



Geochemical characterization and the assessment of trace element retention in sediments of the Reconquista River, Argentina

Cecilia Gisela Cantera · Ana Elisabeth Tufo · Roberto Adrián Scasso ·
Maria dos Santos Afonso

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Abstract The mineralogical and geochemical characterization of sediments of the Reconquista River allows analyzing the geochemical partition of trace elements in one of the most polluted water courses of Argentina. The low dissolved oxygen and high ammonia contents, together with the high chemical oxygen demand, attest to the poor water quality. Ammonia, Cd and Cu content in surficial water exceeds the maximum guidelines for freshwater in Argentina. The recent sediments of the uppermost bed

are enriched in organic matter (OM), sulfur, Zn, Cu and Pb. The enrichment factor is moderate, and the geoaccumulation index (I_{geo}) for Cu and Pb indicates uncontaminated to moderately contaminated sediments. The positive and significant correlation between As, Cr, Pb and Zn with the iron content suggests that their retention is controlled by the amount of iron oxy (hydr)oxides in the sediments, probably combined with the silt + clay abundance. In comparison with its tributary, the Las Catonas Stream, the Reconquista River, has less OM and trace elements in the sediments and more dissolved trace elements in the interstitial water. We interpret that OM is the main

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C. G. Cantera · R. A. Scasso
Instituto de Geociencias Básicas, Aplicadas y Ambientales de Buenos Aires (IGEBA), CONICET-Universidad de Buenos Aires, Ciudad Universitaria Pabellón II 1er Piso, Int. Guiraldes 2160, C1428EHA, Ciudad Autónoma de Buenos Aires, Argentina
e-mail: ceciliacantera@gmail.com

R. A. Scasso
e-mail: rscasso@yahoo.com.ar

A. E. Tufo
Instituto de Investigación e Ingeniería Ambiental (3iA), Universidad Nacional de San Martín, Campus Miguelete, 25 de Mayo y Francia, San Martín 1650, Buenos Aires, Argentina
e-mail: anaetufo@gmail.com

R. A. Scasso
Departamento de Ciencias Geológicas, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria Pabellón II 1er Piso, Int. Guiraldes 2160, C1428EHA, Ciudad Autónoma de Buenos Aires, Argentina

M. dos Santos Afonso (✉)
Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Instituto de Química Física de los Materiales, Medio Ambiente y Energía (INQUIMAE), CONICET-Universidad de Buenos Aires, Ciudad Universitaria Pabellón II 3er Piso, Universidad de Buenos Aires, Int. Guiraldes 2160, C1428EHA, Ciudad Autónoma de Buenos Aires, Argentina
e-mail: dosantos@qi.fcen.uba.ar

sorbent of the trace element. In the absence of OM, the iron oxy (hydr)oxides and the silt + clay fraction are a less efficient substitute. Consequently, the interstitial waters of the Reconquista River are enriched in these elements. Therefore, minor changes in the environmental conditions may generate significant release of hazardous trace elements from the sediments to the interstitial water and, in turn, to the surficial water of the river. As most of the big cities and the agricultural activities of Argentina are developed on the loessic substrate, the understanding of its interaction with polluted waters is crucial.

Keywords Aquatic sediments · Reconquista River · Geochemistry · Trace elements · Interstitial water

Introduction

The Reconquista River is one of the most polluted water resources of Argentina because of agricultural runoff, livestock watering and discharge of mostly untreated household and industrial waste generated by the anthropogenic activity on the densely populated areas by the riverbank. It has thus become a typical example of the adverse impact of human activities on the health of aquatic environment (Salibián, 2006). Previous studies (Nader, 2015; Ossana et al., 2013, 2016; Rigacci et al., 2013; Tufo et al., 2021; and references therein) have determined that trace elements such as chromium (Cr), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn) and arsenic (As) are the main pollutants in the water of the Reconquista River. The introduction of these trace elements is a consequence of the waste of fossil fuel combustion, leakage of metal-containing motor oils and untreated sewage discharged by electroplating, electrical, paint, food, tannery, chemistry and nonferrous smelting industries (Mondino, 2007; Pescuma & Guaresmi, 1992). The heavy metals are the most toxic and persistent elements because they increase their concentration through biomagnification in aquatic habitats (Ahmed et al., 2005). Many authors have studied their toxicological impacts on the biota (Herkovits et al., 1996; Loez & Topalián, 1999; Ossana et al., 2013, 2016; Rigacci et al., 2013). Of note, heavy metals retained in sediment particles (Cantera et al., 2018; Tufo et al., 2021) may eventually be released to water and

generate adverse effects in exposed animals and humans (e.g., Ferraro et al., 2012).

The composition of the river water is affected by the flow of constituent or polluting elements from the water to the sediments, and vice versa, affecting the quality of the water and the organisms that live in it. Former studies in the Reconquista River have highlighted the importance of the analysis of geochemical partition processes to understand the mechanisms that determine the association of pollutants with sediments, their mobilization and bioavailability (Rendina et al., 2001). It is well known that biogeochemical reactions, mainly controlled by the microbiological mineralization of OM, can increase the concentration of trace elements in interstitial water, which can be subsequently transferred to the water column (e.g., Rigaud et al., 2013). Trace elements are some of the most ubiquitous anthropogenic contaminants, and a better understanding of their water–sediment interchange is needed to improve water quality and ecosystem health (Canavan et al., 2007).

River bed sediments may behave either as contaminant acceptors or as secondary sources of contamination (Burton, 2002). The retention capacity of river sediments mainly depends on their composition, texture, surface area and the hydraulic processes of the water course. Therefore, the characterization of sediments is extremely useful to understand the retention and mobilization processes of pollutants between river waters and sediments. Moreover, the mobilization of trace elements in sediments depends on the prevailing physicochemical conditions, both in the sediment and in the water column, as well as the biogeochemical processes that occur in the early diagenesis of the sediments.

In this paper, the general geochemical and trace element characterization of the water, interstitial water and bed sediments of the Reconquista River is carried out in order to highlight the water–sediment interactions. Cores show that bed sediments are not homogeneous and include loessic Late Pleistocene–Holocene sediments besides the modern river deposits. This gives an additional interest to our analysis because most of the anthropogenic activities in the extended plains of the Pampa Húmeda region (e.g., agriculture) as well as the main cities of Argentina are developed on the loessic substrate. This type of studies is therefore crucial to understand the interaction

between polluted waters and sediments for the entire region.

Materials and methods

Study area and geological background

The studied tract of the Reconquista River is located at the Moreno District in the northeast of Buenos Aires Province, Argentina (Fig. 1a). This lowland water course joins the Luján River, which finally flows into the Río de la Plata Estuary. 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 Reconquista River is similar to the well-known stratigraphic succession in the Luján River (Toledo, 2011). According to this author, the La Plata, Luján, Buenos Aires Formations and, to a lesser extent, the Ensenada Formation crop out in the Reconquista River. The La Plata Formation is poorly exposed in the uppermost part of the column because of anthropic modifications and mixing with recent alluvial sediments (Toledo, 2011). In the studied area, the cliffs of the Reconquista River expose the La Plata Formation and the Luján Formation, which can be subdivided in the Luján Verde Superior, Lujan Rojo and Luján Verde Inferior sequences (Online Resource 1) according to Toledo (2011).

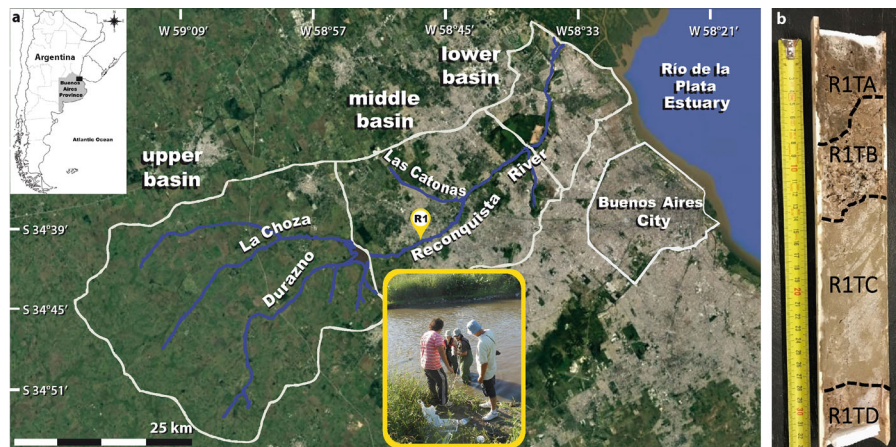
Sampling design

Water and sediment samples were collected in March 2015 at R1 site (34° 39' 58.5" S, 58° 46' 52.4" W), as part of a general survey in the Middle–Upper Basin of the Reconquista River (Fig. 1a). Surface water samples at R1 site were collected by duplicate, in plastic bottles, transported to the laboratory on ice packs and stored at 4 °C in dark conditions prior to analysis. Sediment sampling was performed manually by pushing down into the bed sediment a PVC tube (150 cm long and 10 cm bore). Eight cores were extracted in this study area. The corer penetrated the soft, unconsolidated recent sediments and the wet, softened upper part of the semi-consolidated Pleistocene–Holocene sediments. It was stopped by the dry, harder underlying part of these sediments. Sediment cores were sampled in PVC tubes, preserved and transported to the laboratory at 4 °C. Sedimentary beds were differentiated according to their sedimentological attributes, and one sample of every bed in the core R1T was studied (Fig. 1b), from top to base, namely R1TA, R1TB, R1TC and R1TD.

Physical and chemical analyses of water and sediments

All the analytical methods are described in the Standard Methods for the Examination of Water and Wastewaters (Rice et al., 2012), U.S. Environmental Protection Agency (EPA) methods (USEPA, 2019), or their equivalent as developed by Hach (2021).

Fig. 1 **a** Location of the study area and sampling site R1 in the Reconquista River Basin, Buenos Aires Province, Argentina, with inset showing sampling operations. **b** Core R1T obtained in site R1



River water

Physicochemical parameters such as temperature, conductivity, pH, dissolved oxygen (DO) and turbidity were measured in water samples by in situ duplicate analysis. 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.

Water samples were filtered through 0.45- μm pore membranes to carry out the chemical analyses. Available phosphorus, nitrate, nitrite and ammonium were determined by UV-visible spectrophotometric techniques (APHA 4500-P E, Hach 8203 MR, Hach 8507 and Hach 8155). The hardness and alkalinity parameters were determined by the titration method, based on complexation and acid base reactions, using Hach brand field burettes (Hach 8213 and Hach 8203). Chemical oxygen demand (COD) was performed with a photometric method using potassium dichromate to oxidize organic compounds (Hach 8000). 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). ASRS-ULTRA II micromembrane was employed as suppression. A mixture of 4.5 mM Na_2CO_3 /1.4 mM NaHCO_3 was used as eluent with a flow rate of 1 mL min^{-1} (APHA 4110).

Trace element determinations were performed in filtered water samples (0.45- μm pore diameter) acidified with HNO_3 (free of metals). The Cr, Cd, Cu and As content was analyzed by atomic absorption spectrometry (APHA 3005a) with graphite furnace (AAS-GF) in a Perkin Elmer AA800 equipment. A standard reference material SRM 1643e was used for calibration purposes.

Interstitial waters

Interstitial water extraction was performed by the cold centrifugation method (Bufflap & Allen, 1995) using 50-mL polycarbonate centrifuge tubes with sealing

caps in a Sigma 3–18 K refrigerated centrifuge at 4 °C and 3500 rpm (2800 g) for 40 min. The supernatant was filtered through a 0.45- μm filter and stored in the dark at 4 °C. Trace elements were measured as in the river water samples.

Sediments

After interstitial water extraction, bulk sediment samples were divided into two fractions. The first fraction was air-dried, mixed and homogenized by the cone and quartering technique for total organic carbon (TOC), X-ray diffraction (XRD), particle size and X-ray fluorescence (XRF) analysis. The second fraction was used for determining the moisture content, which was calculated by heating in oven at 105 ± 2 °C to constant weight.

TOC was determined by treating an aliquot of each dried sample with acid to remove inorganic carbon prior to instrument analysis. Then, samples were dried, and the percentage of TOC was determined using a LECO Carbon Analyzer at GeoLab Sur Laboratory.

XRD analysis on bulk samples was performed by means of a Siemens D5000 diffractometer using graphite-monochromated $\text{Cu-K}\alpha$ radiation. Samples were run from $2\theta = 10^\circ$ – 70° interval, using steps of 0.02° and 2 s per step for reading time. A voltage of 40 kV and amperage of 30 mA were used.

Clay-sized (fraction below 2 μm) and coarse clay, silt and sand-sized (fraction between 2 and 2000 μm) were separated by gravitational sedimentation in Atterberg tubes. Air-dried oriented (N), glycolated (EG) and heat-treated (HT) samples were prepared for the clay-sized fraction. The ethylene glycol solvation was accomplished by exposure to vapor at 25 °C for 24 h, whereas the heat-treated samples were kept at 550 °C for 1 h and, subsequently, examined by XRD. The range for 2θ was 5° – 35° , using steps of 0.02° and 3 s per step for reading time. Voltage of 40 kV and amperage of 35 mA were used. X-ray patterns were analyzed using the JADE software X-ray diffractometry (XRD) Pattern Processing software (Materials Data Inc. 2004).

The textural properties of the clay-sized fraction were determined by N_2 adsorption-desorption experiments at 77 K using a manometric adsorption apparatus (AccuSorb 2100, Micrometrics). The measurements were conducted on solids previously outgassed at 60 °C for 15 h. Higher outgassing

temperatures were avoided to prevent phase changes in the samples. The specific surface area (SSA), the micropore volume ($V_{\mu P}$), the total pore volume (V_{TP}) and the modal pore size (w_p^*), that includes the pore and the interparticle volume, were obtained for all samples from the nitrogen adsorption isotherms data at 77 K. The SSA was obtained by the Brunauer, Emmet and Teller (BET) method (Brunauer et al., 1938), using the relative pressure range 0.05–0.25. The micropore volume ($V_{\mu P}$) was estimated by the α_S -plot method (Sing, 1985) using a natural calcined clay as a reference material. The total pore volume (V_{TP}) was obtained by applying the Gurvich rule to the N_2 adsorption data at a relative pressure of 0.99 (Rouquerol et al., 2013). The mesopore volume (V_{mes}) was obtained by difference between V_{TP} and $V_{\mu P}$. The pore size distribution (PoreSD) of the samples (micropores and mesopores) was obtained by a macroscopic method (Villarroel Rocha et al., 2011, 2014) using the desorption branch data and assuming slit pores.

The particle size was determined with a laser diffraction particle size analyzer (Shimadzu brand model SALD-3101). The WingSALD II version 3.1.1 software calculated the grain size distribution.

Major (Fe, Ti, Ca, K, S, P, Mn) and trace (As, Pb, Cr, Cu, Cd, Zn) elements were determined by X-ray fluorescence (XRF) using a Niton XL3 GOLDD + XRF analyzer, which was tested with a TILL4 reference sample between each sample analysis. Element composition was quantified by XRF as an average of multiple determinations ($9 < n < 11$).

Enrichment factor and geoaccumulation index

The normalized enrichment factor (EF) was defined according to Eq. 1:

$$EF = \frac{\left(\frac{M}{Al}\right)_{Sample}}{\left(\frac{M}{Al}\right)_{Loess}} \quad (1)$$

where $(M/Al)_{sample}$ is the ratio of the trace elements and aluminum content of the sediments, while $(M/Al)_{Loess}$ is the ratio between the concentrations of the trace elements and aluminum of selected background (Castro et al., 2018; Simex & Helz, 1981). The $0 \leq EF < 1$ indicates no enrichment (Level I), $1 \leq EF < 3$ indicates minor enrichment (Level II), $3 < EF < 5$ indicates moderate enrichment (Level

III), $5 \leq EF < 10$ indicates moderately severe enrichment (Level IV), $10 \leq EF < 25$ corresponds to severe enrichment (Level V), $25 \leq EF < 50$ is assigned to very severe enrichment (Level VI), and $EF \geq 50$ is attributed to extremely severe enrichment (Level VII).

The trace element geoaccumulation index (Igeo) was calculated as follows:

$$Igeo = \log_2 \left(\frac{C_n}{1.5 * B_n} \right) \quad (2)$$

where C_n and B_n refer to the concentration of the metal and the baseline levels of the metal, respectively (Castro et al., 2018; Müller, 1979). Igeo values were associated with the qualitative scale of contamination (Müller, 1979). Consequently, samples may be classified as uncontaminated (U: Igeo < 0, Class 0), uncontaminated to moderately contaminated (U-MC: $0 \leq Igeo < 1$, Class 1), moderately contaminated (MC: $1 \leq Igeo < 2$ Class 2, moderately to strongly contaminated (M-SC: $2 \leq Igeo < 3$, Class 3), strongly contaminated (SC: $3 \leq Igeo < 4$, Class 4), strongly to extremely contaminated (SC-E: $4 \leq Igeo < 5$, Class 5) and extremely contaminated (EC: $Igeo \geq 5$, Class 6).

Statistical analysis

The statistical analysis involved a nonparametric ANOVA test ($\alpha = 0.05$) for sediments samples. Sediments data were reported on a dry weight basis. In addition, Pearson's correlation coefficient (r) was determined between sediments and interstitial water parameters.

Results

Characterization of surficial waters

Surficial water samples were collected at R1 site (Fig. 1a) and were characterized throughout the determination of numerous physicochemical parameters, which are shown in Table 1. Surficial waters show extremely low DO concentration (less than 6% of the maximum expected DO at the 31.6 °C water temperature), COD values higher than those previously reported in nearby sites and the nitrogen in ammonia is the 92% from the total inorganic nitrogen.

Table 1 Physicochemical parameters for the surface waters in the Reconquista River site and interstitial water (R1T)

Parameter	Surface waters	SRM 1643e measured	SRM 1643e certified value	Argentina guidelines ^a	Interstitial water			
					R1TA	R1TB	R1TC	R1TD
Temperature (°C)	31.6 ± 0.1							
Dissolved oxygen (mg O ₂ L ⁻¹)	0.4 ± 0.1							
pH	7.7 ± 0.1							
Electrical conductivity (µS cm ⁻¹)	1140 ± 7							
Turbidity (NTU)	167.5 ± 0.7							
Alkalinity (mg CaCO ₃ L ⁻¹)	417 ± 7							
Hardness (mg CaCO ₃ L ⁻¹)	105 ± 21							
COD (mg O ₂ L ⁻¹)	100 ± 4							
Nitrate (mg N L ⁻¹)	0.75 ± 0.01							
Nitrite (mg N L ⁻¹)	0.04 ± 0.02			0.06				
Ammonia (mg N L ⁻¹)	9.1 ± 0.4			1.37				
Ortho-phosphate (mg P L ⁻¹)	1.98 ± 0.01							
Chloride (mg Cl ⁻ L ⁻¹)	53.4 ± 0.4							
Sulfate (mg SO ₄ ²⁻ L ⁻¹)	64.6 ± 0.5							
Sodium (mg Na L ⁻¹)	200 ± 9							
Magnesium (mg Mg L ⁻¹)	11.1 ± 0.2							
Calcium (mg Ca L ⁻¹)	23 ± 2							
Potassium (mg K L ⁻¹)	14.9 ± 0.4							
Arsenic (µg As L ⁻¹)	38 ± 3	67 ± 3	60	50	56 ± 1	69 ± 2	61 ± 6	51.3 ± 0.9
Cadmium (µg Cd L ⁻¹)	2 ± 1	7 ± 1	7	0.2–1.8	< DL	< DL	< DL	< DL
Chromium (µg Cr L ⁻¹)	0.6 ± 0.3	19 ± 3	20	2	0.7 ± 0.2	12 ± 1	1.60 ± 0.01	1.00 ± 0.02
Copper (µg Cu L ⁻¹)	22 ± 4	21 ± 2	23	2	29 ± 3	30.1 ± 0.6	12.8 ± 0.2	17.9 ± 0.6

^aMaximum allowed values according to the Argentina Surface Freshwater Guidelines for aquatic life protection. Data expressed as mean ± SD of duplicates. Cadmium detection limit (DL) was 0.05 µg Cd L⁻¹

The order of abundance of major ions is $\text{HCO}_3^{--} > \text{Cl}^- > \text{SO}_4^{2-}$ for anions and $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ for cations. Bicarbonate is the dominant anion (58.9%), whereas chloride and sulfate are 21.3% and 19.0%, respectively. Among the major cations, Na^+ plays a dominant role in surficial water, while the concentrations of Ca^{2+} , Mg^{2+} and K^+ are relatively low compared to the sodium content (78.0%).

Trace element profiles in surficial and interstitial waters

The concentration profiles of trace elements in interstitial and surficial water are shown in Fig. 2a. All profiles present a maximum concentration value at the R1TB fraction (5–13 cm deep). Moreover, the concentration profiles follow the sequence $\text{As} > \text{Cu} > \text{Cr}$ in all the fractions which are generally higher in interstitial water than in surficial water. Arsenic concentration in interstitial water ($51\text{--}69 \mu\text{g L}^{-1}$) nearly duplicates the surficial water content for all the samples ($38 \mu\text{g L}^{-1}$). Cu content is higher than in the surficial water for the upper two samples ($22 \mu\text{g L}^{-1}$ for surficial water and ca. $30 \mu\text{g L}^{-1}$ for interstitial water in samples R1TA and R1TB). Cr concentration in interstitial water ($0.7\text{--}11.7 \mu\text{g L}^{-1}$) is higher than in surficial water ($0.6 \mu\text{g L}^{-1}$) for all samples. Noticeably, Cd was only detected in surficial water samples.

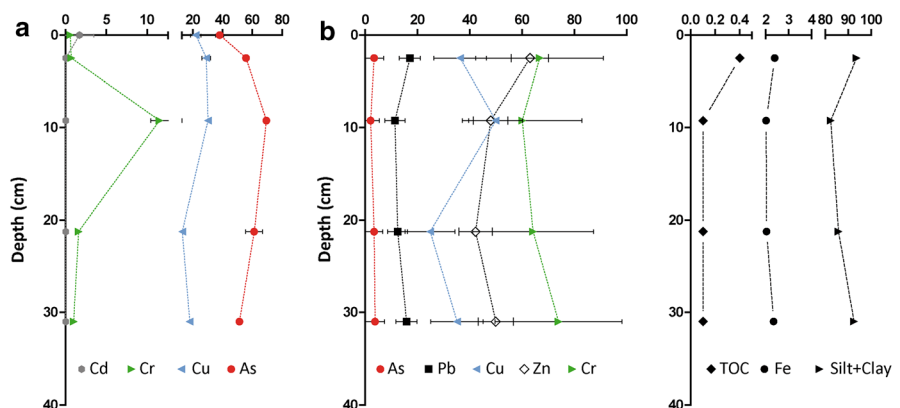
Sedimentological characterization of the sediments

Four stratigraphic intervals separated by bedding planes were distinguished in all the cores of the study area (Fig. 1b). The 5-cm-thick, topmost interval, at the river bed, is formed by a black, massive, stinky, silty sediment (sample R1TA). Its base is irregular (probably erosive), and the black sediment is loaded into the underlying conglomerate. This intraformational, granule conglomerate is 8 cm thick and has a sandy matrix (sample R1TB). Its base is an irregular, erosive bedding plane carved in the underlying 16-cm-thick green, massive, silty bed (sample R1TC), which is separated by a sharp bedding plane from the lowermost part of the core, formed by reddish brown, massive, silty sediments (sample R1TD).

Quartz, feldspar and illite are recognized in all the bulk sediment samples by XRD analysis (Fig. 3a). Calcite is identified in sample R1TB. According to the displacement of d_{104} peak (Goldsmith et al., 1961), it has about 20% of Ca^{2+} substitution by Mg^{2+} ion. R1TC diffractogram presents a peak near $31.5^\circ 2\theta$, which may correspond to a mineral of the carbonate group (huntite). This identification must be considered preliminary since it relies on the presence of a single peak of 100% intensity.

Quartz, feldspar and illite are identified in the fraction below $2 \mu\text{m}$ of all the samples. Illite is identified by its characteristic reflections at 8.7° and $17.8^\circ 2\theta$ (Moore & Reynolds, 1997). Lower contributions of interstratified illite/smectite and kaolinite are found for samples R1TA, R1TB and R1TC (Fig. 3b, R1TA, R1TB, R1TC), whereas a minor contribution of kaolinite is found in R1TD (Fig. 3b). A peak at

Fig. 2 **a** Profiles of As, Cu, Cr and Cd in surface (0 cm) and interstitial sediment waters of the Reconquista River expressed in $\mu\text{g L}^{-1}$. **b** Distribution profiles of As, Pb, Cu, Cr, Zn and TOC, Fe and silt + clay in the bed sediments of the Reconquista River (core R1T) expressed in mg kg^{-1}



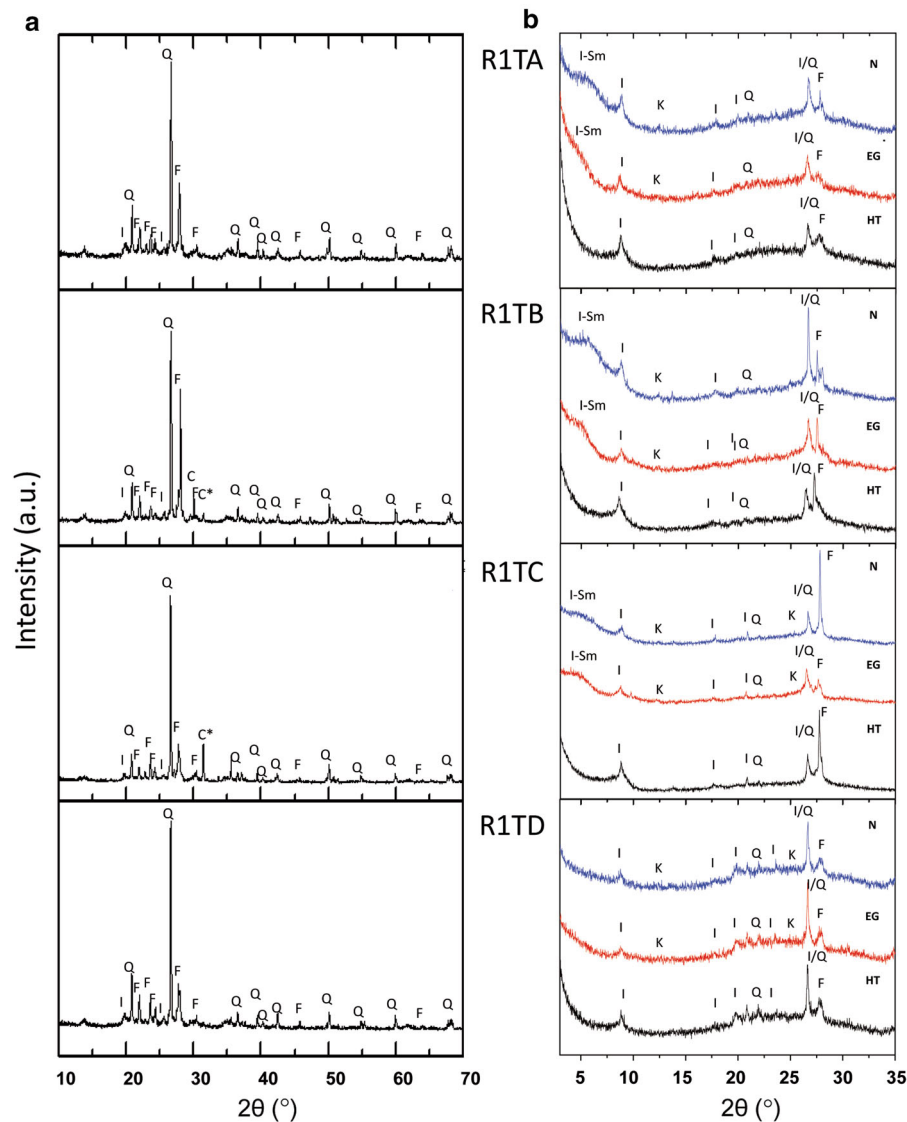


Fig. 3 **a** Diffractograms of bulk sediments at different depths in the R1T core. The minerals identified are quartz (Q), feldspar (F), calcite (C), illite (I) and a carbonate mineral preliminary determined as huntite (C*). **b** Diffractograms for the fraction

$2\theta \sim 8.89^\circ$ and a pronounced shoulder at $2\theta \sim 5\text{--}7^\circ$ are observed in N and EG samples in R1TA, R1TB and R1TC. This, together with the fact that the peak and the shoulder collapse into a single peak at $8.99^\circ 2\theta$ in HT samples, confirms the presence of illite and randomly cross-linked interstratified illite/smectite (Bergaya & Lagaly, 2013; Moore & Reynolds, 1997). Small peaks at 12.5° and $25^\circ 2\theta$ in all the N and EG samples indicate little kaolinite content. These peaks might also correspond to chlorite, or

below $2\ \mu\text{m}$ in the R1T core: A (R1TA); B (R1TB); C (R1TC) and D (R1TD). N, oriented, air-dried; EG, glycolated and HT, calcined samples. The main compounds identified are illite (I), illite-smectite (I-Sm), kaolinite (K), quartz (Q) and feldspar (F)

alternatively, to a mixture of chlorite and kaolinite. However, the disappearance of these peaks due to the collapse of the crystalline structure after calcination is diagnostic for kaolinite (Moore & Reynolds, 1997).

Grain size characterization of sediments

Most of the sediment samples from the core RT1 present a bimodal pattern, with main frequencies in both the coarse-silt and clay fractions (Online

Resource 2). The upper and bottom samples (R1TA and R1TD) consist of silt and the intermediate samples (R1TB and R1TC) of sandy silt (Folk et al., 1970). R1TB and R1TC contain relatively lower silt + clay proportion (below 90%), whereas the samples R1TA and R1TD are relatively enriched in silt + clay (94 and 92%, respectively; Table 2).

Surficial characterization of the fine fraction

According to the BET model, the SSA determined in the fine fraction (below 2 μm) of the sediment is between 101 and 156 m² g⁻¹ (Table 2). The N₂ adsorption–desorption isotherms at 77 K (Online Resource 3) exhibit a type IV shape according to the IUPAC classification, which is characteristic of mesoporous adsorbents (Sing, 1985). In all cases, the isotherms show similar curves and a type H3 hysteresis loop. This type of hysteresis presents an abrupt increase of the amount of nitrogen adsorbed at $p/p_0 > 0.8$, which reveals the presence of slit-like pores, characteristic of mesoporous materials with pores between parallel plates (slit-shaped), classical features of aggregates of platy particles (Rouquerol et al., 2013). This type of hysteresis is also indicative of non-uniform pore size distribution (Kuila & Prasad, 2013). The descending branch of the hysteresis loop shows an abrupt desorption near to 0.45 of p/p_0 , which may be associated with a cavitation-induced evaporation (spontaneous nucleation of vapor bubbles), indicating the presence of a mesoporous network with mesopore sizes smaller than 5 nm (Groen et al., 2003). The isotherm also shows the absence of a plateau at high p/p_0 , which is indicative of the presence of macropores.

The mesopore volumes (V_{MESOP}), the micropore volumes ($V_{μP}$), the modal pore size (w_P^*) and the total

pore volumes (V_{TP}) are summarized in Table 2. The volume of micropores was almost null in all the samples, and thus, the estimated total pore volume was attributed to the presence of mesopores. The V_{TP} and V_{MESOP} were higher for R1TB and R1TC, consistent with the elevated SSA. The w_P^* values slightly vary from 2.3 nm for R1TA up to 2.5 nm for R1TD.

Chemical characterization of sediments

The Reconquista River sediments show similar profiles for the concentrations of Fe, Ti, Ca and Mn (Table 3) with a significant decrease from R1TA to R1TB. Values of R1TC are similar to R1TB and they subsequently increase in R1TD. In contrast, sulfur content shows a marked decrease with depth, from 0.21 to 0.08% SO₃. Phosphorus content is relatively constant in the upper samples (R1TA to C) and increases in the bottom sample. Potassium content is maximum in R1TB and R1TC (1.85 and 1.82% K₂O, respectively).

TOC levels have a maximum value of 0.41% for the upper sample (R1TA). In the rest of the samples, the TOC values did not exceed detection limit (0.1%).

The concentration of trace elements is observed in Fig. 2b. Arsenic presents a fairly constant concentration between 2 and 4 mg kg⁻¹. Pb values keep between 11 and 17 mg kg⁻¹, while Zn and Cu range between 43 and 63 mg kg⁻¹ and 25 and 50 mg kg⁻¹, respectively. Cr concentrations are between 60 and 74 mg kg⁻¹, the highest among the trace elements analyzed. Several trace element profiles, i.e., As, Pb, Zn and Cr, show a slight decrease with depth and then, an increase in R1TD. Their concentrations correlate well with the Fe content ($r_{As} = 0.667$, $r_{Pb} = 0.989$, $r_{Zn} = 0.791$ and $r_{Cr} = 0.769$; Fig. 2b; Online

Table 2 Specific surface area (SSA) values and textural parameters from the fraction below 2 μm at different beds in the R1T core and grain size analyzed for bulk samples (% average and standard deviation expressed as dried weight)

	Fine fraction					Bulk samples		
	SSA (m ² g ⁻¹)	V_{TP} (cm ³ g ⁻¹)	$V_{μP}$ (cm ³ g ⁻¹)	V_{MESOP} (cm ³ g ⁻¹)	w_P^* (nm)	Clay (%)	Silt (%)	Sand (%)
R1TA	117	0.14	0.04	0.10	2.3	29 ± 5	65 ± 2	6 ± 1
R1TB	156	0.18	0.05	0.13	2.3	25 ± 4	57 ± 2	18 ± 1
R1TC	143	0.17	0.04	0.13	2.4	25 ± 2	61 ± 2	14 ± 1
R1TD	101	0.13	0.03	0.10	2.5	15 ± 2	77 ± 2	8 ± 1

Table 3 Concentration of major elements (dried weight %) in the R1T core*

	Fe ₂ O ₃	TiO ₂	CaO	K ₂ O	SO ₃	P ₂ O ₅	MnO	TOC
R1TA	3.42 (0.12) ^a	0.60 (0.02) ^a	1.90 (0.10) ^a	1.68 (0.05) ^a	0.21 (0.03) ^a	0.13 (0.02) ^a	0.051 (0.004) ^a	0.41 (0.05) ^a
R1TB	2.88 (0.13) ^b	0.56 (0.01) ^b	1.69 (0.07) ^b	1.85 (0.02) ^b	0.11 (0.01) ^b	0.15 (0.01) ^{ab}	0.046 (0.004) ^b	< DL ^b
R1TC	2.91 (0.12) ^b	0.58 (0.03) ^{ab}	1.60 (0.08) ^b	1.82 (0.06) ^{bc}	0.08 (0.01) ^c	0.13 (0.02) ^a	0.042 (0.003) ^b	< DL ^b
R1TD	3.35 (0.12) ^a	0.60 (0.02) ^a	1.87 (0.07) ^a	1.76 (0.05) ^c	0.08 (0.01) ^c	0.24 (0.02) ^c	0.057 (0.003) ^c	< DL ^b
TILL 4 Measured	5.99 (0.04)	0.77 (0.02)	1.23 (0.03)	2.86 (0.03)	0.50 (0.01)	0.42 (0.07)	0.058 (0.003)	
TILL 4 Certified value	5.43	0.81	1.25	3.25	NR	0.2	0.06	

Standard deviation is reported in parentheses. The different letters indicate significant differences between the mean values for each control according to the nonparametric tests ($p < 0.05$). TILL 4 corresponds to a certified reference material. NR, not reported. TOC detection limit (DL) was 0.1%

Resource 4). Cu shows a different profile with a marked increase in the sample R1TB. Iron shows no significant Pearson correlation with Cu ($r_{\text{Cu-Fe}} = -0.130$).

Enrichment factor and geoaccumulation index

The normalized EF was calculated using a baseline value obtained averaging the chemical composition of five loessic samples from the La Plata and Lujan sequences cropping out in the cliffs of the river (Cantera, 2019; Online Resource 1). The EF in the Reconquista River bed sediments (Fig. 4a) shows minor enrichment for S and Mn in the upper sample (R1TA) and minor enrichment for P and Mn for the lower sample (R1TD), while the remaining major elements show no enrichment. The EF for trace elements indicated minor enrichment for Pb, Zn and Cu and no enrichment for As and Cr.

The Igeo for the sediments was also calculated for trace elements using the same baseline value (Fig. 4b). The Igeo indicates the Reconquista River sediments are uncontaminated to moderately contaminated with Pb for R1TA and R1TD and with Cu for the R1TB. The remaining Igeo for As, Zn and Cr shows values that are indicative of no contamination.

Discussion

Surficial water

Surficial water is of sodium-bicarbonate type (NaHCO₃). This type of water was also found downstream in the Reconquista River, and in other rivers of the region like the Lower Luján River and the Lower Paraná River (Depetris & Pasquini, 2007; Lombardo et al., 2010). The dissolution of carbonates from the loessic sediments of the basin and its neutralization by carbonic acid of atmospheric origin increases bicarbonate in surficial water (Prasanna et al., 2011). In addition, Stumm and Morgan (1996) found that high CO₂ partial pressure, most precisely, between 10^{-3.5} and 10⁻² (Online Resource 5), might be attributed to organic loading of the waste waters and/or the inflow of groundwater.

The Na⁺/(Na⁺ + Ca²⁺) falls in the field of rock weathering in the Gibbs cationic diagram (Gibbs, 1970) modified by Wetzel (2001), for natural river water (Online Resource 6) (Wetzel, 2001). The cationic ratio in the Southern Hemisphere, and particularly in the pampasic lakes, determines the existence of cation exchange between Ca²⁺ and Na⁺ in the hydrochemical evolution of groundwater in loessic sediments (Volpedo & Fernández Cirelli, 2013). This exchange process produces the increase in sodium and

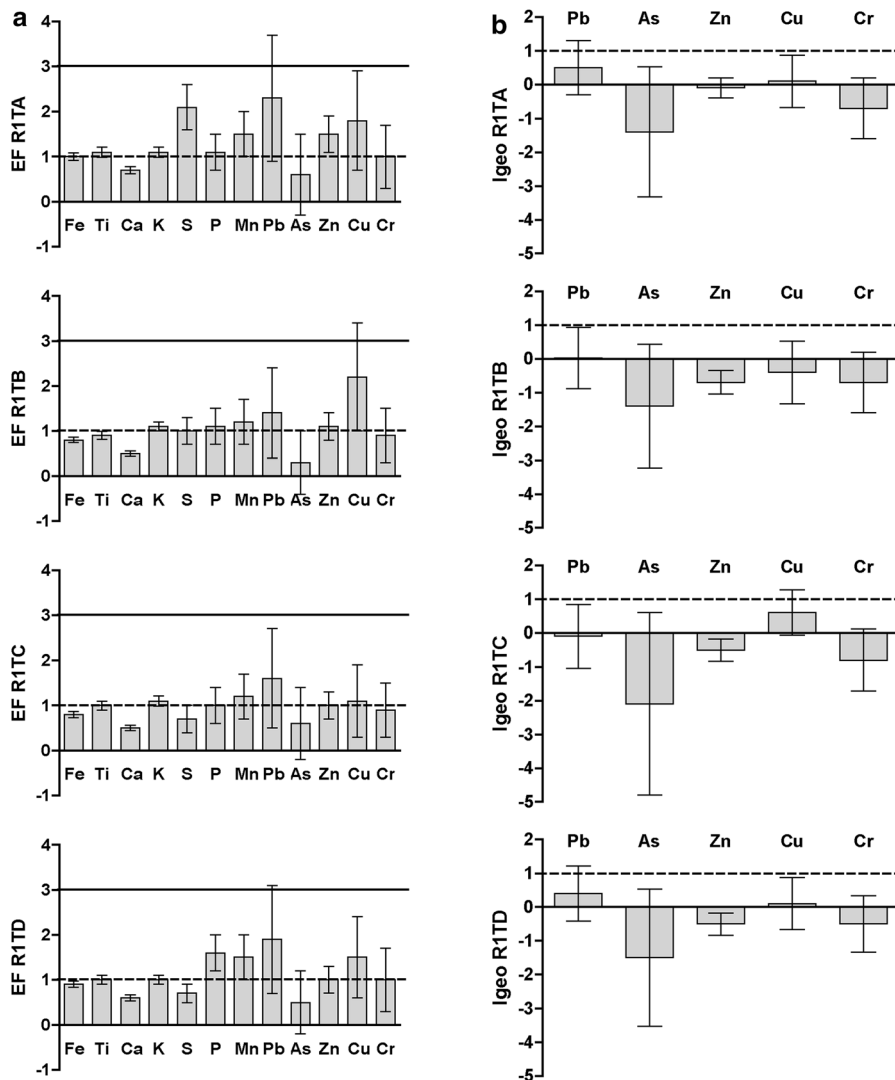


Fig. 4 **a** EF values for major (Fe, Ti, Ca, K, S, P, Mn) and trace elements (Pb, As, Zn, Cu and Cr) for all analyzed sediment samples. No enrichment (Level I, $EF < 1$), minor enrichment (Level II, $1 \leq EF < 3$), moderate enrichment (Level III, $3 < EF < 5$), moderately severe enrichment (Level IV, $5 \leq EF < 10$), severe enrichment (Level V, $10 \leq EF < 25$), very severe enrichment (Level VI, $25 \leq EF < 50$) and extremely severe enrichment (Level VII, $EF \geq 50$). **b** Igeo values of Pb,

As, Zn, Cu and Cr for all analyzed sediment samples. Uncontaminated (U: $I_{geo} \leq 0$), uncontaminated to moderately contaminated (U-MC: $0 \leq I_{geo} \leq 1$), moderately contaminated (MC: $1 \leq I_{geo} \leq 2$), moderately to strongly contaminated (M-SC: $2 \leq I_{geo} \leq 3$), strongly contaminated (SC: $3 \leq I_{geo} \leq 4$), strongly to extremely contaminated (SC-E: $4 \leq I_{geo} \leq 5$) and extremely contaminated (EC: $I_{geo} \geq 5$)

the equivalent decrease in calcium in the water of the pampasic ecosystems.

The DO values ($0.4 \text{ mg O}_2 \text{ L}^{-1}$) are extremely low, less than 6% of the maximum expected DO ($7.4 \text{ mg O}_2 \text{ L}^{-1}$ according to Wetzel, 2001) at the temperature of sample extraction (31.6° C) in the water of the Reconquista River. The DO concentration is lower than that reported in previous studies in the river

(Ossana et al., 2019; Rigacci et al., 2013). The COD values are higher than those previously reported in nearby sites (Rigacci et al., 2013), and ammonia concentration exceeds the maximum levels established in the guidelines for aquatic life protection in freshwater according to the Argentine legislation (Argentina Hazardous Waste Law N° 24,051). Nitrogen in ammonia represents the 92% of the total

inorganic nitrogen (ammonia, nitrite and nitrate). The DO, COD and ammonia values at this site point to the low quality of the river water and its gradual historical deterioration in the Middle–Upper basin.

In addition, Cd and Cu concentrations are higher than the maximum guideline levels for aquatic life protection in freshwater (Argentina Hazardous Waste Law N° 24,051), while the As and Cr content did not exceed the maximum levels. The concentrations of Cu found in the Reconquista River are about six times higher than those in the Las Catonas Stream, while the As and Cd are slightly higher and Cr is a bit lower (Cantera et al., 2018). According to the qualitative classification for the evaluation of heavy metal contamination in river ecosystems (Wachs, 1998), this water system is moderately polluted for Cr, very heavily polluted for Cd and excessively polluted for Cu. Water pollution in the Reconquista River is attributed either to the release of numerous industrial effluents into the river with little or no previous treatment (Mondino, 2007; Rigacci et al., 2013), or to other anthropogenic sources, such as domestic wastewaters, fossil fuel combustion, leakage of metal-containing motor oils, municipal waste disposal and building, which are currently encountered in the basin (Mondino, 2007). On the other hand, high As levels are not related to anthropogenic activities but ascribed to the volcanic origin of the Pampean loess sediments of the Reconquista Basin (e.g., Rosso et al., 2013).

Interstitial water

The concentration profile of trace elements follows the sequence $Cr < Cu < As$ in the interstitial water samples of the Reconquista River core, and the maximum concentrations of trace elements are found at R1TB. The concentration of these trace elements is generally higher in interstitial water than in surficial water.

The trace elements analyzed exceeded the maximum guideline concentrations established for interstitial freshwater (Argentina Hazardous Waste Law N° 24,051, Table 1) and represent a risk for benthonic organisms. According to the Argentine legislation, arsenic content in all the samples is higher than the maximum guideline level, while Cu in R1TB and R1TD shows concentrations that are 10 to 20 times higher than the maximum level. Cr concentration in

R1TB was six times higher than the allowed maximum for the same legislation. Cd is not detected. Compared with the interstitial water of the Las Catonas Stream sediments (Cantera et al., 2018), As is two times higher and Cu ten times higher in the Reconquista River. Downstream, close to the mouth of the Reconquista River, Cataldo et al. (2001) found similar Cu and ten times higher Cr levels in the interstitial waters. Higher Cr levels can be attributed to the gradual increasing of pollution along the course of the rivers.

Sediments

Mineralogy and sedimentology

Quartz, feldspar and illite are the main minerals in the bulk sediment samples of the Reconquista River. Illite and, to a lesser extent, kaolinite are present in the clay fraction of all the samples, whereas interstratified illite/smectite is found in the samples R1TA to R1TC. Tufo et al. (2018) and Porzionato et al. (2016) found a similar composition in sediments of the José León Suarez Channel and in the Ing. Roggero Reservoir of the Reconquista River Basin. On the other hand, this mineral assemblage is also common in the outcrops at the river margins (Cantera, 2019). The bulk and the clay mineral assemblages are typical of the Pleistocene Pampean Loess (Teruggi, 1957) and of the younger Late Pleistocene/Holocene sediments (e.g., Buenos Aires and Luján sequences) derived from its reworking. The latter have been named “loessoid deposits” (Zárate, 2003), associated with a multistage transport mechanism, involving several episodes of reworking of the original loess deposits by fluvial and aeolian processes (Zárate, 2003).

Illite is the predominant clay mineral in the soils and sediments of the Pampa region. According to Gonzalez Bonorino (1966), the illite in the Pampean Loess (Pampeano Formation) was originated mostly from weathered, acidic volcanic and plutonic rocks in the periphery of the Pampa region. The presence of subordinated amounts of kaolinite and smectite is linked to the alteration of volcanic glass in the Pampean soils. On the other hand, the random mixed layer clay illite/smectite could be associated with the moderate and incomplete hydrolysis during weathering of illitic clays (Chamley, 1989).

The uppermost, black muddy bed (R1TA) of the Reconquista River is the result of decantation of fine-

grained sediments during periods of low current speed (and low water level) in the river. This bed is enriched in clay, silt (Table 2) and TOC (Fig. 2 and Table 3) as well as in trace elements (especially in Pb, Cr, Cu and Zn, Fig. 2 and Table 3) in comparison with the other beds of the core, recording the anthropogenic influence in the modern sedimentation at the river bed. The erosive surface at the base of that bed indicates this is a transient deposit that can be easily eroded during the periodic river floods. The intraformational conglomerate below (R1TB) is a modern lag conglomerate associated with the erosion and entrenchment of the river into the surrounding plain (Fig. 1b, Online Resource 1). The intraclasts of this conglomerate are formed by fragments of the underlying beds and typically include reworked calcretes rich in calcite. The erosion surface at the base of this bed has been related to a sea-level drop in recent times (Toledo, 2011). The uppermost two beds are bounded by erosive surfaces and indicate that modern sedimentation is in an unstable equilibrium with erosion. The underlying, massive, green silty bed (R1TC) has the typical attributes of the Luján Verde Inferior Sequence, a loessic, fluvial–palustrine–lacustrine unit of Quaternary age (16/17–13 ka BP; Toledo, 2011). The reddish brown, massive and silty sediments at the lowermost part of the core (R1TD) should correspond to the Buenos Aires Sequence (Cantera, 2019), a loessic silt deposited about 50–70 ka BP, that constitutes the older filling of the valleys cut into the underlying Ensenada Formation (Toledo, 2011). The similar mineralogical and chemical composition of the recent sediments of the upper two beds of the core, the Pleistocene sediments of the lower two beds of the core and the Pleistocene sediments at the river cliffs suggests that the recent sediments are mainly constituted of materials from the erosion and rework of the older Pleistocene beds during the river entrenchment (Cantera, 2019).

Specific surface area (SSA) of the fine fraction

The SSA for the fine fraction ($< 2 \mu\text{m}$) is comparatively higher than that previously found in fine sediments of Las Catonas Stream (Cantera et al., 2018), and in the same order of magnitude than pristine sediments with similar mineral composition and TOC amount, described by Tufo et al. (2018) and Porzionato et al. (2016). The SSA values are in good

agreement with samples poor in OM and rich in illite and smectite, among other clay minerals (Fonseca et al., 2016; Omotoso & Mikula, 2004; Saidian et al., 2016). Kuila and Prasad (2013) reported that the abundance of micropores and fine mesopores in natural shales can be correlated with the dominance of the illite–smectite clays. In addition, the variation of w_p^* among samples is very subtle and similar to that reported by Tufo et al. (2018), who found w_p^* values from 2.2 and 2.5 nm for the sediments and their respective clay fractions in a site considered pristine, the Ing. Roggero Reservoir.

Geochemistry

The concentration of trace elements in the sediments of the Reconquista River is $\text{As} < \text{Pb} < \text{Cu} < \text{Zn} < \text{Cr}$, similar to that previously found in its tributary, the Las Catonas Stream excepting for Zn, which was higher than Cr there (Cantera et al., 2018). However, the trace element concentrations are significantly lower in the Reconquista River.

According to the current legislation in Argentina for urban, residential, or industrial disposal (Argentina Hazardous Waste Law N° 24,051), the concentration levels of trace elements in sediments of the Reconquista River did not exceed the threshold levels. However, As, Cu and Cr concentrations indicate mild to moderate pollution according to the sediment quality guidelines of the Instituto Nacional del Agua for Argentina (INA, 1998), whereas the Pb and Zn concentrations do not exceed the maximum levels. On the other hand, the Igeo calculated on the baseline of pristine sediments in the cliffs shows tiny contamination. This indicates that absolute thresholds for contamination, like those proposed by the INA, should be carefully taken if no background information is available.

The EF shows minor enrichment for Pb, Zn and Cu and no enrichment for As and Cr in the Reconquista River. In the Las Catonas Stream, the EF shows a minor to moderately severe enrichment for Pb, Zn and Cu, minor to moderate enrichment for As and minor enrichment for Cr (Cantera, 2019; Cantera et al., 2018; Online Resource 7). The Igeo in the Reconquista River sediments (Fig. 4b) indicates they are uncontaminated to moderately contaminated with Pb for R1TA and R1TD and with Cu for the R1TB sample. The higher levels of Pb, Cu and Zn in the uppermost sample

suggest that these elements were directly incorporated from the surficial waters. In the Las Catonas Stream, the maximal Igeo values fall in the fields of moderate contamination for Pb, As, Zn and Cu and uncontaminated to moderate contamination for Cr (Cantera, 2019; Cantera et al., 2018; Online Resource 8) exceeding the contamination levels found for Reconquista River sediments.

The EF and the Igeo for trace elements in the Reconquista River are lower than in its tributary, the Las Catonas Stream (Online Resource 7 and 8). Therefore, the composition of their sediments has to be compared in order to explain that difference. On the other hand, the large differences found in the trace element content among several localities in the Reconquista River Basin are probably a function of hotspots of local pollution (Mondino, 2007; Rigacci et al., 2013; Salibián, 2006).

The concentration of TOC in the core RT1 is lower than those found downstream in the Reconquista River (Cataldo et al., 2001; Porzionato et al., 2016) and the Las Catonas Stream (Cantera et al., 2018). This is partially explained by the low content of OM, typical of the Pleistocene/Holocene sediments in samples R1TC and R1TD. However, the TOC content is also lower in the Recent sediments of R1TA (black mud) and R1TB (intraformational conglomerate). These low TOC levels were found neither in the neighboring Luján nor in the Matanza–Riachuelo rivers (Cataldo et al., 2001; Rendina & Fabrizio de Iorio, 2012) and may be caused by the sulfur-reducing bacteria (Porzionato et al., 2016) that degrade OM and precipitate sulfides. Consistently, sulfur is more abundant in the sample R1TA, and this may account for the black color of the sediment (in spite of the low OM content). The precipitation of metal sulfides may occur under anoxic conditions like those in surficial waters of the Reconquista River in the site R1 (0.4 ppm of DO and < 6% of DO saturation). Sulfide precipitation was detected by Porzionato et al. (2016) in the José León Suarez Channel located in the Middle Reconquista River Basin. In the Las Catonas Stream sediments, S is even higher than in the sample R1TA, indicating that these sediments may also have anomalously high sulfide content (Cantera, 2019; Cantera et al., 2018; Online Resource 7).

Cantera et al. (2018) reported that the amount of trace elements in the sediments of the Las Catonas Stream has a strong correlation with the OM

abundance. In the Reconquista River, however, the OM content is negligible and the trace elements must be attached to other components of the sediments. According to Borovec (2000), the content of trace elements may increase with the increasing content of the fine fraction (grain size below 4 μm). Moreover, Unda-Calvo et al. (2019) described that the particle size influences the availability, and by extension, the toxicity of metals in surface sediments. In the Reconquista River, the clay fraction in the upper samples (R1TA-C) nearly doubles that found in R1TD, but the abundance of trace elements has little correlation with the clay content. Instead, the trace elements have positive correlation with the silt + clay fractions ($r_{\text{As}} = 0.803$, $r_{\text{Pb}} = 0.988$, $r_{\text{Zn}} = 0.701$ and $r_{\text{Cr}} = 0.814$; Cu did not correlate with the silt + clay fraction). The silt + clay content in the Reconquista River is very similar to that found in the Las Catonas Stream sediments (Cantera, 2019; Online Resource 9). The positive correlation between several trace elements and silt + clay fraction suggests it may be significant for trace element retention in the OM-poor sediments of the Reconquista River.

As, Pb, Zn and Cr show a strong Pearson correlation with the iron content ($r_{\text{As}} = 0.667$, $r_{\text{Pb}} = 0.989$, $r_{\text{Zn}} = 0.791$ and $r_{\text{Cr}} = 0.769$) in the Reconquista River sediments, while Cu shows no significant correlation ($r = -0.130$). The significant correlation of As and Cr with iron (Fig. 2b) suggests that their retention is controlled by the iron present in the sediments. It is well known that As and Cr oxyanion species are often sorbed on Al, Fe and Mn oxides and hydroxides hosted as cement or coatings in lithic fragments of loess sediments (Hmamou et al., 2020; Li et al., 2017; Nicolli et al., 2012; Tufo, 2013). In addition, these trace elements may also be retained by clays (Goldberg, 2002; Lin & Puls, 2000; Uddin, 2017; Unda-Calvo et al., 2019). We can state that the As and Cr are positively correlated with the sum of both, iron oxy (hydr)oxides and silt + clay fraction, in the Reconquista River, although we cannot discriminate how much As and Cr are retained by the iron oxy (hydr)oxides and silt + clay fraction separately.

The positive correlation between Pb and/or Zn with Fe also suggests their retention in the sediments is also enhanced by the iron oxy (hydr)oxides. Saeedi et al. (2011) reported similar results for Pb and Zn sorption in the Jajrood River (Iran) although Zn may be present, at least in part, in sulfur minerals.

Cu and Fe concentrations do not present a significant Pearson correlation in the core R1T mainly because Cu shows a remarkably increase in the sample R1TB. As the remaining samples follow the trend of Fe (Fig. 4b), Cu retention might be broadly related to the iron content, but the Cu excess in the sample R1TB has to be associated with another phase in the sediments. Du et al. (1997) studied the Cu adsorption in illite by formation of surface complexes followed by bulk or surface precipitates. In addition, this study also found that the Cu–illite interaction in presence of carbonates produced surface complexes, which led to the precipitation of a copper hydroxycarbonate [$\text{Cu}_2(\text{OH})_2\text{CO}_3(\text{s})$], suggesting that Cu can be associated with the carbonate phase in the sediments as well (Du et al., 1997). The Reconquista River is a buffered carbonate–bicarbonate system, with sediments presenting low OM content, as is also reported for the Yellow River (Fan et al., 2007), which could cause the association of Cu with carbonate on the surface of particulate matter. Thus, given the presence of calcite exclusively in the sample R1TB (Fig. 3), the high Cu content in this sample can be attributed to the presence of carbonate-bound Cu.

Sediment–water interactions

The Reconquista River sediments have lower trace element, TOC and Fe than those of Las Catonas Stream (Cantera et al., 2018). Conversely, the interstitial waters of the Reconquista River show higher concentrations for As, Cr and Cu. The concentration profiles of As and Cr show an inverse trend (Fig. 2) compared to their concentration in interstitial water samples ($r_{\text{As}} = -0.938$ and $r_{\text{Cr}} = -0.729$, respectively), similar to the trend also noted in groundwater of other Pampean sediments (Sierra et al., 2016). This suggests that the strong association of As and Cr to the solid phase might restrain its release to the interstitial water.

The sediments of the Las Catonas Stream show positive correlation between TOC and trace element (i.e., As, Pb, Cu, Cr, Zn), suggesting that the OM played a main role for the retention of trace elements (Cantera et al., 2018), decreasing their abundance in the interstitial waters. Thus, high TOC in sediments corresponds to low trace elements dissolved in the interstitial water. The trace elements complexation with the OM by binary (trace element–OM; Fakour &

Lin, 2014) or ternary surface complexes (trace element–OM–Fe or OM–trace element–Fe; Li et al., 2017; Sharma et al., 2010) have an important contribution in the retention of these elements in the sediments. If the OM is absent or negligible, as in the Reconquista River sediments, the iron oxy (hydr)oxides and the silt + clay fraction are the main phases that control the trace element retention.

An overall assessment of the results suggests that minor changes in the sediment conditions at the streams in the Reconquista River basin, e.g., anoxic redox conditions, can generate iron oxy (hydr)oxides minerals dissolution, causing a significant release of hazardous trace elements from the sediments to the interstitial water and, in turn, to the surficial water of the river. In the loessic substrate, a considerable fraction of the trace elements is probably retained by iron oxy (hydr)oxides labile to redox potential (Eh) changes. This is important because on the loessic substrate of the Pampa Húmeda most of the agriculture are carried out, as well as the main cities of Argentina are settled.

Conclusions

The water in the Middle–Upper Basin of the Reconquista River shows poor quality. The DO concentration decreases to less than 6% of total saturation, the COD increases to 34%, and the level of ammonia is 54% higher compared to previous reports. Cd and Cu concentrations exceed the maximum guideline levels for aquatic life protection allowed for freshwater (Argentina Hazardous Waste Law N° 24,051). The content of Cu, Cd and As is higher than that previously found in the Las Catonas Stream, a tributary of the Reconquista River. According to Wachs' qualitative classification, the Reconquista River is a moderately to excessively polluted water system. Trace element concentrations are generally higher in the interstitial than in the surficial water. In this sense, As content exceeds the maximum guideline level established by the Argentine legislation in all interstitial water samples, while Cr and Cu exceed these levels in some samples, which could represent a risk for the benthonic organisms.

The cored riverbed sediments include recent fluvial and Pleistocene/Holocene loessic sediments. The uppermost bed represents the modern,

anthropogenically influenced sedimentation, and it is enriched in OM, sulfur and trace elements. This bed also represents a transient deposit above an intraformational conglomerate formed during recent river entrenchment.

According to the sediment quality guidelines for Argentina proposed by INA, As, Cu and Cr concentrations indicate mild to moderate pollution for the Reconquista River sediments (INA, 1998). However, the Igeo calculated on the baselines of pristine sediments in the cliffs shows low trace element contamination. This indicates that absolute thresholds for contamination should be carefully taken if no background information is available.

The OM seems to be the main control on trace element retention in sediments of the Reconquista River basin. In the absence of OM, as occurs in the loessic substrate of the studied site in the Reconquista River, the iron abundance plays the same role, probably in combination with the silt + clay content. However, they seem to be less efficient for trace element retention than the OM, and the interstitial waters are consequently enriched in these elements. As most of the big cities and the agricultural activities of Argentina are developed on the loessic substrate of the Pampa Húmeda, the study of these processes is crucial to understand the interaction between polluted waters and sediments in that region.

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Author’s contribution CGC, RAS and MdSA designed research; CGC, AET and RAS performed research; CGC, AET, RAS and MdSA analyzed and interpreted data; and CGC, AET, RAS and MdSA wrote the paper and revised the manuscript critically.

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Availability of data and materials Any additional data will be available as required.

Declaration

Conflict of interest No conflict of interest has been declared by the authors.

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