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Phosphorus Forms in Sediments as Indicators of Anthropogenic Pressures in an Agricultural Catchment in Southern Brazil

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ABSTRACT: Phosphorus (P) fractionation is a suitable procedure to ascertain P lability in sediments and is able to distinguish sources of P under different soil management practices in a catchment. Brazil is the second largest producer and the largest exporter of tobacco in the world. Inadequate management of cultivated areas exposes the soil to erosion processes, accelerating the transfer of sediment and P to water bodies, which leads to eutrophication. We evaluated the P forms in suspended sediments collected at two rainfall events in the stream of a small catchment in the state of Rio Grande do Sul. The samples were collected upstream and downstream areas in three sub-catchments with different degrees of anthropogenic pressure and in three phases of the hydrograph in the catchment outlet. The first rainfall event occurred during the fallow period, and the second one, during the period of transplanting the tobacco crop. The sediment P forms were evaluated by successive extractions, following the Hedley method. The results showed that an increase in anthropogenic pressure leads to an increase in total inorganic P and a decrease in the levels of organic C and total organic P in sediments. In the control area, the quantity and quality of the eroded material remained the same in both rainfall events. The levels of total P in sediment alone were not sufficient to evaluate the influence of the soil management practices prevalent in each sampling period. However, P fractionation shows that during the tobacco transplanting period, P in sediments was mainly in labile fractions, and rainfall during this period was more likely to promote the eutrophication process. Sediments carried in runoff during the tobacco transplanting period have larger amounts of available P than those borne during rainfall in the fallow period.

Keywords: phosphorus fractionation, watershed, nonpoint source pollution, eutrophication, land use.

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INTRODUCTION

Degradation of natural resources caused by human activities has increased in recent decades. Agricultural activities are among those that most disturb the environment, exposing soil to erosion processes and accelerating the transfer of sediments (Magnusson et al., 2013; Yahia and Elsharkawy, 2014) and nutrients, such as N (Cameron et al., 2013) and P (Dodd et al., 2014), into water bodies.

In Southern Brazil, about 160 thousand families cultivate tobacco (Afubra, 2015), the majority of them in the state of Rio Grande do Sul, under conventional tillage, with no conservationist practice, which leads to negative environmental impacts at the local level (Lecours et al., 2012). These fields are in steeply sloped areas, resulting in a large amount of sediment (Pellegrini et al., 2010; Bonumá et al., 2012; Bonumá et al., 2014; Tiecher et al., 2014).

Nutrient enrichment of water bodies arising from human activities is considered the main problem for most surface waters in the world (Smith and Schindler, 2009). In waters with a high level of eutrophication, periods of high temperature accelerate multiplication of microorganisms, which impairs the limnological conditions of rivers (Salomoni et al., 2007) and may cause episodes of high fish mortality (Chellappa et al., 2008). In Brazil, P eutrophication has been responsible for some events of excessive macrophyte growth in rivers (Kobayashi et al., 2008) or algae blooms in lakes (Ribeiro et al., 2012), coastal waters (Teichberg et al., 2010), and dam reservoirs (Chellappa et al., 2008; Matsumura-Tundisi et al., 2010).

Eutrophication affects the resident biota, and the intensity of this impact depends on nutrient loading but also on the environmental conditions of the water body. Rivers, lakes, and estuaries have different characteristics. Along transport pathways within a catchment, some P input from nonpoint and point sources can accumulate in various locations, such as soils in downslope areas, sediments, or biomass (Sharpley et al., 2013). This has been referred to as the P legacy of the catchment. These hotspots can release, remobilize, or recycle the P legacy, impacting the water quality of downstream water bodies for years, decades, or centuries (Heisler et al., 2008).

The internal capacity of river systems to remove P from or release P to the water column is a result of physical, chemical, and biological processes that can transform P among organic, inorganic, particulate, and dissolved forms. The diffuse agricultural P inputs also have within-river ecological impacts (Jarvie et al., 2005). Large amounts of sediment-associated P from agricultural sources are transported to the stream channel during storm events. Along the downstream pathway, part of these particles is deposited and stored on the river bed. Later, these river bed sediments can release dissolved P, playing an important role as buffers of soluble reactive phosphorus (SRP) in surface waters (Jarvie et al., 2005).

In the watershed studied, the Lino Stream is a tributary of the Jacuí River, which is the main affluent of Guaíba Lake, a freshwater shallow lake in which wave-created resuspension of environment sediments are frequently observed (Nicolodi et al., 2010). During cyanobacterial summer blooms observed in Guaíba Lake, Ribeiro et al. (2012) identified SRP limitation and indicated the total P increase as an environmental driving factor. That said, it is likely that the internal P load stored in the bottom sediments of Guaíba Lake contributed to these algal blooms since in freshwater lakes, P is usually the limiting nutrient for eutrophication (Hilton et al., 2006).

Many studies in catchments areas have been conducted to evaluate P transport associated with suspended sediments during rainfall events, but most of these studies assessed only the total P levels in the sediments. The analysis of total P is ineffective for measuring the degree of availability of this element for algal absorption and, consequently, the capability of promoting the water eutrophication process (Sharpley et al., 1992). Phosphorus transferred from soil to aquatic environments is commonly divided into two forms: soluble and particulate P. Losses of P in the particulate form associated with sediment usually

range from 75 % (Horowitz, 2009) to 90 % (Sharpley et al., 2000). Moreover, more than 90 % of the sediment losses in a catchment occur during rainfall events (Horowitz, 2009). To access the P bioavailability of suspended sediments, selective sequential extraction based on the difference in reactivity of sediment P with different chemical extractors should be used (Kerr et al., 2011).

Therefore, our hypothesis is that the analysis of sediment P forms obtained by selective sequential extraction can be a useful tool for assessing the magnitude of P pollution in agricultural catchments, and consequently, the ability of these forms to promote the water eutrophication process. The aim of the present study was to verify the effect of anthropic activity on the P forms in sediments by comparing areas with distinct land uses under different seasonal soil management practices.

MATERIALS AND METHODS

Site description

The Agudo catchment has 480 ha and the main watercourse is the Arroio Lino stream, located in the municipality of Agudo, state of Rio Grande do Sul, in southern Brazil (29° 30' S and 53° 15' W). The Arroio Lino Stream is a tributary of the Jacuí River, which is responsible for 85 % of the water input in Guaíba Lake, the most important water supply for the municipality of Porto Alegre, which has a population of 1.5 million inhabitants.

The channel network is characterized by step-pool channels with high roughness and turbulent flux, composed of cobbles and boulders that protect finer bed material. The average stream width is 3 m, with a depth of 0.5 m in the catchment outlet. There are no water control structures along the stream.

The altitude in the catchment ranges from 120 to 480 m, while the topography is hilly with long and short slopes, usually greater than 25°. The climate is humid subtropical (Cfa, according to the Köppen classification system) with an average annual temperature of 20 °C. Annual rainfall ranges from 1,300 to 1,800 mm. The catchment is underlain by acid volcanic rocks in the upper part and sandstone in the lower zones.

Clay content in all soils was lower than 210 g kg⁻¹. Organic matter contents ranged from 7.0 to 34.0 g kg⁻¹. The soil pH in water ranged from 5.1 to 6.1. In the soil clay fraction, 2:1 clay minerals are predominant; however, illite and kaolinite are present in lower amounts (Bortoluzzi et al., 2013). The main soil types in the watershed are Chernozem, Regosol, and Arenosol (WRB, 2014), which are classified as *Chernossolo Argilúvico férreo*, *Neossolo Litólico eutrófico*, and *Neossolo Quartzarênico órtico*, respectively, accordingly to the Brazilian System of Soil Classification (Santos et al., 2013).

Approximately 90 % of the 36 agricultural production units belong to family farmers dedicated to tobacco production. Fertilizers are still added based on the system of precaution and approximately 180, 60, 210, and 20 kg ha⁻¹ of N, P, K, and S, respectively, are applied annually. Tobacco cultivation usually includes two to six soil operations per year, as well as the use of many pesticides for weed control.

The different land uses were grouped into annual crops, native forest cover, and other uses, which include perennial pasture, subsistence crop fields, orchards, buildings and facilities, and roads (Figure 1 and Table 1). In the present study, we selected some areas within the catchment to investigate sediment P forms in areas differing in land use proportions. The selected areas were Sub-basin A, B, and C. The Sub-basin A has steep slopes, high human activity, and cropping areas located next to streams, without riparian vegetation. In Sub-basin A, two points were sampled: the first one (A1) was located upstream, where there was a low proportion of cropland; the second one (A2) was situated in a downstream area, more anthropized than A1.

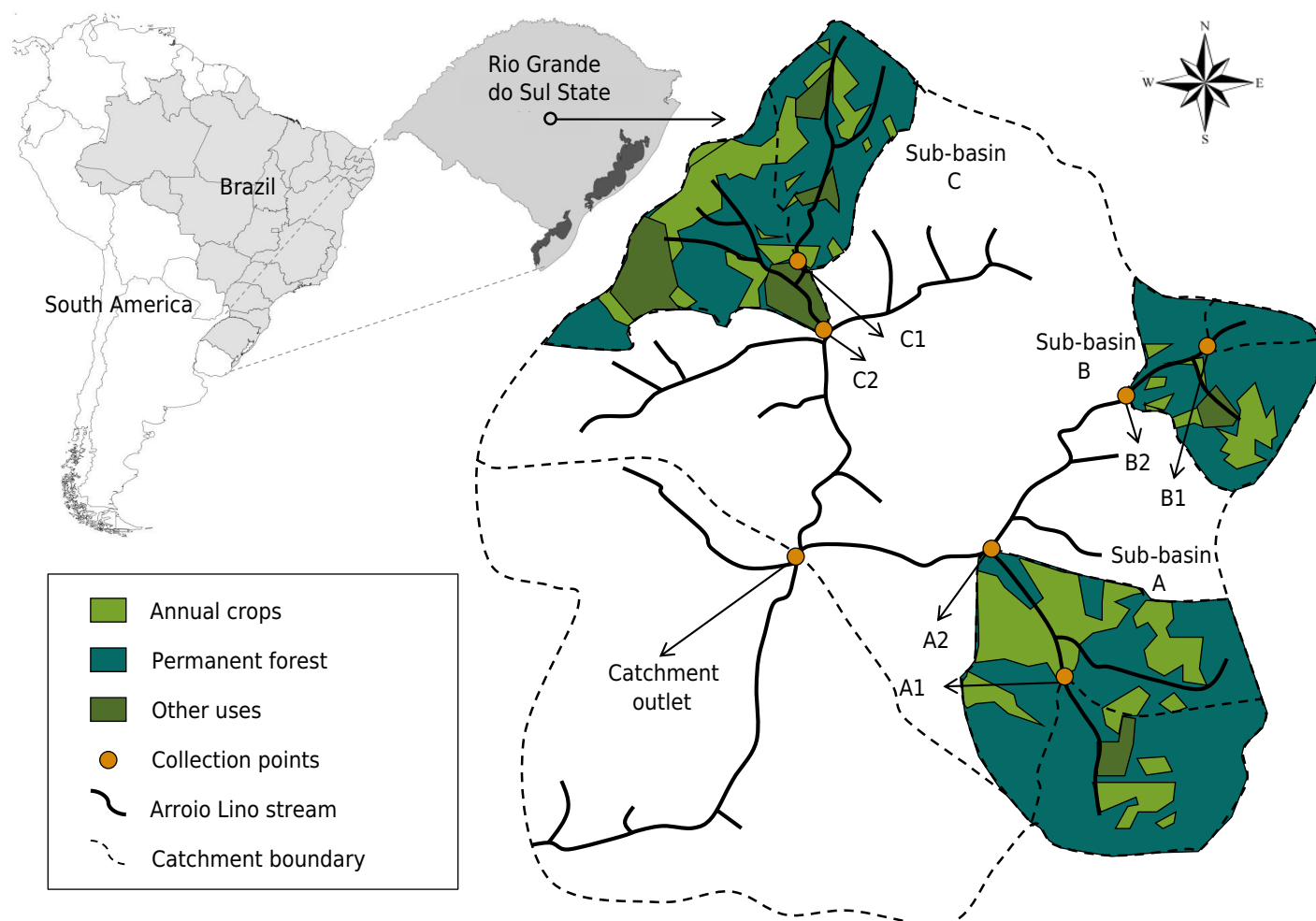


Figure 1. Arroio Lino stream, collection points of suspended sediments, catchment boundary, and land use (annual crops, permanent forest, and other uses) in the three Sub-basins (A, B, and C) monitored in Agudo catchment, Rio Grande do Sul, Brazil.

Table 1. Areas and relative contribution of the land uses at each point of the three sub-basins monitored in the Agudo catchment, Rio Grande do Sul, Brazil

Sub-basins	Collection point	Anthropic condition	Total area	Annual crops		Permanent forest		Other uses ⁽¹⁾	
			ha	ha	%	ha	%	ha	%
A	A1	Disturbed	26.9	3.2	11.9	21.4	79.6	2.3	8.5
	A2	Disturbed	69.2	17.1	24.7	48.1	69.5	4.0	5.8
B	B1	Undisturbed	3.1	0.0	0.0	3.1	100.0	0.0	0.0
	B2	Disturbed	24.3	3.9	16.1	18.5	76.1	1.9	7.8
C	C1	Disturbed	21.2	4.2	19.8	16.0	75.5	1.0	4.7
	C2	Disturbed	48.3	12.0	24.8	29.5	61.1	6.8	14.1

⁽¹⁾ Perennial pasture, subsistence cultivation, orchards, gardens, installations, and roads.

The Sub-basin B has landscape based on highly sloped topography with a low level of human activity. In Sub-basin B, one point was sampled upstream (B1), which corresponds to the only area undisturbed by human activity in the present study, where 100 % of the land is covered with native forest (assumed as a control area). Another point was collected downstream (B2), in a region with few cropping areas. The Sub-basin C has highly sloped topography and high level of human pressure. Two sampling points were chosen, one located in an upstream area (C1) and another in a downstream area (C2).

Sediment sampling

Suspended sediments were sampled during storm events that occurred during the fallow period (April 2008 - figure 2a) and during the tobacco transplanting period (August 2008 - figure 2b) in order to represent the different seasonal soil management practices in the catchment. The samples were collected in two ways. First, at the upstream and downstream points of the three sub-basins (A, B, and C), US U-59 suspended sediment samplers were installed at 0.05 m above the baseflow. This methodology consists of the automatic capture of water and suspended sediment when the water level rises. Secondly, in the catchment outlet, suspended sediment samples were collected at different phases of the hydrograph: rising limb (1), peak discharge (2), and recession limb (3) through use of a US DH-48 manual sampler. Phases sampled during the fallow period were named F1, F2, and F3, and the phases sampled during tobacco transplanting were named T1, T2, and T3. After the rainfall event, the containers with the samples were kept at $\pm 4^{\circ}\text{C}$ and immediately taken to the laboratory where they were analyzed.

In the catchment outlet, a Parshall flume was installed in which the water level was monitored during the storm event. Later, water discharge was calculated using equation 1 obtained by Sequinato (2007) relating the height of the water level (h) and the water discharge with a determination coefficient of 0.982.

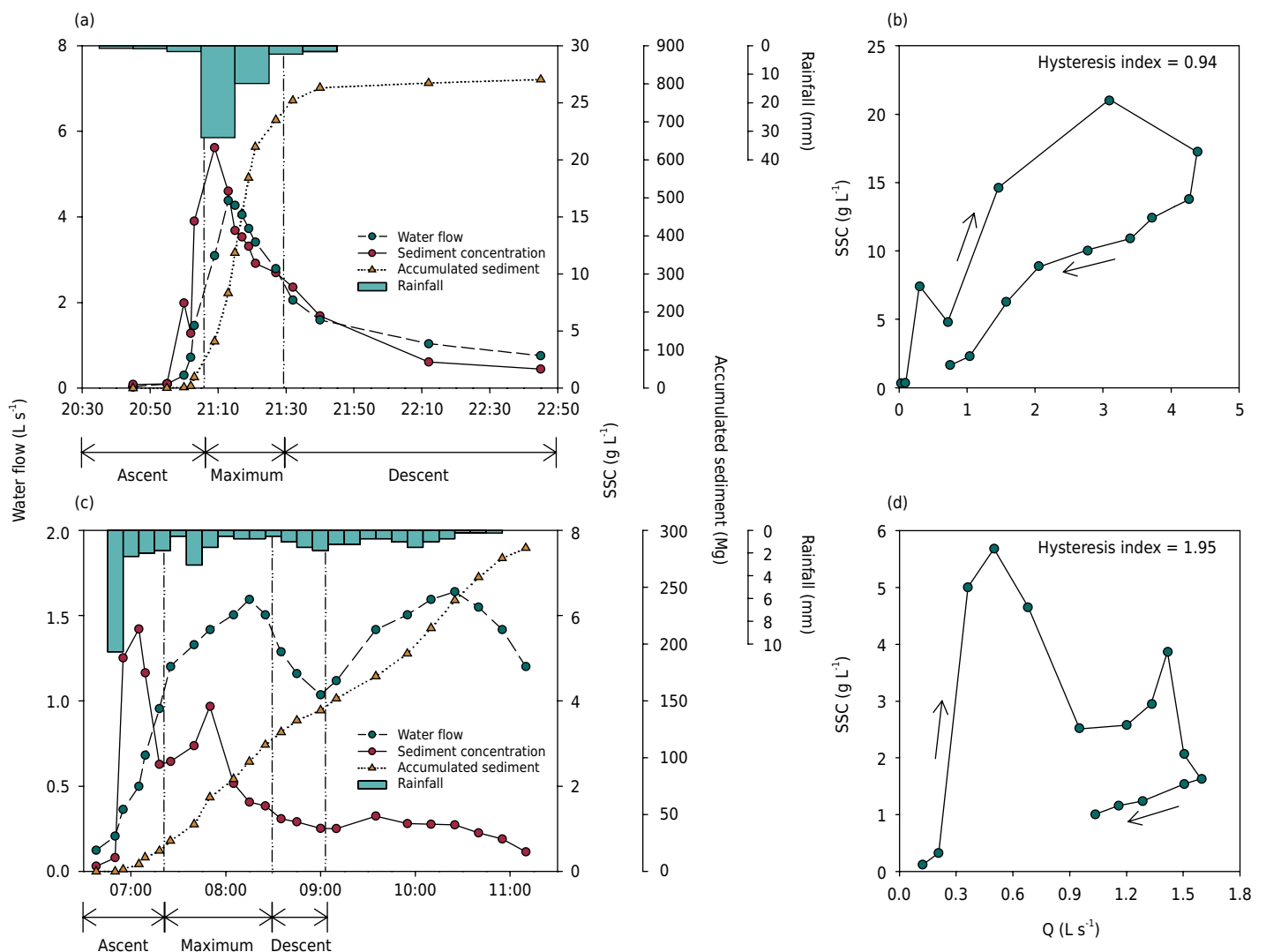


Figure 2. Rainfall, water flow, and suspended sediment concentration (SSC) at the monitoring station in the catchment outlet during the storm events occurred during the fallow (a) and tobacco transplanting (c), and hysteresis loops during the storm events occurred during the fallow (b) and tobacco transplanting (d) periods in Agudo catchment, Rio Grande do Sul, Brazil.

$$\text{Water discharge (m}^3 \text{ s}^{-1}\text{)} = 10.544 \times h^{1.267} \quad \text{Eq. 1}$$

The hysteresis index (*HI*) between suspended sediment concentration (*SSC*) and water flow rate (*Q*) was calculated by using the two single stages of calculation for any given hysteresis loop, as suggested by Lawler et al. (2006). First, the value of *Q* central (*Q_{cen}*) was calculated by using the values of maximum (*Q_{max}*) and minimum (*Q_{min}*) water flow in the ascending branch of the hydrograph (*Q_{max}* is the peak discharge and *Q_{min}* is the starting discharge for the storm event) (Equation 2):

$$Q_{\text{cen}} = 0.5 \times (Q_{\text{max}} - Q_{\text{min}}) + Q_{\text{min}} \quad \text{Eq. 2}$$

Then, the values of *SSC* for *Q_{cen}* is found for the rising stage (*SSC₊*) and the recession phase (*SSC₋*) by using the *Q* × *SSC* plot. If the hysteresis curve is in a clockwise direction, the *HI* will be positive and calculated by equation 3, but if the hysteresis curve is in a counterclockwise direction, the *HI* will be negative and calculated by equation 4.

$$HI = (SSC_{+}/SSC_{-}) - 1 \quad \text{Eq. 3}$$

$$HI = [-1/(SSC_{+}/SSC_{-})] + 1 \quad \text{Eq. 4}$$

Sediment analysis

Suspended sediment concentration was calculated after drying an aliquot of water + sediment sample at 105 °C. For physicochemical characterization and P fractionation, another aliquot was dried at ±50 °C. A third aliquot was filtered through a 0.45 µm cellulose membrane to estimate soluble P (Murphy and Riley, 1962).

Particle size distribution was analyzed by laser granulometry (Muggler et al., 1997). Aluminum and Fe crystalline oxides were estimated by extraction with dithionite-citrate-bicarbonate (Mehra and Jackson, 1960). Aluminum and Fe amorphous oxides were estimated by extraction with ammonium oxalate (Claessen, 1997). The Al and Fe in the extracts were determined using an atomic absorption spectrometer (AAS). Total organic carbon (TOC) content was determined by wet oxidation (Walkley and Black, 1934).

Sediment P forms were evaluated by sequential chemical fractionation proposed by Hedley et al. (1982). Briefly, the sequential extractions were (1) distilled water with one anion exchange resin membrane (identified as Av-P); (2) 0.5 mol L⁻¹ NaHCO₃ at pH 8.5 (identified as Bic-P); (3) 0.1 mol L⁻¹ NaOH (identified as Hid_{0.1}-P); (4) 1.0 mol L⁻¹ HCl (identified as HCl-P); and (5) 0.5 mol L⁻¹ NaOH (identified as Hid_{0.5}-P). After each extraction, the soil suspensions were centrifuged at 2,510 × *g* for 15 min to collect clear supernatants. After centrifugation and storage of the supernatant from each extraction, the soil tubes were washed with the addition of 0.5 mol L⁻¹ NaCl and then centrifuged once more; this supernatant was added to the previous extract. After extractions, the remaining sediment was dried at ± 50 °C, ground, and digested with H₂SO₄ and H₂O₂ in the presence of saturated MgCl₂; after that, the P content was determined (identified as Residual-P) (Olsen and Sommers, 1982). Inorganic P from the acid extractions was determined according to the Murphy and Riley (1962) method. In the NaHCO₃ and NaOH extractions, total P was estimated by digestion with H₂SO₄ and ammonium persulfate in an autoclave at 121 °C (Usepa, 1971), with subsequent determination of P by the Murphy and Riley (1962) method.

Total organic P (Organic-P) estimated by the ignition method was obtained by the difference between the amount of P extracted with 0.5 mol L⁻¹ H₂SO₄ from ignited (550 °C, 2 h) and non-ignited soil samples (Olsen and Sommers, 1982). Total P was estimated by digestion with H₂SO₄ and H₂O₂ in the presence of saturated MgCl₂, as proposed by Olsen and Sommers (1982). Then, total inorganic P (Inorganic-P) was estimated by the difference between total P and total organic P. Inorganic P from the extracts was determined according to the Murphy and Riley (1962) method.

Statistical analysis

All the P forms in sediments passed in the Lilliefors and Kolmogorov-Smirnov test for normality. Pearson's correlation analysis of the P forms with the land use and the physicochemical properties of sediments was performed using the data from the six points sampled in the three sub-basins in both rainfall events ($n = 2$). To evaluate the effect of the seasonal soil management practices, the means of the P forms and physicochemical properties were compared by the nonparametric Mann-Whitney U test. This test was used because non-parametric models differ from parametric models in that the model structure is not specified *a priori* but is instead determined from data.

Principal Component Analysis (PCA) based on the correlation matrix and Discriminant Analysis Function (DAF) was performed using all the sediment samples ($n = 18$) and all the sediment P forms. The DAF was performed in the backward mode to determine the minimum number of P forms that maximizes the discrimination among the sediments collected at different land uses and seasons. The groups tested were: undisturbed sites (B1 during fallow and transplanting); disturbed sites in fallow (A1, A2, B2, C1, C2, F1, F2, and F3), and disturbed sites during transplant (A1, A2, B2, C1, C2, T1, T2, and T3). The multivariate discriminant function is based on the Wilks' Lambda (Λ^*) value from analysis of variance, where the criterion used by the statistical model is the minimization of Λ^* . A Λ^* of 1 occurs if all the group means are the same, while a low Λ^* value means that the variability within the groups is small compared to the total variability. At each step, the P-form which minimized the overall Wilks' Lambda was entered. The maximum significance of F to enter a property was 0.01. The minimum significance of F to remove a property was 0.01. All statistical analysis was performed using Statistica software (StatSoft, USA).

RESULTS AND DISCUSSIONS

Effect of land use and soil management on suspended sediment concentration

Total rainfall and its intensity can be more important than seasonal soil management in determining suspended sediment content (SSC), as highlighted by data collected during the storm events that occurred in the fallow and tobacco transplanting periods (Figures 2a and 2b), particularly considering the erosivity (R) value of $7.866 \text{ MJ mm ha}^{-1} \text{ h}^{-1}$, calculated for the Santa Maria municipality (Cogo et al., 2003), next to the area of study. In the storm event that occurred during the fallow period, the total rainfall was 55 mm, the mean intensity was 47 mm h^{-1} , the maximum intensity was 192 mm h^{-1} , and the sediment yield was 845 Mg. In the storm event that occurred during tobacco transplanting, the total rainfall was 38 mm, the mean intensity was 17 mm h^{-1} , the maximum intensity was 124 mm h^{-1} , and the sediment yield was 284 Mg.

As expected, in both storm events, the SSC was lower upstream in Sub-basins A and B than downstream due to the higher proportion of forest and low human pressure in the upstream areas (Figure 1 and Table 1). In Sub-basin C, the proportions of forest and croplands upstream and downstream were almost the same, resulting in similar SSC. Moreover, as there was no correlation between SSC and the proportions of cropland and/or forest, it was evident that other factors play an important role in sediment yield, such as distribution of croplands and forests in the landscape. Indeed, the shape of the landscape strongly influences sediment concentration in the catchment, and preserved riparian vegetation can serve as a barrier, decreasing the amount of sediments transferred to the water bodies (Pellegrini et al., 2010). Even when almost all crop fields of the catchment were plowed to transplant tobacco, the values of SSC in all six sampling sites in the three sub-basins and in the catchment outlet were lower than those observed during the storm event that occurred in the fallow period (Table 2).

Table 2. Physicochemical properties and phosphorus forms in sediments eroded from undisturbed areas (B1) and disturbed areas (A1, A2, B2, C1, and C2) and during the phases of ascension (1), maximum flow rate (2), and recession (3) at the watershed outlet during the rainfall events that occurred during the fallow and transplanting period in the Agudo catchment, Rio Grande do Sul, Brazil

Variable	Sub-basins					Watershed outlet						U-test ⁽²⁾
	Undisturbed		Disturbed		U-test ⁽¹⁾	Fallow			Transplant			
	Fallow	Transplant	Fallow	Transplant		F1	F2	F3	T1	T2	T3	
SSC (g L ⁻¹)	0.1	0.1	8.0	2.1	*	4.8	13.5	5.3	1.7	2.1	1.1	*
TOC (g kg ⁻¹)	74.7	103.2	26.7	36.9	ns	24.0	23.2	27.0	16.9	24.7	25.9	ns
Clay (g kg ⁻¹)	7.8	7.1	17.5	16.1	ns	18.8	18.7	18.4	20.4	21.9	25.7	*
Silt (g kg ⁻¹)	77.1	80.8	78.5	79.4	ns	75.6	76.0	75.5	79.6	78.1	70.2	ns
Sand (g kg ⁻¹)	15.0	12.0	4.0	4.5	ns	5.5	5.3	6.1	0.0	0.0	4.1	*
CDB-Fe (g kg ⁻¹)	19.5	12.3	75.3	24.3	**	102.3	96.3	78.8	37.6	33.5	29.1	*
CDB-Al (g kg ⁻¹)	1.0	0.6	3.6	1.7	*	5.6	4.6	4.0	2.6	2.5	2.4	*
Oxalate-Fe (g kg ⁻¹)	0.8	0.6	3.2	5.1	*	3.2	4.2	2.5	3.4	5.4	3.6	ns
Oxalate-Al (g kg ⁻¹)	0.2	0.4	0.5	1.2	**	0.5	0.7	0.5	1.6	1.7	1.6	*
Phosphorus form												
Soluble-P (μg L ⁻¹)	17	14	49	137	*	25	20	35	181	100	256	*
Resin-P (mg kg ⁻¹)	9	13	79	176	*	121	148	102	166	185	362	*
Bic-P (mg kg ⁻¹)	91	110	35	78	*	31	37	39	32	73	62	ns
Hid _{0.1} -P (mg kg ⁻¹)	216	147	281	404	*	182	199	232	155	276	253	ns
HCl-P (mg kg ⁻¹)	18	23	120	120	ns	165	142	153	140	132	121	ns
Hid _{0.5} -P (mg kg ⁻¹)	117	130	266	278	ns	196	155	160	123	172	125	ns
Residual-P (mg kg ⁻¹)	484	333	314	247	*	372	395	345	297	275	300	*
Organic-P (mg kg ⁻¹)	498	513	177	239	ns	103	148	148	162	214	271	*
Inorganic-P (mg kg ⁻¹)	123	147	815	658	ns	823	1,020	1,167	931	910	662	ns
Total-P (mg kg ⁻¹)	622	660	992	897	ns	927	1,167	1,316	1,094	1,124	933	ns

⁽¹⁾ Comparison between fallow and transplanting periods in the disturbed areas. ⁽²⁾ Comparison between fallow and transplanting periods in the watershed outlet. * and **: significant at $p < 0.05$ and $p < 0.01$ by the Mann-Whitney U test, respectively. SSC: suspended sediment concentration. TOC: total organic carbon (Walkley and Black, 1934). CDB-Fe and CDB-Al: Fe and Al extracted by dithionite-citrate-bicarbonate, respectively. Oxalate-Fe and Oxalate-Al: Fe and Al extracted by ammonium oxalate. Soluble-P: P soluble in water. Resin-P: available P extracted by anion exchange resin membrane. Bic-P: P extracted by 0.5 mol L⁻¹ NaHCO₃ at pH 8.5. Hid_{0.1}-P: P extracted by 0.1 mol L⁻¹ NaOH. HCl-P: P extracted by 1.0 mol L⁻¹ HCl. Hid_{0.5}-P: P extracted by 0.5 mol L⁻¹ NaOH. Residual-P: P residual obtained after digestion with H₂SO₄ and H₂O₂. Organic-P: total organic P. Inorganic-P: total inorganic P. Total-P: total P content.

Both storm events had a clockwise hysteresis loop, with a higher SSC in the rising limb than in the recession limb (Figures 2c and 2d). The index, calculated according to Lawler et al. (2006), was 0.94 for the storm event that occurred during the fallow period and 1.95 for the transplanting period. That means sediments were quickly mobilized, transported, and deposited (Seeger et al., 2004). This indicates that the main sediment source is close to the stream, such as the particles deposited in the bottom of the river channel (Minella et al., 2011). It was observed especially in the rainfall occurring during the tobacco transplant, which showed the highest hysteresis index.

In the undisturbed site, the SSC, the physicochemical properties, and the P forms in the suspended sediment transported in both storm events were very similar, whereas in the disturbed areas, the SSC is highly influenced by the intensity of the rainfall events. These findings show that, under natural conditions, the quantity and quality of the eroded material are largely unaltered, even under extremely different rainfall events. In contrast, when virtually all crop fields were plowed for tobacco transplanting, the measured values of SSC were approximately four times lower than those under an event with higher total rainfall and rainfall intensity, such as in the fallow period (Table 2).

The influence of the magnitude of the rainfall is also evidenced by the particle size distribution of the sediment. The fallow period can be characterized by transport of sediments with higher sand and lower clay contents, which can be ascribed to an increase in rainfall transport capacity. The Fe_d content was one third of that obtained during the

fallow period (Table 2) at the time of tobacco transplant, indicating a qualitative difference in the sediment. In a study conducted in the same catchment, Minella et al. (2007) found that soils from croplands have two times more Fe_d content than sediments from the road and river banks.

Effect of land use and soil management on sediment P forms

The change in land use from forest to tobacco fields results in an increase in Inorganic-P and a decrease in Organic-P and TOC in the suspended sediments. The Total-P content in sediments in the downstream area of Sub-basins A and B was higher than the content in the upstream area in both storm events (Figure 3). In Sub-basin C, Total-P content was almost the same upstream and downstream, due to the similar land use. Nevertheless, the percentage of Organic-P downstream was always lower, while the proportion of Inorganic-P was always higher than the analogous values upstream. Furthermore, the TOC content in sediments upstream was always higher than the content downstream. This occurs because transformation of natural ecosystems into cultivated areas changes the distribution of soil P forms (Tiecher et al., 2012a,b); generally organic P and TOC decrease quickly in continuous cultivation systems (Solomon et al., 2002).

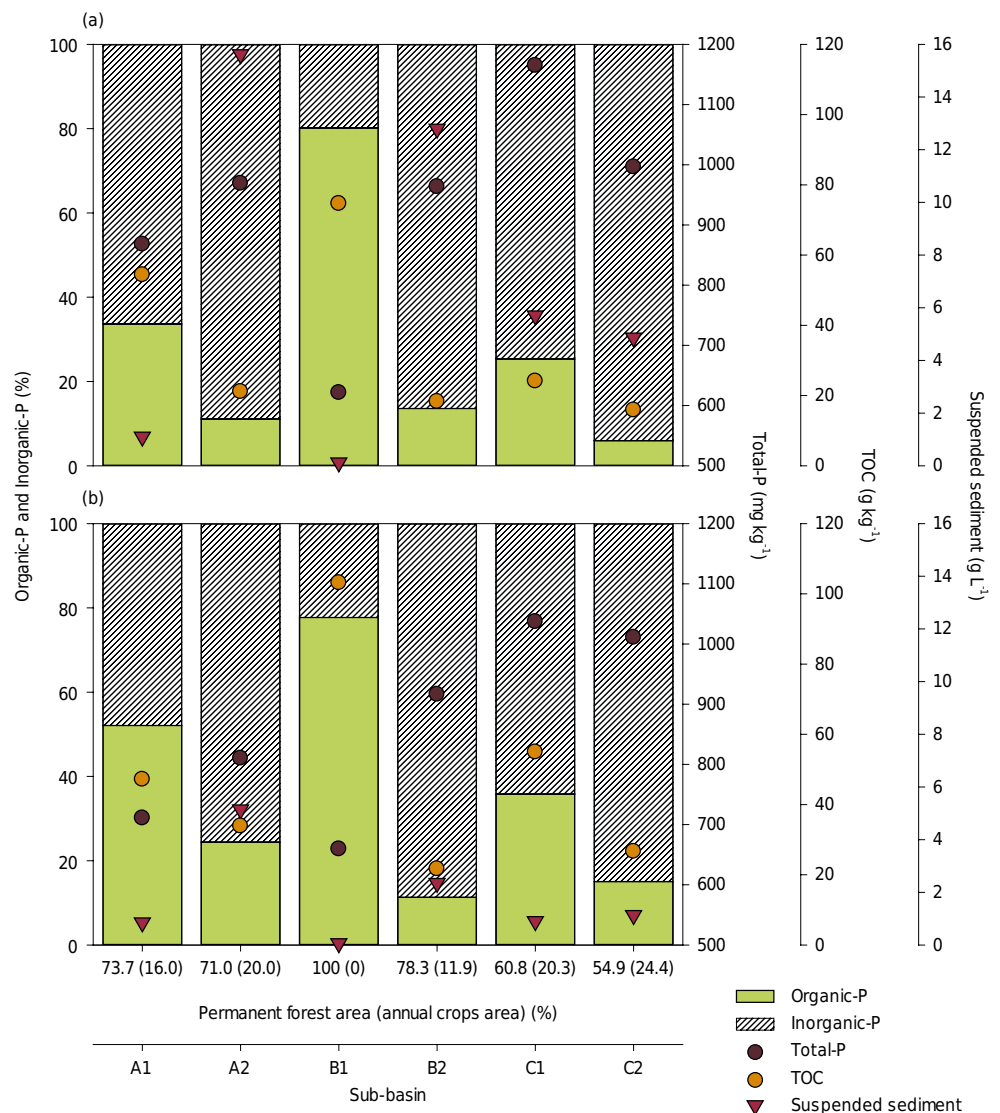


Figure 3. Suspended sediment concentration, total phosphorus content (Total-P), total organic carbon (TOC), and proportion of organic (Organic-P) and inorganic (Inorganic-P) P in relation to the total P content upstream and downstream the Sub-basins A, B, and C, in the storm event occurred in fallow (a) and tobacco transplant period (b) in Agudo catchment, Rio Grande do Sul, Brazil.

The tobacco crop requires large amounts of phosphate, 60 kg ha⁻¹ yr⁻¹ of P are applied in the fields, an amount much higher than that exported by tobacco leaves, which leads to an accumulation of soil P, mainly in inorganic forms (Rheinheimer and Anghinoni, 2001; Guardini et al., 2012), in highly weathered subtropical soils. An increase in the proportion of Inorganic-P at the expense of Organic-P in suspended sediments as the proportion of cropland increases in relation to forest areas can be observed in figure 3 and table 2. These data analyzed together with correlation analysis (Table 3) clearly demonstrate that an increase in Inorganic-P and decrease in Organic-P and TOC in suspended sediments were caused by anthropic pressure. Linear correlation also showed an increase in the contents of Organic-P, Residual-P, and TOC as the proportion of the area occupied by forests increased, whereas Inorganic-P, Total-P, HCl-P, and Hid_{0.5}-P content increases with an increasing proportion of cropped area.

Evaluating only the Total-P content in the disturbed areas and at the catchment outlet, the influence of seasonal soil management could not be verified. Resolution No. 357/2005 of the National Environmental Council of Brazil (Conama, 2005) stipulates that water bodies with concentration above 0.1 mg L⁻¹ of total P cannot be classified as fresh waters; however, it does not mention values of specific P fractions. In the disturbed areas and at the catchment outlet, the soluble P concentration was over this limit during the rainfall event in the tobacco transplanting period (Table 2), highlighting the high pollutant load and the real potential for impact on important areas located downstream. For example, the water drained from the watershed under study goes to Guaíba Lake, an important waterbody that is the main source of water for the metropolitan region of Porto Alegre (more than four million people). Despite its importance, this lake receives a high load of pollutants, and phytoplankton blooms are frequent (Andrade and Giroldo, 2014).

Table 3. Linear correlation of the variables evaluated at the downstream and upstream points of Sub-basins A, B, and C (*n* = 12) in the Agudo catchment, Rio Grande do Sul, Brazil

Variable	P forms										Forest	Annual crops
	Soluble	Resin	Bic	Hid _{0.1}	HCl	Hid _{0.5}	Residual	Organic	Inorganic	Total		
Resin-P	0.76**											
Bic-P	ns	ns										
Hid _{0.1} -P	ns	ns	ns									
HCl-P	ns	ns	ns	ns								
Hid _{0.5} -P	ns	ns	ns	ns	ns							
Residual-P	ns	-0.65*	ns	ns	ns	ns						
Organic-P	ns	ns	0.68*	ns	-0.69*	-0.76**	ns					
Inorganic-P	ns	ns	-0.62*	ns	0.63*	0.82**	ns	-0.89***				
Total-P	ns	ns	ns	ns	ns	0.72**	ns	-0.61*	0.90***			
Forest	ns	ns	ns	ns	-0.67*	-0.78**	0.60*	0.85***	-0.88***	-0.72**		
Annual crop	ns	ns	ns	ns	ns	0.89***	ns	-0.81**	0.88***	0.76**	-0.96***	
SSC	ns	ns	-0.59*	ns	ns	ns	ns	-0.60*	ns	ns	ns	ns
TOC	ns	ns	0.70*	ns	ns	-0.78**	ns	0.91***	-0.91***	-0.72**	0.85***	-0.84**
Clay	ns	ns	-0.58*	ns	ns	ns	ns	-0.66*	0.64*	ns	-0.65*	0.63*
Silt	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Sand	ns	ns	0.62*	ns	ns	ns	0.71**	0.67*	ns	ns	0.70*	-0.58*
CDB-Fe	ns	ns	-0.72**	ns	ns	ns	ns	ns	0.64*	0.59*	ns	ns
CDB-Al	ns	ns	-0.64*	ns	ns	0.65*	ns	-0.62*	0.70*	0.64*	ns	0.61*
Oxalate-Fe	ns	0.71**	ns	ns	ns	ns	-0.73**	ns	ns	ns	-0.62*	ns
Oxalate-Al	0.71**	0.70*	ns	0.58*	ns	0.60*	-0.66*	ns	ns	ns	ns	0.57*

ns: not significant. *, ** and ***: significant at *p* < 0.05, *p* < 0.01, and *p* < 0.001, respectively. SSC: suspended sediment concentration. TOC: total organic carbon. CDB-Fe and CDB-Al: Fe and Al extracted by dithionite-citrate-bicarbonate, respectively. Oxalate-Fe and Oxalate-Al: Fe and Al extracted by ammonium oxalate. Soluble-P: P soluble in water. Resin-P: available P extracted by anion exchange resin membrane. Bic-P: P extracted by 0.5 mol L⁻¹ NaHCO₃ at pH 8.5. Hid_{0.1}-P: P extracted by 0.1 mol L⁻¹ NaOH. HCl-P: P extracted by 1.0 mol L⁻¹ HCl. Hid_{0.5}-P: P extracted by 0.5 mol L⁻¹ NaOH. Residual-P: P residual obtained after digestion with H₂SO₄ and H₂O₂. Organic-P: total organic P. Inorganic-P: total inorganic P. Total-P: total P concentration.

However, the results of P fractionation clearly show that the suspended sediments transported during tobacco transplanting were enriched with more labile P forms than the sediments transported during the fallow period. This can be verified in the disturbed areas by an approximate doubling of the levels of Av-P and Bic-P in sediments carried in the runoff from rainfall during tobacco transplanting. In addition, in the sediments sampled in the disturbed areas, the levels of Hid_{0.5}-P (P of intermediate lability) were also higher during tobacco transplanting (Table 2). These results highlight that the P applied in the soil in the tobacco transplanting period remains loosely bound to the sediment in the catchment runoff, which means it is easily available to the aquatic biota. Furthermore, in the rainfall event that occurred during the tobacco transplanting period, there was an increase in Av-P in the descent phase of the hydrograph, which corresponds to twice the analogous value observed in the ascent and maximum flow phases. This result indicates that most of the sediment reaching the water bodies at the end of the rainfall event came from distant recently-fertilized crop fields.

Frequent application of high rates of P in tobacco fields leads to saturation of the sites with high affinity for P in the soil surface layers. For that reason, there was higher content of Total-P, Inorganic-P, Av-P, Bic-P, HCl-P, Hid_{0.1}-P, and Hid_{0.5}-P in the suspended sediment from disturbed areas compared to the undisturbed site (Table 2). In addition to the P content being lower in the sediment from the undisturbed area, the P is mostly in recalcitrant and organic forms. Furthermore, the sediment from the undisturbed area has low levels of Fe oxides and low content of Hid_{0.1}-P and Hid_{0.5}-P, which are considered as the P that is associated with Fe oxides (Hedley et al., 1982).

In rivers, biogeochemical activation and release of P stores can be triggered by organic C input from wastewater or septic tank effluents, particularly under baseflow conditions (Sharpley et al., 2013). Under high temperatures and low-flow conditions, microbial activity increases, spurring degradation of the organic C load, which elevates the biochemical O₂ demand. Consequently, in these anoxic conditions, reductive dissolution of ferric iron minerals occurs, releasing the bound P stored in sediments into the water column, which increases the algal available P and may promote eutrophication. Molot et al. (2014) argue that internal Fe²⁺ loading from anoxic sediments is also an important factor that regulates the ability of cyanobacteria to compete with eukaryotic phytoplankton. Linking this to our results, even if the sediment coming from the undisturbed site reaches a lentic environment, such as Guaíba Lake, the probability of P release promoted by the dissolution of Fe oxides in a reduced environment will be very small. However, the sediment from disturbed areas not only has higher content of labile P (Av-P and Bic-P), it also has higher content of Fe oxides and higher content of Hid_{0.1}-P and Hid_{0.5}-P, representing high pollution potential, especially if it reaches anoxic environments (Schärer et al., 2009).

Labile P contained in the sediment acts as a source of phosphate readily available to organisms in the water column (Kerr et al., 2011). In this respect, we found a positive correlation between the Av-P content in the sediments and soluble P (Table 3). Furthermore, the increase in labile P content during transplanting also resulted in increased content of soluble P in the disturbed areas and in the catchment outlet (Table 2). Further evidence of this phenomenon can be found in the rainfall event that occurred during tobacco transplanting, in which there was an increase in soluble P that accompanied the increase in Av-P in the final third of the hydrograph in the catchment outlet.

Potential use of P forms as an indicator of anthropic pressures

In areas without human activity (sampling site B1), the sediment P forms were not affected by the different periods of the year, nor by the magnitude of the rainfall event. However, in areas disturbed by anthropic activity, the P forms in the sediments were altered by the seasonal soil management practices. In the projection of the first factorial plan of the PCA, sediment samples collected at the catchment outlet were near those collected in the disturbed areas. These results clearly showed that the predominant source of sediments in the catchment are the disturbed areas, in both periods.

The first two principal components of PCA explained 64 % of the total variation in sediment P forms among all the suspended sediment samples collected in both rainfall events (Figure 4). The P fractions that were more closely associated with PC1 and thus more discriminant in forming the heterogeneous groups (Aleixo et al., 2017) were Organic-P,

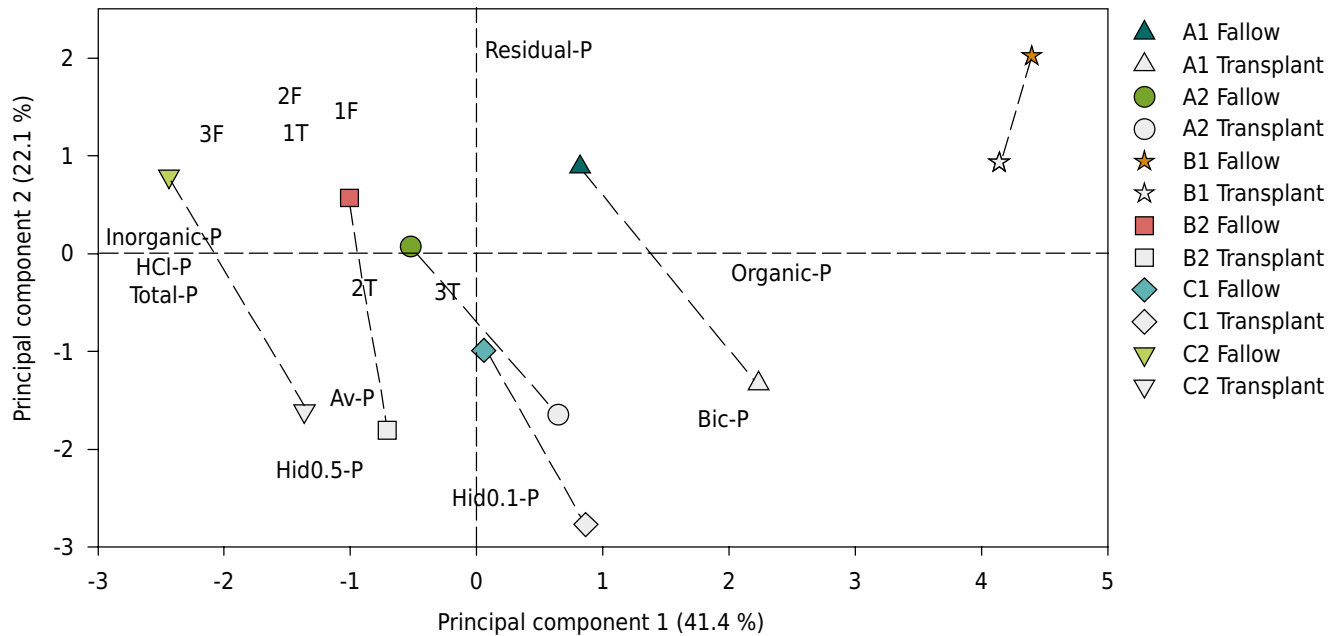


Figure 4. Projection of sediment P forms in the first factorial plan of the Principal Component Analysis (PCA) of the suspended sediment collected upstream and downstream in the Sub-basins A, B, and C, and during rising limb (1), peak discharge (2), and recession limb (3) at the catchment outlet, in two storm events occurred in the periods of fallow (F) and tobacco transplantation (T), in Agudo catchment, Rio Grande do Sul, Brazil. Numbers in parentheses indicate the percentage of variance explained by each axis.

Table 4. Factor analysis of soil P in different fractions

Factor loading ⁽¹⁾	Factor		
	1	2	3
Resin-P	-	-	0.446
Bic-P	-	-	-
Hid _{0.1} -P	-	0.346	-
HCl-P	-	-	-
Hid _{0.5} -P	-	0.182	0.359
Residual-P	-	0.243	-
Organic-P	0.230	-	-
Inorganic-P	0.233	-	-
Total-P	0.176	-	-

⁽¹⁾ Only loadings ≥ 70 % of the maximum are given. Resin-P: available P. Bic-P: P extracted by 0.5 mol L⁻¹ NaHCO₃ at pH 8.5. Hid_{0.1}-P: P extracted by 0.1 mol L⁻¹ NaOH. HCl-P: P extracted by 1.0 mol L⁻¹ HCl. Hid_{0.5}-P: P extracted by 0.5 mol L⁻¹ NaOH. Residual-P: P residual obtained after digestion with H₂SO₄ and H₂O₂. Organic-P: total organic P. Inorganic-P: total inorganic P. Total-P: total P concentration.

Table 5. Results of the stepwise discriminant function analysis as indicated by the Wilks' Lambda values

Step	P-form	p to remove	Wilks' Lambda	Cumulative of sediment samples correctly classified
				%
1	Bic-P	<0.0001	0.3100	89
2	Resin-P	0.0012	0.1340	94
3	Hid _{0.1} -P	0.0025	0.0610	94
4	Residual-P	0.0037	0.0239	94

Resin-P: available P extracted by anion exchange resin membrane. Bic-P: P extracted by 0.5 mol L⁻¹ NaHCO₃ at pH 8.5. Hid_{0.1}-P: P extracted by 0.1 mol L⁻¹ NaOH. Residual-P: P residual obtained after digestion with H₂SO₄ and H₂O₂.

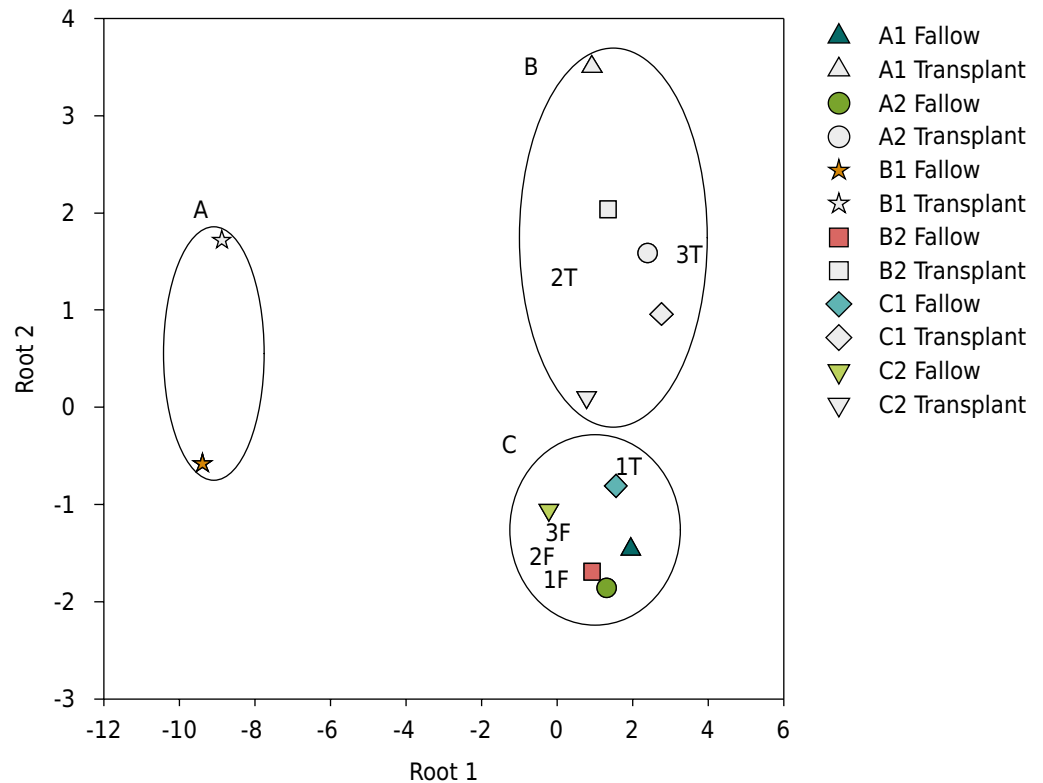


Figure 5. Two-dimensional scatter plot of the first and second discriminant functions from stepwise Discriminant Function Analysis (DFA) using P forms in suspended sediment collected upstream and downstream in the Sub-basins A, B, and C, and during rising limb (1), peak discharge (2), and recession limb (3) at the catchment outlet, in two storm events occurred in the periods of fallow (F) and tobacco transplantation (T), in Agudo catchment, Rio Grande do Sul, Brazil.

Table 6. Classification of sediment samples by discriminant analyses using the P forms of sediments eroded from the Agudo catchment, Rio Grande do Sul, Brazil

Period	Anthropic condition	Sub-basins/ phase	Groups of suspended sediment					
			Undisturbed		Disturbed fallow		Disturbed transplant	
			SMD ⁽¹⁾	p-value	SMD	p-value	SMD	p-value
Fallow								
	Disturbed	A1	117.6	<0.0001	2.9	0.8280	6.0	0.1720
	Disturbed	A2	82.5	<0.0001	1.3	0.9844	9.6	0.0156
	Undisturbed	B1	3.0	1.0000	102.1	<0.0001	127.6	<0.0001
	Disturbed	B2	106.6	<0.0001	0.6	0.9905	9.8	0.0095
	Disturbed	C1	132.5	<0.0001	7.6	0.9488	13.4	0.0512
	Disturbed	C2	115.7	<0.0001	1.4	0.9909	10.8	0.0091
	Disturbed	F1	87.5	<0.0001	1.4	0.9974	13.3	0.0026
	Disturbed	F2	81.0	<0.0001	3.0	0.9967	14.5	0.0033
	Disturbed	F3	85.5	<0.0001	0.5	0.9901	9.7	0.0099
Transplant								
	Disturbed	A1	143.2	<0.0001	12.0	0.0105	2.9	0.9895
	Disturbed	A2	101.1	<0.0001	5.1	0.4797	5.0	0.5203
	Undisturbed	B1	3.0	1.0000	101.3	<0.0001	113.1	<0.0001
	Disturbed	B2	113.1	<0.0001	13.8	0.0026	1.9	0.9974
	Disturbed	C1	111.6	<0.0001	26.5	0.0001	7.5	0.9999
	Disturbed	C2	134.5	<0.0001	12.9	0.0029	1.2	0.9971
	Disturbed	T1	121.1	<0.0001	3.1	0.7890	5.8	0.2110
	Disturbed	T2	86.0	<0.0001	8.1	0.0609	2.7	0.9391
	Disturbed	T3	164.0	<0.0001	22.4	0.0010	8.6	0.9990

⁽¹⁾ SMD: squared Mahalanobis distance.

Inorganic-P, and Total-P, whereas the $Hid_{0.1}$ -P, $Hid_{0.5}$ -P, and Residual-P were associated with PC2 (Table 4). In both rainfall events, the P forms of sediments collected during different flow rates in the catchment outlet resemble more the P forms of sediment sampled in the disturbed areas than those in the undisturbed area (Figure 5).

The table 5 shows the progressive change in the Wilks' Lambda value (Λ^*) as the variables are introduced into the analysis. The set of P forms selected by Discriminant Analysis Function (DAF) comprised four P forms, namely Bic-P, Resin-P, $Hid_{0.1}$ -P, and Residual-P. The final value of the Λ^* parameter was 0.0239. As the value of Λ^* is the proportion of the total variance due to the error of sample discrimination, the selected variables provided an error of $\approx 2.4\%$. That means the set of selected P forms explains approximately 97.6 % of the differences between the samples.

The results of DA showed that suspended sediment samples were correctly classified in their groups according to the degree of disturbance by human activities and evaluation periods (Table 6). Only one sample was not correctly classified: the sediment collected during the rise in water flow in the rainfall event of the tobacco transplanting period. There is higher probability of this sample belonging to the group of sediments from disturbed areas during the fallow period ($p=0.789$) than to the group of sediments from disturbed areas during the transplanting period ($p=0.211$).

CONCLUSIONS

Human activities lead to an increase in inorganic P in sediments, and a decrease in total organic carbon and total organic P. The areas without human interference had the same quantity and quality of the material eroded in both rainfall events studied.

The impact of seasonal soil management practices on stream water quality cannot be determined only on the basis of the total P levels present in suspended sediments; the method of chemical fractionation of P was useful for distinguishing sediments from sub-basins with different land uses that were affected by seasonal soil management practices.

Suspended sediments carried by rainfall during tobacco transplanting had higher P availability. These sediments are more likely to act as pollution agents, promoting the water eutrophication process, than those transported during rainfall in the fallow period.

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