Marine Chemistry 177 (2015) 742–752

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

A comprehensive assessment of the mercury budget in the Marano–Grado Lagoon (Adriatic Sea) using a combined observational modeling approach

Donata Melaku Canu [a,*], Ginevra Rosati [a], Cosimo Solidoro [a,b], Lars-Eric Heimbürger [c,e], Alessandro Acquavita [d]

[a] OGS—National Institute of Oceanography and Experimental Geophysics, Borgo Grotta Gigane 42 c. Sgonico, Trieste, Italy
[b] ICTP, The Abdus Salam International Centre for Theoretical Physics — Strada Costiera, 11 I-34151 Trieste, Italy
[c] Geochemistry and Hydrogeology Group, Department of Geosciences, University of Bremen Klagenfurter Straße, 28359 Bremen, Germany
[d] O.A.A. — Osservatorio Alto Adriatico Via Lamarmora, 13–34139 Trieste, TS, Italy
[e] Mediterranean Institute of Oceanography Campus de Luminy, 13288 Marseille, France

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form 30 October 2015
Accepted 30 October 2015
Available online 31 October 2015

Keywords:
Mercury modeling
Lagoon
Budget
Transformation
Transport
Mercury hot spot
WASP7

ABSTRACT

In this study, a biogeochemical model of the mercury cycle is applied to the Marano–Grado Lagoon (North Adriatic Sea, Italy) to 1) integrate the ensemble of disconnected and snap shot measurements collected over the last decade into a common and coherent framework, 2) assess the concentration of mercury species (Hg^{II}, MeHg, Hg^0) in water, sediment and particulates, and 3) quantify the mercury fluxes and budgets within the lagoon and among the lagoon, the atmosphere and the Adriatic Sea. As a result of long-term industrial and natural contamination, the Marano–Grado Lagoon is a hot spot of mercury contamination in the Mediterranean Region. Several monitoring activities have been undertaken to evaluate the environmental impacts and to better understand mercury cycling in this region. We used the results from these studies to build a mercury biogeochemical model and assess its ability to accurately predict mercury concentrations and fluxes. The results indicate that 1) the lagoon is a contaminated site, with water and sediment concentrations of Hg and MeHg higher than those of comparable environments; 2) there is substantial production of MeHg favored high productivity, occurrence of seasonal anoxia, and shallow conditions; and 3) the lagoon is a source of mercury contamination for the Mediterranean Sea, contributing to about 5% of the total Hg_T load. Research also indicates that the most critical shortcoming of the currently available data sets is the lack of complete synoptic measurements, even for short time periods. Future research programs must also include information on the photo-transformation rates, such as of photo-reduction, photo-oxidation and photo-demethylation.

1. 1. Introduction

Mercury (Hg) is a persistent pollutant of global concern that is mainly emitted as the volatile elemental form Hg^0 from anthropogenic and natural sources. Upon oxidation to Hg^{2+}, Hg deposits on land and oceans, where it can undergo multiple biotic and abiotic transformations, such as photochemical and microbial reduction as well as microbial methylation to organic methylmercury (MeHg) (Sonke et al., 2013). Biological MeHg production (methylation) and degradation (demethylation) in coastal environments occur predominantly in sediment (Monperrus et al., 2007a; Merritt and Amirbahman, 2009 and references therein). However, there is increasing evidence of MeHg biotic production in oxic surface water, especially during or after periods of high productivity when heterotrophic activity is elevated (Bouchet et al., 2013; Heimbürger et al., 2015, Heimbürger et al., 2010, Lehnherr et al., 2011; Monperrus et al., 2007a; Monperrus et al., 2007b; Sharif et al., 2014).

MeHg is assimilated by living organisms and tends to bioaccumulate and biomagnify along freshwater and marine trophic webs (Watras et al., 1998; Cossa et al., 2012). Human MeHg exposure can subsequently occur through fish intake (Black et al., 2012; Fitzgerald et al., 2007; Mason et al., 2012; Sunderland et al., 2009). The health risks for human and wildlife posed by chronic exposure to MeHg and its related socio-economic consequences have led to an increase in attention to this issue. The health risks for human and wildlife posed by chronic exposure to MeHg and its related socio-economic consequences have led to an increase in attention to this issue, such as those agreed upon by the United Nation Environment Programme (UNEP) during the Minamata Convention. These global efforts to reduce anthropogenic Hg emissions highlight the importance of this issue and there has been a concerted effort among researchers to quantify the concentration and flux of Hg species and understand Hg transformations. We

* Corresponding author.

http://dx.doi.org/10.1016/j.marchem.2015.10.013

now have abundant field observations that can be modeled in an effort to develop predicative models to assess long-term ecological impacts and to better focus future research efforts.

Hg is a pollutant of great concern in the North Adriatic Sea, particularly in the Marano–Grado Lagoon, where high productivity, occurrence of seasonal anoxia, and shallow conditions could promote the transformation of Hg into bio-available compounds, as previously observed in other shallow lagoon systems (Bloom et al., 2004; Monperrus et al., 2007a, 2007b). To date, the dynamics of Hg species in the benthic compartment of this lagoon have been investigated in some detail (Acquavita et al., 2012a; Bramabati, 1996; Covelli et al., 2012; Covelli et al., 2008a, 2008b; Emili et al., 2012; Giani et al., 2012; Hines et al., 2012; Piani et al., 2005), although a limited number of sampling stations have been considered in most cases and the emerging data are fragmented. Less is known regarding the fate of Hg species in water columns. In this media, several transformations can occur (i.e., photo-reduction, photo-oxidation, photo-demethylation and possibly biotic methylation and demethylation), which can increase Hg evasion, deposition or bioaccumulation rates. The water column is also where bioconcentration by phytoplankton takes place (i.e., the first step of Hg biomagnification in the pelagic trophic web. Therefore, collating and integrating the available information into a common framework would be timely and useful for enhancing our current understanding of Hg pollution, identifying possible gaps, and informing effective management policies.

Characterizing Hg speciation and fluxes among environmental compartments is difficult, expensive and time consuming. Consequently, even in hot spot environments, data sets are often incomplete, and robust measurement assessments are often unavailable. Moreover, quantifying the transfer of Hg from environmental matrices to biota is a challenging task. Simple correlative approaches do not give a correct assessment of bioaccumulation because environmental parameters influence transfer kinetics. Modeling approaches may help overcome some of these limitations and are highly encouraged (Sonke et al., 2013; Black et al., 2012), although the lack of comprehensive data sets often hinder the development and application of models (Black et al., 2012). Currently a few attempts have been made to model the budget and biogeochemical cycling of total Hg in marine environments at global, regional and subregional scales (Amos et al., 2014; Soerensen et al., 2014; Sunderland et al., 2009), including the Mediterranean Sea (Rajar et al., 2007; Žagar et al., 2007). However, additional efforts are needed to model MeHg budgets in coastal areas (Bloom et al., 2004), where more accurate quantification of pollutant sources, transformation, and transport would be required.

Hg cycling in the Marano–Grado Lagoon has been previously modeled with the 0-D model SERAFM (Melaku Canu et al., 2012) to compile an initial overview of the processes that govern Hg fluxes into and out of the lagoon and to assess the relative importance of different contamination sources. However, this model lacked the ability to resolve spatial and temporal trends/characteristics. Incorporating finer spatial and temporal resolutions into the model would generate a better representation of local characteristics such as biogeochemical and transport processes and would improve the Hg model to provide a better assessment of the fluxes of Hg species among the compartments. However, this would also require more information on the spatial distribution of chemical and biogeochemical parameters and processes, as well as detailed information on the hydrology, and solid transport within the system. Therefore, a sensible trade-off is needed. Here, we decided to model Hg dynamics by subdividing the lagoon in 21 boxes, and the transport between boxes was modeled using a high-resolution hydrodynamic model.

In this study, we collated available information on the Hg cycle in the Marano–Grado Lagoon, estimated missing information through an extensive literature review, and implemented the dynamic Hg module of WASP7 (Water Analysis Simulation Program, US EPA, 1988) to investigate Hg dynamics and establish a mass balance. We also aimed to determine whether and to what extent the lagoon could represent a site of net MeHg production and a secondary source of bioavailable Hg contamination to the Adriatic.

1.1. Study area

The Marano–Grado Lagoon (Northern Adriatic Sea, Italy) is a large wetland environment in the Mediterranean region (Fig. 1). It covers an area of 160 km^2 and provides important ecosystem services, which sustains economic development, tourism, and fishery activities. The watershed supports approximately 32,000 inhabitants (Pirastu et al., 2014). The lagoon is an optimal nursery and recruitment zone for some fish species and provides shelter to many bird colonies. It has been recognized as a Special Area of Conservation (SAC — IT3320037) by the EU Habitat Directive 92/43/EEC.

The lagoon dynamically exchanges water with the Northern Adriatic Sea through six inlets, namely Lignano, S. Andrea, Buso, Morgo, Grado and Primero (Fig. 1). An increasing salinity gradient occurs from the inland regions of the lagoon toward the inlets. Due to its shallowness, the lagoon also experiences strong seasonal fluctuations in water temperature spanning from approximately 0 to 30 °C.

The western and the eastern sectors, also called the Marano and Grado Lagoons, exhibit some different physico-chemical features: the Marano Lagoon receives a greater input of freshwater from its tributaries (Stella, Turgnano, Zellina, Cormor, Corno–Aussa rivers) and is characterized by lower salinity and higher nutrient concentrations compared with the Grado Lagoon, which receives small freshwater inputs from the Natissa River (Fig. 1). The Grado Lagoon is shallower, and presents weaker hydrodynamics and more complex morphologies such as saltmarshes and a tidal flat.

The Marano–Grado Lagoon acts as a sink for various contaminants released from different anthropogenic activities, including large amounts of Hg compounds that have led to high total Hg (Hg_T) concentrations in the lagoon sediment (2.49–69.8 nmol/g; Acquavita et al., 2012a, 2012b; Regional Protection Agency-Friuli Venezia Giulia-ARPAFVG), pore water (Covelli et al., 2008a, 2008b; Emili et al., 2012) and local biota (Bramabati, 1996; Giani et al., 2012). Sediment values are 10 to 280 times higher than those of the open Mediterranean Sea sediments (Heimbürger et al., 2012).

The historic source of Hg was the Idrija cinnabar mine in western Slovenia, which operated from the 16th century until 1994. Dizdarevič (2001) estimated that approximately 37,000 tons of Hg (equivalent to 1.84×10^5 Kmol of Hg) were discharged during the lifetime of the mine. Much of the released Hg persists in the Soča/Isonzo River banks and is slowly released into the Gulf of Trieste (the northern part of Adriatic Sea), especially during flooding events. Once Hg reaches the Gulf of Trieste, it is transported through general water circulation and in the sediment. When the river plume is diverted to the SW under the influence of E–NE winds, the tidal flux carries particulate Hg (Hg_P), which is mostly inorganic, into the Grado Lagoon (Covelli et al., 2007). The second most relevant Hg source is a chlor-alkali plant (see Fig. 1) that dumped approximately 190 tons of Hg (equivalent to 9.5×10^2 Kmol) directly into the lagoon through the Aussa–Corno River (Acquavita et al., 2012a, 2012b) during its 45 years of operation. As a result of historical and more recent Hg emissions, it is estimated that 251 tons of Hg (equivalent to 1.25×10^3 Kmol) are buried in the sediments of the lagoon (Covelli et al., 2012). Therefore, the lagoon sediment, together with the sediment stored in the Aussa–Corno River and in the Gulf of Trieste, has the potential to act as a secondary source of Hg.

2. Materials and methods

To investigate Hg cycle dynamics and estimate Hg species fluxes in the Marano–Grado Lagoon ecosystem, we implemented the water quality model WASP7, which was released by the US EPA and is publicly