Water quality analysis based on phytoplankton and metal indices: A case study in the Sauce Grande River Basin (Argentina)

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Abstract

This study presents the first integrated water quality assessment of the Sauce Grande River Basin. This South American freshwater environment contains two water bodies that interrupt its course before the river discharges into the ocean: a dam for water supply and a shallow lake. We analyzed the spatial distribution of the phytoplankton community, the physicochemical parameters, and the metal concentrations in the particulate fraction. According to the trophic indices and the phytoplankton abundance, composition and diversity, the water quality showed significant deterioration in the lower basin after the Sauce Grande lake. The conductivity, turbidity and most metal concentrations increased towards the downstream area, even exceeding recommended levels for some metals. This study generates a database for the water quality of the Sauce Grande River Basin and its contribution to the sea. It shows an example of how the water quality varies along a basin that crosses different topographic environments and land covers.

Introduction

Watersheds are systems where natural factors, such as climate, geomorphology, soil, water, and fauna, interact with anthropogenic productive developments. The different land uses, irrigation, and water supply for human consumption tend to deteriorate the landscape and land cover organization and water quality. Population growth near the rivers enhances the impact of pollutants in the streams, from domestic activities, industries, effluent discharges, agricultural chemicals and eroded soils (Kazi et al. 2009; Yadav and Pandey 2017). Moreover, dam flow regulation is a significant cause of disturbance of the hydrological regimen of the river and has direct ecological consequences (Petts 2018).

Evaluation of the health of an aquatic ecosystem is complex because pollution is diffuse due to numerous contamination sources. It has been based mainly on biological quality elements such as phytoplankton, which stands out as a useful biomarker of environmental conditions, trophic status, and water quality within rivers and lakes (Katsiapi et al. 2011, Nöges and Tuvikene 2012, O'Farrell et al. 2002, Padisák *et al.* 2006). Most studies have shown that the phytoplankton structure and distribution in aquatic environments are driven by the combination of and interactions between physical, chemical, and biological factors (Duong et al. 2019, Li et al. 2016). Moreover, as these environments are commonly used for disposal and dilution of terrestrial wastes (Spencer et al. 2006), metal contamination of the surface water is also a serious ecological problem deteriorating the watersheds. The metals are possibly potentially toxic to the water system and bio-accumulation through the food chain (Papagiannis et al. 2004, Velusamy et al. 2014). Therefore, metal contamination might be used as an additional physicochemical indicator of water quality.

In the last twenty years, extreme climatic events in the southwest of Buenos Aires province, Argentina, caused water crises due to both deficit and excess of water, which greatly affected the population and agribusiness throughout the basin (Casado 2013). Consequently, the Sauce Grande River Basin located in central-eastern Argentina has achieved increasing regional importance, and the absence of integrated

studies to assess the river water quality became evident. To our knowledge, there are no studies based on the analysis of the phytoplankton and metal concentrations, evaluating the water quality of the entire basin, including the area where the river discharges into the Atlantic Ocean. There are only isolated studies of the Sauce Grande shallow lake (Cony *et al.* 2016), the Paso de las Piedras Dam (Fernandez 2010), and in the middle basin of the Sauce Grande river (Rosso *et al.* 2011).

We analyzed physicochemical parameters and biotic data with a spatial perspective on the characteristics along a 187 km stretch of the river in the Sauce Grande River Basin. The objectives of this study were to assess the water quality status of the Sauce Grande River Basin by evaluating the trophic conditions and physicochemical water parameters, the abundance and diversity of phytoplankton, and the metal concentrations (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) in the particulate fraction.

Materials And Methods

Study area

The Sauce Grande River Basin is located in the south of Buenos Aires province (Argentina). It has a total area of 4856 km² (Brendel *et al.* 2019) (Fig. 1a) and is 200 km long (Casado 2013) to the mouth in the Atlantic Ocean. It is the most important of all the rivers originating in the Ventania System, a 30 km wide mountain chain surrounded by plains that are locally known as the pampas, and which has a length of 180 km with a W–NW trend (Ramos *et al.* 2014). The plains are the most productive subareas and are highly appropriate for agricultural activities. The basin is divided into three sectors (Fig. 1b): the upper basin extends from its source in the hills to the Paso de las Piedras dam; the middle basin includes the dam and extends down to the Las Oscuras stream; and the lower basin, the most extensive one, extends downstream until it reaches the Atlantic Ocean, close to a tourist town, Monte Hermoso. Since 1978, the Paso de la Piedras dam has taken up the middle river section and it constitutes the primary source of drinking water supply for Bahía Blanca and Punta Alta cities and the nearby industrial complex. It has a surface area of 36 km² and a maximum depth of 25 m (Schefer 2004). There is one more disruption before reaching the sea: the Sauce Grande shallow lake, a natural water body with a surface area of 18.5 km² and an average depth of 1.6 m, with highly touristic development (Cony *et al.* 2014).

The basin is divided into three subareas according to their geomorphologic characteristics, hills, plains, and dunes (Fig. 1c). The regional climate is semiarid, with a mean annual precipitation of 705 mm (Brendel *et al.* 2019). The yearly mean temperature oscillates between 14°C and 20°C (Aliaga *et al.* 2017). The primary land use in the basin is rainfed agriculture with crop rotation and livestock grazing. The most extensive winter crop is wheat, followed by barley and oats. A land cover map modified from Brendel *et al.* (2019) is shown in Fig. 1d. For details of how it was created, see Brendel *et al.* (2019).

Sample collection and physicochemical analysis

Sampling was carried out in November 2017 at 13 sampling sites along the Sauce Grande River Basin (Fig. 1b). The samples were collected manually from within the river when possible or from the shoreline.

The water depth was measured with a metal ruler. Physicochemical variables of the water column, such as conductivity, pH, temperature, and dissolved oxygen (DO), were measured *in situ* at each sampling site with a multi-parameter HORIBA U-10. Water samples (1000 ml bottle) were taken for Chlorophyll *a* and for suspended particulate matter (seston) analysis. The Chlorophyll *a* concentration (Chl *a*) was estimated from water samples filtered through glass-fiber filters (GF/F Whatman TM); the filters were stored in aluminium foil at -20° C; Chl *a* was extracted using 90% acetone in darkness, and overnight storage at 4° C; then the extracts were cleared by centrifugation at 3,000 rpm for 3 min and the concentrations were estimated by the spectrophotometric method (Marker et al., 1980). Seston was determined by the gravimetric method with precombusted Whatman TM GF/F filters. Organic matter content in the sediment (OM) was obtained by calcination in a muffle furnace at 550 °C. Carlson's trophic state index using Chl *a* (TSI chl *a*) (Carlson 1977) was estimated according to the following equation:

$$TSI (Chl\ a) = 10(2.46 + \ln Chl\ a \times \ln 2.5) \quad (1)$$

Carlson's Index has the advantage of presenting the trophic state on a continuous numeric scale (Oligotrophic: TSI < 40, mesotrophic: 40 ≤ TSI < 50, eutrophic: 50 ≤ TSI < 70, hypereutrophic: 70 ≤ TSI).

Metal determinations in the particulate fraction

Water samples were collected at each sampling site using polyethylene-terephthalate (PET) bottles pre-cleaned with acid. S10 could not be sampled due to failure in the sampling equipment. Before water collection, the bottles were rinsed three times with river water and were then filled by moving them upwards through the water column, from a typical initial depth of 20–50 cm. The samples were then transported to the laboratory in refrigerated boxes and immediately filtered through the pre-weighed cellulose acetate filters (Millipore HNWP04700, 47 mm diameter and 0.45 µm pore size) in duplicate. The suspended particulate matter fraction retained in the filters was dried at room temperature until constant weight, weighed in an analytical balance (OHAUS, Adventurer), and stored in dry conditions.

For the particulate metal analyses (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn), the filters were subjected to acid digestion following La Colla et al. (2015). The protocol includes an acid pre-digestion with 5.0 ml of HNO₃ (65% Merck, Darmstadt, Germany) for at least three h. Then, 1.0 ml of HClO₄ was added, and the samples were put into a glycerin bath at 110 ± 10°C for at least 72 h. The acidic extracts were transferred to centrifuge tubes and made up to 10 ml using 0.70% HNO₃. Metals were determined using a Perkin-Elmer Optima 2100 DV inductively coupled plasma-optical emission spectrometer (ICP OES).

For metal analyses, all glassware material and cellulose acetate filters used in the laboratory were cleaned according to APHA (2005). The potential presence of metals in chemicals used for digestion was determined; thus, blanks were used simultaneously in each batch of analysis to authenticate the analytical quality. All analyses were performed in duplicate, and the uncertainty based on one relative standard deviation of replicates was < 15%. The analytical method detection limit (MDL) for each particulate metal (µg g⁻¹) was 0.99 for Cd; 2.2 for Cr; 3.5 for Cu; 12 for Fe; 2.9 for Mn; 6.7 for Ni; 9.3 for

Pb; 4.0 for Zn. The analytical quality was tested against reference materials (pond sediment flour R.M.No. 82) provided by the National Institute for Environmental Studies (NIES). The recovery percentages were within 85–115% of the certified values for the measured elements.

Phytoplankton community analysis

Quantitative phytoplankton samples were collected below the surface with a bottle and preserved with Lugol's iodine solution. Qualitative samples were obtained with a 17 µm mesh net and fixed in a 4% formaldehyde solution. Phytoplankton was counted according to Utermöhl (1958). The results of phytoplankton abundance are expressed in ind mL⁻¹.

Diversity indexes were used to evaluate the phytoplankton community structure and ecological status of the water. We used the dominance index (D, Eq. 2) (Simpson 1949), the Shannon index to calculate the specific diversity (H, Eq. 3) (Shannon and Weaver, 1949), and the evenness index (J, Eq. 4) according to Pielou (1975)

$$D = \frac{1}{\sum p_i^2} \quad (2)$$

$$H = - \sum p_i \ln p_i \quad (3)$$

Where; p_i is the proportional abundance of a taxon in each sample.

Furthermore, evenness (J) was determined using the following formula:

$$J = H'/H_{max} \quad (4)$$

where; H_{max} is the maximum value of diversity: $\ln S$, and S is the total number of species in the sample.

Statistical analysis

For statistical metal purposes, the sampling sites were grouped according to their positions in the upper (S1 to S6) or middle-lower (S7 to S13) sectors of the Sauce Grande River Basin. As the data analyzed did not meet the assumptions of the parametric statistics, and there were no possible transformations, the non-parametric test Kruskal-Wallis ANOVA were used to evaluate differences in the particulate fractions. Metal concentrations reported as being below MDL were substituted by one-half of the MDL for statistical analyses (Jones and Clarke, 2005) but if 50% or more of the metal concentrations under evaluation were below the MDL, no statistical analyses were performed according to EPA (2000). Also, as metals might have originated from similar sources or have similar reactivity towards physicochemical parameters, a Spearman correlation was used to evaluate the relation between the metals in the particulate fraction and the physicochemical parameters.

The descriptive statistics and correlation matrix were computed using StatSoft Statistica (Version 7.0) software. A Multivariate Redundancy Analysis (RDA) was performed to explore the temporal associations between the abundance of different taxonomic groups of phytoplankton and the physicochemical parameters (seston, conductivity, temperature, and all metals: Cd, Cu, Pb, Zn, Mn, Ni, Cr, Fe). The RDA was performed after confirming that the length of the obtained gradient in units of standard deviation was lower than 4 through a preliminary Detrended Correspondence Analysis (DCA) (Lepš and Šmilauer, 2003). In these analyses, the variance inflation factor gives a measure of the impact of collinearity between the variables. Values exceeding 20 are often regarded as indicators of multicollinearity. The canonical coefficients of the explanatory variables on each axis show which variables are most important for explaining the ordination of the biological variables on the first and second axes. The significance of the first two axes was tested with a Monte-Carlo permutation test. This analysis was performed with CANOCO Version 4.5.

Results And Discussion

Land uses and physicochemical water characteristics

The classification of land cover during the period 2000 to 2016 is according to Brendel et al. 2019. The dominant land cover was grassland (with an area of 1537.8 km², 37.9%) on the plains. On the other hand, the most typical land cover type in the hills throughout this period was exposed rock (around 231.9 km², 44.8%) and sand was the most extensive land cover in the dunes (169.1 km², 66.5%). As in most developing countries, the agricultural sector is highly dependent on rain-fed production. In this context, knowledge of land cover in semiarid regions acquires relevant importance as the changes determine, in part, the vulnerability of places and people to climatic, economic, and sociopolitical changes. The land cover variations even affect the climate and, consequently, the biodiversity and sustainability of the surrounding ecosystem.

The degree of human impact in the Sauce Grande River Basin was related to the water flow direction, and the consequent spatial variation in the variables studied. The middle and lower reaches of the river were characterized by crop areas (Fig. 1.d), whereas the upper basin was the least affected by human activities, given that a considerable area corresponds to a protected nature reserve. Table 1 shows the sampling site identifications with a brief description and the physicochemical values.

Table 1

Sampling sites description and corresponding water quality parameters measured *in situ* (UB: upper basin, MB: middle basin, LB: lower basin, SL: shallow lake) (m: meters above sea level; WT: water temperature (°C); Chla: chlorophyll ($\mu\text{g L}^{-1}$); DO: dissolved oxygen (mg L^{-1}); Water level (m).

Sampling sites	Location in Basin	Characteristics	m.	WT	Chla	pH	DO	Water depth
S1	UB	Natural Reserve	445	18.9	nd	7.4	9.6	0.2
S2	UB	Peralta Bridge. High water flow, with very low anthropogenic activity	247	16.6	1.6	7.8	8.1	0.8
S3	UB	El Retiro residence, before an old dump	236	15.6	1.8	7.9	7.3	0.6
S4	UB	Area after the old dump	271	18.1	1.2	8.3	5.3	0.6
S5	UB	Touristic area downstream Saldungaray city	210	19.8	1.3	8.2	8.3	1.1
S6	MB	Upstream of Paso de las Piedras dam	170	20.1	2.3	8.8	6.2	1.9
S7	MB	Downstream of Paso de las Piedras dam	145	17.0	2.2	7.4	4.9	0.2
S8	MB	Las Oscuras stream	65	12.3	0.6	9.8	8.9	1.4
S9	MB	Las Mostazas stream. Receives sewage from Dorrego city	65	14.4	1.5	10.0	5.1	0.8
S10	SL	Sauce Grande shallow lake. Fishing and recreational area	7	15.6	73.6	9.0	9.5	1.3
S11	LB	Monte Hermoso Bridge, close to Monte Hermoso city	10	14.2	1.5	9.8	6	1.2
S12	LB	Confluence between Sauce Grande river and Las Mostazas stream	10	14.3	6.1	9.6	6.1	0.9
S13	LB	Sewage discharges from Monte Hermoso city	10	16.1	8.6	9.9	5.9	0.6

Conductivity, along with the seston values, was the main physicochemical factor that defined a spatial gradient in Sauce Grande River Basin. Figure 2a shows that conductivity showed a marked increase from S1 (0.03 mS cm^{-1}) to S13 (3.3 mS cm^{-1}). The observed increase at S4 (an old dump) may be due to the garbage contribution to the soil in this sector. The significant increase in the conductivity observed downstream of the dam (S6) could be explained by the topography and the hydrological changes in the water flow, which contributes to the accumulation of salts downstream. Moreover, the lower basin might be exposed to evaporation processes due to an increase in the wind effect as a result of the flat

geomorphology. At S9 and S13, the high conductivity values could also be related to household waste disposal.

The water in the upstream stretch of the Sauce Grande River (S1-S6) was transparent due to the low seston values (Fig. 2b). In contrast, the water was markedly turbid downstream of the dam, with higher seston concentrations, reaching maximum values after the shallow lake (S10) (Fig. 2b). Anthropogenic activities, such as agricultural activities and domestic dumping, might also contribute to an increase in the seston and OM concentrations. The differences in land use between sites could be responsible for the spatial changes (Orioli et al. 2008), as observed here. These results are similar to those found in a river basin in Vietnam (Strady et al. 2017) with untreated wastewater combined with industrial water. These authors showed the same increasing trend downstream for seston, OM and conductivity as in our study, concluding that such discharges contribute to the degradation of the water quality from the canals of the Saigon River.

According to the TSI (*chl a*), the water was oligotrophic in 10 out of the 13 sampling sites, increasing downstream, where S12 and S13 were characterized as mesotrophic, and S10 was described as hypertrophic (Fig. 2c). The increasing TSI values might indicate that the river is becoming eutrophic downstream. The oligotrophic conditions found in the upper basin agree with the data previously recorded by Orioli et al. (2008). *Chl a* presented a gradual increase along the river, down to the Sauce Grande shallow lake ($73.6 \mu\text{g L}^{-1}$ at S10). According to Cony et al. (2014), this lake is a hypertrophic system with *Chl a* mean values of $359.2 \mu\text{g L}^{-1}$. The maximum amount of *Chl a* after the Sauce Grande lake was found at S13 ($8.6 \mu\text{g L}^{-1}$), before its discharge into the Atlantic Ocean; meanwhile, the upper and middle basins were characterized by low concentrations, with values between $0.6 \mu\text{g L}^{-1}$ at S8 and $2.3 \mu\text{g L}^{-1}$ at S6, upstream of the lake.

Metal concentrations in the particulate fraction

The metal (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) concentrations found in the particulate fraction are presented in Table 2. No sediment samples were taken for metal analysis in the Sauce Grande shallow lake (S10) because the procedure would not have been compatible with the rest of the samples along the river. The average concentration of the studied metals followed a decreasing order: $\text{Fe} > \text{Mn} > \text{Zn} > \text{Cu} > \text{Cr} > \text{Ni} > \text{Pb} > \text{Cd}$, where the relative abundance of Fe and Mn is because they are the two most abundant metal components in nature (Forstner and Wittmann, 2012). Moreover, they are hydroxides that play particularly essential roles in cycling and transporting metals due to their large surface areas and high capacity to adsorb and coprecipitate other metals (Liang et al. 2013).

Table 2

Metal concentrations in the seston fraction ($\mu\text{g g}^{-1}$) from the Sauce Grande River Basin. <MDL: below method detection limits.

Sampling sites	Cd	Cu	Cr	Fe	Mn	Ni	Pb	Zn
S1	1.2	40	16	31000	800	63.0	<MDL	39
S2	18	40	22	21000	750	<MDL	<MDL	10
S3	0.80	37	5.6	15000	1000	<MDL	<MDL	0
S4	0.80	30	11	20000	970	<MDL	<MDL	0
S5	1.1	25	85	20000	1040	<MDL	<MDL	31
S6	5.2	27	15	22000	1130	<MDL	<MDL	42
S7	<MDL	21	17	28000	30000	17.0	<MDL	63
S8	1.8	25	12	21000	1550	<MDL	<MDL	49
S9	<MDL	34	23	33000	920	20.0	11	95
S11	1.5	13	9.1	10000	3630	9.6	<MDL	51
S12	<MDL	25	18	24000	1535	9.6	<MDL	84
S13	<MDL	23	17	24000	1755	8.5	7.9	62

Metal contents in the particulate fraction showed variability between the sampling sites (Table 2), with Cu achieving statistically higher values ($p < 0.05$) in the upper basin, whereas Cd also showed higher values upstream but with no statistical difference. On the other hand, Zn and Mn showed statistically higher values in the middle and lower reaches of the basin ($p < 0.01$ for Zn and $p < 0.05$ for Mn) and metals such as Cr and Fe tended to higher amounts downstream of the Paso de las Piedras dam but with no statistical differences. Statistical analysis of Ni and Pb could not be undertaken since most values were below the method detection limits.

The metal composition of the particulate fraction can reflect the rock types, climatic conditions, and biological processes in a river basin (Yang et al., 2004). They are also affected by human-induced pollution, such as wastewater discharges, sewage sludge emissions, and agricultural practices, e.g. inputs of phosphate fertilizers and fungicides (Benabdelkader et al. 2018) that may release metals (Hou et al. 2014, Song et al. 2010). The results from this study inferred that there were significant differences in the release or behavior of metals along the river, with Cu and Zn being the distinctive metals in the upstream and downstream waters, respectively. The downstream area is characterized by a shift in the physicochemical parameters accompanied by increased particulate metal concentrations. The metals found in the middle-lower basin (Cr, Fe, Ni, Pb, and Zn), except for Mn, all achieved the highest value at sampling site S9, which belongs to the Las Mostazas stream, a course of water that receives waste discharges from Dorrego city.

Conversely, sampling site S3 achieved the lowest concentrations for these same five metals, a site with high water flow and low anthropogenic activity. As mentioned previously, the middle and lower reaches of the river are characterized by zones of crops. In contrast, the upper basin is not affected by human activities, given that a large area corresponds to a protected nature reserve.

A Spearman correlation analysis between the physicochemical parameters and the concentrations of particulate metals indicated that, in most cases, there were no significant associations. Positive significant correlations were found between Zn and Ni ($r = 0.85$, $p < 0.05$), Zn and Cr ($r = 0.67$, $p < 0.05$), Cr and Fe ($r = 0.79$, $p < 0.05$), conductivity and Zn ($r = 0.78$, $p < 0.05$), and between pH and Pb ($r = 0.65$, $p < 0.05$). Moreover, a highly significant negative correlation was found between Cu and Mn ($r = -0.95$, $p < 0.05$). The closer between-element correlations observed for the elements Zn, Cr, and Ni may result from similar sources or be a function of bottom-sediment resuspension and the release of previously adsorbed contaminants. Positive correlations between Cr, Ni, and Zn have already been mentioned in studies performed in water systems (e.g., Beltrame et al. 2009, La Colla et al. 2018). Also, the relationship between Pb and pH may rely on the fact that Pb solubility in the water column decreases with pH (Turner *et al.* 1981), thus increasing Pb in the particulate fraction.

Metal concentrations in the entire river basin were compared with the world river values. These guidelines mention the worldwide average major and trace element chemistry of riverine particulate matter compared with the composition of the continental crust (Viers et al. 2009). Cd and Mn values from this study were indeed above the limits of 1.55 and 1679 $\mu\text{g g}^{-1}$, respectively. The results from this study were also compared with the Argentinean National Guidelines for the Aquatic Biota Protection (Law 24051, 1993 -disposal of hazardous wastes), in order to assess the risks associated with the aquatic life inhabiting superficial waters that contain metals. These guidelines set maximum permitted values for metals in the whole water column matrix (Cd: 0,20 $\mu\text{g L}^{-1}$; Cu: 2,0 $\mu\text{g L}^{-1}$; Cr: 2,0 $\mu\text{g L}^{-1}$; Mn: 100 $\mu\text{g L}^{-1}$; Ni: 25 $\mu\text{g L}^{-1}$; Pb: 1,0 $\mu\text{g L}^{-1}$; Zn: 30 $\mu\text{g L}^{-1}$). According to the data, the metal values found in the particulate fraction from this study were related to the amount of the filtered water, and thus expressed as metal concentrations in the whole water matrix. Values for Cu, Cr, Mn, and Pb found at sampling site S9 were above the legal thresholds (Cu: 3,5 $\mu\text{g L}^{-1}$; Cr: 2,4 $\mu\text{g L}^{-1}$; Pb: 1,2 $\mu\text{g L}^{-1}$; Mn 170 $\mu\text{g L}^{-1}$). Consequently, metal concentrations should be carefully monitored in the watershed in order to avoid dangerous increments.

Phytoplankton community structure

The total abundance of phytoplankton and the community structure at each sampling site is shown in Fig. 3. The total phytoplankton abundance varied from 33319 ind mL^{-1} at S13 to 973.2 ind mL^{-1} at S2 (Fig. 4, Table 3). All the species reflected low abundance (≤ 900 ind mL^{-1}), except the diatoms, such as *Rhoicosphenia* sp. (1946 ind mL^{-1}) and *Navicula* sp. (1065 ind mL^{-1}), the Chlorophyta *Monoraphidium circinale* (15060 ind mL^{-1}), which is considered a species that is tolerant to a wide range of ecological conditions (Izaguirre et al. 2004) and the Cyanobacteria *Synechocystis salina* (1217 ind mL^{-1}). Several authors have previously documented the dominance of diatoms found in this study in the Pampean

regions of the Parana River Basin (Izaguirre and Vinocur, 1996, Izaguirre et al. 2001). The diatoms are one of the algal groups best adapted to turbulent and turbid systems with high nutrient concentrations (Reynolds, 1994).

Table 3

Total Abundance (ind mL⁻¹), diversity indexes (D: Simpson; Hmax: Maximum diversity; H: Shannon index; J: Pielou index) and number of species (S) on sampling sites from the Sauce Grande River Basin.

Sampling sites	Abundance	D	Hmax	H	J	S
S2	973	0.4	2.1	3.0	1.5	8
S3	2919	0.1	2.8	3.7	1.4	16
S4	3012	0.1	2.7	3.5	1.3	15
S5	11863	0.1	3.1	3.6	1.2	22
S6	2502	0.2	2.3	2.8	1.2	10
S7	2038	0.2	2.7	2.8	1.0	15
S8	2317	0.1	2.6	3.4	1.3	18
S9	4495	0.1	2.9	3.4	1.2	13
S10	31697	0.1	3.5	4.3	1.2	32
S11	1714	0.2	2.2	3.0	1.4	9
S12	2595	0.1	2.6	2.8	1.4	14
S13	33319	0.2	3.0	3.6	0.9	20

The phytoplankton community was dominated by diatoms, followed by Chlorophyta, showing downstream variations in response to changes in water parameters. Notably, a remarkable difference was observed in the number and species composition of phytoplankton. Bacillariophyta was dominant in most places, especially in the upper and middle basins, contributing more than 50% of the total phytoplankton abundance. Chlorophyta was predominant at S10 and S13 and contributed about 50% and 83%, respectively, to the quantity of phytoplankton. At S3, S9, and S10, we detected the presence of species of the Euglenophyta group, which is generally associated with organic matter (Conforti 1998). Site S9 receives the contribution of household wastes from Dorrego city, which could explain the presence of the Euglenophyta at S9 and S10. In regard to S1 (pristine zone,) it was impossible to take a representative sample of phytoplankton because the watercourse was low. Moreover, S2 presented low phytoplankton abundance (973 ind mL⁻¹).

We found that the phytoplankton community was significantly modified by high eutrophication levels along the Sauce Grande River Basin. The spatial dynamics of phytoplankton showed higher

Bacillariophyta (diatoms) abundance in zones with low anthropogenic impact, low conductivity values, and the most elevated turbulence (S2-S7). Higher densities of Chlorophyta and Cyanobacteria were found in the highly eutrophic and polluted sites with domestic effluents (S9 and S13) and downstream of the dam (S6).

Cyanobacteria thrive in rich nutrient environments (Paerl *et al.* 2006). Indeed, although they only represented only 22% of the total phytoplankton abundances in this study, their most significant contribution was at S10 where the most frequent genera were *Aphanocapsa*, *Microcystisaeruginosa*, and *Synechocistissalina*. These genera and some potentially toxic individual species like *Planktothrix agardhii* have already been reported in Pampean eutrophic shallow lakes (Izaguirre *et al.* 2014). They were also recorded in polluted zones in the Río de la Plata (Garcia and Bonel 2014). Like the Chlorophyta, the Cyanobacteria tolerate high nutrient uptakes, a condition that allows them to inhabit polluted environments. Thus, these would explain why their abundance was higher in eutrophic and less turbulent sites. The phytoplankton spatial dynamics in the Sauce Grande River were similar to those found in large temperate rivers (e.g., Descy *et al.* 2017), with low or nil phytoplankton abundance upstream, but increasing downstream with maximum values in the middle section.

Some studies have reported many algal species as indicators of water quality, e.g. Zargar and Ghosh (2006), in a study on Karnataka's Kadra reservoir, cited numerous algae belonging to the Chlorophyta, Cyanobacteria, Euglenophyta and Bacillariophyta, as indicators of water pollution. Nandan and Aher (2005) also mentioned the genera, *Euglena*, *Oscillatoria*, *Scenedesmus*, *Navicula*, *Nitzschia* and *Microcystis* as being typical of organically polluted waters, which coincides with our findings. Moreover, the concentration of Chla has been widely used in aquatic studies as an indicator of phytoplankton abundance (e.g., Bettencourt *et al.* 2004, Devlin *et al.* 2007). However, Chla and abundance are two different variables (Dominguez *et al.* 2008). Our results showed that the characterization of water quality using the amount of phytoplankton seems more consistent compared to Chla.

Phytoplankton diversity index and water quality

The H index value in the Sauce Grande River Basin ranged between 4.3 (S10) and 2.8 (S6, S7, and S8). This index is commonly used to reflect the complexity and stability of the community. Higher H values were associated with higher TSI values; meanwhile, Shannon's index seemed to be primarily a function of changes in species richness (Table 3). The D index (Simpson 1949) was also considered because previous studies reported a close relationship with the H index (Ludwig *et al.* 1988). However, Simpson's index values were low and similar in all sampling sites, with unclear information about the sampling sites with different eutrophication levels. This could be explained because the D index gives more relevance to abundant species and underestimates rare species. Many authors showed that Simpson's index responses do not adequately interpret changes in community diversity (Karydis and Tsirtsis 1996; Danilov and Ekelund 1999). Similarly, Pielou's evenness (J) represents how equal a community is based on the relative abundances of each taxon, but it does not take account of the number of taxa. The lower evenness occurred at S13, which presented higher total abundances (Table 3).

Numerous studies have proposed that high H values (≥ 4) are associated with a rich species diversity and low pollution levels, whereas lower H (≤ 1.5) values suggest higher pollution levels (Spatharis *et al.* 2011, Wang *et al.* 2019). The H values found in this study are not in agreement with these assumptions in terms of contamination. As a contamination term, in this study it would be eutrophication. In this way, the highest values of TSH chl *a* agree with the highest amounts of H. The S10 is a shallow lake with a high level of eutrophication (Cony *et al.* 2017, Alfonso *et al.* 2018), possibly due to the discharge of runoff throughout the basin, in the same way as at S13. However, as a lake, it is expected that the H index would be higher than in the river. Even so, the rivers are not isolated ribbons of water. They are essential parts of the landscape connecting with other water bodies. The various waters of river catchments, including small pools, bordering shallows of the rivers, and artificial impoundments, continuously enrich the river (Borics *et al.* 2007).

Community level indices may give a misleading interpretation of the biological data; diversity indices are only recommended to be used in conjunction with other indices (Spatharis *et al.* 2011), as was applied in this study with the TSI. According to our results, the Shannon index (H) seems to be more appropriate for assessing the Sauce Grande River Basin, however the S and D indices provided necessary ecological information.

Assemblages and environmental associations

The RDA (Fig. 4) revealed that the changes in conductivity and seston shaped the structure of the phytoplankton community. The first two ordination axes represented more than 67% of the total variance. The variance inflation factor was less than 20 for all the included variables. Axis 1 was positively correlated with Fe ($r = 0.41$), Zn ($r = 0.28$) and negatively correlated with seston ($r = -0.59$) and conductivity ($r = -0.34$). The analysis of axis 1 indicated an environmental gradient with two distinct spatial groups; the first one, formed by S10, S12 and, S13, was associated with high conductivity, seston and high Chlorophyta abundance, which are related to the higher eutrophication values found at those sites. The second group, of S5, S6, and S8, presented higher diatom abundance and lower seston and conductivity (Bacillariophyta). The axis 2 was positively correlated with Pb ($r = 0.23$), Ni ($r = 0.17$), and negatively correlated with temperature ($r = -0.46$), TSI ($r = -0.44$), H' ($r = -0.39$) and Cd ($r = 0.33$). Strong associations between S11 and Cyanobacteria, and between S9 and Euglenophyta, were observed (Fig. 4) at the sites downstream of the dam that are subjected to stronger anthropogenic influence. The sites S4 and S11 showed a higher TSH value reflecting the anthropogenic effect on these sites.

Conclusions

This research represents the first integrated water quality assessment of the Sauce Grande River Basin. The results showed marked spatial variations in the physicochemical and biological conditions, where the water quality decreased downstream towards the Atlantic Ocean, emphasizing the areas with higher anthropogenic effects. The phytoplankton community was an excellent ecological indicator of water quality, showing significant modifications with the increased eutrophication along the Sauce Grande River Basin, with more abundance of Bacillariophyta (diatoms) in zones with a low anthropogenic impact,

conductivity, and high turbulence. Meanwhile, higher densities of Euglenophyta, Chlorophyta, and Cyanobacteria were found in the middle-lower basin, associated with higher organic matter, eutrophication, and metal pollution values. Moreover, Cu, Cr, Mn, and Pb concentrations in the middle basin achieved values above the legal thresholds, with potential risk to the aquatic life. Metal concentrations should be carefully monitored in the watershed for the next few years, whereas the nutrient concentration must be considered in future studies in order to determine its contribution to the trophic conditions. Our research generated a relevant database for the Sauce Grande River Basin management.

Declarations

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Authors contribution **Josefina Zunino**: Conceptualization, Analyses and interpretation, Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Noelia S. La Colla**: Conceptualization, Analyses and interpretation, Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Andrea S. Brendel**: Conceptualization, Analyses and interpretation, Investigation, Methodology, Writing - review & editing. **Maria B. Alfonso**: Analyses and interpretation, Methodology, Writing - review & editing. **Sandra E. Botté**: Visualization, Methodology, Writing - review & editing. **Gerardo M.E. Perillo**: Visualization, Methodology, Writing - review & editing, **Maria C. Piccolo**: Funding acquisition, Resources, Writing - review & editing.

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Figures

Figure 1

The geographical location of a) Sauce Grande River Basin, b) sampling sites, c) topography and location of the main cities located in the basin, and d) land cover in the Sauce Grande River Basin (modified from Brendel *et al.* 2019).

Figure 2

Spatial variations of (a) water conductivity, (b) seston and organic matter (OM) and (c) trophic state index (TSI) in the Sauce Grande River Basin.

Figure 3

Spatial dynamics of phytoplankton abundance values and composition groups in the Sauce Grande River Basin.

Figure 4

Redundancy analyses (RDA) in the Sauce Grande River Basin. Conducti (Conductivity), seston (suspended particulate matter), TSI (Carlson index), H (Shannon and Weber index), T (water temperature). Eugle (Euglenophyta) Dino (Dinoflagellates), Bacil (Bacillariophyta), Chloro (Chlorophyte), Cyano (Cyanophyte), Eugl (Euglenophyta), Crypto (Cryptophyta).