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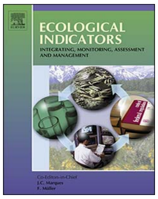

Original Articles

Multidisciplinary approach to a study of water and bottom sediment quality of streams associated with mixed land uses: Case study Del Gato Stream, La Plata (Argentina)

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ABSTRACT

Surface water bodies receive a basin's wide diversity of pollutants, especially when there are mixed land uses. Among the many environmental tools to assess a body water quality, most studies use only a few. In addition these studies, usually, are focused only on a set of pollutants and an environmental matrix. The Del Gato Stream – a surface watercourse within of more populated area of Argentina – exemplifies the typically contrasting land uses around this area's streams. The predominant land uses along of the stream are agricultural in the upper, urban and industrial the middle, and animal husbandry in the lower subbasin. The aim of this study was to use a multidisciplinary approach to evaluate the environmental quality of that stream as a model of surface-water bodies within mixed-land-use regions in the Buenos-Aires metropolitan area. At each of the sampling sites – distributed along the stream as follows: 3 in the upper, 4 in the middle, 3 in the lower subbasin – general water parameters were measured; water and sediment samples taken for physical, chemical, microbiological, and ecotoxicological analysis; and the variables in each environmental matrix, analyzed separately and jointly. The stream presented a significant general deterioration, the middle subbasin with urban-industrial land use being the most impacted, where metals and metalloids recorded highest levels, and the rest of the measured parameters were also found at high levels. The upper subbasin had the highest quality, and the lower subbasin proved poor quality regarding microbiological variables, nutrients, and general water parameters. The tests included in the toxicity battery did not reflect a common pattern of toxicity along the watercourse. However, when they were integrated in the EDAR index, the middle subbasin was the most affected sector of the stream. Although, the usefulness of each analysis tool must be evaluated taking into account the objective of the study, if the aim is to know the general environmental quality of a stream, the multiple-factor analysis proved to be the most effective means in complex systems under the influence of great diversity of pollution sources. This study provides relevant information about the ecological quality of a stream representative of a region with scarce environmental information.

1. Introduction

The exponential increase in the world population, its concentration in large urban centers, and the gamut of anthropic activities involved in meeting its demands (industrialization, agriculture, raising livestock), all contribute to the present imbalance in natural systems resulting from an increase in sewage drainage, urban and agricultural runoff, and technological advances that release synthetic products into the environment (Seilheimer et al., 2007; Zeitoun et al., 2014; Miao et al., 2015). Large urban settlements have historically been closely linked to water sources that are used as resources for the subsistence of populations, and in turn, become the ultimate receptacle of the by-products and waste materials from most human activities. Therefore, anthropic activities disturb the natural state of water resources with resulting detrimental effects on the associated biota and, in turn, on the human effector populations themselves (Ronco et al., 2008; Peluso et al., 2013a; Mugni et al., 2015).

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The evaluation of the quality of water bodies is approached by different disciplines within the environmental sciences. The environmental physical chemist uses the concentration of compounds and other indirect variables to characterize the quality of a resource. The microbiologist, analyzes water quality based on the presence and relative abundance of different functional groups, even up to identifying the specific nature of a contamination from a determination of the taxa present; whereas the ecotoxicologist, in studying the biologic effects of pollutants on organisms, provides a simple and practical way of estimating the quality of water systems (APHA, 1998; Environment Canada, 1999; Newman and Clements, 2008). Regardless of the environmental approach used, the difficulty of the study increases with the diversity of land uses in a given basin (Islam et al., 2015). In such instances, a combined approach is needed to determine the overall environmental quality of water bodies and implement the appropriate management policies for their recovery.

Previous experience dictates that contaminated urban rivers can be recovered if technical, economic, and human resources are implemented adequately under coordinated and long-term, sustained policies, with the Thames River being an example of this principle (Sheehan et al., 1984). A proper design of remediation strategies requires a precise diagnosis of the socio-environmental situation in order to facilitate decision-making and avoid unsuccessful activities, and even more so in developing countries such as in the example of Argentina, where decision-making in terms of environmental policies is faced with characteristic socioeconomic problems.

Most of the studies involving the environmental diagnosis of surface water bodies do not analyze the quality of the water and bottom sediments in a comprehensive way (Sekabira et al., 2010; Zhang et al., 2010; Azhar et al., 2015); and when such investigations do, they usually take into account the groups of compounds associated with only one or just a few of the sources of pollution (*i.e.*, urban, industrial, agricultural) (Islam et al., 2015; Etchegoyen et al., 2017).

Buenos Aires city and its metropolitan area clearly exemplifies the process of transformation from an initial geographic area of high social and economic prosperity to a mega-urbanization with extensive problems of territorial planning and the occupation of the land along with the concomitant pollution of the water resources (Vapñarsky, 2000). The repeated social, economic, and financial crises in this country generated large settlements of low-income populations with significant shortages of the basic utilities such as electricity, drinking water, sewage, and rain-drainage networks (INDEC, 2010). Some of these emergency settlements were installed on marginal areas near watercourses, generating the uncontrolled growth of urbanization in the absence of a bioholistic vision by the territorial-planning and environmental-control agencies that allowed the establishment of those settlements along with the gradual development of prodigious cities and industrial poles without clear guidelines for urban planning.

The Buenos-Aires area contains a large number of stream microbasins that cross the urban centers in west-east direction before flowing into the Río de la Plata estuary. Most of these minicatchments have a high degree of anthropization, including agricultural areas (generally around the headwaters), industries, and an extensive urbanization (usually in the middle and lower sections) (Banda-Noriega and Ruiz de Galarreta, 2002). Many of these streams have been partially channeled and/or piped with the flood plains being occupied by houses that are therefore frequently flooded.

The Del Gato Stream exemplifies, on a small scale, the variability of activities and conflicts of land use that occur in a basin of that type, being fraught with problems common to other regional basins that cross rural, suburban, and urban areas.

Within this context, the aim of this study was to evaluate through several indicators, the physical, chemical, microbiological and ecotoxicological quality of the water and sediment of Del Gato Stream, as a case study of water bodies surrounded by mixed uses of the land.

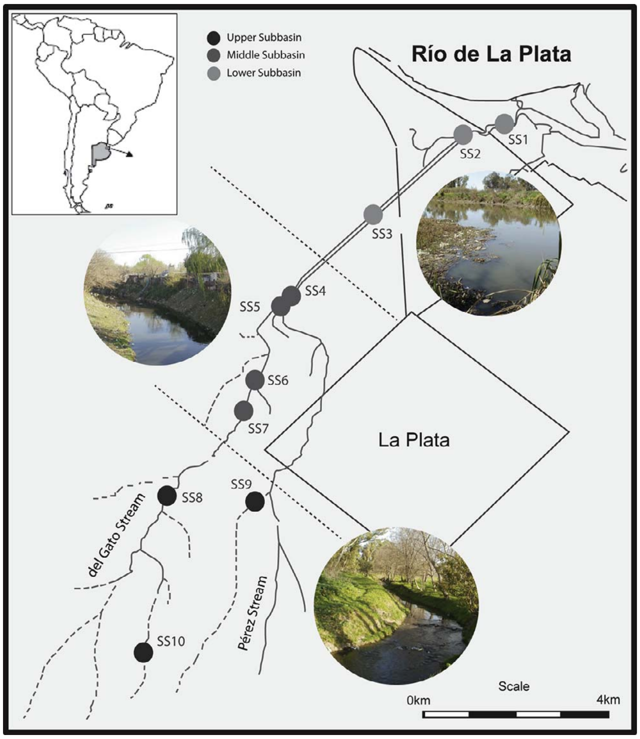

Fig. 1. Scheme of the course of the Del Gato Stream used as a model example of the environmental quality of surface water bodies surrounded by mixed land uses within the Buenos-Aires metropolitan area. The locations of the ten sampling sites and the limits of the subbasin are indicated. The associated photographs illustrate the general characteristics of each subbasin within the vicinity of the stream.

2. Materials and methods

2.1. Study area

The basin of the Del Gato Stream – with an area of approximately 98 km^2 and a length of 25 km – is a typical plains stream of the Río de la Plata basin with a general southwestern-northeastern runoff course. In many sectors, the Del Gato has been rectified to allow normal drainage to the estuary. In the lower sector of the middle subbasin, the stream receives input from the Regimiento and Pérez streams, which are incorporated into the underground drainage system in the urban areas (Guimaràes et al., 2009). Almost 380,000 people live in the Del Gato floodplain, with housing in many instances located on the stream's banks (Bazán et al., 2011; Fig. 1).

Studies carried out by Andrade et al. (2012) indicated that in the basin of the Del Gato Stream a conflict existed between the informal and the correct legal uses of the bordering land. The upper subbasin is characterized by agricultural use combined with discontinuous residence along with a very low industrial activity; the middle subbasin is the most intensively populated with the greatest concentration of industrial activity; while the lower subbasin involves the raising and grazing of livestock (*i.e.*, farm-animal husbandry) along with discontinuous residential areas, low industrial activity, and an open-pit landfill (Fig. 1).

2.2. Sampling sites

The sampling was carried out during in November 2011. The sampling sites (SSs) have been located according to the different land uses within the stream's basin. Thus, the SSs 1, 2, and 3 are characteristic of the lower subbasin; 4, 5, 6, and 7 represent the most complex sector of the watercourse because of the multiplicity of land uses (middle subbasin); while 8, 9, and 10 exemplify the activities associated with the

Table 1
Measured physical, chemical, microbiological and ecotoxicological parameters and analytical methodologies used to analyze the water and sediment samples of the Del Gato Stream. The last columns correspond to the grouping of the variables in the Multiple-factor Analysis.

Measured parameters	Applied methodology	Groups for Multiple-factor Analysis	
		Water (W)	Sediment (S)
In situ water parameters: Temperature, pH, Dissolved Oxygen, Electrical Conductivity		*In-situ_W*	–
General water parameters: Alkalinity, Chlorides, Sulphate, Total dissolved solids (TDS), Phosphorus, Nitrite, Nitrates, Ammonium, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD).	APHA, 1998 (SM 2320, SM 4500-Cl- B, SM 4500-SO4-2B, SM 2540B, SM 4500- F, SM 4500-NO2-, 4500-NO3-, SM 4500-NH3 D SM-5220B and SM-5210B)	*Nutrients_W* (*Nitrite*, *Nitrates*, *Ammonium* and *Phosphorus*) *General_W* (everyone else)	– –
General sediment parameters: Nitrates, Total Phosphorus, Sulphures, Organic Matter by Loss on Ignition (LOI), Sediments classes	Nitrates: (Black, 1965) Total Phosphorus: Colorimetric analysis (Andersen, 1976) Sulphures: M9030 (USEPA, 1996a,b) LOI (Peluso et al., 2013a) *Sediments classes* (Peluso et al., 2013a)	– –	*Nutrients_S* (*Nitrates* and *Total Phosphorus*) *General_S* (everyone else)
Microbiological parameters: Total coliforms and Fecal coliforms (most probable number-MPN)	APHA, 1998 (SM9221B y E)	*Microbiological_W*	–
Metals, metalloids and major elements in water and sediment: Mg-Zn-Cr-Cu-Ba-Ag-Ar-Ni-Fe-Pb-Cd-V-Al-Se-Mo-Bo-Ca-K-Na-Hg-Mn-Co	Inductively Coupled Plasma Mass Spectrometry (ICP-MS), with microwave assisted acid digestion for sediments (USEPA, 3050, 3051)	*Metals_W*	*Metals_S*
Pesticides: αHCH, HCB, Lindane, Heptachlor, Chlorpyriphos, Endosulfan I and II, Dieldrin, Cypermethrin and Tetramethrin	Extraction by dichloromethane. For sediment extraction solid-liquid M3550 (USEPA, 1996a,b) and quantified by Gas chromatography electron-capture detector (GC-ECD) (Marino and Ronco, 2005).	*Pesticides_W*	*Pesticides_S*
Ecotoxicity: lethality (*Daphnia magna* – 48 h, *Hydra attenuata* – 96 h, *Cnesterodon decemmaculatus* – 96 h, *Hyalella curvispina* – 10 d) and sublethality (*Hyalella curvispina* – 10d – growth inhibition, *Lactuca sativa* – 120 h – root elongation inhibition)	*D. magna.* (USEPA, 2002), *H. attenuata* (Trottier et al., 1997), *C. decemmaculatus* (modified USEPA, 1996), *L. sativa* (USEPA, 1996a,b), *H. curvispina* (Peluso et al., 2011)	*Ecotoxicological_W* (*D. magna, H. attenuata, C. decemmaculatus* and *L. sativa)*	*Ecotoxicological_S* (*H. curvispina)*

(–): not applicable/not measured.

upper subbasin (Fig. 1). SS 5, in particular, is located at the mouth of the streams Regimiento and Pérez; so the characteristics recorded at that point will directly reflect the contribution of those tributaries.

2.3. Physical-chemical and bacteriological parameters

In each SS, the dissolved-oxygen (DO-mg L^{-1}) concentration, electrical conductivity (EC-μS cm^{-1}), total dissolved solids (TDS-mg L^{-1}), and pH, were measured with a multiparametric Horiba U52 meter and water and sediment samples taken for physical, chemical, microbiological, and ecotoxicological analysis. The samples collected were maintained at 4 °C until analysis.

Table 1 summarizes the physical-chemical and microbiological parameters analyzed and their experimental protocol.

To assess the contamination level of sediments by heavy metals, the enrichment factor of the sediments tested was calculated. The data on the metal levels was normalized to the iron concentration in each sample to differentiate pollution loads from background levels (Mucha et al., 2003). We employed the average metal levels in the earth's crust to calculate the enrichment factor of the metals investigated except for Hg because that metal did not correlate with the Fe concentrations. The sediment qualities were categorized according to the criteria prescribed by Sutherland (2000). The metal enrichment factor is defined as follows (Rubio et al., 2000):

$$EF = \frac{(M/Fe)sample}{(M/Fe)background}$$

where EF is the enrichment factor, (M/Fe)sample is the ratio of metal-to-Fe concentration of the sample, and (M/Fe)background is the ratio of metal-to-Fe concentration of the background (*i.e.*, the earth's crust).

2.4. Toxicity bioassays

The toxicity of water and sediment samples was evaluated by a battery of standardized toxicity bioassays. The crustacean *Daphnia magna* (Straus Cladocera: Daphnidae), the coelenterate *Hydra attenuata* (Dioni Anthomedusae: Hydriidae), the fish *Cnesterodon decemmaculatus* (Jenyns Cyprinodontiformes: Poecilidae), and the vascular plant *Lactuca sativa* (L. Asterales: Asteracea) were used to assess the toxicity of the water matrix. All bioassays were performed in triplicate with at least four dilutions plus negative control, according to the criteria required for the preparation of the effects-dilution–average ratio (EDAR) index (Ronco et al., 2005). In all cases, the requirements of QC & QA (control charts) and criteria of acceptability of results were followed (effect $< 10\%$ in the negative control and coefficient of variation $< 30\%$ in negative control of the *L. sativa* test) according to the protocols detailed in Table 1.

For the sediment matrix, the amphipod *Hyalella curvispina* (Schomeker Amphipoda: Gammaridae), was used. Toxicity test procedure was previously described by Peluso et al. (2011) (Table 1). Briefly, five replicates were used for each sediment sample; 100 mL of sediment and 175 mL of overlying water were placed in each replicate (24-h stabilization period), with ten individuals each. Exposure was conducted for 10 days at 21 °C on a 16:8 light/dark photoperiod. The lethal effects of the sediment samples were evaluated, and in those instances in which the mortality did not exceed 50%, the percentage of growth inhibition was also assessed as constituting a sublethal effect.

2.5. Data analysis

2.5.1. Quality indices

In order to ascertain and quantify the quality of the water body, the parameters analyzed were scored by means of the different indices commonly used in these types of ecosystems. For the water matrix, the water-quality index (WQI) developed by the National Sanitation Foundation of the United States was used. This index takes into account the levels of dissolved oxygen, biochemical-oxygen demand (BOD), fecal coliforms, nitrates, phosphates, pH, and total solids along with the temperature changes, as described by the following equation:

$$\mathrm{WQI\,(NSF)} = \sum_{i=1}^{n} \mathrm{WI\,Qi}$$

where *Wi* is the weighting factor that can take on values between 0 and 1; *Qi* represents the scale factor; and *i* is a parameter that goes from 1 to n, with n being the total number of parameters considered in the calculation (Carrillo Castro and Villalobos Alcazar, 2011).

To estimate the ecotoxicological quality of the water, the toxicity tests were integrated in the EDAR index (Ronco et al., 2005). This index makes use of the sample concentration for each test that induces an effect of 20%, considering the LC/IC/EC20. When it is not possible to determine an LC/IC/EC20, the highest dilution showing a toxic effect of 15% or higher, or the undiluted sample (100%) when toxic responses at this concentration are below 15%, are used. Dilutions producing a 100% toxic effect are not used in the index calculation. To calculate an EDAR value for the given battery, each estimated effect is included as follows:

$$\frac{\sum_{i=1}^{n} (ei + 1)di}{\sum_{i=1}^{n} pi}$$

where *Pi* is the weight assigned to the endpoint assessed (in this study, one to all endpoints), *ei* is the measured effect at a *di* dilution, and *n* is the number of endpoints tested in the battery.

For the sediment matrix, the ecotoxicological–sediment-hazard index (ESHI) proposed by Peluso et al. (2016) was used to assess the sediment quality, as described by the following equation:

$$ESHI = \frac{(\sum (Mc/G)/n)}{Tox}$$

where *Mc* corresponds to the measured concentration of each compound in the sample, *G* is the corresponding guidelines (interim sediment-quality guideline-ISQG) (CCEM, 2002), *n* is the number of compounds analyzed, and *Tox* is the biologic response taking into account lethal and sublethal effects according to Peluso et al. (2016).

2.5.2. Multivariate analysis

In order to evaluate if a correspondence existed between the sectorization of the basin established by Andrade et al. (2012) and the quality of the stream, we made a cluster analysis of the water, the sediment, and the combination of both matrices; taking in count 42, 30, and 72 variables, respectively.

In addition, a multiple-factor analysis (MFA) (Escofier and Pages, 1994) was performed with all the variables corresponding to the two environmental matrices, thus enabling a combined presentation of the observations made and the relationships between the variable groups. The MFA is an extension of the principal-component analysis (PCA) that provides an analysis of the same set of observations by different combinations and types of variables. MFA proceeds in two steps: first, it computes a PCA of each data table (Table 1 itemizes the various groups of variables) and ‘normalizes’ each data table by dividing all its elements by the first singular value obtained from its PCA. Second, all the normalized data tables are aggregated into a grand data table that is analyzed via a (non-normalized) PCA that gives a set of factor scores for the observations and loadings for the variables.

With the same data matrix, a hierarchical-grouping analysis (Q mode) was applied according to Ward's algorithm and the corresponding dendrogram generated (Borcard et al., 2011). All analysis were performed with the R (R Core Team, 2017) software and FactoMineR functions package (Le et al., 2008).

3. Results and discussion

3.1. Water analysis

3.1.1. General physical, chemical and microbiological parameters

In general, in the present study, physical, chemical and microbiological parameters, proved to be within the range of those found in other urban streams of the area with similar characteristics (Salibian, 2006; Feijoó and Lombardo, 2007; Elordi, 2016; Kuczynski, 2016; ACUMAR, 2017; *cf.* Table 2).

In-situ measurements enable a prompt approximation of the physicochemical characteristics of a given system at the sampling time (USGS, 2015). In the study reported here, the pH did not vary greatly along to the stream, but the levels of EC and TDS, increase from SS 5 to mouth (Table 2). The EC and TDS range between the parameters that are most closely related to changes in water quality and input from urbanization-related processes. Kaushal et al. (2005), in a study of urban and suburban surface water bodies in Frostburg, MD, USA, measured chloride concentrations 100 times higher than those normally occurring in rivers and streams of agricultural and forestry sites. Several authors have reported that chloride ions are the major constituents of water that directly affect the EC (Abyaneh et al., 2005; Alhumoud et al., 2010). At all SSs the DO levels were well below the mean values recorded in other streams of the pampean region of Argentina (Feijoó and Lombardo, 2007). In the most of the SSs, the values did not satisfy the guidelines criteria ($5\,\mathrm{mg\,L^{-1}}$) for aquatic biotic protection adopted by the Authority of the Matanza-Riachuelo Basin (Autoridad de Cuenca Matanza Riachuelo: ACUMAR) in Resolution 3/2009 (ACUMAR, 2017). Because this combination of low DO concentrations and high CEs and TDSs is typical of streams that receive wastewater (Mariely et al., 2002), the observed correlation of this pattern with the SSs associated with urban-industrial land uses was within expectations.

In view of the mean values of the nutrients recorded for streams of the pampean region by Feijoó and Lombardo (2007), the Del Gato Stream exhibited a high degree of eutrophication. The nitrite levels – those being linked to bacterial metabolism – were generally higher in the middle and upper subbasins, while the total- and fecal-coliform counts and the BOD_5, were higher in the middle and lower subbasins. Particularly, BOD_5 values were close to the highest permissible level in the ACUMAR guidelines – *i.e.*, $15\,\mathrm{mg\,L^{-1}}$ for passive recreational use of the resource (Resolution 3/2009, ACUMAR, 2017). Mouri et al. (2011) studied the temporal and spatial variations in nutrient concentrations and related parameters in the water of an urban-rural catchment and found – as we have in this present study – higher BOD_5 values in urban areas.

The microbiological quality indicates that fecal contamination was significantly greater in areas of residential use and still remained at high levels below the source of pollution. In several sectors of the riparian zone corresponding to the middle subbasin of the stream, informal urban settlements were present that released sewage directly into the stream (Fig. 1). Moreover, a government report (SPA, 2007) had indicated that clandestine sewer connections existed in the region, which outlets joined the rainfall system and were able to reach the stream in that manner. The presence of pathogenic bacteria in urban surface water bodies around the world and the problems associated with those microorganisms has been well documented (Nwachcuku and Gerba, 2004; Abraham, 2011; Divya and Solomon, 2016).

3.1.2. Metals and metalloids

Table 3 summarizes the concentrations of metals and metalloids in the surface water of the stream. The loss of surface-water quality associated with metal contamination is a global problem related to the advance of urbanization and industrialization (Boran and Altinok, 2010). Klavins et al. (2000) reported average world background concentrations of several of the metals analyzed in the present work. In all instances the levels recorded for the Del Gato Stream were in excess of

Table 2
Results obtained from analysis of general physical, chemical and microbiological parameters of water and sediment samples belonging to Del Gato Stream.

*	Sampling sites									
	1	2	3	4	5	6	7	8	9	10
Water										
pH	7.47	7.53	7.48	7.58	7.81	8.12	8.14	8	8.45	7.8
DO (mg/L)	6.9	3.3	4.1	1.3	1.1	0.8	0.5	5.5	5.5	5.8
Conductivity ($\mu S\,cm^{-1}$)	1374	1309	1284	1210	1447	1089	1066	1063	772	1084
TDS ($mg\,L^{-1}$)	915	857	852	809	963	713	665	709	507	692
Alkalinity ($mg\,CaCO_3\,L^{-1}$)	577	491	555	534	534	619	534	427	438	535
Chloride ($mg\,L^{-1}$)	109	156	81	81	107	37	42	67	17	105
Sulfate ($mg\,L^{-1}$)	78.5	67.8	64.8	60.8	89.9	28.1	21.6	6.84	3.04	25.1
Phosphorus ($mg\,L^{-1}$)	1.03	1.78	1.76	2.09	1.37	1.94	1.56	1.30	0.88	1.38
Nitrates ($mg\,L^{-1}$)	9	21	13	10	8	11	18	20	19	15
Nitrites ($mg\,L^{-1}$)	0.032	0.052	0.043	0.052	0.044	1.780	1.690	1.670	0.055	1.670
Ammonium ($mg\,L^{-1}$)	18.93	10.18	26.41	11.46	18.90	11.06	12.34	14.06	< DL	0.49
BOD_5 ($mg\,L^{-1}$)	10	17	16	13	7	18	11	11	3	4
COD ($mg\,L^{-1}$)	83	45	50	34	59	10	53	34	83	47
Na ($mg\,L^{-1}$)	238	224	126	186	254	183	216	184	131	195
K ($\mu g\,L^{-1}$)	10.5	10.8	11.8	9.8	10.8	8.7	6.7	9.7	9.8	7.2
Ca ($\mu g\,L^{-1}$)	41.6	32.6	35.4	31.8	29.7	25.1	30.0	25.1	23.4	31.1
Mg ($\mu g\,L^{-1}$)	13.3	11.7	12.1	10.9	12.0	8.2	10.7	7.6	5.9	9.5
Total coliforms (MPN/100 ml)	$3E^{+06}$	$1.6E^{+06}$	$3E^{+06}$	$9E^{+06}$	$3E^{+06}$	$5E^{+06}$	$1.1E^{+06}$	$8E^{+05}$	$3E^{+05}$	$1.70E^{+03}$
Fecal coliforms (MPN/100 ml)	$1.3E^{+05}$	$2.4E^{+05}$	$1.6E^{+06}$	$3.5E^{+05}$	$5E^{+05}$	$5E^{+05}$	$5E^{+04}$	$2.8E^{+05}$	$1.1E^{+03}$	$3E^{+01}$
Sediment										
LOI (%)	16.8	11.4	62.1	3.5	61.8	10.5	NM	4.1	3.9	13.2
Sulphures ($mg\,kg^{-1}$)	216.8	214.7	109.6	456.8	351.2	22.4	444.0	136.3	174.4	219.2
Nitrates ($mg\,kg^{-1}$)	1.1	0.1	0.6	3.8	40.8	2.5	22.5	33.9	21.3	31.8
Phosphorus ($mg\,kg^{-1}$)	89.4	69.0	84.7	19.2	84.4	16.1	6.9	21.4	14.1	20.4
Sand (%)	70.7	63.7	56.8	70.9	87.5	50.5	91.1	56.9	70.2	45.9
Silt (%)	20.6	29.3	35.1	21.2	5.9	31.3	1.80	35.2	22.0	41.0
Clay (%)	8.7	6.9	8.0	7.8	6.5	18.2	7.1	7.8	7.7	13.0
Sediment class	Sandy loam	Sandy loam	Sandy loam	Sandy loam	Sandy	Loam	Sandy	Sandy loam	Sandy loam	Loam

* In this column the measured parameter (units). Meaning of abbreviations: DO (Dissolved oxygen); TDS (Total dissolved solids); BOD (Biochemical Oxygen Demand); COD (Chemical Oxygen Demand); LOI (Organic Matter by Loss on Ignition); MPN (most probable number); < DL: Concentration below of the detection limit.

those values, which finding could be interpreted as indicating that a part of that increment was the result of anthropic input.

The use of guideline levels as an indicator for assessing water quality is a strategy adopted throughout the world (Islam et al., 2015). We observed that, in general, the Cu, Pb, and Mn values were above the guideline levels for the protection of aquatic biota indicated in Argentina by Law N° 24.051 (National Decree 831/93: www.ambiente.gob.ar/), evidencing that the problem associated with the metals cited here is more general. The Zn, Ag and Cr exceeded the guideline levels only in some SSs, showing a more local impact. High concentrations of heavy metals in the surface water from urban rivers within the Buenos-Aires area have also been reported by Topalián et al. (1999) for the Reconquista River and ACUMAR (2017) for the Matanza-Riachuelo River, which waterways are among the most contaminated surface water bodies of Latin America.

3.1.3. Pesticides

The pesticide analysis did not indicate a relevant contribution to the deterioration of stream-water quality. Among all the water samples analyzed, we obtained quantifiable values for some of the pesticides monitored at only SS 1, where 57 $\mu g\,L^{-1}$ of heptachlor, 125 $\mu g\,L^{-1}$ of endosulfan I, and 79 $\mu g\,L^{-1}$ of endosulfan II were measured. Previous studies have demonstrated a low frequency of detection of this type of contaminant within that particular environmental matrix (Papadakis et al., 2015). Similarly, Ronco et al. (2008) and Demetrio (2012) had

Table 3
Results obtained from analysis of metals and metalloids ($\mu g\,L^{-1}$) in water samples of Del Gato stream. *Guideline levels of Environmental Agency of Argentina for protection of aquatic biota (Law N° 24.051 National Decree 831/93 – http://ambiente.gob.ar/). The values in bold indicate that they exceed the guide value adopted.

Metals and metalloids ($\mu g\,L^{-1}$)																
Sampling sites	Ag	As	B	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	V	Zn	Se
1	< DL	< QL	123.1	84.2	< DL	< DL	< QL	**3.42**	686.5	< DL	**183.6**	< QL	< DL	< DL	15.56	< QL	< QL
2	< DL	< QL	126.6	81.5	< DL	< DL	< QL	< QL	76.1	< DL	**105.6**	< QL	< DL	< DL	18.18	< QL	< QL
3	< DL	< QL	121.0	100.2	< DL	< QL	< QL	< QL	799.5	< DL	**138.4**	< QL	< DL	**4.02**	29.92	**57.55**	< QL
4	< DL	< QL	128.1	83.8	< DL	< DL	< QL	< QL	52.6	< DL	60.5	2.36	< DL	< DL	29.87	< QL	< QL
5	< DL	20.6	131.1	92.1	< DL	< QL	< QL	**7.05**	332.0	< DL	**110.5**	< QL	< DL	**5.95**	36.95	**94.15**	< QL
6	< DL	< QL	115.7	85.1	< DL	< DL	< QL	< QL	14.2	< DL	62.4	6.01	< DL	< DL	39.71	< QL	< QL
7	0.181	19.5	167.0	88.0	< DL	0.673	< QL	**4.10**	163.0	< DL	88.9	8.20	1.85	**3.21**	56.30	23.3	< QL
8	< DL	18.8	103.9	62.9	< DL	< QL	0.82	**2.48**	117.1	< DL	**133.8**	9.82	< DL	< DL	38.17	< QL	< QL
9	< DL	< QL	102.4	78.6	< DL	< QL	**2.72**	**5.00**	433.9	< DL	**168.3**	6.05	< QL	**9.72**	27.78	< QL	< QL
10	< QL	21.50	81.7	46.3	< DL	ND	< QL	**2.72**	27.1	< DL	9.6	30.52	ND	ND	63.95	ND	< QL
Guideline*	0.1	50	750		0.2		2	2		0.1	100		25	1	100	30	

< QL: Concentration below of the quantification limit.
< DL: Concentration below of the detection limit.

also obtained low frequencies of detectable levels of chlorpyrifos, endosulfan, cypermethrin, and glyphosate in other streams of La Plata (Argentina) within areas of substantial agricultural influence.

3.1.4. Toxicity

The ecotoxicological evaluation of water, insures the establishment of the existing water quality regardless of the type and concentration of contaminants present in a given sample. Moreover, that type of analysis reflects – at once – additive, synergistic, and antagonistic relationships among the pollutants – aspects related to the bioavailability of the compounds – and provides criteria that are more relevant to the protection of the biota. Other authors have also employed ecotoxicological tools to provide evidence for evaluating the quality of surface water or of complex urban effluents and in that manner have obtained satisfactory results (Becouze-Lareure et al., 2012; De Melo Gurgel et al., 2016). In the present study, we used a battery of ecotoxicological tests in order to expand the range of toxicity monitoring and complement the methods described thus far. The toxicity tests do not reflect a common patter along the watercourse. *H. attenuata* was the most sensitive organism, showing mortalities of 100% in most of the SSs. While, *L. sativa* proved to be the least sensitive bioassay with inhibition of radicle elongation below to 35%. The higher toxicity to *D. magna* was recorded in the upper subbasin where the average mortality was 64 ± 13.6% (mean ± standard error). While to *C. decemmaculatus*, the samples from middle subbasin induced the higher mortalities (60 ± 8.6%).

3.1.5. Quality indices

Scientific investigators and environmental authorities, advocate to environment diagnostic methodologies that are easily applicable and do not require excessive effort, financial resources, or expertise. Thus, the use of water-quality indices is quite extensive since those data simply reflect the general quality of surface waters (Kocer and Sevgili, 2014). In the work reported here, we used the water-quality index WQI developed by the National Sanitation Foundation of the United States in 1970 for our evaluations. This index revealed that the upper subbasin and the stream's mouth have the best water quality in the stream; although, according to the WQI criteria, those sectors should nevertheless be classified as “bad”. The rest of the sectors presented either “bad” or “very bad” quality, but in the former areas the values registered were still close to the lower limit (Fig. 2a). The categorization established by these criteria did not provide a sufficient sensitivity for a clear separation of the quality of the different SSs associated with the various types of land use. In addition, the absence of ecotoxicological variables and of certain specific analysis associated with industrial activity (for example, the presence of metals) suggested that this index did not fully detect the degree and types of contamination generally present in the streams of the Buenos-Aires metropolitan area (Elordi, 2016).

The results obtained from the ecotoxicological tests were combined to generate the EDAR index (Fig. 2b). According to the nominal categorization criteria of this index, from SS 6 to the mouth of the stream, all the SSs were classified as “hazardous”, whereas the rest of the SSs were considered “slightly hazardous”, except for SS 9 indicated as “nonhazardous”. If the numeric value of the index obtained at each SS is considered independently of the nominal categorization criteria, the water ecotoxicological quality of the Del Gato Stream in general is indicated as declining approximately from the middle of the course to the mouth. When the EDAR index was used previously in natural waters, satisfactory results were obtained (Ronco et al., 2005; Manusadžianas et al., 2010). If the protection of aquatic biota is taken as a criterion for the use of a resource, this index constitutes one of the most useful tools among those evaluated so far; though the constituent data do not, however, provide information related to specific pollutants.

3.2. Bottom-sediment analysis

3.2.1. General physical and chemical parameters

The sediments of the Del Gato Stream are mainly of the sandy-loam type (Table 2). The levels of organic matter and phosphorus were higher in the middle and lower subbasin, sulfides in the middle subbasin, and nitrates in middle and upper subbasins. These variables play a key role in the dynamics of pollutants within this matrix (Eggleton and Thomas, 2004; Rendina and Iorio, 2012) and reflect a direct relationship to land use as a potential source of contamination of organic origin (Di Marzio et al., 2005). As mentioned above, several sectors of the middle subbasin evidenced sewage pollution associated with informal urban settlements, which relationship would necessarily point to that housing situation as being an anthropic source of organic loading into the stream system. In general, the values found in the Del Gato Stream for organic matter and sulfides are in the order of the levels recorded in other rivers and streams of the greater-Buenos-Aires region (Ronco et al., 2008; Peluso et al., 2013a), although in the middle subbasin higher values of organic matter were measured.

3.2.2. Metals, metalloids and major elements

In general, we found a higher frequency of metals and metalloids above the limit of quantification in the sediment samples as opposed to those observed in surface water (Table 4). This difference likely occurred because the sediments are the final destination of most of the pollutants, and metals in particular form complexes with several components of that matrix (Ogunfowokan et al., 2013).

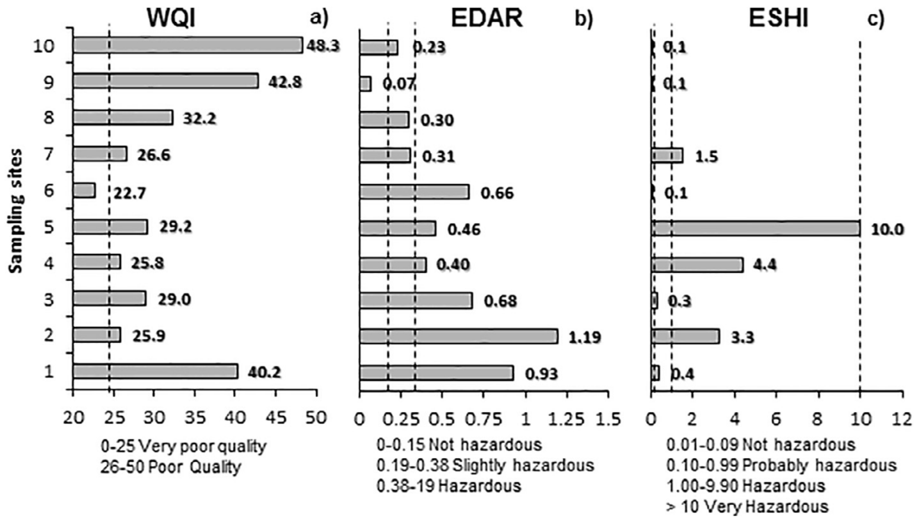

Fig. 2. Environmental quality of the Del Gato Stream for each sampling site expressed according the following indices: Panel a: Water-quality index (WQI) developed by the National Sanitation Foundation of the United States in 1970. Panel b: -dilution-effect-average-ratio (EDAR) index. Panel c: Ecotoxicological–Sediment-Hazard Index (ESH). In each panel the quality categories obtained are indicated on the basis of the classification criteria proposed by the authors. The broken vertical lines mark the threshold values for the different criteria denoted in each panel.

Table 4
Results obtained from analysis of metals and metalloids (mg kg^{-1}) in sediment samples of Del Gato stream. *[1] Guideline level: Interim sediment quality guideline (ISQG).*[2] Guideline level: Probable effect level (PEL) (Environment Canada – CCEM, 2002).

Sampling sites	Metals and metalloids (mg kg^{-1} dry weight)																
	Ag	Al	As	B	Ba	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	V	Zn	Se
1	2.7	8100	< QL	< DL	292	2.05[a]	2.3	25.2	14.8	8100	2.1[b]	143.2	1.6	4.3	146.1	22.8	93.9	< QL
2	1.9	7600	< QL	< DL	260	< DL	2.2	16.1	13.6	7600	1.2[b]	96.6	1.8	< QL	75.8[a]	24.9	76.7	< QL
3	2.4	8376	< QL	< DL	305	1.05[a]	2.3	15.8	12.5	8376	1.2[b]	149.0	1.2	< QL	99.8[b]	22.5	79.5	< QL
4	< DL	6544	< QL	< DL	242	< DL	2.1	10.0	13.6	6544	0.8[b]	135.0	1.0	< QL	71.1[a]	17.3	99.7	0.9
5	< DL	4165	< QL	< DL	99	< DL	1.6	5.2	27.0	4165	0.4[a]	152.0	< QL	< QL	23.2	12.7	144.7[a]	1.0
6	< DL	6704	< QL	< DL	142	< DL	2.5	6.4	4.6	6704	< QL	103.9	< QL	< QL	24.6	11.3	15.3	< QL
7	< DL	3364	< QL	< DL	30	0.91[a]	0.9	3.6	11.4	3364	0.3[a]	64.3	< QL	< QL	27.2	5.3	135.1[a]	0.8
8	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
9	< DL	6402	< QL	< DL	155	< DL	3.1	6.2	6.0	6402	< QL	258.0	< QL	< QL	27.9	15.6	24.9	0.8
10	< DL	6654	< QL	< DL	164	< DL	3.3	10.3	13.7	6654	0.6[b]	72.0	8.0	< QL	45.2[b]	47.1	37.1	< QL
*[1]ISQG						0.6		37.3	35.7		0.17				35		123	
*[2]PEL						3.5		90	197		0.48				91.3		315	

< QL: Concentration below of the quantification limit.
< DL: Concentration below of the detection limit.
NM: Sample not measured by operative problems.
[a] Indicate values that exceed the guideline ISQG.
[b] Indicate values that exceed both ISQG and PEL guideline.

With the aim at using guidelines as a quality reference for sediments in view of the lack of such criteria for freshwater sediments in Argentina, we considered the Canadian sediment quality guidelines, the interim sediment-quality guideline (ISQG) and the probable effect level (PEL) (CCEM, 2002). By this means, the Hg, Zn, Pb and Cd, exceeded at least one of the adopted guidelines (Table 4).

The enrichment factor is considered an effective means of evaluating the magnitude of contamination by metals in the environment (Franco-Uria et al., 2009). Previous studies have reported high levels of enrichment in rivers and streams with urban-industrial influences (Amano et al., 2011; Islam et al., 2015). In this study, we also detected the highest levels of enrichment in the middle subbasins, where this land use predominate. The highest levels of enrichment were recorded for Cd and Pb, with the latter being the metal of the greatest anthropic contribution whose values were considered significant in the middle and upper subbasins and very high in the lower subbasin, according to the classification proposed by Sutherland (2000) (Table 5). In the Buenos-Aires region, where the metals were studied at the mouths of rivers with industrial surroundings, enrichments in Pb, Zn, and Cu had been found previously (Peluso et al., 2013b); but those enrichment factors were lower than the ones obtained in the present study for the middle subbasin of the Del Gato Stream. In the urban river in Bangladesh that Islam et al. (2015) studied, a similar pattern of heavy-metal contamination was present, where the metal concentrations – mainly of Cr, Cu, and Pb – increased from the sources to the mouth, in agreement with the gradient we observed in this work.

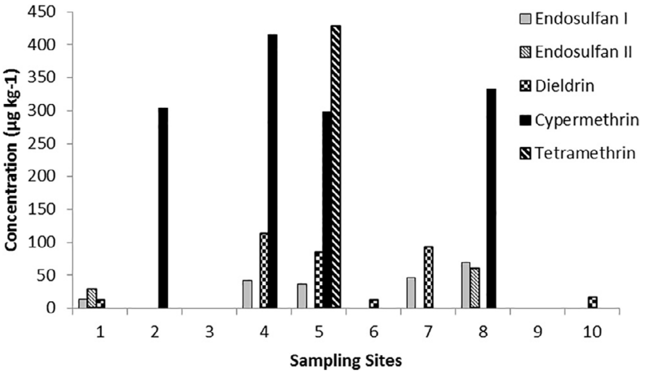

Fig. 3. Concentrations pesticides in bottom sediments of the Del Gato Stream. Only the pesticides that were detected in at least one sampling site are presented.

3.2.3. Pesticides

Among the pesticides investigated, measurable concentrations of only endosulfan (I and II), dieldrin, cypermethrin, and tetramethrin were recorded. At none of the sites is a clear trend apparent in the distribution of pesticides in the sediments measured along the stream (Fig. 3). The pyrethroids seem to be the major contributors to the deterioration of sediments quality due its high concentration and frequency of detection. We associate these levels with domestic use, as those compounds are found mainly at the sites associated with urban

Table 5
Enrichment of metals in sediment samples of Del Gato stream. Values correspond to Enrichment Factor calculated according Rubio et al. (2000). Sampling sites were classified in followed six categories are recognized: [a] < 1 background concentration, [b] 1–2 depletion to minimal enrichment, [c] 2–5 moderate enrichment, [d] 5–20 significant enrichment, [e] 20–40 very high enrichment and [f] > 40 extremely high enrichment (Sutherland, 2000).

Sampling sites	Ba	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	V	Zn
1	0.23[a]	9.37[d]	1.00[b]	3.20[c]	2.61[c]	1.58[b]	0.24[a]	0.94[a]	32.2[e]	1.68[b]	5.85[c]
2	0.22[a]	–	1.05[b]	2.17[c]	2.55[c]	0.76[a]	0.24[a]	–	17.8[d]	1.96[b]	5.09[c]
3	0.23[a]	4.64[c]	0.99[a]	1.94[b]	2.12[c]	1.06[b]	0.28[a]	–	21.2[e]	1.60[b]	4.79[c]
4	0.24[a]	–	1.15[b]	1.57[b]	2.96[c]	1.23[b]	0.16[a]	–	19.4[d]	1.58[b]	7.69[d]
5	0.15[a]	–	1.40[b]	1.30[b]	9.26[d]	2.18[c]	0.18[a]	–	9.94[d]	1.82[b]	17.5[b]
6	0.13[a]	–	1.31[b]	0.98[a]	0.97[a]	0.92[a]	–	–	6.55[d]	1.00[b]	1.15[b]
7	0.05[a]	10.0[d]	0.92[a]	1.09[b]	4.82[c]	1.14[b]	–	–	14.4[d]	0.94[a]	20.2[e]
8	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
9	0.15[a]	–	1.73[b]	1.33[b]	1.33[b]	2.41[c]	–	–	7.78[d]	1.45[b]	1.96[b]
10	0.16[a]	–	1.78[b]	2.94[c]	2.94[c]	0.64[a]	1.43[b]	–	12.1[d]	4.23[c]	2.81[c]

NM: Sample not measured by operative problems.

land use (Ding et al., 2010; Weston and Lydy, 2010). Among the organochlorines, endosulfan I and dieldrin were the most frequently registered, but the recorded concentrations were lower than pyrethroids.

3.2.4. Toxicity

The ecotoxicological evaluation of this matrix was made through the use of the amphipod crustacean *H. curvispina* as a diagnostic organism. The sediments of the middle subbasin exhibited the worst water quality in the stream, with mortalities greater than 90% at the most of the SSs, although we were able to evaluate the sublethal effects at only SS 6, where the growth inhibition reached 33.8%. Conversely, the lower and upper subbasins evidenced lethality at only SS 2 (98% mortality) and SS 8 (100% mortality). The remaining SSs did not exhibit significant mortalities, while the sublethal effects averaged 57.3 ± 4.6% of growth inhibition.

3.2.5. Quality index

The variables of this environmental matrix analyzed in the preceding sections were combined in the ecotoxicological–sediment–hazard index (ESHI). Fig. 2c illustrates that the best sediment quality was found in the upper sectors of the stream (SS 10 through SS 6). The sediments having the worst quality were those starting at SS 5, from which point on a pattern of general decrease in the quality of the sediments occurred in the direction of the mouth. Site S 3, however, did not follow that trend, rather, that site registered sediments of good quality, which difference might be reflecting certain of its particular characteristics. For example, SS 3 was the only site within the SSs of the middle and lower subbasin that did not exhibit quantifiable levels of pyrethroids, and those pesticides are highly toxic to the organisms evaluated here. Although Hg, Cd, and Pb were found at that site, the organic matter content was very high, which feature could reduce the availability of these pollutants (Peluso et al., 2013c).

3.3. Multifactorial analysis as a diagnostic tool for the environmental quality

The use of cluster analysis in studies on the quality of water bodies is a widespread modality for the differential classification of sampling sites (Zhang et al., 2010; Arslan, 2013; Azhar et al., 2015). In the study reported here, we used multifactorial analysis to identify if the sectorization of the basin according to land use established by Andrade et al. (2012) corresponded to the quality of the water body.

When only the variables associated with the water *per se* were considered, the groups generated by the analysis did not match the distinction of land uses proposed by those authors since the various SSs of the upper subbasin simply segregated together, but did so in a heterogeneous way upon the incorporation of SS 7 from the middle subbasin (Fig. 4a).

With respect to the sediment, the grouping obtained was much more consistent with that made *a priori* since 3 groups were observed that represented the low, middle, and upper subbasins. We wish to emphasize that although SS 8 was located along with the SSs corresponding to the middle subbasin, owing to certain technical problems, the metals and metalloids at this spot could not be measured in the sediments so that those variables could not be included in the analysis; which omission, in our opinion, must have influenced the final distribution. Nevertheless, SS 6 manifested features similar to those of the upper subbasin (Fig. 4b).

When the variables were analyzed for both matrices together, the substantial consistency observed in the sediment analysis became distorted. In this analysis, the SSs corresponding to only the upper subbasin segregated together; moreover, although the SSs corresponding to the lower subbasin were likewise still grouped together, that cluster was now more heterogeneous (Fig. 4c).

Previous studies have suggested that sediments act as indicators – or a form of ecologic memory – of local pollutant inputs, indicating that this matrix can be used to locate point sources of contaminants that, after discharge into surface waters, do not remain in solution but are instead quickly adsorbed by the particles, thus escaping detection by water monitoring (Westrich and Förstner, 2005). Therefore, we can hypothesize that the most consistent grouping among the SSs observed when only the variables corresponding to the sediments were analyzed, could be explained by a rapid sorption of such pollutants to particulate material and a subsequent sedimentation. A further consideration is that, in the water, mixing is favored because of the dynamic of movement characteristic of that matrix. In general, in all the cluster analysis, the SSs corresponding to the upper subbasin grouped together more consistently, which result could be related to the sole influence of rural land use on those SSs; whereas the SSs of the middle and lower subbasins received the impact of the further forms of land use characteristic of each of the two sectors in addition to those developed upstream. In contrast, the middle subbasin in all the analysis exhibited less consistency in the grouping of the SSs, which pattern could be attributed to the wide variety of pollutants generated in a sector with both urban and industrial land use (Islam et al., 2015; ACUMAR, 2017; Kuczynski, 2016). Similarly, Volaufova and Langhammer (2007) studied the water and sediment quality associated with organic substances and heavy metals in the Klabava-River basin of the Czech Republic and reported that the sectors of lower quality were associated with urban and industrial land use.

PCA is widely used in water-quality studies where a large number of variables are involved (Ouyang, 2005; Zhang et al., 2010; Fahmi et al., 2011). In general, that form of analysis is used to reduce the number of variables and emphasize those of the greatest influence on the distribution of sampling sites. As mentioned above, MFA is an extension of the PCA that allows the analysis of the same set of observations by different groups and types of variables. Although we did not find studies on water quality that have used this tool, we believe that this methodology provides extremely relevant and pertinent information since the MFA produces global conclusions in such complex systems as those studied here.

The MFA was accordingly performed on the basis of the sets of parameters within each matrix, as described in Materials and Methods (Fig. 5, Figs. S1 and S2). We need to mention that although in this analysis the grouping of variables is associated with a certain degree of subjectivity; we did organize the structure upon consideration of the different classes of contaminants that could exist in the basin.

This analysis enabled the generation of a consensus plane of SSs in order to associate those locations with gradients of environmental relevance that explained 42.9% of the variability (Fig. 5). Thus, in general terms and on the basis of only the parameters that are frequently used to monitor the quality of water bodies, we can identify a gradient of increasing environmental quality that can be projected from quadrants 1 through 3 of the consensus plane. On the basis of the SS distribution within this plane, the upper subbasin manifested the best environmental quality, but no major differences existed in the environmental qualities of the middle and lower subbasins (Fig. 5). Axis 1 (24.8%) comprised contributions of mainly the general *in-situ* and microbiologic parameters measured in water, as well as the nutrients (*i.e.*, nitrogen species and phosphorus) in both matrices. These parameters, commonly measured in water quality monitoring, are those that allowed a good separation of each subbasin. Due to these variables are associated to the contribution of organic matter, we can hypothesize that the informal settlements found mainly in the middle subbasin, are playing an important role in the input of organic matter to the system. The lower subbasin was the sector that evidenced the worst quality when the microbiologic contamination of the stream and the nutrient concentration in the water were considered (Fig. 5). These higher levels could be consequence of discharges that are added in this sector. Since this stream discharges into the Río de la Plata estuary, the quality of the lower subbasin is the relevant portion of the Del Gato in determining the impact on the river as the recipient of the stream's effluence.

The general sediment parameters and the ecotoxicity of both matrices were the elements that most contributed to the axis 2 (18.07%). Taking into account that: the ecotoxicology allow to assessing the environment quality in a more integral way, and if protection of the biota

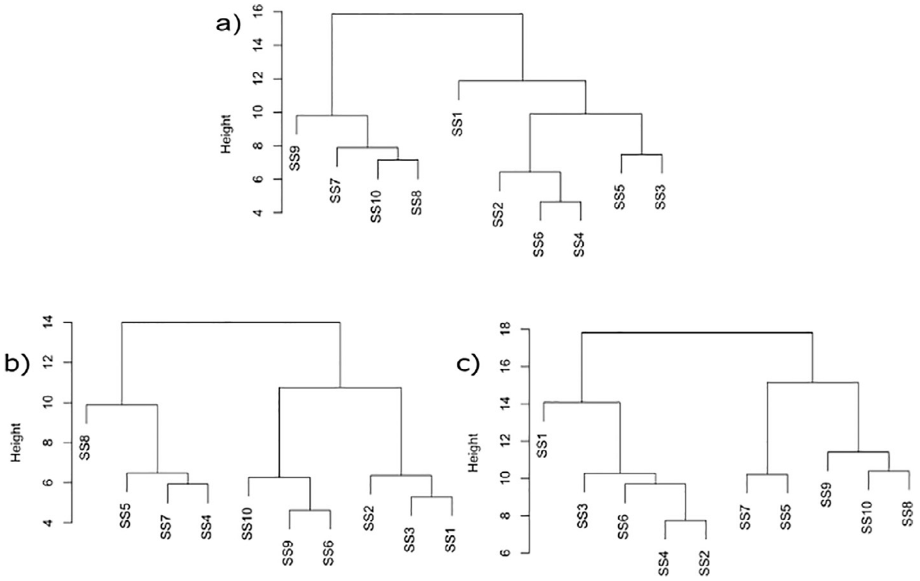

Fig. 4. Dendrograms demonstrating the similarities of sampling sites (SS) distinguished by cluster analysis on the basis of (Panel a) water parameters, (Panel b) sediment parameters, and (Panel c) both sets of parameters.

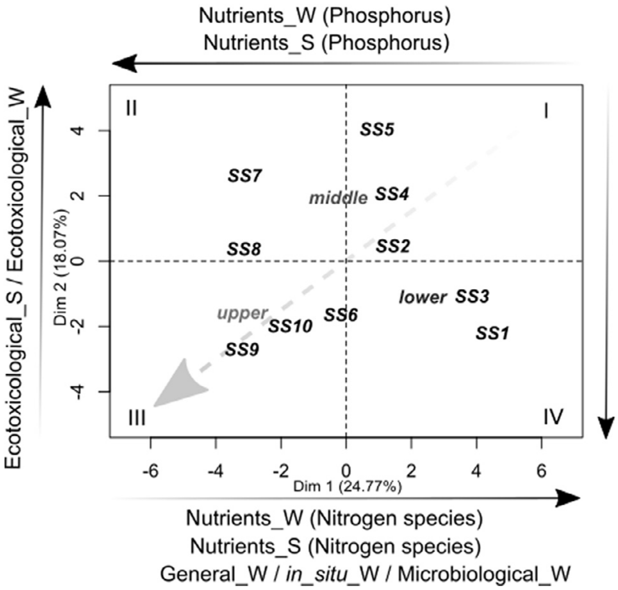

Fig. 5. Multiple-factor analysis (MFA) performed to ascertain the relationship among the sampling sites (SS) in terms of the variable groups established *a priori*. The consensus plane generated by the two principal dimensions and relative distribution of the SSs and the mean values. The arrows on the axes indicate the direction of change of the variables that contribute the most within this component. The arrow in the center of the figure denotes the general gradient of quality improvement in the Del Gato Stream.

is taken as major criterion of environmental quality, then the middle subbasin exhibited the worst quality. Due the diagnostic organisms used in this study are particularly sensitive to pesticides and metals, we believe that the greater toxicity of the samples from the middle subbasin, could be associated with the higher levels of these pollutants recorded in this sector.

4. Conclusions

On the basis of the general behavior of the pollutants in the environment, we observed that in the water of the Del Gato Stream those contaminants appeared in gradients along the stream, whereas in the sediment the compounds were distributed more according to the sector of the stream. This pattern probably obtained because the sediments have a longer residence time in a body of water so that the pollutants accumulate within that matrix (Taylor and Owens, 2009) and in so doing reflect the impact of those contaminants from previous sources.

The different ecotoxicological tools used to ascertain the general environmental quality of this water body indicated a significant deterioration throughout the stream. In particular the sector most highly impacted was the middle subbasin, where the urban-industrial land use predominates.

In view of the complexity of the system under investigation and the great diversity of the variables analyzed, the MFA proved to be the most effective means of evaluating the environmental quality of the Del Gato.

The study reported here provides relevant information on the environmental quality of a stream representative of a region where ecological information is scarce. Moreover, the multidisciplinary evaluation used in this work constitutes an all-inclusive strategy that can provide essential information for decision making on which methods to use in studies on the environmental quality of streams associated with mixed uses of the surrounding land.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ecolind.2018.01.063.

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