



# Mobility of trace elements between the river water, the sediments, and the pore water of Las Catonas Stream, Buenos Aires Province, Argentina

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## Abstract

The composition of river water, sediments, and pore waters (down to 30 cm below the bed) of Las Catonas Stream was studied to analyze the distribution of trace elements in a peri-urban site. The Las Catonas Stream is one of the main tributaries of Reconquista River, a highly polluted water course in the Buenos Aires Province, Argentina. The semi-consolidated Quaternary sediments of the Luján Formation are the main source of sediments for Las Catonas Stream. The coarse-grained fraction in the sediments is mainly composed of tosca (calcretes), intraclasts, bone fragments, glass shards, quartz, and aggregates of fine-grained sediments together with considerably amounts of vegetal remains. The clay minerals are illite, illite–smectite, smectite, and kaolinite. For the clay-sized fraction, the external surface area values are mostly between 70 and 110 m<sup>2</sup>g<sup>-1</sup>, although the fraction at 15 cm below the bottom of the river shows a lower surface area of 12 m<sup>2</sup>g<sup>-1</sup>. The N<sub>2</sub> adsorption–desorption isotherms at 77 K for this sample display a behavior indicative of non-porous or macroporous material, whereas the samples above and below present a typical behavior of mesoporous materials with pores between parallel plates (slit-shaped). As, Cr, Cu, and Cd concentrations increase down to 15 cm depth in the sediments, where the highest trace element and total organic carbon (TOC) concentrations were found, and then decrease toward the bottom of the core. Except for As, the levels of the other heavy metals show higher concentration in surficial waters than in pore waters. Distribution coefficients between the sediments, pore water, and surficial water phases indicate that As is released from the sediments to the pore and surficial waters. Cu content strongly correlates with TOC (mainly from vegetal remains), suggesting that this element is mainly bound to the organic phase.

**Keywords** Geochemistry · Clay minerals · Partitioning coefficient · Heavy metals

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## Introduction

River water quality may be altered by the flux of constituents (or contaminants) from the sediments into the water column, and backward, affecting living organisms in the rivers. Trace metals or metalloids are among the most ubiquitous anthropogenic contaminants. Their remobilization in sediments depends on the prevailing physico-chemical conditions in both the sediment and the water column, and on the biogeochemical processes occurring during the early diagenesis of the sediments: biogeochemical reactions [e.g., sorption, (co)precipitation, and dissolution], and physical (e.g., diffusion and advection) or biological (e.g., bioirrigation and bioturbation) transport mechanisms. Biogeochemical reactions, primarily controlled by microbial mineralization of organic matter, can increase the concentration of trace elements in pore water, and transport mechanisms can induce their transfer to the water column (Rigaud et al. 2013). The knowledge of the processes that control the dynamics of contaminants in the sediment, pore waters, and river waters improves our understanding of the environmental risk produced by the presence of contaminated sediments and would help public administration to select adequate action for remediation or contamination control.

The Río de la Plata Estuary, one of most important rivers in Argentina, provides drinking water for about 10 million people in Buenos Aires City and its surroundings (Ronco et al. 2001). One-third of its contamination is contributed by a relatively small tributary, the Reconquista

River, which runs through a densely populated region (13% of the Argentina's total population).

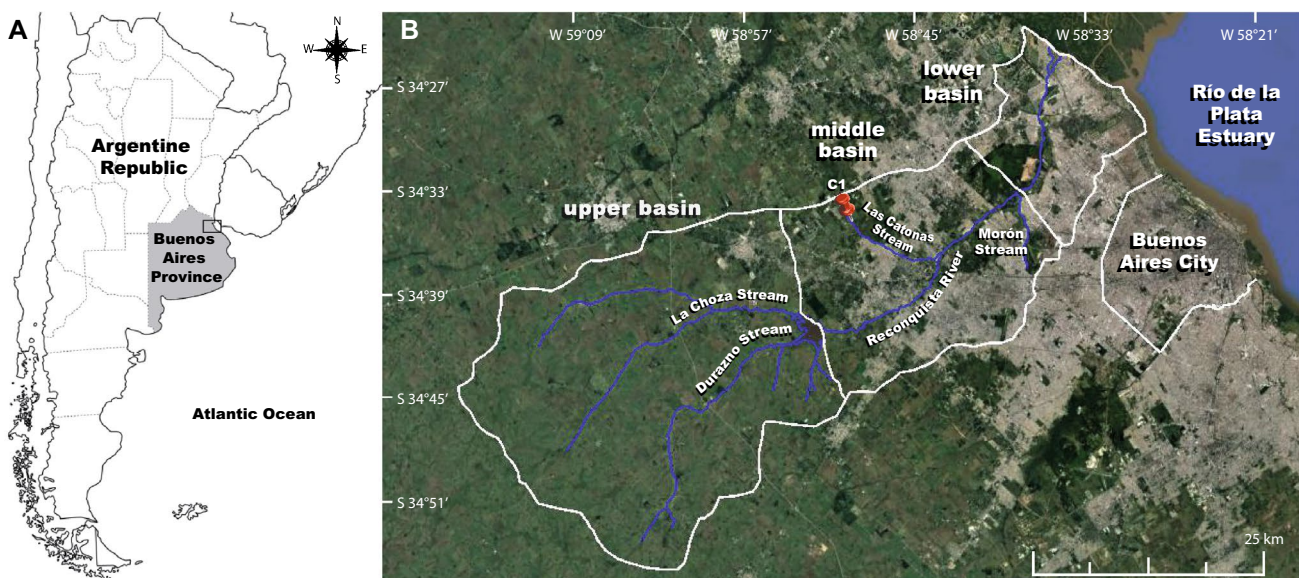
The water quality of the Reconquista River has been described in some former studies (Castañé et al. 2006; Salibián 2006, and the references cited therein), which proposed that the pollution is mainly composed of trace elements such as Cr, Cd, Pb, Cu, Zn, and As. However, no studies about the interrelation between the river water and the river sediments have been carried out up to now.

The Las Catonas Stream, one of the main tributaries in the middle basin of the Reconquista River, was chosen for this study because it is located in a peri-urban zone free of heavy industrial pollution that allows a good estimation of a geological baseline. The aim of the present study is to characterize the presence of Cr, Cd, Cu, and As in the surficial river water, the pore water, and the river bed sediments to assess the transference of elements between the water column and the sediments.

## Materials and methods

### Study area and geological background

The basin of the Reconquista River is a relatively small basin developed on a flat, lowland area near Buenos Aires City (Fig. 1). It has 134 water courses that run over a total of 606 km and contribute to the 82-km-long main course of the river. The two main tributaries are Morón and Las Catonas Streams. The Morón stream is considered the second most polluted watercourse of Argentina and one of the most polluted



**Fig. 1** Geographic location of the Reconquista River basin in the Buenos Aires Province, Argentina (a). The inset map shows Las Catonas Stream sample location (b)

of South America (Kuczynski 2016). On the other hand, the water quality of Las Catonas catchment, with a drainage area of approximately 180 km<sup>2</sup> in the Moreno District of the Buenos Aires Province, is less known (Vullo et al. 2005).

It is possible to differentiate two patterns of territory use in the Reconquista River basin. The upper basin is a predominantly agricultural area with low population density and less pollution, while the middle and lower basin are heavily urbanized and industrialized areas with high population density. Although the Las Catonas Stream belongs to the middle basin, the conditions in the studied site, close to the stream source, are similar to those of the upper basin (Fig. 1).

The region has a temperate humid climate with a monthly mean temperature of  $25 \pm 1$  °C in January, February, and March. The precipitation achieved during these months in 2015 was about 230 mm, while the average annual rainfall is 1100 mm (INTA 2015).

The Las Catonas Stream, as well as the Reconquista River, is entrenched in a thick mantle of semi-consolidated Quaternary sediments called loess pampeano (INTA 1990). The stratigraphic succession exposed in the cliffy margins of the Reconquista River is similar to the well-known stratigraphic succession in the Luján River (Toledo 2011). According to Toledo (2011), the La Plata Formation, Luján Formation, Buenos Aires Formation, and Ensenada Formation crop out in the Reconquista River. The La Plata Formation is poorly developed in the uppermost part of the column because of anthropic modifications and mixing with recent alluvial sediments (Toledo 2011). Only the uppermost part of that column, the Luján Formation, is exposed at the margins of Las Catonas Stream.

## Sampling design

Water and sediments samples were taken in March 2015 in C1 site (Fig. 1), which is located at S 34°34'51.0" W 58°49'25.6". Water samples were collected by duplicate, in plastic bottles, transported to the laboratory on ice packs, and stored at 4 °C in dark conditions. Major inorganic anions plus ammonium were determined in water samples without preservation, while trace elements were determined in water samples treated and preserved as is indicated in "Physical and chemical analyses of water samples" section. Sediment cores were sampled in PVC tubes, preserved and transported to the laboratory at 4 °C. A 30-cm-long sediment core was sampled every 5 cm, from top to base, namely C1T5, C1T10, C1T15, C1T20, C1T25, and C1T30.

## Physical and chemical analyses of water samples

All the analytical methods are described in the Standard Methods for the Examination of Water and Wastewaters (APHA 1992).

Physicochemical parameters such as temperature, conductivity, pH, dissolved oxygen (DO), and turbidity were measured by duplicate in situ in the field. Temperature, pH, and electrical conductivity were measured using a Hanna HI9812-5 Multiparameter Meter; DO and turbidity were measured using a Hach HQ30d Portable Oximeter and a Hach 2100P Portable Turbidimeter, respectively.

A portion of the sample was filtered through cellulose acetate membranes of 0.45 µm pore diameter to carry out the chemical analyses. Available phosphorus, nitrate, nitrite, and ammonium were determined by UV-visible spectrophotometry techniques. The hardness and alkalinity parameters were determined by the analytical method based on complexation reactions and acid base titration using Hach brand field burettes. Chemical oxygen demand (COD) was performed with a photometric method using potassium dichromate to oxidize organic compounds. All the chemical analyses were performed within a 48-h period after sampling.

Chloride and sulfate determinations were performed by ion exchange chromatography using a DIONEX DX-100 chromatograph with a conductivity detector, a sample injection valve, and a 25 µL sample loop. Two plastic anion columns were coupled in series to serve both as pre-column (DIONEX AG-22) and analytical chromatographic column (DIONEX AS-22). The suppression was made using a micromembrane ASRS-ULTRA II. A mixture of 4.5 mM Na<sub>2</sub>CO<sub>3</sub>/1.4 mM NaHCO<sub>3</sub> was chosen as eluent with a flow rate of 1 mL min<sup>-1</sup>.

For Cr, Cd, Cu, and As determination, samples were filtered with cellulose acetate membranes of 0.45 µm pore diameter, acidified with HNO<sub>3</sub> (free of metals) to pH 2, and analyzed by atomic absorption spectrometry with graphite furnace (AAS-GF) in a Perkin Elmer AA800 equipment. Flame atomic absorption spectrometry mode (FAAS) was used for Zn content measurements. A standard reference material SRM 1643e was used for calibration purposes.

## Pore water samples

The pore water extraction was performed at different depths of the sediment core, using the cold centrifugation method (Bufflap and Allen 1995). Centrifugation was conducted using 40 mL polycarbonate centrifuge tubes with sealing caps in a Sigma 3-18K refrigerated centrifuge at 4 °C and 3500 r.p.m. (2800g) for 40 min. The supernatant liquid was filtered through a 0.45 µm filter and stored in the dark at 4 °C.

The available phosphorus and trace element concentrations were measured using the techniques previously mentioned for water analysis.

## Sediments samples

After pore water extraction, sediment samples were air-dried, mechanically disaggregated, and then sieved in 200  $\mu\text{m}$  mesh for X-ray fluorescence (XRF), X-ray diffraction (XRD), and total organic carbon (TOC) analysis.

The sediment samples were mixed and split with the cone and quartering technique and then cupped in the sample cups for further analysis. The NITON XL3 Gold + X-ray Fluorescence analyzer was tested with a TILL4 certified reference sample between each sample analysis. Element composition was quantified by XRF as an average of multiple determinations ( $9 < n < 11$ ). The statistical analysis involved a parametrical ANOVA test, whereas the averages were compared through the Tukey test ( $\alpha = 0.05$ ).

XRD analysis on bulk samples was performed by means of a Siemens D5000 diffractometer using graphite-monochromated Cu-K $\alpha$  radiation. The samples were run in the  $2\theta$  range  $10^\circ$ – $70^\circ$ , using steps of  $0.02^\circ$  and 2 s per step for reading time. A voltage of 40 kV and amperage of 30 mA were used. XRD patterns were analyzed using the X-ray diffraction Pattern Processing software from JADE package (Materials Data Inc. 2004).

Total organic carbon (TOC) was determined by treating an aliquot of dried sample with concentrated hydrochloric acid to remove inorganic carbon prior to instrument analysis (Nelson and Sommers 1996). The sediments were dried at around  $1000^\circ\text{C}$  and the percentage of TOC was determined using a LECO C230CH Carbon Analyzer. The equipment was calibrated during TOC determination using certified standards every five samples. The analytical error was lower than 10%.

Clay-sized sediments samples (fraction below 2  $\mu\text{m}$ ) and silt-/sand-sized sediments samples (fraction between 2 and 2000  $\mu\text{m}$ ) were obtained from the sediments by gravitational sedimentation in Atterberg tubes. The sediments silt-/sand-sized fractions were described by observation under a binocular microscope. Clay-sized representative air-dried oriented (N), glycolated (EG), and heat-treated (HT) samples have been prepared. The ethylene glycol solvation was accomplished by exposure to vapor at  $25^\circ\text{C}$  for 24 h, whereas the heat-treated samples were kept at  $550^\circ\text{C}$  for 1 h and, subsequently, examined by XRD. The range for  $2\theta$  was equal to  $5^\circ$ – $35^\circ$ , using steps of  $0.02^\circ$  and 3 s per step for reading time. Voltage of 40 kV and amperage of 35 mA were used.

Specific surface areas (SSA) were determined by  $\text{N}_2(\text{g})$  adsorption–desorption experiments at 77 K, using a manometric adsorption apparatus (AccuSorb 2100, Micromeritics). The measurements were conducted on the fine fraction below 2  $\mu\text{m}$  previously outgassed at  $60^\circ\text{C}$  during 15 h. Higher outgassing temperatures were avoided to prevent phase changes in the samples. The SSA values were obtained

by the Brunauer–Emmett–Teller (BET) method, using a relative pressure range of 0.05–0.25 (Brunauer et al. 1938).

## Partitioning coefficients

A better understanding of trace elements behavior is needed to guide management efforts to improve water quality and ecosystem health (Canavan et al. 2007). According to Perriñez (2009), dissolved metals from the water column have a certain affinity to the river bed sediments. Thus, metals adsorbed on the sediment surface will be buried by particle deposition of younger sediments and will migrate below the mixed sediment layer which directly interacts with the dissolved phase.

Once the metal and metalloid contents of each phase were determined, the relations between the sediment (Sd), pore water (PW), and surficial water (SW) phase contents were assessed in terms of distribution coefficients (Fernández-Ortiz de Vallejuelo et al. 2014). The distribution or partitioning coefficient  $K_{\text{PW}/\text{SW}}$  denotes the ratio between the dissolved metal content in surficial water ( $C_{\text{SW}}$ ,  $\mu\text{g L}^{-1}$ ) and pore water ( $C_{\text{PW}}$ ,  $\mu\text{g L}^{-1}$ ), and could be defined by Eq. (1) (Duursma and Carroll 2012; Fernández-Ortiz de Vallejuelo et al. 2014)

$$K_{\text{PW}/\text{SW}} = C_{\text{PW}} / C_{\text{SW}} \quad (1)$$

Likewise, a second partitioning coefficient ( $K_{\text{S}/\text{PW}}$ ) was defined.  $K_{\text{S}/\text{PW}}$  denotes the ratio between the metal content in sediment ( $C_{\text{Sd}}$ ,  $\mu\text{g kg}^{-1}$ ) and pore water ( $C_{\text{PW}}$ ,  $\mu\text{g L}^{-1}$ ), and could be defined by the following equation:

$$K_{\text{Sd}/\text{PW}} = C_{\text{Sd}} / C_{\text{PW}} \quad (2)$$

## Results and discussion

### Chemical characterization of sediment samples

Major element composition (Fe, Ti, Ca, K, S, P, and Mn) is expressed as percentage of the corresponding oxide in Table 1. Mn concentration was relatively constant from C1T5 to C1T20, further down increased with increasing depth. Fe content decreased slightly downcore with less than 10% difference from the mean Fe content value ( $4.8 \pm 0.4\%$   $\text{Fe}_2\text{O}_3$ ). The Fe content was similar to that found in the Matanza-Riachuelo River sediments,  $4.3 \pm 0.4\%$   $\text{Fe}_2\text{O}_3$ , (Rendina and Iorio 2012). Minimum levels of K and a singularly high level of S were found in the sample C1T15. Calcium levels were higher in the upper samples (C1T5 = 2.83 and C1T10 = 3.03) and varied between 1.82 and 2.30% in the three lower samples. Phosphorous level strongly increased downcore. TOC percentages (Table 2) showed a maximum at C1T15, which was at least two times higher than the percentages of the other samples.



**Table 1** Major element composition (in wt%) for sediments in C1 site at different depths below the river bed

	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	K <sub>2</sub> O	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	MnO
C1T5	5.31 (0.03) <sup>a</sup>	0.69 (0.01) <sup>a</sup>	2.83 (0.07) <sup>a</sup>	1.79 (0.02) <sup>a</sup>	0.47 (0.07) <sup>a</sup>	0.12 (0.02) <sup>a</sup>	0.068 (0.002) <sup>a</sup>
C1T10	5.11 (0.10) <sup>b</sup>	0.65 (0.03) <sup>b</sup>	3.03 (0.12) <sup>b</sup>	1.65 (0.08) <sup>b</sup>	0.82 (0.08) <sup>b</sup>	0.16 (0.04) <sup>b</sup>	0.068 (0.002) <sup>a</sup>
C1T15	4.93 (0.03) <sup>c</sup>	0.68 (0.01) <sup>b</sup>	1.92 (0.03) <sup>c</sup>	1.55 (0.02) <sup>c</sup>	1.43 (0.11) <sup>c</sup>	0.20 (0.02) <sup>c</sup>	0.063 (0.003) <sup>a</sup>
C1T20	4.44 (0.06) <sup>d</sup>	0.65 (0.01) <sup>b</sup>	1.88 (0.09) <sup>c</sup>	1.59 (0.03) <sup>b</sup>	0.85 (0.09) <sup>b</sup>	0.22 (0.03) <sup>cd</sup>	0.064 (0.002) <sup>a</sup>
C1T25	4.77 (0.04) <sup>e</sup>	0.69 (0.01) <sup>b</sup>	1.82 (0.03) <sup>c</sup>	1.62 (0.03) <sup>b</sup>	1.18 (0.04) <sup>d</sup>	0.25 (0.02) <sup>d</sup>	0.073 (0.002) <sup>b</sup>
C1T30	4.44 (0.10) <sup>d</sup>	0.68 (0.06) <sup>b</sup>	2.30 (0.06) <sup>d</sup>	1.63 (0.03) <sup>b</sup>	1.08 (0.11) <sup>d</sup>	0.21 (0.02) <sup>c</sup>	0.093 (0.008) <sup>c</sup>
TILL 4 measured	5.53 (0.98)	0.91 (0.18)	0.85 (0.45)	3.11 (0.53)	1.8 (0.3)	0.45 (0.10)	0.057 (0.004)
TILL 4 certified value	5.43	0.81	1.25	3.25	NR	0.2	0.06

Standard deviation is reported between parentheses. Values followed by the same letter indicate no significant differences between mean values according to Tukey test ( $p < 0.05$ )

NR not reported

**Table 2** TOC and surface area of the fractions below 2  $\mu\text{m}$  in sediments at different depths under the river bed

Sample	TOC (%)	Surface area ( $\text{m}^2 \text{g}^{-1}$ )
C1T5	$0.1 \pm 0.1$	ND
C1T10	$2.7 \pm 0.3$	$72.60 \pm 0.20$
C1T15	$7.2 \pm 0.7$	$12.33 \pm 0.03$
C1T20	$3.7 \pm 0.4$	ND
C1T25	$3.5 \pm 0.3$	ND
C1T30	$1.4 \pm 0.1$	$110.00 \pm 0.20$

ND not determined

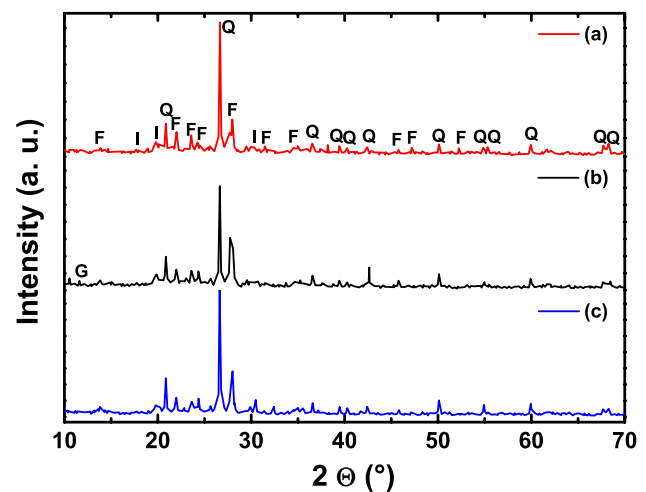
**Table 3** Composition of the sediments in the sand-sized fraction

	C1T10	C1T15	C1T30
Quartz	40	1	45
Intraclasts/aggregates	35	69	15
Tosca (calcretes)	10	NP	25
Glass shards	NP	NP	<1
Vegetal remains/organic debris	13	30	15
Other components	2	<1	<1

NP no presence

## Sedimentology of the river sediments

Binocular microscope analysis (Table 3) showed that sediments in the river bed were mainly formed by erosion of the Pleistocene–Holocene units, cropping out on the river margins and recent soils on top of them. This was evidenced by the presence of pedogenic fragments (tosca), intraclasts, fossilized bone fragments, glass shards, and well-rounded quartz clasts derived from older aeolian sediments in the sand-sized fraction. Aggregates of fine-grained sediments were common and suggest pelletization of sediments prior to final sedimentation. Considerable amounts of minute



**Fig. 2** Diffractograms of the C1 core bulk sediments samples at different depths. a C1T10. b C1T15. c C1T30. Main compounds identified are marked by Q (quartz; SiO<sub>2</sub>); F [feldspar; XAl(Si,Al)Si<sub>2</sub>O<sub>8</sub> with X=K, Na, Ca, Ba, Sr]; and I (illite; (K,H<sub>3</sub>O)(Al,Mg,Fe)<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>[(OH)<sub>2</sub>(H<sub>2</sub>O)])

debris from plants of the natural grasslands, exotic trees planted at the river margin, and aquatic plants, as well as some anthropic remains (e.g., brick and plastic fragments) were found in some levels. Small valves of ostracodes were also found in the sediments.

## Mineralogical characterization of sediment samples

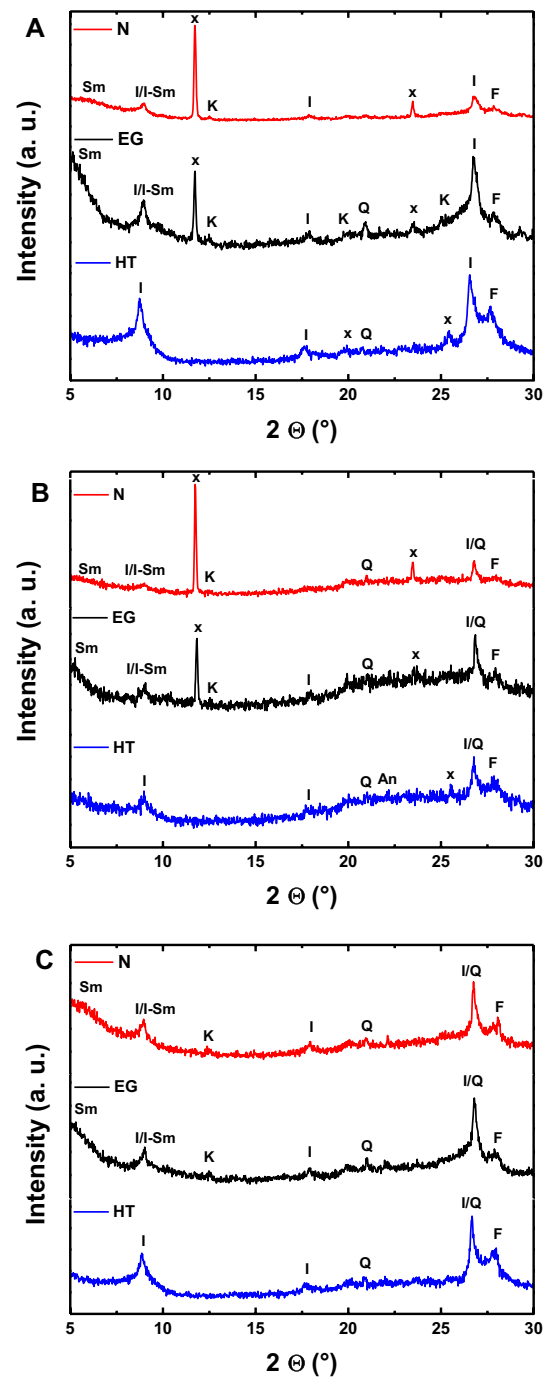
The main quartz peaks were easily recognized in the XRD analysis on bulk sediments samples (Fig. 2). Several feldspar peaks around  $2\theta$  27.8° were also clearly visible. Faint peaks ascribable to clay minerals ( $2\theta$  17.7, 19.8°) and calcium sulfate ( $2\theta$  11.7°) were also observed in the XRD patterns. A similar qualitative mineral composition was found by Porzionato et al. (2017).

Illite, smectite, randomly interstratified illite–smectite, and kaolinite were determined in the clay fraction. Clay minerals are important for the mobilization of heavy metals, mainly due to their physical and chemical properties such as small particle size, large specific area, and agglutinated texture. Then, considering that the bulk sediment XRD patterns suggested the occurrence of different types of clays, the fine-grained fraction of the sediments was extracted and analyzed by XRD. It corresponds to particles smaller than 2  $\mu\text{m}$ , in which minerals such as carbonates, feldspars, quartz, and Fe/Al hydroxides could also be present (Heller-Kallai et al. 2006).

Illite was identified by its characteristic reflection at  $2\theta$  8.7 and 17.8° (Fig. 3) (Moore and Reynolds 1997). The air-dried-oriented sample (N) showed a reflection at about 6°  $2\theta$ , which under ethylene glycol treatment (EG) shifted toward  $2\theta$  5.2°. This reflection collapsed to  $2\theta$  10° in the heat-treated sample (HT), indicating the presence of smectite. According to the diffraction patterns analyzed, this clay mineral might belong to a montmorillonite type of smectite. A reflection at  $2\theta \sim 8.89^\circ$  and a pronounced shoulder at  $2\theta \sim 5^\circ$  to 7° could be observed under the N and EG conditions. The interpretation for both diffractograms along with the fact that the peak and the shoulder collapse into a single peak at  $2\theta$  8.99° (under HT condition), confirmed the presence of randomly interstratified illite–smectites (I–Sm) layers (Lagaly et al. 2013; Moore and Reynolds 1997). Kaolinite was also identified because of its reflection at  $2\theta$  12.5° and 25°. These reflections may also correspond to chlorite, or a mixture of chlorite and kaolinite. However, the disappearance of the diffraction peaks after the heating treatment, because of the collapse of the crystalline structure, was diagnostic for kaolinite (Moore and Reynolds 1997).

The diffractograms of the upper samples (C1T10 and C1T15) showed the characteristic gypsum peaks at  $2\theta$  11.7° and  $2\theta$  23.45° in N samples, also observed in the bulk C1T15. The gypsum peaks collapsed to a main peak of anhydride calcium sulfate (An;  $2\theta$  25.6°) in the HT samples. Small amounts of quartz and feldspar were also found in the fine fraction. In conclusion, the minerals identified in the clay-sized sediments samples were I (illite), I–Sm (illite–smectite), Sm (smectite), K (kaolinite), Q (quartz), and F (feldspar).

The mineralogical analysis revealed that the main source of sediments for the Las Catonas Stream and Reconquista River were the semi-consolidated Quaternary sediments of the La Plata, Luján, Buenos Aires, and Ensenada Formations. The erosion of these units, which often contain paleosols as well as recent soils on top of the succession along the river entrenchment, provides most of the clastic materials found in the river bed. This kind of reworking was common all over the Quaternary and it is still going on. Consequently, the clay mineral association in Las Catonas



**Fig. 3** Diffractograms for the fraction below 2  $\mu\text{m}$  of the core samples: **a** 10 cm depth (C1T10), **b** 15 cm depth (C1T15), and **c** 30 cm depth (C1T30). *N* air-dried, *EG* glycolated, *HT* heat treated. Main compounds identified are marked by I (illite), I–Sm (illite–smectite), Sm (smectite), K [kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ], and F [feldspar;  $\text{XAl}(\text{Si},\text{Al})\text{Si}_2\text{O}_8$  with  $\text{X}=\text{K}, \text{Na}, \text{Ca}, \text{Ba}, \text{Sr}$ ]. The peak identified with an “x” corresponds to a phosphate compound precipitated during the sample preparation

Stream corresponds to a mixture of different sources. Illite is the dominant clay mineral in most argentine Pleistocene–Holocene loess sequences, whereas smectite and kaolinite are minor components (Camili3n 1993). For example, Gonz1lez Bonorino (1966) found that clay minerals in the Lujanense facies had a predominant illitic composition with subordinate amounts of smectite and kaolinite. In the Matanza River, 20 km SE of the Reconquista basin, this author found about 70% of illite, 10% of kaolinite, and 20% montmorillonite in the clay fraction below 2  $\mu\text{m}$ . Manassero et al. (2008) also reported a similar clay composition in sediments of the rivers Areco and Arrecifes, 60 km NW of the study area. Mixed layer clay illite–smectite could be associated with abundant and previous smectitic clay alteration by weathering or diagenetic origins (Manassero et al. 2008).

### Surficial characterization of fine fraction samples

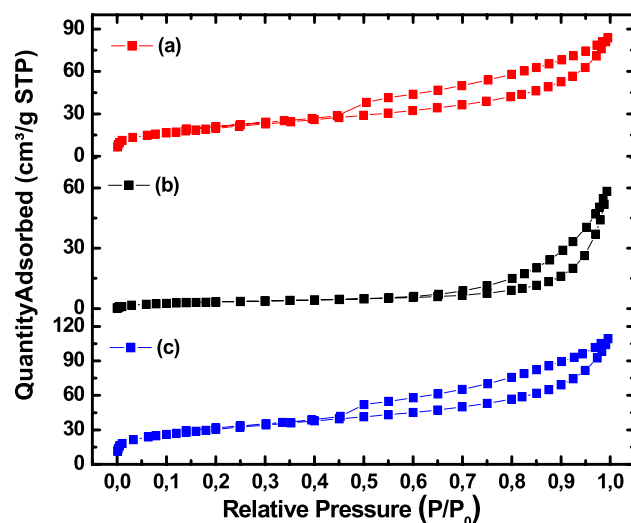
Understanding sorption processes in natural substrates requires specific surface area measurements, especially in the fine sediment fraction. SSA determinations of the fractions below 2  $\mu\text{m}$  are reported in Table 2. According to the BET model, the external surface area values determined were between 70 and 110  $\text{m}^2 \text{g}^{-1}$  for the different samples. The sample C1T15 showed a particular low surface area value of 12  $\text{m}^2 \text{g}^{-1}$ .

The  $\text{N}_2$  adsorption–desorption isotherms at 77 K for C1T10 and C1T30 (Fig. 4a, c) presented Type IV shape and a Type H3 hysteresis loop according to the IUPAC classification (Sing 1985). These features are typical of mesoporous materials with pores between parallel plates (slit-shaped), as are the pillared clays (Sing 1985; Kuila

and Prasad 2013; Rouquerol et al. 2013). The isotherms also showed the “force closure” of the desorption branch at  $0.35 < P/P_0 < 0.55$  due to the “tensile strength effect”. Conversely, the C1T15 displayed a Type II isotherm and a hysteresis (Type H3) extremely narrow, indicating a non-porous or a macroporous material (Fig. 4b). The amount adsorbed at very low-relative pressure ( $P/P_0 < 0.01$ ) was very low, indicating that the sediment had negligible or nonexistent micropores (Sing 1985; Kuila and Prasad 2013; Rouquerol et al. 2013). This result was consistent with the low SSA value found in the C1T15 sample (12  $\text{m}^2 \text{g}^{-1}$ ). In all cases, the absence of a plateau at high  $P/P_0$  also indicated the presence of macropores.

### Characterization of surficial water samples

The surface water quality in C1 showed levels of dissolved oxygen around 72% of oxygen saturation and turbidity of 23.6 NTU. COD and inorganic nitrogen (ammonium, nitrite, and nitrate) and available phosphorus (ortho-phosphate) concentrations are shown in Table 4. These concentrations do not exceed the maximum guidelines established for fresh surface water for aquatic life protection according to the Recommended Aquatic Life Criteria, US EPA (2016). Similar results were found in Roggero Reservoir and upstream Reconquista River by Rigacci et al. (2013). However, these authors found a decrease in water quality in Reconquista River downstream. The concentration of dissolved oxygen was lower than the results found in Las Catonas Stream and there was an increase in several contamination parameters such as COD, nitrite, ammonia, and phosphorus concentration compared to the results found in C1.



**Fig. 4**  $\text{N}_2$  adsorption–desorption isotherms exhibited for the fractions below 2  $\mu\text{m}$  sediment samples; C1T10 (dashed red square, a), C1T15 (dashed black triangle, b), and C1T30 (dashed blue circle, c)

**Table 4** Physicochemical parameters for the surface waters in C1 site

Parameter	C1
Temperature ( $^{\circ}\text{C}$ )	$23.1 \pm 0.3$
Dissolved oxygen ( $\text{mg O}_2 \text{L}^{-1}$ )	$6.2 \pm 0.2$
pH	$7.8 \pm 0.1$
Electrical conductivity ( $\mu\text{S cm}^{-1}$ )	$1130 \pm 7$
Turbidity (NTU)	$23.8 \pm 0.4$
Alkalinity ( $\text{mg CaCO}_3 \text{L}^{-1}$ )	$418 \pm 20$
Hardness ( $\text{mg CaCO}_3 \text{L}^{-1}$ )	$155 \pm 7$
COD ( $\text{mg O}_2 \text{L}^{-1}$ )	$1 \pm 1$
Nitrite ( $\text{mg N L}^{-1}$ )	$0.039 \pm 0.002$
Nitrate ( $\text{mg N L}^{-1}$ )	$1.0 \pm 0.1$
Ammonia ( $\text{mg N L}^{-1}$ )	$0.02 \pm 0.01$
Ortho-phosphate ( $\text{mg P L}^{-1}$ )	$1.1 \pm 0.1$
Chloride ( $\text{mg Cl}^{-} \text{L}^{-1}$ )	$78 \pm 5$
Sulfate ( $\text{mg SO}_4^{-2} \text{L}^{-1}$ )	$29 \pm 2$

## Distribution of trace elements with depth in the sediment core

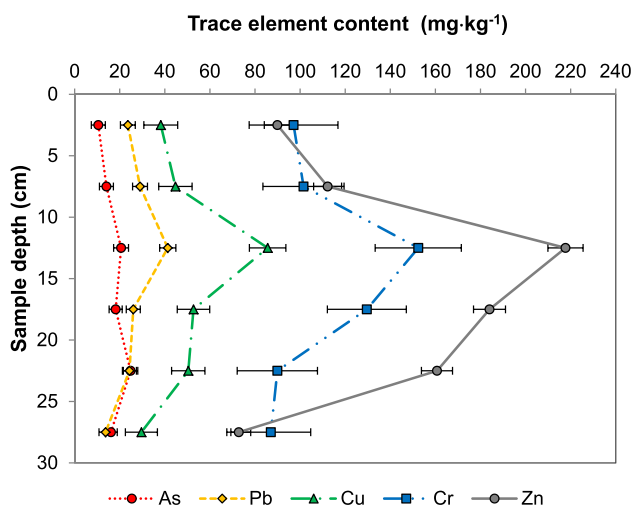
Hazardous element accumulation and sorption capacity in bottom and suspended sediments from different types of aquatic environments have been intensively studied for several decades (Salomons and Förstner 1984; Horowitz 1985; Fergusson 1991; Ronco et al. 2008).

Trace element profiles in Las Catonas Stream sediments showed a similar variation with depth (Fig. 5). The element concentrations increased down to the sample C1T15, where the highest trace element concentrations were found, and then decreased down to the bottom of the core.

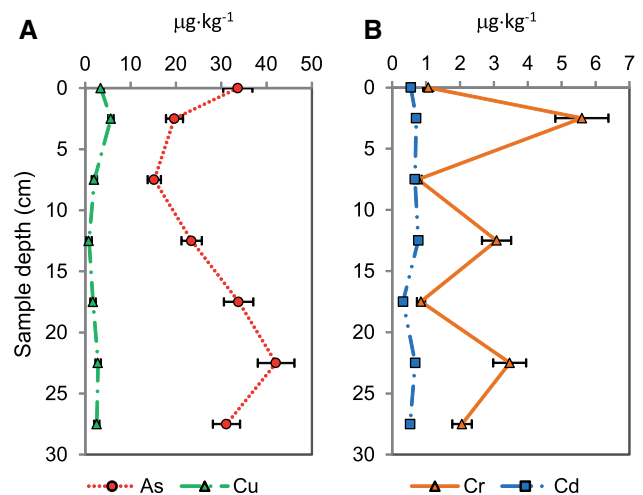
The concentration of Pb and Zn determined in the top sediments (0–5 cm) were similar to those found in the farming and cattle grazing areas in the Matanza-Riachuelo upper basin, while the Cu content was similar to the peri-urban and industrial area in the Matanza-Riachuelo middle basin (Rendina and Iorio 2012). Except for Cr, the levels were lower than those reported for Reconquista River downstream by Porzionato et al. (2017).

In any case, these results do not exceed the threshold levels established according to current legislations (Ley N° 24.051 1993) for urban, residential or industrial use and acceptable background levels.

Dissolved metal and As concentrations in the river and pore waters are shown in Fig. 6. The values of dissolved Cd and most of the Cu and Cr values exceeded the total concentration limits allowed in Argentina for freshwater aquatic life protection (Ley N° 24.051 1993). Despite the fact that arsenic levels did not exceed the recommended concentration established by this current Argentinian regulations (50



**Fig. 5** Sediment distribution of As, Pb, Cu, Cr, and Zn from sediments core samples expressed in  $\text{mg kg}^{-1}$ . Cd content was less than  $7 \text{ mg kg}^{-1}$



**Fig. 6** Vertical distribution of Cr and Cd (a); As and Cu (b) in surficial (depth 0) and pore waters expressed in  $\mu\text{g L}^{-1}$

$\mu\text{g L}^{-1}$ ), the concentrations found were higher than the level recommended by the WHO (1996) ( $10 \mu\text{g L}^{-1}$ ) in all cases.

The retention capacity of the bottom sediments is controlled by three factors: the composition (e.g., Fe and Mn oxides/hydroxides, carbonates, organic substances, and biological materials), the specific surface area of clays, and the hydraulic processes within the stream (Ronco et al. 2001).

Fe content showed similar concentrations than those previously reported by Rendina and Iorio (2012) for Matanza-Riachuelo River. Nevertheless, the iron content exhibited a slightly decreasing depth profile. This implied that there was a little additional Fe input in the study area and that most of the Fe in the sediments may have been of lithogenic origin. However, other results (e.g., large vertical variations in Si, Mn, and TOC contents and clay-specific surface area) suggested that there was some heterogeneity in the sediments composition with depth.

Chemical and mineralogical analyses showed a distinctive sediment layer between 15 and 20 cm depth (C1T15). In this fraction, FRX determinations indicated particularly high levels of trace elements such as Pb, Cr, Zn, and Cu. They could have been adsorbed in the fine sediment fraction (below  $2 \mu\text{m}$ ). However, nitrogen adsorption in C1T15 indicated that it had the lowest surface area ( $12 \text{ m}^2 \text{ g}^{-1}$ ) compared to the rest of the samples. On the other hand, C1T15 sample exhibited the highest TOC percentages (7.21%), at least duplicating the values of the rest of the samples, consistent with the high content of plant remains observed. Vegetal organic matter content in silt-/sand-sized sediment samples ( $\sim 30\%$ ) compared to C1T10 and C1T30 ( $\sim 15\%$ ). Iron was a major element in sediments showing a concentration several times higher than the concentration of trace elements. As it has a good affinity to clay minerals, this metal might saturate the binding capacity of clays, as previously reported



**Table 5** Logarithmic partitioning coefficients for surficial water ( $K_{Pw/SW}$ ) and sediment–pore water ( $K_{Sd/PW}$ ) for As, Cd, Cr, and Cu

	As	Cd <sup>a</sup>	Cr	Cu
PW05/SW	0.23	−0.11	−0.72	−0.22
C1T/PW 05	2.73	ND	4.24	3.83
C1T/PW 10	2.97	ND	5.13	4.35
C1T/PW 15	2.94	ND	4.69	5.02
C1T/PW 20	2.73	ND	5.18	4.49
C1T/PW 25	2.77	ND	4.41	4.26
C1T/PW 30	2.71	ND	4.63	4.07

<sup>a</sup>Cd logarithmic partitioning coefficients for sediment–pore water were not determined (ND) because Cd concentration in sediment samples were lower than the detection limit ( $<7 \text{ mg kg}^{-1}$ )

by Ronco et al. (2001) at the Río de la Plata Estuary. As a consequence, the high trace element values found could not only be associated with the sediment fraction but, more probably, retained by vegetal organic matter.

### Partitioning coefficients

Partitioning coefficients found for As, Cd, Cr, and Cu in this study are shown in Table 5 in a logarithmic scale.

Arsenic concentration in the upper sediment pore water nearly duplicated the levels found in surficial water samples due to the effect of the partition with the sediments ( $\log K_{Sd/PW} = 2.73$ ). The arsenic levels in the pore water decreased with depth, this is consistent with the As content increase in sediments, which is observed in the increase of the partitioning coefficient  $K_{Sd/PW}$  up to  $\sim 900$  ( $\log K_{Sd/PW} \sim 2.9$ ). Then,  $K_{Sd/PW}$  decreased with coefficients values similar to those of the upper samples, around 500–600 ( $\log K_{Sd/PW} \sim 2.7$ ). The fact that anoxic environment could cause microbial degradation of organic matter could contribute to reductive metal oxides dissolution and consequently release of arsenic bound to oxides and organic phases as well (Harvey et al. 2002). Hence, these results could be indicating that there is an arsenic release effect from the sediments to the pore waters and, eventually, surficial water.

Among the trace elements measured in sediment samples, Cu had the highest levels of  $K_{Sd/PW}$ , particularly in the fraction C1T15. As presented in the above results, copper content profile strongly correlated to TOC percentage profile suggesting that this element was mainly bound to the organic phase in these sediments. Similar results were reported in the Matanza-Riachuelo River by Rendina and Iorio (2012).

Chromium partitioning coefficients showed higher  $K_{S/PW}$  levels in C1T10 and C1T20 samples. As other cationic metals, this element is rapidly and strongly adsorbed by clay minerals, Fe and Mn oxides, and the organic matter content of sediments. Particularly, C1T15 lower  $K_{S/PW}$  level could be explained by competitive adsorption with other cationic

metals. Saeedi et al. (2011) reported low adsorption capacity (26%) of this metal in presence of Pb, Cu, Zn, Cd, and Ni.

With the exception of As, the levels of Cd, Cr, and Cu showed higher concentration in surficial waters than in pore waters.

### Conclusions

Sediment characterization of the coarse-grained fraction at the bed and down to 30 cm below of the Las Catonas Stream revealed that they are mainly composed of tosca (calcretes), intraclasts, bone fragments, glass shards, quartz, aggregates of fine-grained sediments, and vegetal remains. The latter was especially abundant at 15 cm below the bottom of the river, consistent with the high TOC level found at this depth. The clay mineral association is formed by a mixture of illite, together with smectite and kaolinite as minor components. Trace element profiles in sediments, i.e., Cr, Cu, Zn, Pb, and As, showed similar variation with depth. The concentration increased down to 15 cm below the bottom of the river, where the highest concentrations were found, and then decreased down to the bottom of the core.

The partitioning coefficients between the sediment–pore water and pore water–surficial water were defined and calculated. Arsenic concentration in pore water of the shallower sediments nearly duplicates the levels found in surficial water due to the partition with sediments. Cu had the highest concentration in sediments and pore water, particularly at the depth of 15 cm. Cu and TOC profiles are positively correlated suggesting that this element is bound to the organic matter, probably through coordination to form copper complexes. Also, chromium partitioning coefficients showed higher sediment–pore water distribution levels at 10 and 20 cm of depth. This metal, as other cationic elements, is rapidly and strongly adsorbed by clay minerals, Fe and/or Mn (hydr)oxides, and the organic matter content of sediments. In particular, Cr lower distribution coefficient value at 15 cm depth could be explained by competitive adsorption with other cationic metals.

The levels of Cd, Cr, and Cu showed higher concentration in surficial waters than in pore waters, which can be attributed to anthropogenic contamination. On the contrary, As concentration was slightly higher in pore water than in surficial water. These results suggest that arsenic is released from the sediments to the pore waters and, eventually, to the surficial water, consistent with a naturally occurring source.

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