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Dissolved and particulate heavy metals distribution in coastal lagoons. A case study from Mar Chiquita Lagoon, Argentina

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ABSTRACT

Mar Chiquita Coastal Lagoon is located on the Atlantic coast of Argentina, and it has been declared a Biosphere Reserve under the UNESCO Man and Biosphere Programme (MAB). This coastal lagoon constitutes an estuarine environment with a very particular behaviour and it is ecologically important due to its biological diversity. The aim of the present study was to evaluate the distribution and geochemical behaviour of several heavy metals in this coastal system, focusing on their distribution in both the dissolved phase (<0.45 μm) and the suspended particulate matter. Therefore, the general hydrochemical parameters (salinity, temperature, turbidity, pH and dissolved oxygen) and concentration of total particulate and dissolved metals (Cd, Cu, Ni, Zn, Fe, Pb, Cr and Mn) were measured along 2 years (2004–2006) at two different sites. As regards their distribution, hydrological parameters did not present any evidence of deviation with respect to historical values. Suspended particulate matter showed no seasonal variation or any relationship with the tide, thus indicating that in this shallow coastal lagoon neither tides nor freshwater sources regulate the particulate matter input. Heavy metals behaviour, both in dissolved and particulate phases did not reveal any relationship with tide or seasons. Mar Chiquita Coastal Lagoon showed a large input of dissolved and particulate metals, which is probably due to intensive agriculture within the drainage basin of this system.

1. Introduction

Coastal lagoons are transitional ecosystems that couple both continental and marine environments, and they receive biogeochemical active inputs from land, rivers and marine coasts. As such, they reach up 13% of the world's coastline and range in location from tropical zones to the highest latitudes. They are among the most productive ecosystems within the biosphere and are particularly complex environments, due to their location between the land and the sea. These ecosystems are controlled by tangled interactions among land, ocean and atmosphere, resulting in high changeable and vulnerable environments (Viaroli et al., 2007). They are characterized by high fluctuations in chemical and physical parameters and, in most cases, there exists a significant occurrence of human activities including industrial, domestic and agricultural waste discharges, thus strongly influencing these processes and interactions.

Trace elements of natural and/or anthropogenic origin, including heavy metals, are transported by rivers and transferred to the coastal marine system through estuaries. Among the various contaminants, trace metals are of particular concern due to their environmental persistence, biogeochemical recycling and ecological risks. Heavy metals such as Zn, Fe and Cu, are essential biological micronutrients required for the growth of many aquatic organisms. These micronutrients can become toxic at high concentrations (Sunda, 1989). Other metals, for example Pb and Cd, are not required for growth and are highly toxic in trace amounts. Therefore, the types and levels of heavy metals that enter into the coastal lagoon are critically important.

Besides, different environmental conditions in estuarine systems can affect trace metal speciation, removal rates, and thus fluxes of trace metals that reach the ocean (Dai et al., 1995; Sanudo-Wilhelmy et al., 1996; Wen et al., 1999; Zhou et al., 2003; Jiann et al.,

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2005). Furthermore, estuaries constitute a natural reactor in which heterogeneous processes at the interface between dissolved phase and suspended particulate matter (SPM) constitute an important part of the trace elements geochemical cycles. This redistribution process is a key issue as it determines the mobility and the toxicity of trace metals within estuaries and coastal oceans (Turner and Millward, 1993; Zhou et al., 2003; Landajo et al., 2004; Audry et al., 2006; Censi et al., 2006). The chemical composition of SPM in estuaries is influenced by physical mixing, coupled with biogeochemical processes existing in transitional waters. In addition, chemical composition of SPM is related to chemical or mineralogical compositions of surrounding soils or sediments, which are the main sources of SPM to the system. Estuaries can be efficient filters for SPM and trace metals, due primarily to particle/solute interactions, flocculation and coagulation, and sedimentation of particle-bound trace metals (Bewers and Yeats, 1989; Turner and Millward, 1993). Other processes such as resuspension of bed sediments, desorption of metals from particles and diffusion of metals from sediment pore water to overlying water, mobilization of Fe and Mn in reducing sediments (Feely et al., 1986), sorption in low salinity and high turbidity zones (Balls, 1990; Liu et al., 1998; Turner et al., 1998) will also affect the behaviour of trace metals in estuaries. Evidently, estuarine chemistry is very complex due to the highly dynamic nature of the estuarine environment, and the heterogeneous reactions and hydrodynamic time scales (Morris, 1986). Hence, there is no universal pattern of trace metal behaviour within estuaries (van der Berg, 1993). Bearing in mind this behaviour diversity, it is important to investigate the full range of estuary types, across the entire spectrum of climates, flow regimes, geomorphology and biological communities, to better assess natural variability as well as to provide a basis for differentiating natural from anthropogenic loads.

Mar Chiquita Coastal Lagoon is unique of this type of environment in Argentina. It is a shallow body of brackish water affected by low amplitude tides (<1.5 m) (Fasano et al., 1982). It has a drainage basin of 10,000 km^2 characterized by intensive agricultural activities. This coastal lagoon constitutes an estuarine environment with a very particular behaviour within its physical-chemical parameters distribution (Marcovecchio et al., 2006). In addition, the biogeochemical dynamic of heavy metals have not yet been studied within this environment. The aim of the present study was to evaluate the distribution, potential seasonal variations and partitioning of several heavy metals in this coastal system, focusing on their distribution in both the dissolved phase (<0.45 μm) and the SPM. In this concern, the hydrological parameters (salinity, temperature, turbidity, pH and dissolved oxygen) and the concentrations of total metals (Cd, Cu, Ni, Zn, Pb, Cr, Fe, and Mn) were determined at two sampling stations within Mar Chiquita Coastal Lagoon during nineteen samplings (May 2004–June 2006), at high and low tide.

2. Materials and methods

2.1. Study area

Mar Chiquita Coastal Lagoon is located between 37° 33′ and 37° 43′ S, and 57° 15′ and 57° 30′ W, on the Atlantic coast of Buenos Aires Province, Argentina (Fig. 1); it has recently been declared a Biosphere Reserve under the UNESCO Man and Biosphere Programme (MAB). This coastal lagoon constitutes an estuarine environment with a very particular behaviour. It has an area of ≈60 km^2, with a tributary basin of 10,000 km^2. Its shape is irregular, and bottom topography very smooth, reaching a maximum depth of 1.50 m (Lanfredi et al., 1981). The lagoon is connected to the sea through an elongated inlet channel of approximately 6 km long and more than 200 m wide. Freshwater influence is quantitatively more important than that of seawater, and its main input is the continental drainage, which collects rainwater from a large basin including the Tandilia orographic system, where a very important agricultural land use is developed and different residues are incidentally discharged within its body (Menone et al., 2000). Average rainfall for this area is about 900 mm year^{-1}, with a homogeneous distribution throughout the year. Even though the greatest rainfall has been historically recorded during summer (December–March), very significant rains occurred not only in summer time (particularly in February, for both years of the study) but also in August (winter), during the study period. Moreover, the role of the phreatic reservoir that regulates not only the lagoon water level but also the standard meteorological conditions within the area has been fully recognized (Fasano et al., 1982). This coastal lagoon is a microtidal estuary, characterized by semidiurnal tides and shows strong salinity fluctuations (Marcovecchio et al., 2006). In addition, it provides refuge and food for numerous native and migratory species (e.g. crustaceans, fishes, birds).

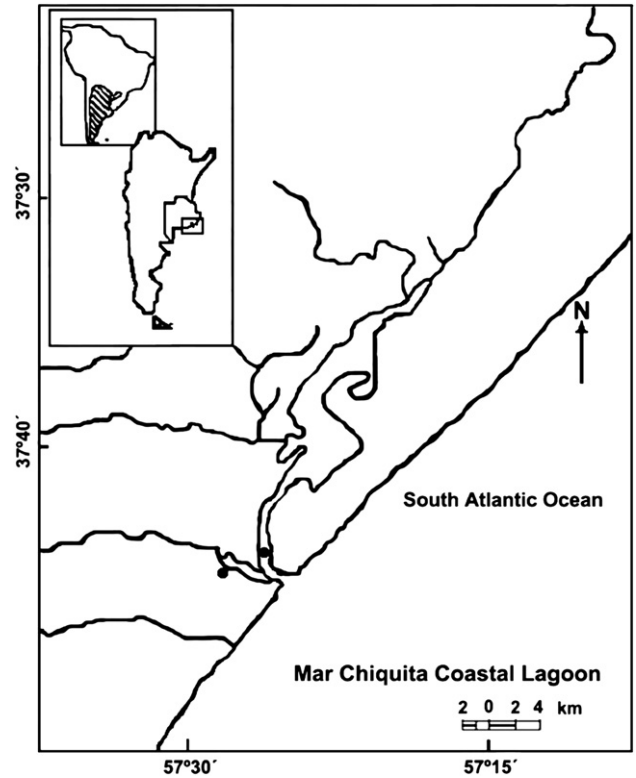

Fig. 1. Location of Mar Chiquita Coastal Lagoon, Argentina. The sampling stations (dots) are shown on the map.

2.2. Sampling and analysis

Two sample stations (Station A and Station B) have been settled (Fig. 1), representing two different zones within the coastal lagoon. Station A is a coastal site within the lagoon where several tributaries converge, while Station B is located on one of these tributaries.

By means of clean techniques, samples were collected during the whole study period (May 2004–June 2006) on the basis of a variable frequency: monthly, the first year and bimonthly, the second year. Tidal effects were assessed by sampling at high and low tide. Two fractions were obtained for each surface water

sample: (i) dissolved fraction; and (ii) suspended particulate matter.

Hydrological general hydrochemical parameters such as temperature, salinity, pH, turbidity and dissolved oxygen were in situ measured with a Horiba U-10 multisensor device. The salinity was measured using the Practical Salinity Scale.

Surface water was sampled by hand at <1 m depth using acid-washed polyethylene bottle samplers (1.5 L), previously rinsed with lagoon water of the sampling site. Water samples were filtered immediately through dry pre-weighted Millipore HA filters (0.45 μm pore size), pre-cleaned with ultrapure 0.7% HNO_3 in order to obtain dissolved and SPM fractions. Filtrates were collected in acid-washed polypropylene bottles, acidified to pH <2 (HCl analytical quality) and stored in the dark at 4 °C until analysis. On the other hand, filters were dried up to constant weight (45 °C) and then re-weighted. The SPM concentration was estimated by the difference between the filter with and without particles.

All materials associated with trace metal extraction were thoroughly acid-cleaned before use, following internationally recommended protocols (APHA, 1998). The extraction of dissolved metals from filtered water samples was performed by chelation with ammonium pyrrolidine-dithiocarbamate (APDC) followed by methyl isobutyl ketone (MIBK) extraction according to the method described by Koirtyohann and Wen (1973), modified by Botté et al. (2008).

The SPM were digested in a mixture of concentrated acids, according to the method described by Marcovecchio et al. (1988), and modified by Marcovecchio and Ferrer (2005). Subsamples were removed and mineralized with a 1:3 perchloric-nitric acid mixture in a thermostatic bath (at 120 ± 10 °C) up to minimum volume. Solutions were made up to 10 ml with 0.7% nitric acid. The same digestion procedure was performed for filters without particles to act as procedural blanks. Samples digestion was carried out in duplicate to ensure the reproducibility of the method.

Heavy metals concentrations (Cd, Cu, Zn, Pb, Fe, Cr, Ni and Mn) were determined using a Perkin–Elmer AA-2380 atomic absorption spectrophotometer with air/acetylene flame. Analytical grade reagents were used to build up the relevant blanks and calibration curves, and the analytical quality (AQ) was tested against reference materials (pond sediments, R.M.N°2) provided by The National Institute for Environmental Studies (NIES) from Tsukuba (Japan), as well as "estuarine water BCR-505" by Institute for Reference Materials and Measurements, Geel, from Belgica (IRMM). The obtained values from the analysis of the reference materials were within the range of the certified ones. Within the scope of an analytical assessment quality, percentages of recovery of same materials were higher than 90% for all the considered metals. The analytical precision expressed as coefficients of variance is <10% for all the metals, based on replicate analysis. The method detection limits (MDL) for each dissolved metal (in μg L^{-1}) are Cd: 0.18, Pb: 0.38, Cr: 0.89, Ni: 0.81, Cu: 0.44, Zn: 1.60 and Fe: 3.10. The MDL (in μg g^{-1}) for each particulate metal are Cd: 0.99, Pb: 9.26, Cr: 2.21, Ni: 6.67, Cu: 3.5, Zn: 3.97, Mn: 2.87 and Fe: 12.05.

3. Results and discussion

3.1. General hydrochemical parameters

In both stations, the water temperature showed a strong seasonal variation. In Station B, it varied from 7.7 (in July 2004, winter) to 30.7 °C (in January 2005, summer). Meanwhile, in Station A the temperature varied between 8.2 in winter and 28.8 °C in summer. The reduced depth of the system, as well as weak water movements due to limited tidal influence, contributed to these high temperatures, mainly sustained by solar radiation and convective processes within the homogeneous water column (Marcovecchio et al., 2006). These characteristics are still more pronounced in Station B, where a higher variation within the temperature range has been observed (Fig. 2a).

The temporal distribution of salinity was found to fluctuate both daily and seasonally, varying over a wide range of values (Fig. 2b). Salinity distribution was largely dependent on environmental factors, such as meteorological conditions (rains and temperatures) and hydrographic circulation. In Station B, the higher salinity in surface waters was 34.5, in April 2005 (autumn) and the lower one was 2.46, in August (winter) 2004. In Station A, the salinity range was between 1.15 during in May 2004 and 34.36 in April 2005.

When high tide, the salinity at Station A showed to be higher than at low tide, indicating the influence of tide on this parameter. Salinity gradients showed pronounced differences between low and high tide on a semidiurnal time scale. Nevertheless, in only a few sampling days, it could be observed that salinity levels were similar or even lower during high tide as compared to low tide values, while in other cases it proved to be very low (minor than 10) during all the tidal cycle. Therefore, these particular results showed that in eventual environmental conditions the tide has negligible influence on the water lagoon (i.e. inland sustained wind blocking seawater input) or even that the freshwater runoff influence could be higher than the tidal one. In Station B, several sampling days showed much higher salinities during the low tide than those of the high tide.

In both Stations, the salinity increased during summer, when temperatures were higher. Because of the specific shallow conditions of the system, the evaporation levels were relevant, even though heavy rainfalls during summer. On the contrary, during winter, when the evaporation was very low, the maximum precipitations resulted in low salinity at both stations.

Dissolved oxygen concentrations varied between 6.57 and 14.07 mg L^{-1} in Station A and between 5.32 and 14.99 mg L^{-1} in Station B, which is indicative of well oxygenated estuarine waters (Fig. 2c). In both Stations dissolved oxygen has showed a seasonal distribution pattern, being the maximum value in winter, in agreement with the lowest water temperature. These results allow to support that this environment does not evidence oxygen deficiency, considering that values recognized as proper for "severe hipoxia" (<4 mg L^{-1}) or below "minimum acceptable level" (<2 mg L^{-1}) for coastal and estuarine waters (Windsor, 1985) have not been recorded during the studied period. Nevertheless, it is worth mentioning that Station B has once presented a value of 1.93 mg L^{-1} during low tide (October 2005), considering it was below the "minimum acceptable level", and keeping in mind that this type of condition is one of the most prominent stressors of estuarine and coastal aquatic biota. In general, the water of the coastal lagoon was well oxygenated along the whole year (saturation 67–182%) of the study period.

pH values in the superficial water ranged from 7.06 to 9.68, in Station A and between 6.97 and 9.98, in Station B, though they were relatively constant within each tidal situation (Fig. 2d).

Generally speaking, data obtained in the present study about these general hydrochemical parameters are comparable to/do resemble those previously reported by Marcovecchio et al. (2006) for the same area.

3.2. Suspended particulate matter concentration (SPM)

The amount of the particulate fraction is often high in the studied area (Fig. 3). SPM concentrations ranged between 19–273.58 and 20.75–112.42 mg L^{-1} during low and high tide, respectively, in Station A. In Station B, concentrations ranged between 29–198.17 and 17.86–114.89 mg L^{-1} during low and high

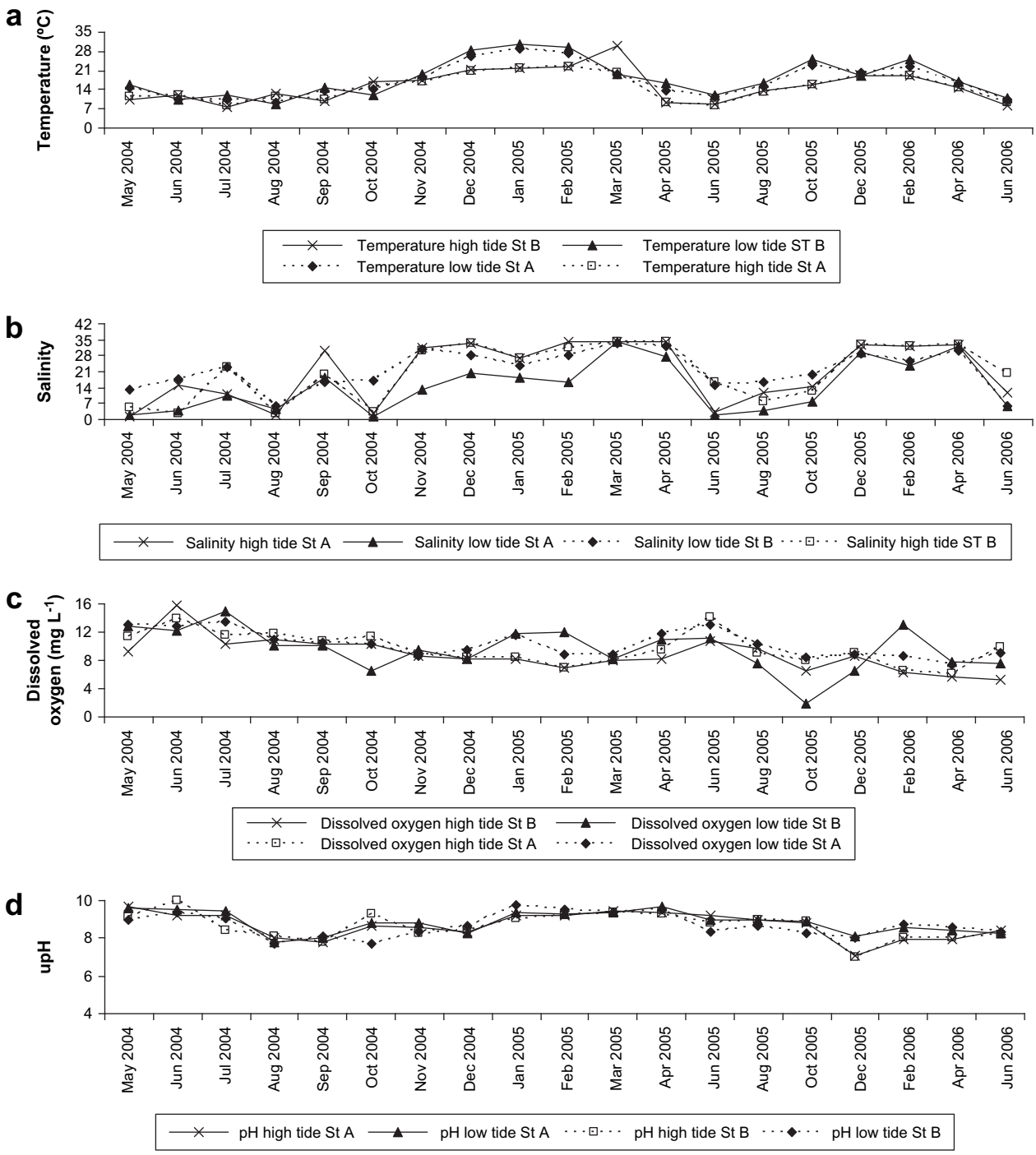

Fig. 2. Distribution of hydrographic parameters in Mar Chiquita Coastal Lagoon during May 2004–June 2006: (a) temperature; (b) salinity; (c) dissolved oxygen; and (d) pH.

tide, respectively. No relevant variations in SPM concentrations between low and high tide were observed during the studied period. This fact suggested that tide did not significantly influenced SPM concentrations. Furthermore, large SPM variations along the year have not been recorded, thus suggesting that several processes previously described as strongly linked to SPM occurrence within estuaries (i.e. hard rainfall or phytoplankton blooms) (Zwolsman and van Eck, 1999) would not affect it at Mar Chiquita Coastal Lagoon.

On the other hand, the obtained results suggested that sediment resuspension due to the shallow water column of the coastal lagoon, which may influence the SPM distribution, leading to these relatively stable SPM concentrations throughout the year. In addition, it must be remarked that river mouths, estuaries and the coastal zone have been recognized as a trap for the terrigenous particulate matter, with estimations of a ~90% of the SPM there deposited, and the remaining 10% being transported to the open sea (Martin et al., 1989).

SPM concentrations, as measured at Mar Chiquita Coastal Lagoon, were similar to those from the Changjiang Estuary (Wang and Liu, 2003), and higher than those from the Port Jackson Estuary (Hatje et al., 2003) and the Scheldt Estuary (Zwolsman and van Eck, 1999).

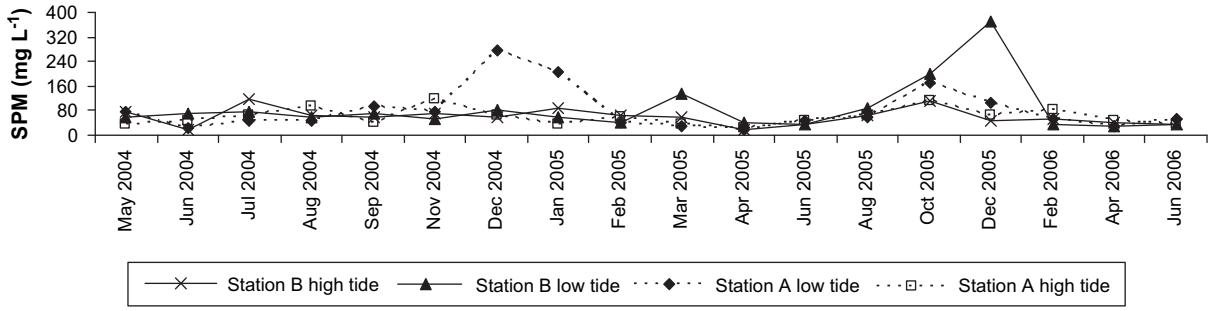

Fig. 3. Suspended particulate matter distribution (mg L^{-1}) along the study period in Mar Chiquita Coastal Lagoon.

3.3. Dissolved trace metals

Since Mar Chiquita drainage basin flows through an agricultural area, trace metal concentrations in the lagoon account for potential concerns of pollution. Although trace metals behaviour in estuaries can be very dynamic, and their concentrations may vary over large ranges, temporal distribution provides information for defining temporal variations of a specific element, regional concentration differences, and different elemental behaviours.

Seven dissolved trace metals were analysed: Zn, Ni, Cr, Fe, Cu, Pb and Cd. Trace metals did not show strong seasonal variations, as it was observed in other estuaries such as Port Jackson Estuary (Hatje et al., 2003) and Scheldt monthly and daily variations. The measured concentrations of such metals presented different trends (Fig. 4), suggesting different behaviours and origins. Mar Chiquita Coastal Lagoon is a dynamic system where seasons and tides do probably not influence the biogeochemical processes that control metal concentrations, unlike observed in other estuaries such as Alvarado Lagoon in México (Vazquez et al., 1998), the Gironde Estuary in France (Michel et al., 2000) and Port Jackson Estuary (Hatje et al., 2003). There are other factors that deserve to be studied such as winds, rains, geomorphology, subterranean waters, phytoplankton, among others, which have a great importance too in determining the heavy metals behaviour.

Levels of Cd were generally close or even below the limit of detection, with the exception of May 2004 samples, when Cd reached the highest values. Pb concentrations in November 2004 in Station A, and in September and December 2004 in Station B were significantly higher than those from the rest of the study period, with concentrations of 850, 253.95 and 188.68 μg L^{-1} respectively. Levels of dissolved Ni in this coastal lagoon waters have varied from <0.81 μg L^{-1} to 74.16 and 79.84 μg L^{-1} in Stations A and B, respectively. Moreover, high Cu concentrations were observed during some months (July 2004, September 2004, November 2004, December 2004, January 2005, February 2005, April 2005) in both stations. The highest values recorded were 1000.23 and 462.51 μg L^{-1} in Stations A and B, respectively. The range of dissolved Zn values has varied between non-detectable values up to more than 1 000 μg L^{-1} (in both stations). In addition, higher dissolved Zn values were in the same order of magnitude than those reported for the Zn chronic toxicity value for *Neohelice granulata* from Mar Chiquita Coastal Lagoon (7.07 mg Zn^{+2} L^{-1} at 5 of salinity) (Beltrame et al., 2008); hence, it allowed to sustain that the present dissolved Zn concentrations could represent a critical environmental stressor. Consequently, its continuous monitoring is highly recommended. Dissolved Fe concentrations were between non-detectable values and 227.15 μg L^{-1}.

Finally, dissolved Cr in this coastal lagoon has shown extreme values, from undetectable levels (<0.89 μg L^{-1}; at both sites) to 35.25 and 33.09 μg L^{-1} in Stations A and B, respectively. Dissolved Cr concentrations did not represent important fluctuations between stations, and the concentrations observed in each sampled month were similar at low and high tide.

The present concentrations of metals as measured in the coastal lagoon were higher than metal levels reported in pristine estuarine environments (Martin et al., 1994; Powell et al., 1996). Trace metal enrichments in coastal waters have been measured in other studies (Sanudo-Wilhelmy et al., 1996; Vazquez et al., 1998; Ferrer et al., 2002; Botté et al., 2008). The greater metal concentrations in the lagoon were probably related to anthropogenic inputs from rivers and adjacent lands. Agriculture has been identified as a source of heavy metals via fertilizers and pesticides (Micó et al., 2006; Huang et al., 2007; Kidd et al., 2007), and appeared to be the main potential source of metals to this coastal lagoon through its catchment. These types of inputs have shown to be major pathways for heavy metal contamination in some estuarine environments such as the Terminos Lagoon, in México (Vazquez et al., 1999), or the Guadalquivir River in Spain (Mendiguchía et al., 2007).

The estuarine and coastal systems listed in Table 1 are located near large urban centers or recognized polluted areas. In comparison to other studies, and considering all seven studied metals in Mar Chiquita Coastal Lagoon, only Cd was similar or even lower than average values reported for other systems, while Zn, Ni, Fe, Cr, Cu and Pb concentrations were on the same order of magnitude or even higher than those reported for other polluted estuaries.

Recordable levels of dissolved heavy metals have been measured during most of the whole period of study; these indicated the occurrence of different continuous (or almost continuous) sources of this kind of contaminants within this area of the estuary.

3.4. Metals in SPM

A total of eight metals including Cd, Pb, Ni, Zn, Mn, Fe, Cu, and Cr were determined in SPM. The distributions of total trace metals in SPM along the study period are shown in Fig. 5. Like the dissolved phase, concentrations of trace metals in SPM showed strong monthly and, in some cases, daily variations, but did not show significant seasonal variations. Different metals displayed different behaviours. The concentrations of metals in SPM fluctuated throughout the study time.

In May 2004, August 2004 and July 2005, Cd concentrations were significantly higher than in the rest of the study period. In general, Cd concentrations in SPM were high all along the research, and varied between non-detectable values to 58.64 μg g^{-1} in both stations. The fluctuations of the particulate Cu were very high, ranging between nd and 16,885 μg g^{-1}, in Station A and nd and 22,921 μg g^{-1}, in Station B; they showed the highest values (more than 20,000 μg g^{-1}) in July and August 2004. In the case of particulate Pb, the highest values were recorded during June 2004, both Station A (342 μg g^{-1}) and Station B (276 μg g^{-1}), although its fluctuation was rather scattered, it presented high concentrations

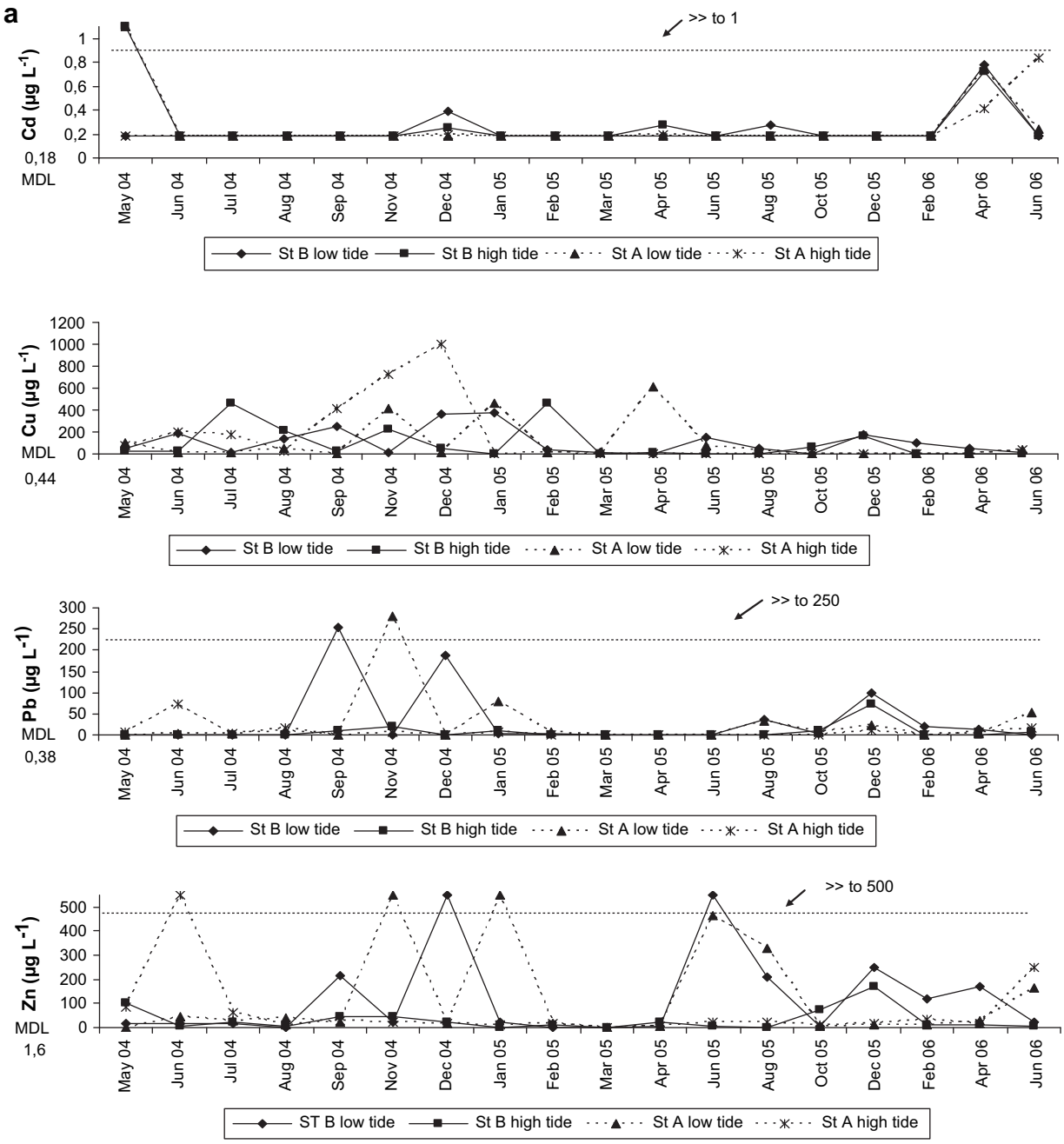

Fig. 4. Temporal distribution of dissolved heavy metals (µg L^{-1}) in Mar Chiquita Coastal Lagoon.

along the study period. Particulate Zn concentrations showed extreme values between <3.97 and 16,922 µg g^{-1}, in Station B and between <3.97 and 3177 µg g^{-1}, in Station A, with high fluctuations throughout the year. In the case of particulate Ni, the temporal trend was similar to that of Zn, including the highest value recorded in August 2004 (16,327 µg g^{-1} only in Station B). Levels of particulate Cr in Mar Chiquita Coastal Lagoon water have varied from <2.21 µg g^{-1} to almost 60 µg g^{-1} in both stations. The fluctuations of particulate Fe were similar in both Stations, with concentrations ranging between 48.71 and 54,684 µg g^{-1}, in Station A and between 49.24 to 39,396 µg g^{-1}, in Station B. Finally, particulate Mn showed high concentrations during all the period, including two extreme values: June 2004 (1947 µg g^{-1}) and October 2005 (2415 µg g^{-1}). Fe and Mn are commonly associated with particles (Rue and Bruland, 1995); therefore, concentrations in SPM of both metals are usually much greater than in dissolved form.

Trace metal concentrations in the SPM from Mar Chiquita Coastal Lagoon were compared to those reported for other polluted estuaries and coastal zones (Table 2), all of them related to both agricultural areas and industrialized and urbanized regions. Considering the low urbanization/industrialization impact on Mar Chiquita Coastal Lagoon compared to other estuaries, the obtained results suggested important metal input due to other anthropogenic activities within this region, being agriculture the main potential source. This type of input has been reported as one of the major pathways for heavy metal contamination in the lagoons of Jacarepagua, Brazil (Barcellos et al., 1988) and Terminos Lagoon, México (Vazquez et al., 1999), among others. The Cd contents of SPM was relatively high, with the maximum

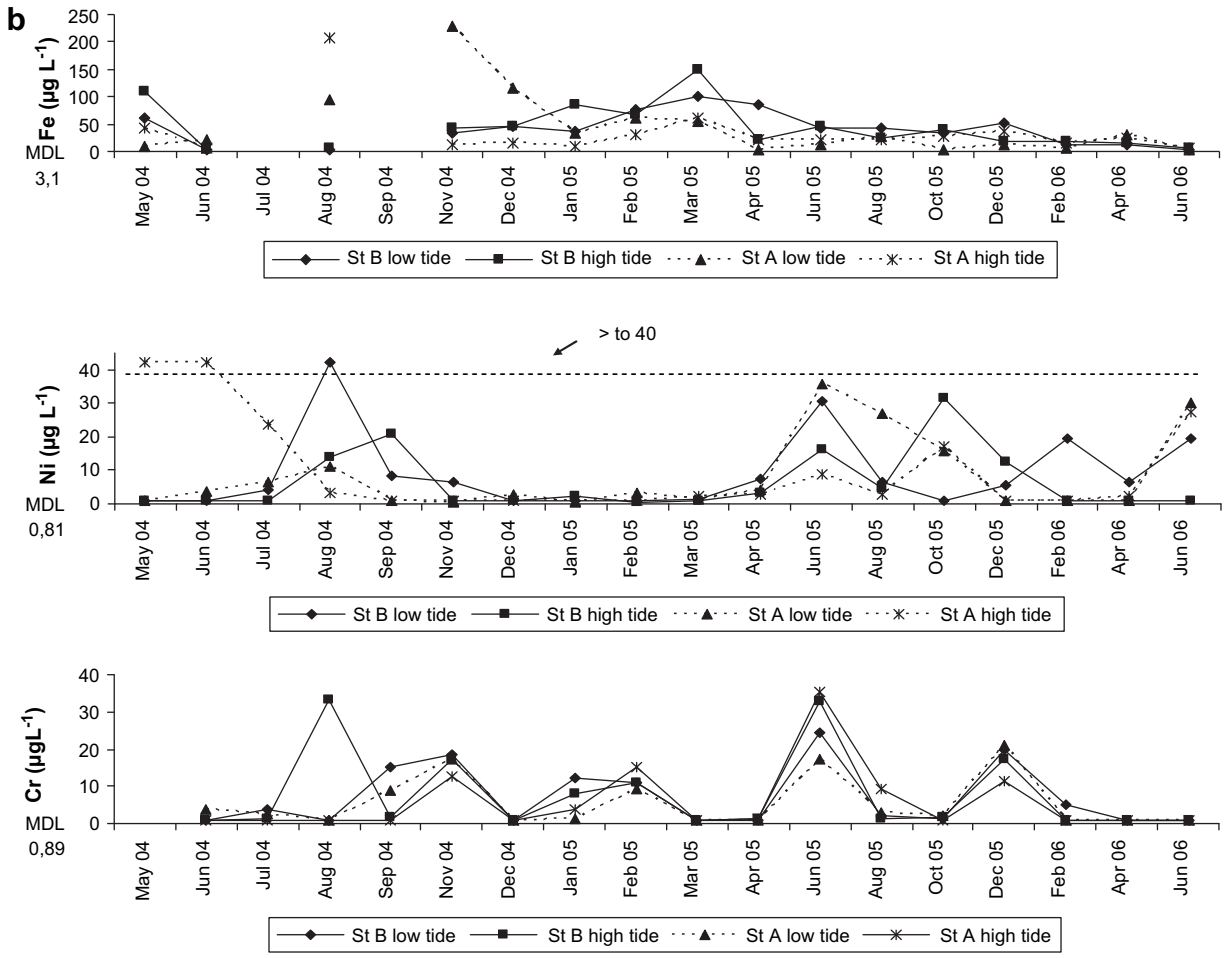

Fig. 4. (*continued*).

value one or two orders of magnitude greater than the highest concentration recorded for the other polluted systems; in addition, these values were similar to those reported in Conwy estuary, India (Zhou et al., 2003). Zn, Cu and Ni levels were much higher than those previously informed, suggesting significant sources of these elements within our study area. Pb and Cr levels in SPM are comparable to those in Table 2. Particulate Mn and Fe values in the SPM in Mar Chiquita Coastal Lagoon were comparable to those reported for most major estuaries, reflecting the well established main natural origin (mineral particles) of these elements. Hence, SPM trace metal data indicates that Mar Chiquita Coastal Lagoon is a moderately-high polluted environment. These comparisons, however, should be carefully considered due to the high variability displayed by SPM. Water dynamics, including the influence of tides and water discharge, together with anthropogenic activities may have dramatic effects over the particulate chemical composition determining strong temporal and spatial changes. The shallow water column of the lagoon promoted resuspension of the sediments due to constant wind, which generates both waves and tidal mixing. This type of processes encouraged the release of the metals from sediments into the water column.

3.5. Inter-element relationships

Since some trace metals may be originated from similar sources, and have similar reactivities towards biological and non-biological

Table 1
Dissolved metals concentrations (µg L^{-1}) in Mar Chiquita Coastal Lagoon and other polluted estuaries and coastal zones elsewhere. References data are given as range data or the higher values ± standard deviation; nd: non-detectables.

Study area	Dissolved metals							References
	Cd	Cu	Pb	Zn	Fe	Ni	Cr	
MCH Coastal Lagoon (estuary)	nd–7.1	nd–1000.23	nd–850	nd–1001.77	nd–227.15	nd–79.84	nd–35.25	This study
Bahía Blanca Estuary	nd–3.41	0.65–13.40	nd–7.53	nd–56.56	nd–3.49	nd–3.49	nd–5.86	Botté, 2005
Terminos Lagoon (estuary)	2–93	3–77	–	3–97	181–1201	6–399	–	Vazquez et al., 1999
Alvarado Lagoon (estuary)	1.44–2.97	0.19–61.4	0.40–116	–	0.11–0.98	–	2.82–6.79	Vazquez et al., 1998
Gulf of Cambay	561 ± 17	3939 ± 123	2036 ± 167	5832 ± 123	3662 ± 132	944 ± 132	765 ± 24	Srinivasa et al., 2005
Changjiang Estuary	0.00241–0.04117	1.221–1.682	0.475–0.710	0.997–1.794	6.06–35.86	1.027–1.651	–	Wang and Liu, 2003
Port Jackson Estuary	0.01–0.10	0.93–2.55	–	nd–9.66	–	0.18–1.61	–	Hatje et al., 2003
Guadalquivir River	0.00136–0.07023	0.74–7.40	0.013–3.29	nd–7.28	–	nd–4.63	nd–134.65	Mendiguchía et al., 2007

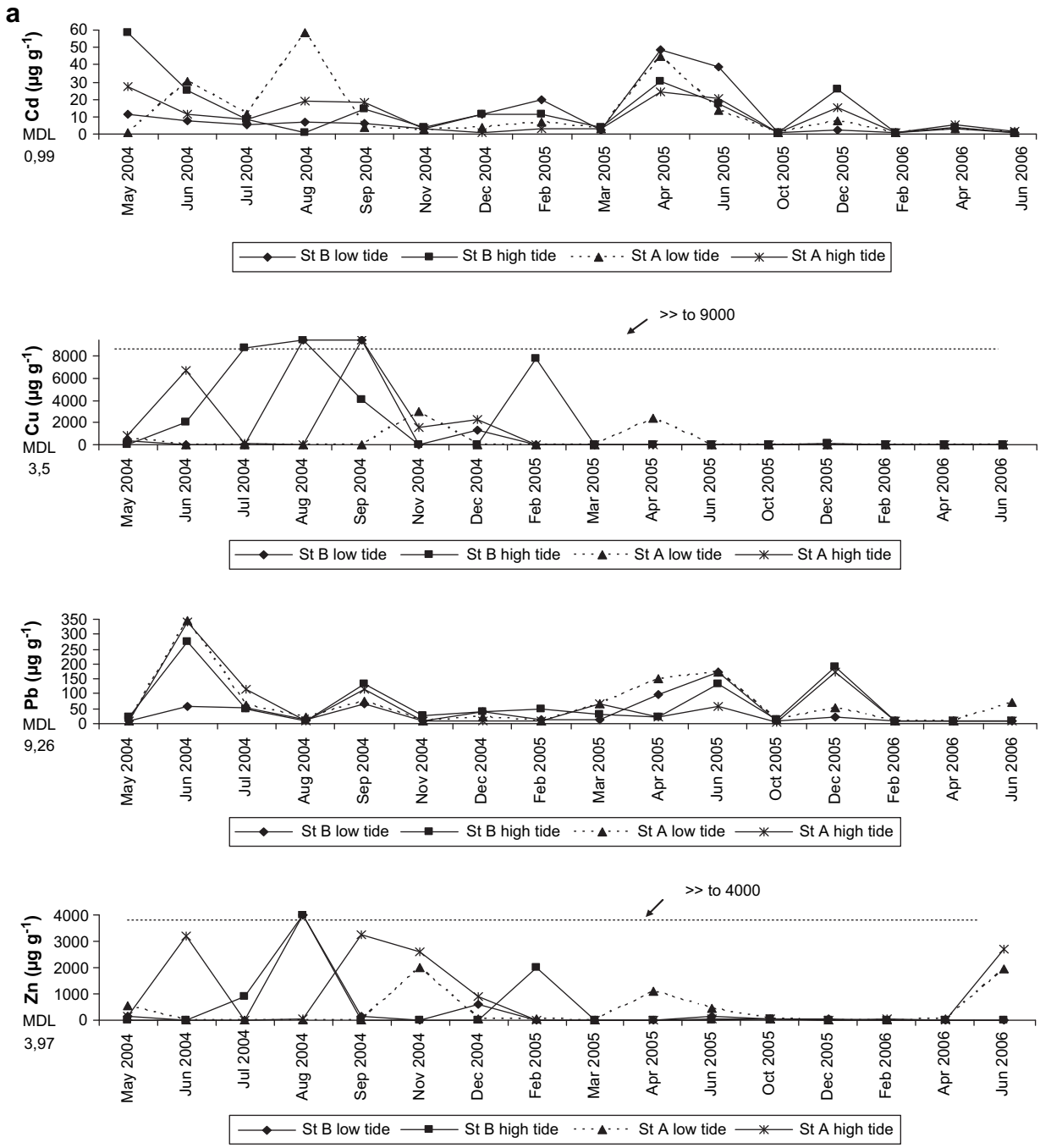

Fig. 5. Temporal distribution of particulate heavy metals Cd, Cu, Zn, Pb, Fe, Cr, Ni and Mn (µg g^{-1}) in Mar Chiquita Coastal Lagoon.

particles, it is probable that some of them may have their particulate-bound concentrations closely related to each other. The concentrations of each total trace metal in both stations were regressed against every other one to assess the significance of any co-association. As shown in Table 3, a significant relationship was found between particulate Cu and Zn ($r^2 = 0.6806$ and $r^2 = 0.7190$ in Stations A and B, respectively) and between Cu and Ni ($r^2 = 0.9460$ and $r^2 = 0.7830$ in Stations A and B, respectively). Moreover, highly significant correlations existed between total Zn and Ni in SPM in both stations ($r^2 = 0.726$ Station A and $r^2 = 0.978$ Station B). Some other relationships are also shown in Table 3.

On the other hand, significant relationships were found between dissolved heavy metals, but different that particulate ones, for example between dissolved Pb and Zn in Stations A and B ($r^2 = 0.702$ and $r^2 = 0.572$, respectively). Some other relationships are also shown in Table 3.

A non-significant relationship was found between dissolved and particulate metals and SPM.

3.6. Partitioning of trace metals between SPM and the dissolved phase

The distribution coefficients (KD) provide empirical information on the combined effect of heterogeneous reactions on the solid-solution distribution of an element. An elevated KD value indicates affinity of an element to be associated and transported with the

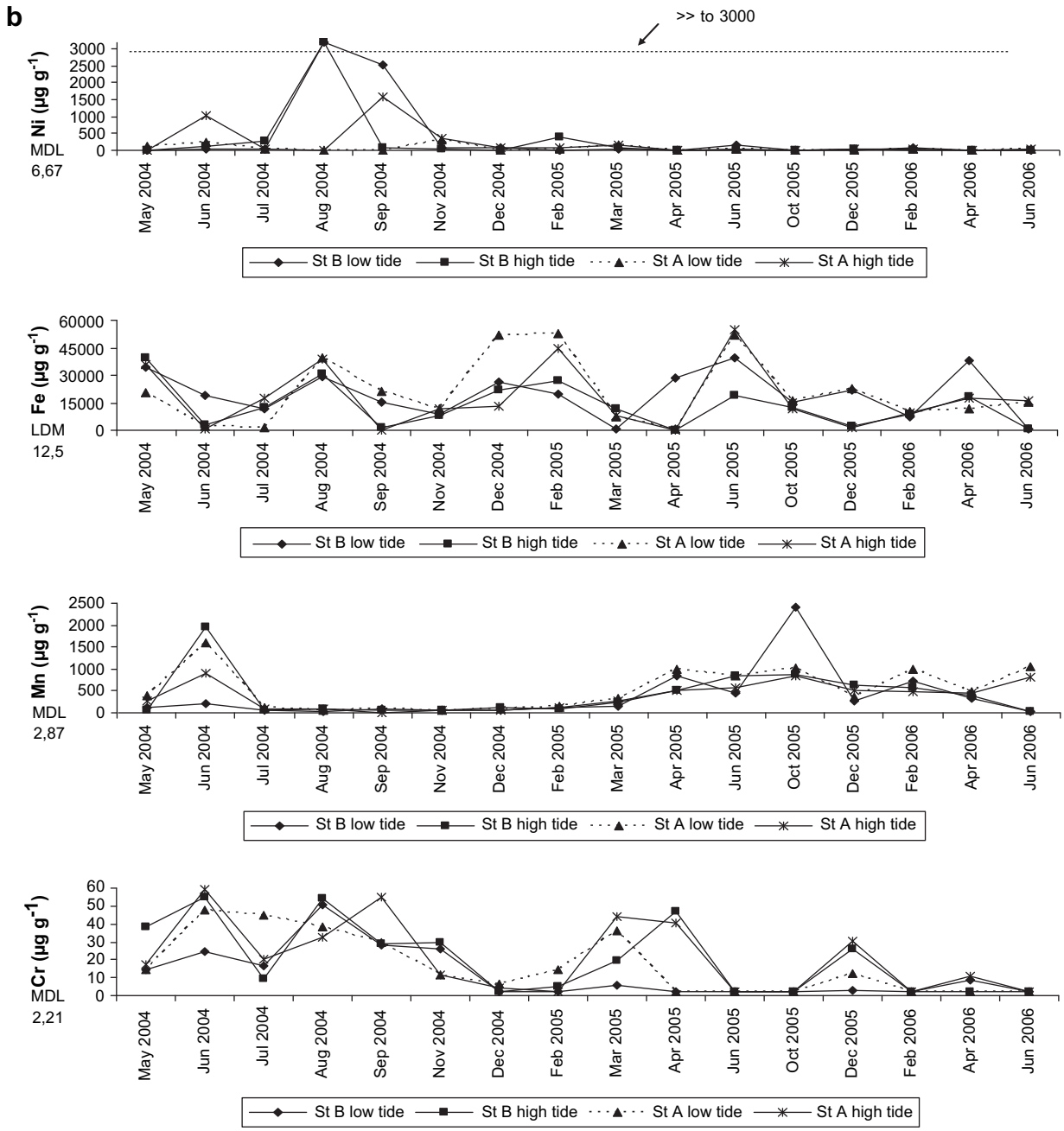

Fig. 5. (*continued*).

Table 2
Particulate metals concentrations (µg g^{-1}) in Mar Chiquita Coastal Lagoon and others polluted estuaries and coastal zones elsewhere. References data are given as range data or the higher values ± standard deviation; nd: non-detectables.

Estuary	Metals in suspended particulate matter								References
	Cd	Cu	Pb	Zn	Fe	Ni	Cr	Mn	
MCH Coastal Lagoon	nd–58.64	nd–22921,37	nd–345.84	nd–16922.69	48.71–54684.37	nd–16327.91	nd–59.36	nd–2415.88	This study
La Plata River	–	7.4–109	–	–	–	–	75–408	525–1341	Bilos et al., 1998
Danshuei River Estuary	0.19–2.34	52–745	40–179	–	–	39–347	–	–	Jiann et al., 2005
Conwy Estuary	58 ± 10	177 ± 94	546 ± 536	554 ± 185	32000 ± 2700	282 ± 165	86 ± 26	1300 ± 146	Zhou et al., 2003
Hudson River Estuary	0.93 ± 0.06	185 ± 11	254 ± 23	2543 ± 234	–	–	–	–	Feng et al., 2002
Mae Klong River	–	1.14–22.27	–	7.66–339.54	570–76500	nd–55.39	7.77–85.14	18.33–724.12	Censi et al., 2006
Scheldt Estuary	<0.5–13.9	10–288	12–279	32–1196	–	3–66	20–306	136–1347	Zwolsman and van Eck, 1999
Severn Estuary	0.32–0.49	29.8–37	65.4–77.5	191–238	–	31.2–36.9	67.2–81.3	–	Duquesne et al., 2006

Table 3
Correlation matrix (Pearson-product correlation): (a) particulate; and (b) dissolved metal concentrations ($n = 38$) in Stations A and B in Mar Chiquita Coastal Lagoon. Bold-type values are significant ($P \leq 0.05$).

(a)

	Station A								Station B							
	Cd_{SPM}	Cu_{SPM}	Pb_{SPM}	Zn_{SPM}	Ni_{SPM}	Fe_{SPM}	Cr_{SPM}	Mn_{SPM}	Cd_{SPM}	Cu_{SPM}	Pb_{SPM}	Zn_{SPM}	Ni_{SPM}	Fe_{SPM}	Cr_{SPM}	Mn_{SPM}
Cd_{SPM}	1								1							
Cu_{SPM}	0.112	1							−0.165	1						
Pb_{SPM}	0.321	0.28	1						**0.494**	−0.0371	1					
Zn_{SPM}	−0.0844	**0.686**	0.227	1					−0.14	**0.719**	−0.155	1				
Ni_{SPM}	0.038	**0.946**	0.42	**0.726**	1				−0.156	**0.783**	−0.151	**0.978**	1			
Fe_{SPM}	0.0796	−0.306	−0.304	−0.316	−0.0335	1			**0.35**	0.197	−0.102	0.297	0.283	1		
Cr_{SPM}	**0.352**	**0.418**	**0.53**	0.145	**0.54**	**−0.372**	1		0.202	**0.496**	0.253	**0.505**	**0.551**	−0.0488	1	
Mn_{SPM}	0.076	−0.161	**0.5**	0.043	−0.086	−0.28	−0.165	1	0.101	−0.231	**0.369**	−0.178	−0.175	−0.144	0.0396	1
SPM	−0.307	0.0535	−0.261	−0.0259	−0.0587	0.139	−0.289		−0.253	−0.0236	−0.233	−0.0361	−0.0436	0.0550	−0.229	0.118

(b)

	Station A							Station B							
	Cd_{DIS}	Cu_{DIS}	Pb_{DIS}	Zn_{DIS}	Ni_{DIS}	Fe_{DIS}	Cr_{DIS}	Cd_{DIS}	Cu_{DIS}	Pb_{DIS}	Zn_{DIS}	Ni_{DIS}	Fe_{DIS}	Cr_{DIS}
Cd_{DIS}	1							1						
Cu_{DIS}	−0.0316	1						−0.124	1					
Pb_{DIS}	−0.0480	0.206	1					−0.0594	**0.414**	1				
Zn_{DIS}	−0.0745	0.151	**0.702**	1				0.0375	**0.380**	**0.572**	1			
Ni_{DIS}	−0.0948	−0.0733	−0.0394	**0.493**	1			−0.125	−0.00935	−0.0639	0.0674	1		
Fe_{DIS}	−0.133	−0.0153	**0.630**	0.0976	−0.193	1		0.315	−0.0725	−0.0146	0.00977	−0.0290	1	
Cr_{DIS}	−0.132	−0.0354	0.249	0.153	−0.0993	0.0346	1	−0.236	0.204	0.149	0.155	0.0869	−0.0156	1
SPM	−0.00964	0.325	−0.0139	−0.144	−0.105	0.0666	−0.0720	−0.0242	0.181	0.241	0.0906	−0.09	0.175	−0.229

solid phase. Hence, KDs are usually used for understanding geochemical and contaminant fluxes in estuaries and coastal waters (Ng et al., 1996; Turner, 1996; Veselý et al., 2001). Trace metals concentrations in both SPM and water have been determined, providing a good opportunity to study the equilibrium distribution of metals. This was performed by calculating the partition coefficients, KD (ml g^{-1}), which is defined as follows: KD = Total Concentration of a metal in SPM ($\mu g\ g^{-1}$)/Concentration of a metal in water ($\mu g\ ml^{-1}$).

Partition coefficients in Station B ranged from 4.12×10^3 to 2.7×10^5 for Cd; 52 to 1.7×10^5 for Cu; 2.1×10^2 to 7.3×10^5 for Pb; 23 to 1.06×10^7 for Zn; 2.1×10^2 to 1.08×10^6 for Ni; 2.4×10^3 to 7.3×10^6 for Fe; and, 67 to 5.7×10^4 for Cr. In Station A ranged from 1.4×10^2 to 2.51×10^5 for Cd; 3.1×10^2 to 4.06×10^4 for Cu, 5.4×10^2 to 3.9×10^5 for Pb; 63 to 3.6×10^5 for Zn; 2.4×10^2 to 1.9×10^6 for Ni; 2.4×10^3 to 5.1×10^6 for Fe; and, 62 to 6.1×10^4 for Cr. Such results suggest that Zn was the most strongly bound by SPM, although some other times it was also the most weakly bound by SPM; such duality of behaviour was presumably related to changes in physical-chemical parameters or environmental processes which could conditionate it.

3.7. Discussion

This study presents the first systematic research on dissolved and particulate heavy metals concentrations within Mar Chiquita Coastal Lagoon. After understanding the preliminary geochemical behaviour of dissolved and particulate trace metals in the Lagoon, the following conclusions can be sustained:

- The annual average of general hydrochemical parameters were in full agreement with historical values for the area, and did not present any evidence of abnormal distribution. This could support the notion that no gross change in the chemical species of trace metals occurred during the time of the measurements.
- Salinity behaviour in both study sites was different, suggesting that the whole coastal lagoon has not the same water dynamic.
- Suspended particulate matter showed neither a seasonal variation nor a relationship with tide, indicating that in these shallow coastal lagoon tidal features or freshwater sources do not dominate the particulate matter inputs.
- Concentrations of dissolved and particulate heavy metals did not denote a seasonal variation.
- A comparison with other world estuaries and coastal areas showed great input of metals in both the dissolved and particulate phases. Therefore, human activities, especially intense agriculture in the drainage basin of Mar Chiquita Coastal Lagoon are believed to be responsible for serious metal impacts.
- Concentrations of dissolved and particulate Zn, Ni and Cu were significantly higher than those reported in other polluted environments in several months.
- The concentration of trace metals did not tend to increase or decrease with the tide, again suggesting that other factors regulated this behaviour.
- High metal concentrations in water column such as particulate Zn, Cu and Ni found in this study implied temporary discharge of these contaminants from land-based sources or advective input from areas with high metal concentrations.
- Significant inter-relationships existed between concentrations of certain metals in SPM, namely between Cu and Zn, Cu and Ni, and Zn and Ni in the SPM; and, between dissolved Zn and Pb, suggested similar sources for and/or similar geochemical processes controlling such metals.

– Dissolved phase is the major metal carrier for Cd, Cu, Ni, Pb and organic carbon, while Fe and Mn are mainly transported in the particulate phase.

4. Conclusions

Just like for every site of the kind, heavy metals environmental status of Mar Chiquita Coastal Lagoon is really important in order to identify its main threats, as well as to prioritize its needs on environmental management. It is known that within certain thresholds, these ecosystems can show a buffer capacity to tolerate external stress. However, high levels of pressure during prolonged periods can lead to their irreversible deterioration (Viaroli et al., 2007). Since lagoons have significantly different characteristics from other estuaries and because they represent a significant portion of the land–sea interface, a better understanding of the biogeochemistry of these systems is desirable. Due to the particular characteristics of this type of environments, a great amount of heavy metals can be trapped here and attempt to their environmental status.

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