The Handbook of Environmental Chemistry 62
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Daniel A. Wunderlin *Editor*

The Suquía River Basin (Córdoba, Argentina)

An Integrated Study on its Hydrology, Pollution, Effects on Native Biota and Models to Evaluate Changes in Water Quality

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The Handbook of Environmental Chemistry

Founded by Otto Hutzinger

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Volume 62

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Volume Editor: Daniel A. Wunderlin

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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry*, there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry*, the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of Environmental Chemistry* provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Preface

The Suquía River is a closed basin located in a the semi-arid region of the Province of Córdoba (Argentina). The basin starts at a *quasi* pristine mountain area, which streams form two main rivers controlled by an artificial dam (San Roque). The dam area is under high anthropic pressure because of touristic activities, and increased urbanization with poor wastewater treatment. After the dam wall, the Suquía River begins, passing through a mountain area first, then flowing across the city of Córdoba (ca. 1.5 Mill inhabitants), receiving the city run-off and other non-point pollution sources. At the east city corner, the river starts its lower basin, changing its hydrology to a plain-area river, receiving the input from the WWTP of the city at the beginning of this lower basin. Downstream, the river flows through fields having intensive agricultural activity, until reaching the hypersaline lagoon of Mar Chiquita, where the river ends.

This geographical and hydrological characteristics have produced a progressive increase in the pollution degree from the upper basin to the end of the lower basin, including almost any kind of pollutants, from typical sewage pollution to the presence of cyanotoxins, heavy metals, toxic organic compounds (including agrochemicals) to pharmaceuticals compounds. This pollution is evidenced in several compartments from the water, sediment, until the aquatic biota are affected. Thus, the Suquía River presents a bad example of diverse pollution sources, human driven, and a good opportunity to verify almost any kind of state-of-the-art analytical method to evaluate changes in the water quality, including intensive data mining by multivariate statistics. Many of the methods used for the study of this basin are presented in this book, looking for an integrated approach on the evaluation of a river basin affected by anthropic pressure at several levels.

Results summarized in this book were obtained along 20 years monitoring, by different persons, belonging to different institutions and with diverse purposes. Thus, this book looks to be a guide for river monitoring in developing countries, where the budget for controlling the water quality is limited but the pollution is still unlimited.

Cordoba, Argentina Daniel Alberto Wunderlin

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Hydrology and Hydraulics of the Suquía River Basin

Érica Díaz, Mariano Corral, María Lábaque, Leticia Vicario, Cecilia Pozzi Piacenza, Gonzalo Moya, Carlos Marcelo García, Leticia Tarrab, and Andrés Rodríguez

Abstract The Suquía River Basin is regulated by the San Roque Dam, which is located in its upper basin. With a basin area of over 1,750 km^2 and a mean streamflow of 9.8 m^3 s^{-1}, the Suquía is the second river of the Province of Córdoba (Argentina), according to its streamflow. Downstream from the dam, the river, in its middle basin, runs across a mountain area and then through the city of Córdoba. After leaving the city, in its lower basin, it flows for approximately 150 km towards the northeast until its mouth in the Mar Chiquita Lake. Therefore, the Suquía River has an endorheic basin. The San Roque Dam was designed as a multipurpose dam, and its priority uses include flood mitigation, water supply, irrigation and power generation. On its journey through the city of Cordoba, the Suquía River is urbanised with bridges, fords, coastal roads and a flood plain that is used for recreational purposes. Several studies were conducted to estimate extreme basin

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events. The basin characteristics were determined by both conventional methods and hydrological modelling. The maximum rainfall records arose from the frequency analysis of 21 rainfall stations installed along the basin.

From the hydraulic point of view, several studies were conducted to assess the maximum streamflow and levels on its way through the city of Córdoba. An emergency action plan (EAP) has also been developed to cover a potential failure at the San Roque Dam; so, EAP contains maps of different flooding scenarios in the city. Hydrometeorological drought studies were also carried out in the upper basin (San Roque Dam), considering the analysis of precipitation and stream flows series.

Keywords Droughts, EAP, Hydrology, San Roque Dam, Suquía River

Contents

1 The Suquía River Basin

1.1 Description of the Basin

The Suquía River is located in the Province of Córdoba (Argentina). It is formed by the confluence of the San Antonio and Cosquín Rivers, with smaller contributions from Los Chorrillos and Las Mojarras streams. Today its waters are dammed by the San Roque Dam (Fig. 1).

The upper basin is located at 31° south latitude and 64° west longitude, covering almost the entire Punilla Valley. It is bounded on the north by the back of La

Fig. 1 Downstream view of the San Roque Reservoir and beginning of the Suquía's middle basin

Cumbre; on the south by the crest of La Sierrita or Cordón de Santiago, which separates its basin from the Anizacate River; and on the west by the watershed of the Pinto River, the Pampa (plain) of San Luis and Sierra Grande (big hill) (Fig. 2). The region included in the Suquía River Basin is relatively small, but it contains the second demographic concentration of the country, Córdoba city, with ca. 1.4 million inhabitants. This city has an important and solid industrial and touristic activity. The upper basin also offers great touristic activities along the year, mainly in summer, and less mining activities (only mineral extraction).

At the end of its upper basin, the Suquía River is formed by the San Roque Dam, producing a reservoir located upstream from Córdoba city, which regulates the river flow and attenuates drought periods (April–October). In addition, upstream from Córdoba city, the river has two small dams: (a) Diquecito, constructed to provide raw water for purification (drinking water), and (b) Mal Paso, constructed to provide water for irrigation channels. Additionally, various bridges outside and inside the metropolitan area are constructed over the river waters. During the rainy season (November–March), the Suquía River and its tributaries cause significant flooding problems upstream and downstream from the San Roque Dam.

The Cosquín River is formed by the confluence of two main rivers, Grande and Yuspe, being the main tributary to the San Roque Dam. It has a basin area of over 905 km^2 and a mean streamflow of 5.5 m^3 s^{-1}. The Cosquín River meanders southwards through the town bearing its same name; it receives water from several streams and finally flows into the San Roque Reservoir (Figs. 2 and 3).

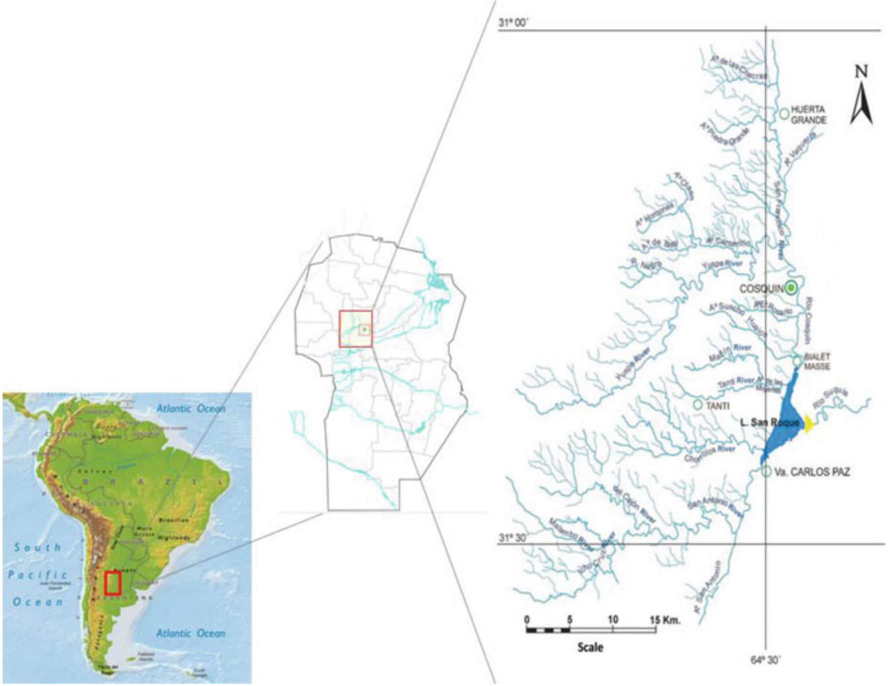

Fig. 2 Location of the Suquía River Basin

The southern sector of the Punilla Valley is drained by the San Antonio River Basin. It is formed by the confluence of the Icho Cruz and Malambo Rivers, meanders eastwards until reach the San Roque Reservoir (Figs. 2 and 3). The San Antonio River has a basin area of over 530 km^2 and a mean streamflow of 3.5 m^3 s^{-1}.

The Mojarras and Chorrillos streams reach the San Roque Dam between the San Antonio and Cosquín Rivers' mouths (Fig. 3). Las Mojarras stream has a length of 15 km, a modulus of 0.3 m^3 s^{-1} and an area of 84 km^2. Los Chorrillos stream has the same module as Las Mojarras, a length of 23 km and a basin area of 130 km^2.

Downstream from the San Roque Dam, the Suquía River crosses the Sierras Chicas through the defile of San Roque. After 26 km, the river reaches the city of La Calera and 4 km downstream the city of Saldán, receiving the waters of the Saldán stream, as well as of other numerous streams on the eastern slope of the Sierras Chicas. The Saldán stream contributes with an important volume during heavy rain periods, thanks to its large basin on the close mountain area (Fig. 2). Then, the Suquía River enters the plain area of Cordoba city. Once in the city downtown, the riverbed is reduced to a narrow concrete channel. In addition, when flowing through the city, the Suquía River incorporates water from La Cañada stream, also receiving part of the urban run-off.

La Cañada stream, formed in the tectonic depression of La Lagunilla, crosses the southern part of the city, from SW to NE (Fig. 4).

After the city east edge, the lower basin receives the effluent from the wastewater treatment plant (WWTP) of Córdoba city, further flowing by approximately

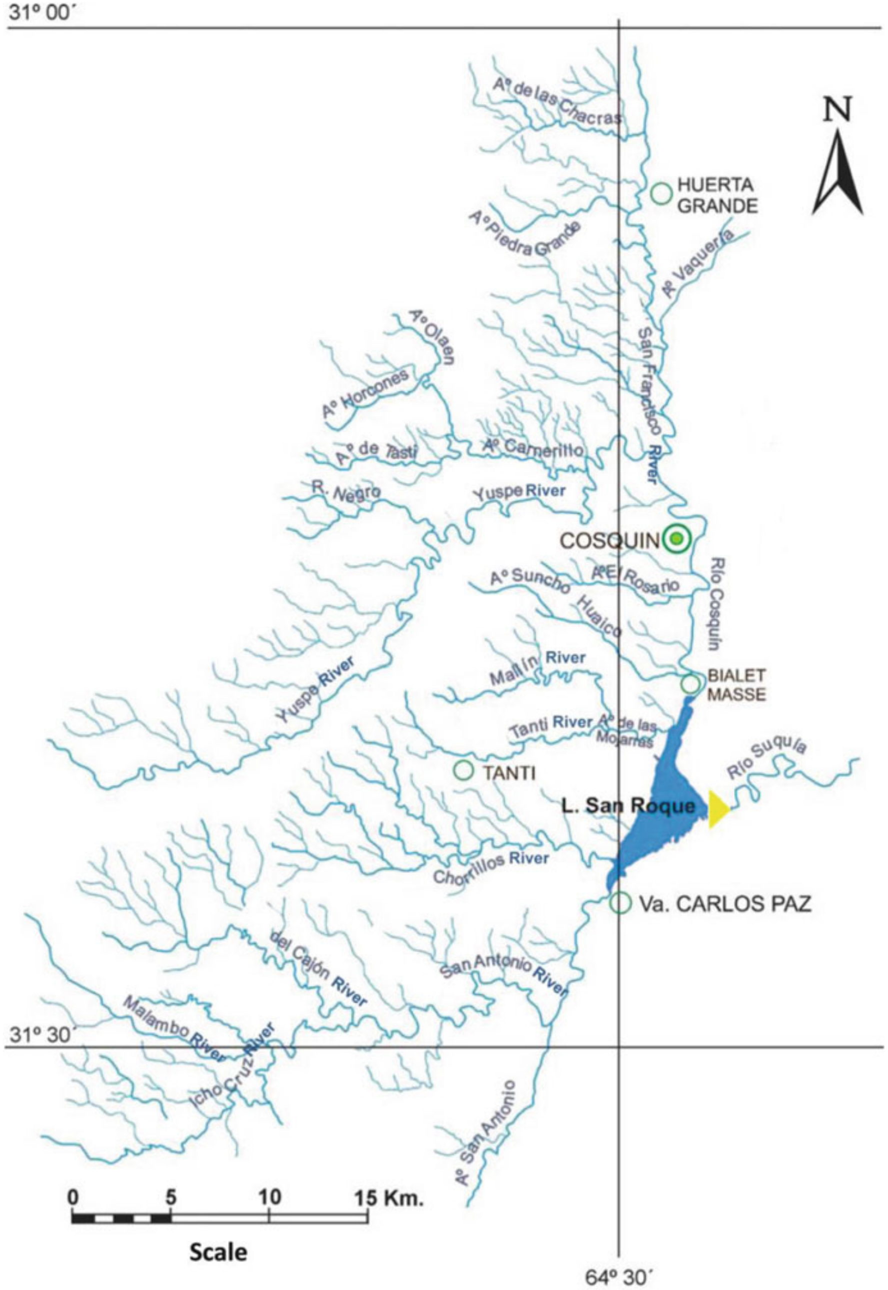

Fig. 3 Suquía River upper basin, including San Roque Reservoir and Dam

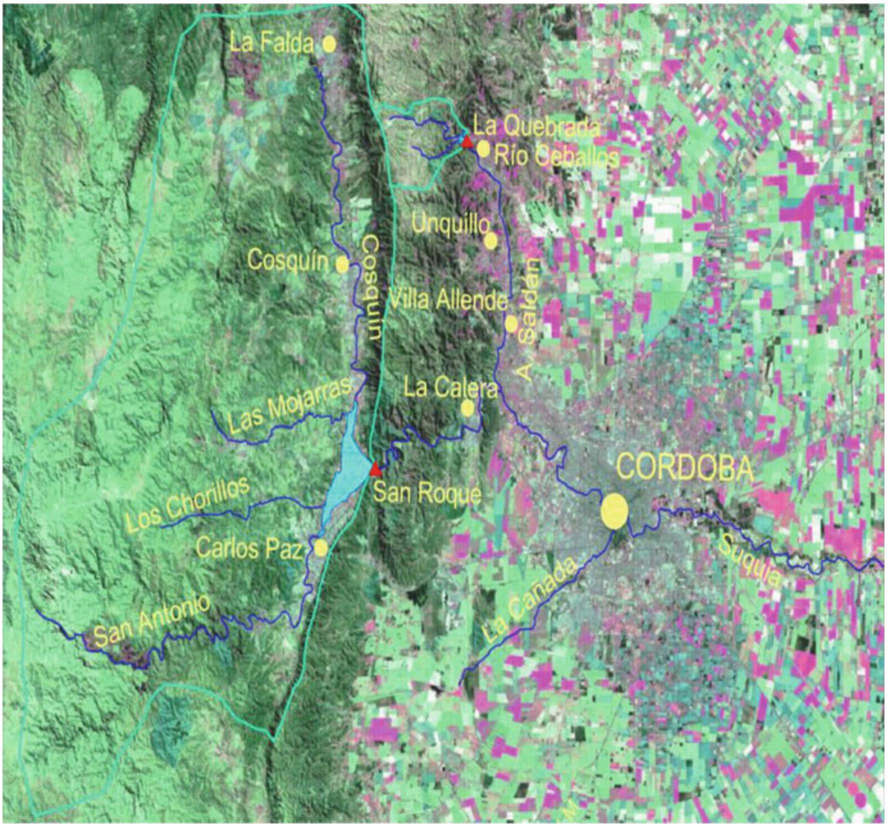

Fig. 4 Suquía River upper and middle basin

150 km to the northeast, until its mouth in the southwestern edge of the Mar Chiquita Lake [1], completing, in this way, an endorheic basin. The total course of the river from the San Roque Dam to the Mar Chiquita Lake is 203 km.

The average slopes of the Cosquín and San Antonio Rivers, at the bottom of their courses, are of 2.70 m km^{-1} and 3.45 m km^{-1}, respectively. The slope of the Suquía River between the San Roque Dam and La Calera (upstream from Córdoba city) is 5.75 m km^{-1}, decreasing downstream to 3 m km^{-1} between Córdoba city and Capilla de los Remedios town (ca. 20 km downstream from Córdoba city) (Figs. 3 and 4).

1.2 San Roque Dam and Reservoir

The San Roque Dam is a gravity dam and plant curve (Fig. 1). The closure height is 51.30 m, the length of the crest is 145 m, the volume of the reservoir is 201 hm^3, and the surface of the lake is 1,501 ha. The watershed area is 1,750 km^2. Figure 5 shows the curve elevation–volume of the San Roque Reservoir.

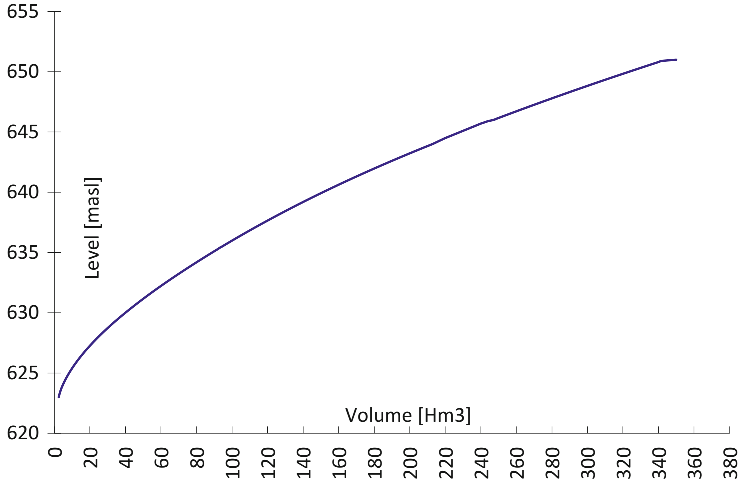

Fig. 5 Curve elevation–volume of the San Roque Reservoir

It was originally designed to serve more than one function ("multipurpose reservoir"), but its priority uses include water supply for Córdoba city, irrigation and power generation.

Its designers were Engrs. Ballester, Volpi and Suarez; the construction company was Enrique J. Bonneu. The construction of the dam started in 1939 and finished in 1944.

Some of its main features are listed in Fig. 6:

- Coat of foundation: 601 m.a.s.l. (above sea level)
- Channel bottom elevation: 608.00 m.a.s.l.
- Level spillway lip: 643.30 m.a.s.l.
- Maximum reservoir elevation: 651.00 msn m
- Level of crest: 652.30 m.a.s.l.
- Lake spillway lip surface elevation: 1,501 ha
- Maximum reservoir lake surface elevation: 2,478 ha
- Volume reservoir spillway lip height: 201 hm^3
- Maximum reservoir volume 350 hm^3

1.2.1 Objectives of the Dam

The San Roque Dam was built in order to exploit and dominate the waters of the Cosquín and San Antonio Rivers at their confluence, giving rise to the current Suquía River.

The dam was built mainly for:

- Mitigation of flood damage to the city of Córdoba and surrounding areas (flood control)
- Provision of drinking water to the city of Cordoba

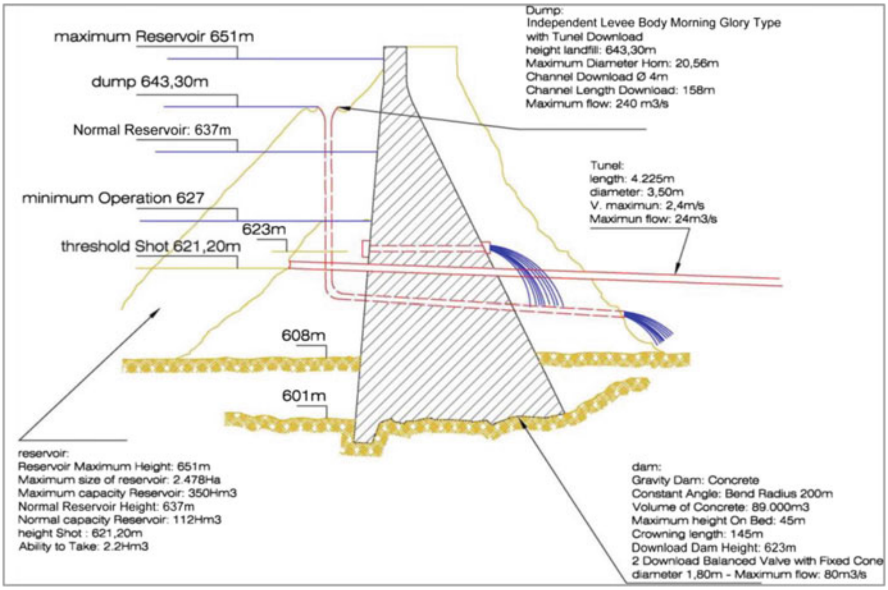

Fig. 6 Schematic section of the San Roque Dam [2]

- Irrigation in times of drought
- Hydroelectricity: to allow the industrial development of the city of Córdoba and surroundings areas

1.2.2 Intake and Pipeline Works

It has two intake and pipeline works, one for the hydroelectric plant and another for irrigation.

The intake for the hydroelectric plant is functioning normally, and the water that was used for the hydroelectric plant is then used for irrigation.

The intake for irrigation is used only for emergencies.

The intake to the hydroelectric plant consists of:

- Two metal ducts of circular section, running through the mountain wall, with a diameter of 1.80 m, with balanced wagon-type valves, size 3.40 m × 4.70 m each, preceded by a sluice valve which is activated in case of emergency
- Coated tunnel: 3.50 m diameter and 4,210 m length, maximum speed 2.4 m s^{-1} with a flow of 24 m^3 s^{-1}
- Surge chamber-type spillway channel with auxiliary tank. Height above the tunnel axis 44 m (6.50 m internal diameter). Maximum level 660 m.a.s.l. Level of maximum pressure altitude of 619 m.a.s.l. Level of threshold of tunnel 613.85 m.a.s.l.
- Hose of valves: two butterfly-type valves commanded from the hydroelectric plant. Bridge crane 7.5 t. Winch for funicular

- Pressure pipe: two metal penstocks with a diameter of 2.05 m each. Flow 24 $m^3\ s^{-1}$ and length 290 m
- Pants 1,025 m^2 each
- Four access lines

The level of this intake is 624 m.a.s.l. Therefore, the capacity of the reservoir is 4.8 hm^3. Loading height at normal reservoir is 118 m and a flow rate of 24 $m^3\ s^{-1}$; loading height at minimum reservoir is 106 m. The hydroelectric plant discharges upstream from La Calera town into the Diquecito small dam, where water is collected for the water treatment plant that supplies drinking water to most part (ca. 75%) of Córdoba city. There is also a second water plant at La Calera town, which produces drinking water for this and other towns surrounding Córdoba city.

The irrigation intake is composed of two metal pipes of 1.30 m diameter. It is located in the body of the San Roque Dam with two-lock hollow jet-type valves. The discharge of these valves goes directly to the Suquía riverbed (downstream from the San Roque Dam) (Fig. 7).

The irrigation work begins at the Mal Paso diverter dam, downstream from La Calera town, where two master channels and a network of secondary irrigation channels start. The Mal Paso regulator dam consists of a fixed masonry dam with 7 m high and 88.05 m length landfill.

1.2.3 Spillway

The San Roque Dam has a morning glory spillway located on the right bank upstream from the San Roque Dam (Fig. 8); its maximum flow rate is 280 $m^3\ s^{-1}$; and the tunnel crossing the body of the San Roque Dam discharges into the Suquía River (Fig. 5). The choice of this type of discharge structure reflected the need to limit the discharge water downstream, in order to avoid inconveniences to the population downstream from Córdoba city (floods).

This spillway consists of a vertical tunnel, dug into the rock, of 4 m in diameter, connected by a circular curve of 10 m radius to a horizontal tunnel with a 1% slope that discharges downstream from the San Roque Dam. The storage capacity in the weir crest is 200 hm^3.

The Howell-Bunger valve on the wall of the dam allows an additional reservoir management in case of emergency.

1.3 The Reach of the Suquía River Through Córdoba City

The flood plain of the Suquía River has little development in most of its route through the city of Córdoba. It has a low, sporadically flooded terrace, which used to be its flood plain.

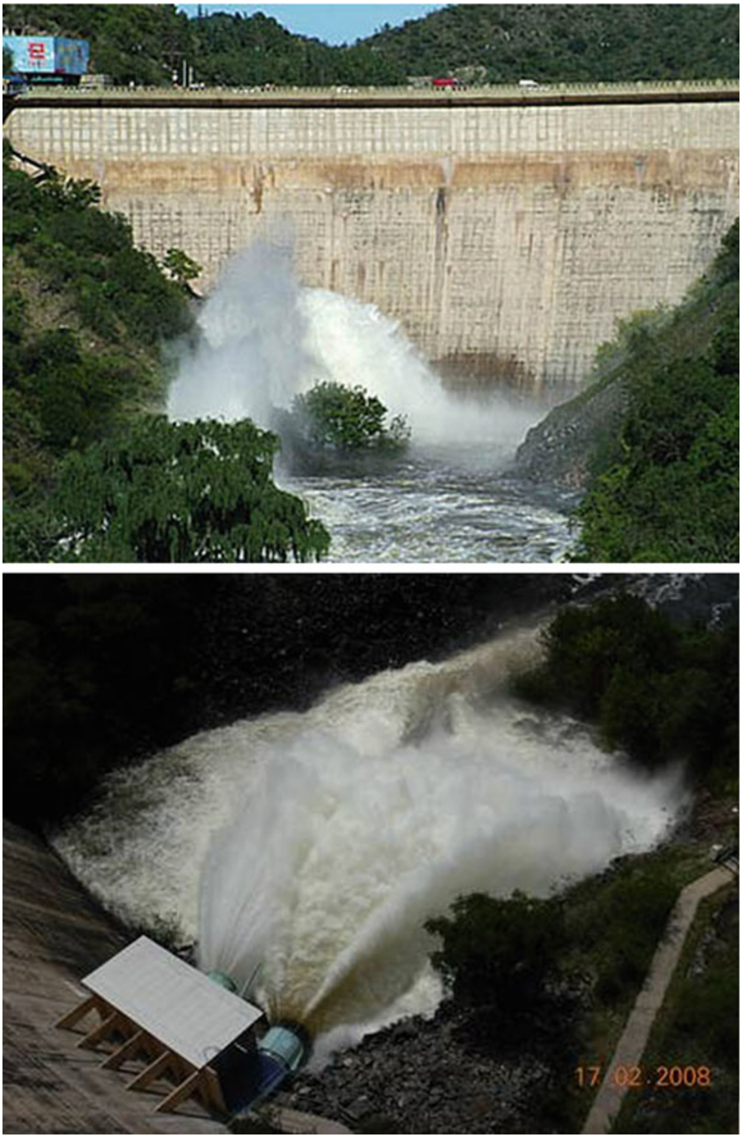

Fig. 7 View of the discharge and discharge valves of the irrigation intake (2008)

From the study of the fluvial environment and the evolution of the river on the plain, two alluvial plains are distinguished: an ancient alluvial plain and a modern alluvial plain.

The old plain has two main terrace levels: high and middle level. The new plain defines the level of the low terrace. This level comprises almost the entire downtown area of Córdoba city, including its main districts (Alberdi, San Vicente and General Paz) [3].

Fig. 8 View of the morning glory spillway of the San Roque Dam

Fig. 9 The Suquía River upstream from the Sagrada Familia Bridge

On its journey through the city, the river is crossed by numerous bridges and fords (around 16). It also has landscaped margins and a small island, which are used for recreation by the residents. In almost all its way through the city (from the Turín Bridge to the junction of Circulvalación Avenue), the Suquía River is accompanied by two coastal vehicular routes, one on each bank: Av. Mayor Mestre (an alternative route to avoid entering downtown Cordoba) and a pedestrian pathway, the cycle path. In the first portion of its passage through the city, the river runs in its natural course (see Fig. 9).

From the Santa Fe Bridge, about halfway into the city, river margins are coated. These coatings are often displaced by floods.

Fig. 10 View of the Suquía River upstream from the Antártida Bridge, showing the mouth of the La Cañada stream (*left side*) and its discharge to the Suquía River (*right side*)

La Cañada stream, formed in the tectonic depression of La Lagunilla, crosses the southern part of the city, from SW to NE, finally flowing into the Suquía River (Figs. 4 and 10).

This harmless-looking stream was the cause of several disastrous floods in the history of the city; the last flooding event occurred in the 1930s, prompting the construction of a channel, formed by two high sidewalls, which efficiently helped to control the behaviour of the stream during flash floods caused by summer storms [3].

The river then continues its journey eastwards, passing through Chacra de La Merced and entering in a broad (ca. 200 m length), gently sloping alluvial valley, which characterises the beginning of the lower river basin (Fig. 2).

The alluvial valley gradually narrows down and reaches a small town: Capilla de Los Remedios, 30 km eastwards. Downstream from Capilla de Los Remedios, the river course is shallow and restricted to 50 m wide.

The river meanders northeastwards, with an increasingly narrow bed, limited by low-rise ravines, with a low flow that decreases progressively.

At El Salto, the river is divided into several branches, nowadays hardly noticeable. These branches have different names, such as Nuevo (new) River, Parva and Río Viejo (old river). Downstream, near Mistoles, the bed becomes visible once more in the form of a well-marked furrow, first isolated after ponds, and finally as a 5 m wide stream running between 2 m high ravines.

The river continues meandering east and southeastwards for about 10 km until Loma Alta hill and then with brackish water until its mouth in the Mar Chiquita Lake (also called Ansenuza Sea).

Finally, it should be noted that this river is not and never has been navigable, but its waters provide numerous services to the neighbouring population. It supplies water and electricity to the capital of the province and serves to irrigate large areas around the capital and neighbouring departments.

2 Regionalisation of Maximum Precipitation

2.1 Background

A designed storm is a sequence of rainfall capable of causing a designed flood in the basin analysed. To calculate this designed storm, it is necessary to define the duration of the rain, the total precipitated sheet, their temporal and spatial distribution and the portion of said sheet that effectively contributes to the generation of run-off.

The Province of Córdoba has valuable studies on designed storms, most of them conducted by the Research Centre for Semi-Arid Regions, belonging to the National Institute of Water (CIRSA). Thus, CIRSA conducted the work entitled “Regionalization of Maximum Precipitation for the Province of Córdoba”, which includes records from 141 rainfall and 7 pluviographic stations across the province (Fig. 11).

According to the CIRSA analysis, the upper basin of the Suquía River falls within the Sierras’ zone (mountain area), which has as pluviographic station in the station La Suela, located in the San Antonio Basin (Fig. 4), while the lower basin has a pluviographic station in the Cordoba Observatory (Córdoba city downtown). Figures 12 and 13 show intensity–duration–recurrence time curves (IDT) for both stations mentioned above.

3 Hydrologic and Hydraulic Modelling

3.1 Background

The main hydrological studies in the upper basin of the Suquía River have been conducted by Engr. Bernasconi, from the Ministry of Water Resources [4], while studies in the middle basin, downstream from the San Roque Dam, have been carried out by Reyna and Tarditti [5, 6], from the National Water Institute (INA). The HEC-1 model was used for the transformation rain flow. The precipitation used for modelling was taken from the study on maximum precipitation by García [7].

Furthermore, there are several studies showing the hydraulic behaviour of the Suquía River downstream from the San Roque Dam towards Córdoba city (Reyna et al. 1997; [5, 6, 8–10]).

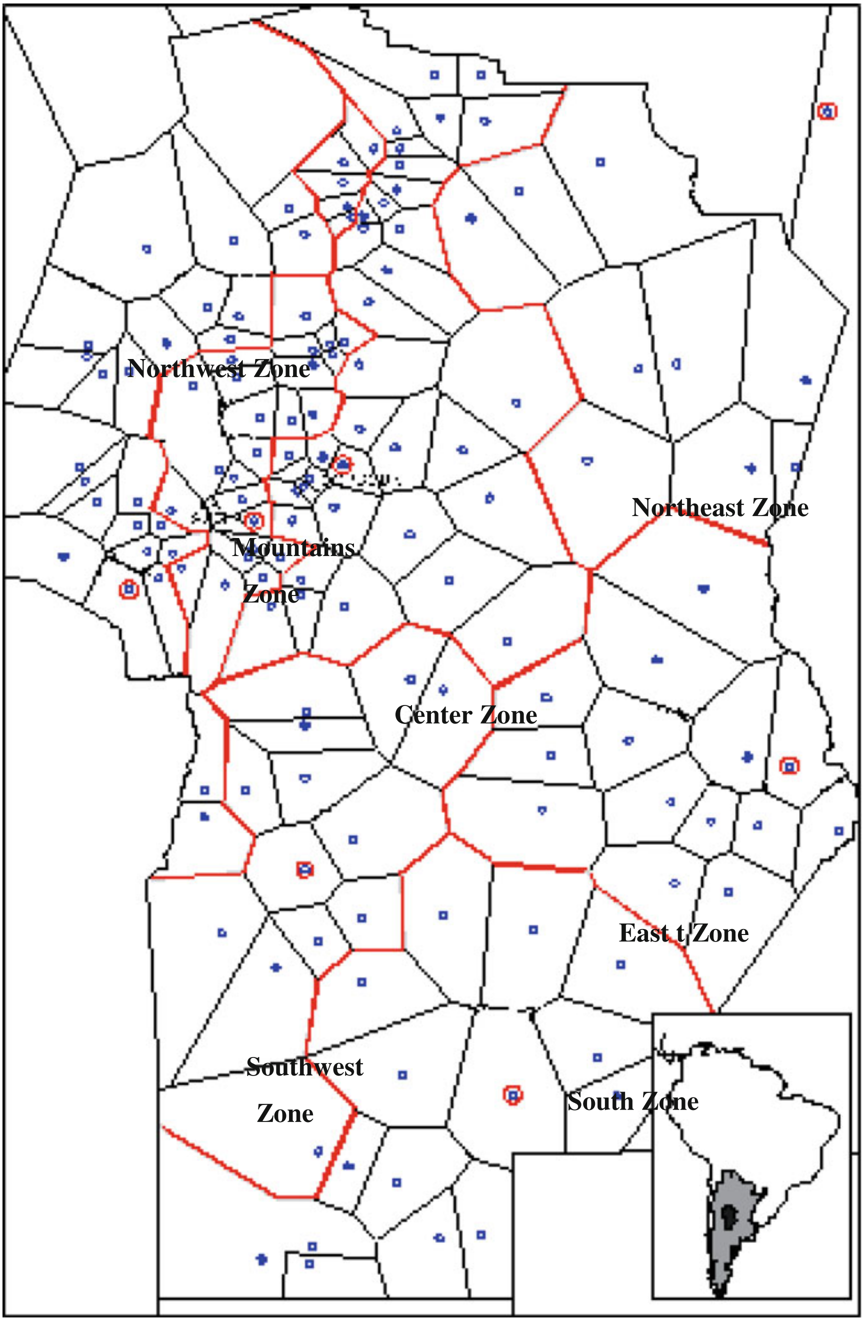

Fig. 11 Regionalisation of maximum precipitation for the Province of Córdoba (CIRSA)

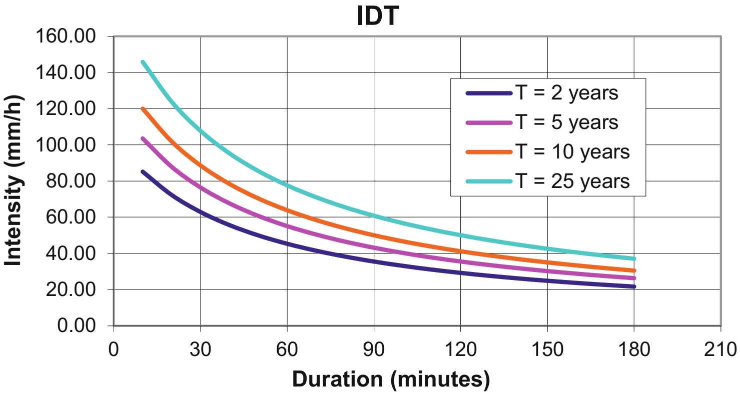

Fig. 12 IDT curves at La Suela – Sierra station

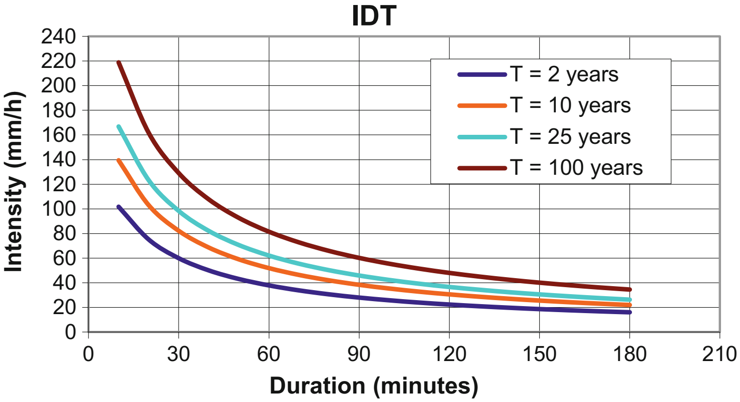

Fig. 13 IDT curves at the Córdoba Observatory – centre station

A comprehensive work on the hydrological and hydraulic operation of the Suquía River resulted in the emergency action plan (EAP) for Cordoba City (failure of the San Roque Dam), prepared by Giménez [11] and updated by Lábaque [12].

Hydrological studies mostly focused on the upstream area of the San Roque reservoir, whereas hydraulic studies are focused on the downstream area of the dam, evaluating the behaviour of the river in the presence of obstructions such as bridges.

3.2 Hydrological Studies Upstream from the San Roque Reservoir

Based on the work of Bernasconi [13], Reyna et al. ([9, 10]; 1997) and Reyna and Tarditti [5, 6], the delimitation of basin and stream systems was verified. A total of 43 subbasins, which make a total area of 1,616 km^2, were obtained.

The total concentration time of the basin was calculated as the sum of concentration time and the transit flood time of each subbasin. The final conclusion was that the concentration time of the entire upper basin of the Suquía River is about 7 h.

3.2.1 Design Rainfall Determination

For the hydrological modelling of the San Roque Dam, the probable maximum precipitation model (PMP) was used.

Probable maximum precipitation (PMP) is the estimated precipitation threshold. Consequently, it can be defined as the greatest precipitation analytically estimated that is physically possible and that reasonably characterises a particular geographic region for a given time, in a specified period of the year. In practice, the effects of climate change in the long term are not taken into account to estimate the PMP. It should be noted that the concept of PMP is not completely reliable and cannot be well estimated, as its likelihood of occurrence is unknown. However, for practical applications, it has been found useful, and its use will continue due to the public concern about the safety of projects such as large dams.

There is a variety of methods to determine the PMP. Because of the uncertainties and limitations on data and knowledge, PMP can be considered as an estimate where judgement and experience should be used to set its value.

In this work, we have estimated PMP values through "generalised PMP charts". They are isohyet maps that describe regional PMP variation for a specified duration, basin size and annual or seasonal variations. In this case, we have determined the PMP value for a duration of 6 h (Fig. 14): probable maximum precipitation – 6 h duration with 230 mm of total precipitation [7].

3.2.2 Hydrological Computational Modelling

To verify the safety of the dam during extreme hydrological events (e.g. overtopping), computational modelling was performed using the HEC-1 program US Army Corps of Engineers [14]. The scenario for this situation, according to international recommendations, was to consider the reservoir at landfill level and to precipitate a storm like the PMP on the Suquía upper basin.

The HEC-1 program calculates input and output hydrographs of the dam to different recurrences and continuous events. These hydrographs allow the operation

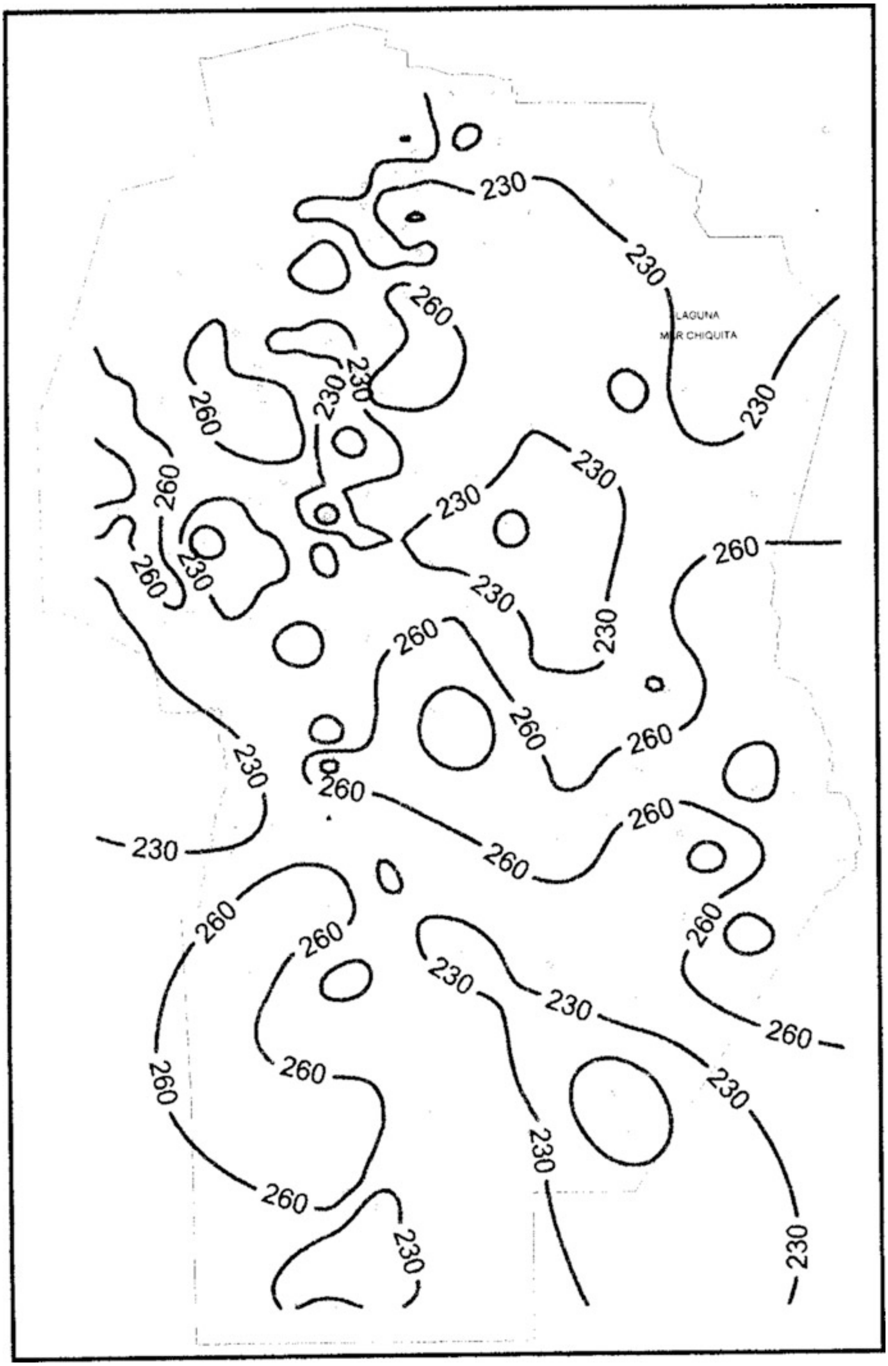

Fig. 14 Probable maximum precipitation – 6 h duration [7]

Table 1 Results from the HEC-1 modelling, Suquía River upper basin (upstream from San Roque Reservoir)

Maximum reservoir elevation (m.a.s.l.)	Maximum peak flow storage (hm^3)	Peak flow out (m^3 s^{-1})	Peak time (hours)
651.99	372,350	318	18.83

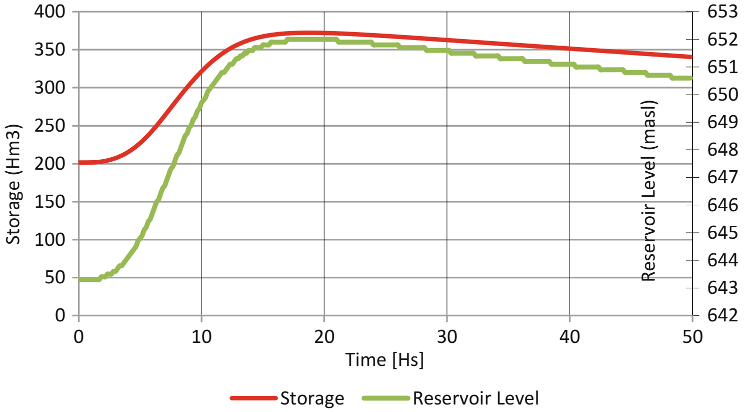

Fig. 15 Storage curve and reservoir level (HEC-1) considering PMP

and safety of the dam. The simulated hydrographs were obtained by computational models of transformation rain flow and transit flow.

The scenario chosen for the modelling was the probable maximum precipitation 230 mm in the upper basin [7], causing a height of weir dam (643.30 m.a.s.l.).

Thus, the complete hydrologic modelling of the entire upper basin of the Suquía River was performed using HEC-1 model. The results indicate that the peak flow entering the reservoir for this situation is 8,220 m^3 s^{-1}, which does not produce overflow before the PMP.

The results are presented in Table 1 and Figs. 15 and 16.

Hydrological studies showed that the dam would not present problems if an event like the PMP occurs in the upper basin, considering the reservoir at landfill level. It can be said that the design satisfies the requirements of current criteria, and there is no possibility of failure by overtopping [12].

3.3 *Hydraulic Studies Downstream from the San Roque Dam*

3.3.1 Background

The Study of Hydraulic Performance of the Suquía River was presented by Engrs. Guillermo Tarditti and Santiago Reyna in the II National Conference on Urban Storm Drainage, in 1996. In this paper, a topographic campaign work was

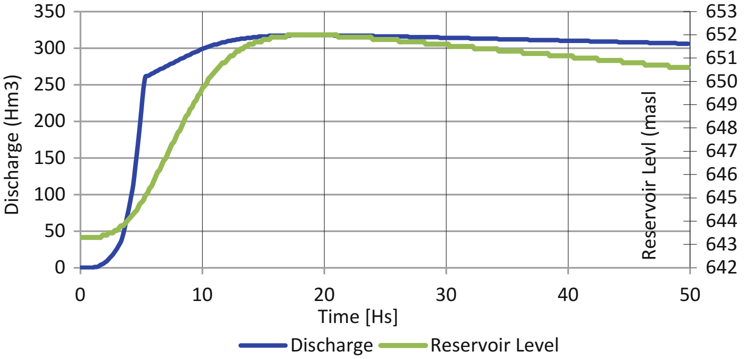

Fig. 16 Discharge curve and reservoir level (HEC-1) considering PMP

conducted measuring sections from La Tablada Bridge to Antártida Bridge (covering eight intermediate bridges along approx. 4 km) in the city of Córdoba. A hydrological study was carried out with the primary purpose of determining the flow through the city of Córdoba caused by rainfall in the intermediate basin (between the dam and the city, Fig. 4), for different recurrences, considering the contribution of base flows and flow evacuated by the San Roque Dam. The determination of these flows was performed using the computer model HEC-1.

Tarditti and Reyna [5, 6] also performed a mathematical modelling of the Suquía River using the HEC-2 model, in order to study and predict the hydraulic behaviour of the river as it crosses the city of Córdoba, particularly the water level at different bridges in the urban area. The study was also conducted between La Tablada and Antártida Bridges, because this is one of the most compromised areas during hard rainfall events. Other objectives of this work were to determine the possible river level, to know how the bridges work during flooding events, to know the maximum flow through them and to raise the level of the water profile when the bridges start working as landfills.

A summary flow chart for different recurrences at the intersection between the Suquía River and La Cañada stream, sector located at Córdoba city downtown, in the middle river basin is presented below (Fig. 17 and Table 2).

In the cited studies, the effects of introducing the contributions of secondary basins to the main basin, downstream from the San Roque Dam, were also studied. Two of these secondary basins have defined entry points, Saldán and La Cañada streams, while other small basins have a distributed flow along the way (Fig. 4). Individual hydrographs of these secondary basins at the confluence with the Suquía River, to a recurrence of 25 years, are presented in Figs. 18 and 19.

Fig. 17 Stream channelled at the intersection of La Cañada stream (*lower part of the picture*) and the Suquía River (*upper, traversal, part of the picture*). At this area, the Suquía River flows within a channel, which is crossed by the Antártida Bridge (*upper-right part of the picture*)

Table 2 Flow rates for different recurrences

Tr (years)	Suquía River ($m^3 s.^{-1}$)	La Cañada stream (m^3 $s.^{-1}$)
2	278	88
5	367	147
10	454	210
25	675	328
50	755	344
100	1,094	488

Source: SSRRHH (2011)

3.3.2 Hydraulic Modelling of the Suquía River Downstream from the San Roque Dam

In general, the geometry of the water valley below the dam comes from the topography obtained from the studies cited in Sect. 3.3.1.

From the computational point of view, different works were performed using the following models:

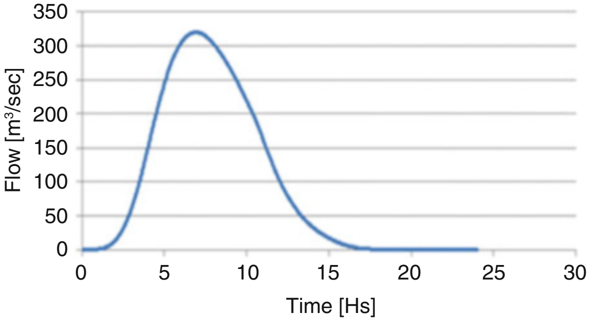

Fig. 18 Hydrograph contribution of the Saldán stream Tr = 25 years

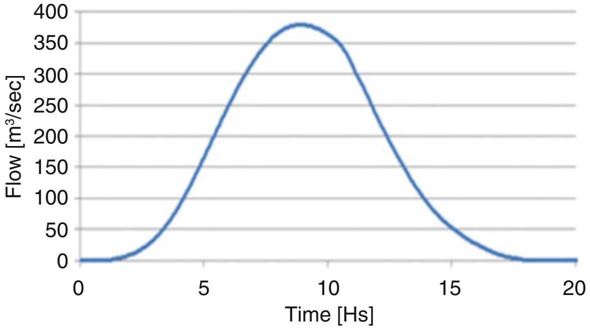

Fig. 19 Hydrograph contribution of La Cañada stream Tr = 25 years

- HEC-1 program/HEC-HMS works only with simple models. It is used to determine input hydrograph basins, the modelling of the gap and transit on the Muskingum–Cunge model.
- FLDWAV program: the simulation of the gap and flow routing gradually varied unsteady open-channel flow is performed.
- HEC-RAS program: one modelling is performed in steady state and it is not permanent.

Some results obtained from these computational models are presented in Figs. 20 and 21.

In section located 3.5 km downstream from the dam, the estimated peak flow is 16,210.50 $m^3\ s^{-1}$/s and the time of arrival in the section is 0.40 h.

In section located 24 km downstream from the dam (in the city of Cordoba), the estimated peak flow is 13,635.40 $m^3\ s^{-1}$/s and the time of arrival in the section is 1.77 hs. This indicates that if the dam is broken, it has almost 2 h to deal with the emergency in Cordoba city.

Faced with emergencies caused by floods generated by the San Roque dam break, the city would be in a serious situation. So an updated EAP is essential for this dam.

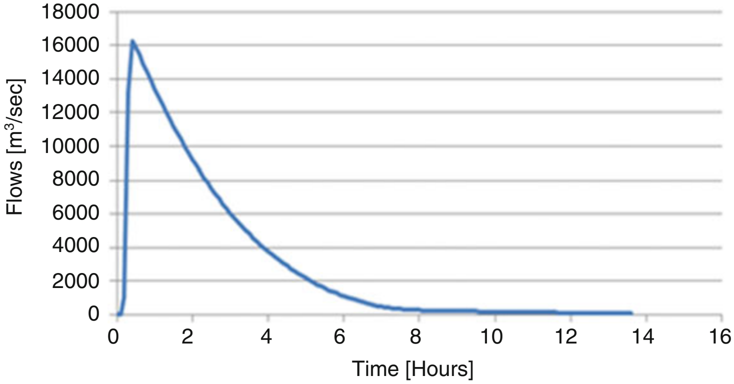

Fig. 20 Hydrograph break in a section located 3.5 km downstream from the dam

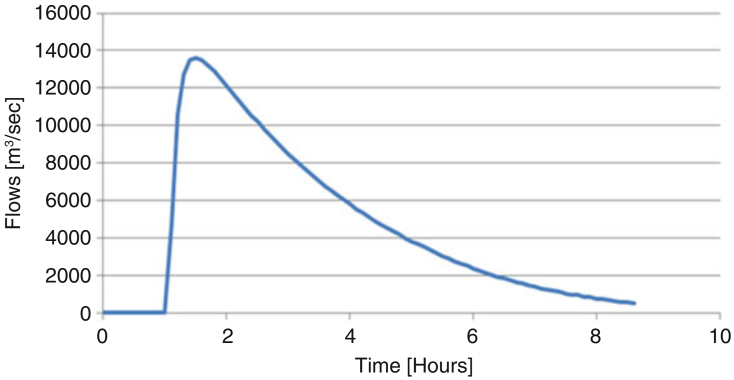

Fig. 21 Hydrograph break in section located 24 km downstream from the dam

3.3.3 Preparation of the Action Plan for Emergencies

Flood maps obtained from Lábaque [12] show a detailed dam break analysis, providing valuable information for control agencies to manage flood emergencies. For this purpose, the scale and scheme of flood plain that clearly demarcate the flood area were considered as criteria for making maps. The maps contain all the information about the riverbank area and the potential flood conditions (Fig. 22).

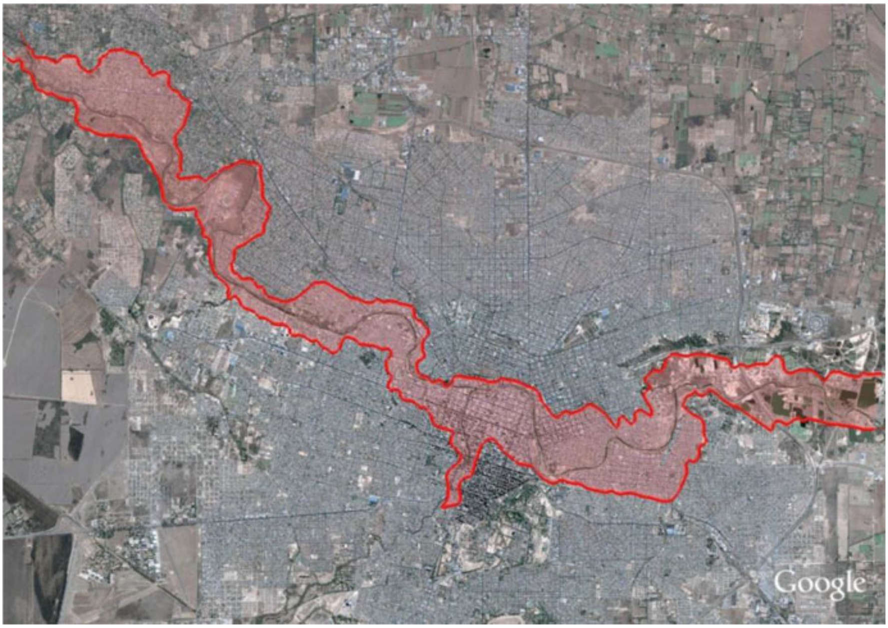

Fig. 22 Map of flooding area in the city of Cordoba due to a break of the San Roque Dam

4 Analysis of Drought in the Basin

4.1 Introduction

Droughts are complex phenomena that affect the normal development and utilisation of water resources of a region. Due to the slow and progressive nature of droughts, they only become evident long after they began. For this reason, advanced knowledge about them over the time is essential for water management in a semiarid region [15].

This extreme hydrological phenomenon called "drought" is defined as an extended period of low rainfall in an area.

Droughts can be classified according to the water variables involved. In this regard, Wilhite and Glantz [16] have defined four categories of drought:

- Meteorological: based on climatic data, it is an expression of the deviation of rainfall from the average value over a period of time.
- Agricultural: when there is not enough soil moisture to allow the normal development of a crop in any stage of growth.
- Hydrological: a deficiency in the flow or volume of surface and groundwaters (rivers, lakes, springs, etc.).

- Socio-economic: occurs when water availability decreases to the point of causing (financial or personal) damage to the population of an area affected by low rainfall.

Meteorological droughts are a necessary precondition of agricultural and hydrological droughts, and socio-economic droughts are an inevitable consequence of the above, still under study management and planning area [17]. The identification and characterisation of meteorological and hydrological droughts in the Suquía River through different methodologies are addressed here. The knowledge of the characteristics of droughts helps providing the necessary measures for such events in the future, as well as plan for water resources.

4.2 Identification and Characterisation of Hydrometeorological Droughts

Hydrometeorological droughts in the San Roque River Basin were evaluated and characterised through the Palmer Drought Index (PDI) [17]. The PDI is based on the water anomalies of serial water balance, and the study was conducted with a series of monthly mean precipitations (1943–1999), corresponding to the San Roque dam station.

The PDI index allows, among other applications, to determine periods of drought and water excess. The dry period begins when the index value is below −0.5 and ends when it is greater than −0.49 (Table 3). The values of the PDI are classified into categories according to the drought intensity ([18], Table 4).

Figure 23 shows the results of PDI for the period 1943–1999 at San Roque Dam station. Several multi-year periods with severe and extreme droughts are observed. Years 1949, 1951, 1970 and 1999 are particularly important drought periods with values less than −4.0.

Table 3 PDI index of drought categories

PDI drought category	
>4	Extremely wet
3.0–3.9	Very wet
2.0–2.9	Moderately wet
1.0–1.9	Slightly wet
0.5–0.9	Incipient wet spell
−0.4 to 0.4	Near normal
−0.5 to −0.9	Incipient dry spell
−1.0 to −1.9	Mild drought
−2.0 to −2.9	Moderate drought
−3.0 to −3.9	Severe drought
<−4.0	Extreme drought

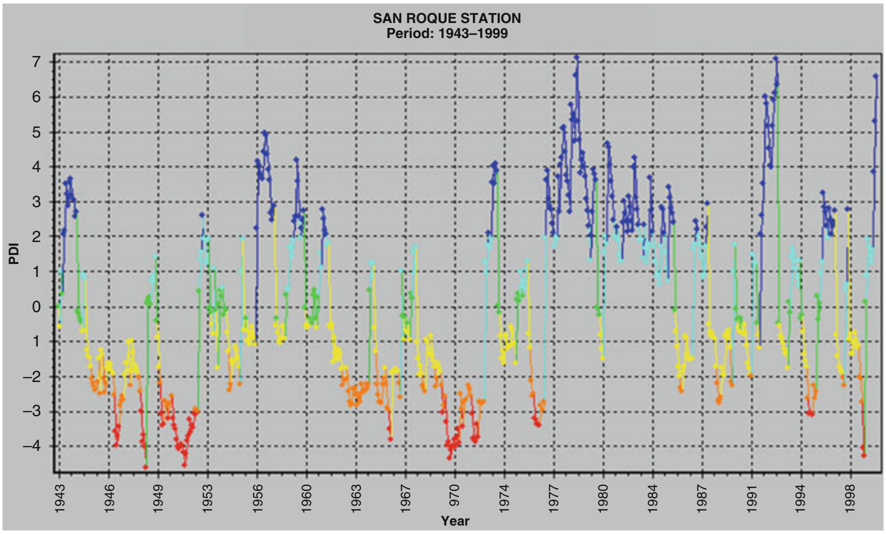

Fig. 23 Palmer Drought Index (PDI) on the San Roque station (1943–1999). Colour of period: *blue*, very wet; *light blue*, slightly wet; *green*, normal; *yellow*, incipient dry spell; *orange*, moderate drought; and *red*, severe drought

We also observe drought periods of about 10 years, cyclically alternating with wet periods of 10 years.

This effect is softened from the 1980s on, where, although there are drought events of varying magnitude, they are rare and less severe.

To identify the type of drought with greater probability of occurrence, a frequency study of the different categories of PDI is performed. The results are presented in Table 4 and Fig. 24.

Defined categories of drought for the PDI show that emerging and moderate droughts are the most frequent. Severe and extreme droughts are 7.60% and 2.05%, respectively, of the total studied period.

Thus, it is estimated that the recurrence time (Tr), in a month with severe drought in the San Roque River Basin, is 13.2 months and 1.1 years. While for the occurrence of a month with extreme drought, Tr Achala is 49 months (about 4 years).

Table 5 shows the frequencies (%) of different types of drought by the PDI classification index for each month of the year in the San Roque River Basin.

Except for November and December, the rest of the months have a higher probability (to 50%) to be characterised as dry. Severe droughts are more common in the month of March, even though not extreme droughts occurred in that month. Extreme droughts occurred with equal frequency in 6 months of the year: January, February, April, May, June and September, even when January and February belong to the rainy season (summer).

Table 4 Frequency study of PDI in the San Roque River Basin (1943–1999)

PDI values					
Ordered by class			Ordered by frequency		
Class	Frequency	% accumulated	Class	Frequency	% accumulated
−8	0	0.00	−1	116	16.96
−4	14	2.05	−2	107	32.60
−3	52	9.65	2	82	44.59
−2	107	25.29	−0.5	71	54.97
−1	116	42.25	3	69	65.06
−0.5	71	52.63	0.5	61	73.98
0.5	61	61.55	−3	52	81.58
1	30	65.94	4	42	87.72
2	82	77.92	8	40	93.57
3	69	88.01	1	30	97.95
4	42	94.15	−4	14	100.00
8	40	100.00	−8	0	100.00

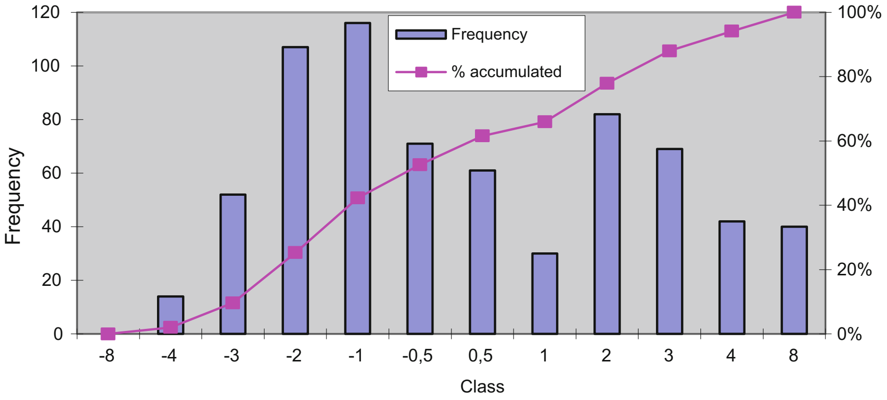

Fig. 24 Histogram and accumulated frequencies curve of PDI index in the San Roque River Basin (1943–1999)

4.3 *Identification and Characterisation of Hydrological Droughts*

This section focuses on the identification and characterisation of hydrological droughts, in terms of a deficit of annual run-off, following a methodology of time series analyses known as “theory of runs”.

The theory of runs has been proposed as an objective method to identify drought periods and to evaluate its statistical properties. This methodology has been used

Table 5 Matrix of drought frequencies (%) for each month of the year in the San Roque River Basin (1943–1999)

PDI classification	Jan	Feb	March	April	May	June	July	Aug	Sept	Oct	Nov	Dec
Extreme drought	3.51	3.51	0.00	3.51	3.51	3.51	0.00	0.00	3.51	1.75	1.75	0.00
Severe drought	8.77	10.53	15.79	7.02	7.02	5.26	7.02	5.26	1.75	7.02	5.26	10.53
Moderate drought	12.28	12.28	8.77	15.79	17.54	17.54	17.54	19.30	21.05	12.28	17.54	15.79
Mild drought	17.54	22.81	15.79	21.05	17.54	17.54	15.79	15.79	14.04	15.79	15.79	14.04
Incipient dry spell	12.28	7.02	10.53	7.02	10.53	12.28	10.53	12.28	12.28	15.79	5.26	8.77
Near normal	7.02	7.02	10.53	8.77	7.02	3.51	12.28	12.28	12.28	5.26	8.77	12.28
Incipient wet spell	3.51	1.75	3.51	3.51	0.00	7.02	5.26	1.75	3.51	10.53	8.77	3.51
Slightly wet	12.28	14.04	14.04	10.53	10.53	8.77	10.53	15.79	14.04	8.77	15.79	8.77
Moderately wet	10.53	8.77	8.77	8.77	14.04	12.28	7.02	5.26	7.02	12.28	12.28	14.04
Very wet	7.02	7.02	7.02	3.51	7.02	3.51	8.77	10.53	7.02	7.02	1.75	3.51
Extremely wet	5.26	5.26	5.26	10.53	5.26	8.77	5.26	1.75	3.51	3.51	7.02	8.77
Total	100	100	100	100	100	100	100	100	100	100	100	100

for the analyses and stochastic characterisation of droughts since Yevjevich [19] proposed the definition of drought events. According to this, "An event of drought is defined as the period during which the variable indicating water availability, Xt, (contributions, rain, humidity of soil, etc.) is below a certain threshold, Xo".

This threshold value can be the mean or median number of hydrological data used, a mean fraction [20], a defined level (as the least mean standard deviation) or a value equivalent to a given exceedance probability [21]. In any case, the threshold must be chosen so that it is representative of the water demand [22].

These analyses help to obtain useful parameters for the quantification of droughts, including duration (L), severity and magnitude (M) (accumulated number of differences between the threshold and the values of the variable), temporal variations in absolute time (beginning and end), maximum intensity (Imax, defined as the maximum differences between the threshold and the relations to the event) and average intensity (Iavg, the relation between magnitude and duration). These parameters are observed in Fig. 25.

Selecting a demand value, or truncation, linked to the probability of exceeding series offer allows uniform drought conditions in a climatically inhomogeneous region, since the level of resources available in each area and the offer variability are incorporated. In this way, given an α level, there is equal probability of observing a drought in any point of the region. If considered as a truncation level for the definition of droughts, a percentage of the average resource will be placed where droughts frequently occur, while in others they do not exist, depending on the statistical variance of the offering series at each place. All of this makes the regional analysis more complex in large, not homogeneous areas [21].

An analysis of successions with annual contributions to the basin is exposed. This was performed using series of annual average contributions of the San Roque Dam station (latitude 31°22′00.0″, longitude 64°27′00.0″).

Periods of drought and excess (Xt-Xo) are represented in the graphic, where Xo is a threshold that represents a level equivalent to the average annual contributions to probability of exceedance of a 0.6 demand.

Figure 26 clearly distinguishes a period characterised by deficits and others with excesses of annual contributions, where breaks occurred in 1975. In the first period, more than 60% of the contributions are deficits, and in the second, over 65% are

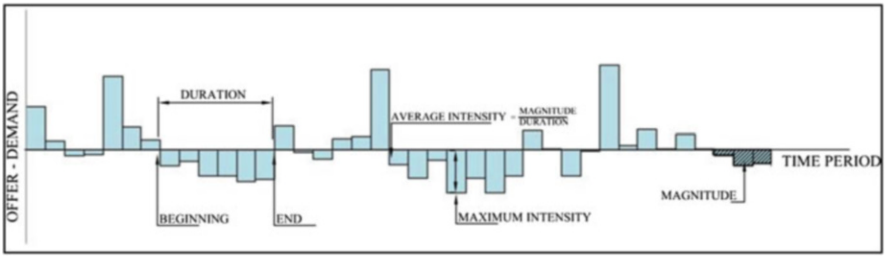

Fig. 25 Time series offer without demand in a place for the identification and characterisation of droughts according to sequence method

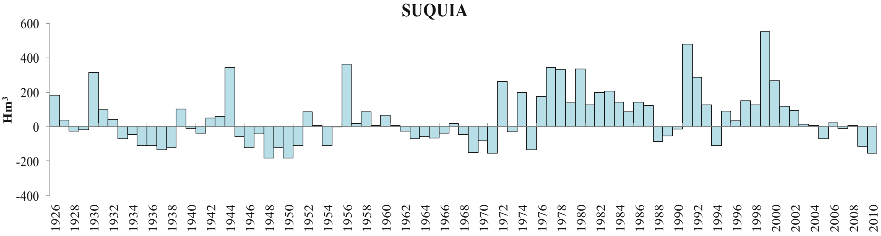

Fig. 26 Time series offer less demand in a place for the identification and characterisation of droughts according to the sequence method

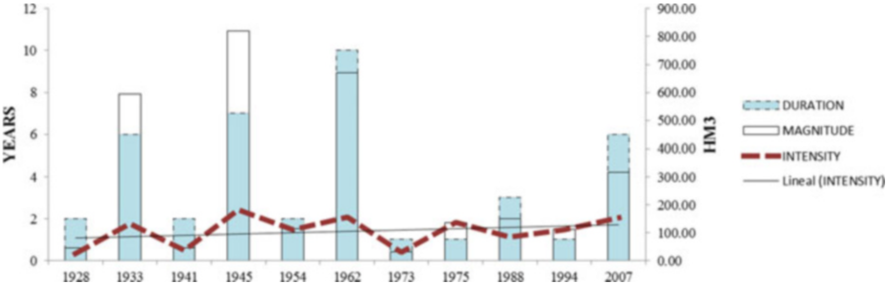

Fig. 27 Duration, magnitude and intensity of main droughts in the Suquía River Basin. With Probability $= (X_{jt} > x_{jt}) = 0.6$

water excesses. Four major droughts were identified: in the 1930s (6 years), 1940s (7 years), 1960s (10 years) and late 2000 (6 years) (Fig. 27).

This break in the 1970s coincides with the change in mean temperature conditions of the central equatorial Pacific 1976/1977, with a climate transition that affected more than 40 bioenvironmental variables in the Pacific and the Americas, which are expressions of variability-“type” El Niño Southern Oscillation (ENSO) [23].

It is also noted that the annual contributions of the Suquía River had cyclical drought events with large temporal extension, a positive trend in terms of duration and magnitude up to the 1970s. After that decade, drought periods become shorter in duration and magnitude, but the intensity remains constant, even with a slight positive trend.

Intensity is the maximum deficit experienced by the basin in a year. Moreover, it can be seen that the intensity of the drought of 2010 (153.68 hm^3) is close to that of 1971 (155.14 hm^3).

The severe droughts of the 1930s, 1940s and 1960s coincide with severe droughts that affected ten basins of central and northern Argentina [15].

In the last decade, drought events have impacted society: economic losses in the productive activity of the soil, impairment of engineering for water supply and loss of generating capacity of hydroelectric plants (because the levels of reservoirs are reduced). It is emphasised that the droughts that have generated these impacts have not reached the order of those registered before 1975, although it is important to remark that the anthropic pressure was lower in 1975 than nowadays.

4.4 Spatial and Temporal Analysis of Drought in the Suquía River Watershed and Surrounding Watersheds

In order to make a comparative analysis of the phenomena of hydrometeorological droughts in similar periods, the same technique (PDI) was applied to the basin of the Los Molinos Dam/Reservoir, which constitutes the second water supply of Córdoba city, behind the San Roque Reservoir.

The Los Molinos Basin is located among the peaks of Achala (west) and Sierras Chicas (east). It is bounded on the north by the Sierrita or Cordón de Santiago (small mountain division), which separates the Punilla Valley (where the San Roque Dam is located), and on the south by a continuation of the Achala summit that separates the Ctalamuchita Valley (where the Los Molinos Dam is located) (Fig. 2). Some typical data are shown in Table 6 for this stage of study. The time period used is 1943–1980.

The results of the analysis of hydrometeorological droughts in the basins of the San Roque and Los Molinos Dams have similarities. At the end of the 1940s and early 1950s, extreme droughts occurred throughout the system.

Table 6 summarises some of the hydrometeorological characteristics for each case to facilitate the comparison between both basins.

As for hydrological droughts, nearby basins like Los Molinos, Ctalamuchita and Anizacate Rivers are analysed. This spatial and temporal analysis is based on a matrix system with columns, corresponding to the geographical location of the basins, and chronologically ordered rows. It is identified with a coloured scale with varying thresholds of drought. Table 7 and Fig. 28 summarise the characteristics of the selected watersheds.

Table 6 Comparative table of some characteristics analysed in the basins of the San Roque Dam (period 1943–1999) and Los Molinos Dam (period 1943–1999)

Characteristic	San Roque (1943–1999)	Los Molinos (1943–1980)
Average monthly precipitation	60.4 mm	74.3 mm
Maximum monthly rainfall record	316 mm	319 mm
Range precipitation with > frequency	0.1–20 mm	0.1–20 mm
Years with severe droughts	1940, 1950, 1960, 1970 and 1995	1940, 1950, 1970
Years with extreme drought	1949–1951–1970–1999	1949–1951–1972–1980

Table 7 Characteristics of the analysed basins

	Station						
Basin	Name	Latitude	Longitude	Altitude [m.a.s.l.]	Area [km^2]	Module [m^3s^{-1}]	Vol supply average annual [hm^3]
Suquía	San Roque	31°22′	64°27′	650	1,350	10	353.6
L. Molinos	L. Molinos	31°05′	64°30′	770	980	9.5	321.2
Anizacate	Santa Ana	31°40′	64°34′	900	465	4.83	152
Ctalamuchita	Embalse	32°09′	64°23′	650	3,300	27	858.5

The values of each matrix unit are obtained by calculating the probability of exceedance of annual average contributions in the chronological series of the available supply:

$$\text{Probability}\left(Q_{jt} > q_{jt}\right) = \propto$$

being

q_{jt}: value of the annual contribution observed in t year in basin j

$\propto$: probability thresholds

In this way, a general vision of the temporal and spatial characteristics of superficial resources is visualised:

$0.00 < \propto < 0.20$ very humid.
$0.20 < \propto < 0.40$ humid.
$0.40 < \propto < 0.60$ normal.
$0.60 < \propto < 0.80$ dry.
$0.80 < \propto < 1.00$ very dry.

The results obtained in the study, from the identification and characterisation of droughts at the regional level, indicate that a temporal and spatial clustering of periods with water excess and deficit is pronounced. At temporal level, it was detected that the most persistent droughts experienced by four basins started in the years 1933, 1944 and 1962, while common wet periods are observed in the mid 1950s, 1970s and late 1990s. A break in the middle of the 1970s between dry and wet seasons is evident, in agreement with previous studies on basins of central and northern Argentina [24].

The history of water resources available shows that periods of drought are of significant duration.

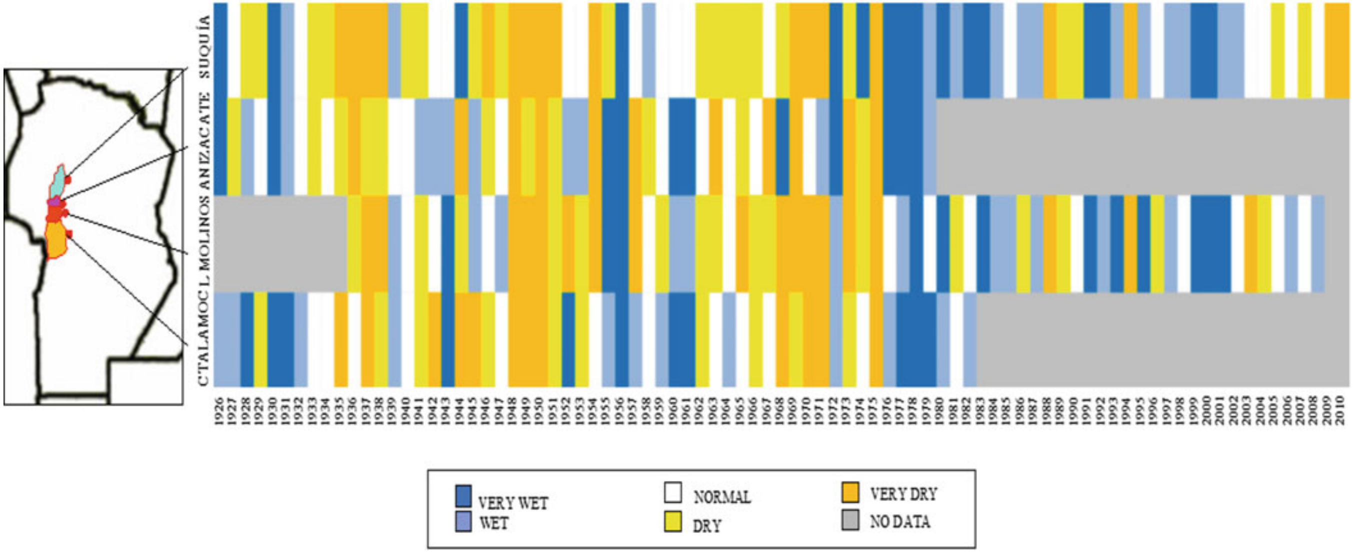

Fig. 28 Identification of droughts based on temporal and spatial distribution of the probability of exceeding the annual supply of water resources in all the basins analysed

4.5 Concluding Remarks

Through the analysis of identification of droughts, it can be seen that meteorological and hydrological droughts indicate that there have been periods of severe multiyear droughts until 1975. After this period, although drought events of different magnitudes occurred, they were rare and shorter in relation to the period before 1975.

The analysis shows that there is a spatial and temporal grouping of water excess and deficit events. A break in the middle of the 1970s, between dry and wet seasons, is evident. This break in the 1970s coincides with the change in mean temperature conditions of the central equatorial Pacific 1976/1977 and climate transition that affected more than 40 bioenvironmental variables in the Pacific and the Americas, which are expressions of variability-"type" ENSO (El Niño/Southern Oscillation) [23].

This change in the previous deficit–excess of water in the Suquía River Basin, occurring in the middle 1970s, is raising questions on the long-time capacity of the basin to support human activities in the city of Córdoba and surrounding area, mainly because of the increased population inhabiting this area at the beginning of the twenty-first century. Further anthropic pressure on the basin, resulting in higher load of nutrients and contaminants, could result in severe damage to both aquatic biota and human depending on this water resource for subsistence. Thus, hydrological and hydrographic studies help to better understand the behaviour of the basin in terms of water scarcity, conditioning the future social development along the basin.

For the management of water resources of the Great Cordoba, it is very important to know that provincial watersheds that supply the same region can be simultaneously affected by severe drought.

References

1. Vázquez JB, Miatello RA, Roqué ME (1979) Geografía Física de la Provincia de Córdoba. Editorial Boldt, Argentina
2. Castelló E, Moya G, Rodríguez A, Bartó C, Menajovsky S (2000) Simulación para la Optimización de los Recursos Hídricos Superficiales en el Área del Gran Córdoba, Argentina. XVIII Congreso Nacional del Agua. Santiago del Estero. Argentina
3. Barbeito OL, Quintana Salvat F (1998) Carta Geologica Geomorfologica de la Ciudad de Córdoba y su Entorno. Fotointerpretacion 7(1):324–339. ISSN/ISBN: 03277410. Córdoba, Argentina
4. Bernasconi I (1998) Estudio Hidrológico de la cuenca alta del Dique San Roque. Informe. Área de Recursos Hídricos Superficiales de la DIPAS, Córdoba, Argentina
5. Reyna S, Tarditti G (1996) Estudio del Comportamiento Hidráulico del Río Suquía Tramo Puente Tablada – Puente Antártida. II Jornadas de Saneamiento Pluvial Urbano. Córdoba, Argentina
6. Reyna S, Tarditti G (1996) Hidrología de las Cuencas del Río Suquía. II Jornadas de Saneamiento Pluvial Urbano. Córdoba, Argentina

7. García CM (2000) Lámina de Lluvia Puntual para Diseño Hidrológico. Tesis de Maestría. Facultad de Ciencias Exactas, Físicas y Naturales. Universidad Nacional de Córdoba. Córdoba, Argentina
8. Pozzzi C, Plencovich G (2002) Modelación Hidráulica del Río Suquía. Trabajo final de grado. Facultad de Cs. Exactas, Físicas y Naturales. Universidad Nacional de Córdoba, Argentina
9. Reyna S, Reyna T, Reyna E (1997) Estudios hidrológicos hidráulicos de la Obra Avenida Costanera Margen Sur, tramo: Puente Sagrada Familia – Puente Turín. Informe de Consultoría externa para la Municipalidad de Córdoba. Córdoba, Argentina
10. Reyna S, Reyna T, Reyna E (1997) Informe Técnico para la Determinación de Caudales y Recurrencias en el Río Suquía a la Altura del Puente Turín. Informe de Consultoría Externa para la DIPAS. Córdoba, Argentina
11. Giménez R (2008) Plan de Acción de Emergencia para la Ciudad de Córdoba por Rotura de la Presa San Roque. Trabajo final de grado. Facultad de Ciencias. Exactas, Físicas y Naturales. Universidad Nacional de Córdoba, Argentina
12. Labaque M (2008) Propuesta para la Confección de Planes de Emergencia por Rotura de Presa en la Provincia de Córdoba. Aplicación al Dique San Roque. Tesis de Maestría. Facultad de Ciencias Exactas, Físicas y Naturales. Universidad Nacional de Córdoba. Córdoba, Argentina
13. Bernasconi I (1998) Estudio Hidrológico de la cuenca alta del Dique San Roque. Informe. Área de Recursos Hídricos Superficiales de la DIPAS. Córdoba. Argentina
14. U.S. Army Corps of Engineers (1985, 1997) Manual. HEC-1. Simulación de Eventos Hidrológicos. Hydrologic Engineering Center, USA
15. Díaz E (2013) Identificación y Caracterización de Sequías hidrológicas en el centro y norte de la República Argentina - Córdoba, Argentina : FCEFyN-UNC, 2013. - Tesis de Maestria en Cs de la Ing. Mención Rec. Hídricos
16. Wilhite D, Glantz M (1985) Understanding the drought phenomenon: the role of definitions. Water Int 10:111–120
17. Vicario L (2008) Evaluación de las sequías Hidro-Meteorológicas en la cuenca del Dique San Roque- Córdoba. Tesis de Maestría en Recursos Hídricos, FCEFyN-UNC. Córdoba, Argentina
18. Palmer WC (1965) Meteorological drought. Weather Bureau research paper no. 45. p 58
19. Yevjevich V (1967) An objective approach to definition and investigation of continental drought. Hydrology Paper 23. Colorado State University, Fort Collins, Colorado
20. Clausen B, Pearson CP (1995) Regional frequency analysis of annual maximum streamflow drought. J Hydrol 173:111–130
21. Fernández B (1997) Identificación y caracterización de sequías hidrológicas en Chile Central. Ingeniería del Agua 4(4):37–46
22. Tsakiris G, Loukas D, Pangalou H, Vangelis H, Tigkas D, Rossi G, Cancelliere A (2007) “Drought characterization”. Drought management guidelines technical. Vols. Capitulo 7, (85–102). Zaragoza, España
23. Compagnucci R, Agosta E (2008) La precipitación de verano en el centro-oeste de argentina y los fenómenos interanual el niño/oscilación sur (enos) e interdecádico “tipo” enos. GEOACTA. págs. 97–103
24. Díaz E, Rodríguez A, Dölling O, Moya G, Bertoni JC, Hillman G (2012). Análisis de simultaneidad de extremos hídricos en el centro y norte de la República Argentina. IV Congreso Internacional sobre Gestión y Tratamiento Integral del Agua. Córdoba, Argentina
25. Camaño Nelli G, Dassso CM (2003) Lluvias de Diseño; Conceptos, técnicas y experiencias. Ed. Científica Universitaria, Córdoba
26. Caamaño Nelli G (2000) Hidrología Avanzada. Apuntes de Clases, Maestría en Ciencias de la Ingeniería Civil – Mención en Recursos Hídricos, FCEFyN, UN de Córdoba
27. Caamaño Nelli G et al (1993) Regionalización de Precipitaciones Máximas para la Provincia de Córdoba. INCYTH, CIHRSA, CONICET, SMN, DPH, CONICOR

28. Catalini C, Camaño Nelli G (2005) Predicción de Crecientes en Embalses de Córdoba. XX Congreso Nacional de Agua. III Simposio de Recursos Hídricos del Cono Sur. Mendoza. Argentina
29. Dirección Provincial de Agua y Saneamiento – DiPAS – Subsecretaría de Obras Públicas (2001) Normas de Operación de Embalses de Uso Múltiple en la Provincia de Córdoba. Informe Técnico. Córdoba, Argentina

Limnology of the San Roque Reservoir

María Inés Rodriguez and Marcia Ruiz

Abstract This chapter presents a summary of the main limnologic aspects of the San Roque reservoir performed over more than 15 years of monitoring and analysis of its water quality. Sampling, transportation and analysis has been jointly performed by members of the National Water Institute, Department of Applied Limnology and Water Quality of INA-CIRSA in collaboration with numerous institutions including Aguas Cordobesas SA (Water Company), the water authority of the Province of Córdoba (DiPAS), the National University of Córdoba (UNC), the Catholic University of Córdoba (UCC), the Office of Boating Safety and the Police Task Force (CEP) of the local government, among others.

Results presented here demonstrate that the San Roque reservoir can be classified as eutrophic to hypereutrophic. The annual values of transparency are usually close to 1 m, chlorophyll-a exceeds 20 μg L^{-1}, and total phosphorus (TP) concentration is higher than 48 μg L^{-1}. The reservoir can also be defined as a warm monomictic lake, whose stratification can begin in September and be established during the summer (December–February), with a warmer surface layer between 0 and 6–9 m deep. Because of its eutrophic status, frequent algae blooms occur in the reservoir. Cyanobacteria, mainly represented by *Dolichospermum* spp. and *Microcystis* spp., grow mainly during the spring, summer and fall and alternate with blooms of the dinoflagellate *Ceratium hirundinella*. When the reservoir is mixed, typically in late autumn, winter and early spring, there is a prevalence of chrysophytes (Bacillariophyceae), being *Cyclotella* sp. the species most often present. Cyanobacteria produce toxins, mainly microcystins (MC),

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whose concentration can reach 32.7 μg L^{-1}, exceeding the safe limit suggested by the WHO (*Guidelines for Safe Recreational Water Environments. Coastal and Freshwaters*. World Health Organization, Geneva, 2003), posing a risk for both touristic activities and sport fishing at the reservoir.

More information about the study area, monitoring design, characteristics of the study area and scope of results can be found in the official website of the National Water Institute (www.ina.gob.ar).

Keywords Algal blooms, Eutrophication, Monitoring, Reservoir, Sediments

Contents

1 Description of Environmental Issues in the San Roque Watershed and Reservoir

The problem of eutrophication of the reservoir is an emerging environmental problem that involves both the type of land use in the basin and the use of the waterbody itself.

The basin is highly altered by human activities, including intense urban development without adequate infrastructure and planning, added to a frequent loss of soil and vegetation caused by fire in the watershed. Because of these problems, the reservoir shows little transparency, frequent presence of colour and off-odours mainly caused by algal blooms, which are, in turn, the cause of death of fish. These are the only visible manifestations of problems in the waterbody (Fig. 1), which can be defined as eutrophic to hypereutrophic [1].

Eutrophication has a negative impact on the biota, the aesthetic quality of the waterbody, the water treatment process and the health of the population. It is worth to mention here that this reservoir serves as a source of drinking water for over one

Fig. 1 Cyanobacteria bloom in the San Roque reservoir – December 2010. Source: www.funeat.org.ar

million inhabitants of Córdoba city; thus, monitoring the water quality is a high priority for human health and drinking water quality.

Monitoring is one of the cornerstones for understanding the status of the system, evaluating temporal changes as well as the degree of success of corrective measures implemented in the basin (e.g. sanitation in towns and cities located along its basin), or in the reservoir itself (e.g. installation of air diffusers to reduce anoxia). The case of the San Roque reservoir and its watershed should be considered a leading case for numerous waterbodies in the region that are at risk of eutrophication.

2 Description of the Study Area

The reservoir is located in a semiarid region of the Punilla Valley (31° 22′ S and 64° 27′ W), 608 m above sea level, between Sierras Grandes and Sierras Chicas in the province of Córdoba (Argentina) (Fig. 2). It is an artificial waterbody whose first dam was constructed in 1891. This first dam was replaced in 1944 by the current dam. When the water reaches the chute level, the lake surface is 15 Km^2, with a volume of 201 Hm^3 [2] and an average depth of 13 m. The approximate average residence time is 0.6 years. The Suquía River upper basin consists of the sub-basins

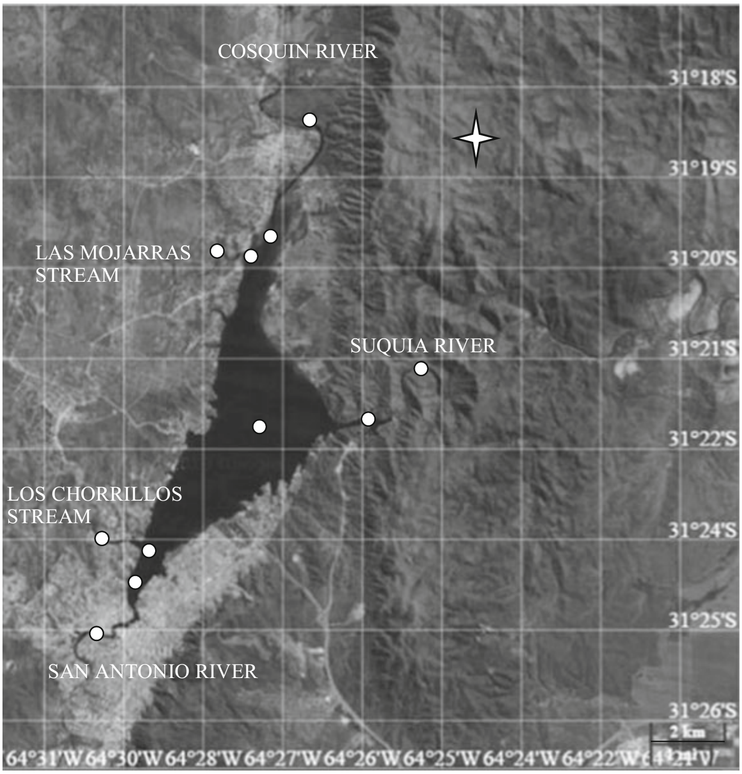


Fig. 2 Monitoring sites at the San Roque reservoir and watershed. *Base map*: www.segemar.org.ar

corresponding to four tributaries that drain into the San Roque reservoir, with a total area of 1,750 Km^2. These tributaries are San Antonio River (515 Km^2 basin), Cosquín River (827 Km^2 basin), Las Mojarras Stream (89 Km^2 basin) and Los Chorrillos Steam (138 Km^2 basin), being the Suquía River its only effluent.

From a climate perspective, the precipitation regime in the basin presents large temporal-spatial variation. Rainfall along the hydrological year is divided into two distinct cycles, a wet season (November–April) and a dry season (May–October). Also on an annual basis, an alternation between wet years (annual rainfall exceeding 1,000 mm) and dry years (annual rainfall barely exceeding 400 mm) is observed. The basin is characterized by an average annual rainfall of 780 mm [3].

Dominated by a temperate climate, the average annual temperature is 14°C, and the prevailing winds come from the south and north quadrants [4].

The dam is mainly used to supply water to the second largest city of the country (Córdoba city). Other common uses include flood control, irrigation and hydroelectric use, in addition to multiple recreational activities (sport fishing, sailing, etc.).

3 Monitoring Design

Monitoring was performed on a monthly basis. Each tributary was regularly monitored upstream from its entry to the reservoir (Fig. 2).

The following Table 1 *shows the* monitored parameters and applied techniques:

Following the morphology of the reservoir, a horizontal spatial monitoring design was applied. According to this design, the centre of the reservoir, mouths of tributaries and areas close to the dam are identified as sites that may present differences. For instance, the characteristics of the mouth of the San Antonio River are more critical in relation to water quality because of the surrounding city of Carlos Paz, an area with intensive tourism along the year, mainly in summer. On the

Table 1 Parameters and applied methodologies

Parameters in situ	Method and instruments
pH	Multiparametric Probe WTW 350i; U-10 and U-23
Temperature (°C)	
Dissolved oxygen (mg L^{-1})	
Conductivity (µS cm^{-1})	
Transparency (m)	Secchi disk visibility
Flow velocity (m s^{-1}) and section geometry	Wading gauging flow Current meter A-OTT Kempten Midsection method
Parameters measured in water	
Ionic composition (Na^+, K^+, Ca^{++}, Mg^{++},Cl^-, SO_4^- mg L^{-1})	Ionic chromatography
F^- (mg L^{-1})	Espectrophotometry – segmented flow
Alkalinity (mg L^{-1})	Titration
Ammonium nitrogen N–NH_4^+ (µg L^{-1})	Espectrophotometry – segmented flow
Nitrite nitrogen N–NO_2^- (µg L^{-1})	Espectrophotometry – segmented flow
Nitrate nitrogen N–NO_3^- (µg L^{-1})	Ionic chromatography
Soluble reactive phosphorus (SRP) (µg L^{-1}),	Espectrophotometry – segmented flow
Total soluble phosphorus (TSP) and Total phosphorus (TP) (µg L^{-1})	Espectrophotometry – segmented flow
Chl *a* (µg L^{-1})	Espectrophotometry
Fe^{++} y Mn^{++} (mg L^{-1})	Atomic absorption
Identification and quantification phytoplankton (cells per L^{-1})	Sedimentation
Total coliforms, faecal and *E. coli* (MPN 100 ml^{-1})	Multiples tubes lauryl sulphate and EC MUG
Mesophylls bacteria (MPN 100 ml^{-1})	Agar plate count
Total microcystins (µg L^{-1})	ELISA
Laboratory parameters measured in sediments	
Inorganic phosphorus (IP) and Total phosphorus (TP) (mg L^{-1})	NAQUADAT
Organic matter (OM) (%)	Ignition 550°C/Nelson and Sommers

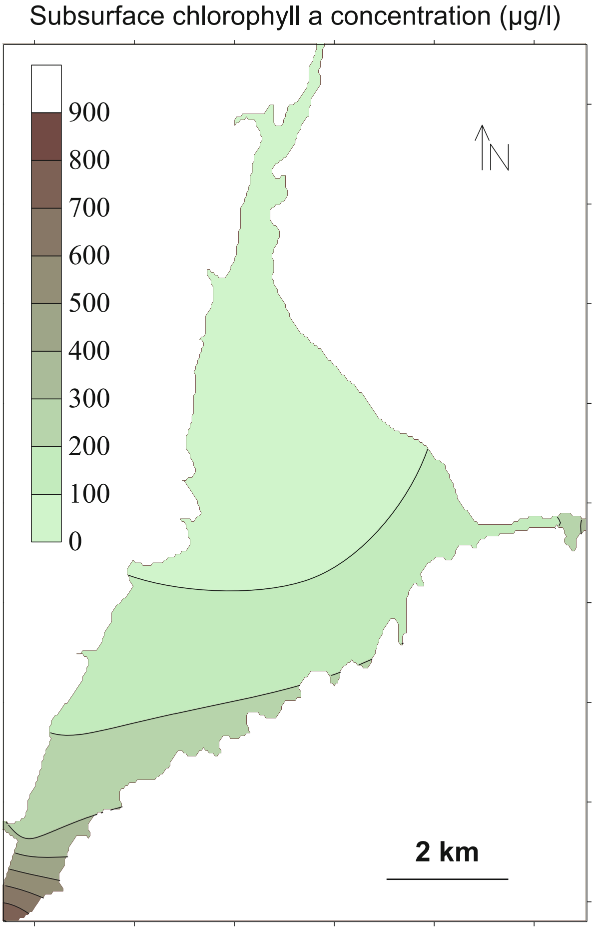


Fig. 3 Extreme concentrations of chlorophyll observed during summer 1999–2000

other hand, the mouth of the Cosquín River has some peculiarities associated with the soil characteristics of the basin [5]. Moreover, the presence of the submerged ancient dam, close to the current dam, shows some variations at this point with respect to the rest [6]. The centre of the reservoir is presented as a point at which any of the critical or extreme aspects observed in other areas, such as nutrient concentration, dissolved oxygen and chlorophyll-a (Fig. 3), is generally softened. The values obtained at the centre of the reservoir could be used as an approximate average value of the behaviour of the reservoir, although in the case of cyanobacteria blooms the dominant wind makes changes, concentrating the bloom on an edge of the reservoir.

The vertical spatial design (water column) comprises both subsurface (0.2 m) and deeper water (1 m above the sediment), including a variable number of intermediate samples, depending on the climatic situation that causes thermal mixing or stratification. One of these vertical samples corresponds to a depth limit in the photic zone estimated as the product of the depth of Secchi disc visibility by a factor of 2.5.

When the reservoir is stratified, additional variability is observed because of the formation of two layers (epilimnion and hypolimnion), clearly definable from the construction of a temperature profile at different water depths. It is important to know that these layers or strata have different water qualities, with the corresponding implications in the exacerbation of eutrophication. Thermocline is defined by the presence of a maximum temperature gradient (decreasing 1°C per meter of depth), determining the need to get water samples 1 m above and 1 m below the thermocline. Samples were taken in both the central and dam area of the reservoir [7]. Another water sample was taken close to the dam, at the depth of pipes that carry the reservoir water to the hydroelectric plant.

Water samples (10 L) were extracted using a Niskin sampler (vertical), while sediments were sampled using an Eckman dredge. Some physical and chemical parameters were measured in situ using Horiba and WTW multiparameter probes (Table 1).

4 Dissolved Oxygen and Thermal Dynamics

Reservoir stratification can begin in September and be established during the summer (December–February), with a warmer surface layer between 0 and 6–9 m deep. This behaviour defines the reservoir as a warm monomictic lake (Fig. 4). Mixing events are possible during the summer by the presence of strong winds that can alter the stratification [8].

The distribution of dissolved oxygen in the water column during the year mainly depends on the physical condition of the system, and its biological activity. The lower stratum of the reservoir frequently shows little or no presence of oxygen due to the prevalence of bacterial decomposition processes, and usually in coincidence with concomitant stratification (Fig. 5). In critical situations, when oxygen concentration falls below 4 mg L^{-1}, some events of fish death can be observed, particularly in combination with the presence of algae or cyanobacteria blooms at the surface of the reservoir.

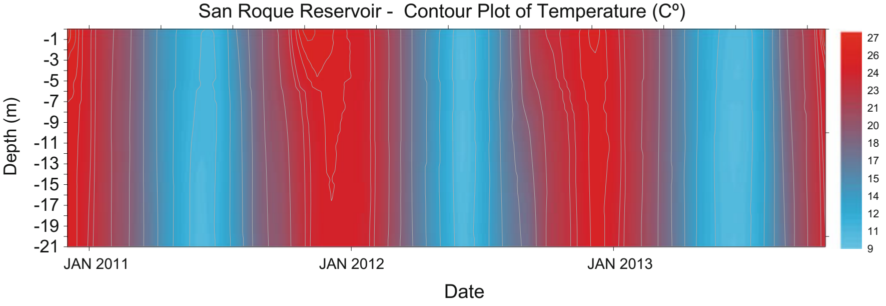


Fig. 4 Contour plot of temperature in the San Roque reservoir during 2011–2014

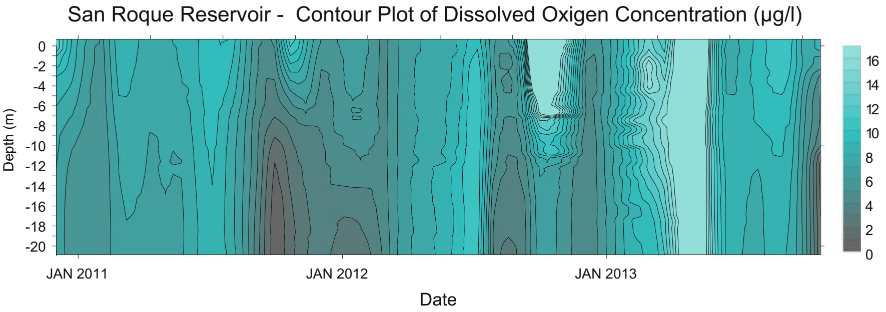


Fig. 5 Contour plot of dissolved oxygen in the centre of the San Roque reservoir during 2011–2014

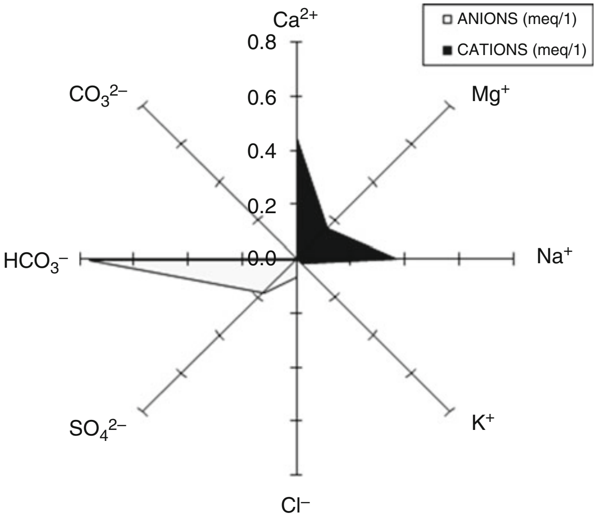


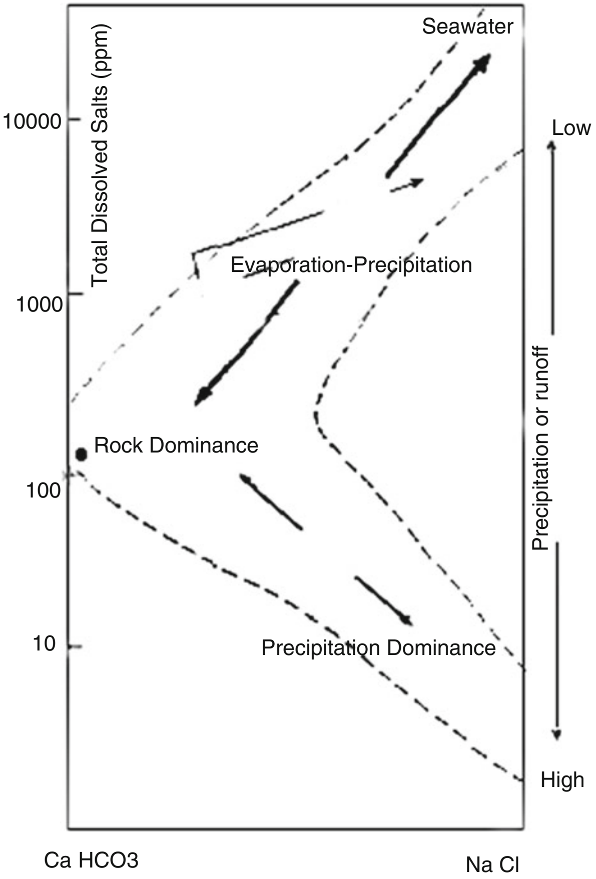
Fig. 6 Ionic mean composition (meq L^{-1}) of the San Roque reservoir

5 Ionic Composition of Water in the Reservoir

The reservoir water is dominated by calcium and sodium bicarbonate, where the order of ions concentration is as follows: $HCO_3^- >> Ca^{2+} > Na^+ >> SO4^{2-} > Mg^{2+} > Cl^- > K^+$ (Fig. 6).

Thus, the resulting salinity of the reservoir can be analysed using the Gibbs model [9], which establishes the salinity control processes, depending on the concentration of major ions. The data for the San Roque reservoir, rich in calcium bicarbonate, indicate a high dependence on the hydrochemistry of the waterbody, with respect to the geochemistry and chemical weathering processes occurring in

Fig. 7 Gibbs diagram. San Roque reservoir ($y = 118.5$ ppm, $x = 0.35$)



the upper basin (Fig. 7). The differences in ionic concentration between surface and deep waters are vertically controlled by the regime of thermal stratification and temporary rainfall. The high level of water in the reservoir during the rainy season causes an overall dilution, with variants that respond to the particularities of each ion [10].

6 Algal Blooms

The seasonal dynamics of phytoplankton is shown in Fig. 8. Cyanobacteria, mainly represented by *Dolichospermum* spp. and *Microcystis* spp., grow mainly during the spring, summer and fall and alternate with blooms of the dinoflagellate *Ceratium hirundinella*. When the reservoir is mixed, typically in late autumn, winter and early spring, there is a prevalence of chrysophytes (Bacillariophyceae), being

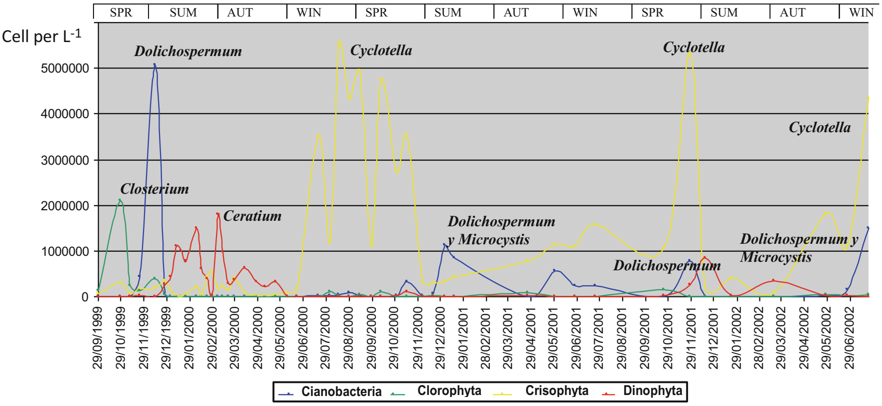


Fig. 8 Temporal dynamics of main genera of phytoplankton in the San Roque reservoir

Table 2 Favourable environmental conditions for the blooming of different genera in the San Roque reservoir (*Ts*: subsurface temperature, *Tm*: temperature at 1 m above the bottom)

Critical areas in the reservoir with greater algal growth	San Antonio River mouth and dam area			
Range of variables for relevant blooming species	*Cyclotella* sp. 	*Ceratium hirundinella* 	*Dolichospermum spiroides* 	*Microcystis aeruginosa* 
Abundance (cells per L^{-1})	2.10^6–4.10^7	300,000–$5.8.10^6$	10^6–5.10^6	10^6–$5.5.10^6$
Chl *a* ($\mu g\ L^{-1}$)	10–52	40–810	50–160	10–70
Secchi Disc (m)	0.5–1.5	0.3–1	0.6–1	0.9–2
Temperature (°C)	<12	22–26	14–25	11–26
Stratification ($Ts - Tf$)	<1	>2	0–4	0–5
Reservoir level (m)	<34	>34 *y* < 35.3	<35.3	<35.30
Water colour	Yellowish green	Brownish red	Green	Green
Total phosphorous ($\mu g\ L^{-1}$)	>30	>75	>20	>30
Dominance (%)	>90	>90	>50	>50

Cyclotella sp. the species most often present. Other common genera are *Aulacoseira* sp., *Stephanodiscus* sp. and *Navicula* sp. [11].

The record of blooms along several years revealed the conditions that favour algae most significantly (Table 2). The extensive mix in the water column favours the dominance of diatoms that have a high reproductive rate, allowing them to get the light and nutrients necessary for growth. Under conditions of stratification, its high specific density, together with the lack of mobile media, determines its sinking beyond the euphotic zone.

C. hirundinella adapts itself to a wide range of conditions, but it is most often associated with conditions of stratification and high concentrations of phosphorous in the reservoir. Thanks to its flagella, it is competitively more effective in the pursuit of light and nutrients that are not available for other algae.

The genera of cyanobacteria detected in the reservoir are *Microcystis* spp., *Dolichospermum* spp., *Merismopedia* sp., *Oscillatoria* sp., *Chroococcus* sp., *Lyngbya* sp., *Planktothrix* sp., *Anabaenopsis* sp., *Aphanothece* sp., *Raphidiopsis* sp., *Pseudanabaena sp.* and *Spirulina* sp., being *Microcystis* sp. and *Dolichospermum* sp. the first two more frequent and abundant than the rest.

The maximum values of *Microcystis aeruginosa* have been recorded in the spring, at temperatures between 11 and 26°C, with the onset of stratification and concentrations of total phosphorous greater than 30 μg L^{-1}. Occasionally, chlorophytes may dominate in winter and spring, including *Closterium* sp., *Carteria* sp., *Chlorella* sp. and cryptophyta *Cryptomonas* sp.

7 Cyanotoxins

Massive development of cyanobacteria in inland waterbodies causes serious problems for resource use, as many strains produce toxins, called cyanotoxins, which are a major concern for public health.

Cyanotoxins could be classified into two categories of water-related diseases [12]: (a) waterborne diseases when ingested, (b) direct contact diseases through exposure during recreational use. They belong to different groups of chemicals. Some are strong neurotoxins that attack the nervous system [anatoxin-a, anatoxin-a (S) and saxitoxin]; others are primarily toxic to the liver (microcystins, nodularin and cylindrospermopsin) and others, like lipopolysaccharide, seem to be the cause of health disorders such as gastroenteritis, but their action has not been clarified.

7.1 Microcystins

Previous studies [1, 13] indicate that the algae in the San Roque reservoir produce toxins. The reservoir water is used not only for the provision of drinking water to Córdoba city, but also for sports and domestic activities by the populations living along its coasts [14–17]. Since the toxins concentrations in both water [18] and fish [19] exceed the guideline values suggested by WHO, representing a real risk to the population, further studies on the level of toxins in this particular environment become necessary.

As shown in Table 3, during the studied period, microcystin (MC) was present from year to year. Maximum concentrations were detected in summer and autumn. The values obtained in the centre of the lake, in the Rio San Antonio River mouth and in the dam area ranged from ND (non-detectable) to 789 μg L^{-1}.

Table 3 Microcystins (MCs) concentration range in the San Roque Dam

Place	Studied period	MCs rank μg L^{-1}
San Antonio River mouth	1997–2007	ND–798.9
Centre of the reservoir	1997–1998	ND–450.9
Reservoir close to the dam (surface)	1997–2007	ND–119
Reservoir close to the dam photic zone	2004–2005	<0.16–4.3
Reservoir close to the dam (deep of water pipe to hydroelectric central)	2003–2006	<0.16–0.89
Reservoir close to the dam (bottom)	2003–2006	<0.16–22

ND Not detected

From October 1998 to June 2002, 35 samples were taken during blooming events. The presence of MC-LR and MC-RR was confirmed in 97% of the cases, with concentrations between 5.8 and 2,400 μg g^{-1} on freeze-dried material. The highest concentrations corresponded to MC-RR [1]. Ruibal Conti et al. [18] reported similar results for samples collected in the same period.

Studies conducted at the coast of the San Roque reservoir (La Calera Club, El Gitano bay and Los Mimbres bay) showed the presence of cyanobacteria in 66% of samples analysed during the summer time [20, 21]. The concentration for total MC ranged from ND to 32.7 μg L^{-1}. These values exceed by far the safe limit suggested by the WHO [22] of 4 μg L^{-1}. Cyanobacteria dominance was frequent on the beaches, corresponding mainly to the genera *Microcystis* sp. and *Dolichospermum* sp.

7.2 Anatoxin-a

Studies conducted in 2006/2007 recorded the presence of anatoxin-a in the reservoir. The average concentration in the autumn period (March–May 2006) was 2.70 ng L^{-1}, which was associated with the presence of *Oscillatoria* sp. and *Dolichospermum* sp. [23, 24]. This is the first report on the presence of anatoxin-a in fresh waterbodies of South America, and it is the first time that the presence of anatoxin-a is reported in this waterbody, but the concentrations found are well below the New Zealand recommended limit (6 μg L^{-1}), because of its lability.

8 Nutrients

Table 4 presents the average characteristics of the reservoir in relation to limnologic aspects.

Concentrations of phosphorous (P) and nitrogen (N) in the reservoir are high, and have a high variability in many sectors of the reservoir as well as in the water

Table 4 Statistics of monitored variables considering subsurface data from the centre of the San Roque reservoir during the period 1999–2013

	Valid *n*	Mean	Median	Minimum	Maximum	Quartile range	Std. dev.	Standard error
pH	143	7.9	7.9	6.0	9.9	0.91	0.72	0.06
Dissolved Oxygen (DO) (mg L^{-1})	114	9.5	8.7	2.9	30.0	3.59	4.37	0.41
Conductivity (μS cm^{-1})	149	243	239	114	492	77.00	63.76	5.22
Temperature (°C)	150	19.2	20.0	8.7	27.6	9.60	5.14	0.42
Secchi disk (m)	144	1.2	1.1	0.0	2.7	0.36	0.35	0.03
$N–NH_4^+$ (μg L^{-1})	151	54	40	10	460	6.00	48.09	3.91
$N–NO_3^-$ (mg L^{-1})	152	0.32	0.30	0.05	0.80	0.40	0.21	0.02
$N–NO_2^-$ (μg L^{-1})	152	11	6	4	58	6	8.95	0.73
SRP (μg L^{-1})	155	24	20	5	84	21	15.80	1.27
TP (μg L^{-1})	155	83	67	10	522	47	67.16	5.39
Alkalinity (mg L^{-1})	153	74	74	47	116	20	14	1.15
Hardness (mg L^{-1})	140	59	58	37	87	17	12	0.98
Ca^{2+} (mg L^{-1})	153	18.0	17.7	11.4	29.5	5.0	3.56	0.29
Mg^{2+} (mg L^{-1})	153	3.7	3.7	2.0	6,8	1.2	0.95	0.08
Na^+ (mg L^{-1})	153	21.4	20.7	9.0	39.2	10.1	6.36	0.51
K^+ (mg L^{-1})	153	2.3	2.3	1.5	3.6	0.5	0.38	0.03
SO_4^- (mg L^{-1})	153	24.8	22.0	8.0	53.0	15.0	9.96	0.81
Cl^- (mg L^{-1})	153	5.8	5.7	3.1	10.7	2.2	1.60	0.13
F^- (mg L^{-1})	144	0.8	0.8	0.2	1.1	0.2	0.13	0.01
TFe (mg L^{-1})	153	0.15	0.13	0.05	0.95	0.10	0.11	0.01
TMn (mg L^{-1})	153	0.04	0.03	0.03	0.12	0.01	0.01	0.00
TOC (mg L^{-1})	149	5.74	5.20	3.00	24.80	1.60	2.94	0.24
Chlorophyll a (μg L^{-1})	152	51	20	2	528	52	80.38	6.52

SRP soluble reactive phosphorous, *TP* total phosphorous, *TFe* total iron, *TMn* total manganese, *TOC* total organic carbon column. This is related to thermal dynamics and metabolic processes as observed in the variables of DO and SRP (Figs. 9 and 10).

The Total Inorganic Nitrogen (TIN) median value is higher than 300 μg L^{-1}, while the Soluble Reactive Phosphorous (SRP) is higher than 15 μg L^{-1}, with Total

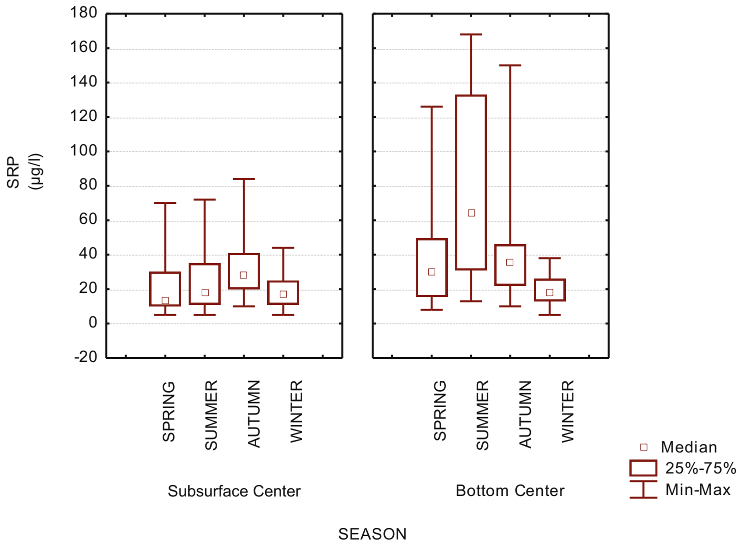


Fig. 9 Soluble Reactive Phosphorous (SRP), seasonal variability in the San Roque reservoir (monitored at the centre of the reservoir, surface and bottom)

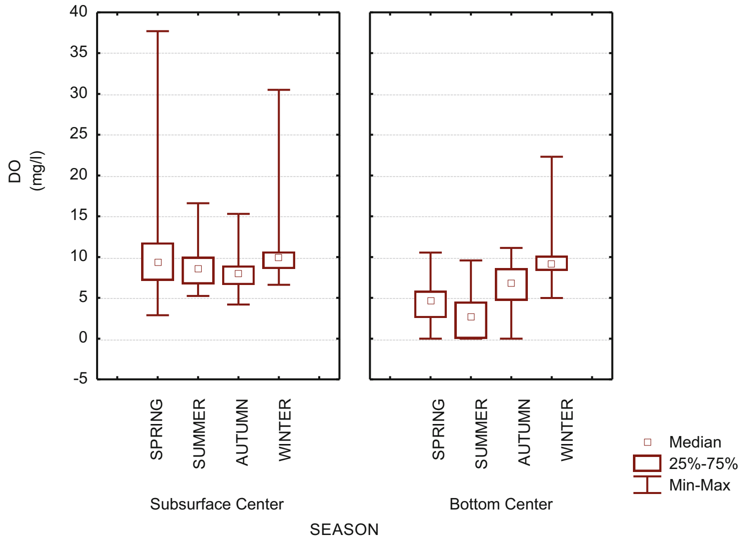


Fig. 10 DO seasonal variability in the San Roque reservoir (monitored at the centre of the reservoir, surface and bottom)

Phosphorous (TP) is higher than 50 μg L^{-1}. It is commonly accepted that values lower than 5 μg L^{-1} for SRP, and 20 μg L^{-1} for TIN are limiting concentrations for the algae growth [25].

9 Transparency and Euphotic Zone

The lack of transparency of the lake, with an average around 1 m (Fig. 11), determines that the euphotic zone is limited to a few meters thick. The maximum depth of this layer is between 1.2 and 5.6 m (Fig. 12). This water layer is included in the mixed layer (Z_{mix}), being the $Z_{\mathrm{eu}}/Z_{\mathrm{mix}}$ relationship always lower than 1. Thus, the uptake is below the mixed layer during stratification periods. However, this sector is not free from the impact of algal blooms. Figure 13 shows cyanobacteria abundance in the uptake area at three depths: subsurface, photic zone and uptake. In the spring of 2010, there was a massive cyanobacteria bloom in the reservoir, and its abundance was increased both in absolute and relative values at greater depths, compared to other periods in which the maximum values were found in the photic

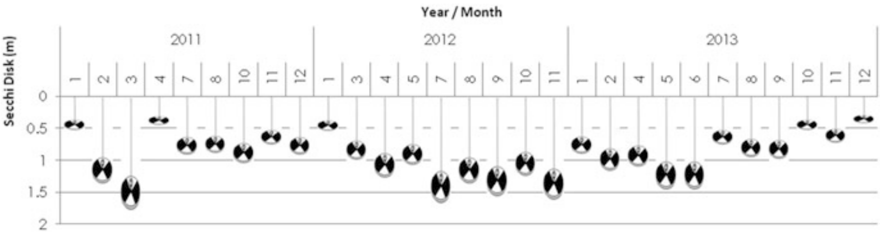


Fig. 11 Secchi disc transparency variability in the centre of the San Roque reservoir 2011–2013

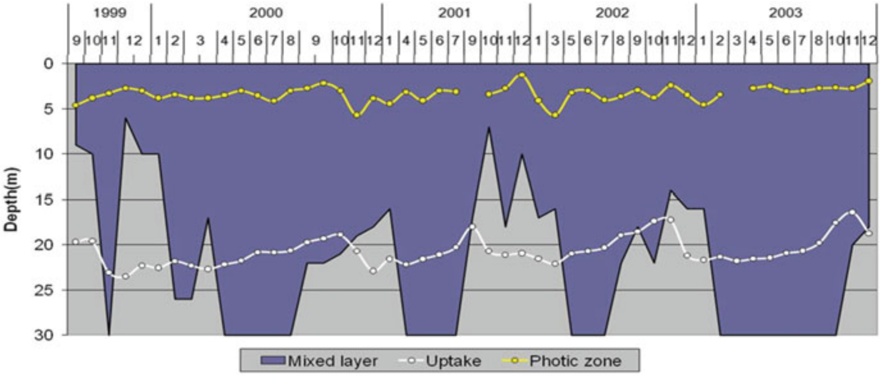


Fig. 12 Variation of mixed and photic layers in the reservoir at the uptake area close to the dam (TAC)

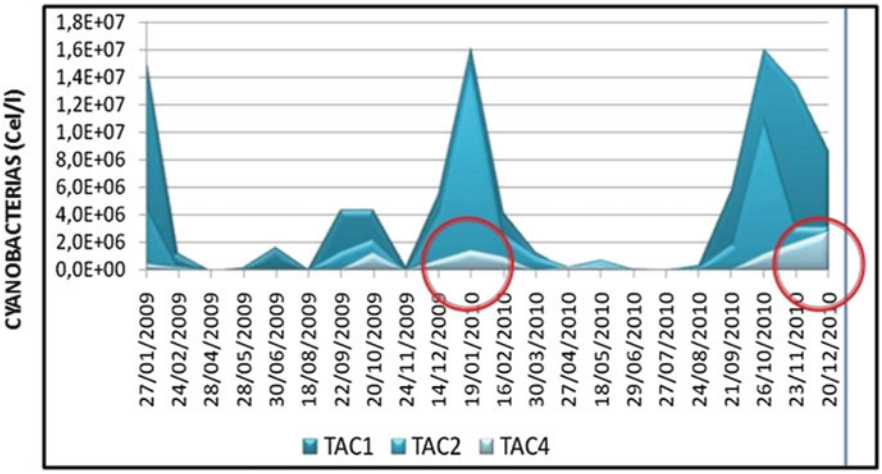


Fig. 13 Variation of cyanobacteria abundance at the uptake area at three depths TAC_1: subsurface, TAC_2: photic zone and TAC_4: uptake depth. *TAC* uptake area close to the dam

layer (Fig. 13). This event was associated with SRP extraordinary concentration of 567 μg L^{-1} released from sediments in the hypolimnion, which became available for algae to mix the water column. Nutrient availability and intake lead to one of the greatest cyanobacterial blooms recorded in the waterbody (*Dolichospermum* sp. and *Microcystis* sp.).

10 Sediments and Organic Matter

P exchange between sediment and water is a determining factor in the trophic status of lakes and reservoirs. Its importance is based on an apparent net movement of P towards the water, because sediments act as a reservoir of phosphorous and, under particular conditions of anoxia and change of redox potential (ORP), it is released, creating an important internal source of nutrients.

The amount of released phosphorous is generally called the internal phosphorous load. Its estimation is of vital importance because of the magnitude of the contribution of phosphorous from the sediments during the summer. The selected methodology for this calculation was Jorgensen's [26]. A maximum coefficient of 1.33 mg SRP m^2 day^{-1} at a temperature of 18°C, and DO of 0 mg L^{-1}, with pH between 6 and 7, was obtained. These conditions are commonly seen in the hypolimnion of the San Roque reservoir every summer [27]. The centre and the old wall (dam) area show a higher TP quantity compared to the water uptake area, which is protected from the internal currents of the reservoir by the submerged structure of the old dam. The uptake station recorded an annual average content of

Fig. 14 Seasonal variation in phosphorous content in sediments of the San Roque reservoir

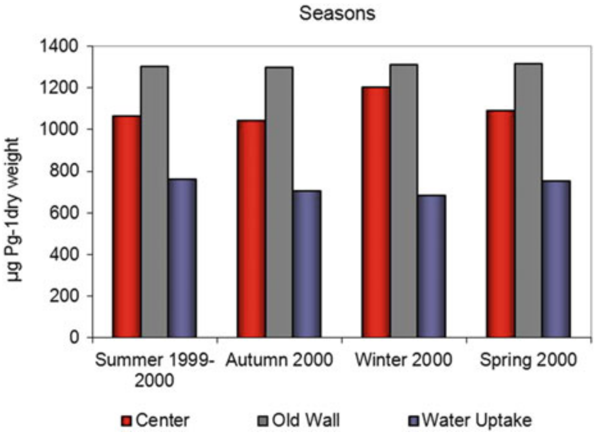


Table 5 Phosphorous mean values (dry sediment)

Station name	IP (µg P g^{-1})	TP (µg P g^{-1})
TAC	950	1,069
Centre	869	1,003
SAM	701	901
CQM	431	497

TAC uptake area close to the dam, *SAM* San Antonio River mouth, *CQM* Cosquín River mouth

722 µg phosphorous g^{-1} (dry sediment), while the centre and old wall recorded 1,076 and 1,342 µg phosphorous g^{-1} (dry sediment), respectively (Fig. 14).

In subsequent studies [28], the values obtained between TP and IP (inorganic phosphorous) were very similar. The average concentrations are detailed in Table 5. Higher values correspond to silt-clay sediments of the centre and uptake area, in addition to sandy sediments of Cosquín and San Antonio Rivers mouths. Another aspect evaluated in the sediment was the organic matter (OM). Mostly produced by algae in the lake, OM is deposited on them and then broken down by aerobic and anaerobic processes, producing different carbon, nitrogen and phosphorous compounds. The water uptake sector has a high percentage of OM (18–19%), presenting a peak of 34%. Conversely, in the centre of the reservoir, OM is around 15%, with a maximum of 18%, but always remaining constant and stable because of the composition of the pellets in this area (Fig. 15).

During the study period 1999–2006, it has been verified that sediments acted as a reservoir, promoting the enrichment of the water, and favouring eutrophication. Phosphorous concentrations measured in sediment did not show great variability over the time, but it is important to continue studying them to provide relevant information for a lake-basin integrated management system.

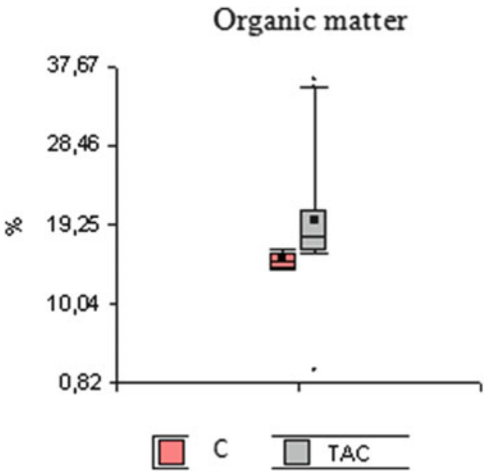


Fig. 15 Percentage of Organic matter (OM) in centre of the reservoir (C) and in the uptake area close to the dam (TAC) of the reservoir

11 Estimate of Phosphorus Loads

Nutrient inputs can enter through affluents, diffusive load or punctual sources on the shores of the lake.

Urban sewage usually provides a significant amount of nutrients, including tensioactives and food debris. Load per domestic effluents can vary as it depends on many factors, such as community composition, type of treatment plants, living standards, geographic location, climate, season and presence or absence of garbage deposits. In 1999–2000, Rodriguez et al. [29] estimated the contribution of phosphorous indicating that the main source of phosphorous was the direct contribution by diffusive load to the reservoir (66%), resulting from the urbanization of the river banks (Fig. 16). According to the mass balance performed, the sediments, while having a reservoir role under frequent anoxia situations, produced a critical nutrient release by its magnitude that lead to algal blooms (Fig. 17).

Table 6 shows the results of other phosphorous load estimates made in this reservoir. The observed variability in values may be due to the inclusion or non-inclusion of overflowing events; the different methods applied, the different periods evaluated, the contribution of the coefficients used, as well as the quality and quantity of data.

In addition to the mentioned loads, the amount of phosphorous may increase as a result of fires affecting the basin, often during winter and before the rainy season. Combustion consumes part of the soil organic matter in the surface layers or mulch, producing its mineralization. This sudden release of nutrients causes loss by volatilization or washing. It has been observed that the TP load increases significantly in the summer, after the fires. In August 2003, the burned vegetation in the basin was mostly grassland, natural forest and scrub, with a total of 15,000 ha, of which 99% corresponded to the Cosquín River watershed. At that time, TP concentrations were well above the historical values registered.

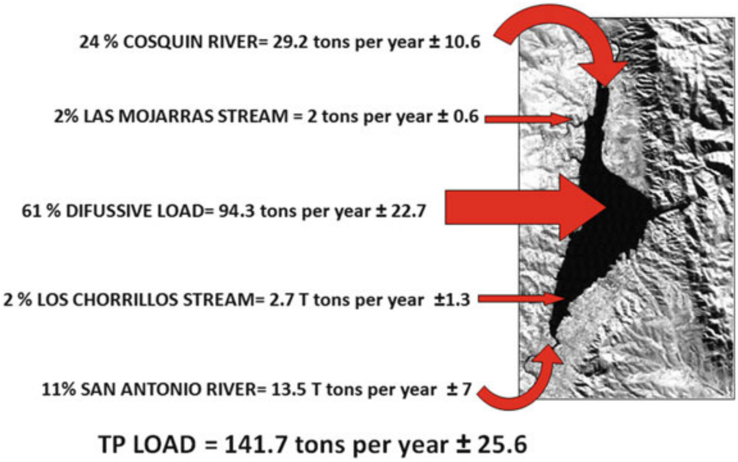


Fig. 16 Discrimination of P loads to the reservoir

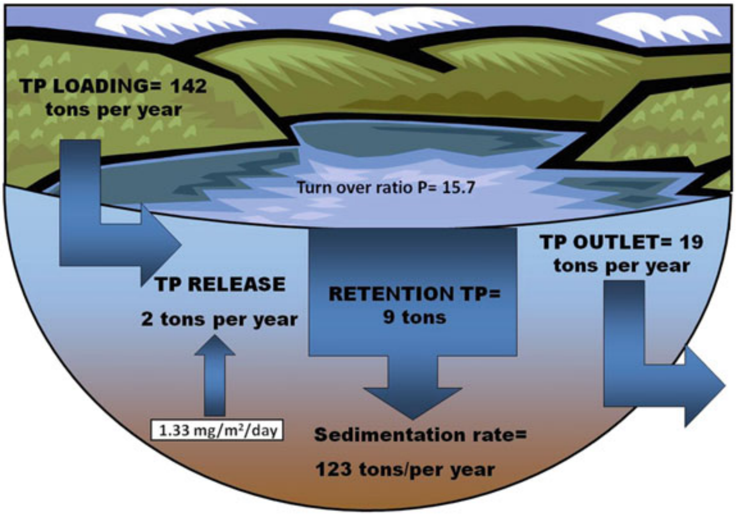


Fig. 17 Mass balance of phosphorous estimated for the San Roque reservoir

Table 6 Load estimates at the San Roque reservoir (source: [30])

Phosphorous load (ton year^{-1})	Total
Gavilán [31]	190
INYPSA [32]	100
Bechtel and Benito Roggio e Hijos S.A. [33]	91
Bustamante et al. [34]	246.1
Rodriguez [30]	141.7

12 Trophic Status

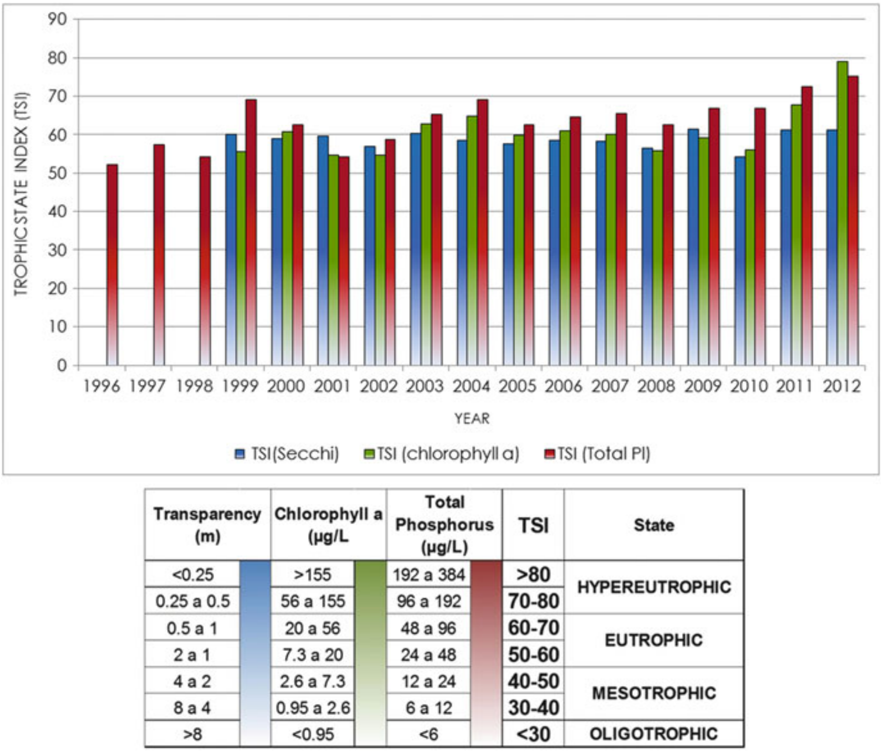
One way to establish the trophic condition of reservoirs is through Trophic Status Carlson Indexes [35]. These indexes are simple calculations that help to understand the evolution of the waterbody over the time, in a clear manner. The transparency (1), chlorophyll-a (2) and total phosphorus (3) values are included in these calculations. The annual surface data at the centre of the reservoir are considered in the index.

$$\mathrm{ICT(DS)} = 60 - 14.41\ln(\mathrm{DS}) \tag{1}$$

$$\mathrm{ICT(Chl\ a)} = 9.81\ln(\mathrm{Chl\ a}) \tag{2}$$

$$\mathrm{ICT(PT)} = 14.42\ln(\mathrm{PT}) \tag{3}$$

Figure 18 shows the variation of the Carlson indexes in the reservoir during the period 1996–2012. A waterbody is considered eutrophic from an indicative value of 50, while an index above 70 indicates that the waterbody becomes hypereutrophic. The San Roque reservoir has historically values above 50 and, for the most recent



Transparency (m)	Chlorophyll a (µg/L	Total Phosphorus (µg/L)	TSI	State
<0.25	>155	192 a 384	>80	HYPEREUTROPHIC
0.25 a 0.5	56 a 155	96 a 192	70-80	
0.5 a 1	20 a 56	48 a 96	60-70	EUTROPHIC
2 a 1	7.3 a 20	24 a 48	50-60	
4 a 2	2.6 a 7.3	12 a 24	40-50	MESOTROPHIC
8 a 4	0.95 a 2.6	6 a 12	30-40	
>8	<0.95	<6	<30	OLIGOTROPHIC

Fig. 18 Carlson trophic index of the San Roque reservoir (centre) for the period 1999–2012

years, it shows a hypereutrophic condition. This indicates that the reservoir is characterized by frequent hypolimnetic anoxia, dominance of cyanobacteria, presence of scum, frequent fish death, macrophytes problems and algae productivity, which is limited by light and not by nutrients, since the latter are sufficiently available for algae development. The annual values of transparency are usually close to 1 m, chlorophyll-a exceeds 20 μg L^{-1} and total phosphorus concentration (TP) is higher than 48 μg L^{-1}.

References

1. Amé MV, Díaz MP, Wunderlin DA (2003) Occurrence of toxic cyanobacterial blooms in San Roque Dam (Córdoba, Argentina): a field and chemometric study. Environ Toxicol 18 (3):192–201
2. Dasso CM, Piovano EL, Pasquini AI, Córdoba FE, Lecomte KL, Guerra L, Campodónico VA (2014) *Recursos Hídricos Superficiales*, Relatorio del XIX Congreso Geológico Argentino. Rev Asoc Geol Argent 1:1209–1231
3. Colladón L (2014) Síntesis pluviométrica 1992–2012, Cuenca del río San Antonio: Sistema del Río Suquía, Provincia de Córdoba. Instituto Nacional del Agua, Ezeiza, 28 pp. ISBN: 978-987-45194-4-3
4. Colladón L (2004) Estadística Meteorológica, Temperaturas Medias Mensuales, 1994–2003, Cuenca del Río San Antonio. INA-CIRSA, Villa Carlos Paz, Córdoba, 40 pp
5. Gaiero D (1998) Hidrogeoquímica de un sistema de la región semiárida: el Río Suquía, Córdoba, 2, Transporte de sólidos disueltos, meteorización y consumo de CO_2. Rev Asoc Geol Argent 53(3):337–347
6. Granero M, Bustamante M, López F, Ruibal AL (2000) Impacto del Antiguo Muro del Embalse San Roque (Córdoba, Argentina) en la Calidad de Agua de la Toma. Memorias del XIX Congreso Latinoamericano de Hidráulica 1:181–190
7. Rodriguez MI, Ruiz M, Vilchez G, Crema N, Ruibal Conti AL, Bustamante MA, Angelaccio CM (2006) Monitoreo Integral de un Cuerpo de Agua Eutrófico: Embalse San Roque (Córdoba, Argentina). In: I Congreso Internacional sobre Gestión y Tratamiento Integral del Agua, Córdoba, Argentina
8. Helmbretch J, López F (2000) Predictores Físicos de la Calidad del Recurso en el Lago San Roque (Córdoba, Arg). XIX Congreso Latinoamericano de Hidráulica 1:75–84. Córdoba, Argentina
9. Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170:1088–1090
10. Rodriguez MI, Granero M, Bustamante A, Avena M, Bonfanti E, Busso F, Girbal A (2002) Análisis de la Composición Iónica de las Aguas del Embalse San Roque, Córdoba. In: XIX Congreso Nacional del Agua, Córdoba, Argentina
11. Rodriguez MI, Busso F, Bustamante MA, Ruibal Conti AL, Ruiz M, Angelaccio CM (2005) Floraciones de algas en el Embalse San Roque (Córdoba). In: XX Congreso Nacional del Agua y III Simposio de Recursos Hídricos del Cono Sur, Mendoza, Argentina
12. Chorus I, Bartram J (1999) Toxic cyanobacterias in water: a guide to their public health consequences, monitoring and management. Published on the behalf of WHO by E&FN Spon, London
13. Ruibal Conti AL (2003) Seasonal variation of microcystins in Argentinean Inland waters. Tesis de Maestría, Universidad de Kyoto, Kyoto, 88 pp
14. Ruibal Conti AL, Rodríguez MI, Ruiz MA, Centineo ME, Angelaccio CM, Lerda D (2007) Survey on health problems in a comunity exposed to Cyanobacteria (Córdoba, Argentina). In: Congreso Internacional de Cianobacterias tóxicas, Rio de Janeiro

15. Ruiz M, Rodríguez MI, Ruibal AL, Centineo E, Alasia V, Lerda D, Aguilera, S (2008) Estudio del Impacto en la Salud de una Población Expuesta al Uso de Agua con Cianobacterias. In: CAL 4 Bariloche, Río Negro, Argentina
16. Ruiz M, Rodríguez MI, RuibalAL, Gonzalez I, Alasia V, Pellicioni P, Biagi M, Lerda D (2009) Exposición al Uso y Consumo de Agua con Cianobacterias: Efectos en la Salud. In: 1 Congreso Internacional de Ambiente y Energías Renovables, Universidad Nacional de Villa María, Villa María, Córdoba
17. Ruiz M, Rodríguez MI, Ruibal AL, González I, Pellicioni P, Biagi M, Lerda D (2010) Efectos en la Salud por Exposición al Agua con Microcistinas. In: III Congreso Internacional de Gestión y Tratamiento, Córdoba, Argentina, ISBN: 978-987
18. Ruibal Conti AL, Regueira M, Guerrero JM (2005) Levels of microcystins in two reservoirs used for water suply and recreation: differences in the implementation of safe levels. Environ Toxicol 20:263–269
19. Cazenave J, Wunderlin DA, Bistoni MA, Amé MV, Krause E, Pflugmacher S, Wiegand C (2005) Uptake tissue distribution and accumulation of microcystin-RR in Corydoras paleatus, Jenynsia multidentata and Odontesthes bonariensis. A field and laboratory study. Aquat Toxicol 75:178–190
20. Rodriguez MI, Ruiz M, Ruibal AL, Bustamante MA, González I, Olivera P, Halac S, Sada C (2010) Calidad de Agua Recreativa Afectada por Floraciones de Cianobacterias en el Embalse San Roque (Córdoba). In: III Congreso Internacional sobre Gestión y Tratamiento Integral del Agua, Córdoba, Argentina.
21. Ruiz M, Rodriguez MI, Olivera P, Halac S, Nadal F, Larrosa N, Brandalise V (2012) Importancia de la Calidad del Agua Recreativa y su Impacto en Salud. In: V Taller de Cianobacterias Toxígenas en Argentina – I Simposio Interdisciplinario sobre Cianobacterias y Salud, Mar del Plata, Argentina
22. WHO (2003) Guidelines for safe recreational water environments. Coastal and freshwaters, vol 1. World Health Organization, Geneva
23. Ruiz M, Galanti L, Ruibal Conti AL, Rodriguez MI, Wunderlin D, Amé V (2013) First report of microcystins and anatoxin-a co-occurrence in San Roque Reservoir (Córdoba, Argentina). Water Air Soil Pollut 224:1593
24. Amé V, Ruiz M, Galanti LN, Ruibal AL, Rodriguez MI, Wunderlin DA (2010) Microcistinas y anatoxina-a en el Embalse San Roque (Córdoba-Argentina). In: III Congreso Argentino de SETAC, 10 al 14 de Mayo, Santa Fe, Argentina
25. Ryding S, Rast W (1992) El Control de la Eutrofización en Lagos y Pantanos. Ed. Pirámide, Madrid, 375 pp
26. Jorgensen SE (1980) Lake management, 14 edn. Pergamon Press, London
27. Granero M, Bustamante MA, López F, Ruiz M (2002) Internal load and hypolimnion water quality of San Roque Reservoir. J Hydraul Res 42(3):310–315. International Association of Hydraulic Engineering and Research
28. Ruiz M, Granero M, Rodriguez MI, Bustamante MA, Ruibal Conti AL (2005) Importancia de los Sedimentos como Fuente interna de Fósforo en el Embalse San Roque (Córdoba): Determinación de una Metodología para su Estudio. In: XX Congreso Nacional del Agua y III Simposio de Recursos Hídricos del Cono Sur, Mendoza, Argentina
29. Rodriguez A, Avena M, Rodríguez MI, Cossavella A, Oroná C, del Olmo S, Larrosa N, Bazán R, Corral M (2002) Estimación de Aportes de Nutrientes de Fósforo a los Embalses San Roque y Los Molinos en Córdoba, Argentina e Implicancias en su Gestión. Ingeniería Sanitaria y Ambiental 60:45–51
30. Rodriguez MI (2003) Estudio de la Problemática Ambiental de la Eutroficación del Embalse San Roque (Córdoba). Aportes para la Gestión del Recurso. Tesis de Maestría en Gestión Ambiental del Desarrollo Urbano, Facultad de Arquitectura Diseño y Urbanismo, Universidad Nacional de Córdoba, Córdoba, Argentina, p 164
31. Gavilán JG (1981) Study water quality in the san Roque reservoir. Water Qual Bull Environ 6 (4):136–158

32. INYPSA (1987) Estudio de la problemática y viabilidad de tratamiento de vertidos de la Ciudad de Carlos Paz en Córdoba (Arg). Informe inédito, Córdoba, Argentina
33. Bechtel G, Hansen BR (1992) Comité de la Cuenca del Lago San Roque: Informe Interino Número 6, Estudio de factibilidad/Diseño conceptual para el manejo de descargas de aguas cloacales en la Cuenca del Lago San Roque. Informe inédito, Córdoba, Argentina
34. Bustamante MA, López F, Bonetto C, Granero M (2002) Limnology of mountain rivers and transport of phosphorus and nitrogen to an enriched reservoir. Verh Internat Verein Limnol 28:1779–1782
35. Carlson RE (1977) Trophic State Index. Limnol Oceanogr 22(2):361–369

Biota Along the Suquía River Basin

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Abstract The biota inhabiting the Suquía River Basin is described in this chapter. Comments on the species of fish, birds, invertebrates and aquatic plants registered in this system are included. Along the basin, different factors generate a noncontinuous mosaic of abiotic conditions at temporal and spatial levels, which, in turn, structure the biotic communities. The Suquía hydrological system consists of three sections: the upper basin in a mountainous area with headwaters and torrential rivers flowing into the San Roque Reservoir; the middle basin with drainage areas belonging to the eastern slope of the Sierras Chicas, together with the drainage area of the city of Córdoba; and the lower basin which is located downstream from the city of Córdoba flowing into the Mar Chiquita Lake, where the river meanders exhibit little flow. The species of the different groups change according to the characteristics of each section. In this chapter, endemic and

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introduced species are discussed. The bivalve species that inhabit the Suquía River are not native, and the cause of their introduction is explained. Authors also specify the anthropic factors that negatively impact water, bird and invertebrate species in the river.

Keywords Aquatic birds, Aquatic biotic, Aquatic macroinvertebrates, Aquatic plants, Ichthyofauna

Contents

1 Ichthyofauna

In the Suquía River Basin, 24 fish species, in permanent and casual forms, are accepted in the literature (Table 1). These species are distributed in 14 families and 8 orders [1]. The richest groups were the Characiformes (10 species) and the Siluriformes (6 species). Regarding the abundance of each order, the Cyprinodontiformes was the best represented order (50%), followed by the Siluriformes and the Characiformes (24.68% and 24.18%, respectively). However, the Cyprinodontiformes have only four species.

It is important to note that *Phalloceros* sp. was registered for the first time by Hued and Bistoni [1]. This is important because, according to Ringuelet et al. [2], the geographical distribution of this species comprises the Province of Misiones and the city of La Plata, in the Province of Buenos Aires, Argentina. It is also found in southern Brazil, Uruguay and Paraguay [2]. Hued and Bistoni [1] mentioned that only two females were found in the Villa Giardino area (upper basin) (31°02′00″S 64°29′00″O) on the San Francisco Stream (tributary of the Suquía River Basin) (Fig. 1). Further studies are necessary to determine if this species is established in the basin.

Table 1 Fish species richness in Suquía river, Córdoba province, Argentine

Order	Family	Species
Cypriniformes	Cyprinidae	*Cyprinus carpio*
		Ctenopharyngodon idellis
Characiformes	Characidae	*Cheirodon interruptus*
		Oligosarcus jenynsi
		Astyanax eigenmanniorum
		Astyanax hermosus
		Astyanax cordovae
		Bryconamericus iheringi
		Bryconamericus eigenmanni
		Odontostilbe microcephala
		Parodon tortuosus
	Erythrinidae	*Hoplias malabaricus*
Siluriformes	Heptapteridae	*Pimelodella laticeps*
		Rhamdia quelen
	Pimelodidae	*Pimelodus albicans*
	Trichomycteridae	*Trichomycterus corduvense*
	Callichthyidae	*Corydoras paleatus*
	Loricariidae	*Rineloricaria catamarcensis*
		Hypostomus cordovae
Atheriniformes	Atherinidae	*Basilichthyes bonariensis*
Cyprinodontiformes	Anablepidae	*Jenynsia multidentata*
	Poecilidae	*Gambusia affinis*
		Cnesterodon decenmaculatus
		Phalloceros sp.
Synbranchiformes	Synbranchidae	*Synbranchus marmoratus*
Perciformes	Cichlidae	*Australoheros facetum*
Salmoniformes	Salmonidae	*Oncothynchus mykiss*
		Salvelinus fontinalis

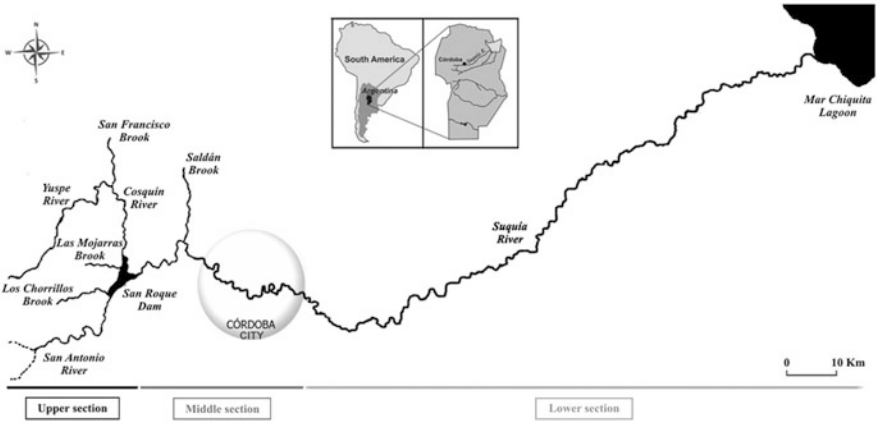

Fig. 1 Rio Suquia Basin showing different sections along of the basin

Fig. 2 Ichthyological provinces of Argentina. Adapted from López et al. [3] with permission

At the biogeographical level, five ichthyological provinces of the Argentinean freshwater fauna are recognised [3] (Fig. 2): Andino-Cuyana, Patagónica, Aymara, Grandes Ríos and Pampeana. According to these authors, the Pampeana province includes the Provinces of Tucumán and Córdoba, as well as an extensive area of the Provinces of Santiago del Estero, San Luis, Buenos Aires and La Pampa. It also includes the south-eastern region of the Provinces of Salta, Catamarca and La Rioja and the south-western region of the Province of Santa Fe. According to this classification, the Suquía River Basin is located fully in the Pampeana ichthyological province (Fig. 2).

1.1 Distribution of the Ichthyofauna Along the Suquía River Basin

From the headwaters down, communities are structured along the abiotic factors that characterise each section, such as altitude, river order, stream gradient and distance from the source. These abiotic factors influence not only species richness but also trophic composition [4]. In the Suquía River Basin, three sections can be recognised according to their geomorphological conditions: upper, middle and lower sections (Fig. 1). The upper section extends from 1,900 m.a.s.l. to 650 m.a.s.l. and the middle section from 643 m.a.s.l. to 352 m.a.s.l. The lower section starts at 300 m.a.s.l. and runs down to the mouth of the Suquía River in the Mar Chiquita Lake (70 m.a.s.l.). Fish fauna of the middle and lower sections was comprehensively surveyed by Haro and Bistoni [5] and the upper section by Hued and Bistoni [1]. Streams located in high altitude places support cold water fish assemblages, and as streams run down the mountains, this assemblage changes to warm-water taxa. In the first case, the dominant species is trout. Trout inhabits areas near the headwaters because of their specific living requirements of oxygen, pH and temperature [6]. Thus, the headwaters can be classified as ‘trout zones’. A few kilometres downstream from the headwaters, this species rapidly declines in abundance, mainly because stream temperatures become warmer [7, 8]. Numerous studies indicate injury to native fish communities by the introduction of salmonids [9–11]. These studies indicate that trouts change the communities’ composition of native fish by competing for resources or predation. Further studies in the mountain river in the Province of Córdoba are necessary to confirm this aspect.

Continuous change in fish assemblages along the river seems to prevail in the middle and lower sections. Among the fish species present in downstream areas, *Hoplias malabaricus* and *Cyprinus carpio* are observed in the plains from 600 m downstream. The Siluriformes order is registered along the basin, but they are more diverse in the lower section of the basin with respect to upstream locations.

1.2 Endemism

Astyanax cordovae is a remarkable endemism in the Córdoba province, and it was described for the first time by Gunther in 1881 for Córdoba rivers (Fig. 3). Ringuelet [12] stated that this species had not been seen since its original description. In 1988, Bertolio and Gutiérrez published a detailed redescription of this fish. They note that *A. cordovae* has a geographical distribution restricted to the basins of the Suquía and Xanaes Rivers. Its presence is more easily observable in the Suquía River, even though it is not as common as the other two species of the same family, *Astyanax eigenmanniorum* and *Bryconamericus iheringi*. It inhabits deep wells and has also been captured in flowing water in the channelized area of the Suquía River, running through the city of Córdoba (middle basin, Fig. 1) [13].

Miquelarena et al. [14] described for the Suquía River Basin a new endemic species, *Astyanax hermosus* that was registered only in the San Francisco River, in the Valle Hermoso locality (37° 07’ S-64° 29’ W). This site is located at 900 m.a.s.l. and it is a typical mountain stream with a fast-flowing current and gravelly, rocky and sandy bottoms (upper basin, Fig. 1).

1.3 Introduced Fish in the Suquía River

Species that move, whether intentionally or accidentally, due to human activities, from its native area to a different region are considered alien species [15].

Fig. 3 *Astyanax cordovae*. Endemic species in the Suquía River. Scale bar, 3 cm

Out of 28 fish species, five were introduced: *Cyprinus carpio*, *Ctenopharyngodon idella*, *Gambusia affinis*, *Odontesthes bonariensis*, *Oncorhynchus mykis*s and *Salvelinus fontinalis*. The last two mentioned species were introduced in Argentina from the United States for sport fishing. They were introduced as embryonated eggs at the beginning of the twentieth century [16]. Nowadays, they are distributed in almost all mountain rivers of the Province of Córdoba. On the same hand, *C. carpio*, a species indigenous to China, was introduced in Argentina in 1930. It is considered a naturalised species because it sustains self-replacing populations for several life cycles. Besides, another cyprinid, *C. idella*, was introduced in the San Roque Dam since 1989, and it is considered a casual species because it does not form self-replacing populations in the invaded region and its persistence depends on repeated introductions. It is detected in sporadic catches by sport fishermen in the San Roque Dam.

G. affinis, a species native to Mexico and the southern region of the United States, was introduced in Argentina to fight diseases such as malaria and yellow fever, because of its recognised deficiency as a larvivorous fish. It is a small-sized fish (3–4 cm), common along the Suquía River, which inhabits pristine as well as contaminated sites, where it becomes the dominant species [17]. Silverside (*O. bonariensis*) is native to the Río de la Plata River (Argentina). This fish species was introduced, mainly in lakes of the Province of Córdoba, for sport fishing. Now, it is considered a naturalised species, with a permanent population in the lakes. From the San Roque Lake and through the Suquía River as a dispersal route, silverside arrived to the Mar Chiquita Lake, where it settled. This last lake showed a hypersaline condition 20 years ago [18]. At the time, the average concentration of salt in the lake was around 300 g/L (hypersaline stage), making it impossible for this species to settle there. Around 1970, the Mar Chiquita Lake received a significant amount of freshwater from their tributaries, as a result of a marked increase in precipitation throughout the basin, and its salinity decreased to 30 g/L, a concentration similar to seawater levels. This mesohaline condition allowed *O. bonariensis* and others species, such as *Jenynsia multidentata*, to colonise this lake [18]. The silverside population grew rapidly in the lake; therefore, the Government of the Province of Córdoba authorised commercial fishing in the area [19]. These authors note that in 1997 the level of the Mar Chiquita Lake decreased, and the salinity increased again. These reasons, among others like fishing pressure, population dynamics and limnology, caused a decrease in the silverside population in the lake, so commercial fishing was markedly affected. Nowadays, it is difficult for local fishermen to find silversides in the Mar Chiquita Lake (personal observation). Reati et al. [18] estimated that *O. bonariensis* will disappear from the Mar Chiquita Lake in a few years if the increasing trend raising the water salinity continues, probably before concentrations of 60 g/L are reached. Therefore, the presence of silverside in the Mar Chiquita Lake seems to be cyclical. During extended periods of low salinity, this species adds economic importance to the region.

1.4 Ecological Types

Ringuelet [12] made a classification integrating habitat and trophic level of freshwater fish in Argentina, and they denominated it ‘ecological types’. We modified the classification made by these authors according to our experience. Therefore, the Suquía River species can be classified into several ‘ecological types’. So ‘bottom fish’ includes species with an iliophagus diet, such as *Prochilodus lineatus*, and it also includes the most characteristic species of this group: the armoured catfish *Rineloricaria catamarcensis*, *Hypostomus* sp. and *Corydoras paleatus*. Besides, the ecological type comprising ‘fish that frequent the bottom’ encounters opportunistic carnivores, which are very common in the bottom of streams with a slow velocity. This type includes species such as catfish *Rhamdia quelen*, *Pimelodella laticeps* and *Pimelodus albicans*, which have long sensitive barbells that allow them to perceive their preys. Considering the diet and habitat of *C. carpio*, it could be included in this ecological type. The ecological type ‘open and vegetated waters’ includes the predator *H. malabaricus* as well as a group of small fish with an insectivorous diet. This group also includes a different genus such as *Astyanax*, *Bryconamericus* and *Cheirodon*. Other species included in this group are *Australoheros facetum* and small fish of the order Cyprinodontiformes such as *J. multidentata*, *Cnesterodon decemmaculatus* and *G. affinis*. In recent times, it has been observed that mosquitofish (*G. affinis*) is the most resistant to pollution among all the Cyprinodontiformes species, and it seems that native species decline in abundance while alien species increase. However, no studies have been conducted yet to confirm this observation. Also, a special ecological type called ‘air-breathing fish’ includes species with the ability to breathe atmospheric oxygen. Members of this ecological type found in the Suquía River Basin include *Synbranchus marmoratus* and *C. paleatus*. Finally, the ecological type ‘cold water fish’ includes *Trichomycterus corduvense*. This species inhabits the fastest section of the river, with rocky and sandy bottom. This little catfish shares the habitat with trouts, which have the same environmental requirements and can compete for different resources.

2 Aquatic Birds

The literature about waterbirds specifically present in the Suquía River Basin is almost non-existent; much of the concepts expressed herein correspond to observations made by the authors.

2.1 Species Richness

Birds, and particularly aquatic birds, are known for their great dispersal capability compared to other groups of vertebrates. In this way, 69% of aquatic birds cited for the Province of Córdoba can be observed in the Suquía River Basin ([20–24], [25, pers. obs.]), totalling 79 species belonging to 18 families in eight orders. However, it is possible that the remaining 35 species, which are rare or occasional in Córdoba, will ever be observed.

Some families are particularly rich around the world and the situation in the Suquía River Basin is not an exception. Thus, most waterbird species belong to the families Anatidae (15 species) and Scolopacidae (13 species, Table 2).

Additionally, 25 species of birds not considered as aquatic birds sensu stricto (i.e. those with physiological and anatomical adaptations to aquatic habitats) also inhabit the basin. These species, however, exhibit behavioural adaptations for living in wetlands and rivers and can hardly be observed outside such environments. Nine families, in three orders, contain species of this type in the basin, being six species of the family Tyrannidae the richest ones (Table 3).

2.2 Distribution Along the Suquía River Basin

As mentioned previously (Sect. 1), from the headwaters in the highlands of the Sierras Grandes at 1,900 m.a.s.l. to the mouth in Mar Chiquita, a saline lake at 70 m. a.s.l., the Suquía River runs through markedly different regions (Fig. 1). The upper portion of the basin is part of a highland plateau dominated by grasslands interspersed with rocky outcrops (locally named 'Pampa de Achala'), where the headwaters flow as small streams. The flat topography in this region makes watercourses flow at a low speed and allows the formation of small wetlands with palustrine vegetation. These wetlands are inhabited by some birds that colonised them from lowland regions, as the plumbeous rail (*Pardirallus sanguinolentus*) and the sedge wren (*Cistothorus platensis*). Instead, birds like the Córdoba cinclodes (*Cinclodes comechingonus*), the white-winged cinclodes (*C. atacamensis schocolatinus*) and the Olrog's cinclodes (*C. olrogi*), which travel along the rocky banks of streams, searching for small aquatic invertebrates, are endemic to the highlands of the mountains of Central Argentina [22]. Two species, the buff-necked ibis (*Theristicus caudatus*) and the tawny-throated dotterel (*Oreopholus ruficollis*), inhabit the humid grasslands near streams and constitute biogeographic singularities since they belong to local, isolated breeding populations, separated by hundreds or even thousands of kilometres from the nearest breeding populations in the lowlands of Eastern Argentina and Patagonia, respectively [22, 26]. The cast of grassland birds is completed with the widely distributed southern lapwing (*Vanellus chilensis*), as common here as in the lowlands.

Table 2 Aquatic birds sensu stricto in the Suquía River basin

Order	Family	Species
Anseriformes	Anhimidae	*Chauna torquata*
	Anatidae	*Coscoroba coscoroba*
		Cygnus melancoryphus
		Dendrocygna bicolor
		Dendrocygna viduata
		Anas bahamensis
		Anas cyanoptera
		Anas discors
		Anas flavirostris
		Anas georgica
		Anas platalea
		Callonetta leucophrys
		Amazonetta brasiliensis
		Netta peposaca
		Oxyura vittata
		Nomonyx dominicus
Podicipediformes	Podicipedidae	*Podicephorus major*
		Podilymbus podiceps
		Rollandia rolland
Phoenicopteriformes	Phoenicopteridae	*Phoenicoparrus andinus*
		Phoenicoparrus jamesi
		Phoenicopterus chilensis
Suliformes	Phalacrocoracidae	*Phlacrocorax brasilianus*
Pelecaniformes	Ardeidae	*Ardea cocoi*
		Ardea alba
		Egretta thula
		Bubulcus ibis
		Butorides striata
		Nycticorax nycticorax
		Syrigma sibilatrix
		Tigrisoma lineatum
	Threskiornithidae	*Plegadis chihi*
		Phimosus infuscatus
		Theristicus caudatus
		Platalea ajaja
Gruiformes	Aramidae	*Aramus guarauna*
	Rallidae	*Aramides cajanea*
		Pardirallus sanguinolentus
		Gallinula galeata
		Gallinula melanops
		Porphyrio martinicus
		Fulica armillata
		Fulica leucoptera
		Fulica rufifrons

(continued)

Table 2 (continued)

Order	Family	Species
Charadriiformes	Charadriidae	*Vanellus chilensis*
		Pluvialis dominica
		Pluvialis squatarola
		Charadrius semipalmatus
		Charadrius collaris
		Charadrius falklandicus
		Charadrius modestus
		Oreopholus ruficollis
	Recurvirostridae	*Himantopus mexicanus*
	Scolopacidae	*Gallinago paraguaiae*
		Limosa haemastica
		Bartramia longicauda
		Tringa melanoleuca
		Tringa flavipes
		Tringa solitária
		Calidris alba
		Calidris fuscicollis
		Calidris bairdii
		Calidris melanotos
		Calidris himantopus
		Tryngites subruficollis
		Phalaropus tricolor
	Jacanidae	*Jacana jacana*
	Rostratulidae	*Nycticryphes semicollaris*
	Stercorariidae	*Stercorarius parasiticus*
	Laridae	*Chroicocephalus maculipennis*
		Chroicocephalus cirrocephalus
		Larus atlanticus
		Larus dominicanus

Downstream from Pampa de Achala, watercourses become faster as the slope becomes steeper. The aquatic birds at these sites are limited to the backwaters, where fish, tadpoles and invertebrates are caught by Neotropic cormorants (*Phalacrocorax olivaceous*), snowy egrets (*Egretta thula*) and striated herons (*Butorides striata*). Among ducks, the speckled teal (*Anas flavirostris*) is by far the most common in this region. In some sites, the cliffs over rivers, both rocky and gravelly, are utilised for nesting by the Speckled Teal, the buff-necked ibis and the ringed kingfisher (*Megaceryle torquata*), together with several nonaquatic species (not listed in Tables 2 and 3) like the peregrine falcon (*Falco peregrinus*) and the introduced rock dove (*Columba livia*). In this section of the basin, several reservoirs of variable dimensions add a previously non-existent feature to the original

Table 3 Other birds dependent on aquatic environments in the Suquía River basin

Order	Family	Species
Accipitriformes	Pandionidae	*Pandion haliaetus*
	Accipitridae	*Rostrhamus sociabilis*
Coraciiformes	Alcedinidae	*Megaceryle torquata*
		Chloroceryle amazona
		Chloroceryle americana
Passeriformes	Furnariidae	*Cinclodes fuscus*
		Cinclodes comechingonus
		Cinclodes olrogi
		Cinclodes atacamensis
		Phleocryptes melanops
	Tyrannidae	*Serpophaga nigricans*
		Pseudocolopteryx dinelliana
		Tachuris rubrigastra
		Lessonia rufa
		Hymenops perspicillatus
		Fluvicola pica
	Hirundinidae	*Tachycineta leucorrhoa*
		Riparia riparia
		Petrochelidon pyrrhonota
	Troglodytidae	*Cistothorus platensis*
	Thraupidae	*Sporophila collaris*
		Sporophila hypoxantha
	Icteridae	*Amblyramphus holosericeus*
		Agelasticus thilius
		Chrysomus ruficapillus

landscape. These deep waters were colonised mainly by Neotropic cormorants, great grebes (*Podicephorus major*) and pied-billed grebes (*Podilymbus podiceps*). At the mouths of rivers, the marshy vegetation thrives and birds like the red-gartered coot (*Fulica armillata*), the white-winged coot (*F. leucoptera*) and some ducks are commonly associated with it.

When the river reaches the lowlands, it becomes very sinuous and forms a broad alluvial plain, with marshes and small lagoons as associated wetlands (lower basin, downstream from Córdoba City, Fig. 1). The aquatic avifauna is richer than in the previous regions. Besides Neotropic cormorants, snowy egrets and striated herons, other piscivorous birds, such as the great egret (*Ardea alba*) (Fig. 4) and the beautiful cocoi heron (*A. cocoi*), are frequently observed along the river. The lagoons exhibit a great spatial heterogeneity, and several distinct habitats (open deep waters, shallow waters, reed beds, floating plants and humid grasslands) allow the coexistence of a diverse fauna of birds. Thus, open deep waters are mainly frequented by the pied-billed grebe, the white-tufted grebe (*Rollandia rolland*), the white-cheeked pintail (*Anas bahamensis*), the lake duck (*Oxyura vittata*), the rosy-

Fig. 4 Great egret (*Ardea alba*)

billed pochard (*Netta peposaca*), the red-gartered coot and the white-winged coot, whereas shallow waters are visited by several egrets and herons, the white-faced ibis (*Plegadis chihi*), the southern screamer (*Chauna torquata*) and the black-necked stilt (*Himantopus mexicanus*). The red-fronted coot (*Fulica rufifrons*), the common gallinule (*Gallinula galeata*) and the spot-flanked gallinule (*G. melanops*) swim through the dense reeds, whereas the plumbeous rail prefers walking, pushing through them. The limpkin (*Aramus guarauna*) and the snail kite (*Rostrhamus sociabilis*) search for amphibious snails that lay their eggs on the reeds. Reedbeds are also inhabited by a diverse fauna of small birds that eat and nest in them, like the wren-like rushbird (*Phleocryptes melanops*), the many-coloured rush tyrant (*Tachuris rubrigastra*) and the yellow-winged blackbird (*Agelasticus thilius*). Finally, floating plants are the substrate for the specialised wattled jacana (*Jacana jacana*), while humid grasslands are the home of the South American painted-snipe (*Nycticryphes semicollaris*), the South American snipe (*Gallinago paraguaiae*) and the whistling heron (*Syrigma sibilatrix*).

In its final section, the Suquía River is divided into two branches, both of which flow into the Mar Chiquita Lake (lower section, Fig. 1). Several small lagoons near the mouths harbour an avifauna similar to the one described above, while in the mouth itself, the silty beaches are exploited by a great number of shorebirds species, both permanent and migratory. The collared plover (*Charadrius collaris*) is one of the few breeding permanent species, together with the two-banded plover (*C. falklandicus*), which have an isolated breeding population in Mar Chiquita [27], a thousand kilometres away from the nearest breeding population in Patagonia and, thus, constituting another biogeographic singularity. The rufous-chested dotterel (*C. modestus*) can be observed in winter as coming from Patagonia, but the vast majority of species arrive from North America in spring, being the Wilson's phalarope (*Phalaropus tricolor*), the greater yellowlegs (*Tringa melanoleuca*), the lesser yellowlegs (*T. flavipes*), the white-rumped sandpiper (*Calidris fuscicollis*), the Baird's sandpiper (*C. bairdii*) and the pectoral sandpiper (*C. melanotos*) the most common ones. The brackish waters in estuaries are used by the Chilean flamingo (*Phoenicopterus chilensis*) for feeding, and they are visited in winter by the Andean flamingo (*Phoenicoparrus andinus*) and the James's flamingo (*P. jamesi*), which come from their breeding grounds in the Andean puna. As beautiful as flamingos are the black-necked swans (*Cygnus melancoryphus*) and the coscoroba swan (*Coscoroba coscoroba*), which, together with the brown-hooded gull (*Chroicocephalus maculipennis*) and the grey-hooded gull (*C. cirrocephalus*), prefer deeper waters near the mouths.

2.3 Anthropic Factor Influencing the Occurrence of Waterbirds in the Basin

Contamination and deforestation are the main pressures on the biota of the Suquía River Basin. The headwaters in the upper section of the basin are the more pristine habitats; however, overgrazing magnifies water erosion, leading to an increase in the sediments transported towards the lower sections of the basin. When these nutrients reach the San Roque Reservoir, they get combined with sewage from Carlos Paz city, causing an increase in the densities of bacteria and algae, with occasional blooms, whose toxins are dangerous to all living beings, including waterbirds. Nevertheless, the main sources of contamination of the Suquía River are the industrial activities and sewage discharges of Córdoba City. Some data indicate a great reduction in richness, abundance and diversity of aquatic birds in the river in Córdoba city when compared to sections upstream and downstream [20]. This reduction, however, is also influenced by others anthropic disturbances, as the presence of homes and busy routes close to the river and the reduction in the cover of riparian vegetation. In any case, the community composition was quite different between the sections' upstream and downstream of the city, with predominance of piscivorous species upstream from the city and of invertivorous species downstream from the city, probably reflecting a rise in invertebrate abundance and a decline of fish as a consequence of pollutants in the water [20].

Deforestation was widespread in all plains of the centre and east of the Province of Córdoba, including the Suquía River Basin. The remnant forest fragments are dispersed throughout the plains, the riparian zones of the river and the associated lagoons. These forests form a corridor that allows the penetration from the North of aquatic birds, typical of subtropical areas. In this way, in the lagoons near Río Primero city, it is possible to observe species such as the Brazilian teal (*Amazonetta* *brasiliensis*), the rufescent tiger heron (*Tigrisoma lineatum*) and the purple gallinule (*Porphyrio martinicus*), all of them common and widespread in Northern and Eastern Argentina but rare in Córdoba. Finally, in lagoons close to Córdoba City (downstream, in Chacra de la Merced, Fig. 1), species like the bare-faced ibis (*Phimosus infuscatus*) are observable.

3 Aquatic Macroinvertebrates

Rivers are dynamic systems where communities respond spatially and temporally to the interaction between external factors, determined by their drainage basin, and internal factors, defined by the riverbed and valley characteristics [28]. According to the size and type of lotic environment, these factors generate a noncontinuous mosaic of biotic and abiotic conditions at the temporal and spatial levels [29], which determines the distribution of the populations, especially those related to the bottom of the river [30].

The biological quality of rivers can be evaluated through the biotic communities they harbour. Macroinvertebrates, particularly insects, are an important component of both biodiversity and the functioning of freshwater ecosystems [31]. Several authors studied the communities of aquatic invertebrates in lotic environments in the Province of Córdoba, considering different aspects such as distribution and ecology [32–36]. Regarding the Suquía River, the most comprehensive studies were approached by Mangeaud [37].

Here, the relative composition in phyla and orders of the macroinvertebrate community is similar to other rivers in the central region of Argentina. Even though the number and abundance of the taxa differ, its comparable to rivers in other regions but under arid or semi-arid climates. Along the basin, a total of 51 taxa were recorded distributed in six phyla, nine classes and 41 families (Table 4), with diversity (H') values ranging from 0.8 to 3.2 in different points. Diversity and number of taxa increase from the headwaters to the mouth, and when contaminants enter the basin, these variables decrease.

In the entire basin, Arthropoda is well represented (more than 88%), followed by Annelida and Mollusca with much lower relative abundances (8% and 2%, respectively). In the basin sites considered as contaminated (mainly downstream from cities), a higher proportion of Annelida and a decreased proportion of Arthropoda is observed, which might be possible since the first group is more tolerant to pollution. The non-polluted sites mark the general tendency of the basin.

Insecta is the most numerous group of macroinvertebrates in the Suquía River, with 37 recognised Families of benthic insects, belonging to eight orders, and constituting about 99% of the arthropods of the watershed. Diptera is the order with the highest abundance (more than 50% of the benthos abundance), followed by Ephemeroptera (33%), Trichoptera (10%) and Coleoptera (4%). Such composition varies in the different subbasins of the upper section (Fig. 1) with small changes in the community structure, but more important ones regarding dominant taxa.

Table 4 Benthos in the Suquía River basin

Phylum	Class	Order	Suborder	Family
Annelida	Hirudinea			Glosiphoniidae
	Oligochaeta			Lumbriculidae
				Naididae
				Tubificidae
Arthropoda	Arachnida	Acarina		Hygrobatidae
	Insecta	Coleoptera		Elmidae
				Dytiscidae
				Psephenidae
				Gyrinidae
				Hidrophilidae
		Diptera		Chironomidae
				Ceratopogonidae
				Dolichopodidae
				Empididae
				Ephydridae
				Psychodidae
				Simuliidae
				Syrphidae
				Tipuliidae
		Ephemeroptera		Baetidae
				Caenidae
				Leptohyphidae
		Hemiptera		Naucoridae
				Notonectidae
				Nepidae
				Corixidae
				Belostomatidae
				Veliidae
		Lepidoptera		Pyralidae
		Neuroptera		Sysiridae
		Odonata	Anisoptera	
			Zygoptera	Coenagrionidae
		Plecoptera		Perlidae
		Trichoptera		Calamoceratidae
				Glossosomatidae
				Helicopsychidae
				Hidrobiosidae
				Hidropsychidae
				Hydroptilidae
				Leptoceridae
				Odontoceridae
				Philopotamidae
				Polycentropodidae

(continued)

Table 4 (continued)

Phylum	Class	Order	Suborder	Family
Crustacea	Malacostraca	Amphipoda		
Mollusca	Gastropoda			Physidae
				Ancylidae
				Hydrobiidae
	Bivalvia			Corbiculidae
				Mytilidae
Platyhelminthes	Turbellaria	Tricladida		Dugesiidae
Nematomorpha	Gordiacea			

Camelobaetidius (Ephemeroptera: Baetidae) seems to be one of the dominant genus upstream in the upper section, but it is poorly represented downstream of the same section of the river. On the other hand, in this last part of the basin, the dominant genus is *Leptohyphes* (Ephemeroptera: Leptohyphidae), while Chironomidae is dominant in all the upper section.

3.1 Distribution Along the Suquía River Basin

Variation in diversity, number of taxa and abundance is observed when the stream order increases and the altitude decreases. Causes of this zonation are given by a complex combination of variables such as current velocity, substrate, stream flow, temperature, dissolved oxygen and nutrients, alkalinity and other chemical factors, as well as interactions with other organisms [37, 38].

The altitude range in which taxa are recorded presents great variability. Hirudinea, Annelida, Chironomidae, Acari, Elmidae, Dytiscidae, *Smicridea* (Trichoptera: Hidropsychidae) and *Leptohyphes*, among others, are well represented in the upper section of the river (from 600 up to 1,800 m.a.s.l.). Even though some taxa like *Leptohyphes*, Hirudinea, *Hydroptila* (Trichoptera: Hydroptilidae) and Dytiscidae present an inverse relationship between abundance and altitude, meaning that, although their optimal conditions come from the middle or lower sections, some individuals are able to tolerate conditions the upper section Another group develops only in the lower or middle sections area, and in the upper section up to 1,000–1,200 m.a.s.l. They are *Protoptila* (Trichoptera: Glossosomatidae), Zygoptera, Anisoptera (Fig. 5), *Nectopsyche* (Trichoptera: Leptoceridae), *Marilia* and Mollusca. A third group only inhabits mainly the middle section: Empididae, *Maruina* (Diptera: Psychodidae) and *Polycentropus* (Trichoptera: Polycentropodidae), while *Ochrotrichia* (Trichoptera: Hydroptilidae) develops in the upper section exclusively above 1,200 m.a.s.l.

Supraspecific groups such as Trichoptera, Leptohyphidae, Ephemeroptera and Mollusca show a significant decrease in abundance in relation to altitude. On the other hand, Coleoptera decreases in abundance when the order of the river

Fig. 5 Dragonfly (*Odonata, Anisoptera*). Scale bar, 3 cm

increases. The abundance of Diptera and Annelida seems unrelated to these two variables.

Plecoptera is known worldwide as a species exclusive of upstream regions since their nymphs depend intimately on cold temperatures to develop [39]. In spite of the appropriate environmental conditions, this Order is poorly represented in Córdoba. Summer droughts can cause significant increases in macroinvertebrates abundance. When this occurs, algae and macrophytes that are attached to the rocky bottom of streams are not removed by summer floods, as is the case with aquatic invertebrates. An abundant layer of plants covers the bottom of streams leading to a great heterogeneity of benthic habitats [40], and the higher the plant biomass, the greater the number of macroinvertebrates [41].

To summarise, benthic macroinvertebrate communities are neither stable nor constant with regard to diversity, number of taxa and abundance in the Suquía River, presenting a great temporal and spatial variability. Community structure becomes more complex in an altitudinal gradient, from up to downstream. In the places where contaminants enter the basin, diversity and number of taxa decrease. Some taxa are more abundant in the upper section, while others increase their abundance in the middle and lower sections. Some others are present along the basin, regardless of altitude. In the upper section there is a limit (1,000–1,200 m.a.s.l.) above which a change in fauna is produced.

3.2 Invasive Bivalves

Invasive species are one of the most significant causes of biodiversity loss and changes in ecosystem services, which underline the importance of their detection and study. Freshwater systems are particularly subject to invasion by exotic invertebrate species, which use water current for dispersion throughout these systems. Among these invertebrates, bivalve molluscs are a group with high potential for invasion: they can develop massive populations in all kinds of fresh waters, consuming microalgae and substantially affecting the amount and composition of primary producers. Interactions radiating out from the primary producers can affect nearly every part of the ecosystem. Their activity also entails habitat modification, competition and extinction. Besides the characteristics of natural ecosystems, they can affect human structures, impeding domestic and industrial water supply infrastructure. Human activity, such as the construction of shipping canals for trade, building of reservoirs for water storage and power production, promotes the spreading of these species and facilitates pulses of spreading which seem to be not continuous [42].

In the last decades, two species of freshwater bivalves have been reported as invasive in inland waters of South America: the golden mussel, *Limnoperna fortunei* (Dunker 1857), and the Asian clam, *Corbicula fluminea* (Müller 1774).

In the case of *Limnoperna fortunei*, its sudden appearance in the Río de La Plata Estuary was first reported at the beginning of the 1990s [43], spreading into Argentina, Uruguay, Paraguay, Bolivia and Brazil. *Corbicula fluminea* started to colonise South America in the 1960s, when the bivalve arrived in Argentina and Brazil, through the Río de La Plata River, and subsequently spread into Venezuela, the northern part of the Pantanal in Southwest Brazil, and lower areas of the Amazon River Basin, among other areas [44]. Nowadays, they are one of the dominant freshwater benthic macrofauna in an area extending from Lake Superior in North America to Patagonia in South America. Such golden mussels and Asian clams have been reported in central Argentina. In Córdoba, their distribution is still scattered, not having been observed, for instance, in the upper reaches of the main rivers and reservoirs. It is estimated that their distribution will be more extensive in the case of species with a wide range of physiological tolerance and adaptability to different environments.

The mechanism that enabled the introduction of invasive bivalves in the Suquía River and other basins of central Argentina is uncertain, since they are geographically disconnected from the arrival area. Thus, the accidental introduction by human activities is the most probable cause. They are successful invaders that can be dispersed through natural means over large areas in a short time. Through their larvae, they could spread into reservoirs connected to the arrival area and from there, to other rivers and reservoirs like the San Roque Reservoir, most probably transported in hulls of boats for recreational or fishing purposes.

The systematics of *Corbicula* is controversial and especially the study of lineages in the New World, where three morphotypes have been distinguished. These are forms A and B, present throughout the continent, and form C, only present in South America and known as *C. largillierti*. According to Lee et al. [45], there are hybrids between the different forms. Pfenninger et al. [46] proposed that different lineages of *Corbicula* may be an initial state of a group of species rather than a defined species. Morton [47] considered that the observed variability could correspond to a single species. Following the analyses of different outer and inner characters suggested by previous authors [48–50], Reyna et al. [51] reported the presence of two corbiculid species, *C. largillierti* and *C. fluminea* in the Suquía River Basin. Among the previously reported characters, rib number was useful to differentiate the two species. Besides, conventional and geometric morphometric analyses to assess inter- and intraspecific differences in shell shape revealed a clear morphometric differentiation between *C. fluminea* and *C. largillierti* (Morán et al. in prep) (Fig. 6).

When present in high abundance, *L. fortunei* produces occlusions in piping systems, such as pipes or hoses, as well as in bars, turbines and water intakes with imaginable consequences. They can also affect the speed of vessels due to a loss in hydrodynamics. In all cases, a necessary step then is to spread the problem to take preventive measures. The invasions of freshwater molluscs are a real problem in different areas of the world: in the Northern Hemisphere, the zebra mussel

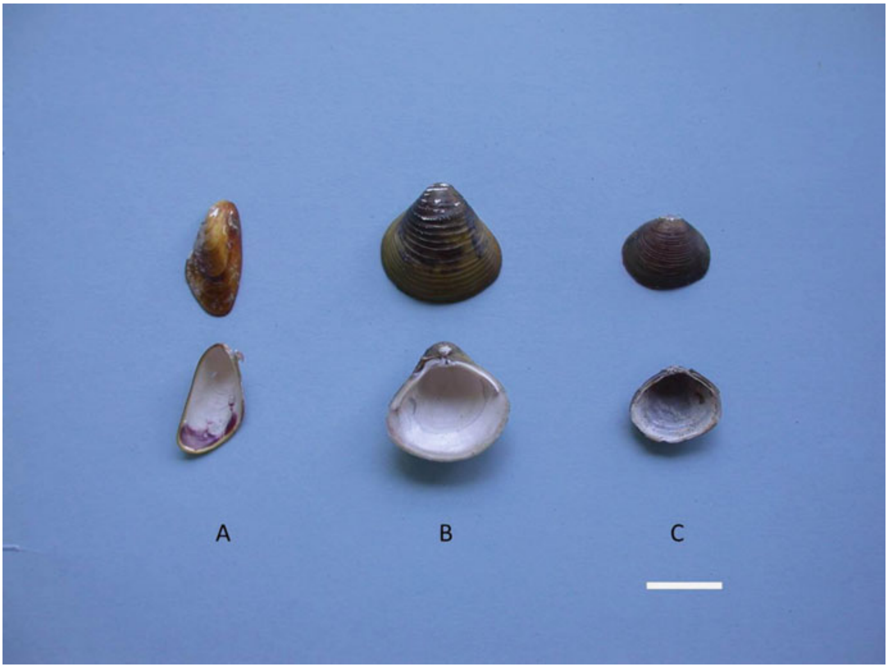

Fig. 6 Inner and outer sides of shells from different bivalves. (**a**) *Limnoperna fortunei;* (**b**) *Corbicula fluminea*; (**c**) *C. largillierti*. Scale bar, 3 cm

Dreissena polymorpha produces similar effects as the golden mussel. In the United States, the use of aggregates with abundant dead *Corbicula fluminea* shells in the construction business caused the weakening of concrete structures. From an ecological perspective, the filtering capacity of freshwater molluscs (necessary for the feeding activity) causes a decrease in the turbidity of water bodies since they eat phytoplankton and particulate matter in general, and their droppings can be an important part of the nutrient cycling. While the golden mussels are typically epifaunal animals that normally attach themselves to hard substrates through byssal threads, the Asian clams are infaunal species. In both cases, they potentially constitute a substrate competitor for other species, since they can colonise large areas. Although native bivalves are present in other areas of Argentina (i.e. clams *Cyanocyclas* and *Anodontites*), none were reported in the Suquía River. So far, the vector of parasites that affects human health or other species is unknown. In other close areas, certain species of birds and teleost fish, such as *Pterodoras granulosus* and *Leporinus obtusidens*, predators of clams and mussels, respectively [44], can constitute natural controls for mollusc populations.

Strategies for the prevention and control of mollusc populations must be adapted to each circumstance, because once they appear, they are difficult to eliminate. Regular cleaning or the use of anti-fouling paints on the hulls of boats used for recreational or fishing purposes may limit accidental spillage. Other uses of these organisms, such as fishing bait or aquarium, should be avoided. In closed systems, biocides (chemicals), temperature or salinity alteration can be used. In natural environments, the control of these factors becomes difficult, and the predator action is limited. For this reason, the most effective method is manual removal.

Bivalve density varies with substrate type: while golden mussels typically attach themselves to natural and artificial hard substrates, clams bury themselves in sediments, preferably in sandy substrates. However, *C. fluminea* can colonise a wide variety of substrates: rocks, gravel, boulders, sand and clay. Darrigran [52] found that in environments with a substrate composed of silt sediment, *C. largillierti* dominates over *C. fluminea*.

Other parameters, such as fluctuation in water level and contamination, can also determine the presence and density of these animals and produce alterations in their population structure. Given the particular characteristics of the Suquía River Basin, i.e. presence of diverse substrate types, fluctuations in the flow regime and the impact of human activities, the presence, distribution and density of invasive bivalves vary throughout this extensive area.

Making a first diagnosis on the status of the invasion of corbiculids in the Suquía River Basin, Reyna et al. [51] studied their distribution and density at different sites. Variations in population structure (density, biomass, spatial distribution and size classes) during a whole year were also studied in Córdoba city. Results of that study revealed that *C. fluminea* is restricted to a lentic environment (the San Roque Reservoir), apparently coexisting with *C. largillierti*, although only empty shells of this latter species have been found in this site. In rivers and brooks, only *C. largillierti* was detected. The absence of living specimens and the presence of empty shells in diverse sites could be due to the water dynamics and flow, which depend on rainfall that mostly occurs during summer time in the Southern Hemisphere (from November to March). The reduction of the river flow during the dry winter season exposes the sandbanks where molluscs live buried and causes their death. The species *C. largillierti* showed variations in average density between the different sites and also variations in biomass and size classes throughout the year period. The average density of 302 ind./m^2observed in Córdoba city was similar to the density observed in a tributary lentic environment of the Río de La Plata Basin (459 ind./m^2 [52]), but it was considerably less than the mean density of *Corbicula* observed in the Río de La Plata Basin (2.5 ind./m^2 [53]). A great number of medium-sized animals were found in Córdoba city during the year period. As stated by Boltovskoy et al. [54], the absence of small and large-sized individuals and the high density of medium-sized individuals may be caused by contamination, affecting the larvae and preventing the growth of individuals. This site is located in Córdoba city, where the river is flanked on both sides by frequently used highways and is connected to the city rainwater channels, through which garbage and sewage waters are illegally introduced.

Darrigran [52] found *Corbicula* in lentic environments, with *C. fluminea* restricted to shallow, well-oxygenated coastal waters. Besides, abundant populations of *C. fluminea* were detected in the headwaters of micro-basins and rivers with a stronger flow [55]. The distribution of *C. fluminea,* restricted to the San Roque Reservoir, within the Suquía River Basin is surprising, considering the wide, rapid spread of this species in other areas. On the other hand, *C. largillierti*, which was distributed in most of the sampling sites along the Suquía River, was restricted to a few sites in Argentina [52, 56]. That species seems to be better adapted to brook environments. The absence of *Corbicula largillierti* downstream of Córdoba city (31° 25′50″S/64°01′57″W) could be due to high contamination. The accumulation of city garbage and agricultural pesticides, sewage discharge (WWTP) of Córdoba city at Bajo Grande with low oxygen levels (5 ± 2.1 mg l^{-1}) detected in that area [57] are probable stress conditions. They would limit the survival of juvenile and adult bivalves and, therefore, their dispersion from the upper to the lower basin. Studies on the potential distribution and the influence of contamination are necessary in order to comprehend the processes structuring changes along the Suquía River.

4 Aquatic Plants

Despite having conquered the land, some vascular plants have ventured back into fresh waters: it is estimated that they represent ca. 1% of the angiosperms and 2% of the pteridophytes, according to how strictly an aquatic plant is defined. Since plants from aquatic environments have a diversity of habitats and plasticity, it is difficult to determine a biological classification for such a heterogeneous group. However, a more generalised scheme divides them into the following categories [58–60]:

Hydrophytes or Strictly Aquatic Plants They live in the water or on a substrate that is at least periodically anaerobic due to water excess, and they can be: (a) Emergent (11 genera and 19 species in the Suquía River): they are attached to submerged soils where the water depth is 50–150 cm, mainly rhizomatous perennials, usually with heterophylly, and all producing aerial reproductive organs; (b) Submerged (7 genera and 11 species): they grow on submerged soils at a water depth of ± 10 m, leaves are usually filiform and totally submerged, and reproductive organs may be submerged, floating or aerial; (c) Floating (6 genera and 9 species): they grow mainly in sheltered sites and are typically unattached, very diverse in life forms, reproductive organs floating or aerial (rarely submerged).

Riparian (ca. 87 genera and 162 species in the Suquía River): They are completely terrestrial plants but require a high level of soil moisture, which they find on river banks. Plants have been classified by their presence in riparian areas as obligate riparian, facultative riparian and non-riparian, with some variations according to the author [61, 62].

A riparian area is the one that is adjacent to or directly influenced by a water body. Riparian means ‘belonging to the bank of a river’; therefore, it refers to biotic communities living on both sides of rivers, streams or lakes [63, 64]. Riparian areas usually maintain a high biodiversity of flora and fauna compared to other areas, working in many cases as a shelter for vulnerable species of both, plants and animals. Species richness of herbaceous plants is usually greater in the zone adjacent to the stream bank than in other zones, and species composition of herbaceous plants is statistically different from more distant zones [65]. These areas provide habitat for rich wildlife, since they function as corridors among vegetation patches in fragmented landscapes [66, 67]. Riparian areas are generally fertile and productive, with high soil quality, and are the last line of defence for the protection of water quality and aquatic ecosystems [68, 69].

Riparian vegetation is unique and different, being generally higher, denser and structurally more complex than the surrounding vegetation [68]. Microclimate in most cases is moister. The shadow produced by the riparian vegetation is critical for fluctuations in water temperature and amount of sunlight, affecting the growth of plants that live along the streams, and consequently, fish and vertebrates that feed on them [68].

Another characteristic of riparian areas is the excess of sediment and nutrients, mainly phosphorus and nitrogen from crop areas. The main functions of a riparian forest are to slow and reduce runoff by using the excess of nutrients, trapping sediments and other pollutants that flow from bare soil or crop land, protecting water bodies, and also enhancing infiltration [68].

The composition and amount of vegetation in riparian areas differ from terrestrial upland vegetation. These differences reflect the influence of water from the adjacent water body, primarily in terms of increased soil moisture in the riparian areas. At the same time, rivers or sections of a river can be characterised according to the slope as: torrential upper, swift middle and sluggish lowland. In the case of the Suquía River, two sections could be distinguished: a first one, before crossing the ravine above Bamba, where the river runs through the Pampean Hills (Sierras Grandes and Sierras Chicas), and a second one that begins when the river enters the Córdoba peneplain, where most of the city of Córdoba is located (Fig. 1). When the Suquía River leaves the city, it is already a typical lowland river. At the upper end of the Suquía River basin, riparian vegetation has elements of the Chaco Serrano biogeographical district, in which it is embedded [70, 71]. The tree stratum includes non-riparian species like *Schinus areira*, *Manihot grahamii*, *Celtis ehrenbergiana*, *Acacia* spp., *Prosopis* spp., *Zanthoxylum coco* and *Lithraea molleoides*, but there are also exotic species growing in the riverbanks, like *Salix babylonica*, *Acer negundo*, *Gleditsia triacanthos*, *Melia azedarach*, *Ligustrum lucidum*, *L. sinense*, *Morus alba*, *Fraxinus pennsylvanica* and *Ulmus* spp., which exploit the water availability and shelter of this habitat. *Rubus* spp. and *Ligustrum lucidum* are particularly troublesome and considered as dangerous invasive plants [71, 72]. A few native riparian tree species (both obligate and facultative) are dominant: *Salix humboldtiana*, *Sapium haematospermum* and *Sebastiania commersoniana*. When the river enters the peneplain, tree species become less frequent, being shrubby or herbaceous the dominant plants. Within the herbaceous stratum, the Poaceae, with 20 genera (e.g. *Cynodon*, *Eragrostis*, *Paspalum*) and ca. 45 spp. are remarkable in the Suquía Riverbank. Outstanding representatives of this family are the showy "Pampas grasses" (*Cortaderia* spp.) which beautify the landscape. Cyperaceae (e.g. *Carex*, *Cyperus*, *Eleocharis*, *Bulbostylis*, *Fimbristylis*) is also important because of its species number, while within the dicots, the Plantaginaceae (e.g. *Plantago*, *Bacopa*, *Stemodia*, *Veronica*) and many other species scattered among several families (Caryophyllaceae, Lamiaceae, Brassicaceae, Asteraceae, Apiaceae, etc.) are also worth mentioning.

Rivers have a relative constant flow; they drain a great variety of rocks and encounter geological irregularities and artificial obstacles which progressively modify their course and chemical composition, introducing a multitude of local peculiarities. As a result, it is difficult to characterise a single river as a whole. As mentioned above, slope is important in determining the type of plant communities along the river, but there are also micro-environmental variations which are very significant for the development of the Flora [59]. Among the main factors affecting the plant communities composition and the penetration of rooted vegetation are:

(a) Light transmission in the water. The depth at which the limiting intensity is reached varies from site to site, according to the colour of the water (due to dissolved organic matter), the concentration of suspended particles, and the amount of phyto- and zooplankton. These factors may interact with each other and vary seasonally. Aquatic plants can be used to indicate water ecological conditions because some of them are perennial and integrate periodic changes in water clarity and nutrient status, which are reflected in the depth that plants grow down [73]. That is why in the Suquía River some plants (as *Utricularia gibba* or *Limnobium laevigatum*) can only be found in certain intact micro-habitats.

(b) Water temperature: fluctuations of temperature in aquatic habitats are generally much less pronounced than in aerial environments, and are partially responsible for the extensive geographical range of many hydrophytes of all life forms. Some genera, such as *Myriophyllum* (submerged, Haloragaceae), *Lemna* (floating, Lemnaceae) and *Echinocloa* (emergent, Poaceae) are cosmopolitan. In fact, *Lemna gibba* and *Echinochloa colona* are worldwide spread species that can be found in the Suquía River.

(c) Dissolved substances (including organic and inorganic nutrients, salts, oxygen and toxic compounds) have a notable influence on the developments of aquatic plants. Rooted emergent species obtain nutrients exclusively from substrate, whereas submerged ones may absorb ions from both, the substrate and the water. Floating species must obtain all their nutrients from water. Although some species seem to be generalists, there are some others in which the general water chemistry controls whether they can grow or not [59, 74].

4.1 Distribution Along the Suquía River Basin

The distribution of aquatics is intriguing. Although about 40% of the known aquatic plants display relatively small ranges confined within the limits of a single continent or major land mass, there are several plants that are worldwide spread, and about 25–30% are endemic [59]. South America seems to be relatively rich in endemics and poor in widespread hydrophytes. The general picture of their status and distribution with regard to the Suquía River is as follows:

(a) Extensive hydrophytes. Mostly monocots (emergent, submerged and floating), some of them are among the most widely distributed of all vascular plants. Present in the Suquía River are: *Lemna gibba*, *Phragmites* spp., *Zannichellia palustris*, *Phalaris* spp., *Bacopa monnieri*, *Cyperus digitatus*, *C. esculentus*, *C. rotundus*, *Echinochloa colona*, *E. crus-galli*, *Leersia hexandra*, *Pistia stratiotes* and *Utricularia gibba*.

(b) Hydrophytes with continental ranges. The majority of aquatic plants fall within this category and they have representatives of all life forms. Some of the most remarkable South American aquatic plants that are present in the Suquía River are *Echinodorus grandiflorus*, *Elodea callitrichoides*, *Sagittaria montevidensis*, *Potamogeton* spp., *Stuckenia* spp., *Heteranthera* spp., *Marsilea ancylopoda*, *Bulbostylis* spp., *Eleocharis bonariensis*, *Equisetum giganteum*, *Ludwigia uruguayensis*, *Myriophyllum quitense*, *Schoenoplectus californicus*, and *Wolffia brasiliensis*.

(c) Endemics. By endemism is meant the possession of a remarkable confined geographical range, clearly smaller than the average for related species. The term is usually applied in a comparative sense and there is an appreciable element of arbitrary choice in its use. Since aquatic plants are generally more sporadic than terrestrials, the concept of endemic in this case is narrower.

There are several species of aquatic plants endemic to Argentina or Southern South America, but just a few reach the Suquía River: *Egeria densa* (submerged), *Hydrocotyle modesta* (emergent) (Fig. 7), *Cerastium rivulariastrum*, *Poa ligualris* var. *resinulosa*, *Sesbania punicea* and *Cyperus meridionalis* (riparian species). Finally, there are two more riparian species, exclusive to Central Argentina, which can be found in the banks of the Suquía River: *Carex bonariensis* var. *glabrescens* and *Cerastium argentinum*.

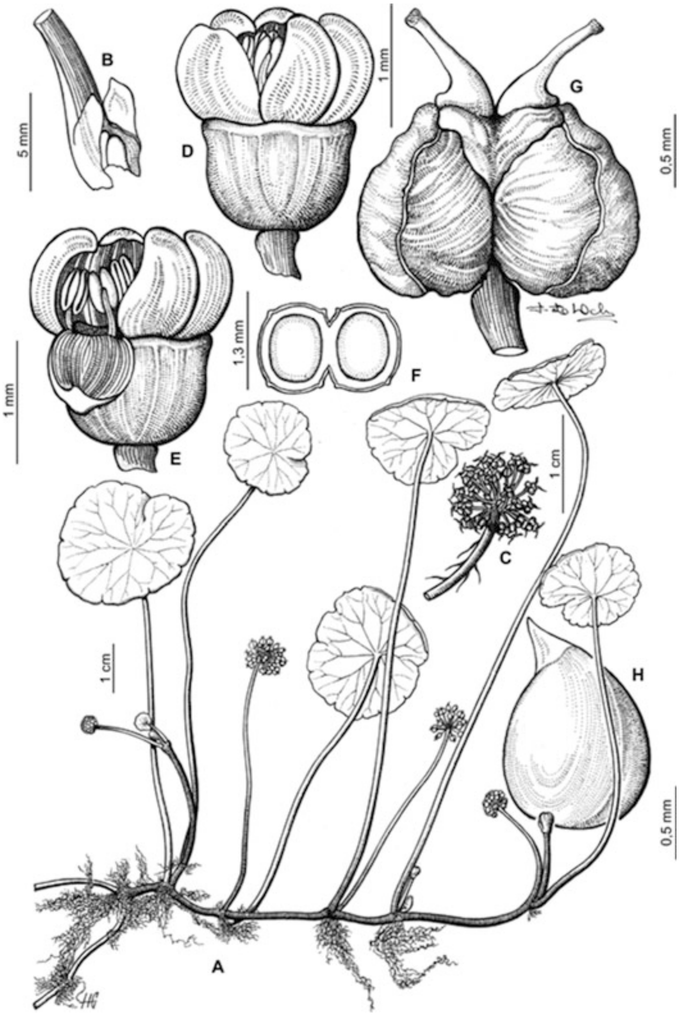

Fig. 7 *Hydrocotyle modesta* Cham. & Schltdl. (**a**) Habit. (**b**) Stipules. (**c**) Inflorescence. (**d**, **e**) Flower. (**f**) Fruit, transverse section. (**g**) Fruit. (**h**) Seed. With the permission of Museo Botánico de Córdoba

(d) Exotics, invasive plants or weeds. Like all other ecosystems, aquatic environments are susceptible to invasion by exotic (alien or non-indigenous) species. Exotic species are entities from one part of the world that are transported beyond their natural range and become established in a new area. Categories within exotic species are difficult to establish because of the lack of consensus and inaccuracy of terms [75, 76]. When exotic plants reproduce outside cultivation, maintaining populations over several generations without direct human intervention, but without adverse effects on the invaded habitat, they are considered as 'adventive' or 'naturalised'. On the contrary, invasive plants or weeds are usually understood as exotic plants that produce new breeding individuals in large numbers, inducing significant changes in the structure, composition and functioning of ecosystems [75, 76]. Among the plants of aquatic environments, the list of species recognised as weeds is long and includes all life forms, but the most severe problems are caused by stoloniferous free-floating species, since they form large impenetrable colonies which block drainage channels and hydroelectric installations and compete with local species [59]. For the Suquía River, *ca*. 50 exotic species are recorded, among riparian, emergent, submerged and floating. Some of them are important for causing serious problems in other parts of the world: *Alternanthera philoxeroides*, *Cyperus esculentus*, *C. rotundus* and *Pistia stratiotes*. However, they seem not to be proliferating too much in the area. *Eichhornia crassipes*, an aquatic weed with critical importance over the world, has been recorded once in the river, but apparently its presence was occasional and the species would not be propagating. On the contrary, an invasive plant always associated with river banks that is present in the margins of the Suquía River is *Gleditsia triacanthos*, a tree which grows rapidly, replacing the natural vegetation [77].

4.2 Systematics

Within vascular plants, a few families consisting exclusively of hydrophytes (ca. 30) are observed. They are small families, each one with less than ten genera, and most of them being monotypic or with a few species. Only Podostemaceae (absent in Córdoba) and Haloragaceae have more than 100 species (two in the Suquía River). By contrast, there are many more hydrophytes, too numerous to list fully, scattered throughout other terrestrial families of ferns and angiosperms.

Considering the plants of the entire Suquía ecosystem (the river itself and the banks), there are 49 families with ca. 200 species recorded, including emergent, submerged, floating and riparian. Overall, the most important family is Poaceae, with 23 genera and 46 species, followed by Cyperaceae, with six genera and 30 species. The remaining records are scattered among several families, each one with few representatives. Strictly considering aquatic plants, the Suquía River satisfies the general rule that the majority of species are Monocots: 11 families with 30 species, out of a total of 18 families with 40 species. The remaining species are dicots, with the exception of *Marsilea ancylopoda* and *Azolla filiculoides* (ferns). *Floating* life form is dominated by two families of exclusively aquatic plants, Lemnaceae (5 spp.) and Pontederiaceae (2), but at the same time, *A. filiculoides* and *Pistia stratiotes*, which are native to South America but probably alien to the Suquía Basin, also live in the river. *Submerged* life form is also dominated by two exclusively aquatic families, Potamogetonaceae (with 6 spp.) and Hydrocharitaceae (with 3 spp.), but *Utriculariagibba* (Lentibulariaceae) and *Zannichellia palustris* (Zannichelliaceae) are also present. Finally, *Emergent* species reach a total of 19, scattered among 10 families, but the genus *Juncus* (Juncaceae) is remarkable for having the highest number of species (6).

References

1. Hued AC, Bistoni MA (2007) Abundancia y distribución de la fauna íctica en la cuenca del río Suquía (Córdoba, Argentina). Iheringia Ser Zool 97:286–292
2. Ringuelet RA, Aramburu RH, Alonso de Aramburu A (1967) Los peces Argentinos de agua dulce, Com. Inv. Cient. Prov. Buenos Aires, La Plata, 602 pp
3. López H, Menni R, Donato M, Miquelarena A (2008) Biogeographical revision of Argentina (Andean and Neotropical Regions): an analysis using freshwater fishes. J Biogeogr 35:1564–1579
4. Bistoni MA, Hued AC (2002) Patterns of fish species richness in rivers of the central region of Argentina. Braz J Biol 62:1–12
5. Haro JG, Bistoni MA (1986) Ictiofauna del Río Primero (Suquía) (Córdoba, Argentina). Historia Natural 6:53–63
6. Huet M (1983) Tratado de Piscicultura. Mundi-Prensa, Madrid, 736 pp
7. Hued AC, Bistoni MA (2001) Ictiofauna del río San Francisco-Cosquín en la provincia de Córdoba (Argentina) (Pisces, Osteichthyes). Iheringia Ser Zool 91:75–78
8. Videla M, Bistoni MA (1999) Composición y estructura de las comunidades ícticas de un río serrano a lo largo de un gradiente altitudinal. Iheringia Ser Zool 87:171–180
9. Fernandez HR, Fernandez LA (1995) La biodiversidad del zoobentos en ríos de montaña de Tucumán, la trucha como amenaza. In: Brown AD, Grau HR (eds) Investigación, Conservación y Desarrollo en Selvas Subtropicales de Montaña. Proyecto de desarrollo-forestal, LIEY, Tucumán, pp 149–156
10. Krueger CC, May B (1992) Ecological and genetics effects of salmonid introductions in North America. Can J Fish Aquat Sci 48:66–77
11. Wegryn D, Ortubay S (1991) Nuestros salmónidos. Dirección de Pesca de la provincia de Río Negro, Viedma, 120 pp
12. Ringuelet RA (1975) Zoogeografía y ecología de los peces de aguas continentales de la Argentina y consideraciones sobre las áreas ictiológicas de América del Sur. Ecosur 2:1–151
13. Haro JG, Bistoni MA (2007) Peces de Córdoba. Universidad Nacional de Córdoba, 246 pp
14. Miquelarena A, Protogino L, López H (2005) Astyanax hermosus, for a new speciesfrom primero river basin, Córdoba, Argentina (Characiformes, Characidae). Revue Suisse de Zoologie 112:13–20
15. Richardson DM (ed) (2011) Fifty years of invasion ecology: the legacy of charles elton. Blackwell, Hoboken

16. Haro JG, Bistoni MA (1996) In: Di Tada I, Bucher E (eds) Biodiversidad de la Provincia de Córdoba. Fauna. Córdoba, Argentina. Universidad Nacional de Río Cuarto, Córdoba, pp 169–190
17. Hued AC, Bistoni MA (2005) Development and validation of a Biotic Index for evaluation of environmental quality in the central region of Argentina. Hydrobiologia 543:279–298
18. Reati G, Florin M, Fernandez GJ, Montes C (1997) The Laguna de Mar Chiquita (C6rdoba, Argentina): a little known, secularly fluctuating, saline lake. Int J Salt Lake Res 5:187–219
19. Bucher EH (ed) (2006) Bañados del Río Dulce y Laguna Mar Chiquita (Córdoba, Argentina). Academia Nacional de Ciencias, Córdoba
20. Andrada G (2004) Efectos de diversos disturbios sobre las comunidades de aves acuáticas del Río Suquía en la ciudad de Córdoba. Unpublished Degree Thesis, Universidad Nacional de Córdoba, 39 pp
21. Michelutti P, Torres R (2006) Nuevos registros y comentarios sobre aves acuáticas fuera de su rango de distribución conocido en el centro de Argentina. Nuestras Aves 51:32–34
22. Nores M (1996) Avifauna de la provincia de Córdoba. In: Di Tada IE, Bucher EH (eds) Biodiversidad de la provincia de Córdoba. Fauna, vol I. Universidad Nacional de Río Cuarto, Río Cuarto
23. Nores M, Yzurieta D, Miatello R (1983) Lista y distribución de las aves de Córdoba, Argentina. Boletín de la Academia Nacional de Ciencias, Córdoba 5:1–114
24. Torres R, Michelutti P (2001) Las aves de ambientes acuáticos del sistema Laguna Mar Chiquita – Bañados del río Dulce (provincias de Córdoba y Santiago del Estero, Argentina). Boletín de la Academia Nacional de Ciencias, Córdoba 66:61–73
25. Torres R, Michelutti P (2001) Nuevos registros de aves escasas en la región central de Argentina. Nótulas Faunísticas – Segunda Serie 1:1–5
26. Hancock J, Kushlan J, Kahl MP (1992) Storks, ibises and spoonbills of the world. Academic, London, 385 pp
27. Torres R, Michelutti P (2006) Aves acuáticas. In: Bucher EH (ed) Bañados del río Dulce y Laguna Mar Chiquita. Academia Nacional de Ciencias, Córdoba, pp 237–249
28. Wantzen KM, Rueda-Delgado G (2009) Técnicas de muestreo de macroinvertebrados-bentónicos. In: Domínguez E, Fernández HR (eds) Macroinvertebradosbentónicos sudamericanos. Sistemática y biología. Fundación Miguel Lillo, Tucumán, pp 17–45, ISBN 978-950-668-015-2
29. Wantzen KM, Sá MFP, Siqueira A, Nunez da Cunha C (2006) Stream-valley systems of the Brazilian Cerrado: impactassessment and conservationscheme. AquatConserv 16:713–732
30. Allan JD, Castillo MM (2007) Stream ecology: structure and function of running waters. Springer, New York, 436 pp
31. Barba-Álvez R, De la Lanza-Espino G, Contreras-Ramos A, González-Mora I (2013) Insectos acuáticos indicadores de calidad de agua en México: casos de estudio, ríos Copalita, Zimatán y Coyula, Oaxaca. Rev MexBiodiv 84:381–383
32. Gualdoni CM, Duarte CA, Medeot EA (2011) Estado ecológico de dos arroyos serranos del sur de Córdoba, Argentina. Ecol Austral 21:149–162
33. Gualdoni CM, Oberto AM (1998) Biological quality assessment of the lotic environment of Carcarañá River tributaries (Córdoba, Argentina). VerhInternat Verein Limnol 26:1219–1222
34. Gualdoni CM, Oberto AM (2012) Estructura de la comunidad de macroinvertebrados del arroyo Achiras (Córdoba, Argentina): análisis previo a la construcción de una presa. Iheringia, Série Zoología, Porto Alegre 102(2):177–186
35. Principe RE, Gualdoni CM, Oberto AM, Raffaini GB, Corigliano MC (2010) Spatial-temporal patterns of functional feeding groups in mountain streams of Córdoba, Argentina. Ecol Austral 20:257–268
36. Principe RE, Raffaini GB, Gualdoni CM, Oberto AM, Corigliano MC (2007) Do hydraulic units define macroinvertebrate assemblages in mountain streams of central Argentina? Limnológica 37:323–336

37. Mangeaud A (1998) Macroinvertebrados bentónicos como bioindicadores de la calidad del agua en la cuenca del Suquía, Ph.D. Thesis, Facultad de Ciencias Exactas, Físicas y Naturales, Universidad Nacional de Córdoba, Córdoba, Argentina
38. Vannote R, Minshall G, Cummins K, Sedell J, Cushing C (1980) The river continuum concept. Can J Fish Aquat Sci 37:130–137
39. Roback S (1974) Insects (Arthropoda: Insecta). In: Hart CW, Fuller SH (eds) Pollution ecology of freshwater invertebrates. Academic, New York, pp 313–376
40. Minshall W (1984) Aquatic Insects-substratum relationships. In: Resh VH, Rosemberg DM (eds) The ecology of aquatic insects. Praeger, New York, pp 358–400
41. Campeau S, Murkin H, Titman R (1994) Relative importance of algae and emergent plant litter to freshwater marsh invertebrates. Can J Fish Aquat Sci 51:681–692
42. Karatayev AY, Padilla DK, Minchin D, Boltovskoy D, Burlakova LE (2007) Changes in global economies and trade: the potential spread of exotic freshwater bivalves. Biol Invasions 9:161–180
43. Pastorino G, Darrigran G, Martin SM, Lunaschi L (1993) *Limnoperna fortunei* (Dunker, 1857) (Mytilidae), nuevo bivalvo invasor en aguas del Río de la Plata. Neotropica 39:34
44. Darrigran G (2002) Potential impact of filter-feeding invaders on temperate inland freshwater environments. Biol Invasions 4:145–156
45. Lee T, Siripattawan S, Ituarte C, Foighle D (2005) Invasion of the clonal clams *Corbicula* lineages in the New World. Am Malacol Bull 20:113–122
46. Pfenninger M, Reinhardt F, Streit B (2002) Evidence for cryptic hybridization between different evolutionary lineages of the invasive clam genus *Corbicula* (Veneroida, Bivalvia). Evol Biol 15:818–829
47. Morton B (1986) Corbicula in Asia an updated synthesis. Am Malacol Bull 2:113–124
48. Ituarte C (1994) *Corbicula* and *Neocorbicula* (Bivalvia: Corbiculidae) in the Paraná, Uruguay, and Río de La Plata basins. Nautilus 107(4):129–135
49. Mansur M, Pereira D (2006) Bivalves límnicos da bacia do rio dos Sinos, Rio Grande do Sul, Brasil (Bivalvia, Unionoida, Veneroida e Mytiloida). Revista Brasileira de Zoologia 23 (4):1123–1147
50. Martins DS, Veitenheimer-Mendes IL, Faccioni-Heuser C (2006) Aspectos morfológicos e de incubação em três espécies de *Corbicula* Mühlfeld, no lago Guaíba, Rio Grande do Sul, Brasil (Bivalvia, Corbiculidae). Biota Neotropica 6(2):1–11
51. Reyna P, Morán G, Tatián M (2013) Taxonomy, distribution and population structure of invasive Corbiculidae (Mollusca, Bivalvia) in the Suquía River basin, Córdoba, Argentina. Iheringia, Série Zoología 103(2):77–84
52. Darrigran G (1992) Nuevos datos acerca de la distribución de las especies del género *Corbicula* (Bivalvia, Sphaeriacea) en el área del Río de La Plata, República Argentina. Notas del Museo de La Plata 21(210):143–148
53. Darrigran G (1991) Competencia entre dos especies de pelecípodos invasores *Corbicula-fluminea*, (MÜLLER, 1774) y *C. largillierti* (PHILIPPI, 1844) en el litoral argentino del estuario del Río de La Plata. Notas Científicas de la Segunda Reunión Argentina de Limnología 498:214–215
54. Boltovskoy D, Correa N, Cataldo D, Stripeikis J, Tudino M (1997) Environmental stress on *Corbicula fluminea* (Bivalvia) in the Paraná River Delta (Argentina): complex pollution-related disruption of population structures. Arch Hydrobiol 138:483–507
55. Aroceno R, Chalar G, Fabián D, De Léon L, Brugnoli E, Silva M, Rodó E, Machado I, Pacheco J, Castiglioni R, Gabito L (2008) Distribución y descripción poblacional de moluscos invasores. In: Evaluación Ecológica de Cursos de Agua y Biomonitoreo. Informe final del Convenio DINAMA – Facultad de Ciencias (Sec. Limnología), Uruguay, p 17
56. Torre L, Reyna P (2013) Bivalvia, Veneroidea, Corbiculidae, *Corbicula largillierti* (Philippi, 1844): New distribution record in the Del Valle Central basin, Catamarca Province, Argentina. Check List 9(1):165–166

57. Wunderlin D, Amé M, Pesce S, Hued A, Bistoni M (2001) Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquía River Basin (Córdoba, Argentina). Water Res 35:2881–2894
58. Lovett S, Price P (1999) Riparian land management technical guidelines. In: Principles of sound management, vol 1. LWRRDC, Canberra
59. Sculthorpe CD (1985) The biology of aquatic vascular plants. Edward Arnold, London. Koeltz Scientific Books, Königstein
60. Tiner R (1991) The concept of a hydrophyte for wetland identification. BioScience 41:236–247
61. Johnson RR, Carothers SW, Simpson JM (1984) A riparian classification system. In: Warner RE, Hendrix KM (eds) California riparian systems: ecology, conservation, and productive management. University of California Press, Berkeley, pp 376–382
62. McLaughlin SP (2004) Riparian Flora. In: Baker BM, Folliott PF, Debano LF, Neary DG (eds) Riparian areas of the Southwestern United States Hydrology Ecology and Management. CRC, Boca Raton, pp 127–168
63. Clerici N, Weissteiner CJ, Paracchini ML, Boschetti L, Baraldi A, Strobl P (2013) Pan-European distribution modelling of stream riparian zones based on multi-source Earth Observation data. Ecol Indic 24:211–223
64. Naiman RJ, D'ecamps H (1997) The ecology of interfaces: riparian zones. Annu Rev Ecol Syst 28:621–658
65. Hagan JM, Pealer S, Whitman AA (2006) Do small headwater streams have a riparian zone defined by plant communities? Can J For Res 36:2131–2140
66. Naiman RJ, D'ecamps H, Pollock M (1993) The role of riparian corridors in maintaining regional biodiversity. Ecol Appl 3:209–212
67. Robert J, Naiman RJ, Bilby E, Peter A, Bisson P (2000) Riparian ecology and management in the pacific coastal rain forest. BioScience 50:996–1010
68. Lovett S, Price P (eds) (2007) Principles for riparian lands management. Land and Water Australia, Canberra
69. Núñez CO, Cantero JJ, Petryna L (1998) Los hidrófitos del sur de la provincia de Córdoba (Argentina). Rev UNRC 18:37–82
70. Cabrera AL (1971) Fitogeografía de la República Argentina. Bold Soc Argent Bot 14:1–42
71. Giorgis MA, Cingolani AM, Chiarini F, Chiapella J, Barboza G, Ariza Espinar L, Morero R, Gurvich DE, Tecco P, Subils R, Cabido M (2011) Composición florística del Bosque Chaqueño Serrano de la provincia de Córdoba, Argentina. Kurtziana 36:9–43
72. Gavier-Pizarro GI, Kuemmerle T, Hoyos LE, Stewart SI, Huebner CD, Keuler NS, Radeloff VC (2012) Monitoring the invasion of an exotic tree (*Ligustrum lucidum*) from 1983 to 2006 with Landsat TM/ETM+ satellite data and support vector machines in Cordoba, Argentina. Remote Sens Environ 122:134–145
73. Clayton J, Edwards T (2006) Aquatic plants as environmental indicators of ecological condition in New Zealand Lakes. Hydrobiologia 570:147–151
74. Seddon B (1965) Occurrence of *Isoetes echinospora* in eutrophic lakes in Wales. Ecology 46:747–748
75. Colautti RI, Mac Isaac HJ (2004) A neutral terminology to define 'invasive' species. Divers Distrib 10:135–141
76. Richardson DM, Pysek P, Rejmánek M, Barbour MG, Panetta FD, West CJ (2000) Naturalization and invasion of alien plants: concepts and definitions. Divers Distrib 6:93–107
77. Marco DE, Páez SA (2000) Invasion of *Gleditsia triacanthos* in *Lithraea ternifolia* montane forests of central Argentina. Environ Manag 26:409–419

Spatial and Temporal Changes in Water Quality Along the Basin

María Valeria Amé and Silvia Fabiana Pesce

Abstract The hydrological system of the Suquía River comprises three drainage areas with different anthropogenic impacts. A water quality index proposed for the Suquía River Basin was calculated in order to characterise the condition of 23 sampling sites based on the physicochemical and bacteriological variables studied from 1995 to 2011. The data analysis indicates that the river water has good quality along the upper and middle basins, but suffers a significant degradation (to medium quality) while crossing Córdoba City. Even after 100 km downstream from the discharge of the wastewater treatment plant (WWTP) of the city, the water exhibits bad quality, without recovering the good levels observed upstream from the city. Moreover, some water quality parameters surpass the water quality guidelines established for the protection of the aquatic biota.

Keywords Physicochemical analysis, Sewage pollution, Urban pollution, Water quality index

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Contents

1 Introduction

Water is essential for human life and for the health of the environment. As a valuable natural resource, it comprises marine, estuarine, freshwater (rivers and lakes) and groundwater environments. Water has two dimensions that are closely linked: quantity and quality. Therefore, water quality is commonly defined as a set of concentrations, speciations and physical partitions of inorganic and organic substances and the composition and state of the aquatic biota found in a waterbody [1]. A healthy environment is one in which the water quality supports a rich and varied community of organisms and, at the same time, protects the public health.

The quality of an aquatic environment shows temporal and spatial variations due to internal and external factors of the water body [1]. It is known that the composition of natural waters is regulated by biogeochemical cycles, including climatic, geological and biological factors. The dissolved mineral load carried by a river has its origin in the weathering of rocks found in the basin and is a function of climatic and biological processes. Rainfall plays a dual role in controlling the chemical composition of the river water. On the one hand, it can contribute significant amounts of solutes and suspended particulate matter from the atmosphere and, on the other, the dissolution of CO_2 in atmospheric water participates in the chemical weathering of minerals. Besides, precipitations in densely populated areas tend to be more acidic than in a ‘clean’ atmosphere, due to the acids formed from the oxides originated by urban and industrial emissions. Human activities, including but not limited to agriculture, municipal landfilling, industrial waste and dams, interrupt the continuity of the characteristics of the river water and cause changes (usually deterioration) in ecosystems, with the consequent increase of problems related to the use of water resources [2].

Restoration of the natural water quality often takes many years depending on the geographical scale and intensity of the event [1]. For this reason, the evaluation of water quality in developing countries has become a critical issue in recent years, especially due to the concern that freshwater will be a scarce resource in the future [3].

2 Water Quality Assessment in the Suquía River

2.1 *Suquía River Basin*

The Suquía River is located in a semi-arid region of the Province of Córdoba (Argentina) and drains into the depression of the Mar Chiquita Lake (Fig. 1). 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 December 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 into a large and shallow hypersaline lake called Mar Chiquita. The San Roque Dam forms a reservoir where fishing, swimming, boating and sailing are practised. These recreational activities have promoted the urbanisation of its shorelines and surroundings. This reservoir is the main drinking water source for Córdoba City (1.29 million inhabitants).

Thirty kilometres downstream from the dam, the Suquía River enters Córdoba City flowing through a cement channel for approximately 6 km and then alternating with open banks for about 40 km. In the last 20 years, the city's population has almost doubled, and the growing industrialisation has increased the risk of having toxic effluents discharged into the river. La Cañada Brook, located in Córdoba City downtown, contributes to the river flow, and further, downstream, near the eastern edge of the city, the Suquía River is affected by the city's sewage discharge from the municipal wastewater treatment plant (WWTP) [3, 4] (Fig. 1).

The flow regime of rivers and brooks that form the Suquía River drainage network is exclusively pluvial in origin, with a marked flow seasonality due to the irregular distribution of rainfall throughout the year [5]. 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

Fig. 1 Suquía River Basin located in the Province of Córdoba (Argentina)

April, with an estimated flow greater than 15 $m^3 s^{-1}$, whereas during the dry season, from May to November, the estimated flow is 2.7 $m^3 s^{-1}$ [6].

With the exception of the Suquía River Basin headwaters (mean altitude of 1,000 m.a.s.l. and almost totally covered with granitic and high-grade 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. The western edge of the loess-mantled Pampa plains lies downstream from Córdoba City. Moreover, in the middle–low basin, sediments are introduced into the mainstream by bank erosion [7].

The hydrological system of this river comprises three drainage areas: (1) the upper basin, in a mountainous area with headwaters and streams of torrential character, flowing into the San Roque Reservoir; (2) 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 (3) the lower basin, running from Córdoba City into the Mar Chiquita Lake, in a level area, where the river exhibits typical meanders and a shallow and scarce flow.

Based on the hydrologic river features and on our previous results [3, 8], the water quality of the river will be presented in three sections: (1) upper basin (UB), (2) middle basin (MB) and (3) lower basin (LB). As a lentic water body, the San Roque Reservoir should be analysed differently than the rivers.

2.2 Water Quality Assessment in the Suquía River Basin

2.2.1 Monitoring and Data Analysis

Water samples were taken from at least 40 cm under the water surface and from the centre of the stream, where possible. Samples were never taken during rainfall but at least 72 h after the rain had stopped, to allow the river to return to its regular flow condition. Collection receptacles, sample stabilisation and transportation to the laboratory as well as sample storage were done considering Pesce and Wunderlin [3].

Water samples were collected in the Suquía River Basin between 1995 and 2011. However, different periods were studied for each section, being indicated in following sections.

In order to assess the river water quality, 18 physical, chemical and bacteriological parameters were determined at each sampling site. Dissolved oxygen, conductivity, pH and temperature were monitored in the field, while in the laboratory, the following variables were measured: 5-day biological oxygen demand (BOD-5), chemical oxygen demand (COD), ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, orthophosphate phosphorus, chloride, sulphates, hardness, calcium, magnesium, dissolved and total solids and total coliforms (all determinations were performed according to [9–11]).

To evaluate the changes in water quality due to combined effects of many parameters, a WQI proposed for the Suquía River Basin was calculated [3], in order to characterise the conditions of sampling sites based on the physicochemical and bacteriological variables. The construction of WQI requires first a normalisation step, where each parameter is transformed into a 0–100% scale, with 100% representing the highest quality. The next step is to apply weighting factors that reflect the importance of each parameter as an indicator of the water quality. The constructed WQI, based on scientific criteria for water quality, provides an easy to understand number that can be associated with a quality percentage.

The calculation was as follows:

$$\mathrm{WQI} = \Sigma(Ci \cdot Pi)/\Sigma Pi$$

Ci is the value assigned to each parameter after normalisation. Pi value ranges from 1 to 4, where 4 represents a parameter that has the most importance for aquatic life preservation (e.g. dissolved oxygen) and 1 means that such parameters have a smaller impact (e.g. chloride).

For each section of the Suquía River Basin, spatial and temporal analyses were performed. Water samples were grouped in dry or wet seasons for temporal analysis.

Differences among sites, seasons or years were evaluated using the Kruskal–Wallis nonparametric test, followed by Dunn's post test ($P \leq 0.05$), since some variables did not show normality or variance homogeneity.

3 Water Quality in the Upper Basin of the Suquía River

The Suquía River Watershed includes two main tributaries, the Cosquín River (estimated annual mean flow = 4.5 $m^3\ s^{-1}$) and the San Antonio River (estimated annual mean flow = 3 $m^3\ s^{-1}$), and two minor tributaries, Los Chorrillos Brook (estimated annual mean flow = 1.2 $m^3\ s^{-1}$) and Las Mojarras Brook (estimated annual mean flow = 0.5 $m^3\ s^{-1}$), all flowing into the San Roque Reservoir [12]. These rivers/brooks form a reservoir that attracts a good deal of tourists to the area and has significantly increased the population settled in its surroundings in the last years (Fig. 2).

The Cosquín River is formed by the union of the Yuspe River and San Francisco Brook. Small towns are established along these waterbodies, being La Falda and Cosquín the most important ones. Villa Giardino, Huerta Grande, La Falda and Valle Hermoso have a treatment plant that processes 60% of their sewage. On the other hand, Cosquín, Santa María de Punilla and Bialet Massé and other communities do not treat their domestic effluents.

The Icho Cruz and Malambo Rivers converge to form the San Antonio River. Small towns are also settled all along its watercourse, being Cuesta Blanca, Icho

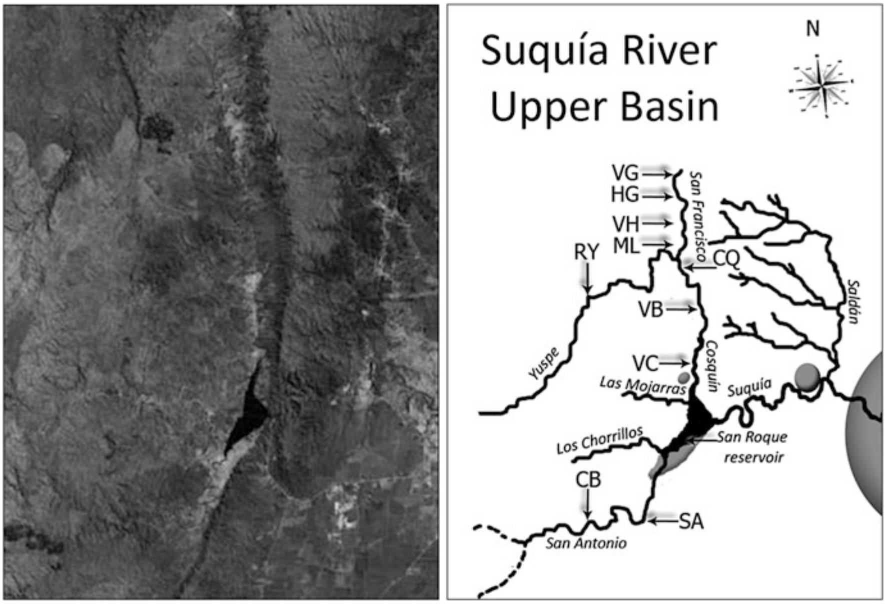

Fig. 2 Suquía River upper basin. Names of rivers, brooks and reservoir are indicated in *italics*. Sampling sites: *VG* Villa Giardino, *HG* Huerta Grande, *VH* Valle Hermoso, *ML* Molinari, *RY* Yuspe River, *CQ* Cosquín, *VB* Villa Bustos, *VC* Villa Caeiro, *CB* Cuesta Blanca, *SA* San Antonio de Arredondo

Cruz and San Antonio de Arredondo the main ones. None of them process their sewage.

Water samples were collected between 1998 and 2001. A total of eight sampling sites were studied in the Cosquín River and its tributaries (Fig. 2): in the San Francisco Brook, Villa Giardino (VG, 31°3′ 0.24″ south; 64°30′ 36.22″ west) and Huerta Grande (HG, 31°3′ 54.22″ south; 64°30′ 51.68″ west), both located upstream from La Falda City, and Valle Hermoso (VH, 31°6′ 59.80″ south; 64° 29′36.27″ west) and Molinari (ML, 31°11′ 33.32″ south; 64°28′ 35.57″ west), both located downstream of the mentioned city; in the Yuspe River (RY, 31°14′ 18.55″ south; 64°31′ 13.31″ west); and in the Cosquín River, Cosquín (CQ, 31°13′ 6.36″ south; 64°28′ 54.26″ west) and Villa Bustos (VB, 31°15′ 27.33″ south; 64°27′ 43.74″ west), located upstream and downstream of Cosquín City, respectively, and Villa Caeiro (VC, 31°17′ 36.04″ south; 64°27′ 36.50″ west), also located downstream of Cosquín City. Two sites were sampled in the San Antonio River: Cuesta Blanca (CB, 31°28′ 58.52″ south; 64°34′ 32.71″ west) and San Antonio de Arredondo (SA, 31°28′ 45.71″ south; 64°31′ 32.75″ west), located nearby the cities bearing the same names.

The WQI in the UB did not show significant changes among the studied years (1998–2001); therefore, the water samples collected along the different years were analysed together. Moreover, differences between the dry and wet seasons were

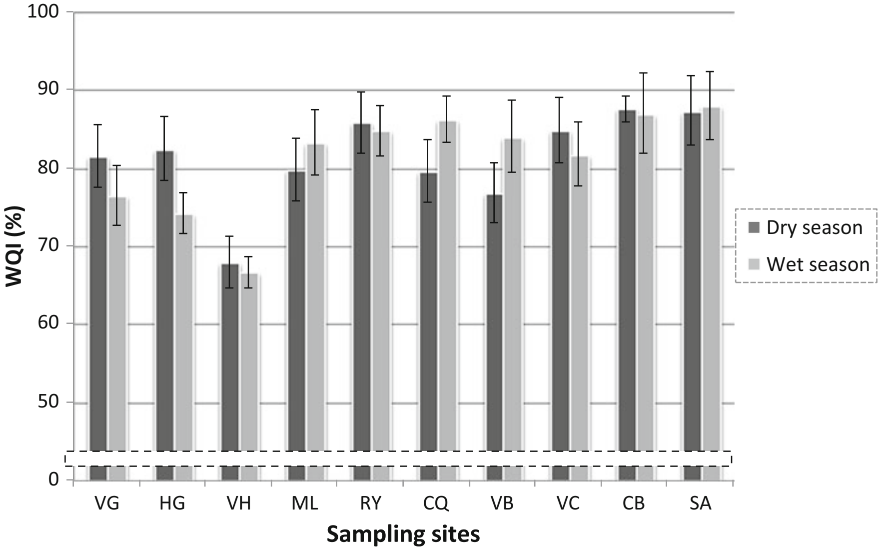

Fig. 3 Mean WQI values and standard deviation for each sampling site along the Suquía River upper basin. *VG* Villa Giardino, *HG* Huerta Grande, *VH* Valle Hermoso, *ML* Molinari, *RY* Yuspe River, *CQ* Cosquín, *VB* Villa Bustos, *VC* Villa Caeiro, *CB* Cuesta Blanca, *SA* San Antonio de Arredondo

significant only in HG, with a better water quality during the dry season (Fig. 3). The decrease in water quality during the wet season (summer time) could be associated with a higher domestic sewage generation by touristic activities and a low capacity of wastewater treatment in the town.

Considering the whole studied period, the highest WQI was calculated in the two sampling stations of the San Antonio River (CB and SA) and in the Yuspe River (RY), one of the tributaries of the Cosquín River located in a quasi-pristine area. The site with the lowest WQI (VH) is located in the San Francisco Brook, the other tributary of the Cosquín River. Water quality decreased downstream from the San Francisco Brook, showing the lowest mean value in Valle Hermoso, after La Falda City (Fig. 3). This sampling site (VH) is negatively influenced by the impact of Valle Hermoso City, having low capacity to treat its domestic sewages, which are discharged into the river like other localities situated along the San Francisco Brook. The self-purification processes, downstream from VH, and the mix with the Yuspe River to form the Cosquín River promote an increase of WQI from ML to the mouth of the Cosquín River in the San Roque Reservoir.

The decrease in the WQI observed for VH could be better understood by the individual analysis of some water quality parameters. Ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, orthophosphate phosphorus, BOD-5 and total coliforms are the variables responsible for this change. All of them showed a significant increase in VH when compared to the other sites, being a general indication of the

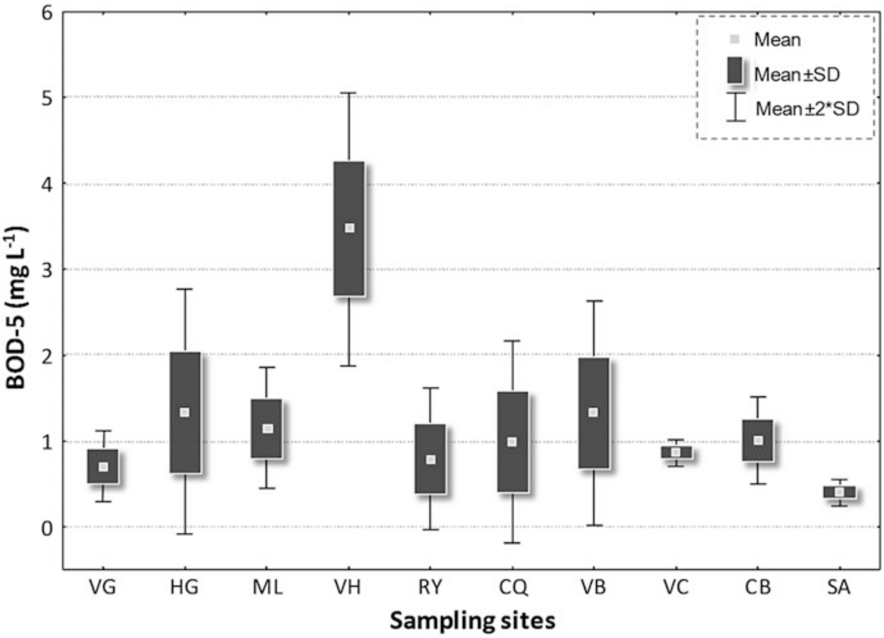

Fig. 4 Box plot of BOD-5 (mg L^{-1}) levels for each sampling site along the Suquía River upper basin. *VG* Villa Giardino, *HG* Huerta Grande, *VH* Valle Hermoso, *ML* Molinari, *RY* Yuspe River, *CQ* Cosquín, *VB* Villa Bustos, *VC* Villa Caeiro, *CB* Cuesta Blanca, *SA* San Antonio de Arredondo

nutrient status of the surface water and the level of organic pollution and municipal waste. BOD-5 average values are shown in Fig. 4 as an example of this pattern.

Another pattern that should be noted was observed in the Cosquín River. Conductivity, pH, chloride, sulphates, hardness, calcium, magnesium and total solids showed higher levels in the San Francisco Brook, lower levels in the Yuspe River and medium values in the Cosquín River, after the convergence of both affluents. This pattern could correspond to natural drainage. As previously stated, the San Francisco Brook drains along a valley covered by tertiary and modern sediments. The sediment erosion and the presence of marble quarries confer a clear alkaline character to its waters [7]. The mean water pH in the San Francisco Brook is 8.7 ± 0.2 with high abundance of $CaCO_3$. An example of this pattern is shown for total solids in Fig. 5 as representative of those other variables.

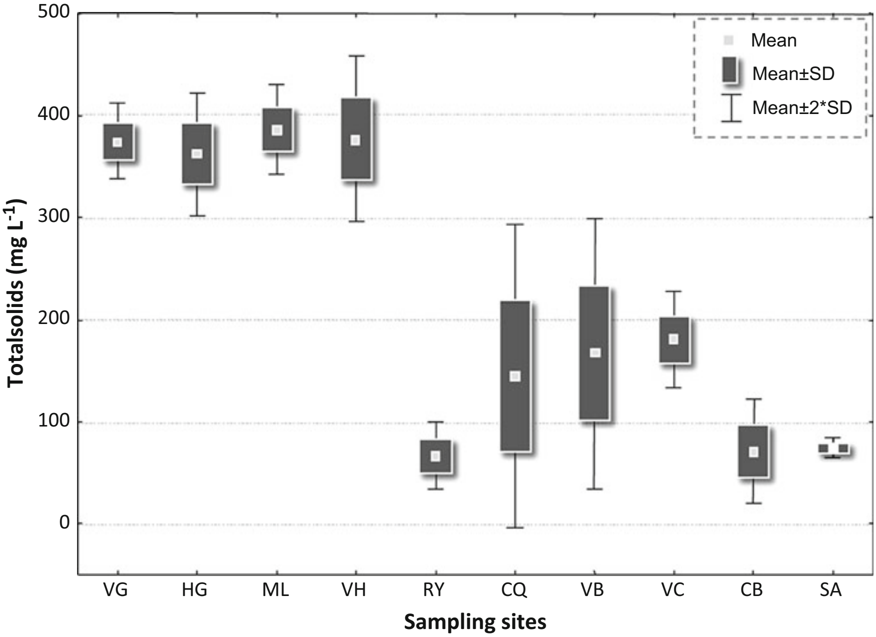

Fig. 5 Box plot of total solid (mg L^{-1}) levels for each sampling site along the Suquía River upper basin. *VG* Villa Giardino, *HG* Huerta Grande, *VH* Valle Hermoso, *ML* Molinari, *RY* Yuspe River, *CQ* Cosquín, *VB* Villa Bustos, *VC* Villa Caeiro, *CB* Cuesta Blanca, *SA* San Antonio de Arredondo

4 Water Quality in the Middle Basin of the Suquía River

The first sampling site of the middle basin was located in a place named La Calera (LC, 31°21′ 5.28″ south; 64° 21′ 0.24″ west; Fig. 6), 18 kilometres downstream from the San Roque Dam. This site is close to La Calera City (ca. 35,000 inhabitants), which is situated along the river's margins. This area exhibits a low impact from human population, and it is considered nearly pristine in terms of a potential man-made source of heavy metals [13]. Six kilometres upstream from LC, a place named El Diquecito is located, where the water supply company withdraws surface water for purification to produce potable water for 70% of Córdoba City [14]. Additionally, eight kilometres downstream from LC, the Suquía River receives the waters of the Saldán Brook. The second sampling site in the middle basin is located before the mouth of this stream (Saldán, SLD, 31°19′ 23.18″ south; 64°18′ 32.18″ west). So far, water samples collected at LC and SLD are representative of raw drinking water quality of Córdoba City.

The Saldán Brook receives the waters of numerous streams of the eastern slope of the Sierras Chicas and, consequently, contributes to the Suquía River with an important volume, particularly in days of heavy rainfall. One kilometre downstream from SLD, the western edge of the Córdoba City is located. Downstream, in the

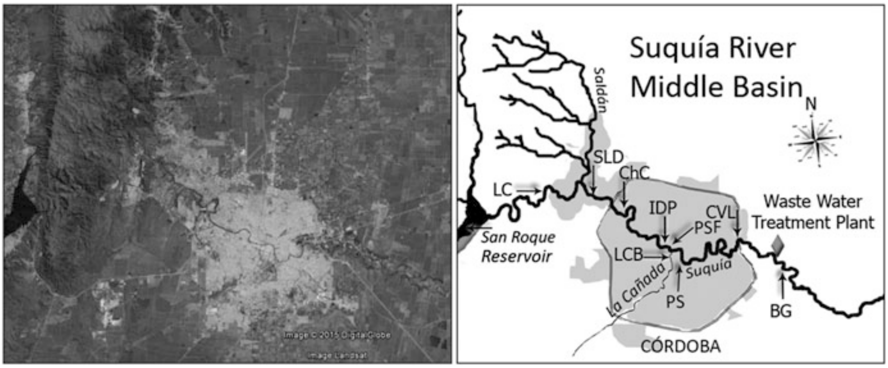

Fig. 6 Suquía River middle basin. Names of rivers, brooks and reservoir are indicated in *italics*. Sampling sites: *LC* La Calera, *SLD* Saldán, *ChC* Chateau Carreras, *IDP* Isla de los Patos, *PSF* Puente Santa Fe, *LCB* La Cañada Brook, *PS* Puente Sarmiento, *CVL* Circunvalación, *BG* Bajo Grande

section of the river that flows through the city, six sampling sites were located: Chateau Carreras (ChC, 31°22′ 1.99″ south; 64°15′ 5.44″ west), Isla de los Patos (IDP, 31°23′ 59.20″ south; 64°12′ 15.30″ west), Puente Santa Fe (PSF, 31°24′ 17.78″ south; 64°11′ 56.73″ west; at this point, a cement channel begins, replacing the natural riverbed), La Cañada Brook (LCB, 31°24′ 28.65″ south; 64°11′ 23.48″ west; affluent of the Suquía River), Puente Sarmiento (PS, 31°24′ 44.94″ south; 64°10′ 29.45″ west; at this site, the Suquía River has already joined La Cañada Brook) and Circunvalación (CVL, 31°24′ 22.70″ south; 64°7′ 22.56″ west). After the city, one last sampling site was located in the middle basin: Bajo Grande (BG, 31°24′ 32.98″ south; 64°4′ 49.26″ west), 5.1 km downstream from CVL and 3.5 km downstream from the discharge of the WWTP into the river. According to Mancini [15], the average flow of the river 0.7 km upstream from the WWTP discharge is 2.45 $m^3\ s^{-1}$ (2011–2012), while downstream, the average river flow is 5 $m^3\ s^{-1}$ in the same period.

Thus, the ratio between the WWTP effluent flow and the river flow is almost 1:1, which exceeds the purification capacity of the river. The water quality assessment of the middle basin includes sample analyses performed between 1995 and 2011 [3, 5, 8, 13, 14, 16].

The WQI in the MB did not show significant changes among the studied years (1995–2011); therefore, the water samples collected along different years were analysed together. Moreover, none of the sampling sites showed differences between the calculated WQI for dry and wet seasons (Fig. 7).

Significant differences of WQI among sampling sites were observed (Kruskal–Wallis, $P < 0.0003$). The multiple-comparison test determined three groups comprising sites with similar water quality. The first group is composed of sites with high water quality (LC and SLD). The second group was classified as having good water quality, and it comprised sampling sites with WQI mean values significantly different but slightly lower than the first group (ChC, IDP, PSF and PS). Only three

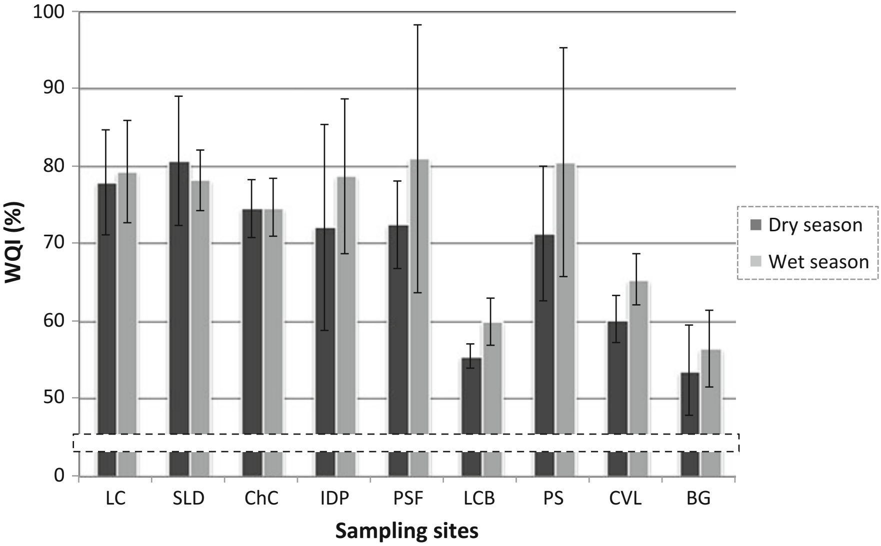

Fig. 7 Mean WQI values and standard deviation for each sampling site along the Suquía River middle basin. *LC* La Calera, *SLD* Saldán, *ChC* Chateau Carreras, *IDP* Isla de los Patos, *PSF* Puente Santa Fe, *LCB* La Cañada Brook, *PS* Puente Sarmiento, *CVL* Circunvalación, *BG* Bajo Grande

sites (LCB, CVL and BG) constitute the last group, with the lowest water quality of the MB.

The river sections studied on the Suquía River varied significantly, with a decrease in water quality conditions in downstream sites. According to the WQI, the WWTP would not be the only source of pollution. The waters of La Cañada Brook are contaminated by industrial effluents, sewage waters and run-off from the downtown commercial area [5]. However, according to the WQI, no clear evidences of this impact can be identified in PS, the first sampling site located downstream from the LCB mouth. Another source of pollution is the urban run-off. This effect is shown by a decrease in the WQI of approximately 16% between the sites located upstream the city (LC and SLD) and CVL, the sampling site located in the eastern border of the city. The WWTP discharge into the river is another identified source of pollution. The WQI declines an additional 8 % in only 5 km when the river receives the effluent. The WQI lowest value corresponds to RP during the dry season. Moreover, it has been indicated that WQI values of approximately 50% are hardly compatible with aquatic life [17]. Therefore, the observed values at BG mean the degraded condition of this site with an associated inhabiting biota at risk.

The pattern of variation of some variables included in the WQI along the river shows these effects. The first pattern exhibits little variation from LC until the sewage exit and a significant variation (deterioration) downstream. In addition, high values are observed in LCB. This is the case with ammonia nitrogen (Fig. 8), orthophosphate phosphorus, dissolved oxygen, BOD-5 and pH (not shown). Most

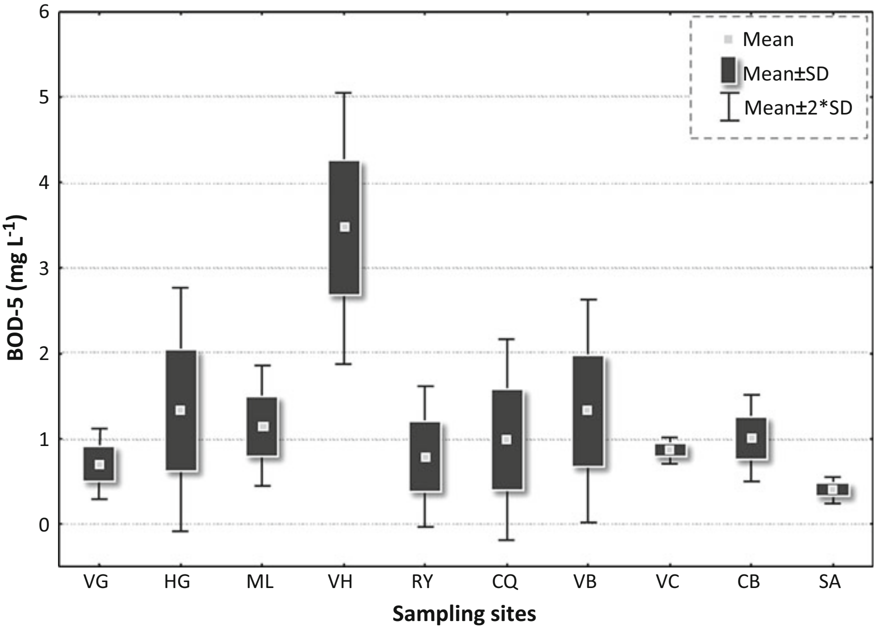

Fig. 8 Box plot of 5-day biological oxygen demand (mg L^{-1}) levels for each sampling site along the Suquía River middle basin. *LC* La Calera, *SLD* Saldán, *ChC* Chateau Carreras, *IDP* Isla de los Patos, *PSF* Puente Santa Fe, *LCB* La Cañada Brook, *PS* Puente Sarmiento, *CVL* Circunvalación, *BG* Bajo Grande

of these parameters are identified as associated with pollution coming from the sewage [4].

The second pattern shows little variation upstream from Córdoba City and a significant deterioration when the river flows across the city downtown, with little changes due to the sewage exit. Furthermore, high values are observed in LCB, showing the complex mixture of pollutants in this stream. This second pattern is then associated with the urban run-off; this is the case with chloride (Fig. 9), conductivity, calcium, hardness, magnesium, nitrate nitrogen, sulphates and dissolved solids (data not shown).

The variables that did not fit these patterns also showed changes along the river that could be associated with a mixture of sewage pollution, urban run-off, natural drainage and other unidentified sources [4].

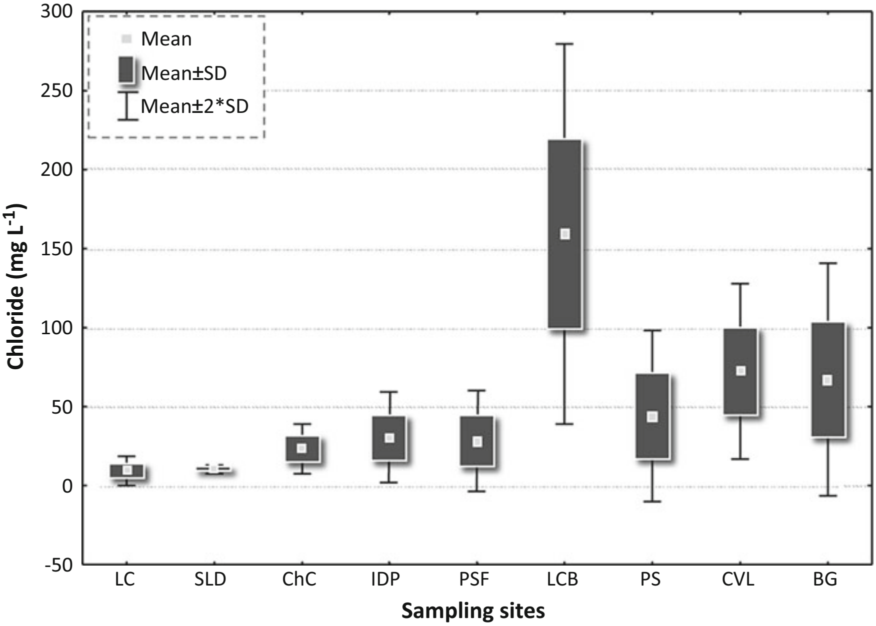

Fig. 9 Box plot of chloride (mg L^{-1}) levels for each sampling site along the Suquía River middle basin. *LC* La Calera, *SLD* Saldán, *ChC* Chateau Carreras, *IDP* Isla de los Patos, *PSF* Puente Santa Fe, *LCB* La Cañada Brook, *PS* Puente Sarmiento, *CVL* Circunvalación, *BG* Bajo Grande

5 Water Quality in the Lower Basin of the Suquía River

The third area, named the lower basin (LB), coincides with the beginning of the Suquía River lower basin and includes four monitoring stations located downstream from the WWTP of Córdoba City: 13 km, at Villa Corazón de María (VCM, 31°26′ 50.19″ south; 63°59′ 26.58″ west; Fig. 10); 34.3 km, at Capilla de los Remedios (CR, 31°26′ 4.83″ south; 63°49′ 53.61″ west); 68.5 km, at Río Primero (RP, 31°20′ 16.53″ south; 63°36′ 31.01″ west); and 108 km, at Santa Rosa de Río Primero (SR, 31°9′ 26.99″ south; 63°23′ 38.06″ west). Then, the river flows another 87.5 km until Laguna del Plata Bay, the mouth of the Suquía River into the Mar Chiquita Lake. This area has intensive agricultural activity surrounding the river, dedicated mainly to soybean and corn production. Only small towns with less than 6000 inhabitants are settled along the river margins (Fig. 10).

In the LB, the WQI did not show significant changes among the studied years (1995–2007). Consequently, the analysis of water samples was conducted without grouping by years. Furthermore, no significant differences were observed for each sampling site between dry and wet seasons (Fig. 11).

Changes in the WQI showed a gradual increase with significant differences between the most polluted sites (VCM and CR) and the last studied site, SR. Río Primero showed an intermediate level between both areas. The average WQI at

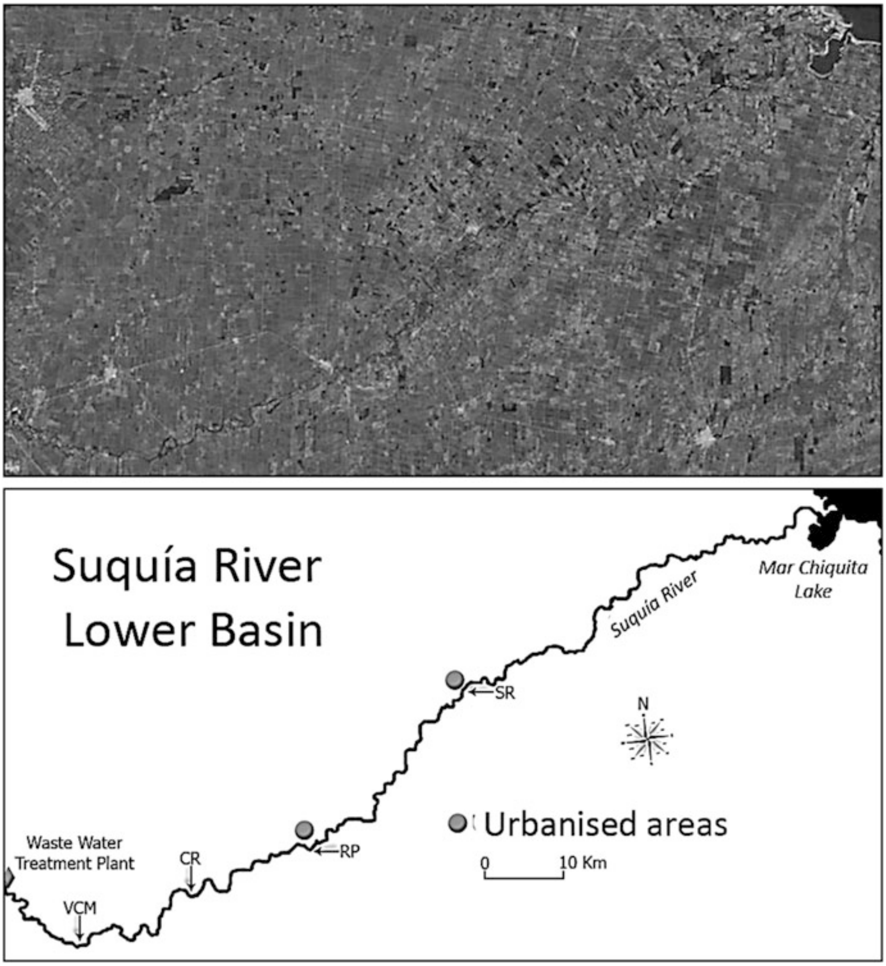

Fig. 10 Suquía River lower basin. Names of rivers, brooks and reservoir are indicated in *italics*. Sampling sites: *VCM* Villa Corazón de María, *CR* Capilla de los Remedios, *RP* Río Primero, *SR* Santa Rosa de Río Primero

VCM and CR is below 50%, evidencing the strong impact of human activities on the aquatic ecosystem. During the studied period, the WWTP of Córdoba City had an irregular activity. The infrastructure of the plant was expanded and adapted to the increasing population, and these activities resulted in long periods of release of raw or partially treated effluents to the river. The distance between VCM and CR (21 km) was not enough to produce amelioration in the water quality of the river, exceeding the river dilution and self-purification capacity. It is not until 108 km downstream from Córdoba City (SR) that the water reaches the quality levels detected at the eastern edge of the city (CVL), before the WWTP discharge.

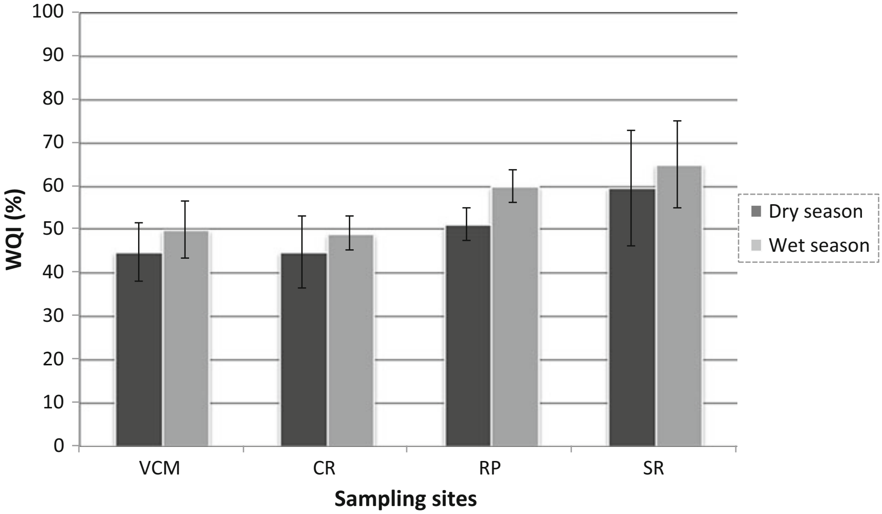

Fig. 11 Mean WQI values and standard deviation for each sampling site along the Suquía River lower basin. *VCM* Villa Corazón de María, *CR* Capilla de los Remedios, *RP* Río Primero, *SR* Santa Rosa de Río Primero

Nevertheless, it is important to mention that the WQI at SR is still far away from the levels observed at LC.

The recovery of the WQI downstream can also be observed through the analysis of individual water quality parameters. Significant differences were found for dissolved oxygen (Fig. 12), ammonia nitrogen, nitrite nitrogen, total coliforms, BOD-5 and pH (data not shown).

The levels of inorganic nitrogen compounds observed along the LB indicate an anthropogenic origin. The relative contributions of each dissolved inorganic nitrogen species measured to the total inorganic nitrogen are shown in Fig. 13. It is evident that the nitrate nitrogen increases its relative contribution downstream, from 20 to 30% at CR and VCM and to 92% at SR, with a consequent decrease in ammonia nitrogen from 78 to 66% and to 8%, respectively. This fact corroborates that the nitrification process occurs from the ammonium oxidation to nitrite and, subsequently, to nitrate. Ammonia nitrogen concentrations are an indication of organic pollution, coming from domestic sewage, industrial waste and fertiliser run-off, among other sources. High nitrate concentrations are associated with diffuse rather than point sources; thus, the highest concentrations of nitrate at CR, RP and SR could be associated with agricultural sources [5].

Nevertheless, there are many internal processes regulating the concentrations of dissolved water quality variables in rivers [1]. Many of the freshwater constituents can undergo biological and non-biological transformations. The full comprehension of these complex phenomena needs the integration of both kinds of processes.

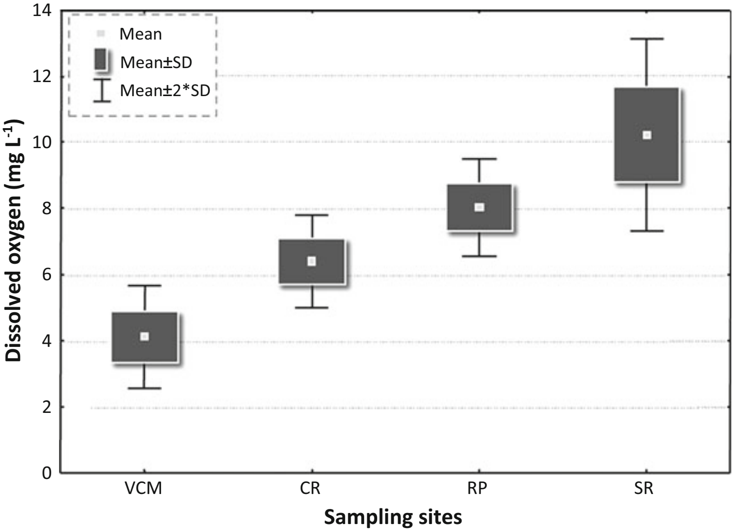

Fig. 12 Box plot of dissolved oxygen (mg L^{-1}) levels for each sampling site along the Suquía River lower basin. *VCM* Villa Corazón de María, *CR* Capilla de los Remedios, *RP* Río Primero, *SR* Santa Rosa de Río Primero

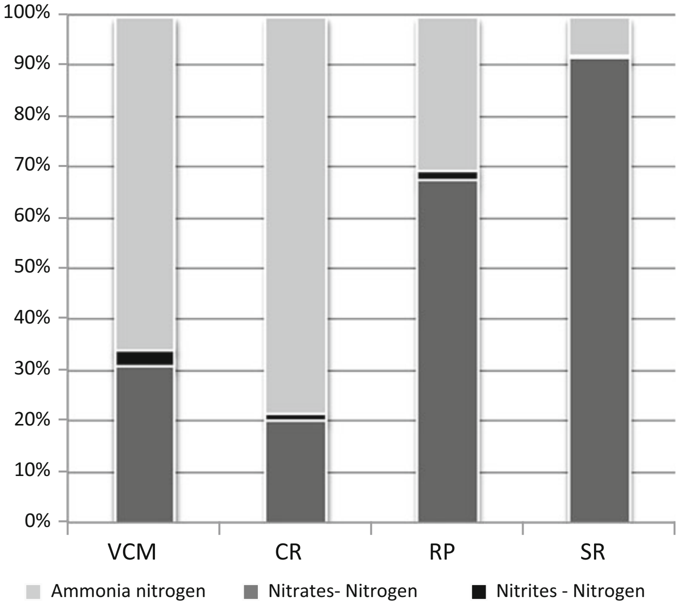

Fig. 13 Variability of relative dissolved inorganic nitrogen species concentrations for each sampling site along the Suquía River lower basin. *VCM* Villa Corazón de María, *CR* Capilla de los Remedios, *RP* Río Primero, *SR* Santa Rosa de Río Primero

6 Human Impact on Water Quality of the Suquía River

During the last twenty years, the Suquía River Basin has coped with several environmental problems, including but not limited to (1) the negative influences of cattle grazing, (2) forest land clearing, (3) sporadic accidental fires or inadequate use of fire, (4) intensive agricultural activities at the middle and lower sections of the basin, (5) the high population density along the watershed and tourism activities in the most important cities, (6) the presence of the wastewater treatment plant at Bajo Grande (eastern edge of Córdoba City), (7) clandestine discharges of industrial effluents as well as sewage discharges from residential villages and (8) sand extraction and sand washing at the eastern edge of Córdoba City [16].

These sources of pollution have significantly affected the water quality of the Suquía River, which is evident from the drop in the WQI analysed here. According to the National Sanitation Foundation, with the WQI defined by Ott [18] and applied by Golge et al. [19], the water quality of a river could be defined considering the following ranges in this WQI: 90–100, excellent; 70–90, good; 50–70, medium; 25–50, bad; and 0–25, very bad. The application of this criterion indicates that the river water has good quality along the upper and middle basin, but suffers degradation to medium quality while running through Córdoba City. After the discharge of the WWTP, the water reaches bad quality without recovering the good levels observed upstream from the city (Fig. 14).

Similar changes in a WQI were measured in the Sabarmati River, one of the biggest and major rivers of Gujarat (India), that runs through two major cities of Gujarat, Gandhinagar and Ahmedabad and finally meets the Gulf of Khambhat in the Arabian Sea [20]. The authors indicate that the river has a WQI around 80 % upstream from the urbanisations and falls to 35% downstream from the highly polluted areas with perennial waste discharges mainly from municipal drainage and industries.

Streams around São Carlos (Brazil) showed the same trend, with a WQI around 85% in less impacted areas and 70% in moderately polluted urban areas, while levels of 40 % where measured in highly polluted areas located downstream from the urbanisations [21].

Some of the variables measured in the Suquía River waters were above the limits for the protection of the aquatic biota. For example, ammonia nitrogen concentrations were above the Argentinean environmental water quality guideline for aquatic biota protection (0.06–0.60 mg L^{-1} NH_4^+; [22]). Possible health risks to aquatic biota associated with nitrate and nitrite nitrogen were also sporadically detected. Moreover, according to the CCME [23], dissolved oxygen levels are below the lowest acceptable concentration (5.5 mg L^{-1}, for warm water biota).

The present study constitutes a good model to be applied in other basins with a mixed source of pollution. The WQI applied here is in agreement with the changes observed in the local biota [14, 16]. However, the conduction of integral investigations becomes one of the most complete and valid strategies for assessing water quality, possible sources of contamination and the effect the latter has on biota at all levels of organisation. Only a comprehensive approach like this would constitute an effective tool to construct preventive and palliative policies.

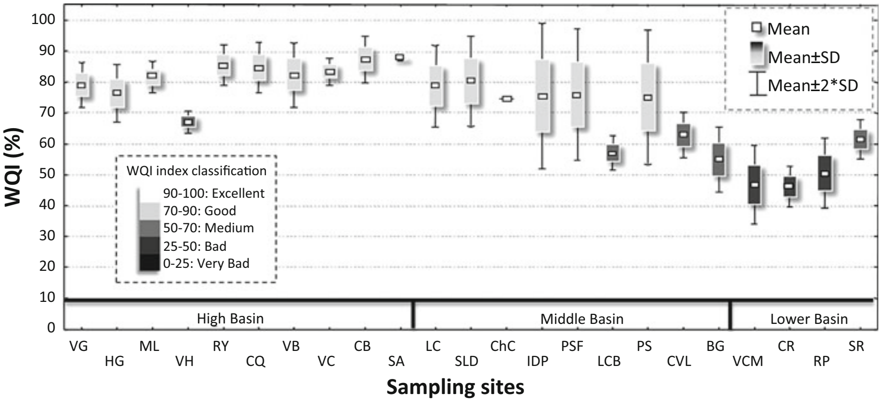

Fig. 14 Box plot of WQI values and standard deviation for each sampling site along the Suquía River lower basin with an indication of water quality. *VG* Villa Giardino, *HG* Huerta Grande, *VH* Valle Hermoso, *ML* Molinari, *RY* Yuspe River, *CQ* Cosquín, *VB* Villa Bustos, *VC* Villa Caeiro, *CB* Cuesta Blanca, *SA* San Antonio de Arredondo, *LC* La Calera, *SLD* Saldán, *ChC* Chateau Carreras, *IDP* Isla de los Patos, *PSF* Puente Santa Fe, *LCB* La Cañada Brook, *PS* Puente Sarmiento, *CVL* Circunvalación, *BG* Bajo Grande, *VCM* Villa Corazón de María, *CR* Capilla de los Remedios, *RP* Río Primero, *SR* Santa Rosa de Río Primero

References

1. Chapman D (1992) In: Chapman D (ed) Water quality assessment. On behalf of UNESCO, WHO, and UNEP. Chapman & Hall, London 585 pp
2. León J (2013) Efecto de la dinámica de nutrientes sobre el fitoplancton en el embalse El Carrizal. Relación con la calidad y el uso del agua. Universidad Nacional de Córdoba, Mendoza
3. Pesce SF, Wunderlin DA (2000) Use of water quality indices to verify the impact of Cordoba City (Argentina) on Suquia River. Water Res 34:2915–2926
4. Wunderlin DA, Diaz MP, Amé MV, Pesce SF, Hued AC, Bistoni MA (2001) Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquía River Basin (Cordoba, Argentina). Water Res 35:2881–2894
5. Pasquini AI, Formica SM, Sacchi G (2011) Hydrochemistry and nutrients dynamic in the Suquía River urban catchment's, Córdoba, Argentina. Environ Earth Sci 65(2):453–467
6. Vázquez JB, Lopez-Robles A, Saez MP (1979) Aguas. In: Vázquez JB, Miatello RA, Roque M, (eds) Geografía física de la provincia de Córdoba. Banco Provincia de Córdoba, Córdoba, pp 139–211
7. Gaiero D, Roman Ross G, Depetris PJ, Kempe S (1997) Spatial and temporal variability of total non-residual heavy metals content in stream sediments from the Suquía River system, Córdoba, Argentina. Water Air Soil Pollut 93:303–319
8. Merlo C, Abril A, Amé MV, Argüello GA, Carreras HA, Chiappero MS et al (2011) Integral assessment of pollution in the Suquía River (Córdoba, Argentina) as a contribution to lotic ecosystem restoration programs. Sci Total Environ 409(23):5034–5045
9. Association Official Analytical Chemists (AOAC) (1995) AOAC official methods of analysis. 16th edn. (March 1999 revision). AOAC International, Gaithersburg
10. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF) (1998) In: Clesceri LS, Greenberg AH, Eaton AD (eds)

Standard methods for the examination of water and wastewater, 20th edn. American Public Health Association, Washington, DC

11. American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF) (2005) In: Eaton AD, Clesceri LS, Rice EW, Greenberg AH (eds) Standard methods for the examination of water and wastewater. APHA, Baltimore
12. Dasso C (1998) CIRSA (Centro de la Región Semiárida-Semiarid Region Center) INA (Instituto Nacional del Agua y del Ambiente-National Water and Environment Institute), unpublished results
13. Monferrán MV, Galanti LN, Bonansea RI, Amé MV, Wunderlin DA (2011) Integrated survey of water pollution in the Suquía River basin (Córdoba, Argentina). J Environ Mon 13 (2):398–409
14. Contardo-Jara V, Galanti LN, Amé MV et al (2009) Biotransformation and antioxidant enzymes of Limnoperna fortunei detect site impact in watercourses of Córdoba Argentina. Ecotoxicol Environ Saf 72:1871–1880
15. Mancini C (2012) Impacto del Vertido de la Estación Depuradora de Aguas Residuales (EDAR) Bajo Grande sobre el Río Primero (Suquía). Technical report Centro de Tecnología de Química Industrial. Facultad de Ciencias Exactas Físicas y Naturales, Universidad Nacional de Córdoba
16. Hued AC, Bistoni MA (2005) Development and validation of a Biotic Index for evaluation of environmental quality in the central region of Argentina. Hydrobiologia 543(1):279–298
17. Hued AC, Dardanelli S, Bistoni MA (2010) Temporal and spatial variability of fish assemblages in a river basin with an environmental degradation gradient. Community Ecol 11 (1):41–50
18. Ott WR (1978) Water quality indices: a survey of indices used in the United States, EPA-600/4-78-005. U.S. Environmental Protection Agency, Washington DC
19. Golge M, Yenilmez F, Aksoy A (2013) Development of pollution indices for the middle section of the Lower Seyhan Basin (Turkey). Ecol Ind 29:6–17
20. Haldar S, Mandal SK, Thorat RB, Goel S, Baxi KD, Parmer NP et al (2014) Water pollution of Sabarmati River-a harbinger to potential disaster. Environ Mon Assess 186(4):2231–2242
21. Bere T, Tundisi JG (2011) Applicability of borrowed diatom-based water quality assessment indices in streams around São Carlos-SP, Brazil. Hydrobiologia 673(1):179–192
22. Argentinean Environmental Water Quality Guidelines (AEWQG); Niveles Guía Nacionales de Calidad de Agua Ambiente. Subsecretaría de Recursos Hídricos de la Nación, República Argentina (2003) www.hidricosargentina.gov.ar/NivelCalidad1.html. Accessed 27 July 2012
23. Canadian Council of Ministers of the Environment (CCME) (2002) Canadian water quality guidelines for the protection of aquatic life. In: Canadian Environmental Quality, Quality, 1999, Canadian Council of Ministers of the Environment, Winnipeg

Metals and Metalloids in Water and Sediment of the Suquía River Basin: Spatial and Temporal Changes

Magdalena Victoria Monferrán

Abstract Metals, metalloids and nonmetals concentrations along the Suquía River basin have been monitored in sediment and surface water, during the wet and dry season, at different points and by different authors since 1997 until 2014. The potential ecological risk (PER) in surface sediments along some studied stations is presented on the basis of measured data.

In general, metal/loids concentrations were highest in sediments and lower in water, being sediments the major sink for metal/loids pollution in this river. The concentrations of metal/loids from the Suquía River pristine areas (upper catchment) were, as expected, the lowest measured. It was also demonstrated how the environmental impact of Córdoba City (e.g. WWTP discharge) becomes evident in the Suquía River basin, which is not only marked by the presence of metals at a sampling station located few kilometres downstream the WWTP but also by the influence of agricultural and small industrial activities downstream from Córdoba City.

According to ecological risk indexes of metal/loids in the *pseudo*-total fraction of sediments, the best scenario was found in La Calera (LC), upstream from Córdoba City. Results indicate that this site presented low to moderate ecological risk. On the other hand, the worse situation is observed in Corazón de María (CM), ca. 16 km downstream the WWTP, where the ecological risk ranges from moderate to severe.

The use of Generalised Procrustes analysis (GPA) shows that the different ecological compartments studied (water and sediment) are closely related and that the interaction between them determines the characteristics of each site.

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Keywords Metalloids, Metals, Sediment, Suquía River basin, Water

Contents

1 Introduction

In recent decades, studies have been conducted to evaluate the pollutants that are discharged into different water sources. Many of these contaminants are not detected in the water column, and, in order to know their fate and effect on the environment, numerous studies have been carried out worldwide in the last decade to assess concentrations of contaminants not only in waterbodies but also in sediments, suspended material, etc. Sediment has been considered a sink of contaminants, and a record of anthropogenic pollution, since the input of diverse contaminants in the water column is many times stored in the sediment (settling) or transported (adsorbed–absorbed) associated with particulate matter [1]. However, available metals in the sediment could be also reintroduced into the water or be uptaken by plants and benthic organisms [2].

Metals are among the main pollutants, since they are easily transported and accumulated in the environment. They are considered serious pollutants due to their persistence in the environment, bioaccumulation and high toxicity [3]. These compounds may be biomagnified through the food chain, resulting in sublethal concentrations affecting the biota, or even reaching concentrations that are lethal to local populations [4].

The study of metal/loids in river waters and sediments is a contribution to the provision of information on the environmental character of these rivers and also to the diagnosis of each of their catchment areas, facilitating the decision making, especially at the government level. Toxic metal/loids are a major environmental concern because of their toxicity to both humans and animals as in the case of fish impact. Investigating the presence of toxic metal/loids in certain water reservoirs can improve the knowledge about the routes of contaminants and their interaction with other substances and organisms in the water.

The presence of toxic metal/loids in waters and sediments of rivers also causes a serious health problem to the inhabitants of populations served by these rivers, which implies an increased spending on medical treatments, a reduction in the productive capacity of residents and, of course, a negative economic impact.

The origin or presence of metal/loids in coastal sediments can be originated from physical and chemical weathering of parent rocks, wastewater discharge and atmospheric deposition [5]. Metal/loids discharged into aquatic systems are distributed between the aqueous phase and sediments during their transport. Due to adsorption, hydrolysis and co-precipitation of soluble ions, a large quantity of these metal/loids are deposited in the sediment, while only a small portion of free ions stay dissolved in the water column. The accumulation and mobility of elements in sediments is controlled by various factors, such as the nature of the sediment, properties of adsorbed compounds, metal/loid characteristics, redox reactions and biodegradation of sorptive substances under specific conditions [6–10]. Hence, sediments are enumerated as a major source of metal/loids in the environment, playing a key role in their transmission and deposition. Accumulated metal/loids in sediments can be chemically altered by aquatic organisms and converted into organic complexes, some of which may be more hazardous to animal and human life, via the food chain.

When environmental conditions change (pH, cationic exchange capacity, nutrient status, redox potential, etc.), some of the sediment-bound elements may be remobilised and released back into the water, where they can have adverse effects on living organisms [11]. In fact, the mobility of metal/loids in the environment strongly depends on their chemical forms or types of binding of the elements [12]. Numerous analytical techniques have been used to identify the key factors that control distribution and speciation of metal/loids in coastal and estuarine sediments in order to understand their mobility and potential ecological risks [13].

Sediments from various water environments reveal the differences in hydrodynamic regime, redox potential, sorting process, mineral and chemical components. These differences are reflected by geochemical properties of sediments [14]. River sediments usually derive from ambient soils and road deposits [15]. These sediments undergo the effect of one-way water flow and exhibit a relatively high proportion of coarse matter [16].

The sediment contamination by inorganic elements is traditionally evaluated in terms of total concentrations or *pseudo*-totals of each element; however, it is shown that the danger that toxic elements pose to living organisms is determined more by their availability to living organisms than by their total concentration [17]. For the extraction of the *pseudo*-total fraction of sediments, a mix of HCl and HNO3 at different proportions is commonly used, being the extraction performed during long times at high temperatures. Conversely, the available fraction is extracted using various reagents and different extraction methods. Among the methods reported in the literature, the use of diluted hydrochloric acid (0.5 M) is a low-cost and widely used procedure to extract the available fraction [18]. In connection with this last method, the use of 0.5 M HCl [19] satisfies the minimum requirements for the extraction of metal/loids that are part of the exchangeable fraction, with minimum disturbance of the silicate matrix [17, 18, 20]. Thus, metal/loids extracted by this method can be interpreted as the mobilisable fraction of metal/loids in soil, mainly because diluted HCl releases the metal/loid carbonates associated with Fe and Mn oxides [20]. Studies of metal/loids in the sediment of the Suquía River basin include both total and bioavailable fractions; so, from now on, the discussion will explain to which sediment fraction the metal/loid belongs.

2 Metals, Metalloids and Nonmetals

"Heavy metal" is a somewhat imprecise term commonly used to refer to certain metals and some of their related compounds, to which certain environmental pollution, toxicity and ecotoxicity effects are attributed.

According to the International Union of Pure and Applied Chemistry (IUPAC), the term "heavy metal" may be a "meaningless term", because there is no standardised definition for a heavy metal. In fact, some light metals or metalloids are toxic, while some high-density metals are not. For a given metal/loid, the toxicity varies widely depending on its allotrope or oxidation state. For instance, hexavalent chromium is deadly; while trivalent chromium is nutritionally significant in many organisms, including humans. Today, a new classification is being used:

- Metals are generally shiny, malleable and hard. Metals are also good conductors of electricity. Examples of metals are gold, silver, iron, uranium and zinc.
- Nonmetals do not conduct heat or electricity very well. Nonmetals are typically brittle and are not easily moulded into shapes. Examples of nonmetal elements are selenium and phosphorous.
- Metalloids share characteristics of both metals and nonmetals and are also called semimetals. Metalloids are typically semiconductors, meaning that they both insulate and conduct electricity. This semiconducting property makes metalloids very useful as a computer chip material. Examples of metalloid elements are arsenic and boron.

So, metals, metalloids and nonmetals are naturally present in the soil, at concentration levels called background levels or simply "background", whose origin is not external. Background levels come from the original parent rocks. Often found as cations, they strongly interact with the soil matrix, which sometimes means that even at high concentrations they can be found in harmless concentrations or as chemically inert forms. However, these elements can move and change their shape due to chemical changes in response to different environmental conditions [21].

For the exposed general characteristics, it is necessary to identify the source of these elements in benthic sediments of waterbodies. There are different sources of metals, metalloids and nonmetals in the environment. These sources can be either of natural or anthropogenic origin [5, 22].

The weathering of rocks and soils, directly exposed to the action of water, is the major contribution from natural sources. On the other hand, human activities such as agriculture, industry and urban waste are of great importance to the contribution of these inorganic compounds in the sediment of natural water courses [5].

2.1 Anthropogenic Sources of Inorganic Compounds

Metals, metalloids and Se are released into the environment by many human activities. They are also used in a large variety of industrial products, which in the long term have to be deposited as waste. They are released into the environment at the beginning of the production chain, whenever ores are mined, or during the use of products containing them, and also at the end of the production chain (trash, etc.). Here, we present an overview on anthropogenic sources and uses of these inorganic compounds, through which they can be introduced into the environment. The natural sources are dominated by parent rocks and metallic minerals, while the main anthropogenic sources are agricultural activities, where fertilisers, animal manures and pesticides containing metal/loids are widely used. Also, metallurgical activities, including mining, smelting, metal finishing among others, in addition to energy production and transportation, microelectronic products and waste disposal, contribute as anthropic sources of metal/loids. Furthermore, metals, metalloids and nonmetals can be released into the environment in gaseous, particulate, aqueous or solid form, emanating from both diffuse and point sources [5].

As: Used as additive to animal feed, wood preservative (copper chrome arsenate), special glasses, ceramics, pesticides, insecticides, herbicides, fungicides, rodenticides, algaecides, sheep dip, electronic components (gallium arsenate semiconductors, integrated circuits, diodes, infrared detectors, laser technology), nonferrous smelters, metallurgy, coal-fired and geothermal electrical generation, textile and tanning, pigments and anti-fouling paints, light filters, fireworks, veterinary medicine

Be: Used in alloys (with Cu), electrical insulators in power transistors, moderator of neutron deflectors in nuclear reactors

Cd: Used in Ni/Cd batteries, pigments, anticorrosive metal coatings, plastic stabilisers, alloys, coal combustion, neutron absorbers in nuclear reactors

Co: Used in metallurgy (superalloys), ceramics, glasses, paints

Cr: Manufacturing of iron alloys (special steels), plating, pigments, textiles and leather tanning, passivation of corrosion of cooling circuits, wood treatment and audio, video and data storage

Cu: Good conductor of heat and electricity, water pipes, roofing, kitchenware, chemicals and pharmaceutical equipment, pigments, alloys

Fe: Cast iron, wrought iron, steel, alloys, construction, transportation, machine manufacturing

Hg: Extracting of metals by amalgamation, mobile cathode in the chloride–alkali cell for the production of NaC1 and Cl_2 from brine, electrical and measuring apparatus, fungicides, catalysts, pharmaceuticals, dental fillings, scientific instruments, rectifiers, oscillators, electrodes, mercury vapour lamps, X-Ray tubes, solders

Mn: Production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys, catalysts, fungicides, antiknock agents, pigments, dryers, wood preservatives, coating welding rods

Mo: Alloying element in steel, cast irons, nonferrous metals, catalysts, dyes, lubricants, corrosion inhibitors, flame retardants, electroplating

Ni: Alloying element in the steel industry, electroplating, Ni/Cd batteries, arc-welding, rods, pigments for paints and ceramics, surgical and dental prosthesis, moulds for ceramic and glass containers, computer components, catalysts

Pb: Antiknock agents, tetramethyllead, lead–acid batteries, pigments, glassware, ceramics, plastic, in alloys, sheets, cable sheathings, solder, ordinance, pipes or tubing

Sb: Type-metal alloy (with lead to prevent corrosion), in electrical applications, Britannia metal, pewter, Queen's metal, in primers and tracer cells in munition manufacture, semiconductors, flameproof pigments and glass, medicines for parasitic diseases, as an expectorant, combustion of fossil fuels

Se: In the glass industry, semiconductors, thermoelements, photoelectric and photo cells, and xerographic materials, inorganic pigments, rubber production, stainless steel, lubricants, dandruff treatment

Sn: Tin-plated steel, brasses, bronzes, pewter, dental amalgam, stabilisers, catalysts, pesticides

Ti: For white pigments (TiO2), as UV-filtering agents (sun cream), nucleation Agent for glass ceramics, as Ti alloy in aeronautics

Tl: Used for alloys (with Pb, Ag or Au) with special properties, in the electronics industry, for infrared optical systems, as a catalyst, deep temperature thermometers, low melting glasses, semiconductors, supra conductors

V: Steel production, in alloys, catalyst

Zn: Zinc alloys (bronze, brass), anticorrosion coating, batteries, cans, PVC stabilisers, precipitating Au from cyanide solution, in medicines and chemicals, rubber industry, paints, soldering and welding fluxes

3 Metals, Metalloids and Se in Water and Sediment from the Suquía River Basin: Studies Over the Years

The Suquía River basin has been monitored since 1991. The first study on metals (Mn, Fe, Zn, Pb, Cu and Ni) in the available fraction of Suquía River sediments was reported by Gaiero et al. [23].

In this study, river sediments were sampled in two seasons. Samples were collected in June 1991 (autumn), after the rainy season, and in October 1991 (spring), after the dry winter period, coinciding with the initial phase of the rainy season. Eight sampling stations (S1 to S6, and LI–L2) were established along the main course. Two of these stations (L1 and L2) were located in the mixing zone of the Mar Chiquita Lake, where the Suquía Rivers discharges its water into the lake. The active upper catchment was also sampled in eight additional stations: IC1–IC2, Y1–Y2, SFI–SF2 and LM 1–LM2 (Fig. 1).

Stations IC1, Y1, LM1 and SF1 were representative of the conditions dominating in the upper catchments of the main tributaries.

These stations, located in the Punilla Valley, were mainly placed on modern sedimentary terrain and were subjected to various degrees of environmental impact (Table 1). The city of Córdoba is Argentina's second largest urban and industrial centre. To show its impact on the river, stations S1 and S2 were located upstream and downstream from the city. Stations S3, S4 and S5 were distributed along the lower 100 km section, upstream from the river mouth in the Mar Chiquita Lake. Small towns, with less than 6,000 inhabitants, justified the location of S3 and S4. Stations S5, S6, Ll and L2 were influenced by extensive farming activities.

Table 1 lists Mn, Fe, Zn, Pb, Cu and Ni concentrations in sediment measured during the wet and dry season at the different sampling sites from the Suquía River basin.

During this first study, the uppermost area exhibited a low population impact; thus, it was considered a nearly pristine basin in terms of potential man-made sources of metals.

The concentrations of these metals in sediment at sites located in the upper basin showed many similarities; this could be attributed to the similarity in the geochemical conditions in these places (Table 1). The concentrations of some metals were slightly affected by the different hydrological conditions (dry or wet/rainy seasons).

As expected, concentrations of some metals like Pb and Ni exhibited lower values along the entire basin, probably due to the generation of hydrous oxides by weathering reactions, while Fe and Mn exhibited a highly relative abundance in the sediment fraction.

In the upper basin, areas considered as representative between the transition of low and moderate population were stations LM1, LM2, IC2 and Y2.

The increase in the concentrations of some elements (e.g. Pb, Cu, Zn) in these transition zones is clearly related to the increase in urban settlements with respect to the pristine areas. In contrast, Fe and Mn showed no significant changes with values recorded in the upper pristine basin.

Sampling stations SF1 and SF2 correspond to the San Francisco River (Fig. 1a). This river drains through a valley (Punilla Valley), where urban activities release different wastes, with little or no treatment, into the riverbed. In these sampling sites, increased levels of Pb, Cu and Zn during the rainy season were observed, in agreement with increased levels of organic matter and, to a lesser extent, precipitated carbonates [23]. In the dry season, a drop in Pb, Cu and Zn concentrations was observed [23]. On the other hand, concentrations of Fe and Mn in these sites were among the lowest throughout the entire basin; a possible explanation for this might be associated with reducing conditions in this area. Ni concentrations showed minimal temporal and spatial changes.

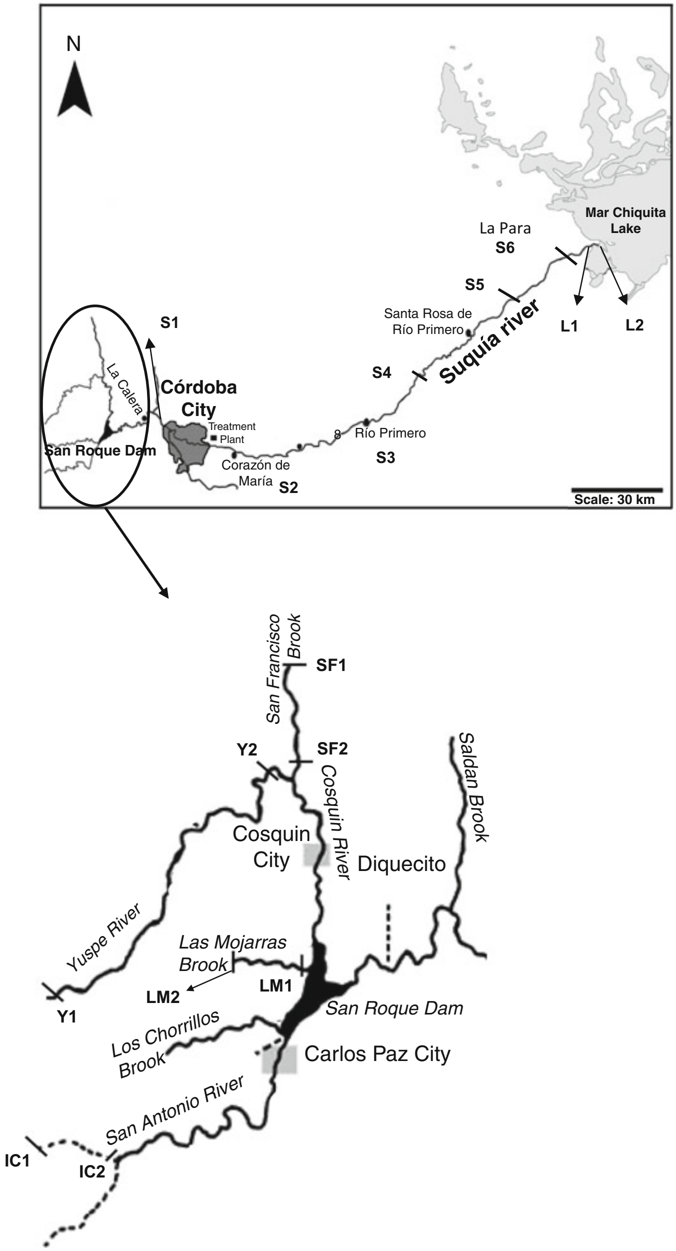

Fig. 1 Map of the Suquía River basin (Córdoba–Argentina) with indication of the studied area and monitoring stations

Table 1 Bioavailable metals concentrations in Suquía bed sediments during autumn (A) and spring (B)

		Metal concentration (μg g^{-1})															
		Upper catchment								Main channel						Mouth	
Stream		Icho Cruz		Yuspe		Las Mojarras tributary	Las Mojarras	San Francisco		Suquía River						Mar Chiquita lake	
Environmental type		Pristine	Urban	Pristine	Farm	Municipal	Urban	Sewage	Municipal	Municipal wastes	Sewage	Municipal wastes	Farm	Farm	Farm	Farm	Farm
Samples		IC1	IC2	Y1	Y2	LM1	LM2	SF1	SF2	S1	S2	S3	S4	S5	S6	L1	L2
Ni	A	0.8 ± 0.0					1.2 ± 0.0	3.3 ± 0.2	4.5 ± 0.2	4.2 ± 0.1	6.0 ± 0.3	4.3 ± 0.1		0.7 ± 0.0	5.7 ± 0.2	3.1 ± 0.1	1.7 ± 0.1
	S	0.6 ± 0.0		1.2 ± 0.0	3.3 ± 0.1		1.8 ± 0.1	3.4 ± 0.1	4.5 ± 0.2	5.3 ± 0.2	12 ± 0.5	5.2 ± 0.2		3.3 ± 0.1	3.3 ± 0.1	0.4 ± 0.1	1.7 ± 0.1
Cu	A	6.9 ± 0.1	18.0 ± 0.7	7.8 ± 0.4		21.0 ± 0.5	8.9 ± 0.1	3.9 ± 0.1	2.3 ± 0.1	5 ± 0.8	21 ± 1	10 ± 0.3	8.4 ± 0.3	3.5 ± 0.2	9.3 ± 0.8	5.0 ± 0.3	6.5 ± 0.3
	S	13 ± 0.3		10 ± 0.3	7.0 ± 0.2	27.0 ± 1.2	1.8 ± 1.0	6.5 ± 0.3	9.3 ± 0.3	4.3 ± 0.2	52 ± 0.8	19 ± 0.3		4.5 ± 0.9	5.5 ± 0.2	4.8 ± 0.2	9.3 ± 0.3
Pb	A	2.8 ± 0.1		3.4 ± 0.2		18 ± 1.2	9.8 ± 0.5	13 ± 0.7	9.2 ± 0.3	15 ± 0.8	40 ± 2.7	31 ± 2.0	17 ± 0.6	7.6 ± 0.3	6.9 ± 0.3	5.8 ± 0.3	9.0 ± 0.33
	S	2.6 ± 0.1		2.5 ± 0.1	8.5 ± 0.4		11 ± 0.5	11 ± 0.7	20 ± 1.1	22 ± 1.1	92 ± 3.2	16 ± 1.0		5.6 ± 0.3	8.9 ± 0.3	5.3 ± 0.3	10 ± 0.5
Zn	A	13 ± 0.1	24 ± 0.4	13 ± 0.2		34 ± 0.2	24 ± 0.9	8.8 ± 0.2	4.9 ± 0.1	25 ± 0.9	42 ± 0.4	48 ± 0.1	44 ± 0.4	3.0 ± 0.0	11 ± 0.2	6.2 ± 0.1	9.5 ± 0.2
	S	14 ± 0.3		12 ± 0.3	14 ± 0.4	34 ± 1.2	21 ± 0.6	15 ± 0.5	23 ± 0.3	11 ± 0.1	125 ± 0.8	37 ± 0.2		4.9 ± 0.1	2.4 ± 0.1	4.1 ± 0.1	7.3 ± 0.2
Mn	A	276 ± 2.5	254 ± 3.3	149 ± 1.8		356 ± 6	88 ± 1.6	26 ± 1.6	53 ± 1.3	37 ± 1.2	32 ± 1.1	601 ± 11	533 ± 7.3	100 ± 1.4	118 ± 2.2	92 ± 1.1	210 ± 6.3
	S	198 ± 1.8		286 ± 5.1	532 ± 5.4	798 ± 13	46 ± 1.0	73 ± 1.6		462 ± 8.8	100 ± 2.1	311 ± 24		140 ± 1.4	162 ± 3.1	63 ± 0.1	123 ± 2.4
Fe	A	2,257 ± 41	1693 ± 30	2,073 ± 48			1,286 ± 22	15 ± 0.1	13 ± 0.2	13 ± 0.2	2,714 ± 56		424 ± 10	313 ± 5.6	389 ± 4.0	1,318 ± 20	
	S	1,715 ± 31		1,676 ± 15		265 ± 2.4	161 ± 2.0	11 ± 0.1	8 ± 0.1	19 ± 0.3	4,549 ± 90	926 ± 21		289 ± 5.0	42 ± 0.8	407 ± 6.0	208 ± 4.2

Adapted from Gaiero et al. [23]

During the wet season, an increase in the concentrations of metals downstream from sampling sites SF1 and SF2 was observed, in addition to an increase in the content of organic matter and carbonates.

The upper basin supplies the water stored at the San Roque reservoir (Fig. 1). This dam is considered the limit between the upper and the medium drainage basin, where the city of Córdoba is located. The river crosses the city, receiving industrial and municipal effluents as well as urban runoff inputs.

The concentrations of most of the measured elements (with the sole exception of Mn) were higher downstream from Córdoba City, while a subsequent decrease in the downstream direction was also observed (Table 1). Metal concentrations, measured at the sampling point S2, were higher during the wet season compared to the dry one, in opposition to values recorded in both the upstream and downstream sections. This increase was approximately 40% above base values during the dry season, and it can be attributed to metals washed out from the city via urban runoffs.

Downstream from the city of Córdoba, in S2 monitoring station, a marked reducing environment determines low concentrations of Mn and high concentrations of Fe. Such reducing environment is likely to be caused by the discharge of the wastewater treatment plant (WWTP), which causes a severe oxygen drop downstream, leading to such reducing conditions. Under these conditions, Fe, along with other metals, probably precipitates as sulphide, given the presence of bioavailable organic matter, sulphates and other oxidising compounds – such as Fe^{+3} [24].

A reasonable explanation for the observed decrease of most heavy metals, further downstream from S2, is the dilution by "native sediments", relatively free from heavy metals, introduced into the main stream by bank erosion from the surrounding area. This river section does not present major point sources of metals, although minor fluctuations can be attributed to the presence of small towns located along the riverbank.

Finally, stations L1 and L2 represented the transition zone between the freshwater river mouth (L1, conductivity: 23,754 μS) and the Mar Chiquita saline lake (L2, conductivity: 27,000 μS). Settling of small particles determined the increase observed with most metal concentrations (Fig. 1).

As in some estuaries (e.g. [25]), the concentrations of Fe appeared to be higher in the low-salinity river mouth than in the high-salinity sector. Probably, Fe (along with A1 and Ti) remained associated with fine colloidal particles in offshore waters [26]. An increase of organic matter and carbonates in bottom sediments (L2) from the saline river mouth was also observed [23].

Some years later, Contardo-Jara et al. [27] also reported the amounts of the available metal fraction, extracted from field-sampled sediments and surface water during the spring of 2007. In this case, four sampling sites were monitored, covering a pollution range from *quasi*-pristine to heavily polluted areas. The monitoring station at Río Yuspe corresponds to the Y2 station in Gaiero et al. [23]. A second station, El Diquecito, located 30 km upstream from Córdoba City, is slightly polluted as a consequence of less treated sewage and urban runoff from smaller cities further upstream from the eutrophic San Roque reservoir [28], where the Suquía River is born (Fig. 1). A third monitoring station was Isla de los Patos, located close to Córdoba City downtown, where the river is flanked on both sides by frequently used highways. Further reasons for the pollution at Isla de los Patos are in connection with urban drainage (runoff), where illegal garbage and domestic sewage is sometimes introduced. The most polluted site reported by Contardo-Jara et al. [27] was Corazón de María, located ca. 16 km downstream the WWTP (Fig. 1). It is worth noting that only 0.7 out of 1.2 million inhabitants of Córdoba City are connected to the municipal sewage, with the rest discharging home-treated sewage (septic tanks) into cess pools, which then infiltrate the ground and pollute the groundwater. This last site (Corazón de María) corresponds to the S2 sampling site in the work of Gaiero et al. [23].

Contardo-Jara et al. [27] showed that metals tend to concentrate in the sediment, where they reach concentrations of several magnitudes higher than in the overlaying water.

Conversely, iron showed the highest concentration in sediments of the Yuspe River (514 μg g^{-1}), which could be a consequence of the geological composition of the surrounding soil (metamorphic granite with gneiss ducts). This result cannot be compared with previous studies [23], since Fe was not reported during spring monitoring in this previous work.

Iron content in surface water in Yuspe River (24.1 μg L^{-1}) was in the same magnitude as the most polluted site Corazón de María (33.5 μg L^{-1}). At Isla de los Patos, even higher amounts were detected (55.2 μg L^{-1}), while at El Diquecito values were below detection limit. In some cases, metal content in sediments did not show a clear increasing or decreasing trend throughout the studied basin section (e.g. Co, K, Mn, Na). Others metals are strongly associated with human activities or sewage, showing their highest levels at Corazón de María compared to the other studied basin sections (Cr, 1.36 μg g^{-1}; Cu, 17.45 μg g^{-1}; Mg, 913 μg g^{-1}; Ni, 7,08 μg g^{-1}; Pb, 11.8 μg g^{-1}; and Zn, 160 μg g^{-1})

Changes in copper concentration in basin sediments seem to be associated with urban activities, changing by almost sixfold from Río Yuspe (1.52 μg g^{-1}) to El Diquecito (8.64 μg g^{-1}) and Isla de los Patos (8.64 μg g^{-1}), with a further increase by more than tenfold at Corazón de María (17.45 μg g^{-1}) with respect to Yuspe River. This trend was also reported by [23] some years before during the spring time (Table 1).

Concentrations of Fe, Cu, Ni and Pb in sediment collected during spring time at both Y1 and S2 stations in Gaiero et al. [23] were higher in all cases than concentrations reported by Contardo-Jara et al. [27] in the same site, with the exception of Mn and Zn in S2 (Corazón de María) station, where in both papers they showed similar concentrations.

Nickel amounts in surface water of Yuspe River (17.8 μg L^{-1}) are strikingly high, being sixfold higher than in Corazón de María (2.6 μg L^{-1}), which can be explained by the geochemical background of the surrounding soils [27].

Two years later, Monferrán et al. [29] reported concentrations of Ag, Cr, Cu, Mn, Ni, Pb, Fe and Zn in the available fraction of sediments and surface water throughout five stations studied for the period 2008–2009 at the Suquía River basin, during the dry and rainy season.

Sampling areas used by Monferrán et al. [29] were selected, considering previous reports on pollution sources and water quality of the Suquía river basin [23, 27, 30, 31]. All of these reports point out to Córdoba City as the main responsible area for the pollution of the Suquía River. So far, a reference area located upstream from the city (La Calera,LC; Fig. 1) was established. The four sampling areas located downstream from Córdoba City, Corazón de María (CM), Capilla de los Remedios (CR), Río Primero (R_1) and Santa Rosa de Río Primero (SR) are primarily affected by the input of pollutants from the city sewage [30, 31]. Closer to the WWTP, downstream from Córdoba City, the basin could receive agricultural runoffs or additional domestic wastes [23].

The mean values, determined in both water and sediment by Monferrán et al. [29], are given in Table 2. Clearly, sediments show the negative impact of the city, with increased amounts of Pb, Cu, Cr and, particularly, Zn. Considering previous reports [23, 27, 31], it is likely to think that these metals arise from the city WWTP, though this point cannot be definitively concluded because the sewage exit was not analysed during these works. On the other hand, Ni remained roughly constant in sediments throughout the studied area; this trend was also reported by [23] some years before (Table 1). It is worth to mention that the amount of Fe is drastically reduced in sediments downstream from Córdoba City but proportionally increased in the water. Thus, in agreement with reports by [23], it is demonstrated that the tendency remained unchanged over the time ($>$10 years).

Additionally, higher values of dissolved Cr, Cu, Mn, Ni and Pb are observed during the wet (rainy) season, probably due to the increased amount of these metals coming from the urban runoffs at the beginning of the rainy season.

The uppermost area (La Calera) exhibits low population impact, and it is considered *quasi*-pristine in terms of potential man-made source of toxic metal/loids. Thus, current results show that the riverbed sediment is projecting a clear image of the impact produced by diverse activities, but it is mainly affected by the city sewage.

In some cases, as previously reported by others authors, the levels of soluble metals show the impact of the WWTP discharge, followed by a drop downstream from this point (i.e. Cr and Mn at Corazón de María – CM – and further downstream, Table 2). However, other metals like Cu showed the highest values at R_1 during the wet season (Table 2), which is less influenced by the sewage discharge. In this case, high concentrations of soluble Cu could be the consequence of agricultural runoffs ($CuSO_4$ is used as a common fungicide in this area) or any other point source pollution.

Considering the studied metals in stream sediments by Monferrán et al. [29], it can be seen that concentrations of Cu, Zn and Pb were lowest at the reference site (LC). The environmental impact caused by Córdoba City (e.g. WWTP) became evident in the Suquía River system because of some toxic metals (Zn, Cu and Pb) at CM, with moderate or less drop further downstream (Table 2). Thus, the impact of sewage point source pollution is reflected downstream in river sediments, though

Table 2 Concentrations of metal measured in water (μg L^{-1}) and sediments (μg g^{-1} dry weight-DW) of the Suquía River

Parameter	Matrix	Season	Monitoring station				
			La Calera (LC)	Corazón María (CM)	Capilla Remedios (CR)	Rio 1° (R$_1$)	Sta Rosa Rio 1° (SR)
Ag	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
	Sediment	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Sediment	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Cr	Water	Wet	2.7 ± 0.4^{b}	5.9 ± 0.6^{e}	4.7 ± 0.2^{d}	2.2 ± 0.2^{a}	3.8 ± 0.14^{c}
	Water	Dry	<LOD	1.2 ± 0.1^{b}	2.5 ± 0.4^{c}	0.8 ± 0.1^{a}	1.2 ± 0.1^{b}
	Sediment	Wet	1.9 ± 0.1^{a}	3.5 ± 0.8^{b}	3.0 ± 1.3^{b}	4.3 ± 1.6^{c}	1.7 ± 0.1^{a}
	Sediment	Dry	3.7 ± 0.2^{a}	17.6 ± 0.4^{c}	18.8 ± 0.7^{c}	17.1 ± 0.6^{c}	6.2 ± 0.3^{b}
Cu	Water	Wet	3.8 ± 0.1^{a}	3.5 ± 0.1^{a}	6.5 ± 0.8^{c}	20.3 ± 1.3^{d}	5.4 ± 0.6^{b}
	Water	Dry	<LOD	1.3 ± 0.1^{b}	1.2 ± 0.2^{b}	1.4 ± 0.1^{b}	0.5 ± 0.1^{a}
	Sediment	Wet	7.4 ± 1.5^{a}	16.5 ± 0.4^{b}	15.1 ± 0.1^{b}	14.5 ± 0.3^{b}	8.5 ± 0.4^{a}
	Sediment	Dry	1.9 ± 0.3^{a}	17.5 ± 0.4^{c}	20.1 ± 0.3^{d}	22.1 ± 0.7^{f}	8.6 ± 0.4^{b}
Fe	Water	Wet	181 ± 54^{a}	$2,870 \pm 68^{b}$	$1,770 \pm 45^{a}$	$3,980 \pm 71^{d}$	$3,141 \pm 65^{c}$
	Water	Dry	140 ± 12^{a}	444 ± 28^{c}	310 ± 15^{b}	101 ± 11^{a}	640 ± 35^{d}
	Sediment	Wet	$3,388 \pm 349^{d}$	$1,703 \pm 16^{b}$	$1,569 \pm 52^{c}$	$1,021 \pm 38^{b}$	839 ± 9^{a}
	Sediment	Dry	$3,457 \pm 96^{d}$	$1,514 \pm 54^{c}$	$1,424 \pm 34^{c}$	$1,036 \pm 104^{b}$	445 ± 51^{a}
Mn	Water	Wet	31 ± 3^{a}	75 ± 5^{e}	50 ± 1^{b}	60 ± 2^{c}	70 ± 3^{d}
	Water	Dry	8 ± 1^{a}	71 ± 3^{d}	74 ± 5^{e}	21 ± 3^{c}	18 ± 2^{b}
	Sediment	Wet	125 ± 21^{b}	217 ± 4^{b}	269 ± 2^{b}	474 ± 4^{c}	138 ± 6^{a}
	Sediment	Dry	193 ± 6^{b}	121 ± 4^{a}	174 ± 3^{b}	346 ± 11^{c}	131 ± 5^{a}
Ni	Water	Wet	10.3 ± 1.2^{d}	5.1 ± 0.4^{b}	4.0 ± 0.2^{a}	<LOQ	8.3 ± 1.0^{c}
	Water	Dry	<LOD	<LOQ	<LOQ	<LOQ	<LOD
	Sediment	Wet	5.1 ± 0.7^{c}	5.3 ± 0.3^{b}	4.8 ± 0.4^{b}	6.3 ± 1.0^{c}	4.2 ± 0.2^{a}
	Sediment	Dry	4.8 ± 0.2^{a}	17.3 ± 0.9^{c}	16.1 ± 0.8^{c}	17.6 ± 0.6^{c}	6.9 ± 0.8^{b}

(continued)

Table 2 (continued)

			Monitoring station				
Parameter	Matrix	Season	La Calera (LC)	Corazón María (CM)	Capilla Remedios (CR)	Rio 1° (R_1)	Sta Rosa Rio 1° (SR)
Pb	Water	Wet	8.7 ± 0.2^{d}	8.0 ± 0.2^{c}	4.8 ± 0.3^{a}	4.9 ± 0.1^{b}	5.1 ± 0.1^{b}
	Water	Dry	<LOD	2.2 ± 0.2^{a}	<LOQ	<LOQ	<LOQ
	Sediment	Wet	16.6 ± 1.6^{a}	23.5 ± 1.3^{c}	25.5 ± 3.8^{c}	21.0 ± 0.1^{b}	17.0 ± 0.3^{a}
	Sediment	Dry	8.7 ± 0.5^{a}	16.9 ± 0.7^{b}	14.5 ± 0.2^{b}	17.6 ± 0.6^{b}	9.7 ± 0.6^{a}
Zn	Water	Wet	<LOQ	0.08 ± 0.01^{a}	<LOQ	<LOQ	<LOQ
	Water	Dry	<LOQ	0.05 ± 0.01^{a}	<LOQ	<LOQ	<LOQ
	Sediment	Wet	13.9 ± 1.9^{a}	78.3 ± 2.3^{b}	85.7 ± 1.5^{c}	63.7 ± 2.9^{b}	22.3 ± 2.9^{a}
	Sediment	Dry	9.0 ± 0.5^{a}	92.9 ± 5.2^{c}	93.5 ± 1.9^{c}	107.1 ± 3.5^{d}	26.7 ± 1.3^{b}

Values are expressed as means ± SD. <LOD (below detection limit); <LOQ (below quantification limit). Different letters indicate significantly different values at different monitoring stations (DMRT, $P \leq 0.05$). Adapted from Monferrán et al. [29]

values in water tend to decrease (Table 2). This trend was also observed in previous years [23, 27].

Many pollutants measured during the work of Monferrán et al. [29] are well above levels considered as hazardous for aquatic life, exceeding the levels of the Argentinean Environmental Water Quality Guidelines [32]. For instance, values observed for Cr at LC, CM, CR and SR during the wet season (Table 2) clearly exceed the threshold-regulated value of 2.5 μg L^{-1}. A similar situation is observed with Pb, which exceeds the threshold value (1.6 μg L^{-1}) throughout the entire basin during the wet season and at CM during the dry season. In the sediment, some metals exceed the risk levels defined by the Management of Aquatic Sediment Quality ([33]; Argentinean regulations do not stipulate guideline values for sediments). Concentrations of Cu (17.5, 20.1 and 22.1 μg g^{-1} DW at CM, CR and R_1, respectively; Table 2) were in excess up to 1.4-fold (threshold value, 16 μg g^{-1} DW), while loadings of Ni (ca. 17 μg g^{-1} DW at CM, CR and R_1; Table 2) also exceeded levels for the protection of the aquatic biota established in Canada (16 μg g^{-1} DW).

These results complement the previous measurements of metal levels in available fraction in sediments of the Suquía River basin [23, 27]. Thus, current Cu, Ni and Pb concentrations in sediments are similar to those previously reported by Gaiero et al. [23] at similar monitoring places. Current concentrations of Zn present lower values upstream from Córdoba City but higher values downstream. It is worth to mention that Fe in sediments presents much higher values during this work in comparison to previous reports by Gaiero et al. [23].

Later on, Monferrán et al. [34, 35] reported concentrations of metals, metalloids and Se (Li, B, Be, Al, V, Cr, Mn, FMo, Ag, Cd, Ce, Hg, Tl, e, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Pb, Bi, U, Pd, Sn, Sb, Pt and Au) in the *pseudo*-total fraction of sediments and water throughout five studied stations at the Suquía River basin: La Calera (LC) was established as the reference area located upstream from the city and four sampling areas downstream from Córdoba City, Corazón de María (CM), Rio Primero (R_1), Santa Rosa de Rio Primero (SR) and La Para (LP) (Fig. 1).

Higher values of dissolved Al, V, Mn, Co, Ba and Ce were observed during the wet season; this could be attributed to runoffs of the basin area during rainfall (Table 1); higher values of dissolved elements were observed in the dry season in comparison to the wet season. In some cases, the levels of soluble metal/loids showed the impact of the WWTP discharge, followed by a drop downstream from this point source (i.e. Cr, Mn, Hg, Ni, Cu, Zn, Pb and Sn at CM and further downstream) (Table 3). These results agree with those reported by Contardo-Jara et al. [27] and Monferrán et al. [29].

It can be seen that levels of As in the water increase as the river flows towards the Mar Chiquita lake (1.8 to 14.6 μg g^{-1} from west to east). The Chaco–Pampas plain in Argentina is considered the largest region in the world (one million km^2) affected by the presence of arsenic in groundwater. Within this region, the eastern part of the Province of Cordoba is one of the most affected areas. Levels of As reported by different authors in surface waters from this area are generally lower than those reported in groundwater. In rivers and lakes, the average concentration of As

Table 3 Concentrations of metal measured in water (μg L^{-1}) and sediments (μg g^{-1} dry weight-DW) of the San Roque reservoir

Matrix	Season	Analysed elements								
		Ag	Al	As	Cd	Ce	Cr	Cu	Fe	Hg
Water	Dry	<LOD	2,434 ± 26 *	3.8 ± 0.1 *	<LOD	0.62 ± 0.01	2.6 ± 0.7 *	5.5 ± 0.1 *	2,087 ± 10 *	<LOD
	Wet	<LOD	60 ± 2	<LOD	1.97 ± 0.08*	4.7 ± 0.1 *	<LOD	3.5 ± 0.6	51 ± 4	<LOD
Sediment	Dry	0.018 ± 0.02	1,051 ± 68	0.76 ± 0.11 *	0.073 ± 0.014	12.5 ± 0.1 *	0.52 ± 0.17	4.1 ± 0.1 *	724 ± 48 *	<LOQ
	Wet	0.014 ± 0.02	780 ± 58	0.34 ± 0.07	0.059 ± 0.014	7.8 ± 0.1	0.41 ± 0.17	2.5 ± 0.1	269 ± 1	<LOQ
		Mn	**Mo**	**Nd**	**Ni**	**Pb**	**Pt**	**Sr**	**Zn**	
Water	Dry	224 ± 2 *	9.1 ± 0.1	0.31 ± 0.05 *	5.5 ± 0.6 *	2.35 ± 0.01	<LOD	105 ± 1 *	15.8 ± 1.1	
	Wet	24 ± 4	11.2 ± 0.6	0.17 ± 0.01	2.2 ± 0.6	2.53 ± 0.02	0.008 ± 0.002*	67 ± 2	20.2 ± 0.8 *	
Sediment	Dry	326 ± 25 *	<LOD	6.3 ± 0.1 *	2.2 ± 0.1 *	4.72 ± 0.06	<LOD	17 ± 1	23.4 ± 0.2 *	
	Wet	109 ± 4	<LOD	4.4 ± 0.1	1.3 ± 0.1	7.85 ± 0.17 *	<LOD	15 ± 1	8.9 ± 0.5	

Values are expressed at means ± SD. <LOD (below detection limit); <LOQ (below quantification limit). (*) indicate significantly different values at different monitoring stations (DGC, $P \leq 0.05$). Data adapted from Monferrán et al. [34]

reported in the literature is generally less than 0.8 μg L^{-1}. However, downstream from Córdoba City, the Suquía River flows through an area with intensive agriculture and stockbreeding, where there is a frequent extraction of groundwater for irrigation purposes and the provision of drinking water to cattle. Thus, As contained in this groundwater can reach the river in this area, increasing levels of this metalloid in surface waters [36].

Finally, Harguinteguy et al. [37] also reported levels of some metals (Co, Cu, Fe, Mn, Ni, Pb and Zn) in surface water and sediment samples of the Suquía River. In this case, sampling was carried out in July 2006 and February 2009, during the dry and wet seasons. To evaluate the spatial variation, they selected seven sampling sites:

Site 1 (31°21′60″ S, 64°30′52″ W, 766 m), established as the reference, was located on Los Chorrillos brook before the San Roque reservoir (Fig. 1).
Site 2 (31°20′36″ S, 64°21′18″ W, 539 m) was located 18 km upstream from Córdoba City, before La Calera town.
Site 3 (31°17′54″ S, 64°19′53″ W; 594 m) was located 15 km upstream from Córdoba City, before the Saldán brook.
Site 4 (31°19′16″ S, 64°18′58″ W, 516 m) was located on the Saldán brook, before the mouth of the Suquía river.
Site 5 (31°20′46″ S, 64°16′58″ W; 463 m) was located 12 km upstream from Córdoba City, after Villa Rivera Indarte, upstream from Córdoba downtown.
Site 6 (31°24′19″ S, 64°05′29″ W, 397 m) was located 1 km downstream the WWTP.
Site 7 (31°25′48″ S, 64°01′22″ W, 360 m) was located 9 km downstream from Córdoba City, after the discharge of a channel containing industrial effluents (automotive, metallurgical and metal–mechanical industries) in the southeast of Córdoba City.

Metal concentrations in surface waters found by Harguinteguy et al. [37] in 2006 and 2009 revealed significant differences between the sampling sites. In general, metal concentrations were higher downstream from Córdoba City (Sites 6 and 7) in both sampling campaigns, which was probably related to the contribution of pollutants from effluent discharges from anthropogenic sources (WWTP and the industrial channel). The mean concentrations of all metals in river water, except for Cu and Pb, were well above the levels considered hazardous for aquatic life, exceeding the levels established by the Argentinean Environmental Water Quality Guidelines [32].

It should be mentioned that metals in sediment in this work resulted in concentration values much higher than those observed in previous studies conducted in the same river and in the same sampling stations [23, 27, 29]. This could be due to methodological differences as Harguinteguy et al. [37] measured the *pseudo*-total fraction in sediment, while previous works reported the labile fraction [23, 27, 29]. The evaluation of *pseudo*-total concentrations involves a more exhaustive extraction than the one performed to determine the bioavailable or labile fraction.

However, results by Harguinteguy et al. [37] can be compared to those reported by Monferrán et al. [34, 35].

Reports by Harguinteguy et al. [37] and Monferrán et al. [34, 35] show the negative impact of Córdoba City, particularly through the WWTP and industrial channel discharges. Thus, downstream from the city, increased amounts of Pb, Cu, Cr, Zn, Cd, Ni, Hg, Bi, Sn and Pt were observed. On the other hand, Be, Co, V, Rb, Tl and Pd remained roughly constant in sediments throughout the studied area.

It is worth to mention that Harguinteguy et al. [37] reported that levels of Fe in sediments were higher in 2009 than in 2006 (5,842 and 7,892 $\mu g\ g^{-1}$, respectively), with the maximum concentrations of this metal being registered in 2009 in areas where large amounts of organic matter were deposited (site 6 and 7, corresponding to the site CM in Monferrán et al. [34, 35] work). In this regard, Charzeddine et al. [38] noted that the external supply of Fe in the rainy season was able to form colloidal dispersions of amorphous iron hydroxide, $Fe(OH)_3$ and goethite, α-FeO (OH), which were retained by the organic matter in sediments. Similarly, Wedepohl [39] indicated that this element is found in large proportions in the upper crust, and consequently, its concentrations in aquatic environments tend to increase considerably due to the drag action exerted by rainfall, surface runoff and/or leaching. This increase in iron concentration in sediments during the wet season, compared to the dry season, is not as marked in Monferrán et al.'s [34, 35] work, probably because of methodological differences, as Monferrán et al. [34, 35] monitored dry and wet season within the same year (2012), while Harguinteguy et al. [37] reported results from the dry season of 2006 and the rainy season of 2009. So far, consideration of the hydrological issues and the analytical method used is necessary to compare results by different authors, taken in different years, under different weather conditions. A normalisation of data should be attempted considering the total load of metals and metalloids transported by the river. Unfortunately, the lack of hydrological stations coincident with monitoring sites precludes such data normalisation.

3.1 Metals and Metalloids Concentrations in Water and Sediment of the San Roque Reservoir

Seventeen elements (Mn, Fe, Zn, Cu, Cd, Cr, Ni, Ag, Mo, Nd, Al, Ce, As, Sr, Pb, Pt and Hg) were sampled from water and sediment on the San Roque reservoir (Fig. 1) during both wet and dry seasons throughout 2012 [35]. In this case, the available fraction of sediments was analysed.

The mean values, determined in both water and sediment, are given in Table 3. In general, the highest concentrations for measured metal/loids in water were detected during the dry season ($P < 0.05$) (Table 3). This could be the result of low water volumes supplied by tributaries during the dry season, resulting in a concentration of studied elements in the reservoir because of the lower water amount. Conversely, higher flows observed during the wet season could dilute elements in the reservoir (Table 3). These results are in agreement with the previously detected trend, measuring several physical and chemical parameters in the lake [31]. Some of the measured elements exceed the limit considered dangerous to aquatic wildlife, established by the Argentinean Environmental Water Quality Guidelines [32]. For instance, values observed for Al, Cu, Cr, Fe, Ni and Zn, during the dry season (Table 3), clearly exceed the threshold regulated (100, 2.87, 2.5, 1.37*, 4.2, 4.54 μg L^{-1}, respectively, with the exception of Fe, where values are expressed as mg L^{-1}). A similar situation is observed with Cu and Zn during the wet season, exceeding the threshold value (2.87 and 4.54 μg L^{-1}, respectively).

Water pollution has also affected the upper layer of sediment (0–15 cm). The highest concentrations for most measured metals in reservoir sediments were detected during the dry season ($P < 0.05$) (Table 3). Sediment samples presented different textures along the studied period, varying from low to high silt sludge. It is noticeable that the deposition of suspended material, due to the slow water flow (larger residence time) during the dry season, determined a high metal concentration in sediments, in contrast with more sandy sediments typical of the rainy season (Table 1). These results complement the few previous measurements of metal/loids in sediments of the San Roque reservoir. Thus, current Cr, Cu, Ni and Fe concentrations in sediments are lower than those previously reported by Monferrán et al. [29], in sediments of the Suquía River, close to the San Roque dam (La Calera) (Fig. 1) during both wet and dry seasons (Table 2). Although Zn concentration presents higher values in the San Roque reservoir than those previously found in La Calera, both concentrations do not exceed the risk levels defined by the Canadian Guidelines for the Protection and Management of Aquatic Sediment Quality ([33], Argentinean regulations do not stipulate guideline values for sediments).

4 Ecological Risk Assessment

Potential ecological risk was calculated using Håkanson [8] methodology in which the sensitivity of the aquatic system depends on its productivity. The potential ecological risk index ($\mathrm{R_I}$) was introduced to assess the degree of heavy metal pollution in sediments, according to the toxicity of metal and metalloids pollution and the response of the environment:

$$\mathrm{R_I} = \sum E_{\mathrm{r}}^{\mathrm{i}} \tag{1}$$

$$E_{\mathrm{r}}^{\mathrm{i}} = T_{\mathrm{ir}} C_{\mathrm{if}} \tag{2}$$

$$C_{\mathrm{if}} = C_{\mathrm{io}} / C_{\mathrm{in}} \tag{3}$$

where $\mathrm{R_I}$ is calculated as the sum of all risk factors for metals studied in sediment,

Table 4 Concentrations of metal/loids measured in water (μg L^{-1}) of Suquía River basin

Parameter	Matrix	Season	Monitoring station				
			La Calera (LC)	Corazón María (CM)	Rio 1° (R_1)	Sta Rosa Rio 1° (SR)	La Para (LP)
Li	Water	Wet	10.6 ± 2.4^{a}	16.0 ± 0.8^{b}	15.4 ± 2.8^{b}	16.6 ± 0.6^{b}	18.8 ± 0.4^{c}
	Water	Dry	7.1 ± 0.7^{a}	16.7 ± 0.4^{b}	15.7 ± 1.3^{b}	16.3 ± 2.1^{b}	17.7 ± 0.6^{c}
Be	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	0.22 ± 0.01^{a}	0.22 ± 0.01^{a}	0.22 ± 0.01^{a}	0.22 ± 0.1^{a}	0.22 ± 0.01^{a}
B	Water	Wet	136 ± 69^{a}	317 ± 12^{c}	322 ± 94^{c}	237 ± 11^{b}	329 ± 9^{c}
	Water	Dry	<LOD	162 ± 32^{a}	113 ± 12^{a}	<LOD	229 ± 69^{b}
Al	Water	Wet	34 ± 1^{a}	59 ± 7^{a}	87 ± 1^{a}	351 ± 10^{b}	$1,255 \pm 165^{c}$
	Water	Dry	10 ± 1^{a}	47 ± 2^{b}	44 ± 2^{b}	61 ± 5^{c}	111 ± 4^{d}
V	Water	Wet	3.2 ± 0.1^{a}	4.8 ± 0.6^{a}	5.8 ± 0.1^{a}	11.9 ± 0.3^{b}	32.8 ± 4.2^{c}
	Water	Dry	2.4 ± 0.1^{a}	4.1 ± 0.2^{b}	4 ± 0.1^{b}	10.6 ± 0.9^{c}	25.3 ± 0.5^{d}
Cr	Water	Wet	0.41 ± 0.01^{a}	1.54 ± 0.23^{c}	0.53 ± 0.02^{a}	0.94 ± 0.02^{b}	1.71 ± 0.23^{d}
	Water	Dry	0.87 ± 0.02^{a}	29 ± 1^{c}	4.5 ± 0.1^{b}	0.83 ± 0.09^{a}	1.38 ± 0.05^{a}
Mn	Water	Wet	25 ± 1^{a}	187 ± 21^{e}	49 ± 1^{b}	65 ± 1^{c}	124 ± 16^{d}
	Water	Dry	6.3 ± 0.2^{a}	133 ± 7^{e}	50 ± 1^{d}	23 ± 2^{c}	17 ± 1^{b}
Fe	Water	Wet	50 ± 1^{a}	85 ± 11^{a}	75 ± 6^{a}	230 ± 6^{b}	705 ± 80^{c}
	Water	Dry	12 ± 1^{a}	152 ± 8^{e}	99 ± 2^{d}	38 ± 5^{c}	56 ± 2^{b}
Co	Water	Wet	<LOQ	0.62 ± 0.04^{b}	0.50 ± 0.02^{a}	0.60 ± 0.05^{b}	1.17 ± 0.15^{c}
	Water	Dry	<LOD	0.29 ± 0.02^{a}	0.23 ± 0.03^{a}	<LOD	<LOD
Ni	Water	Wet	<LOD	5.4 ± 0.8^{b}	1.9 ± 0.1^{a}	<LOD	2.1 ± 0.5^{a}
	Water	Dry	2.5 ± 0.1^{a}	13.6 ± 0.7^{e}	9.0 ± 0.1^{d}	3.1 ± 0.2^{b}	4.8 ± 0.1^{c}
Cu	Water	Wet	<LOQ	2.9 ± 0.4^{b}	1.9 ± 0.1^{a}	3.0 ± 0.1^{b}	5.4 ± 1.0^{c}
	Water	Dry	2.4 ± 0.1^{b}	4.7 ± 0.2^{e}	3.2 ± 0.01^{c}	1.9 ± 0.3^{a}	4.4 ± 0.1^{d}
Zn	Water	Wet	<LOQ	23 ± 5^{a}	<LOD	<LOD	<LOQ
	Water	Dry	10.5 ± 0.4^{a}	133 ± 6^{d}	38 ± 1^{c}	14 ± 1^{a}	17 ± 1^{b}
As	Water	Wet	<LOD	<LOD	<LOD	<LOD	13 ± 1
	Water	Dry	<LOD	1.8 ± 0.1^{a}	1.9 ± 0.1^{a}	4.4 ± 0.4^{b}	14.6 ± 0.2^{c}

Se	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Rb	Water	Wet	2.1 ± 0.1^{a}	5.0 ± 0.4^{c}	5.0 ± 0.1^{c}	4.3 ± 0.3^{b}	4.8 ± 0.7^{c}
	Water	Dry	1.6 ± 0.1^{a}	4.9 ± 0.3^{e}	4.0 ± 0.2^{d}	3.7 ± 0.3^{c}	2.3 ± 0.1^{b}
Sr	Water	Wet	113 ± 3^{a}	494 ± 66^{c}	429 ± 6^{b}	436 ± 6^{b}	513 ± 78^{c}
	Water	Dry	155 ± 2^{a}	536 ± 22^{b}	519 ± 12^{b}	540 ± 27^{b}	520 ± 12^{b}
Mo	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	3.6 ± 0.1^{a}	<LOD	3.2 ± 0.2^{b}	5.4 ± 0.3^{c}
Ag	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Cd	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Ba	Water	Wet	26 ± 4^{a}	52 ± 1^{b}	62 ± 9^{c}	55 ± 1^{b}	68 ± 1^{d}
	Water	Dry	32 ± 2^{a}	40 ± 1^{b}	54 ± 2^{d}	55 ± 2^{d}	47 ± 1^{c}
Ce	Water	Wet	0.10 ± 0.02^{a}	0.31 ± 0.01^{b}	0.43 ± 0.07^{c}	1.4 ± 0.2^{d}	5.5 ± 0.1^{e}
	Water	Dry	0.04 ± 0.01^{a}	0.16 ± 0.01^{b}	0.33 ± 0.01^{c}	0.53 ± 0.02^{d}	1.09 ± 0.03^{e}
Hg	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	0.54 ± 0.04a	1.53 ± 0.05b
Tl	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Pb	Water	Wet	0.77 ± 0.21^{a}	0.95 ± 0.03^{a}	0.86 ± 0.24^{a}	1.85 ± 0.03^{b}	3.47 ± 0.05^{c}
	Water	Dry	0.67 ± 0.06^{a}	3.09 ± 0.04^{e}	2.11 ± 0.09^{c}	1.07 ± 0.02^{b}	2.34 ± 0.04^{d}
Bi	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
U	Water	Wet	2.3 ± 0.4^{a}	14.9 ± 0.2^{c}	13.9 ± 2.2^{c}	12.6 ± 0.1^{b}	16.8 ± 0.2^{d}
	Water	Dry	2.6 ± 0.2	12.5 ± 0.1	13.5 ± 0.5	13.5 ± 0.5	15.2 ± 0.4
Pd	Water	Wet	0.11 ± 0.01^{a}	0.43 ± 0.01^{b}	0.39 ± 0.03^{b}	0.40 ± 0.06^{b}	0.50 ± 0.04^{c}
	Water	Dry	0.10 ± 0.01^{a}	0.43 ± 0.11^{c}	0.31 ± 0.01^{b}	0.31 ± 0.01^{b}	0.35 ± 0.01^{b}

(continued)

Table 4 (continued)

Parameter	Matrix	Season	Monitoring station				
			La Calera (LC)	Corazón María (CM)	Rio 1° (R_1)	Sta Rosa Rio 1° (SR)	La Para (LP)
Sn	Water	Wet	<LOD	0.046 ± 0.004^b	0.015 ± 0.003^a	<LOQ	<LOQ
	Water	Dry	<LOQ	0.103 ± 0.019^b	0.09 ± 0.01^a	<LOD	0.031 ± 0.006
Sb	Water	Wet	0.028 ± 0.003^a	0.131 ± 0.007^b	0.119 ± 0.008^b	0.154 ± 0.034^c	0.141 ± 0.012^c
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Pt	Water	Wet	<LOD	<LOQ	<LOD	<LOD	<LOD
	Water	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Au	Water	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Water	Dry	0.08 ± 0.01^a	0.08 ± 0.01^a	<LOD	<LOD	<LOD

Values are expressed at means ± SD; <LOD (below detection limit); <LOQ (below quantification limit). LODs. Different letters indicate significantly different values at different monitoring stations in each season (DGC, $P \leq 0.05$). Data adapted from Monferrán et al. [35]

$E_{\mathrm{r}}^{\mathrm{i}}$ is the monomial potential ecological risk factor, T_{ir} is the toxic-response factor for a given substance, which accounts for the toxic and sensitivity requirements. C_{if} is the contamination factor, C_{io} is the concentration of metals in sediment and C_{in} is a reference value for metals (Table 3).

The risk factor $\mathrm{R_I}$ proposed by Håkanson [8] was based on eight parameters (PCB, Hg, Cd, As, Pb, Cu, Cr and Zn) measured in total or *pseudo*-total fraction of sediments. To calculate the ecological risk assessment, the data presented in Table 4 [34, 35] was used, since this study contains much elements measured in *pseudo*-total fraction, excluding PCB that was not measured during this work. Using Eq. (1) and the parameters listed in Table 4, the potential ecological risk indexes $E_{\mathrm{r}}^{\mathrm{i}}$ and $\mathrm{R_1}$ for each sampling site were calculated. T_{ir} is the toxicity coefficient, which represents the toxic-response factor for a given metal/loid. The value of T_{ir} for Hg, Cd, As, Cu, Pb, Cr and Zn was 40, 30, 10, 5, 5, 2 and 1, respectively [40]. C_{if} is the contamination factor, C_{io} is the concentration of metal in the sediment of the Suquía River and C_{in} is the background value of the heavy metal in coastal sediments [41].

Based on Eqs. (1)–(3), ecological risk indexes of metal/loids in the five monitoring stations, considering dry and wet seasons, were calculated and are listed in Table 4. The results indicated that there was a relatively low degree of ecological risk associated with toxic metal/loids in LC, $\mathrm{R_1}$, SR and LP during the wet season. Conversely, moderate ecological risk was found in LC, $\mathrm{R_1}$, SR and LP in the dry season and in CM in the wet season. It is worth noting that severe ecological risk was determined for CM during the dry season. The potential ecological risk index of a single-element $E_{\mathrm{r}}^{\mathrm{i}}$ showed that Hg exhibited the most severe risk for potential pollution risk out of seven studied metal/loids in the sediments of the Suquía River basin, mainly due to the highest toxicity coefficient of Hg.

5 Multivariate Statistical Analysis

Looking for evidence on the correspondence between the two studied matrixes (water and sediment), we decided to apply the Generalised Procrustes analysis (GPA). 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 (metals and metalloids in this case), measured in different matrixes, namely, water and sediment in this case. Additionally, GPA produces a configuration corresponding to different studied sites that reflect the consensus among the two matrixes (metal/loids in water and sediment from different sites). The result is a consensus alignment that uses all the variables from both datasets.

Variables used are those from Tables 5 and 6, since these datasets contain the highest number of measured elements. So far, all the variables showed in Tables 5 and 6 were used as descriptors for grouping water and sediments. In Fig. 2a, b, the consensus configuration projected onto the plane defined by its first and second

Table 5 Concentrations of metal/loids measured in sediments (μg g^{-1} dry weight-DW) of the Suquía River basin

			Monitoring station				
Parameter	Matrix	Season	La Calera (LC)	Corazon María (CM)	Rio 1° (R_1)	Sta Rosa Rio 1° (SR)	La Para (LP)
Li	Sediment	Wet	27 ± 3^a	37 ± 2^c	38 ± 1^c	37 ± 2^c	33 ± 1^b
	Sediment	Dry	18 ± 1^a	23 ± 5^b	36 ± 2^c	26 ± 2^b	26 ± 3^b
Be	Sediment	Wet	0.38 ± 0.01^a	0.43 ± 0.01^c	0.45 ± 0.01^d	0.45 ± 0.01^d	0.41 ± 0.01^b
	Sediment	Dry	0.77 ± 0.01^a	0.82 ± 0.02^b	0.89 ± 0.01^d	0.85 ± 0.01^c	0.82 ± 0.02^b
B	Sediment	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Sediment	Dry	11 ± 5^a	75 ± 17^b	75 ± 26^b	<LOD	<LOD
Al	Sediment	Wet	$14{,}550 \pm 220^a$	$22{,}806 \pm 648^c$	$22{,}651 \pm 651^c$	$22{,}265 \pm 1{,}140^c$	$21{,}285 \pm 673^b$
	Sediment	Dry	$11{,}224 \pm 506^a$	$22{,}121 \pm 736^b$	$22{,}793 \pm 1{,}451$	$20{,}282 \pm 908$	$19{,}157 \pm 771$
V	Sediment	Wet	38 ± 1^c	31 ± 1^a	32 ± 1^b	30 ± 2^a	33 ± 1^b
	Sediment	Dry	58 ± 2^b	36 ± 6^a	34 ± 2^a	37 ± 2^a	34 ± 2^a
Cr	Sediment	Wet	21 ± 1^b	26 ± 1^c	26 ± 1^c	26 ± 2^c	19 ± 1^a
	Sediment	Dry	28 ± 1^c	36 ± 6^d	31 ± 2^c	22 ± 1b	17 ± 1^a
Mn	Sediment	Wet	474 ± 10^c	334 ± 9^a	736 ± 16^e	670 ± 36^d	381 ± 11^e
	Sediment	Dry	386 ± 9^b	429 ± 71^b	$1{,}720 \pm 110^d$	633 ± 28^c	298 ± 12^a
Fe	Sediment	Wet	$18{,}443 \pm 376^a$	$18{,}807 \pm 513^a$	$19{,}890 \pm 745^a$	$19{,}526 \pm 836^a$	$17{,}462 \pm 474^a$
	Sediment	Dry	$20{,}412 \pm 880^c$	$16{,}892 \pm 684^a$	$18{,}241 \pm 1{,}189^b$	$17{,}315 \pm 795^b$	$15{,}398 \pm 619^a$
Co	Sediment	Wet	6.4 ± 0.1^c	5.8 ± 0.1^b	6.5 ± 0.2^c	6.3 ± 0.4^c	5.3 ± 0.1^a
	Sediment	Dry	6.6 ± 0.4^c	4.3 ± 0.7^a	6.7 ± 0.5^c	5.4 ± 0.2^b	4.3 ± 0.2^a
Ni	Sediment	Wet	10.4 ± 0.4^b	13.2 ± 0.6^d	12.1 ± 0.4^c	11.6 ± 0.9^c	9.4 ± 0.8^a
	Sediment	Dry	11 ± 0.6^b	15.1 ± 2.8^c	13.8 ± 1.1^c	10.1 ± 0.5^b	8.2 ± 0.3^a
Cu	Sediment	Wet	18 ± 1^b	38 ± 2^e	30 ± 1^d	27 ± 2^c	16 ± 1^a
	Sediment	Dry	13 ± 1^a	74 ± 13^c	44 ± 3^b	20 ± 1^a	17 ± 1^a
Zn	Sediment	Wet	27 ± 2^a	131 ± 5^e	78 ± 4^d	67 ± 5^c	37 ± 2^b
	Sediment	Dry	38 ± 2^a	254 ± 42^c	126 ± 9^b	59 ± 3^a	49 ± 2^a
As	Sediment	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Sediment	Dry	<LOD	<LOD	<LOD	<LOD	<LOD

Se	Sediment	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Sediment	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Rb	Sediment	Wet	26 ± 1^{a}	39 ± 2^{a}	42 ± 1^{a}	46 ± 1^{b}	39 ± 1^{a}
	Sediment	Dry	24 ± 2^{a}	35 ± 2^{b}	39 ± 3^{c}	34 ± 2^{b}	31 ± 1^{b}
Sr	Sediment	Wet	76 ± 1^{a}	119 ± 1^{a}	141 ± 4^{a}	139 ± 4^{b}	145 ± 40^{a}
	Sediment	Dry	27 ± 2^{a}	118 ± 2^{b}	117 ± 7^{c}	126 ± 6^{c}	119 ± 5^{c}
Mo	Sediment	Wet	<LOD	<LOD	<LOD	<LOD	<LOD
	Sediment	Dry	<LOD	2.1 ± 0.4^{b}	1.3 ± 0.1^{a}	<LOD	<LOD
Ag	Sediment	Wet	<LOQ	$1.46\ 0.02^{b}$	1.43 ± 0.02^{b}	1.51 ± 0.06^{b}	0.75 ± 0.02^{a}
	Sediment	Dry	<LOQ	1.9 ± 0.1^{b}	4.7 ± 1.4^{c}	1.1 ± 0.1^{a}	<LOQ
Cd	Sediment	Wet	<LOQ	0.74 ± 0.03^{c}	0.59 ± 0.04^{b}	0.56 ± 0.05^{b}	0.45 ± 0.01^{a}
	Sediment	Dry	<LOQ	<LOQ	<LOQ	0.34 ± 0.11	<LOD
Ba	Sediment	Wet	304 ± 11^{d}	236 ± 5^{a}	278 ± 3^{b}	289 ± 14^{c}	229 ± 3^{a}
	Sediment	Dry	130 ± 2^{a}	315 ± 2^{c}	321 ± 5^{b}	201 ± 13^{a}	168 ± 14^{a}
Ce	Sediment	Wet	67 ± 2^{b}	53 ± 2^{a}	73 ± 1^{c}	75 ± 4^{c}	69 ± 1^{b}
	Sediment	Dry	178 ± 8^{d}	37 ± 7^{a}	60 ± 1^{b}	85 ± 6^{c}	61 ± 5^{b}
Hg	Sediment	Wet	<LOD	0.64 ± 0.09^{a}	0.53 ± 0.11^{a}	0.55 ± 0.11^{a}	0.58 ± 0.08^{a}
	Sediment	Dry	1.46 ± 0.15^{a}	1.88 ± 0.5^{b}	1.42 ± 0.15^{a}	1.22 ± 0.07^{a}	1.26 ± 0.07^{a}
TI	Sediment	Wet	0.32 ± 0.01^{a}	0.46 ± 0.02^{b}	0.45 ± 0.01^{b}	0.43 ± 0.03^{b}	0.4 ± 0.02^{b}
	Sediment	Dry	0.46 ± 0.03^{a}	0.52 ± 0.06^{b}	0.62 ± 0.02^{b}	0.53 ± 0.03^{c}	0.52 ± 0.02^{b}
Pb	Sediment	Wet	10 ± 1^{a}	48 ± 1^{e}	34 ± 1^{d}	29 ± 2^{c}	17 ± 1^{b}
	Sediment	Dry	9 ± 2^{a}	39 ± 7^{d}	39 ± 1^{d}	18 ± 1^{c}	13 ± 1^{b}
Bi	Sediment	Wet	0.14 ± 0.01^{a}	0.90 ± 0.02^{e}	0.62 ± 0.02^{d}	0.57 ± 0.03^{c}	0.37 ± 0.01^{b}
	Sediment	Dry	0.50 ± 0.02^{a}	1.91 ± 0.31^{d}	1.28 ± 0.02^{c}	0.783 ± 0.028^{b}	0.71 ± 0.03^{b}
U	Sediment	Wet	4.1 ± 0.1^{b}	4.7 ± 0.2^{c}	5.1 ± 0.1^{d}	4.1 ± 0.2^{b}	2.5 ± 0.1^{a}
	Sediment	Dry	4.8 ± 0.2^{c}	7.3 ± 1.5^{d}	5.6 ± 0.1^{c}	2.8 ± 0.2^{b}	1.8 ± 0.2^{a}
Pd	Sediment	Wet	0.54 ± 0.02^{b}	0.46 ± 0.02^{a}	0.53 ± 0.01^{b}	0.57 ± 0.01^{c}	0.61 ± 0.01^{d}
	Sediment	Dry	1.33 ± 0.16^{d}	0.56 ± 0.11^{a}	0.82 ± 0.05^{b}	1.05 ± 0.14^{c}	0.87 ± 0.08^{b}

(continued)

Table 5 (continued)

Parameter	Matrix	Season	Monitoring station				
			La Calera (LC)	Corazon María (CM)	Rio 1° (R_1)	Sta Rosa Rio 1° (SR)	La Para (LP)
Sn	Sediment	Wet	0.13 ± 0.01^{a}	0.41 ± 0.03^{c}	0.25 ± 0.02^{b}	0.24 ± 0.02^{b}	0.13 ± 0.03^{a}
	Sediment	Dry	0.08 ± 0.02^{a}	2.06 ± 0.44^{c}	0.97 ± 0.09^{b}	0.27 ± 0.10^{a}	0.24 ± 0.04^{a}
Sb	Sediment	Wet	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Sediment	Dry	<LOD	<LOD	<LOD	<LOD	<LOD
Pt	Sediment	Wet	0.005 ± 0.001^{a}	0.014 ± 0.001^{c}	0.012 ± 0.001^{b}	0.013 ± 0.010^{b}	0.014 ± 0.001^{c}
	Sediment	Dry	<LOD	0.012 ± 0.003^{a}	0.018 ± 0.002^{a}	0.015 ± 0.002^{a}	0.013 ± 0.003^{a}
Au	Sediment	Wet	<LOQ	0.019 ± 0.002^{c}	0.016 ± 0.002^{b}	0.014 ± 0.002^{b}	0.009 ± 0.001^{a}
	Sediment	Dry	<LOD	0.186 ± 0.022^{b}	0.151 ± 0.067^{b}	0.027 ± 0.005^{a}	0.033 ± 0.004^{a}

Values are expressed as means ± SD. <LOD (below detection limit); <LOQ (below quantification limit). Different letters indicate significantly different values at different monitoring stations in each season (DGC, $P \leq 0.05$). Data adapted from Monferrán et al. [35]

Table 6 Standards of the potential ecological risk according to E_r^i and R_I

Scope of potential ecological risk index (E_r^i)	Ecological risk level of single-factor pollution	Scope of potential toxicity index (R_I)	General level of potential ecological risk
$E_r^i < 40$	Low	$R_I < 150$	Low-grade
$40 \le E_r^i < 80$	Moderate	$150 \le R_I < 300$	Moderate
$80 \le E_r^i < 160$	Higher	$300 \le R_I < 600$	Severe
$160 \le E_r^i < 320$	High	$600 \le R_I$	Serious
$320 \le E_r^i$	Serious		

Note: E_r^i was classified by Håkanson [8]. E_r^i is the monomial potential ecological risk factor. R_I is calculated as the sum of all risk factors for heavy metals in sediment, which represents the sensitivity of the biological community to the toxic substance and illustrates the potential ecological risk caused by the overall contamination

Table 7 Potential ecological risk indices of metal/loids in sediments from five monitoring sites of Suquía River

		E_r^i							
Monitoring station	Season	As	Cu	Cd	Cr	Pb	Zn	Hg	R_I
La Calera (LC)	Wet	0.0	3.0	0.0	0.7	2.0	0.3	0.0	6
	Dry	0.0	2.2	0.0	0.9	1.8	0.5	233.6	239
Corazón de Maria (CM)	Wet	0.0	6.3	44.4	0.9	9.6	1.6	102.4	165
	Dry	0.0	12.3	0.0	1.2	7.8	3.2	300.8	325
Río Primero (R_1)	Wet	0.0	5.0	35.4	0.9	6.8	1.0	84.8	134
	Dry	0.0	7.3	0.0	1.0	7.8	1.6	227.2	245
Santa Rosa de Rio Primero (SR)	Wet	0.0	4.5	27.0	0.9	3.4	0.8	88.0	125
	Dry	0.0	3.3	0.0	0.7	2.6	0.7	195.2	203
La Para (LP)	Wet	0.0	2.7	27.0	0.6	3.4	0.5	92.8	127
	Dry	0.0	2.8	0.0	0.6	2.6	0.6	201.6	208

principal axis is shown, explaining 68.4% of variability between samples during the wet season and 73.7% during the dry season.

We can observe that the five monitoring sites considered are well separated in terms of levels of metals and metalloids measured in both water and sediment. This last result gives further indication of the connection between both studied matrixes.

Through this multivariate statistical technique (GPA), we can presume that the different ecological compartments (water and sediment) studied along the Suquía River basin are closely related and that the interaction between them determines the characteristics of each site. These results allow us to highlight the importance of integrating studies from different compartments to determine the quality of water resources by means of a pollution gradient as the one observed along the Suquía River basin from upper to lower sections.

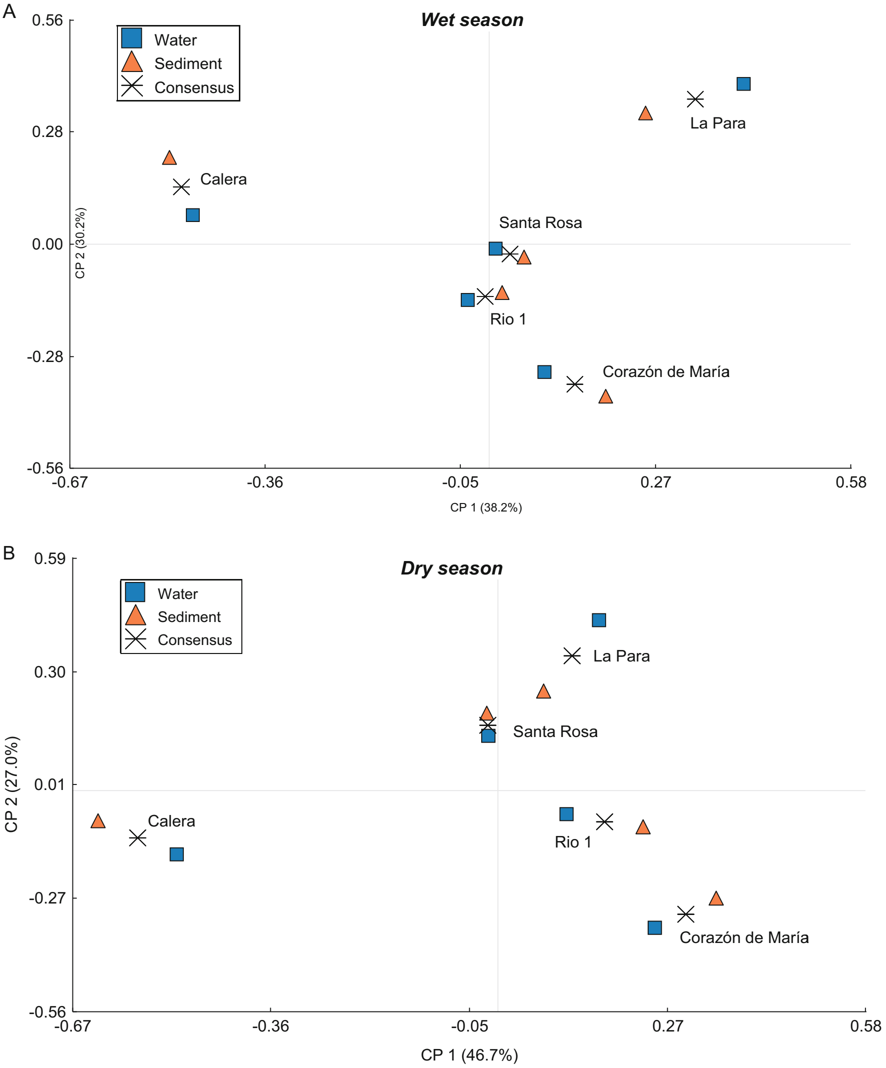

Fig. 2 Consensus space from Generalised Procrustes analysis: plot in the plane formed by the first two dimensions: (**a**) wet season and (**b**) dry season

6 Conclusions

According to studies conducted by different authors over 17 years, it can be concluded that, although not all mentioned reports sampled at the same monitoring sites, or at the same time, when analysing them all together, a wide overview of metal/loids concentrations in water and sediment along the Rio Suquía basin is observed, showing differences between the dry and wet season throughout the studied years. A brief summary of all these studies allow the following conclusions:

The concentrations of metal/loids in stream available sediments from the pristine areas were similar in both sampling seasons.

Some metal/loids values (e.g. Pb and Ni) in the upper catchment were, as expected, the lowest, considering the entire drainage basin. Conversely, Cu and Zn exhibited moderate concentrations, especially in LM1 and LM2 (Table 1) sites when compared to levels for the protection of the aquatic biota established in Canada (16 μg g^{-1} DW).

The environmental impact of Córdoba City (mainly from the WWTP) became evident in the Suquía River system with the increase of toxic metal/loids at the sampling stations located downstream the WWTP, with a greater impact closer to the sewage exit.

A reduced number of point sources of pollutants further downstream the WWTP and the industrial effluents determine a decreasing metal/loids concentration trend downstream from these points. Other processes, such as dilution by relatively metal-free sediment supplied by bank erosion, may also support the observed decreasing concentration trend.

The increase in As concentration observed between Córdoba City and the river mouth at the Mar Chiquita lake could be explained by nonpoint sources, arising from runoffs from surrounding fields dedicated to both agriculture and stock breeding, which use groundwater for irrigation and provision of water to cattle.

The concentrations of some elements in river waters are also characterised by a seasonal dependence. Namely, higher concentrations are observed during the wet/rainy season for some elements, probably due to increased urban runoffs at the beginning of the rainy season, while other elements present higher values during the dry season, probably as a consequence of a lower amount of water, causing a concentration effect when an almost constant charge is released into the water.

Ecological risk indexes of metals in sediments indicate that sediments located few kilometres downstream from the WWTP have moderate to severe ecological risk. Therefore, the downstream area close to the WWTP can be considered as the most polluted site.

Using multivariate statistical analysis (GPA), it can be demonstrated that the different ecological compartments studied (water and sediment) are closely related and that the interaction between them determines the quality of the aquatic environment at each studied site.

References

1. El-Said GF, Youssef DH (2013) Ecotoxicological impact assessment of some heavy metals and their distribution in some fractions of mangrove sediments from Red Sea, Egypt. Environ Monit Assess 185:393–404

2. DeWolf H, Rashid R (2008) Heavy metal accumulation in Littoraria scabra along polluted and pristine mangrove areas of Tanzania. Environ Pollut 152:636–643
3. Chen Y, Siyue L, Yulong Z, Quanfa Z (2011) Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China. J Hazard Mater 191:366–372
4. Yi Y, Yang Z, Zhang S (2011) Ecological risk assessment of heavy metals in sediment and human health risk assessment of heavy metals in fishes in the middle and lower reaches of the Yangtze River basin. Environ Pollut 159(10):2575–2585
5. Bradl HB (2005) Sources and origins of heavy metals. In: Bradl HB (ed) Heavy metals in the environment. Elsevier, Amsterdam, pp 1–27
6. Bastami KD, Bagheri H, Haghparast S, Soltani F, Hamzehpoor A, Bastami MD (2012) Geochemical and geo-statistical assessment of selected heavy metals in the surface sediments of the Gorgan Bay, Iran. Mar Pollut Bull 64:2877–2884
7. ElNemr AH, El Sikaily A, Khaled A (2007) Total and leachable heavy metals in muddy and sandy sediments of Egyptian coast along Mediterranean Sea. Environ Monit Assess 129:151–168
8. Håkanson L (1980) An ecological risk index for aquatic pollution control of sediment ecological approach. Water Res 14:975–1000
9. Maher WA, Aislabie J (1992) Polycyclic aromatic hydrocarbons in near shore marine sediments of Australia. Sci Total Environ 112:143–164
10. Rivail Da Silva M, Lamotte M, Donard OFX, Soriano-Sierra EJ, Robert M (1996) Metal contamination in surface sediments of mangroves, lagoons and southern Bay in Florianopolis Island. J Environ Technol 17:1035–1046
11. Peng JF, Song YH, Yuan P, Cui XY, Qiu GL (2009) The remediation of heavy metals contaminated sediment. J Hazard Mater 161:633–640
12. Yu RL, Hu GY, Wang LJ (2010) Speciation and ecological risk of heavy metals in intertidal sediments of Quanzhou Bay, China. Environ Monit Assess 163:241–252
13. Cuong DT, Obbard JP (2006) Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Appl Geochem 21:1335–1346
14. Wu YH, Hou XH, Cheng XY, Yao SC, Xia WL, Wang SM (2007) Combining geochemical and statistical methods to distinguish anthropogenic source of metals in lacustrine sediment: a case study in Dongjiu Lake, Taihu Lake catchment. China Environ Geol 52:1467–1474
15. Taylor KG, Owens PN (2009) Sediments in urban river basins: a review of sediment-contaminant dynamics in an environmental system conditioned by human activities. J Soils Sediments 9:281–303
16. Pettine M, Camusso M, Martinotti W, Marchetti R, Passino R, Queirazza G (1994) Soluble and particulate metals in the Po River: factors affecting concentrations and partitioning. Sci Total Environ 145:243–265
17. Sutherland RA, Tack FMG, Ziegler AD, Bussen JO (2004) Metal extraction from road-deposited sediments using nine partial decomposition procedures. Appl Geochem 19:947–955
18. Sutherland RA (2002) Comparison between non-residual Al, Co, Cu, Fe, Mn, Ni, Pb and Zn released by a three-step sequential extraction procedure and a dilute hydrochloric acid leach for soil and road deposited sediment. Appl Geochem 17:353–365
19. Agemian H, Chau A (1977) A study of different analytical extraction methods for nondetrital heavy metals in aquatic sediments. Arch Environ Contam Toxicol 6:69–82
20. Andrews S, Sutherland RA (2004) Cu, Pb and Zn contamination in Nuuanu watershed, ahu, Hawaii. Sci Total Environ 324:173–182
21. Yuan X, Zhang L, Li J, Wang C, Ji J (2014) Sediment properties and heavy metal pollution assessment in the river, estuary and lake environments of a fluvial plain, China. Catena 119:52–60
22. Siegel FR (2002) Environmental geochemistry of potentially toxic metals. Springer, Berlin

23. Gaiero D, Ross GR, Depetris P, Kempe S (1997) Spatial and temporal variability of total non-residual heavy metals content in stream sediments from the Suquia River system, Cordoba, Argentina. Water Air Soil Pollut 93:303–319
24. Marnette ECL, Van Breemen N, Hordjijk KA, Cappemberg TE (1993) Pyrite formation in two freshwater systems in the Netherlands. Geochim Cosmochim Acta 57:4165–4177
25. Eaton A (1979) Leachable trace elements in San Francisco Bay sediments: indicators of sources and estuarine processes. Environ Geol 2:333–339
26. Yan L, Stallard RF, Key RM, Crerar DA (1991) Trace metals and dissolved organic carbon in estuaries and offshore waters of New Jersey, USA. Geochim Cosmochim Acta 55:3647–3656
27. Contardo-Jara V, Galanti LN, Amé MV, Monferrán MV, Wunderlin DA, Wiegand C (2009) Biotransformation and antioxidant enzymes of Limnoperna fortunei detect site impact in watercourses of Córdoba, Argentina. Ecotoxicol Environ Saf 72:1871–1880
28. Amé MV, Díaz MD, Wunderlin DA (2003) Occurrence of toxic cyanobacterial blooms in San Roque Reservoir (Córdoba, Argentina): a field and chemometric study. Environ Toxicol 18:192–201
29. Monferrán MV, Galanti LN, Bonansea RI, Amé MV, Wunderlin DA (2011) Integrated survey of water pollution in the Suquía River basin (Córdoba, Argentina). J Environ Monit 13:398–409
30. Pesce SF, Wunderlin DA (2000) Use of water quality indices to verify the impact of Cordoba City (Argentina) on Suquia River. Water Res 34:2915–2926
31. Wunderlin DA, Diaz MP, Amé MV, Pesce SF, Hued AC, Bistoni MA (2001) Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquía River basin (Córdoba-Argentina). Water Res 12:2881–2894
32. Argentinean Environmental Water Quality Guidelines (AEWQGNiveles Guı'a Nacionales de Calidad de Agua Ambiente) (2003) Subsecretaria de Recursos Hídricos de la Nación, República Argentina. www.hidricosargentina.gov.ar/NivelCalidad1.html. Accessed 27 July 2012
33. Canadian Council of Ministers of the Environment (2001) Canadian sediment quality guidelines for the protection of aquatic life: introduction. Updated. In: Canadian environmental quality guidelines, 1999. Canadian Council of Ministers of the Environment, Winnipeg, Canada
34. Monferrán MV, Garnero P, Bistoni MA, Ambar AD, Gordon GW, Wunderlin DA (2012) Acumulación de metales pesados y metaloides en diferentes matrices del lago San Roque (Córdoba, Argentina). Implicancias asociadas al consumo de peces. IV Congreso Argentino de la Sociedad de toxicología y química ambiental SETAC-Argentina. Buenos Aires, Argentina
35. Monferrán MV, Pignata ML, Wunderlin DA (2012) Bioaccumulation of heavy metal and trace elements by Potamogeton pusillus as bioindicator of aquatic pollution. VI SETAC Word Congress, SETAC Europe 22nd Annual meeting. Berlin, Germany
36. Pérez-Carrera A, Fernández A (2013) Cirelli1,2. http://revistas.unlp.edu.ar/index.php/domus/issue/current/showToc
37. Harguinteguy CA, Fernández Cirelli A, Pignata ML (2014) Heavy metal accumulation in leaves of aquatic plant Stuckenia filiformis and its relationship with sediment and water in the Suquía river (Argentina). Microchem J 114:111–118
38. Charzeddine L, Andrade J, Martins C, Gharseddine S, Pérez M (2002) Variación estacional demetales pesados en Americonuphismagna (Annelida: Polychaeta) y en sedimentos de la región nororiental de Venezuela, Saber 14
39. Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232
40. Hilton J, Davison W, Ochsenbein U (1985) A mathematical model for analysis of sediment coke data. Chem Geol 48:281–291
41. Li J, Zheng C (1988) Handbook of environmental background values. China Environmental Science Press, Beijing

Organic Pollutants in the Suquía River Basin

Ana Noemí Santiago, Rocío Inés Bonansea, and María Eugenia Valdés

Abstract Organic pollutants have been detected in water, sediment, suspended particulate matter (SPM) and biota of the Suquía River Basin. It has been observed that the presence of these pollutants is closely related to the anthropic activity carried out at the basin. The upper basin shows the presence of cyanotoxins in water reservoirs due to water eutrophication caused by urban and touristic activities. In the middle basin, Córdoba City is the main source of organic pollutants. Downstream from this city, its wastewater treatment plant (WWTP) releases the highest amount and variety of organic pollutants, which are associated with human activities. Downstream from the WWTP, after the beginning of the lower basin, the riverbank is dominated by farms with diverse agricultural practices, including the use of several agrochemicals, like glyphosate and its metabolite AMPA, chlorinated pesticides and some veterinary medicines, all of them detected in the river water, sediment and biota. Some of these pollutants are retained in the sediment along the lower basin, while others are

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transported until reaching the river mouth at the Mar Chiquita Lake. Exposure to these pollutants, whether by drinking or ingesting them from polluted biota, represents a health risk to aquatic organisms, wildlife, domestic animals and humans.

Keywords Cyanotoxins, Organic pollutants, Organochlorides, Pesticides, Pharmaceuticals

Contents

1 Introduction

The Suquía River Basin covers a wide region, starting in a quasi-pristine mountain area, receiving the input from several small rivers and streams, forming two main tributaries, the Cosquín River and the San Antonio River, which, in turn, form the San Roque Reservoir with a dam, where the Suquía River is born. The reservoir and its tributaries receive both treated and untreated sewages from residential and touristic areas. This reservoir is the main supplier of drinking water for Córdoba City, as well as of electric power. It is also an important recreational area, thus promoting an increase in the urbanisation of the lake surroundings. Downstream from the San Roque Reservoir, the Suquía River runs through several cities, including Córdoba City, with almost 1.5 million inhabitants, which contributes with an important sewage water input from its wastewater treatment plant (WWTP), discharging residues from human activities, such as human and veterinary medicines (HMs and VMs) and their metabolites, personal care products (PPCPs), etc. After leaving the city, the river runs through small towns and an

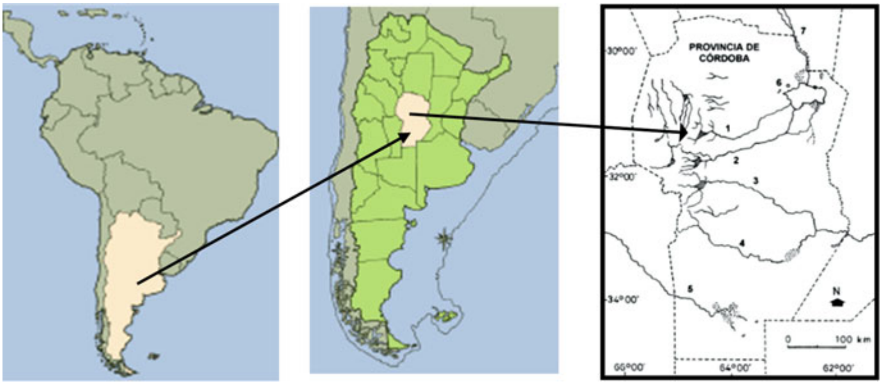

South America Argentina Córdoba

Fig. 1 Localisation of the Suquía River Basin in the world

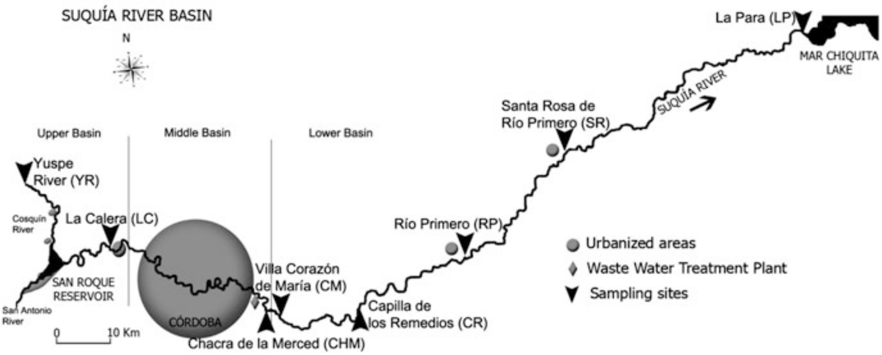


Fig. 2 The entire Suquía River Basin with three areas: upper, middle and lower basins

extensive agricultural area, where the use of agrochemicals and VMs also contributes to the contamination of the river with different organic compounds. Figure 1 shows the localisation of the Suquía River in South America, specifically in the province of Córdoba, Argentina.

Figure 2 shows the basin, including three areas: upper, middle and lower basins. The upper basin starts in a quasi-pristine area located upstream from Córdoba City. It is a touristic area and its pollution is principally caused by human activities. The San Roque Reservoir, which is an artificial lake with a storage capacity of 350 hm^3, is located in this upper basin. The surface area of the lake is 2,478 ha, with a maximum depth of 35.5 m. It has two main tributaries: the San Antonio River (estimated annual mean flow $= 3$ m^3 s^{-1}) and the Cosquín River (estimated annual mean flow $= 4.5$ mm^3 s^{-1}). It also has two minor tributaries: Los Chorrillos Stream (estimated annual mean flow $= 1.2$ m^3 s^{-1}) and Las Mojarras Stream (estimated annual mean flow $= 0.5$ m^3 s^{-1}).

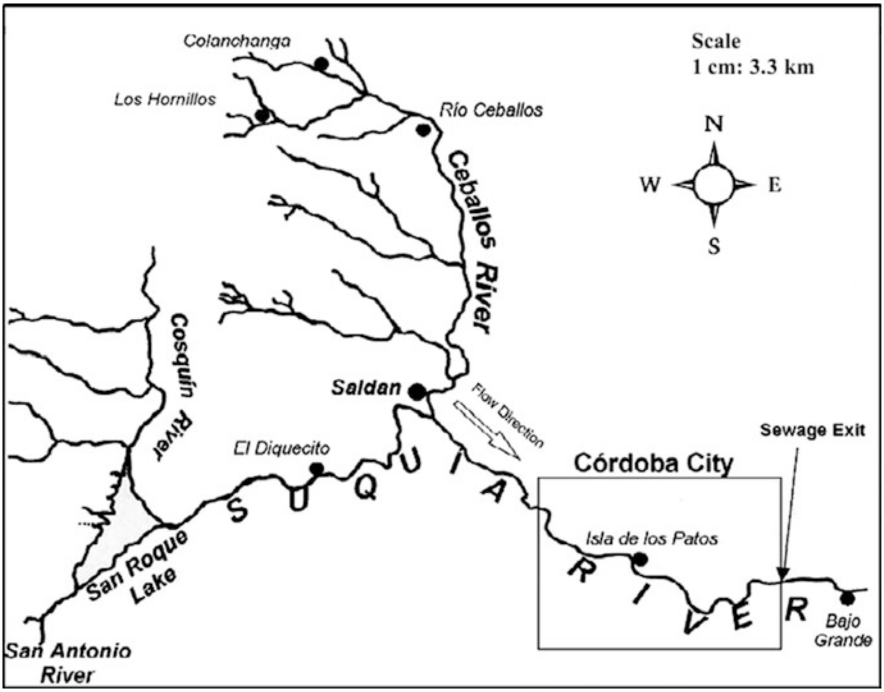


Fig. 3 The Suquía River's upper and middle basins, with indication of monitoring stations. The *box* represents Córdoba City

The middle basin corresponds to the passage of the river through Córdoba City, finishing in a highly polluted area downstream from the outlet of the WWTP of Córdoba City.

The lower basin is in an extensive crop-cultivated area which comprises Villa Corazón de María, nearly 13 km downstream from the WWTP, where vegetables are cultivated for consumption of Córdoba's inhabitants, Capilla de los Remedios, Río Primero, Santa Rosa de Río Primero and La Para (Fig. 2). The Suquía River Basin ends in the Mar Chiquita Lake, located at 150 km NE from Cordoba City, with a surface of 5,770 km^2, which has been classified as a hypersaline lake (>35 g L^{-1} salt).

Figure 2 shows monitoring stations located in the upper and medium basins. These monitoring points account for the presence of quasi-pristine areas, located upstream from Córdoba City, as well as an important pollution gradient caused by human activities downstream, along the basin.

Figure 3 shows in details six monitoring stations: four corresponding to less polluted sites (Los Hornillos, Colanchanga, Río Ceballos and El Diquecito), one with moderate pollution (Isla de los Patos within Córdoba City) and one highly polluted downstream from the Córdoba City WWTP (Bajo Grande).

2 Organochlorides in the Upper and Middle Basins of the Suquía River

Several organochlorides, such as lindane and dichlorobenzene, are persistent organic pollutants (POPs), which are dangerous when released into the environment. They are highly toxic to plants and animals, including humans. Among xenobiotics, chlorinated compounds have high persistence in water and sediments, which can be accumulated by the aquatic biota.

Lindane (γ-hexachlorocyclohexane, or γ-HCH) is a halogenated organic insecticide that has been used worldwide. Most countries have prohibited its use, but some are still using γ-HCH for economic reasons. Consequently, new sites are being contaminated. Furthermore, γ-HCH is used against lice infestations [1], which is a popular infestation among young students in Argentina; thus, the illegal use of γ-HCH against lice cannot be discarded along the basin. A first preliminary report on the presence of γ-HCH in the Suquía River was done by Pesce and Wunderlin [2] at Bajo Grande (Fig. 3). More recent studies confirmed the presence of HCHs at the mouth of the Suquía River in Mar Chiquita Lake (Figs. 2 and 3). It is worthy to mention that γ-HCH accounts for 90% of total HCHs detected, overpassing quality guidelines, and represents a risk to aquatic biota [3].

2.1 *Presence of DCBs in the Suquía River Basin*

Dichlorobenzene isomers (DCBs) are hazardous to health and have been ranked as priority pollutants by the USEPA and public health authorities in the USA (http://www.atsdr.cdc.gov/substances/toxsubstance.asp?toxid=126). DCBs can be introduced into the environment following their use as solvents in deodorants or as intermediates in the manufacture of pesticides [4]. DCBs are found in water [5, 6], sediment [7], sewage sludge [8], air [9] and aquatic biota [10], demonstrating their widespread distribution among all the components of the aquatic environment. Among DCB isomers, 1,4-DCB has a range of domestic uses, namely, as moth repellent and toilet deodorant block. Besides, it has several industrial uses as intermediate in dye and pesticide manufacture, and it is also used in heat transfer media. 1,2-DCB is used as a sewer and septic tank cleaner [6].

Until the year 2000, chlorinated pesticides were not found in the Suquía River, with the exception of the previously mentioned report from Pesce and Wunderlin [2]. However, in the year 2009, the presence of DCBs was observed and evaluated in the Suquía River Basin for over one year. DCBs were not detected in water or sediments of samples collected from quasi-pristine areas, belonging to a protected reserve with less human activities (Los Hornillos and Colanchanga, Fig. 3) [11].

Los Hornillos and Colanchanga Brooks form a small reservoir (La Quebrada), where Ceballos River begins (Fig. 3). Water and sediments of the Ceballos River, sampled in July (drought season), evidenced the presence of 1,2-DCB and 1,3-DCB in both water and sediment, while 1,4-DCB was present only in sediment samples. The presence of DCBs in Ceballos River in July can be explained considering that La Quebrada Reservoir could be acting as a concentrator of DCBs, coming from a small village located upstream (Colanchanga, Fig. 3), and also considering the low river flow during the drought season, which increases the concentration of pollutants in the water [11].

Moreover, water and sediment samples from El Diquecito, located in the Suquía River course, upstream from Córdoba City (Fig. 3), also evidence the presence of DCBs, showing the highest DCB concentrations in the sediment. This station is also located downstream from the San Roque Reservoir, which receives water from San Antonio River and Cosquín River, both surrounded by small to medium touristic towns (Fig. 3). Considering that there are no important human activities between the San Roque Reservoir and El Diquecito, the presence of DCBs in this station could be attributed to pollution from the San Roque Reservoir, which could be concentrating pollutants produced either upstream or along its coasts as a consequence of touristic activity in this area.

An even worse situation was found when analysing stations located in Isla de Los Patos (close to Córdoba downtown) and Bajo Grande (downstream from the city WWTP) (Fig. 3). Both stations presented high DCB levels in water and sediments, confirming that urban–domestic activities could be the main source for DCBs along the Suquía River Basin. However, El Diquecito, Isla de Los Patos and Bajo Grande showed DCB levels that did not exceed limits reported by other authors as having negative effects on the aquatic biota (19,900 $\mu g\ kg^{-1}$ dry weight) [12]. In most of the samples, DCB levels were higher in sediment than in water. Mean concentrations of DCBs in the water of the Suquía River Basin were 1.84 $\mu g\ L^{-1}$for 1,4-DCB and 6.33 $\mu g\ L^{-1}$for 1,2-DCB, which are values comparable to those reported for rivers in heavily populated or industrialised areas, such as the Besos River (Catalonia, Spain) [13].

The contribution of 1,4-DCB to the basin during the dry season reflects the input of DCBs from domestic origin. However, the presence of 1,2-DCB and 1,3-DCB is not understandable, because there are no intensive industries located in the area. Thus, the presence of these two isomers could be due to the biological reduction of highly chlorinated compounds [14]. A high level of DCBs found in sediments involves absorption of these xenobiotics in the natural organic matter (NOM) of sediments, which helps in spreading the pollution throughout the basin.

It is worth to mention that native bacteria of the Suquía River are able to perform biodegradation of DCBs after an acclimation period [15], which can explain why a large accumulation of these xenobiotics is not observed in the basin, although DCBs are being transported by the river, associated with the NOM.

3 Presence of Cyanotoxins in the San Roque Reservoir

Among cyanotoxins, microcystins (MCs) and nodularins (Nods) are potent hepatotoxins [16] and tumour promoters [17]. MCs are cyclic heptapeptides (containing one characteristic amino acid, 3-amino-9-methoxy-2,6,8-trimethyl-10-phenyl-4,6-decadienoic acid-ADDA), while Nod is a cyclic pentapeptide formed by five amino acids (preserving the characteristic ADDA) [18]. MCs present more than 85 variants, including different amino acids at positions 2 and 4; namely, MC-LR contains lysine and arginine at these positions, MC-RR contains two arginines, etc. [19]. Exposure to cyanotoxins represents a health risk to aquatic organisms, wildlife, domestic animals [20] and humans if there is a long-term and frequent exposure through food [21, 22].

Cyanobacterial blooms have occurred in the San Roque Reservoir for about 40 years [23, 24]. *Dolichospermum* sp., *Microcystis* sp., *Chroococcus* sp., *Oscillatoria* sp., *Pseudanabaena* sp., *Phormidium* sp., *Lyngbya* sp. and *Nodularia* sp. are among the cyanobacteria genera more frequently described in this water body [25]. In addition to recreational uses, the San Roque Reservoir is used as raw water source for drinking water; thus, it is necessary to verify the human exposure to cyanobacterial toxins. The presence of MCs in the San Roque Reservoir has been informed since 1997, with maximum values in summer and autumn [26, 27].

From October 1998 to June 2002, 35 cyanobacteria samples were collected during bloom events. The presence of MC-LR and MC-RR was confirmed in 97% of the studied samples, with concentrations ranging from 5.8 to 2,400 μg g^{-1} of freeze-dried material. Four areas of the San Roque Reservoir were monitored. Three stations were on the tributaries' mouths: San Antonio River, Los Chorrillos Brook and Cosquín River. The fourth station was located before the dam exit (Fig. 3). Though the occurrence of MC-LR and MC-RR was similar, the highest concentrations found corresponded to MC-RR [26]. The highest MC levels in cyanobacteria cells in Los Chorrillos Brook's mouth reached 2,400.6 μg g^{-1}, with 721.0 μg g^{-1} and 1,679.6 μg g^{-1} for MC-LR and MC-RR, respectively (expressed in dry weight of freeze-dried cells).

Similar results were reported by Ruibal Conti et al. [27] in water samples collected from 1998 to 2000 in the same reservoir. MC concentration varied from very low (<0.050) to 450 μg L^{-1} in the centre of the reservoir to 923 μg L^{-1} in the east shore. Further studies in the San Roque Reservoir beaches (Club La Calera, the Gypsy Bay, Los Mimbres Bay), where many people practice recreational baths, rod fishing, etc., showed the presence of cyanobacteria in 66% of the cases during the summer, with an MC total concentration in water ranging from non-detectable (nd) to 32.7 μg L^{-1} (unpublished results). This value exceeds by far the guidelines suggested by WHO for drinking water (1 μg L^{-1}) and recreational exposure (20 μg L^{-1}) [28]. On these beaches, dominance of cyanobacteria was common, mainly of the genera *Microcystis* sp. and *Dolichospermum* sp. Considering all these results, it is evident that the San Roque Reservoir is dangerous for practising recreational activities during cyanobacteria blooms. Even the production of drinking water must be carefully controlled during cyanobacteria blooms, where an additional purification procedure must be used (e.g. ozone oxidation, with further activated carbon filtration to remove both MCs and odour, etc.).

In the year 2006, water quality parameters and concentrations of microcystin-LR (MC-LR), MC-RR, MC-LA, MC-YR and Nod were measured in both water and shrimps (*Palaemonetes argentinus*), during field exposure in the San Roque Reservoir [29]. The concentrations of diverse MC variants, evaluated in the water, were below the detection limit (< LOD). The presence of MC-RR and MC-LA in the water was not detected during the exposure of shrimps. Conversely, MC-YR and MC-LR were present during the first two exposure weeks, being below the limit of quantification (<LOQ) afterwards. On the other hand, Nod was the only cyanotoxin quantified in the water throughout the exposure time (0.24 ± 0.04 μg L^{-1}), showing significant differences among the first and the fourth week of exposure. Besides, Nod was detected in all water samples analysed during the exposure time [29]. No guidelines have been set for Nod [28], but since its toxicity resembles that of the MCs, the same guidelines can be applied [30]. Therefore, levels of Nod found in San Roque Reservoir did not surpass those suggested by WHO for drinking water nor exceeded the suggested recreational exposure guideline [28]. These results are in good agreement with Nod levels reported by other authors in the Baltic Sea (0.004–565,000 μg L^{-1}; [31, 32]). According to Dörr et al. [33], the presence of Nod had not been reported in South America; so, the article from Galanti et al. [29] is the first evidence on the presence of Nod in South American freshwaters.

The distribution of MC-LR, MC-RR, MC-YR and the neurotoxin anatoxin-a in water samples was also reported in the San Roque Reservoir from February 2006 to March 2007 [34]. Two monitoring sites were selected: station 1 located at the mouth of the San Antonio River (a visited recreational area, commonly affected by algae blooms) and station 2, nearby the main water intake for Córdoba City (1.3 million of inhabitants). Microcystin concentrations varied from non-detectable levels to 119.0 μg L^{-1}. The highest concentrations of MCs were measured in the San Roque Dam in the spring and summer time. These concentrations frequently surpassed the guidelines suggested by WHO for drinking water and recreational exposure.

The first report of anatoxin-a in freshwaters in South America (2006–2007) informed that anatoxin-a concentrations ranged from non-detectable levels to 6.6 ng L^{-1}, a thousand times below the provisional guideline adopted by New Zealand for drinking water (6 μg L^{-1}) [34]. Anatoxin-a was detected at low concentrations; however, its presence should always be considered as a potential health hazard to humans, aquatic animals, livestock and wildlife.

Also, Galanti et al. [29]) reported the dynamics of bioaccumulation–detoxification of MC-LR by *Palaemonetes argentinus*, showing that after a 3-day exposure in an aquarium to 50 μg L^{-1} MC-LR, this shrimp was able to accumulate MC-LR (0.7 μg g^{-1} FW or 2.8 μg g^{-1} dry weight), showing similar MC accumulation as measured in *Procambarus clarkii* during a laboratory exposure (2.9 μg g^{-1} dry weight; [35]). After a 3-day exposure, Galanti et al. [29]) moved the shrimps to another aquarium without the presence of MC-LR, observing a drop to

0.18–0.01 μg MC-LR g^{-1} after three days, which means that this cyanotoxin can be rapidly detoxified after relocation in water without MCs.

4 Presence of Pesticides in the Lower Basin of the Suquía River

In the last few decades, pesticides have been used on an increasingly wider scale throughout the world. Argentina is not out of this trend; hence, it has significantly expanded the agricultural area and the use of the technological package based on genetically modified seeds. Thus, the use of agrochemicals has pumped up in the last decade from 73 million litres of pesticides to 281 million L/year [36]. The province of Córdoba, where the Suquía River Basin is located, is in the centre of Argentina, with about 50% of its total surface dedicated to agriculture (ca. 165.321 km^2) [37].

Pesticides are a family of compounds characterised by different physical and chemical properties, various modes of action and diverse uses. Plagues develop resistance to regularly used agrochemicals. Thus, developing new pesticides or spreading greater quantities of them has become necessary to keep plagues under control. The importance of pesticides goes further than to reduce costs or produce more with the less handwork; they are also important because they have become harmful to the biota as they pollute different environmental compartments.

There are several studies evaluating the levels of the most widespread commercialised pesticides in Argentina [38]. Additionally, temporal and spatial distributions of agricultural contaminants in the Suquía River Basin have been reported [39–41]. Five sampling sites were selected along this river, considering low and high application periods over the year 2010–2011. The first site is located upstream from Córdoba City, in a mountainous area (La Calera), and the second site is located in Villa Corazón de María, nearly 13 km downstream from the WWTP, next to a vegetable-growing area. In an extensive crop-cultivated area located in the lower basin, three sites were selected: Río Primero, Santa Rosa de Río Primero and La Para (Fig. 2).

Atrazine, acetochlor, chlorpyrifos, α-endosulfan, β-endosulfan, endosulfan sulphate and α-cypermethrin were measured in water [40] and sediment samples [39].

The distribution of glyphosate and its metabolite, aminomethylphosphonic acid (AMPA), was also measured in different compartments of the Suquía River Basin. Monitoring was carried out in water, sediments and suspended particulate matter (SPM) [3]. This investigation revealed the presence of glyphosate and AMPA in all the studied samples. Glyphosate concentrations were the highest in all the matrices: in water from 70.0 to 125.0 μg L^{-1}, in sediments from 23.1 to 1,882.3 μg kg^{-1} and in SPM from non-detectable to 1,570.7 μg kg^{-1}. Glyphosate is the first top pesticide used in Argentina, where approximately 182 million litres are employed per year [36]. Its characteristics of being polar and highly water soluble (11.6 g L^{-1} at 25°C) favour the pollution of the aquatic system. Even though its persistence is relatively short compared to other pesticides (its half-life ranges from 2 to 91 days), when combined with soil particles or sediments, glyphosate becomes more persistent and it may last up to 215 days [42].

AMPA, the main degradation metabolite of glyphosate, was the second most concentrated in water and SPM samples and the third in sediment samples. In water, AMPA ranged from 2.2 to 4.8 μg L^{-1}; in SPM, from 473.5 to 684.9 μg kg^{-1} and in sediments, from 23.9 to 266.1 μg kg^{-1}. AMPA is more persistent than glyphosate, with a longer half-life range in soil from 76 to 240 days [43]. The greater affinity of glyphosate and AMPA to SPM and sediment can be verified in contrast with its presence in water [44].

The third most concentrated compound in water and the second in sediment was α-cypermethrin, ranging from 0.078 to 0.122 μg L^{-1} in water and from 305.8 to 1,333.7 μg kg^{-1} in sediment. The presence of cypermethrin in the river basin can be attributed to its use as both agricultural and urban (domestic) insecticide. Cypermethrin was found in higher concentrations in sediment than in water of the Suquía River, confirming its greater affinity to sediment [45].

The concentration of atrazine in river water, ranging from 0.0048 to 0.434 μg L^{-1}, is mainly related to its extensive use as an agricultural herbicide and also to its relative persistence in surface waters. Atrazine has a half-life of 159 days [46].

The concentration of endosulfan sulphate in water, ranging from 0.6 to 107 ng L^{-1}, was higher than those of their precursors, α- and β-endosulfan, which had a concentration in water from 0.7 to 9.2 ng L^{-1}. Endosulfan has a half-life of 3 to 7 days in water, but its toxic biological metabolite, endosulfan sulphate, has an aqueous half-life of several weeks [47]. These results correlate with the concentrations of endosulfan and endosulfan sulphate quantified in water samples collected in the Mar Chiquita Lake, at the mouth of the Suquía River (Fig. 2), by Ballesteros et al. [3].

The surveys done with the herbicide acetochlor provided a concentration range in water from 0.5 to 3.0 ng L^{-1}. It is a common herbicide used worldwide and, due to its low adsorption coefficients, its turns into a rather mobile pollutant from the soil, becoming a potential threat to the aquatic environment [48]. The presence of this compound in areas without agricultural activity (e.g. at La Calera, upstream from Córdoba City, Fig. 2) shows how widely this pollutant may be distributed throughout the Suquía River Basin.

Chlorpyrifos is a broad-spectrum organophosphate insecticide with widespread usage on grains, cotton, fruits and vegetable crops as well as on lawns and ornamental plants. Chlorpyrifos has a half-life of 35 to 78 days in water [49]. The concentration of this insecticide in river water ranged from 2.5 to 5.6 ng L^{-1}.

Atrazine, acetochlor, chlorpyrifos, α-endosulfan, β-endosulfan and endosulfan sulphate were not detected in sediment samples in the Suquía River Basin.

The comparison of the total amounts of studied pesticides, calculated by summarising the average concentration of each pesticide at each sample site [39–41], reflects that the most polluted location was Villa Corazón de María,

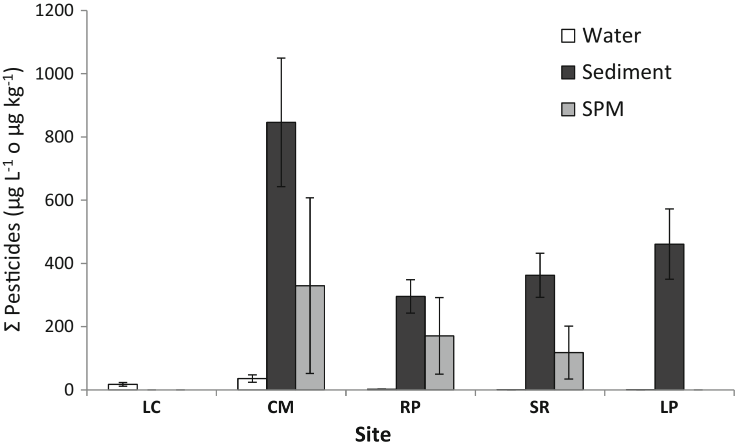


Fig. 4 Concentration of total pesticides (∑ individual pesticides) quantified in the Suquía River Basin. Data from Bonansea et al. [39–41]

downstream from Córdoba City (Fig. 2), with total pesticide concentration of 35.8 μg L^{-1} in water, 846.5 μg kg^{-1} in sediment and 392.7 μg kg^{-1} in SPM (Fig. 4). It was inferred that the measured concentrations of pollutants could be attributed to two sources: the use of studied pesticides in the neighbouring area, dedicated to produce fresh vegetables for urban consumption (close to Córdoba City), in addition to their urban use for home plagues, being later discharged into the water by the WWTP or drained through the urban run-off of Córdoba City, with a population of about 1.5 million people.

In addition to Villa Corazón de María, other sites that showed an intermediate contamination rate were located in the lower basin: Santa Rosa de Río Primero, Río Primero and La Para (Fig. 2). The first one had a total pesticide concentration of 0.14 μg L^{-1} in water, 362.6 μg kg^{-1} in sediments and 118.4 μg kg^{-1}in SPM (Fig. 4). Río Primero showed 2.2 μg L^{-1} total pesticides in water, 296.0 μg kg^{-1} in sediments and 171.2 μg kg^{-1} in SPM, while in La Para the total pesticide concentrations were 0.07 μg L^{-1} in water, 461.1 μg kg^{-1} in sediments and without measurable quantities in SPM (Fig. 4). These three last sites are situated in the main agricultural area of the province of Córdoba, where the cultivated fields reach the riverbank.

Finally, the least polluted area studied was La Calera, upstream from Córdoba City, with a mean of 17.5 μg L^{-1} total pesticides in water and non-detectable amounts of studied pesticides in both sediments and SPM. The most contributing pesticides in this site were glyphosate and α-cypermethrin. The presence of glyphosate in the water of La Calera could be attributed to sporadic domestic usage in house gardens, while the presence of α-cypermethrin could be associated with urban uses to control domestic plagues.

There were no significant differences between application and non-application periods.

Comparing results observed in the Suquía River Basin with other studies carried out in other river basins of the world, it can be observed that concentrations of atrazine found in the Suquía River were similar to those found in the Ebro River Basin in Spain (0.062 μg L^{-1}; [50]). On the contrary, higher concentrations of chlorpyrifos (0.031 μg L^{-1}, [50]) and lower levels of cypermethrin were also reported in the Ebro River (0.00073 μg L^{-1} to 0.0572 μg L^{-1}; [51]). In African basins, the concentrations of endosulfan and endosulfan sulphate were higher than those detected in the Suquía River [52]. On the other hand, Gómez et al. [53] found similar amounts of endosulfan (3 ng L^{-1}) in water samples of the Henares River Basin in Spain.

Comparing the Suquía River Basin data with those of other Argentinean rivers, the Brown and Horqueta Streams, both located in the province of Buenos Aires, had higher concentrations of chlorpyrifos (0.450–10.8 μg L^{-1}) and cypermethrin (0.710–194 μg L^{-1}) [54, 55]. On the other hand, Gonzalez et al. [56] reported endosulfan in the Quequén Grande River (south of the province of Buenos Aires, Argentina) in similar proportions to those found in the Suquía River waters. Concentrations of glyphosate and AMPA similar to those found in the Suquía River were reported in agricultural areas of the northwest of the province of Buenos Aires [57], which were higher than those found in the southeast of the same province [58]. All in all, these results demonstrate the generalised use of pesticides during agricultural activities in Argentina, which is causing pollution of neighbour water courses, impairing risk for the inhabiting biota and for humans using these water resources for diverse uses. For instance, the concentrations of chlorpyrifos and cypermethrin in the Suquía River surpassed the maximum concentrations of pesticides permitted by guidelines established for the protection of the aquatic biota in freshwaters [59, 60]. These results show that remedial action plans for a sustainable management of the Suquía River Basin are urgently needed, including a sustainable use of pesticides in agriculture.

5 Persistent Organic Pollutants (POPs) in the Mar Chiquita Lake

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) represent persistent, bioaccumulative and toxic compounds of global concern [61]. The production and intensive agricultural or industrial use of these compounds during decades have led to a widespread contamination of the environment. Most of these substances have been restricted and forbidden in most countries since the late 1970s, but some developing countries are still using them [62]. In Argentina, most of the OCPs' uses have been banned since 1998 and PCBs since 2005, but their residues are still found in aquatic environments. Endosulfan was highly used in agriculture during the last decades in Argentina, until it was phased out in July 2013.

5.1 Mar Chiquita Lake

Sampling at this hypersaline lake was performed at two stations: Laguna del Plata and Campo Mare (both at the mouth of the Suquía River). Selection of these sites was done with the land use along the river basin: agricultural, urban and industrial. POPs were analysed in superficial water, SPM, bottom sediment and fish tissues (silverside, *Odontesthes bonariensis*) captured in the lake [3]. HCHs, endosulfans, dichlorodiphenyltrichloroethanes (DDTs), PCBs and PBDEs were found in all matrices at both sampling stations. The high persistence and transport processes are responsible for the occurrence of HCHs, DDTs and PCBs in sediment, SPM and fish tissues, even many years after their prohibition.

Superficial water and SPM showed the highest HCH levels during the post-rainy season at both Laguna del Plata (31.8 ng L^{-1} and 17.8 ng g^{-1} dry wt) and Campo Mare (15.7 ng L^{-1} and 25.8 ng g^{-1} dry wt), while for bottom sediments the concentrations remained constant between 0.4 and 1.3 ng g^{-1} dry weight, during all sampling periods. Among HCHs, 90% corresponded to the γ-HCH isomer (lindane), confirming the presence of γ-HCH previously found downstream from the WWTP of Córdoba City [2]. Although the use of HCHs was forbidden in 1998 for different activities, the γ-isomer was allowed until 2011 as an active ingredient in lotions used for lice and scabies control in Argentina [63], which can explain its presence in the basin downstream from Córdoba City [2, 3]. Fish tissues were also studied to verify the follow-up of POPs from the aquatic environment to the inhabiting biota. The maximum permitted level of γ-HCH for the protection of the aquatic biota in saline waters, proposed by the National Argentinean Water Council [64], is 4 ng L^{-1}.This value was exceeded during the post-rainy season at both Laguna del Plata and Campo Mare, where γ-HCH levels in water reached 21.7 ng L^{-1} and 5.8 ng L^{-1}, respectively. Therefore, the aquatic biota inhabiting the Mar Chiquita Lake is exposed to the risk level of lindane in water and sediment. Fish muscle does not represent a risk for human consumption, since the levels of this contaminant did not overpass the daily allowed intake [3]. However, the presence of lindane in fish muscle warns on the probable bioaccumulation of similar compounds in edible fish, which can continue to increase if a more intensive surveillance and control is not applied soon in the basin.

Endosulfan showed variable amounts (0.9–11.6 ng L^{-1}) in water, in agreement with its application in this area until a few years ago. The highest endosulfan levels in water were registered during the rainy season at both sites (11.6 ng L^{-1} and 8.9 ng L^{-1}, respectively). The highest endosulfan levels in SPM, observed during the post-rainy season, reached 37.5 ng L^{-1} and 57.3 ng L^{-1} at both Laguna del Plata and Campo Mare, respectively. When evaluating fish, the highest endosulfan levels were detected in liver (166.3 ng g^{-1}) during the post-rainy season at Laguna del Plata. The residue levels in fish muscle were between 0.3% and 3% of the acceptable daily intake (ADI) and, therefore, do not represent an imminent risk to human health [3].

DDT levels in water ranged from 0.2 to 3.2 ng L^{-1}, with a predominance of *p*,*p*'-DDE (>90%, 0.2–2.9 ng L^{-1}), followed by *p*,*p*'-DDT (0.5–1.7 ng L^{-1}).

The highest DDT levels in SPM in the post-rainy period reached 5.6 ng L^{-1} and 4.8 ng L^{-1} at both Laguna del Plata and Campo Mare, respectively. DDT levels in silverside muscle reached 1.0 ng L^{-1} and 1.5 ng L^{-1} at both Laguna del Plata and Campo Mare, respectively, thus not representing a risk for human consumption [3].

PCBs were registered in superficial water at all sampling periods at both studied sites without significant spatial and temporal differences. The highest PCB levels in water reached 7.3 ng L^{-1} and 8.8 ng L^{-1} at Laguna del Plata and Campo Mare, respectively. Although the maximum allowed levels for saline water are not available, the total concentrations of PCBs did not overpass the maximum permitted for freshwater environments, proposed by the Argentinean National Water Institute (INA) ($\leq$9 ng L^{-1}). Considering these values, PCBs would not represent a risk to the aquatic biota inhabiting the lake under these conditions [3]. On the contrary, levels of PCBs in SPM were higher than in water during the post-rainy season, being 32.4 ng L^{-1} and 21.6 ng L^{-1} at Laguna del Plata and Campo Mare, respectively. PCB levels in fish muscle overpassed the acceptable daily intake for human consumption, posing a risk to human health during the post-rainy season at both Laguna del Plata (10.8 ng g^{-1}) and Campo Mare (10.9 ng g^{-1}). PBDEs showed lower levels (0.2–1.3 ng L^{-1} in water), in agreement with the scarcity of point sources in the area.

The occurrence of POPs in the Mar Chiquita Lake alerts on the contribution of agricultural and urban pollutants in a site protected by the Convention of Wetlands (Ramsar, www.ramsar.org). The studies also raise concerns on biomagnification processes through the food web, reaching values of PCBs in edible fish (silverside, *Odontesthes bonariensis*) that would exceed safe consumption in the absence of adequate surveillance programmes and strict control on the release of POPs from diverse sources.

6 Presence of Pharmaceuticals in the Lower Basin of the Suquía River

Contaminants of emerging concern are chemicals that pose some potential risks to human health or the environment and which are not yet subjected to regulatory criteria or norms for the protection of human health or the environment [65]. Pharmaceuticals are a class of emerging environmental contaminants which have gained a lot of attention in the last 20 years, mainly because of their potential to cause adverse effects on the environment and human health, since they are biologically active compounds, designed to interact with specific pathways and processes in target humans and animals. Pharmaceutical ingredients are widely used in human and veterinary medicine and, after usage or consumption, they are excreted via urine or faeces, as either parent compounds or their metabolites. WWTPs that treat domestic sewage, wastewater from hospital effluents and/or chemical manufacturing plants as well as wastewaters from livestock and agriculture are recognised as the principal sources of pharmaceuticals in the environment, because they are not commonly designed to eliminate micropollutants like pharmaceuticals [66, 67]. Depending on the WWTP nature and on the process design, the elimination rates range from $<10\%$ to almost complete removal [68]. As a consequence, pharmaceuticals are found in concentrations of ng L^{-1} to μg L^{-1} in surface waters [69, 70]. Over the past 20 years, a substantial amount of work has been done (mostly in North America, Europe and Asia), to determine the occurrence, fate, risks and effects of pharmaceuticals on the environment [71]. In South America and particularly in Argentina, there are few studies conducted on this topic, even though tons of medicinal components (i.e. active principles and excipients) are produced annually [72]. Elorriaga et al. [73] conducted the first survey on pharmaceuticals in sewage and WWTP effluents (primary treatment) at 6 locations in Argentina: Palo Blanco (La Plata-Berisso, Buenos Aires), Chascomús (Buenos Aires), Guaminí (Buenos Aires), Bell Ville (Córdoba), Monte Maíz (Córdoba) and Río Tercero (Córdoba). The authors measured the occurrence and concentration range of five widely used pharmaceuticals: caffeine (0.9–44.2 μg L^{-1}), ibuprofen (0.4–13.0 μg L^{-1}), carbamazepine (0.2–2.3 μg L^{-1}), atenolol (0.2–1.7 μg L^{-1}) and diclofenac (0.03–1.2 μg L^{-1}). Pharmaceuticals were detected in all the samples analysed, with similar profiles, even though they corresponded to different urbanised locations. Over half of the total burden of the 5 pharmaceuticals corresponded to caffeine, whereas ibuprofen accounted for 25–30 % and the rest of the compounds represented less than 10 %. This study demonstrated the presence of pharmaceutical compounds in sewer discharges from urban areas in Argentina (μg L^{-1} levels), indicating inputs of these compounds into surface waters of the region.

6.1 Surface Water

Pharmaceuticals are of special concern in areas where treated effluent discharges contribute to a significant portion of the river flow or to streams that are used for the production of drinking water [74]. Both are the case of the Suquía River Basin. As mentioned previously, the ratio between the WWTP effluent flow (mean: 2.45 m^3 s^{-1} in the period 2011–2012) and the river flow (mean: 2.5 m^3 s^{-1} in the same period) is almost 1:1, which exceeds the purification capacity of the river [75]. Valdés et al. [76] measured 15 compounds (pharmaceuticals and steroid hormones) at six sampling stations along the Suquía River and one tributary, the Yuspe River (as control site), during the wet and dry seasons (2011–2012). The concentrations of studied pharmaceuticals were below the detection limit in water samples from sites located upstream from Córdoba City, Yuspe River and La Calera (near the intake of the drinking water facilities of Córdoba City). Conversely, 8 compounds were detected in water samples of the 4 stations downstream

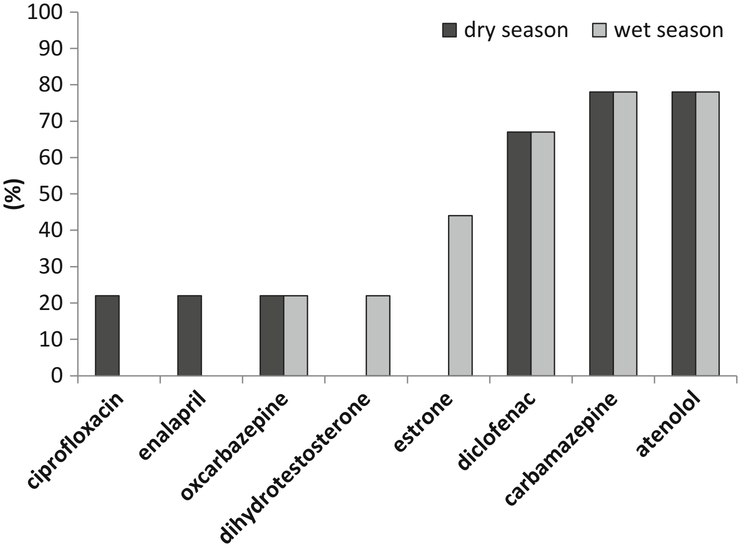


Fig. 5 Frequency of detected pharmaceuticals in the Suquía River water samples. Frequency was calculated as percentage of positive findings in La Calera, Chacra de la Merced, Villa Corazón de María, Capilla de los Remedios and Río Primero samples, within each season. Propranolol, clarithromycin, furosemide, 17β-estradiol, testosterone, androstenedione and methyltestosterone concentrations were below the limit of detection in all studied samples. Data from Valdés et al. [76]

from the WWTP of Cordoba City: ciprofloxacin, enalapril, estrone, dihydrotestosterone, oxcarbazepine, carbamazepine, atenolol and diclofenac. The stations analysed were Chacra de la Merced, Villa Corazón de María, Capilla de los Remedios and Río Primero (Fig. 2). The results found were in accordance with the pollution of the lower river basin previously reported, measuring physical–chemical parameters, metals and pesticides, etc., showing the negative impact of the WWTP on the river water quality, raising concerns about its use for domestic or recreational activities [2, 40, 77–80]. The anti-inflammatory diclofenac, the antiepileptic carbamazepine and the β-blocker atenolol were ubiquitous throughout the studied period, in the 4 stations downstream from Córdoba City, from Chacra de la Merced to the Rio Primero station (67–78% frequencies of detection) (Figs. 2 and 5). Diclofenac ranged from 14 to 145 ng L^{-1}, while carbamazepine 15–113 ng L^{-1} and atenolol 9–581 ng L^{-1} showed the highest levels in the river water. As regards seasonal comparison, higher concentrations of atenolol and diclofenac occurred during the dry season, which could be explained by the lower river flows at this time of the year. Concerning spatial distribution, the general trend for diclofenac and atenolol was a decrease in the concentration with increasing distance from the WWTP of Cordoba City, whereas carbamazepine showed an opposite spatial pattern, increasing its concentration in the last station, Rio Primero (Fig. 2). Moreover, oxcarbazepine levels ranged from non-detectable (nd) to 51 ng L^{-1}, following a similar distribution pattern than carbamazepine, probably given their structural similarities.

Similar levels of carbamazepine, atenolol and diclofenac have been detected in river waters of the Pampas region (province of Buenos Aires and southern area of the province of Cordoba, Argentina) in the first study describing the presence of pharmaceuticals in surface waters of Argentina [81]. The authors detected these 3 pharmaceuticals within the range 0.05–0.36 μg L^{-1} in 10 sampling stations receiving urban wastewater effluents, together with caffeine and ibuprofen, the two most frequently detected pharmaceuticals, in the range 0.86–5.44 μg L^{-1} (not measured in the Suquía River). They also mentioned that, although the half-life of carbamazepine in the environment is higher than atenolol [82], both compounds are usually found at similar levels, since atenolol is more consumed than carbamazepine, being the second most consumed pharmaceutical within the heart therapy and arterial pressure group in Argentina. These three compounds have been reported in other surface waters of the world at similar levels [66, 83–85].

The least frequent emerging contaminants found in the Suquía River were ciprofloxacin, enalapril, estrone and dihydrotestosterone (22–33% frequency) (Fig. 5). Ciprofloxacin (nd–36 ng L^{-1}) and enalapril (nd–4 ng L^{-1}) were present during the dry season in two sites downstream from the WWTP discharge. Similar concentrations have been detected in the Ebro River and its tributaries [84]. Estrone and dihydrotestosterone (nd–8 and nd–10 ng L^{-1}, respectively) were quantified during the wet season, in similar values than previous reports from other parts of the world [86, 87]. The authors explained that cattle farms (more frequent around the area of the Rio Primero station) could be contributing to the steroid load into the Suquía River by run-off.

6.2 Biota

Once in the aquatic environment, the exposure of biota to pharmaceuticals is of particular concern, since these compounds are manufactured with the intention of having a beneficial effect on human/animal health, which is not necessarily the case for aquatic organisms subjected to continual life-cycle exposure. Pharmaceuticals often have the same type of physical–chemical behaviour; e.g. they are lipophilic (to pass membranes) and persistent (to avoid the active principle from becoming inactive before having a curing effect) as other harmful xenobiotics; therefore, they have many of the necessary properties to bioaccumulate and provoke effects on aquatic or terrestrial ecosystems [88]. Studies published in the last ten years have revealed residues of pharmaceuticals in fish downstream from sewage treatment plants [89–92].

Valdés [93] measured accumulation of pharmaceuticals in fish from the Suquía River, covering 20 human and veterinary pharmaceuticals. They were atenolol, carazolol, metoprolol, nadolol, propranolol, sotalol, carbamazepine, 10,11-epoxycarbamazepine, 2-hydroxycarbamazepine, citalopram, diazepam, lorazepam, sertraline, venlafaxine, clopidogrel, codeine, diclofenac, hydrochlorothiazide, levamisole and salbutamol. Fish were captured during the wet and dry seasons in polluted sites where pharmaceuticals had been quantified in river water samples [76]. When monitoring sites closer to the WWTP of Cordoba City, the authors did not find fish, which is probably the consequence of heavy pollution at this area caused by WWTP discharge. Thirty-five kilometres downstream from the WWTP, in Capilla de los Remedios (Fig. 2), only *Gambusia affinis* individuals were present (in the wet season only) and, 70 km downstream, in Río Primero, *G. affinis* and *Jenynsia multidentata* individuals were collected (in both seasons). Both species are abundant along the Suquía River Basin [94]. The first one is an introduced species, very resistant to unfavourable conditions [95]. The second one is a native species, previously proposed as a bioindicator of pollution in the basin [78, 80].

The 20 pharmaceuticals analysed were detected in fish samples in the range nd–41 ng g^{-1} (highest value for codeine), 7 of them being detected in all samples (atenolol, nadolol, diazepam, lorazepam, clopidogrel, hydrochlorothiazide and salbutamol, range 0.4–17 ng g^{-1}ww). The results were in agreement with or higher than previously reported pharmaceutical values in whole fish, except for lower values of diclofenac [92, 96]. Eleven out of the 20 pharmaceuticals analysed were reported in fish tissues from effluent-dominated surface waters worldwide, while 9 of them were reported for the first time to the authors' knowledge [89, 91, 97–100]. The authors mentioned higher levels of pharmaceuticals in fish from Capilla de los Remedios (shorter distance to the WWTP of Cordoba City) compared to Río Primero and a higher accumulation tendency in *G. affinis* during the dry season, similar to pharmaceuticals' behaviour in the water-dissolved phase of the river [76]. However, *J. multidentata* results showed greater variability in the accumulation of pharmaceuticals in both seasons, evidencing a noticeable difference in the accumulation pattern of both species. The authors could not attribute the differences to lipid content (higher in *G. affinis*) and mentioned that other mechanisms (rather than lipophilicity), such as differences in the biotransformation rates by fish, could be involved in the accumulation of polar pharmaceuticals [100]. Finally, they concluded that *G. affinis*, even though it is an introduced species in the region, can be a good bioindicator of the presence of pharmaceuticals in urban impacted rivers, given its presence in polluted sites and its ability to accumulate pharmaceuticals.

7 Methodology of Analysis of Organic Compounds in the Suquía River Basin

Several advanced analytical methods have been developed in recent years for water and wastewater matrices, aimed to obtain a better precision and sensitivity, leading to accurately quantify pollutants at trace concentrations in the aquatic environment. Different alternative methods and materials of extraction and cleanup are known [101]. Solid-phase extraction (SPE) is a well-established sample preparation technique with high sensitivity. Alternative techniques, e.g. SPME (solid-phase microextraction) and LPME (liquid-phase microextraction), have been applied more recently due to their several advantages over SPE in terms of speed, ease of sample handling and minimal solvent use. Monitoring of volatile organic compounds (VOCs) in environmental samples requires the use of highly sensitive techniques to ensure low detection limits as well as an accurate quantification of contaminants.

SPME is a rapid, less expensive, solvent-free and easily automated technique for the isolation of organic compounds from gaseous, liquid and solid samples [102, 103]. Moreover, analyses of organic compounds using SPME were known in soils [104]. The extraction times can be reduced by using the headspace (HS) technique [105]. Another advantage of the HS–SPME approach is that samples from virtually any matrix can be analysed since the fibre is not in direct contact with the sample, although care should be taken when releasing analytes efficiently into the headspace [106]. Thus, optimisation of procedure for headspace solid-phase microextraction (HS–SPME) is mandatory to achieve good results with this technique, especially when analysing low levels of environmentally relevant chemicals [11].

Some other techniques of extraction of organic compounds used in homogenised fish are ultrasonic extraction (USE), QuEChERS (quick, easy, cheap, effective, rugged and safe) and pressurised liquid extraction (PLE) with ASE 350®. Ultrasonic extraction can be achieved using a mixture of 0.1 M aqueous acetic acid/methanol (1:1) as extraction solvent. The extraction included 3 cycles (15 min each), collecting the supernatant after each cycle [92].

QuEChERS involved microscale extraction and purification of the extract using dispersive solid-phase extraction (d-SPE) [92]. Water and acetonitrile are commonly added for the extraction. Magnesium sulphate and sodium acetate are normally used as extraction salts. The mixture is shaken intensively for 1 min and centrifuged (11,000 rpm, 5 min, 4°C) for the separation of the organic and aqueous phases. An aliquot of the organic phase is further purified by d-SPE, employing sorbent mixture of PSA, C18 and magnesium sulphate sorbents for the removal of interfering compounds [92]. The pressurised liquid extraction (PLE) system is a sample preparation technique used for the extraction of analytes from solid materials. The major driving force is the increasing demand from authorities to reduce volumes of organic solvents consumed by classical extraction methods such as Soxhlet. PLE is usually carried out with organic solvents, using a sample cell heated to a selected extraction temperature. A pump valve is opened after the heat-up time, allowing the introduction of the solvent into the cell. Then, the static valve is closed and the cell continued to pressurise to the set point. After the static period, the static valve is reopened, fresh solvent is introduced to flush the lines and cell, and the extract is collected in a vial. PLE, commonly mentioned as accelerated solvent extraction (ASE®), gives recoveries comparable to those obtained with Soxhlet and other techniques in use, while spending only a fraction of the time and solvents needed for those techniques. ASE shows good potential for the recovery of volatile as well as semivolatile compounds [107, 108]. PLE offers several advantages over the traditional methods for the extraction of contaminants from complex environmental matrices, including rapid rates of extraction, high recoveries and low solvent use [90].

A number of studies have demonstrated that isotope dilution (i.e. the use of isotopically labelled internal standards for each analyte or group of compounds sharing similar structures) is the preferred approach to alleviating matrix interference, when labelled analogues for each target analyte are commercially available. However, standard and labelled analogues are required to carry out this technique, whose cost is significantly higher compared to the use of non-labelled compounds [99].

7.1 Quantification of Volatile Organic Compounds (VOCs) by HS/SPME/GC–MS

The following procedure is representative of the analysis of volatile organic compounds (*VOCs*): The quantification of dichlorobenzenes was described by Monferrán et al. [11]). Dichlorobenzene assays were carried out by HS/SPME/GC–MS, using a polydimethylsiloxane (PDMS) SPME, and 3-chloro-1-bromobenzene as the internal standard. Gas chromatographic analyses were performed with a fused silica capillary column HP-5. The GC temperature programme was between 80 and 280°C using helium as carrier gas. Samples were injected manually using the splitless mode with a special fibre holder obtained from Supelco, USA. More accurate results can be obtained in the analysis of VOCs using modern autosamplers designed to inject samples to a GC from either headspace or liquid phase. To increase sensitivity and specificity, the MS detector was operated in the single-ion monitoring (SIM) mode, selecting ions at m/z 146, 148 and 151 for all DCBs, while 3-chloro-1-bromobenzene was monitored at m/z 190, 192 and 194 [11].

7.2 Quantification of Organochlorine Pollutants by GC/ECD

The following procedure is representative of these analyses: Pollutants were liquid–liquid extracted from superficial water using the liquid–liquid method. Briefly, 500 mL of water was spiked with 20 ng of PCB no. 103 as an internal standard, shaked with 300 mL of hexane/dichloromethane for 2 h in a Teflon-lined cap glass amber bottle. After keeping overnight at 4°C, the organic layer was separated and evaporated to 2 mL. Further cleanup was performed by chromatography on activated (200°C, 24 h) silica gel. Elution was carried out with hexane and hexane/dichloromethane (50:50) mixtures. Eluted fractions were concentrated under vacuum. Organochlorine pesticides (OCPs), polychlorinated biphenyls

(PCBs) and polybrominated diphenyl ethers (PBDEs) were analysed using a Shimadzu 17-A chromatograph, equipped with an SPB-5 capillary column, splitless injector (275°C) and EC detector at 290°C. The oven temperature was held at 100°C for 1 min, increased to 150°C at 5°C min^{-1} (held for 1 min), further increased to 240°C at 1.5°C min^{-1} and followed by a final heating up to 300°C at 10°C min^{-1} (held for 10 min) [3].

7.3 *Quantification of Pesticides by GC–MS*

Atrazine, acetochlor, chlorpyrifos, α-endosulfan, β-endosulfan, endosulfan sulphate and α-cypermethrin were measured in water [40] and sediment samples [39]. A combined SPE–SPME method was developed. A starting SPE step was performed to remove pesticides from water samples, with further concentration of the extract by SPME to reach quantitation limits according to the environmental relevant levels using GC–MS. This technique allows measuring pesticides in water at ng L^{-1} levels by GC–MS, enabling structural confirmation by spectral analysis [40]. For removal and pre-concentration of pesticides from sediments, the HS–SPME method was used, similarly to the method previously described for VOCs. The identification and quantification of the compounds were carried out by means of gas chromatography–tandem mass spectrometry (GC–MS/MS) [40].

7.4 *Quantification of Glyphosate and Its Metabolite AMPA by HPLC/ESI-MS*

The distribution of glyphosate and AMPA was measured in different compartments of the Suquía River Basin: water, sediments and suspended particulate matter (SPM) [41]. The sediments and particulate matter samples were extracted with a buffer solution and then derivatised with 9-fluorenmethylcholoroformate (FMOC-Cl) and injected into the high-performance liquid chromatography coupled to mass spectrometry (HPLC/ESI-MS) system. Water samples were directly derivatised and measured.

7.5 *Quantification of Cyanotoxins by HPLC–MS/MS*

The following procedure is representative of these analyses: Extraction and cleanup were performed by SPE, followed by the quantification of cyanotoxins [109]. Cyanotoxins were quantified by HPLC coupled to an ESI ionisation source, followed by MS/MS analysis (triple quadrupole). HPLC was carried out using a column Varian Polaris 5 mm C18-A (50 mm × 2.0 mm). Solvent delivery was performed at 0.25 mL min^{-1} by a binary HPLC using water supplemented with 0.1% formic acid and acetonitrile with 0.1% formic acid (total runtime: 25 min).

7.6 Quantification of Pharmaceuticals by HPLC–MS/MS

The occurrence and concentration range of pharmaceuticals and steroids in water samples were measured by high-performance liquid chromatography coupled to high-resolution mass spectrometry (HPLC/ESI-Q-TOF-MS): ciprofloxacin, enalapril, estrone, dihydrotestosterone, oxcarbazepine, carbamazepine, atenolol and diclofenac were identified by this method [76].

Homogenates of *Gambusia affinis* and *Jenynsia multidentata* were analysed by pressurised liquid extraction, gel permeation purification and separation by ultra-high-performance liquid chromatography coupled to tandem mass spectrometry analysis for detection (UPLC/ESI-QqLIT-MS/MS) [92, 93, 110].

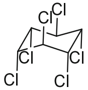
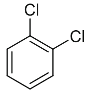
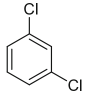
8 Conclusions

A wide range of organic pollutants have been found in water, sediment, SPM and biota of the Suquía River Basin (Table 1). The type and concentration of these pollutants are closely related to the anthropic activity carried out at the respective basin section. For instance, the upper basin mainly shows the presence of cyanotoxins, which can be associated with the eutrophication of the San Roque Reservoir, due to urban and touristic activities along the reservoir catchment. The presence of cyanotoxins in this reservoir poses a threat to humans, whether by water or fish consumption. Furthermore, the recreational use of this reservoir is compromised by the presence of cyanotoxins.

Córdoba City is by far the main source for organic pollutants throughout the Suquía River Basin. The range of organic pollutants detected in the urban section of the river includes chlorinated benzenes and low concentrations of some agrochemicals. Immediately after the city, the WWTP releases the highest amount and variety of organic pollutants, which are associated with human activities. In this section of the river, the presence of some domestic disinfectants (e.g. cypermethrin), pharmaceuticals and personal care products (mainly carbamazepine and atenolol but with many others present) becomes evident.

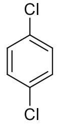
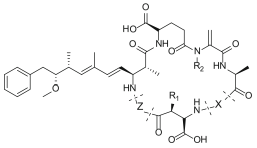
Downstream from the city and its WWTP, the riverbank is dominated by farms, with diverse agricultural practices. The consequence of these farms is the release of several agrochemicals, like glyphosate, AMPA, chlorinated pesticides (e.g. endosulfan), etc., into the river. Some of these pollutants are water soluble (e.g. glyphosate), while others are absorbed/adsorbed into the sediment and suspended particulate matter (SPM) and later deposited in the riverbed or

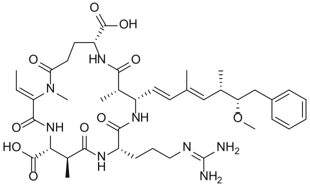
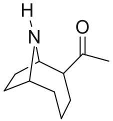
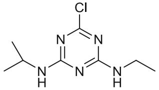
Table 1 Organics Pollutants in the Suquía River Basin

Compounds		Monitoring station	Concentration	References
	Lindane	Chacra de la Merced – sediment	Presence	[2]
		Laguna del Plata – water	2.9–31.8 ng L^{-1}	[3]
		Laguna del Plata – SPM	2.0–17.8 ng g^{-1}	
		Laguna del Plata – sediment	0.4–1.3 ng g^{-1}	
		Laguna del Plata – biota (muscle)	nd–2.5 ng g dw^{-1}	
		Campo Mare – water	3.8–15.7 ng L^{-1}	
		Campo Mare – SPM	4.5–25.8 ng g^{-1}	
		Campo Mare – sediment	0.5–0.9 ng g^{-1}	
		Campo Mare – biota (muscle)	nd–3.1 ng g dw^{-1}	
	1,2-Dichlorobenzene	Ceballos River – water	nd–2.36 µg L^{-1}	[11]
		Ceballos River – sediment	nd–95.00 µg kg^{-1}	
		El Diquecito-water	nd–17.72 µg L^{-1}	
		El Diquecito – sediment	nd–245.20 µg kg^{-1}	
		Isla de los Patos – water	nd–9.0 µg L^{-1}	
		Isla de los Patos – sediment	nd–81.30 µg kg^{-1}	
		Chacra de la Merced – water	nd–24.1 µg L^{-1}	
		Chacra de la Merced – sediment	nd–62.10 µg kg^{-1}	
	1,3-Dichlorobenzene	Ceballos River – water	nd–0.6 µg L^{-1}	[11]
		Ceballos River – sediment	nd–12.00 µg kg^{-1}	
		El Diquecito – water	nd–0.42 µg L^{-1}	
		El Diquecito – sediment	nd–73.60 µg kg^{-1}	
		Isla de los Patos – water	nd–0.82 µg L^{-1}	
		Isla de los Patos – sediment	nd–55.0 µg kg^{-1}	
		Chacra de la Merced – water	nd–7.75 µg L^{-1}	
		Chacra de la Merced – sediment	nd–15.40 µg kg^{-1}	

(continued)

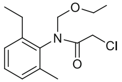
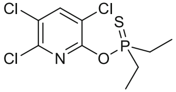
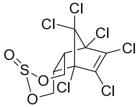
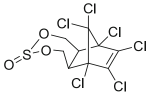
Table 1 (continued)

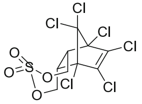
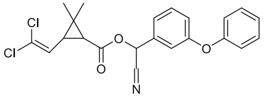
Compounds		Monitoring station	Concentration	References
	1,4-Dichlorobenzene	Ceballos River – sediment	nd–6.30 μg kg^{-1}	[11]
		El Diquecito – water	nd–3.42 μg L^{-1}	
		El Diquecito – sediment	nd–44.70 μg kg^{-1}	
		Isla de los Patos – water	nd–2.14 μg L^{-1}	
		Isla de los Patos – sediment	nd–764.70 μg kg^{-1}	
		Chacra de la Merced – water	nd–6.34 μg L^{-1}	
		Chacra de la Merced – sediment	nd–13.20 μg kg^{-1}	
	Total MC	Dam exit – biota (bloom)	nd–2,366.5 μg g^{-1}	[26]
		San Antonio River mouth – biota (bloom)	5.8–1,232.54 μg g^{-1}	[34]
		Los Chorrillos Brook mouth – biota (bloom)	11.3–2,400.6 μg g^{-1}	
		San Roque Reservoir station 1 – water	0.15–9.21 μg L^{-1}	
		San Roque Reservoir station 2 – water	nd–20.23 μg L^{-1}	
	MC-LR	Dam exit – biota (bloom)	nd–589.8 μg g^{-1}	[26]
		San Antonio River mouth – biota (bloom)	nd–315.8 μg g^{-1}	[34]
		Los Chorrillos Brook mouth – biota (bloom)	nd–721.0 μg g^{-1}	
		San Roque Reservoir station 1 – water	nd–2.02 μg L^{-1}	
		San Roque Reservoir station 2 – water	nd–0.27 μg L^{-1}	

	MC-RR	Dam exit – biota (bloom)	nd–1,776.7 μg g^{-1}	[26]
		San Antonio River mouth – biota (bloom)	nd–916.6 μg g^{-1}	[34]
		Los Chorrillos Brook mouth – biota (bloom)	nd–1,679.6 μg g^{-1}	
		San Roque Reservoir station 1 – water	nd–7.19 μg L^{-1}	
		San Roque Reservoir station 2 – water	nd–19.92 μg L^{-1}	
	MC-YR	San Roque Reservoir station 1 – water	nd–0.25 μg L^{-1}	[34]
		San Roque Reservoir station 2 – water	nd–0.25 μg L^{-1}	
	Nodularin	San Roque Reservoir – water	0.1–0.2 μg L^{-1}	[29]
		San Roque Reservoir – biota	nd–0.09 μg L^{-1}	
	Anatoxin-a	San Roque Reservoir station 1 – water	nd–2.7 ng L^{-1}	[34]
	Atrazine	La Calera – water	nd–0.0048 μg L^{-1}	[40]
		Villa Corazón de María – water	nd–0.0640 μg L^{-1}	
		Río Primero – water	nd–0.1900 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.4340 μg L^{-1}	
		La Para – water	nd–0.0696 μg L^{-1}	

(continued)

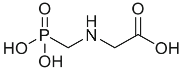
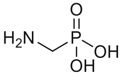
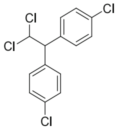
Table 1 (continued)

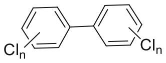
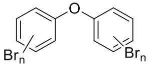
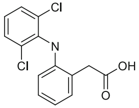
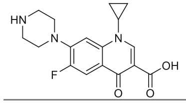
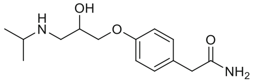
Compounds		Monitoring station	Concentration	References
	Acetochlor	La Calera – water	nd–0.0124 μg L^{-1}	[40]
		Corazón de María – water	nd–0.0170 μg L^{-1}	
		Río Primero – water	nd–0.0158 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.0310 μg L^{-1}	
		La Para – water	0.0005–0.0020 μg L^{-1}	
	Chlorpyrifos	La Calera – water	nd–0.0026 μg L^{-1}	[40]
		Villa Corazón de María – water	nd–0.0055 μg L^{-1}	
		Río Primero – water	0.0025–0.0056 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.0031 μg L^{-1}	
		La Para – water	nd–0.0026 μg L^{-1}	
	α-Endosulfan	La Calera – water	nd–0.0046 μg L^{-1}	[40]
		Villa Corazón de María – water	nd–0.0020 μg L^{-1}	
		Río Primero – water	nd–0.0020 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.0015 μg L^{-1}	
		La Para – water	nd–0.0064 μg L^{-1}	
	β-Endosulfan	Villa Corazón de María – water	nd–0.0049 μg L^{-1}	[40]
		Río Primero – water	nd–0.0092 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.0007 μg L^{-1}	

	Endosulfan sulphate	La Calera – water	nd–0.0178 μg L^{-1}	[40]
		Villa Corazón de María – water	nd–0.0190 μg L^{-1}	
		Río Primero – water	nd–0.0417 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.0038 μg L^{-1}	
		La Para – water	nd–0.1067 μg L^{-1}	
	∑ α- + β- + Endosulfan sulphate	Laguna del Plata – water	0.9–11.6 ng L^{-1}	[3]
		Laguna del Plata – SPM	1.5–37.5 ng g^{-1}	
		Laguna del Plata – sediment	0.5–2.2 ng g^{-1}	
		Laguna del Plata – biota (muscle)	1.3–6.4 ng g dw^{-1}	
		Campo Mare – water	3.1–8.9 ng L^{-1}	
		Campo Mare – SPM	3.3–57.3 ng g^{-1}	
		Campo Mare – sediment	0.8–2.1 ng g^{-1}	
		Campo Mare – biota (muscle)	nd–3.1 ng g dw^{-1}	
	α-Cypermethrin	La Calera – water	nd–0.1217 μg L^{-1}	[39]
		Villa Corazón de María – water	nd–0.0930 μg L^{-1}	[40]
		Río Primero – water	nd–0.1050 μg L^{-1}	
		Santa Rosa de Río Primero – water	nd–0.1120 μg L^{-1}	
		La Para – water	nd–0.1070 μg L^{-1}	
		Villa Corazón de María – sediment	nd–352.6 μg kg^{-1}	
		Río Primero – sediment	nd–548.5 μg kg^{-1}	
		Santa Rosa de Río Primero – sediment	nd–800.6 μg kg^{-1}	
		La Para – sediment	nd–1,333.7 μg kg^{-1}	

(continued)

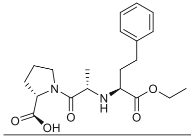
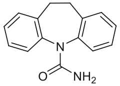
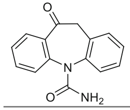
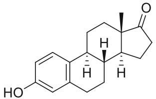
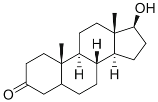
Table 1 (continued)

Compounds		Monitoring station	Concentration	References
	Glyphosate	La Calera – water	nd–70.0 μg L^{-1}	[41]
		Villa Corazón de María – water	nd–125.0 μg L^{-1}	
		Villa Corazón de María – sediment	nd–1,882.3 μg kg^{-1}	
		Río Primero – sediment	nd–168.7 μg kg^{-1}	
		Santa Rosa de Río Primero – sediment	nd–139.0 μg kg^{-1}	
		La Para – sediment	nd–381.9 μg kg^{-1}	
		Villa Corazón de María – SPM	nd–1,570.7 μg kg^{-1}	
	Aminomethylphosphonic acid (AMPA)	Villa Corazón de María – water	nd–2.2 μg L^{-1}	[41]
		Río Primero – water	nd–4.8 μg L^{-1}	
		Corazón de María – sediment	nd–266.1 μg kg^{-1}	
		Río Primero – sediment	nd–222.2 μg kg^{-1}	
		Santa Rosa de Río Primero – sediment	nd–196.4 μg kg^{-1}	
		La Para – sediment	nd–90.2 μg kg^{-1}	
		Río Primero – SPM	nd–684.9 μg kg^{-1}	
		Santa Rosa de Río Primero – SPM	nd–473.5 μg kg^{-1}	
	1-Chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene (DDT)	Laguna del Plata – water	0.2–3.2 ng L^{-1}	[3]
		Laguna del Plata – SPM	nd–5.6 ng g^{-1}	
		Laguna del Plata – sediment	0.03–0.3 ng g^{-1}	
		Laguna del Plata – biota (muscle)	0.1–2.1 ng g dw^{-1}	
		Campo Mare – water	0.2–1.6 ng L^{-1}	
		Campo Mare – SPM	nd–4.8 ng g^{-1}	
		Campo Mare – sediment	0.1–0.3 ng g^{-1}	
		Campo Mare – biota (muscle)	0.1–2.5 ng g dw^{-1}	

	Polychlorinated biphenyls (PCBs)	Laguna del Plata – water	3.2–7.3 ng L^{-1}	[3]
		Laguna del Plata – SPM	2.3–32.4 ng g^{-1}	
		Laguna del Plata – sediment	0.4–1.4 ng g^{-1}	
		Laguna del Plata – biota (muscle)	1.7–14.4 ng g dw^{-1}	
		Campo Mare – water	0.9–8.8 ng L^{-1}	
		Campo Mare – SPM	3.2–21.6 ng g^{-1}	
		Campo Mare – sediment	0.4–1.2 ng g^{-1}	
		Campo Mare – biota (muscle)	0.2–32.7 ng g dw^{-1}	
	Polybrominated diphenyl ethers (PBDEs)	Laguna del Plata – water	0.2–1.3 ng L^{-1}	[3]
		Laguna del Plata – SPM	0.2–4.0 ng g^{-1}	
		Laguna del Plata – sediment	0.6–3.0 ng g^{-1}	
		Laguna del Plata – biota (muscle)	nd–12.0 ng g dw^{-1}	
		Campo Mare – water	0.2–1.1 ng L^{-1}	
		Campo Mare – SPM	1.1–14.3 ng g^{-1}	
		Campo Mare – sediment	0.7–1.4 ng g^{-1}	
		Campo Mare – biota (muscle)	0.4–8.1 ng g dw^{-1}	
	Diclofenac	Chacra de la Merced – water	58–130 ng L^{-1}	[76]
		Villa Corazón de María – water	62–136 ng L^{-1}	
		Capilla de los Remedios – water	34–145 ng L^{-1}	
		Río Primero – water	nd–88 ng L^{-1}	
	Ciprofloxacin	Villa Corazón de María – water	nd–35 ng L^{-1}	[76]
		Capilla de los Remedios – water	nd–36 ng L^{-1}	
	Atenolol	Chacra de la Merced – water	161–353 ng L^{-1}	[76]
		Villa Corazón de María – water	255–581 ng L^{-1}	
		Capilla de los Remedios – water	289–453 ng L^{-1}	
		Río Primero – water	9–261 ng L^{-1}	

(continued)

Table 1 (continued)

Compounds		Monitoring station	Concentration	References
	Enalapril	Capilla de los Remedios – water	nd–4 ng L^{-1}	[76]
	Carbamazepine	Chacra de la Merced – water	15–30 ng L^{-1}	[76]
		Villa Corazón de María – water	16–22 ng L^{-1}	
		Capilla de los Remedios – water	17–113 ng L^{-1}	
		Río Primero– water	33–110 ng L^{-1}	
	Oxcarbazepine	Capilla de los Remedios – water	nd–39 ng L^{-1}	[76]
		Río Primero – water	nd–51 ng L^{-1}	
	Estrone	Río Primero – water	<LOQ–8 ng L^{-1}	[76]
	Dihydrotestosterone	Río Primero – water	nd–10 ng L^{-1}	[76]

transported during flooding events (rainy season) until reaching the river mouth at the Mar Chiquita Lake. The presence of several pesticides in water, sediment and biota close to the river mouth in the Mar Chiquita Lake shows the final destination of organic pollutants and their longer half-life associated with SPM/sediment. The presence of POPs in Mar Chiquita challenges the potential use of this lake for growing edible fish (aquaculture), as endosulfan and its metabolite were found in edible fish (silverside, *Odontesthes bonariensis*).

The most relevant results of organic pollutants in the Suquía River Basin are summarised in the Table 1.

References

1. Nagata Y, Miyauchi K, Damborsky J, Manova K, Ansorgova A, Takagi M (1997) Purification and characterization of a new substrate class from a γ-hexachlorocyclohexane-degrading bacterium, *Sphingomonas paucimobilis* UT26. Appl Environ Microbiol 63:3707–3710
2. Pesce SF, Wunderlin DA (2000) Use of Water quality indices to verify the impact of Córdoba city (Argentina) on Suquía river. Water Res 34(11):2915–2926
3. Ballesteros ML, Miglioranza KSB, Gonzalez M, Fillmann G, Wunderlin DA, Bistoni MA (2014) Multimatrix measurement of persistent organic pollutants in Mar Chiquita, a continental saline shallow lake. Sci Total Environ 490:73–80
4. Beurskens JE, Dekker CGC, van den Heuvel H, Swart M, de Wolf J (1994) Dechlorination of chlorinated benzenes by an anaerobic microbial consortium that selectively mediates the thermodynamic most favourable reactions. Environ Sci Technol 28:701–706
5. He Y, Wang Y, Lee HK (2000) Trace analysis of ten chlorinated benzenes in water by headspace solid-phase microextraction. J Chromatog A 874:49–154
6. Meharg AA, Wright J, Osborn D (2000) Chlorobenzenes in rivers draining industrial catchments. Sci Total Environ 251(252):243–253
7. Beck AJ, Johnson DL, Jones KC (1996) The form and bioavailability of non-ionic organic chemicals in sewage sludge-amended agricultural soils. Sci Total Environ 185:125–149
8. McPherson CA, Tang A, Chapman PM, Taylor LA, Gormican SJ (2002) Toxicity of 1,4-dichlorobenzene in sediment to juvenile polychaete worms. Mar Pollut Bull 44:1405–1414
9. Juang DE, Yuan CS, Hsueh SC, Chiou LJ (2009) Distribution of volatile organic compounds around a polluted river. Int J Environ Sci Technol 6(1):91–104
10. Van Wezel AP, Opperhuizen A (1995) Thermodynamics of partitioning of a series of chlorobenzenes to fish storage lipids, in comparison to partitioning to phospholipids. Chemosphere 31:3605–3615
11. Monferrán MV, Cortina PR, Santiago AN, Wunderlin DA (2009) Distribution of dichlorobenzenes in sediment and water of Suquía River basin (Córdoba-Argentina). Int J Environ Health 3:363–378
12. Malcolm HM, Howe PD, Dobson S (2004) Chlorobenzenes other than hexachlorobenzene: environmental aspects. World Health Organization, Concise International Chemical Assessment Document 60, http://whqlibdoc.who.int/publications/2004/924153060X.pdf
13. Gomez Belichon JI, Grimalt JO, Albaiges J (1991) Volatile organic compounds in two polluted rivers in Barcelona (Catalonia, Spain). Water Res 25:577–589
14. Fathepure BZ, Tiedje JM, Boyd SA (1988) Reductive dechlorination of hexachlorobenzene to tri- and dichlorobenzenes in anaerobic sewage sludge. Appl Environ Microb 54:327–330
15. Monferrán MV, Echenique JR, Wunderlin DA (2005) Degradation of chlorobenzenes by a strain of Acidovorax avenae isolated from a polluted aquifer. Chemosphere 61:98–106

16. Wiegand C, Pflugmacher S (2005) Ecotoxicological effects of selected cyanobacterial secondary metabolites a short review. Toxicol Appl Pharm 203:201–218
17. Nishiwaki-Matsushina R, Oht T, Nishiwaki S, Suganuma M, Yoszawa S, Kohyama K, Ishikaawa Y, Carmichael WW, Fujiki H (1992) Liver tumor promotion by the cyanobacterial cyclic peptide toxin microcystin-LR. J Canc Res Clin Oncol 118:420–424
18. Sivonen K, Kononen K, Carmichae WW, Dahlem AM, Rinehart KL, Kiviranta J, Niemela SI (1989) Occurrence of the hepatotoxic cyanobacterium *Nodularia spumigena* in the Baltic sea and structure of the toxin. Appl Environ Microbiol 55(8):1990–1995
19. Rastogi RP, Sinha RP, Incharoensakdi A (2014) The cyanotoxin-microcystins: current overview. Rev Environ Sci Biotechnol 13:215–249
20. Malbrouck C, Kestemont P (2006) Effects of microcystins on fish. Environ Toxicol Chem 25:72–86
21. Magalhäes VF, Soares RM, Azevedo SMFO (2001) Microcystin contamination in fish from the Jacarepaguá Lagoon (Rio de Janeiro, Brazil): ecological implication and human health risk. Toxicon 39:1077–1085
22. Quiblier C, Wood S, Echenique-Subiabre I, Heath M, Villeneuve A, Humbert J-F (2013) A review of current knowledge on toxic benthic freshwater cyanobacteria-Ecology, toxin production and risk management. Water Res 47:5464–5479
23. Scarafia ME, Agnese AM, Cabrera JL (1995) Microcystis aeruginosa: behavior and toxic features in San Roque Dam (Argentina). Natural Toxins 3:75–77
24. Pizzolón L, Tracanna B, Silva H, Prósperi C, Fabricius ALM, Emiliani MOG, Otaegui AV, Amalfi M, Labollita H, Santinelli N, Sastre V (1997) Inventario de ambientes dulceacuícolas de la Argentina con riesgo de envenenamiento por cianobacterias (toxic cyanobacterial blooms in Argentinean freshwaters). Ingeniería Sanitaria Ambiental 33:26–34
25. Brandalise MV, Nadal F, Rodriguez MI, Larrosa N, Ruiz M, Halac S, Olivera P, Licera C (2007) Índice de Calidad de Agua para uso Recreativo en Ambientes con Cianobacterias. http://www.ina.gov.ar/pdf/ifrrhh/02_007_Brandalise.pdf
26. Amé MV, Díaz MP, Wunderlin DA (2003) Occurrence of toxic cyanobacterial blooms in San Roque Reservoir (Córdoba–Argentina): a field and Chemometric study. Environm Toxicol 18:192–201
27. Ruibal Conti AL, Reguerira M, Guerrero JM (2005) Levels of microcystins in two reservoirs used for water supply and recreation: differences in the implementation of safe levels. Environ Toxicol 20:263–269
28. World and Health Organization (WHO) (2011) Guidelines for drinking-water quality, 4th edn. WHO, Geneva, Switzerland, p 564
29. Galanti LN, Amé MV, Wunderlin DA (2013) Accumulation and detoxification dynamic of cyanotoxins in the freshwater shrimp *Palaemonetes argentinus*. Harmful Algae 27:88–93
30. Kuiper-Goodman T, Falconer I, Fitzgerald J (1999) Human health aspects. In: Chorus I, Bartram J (eds) Toxic cyanobacteria in the water. E & FN Spon, London pp 113–153
31. Mazur H, Plinski M (2003) Nodularia spumigena blooms and the occurrence of hepatotoxin in the Gulf of Gdansk. Oceanologia 45(1):305–316
32. Henriksen P (2005) Estimating nodularin, content of cyanobacterial blooms from abundance of *Nodularia spumigena* and its characteristic pigments – a case study from the Baltic entrance area. Harmful Algae 4:167–178
33. Dörr FA, Pinto E, Soares RM, de Feliciano Olivera e Azevedo SM (2010) Microcystins in South American aquatic ecosystems: occurrence, toxicity and toxicological assay. Toxicon 56:1247–1256
34. Ruiz M, Galanti L, Ruibal AL, Rodriguez MI, Wunderlin DA, Amé MV (2013) First report of microcystins and anatoxin-a co-occurrence in San Roque Reservoir (Córdoba, Argentina). Water Air Soil Pollut 224:1593
35. Vasconcelos V, Aliveira S, Oliva Teles F (2001) Impact of a toxic and non-toxic strain of *Microcystis aeruginosa* on the crayfish *Procambarus clarkii*. Toxicon 39:1462–1470
36. Cámara de Sanidad Agropecuaria y Fertilizantes (CASAFE) (2013) http://www.casafe.org/

37. Sistema integrado de información agropecuaria (SIIA) (2013) http://www.siia.gov.ar/
38. Cámara de Sanidad Agropecuaria y Fertilizantes (CASAFE) (2011) http://www.casafe.org/
39. Bonansea RI, Wunderlin DA, Amé MV (2012) Determinación de pesticidas en sedimentos del río Suquía (Córdoba, Argentina) usando microextracción en fase sólida (HS-SPME) acoplada a GC-MS. IV Congreso Argentino de la Sociedad de Toxicología y Química Ambiental (SETAC). Buenos Aires, p 51
40. Bonansea RI, Amé MV, Wunderlin DA (2013) Determination of priority pesticides in water samples combining SPE and SPME coupled to GC/MS. A case study: Suquía River basin (Argentina). Chemosphere 90:1860–1869
41. Bonansea RI (2015) Evaluación de Plaguicidas en un ambiente acuatico contaminado, su acumulación en biota y aplicación de Biomarcadores para su detección. PhD. Thesis, Universidad Nacional de Córdoba, Córdoba-Argentina
42. Grunewald K, Schmidt W, Unger C, Hanschmann G (2001) Behavior of glyphosate and aminomethylphosphonic acid (AMPA) in soils and water of reservoir Radeburg II catchment (Saxony/Germany). J Plant Nutr Soil Sci 164:65–70
43. Annett R, Habibi HR, Hontela A (2014) Impact of glyphosate and glyphosate-based herbicides on the freshwater environment. J Appl Toxicol 34:458–479
44. Wauchope RD, Buttler TM, Hornsby AG (1992) Augustijn beckers PWM. The SCS ARS CES pesticide properties database for environmental decision making. Rev Environ Contam Toxicol 123:1–155
45. Mugni H, Ronco A, Bonetto C (2011) Insecticide toxicity to *Hyalella curvispina* in runoff and stream water within a soybean farm (Buenos Aires, Argentina). Ecotoxicol Environ Saf 74:350–354
46. Solomon KR, Carr JA, Du Preez LH, Giesy JP, Kendall RJ, Smith EE, Van Der Kraak GJ (2008) Effects of Atrazine on fish, amphibians, and aquatic reptiles: a critical review. Crit Rev Toxicol 38:721–772
47. Leonard AW, Hyne RV, Lim RP, Pablo F, Van den Brink PJ (2000) Riverine endosulfan concentrations in the Namoi River, Australia: link to cotton field runoff and macroinvertebrate population densities. Environ Toxicol Chem 19:1540–1551
48. Lengyel Z, Földényi R (2003) Acetochlor as a soil pollutant. Environ Sci Pollut Res 10:13–18
49. EXTOXNET (1996) Extension toxicology network pesticide information. http://ace.ace.orst.edu/info/extoxnet
50. Navarro A, Tauler R, Lacorte S, Barceló D (2010) Occurrence and transport of pesticides and alkylphenols in water samples along the Ebro River Basin. J Hydrol 383:18–29
51. Feo ML, Ginebreda A, Eljarrat E, Barceló D (2010) Presence of pyrethroid pesticides in water and sediments of Ebro River Delta. J Hydrol 393:156–162
52. Kuranchie-Mensah H, Atiemo SM, Palm LMND, Blankson-Arthur S, Tutu AO, Fosu P (2012) Determination of organochlorine pesticide residue in sediment and water from the Densu river basin, Ghana. Chemosphere 86:286–292
53. Gómez MJ, Herrera S, Solé D, García-Calvo E, Fernández-Alba AR (2012) Spatio-temporal evaluation of organic contaminants and their transformation products along a river basin affected by urban, agricultural and industrial pollution. Sci Total Environ 420:134–145
54. Jergentz S, Mugni H, Bonetto C, Schulz R (2005) Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina. Chemosphere 61:817–826
55. Marino D, Ronco A (2005) Cypermethrin and chlorpyrifos concentration levels in surface water bodies of the Pampa Ondulada, Argentina. Bull Environ Contam Toxicol 75:820–826
56. Gonzalez M, Miglioranza KSB, Shimabukuro VM, Londoño OMQ, Martinez DE, Aizpún JE, Moreno VJ (2012) Surface and groundwater pollution by organochlorine compounds in a typical soybean system from the south Pampa, Argentina. Environ Earth Sci 65:481–491
57. Peruzzo PJ, Porta AA, Ronco AE (2008) Levels of glyphosate in surface waters, sediments and soils associated with direct sowing soybean cultivation in North Pampasic Region of Argentina. Environ Pollut 156:61–66

58. Aparicio VC, DeGerónimo E, Marino D, Primost J, Carriquiriborde P, Costa JL (2013) Environmental fate of glyphosate and aminomethylphosphonic acid in surface waters and soil of agricultural basins. Chemosphere 93:1866–1873
59. Canadian Council of Ministers of the Environment (CCME) (2002) Canadian water quality guidelines for the protection of aquatic life. In: Canadian environmental quality (1999) Canadian Council of Ministers of the Environment, Winnipeg
60. Subsecretaria de Recursos Hídricos de la Nación, República Argentina (SSRH) (2003) http://www.hidricosargentina.gov.ar/NivelCalidad1.html
61. UNEP (2011) Stockolm Convention. The 9 New POPs under the Stockholm Convention. http://chm.pops.int/Programmes/NewPOPs/The9newPOPs/tabid/672/language/en-US/Default.aspx
62. Loganathan BG, Kannan K (1994) Global organochlorine contamination trends: an overview. Ambio 23:187–191
63. ANMAT (2011) Disposición 617/11. http://www.anmat.gov.ar/webanmat/legislacion/medicamentos/Disposicion_617-2011.pdf
64. INA (2005) Desarrollos de niveles guia nacionales de calidad de agua ambiente correspondientes a lindano http://www.pnuma.org/agua-miaac/CODIA%20CALIDAD%20DE%20LAS%20AGUAS/MATERIAL%20ADICIONAL/PONENCIAS/PONENTES/Tema%205%20Niveles%20Guias%20Calidad%20de%20Aguas/NIVELES%20GUIA/4%20-%20Desarrollos/lindano.pdf
65. Sauvé S, Desrosiers M (2014) A review of what is an emerging contaminant. Chem Cent J 8:1–7
66. Pal A, Gin KYH, Lin AYC, Reinhard M (2010) Impacts of emerging organic contaminants on freshwater resources: review of recent occurrences, sources, fate and effects. Sci Total Environ 408:6062–6069
67. Fent K, Weston A, Caminada D (2006) Ecotoxicology of human pharmaceuticals. Aquatic Toxicol 76:122–159
68. Miège C, Choubert JM, Ribeiro L, Eusèbe M, Coquery M (2009) Fate of pharmaceuticals and personal care products in wastewater treatment plants conception of a database and first results. Environ Pollut 157:1721–1726
69. Mompelat S, Le Bot B, Thomas O (2009) Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water. Environ Int 35:803–814
70. Li WC (2014) Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. Environ Pollut 187:193–201
71. Boxall ABA, Rudd MA, Brooks BW, Caldwell DJ, Choi K, Hickmann S, Innes E, Ostapyk K, Staveley JP, Verslycke T, Ankley GT, Beazley KF, Belanger SE, Berninger JP, Carriquiriborde P, Coors A, DeLeo PC, Dyer SD, Ericson JF, Gagné F, Giesy JP, Gouin T, Hallstrom L, Karlsson MV, Larsson DGJ, Lazorchak JM, Mastrocco F, McLaughlin A, McMaster ME, Meyerhoff RD, Moore R, Parrott JL, Snape JR, Smith RM, Servos MR, Sibley PK, Straub JO, Szabo ND, Topp E, Tetreault GR, Trudeau VL, Kraak GVD (2012) Pharmaceuticals and personal care products in the environment: what are the big questions? Environ Health Perspectives 120:1221–1229
72. National Institute of Statistics and Censuses; Instituto Nacional de Estadística y Censos (NISC) (2013) Ministerio de Economia y Finanzas Públicas. República Argentina. http://www.indec.mecon.ar. Accessed June 2013
73. Elorriaga Y, Marino DJ, Carriquiriborde P, Ronco AE (2013) Screening of pharmaceuticals in surface water bodies of the Pampas region of Argentina. Int J Environ Health 6:330–339
74. Garcia SN, Foster M, Constantine L, Huggett DB (2012) Field and laboratory fish tissue accumulation of the anti-convulsant drug carbamazepine. Ecotoxicol Environ Saf 84:207–211
75. Mancini C (2012) Impact of Discharge of Wastewater Treatment Plant in Suquía River Basin. Technical report. Centro de Tecnología de Química Industrial. Facultad de Ciencias Exactas Físicas y Naturales, Universidad Nacional de Córdoba

76. Valdés ME, Amé MV, Bistoni MDLA, Wunderlin DA (2014) Occurrence and bioaccumulation of pharmaceuticals in a fish species inhabiting the Suquía River basin (Córdoba, Argentina). Sci Total Environ 472:389–396
77. Wunderlin DA, Díaz M del P, Amé MV, Pesce SF, Hued AC, Bistoni MDLÁ (2001) Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquía River basin (Córdoba-Argentina). Water Res 35:2881–94
78. Monferrán MV, Galanti LN, Bonansea RI, Amé MV, Wunderlin DA (2011) Integrated survey of water pollution in the Suquía River basin (Córdoba, Argentina). J Environ Monit 13:398–409
79. Merlo C, Abril A, Amé MV, Argüello GA, Carreras HA, Chiappero MS, Wannaz E, Galanti LN, Monferrán MV, González CM, Solís VM (2011) Integral assessment of pollution in the Suquía River (Córdoba, Argentina) as a contribution to lotic ecosystem restoration programs. Sci Total Environ 409:5034–5045
80. Maggioni T, Hued AC, Monferrán MV, Bonansea RI, Galanti LN, Amé MV (2012) Bioindicators and biomarkers of environmental pollution in the middle-lower basin of the Suquía River (Córdoba, Argentina). Arch Environ Contam Toxicol 63:337–353
81. Elorriaga Y, Marino DJ, Carriquiriborde P, Ronco AE (2013) Human pharmaceuticals in wastewaters from urbanized areas of Argentina. Bull Environ Contam Toxicol 90 (4):397–400
82. Yamamoto H, Nakamura Y, Moriguchi S, Nakamura Y, Honda Y, Tamura I, Hirata Y, Hayashi A, Sekizawa J (2009) Persistence and partitioning of eight selected pharmaceuticals in the aquatic environment: laboratory photolysis, biodegradation, and sorption experiments. Water Res 43:351–362
83. Vieno NM, Härkki H, Tuhkanen T, Kronberg L (2007) Occurrence of pharmaceuticals in river water and their elimination in a pilot-scale drinking water treatment plant. Environ Sci Technol 41:5077–5084
84. López-Serna R, Petrović M, Barceló D (2012) Occurrence and distribution of multi-class pharmaceuticals and their active metabolites and transformation products in the Ebro river basin (NE Spain). Sci Total Environ 440:280–289
85. Osorio V, Marcé R, Pérez S, Ginebreda A, Cortina JL, Barceló D (2012) Occurrence and modeling of pharmaceuticals on a sewage-impacted Mediterranean river and their dynamics under different hydrological conditions. Sci Total Environ 440:3–13
86. Lei B, Huang S, Zhou Y, Wang D, Wang Z (2009) Levels of six estrogens in water and sediment from three rivers in Tianjin area, China. Chemosphere 76:36–42
87. Liu S, Ying GG, Zhao JL, Chen F, Yang B, Zhou LJ, Lai HJ (2011) Trace analysis of 28 steroids in surface water, wastewater and sludge samples by rapid resolution liquid chromatography-electrospray ionization tandem mass spectrometry. J Chromatogr A 1218:1367–1378
88. Halling-Sorensen B, Nors Nielsen S, Lanzky PF, Ingerslev F, Holten Lützhoft HC, Jorgensen SE (1998) Occurrence, fate and effects of pharmaceutical substances in the environment – a review. Chemosphere 36:357–393
89. Brooks BW, Chambliss CK, Stanley JK, Ramirez A, Banks KE, Johnson RD, Lewis RJ (2005) Determination of select antidepressants in fish from an effluent-dominated stream. Environ Toxicol Chem 24:464–469
90. Chu S, Metcalfe CD (2007) Analysis of paroxetine, fluoxetine and norfluoxetine in fish tissues using pressurized liquid extraction, mixed mode solid phase extraction cleanup and liquid chromatography-tandem mass spectrometry. J Chromatogr A 1163:112–118
91. Ramirez AJ, Brain RA, Usenko S, Mottaleb MA, O´Donnell JG, Stahl LL, Wathen JB, Snyder BD, Pitt JL, Perez-Hurtado P, Dobbins LL, Brooks BW, Chambliss CK (2009) Occurrence of pharmaceuticals and personal care products in fish: results of a national pilot study in the United States. Environ Toxicol Chem 28:2587–2597

92. Huerta B, Jakimska A, Gros M, Rodríguez-Mozaz S, Barceló D (2013) Analysis of multi-class pharmaceuticals in fish tissues by ultra-high-performance liquid chromatography tandem mass spectrometry. J Chromatogr A 1288:63–72
93. Valdés ME (2015) Evaluación de Compuestos de Origen Farmacéutico en la cuenca del Río Suquía, Efectos tóxicos sobre la Ictiofauna. PhD. Thesis, Universidad Nacional de Córdoba, Córdoba-Argentina. Chapter 3 in collaboration with Huerta B, Rodriguez-Mozaz S, and Barcelò D. (Catalan Institute of Water Research-ICRA, Girona, Spain)
94. Hued AC, Bistoni MDLÁ (2005) Development and validation of a Biotic Index for evaluation of environmental quality in the central region of Argentina. Hydrobiologia 543:279–298
95. Pyke GH (2005) A review of the biology of *Gambusia affinis* and *G. holbrooki*. Rev Fish Biol Fish 15:339–365
96. Wang MJ, Mc Grath SP, Jones KC (1995) Chlorobenzenes in field soil with a history of multiple sewage sludge applications. Environ Sci Technol 29:356–362
97. Ramirez AJ, Mottaleb MA, Brooks BW, Chambliss CK (2007) Analysis of pharmaceuticals in fish using liquid chromatography-tandem mass spectrometry. Anal Chem 79:3155–3163
98. Schultz MM, Furlong ET, Kolpin DW, Werner SL, Schoenfuss HL, Barber LB, Blazer VS, Norris DO, Vajda AM (2010) Antidepressant pharmaceuticals in two U.S. effluent-impacted streams: occurrence and fate in water and sediment, and selective uptake in fish neural tissue. Environ Sci Technol 44:1918–1925
99. Du B, Perez-Hurtado P, Brooks BW, Chambliss CK (2012) Evaluation of an isotope dilution liquid chromatography tandem mass spectrometry method for pharmaceuticals in fish. J Chromatogr A 1253:177–183
100. Tanoue R, Nomiyama K, Nakamura H, Hayashi T, Kim JW, Isobe T, Shinohara R, Tanabe S (2014) Simultaneous determination of polar pharmaceuticals and personal care products in biological organs and tissues. J Chromatogr A 1355:193–205
101. Fatta D, Nikolaou A, Achilleos A, Meric S (2007) Analytical methods for tracing pharmaceutical residues in water and wastewater. Trends Anal Chem 26(6):515–533
102. Arthur CL, Pawliszyn J (1990) Solid phase microextraction with thermal desorption using fused silica optical fibers. Anal Chem 62:2145–2148
103. Louch D, Motlagh S, Pawliszyn J (1992) Dynamics of organic compounds extraction from water using liquid-coated fused silica fibers. Anal Chem 64:1187–1199
104. Santos FJ, Sarrión MN, Galceran MT (1997) Analysis of chlorobenzenes in soil by headspace solid-phase microextraction and gas chromatography-ion trap mass spectrometry. J Chromatogr A 771:181–189
105. Zhang Z, Pawliszyn J (1993) Headspace solid-phase microextraction. Anal Chem 65:1843–1852
106. Liu J, Hara K, Kashimura S, Hamanka T, Tomojiri S, Tanaka K (1999) Gas chromatographic-mass spectrometric analysis of dichlorobenzene isomers in human blood with headspace solid-phase microextraction. J Chromatogr B 731:217–221
107. Richter BE, Jones BA, Ezzell JL, Porter NL (1996) Accelerated solvent extraction: a technique for sample preparation. Anal Chem 68:1033–1039
108. Petrovic M, Lacorte S, Viana P, Barcelo D (2002) Pressurized liquid extraction followed by liquid chromatography–mass spectrometry for the determination of alkylphenolic compounds in river sediment. J Chromatogr A 959:15–23
109. Amé MV, Galanti LN, Menone M, Gerpe MS, Moreno VJ, Wunderlin DA (2010) Microcystin-LR, -RR, -YR and -LA in water samples and fishes from a shallow lake in Argentina. Harmful Algae 9:66–73
110. Gros M, Rodríguez-Mozaz S, Barceló D (2012) Fast and comprehensive multi-residue analysis of a broad range of human and veterinary pharmaceuticals and some of their metabolites in surface and treated waters by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem. J Chromatogr A 1248:104–121

Integrating Data from Suquía River Basin: Chemometrics and Other Concepts

María Verónica Baroni and Daniel A. Wunderlin

Abstract Assessing the water quality in a river basin seems to be an easy tool. However, some degree of expertise is required when planning and executing several tasks necessary to avoid either excessive or insufficient data. In this chapter we briefly describe some aspect of sampling and sample preparation, which have been discussed in deep in previous chapters. However, after sampling a river, it is necessary to analyse several parameters, arising from many monitoring stations, sampled at different time, etc. All of this generates an amazing database that needs to be carefully explored, looking to extract the most relevant information on changes in the water quality, probable pollution sources, temporal and spatial changes and so on. One simple approximation is the construction of water quality indices from both chemical and biological data, deep discussed in Bistoni et al. (Handb Environ Chem. https://doi.org/10.1007/698_2016_455, 2016) and Amé and Pesce (Handb Environ Chem. https://doi.org/10.1007/698_2015_434, 2015). The other way is using multivariate statistics (chemometrics), trying to evidence which changes are occurring, where and when. Here we discuss several chemometrics methods used to verify changes in the water quality of the Suquía River basin, starting with non-supervised methods, like cluster analysis (CA), factor analysis (FA, including principal components analysis – PCA) and going to supervised methods, namely, discriminant analysis (DA) and generalized procrustes analysis (GPA). Although PCA has become the most popular method of analysis for the evaluation of water quality, we think that PCA should be complemented with other methods that help to corroborate results from PCA. In this case, we used CA as a primary tool to evidence

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spatial differences in the water quality along the basin, confirming these results by PCA, which also added evidence on temporal differences. DA allowed further confirmation of both temporal and spatial changes, with an important data reduction, which is important for the survey of a river basin when the budget is restrictive. Finally, GPA brings further confirmation of other chemometrics methods, enabling a clear differentiation between water quality at diverse river sections, during both dry and rainy season. So far, we truly expect that this chapter helps readers to better design future surveys to evaluate changes of the water quality in other rivers worldwide.

Keywords Chemometrics, Integrated evaluation, Multivariate statistics, River basin, Water quality

Contents

1 Introduction

River basins function with complex interactions between biotic and abiotic components. In order to understand these complex interactions, it is often necessary characterizing the basin considering its geology, hydrology, biology and human activities. Some measurements can be made directly in the basin by using sensors or collecting samples that can be analysed at the laboratory and in the field as well. For instance, pH, conductivity, water flow, temperature, etc. can be field measured; while organic and inorganic elements require laboratory work for measuring. Furthermore, the community structure of fish can be field obtained but needs further analysis at the laboratory to point out changes, etc. Other biological elements need to be sampled in the field but transferred to the laboratory for a detailed analysis (plankton structure, macroinvertebrates, microorganisms, etc.). Thus, an integrated analysis of a river basin requires the assemblage of several data, from different origin, units, magnitude, etc. So, it will be necessary to have appropriate statistical methods to examine the relationships among the parameters measured to describe the functioning of the chemical-biological processes that gave rise to the observed values, behaviour and changes [1].

It is noteworthy that the use of mathematical and statistical methods, including chemometrics and many other statistical methods/algorithms, in environmental and other sciences has increased steeply during the last years. Conducting a quick search in the most recognized scientific databases (PubMed, ScienceDirect, Scopus), it is possible to observe that statistical methods have gained a huge space in different areas. Statistical analysis is at the core of most modern data mining models [2, 3].

During the last years, with the development of computational software, we can perform more complex statistical analysis, exploring our data deeper and in a more complex way. However, this means that the statistical models and analysis are complex too; therefore, we need to be familiar with the potential and limitations of a much greater range of statistical approaches [2, 4].

Furthermore, scientific journals demand proving that the experimental differences between data sets are statistically significant; thus, an increasing number of software tools and packages have been developed to cover this need. However, modern, user-friendly software has led to a generation of “click and go” users, who are eagerly destined to obtain the *P*-values and multivariate plots (projection of samples and variables on the factor plane) but with less or no idea on how the statistical parameters are calculated. Furthermore, some researchers do not know the theoretical and practical reasons for performing such tests [2, 5, 6].

Computational tools available can be used not only to run statistical analysis such as univariate and bivariate tests but also multivariate calibration and development of complex models, simulating different scenarios that consider a set of inputs or simply making predictions for specific data sets or conditions. Therefore, one should avoid and forget the word “test” and replace it with analysis. A test implies something simple and unified and gives a clear answer related to a *P*-value, something rarely for environmental data. In practice, one has to apply data exploration, check assumptions, validate the models, perhaps apply a series of methods and most importantly interpret the results [7].

For instance, ecologists evaluating the community composition in aquatic systems need to include the characterization of individual populations, the environment and, of course, relating the observed biological variation to the environmental characteristics. One has to take into account this multidimensionality, so a univariate analysis does not work in most cases. The most appropriate methods for statistical analysis of such data are the “multivariate statistical methods” [8].

One important point when analysing an extensive data set, like those produced during basin monitoring, is the data reduction. Data reduction means that not all obtained data are to be used to show the main basin characteristics, its variations and changes (e.g. temporal and spatial changes). In spite of using the whole data set, mathematically- statistically methods can be used to select those variables that are most representative of such changes, enabling a good analysis from a reduced data set, which points out critical variables that fit for the analysis purpose. Multivariate statistics helps scientists to discover the data structure, helping to reduce the amount of data but keeping the important information for easier comprehension. Multivariate analysis uses relationships between variables to order the objects of study according to the results of the measured variables and to classify monitoring sites, biological species or ecosystems in distinct classes, each containing entities with similar chemical and/or physiological characteristics. However, multivariate analysis is complicated in theoretical structure and in operational methodology [8].

Most of the statistical tests are based on a set of assumptions about the data that must be met prior to the application of the statistical analysis and testing of a hypothesis. For example, most of the parametric statistics analyses have an assumption that the data follow a certain distribution. Other assumptions include homoscedasticity, linearity and independence. The non-compliance of these assumptions may have little impact on the results or conclusions; yet others may arise the possibility of making errors type I or II (false positive and false negative), leading to incorrect inferences about the results and thus undermine meaningful research [3, 9]. In this sense, statistical procedure should be use to check that the statistical analyses meet the assumptions, and the results from these procedures need to be reported to verify that the conclusions raised from the statistical analysis are valid [9].

There are new statistical methods that can be applied to answer almost every concern in studies related to aquatic systems; however, the greatest challenge is to figure out how the various statistical methods relate to each other, determining which method is most appropriate for any particular problem.

Before questioning which statistical analysis should I apply? The scientist should answer: What are the underlying questions? What do I want to show? What am I looking for? Answering these questions will give you the basis for deciding the most appropriate statistical approach. Our objective as scientists is to be able to use these tools efficiently, without losing sight of the vision, that is, the motivation of the research done (e.g. base chemical/biological monitoring, evaluation of temporal and spatial changes along a basin, integrating chemical with biological data, etc.).

On the other hand, sometimes it is necessary to present our results in a simple way, which can be easily understood by the people, policy makers, magistrates, etc. Under these circumstances, we can choose non-statistical models, like the use of an index that reflects the overall quality status of a basin, temporal and spatial changes, etc. The use of water quality indice, for instance, can provide this kind of practical approach to show changes along a basin, a temporal trend during monitoring surveys, etc. [10]. However, it is worth to mention that the validity of these indices needs to be confirmed by a more strength mathematical-statistical model to demonstrate their usefulness and accuracy when informing results to the population.

This chapter will provide both a conceptual and practical understanding of the application of quality indices and multivariate statistics in the evaluation of changes along a river basin.

We hope that, after reading this chapter, you should be able to understand and know the validity and limitations of water quality indices as well as the assumptions of different statistical methods, identify the appropriate model for the sampling design, interpret the output of the method used for data mining and design the monitoring and analysis programme that best fits for the purpose, lowering cost and maximizing information.

2 Monitoring a River Basin

The design of a monitoring programme should fit for purpose. If the aim of the survey is bringing baseline information on the current status of the basin, or checking changes with respect to previous monitoring campaigns or evaluating the usefulness of the water for a specific purpose (e.g. drinking water, irrigation, industrial uses, tourism/recreation, aquaculture, etc.), it should be considered that each of these different purposes involves different water quality requisites, and, thus, the sampling strategy and analytical methods may differ. Some classical literature can be advised for those intending to start with the monitoring of a river basin [11, 12]. However, few practical tips are presented as follows:

1. Consider the river hydrology and its seasonal changes [13]. It is important to evaluate temporal changes considering variations in the river flow, which leads to dilution/concentration of contaminants, different degree of toxicity (related to the dilution of toxics), presence of particulate matter (PM) (affecting the absorption of diverse pollutants to its surface, in addition to transport phenomena of pollutants attached to PM, etc.), different land uses during winter and summer, different environmental conditions for the river biota, etc. (from bacteria to higher organisms, etc.). River hydrology also involves different areas within a basin (high, medium, lower basin), usually associated with different flow, turbulence, sediment structure (sand, clay, etc.) and many other conditions that can change from upper to lower basin. Consider that both native and non-native biotas are also affected by hydrological changes along the basin [14].
2. If natural or artificial lakes are present in the basin, their limnology should also be studied [15]. The study of limnologic issues can help to understand and prevent algae blooms, including those producing toxins that can affect both the native biota and human health. In addition, the study of the limnology helps to predict the quality of drinking water if the lake/reservoir is used for such purpose, etc.
3. Make an inventory of human activities along the basin. It helps to identify point pollution sources (industries, sewage exits, urban or agricultural run-off, etc.). This inventory usually helps to avoid unnecessary analyses in areas where some pollutants could not be expected. Of course, for a scientific work, it is necessary to consider pristine (reference) points to compare changes with respect to more impacted areas.
4. If possible, make an inventory of the biota inhabiting different basin areas, including both native and introduced biota. This is very helpful to evaluate how water quality changes are affecting the assemblages between different species, changes in dominance, endangered species, etc. [14].
5. Be prepared to evaluate changes in the water quality at different levels (surface water, sediment, interstitial water, etc.), at different areas (upper, middle and lower basin), with different pollution sources (human eutrophication, urban run-off, industrial effluents, wastewater, agricultural run-off, etc.). Each of these pollution sources could require different analytical methods and, accordingly, different budget to perform the monitoring survey [16–18]. In addition,

temporal changes should be considered as previously stated. To this point, when the budget is restrictive or even with less restrictive resources, a very careful analysis of requested information should be performed before sampling, never after sampling. Sometimes, professionals with less experience in water quality assessments just decide to get hundred samples, analysing a restricted set of parameters, losing valuable information that could be obtained from the same sampling campaign. Additionally, the possibility for safe sample storage should be considered, since after a first preliminary analysis, further elements could help to get a better diagnostic of the basin. If well-stored samples are available, preliminary results can be later completed with additional information without repeating the sampling, which would require the entire analysis of the new sample set. Moreover, stored samples can be used to compare changes along years when introducing new analytical methods, enhancing the scope of analysed parameters, etc.

6. Get enough number of samples from each environmental compartment (water, sediment, biota, etc.) at each area. Sampling campaigns are expensive, time consuming, requiring appropriate weather conditions, etc.; thus, getting only one sample from each area will be not enough if you need a serious, scientific-based, statistically sound result to be presented. On the other hand, excessive number of samples can be expensive to analyse, can be negative for endangered biota, etc. Just consider the appropriate number of samples necessary to get statistically representative results from your survey.
7. Repeat monitoring campaign for at least 2 years, better 3–4 different years. This is just for consider inter-year variations caused by different climatic conditions, etc.
8. Use appropriate tools for monitoring. Some practical tips can be found at WHO [12], Chapman [11] and recent scientific literature (see, for instance, [19–23]). It is quite common to find the use of metallic tools used to get samples designed for metal analysis. Particularly with trace elements, the use of metallic tools results in contamination of samples. In this case, pre-cleaned plastic tools should be used. On the contrary, to analyse organic elements, the use of plastic tools should be avoided as many organic compounds can be adsorbed onto some plastic surfaces, etc. [18]. Some particular cases need to be addressed. For instance, using glass bottles for sampling water for boron analysis should be avoided as the glass usually contains boron-silicate, which interferes with the measurement of boron. In addition, the common practice of adding mineral acids to stabilize samples should be considered using ultra-pure acids (ICP-MS grade) to avoid interferences when analysing trace elements by ICP-MS and related methods [17].

3 Data Mining from Monitored Basins

3.1 Use of Indices

Water monitoring for different purposes is well defined (e.g. aquatic life preservation, contact recreation, drinking water use) [11, 12]. However, the overall water quality is sometimes difficult to assess from a large number of samples, each containing concentrations for many parameters, including different magnitudes within analysed parameters [11]. Although any measured parameter is worth to be analysed by itself (univariate change using a single parameter, e.g. changes in water conductivity along a river basin), it is also quite common to analyse groups of parameters sharing a common feature (e.g. nitrogen load through the analysis of ammonia, nitrites, nitrates and organic nitrogen). Even so, the analysis of a single parameter provides only partial information on the overall water quality. Thus, the integration of several parameters to afford a better idea of changes along the basin seems a reasonable approach [10].

Mathematical-computational modelling of river water quality is possible but requires a previous knowledge of hydraulics and hydrodynamics [13]. Besides, mathematical models require extensive validation (see, for instance, [11, 24–32]).

The use of water quality indices (WQI) is a simple practice that overcomes many of the previous mentioned problems and allows the public and decision makers to receive water quality information, based on scientific criteria, from a complex data set, but presented in a simple form that can be used for regulatory purposes, public information, etc. [10]. WQI also permit assessing changes in the water quality along the basin, identifying trends and sudden changes produced by point pollution sources [11].

The use of WQI to assess the water quality in the Suquía River basin has been explained in [16] and will not be repeated here.

It is worth mentioning that other indices, like a Biotic Index, can be constructed using different parameters (e.g. fish diversity, etc.), not only chemical or physical parameters. This biotic index has been constructed for the Suquía River basin [33], considering valuable information on the biota present in the basin [14].

3.2 Multivariate Statistics (Chemometrics)

Even though WQI provide a useful way to predict changes and trends in the water quality considering multiple parameters, WQI do not provide evidences on the pollution sources, mainly because they are calculated after normalization of analytical values and weighting of such normalized values, according to the importance of the measured parameter for the aquatic life preservation [10, 14]. The use of multivariate techniques (also called chemometrics) is another method that can be adopted to evaluate water quality changes [11]. Other words used to describe some multivariate methods is “pattern recognition techniques” as these methods allow discovering different patterns, representing different behaviour of the data set (although not all multivariate methods led to patterns). In the case of the Suquía River basin, the use of chemometrics allowed differentiating different parameters associated with diverse point and non-point pollution sources [34].

3.2.1 Exploratory Methods: Cluster Analysis

Cluster analysis (CA) can be divided in hierarchical and non-hierarchical. Hierarchical CA forms clusters sequentially, starting with the most similar pair of objects and forming higher clusters step by step. The similarity between two samples is usually given by the Euclidean distance, and a “distance” can be represented by the “difference” between analytical values from both samples [35]. One efficient way to calculate such distance is the Wards method, which uses analysis of variance to verify the distances between clusters, minimizing the sum of squares of any two (hypothetical) clusters that can be formed at each step.

Non-hierarchical CA methods, including fuzzy clustering, evaluate overall distributions of objects by pairs, classifying them into groups.

CA repeats the process of forming and joining clusters until obtaining a single cluster containing all samples. CA results in a dendrogram (tree diagram), providing a picture of the groups and its proximity, in addition to data reduction.

Many times, it is convenient to standardize the data set to obtain better results with CA [35–40]. Thus, grouped data presented in a dendrogram can be recognized as belonging to dry or wet season in seasonal analysis or belonging to the upper, middle or lower river basin during spatial analysis.

Some examples of other river basins studied using CA can be found in Astel et al. [41]; [42–51]. CA can be also used for the study of variations in groundwater, lakes, etc. (e.g. [52, 53])

Figure 1 presents results of both temporal and spatial analyses of samples corresponding to the Suquía River basin. Figure 1 was constructed using the same chemical and microbiological parameters used to construct WQI [16]; however, using biological and biochemical parameters is also possible (see, for instance, [54]). But here comes one of the first limitations of chemometrics methods: increasing the number of parameters considered (translated into columns in the matrix used for statistical calculation) also requires increasing the number of samples (each sample represents a row in the matrix, although data arising from different analytical replicates can be used as separate rows, accounting for both sample and analytical variations). In Fig. 1 samples belonging to a common area/season were grouped, namely, group “A” accounts mainly for samples from the lower basin (with 15% samples corresponding to the middle basin); group “B” accounts for samples from the high basin (with 25% samples from the middle basin). Thus, this approach helps to better visualize differences/similitudes between studied areas/seasons.

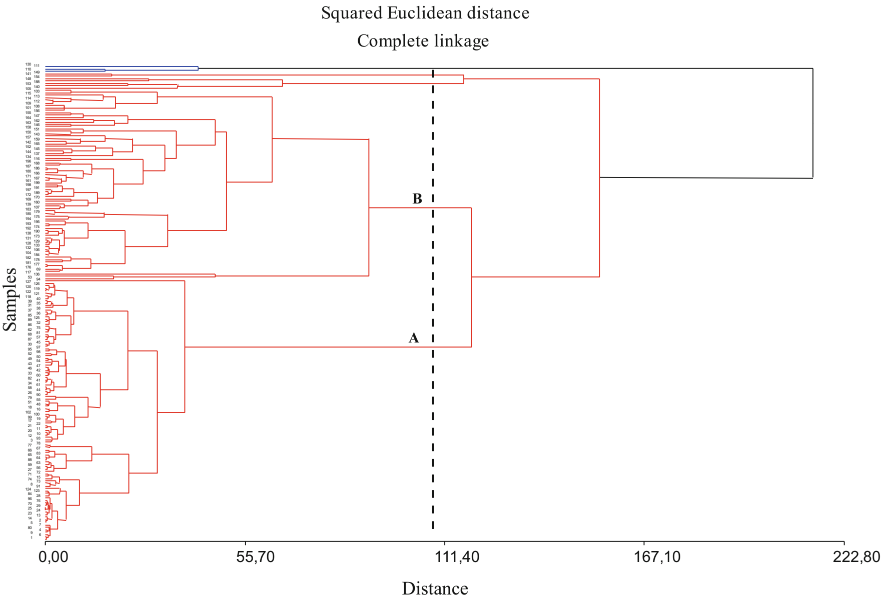

Fig. 1 Dendrogram constructed by cluster analysis (CA) of chemical and microbiological data evaluated in the Suquía River basin

As we can see from Fig. 1, data arising from 201 samples, taken along several years at the Suquía River basin (grouped according to basin area), are separated into two main groups, at approximately 50% of the maximal Euclidean distance (dotted line). What we can say from this plot is that the Suquía River Basin shows a clear difference in the water quality between the high and lower basin, meanwhile medium basin overlaps the other two zones.

It is also interesting to remark that CA does not show those parameters leading to the constructed dendrogram (Fig. 1). Thus, although CA can be used as a primary tool to see how to divide (grouping) our data set, it fails to show what is important and what is less important, to measure to reach such group separation.

3.2.2 Exploratory Methods: Factor Analysis/Principal Component Analysis

Factor analysis (FA), which includes principal components analysis (PCA), is used for data reduction without loss of information. Large data sets are common when evaluating temporal-spatial changes in river water quality, where several stations are included along the river basin to account for diverse environmental issues. In addition, several samples are taken at each site during one monitoring campaign, and many monitoring campaigns are organized to account for temporal changes, etc. In addition to the number of samples, several physical, chemical and biological parameters are usually evaluated, with two to five analytical replicates, etc. This construct a big database that must be considered, evidencing changes along the basin or between seasons, pointing out key parameters to distinguish between different areas/seasons, etc.

PCA mathematically operates from the covariance matrix, which describes the dispersion of the multiple measured parameters, to obtain eigenvalues and eigenvectors. Linear combinations of the original variables and eigenvectors result in new variables, called principal components (PCs). A new set of axes, called factor axes, are obtained in a lower dimensional space onto which the original space of variables can be projected. Further rotation of the axis defined by PCA produces new groups of variables called varifactors (VFs). This last procedure is frequently known as factor analysis (FA), which is not the same with PC. The basic features associated with FA/PCA are data reduction and data grouping. Data reduction is obtained because we usually need only a few VFs/PCs to get a good description of the entire data set variability with a minimum of loss of information. Mathematically speaking, it is a linear combination of the variables that are most correlated with it. This further implies that the factor coordinates (or factor loadings) of a variable are the correlations between the variable and the factor or principal axes. Accordingly, interpretation of the PCs must be done in terms of the correlation. With this fact and the objective of factor interpretation in mind, given a set of variables, we should naturally be looking for those variables that have the highest (absolute) values of the factor coordinates for the given factors. Some other statistics that are useful for the purpose of interpretation are relative contribution of the factor axis to the eccentricity of the variables and the relative contribution of a variable to the variance of the factor axis. Besides, in FA, VFs usually group the studied variables in accordance with common features (i.e. soluble salts, organic pollutants, etc.). So FA and PCA are particularly valuable when a chemical, physical or biological interpretation of the data grouped in VFs/PCs is possible [11, 34, 40, 46–48].

Principal components analysis (PCA) has become one of the most popular methods used in multivariate statistics. Many reports on the use of PCA for the evaluation of changes in river water quality have been published (e.g. [34, 41, 43, 45, 46, 48, 49, 55–57]), including the combined use of physical, chemical, biological and biochemical parameters [58].

When PCA was applied to the same data set used to calculate WQI [16] and CA (Fig. 1), we obtained two complementary information on the water quality of the Suquía River. Figure 2 shows only spatial differences along the basin, pointing out high, medium and low basin areas as well as physical and chemical parameters associated with such basin areas. From Fig. 2 we can see that using only two principal components (PC1 and PC2), it is possible to account for 59% of the variance.

Different symbols and colours indicate different basins and seasons. Even though only 59% of the variance is explained, analysing PC1, samples from the high basin (wet and dry season) and samples from medium basin (wet season) are located to the left of the graph, in agreement with results obtained in CA (Fig. 1). On the right side of PC1, samples from the low basin (dry season) are located, while

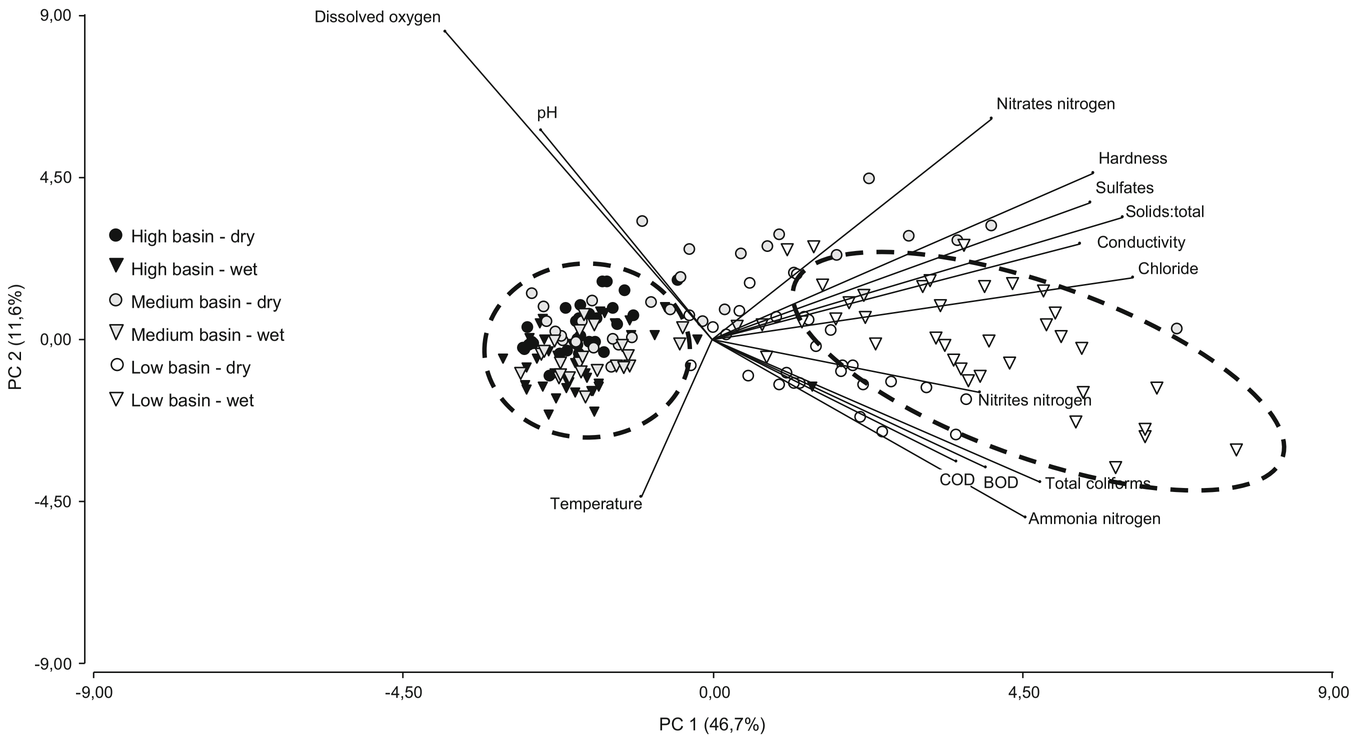

Fig. 2 Biplot produced from the entire data set used to calculate the water quality indice [16], obtained by PCA of this data matrix. Each point represents a sample (replicates are averaged), belonging to the high, medium or lower river basin

close to the zero point are samples belonging to middle basin (dry season) and to the low basin (wet season). It is worth to remark that samples located close to the zero point are not characterized by any of the analysed variables; instead, samples located to the left of PC1 are characterized by dissolved oxygen, pH and temperature. Conversely, samples located to the right of PC1 are characterized by ammonia nitrogen, conductivity, dissolved oxygen, chloride, COD, hardness, nitrates nitrogen, nitrites nitrogen, total solids, sulphates, total coliforms and BOD.

When data belonging to a particular area are averaged, the PCA biplot looks like Fig. 3. In Fig. 3 we can see even better differences between the low and the high basin, with the middle basin in the middle. When comparing Fig. 2 with Fig. 3, it is evident that real data points (Fig. 2) show some degree of overlaps, which is the natural situation as small changes are observed along the year, between years, etc. However, Fig. 3 better summarizes the trend observed along the basin. Similar interpretation as in Fig. 2, related to the variables and samples distribution along the axes, can be made.

Figure 3 shows that principal components 1 and 2 account for ca. 90.9% of the total variance. So far, PCA is able to differentiate well between higher, middle and lower basin, with most of the chemical parameters showing a strong change from higher to lower basin (from left to right along CP1 in this case). In addition to spatial differences, Fig. 3 also shows that the Suquía River basin also presents temporal variations. As it is evident from Fig. 3, variations along CP1 are much more pronounced than the corresponding to CP2, which means that temporal variations are less significant than spatial variations. However, further analysis evidences that the lower basin has bigger differences between wet (rainy) and dry season along CP1. So far, Fig. 3 resembles results obtained by CA (Fig. 1), showing that similar results are possible by two independent methods, using different mathematical approaches, diverse modes of graphical representation but same trends. This provides with additional certainty on the analysis of results, which is important to reinforce our conclusions but not so frequently performed by many researchers, policy makers, etc.

3.3 Supervised Methods: Discriminant Analysis (DA)/ Generalized Procrustes (GPA)

3.3.1 Discriminant Analysis (DA)

In contrast with CA, PCA and FA, which can be carried out without previous indication of the group to which a particular sample/data belongs, supervised methods require a grouping variable. In river monitoring this grouping variable is usually the monitoring station or the sampling period (summer/winter, etc.), although grouping variable can also refer to a group of monitoring stations (high basin, low basin, etc.) or to a group of months with some common characteristic (dry season/wet season, etc.).

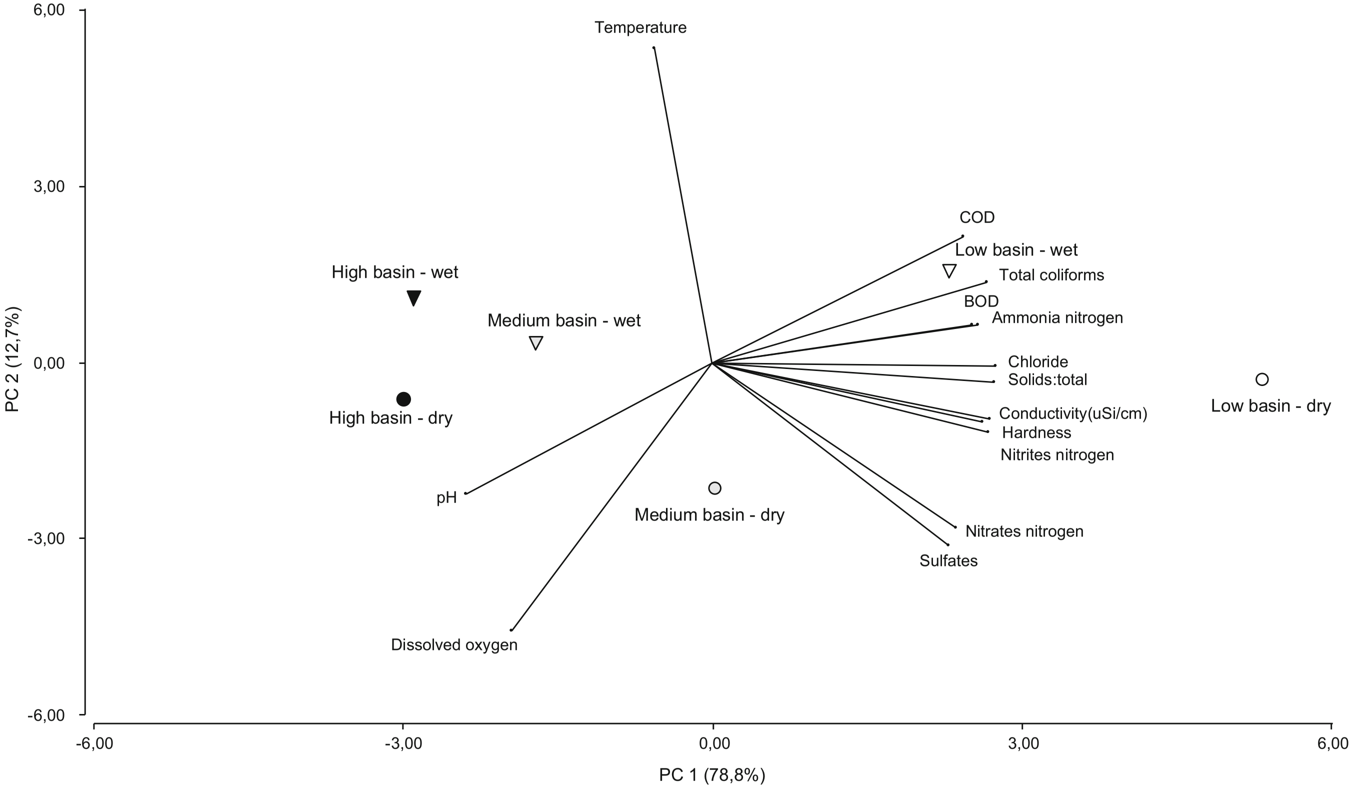

Fig. 3 Biplot produced from the entire data set used to calculate the water quality indice [14], obtained by PCA of this data matrix. Each point represents the average of samples belonging to the high, medium or lower river basin

Among others, DA technique is probably the most popular for evaluating changes along a river basin, within different seasons, etc. [34, 46, 48, 49]. DA builds up a discriminant function for each group, this function has the form presented in Eq. (1), and it is similar to a mathematical function having multiple terms (to the corresponding variables parameters analysed), with different load (weight) each for the final result [34, 39].

$$f(\mathrm{G}i) = k1 + \sum_{J=1}^{n} w_{ij}.p_{ij} \tag{1}$$

where

i is the number of groups (G).
ki is the constant inherent to each group.
n is the number of parameters used to classify a data set into a given group.
w_{ij} is the weight coefficient, assigned by DA, to a given parameter/variable (j), measured within a particular group (i).
(p_{ij}) is the analytical value of the parameter/variable (j), corresponding to a particular group (i).

During river monitoring it is necessary to measure parameters having different magnitudes in their value (e.g. pH, 1–14 and conductivity, 100–>1,000, etc.). Although these differences in magnitudes can be compensated assigning different values to w_{ij}, it is very frequent to standardize the entire data set (matrix) to mean 0 and variance 1 [34, 39].

The efficiency of these discriminant functions (DF) needs to be checked. Here two alternative procedures can be used:

(a) Construct the DF using one part of the data set; check its goodness with the remaining data (which implies a large number of samples to be able to divide the data set in two).
(b) Use the entire data set for constructing DF, but use the cross-validation method to verify it, which refers to the process of assessing the predictive accuracy of the model in a test sample (cross-validation), relative to its predictive accuracy in the learning sample from which the model was developed. If the model performs as well in the test sample as in the learning sample, it is said to cross-validate. One common method for cross-validation is the so named "one in, one out," which first constructs the discriminant function with the entire data set, removes one data line (set of variables corresponding to a particular site, monitored at a particular time), recalculates new DFs and checks if the removed data fits to its original group using the new constructed function. This procedure is repeated for each data line from the original matrix.

One additional feature that DA offers is the possibility to include all the variables measured to calculate DFs (standard mode), or constructing DFs by a stepwise procedure. Stepwise mode can be also divided into two alternatives, forward or backward stepwise. Forward stepwise mode starts including only one parameter within DF (the most significant to differentiate among groups); in the next step, it adds the second most significant parameter and verifies significant changes (improvements) in the ability to discriminate groups. If so, a third step is performed and so on until adding a new variable does not significantly improve the previous discriminating power, which causes that the stepwise procedure is stopped and DFs are constructed using only those parameters significant to the discrimination. The second alternative is the backward stepwise mode, which starts with all the variables measured (as in the standard mode) and then removes the less significant variable in a second step and so on until removing a variable causes a significant drop in the predictive ability. So far, stepwise modes allow reducing the starting number of variables, keeping only those that are significant to discriminate among river sections, seasons, etc. This is an important issue of DA, because it allows reducing the number of parameters to be measured in monitoring campaigns but keeping the same valuable information on changes in the river water quality, identification of both point and non-point pollution sources, etc. [34].

DA was applied to the same data set used in [16] for calculating water quality indice and in this chapter to show how CA (Fig. 1) and PCA (Figs. 2 and 3) perform. Results from DA, corresponding to the Suquía River basin, are shown in Table 1 and Fig. 4.

From Table 1 it is evident that the classification power of DA did not change so much from the standard to the backward stepwise mode, which rendered the best compromise between right assignations (classification) and number of parameters to be used. In this case, using only six parameters would be enough to distinguish water from the high, medium or lower basin of the river and according to the season of sampling. Moreover, these six parameters are relatively simple to measure and could be used in a surveillance programme of the basin, at low cost.

Table 1 Parameters used by DA in different modes to evaluate spatial and temporal changes in the water quality of the Suquía River basin

Parameters used	Standard mode	Forward stepwise	Backward stepwise
Ammonia nitrogen	✓*		
BOD-5	✓*		
Chloride	✓	✓	✓
Chem.Oxig.demand	✓	✓	
Conductivity	✓*		
Dissolved oxygen	✓	✓	✓
Hardness	✓	✓	✓
Nitrates nitrogen	✓	✓	
Nitrites nitrogen	✓	✓	
pH	✓	✓	✓
Solids: total	✓*	✓*	
Sulphates	✓	✓	
Temperature	✓	✓	✓
Total coliforms	✓*		✓*
Classification goodness	87.2%	87.5%	85.2%

* $P > 0.05$

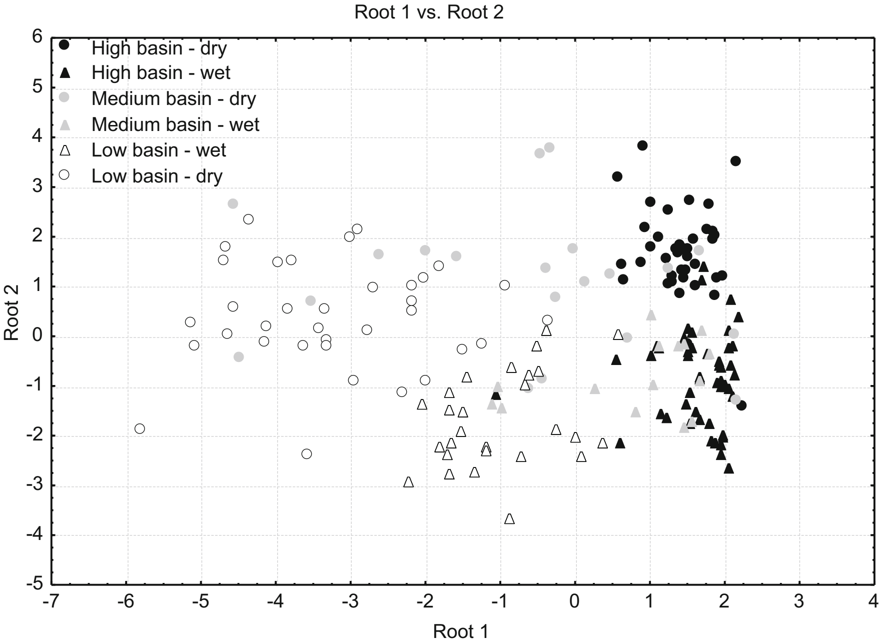

Fig. 4 Biplot obtained from DA (backward stepwise mode), corresponding to monitoring stations throughout the basin at both dry and wet season

From Fig. 4 it is clear that the best separation is obtained between the higher and the lower basin, which is expected considering the presence of the big city in the middle. Also from Fig. 4 we can see that the middle basin is overlapped with both high and lower basins. Additionally, Root 1 separates spatially well the river (from right = high basin to left = low basin). Conversely, Root 2 separates the basin according to the season (dry vs. wet). So far, DA affords similar results than those obtained with CA and PCA but now with a notorious reduction in the amount of data necessary to point out both spatial and temporal differences observed along the river basin throughout a year.

3.3.2 Generalized Procrustes Analysis (GPA)

Generalized procrustes analysis (GPA) is one of the family of methods that are concerned with the analysis of data arising from different group of variables/parameters, and it is frequently used to find a consensus from different set of variables analysed to a sample. In other words, the main goal is to acquire a consensus from the different groups of variables after they have undergone procrustes transformations that reduce individual differences by means of translation, rotation and reflection as well as isotropic scaling [59].

The statistical problem is to find a set of transformations (rotation, reflection, translation and an optional isotropic scaling factor), so that there is maximal agreement among the transformed configurations. The consensus is simply the average of all the transformed configurations. Here we used the Grower algorithm that minimizes within-samples variance by applying translation, scaling and rotation to generate a p-dimensional average configuration Yc. Following this, a q-dimensional group average space ($q \leq p$) is constructed from Yc by PCA. Therefore, GPA theory and algorithms can be applied to match chemical, physical and microbiological data arising from the different basin locations.

The aim of GPA is to evaluate the correspondence between different data from the same object, in this case the different river basin and stations. We evaluate the correspondence between microbiological parameters (Configuration 1; Fig. 5: includes BOD and total coliforms, accounting for changes in the microbiological quality of the river water), chloride (Configuration 2; Fig. 5: representing changes in the water quality probably due to urban run-off [34]) and chemical parameters (Configuration 3; Fig. 5: includes several variables: conductivity, temperature, pH, dissolved oxygen, ammonia nitrogen, COD, hardness, nitrates and nitrites nitrogen, total solids and sulphates). This last group generally accounts for chemical changes in the water quality, sometimes related to urban activities but in many cases related with sewage pollution. In this analysis, two components explained almost 97% of the total variance, contributed by three groups of variables: CP1 explains 94.2%, while the CP2 explained 2.7% (see Fig. 5). As shown in Fig. 4, similar results to PCA analysis are obtained. Samples from the high basin during both seasons are differentiated from the rest. On the other hand, the low basin (dry season) is on the opposite side of the biplot, while the rest is around the zero point. Table 2 shows the consensus values for each basin and season among the different groups of variables under study. The average consensus was 88.7%, which means that the three groups of variables (configurations 1–3) describe samples in similar ways. The low basin showed the highest level of consensus (97.1%) during the dry season, followed by the high basin in both seasons, while the lowest values were for the middle basin. This is in accordance with the results obtained along all the statistical analysis, which always showed that samples from the middle basin are overlapped, sometimes with the higher basin and sometimes with the lower one. This overlapping of the middle basin is expected, as previously stated, because of seasonal differences in the river flow, causing more or less dilution of different analytes, more or less turbidity; also changes in the water temperature from winter to summer cause changes in dissolved oxygen, etc. So far, the middle basin is by far the most difficult area to characterize in the Suquía River basin. We were not able to find other reports on the use of GPA in water quality assessment, being this probably the first.

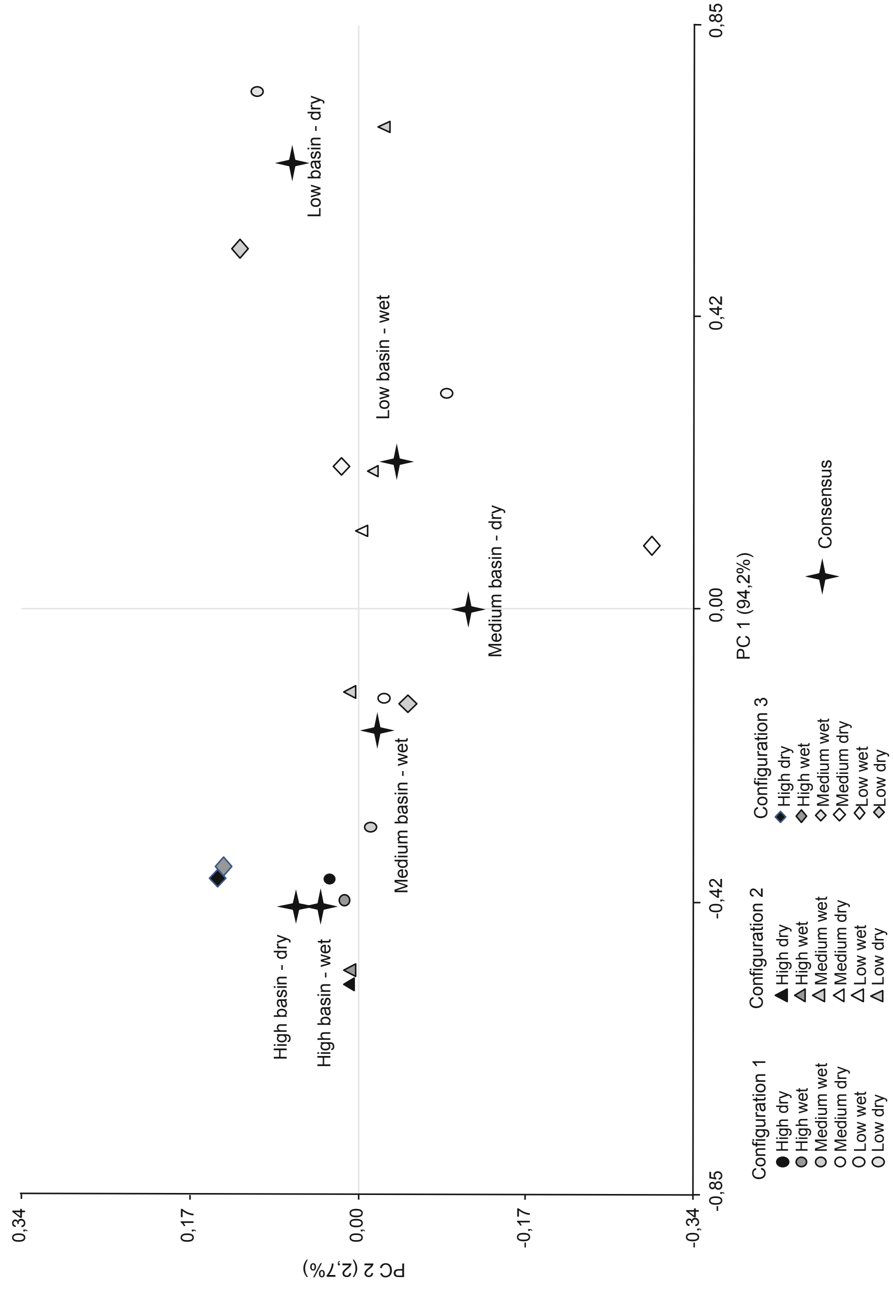

Fig. 5 Generalized procrustes analysis of the water quality in the Suquía River basin

Table 2 GPA: analysis of variance: sum of squares within each case

	Consensus	Residual	Total	Prop cons
High basin – dry	0.499	0.039	0.539	0.927
High basin – wet	0.486	0.038	0.524	0.928
Medium basin – dry	0.06	0.13	0.19	0.314
Medium basin – wet	0.082	0.046	0.129	0.64
Low basin – wet	0.228	0.041	0.269	0.849
Low basin – dry	1.311	0.039	1.35	0.971
Total	2.667	0.333	3	0.889

4 Conclusions

Monitoring and analysing a river for different purposes are difficult tasks. A rational analysis of the river hydrology, climate, urbanization, industries, etc. is required before starting a surveillance programme. After deciding the monitoring stations and a set of parameters to be monitored and measured, a big data set is constructed. This big data set can be simplified and transformed to a water quality indice (WQI), reflecting the change in the water quality along the basin or between seasons. Although WQI are easy to explain, there is a deficit of detailed information in a WQI. Thus, multivariate statistical methods (chemometrics, pattern recognition methods, etc.) help to fully evaluate changes in the water quality at many levels, in our case spatial and temporal changes. Among multivariate methods, CA can be used as a primary, unsupervised method to verify bulk differences in the water quality, for instance, between the higher and the lower basin in the Suquía River. However, CA does not indicate which parameters are causing such differences. PCA/FA can also be used to evaluate differences between areas (spatial changes) and seasons in an unsupervised way (without indicating the real origin of each sample). PCA and FA enable differentiating spatial areas and/or seasons or both, pointing out a set of parameters (variables) associated with each area/season. This is usually visualized through a biplot (Figs. 2 and 3), showing the dispersion of data points and their association with a group of variables. Finally, supervised methods (DA and GPA) enable a better differentiation between areas and seasons (or both), using the entire data set but also leading to an important data reduction, with less deficiency of information, in many cases. So far, DA and GPA are, in our criteria, best-suited methods for the evaluation of changes in the water quality of a river basin. In the case of the Suquía River basin, DA enables differentiating both spatial and temporal changes, with 85% certainty, using only six parameters. In addition, GPA evidenced that less changes are observed in the high basin during both spatial and temporal analyses, which means that the Suquía River maintains a relative constant water quality along the year in the high basin. Conversely, GPA shows big temporal differences in the lower basin. So far, the water quality of the Suquía River is better during the rainy season (more close to the higher basin quality) than during the dry season, where the low river flow causes concentration of most of the pollutants, decrease in the dissolved oxygen, etc. Finally, also GPA shows that the middle basin has an intermediate water quality, being more similar to the quality of the lower basin during the dry season and close to the quality observed in the high basin during the wet season.

References

1. Hopke PK (2015) Chemometrics applied to environmental systems. Chemom Intel Lab Syst 149:205–214
2. Nunes CA, Alvarenga V, de Souza Sant'Ana A, Sousa Santos J, Granato D (2015) The use of statistical software in food science and technology: advantages, limitations and misuses. Food Res Int 75:270–280
3. Zuur AA, Ieno EL, Elphick CS (2010) A protocol for data exploration to avoid common statistical problems. Methods Ecol Evol 2010(1):3–14
4. Quinn GP, Keough MJ (2002) Experimental design and data analysis for biologists. Cambridge University Press, New York, NY, 539 p
5. Daszykowski M, Walczak B (2006) Use and abuse of chemometrics in chromatography. Trends Anal Chem 25(11):1081–1096
6. Pretsch E, Wilkins CL (2006) Use and abuse of chemometrics. Trends Anal Chem 25(11):1045
7. Zuur AF, Ieno EN, Smith GM (2007) Analysing ecological data. Springer, New York, 672 p
8. Leps J, Smilauer P (2003) Multivariate analysis of ecological data using CANOCO. Cambridge University Press, New York, NY, 283 p
9. Bilotta GS, Milner AM, Boyd IL (2015) How to increase the potential policy impact of environmental science research. Environ Sci Eur 27:9
10. Pesce SF, Wunderlin DA (2000) Use of water quality indices to verify the impact of Córdoba City (Argentina) on Suquía River. Water Res 34:2915–2926
11. Chapman D (1992) In: Chapman D (ed) Water quality assessment. Chapman & Hall, London, p 585. (On behalf of UNESCO, WHO and UNEP)
12. WHO (World and Health Organization) (1987) GEMS/WATER operational guide. World Health Organization, Geneva
13. Díaz É et al (2016) Hydrology and hydraulics of the Suquía River Basin. Handb Environ Chem. https://doi.org/10.1007/698_2016_466
14. Bistoni MA et al (2016) Biota along the Suquía River Basin. Handb Environ Chem. https://doi.org/10.1007/698_2016_455
15. Rodriguez MI, Ruiz M (2016) Limnology of the San Roque Reservoir. Handb Environ Chem. https://doi.org/10.1007/698_2016_467
16. Amé MV, Pesce SF (2015) Spatial and temporal changes in water quality along the basin. Handb Environ Chem. https://doi.org/10.1007/698_2015_434
17. Monferrán MV (2015) Metals and metalloids in water and sediment of the Suquía River Basin: spatial and temporal changes. Handb Environ Chem. https://doi.org/10.1007/698_2015_444
18. Santiago AN et al (2015) Organic pollutants in the Suquía River Basin. Handb Environ Chem. https://doi.org/10.1007/698_2015_431
19. Aboutalebi M, Bozorg-Haddad O, Loáiciga HA (2017) Multiobjective design of water-quality monitoring networks in river-reservoir systems. J Environ Eng 143(1), art. nr. 04016070
20. McCarthy DT, Jovanovic D, Lintern A, Teakle I, Barnes M, Deletic A, Coleman R, Rooney G, Prosser T, Coutts S, Hipsey MR, Bruce LC, Henry R (2017) Source tracking using microbial community fingerprints: method comparison with hydrodynamic modelling. Water Res 109:253–265
21. Stipaničev D, Dragun Z, Repec S, Rebok K, Jordanova M (2017) Broad spectrum screening of 463 organic contaminants in rivers in Macedonia. Ecotox Environ Safety 135:48–59

22. Tousova Z, Oswald P, Slobodnik J, Blaha L, Muz M, Hu M, Brack W, Krauss M, Di Paolo C, Tarcai Z, Seiler T-B, Hollert H, Koprivica S, Ahel M, Schollée JE, Hollender J, Suter MJ-F, Hidasi AO, Schirmer K, Sonavane M, Ait-Aissa S, Creusot N, Brion F, Froment J, Almeida AC, Thomas K, Tollefsen KE, Tufi S, Ouyang X, Leonards P, Lamoree M, Torrens VO, Kolkman A, Schriks M, Spirhanzlova P, Tindall A, Schulze T (2017) European demonstration program on the effect-based and chemical identification and monitoring of organic pollutants in European surface waters. Sci Total Environ 601–602:1849–1868
23. van der Oost R, Sileno G, Janse T, Nguyen MT, Besselink H, Simoni BA (2017) (Smart integrated monitoring) as a novel bioanalytical strategy for water quality assessment: part II-field feasibility survey. Environ Toxicol Chem 36:2400–2416
24. Arnold JG, Fohrer N (2005) SWAT2000: current capabilities and research opportunities in applied watershed modelling. Hydrol Process 19(3):563–572
25. Gassman PW, Reyes MR, Green CH, Arnold JG (2007) The soil and water assessment tool: historical development, applications, and future research directions. Transact ASABE 50(4): 1211–1250
26. Hawkins CP, Norris RH, Hogue JN, Feminella JW (2000) Development and evaluation of predictive models for measuring the biological integrity of streams. Ecol Appl 10(5): 1456–1477
27. Moriasi DN, Arnold JG, Van Liew MW, Bingner RL, Harmel RD, Veith TL (2007) Model evaluation guidelines for systematic quantification of accuracy in watershed simulations. Transact ASABE 50(3):885–900
28. Rauch W, Henze M, Koncsos L, Reichert P, Shanahan P, Somlyódy L, Vanrolleghem P (1998) River water quality modelling. I. State of the art. Water Sci Technol 38:237–244
29. Romagnoli M, Portapila M, Rigalli A, Maydana G, Burgués M, García CM (2017) Assessment of the SWAT model to simulate a watershed with limited available data in the Pampas region. Argentina Sci Total Environ 596–597:437–450
30. Shanahan P, Henze M, Koncsos L, Rauch W, Reichert P, Somlyódy L, Vanrolleghem P (1998) River water quality modelling II. Problems of the art. Water Sci Technol 38:245–252
31. Somlyódy L, Henze M, Koncsos L, Rauch W, Reichert P, Shanaham P, Vanrolleghem P (1998) River water quality modelling III. Future of the art. Water Sci Technol 38:253–260
32. Zhai X, Xia J, Zhang Y (2017) Integrated approach of hydrological and water quality dynamic simulation for anthropogenic disturbance assessment in the Huai River Basin. China Sci Total Environ 598:749–764
33. Hued AC, Bistoni MA (2005) Development and validation of a biotic index for evaluation of environmental quality in the central region of Argentina. Hydrobiologia 543:279–298
34. Wunderlin DA, Díaz MP, Amé MV, Pesce SF, Hued AC, Bistoni MA (2001) Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquía River basin (Córdoba-Argentina). Water Res 35(12):2881–2894
35. Otto M (1998) Multivariate methods. In: Kellner R, Mermet JM, Otto M, Widmer HM (eds) Analytical chemistry, Wiley-VCH, Weinheim, Germany, 916 p
36. Adams MJ (1998) The principles of multivariate data analysis. In: Ashurst PR, Dennis MJ (eds) Analytical methods of food authentication. Blackie Academic & Professional, London, UK, 350 p
37. Graça MAS, Coimbra CN (1998) The elaboration of indices to assess biological water quality. A case study. Water Res 32:380–392
38. Helena B, Pardo R, Vega M, Barrado E, Fernandez JM, Fernandez L (2000) Temporal evolution of groundwater composition in an alluvial aquifer (Pisuerga River, Spain) by principal component analysis. Water Res 34:807–816
39. Johnson RA, Wichern DW (1992) Applied multivariate statistical analysis. 3rd edn. Prentice–Hall International, Englewood Cliffs, NJ, USA, 642 p
40. Vega M, Pardo R, Barrado E, Debn L (1998) Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. Water Res 32:3581–3592

41. Astel A, Tsakovski S, Barbieri P, Simeonov V (2007) Comparison of self-organizing maps classification approach with cluster and principal components analysis for large environmental data sets. Water Res 41(19):4566–4578
42. De Las Heras Jiménez A, Melgar Riol MJ (2005) Rivers water quality at Galicia-Cost River Basin during 1973-2002. Predictive analysis to 2010 [Calidad del agua de los ríos de la Cuenca Hidrográfica Galicia-Costa durante el período 1973-1995. Análisis predictivo a 2010]. Tecnologia del Agua 25(261):54–61
43. Kannel PR, Lee S, Kanel SR, Khan SP (2007) Chemometric application in classification and assessment of monitoring locations of an urban river system. Anal Chim Acta 582(2):390–399
44. Khalil B, Ouarda TBMJ, St-Hilaire A (2011) A statistical approach for the assessment and redesign of the Nile Delta drainage system water-quality-monitoring locations. J Environ Monit 13(8):2190–2205
45. Kowalkowski T, Zbytniewski R, Szpejna J, Buszewski B (2006) Application of chemometrics in river water classification. Water Res 40(4):744–752
46. Shrestha S, Kazama F (2007) Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan. Environ Model Softw 22(4):464–475
47. Simeonov V, Stratis JA, Samara C, Zachariadis G, Voutsa D, Anthemidis A, Sofoniou M, Kouimtzis T (2003) Assessment of the surface water quality in Northern Greece. Water Res 37(17):4119–4124
48. Singh KP, Malik A, Mohan D, Sinha S (2004) Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India) – a case study. Water Res 38(18):3980–3992
49. Singh KP, Malik A, Sinha S (2005) Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques – a case study. Anal Chim Acta 538(1–2):355–374
50. Sundaray SK, Nayak BB, Lin S, Bhatta D (2011) Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments-a case study: Mahanadi basin, India. J Hazard Mater 186(2–3):1837–1846
51. Varol M (2011) Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques. J Hazard Mater 195: 355–364
52. Devic G, Djordjevic D, Sakan S (2014) Natural and anthropogenic factors affecting the groundwater quality in Serbia. Sci Total Environ 468-469:933–942
53. Li G, Liu G, Zhou C, Chou C-L, Zheng L, Wang J (2012) Spatial distribution and multiple sources of heavy metals in the water of Chaohu Lake, Anhui, China. Environ Monit Assess 184(5):2763–2773
54. Cao Y, Bark AW, Williams WP (1997) A comparison of clustering methods for river benthic community analysis. Hydrobiologia 347(1–3):25–40
55. Chabukdhara M, Nema AK (2012) Assessment of heavy metal contamination in Hindon River sediments: a chemometric and geochemical approach. Chemosphere 87(8):945–953
56. Clarke RT, Wright JF, Furse MT (2003) RIVPACS models for predicting the expected macroinvertebrate fauna and assessing the ecological quality of rivers. Ecol Model 160(3):219–233
57. Marchant R, Hirst A, Norris RH, Butcher R, Metzeling L, Tiller D (1997) Classification and prediction of macroinvertebrate assemblages from running waters in Victoria, Australia. J N Am Benthol Soc 16(3):664–681
58. Monferrán MV, Galanti LN, Bonansea RI, Amé MV, Wunderlin DA (2011) Integrated survey of water pollution in the Suquía River basin (Córdoba, Argentina). J Environ Monit 13: 398–409
59. Tomic O, Berget I, Næs T (2015) A comparison of generalised procrustes analysis and multiple factor analysis for projective mapping data. Food Qual Prefer 43(2015):34–46

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