



Recent contamination of mercury in an estuarine environment (Marano lagoon, Northern Adriatic, Italy)

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ABSTRACT

The Marano Lagoon, in the northern Adriatic Sea (Italy), has been affected by mercury (Hg) contamination from industrial and mining activities. It has been estimated that 186,000 kg of Hg were deliberately discharged into the main drainage system (Aussa–Corno River) by a chlor-alkali plant (CAP) from 1940s to 1984. The lagoon has also experienced a secondary long-term Hg input, originated from mining activity in Idrija (Slovenia), due to the supply of fluvial suspended particles carried by the Isonzo River in the Gulf of Trieste. Since local fishing activities are extensively conducted, there is great concern on the risk posed by potentially harmful effects of Hg to the trophic chain.

Present inputs of this metal, both in dissolved ($52.4\text{--}4.1\text{ ng L}^{-1}$) and particulate ($130.8\text{--}3.4\text{ ng L}^{-1}$) phases, were preliminary investigated in the water column. Although direct discharge of Hg from the CAP no longer exists, the metal is still released from the source area into freshwaters, and its distribution and abundance is controlled by the salt-wedge circulation system, which is tide-influenced.

Remobilization from bottom sediments can also be a secondary source of Hg into the aquatic environment. A speciation technique, used to investigate the main binding sites and phase associations of Hg in sediments ($5.69\text{--}0.82\text{ }\mu\text{g g}^{-1}$), evidenced the presence of mobile (1.8–11%) and potentially available species for methylation processes. The results are particularly important if related to resuspension effects caused by natural events and anthropogenic activities. Preliminary considerations on Hg behaviour in this estuarine environment are reported.

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1. Introduction

Among pollutants, mercury (Hg) has received a worldwide attention due to its significant global adverse impact on both, environment and human health. Indeed, even areas with minimal Hg releases may be adversely affected owing to its relative global transport (Asmund and Nielsen, 2000; Jewett et al., 2003). Beside the atmospheric pathway (e.g. Schlüter, 2000; Böhme et al., 2005), the main concern arises from abiotic or biologically mediated transformations of inorganic Hg into the potent neurotoxin monomethylmercury (MeHg) (Fitzgerald and Clarkson, 1991; Clarkson, 1997; Bloom et al., 1999, 2004).

It is well known that the advent of massive industrialization during the last century increased Hg release from 2 to 5 orders of magnitude (Mason et al., 1994). The main anthropogenic sources include fuel combustion, waste incineration, waste water discharge

and industrial processes such as wood pulping and chlor-alkali plants (CAPs). Although the industrial use of Hg has been drastically reduced in recent years due to strict law regulations, high concentrations are still present in atmosphere, soils, water and sediments located nearby industrial activities involving Hg applications.

The Marano and Grado lagoon, along the northern Adriatic coast, experienced a significant double historic Hg input. First, the presence of this element arises from the total suspended matter (TSM) vehiculated from the Isonzo River draining the cinnabar deposits of the world's second largest Hg mine in Idrija (Slovenia), which has been in activity for 500 years. Several studies demonstrated that a high quantity of Hg reaches the Gulf of Trieste (Horvat et al., 1999; Rajar et al., 2000; Covelli et al., 2006) and it was verified that considerable amounts of the metal enter the nearby lagoon system when peak river discharges and specific wind conditions simultaneously occur (Covelli et al., 2007). Moreover, the lagoon environment was affected by the activities of the industrial site located further inland. Here, cellulose production from cane (*Arundo donax* sp) was active from 1940 until 1992. A CAP, using

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metallic Hg for electrolytic production of Cl₂, became active since 1949 and it was estimated that a total amount of 186,000 kg of Hg (with a maximum of about 20 kg day⁻¹) was deliberately discharged into the Aussa–Corno River system in connection with the lagoon (Piani et al., 2005). In 1984, due to application of law rules, a modern wastewater system treatment was installed; hence no more inputs of Hg should have been released into the environment. Nevertheless, both diffuse and punctual persistent cases of contamination still subsist in several areas (Maserti and Ferrara, 1992; Lodenius, 1998; Biester et al., 2000; Hissler and Probst, 2006). Previous studies revealed high Hg levels in sediments, showing a net westward decrease from the Grado to the Marano basin (from 10 to 1 mg kg⁻¹, respectively) and they emphasized the bio-accumulation effects along the whole trophic chain (Brambati, 2001).

Piani et al. (2005) made a first effort to investigate Hg speciation in bottom sediments of the Marano lagoon to predict harmful effects on fish farms and shellfish cultivation areas. Results showed that cinnabar (HgS), mostly stable and insoluble, dominates the central sector of the lagoon entering from the sea through the tidal inlet; on the other hand, organically bound Hg, which can be transformed into bioavailable compounds (e.g. MeHg), was found to be enriched up to 98% in fine grained material in the Aussa River. These evidences suggested that the Aussa–Corno River system acts as a “transport belt” of non-cinnabar Hg compounds originating from the industrial complex and potentially bioavailable, both in the fluvial and in the lagoon environment. Despite this evidence, the present input of Hg from the Aussa–Corno River system downstream in the Marano lagoon has never been evaluated.

In this study, due to the importance of local fishing activities and the risk posed by harmful effects of Hg to the trophic chain, an assessment of the contribution of Hg to the water column, both in its dissolved phase and bound to sediment particles, has been attempted. Besides, we have hypothesized that remobilization from river sediments could be a secondary source of Hg release into the water column. In order to verify this hypothesis, one of the aims of this study is to differentiate the Hg compounds in sediments, classifying them in diverse behavioural classes by means of the sequential extraction scheme adopted by Bloom et al. (2003) and modified for river sediments by Shi et al. (2005).

2. Materials and methods

2.1. Study site

The Grado–Marano wetland system, with an average width of 5 km extending for about 35 km, covers an area of 160 km² located along the northern Adriatic coast between the Tagliamento and Isonzo River deltas. The lagoon is characterized by semi-diurnal tidal fluxes (65 cm and 105 cm mean and spring tidal range, respectively). Salinity values are very low (2–7) in the areas close to the river mouths; they increase towards the tidal inlets, where values between 24 and 36 were recorded (Brambati, 2001). Freshwater inputs are very scarce and mostly limited to the western sector (Marano lagoon). The overall amount of average freshwater discharge was estimated in about 70–80 m³ sec⁻¹ average, with a maximum peak of 100 m³ sec⁻¹ (Mosetti, 1983). The sedimentary contribution of these small rivers is fine suspended matter represented by material washed out of the groundwater table (Brambati, 1972), whereas a more relevant source of sediments comes from the sea, through the tidal inlets, as contribution of the two river deltas (silty and clayey particles) and from erosion of the barrier islands (sands) (Brambati, 1970).

The Aussa and Corno rivers originate from the spring line area located in the southern part of the coastal plain, and flow into the

central sector of the lagoon (45 km²). The Corno River, which has a total length of 17 km, drains a basin of about 5000 ha and receives few tributaries, hence its degree of discharge is very limited; actually, it ranges about 5–8 m³ s⁻¹. On the contrary, the Aussa River is characterized by the presence of several tributaries, drainage channels and irrigation ditches; the total discharge reaches 8–20 m³ s⁻¹. The suspended load during normal run off periods is limited (8–10 mg L⁻¹; Piani, pers. comm.). Maximum and minimum discharges are registered in October/December and February/September for Corno and Aussa River, respectively. During dry periods, relevant phenomena of thermo-haline stratification occur and the presence of a net salt-wedge tip can be detected. In addition, downflowing is often hindered when particular weather conditions and high tides occur.

Due to the presence of economic activities such as local fishing, clams and mussels collection and edible fish cultivation (17 and 38 fishfarms in Marano and Grado lagoons respectively, in a total area of 1730 ha), this area represents an important site for inhabitants.

2.2. Sampling

Water and sediment samples were collected in October 2004. Sampling was performed by boat at six sampling stations along the main axis of the Aussa–Corno River system (Fig. 1) during spring ebb-tide conditions (tidal range +55/–56 cm).

Measurements of temperature, salinity and turbidity along the water column were acquired by means of a CTD Hydrolab H20 Multiprobe with a 0.1 dbar pressure step.

Surface and bottom water samples were collected by means of a 5-L acid precleaned Teflon-lined Niskin bottle. Water samples were subsampled for the determination of oxygen (O₂), dissolved inorganic (DIC) and organic (DOC) carbon, total suspended matter (TSM), particulate organic carbon (POC) concentrations and grain-size. Another aliquot was transferred to borosilicate bottles previously subject to hot acid precleaning steps as recommended by EPA Standard Methods (2002) and processed for total (THg), particulate (PHg) and dissolved mercury (DHg). DHg is defined as the fraction of water sample filtered through a 0.45 µm filter. Surface sediments (0–2 cm) were also sampled using a stainless steel Van Veen grab. Two aliquots of the sediments were freeze-dried and used for grain-size determination and organic carbon (C_{org}), total nitrogen (N_{tot}) and mercury (Hg) analyses.

2.3. Analysis of the dissolved and particulate phases

Dissolved O₂ concentrations in the water samples were determined by Winkler method (Grasshoff et al., 1983) using an automated titration system (Mettler Toledo, DL 21).

Dissolved inorganic (DIC) and organic (DOC) carbon were analyzed using a commercial unit (Shimadzu TOC 5000A). Briefly, for DIC determination the samples were injected into the IC instrument port and directly acidified with phosphoric acid (25%). For DOC analysis, water samples were previously acidified (HCl 6 M, 200 µL) and after CO₂ elimination, the concentration was determined by a high temperature catalytic method (Covelli et al., 2008). Solutions of carbonate/hydrogencarbonate and potassium hydrogen phthalate were used as reference standard for DIC and DOC, respectively.

The total suspended matter (TSM) was measured using vacuum filtration through Whatman fiberglass GF/F filters (diameter 47 mm, 0.7 µm nominal pore size), previously pre-ignited at 450 °C to eliminate organic contaminants (Strickland and Parsons, 1972), and preweighted. All filters were frozen at –20 °C and stored for particulate organic carbon (POC) content determinations. The

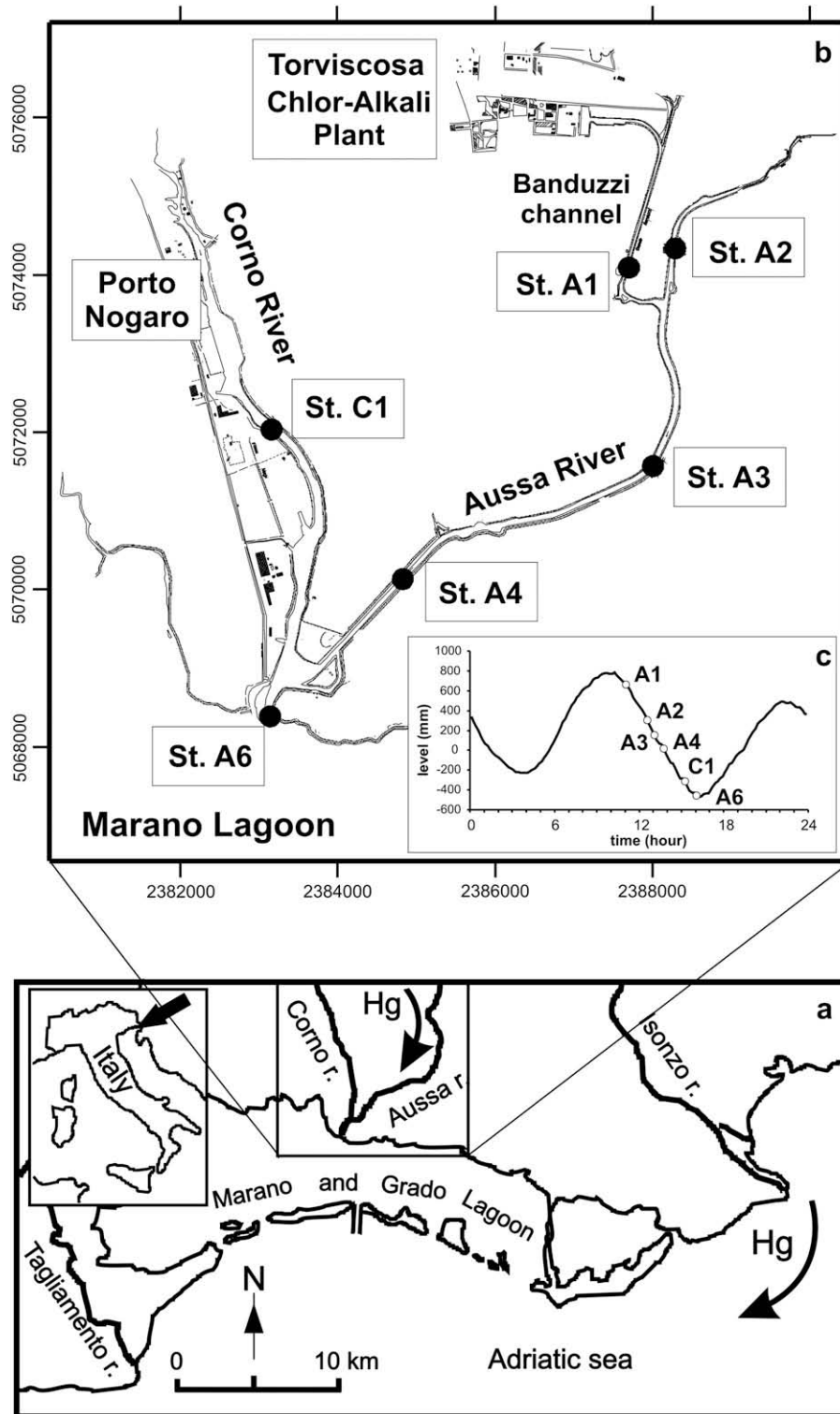


Fig. 1. Index map of the study area showing mercury inputs in the Marano and Grado lagoon (a). Location of sampling points along the Aussa–Corno River system (b). Tidal curve (a time lag of about 1 h was applied to real data recorded at Trieste) and related sampling time in the fluvial system on 28th October 2004 (c).

analysis was performed using a CHN Elemental Analyzer (Perkin Elmer). Samples were previously acidified with 1 M HCl, as reported in Hedges and Stern (1984) before POC analytical determination.

The particle size analysis in the range 9–4 ϕ (1.95–62.5 μ m) was conducted by using a Coulter Multisizer II (Coulter Electronics

Ltd., 1972). The Accucomp programme was used to acquire and process grain-size spectra.

Particulate Hg (PHg) was determined after filtering on pre-weighted Millipore HA (cellulose nitrate) membrane filters (diameter 47 mm, 0.45 μ m pore size). Filters with particles were lyophilized (Lyphlock, Labconco), accurately weighted, and

a complete dissolution (HF + aqua regia) procedure was conducted in a closed microwave system (Multiwave 3000, Anton Paar). Analytical determination was performed by CVAFS (Tekran mod. 2500) coupled with a gold trap preconcentration system, after a pre-reduction step (SnCl_2 10%; Ferrara et al., 1986). The detection limit calculated was <0.1 pg. The accuracy for PHg determination was controlled using a certified reference material (PACS-2, mean value 3.04 ± 0.2 mg kg⁻¹, National Research Council Canada). Results obtained on the basis of three replicates (2.92 ± 0.09) were in good agreement with the certified material value.

Total (THg) and dissolved (DHg) mercury in water samples were determined by CVAFS (Tekran mod. 2500) after a first oxidation step of all Hg compounds to Hg^{2+} adding a BrCl solution (0.5 mL/100 mL sample, $t = 12$ h). A pre-reduction step using $\text{NH}_2\text{OH}\cdot\text{HCl}$ (30%, 0.25 mL), until yellow colour disappeared, was followed by SnCl_2 (10%) reduction and gold trapping (Horvat et al., 1991). For measuring DHg, the water sample was previously filtered through Nalgene filtration units on Millipore HA (cellulose nitrate) membrane filters with a pore size of 0.45 μm .

2.4. Analysis of solid phase

Sediment samples for grain-size analysis (15–20 g wet sediment) were treated with hydrogen peroxide (10%, $t = 24$ h) to remove organic matter and subsequently wet-sieved through a 2000 and 63 μm sieve. The obtained sandy fraction was analyzed using a Macrogranometer. The fraction <63 μm was collected, filtered through 50 grade Whatman cellulose filters (R 185 mm) and dried at 40 °C. In this fraction, grain-size distribution was determined on the basis of the suspension of the sample in distilled water to which 0.5 g dm⁻³ Na-hexametaphosphate antiflocculant solution was added and then analyzed by a Micromeritics Sedi-graph 5100 Particle Size Analyzer.

The analyses of organic C (C_{org}) and total N (N_{tot}) in freeze-dried and homogenized sediment samples were performed using a Perkin Elmer 2400 CHNS/O Elemental Analyzer after acidification of samples with 1 M HCl (Hedges and Stern, 1984) at a combustion temperature of 975 °C.

The determination of total mercury (THg) in sediments was achieved upon completion of the total decomposition method as recommended by Loring and Rantala (1992). About 300 mg of dry sediment were treated with a mixture of 1.5 ml HF + 5 ml aqua regia in a closed microwave system (Multiwave 3000, Anton Paar). The solutions obtained were analyzed by the CVAAS technique (MHS-15, Perkin Elmer 5100PC) after a reduction step (NaBH_4 3% in NaOH 1%). Quality control was tested using certified reference materials (PACS-2 harbour sediment, NCR-CNR, Canada). Recovery of Hg was $97 \pm 5\%$ ($n = 3$ replicates). The detection limit was 0.25 $\mu\text{g g}^{-1}$ on the basis of 0.3 g dry sediment.

The selective extraction procedure employed is based on Bloom's five-step scheme (Bloom et al., 2003) adapted for sediments river by Shi et al. (2005). Briefly, 2 g of dry sediment were placed into a 50 mL borosilicate centrifuge tube. An exact volume of the selective extractant ($V = 20$ mL) was added and the centrifuge tube was subject to an end-over shaker action for 18 h at room temperature (Rotomix, PBI International). A known volume of extraction was then filtered, 1 mL of HNO_3 trace select and 0.1 mL of BrCl were added and, finally, volume was made up with Milli-Q. The residue was washed with Milli-Q, centrifuged and rinse was discarded. The four extractants used were: (1) Milli-Q water for "water soluble" (Hg-w); (2) 0.1 mol L⁻¹ $\text{CH}_3\text{COOH} + 0.01$ mol L⁻¹ HCl for "human stomach acid soluble" (Hg-h); (3) 1 mol L⁻¹ KOH for "organo-chelated" (Hg-o); (4) 12 mol L⁻¹ HNO_3 for "elemental Hg" (Hg-e). In the last step (5), the residue was air dried at room temperature and total Hg digestion with aqua regia was

performed for "mercuric sulfide" (Hg-s) and mercury immobilized by pyrite (FeS_2 ; Huerta-Diaz and Morse, 1992). The total Hg in each obtained solution was determined by CVAFS (Mercur AFS, Analytic Jena). The method was verified for all samples with the sum of the ratio of Hg extracted in all phase to Hg_{tot} obtained as $\Sigma\text{Hg}/\text{Hg}_{\text{tot}}$. These ratios ranged from 75.1 to 104% (mean value $82.3 \pm 12.8\%$).

3. Results

3.1. Water column

A clear thermo-haline stratification of the water column was recognized on the basis of CTD profiles (Fig. 2). A colder (14.1–16.0 °C) layer of freshwaters (salinity ranging between 0.3 and 7.0) flowed on the underlying warmer saltwaters (16.4–17.4 °C; 25.0–30.5 °C), thus forming a "saltwedge", which shifts its position landward according to tidal range. The dissolved O_2 concentrations in bottom waters exhibit a general decrease moving upstream to the salt-wedge tip (Fig. 3a), whereas they appear rather constant in surface waters. Undersaturated values at the bottom are lower in the chlor-alkali channel (33%, station A1) compared to the river mouth (84%, station A6).

The DOC in freshwaters shows the highest values in station A1 and A2 (2.84 and 4.09 mg L⁻¹, respectively), whereas lower and constant concentrations (about 1.5 mg L⁻¹) were measured downstream (Fig. 3b). Conversely, the DOC phase increased upstream within the salt-wedge, and the results obtained (3.32–2.52 mg L⁻¹) are well correlated with the observed O_2 depletion ($r = 0.863$, $n = 6$; $P \leq 0.05$).

Total suspended matter (TSM) in superficial freshwaters (1.9–8.13 mg L⁻¹) is slightly lower than in saltwaters (4.7–25.9 mg L⁻¹) except at the river mouth (station A6), suggesting an increase in mixing between the fresh and saltwater layers as the lagoon basin is approached (Fig. 3c). This can be explained in terms of breaking of internal waves (Wright and Coleman, 1974; Dyer, 1991), which also causes turbulence, a gradual halocline and constant turbidity values of 5 NTU (Nephelometric Turbidity Unit) along the whole water column at the river mouth.

Particulate organic carbon (POC) in the superficial layer varied within the ranges 4.6–14.2% (267–506 $\mu\text{g L}^{-1}$) (Fig. 3d). These values are very close to the results obtained for the Adige, Po and Isonzo Rivers, among the main watercourses flowing into the Adriatic Sea (Boldrin et al., 1992; Pettine et al., 1998; Covelli et al., 2004).

The highest total Hg (THg) content in freshwaters (Fig. 3e) was detected in the chlor-alkali channel (144.7 ng L⁻¹). Concentrations decreased to less than one fifth immediately downstream the confluence with the Aussa River, where THg reached, at most, 64.7 ng L⁻¹ (station A4). These values are similar to those observed in superficial waters at the Isonzo River mouth, which represents the secondary long-term Hg input in the nearby area, during low-normal river discharge (Covelli et al., 2006). Conversely, the highest contents of THg, in the bottom saltwaters (283.0 ng L⁻¹), were found at the Aussa-Corno River mouth. This was probably caused by accidental bottom sediment resuspension due to shipping traffic and subsequent Hg remobilization to the water column. THg concentrations in the salt-wedge along the river course generally ranged between 50.0 and 80.0 ng L⁻¹, which are double than those observed for the salt-wedge inside the Isonzo River mouth (Covelli et al., 2006).

PHg contents decreased from the chlor-alkali channel downstream in the superficial freshwaters (from 130.8 to 3.4 ng L⁻¹) as well as in the underlying saltwaters (from 32.1 to 4.8 ng L⁻¹; Fig. 3f). This trend in freshwaters is even more evident when PHg concentrations are normalized for suspended load (Fig. 3g). The

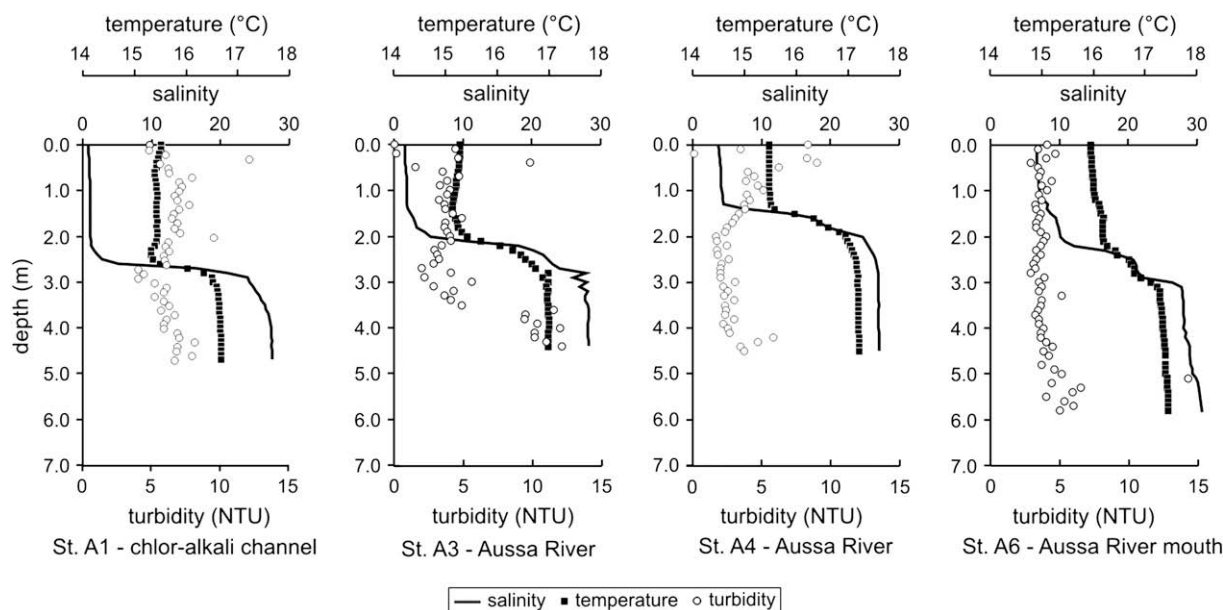


Fig. 2. Vertical profiles of turbidity (NTU, Nephelometric Turbidity Unit), Salinity (Practical Salinity Scale) and Temperature ($^{\circ}\text{C}$) in four selected sampling stations along the Aussa-Corno river system (28th October 2004).

highest PHg values at the surface ($20.3 \mu\text{g g}^{-1}$) as well as at the bottom ($2.2 \mu\text{g g}^{-1}$), were observed at station A1. The range of bottom values was very narrow, showing a minimum concentration of $1.1 \mu\text{g g}^{-1}$ at the river mouth (station A6), which is very similar to the one found at the surface ($1.3 \mu\text{g g}^{-1}$).

Dissolved Hg concentrations (DHg) do not show evidences of spatial distribution along the estuary if samples collected in the chlor-alkali channel (52.4 ng L^{-1} and 48.0 ng L^{-1} , at the surface and at the bottom, respectively) are not considered (Fig. 3h). In addition, the dissolved component in the bottom water samples appeared to be more abundant ($9.1\text{--}34.9 \text{ ng L}^{-1}$) than in the superficial freshwaters ($4.1\text{--}23.7 \text{ ng L}^{-1}$) after the confluence with the Aussa River, where dilution of waters from the chlor-alkali channel occurs.

3.2. River sediments

Bottom sediment samples proved to be rather uniform from the textural point of view (Fig. 4a). The sandy fraction was always lower than 8%. The only exception was station A6, at the river mouth, where sand accounted for 59.2% (mode at 3 phi or $125 \mu\text{m}$), silt and clay for 32.7% and 8.1%, respectively. Within the muddy component, the silty fraction was dominant (70.0–84.9%), progressively decreasing downstream along the river channel. In this context, the main modal class (from 9 to 14%) is represented by particles falling between 6.5 phi ($11 \mu\text{m}$) and 8 phi ($4 \mu\text{m}$) (Fig. 4b). The clay component, which is very important in controlling metal–solid interaction due to its high surface area reactivity compared to the coarser fractions, ranged from 13.3 to 26.9%.

The sedimentary contents of C_{tot} , C_{org} and N_{tot} in our samples exhibited a high degree of variability. C_{tot} ranged from 5.34 to 8.21%, in A4 and A1, respectively, with a slight decrease downstream. This trend was confirmed for both C_{org} (Fig. 4c) and N_{tot} (ranging from 4.04 to 0.53% and from 0.49 to 0.11%, respectively), thus suggesting the importance of inputs from the surrounding agriculture sites.

The highest THg content ($5.69 \mu\text{g g}^{-1}$) in bottom sediment samples was detected at station A3, whereas the lowest value ($0.82 \mu\text{g g}^{-1}$) was found out at station A2, just upstream the confluence between the wastewater system discharge and the Aussa River (Fig. 4c). The results obtained are similar to those

reported for other sites impacted by the chlor-alkali plants activities (Hintelmann and Wilken, 1995; Bloom et al., 1999, 2004; Odzak et al., 2000; Canario et al., 2005). The high pollution degree of this river system has been recently estimated from deep core sediments. THg values ranged from 80 to $300 \mu\text{g g}^{-1}$ at the core bottom (180–200 cm depth) only in a restricted area close to the point source (Banduzzi chlor-alkali channel), whereas local background values usually ranged from 0.03 to $0.10 \mu\text{g g}^{-1}$ (unpublished data).

The amount of THg in sediments is not by far the most important factor to bear in mind, as the different chemical species of Hg behave also distinctly, thereby affecting its biogeochemical behaviour and toxicity to organisms (Cai et al., 1997). According to this evidence, the last step of our research was to distinguish among different Hg fractions which biogeochemically “make sense”, aiming to determine its bioaccessibility. The latter refers to the potential of a generic substance to dissolve in aqueous media, thus becoming an exposure route for organisms, whereas bioavailability is the capability to evoke biological effects during *in vitro* tests. The chemical–physical properties of Hg are very peculiar, thus traditional procedures employed in speciation studies for trace elements are almost useless. Bloom et al. (2003) developed and validated a method based upon sequential selective extractions (SSE), distinguishing Hg compounds into behavioural classes, namely water soluble (Hg-w), “human stomach acid” soluble (Hg-h), organo-chelated (Hg-o), elemental Hg (Hg-e) and mercuric sulphide (Hg-s). In a simplistic manner, the extractants obtained can be classified on the basis of their relative exchange properties within the water column. Briefly, Hg-w + Hg-h (exchangeable fractions) pose the highest risk because they can easily enter the aquatic media and bioaccumulate. Hg-o has a moderate mobility, whereas Hg-e + Hg-s have a very low mobility and, consequently, they can be considered unavailable species.

Our results showed that Hg-e is the predominant form in all the sites investigated except for A6 (Fig. 5a,b). In terms of percentage, Hg-e contents ranged from 63.5 (station A2) to 90.6% (station A3), respectively.

The Hg-o fraction, the one related to organo-chelated Hg(II) compounds, is the second most abundant, ranging from 5.6 (station A6) to 24.2% (station A2).

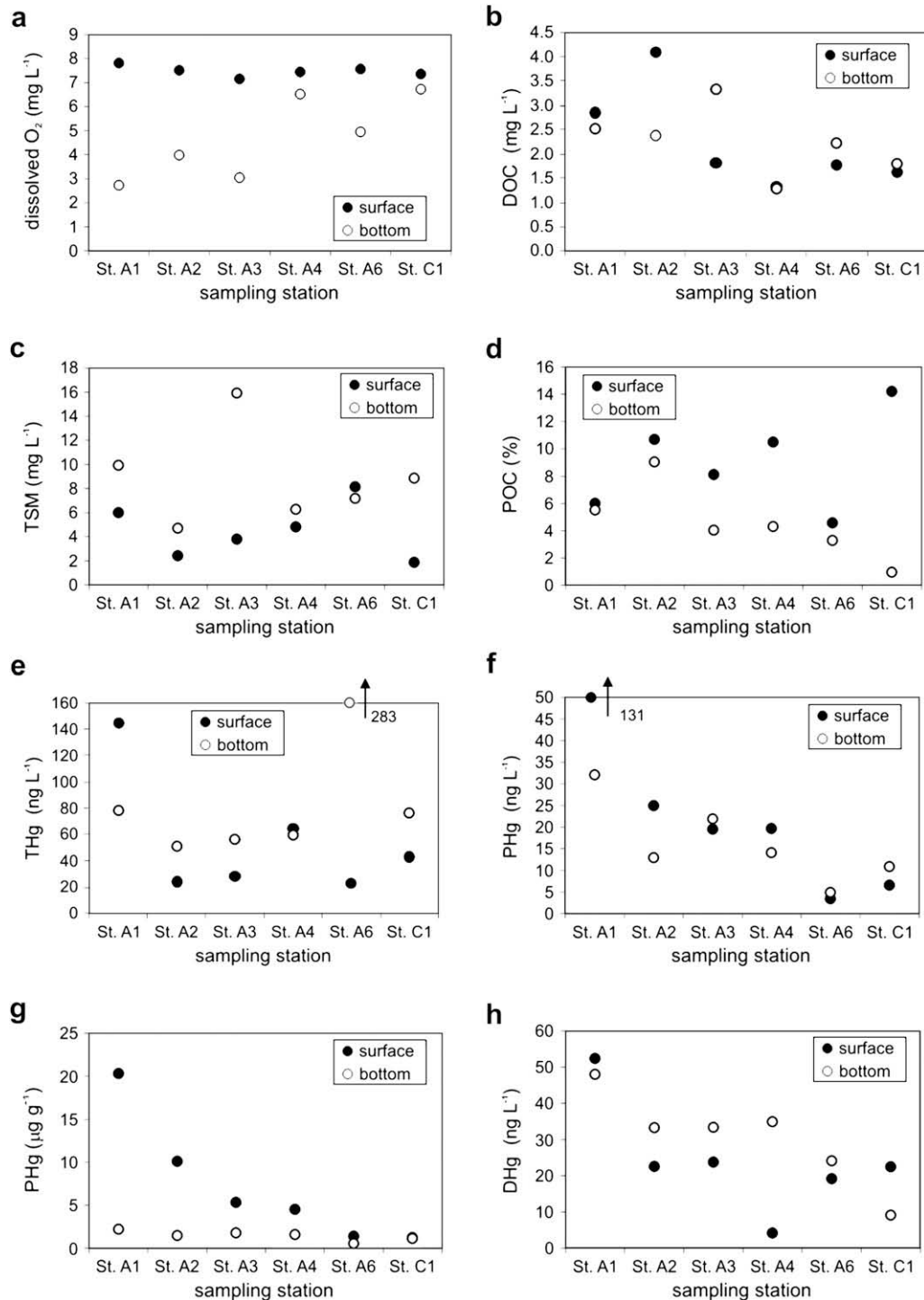


Fig. 3. Variability of the principal parameters measured in the surface and bottom layers of the water column in the Aussa–Corno River system: (a) dissolved O₂, (b) DOC (Dissolved Organic Carbon), (c) TSM (Total Suspended Matter), (d) POC (Particulate Organic Carbon), total mercury (THg) (e), particulate mercury (PHg as ng L⁻¹ (f) and μg g⁻¹ (g)) and (h) dissolved mercury (DHg).

These results were similar to those reported by other authors. Shi et al. (2005) found an average value of 13.3% in river sediments. However, this fractionation method resulted in a wide range of values. In fact, Peng and Wang (1985) reported contribution from 2.7 to 77.4% in some Chinese rivers. Generally, the lowest contribution is usually found in samples recovered close to CAPs, whereas greater contributions are found in sediments from non-polluted rivers (Lechler et al., 1997).

The contribution of water-soluble Hg species (Hg-w + Hg-h) in our sediment samples was found very small, ranging from 1.8 (station A3) to 11% (station A2).

The mercuric sulphide (Hg-s) fraction was only detected at the river mouth (A6), accounting for about 58% (Fig. 5a,b). Since Hg has an extremely high affinity for S-containing ligands, compounds such as cinnabar (red Hg-S) and metacinnabar (black Hg-S), were only leached in the Hg-s class (Hintelmann and Wilken, 1995).

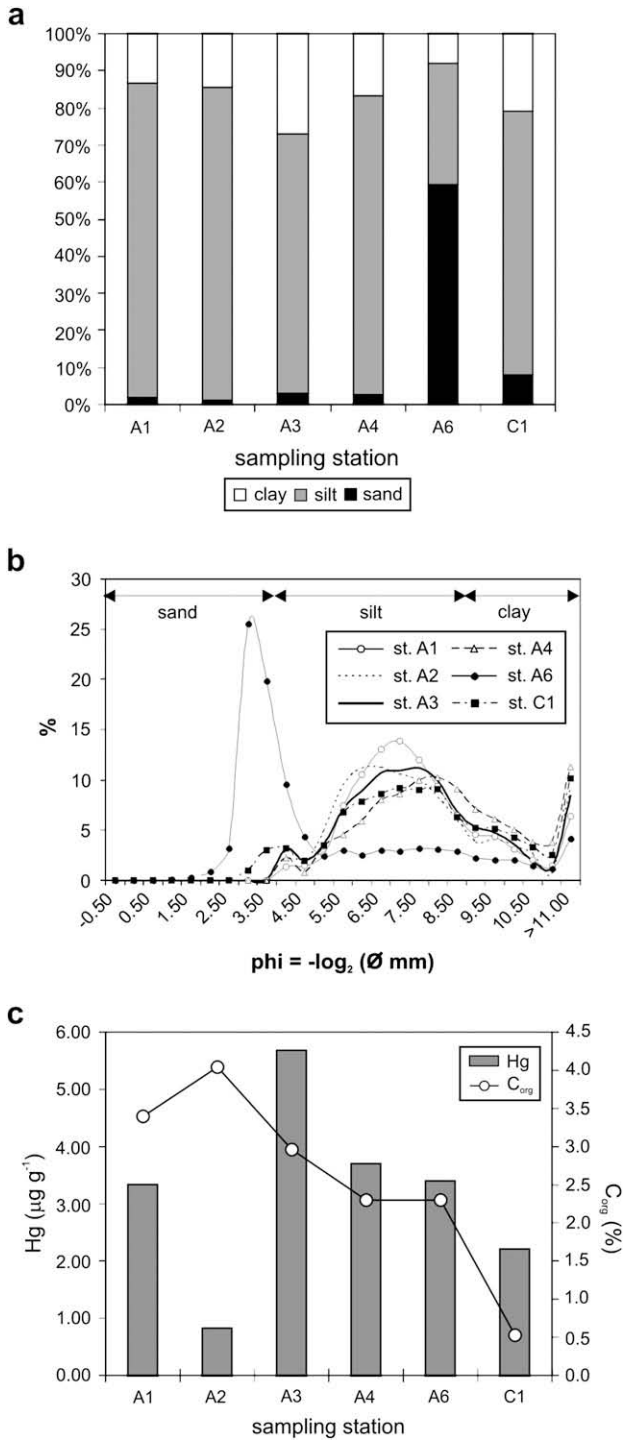


Fig. 4. Grain-size of bottom sediment samples expressed in terms of sand, silt and clay percentages (a); particle size distributions (b), total mercury (Hg) and organic carbon (C_{org}) concentrations in bottom sediment samples (c).

4. Discussion

4.1. Water column

Since these two rivers flowing into the lagoon drain waters coming from the aquifers of the alluvial plain, their discharges are scarce and constant within the year, thus determining the highly stratified water column and related hypopycnal flux to be

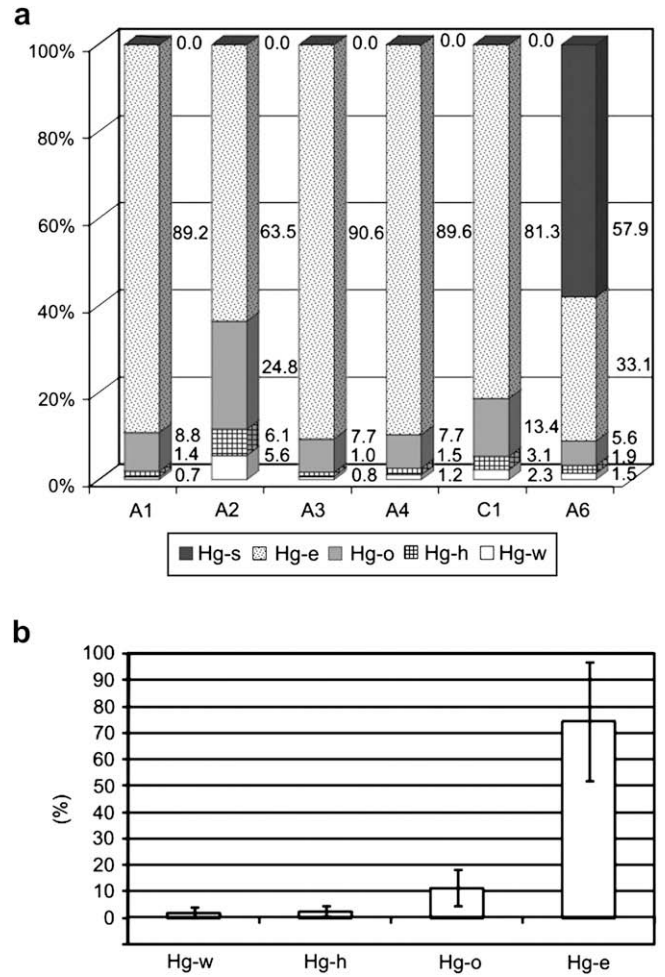


Fig. 5. Partitioning of Hg in the solid phase of bottom sediments according to the selective extraction procedure (a) and average percentage (±sd) for each fraction in the six samples analyzed (b) except Hg-s since it was only detected in one station at the river mouth (A6).

permanent within the “estuarine” zone (Fig. 2). The low rate of water exchange across the halocline implies that the residence time of the saline bottom water in the fluvial channel is certainly long. The water might only be renewed and it might receive new O₂ supplies during the spring tide period of high current flows. Thus, this suggests that both respiration and resulting mineralization of organic matter processes occur in the salt-wedge (Fig. 3a).

The low freshwaters suspended load and the thermo-haline stratification in the estuary help to emphasize the important role of tidal currents in carrying TSM from the lagoon basin upstream through the salt-wedge. Particle size distributions of TSM along the river course and, vertically, in the water column, are also affected by the well marked stratification. Grain-size spectra in the freshwater layer showed that TSM is usually finer than 40 µm with the mode size of about 10 µm (Fig. 6). In the salt-wedge, the size spectra are skewed with the finer modal class between 5 and 9 µm. With the exception of sampling stations A1 and A4, the fine/coarse ratio (16–2/62.5–16 µm) is up to twice higher in the saltwater TSM. This evidence, along with a better sorting, testifies the role of the selective processes acting on lagoon originated TSM.

Most of the Hg transported by fluvial waters was in association with the suspended particulate phase (PHg). The average relative abundance of PHg to THg in freshwaters varied from about 90% (station A2) to 15% (station A6), whereas it was lower in the

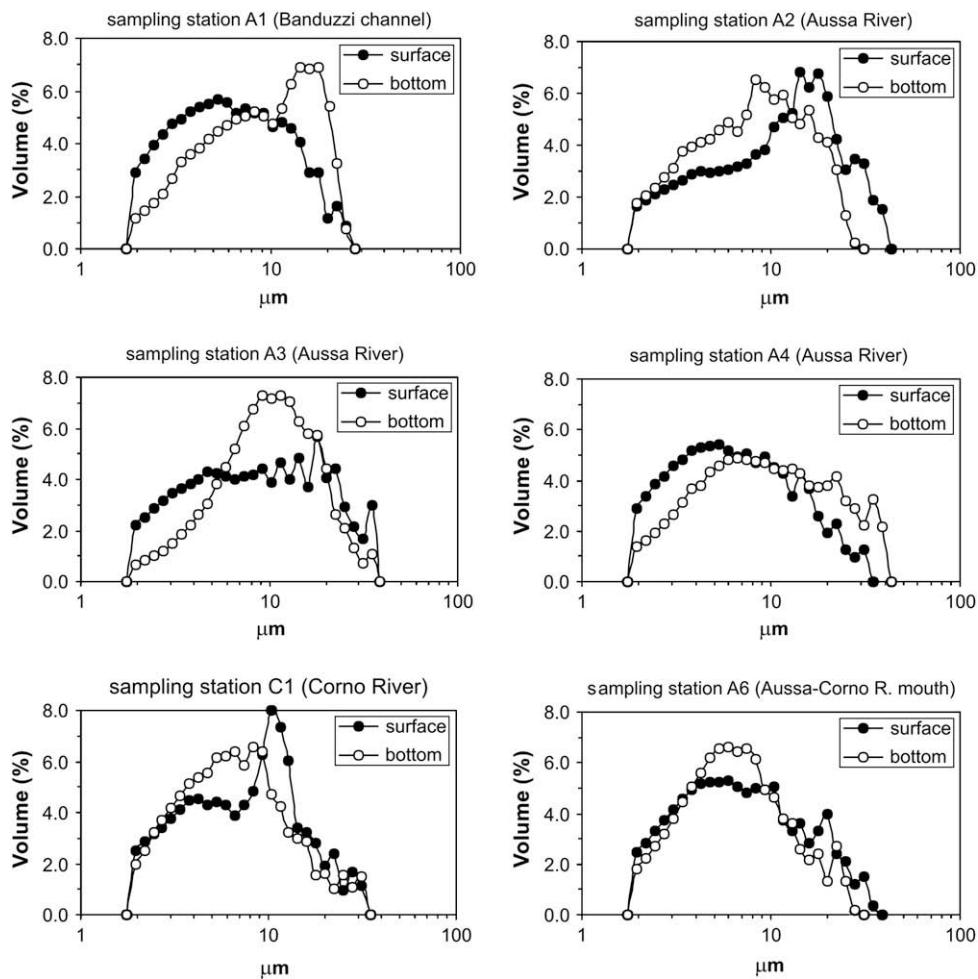


Fig. 6. Grain-size spectra of total suspended matter (TSM) samples collected at the surface and at the bottom in the fluvial system on 28th October 2004.

salt-wedge (from 40% to 2%). The decreasing trend of THg and, especially, PHg downstream station A1 (Fig. 3e, f, g), seems to be influenced by a progressive dilution of the suspended particles originated from the chlor-alkali channel after the confluence with the Aussa River, and, subsequently, by the presence of a higher mixing of riverine and lagoon waters occurring near the river mouth. PHg shows to be correlated with particles ranging between 16 and 32 μm (medium silt) mostly in saltwaters ($r = 0.933$, $n = 5$; $P \leq 0.01$) rather than in the superficial freshwaters ($r = 0.879$, $n = 5$; $P \leq 0.05$), if the sampling station A1 in the chlor-alkali channel is not considered (Fig. 7a). In fact, TSM at this site shows an unusually high fine/coarse ratio ($16\text{--}2\ \mu\text{m}/16\text{--}62.5\ \mu\text{m} = 8.3$) whereas an understandable downstream decrease in the 16–32 μm content in freshwaters, and a concomitant increase of the fine component, are observed from station A2 (ratio from 1.7 to 4.5).

The relative distribution of Hg between the dissolved and particulate phases is usually described by the K_d coefficient (ratio between the Hg concentration in the particulate ($\mu\text{g g}^{-1}$) and the dissolved phase (ng L^{-1})), which is also predictive for understanding Hg behaviour in aquatic systems (Benoit, 1995).

The relative affinity of Hg to the riverine fine suspended particles is confirmed by the higher $\log K_d (= [\text{PHg}]/[\text{DHg}], \text{L kg}^{-1})$ values range (4.5–6.0) at the surface compared to the salt-wedge waters (4.3–4.7), if the Corno River station (C1) is excluded (Fig. 7b). The partitioning of Hg can be affected by several factors such as TSM, pH and complexation with dissolved organic matter (DOM), humic acids and inorganic ligands (Ravichandran, 2004). In the Aussa

River, the K_d coefficient is not correlated to TSM and DOC concentrations. On the contrary, a slightly direct relationship is detectable if K_d values are plotted against POC contents in the surface freshwater samples (Fig. 7c). Although POC is not significantly correlated to PHg, a minor general increasing trend is discernible, thus suggesting that the organic component probably plays a minor role as a metal carrier in freshwaters as well as in the salt-wedge (Fig. 7d).

According to Morel et al. (1998), hydroxide ($\text{Hg}(\text{OH})^+$, $\text{Hg}(\text{OH})_2$, $\text{Hg}(\text{OH})_3^-$) and chloride (HgCl^+ , HgClOH , HgCl_2^- , HgClOH_2^-) species in variable amounts are the dominant Hg forms in natural waters. The OH^- -complexes prevail where low Cl^- contents are present. When the Cl^- concentration increases, OH^- -complexes are replaced by Cl^- -complexes; the latter are less adsorbed on particles than OH^- -Hg, thus decreasing Hg adsorption in the aquatic particulate.

If sample A2 is excluded, there is a weak positive trend ($r = 0.617$; $P \leq 0.5$) between DHg and DOC values (Fig. 7e). In our case, saltwaters seem to be enriched in DOC compared to the freshwaters, but this correlation is surprising. In fact, the stability constants for Hg–DOC complexes reported are about 10^{20} – 10^{28} in the aquatic environment (Benoit et al., 2001). These values are much larger than the values reported for Hg–Cl complexes (10^7 – 10^{14}) and Hg–OH complexes (10^{10} – 10^{22}). Moreover, it appears that DOC would constitute the main ligand for Hg complexation when its concentration is $>10\ \text{mg L}^{-1}$ (even $5\ \text{mg L}^{-1}$!); this is not the case of the Aussa–Corno River system. Besides, in this context, the effect of DOC on Hg partitioning could be affected by the pH of the solution. At a pH higher than 7, DOC is more negatively charged and

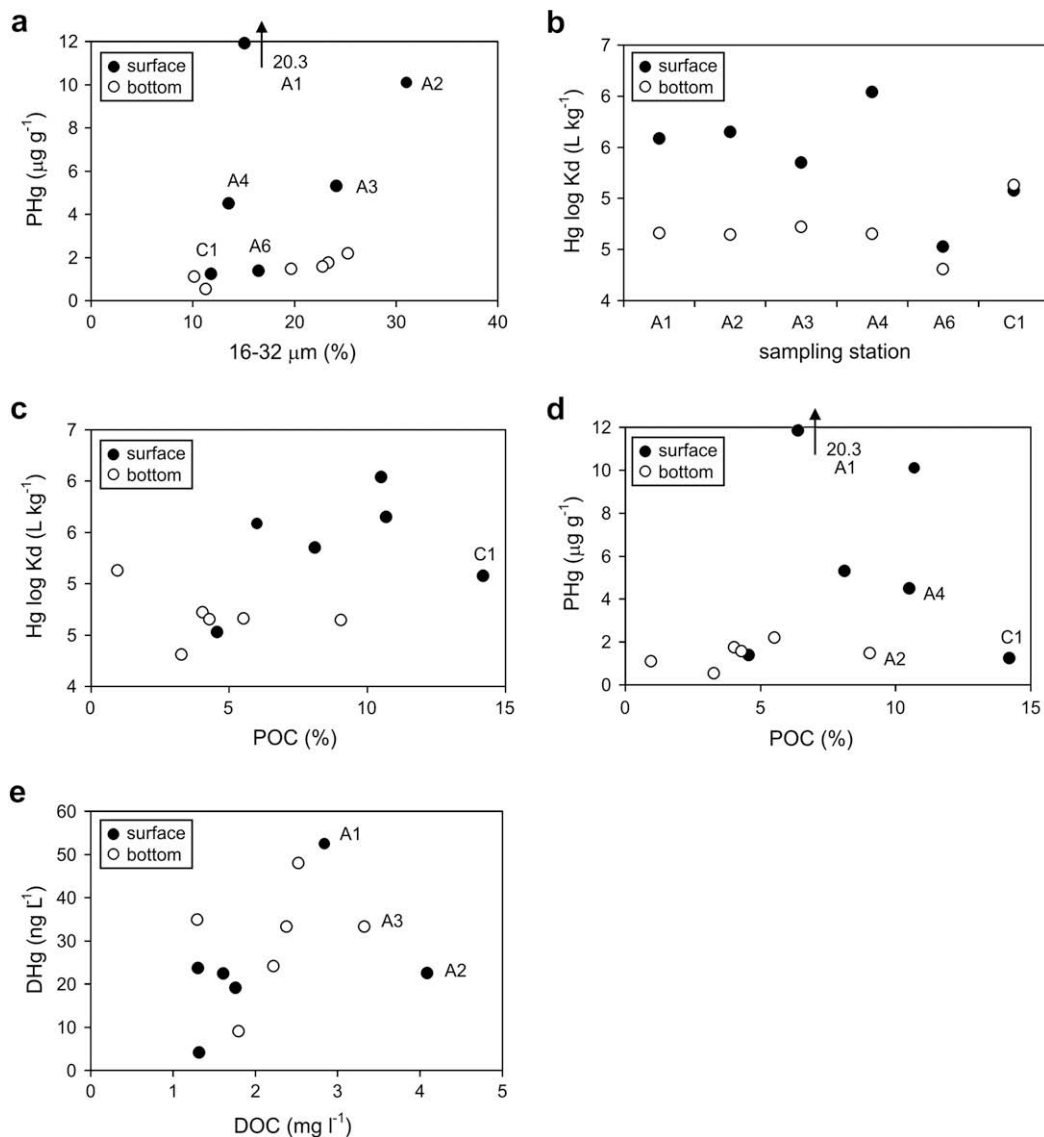


Fig. 7. The relationship between particulate mercury concentration (PHg as $\mu\text{g g}^{-1}$) and the medium silty fraction (16–32 μm) in the water samples (a). The partitioning of Hg, expressed as log K_d ($=[\text{PHg}]/[\text{DHg}]$, L kg^{-1}) is reported as spatial variability (b) along the river courses and against the particulate organic Carbon (POC) content (c). Particulate (d) and dissolved (e) mercury concentrations are also related to the corresponding organic Carbon component in the water samples.

therefore it is more likely that it complexes Hg. Accordingly, it is probable that DHg may also be present in association with inorganic ligands and, presumably, with important quantities in reactive form, at least in the salt-wedge, thus rendering Hg available for methylation processes (Mason and Fitzgerald, 1990).

4.2. River sediments

The flood tide, entering the lagoon system through the inlet and the main channel, is effective in transporting coarse particles up to the river mouth (Piani and Covelli, 2000) where they eventually accumulate at the bottom. The sand-sized particles are mainly composed by carbonates with the calcitic component prevailing over the dolomitic one (Brambati, 1970). On the contrary, the high contents of fine particles (silt and clay-sized) found along the two rivers are due to the suspended load associated with spring water supply along with the flow of residual tides from the sea (Brambati, 1969). The clay association in the lagoon sediments was found to be illite > chlorite > kaolinite with small percentages of smectite (Brambati, 1972). The same author also suggests that the clay

minerals are mainly of marine origin, whereas the contribution from spring rivers due to soil erosion of the alluvial plain is prevalently constituted of silty particles.

The $C_{\text{org}}/N_{\text{tot}}$ ratios (atomic) are often used in order to explain the source of sedimentary particulate organic matter (POM; Trask, 1939; Pocklington and Leonard, 1979). It was observed that $C_{\text{org}}/N_{\text{tot}}$ ratios >12 are associated to land-derived organic matter, whereas values <10 may be defined as autochthonous marine. Our ratios ranged from 9.2 to 12.3, thus confirming the origin of sedimentary material from riverine POM as previously reported in Faganeli et al. (1988). Factors contributing to such high $C_{\text{org}}/N_{\text{tot}}$ ratios are especially terrestrial plants and wood debris containing lignin (Pocklington and Leonard, 1979). The only exception was the ratio of 5.6, typical of autochthonous marine POM, obtained for A6 which is clearly consequence of the flood tide TSM contribution within the lagoon basin.

In relation with anthropogenic sources, it has been often reported that the THg abundance in sediments is controlled by both organic matter and fine grained particles (Devai et al., 2005). In fact, it is generally assumed that, due to their greater surface to volume

ratio, smaller particles tend to bind high concentrations of heavy metals, whereas strong interactions between Hg and organic matter are attributed to the presence of sulphur-containing functional groups (Förstner and Wittman, 1979; Horowitz and Elrick, 1987; Ravichandran, 2004). In this study, THg showed to be correlated only with 2–8 μm size (silt) ($r = 0.928$, $n = 6$; $P \leq 0.05$). On the contrary, no significant correlation was found between THg and C_{org} (Fig. 4c). This is probably due to the high enrichment of organic substances discharged from the industrial site, mainly in form of lignin-sulphonate. These compounds are very refractory to humification processes and do not offer any sulphur binding site for Hg. Despite the lack of correlation between total Hg and C_{org} , the latter could play an important role in enhancing methylation processes, both in biotic and abiotic ways (Ullrich et al., 2001).

In the nearby Gulf of Trieste, affected by the Isonzo River inputs, microcrystalline red cinnabar is prevalently bound to the coarse fraction of the bottom sediments (Biester et al., 2000). Hg as sulphide has probably the same origin at station A6 (Fig. 5a), where grain-size composition showed accumulation of coarse particles (sand; Fig. 4a). This result is in agreement as previously reported in Piani et al. (2005) for the Marano lagoon. The authors pointed out the role of tidal fluxes in controlling dispersion and accumulation of cinnabar bound to TSM from the Isonzo River and entering the lagoon through the inlets. These evidences should exclude the presence of appreciable quantities of Hg in the pyrite fraction, due to the availability of sulphate for sulphate reduction in marine reducing environment (Huerta-Diaz and Morse, 1992; Bower et al., 2008).

Although the scarce availability of HgS for methylation processes is well recognized (Morel et al., 1998), it should be emphasized that anaerobic conditions due to both, low renewal of bottom waters and increase in organic load, can effectively occur in lagoon environments. The chemical oxidation of sulphides can lead to the formation of sulphate, thiosulphate or even elemental sulphur (Gagnon et al., 1996), thus releasing Hg in the form of Hg(II), which is then eventually available for methylation (Ullrich et al., 2001).

Hg-e is considered a good estimation of the free Hg(0) present in the sediment matrix, although some interferences of Hg(I), amorphous organo-sulphur and crystalline Fe/Mn oxide phases could yield an overestimation. Our results (Fig. 5a, b) are not in agreement with those obtained from Biester et al. (2002b), but they are very similar to those reported for top soils near an abandoned Hg cell chlor-alkali plant (Bloom et al., 2003). Hg accumulation in soils near CAPs may occur as a consequence of wet and dry deposition of Hg(II) and Hg(0) respectively, along with particulate Hg. After deposition, Hg is subject to a wide array of chemical and biological

processes such as Hg(0) oxidation, and Hg(II) reduction or methylation (Weber, 1993). Biester et al. (2002a) investigated the main binding forms and mobility of Hg in this kind of soils and demonstrated that Hg(0), which is the main form emitted, was almost absent. This was probably due to a quantitative re-emission and oxidation of Hg(0) species in the atmosphere from soils, either directly (Biester et al., 2002a,b) or by biotic and abiotic reduction of Hg(II) (Alberts et al., 1974; Allard and Arsenie, 1991). These processes seem not to have occurred in our study area, since Hg as Hg(0) was directly discharged in large quantity in the fluvial system.

The Hg-o fraction includes Hg(II) complexes with humic, fulvic and amino acids, living and dead biota and the relative small fraction of methylated species. Nevertheless, it is well known that each sediment type has a unique methylation potential, so we can only speculate about the relevance of the Hg-o. For instance, Bloom et al. (2003) reported a strong positive and negative correlation of MeHg contents with Hg-o and Hg-e + Hg-s fractions, respectively. In this context, our data suggest that the Aussa-Corno River sediment could represent an important site for methylation processes.

The sum of Hg-w + Hg-h phases consists of Hg compounds with relatively high water solubility such as HgCl_2 , HgSO_4 and HgO. These compounds are not usually present in form of water-soluble ionic species, but bound to organic matter (without a Hg-C bond) or suspended mineral particles. This assumption makes arise the importance of these fractions for the bioavailability of Hg, from sediments to the river and marine fauna, being this extracted Hg forms often considered as the substrate for Hg methylation processes (Stein et al., 1996; Ullrich et al., 2001; Devai et al., 2005). In addition, Hg-w and Hg-h compounds are fully dissolved by an operationally defined method, employed to determine the “*in vitro human stomach simulation*” accepted by state regulatory agencies for the purpose of site-specific exposure assessment (Ruby et al., 1996; Bloom et al., 2003).

Generally, the sum in our samples does not exceed 3.5–4.0% of the total Hg (mean value $2.0 \pm 1.9\%$; Fig. 5b). These data are similar to those obtained in marine sediments from the Gdansk Bay and Vistula River in Poland (Bełdowski and Pempkowiak, 2003; Boszke and Kowalsky, 2007), but slightly higher than values reported for the River Ji Yun in China (from 0.05 to 1.22%; Ching-I and Hongxiao, 1985). However, it should be emphasized that this comparison could be only speculative, due to the application of different extraction procedure schemes. From a global point of view, it would be useful to establish a simplified protocol and to test analytical results through appropriate reference materials (Issaro et al., 2009). As a result, it seems there is no high risk of direct contamination of the river sediments except for the site A2 which, in spite of having

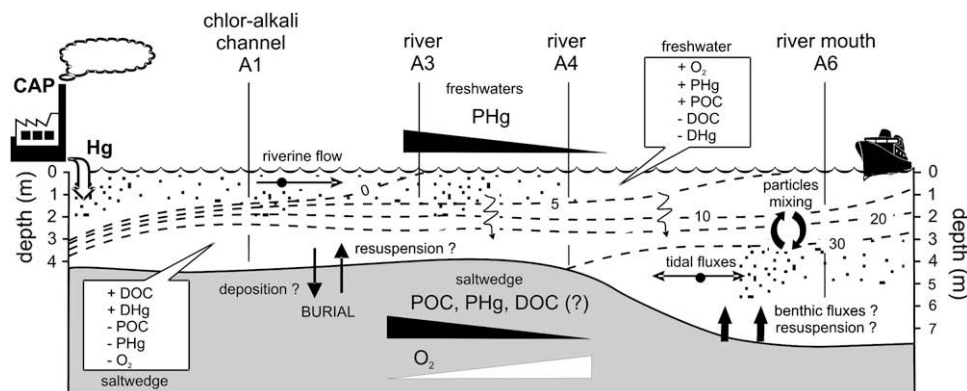


Fig. 8. Conceptual representation of the geochemical processes controlling mercury behaviour and transport in the estuarine environment of the Aussa-Corno River mouth. Abundances of chemical species are only relative and indicated by the + (high) and - (low) notations. Salinity is reported as dotted-line.

the lowest total Hg level ($0.86 \mu\text{g g}^{-1}$), shows the highest level of both exchangeable and Hg-o fractions.

5. Conclusions

Although uncontrolled Hg discharge from a CAP within the Aussa–Corno River system stopped in 1984, the artificial channel connecting the industrial area to the upper river course still remains an active contamination source for the Marano lagoon environment. The results provided an insight into the geochemical processes controlling Hg behaviour in the estuarine zone (Fig. 8).

Hg seems to be scavenged by fine particles transported by surface freshwaters, flowing on the salt-wedge, to the river mouth. PHg concentrations decrease downstream as a consequence of progressive dilution in the underlying saltwaters. Some particulate-bound Hg may, however, undergo slowly, settling through the halocline where water mixing is allowed. However, the PHg contents in the salt-wedge would be rather controlled by resuspension of fine bottom sediments due to tidal currents and, periodically, to recurring shipping traffic.

The internal part of the salt-wedge is systematically oxygen depleted and particularly rich in DHg. The Hg dissolved phase would be mainly complexed by inorganic ligands, whereas the role of DOC, although in low concentrations, cannot be excluded. Presumably, DHg would be present with important quantities in reactive form, thus rendering the metal available also for methylation processes in the water column. Specific studies should be conducted to understand these aspects.

The influence of tidal fluxes in transport and sedimentation processes affecting Hg is pointed out by the absence of a clear gradient for metal concentrations in bottom sediments. This evidence is also supported by the presence of Hg contents in the Corno River, which is not affected by direct metal inputs from CAP. Resuspension due to periodical dredging operations, essential for shipping traffic, could play an important role in Hg remobilization. In fact, speciation techniques highlighted the presence of potentially available Hg species for methylation processes. Further investigations should focus on the environmental conditions most favourable to the recycling of Hg accumulated in river sediments, in order to individuate the potential risk affecting the trophic chain.

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