

Phosphorus seasonal sorption-desorption kinetics in suspended sediment in response to land use and management in the Guaporé catchment, Southern Brazil

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Abstract Phosphate sorption-desorption parameters like maximum phosphorus (P) adsorption capacity (P_{\max}), equilibrium phosphorus concentration (EPC), water desorbable P (α), potentially bioavailable P (β), and mobility index (α/β ratio) were determined in order to understand the sediment source-sink nature in Guaporé catchment in southern Brazil during summer and winter 2013 and 2014. The result showed a significant ($p = 0.05$) variation across sediment site or seasons and revealed the most sorption-desorption parameters (P_{\max} , α , β) with the

increments following the order urban sediments > intensive agriculture under CT > intensive agriculture under NT > low agriculture sub-catchments (sub1 and sub2) > native forest. In the main river points, these parameters decreased along the river (P1 to P5). The results were more obvious in winter than the summer season. In contrast, the low values of λ and α/β ratio in the sediment from native forest and relatively less polluted catchment (sub1) during summer season show the quick P desorption when compared to specific Fe and Al oxides bound to stable P in intensive agriculture sediments. These findings clearly indicated that agricultural practices, sediment characteristics, and hydrological factors have a major impact on seasonal sediment P bioavailability and mobility. The urban untreated discharges may be a single major P source and, if it is not wisely managed, proves a major threat to water quality. These results have serious implications for the river ecosystem and will be of great importance to improve the environmental and economic performance of agricultural practices aiming to reduce soil-based P legacy to surface waters.

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Introduction

Eutrophication of fresh waters is mainly linked to upstream anthropogenic activities in the catchment

like overfertilization and untreated urban and or industrial sewage discharge containing high amounts of dissolved nutrients, which pose a serious threat to the ecological environment (Sharpley et al. 2013; Withers et al. 2015). Non-point phosphate reaching to fresh water rivers and streams is more difficult to manage as it is bound to sediments and organic materials. However, due to land-use change, catchment geographical features like rainfall and runoff, seasonal pH and dissolved oxygen (DO) shifts, and sediment chemical composition, this sediment-bound P could be released into surrounding water by ion exchange (Withers and Jarvie 2008; Upreti et al. 2015). The sorption-desorption P balance considerably contributes to the final trophic level of water bodies (Jarvie et al. 2006; Zhang et al. 2014).

It is a fact that the P adsorption capacity to a larger extent is dependent on the sediment composition. Therefore, the most reactive sites for phosphate interaction are those minerals such as Fe and Al oxyhydroxides and surface hydroxyl groups that could be exchanged by phosphate anions on these sites of sediments. These variations are more obvious under highly weathered ferralsol under subtropical environments like most of the Southern Brazil. The high affinity of these soils for P adsorption has been reported in recent studies (Bortoluzzi et al. 2015; Tiecher et al. 2015; Fink et al. 2016). Their results have shown that these soils are predominant in Fe and Al sesquioxides, kaolinite clay, and 2:1 clay type with interlayer hydroxy-Al (Caner et al. 2014).

Furthermore, particle physical characteristics like size distribution are linked to the total surface area and must be considered while determining P retention. Results from the previous studies (Zhang and Huang 2007; Bortoluzzi et al. 2015) have shown that the P adsorption increases exponentially with decreasing particle size i.e., increasing clay fraction. Consequently, the sediment originating from these acidic soils facilitates the P sorption preferably via bidentate binding with active Fe and can contribute to as much as 50 to 70 % of total adsorbed P in sediment (Kim et al. 2011; Jan et al. 2015).

The determination of sediment-bound total phosphorus (TP) to predict either they act as source or sink in the river is ambiguous, as only some P is desorbed and become biologically available. For a better understanding of the sediment P mobilization, maximum

phosphorus adsorption capacity (P_{\max}) and equilibrium phosphorus concentration (EPC) have been used to estimate river-sediment P dynamics. Several mathematical models have been developed and reported in literature (Lopez et al. 1996; Rheinheimer et al. 2000; Tu et al. 2002) for this purpose, but the superiority and wide adoption of nonlinear model of Langmuir have already been reported in many studies to describe the best P adsorption (House and Denison 2000; Bubba et al. 2003; Guardini et al. 2012). However, when the sediment has a considerable amount of native desorbable P (Q_0), it affects the Langmuir model validity to quantify accurately the P adsorption, as a fact that water desorbable P also participates in the adsorption equilibrium and, therefore, it must be accounted. To overcome this situation, several modifications in Langmuir model have been proposed depending on the sediment type (Zhu et al. 2011); however, the modification introduced by Koski-Vahala and Hartikainen (2001) is more practicable as it visually separates the P desorbed in distilled water (Q_0).

In freshwater river sediments, both total P (TP) and bioavailable P (BAP) contents also vary according to land-use heterogeneity and catchment characteristics and are not clear indicators of the eutrophic state of water. All P adsorbed into the sediment can be thermodynamically desorbed (Barrow 1983), yet, the determination of P adsorption capacity and EPC does not fully reveal the P release at the sediment-water interface. However, McKean and Warren (1996) proposed first-order kinetics equation which allows to estimate the instantaneous particulate bioavailable P (α), potential particulate bioavailable P or P buffering capacity (β), and desorption rate constant (λ) sediment-water interface and is used in many recent studies (Rheinheimer and Anghinoni 2001; Rheinheimer et al. 2008; Pellegrini et al. 2010; Bortoluzzi et al. 2013).

So far, few studies focusing on water and sediment-bound P transportation have been conducted in Southern Brazil and were limited to field/plot or small catchment scale to understand the land use (Pellegrini et al. 2010), rain event basis (Bortoluzzi et al. 2013), high-intensity cropland (Capoane et al. 2015), successive slurry application under no-till soil management (Guardini et al. 2012), and sediment source finger printing (Tiecher et al. 2015); yet, a comprehensive catchment scale temporal study integrating all these aspects is lacking.

The main objectives of current study were (a) to determine whether the surface sediments act as sink or source for river water, (b) to predict the particulate bioavailable P (algal bioavailable) and sediment P buffering capacity in response to the land use and management for each monitoring site, and (c) to assess and differentiate the overall seasonal variations in P adsorption-desorption kinetics based on geochemical composition in order to refine the upstream fertilization plan and soil management in the Guaporé catchment which is currently under highly anthropic and intensive agriculture region in Southern Brazil.

Materials and methods

Description of Guaporé catchment

The study area Guaporé catchment is located at coordinates 28°54'41"S and 51°57'10"W in the south of the Brazil. The basin altitude varies from 40 to 800 m from south to north (Fig. 1). The climate of the region is humid subtropical climate with average annual rainfall from 1400 and 2000 mm and well distributed throughout the year, but high winter rain events are frequent from August to October months, and the average annual temperature is 17.4 °C. It has a total basin area of over 2000 km² with areas under representative land uses for cropping pattern and fertilization management. The basin has high heterogeneity in soil geology and lithology, and many soil classes like Entisols, Luvisol, Cambisol, Oxisol, Ultisol, Chernosol are present due to specific pedo-climatic variations (Didoné et al. 2014). The region is characterized with intensive agriculture and high anthropic activities including rapid expansion in dairy and poultry industry over past 30 years. Therefore, surface water reservoirs are under threat of severe impairment due to high rainfall, sloppy landforms, high water erosion and sediment loads, and increased P discharges either from intensive agriculture lands or untreated urban sewage reaching to headwater streams (Didoné et al. 2014). It is a major source of drinking water for Marau town and a population of over 0.5 million residing in Guaporé region and have great importance for livestock, fisheries, and recreation in the region. Being a tributary of river Taquari, and a key contributor to the regional hydrographic of

Guaíba Lake, the high sediment production and associated P drain to the Atlantic Ocean near Porto Alegre city, Rio Grande do Sul Brazil. The Guaporé catchment thus has a great importance both for regional and international water resource management.

Sediment samplings

To collect representative suspended sediment samples, a total of 11 monitoring stations, of which 6 were installed on sub-catchment scale and 5 monitoring stations on the main river, were selected after analyzing the land use and geographical location with the help of a digital elevation model originating in mapping mission of Earth relief-SRTM (Shuttle Radar Topography Mission) using the software ArcGIS 10 (ESRI 2011), and maps were developed. Suspended sediments were collected from summer (early February) and winter (late July) during 2013 and 2014 with the time-integrated suspended sediment samplers (Maier 2013). The samples were taken into acid-washed 20-L gallon and brought to soil and water chemistry laboratory of Federal University of Santa Maria, Brazil, and then oven-dried at 50 °C, gently disaggregated using a rubber head pestle and mortar, and sieved through a 63- μ m mesh before chemical analysis. A set of original oven-dried sample was passed through 2-mm mesh and kept for particle size analysis.

Sediment characterization

Sediment (<63- μ m) TP was determined with H₂SO₄ and H₂O₂ digestion in the presence of saturated MgCl₂ (Olsen and Sommers 1982), while the organic P (OP) was estimated by ignition at 550 °C for 6 h and subsequently determined by colorimetry (Murphy and Riley 1962). The inorganic P (IP) was calculated as the difference of OP to TP. The total organic carbon (TOC) was analyzed by wet oxidation with K₂Cr₂O₇ and H₂SO₄ following Walkley and Black method (1934). Amorphous Fe and Al were extracted with 0.2 mol L⁻¹ ammonium oxalate at pH 3 in the dark (Fe_{ox} and Al_{ox}), as described by Schwertmann (1964). The crystalline forms of Fe oxyhydroxides (Fe_{dcb}) and Al (Al_{dcb}) were estimated in dithionite-citrate-bicarbonate (DCB) extraction as explained by Mehra and Jackson (1960). The particle size distribution was

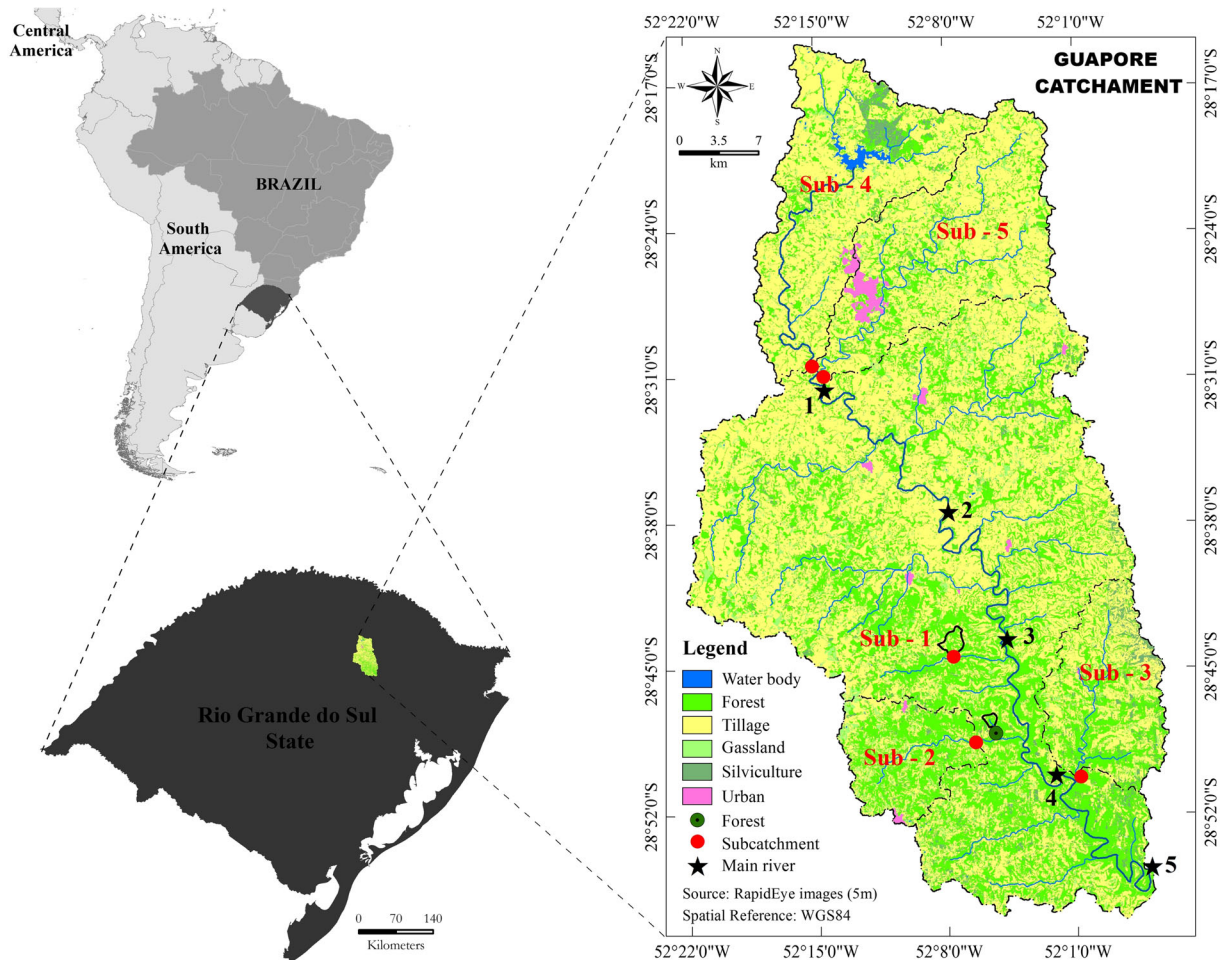


Fig. 1 Geographical location of the study catchment Guapore in Rio Grande do Sul State, Southern Brazil. The *right map* summarizes the location and land use of each monitoring station while *dotted black line* indicates demarcation of sub-catchments

determined in 2-mm sediment by the laser particle size analyzer (Muggler et al. 1997) after oxidation of soil organic matter with H_2O_2 and subsequent dispersion with 6 % NaOH solution.

Phosphorus sorption study

To determine the P adsorption behavior, only summer sediments were selected, and 0.5 g of powdered suspended sediment ($<63 \mu\text{m}$) was weighed into 15 mL polypropylene centrifuge tube. Thereafter, 10 mL of 0.01 M L^{-1} CaCl_2 solution containing 0, 2, 5, 10, 20, 50, 100, 200, 400, 800, 1200, and 1600 mg L^{-1} of equivalent P concentration from KH_2PO_4 was added, respectively. The samples were shaken for 16 h on an end-over-end shaker at 33 rpm at 25 °C, and subsequently the samples were

centrifuged and P concentration was colorimetrically measured in the supernatant (Murphy and Riley 1962). The amount of adsorbed P was calculated as the difference of quantity added to P remaining in the solution at equilibrium. The sorption data was fitted to Langmuir equation with modification of the Koski-Vahala and Hartikainen (2001) and given as follow:

$$P_{\text{sorbed}} = \frac{P_{\text{max}} \times P_{\text{solution}}}{1 + km \times P_{\text{solution}}} - Q_0 \quad (1)$$

where

P_{max} is the maximum P adsorption capacity (mg kg^{-1}); km is the P concentration in the solution that allows half of the maximum P adsorption (mg L^{-1}); P_{solution} is the equilibrium P concentration in solution

(mg L⁻¹); and Q_0 is water desorbed P (mg L⁻¹). The EPC was calculated by the expression:

$$EPC = \frac{(Q_0 \times km)}{(P_{max} \times Q_0)} \tag{2}$$

Desorption kinetics study

Bioavailable particulate phosphorus in suspended sediments was estimated by a single extraction with anion exchange resin (AER) strips (AMI-7001S; Membranes International Inc., NJ) as described by Rheinheimer et al. (2000). Briefly, 0.5 g of powdered suspended sediment (<63-µm) and 10 mL of distilled water were taken in 15-mL falcon tube. Then 0.5 mol L⁻¹ NaHCO₃-saturated anion exchange resin strip was added (Gatiboni et al. 2005), and the tubes were shaken for 16 h on an end-over-end shaker at 33 rpm and 25 °C. The anion resin membrane was removed and washed with water before transferring into a 15-mL glass tube with 10 mL of 0.5 M L⁻¹ HCl. After leaving for 2 h, the tubes were shaken on an oscillating agitator for further 30 min and P concentration was determined on an aliquot of the solution by Murphy and Riley (1962) method, and this P concentration is considered as bioavailable particulate P. To attain the cumulative amount of P sorbed, the successive extraction was carried out for 13 days in the same sediment samples until the P concentration in extract became constant and reached zero.

To estimate P desorption parameters, the first-order kinetic model proposed by the McKean and Warren (1996) in Eq. 3 was employed.

$$P_{des} = \beta(\beta - \alpha)e^{-\lambda t} \tag{3}$$

where

(P_{des}) is amount of P desorbed; (β), potentially bioavailable particulate P; (α), instantaneous bioavailable particulate P; (λ), desorption rate constant, and (t), extraction time in minutes. The P mobility index was calculated as = ($\alpha \times 100/\beta$).

Statistics

One-way analysis of variance (ANOVA) followed by Scott-Knott test ($p < 0.05$) was conducted using Sisvar statistical software (version 5.3) to determine the significant differences between seasons and sampling stations (Ferreira 2011). The correlation coefficient was

determined, and principal component analysis between a pair of means of P sorption-desorption parameters and sediment characteristics was also performed.

Results

Sediment characteristics

Under the acidic environments, the sediment P retention is closely related to and or influenced by metal oxides (Al and Fe) and clay contents. In this study, the seasonal variation in Fe and Al oxides is presented in Tables 2 and 3 while particle size distribution is shown in Fig. 2. The rank order of the Fe and Al oxides and most of chemical components concentration for the sediments generally followed a pattern as highly anthropic sediments (sub5) > intense agriculture under Ct (sub3) > agriculture under no tillage (NT) (sub4) > low agriculture sub-catchments (sub1, 2) > native forest. The main river sediments (P1 to P5) showed a descending order along river continuum for most of the chemical characteristics. Average across four seasons and 11 monitored locations, the sediment Fe_{ox} ranged (4.4 to 7.4 g kg⁻¹), Fe_{dcb} (33.7 to 53.6 g kg⁻¹), Al_{ox} (1.1 to 2.2 g kg⁻¹), Al_{dcb} (2.8 to 5.9 g kg⁻¹), TOC (18.2 to 33.7 g kg⁻¹), and clay (43.3 to 137.7 g kg⁻¹).

Individually, the sediment amorphous Fe (Fe_{ox}) concentration collected in 2013 was higher during winter for agriculture sub-catchments (sub1 < sub2 < sub3 < sub4) and in the summer for main river sediment (P1 to P5); whereas, during 2014, most of the sediments from all monitoring stations showed higher Fe_{ox} concentration in the summer. The relative increase in Fe_{ox} content varied from 8.5 to 49.2 % summer and 37.8 to 113.5 % winter during 2013 and from 37.2 to 93 % summer and 59.5 to 110.8 % winter during 2014, over control (forest). The crystalline Fe (Fe_{dcb}) was higher in summer sediments than winter during both years, and higher concentration for highly anthropic followed by the both CT and NT intensive agriculture sediments was observed over the rest of the locations. The relative increase in Fe_{dcb} due to land use or seasonal changes ranged between 31 to 94.5 % and 16.5 to 30.9 % (summer and winter 2013) and between 22.4 to 71.1 % and 16.6 to 39.8 % (summer and winter 2014) over the reference forest site (Table 1).

The Al_{ox} did not showed much variation either for seasons or among sampling sites and differed between 1

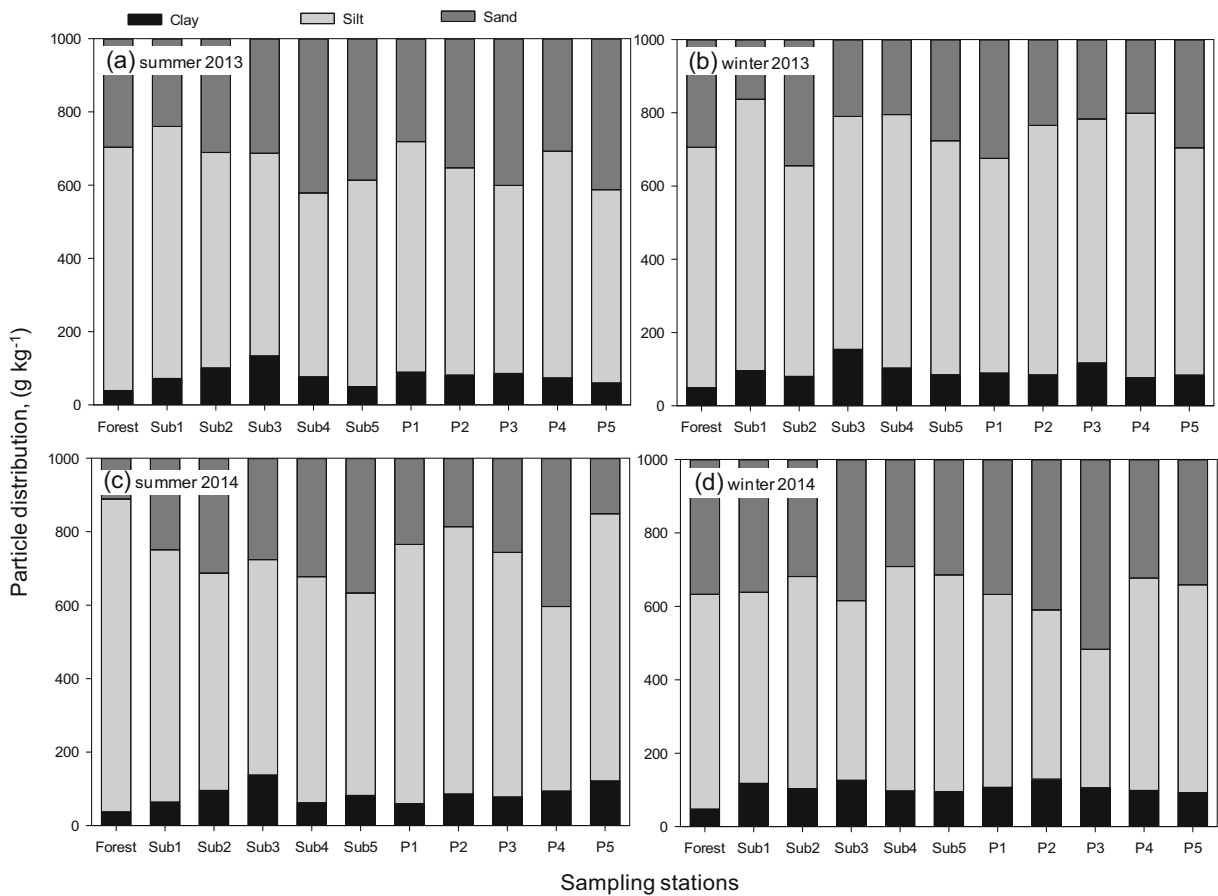


Fig. 2 Particle size distribution of suspended sediment samples during summer 2013 (a), winter 2013 (b), summer 2014, and winter 2014 (d) across 11 different monitoring sites in Guapore catchment, Southern Brazil

and $2 \text{ g kg}^{-1} \text{Al}_{\text{ox}}$ for most of the sediments except highly anthropic (sub5) which showed as much as $3.37 \text{ g kg}^{-1} \text{Al}_{\text{ox}}$. However, Al_{dc} showed a significant difference, and a relative increase lies between 12.2 to 109 % and 20.9 to 88.1 % (summer and winter 2013) and 18.3 to 189 % and 7.6 to 96.6 % (summer and winter 2014) over the forest site (Table 1).

The TOC content was higher in most of winter sediments for both years, except a relatively higher TOC content in main river sediments during summer 2013. The relative increase in TOC content over the forest varied between 4.6 to 248.9 % in summer and 5.8 to 80.6 % in winter during 2013, and from 7.2 to 78.4 % and 10.6 to 308.9 % during summer and winter 2014, respectively (Tables 2 and 3).

The particle size distribution of different sediments collected over four seasons is presented in Fig. 2. The silt fraction appeared as the major proportion in the sediments, and it accounts for 50 to

70 % of the total while the clay showed a small contribution, accounting for 4 to 15 % of the total. The seasonal trend revealed that the high clay and sand proportion was recorded for intensive sub-catchment under CT (sub3) during winter period in both 2013 and 2014.

Sediment organic, inorganic, and total phosphorus fractions

The seasonal variations in OP, IP, and TP concentrations showed significant differences according to Scott-Knott test ($p < 0.05$) for 11 monitored sites and four seasons and are summarized in Tables 4 and 5. Along different land uses, the OP contents followed an order: intense agriculture under NT (sub4) > intense agriculture under CT (sub3) > highly anthropic sediments (sub5) > low agriculture sub-catchment (sub2) > native forest > sub1. The main

Table 1 General characteristics of the monitoring locations in the Guapore catchment, Southern Brazil

Monitoring location	Area (km ²)	Coordinates		Dominant soil type ^b	Farming system and land use ^c	Land use (%)					
		E	S			Water bodies	Arable	Forest	Pasture	Silviculture	Urban
Forest	0.998	393,475	6,814,063	Alfisols	Forest, with few pasture and minimum anthropic disturbance	–	–	68.4	29.5	2.2	–
Sub1 ^a	3.29	389,998	6,820,260	Ultisols	Newly established low arable with maize under CTS, no swine/poultry	–	34.5	57.9	7.0	0.7	–
Sub2	99.04	391,861	6,812,458	Alfisols	Low arable with tobacco and CTS, erva-mate plantation, low maize and tobacco, few poultry, beef and swine	0.1	34.6	50.0	11.1	3.0	1.2
Sub3	144.68	401,071	6,809,790	Oxisols	Intensive arable with tobacco and CTS, low poultry + beef	0.1	49.6	37.0	4.6	8.7	0.0
Sub4	269.39	377,260	6,846,103	Oxisols	Intensive arable with soybean under NTS, slight beef and poultry	1.9	70.7	17.4	4.2	5.1	0.8
Sub5	257.23	378,257	6,845,049	Ultisols	Point source, highly anthropic, city effluent being directly added to river, medium intensity arable, soybean under NTS	0.13	69.12	20.07	5.66	1.77	3.24
P1	532.43	377,786	6,844,236	Oxisols	Diffuse source receiving city effluent and inputs from NTS (main river upstream)	1.0	69.9	18.8	4.9	3.4	2.0
P2	1042.81	389,008	6,832,785	Oxisols	Diffuse with intense swine production areas	0.6	68.7	21.3	5.6	2.6	1.2
P3	1441.38	394,744	6,821,782	Alfisols	Diffuse with mix land use and dairy + poultry	0.5	66.2	24.2	5.8	2.3	0.9
P4	1697.67	400,749	6,809,187	Entisols	Diffuse with tobacco under CTS	0.5	61.5	28.5	6.2	2.4	0.9
P5	2029.91	407,170	6,801,390	Entisols	Diffuse, catchment outlet receiving all upstream contribution	0.5	58.5	31.2	5.9	3.2	0.7

^a Sub sub-catchments (tributaries), P main river monitored locations

^b IUSS Working Group WRB (2015)

^c CTS conventional tillage system, NTS no-tillage system

Table 2 Seasonal changes in Fe_{ox} and Fe_{dcb} of suspended sediments from different land uses in Guapore catchment, Southern Brazil

Stations	Fe_{ox} (g kg ⁻¹)						Fe_{dcb} (g kg ⁻¹)					
	2013			2014			2013			2014		
	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean
Forest	5.9k	3.7h	4.8H	4.3k	3.7h	4.1I	34.8e	34.6d	34.7E	32.1d	33.2f	32.6F
Sub1	6.4j	6.9d	6.6G	5.9j	6.3f	6.1H	47.8d	41.1c	44.5D	39.3c	44.7b	42.1D
Sub2	6.6i	7.4b	7.1F	6.2i	6.3f	6.2G	56.7c	43.7b	50.2C	43.2b	38.7e	41.0E
Sub3	8.6b	7.5b	8.1B	7.1f	5.9g	6.5F	61.5b	43.1b	52.4B	44.5a	44.1c	44.3B
Sub4	7.6h	7.8a	7.7C	7.8c	6.7c	7.3D	53.6c	44.8a	49.2C	44.9a	46.1a	45.4A
Sub5	8.4d	7.9a	8.1A	8.3a	6.6d	7.4C	67.7a	45.3a	56.5A	55.1a	46.4a	45.7A
P1	8.5c	7.2c	7.8C	8.1b	7.8a	7.9A	55.7c	44.8a	50.2C	44.4a	42.9d	43.7B
P2	8.1f	5.8f	7.0F	7.3e	7.4b	7.4C	46.7d	40.3c	43.5D	43.6b	43.7c	43.7B
P3	8.0g	6.6e	7.3E	6.8h	6.4e	6.6E	46.5d	43.0b	44.7D	44.1a	42.1d	43.1C
P4	8.2e	6.7e	7.5D	6.9g	6.3f	6.6E	45.6d	44.4a	45.1D	42.3b	42.2d	42.3D
P5	8.8a	5.1g	6.9F	7.7d	7.8a	7.7B	43.4d	43.6b	43.5D	43.1b	45.7a	44.3B
CV (%)	0.38	2.05	0.92	0.64	0.86	0.64	4.39	1.49	2.42	1.51	1.41	1.08

Lowercase letters in a column show seasonal variation while uppercase letters indicate annual variation and the values followed by the same letter in a column are not significant at $p < 0.05$ by the Scott-Knott test

Fe_{ox} extracted with ammonium oxalate, Fe_{dcb} extracted with dithionite–citrate–bicarbonate, CV Coefficient of variation

river sediments (P1 to P5) showed descending trend along the river downstream except P4, which showed maximum values for OP over rest of the main river sediments. The

relative increase in OP of disturbed sediment over native forest varied from 6.2 to 98.8 % in summer and 70.6 to 129.0 % in winter during the year 2013, while from 35.3

Table 3 Seasonal changes in Al_{ox} and Al_{dcb} of suspended sediments from different land uses in Guapore catchment, Southern Brazil

Stations	Al_{ox} (g kg ⁻¹)						Al_{dcb} (g kg ⁻¹)					
	2013			2014			2013			2014		
	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean
Forest	1.49b	0.81d	1.15C	1.00e	1.07c	1.03E	2.79d	2.53d	2.66E	3.01e	3.16e	3.08E
Sub1	1.51b	1.14c	1.32B	1.30d	1.52b	1.41C	4.21b	3.33c	3.76B	3.73d	4.26c	4.00C
Sub2	1.40c	1.48b	1.45B	1.37c	1.61b	1.49C	3.96b	4.16b	4.06B	3.90c	4.14c	4.02C
Sub3	1.17d	1.73a	1.45B	1.48c	1.16c	1.32C	3.40c	4.76a	4.08B	4.16c	3.40d	3.78D
Sub4	1.40c	0.65d	1.03D	2.42b	1.73b	2.07B	3.97b	2.16d	3.06D	6.40b	4.76b	5.58B
Sub5	2.18a	1.27b	1.73A	3.37a	1.98a	2.68A	5.83a	3.66b	4.75A	8.70a	5.36a	7.03A
P1	1.36c	1.37b	1.37B	1.52c	1.01c	1.26D	3.86b	3.90b	3.88B	4.26c	3.00e	3.63D
P2	1.11d	1.68a	1.40B	1.27d	1.52b	1.40C	3.26c	4.63a	3.95B	3.66d	4.26c	3.96C
P3	1.05d	1.23b	1.15C	1.23d	1.62b	1.43C	3.13c	3.56b	3.35C	3.56d	4.50b	4.03C
P4	1.09d	1.03c	1.06D	1.26d	1.28c	1.27D	3.23c	3.06c	3.15C	3.63d	3.66d	3.65D
P5	1.05d	1.34b	1.20C	1.29d	1.69b	1.49C	3.13c	3.83b	3.48C	3.70d	4.66b	4.61C
CV (%)	5.32	8.95	5.40	6.75	8.85	6.14	4.52	7.45	4.54	5.85	5.62	4.79

Lowercase letters in a column show seasonal variation while uppercase letters indicate annual variation and the values followed by the same letter in a column are not significant at $p < 0.05$ by Scott-Knott test

Al_{ox} extracted with ammonium oxalate, Al_{dcb} extracted with dithionite–citrate–bicarbonate, CV Coefficient of variation

Table 4 Seasonal changes in organic P and inorganic P of suspended sediments from different land uses in Guapore catchment, Southern Brazil

Stations	Organic P (mg kg ⁻¹)						Inorganic P (mg kg ⁻¹)					
	2013			2014			2013			2014		
	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean
Forest	172.1d	172.7b	172.4C	81.2e	151.9c	116.6F	601.8h	691.3h	646.6J	717.7e	600.1d	658.8F
Sub1	152.8d	122.3b	132.6C	72.4e	199.0c	135.7F	747.4g	858.7g	803.1I	807.5d	694.7d	751.1E
Sub2	182.7d	359.3a	271.1B	117.7d	207.0c	162.4E	753.9g	979.0f	866.4H	720.9e	830.9c	775.9E
Sub3	318.8a	356.3a	337.5A	163.2c	308.3b	235.8C	1198.6e	1410.2c	1304.4D	1210.2c	1149.3a	1179.7C
Sub4	315.1a	334.9a	325.0A	61.9e	410.9a	236.4C	1573.1b	1598.1b	1585.6B	1166.4c	954.4b	1060.4B
Sub5	274.6b	294.6a	284.6B	75.4e	364.2a	219.8C	1766.2a	1927.5a	1846.8A	1524.5a	1167.9a	1346.2A
P1	294.7b	322.6a	308.6A	240.5b	319.3b	279.9B	1408.8c	1450.1c	1429.5C	1379.2b	1116.4a	1247.8B
P2	342.2a	274.1a	308.1A	149.9c	296.8b	223.3C	1096.2f	872.5 g	984.3G	1165.7c	1199.1a	1182.4C
P3	276.6b	304.6a	290.6B	123.8d	283.6b	203.7D	1105.1f	1177.5d	1141.2F	1169.1c	1097.4a	1133.2C
P4	289.6b	395.5a	342.5A	375.1a	305.4b	340.2A	1196.3e	1230.5d	1213.4E	1151.7c	1054.9b	1103.3D
P5	223.5c	310.9a	267.2B	109.9d	264.3b	187.1D	1284.9d	1107.5e	1196.2E	1129.9c	976.5b	1053.2D
CV (%)	8.33	16.13	8.98	13.65	11.60	8.13	3.12	3.67	2.46	3.36	6.15	3.54

Lowercase letters in a column show seasonal variation while uppercase letters indicate annual variation and the values followed by same letter in a column are not significant at $p < 0.05$ by Scott-Knott test

CV Coefficient of variation

Table 5 Seasonal changes in total P and total organic C of suspended sediments from different land uses in Guapore catchment, Southern Brazil

Stations	Total P (mg kg ⁻¹)						Total organic carbon (g kg ⁻¹)					
	2013			2014			2013			2014		
	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean	Summer	Winter	Mean
Forest	773.9g	864.2g	819.1J	799.0e	752.0e	775.5E	19.5i	24.2f	21.9F	16.7g	12.3f	14.5F
Sub1	900.2f	971.1g	935.7I	880.1e	893.7d	886.8D	20.4i	25.6f	22.9F	19.6e	13.6f	16.6E
Sub2	936.7f	1338.3e	1137.5H	838.6e	1037.9c	938.3D	55.9c	41.3b	48.6B	19.8e	23.3e	21.6D
Sub3	1517.4d	1766.5c	1642.0D	1373.5c	1457.6a	1415.5B	38.5e	43.3a	40.8C	18.3f	43.1b	30.7B
Sub4	1888.1b	1933.1b	1910.6B	1228.4d	1365.4b	1296.9C	24.1h	38.1c	31.1E	22.4c	29.8d	26.1C
Sub5	2040.7a	2222.2a	2131.5A	1599.9a	1332.1a	1566.1A	25.6g	37.6c	31.6E	22.3c	32.9c	27.6C
P1	1703.5c	1772.8c	1738.1C	1619.8a	1435.8a	1527.8A	47.4d	36.2d	41.8C	24.8b	34.9c	29.9B
P2	1438.4e	1146.6f	1292.5G	1315.6c	1496.1a	1405.8B	64.8b	30.6e	47.7B	21.2d	50.3a	35.7A
P3	1381.6e	1482.3e	1431.9F	1292.9c	1381.0b	1337.0C	67.9a	40.3b	54.1A	19.4e	35.4c	27.4C
P4	1485.9d	1626.1d	1556.1E	1526.8b	1360.4b	1443.6B	30.6f	35.2d	32.9D	29.8a	29.5d	29.6B
P5	1508.5d	1418.5e	1463.5F	1239.9d	1240.8b	1240.4C	38.5e	43.7a	41.1C	17.9c	34.6c	26.2C
CV (%)	2.73	4.87	2.81	3.87	6.35	3.64	1.49	2.83	1.78	2.05	5.36	3.5

Lowercase letters in a column show seasonal variation while uppercase letters indicate annual variation and the values followed by same letter in a column are not significant at $p < 0.05$ by Scott-Knott test

CV Coefficient of variation

to 361.9 % in summer and 31.0 to 170.5 % in winter during 2014 was recorded.

The highest IP content was 1927.5 mg kg⁻¹ in urban sub-catchment during summer 2013, while a minimum of 600.1 mg kg⁻¹ was found in the native forest during winter in 2014 (Tables 2 and 3). A higher IP in sub-catchment with intensive agriculture under CT (sub3) was observed in the winter season in both years. The intensive agriculture sub-catchments (sub3 and sub4) showed relatively higher IP values during winter 2013 while higher IP contents were recorded in summer 2014. A similar trend for main river sediment (P1 to P5) was also observed. Across different sediment locations, the relative increase in IP contents varied between 24.2 to 193.5 % and 24.2 to 178.8 % (summer and winter 2013) and from 0.4 to 112.4 % to 15.8 to 99.8 % (summer and winter 2014) over the forest sediments (Tables 4 and 5).

A high TP during winter period was detected during both years and anthropogenic activity almost tripled the TP (2222.2 mg kg⁻¹) in urban sub-catchment when compared to the reference forest sediment (864.2 mg kg⁻¹) in winter 2013. The intensive agriculture site either under CT (sub3) or NT (sub4) also showed the higher 1642.0 and 1910.6 mg kg⁻¹ during 2013, and 1415.5 and 1296.9 mg kg⁻¹ TP during 2014 over the rest of sediments and the winter months retained higher TP in both years. The percent relative increase over forest site varied from 16.3 to 163.7 % (summer 2013), 12.4 to 157.7 % (winter 2013), 5.0 to 102.7 % (summer 2014), and from 18.8 to 98.9 % in winter 2014, respectively.

Phosphorus adsorption

The P adsorption behavior of suspended sediment was carried on sediments collected during the summer period for both 2013 and 2014. The time was selected since there are low flow conditions in the Guaporé River during this period, and it is also considered as an ecologically sensitive period. The land uses and seasonal changes showed a significant effect on the P sorption parameters (i.e., P_{\max} , km, Q_0 and EPC) according to Scott-Knott test ($p < 0.05$), and the results are presented in Table 6. Across the sediment origin, the highest values for sorption parameters were recorded for the intensive agriculture sub-catchment (sub3) under CT ($P_{\max} = 4032$ and 2342 mg kg⁻¹), (km = 29.9 and 13.6 mg L⁻¹), and ($Q_0 = 2.4$ and 2.2 mg L⁻¹) during 2013 and 2014, respectively. The low agriculture catchment (sub2) also showed increasing trend for P sorption and P_{\max} (3258

and 2608 mg kg⁻¹), km (27.40 and 15.68 mg L⁻¹), and Q_0 (0.70 and 2.08 mg L⁻¹) were recorded in both years. The main river sediments (P1 to P5) showed the second highest category for the P_{\max} , km, and Q_0 , followed by the highly urban sub5, then by the NT (sub4), and least in sub1 and forest, respectively (Tables 4 and 5).

The sediments have finite P retention capacity and when saturated with P will reach the environmental limit, and the EPC estimation can differentiate this limit. The results indicated that in forest control sediments, the EPC was 2.73 and 3.01 µg L⁻¹ during 2013 and 2014, respectively. The intensive agriculture sub-catchment under CT during both years (2013–2014) showed highest EPC (17.2 and 12.5 µg L⁻¹), while low agriculture sub-catchment showed only high EPC (12.5 µg L⁻¹) during 2014. Similarly, the sediments from highly punctual urban P source showed high equilibrium concentration (5.5 and 6.7 µg L⁻¹) when compared to the forest. The sediments collected on the main river showed lower EPC concentration when compared to the highly impacted catchments. However, the intermediate P2 and P4 showed higher value over rest of the three points (Tables 4 and 5).

Phosphorus desorption kinetics

Results regarding seasonal P desorption kinetics from different land uses in Guaporé region are presented in Figs. 3, 4, 5, and 6. Individually, across the four seasons, the highest (96.3 mg kg⁻¹) instantaneous bioavailable particulate P (α) was recorded for highly anthropic urban site during winter 2013, followed by the intensive agriculture site under CT with the (57.8 mg P kg⁻¹) during winter 2014. While on the main river points from P1 to P5, a descending trend in α content was observed. The relative increase in α of disturbed sediment over native forest ranged from 19.6 to 175.3 % in summer and 8 to 235.5 % in winter during 2013, while it ranged from 53.2 to 165.8 % in summer and 15.1 to 123.2 % in winter during 2014 (Fig. 3).

Similarly, the potentially bioavailable P (β) exhibited varied response and showed an order in land use as highly anthropic sediments > intense agriculture under CT > intense agriculture under NT > low agriculture sub-catchments (sub1 and sub2) > native forest. The main river points (P1 to P5) showed relatively higher amount than agriculture treatments due to receiving highly diffused P inputs but followed the descending order along the river continuum (Fig. 4). The relative increase in potentially

Table 6 Phosphorus adsorption parameters of suspended sediments collected during summer 2013 and 2014 from Guapore catchment, Southern Brazil

Stations	P_{max} (mg kg ⁻¹)			km (mg L ⁻¹)			Q_0 (mg L ⁻¹)			EPC ₀ (µg L ⁻¹)		
	2013	2014	Mean	2013	2014	Mean	2013	2014	Mean	2013	2014	Mean
Forest	1694g	1497f	1596I	7.11d	5.86c	6.48D	0.65e	0.77f	0.71F	2.73c	3.01d	2.87D
Sub1	1093i	1802e	1448J	3.52e	8.15c	5.84D	0.62e	0.93d	0.77F	2.00c	4.21c	3.10D
Sub2	3258b	2608a	2933B	27.40a	15.68a	21.54A	0.70e	2.08a	1.39C	5.88b	12.50a	9.19B
Sub3	4032a	2342c	3187A	28.99a	13.62b	21.31A	2.40a	2.16a	2.28A	17.25a	12.55a	14.90A
Sub4	1308h	1512f	1410J	3.20e	3.56d	3.38E	0.93d	1.33b	1.13D	2.21c	3.12d	2.67D
Sub5	1791f	2524b	2157F	5.36d	12.08b	8.72C	1.84b	1.39b	1.62B	5.50b	6.65b	6.08C
P1	2403d	2355c	2379E	3.76e	4.47d	4.11E	0.62e	0.59f	0.61G	0.97c	1.12e	1.04E
P2	2380d	2524b	2452D	11.60b	12.08b	11.84B	0.54f	1.39b	0.97E	2.63c	6.65b	4.64C
P3	2108e	1914d	2011G	9.16c	7.93c	8.54C	0.46f	0.74e	0.60G	2.00c	3.07d	2.53D
P4	2639c	2497b	2568C	13.30b	12.06b	12.68B	1.32c	1.04c	1.18D	6.65b	5.02c	5.83C
P5	1830f	1814e	1822H	1.86e	1.99d	1.92E	1.39c	1.14c	1.27D	1.41c	1.25e	1.33E
CV (%)	1.15	1.29	1.18	16.35	18.23	16.60	6.13	6.99	6.33	27.10	16.24	19.53

P_{max} is the maximum P adsorption capacity (mg kg⁻¹); km (mg L⁻¹) is the P concentration in the solution which allows half of the maximum P adsorption, Q_0 is water desorbed P (mg L⁻¹), and EPC₀ is the zero equilibrium P concentration in solution (µg L⁻¹). Lowercase letters in a column show yearly variation while uppercase letters indicate mean variation, and the values followed by same letter in a column are not significant at $p < 0.05$ by Scott-Knott test

CV Coefficient of variation

bioavailable P varied from 19.6 to 146 % in summer and 31.4 to 312.2 % in winter during the year 2013, and during 2014 from 39.6 to 148.3 % in summer and 31.3 to 110.9 % in winter. Among seasons, winter sediment considerably showed higher values than the summer at sub-catchment scale, while a less

clear difference in the main river sediments was observed.

The results of the desorption rate constant (λ) revealed that the highest values were recorded for downstream main river sediments (P3 and P4) during winter 2013. The less anthropic sediments

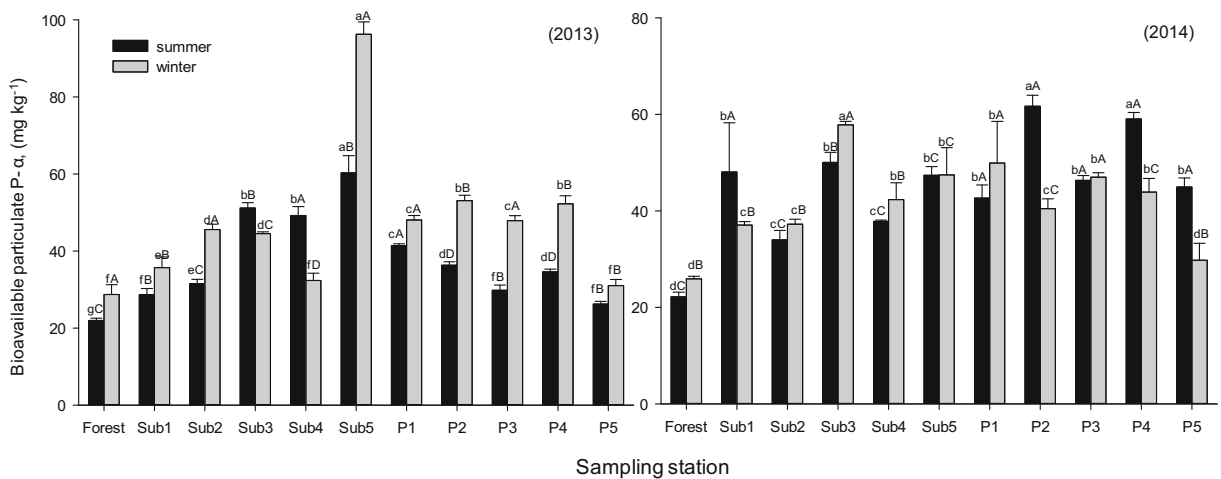


Fig. 3 Changes in the readily desorbable P (α , bioavailable P) of suspended sediment samples during summer-winter of 2013 and 2014 across 11 different monitoring sites in Guapore catchment, Southern Brazil. Lowercase letters on each bar show seasonal

variation among different land use, while uppercase letters indicate annual variation within monitoring site and the values followed by the same letter are not significant at $p < 0.05$ according to the Scott-Knott test

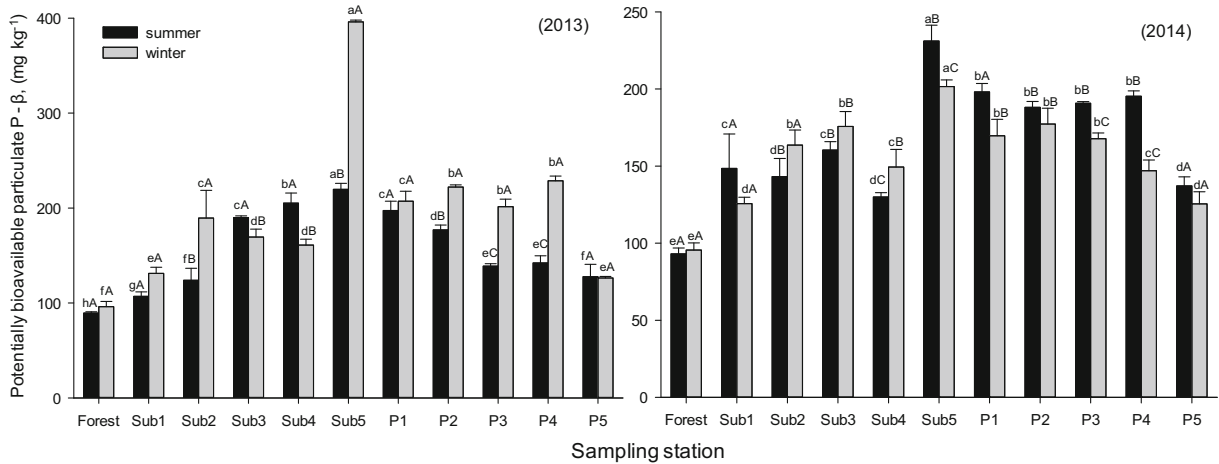


Fig. 4 Changes in the potentially available P (β , potentially available P) of suspended sediment samples during summer-winter of 2013 and 2014 across 11 different monitoring sites in Guapore catchment, Southern Brazil. Lowercase letters on each

bar show seasonal variation among different land use, while uppercase letters indicate annual variation within monitoring site and the values followed by the same letter are not significant at $p < 0.05$ according to the Scott-Knott test

(forest, sub1 and sub2) showed lower λ values when compared to the intense agriculture and highly anthropic sediments (Fig. 5). To estimate the sediment eutrophication hazard, the ratios between α and β have been used as a useful tool to describe the P mobility index. Averaging across seasons, among the monitored sites, the sediments from low anthropic sub-catchments have higher values for α/β ratios (forest = 26.4 %, sub1 = 29 % and sub2 = 25 %) than the highly anthropic sub5 (23.9 %). The sediments from the main river showed higher value of P mobility index than the native forest but they did not

follow the upstream-downstream phenomena (Fig. 5).

The cumulative P release revealed that the different sediments showed a clear desorption behavior for all four seasons during the 2013 and 2014 (Fig. 7). To attain the nearly complete removal of sediment-bound P from all sediments, 13 successive (192 h) AER extractions were performed to reach nearly a constant P concentration, although the sediment of low anthropic activity (forest, sub1, and sub2) attained this level between 7 to 10 extractions. Figure 7 indicates that in each season, the successive resin extraction resulted in maximum of

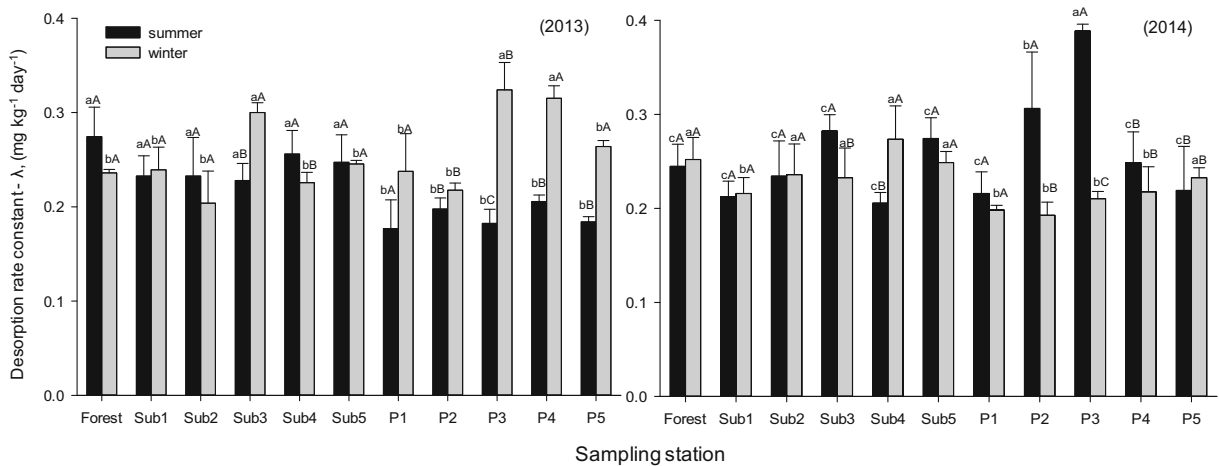


Fig. 5 Changes in the desorption rate constant (λ) of the first-order desorption reaction of suspended sediment samples during summer-winter of 2013 and 2014 across 11 different monitoring sites in Guapore catchment, Southern Brazil. Lowercase letters on

each bar show seasonal variation among different land use, while uppercase letters indicate annual variation within monitoring site and the values followed by the same letter are not significant at $p < 0.05$ according to the Scott-Knott test

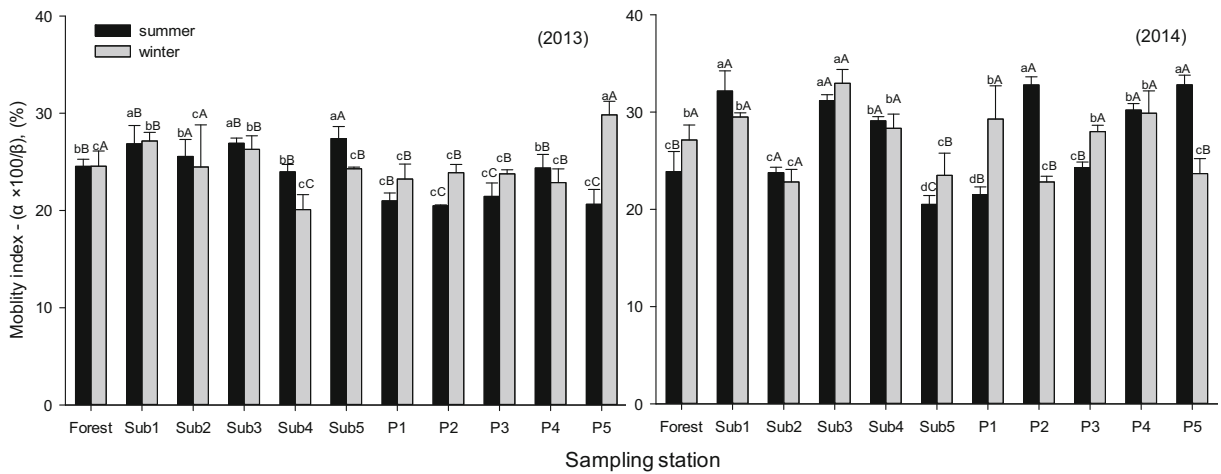


Fig. 6 Variation in the mobility index ($\alpha \times 100/\beta$) of suspended sediment samples during summer-winter of 2013 and 2014 across 11 different monitoring sites in Guapore catchment, Southern Brazil. Lowercase letters on each bar show seasonal variation

among different land use, while uppercase letters indicate annual variation within monitoring site and the values followed by the same letter are not significant at $p < 0.05$ according to the Scott-Knott test

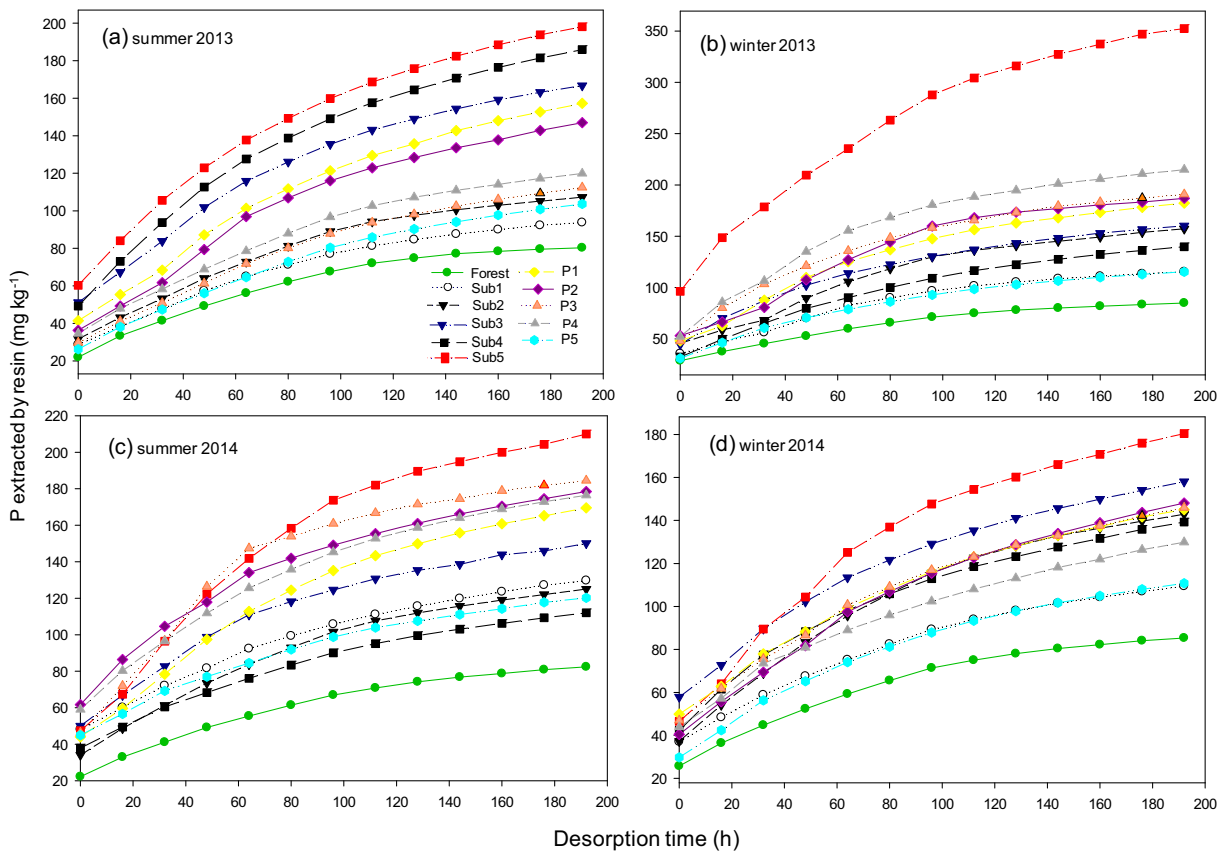


Fig. 7 Cumulative phosphorus desorbed by successive anion exchange resin extractions in suspended sediment samples during summer 2013 (a), winter 2013 (b), summer 2014, and winter 2014 (d) across 11 different monitoring sites in Guapore catchment, Southern Brazil

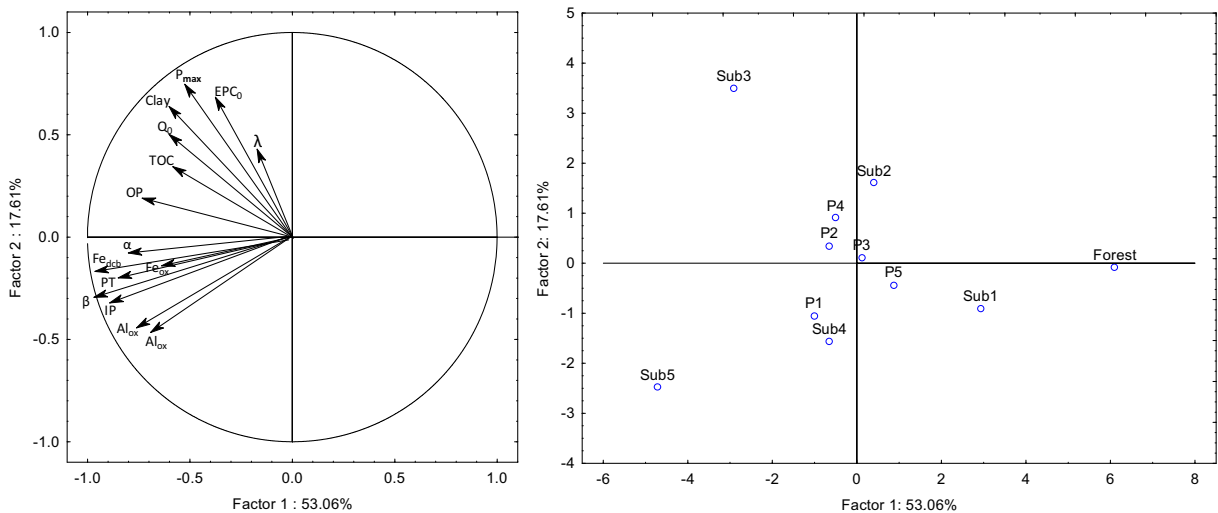


Fig. 8 Principal component analysis (PCA) of the sediment adsorption-desorption parameters and related physico-chemical characteristics

cumulative P in highly anthropic urban sub5 sediments while lowest in the native forest sediments.

Principal component analysis and correlations

The principal component analysis (PCA) of P sorption-desorption parameters and sediment characteristics helped to identify the main factor that control the P transformations at the sediment-water interface. The sum of the first two factors accounted for 70.7 % of the variance of sediment data (Fig. 8). Factor 1 showed 53.1 % of total variance and was mainly related with Fe_{dcb} , Fe_{ox} , α , β , IP, and Al_{dcb} . As α and β are the fractions of IP and ultimately of TP, they are naturally correlated. Therefore, the important factor that correlates them under these environments is Fe/Al oxides. This indicates that the instantaneous bioavailable P and potentially bioavailable P concentration are strongly controlled by Fe_{dcb} and Fe_{ox} . Factor 2 accounting for 17.6 % of total variability and EPC and P_{max} was strongly correlated to clay and TOC contents. The PCA further revealed that at sub-catchment scale, the intense agriculture under NT (sub4), highly anthropic-urban (sub5), and P1 sediment showed the highest values for P sorption-desorption parameters, while intensive agriculture under CT (sub3) and main river P2 and P4 ranked in the second highest group.

The Pearson correlation revealed that many P sorption-desorption parameters and sediment characteristics have a significant correlation. The highest significant correlation coefficients between α and β with Fe

and Al extracted by ammonium oxalate and dithionite-citrate-bicarbonate were recorded ($r = 0.68$ to 0.84). The P_{max} was correlated with clay content ($r = 0.65$) and TOC content ($r = 0.60$), while EPC was only correlated with clay content ($r = 0.67$; Table 7).

Discussion

Variation in sediment phosphorus and chemical characteristics

Phosphorus mainly reaches the river system through domestic wastes and agricultural runoff; however, several biogeochemical factors and landscape hydrodynamics control this phenomenon. Firstly, the land use and managements play a key role. The study landscape showed a great variation in land use and soil management. The land cover variations are key contributor, and a shift from forest sub-catchment (0 % arable vs. 69 % forest) to intensive agriculture either under CT-sub3 (50 % arable vs. 37 % forest) or under NT-sub4 (71 % arable vs. 17 % forest) showed direct influence on the runoff and sediment delivery resulting in higher amount of TP, IP, and OP transport from these catchments. Similarly, the urban source (sub5) is directly receiving untreated city discharges into the river. Recent studies in the Guaporé catchment have shown high hydrological inundation, steep slope in CT sub-catchment, and high sediment production from agriculture catchments even under the NT management (Didoné et al. 2014; Minella

Table 7 Pearson correlation coefficient (*r*-value) and significance * between P sorption-desorption parameters and sediment characteristics.

Variables	P_{max}	Q_0	EPC_0	α	β	λ	OP	IP	TP	TOC	Fe_{ox}	Fe_{dcb}	Al_{ox}	Al_{dcb}
Q_0	0.59													
EPC_0	0.78**	0.85***												
α	0.45	0.47	0.39											
β	0.39	0.32	0.21	0.96***										
λ	0.06	0.25	0.34	0.21	0.13									
OP	0.52	0.31	0.23	0.61*	0.60*	0.08								
IP	0.18	0.36	0.07	0.82**	0.84**	0.13	0.72*							
TP	0.26	0.36	0.10	0.80**	0.82**	0.12	0.82**	0.99***						
TOC	0.60*	0.16	0.20	0.43	0.49	0.05	0.63*	0.43	0.51					
Fe_{ox}	0.30	0.32	0.07	0.72*	0.74**	-0.19	0.71*	0.85***	0.87***	0.62*				
Fe_{dcb}	0.34	0.63*	0.33	0.84**	0.83**	0.00	0.52	0.84**	0.80**	0.40	0.88***			
Al_{ox}	0.02	0.42	0.17	0.69*	0.75**	0.08	0.09	0.65*	0.54	0.05	0.51	0.80**		
Al_{dcb}	0.05	0.52	0.17	0.74**	0.78**	0.06	0.17	0.70*	0.60*	0.13	0.61*	0.86***	0.99***	
Clay	0.65*	0.62*	0.67*	0.45	0.29	0.13	0.45	0.32	0.37	0.62	0.57	0.53	0.07	0.16

P_{max} maximum P adsorption capacity, Q_0 water desorbed P, EPC_0 equilibrium P concentration in solution, α , bioavailable particulate P, β Potentially bioavailable particulate P, λ desorption rate constant, OP organic P, IP inorganic P, TP total P, TOC total organic carbon, Fe_{ox} extracted with ammonium oxalate, Fe_{dcb} extracted with dithionite–citrate–bicarbonate, Al_{ox} extracted with ammonium oxalate and Al_{dcb} extracted with dithionite–citrate–bicarbonate

* Significant at $p < 0.05$; ** significant at $p < 0.01$; *** significant at $p < 0.001$

et al. 2015). Similarly, Blanc et al. (2014) have shown a significant variation in the upstream and downstream river P concentration in urban Brazil. The landscape geology, geographical heterogeneity, and hydrological feature have a great control on the surface erosion and sediment transportation, and it can also be described that increasing area under NT can enhance the P export due to P saturation of top layer as recently reported by Sprague and Gronberg (2012) and Upreti et al. (2015).

Similarly, particle size distribution is also crucial while accounting for sediment-bound P. In our study, the sub-catchments under CT and steep slopes (sub2 and sub3) showed higher clay content than the NT (sub4) and urban catchment. The increased clay content in the CT catchments could be the result of tobacco cultivation during the winter months, and soil is thoroughly tilled and more vulnerable to water erosion and thus transports higher amounts of clay in the suspended colloids. Similar results were found by the Kröger et al. (2012) with changing land use and geography, while Zhang and Huang (2007) and Cooper et al. (2015) have reported that at even a small percentage (16–20) of the total weight, the clay fraction can account up to 70 % of the total surface area.

A complex overall situation with respect to defining P loss arises as a result of the size selective nature of soil erosion events. The loss of total P in the finer-eroded fraction would be greater relative to the original whole soil; however, this more easily transported material may support a lower solution P concentration compared to coarser-sized fractions (Scalenghe et al. 2007).

The mineralogical heterogeneity and geochemical composition, particularly Fe/Al content in the landscape, are other key features that regulate the form and fate of P along the river continuum. In the 1:1 type clays, specially kaolinite, the aluminum groups strongly attract proton that is generally protonated ($Al-OH_2^+$), and it can be easily displaced by phosphate causing strongly bonded specific adsorption with and low equilibrium concentration (Chen et al. 1973). The P sorption-desorption parameters indicate that the iron hydroxides are the major binding agent of ion phosphate in these soils (Parfitt 1978; Sposito 2008).

Most soils of the study area are Oxisols/Ultisols, and these soils have a high content of Fe and Al oxides. The intensive site under CT (sub3) lies in Ultisols while that under NT and urban are located under Oxisols. Earlier studies in the region on many soils and sediments have shown similar geochemical behavior of P due to their

high clay and Fe/Al contents (Bortoluzzi et al. 2013, 2015; Fink et al. 2014, 2016).

Another factor that might influence the P export is the successive surface application of manure and slurry under NT over prolonged time on small landholdings (sub4). This can saturate the surface charges and thus create a high risk to water quality (Sharpley 2003). Similarly, the highest OP concentration in NT sediment explains the evidence of soil OP in the top carbon stratified layer in the area. Many recent studies have proved that the fertilization and crop management in NT accelerate particulate bound P and its desorption from soils and suspended sediments (Kaiser et al. 2009; Borda et al. 2014; Couto et al. 2015; Fink et al. 2016). On the other hand, under CT, the freshly applied industrial P fertilizer had great risk to be lost during the tobacco cultivation. The impact is coincidentally accelerated by the high rainfall during the same period (July to October) as observed in an earlier study (Pellegrini et al. 2010).

Phosphorus sorption

Land-based P enters to the river water mainly found as particulate P (PP) and often exceeds 80 % of the TP, as it can be stored in sediments via adsorption. Under acidic subtropical environments, the greater portion of PP is present as IP and occurs principally as Al-P or Fe-bound P and also as Ca-P in relatively small proportions. Many studies have documented that relationship (Némery and Garnier 2007; Withers and Jarvie 2008; Jing et al. 2012; Meng et al. 2015).

In this study, we used paired forest (natural) sediments as a reference for the comparison with anthropically impacted sediments. The relatively lower values of P_{max} , km, Q_0 , and EPC in forest sediments are attributed to the low clay content and low Al/Fe oxides and the fact that this area was never fertilized with external P and no anthropic activity. This leads to a very low release of P when these sediments reach to the river waters. A similar trend of P release in forest sediment was recorded by Pellegrini et al. (2010) and Zhu et al. (2011), and the latter authors found less seasonal variability in P release from forest sediments as they are nearly under balanced equilibrium.

Conversely, the sediments coming from intensively cultivated site under CT (sub3 = 50 % arable) located on steep slope landform and coupled with high rainfall generating very high erosion (Didoné et al. 2014) with

a higher clay content, and higher amount of ammonium oxalate and or dithionite–citrate–bicarbonate extracted Al and Fe. Moreover, this site receives a high dose of industrial fertilizers and animal waste. Consequently, the sediments originated yet showed the higher capacity to absorb free P from the river water. Many authors have shown the high P retention capacity of the colloids under 1:1 type clays and where Al and Fe predominance (Bortoluzzi et al. 2013, 2015; Jan et al. 2015; Fink et al. 2016).

Similarly, the low agriculture catchment under CT (sub2) is located in the hilly area, and sediment predominantly comes from conventional cultivation areas (Tiecher et al. 2015). Due to the smaller area under cultivation in relation to sub3 (35 vs. 50 %), and the variation in forest coverage (50 % vs. 37 %), it justifies sediments' intact nature with lower clay, low Al_{ox} , Fe_{ox} and Al_{dcb} , Fe_{dcb} that leads to lower P_{max} , Q_0 , and EPC (Tables 4 and 5). The sediments of the sub1, although with the same percent of the arable area as that cultivated in sub3 but high coverage with native vegetation, emphasize the importance of the distribution of arable and forest vegetation in the landscape ecology (Table 6). A similar result in earlier studies explaining the connectivity of P source and the river is critical and that upstream land use is influential and regulates the sediment P retention (Buck et al. 2004; Withers and Jarvie 2008; Pellegrini et al. 2010).

The sediment originated from intensive agriculture under NT (70 % arable and only 17 % forest) has low P_{max} , very low km, lower Q_0 and especially much smaller value of EPC in comparison to under CT (50 % arable and 37 % forest).

This indicates the physical conservation of soil under NT (low erosion) but higher P loss risk due to increased fine sediment transportation from top phosphate saturated soil layer. A similar observation in recent studies has raised a serious question on the suitability of prolonged NT (>15 years) in relation to P release and water quality (Sharpley et al. 2013; Borda et al. 2014; Gatiboni et al. 2015).

Untreated domestic and city discharges are also a major source of P to rivers. In this study, we can compare two sub-catchments with the same proportion of arable area (70 %) and are under similar land use and soil management system (NT-soybean) (sub4 and sub5). The urban site receives untreated domestic sewage and agro-industrial discharges of the Marau city (45,000 inhabitants). This induces a high physico-chemical

variation in sediments' behavior and affect the sediment P dynamics over time. The adsorption results reported here reflect this effect, and many authors have shown urban P pollution in sediment with higher P_{\max} , K_m , Q_0 , and EPC_0 with lower clay content. Therefore, these sediments can easily act as a P source in the river system (Peterse et al. 2003; Jarvie et al. 2012; Blanc et al. 2014).

The overall particle size distribution indicated that the sediment from intensive agriculture and CT sub-catchment (sub3) with higher clay content showed higher values of modified Langmuir parameters i.e., P_{\max} , K_m , Q_0 , and EPC_0 . Earlier studies under the similar soil and management system have shown a relationship between clay content and P sorption for high P_{\max} value (Agudelo et al. 2011; Bortoluzzi et al. 2013; Eriksson et al. 2015; Fink et al. 2016).

The main river sediments showed a great variability along the river continuum for P sorption. As the diffuse sources are invariably related to the land use, agriculture, animal production, there are several individual sources which define the P export potential of that all upstream drainage area. A better interpretation of these anthropogenic sources in relation to their runoff and sediment loss can help to differentiate their rate of P delivery and its composition (Minella et al. 2015; Tiecher et al. 2015). In this study, the P1 sediments receiving P input from the 70 % arable under NT and urban contributions showed high P_{\max} and showed a decreasing trend downstream except P4. This point of the river lies downstream too much of the conventional cultivation and receives the similar sediment as of two neighboring sub-catchment under CT (sub2 and sub3). Therefore, it was likely obvious that runoff from these CT sediments showed higher seasonal values for P_{\max} .

Phosphorus desorption

The significant variability in AER-extracted P in the different sediments is a useful tool to predict the instant bioavailable P and P buffering capacity and has been used in many soil and sediment P desorption studies (McKean and Warren 1996; Rheinheimer and Anghinoni 2001; Pellegrini et al. 2010; Su et al. 2014; Fink et al. 2016).

P-desorption-based indices require careful calibration for each desorption scenario. Torrent and Delgado (2001) proposed an index relatively

insensitive to soil type, which makes it potentially useful in areas with high soil diversity. The low values of α and β in the forest and low anthropic sub1 were detected when compared to the intensive agriculture sub2 and sub3. This indicates that P is poorly retained in the forest and sub1 sediment than sub3 and sub4. This phenomenon can be contributed to the presence of high amount of binding partners of P in the form of amorphous and crystalline Fe or Al in intensively cultivated soils. This is also indicated by the higher correlation between α and Fe_{ox} , Fe_{dcb} and Al_{ox} , Al_{dcb} ($r = 0.72, 0.84; 0.69, 0.74$ —Fig. 8, Table 6) and between β and Fe_{ox} , Fe_{dcb} and Al_{ox} , Al_{dcb} ($r = 0.74, 0.83; 0.75, 0.78$ —Fig. 7, Table 6). The high potential of bioavailable P and cumulative desorbed P during winter months can be attributed to the high rainfall erosivity and increased sediment production during the tobacco cultivation (Pellegrini et al. 2010; Didoné et al. 2014).

The higher α and β in urban sediment (sub5) are directly related to the higher amount of untreated sewage and P discharges but are variable and are a combined function of both background agricultural loads and intensity of urban P export. This trend is very obvious in sub5 as indicated by the continuous higher β values (i.e., 396 vs. 96 mg kg⁻¹) than in forest during winter 2013 as well as overall sub5 which showed highest P buffering capacity in all four seasons during 2013 and 2014 (Fig. 6). The inconsistent pattern of the main river sediment towards the α and β again shows the ambiguity and overlapping of several factors contributing to sediment and P transport. However, when compared to the forest, all five sediments showed a double increase for α and β values.

These results imply that at sub-catchment scale, the intensive agriculture (sub3 and sub4) and urban (sub5) monitoring locations have specifically sediment-bound P which is stable and can be transported over longer distances in the landscape and or receiving water bodies as later evidenced by the consistent high values of α and β in the main river sediments along the river continuum than forest. The similar results for P desorption parameters were found in conditions (Tiessen et al. 1984; Agudelo et al. 2011).

The relatively higher desorption rate constant (λ) values in downstream sediment are indicative of higher organic carbon in these sediments with increasing

drainage area and to some extent, also, higher surface runoff during winter months. However, during the summer season, relatively higher λ values in forest sediment than agriculture sediments are indicative that forest sediment can rapidly desorb P than the specifically bound P in agriculture sediment. Similarly, the higher values for the P mobility index (α/β ratios) both in the reference forest and relatively less disturbed (sub1) sediments than those of intensive agriculture (sub3 and sub4) and urban (sub5) clearly indicate that forest and low anthropic sediments easily desorb P than the sediments from the high agriculture and anthropic influence. Our results are in accordance with the Pellegrini et al. (2010), Guardini et al. (2012), and Fink et al. (2016) and authors observed a similar trend for P desorption parameters for low and high P conditions.

Conclusions

This intra-catchment comparison study has reflected the seasonal P sorption-desorption potential of sediments in relation to landscape controls using a range of sediment properties, catchment land use, and demographic characteristics to estimate P release potential and improve different upstream land use and management approaches. The seasonal and intra-catchment variation in TP and sediment-bound P release appeared as the combined effect of sediment mineralogical composition, landscape geographic features, and land use and management. However, the TP and IP showed higher correlation towards Fe_{ox} concentration. Within the different monitored sites, the suspended sediment from intensive agriculture site under CT presented higher P storage (P_{max}) which is closely associated with the high Al/Fe-P complexes. This leads to the lower EPC values indicating the high P release to the river waters. The desorption kinetics showed that urban (sub5) intensive agriculture (sub3 and sub4 including sub2) and P1 to P5 (main river) showed higher bioavailable P (α) and total desorbed P (β), which can pose a greater threat to stream waters by acting as P source during seasonal shifts and oxic-anoxic variations on sediment-water interface in the presence of high Fe, Al, and Mn ions. Finally, desorption rate (λ) and the P mobility index ($\alpha \times 100/\beta$) were highest in intensive agriculture sediment (sub3) as well as in highly anthropic

(sub5), and main river sediment, though less pronounced variation was observed. The results clearly suggest that improvement in reduction of soil-based P is required to maintain water quality and implement the conservation practices to understand eutrophication process for wise hydrological source management.

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