Limnologica 82 (2020) 125762

Contents lists available at ScienceDirect

Limnologica

journal homepage: www.elsevier.com/locate/limno

Riparian land use and stream habitat regulate water quality

José Pedro Ramião[a,b,*], Fernanda Cássio[a,b], Cláudia Pascoal[a,b]

[a] Centre of Molecular and Environmental Biology (CBMA), Department of Biology, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal
[b] IB-S, Institute of Science and Innovation for Bio-Sustainability, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal

ARTICLE INFO

Keywords:
Land cover
Habitat assessment
Water chemistry
Streams

ABSTRACT

Riparian land use is a key driver of stream ecosystem processes but its effects on water quality are still a matter of debate when proposing measures to improve freshwater quality. The aim of this study was to examine the influence of riparian land use on stream habitat and water chemistry, and to assess in what extent stream habitat also affects water quality. To that end, we selected eight reaches in the Ave River basin (northwestern Portugal) and compared longitudinal variations in water chemistry and stream habitat between reaches with different land use (urban, agricultural and natural), and between reaches with natural riparian areas and different habitats. Stream habitat was assessed using the Fluvial Functional Index, the HABSCORE, and the Riparian Forest Quality Index. Longitudinal variations in water chemistry were determined measuring differences in concentrations of ammonium, nitrate, phosphate and oxygen, and conductivity, pH and temperature between the downstream and the upstream ends of each reach. Nitrate concentration tended to decrease along reaches with more natural riparian areas and to increase along reaches with more urban and agricultural land uses. Longitudinal variations in water chemistry also differed between reaches with natural riparian areas, suggesting that water quality also depends on stream habitat. Moreover, longitudinal variation in water chemistry was proven a simple, useful and low-cost approach to assess the influence of land cover and stream habitat on water quality. Overall results demonstrated that both riparian land use and stream habitat influence water quality and that riparian forests are essential to reduce nutrient export to downstream ecosystems.

1. Introduction

Freshwater ecosystems account for less than 1 % of the planet surface area but support more than 10 % of the actual described species (Strayer and Dudgeon, 2010) and provide vital ecosystem services, such as food, water purification and erosion control (Aylward et al., 2005). Streams are among the most vulnerable and endangered ecosystems worldwide due to climate change, water pollution, land use change, habitat degradation and introduction of invasive alien species (Carpenter et al., 2011).

Land use is a key driver of stream ecosystem processes by influencing pollutant inputs, riparian vegetation and stream habitat. An increase in nitrogen and phosphorus inputs from agricultural and urban land uses is well documented and it is a major cause of eutrophication (Broussard and Turner, 2009; Karmakar et al., 2019; Paul and Meyer, 2008). Eutrophication impairs freshwater ecosystems and can have high economic costs due to high water treatment costs and limiting water usages (Dodds et al., 2008).

Riparian areas have a major influence on stream ecosystems and it is generally assumed that stream water quality is mainly related to the land use of riparian areas. However, while some authors have confirmed this hypothesis (Amuchástegui et al., 2016; Tran et al., 2010), others found that stream water quality is more related to the land use of the whole catchment (Ding et al., 2016; Mello et al., 2018). The influence of riparian versus catchment land use may depend on the riparian buffer width, and/ or the land use class or the examined water quality parameter (Mello et al., 2018; Ou et al., 2016; Shi et al., 2017). The relationship between land use and water quality is difficult to establish because it depends on many factors, such as hydrology, soil properties, topography, seasonality and historical land use or its spatial distribution in the catchment (Allan, 2004; Rodrigues et al., 2018). Predicting the influence of land use on water quality is challenging and a major issue if we aim to improve freshwater quality. In this sense, rehabilitation of riparian areas may not be sufficient to improve freshwater quality, while catchment-wide rehabilitation measures may have high associated costs with no significant ecological benefits. Therefore, examining the influence of riparian land use on stream habitat and water quality is essential to ascertain the importance of

* Corresponding author at: Centre of Molecular and Environmental Biology (CBMA), Department of Biology, University of Minho, Campus de Gualtar, 4710-057, Braga, Portugal.
E-mail address: zepedroramiao@gmail.com (J.P. Ramião).

https://doi.org/10.1016/j.limno.2020.125762
Received 4 November 2019; Received in revised form 26 February 2020; Accepted 27 February 2020
Available online 04 March 2020
0075-9511/

maintaining natural riparian areas and assess the cost-effectiveness of small-scale rehabilitation measures.

Riparian forests can reduce nutrient export to downstream ecosystems by reducing surface runoff and intercepting nutrients from subsurface and the stream channel (Balestrini et al., 2011; Larson et al., 2019; Schade et al., 2005). Streams can further reduce nutrient export due to in-stream processes that retain and remove nutrients and thus affect water quality (Bernal et al., 2012). In-stream processes depend on riparian land cover and stream habitat (Mulholland and Webster, 2010), so both should be considered if we aim to improve freshwater quality.

Urban land cover is expected to increase 200 % between 2000 and 2030 (Fragkias et al., 2013) and 67 % of the world population will probably live in urban areas by 2050 (United Nations, 2012). Global crop demand is expected to increase 100 % from 2005 to 2050, causing 0.2–1 billion ha of land to be cleared and 225–250 Mt y^{-1} of nitrogen to be used to meet increasing crop demands (Tilman et al., 2011). Therefore, understanding how urban and agricultural areas affect ecosystems and how key ecosystem structures, such as riparian forests and stream habitats, may reduce the impact of urban and agricultural activities is essential to ensure human welfare while reducing its environmental costs.

The aim of this study was to examine the influence of riparian land use on stream habitat and water chemistry, and to assess in what extent stream habitat also affects water quality. To that end, we compared longitudinal variations in water chemistry and stream habitat between reaches with different dominant land use (urban, agricultural and natural), and between reaches with natural riparian areas and different habitats. Most studies examined the effect of land use on water quality considering the land use upstream in the whole catchment or upstream in riparian areas (Amuchástegui et al., 2016; Dodds and Oakes, 2008; Tromboni and Dodds, 2017). Here, we examined the effects of land use considering changes in water chemistry along reaches with different riparian land use, so we could avoid spatial autocorrelation in land use composition (Monteagudo et al., 2012), and get more information about other factors that could also influence water quality (e.g. point-sources of pollution or local land use practices along each reach). Furthermore, we compared reaches from the same and from different sub-catchments and included data from autumn and spring. We expected that the stream habitat and longitudinal variations in water chemistry would be more similar between reaches with similar land use than between reaches from the same sub-catchment, if riparian land use was a key driver of the stream habitat and water quality.

2. Materials and methods

2.1. Study area

We selected eight reaches in the Ave River basin (northwestern Portugal), three contiguous reaches in the Pequeno Stream, one reach in the Ave River, and two contiguous reaches both in the Vizela and the Ferro streams (Fig. 1). Reaches had different dominant land uses (Appendix A, Fig. A.1-A.4) and none or very small tributaries, so we could assess the influence of selected land uses while minimizing the effect of tributaries on water chemistry and stream discharge.

The Ave River basin has a drainage area of 1391 km^2 and the climate in the Ave region is warm-summer Mediterranean (Portuguese Institute for Sea and Atmosphere, IPMA: www.ipma.pt/en). All reaches were located upstream in the Aver River basin (Fig. 1), where granite dominates the geological substratum (APA, 1982) and human presence is sparse. The Pequeno Stream and the Ave River had a poor ecological status according to the Water Framework Directive, whereas the Vizela and the Ferro streams had a good ecological status (Fig. 1).

The upstream reach in the Pequeno Stream (ArP) had 3562 m length and crossed sparse habitations and arable lands of forage crops that were not related to intensive practices but to small producers (Table 1). The middle reach in the Pequeno Stream (UrP) had 698 m length and crossed a small group of houses, whereas the downstream reach (NrP) had 1708 m length and natural riparian areas (Table 1). All reaches in the Pequeno Stream had riffle-pool sequences and turbulence zones, and streambeds dominated by pebbles, cobbles and sand (Table 1). Upstream the study reaches, the Pequeno Stream had natural riparian areas but there were two WWTPs (Fig. 1).

The reach in the Ave River (NrA) had 2746 m length, natural riparian areas, a shallow and wide stream channel with macrophytes and mosses, and a streambed dominated by cobbles and boulders (Table 1). The NrA reach was downstream two WWTPs and two dams (Fig. 1), and just 300 m downstream a gravity type dam that creates a reservoir of 21 ha.

The upstream reach in the Vizela Stream (ArV) had 1595 m length and crossed a golf course and agricultural areas of forage crops and vineyards, whereas the downstream reach (NrV) had 1897 m and steep banks with a dense coverage of forest trees (Table 1). The upstream reach in the Ferro Stream (ArF) had 1227 m length and crossed arable lands of forage crops, whereas the downstream reach (NrF) had 1931 m and steep banks with a dense coverage of forest trees (Table 1). The ArV and the ArF reaches had a laminar flow and the streambed dominated by pebbles and sand, whereas the NrV and the NrF reaches had a turbulent flow and the streambed dominated by sand and boulders (Table 1). Upstream the study reaches, the Vizela and the Ferro streams crossed urban areas and there was one WWTP in the Vizela Stream (Fig. 1). All WWTPs located upstream our study reaches used secondary treatment levels.

2.2. GIS data

Reaches with different land cover were selected in QGIS version 2.10.1 using Bing aerial images (OpenLayers QGIS plugin 1.1.0), a vector map of the stream network (1:25000) (APA, 2015), and the Land use and land cover map for Continental Portugal 2007 (COS2007); (IGP, 2007; COS2007 has a minimum mapping unit of 10,000 m^2 and a land cover nomenclature consistent with CORINE land cover.

The percentage of each land cover class in every reach was determined by intersecting 50 m buffer strips adjacent to both reach margins with COS2007, and then improving the geometric and thematic accuracy of land cover based on Bing aerial images and field observations, to have a detailed map for the land cover classes (minimum mapping unit of 50 m^2). A riparian buffer width of 50 m was chosen because it refers to an intermediate width used to define riparian areas (Munné et al., 2003; Siligardi et al., 2007), and because it allowed us to analyze the land cover in a reasonable extension.

The area of each land cover class from level 2 in every reach was determined using QGIS, and then the area of each land cover class from level 1 was determined by summing up the areas of detailed land cover classes that were together at the higher level (i.e., the area of a land cover class from level 1 is the sum of its detailed land cover class from level 2). The area of each land cover class from levels 1 and 2 of a reach was then divided by the reach total area, to calculate the percentage of each land cover class.

To examine whether the slope of agricultural areas within the 50 m buffer strips could be related to changes in water chemistry along reaches, we first intersected the map of the land cover with a vector map of slopes divided in 7 classes (LEAF, 2013). Then, for each reach, we summed up the area of the agricultural lands with a similar slope and divided by the total agricultural area. The percentage of agricultural areas with a certain slope was multiplied by the corresponding slope value, and then, by summing up the results for each slope class, it was possible to determine the weighted mean slope of the agricultural areas in each reach.

Reaches were georeferenced using Bing aerial images, field observations and the stream network map, so we could determine the length of every reach in great detail (1:1000) using QGIS.

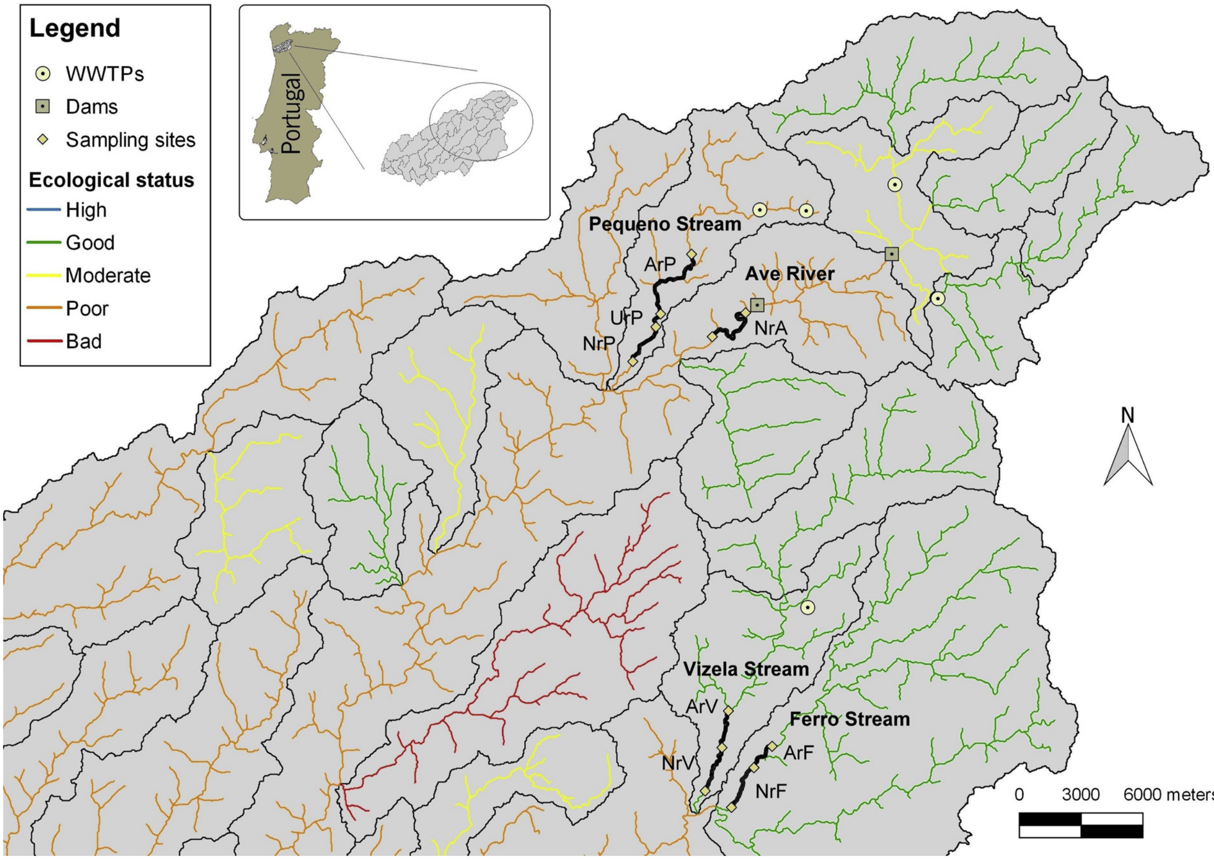

Fig. 1. Map showing the location of the study reaches and sampling sites, the dams and waste water treatment plants (WWTPs) located upstream, and the ecological status of rivers in the Ave River basin according to the Portuguese Environment Agency (APA). For interpretation of the map legend, the reader is referred to the web version of this article.

Location of water bodies and WWTPs, and information about the ecological status of water bodies, WWTPs and dams were provided by the Portuguese Environment Agency (APA).

2.3. Stream habitat

The stream habitat was assessed in smaller homogeneous sections within each reach using the Fluvial Functioning Index (FFI) (Siligardi et al., 2007), the HABSCORE (RBP) (Barbour et al., 1999) and the Riparian Forest Quality Index (QBR) (Munné et al., 2003). Three habitat condition indices were used to better discriminate the effects of land cover on stream habitat. The number of homogeneous sections where the habitat quality was assessed in each reach depended on the reach homogeneity regarding habitat quality.

The score of each habitat parameter and habitat condition index final score in each reach was determined by summing up the scores of the respective small sections, which were first multiplied by the small section length (meters) and then divided by the length of the corresponding reach (meters).

The stream habitat was mostly assessed in November 2013 and then monitored in March and June 2014, so the final scores of all habitat parameters took into account the season. To complete the habitat assessment of FFI, macroinvertebrates were sampled in June 2014. Benthic macroinvertebrates were sampled with a hand net (60 × 30 cm; 0.5 mm mesh size) along 1 m length transects taking into account the proportion of the existing habitats. Biological samples were preserved in ethanol (97 % v/v) and stored at 4 °C in the laboratory before identified and counted according to the FFI protocol (Siligardi et al., 2007).

2.4. Physical and chemical parameters of the stream water and stream discharge

The physical and chemical parameters of the stream water were determined twice in November 2013 and twice in March 2014, at the upstream and the downstream ends of each reach. Conductivity,

Table 1
Reaches length, ecological status, number of WWTPs upstream, dominant land cover, flow type, and riverbed substrate.

Stream	Reach	Length	Ecological status	WWTPs	Land cover	Flow type	Substrate
Pequeno	ArP	3562	Poor	2	Forage crops	Riffle-pools	Pebbles, cobbles, sand
	UrP	698	Poor	2	Houses	Riffle-pools	Pebbles, cobbles, sand
	NrP	1708	Poor	2	Forest trees	Riffle-pools	Pebbles, cobbles, sand
Ave	NrA	2746	Poor	2	Forest trees	Laminar	Cobbles, boulders
Vizela	ArV	1595	Good	1	Forage crops	Laminar	Pebbles, sand
	NrV	1897	Good	1	Forest trees	Laminar	Pebbles, sand
Ferro	ArF	1227	Good	0	Forage crops	Turbulent	Sand, boulders
	NrF	1931	Good	0	Forest trees	Turbulent	Sand, boulders

dissolved oxygen, pH, and temperature were determined in situ with field probes (Multiline F/set 3 no. 400327, WTW, Weilheim, Germany). Stream water samples were collected to determine concentrations of ammonium (HACH kit, program 385), nitrate (HACH kit, program 353), and phosphate (HACH kit, program 490) in the laboratory with a HACH DR/2000 spectrophotometer (HACH Company, Loveland, CO, USA).

The stream discharge was determined at the upstream sampling site of every stream by multiplying the cross-sectional area of the stream channel by the length of a defined stream section, and then dividing by the time for a float to travel this length (Gore, 2006). The cross-sectional area was determined by measuring the stream channel depth every 30 cm from one margin to the other, and then by summing the area of the sections (intervals) comprising the cross-sectional area (Gore, 2006). The time for a float to travel a defined stream section was four times measured at the site where the cross-sectional area was measured.

2.5. Statistical analysis

Changes in water chemistry along streams (longitudinal variations) were determined as the difference between the downstream and the upstream sampling site of each reach (μg L^{-1}). Results were further divided by the reach length (μg L^{-1} km^{-1}), to compare reaches with different lengths.

The scores of the habitat parameters related to river bank erosion, vegetation in the wet riverbed, pulpy and anaerobic plant detritus, and channel alteration (FFI parameters 8, 12 and 13, and RBP parameter 6, respectively) were reversed, since lower scores meant an increase in their presence/intensity.

A cluster analysis was used to group the reaches according to the percentage of artificial surfaces, agricultural areas and forest and semi-natural areas (CORINE land cover classes 1, 2 and 3, respectively), using the Ward´s clustering method. An analysis of similarity (ANOSIM) (Oksanen et al., 2013) was used to test for significant differences among groups. The cluster analysis and the ANOSIM were performed using standardized data and Euclidian distance.

One-way ANOVAs were used to test for significant differences in i) physical and chemical parameters of the stream water among streams, ii) longitudinal variations in physical and chemical parameters of the stream water among reaches and among the groups of reaches, and iii) the final score of the habitat condition indices among the groups of reaches. ANOVAs were followed by Tukey's post-hoc tests to discriminate where significant differences occurred (Zar, 2010). Data were previously tested for Gaussian distribution (Shapiro-Wilk test) and homoscedasticity (Bartlett test). Kruskal-Wallis tests, followed by a Dunn´s test from dunn.test package (Dinno, 2015) were used whenever data did not achieve normal distribution or were not homoscedastic.

To determine the habitat parameters best represented in each group of reaches, the scores of each habitat parameter were first standardized and then ordered, so we could have the scores for each group considering the scores in the other groups. A Principal Component Analysis (PCAs) was performed with standardized data to ordinate the reaches according to the land cover classes and the habitat parameters that best distinguished the groups of reaches. Regression plots were created using the ggplot2 package (Wickham, 2009). Statistical analyses were done in R version 3.0.2 (R Foundation for Statistical Computing, Vienna, Austria).

3. Results

The study reaches were classified as urban (UrP), agricultural (ArP, ArV, ArF) and natural (NrP, NrA, NrV, NrF) based on the percentage of artificial surfaces (CORINE land cover class 1), agricultural areas (CORINE land cover class 2) and forest and semi-natural areas (CORINE land cover class 3) as revealed by cluster analysis (ANOSIM, R = 0.98; Fig. 2). Forests (CORINE land cover class 3.1) was the land cover that best distinguished natural from agricultural and urban reaches, suggesting that human activities most altered this land cover.

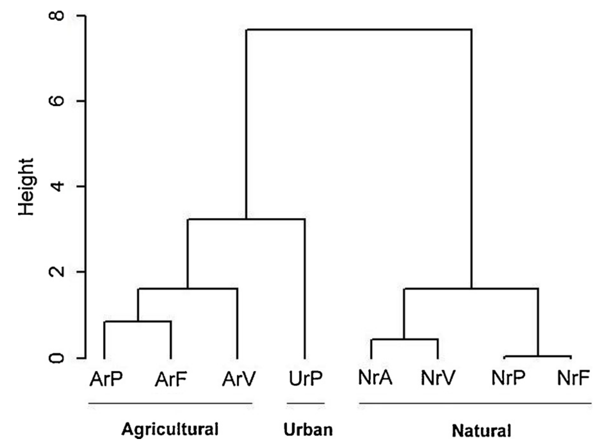

Fig. 2. Cluster dendogram based on the percentage of artificial surfaces, agricultural areas and forest and semi-natural areas (CORINE land cover classes 1, 2 and 3, respectively). The first letter indicates the group of the reach according to the cluster analysis (A, agricultural; U, urban; N, natural), while the last letter refers to the corresponding stream (P, Pequeno Stream; F, Ferro Stream; V, Vizela Stream; A, Ave River).

The reaches also differed in their habitat condition, which varied from very poor (FFI), suboptimal (RBP) or bad quality (QBR) in agricultural reaches to optimal (RBP) or good quality (FFI and QBR) in natural reaches (Table 2). The scores of the habitat assessment were significantly higher in the natural reaches than in the agricultural or urban reaches, regardless the habitat assessment method used (one-way ANOVA, $P < 0.05$; Table 2).

The width of the functional vegetation, the bank vegetative protection and the riparian cover structure and quality were among the habitat parameters most affected by agricultural and urban land uses (Fig. 3). Urban and agricultural reaches had more erosion, channel alterations, anaerobic detritus, and lower hydromorphological diversity and flooding efficiency than natural reaches (Fig. 3). Stream habitat also differed among the natural reaches: NrV and NrF had higher hydromorphological diversity and a denser coverage of forest trees, while NrA had more vegetation in the wet riverbed (Fig. 3).

The physical and chemical parameters of the stream water, the current velocity, and the stream discharge of each stream are presented

Table 2
Scores of each stream reach according to each habitat assessment method (FFI, Fluvial Functioning Index; RBP, HABSCORE; and QBR, Riparian Forest Quality Index). The first letter indicates the group of the reach according to the cluster analysis (A, agricultural; U, urban; N, natural), while the last letter refers to the corresponding stream (P, Pequeno Stream; F, Ferro Stream; V, Vizela Stream; A, Ave River).

Stream reach	FFI		RBP		QBR	
	Stream functioning	Score	Habitat condition	Score	Riparian habitat	Score
ArP	Fair	131	Suboptimal	134	Bad quality	29
UrP	Fair	150	Suboptimal	130	Bad quality	21
NrP	Good - fair	195	Suboptimal	135	Fair quality	59
NrA	Good	239	Optimal	164	Good quality	86
ArV	Fair	138	Suboptimal	118	Bad quality	19
NrV	Good	221	Optimal	166	Good quality	84
ArF	Very poor	47	Suboptimal	106	Bad quality	10
NrF	Good	241	Optimal	175	Good quality	85

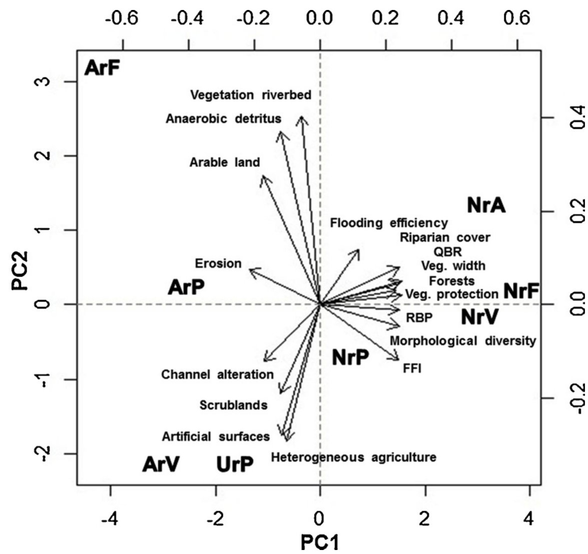

Fig. 3. Principal Component Analysis (PCA) of the most distinct land cover classes and habitat parameters among the groups of reaches. The upper and the right axes refer to the variable loadings, while the lower and the left axes refer to the PC1 and PC2 scores. Land cover is represented as Artificial surfaces, Arable land, Heterogeneous agriculture, Forests, and Scrublands (CORINE land cover classes 1, 2.1, 2.4, 3.1, 3.2). Habitat parameters are represented as Veg. (vegetation) width, Flooding efficiency, Erosion, Morphological diversity, Vegetation riverbed, Anaerobic detritus (FFI, parameters 3, 6, 8, 9, 12, 13), Veg. (vegetation) protection (RBP, parameter 9), Riparian cover, Channel alteration (QBR, parameters 2 and 4), FFI, RBP and QBR (habitat condition indices final scores). Reaches are represented as ArP, UrP, NrP, NrA, ArV, NrV, ArF, and NrF; the first letter indicates the group of the reach according to the cluster analysis (A, agricultural; U, urban; N, natural), while the last letter refers to the corresponding stream (P, Pequeno Stream; F, Ferro Stream; V, Vizela Stream; A, Ave River).

in Table 3. The Vizela and the Ferro streams had the highest concentrations of ammonium (0.07 and 0.06 mg L^{-1}, respectively) (Dunn´s test, $P < 0.05$) and the highest current velocity (53 and 86 cm s^{-1}, respectively) (Tukey's post-test, $P < 0.01$). The Ave River had the highest concentrations of nitrate (11.9 mg L^{-1}) and the lowest current velocity (11 cm s^{-1}) (Tukey's post-test, $P < 0.05$).

Changes in nitrate (one-way ANOVA, $P < 0.05$) and oxygen (Kruskal-Wallis test, $P < 0.05$) concentrations along streams were different among urban, agricultural and natural reaches (Fig. 4). Nitrate concentration tended to decrease along natural reaches and to increase along urban and agricultural reaches (Fig. 4a). Nitrate concentration had the highest increments along UrP and ArP, and the highest declines along NrA (Dunn´s test, $P < 0.05$; Fig. 4a and Appendix A, Fig. A.5b). Oxygen concentration tended to increase along natural reaches and to decrease along urban and agricultural reaches (Fig. 4b). Ammonium concentration often decreased along reaches regardless the land use and had the highest declines along NrV and NrF (Dunn´s test, $P < 0.05$; Appendix A, Fig. A.6a and Fig. A.5a). Phosphate declines were more frequent along natural reaches (Appendix A, Fig. A.6b). Conductivity had the highest increments along agricultural reaches (Appendix A, Fig. A.6c), while temperature had the highest increments along the urban reach (Appendix A, Fig. A.6d).

4. Discussion

Our results demonstrate that nitrate concentration tended to decrease along natural reaches and to increase along urban and agricultural reaches, and further suggest that longitudinal variations in water chemistry can constitute a simple, useful and low-cost approach to assess the influence of land cover and stream habitat on water quality. Streams can increase downstream export of nutrients as a result of natural processes, such as organic matter mineralization and nutrients desorption from bed sediments (Bernal et al., 2012; von Schiller et al., 2015). In our study, nitrate concentration tended to increase along urban and agricultural reaches and to decrease along natural reaches (Fig. 4a), suggesting that changes in nitrate concentration might have been influenced directly by human activities or indirectly via organic matter mineralization followed by nitrification, and/ or groundwater enrichment.

Nitrate concentration had the highest increments along the urban reach (UrP) (Fig. 4a). Previous studies found that even sparse and isolated groups of houses are sufficient to cause nutrient pollution (Jarvie et al., 2010), which might have been the case in the UrP reach. Nitrate concentration also increased along agricultural reaches especially along ArP (Fig. 4a). Nitrate concentration has been related to the percentage and slope of agricultural areas (Amuchástegui et al., 2016; Sliva and Williams, 2001; Tanaka et al., 2016), but the ArP reach, which had the highest increments in nitrate, had a lower percentage and slope of agricultural areas than the ArF reach (not shown), suggesting that the relationship between land use and water quality actually depends on several factors.

In our study, changes in ammonium concentration were unexpected since ammonium decreased along reaches regardless the land use (Appendix A, Fig. A.6a). This might have occurred because ammonium is a preferable source of N and can be retained within a few meters by

Table 3
Physical and chemical parameters of the stream water, current velocity, and stream discharge at the upstream sampling site of each stream. Data represent mean values ± SD (n = 4, except for ammonium and conductivity, n = 3).

	Pequeno Stream	Ave River	Vizela Stream	Ferro Stream
Ammonium (mg L^{-1} NH_4^+)	0.01 ± 0.01	0.01 ± 0.01	0.07 ± 0.06	0.06 ± 0.03
Nitrate (mg L^{-1} NO_3-)	3.5 ± 1.1	11.9 ± 0.9	8.3 ± 0.4	6.5 ± 1.9
Phosphate (mg L^{-1} PO_4^{3-})	0.01 ± 0.01	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01
Conductivity (µS cm^{-1})	40 ± 2	72 ± 4	79 ± 19	84 ± 6
Oxygen (mg L^{-1})	11.15 ± 0.79	9.94 ± 0.58	10.53 ± 0.51	10.63 ± 0.22
pH	6.74 ± 0.24	6.42 ± 0.18	6.69 ± 0.05	6.95 ± 0.09
Temperature (°C)	11.10 ± 1.06	12.38 ± 1.85	11.35 ± 1.01	11.13 ± 1.11
Current velocity (cm s^{-1})	46 ± 6	11 ± 1	53 ± 5	86 ± 4
Stream discharge (L s^{-1})	718	78	1731	1474

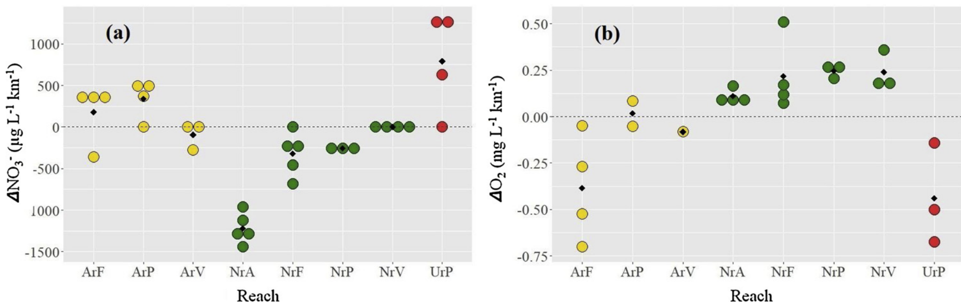

Fig. 4. Changes in nitrate (a) and oxygen (b) concentrations along agricultural (ArF, ArP, ArV), natural (NrA, NrF, NrP, NrV), and urban (UrP) reaches. Negative values refer to a decrease in nitrate or oxygen concentration, while positive values refer to an increase in nitrate or oxygen concentration along the reaches. Black dots refer to mean values.

nitrification or biota uptake (Mulholland et al., 2000). Ammonium is also toxic for some aquatic organisms especially under high pH (Passell et al., 2007), and nitrification is an important sink for ammonium in streams and it is favored under oxidized conditions (Mulholland et al., 2000). Therefore, oxygen declines together with pH increments along some agricultural and urban reaches (Fig. 4b and Appendix A, Fig. A.6e) might impact stream ecosystems by reducing ammonium retention and increasing its toxicity.

Phosphate concentration increased along both agricultural (ArV) and natural (NrV) reaches of the Vizela Stream (Appendix A, Fig. A.6b), suggesting that natural processes rather than human activities were determinant for the concentration of this nutrient. Our results agree with previous findings where the most pronounced effects of changes in land use were on nitrate fluxes (Amuchástegui et al., 2016). Phosphate and ammonium readily adsorb to sediments and are mainly transported into streams via surface runoff, while nitrate is more prone to leaching and is mainly transported via subsurface flow (Pärn et al., 2012). Reaches were sampled during dry weather conditions when surface runoff was expected to be low, which might further explain differences in longitudinal variation in ammonium, phosphate and nitrate concentrations among reaches.

Riparian forests can reduce erosion and increase the diversity and availability of in-stream habitats (Sweeney et al., 2004). In our study, the higher river bank erosion and the lower morphological diversity in urban and agricultural reaches was associated with a low coverage of forest trees. A low coverage of forest trees may also explain the increments in temperature and the decrease in oxygen concentration along urban and agricultural reaches, especially along UrP (Appendix A, Fig. A.6d and Fig. 4b). Oxygen and temperature are determinant to the survival and activity of living organisms (Brown et al., 2004), so the stream ecological condition of urban and agricultural reaches might be more vulnerable to changes in climate associated with these environmental factors.

In our study, changes in water chemistry along streams also differed between reaches with natural riparian areas (Appendix A, Fig. A.5), suggesting that water quality further depends on stream habitat. In fact, Bernal et al. (2015) showed that despite a strong hydrological connectivity between the stream and riparian groundwater, changes in nutrient concentrations along reaches cannot be explained solely by hydrological mixing, supporting the idea that in-stream processes are relevant to stream water chemistry and downstream export of nutrients.

Forest cover and stream hydromorphology are expected to influence in-stream processes. NrA had more sparse forests, a longer water residence time and a higher ratio of streambed area per total water volume, which could favor nutrient retention and photoautotrophs (Mulholland and Webster, 2010). On the other hand, NrV and NrF had a dense coverage of forest trees, a turbulent flow, and a lower ratio of streambed area per total water volume, which may limit nutrient retention and photoautotrophs. Differences in water chemistry and hydromorphology among natural reaches are expected to cause differences in nutrient uptake, which might be higher in urban and agricultural reaches due to a lower canopy coverage favoring photoautotrophs (Sabater et al., 2000). Streams can actually reduce nutrient export even when longitudinal variations in nutrient concentrations are low, because in-stream processes can balance nutrient inputs from groundwater and nutrients release from bed sediments (Bernal et al., 2015; von Schiller et al., 2015), which might have been the case in our study. However, a lower coverage of forest trees can also increase the risk of eutrophication, leading to the loss of other vital ecosystem services. Furthermore, urban and agricultural land use can increase nutrient inputs more than the stream uptake capacity (Merseburger et al., 2005), as suggested by our results. Therefore, streams should be managed considering all processes and services they can actually support.

Our findings should be interpreted with caution because we did not use conservative solutes to account for dilution nor stable isotopes to investigate pathways of nutrient retention and removal (von Schiller et al., 2009). Furthermore, we did not measure stream discharge at the upstream and downstream ends of each reach to estimate groundwater inputs and nutrient export (Roberts and Mulholland, 2007; von Schiller et al., 2011), and our data were not sufficient to assess temporal variation of net nutrient uptake (Bernal et al., 2012 and 2015). Therefore, additional studies are needed to better determine the factors explaining the differences in nutrients decline among reaches and their contribution to nutrient export at large temporal scales.

Overall results demonstrated that both riparian land use and stream habitat influence water quality, and that riparian forests are essential to reduce nutrient export to downstream ecosystems. Our study thus suggests that the rehabilitation of riparian forests and stream habitats is essential to reduce the environmental costs resulting from the increasing urban and agricultural land uses.

CRediT authorship contribution statement

José Pedro Ramião: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Project administration. **Fernanda Cássio:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Funding acquisition. **Cláudia Pascoal:** Conceptualization, Methodology, Resources, Writing - review & editing, Supervision, Funding acquisition.

Acknowledgments

This study was supported by the CLIMALERT project (ERA4CS) funded by JPI-CLIMATE, the EU Commission and the Portuguese Foundation for Science and Technology (FCT), the EcoAgriFood project (NORTE-01-0145-FEDER-000009) supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF), and the strategic programme UID/BIA/04050/2019 (POCI-01-0145-FEDER-007569), funded by national funds through FCT, and by the ERDF through the COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI). The authors thank to Francisco Carvalho, Eva Lima-Fernandes, Rocco Scolozzi, Paulo Geraldes, Isabel Fernandes, José Trabulo, Bruno Antunes, Ana Pereira, and Sofia Duarte for field and laboratory assistance, and to the Portuguese Environment Agency (APA) for providing GIS data for the Ave River Basin.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.limno.2020.125762.

References

[dataset] APA (Portuguese Environment Agency), 1982. Lithological map. Environmental Atlas. details.page?uuid={15A7CB73-BCF1-4541-9671-0F07C9690FC6}. https://sniambgeoportal.apambiente.pt/geoportal/catalog/search/resource/.

[dataset] APA (Portuguese Environment Agency), 2015. Total hydrographic network. Water Atlas. details.page?uuid={F199A8DA-ECE8-44FF-B753-37DDD9A70240}. https://sniambgeoportal.apambiente.pt/geoportal/catalog/search/resource/.

[dataset] IGP (Portuguese Geographic Institute), 2007. Land Use and Land Cover Map for Continental Portugal 2007. http://www.dgterritorio.pt/cartografia_e_geodesia/cartografia/cartografia_tematica/cartografia_de_uso_e_ocupacao_do_solo__cos_clc_e_copernicus_/.

[dataset] LEAF - Linking Landscape, Environment, Agriculture and Food, 2013. Slope. http://epic-webgis-portugal.isa.ulisboa.pt/.

Allan, J.D., 2004. Influence of land use and landscape setting on the ecological status of rivers. Limnetica 23, 187–197. https://doi.org/10.1146/annurev.ecolsys.35.120202.110122.

Amuchástegui, G., di Franco, L., Feijoó, C., 2016. Catchment morphometric characteristics, land use and water chemistry in Pampean streams: a regional approach. Hydrobiologia 767, 65–79. https://doi.org/10.1007/s10750-015-2478-8.

Aylward, B., Bandyopadhyay, J., Belausteguigotia, J.C., Borkey, P., Cassar, A.Z., Meadors, L., Saade, L., Siebentritt, M., Stein, R., Tognetti, S., Tortajada, C., 2005. Freshwater ecosystem services. In: Chopra, L., Leemans, R. (Eds.), Ecosystems and Human Well-Being: Policy Responses. Island Press, Washington DC, pp. 213–256.

Balestrini, R., Arese, C., Delconte, C.A., Lotti, A., Salerno, F., 2011. Nitrogen removal in subsurface water by narrow buffer strips in the intensive farming landscape of the Po River watershed. Italy. Ecol. Eng. 37, 148–157. https://doi.org/10.1016/j.ecoleng.2010.08.003.

Barbour, M.T., Gerritsen, J., Snyder, B.D., Stribling, J.B., 1999. Rapid Bioassessment Protocols for Use in Streams and Wadeable Rivers: Periphyton, Benthic Macroinvertebrates and Fish, second ed. U.S. Environmental Protection Agency, Washington DC.

Bernal, S., von Schiller, D., Martí, E., Sabater, F., 2012. In-stream net uptake regulates inorganic nitrogen export from catchments under base flow conditions. J. Geophys. Res. Biogeosciences 117, 1–10. https://doi.org/10.1029/2012JG001985.

Bernal, S., Lupon, A., Ribot, M., Sabater, F., Martí, E., 2015. Riparian and in-stream controls on nutrient concentrations and fluxes in a headwater forested stream. Biogeosciences 12, 1941–1954. https://doi.org/10.5194/bg-12-1941-2015.

Broussard, W., Turner, R.E., 2009. A century of changing land-use and water-quality relationships in the continental US. Front. Ecol. Environ. 7, 302–307. https://doi.org/10.1890/080085.

Brown, J.H., Gillooly, J.F., Allen, A.P., Savage, V.M., West, G.B., 2004. Toward a metabolic theory of ecology. Ecology 85, 1771–1789. https://doi.org/10.1890/03-9000.

Carpenter, S.R., Stanley, E.H., Vander Zanden, M.J., 2011. State of the world's freshwater ecosystems: physical, chemical, and biological changes. Annu. Rev. Environ. Resour. 36, 75–99. https://doi.org/10.1146/annurev-environ-021810-094524.

Ding, J., Jiang, Y., Liu, Q., Hou, Z., Liao, J., Fu, L., Peng, Q., 2016. Influences of the land use pattern on water quality in low-order streams of the Dongjiang River basin, China: a multi-scale analysis. Sci. Total Environ. 551, 205–216. https://doi.org/10.1016/j.scitotenv.2016.01.162.

Dinno, A., 2015. dunn.test: Dunn's Test of Multiple Comparisons Using Rank Sums. R Package Version 1.2.2. http://CRAN.R-project.org/package=dunn.test.

Dodds, W.K., Oakes, R.M., 2008. Headwater influences on downstream water quality. Environ. Manage. 41, 367–377. https://doi.org/10.1007/s00267-007-9033-y.

Dodds, W.K., Bouska, W.W., Eitzmann, J.L., Pilger, T.J., Pitts, K.L., Riley, A.J., Schloesser, J.T., Thornbrugh, D.J., 2008. Eutrophication of US freshwaters: analysis of potential economic damages. Environ. Sci. Technol. 43, 12–19. https://doi.org/10.1021/es801217q.

Fragkias, M., Güneralp, B., Seto, K.C., Goodness, J., 2013. A synthesis of global urbanization projections. In: Elmqvist, T., Fragkias, M., Goodness, J., Güneralp, B., Marcotullio, P.J., McDonald, R.I., Parnell, S., Schewenius, S., Sendstad, M., Seto, K., Wilkinson, C. (Eds.), Urbanization, Biodiversity and Ecosystem Services: Challenges and Opportunities. Springer, Nehterlands, pp. 409–435. https://doi.org/10.1007/978-94-007-7088-1_21.

Gore, J.A., 2006. Discharge measurements and streamflow analysis. In: Hauer, F.R., Lamberti, G.A. (Eds.), Methods in Stream Ecology. Academic Press, Massachusetts, pp. 51–77.

Jarvie, H.P., Withers, P.J.A., Bowes, M.J., Palmer-Felgate, E.J., Harper, D.M., Wasiak, K., Wasiak, P., Hodgkinson, R.A., Bates, A., Stoate, C., Neal, M., 2010. Streamwater phosphorus and nitrogen across a gradient in rural–agricultural land use intensity. Agric. Ecosyst. Environ. 135, 238–252. https://doi.org/10.1016/j.agee.2009.10.002.

Karmakar, S., Haque, S.S., Hossain, M.M., Sen, M., Hoque, M.E., 2019. Water quality parameter as a predictor of small watershed land cover. Ecol. Indic. 106, 105462. https://doi.org/10.1016/j.ecolind.2019.105462.

Larson, D.M., Dodds, W.K., Veach, A.M., 2019. Removal of woody riparian vegetation substantially altered a stream ecosystem in an otherwise undisturbed grassland watershed. Ecosystems 22, 64–76. https://doi.org/10.1007/s10021-018-0252-2.

Mello, K., Valente, R.A., Randhir, T.O., dos Santos, A.C.A., Vettorazzi, C.A., 2018. Effects of land use and land cover on water quality of low-order streams in Southeastern Brazil: watershed versus riparian zone. CATENA 167, 130–138. https://doi.org/10.1016/j.catena.2018.04.027.

Merseburger, G.C., Martí, E., Sabater, F., 2005. Net changes in nutrient concentrations below a point source input in two streams draining catchments with contrasting land uses. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2004.12.022.

Monteagudo, L., Moreno, J.L., Picazo, F., 2012. River eutrophication: irrigated vs. Non-irrigated agriculture through different spatial scales. Water Res. 46, 2759–2771. https://doi.org/10.1016/j.watres.2012.02.035.

Mulholland, P.J., Webster, J.R., 2010. Nutrient dynamics in streams and the role of J-NABS. J. North Am. Benthol. Soc. 29, 100–117. https://doi.org/10.1899/08-035.1.

Mulholland, P.J., Tank, J.L., Sanzone, D.M., Wollheim, W.M., Peterson, B.J., Webster, J.R., Meyer, J.L., 2000. Nitrogen cycling in a forest stream determined by a ^{15}N tracer addition. Ecol. Monogr. 70, 471–493. https://doi.org/10.1890/0012-9615(2000)070[0471:nciafs]2.0.co;2.

Munné, A., Prat, N., Sola, C., Bonada, N., Rieradevall, M., 2003. A simple field method for assessing the ecological quality of riparian habitat in rivers and streams: QBR index. Aquat. Conserv. Mar. Freshw. Ecosyst. 13, 147–163. https://doi.org/10.1002/aqc.529.

Oksanen, J., Blanchet, F.G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., Minchin, P.R., O'Hara, R.B., Simpson, G.L., Solymos, P., Stevens, M.H., Szoecs, E., Wagner, H., 2013. Vegan: Community Ecology Package. R Package Version 2.0-10. http://CRAN.R project.org/package=vegan.

Ou, Y., Wang, X., Wang, L., Rousseau, A.N., 2016. Landscape influences on water quality in riparian buffer zone of drinking water source area. Northern China. Environ. Earth Sci. 75, 114. https://doi.org/10.1007/s12665-015-4884-7.

Pärn, J., Pinay, G., Mander, Ü., 2012. Indicators of nutrients transport from agricultural catchments under temperate climate: a review. Ecol. Indic. 22, 4–15. https://doi.org/10.1016/j.ecolind.2011.10.002.

Passell, H.D., Dahm, C.N., Bedrick, E.J., 2007. Ammonia modeling for assessing potential toxicity to fish species in the Rio Grande, 1989–2002. Ecol. Appl. 17, 2087–2099. https://doi.org/10.1890/06-1293.1.

Paul, M.J., Meyer, J.L., 2008. Streams in the urban landscape. In: Marzluff, J.M., Shulenberger, E., Endlicher, W., Alberti, M., Bradley, G., Ryan, C., Simon, U., ZumBrunnen, C. (Eds.), Urban Ecology: An International Perspective on the Interaction Between Humans and Nature. Springer, U.S., Boston, pp. 207–231. https://doi.org/10.1007/978-0-387-73412-5.

Roberts, B.J., Mulholland, P.J., 2007. In-stream biotic control on nutrient biogeochemistry in a forested stream, West Fork of Walker Branch. J. Geophys. Res. Biogeosciences 112. https://doi.org/10.1029/2007JG000422.

Rodrigues, V., Estrany, J., Ranzini, M., de Cicco, V., Martín-Benito, J.M.T., Hedo, J., Lucas-Borja, M.E., 2018. Effects of land use and seasonality on stream water quality in a small tropical catchment: the headwater of Córrego Água Limpa, São Paulo (Brazil). Sci. Total Environ. 622, 1553–1561. https://doi.org/10.1016/j.scitotenv.2017.10.028.

Sabater, F., Butturini, A., Martí, E., Muñoz, I., Romaní, A., Wray, J., Sabater, S., 2000. Effects of riparian vegetation removal on nutrient retention in a Mediterranean stream. J. North Am. Benthol. Soc. 19, 609–620. https://doi.org/10.2307/1468120.

Schade, J.D., Welter, J.R., Martí, E., Grimm, N.B., 2005. Hydrologic exchange and N uptake by riparian vegetation in an arid-land stream. J. North Am. Benthol. Soc. 24, 19–28. https://doi.org/10.1899/0887-3593(2005)024<0019:HEANUB>2.0.CO;2.

Shi, P., Zhang, Y., Li, Z., Li, P., Xu, G., 2017. Influence of land use and land cover patterns on seasonal water quality at multi-spatial scales. Catena 151, 182–190. https://doi.org/10.1016/j.catena.2016.12.017.

Siligardi, M., Bernabei, S., Cappelletti, C., Chierici, E., Ciutti, F., Egaddi, F., Franceschini, A., Maiolini, B., Mancini, L., Minciardi, M.R., Monauni, C., Rossi, G., Sansoni, G., Spaggiari, R., Zanetti, M., 2007. I.F.F. 2007: Indice di Funzionalità Fluviale, Manuale APAT. Trento.

Sliva, L., Williams, D.D., 2001. Buffer zone versus whole catchment approaches to studying land use impact on river water quality. Water Res. 35, 3462–3472. https://doi.org/10.1016/S0043-1354(01)00062-8.

Strayer, D.L., Dudgeon, D., 2010. Freshwater biodiversity conservation: recent progress and future challenges. J. North Am. Benthol. Soc. https://doi.org/10.1899/08-171.1.

Sweeney, B.W., Bott, T.L., Jackson, J.K., Kaplan, L.A., Newbold, J.D., Standley, L.J., Hession, W.C., Horwitz, R.J., 2004. Riparian deforestation, stream narrowing, and loss of stream ecosystem services. Proc. Natl. Acad. Sci. U. S. A. 101, 14132–14137. https://doi.org/10.1073/pnas.0405895101.

Tanaka, M.O., de Souza, A.L.T., Moschini, L.E., de Oliveira, A.K., 2016. Influence of watershed land use and riparian characteristics on biological indicators of stream water quality in southeastern Brazil. Agric. Ecosyst. Environ. 216, 333–339. https://doi.org/10.1016/j.agee.2015.10.016.

Tilman, D., Balzer, C., Hill, J., Befort, B.L., 2011. Global food demand and the sustainable intensification of agriculture. Proc. Natl. Acad. Sci. 108, 20260–20264. https://doi.org/10.1073/pnas.1116437108.

Tran, C.P., Bode, R.W., Smith, A.J., Kleppel, G.S., 2010. Land-use proximity as a basis for assessing stream water quality in New York State (USA). Ecol. Indic. 10, 727–733. https://doi.org/10.1016/j.ecolind.2009.12.002.

Tromboni, F., Dodds, W.K., 2017. Relationships between land use and stream nutrient concentrations in a highly urbanized tropical region of Brazil: thresholds and riparian zones. Environ. Manag. 60, 30–40. https://doi.org/10.1007/s00267-017-0858-8.

United Nations, 2012. World Urbanization Prospects the 2011 Revision, Department of Economic and Social Affairs of the United Nations. New York. .

von Schiller, D., Martí, E., Riera, J.L., 2009. Nitrate retention and removal in

Mediterranean streams bordered by contrasting land uses: a ^{15}N tracer study. Biogeosciences 6, 181–196. https://doi.org/10.5194/bg-6-181-2009.
von Schiller, D., Bernal, S., Martí, E., 2011. Technical Note: a comparison of two empirical approaches to estimate in-stream net nutrient uptake. Biogeosciences 8, 875–882. https://doi.org/10.5194/bg-8-875-2011.
von Schiller, D., Bernal, S., Sabater, F., Martí, E., 2015. A round-trip ticket: the importance of release processes for in-stream nutrient spiraling. Freshw. Sci. 34, 20–30. https://doi.org/10.1086/679015.
Wickham, H., 2009. ggplot2: Elegant Graphics for Data Analysis. Springer-Verlag, New York.
Zar, J.H., 2010. Biostatistical Analysis, fifth ed. Pearson Prentice – Hall, New Jersey.