The impact of agricultural land use on stream chemistry and inputs to an inland reservoir: case of the Sauce Grande River, Argentina

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Abstract Water quality in the Paso Piedras Reservoir has deteriorated, primarily due to periodic blue-green algal blooms, making it temporarily unfit for human consumption. This phenomenon results from the eutrophication of waters of the watershed, and nutrients are considered to be the primary contributors to degradation of freshwater quality. In order to reduce the levels of nitrogen and, most of all, phosphorus, entering the Paso Piedras Reservoir, it is necessary to understand the incidence of diffuse transfers of nutrients from agricultural soils. The nitrogen composition, soluble reactive phosphorus (SRP) and other physico-chemical parameters of the water were analysed in various different parts of the watershed in order to characterize water input to the reservoir from areas with different anthropogenic activity. The upper Sauce Grande basin was divided into three areas with different edaphic characteristics. The physico-chemical parameters measured in sampling surveys included: SRP, ammonium and nitrate, pH, conductivity, turbidity, and total solids. The results showed that the water of the Sauce Grande (areas 1 and 2) was not strongly contaminated, but in El Divisorio (Area 3, which is a sub-watershed whose stream flows directly into the Paso Piedras Reservoir), the levels of conductivity, total suspended sediments and SRP were so high that its contribution to the reservoir accounts for nearly 50% of the total SRP input. The main characteristics of El Divisorio watershed that make it a diffuse source of SRP were not only that its soils, under agricultural-livestock production, have significant slopes, so that water and wind erosion are faster, but also that human intervention had caused the destruction of aggregates. The results showed the influence of the soil characteristics, production systems and the micro-environment developed in the reservoir on the characteristics of waters flowing out of the reservoir. The two villages located in Area 2 had no significant influence on the concentration of nitrogen compounds and SRP found downstream.

Key words ammonium; diffuse source; eutrophication; nitrate; phosphorus; water chemistry

Impact de l'occupation agricole du sol sur la chimie de l'eau de rivière entrant dans un réservoir continental: cas de la Rivière Sauce Grande, Argentine

Rèsumé La qualité de l'eau dans le barrage de Paso Piedras s'est détériorée, essentiellement en raison de blooms d'algues bleu-vert, ce qui l'a rendue temporairement non potable. Ce phénomène est dû à l'eutrophisation des eaux provenant du bassin versant, et les nutriments sont considérés comme étant les premiers responsables de la dégradation de la qualité de l'eau douce. Afin de réduire les niveaux d'azote et surtout de phosphore entrant dans le barrage de Paso Piedras, il est nécessaire de comprendre l'incidence des transferts diffus des nutriments des sols agricoles. La composition des formes azotées, le phosphore réactif soluble (PRS) et d'autres paramètres physico-chimiques de l'eau ont été analysés en différents points du bassin versant afin de caractériser l'eau entrant dans le réservoir depuis des zones présentant des activités anthropiques différentes. Le bassin supérieur de Sauce Grande a été divisé en trois zones aux caractéristiques édaphiques différentes. Les paramètres physico-chimiques mesurés lors des campagnes d'échantillonnage comprennent: le PRS, l'ammonium et le nitrate, le pH, la conductivité, la turbidité et la charge solide totale. Les résultats montrent que l'eau de Sauce Grande (zones 1 et 2) n'est pas fortement contaminée, mais que les niveaux de conductivité, charge solide totale et PRS sont si élevés dans la zone de El Divisorio (Zone 3, qui est un sous-bassin qui alimente directement le réservoir de Paso Piedras) que sa contribution au réservoir représente près de 50% de l'apport total de PRS. Les caractéristiques principales du bassin de El Divisorio qui en font une source diffuse de PRS sont non seulement les pentes significatives des sols supportant la production en agriculture–élevage, qui accélèrent l'érosion hydrique et éolienne, mais aussi la destruction des agrégats due aux interventions humaines. Les résultats montrent l'influence des caractéristiques des sols, des systèmes de production et du micro-environnement développé dans le réservoir sur les caractéristiques des eaux sortant du réservoir. Les deux villages situés dans la zone 2 n'ont pas d'influence significative sur la concentration en composants azotés et en PRS observés à l'aval.

Mots clefs ammonium; source diffuse; eutrophisation; nitrate; phosphore; chimie de l'eau

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INTRODUCTION

Even though artificial regulation of freshwater streams has been undertaken for thousands of years, the necessity to supply water for human consumption, or for producing energy, or to disperse undesirable material has greatly increased the number of management projects in more recent times. At the same time, the larger number of freshwater sources has resulted in an increase in population, of living standards, and of land use and irrigation.

The Paso Piedras Reservoir in the upper basin of the Sauce Grande River in Argentina supplies water to the city of Bahía Blanca and much of the surrounding area. The quality of the reservoir water has deteriorated sharply during recent years, basically due to periodic blue-green algal blooms, which render the water temporarily unfit for human consumption. It has been suggested that this phenomenon results from the eutrophication of waters of the watershed, caused by nutrient inputs from diffuse sources, comprising areas with an intensive agricultural and livestock activity, or, less probably, by three small urban areas in the upstream part of the watershed.

Nutrients are considered primary contributors to the eutrophication and degradation of freshwater quality (Daniel *et al*., 1998), so the ultimate goal is to reduce the levels of nitrogen and, most of all, phosphorus (P), entering the Paso Piedras Reservoir. The understanding of the incidence of diffuse transfers of phosphorus from agricultural soils and the role of hydrology in P transfer is crucial to enable an effective management of a grassland soil (Haygarth & Jarvis, 1999; Preedy *et al*., 1999; Haygarth *et al*., 2000). In fact, the adoption of integrated crop management practices could help to improve the quality of the water in the reservoir as well as to maintain good water quality in aquifers. To accomplish this goal, it is necessary to undertake basic surveys to understand the functioning of the watershed, which would help find the solutions to a major regional problem, via the adoption of integrated agricultural and cattle management practices throughout the watershed.

The aim of this study was to analyse, at various sites within the watershed, nitrogen composition, soluble reactive P and other physico-chemical parameters of the water to characterize water input to the reservoir from areas where different human activities were taking place.

MATERIALS AND METHODS

Description of the upper Sauce Grande River basin

The Sauce Grande basin is a small lowland river watershed (4181 km^2) located in the south of the Province of Buenos Aires, Argentina, with the main stream flowing from the Sierras Australes (Sierras de la Ventana) to the Atlantic Ocean. The upper watershed (Fig. 1), about 1840 km^2 in area, includes the Paso Piedras Reservoir (38°41′S, 62°15′W), which is the primary water supply source for the city of Bahía Blanca and its industrial settlement area. The Sauce Grande River (62 km in length from its source to the reservoir) collects water from 12 main tributaries entering the river upstream of the reservoir and constitutes the major water supply to the reservoir. An additional stream is El Divisorio, which presently flows directly into the reservoir, draining most of the lower part of the watershed.

The maximum and minimum mean annual air temperatures are around 25°C and 15°C, respectively. The mean total annual precipitation is a little higher than 1000 mm, distributed in a humid autumn and spring, with lower rainfall during winter and summer.

The edaphic domains of the upper Sauce Grande River basin (Fig. 1) were established based on the soil map of INTA (INTA, 1989) and a characterization made by Adúriz *et al*. (2003), and three areas were determined with the following characteristics:

– **Area 1** (613 km^2; 33.3% of the total area), where sites 1 and 3 are located, has the highest elevations of the watershed, around 600–700 m a.s.l. Most of the area is formed by high outcropping rocks and steep slopes without soil. The percentage of cultivable land (loam-clay-sandy) in this area is about 10%. The rest of the area is mostly rock (60%) or shallow soil with natural vegetation, for the most part used for animal husbandry. In one of the valleys, there is a small conglomeration of weekend tourist houses with a permanent population of about 350 persons.

Fig. 1 The upper Sauce Grande basin, showing the main edaphic domain (areas 1, 2 and 3) and the nine sampling sites. Top right: basin location in Buenos Aires Province, Argentina. For details see text.

– **Area 2** (944 km^2; 51.3% of the total area) is the middle area where sites 2, 4, 5, 6 and 7 are located. Many of these soils are limited by their shallow depth; they are prone to water erosion and the percentage of workable land (loam or loam-clay-sand) is about 50%. Historically, the land use is mixed: 60% of the total area is used for agriculture, and 40% predominantly for animal husbandry. The soils are under intensive use, have good fertility, and show no significant degradation; this is the area where more technological resources are applied to control water erosion. There are two villages in the area (Sierra de la Ventana and Saldungaray) with permanent populations of 5000 and 4000, respectively.

– **Area 3** (283 km^2; 15.4% of the total area) is the unit that corresponds to the sub-watershed of El Divisorio stream (Site 8), a tributary that flows directly into the Paso Piedras Reservoir. In the main river, downstream of the reservoir, at a short distance from the weir, Site 9 was installed. The limitations are the shallow depth in the high locations and water erosion on the slopes. The percentage of workable land (loam or loam-clay-sand) is about 75%; this area is less fertile than Area 2 and about 80% is used predominantly for animal husbandry. However, these soils have been periodically ploughed, so their original structure has been altered and their stability is very low.

Differences in the percentages of cultivable soil and production systems in four contrasting sub-watersheds located in areas 1 and 2 were estimated using charts nos 3963-6-1, 3963-6-2, 3963-6-3 and 3963-6-4 from the Instituto Geográfico Militar of Argentina (http://www.igm.gov.ar).

Field and laboratory methods

The first sampling survey was conducted between November 1999 and December 2001 at eight selected sites: sites 1, 2 and 7 along the main river; sites 3, 4, 5 and 6 on four small tributaries, and Site 8 located on El Divisorio. A second survey was done between November 2002 and December 2004 at sites 7 and 8, and a new site, 9, located downstream of the reservoir. These locations are shown in Fig. 1 and the soil characteristics and predominant production systems are given below. In both surveys, samples were collected for water quality analysis using manual field sampling methods and the frequency of sampling was between 20 and 25 days. On each sampling date, physico-chemical parameters, including water conductivity, turbidity, dissolved oxygen and pH were measured *in situ* using a Horiba U-10 meter.

Water samples were preserved by the addition of concentrated sulphuric acid, then transported to the laboratory in ice and kept in a cold chamber (4°C) until they were processed—within a period of three days. Prior to analysis the collected samples were filtered through a 0.45-micron polycarbonate filter and the suspended sediment filtered was oven dried and weighed. Phosphate (soluble reactive phosphorus, SRP) was determined according to the methods of Eberlein & Kattner (1987), which are based on the original method with molybdenum blue; ammonium and nitrate were determined according to Treguer & Le Corre (1975); and nitrite was determined by the Grasshoff method (1983). In the first survey, ammonium was only measured at sites 7 and 8. Particulate material was only measured in the second survey.

During the first survey in the main river close to Site 7, and in El Divisorio close to Site 8, the streamflow was measured and recorded every 15 min using an electronic data logger. Continuous limnigraphs (model LF-103 and LF-324 EEPROM type; Génica Ingeniería, Bahía Blanca, Argentina) were operated at both stations. Using available software, and the HYMO model, flow curves/water level (H–Q curves) were obtained for each of the profiles.

The data were tested for normality and homogeneity of variance with the Lilliefors and Bartlett tests, respectively (Sokal & Rohlf, 1995). In some cases, where lack of normality or homogeneity was observed, different transformations were applied to the data and the ln transformation was found adequate for both tests. Each variable underwent a simple variance analysis (ANOVA; $p \leq 0.05$) and the difference between the average values was analysed by using the SNK method of multiple comparisons ($p \leq 0.05$).

RESULTS

Mean values of the parameters evaluated in the 1999–2001 survey

The values of the parameters measured at eight sites in the upper Sauce Grande basin, throughout the two years of the first survey, are presented in Table 1, and show the trophic condition of the system.

Table 1 Means of nutrient content and environmental parameters measured in 35 water samples periodically taken in the eight sites selected in the Sauce Grande system during the 1999–2001 survey.

Site	NO_3-N (µg L^{-1})	NO_2-N (µg L^{-1})	PO_4-P (µg L^{-1})	Conductivity (µS cm^{-1})	Turbidity (NTU)	pH	Dissolved oxygen (mg L^{-1})
1	27.76 a	1.44 a	4.23 a	85.62 a	3.27 a	7.46 a	9.65 a
2	206.12 ab	2.17 ab	17.55 ab	200.63 b	4.66 a	7.58 a	10.42 a
3	1137.75 d	6.55 bcd	37.62 b	357.25 d	4.65 a	7.67 a	9.90 a
4	448.62 bc	6.29 bcd	24.90 b	286.02 c	6.66 a	7.55 a	11.23 a
5	1852.50 e	6.70 bcd	26.34 b	412.87 e	2.11 a	7.44 a	10.09 a
6	1815.62 e	10.36 d	32.27 b	421.87 e	4.84 a	7.34 a	9.65 a
7	708.62 c	5.16 abc	37.44 b	304.00 c	5.87 a	7.33 a	10.87 a
8	1027.87 d	8.54 cd	168.87 c	1056.37 f	14.64 b	7.71 a	9.23 a

Means labelled in each column with different letters (a–f) are significantly different (SNK test, $p < 0.05$).

Even though the concentrations of the two forms of inorganic nitrogen and soluble reactive phosphorus (SRP) are only part of the total of N and P present in the water column, many classifications of the trophic condition of water are made based on these indicators. In this sense, the data on the last row of Table 1 would show that the water in the watershed of the Sauce Grande was not strongly contaminated since the average values of both nutrients were below the limits established by Omermik (1976) for agricultural land.

However, the classification of the waters in a region by their general characteristics might lead to mistakes, since these can differ greatly from one site to another. In fact, when nutrients concentration values and other physico-chemical parameters of each particular site (Table 1) were analysed, it was possible to determine areas with different degrees of trophic state. The level of SRP in the El Divisorio waters was near 170 µg L^{-1}; that is three times the value of 50 µg L^{-1} established by Mueller & Helsen (1996) for waters entering a reservoir or a lake. The same tendency was observed for conductivity (dissolved salts) and turbidity (total suspended sediments).

It must be highlighted that, in general, N-NO_3 concentrations found during the two years were lower than 2000 µg L^{-1}—well below those considered as being in the polluted water category. However, levels exceeding 1000 µg L^{-1} indicate anthropogenic influence, e.g. agricultural runoff (European Environment Agency, 1995). The data also show that the N-NO_3 concentrations in the water of the Sauce Grande River (Site 7) were significantly lower than that in El Divisorio (Site 8). As regards N-NH_4 concentrations (not shown in Table 1), the average values were generally below 100 µg L^{-1}. There was no N-NO_2 accumulation, since its concentration was low (10 µg L^{-1} or less), showing that the nitrite oxidation to nitrate occurs normally. The data of Table 1 allowed us to classify the watershed into two main types: (a) the waters located in areas 1 and 2 as mesotrophic; and (b) waters located in Area 3, in El Divisorio, as eutrophic.

Flow and nutrient input to the reservoir in the 1999–2001 survey

As stated above, the water from the high watershed reaches the Paso Piedras Reservoir through the main river and through El Divisorio stream. The seasonal flow values at sites 7 and 8 (Table 2) measured during the first two sampling years show that the main river stream contributes most of the flow; in 2001 (high rainfall, 1480 mm), the flow was almost double that of the previous year

Table 2 Seasonal values of flow (m^3 s^{-1}) and total annual volume (Hm^3 $year^{-1}$) measured at sites 7 and 8 in the 1999–2001 survey.

Site	Year	Flow: Summer	Autumn	Winter	Spring	Annual volume
7	1999/2000	1.93	4.65	2.66	3.75	102.40
	2000/2001	3.23	11.10	5.26	6.03	201.90
8	1999/2000	0.36	0.80	0.62	0.73	19.80
	2000/2001	0.63	1.43	1.29	1.34	37.00

Table 3 Mean annual concentration (μg L^{-1}) values of $N\text{-}NO_3$, $N\text{-}NH_4$ and $P\text{-}PO_4$ (SRP) measured at sites 7 and 8 during the 1999–2001 survey.

		$N\text{-}NO_3$	$N\text{-}NH_4$	$P\text{-}PO_4$ (SRP)
1999/2000	Site 7	550	28	37
	Site 8	1060	30	142
2000/2001	Site 7	870	54	39
	Site 8	997	54	196

Table 4 Mean annual nutrient losses by surface runoff and baseflow of $N0_3$-N, NH_4-N and SRP, estimated at the main river (Site 7) and in El Divisorio (Site 8) during the first survey (1999–2001).

		Nutrient losses (kg ha^{-1})		Input to the dam (mg $year^{-1}$)	
		Site 7	Site 8	Site 7	Site 8
1999/2000	NO_3-N	0.36	0.74	56.30	20.96
	NH_4-N	0.03	0.04	5.74	1.20
	PO_4-P	0.03	0.10	3.74	2.80
2000/2001	NO_3-N	1.13	1.30	175.30	36.84
	NH_4-N	0.14	0.14	21.64	3.96
	PO_4-P	0.05	0.25	7.76	7.24

(normal rainfall, 910 mm). The average flow follows the typical seasonal pattern characterized by higher precipitation during autumn and spring months than that registered during winter and summer. There were occasional storms, which caused quick and strong flow increases.

In order to calculate the loss of nutrients from the watershed to the reservoir, we used the flow measurements made at sites 7 and 8 (Table 2) and the mean annual concentrations of different nitrogen species and SRP at the same sites (Table 3). All the water from areas 1 and 2 passes through Site 7 and the water coming from El Divisorio sub-basin passes through Site 8 (Fig. 1).

As shown in Table 4, the loss of nutrients due to surface runoff and from baseflow (expressed in kg ha^{-1}) was higher in El Divisorio than in areas 1 and 2. The amount of nutrients (mg $year^{-1}$) that reached the reservoir from the main riverbed of the Sauce Grande (Site 7) and El Divisorio stream (Site 8) can be seen in Table 4. Although annual runoff for El Divisorio stream is low compared to that of the Sauce Grande River, the contribution of SRP from El Divisorio to the reservoir accounts for nearly 50% of the total SRP input; however, the main source of nitrogen ($N\text{-}NO_3 + N\text{-}NH_4$) was the main river of the system (Table 4).

The annual average values of turbidity and conductivity determined at sites 7 and 8 (Table 1) showed that the water of the Sauce Grande River was clear, while El Divisorio stream water was turbid, as it had a considerable amount of total particulate material and dissolved salts.

Anthropogenic activities and nutrient concentrations in water

As already mentioned above, the non-cultivable soils are purely devoted to animal husbandry on natural grassland. Meanwhile, the cultivable soil supports mixed production systems with extensive crops and/or cattle farming, in different ratios. The use of fertilizers (N and P) in the entire watershed was less than 5 kg ha^{-1} applied to 22% of the total area of the upper basin (Adúriz *et al.*, 2003). Over a similar surface, chemical control of weeds, insects and fungi was used according to the crop requirements.

In order to establish different diffuse sources among the sub-watersheds, four contrasting sub-watersheds were identified in areas 1 and 2 (Table 5) based on the different percentages of cultivable soil and production systems used. The sub-watershed Nacientes, (where Site 1 was located) was characterized as the most contrasting one: it is located near the river source, has less than 10% of cultivable land, agricultural activity is almost nil and cattle farming is very limited (it was estimated as being able to support no more than 0.1–0.2 head of animals per ha). The San Teófilo sub-watershed (where Site 4 was located), had workable soil covering less than 20% of its

Table 5 Length of the tributary (km), total area (km^2), total farmland area (km^2) and the farmland area (km^2) devoted each year to agriculture in each sub-watershed.

Site	Sub-watershed	Length (km)	Total area (km^2)	Farmland (km^2)	Agriculture (km^2)
1	Nacientes	25	120.0	12	2
4	San Teófilo	21	56.0	12	8
5	Rivera	20	173.0	140	85
6	Toro	46	180.0	110	66

Table 6 Mean concentration values of $N\text{-}NO_3$ and $P\text{-}PO_4$ measured during the 1999–2001 survey at sites 1, 4, 5 and 6 of the sub-watersheds described in Table 5.

		Site 1	Site 4	Site 5	Site 6
$N\text{-}NO_3$ (μg L^{-1})	1999/2000	28.86	469.24	1783.40	1709.75
	2000/2001	26.71	429.06	1922.40	1353.92
$P\text{-}PO_4$ (μg L^{-1})	1999/2000	3.95	21.75	23.86	24.55
	2000/2001	4.51	28.13	28.87	41.88

total area: agricultural activity was minimal; cattle farming was limited by the topography and the quality and quantity of natural grassland. In contrast, in the sub-watersheds Rivera and Toro (locations of sites 5 and 6, respectively), the area devoted each year to agriculture was greater than 60% and the agricultural-livestock activity is significant and increasing.

At Site 1 near the river source, the concentrations of $N\text{-}NO_3$ found were 16 times lower than those found at Site 4 (Table 6). However, at sites 5 and 6, where farming activities are high, the $N\text{-}NO_3$ values were about three times greater than those in Site 4. These low values can be attributed to the fact that the percentage of cultivable soil and the agricultural-livestock activity were very low in sites 1 and 4. At the four sites, the concentrations of $N\text{-}NH_4$ were one tenth of that of $N\text{-}NO_3$ and followed a pattern similar to that of nitrate (not shown in Table 6).

Similar to the measured nitrate concentrations, the content of SRP (Table 6) at Site 1 was significantly lower, compared to that at sites 4, 5 and 6; the concentrations at these three sites did not differ much, either from each other or from those at the stations located on the main river.

Production systems and soil characteristics

Table 7 shows the results of the second survey: (a) the influence of areas 1 and 2 (Site 7) and El Divisorio (Site 8) on some parameters of the water that reaches the reservoir; and (b) the influence of the micro-environment developed in the reservoir upon the characteristics of outflow water from the reservoir (Site 9). Ammonium values (Table 7) were similar at the three sites. In turn, the

Table 7 Means of environmental parameters measured in 32 water samples periodically taken in the three sites selected in the Sauce Grande system during the 2002/2004 survey.

	Site 7 (main river upstream of the reservoir)	Site 8 (El Divisorio upstream of the reservoir)	Site 9 (main river downstream of the reservoir)
$NO_3\text{-}N$ (μg L^{-1})	529.36 b	923.56 c	367.44 a
$NO_2\text{-}N$ (μg L^{-1})	4.96 b	6.13 c	3.40 a
$NH_4\text{-}N$ (μg L^{-1})	72.64 a	94.61 a	85.01 a
$PO_4\text{-}P$ (μg L^{-1})	15.59 a	76.88 b	77.76 b
pH	7.60 a	7.90 a	7.60 a
Turbidity (NTU)	4.00 a	32.80 b	3.90 a
Conductivity (μS cm^{-1})	388.10 a	947.90 b	788.70 b
Part. mat. (mg L^{-1})	6.60 a	45.70 b	6.40 a

Means labelled in each row with different letters (a–c) are significantly different (SNK test, $p < 0.05$).

highest values of nitrate and nitrite values were found at Site 8 and the lowest at Site 9. In El Divisorio (Site 8) and at the outlet of Paso Piedras Reservoir (Site 9), the SRP concentrations were high. Turbidity and conductivity values showed that water in the main stream of the Sauce Grande (Site 7) was clear, with low dissolved salts and total particulate material concentrations. In contrast, the water of El Divisorio stream (Site 8) was markedly turbid, with a significant amount of total particulate material and dissolved salts. At Site 9, at the outlet of the reservoir, the particulate material and, consequently, turbidity decreased to the values of Site 7, while the amount of dissolved salts (conductivity) was similar to that of Site 8 (Table 7).

It must be highlighted that: (a) the SRP and conductivity determinations made for El Divisorio stream and downstream of the dam were not only high but also very similar; and (b) a significant amount of solids transported by El Divisorio waters were deposited in the reservoir, as the amount of particulate material exiting the reservoir was much lower. These results agree with the results in Table 5, in that the sub-watershed of El Divisorio stream, in spite of its smaller area, was an important source of nutrient inputs into the reservoir, mainly SRP and phosphorus sorbed onto the deposited solids.

DISCUSSION

When nutrient concentrations in the tributaries (Table 1, sites 3, 4, 5 and 6) are compared with those of Site 7 on the main river, it is clear that the two inhabited areas (Sierra de la Ventana and Saldungaray in Area 2) have no influence over the concentrations of nitrogen compounds and SRP found downstream. Ammonium concentration generally is extremely low in surface water, but high $N\text{-}NH_4$ concentrations are typical of urban runoff and inadequate waste treatment. In our study, the inputs of sewage into the Sauce Grande River from these small towns caused no significant variations in the nutrient values. So it can be concluded that inhabited areas were not significant point sources.

However, nitrate concentrations in the tributaries (Table 6) were related to the percentage of farmland in the sub-watersheds (Table 5): water $N\text{-}NO_3$ levels in affluent draining watersheds with less than 10% agricultural land were below 30 μg N L^{-1}, whereas those in watersheds with about 20% agricultural land were around 450 μg N L^{-1}. In streams draining watersheds with about 70% agricultural land, the nitrate levels were even higher, as in sub-watersheds Rivera and Toro (sites 5 and 6, respectively), where the concentrations of nitrate in the affluent were between 1300 and 2000 μg N L^{-1}.

The concentrations of SRP in the main river and in El Divisorio stream can only be considered as indicative as regards the phosphorus contribution made to the watershed of the Paso Piedras Reservoir. SRP is one of the fractions of the phosphorus labile forms originating from the watershed, which after undergoing transformations or various recycling pathways, are made available for uptake by the biota. SRP is easily accessible for aquatic plants to the extent that, when measured in surface waters, it might only represent a residual percentage since it has been mostly absorbed by plants (Ongley, 1997). Variations in flow, total suspended sediment, and the proportion that is in soluble and particulate forms will account for the loading of phosphorus in labile forms.

Even though SRP is a part of the total-P transported, the SRP values at Site 8 exceeded 50 μg P L^{-1}, which is considered as the limit above which the water can be classified as contaminated, indicating anthropogenic influence such as from sewage effluent or intensive agriculture. In order to control eutrophication, the US EPA (Environmental Protection Agency) recommendations are that total phosphate should not exceed 50 μg P L^{-1} in a stream at a point where it enters a lake or reservoir, and should not exceed 100 μg P L^{-1} in streams that do not discharge directly into lakes or reservoirs (Mueller & Helsel, 1996).

The main characteristics of the El Divisorio watershed that would account for its importance as a diffuse source of SRP were due not only to human intervention, but also to the runoff, which causes significant erosion because of the topography and type of soils in this area. The soils under crop cultivation/livestock production have steep slopes where water and wind erosion process are speeded up by the farming practises. The prevailing mixed agro-systems, with agricultural activity and strong animal husbandry (calf raising and cattle finishing), and the fine-particled soils with high P content and high desorption capacity, explain why the El Divisorio sub-watershed contributes much of phosphorus and sediments that reach the Paso Piedras Reservoir. Even though the soils in the El Divisorio sub-watershed have acceptable structural stability values (Cacchiarelli *et al*., 2004a), they are cyclically used for animal husbandry followed by conventional sowing of intensive crops (Adúriz *et al*., 2003). This agricultural activity has caused the destruction of soil aggregates, resulting in potentially erodible soils with great amounts of fine particles which, upon interaction with water, release the P fraction held by labile bonds (Cacchiarelli *et al*., 2004b). This explains the values shown in Table 4.

The fact that the high SRP concentration in the El Divisorio and reservoir waters is equal to that in the waters at the reservoir outlet (Table 7) can be explained because: (a) the sediments are transported to and deposited and stored in the El Divisorio river bed; (b) the soils beneath the reservoir are the same; and (c) the sediments transported downstream in El Divisorio sub-watershed and deposited in the reservoir, have similar physicochemical characteristics.

Close to the stream and due to lack of protection against soil erosion (Echeverría *et al*., 2004), a proportion of the sediment-associated P coming from agricultural diffuse sources, which is flushed into the stream channel under high flows, will be deposited and stored on the river bed during downstream transport and potentially be available for release as dissolved P under stable low-flow conditions. Sediments in the river bed can play an important role in buffering concentrations of SRP under low-flow conditions (House & Denison, 2002) and when the stream water enters the reservoir, the P in the sediments begins to re-equilibrate with the SRP already dissolved in the reservoir (Correll, 1998). At this critical time, once the sediment-associated P from diffuse sources has settled to the bottom, internal processes within the reservoir may significantly influence the concentration and availability of P and hence algal growth (Correll, 1998; Schernewski, 2003).

Thus, if the P desorption process that takes place during soil particle transport continues at its destination (the Paso Piedras Reservoir), it should not be ignored that this, plus the P being continuously liberated from the submerged soils within the reservoir, is maintaining a high concentration of SRP in the eutrophicated water of the Paso Piedras Reservoir. In other words, the dynamic balance of dissolved/absorbed P in the sediment stored in the reservoir bed corresponds to that in El Divisorio sub-watershed and so is potentially available for re-release as soluble P when its concentration is reduced by dilution with the low-SRP water of the Sauce Grande River.

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