

Estuary-ria exchange of cadmium, lead and zinc in the coastal system of the Ria of Vigo (NW Iberian Peninsula)

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SUMMARY: Little research has been done on the land-sea exchange of trace elements, which is particularly applicable to ria coasts. In particular, trace metal enrichment in the inner part of the Ria of Vigo (the San Simon Inlet) has been observed from sediment studies but there is no information about Cd, Pb and Zn fluxes through the Rande Strait, which is the natural boundary of the estuary-ria water exchange. In order to assess metal exchanges in a ria-type system, six sampling cruises on board the R/V *Mytilus* (IIM-CSIC) were carried out. Water column profiles of salinity, temperature and tidal currents were obtained every 30 min. The water column for dissolved and particulate metals was sampled every two hours over a complete tidal cycle. Dissolved metal concentrations were 0.01–0.18 nM for Cd, 0.5–1.9 nM for Pb and 4–44 nM for Zn. Compared with Zn (16±12%) and especially with Cd (5.4±5.0%), particulate metal represented a significant fraction of the total concentration for Pb (41±21%). Net fluxes of dissolved Cd and Zn are higher than in the particulate phase, whereas for Pb an inverse situation was observed. The net metal exchange in the Vigo estuary-ria environment was not seasonally controlled. Dissolved Cd and Pb were driven by tidal ranges and particulate Pb by the Oitavén River flow. On the other hand, Zn did not show a defined trend. The budgets obtained for the Ria of Vigo, with the exception of Pb, were one or two orders of magnitude lower than those measured in other large European estuaries.

Keywords: dissolved metals, particulate metals, land-sea exchange, flux, budget, estuary, Ria, Spain.

RESUMEN: INTERCAMBIO ESTUARIO-RÍA DE ELEMENTOS TRAZA EN EL SISTEMA COSTERO DE LA RÍA DE VIGO (NO PENÍNSULA IBÉRICA). – Existen pocos estudios sobre los elementos traza en el intercambio tierra-océano, lo que es especialmente aplicable a las zonas costeras de las rías. En particular, respecto a la ría de Vigo se ha observado un enriquecimiento de metales traza en sedimentos pero se carece de información acerca de los flujos de Cd, Pb y Zn a través del estrecho de Rande, que es la frontera natural para el intercambio estuario-ría. A fin de evaluar este tipo de intercambios se realizaron seis campañas oceanográficas a bordo del B/I *Mytilus* (IIM-CSIC) para cuantificar los flujos de Cd, Pb y Zn en diferentes estaciones del año. Se obtuvieron perfiles verticales de salinidad, temperatura y corrientes cada 30 min en el centro del estrecho de Rande durante un ciclo de marea. Además, se recogieron muestras de agua en cuatro niveles cada 2h. Las concentraciones de metales disueltos oscilaron entre 0.01 y 0.18 nM para Cd, 0.5 y 1.9 nM para Pb y 4 y 44 nM para Zn. Los metales particulados supusieron una fracción pequeña respecto del contenido total de metal (5.4±5.0% para Cd y 16±12% para zinc) salvo para el plomo (41±21%). Los flujos netos de Cd y Zn disueltos fueron superiores a los del particulado mientras que para Pb ocurrió lo contrario. El intercambio de metales en el entorno estuario-ría no parece depender de las estaciones del año sino de la altura de la marea en el caso de Cd y Pb disueltos y del caudal fluvial para Pb particulado mientras que Zn no presentó una tendencia definida. Excepto para Pb, los balances obtenidos son de uno a dos órdenes de magnitud inferiores a los de otros estuarios europeos.

Palabras clave: metales disueltos, metales particulados, intercambio tierra-océano, flujo, balance, estuario, ría, España.

INTRODUCTION

The biogeochemical cycles of many trace elements have been significantly impacted by anthro-

pogenic activities. Cd and Zn take part in important biogeochemical processes in the marine environment, such as CO₂ concentration/acquisition or silica uptake by large diatoms (Morel *et al.*, 2003 and Morel and

Price, 2003, and references therein). Cd and Pb may become harmful to the natural and human environment at high concentrations owing to their toxicity (Merian, 1991). Therefore, the understanding of the processes controlling the transport of these potential contaminants is important for the management of the coastal environment.

Major urban and industrial activities are concentrated on the littoral of the Vigo and Ferrol rias in NW Spain. However, little research has been done on the land-sea exchange of trace elements compared with nutrients (e.g. Prego, 1993; 1994; Prego *et al.*, 1995). Recent studies have highlighted the ria-ocean exchange (Cobelo-García *et al.*, 2005; Prego *et al.*, 2006) but many authors, based on sediment data, emphasize that the most contaminated areas are located in the inner part of the rias (Carballeira *et al.*, 2000; Rubio *et al.*, 2000; Cobelo-García and Prego, 2004; Prego *et al.*, 2008a). In particular, trace metal enrichment in the inner part of the Ria of Vigo (the San Simon Inlet) has been observed from sediment analysis (Belzunce-Segarra *et al.*, 1997; 2008; Evans *et al.*, 2003; Howarth *et al.*, 2005; Álvarez-Iglesias *et al.*, 2006; 2007). However, only one study has been published on trace metals in the water column of the San Simon Inlet (Santos-Echeandía *et al.*, 2008a), focusing on the dissolved copper speciation trend across the estuarine zone of the Ria of Vigo and its relation to particulate matter. Furthermore, no information about Cd, Pb and Zn concentration and fluxes in the estuarine ria area is available. The metal presence in this zone is affected by sewage dumping (Filgueiras and Prego, 2007) and harbour-shipyard activities (Prego *et al.*, 2008b). The sources and sinks of material to and from coastal systems are one of the pathways defined for the ocean inputs of trace elements (Bruland and Lohan, 2003), as has been observed for other European estuaries (Turner *et al.*, 1991; Millward and Glegg, 1997; Chiffoleau *et al.*, 1999; Cotté-Krief *et al.*, 2000; Michel *et al.*, 2000; Waelles *et al.*, 2005), but little is known about them in the rias (Prego and Cobelo-García, 2003). As in any other estuary, the estuarine ria area may be a critical boundary zone that could behave as a source or a sink of metals. For this reason, the aim of this study was to evaluate the role of season periods and tidal cycles in the exchange of Cd, Pb and Zn in a ria-type system. To this end, the estuary-ria exchange through the Rande Strait in the Ria of Vigo was quantified in order to achieve the following objectives:

(i) To determine the seasonal concentrations and distributions of metals in both the dissolved and the particulate phases.

(ii) To calculate the fluxes of metals between the San Simon Inlet and the rest of the Ria of Vigo, combining metal concentrations with current velocity data measured in the Rande Strait.

(iii) To determine whether the San Simon Inlet exports trace metals to the Ria or, in contrast, acts as a sink of metals.

Study Site

The Ria of Vigo (Fig. 1) is the southernmost of the Galician Rias, with a surface area of 156 km² and a water volume of 3.12 km³. The ria's axis is 33 km long and faces WSW. The catchment basin covers an area of 578 km², of which 75% discharges freshwater into the inner ria, i.e. the San Simon Inlet (length, 7.3 km; area, 18.3 km²; water content, 90 Hm³ at high tide). The greatest contribution is made by the Oitaven River, with an average monthly flow that ranges from 1.8 m³ s⁻¹ in August to 55.5 m³ s⁻¹ in February (Río and Rodríguez, 1992).

The inner ria zone can be considered as an estuary from both a hydrographic and a sedimentological point of view (Evans and Prego, 2003). The middle and outer ria zones are usually under marine conditions, with salinities higher than 35 (Álvarez *et al.*, 2005). In spite of the low flow rate of secondary rivers (annual average flow lower than 4 m³ s⁻¹), it is important to note that the River Lagares plays an important role in metal inputs to the ria (Filgueiras and Prego, 2007; Santos-Echeandía *et al.*, 2008b), and that the main terrigenous sediment source is the Alvedosa River, which drains a basin mainly dedicated to agriculture (Evans *et al.*, 2003).

The ria is under a mesotidal regime and its water column is partly stratified, showing a positive residual circulation in two layers (Prego and Fraga, 1992; Taboada *et al.*, 1998) which is the result of river outflow (Prego *et al.*, 1990) and seasonal upwelling events (Prego and Bao, 1997). The water exchange between the San Simon Inlet and the rest of the ria occurs through the Strait of Rande (600 m wide) controlled by tide: approximately 50% of the inlet's water is exchanged during each tidal cycle (Romero and Prego, 1995).

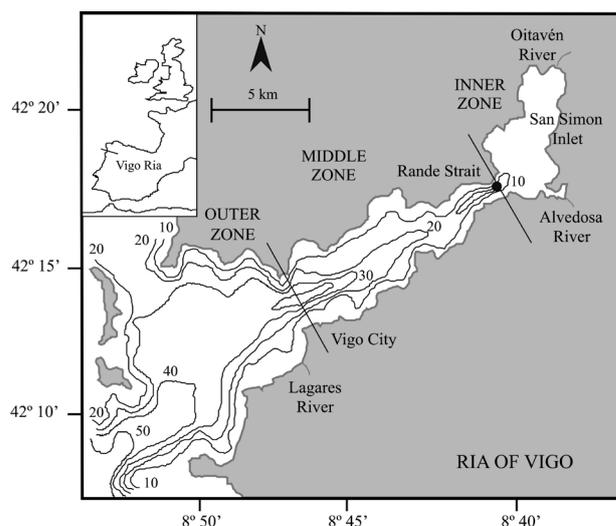


FIG. 1. – Map of the Ria of Vigo showing the bathymetry, inner, middle and outer ria zones and the anchoring station fixed on the Rande Strait (black point).

The middle ria zone is the one most affected by anthropogenic activities. On its shoreline are the city of Vigo (population, 295700) and the towns of Cangas (population, 25500) and Moaña (population, 18500). Inputs come from food factories and metal industries linked to shipyard and dock activities on the southern bank. Another aspect to be highlighted is the presence of six sewage treatment plants (STPs). After six years of operation of the STPs (1999-2005), particulate metal in surface sediments (Cd, Cu, Ni and Zn) was generally observed to decrease, while labile metal presence increased (Prego *et al.*, 2008a). Moreover, ligand concentrations were higher in sewage than in the rivers. Thus, the natural continental inputs of copper, for example, and ligands into the ria were magnified by anthropogenic inputs (Santos-Echeandía *et al.*, 2008a, b).

MATERIALS AND METHODS

Sampling and analysis

Six cruises (C1 to C6) were carried out in the Strait of Rande on board the R/V *Mytilus* during 2004, twice in winter (C1 on 29 January and C2 on 4 February), twice in spring (C3 on 6 May and C4 on 12 May), and twice in summer (C5 on 6 September and C6 on 13 September). The research vessel was anchored at a fixed station (42°17.26'N; 08°39.78'W) in the middle of the strait (Fig. 1), where temperature and salinity profiles were obtained from a current-temperature-depth (CTD) sounder (SBE 19, Sea-Bird) every hour during a complete tidal cycle. Water current was measured with a ship-mounted broadband acoustic Doppler current profiler (RDI, Vessel-mounted ADCP300 kHz), except for surface water, for which an electromagnetic current meter (Valeport 808) was used.

At the fixed station, water column samples were collected using Go-Flo bottles (General Oceanic of 5 L) every two hours during the same CTD tidal cycle at 5, 10, 17 and 24 m depth for each sampling date. Surface samples were taken from the gunwale with a telescopic arm. Samples were collected in 0.5-L acid-washed low-density polyethylene bottles kept in zip-lock bags and stored at 4°C in a cooler to be transported back to the on-shore lab for subsequent filtration, storage and analysis. Samples for dissolved oxygen were taken on-board from the Go-Flo bottles, immediately fixed and analyzed within 24 h at the IIM lab according to the Winker method (Aminot, 1983).

Samples were vacuum-filtered inside a Class 100 laminar flux cabin using pre-weighed 0.45 µm polycarbonate filters (Pall Gelman) mounted in an acid-washed polycarbonate filter holder (Sartorius AG). Filters were acid-washed just before filtration by passing 50 mL of HNO₃ 1% (Panreac Hiperpur 69%) by gravity and then rinsed with 250 mL of Milli-Q water. The first 100 mL of the sample was used to rinse the sample bottle, and was later discarded. Subsequent filtrate was kept in the

TABLE 1. – Accuracy control of the analytical procedures employed for dissolved and particulate metal determinations. Certified reference materials were CASS-4 (coastal seawater), SLRS-4 (riverine water) and PACS-2 (marine sediment) from NRC of Canada.

		Cd	Pb	Zn
Dissolved		pM	pM	nM
CASS-4	Obtained	236 ± 33	68 ± 12	5.8 ± 1.0
	Certified	231 ± 27	47 ± 17	5.8 ± 0.9
SLRS-4	Obtained	-	458 ± 73	15.6 ± 1.8
	Certified	-	415 ± 34	14.2 ± 1.5
Particulate		µg g ⁻¹	µg g ⁻¹	µg g ⁻¹
PACS-2	Obtained	2.47 ± 0.36	183 ± 3	345 ± 24
	Certified	2.11 ± 0.15	183 ± 8	364 ± 23

same bottle, acidified to pH 2 (HNO₃ Panreac Hiperpur 69%), and stored in zip-lock bags until analysis. In order to avoid overestimation of the suspended particulate matter (SPM), the salt was removed from the filters by passing a few millilitres of Milli-Q water. The filters containing the SPM were then removed from the holder using acid-washed polypropylene tweezers and stored frozen at -20°C in acid-washed Petri dishes until analysis.

The determination of trace metals (Cd, Pb and Zn) in the dissolved phase was carried out by means of differential pulse anodic stripping voltammetry (DPASV) using a hanging mercury dropping electrode (HMDE). Ag/AgCl (KCl) was used as the reference electrode and Pt wire as the auxiliary electrode. The equipment consisted of a Stand VA694 and an Autosampler 695 from Metrohm. Before determination, samples were digested for 1 hour using an UV-digestion apparatus (Achterberg and van den Berg, 1994) to break down the organic matter. Blanks were measured every ten samples and the accuracy of the analytical procedure was assessed by analysis of certified reference material (Table 1).

Analysis of metals in SPM was carried out using two different methods according to the metal concentrations and the detection limits of the equipment. For Zn, Varian 220FS flame-atomic absorption spectrometry (FAAS) was used. Cadmium and Pb concentrations were measured using electro-thermal atomic absorption spectrometry (ET-AAS) by means of a Varian 220 apparatus equipped with Zeeman background correction. Before the determinations, samples were microwave-digested (Milestone 1200 Mega) in Teflon® bombs using a mixture of HNO₃ (69%; Panreac Hiperpur) and HF (40%; Merck, Suprapur) according to the EPA 3052 method. The accuracy of the analytical procedure was checked with certified reference material (Table 1).

Estimation of metal fluxes

In order to calculate the fluxes of metals in dissolved and particulate phases at the estuary-ria boundary in the Rande Strait, the following equation was used:

$$F_M = \int_t \int_z V_{(z,t)} \cdot M_{(z,t)} dz \cdot dt \quad (1)$$

where V is the instantaneous velocity in the direction of the main axis of the ria and M is the dissolved or particulate metal concentration at a given depth z and at a given time t .

It was assumed that currents and metal concentrations were quasi-homogenous across the horizontal channel section. One sample point, at the centre of the Rande Strait section was used to calculate the metal fluxes across it. This assumption is due to the narrowness of the channel (600 m wide) and because currents are almost completely induced by tidal forcing and flow in the ria axis direction (Taboada *et al.*, 1998; Gomez-Gesteira *et al.*, 1999).

Equation (1) was simplified (Statham *et al.*, 1993) since the non-continuous metal concentration record was made during the tidal cycle, and the fluxes of elements per tidal cycle were estimated as:

$$F_M = \sum_{n=1}^{24} \sum_{i=1}^4 V_{i,n} \cdot M_{i,n} \cdot A_i \quad (2)$$

where subscripts i represent the number of layers into which the cross-section of channel was divided, n the number of samples taken in every tidal cycle, and A the area of the cross-section layer.

For the flux calculation, the channel cross-section was divided into four layers of 5 m depth approximately, from 0 to 24 m depth. In order to calculate the area of each layer a bathymetric map of the channel at the sampling section was used. The velocity current data were continuously recorded and averaged from 15 min before to 15 min after the time of water sampling. The current speed of each channel layer was calculated as the average between the velocities through it. The metal concentration of each layer was calculated as the average of the upper and the lower limit metal concentration of this layer.

Six seasonal samplings were carried out during each tidal cycle; the metal fluxes in each layer were calculated by multiplying the appropriate metal concentration by the water flux through this layer. The water flux was obtained by multiplying the current velocity by the area of the layer. The sum of the metal flux through the section layers every two hours gives the total metal flux in one tidal cycle.

RESULTS

In 2004 twin sampling campaigns were carried out in winter (C1 and C2), spring (C3 and C4) and summer (C5 and C6), the seasonally characteristic periods in the western Galician rias. Tidal currents along the main axis of the Rande Strait varied in the range of $\pm 35 \text{ cm s}^{-1}$ during spring tide and $\pm 20 \text{ cm s}^{-1}$ during neap tide. Tidal speeds were higher near the surface at the ebb tide and near bottom at the rising tide (see, for example, Cruise C3 in Fig. 4). Moreover, a tidal asymmetry was observed. Rising tide lasted around one hour more than the ebb tide. In addition, the San Simón

Inlet outflow started near the surface, while the inflow started through lower layers. Changes in the observed thermohaline properties and metal concentrations during six tidal cycles are explained next.

Winter cruises

In the January 29 campaign (Cruise C1) a thermal inversion was measured with surface temperatures of 13.5°C increasing with depth to 13.9°C . Salinity varied between 33.1 and 35.5 and a surface significant gradient was observed. Total metal concentrations (dissolved phase + particulate phase) were in the range of $0.02\text{--}0.14 \text{ nM}_{\text{Cd}}$, $0.6\text{--}6.0 \text{ nM}_{\text{Pb}}$ and $7\text{--}44 \text{ nM}_{\text{Zn}}$ (Fig. 2). The percentage of particulate metal was 2–92% for Pb, but only only 5–34% and <28%, respectively, for Zn and Cd. The lowest concentrations of dissolved metals were found when the San Simón Inlet was ebbing, and these values increased when the tide begun to rise. In the particulate phase, Cd concentrations showed a similar trend to that in the dissolved one. However, high particulate concentrations of Pb in the bottom layer were measured when the inlet was ebbing.

In the February 4 campaign (Cruise C2, Fig. 3) the thermal inversion of the previous week disappeared, temperatures ranged from 14.1°C to 12.9°C , and salinities varied between 25.1 at surface and 33.2 near bottom as a consequence of the large Oitavén River flow during the previous week (average: $64 \text{ m}^3 \text{ s}^{-1}$). Metal concentrations, both in particulate and dissolved phases, were of the order of the ones measured during Cruise C1 (Fig. 2), with the lowest concentrations when the inlet was flooding. Dissolved Pb concentrations were highest ($0.8\text{--}1.5 \text{ nM}$) at the top and at the-bottom of the water column. Particulate Pb only reached maximum values in deeper waters.

Spring cruises

In the May 6 campaign (Cruise C3; Fig. 4), the temperature gradient was very low in the whole water column ($13.1\text{--}13.7^\circ\text{C}$), but salinity varied between 32.6 and 35.5, with the lowest values near the surface during flood tide. The ranges of total metal were $0.02\text{--}0.16 \text{ nM}_{\text{Cd}}$, $0.4\text{--}2.0 \text{ nM}_{\text{Pb}}$ and $5\text{--}19 \text{ nM}_{\text{Zn}}$. The ranges of particulate metal were 0–10% (Cd), 2–71% (Pb) and 6–41% (Zn). The minimum values of dissolved Cd and Pb concentrations were found during the San Simón Inlet flooding and the maximum ones when the tide was going out (Fig. 2). In contrast, the water exported from the inlet was richer in Zn than the incoming water. The highest concentrations of Pb were measured at the surface and bottom, as occurred in the winter sampling (Fig. 4). Particulate distributions of Pb and Zn were similar, decreasing during flood tide. Particulate Cd showed the same trend as dissolved Cd, i.e. it showed a clear influence with the tide.

In the May 12 campaign (Cruise C4), temperature was quasi-homogeneous in the whole water column ($13.2\text{--}13.6^\circ\text{C}$) and salinity showed a marked gradient

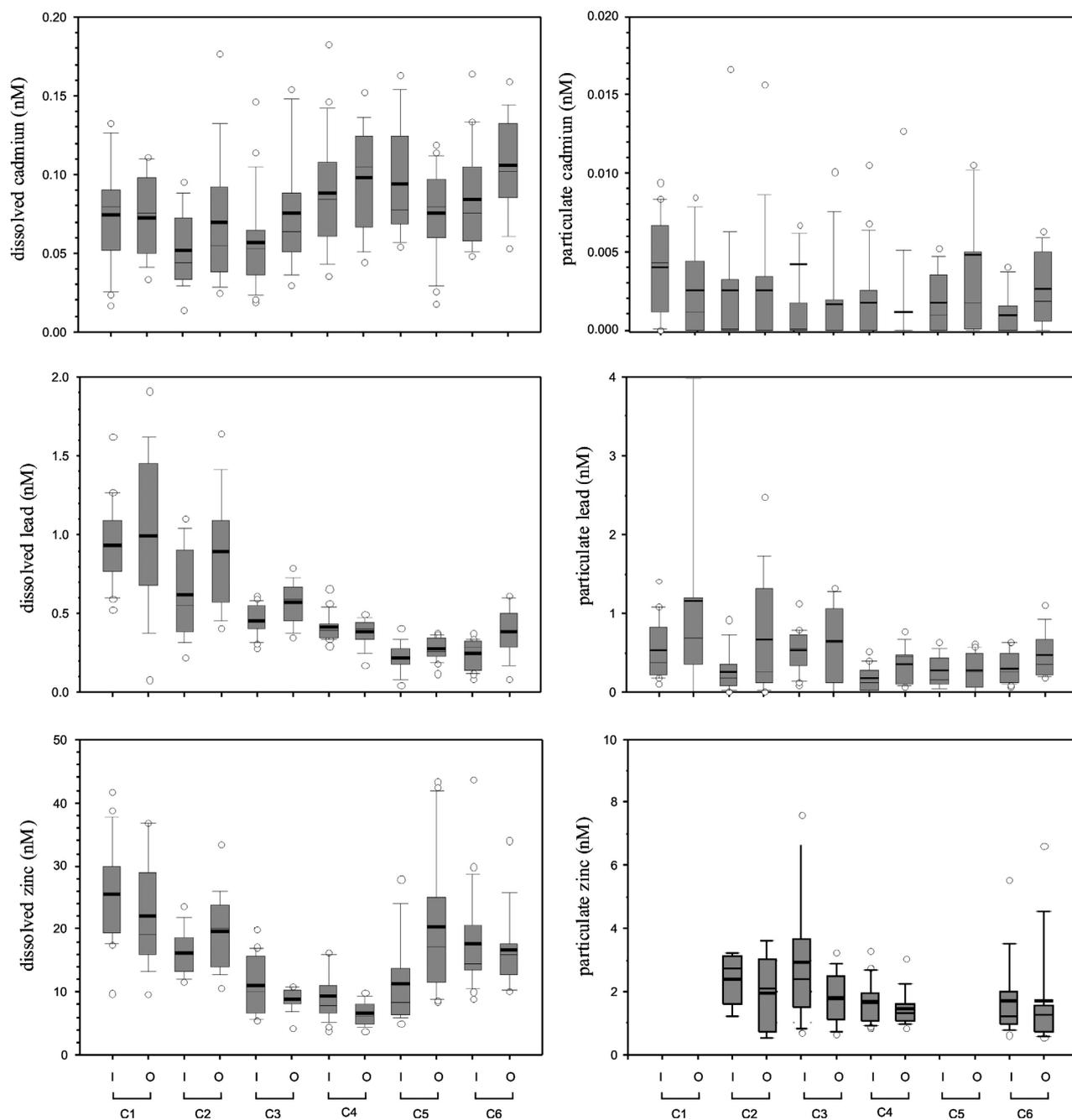


FIG. 2. – Box-and-whisker plots of concentration for incoming (I) and outgoing (O) water for each metal (dissolved and particulate) in each cruise (winter, C1 and C2; spring, C3 and C4; summer, C5 and C6). The length of the box represents the interquartile range, which contains 50% of the values. The thin horizontal line inside the box indicates the median, whereas thick horizontal line represents the mean.

(32.6–35.4), with the lowest values of temperature and salinity near the surface when the tide was ebbing. Total metal range was 0.02–0.18 nM_{Cd} , 0.3–1.1 nM_{Pb} and 5–18 nM_{Zn} (Figure 2). The particulate metal ranges were 0–17% (Cd), 2–73% (Pb) and 7–31% (Zn). A common trend was observed for dissolved Pb and Zn: their concentrations were lower during ebb tide and higher during flood tide. The distributions of particulate and dissolved Zn was similar, but those of Pb were not.

Dissolved (particulate) Cd increased when the tide was going out (coming in).

Summer cruises

In the September 6 campaign (Cruise C5), an increase in water surface temperatures (18.8°C) was observed in comparison with the previous campaigns. This fact contrasts with the temperature near the bed (13.7°C), which

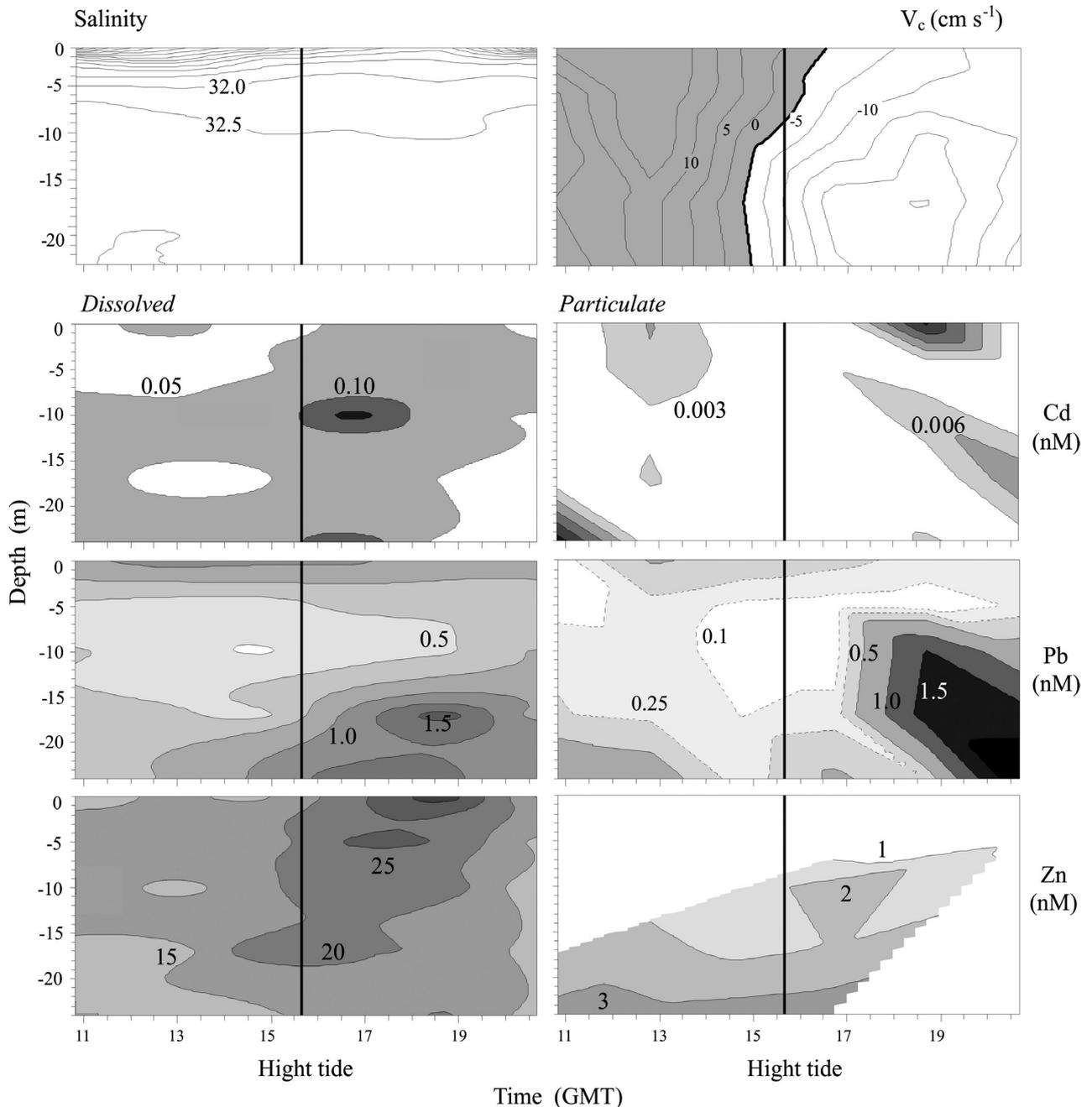


FIG. 3. – Isoline map at the anchored station in the estuary-ria boundary during the C2 winter cruise. Salinity, currents and dissolved and particulate concentrations of Cd, Pb and Zn are shown for winter. The vertical lines represent high and low waters according to the tide table for Vigo harbour.

may be associated with an upwelling event. Salinities found in the strait were in the range of 34.8-35.7. The column stratification was mainly a result of temperature. Total metal concentration ranges were 0.02-0.16 nM_{Cd} (4.4% of particulate) and 0.2-0.9 nM_{Pb} (around 45% of particulate) (Fig. 2). Dissolved Cd showed its lowest concentrations when the inlet was ebbing, whereas the opposite was observed for dissolved Pb and Zn. Cd particulate concentrations were higher in the incoming waters near the bed, whereas particulate Pb concentra-

tions were very similar in both water bodies.

In the September 13 campaign (Cruise C6; Fig. 5), hydrographical parameters showed similar trends to the previous cruise. The total metal concentration ranges were 0.02-0.14 nM_{Cd}, 0.6-6.0 nM_{Pb} and 7-44 nM_{Zn} (Fig. 2). The particulate ranges were <28%, 2-92% and 5-34% for Cd, Pb and Zn, respectively. Pb and Cd showed the same behaviour in both the dissolved and particulate phases: their highest concentrations were found when the tide was ebbing.

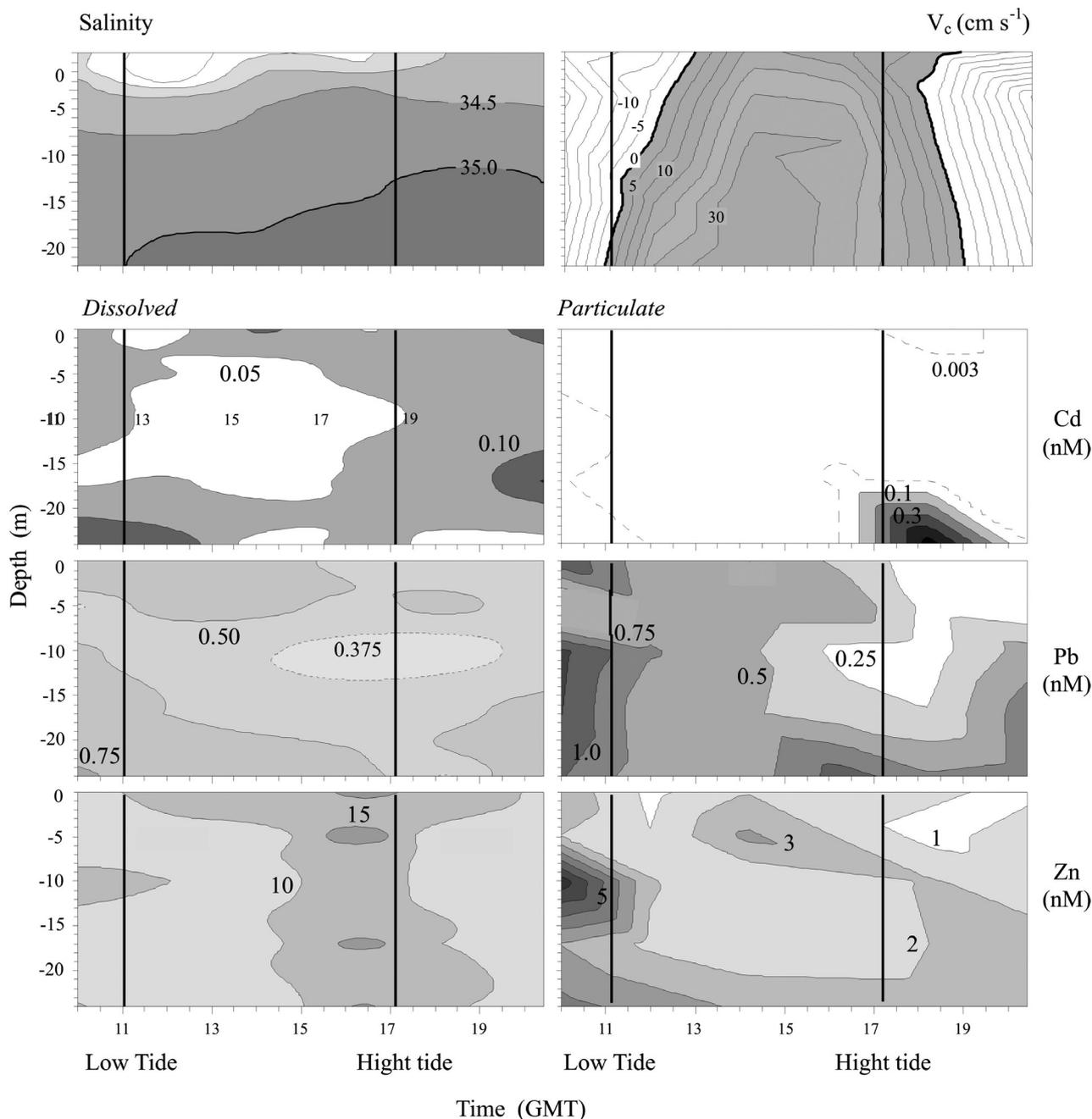


FIG. 4. – Isoline map at the anchored station in the estuary-ria boundary during the C3 spring cruise. Salinity, currents and dissolved and particulate concentrations of Cd, Pb and Zn are shown for spring. The vertical lines represent high and low waters according to the tide table for Vigo harbour.

DISCUSSION

Seasonal concentrations and distributions of trace metals

The dissolved metal concentration ranges (Fig. 2) were 0.01–0.18 nM for Cd, 0.5–1.9 nM for Pb and 4–44 nM for Zn. These levels are of the order of those measured in other near-shore European areas. Dissolved Zn concentrations were similar to the ones observed in

Iberian coastal waters (Braungardt *et al.*, 1998; Cottè-Krief *et al.*, 2000; Elbaz-Poulichet *et al.*, 2001; Cobelo-García *et al.*, 2005) and in other European Atlantic coastal zones (Chiffoleau *et al.*, 1994; Muller *et al.*, 1995; Boutier *et al.*, 2000), whereas the dissolved Cd range was around half. In contrast, Pb concentrations were two times higher in the Rande Strait. This fact was also observed in the industrialized Ria of Ferrol (Cobelo-García *et al.*, 2005) and highlighted in a previous work at the Ria of Vigo–ocean boundary (Prego *et al.*

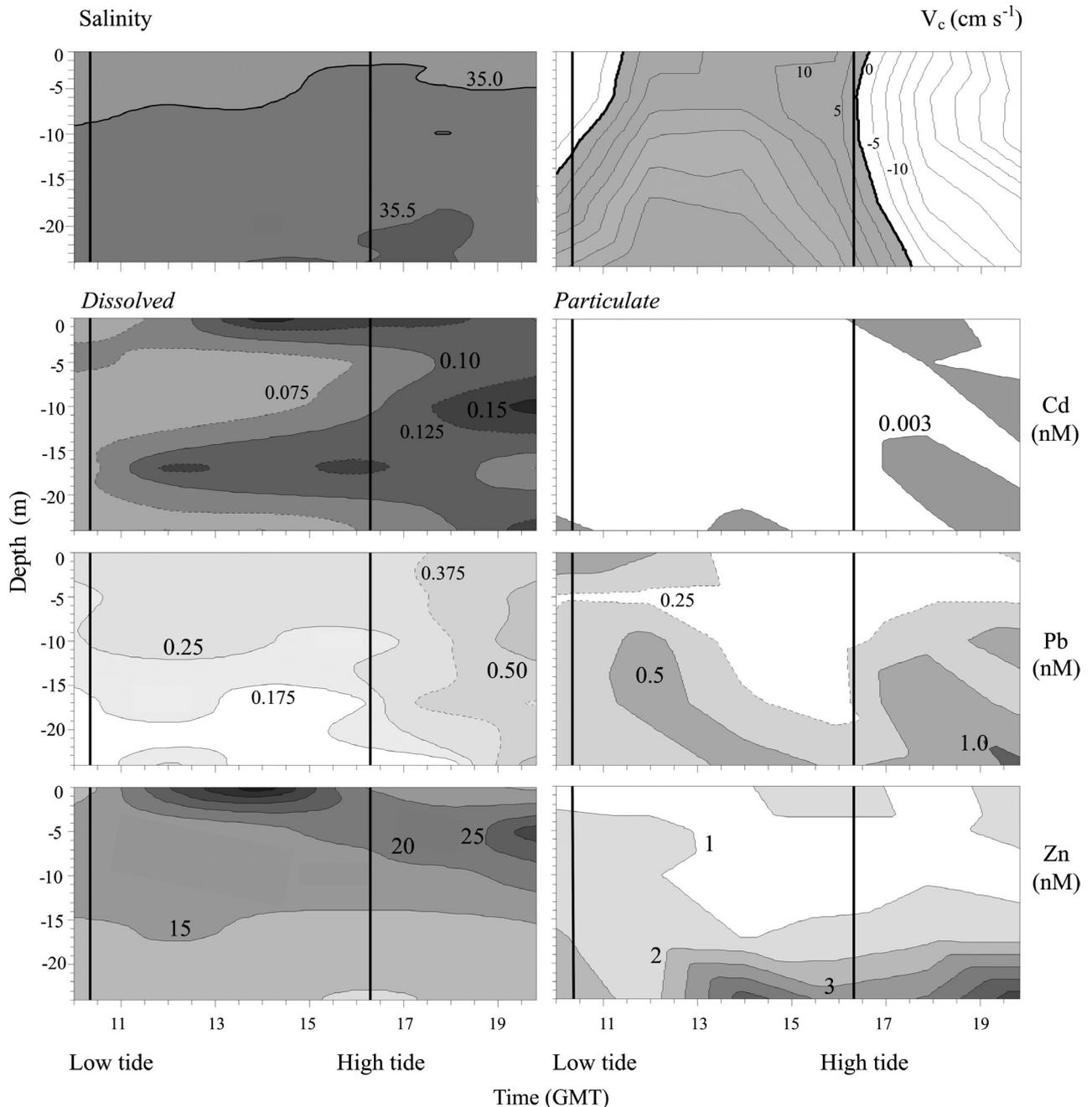


FIG. 5. – Isoline map at the anchored station in the estuary-ria boundary during the C6 summer cruise. Salinity, currents and dissolved and particulate concentrations of Cd, Pb and Zn are shown for summer. The vertical lines represent high and low waters according to the tide table for Vigo harbour.

et al., 2006). The high Pb concentration is suspected to be a consequence of the high Pb contamination in the sediments of the San Simón Inlet. Accordingly, Belzunce *et al.* (1997) and Álvarez-Iglesias *et al.* (2003) showed the local existence of heavy contamination with Pb in the San Simón Inlet.

Particulate metal concentrations in the strait waters are also shown in Figure 2. Cadmium and Pb concentrations are within the values found for NE Atlantic shelf waters, whereas particulate Zn was lower in

the strait but similar to values recorded in the Ria of Ferrol, where the average Pb concentration was three times lower than in the Vigo inner-middle boundary. This significant difference may again be due to the Pb contamination at the San Simón Inlet. This influence was also observed, although to a minor extent, in the middle-outer ria, as Prego *et al.* (2006) suggested.

The relative affinity of trace metals for dissolved and particulate phases can be evaluated from the respective partition coefficient, $K_D = P/D$, where P is the

TABLE 2. – Flow of metals in the dissolved (D) and particulate (P) phase through the Rande Strait for each campaign. Values are expressed in kg·d⁻¹ (two tidal cycles per day). A positive sign denotes incoming flux towards the San Simón Inlet and vice versa.

Cruise	flux	D Cd	P Cd	D Pb	P Pb	D Zn	P Zn
C1 (winter)	Incoming	1.38	0.11	34.8	16.0	299	-
	Outgoing	-1.47	-0.05	-34.9	-32.5	-218	-
C2 (winter)	I	1.83	0.11	42.4	16.6	366	-
	O	-2.77	-0.08	-65.8	-54.6	-445	-
C3 (spring)	I	3.27	0.46	54.7	65.0	442	38
	O	-4.87	-0.13	-64.8	-87.7	-346	-112
C4 (spring)	I	2.68	0.02	23.0	8.9	167	29
	O	-2.37	-0.02	-17.4	-14.7	-101	-20
C5 (summer)	I	2.91	0.04	12.4	11.9	194	-
	O	-2.25	-0.23	-14.6	-11.6	-291	-
C6 (summer)	I	4.59	0.04	26.6	31.6	520	46
	O	-5.95	-0.13	-42.6	-39.7	-602	-40

TABLE 3. – Oitavén River flow, tidal range and dissolved (D) and particulate (P) fluxes of Cd, Pb and Zn in each cruise (in moles per tidal cycle). Negative and positive values correspond to outgoing and incoming flux, respectively, in the San Simon Inlet.

Cruise	Oitavén flow (m ³ ·s ⁻¹)	tide Δh (m)	Cd			Pb			Zn		
			D	P	Total	D	P	Total	D	P	Total
C1 (winter)	63	1.53	-0.4	0.3	-0.1	-0.3	-40.0	-40.3	621	-	-
C2 (winter)	32	2.02	-4.1	0.2	-4.0	-56.0	-92.0	-148.0	-599	-	-
C3 (spring)	26	3.48	-7.1	-0.4	-7.5	-24.0	-55.0	-79.0	741	-567	174
C4 (spring)	5	1.42	1.4	0.02	1.4	13.0	-14.0	-0.5	510	64	548
C5 (summer)	4	1.37	2.9	-0.2	2.7	-5.2	0.9	-4.3	-746	-	-
C6 (summer)	4	2.64	-6.1	-0.4	-6.5	-39.0	-20.0	-59.0	-636	47	-597

metal concentration in SPM, and D is the dissolved phase concentration on a weight/weight basis. In the Rande Strait the sequence for log K_D was Pb (5.29 ± 0.69) > Zn (4.52 ± 0.47) > Cd (3.92 ± 0.92), which is of the order of other similar coastal zones (Chiffoleau *et al.*, 1994; Wen *et al.*, 1999; Gee and Bruland, 2002). If these relationship are stated as percentages of particulate fraction versus total they are $41 \pm 21\%$ for Pb, $16 \pm 12\%$ for Zn and $5.4 \pm 5.0\%$ for Cd, which are analogous to the ones found in previous studies in the ria (Cobelo-García *et al.*, 2005; Prego *et al.*, 2006).

The highest concentrations of dissolved and particulate trace metals were found in winter (cruises C1 and C2, Fig. 2), except for dissolved Cd, which was slightly higher in the other seasons. This may be a consequence of sediment resuspension during the wet period when the continental run-off is significant in the ria (Filgueiras and Prego, 2007). On the other hand, the lowest particulate metal levels occurred when the primary productivity was the highest ($20 \text{ mgC m}^{-3} \text{ h}^{-1}$, Varela, pers. com.), and therefore could be diluted by phytoplankton blooms.

Estuary-ria exchange of trace metals

On average, a net output from the estuarine zone was observed for total Cd and Pb (Table 3), although during neap tides their dissolved budgets had the opposite direction. Particulate Pb output was two times higher than dissolved Pb output, as a result of the strong particle reactivity of this element (Cobelo-García *et al.*, 2005) and its greater association with the residual fractions of the San Simon and ria sediments (Belzunce *et*

al., 1997; 2008), which prevents the remobilization of the dissolved phase of the water column. Zinc showed no clear pattern and this element was imported or exported from the estuary independently of river or tidal flows. The irregular intervals of industrial and shipyard activities—which are the main Zn source—during the year may account for this variability. On the other hand, current speed seemed to be a more relevant factor than metal concentration in Cd, Pb and Zn fluxes through the Rande Strait (Fig. 3). This can be exemplified with the Pb fluxes (Table 3). Due to its innermost source of contamination, the highest fluxes of Pb occurred during spring tides and the wet season. This result was also observed by Michel *et al.* (2000) in the dissolved fluxes of Cd and Zn in the Gironde Estuary, France, where the fluxes of these elements were mainly dependent on river flow and winter floods.

The estuary-ria net exchange of these three metals did not appear to be driven by seasonal changes, according to the mixed budget results indicated in Table 3. On the other hand, tidal range could be responsible for the net exchange. When the tidal range increased, the dissolved Cd and Pb exportation, i.e. negative budget, was also intensified to reach a value at which it became practically invariable, according to the following equations obtained from the tidal ranges and metal concentrations of Table 3:

$$\begin{aligned}
 [B]_{DCd} &= 3.13 \text{ h}^2 - 19.4 \text{ h} + 23 & (r = 0.989) \\
 [B]_{DPb} &= 12.7 \text{ h}^2 - 93.6 \text{ h} + 94 & (r = 0.926)
 \end{aligned}$$

where $[B]_{DCd}$ and $[B]_{DPb}$ are the budget of dissolved Cd and Pb, respectively, in mol per tidal cycle and h is

TABLE 4. – Budget (kg·day⁻¹) of dissolved (D) and particulate (P) metals in some European estuaries. A positive value denotes a net import into the estuary and negative exportation from the estuary.

Estuary (Country)	D Cd	P Cd	D Pb	P Pb	D Zn	P Zn	Reference
Ria of Vigo (Spain)	-0.50	+0.02	-7.7	-15.1	-2.5	-19.7	This study
Seine estuary (France)	-10.1	-	-9.3	-	-384	-	Chiffolleau <i>et al.</i> , 1999
Tagus estuary (Portugal)	-22.3	-	-	-	-695	-	Cottè-Krief <i>et al.</i> , 2000
Gironde estuary (France)	-16.3	-	-	-	-140	-	Michel <i>et al.</i> , 2000

the tidal range expressed in metres (1.4<h<3.5). In the exportation pulses during tidal cycles the fluxing of dissolved metals across the sediment-water interface from intertidal flats (one third of the San Simón Inlet surface) can play a key role, as has been observed for nutrients (Falcão and Vale, 1995; Cabrita *et al.*, 1999) and some metals (Caetano *et al.*, 2007) in estuaries. On the other hand, the particulate Cd budget was low (10–20 times lower than the dissolved Cd budget) and was not important in the exchange. Particulate Pb was significant in the net export from the estuary. In this case it was not conducted by tide but by river flow. In the San Simón Inlet, contaminated lead sediments are close to the Oitavén River mouth (Belzunce-Segarra *et al.*, 1997; Álvarez-Iglesias *et al.*, 2003), so they are mainly transported during the wet season according to the equation:

$$[B]_{ppb} = 0.0612 Q^2 - 4.6 Q + 9 \quad (r = 0.937)$$

where $[B]_{ppb}$ is the budget of particulate Pb in mol per tidal cycle and Q is the Oitavén River flow in m³ s⁻¹ (Table 3). Lastly, Zn did not show a defined trend, probably due to the diffusion of Zn along the whole southern ria shoreline—i.e. from the San Simón Inlet to the city of Vigo—due to harbour and shipyard activities which, are the main Zn sources (Prego *et al.*, 2008b).

The budgets obtained for the Ria of Vigo are one or two orders of magnitude lower than the ones measured in other large European estuaries (Table 4), with the exception of Pb, which is similar. The Pb contribution from the San Simon Inlet, both in dissolved and particulate phases, should be considered in the assessment of the land-based mass flow of trace elements to the European continental margin.

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