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

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Abstract

The increasing landscape alterations due to anthropogenic activities is of global concern since it affects aquatic ecosystems, often resulting in compromise of the ecological integrity and the water quality. In this sense, the evaluation, monitoring, and prediction of the aquatic ecosystem quality becomes an important research subject. This study presents the first integrated water quality assessment of the Sauce Grande River Basin, in Argentina, based on the spatial distribution of the phytoplankton community, the physicochemical parameters, and the metal concentrations (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) found 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 trophic state index indicated that water was oligotrophic in over 75% of the sampling sites, increasing downstream, where two sites were characterized as mesotrophic, and one described as hypertrophic. The phytoplankton community was dominated by diatoms in zones with low anthropogenic impact and conductivity, whereas high densities of Euglenophyta, Chlorophyta, and Cyanobacteria were found in the middle-lower basin, associated with higher organic matter and eutrophication. The conductivity, turbidity, and most metal concentrations also increased towards the downstream area, even exceeding recommended levels for the metals Cu, Cr, Mn, and Pb in the middle and lower reaches of the basin (Cu: 3.5 µg L⁻¹; Cr: 2.4 µg L⁻¹; Pb: 1.2 µg L⁻¹; Mn 170 µg L⁻¹). This study generates a database for the water quality of the Sauce Grande River Basin and sets an example of how the water quality varies along a basin that crosses different topographic environments, land covers, and anthropogenic influences.

Keywords Anthropogenic uses · Chlorophyll a · Biological biomarker · Pollution · Trophic condition · Freshwater

Introduction

Watersheds are systems shaped by multiple factors, such as climate variability, hydrological, biogeochemical, and anthropogenic variables (Abdul-Aziz and Ahmed 2019; Alnahit et al. 2020). The landscape alterations, driven through urban and agricultural conversion, play a key role in the degradation of water quality (Qiu et al. 2019; Yu et al. 2013). Population growth at rivers margins and the related economic activities have increased the environmental pressure over these freshwater ecosystems with time (Kazi et al. 2009; Mangadze et al. 2019; 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 and Gurnell 2005).

Evaluation of the health of an aquatic ecosystem is complex because pollution is diffuse due to numerous contamination sources. Although chemical analyses of water provide
a good indication of the quality of the aquatic systems, they do not necessarily reflect the ecological state of the system (El-Kassas and Gharib 2016). Thus, water quality 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 (Celakli et al. 2019; Katsiapi et al. 2011; Lopes et al. 2021). Most studies have shown that the phytoplankton structure and distribution in aquatic environments are driven by the combination and interactions between physical, chemical, and biological factors (Duong et al. 2019; Li et al. 2016). Indeed, phytoplankton is generally more sensitive to pollution than other assemblages (Pourafrasyabi and Ramezanpour 2014). In addition, 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, considering that metals may bioaccumulate through the food chain (Velusamy et al. 2014). It is important to stress out that metals also interact with the phytoplankton community, and their concentrations in the water column may cause a shift in composition towards species less susceptible to these elements (Cabrita 2014; Yang et al. 2018). Therefore, metal contamination might be used as an additional physicochemical indicator of water quality.

In the last 20 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) Increasing water demand due to population growth and decreasing water availability due to recurrence of drought combine to generate low resilience to water scarcity, and has seriously impacted on the efficiency and sustainability of local water resources management (Casado et al. 2018). 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, and including the area where the river discharges into the Atlantic Ocean. There are only isolated studies of the phytoplankton community in the Sauce Grande shallow lake (Cony et al. 2017) and the Paso de las Piedras reservoir (Fernández et al. 2009), and of dissolved metal values in the middle basin of the Sauce Grande river (Rosso et al. 2011).

The goals of this study were to assess, for the first time, the water quality status along a 200-km stretch of the Sauce Grande River Basin, by evaluating the trophic conditions and the physicochemical water parameters, the abundance and diversity of the phytoplankton, and the metal concentrations (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) in the particulate fraction. The results from this study were expected to shed light on the water quality status of the river basin as a result of anthropogenic developments, different topographic environments and land covers along the basin, and their possible influence on the phytoplankton community.

### Materials and methods

#### Study area

The Sauce Grande River Basin is located in the south of the 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 -ide mountain chain surrounded by plains that are locally known as the pampas (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 reservoir; the middle basin includes the water reservoir 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 reservoir 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 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.

#### 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 aluminum foil at –20º C; chl-a was extracted using 90% acetone in darkness, and

Fig. 1 The geographical location of a the Sauce Grande River Basin, b the 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)
overnight storage at 4°C; then the extracts were cleared by centrifugation at 3000 rpm for 3 min and the concentrations were estimated by the spectrophotometric method (Marker 1980). The concentration of seston was estimated gravimetrically after filtration of water samples (1000 ml) through pre-combusted (500 °C for 1 h) filters (GF/F Whatman TM) and drying to a constant weight at 105 °C (APHA 2005). Organic matter content in seston (OM) was obtained by calcination of the filters in a muffle furnace at 550 °C.

Carlson’s trophic state index (TSI) commonly uses three variables, chl-a, Secchi depth, and total phosphorus, which independently estimate the trophic level. According to Carlson and Simpson (1996), even though any of the three variables can therefore theoretically be used to classify a waterbody, for the purpose of classification, priority is given to chl-a, because this variable is the most accurate of the three at predicting algal biomass. Total phosphorus may be better than chl-a at predicting summer trophic state from winter samples, and the Secchi disc depth should only be used if there are no better methods available. Accordingly, the TSI using chl-a (TSI chl-a) (Carlson 1977) was estimated in agreement with the following equation:

$$\text{TSI(chl-a)} = 10(2.46 + \ln \text{chl-a} $X \ln 2.5)$$

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 (1500 ml), pre-cleaned with acid. No samples were taken for metal analysis in the Sauce Grande shallow lake (S10) due to difficulties in the sampling procedure. 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 3 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; and 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 sampling and community analysis**

Sub-surface water samples for quantitative phytoplankton analyses were collected in bottles (250 ml) 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) (Simpson 1949), the Shannon index to calculate the specific diversity (H) (Shannon 1948), and the evenness index (J) according to Pielou (1975).

**Statistical analysis**

Sampling sites were grouped according to their locations in the upper (S1 to S6) or middle-low (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 US (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 spatial associations between the abundance of different taxonomic groups of phytoplankton and the physicochemical parameters (seston, conductivity, temperature, and metals: Cd, Cu, Cr, Fe, Mn, and Zn). 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), and phytoplankton values were log-transformed. 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 degree of human impact in the Sauce Grande River Basin was related to the water flow direction, and the consequent spatial variations in the studied variables. Land use and cover changes driven by human activities have effects on the biodiversity, dynamics, and sustainability of the surrounding ecosystem (Kalantari et al. 2019; Li et al. 2018; Mangadze et al. 2017; Meng et al. 2020). The middle and lower reaches of the river were characterized by crop areas (Fig. 1d), whereas the upper basin was the least affected by human activities, given that a considerable area corresponds to a protected nature reserve (Brendel et al. 2019). Table 1 shows the sampling site identifications with a brief description and the physicochemical values.

Conductivity, along with the seston and organic matter values, were the main physicochemical factors that defined a spatial gradient in Sauce Grande River Basin. Figure 2a shows that conductivity presents a marked increase from S1 (0.03 mS cm⁻¹) to S13 (3.3 mS cm⁻¹). The observed increased 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 Paso de las Piedras reservoir (S6) could be explained by the topography and the hydrological changes in the water flow, which contributes to the accumulation of salts downstream (Leibowitz, et al. 2018). 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 (Przydatek and Kanownik 2019).

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 Paso de las Piedras reservoir, with higher seston and OM concentrations, reaching maximum values after the shallow lake (S10) (Fig. 2b). Anthropogenic activities, such as agricultural activities and domestic dumping, might

| Sampling sites | Location in the basin | Characteristics | M | WT | chl-a | pH | DO | WD |
|---------------|-----------------------|----------------|---|----|-------|----|----|----|
| 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 reservoir| 170 | 20.1 | 2.3 | 8.8 | 6.2 | 1.9 |
| S7            | MB                    | Downstream of Paso de las Piedras reservoir| 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 | 6.0 | 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 |
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 or that the water flow gets slower, enabling phytoplankton to accumulate 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 µg L⁻¹ at S10). According to Cony et al. (2014), this lake is a hypertrophic system with chl-a mean values of 359.2 µg L⁻¹. The maximum amount of chl-a after the Sauce Grande lake was found at S13 (8.6 µg 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 µg L\(^{-1}\) at S8 and 2.3 µg L\(^{-1}\) at S6, upstream of the lake.

**Metal concentrations in the particulate fraction**

The metals (Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn) concentration found in the particulate fraction are presented in Table 2. The average concentration of the studied metals followed a decreasing order: Fe > Mn > Zn > Cu > Cr > Ni > Pb > Cd, where the relative high concentrations of Fe and Mn are due to their characteristic abundances 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).

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 reservoir 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 (Benabdellakader 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 Cr \((r = 0.67, p < 0.05)\), Cr and Fe \((r = 0.79, p < 0.05)\), and conductivity and Zn \((r = 0.78, p < 0.05)\). 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 and Cr may result from similar sources or be a function of bottom-sediment resuspension and the release of previously adsorbed contaminants. Positive correlations between Cr and Zn have already been mentioned in studies performed in water systems (e.g., Beltrame et al. 2009; La Colla et al. 2018).

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 µg g\(^{-1}\), respectively. The results from this study

| Sampling sites | Cd  | Cu  | Cr  | Fe   | Mn  | Ni  | Pb  | Zn  |
|---------------|-----|-----|-----|------|-----|-----|-----|-----|
| S1            | 1.2 | 40  | 16  | 31,000 | 800 | 63.0 | <MDL | 39  |
| S2            | 18  | 40  | 22  | 21,000 | 750 | <MDL | <MDL | 10  |
| S3            | 0.80| 37  | 5.6 | 15,000 | 1000| <MDL | <MDL | 0   |
| S4            | 0.80| 30  | 11  | 20,000 | 970 | <MDL | <MDL | 0   |
| S5            | 1.1 | 25  | 85  | 20,000 | 1040| <MDL | <MDL | 31  |
| S6            | 5.2 | 27  | 15  | 22,000 | 1130| <MDL | <MDL | 42  |
| S7            | <MDL| 21  | 17  | 28,000 | 30,000| 17.0| <MDL | 63  |
| S8            | 1.8 | 25  | 12  | 21,000 | 1550| <MDL | <MDL | 49  |
| S9            | <MDL| 34  | 23  | 33,000 | 920 | 20.0| 11  | 95  |
| S11           | 1.5 | 13  | 9.1 | 10,000 | 3630| 9.6 | <MDL | 51  |
| S12           | <MDL| 25  | 18  | 24,000 | 1535| 9.6 | <MDL | 84  |
| S13           | <MDL| 23  | 17  | 24,000 | 1755| 8.5 | 7.9 | 62  |
were also compared with the Argentinian National Guidelines for the Aquatic Biota Protection (Law 24,051, 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 µg L⁻¹; Cu: 2.0 µg L⁻¹; Cr: 2.0 µg L⁻¹; Mn: 100 µg L⁻¹; Ni: 25 µg L⁻¹; Pb: 1.0 µg L⁻¹; Zn: 30 µg 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 µg L⁻¹; Cr: 2.4 µg L⁻¹; Pb: 1.2 µg L⁻¹; Mn 170 µg 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 973.2 ind ml⁻¹ at S2 to 33,319 ind ml⁻¹ at S13 (Fig. 3, Table 3). All the species reflected low abundance (< 900 ind ml⁻¹), except the diatoms (Bacillariophyta), such as *Rhoicosphenia* sp. (1946 ind ml⁻¹) and *Navicula* sp. (1065 ind ml⁻¹), the Chlorophyta *Monoraphidium circinale* (15,060 ind ml⁻¹), which is considered a species 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 1994; 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).

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 the phytoplankton, with Bacillario phyta as the dominant species in most places, especially in the upper and middle basins, contributing to more than 50% of the total phytoplankton abundance. Chlorophyta was predominant at S10 and S13 and contributed about 50% and

![Fig. 3 Spatial dynamics of phytoplankton abundance values and composition groups in the Sauce Grande River Basin](image)

**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. Data from Sampling site 1 (S1) was not available since it was not possible to take a representative sample

| 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            | 11,863    | 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           | 31,697    | 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           | 33,319    | 0.2 | 3.0  | 3.6 | 0.9 | 20  |
83%, respectively, to the quantity of phytoplankton. S3, S9, and S10 were 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 Euglenophyta at S9 and S10. Regarding 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 m−1).

River systems are often dominated by Bacillariophyta, Chlorophyta and Cyanophyta, with the succession between these three phyla as the dominants, as was found in many river throughout the world (Elshobary et al. 2020; Inyang and Wang 2020; Koekemoer et al. 2021). Among them, Cyanophyta is potentially problematic since blooms can result in unacceptable scum formations, recreational problems, such as skin and eye irritations, and the production of tastes, odors, and toxins (Koekemoer et al. 2021).

The phytoplankton community might be significantly modified by high eutrophication levels along the Sauce Grande River Basin since they have great sensitivity towards environmental stressors due to their short life-span and the ability to respond to changes in the environment (El-Kassas and Gharib 2016). The spatial dynamics of phytoplankton showed higher Bacillariophyta abundance in zones with low anthropogenic impact, low conductivity values, and the least turbulence. Higher densities of Chlorophyta and Cyanobacteria were found in the highly eutrophic and polluted sites with domestic effluents (S9–S13) and upstream of the reservoir (S6).

Cyanobacteria thrive in rich nutrient environments (Paerl and Fulton 2006). Indeed, although they only represented 22% of the total phytoplankton abundances in this study, their most significant contribution was at S10 where the most frequent genera were Aphanocapsa, Microcystis, and Synechocystis. These genera and many 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 concentrations, a condition that allows them to inhabit polluted environments. According to Inyang and Wang (2020), Cyanobacteria species like Microcystis spp., could be used as indicator species of nitrate in the aquatic system, for instance.

Moreover, pollution can change the structure of an ecosystem by reducing the number of species in a community (Piranti and Wibowo 2020) or by causing a shift in composition towards species less susceptible to these elements (Cabrita 2014). In this study, the shift in the phytoplankton community between the upper and middle-lower sites could be, at least in part, related to the metal concentrations achieved in the particulate fraction, whose values also increased towards the middle-lower sites, with a maximum in S9.

Moreover, the phytoplankton spatial dynamics in the Sauce Grande River were similar to those found in other 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.

Even though the concentration of chl-a has been widely used in aquatic studies as an indicator of phytoplankton abundance (e.g., Bettencourt et al. 2004; Devlin et al. 2007), the results from this study showed that the characterization of water quality using the amount of phytoplankton seems more consistent compared to chl-a.

**Phytoplankton diversity index and water quality**

Phytoplankton species can be very sensitive to slight modifications in its environment and hence, may provide good insight about water quality before it reaches extreme visible condition like eutrophication (Brettum and Andersen 2005). The quality and quantity of phytoplankton have been successfully utilized to assess the quality of water and its capacity to sustain heterotrophic communities (Gao and Song 2005; Inyang and Wang 2020). Species diversity within aquatic communities is strongly associated with the trophic state of the water body (e.g., Li et al. 2019). Diversity, distribution, abundance, and variation of phytoplankton provide information on the aquatic system (El-Kassas and Gharib 2016), whereas physical and chemical water quality measurements represent only a “snapshot” of the current conditions in aquatic systems by giving only a transient picture of prevailing environmental conditions (Gökçe 2016).

The $H$ index value in the Sauce Grande River Basin ranged between 2.8 (S6, S7, and S8) and 4.3 (S10). 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).

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). Nevertheless, the $H$ values found in this study are not in agreement with these assumptions in terms of contamination since in this study, contamination is synonymous of eutrophication. In this way, the highest values of TSI (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).

The $D$ index 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 the sampling sites, with lack of information about the eutrophication levels in the sampling sites. 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).

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 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 ($r = 0.41$) and 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 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 water reservoir that are subjected to stronger anthropogenic influence. The sites S4 and S11 showed a higher TSI 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 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.

This article intended to shed light on the water quality of aquatic environments and create the basis for further researches, which could include the use of sessile algae or benthic organisms as biological indicators of water quality, since they can be relatively fixed in the river, avoiding being washed out by the current.

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Author 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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