

## Mercury distribution in Douro estuary (Portugal)

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### Abstract

Determinations of dissolved reactive and total dissolved mercury, particulate and sedimentary mercury, dissolved organic carbon (DOC), particulate organic carbon (POC) and suspended particulate matter (SPM) have been made in the estuary of river Douro, in northern Portugal. The estuary was stratified by salinity along most of its length, it had low concentrations of SPM, typically  $<20 \text{ mg dm}^{-3}$ , and concentrations of DOC in the range  $<1.0\text{--}1.8 \text{ mg dm}^{-3}$ . The surface waters had a maximum dissolved concentration of reactive mercury of about  $10 \text{ ng dm}^{-3}$ , whereas for the more saline bottom waters it was about  $65 \text{ ng dm}^{-3}$ . The surface waters had maximum concentrations of total suspended particulate mercury of  $\sim 7 \mu\text{g g}^{-1}$  and the bottom waters were always  $<1 \mu\text{g g}^{-1}$ . Concentrations of mercury in sediments was low and in the range from  $0.06$  to  $0.18 \mu\text{g g}^{-1}$ . The transport of mercury in surface waters was mainly associated with organic-rich particulate matter, while in bottom waters the dissolved phase transport of mercury is more important. Lower particulate organic matter, formation of chlorocomplexes in more saline waters and eventually the presence of colloids appear to explain the difference of mercury partitioning in Douro estuarine waters.

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### 1. Introduction

Estuarine circulation determines the mixing of solutes and SPM (Dyer, 1997), and ultimately modifies the composition of the riverine signal to the adjacent marine waters (Chester, 2000). Mixing diagrams, where the concentrations of dissolved constituents are plotted against salinity, often show considerable inter-estuarine variability due to their sensitivity to strong gradients in ionic strength, pH and particle character and concentration (Millward and Turner, 1995). Dissolved mercury concentrations are affected by the presence of a turbidity maximum zone, particularly in macro-tidal estuaries characterised by a long residence time for suspended particles (Cossa et al., 1988; Leemarkers et al., 1995). Here adsorption reactions are always in competition

with the effects of gradient of the major ions of seawater because of the formation of chlorocomplexes and competition for active sites from  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Millward and Turner, 1995). However, there is no substantial evidence from field studies for the prevalence of mercury chlorocomplexes in the presence of organic matter (Coquery et al., 1997; Turner et al., 2001), rather the significance of colloidal organic matter on mercury speciation in estuarine systems of different characteristics becomes more important (Martin et al., 1995; Stordal et al., 1996). In laboratory studies, Turner et al. (2001) have suggested that mercury behaviour is influenced by a coupled salting out-sorption mechanism, involving neutral mercury chlorocomplexes (e.g.  $\text{HgCl}_2$ ) and  $\text{Hg(II)}$ –hydrophobic organic complexes. Thus, it appears that mercury speciation in estuaries will be dominated by the presence of dissolved and particulate organic matter.

The Douro estuary has a single, narrow channel approximately 20 km in length, an average depth of

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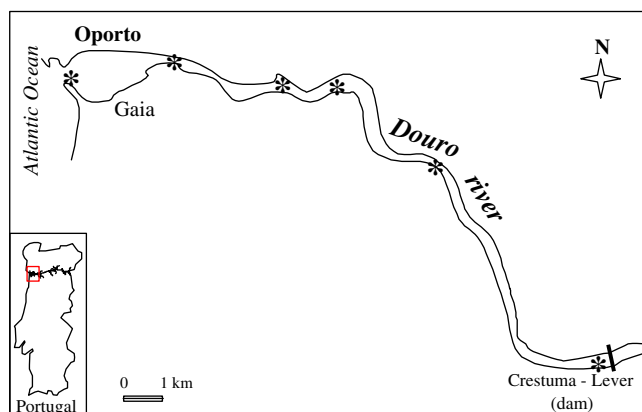


Fig. 1. Map of Douro estuary and of sampling stations.

10 m and, at the present time, the upper limit of the estuary is defined by the dam at Crestuma-Lever (Fig. 1). The mean flow in August is normally about  $80 \text{ m}^3 \text{ s}^{-1}$ , while in January it increases to about  $1230 \text{ m}^3 \text{ s}^{-1}$ . The tides are semidiurnal with an amplitude of 3.5 m at spring tide. The bottom sediment is generally uncontaminated with metals (Mucha et al., 2003) and consists of a thin layer of mixtures of sand and gravel overlying bedrock. During 1998 a new system for the treatment of domestic sewage was installed in the city of Oporto, presumably reducing the inputs of anthropogenic materials to the estuary, such that along the Oporto coast the concentrations of dissolved metals are relatively low (Vasconcelos and Leal, 1997). As a consequence, the Douro estuary has been classified as “pristine”, as regards the organic carbon content of its waters (Abril et al., 2002).

The aim of this study is to examine the mercury distribution in the Douro estuary and its relationship with relevant estuarine master variables (salinity, SPM, dissolved and particulate organic carbon).

## 2. Materials and methods

### 2.1. Sample collection and pre-treatment

Water samples were collected at six stations along the longitudinal axis of Douro estuary, between the mouth and the dam Crestuma-Lever (Fig. 1). The sampling was performed in September 1997 and in April 1999, during neap tides with a tidal range of 1.5 m. A calibrated sensor was used to measure salinity in situ. Surface and bottom waters were collected with an acid-washed  $5 \text{ dm}^3$  PVC “Niskin” bottle, a type that has been found to be suitable for collecting water samples for mercury analysis (Plaschke et al., 1997). Samples for DOC analysis were only collected in the April survey. Surface sediments were collected along the estuary at the lower four stations in Fig. 1 and

samples were not taken where the estuary had a rocky bottom.

Sampling, sample treatment and analysis were performed using ultra-clean protocols (adapted from Bloom, 1995). Ultra-pure water was obtained from a Millipore Milli-Q model 185 system. All glassware was previously soaked for at least 24 h in a bath containing 5% Decon, then in 25%  $\text{HNO}_3$  and finally thoroughly rinsed with ultra-pure water. After sampling, water samples were transported to the laboratory and processed within a few hours. The water samples were filtered and the suspended particulate matter was collected on pre-weighed,  $0.45 \mu\text{m}$  pore size Millipore filters for mercury determinations. For DOC and POC determinations, the water samples were filtered through pre-combusted, pre-weighed glass fibre (GF/C) filters. The filtrates for mercury determinations were acidified to  $\text{pH} < 2$  using concentrated  $\text{HNO}_3$  (Merck, “mercury-free”). In order to examine for any possible contamination during the filtration procedure, two blank solutions ( $100 \text{ cm}^3$  of Milli-Q water) were acidified with  $50 \mu\text{L}$  concentrated  $\text{HNO}_3$  (Merck, “mercury-free”) and were filtered in between the water samples through the same filtration unit used for those samples.

### 2.2. Analytical approach

Reactive mercury was determined directly on samples from both surveys by cold vapour-atomic fluorescence spectrometry (CV-AFS; PSA, model 10.003, associated with a detector Merlin PSA model 10.023). In the filtered waters of the April survey, total dissolved mercury concentrations were also measured. These determinations were made using the method described above, but after addition of  $500 \mu\text{L}$  of a saturated solution of potassium persulfate to  $50 \text{ cm}^3$  of filtered water and irradiation by a UV lamp (1000 W) for 30 min. Following irradiation, the excess of oxidant was reduced with  $40 \mu\text{L}$  of hydroxylamine solution 12% (w/v) (Mucci et al., 1995).

The variability of replicates for filtration was assessed in the following manner: two replicates of filtered water samples were obtained and analysed three to four times each; the coefficient of variation was in the range from 2% to 6%. The CV-AFS method for the analysis of mercury in water has a mean analytical detection limit (defined as three times the standard deviation of the blank signal) of  $0.42 \text{ ng dm}^{-3}$  ( $n = 10$ ).

For DOC analyses, all the glassware was cleaned with sulfochromic solution and analysis blanks of DOC and samples were performed. Dissolved organic carbon determinations were made by an automated procedure (Alliance, model Evolution II) in which the sample is acidified and the inorganic carbon, as  $\text{CO}_2$ , removed by  $\text{N}_2$ . Subsequently, a buffered persulfate solution was added and the solution was irradiated in an UV

digester (Skalar, model SA 5550). A hydroxylamine solution was then added and the carbon dioxide generated diffused through a gas silicone membrane. A weakly buffered phenolphthalein indicator solution was used as a recipient stream. The colour intensity of this solution decreased proportionately to the change in pH caused by the absorbed carbon dioxide gas (Wangersky, 1993).

Total particulate mercury was determined after digestion of the filters in closed glass reactors with 50 cm<sup>3</sup> of a solution 4 mol dm<sup>-3</sup> HNO<sub>3</sub>, at 70 °C for 2 h (Pereira et al., 1995, 1998). The digests were analysed by cold vapour-atomic absorption spectrophotometry (CV-AAS; Perkin Elmer, model 3030B associated to a MHS-20 system), using stannous chloride as the reducing agent and a pre-concentration step on a gold gauze. The sediment samples were freeze-dried, homogenised and mineralised using the same method. The analysis method for particulate mercury had an analytical detection limit of 22 ng dm<sup>-3</sup> and the accuracy for particulate mercury was checked using certified reference material MESS-2 (National Research Council of Canada-NRCC). The value found was 0.090 mg kg<sup>-1</sup>, which compared favourably ( $p < 0.05$ ) with the certified concentration of  $0.092 \pm 0.009$  mg kg<sup>-1</sup>. The POC content was estimated by chemical oxidation with a sulfochromic mixture of the GF/C filters. The excess of oxidant was titrated with an iron solution.

### 3. Results

#### 3.1. Water column characteristics

The axial salinity distribution in the Douro estuary in both surveys is presented in Fig. 2. Surface waters had salinity values lower than 5‰, except near the estuary mouth, where it reached 14‰, whereas the salinity of bottom waters was normally higher than 10‰ up to 12 km from the mouth. Further upstream differences of salinity between upper and lower waters decreased owing to the influence of freshwater discharge. The dis-

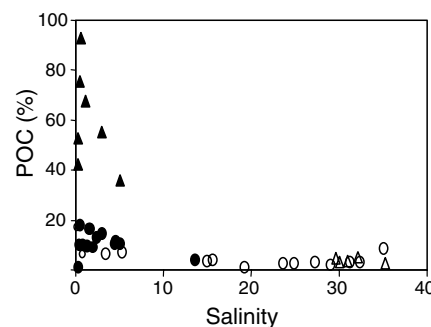


Fig. 3. Particulate organic carbon (POC in %) in the Douro estuary in September 1997 (circles) and April 1999 (triangles); surface waters represented by full symbols (●, ▲) and bottom waters by open symbols (○, △).

tribution of SPM concentrations showed a similar pattern (Fig. 2), such that SPM concentrations in surface waters were uniformly low (<5 mg dm<sup>-3</sup>) and bottom waters had higher concentrations up to 25 mg dm<sup>-3</sup>. Concentrations of DOC in surface waters, in April, were between 1.6 and 1.8 mg dm<sup>-3</sup>, whereas in bottom waters it was <1 mg dm<sup>-3</sup>. Particulate organic carbon in surface waters in September was in the range 6–20%, whereas during the spring phytoplankton bloom in April it was up to 90%. In bottom waters, the POC concentrations were always between 3% and 6% and decreased with salinity (Fig. 3).

#### 3.2. Mercury distributions

Most of the sediments were composed of sand, with the fine fraction (<63 μm) being less than 12%. Total mercury in the sediments varied from 0.06 to 0.18 μg g<sup>-1</sup>. The higher concentrations were found in samples with a higher proportion of mud and no longitudinal variation was observed. Suspended particulate mercury concentrations varied from 0.3 to 6.5 μg g<sup>-1</sup>, and in general were higher in surface waters (Fig. 4) and the particulate mercury-salinity relationship had a similar trend to that found for POC-salinity (Fig. 3). For surface samples the suspended particulate mercury

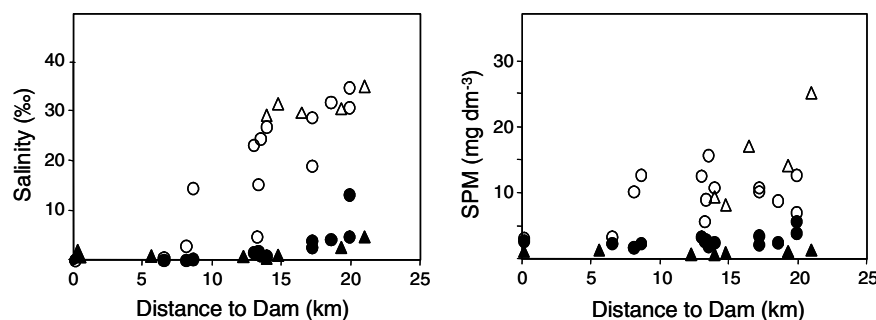


Fig. 2. Axial distribution of salinity (‰) and suspended particulate matter concentrations (SPM in mg dm<sup>-3</sup>) in the Douro estuary in September 1997 (circles) and April 1999 (triangles); surface waters represented by full symbols (●, ▲) and bottom waters by open symbols (○, △).

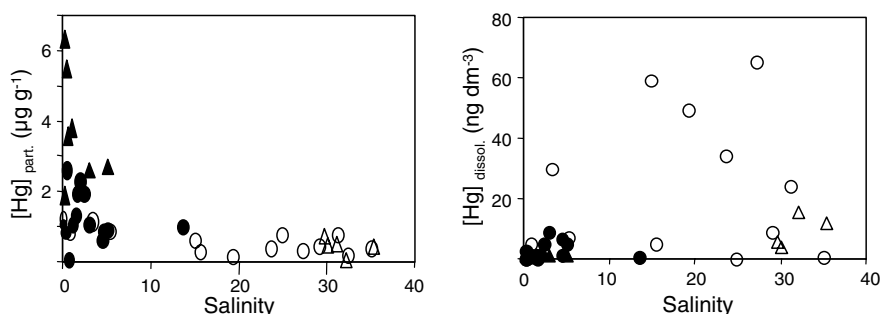


Fig. 4. Particulate ( $\mu\text{g g}^{-1}$ ) and dissolved reactive ( $\text{ng dm}^{-3}$ ) mercury concentrations in the Douro estuary in September 1997 (circles) and April 1999 (triangles); surface waters represented by full symbols ( $\bullet$ ,  $\blacktriangle$ ) and bottom waters by open symbols ( $\circ$ ,  $\triangle$ ).

is positively correlated to POC ( $r^2 = 0.53$ ,  $p < 0.05$ ) and as consequence particles transported by surface waters are enriched in suspended particulate mercury.

The distribution of reactive dissolved mercury concentrations along the estuary differed from that of particulate mercury (Fig. 4): reactive mercury in surface waters was uniformly low ( $0.5\text{--}10 \text{ ng dm}^{-3}$ ), while concentrations in bottom waters were in general higher and in the samples collected in September 1997 showed concentrations up to  $65 \text{ ng dm}^{-3}$ . Total dissolved mercury was measured only in the waters sampled in April and the pattern observed is comparable to the distribution of reactive forms. The total concentrations of mercury in surface waters were lower ( $0.6\text{--}6.5 \text{ ng dm}^{-3}$ ) than bottom waters ( $61\text{--}92 \text{ ng dm}^{-3}$ ). Comparing total and reactive mercury concentrations it was found that bottom waters contained more than 80% of non-labile mercury forms, while lower percentage and broader range was encountered in upper waters (45–80%). The solid-solution interactions of mercury may be interpreted in terms of the conditional partition coefficient defined as  $K_D = ([\text{Hg}]_{\text{particulate}}/[\text{Hg}]_{\text{reactive soluble}}) \text{ dm}^3 \text{ kg}^{-1}$  (Turner, 1996). The  $K_D$  varied by three orders of magnitude along the Douro estuary from  $5.2 \times 10^3$  to  $3.3 \times 10^6 \text{ dm}^3 \text{ kg}^{-1}$ . The highest  $K_D$  values were found in surface waters in both surveys, with a mean  $\pm$  standard deviation of  $1.3 \pm 1.0 \times 10^6 \text{ dm}^3 \text{ kg}^{-1}$ , while the lowest mean  $K_D$  values,  $3.2 \pm 5.9 \times 10^5 \text{ dm}^3 \text{ kg}^{-1}$ , were found in bottom waters.

#### 4. Discussion

The distribution of mercury in dissolved and particulate fractions of the Douro estuary allow us to examine the behaviour of mercury in surface and bottom waters of a well-stratified estuary with low suspended matter concentration and relatively high POC concentrations.

The range of the concentrations of dissolved reactive mercury in the Douro estuarine waters are similar to the values reported for the low-contaminated Atlantic coast of Galicia (Beiras et al., 2002). However, the dissolved

reactive mercury concentrations in bottom waters are significantly above the values reported for the Seine and Loire estuaries (Coquery et al., 1997) and three estuaries in Texas (Stordal et al., 1996). The enhancement for the Douro possibly reflects the influence of anthropogenic discharges, into the bottom waters, at various points along the estuary. Reactive mercury in the bottom waters had a maximum of  $65 \text{ ng dm}^{-3}$  in September 1997, before the installation of a new sewage treatment for Oporto, and although values were lower in April 1998 ( $<20 \text{ ng dm}^{-3}$ ), concentrations still remained higher than in surface waters. Aside from anthropogenic sources the higher reactive mercury in bottom waters compared to surface waters is probably related to salinity that facilitates the formation of dissolved mercury chlorocomplexes. More than 80% of “filter-passing” mercury in non-reactive forms may reflect the presence of other ligands, mainly dissolved humic substances, which complement the chlorocomplexation process in releasing mercury from SPM. However, higher concentrations of dissolved mercury in bottom waters that contain low dissolved organic carbon in conjunction with the increase of the proportion of non-labile forms suggest that mercury may be also tied to colloidal organic matter (Stordal et al., 1996). Colloids presumably formed in the mid-water interface along the almost entire Douro estuary, may contain mercury that is quantified in the “dissolved” fraction (Stordal et al., 1996). It is unlikely that release of mercury from sediments contributes to higher concentrations in bottom waters because of the low mercury concentrations in sand and muddy sand comprising the deposits in the Douro.

The relatively low concentrations of dissolved reactive mercury in surface waters indicate that only small quantities of mercury might be in the chlorocomplex forms (Turner et al., 2001). A large proportion of the total dissolved mercury (45–80%) appears to be in non-labile forms highlighting the possible relevance of humic complexes in the speciation of surface waters in Douro estuary. This hypothesis is in accordance with other studies (Leemarkers et al., 1995) and thermodynamic calculations showing that “filter-passing”

mercury in the low-salinity waters includes humic complex forms (Stordal et al., 1996).

Lower suspended particulate mercury concentrations were found in bottom waters, compared to surface waters, due to the lower POC concentrations. Dissolved mercury mixed across the freshwater–seawater interface and becomes preferentially associated with the suspended particles in the surface waters. During periods of phytoplankton blooms and high POC concentrations this association is enhanced (Monterroso et al., 2003), as in the April survey. The values of  $K_D$  in surface waters were 1–2 orders of magnitude higher than those in the bottom waters, indicating a greater exchangeability. These factors suggest a complex set of chemical processes where adsorption and desorption are controlled by the interplay between the competitive effects of complexation with chlorides and DOC and the tendency of mercury to adsorb onto organic-rich particles. In order, to resolve the fate of mercury in the Douro estuary further process-oriented studies are required.

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