Water quality assessment of a polluted urban river

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Abstract: Urban rivers in Latin America are heavily impacted by human activities that affect their functions and services. This paper shows the results of a water quality assessment for the Reconquista River, the second most polluted urban river in Argentina. They allowed the identification of the main processes of transport of pollutants and the prioritisation of different areas of the basin for interventions in a future sanitation plan. The following assessment tools were used: a Water Quality Index (WQI); geospatial and statistical analysis of the environmental parameters; and determination of critical points of the system. The implementation of these tools required 32 physicochemical and microbiological parameters that were measured in six monitoring campaigns from a monitoring network composed of 12 sites. Results show that water quality decreased from fair to very poor, with reference to protection of aquatic life; mainly due to the impact produced by the discharge of organic untreated effluents.

Keywords: urban rivers; water quality assessment; contamination critical zones; pollutants transport.

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1 Introduction

Most of the Latin American urban rivers are heavily impacted by anthropogenic activities that affect the aptitude of use of the resource: water source for human consumption, protection of aquatic life, irrigation, recreation; and, source of drinking water for livestock, among others; also affecting the health of people living in the basin.

The process of urbanisation of the surroundings of Buenos Aires city (the so-called Gran Buenos Aires) has modified the relationship between the water course and the environment of the Reconquista River basin. The area has been subject to major interventions to attend the problematic of flood. Thus, infrastructure has been developed for the regulation of the water course that controls the risk of events of 100 years of recurrence (Sadañiowski, 2003; Banco Interamericano de Desarrollo, 2006).

The irregular land occupancy for residential, industrial and commercial activities has transformed the Reconquista River into an urban river, without solving the issues that influence this new environmental situation yet. New required interventions for water quality improvement need the development of an environmental baseline that identifies the source, fate and transport of contaminants in the basin.

This study presents the environmental data corresponding to six (6) monitoring campaigns of the Reconquista River (middle basin), developed from 2009 to 2011, that were used for the water quality assessment. Data were stored in an environmental database to perform a statistical analysis of the spatial and temporal behaviour of the measured parameters; their possible correlations; and, the application of a Water Quality Index (WQI) for the assessment of contaminated sites in the studied system. Thus, there have been identified and prioritised areas for intervention, in the framework of a future sanitation plan.

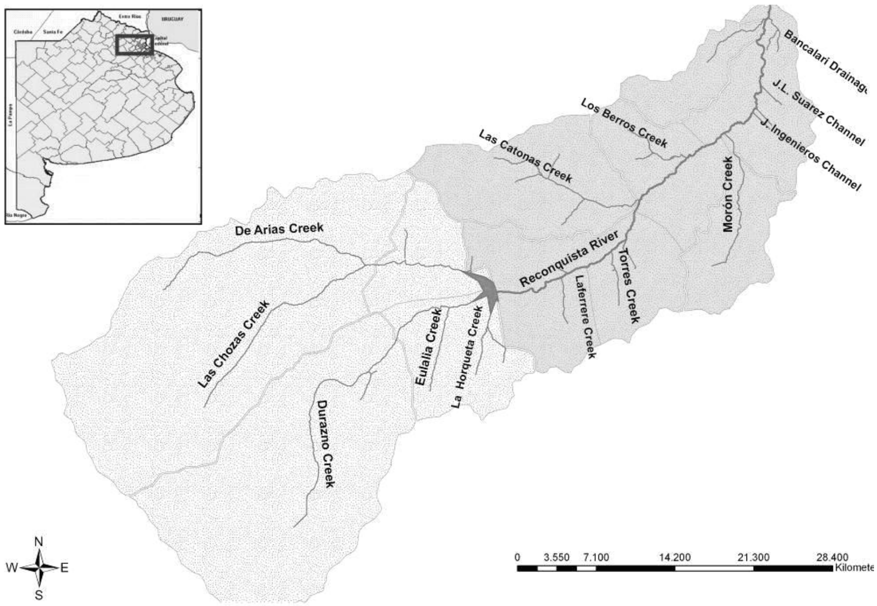
2 Materials and methods

2.1 Study site description

The basin of the Reconquista River is located in the Buenos Aires Province, Argentina (see Figure 1). It has ~167,000 hectares, from 18 counties of the Gran Buenos Aires area.

The river is a typical plain water course that originates in the confluence of the creeks La Choza, Durazno and La Horqueta in the county of General Rodríguez. Once the main course is formed, it received, in the middle basin, the flows of the creeks Torres, Saladero, Las Catonas, Los Berros and Morón; and the discharge channels of José Ingenieros, José León Suarez and Bancalari (Figure 1). Finally, its waters enter to Luján River, through which they reached Río de la Plata River. From the national census developed in 2010, it is known that 4,634,433 people lived in the 18 counties that form the basin (INDEC, 2010). Around 330 industries of third category (which include those establishments that are considered hazardous because its operation constitutes a hazard to safety, health and hygiene of the population or cause serious damage to property and the environment) are in the counties of the middle and low basin, close to the water courses. The Reconquista River is presently the second most contaminated river of Argentina; being the main cause of contamination the discharges of sewage and industrial effluents with poor or no treatment (Salibián, 2006; Defensoría del Pueblo de la Nación, 2007).

Figure 1 Upper and middle basin of Reconquista River



This work put its attention on the 38 km of the Reconquista River that conform the middle basin (system under study). This is owing to:

- in the middle basin, the Reconquista River has the typical characteristics of a urban river (Dourojeanni and Jouravlev, 1999; EPA, 2002)
- the availability of historical data
- the watershed committee, which is presently preparing the programme for the sanitation of the basin, required of different academic institutions, the input data to design and implement this management tool.

2.2 Design and implementation of a surface water quality monitoring network

The tributaries that were considered relevant for the design of the water quality monitoring network, taking into account the preliminary information of the system (Salibián, 2006 and references therein; Nader, 2009; Cappari, 2009), include the creeks Torres, Las Catonas, Los Berros, Morón, the channels José Ingenieros and José León Suárez, and a pluvial drainage. The implemented network has 12 monitoring stations: five located on the Reconquista River and seven on the tributaries (see Figure 2). Their final locations were determined considering accessibility and security issues (Table 1).

Figure 2 Stations of the water quality monitoring network of the middle basin of the Reconquista River. It also shows the georeferenced values of water quality evaluated in this work

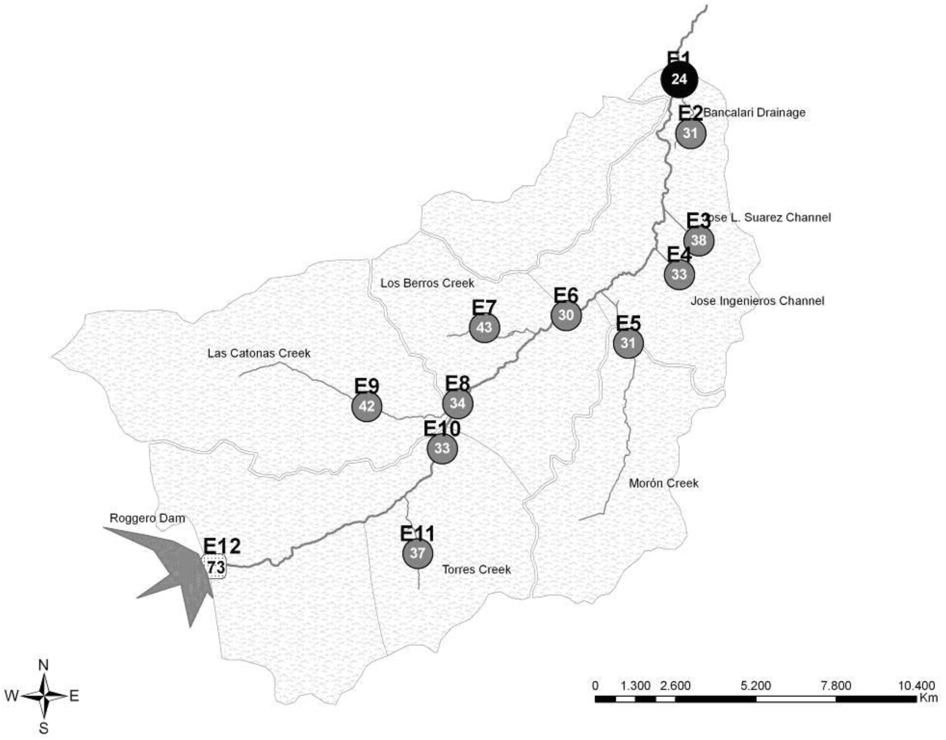


Table 1 Stations of the water quality monitoring network

Station	*Location*
E1	Reconquista River (km 37.8)
E2	Bancalari pluvial drainage
E3	José León Suárez Channel
E4	José Ingenieros Channel
E5	Morón Creek
E6	Reconquista River (km 25.5)

Table 1 Stations of the water quality monitoring network (continued)

Station	*Location*
E7	Los Berros Creek
E8	Reconquista River (km 17.9)
E9	Las Catonas Rreek
E10	Reconquista River (km 15.6)
E11	Torres Creek
E12	Reconquista River (after Roggero Dam, km 0)

Thirty-two physicochemical and microbiological parameters were measured in six campaigns developed between the years 2009 and 2011, as it can be seen in Table 2. These parameters include pH, Electrical Conductivity (EC), dissolved oxygen (DO), water temperature (T), turbidity, Total Suspended Solids (TSS), flow, Biological Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), nitrogen as nitrates ($N–NO_3^-$), nitrogen as ammonia ($N–NH_4^+$), reactive phosphate ($P–PO_4^{3-}$), faecal coliform bacteria (Fec Coli), lithium (Li), magnesium (Mg), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), strontium (Sr), molybdenum (Mo), cadmium (Cd), antimony (Sb) and lead (Pb).

Table 2 Sampling campaigns

	1st campaign	*2nd campaign*	*3rd campaign*	*4th campaign*	*5th campaign*	*6th campaign*
Date	03/11/2009	11/05/2010	08/09/2010	01/03/2011	06/07/2011	11/10/2011
Station	Spring	Autumn	Winter	Summer	Winter	Spring

2.3 Monitoring plan

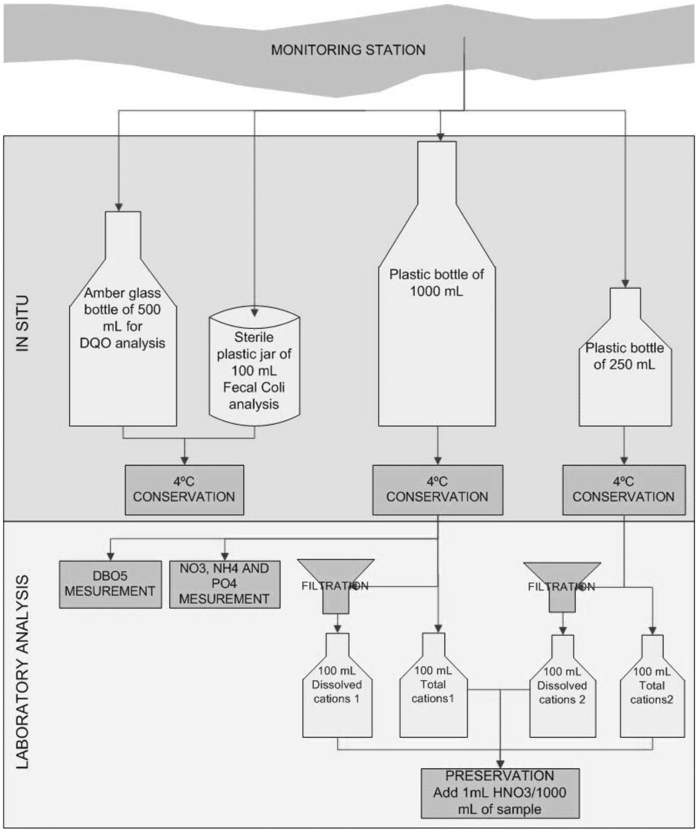
2.3.1 Sampling plan

The sampling plan for water, suspended particulate matter and sediment was designed following the procedure PT-Mu-01 “Plan de muestreo para aguas superficiales y sedimentos” (Alberro et al., 2011). Samples were collected from the main course of the river and tributaries. In the framework of the Quality Assurance/Quality Control Plan, were prepared two field blank samples and replicates of each sample taken, to take into account the uncertainty due to the possible contamination during the sampling and transport.

2.3.2 Sampling, fractionation, preservation and conservation

Sampling followed the procedure PT-Mu-02 “Muestreo de aguas superficiales” (Alberro et al., 2011). Figure 3 presents the scheme of the process of fractionation, preservation and conservation of the water samples.

Figure 3 Scheme of the procedure for sampling, fractionation, preservation and conservation of the water samples



2.3.3 In situ measurement procedures

The EC was measured with a cell of conductance following the procedure Hach 8160, equivalent to Standard Method 2510-B for wastewater; the pH, with a combined glass electrode following the procedure Hach 8156, based on the Standard Method 4500-H+B, ASTM D1293-84(90)/(A or B) and USEPA 150.1; the DO, with an amperometric Clark type sensor, following the procedure Hach 8157; water temperature, with the sensors provided by the EC, pH and DO probes. The turbidity was measured by a portable turbidimeter with a tungsten filament following the procedures suggested by the manufacturer, based on USEPA method 180.1; the flow, with a horizontal axe current meter following a procedure based on the ASTM D3858 for Open-Channel Flow Measurement of Water by the Velocity-Area Method.

2.3.4 Laboratory measurements

To guarantee that the measurements represent nitrogen as NO_3^- and NH_4^+, and reactive phosphorus as PO_4^{3-}, the concentrations were determined in <6 h since their collection, in water samples conserved at 4°C.

Spectrophotometric techniques were used to determine PO_4^{3-} (procedure based on the Standard Methods 4500-P E); NO_3^- (procedure based on the Standard Methods 4500 E); and NH_4^+ (procedure based on the salicylate method adapted from Reardon et al., 1966).

The determination of BOD5 was done in 12 respirometers located in a controlled temperature cabinet, following a procedure based on the Standard Methods 5210 D. The measurements of DQO and faecal coliform bacteria were done following the procedures of the Standard Method 5220D and 9221 C/E, respectively.

The samples used for the determination of total and dissolved cations were digested by following a procedure based on the USEPA Method 3005A (Acid digestion of waters for total recoverable or dissolved metals for analysis by Flame Atomic Absorption or Inductive Coupled Plasma spectroscopy). The digested samples were analysed with an Inductive Coupled Plasma Mass Spectrometer from the Environmental Analysis Laboratory of University of San Martín. The results were verified by using certified reference materials.

2.3.5 Environmental database and statistical analysis

The 2376 primary data obtained after the development of six campaigns of water quality monitoring, were loaded to an Environmental Database (EDB), which was previously designed taking into account the characteristics of the study system, the measured parameters and the requirements of the analysis tools that were used in this study.

The variables were normalised for further analysis by auto scaling the values using equation (1):

$$xa_i = (x_i - x_{\text{mean}}) / s, \tag{1}$$

where x_i is the original value, x_{mean} the mean value of the variable and s, its standard deviation.

The coefficients of the Pearson correlation were determined for each possible pair of normalised variables using the command 'corrcoef()' of the calculation Matlab programme. Then, the correlation matrix was analysed to determine the lineal correlation among the variables.

The matrix of eigenvalues and eigenvectors were calculated from the generated matrix of correlations by using the command '[V, D] = eig()' of the calculation Matlab programme. Once determined the eigenvalues were used to calculate the number of principal components (PC) that are necessary to represent more than 60% of the variability of the data in the EDB. Finally, the matrix of scores was calculated to determine the possible presence of clusters in the EDB.

2.3.6 Water Quality Index

The water quality of the Reconquista River was evaluated using a WQI, developed by the Canadian Council of Ministers of the Environment (CCME, 2001). Twelve countries of Latin America and the Caribbean have harmonised its use for the evaluation of contamination in polluted rivers of the region, in a Workshop developed in Río de Janeiro in 2007, in the framework of the IAEA Project RLA/1/010 "Improved management of the pollution of surface water bodies contaminated with metals" (IAEA, 2012; Aguacal, 2012).

The index determines the quality of a water body, with reference to an objective of quality of the resource. It is composed of three normalised factors to obtain a maximum value of 100. Table 3 shows the relation between the numerical values of the WQI and the classification of the water quality. The formulation of the index is presented in equation (2).

$$\text{CCMEWQI} = 100 - \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1732}. \tag{2}$$

The F1 factor (scope) represents the extent of water quality guideline non-compliance over the time period of interest (number of variables that did not accomplish objectives); the F2 factor (frequency) represents the percentage of individual tests that do not meet objectives ("failed tests or measurements"); and, the F3 factor (amplitude) represents the amount by which failed test values do not meet their objectives.

Table 3 Classification of the WQI values

CCME-WQI	*Category*
95–100: Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels. These index values can only be obtained if all measurements are within objectives virtually all of the time	Excellent
80–94: Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels	Good
65–79: Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels	Fair
45–64: Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels	Marginal
30–44: Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels	Poor
0–29: Water quality is always threatened or impaired; conditions always depart from natural or desirable levels	Very Poor

This study used the quality objectives corresponding to protection of aquatic life presented in a local regulation (Decreto 831/93, Anexo II, Tabla 2, 1993). For those parameters for which there are no local guidelines, we have picked up regional (Latin America and the Caribbean, Ávila Pérez et al., 2011) standards.

2.3.7 *Spatial and temporal analysis, mass fluxes and evaluation of critical points*

The temporal and spatial variability of the parameters that define the system were evaluated, considering the four typical seasons of the year, and the distance from Roggero dam. The values were compared with the guidelines for protection of aquatic Life (Decreto 831/93, Anexo II, Tabla 2, 1993), in the cases that the local guidelines of the parameters exist.

The contribution of each of the Reconquista River tributaries, to the contamination of the main river course, was evaluated through the mass flux of pollutants, calculated from the flow and concentrations of the parameters considered as indicators of pollution.

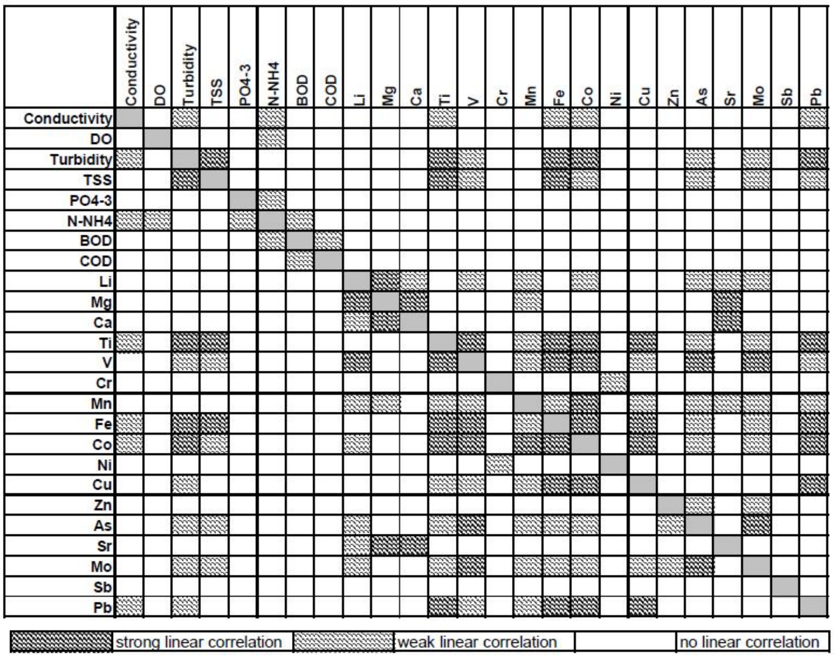
Total Dissolved Solids (TDS) and TSS were used as inorganic pollution indicators; while biodegradable organic matter (BOD5) and faecal coliform, as indicators of organic pollution. Thus, the criteria used to classify the critical points of the system rely in their contribution to decrease the aptitude of use of the resource.

3 Results and discussion

3.1 Statistical analysis

The analysis of the matrix of correlation (Figure 4) allowed determining that turbidity is, as expected, related to total suspended solid, but also to metals like Ti, Fe, Co, Pb, V, Cu, As, Mo and Pb; showing their transport through the water courses of the basin is associated to inorganic/organic particles. Thus, a conceptual model for the evaluation of the water quality of the Reconquista River must include suspended solids and metals.

Figure 4 Correlation matrix of the environmental variables/indicators measured in this study



	Conductivity	DO	Turbidity	TSS	PO4-3	N-NH4	BOD	COD	Li	Mg	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Mo	Sb	Pb
Conductivity	■		░			░						░				░	░								░
DO		■				░																			
Turbidity	░		■	▓								▓	░			▓	▓				░		░		▓
TSS			▓	■								▓	░			▓	░				░		░		░
PO4-3					■	░																			
N-NH4	░	░			░	■	░																		
BOD						░	■	░																	
COD							░	■																	
Li									■	▓	░		░		░		░				░	░	░		
Mg									▓	■	▓				░							▓			
Ca									░	▓	■											▓			
Ti	░		▓	▓								■	▓		░	▓	▓		▓		░		░		▓
V			░	░					▓			▓	■		░	▓	▓		░		▓		▓		░
Cr														■				░							
Mn									░	░		░	░		■	░	▓		░		░	░	░		░
Fe	░		▓	▓								▓	▓		░	■	▓		▓		░		░		▓
Co	░		▓	░					░			▓	▓		▓	▓	■		▓		░		░		▓
Ni														░				■							
Cu			░									░	░		░	▓	▓		■						▓
Zn																				■	░		░		
As			░	░					░			░	▓		░	░	░			░	■		▓		
Sr									░	▓	▓											■			
Mo			░	░					░			░	▓		░	░	░		░	░	▓		■		
Sb																								■	
Pb	░		░									▓	░		░	▓	▓		▓						■

▓ strong linear correlation ░ weak linear correlation ☐ no linear correlation

It can also be seen that there are two major clusters of metals: one formed by Ti, V, Fe, Co, Cu and Pb; another by Li, Mg, Ca and Sr. From the point of view of chemical reactivity, the first group includes transition metals (except Pb), that stabilise as strongly hydrated soluble cations (Co, Cu and Pb) and oxides and hydroxides (Ti, V and Fe); whereas the second one is composed of alkaline and alkaline earth elements that stabilise as strongly hydrated soluble cations. They have the ability to form ionic bonding (Ti, Fe(III), Li, Mg, Ca and Sr), covalent bonding (Pb) or both (Fe(II), V, Co, Cu) (Duffus, 2002; Cicerone et al., 2006, 2011).

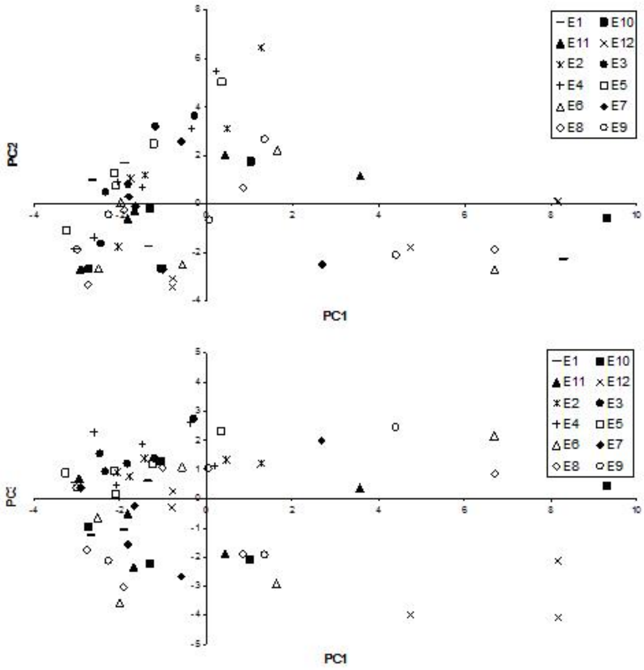
Regarding the origin of metals, Li, Mg, Ca and Sr could be associated to meteorisation processes. The soils adjacent to the main course, among which we can find Natracualfs and typical Natracuols, are formed by alluvial sediments distributed in flat and concave areas, being their main limiting factors the sodium alkalinity, the presence of a calcareous horizon and the consequent risk of flooding (SEAGYP-INTA, 1990).

García Reiriz et al. (2011) have found that other metals like Fe and Mn could have a geochemical origin. In Figure 4, it can be seen that Ti and Fe strongly correlate with TSS; thus, it is reasonable to assume that they might be the constituents of suspended particulate material of the Reconquista River. The strong correlation of Pb with the turbidity could be attributed to its capacity of forming surface complexes with clays and organic material (McBride, 1994). Like Cu, Zn, Sb and Cr, it comes from deficient or non-treated industrial effluents.

Organic matter pollution has its own indicators: $\mathrm{N{-}NH_4^+}$, $\mathrm{P{-}PO_4^{3-}}$, $\mathrm{BOD_5}$ and COD. The correlation of $\mathrm{N{-}NH_4^+}$ with EC, DO, $\mathrm{P{-}PO_4^{3-}}$ and $\mathrm{BOD_5}$ could be attributed to the presence of one of the major pollutants in the Reconquista River: the effluents without treatment or deficiently treated coming from sewage. The slight correlation between $\mathrm{BOD_5}$ and COD recognises that there are other sources for organic matter: meat processing plants, and textile industries (Defensoría del Pueblo de la Nación, 2007; Salibián, 2006).

The matrix of eigenvalues allowed determining that the three principal components, PC1, PC2 and PC3, describe the 60% of variability of the stored values in the EDB. Figure 5 presents the analysed observations in terms of linearly uncorrelated variables PC1 vs. PC2 and PC3. The values formed one cluster for the most polluted monitoring stations: E1, E2, E3, E4, E5 and E7.

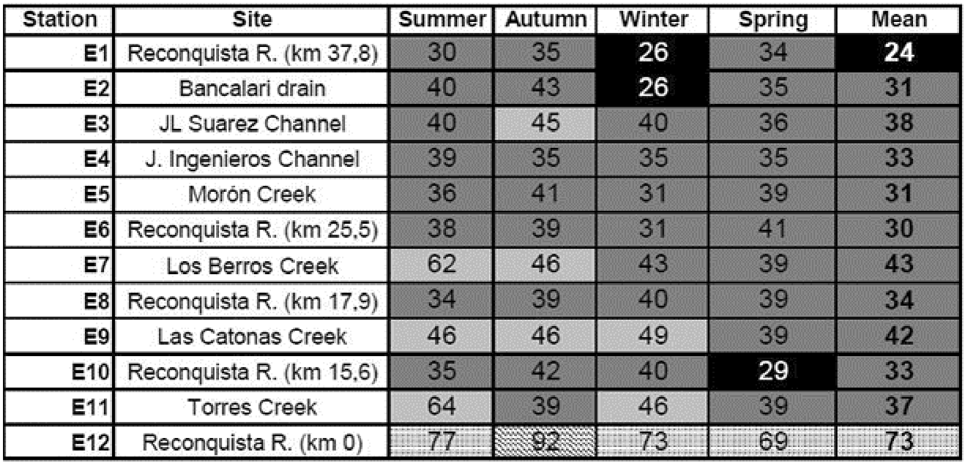
Figure 5 PCA spatial distribution of the observations in the EDB. PC1 vs. PC2 and PC3



3.2 Water quality

Figure 2 and Table 4 show water quality georeferenced values, calculated taking into account the quality objective for protection of aquatic life.

Table 4 Water quality values evaluated for the middle basin of the Reconquista River



Station	Site	Summer	Autumn	Winter	Spring	Mean
E1	Reconquista R. (km 37,8)	30	35	26	34	24
E2	Bancalari drain	40	43	26	35	31
E3	JL Suarez Channel	40	45	40	36	38
E4	J. Ingenieros Channel	39	35	35	35	33
E5	Morón Creek	36	41	31	39	31
E6	Reconquista R. (km 25,5)	38	39	31	41	30
E7	Los Berros Creek	62	46	43	39	43
E8	Reconquista R. (km 17,9)	34	39	40	39	34
E9	Las Catonas Creek	46	46	49	39	42
E10	Reconquista R. (km 15,6)	35	42	40	29	33
E11	Torres Creek	64	39	46	39	37
E12	Reconquista R. (km 0)	77	92	73	69	73

During the first 15 km, water quality of the main course of the Reconquista River decreased 50 %, from 73 in E12–33 in E10; which means that not all pollutants are coming from Torres Creek. Thus, there is a substantial input of contaminants that are directly unloaded from unknown sources to the Reconquista River. For the following 22 km, water quality decreased 30% from 33 to 24 in E1. There is no pattern of water quality variation dealing with seasonal changes.

The F1 factor of the index (see equation (2)) showed that nine variables from 12 did not meet the quality objectives for protection of aquatic life. These are: DO, EC, BOD, Fec Coli, $N\text{–}NH_4^+$, Pb, Cd, Cr and Cu.

The F2 factor of the index showed that 238 from 576 tests did not meet the objectives. It also showed that Fec Coli has exceeded the objectives, 91.6% of the times that was tested; BOD and $N\text{–}NH_4^+$, 81.25% of the times; and DO, 64.6% of total tests for this indicator.

The same analysis can be done for metals. Cr, Cu, Cd and Pb exceeded objectives in the 68.8, 60.4, 16.7 and 10.4% of the tests of these variables, respectively.

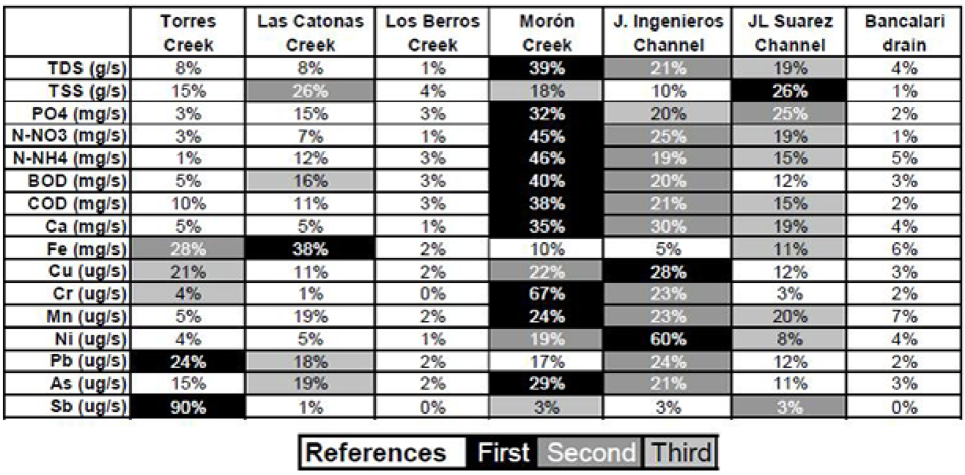
The F3 factor shows that Fec Coli have exceeded the value of the quality objectives more than 25 times, for protection of aquatic life; while the rest of the variables, in <10 times.

By taking into account all the results presented in this section, it is concluded that water quality of the Reconquista River in the middle basin, has lost its aptitude for protecting aquatic life due to the impact produced by the discharge of organic untreated effluents coming from sewage and meat processing plants. The water quality of E1 might increase from 24 to 72.6 if this impact is mitigated by taking action in territorial planning and land use.

3.3 Mass flux analysis and determination of critical points

Table 5 presents the contribution of each tributary of the Reconquista River in the middle basin to the mass flux of the different pollutants received by the main river course. Their percentages of contribution are shown by a colour scale (black: first; grey: second; light grey: third).

Table 5 Discharges of the tributaries of the Reconquista River in the middle basin, in percent of the total mass flux. See text for more details



	Torres Creek	Las Catonas Creek	Los Berros Creek	Morón Creek	J. Ingenieros Channel	JL Suarez Channel	Bancalari drain
TDS (g/s)	8%	8%	1%	39%	21%	19%	4%
TSS (g/s)	15%	26%	4%	18%	10%	26%	1%
PO4 (mg/s)	3%	15%	3%	32%	20%	25%	2%
N-NO3 (mg/s)	3%	7%	1%	45%	25%	19%	1%
N-NH4 (mg/s)	1%	12%	3%	46%	19%	15%	5%
BOD (mg/s)	5%	16%	3%	40%	20%	12%	3%
COD (mg/s)	10%	11%	3%	38%	21%	15%	2%
Ca (mg/s)	5%	5%	1%	35%	30%	19%	4%
Fe (mg/s)	28%	38%	2%	10%	5%	11%	6%
Cu (ug/s)	21%	11%	2%	22%	28%	12%	3%
Cr (ug/s)	4%	1%	0%	67%	23%	3%	2%
Mn (ug/s)	5%	19%	2%	24%	23%	20%	7%
Ni (ug/s)	4%	5%	1%	19%	60%	8%	4%
Pb (ug/s)	24%	18%	2%	17%	24%	12%	2%
As (ug/s)	15%	19%	2%	29%	21%	11%	3%
Sb (ug/s)	90%	1%	0%	3%	3%	3%	0%

References First Second Third

Thus, the contribution to the pollution of the main course of the Reconquista River in the middle basin, owing to the tributaries, follows the order: Morón > José Ingenieros > José León Suárez > Torres > Las Catonas.

4 Conclusions

A monitoring network of surface water quality was designed and implemented in the middle basin of the Reconquista River.

An environmental database was designed and implemented for physical, chemical and biological indicators measured in water and suspended solids.

Four groups (transition metals, alkaline and alkaline earth elements, suspended particulate material and effluents from sewage) of correlated variables that pointed out potential sources and origin of chemical compounds in the chemical matrix the Reconquista River were identified.

The water quality decreased from fair to very poor, with reference to protection of aquatic life; mainly owing to the impact produced by the discharge of organic untreated effluents, probably coming from sewage and meat processing plants.

The most polluted monitoring stations were E1, E2, E3, E4, E5 and E7. The variables DO, EC, BOD, Fec Coli, N-NH_4^+, Pb, Cd, Cr and Cu were those that did not meet the quality objectives.

The water quality of E1 might increase from 24 to 72.6 if this impact is mitigated by taking action in territorial planning and land use.

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