IASWS2022: INTERACTIONS BETWEEN SEDIMENTS AND WATER



Fluxes of settling sediment particles and associated mercury in a coastal environment contaminated by past mining (Gulf of Trieste, northern Adriatic Sea)

Elena Pavoni¹ • Elisa Petranich¹ • Sergio Signore² • Giorgio Fontolan¹ • Annelore Bezzi¹ • Stefano Covelli¹

Received: 26 October 2022 / Accepted: 27 January 2023 / Published online: 8 February 2023 © The Author(s) 2023

Abstract

Purpose As the result of historical mining at Idrija (Slovenia), mercury (Hg) contamination in the Gulf of Trieste (northern Adriatic Sea) is still an issue of environmental concern. The element has been conveyed into the coastal area by the Isonzo/Soča River inputs of freshwater and suspended particles for centuries. This research aims to investigate the occurrence of Hg bound to the settling sediment particles (SSP) in the coastal water and to assess the sedimentary Hg fluxes.

Methods Settling sediment particles were collected at four sites located in the innermost sector of the Gulf, a shallow and sheltered embayment where the accumulation of fine sediments is promoted. Six sampling campaigns were performed under different environmental conditions in terms of discharge from the Isonzo River and 12 sediment traps were installed in the upper and bottom water column for SSP collection. Settling sediment particles (SSP) were collected approximately every 2 weeks and analysed for grain size and total Hg.

Results Settling sediment particles (SSP) consisted predominantly of silt $(77.7 \pm 10.1\%)$, showing a concentration of Hg ranging overall between 0.61 and 6.87 µg g⁻¹. Regarding the daily SSP fluxes, the minimum $(7.05 \pm 3.26 \text{ g m}^{-2} \text{ day}^{-1})$ and the maximum $(92.4 \pm 69.0 \text{ g m}^{-2} \text{ day}^{-1})$ values were observed under conditions of low and high river discharge, respectively. The daily Hg fluxes displayed a notable variability, up to an order of magnitude, both in the surface water layer $(3.07-94.6 \text{ µg m}^{-2} \text{ day}^{-1})$ and at the bottom $(11.3-245 \text{ µg m}^{-2} \text{ day}^{-1})$, reaching the maximum values following periods of high river flow.

Conclusions The Isonzo River inputs of suspended particulate matter continue to convey Hg into the Gulf of Trieste, especially following river flood events, which represent one of the most relevant natural factors affecting the variations of the Hg flux in the investigated area.

Keywords Mercury · Water column · Settling sediment particles · Sediment traps

1 Introduction

The accumulation of contaminants in sediments as well as their potential remobilisation due to resuspension events represents one of the most relevant environmental issues

Responsible editor: Jadran Faganeli

- Department of Mathematics and Geosciences, University of Trieste, Via E. Weiss 2, 34128 Trieste, Italy
- Autorità di Sistema Portuale del Mare Adriatico Orientale-Porto di Trieste, Via Karl Ludwig Von Bruck 3, 34144 Trieste, Italy

in marine-coastal areas (Che et al. 2003; Caplat et al. 2005; Zhao et al. 2018; Acquavita et al. 2021; Le et al. 2022). These processes are especially active in estuaries and semienclosed coastal water basins where aggregation and settling of the riverine inputs of suspended particulate matter (SPM) are promoted by several factors including density/salinity gradients and variations in flow velocity (Wright 1977; Menon et al. 1998; Santos-Echeandía et al. 2012 and references therein). Indeed, these environments often act as a sedimentary trap for particles transported in suspension and for a variety of organic and inorganic contaminants adsorbed on their surface, including potentially toxic trace elements (PTEs) (Turner et al. 1991) among which mercury (Hg) is of major concern due to the potential bioaccumulation of



its most toxic chemical form, methylmercury, in the aquatic trophic chain (Raj and Maiti 2019).

Mining and industrial activities (e.g. chlor-alkali plants) have been recognised among the most relevant anthropogenic sources of Hg (Baumann and Mason 2019; Hatje et al. 2019) which is easily released in the atmosphere during mineral processing (mostly cinnabar, HgS), accumulated on the soil surface through atmospheric deposition and transported over long distances from the source (Kotnik et al. 2005). Runoff and erosion of contaminated river banks and floodplain deposits in the vicinity of decommissioned mining districts and industrial plants may also contribute to the conveyance of solid particles enriched in Hg to marine-coastal areas (Biester et al. 2000; Kocman et al. 2011; Gosar and Žibret 2011; Rimondi et al. 2014; Dickson et al. 2019; Dellapenna et al. 2020; Pavoni et al. 2021a) posing a potential risk for aquatic biota. Indeed, the increased hydrological regime of a river contaminated by Hg may result in increasing Hg concentrations in mussels as found at the Ebro River estuary (Spain; Campillo et al. 2019). In aquatic systems, Hg was found to be mainly associated with the SPM and easily accumulated in the bottom sediments by settling (Benoit et al. 1998; Hatje et al. 2019; Acquavita et al. 2021). One of the main factors governing the distribution of major and trace elements associated with the settling particles in marinecoastal areas is represented by the magnitude and variability in the flux of the settling particles (Buesseler et al. 2007) which may be collected by means of sediment traps (Bloesch and Burns 1980; Broman et al. 1994; Leivuori and Vallius 1998; Matthai et al. 2002; Ergül et al. 2008; Nordmyr et al. 2008; Santos-Echeandía et al. 2012; Helali et al. 2016; Bellucci et al. 2016; Gascón Díez et al. 2016, 2018; Paladini de Mendoza et al. 2018). In this context, few studies are currently available regarding the assessment of the Hg sedimentary flux in both marine and freshwater systems by using sediment traps (Broman et al. 1994; Gascón Díez et al. 2016, 2018; Botwe et al. 2018).

The aim of this research is to evaluate the occurrence of Hg associated with the settling sediment particles (SSP) in the Bay of Panzano, the innermost sector of the Gulf of Trieste which is known to be affected by Hg contamination as a result of long-term mining activity at Idrija (Slovenia), the world's second-largest Hg mine (Horvat et al. 1999; Covelli et al. 2001, 2006b, 2007, 2021; Pavoni et al. 2021b). Another goal of this study is to improve the use of sediment traps to evaluate background levels of SSP and associated contaminants such as Hg. This is especially important at the bottom of the water column and may represent a valuable technical tool in the management of future dredging operations. In this context, the environmental issues related to the occurrence and distribution of Hg in the investigated area are of relevant concern since dredging is planned for the main access channel to the Port of Monfalcone (the busiest port of the northern Adriatic Sea). Indeed, the assessment of the sedimentary Hg fluxes in this relatively shallow embayment prone to the accumulation of fine sediments will provide useful scientific support for environmental management and risk assessment as well as for the future evaluation of the impact of Hg in the Gulf of Trieste.

2 Materials and methods

2.1 Environmental setting

The semi-enclosed water basin of the Gulf of Trieste is located in the northern Adriatic Sea (Italy), covering an area of approximately 500 km². The water depth is relatively shallow, (maximum depth of 25 m) and the anticlockwise circulation pattern of the Adriatic Sea mainly governs the water circulation which is further affected by tides, seasonal variations in freshwater inputs and winds including Bora (E-NE), Libeccio (SW) and Sirocco (SE) (Olivotti et al. 1986; Malačič and Petelin 2009). The salinity is typical of brackish and marine waters, ranging between 25 and 38 PSU (using the Practical Salinity Scale), as the result of the interaction between seawater and freshwater (Cozzi et al. 2012). The main freshwater input is provided by the Isonzo/ Soča River (average discharge of 123 m³ s⁻¹, for the period 1998–2005, at Turriaco, 13 km from the mouth, Comici and Bussani 2007), with two main flood periods during spring and autumn as the result of snowmelt and rainfall respectively, followed by the Timavo/Reka River (average discharge of 29.3 m³ s⁻¹, Petrič and Kogovšek 2016). During flood events, the Isonzo River flow develops a turbidity plume characterised by a strong correlation between low salinity and turbidity in the surface water layer (Covelli et al. 2007). Following a river plume event, the distribution of the suspended particles appeared to be heavily affected by wind. In detail, the river plume is stretched NE-SW under prevailing E-NE wind (Bora) towards the Marano and Grado Lagoon (Covelli et al. 2001; Turritto et al. 2018). Conversely, the plume heads east, affecting the Panzano Bay, especially in the absence of wind or under prevailing SE wind (Sirocco) (Covelli et al. 2001; Tondello 2017, 2020).

As the result of its karst nature, the Timavo River has particularly complex hydrological characteristics, since the flow at the mouth also depends on underground circulation in the Karst aquifer. The river can still produce a turbidity surface plume that affects the northern part of the Bay of Panzano especially under conditions of prevalent SE wind (Tondello 2017, 2020).

The Hg contamination in the Gulf of Trieste is well known (Horvat et al. 1999) due to over 500 years of cinnabar (HgS) mining at the Idrija mining district which seriously affected the environmental quality in the areas surrounding the mine



as well as along the Isonzo River drainage basin (Kocman et al. 2011; Gosar and Žibret 2011; Gosar and Teršič 2012; Baptista-Salazar et al. 2017). As the result of the erosion of Hg-enriched river banks and floodplains, the element was and continues to be conveyed into the Gulf of Trieste mainly in association with the SPM, especially following periods of high river discharge (Covelli et al. 2004, 2006b, 2007, 2021; Pavoni et al. 2021b). Subsequently, remarkable Hg concentrations, up to one order of magnitude higher than the natural local background $(0.13 \pm 0.04 \,\mu g \, g^{-1}; \, \text{Covelli})$ et al. 2006a), were found in the surface sediments in front of the mouth of the Isonzo River (23.3 μg g⁻¹; Covelli et al. 2001), along the main access channel approaching the port of Monfalcone (0.30–13.5 µg g⁻¹; Covelli et al. 2021) and in the Bay of Panzano $(0.77-6.39 \,\mu g \, g^{-1}; Pavoni et al. 2021b)$, a shallow embayment suitable for the accumulation of fine particles. Indeed, the supply of suspended particles enriched in Hg from the Isonzo River to the Bay of Panzano appears to be more effective with respect to the other directions of SPM dispersion in the Gulf of Trieste (Covelli et al. 2001).

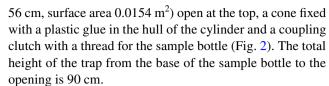
2.2 Sampling strategy

Installation of the sediment traps and sampling campaigns were performed from February to May 2016 at four sites (P1, P2, P4 and P5) located in the vicinity of the main access channel to the Port of Monfalcone in the northernmost sector of the Gulf of Trieste (Bay of Panzano) (Fig. 1, Table 1).

Sites P1 and P2 are located in a mussel farm (6 and 10 m depth, respectively) and more precisely in front of the mouth of the Timavo River at the northwestern end of the mussel farm (site P1) and in its central sector among the mussel longlines (site P2). Indeed, site P2 appears to be more protected among the investigated sites. Site P4 (5 m depth) is characterised by the occurrence of seagrass and is located in the coastal sector near a confined disposal area suitably arranged for the storage of dredged sediments. Site P5 is the shallowest site (4 m depth) and is representative of the coastal area in front of the tourist sandy beach of Marina Julia (Fig. 1). All the sampling sites may be affected by both Isonzo River plume events as well as the resuspension of fine sediments induced by both natural (e.g. waves) and anthropogenic factors (e.g. dredging, transit of ships with large draught) (Pavoni et al. 2021b).

Generally, low turbidity values (below 20–25 NTU) were observed along the water column at the investigated area, suggesting that both natural and anthropogenic perturbations do not appear to promote a lasting increase in turbidity with the subsequent quick restoration of unperturbed conditions (Pavoni et al. 2021b).

Sediment traps were built in-house, adapting suggestions reported in Lukashin et al. (2011). Each trap consisted of an opaque cylindrical PVC tube (diameter 14 cm, height



Each trap was equipped with a dismountable baffle grid at the opening in order to reduce turbulence and avoid wash-out of the sediment from the upper part of the cylinder. The sample bottle was a standard recycled plastic bottle for chemical reagents with a volume of 500 mL. The clutch was piled up onto the cone, and the sample bottle was inserted into the clutch. The water above the collecting bottle can be drained via two stopcocks. The traps were used pairwise (Fig. 2) and can operate at a selected depth by hanging vertically from one of the mussel longlines in the mussel farm. Sediment traps placed on the seabed consisted of the same cylindrical sampling tubes mounted on a vertical stainless-steel structure fixed to a reinforced concrete base laid on the seabed. Considering the complete geometry of the trap with its base, the opening is placed approximately at 100 cm from the bottom. The sampling tubes are easily detached and repositioned by a scuba diver for recovery and transport aboard the boat without removing the base. The deployment of the sediment traps was set from the boat using an electric winch.

Once on board, each tube was emptied of its internal water down to the cone with the help of the two stopcocks. The water was collected in 2-L polyethylene containers. The bottle with the sample was then unscrewed from the cone into a bucket in order to recover the remaining water with the SSP. A final rinse was performed from the inside walls of each tube. In conclusion, each SSP sample consisted of the sum of the material in the bottle and in the 2-L containers, which were left to decant in the laboratory to eliminate excess water and then to combine the different SSP aliquots.

In summary, eight sediment traps (two in the surface water layer at a depth of approximately 2 m and two at the bottom) were placed in the mussel farm (sites P1 and P2). In this way, the amount of the trapped material as well as the corresponding daily SSP and Hg fluxes were measured in replicates. Additional four sediment traps (two at each site) were placed at the bottom in the shallowest sites (P4 and P5). The SSP accumulated into each sediment trap were collected approximately every 2 weeks according to Buesseler et al. (2007) and Botwe et al. (2018), during six sampling campaigns under various environmental conditions in terms of the level of discharge from the Isonzo River (Fig. 1, Table 1).

2.3 Analytical determinations: grain size composition and total Hg content

The SSP samples were stored in a dark room at 4 °C until complete decantation of the solid material, the water was removed and the remaining solid fraction was collected.



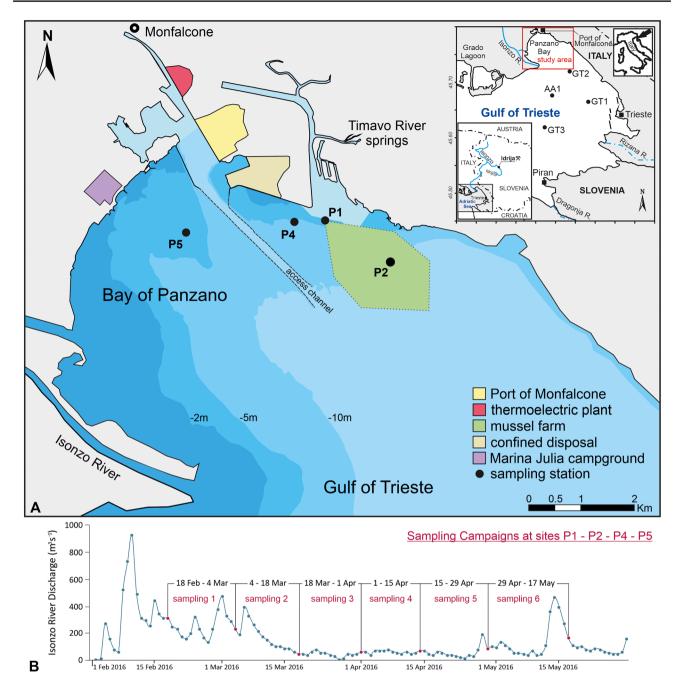


Fig. 1 A Index map of the study area and location of the sampling sites (P1, P2, P4 and P6) near the main access channel to the Port of Monfalcone (Bay of Panzano, Gulf of Trieste). Location of sampling stations GT1, GT2, GT3 and AA1 in the Gulf of Trieste where previous investigations were performed by Faganeli et al. (2003) and

Covelli et al. (2006a). **B** Isonzo River daily discharge (m^3 s $^{-1}$) from January 1, 2016, to May 30, 2016, during six sampling campaigns, as measured at the Pieris Station (Gorizia), located approximately 15 km upstream from the river mouth

Grain size analysis was performed in replicates (two SSP samples collected by means of two sediment traps at each sampling site and at the same depth) using an aliquot of each fresh sample which was treated with $\rm H_2O_2$ (3%) for 24 h to eliminate the majority of the organic matter and wetsieved through a 2-mm sieve. A laser granulometer (Malvern

Mastersizer 2000) was used for the grain size analysis of the resulting < 2 mm fraction.

For total Hg determination, the remaining amount of each fresh sample was frozen, freeze-dried (CoolSafe 55–4, SCANVAC) and homogenised. Three aliquots of each sample were directly analysed using a Direct Mercury



Table 1 Environmental conditions (perturbed: high river flow; unperturbed: medium-low river flow) and daily discharge from the Isonzo River (m³ s⁻¹) during the six SSP sampling campaigns at the four investigated sites in the Bay of Panzano

Sampling campaign		Environmen- tal condition	Isonzo River discharge (m³ s ⁻¹)	
			Min – max	Average
1	February 18–March 4	Perturbed	131–471	256±89
2	March 4-18	Perturbed	49.3-391	169 ± 101
3	March 18-April 1	Unperturbed	2.93-76.0	44.0 ± 18.3
4	April 1–15	Unperturbed	40.1-74.7	61.5 ± 10.8
5	April 15–29	Unperturbed	16.1-188	55.5 ± 42.5
6	April 29–May 17	Perturbed	33.6–462	143 ± 130

Analyser (DMA-80, Milestone) following EPA Method 7473 (EPA 1998). Certified reference material (PACS-3 Marine Sediment CRM, NRCC) was analysed for quality control obtaining acceptable recoveries (ranging between 88 and 101%). The limit of detection (LOD) was approximately 0.004 μ g g⁻¹ and the precision of the analysis expressed as RSD% was < 2%.

2.4 Daily fluxes of settling sediment particles and associated Hg

The daily SSP fluxes ($F_{\rm SSP}$) were estimated according to the following Eq. (1) (Botwe et al. 2017, 2018) where M is the mass (g) of the SSP accumulated into each sediment trap, A is the cross-sectional area of the trap (m^2) and D is the duration (days) of the trap deployment in situ.

Fig. 2 Sediment traps placed at the **A** seabed and **B** hanging vertically from the mussel longline at approximately 2 m depth

$$F_{SSP} = \frac{M}{A * D} \tag{1}$$

The corresponding daily Hg fluxes (F_{Hg}) were calculated according to Eq. (2) (Botwe et al. 2018), where F_{SSP} is the daily SSP flux and (Hg) is the concentration of Hg in each SSP sample:

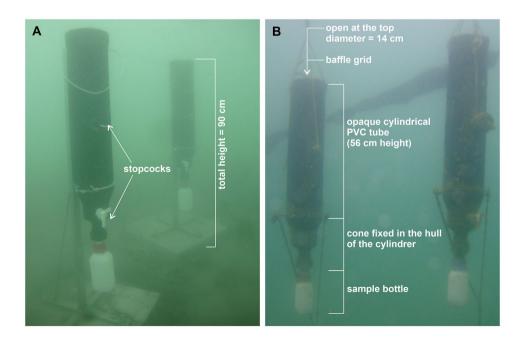
$$F_{Hg} = F_{SSP} * [Hg] \tag{2}$$

Although a certain contribution from sediment resuspension cannot entirely be excluded, especially in shallow water, the SSP and Hg fluxes were calculated assuming that the trapped material was accumulated by settling along the water column.

3 Results and discussion

3.1 Settling sediment particles: grain size composition and daily fluxes

Settling sediment particle (SSP) contents in the traps placed in the surface water layer ranged between 1.04 ± 0.46 and 12.7 ± 7.5 g (sampling campaign 4 and 2, respectively) and between 1.76 ± 0.68 and 28.4 ± 19.0 g (sampling campaign 4 and 2, respectively) at the bottom. Settling sediment particles (SSP) were generally found to be composed predominantly of silt (77.7 $\pm10.1\%$) followed by sand (13.8 $\pm11.4\%$) and clay (8.46 ±1.87) (Fig. 3) taking into account the main textural components (Shepard 1954). Significant differences in the grain size composition were not observed between





replicates at the same site and among different sites and sampling campaigns. There was an exception during sampling campaign 6 which showed a higher average content of sand $(29.4 \pm 14.4\%)$, especially in the surface water at the mussel farm (sites P1 and P2, $47.0 \pm 1.7\%$). In detail, the bimodal size distribution observed at the bottom of sites P1 and P2 (sampling campaign 6) and to a lesser extent at site P4 (sampling campaign 5) may be related to settling processes from the surface water layer to the bottom (Fig. 3). In addition to the SPM entering the Gulf from the Isonzo River, this grain size distribution could also be affected by the coarse (very fine sand) suspended particle supply from the Timavo River during high river discharge (unpublished data), since the mussel farm is located in front of the river mouth (Fig. 1). The grain size composition was generally consistent with previous results focused on the surface sediments collected from the same investigated area (Covelli et al. 2021; Pavoni et al. 2021b) thus confirming that the fine suspended particles entering the Gulf of Trieste in association with the Isonzo River inputs were trapped in the Panzano Bay where settling may be completed in a couple of days (Covelli et al. 2001). Nevertheless, the generally low sand content suggested that the sampling sites are far from the beach's most active zone, within a depth of 5-6 m, where the majority of sand movement is brought on by typical waves and storms (Marocco 1989; Gordini et al. 2003).

Among the investigated sites, sampling campaigns 4 and 2 showed the minimum $(7.05\pm3.26~{\rm g~m^{-2}~day^{-1}})$ and the maximum $(92.4\pm69.0~{\rm g~m^{-2}~day^{-1}})$ average daily SSP flux, respectively (Fig. 4). The particle fluxes observed in this research were generally elevated with respect to other estuarine and marine environments, although with different SPM supplies, such as the Gulf of Taranto $(2.78-22.5~{\rm g~m^{-2}~day^{-1}};$ Bellucci et al. 2016), estuarine environments in the Iberian Peninsula $(8.8-91.3~{\rm g~m^{-2}~day^{-1}};$ Santos-Echeandía et al. 2012), in Finland $(5-120~{\rm g~m^{-2}~day^{-1}};$ Nordmyr et al. 2008) in the Black Sea $(9.4-56.4~{\rm g~m^{-2}~day^{-1}};$ Ergül et al. 2008) and in the Baltic Sea $(1.1-7.2~{\rm g~m^{-2}~day^{-1}};$ Broman et al. 1994; $0.55-1.6~{\rm g~m^{-2}~day^{-1}};$ Leivuori and Vallius 1998).

Generally, the highest fluxes of SSP were observed following periods of high discharge from the Isonzo River at site P4 ($188 \pm 1 \text{ g m}^{-2} \text{ day}^{-1}$, sampling campaign 2) followed by site P1 both in the surface water (maximum values of 93.7 and $83.1 \pm 8.1 \text{ g m}^{-2} \text{ day}^{-1}$ during sampling campaigns 1 and 2, respectively) and at the bottom (maximum values of 77.4 ± 39.8 and $167 \pm 8 \text{ g m}^{-2} \text{ day}^{-1}$ during sampling campaigns 1 and 2, respectively).

Conversely, notably lower values were observed under unperturbed environmental conditions, especially during sampling campaigns 3 and 4. This suggested that a relationship existed between the SSP fluxes and the Isonzo River discharge, as also confirmed by the significant correlations between the two parameters during the trap deployment at each site (Fig. 5).

This is especially evident at site P4 (r = 0.823, N = 5, P < 0.5) showing a greater SSP flux (ranging between 7.72 and 188 g m⁻² day⁻¹ during sampling campaigns 4 and 2, respectively), as also suggested by the elevated slope of the regression line (1.04). The situation is similar at the nearby site P1 (r=0.932, N=6, 0.01 < P < 0.1, slope = 0.40)(Fig. 5). Although an equally significant correlation was observed at site P2 (r = 0.891, N = 6, 0.1 < P < 0.5), the minimum values of SSP fluxes (ranging between 3.16 and 27.0 g m⁻² day⁻¹ during sampling campaigns 4 and 2, respectively) as well as the minimum slope (0.11) of the regression line were observed at this site. This evidence suggested that site P2 was more protected and less affected by the SSP river surface supply due to its location in the central sector of the mussel farm where the mussel longlines may have a protective effect towards the traps. Conversely, a weak correlation was observed at site P5 (r=0.555, N=5, P<0.5)most likely due to the shallow water depth which may promote permanence in the suspension of the suspended particles and/or resuspension events, as also suggested by the low value of the slope of the regression line (0.20) (Fig. 5).

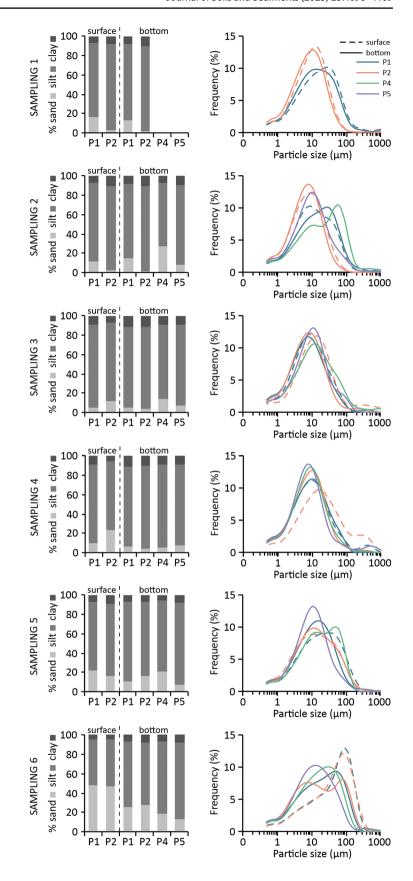
3.2 Mercury content and daily fluxes

The overall concentration of Hg in the SSP varied between 0.61 and $6.87 \mu g g^{-1}$ (Fig. 4), showing values of the same order of magnitude with respect to previous investigations focused on the surface sediments collected from the same area (Acquavita et al. 2010; Covelli et al. 2021; Pavoni et al. 2021b), in the offshore sector of the Gulf (ranging between 0.10 and 11.7 µg g⁻¹, Covelli et al. 2001) as well as in the northern Adriatic Sea (ranging between 0.05 and 8.63 μ g g⁻¹, (Ferrara and Maserti 1992). Conversely, the amount of Hg in the SSP was found to be notably lower compared to surface sediments collected at the mouth of the Isonzo River (ranging between 4.45 and 23.3 μg g⁻¹; Covelli et al. 2001) where the occurrence of detrital Hg, i.e. cinnabar particles, was recognised in association with the sandy fraction which is predominant in this area (Biester et al. 2000; Covelli et al. 2001).

No notable differences in the amount of Hg associated with the SSP were observed among the different sampling campaigns at the mussel farm (1.37 \pm 0.39 and 1.85 \pm 0.59 μg g $^{-1}$ at sites P1 and P2, respectively) although slightly higher Hg concentrations were found at site P2, especially at the bottom (2.10 \pm 0.50 μg g $^{-1}$). Comparable Hg concentrations were also found at site P4 (1.22 \pm 0.37 μg g $^{-1}$) which is quite close to the mussel farm, whereas the highest concentrations of Hg were observed at site P5 (4.80 \pm 1.36 μg g $^{-1}$) (Fig. 4). Indeed, this site appeared to be particularly affected by resuspension



Fig. 3 Mean grain size distribution and composition of SSP collected at the four investigated sites in the Bay of Panzano under different environmental conditions. Significant differences in the grain size distribution and composition of the samples collected at the same depth at each site were not observed





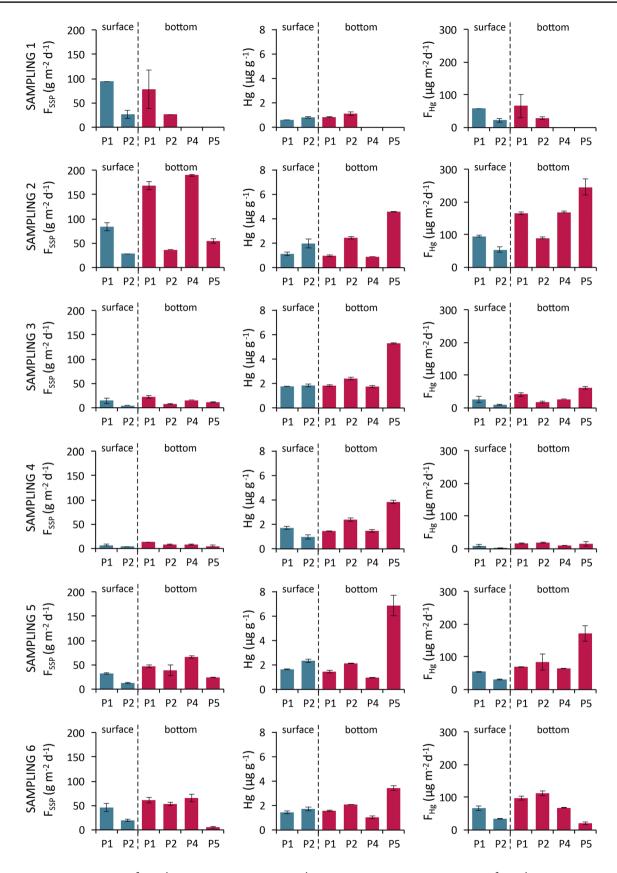


Fig. 4 Daily fluxes of SSP (g m⁻² day⁻¹), concentration of Hg (μ g g⁻¹) in the SSP and daily Hg fluxes (μ g m⁻² day⁻¹) at the four investigated sites in the Bay of Panzano under perturbed (sampling campaigns 1, 2, 6) and unperturbed (sampling campaigns 3, 4, 5) conditions



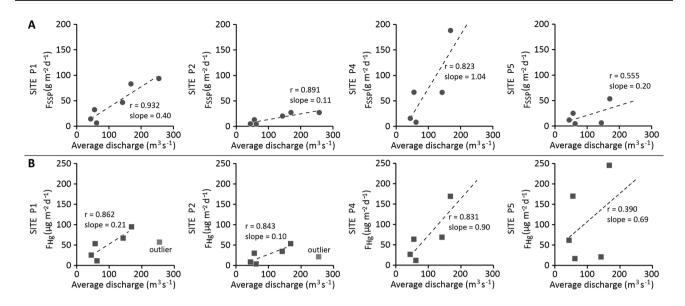


Fig. 5 Correlation between the Isonzo River average discharge (m³ s⁻¹) during each campaign of trap deployment and **A** the daily fluxes of SSP (g m⁻² d⁻¹) (circles) and **B** daily fluxes of Hg (μ g m⁻² d⁻¹)

(squares) at the four investigated sites in the Bay of Panzano. Surface SSP and Hg fluxes are displayed for sites P1 and P2

events which could increase the amount of material in the traps, most likely due to the shallow water depth.

The estimated daily Hg fluxes associated with the SSP showed a notable variability, up to an order of magnitude, and ranged overall between 3.07 ± 0.86 and 245 ± 25 µg m⁻² day⁻¹ during sampling campaigns 4 and 2 (unperturbed and perturbed conditions, respectively) (Fig. 4).

Results were found to be comparable to those observed in the fine sedimentary fraction collected through sediment traps placed in a harbour area which may act as a sink for contaminants associated with suspended particles in the Gulf of Guinea, Ghana (from 13.0 ± 4.5 to 114 ± 85 µg m⁻² day⁻¹; Botwe et al. 2018).

Moreover, the temporal variability during the 6 sampling campaigns suggested that there were periods of enhanced Hg accumulation, especially under perturbed conditions (sampling campaign 2), whereas the lowest Hg fluxes were observed under unperturbed conditions (sampling campaigns 3 and 4). With the only exception being sampling campaign 6, the highest Hg fluxes were observed at site P5 especially following periods of high discharge from the Isonzo River (sampling campaign 2). In addition, the Hg fluxes appeared to be related to the Isonzo River discharge as evidenced by the strong correlation with the average discharge during the trap deployment in the surface water at sites P1 (r=0.862, N=5, P<0.5) and P2 (r=0.843, N=5, P<0.5) (Fig. 5). Sampling campaign 1 (perturbed conditions with the highest average discharge of 256 m³ s⁻¹) represents an outlier since it appears to be depleted in terms of Hg concentrations and fluxes. This may be due to dilution effects in the SSP which were likely composed of different material deriving from enhanced erosion processes along both the Isonzo River drainage basin and those of its major tributaries not affected by Hg contamination. Although the Hg fluxes and the river discharge are significantly correlated, the surface Hg fluxes were found to be relatively low in the mussel farm with respect to sites P4 and P5, especially at site P2 (ranging between 3.07 and 53.8 µg m⁻² day⁻¹ during sampling campaigns 4 and 2, respectively). This further confirms that site P2 was the most protected and less affected in terms of both SSP and Hg fluxes, as also suggested by the low slope value of the regression line between the Hg flux in the surface water and the river discharge (0.21, Fig. 5). Conversely, site P4 showed the maximum values of Hg fluxes (ranging between 11.3 and 169 µg m⁻² day⁻¹ during sampling campaigns 4 and 2, respectively) which were strongly correlated to the river discharge (r = 0.831, N = 5, P < 0.5). Moreover, the elevated slope value (0.90) suggested that site P4 was the most affected by both SSP and Hg fluxes. This was similar at site P5, although a weaker correlation between the daily fluxes of Hg and the average discharge was observed most likely due to the shallow water depth and potential contributions from resuspension events (Fig. 5).

An estimation of the annual Hg fluxes made on the basis of the average daily Hg fluxes at each site during the entire sampling period ranged between 15.3 and 37.5 mg m⁻² y⁻¹ at sites P2 and P5, respectively (Table 2). In this context, a comparison can be made with the Hg fluxes estimated by sediment cores collected from different sectors of the Gulf of Trieste (Covelli et al. 2006a; Fig. 1, Table 2).

According to Covelli et al. (2006a), the annual Hg fluxes ranged between 1.77 mg m⁻² y⁻¹, in the deepest sector of



Table 2 Annual Hg fluxes (mg m⁻² y⁻¹) and concentrations of Hg (μg g⁻¹) in the SSP and in the surface sediments (Pavoni et al. 2021a, b) at the four investigated sites in the Bay of Panzano compared to previous results from the Gulf of Trieste (Faganeli et al. 2003; Covelli et al. 2006a)

Sampling site		Hg—SSP μg g ⁻¹	Hg—sediment μg g ⁻¹	Annual Hg flux mg m ⁻² y ⁻¹	Reference
P1	Bay of Panzano	1.37 ± 0.39	0.77*	23.2	This study *Pavoni et al. 2021b
P2		1.85 ± 0.59	2.46*	15.3	
P4		1.22 ± 0.37	0.78*	24.7	
P5		4.80 ± 1.36	4.23*	37.5	
AA1	Gulf of Trieste	2.68 ± 0.42	3.21	14.0**	**Faganeli et al. 2003
GT1	Gulf of Trieste	n.d	2.34	3.75	***Covelli et al. 2006a
GT2		n.d	8.45	31.5	
GT3		n.d	1.56	1.77	

nd not determined

the Gulf (site GT3, 25 m depth), and 31.5 mg m⁻² year⁻¹, just in front of the mouth of the Isonzo River (site GT2; 15 m wwdepth), respectively. Although the estimation approaches are different, the same orders of magnitude for the annual Hg fluxes observed in this study suggested that the contribution of settling particles in terms of Hg accumulation at the sea bottom has not showed notable changes in the last 20-25 years. Moreover, results from this research are also comparable with the annual Hg flux estimated by means of sediment traps placed 4.5 miles SE from the mouth of the Isonzo River (14 mg m⁻² year⁻¹, site AA1; Faganeli et al. 2003; Fig. 1, Table 2). This is consistent with the dynamics of Hg dispersion in the Gulf which is affected by several factors and wind in particular (Covelli et al. 2001). Indeed, under conditions of a prevailing SE wind, the supply of suspended particles enriched by Hg from the Isonzo River to the Bay of Panzano appears to be promoted. However, it cannot be excluded that a non-negligible contribution from sediment resuspension may occur, especially at the shallowest site (P5) where the shallow water depth may favour permanent particle suspension, according to observations of other shallow coastal areas (Bellucci et al. 2016). Moreover, the opening of the sediment traps was high enough (approximately 120 cm from the bottom) to avoid most of the contribution from sediment resuspension. This is also confirmed by the average concentration of Hg in the SSP which was generally found to be of the same order of magnitude with respect to the surface sediments at the same sites (Pavoni et al. 2021b; Table 2).

4 Conclusions

Although the Idrija mining district closed in 1996, Hg is still conveyed into the marine-coastal area of the Gulf of Trieste by freshwater inputs from the Isonzo River.

Results from this research suggested that notable fluxes of SSP (max 188 ± 1 g m⁻² day⁻¹) and associated Hg (max 245 ± 25 µg m⁻² day⁻¹) may occur but they were limited to brief periods of elevated river discharge, which was confirmed as a still active and relevant source of Hg in the Gulf.

Moreover, Hg concentrations in the SSP $(0.61-6.87 \ \mu g \ g^{-1})$ were found to be of the same order of magnitude with respect to the amount of Hg observed in the surface sediments in previous investigations. This suggests that settling processes in relatively shallow water still play a crucial role in the quick transfer of Hg-enriched suspended particles from the water column to the seabed compartment.

Insights from this research suggest that variations in the Hg fluxes appeared to be predominantly governed by natural factors such as flood events from the Isonzo River and, to a lesser extent, by physical resuspension in shallow water due to increased wave motion. This is of relevant concern since local anthropogenic perturbations, such as those projected to occur in the future during dredging operations planned along the navigation channel approaching the Port of Monfalcone, would be most likely be constrained and are not expected to seriously affect natural Hg fluxes from the water column to the seabed.

Acknowledgements The authors are grateful to Giacomo Casagrande and the Servizio Gestione Risorse Idriche of the Friuli Venezia Giulia Region for providing discharge data for the Isonzo River. We are also grateful to Gabriele Crevatin, Walter De Walderstein and Paolo De Carli for their technical assistance during sampling. The authors want also to thank Daniele Karlicek and Lorenzo Furlan for their invaluable technical support for the sediment trap assemblage. Karry Close is warmly acknowledged for proofreading the manuscript. The anonymous reviewers are greatly acknowledged for their thoughtful reviews and useful suggestions which improved the quality of the manuscript.

Funding Open access funding provided by Università degli Studi di Trieste within the CRUI-CARE Agreement.

Data Availability The datasets generated in the framework of this study are available from the corresponding author on reasonable request.



^{*}Previous results on surface sediments (Pavoni et al. 2021b) **Estimated from sediment traps (Faganeli et al. 2003) ***Estimated from sediment cores (Covelli et al. 2006a)

Declarations

Conflict of interest The authors declare no competing interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

- Acquavita A, Floreani F, Covelli S (2021) Occurrence and speciation of arsenic and mercury in alluvial and coastal sediments. Curr Opin Environ Sci Health 22:100272. https://doi.org/10.1016/j.coesh.2021.100272
- Acquavita A, Predonzani S, Mattassi G et al (2010) Heavy metal contents and distribution in coastal sediments of the Gulf of Trieste (northern Adriatic Sea, Italy). Water Air Soil Poll 211:95–111. https://doi.org/10.1007/s11270-009-0284-5
- Baptista-Salazar C, Richard J-H, Horf M et al (2017) Grain-size dependence of mercury speciation in river suspended matter, sediments and soils in a mercury mining area at varying hydrological conditions. Appl Geochem 81:132–142. https://doi.org/10.1016/j.apgeochem.2017.04.006
- Baumann JS, Mason RP (2019) Geochemistry of mercury in the marine environment. In: Cochran JK, Bokuniewicz HJ, Yager PL (eds) Encyclopedia of Ocean Sciences, 3rd. Academic Press, Cambridge, MA, USA, pp 301–308
- Bellucci LG, Cassin D, Giuliani S et al (2016) Sediment pollution and dynamic in the Mar Piccolo of Taranto (southern Italy): insights from bottom sediment traps and surficial sediments. Environ Sci Pollut Res 23:12554–12565. https://doi.org/10.1007/s11356-016-6738-6
- Benoit JM, Gilmour CC, Mason RP et al (1998) Behavior of mercury in the Patuxent River estuary. Biogeochemistry 40:249–265
- Biester H, Gosar M, Covelli S (2000) Mercury speciation in sediments affected by dumped mining residues in the drainage area of the Idrija mercury mine, Slovenia. Environ Sci Technol 34:3330–3336. https://doi.org/10.1021/es991334v
- Bloesch J, Burns NM (1980) A critical review of sedimentation trap technique. Schweiz Z Hydrol 42:15–55
- Botwe BO, Abril JM, Schirone A et al (2017) Settling fluxes and sediment accumulation rates by the combined use of sediment traps and sediment cores in Tema Harbour (Ghana). Sci Total Environ 609:1114–1125. https://doi.org/10.1016/j.scitotenv. 2017.07.139
- Botwe BO, Nyarko E, Lens PNL (2018) Settling fluxes and ecotoxicological risk assessment of fine sedimentary metals in Tema Harbour (Ghana). Mar Pollut Bull 126:119–129. https://doi.org/10.1016/j.marpolbul.2017.11.001
- Broman D, Lundbergh I, Näf C (1994) Spatial and seasonal variation of major and trace elements in settling particulate matter in an estuarine-like archipelago area in the Northern Baltic proper. Environ Pollut 85:243–257

- Buesseler KO, Antia AN, Chen M et al (2007) An assessment of the use of sediment traps for estimating upper ocean particle fluxes. J Mar Res 65:345–416. https://doi.org/10.1357/002224007781567621
- Campillo JA, Santos-Echeandía J, Fernández B (2019) The hydrological regime of a large Mediterranean river influences the availability of pollutants to mussels at the adjacent marine coastal area: implications for temporal and spatial trends. Chemosphere 237:124492. https://doi.org/10.1016/j.chemosphere.2019.124492
- Caplat C, Texier H, Barillier D, Lelievre C (2005) Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. Mar Pollut Bull 50:504–511. https://doi.org/10.1016/j.marpolbul. 2004.08.004
- Che Y, He Q, Lin W-Q (2003) The distributions of particulate heavy metals and its indication to the transfer of sediments in the Changjiang Estuary and Hangzhou Bay, China. Mar Pollut Bull 46:123–131. https://doi.org/10.1016/S0025-326X(02)00355-7
- Comici C, Bussani A (2007) Analysis of the river isonzo discharge (1998–2005). Boll Geofis Teor Appl 48:435–454
- Covelli S, Faganeli J, Horvat M, Brambati A (2001) Mercury contamination of coastal sediments as the result of long-term cinnabar mining activity (Gulf of Trieste, northern Adriatic sea). Appl Geochem 16:541–558. https://doi.org/10.1016/S0883-2927(00) 00042-1
- Covelli S, Fontolan G, Faganeli J, Ogrinc N (2006a) Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (northern Adriatic Sea). Mar Geol 230:29–51. https://doi.org/10.1016/j.margeo.2006.03.013
- Covelli S, Petranich E, Pavoni E, Signore S (2021) Can sediments contaminated by mining be a source of mercury in the coastal environment due to dredging? Evidence from thermo-desorption and chemical speciation. Bull Environ Contam Toxicol 106:942–948. https://doi.org/10.1007/s00128-021-03159-x
- Covelli S, Piani R, Acquavita A et al (2007) Transport and dispersion of particulate Hg associated with a river plume in coastal Northern Adriatic environments. Mar Pollut Bull 55:436–450. https://doi.org/10.1016/j.marpolbul.2007.09.006
- Covelli S, Piani R, Faganeli J, Brambati A (2004) Circulation and suspended matter distribution in a microtidal deltaic system: the Isonzo river mouth (northern Adriatic Sea). J Coastal Res 41:130–140
- Covelli S, Piani R, Kotnik J et al (2006b) Behaviour of Hg species in a microtidal deltaic system: the Isonzo River mouth (northern Adriatic Sea). Sci Total Environ 368:210–223. https://doi.org/10. 1016/j.scitotenv.2005.09.089
- Cozzi S, Falconi C, Comici C et al (2012) Recent evolution of river discharges in the Gulf of Trieste and their potential response to climate changes and anthropogenic pressure. Estuar Coast Shelf Sci 115:14–24. https://doi.org/10.1016/j.ecss.2012.03.005
- Dellapenna TM, Hoelscher C, Hill L et al (2020) How tropical cyclone flooding caused erosion and dispersal of mercury-contaminated sediment in an urban estuary: the impact of Hurricane Harvey on Buffalo Bayou and the San Jacinto Estuary, Galveston Bay, USA. Sci Total Environ 748:141226 https://doi.org/10.1016/j.scitotenv.2020.141226
- Dickson JO, Mayes MA, Brooks SC et al (2019) Source relationships between streambank soils and streambed sediments in a mercury-contaminated stream. J Soils Sediments 19:2007–2019. https://doi.org/10.1007/s11368-018-2183-0
- EPA (1998) Method 7473 (SW-846) Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry. EPA, Washington
- Ergül HA, Topcuoğlu S, Ölmez E, Kırbaşoğlu Ç (2008) Heavy metals in sinking particles and bottom sediments from the eastern Turkish coast of the Black Sea. Estuar Coast Shelf Sci 78:396–402. https://doi.org/10.1016/j.ecss.2008.01.006
- Faganeli J, Horvat M, Covelli S et al (2003) Mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea). Sci Total Environ 304:315–326. https://doi.org/10.1016/S0048-9697(02)00578-8



- Ferrara R, Maserti BE (1992) Mercury concentration in the water, particulate matter, plankton and sediment of the Adriatic Sea. Mar Chem 38:237–249
- Gascón Díez E, Graham ND, Loizeau J-L (2018) Total and methylmercury seasonal particulate fluxes in the water column of a large lake (Lake Geneva, Switzerland). Environ Sci Pollut Res 25:21086–21096. https://doi.org/10.1007/s11356-018-2252-3
- Gascón Díez E, Loizeau J-L, Cosio C et al (2016) Role of settling particles on mercury methylation in the oxic water column of freshwater systems. Environ Sci Technol 50:11672–11679. https:// doi.org/10.1021/acs.est.6b03260
- Gordini E, Caressa S, Marocco R (2003) Nuova carta morfo-sedimentologica del Golfo di Trieste (Da Punta Tagliamento alla foce dell'Isonzo). Gortania, Atti Museo Friul di Storia Nat 5–29
- Gosar M, Teršič T (2012) Environmental geochemistry studies in the area of Idrija mercury mine, Slovenia. Environ Geochem Health 34:27–41. https://doi.org/10.1007/s10653-011-9410-6
- Gosar M, Zibret G (2011) Mercury contents in the vertical profiles through alluvial sediments as a reflection of mining in Idrija (Slovenia). J Geochem Explor 110:81–91. https://doi.org/10.1016/j.gexplo.2011.03.008
- Hatje V, Andrade RLB, Jesus RM et al (2019) Historical records of mercury deposition in dated sediment cores reveal the impacts of the legacy and present-day human activities in Todos os Santos Bay, Northeast Brazil. Mar Pollut Bull 145:396–406. https://doi. org/10.1016/j.marpolbul.2019.06.041
- Helali MA, Zaaboub N, Oueslati W et al (2016) Suspended particulate matter fluxes along with their associated metals, organic matter and carbonates in a coastal Mediterranean area affected by mining activities. Mar Pollut Bull 104:171–181. https://doi.org/10.1016/j. marpolbul.2016.01.041
- Horvat M, Covelli S, Faganeli J et al (1999) Mercury in contaminated coastal environments; a case study: the Gulf of Trieste. Sci Total Environ 237–238:43–56. https://doi.org/10.1016/S0048-9697(99)00123-0
- Kocman D, Kanduč T, Ogrinc N, Horvat M (2011) Distribution and partitioning of mercury in a river catchment impacted by former mercury mining activity. Biogeochemistry 104:183–201. https:// doi.org/10.1007/s10533-010-9495-5
- Kotnik J, Horvat M, Dizdarevič T (2005) Current and past mercury distribution in air over the Idrija Hg mine region, Slovenia. Atmos Environ 39:7570–7579. https://doi.org/10.1016/j.atmosenv.2005.06.061
- Le ND, Hoang TTH, Phung VP et al (2022) Evaluation of heavy metal contamination in the coastal aquaculture zone of the Red River Delta (Vietnam). Chemosphere 303:134952. https://doi.org/10.1016/j.chemosphere.2022.134952
- Leivuori M, Vallius H (1998) A case study of seasonal variation in the chemical composition of accumulating suspended sediments in the central Gulf of Finland. Chemosphere 36:503–521
- Lukashin VN, Klyuvitkin AA, Lisitzin AP, Novigatsky AN (2011) The MSL-110 small sediment trap. Oceanology 51:699–703. https:// doi.org/10.1134/S0001437011040126
- Malačič V, Petelin B (2009) Climatic circulation in the Gulf of Trieste (northern Adriatic). J Geophys Res 114:C07002. https://doi.org/ 10.1029/2008JC004904
- Marocco R (1989) Lineamenti geomorfologici della costa e dei fondali del Golfo di Trieste e considerazioni sulla loro evoluzione tardoquaternaria. Int J Speleol 18:87–110
- Matthai C, Birch GF, Bickford GP (2002) Anthropogenic trace metals in sediment and settling particulate matter on a high-energy continental shelf (Sydney, Australia). Mar Environ Res 54:99–127. https://doi.org/10.1016/S0141-1136(02)00098-3
- Menon MG, Gibbs RJ, Phillips A (1998) Accumulation of muds and metals in the Hudson River estuary turbidity maximum. Environ Geol 34:214–222. https://doi.org/10.1007/s002540050273
- Nordmyr L, Österholm P, Åström M (2008) Estuarine behaviour of metal loads leached from coastal lowland acid sulphate soils. Mar

- Environ Res 66:378–393. https://doi.org/10.1016/j.marenvres. 2008.06.001
- Olivotti R, Faganeli J, Malej A (1986) Impact of 'organic' pollutants on coastal waters, Gulf of Trieste. Water Sci Technol 18:57–68
- Paladini de Mendoza F, Fontolan G, Mancini E et al (2018) Sediment dynamics and resuspension processes in a shallow-water Posidonia oceanica meadow. Mar Geol 404:174–186. https://doi.org/10.1016/j.margeo.2018.07.006
- Pavoni E, García-Ordiales E, Covelli S et al (2021a) Legacy of past mining activity affecting the present distribution of dissolved and particulate mercury and methylmercury in an estuarine environment (Nalón River, Northern Spain). Appl Sci 11:4396
- Pavoni E, Petranich E, Signore S et al (2021b) The legacy of the Idrija mine twenty-five years after closing: is mercury in the water column of the Gulf of Trieste still an environmental issue? Int J Environ Res Public Health 18:10192. https://doi.org/10.3390/ijerph181910192
- Petrič M, Kogovšek J (2016) Identifying the characteristics of groundwater flow in the Classical Karst area (Slovenia/Italy) by means of tracer tests. Environ Earth Sci 75:1446. https://doi.org/10.1007/ s12665-016-6255-4
- Raj D, Maiti SK (2019) Sources, toxicity, and remediation of mercury: an essence review. Environ Monit Assess 191:566. https://doi.org/ 10.1007/s10661-019-7743-2
- Rimondi V, Costagliola P, Gray JE et al (2014) Mass loads of dissolved and particulate mercury and other trace elements in the Mt. Amiata mining district, Southern Tuscany (Italy). Environ Sci Pollut Res 21:5575–5585. https://doi.org/10.1007/s11356-013-2476-1
- Santos-Echeandía J, Prego R, Cobelo-García A, Caetano M (2012) Metal composition and fluxes of sinking particles and postdepositional transformation in a ria coastal system (NW Iberian Peninsula). Mar Chem 134–135:36–46. https://doi.org/10.1016/j. marchem.2012.02.006
- Shepard FP (1954) Nomenclature based on sand-silt-clay ratios. J Sediment Petrol 24:151-158
- Tondello M (2017) Clima meteomarino e scenari di circolazione nell'area del Golfo di Panzano. Escavo del canale del porto di Monfalcone. Servizio di monitoraggio sull'ambiente marino. Unpublished technical report HydroSoil S.r.l. p 183
- Tondello M (2020) Utilizzo della modellistica numerica a supporto dell'ottimizzazione progettuale delle attività di dragaggio. Dalla teoria alla pratica: capitalizzazione dei risultati ottenuti dai progetti Interreg Italia Francia Marittimo SEDRIPORT, SEDITERRA E GRAMAS https://www.isprambiente.gov.it/files2020/eventi/sedriport/sedriport_webinar-10-12-20_hsmmarine.pdf
- Turritto A, Acquavita A, Bezzi A et al (2018) Suspended particulate mercury associated with tidal fluxes in a lagoon environment impacted by cinnabar mining activity (northern Adriatic Sea). J Environ Sci 68:100–113. https://doi.org/10.1016/j.jes.2017. 12.009
- Turner A, Millward GE, Morris AW (1991) Particulate metals in five major North Sea estuaries. Estuar Coast Shelf Sci 32:325–346
- Wright LD (1977) Sediment transport and deposition at river mouths: a synthesis. Geol Soc Am Bull 88:857–868
- Zhao B, Wang X, Jin H et al (2018) Spatiotemporal variation and potential risks of seven heavy metals in seawater, sediment, and seafood in Xiangshan Bay, China (2011–2016). Chemosphere 212:1163–1171. https://doi.org/10.1016/j.chemosphere.2018.09. 020

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

