

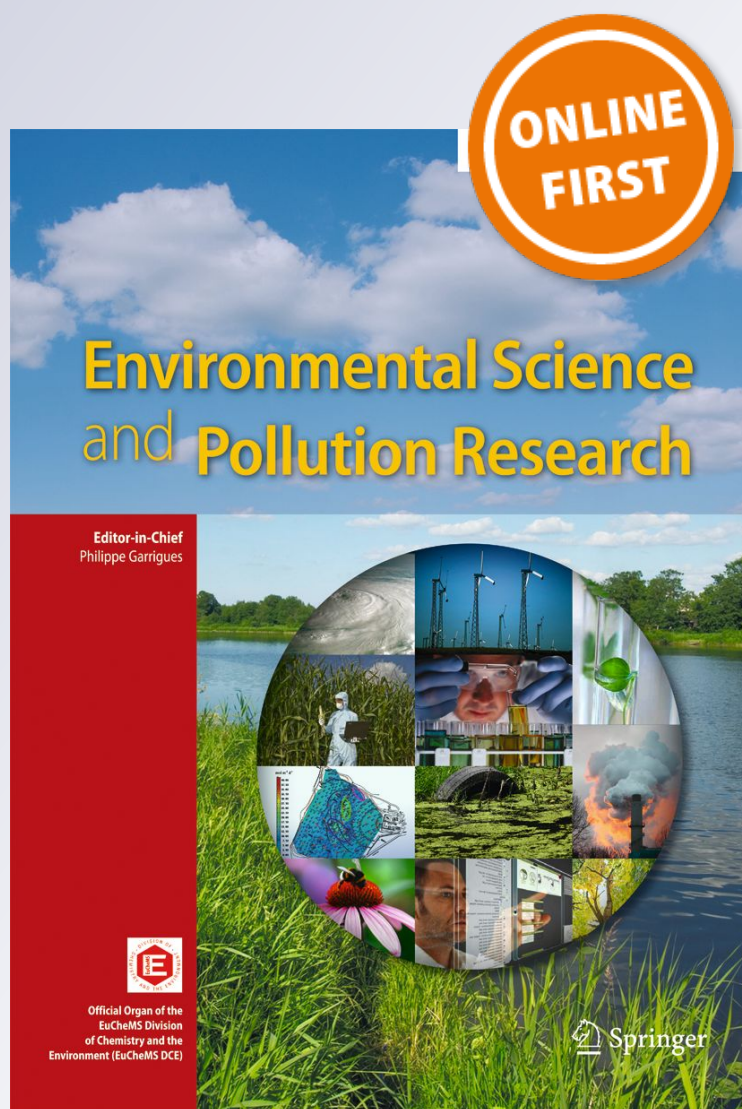
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# Water and sediment quality assessment in the Colastiné-Corralito stream system (Santa Fe, Argentina): impact of industry and agriculture on aquatic ecosystems

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## Abstract

The present study focuses on the evaluation of metal (chromium, copper, and lead), arsenic, and pesticide (atrazine and endosulfan) contamination in freshwater streams of one of the most important agricultural and industrial areas of central-eastern Argentina, which has not been reported earlier. The environmental fate of inorganic microcontaminants and pesticides was assessed. Samples were collected monthly for a year. Pesticide concentrations were measured in water; metal and arsenic concentrations were measured in water and sediments, and physicochemical variables were analyzed. In most cases, metals and arsenic in water exceeded the established guideline levels for the protection of aquatic biota: 98 and 56.25% of the samples showed higher levels of Cr and Pb, while 81.25 and 85% of the samples presented higher values for Cu and As, respectively. Cr, Pb, Cu, and As exceeded 181.5 times, 41.6 times, 57.5 times, and 12.9 times, respectively, the guideline level values. In sediment samples, permitted levels were also surpassed by 40% for Pb, 15% for As, 4% for Cu, and 2% for Cr. Geoaccumulation Index (*I<sub>geo</sub>*) demonstrated that most of the sediment samples were highly polluted by Cr and Cu and very seriously polluted by Pb, which indicates progressive deterioration of the sediment quality. Atrazine never exceeded them, but 27% of the 48 water samples contained total endosulfan that surpassed the guidelines. The findings of this study suggest risk to the freshwater biota over prolong periods and possible risk to humans if such type of contaminated water is employed for recreation or human use.

## Highlights

- Metals, arsenic, and pesticides in surface waters and sediments of central-eastern Argentina were monitored for 1 year. The status of pollution in relation to standard levels was considered in conjunction with other assessment methods.
- Similarly, to physicochemical variables, microcontaminant concentrations in sediments between sites were more informative about the impairment of the system than those between months.
- In water samples, findings suggest a serious level of metal pollution—mainly Cr, Pb, Cu and As, and pesticides mostly by endosulfan. In sediment samples, Pb, As, Cu, and Cr also surpassed the established international guideline levels.
- Proper measures in terms of technological innovations or improvements of public and private policies must be taken immediately in order to protect aquatic resources and human health.

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Improper disposal of industrial effluents and agricultural runoffs need to be controlled, and proper treatment should be done before disposal to avoid further deterioration of the aquifers of this area.

**Keywords** Aquatic system assessment · Pesticides · Metals · Arsenic · Environmental pollution

### Abbreviations

AEQGs	Argentine Environmental Quality Guidelines
As	Arsenic
Atr	Atrazine
BOD	Biological oxygen demand
CEQGs	Canadian Environmental Quality Guidelines
COD	Chemical oxygen demand
Cr	Chromium
Cu	Copper
DO	Dissolved oxygen
EEA	European Environment Agency
End	Endosulfan
EPA	Environmental Protection Agency
EQGs	Environmental quality guidelines
FD	Frequency of detection
IC	Inorganic carbon
<i>Igeo</i>	Geoaccumulation Index
INIDEP	Instituto Nacional de Investigación y Desarrollo Pesquero
LAQUIGE	Laboratorio de Química Geológica y Edafológica
MAC	Maximum allowable concentration
MC	Maximum concentration
NA	Not available
ND	No data
Pb	Lead
PCA	Principal component analysis
S1	Site one
S2	Site two
S3	Site three
S4	Site four
SD	Standard deviation
Sed.	Sediment
SRP	Soluble reactive phosphorus
T. End	Total endosulfan ( $\alpha$ END, $\beta$ END and END. SULFATO)
TOC	Total organic carbon
TSS	Total suspended solids
WHO	World Health Organization

### Introduction

Aquatic ecosystems are affected by the introduction of contaminants of different origins such as domestic, industrial effluents and washing water from polluted areas, and agriculture runoff (Dudgeon et al. 2006; Bonansea et al. 2012), making environmental pollution one of the current priority issues around the world. Many environmental institutions (e.g., WHO, EPA, EEA) and governments of several countries request further knowledge on the status of freshwater ecosystems to propose adequate and feasible management measures.

Recent studies have focused on the central-eastern area of Argentina due to the great economic importance of this region. In the Salado River and some of its tributaries, Cu, Cr, and Pb

in water exceeding permitted standard values were recorded (Gallo et al. 2006; Gagneten and Paggi 2009; José de Paggi and Devercelli 2011). Gagneten et al. (2007) have suggested that the main industrial contamination could be due to tannery effluent discharges from industries located in this area.

Considering the increment of the population, the big area occupied, and the industrial and agricultural activities developed in the basin over the last decades, it is possible that at present, other sources of input (occasional and diffuse) could have impaired these freshwater ecosystems. After more than 10 years of studies in this region, there is a clear need to continue monitoring those courses and furthermore, to widen the study area. This will contribute to gaining knowledge about the degree of disturbance of the water courses of Santa Fe Province (central-eastern Argentina) and knowing more about punctual and diffuse contamination of aquatic ecosystems.

Most of the productivity achievements of the developed countries were due to the displacement of the more polluting industries to the underdeveloped ones. In this way, these countries have been able to maintain their way of life by consuming valuable natural resources of underdeveloped countries (Novo 2006). Thus, it is perfectly possible for a nation to ensure its sustainable development at the expense of unsustainable development in another country (Coria et al. 1998). It is important for sustainability-exporting countries, such as Argentina and other Latin American ones, to provide information on the state of their ecosystems. The international relevance of this study remains on the high extended practices of discharging wastes of industrial and agricultural origin on surface water courses without previous treatment and/or control.

The growing demand for grains (mainly soy) that are exported to Asian and European countries to feed cattle and pigs requires extensive areas sown with monoculture and the use of huge volumes of pesticides and fertilizers, such as the herbicides glyphosate and atrazine and the insecticide endosulfan (CASAFE, Chamber of Agricultural and Fertilizer Health 2013). These two last ones were selected to seek for them in superficial freshwater.

Pesticides frequently reach the aquatic environment via runoff or infiltration, by container washing, or by direct spraying on rivers, lagoons, or streams, with possible negative impact on native biota (Jergentz et al. 2005; Marino and Ronco 2005; Romero et al. 2011). The economy of Argentina rests on the production of raw materials, mainly based on the agricultural industry—being soy, maize, and



wheat the most important—and that requires huge amounts of pesticides.

With 31 million hectares devoted to agriculture, Argentina ranks behind the USA, India, Russia, China, Brazil, and Australia (de Gerónimo et al. 2014), being the third worldwide soy oilseed producer. Along with the expansion of the agricultural area, the agrochemicals market in Argentina has expanded strongly in recent years, with the increase in consumption from 73 to 236 million kilogram per year in the last 10 years (64% herbicides, 16% insecticides, 20% fungicides, acaricides, and seed treatments).

Glyphosate represents 65% (182.484.206 L) of the total of pesticides used (281.652.245 L). However, it increased in a greater proportion than other herbicides owing to the presence of resistant undergrowth. The six products of greater use during 2013 were glyphosate, 2,4-D, atrazine, diclosulam, clethodim, and lambda-cyhalothrin (Aparicio et al. 2015). Argentina is considered the second country in the world in the amount of herbicides used per hectare cultivated and is the first less efficient in the amount of grains obtained (FAO 2015). The intensive use of herbicides is not reflected in a greater performance (Tons of grains obtained per hectare) if compared with that of other countries such as the USA, Germany, France, Denmark, or Australia (World Bank 2015).

On the other hand, the leather industry is the oldest of which settle in Argentina; its beginnings goes back to the end of the seventeenth century. It is currently the seventh largest exporter of leather, with factories located on several continents. The leathers of Brazil and Argentina are exported to China, Italy, the USA, and Germany (Industrial Chamber of Leather Manufactures and Allied (ICLA) (2017). However, it is important to analyze the life cycle of products that are demanded internationally. Although the animal leather tanning industry contributes significantly to the regional and global economy, the conventional technology employed is highly pollutant and produces large amounts of wastes, posing serious threats to the environment (Kabdasli et al. 2002).

The 21% of the industrial production of the region are tanneries. Chromium and other potential toxic elements, such as Cu and Pb, are used in the stainless steel production, and in the manufacture of glass, pigments, fungicides, and batteries (Gagneten et al. 2007). Although some industries certify under the international norms ISO 14001, the metals used in the processes are still found in sediments and water due to their persistence.

Besides considering contaminants of anthropogenic source, this survey assesses the concentration of arsenic in surface fresh water and sediments. Arsenic is largely naturally occurring due to elevated background content of the metalloid in volcanic sediments, although, in some regions, mining can contribute (Siegfried et al. 2015).

Owing to the toxicity, persistence, and high bioaccumulative potential, metal pollution of water and sediments is of serious

environmental concern. Their ions can enter the cells through the same transport channels used by physiologically important cations such as Ca, Mg, Fe, Cu, and Zn (Luoma and Rainbow 2005), competing with them for the adsorption sites and subsequent absorption on the cell (Castañe et al. 2003), causing deficiency of these elements (Regaldo et al. 2009), alterations in enzymatic activities, and interruption of metabolic processes (Visviki and Rashlin 1991). Some of the metals are essentially required in traces for the growth and functions of living organisms; however, exposures to higher concentrations are toxic to human and aquatic life (Ouyang et al. 2002).

The inappropriate application of pesticides and the little control of the fate of heavy metal effluents pose risks to population health and ecosystem sustainability, so there is a need of widening environmental monitoring to gather information on the possible impact that industrial and agricultural activities could have on freshwater ecosystems. Pesticide monitoring in freshwater ecosystems has increased in the last years in Argentina (Jergentz et al. 2005; Marino and Ronco 2005; Bonansea et al. 2012; Gonzalez et al. 2012; Moreno 2012; Ronco et al. 2016; Hunt et al. 2016, 2017; Primost et al. 2017). However, surveys on water and sediment quality—due to the interdependence of both compartments—considering both metal and pesticides to assess the impact of industry and agriculture on aquatic ecosystems are still scarce.

The present study focuses on the evaluation of selected metal, arsenic, and pesticide contamination in freshwater streams of one of the most important agricultural and industrial areas of Argentina, which has not been reported earlier. The comparison with permissible levels and the identification of the compartments where these microcontaminants and pesticides accumulate can help to guide further field ecotoxicological studies and to improve policies and control measures.

## Materials and methods

### Environmental context

#### Study area

The Colastiné-Corralito stream system is situated in central-eastern Argentina and is an exoreic basin that flows into the Coronda River; both of them are part of the Paraná River system that, together with the La Plata, Uruguay, and Paraguay rivers form the La Plata Basin. The Colastiné-Corralito system includes an area with low slope of approximately 6490 km<sup>2</sup> with rainfall-dependent water courses. This region is characterized by waterbodies of different depths, areas, and connectivities, with numerous lagoons and marshes and a hydrographic network formed by interconnected gullies (Iriondo and Kröhling 2007). It receives an important flow from the Corralito Stream that is born in secondary channels

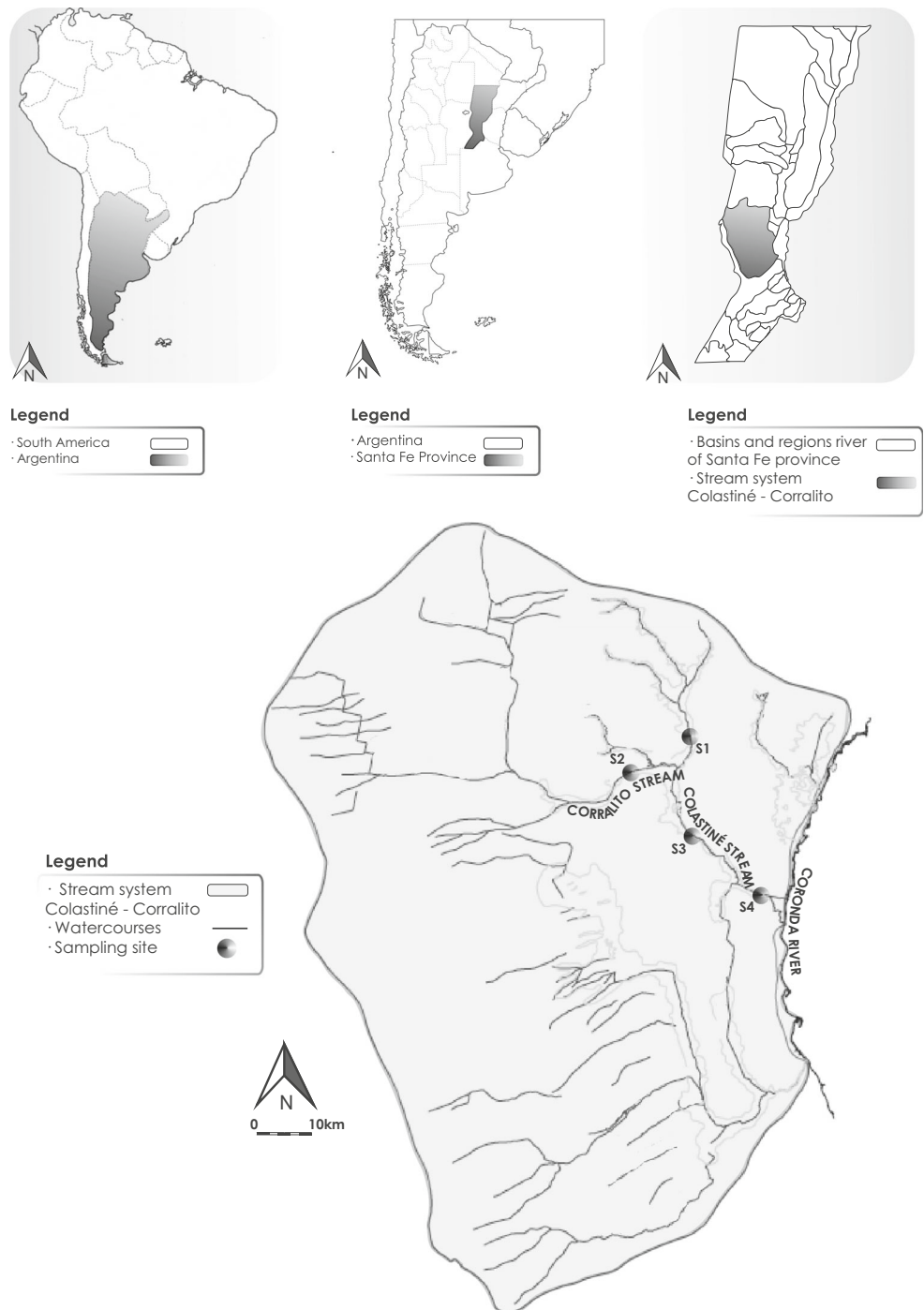
and has a maximum flow rate of  $38.7 \text{ m}^3/\text{s}$  (Castelao and Glur 2012) (Fig. 1).

The climate and geomorphology allows the production of raw materials with soy, sunflower, and corn as the predominant crops (Giraut et al. 2000; Giunta et al. 2005). The soil has sodium clay and blocks are formed in the presence of high sodium content; underground

water composition affects the soil profile and modifies its salt content (Manzi and Gallardo 1970).

The Colastiné-Corralito stream system covers 48 localities in the province of Santa Fe. Its hydrographic network is approximately 963 km and is crossed by 1509 km of road and rail networks (Castelao and Glur 2012). The urban areas are mostly dominated by small-scale industries: most of the

**Fig. 1** Location map of the sampling sites (S1, S2, S3, and S4)



industrial production is composed of tanneries, milk product factories, and manufacture of glass, pigments, fungicides, and batteries (Gagneten et al. 2007). A significant number of hectares of livestock or mixed farming operations have become exclusively agricultural. In addition, pesticides reach the basin via runoff, where recreational activities are developed (e.g., hunting and fishing). In the Coronda River, a water intake for purification and supply is projected to assist a population of over 400,000 inhabitants, living in 120 localities (Portal of the Government of the Santa Fe Province (2013b): [https://www.santafe.gov.ar/index.php/web/content/view/full/120719/\(subtema\)/93824](https://www.santafe.gov.ar/index.php/web/content/view/full/120719/(subtema)/93824)), hence the urgency to quantify the degree of pollution of the area.

### Sampling sites

Figure 1 shows the location map of the four sampling sites (S1, S2, S3, and S4). Site 1 (S1): Colastiné Stream (31° 43' 03, 3" S/61° 10' 01, 1" W); site 2 (S2): Corralito Stream (31° 47' 13, 44" S/61° 18' 40" W); site 3 (S3): Colastiné Stream (31° 54' 36, 80" S/61° 08' 49, 54" W); and site 4 (S4): Colastiné Stream, close to the Coronda River (31° 01' 02, 15" S/60° 59' 24, 97" W).

### Environmental parameters and sampling of surface waters and sediments

Physicochemical parameters were recorded monthly for a year (August 2011 to August 2012) at S1, S2, S3, and S4. In situ physicochemical measurements (water temperature, pH, conductivity, and dissolved oxygen) were carried out using LabQuest Vernier portable multiparameter equipment.

In water, the following parameters were measured: depth (m); mean velocity of the flow ( $\text{m sec}^{-1}$ ) recorded at the center of the watercourse; temperature ( $^{\circ}\text{C}$ ); transparency (Secchi disc, m); pH; conductivity ( $\mu\text{S cm}^{-1}$ ); dissolved oxygen ( $\text{mg L}^{-1} \text{O}_2$ ); total suspended solids (TSS,  $\text{g L}^{-1}$ ); chemical oxygen demand (COD,  $\text{mg L}^{-1} \text{O}_2$ ); biological oxygen demand (BOD,  $\text{mg L}^{-1} \text{O}_2$ ); total organic carbon (TOC,  $\text{mg L}^{-1}$ ); inorganic carbon (IC,  $\text{mg L}^{-1}$ ); nitrate ( $\text{mg L}^{-1} \text{NO}_3^-$ ); nitrite ( $\text{mg L}^{-1} \text{NO}_2^-$ ); and soluble reactive phosphorus ( $\text{mg L}^{-1} \text{SRP}$ ).

Total concentrations of chromium (Cr), copper (Cu), lead (Pb), arsenic (As), and pesticides [atrazine (Atr) and endosulfan (End)] were analyzed from water samples; metal (Cr, Cu, Pb) and arsenic concentrations were also recorded in sediments.

The Canadian Environmental Quality Guidelines for Aquatic Life Protection (expressed for sediments and unfiltered surface water samples) (Canadian Council of Ministers of the Environment 2003, 2008) and the Guidelines of the Undersecretariat of Hydric Resources of Argentina (expressed for filtered water) (2003a, b; 2004a, b; and 2005a, b) were

considered to evaluate pollution by metal, arsenic, and pesticide in water and sediments. The mean monthly rainfalls (mm) were surveyed at Portal of the Government of the Santa Fe Province (2013a): <http://www.santa-fe.gov.ar/gbrn/regpluv/> to consider the possible runoff of contaminants by rainfall.

### Collection and processing of samples

**Surface water sampling** Ninety-six water samples (one replicate per each site and month for metals and pesticides sampled) were taken approximately 10 cm below the surface of the stream water to measure Cr, Cu, Pb, As, Atr, and End. Forty-eight plastic bottles previously washed with  $\text{HNO}_3$  (10% v/v) and afterwards rinsed with deionized water were used to analyze inorganic microcontaminants (Cr, Cu, Pb, and As). For pesticide analysis, 48 amber glass bottles previously rinsed twice with stream water were used. Water samples were collected in plastic bottles, washed with deionized water, and rinsed twice with stream water before their filling to analyze TSS, DOC, BOD, TOC,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and SRP. The collected samples were stored in airtight ice-cold containers at 4  $^{\circ}\text{C}$  and transported to the laboratory within 24 h of collection.

**Sediment sampling** A total of 48 surface sediment samples were taken using a manual dredge (i.e., mud-snapper) with an effective extraction surface of  $100 \text{ cm}^2$ . The collected samples were placed in plastic containers, maintained refrigerated at 4  $^{\circ}\text{C}$ , and transported until being digested in the laboratory for their subsequent analyses.

### Metals and arsenic in surface water and sediment samples

Metals and arsenic were analyzed in water and sediments were performed following Martin et al. (in Environmental Protection Agency 1994). Each water sample was preserved in acid medium (nitric acid  $\text{pH} < 2$ ) until analysis. For total Cr, Cu, Pb, and As analysis, a homogenized aliquot of 100 mL was transferred to a 250-mL Erlenmeyer flask. Afterwards, 2 mL nitric acid and 1 mL hydrochloric acid were added. The Erlenmeyer flasks were placed on a heating plate at 85  $^{\circ}\text{C}$  for evaporation. The sample volumes were reduced to approximately 20 mL. After the solutions were allowed to cool at an ambient temperature, they were quantitatively transferred to 100-mL containers to complete the water volume for analyses and carefully mixed.

Metals and arsenic analyses in sediments were performed after each sample ( $< 20 \text{ g}$ ) was dried until constant weight at 60  $^{\circ}\text{C}$  in an oven and homogenized in a mortar. Aliquots of  $1.0 \pm 0.01 \text{ g}$  taken from dry and homogeneous material from each sample were weighed and transferred to 250-mL Erlenmeyer flasks in which the acid extraction with 4 mL  $\text{HNO}_3$  and 10 mL  $\text{HCl}$  was carried out. Samples were then

heated and slightly agitated for 30 min until obtaining an approximate volume of 3–4 mL. Afterwards, samples were allowed to cool, and the extract was first filtered, to eliminate the insoluble silicates, and then transferred to a flask to complete the volume up to 50 mL with ultrapure distilled water.

The Cr, Cu, Pb, and As concentrations were measured in water samples, as well as in sediment samples, according to Creed et al. (in Environmental Protection Agency 1994) using a Perkin Elmer (model PE 8000) atomic absorption spectrophotometer equipped with a graphite oven, using standardized techniques for calibration. Detection limits were  $< 5 \mu\text{g L}^{-1}$  for Cr, Cu, and Pb, and  $< 2 \mu\text{g L}^{-1}$  for As. Certified analytical-quality reagents were used. Blanks were used for all analyses. Blank calibration was controlled at the beginning and end of determinations to test the possible level of variation in the calibration of instruments.

### Geoaccumulation Index

Geoaccumulation Index (*I<sub>geo</sub>*) was used as a measure of metal and arsenic pollution in sediments. It was calculated based on the values of metals from sediments of the study area (background levels). The reference levels on sediment samples for Cr, Pb, Cu, and As were established on the basis of analyses carried out by Arribère et al. (1997), LAQUIGE, and INIDEP (unpublished data, Argentina) taken from streams belonging to the Paraná River basin, which includes the Salado River. The samples were taken from the main and secondary channels of the Paraná River, 0.5–5 km upstream the Salado River outlet. *I<sub>geo</sub>* was calculated using this data for all the study sites.

Müller (1981) assessed the degree of metal pollution by means of seven different grades based on the numerical values of the Geoaccumulation Index:  $I_{geo} = \log_2 (C_n/1.5B_n)$ , where  $C_n$  is the measured concentration of element  $n$  in the sediment and  $B_n$  is the geochemical background value of element in the background sample. The factor 1.5 was introduced to minimize the possible variations in the background values which may be attributed to lithogenic effects. Geoaccumulation Index consists of seven grades ranging from unpolluted to very seriously polluted environments:  $< 0$ , 1–2, 3–4, and  $> 5$  and can be interpreted as “uncontaminated,” “moderately polluted,” “highly polluted,” and “very seriously polluted,” respectively (Muniz et al. 2004).

### Quantification of pesticides in surface water samples

The atrazine analysis was carried out using an ultrahigh-pressure liquid chromatograph (UHPLC) coupled to an ionization source by electrospray with quantification by tandem mass spectrometry (MS/MS). Water samples were subjected to a preparation and cleaning process by solid phase extraction (SPE), based on the method described by Min et al. (2008),

prior to the chromatographic injection. Moreover, aspects related to chromatographic methodology, mobile phases, ionization conditions, and operative variables of detection of the triple quadrupole mass spectrometer in multiple-reaction monitoring (MRM) mode were evaluated. Separation was carried out in a rapid resolution column (C18, 2.1 mm  $\times$  100 mm, 1.7  $\mu\text{m}$ ) using gradient elution, with an acetonitrile and water mix mobile phase, both with 0.1% (v/v) formic acid. In relation to mass detection, two transitions from the atrazine pseudomolecular ion ( $[M + H]^+$ ,  $m/z = 216.1$ ) were used for its identification:  $216.1 > 174.1$  and  $216.1 > 104.0$ , which come from losses of  $\text{CHCH}_3\text{CH}_3$  and from the group  $\text{CH}_3\text{CH}_2\text{NH}$ , in addition to the time of retention, while for its quantification, the most abundant transition,  $216.1 > 174.1$ , was used. The detection and quantification limits reached were 0.001 and 0.002  $\mu\text{g L}^{-1}$ , respectively. The proposed methodology was validated carrying out recovery, repeatability, reproducibility, and ionization efficiency studies. Moreover, the influence of the matrix on the analyte signal was evaluated by carrying out calibration curves in solvent and matrix.

Total endosulfan ( $\alpha$  End,  $\beta$  End, and End sulfate) was assessed by gas chromatography (GC-ECD) following the ASTM D 6520-06 method proposed by APHA (1976). The detection and quantification limits reached were 0.002 and 0.004  $\mu\text{g L}^{-1}$  for  $\alpha$  End; 0.010 and 0.020  $\mu\text{g L}^{-1}$  for  $\beta$  End; and 0.030 and 0.060  $\mu\text{g L}^{-1}$  for End sulfate.

### Total suspended solids (TSS), chemical oxygen demand (COD), biological oxygen demand (BOD), total organic and inorganic carbon (TOC-IC), nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), and soluble reactive phosphorus (SRP)

These variables were measured following standardized methodologies proposed in international protocols:

TSS: according to method 160.3 proposed by APHA (1975a). Aliquots of 50 mL of the sample (previously homogenized) were placed in porcelain capsules and dried until constant weight at 103–105  $^\circ\text{C}$ ; afterwards, TSS were estimated by weight differences using a high-resolution analytical balance (determination range 10–20,000  $\text{mg L}^{-1}$ ).

COD: according to method 410.1 (APHA 1975b). Potassium dichromate in a solution of sulfuric acid (50%) at a controlled temperature was used as oxidation agent. Silver sulfate was added as catalyzer, and mercuric sulfate was added to eliminate chloride interferences. The excess of dichromate was assessed with standard ferrous ammonium sulfate, using a ferrous complex as indicator. BDO: according to method 405.1 (5 days, 20  $^\circ\text{C}$ ) (APHA 1980). Samples were incubated in dark conditions for 5 days; afterwards, the reduction in dissolved oxygen



concentration in this period was recorded using the Winkler test.

TOC and IC: according to method 415.1 proposed by APHA (1975c). Fifty milliliters of sample was acidified with hydrochloric acid until  $\text{pH} \leq 2$ . Afterwards, readings were carried out with a total organic carbon analyzer—5000-A (Shimadzu).

$\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and SRP: according to techniques SM 4500-P-E, SM 4500- $\text{NO}_2$ -B, and SM 4500- $\text{NO}_3$ -D proposed by APHA (1998).

## Statistical analysis

Normality of data distribution and homogeneity of variances were corroborated prior to the analysis using the Kolmogorov-Smirnov test and Bartlett test, respectively. One-way analysis of variance (ANOVA) and a posteriori Bonferroni test were applied to analyze the significant differences among various physicochemical parameters and metal, arsenic, and pesticide concentrations recorded at the different sampling sites and months (Sokal and Rohlf 1969). Linear and Spearman correlation analyses were performed to establish comparisons among different environmental parameters, physicochemical parameters, and potential toxic metals, arsenic, and pesticide concentrations. Differences were considered significant when  $p < 0.05$ . In order to synthesize the information provided by the pollutants and physicochemical parameters on each studied site, we used principal component analysis (PCA) after standardizing the variables.

## Results and discussion

A spatial- and temporal-dependent integral study of physicochemical variables, microcontaminants, and pesticides showed that the spatial approach (sampling sites) provided more information than the temporal one (months of sampling).

The incidence of each of the variables and pollutants measured at the four sites and 12 months is analyzed and discussed with background levels—if available—and guideline levels.

### Water physicochemical parameters

Mean depth at sites S1, S2, and S3 was low ( $< 1$  m), significantly different from that of S4, where depth exceeded 2 m (ANOVA,  $p < 0.001$ ). The results revealed that the mean annual flow velocity was similar at S1 and S4 (0.09 and 0.06  $\text{m sec}^{-1}$ , respectively) and lower than that recorded at S2 and S3 (0.45 and 0.47  $\text{m sec}^{-1}$ , respectively).

Water temperature along the year varied from 11 to 29 °C, with a mean of 22.4 ( $\pm 1.2$ ) °C. In relation to monthly records, this parameter showed variations according to the regional

seasonal dynamics. Differences in water transparency were recorded among sampling sites, being higher at S1 and decreasing progressively at S2, S3, and S4 (ANOVA, S1 vs. S3 and S4,  $p < 0.05$  and  $p < 0.01$ , respectively) (Table 1).

The annual mean pH level was 8.25 ( $\pm 0.5$ ), 8.04 ( $\pm 0.5$ ), 8.01 ( $\pm 0.5$ ), and 8.16 ( $\pm 0.7$ ), from S1 to S4, respectively. There was no significant difference between sites (ANOVA,  $p > 0.05$ ) (Table 1).

Conductivity was very high (exceeding 1000  $\mu\text{S cm}^{-1}$ ), with annual means of 8576.2; 13,666.7; 11,429.8; and 3541.6  $\mu\text{S cm}^{-1}$  at S1, S2, S3, and S4, respectively (Table 1). No significant differences were found between S2 and S3 (ANOVA,  $p > 0.05$ ), although there were significant differences between S1 vs. S2 and S4, and between S2 and S3 vs. S4 (ANOVA,  $p < 0.001$ ). The conductivity was higher at S2 and S3, reaching maximum values of 18,240 and 17,330  $\mu\text{S cm}^{-1}$  in September, in coincidence with scarce precipitations (16 and 6 mm, respectively). Maximum conductivity values recorded in the Corralito Stream (S2) and in the Colastiné Stream (S3) in September showed an extremely significant positive correlation with total suspended solid (TSS) concentrations ( $r = 0.6637$ ;  $p < 0.0001$ ). The highest concentrations of TSS were recorded at S2 and S3, with annual mean values of 11.88 ( $\pm 0.88$ ) and 11.05 ( $\pm 1.9$ )  $\text{g L}^{-1}$ , being lower at S1 and S4: 6.52 ( $\pm 0.53$ ) and 3.24 ( $\pm 1.37$ )  $\text{g L}^{-1}$ . No significant differences were recorded between S2 and S3, although there were significant differences among the other sampling stations (ANOVA,  $p < 0.001$ ). Conductivity is sometimes used as an indirect measure of water salinity (Montes and Martino 1987). Variations in conductivity demonstrated a significantly inverse relationship with monthly precipitations (Spearman rank correlation:  $r = -0.68$ ;  $p = 0.01$ ). The studied environments can be characterized as alkaline waters, with annual mean pH level  $> 8$ . Periods of maximum conductivity coincided with scarce precipitations. According to Manzi and Gallardo (1970), soil salts ascend by capillarity in drought periods and, afterwards, descend when precipitations increase, being able to modify the conductivity of aquatic systems.

Low levels of dissolved oxygen are indicative of impairment of aquatic environments (Wilcock et al. 1995; Huggins and Anderson 2005). Records of dissolved oxygen included a wide range, although most were higher than 5  $\text{mg L}^{-1}$ . Minimum values were recorded in October and November at S1 (5.2 and 5.7  $\text{mg L}^{-1}$ ), and in November at S4 (4.4  $\text{mg L}^{-1}$ ), while the other months showed higher and similar values among them. No significant differences were found among the sampling sites (ANOVA,  $p > 0.05$ ) (Table 1).

Water quality may be affected by the input of organic matter coming from urban wastes and from agricultural and cattle raising activity. COD presented high annual mean values (623–835  $\text{mg L}^{-1}$ ), while BOD was higher at sites 2 and 3, and slightly lower at sites 1 and 4 (Table 1), corresponding to

**Table 1** Physicochemical parameters recorded at each sampling site (S1, S2, S3, and S4), mean values ( $N = 12 \pm 1$  SD standard deviation): temperature ( $^{\circ}\text{C}$ ), depth (m), transparency (Secchi, m), current velocity ( $\text{m seg}^{-1}$ ), conductivity ( $\mu\text{S cm}^{-1}$ ), pH, dissolved oxygen (DO,  $\text{mg L}^{-1}$ ), rain (monthly mean, mm), total suspended solids (TSS,  $\text{g L}^{-1}$ ), totalorganic carbon (TOC,  $\text{mg L}^{-1}$ ), inorganic carbon (IC,  $\text{mg L}^{-1}$ ), chemical oxygen demand (COD,  $\text{mg L}^{-1}$ ), biological oxygen demand (BOD,  $\text{mg L}^{-1}$ ), nitrates ( $\text{NO}_3^-$ ,  $\text{mg L}^{-1}$ ), nitrites ( $\text{NO}_2^-$ ,  $\text{mg L}^{-1}$ ), soluble reactive phosphorus (SRP,  $\text{mg L}^{-1}$ )

	Site 1	Site 2	Site 3	Site 4
Temperature ( $^{\circ}\text{C}$ )	21 ( $\pm 4.58$ )	22.23 ( $\pm 4.8$ )	22.43 ( $\pm 4.5$ )	24 ( $\pm 4.3$ )
Depth (m)	0.825 ( $\pm 0.11$ )	0.41 ( $\pm 0.23$ )	0.56 ( $\pm 0.28$ )	2 ( $\pm 1.08$ )
Transparency (Secchi, m)	0.63 ( $\pm 0.26$ )	0.39 ( $\pm 0.37$ )	0.34 ( $\pm 0.2$ )	0.26 ( $\pm 0.12$ )
Current velocity ( $\text{m seg}^{-1}$ )	0.09 ( $\pm 0.06$ )	0.45 ( $\pm 0.23$ )	0.47 ( $\pm 0.2$ )	0.06 ( $\pm 0.03$ )
Conductivity ( $\mu\text{S cm}^{-1}$ )	8576.25 ( $\pm 2226$ )	13,666.75 ( $\pm 5509$ )	11,429.83 ( $\pm 5832$ )	3541.6 ( $\pm 19.74$ )
pH	8.25 ( $\pm 0.5$ )	8.04 ( $\pm 0.5$ )	8.01 ( $\pm 0.5$ )	8.16 ( $\pm 0.7$ )
Dissolved oxygen (DO, $\text{mg L}^{-1}$ )	8.27 ( $\pm 2.18$ )	9.32 ( $\pm 2.5$ )	9.85 ( $\pm 3.5$ )	9.04 ( $\pm 3.08$ )
Rain (monthly averages, mm)	90.5 ( $\pm 76.4$ )	67.3 ( $\pm 42.3$ )	70.5 ( $\pm 51.6$ )	76.5 ( $\pm 63.4$ )
Total suspended solids (TSS, $\text{g L}^{-1}$ )	6.5 ( $\pm 0.5$ )	11.8 ( $\pm 0.8$ )	11.05 ( $\pm 1.9$ )	3.24 ( $\pm 1.37$ )
Total organic carbon (TOC, $\text{mg L}^{-1}$ )	27.1 ( $\pm 25$ )	21.5 ( $\pm 20.42$ )	24.8 ( $\pm 18.3$ )	25.3 ( $\pm 17.11$ )
Inorganic carbon (IC, $\text{mg L}^{-1}$ )	35 ( $\pm 26.7$ )	34.63 ( $\pm 26.85$ )	30.31 ( $\pm 27.2$ )	23.45 ( $\pm 19.38$ )
Chemical oxygen demand (COD, $\text{mg L}^{-1}$ )	623.43 ( $\pm 707$ )	835.4 ( $\pm 1007$ )	757.13 ( $\pm 947$ )	748.9 ( $\pm 931.7$ )
Biological oxygen demand (BOD, $\text{mg L}^{-1}$ )	74.53 ( $\pm 55.6$ )	95.7 ( $\pm 74.62$ )	99.8 ( $\pm 99$ )	60.9 ( $\pm 44.13$ )
Nitrates ( $\text{NO}_3^-$ , $\text{mg L}^{-1}$ )	1.16 ( $\pm 1.5$ )	4.7 ( $\pm 4.7$ )	2.74 ( $\pm 3.5$ )	1.16 ( $\pm 0.92$ )
Nitrites ( $\text{NO}_2^-$ , $\text{mg L}^{-1}$ )	0.1 ( $\pm 0.2$ )	0.228 ( $\pm 0.18$ )	0.07 ( $\pm 0.04$ )	0.002 ( $\pm 0.0$ )
Soluble reactive phosphorus (SRP, $\text{mg L}^{-1}$ )	0.3 ( $\pm 0.2$ )	0.64 ( $\pm 0.29$ )	0.51 ( $\pm 0.26$ )	0.47 ( $\pm 0.23$ )

polysaprobic environments (Margalef 1983). This situation was the same as that recorded in previous studies in the lower Salado River basin (Gagneten and Ceresoli 2004; Gagneten and Paggi 2009), although records were higher in this study, indicating an impairment of water quality after a decade.

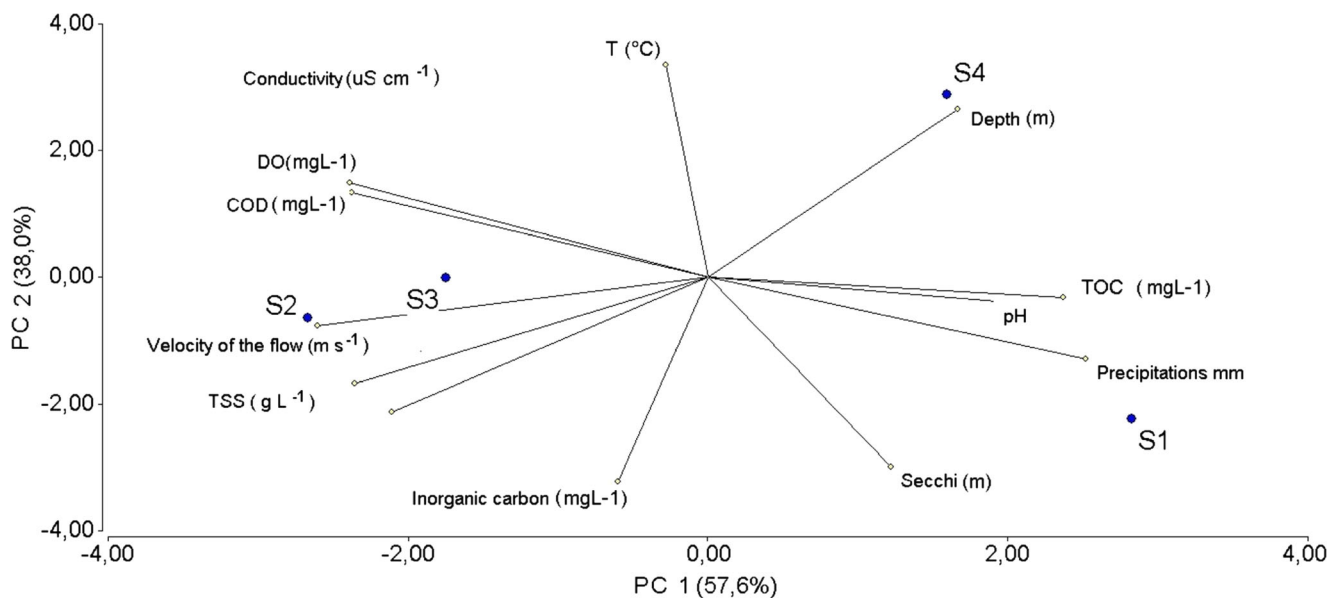
COD values were high in January, February, and April (means of four sites for the 3 months: 1750, 2250, and 1600  $\text{mg L}^{-1}$ , respectively), showing significant differences in relation to the other months (ANOVA,  $p < 0.001$ ). No differences were found among the studied sites (ANOVA,  $p > 0.05$ ). The highest BOD values were recorded in January, February, March, April, and September. The maximum value was found at S3 in April (300  $\text{mg L}^{-1}$ ). No differences were found among the studied sites (ANOVA,  $p > 0.05$ ).

TOC values were higher in March, showing highly significant differences when compared with those recorded in August and September (ANOVA,  $p < 0.0001$ ), reaching 97.19, 80.07, 58.92, and 72.1  $\text{mg L}^{-1}$  at S1, S2, S3, and S4, respectively. No differences were found among the studied sites (ANOVA,  $p > 0.05$ ). Organic carbon concentration is an indicator of decomposed organic matter, which in epicontinental waters generally oscillates from 1 to 30  $\text{mg L}^{-1}$  (Margalef 1983). When these values are exceeded—as in this study—the system generally contains an organic matter input from peripheral ecosystems, which can reach the aquatic systems via runoff. In this study, a significantly positive correlation among TOC values and precipitations was found ( $r = 0.60$ ;  $p = 0.03$ ).

High variable values of nitrates were recorded at the studied sites, with higher concentrations at S2, which were significantly different to those at S1 and S4 (ANOVA,  $p < 0.05$ ) (Table 1). The lowest value was recorded at S2 in September 2011 (0.4  $\text{mg L}^{-1}$ ), and the highest value was recorded in August 2012 (15.3  $\text{mg L}^{-1}$ ), showing significant differences between the 2 months (ANOVA,  $p < 0.01$ ).

Nitrite concentrations had no significant differences among the studied months (ANOVA,  $p > 0.05$ ). SRP had significantly different concentrations between S1 and S2. The lowest records were found in June (mean of the four sites 0.11  $\text{mg L}^{-1}$ ), showing significant differences with the other months (ANOVA,  $p < 0.01$ ), while maximum values were found in March (mean of the four sites 0.74  $\text{mg L}^{-1}$ ). The correlations performed between precipitations and nutrients (nitrates, nitrites, and SRP) were positive but not significant (ANOVA,  $p > 0.05$ ).

The analysis of the physicochemical variables showed greater effect of the space (sites) than of the time (months). According to the PCA (Fig. 2), 96% of the total variation of the data is explained by the first two components. The first component explains 58% of the variation: the most important variables in this component were pH, flow velocity (negative), rainfall, DO, and COD (negative). Towards the positive region of the first component, sites 1 and 4 are characterized by higher pH values, lower current velocities and lower DO and COD, and lowest organic contamination. To the negative region of this component, sites 2 and 3 had higher current



**Fig. 2** PCA loading plot with the environmental variables included in the analyses and sampling sites (points). (Principal components—PC—1 and 2, explaining 96% of the total variation)

velocities, which in turn produce higher OD with higher organic load. The second component explains 38% of the total variation, and towards the positive region, the site 4 is characterized by higher  $T^{\circ}$  and lower transparency (Fig. 2).

### Metals, arsenic, and pesticides in water and sediments

At present, there is no available information related to background metals, arsenic, and pesticide concentrations in the Colastiné-Corralito stream system. There is also no information on the possible effects on aquatic communities (e.g., plankton, benthos, fishes). In order to fill this gap, the mean and maximum concentrations recorded in surface water and sediment samples analyzed in this study are listed in Table 2. The maximum allowable concentrations of metals, arsenic, and pesticides, according to Canadian and Argentine Environmental Quality Guidelines (CEQGs/AEQGs), and the frequency at which they were recorded, are also included. The environmental quality guidelines (EQGs) were discussed in conjunction with other assessment methods (e.g., comparison to background values, characterization of other factors controlling bioavailability, and toxicity tests). As can be seen in Table 2, in general, Canadian guideline levels are stricter (lower) than Argentine ones.

According to the PCA (Fig. 3), 88% of the total variation is explained by components 1 and 2. The first component explained 65% of the total variation, being metals the parameters which more information provided, specifically Cu and Cr in sediments, Pb in water, and As and Pb in sediments. In the positive axis, site 1 had the highest values of metals and site 4 had the lowest in the negative axis.

The second component accounted for 23% of the remaining variation, being As, endosulfan, and Cr in water the most important. In the positive axis, sites 2 and 3 showed the highest records. To the negative region, site 4 had higher concentrations of Cu in water (Fig. 3).

### Metals and arsenic in water

At S1, S2, and S3, the decreasing order was:  $Cr > Pb > As > Cu$ , and at S4,  $Cr > Cu > Pb > As$ . S1 showed the maximum annual mean concentration of Pb ( $41.4 \mu\text{g L}^{-1}$ ), S2 showed the maximum annual mean concentrations of Cr ( $77.6 \mu\text{g L}^{-1}$ ) and As ( $20.9 \mu\text{g L}^{-1}$ ), while S4 showed the maximum annual mean concentration of Cu ( $28.1 \mu\text{g L}^{-1}$ ) (Table 2). Among the studied microcontaminants, no significant variations between sampling sites were observed for Cr, Cu, Pb, and As in water (ANOVA,  $p > 0.05$ ). Similarly, Gagneten et al. (2007) showed that sediments act as sinkers of Cr, Cu, and Pb, since those metals were measured in low concentrations in the water column.

The concentrations of Cr, Cu, Pb, and As in water varied greatly among months (Fig. 4). At S1 and S4, significant differences were found among annual concentrations of Cr, Cu, Pb, and As (ANOVA,  $p = 0.01$  and  $p = 0.003$ , respectively). Among the studied sampling sites, no significant variation was observed for S2, but  $p$  value was close to the significance level for S3 (ANOVA,  $p = 0.14$  and  $p = 0.07$ , respectively).

Maximum Cr and Pb values were recorded in August and September 2011 at all sites. Cr and Pb concentrations were 176–181.5 times higher and 24.4–41.6 times higher, respectively, than the guideline levels proposed by the Canadian guideline levels (Canadian Environmental Quality

**Table 2** Summary of Canadian and Argentine Environmental Quality Guidelines (CEQGs—expressed for sediments and unfiltered surface water samples/AEQGs—expressed for filtered water): maximum allowable concentration (MAC  $\mu\text{g L}^{-1}$ ); frequency of detection (FD, %); mean ( $\mu\text{g L}^{-1}$ ); and maximum concentration (MC;  $\mu\text{g L}^{-1}$ ) of metals (Cr, Cu, Pb), arsenic (As), and pesticides (atrazine—Atr—and total endosulfan—T.End) in water and sediments (sed.) from four sampling sites along a year (August 2011–August 2012)

CEQGs	Site 1			Site 2			Site 3			Site 4				
	MAC ( $\mu\text{g L}^{-1}$ )	AEQGs	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )
Cr	1–8.9 <sup>e</sup>	2.5 <sup>a</sup>	100	66.7	357	100	77.6	363	100	67.9	360	100	74.2	352
Cu	2–4	6.6 <sup>b</sup>	100	13	26	100	14.7	36	100	14.6	43	100	28.1	230.8
Pb	1–7	1.59	100	41.4	291	100	27.8	131	100	32	164	100	24.2	155
As	5	15	100	16.9	31.4	100	20.9	64.3	100	18.7	52.8	100	10	18
Sed.	MAC ( $\mu\text{g g}^{-1}$ )	MAC ( $\mu\text{g g}^{-1}$ )	FD (%)	Mean ( $\mu\text{g g}^{-1}$ )	MC ( $\mu\text{g g}^{-1}$ )	FD (%)	Mean ( $\mu\text{g g}^{-1}$ )	MC ( $\mu\text{g g}^{-1}$ )	FD (%)	Mean ( $\mu\text{g g}^{-1}$ )	MC ( $\mu\text{g g}^{-1}$ )	FD (%)	Mean ( $\mu\text{g g}^{-1}$ )	MC ( $\mu\text{g g}^{-1}$ )
Cr	37.3	ND	100	17.2	71.1	100	10.4	16.4	100	11.2	16.8	100	9.6	14.1
Cu	35.7	ND	100	26.1	46.8	100	20.2	23.8	100	20.5	30.2	100	16.7	25.6
Pb	35	ND	100	26.6	42.2	100	26.5	47.4	100	26.1	46	100	23.3	45.7
As	5.9	ND	100	6.7	31.5	100	4.6	7.8	100	4.1	5.8	100	4.3	6
Water	MAC ( $\mu\text{g L}^{-1}$ )	MAC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )	FD (%)	Mean ( $\mu\text{g L}^{-1}$ )	MC ( $\mu\text{g L}^{-1}$ )
Atr.	1.8	3	100	0.036	0.13	100	0.05	0.14	75	0.21	0.86	100	0.16	1.73
T.End	0.003	0.007	33.33	0.009	0.05	25	0.014	0.102	25	0.015	0.13	25	0.012	0.13

ND no data

<sup>a</sup> When recording the total concentration of Cr (Cr<sup>+6</sup> and Cr<sup>+3</sup>) only, the guideline level is derived for Cr<sup>+6</sup>

<sup>b</sup> Hardness value at which the data fit: 100 CaCO<sub>3</sub> (mg L<sup>-1</sup>)

<sup>c</sup> 1  $\mu\text{g L}^{-1}$  for Cr<sup>+6</sup> and 8.9  $\mu\text{g L}^{-1}$  for Cr<sup>+3</sup>

Guidelines 2008). The highest Cu concentration was recorded in August 2011 at S4 (230.8  $\mu\text{g L}^{-1}$ ), exceeding 57.7 times the values proposed for the protection of the aquatic biota (Canadian Environmental Quality Guidelines 2008). Conversely, the maximum As concentration (64.34  $\mu\text{g L}^{-1}$ ) recorded in April in the Corralito Stream (S2) was 12.9 times higher than the Canadian guideline levels (Tables 2 and 3).

According to the Undersecretariat of Hydric Resources of Argentina (2004a), mean As concentrations recorded in surface freshwater (Uruguay, Iguazú, Paraná, and La Plata rivers, 1988–1995 period) ranged from 10 to 17  $\mu\text{g L}^{-1}$ . In this study, higher concentrations were recorded: 64.3  $\mu\text{g L}^{-1}$  in the Corralito Stream, 52.83  $\mu\text{g L}^{-1}$  at S3, 31.45  $\mu\text{g L}^{-1}$  at S1, and 18.07  $\mu\text{g L}^{-1}$  at S4, in the Colastiné Stream.

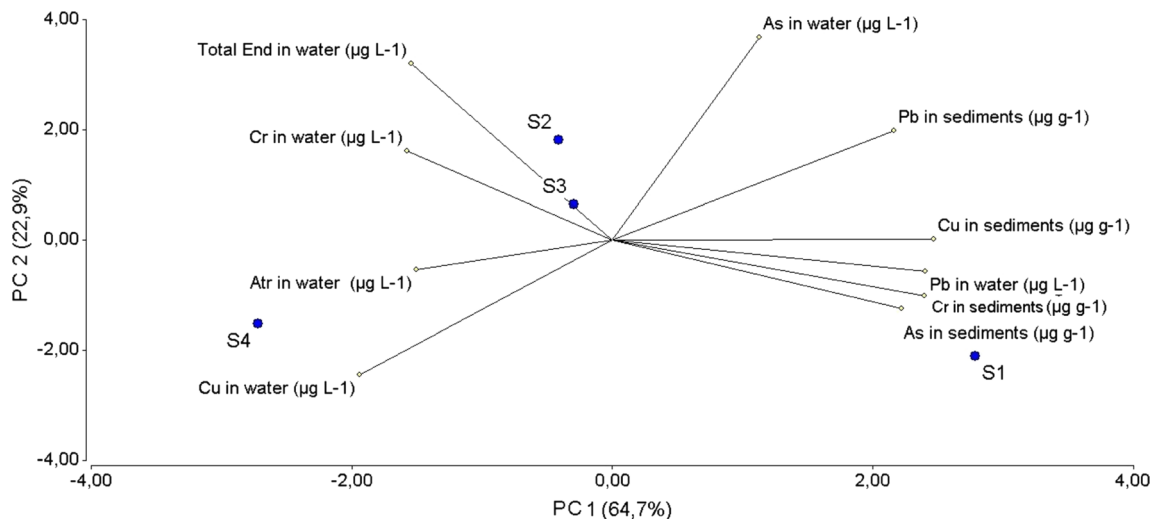
Metal concentrations recorded in water were higher than those found by other authors at the lower section of the Salado River (Gagneten et al. 2007; Gagneten and Paggi 2009; José de Paggi and Devercelli 2011). Gallo et al. (2006) found high variations in the mean Cr concentration: values of < 10–30 and 12.1–18.8  $\mu\text{g L}^{-1}$  were observed in the Cululú Stream and in the Salado River, respectively, with maximum values of 4573  $\mu\text{g L}^{-1}$  at the site close to Esperanza city. In this study, Cr in water was always in higher concentrations than other metals, with 98% of the samples exceeding the guideline levels proposed for the protection of the aquatic biota. This finding alerts that, besides the historical and background Cr pollution already recorded by the authors more than a decade ago, there is also current input of Cr in water, coming from industrial activities and persisting by lack of controls.

The literature that demonstrates the impact of metals on aquatic biota is extensive (Gagneten and Paggi 2009; Gutierrez and Gagneten 2011; Bajguz 2011; Gutiérrez et al. 2012; Regaldo et al. 2013, 2014; among many others). Direct toxic effects on survival, fecundity, sexual maturity, and growth of native cladocerans were observed in chronic assays when they were exposed to lower concentrations than those recorded in this study ( $\geq 5 \mu\text{g L}^{-1}$  Cu and Cr, and  $\geq 30 \mu\text{g L}^{-1}$  Pb; Regaldo et al. 2014). It should be pointed out that the limits established for Pb are similar to or even more strict than those for Cu and Cr, but Cu and Cr are the most toxic ones (Wong and Pak 2004; Gutiérrez et al. 2010).

### Metals and arsenic in sediments

In sediments, in contrast to water results, Cr had lower concentrations than Cu and Pb, although higher than As. The order for decreasing mean concentrations of metals and arsenic in sediments was Pb > Cu > Cr > As for all the studied sites. S1 showed the maximum annual means for Pb, Cu, Cr, and As (Table 2). Significant differences in concentrations of Cr, Cu, Pb, and As in sediments were found among sites (ANOVA,  $p = 0.006$ ).





**Fig. 3** PCA loading plot with the potential toxic elements in water and sediment included in the analyses and sampling sites (points) (principal components—PC—1 and 2, explaining 88% of the total variation)

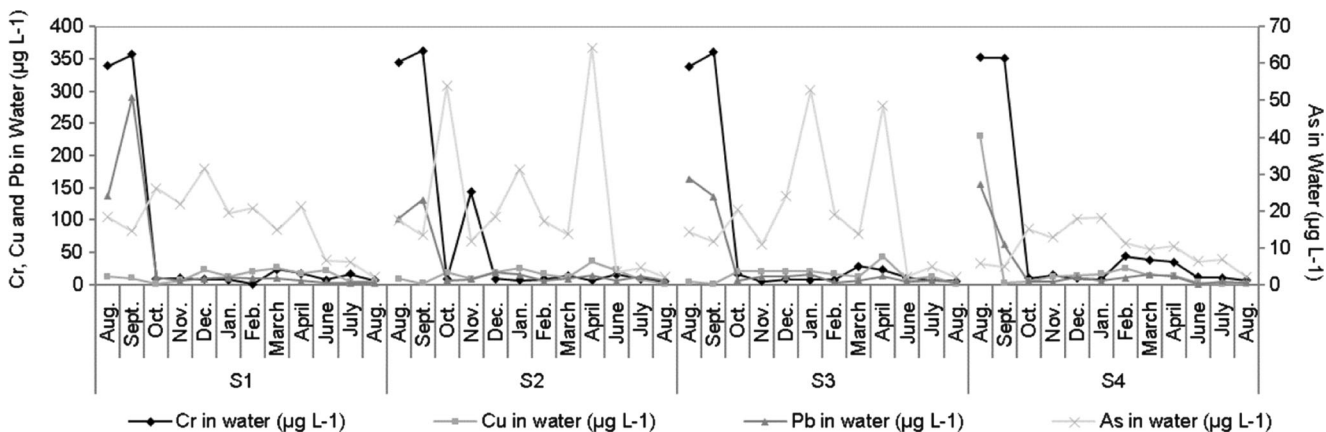
The concentrations of metals and arsenic recorded in sediments for the different months were very variable (Fig. 5). The highest Pb concentrations were recorded from October to April. The maximum Pb value was recorded in November 2011 at S2 ( $47.43 \mu\text{g g}^{-1}$ ). In contrast to the results obtained in water samples, Pb concentrations in sediments were low in September 2011 ( $6.27 \pm 4 \mu\text{g g}^{-1}$ ). Sediments at S1 showed maximum Cr concentrations in August 2012 ( $71.14 \mu\text{g g}^{-1}$ ), maximum Cu concentrations in July 2012 ( $46.8 \mu\text{g g}^{-1}$ ), and maximum As concentrations in April 2012 ( $31.47 \mu\text{g g}^{-1}$ ). In April, at the Colastiné Stream (S1), Cu, Pb, and As values exceeded the guideline levels (1.05, 1.09, and 5.33 times, respectively (Canadian Environmental Quality Guidelines 2003) (Fig. 5, Table 3). An alternation in Pb concentration between the water and sediment matrices was observed at all sites. Pb recorded in water and sediments had significantly negative correlation between the two matrices ( $r = -0.4, p = 0.004$ ).

Similar to physicochemical variables, microcontaminant concentrations in sediments between sites were more informative about the impairment of the system than those between months.

The Geoaccumulation Index (*Igeo*) revealed that sediments in the four sites were seriously polluted by Pb and highly polluted by Cr and Cu. The values of the *Igeo* for As were lower because it is a metalloid of natural origin, therefore the background of this element in the studied environments is greater (Fig. 6). Similarly, studies carried in Santa Fe province by Gagneten et al. (2007) indicated that the values of the *Igeo* for Cr and Pb varied between “highly polluted” and “seriously polluted.” On the other hand, contamination by Cu, as indicated by *Igeo*, was high everywhere.

**Pesticides in water**

In contrast with physicochemical variables and microcontaminants in water, pesticide concentrations in water



**Fig. 4** Cr, Cu, Pb, and As concentration ( $\mu\text{g L}^{-1}$ ) in stream water at each sampling site (S1, S2, S3, and S4). Cr, Cu and Pb in the principal axis, As in the secondary axis

**Table 3** Number of times (in italics) that the concentrations of metals, arsenic, and pesticides in water and sediments exceeded the environmental quality guidelines (EQGs). Figures were obtained through the ratio between the concentrations of metals, As, and pesticides recorded in water (expressed for unfiltered surface water

samples) and sediments and the guideline levels proposed by the Canadian Environmental Quality Guidelines (2003) (–) under environmental quality guidelines. EQGs for Cr  $2 \mu\text{g L}^{-1}$ , to protect aquatic life including zooplankton and phytoplankton; EQGs for Cu and Pb 4 and  $7 \mu\text{g L}^{-1}$ , respectively, hardness  $> 180 \text{ mg L}^{-1}$  ( $\text{CaCO}_3$ )

## Metals and As in water

	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
S1	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	<i>169.5</i>	<i>178.5</i>	<i>4.3</i>	<i>5</i>	<i>3.9</i>	<i>3.5</i>	–	<i>11.7</i>	<i>8.4</i>	<i>3.6</i>	<i>7.9</i>	<i>3.3</i>
Cu	<i>3</i>	<i>2.3</i>	–	<i>1.5</i>	<i>5.8</i>	<i>3</i>	<i>5</i>	<i>6.5</i>	<i>4.3</i>	<i>5.5</i>	<i>1</i>	<i>1</i>
Pb	<i>19.7</i>	<i>41.6</i>	<i>1.6</i>	–	<i>1.2</i>	<i>1.5</i>	<i>1.4</i>	<i>1.4</i>	–	–	–	–
As	<i>3.7</i>	<i>2.9</i>	<i>5.2</i>	<i>4.4</i>	<i>6.3</i>	<i>3.9</i>	<i>4.1</i>	<i>3</i>	<i>4.2</i>	<i>1.3</i>	<i>1.2</i>	–
S2	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	<i>172.5</i>	<i>181.5</i>	<i>4.1</i>	<i>71.7</i>	<i>4.4</i>	<i>3.3</i>	<i>4.2</i>	<i>6.8</i>	<i>3</i>	<i>7.6</i>	<i>4.3</i>	<i>2.6</i>
Cu	<i>2.2</i>	–	<i>4.8</i>	<i>2.3</i>	<i>4.8</i>	<i>6.3</i>	<i>4</i>	<i>2.8</i>	<i>9</i>	<i>5.8</i>	<i>2</i>	–
Pb	<i>14.6</i>	<i>18.7</i>	–	<i>1.2</i>	<i>2.6</i>	<i>2.2</i>	–	<i>1.3</i>	<i>1.9</i>	–	<i>1.8</i>	–
As	<i>3.5</i>	<i>2.7</i>	<i>10.8</i>	<i>2.4</i>	<i>3.7</i>	<i>6.2</i>	<i>3.5</i>	<i>2.7</i>	<i>12.9</i>	–	–	–
S3	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	<i>169</i>	<i>180</i>	<i>8.2</i>	<i>2.3</i>	<i>4</i>	<i>3.6</i>	<i>3.8</i>	<i>14.1</i>	<i>11.3</i>	<i>5.4</i>	<i>3.1</i>	<i>2.9</i>
Cu	<i>1</i>	–	<i>5</i>	<i>5</i>	<i>5</i>	<i>5</i>	<i>4</i>	<i>3</i>	<i>10.8</i>	<i>1.8</i>	<i>3</i>	–
Pb	<i>23.4</i>	<i>19.4</i>	–	<i>1.7</i>	<i>1.8</i>	<i>2.3</i>	–	–	<i>1.9</i>	–	–	–
As	<i>2.8</i>	<i>2.3</i>	<i>4</i>	<i>2.2</i>	<i>4.8</i>	<i>10.6</i>	<i>3.8</i>	<i>2.7</i>	<i>9.7</i>	–	<i>1</i>	–
S4	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	<i>176</i>	<i>175.5</i>	<i>4.8</i>	<i>7.4</i>	<i>4.7</i>	<i>3.9</i>	<i>22</i>	<i>19.1</i>	<i>17.6</i>	<i>5.8</i>	<i>5.4</i>	<i>3.3</i>
Cu	<i>57.7</i>	–	<i>1.3</i>	<i>3</i>	<i>3.5</i>	<i>4</i>	<i>6.3</i>	<i>3.5</i>	<i>3.5</i>	–	–	–
Pb	<i>22.1</i>	<i>8.8</i>	–	–	<i>1.6</i>	–	<i>1.4</i>	<i>2.2</i>	<i>1.8</i>	–	–	–
As	<i>1.1</i>	<i>1</i>	<i>3</i>	<i>2.6</i>	<i>3.6</i>	<i>3.6</i>	<i>2.2</i>	<i>1.9</i>	<i>2.1</i>	<i>1.2</i>	<i>1.4</i>	–

## Metals and As in sediments

	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
S1	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	–	–	–	–	–	–	–	–	–	–	–	<i>1.91</i>
Cu	–	–	–	–	–	–	–	–	<i>1.06</i>	–	<i>1.31</i>	–
Pb	–	–	–	<i>1.19</i>	–	–	<i>1.09</i>	<i>1.21</i>	<i>1.09</i>	–	–	–
As	–	–	–	<i>1.08</i>	–	–	–	–	<i>5.34</i>	–	–	–
S2	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	–	–	–	–	–	–	–	–	–	–	–	–
Cu	–	–	–	–	–	–	–	–	–	–	–	–
Pb	–	–	<i>1.25</i>	<i>1.36</i>	<i>1.33</i>	–	<i>1.25</i>	<i>1.16</i>	<i>1.14</i>	–	–	–
As	–	<i>1.02</i>	–	–	<i>1.04</i>	–	–	–	–	–	<i>1.32</i>	–
S3	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	–	–	–	–	–	–	–	–	–	–	–	–
Cu	–	–	–	–	–	–	–	–	–	–	–	–
Pb	–	–	<i>1.23</i>	<i>1.21</i>	<i>1.32</i>	<i>1.03</i>	–	<i>1.04</i>	<i>1.28</i>	–	–	–
As	–	–	–	–	–	–	–	–	–	–	<i>1.32</i>	–
S4	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Cr	–	–	–	–	–	–	–	–	–	–	–	–
Cu	–	–	–	–	–	–	–	–	–	–	–	–
Pb	–	–	–	–	<i>1.14</i>	<i>1.31</i>	–	<i>1.09</i>	–	–	–	–
As	<i>1.02</i>	–	–	–	–	–	–	–	–	–	–	–

## Pesticides in water

	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
S1	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Atr	–	–	–	–	–	–	–	–	–	–	–	–
End	–	<i>13.33</i>	–	–	<i>2.33</i>	<i>16.67</i>	–	–	–	<i>5.33</i>	–	–

**Table 3** (continued)

	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
S2	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Atr	–	–	–	–	–	–	–	–	–	–	–	–
End	–	–	<b>10</b>	–	<b>34</b>	–	–	–	–	<b>15.67</b>	–	–
S3	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Atr	–	–	–	–	–	–	–	–	–	–	–	–
End	–	–	–	–	<b>1.67</b>	–	–	–	–	<b>10.67</b>	–	<b>44</b>
S4	Aug. 11	Sept. 11	Oct. 11	Nov. 11	Dec. 11	Jan. 12	Feb. 12	March 12	April 12	June 12	July 12	Aug. 12
Atr	–	–	–	–	–	–	–	–	–	–	–	–
End	–	–	<b>4.67</b>	–	–	–	<b>1.33</b>	–	–	<b>43.33</b>	–	–

(Atr,  $\alpha$  End,  $\beta$  End, and End sulfate) were not significantly different between sampling sites (ANOVA,  $p > 0.05$ ). Although atrazine was always found at higher concentrations than endosulfan (ANOVA,  $p < 0.001$ ), atrazine concentrations were not above the desirable Argentine Environmental Quality Guidelines (AEQGs) limits ( $3 \mu\text{g L}^{-1}$ ) or the Canadian Environmental Quality Guidelines (CEQGs) limits ( $1.8 \mu\text{g L}^{-1}$ ). Conversely, the endosulfan values exceeded both permitted limits ( $0.007$  and  $0.003 \mu\text{g L}^{-1}$ ).

S3 and S4 showed maximum averages of atrazine ( $0.21$  and  $0.16 \mu\text{g L}^{-1}$ , respectively), and S2 and S3 maximum total endosulfan ( $0.014$  and  $0.015 \mu\text{g L}^{-1}$ , respectively), with the predominance of  $\alpha$  End and  $\beta$  End (Table 2).

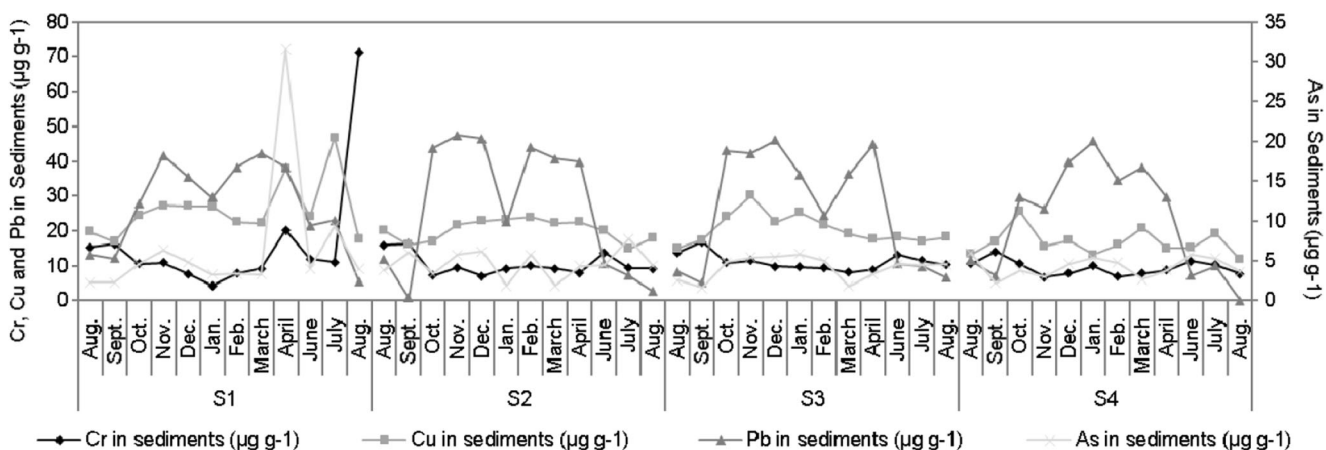
Figure 7 shows the annual variation of the pesticides recorded in water together with the permitted guideline levels. The maximum Atr concentrations were recorded in October ( $0.86 \mu\text{g L}^{-1}$  at S3), November ( $1.73 \mu\text{g L}^{-1}$  at S4), and December ( $0.13$  and  $0.14 \mu\text{g L}^{-1}$  at S1 and S2, respectively), and the maximum total End was recorded in August and June 2012 ( $0.13 \mu\text{g L}^{-1}$  at S3 and S4) (Table 2, Fig. 7).

Table 3 shows the frequency (in bold) at which the concentrations of metals, arsenic, and pesticides in water and sediments exceeded the permissible limits. These values were calculated through the ratio between the concentrations recorded in water and sediments and the desired limits.

In August and September 2011, low atrazine values were recorded in water (ranging from  $0.006$  to  $0.3 \mu\text{g L}^{-1}$ ), which was possibly related to the scarcity of monthly precipitations (means of the four sites for both months  $40$  and  $12$  mm, respectively). In September, in the Colastiné Stream (S1), endosulfan exceeded  $13.3$  times the Canadian guideline levels, respectively (Table 3).

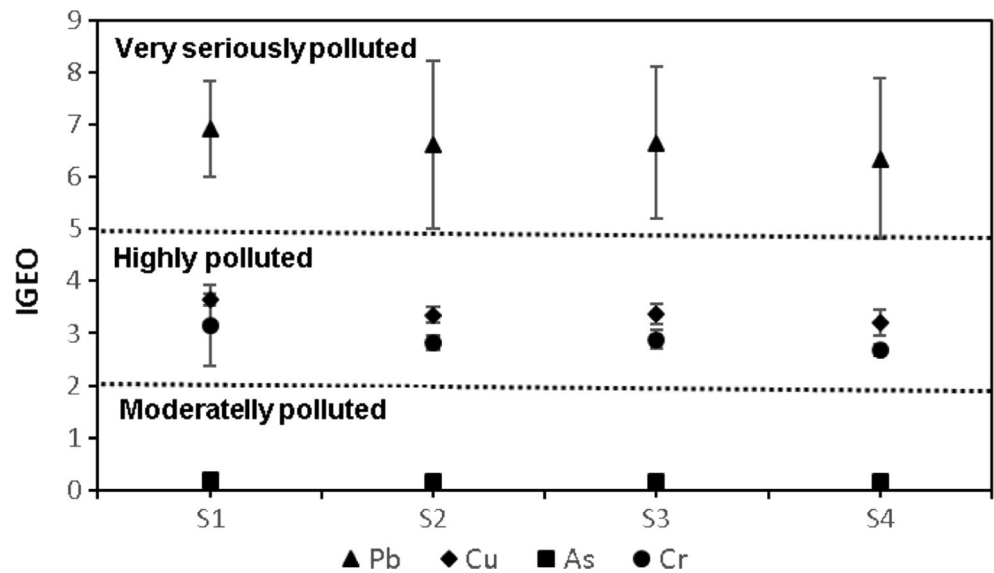
In October, November, and December, precipitations started to increase progressively (means of the four sites for the 3 months  $98$ ,  $78$ , and  $101$  mm, respectively). These increments probably caused the runoff of pesticides into the water bodies. Several studies have emphasized that rainfall greater than  $10 \text{ mm day}^{-1}$  is the most important driving cause for the input of pesticides into freshwater ecosystems as a result of flow runoff (Nakano et al. 2004). Epstein and Grant (1968) indicated that if it rains within 4 days after the application of endosulfan ( $3.5 \text{ kg ha}^{-1}$ ), the mean concentrations of this pesticide that can be observed in surface runoff can be up to  $16 \mu\text{g L}^{-1}$ . Pesticides can also enter the water courses directly via container washing or negligent application, e.g., without considering the direction of the predominant winds.

In November, only atrazine was present at all sites, with maximum values at S4 where, although it did not exceed the Canadian guideline level, it was close to the proposed limit ( $1.73 \mu\text{g L}^{-1}$ ). Also, the minimum value of dissolved oxygen ( $4.4 \text{ mg L}^{-1}$ ) was recorded. According to Solomon et al.



**Fig. 5** Cr, Cu, Pb, and As concentration ( $\mu\text{g g}^{-1}$ ) in sediments at each sampling site (S1, S2, S3, and S4). Cr, Cu, and Pb in the principal axis, As in the secondary axis

**Fig. 6** Geoaccumulation Index (*Igeo*) value for Cr, Pb, Cu, and As in sediment of the four sampling sites (Colastiné-Corralito stream system, Santa Fe, Argentina)

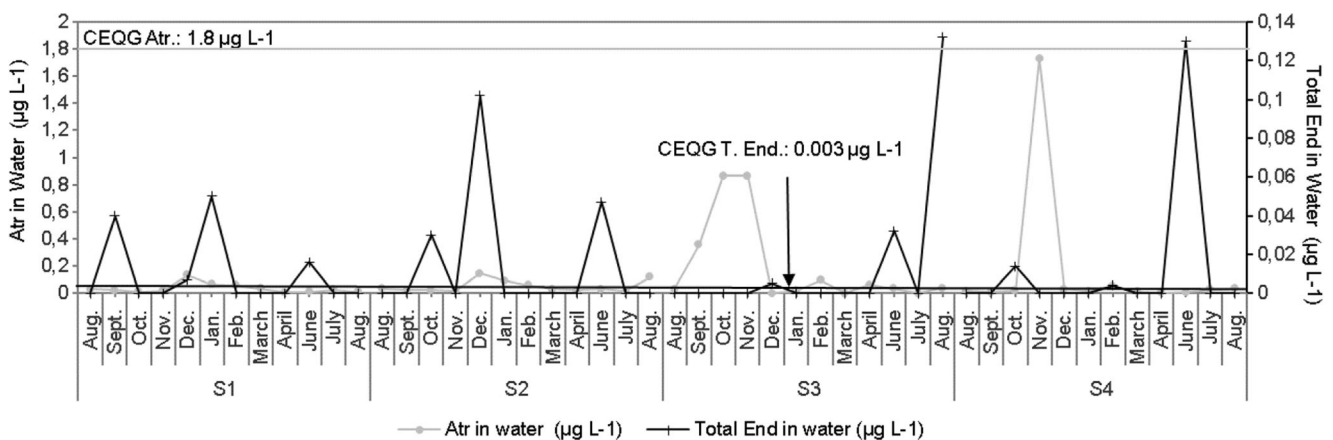


(1996), the first sign for the presence of atrazine in the aquatic ecosystem is a reduction in dissolved oxygen, caused by a decrease in primary production. In this survey, a negative and significant correlation between atrazine concentration and dissolved oxygen in water ( $r = -0.42$ ;  $p = 0.002$ ). This herbicide mainly produces direct effects on phototrophic communities, such as phytoplanktonic algae and periphyton, reducing the primary activity of the ecosystem (Hamilton et al. 1988; Graymore et al. 2001) by blocking the electron transport from photosystem II (Woolhouse 1981; Forney and Davis 1981; De Lorenzo et al. 2001). In this sense, Lakshminarayana et al. (1992) found that concentrations ranging from 1 to 10  $\mu\text{g L}^{-1}$  decreased the photosynthetic rate and indirectly affected the zooplankton. Studies carried out by De Noyelles et al. (1982) at a microcosm scale showed that very low atrazine concentrations ( $< 1 \mu\text{g L}^{-1}$ , close to the values measured in this study) affected phytoplankton photosynthesis and biomass, and produced changes in the zooplanktonic community structure.

Maximum atrazine values in December were recorded in the Colastiné Stream and in the Corralito Stream. At this last site, endosulfan was also recorded, exceeding 34 times the Canadian standards, respectively (Table 3).

For several decades, pesticides have also been detected in aquatic systems in different parts of the world. For example, atrazine concentrations of  $< 0.2\text{--}1000 \mu\text{g L}^{-1}$  were recorded by different authors (Christopher and Bird 1992; Maguire and Tkacz 1993; Davis et al. 1994). Little is known about their impact on the structure and dynamics of aquatic communities and on the persistence and toxicity of their degradation products; there are even contradictory responses. According to Stratton (1984), metabolites present lower toxicity than atrazine, while Winkelmann and Klaine (1991) postulated that the metabolite deethylatrazine is more toxic.

In this study, in June, endosulfan concentrations exceed 5–43 times the Canadian guideline levels at all sites (Table 3). This insecticide has proven negative effects on the aquatic biota. It is known that  $\beta$  End and  $\alpha$  End isomers are degraded



**Fig. 7** Atrazine concentration ( $\mu\text{g L}^{-1}$ , principal axis) and total endosulfan ( $\alpha$  END,  $\beta$  END, and END sulfate) ( $\mu\text{g L}^{-1}$ , secondary axis) at four sampling sites (S1, S2, S3, and S4) during 12 months. Guideline levels are shown (Atr: gray line; End: dark line)



at different velocities in the aquatic systems depending on the environmental conditions. Due to their semivolatility, they have been recorded in the atmosphere in different regions of the world (Weber et al. 2006). Gutiérrez et al. (2012) found that sublethal concentrations of this pesticide provoked alterations in the behavior of different zooplankton species of the Neotropical fauna, affecting swimming and generating disorientation. According to Palma et al. (2009), this pesticide affects the activity of endocrine signaling molecules (ecdysteroids) that participate in molting processes and in the regulation of the embryonic development in *Daphnia magna*.

In agreement with Palma et al. (2014), a good chemical condition will be reached when the concentrations of the priority compounds (such as atrazine) are below the environmental quality standards, and the hazardous compounds (such as endosulfan) are not found in water bodies. Through all the data presented here, it is quite evident that this is not the current status of the studied ecosystems: metal concentrations were higher than those recorded by Gagneten et al. (2007) a decade ago in the low basin of the Salado River, and also higher than those recorded in other aquatic systems (Chen et al. 2017). These results reaffirm that there is a historical and background metal contamination in central-eastern aquatic systems of Argentina, impaired by the diffuse input of a forbidden insecticide. The recommendation for managers of this system and other similar ones worldwide—with historical and diffuse pollution—is to improve legislation or, as in the case of Argentina, to respect preexisting regulatory standards and strengthen them with rigorous controls.

## Conclusions

This is the first report on the simultaneous temporal and spatial distribution of pesticides and microcontaminants in water and sediments in an Argentinean stream system. Metals and arsenic in water and sediments exceeded the established national and international guideline levels for the protection of the aquatic biota. Canadian guides for the protection of the aquatic life are expressed as element concentrations for unfiltered surface water samples, while the Argentine values are expressed for filtered water, in this sense, it is important to consider that some of the metals may not be available for biota. Cr in water was always recorded at higher concentrations than other metals, with 98% of the samples exceeding the guideline levels. The sediment samples were highly polluted with Cr and Cu and very seriously polluted with Pb, which suggests a deterioration of the sediment quality.

There is ancient and recent contamination by metals and recent diffuse contamination by pesticides. Twenty-seven percent of the analyzed water samples contained higher concentration of total endosulfan than the guideline levels.

Site 1 had the highest values of Pb, Cu, Cr, and As in sediments, and Pb in water and site 4 had the lowest. Sites 2 and 3 showed the highest records of As, endosulfan, and Cr in water, while site 4 had higher concentrations of Cu in water.

Based on the findings of this study, it can be concluded that the freshwater of the studied area is not suitable for aquatic biota and may be harmful to human life. Contaminants reach the water courses causing impacts on the ecosystems and possibly on population health, since inhabitants are directly or indirectly affected. These results are relevant for planning the future uses of the studied systems (e.g., extraction for drinking water, fishing, re-creation activities). It should be considered that the organic and inorganic contaminants in water for human consumption are linked to high treatment costs, possible toxicological incidents, and even prohibition of its use.

The findings of this study alert about the threat of contamination by metals, arsenic, and pesticides, not only by extensive agricultural activities but also by industrial wastewaters. In this study, water bodies showed low dilution capacity and high contaminant loads from anthropogenic activities. Proper measures in terms of technological innovations or improvements of public and private policies must be taken immediately in order to protect aquatic resources and human health. Improper disposal of industrial effluents and agricultural runoff need to be controlled, and proper treatment should be done before disposal to avoid further deterioration of the aquatic ecosystems.

To conclude, let us remember a strong suggestion by Trevors and Saier (2010): “We must avoid short-term solutions that have long-term detrimental consequences. It must be a national and an international priority. Manage humans and their damaging actions, not just “the environment” and we have a chance for sustainability and species survival. Educate and manage human activities, not just the environment. This is the challenge.”

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