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# Suspended particulate mercury associated with tidal fluxes in a lagoon environment impacted by cinnabar mining activity (northern Adriatic Sea)

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ABSTRACT

The Isonzo River has been demonstrated to be a continuing point source of mercury (Hg) in the Gulf of Trieste although the Idrija mine was last active in 1996. The present study aims to investigate the role of the suspended particulate matter (SPM) associated with tidal fluxes to disperse particulate Hg (PHg) into the Grado coastal lagoon system. PHg concentrations (avg. 3.11 ± 2.62 μg/g, d.w.), notwithstanding the ebb or flood tides, were significantly higher than the local sediment background (0.13 μg/g). The relative affinity of Hg for the particulate phase in surface waters was confirmed by higher average distribution coefficient ($K_d$) values (5.6–6.7). PHg contents showed the highest values in ebb tide conditions, thus suggesting their origin from the erosion of tidal flats and saltmarshes of the lagoon. When compared to river discharge, high PHg surface concentrations in flood tide are related to rainfall events occurring within the river basin. Results can be used to make an indicative assessment of the amount of Hg bound to SPM which is transported in and out of the lagoon basin following the action of tidal fluxes. A simple estimation provides a negative budget for the Grado lagoon sub-basin which loses between 0.14 and 1.16 kg of PHg during a tidal semi-cycle. This conclusion is in agreement with the evidence of morphological deterioration which has emerged from recent studies on the lagoon environment, and which testifies to a current sedimentary loss from the lagoon into the northern Adriatic Sea.


## Introduction

Like estuaries, coastal lagoons are often efficient traps for sediments from marine and fluvial origin due to their shallowness and the reduced water exchange with the open sea. Lagoons are also recognised as reservoirs for associated contaminants which result from anthropogenic activities in their hinterland and along their shores (Ridgway and Shimmield, 2002). Several trace metals are primarily associated with suspended particulate matter (SPM) in aquatic systems largely due to processes of adsorption onto mineral surfaces, absorption onto organic coatings on particles, ion-exchange, and salting-out effects in estuarine environments (Turner and Millward, 2002). The total concentration of trace

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metals considerably increases during riverine flood events, following the trend of SPM as a result of materials delivered from the runoff on soils, which are essentially constituted by sediments with a large percentage of fine particles (Zonta et al., 2005; Turner et al., 2008). Since riverine suspended particulate matter is often carried by longshore currents and entrapped in these transitional environments, it provides a preferential pathway for the transport and dispersion of associated contaminants. Contaminant and SPM concentrations at any point in coastal lagoons are expected to change according to tidal range and other variable local factors such as wind and fluvial inputs (Pato et al., 2008). Major movements of SPM occur at the lagoon inlet where tidal fluxes convey suspended particles out into the lagoon where they eventually accumulate on tidal flats and saltmarshes. Natural and anthropogenic processes may also be responsible for changes in hydrodynamics and the subsequent sediment erosion and resuspension from the above-mentioned morphologies (Fontolan et al., 2012). These contaminants negatively affect lagoon ecosystems where bioaccumulation in the trophic chain is also increased by the abundance of animal and plant species (Brambati, 2001; Monterroso et al., 2003; Petranich et al., 2016). The final uptake of contaminants by humans through for instance fishing and clam and mussel collection, is then perceived as a potential health risk (Whyte et al., 2009; Giani et al., 2012).

The Marano and Grado Lagoon (hereafter referred to simply as "the Lagoon") is one of the most important transitional environments along the Northern Adriatic coastline (Italy), and has been extensively contaminated by a double source of mercury (Hg) (Covelli, 2012). This metal was employed as a catalyst in a chlor-alkali plant (CAP) and deliberately discharged from 1949 to 1984 into the Aussa-Corno River system, which is connected to the central sector of the Lagoon and received approximately 186 t of Hg (RAFVG, 1991). Although direct discharge of Hg from the CAP no longer occurs, the metal is still released mainly in particulate form from the source area into freshwaters flowing into the central sector of the Lagoon (Covelli et al., 2009). The main source of Hg for the whole Lagoon, however, has been identified in contaminated sediment eroded from the river banks and the floodplain deposits (Gosar and Zibret, 2011; Kocman et al., 2011) of the Soča/Isonzo River drainage basin where the Idrija mining district is located (western Slovenia). For almost 500 years, until 1996, 12 million t of Hg ore, mostly cinnabar, were excavated. More than 35,000 t of Hg have been lost into the environment during roasting processes (Dizdarevič, 2001). The predominant and long-term impact of the cinnabar-rich Isonzo River sediment is evident not only in the bottom sediments of the Gulf of Trieste (Horvat et al., 1999; Covelli et al., 2001, 2006b) but also of the Lagoon and confirmed by a decreasing concentration gradient in surface sediments from east (>11 μg/g) to west (0.7 μg/g) (Acquavita et al., 2012). In addition, the highest concentrations of Hg (up to 28 μg/g) in the Grado sector occur in the subsurface sediments of the saltmarshes (Covelli et al., 2017). Žagar et al. (2006) estimated that a total amount of 10,000 t of Hg is still stored in riverbed, riverbanks and flood plains between the Idrija mining site and the Isonzo River mouth. Research performed at the mouth of the Isonzo River has demonstrated that dissolved and particulate Hg concentrations are still very high during low and normal river discharge throughout the year (Faganeli et al., 2003; Covelli et al., 2006a). Despite the fact that flood events are rare during the year, they account for most of the particulate Hg influx into the Gulf of Trieste (Rajar et al., 2000; Covelli et al., 2007). Preliminary assessments suggest that considerable amounts of Hg enter the Lagoon following peaks in the discharge from the Isonzo River, whereas specific wind conditions from E-NE concurrently occur in the Gulf of Trieste and disperse fluvial input westwards (Covelli et al., 2007).

Monitoring and modelling of sediment transport in the coastal systems are critical for understanding the fate of contaminants associated with particles. The aim of this work was to understand the present role of SPM at the tidal inlets as a main pathway for Hg load from the Isonzo River drainage basin into the eastern sector of the Lagoon system and, conversely, from this large contaminated reservoir into the Adriatic Sea. An annual mass-balance assessment of Hg was also performed on the basis of seasonal measurements of particulate Hg concentrations associated with tidal fluxes at the Grado tidal inlet in order to establish whether the Lagoon environment may also be considered a secondary source for the metal to the Adriatic Sea. The direct observation of these dynamics is crucial although it requires a great effort in terms of field work. A better understanding of sediment-associated Hg behaviour can be explained only partially by applying models which are clearly limited and misleading, if not wrong, when field information is missing (Melaku Canu et al., 2015).

## 1. Experimental

### 1.1. *Environmental setting*

The Lagoon covers an area of 160 km$^2$ reaching up to 5 km in width and extending for about 32 km, between the Tagliamento and Isonzo river mouths. The main hydraulic forcing of the system are the tide and the wind. The predominant wind in the area is the Bora from the NE with typical speeds of 10 m/sec (Petti and Bosa, 2004). Semi-diurnal tidal fluxes (65 cm and 105 cm mean and spring tidal range, respectively) affect the Lagoon system and control sediment dispersion through six tidal inlets (Brambati et al., 1983). Salinity values range from 0.21 in the areas close to the river mouths, to 36.0 towards the tidal inlets (Acquavita et al., 2015). Most of the Lagoon is very shallow (<1 m on average), and some areas are constantly submerged (tidal channels and subtidal zones), whereas others are included in tidal flats and saltmarshes. The estimated overall amount of average freshwater discharge is about 70–80 m$^3$/sec, mostly in the western sector of the Lagoon, and does not show any significant seasonal variability (Ret, 2006).

The hydrodynamics of the Lagoon have recently been modelled numerically (Ferrarin et al., 2010) showing that a total average water exchange rate of 5000 m$^3$/sec through all the Lagoon's inlets as a result of the tidally-induced flow. The hydrodynamic model results reveal that the Lignano, Buso and Grado inlets are the most significant in terms of water fluxes, with approximately 35%, 30% and 22% respectively of the total water discharge between the Lagoon and the sea. In