Impact of anthropogenic activities on an urban river through a comprehensive analysis of water and sediments

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Abstract

The aim of this study was to assess the impact of urban and industrial areas on an urban river through a comprehensive analysis of water and sediments. Six different sites along the San Luis River, Argentina, were characterized by measuring 12 physical-chemical parameters and nine heavy metals according to standard protocols. Metal pollution in sediment samples was evaluated with several indices. Cluster analysis was applied to standardized experimental data in order to study spatial variability. As, Cu, Cr, Mn, Pb, and Zn were the main contributors to sediment pollution, and the industrial zone studied showed moderate enrichment of Co, Cu, and Zn, probably due to anthropogenic activities. Cluster analysis allowed the grouping of the sites: sediment samples were classified into two clusters according to the metal content; water samples were arranged into three groups according to organic matter content. The results were compared with sediment and water quality guidelines. They indicated progressive deterioration of water and sediment quality compared with the background area, mainly in the sites following the industrial park and domestic discharge areas. Moreover, the results showed that the analysis of both water and sediment should be considered to achieve a watershed contamination profile.

Keywords Heavy metals · Physical-chemical characteristics, Urban river · Anthropogenic activities

Introduction

The world population has rapidly grown, from 220 million to 2.8 billion over the twentieth century, and this figure will continue to rise in developing countries mainly (UNFPA 2007). This expanding urbanization was due in part to the growth of industrialization activities which created

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employment opportunities that attracted people to the cities. Throughout the history of human civilization, urbanization patterns have been configured mainly near water sources because waterways are vital resources for human benefit (Li et al. 2017). Urban rivers are essential components of the global geochemical cycle as well as complex and dynamic ecosystems. They provide necessary resources for human life such as drinking water, aquatic products, and agricultural activities. For this reason, in most cities, industrial and agricultural centers have been established very close to rivers and streams (Dubois 2011). However, industrial and domestic wastewater, agricultural runoff, and air pollutant depositions are the most important and frequently anthropogenic sources of heavy metal pollution (Maceda-Veiga et al. 2012; Roig et al. 2016; Khodami et al. 2017). After being released into the environment, heavy metals can be distributed to the soils, sediments, and surficial waters. Then, metals can be recycled by chemical and biological processes or may be incorporated by the biota and easily propagated through the trophic chain (Maceda-Veiga et al. 2012; Souza and Silva 2016). Urban river quality monitoring programs are necessary in order to protect public health and to safeguard water resources. Heavy

metals analyses of water samples have been demonstrated to be insufficient to establish anthropogenic influences on the urban river quality because of the inherent variability of flow. Sediments are an integral and dynamic part of rivers and streams characterized by extreme complexity and high capability to accumulate metal compounds (Islam et al. 2015a). Sediments contain substances, such as clay, humic acid, and organic matter that complex with metal ions. Metal-organic matter complexes and adsorption of metals to fine grains are important mechanisms for the dispersion of metals in the aquatic environment (Kennish 2002). Therefore, sediments have a high retention capacity, as well as the potential to release accumulated contaminants back into the water (Shafie et al. 2014). Thus, they are considered a major repository of natural and anthropogenic metals (Maceda-Veiga et al. 2012; Sakan et al. 2015). For this reason, their analysis can allow to know the contamination history of the river and its potential as a pollution source. Nevertheless, heavy metal mobility depends on sediment composition and physical-chemical properties of the water body, such as pH, temperature, salinity, and redox potential (Cheng 2003). Hence, sediment quality could be regarded as an important indicator of water pollution.

Traditional approaches to urban river quality assessment only considered the water samples analysis and their evaluation is commonly based on a comparison of experimental values with established water quality. However, urban river quality monitoring programs that integrate water and sediment analysis simultaneously are needed to protect valuable fresh water resources. This approach is insufficient for reporting on the water quality status and its evolution along the basin and over time (Simeonov et al. 2003; Finotti et al. 2015). The water quality index consists of an important tool to summarize and simplify different values of analytical determination and indicates the quality of a water resource (Finotti et al. 2015). For this reason, several surface water quality indexes have been developed and applied to estimate the water river quality (Finotti et al. 2015; Glińska-Lewczuk et al. 2016; Wu et al. 2018; Tian et al. 2019; Unda-Calvo et al. 2020; Ustaoğlu et al. 2020).

In the same way, sediment quality guidelines (SQGs) and numerous indices are used for assessing the level of contamination, estimating the possible biological adverse effects and ecological risks of sediments (Suthar et al. 2009; Wan et al. 2013; Islam et al. 2015a; Zhuang et al. 2016). An effective assessment of sediment contamination can be achieved by the use of pollution indices, which are widely used in the comprehensive geochemical evaluation of soil conditions (Okay et al. 2016; Mazurek et al. 2017). Pollution indices are classified into two groups: individual and complex ones. The first group contains indices which are calculated for each individual heavy metal separately, and they can be used for the unitary assessment of soil pollution with particular heavy metals

(Suthar et al. 2009; Wan et al. 2013; Zuzolo et al. 2017). On the other hand, the second group of indices describes soil contamination in a more comprehensive way, since it considers the content of more than one heavy metal or a sum of individual indices (Kowalska et al. 2018).

However, total metal concentration in water or sediment samples provides a poor indicator of environmental risk. Both data, simultaneously, are necessary to estimate the general status of waterways.

San Luis River is located in the homonymous province of Argentina and runs through the capital city. Urban and industrial areas have increased substantially, influencing the quality of the river that is currently used as a source of irrigation and recreation. Therefore, the management of river quality has become more important. When referring to the quality of a river, its main components—sediment and water—must be taken into account simultaneously: There are no previous data that integrally analyze the quality of water and sediments in this river.

The impact of anthropogenic activities on this urban river can be minimized through the early diagnosis of its quality and the potential disturbance sources identification; thus, it is crucial to develop an integral study in such vulnerable areas. Since the San Luis River constitutes the main inland water resource for domestic, industrial, and irrigation purposes, it is imperative to prevent and control its pollution. It is thus important to present reliable information on its quality for effective management.

Therefore, the main objective of this study was to assess the effects of anthropogenic activities on urban river quality through a combined physical-chemical analysis of both water and sediment quality. Also, in this work, the correlation between the heavy metals and physical-chemical parameters in the sediment was realized.

Materials and methods

Study area

This study has been performed along the San Luis river (33° 36′ 67″ S–66°46′ 67″ W) located in the center zone of San Luis city, Argentina. This river flows through this city whose population is approximately 170,000 inhabitants, and its industrial zone. The river has an annual flow of about 0.728 m3 s^{-1} (Casín 2015). The climate of the area is semi-arid with an average annual rainfall of about 48 mm. In the present study, six stations were chosen considering a preliminary study (data not shown) and river accessibility (Fig. 1). Only R1 (33° 15′ 47, 67″ S–66° 13′ 07.27″ W) is known to be an area with little anthropogenic activity, while R2 (33° 18′ 04, 88″ S–66° 17′ 52.79″ W) and R3 (33° 18′ 37.97″ S–66° 19′ 28.68″ W) correspond to an urban area; R4 (33° 20′ 45.83″ S–66° 23′ 17.12″
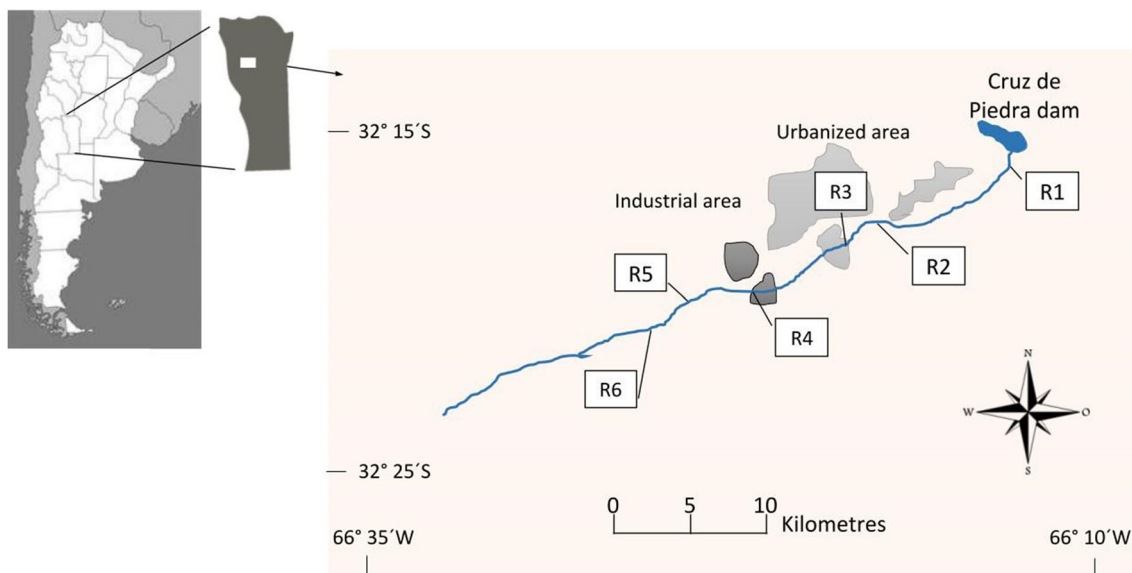
Fig. 1 Sampling sites along the San Luis River, San Luis province, Argentina

W) is located in the industrial parks, without direct discharge of effluents. Sites R5 (33° 20′ 44, 99″ S–66° 25′ 11.60″ W) and R6 (33° 22′ 06, 83″ S–66° 28′ 25.17″ W) correspond to an area of the river which has received the discharge of treated domestic effluents with a flow about 0.325 m³ s⁻¹ (Casín 2015). Near R5 and R6, little agriculture activity was observed. Finally, the San Luis River drains near Salinas del Bebedero, which is a salt mine for domestic consumption located 42 km south of the city.

Water and sediment sample collection and their preliminary preparation

The water samples were collected from the center of the river and up to 15 cm deep from the surface. The samples were taken during the months of May and November of 2018. The preservation and transportation of samples were performed according to Standard Methods for the Examination of Water and Wastewater (Rice et al. 2012).

Sediment samples were collected from the upper 0–2 cm of undisturbed bottom sediment using a mud grab sampler, collected in plastic containers, and stored at 4 °C until analysis. Then, sediment samples were dried at 60 °C for 24 h, sieved, and homogenized before analysis.

Physical-chemical characterization

Water and sediment samples (three replicates) were characterized by measuring 11 parameters according to standard protocols (Rice et al. 2012). In situ: temperature (T), pH, and redox potential (RP) of water samples were measured using the Waterproof tester HI 98121-HANNA. Ex situ: dissolved oxygen (DO), 5-day biochemical oxygen demand (BOD),

chemical oxygen demand (COD), turbidity (Tu), sulfate (SO_4^{2-}), nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) were determined in the laboratory.

For sediment characterization, the previously saturated sediment paste from 200 g of dry and sieved samples were prepared, and distilled water was added until saturation of the sample. The parameters analyzed were electric conductivity (EC), chlorides, alkalinity, sodium, potassium, calcium, and magnesium. A previous extraction was performed to determine the levels of nitrate, nitrite, and ammonium. The extraction was performed using 10 g of sediments and 20 mL of KCl 1M. The mixture was shaken for 10 min and finally was vacuum-filtered using Whatman black filter paper (grade 589/1). The resulting filtering was used for the determinations. The pH value was determined in a soil:water ratio of 3 to 1 (w/w). The organic matter (OM) content (g %, w/w) was determined using the chromic acid oxidation method followed by titration with ammonium ferrous sulfate (Khan et al. 2012).

Sediment textural characterization

For textural characterization, fresh sediments were dried at 110 °C for 12 h. The completely dried sediment samples (three replicates) were analyzed for particle size distribution. The samples were passed through a series of six sieves with openings, ranging from 75 to 4750 μm. The sieves were agitated by a mechanical shaker (EMS -8 Electromagnetic Sieve Shaker) for 2 h. At the end of the shaking time, the sediments that remained on the sieves were collected and weighed. Finally, each sample was separated into three size groups of particles including gravel (> 4750 μm), sand (4750 - 75 μm), and fines (< 75μm).

Analysis of heavy metal concentrations

Acid digestion of water samples for total metal concentration analysis was performed with nitric acid in 25 mL of filtered sample. To determine metal in sediment, 0.25 g of sample was digested with a mixture of acids (HNO_3/ HF; 3:1) in a microwave heating closed system (MILESTONE-START D model) according to EPA Method 3052 (EPA 1995). The digested solutions were filtered and adjusted to HNO_3 1% at the final concentration in order to avoid interference with the measurement of metal concentrations. A total of nine heavy metals (As, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) were determined using an ELAN DRC-e quadrupole ICP-MS instrument (Perkin Elmer SCIEX, Thornhill, Canada).

Canadian Water Quality Guidelines (CWQG) (Macdonald et al. 1996; Pawlisz et al. 1997) and CONAMA-Brazil Guidelines (Brasil 2012) were used to evaluate water quality, while sediment quality was assessed following the Canadian Council of Ministers of the Environment Sediment Quality Guidelines (CCME 2002).

Assessment of sediment quality using indices

Contamination factor and pollution load index determination

Contamination factor (CF) indicates the level of contamination in sediments, and it was calculated as the ratio of the metal concentration at a given sampling station to the natural background values (Moore et al. 2011). The CF was obtained by the following equation:

$$CF_{metals} = C_{metal}/C_{backroundarea}$$

CF values are classified into four grades for monitoring sediment pollution (Hakanson 1980): low degree (CF<1), moderate degree ($1 \leq CF \geq 3$), considerable degree ($3 \leq CF \geq 6$), and high degree ($CF \geq 6$).

The pollution load index (PLI) (Tomlinson et al. 1980) allows assessing the extent of the pollution status of the trace metal in a site of interest. Moreover, PLI allows the determination of the overall toxicity status of the samples and the contribution of all heavy metals analyzed. The PLI is defined as the nth root of the multiplications of the CF of metals.

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}$$

According to Tomlinson et al. (1980), values of PLI=0 indicate perfection, PLI=1 indicate the presence of only baseline level of pollutants, and PLI>1 would indicate progressive deterioration of quality states of the site.

Geoaccumulation index and enrichment factor determination

Geoaccumulation index (I_{geo}) is defined by the following equation (Muller 1981 cited by Khodami et al. 2017):

$$I_{geo} = \log_2 (C_n/1.5B_n)$$

where C_n is the concentration of the metal n in the sediment and B_n is the geochemical background concentration of the metal n in the background sample. Factor 1.5 is the background matrix correction factor due to lithogenic effects (Nasrabadi et al. 2010). I_{geo} values are categorized into seven classes: $I_{geo} \leq 0$– practically uncontaminated; $0 \leq I_{geo} \leq 1$ –uncontaminated to moderately contaminated; $1 \leq I_{geo} \leq 2$–moderately contaminated; $2 \leq I_{geo} \leq 3$ moderately to heavily contaminated; $3 \leq I_{geo} \leq 4$–heavily contaminated; $4 \leq I_{geo} \leq 5$–heavily to extremely contaminated; and $5 < I_{geo}$–extremely contaminated (Yap and Pang 2011; Mohammad Ali et al. 2015).

On the other hand, enrichment factor (EF) also was calculated to estimate the degree of sediment pollution and to identify natural or anthropogenic contaminants sources (Wan et al. 2013; Mohammad Ali et al. 2015; Khodami et al. 2017). This index was calculated using the following equation:

$$EF = \left[(C_n/C_{Fe})_{sample}/(C_n/C_{Fe})_{back}\right].$$

where $(C_n/C_{Fe})_{sample}$ is the ratio of the concentration of the element n (C_n) to that of Fe (C_{Fe}) in the sediment sample and $(C_n/C_{Fe})_{back}$ is the same relation in the background zone or pre-industrial area in the present work. As the normalizing element for determining EF values, Fe was selected. Normalization with a reference element is used to reduce the variability caused by particle size and mineralogy of sediments (Teixeira et al. 2019).

The EFs values are used to identify anthropogenic influences on sediments based on the use of normalized elements and therefore allow for the distinction of the origin of metal pollution (Yuan et al. 2012). EF values between 0.5 and 1.5 indicate that heavy metal is entirely provided from crustal contribution in sediment, such as weathering products. Values greater than 1.5 establish that an important proportion of non-crustal materials are released by any natural process, such as biota contributions, and/or anthropogenic influences (Zhang and Liu 2002). Sutherland (2000) proposed five established contamination categories based on EF values. (i) EF < 2 depletion of mineral enrichment; (ii) $2 \leq EF < 5$, moderate enrichment; (iii) $5 \leq EF < 20$, significant enrichment; (iv) $20 \leq EF < 40$, very high enrichment; (v) EF > 40, extremely high enrichment.

Assessment of water quality using indices

Comprehensive pollution index

Comprehensive pollution index (CPI) is used to assess the level of water pollution in a watershed and classify the overall water quality into five categories (Zhao et al. 2012). This method reflects the kind and level of main pollutions according to water pollution level standards. The comprehensive pollution index method can be formulated as:

$$CPI = \frac{1}{n}\sum_{i=1}^{n} Pli$$
$$Pli = \frac{Ci}{Si}$$

where CPI is the comprehensive pollution index, and Ci is the measured concentration of the pollutant in water; Si is the limit allowed according to the regulations considered in this study.

CPI classifies the level of watershed pollution into five categories: (I to V): (i) CPI from 0 to 0.20 (clean); (ii) CPI from 0.21 to 0.40 (sub clean); (iii) CPI from 0.41 to 1.00 (slightly polluted); (iv) CPI from 1.01 to 2.00 (medium polluted); and (v) CPI>2.01 (heavily polluted).

Statistical analysis

One-way ANOVA was applied to analyze the significant differences among sampling stations for different metal levels. Tukey's t test was also performed to identify the homogeneous type of the data sets. Cluster analysis was applied to standardized experimental data in order to study spatial variability over the San Luis River. Euclidean distances as a measure of similarity were applied both for water and sludge samples. The Minitab 17 software was used for statistical calculations.

Results and discussion

Physical-chemical characterization and heavy metal concentrations of water samples

The water physical-chemical parameters values are presented in Table 1. R1 is a site with little anthropogenic activity; therefore, it was selected as the reference site. Significant differences were found among the sampling sites (ANOVA, $p<0.05$), except for temperature and pH measurements. The temperature ranged between 12.5 and 15.0 °C, pH values indicated slightly alkaline properties in all samples, and they were within the recommended standard values. DO values decreased significantly in the industrial zone (R5 and R6), which exhibited values below those recommended for a good water quality by CONAMA–Brazil (6 mg L^{-1} O$_2$) and by CWQG (5.5–6.0 mg L^{-1} O$_2$). Similar results were reported by Glińska-Lewczuk et al. (2016) who observed a significant decrease in DO values in an urban river exposed to intense urban and agricultural activities. Significant reduction in DO values at R5 and R6 sites may be explained by an increase in ammonium oxidation for nitrate formation and organic matter decomposition. BOD and COD tests are major indicators of the environmental health of water bodies. According to some authors, if the BOD and COD concentrations are high, then water is considered polluted (Amneera et al. 2013). COD is widely used for determining the waste concentration and is primarily applied to pollutant mixtures, such as domestic sewage, agricultural, and industrial waste (Kazi et al. 2009). In this study, the drastic increase in COD values at sites R5 and R6 indicated a severe deterioration of water quality. Furthermore, BOD values exceeded ten times the established limits by CONAMA-Brazil (2012) for aquatic life protection. These values can be produced by inefficient treated domestic waste discharge and local industrial activities. Regaldo et al. (2017) determined three parameters: DO, COD, and BOD in Colastiné-Corralito stream system in Santa Fe, Argentina.

Table 1 Physical-chemical characterization of water samples

Variable	R1	R2	R3	R4	R5	R6
pH	8.2 ±0.4	8.2 ±0.2	8.1 ±0.2	8.2 ±0.2	7.4 ±0.4	7.2 ±0.7
T (°C)	13 ±0.4	12 ±0.6	13 ±1	13 ±0.6	15±0.3	14 ±0.6
RP (mV)	45 ±5.7	49 ±2.8	80 ±4.2	100±3.1	-180±2.8	-134±8.5
DO (mg L^{-1} O$_2$)	8.4 ±0.2	8.2 ±0.5	8.0 ±0.5	7.7 ±0.5	1.5 ±0.5	2.2 ±0.6
BOD$_5$ (mg L^{-1} O$_2$)	3.1 ±0.3	4.2 ±0.9	4.2±0.9	5.2 ±0.3	58 ±5.6	57 ±4.9
COD (mg L^{-1} O$_2$)	4.8 ±0.2	5.7 ±0.6	6.4 ±0.5	7.1 ±0.4	85 ±9.4	86 ±8.7
Tu (NTU)	31 ±4.8	130 ±72	71 ±14	64±14	114±16	106±14
SO$_4^{2-}$ (mg L^{-1})	130 ±12	170±39	180±32	200±49	82 ±14	74 ±21
NO$_2^-$ (mg L^{-1})	0.01±0.0	0.01±0.0	0.01±0.0	0.02±0.0	0.08±0.0	0.07±0.0
NO$_3^-$ (mg L^{-1})	0.9 ±0.1	1.2 ±0.1	1.9 ±0.3	1.7 ±0.3	12 ±1	6.3 ±2.5
NH$_4^+$ (mg L^{-1})	0.1 ±0.0	0.7 ±0.1	0.8 ±0.1	0.8 ±0.1	18 ±2	7.3 ±5.6

They detected low DO values and high COD and BOD values and the water quality decrease was related to high industrial and agricultural activity.

On the other hand, high turbidity values reduce sunlight penetration, which affects food supplies and growth of aquatic organisms (Mackie and Walsh 2012). The results obtained in the present work showed that turbidity values were four times higher in R2, and three times higher in R5 and R6 with respect to the reference site (R1). According to standard references (CONAMA-Brazil), these results suggested a good water quality in R1, R3, and R4 sampling sites and a deterioration of the water quality at the industrial zone. Taking into account the provisions of CONAMA-Brazil (2012) in relation to SO_4^{2-} concentration, water would have a good quality because the range was from 74.5 to 203.3 mg L^{-1}. Finally, R5 exhibited the maximum concentrations of NH_4^+, NO_3^-, and NO_2^-, and these values were several times higher than those found in R1. It is worth mentioning that between sites R4 and R5 the river receives the treated domestic waste. Recent studies found nitrogenous compound concentrations above the permitted values in areas of intense industrial activity or effluent discharge with little or no treatment (Mahadevan et al. 2020; Unda-Calvo et al. 2020).

The box plots shown in Fig. 2 summarize the basic statistics for the concentrations of heavy metals. The average concentration followed the decreasing order of Mn> Zn > Cu > As > Ni > Cr > Cd > Co >Pb. The flow of river water affects surface heavy metal dissolution, resulting in different concentrations of heavy metals along the course of the river (Nguyen et al. 2013). In this sense, maximum heavy metal concentration values in water samples showed a heterogeneous distribution along the sampling sites. The general trend evidenced a decrease in water quality at sites R4, R5, and R6 belonging to the described industrial area. According to CONAMA-Brazil (2012), all metal concentrations were below the permissible limits. However, considering the Canadian Water Quality Guidelines (CCME 2002), Mn, Cu, Zn, Cd, and Cr were above the permissible limits. The results revealed water quality deterioration in the industrial zone, probably due to low effectiveness in the treatment of discharged wastewater.

Physical-chemical characterization and heavy metal concentrations of sediment samples

The results of physical-chemical sediment analysis are presented in Table 2. This is the first study about heavy metals in San Luis River sediments. The pH values ranged from 7.07 to 8.26 (i.e., slightly acidic to alkaline) and no significant differences were found. The results indicated a relative secure environment according to CCME (2002), which provided a pH of 6.50 to 9.00 for the protection of aquatic life. Sites R4, R5, and R6 exhibited a higher concentration of Cl^-, HCO_3^-, Ca^{2+}, Mg^{2+}, and NH_4^+ with respect to the other sites. These sites correspond to the area affected by the industrial park and domestic discharge. In addition, low organic matter content was found in all samples. However, it is important to note that these values fluctuated in the river bed; R6 presented the highest possibly due to the accumulation of organic matter from the domestic discharge in the R5 site. EC rose linearly on the river bed from 156 (R2) to 264 μS cm^{-1} (R6). The values were statistically significant (p <0.05) for all measured parameters among the sampling sites.

Fig. 2 Heavy metal concentration (μg L^{-1}) in water along the San Luis River (1, 2, 3, 4, 5, and 6 correspond to R1, R2, R3, R4, R5, and R6, respectively). Values resulting from campaigns during 2018
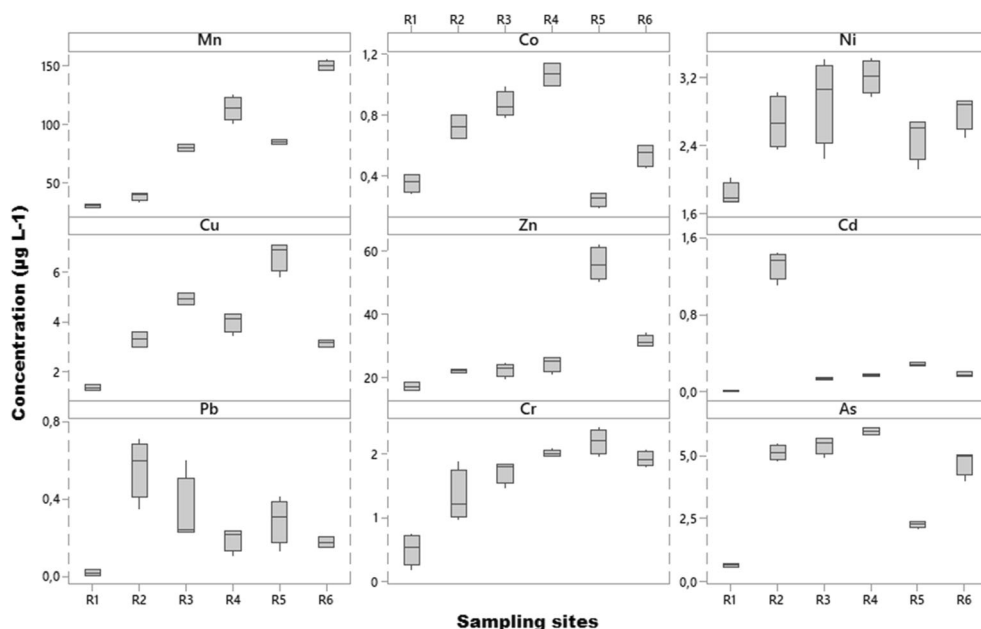
**Table 2** Physical-chemical values of sediments samples

Parameters	R1	R2	R3	R4	R5	R6
pH	8.3 ±0.1	8.2 ±0.0	8.2 ±0.0	7.1 ±0.1	7.1 ±1.0	7.7 ±0.1
Cl⁻(mg kg⁻¹)	3.8 ±0.1	5.2 ±0.1	3.2 ±0.1	30 ±1.0	19 ±1.2	22 ±0.5
OM (%)	0.1 ±0.0	0.1 ±0.0	0.3 ±0.3	0.1 ±0.0	0.9±0.1	0.2 ±0.1
HCO₃⁻ (mg kg⁻¹)	26 ±1.0	32 ±0.4	26 ±1.3	49 ±1.0	51 ±2.0	54 ±1.0
EC (µS cm⁻¹)	170±5.4	170±6.9	190±1.9	160±2.6	250±31	260±18
Na (mg kg⁻¹)	2.6 ±0.4	3.7 ±0.2	3.6 ±0.1	10±0.6	1.9±0.2	8.9±0.5
K (mg kg⁻¹)	0.6±0.1	0.6 ±0.0	0.8±0.0	1.5 ±0.1	1.6 ±0.3	2.5 ±0.6
Ca (mg kg⁻¹)	3.6 ±0.7	4.1±0.6	5.6±0.4	15 ±1.8	20 ±1.3	36 ±1.9
Mg (mg kg⁻¹)	0.4 ±0.1	0.3 ±0.1	0.4 ±0.0	1.5 ±0.1	1.6 ±0.1	1.9 ±0.0
NO₂⁻ (mg kg⁻¹)	0.1 ±0.0	0.1 ±0.0	0.1 ±0.0	0.1 ±0.0	0.1 ±0.0	0.1 ±0.0
NO₃⁻ (mg kg⁻¹)	1.2 ±0.2	2.1 ±0.1	2.8 ±0.3	1.4 ±0.1	5.8 ±0.5	5.4 ±0.4
NH₄⁺(mg kg⁻¹)	3.4 ±0.4	15 ±1.1	21 ±0.7	170±1.7	19 ±0.7	110±2.3

Figure 3 shows the average and standard deviation of total metal concentrations in sediments. The distribution of metals was heterogeneous along the river, which is probably related to the variability of mineralogical composition among the sampling sites and the potential sources of metallic contamination. The results in relation to heavy metal concentration in sediments and water samples were notoriously discordant, indicating that the metal balances in the sedimentary and aquatic systems are different. The increased heavy metal concentration in sediment samples could be explained by some characteristics of the water column such as the pH. High pH values can promote the adsorption and precipitation of heavy metals from water into river sediment (Zhang et al. 2014). Mn, Co, Ni, Zn, and Pb concentrations were significantly different among sampling stations ($p<0.05$), while Cu, Cr, and As did not show significant differences ($p>0.05$). The concentration of heavy metal in sediment was in the following order: Zn >Mn> Cu >Pb> Cr > As > Ni > Co > Cd. The highest mean concentrations of Mn, Co, Ni, Zn, and Pb were found at the R4 site. Similarly, Cu, Cr, and As showed the maximum concentration at R5 and R6. It should be noted that all analyzed element concentrations were the greatest in industrial areas with respect to the reference site. These results are in agreement with other authors (Islam et al. 2015a; Haris et al. 2017; Wei et al. 2019; Yi et al. 2020; Zeng et al. 2020) in that they demonstrated a significant increase in heavy metals concentration in areas of intense urban and industrial activities.

Sediment quality guidelines (SQGs) are frequently used to estimate possible environmental consequences of heavy metals in sediment (Wan et al. 2013). To protect aquatic life,

Fig. 3 Total heavy metal concentrations in sediment samples (1, 2, 3, 4, 5, and 6 correspond to R1, R2, R3, R4, R5, and R6, respectively). Values resulting from campaigns during 2018
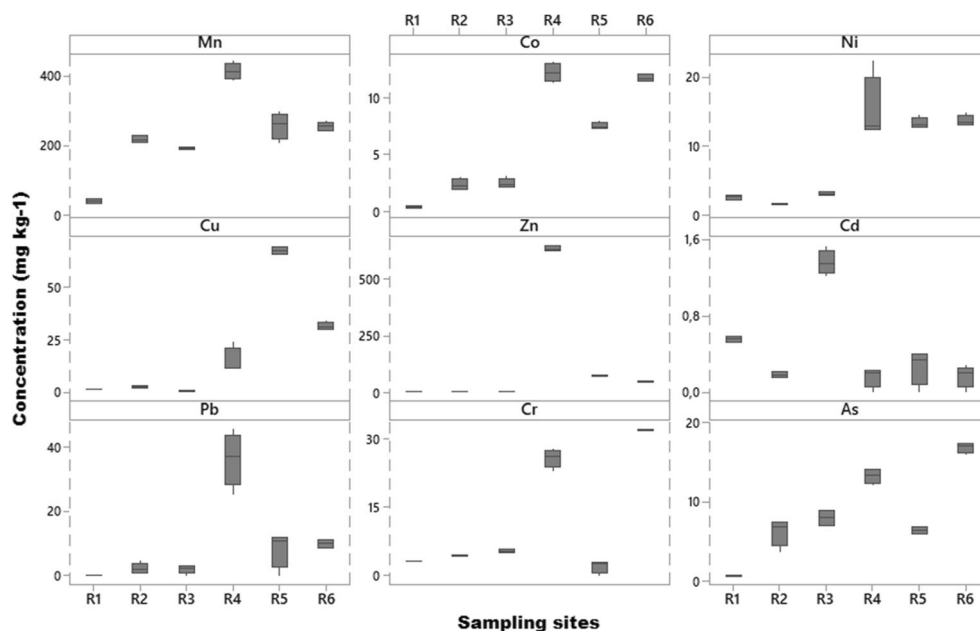
the CCME derived two reference values for about 30 substances in freshwater and marine sediments: a threshold effect level (TEL) below, which adverse effects are rarely observed, and probable effect level (PEL) that defines the level above which adverse effects are expected to occur frequently. Three ranges of chemical concentrations are defined for the TEL and the PEL: (1) the lowest range of concentrations (below TEL), within which adverse effects are rarely observed; (2) the possible effects range (between TEL and PEL), within which adverse effects are occasionally observed; and (3) the probable effects range (above PEL), within which adverse biological effects are frequently observed. According to this guideline, total concentrations of As and Cu were between TEL and PEL values in all the analyzed sites. Conversely, Zn and Pb concentrations were below TEL in all sampling sites, except in site R4. Sites R2 and R4 exhibited Cd concentrations close to TEL value (0.68 mg kg^{-1}), coinciding with that reported by Zahra et al. (2014). In general, the comparisons suggest that R4 was the most affected site by all heavy metals. It can be concluded that Zn and As concentrations (above PEL) in the area have a high probability of harm to the environment.

Textural characterization of sediment samples

The size of the sediment particles is a factor that can affect the concentrations of metals found in the sediment (Bábek et al. 2015; Mokwe-Ozonzead et al. 2018). The results of the analysis of particle size distribution indicated that sediments from sites R1, R2, and R3 did not contain gravel-sized particles. Although R1 presented a considerable percentage of sand (70.90 % ± 23.15) followed by a smaller quantity of fines (29.10 % ± 6.42), the sediments from R2 and R3 exhibited a higher quantity of sand and lower quantity of fines. R2 and R3 had 91.50 % ± 5.74 and 92.50 % ± 8.23 of sand and 8.50 % ± 1.32 and 7.40 % ± 2.67 of fines respectively. The similarity in particle size distribution between R2 and R3 could be due to the nearness of the sampling sites. On the other hand, R4, R5, and R6 presented gravel fraction, being R4 the site with the smallest percentage of this size of particle (0.3 % ± 0.18), while R5 and R6 presented a slightly higher quantity of gravel: 8.60 % ± 4.76 and 12.60 % ± 2.32 respectively. Furthermore, R4 was characterized for its equitable content of sand and fines (49.0 % ± 7.78 and 50.70 % ± 9.23). As R5 and R6 are concerned, the results showed that both had sandy sediments (content sand upper to 50%) with smaller presence of fines (lower than 50%). It is important to consider that the highest concentrations of heavy metals were found at the R4 site, which presented the highest percentage of fine particles. Similar results were found by numerous authors who reported an increase in the concentrations of some heavy metals with a decrease in the size of the sediment particles (Yao et al. 2015; Yutong et al. 2016; Guo et al. 2019; Huang et al. 2020), while other authors showed a negative

correlation between the size of the sediment particles and the concentration of some metals (Xiao et al. 2016; Huang et al. 2019; Zeng et al. 2020). These results suggest that sediment particle size is not a useful tool for predicting the distribution of heavy metals between sediments and water.

Spatial variation in water and sediment samples

Cluster analysis (CA) was performed in order to categorize and group the sites on the basis of similarities of water and sediment heavy metal, organic matter, nitrite, nitrate, and ammonium concentrations. Ward's method and Euclidean distances as a measure of similarity were used, which is a widely accepted method for grouping (Sundaray et al. 2011). For sediment samples, the study area was classified into two main clusters: groups A and B (cophenetic correlation coefficient: 0.92, $p \leq 0.05$) (Fig. 4a). Four major clusters were recognized, in which R1 and R4 were clustered as a single entity. The CA analysis separated the R1 site from the remaining sites and formed the first group, since this site showed the lowest concentrations of heavy metals. R2 and R3 formed the second group; they are located in highly urbanized areas and showed intermediate concentrations of all heavy metals and analyzed parameters. The CA analysis separated the R1 site from the remaining sites and formed the first group, since this site showed the lowest concentrations of heavy metals. R2 and R3 formed the second group; they are located in highly urbanized areas and showed intermediate concentrations of all heavy metals and all parameters analyzed. These values are possibly due to the fact that in this area the river does not receive any affluent and is only affected by urbanization. The third group included sites R5 and R6, located after the industrial area. These sites are mainly affected by the discharge of poorly treated domestic effluents and showed the maximum concentrations of Cu, Cr, and As. The last group, which included R4, showed the maximum concentrations of Mn, Co, Ni, Zn, and Pb in the industrial zone. The content of individual elements depends on the wastewater origin. For example, Cu, Cr, and Zn are used in the textile and plastic industry, while Ni is used in the paper industry and Pb in battery production. As mentioned before, San Luis is an industrial zone and has a delimited industrial zone. However, the city grew around some industries, and this caused its wastewater to be dumped into the urban effluent sewer system, many times without being properly treated, increasing metal concentration in these sites. In relation to the physical-chemical parameters, only a decrease in pH was observed from the R5 site with an increase in turbidity, concentration of sulfate ions, and organic matter, typical of wastewater.

The clustering pattern of water samples (Fig. 4b) was arranged into three groups. Sites R1 and R2 formed the first group and presented the lowest heavy metal, organic matter, nitrite, nitrate, and ammonium concentrations. The second group included sites R3 and R4, which showed intermediate quantities of all analyzed parameters. The third group included sites R5 and R6, which were mainly affected by

Fig. 4. Dendrograms showing clustering of sampling sites according to the characteristics of sediments (**a**) and water quality (**b**) (1, 2, 3, 4, 5, and 6 correspond to R1, R2, R3, R4, R5, and R6, respectively)
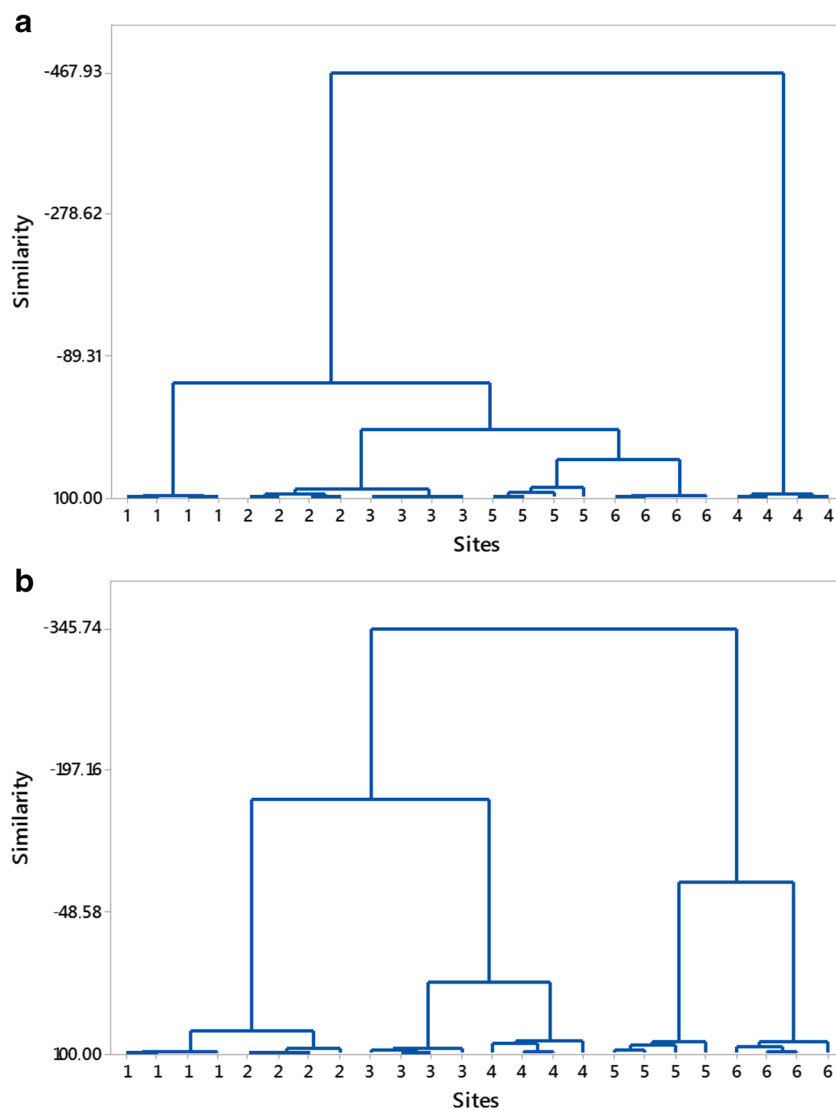
poorly treated domestic effluent discharges. This group is characterized by the high content of organic matter, NO_3^-, NH_4^+, Mn, and Zn concentrations. These clustering patterns clearly show the influence of anthropogenic activities in the analyzed sites. Although the increase in nitrates and ammonium are typical of urban effluents, the increase in Mn and Zn could be due to two probable causes. The first direct cause is that the metals come from the same effluent, while the second cause is a result of the solubilization of metals present in the sediment favored by lower pH (Haynes and Swift 1985). At sites R5 and R6, organic matter high content could increase algae blooms. Previous studies (Peel et al. 2009; Baptista et al. 2014; Jin et al. 2019) confirmed that algal blooms have a significant effect on Zn mobility. Moreover, Jin et al. (2019) found that under reducing conditions and low oxygen concentrations, the Mn and Zn contents in the pore water of the sediment simultaneously increased.

According to the sediment and water cluster analysis, it is observed that the classification of the different sites is carried out in water according to the content of organic matter. However, in sediments, the classification was conducted according to heavy metal content. This indicates that the analysis of both water and sediment should be taken into account to achieve a watershed contamination profile. The water quality reflects an instantaneous state of the river because it is subject to the contribution of other sources of water (rain, runoff, rivers). On the contrary, the sediments could be considered an additional system of the static type which allows for the evaluation of river quality over time.

Assessment of water quality using indices

The CPI index has been applied in different studies to assess the overall water quality of a watershed. For example, CPI values found by Matta et al. (2018) showed

slight to moderate pollution of the Henwal River. Similarly, a study conducted by Imneisi and Aydin (2018) successfully applied the CPI index to assess the water quality of the Elmali and Karacomak streams in Turkey. In the present study, CPI values ranged from 0.3 to 2.3, indicating the progressive contamination of the San Luis River. According to the CPI index, site R1 was classified as sub clean, R2 to R4 slightly polluted, R5 as highly contaminated, and R6 moderately contaminated. These results suggest that the anthropogenic activity and mainly the contribution of nutrients from domestic waste treatment systems affect the water quality.

Assessment of sediment quality using indices

In this study, metal pollution in sediment samples was evaluated by determining pollution indicators. Some of these indices use heavy metal background values but these tend to be very general and can be inadequate in certain areas. Therefore, several researchers have recommended the use of reference regional values (Xu et al. 2016). In the present work, taking into account the results of CA analysis, the calculation of the pollution indices was performed considering the metals found in all the sites with respect to the concentration in R1. In the case of Pb, no values were detected in R1; thus, the Pb limit of detection of the equipment was used as a background value. The CF and PLI values are summarized in Table 3. The CF values showed a high degree of pollution for Pb in all the analyzed sites (CF> 6). On the contrary, the CF values for Cd presented values lower than 1, indicating a low degree of contamination with this metal. The CF values in the industrial zone for the remaining metals showed a higher degree of pollution than the urban zone. In addition, PLI values indicated progressive deterioration of sediment quality with respect to the R1 site. The metals Pb, Co, Cu, Zn, and As were the main contributors to sediment pollution.

Along the river route, great variations of the geoaccumulation index were observed (uncontaminated to extremely contaminated) for most heavy metals (Table 4). Furthermore, I_{geo} indicated that all sites were extremely contaminated with Pb and showed that R4, R5, and R6 were the most affected sampling sites in terms of metal pollution. However, sites R2 and R3 were categorized as unpolluted ($I_{geo} < 0$) for Cu, Ni, and Zn (Fig. 5).

In general, the EF values for As, Cd, Cr, Mn, and Ni did not show modifications (EF $\leq$ 1.5), while Zn, Cu, and Co presented a moderate enrichment at sites R4, R5, and R6, respectively (Table 4). In addition, the highest EF values appeared in all sites for Pb, showing an extremely high enrichment. These significant levels of Pb in all sediments, including upstream, suggest that the potential sources could be from the adjacent motorway and surface water runoff from San Luis city. The contribution of heavy metals by anthropogenic influence to sediment is in agreement with the values reported by other authors (Li et al. 2009; Liu et al. 2011; Grba et al. 2017; Lynch et al. 2017; Taghavi et al. 2019).

The assessment of surface water quality along with the heavy metal pollution load in sediments is of immense importance for the protection of the environment and human health. The increase of heavy metal concentration in water samples exerts severe toxic effects on aquatic organisms, which leads to the complete disruption of normal ecosystem function (Islam et al. 2015b; Kumar et al. 2019). Moreover, these toxic heavy metals can enter the human body not only through ingestion of contaminated water and/or aquatic organisms but also via dermal contact with the contaminated water (Priti and Biswajit 2019).

In future studies, it would be interesting to analyze heavy metal bioavailability in both sediments and water and to correlate with microbial diversity or another organism as a biological indicator. This will provide a more accurate assessment of the risk of heavy metals in aquatic ecosystems.

Table 3 Contamination factor (CF) and Pollution load index (PLI)

Site	CF									PLI
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	
R2	8.4±1.9	0.3±0.1	8.0±3.4	1.3±0.1	1.5±0.3	5.9±1.0	0.6±0.1	103.8±0.8	0.7±0.1	2.6±0.2
R3	10.9±1.6	2.5±0.4	8.7±2.8	1.7±0.2	0.4±0.2	5.2±0.8	1.2±0.3	96.50±2.4	0.9±0.1	3.2±0.2
R4	18.1±1.7	0.3±0.2	41.4±7.1	8.2±1.8	9.1±3.7	11.4±2.1	6.3±2.1	1833.75±2.3	115.6±2.6	15.4±4.9
R5	8.7±0.7	0.5±0.3	26.0±5.7	0.6±0.4	42.6±1.7	7.0±1.1	5.4±0.8	425.88±2.7	13.6±0.9	7.1±3.8
R6	23.2±2.9	0.3±0.2	40.0±6.8	10.2±0.2	19.8±0.8	7.0±1.4	5.5±0.8	495.63±5.5	8.8±0.4	11.3±2.8

Fig. 5 Geoaccumulation index (I_{geo})
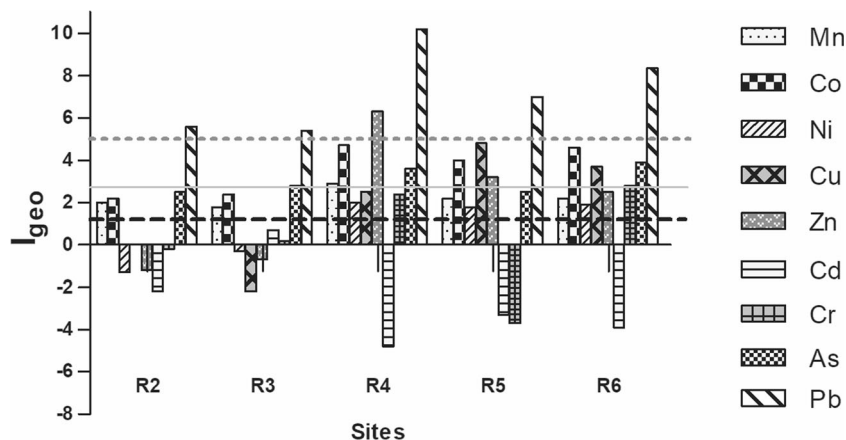
Conclusion

Our study investigated the influence of urban and industrial areas on the physical-chemical water and sediment quality. For this purpose, the application of an integrated approach of pollution indices and cluster analysis proved to be useful to understand the current San Luis River quality status. The water pollution index showed the progressive deterioration in the San Luis River in the greatest anthropogenic activity areas mainly due to organic contamination. Sediment pollution in the present study was assessed using several indices: geoaccumulation index, contamination factor, enrichment factor, and pollution load index. The elevated values identified for Pb, Co, Cu, and Zn are probably a result of anthropogenic activities in the catchment area of the dam site. Moreover, the calculation of pollution indices and SQGs shows a progressive deterioration of sediment quality along the San Luis River. Hierarchical CA helped to group the sampling sites into different clusters of similar characteristics pertaining to sediments and water quality characteristics and pollution sources. Moreover, CA confirmed R1 as a low contamination site and its correct use as a reference site. However, classifications according to sediment quality and water quality were different because water quality reflects an instantaneous state, whereas the sediments allow us to evaluate river quality over time. This work highlights the importance of an integral study: water sediments for complete information about the status of the river.

The sites following the industrial park and the domestic discharge (R4, R5, and R6) areas showed a high degree of pollution, which can be harmful to biota, in particular for benthic organisms. Based on the results obtained, it is necessary to reinforce the treatment of domestic effluents before being discharged into the San Luis River.

Therefore, continuous monitoring should be done and further studies in the area conducted to ascertain the long-term effects of anthropogenic impact.

Authors' contribution All authors contributed to the study conception and design of the work. Villegas Liliana and Almeida César: designed and supervised all the work. Castro María and Delfini Claudio: pre-sampled the river bed and were in charge of the selection and collection of the final sampling sites. Bazán Cristian: analyzed the heavy metal concentrations in water and sediment samples. Vidal Juan: characterized the texture of sediment samples. Castro María and Almeida César: carried out treatment of samples and physical-chemical tests. Castro María, Almeida César and Villegas Liliana: drafted and prepared the original draft. The final manuscript has been read, modified, and approved by all named authors.

Table 4 Enrichment factor (EF) analysis

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
R2	1.2±0.2	0.04±0.1	1.1±0.6	0.2±0.0	0.2±0.0	0.8±0.1	0.08±0.0	14.4±2.3	0.1±0.0
R3	1.4±0.2	0.3±0.3	1.1±0.6	0.2±0.1	0.1±0.0	0.7±0.1	0.2±0.0	12.7±4.2	0.1±0.0
R4	0.4±0.1	0.01±0.0	0.8±0.3	0.2±0.0	0.2±0.1	0.2±0.0	0.1±0.1	37.2±6.2	2.3±0.0
R5	0.6±0.1	0.03±0.0	1.7±0.8	0.04±0.0	2.8±0.1	0.5±0.1	0.4±0.1	28.5±3.3	0.9±0.1
R6	1.5±0.2	0.02±0.0	2.4±1.0	0.6±0.1	1.2±0.0	0.4±0.1	0.3±0.1	29.8±2.5	0.5±0.0

Data Availability All data generated or analyzed during this study are included in this published article.

Declarations

Ethics approval and consent to participate   Not applicable

Consent for publication   Not applicable

Competing interests   The authors declare no competing interests.

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