Agriculture influences ammonium and soluble reactive phosphorus retention in South-American headwater streams

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Short title: Agriculture influences instream nutrient retention

ABSTRACT

Agricultural activities can affect the delivery of nutrients to streams, riparian canopy cover, and the capacity of aquatic systems to process nutrients and sediments. There are few measures of nutrient uptake and metabolism from tropical or sub-tropical streams in general, and even fewer from tropical regions of South America. We examined ammonium (NH_4^+) and soluble reactive phosphorus (SRP) retention in streams in Brazil and Argentina. We selected twelve streams with relatively little or extensive agricultural activity and conducted whole-stream nutrient additions and measurements of Gross Primary Production (GPP) and Ecosystem Respiration (ER). We used multiple linear regression to determine potential drivers of nutrient uptake metrics across the streams. Nutrient concentrations and retention differed significantly between land use categories. Both NH_4^+ and SRP concentrations were higher in the agricultural sites (means of 161 and 495 μg L^{-1}, respectively), whereas metabolic rates were slower and transient storage smaller. Our analysis indicated that agriculture increased ambient uptake lengths and decreased uptake velocities. The regression models revealed that ambient SRP had a positive effect on NH_4^+ uptake and vice-versa, suggesting strong stoichiometric controls. Drivers for nutrient uptake in streams with low-intensity agriculture also included canopy cover, temperature, and ER rates. Nutrient assimilation in agricultural sites was influenced by a higher number of variables (GPP for SRP, and discharge, and transient storage for both nutrients). Our results indicate agricultural activity changes both the magnitude of in-stream nutrient uptake and the mechanisms that control its variation, with important implications for South American streams under agricultural intensification.

Keywords: Agricultural watersheds; Aquatic metabolism; Low-order streams; Macronutrient assimilation; Nitrogen; Phosphorus.

INTRODUCTION

In a classic citation from the 1960s, Leopold et al. (1964) stated that rivers and streams are "*the gutters down which flow the ruins of continents*". These aquatic systems are still frequently used as the final destination for point source and non-point source effluents from human activities, with negative implications for their structure and function. Because rivers and streams provide a wide range of direct and indirect benefits to humans (Arthington et al. 2015), there has been a paradigm shift in recent years towards direct estimations of those services rather than solely relying on traditional measures of water quality and biotic community structure for assessing lotic conditions (Cosgrove and Loucks, 2015). Ecosystem services provided by rivers and streams include the provision of drinking water, food, and water for industrial and agricultural activities, as well as navigation, recreation, and pollution abatement (Dodds et al. 2013). The retention and processing of organic matter, nutrients, and other pollutants by these water bodies reduce export of pollutants and thus mitigate their undesirable effects on downstream water quality (Peterson et al. 2001).

Smaller streams can be especially active in nutrient cycling as compared to their high-order counterparts (Alexander et al. 2000, Yeakley et al. 2016). Phosphorus and nitrogen uptake rates in streams are associated with a suite of physical and chemical (e.g., sedimentation, adsorption and volatilization) and biological (e.g., assimilation and transformation by aquatic biota) processes (Valett et al. 2008, Potter et al. 2010, Webster et al. 2016). The contribution of biological activity to nutrient retention is expected to vary with rates of metabolic activity of the aquatic ecosystem (Fellows et al. 2006, Arce et al. 2014). Ecosystem metabolism consists of gross primary production (GPP) and ecosystem respiration (ER) and is most often derived from diel changes in dissolved oxygen concentrations. Chronic inputs of sewage effluent (Gücker et al. 2006, Sánchez-Pérez et al. 2009) or nutrient enrichment from agricultural runoff (Gücker et al. 2009) alter GPP and ER and these effects have been well documented in rivers and streams. In contrast, fewer studies have focused on the relationship between metabolic activity and the capacity of streams to retain nutrients (but see Hall and Tank 2003, Dodds et al. 2008, and Stutter et al. 2010).

Geomorphic, hydrologic, and hydraulic factors such as discharge, channel size, and transient storage are also relevant for nutrient uptake because they influence water residence time and therefore the contact time between dissolved nutrients and reactive substrates (Valett et al. 1996, Gücker and Boëchat 2004, Thomas et al. 2005, Ensign and Doyle 2006, Tromboni et al. 2017, Cunha et al. 2018). Increasing hydrologic connectivity between the channel and the hyporheic zone and promoting hydrological exchange between the stream and its floodplain increase nutrient retention through biological assimilation, denitrification and/or adsorption to clay particles. Increasing the dimensions and activity of the hyporheic zones has been identified as important restoration techniques for nutrient-impacted streams (Klocker et al. 2009, Johnson et al. 2016).

Agricultural activities alter stream features associated with nutrient uptake. These impacts include increased loading of fine sediment (Naden et al. 2016), direct nutrient enrichment from fertilizer application and runoff (Mulholland et al. 2008, Connolly et al. 2015), and changes in canopy cover and riparian vegetation (Goss et al. 2014, Feijó-Lima et al. 2018). Significant reduction of nutrient retention efficiency in streams draining agricultural landscapes is expected (e.g., see Royer et al. 2006, Weigelhofer et al. 2013). Increases in incident light due to riparian deforestation, often associated with agricultural activity, can lead to higher rates of GPP and influence in-stream nutrient uptake (Feijoó et al. 2018). The loss of riparian vegetation also alters the temperature regime, supply of terrestrial leaf litter and large wood, and bank stability (Burrell et al. 2014), with significant consequences for aquatic metabolism and processing of phosphorus and nitrogen (Niyogi et al. 2007, Bleich et al. 2015). In addition, agricultural development often results in flashier hydrographs, and altered baseflow compared to undeveloped segments due to channel straightening, bank stabilization and hardening, water withdrawals, and water storage (Laws and Roth 2004, Poff et al. 2006).

A reasonable number of investigations have already linked agricultural practices with lower capacity of whole-stream nitrogen and phosphorus uptake, but the vast majority of these were conducted in the Northern Hemisphere (e.g., Bernot et al. 2006, Mulholland et al. 2008, Weigelhofer et al. 2012). In developing countries like Brazil and Argentina, the impacts of agricultural expansion and increasing fertilizer use on the ability of streams to mediate external nutrient loads remains unclear (but see Gücker and Boëchat, 2019), and there is a pressing need to assess stream functioning across a gradient of nutrient supply and stream conditions. More specifically, many regions in South America have been largely converted to arable land for sugarcane, maize, coffee, cotton, rice, soybean, and vegetable production over the last few decades (Tabarelli et al. 2010, Piquer-Rodríguez et al. 2018, Rodriguez et al. 2018), establishing countries as Brazil and Argentina among the world leaders in agricultural production. Hydrologically, low-order streams respond rapidly to precipitation and extreme weather events, which are more intense and frequent in tropical and sub-tropical areas in comparison to higher latitude zones (Taniwaki et al. 2017). Also, the influence of land use changes on water quality might be especially relevant in the tropics because organic matter mineralization is more rapid, and erosion and sedimentation rates are usually greater in such regions (Connolly and Pearson 2007, Rodrigues et al. 2018). An assessment of nutrient transformations in streams and rivers in South America is needed to guide water resources planning and land use management. Alteration of ecosystem processes is often influenced in regionally-specific ways. Currently, it is unclear how accurately conclusions from the United States and Europe extend to South-American water bodies.

Here, we quantified the effects of agricultural activity on retention of ammonium (NH_4^+) and soluble reactive phosphorus (SRP), and on metabolic rates in headwater streams located in South-America. Agricultural production in tropical and sub-tropical regions differs from temperate areas in that different crops are grown (e.g. sugar cane), different strains of cattle are used, tropical soils are poorer in nutrients, growing seasons are longer or year-round, and pests may be more intense. We conducted whole-stream nutrient additions and measured metabolic rates in twelve streams in Brazil and Argentina with contrasting land use in their watersheds. We used regression models to analyze potential drivers of nutrient uptake in these streams, including GPP and ER rates, and examined the influence of agricultural activity on these relationships. We hypothesized that the agricultural streams in South America would become less efficient in retaining NH_4^+ and SRP, indicated by longer uptake lengths, lower areal uptake rates, and reduced uptake velocities compared to sites with low-intensity agriculture. We also expected that drivers of variation in nutrient uptake would differ among streams located in different land use categories (intensive, hereafter referred to as “agricultural”, or low-intensity agricultural) as they have contrasting conditions regarding water chemistry, metabolic rates and geomorphological features.

METHODS

Study sites

We studied reaches of 12 streams located in Minas Gerais and São Paulo States (Brazil) and Buenos Aires Province (Argentina), with four streams in each state/province (two agricultural and two with low-intensity agriculture). Photographs of each stream are available as online Supplementary Material. We determined the relative composition of land use for the watersheds of each stream using ArcGIS 10.1 (ESRI) geographic information systems (GIS) software. The watershed boundaries were delineated using flow path analysis of digital elevation models and 1:25,000 topographic maps. The percentage of land use in each watershed was determined using maximum likelihood classification with data from U.S. Geologic Survey (LANDSAT 8 Thematic Mapper, obtained at: https://earthexplorer.usgs.gov/) for the following classes: water, agriculture, urban area and natural vegetation. In general, half of the streams were predominantly agricultural, with intensive agriculture on 37-65% of the catchment area and low contributions of natural vegetation (25-44%). The other half was less impacted and with greater contributions of natural areas (55-87% natural vegetation; 0-28% agricultural area with low mechanization and also smaller fields interspersed with pasture and forest), hereafter referred to as low-intensity agricultural streams (Table 1). The studied aquatic systems spanned a wide range of water depths (averages from 0.03-0.36 m) and wetted widths (from 0.63-2.81 m) (Table 1). The Brazilian streams had denser riparian vegetation (canopy cover >60%), while the Argentinian ones were less shaded (canopy cover <20%), in accordance with the terrestrial biome in which they are embedded. Fine sediments (e.g., silts and clay) were more abundant in the Argentinian sites, whereas sand was predominant in the Brazilian sites.

Four streams are located in São Paulo State in the São Carlos municipality and representative of the Cerrado biome. The climate is tropical semi-humid with dry winters (*Aw* according to Köppen-Geiger classification, Kottek et al. 2006). Total precipitation is usually about 1,300 mm year^{-1}, with drier periods from April to September, and mean air temperatures usually range from 19-25^{o}C. Macrophytes were absent in the São Paulo streams, with sand and silt as the dominant substrate types. The streams were typical meandering channels with alternating runs and pools. Benthic chlorophyll-a is usually not greater than ~35 mg m^{-2} (Saltarelli et al. 2018) Four other sites are located in the State of Minas Gerais, in the Campo das Vertentes region (municipalities of São João del-Rei, Tiradentes, Prados, and Resende Costa), in the Cerrado/Atlantic Rainforest transition. Climate type is humid subtropical climate (*Cwa*, Köppen), also with drier months from April to September. Total precipitation is higher in comparison to São Paulo sites (~1,470 mm year^{-1}) and air temperatures typically vary between 16-22^{o}C. There were no macrophytes in these Minas Gerais run-pool type mountain streams, and dominant sediments ranged from silt to medium sands in pools, and fine sands to cobbles in runs. Benthic chlorophyll-a in the studied streams ranges from 6 to 54 mg m^{-2} (unpublished data).

Finally, four streams are located in the Pampas biome, Buenos Aires Province, which has 39% of total Argentinian population and where more than 50% of country's industrial activities (e.g., metal and leather production) are established (INDEC, 2010). These streams have low slope gradients, but limited connection with wetlands along the floodplains and riparian corridors. Also, the streams are characterized by the lack of riparian forest vegetation (i.e., grasslands predominate on the banks), low current velocities, alternating wet and dry periods, and the development of dense and rich macrophyte communities, mainly palustrine species (Giorgi et al. 2005; Feijoó and Lombardo 2007).

All field activities were carried out two times in each stream to roughly encompass seasonal variations in precipitation and air temperatures, including dry and rainy periods. Besides general characterization of the streams, we conducted nutrient additions and whole-stream metabolism estimates (see details below) over the year 2017: January and July (São Paulo), May and August (Minas Gerais), and February and September (Buenos Aires).

General characterization of the streams

We estimated the canopy cover percentage (CC, %) in each stream reach using a concave densiometer (Forestry Suppliers Inc., Jackson, MS, USA) following Lemmon (1956, 1957). We used salt dilution gauging (Webster and Valett, 1996) to quantify stream discharge (Q, L s^{-1}) and mean water velocity (v, m s^{-1}) within each experimental reach. Salt breakthrough curves used in the discharge calculations were also analyzed using a one-dimensional advection-dispersion model (OTIS, Runkel 1998) to estimate the cross-sectional area of the stream channel (A, m^{2})

using direct measures of wetted widths (w) and depth (h), the cross-sectional area of the transient water storage zone (A_S, m^2) and the exchange rate between the channel and the transient storage zone (α, s^{-1}). Using the OTIS model outputs, we also calculated the ratio between the cross-section of the transient storage zone and advective channel (A_S/A), as well as the storage zone exchange rate (α).

Aquatic metabolism estimation

We estimated whole-stream metabolism for each stream reach, always under stable base-flow and clear sky/sunny weather conditions, by measuring diel changes in dissolved oxygen concentration (DO), water temperature, and light intensity at 10-min intervals over 1- to 3-d deployment periods with an optical dissolved O_2 and temperature probe (Onset-HOBO® U26-001) and a light logger (Onset-HOBO® UA-002- 64, Onset Computer Corporation, Bourne, Massachusetts, USA). Oxygen probes were calibrated to water-saturated air prior to deployment, and post deployment calibrations were used to correct sensor drift. While longer deployments would have been optimal, the threat of theft or vandalism in these areas precluded extended unattended deployments. We estimated daily gross primary production (GPP), net primary production (NPP) and ecosystem respiration (ER) rates and the gas-exchange coefficient (KO_2) by fitting a one-station model to diel O_2 curves, following procedures from Riley and Dodds (2013) and Dodds et al. (2013). Values of barometric pressure were obtained from nearby climatologic stations for each stream.

Stream nutrient uptake

We used the Tracer Additions for Spiraling Curve Characterization (TASCC) approach (Covino et al. 2010) to estimate ambient uptake metrics from a pulsed nutrient addition. We calculated the ambient uptake metrics: uptake length (Sw_{amb}), areal uptake rate (U_{amb}), and uptake velocity (V_{famb}) for NH_4^+ and SRP following the nutrient spiraling concept (Stream Solute Workshop, 1990). We simultaneously added NH_4^+ (as NH_4Cl), and SRP (as K_2HPO_4), both as bioavailable reactive tracers to characterize nutrient dynamics, and Cl^- (as NaCl) as a conservative tracer to account for dilution and to characterize stream hydrodynamics. In our study, we used pulsed additions which estimate ambient uptake rates with results that are comparable to multiple level nutrient additions or isotopic methods (Trentman et al. 2015) to characterize general patterns of nutrient retention across the studied sites and obtain uptake metrics to compare the extent of agricultural influence.

The added mass of the conservative tracer was calculated prior to each experiment in order to increase in-stream electrical conductivity (EC) to detectable levels (i.e., 5–10-fold of background EC), while the added mass of nutrients was calculated to raise in-stream concentrations to promote saturation (Covino et al. 2010). For each experiment, we dissolved all salts in a 5 L bucket with stream water and then poured the solution carefully into a well-mixed run section of the stream at the top of the experimental reach over one minute. EC was measured over the experiment using a multiparameter probe at the downstream end of the reach (Model HI 9829, HANNA Instruments, Woonsocket, RI, USA). At this station, we took water samples over the full pulse, with sampling frequency as a function of EC rate of rise or decline, resulting in 21–26 samples per experiment, in order to obtain well-characterized breakthrough curves. Immediately before the additions, we collected three water background samples to determine ambient nutrient concentrations (C_{amb}). All water samples were filtered immediately upon collection (GF/C Glass Microfiber Membranes, 0.45 µm, Whatman International, Kent, UK) and frozen until analysis. Nutrient concentrations were determined, always in triplicates, via colorimetry methods. The analytical method used for NH_4^+ (as N) was based on Solórzano (1969), modified for a 7 mL sample volume, and the one used for SRP (as P) followed APHA (2012). The detection limits for NH_4^+ and SRP analyses were 1.7 and 0.7 µg L^{-1}, respectively

Statistical analyses

For statistical analyses, data from streams were pooled regardless their location in Brazilian or Argentinian regions, but considering agricultural influence (i.e., land use) as an independent, categorical variable. The discrimination between low-intensity agricultural and agricultural sites was based on the percentages of land use categories in their respective drainage areas (Table 1). All data were transformed [ln (data+1)] to meet normality assumption. Differences among low-intensity agricultural and agricultural streams regarding their physical, chemical, and biological variables, as well as their nutrient uptake metrics and metabolism, were tested through nested design general linear mixed model (GLMM) with a confidence level of 95% ($p < 0.05$). Here, we considered “stream” nested in “land use”, and “region” as a random factor. We performed multiple linear regressions using ambient uptake metrics for NH_4^+ and SRP as dependent variables (only those metrics with significant differences between low-intensity agricultural and agricultural streams, based on the previous GLMM). The tested independent variables were relevant uptake drivers based on a literature review (e.g., Dodds et al. 2002, Hall and Tank 2003, Gibson et al. 2015) and included all variables shown in Table 2 (A_S/A, α, v, Q, NH_4^+, C_{amb}, SRP C_{amb}, GPP, ER, DO, T, and CC). We used a backward stepwise strategy to select the most influential variables ($p < 0.05$ and adjusted $R^2 \geq 0.60$) and controlled for multicollinearity through the VIF (Variance Inflation Factor) calculation in each model. We carried out all statistical analyses with Statistica 10 (Statsoft, Tulsa, OK, USA).

RESULTS

Streams’ physical and chemical characteristics

The raw dataset used in this paper is fully available as online Supplementary Material. Low-intensity agricultural and agricultural sites were significantly different ($p < 0.05$, GLMM) with respect to some of the variables analyzed (Table 2). Low-intensity agricultural sites had significantly higher A_S/A ratios ($p < 0.05$) than agricultural ones. Conversely, ambient NH_4^+ and SRP concentrations were about 3.1 and 9.4 times higher ($p < 0.05$) in agricultural sites. Mean daily dissolved oxygen and water temperature were relatively similar among sites (Table 2). Canopy cover percentages differed among streams, but not between the land use categories ($p = 0.072$), with averages around 60%. Mean discharges were around 11.2 L s^{-1} in agricultural sites and 19.2 L s^{-1} in low-intensity agricultural sites, with significant difference among land used types ($p < 0.05$), while average water velocities were similar in low intensity agricultural and agricultural sites (0.09 m s^{-1}) (Table 2).

Ecosystem metabolism and nutrient dynamics

As for the metabolic rates, ER was 3.1 times greater in the low-intensity agricultural sites than in agricultural sites ($p < 0.05$, Table 2). Rates of GPP were not affected by land use ($p > 0.05$). All streams were net heterotrophic, with GPP:ER ratios varying between 0.0 and 0.27 and 0.0 and 0.57 in the agricultural and low-intensity agricultural streams, respectively. In general, ambient uptake lengths were longer, and ambient uptake rates and velocities were lower in agricultural streams (Figure 1). Both Sw_{amb} for NH_4^+ and SRP were significantly different ($p < 0.05$) among low-intensity agricultural and agricultural sites (mean Sw_{amb} values for NH_4^+ and SRP were about three times shorter in low-intensity agricultural sites) (Figure 1A). U_{amb} values were not statistically different among land use categories ($p = 0.942$ and 0.667, respectively for NH_4^+ and SRP) (Figure 1B). V_{famb} was significantly different between land use categories for SRP but not for NH_4^+, with low-intensity agricultural streams removing SRP more than two times more efficiently than agricultural streams (average V_{famb} 22 versus 9 mm min^{-1}, respectively) (Figure 1C).

The best regression models ($p < 0.05$ and adjusted $R^2 \geq 0.60$) revealed different predictors for nutrient retention metrics associated with agricultural and low-intensity agricultural sites (Tables 3 and 4). In general, ambient SRP concentration had a strong positive effect on NH_4^+ uptake and ambient NH_4^+ concentrations had the same effect on SRP uptake. Overall, our regression models indicated a greater number of variables significantly related with uptake variation in agricultural sites compared to low-intensity agricultural sites (Table 5).

Temperature and canopy cover were the dominant predictors and negatively associated with NH_4^+ retention in low-intensity agricultural sites (Table 3, adjusted $R^2 = 0.61$). Regression models addressing NH_4^+ variation in agricultural sites (adjusted R^2 ranging from 0.82 to 0.91) suggested that canopy cover and a range of hydraulic/geomorphological variables were important explanatory variables (e.g., A_S/A and α had positive effects, while velocity and dissolved oxygen had negative ones). In contrast, SRP retention in low-intensity agricultural sites was more closely associated with variation in ER rates through a positive relationship (Table 4, adjusted R^2 of 0.61). Finally, SRP retention in agricultural streams (adjusted R^2 from 0.69-0.88) was positively associated with dissolved oxygen, GPP, A_S/A, discharge and canopy cover.

DISCUSSION

Trends in South American stream function from a global perspective

Our experimental approach focused on the impacts of agriculture in areas of rapid development in Brazil and Argentina, regardless the streams' location in different biomes. We acknowledge that the small sample size of twelve streams of our study does not allow for testing biome-driven variations in addition to tests of land use effects. Moreover, the studied streams were representative of areas with significant agricultural land conversion in South America, for which scarce information is available to date. The TASCC (Covino et al. 2010) approach we followed explores the pattern in Sw that occurs as nutrient concentrations rise and fall across the downstream breakthrough curve and uses that pattern to extrapolate estimates of Sw under ambient nutrient concentrations thus avoiding, in theory, criticisms associated with traditional nutrient enrichment methods (see Earl et al. 2007).

The effects of intensive agricultural activity on our study streams in Brazil and Argentina were clear and included significant nutrient enrichment, changes in geomorphic characteristics, and shifts in metabolic rates. Agricultural sites had ambient nutrient concentrations (Table 2) that exceeded water quality reference conditions and guidelines established in South America (e.g., Brasil 2005). NH_4^+ concentrations expected in reference tropical rivers and streams in São Paulo State, for example, were estimated between 60-100 μg L^{-1} by Cunha et al. (2011) and the concentrations in our study agricultural streams were frequently higher (see Feijoó and Lombardo 2007 for nutrient baseline conditions in Argentinian streams). Nutrient enrichment of agricultural streams from fertilizer runoff is well documented in North America (e.g. Turner and Rabalais, 1991, Mulholland et al. 2008), but our understanding of fertilizer impacts in South America remains limited (Martinelli and Filoso 2008). This is because different crops are grown than in more studied areas, soil fertility is lower requiring more fertilizer input, and production can occur year round. Our results could serve as a starting point to define nutrient abatement goals in agricultural streams. The crops in the watersheds examined here mainly consisted of sugarcane, soybean, and vegetable production, which demand significant nitrogen, phosphorus and potassium supplementation to increase productivity (Silva et al. 2017). Currently, Brazil and Argentina still need more detailed management strategies for mitigating the detrimental effects of agricultural development and expansion on critical ecosystem services, such as drinking water supply (Rada 2013, Modernel et al. 2016).

The studied agricultural streams also had lower ratios of transient storage areas to stream channel cross sectional area (A_S/A, Table 2) that may be important predictors of ecosystem function in South American streams (Gücker and Boëchat 2004, Gücker et al. 2009). Ensign and Doyle (2006) provided a global synthesis of the nutrient spiraling literature and highlighted that A_S/A represents generic transient storage information and that limited evidence of a causative relationship between transient storage and nutrient uptake was available in the analyzed datasets. The authors reinforced the importance to refine these data and characterize the mechanisms of storage (e.g., dead zones, biofilms or hyporheic contribution). Our study did not address these mechanisms, but as transient storage represented by A_S/A values correlates with the residence time of water, we assumed less exposure of dissolved nutrients to biochemically reactive substrates in the case of our agricultural sites. Similarly, Sheibley et al. (2014) reported small amounts of transient storage in seven agriculturally influenced streams in the United States and found A_S/A values between 0.020 and 0.111, which are even lower than our values (Table 2). Values of A_S/A reported by Gücker et al. (2009) and Tromboni et al. (2017) for agricultural Brazilian Cerrado and pristine Atlantic rainforest streams were in the range of the values found in the present study (from 0.12 to 0.31, and from 0.04 to 0.61, respectively).

In contrast to the global trend, agricultural streams in our study had lower rates of GPP and ER than their low-intensity agricultural counterparts. Silva-Junior (2016) performed a systematic review to evaluate land use effects on stream metabolism worldwide and found that most studies reported increases in GPP and ER rates associated with agriculture. While Gücker et al. (2009) found lower rates of ER in agricultural Cerrado streams as a result of increased bottom shear stress that decreased benthic microbial biomass in the central streambed, we did not find significant differences in current velocity between agricultural and low-intensity agricultural streams in the present study. We suspect this counterintuitive trend in our streams is in part due to the lack of a significant difference in variables expected to increase metabolic rates (temperature and canopy cover) between agricultural and low-intensity agricultural sites. Particularly, the lack of differences in canopy cover between the studied stream types probably influenced our results, since canopy cover significantly drives metabolic rates (Bunn et al. 1999). We also speculate that higher ER rates in the low-intensity agricultural sites result from higher channel complexity and potential differences in the composition and abundance of benthic biofilms (e.g., algae, bacteria and fungi) (Saltarelli et al. 2018), although we did not include biofilm characteristics in this study. Also, herbicides and siltation can be an important issue in agricultural streams as turbidity can absorb light and sediments can scour algae, as highlighted in other studies (e.g., see Wantzen and Mol 2013).

The low-intensity agricultural systems we studied in South America had shorter ambient uptake lengths compared to our agricultural sites, and to streams in North America, Europe or Oceania with similar ranges of stream discharge (e.g., Niyogi et al. 2004, Bernot et al., 2006; Gücker and Pusch, 2006). In their review of 969 nutrient uptake measurements, Hall et al. (2013) observed that nutrient uptake lengths were generally longer in human-impacted streams than in undisturbed systems. The same authors used this global dataset to perform scaling of uptake length with specific discharge (discharge divided by stream width) to examine the relationships between stream size and Sw in a standardized way. When we plotted our data together with the same dataset from Hall et al. (2013), we observed our low-intensity agricultural sites had proportionally shorter Sw_{amb} values, falling below their regression lines of both NH_4^+ and SRP Sw_{amb} against specific discharge. In this study, we were not able to identify the causes of the high uptake efficiency of our low-intensity agricultural streams. We speculate this could be related with the relatively higher and more stable temperatures and insolation throughout the year (see Boulton et al. 2008) in comparison to the streams reported by Hall et al. (2013), which are mostly from the Northern hemisphere. This would lead to more stable biological communities, as well as to possible differences in stoichiometry and nutrient limitation (e.g., Tromboni et al. 2018).

Agricultural effects on nutrient retention in South American streams

Ambient uptake metrics suggested that nutrient retention was lower in our agricultural sites than in low-intensity agricultural sites, with statistically significant differences for Sw_{amb} for NH_4^+ and SRP (Figure 1A) and V_{famb} for SRP (Figure 1C). In our study, the uptake metrics (longer Sw_{amb} for NH_4^+ and SRP and lower V_{famb} for SRP) generally suggested low nutrient retention when compared to metrics reported for more pristine sites in the Brazilian Coastal Atlantic Forest (Tromboni et al. 2017, Tromboni et al. 2018) or even for chronically nutrient-rich Pampean streams in Argentina (García et al. 2017). In general, lower nutrient uptake capacity in agricultural streams than in less impacted/pristine streams can be attributed to i) saturation of the biological community (Bernot et al., 2006); ii) reduced hydrological complexity of the channel (Argerich et al. 2011; Sheibley et al., 2014); iii) loss of riparian vegetation (Weigelhofer 2017); iv) restricted hyporheic water exchange with the sediments (Macrae et al., 2003); and v) reduced adsorption capacities of the sediments (Stutter and Lumsdon, 2008). A rapid development of agriculture has been occurring in South America in recent decades (Ceddia et al. 2013, Garrett et al. 2018) and specific climate/hydrological features make this region more vulnerable to the detrimental effects of croplands (Taniwaki et al. 2017). As our study suggested that agricultural streams are generally less nutrient retentive, progressive agricultural intensification or expansion is expected to increase the role of streams in watershed nutrient export.

In our study, the regression models allowed us to recognize three main factors accounting for differences in nutrient retention among our low-intensity agricultural and agricultural sites: background nutrient concentrations (water chemistry), hydrological and transient storage-related variables (hydro geomorphology), and metabolism (biological activity). To the best of our knowledge, our study is among the first to identify and integrate these relationships in South-American streams, thereby providing important information for mitigation and restoration efforts in this understudied region.

Interestingly, the number of potential drivers of nutrient retention was smaller in low-intensity agricultural sites in our study than in agricultural sites, in which a large number of variables, including ambient nutrient concentrations, hydraulic/geomorphic variables, and metabolic rates affected uptake metrics (Tables 3-5). Thus, if agricultural activities in the low-intensity agricultural catchments were intensified, the controls of nutrient uptake and associated mechanistic relationships to be considered in restoration and mitigation efforts may become more complex.

The uptake metrics for NH_4^+ (Sw_{amb}) and SRP (Sw_{amb} and V_{famb}) indicated that each of these nutrient forms impacted the cycling of the other in our study streams. For the NH_4^+ Sw_{amb}, for example, models suggested that ambient SRP had a positive effect on retention (i.e. shortening the uptake length) in both land use categories. Therefore, we observed a strong relationship between uptake metrics of both NH_4^+ and SRP and ambient concentrations of the other element (i.e., ambient SRP concentration effects NH_4^+ uptake and vice versa). This effect suggests N and P co-limitation in these water bodies, which has been previously reported for streams, but mainly in undisturbed systems (e.g., Schade et al 2011, Appling et al. 2014, Finkler et al. 2018). However, strict co-limitation by N and P in our streams seems unlikely based on background nutrient concentrations (Table 2). We thus suspect that our results suggest that differential availability of nitrogen forms (i.e. NO_3 or NH_4) complicates judgments of nutrient limitation based on simple ratios of dissolved inorganic nutrients. These results suggest that increasing NH_4^+ availability can stimulate phosphorus uptake even when dissolved inorganic nitrogen is stoichiometrically abundant.

Several studies have documented the effects of agricultural land use on the size of transient storage zone (e.g., Bernot et al., 2006, Weigelhofer 2017). Our results support studies (e.g., Runkel 1998; Webster et al. 2003) where A_S/A values were significantly higher in low-intensity agricultural sites (Table 2, $p < 0.05$) and agricultural sites usually have lower A_S/A associated with increased siltation, for example. However, this does not mean that hyporheic/surface water dimensions and activity do not influence nutrient uptake in agricultural streams. To the contrary, A_S/A and α values were positively associated with NH_4^+ and SRP removal in the agricultural streams in South America, in general decreasing Sw_{amb} and increasing V_{famb}. Transient storage zones retain water in eddies, pools, and the hyporheic zone, and storage zone size is related to stream morphology (e.g., swamp, meandering or run streams). Stream hydromorphological features can influence the magnitude of nutrient retention (Gücker and Boëchat 2019), with hydrological retention in metabolically active zones providing additional opportunity for microbial assimilation, thereby increasing nutrient removal (Ensign and Doyle 2006; Webster and Valett 2007). Interestingly, SRP retention was related to discharge in our agricultural streams (Table 4). As agriculture is expected to indirectly change the hydrological regime through modifications of different components of the hydrological cycle (e.g., surface runoff and interception) (Mello et al. 2018), we expect implications for SRP removal as such components directly influence discharge.

In the agricultural sites, we also observed a positive correlation between NH_4^+ retention and the storage zone exchange coefficient (α), which represents the mass-transfer coefficient of water between the channel and the storage zone (Tables 3 and 5). Greater nutrient retention as α increases is consistent with the potential, but limited role of storage exchange in agricultural streams (Sheibley et al.2011). The low storage zone and presumable shorter residence times typical of these streams suggest that NH_4^+ retention can be affected by physical transport and biochemical processing in storage zones. In fact, in other studies, rates of sediment nitrification and denitrification were higher in agricultural than in undisturbed streams (Kemp and Dodds, 2002; Von Schiller et al. 2009), probably because of the long-term N loading and accumulation in groundwater, organic-rich sediments, and aquatic vegetation that are commonly present in agricultural watersheds.

For the low-intensity agricultural sites, canopy cover and water temperature increased Sw_{amb} for NH_4^+. Such negative influence on retention suggests that NH_4^+ uptake was favored by light availability, although GPP was not a significant predictor in our models. Regarding the SRP uptake in low-intensity agricultural streams, ER was positively associated with retention (increasing V_{famb}, Table 4). Respiration influences on SRP uptake have also been described in North-American streams (e.g., Gibson and O'Reilly 2012). In our low-intensity agricultural sites, especially those in Brazil, heterotrophic assimilation associated with leaf litter decomposition is probably an important pathway for microbial phosphorus removal, which in turn may be affected by temperature and precipitation patterns (Tonin et al. 2017). GPP was not related to SRP retention in our low-intensity agricultural sites, though this has been reported in the literature (e.g., Withers and Jarvie 2008, Rasmussen et al. 2011). We suspect this discrepancy is due to light limitation (especially in the Brazilian streams where canopy cover values can exceed 90%). Correlations of Sw_{amb} and Vf_{amb} of SRP with GPP, and not with ER as in the low-intensity agricultural streams, pointed to autotrophic phosphorus assimilation in the studied agricultural streams.

CONCLUSIONS

Recent discussions on the water-energy-food nexus (e.g., Amorim et al. 2018, Reddy et al. 2018) have been including the improvement of agriculture management and practices as a key element to minimize global risks and promote water quality, ecosystem services, and food security. Many regions in Brazil and Argentina have been undergoing significant expansion of the agricultural frontier into natural biomes and rapid conversion of the original vegetation to pastures and croplands. Further, many catchments with low-intensity, rural farming in both countries may undergo agricultural intensification in the next years, with potential significant implications for stream ecosystem functioning. Many aspects of how such land use changes will impact ecosystem function and structure in these areas are unknown. Specifically, limited information is available regarding how in-stream nutrient retention can be affected by fertilizer inputs, geomorphic changes, hydrological alterations and other modifications derived from agricultural land use.

Agricultural streams in Brazil and Argentina exhibited key differences in comparison to the examined low-intensity agricultural water bodies. The former had more nutrient-enriched conditions, less hydrological retention, and apparently less microbial activity as suggested by lower metabolic rates. Agriculture had an overall negative effect on nutrient processing and retention, with overall longer ammonium and phosphate uptake lengths and slower phosphate uptake velocities in agricultural streams. Moreover, the drivers of nutrient retention differed between agricultural and low-intensity agricultural streams, and a larger number of factors affected nutrient retention in our agricultural streams, including factors such as hydraulic variables, GPP and dissolved oxygen concentrations, that were not important in low-intensity agricultural streams. As our dataset is admittedly limited, more studies are required to delineate the nutrient retention capacities of streams in these regions and how they are influenced by agriculture. As the world human population and standard of living grows, there will be even more demand for crops. Much of this growth in demand will occur in tropical and sub-tropical areas, thus we need more data globally in these areas with rapid land use conversion to inform their conservation and restoration.

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Table 1. Characteristics of the study streams in Brazil and Argentina, including their geographic coordinates, average depths and widths, as well as percentages of main land uses in their respective catchments. Other land use categories not shown include urban areas, open spaces, and water bodies.

Site name	Location	Geographic coordinates	Depth (m)	Width (m)	Land use: Agricultural areas (%)	Land use: Natural areas (%)
Broa	São Paulo, Brazil	22°11'40.93"S 47°53'55.78"W	0.31	0.88	0	87
Espraiado		21°58'46.75"S 47°52'23.11"W	0.23	0.63	11	86
Mineirinho		22°00'12.78"S 47°55'40.82"W	0.03	1.01	41	38
Canchim		21°57'54.69"S 47°50'38.02"W	0.04	1.19	65	32
Bichinho	Minas Gerais, Brazil	21°06'08.44"S 44°06'40.12"W	0.14	1.76	23	59
Calçada dos Escravos		21°04'38.49"S 44°10'23.54"W	0.13	1.42	19	76
Correias		20°59'15.17"S 44°11'38.43"W	0.16	1.89	47	35
Nelson		21°03'21.59"S 44°11'33.93"W	0.19	1.59	47	44
Chubichaminí	Buenos Aires, Argentina	35°07'24.09"S 57°41'22.52"W	0.31	1.89	22	66
Cajaravilla		35°02'53.30"S 57°48'38.81"W	0.36	2.81	28	55
Del Gato		34°58'52.79"S 58°03'13.14"W	0.20	1.64	45	25
Carnaval		34°55'02.74"S 58°06'29.69"W	0.24	1.47	37	30

Table 2. Mean ± standard errors of physical, chemical and biological variables in the study streams in Brazil and Argentina at low-intensity agricultural and agricultural sites. Although mean ± standard errors of the original data are shown here, all data were transformed [ln (data+1)] to meet the normality assumption for GLMMs. Results of GLMMs are the effects stream nested in land use, and land use. The symbol * indicates significant differences ($p < 0.05$)

Variable	Low-intensity agricultural sites	Agricultural sites	p value	
			Effect stream (land use)	Effect land use
A_S/A	0.387 ± 0.067	0.187 ± 0.041	0.964	0.028*
α (s^{-1})	0.007 ± 0.004	0.062 ± 0.056	0.502	0.359
v ($m\ s^{-1}$)	0.09 ± 0.03	0.09 ± 0.02	0.023*	0.626
Q ($L\ s^{-1}$)	19.2 ± 6.0	11.2 ± 3.4	<0.001*	0.021*
NH_4^+ C_{amb} ($\mu g\ L^{-1}$)	52.6 ± 19.4	161.3 ± 74.6	0.026*	0.004*
SRP C_{amb} ($\mu g\ L^{-1}$)	93.8 ± 39.7	494.9 ± 191.0	0.086	<0.001*
GPP ($gO_2\ m^{-2}\ d^{-1}$)	2.2 ± 1.2	0.8 ± 0.6	0.771	0.335
ER ($gO_2\ m^{-2}\ d^{-1}$)	13.5 ± 4.4	4.4 ± 1.6	0.251	0.033*
DO ($mg\ L^{-1}$)#	6.6 ± 0.4	7.2 ± 0.6	0.899	0.610
T (^oC)	18.5 ± 1.0	18.8 ± 1.0	0.991	0.820
CC (%)	60.3 ± 12.6	58.6 ± 11.0	<0.001*	0.072

#During nutrient addition period; A_S/A: storage zone area to stream cross-sectional area ratio, α: storage rate, v: water velocity, Q: discharge, NH_4^+ C_{amb}: ambient ammonium, SRP C_{amb}: ambient soluble reactive phosphorus, GPP: gross primary production, ER: ecosystem respiration, DO: dissolved oxygen, T: water temperature, CC: canopy cover

Table 3. Best multiple linear regression models ($p < 0.05$ and adjusted $R^2 \geq 0.60$) for the ambient ammonium (NH_4^+) uptake metric Sw_{amb} as function of environmental variables for the low-intensity agricultural and agricultural stream sites in Brazil and Argentina. Sw_{amb} was significantly different for NH_4^+ between land use categories (see Figure 1). All data were ln-transformed [ln(x + 1)]. Regression coefficients (B), Variance Inflation Factor (VIF), Standard Errors (SE), p values and adjusted R^2 are shown for each case.

Land use category	Dependent variable	Independent variable	B	VIF	SE	p value	Adj. R²
Low-intensity agricultural	NH_4^+ Sw_{amb}	Intercept	-5.26	--	2.30	0.048	0.61
		SRP C_{amb}	-0.18	1.89	0.06	0.030	
		T	3.14	1.89	0.822	0.008	
		Intercept	-3.65	--	1.84	0.047	0.61
		CC	0.15	1.16	0.06	0.032	
		T	2.25	1.16	0.59	0.007	
Agricultural		Intercept	4.92	--	0.76	<0.001	0.91
		A_S/A	-3.73	1.31	1.19	0.020	
		Vel	1.27	1.23	0.29	0.005	
		SRP C_{amb}	-0.56	1.40	0.08	<0.001	
		Intercept	-2.29	--	1.39	0.159	0.82
		A_S/A	-5.24	1.59	1.89	0.039	
		DO	2.55	1.10	0.70	0.015	
		CC	0.59	1.35	0.13	0.007	
		α	-4.77	1.22	1.43	0.020	

C_{amb}: nutrient ambient concentrations; T: temperature; CC: canopy cover; A_S/A: ratio between the cross-section of the transient storage zone and advective channel; Vel: water velocity; DO: dissolved oxygen; α: storage zone exchange rate

Table 4. Best multiple linear regression models ($p < 0.05$ and adjusted $R^2 \geq 0.60$) for the ambient soluble reactive phosphorus (SRP) uptake metrics Sw_{amb} and V_{famb} as function of environmental variables for the low-intensity agricultural and agricultural stream sites in Brazil and Argentina. Sw_{amb} and V_{famb} were significantly different for SRP between land use categories (see Figure 1). All data were ln-transformed [ln(x + 1)]. Regression coefficients (B), Variance Inflation Factor (VIF), Standard Errors (SE), p values and adjusted R^2 are shown for each case.

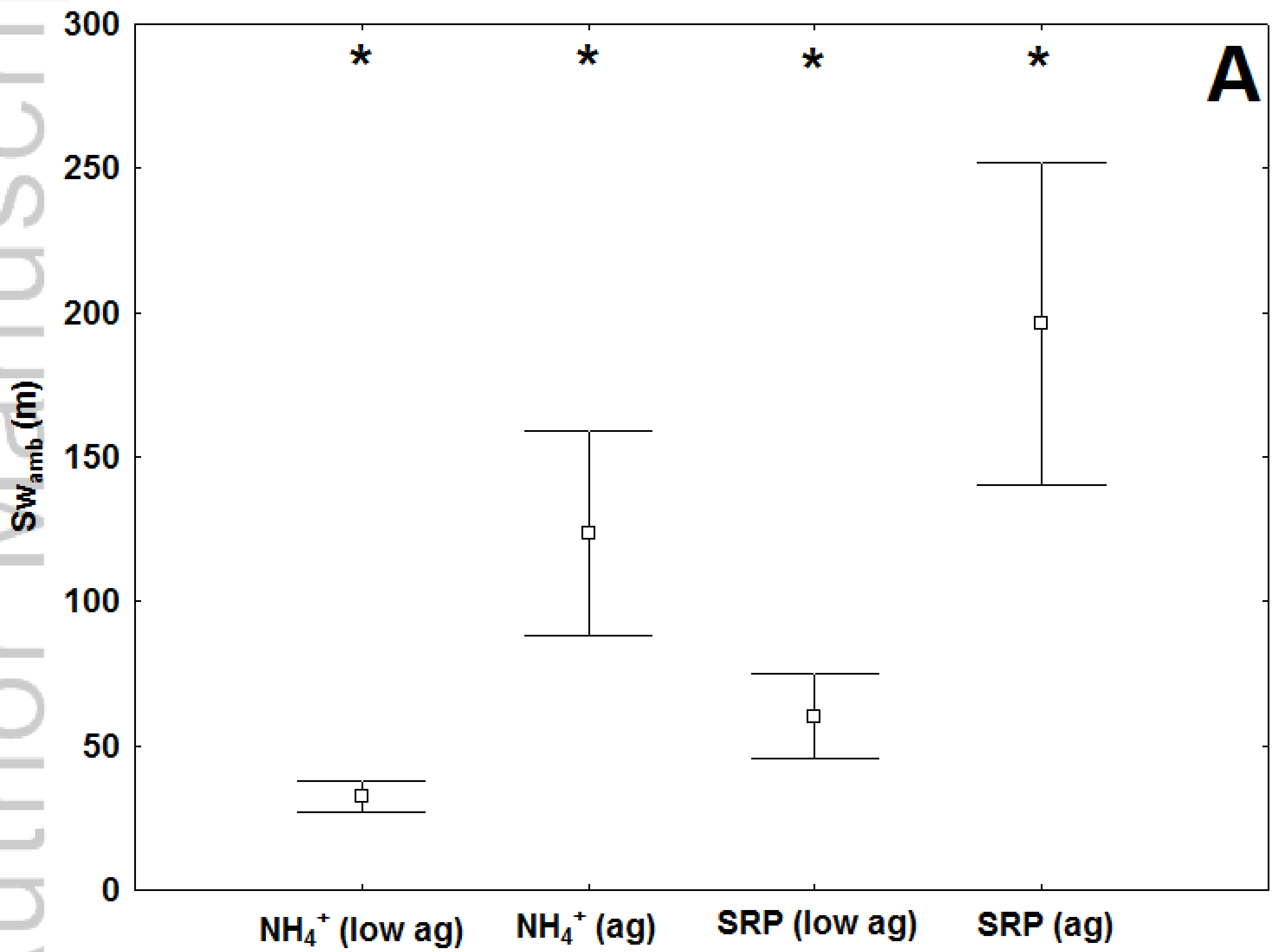
Land use category	Dependent variable	Independent variable	B	VIF	SE	p value	Adj. R²
Low-intensity agricultural	SRP Sw_{amb}	Intercept	5.05	--	0.30	<0.001	0.84
		NH_4^+ C_{amb}	-0.57	1.11	0.08	<0.001	
		SRP C_{amb}	0.20	1.33	0.07	0.018	
	SRP V_{famb}	Intercept	1.26	--	0.38	0.009	0.61
		ER	0.65	--	0.16	0.002	
Agricultural	SRP Sw_{amb}	Intercept	16.07	--	1.80	<0.001	0.80
		Q	-0.98	1.09	0.24	0.005	
		DO	-3.50	1.26	0.69	0.001	
		NH_4^+ C_{amb}	-0.58	1.36	0.12	0.002	
		Intercept	10.56	--	1.26	<0.001	0.75
		A_S/A	-5.98	1.26	1.73	0.014	
		NH_4^+ C_{amb}	-0.38	1.34	0.13	0.029	
		GPP	-2.91	3.47	0.60	0.003	
		CC	-0.75	4.10	0.23	0.019	
	SRP V_{famb}	Intercept	-0.36	--	0.45	0.444	0.69
		A_S/A	8.54	1.19	1.88	0.002	
		GPP	1.42	1.19	0.40	0.007	
		Intercept	-7.43	--	1.41	0.001	0.88
		Q	1.47	1.09	0.19	<0.001	
		NH_4^+ C_{amb}	0.33	1.36	0.09	0.010	
		DO	2.27	1.26	0.54	0.004	
		Intercept	6.72	--	2.97	0.047	0.85
		Q	1.23	1.03	0.21	<0.001	
		GPP	0.66	1.00	0.26	0.003	
		T	-2.70	1.03	0.96	0.026	

C_{amb}: nutrient ambient concentrations; ER: ecosystem respiration; Q: discharge; DO: dissolved oxygen; A_S/A: ratio between the cross-section of the transient storage zone and advective channel; GPP: gross primary production; CC: canopy cover; DO: dissolved oxygen; T: temperature

Table 5. Summary of the results from the multiple regression models, showing the positive (Sw_{amb} decrease and/or V_{famb} increase) or negative (Sw_{amb} increase and/or V_{famb} decrease) effects of the main predictors of NH_4^+ and SRP uptake in agricultural and low-intensity agricultural streams in Brazil and Argentina.

Predictor	Effect on NH_4^+ uptake		Effect on SRP uptake	
	Low-intensity agricultural	Agricultural	Low-intensity agricultural	Agricultural
NH_4^+ C_{amb}	—	—	↑	↑
SRP C_{amb}	↑	↑	—	—
CC	↓	↓	—	↑
DO	—	↓	—	↑
T	↓	—	—	↓
GPP	—	—	—	↑
ER	—	—	↑	—
A_S/A	—	↑	—	↑
α	—	↑	—	—
Q	—	—	—	↑
Vel	—	↓	—	—

↑: positive effect; ↓: negative effect, —: no effect; C_{amb}: nutrient ambient concentrations; CC: canopy cover; DO: dissolved oxygen; T: temperature; GPP: gross primary production; ER: ecosystem respiration; A_S/A: ratio between the cross-section of the transient storage zone and advective channel; α: storage zone exchange rate; Q: discharge; Vel: water velocity



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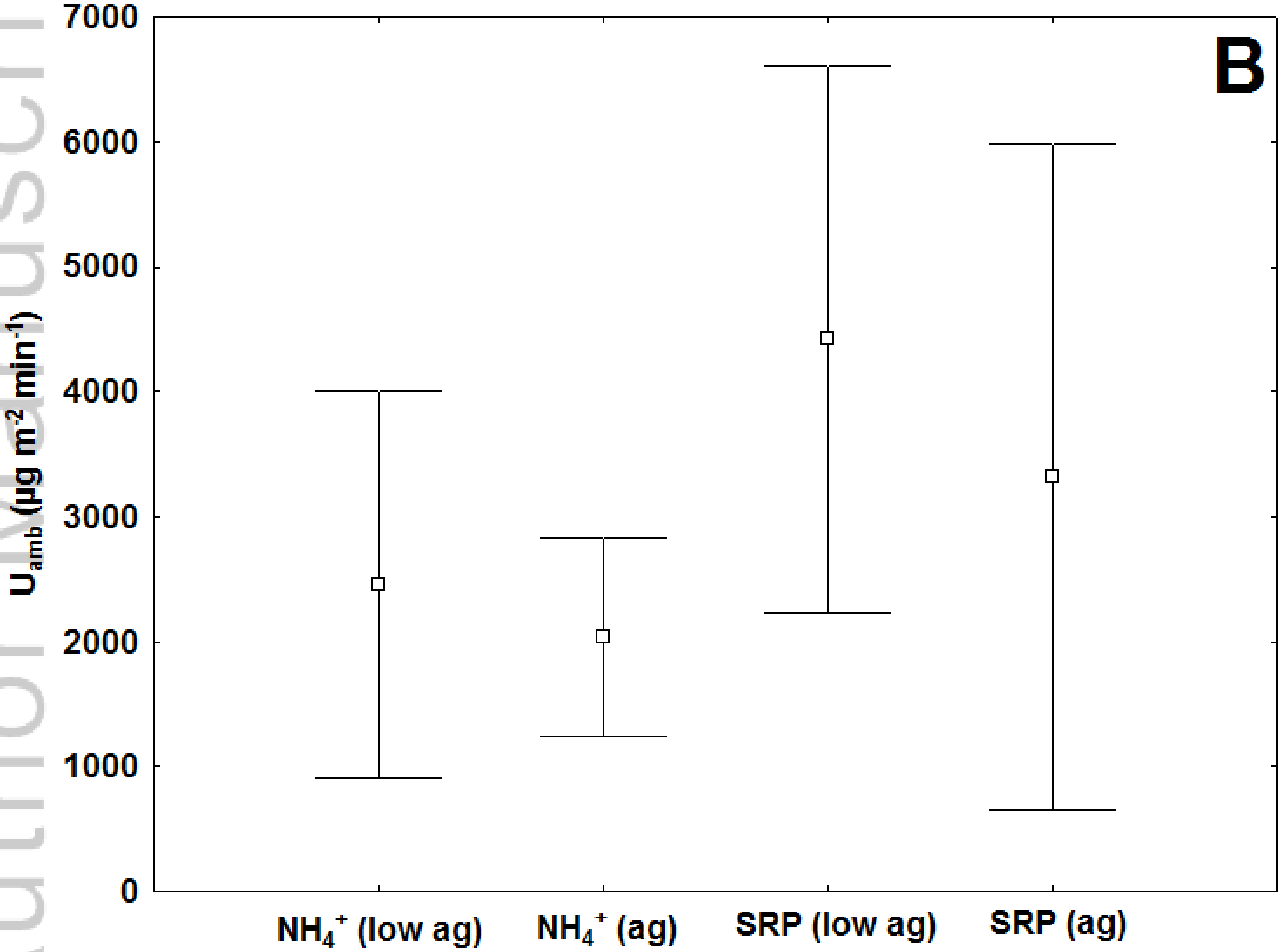

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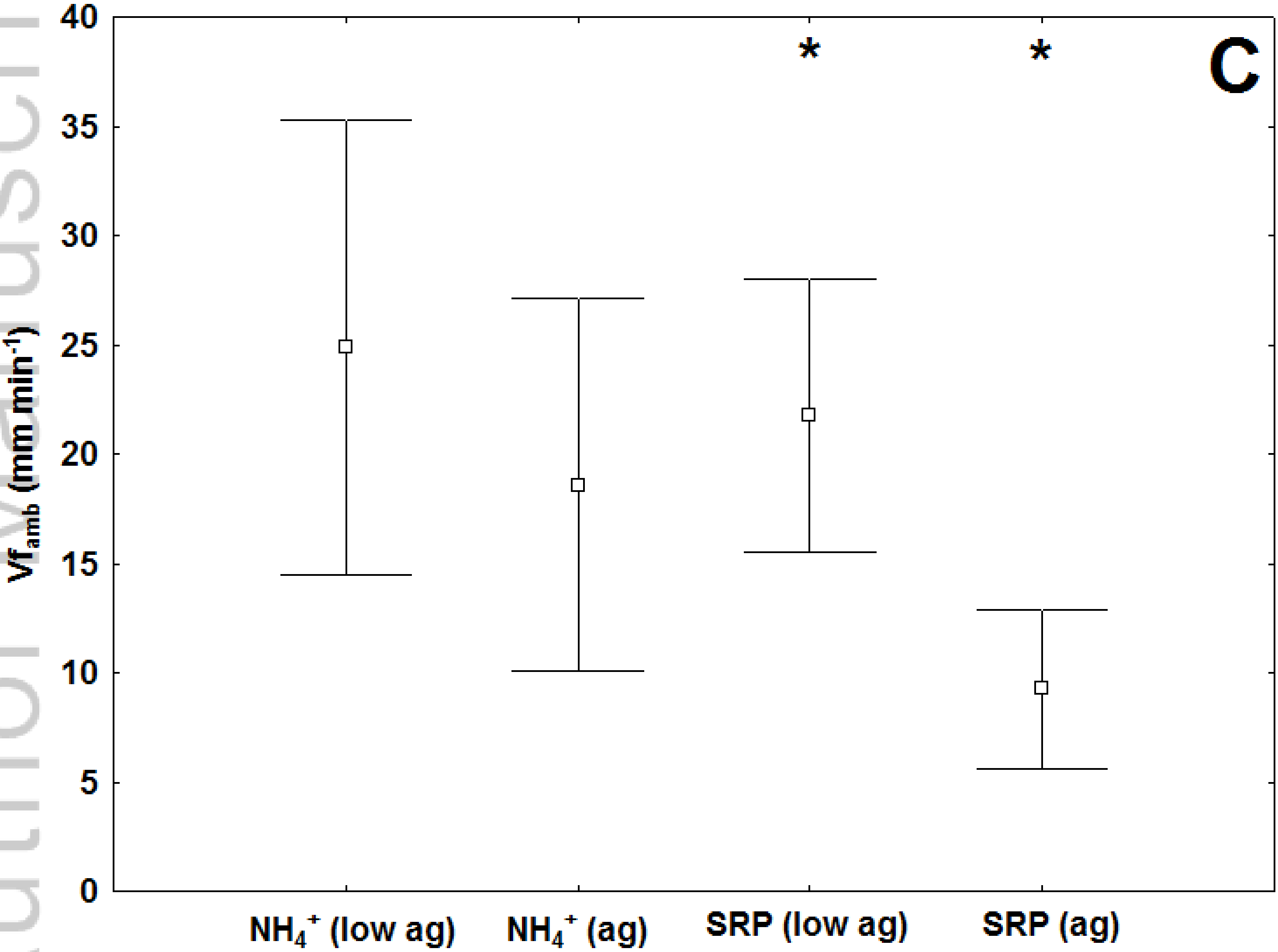

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