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Mercury speciation in the Adriatic Sea

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ABSTRACT

Mercury and its speciation were studied in surface and deep waters of the Adriatic Sea. Several mercury species (i.e. DGM – dissolved gaseous Hg, RHg – reactive Hg, THg – total Hg, MeHg – monomethyl Hg and DMeHg – dimethylmercury) together with other water parameters were measured in coastal and open sea deep water profiles. THg concentrations in the water column, as well as in sediments and pore waters, were the highest in the northern, most polluted part of the Adriatic Sea as the consequence of Hg mining in Idrija and the heavy industry of northern Italy. Certain profiles in the South Adriatic Pit exhibit an increase of DGM just over the bottom due to its diffusion from sediment as a consequence of microbial and/or tectonic activity. Furthermore, a Hg mass balance for the Adriatic Sea was calculated based on measurements and literature data.

1. Introduction

During recent decades special attention has been given to the mercury cycle in marine environments due to the toxicity of its organic compounds. These organic mercury compounds are produced, bioaccumulated and biomagnified in marine organisms. Of particular concern is biomagnifications in fish which are the principal route of human exposure to methyl mercury (Fitzgerald and Clarkson, 1991), thus mercury contamination is an issue of great concern globally and in the Mediterranean sea basin. It is well known that mercury is chemically, biologically and geologically active; therefore, non-conservative distributions have indeed been reported in a number of water bodies (Fitzgerald et al., 2007).

The main Hg species present in the marine environment are elemental Hg (Hg^0), Hg(II) and organic molecules (methyl Hg (MeHg) and dimethyl Hg (DMeHg)). The cycling of Hg in coastal marine systems is comparable to that in the open oceans, although the levels of Hg species are enhanced (Cossa et al., 1996; Fitzgerald et al., 2007). Most mercury enters marine waters by wet or dry deposition or by river discharges, with a significant fraction in oxidized form (Mason et al., 1994; Fitzgerald et al., 2007). It has been found that Hg^0 in marine waters originates from several biotic and abiotic transformations of oxidized Hg(II) (Mason et al., 1995; Costa and Liss, 1999, 2000; Amyot et al., 1997) and decomposition of organo-mercury compounds (Mason and Fitzgerald, 1993; Mason and Sullivan, 1999). Also tectonic activity may be an important source of Hg^0 (Ferrara et al., 2003; Horvat et al., 2003; Kotnik et al., 2007). Between 10% and 30% of total Hg can be present in marine waters as Hg^0 (Kim and Fitzgerald, 1988; Mason and Fitzgerald, 1993). Hg^0 is usually supersaturated with respect to the atmosphere, especially in surface waters, where its evasion represents an important source to the global atmosphere. Moreover, it should be highlighted that part of Hg(II) is also removed due to the processes of methylation and subsequent bioaccumulation along the food chain (Horvat et al., 2003).

MeHg is present in open sea waters at very low levels, ranging from few tens of fM to few pM (Horvat et al., 1999, 2003; Mason et al., 1998; Cossa and Coquery, 2005). Methylated Hg species are primarily formed in deeper ocean waters, but are not restricted to low oxygen zones suggesting that there are additional mechanisms for methylation/demethylation processes (Horvat et al., 2003). Reducing conditions and high salinity are hypothesized to promote demethylation of MeHg (Hines et al., 2000), while it can be efficiently decomposed by photochemical reactions and microbial activity (Horvat et al., 2003). Net MeHg production in coastal marine sediments is substantial (Hammerschmidt and Fitzgerald, 2006; Heyes et al., 2006; Sunderland et al., 2006) and recent

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research suggests that most MeHg in marine fish may have a near-shore sedimentary origin, where it is apparent that biological methylation is more important than abiotic mechanisms (Benoit et al., 2003). The recent oceanic mass balance calculated by Mason et al. (2012) suggests that open ocean production is a greater source of MeHg that near-shore sediments. Also abiotic production of MeHg is likely to occur in hydrothermal fluids as significant levels of MeHg have been observed in hydrothermal vent fluids (Lamborg et al., 2006). DMeHg was reported to be found in deeper ocean waters (Mason and Fitzgerald, 1990; Cossa et al., 1997; Mason et al., 1995; Horvat et al., 2003; Kotnik et al., 2007). Its source at depth is thought to be linked to some heterotrophically driven production of DMeHg (e.g., Mason et al., 1998). In surface waters, it is readily lost from aquatic environments by evasion and is rapidly decomposed by photochemical degradation (Horvat et al., 2003). However, Black et al. (2009) suggest that evasion is far more important that photodecomposition as a loss term for DMeHg from marine surface water.

Closed marine water systems are environments which are very sensitive to Hg pollution due to limited exchange of water between the oceans. The Adriatic Sea is a closed marine system connected to the Mediterranean Sea by the narrow Strait of Otranto and is subject to a high inflow of heavily polluted river water and other direct discharges, especially in its northern and central parts. Its most northern part, the Gulf of Trieste, is influenced by the natural and anthropogenic load of Hg from polluted River Soča (Isonzo), whose watershed contains the world's second largest Hg mine in Idrija. Centuries of drainage of Hg polluted soils, cinnabar deposits, mining and smelting wastes provided the main source of Hg in the Gulf, which is one of the most Hg contaminated areas in the whole Mediterranean region. Mercury that enters the Gulf via the River Soča is mainly in particulate form (Širca et al., 1999). Measurements of different Hg species in the water column, suspended solids and sediments have shown several times higher concentrations than in the Central and Southern part of the Adriatic Sea (Horvat et al., 1999, 2002; Faganeli et al., 2003; Covelli et al., 2007, 2008). It was estimated, that the River Soča contributed approximately 2160 tonnes of Hg to the Gulf of Trieste during the 500 (1490–1995) year mining history of Idrija (Žagar et al., 2006). Elevated Hg levels in water and sediments were found on both western (Italian) and eastern (Croatian) coasts. However, the high Hg levels found in the Ravenna Lagoon sediments were a consequence of direct discharges of the acetaldehyde and vinyl chloride industry. More than 150 tonnes of Hg were released into the Lagoon between 1958 and 1973 (Fabbri et al., 2001; Trombini et al., 2003). The River Po delta area coastal sediments appear to be enriched in Hg as a direct consequence of very extensive industrial inputs from the river drainage basin which represents one quarter of the Italian national territory. Sources of Hg contamination were also identified in the Marghera industrial zone on the western shoreline of the Venice Lagoon. The Lagoon was extensively contaminated with Hg from chlor-alkali discharges (100–300 tonnes of Hg released between 1951 and 1988) (Bloom et al., 2004; Zonta et al., 2007). The Venice Lagoon is now a net exporter of sediments to the Adriatic Sea (1.1 million tonnes per year). The Marano and Grado Lagoons have experienced significant Hg inputs from mining (Idrija, River Soča discharge) and industrial sources (Aussa-Corno river, chlor-alkali plant since 1940–1984) (Piani et al., 2005). Kaštela Bay, located on the eastern Adriatic coast near Split, has been exposed to pollution by inorganic mercury derived from a chlor-alkali plant operating between 1949 and 1989. It was estimated that the total amount of elemental mercury discharged into the Bay was 39 t (Tudor, 1993).

The present study was performed to obtain missing data and improve knowledge on Hg speciation and distribution in central, as well as the coastal regions of the Adriatic Sea. In this paper, we focus on Hg distribution and speciation in the water column of the area investigated. In addition, the concentrations of THg and MeHg in pore waters and sediment profiles down to a depth of 20 cm were determined, and a rough mass balance for THg and MeHg was calculated separately for the Northern and Southern Adriatic.

2. Materials and methods

2.1. Site description

The Adriatic Sea extends northwest from 40° to 45°45′ N, with an extreme length of about 770 km. Its northern part is very shallow, gently sloping with an average bottom depth of about 35 m. The site of maximum depth is south of the central area, and the average depth of the Central and South Adriatic is about 440 m, with a maximum depth of 1399 m. In the northern Adriatic the water column shows a seasonal thermal cycle. The thermocline is present in spring and summer down to 30 m depth. In winter cooling of the whole water column occurs. A freshwater surface plume was observed in spring and summer due to increased runoff and water stratification. There are two typical water masses: the seasonal layer of North Adriatic surface water (NAdSW – low salinity and high temperature in the summer), and the North Adriatic deep water (NAdDW – $T = 11.35 \pm 1.4$ °C, $S = 38.3 \pm 2.8$), which is cooled and renewed in winter (Artegiani et al., 1997), flowing southward and forming Central Adriatic deep water (CAdDW). In the Central Adriatic, the thermocline is formed down to 50 m in spring and summer. Below the thermocline (50 m) Levantine intermediate waters can be found (LIW – $S > 38.5$). The area deeper than 150 m (the Pomo Depression) is filled with CAdDW ($T = 11.62 \pm 0.75$ °C, $S = 38.47 \pm 0.15$). In the southern Adriatic the thermocline can be found down to 75 m. Surface waters (SAdSW) affected by river inflow exhibit a decrease in salinity. From 150 m to the bottom, Mediterranean open sea conditions were found to be modulated by LIW between 150 and 400 m ($T > 13.5$, $S > 38.6$). Bottom water masses in that area are defined as South Adriatic deep water (SAdDW – $T = 13.16 \pm 0.3$ °C, $S = 38.6 \pm 0.09$) (Artegiani et al., 1997). In the Strait of Otranto four water masses can be found: Adriatic surface water (AdSW) with lower salinity, flowing out of the Adriatic along the western side of the strait; Ionian surface water (ISW) flowing into the Adriatic along the eastern side; Levantine intermediate water (LIW) which flows into the Adriatic at intermediate depths; and Adriatic deep water at the bottom, which flows out of the Adriatic feeding the deep waters of the eastern Mediterranean Sea.

The northern Adriatic water circulation (Fig. 1) is dominated by the North Adriatic current (NAd current), flowing southward along the W coast. During winter, it is a segment of the Po River extending only 100 km downstream, while in summer it extends farther south. The central and south Adriatic water circulation is composed of the cyclonic Central and Southern Adriatic gyres (CAd and SAd gyres), the northward flowing eastern South Adriatic current (E-SAd current) and the southward flowing western South Adriatic current (W-SAd current). These four features of the circulation strengthen during summer, while they are weaker in spring and almost absent in winter. During winter, the water circulation is dominated by smooth flow from south to north along the longitudinal centre of the basin (Artegiani et al., 1997).

2.2. Sampling and sample preparation

Sampling procedures and analysis of different Hg species were performed either on board, or in the laboratory at the "Jožef Stefan" Institute (JSI), Ljubljana, Slovenia.