

# Catchment morphometric characteristics, land use and water chemistry in Pampean streams: a regional approach

Graciana Amuchástegui · Leonardo di Franco ·  
Claudia Feijoó

Received: 22 January 2015 / Revised: 1 September 2015 / Accepted: 2 September 2015 / Published online: 9 September 2015  
© Springer International Publishing Switzerland 2015

**Abstract** The Pampean region covers a large surface in central Argentina, but despite the extensive agricultural activities and the high nutrient levels recorded in streams of the region, few authors have analysed the influence of land use on water quality. Here, we evaluated the relationships among catchment attributes (size, morphometry and land cover) and water chemistry in 23 Pampean streams in different seasons (autumn, spring and summer) and at three spatial scales: whole catchment and two scales of riparian buffers (200 and 500 m adjacent to both stream margins). Chloride concentration was positively related to catchment area and negatively related to drainage density. Nitrate level was strongly associated to cropland, but soluble phosphorus concentration showed no relationships with any type of land cover. Land cover at the buffer scale seemed to be more influential than land cover at the whole catchment for nitrogen concentration. The main impact of cropland

was the increase of nitrate concentration, while cattle breeding was negatively associated to photosynthetically active radiation (PAR) in autumn and summer and to dissolved oxygen concentration in spring. Our results highlighted the importance of local land use and riparian conservation on streamwater quality.

**Keywords** Agriculture · Cattle breeding · Scale · Nitrogen · Phosphorus

## Introduction

In 1975, Hynes proposed that “in every respect the valley rules the stream”, meaning that the morphology, geology, type of soils and vegetation in the catchment influence the structure and function of fluvial systems. Since then, this idea has been expanded to include land use into the factors that strongly affect stream characteristics, and several authors have analysed the relationships between land use and nutrient concentration in streamwater. In general, a strong positive association was observed between agricultural cover and nitrate levels and, in some cases, with phosphate concentration too (see, for example, Herlihy et al., 1998; Schilling & Libra, 2000; Ferrier et al., 2001; Jarvie et al., 2008; Broussard & Turner, 2009; Shupe, 2013). Other catchment attributes such as area and morphometric factors have been also proposed to influence water quality, but fewer

---

Handling editor: Sidinei Magela Thomaz

---

G. Amuchástegui · C. Feijoó (✉)  
BED (Biogeoquímica de Ecosistemas Fluviales),  
INEDES, Universidad Nacional de Luján, Rutas 5 y ex 7,  
Luján, Buenos Aires, Argentina  
e-mail: clasife@yahoo.com.ar

L. di Franco  
PRODITEL (Programa de Desarrollo e Investigación en  
Teledetección), Universidad Nacional de Luján, Rutas 5 y  
ex 7, Luján, Buenos Aires, Argentina

studies have addressed this question (Binkley et al., 2004; Stanley & Maxted, 2008).

In addition, the influence of land cover on stream integrity is scale dependent and varies in time and space (Buck et al., 2004). Initially, it was assumed that land cover closer to the stream would influence water quality more than land cover at the catchment scale, but the evidence is controversial. Some authors reported that local land cover is a better predictor of stream water quality (Dodds & Oakes, 2006; Tran et al., 2010), while others observed that whole-catchment land cover is more important (Sliva & Williams, 2001; Park et al., 2011) or even intermediate scales of land cover (Gove et al., 2001). Finally, some authors found no differences in the response of water chemistry to land cover across different spatial scales (Omernik et al., 1981; Lasaletta et al., 2010) or contradictory results within the same database (higher association with land cover at larger scales for some variables or the opposite for other variables; Monteagudo et al., 2012).

The Pampean region is a flat and large region (>50 million hectares) that covers central Argentina. Their arable soils have few limitations to crop production, and the majority are suitable for grazing (Viglizzo et al., 2003). Nutrient concentrations in Pampean streams are high (Feijoó & Lombardo, 2007), and have been generally attributed to the agricultural activities (Gabellone et al., 2005). However, there is some evidence that enriched conditions in Pampean waterbodies existed very much before the arrival of the Spaniards to the region (Feijoó & Lombardo, 2007). To determine the link between nutrient levels and agricultural land cover is an issue of great concern because this will help to elucidate whether Pampean streams are chronically eutrophic systems or not. That is, if Pampean aquatic systems showed eutrophic conditions for centuries or even millennia (which cannot be attributed to the human influence), or they were eutrophicated by the agricultural activities in the last decades. In the former case, biological communities would coexist a very long period with high nutrient levels and should well adapted to enriched conditions. We are also interested in determining if the influence of land cover on physical and chemical parameters of streamwater is more important at a local scale or at a catchment scale, because this information will help to design a more suitable management for the region.

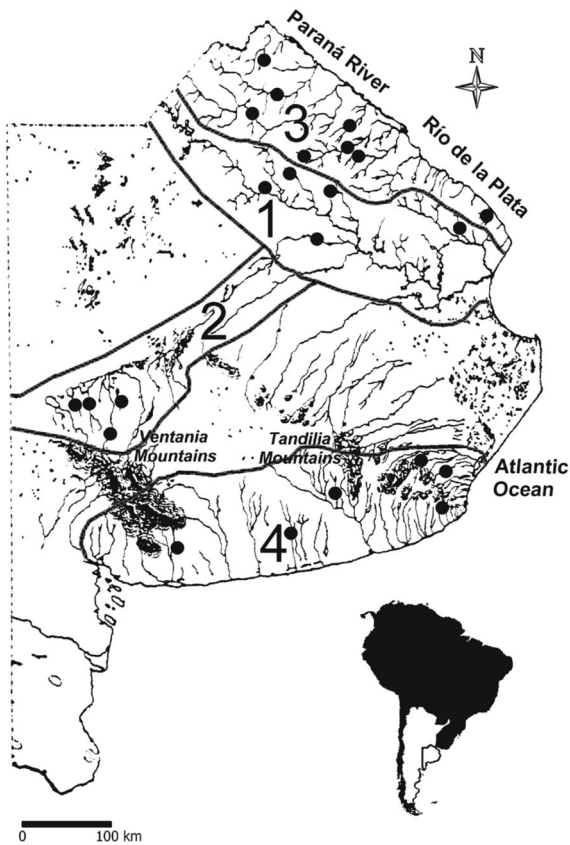
The analysis of the influence of land cover on water chemistry in the Pampean region has been limited due to the lack of land cover maps at regional and local scales. Recently, Rosso & Fernández Cirelli (2013) evaluated the impact of cropland and livestock breeding on streamwater quality, but they only considered the adjacent land use, which was assessed by visual inspection. Here we analysed the influence of catchment attributes (size, morphometry and land cover) on physical and chemical variables in 23 Pampean streams. We also examined the relationship between water chemistry and land cover estimated at three different spatial scales: whole catchment and two scales of riparian buffers in the entire catchment (200 m and 500 m adjacent to both stream margins).

## Materials and methods

### Study region

The study was conducted in the Buenos Aires province, which has a surface of 307.500 km<sup>2</sup>. The relief is flat (0–200 m above sea level) except for Tandilia and Ventania Mountain ranges (500 and 1100 m above sea, respectively) that occupy small areas in the south of the province (Fig. 1). Climate is temperate humid. Mean annual precipitation increased from 700 mm in the SW of Buenos Aires province to 1100 in the NE, and it is almost evenly distributed throughout the year, with slight increases at the end of summer (February) and at the onset of spring (October).

The region is characterized by the presence of a highly productive herbaceous steppe and the almost total absence of autochthonous trees, except for two species (*Celtis tala* Gill. ex Planch and *Salix humboldtiana* Willd.) that are restricted to areas with particular soil conditions. Soils are composed of a sequence of sand and loess deposited during the Tertiary and the Quaternary. The oldest Quaternary sediments ('Pampeano') accumulated by alluvial and eolian action, and included volcanic material transported from the Andes range. The latest sediments ('Postpampeano') are silts rich in sulphates and chloride with calcium carbonate concretions. They have fluvial and eolian origin and form the bed of streams and rivers (Sala et al., 1983). Most Pampean streams originated in wetland areas and are mainly fed



**Fig. 1** Map of Buenos Aires province indicating the fluvial systems proposed by Frenguelli (1956) and the streams considered in this study. *Region 1*: Salado river and its tributaries, *region 2*: Vallimanca stream, *region 3*: tributaries of the Paraná and Río de la Plata rivers, *region 4*: tributaries of the Atlantic Ocean

by groundwater. Streambeds are characterized by hard and homogeneous substrata with fine sediments (primarily silt and clay), and generally lack of stones and pebbles. Flow is slow due to the gentle slope of the region ( $\approx 2.5\%$ ), and dissolved nutrient levels are high ( $0.18 \text{ mg P-PO}_4/\text{l}$  and  $1.60 \text{ mg N-NO}_3/\text{l}$ ) (Feijoó & Lombardo, 2007). These conditions favour the development of dense autotrophic communities that include epipelton, macrophytes, and the associated epiphyton. Macrophyte architecture increases habitat heterogeneity, and provide food and refuge to rich ensembles of consumers (Giorgi et al., 2005).

Fertile soils and humid conditions favoured agricultural activities in the region. There was a rapid conversion of the original grassland to cultivated grasslands and croplands from 1880 to 1930, but until the beginning of the 1990s a low external-input

farming scheme prevailed in the region (Viglizzo et al., 2001). By 2002, main crops in Buenos Aires province where wheat and soybean (39 and 25.4% of the whole cultivated area, respectively) ([www.ec.gba.gov.ar](http://www.ec.gba.gov.ar)), and cattle breeding was principally extensive with a low proportion of feedlots (FAO, 2004). Chemical fertilization was not intensively used in the region due to unfavourable price conditions (Viglizzo et al., 2001). For instance, mean fertilizer use was  $40 \text{ kg N/ha}$  and  $26 \text{ kg P}_2\text{O}_5/\text{ha}$  for wheat and  $2 \text{ kg N/ha}$  and  $6 \text{ kg P}_2\text{O}_5/\text{ha}$  for soybean (FAO, 2004). This may be reflected in the negative balance for nitrogen and phosphorus in the Pampean region estimated by some authors (Viglizzo et al., 2001, 2003). Fertilization period varies according to the type of crop (June for wheat and end of December-beginning of January for soybean). Irrigation is restricted to small areas of horticulture production. In the last two decades, a process of agriculture intensification is occurring in the region with the replacement of mixed cattle grazing–cropping systems by continuous cropping (Viglizzo et al., 2003).

An early attempt to characterize streams of Buenos Aires province was made by Frenguelli in 1956, who proposed four fluvial systems (see Fig. 1). This regionalization was made considering geomorphological and hydrological features of the waterbodies, and did not include regions where the fluvial systems were poorly developed (for instance, NW and centre of the province). It was later observed that the four regions can be discriminated using chemical criteria (Feijoó & Lombardo, 2007).

#### Field survey and physical and chemical data

In this study, we considered 23 streams from the database presented by Feijoó & Lombardo (2007), who attempted to determine chemical basal conditions in Pampean streams. Due to the large extent of agricultural activities, there are no pristine catchments in the region that can be used to establish reference conditions for streamwater. Consequently, we selected streams that represent the whole range of variation in stream morphology, substrate, and flow of the region and show the lower levels of disturbance that can be found in the Pampas. The selection process was performed in three phases. As a first step, streams which do not run across villages or towns were identified. After that, streams were visited and

surveyed to evaluate their level of disturbance. Riparian vegetation, topography, and land use in the surrounding areas were registered, and water sample was taken to evaluate some indicative variables (pH, conductivity, temperature, and dissolved oxygen, soluble reactive phosphorus and ammonium concentrations). After this characterization, streams were selected discarding those streams that:

- (a) were not representative of the natural conditions of the Pampean region; i.e. with high slope or riparian forest vegetation;
- (b) showed an intensive land use close to the sampling site;
- (c) were canalized or their margins showed noticeable level of physical disturbance;
- (d) the physical and chemical water features indicated the possibility of pollution.

Streams were sampled in May (autumn) and November (spring) 2003, and February (summer) 2004. Our sampling periods did not coincide with the typical periods of fertilization in the region (see above). Sampling was not conducted during or following rainfall events so that samples represent base flow conditions. Current velocity, photosynthetically active radiation (PAR) at 15-cm depth (which can be used as a proxy of water transparency), water temperature, pH, conductivity and dissolved oxygen concentration were recorded using field instruments at each sampling site (see Feijoó & Lombardo, 2007, for details). Water samples were also collected and analysed to determine concentrations of chloride, carbonates, bicarbonates, soluble reactive phosphorus (SRP), nitrites, nitrates and ammonia following the methodology of APHA (1992). Chloride concentration was determined by titration with silver nitrate and SRP was determined using the ascorbic acid method. Nitrites and nitrates were measured by reaction with sulphanilamide, with previous cadmium reduction in the case of nitrates, while ammonium was analysed using the phenolhypochlorite method. Total and phenolphthalein alkalinities were determined by titration, and they were used to estimate carbonate and bicarbonate concentrations.

#### Land cover data

Catchment boundaries of the 23 streams were located using topographical maps of the Argentinian Instituto

Geográfico Militar (scale 1:50.000). Boundaries of each catchment were drawn following the ridge tops or topographic divides that separates the stream system from those neighbouring it. The drawing was closed at the sampling point, and the delimited catchment area included all the upstream land and water surface area which drains to this point. Catchment area and stream lines were traced in translucent paper, and geographical coordinates were marked as control points. These points were used later to georeference the catchment with the corresponding remotely sensed image.

Land cover was determined using ETM Landsat 7 images, which were available at the Earth Science Data Interface site of the University of Maryland or that were provided by the Programa de Desarrollo e Investigación en Teledetección (PRODITEL, Universidad Nacional de Luján). Landsat imagery used in this study was obtained between December 1999 and March 2003. Landsat images were projected to the Transverse Mercator reference system and georeferenced using the ERDAS Imagine 8.4 software. Images were geometrically corrected applying the nearest neighbour method (mean square error for the transformation <1 pixel) (Chuvieco, 1996).

Catchment areas delineated from the topographical maps were scanned and georeferenced to the Landsat images using the ERDAS software (mean square error <1 pixel). Contours of the catchment and the fluvial channels (both permanent and temporary) were then manually digitized on the screen with the Arc View GIS 3.2 software.

Catchment area and stream length were calculated from the digitized catchments with the ArcView GIS 3.2 software. The Strahler's method was used to determine stream order, mean slope was calculated as the difference of elevation at source and mouth (standardized by the length of the stream), and drainage density was estimated as the ratio between the total stream lengths for the basin and the catchment area (Gordon et al., 1992).

Land cover was classified in Landsat images with the ArcView software considering several visual criteria (colour, size, form, texture, etc.), temporal cover variation between images and complementary information from topographic maps. Polygons from the same land cover type were digitized manually on the screen. We considered the following land cover classes: cropland, cattle breeding, natural vegetation (grassland) and other covers, which included urban

land (small villages), forest, bare land, mining and ponds. The percentage of each land cover and cover type upstream of the sampling point was calculated at three spatial scales: whole catchment, 500-m buffer and 200-m buffer. Buffers encompassed the riparian corridor extending laterally 500 or 200 m each side of the channel along the entire length of the stream. Land cover classification was verified by visiting some of the studied catchments.

### Statistical analyses

Ordination of samples was performed using principal components analysis (PCA) to explore the structure of data. One PCA was made for each season including landscape attributes, land cover at catchment scale and physical and chemical features of streamwater. Relationships among variables across seasons and scales were evaluated by Pearson's correlations. Percentage of cropland, natural vegetation, cattle breeding and other covers were arcsine square root transformed. Other variables that did not meet the assumption of normality were log transformed. To give more support to our data interpretation, we only considered in our analysis those correlations that were significant at least in two seasons or scales. In addition, given that chloride concentration and conductivity were highly correlated ( $r = 0.97$  and  $P < 0.001$ ), in the correlation analyses, we only included the former variable.

## Results

### Characteristics of the streams

Catchment area ranged from 17 to 2559 km<sup>2</sup>, stream order varied between 2 and 4, and mean slope was generally low and averaged 0.5% (Table 1). Mean slope was higher in streams of regions 2 (Vallimanca) and 4 (tributaries of the Atlantic Ocean) because there headwaters are generally located in the southern mountains (Fig. 1).

Streams were characterized by alkaline waters with high conductivity and elevated nutrient and dissolved oxygen concentrations (Table 2). Conductivity and concentration of ammonia, chloride and carbonates tended to increase in summer, while SRP levels were lower in this season (Table 2).

**Table 1** Catchment area and morphometric characteristics of the 23 studied streams

Stream order	3 (2–4)
Area (km <sup>2</sup> )	223 (17–2559)
Mean slope (m/km)	5.2 (0.9–36.3)
Drainage density (km/km <sup>2</sup> )	0.25 (0.08–0.61)
Distance to origin (km)	24.4 (6.8–85.5)

Mean and ranges (between parentheses) are indicated

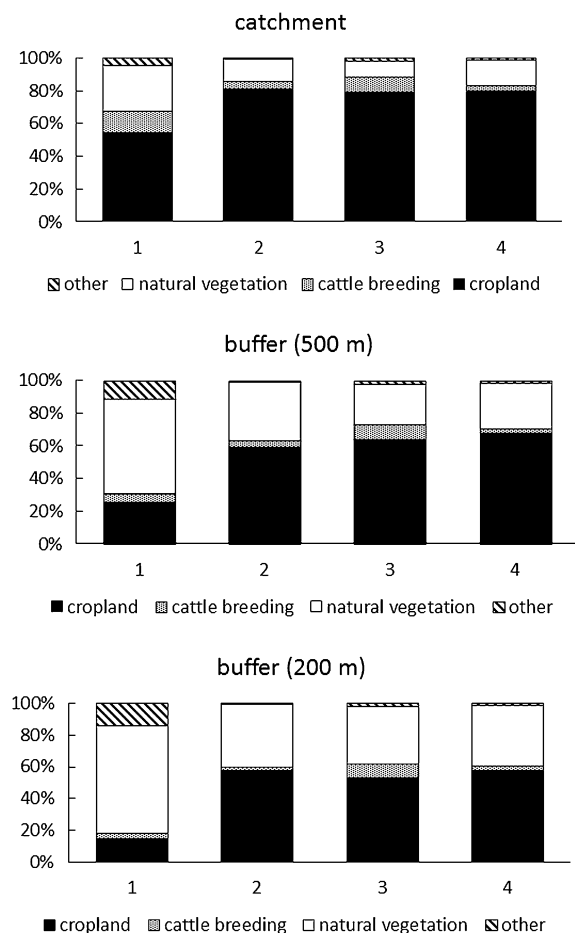
Cropland cover predominated in all regions at the catchment scale with a mean value of 72.5%, followed by natural vegetation (14.9%), cattle breeding (7.2%) and other covers (2.3%). In region 1 (Salado river and tributaries), % cropland was lower, while % cattle breeding and % natural vegetation were higher (Fig. 2). Cattle breeding was also important in region 3 (Paraná and Río de la Plata tributaries) when compared to the other regions. At the buffer scales (500 and 200 m), there was an increase of the natural vegetation cover and a decline of croplands, especially in region 1 (Salado river). Land cover was similar at the buffer scales, with a slight increase of the percentage of natural vegetation cover at the 200-m buffer scale (Fig. 2). At the catchment scale, % cropland was significantly correlated with % cattle breeding and % natural vegetation ( $r = -0.74$  and  $P < 0.001$ , and  $r = -0.81$  and  $P < 0.001$ , respectively), but there is no significant relationship between % cattle breeding and % natural vegetation.

### Relationships between catchment attributes and stream characteristics

One PCA per season including all the variables (including land cover at catchment scale) was made to explore the structure of data. The variance explained by the first two factors was 45.6% in autumn, 48.3% in spring and 45.5% in summer. In all seasons, one of the two axes represented a gradient from streams with high conductivity and chloride concentration (and a larger catchment area and natural vegetation cover) to streams with elevated nitrate concentration (and high drainage density and percentage of cropland) (Fig. 3). The other axis was correlated to the level of dissolved oxygen on one side and the percentage of cattle breeding on the other side.

**Table 2** Mean and ranges (between parentheses) of water characteristics in the sampled streams in the different seasons. DO: dissolved oxygen concentration. N = 23

	Autumn	Spring	Summer
pH	8.24 (6.55–8.93)	8.82 (8.03–10.54)	8.86 (8.07–10.25)
Conductivity ( $\mu\text{S}/\text{cm}$ )	1321 (722–2510)	1581 (230–4900)	2232 (584–10320)
DO (mg/l)	8.64 (4.60–12.75)	7.64 (3.17–13.45)	7.66 (2.80–16.60)
SRP ( $\text{mgP-PO}_4/\text{l}$ )	0.16 (0.04–0.67)	0.18 (0.02–0.61)	0.09 (0–0.54)
Nitrates ( $\text{mgN-NO}_3/\text{l}$ )	2.07 (0–6.64)	1.84 (0–6.96)	1.92 (0–5.92)
Nitrites ( $\text{mgN-NO}_2/\text{l}$ )	0.01 (0–0.03)	0.02 (0–0.09)	0.03 (0–0.10)
Ammonia ( $\mu\text{gN-NH}_4/\text{l}$ )	2.84 (0–17.21)	8.88 (0–36.93)	24.37 (0.10–91.47)
Chloride (mg/l)	91.00 (8–347)	116 (9–669)	246 (9–2072)
Carbonates (meq/l)	0.38 (0–2.58)	0.74 (0–5.25)	1.52 (0–9.73)
Bicarbonates (meq/l)	7.52 (4.43–12.03)	6.98 (1.91–11.45)	8.5 (3.60–13.55)

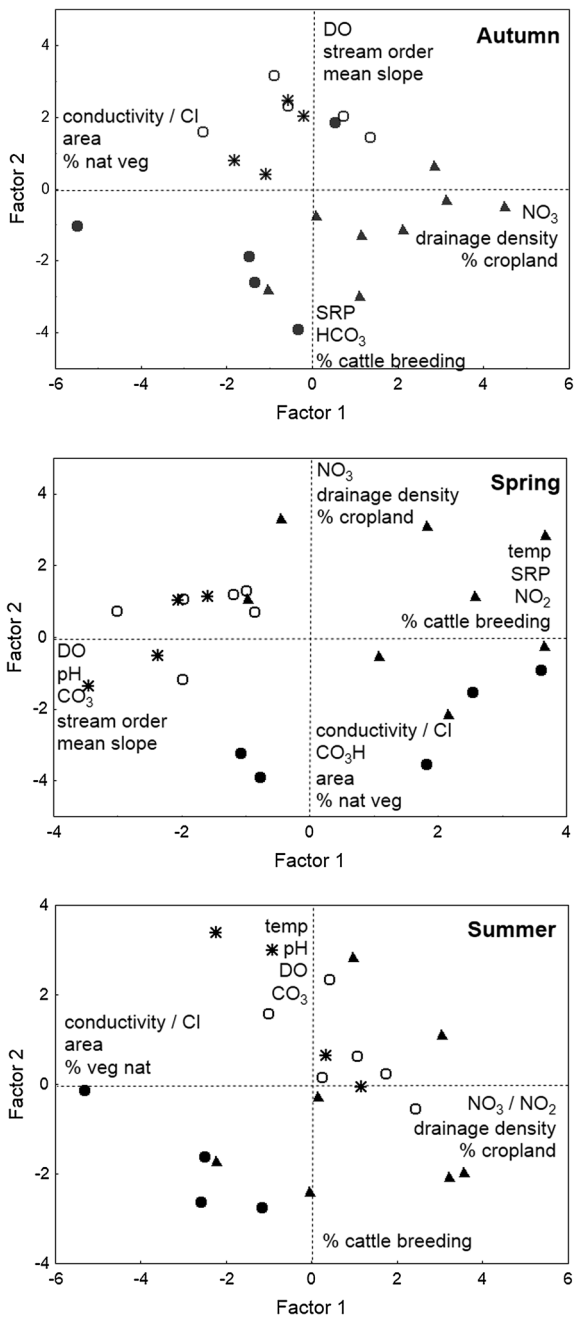


**Fig. 2** Land cover in the streams at the different scales and regions (*region 1* Salado river and its tributaries; *region 2* Vallimanca stream; *region 3* tributaries of the Paraná and Río de la Plata rivers; *region 4* tributaries of the Atlantic Ocean)

Results of the PCA suggested that dissolved oxygen concentration is positively associated to stream order and mean slope and negatively to % cattle breeding. Nitrate concentration was associated to % cropland and drainage density, while SRP concentration was related to % cattle breeding in autumn and spring. Finally, conductivity and chloride concentration were associated to catchment area and natural vegetation (Fig. 3).

In autumn, streams of the four regions are generally well separated in the ordination space, and only streams from regions 2 (Vallimanca) and 4 (tributaries of the Atlantic Ocean) and one stream of region 1 (Salado river) showed some degree of overlap (Fig. 3). In spring and especially in summer, discrimination among regions was lower. Streams of region 1 (Salado river) were associated to cattle breeding and natural vegetation, with high SRP levels and variable values of conductivity and chloride concentration. Streams of region 2 (Vallimanca) showed no clear relationships with the different land covers. Tributaries of the Paraná and Río de la Plata rivers (region 3) were related to cropland and cattle breeding, with higher concentrations of SRP and nitrates, while tributaries of the Atlantic Ocean (region 4) showed a slight association with cropland land cover (Fig. 3).

Results of the correlation analyses in general confirmed the associations suggested by the PCA. When analysing relationships between catchment size and topographical attributes and physical and chemical features of streamwater, we observed that stream order was significant and positively related with PAR



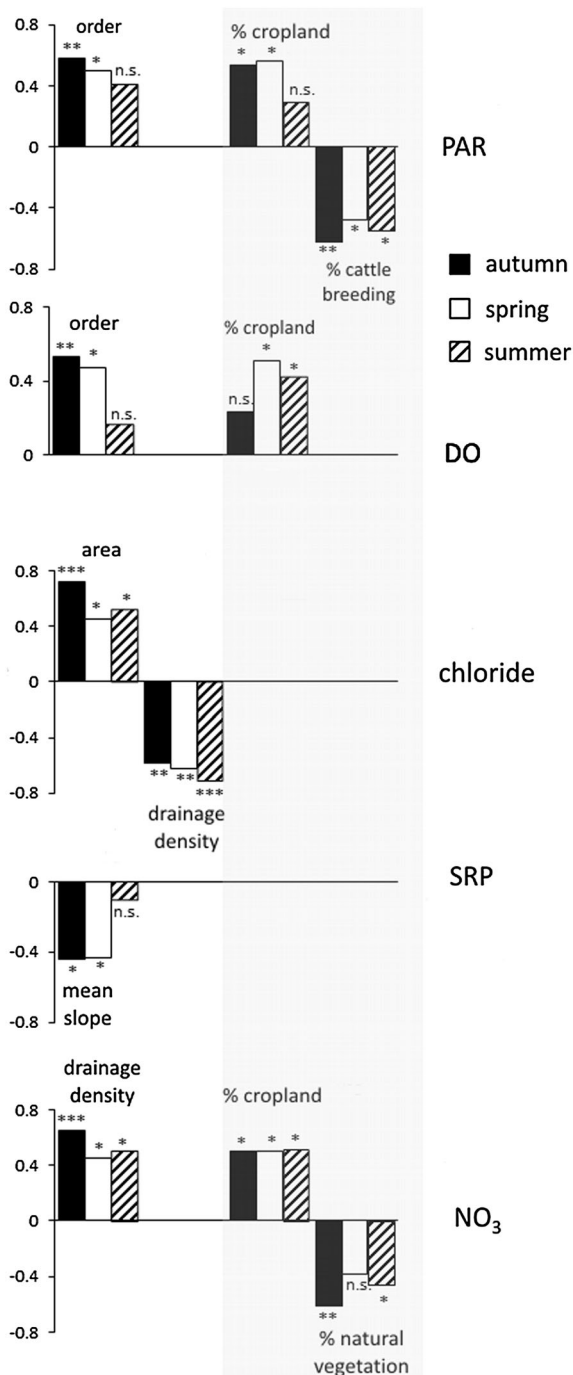
**Fig. 3** Sample ordination resulting from a PCA for each season. Points correspond to streams of the different regions: *Filled circle* Region 1 Salado river and its tributaries; *asterisk* Region 2, Vallimanca stream; *filled triangle* region 3, tributaries of the Paraná and Río de la Plata rivers; *open circle* region 4, tributaries of the Atlantic Ocean. Variables with the higher load in the first two functions are indicated on the axes. DO: dissolved oxygen; temp: temperature; NO<sub>3</sub>: nitrate; NO<sub>2</sub>: nitrite; Cl: chloride; CO<sub>3</sub>: carbonate; CO<sub>3</sub>H: bicarbonate; % nat veg: percentage of natural vegetation cover. N varied among 21 and 23 in the different seasons because in few cases (one for autumn and two for summer) the value of one variable was missed

( $r = -0.50$  and  $P < 0.05$ ). SRP concentration was negatively related with mean slope in autumn and spring, while nitrate concentration was positively related with drainage density in all seasons. When considering land cover at the catchment scale (grey box in Fig. 4), we observed that PAR was negatively associated to % cattle breeding in all seasons and positively related to % cropland in autumn and spring (but it should be remembered that both land covers were negatively related). DO level was positively related to % cropland (except in summer) but was not associated with % cattle breeding as it was suggested by the PCA. SRP concentration showed not relationships with any land cover; thus, the positive association between SRP and % cattle breeding observed in the PCA was not supported by the correlation analysis. Nitrate concentration was positively correlated with % cropland and negatively related to % natural vegetation (again, both land covers were negatively related) (Fig. 4).

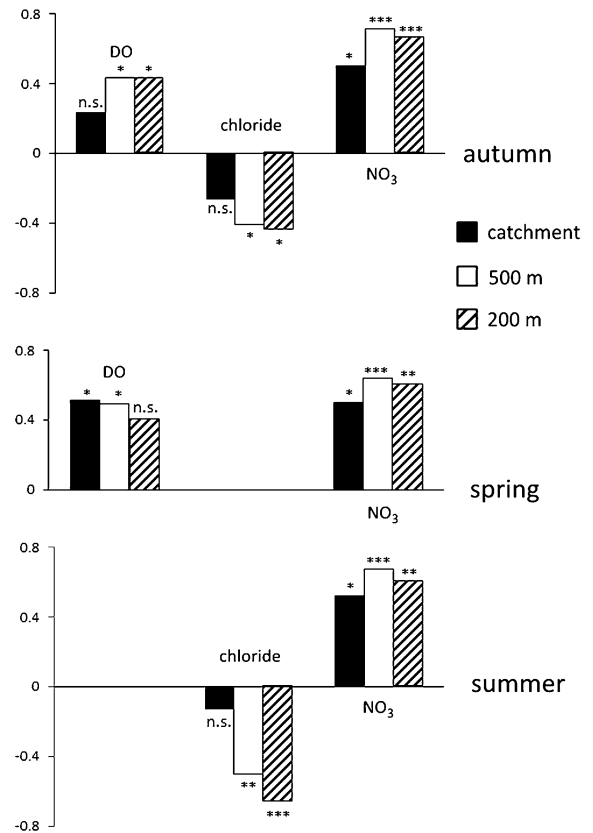
**Influence of the scale of land cover**

The analysis of the influence of land cover on physical and chemical characteristics of streamwater at different scales (catchment, 500 m and 200 m buffers) showed that % cropland in 500 and 200 m buffers was negatively correlated with chloride concentration in autumn and summer, but not in spring (Fig. 5). This association was not observed at the catchment scale in any season. Relationships between % cropland and nitrate concentration were significant at all seasons and scales, but they showed higher correlations coefficients and signification levels and the 200 and 500 m buffers scales than at the catchment scale (Fig. 5). In addition, the linear relationships between

and dissolved oxygen concentration in autumn and spring (Fig. 4). However, dissolved oxygen concentration did not correlate with mean slope even, as it was suggested by the PCA analysis. Chloride concentration increased with catchment area and decreased with drainage density, but it should be noted that area and drainage density were negatively correlated



**Fig. 4** Correlation coefficients (Pearson  $r$ ) of the relationships between catchment attributes and physical and chemical features of streamwater in the different seasons. Relations with land cover are indicated in the grey box. \*\*\*  $P < 0.001$ ; \*\*  $P < 0.01$ ; \*  $P < 0.05$ ; *ns* not significant



**Fig. 5** Correlation coefficients (Pearson  $r$ ) of the relationships between % cropland and physical and chemical features of streamwater at the different scales and seasons. \*\*\*  $P < 0.001$ ; \*\*  $P < 0.01$ ; \*  $P < 0.05$ ; *ns* not significant

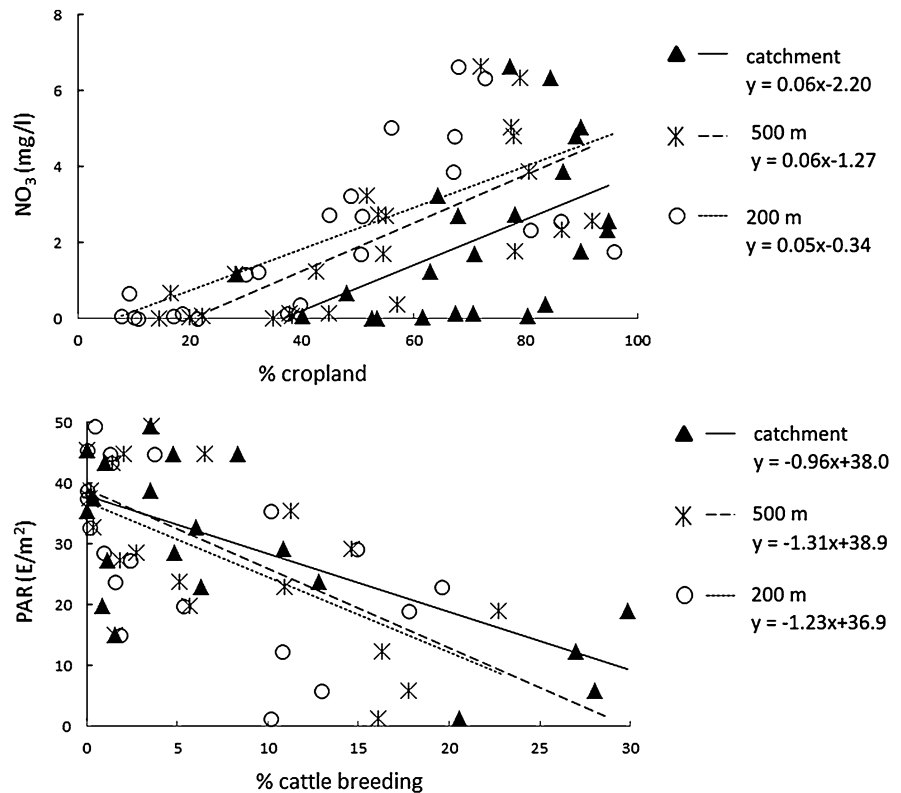
% cropland and nitrate levels showed similar slopes in the different scales, but lines for buffers (200 m a 500 m) intercept the X-axis at lower values than in the case of the catchment scale (Fig. 6). This reflects the lower % cropland observed in buffers in relation to the catchment.

At the catchment scale, streams with a high % cropland (up to 80%) can show low nitrate concentrations in autumn. However, at the buffer scales (200 and 500 m) nitrate concentration tended to exceed 1 mg/l when % cropland is higher than 40% (Fig. 6). A similar behaviour of the relationship nitrate vs. % cropland was observed in spring and summer (data not shown).

Cattle breeding cover was negatively related with PAR at the different scales in autumn and summer but



**Fig. 6** Linear relationships between % cropland and nitrate concentration, and between % cattle breeding and PAR in autumn



not in spring (Figs. 6, 7). The linear relation between this land cover and PAR showed similar intercepts for the different scales but slopes were steeper for buffers than for the catchment scale in autumn (Fig. 6) and summer (data not shown).

## Discussion

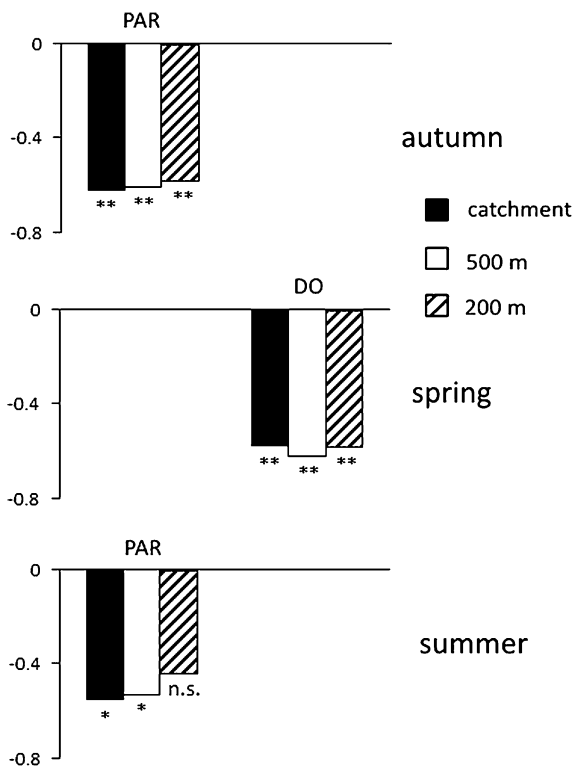
To our knowledge, this is the first study where the influence on catchment attributes (morphometric features and land cover) on water quality in Pampean streams was tested at a wide regional scale. Gabellone et al. (2005) described changes in nutrient concentration along the Salado river and related them to land cover, but these relationships were not statistically analysed. On the other hand, Rosso & Fernández Cirelli (2013) used statistical tests to relate environmental conditions with surrounding land use in 31 Pampean streams, but they did not consider the influence of land use at catchment scale.

Our results indicated that the catchment attributes that had the most influence on water quality in across

seasons were catchment area, drainage density and land cover (especially cropland). Chloride concentration were positively related to catchment area and negatively related to drainage density. Nitrate level was strongly related to percentage of cropland in the different seasons and scales, but the origin of dissolved phosphorus is less clear given that SRP concentration showed no clear relations with any type of land cover. Finally, land cover in the proximity of the streams seemed to be important for some streamwater characteristics, mainly chloride and nitrate concentrations.

## Regional characterization of the streams

Feijó & Lombardo (2007) analysed water features of 41 streams, including the 23 streams studied here. They concluded that streams from the different regions proposed by Frenguelli (1956) can be differentiated by the chemistry of their waters. They reported higher conductivity and chloride concentration in streams from regions 1 (Salado river) and 2 (Vallimanca) and suggested that this might be related to the more arid conditions prevailing in these regions



**Fig. 7** Correlation coefficients (Pearson  $r$ ) of the relationships between % cattle breeding and PAR and DO concentration in streamwater in the different scales and seasons. \*\*\* $P < 0.001$ ; \*\* $P < 0.01$ ; \* $P < 0.05$ ; *n.s.* not significant

and the inflow of saline water from the phreatic aquifer. Indeed, they observed that SRP levels were higher in the northern regions (Salado river and tributaries of the Paraná and Río de la Plata), while nitrate concentration was higher in the streams from regions 3 (Paraná and Río de la Plata) and 4 (tributaries of the Atlantic Ocean) than in the rest of the streams. The PCA analyses that we performed here including land covers showed similar results.

Cropland was the prevailing land cover in all regions, but cattle breeding showed a higher importance in regions 1 (Salado river) and 3 (tributaries of the Paraná and Río de la Plata). Region 1 was also characterized by a higher cover of natural vegetation (mainly grasses).

#### Influence of catchment area and morphometric attributes

Some authors reported a positive relationship between catchment area and dissolved nitrogen concentration

(Dodds et al., 1996; Hossack et al., 2000; Binkley et al., 2004). We did not detect this association, but we observed that catchment area was positively related with chloride concentration. In addition, this variable was negatively related to drainage density, suggesting that chloride ions are not provided by superficial runoff but by subsuperficial phreatic supply. High conductivities were detected in the superficial aquifer that fed Pampean streams possibly due to the weathering of sediments rich in chloride ions (Sala et al., 1983). This would be especially true for the Salado river catchment whose headwater reaches are fed by a sedimentary aquifer with high levels of sodium chloride originated under arid conditions (Gabellone et al., 2005).

In our study, SRP concentration was negatively associated to mean slope in autumn and spring. This differs from data presented by Castillo (2010), who reported a positive relationship between phosphorus level and mean slope in a tropical catchment, and attributed it to agricultural activities and urban discharges in the upper basin. Unlike phosphorus, nitrate concentration was positively related to drainage density. Considering that a fluvial system with a well-developed drainage will be more influenced by the surrounding land use, this result give an additional evidence of the agricultural origin of dissolved nitrogen in the studied streams.

#### Influence of land cover

As land covers are quantified in percentages of a surface, the higher the percentage value for one dominant land cover, the lower the percentage for the next dominant cover (Monteagudo et al., 2012). In our study, this was true for % cropland giving that it showed negative relationships with natural vegetation. In addition, % cropland was also negatively associated to % cattle breeding, but we found no significant association between cattle breeding and natural vegetation. Nitrate concentration in streamwater was positively related to cropland and negatively related to natural vegetation cover, while chloride concentration showed the opposite trend in autumn and summer at the buffer scales (decreasing with cropland and increasing with natural vegetation). The negative association between % cropland and natural vegetation cover will explain the contrasting behaviour of chloride and nitrate concentrations under both land

covers. Hence, streams with higher % cropland in the catchment showed higher levels of nitrate and lower salinity. The relationship between nitrates and arable land cover in the catchment has been observed by several authors (see for example Herlihy et al., 1998; Liu et al., 2000; Schilling & Libra, 2000; Ferrier et al., 2001; Castillo, 2010; Monteagudo et al., 2012; Shupe, 2013). But unlike our results, it has been reported that conductivity increased with cropland due to the decline in water quality (Hunsaker & Levine, 1995; Shupe, 2013). As we pointed out above, it is possible that chloride ions come from groundwater, and a higher salinity in the phreatic water would be reflected in more saline soils with lower suitability for agricultural production. However, more data are needed to support this hypothesis.

Cattle breeding showed a negative relationship with PAR in all seasons at the catchment scale. This relationship was also significant at, at least, two spatial scales in autumn and summer. The association between cattle breeding and PAR can be related to the impact of livestock on water quality via sediment erosion from grasslands and riparian zones, and streambank destabilization and sediment resuspension when cattle has free access to streams (Osmond et al., 2007). We also observed a decrease of dissolved oxygen concentration in spring at all scales, which could be attributed to faecal contamination by livestock (Buck et al., 2004). It is possible that positive associations between % cropland and PAR and dissolved oxygen concentration in some seasons and spatial scales should reflect the negative relationship between this land cover and % cattle breeding.

Pampean streams were eutrophic according to the EPA's criteria (2000) (Table 3). Mean phosphorus level in Pampean streams was two orders higher than those reported for forested streams in USA (Binkley et al., 2004), and within the range observed in 20 impaired streams from different regions of the world (Marcé & Armengol, 2009). Indeed, they exceeded the values found in streams of USA with more than 90% of agriculture use in their basins (Omernik, 1977). Cattle breeding has been suggested as phosphorus source (Mugni et al., 2005), but we cannot link SRP concentration to any land cover. But it must be considered that our sampling was performed under baseflow conditions, when it is difficult to detect relationships between the extent of agriculture practices and phosphorus levels in streamwater. Therefore,

we cannot completely discard the influence of land use on SRP concentration in Pampean streams. But in any case, observed SRP concentrations are much elevated to be solely explained by the agricultural activities prevailing in the region. Nitrate concentrations in these streams were also high compared to forested streams of USA (Binkley et al., 2004), but lower than the concentrations registered in streams with more than 75% of agriculture in their basins (Omernik, 1977) (Table 3). The origin of nitrates may be mostly related to cropland cover in Pampean streams given the strong relation between both variables across seasons and scales. But, when comparing with the data of Omernik (1977), mean nitrate concentration is lower than the expected for the extensive cropland cover in the region (mean = 73%, varying between 28–95%). This discrepancy should be attributed to the low external-input farming scheme prevailed in the region until the beginning of the 1990s (Viglizzo et al., 2001), which was reflected in a low fertilizer use compared to North America and Europe (Mugni et al., 2005) and in negative balances in soil phosphorus and nitrogen in the Pampas (Viglizzo et al., 2001, 2003). Bustamante et al. (2015) also observed a lower dissolved inorganic nitrogen yield in rivers from the Amazon and the La Plata-Paraná basin compared with the more important European rivers, and attributed these differences to a much higher use of N fertilizer per unit of area of arable land in Europe than in South America.

There is palynological evidence that eutrophic conditions in Pampean waterbodies existed very much before the rise of the agriculture in the region. Pollen sequences obtained in different sites of Buenos Aires province revealed the existence of eutrophic waterbodies with abundant macrophytic vegetation in different periods between 10,000y B.P. and 3000y B.P. (Prieto, 1996; Zarate et al., 2000; Vilanova et al., 2006). Aquatic vegetation in these periods included genera typical of enriched conditions such as *Typha*, *Myriophyllum*, *Ranunculus*, *Schoenoplectus* and *Elo-dea* (Palmer & Roy, 2001). Considering this information and the lack of association between SRP concentration and cropland or cattle breeding land cover in the Pampean region, we hypothesized that phosphorus mainly derive from the sedimentary parent material. During the Quaternary, phosphorus-rich volcanic material was transported from the Los Andes range and deposited in the region, and its weathering

**Table 3** Comparison of nutrient concentrations in Pampean streams and those registered in other regions of the world

	Phosphorus (mg/l)	Nitrogen (mg/l)	Reference
Mean (SD) of 41 pampean streams			Feijóo & Lombardo (2007)
Autumn	SRP = 0.22 (0.48)	NO <sub>3</sub> = 1.68 (1.88)	
Spring	SRP = 0.18 (0.21)	NO <sub>3</sub> = 1.59 (1.95)	
Summer	SEP = 0.13 (0.28)	NO <sub>3</sub> = 1.54 (1.90)	
EPA criteria			EPA (2000)
Oligotrophic–mesotrophic boundary	TP = 0.0025	TN = 0.7	
Mesotrophic–eutrophic boundary	TP = 0.075	TN = 1.5	
Median of 300 forested streams (USA)	SRP = 0.004	NO <sub>3</sub> = 0.15	Binkley et al. (2004)
Mean of 928 relatively unpolluted streams (USA)			Omerik (1977)
>50% agriculture	TP <sub>i</sub> = 0.04	TN <sub>i</sub> = 1.2	
>75% agriculture	TP <sub>i</sub> = 0.06	TN <sub>i</sub> = 1.8	
>90% agriculture	TP <sub>i</sub> = 0.07	TN <sub>i</sub> = 4.2	
Mean (range) of streams from different regions			Marcé & Armengol (2009)
46 pristine streams	SRP = 0.006 (0.001–0.029)		
20 impaired streams	SRP = 3.21 (0.11–7.14)		

TP total phosphorus, TN total nitrogen, TP<sub>i</sub> total inorganic phosphorus, TN<sub>i</sub> total inorganic nitrogen

may supply this nutrient to surface waters (Morrás, 1999). However, data of total phosphorus content in Pampean soils obtained in early twentieth century (in the beginning of the expansion of agriculture) suggest a differential rate of material deposition across the region, with higher phosphorus content in the northern Pampa (Morrás, 1999). If high phosphorus levels in Pampean streams were derived from parent materials, then nutrient criteria developed in other regions to determine trophy (such as EPA, 2000) cannot be applied in these systems without being revised. To summarize, we found no evidence that high phosphorus levels in Pampean streams are due to agricultural activities, while nitrate concentration showed a clear link with cropland cover, but values are not as high as expected given the extent of cropland in the Pampas.

#### Importance of scale

Even though it has been generally assumed that fluvial water quality will depend more strongly on land use in the proximity of the streams, results provided by different authors are contradictory. In this study, land cover at lower spatial scales seemed to be more influential for nitrate, given that relationships between cropland and nitrate concentrations showed higher

significances and coefficients of regression at the buffer scales than at the catchment scale. Our results agree with those of other authors who observed that land use at the buffer scale showed a higher impact on stream water quality (Tran et al., 2010; Monteagudo et al., 2012), and with those of Buck et al. (2004) who reported that land use at a 600-m riparian zone showed a higher influence on water quality in small streams than in large ones. Our results also suggest that nitrate concentration exceeded 1 mg/l when % cropland at the buffer scales is higher than 40%, whereas at the catchment scale it can be low even with high cropland cover.

#### Implications and final considerations

In this study, we identified catchment attributes that had the most influence in water chemistry in Pampean streams. The main impact of cropland was to increase nitrate level, while cattle breeding decreased PAR in autumn and summer and dissolved oxygen concentration in spring.

The lack of significant relationships between phosphorus concentration and land cover jointly with palynological evidence give support to the hypothesis that Pampean streams may be chronically enriched

systems (Feijoó & Lombardo, 2007). Hence, biological communities should have a long history of coexistence (centuries to millennia) with an environment with high nutrient availability and should be well adapted to these conditions. Hence, their structure and function should differ from those of eutrophic streams resulting from the impact of human activities in the last decades. In fact, Pampean streams do not show some of the problems associated to the eutrophication process such as low biological diversity or a lower efficiency to process and retain nutrients. Trophic webs are complex in these streams, with several basal compartments and species of macroinvertebrates and fishes (Giorgi et al., 2005), and phosphorus uptake can be high despite the elevated nutrient concentrations (Feijoó et al., 2011; Rodríguez Castro, 2015). Consequently, the concept of what should be considered an eutrophic status (in the sense of being polluted) in Pampean stream deserves more attention.

Monteagudo et al. (2012) pointed out that the election of the spatial scale may have important influences on the results and ecological interpretation of studies assessing the relationship between land cover and stream water quality. In this study, some variables showed significant associations with land cover across spatial scales (e.g., nitrate concentration vs. % cropland), but others were only detectable at some spatial scales and in certain seasons (e.g., PAR vs % cattle breeding). Consequently, this study stress the relevance of not only selecting the adequate spatial scale but also repeating the sampling scheme in different seasons to determine whether the detected relationships are consistently observed across the year or not.

We also observed that local land cover showed a higher impact on nitrate levels in streamwater compare to land cover at the catchment scale. This highlights the importance of regulating land use in the proximity of the streams, a point that is not considered at present in the argentine legislation. According to our results, management measures should be focused on reducing agricultural land use in at least the 200 m buffer adjacent to both stream margins. The maintenance of riparian buffers of natural herbaceous vegetation where livestock and crops are excluded could help to ameliorate the impact of agricultural activities on water quality, improving the whole ecological integrity of Pampean streams.

Despite the fact that this study was performed when the process of agriculture intensification was in their early stages, we observed a response of water chemistry to agricultural activities at least concerning nitrogen pollution. However, in the last years this intensification was consolidated by the expansion of soybean, the reduction of the surface dedicated to extensive cattle breeding, and the increasing of feed lots. An open question is what will be the response of Pampean fluvial ecosystems to the impact of agricultural intensification, and how this will be affecting their structural and functional attributes.

**Acknowledgments** The PRODITEL (Programa de Desarrollo e Investigación en Teledetección, Universidad Nacional de Luján) kindly provided some of the Landsat images used in this study. We thank Adonis Giorgi for their useful comments on the manuscript and Gabriela Romano for the revision of the English text. The manuscript was improved by the comments and suggestion of the Editor (Sidinei M. Thomaz) and two anonymous reviewers. This project was supported by the Universidad Nacional de Luján and the Horatius Foundation.

## References

- APHA, 1992. Standard Methods for the Examination of Water and Wastewater. APHA, Washington DC.
- Binkley, D., G. G. Ice, J. Kaye & C. A. Williams, 2004. Nitrogen and phosphorus concentrations in forest streams of the United States. *Journal of the American Water Resources Association* 40: 1277–1291.
- Broussard, W. & R. E. Turner, 2009. A century of changing land-use and water-quality relationships in the continental US. *Frontiers in Ecology and the Environment* 7: 302–307.
- Buck, O., D. K. Nigoyi & C. R. Townsend, 2004. Scale-dependence of land use effects on water quality of streams in agricultural catchments. *Environmental Pollution* 130: 287–299.
- Bustamante, M. M. C., L. A. Martinelli, T. Pérez, R. Rasse, J. P. H. B. Ometto, F. S. Pacheco, S. R. Machado Lins & S. Marquina, 2015. Nitrogen management challenges in major watersheds of South America. *Environmental Research Letters* 10: 065007.
- Castillo, M. M., 2010. Land use and topography as predictors of nutrient levels in a tropical catchment. *Limnologica* 40: 322–329.
- Chuvieco, E., 1996. Fundamentos de teledetección espacial. Ediciones Rialp S.A, Madrid.
- Dodds, W. K., J. M. Blair, G. M. Henebry, J. K. Koelliker, R. Ramundo & C. M. Tate, 1996. Nitrogen transport from tallgrass prairie watersheds. *Journal of Environmental Quality* 25: 973–981.
- Dodds, W. K. & R. M. Oakes, 2006. Controls of nutrients across a prairie stream watershed: land use and riparian cover effects. *Environmental Management* 37: 634–646.

- EPA, 2000. Nutrient criteria technical guidance manual. Rivers and streams. EPA-822-B-00-002, Washington, DC.
- FAO, 2004. Uso de fertilizantes por cultivos en Argentina. FAO, Roma.
- Feijóo, C. S. & R. J. Lombardo, 2007. Baseline water quality and macrophyte assemblages in Pampean streams: a regional approach. *Water Research* 41: 1399–1410.
- Feijóo, C., A. Giorgi & N. Ferreira, 2011. Phosphorus uptake in a macrophyte-rich pampean stream. *Limnologia* 41: 285–289.
- Ferrier, R. C., A. C. Edwards, D. Hirst, I. G. Littlewood, C. D. Watts & R. Morris, 2001. Water quality of Scottish rivers: spatial and temporal trends. *Science of the Total Environment* 265: 327–342.
- Frenguelli, J., 1956. Rasgos generales de la hidrografía de la Provincia de Buenos Aires. LEMIT, Buenos Aires.
- Gabellone, N. A., M. C. Claps, L. C. Solari & N. C. Neschuk, 2005. Nutrients, conductivity and plankton in a landscape approach to a Pampean saline lowland river (Salado River, Argentina). *Biogeochemistry* 75: 455–477.
- Giorgi, A., C. Feijóo & G. Tell, 2005. Primary producers in a Pampean stream: temporal variation and structuring role. *Biodiversity and Conservation* 14: 1699–1718.
- Gordon, N. D., T. A. McMahon & B. L. Finlayson, 1992. *Stream Hydrology*. Wiley, Chichester.
- Gove, N. E., R. T. Edwards & L. L. Conquest, 2001. Effects of scale on land use and water quality relationships: a longitudinal basin-wide perspective. *Journal of the North American Water Resources Association* 37: 1721–1734.
- Herlihy, A. T., J. L. Stoddard & C. B. Johnson, 1998. The relationship between stream chemistry and watershed land cover data in the Mid-Atlantic region, U.S. *Water, Air, & Soil Pollution* 105: 377–386.
- Hossack, B. R., S. M. Struhs & K. Lohman, 2000. Influence of basin and watershed characteristics on the nutrient chemistry of headwater streams in northern Idaho, USA. *Internationale Vereinigung für Theoretische und Angewandte Limnologie: Verhandlungen* 27: 1095–1100.
- Hunsaker, C. T. & D. A. Levine, 1995. Hierarchical approaches to the study of water quality in rivers. *BioScience* 45: 193–203.
- Hynes, H. B. N., 1975. The stream and its valley. *Internationale Vereinigung für Theoretische und Angewandte Limnologie: Verhandlungen* 19: 1–15.
- Jarvie, H. P., P. J. A. Withers, R. Hodgkinson, A. Bates, M. Neal, H. D. Wickhan, S. A. Hasman & L. Armstrong, 2008. Influence of rural land use on streamwater nutrients and their ecological significance. *Journal of Hydrology* 350: 166–186.
- Lassaletta, L., H. García-Gómez, B. S. Gimeno & J. V. Rovira, 2010. Headwater streams: neglected ecosystems in the EU Water Framework Directive. Implications for nitrogen pollution control. *Environmental Science and Policy* 13: 423–433.
- Liu, Z.-J., D. E. Weller, D. L. Correll & T. E. Jordan, 2000. Effects of land cover and geology on stream chemistry in watersheds of Chesapeake Bay. *Journal of the American Water Resources Association* 36: 1349–1365.
- Marcé, R. & J. Armengol, 2009. Modeling nutrient in-stream processes at the watershed scale using Nutrient Spiralling metrics. *Hydrology and Earth System Sciences* 13: 953–967.
- Monteagudo, L., J. L. Moreno & F. Picazo, 2012. River eutrophication: irrigated vs. Non-irrigated agriculture through different spatial scales. *Water Research* 46: 2759–2771.
- Morrás, H. J. M., 1999. Geochemical differentiation of Quaternary sediments from the Pampean region based on soil phosphorus contents as detected in the early 20th century. *Quaternary International* 62: 57–67.
- Mugni, H., S. Jergentz, R. Schulz, A. Maine & C. Bonetto, 2005. Phosphate and nitrogen compounds in streams of Pampean Plain areas under intensive cultivation (Buenos Aires, Argentina). In Serrano, L. & H. L. Golterman (eds), *Phosphates in Sediments*. Backhuys Publishers, Leiden: 163–170.
- Omernik, J. M., 1977. Nonpoint source-stream nutrient level relationships: A nationwide study. US Environmental Protection Agency, EPA-600/3-77-105.
- Omernik, J. M., A. R. Abernathy & L. M. Male, 1981. Stream nutrient levels and proximity of agricultural and forest land to streams: some relationships. *Journal of Soil and Water Conservation* 36: 227–231.
- Osmond, D. L., D. M. Butler, N. R. Rannels, M. H. Poore, A. Wossink & J. T. Green, 2007. *Grazing practices: A review of the literature*. North Carolina Agricultural Research Service, Technical Bulletin 325-W, Raleigh.
- Palmer, M. A. & D. B. Roy, 2001. A method for estimating the extent of standing fresh water of different trophic states in Great Britain. *Aquatic Conservation: Marine and Freshwater Ecosystems* 11: 199–216.
- Park, S.-R., H.-J. Lee, S.-W. Lee, S.-J. Hwang, M.-S. Byeon, G.-J. Joo, K.-S. Jeong, D.-S. Kong & M.-C. Kim, 2011. Relationships between land use and multi-dimensional characteristics of streams and rivers at two different scales. *International Journal of Limnology* 47: S107–S116.
- Prieto, A. R., 1996. Late quaternary vegetational and climatic changes in the Pampa grassland of Argentina. *Quaternary Research* 45: 73–88.
- Rodríguez Castro, C., 2015. Capacidad de depuración de sustancias bioaprovechables en arroyos de llanura y su relación con el arsénico. PhD thesis, Universidad de Buenos Aires, Buenos Aires.
- Rosso, J. J. & A. Fernández Cirelli, 2013. Effects of land use on environmental condition and macrophyte in prairie lotic ecosystems. *Limnologia* 43: 18–26.
- Sala, J. M., N. González & E. Kruse, 1983. Generalización hidrológica de la provincia de Buenos Aires. Coloquio Internacional sobre Hidrogeología de Grandes Llanuras, Olavarría.
- Schilling, K. E. & R. D. Libra, 2000. The relationship of nitrate concentrations in streams to row crop land use in Iowa. *Journal of Environmental Quality* 29: 1846–1851.
- Shupe, S., 2013. Statistical and spatial analysis of land cover impact on selected metro Vancouver, British Columbia watersheds. *Environmental Management* 51: 18–31.
- Sliva, L. & D. D. Williams, 2001. Buffer zone versus whole catchment approaches to studying land use impact on river water quality. *Water Research* 35: 3462–3472.
- Stanley, E. H. & J. T. Maxted, 2008. Change in the dissolved nitrogen pool across land cover gradient in Wisconsin streams. *Ecological Applications* 18: 1579–1590.

- Tran, C. P., R. W. Bode, A. J. Smith & G. S. Kleppel, 2010. Land-use proximity as a basis for assessing stream water quality in New York State (USA). *Ecological Indicators* 10: 727–733.
- Viglizzo, E. F., F. Lértora, A. J. Pordomingo, J. N. Bernardos, Z. E. Roberto & H. Del Valle, 2001. Ecological lessons and applications from one century of low external-input farming in the pampas of Argentina. *Agriculture, Ecosystems and Environment* 83: 65–81.
- Viglizzo, E. F., A. L. Pordomingo, M. G. Castro & F. A. Lértora, 2003. Environmental assessment of agriculture at a regional scale in the Pampas of Argentina. *Environmental Monitoring and Assessment* 87: 169–195.
- Vilanova, I., A. R. Prieto & M. E. Espinosa, 2006. Palaeoenvironmental evolution and sea-level fluctuations along the southeastern Pampa grassland coast of Argentina during the Holocene. *Journal of Quaternary Science* 21: 227–242.
- Zarate, M., R. A. Kemp, M. Espinosa & L. Ferrero, 2000. Pedosedimentary and palaeoenvironmental significance of a Holocene alluvial sequence in the southern Pampas, Argentina. *The Holocene* 10: 481–488.