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Evaluation of mercury biogeochemical cycling at the sediment–water interface in anthropogenically modified lagoon environments

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ABSTRACT

The Marano and Grado Lagoon is well known for being contaminated by mercury (Hg) from the Idrija mine (Slovenia) and the decommissioned chlor-alkali plant of Torviscosa (Italy). Experimental activities were conducted in a local fish farm to understand Hg cycling at the sediment–water interface. Both diffusive and benthic fluxes were estimated in terms of chemical and physical features. Mercury concentration in sediments (up to 6.81 μg/g) showed a slight variability with depth, whereas the highest methylmercury (MeHg) values (up to 10 ng/g) were detected in the first centimetres. MeHg seems to be produced and stored in the 2–3 cm below the sediment–water interface, where sulphate reducing bacteria activity occurs and hypoxic–anoxic conditions become persistent for days. DMeHg in porewaters varied seasonally (from 0.1 and 17% of dissolved Hg (DHg)) with the highest concentrations in summer. DHg diffusive effluxes higher (up to 444 ng/(m^2 d) than those reported in the open lagoon (~95 ng/(m^2 d), whereas DMeHg showed influxes in the fish farm (up to −156 ng/(m^2 d). The diurnal DHg and DMeHg benthic fluxes were found to be higher than the highest summer values previously reported for the natural lagoon environment. Bottom sediments, especially in anoxic conditions, seem to be a significant source of MeHg in the water column where it eventually accumulates. However, net fluxes considering the daily trend of DHg and DMeHg, indicated possible DMeHg degradation processes. Enhancing water dynamics in the fish farm could mitigate environmental conditions suitable for Hg methylation.

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Introduction

The Mediterranean coastal areas are essential ecological systems that constitute important resources of great recreational and profitable value, in particular, fisheries and aquaculture play a crucial socio-economic role (Abdou et al., 2017). In the Mediterranean, the aquaculture industry has grown rapidly (FAO, 2016; Belias and Dassenakis, 2002), facilitated by the geography and chemical and physical conditions in the zone (FAO, 2016). Over the last decades, aquaculture activities have expanded rapidly throughout the world and the production increased on an average rate of 23.5% from 2009 to 2014 (FAO, 2016). At present, approximately 44% of fish consumed are farmed, and this percentage is predicted to reach 52% by 2025 (FAO, 2016).

One of the main environmental issues affecting the coastal marine environments is the accumulation of contaminants in sediments and their possible mobility (Emili et al., 2016). The sediment, in fact, is a sink for many chemical species potentially toxic to the marine ecosystem, such as heavy metals (*e.g.*, Chen et al., 2013; Kalantzi et al., 2016) or organic compounds (*e.g.*, Fent, 1996; Tas et al., 1996), but it is also the site of early diagenesis biogeochemical processes that can mobilise contaminants, often transforming them into most toxic forms which may subsequently accumulate through the trophic chain.

In the coastal area of the Friuli Venezia Giulia region (Northern Adriatic Sea, Italy), the Marano and Grado Lagoon is well known for a high degree of anomaly in relation to mercury concentration (Hg) in waters and especially sediments (Acquavita et al., 2012). This contamination is due to a double source: the first is located within the Isonzo River basin, the main river flowing into the Gulf of Trieste (Horvat et al., 1999; Covelli et al., 2001, 2007), which is affected by contamination from the Idrija mine (Western Slovenia) which was in operation for approximately 500 years. The second source of contamination is located in the Aussa-Corno River system, the result of chlor-alkali plant effluents discharged into the Marano and Grado Lagoon (Covelli et al., 2009).

Mercury is considered a priority contaminant due to its toxicity (WHO, 1990), mobility and bioaccumulation potential and exhibits complex biogeochemical cycling (Mason et al., 1993; Ullrich et al., 2001; O'Driscoll et al., 2005). Anoxic sediments can become a significant source of methylmercury (CH_3Hg or $MeHg^+$), which is a potent neurotoxin (*e.g.*, Grandjean et al., 2010) and endocrine-disrupting chemical (Tan et al., 2009), highly toxic to humans and other organisms (Crespo-López et al., 2009). This is the most toxic organic form that can be highly biomagnified in the trophic chain, most significantly in edible fish. Other microorganisms in addition to SRB are involved in Hg methylation, such as iron-reducing (Fleming et al., 2006; Kerin et al., 2006) and methanogenic (Gilmour et al., 2013; Hamelin et al., 2011; Podar et al., 2015) bacteria that are capable of Hg methylation. It has been shown that sulphur cycling (Gagnon et al., 1996; Lambertsson and Nilssons, 2006) is important in controlling the transformation of Hg species (*e.g.*, Han et al., 2007; Hollweg et al., 2009) such as the amount and characteristics of dissolved organic matter (Ravichandran, 2004) and sorption/dissolution processes involving Fe/Mn oxy-hydroxides (*e.g.*, Gagnon et al., 1997; Schäfer et al., 2010).

Various research activities were carried out in order to more fully understand the Hg biogeochemical cycle in the northern Adriatic Sea in the last 20 years, from the more extended area of the Gulf of Trieste (Covelli et al., 1999; Horvat et al., 1999) to the Marano and Grado Lagoon (Covelli et al., 2008, 2011; Emili et al., 2012). Despite Hg issue, fishing, along with clam and mussel collection and aquaculture practice are very widespread. All these activities increase the chances of Hg uptake by living aquatic organisms in the nearby area (Covelli et al., 2008). Few studies have been performed in this area regarding Hg impact on the trophic chain. Brambati (2001) considered Hg bioaccumulation in seaweed, edible fish and birds. High Hg concentrations, often one order of magnitude higher than the 0.5 mg/kg European Community limit, were found along trophic chain (especially in seabream and seabass). More recently, a multidisciplinary research project called "MIRACLE" (Mercury Interdisciplinary Research for Appropriate Clam farming in a Lagoon Environment) was conducted to identify which areas pose the least risk of Hg bioaccumulation for commercial Manila clams (Covelli, 2012). To this purpose, Hg and MeHg content in *Tapes philippinarum* was monitored in natural and seeded populations (Giani et al., 2012). Increased bioaccumulation of Hg but not of MeHg with increasing size of wild clam populations was observed at most sites depending on Hg concentrations in bottom sediments but also on biogeochemical processes at the sediment–water interface (SWI).

Fish farming is a historical activity for the local population, covering 14% of the total lagoon area (Acquavita et al., 2015), where mostly sea bass and sea bream are farmed. Fish farms were built by isolating an area of the lagoon with an embankment. They communicate with Lagoon waters through sluice gates, which allow the water exchange between the external lagoon environment and the fish farms. They can be self-contaminated mainly by organic matter and heavy metals due to inappropriate operational practices such as the cultivation of high fish populations, excess of food given and use of antifouling chemical substances (Belias and Dassenakis, 2002).

Since the bottom sediments in the fish farms are highly contaminated by mercury, this study is a first step toward understanding the role of the SWI in recycling mercury in this anthropogenically modified lagoon environment. To this end, an estimate of Hg and MeHg mobility and exchanges between sediment and water column was performed at two different sites located in this environment, in order to 1) highlight differences with the open lagoon system and 2) to provide new insight for future studies on Hg transformations (*e.g.*, methylation/demethylation rates) and bioaccumulation in edible fish. The final aim was to suggest good practices for improving the environmental conditions of the fish farm in order to mitigate the impact of Hg on this complex and highly anthropogenically modified lagoon ecosystem.

1. Sampling strategy

1.1. Study area

The wetland system of the Marano and Grado Lagoon (Northern Adriatic Sea, Italy) is one of the best conserved

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