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Phosphorus and nitrogen fractions during base flow conditions of a Pampean stream and their relationship with land use

María J. Torti; Silvina I. Portela✉ & Adrián E. Andriulo

INTA (Instituto Nacional de Tecnología Agropecuaria), Estación Experimental Agropecuaria Pergamino. Provincia de Buenos Aires, Argentina.

Abstract. During the last decades, population growth and the associated intensification of anthropogenic activities (agriculture, industrialization and urbanization) increased nutrient inputs to Pampean lotic waterbodies. However, few studies evaluated the influence of these changes on water quality. The objectives of this study were to determine nitrogen (N) and phosphorus (P) fractions, trophic status and nutrient limitation of a typical Pampean stream, and to compare nutrient contents and speciation with different land uses (urban/industrial versus agricultural). Stream water samples were obtained monthly between 2010 and 2012 from six locations along the Pergamino stream. The stream was highly productive (eutrophic/hypertrophic) and nutrient concentrations were greater than the environmental quality standards from different parts of the world as a result of point and diffuse source inputs in addition to the naturally high baseline nutrient concentrations. In the case of N, organic and particulate fractions predominated in sites surrounded by agriculture, while inorganic forms predominated in sites dominated by urban/industrial effluent discharges. Nutrients spatial variation along the Pergamino stream presented the lowest concentrations in the headwaters, the highest concentrations when crossing the city of Pergamino and intermediate values towards the mouth. In this basin, despite being located in the most important agricultural region of Argentina, urban and industrial point source discharges resulted in greater impairment of water quality than diffuse sources linked to agriculture. Between the city of Pergamino and the stream mouth, total N and P concentrations decreased by 50% as a result of dilution due to increased flow and other natural self-cleansing mechanisms. It is imperative to design a monitoring programme and to adopt management strategies designed to reduce nutrient input to avoid saturating the stream's capacity to retain and process nutrient inputs.

[Keywords: eutrophication, agriculture, urbanization, Pampean region]

Resumen. Relaciones entre el uso del suelo y fracciones de fósforo y nitrógeno en condiciones de flujo base de un arroyo pampeano. Durante las últimas décadas, la intensificación de las actividades antrópicas (agricultura, industrialización, urbanización) aumentó el ingreso de nutrientes a los sistemas lóticos pampeanos. Sin embargo, pocos estudios evaluaron cómo estos cambios afectaron la calidad del agua. Los objetivos de este estudio fueron determinar las fracciones de nitrógeno (N) y fósforo (P), el estado trófico y el nutriente limitante en un arroyo pampeano típico, y relacionar el contenido de nutrientes y su especiación con los diferentes usos del suelo (urbano/industrial versus agropecuario). Se colectaron muestras de agua del arroyo Pergamino mensualmente entre 2010 y 2012, en seis sitios a lo largo del curso. El arroyo resultó muy productivo (eutrófico/hipereutrófico) y la concentración de nutrientes fue superior a los estándares mundiales de calidad ambiental como resultado del aporte de fuentes puntuales y difusas sumado a concentraciones de base naturalmente elevadas. En el caso del N, las fracciones orgánicas y particuladas predominaron en los sitios con agricultura, mientras que las inorgánicas predominaron en los sitios con aportes urbano/industriales. En cuanto a la variación espacial, la concentración de nutrientes fue mínima en los sitios cercanos a la naciente, máxima luego de atravesar la ciudad de Pergamino e intermedia hacia la desembocadura. En esta cuenca, a pesar de encontrarse en la región productiva más importante de la Argentina, los aportes puntuales urbanos e industriales causaron mayor deterioro de la calidad del agua que los aportes difusos provenientes de las actividades agropecuarias. Desde su paso por la ciudad hasta la desembocadura, las concentraciones de N y P disminuyeron 50% como consecuencia de la dilución por aumento del caudal y de otros mecanismos naturales de autodepuración. Es imperativo el diseño de un programa de monitoreo y la adopción de estrategias de gestión orientadas a reducir los aportes de nutrientes para evitar superar la capacidad autodepuradora del sistema..

[Palabras clave: eutrofización, agricultura, urbanización, Región Pampeana]

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✉ portela.silvina@inta.gob.ar

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Introduction

Small-scale, low-order streams connect the terrestrial environment with large rivers. Nutrients from terrestrial ecosystems enter aquatic ecosystems through these small streams (Figueiredo et al. 2010). In the natural cycle, nutrients come mainly from the decomposition of organic matter, but over the past 60 years, nutrient inputs have increased due to human activity (Dodds 2006). According to Matlock and Morgan (2011), flows of biologically available nitrogen (N) and phosphorus (P) have doubled and tripled, respectively, between 1960 and 2010. Nutrient enrichment (eutrophication) is the primary problem of most surface waters today (Smith and Schindler 2009).

In aquatic ecosystems, the minority elements N and P play the role of nutrients and limit algal growth. As algae are the first link in the food chain, N and P determine the quantity and quality distribution of organisms in surface waters. Therefore, nutrient concentrations exert a strong control on the biological productivity of fresh waters and both of these variables are used to define their trophic state through indexes. The concept of limiting nutrient is based on the fact that the algal growth rate will be restricted by the element that is present in a lower concentration than the proportion required by the algae (Conzonno 2009). In Argentina, a moderate number of studies have evaluated the trophic state of freshwaters. These studies were conducted in lentic (still water) (Quirós 2000; Volpedo et al. 2009) and lotic (flowing water) systems (Feijoó and Lombardo 2007; Mugni et al. 2013; Rosso and Fernández Cirelli 2013; Schenone et al. 2008; Sierra et al. 2013), and most of them were restricted to Pampean waterbodies. Although these waterbodies are naturally eutrophic (highly productive), a large portion of Pampean shallow lakes became hypereutrophic (very highly productive) over the last decades with the intensification of agriculture, urbanization and industrialization (Quirós et al. 2006; Volpedo et al. 2009). Likewise, the water quality of streams is likely to have decreased as a result of land use changes. It could be speculated that lotic systems are more resilient to eutrophication than lentic systems because they have unidirectional flow (Wais de Badgen 1998) and more atmospheric exchange (Dodds 2006). However, Pampean streams show low current velocities (Feijoó et al. 1999), so they probably behave similarly to small, shallow lentic systems (Dodds 2006).

In recent years, significant advances have been made to increase our understanding of stream trophic state and cultural eutrophication (Dodds and Oakes 2004; Dodds and Oakes 2006; Jarvie et al. 1998; Jarvie et al. 2008). However, most studies correspond to temperate water bodies of the Northern Hemisphere. Pampean streams are different from those of the Northern Hemisphere. They show low current velocities and fine bottom sediments (primarily, silt and clay), they originate in shallow depressions, are mainly fed by local subsurface runoff, they usually lack riparian vegetation and have low inputs of allochthonous organic matter (Feijoó et al. 1999). The production system of the Pampas is different too: agricultural intensification began in the 1980s, twenty years later than in industrialized countries (Viglizzo et al. 2011) and average fertilizer rates range between one third and one fifth of those of the United States and United Kingdom (Banco Mundial database); farmers rarely apply fresh manure, and a large proportion of beef production is still forage-based (only one out of four animals slaughtered in the country goes through a confinement system (Moscuza 2010; Robert et al. 2009). These differences suggest that nutrient loads and stream water quality are different from those described in the Northern Hemisphere.

Feijoó and Lombardo (2007) reported that nutrient levels in Pampean streams are between two and four fold those of other lotic systems of the world in the case of P and similar to those of basins with agricultural use in the case of N. Mugni et al. (2005) reported P and N concentrations of four Pampean streams that are higher (between four and tenfold) and lower (less than half), respectively, than those of rivers from intensively cultivated basins of Europe and North America. Feijoó and Lombardo (2007) suggest that the high levels of P are related to the sedimentary origin of the landscape in addition to land use changes. On the other hand, Mugni et al. (2013) suggest that the modest nitrate (NO_3^-) concentrations are the result of low N fertilization rates associated to soybean cultivation. Nevertheless, these authors could be underestimating nutrient contents since they measured dissolved inorganic forms rather than totals (Dodds 2003). According to Jarvie et al. (1998), nutrient speciation varies between rivers draining land with different uses, and nutrient partitioning enables relating water quality to the source areas contributing to nutrient enrichment.

The objectives of this study were to determine water concentrations of different N and P fractions, trophic state and nutrient limitation for algal growth in a typical Pampean stream, and to compare them with different land uses (urban/industrial versus agricultural) along the watercourse. A complete characterization of nutrient contents will contribute to a better understanding of the linkages between nutrient sources and their impact on water quality, to use as a basis for mitigation measures and control strategies.

Materials and Methods

Study region

The study was conducted along the Pergamino stream, in the Rolling Pampas, North Buenos Aires Province in Argentina (Figure 1). The corresponding basin has a surface of 2092 km^2, it has well defined boundaries, a well-developed drainage network and a single outlet (Uriburu Quirno et al. 2010). The Pergamino stream is a tributary of the Arrecifes river, which flows into the Paraná river. It is a second order stream and it has a total length of 109 km and an average slope of 0.046% (Uriburu Quirno et al. 2010). The stream originates in a depressed area that forms a shallow lagoon system with a swamp; it flows along a NW-SE axis, and presents tributaries in both banks. In the mid-section, it passes through the city of Pergamino, with a population of 104.590 (INDEC 2010). Like other Pampean streams, it is effluent, and groundwater discharge constitutes its base flow (Galindo et al. 2007).

The area lies on two horizontal sedimentary sequences: the Plio-Pleistocene Puelches in the lower part and the Middle-Upper Quaternary Pampeano sequence in the upper level (Galindo et al. 2007). The Pampeano sediments include volcanic material transported from the Andes by alluvial and eolian action, which are rich in P (Morrás 1999). The dominant upland soils are Argiudolls. These soils have a silt loam A horizon without eroded phase, they are deep,

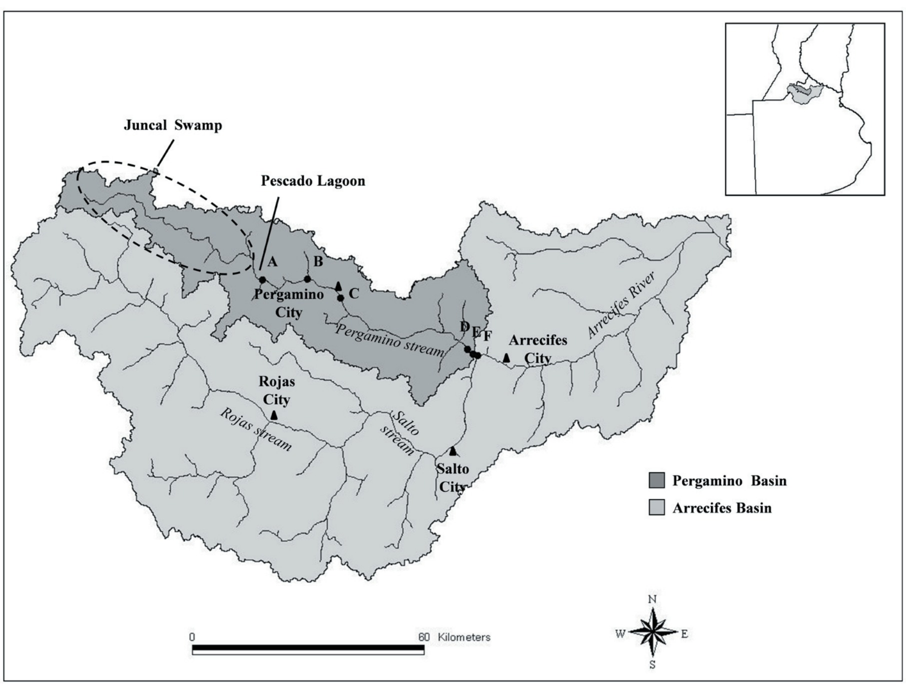


Figure 1. Map of the study region and location of sampling sites. Sites A and B are near the stream source, with agriculture as the dominant land use in the upland and mid-slope landscape and pastures or natural grasslands with livestock in the lowlands; site C is downstream the city of Pergamino (urban and industrial use), and sites D, E and F are at the mouth of the stream, where agriculture is the dominant land use.

Figura 1. Mapa de la región de estudio y ubicación de los sitios de muestreo. Los sitios A y B se encuentran cerca de la naciente del arroyo, representan un área de uso exclusivamente agropecuario con agricultura en la parte alta y media del paisaje, y cría bovina extensiva en los bajos; el sitio C se encuentra aguas abajo de la ciudad de Pergamino (uso urbano e industrial), y los sitios D, E y F se encuentran en la desembocadura del arroyo, donde el uso de la tierra es agropecuario.

well developed and well drained. The long smooth slopes towards the Pergamino Creek have soil complexes containing upland soil intermingled with varying proportions of alkaline and saline alfisols of the stream sides (INTA 1972a).

The climate is temperate humid without a dry season, with mean annual temperature of 16.5 °C. The mean annual rainfall for the 1910-2018 period was 988 mm, with an occurrence of 68% of total rainfall between October and March (spring and summer) (Hall et al. 1992). During the study period, the annual rainfall was 816, 822 and 1486 mm for 2010, 2011 and 2012, respectively (Agroclimatological network database, INTA).

Agriculture is the main land use accounting for 98% of the area. Spring-summer crops are dominant, mainly soybean (77% of the cultivated area is assigned to full-season soybean and 14% to second-season soybean) and secondarily maize (9% of the cultivated area). Winter crops, particularly wheat (17% of the cultivated area) are sown preceding second-season soybean some years. Crops are generally sown without tillage and irrigation is rare. Grasslands and cultivated pastures cover 36% of the cultivated area (GIS network database, INTA, 2014-2015 growing season). Beef cattle production has been displaced to lowlands, including the stream banks (Chagas et al. 2010).

Sampling design and analytical procedures

Six sampling locations were selected along the Pergamino stream. The sampling programme was designed to compare nutrient concentrations at sites with different land-use types (urban/industrial versus agricultural). Sites A and B are near the stream source and surrounded by agricultural farms, with annual crops in the upland and mid-slope landscape (42 and 96% cultivated area in sites A and B, respectively) and pastures or natural grasslands used for cattle rearing in the lowlands (300 and 20-m riparian strips in site A and B, respectively) (Sánchez 2014). Site C is located immediately downstream the city of Pergamino, 2 km downstream the confluence of the tributary Chu-Chú. At this sampling site the watercourse receives point source discharges from the urban wastewater treatment works and the municipal industrial park. Subsequent sampling locations (sites D, E and F) are at the mouth of the stream, approximately 43 km downstream of site C, and agriculture is the dominant land use. In this part of the basin the relief is more undulated than in sites A and B, and continuous agriculture is practiced in ~80% of the area, limiting livestock production to the lowlands (INTA 1972b).

Stream water samples were obtained monthly between June 2010 and August 2011 and between April and May 2012 (n=14 for each site). Samples were collected at least three days after rainfall events so that they represented base flow conditions. Each month, one litre of water was collected at each sampling site from the middle section of the stream and at 15-30 cm depth, using a manual sampler. Samples were stored in polyethylene bottles previously washed with HNO_3 1:1 and rinsed with deionized water, and immediately transported to the laboratory and stored at 4 °C until analysed (APHA 1989). The analytical procedure is outlined in Figure 2. A subsample was filtered through 0.45 μm cellulose membrane filters and used to measure N and P dissolved fractions (Jarvie et al. 2008) and the unfiltered sample was used to measure total nitrogen (TN), total phosphorus (TP) and chloride (Cl^-). Total phosphorus and total dissolved phosphorus (TDP) were determined using the nitric acid-sulphuric acid oxidation technique, after digestion, the released orthophosphate was determined colorimetrically using the ascorbic acid method (APHA 1989). Soluble reactive phosphorus (SRP) was also determined colorimetrically using ascorbic acid method (APHA 1989). Particulate phosphorus (PP) was calculated as the difference between TP and TDP, and dissolved hydrolysable phosphorus (DHP) was calculated as the difference between TDP and SRP (Jarvie et al. 2008). Ammonium-nitrogen (NH_4-N) was measured using nesslerization method with preliminary distillation (APHA 1989). Nitrate-nitrogen was measured colorimetrically using the phenoldisulfonic acid method (Lewis and Freitas 1970). Total nitrogen and total dissolved nitrogen (TDN) were measured through digestion and steam distillation with Devarda's alloy (ISO 10048: 1991). Dissolved inorganic nitrogen (DIN) was calculated as the sum of NO_3-N and NH_4-N concentrations (Jarvie et al. 2008). Dissolved organic nitrogen (DON) was calculated as the difference between the TDN and DIN (Jarvie et al. 2008). Particulate nitrogen (PN) was calculated as the difference between TN and TDN. Chloride concentration was measured using the argentometric method (APHA 1989).

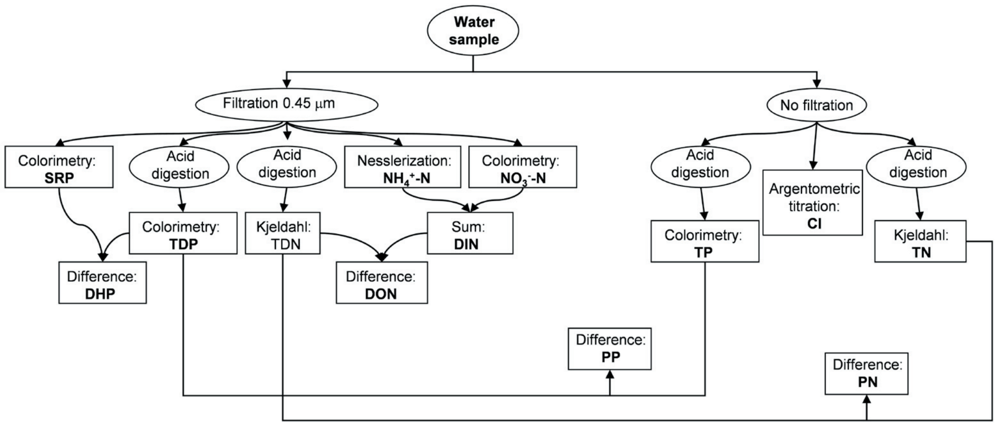


Figure 2. Laboratory analytical procedure. TN: total nitrogen, PN: particulate nitrogen, TDN: total dissolved nitrogen, DON: dissolved organic nitrogen, DIN: dissolved inorganic nitrogen, NO_3-N: nitrate-nitrogen, NH_4-N: ammonium-nitrogen, TP: total phosphorus, PP: particulate phosphorus, TDP: total dissolved phosphorus, SRP: soluble reactive phosphorus, DHP: dissolved hydrolysable phosphorus, Cl^-: chloride.

Figura 2. Esquema del procedimiento de laboratorio. TN: nitrógeno total, PN: nitrógeno particulado, TDN: nitrógeno disuelto total, DON: nitrógeno orgánico disuelto, DIN: nitrógeno inorgánico disuelto, NO_3-N: nitrógeno de nitrato, NH_4-N: nitrógeno de amonio, TP: fósforo total, PP: fósforo particulado, TDP: fósforo disuelto total, SRP: fósforo reactivo soluble, DHP: fosforo disuelto hidrolizable, Cl^-: cloruro.

Data analysis

Stream trophic state was determined using the Forsberg and Ryding index (1980) and the classification suggested by Dodds et al. (1998). The Forsberg and Ryding index is based on four parameters: TN, TP, chlorophyll a and transparency, and although it was originally published for lakes, it has been applied to lentic and lotic systems worldwide. The classification proposed by Dodds was based on the frequency distribution of nutrients (TN and TP) and chlorophyll across a large number of temperate streams from North America, New Zealand and Europe. Although both classifications comprise several parameters, we only used total nutrient contents to determine trophic state of the Pergamino stream. To assess nutrient limitation for algal growth, the N/P ratio was calculated as the molar ratio of TN to TP. Ratios >17 suggest that P is the limiting nutrient, ratios <10 suggest that N is limiting, and ratios between 10 and 17 suggest that both or neither nutrient is limiting (Forsberg and Ryding 1980).

Homogeneity of variance and normality of the residues of each analyzed variable were tested. Analysis of variance was used to compare nutrient fractions among sampling sites and mean values were compared through Duncan's test ($P<0.05$). With the purpose of detecting differences in nutrient speciation between sampling sites, the relative nutrient fractions were calculated at the six sites (Jarvie et al. 1998).

For a preliminary examination of the stream self-cleansing capacity, we suggest a calculation that takes advantage of the conservative behaviour of Cl^-. Chloride concentrations were used to calculate a dilution factor with increasing flow between site C and the stream mouth, as the ratio of average Cl^- concentration in site C to average Cl^- concentration in sites D, E and F. The same ratio was calculated for TN and TP to assess nutrient reduction between site C and sites D, E and F at the stream mouth. These ratios were compared with the calculated dilution factor to estimate how much of the nutrient decrease could be attributed to a dilution effect.

Results

Examining nutrient spatial variation along the Pergamino stream, we found that site C had the highest concentrations of TN, TP and SRP, sites A and B had the lowest concentrations and sites D, E and F had intermediate values (Figure 3 and Supplementary Table). Particulate nitrogen, DHP and NH_4-N also presented higher concentrations in site C compared to all other sites, which showed similar values. Nitrate-nitrogen concentration was highest towards the stream mouth (sites D, E and F), at site C the values were intermediate, and in the stream upper course (sites A and B) it was not detected. Dissolved organic nitrogen concentration at sites C, D, E and F was twice that of sites A and B. The concentration of PN at site C was higher than at sites D, E and F.

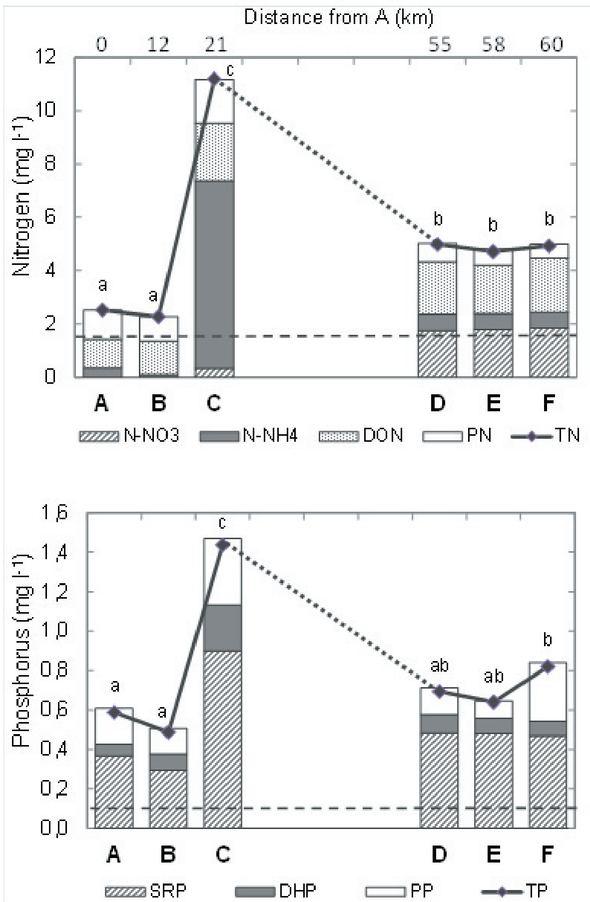


Figure 3. Mean concentration (mg/L) of nitrogen and phosphorus fractions at six sampling sites along the Pergamino stream during 2010-2012. Sites A and B are near the stream source, with agriculture as the dominant land use in the mid-slope and upland landscape and pastures or natural grasslands with livestock in the lowlands; site C is downstream the city of Pergamino (urban and industrial use), and sites D, E and F are at the mouth of the stream, where agriculture is the dominant land use. The dashed line indicates the value of TN and TP above which the course is considered to be hypertrophic according to Forsberg and Riding (1980). Different letters within TN and TP indicate significant differences between sites (P<0.05). TN: total nitrogen, PN: particulate nitrogen, DON: dissolved organic nitrogen, NO_3-N: nitrate-nitrogen, NH_4-N: ammonium-nitrogen, TP: total phosphorus, PP: particulate phosphorus, SRP: soluble reactive phosphorus, DHP: dissolved hydrolysable phosphorus.

Figura 3. Concentración media (mg/L) de fracciones de nitrógeno y fósforo en seis sitios de muestreo a lo largo del arroyo Pergamino entre 2010 y 2012. Los sitios A y B se encuentran cerca de la naciente del arroyo, representan un área de uso exclusivamente agropecuario con agricultura en la parte alta y media del paisaje y cría bovina extensiva en los bajos; el sitio C se encuentra aguas abajo de la ciudad de Pergamino (uso urbano e industrial), y los sitios D, E y F se encuentran en la desembocadura del arroyo, donde el uso de la tierra es agropecuario. La línea punteada indica el valor de NT y PT por encima del cual se considera al curso de agua como hipertrófico de acuerdo al criterio de Forsberg y Riding (1980). Letras diferentes para NT y PT indican diferencias significativas entre sitios (P<0.05). TN: nitrógeno total, PN: nitrógeno particulado, DON: nitrógeno orgánico disuelto, NO_3-N: nitrógeno de nitrato, NH_4-N: nitrógeno de amonio, TP: fósforo total, PP: fósforo particulado, SRP: fósforo reactivo soluble, DHP: fosforo disuelto hidrolizable.

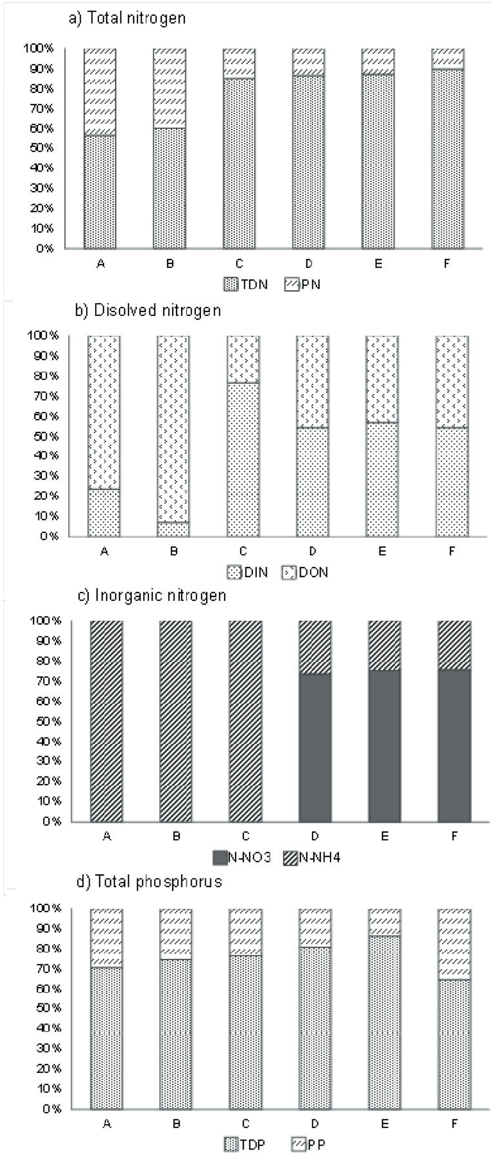
Considering TN and TP concentrations, 93% of the water samples presented a hypertrophic state (>0.1 mg TP/L and >1.5 mg TN/L) according to the criteria of Forsberg and Riding (1980) and an eutrophic state (>0.075 mg TP/L and >1.5 mg TN/L) according to Dodds et al. (1998). The remaining 7% of the samples were mesotrophic or eutrophic, according to the criteria of Dodds et al. (1998) and Forsberg and Riding (1980), respectively. The N/P ratios suggest that P was the limiting nutrient for algal growth in 38% of the samples, N was limiting in 25% of the samples and the remaining 37% could be limited by either or both of elements (Table 1).

The relative contribution of each fraction to the total nutrient concentration was analysed at each sampling site (Figure 4). In the case of P, TP consisted mainly of TDP (between 66 and 86%), and SRP dominated (between 78 and 87%) the dissolved fraction (TDP) in all the sites. In the case of N, there were important

Table 1. Number of samples with N, P and N and/or P limitation for algal growth at each sampling site. Sites A and B are near the stream source, with agriculture as the dominant land use in the mid-slope and upland landscape and pastures or natural grasslands with livestock in the lowlands; site C is downstream the city of Pergamino (urban and industrial use), and sites D, E and F are at the mouth of the stream, where agriculture is the dominant land use.

Tabla 1. Número de muestras con limitación de N, P y N o P para el crecimiento algal en cada sitio de muestreo. Los sitios A y B se encuentran cerca de la naciente del arroyo, representan un área de uso exclusivamente agropecuario con agricultura en la parte alta y media del paisaje y cría bovina extensiva en los bajos; el sitio C se encuentra aguas abajo de la ciudad de Pergamino (uso urbano e industrial), y los sitios D, E y F se encuentran en la desembocadura del arroyo, donde el uso de la tierra es agropecuario.

	A	B	C	D	E	F	Total
N limitation	7	7	1	1	-	4	20
P limitation	2	1	7	7	5	7	29
N and/or P limitation	4	5	5	5	6	2	27



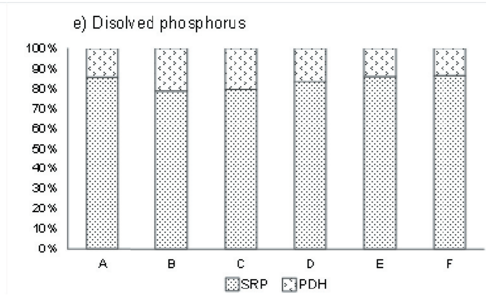


Figure 4. Relative nutrient fractions at each sampling site. Sites A and B are near the stream source, with agriculture as the dominant land use in the upland and mid-slope landscape and pastures or natural grasslands with livestock in the lowlands; site C is downstream the city of Pergamino (urban and industrial use), and sites D, E and F are at the mouth of the stream, where agriculture is the dominant land use. TN: total nitrogen, PN: particulate nitrogen, TDN: total dissolved nitrogen, DON: dissolved organic nitrogen, DIN: dissolved inorganic nitrogen, NO_3-N: nitrate-nitrogen, NH_4-N: ammonium-nitrogen, TP: total phosphorus, PP: particulate phosphorus, TDP: total dissolved phosphorus, SRP: soluble reactive phosphorus, DHP: dissolved hydrolysable phosphorus.

Figura 4. Fracciones relativas de nutrientes en cada sitio de muestreo. Los sitios A y B se encuentran cerca de la naciente del arroyo, representan un área de uso exclusivamente agropecuario con agricultura en la parte alta y media del paisaje y cría bovina extensiva en los bajos; el sitio C se encuentra aguas abajo de la ciudad de Pergamino (uso urbano e industrial), y los sitios D, E y F se encuentran en la desembocadura del arroyo, donde el uso de la tierra es agropecuario. TN: nitrógeno total, PN: nitrógeno particulado, TDN: nitrógeno disuelto total, DON: nitrógeno orgánico disuelto, DIN: nitrógeno inorgánico disuelto, NO_3-N: nitrógeno de nitrato, NH_4-N: nitrógeno de amonio, TP: fósforo total, PP: fósforo particulado, TDP: fósforo disuelto total, SRP: fósforo reactivo soluble, DHP: fosforo disuelto hidrolizable.

differences among sites: there was a higher proportion of PN in agricultural sites A and B compared with the urban/industrial site C, and site C had a higher proportion of DIN within the TDN while sites A and B had higher proportions of DON within the TDN. In sites A, B and C, DIN consisted mainly of NH_4-N. The results of sites D, E and F showed similar trends to those of site C, except that there was not a predominant dissolved fraction, since the proportion of DIN was very similar to that of DON, and NO_3-N dominated the DIN fraction.

Average Cl^- concentration decreased from 14.56 to 8.93 mg/L (39%) between site C and the stream mouth (sites D, E and F). Therefore, it could be considered that between site C and the stream mouth there is a solute decrease of 39% due to dilution. Average TP and TN concentrations decreased from 1.44 to 0.72 mg/L (50%) and from 11.19 to 4.87 mg/L (56%), respectively, between site C and the stream mouth.

Discussion

Average TN and TP concentrations of the Pergamino stream are similar to those reported for other lotic systems of the Humid Pampas (Gabellone et al. 2010; Galindo et al. 2002; Schenone et al. 2008) and exceed the reference thresholds of environmental quality standards from different parts of the world (Table 2). The high nutrient levels can be attributed to natural and anthropogenic factors. On

Table 2. Environmental quality standards from different parts of the world and the results of this work.
Tabla 2. Estándares de calidad ambiental de distintas partes del mundo y los resultados del presente trabajo.

Description	Total nitrogen (mg/L)	Total phosphorus (mg/L)	Source
U.S. Environmental Protection Agency guideline for streams	<1.5	<0.1	Liang et al. (2014)
Threshold level for the good water quality in running surface waters of Estonia	<3.0		Iital et al. (2008)
Nutrient criteria for rivers and streams in the state of New Jersey		<0.1	Hausmann et al. (2016)
Limit value of Germany´s Working Group of the Federal States on Waters Problems Issues for water quality	≤3.0		Volk et al. (2009)
National Rivers and Streams Assessment 2008-2009 Ecoregion Coastal Plains	<0.624	<0.056	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Northern Appalachians	<0.345	<0.017	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Southern Appalachians	<0.240	<0.015	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Upper Midwest	<0.583	<0.036	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Temperate Plains	<0.700	<0.089	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Northern Plains	<0.575	<0.064	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Southern Plains	<0.581	<0.056	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Western Mountains	<0.139	<0.018	US EPA (2016)
National Rivers and Streams Assessment 2008-2009 Ecoregion Xeric Region	<0.285	<0.052	US EPA (2016)
Mean concentration of the Pergamino Stream (n:82)	5.11	0.78	This work

one hand, the Pergamino stream shows some characteristics of naturally enriched waterbodies: it drains a region of fertile soils, with phosphorus rich parent materials (Morrás 1999) and humid climate that favours nutrient loss (Volpedo and Fernández Cirelli 2010); furthermore, it is a shallow water course of low current velocity and without riparian vegetation, conditions that favour eutrophication. According to Amuchástegui et al. (2016), there is palynological evidence that eutrophic conditions of Pampean waterbodies existed before the expansion of agriculture in the region. However, there are virtually no large, completely pristine streams or rivers left to reconstruct baseline conditions before the expansion of agriculture (Quirós 2002). This naturally eutrophic state was probably enhanced, as a consequence of the anthropogenic activities developed in the basin: point source discharges from the urban wastewater treatment works and industries, clandestine discharge of septic tanks, storm-water runoff from the city of Pergamino, and diffuse agricultural runoff. For a better understanding of our results, it is convenient to analyse the spatial distribution of the total nutrients and their fractions along the stream.

Sites A and B exhibited the lowest nutrient contents compared to the other sites. In fact, the only samples that classified as mesotrophic and eutrophic corresponded to these sites. It is possible to speculate that this is because the stream drains a pond system characterized by N and P retention and removal (Baron et al. 2013; Jarvie et al. 2008). Furthermore, these sites are dominated by agricultural farms and there are no urban settlements which generally contribute to increase the nutrient content of water courses due to industrial and municipal discharge (Withers and Jarvie 2008).

With respect to nutrient fractions, it could be expected that particulate and organic fractions and NO_3-N were higher in sites A and B with respect to the other sites, because these fractions are associated with the contribution of agricultural runoff (Jarvie et al. 1998; Outram et al. 2016; Withers and Jarvie 2008). However, the absolute values of these fractions were not higher than those of downstream sites, except for DON, presumably because samples were obtained under base flow conditions, temporally disconnected from runoff events. However, when we analysed the relative contribution of each fraction, we found a higher proportion of PN (within TN) and DON (within the TDN) in sites A and B compared with the urban site C. In contrast with NO_3-N concentrations reported in streams of agricultural basins around the world, this fraction was not detected in sites A and B, presumably due to denitrification in the pond system of the stream source and in the floodplain of these sites and to the modest use of inorganic fertilizers (Table 3). Although agriculture intensification in the Pampas has been accompanied by a dramatic raise of N fertilization, application rates are still low and the region is still under negative N balances (fertilization<harvest exports) sustained by the mineralization of a rich soil organic matter pool, and N losses through leaching and runoff are usually low (Darder et al. 2010; Portela et al. 2006; Portela et al. 2009). In addition, fertilization is mainly related to maize and wheat production, which amounts to 23% of the cultivated area, while soybean, which is the most widespread crop of the region is rarely fertilized with N (Portela et al. 2006), and manure application, which represents another source of nutrients in water courses of the Northern Hemisphere (Withers and Lord 2002), is not frequent (Herrero and Gil 2008). On the other hand, TP concentrations at sites A and B were relatively high in comparison with those of Northern Hemisphere streams (Table 3). Considering that P fertilization rates are also modest in Pampasic basins, it is possible to speculate that stream P concentrations depend more on geochemical reactions of parent material than on land use (Amuchástegui et al. 2016; Feijoó and Lombardo 2007; Mugni et al. 2013). When comparing N and P totals of sites A and B of this study with other results obtained in the region (Amuchástegui et al. 2016; Feijoó and Lombardo 2007; Mugni et al. 2013; Mugni et al. 2005) we realize that quantifying only the dissolved inorganic fractions underestimates nutrient contents although these studies arrive to the same conclusion as we do with regard to the trophic status of Pampean streams.

Table 3. Total nitrogen, nitrate-nitrogen (NO_3-N), total phosphorus (TP) and soluble reactive phosphorus (SRP) concentration in watercourses draining agricultural basins from different parts of the world and the results of this work.

Tabla 3. Concentración de nitrógeno total (TN), nitrógeno de nitrato (NO_3-N), fósforo total (TP) y fósforo reactivo soluble (SRP) en cursos de agua que drenan cuencas agrícolas de distintas partes del mundo y los resultados del presente trabajo.

Stream or river or catchment/country	TN (mg/L)	NO_3-N (mg/L)	TP (mg/L)	SRP (mg/L)	Source
Saginaw River, USA	3.24	0.32	0.315		Einheuser et al. (2012)
Kolstad catchment, Norway	11.2		0.099		Bechmann et al. (2008)
Mørdre catchment, Norway	5.10		0.382		Bechmann et al. (2008)
Tõnga River, Estonia			0.548		Iital et al. (2008)
Räpu River, Estonia	5.41				Iital et al. (2008)
Blackwater River, UK		6.1	0.09		Outram et al. (2016)
Wylye River, UK	8.16		0.126		Yates and Johnes (2013)
Appalachian Region, USA		15			Boyer and Paquarell (1995)*
Seine Upper Basin, France		5.0			Meybeck (1998)*
Herring, North Carolina, USA		5.6			Stone et al. (1995)*
Central Nebraska, USA		5.0			Boyd (1996)*
Girou Basin, France		5.7			Probst (1985)*
Ohebach, Germany		5.9			Schulz and Liess (1999)*
Duero River Basin, Spain		2.53			Vega et al. (1998)
Kerbernez Stream, France		15.1			Molenat et al. (2008)
River Derwent, England		3.85			Jarvie et al. (1998)
Arrecifes Basin, Argentina		2.305		0.106	Mugni et al. (2005)
Arrecifes Basin, Argentina		0.726		0.289	Mugni et al. (2013)
Tributaries of the Paraná and Río de la Plata rivers, Argentina		1.59		0.18	Feijoo and Lombardo (2007)
Streams of Buenos Aires province, Argentina		1.84		0.18	Amuchástegui et al. (2015)
Pergamino Stream, Argentina (average of agricultural sites A and B of this work)	2.39	Not detected	0.54		This work

*From (Mugni et al. 2005)

The urban site C presented the highest concentrations of nutrients (except NO_3-N), reflecting N and P inputs from urban wastewater treatment works (without N and P stripping), industrial effluents without proper treatment and stormwater runoff. Furthermore, at this sampling site the watercourse receives the confluence of the tributary Chu-Chú; a small stream that passes through the city of Pergamino and receives clandestine industrial and domestic effluents and wastes. These discharges are rich in organic matter and release NH_4-N and phosphate (PO_4^{3-}) when decomposed (Wais de Badgen 1998), explaining the high levels of NH_4-N y SRP quantified in site C. We also speculate that high levels of P may originate from detergents that are an important component of municipal wastewater (Vega et al. 1998). The nutrient concentrations at this site are comparable to those of others urban/industrial catchments (Jarvie et al. 1998; Liang et al. 2014; Vega et al. 1998; Withers and Jarvie 2008; Yates and Johnes 2013), and N and P speciation is characteristic of waters receiving sewage effluent (Jarvie et al. 1998).

Towards the stream mouth (sites D, E and F), TN, TP and SRP concentrations were intermediate between the upper and the middle basin sites. Particulate nitrogen, NH_4-N and DHP concentrations decreased between site C and these sites reaching similar concentrations to those of the headwaters, reflecting a river "self-cleansing" process at this reach. Contrary to this trend, NO_3-N concentration was highest towards the stream lower reaches, probably, as a result of the nitrification of the high levels of NH_4-N detected in site C (which is striking because there are 41 km between sites C and F, and normally self-depuration occurs within 10 km) and from agricultural inputs from the whole basin that converge in these three sites (Amuchástegui et al. 2016).

Total N and P concentrations decreased by 50% between site C and sites D, E and F, but did not reach the headwater concentrations. These results indicate that Pergamino stream is unable to self-purify along its length, and that water quality at the stream mouth is influenced by effluent discharge at site C and agricultural activities throughout the basin. Considering that Cl^- concentration exhibited a 39% reduction between site C and the stream mouth, it is possible to speculate that nutrient reduction between these sites might result from a dilution effect due to increased flow (39% reduction) and other natural self-cleansing mechanisms (11% and 17% reduction for TP and TN, respectively).

The high NO_3-N concentrations towards the stream lower reaches and the high NH_4^+-N concentrations at site C explain the conditions of potential P limitation for algal growth at sites C, D, E and F. In contrast, N is the limiting element at site A and B, as described by US EPA (2000) for waters receiving agricultural runoff. Also, cattle accessing stream margins may represent a significant P loading source to the stream in these sites.

Although the absolute P concentrations differed according to land use, there was no difference in the relative contribution of each fraction to the TP concentration between sites, reinforcing the idea that the mobility of P in Pampean basins depends not only on land use but also on geochemical reactions (Amuchástegui et al. 2016; Feijoó and Lombardo 2007; Mugni et al. 2013). Instead, there is a marked difference in the relative contribution of each fraction to the TN concentration between sites with contrasting land use. At sites surrounded by agriculture (A and B) the organic and particulate fractions predominated. On the other hand, in sites with urban/industrial effluent discharges (site C) TN consisted mainly of inorganic forms.

Conclusions

During the study period, the Pergamino stream was highly productive (eutrophic/hypertrophic) as a result of point and diffuse source inputs in addition to the naturally high baseline nutrient concentrations. It is therefore necessary to develop nutrient criteria to determine trophy status that considers these regional conditions. An open question is if biological communities in this stream show signs of eutrophic status (in the sense of being polluted).

This study showed that lotic systems exposed to contrasting land uses in the surrounding landscape display different nutrient speciation and allowed to identify which are the critical fractions that should be monitored. Moreover, our results illustrate that quantifying dissolved inorganic fractions alone underestimates the nutrient enrichment and is insufficient to characterize and understand the lotic system. Total N and TP, as well as all component fractions of both nutrients should be determined in order to generate strong scientific evidence necessary to suggest changes or adjustments to management practices.

In this basin, point source discharge (industrial and domestic effluents) resulted in a great impairment of water quality, and, although the high concentrations quantified downstream the city of Pergamino decreased towards the mouth, they did not reach the values measured at the headwaters. The impact of agricultural activities on the deterioration of the stream's water quality is practically impossible to infer, since there are currently no pristine water courses in the region or data on water quality prior to the introduction of agricultural activities to establish a baseline. At present, there are no statutory targets for N and P concentrations in Argentina, but concentrations in this system were found to be greater than the environmental quality standards from different parts of the world. Therefore, it is imperative to design a programme for monitoring stream water quality at critical points and to adopt management strategies for nutrient input control such as adequate treatment of domestic and industrial effluents with efficient control of discharges, eradication of clandestine discharges and implementation of good agricultural practices.

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