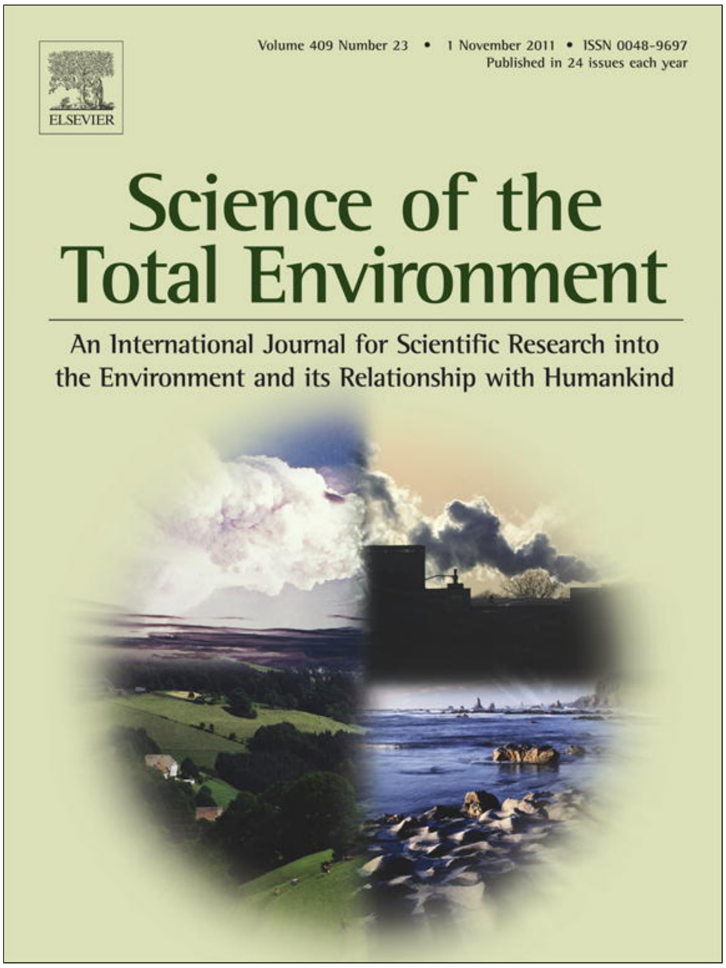

Volume 409 Number 23 • 1 November 2011 • ISSN 0048-9697
Published in 24 issues each year

ELSEVIER

Science of the Total Environment

An International Journal for Scientific Research into
the Environment and its Relationship with Humankind

Science of the Total Environment 409 (2011) 5034–5045

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Integral assessment of pollution in the Suquía River (Córdoba, Argentina) as a contribution to lotic ecosystem restoration programs

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ARTICLE INFO

Article history:
Received 22 June 2010
Received in revised form 12 August 2011
Accepted 15 August 2011
Available online 16 September 2011

Keywords:
Air bioindicators
Coliform bacteria
Heavy metals
Semi-volatile organic compounds
Fish assemblages

ABSTRACT

The Suquía River lower–middle basin (Córdoba, Argentina) is subject to a strong anthropic impact because it receives pollutants from different sources (industries, wastewaters, heavy traffic, agricultural land use, etc.) We have assessed the degree of watershed degradation of Suquía River lower–middle sections through the analysis of different ecosystem compartments (air, water, riparian soil, sediments and biota), in order to provide useful data to be considered in future river restoration programs. Four study sites were selected along the river (La Calera city, Córdoba city, Corazón de María village and Río Primero city) which were sampled during the low- and high-water flow periods. We analyzed: a) chemical and physical characteristics of water, sediments, and riparian soil; b) heavy metal content of water and sediments, and c) semi-volatile organic compounds in air. Besides, pollutant bioindicators such as fish assemblages, lichens (*Usnea amblyoclada*), vascular plants (*Tradescantia pallida*), and microorganisms (fecal coliform and *Escherichia coli*) were used to further assess the status of the river. All analyzed ecological compartments were affected by water pollution, particularly, fish assemblages, sediments and riparian soils by heavy metal and coliform bacteria. Moreover, we detected a possible contribution of sulfur and a high pollutant content in air that merit further research about other air–water exchanges. Accordingly, we strongly suggest that an action to restore or remediate the anthropic effect on the Suquía River be extended to all possible compartments along the river.

1. Introduction

Human activities have greatly altered freshwater ecosystems worldwide. The Suquía River (Córdoba, Argentina), as most water courses running across big cities, receives complex pollutants from different sources. Furthermore, it is particularly vulnerable to pollution due to its scarce and seasonal flow, short length and endorheic basin (Wunderlin et al., 2001; Contardo-Jara et al., 2009). It is well known that watersheds of arid or semiarid regions have scarce capacity of self-purification and drag of pollutants. At the same time, its endorheic condition complicates the output of xenobiotics compounds, contributing to their accumulation in the basin (Gaiero et al., 1997).

Air, water, sediment and soil maintain a close relationship because they are reciprocal sinks and sources of pollutants. Therefore, the pollution of a river basin is not confined to a single compartment or to a nearby source (Swackhamer et al., 2004). The most important mechanisms of pollutant dispersal are volatilization and transport by the atmosphere (Shen et al., 2005; Shoieb et al., 2006; Jahnke et al., 2007a), deposition by rainfall, irrigation for agriculture, and leaching to groundwater (Carpenter et al., 1998; Williamson et al., 2008; Bazargan-Lari et al., 2009).

It is widely accepted that polluted waters affect not only the human population (by agricultural, recreational and drinking water uses; Yau et al., 2009), but also riparian soils, air and biota. From these ecological compartments, more harmful and enduring in time effects have been described (Depledge and Galloway, 2005; Katz et al., 2009).

Nowadays restoration programs for polluted rivers are widespread throughout the world, comprising purification and control of watershed uptakes (Parkyn et al., 2003; Craig et al., 2008; White and Stromberg, 2009). If restoration programs were applied to Suquía River, the scarce information available about the magnitude of the system alteration and its resilience capability would pose severe limitations.

The main problems that the Suquía River basin is coping are anthropogenic activities, sewages, agricultural and industrial effluents from point and nonpoint pollution sources (Wunderlin et al., 2001; Hued and Bistoni, 2005; Nimptsch et al., 2005). In recent years numerous

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doi:10.1016/j.scitotenv.2011.08.037

studies have demonstrated the effects of the watershed degradation on local aquatic biota (Bistoni et al., 1999; Cazenave et al., 2005; Hued and Bistoni, 2005). On the other hand, previous studies have demonstrated the adverse impact of air pollutants on a lichen and a vascular plant species (Carreras et al., 2006; 2009). These toxic effects were associated to the primary air pollution in Córdoba city driven by the traffic, the poor control on emissions and the little use of catalytic converters which produce a great amount of toxic gases and particulate (Olcese and Toselli, 2002). Despite these evidence, no studies have been conducted in order to combine comprehensive information from different compartments (air, water, sediments, soil and biota). These facts generate uncertainty at the moment to plan restoration actions.

Our main goal was to assess the degree of watershed degradation of Suquía River lower–middle sections through the analysis of different ecosystem compartments (air, water, riparian soil, sediments and biota), in order to provide useful data to be considered in future river restoration programs. We carried out a systematized study with an integral approach and applied specific methodologies to characterize each ecological compartment. Air organic pollutants as well as microbial and chemical characteristics of riparian soils are reported for the first time.

2. Materials and methods

2.1. Study area

The Suquía River is located in a semi-arid region of Córdoba province (Argentina) and drains into the depression of the Mar Chiquita Lake. The watershed covers approximately 7.700 km^2, of which almost 900 km^2 corresponds to the Córdoba city drainage area. The mean annual rainfall is in the range of 700 to 900 mm, with a dry season (from May to November) and a wet season (from October to April) with most of the rainfall occurring in January and February. The Suquía River begins at the San Roque Dam and flows mainly from west to east for about 200 km until Mar Chiquita Lake. Thirty kilometers away from the dam, it enters Córdoba city flowing through a cement channel for approximately 6 km, and then alternating with open banks for about 40 km. The hydrological system of this river comprises three drainage areas: a) the high basin, in a mountainous area with headwaters and streams of torrential character, which flow into the San Roque Dam; b) the middle basin with drainage areas belonging to the eastern slope of the Sierras Chicas and their foothills, together with Córdoba city drainage area; and c) the lower basin, from Cordoba city to Mar Chiquita Lake, in a level area, where the river exhibits typical meanders and a shallow and scarce flow.

The San Roque Dam is an artificial lake where fishing, swimming, boating and sailing are practiced. These recreational activities have promoted the urbanization of the lake shorelines and surroundings. This dam is the main drinking water source for Córdoba city (1.29 million inhabitants). In the last 20 years, the city's population has almost doubled and growing industrialization has increased the risk of having toxic effluents discharged into the river. Downtown, La Cañada brook contributes to the river flow, and near the eastern edge of the city the Suquía River is affected by the city's sewage discharge from the Municipal Waste Water Treatment Plant (WWTP) (Pesce and Wunderlin, 2000; Wunderlin et al., 2001) (Fig. 1).

The flow regime of rivers that form Suquía River drainage network is exclusively pluvial origin, with a marked seasonality of the flow due to the irregular distribution of rainfall throughout the year (Pasquini et al., 2011). Though there is not a systematic study, the river flow can be estimated from the water released by the San Roque Dam. The Suquía River has shown a high flow period, from December to April, with an estimated flow greater than 15 $m^3\ s^{-1}$; whereas during the dry season, from May to November, its estimated flow is 2.7 $m^3\ s^{-1}$ (Vázquez et al., 1979).

With the exception of Suquía River basin headwaters (mean altitude of 1000 m.a.s.l. and dominated by high metamorphic rocks), the drainage basin is covered by Tertiary and Modern sediments. Sediment erosion and the ubiquitous presence of marble quarries, confer a clear alkaline character to its waters. According to Gaiero et al. (1997) in the middle–low basin sediments are introduced into the mainstream by bank erosion.

2.2. Study sites

Four study sites were selected in the lower–middle basin of the Suquía River (Fig. 1):

a) Site 1 (31° 21′ 45″ S and 64° 20′ 99″ W, 488 m.a.s.l.): Located in La Calera city, 18.4 km downstream San Roque Dam and 18 km upstream of Córdoba city west border. In this site the river carries contaminants coming from the eutrophic San Roque Dam as well as sewage discharges and urban run-off from villages further upstream (Amé et al., 2003).
b) Site 2 (31° 23′ 82″ S and 64° 14′62 ″ W, 393 m.a.s.l.): Positioned in Córdoba city, 27.8 km downstream Site 1. At this point the river runs through a cement channel that replaces the natural river

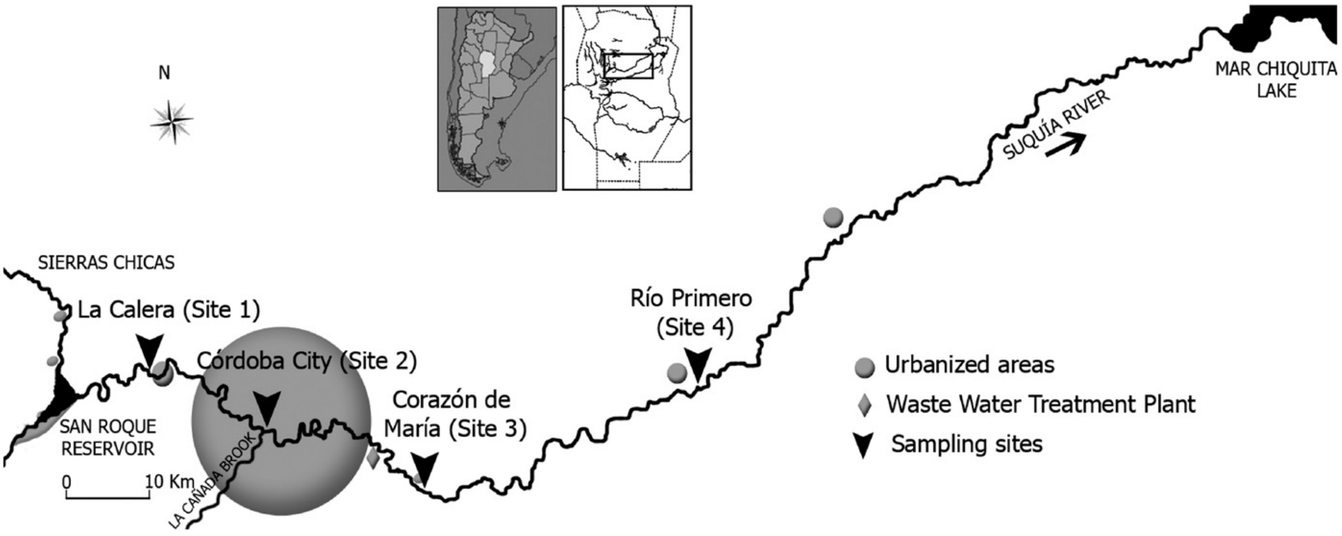

Fig. 1. Study sites in the Suquía River lower–middle basin.

bed. In this segment it is fed by La Cañada brook, which in turn is contaminated by industrial effluents, sewage waters, and run-off from the downtown commercial area (Pasquini et al., 2011).

c) Site 3 (31° 26′ 81″ S and 63° 59′ 45″ W, 430 m.a.s.l.): Situated at Corazón de María village 24.8 and 16 km downstream from Site 2 and the WWTP, respectively. This is the most degraded area of the river. From Sites 2 to 3 the river banks are deeply modified by sand mining (Hued and Bistoni, 2005).

d) Site 4 (31° 20′ 29″ S and 63° 36′ 58″ W, 243 m.a.s.l.): Located in Río Primero city, 51.1 km downstream from Site 3. This site is in an agricultural area and the river is crossed by a high traffic route (Pasquini et al., 2011).

Study sites were sampled during the low- and high-flow periods, August 2008 and March 2009 respectively. Air from all sites was monitored only during the low-flow period. Depending on the ecological compartment and the analyzed parameter, the sampling and analytical procedures described below were carried out.

2.3. Chemical and microbiological analyses

For each study site, five points were randomly selected, along a 100 m linear transect, in each of which "in situ" pH, dissolved oxygen, temperature and conductivity of the water were measured using portable equipment (WTW, Multiline F/Set 3). Moreover, in each point, one sample of water, sediment and riparian soil (0–20 cm) was taken in sterile receptacles and stored at 5 °C until analysis. The following parameters were evaluated in all samples: a) total organic carbon content by wet combustion (Nelson and Sommers, 1982); b) nitrate concentration by colorimetric methods (Kenney and Nelson, 1982); c) abundance of culturable total heterotrophic microorganisms in general culture media (US EPA, 1999a); and d) microbial sewage pollution indicators (fecal coliform and *Escherichia coli*) following USEPA guide (1999a). In addition, ammonia content was measured in water samples (US EPA, 1999a), pH and texture were determined in sediment and soil samples, and conductivity was measured in soil samples, according to the SSSA methodology (Klute, 1986).

2.4. Heavy metal analyses

Water and sediment samples were taken in three out of four study sites because the river's cement channel at Site 2 prevents accumulation of enough sediments. Water samples were collected from approximately 30 cm below the river surface in acid-washed plastic bottles. Sediment samples were collected using a plastic spoon for each, and quickly transferred (with no head space) into clean 1 L plastic containers. All samples were transported on ice to the laboratory within 4 hours, where they were stored at −20 °C until analysis.

Water samples acidified with concentrated HNO_3 (1.5 mL/L) were vacuum-filtered using a 0.45 μm nitrocellulose membrane filter. Sediment samples were initially stored in the same plastic bottle used in the sampling and immediately dried at room temperature. Then, 5 g of the <63 μm dried material were processed by acid leaching using ultra pure HCl 0.5 M, following the methodology described by Gaiero et al. (1997). Controls (only reactants without sample) were prepared using ultrapure water (Arium 611 UV system, Sartorius, Germany). Elemental analyses were performed by either ET-AAS for trace elements (atomic absorption spectrometer, AAnalyst 600, equipped with AS 800 autosampler, Perkin Elmer, USA) or FAAS for abundant metals (air–acetylene flame atomic absorption spectrometer, Perkin Elmer 3110, USA). Metal concentration values were obtained by triplicates (three measurements on each duplicate sample). The limit of detection (LOD) was established considering three standard deviations of blank absorption values.

2.5. Fish assemblage analyses

Fish were captured with backpack electrofisher equipment in each study site (except for Site 2). The collections area covered 150 m of stream length (500 m^2 approximately). The study sites were long enough to encompass several examples of all major macrohabitat types within the reach (pools, runs, riffles, etc.) (Sanders et al., 1999). Fish were identified to the species level, counted, and then released alive back into the water. The abundance of each species was estimated as the number of fish captured per unit area of water surface sampled (100 m^2) (Paller, 1995; Langford and Hawkins, 1997). The total abundance, the species richness and diversity (Shannon–Wienner index) were estimated. Following Hued and Bistoni (2005), it was calculated a Biotic Index (BI) based on fish assemblage attributes. The metrics used for its estimation were: a) abundance of *Astyanax eigenmanniorum, Rineloricaria catamarcensis, Gambusia affinis* and *Cnesterodon decemmacultus*, b) the proportion of sensitive species richness and c) the proportion of tolerant species richness. The sensitive species considered were: *Oligosarcus jenynsi*, *Astyanax eigenmanniorum*, *Bryconamericus iheringi*, *Cheirodon interruptus*, *Pimelodella laticeps*, *Rineloricaria catamarcensis* and *Hypostomus cordovae* whereas *Parodon tortuosus*, *Trichomycterus corduvense*, *Synbranchus marmoratus*, *Corydoras paleatus*, *Gambusia affinis*, *Cnesterodon decemmaculatus* and *Jenynsia multidentata* were considered as tolerant species (Hued and Bistoni, 2005).

2.6. Organic pollutant analyses by active air sampling

The procedures outlined in the standard TO-13 method (US EPA, 1999b) for polyaromatic hydrocarbons (PAH) determination were used to determine the organic semi-volatile compounds using a high-volume active air sampler. Temperature and pressure data were used to obtain the experimental sampled volume (supplied every hour by the National Meteorological Service, Córdoba Airport Station). The air sampler was placed within 50 m from the shoreline. The sampled volumes (m^3) and the corresponding flow rates ($m^3\ min^{-1}$) ranged between 297.4/0.22 and 516.5/0.19.

Particulate matter was retained in quartz-fiber filters (10.16 cm). For the collection of organic semi-volatile compounds, a cartridge assembled with 15.0 g of XAD-2 (trade name for the polymer amberlite, XAD hereinafter) between two slices of polyurethane foam (PUF) were placed in a glass holder, wrapped with aluminum foils and inserted into a stainless steel holder until used (Jahnke et al., 2007a). The aluminum holder of the equipment with the filter and the glass cartridge was put into the air sampler. Previously, 20 μl of a deuterated polyaromatic hydrocarbon standard (500 ng μl^{-1}) was spiked over the PUF in order to check eventual compound loss during the procedure (Jahnke et al., 2007b).

After sampling, quartz filter, XAD, and PUF were analyzed separately. For the extraction procedure, a Soxhlet apparatus was used with 300 mL of CH_2Cl_2 in a XAD case and 300 mL diethyleter/n-Hexane (1/10 v/v) for filters and PUFs, respectively. The concentrated extracts (1 mL) were stored in screw-cap amber vials and maintained at (4 ± 2) °C until analysis. Each extract was analyzed in triplicate by a Shimadzu GCMS GC17A/QP5050 with a Varian VF-5 ms 30 m × 0.25 mm × 0.25 μm capillary column to separate and identify the organic compounds. Each chromatographic peak area was multiplied by an arbitrary factor of 1×10^{-4} in order to work with simpler values of a.u. (arbitrary units).

2.7. Air pollutant bioindicator analyses

2.7.1. Usnea amblyoclada bioindicator

The lichen *U. amblyoclada* had already been employed as a biomonitor of urban pollutants in several studies (Carreras et al., 1998; Carreras and Pignata, 2000, 2002; Carreras et al., 2005) and their results demonstrate that this species is an efficient bioaccumulator of gases and airborne particles. The lichen material was collected in the Cerro Blanco area (1200 m. a. s. l.), located 100 km north-west of Cordoba city. Special attention was taken to collect material of approximately the same size and under similar exposure conditions (south-oriented) with the aim to minimize physiological differences. The lichen bags were prepared separating the thalli from their basal portion and packing them in a fine nylon net, according to González and Pignata (1994). Three lichen bags were placed in each study site on posts at 2 m above the ground and oriented to the south. The samples remained exposed for 3 months in each study period (low- and high-flow periods). At the end of the exposure, they were dried at 50 ± 2 °C to constant weight. Then, the sulfur content was quantified according to the technique described by González and Pignata (1994). Lichens without exposure were considered as the control group.

2.7.2. *Tradescantia pallida* bioindicator

Plant bioassays are best suited for addressing the clastogenic effects of air pollution, because they are more sensitive to environmental stress than other currently available bioassay systems (Gopalan, 1999). *Tradescantia* can assess mutagenic effects by the formation of micronuclei (MCN) in meiotic or mitotic cells and pink mutations in stamen hairs. The Trad-MCN bioassay has been used extensively for monitoring environmental genotoxicity, and it is particularly sensitive to chemical mutagens (Ma et al., 1994; Monarca et al., 2001; Guimaraes et al., 2000). In this study, we used pollen mother cells of *Tradescantia pallida* Rose. Hunt. cv. *purpurea* Boom, which is a popular ornamental plant.

Genotoxicity test were carried out according to Carreras et al. (2009) as follows: *T. pallida* plants were cultivated in pots (20 cm diameter) using the same batch of commercial soil. Ten pots were placed in each study site, in periods coincident with *U. amblyoclada* exposure. All pots were kept on wooden platforms (1 m above ground level) in the open air, without any shade, and watered frequently. During three months young inflorescences were collected twice a month, at each study site. They were fixed overnight in 1:3 glacial acetic acid–ethanol, and then stored in 70% ethanol. The flowers were dissected and young anthers were squashed on a microslide to count the total number of micronuclei formed on each flower. Three-hundred tetrads were examined per slide (10–20 for each site) at a magnification of 400× (Ma et al., 1994). Micronuclei frequencies were calculated by dividing the total number of micronuclei (MCN) by the total number of tetrads, and expressed as MCN/100 tetrads (Fomin and Hafner, 1998).

2.8. Statistical analysis

In order to determine significant differences between variables among sites or between low and high water flow periods it was applied ANOVA test followed by a Tukey's multiple comparison test. Differences were considered significant at $p<0.05$. Generalized Procrustes Analysis (GPA) was applied to datasets (Besada et al., 2011). All the variables measured were used as descriptors for river group (water, sediments and riparian soil), air group (semi-volatile organic compounds) and biota group (microorganisms, fish and air bioindicators). GPA was applied for assessing the relationship among the descriptors. Specifically, GPA constructs the consensus configuration of a group of datasets by applying transforms in an attempt to superimpose them. Therefore, GPA theory and algorithms can be applied to match abiotic parameters to the corresponding biological data. For the statistical analysis Infostat software package (Infostat, 2011) was used.

3. Results

3.1. Water chemical and microbiological characteristics

All the analyzed parameters varied significantly among sites during the two sampling periods. In general, in the low flow period (August 2008), the lowest values registered correspond to Site 1 whereas Site 2 showed the highest ones in all the chemical parameters analyzed, except for the ammonia content which presented the highest values at Site 3. The organic carbon content and conductivity in Site 3 did not significantly differ from those in Site 2, and nitrate and organic carbon in Site 4 did not significantly differ from those in Site 2. Also the microbial parameters were significantly lower in Site 1, but the highest values were registered in Site 3 (Table 1).

Similarly, during the high flow period, Site 1 showed the lowest values for all the parameters measured. On the contrary, Site 4 presented the highest organic carbon, nitrates (no difference with Site

Table 1

Water chemical and biological characteristics (means ± SD) at Suquía River study sites during low and high flow periods. For each parameter, different letters indicate significant differences among sites (Tukey test $p>0.05$). * indicates significant differences between flow periods for each study site (Tukey test $p>0.05$).

	Site 1	Site 2	Site 3	Site 4
Low flow				
pH	7.02 b (±0.11)	7.18 a* (±0.04)	6.79 c* (±0.08)	6.77 c* (±0.14)
Conductivity (μS cm^{-1})	215 c* (±1.92)	1438 a* (±29.06)	1411 a* (±16.99)	1051 b* (±225.24)
Nitrate (mg L^{-1})	3.3 b* (±0.57)	37.0 a* (±2.24)	11.8 b (±0.32)	31.4 a* (±14.28)
Organic C (g L^{-1})	0.36 b* (±0.02)	1.39 a (±0.51)	1.86 a (±0.51)	1.30 a* (±0.64)
Ammonium (mg L^{-1})	0.19 b* (±0.02)	0.72 b (±0.09)	15.32 a* (±0.37)	1.86 ab (±0.37)
Dissolved O$_2$ (mg L^{-1})	10.01 b* (±0.08)	13.29 a* (±0.54)	3.18 d* (±0.36)	4.36 c* (±0.89)
E. coli (log mL^{-1})	0 c	0.47 b* (±0.20)	0.76 a (±0.21)	0.19 c (±0.26)
Fecal coliforms (log mL^{-1})	1.72 d (±0.17)	2.67 b (±0.27)	3.11 a* (±0.17)	2.27 c (±0.37)
Total heterotrophic microorganisms (log mL^{-1})	2.24 d* (±0.32)	2.96 c* (±0.26)	5.44 a* (±0.57)	4.79 b (±0.61)
High flow				
pH	7.07 c (±0.08)	7.34 a (±0.11)	7.12 bc (±0.25)	7.32 ab (±0.12)
Conductivity (μS cm^{-1})	147 c (±1.72)	506 ab (±11.91)	493 b (±11.84)	518 a (±12.88)
Nitrate (mg L^{-1})	1.76 c (±0.81)	9.55 b (±2.18)	10.45 ab (±1.58)	12.25 a (±1.79)
Organic C (g L^{-1})	0.58 c (±0.18)	1.31 b (±0.08)	1.35 b (±0.27)	2.98 a (±0.97)
Ammonium (mg L^{-1})	0.49 b (±0.05)	0.40 b (±0.10)	1.18 a (±0.63)	0.19 b (±0.06)
Dissolved O$_2$ (mg L^{-1})	6.87 b (±0.03)	8.28 a (±0.47)	4.96 c (±0.24)	7.11 b (±1.08)
E. coli (log mL^{-1})	0 b	0 b	0.48 a (±0.32)	0 b
Fecal coliforms (log mL^{-1})	2.08 b (±0.31)	2.72 a (±0.09)	2.65 a (±0.17)	2.48 a (±0.16)
Total heterotrophic microorganisms (log mL^{-1})	3.03 b (±0.36)	3.46 ab (±0.34)	3.89 ab (±0.81)	4.10 a (±0.65)

3), pH and conductivity values (no difference with Site 2). Site 3 presented the lowest dissolved O_2 and the highest ammonia values. The lowest microbial parameters were registered at Site 1, except to *E. coli* which was not detectable in Site 2 and Site 4 (Table 1).

Flow differences strongly modified the water characteristics although their magnitude depended on the sites. During the high flow season the conductivity and soluble N (ammonia and nitrates) decreased in all sites, while dissolved O_2 decreased in Sites 1 and 2, and increased in Site 3 and Site 4. The abundance of heterotrophic bacteria was significantly lower with the low flow in Sites 1 and 2 compared with the same sites during the high flow period. Site 3, on the other hand, showed a significantly higher abundance of heterotrophic bacteria in the low-flow period than it did in the high-flow period, in coincidence with a major abundance of fecal coliform (Table 1).

3.2. Sediment chemical and microbiological characteristics

In general, the characteristics of sediments were more homogeneous than water attributes during both periods. During low flow period, the nitrate content and pH were significantly higher in Sites 2 and 3, while the other parameters did not differ among sites. On the other hand, the abundance of all bacteria groups was significantly higher in Sites 2 and 3 than in Sites 1 and 4 (Table 2).

During the high flow period, however, the chemical characteristics of sediments were more variable than the microbiological values. Site 2 showed the lowest nitrate values, while Site 1 presented the highest values for organic carbon content (though there were no difference with Site 4). At Site 1 the pH values measured in sediment samples were lower than in the other sites. The bacterial abundance did not significantly differ among sites, except the heterotrophic bacteria which were more abundant at Sites 1 and 4 as compared to Sites 2 and 3 (Table 2).

The sediment chemical and microbiological parameters of each study site presented scarcely significantly variations depending on the river flow. Site 1 presented increases in heterotrophic bacteria, organic C and nitrates during high flow period, while Site 3 showed a significantly higher quantity of fecal coliform bacteria during low flow period (Table 2).

3.3. Riparian soil chemical and microbiological characteristics

The soil chemical characteristics, as opposed to those of sediments, were very heterogeneous in the low flow period. Texture differed significantly among sites, and Site 2 presented the highest silt values and the lowest sand values. Nevertheless, at Site 2 the highest organic carbon and pH values were detected. Microbial groups showed scarce differences among sites, except for *E. coli*, which was significantly lower at Site 1 (Table 3).

During the high flow period, the organic carbon, sand content and heterotrophic bacteria abundance differed among sites. The organic carbon content and the heterotrophic bacteria abundance were higher at Sites 1 and 2, while lower sand content of the sediments was observed at Site 2. Similar to sediments, riparian soils presented scarcely significant variations in their characteristics depending on the river flow. At Site 1 the pH, *E. coli* abundance, nitrate and organic C content increase with high flow while at Site 4 only the total heterotrophic microorganisms increased their abundance during the same period (Table 3).

3.4. Heavy metals in sediment and water

In surface water Cu, Cr, Ni, Fe and Mn showed a similar tendency during low flow period with lower values at Sites 1 and 4 and higher levels at Site 3. Pb and Zn where only detected at Site 3 while Cd never reached detectable values in none of the study sites. A completely different pattern was observed in water samples during the high flow period. Cd, Cr, Zn and Ni were never detected in study sites, while Cu and Pb were below the detection limit at Site 1 but reached similar values at Sites 3 and 4. In contrast, Fe and Mn showed the lower values at Site 1, an increase at Site 3 and a decrease but still over Site 1 amounts, at Site 4 (Table 4).

In sediment samples there were also differences between sampling periods. During the high flow metal level measured in water and in sediment samples showed a similar trend. In most cases, the lowest levels were observed at Site 1 and the highest ones at Site 3, with the exception of Fe, Ni and Cr. Maximum values of Fe were observed in Site 1 while Ni and Cr levels did not change along the river. Metal amounts in sediment samples collected during the low

Table 2

Sediment chemical and biological characteristics (means ± SD) at Suquía River study sites during low and high flow periods. For each parameter, different letters indicate significant differences among sites (Tukey test $p>0.05$). * indicates significant differences between flow periods for each study site (Tukey test $p>0.05$).

	Site 1	Site 2	Site 3	Site 4
Low flow				
pH	6.89 b (±0.09)	7.24 a (±0.19)	6.53 c (±0.23)	7.06 ab (±0.20)
Nitrate (mg kg^{-1})	17.5 b* (±5.3)	366.0 a (±36.8)	122.2 ab (±14.2)	30.1 b (±2.15)
Organic C (g kg^{-1})	1.94 * (±1.71)	19.08 (±23.65)	25.67 (±22.75)	2.33 (±3.69)
Sand (%)	92.0 (±3.8)	55.8 (±41.3)	79.7 (±18.7)	87.5 (±12.3)
Silt (%)	5.3 (±2.18)	30.6 (±35.1)	18.3 (±19.6)	11.3 (±12.6)
Clay (%)	2.6 (±2.9)	13.6 (±17.7)	2.0 (±2.9)	1.3 (±1.8)
E. coli (log g^{-1})	0 b	2.30 a (±1.48)	2.27 a (±1.46)	0.55 b (±1.23)
Fecal coliforms (log g^{-1})	3.03 c (±0.88)	4.33 a (±0.93)	4.82 a* (±0.41)	3.76 b (±0.82)
Total heterotrophic microorganisms (log g^{-1})	4.46 b* (±0.14)	5.81 ab (±1.25)	6.64 a (±1.58)	4.28 b* (±0.73)
High flow				
pH	6.81 b (±0.46)	7.65 a (±0.06)	7.44 a (±0.14)	7.42 a (±0.10)
Nitrate (mg kg^{-1})	40.2 b (±16.4)	15.2 c (±7.7)	68.0 a (±45.3)	40.0 b (±16.3)
Organic C (g kg^{-1})	9.81 a (±7.29)	0.72 c (±0.20)	2.01 bc (±2.79)	8.71 ab (±8.03)
Sand (%)	81.3 (±10.7)	98.1 (±0.8)	71.5 (±28.1)	67.3 (±22.9)
Silt (%)	12.3 (±9.3)	1.7 (±0.4)	18.5 (±19.9)	23.7 (±18.8)
Clay (%)	6.4 (±4.7)	0.3 (±0.6)	10.0 (±13.8)	8.9 (±10.5)
E. coli (log g^{-1})	0.81 (±1.12)	1.61 (±0.92)	1.92 (±0.45)	0.47 (±1.06)
Fecal coliforms (log g^{-1})	3.77 (±0.54)	3.67 (±0.18)	4.06 (±0.57)	4.09 (±0.34)
Total heterotrophic microorganisms (log g^{-1})	5.52 a (±0.20)	4.62 c (±0.07)	4.93 bc (±0.70)	5.46 ab (±0.36)

Table 3
Riparian soil chemical and biological characteristics (means ± SD) at Suquía River study sites during low and high flow periods. For each parameter, different letters indicate significant differences among sites (Tukey test $p > 0.05$). * indicates significant differences between flow periods for each study site (Tukey test $p > 0.05$).

	Site 1	Site 2	Site 3	Site 4
Low flow				
pH	6.96 b (±0.29)	7.36 a (±0.25)	6.77 b (±0.28)	6.83 b (±0.14)
Conductivity (µS cm^{-1})	556 (±108)	4493 (±3994)	2333 (±1749)	2378 (±2683)
Nitrate (mg kg^{-1})	36.2* (±15.9)	257.5 (±343.48)	42.5 (±26.4)	44.0 (±41.22)
Organic C (g kg^{-1})	15.35 ab* (±6.52)	24.31 a (±14.24)	2.14 c (±1.65)	10.64 bc (±9.78)
Sand (%)	74.6 ab (±12.6)	57.3 b (±20.5)	89.2 a (±3.8)	68.7 ab (±21.7)
Silt (%)	18.9 ab (±11.4)	34.7 a (±14.6)	8.1 b* (±4.0)	27.6 a (±19.4)
Clay (%)	6.4 (±2.5)	8.0 (±14.2)	2.7 (±2.8)	3.7 (±5.8)
E. coli (log g^{-1})	0 b*	1.32 a (±1.95)	1.46 a (±1.36)	0.45 ab (±1.02)
Fecal coliforms (log g^{-1})	4.37 (±0.36)	4.99 (±1.19)	3.99 (±1.18)	3.59 * (±0.95)
Total heterotrophic microorganisms (log g^{-1})	5.48 (±0.45)	5.99 (±0.92)	5.49 (±0.84)	4.95 (±0.77)
High flow				
pH	7.70 (±0.15)	7.59 (±0.02)	7.51 (±0.13)	7.51 (±0.09)
Conductivity (µS cm^{-1})	1163 (±645)	1064 (±175)	880 (±270)	919 (±252)
Nitrate (mg kg^{-1})	82.7 (±37.5)	76.0 (±67.7)	90.2 (±67.9)	39.5 (±20.6)
Organic C (g kg^{-1})	23.01a (±1.53)	25.17a (±2.22)	6.52 b (±5.83)	10.85 b (±5.73)
Sand (%)	61.0 a (±17.1)	36.7 b (±17.0)	74.0 a (±15.3)	51.3 ab (±20.2)
Silt (%)	35.7 (±16.2)	48.0 (±12.8)	18.7 (±7.7)	41.3 (±22.4)
Clay (%)	3.3 (±4.1)	15.3 (±14.8)	7.3 (±8.6)	7.3 (±5.5)
E. coli (log g^{-1})	1.23 (±1.16)	1.01 (±1.38)	0.93 (±1.29)	1.73 (±1.04)
Fecal coliforms (log g^{-1})	4.55 (±0.36)	4.62 (±0.23)	4.13 (±0.55)	4.54 (±0.27)
Total heterotrophic microorganisms (log g^{-1})	5.76 ab (±0.34)	5.99 a (±0.13)	5.30 b (±0.43)	5.32 b (±0.51)

flow period showed an increase from Site 1 to Site 4. Only Fe with a maximum level in Site 1 and Mn with minimum values in Site 3 did not follow this tendency (Table 5).

3.5. Fish assemblages

The results clearly show differences among sites and sampling periods in almost all the analyzed fish parameters. Site 1 showed the highest values of fish assemblage attributes (Table 6), while Site 3 presented the lowest ones, except for the number of tolerant species proportion. The highest values of the BI were registered at Site 3. Site 4 presented intermediate values respect to the other sites or similar to those at Site 1 (Table 6).

During the high flow period the fish relative abundance was higher than in low flow period. The BI, species richness and diversity presented scarce changes between periods. In contrast, during low flow period the proportion of the number of tolerant species was high whereas sensitive species were not detected at Site 3 (Table 6).

Table 4
Water heavy metals (means ± SD of $n = 6$ analytic repetitions) at three study sites along the Suquía River during low and high flow periods. LOD: limit of detection.

	Site 1 (µg L^{-1})	Site 3 (µg L^{-1})	Site 4 (µg L^{-1})	LOD (µg L^{-1})
Low flow				
Cu	2.24 (±0.15)	7.78 (±0.79)	3.26 (±0.12)	
Cd	<LOD	<LOD	<LOD	0.1
Cr	5.38 (±0.36)	8.73 (±0.92)	3.79 (±0.16)	
Pb	<LOD	3.48 (±0.50)	<LOD	1.3
Zn	<LOD	42.73 (±7.66)	<LOD	0.04
Ni	4.65 (±0.89)	8.69 (±1.31)	4.46 (±1.21)	
Fe	159.9 (±12,0)	264.7 (±12.6)	123.6 (±4.4)	
Mn	15.1 (±3.3)	93.4 (±10.6)	18.1 (±1.9)	
High flow				
Cu	<LOD	5.03 (±0.10)	4.73 (±0.04)	0.5
Cd	<LOD	<LOD	<LOD	0.1
Cr	<LOD	<LOD	<LOD	0.26
Pb	<LOD	5.03 (±0.48)	3.78 (±0.35)	1.3
Zn	<LOD	<LOD	<LOD	0.04
Ni	<LOD	<LOD	<LOD	2.3
Fe	41.25 (±3.50)	303 (±11.00)	181.8 (±16.11)	
Mn	8.71 (±0.90)	158.7 (±1.36)	30.94 (±0.99)	

3.6. Air semi-volatile organic compounds

Sites 1, 2 and 4 showed the highest total area values for all chemical functional groups (around 700 a.u./m^3, Fig. 2), while the values in Site 3 were almost one order of magnitude below (around 70 a.u/m^3). Moreover, Site 3 presented the lowest variability and a smaller quantity of substances for all of the three phases analyzed compared to the other sites.

The monitored substances were gathered by chemical functional group in Fig. 3. Each bar represents the amount of semi-volatile organic compounds in PUF, XAD and filter compartment arranged in blocks of 4 bars, one for each site. The most abundant groups were

Table 5
Sediment heavy metals (means ± SD of $n = 6$ analytic repetitions) at three study sites along the Suquía River during low and high flow periods. LOD: limit of detection.

	Site 1 (µg g^{-1})	Site 3 (µg g^{-1})	Site 4 (µg g^{-1})
Low flow			
Cu	1.96 (±0.27)	12.70 (±0.34)	22.93 (±2.70)
Cd	0.021 (±0.007)	0.055 (±0.01)	0.084 (±0.001)
Cr	3.73 (±0.16)	7.03 (±0.09)	12.88 (±0.08)
Pb	8.72 (±0.50)	20.54 (±0.90)	24.76 (±0.40)
Zn	9.00 (±0.50)	65.77 (±0.20)	118.66 (±7.70)
Ni	4.83 (±0.20)	5.65 (±0.15)	6.09 (±0.17)
Fe	3456.8 (±95.8)	2285.5 (±32.5)	1631.4 (±35.9)
Mn	230.3 (±6.5)	84.5 (±0.6)	319.1 (±5.2)
High flow			
Cu	6.38 (±0.35)	17.55 (±0.50)	15.11 (±0.27)
Cd	0.021 (±0.008)	0.054 (±0.050)	0.084 (±0.004)
Cr	4.86 (±0.38)	4.81 (±0.85)	5.57 (±0.28)
Pb	6.89 (±1.60)	18.96 (±2.73)	16.68 (±0.60)
Zn	13.94 (±1.90)	58.92 (±1.01)	58.78 (±1.32)
Ni	5.00 (±0.80)	4.14 (±0.21)	4.09 (±0.17)
Fe	3387.9 (±349.3)	1947.9 (±119.8)	1863.6 (±81.3)
Mn	124.9 (±20.8)	214.9 (±5.4)	192.6 (±5.4)

Table 6
Distributions, fish species abundance (%) and assemblages attributes collected at each sampling sites along the Suquía River Basin.

Fish species	Sampling sites					
	Low flow period			High flow period		
	1	3	4	1	3	4
CHARACIDAE						
Oligosarcus jenynsii (Günther, 1864)	0.56	0	0	0.29	0	0
Astyanax spp.	6.70	0	0	0.88	0	0.30
Bryconamericus iheringi (Boulenger, 1887)	1.68	0	2.60	0.88	0.35	0.29
Odontostilbe microcephala Eigenmann, 1907	0	0	6.48	0	0	2.96
Cheirodon interruptus (Jenyns, 1842)	0.56	0	0	0	0	0
ERYTHRINIDAE						
Hoplias malabaricus (Bloch, 1794)	2.23	0	0	0	0	0
PARONDONTIDAE						
Parodon nasus Kner, 1859	0	0	3.89	0	0	0
HEPTAPTERIDAE						
Pimelodella laticeps Eigenmann, 1917	0.56	0	0	0.59	0	0
Rhamdia quelen (Quoy & Gaimard, 1824)	0	0	0	1.47	0	0
TRICHOMYCTERIDAE						
Trichomycterus cordubense Wedenbergh, 1877	0	0	7.79	0	0	0
CALLICHTHYDAE						
Corydoras paleatus (Jenyns, 1842)	38.55	0	0	18.47	0	1.78
LORICARIIDAE						
Rineloricaria catamarcensis (Berg, 1895)	0.55	0	0	1.17	0	2.07
Hypostomus cordovae (Günther, 1880)	0	0	1.29	0.87	0	0.89
ANABLEPIDAE						
Jenynsia multidentata (Jenyns, 1842)	35.75	100.00	35.06	34.02	3.52	66.27
POECILIIDAE						
Gambusia affinis (Baird & Girard, 1853)	10.62	0	42.85	37.24	84.51	23.08
Cnesterodon decemmaculatus (Jenyns, 1842)	1.68	0	0	3.81	11.62	2.07
SYNBRANCHIDAE						
Synbranchus marmoratus Bloch, 1795	0	0	0	0	0	0.29
CICHILIDAE						
Australoheros facetus Jenyns, 1842	0.56	0	0	0.29	0	0
Fish assemblages attributes						
Total relative abundance	0.36	0.004	0.24	1.05	0.87	1.04
Diversity Index	1.52	0	1.38	1.48	0.53	1.04
Fish species richness	12	1	7	12	4	10
Number of sensitive species (%)	58.33	0.00	57.14	58.33	25.00	50.00
Number of tolerant species (%)	33.33	100.00	42.80	33.33	75.00	40.00
Biotic Index	62.50	15.42	58.33	54.17	29.16	58.33

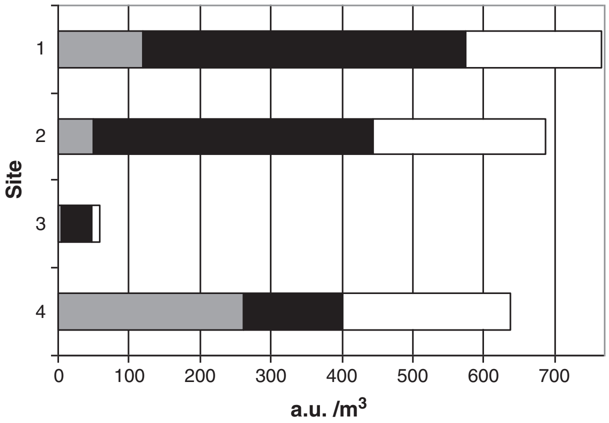

Fig. 2. Total organic semi-volatile compounds in air (a.u./m^3) discriminated by the solid phase retention: PUF (gray); XAD (black); and filter (white), at the four study sites. Site 1: La Calera city; Site 2: Córdoba city; Site 3: Corazón de María village; Site 4: Río Primero city.

phthalates, esters, siloxane and alkanes, independently of either sites sampled or phase analyzed. Around 15–20% of the chromatographic peaks corresponded to unidentified substances (Fig. 3).

Sites 1 and 4 were found to be the most affected by phthalate pollution, followed by Site 2 and 3. Esters are a group of heterogeneous compounds that presented higher amounts at Sites 4, 2 and 1 in decreasing order than at Site 3 whereas siloxanes showed an important presence in air and particulate material at Sites 1 and 2 compared to Sites 3 and 4. Alkanes are the most abundant compounds at Sites 1, 2 and 4 and the second in importance at Site 3.

Among the semi-volatile compounds found in less important area is remarkable the variation pattern of the PAH's which is directly related to the transport automotive. This group was almost five times superior at Site 2 than at Sites 1 and 4 and twenty five times than at Site 3. Furthermore, Site 2 showed a high diversity of these compounds, which is indicative of anthropogenic activities from a great urban center.

3.7. Air pollutant bioindicators

In both sampling periods, Sites 2, 3 and 4 presented a significantly higher sulfur concentration accumulated on lichen thalli (*U. amblyoclada*), with respect to the control group. In the low flow period Site 1 significantly differed from control, and it was the only site that showed significant differences between flow periods (Fig. 4). The highest MCN frequencies were observed in the *T. pallida* individuals located at Site 2 being significantly different than those from Sites 1, 3 and 4 during the high flow period (Fig. 5).

3.8. Multivariate statistical analysis

Looking for additional evidences on the correspondence between three studied matrixes, we decided to apply Generalized Procrustes Analysis (GPA). GPA produces a configuration of the different studied sites that reflects the consensus among the three matrixes (river, air and biota groups). The result is a consensus alignment that uses all the variables from the three data sets. In Fig. 6, the consensus configuration projected onto the plane defined by its first and second principal axis is shown, explaining 100% of variability between samples. We can observe that the three monitoring sites are well separated on the basis of the biotic and abiotic parameters. This result shows that data obtained from biota has a significant consensus (99.3%) with those corresponding to river and air groups, as the three data sets projects the regions in the same way onto the plane defined by its first and second principal axis. This last result gives further indication on the connection between three studied matrices.

4. Discussion

The identification and control of the environmental contaminants generated by point (sewage discharges, industrial effluents and emissions) and dispersed or nonpoint sources (urban runoff, automobile traffic, livestock wastes, fertilizer and pesticide applications) pose

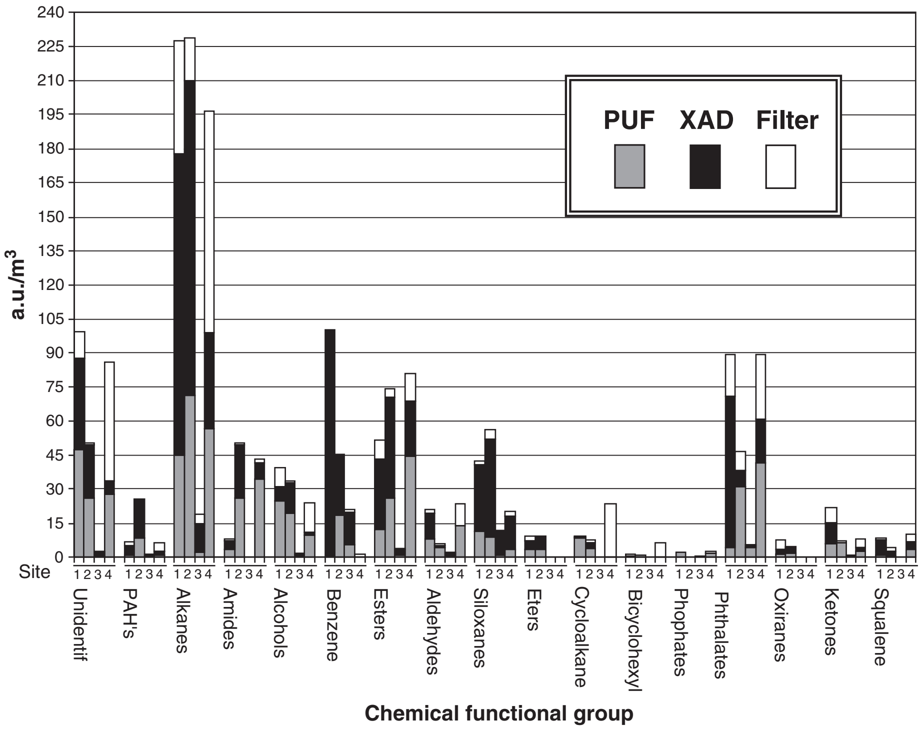

Fig. 3. Chemical functional groups in air (a.u./m^3) are plotted against sampling sites. Each bar discriminates the solid phase retention of the chemical: PUF (gray); XAD (black); filter (white). The differences in the PUF pattern identify the site monitored. 1: Site 1 (La Calera city); 2: Site 2 (Córdoba city); 3: Site 3 (Corazón de María village); 4: Site 4 (Río Primero city).

difficult challenges for watershed restoration programs (Swackhamer et al., 2004). The Suquía River basin, considered as a key element of the central landscape of Córdoba province, suffers the negative impact of different pollution sources that affects the air, water, riparian soil, sediments and biota at different quality degrees.

A natural approach to characterize the problem is to rank the sampling sites of the watershed from best to worst according to a group of environmental variables. Our work comprises a diversity of variables grouped in different compartments that makes this investigation an integral study to evaluate the Suquía River watershed quality.

4.1. Water characteristics

Our results clearly show that Córdoba city negatively impact on water quality compared to the river areas located upstream. Even 50 km downstream the city, the river does not achieve the water quality detected at the reference site (Site 1). According to the parameters measured in water, the WWTP would not be the only source of pollution. For instance, immediately upstream Site 2 the river receives La Cañada Brook. This tributary causes the rise of pH and conductivity because it is born on a limestone bed (Vázquez et al., 1979). On the other hand, La Cañada Brook contributes with high nitrate and organic C content indicating the effects of anthropogenic activities (Das and Kumar, 2009; Pasquini et al., 2011). As the river and brook flow on a cement channel, the nitrate persistence in water could be associated to the scarce riparian and aquatic vegetation at Site 2 (Carpenter et al., 1998; Craig et al., 2008). Other possible effect of the cement channel is the increase of water velocity which causes the rise of dissolved O_2 concentration during both sampling periods.

The presence of bacteria from sewage was registered at all the studied sites and for the both sampling periods. However, the high bacteria content together with the high content of organic C downstream the WWTP indicate: a) the lack of an adequate waste water

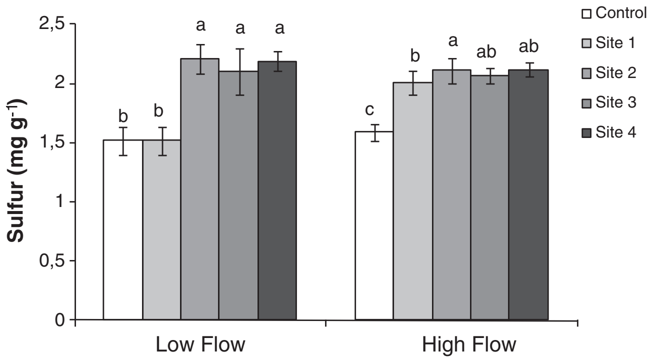

Fig. 4. Sulfur concentration (mg g^{-1} DW) in *Usnea amblyoclada* tissues after 3 months of exposure at study sites along the Suquía River on low- and high-flow periods. Site 1: La Calera city; Site 2: Córdoba City; Site 3: Corazón de María village; Site 4: Río Primero city. Bars indicate SD. Different letters indicate significant differences among sites (Tukey test, $p<0.001$).

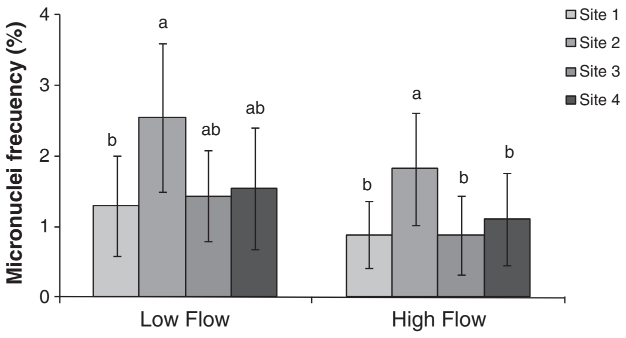

Fig. 5. Micronuclei frequency (100 tetrads) in *Tradescantia pallida* inflorescences after 3 months exposure at study sites along the Suquía River on the low- and high-flow periods. Site 1: La Calera city; Site 2: Córdoba City; Site 3: Corazón de María village; Site 4: Río Primero city. Bars indicate SD. Different letters indicate significant differences among sites (Tukey test, $p<0.05$).

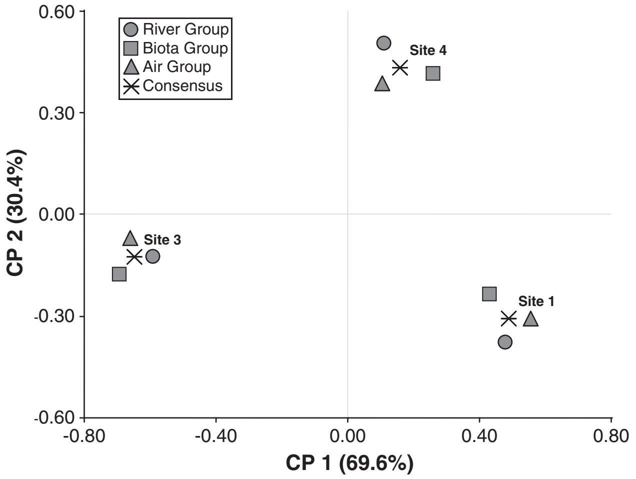

Fig. 6. Consensus space from Generalized Procrustes Analysis: plot in the plane formed by the first two dimensions.

treatment (Graham and Smith, 2004), not only from WWTP but also from discharges of neighborhoods' smaller treatment plants, and b) that water already has an important coliform bacteria content when it enters the city. The San Roque Dam is located in a highly-populated tourist area widely known for its deficiency in waste water treatment (Wunderlin et al., 2001). This aspect is consistent with the fact that fecal coliforms was detected at Site 1, and *E. coli* (recent sewage pollution indicator) was not, while its presence in the other sites indicate permanent sewage contributions along the river in the city (Eamens et al., 2006). The decrease of conductivity, nitrates and ammonia values registered during the high flow period reflect the dilution effect due to high water flows which, together with the high dissolved O_2 concentrations, could also promote the increase of the BI at Site 3.

Oxygen is a key factor for aquatic biota and determines fish distribution in freshwater systems. Only few fish species could tolerate a low oxygen concentration as the one recorded at Site 3, where oxygen reached critical low concentrations. Species like *Jenynsia multidentata, Gambusia affinis* and *Cnesterodon decemmacultus* can tolerate low oxygen concentrations because they have morphological adaptations to aquatic surface respiration such as small size body and mouth turned upwards. Tagliani et al. (1992) have indicated that the vertical distribution of the Poeciliidae family (like *G. affinis* and *C. decemmaculatus*) is restricted to the first centimeters of the water column where the dissolved oxygen concentrations are higher than deeper waters. The same features are present in *J. multidentata* (Anablepidae). Similar conclusions were achieved by Bistoni et al. (1999). These authors worked in the same study area during 1995–1996. Since then, 15 years have passed and the water quality degradation continues and extends many kilometers downstream respect to the data recorded in those years.

Fish assemblage structure changed with increasing water quality degradation, showing a simpler structure at the most polluted area (Site 3) where few species found favorable conditions for their establishment in degraded zones. According to the BI based on fish attributes, our results showed a clear deterioration of the fish assemblages of Suquía River compared to the data published by Hued and Bistoni (2005), particularly at Site 3, after WWTP discharges (1998–2002 = 35.9; 2008–2009 = 16.67). A similar pattern of variation was registered in the other fish assemblages attributes such as species richness and diversity. The changes registered in fish assemblages through the present study have been pointed out by several authors around the world (Karr et al., 1987; Zampella and Bunnel, 1998; Oberdorff et al., 2002) who indicated the simplification of assemblages due to pollution effects.

Variations in heavy metal concentrations between the low and high flow periods suggest the different sources of these elements. For instance, although most of the metals suffer dilution during the high flow period, Pb and Fe increased at sites located downstream from Córdoba city. Moreover, Pb reached values above the levels for life aquatic preservation (SRHN, 2004) at Site 3 during the low flow period. On the other hand, the river receives the urban run-off from the rainfall drainage loaded with traffic pollutants (Baldauf et al., 2009) which increase the Pb levels during the high flow period at Sites 3 and 4. The Pb, Mn and Fe concentrations registered in our study showed an increase respect to the data recorded in 2007 by Contardo-Jara et al. (2009). The other heavy metal measured did not exceed the levels established by the US EPA (1999c).

4.2. Sediments characteristics

The water pollution also has affected the river sediments, particularly at Sites 2 and 3. Although sandy sediments were dominant at all the sites, each of them presented great diversity of textures, varying from sandy to highly silt sludge. It is noticeable, that during the low flow period the high content of fine material registered on the cement channel at Site 2 suggests the removal of the silt sediments by the high water velocity during the high flow period (Dachs and Méjanelle, 2010). On the contrary, the deposition of suspended material due to the slowness of the water flow determined a high organic C content in sediments during the low flow period.

In addition, the high nitrate concentrations registered in sediments from Site 2 in the low flow period could be associated to silt fraction retention. On the other hand, in the high flow period, the water speed on the cement channel prevents the fine material deposition and consequently the nitrate retention (Bernot and Dodds, 2005).

The amount of fecal organisms in sediments is a main indicator for sewage pollution. A similar annual abundance of fecal coliform in sediments and values greater than those found for water, indicates that two processes could be occurring: a) the sediments are substrate for bacteria retention and protection, or b) the coliform bacteria found optimal conditions for reproduction in the sediments from the most polluted sites with sewage discharges. The latter option is based on the fact that coliform bacteria development depends on growth factors of the mammalian intestinal tract (present in organic matter from sewage sludge) and on anoxic conditions in sediments (Bonjoch and Blanch, 2009; Haller et al., 2009).

In accordance with the heavy metal concentrations registered in water, metal levels in sediments did not exceed the Probable Effect Concentration recommended by the USEPA quality guidelines for fresh water sediments (US EPA, 2002; Mdegela et al., 2009; Bird et al., 2010).

The geological composition of original rocks (metamorphic granite with gneiss ducts) determines the high Fe and Mg values detected at Site 1 (Contardo-Jara et al., 2009). Furthermore, the similar high heavy metal values associated to human activities at Sites 3 and 4 could indicate the negative effect of the city and the metal movement from Site 3 toward Site 4 (50 km away) (Bird et al., 2010).

4.3. Riparian soils characteristics

Similar to sediments, riparian soils permanently wet by river waters, receive the negative impact of the polluted water. As well as sediments from Site 2, riparian soils presented high organic C, nitrate and silt fraction contents during the low flow period, which suggests a high deposition of fine material.

.Conductivity showed a similar variation pattern for both water and riparian soil during the high flow period. On the other hand, during the low flow period an increased conductivity level was registered after the river receives the La Cañada brook indicating salt precipitation.

The presence of coliform bacteria in the riparian soils at most sampled sites (with similar or higher values than in sediments) suggests the importance of including the margins of the river in restoration programs (Parkyn et al., 2003; White and Stromberg, 2009).

Riparian vegetation along the Suquía River basin varies among sites. For example, Sites 1 and 4 present abundant vegetation including native and exotic species (dominated by medium size trees and grasses), while Site 2 has a conspicuous marshy species (*Poligonun ssp*) only on summer. Besides, margins of Site 3 are modified by sand mining where the vegetation is scarce contributing to the low nitrate uptake by the riparian vegetation.

The importance of riparian zones in preventing erosion, protecting water quality, providing habitat and wildlife corridors, and maintaining the health of in-stream biota as well as human recreational uses, has led to a surge of restoration activities aimed at riparian ecosystems in the last few decades (Richardson et al., 2007). In general, restoration programs take a fertility approach to riparian soils, which will depend on the success of vegetation management (Parkyn et al., 2003; White and Stromberg, 2009). However, in the Suquía River, a health risk approach must be taken due to the great amount of coliform bacteria (Yau et al., 2009).

4.4. Air characteristics

This is the first study on the presence of semi-volatile organic compounds in air and particulate through the Suquía basin in the province of Córdoba. In all the analyzed sites, phthalates, siloxanes, and esters follow alkanes in terms of their presence in air. Undoubtedly, all of these compounds have an anthropogenic source.

The high amount of other organic compounds (apart from alkanes) at Site 1 could be related to the presence of an important power plant (Dachs and Méjanelle, 2010) in the San Roque reservoir, near which the air sampler was placed. Water discharge, which produces high turbulence in the river, could also mobilize semi-volatile substances from sediments (Swackhamer et al., 2004). Besides, at Site 1 the river flows through mountains, which could accelerate the wind speed, volatilizing the organic compounds from water (Dachs and Méjanelle, 2010). In the case of Site 2, the impact of automotive transport is reflected in the high level of alkanes, benzene derivates, and PAH. Also, it is the site with the widest variability of compounds. Site 3 is roughly 7 km from the highway; it has a low number of permanent inhabitants and is surrounded by farms. All these factors should contribute to the reduced presence of semi-volatile organic compounds, although it lies downstream of the WWTP while pollution at Site 4 was affected by the highest dosage of compounds related to plastic manufacture.

As it is shown in this work the air quality is greatly influenced by modern human activities such as manufacture and widespread use of plastic materials since they promote an increasing release into air and particulate of substances that pose a risk to human health. The release of semi-volatile substances from the river cannot be conclusively assessed, especially when comparing the behavior at Site 3, which presents the highest levels of river pollution with a low concentration of semi-volatile organic compounds.

The high lichen sulfur content detected at all sites (related to control), agree to state that lichen sulfur content is a good estimation of the air SO_2 content (Garty et al., 1988). SO_2 is one of the main products of fuel combustion, which is directly related to vehicles emissions as well as a large amount of industrial process or energy generation. Thus, the higher the sulfur level in the air, the greater the accumulated sulfur level in the lichens and the damage caused in the thalli (Wadleigh and Blake, 1999).

Previous studies on the same species also have shown a significant increase in the accumulated sulfur content in lichen exposed in Córdoba urban zones. For example, Carreras et al. (1998) reported 2.135 ± 0.233 mg/g DW values in samples exposed in Córdoba downtown, close to a heavy vehicular traffic. Similarly, studies on other lichen species also reported an increase in the sulfur content in thalli transplanted to other urban zones (Levin and Pignata, 1995; González et al., 1996; Cañas et al., 1997).

However, the substantial level of sulfur at Site 4 could also be due to agricultural activity. Previous studies reveal that agrochemicals (glyphosate and sulfur fertilizers) are an important contribution of sulfur to the environment (Hitsuda et al., 2004). On the other hand, the differences found in sulfur content accumulated in the lichens exposed at Site 1in the low-flow period, are reflecting seasonal variations in traffic pattern since during this period (summer) La Calera road is one of the tourists preferred route to get to the nearby hills from the city of Córdoba.

Moreover, sulfur levels in the lichen transplanted at Site 3 suggest SH_2 emissions from the river by sulfate reducer microorganism activity (Merlo and Abril, 2010). The water sediments and riparian soil characteristics at this site (siltly texture, high organic C content and O_2 scarcity) agree with the sulfate reducer bacteria requirements (Kosolapov et al., 2003; Leonov and Chicherina, 2008; Reese et al., 2008).

Similarly, the results of the genotoxicity test with *T. pallida* are in good agreement with a previous study conducted in downtown Córdoba city with the same species, where a significantly higher percentage of MCN was found in the study sites located close to high traffic routes (Carreras et al., 2006). In addition, our results are consistent with what Guimaraes et al. (2000) reported in a study conducted in Sao Paulo city. These authors demonstrated that the urban atmospheric pollutant corresponded with changes in the MCN frequency. The higher MCN frequency observed during the low-flow period, could owe to the lack of rainfall and thermal inversions characteristic of wintertime that enhance pollutant permanence in the atmosphere lower layers (Stein and Toselli, 1996; Olcesse and Toselli, 1997).

4.5. Associations between ecological compartments

Through multivariate statistical analysis (GPA) we can presume that the different ecological compartments studied are closely related and that the interaction between them determines the characteristics of each site. The results of this study allow us to conclude the validity of integrating the study of the different compartments to determine the quality of water resources through a pollution gradient.

5. Conclusions

Since the contamination of surface waters is a global concern, the restoration projects of water resources have been widespread in many countries. Their main goals are to improve the water quality and habitats and make an appropriate management of riparian zones (Parkyn et al., 2003; Kang and Lin, 2009; Langendoen et al., 2009; Gift et al., 2010). However it was reported that many of these restoration programs fail to achieve its objectives, in part because of the scarcity of knowledge about the dynamics that characterized each watershed (Parkyn et al., 2003; Langendoen et al., 2009).

One of the key criteria in the planning of restoration programs is the identification of reference areas (undisturbed or minimally disturbed sites) whose values are considered optimal for this kind of programs (Carey and Migliaccio, 2009).

Our interdisciplinary study clearly reflects that water pollution in the Suquía River significantly affects other ecosystem compartments, particularly fish assemblage, and sediments and riparian soils by heavy metals and coliform bacteria. Moreover, we detected a possible contribution of sulfur and high pollutant content in air, which make investigations about other air-water exchanges necessary. Accordingly, our results suggest that actions must be taken not only to restore the Suquía River and remediate the anthropic effect on it, but also to deal with soil, sediment, and air pollution along the river.

Acknowledgements

Financial support was provided to Velia Matilde Solís and fellowship to Carolina Merlo by FONCyT (PICTO UNC 36026). Agencia Nacional de Promoción Científica y Tecnológica. Argentina.

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