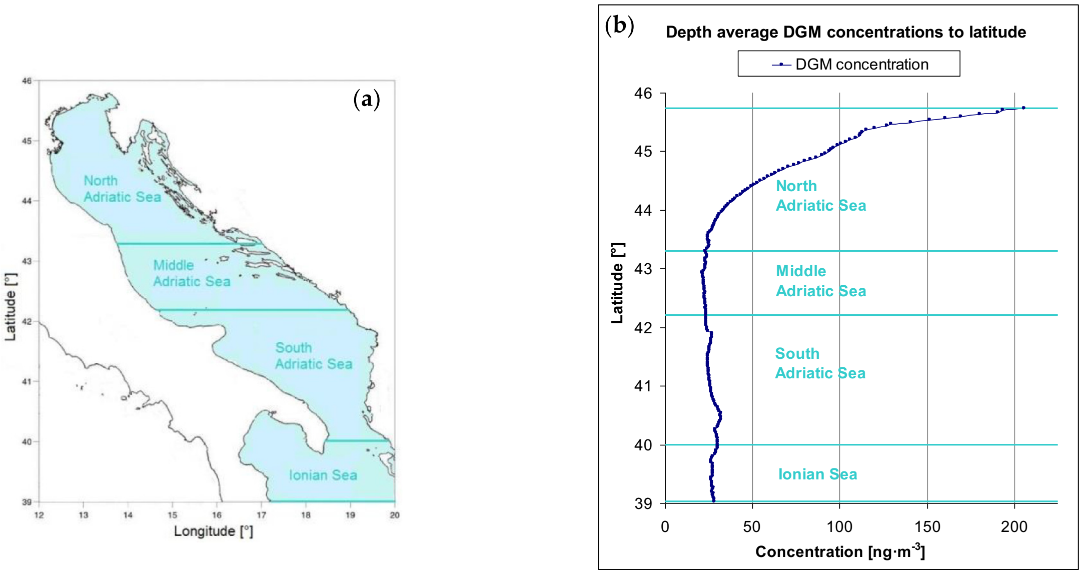

Fig. 1. Boundaries between the Adriatic Sea compartments (a), and depth averaged DGM concentrations related to latitude (b) (Kotnik et al., 2015).

were achieved using several models, calculations, and estimations, although the differences between the models still exceeded 10% (Žagar et al., 2014, Table 2).

So far, all models applied in Hg exchange computations were either atmosphere or ocean models. They employed as good estimations at the atmosphere–ocean boundary as were available at the time of simulations: spatial and/or temporal averaging in either of the compartments was the usual approach (Žagar et al., 2014 and the references therein). To date the only attempt made at coupling an atmosphere and an ocean model for Hg evasion simulations was within the MERCYMS project, where the results of the RAMS-Hg and the PCFLOW3D models were exchanged sequentially in order to enhance the modelling results (Žagar et al., 2007).

As a recent development the atmosphere and the ocean models are coupled in real time; one-way coupling considers atmosphere forcing to the ocean, while the two-way coupled models include ocean feedback to the atmosphere, which affects the computation of air-sea fluxes (momentum, water and heat) (Ličer et al., 2016). Such models offer a promising tool for further computation of Hg exchange. However, equations describing transport and transformation processes within the individual compartments, as well as the gas exchange models must be included in these models. Furthermore, Hg speciation must be taken into account: at least gaseous elemental Hg (*TGM* – total gaseous mercury in the atmosphere; and *DGM* – dissolved gaseous mercury in the water), and reactive Hg (reactive gaseous mercury, *RGM* in the atmosphere; and *RHg* in the water) must be considered. Such an approach is being used for the first time in the present study. The aim of this research is to (i) develop a mercury exchange model in the Adriatic Sea based on the wind parameterisation described by Nightingale et al. (2000); (ii) simulate *DGM* and *RHg* concentrations, and net reduction in the water compartment, considering preciously modelled deposition and concentrations in the atmosphere (Žagar et al., 2007, 2014) and measured concentrations in the ocean (Kotnik et al., 2015); (iii) run Hg exchange simulations using available real-time data from one- and two-way coupled models for a one-month period during the winter 2012 with an extreme Bora-wind event (Ličer et al., 2016); (iv) compare the results based on one- and two-way coupled models with other data on Hg exchange in the Adriatic and Mediterranean Seas (Andersson et al., 2007; Ferrara et al., 2000; Gårdfeldt et al., 2003; Gencarelli et al., 2014; Kotnik et al., 2015; Mastromonaco et al., 2017; Pirrone et al., 2001; Rajar et al., 2007; Žagar et al., 2007; Žagar et al., 2014); and (v) compare the exchange to the quantities estimated by Kotnik et al. (2015). In their manuscript Kotnik et al. (2015) assumed the atmosphere-ocean exchange in the Adriatic Sea to be overestimated. We hypothesise that by using the newly developed exchange model we can improve the exchange term in the mass balance estimation in this region.

2. Materials and methods

2.1. The Adriatic Sea

Adriatic Sea is a closed marine system subject to severe Hg pollution. The most prominent Hg sources are the Soča and Po rivers in its northern part. The Idrijca river, a tributary of the Soča, drains an area in the vicinity of a former mercury mine in Idrija, Slovenia (Horvat et al., 1999; Žagar et al., 2006), and the Po is one of the most Hg polluted rivers in the Mediterranean area (Rajar et al., 2007). A large part of reactive mercury in the Adriatic Sea capable of immediate transformations stems from atmospheric deposition (Kotnik et al., 2015). In the south the water masses of the Adriatic exchange with the Ionian Sea through the Strait of Otranto. The northern part is shallow, with an average depth 35 m, while the depth of the central and southern Adriatic is on average about 440 m, reaching 1399 m in the South Adriatic Pit. The maximum length and the average width of the Adriatic are 770 km and about 200 km, respectively, and the area covered is about 167,700 km^2. The oceanographic characteristics are described in detail in numerous sources (e.g. Artegiani et al., 1997; Kotnik et al., 2015). For the purpose of this study we divided the Adriatic Sea into three parts (Fig. 1a), in accordance with depth-averaged measured DGM concentrations (Fig. 1b) (Kotnik et al., 2015).

Mercury in the Adriatic Sea was sampled during two oceanographic cruises, one in 2004 and one in 2005. All Hg speciation results and statistical analyses from the Adriatic cruises were compiled and presented in Kotnik et al. (2015), and used as the input data for modelling.

2.2. AdriHg model: domain and forcing

To simulate Hg exchange at the ocean-atmosphere boundary we developed AdriHg, a new numerical mercury evasion model, written in Matlab. The AdriHg model runs offline with the input data from the coupled ocean-atmosphere modelling suite described in Ličer et al. (2016). This suite provides the necessary physical parameters in high temporal and spatial resolution for further evasion computation. Ocean