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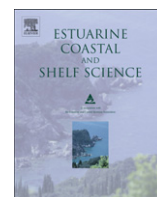
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Spatial and temporal distribution of cadmium and copper in water and zooplankton in the Bahía Blanca estuary, Argentina

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ABSTRACT

Cadmium and copper in the dissolved and particulate phase and in zooplankton were determined in the Bahía Blanca estuary during six surveys from March to December 2005. Temperature, pH, salinity, dissolved oxygen, suspended particulate matter, particulate organic matter and chlorophyll-*a* were also considered. Dissolved Cd was below the detection limit ($0.2 \mu\text{g L}^{-1}$) for almost the entire study period whereas Cu concentrations ($0.5\text{--}2.4 \mu\text{g L}^{-1}$) indicated a continuous dissolved Cu input. Particulate Cd concentrations ranged from below the detection limit (<0.01) to $28.6 \mu\text{g g}^{-1}$ d.w. while particulate Cu ranged from below the detection limit (<0.04) to $53.5 \mu\text{g g}^{-1}$ d.w. Cd in mesozooplankton ranged from below the detection limit (<0.01) to $37.4 \mu\text{g g}^{-1}$ d.w. Some of the Cd levels were higher than those reported for other aquatic ecosystems. Cu in the mesozooplankton ranged from 1.3 to $89.3 \mu\text{g g}^{-1}$ d.w., values which were within the reported values or higher than other studies. The log of the partition coefficients ($\log(K_d)$) of Cd was 0.04 , while $\log(K_d)$ for Cu ranged from -0.39 to 2.79 . These values were lower than both those calculated for other estuaries and the typical coefficients for marine environments. The log of the bioconcentration factor ($\log(\text{BCF})$) of Cd was 1.78 , indicating that Cd concentration was higher in the zooplankton than in the dissolved phase. $\log(\text{BCF})$ of Cu ranged from 1.15 to 3 . The logs of the biomagnification factors ($\log(\text{BMF})$) of Cd were low, with a range between -3.45 and 2.21 and those for Cu ranged from -0.1 to 3.35 . Positive values indicate biomagnification while negative values indicate biodiminution. In general, no significant dissolved Cd concentration appeared to be present in the Bahía Blanca estuary and Cu values did not indicate a critical environmental status. The particulate phase seemed to be the major carrier for Cd and Cu and TPCu values were within the normal values for an anthropogenically stressed estuary but not for a strongly polluted system. This fraction was the most important metal source for the mesozooplankton. Moreover, the highest metal concentrations were in the mesozooplankton since most of the bioconcentration and biomagnification factors were positive, especially for Cu.

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1. Introduction

Estuaries are unique ecosystems with dynamic and complex processes of ecological and economic importance (Kennish, 1991). They are amongst the most productive environments due to the presence of high phytoplankton and zooplankton biomass which are key components in aquatic food webs (Omori and Ikeda, 1984).

These coastal areas are affected by human activities mainly due to the presence of industries, harbours, and cities. Trace metals, polycyclic aromatic hydrocarbons, pesticides and radioactive materials are persistent contaminants which are introduced into

the estuaries through river runoff, atmospheric deposition, hydrothermal venting, diagenetic remobilisation, agricultural activities, and industrial and urban waste-waters discharges (Salomons and Förstner, 1984; Libes, 1992; Gavril and Angelidis, 2005).

In aquatic ecosystems, plankton and suspended particulate matter have an affinity for most of the trace metals (Balls, 1989; Sanders and Riedle, 1998). Thus, these fractions play important roles in the biogeochemical cycle of the metals (Fowler and Knauer, 1986). Suspended particulates are instrumental in controlling the reactivity, transport and biological impacts of substances in aquatic environments, and provide a crucial link for chemical constituents between the water column, bed sediments and food chain (Turner and Millward, 2002). Particulate metals eventually settle to the bottom and may be available to benthic organisms or may be released to the water column through resuspension, adsorption/

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desorption, reduction/oxidation reactions or degradation of organisms. In plankton, metals may be adsorbed onto the cell surface or by crossing the cell walls. The adsorption of metals by plankton is very variable and in general this fraction, presents high surface/volume ratio. Thus, plankton has high concentrations factors, especially for non-reactive particles. Once incorporated into this fraction, metals may be transferred along the food chain and transformed by the organisms, enhancing or alleviating their toxicity (Fisher and Reinfelder, 1995; Monterroso et al., 2003).

On the other hand, to assess the environmental quality of heavy metals, the bioavailable fraction is relevant and is only accessible by determining the concentration of metals within the organisms (Rainbow, 1993; Zauke et al., 1996). In addition, organisms can be used as biomonitors due to both the potential role as indicators of the minimal lethal concentration of metals and also their ability to accumulate such metals (Kahle and Zauke, 2003; Fang et al., 2006). Analysis of metals in plankton organisms is an additional tool for research on metal biogeochemistry in marine ecosystems (Schulz-Baldes, 1992).

Although there are many papers on trace metals concentrations in water and zooplankton, few studies analyse these fractions together (i.e. Fang et al., 2006; Nguyen et al., 2005). In Argentina, there are few studies on metals levels in zooplankton (Scarlato et al., 1993, 1997). With respect to the Bahía Blanca estuary no previous works analyse the metal content in both the zooplankton and the dissolved and particulate phase. The principal aim of the present work is therefore to describe the concentration of cadmium and copper in water (dissolved and particulate) and in the meso-zooplankton ($>200\ \mu\text{m}$ – $<500\ \mu\text{m}$) in the Bahía Blanca estuary, one of the most important estuaries of Argentina.

2. Study area

The Bahía Blanca estuary is a mesotidal coastal plain located between $38^{\circ}45'–39^{\circ}40'S$ and $61^{\circ}45'–62^{\circ}30'W$, on the south-eastern coast of Buenos Aires province in Argentina (Fig. 1). This estuary is elongate with a total length of 80 km characterised by channels, islands and wide tidal flats (Perillo and Piccolo, 1991). It is a highly turbid estuary with fine sand and silt-clay sediments as a result of the combined effects of winds, mainly from the north and northwest, tide currents and river discharges which maintain large amounts of suspended matter (Perillo and Piccolo, 1999). The principal energy input is produced by a quasi-stationary, semi-diurnal tidal wave. The mean tidal amplitude varies between 3.5 and 2.2 m at the head and mouth of the estuary, respectively. The water surface area at low tide is $400\ \text{km}^2$, while at high tide this area rises to nearly $1300\ \text{km}^2$. Several streams and channels flow into the estuary, most of them affected by anthropogenic activities. Two freshwater tributaries enter the estuary from the northern shore. The Sauce Chico River discharges about 3 km downstream from the head and the Napostá Grande Creek reaches the estuary about 1 km downstream of Ing. White Port. The mean annual freshwater contribution of these tributaries is $1.5–1.9\ \text{m}^3\ \text{s}^{-1}$ and $0.5–0.9\ \text{m}^3\ \text{s}^{-1}$, respectively. Based on the salinity and temperature distribution, the estuary is divided in two zones. The inner one, from the mouth of the Sauce Chico River to Ing. White, is classified as a partially mixed estuary during normal runoff conditions, but with a strong tendency to become vertically and even sectionally homogeneous during low runoff. The outer reach (from Ing. White Port to the mouth of the estuary) is sectionally homogeneous (Piccolo et al., 2008).

The Bahía Blanca estuary includes harbours, industries and towns (350,000 inhabitants) that are located to the North. Oil refineries and terminal, petrochemical industries, fish factories and leather, textile plants and wool washing plants, silos and cereal mills discharge their processing residues into the streams or

directly into the estuary. Also, it is extensively used by fishing boats, oil tankers and cargo vessels and requires regular dredging. Thus, this coastal marine ecosystem receives inputs from urban waste-waters, direct industrial discharges, harbour related operations and runoff water that carry material from land development areas and aerial fallout from atmospheric pollutants (Botté et al., 2007).

In the present study, two sampling stations (Cuatrerros Port and Ing. White Port) were considered. The first is least affected by the human activities, while the latter is close to the industrial area and waste-waters discharges (Fig. 1).

3. Materials and methods

Sampling was carried out every 2 months between March and December 2005. Zooplankton samples consisted on two replicates of approximately 750 ml at each sampling station. They were collected from a boat, during ebb and using a Nansen net (200 μm and 30 cm diameter). The tows were oblique (0.5–1 m depth) and at a constant speed (2 knots) for 5 min. Besides, the physico-chemical variables: T° , pH, conductivity and dissolved oxygen were recorded in each sampling station at 1 m depth with a multisensor HORIBA U-10. Salinity was calculated from conductivity and expressed as practical salinity units. Water samples were collected for the determination of chlorophyll-*a*, and particulate organic matter (POM) in the laboratory.

Surface water samples for dissolved and particulate metal determination, were collected manually at $<1\ \text{m}$ depth with 1.5 L polyethylene-terefthalate (PET) bottles. At each sampling station there were considered two subsamples of 750 ml, obtained from the homogenisation of the bottle and dividing the volume (1.5 L) into two equal parts. The samples were immediately transported to the laboratory and filtered through acid treated Millipore HA filters (0.45 μm) with vacuum for the determinations of particulate and dissolved metals. The filtered water was acidified at pH 2, using 1.5 ml HCl analytical quality. These samples were stored in darkness at 4°C up to the analytical treatment. Prior to use, all the sampling and laboratory materials were carefully cleaned with 0.7% HNO_3 , following internationally recommended protocols (APHA, 1998).

The dissolved metals were extracted from the filtered water by chelation with ammonium pyrrolidine-dithiocarbamate (APDC) followed by methyl isobutyl ketone (MIBK) extraction, according to the method described by Koirtyohann and Wen (1973) and updated by El-Moselhy and Gabal (2004). After metal extraction, the residual water samples were combined to provide a homogenous matrix for the preparation of blanks and standards. The corresponding standards were prepared by adding increasing amounts of Cd and Cu to the matrix.

Zooplankton samples for the metal determination were pre-filtered using 1.5 mm and 500 μm mesh size nets in order to analyse only the mesozooplankton. Then the samples were vacuum-filtered following the same procedure as the suspended particulate matter. In both cases, the filters with the retained material (SPM or zooplankton) were dried at $50 \pm 5^{\circ}\text{C}$ to constant weight, weighed in analytical balance and stored in a desiccator until their analytical treatment. Subsequently, the filters were subjected to acid digestion; following the methodology of Marco-vecchio and Ferrer (2005). The material was digested with a mixture of 3 ml of HNO_3 and 1 ml of concentrated HClO_4 and the mineralisation of the samples was performed in a bath of glycerin at $110 \pm 10^{\circ}\text{C}$ to obtain a sample of about 1 ml. Each if these extracts was transferred to a graduated tube and completed with diluted nitric acid 0.7% to a volume of 10 ml.

Metal concentrations were determined with a Perkin–Elmer AA-2380 atomic absorption spectrophotometer with an air/acetylene flame. The method detection limits (MDL) for each metal are

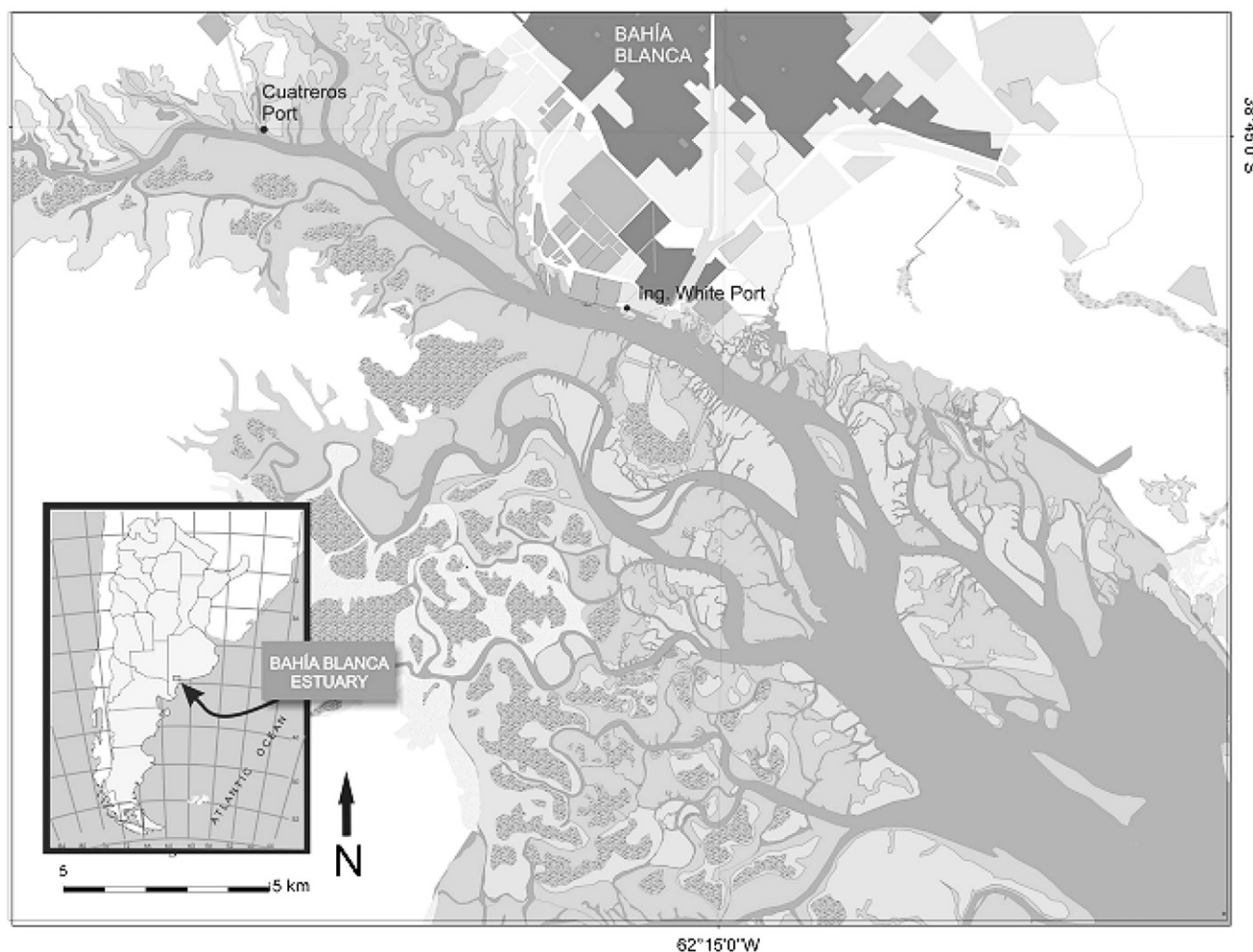


Fig. 1. Study area and sampling stations.

Cd: 0.18; Cu: 0.44 $\mu\text{g L}^{-1}$ for dissolved and Cd: 0.01; Cu: 0.04 $\mu\text{g ml}^{-1}$ for particulate-zooplankton. Analytical grade reagents were used to make up the relevant blanks and calibration curves, and the analytical quality (AQ) was tested against reference materials (Table 1) provided by The National Institute for Environmental Studies (NIES), from Tsukuba (Japan) as well as from the United Nations Environment Programme (UNEP).

Non-parametric statistical procedures were used since the results of the present study did not meet the assumptions of normality and equality of variance. The Mann–Whitney *U*-test was employed to detect statistical differences of the mean values between the sampling stations and the Kruskal–Wallis test find differences among the mean values at each sampling station. Also, the Spearman correlation coefficient was employed to establish relationships between the metal concentrations and the physicochemical variables. For these analyses there were used data corresponding to replicates (mesozooplankton samples) and pseudoreplicates (water samples). On the other hand, in those cases

where 40% or more of the metals values were below the detection limit, no statistical analyses were performed according to Federal Register (1984).

4. Results and discussion

4.1. Physicochemical variables

Temperature in the subsurface layer (0–1 m), ranged between 7.6 °C (in July) and 22.2 °C (in December) and was similar in both stations (Fig. 2). The pH values were homogeneous and varied from 8 to 9.2 while salinity ranged between 29.5 in July (winter) and 35.5 in November (spring) (Fig. 2). Dissolved oxygen concentrations showed a similar distribution pattern between the sampling stations, but with significant differences during the period of study (Fig. 2). The lowest values (5.8 mg L^{-1}) were recorded in December (late spring) while the highest (10.5 and 11.7 mg L^{-1}) were in July (winter) (Fig. 2). The latter is due to both the higher solubility oxygen at low temperatures, and the phytoplankton bloom that develops in the estuary, thereby increasing oxygen concentrations by photosynthesis (Freije and Gayoso, 1988). Suspended particulate matter concentrations ranged between 24.75 and 186.23 mg L^{-1} and these values are typical of this environment, which is characterised by high turbidity, as a result of resuspension of fine sediments (silt-clay) generated by tidal currents, by prevailing winds

Table 1

Percentages of recovery in the analysis of reference materials (NIES and UNEP) to assess analytical quality (ranges).

Metal analyzed	Estuarine water (%)	Seawater (%)	Organisms (%)
Cadmium	91.1–95.3	93.1–95.7	92.4–98.7
Copper	92.9–96.5	92.2–97.5	93.1–97.9

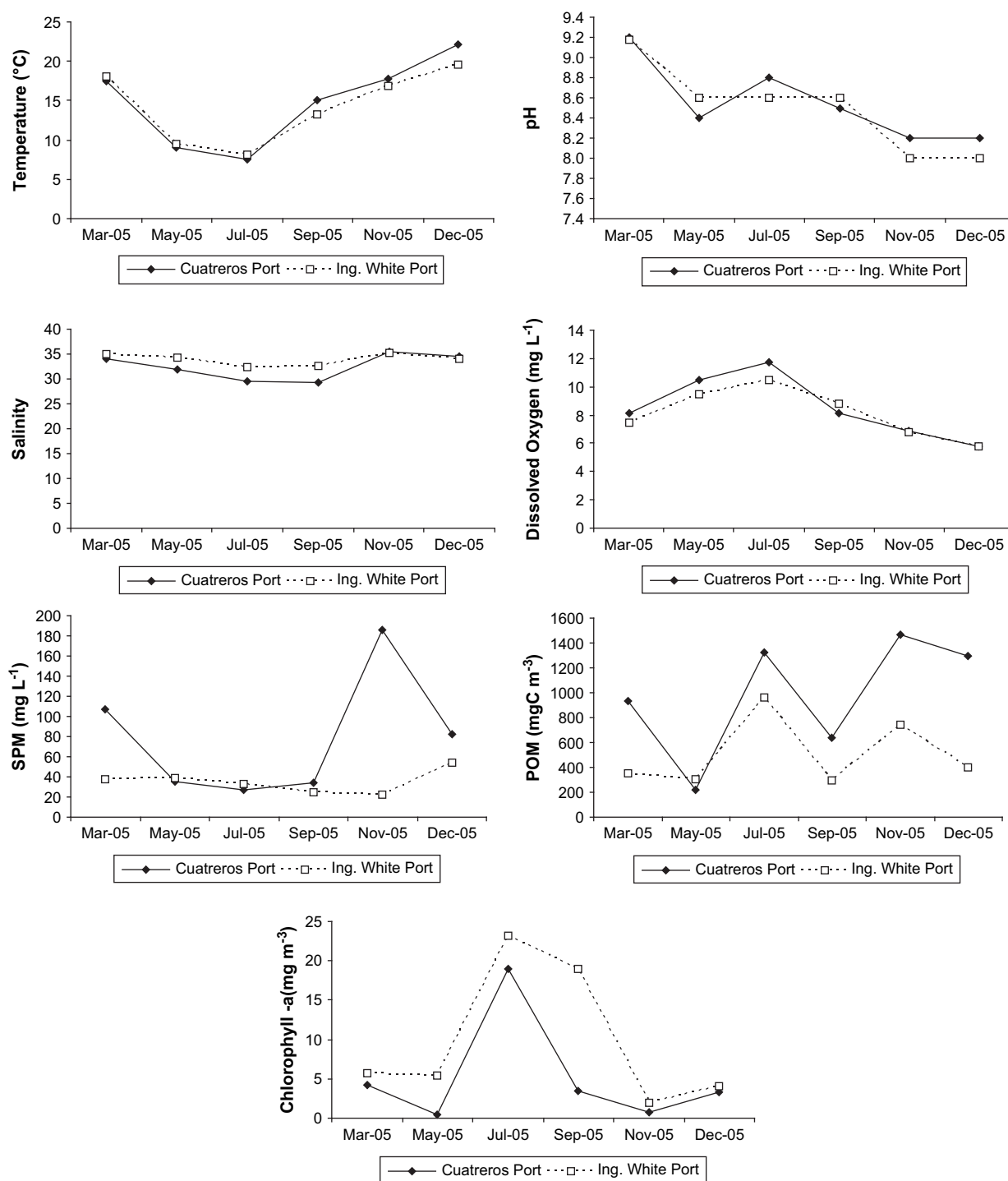


Fig. 2. Temporal distribution of the physicochemical variables in the Bahía Blanca estuary. POM: particulate organic matter. SPM: suspended particulate matter.

from the north and northwest and to a lesser measure the contribution of the flow of fresh water (Piccolo and Perillo, 1990). In addition, the Principal Navigation Channel of the estuary is regularly dredged, increasing the resuspension of particulate matter (Marcovecchio and Freije, 2004). On the other hand, no significant statistical differences were detected in the mean values of the above mentioned variables between the sampling stations ($p > 0.25$, $N = 12$).

The higher concentrations of particulate organic matter (MOP) were at Cuatrerros Port and significant statistical differences were

detected between the sampling stations ($p = 0.03$, $N = 12$) (Fig. 2). The highest values were recorded in July (1325 mg C m^{-3}) mainly due to the phytoplankton bloom and in November–December ($1462\text{--}1297 \text{ mg C m}^{-3}$) probably due to urban effluents and rivers discharges. Mean chlorophyll-*a* concentrations were also statistically different between both stations ($p = 0.02$, $N = 12$) and showed a definite trend throughout the study period (Fig. 2). The higher values ($18.9\text{--}23.2 \text{ mg m}^{-3}$) were recorded in July due to the phytoplankton bloom while in the rest of the study period, the values were much lower ($0.5\text{--}1.9 \text{ mg m}^{-3}$). All these

physicochemical variables are within the levels described as normal for this type of estuary (Marcovecchio and Freije, 2004), and coincided with historical data available for this environment (Pucci et al., 1980; Marcovecchio and Freije, 2004).

4.2. Total dissolved (TD) Cd and Cu

Fig. 3a describes the mean TDCd concentrations at both stations. Almost all the values were below the detection limit and were relatively stable during the sampling period. The only exception was the concentration in December (late spring) at Ing. White Port ($0.3 \mu\text{g L}^{-1}$). Since most of the values were non-detectable, no statistical analysis were performed, however, it is evident that there is no differences between the sampling stations. Moreover, there is no difference at each study site regarding dissolved Cd. These concentrations could indicate the absence of Cd-related land-based pollution sources (industries, urban waste-waters) during the months when particulate Cd levels were also low. On the other hand, in March–May (autumn) and November (spring) dissolved Cd inputs could be rapidly adsorbed onto SPM since in these months high TPCd were recorded at both stations (Fig. 3a). Due to the nature of the concentrations above described, no correlations were established between TDCd and the physicochemical variables.

The concentrations are lower than those previously reported in the estuary by Andrade et al. (1996a) during spring 1995–autumn 1996 (Table 2). Also, Andrade et al. (2000) registered higher concentrations during spring 1997–1999, reaching in autumn maxima values of 4.1 and $3 \mu\text{g L}^{-1}$ at Ing. White Port and Cuatros Port, respectively. However, during the rest of the period, these authors reported TDCd values that varied from undetectable levels ($0.05 \mu\text{g L}^{-1}$) to $1 \mu\text{g L}^{-1}$ at both sampling stations. In accordance with the present study, Ferrer et al. (2000) registered $0.18 \mu\text{g L}^{-1}$ at Cuatros Port, between autumn 1997 and winter 1998. Also at this station, Andrade (2001) during winter 1998–spring 1999, reported similar concentrations; Botté (2005) registered low concentrations during spring 2000–2002, with peak values ($1.50 \mu\text{g L}^{-1}$) in winter

2000 and Botté et al. (2007) reported a mean value of $0.4 \mu\text{g L}^{-1}$. It is important to mention that the methodology used in these works is the same as the employed in the present paper. The TDCd concentrations of the present study are within the lowest values recorded in the Bahía Blanca estuary.

Concentrations from the present study are similar to or lower than other anthropogenically-affected estuaries of the world like the Rosetta estuary, Egypt (0.37 – $0.97 \mu\text{g L}^{-1}$) (Saad and Hassan, 2002), the Río Tinto–Ría Huelva, Spain ($45 \mu\text{g L}^{-1}$) (Achterberg et al., 2003), the Toulon Bay, France ($0.14 \mu\text{g L}^{-1}$) (Rossi and Jamet, 2008) and the Ría de Huelva estuary in Spain (0.64 – $2.18 \mu\text{g L}^{-1}$) (Vicente-Martorell et al., 2009), among others.

TDCu mean values in both sampling stations were similar and no statistical differences were detected between them ($p = 0.82$). Cuatros Port, the site away from the industrial area, had a range of 0.5 – $2.4 \mu\text{g L}^{-1}$, with some fluctuations during the sampling period (Fig. 3b). Maximum values occurred in May (autumn)–November (late spring), with lower concentrations in March (early autumn). However during the study period, there were no significant differences between the concentrations of cadmium at this station ($p = 0.22$). A negative correlation ($r = -0.75$, $p = 0.005$, $N = 12$) was detected between dissolved Cu and pH. This behaviour is commonly observed. A small pH decrease can favour an increase of metal in the dissolved phase (Salomons and Förstner, 1984).

On the other hand, the nearest station to the industrial zone, cereal harbours and urban waste-waters, Ing. White Port, showed a range from 0.6 to $2 \mu\text{g L}^{-1}$, with increased concentrations from March (early autumn) to December (late spring) (Fig. 3b). These values differ statistically during the sampling period ($p = 0.009$). TDCu concentrations in autumn differ from those of spring ($p = 0.009$) and winter ($p = 0.06$); TDCu values in spring also differ from winter ($p = 0.06$). In this site, it was also detected a significant negative correlation ($r = -0.93$, $p = 0.0005$, $N = 12$) between dissolved Cu and pH, indicating the influence of this parameter on the dissolved Cu concentrations.

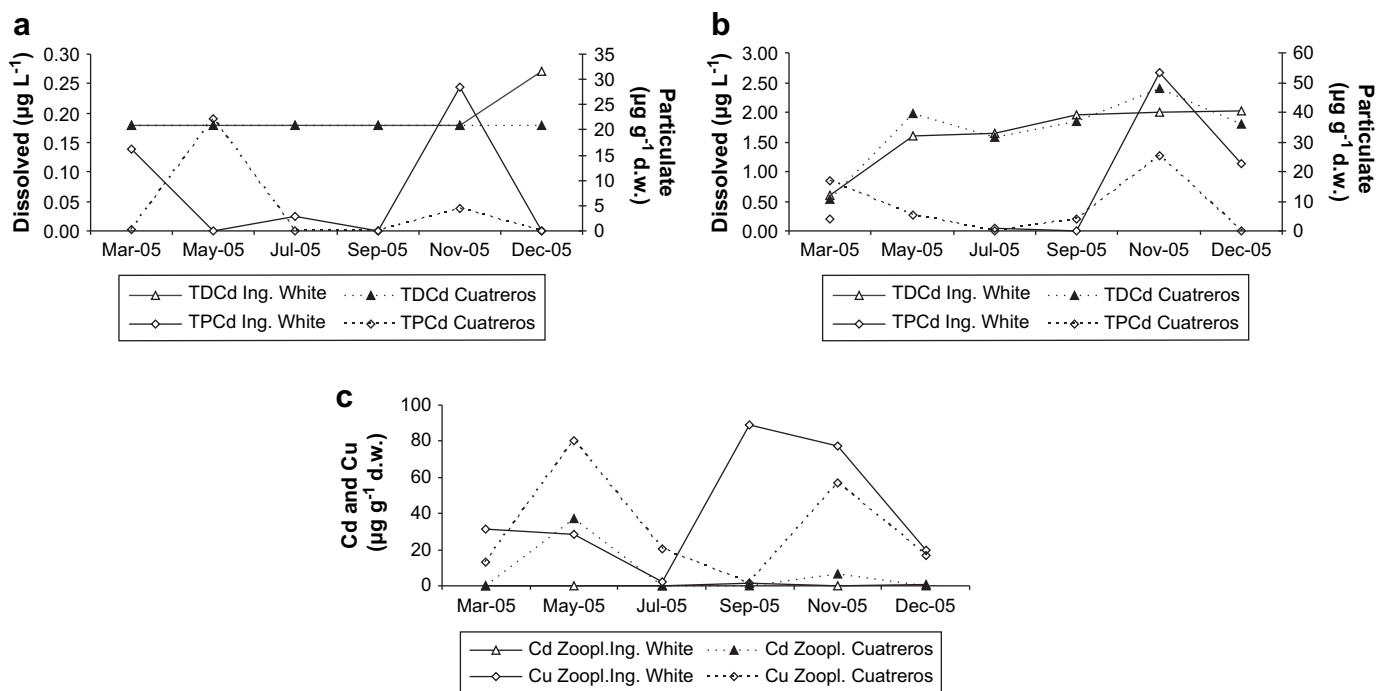


Fig. 3. Cd and Cu concentrations in dissolved ($\mu\text{g L}^{-1}$) and particulate ($\mu\text{g g}^{-1}$ d.w.) phases and zooplankton ($\mu\text{g g}^{-1}$ d.w.) at the sampling stations (Cuatros Port and Ing. White Port).

Table 2Trace metals dissolved and particulate concentrations in the Bahía Blanca estuary. *: general mean; \pm : standard error; su: summer; a: autumn; w: winter; s: spring.

	Dissolved (µg L ⁻¹)				Particulate (µg g ⁻¹ d.w.)				References
	Cd		Cu		Cd		Cu		
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Ing. White Port	n.d.–0.3	0.2 ± 0.01*	0.61–2	1.6 ± 0.14*	n.d.–42.43	7.9 ± 3.7*	<0.04–53.52	16.2 ± 6.9*	Present study
		0.2 (a)	–	1.1 ± 0.3 (a)	–	8.1 ± 4.8 (a)	–	4 ± 0.02 (a)	
		0.2 (w)	–	1.7 (w)	–	2.9 ± 0.8 (w)	–	0.8 ± 0.07 (w)	
		0.2 ± 0.01 (s)	–	2 ± 0.01(s)	–	9.5 ± 7 (s)	–	25.3 ± 10.1 (s)	
	–	0.5 (s-a)	–	5	–	–	–	–	
	<0.05–4	–	–	–	–	–	–	–	
Cuatreros Port	n.d.	<0.2*	0.5–2.4	1.7 ± 0.2*	n.d.–23.85	4.5 ± 2.5*	<0.04–25.5	8.6 ± 3.1*	Present study
	–	0.2 (a)	–	1.3 ± 0.4 (a)	–	11.2 ± 6.4 (a)	–	11.1 ± 3.4 (a)	
	–	0.2 (w)	–	1.6 (w)	–	0.01 (w)	–	0.04 (w)	
	–	0.2 (s)	–	2 ± 0.12 (s)	–	1.5 ± 1.06 (s)	–	9.8 ± 5.6 (s)	
	–	1	3.4–5.8	5.8	–	–	–	–	
	<0.05–3	–	–	–	–	–	–	–	
	–	0.2 ± 0.11	–	–	–	–	–	–	
	0.1–0.3	0.1 (su)	0.5–5.5	5.4 (su)	<0.2–8	3.9 (su)	12–60	31.2 (su)	
	–	0.2 (a)	–	4 (a)	–	5.3 (a)	–	30.1 (a)	
	–	0.2 (w)	–	3.5 (w)	–	2.01 (w)	–	34.1(w)	
	–	0.1 (s)	–	3(s)	–	4.4 (s)	–	31.7 (s)	
	0.2–1.5	0.2 (su)	1.2–11.5	1.9 (su)	0.9–4.9	2.2 (su)	13.3–31	21.8 (su)	
	–	0.2 (a)	–	3.9 (a)	–	3.7 (a)	–	27.5 (a)	
	–	0.2 (w)	–	3.2 (w)	–	2.8 (w)	–	19.2 (w)	
	–	0.2 (s)	–	2.7 (s)	–	1.3 (s)	–	26.4 (s)	
	–	0.4 ± 0.3	–	–	–	–	–	–	

The results indicate a continuous dissolved Cu input, however they are lower than previous studies carried out in this estuary. Andrade et al. (1996b) during spring 1995–winter 1996 and Andrade (2001) during winter 1998–spring 1999 registered higher concentrations in both stations. In addition, Botté (2005) also found higher values than this study (Table 2).

In accordance with TDCd, TDCu values of the present study are within the lowest recorded values in the Bahía Blanca estuary. Much of the dissolved Cu in estuaries is present in a complexed form (Van der Berg et al., 1987) which is less harmful for marine organisms than ionic Cu (Sunda and Guillard, 1976). Previous studies in the Bahía Blanca estuary have demonstrated that this metal is mainly complexed with hydroxides associated with organic compounds (Andrade et al., 2000).

On the other hand, the concentrations presented here are similar to or lower than those obtained in other estuaries of the world with some anthropogenic influence. In the Rosetta estuary (Egypt), Saad and Hassan (2002) reported a range of 5.1 and $26 \mu\text{g L}^{-1}$, while in the Loire estuary (France) Waeles et al. (2004) reported values from 0.5 to $1.34 \mu\text{g L}^{-1}$ and in the Penzé estuary (France), Waeles et al. (2005a) registered a range of 0.11 and $0.60 \mu\text{g L}^{-1}$. In the Toulon Bay (France), Rossi and Jamet (2008) reported a range of 0.62 and $2.82 \mu\text{g L}^{-1}$ and in the Ría de Huelva estuary (Spain), Vicente-Martorell et al. (2009) determined a range of 11 and $23.11 \mu\text{g L}^{-1}$.

4.3. Total particulate (TP) Cd and Cu

Mean concentrations of particulate Cd in the two sampling stations had similar ranges and the mean values between the stations did not differ statistically ($p = 0.75$). At Cuatreros Port (Fig. 3a), TPCd ranged between not detected and $22.3 \mu\text{g g}^{-1}$ d.w., while Ing. White Port ranged between not detected (n.d.) and $28.6 \mu\text{g g}^{-1}$ d.w. (Fig. 3a). Regarding temporal distribution, at Cuatreros Port, higher TPCd values were recorded in May (autumn) and November (spring), while at Ing. White Port peak concentrations occurred in March (early autumn) and November (spring).

However no statistical differences were detected among TPCd concentrations, at each sampling stations (Cuatreros Port: $p = 0.07$; White Port: $p = 0.85$).

In general, phytoplankton blooms play an important role in the enrichment of the particulate fraction with cadmium through biological absorption of the dissolved phase (Balls, 1990; Waeles et al., 2005b). However, in the present study, the July phytoplankton bloom did not appear to affect the Cd concentration in both the particulate and dissolved phase at none of the stations. Moreover, no significant correlation was detected between TPCd and chlorophyll-*a* (Ing. White Port: $r = -0.17$, $p = 0.60$, $N = 12$; Cuatreros Port: $r = 0.51$, $p = 0.08$, $N = 12$), TPCd and SPM (Ing. White Port: $r = -0.52$, $p = 0.07$, $N = 12$; Cuatreros Port: $r = 0.51$, $p = 0.08$, $N = 12$).

On the other hand, the high concentrations of TPCd and Cu recorded in Cuatreros Port in November could be related to metal adsorption upon particles, favoured at this time of the year by the rise in SPM concentration. Also, in this station, it was detected a significant positive correlation between TPCd and Cd in the mesozooplankton ($r = 0.90$, $p = 0.0001$, $N = 12$). This relationship indicates that at Cuatreros Port, the SPM influences on the Cd levels in the mesozooplankton since part of the zooplankton diet is based on this fraction. However, at Ing. White Port no significant correlation was detected between these variables ($r = 0.53$, $p = 0.11$, $N = 12$).

In general, Cd concentrations were similar to those recorded in the Bahía Blanca estuary by Andrade (2001) and Botté (2005) but the maximum values recorded in autumn and spring were higher than those of previous studies carried out in these seasons (Table 2). Moreover, they are among the highest values recorded in the estuary.

The concentrations of TPCd are higher than in other estuarine ecosystems like the Río Tinto–Ría Huelva, where Achterberg et al. (2003) registered a range of 0.8 and $10 \mu\text{g g}^{-1}$ d.w. In the Penzé estuary TPCd ranged between 0.4 and $2.4 \mu\text{g g}^{-1}$ d.w. (Waeles et al., 2005b) and in the Vigo Ria, Prego et al. (2006) reported a mean value of $0.24 \mu\text{g g}^{-1}$ d.w. Recently in the Ría de Huelva estuary

Vicente-Martorell et al. (2009) reported a range of 0.35 and 1.91 $\mu\text{g g}^{-1}$ d.w.

The mean values of TPCu are plotted in Fig. 3b. Cuatreros Port had a range of 0.04 (below the detection limit) to 25.5 $\mu\text{g g}^{-1}$ d.w., while Ing. White Port showed a range of 0.04–53.5 $\mu\text{g g}^{-1}$ d.w. Both study sites had similar temporal distributions, with a peak concentration in March (early autumn) and another in November (spring) and as in the case of TPCd, the mean concentrations of TPCu did not differ statistically between these sampling stations ($p = 0.50$). Also, no significant differences were detected in the Cu concentrations at each station (Cuatreros Port: $p = 0.10$; Ing. White Port: $p = 0.56$). In Cuatreros Port, the significant correlation between TPCu and SPM concentration ($r = 0.71$, $p = 0.008$, $N = 12$) indicated that during the study period, the high Cu concentrations in the particulate phase were related to the high values of SPM. In Ing. White Port, it was detected a significant and negative correlation between TPCu and chlorophyll-*a* concentrations ($r = -0.90$, $p = 0.001$, $N = 12$). This relation in which particulate Cu decrease with phytoplankton (chlorophyll-*a* concentrations) has been reported in other estuaries (Balls, 1990; Zwolsman and van Eck, 1999; Hatje et al., 2001). In this case, TPCu decreases during the bloom, due to the strongly complexing hydrophobic phytoplankton-released ligands which favour Cu desorption from SPM.

The results are lower than historical records at the same study area (Table 2). Andrade (2001) recorded a general range of 12 and 60 $\mu\text{g g}^{-1}$ d.w. with mean values of approximately 30 $\mu\text{g g}^{-1}$ d.w. during all the study period. Botté (2005) reported a range of 13.3 and 31 $\mu\text{g g}^{-1}$ d.w. with mean concentrations of 20 $\mu\text{g g}^{-1}$ d.w.

The concentrations of the present study are similar or lower to the reported in other estuarine systems. In the Port Jackson estuary, Hatje et al. (2001) registered concentrations between 59.1 and 95.7 $\mu\text{g g}^{-1}$ d.w., Waeles et al. (2005a) in the Penzé estuary reported a range of 5 and 98 $\mu\text{g g}^{-1}$ d.w. and in the Ría de Huelva estuary TPCu ranged between 21.2 and 33.1 $\mu\text{g g}^{-1}$ d.w. (Vicente-Martorell et al., 2009).

4.4. Cd and Cu in mesozooplankton

Mean cadmium concentrations in the mesozooplankton are shown in Fig. 3c. In Cuatreros Port the values were below the detection limit and 37.4 $\mu\text{g g}^{-1}$ d.w., while at Ing. White Port, the values were lower (n.d.–1.6 $\mu\text{g g}^{-1}$ d.w.). However, the mean values between these sampling stations were not statistically different ($p = 0.33$).

At Cuatreros Port, no significant differences were detected among the Cd concentrations ($p = 0.07$) in mesozooplankton. However, the peaks of Cd concentrations at Cuatreros Port in May (autumn) and November (spring) can be attributed to the high TPCd registered in those same months because this fraction is part of the zooplankton food. In addition, it was detected a significant and positive correlation which demonstrated the close relation between the metal concentration in both the SPM and mesozooplankton ($r = 0.9$, $p = 0.0001$, $N = 12$). On the other hand, at Ing. White Port, almost all values were below the detection limit and no significant differences were detected among them ($p = 0.07$). Moreover, no significant correlations were detected between the physicochemical variables and the Cd content ($p > 0.25$, $N = 12$).

The temporal variations in Cd concentration can be related to the mesozooplankton taxa present throughout the year, their diet, and changes in the bioavailability of metal. In the Bahía Blanca estuary, the mesozooplankton is represented by the copepods *Acartia tonsa*, which are present throughout the year but with high densities from December to April (summer–autumn). *Eurytemora americana* is the other important copepod but with high densities only in July–September (Hoffmeyer, 2004). The larvae of both the

cirripeds *Balanus* spp. and Decapoda and are also important mainly in July–September and November–December respectively. *Eurytemora americana* is herbivorous (phytoplankton based-diet), while the other ones are omnivorous (SPM, detritus, particulate organic matter) (Hoffmeyer, 2004).

There is no information on metal content in *Eurytemora americana* in other marine or estuarine environments and in the case of *Acartia tonsa* is little. Table 3 suggests that Cd in the autumn and spring mesozooplankton is higher compared with other estuarine or marine systems. In autumn, *A. tonsa* dominated the mesozooplankton with a 98% of the total abundance and the metal content was mainly due to the high particulate Cd concentration recorded during this season. In spring, mixed zooplankton was represented by *A. tonsa* and larvae of Decapoda and *Balanus* spp. with similar percentages of total abundance, and the high metal content are related to the high particulate Cd concentrations.

It is important to consider the different factors that determine metal concentrations such as source of pollution, accumulation strategies, life cycle, assimilation efficiency, efflux rate, and detoxification strategies, among others (Amiard-Triquet et al., 1993; Wang et al., 1996; Marsden and Rainbow, 2004).

The mean Cu concentrations in the mesozooplankton at Ing. White Port ranged between 2.3 and 89.3 $\mu\text{g g}^{-1}$ d.w. (Fig. 3c). As in the case of Cd, the concentrations recorded in the warmer months (November and December) can be linked with both high TPCu and TDCu concentrations. These temporal variations at Ing. White Port were statistically significant ($p = 0.03$) and Cu values in winter differed from those of spring ($p = 0.01$). At Cuatreros Port the values ranged between 1.3 and 80.2 $\mu\text{g g}^{-1}$ d.w. (Fig. 3c) and the high concentration recorded in November in the mesozooplankton, can be explained by the high TDCu and TPCu also recorded in this month. However, no significant differences on the Cu concentrations were detected at this station during the study period ($p = 0.53$). On the other hand, the mean values between these stations did not differ statistically ($p = 0.30$, $N = 12$) and no correlation was found between the physicochemical variables and Cu in the mesozooplankton ($p > 0.25$, $N = 12$) at none of the stations.

Zooplankton Cu values were higher or within the range reported by other authors (Table 3). The highest concentrations were mainly presented at Cuatreros Port in autumn (mean: 46.7 $\mu\text{g g}^{-1}$ d.w.), when *Acartia tonsa* dominated the zooplankton and the highest particulate Cu values were also recorded. However, important values were detected in spring (mean: 24.7 $\mu\text{g g}^{-1}$ d.w.) when *Eurytemora americana* and larvae of *Balanus* spp. dominated plankton and high Cu content in the SPM were recorded (9.8 $\mu\text{g g}^{-1}$ d.w.). In winter *A. tonsa* and larvae of Decapoda and *Balanus* spp. also presented high Cu concentrations (mean: 20.5 $\mu\text{g g}^{-1}$ d.w.) and in the particulate phase Cu was below the detection limit while in the dissolved phase the concentrations were important (1.6 $\mu\text{g g}^{-1}$ d.w.).

4.5. Partitioning of Cd and Cu

Fig. 4a illustrates the partition coefficient K_d , defined as the ratio of particulate metal concentration ($\mu\text{g kg}^{-1}$) divided by the dissolved metal concentration ($\mu\text{g L}^{-1}$). At Cuatreros Port, the TDCd values were below the detection limit so no partition coefficients were calculated. Regarding Cu, the logs of the K_d ranged from -0.35 to 2.79 and the highest coefficients were in March, May and November. At Ing. White Port, only one log (K_d) Cd value was calculated (0.05) while the range for Cu was -0.39 to 2.73 . The highest coefficients were in March, July and November and during most of the study period the partition coefficients were positive, indicating that Cu were mainly in the particulate form.

Table 3
Cd and Cu concentrations in different zooplankton species of the Bahía Blanca estuary and marine ecosystems around the world. *: general mean; \pm : standard error; su: summer; a: autumn; w: winter; s: spring; L: larvae.

	Metals in mesozooplankton (μg g ⁻¹ d.w.)				References
	Cd		Cu		
	Range	Mean	Range	Mean	
Ing. White Port	n.d.–2.2	0.3 ± 0.2*	2.3–104.7	41.4 ± 10.3*	Present study
–	–	0.01(a) (<i>A. tonsa</i>)	–	29.8 ± 0.8 (a) (<i>A. tonsa</i>)	
–	–	0.01(w) (<i>E. americana</i> - <i>Balanus</i> spp.)	–	2.3 (w) (<i>E. americana</i> - <i>Balanus</i> spp.)	
–	–	0.7 ± 0.3 (s) (<i>A. tonsa</i> - <i>Balanus</i> spp.- Decapoda)	–	62.1 ± 16.2 (s) (<i>A. tonsa</i> - <i>Balanus</i> spp.- Decapoda)	
Cuaterros Port	n.d.–50.4	7.3 ± 4.4*	1.3–90.7	31.4 ± 8.6*	Present study
–	–	18.8 ± 11.9 (a) (<i>A. tonsa</i>)	–	46.7 ± 19.8 (a) (<i>A. tonsa</i>)	
–	–	0.01 (w) (<i>E. americana</i> - <i>Balanus</i> spp.)	–	20.5 ± 3.9 (w) (<i>E. americana</i> - <i>Balanus</i> spp.)	
–	–	2.1 ± 1.7 (s) (<i>A. tonsa</i> - <i>Balanus</i> spp.- Decapoda)	–	24.7 ± 10.8 (s) (<i>A. tonsa</i> - <i>Balanus</i> spp.- Decapoda)	
North Sea		1.7 ± 0.2 (a) (<i>Acartia</i> sp.)		15.2 ± 2.1 (a) (<i>Acartia</i> sp.)	Zauke et al. (1996)
German Bight		2.5 ± 0.2 (a) (<i>Acartia</i> sp.)		9.7 ± 1.5 (a) (<i>Acartia</i> sp.)	Zauke et al. (1996)
Hong Kong (China)		7.3 (<i>B. amphitrite</i>)		14.9 (<i>B. amphitrite</i>)	Phillips and Rainbow (1988)
Cheesequake Creek (United States)	–	–	20–30 (S) (<i>Acartia</i> sp.)	–	Chang and Reinfelder (2002)

In general, the $\log(K_d)$ values for Cd and Cu were lower than those calculated for other estuaries and marine environments of the world, which range from 4 to 6 (Balls, 1989). In English estuaries and coasts, Balls (1989) calculated coefficients of 3.5–5. In surface waters around the coasts of England and Wales and in adjacent seas Laslett (1995) calculated $\log(K_d)$ values of 4.4 and 5.1 in the Humber Estuary, while the highest partition coefficients were recorded in the Tees and Tyne estuaries (4.86–6.03 and 4.02–5.74, respectively). In the Scheldt Estuary, the range was 4.3–5.8 (Baeyens et al., 1998), while in estuaries of the Atlantic Ocean, Helmers (1996) recorded values of 5.1–6.2.

The $\log(K_d)$ for Cu was also calculated in the above mentioned estuaries, Balls (1989) reported values between 4 and 5. Baeyens et al. (1998) recorded a range from 4.5 to 5.4;

Helmers (1996) a range between 4.5 and 5.9 and Munksgaard and Parry (2001) in North Australian coastal and estuarine waters a range from 3.7 and 5.4. Hence, the results of the present work are lower than some studies of other aquatic ecosystems with human influence.

4.6. Bioaccumulation of Cd and Cu in mesozooplankton

Log Bioconcentration (BCF) and biomagnification factors (BMF) are displayed in Fig. 4b,c. BCF considers the metal accumulated by an organism from its surrounded water, while BMF describes the metal accumulation in an organism at a higher trophic level than its food source (Fang et al., 2006). Both factors were calculated based on the following formula:

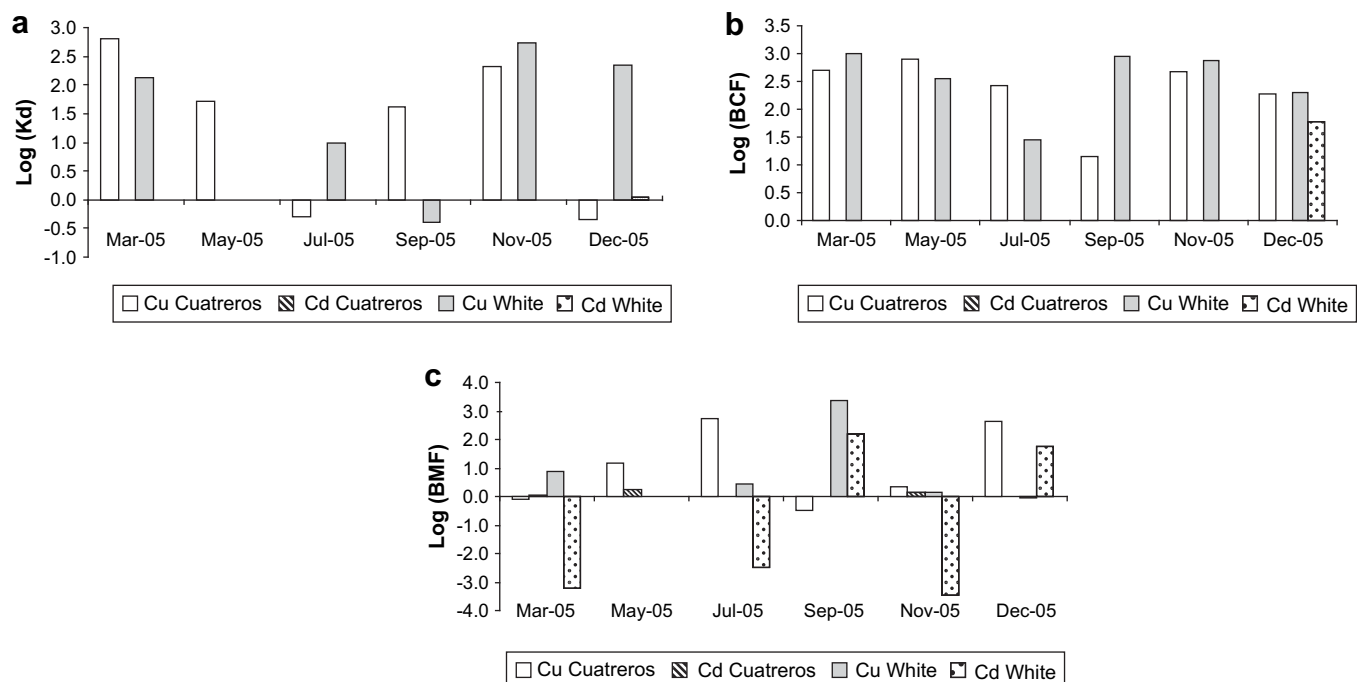


Fig. 4. Trace metal partition coefficients, and bioconcentration (BCF) and biomagnification factor (BMF) at each sampling station.

$$\text{BCF} = \frac{\text{metal concentration in organism } (\mu\text{g g}^{-1})}{\text{dissolved metal concentration } (\mu\text{g ml}^{-1})}$$

$$\text{BMF} = \frac{\text{metal concentration in organism } (\mu\text{g g}^{-1})}{\text{particulate metal concentration } (\mu\text{g ml}^{-1})}$$

At Cuatreros Port, the log (BCF) Cd was not calculated since dissolved Cd was below the detection limit. Log (BCF) of Cu was lower ranging from 1.15 to 2.90. These positive values reveal metal bioconcentration (Fig. 4b). Log (BMF) values of Cd were low, ranging between 0.14 and 0.22; however the positive values indicate only a small degree of biomagnification. The logs of the BMF of Cu range from –0.48 to 2.71 indicating biodiminution in the case of the negative values and biomagnification for the positive ones (Fig. 4c).

At Ing. White Port, log (BCF) values of Cd were calculated only in December (1.78) and log (BCF) of Cu were always positive (1.44–3), indicating bioconcentration of both metals (Fig. 4b). Log (BMF) values of Cd were also low, and thus similar to Cuatreros Port (Fig. 4c). The coefficients ranged between –3.45 and 2.21. Log (BMF) of Cu comprised values between –0.05 and 3.35, with the highest coefficient in September and only a small biomagnification in March, July and November.

5. Conclusions

This study examined, for the first time, trace metals levels in the zooplankton of the Bahía Blanca estuary, one of the most important estuaries of Argentina. Also, it investigated the metal concentrations in dissolved and particulate fraction. The following conclusions can be drawn from the study:

1. Despite their location, the sampling stations did not present significant differences in the metal concentration.
2. In general, no significant dissolved Cd concentrations appeared to be present in the Bahía Blanca estuary.
3. Dissolved Cu concentrations indicated a continuous dissolved Cu input. However, TDCu values in the Bahía Blanca estuary did not indicate a critical environmental status.
4. The particulate phase appears to be the major carrier for Cd and Cu.
5. TPCu values were within the normal values for an anthropogenically stressed estuary but not for a strongly polluted system.
6. Some of the concentrations of Cd and Cu in the mesozooplankton were high and the particulate phase was the most important metal source.
7. In general, the highest metal concentrations were in the mesozooplankton since most of the bioconcentrations and biomagnifications factors were positive, especially for Cu.

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