Behaviour of Hg species in the Isonzo river mouth (northern Adriatic sea)

STEFANO COVELLI[1], RAFFAELLA PIANI[1], JOŽE KOTNIK[2], MILENA HORVAT[2], JADRAN FAGANELI[3], MARTINA LOGAR[2], DARIJA GIBIČAR[2], ALESSANDRO ACQUAVITA[4], ANTONIO BRAMBATI[1]

[1]Dept. of Geol., Environ. & Mar. Sciences, Trieste, Italy; E-mail: covelli@univ.trieste.it
[2]Jožef Stefan Institute, Ljubljana, Slovenia; E-mail: joze.kotnik@ijs.si
[3]National Institute of Biology, Marine Biological Station, Piran, Slovenia; E-mail: jadran.faganeli@uni-lj.si
[4]Laboratory of Marine Biology, Trieste, Italy; E-mail: acquavit@univ.trieste.it

Abstract: The interaction between mercury species and physico-chemical parameters in the estuarine zone of Isonzo river in different seasonal conditions were investigated. Particulate Hg and MeHg are well correlated to medium-coarse silty suspended sediment and organic matter. Desorption of Hg from particles in the brackish layer was observed. Due to the presence of a salt wedge, the lower river course seems to be a trap of Hg carried by fluvial waters. MeHg normally decreases approaching the sea but the local increase in the inner zone of the salt wedge could be related to methylation processes in the bottom water layer.

Key words: mercury, methylmercury, suspended matter, biogeochemical cycling, deltaic system.

INTRODUCTION

The Isonzo river (Fig.1) is affected by long periods of low-medium discharges and short peaks of intense riverine flow, associated with high suspended sediment load, following heavy rainfalls. Most of the year, the highly stratified water column and related hypopycnal flux prevail in the dynamic regime within the lower reach of the distributary mouth (Fig. 2). The Isonzo river mouth may be defined as a microtidal, low energy and fine-grained deltaic system[1]. This type of circulation, and the consequent buoyancy-dominated depositional pattern, is interrupted during extreme river floods. The salt wedge is pushed out of the river mouth and the outflow spreads as a plume above the underlying marine water, transporting fine riverborne material seaward to the prodelta zone. Mercury (Hg) contaminated freshwater inputs of the Isonzo river have affected the Gulf of

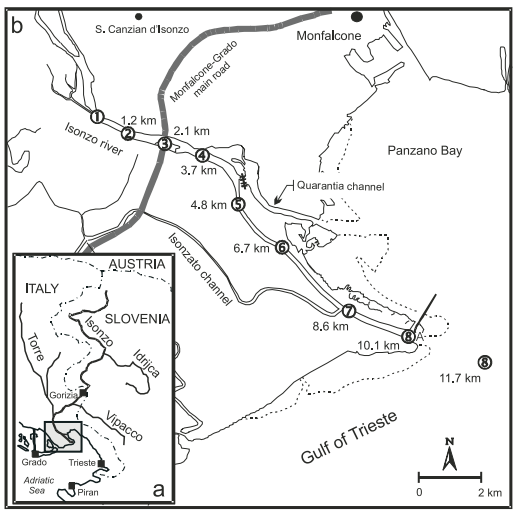

Figure 1. Sampling stations along the Isonzo river.

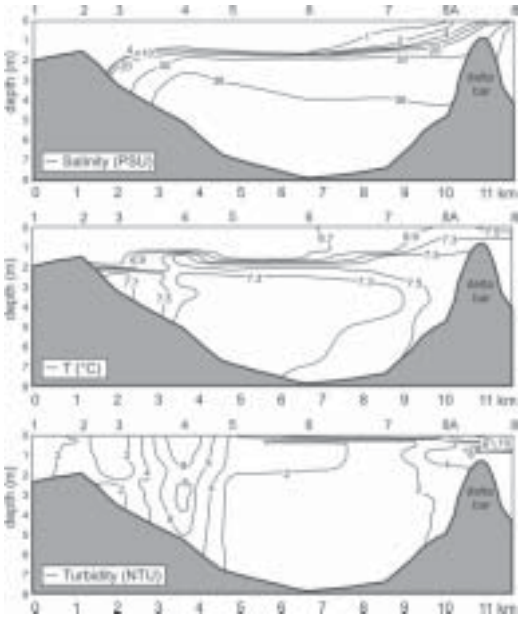

Figure 2. Representation of water stratification in the lower course of the Isonzo river (e.g. February 2002)

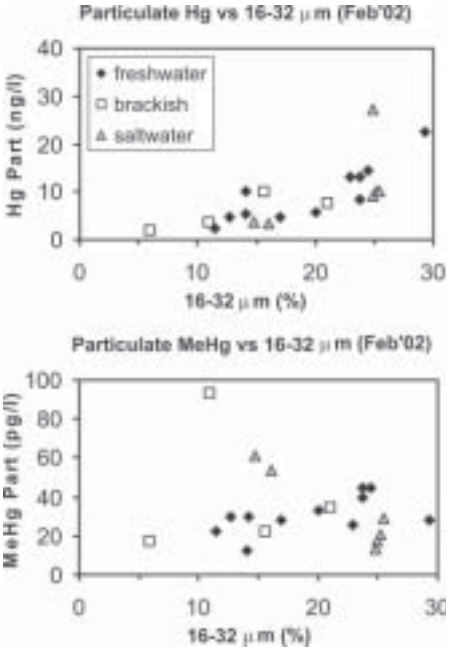

Figure 3. Relationship between particulate Hg and MeHg and grain-size of suspended matter.

Trieste and the northern Adriatic sea since nearly 500 years as a result of excavation of cinnabar rich deposits in the Idrija mining district in western Slovenia.

Although several recent studies have described some aspects of mercury biogeochemistry in the Idrija-Isonzo river system[2], in the coastal waters[3] and sediments[4] of the Gulf of Trieste, little is known about mercury behaviour in the lower course river system. The results of a study on the effects of physical and biogeochemical factors on the distribution of mercury species within the "estuarine zone" of the river mouth in different seasonal conditions are herein presented. Three field samplings were conducted during low (Aug. 2002) and medium river discharges (Feb. and May 2002), and systematic measurements of physico-chemical (salinity, temperature, turbidity, dissolved O_2) and compositional (Hg species, POC, PON, SPM, grain-size) parameters along the water column were investigated at nine sampling stations (Fig.1). Sampling was conducted along the main axis of the river channel moving upstream, during neap tide conditions, in freshwater and saltwater layers and at variable depths (brackish waters), according to the salinity profiles. In May, field operations were performed after one day of heavy rains. As a consequence, a small plume of suspended sediments formed in the river and it was intercepted while sampling was still in progress. Analytical methods used in this study are reported in previous papers on Hg research in the Gulf of Trieste[1, 3].

RESULTS AND DISCUSSION

Total Hg (THg) concentrations in freshwaters increased from February (avg. 18.2 ng/l) to August (avg. 25.7 ng/l). However, the highest contents were found in the bottom saltwaters in late spring (63.5 ng/l) and summer (31.3 ng/l). Most of the mercury transported by the fluvial course is in particulate form (PHg avg. between 51 and 87 % of THg). PHg concentrations in fresh and saltwaters are normally higher than the brackish intermediate layer, especially in May (avg. 18.0 and 37.1 ng/l, respectively), and August (avg. 25.4 and 28.5 ng/l, respectively) indicating that at intermediate salinities a removal process is operative. In bottom saltwaters PHg increases toward the river mouth. Saltwaters entering with tidal fluxes and higher turbulence causing resuspension at lower depth of the mouth may explain this downstream gradient. Looking at the relationships with grain-size of SPM, PHg is positively correlated to the medium-coarse silty fraction (mostly 16-32 μm), no matter the type of water and sampling (Fig. 3). Dissolved mercury (DHg) values appear quite uniform along the water column (avg. ranging from 5.44 to 8.66 ng/l) except in May, where a sharp increase from fresh (avg. 1.78 ng/l) to saltwaters (avg. 31.7) is observed. In terms of percentage of THg, the thin mixing layer always shows higher value of DHg (avg. 39-54 %) in comparison with surface and bottom waters probably due to Hg desorption from suspended matter. Reactive Hg (RHg) concentrations in water samples are usually lower than 1 ng/l. As percentage of THg, RHg is always slightly higher in the brackish waters (avg. 3.8-14.0 %) in comparison with the other two layers. Positive correlation between RHg and DHg in August suggests that part of dissolved Hg is reactive and potentially involved in biogeochemical trans-formations. Estuarine

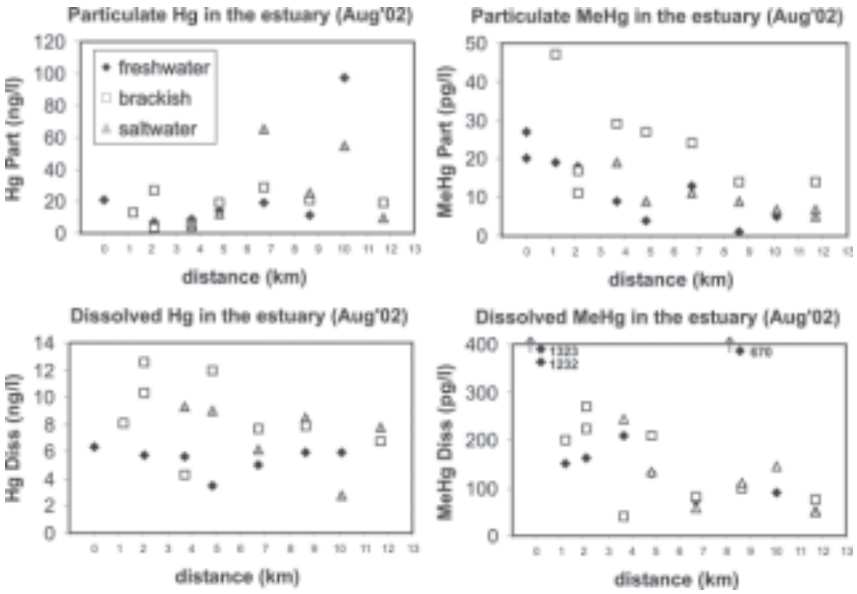

Figure 4. Particulate and dissolved Hg and MeHg along the lower course of the river.

waters show high dissolved gaseous mercury (DGHg) values (avg. 0.68-1.15 ng/l) in winter, whereas low values are observed in spring and summer (avg. 0.09-0.31 ng/l).

Particulate methylmercury (PMeHg) shows the highest values in February (avg. 30.82-41.75 pg/l) in comparison with May (11.79-26.40 pg/l) and August (9.57-22.88 pg/l). It can be noted a decrease of PMeHg from the upper estuary to the river mouth in all sampling periods. PMeHg concentration increases as SPM shows higher amounts in the 16-32 μm fraction in freshwaters, whereas a negative relationship is shown for saltwaters (Fig.3). A good positive correlation was found between POC and PMeHg in water samples except for freshwaters in August, which were negatively correlated. PMeHg was normally < 1% of PHg although higher percentages (up to 2.5%) were found in the brackish layer in February and August. This evidence could be related to phytoplankton component in these two seasons. This was confirmed by microscopic analyses and grain-size spectra of SPM. The dissolved MeHg (DMeHg) shows decreasing concentrations through the water column from the surface to the bottom. Freshwater concentrations of DMeHg were high in August (200-250; max 1350 pg/l) and in February (150-200 pg/l) decreasing downstream (Fig.4). It appears that, in summer, the biological activity and low riverine flow play an important role in MeHg availability in fluvial waters. In May, the surface waters generally show low DMeHg values (10-15 pg/l), although higher values are found in those samples of the upper river course affected by the suspended sediment plume.

The distribution coefficient (Kd l kg^{-1}) of Hg in the freshwaters is 10^5-10^6 showing a stronger association to SPM in comparison with brackish (10^4-10^5) and saltwaters (10^5). The lower Kd for MeHg (10^4) in all waters indicates a weaker binding of organic Hg on particulate matter.

CONCLUSIONS

PHg and PMeHg are mainly carried in medium-coarse silty particles by freshwaters. Brackish waters show the lowest contents of PHg due to removal processes, whereas the lowest values of PMeHg were encountered in saltwater. Seawater enters with tidal fluxes at the bottom, carrying particles with high PHg but as the salt wedge tip is approached, the coarse fraction may accumulate at the river bottom and SPM becomes enriched by the finest fraction. The higher DHg/THg ratio found in the thin mixing layer may indicate desorption of Hg from particles. At the salt wedge tip where dissolved oxygen concentrations are low, methylation processes may possibly act in the bottom water column. The lower course of the river seems to act as a trap, at least for MeHg, and no relevant supply of Hg to the sea during normal flow conditions can be estimated. Resuspension due to turbulence at the river mouth and flocculation of small suspended particles determine enrichment of coarser particles and PHg in the salt wedge within the river channel. Only during very high river floods occurring in autumn, a relevant amount of Hg prevalently bound to suspended sediments is carried into the Gulf of Trieste. Eventually, the river plume diverted by ENE wind-driven surficial currents can be an important way of Hg dispersion and export from the Gulf to the northern Adriatic sea and the adjacent lagoon system.

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