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THEMATIC ISSUE

Comparative approach for trace metal risk evaluation in settling particles from the Uruguay River, Argentina: enrichment factors, sediment quality guidelines and metal speciation

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Abstract The source and potential risks of trace metals in settling material collected with sediment traps in the Uruguay River were evaluated utilizing enrichment factors (EF), sediment quality guidelines (SQG) and speciation using a 4-step sequential extraction procedure. The total organic carbon content of the settling material was relatively high and homogeneous (2.5 ± 0.3 %) and showed no correlation with the metal concentrations. Total trace metal concentrations decrease from Fe (48,969 ± 7380 μg g^{-1}), Mn (1859 ± 233 μg g^{-1}), Zn (84 ± 7.6 μg g^{-1}), Cu (56 ± 6.9 μg g^{-1}), Cr (19 ± 2.7 μg g^{-1}), Ni (16 ± 2.0 μg g^{-1}) and Pb (13 ± 1.2 μg g^{-1}). The average EF of Zn, Cr, Ni and Pb are below 1.5 indicating natural sources, whereas those of Cu and Mn are consistently higher (EF > 2) insinuating some anthropogenic influence. Consistently, Cu concentrations duplicated the SQG (35.7 μg g^{-1}) suggesting that adverse biological effects may be observed occasionally. However, speciation results revealed that most metals are associated with the residual fraction, strongly linked to the mineral matrix, and therefore unavailable to aquatic organisms. The sole exception is Mn which is mainly found in the non-residual fractions ($\sum F1 - F3 = 82$ %). Trace metal mobility/bioavailability decreased from Mn (82 %) $\gg$ Pb (37 %) > Cr (26 %) ~ Ni (25 %) > Zn (20 %) > Cu (14 %) > Fe (10 %). These results demonstrate the utility of metal speciation studies to assess the real risk for aquatic organisms of high Cu concentrations, but associated to relatively immobile fractions of reduced bioavailability.

Keywords Heavy metals · Settling particles · Sequential extraction · Uruguay River

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Introduction

Due to their persistence, toxicity and non-biodegradable properties, trace metals pollution constitute a global environmental problem affecting the urbanized-industrialized water ecosystems around the world (Förnstner and Wittman 1983). The traditional assessment of total metal concentrations does not provide detailed information on metal mobility, bioavailability and potential toxicity for aquatic organisms (Ure and Davidson 2002). To address this problem, sequential extraction procedures have been proposed as validated methods to assess the trace metal speciation in soils and sediments. In these procedures, the sample is successively treated with increasing-strength reagents to dissolve from mobile to residual sediment phases (Davidson et al. 1994). The sequential extraction procedure proposed by the European Community Bureau of Reference (BCR; now the Standards Measurement and Testing Programme) was developed in an attempt to standardize the various schemes described in the literature (Ure et al. 1993). This sequential extraction procedure has been widely applied to determine the speciation of metals in

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different kind of samples including soils (Kaasalainen and Yli-Halla 2003; Pueyo et al. 2008), sediments (Morillo et al. 2004; Yu et al. 2010), sewage sludge (Fuentes et al. 2004; Kazi et al. 2006) and street dusts (Kartal et al. 2006; Li et al. 2013).

The vertical flux of particulated material in aquatic ecosystems transport organic matter and chemical substances from surface layers to the bottom transferring energy and materials to benthic communities constituting the vehicle to sequester excess carbon in sediments (Hargrave and Taguchi 1978; Speranza and Colombo 2009). Sediment traps have been extensively used to determine the downward flux of suspended particles and particle-bound metals in different freshwater and marine environments (Jickells et al. 1984; Sigg et al. 1987; Kuss and Kremling 1999; Caetano et al. 2002; Ergül et al. 2008; Heimbürger et al. 2014). However, the studies of trace metal speciation in settling particles are scarce (Feely et al. 1986; Fischer et al. 1986; Gagnon et al. 2009).

The Uruguay River, with a total length of 1838 km and a drainage area of nearly 3.65×10^5 km^2 (Fig. 1a), is the second tributary in importance of the Río de la Plata basin covering parts of Brazil, Uruguay and Argentina (Di Persia and Neiff 1986). The geology of the basin is complex and includes a mosaic of volcanic (basaltic) and sedimentary rocks together with quaternary alluvial sediments (López Laborde 1998). The Uruguay River basin experienced extensive land use change during the second half of the twentieth century as a result of expansion of agricultural activities (Saurral et al. 2008). The river transports $\sim 11 \times 10^6$ t per year of suspended solids and $\sim 6 \times 10^6$ t per year of dissolved solids to the Río de la Plata (Depetris and Paolini 1991). A recent study of the river discharge and water quality variability related to ENSO episodes revealed that the irregular river discharge (307–28,091 m^3 s^{-1}) produce contrasting environmental conditions with a 1–2 orders of magnitude increase of the solid load during the river floods (Colombo et al. 2015). In this paper, we evaluate the source and potential risks of trace metals in settling material collected with sediment traps in the Uruguay River utilizing enrichment factors, sediment quality guidelines and the BCR sequential extraction procedure.

Materials and methods

Study area and sampling

The study area is located in the Ñandubaysal Bay, a shallow, turbid and little impacted bay located in the Argentinean coast of the Lower Uruguay River (Fig. 1a). The settling material was collected by fixed sediment traps deployed 50 cm below the surface for 1–3 months during 2012–2014 ($n = 9$). Sediment trap consisted in a plastic funnel with a height/diameter ratio of 3:1 coupled to a 50 ml Falcon™ tube. The mooring line was stretched between an anchor and a subsurface float, which is loosely connected to a surface marker buoy, to keep the traps in a stable vertical position throughout the sampling period (Fig. 1b). Due to the short sediment trap deployment periods and to minimize the contamination, no poisoning was used in the traps.

Chemical analyses

The material collected by the traps was immediately centrifuged and split for total organic carbon (TOC; catalytic combustion with a Thermo Finnnigan, CE FlashEA 1112 elemental analyzer) and the determination of trace metals. To determine the pseudo-total concentration of metals,

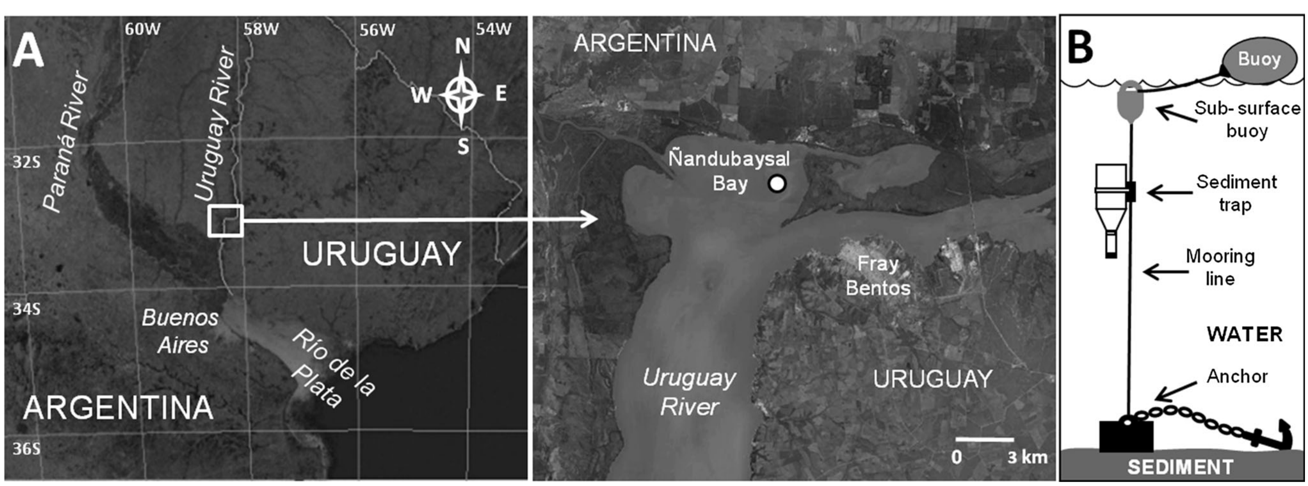

Fig. 1 **a** Study area and location of the mooring site in the Uruguay River. **b** Schematics of the sediment trap deployment

samples were digested with aqua regia (3:1 v/v, HCl to HNO_3) and H_2O_2 at 100 °C in a heating block (Hseu et al. 2002).

The BCR sequential extraction procedure (Ure et al. 1993) was applied, in duplicate, using the reagents and experimental conditions given in Table 1. Wet samples were analyzed since the drying process is known to significantly alter metal speciation (Rapin et al. 1986; Bordas and Bourg 1998). The extractions were performed by mechanical shaking in end-over-end shaker at room temperature. Between each successive extraction, the residue was rinsed with 15 ml of deionized water, shaken for 5 min, and centrifuged for 10 min at 3000 rpm. The supernatant was discarded taking care not to discard any solids. Blank extractions were carried out throughout the complete procedure.

The pseudo-total and fractionated metal concentrations were determined using a Thermo Elemental Solar M5 atomic absorption spectrophotometer equipped with a deuterium background corrector, and an air-acetylene flame. Procedural blanks were negligible. The method recovery tested through the analysis of Certified Reference Soil (CRM020-050 RTC) ranged between 87 and 113 % for Ni and Pb, respectively.

An internal check was performed on the results of the sequential extraction by comparing the total amount of metals removed in the procedure ($\sum$F1 − F4) with the results of the pseudo-total digestion. The sum of the 4 steps was in good agreement with the pseudo-total content (92–106 % for Ni and Pb, respectively) for most trace metals (except Mn 62 %).

Results and discussion

Metal concentration in settling particles

Table 2 presents total organic carbon (TOC) and trace metal contents of the settling particles. The TOC content of the settling material was relatively high and uniform (2.06–2.87 %; mean = 2.5 ± 0.3 %) and showed no correlation with metal concentrations ($p < 0.05$). Average trace metal concentrations were also relatively homogeneous (relative standard deviations <17 %) and decrease from Fe (47,483 ± 7846 $\mu g\ g^{-1}$), Mn (1888 ± 219 $\mu g\ g^{-1}$), Zn (85 ± 8.4 $\mu g\ g^{-1}$), Cu (55 ± 7.0 $\mu g\ g^{-1}$), Cr (19 ± 3.0 $\mu g\ g^{-1}$), Ni (16 ± 2.2 $\mu g\ g^{-1}$) to Pb (13 ± 1.4 $\mu g\ g^{-1}$). These concentrations are 40–80 % lower than previous reports for filtered suspended particulate matter from the Uruguay River (Depetris et al. 2003), reflecting the higher contribution of coarser material with reduced metal concentrations in the traps compared to the finer material transported in suspension.

A first approach used to distinguish between the natural background and anthropogenic influences, was to calculate the enrichment factors relative to the earth crust taking Fe as reference element and upper crust values from Wedepohl (1995):

$$\mathrm{EF} = (\mathrm{metal/ref.\ element})_{\mathrm{sample}} / (\mathrm{metal/ref.\ element})_{\mathrm{uppercrust}})$$

According to Zhang and Liu (2002), EF values between 0.5 and 1.5 indicate that metals are entirely from crustal materials or natural sources, whereas EF values greater than 1.5 suggest a more likely anthropogenic influence. Figure 2 shows EF values of Mn, Zn, Cu, Cr, Ni and Pb in settling particles. The average enrichment factors of Zn, Cr, Ni and Pb (1.1 ± 0.1, 0.4 ± 0.04; 0.6 ± 0.1 and 0.5 ± 0.1, respectively) are below 1.5 indicating natural sources, whereas those of Cu and Mn are consistently higher (2.5 ± 0.3 and 2.4 ± 0.3, respectively) insinuating some anthropogenic influence.

To evaluate the possible risks associated with trace metals, sediment trap concentrations were compared with Canadian sediment quality guidelines for the protection of aquatic life (CCME 2001). The sediment quality guideline (SQG) and the probable effect level (PEL) are used to define three ranges of chemical concentrations: those that are rarely (<SQG), occasionally (between the SQG and the PEL), and frequently (>PEL) associated with adverse biological effects. In Uruguay River settling material, most trace metals are 30–60 % lower than sediment quality guidelines for freshwater sediments (Zn: 123; Cr: 37.3 and

Table 1 Summary of the BCR sequential extraction procedure

Fraction	Extraction reagent and conditions
F1: exchangeable and acid soluble	Acetic acid (0.11 M), shaken at room temperature for 16 h (overnight)
F2: reducible	Hydroxylamine hydrochloride (0.1 M), shaken at room temperature for 16 h (overnight)
F3: oxidizable	(a) Hydrogen peroxide (8.8 M) (twice), 1 h at ambient temperature and 1 h in a water bath at 85 °C
	(b) Ammonium acetate (1 M), shaken at room temperature for 16 h (overnight)
F4: residual	Aqua regia, digested on hotplate at 100 °C

Table 2 Total organic carbon (TOC) and trace metal contents of settling particles

Date	TOC %	Fe $\mu g\ g^{-1}$	Mn	Zn	Cu	Cr	Ni	Pb
June-12	2.06	46,216	1794	80.24	47.94	17.05	13.91	11.49
August-12	2.11	44,466	1643	79.58	45.89	16.13	13.83	11.23
December-12	2.70	42,057	1884	86.11	46.75	16.76	13.63	12.59
March-13	2.54	48,845	2057	95.87	54.98	18.03	15.16	13.23
April-13	2.67	49,163	2342	88.98	64.73	23.03	18.90	14.80
July-13	2.68	46,662	1943	88.54	59.30	21.18	18.26	13.54
August-13	2.18	41,633	1639	74.76	56.06	15.68	16.48	11.34
September-13	2.59	41,431	1768	72.58	56.32	18.00	16.64	10.98
February-14	2.87	66,876	1922	95.17	63.39	23.68	19.04	13.85
Mean	2.5	47,483	1888	85	55	19	16	13
SD	0.3	7846	219	8.4	7.0	3.0	2.2	1.4

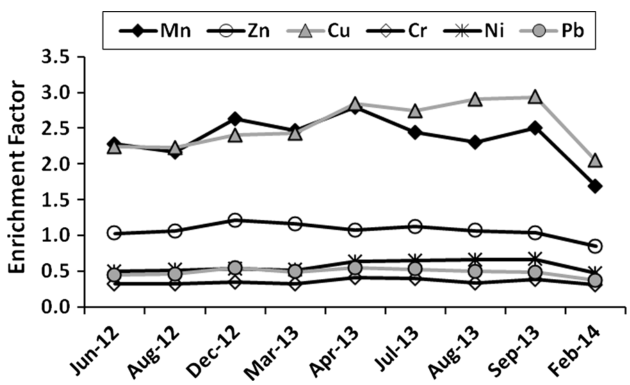

Fig. 2 Enrichment factors of metals in settling particles

Pb: 35.0 $\mu g\ g^{-1}$). Consistent with its higher EFs, the sole exception is Cu whose concentrations are between the SQG and PEL (35.7 and 197 $\mu g\ g^{-1}$, respectively), suggesting that adverse biological effects may be observed occasionally.

Metal speciation

Figure 3 show the average distribution of the heavy metals in the four fractions of the sequential extraction procedure. As total metal concentrations, the speciation patterns of the different metals were relatively homogeneous during the study. Most metals in the settling material are associated to the residual F4 fraction (Fe = 90 ± 2.4 %; Cu = 86 ± 5.0 %; Zn = 80 ± 2.5 %; Ni = 75 ± 4.3 %; Cr = 74 ± 4.0 % and Pb = 63 ± 8.0 %), strongly bound to the mineral matrix, and therefore unavailable to aquatic organisms (Chandra Sekhar et al. 2003). Among non-residual fractions, the organic fraction (F3) was the most important (17 ± 12 % of total concentration), especially for Pb and Cr (F3 = 37 ± 7.8 % and 26 ± 4.0 %, respectively). The most mobile fractions, F1 of exchangeable and carbonate bound metals, and the reducible F2 consisting of metals bound to Fe and Mn oxides, account for a minor percentage of the total (<10 %).

Elevated concentrations of metals in the residual fraction indicate that sediments are relatively unpolluted, and that the elements derive mainly from lithogenic sources (Davidson et al. 1994; Canuto et al. 2013). This agrees with the low EFs calculated for Zn, Cr, Ni and Pb (EF < 1.5) relative to the upper crust. In contaminated river sediments, the speciation patterns differ significantly since most metals are usually associated to non-residual fractions (Farkas et al. 2007; Pandey et al. 2014; Sungur et al. 2014). Anthropogenic metals are predominantly found in the first three fractions (soluble in acid, associated with Fe and Mn oxides, and associated with organic matter and sulfides), which are vulnerable to small changes in environmental conditions (Passos et al. 2010).

Mn speciation in settling particles shows a contrasting pattern and is basically associated with the non-residual fractions (Fig. 3). Non-residual Mn was distributed among the reducible (F2 = 30 ± 3.1 %), oxidizable (F3 = 29 ± 6.1 %) and the exchangeable (F1 = 23 ± 9.8 %) fractions. This is consistent with the elevated EF of Mn (EF > 1.5; Fig. 2) pointing to an anthropogenic enrichment. However, this fractionation pattern has been previously observed by other researchers (Yuan et al. 2004; Rodrigues and Formoso 2006) and was not attributed to anthropogenic sources. This is because Mn tends to be present in less stable phases such as ion-exchangeable Mn^{2+}, easily reducible Mn oxides and Mn enclosed in carbonate minerals (Sakan et al. 2009).

The risk assessment code (RAC), defined as the fraction of exchangeable and carbonate fractions (% F1 for BCR), was used to gain the additional insights in the assessment of environmental risk of trace metal pollution (Perin et al. 1985). Metals in this fraction are weakly bound to the sediment and present a higher environmental risk since they are more available to the aquatic system. According to

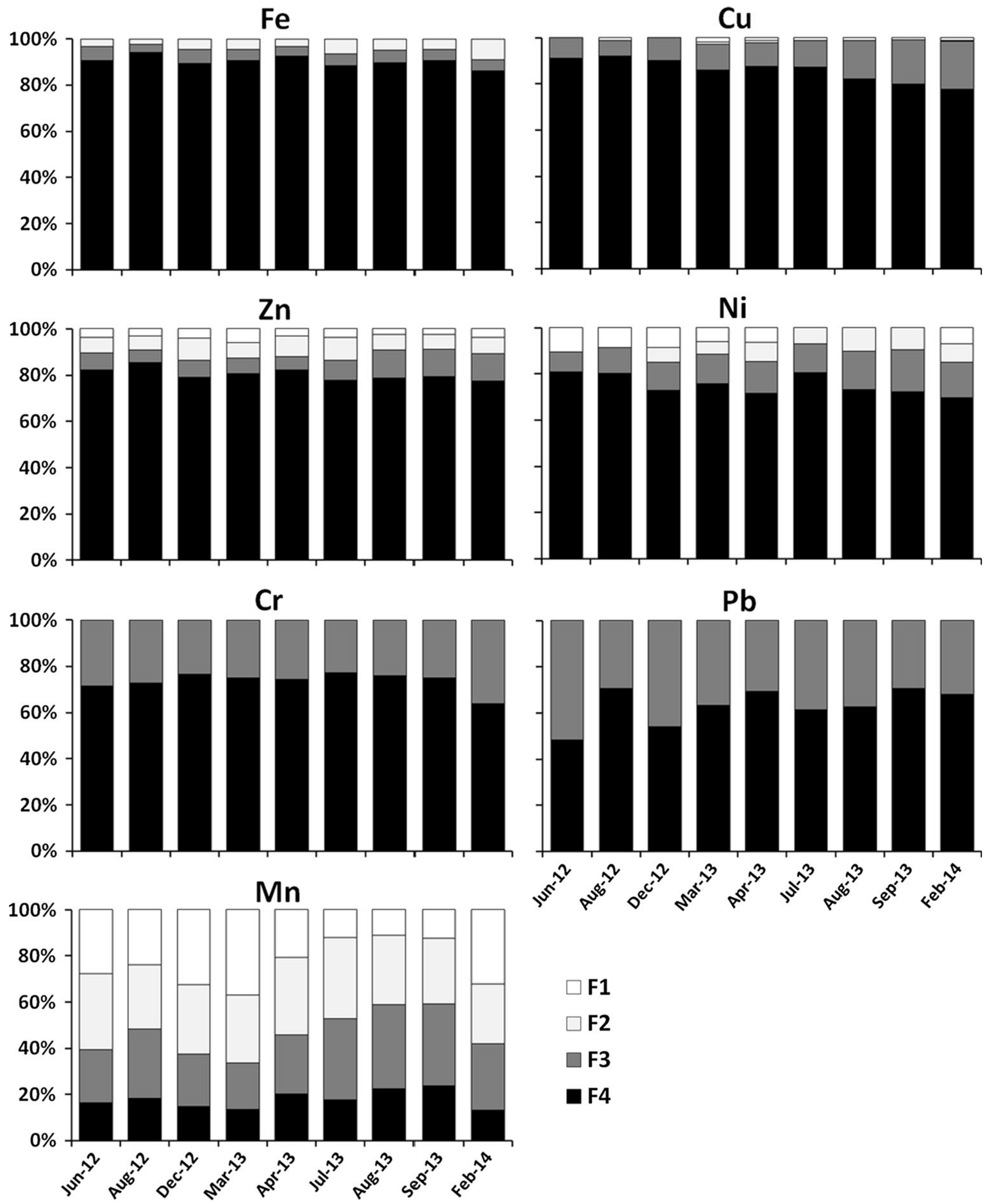

Fig. 3 Speciation of trace metals in settling particles

the RAC scheme, the risk increases from <1 % (no risk) to 1–10 % (low risk), 11–30 % (medium risk), 31–50 % (high risk), and >50 % (very high risk). The results indicate that Fe, Cu, Cr and Pb in settling particles are in the no risk category (<1 %). The speciation pattern of Zn and Ni shows low risk (1–10 %), whereas Mn is in the medium risk category (11–30 %). These results contrast with the risk assessment for Cu using SQG stressing the importance of speciation to predict bioavailability, and hence toxicity of metals.

As indicated above, Cu presented higher EFs and exceeded sediment quality guidelines insinuating a possible anthropogenic contribution. However, a sequential extraction analysis (Fig. 4) revealed that Cu concentrations were mostly in the residual fraction (90 %) yet exceeding sediment quality guidelines; this supports the interpretation of prevailing natural sources with very improbable risks. In fact, a sediment core taken in the bay revealed relatively high and uniform Cu concentrations downcore (Tatone et al. 2014), even in the bottom which presented a high abundance of the typically estuarine bivalve *Erodona mactroides* dated at 6900 ± 100 years before present, thus supporting a natural high abundance of Cu in the basin.

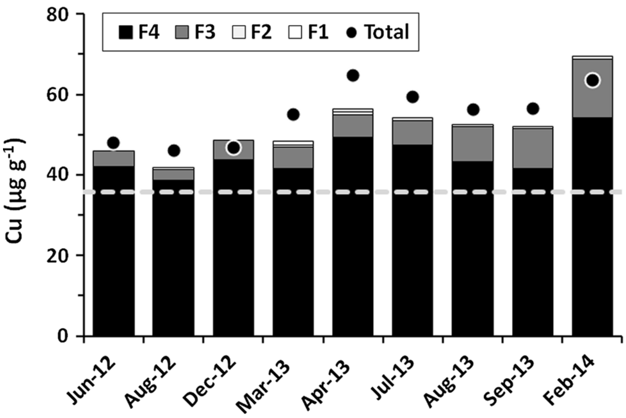

Fig. 4 Fractionation of Cu. The *horizontal line* shows the guideline of sediment quality for protection of aquatic life. *Black dots* indicate the total concentration of Cu

Conclusions

This study presents for the first time a comparative evaluation of trace metal sources and associated potential risks utilizing different criteria; EFs, SQG, speciation and RACs in the settling material from the Uruguay River. The metal contents of settling material are relatively uniform with low enrichment factors, and generally below sediment quality guidelines. The sole exception is Cu whose concentrations duplicated the SQG and presented a higher EF insinuating a possible anthropogenic contribution with occasional adverse biological effects. Contrasting with this evaluation, sequential extraction indicated that Cu is mainly associated to the immobile, residual fraction with low risks to organisms.

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