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Mercury in the food chain of the Lagoon of Venice, Italy

Janusz Dominik[a,b,*], Davide Tagliapietra[a], Andrea G. Bravo[b,1], Marco Sigovini[a], Jorge E. Spangenberg[c], David Amouroux[d], Roberto Zonta[a]

[a] Istituto di Scienze Marine – Consiglio Nazionale delle Ricerche, Arsenale – Tesa 104, Castello 2737/F 30122 Venezia, Italy
[b] Institute F.-A. Forel, Université de Genève, CP 416, 1290 Versoix, Switzerland
[c] Institute of Earth Surface Dynamics, University of Lausanne, CH 1015 Lausanne, Switzerland
[d] IPREM-LCABIE, UMR 5254 CNRS – Université de Pau et des Pays de l'Adour, Hélioparc, 2 av P. Angot, 64053 Pau, France

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ABSTRACT

Sediments and biota samples were collected in a restricted area of the Lagoon of Venice and analysed for total mercury, monomethyl mercury (MMHg), and nitrogen and carbon isotopes. Results were used to examine mercury biomagnification in a complex food chain. Sedimentary organic matter (SOM) proved to be a major source of nutrients and mercury to primary consumers. Contrary to inorganic mercury, MMHg was strongly biomagnified along the food chain, although the lognormal relationship between MMHg and δ^{15}N was less constrained than generally reported from lakes or coastal marine ecosystems. The relationship improved when log MMHg concentrations were plotted against trophic positions derived from baseline δ^{15}N estimate for primary consumers. From the regression slope a mean MMHg trophic magnification factor of 10 was obtained. Filter-feeding benthic bivalves accumulated more MMHg than other primary consumers and were probably important in MMHg transfer from sediments to higher levels of the food chain.

1. Introduction

The contamination of aquatic environments with mercury (Hg) originating from both global and local sources is of concern because this metal accumulates in biota and can be transferred to humans via fish and other sea food. This may lead to serious health problems, especially in cases of prenatal exposure (Harada, 1978; Grandjean et al., 1997; Clarkson, 1998). In aquatic systems, a proportion of the inorganic mercury (IHg) is converted to monomethylmercury (MMHg), which biomagnifies along the food web (Wood, 1974; Fitzgerald et al., 2007). Hg concentrations in aquatic organisms depend not only on the contaminant input to the system, but also on variables and processes such as methylation and demethylation rates, trophic level, food chain structure and other environmental factors (Pelletier, 1995; Ullrich et al., 2001). Numerous studies have examined total mercury (THg) and MMHg concentrations in aquatic food chains in freshwater or coastal marine environments as a function of nitrogen stable isotope composition (δ^{15}N values). The latter reflects the trophic position of organisms (e.g. Power et al., 2002; Lavoie et al., 2010). Only recently has data became available on IHg and MMHg transfer in the trophic chain of lagoons (Jara-Marini et al., 2012; Coelho et al., 2013; Hong et al., 2013). Several Hg-contaminated Mediterranean lagoons have been studied with respect to metal sources, cycling and accumulation in biota (Trombini et al., 2003; Faganeli et al., 2012 and references within). However, little is known about Hg biomagnification along the lagoonal trophic chain in the Mediterranean.

The Lagoon of Venice (Fig. 1) is the largest lagoonal system in Italy, covering an area of ~550 km^2. The average depth is only ~1 m, but a network of deeper channels rooted at the inlets facilitates water exchange with the Adriatic Sea. Anthropogenic nutrient loads to the Lagoon originate mainly from agriculture, industrial activity and urban sewage. Nitrogen sources, annual budget and cycling were modelled by Solidoro et al. (2005) and food web models were proposed by Carrer and Opitz (1999), Libralato et al. (2002), Libralato and Solidoro (2009) and Brigolin et al. (2011, 2014). Because of lack of carbon and nitrogen isotope data for biota these food web models were based only on expert judgement. Nitrogen sources and cycling influence nitrogen isotopic composition of primary producers and consequently the interpretation of the structure of trophic chain based on δ^{15}N isotope values. Therefore, the isotopic data may improve modelling of

* Corresponding author at: Istituto di Scienze Marine – Consiglio Nazionale delle Ricerche, Arsenale – Tesa 104, Castello 2737/F 30122 Venezia, Italy.
E-mail address: janusz.dominik@ve.ismar.cnr.it (J. Dominik).
[1] Present address: Limnology/Department of Ecology and Genetics, Uppsala University, Norbyvägen 18D, 75236 Uppsala, Sweden.

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the trophic chain and the interpretation of mercury accumulation in biota.

The main source of Hg in the Lagoon of Venice has been a chlor-alkali plant operating since 1951 in the Marghera industrial area (Kenyon and Gallone, 1953; Zonta et al., 2007). No Hg emissions from this factory have been reported since the decommissioning of mercury cell technology in 2009 (Eurochlo, 2009), but it is estimated that a total of 200 tons of Hg may have been discharged to the Lagoon in the past (Bloom et al., 2004b). The most contaminated sediments are located close to the Marghera site (Zonta et al., 2007). These have been partially eroded and dispersed to other parts of the Lagoon (Molinaroli et al., 2013). In other coastal sites, it has been observed that after the reduction of Hg load from point sources, the contamination in benthic organisms and fish decreases. However, for semi-enclosed systems the recovery could take decades (Locarnini and Presley, 1996, Munthe et al., 2007). Because Hg is perpetually recycled between water and sediments, it has a long residence time in the Lagoon of Venice and thus the transfer of Hg to biota may persist a long time after the reduction or elimination of point sources. In such a dynamic system with a complex food chain, predicting the fate of Hg contamination and the associated risk is particularly difficult.

Previous studies demonstrated an elevated methylation potential in the Lagoon of Venice sediments (Han et al., 2007). Tide-driven MMHg transfer from sediments to the water column has been observed by Guédron et al. (2012), and MMHg accumulation in several organisms was reported by Bloom et al. (2004a). Here, we report for the first time the results on THg and MMHg concentrations in the food web of the Lagoon of Venice as a function of the trophic level of organisms using $\delta^{15}N$ measurements. The principal objective of this study was to evaluate to what degree relationships established in lakes and coastal seas can be applied to shallow lagoons, which contain distinctive features such as a low number of trophic levels but a large number of interactions in the food web; a high trophic redundancy; overlapping benthic and pelagic food webs; a high biomass of filter and deposit feeders, as well as omnivorous organisms; and continuous resuspension of sediments by tidal currents, waves and anthropogenic activities. Special consideration was given to benthic bivalves since they are often used for monitoring Hg pollution.

2. Methods

2.1. Setting and sampling

Biota and sediment samples were collected between 22 June and 14 July 2011 in the northern part of the Lagoon of Venice (Palude Maggiore, 45°30′20″N, 12°20′20″E) within an area 350 × 200 m (Fig. 1). This sampling area represents a typical shallow lagoon ecosystem (mean depth about 1 m) with seagrass meadows and mud flats next to a natural channel (about 6 m deep). This channel maintains a tidal exchange of water with the Adriatic Sea via the Lido Inlet. The area is euhaline with salinity varying between 27 and 34 psu, with minimum values in spring and maximum in summer (Guerzoni and Tagliapietra, 2006). In terms of water exchange, the area has been defined as restricted to confined (Ghezzo et al., 2011), with mean water residence time of 15–20 days (Molinaroli et al., 2007).

Sediments were recovered manually with a plastic corer (internal diameter of 2 cm) at three different locations representing seagrass meadows, bare mudflats and salt marsh edges. The sediments, mostly sandy silt, are only moderately polluted with Hg (<0.5 mg/kg) as compared to the central part of the Lagoon, where the concentrations can still reach 2 mg kg^{-1}. Because of sediment mixing and re-suspension the concentrations of Hg were fairly constant in the top 30 cm (Zonta et al., 2011). For each location sub-samples were taken at 0–5 cm and 5–10 cm depths. Three replicates were collected, pooled and again subsampled by quartering for analysis. Biota samples included pelagic and benthic organisms from all trophic levels, from primary producers to fish (Table 1). Macrophytes and benthic invertebrates were sampled manually from a boat or by divers. Seston and zooplankton were sampled in the adjacent channel using a 20 µm net (total sampling

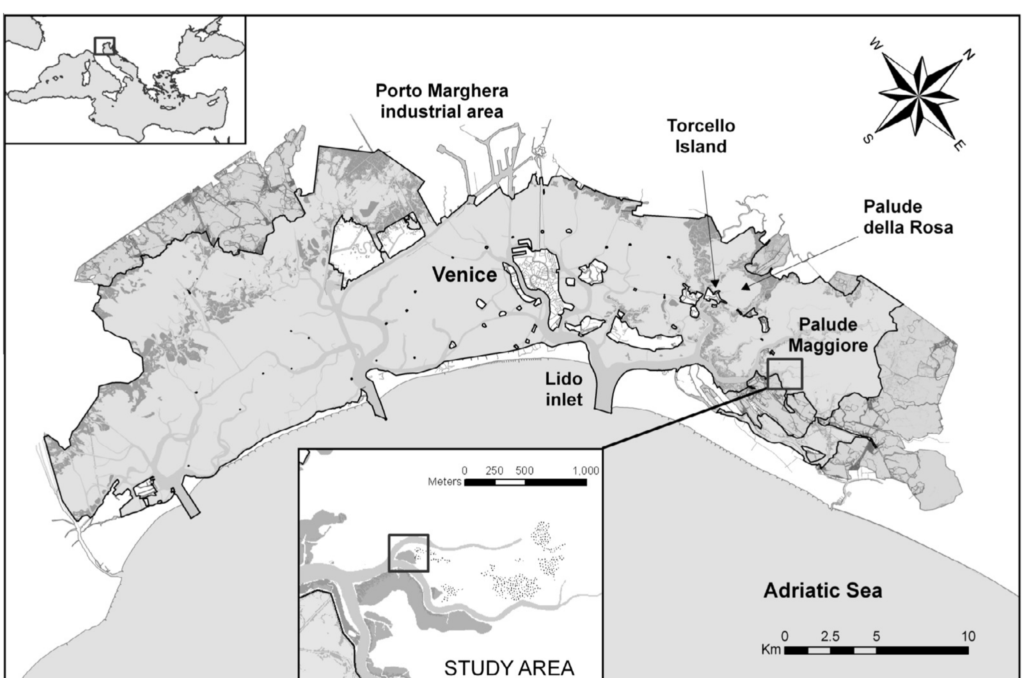

Fig. 1. The area of study in Palude Maggiore, northern part of the Lagoon of Venice (Italy). Morphological features of the study area include salt marshes (dark grey), channels (light grey) and seagrass meadows (dotted).