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Research Article

Geochemical Erosion in Fluvial Channels During Intense Rainfall Events in Southern Brazilian Watersheds

Erosão geoquímica em canais fluviais durante eventos de chuvas intensas em bacias hidrográficas do sul do Brasil

Paulo R. B. da Silva [1], Márcia Luciane Kochem [2], Jean P.G. Minella [3], Tales Tiecher [4], Danilo Rheinheimer dos Santos [5], Viviane Capoane [6], Cláudia Alexandra Peixoto de Barros [7], Elizeu Didoné [8], Leandro Dalbianco [9]

[1] UFSM, Departamento de Solos, Santa Maria -RS, Brasil. E-mail: paulo.bairros-silva@ufsm.br
ORCID: https://orcid.org/0000-0002-2052-4210
[2] UFSM, Departamento de Solos, Santa Maria -RS, Brasil. E-mail: marciakochem@yahoo.com.br
ORCID: https://orcid.org/0000-0002-0328-5561
[3] UFSM, Departamento de Solos, Santa Maria -RS, Brasil. E-mail: jean.minella@ufsm.br
ORCID: https://orcid.org/0000-0001-9918-2622
[4] UFRGS, Departamento de Solos, Porto Alegre -RS, Brasil. E-mail: tales.tiecher@gmail.com
ORCID: https://orcid.org/0000-0001-5612-2849
[5] UFSM, Departamento de Solos, Santa Maria -RS, Brasil. E-mail: danilonesaf@gmail.com
ORCID: https://orcid.org/0000-0003-1085-7617
[6] UEMS, Departamento de Geografia, Dourados -MS, Brasil. E-mail: viviane.capoane@uems.br
ORCID: https://orcid.org/0000-0002-6672-1279
[7] UFRGS, Departamento de Solos, Porto Alegre -RS, Brasil. E-mail: claudia.barros@ufrgs.br
ORCID: https://orcid.org/0000-0002-5375-3095
[8] UFSM, Departamento de Solos, Santa Maria -RS, Brasil. E-mail: elizeu.didone@acad.ufsm.br
ORCID: https://orcid.org/0000-0003-0717-0515
[9] UFSM, Departamento de Solos, Santa Maria -RS, Brasil. E-mail: agro.dalbianco@gmail.com
ORCID: https://orcid.org/0000-0003-1017-0532

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Abstract: The high average load of suspended sediments in rivers in southern Brazil is related to soil degradation in agricultural areas due to erosive processes resulting from inadequate management. In this context, understanding the dimensions of transported particles and their biogeochemical dynamics is essential, as well as their transport capacity, load, concentration, deposition potential, and degradation within the fluvial system. This study analyzed hydrological characteristics, particle size, and chemical properties (TOC, NT, PT, POrg, Pd) in three river basins in Rio Grande do Sul (2012-2013): Arroio Lajeado Ferreira (1.19 km²), Rio Guaporé (1,980 km²), and Rio Conceição (804 km²), all located in southern Brazil. This research revealed that erosion during heavy rainfall in southern Brazil acts as a selective "geochemical erosion" process, preferentially transporting fine sediments (<63 μm) enriched with nutrients. The dynamics of phosphorus, during intense rainfall events can become predominantly organic (>50%), and quantifying significant loads of bioavailable phosphorus and organic carbon to rivers. The Conceição River Basin stood out with the greatest nutrient loss per area, demonstrating that agricultural practices exacerbate this impact. Suspended sediments (< 63 μm) showed high concentrations of organic carbon, nitrogen, and phosphorus (especially Pd, which is of environmental concern). The particle size D(25), D(50), D(75) did not vary significantly between basins or rainfall events. Phosphorus exhibited a dynamic behavior, at basal flow, it was predominantly inorganic, but during rainfall events, more than 50% could be organic.

Keywords: Erosive processes, Gran-Size Analysis, Phosphorus, Carbon, Nitrogen

1. Introduction

The impact of agricultural activities on water resources is strongly influenced by surface runoff generation processes and water erosion. Land use beyond its aptitude, combined with low vegetation biomass production and the absence of mechanical erosion control practices, accelerates soil degradation (Utzig et al., 2023; Naibo et al., 2022; Bender et al., 2018). Eroded soils from highland slopes, rural roads crossing farmlands, and the general drainage network are transported by surface runoff and deposit several pollutants into water bodies, either in soluble form or adsorbed to functional groups: nitrate (Kaiser et al., 2015); phosphorus (P) (Pellegrini et al., 2009; Zafar et al., 2017), pesticides (Fernandes et al., 2021; Fernandes et al., 2019), and pharmaceuticals (Bastos et al., 2020), which, in addition to accumulating in sediments, are transferred to the trophic chain (Naibo et al., 2022; Dambroz et al., 2022; Ramos et al., 2016).

The erosion phenomenon (detachment, transport, and deposition) is a selective process governed by rainfall intensity and the size of soil particles, among other factors such as texture, structure, aggregation, permeability, infiltration, slope and depth of soils, existence of vegetation cover, concentration of organic matter and the presence of root systems (Didoné et al., 2021; Barros et al. 2021; Minella et al., 2007). Smaller and lower-density particles are more easily transported by water influence (Menella et al., 2022; Bender et al., 2018; Owens, Walling, 2002). Fine particles classified as clays (<2 μm) are primarily composed of clay minerals, Fe and Al oxides, and organic matter. These three components, due to their large specific surface area, expose functional groups capable of adsorbing ions and organic compounds, interacting with each other to initiate the aggregation process, making them more resistant to disaggregation by raindrop impact and runoff (Dambroz et al., 2022; Ballantine et al., 2008; Droppo et al., 2005).

Thus, the granulometry of suspended eroded material reflects the active erosive process and its capacity to cause damage to water resources, whether through sedimentation (Müller et al., 2024; Brena, Surian, 2023, Barros et al., 2020) or pollutant transport (Ramos et al., 2016; Pellegrini, 2008). The remobilization of bottom sediments and consequent alterations in their reactivity, due to hydrodynamic influence, are more evident in finer fractions (Rollet et al., 2024, Utzig et al., 2023; Owens, Walling, 2002).

However, recent investigations have emphasized that a substantial proportion of the load generated in a headwater watershed and transported by many rivers is associated with suspended sediments in the coarse fraction (> 63-500 μm) transported in the flow (Minella et al., 2022; Ballantine et al., 2008; Peart, 2003). The quantity and form of P, N, and C transferred from the soil to surface water bodies in an agricultural watershed may vary spatially and temporally, from one rainfall event to another, due to seasonal precipitation variations, land use and management, time intervals between events, crop growth stages, and vegetation cover levels in agricultural soils (Troian et al., 2024; Dambroz et al., 2022; Sharpley, Smith, 1992) The main additional natural factors would be: soil characteristics (texture, structure, organic matter content, pH, and cation exchange capacity), topography and hydrology (slope, length and shape of the basin, connectivity with watercourses, type of runoff), and geological and geomorphological processes (Conceição et al., 2024; Alvarez et al., 2017; Sharpley, 2016).

Studies correlating total nitrogen (TN), total phosphorus (TP), and total organic carbon (TOC) levels with the granulometric distribution of suspended sediments in rural watersheds with different land use and physiographic characteristics are still scarce in the literature. This information is necessary not only to characterize solute discharge but also to describe the origin and propagation mechanisms of these materials from sources to rivers (Minella et al., 2022; Ballantine et al., 2008; Alvarez et al., 2017; Braziera et al., 2005).

During heavy rainfall, rapid runoff generation in source areas (such as agricultural soils with high organic matter and crop residue content) is connected to spillways. This rapidly mobilizes and transports enriched soil particles to the river (Rollet et al., 2024; Brenna, Surian, 2023; Peart, 2003). The hypothesis of this study is that erosion during intense rainfall events is a selective (geochemical) process that transports material to rivers in patterns influenced by the specific characteristics of each watershed. Thus, watersheds with younger soils and high connectivity primarily export coarse particulate matter, nutrients, and organic matter.

This study aims to analyze the hydrometric characteristics (rainfall-runoff-sediment), physical attributes (granulometry), and chemical properties (TN, TOC, TP, organic phosphorus (POrg), and bioavailable phosphorus (Pd)) associated with local suspended sediment load loss (SSSavg) transported during heavy rainfall events in different river basins to characterize its deleterious potential and the impact of agricultural management. The study focuses on the composition present in the fine (<63 μm) and coarse (>63-500 μm) fractions of samples collected from 2012 to 2013 to characterize its harmful potential and the impact of agricultural management in these river basins on water resources in southern Brazil.

3. Materials and Methods

3.1 Study areas

This study covers three watersheds located in the state of Rio Grande do Sul, southern Brazil: the small Arroio Lajeado Ferreira watershed (1.19 km², 28º48′32″S and 52º3′50″W) in the municipality of Arvorezinha, the Rio Guaporé watershed (1,980 km², 28°54′41″S and 51°57′10″W) with its outlet in the municipality of Anta Gorda, and the Rio Conceição watershed (804 km², 28°27′22″S and 53°58′24″W) with its outlet in the municipality of Ijuí.

The Lajeado Ferreira Stream Basin, Figure 1, located in the municipality of Arvorezinha, in southern Brazil, is part of the Southern Plateau geomorphological unit. With an area of 1.2 km², it is drained by the Lajeado Ferreira Stream, a perennial stream approximately 2 km long and with an average slope of 9%. This stream flows into the Guaporé River, which, in turn, is a tributary of the Taquari River, forming part of the South Atlantic Hydrographic Region (Minella et al., 2022; Barros et al., 2021; Minella, 2007).

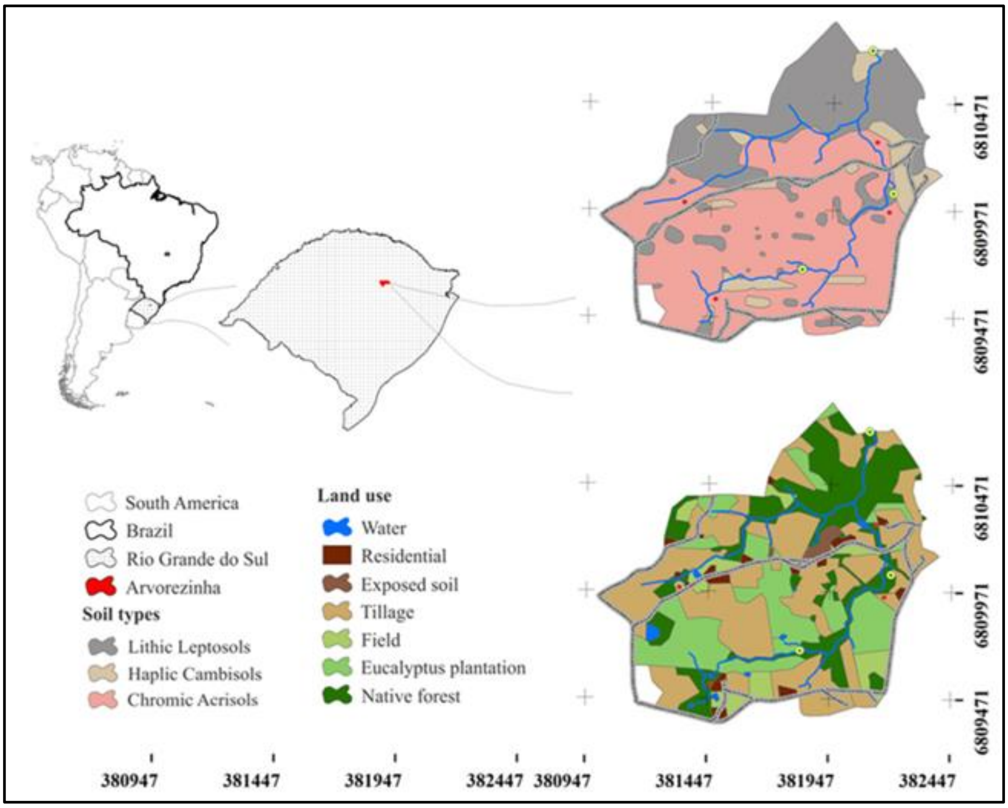

Figure 1. Lajeado Ferreira Stream Basin: land use and soil. Adapted of Bastos et al. (2021).

The basin's geology is characterized predominantly by igneous rocks, such as basalts and rhyodacites, with altitudes ranging from 580 to 730 meters. The topography is gently undulating in the upper third, with an average slope of 7%. The middle and lower thirds are highly undulating, with slopes exceeding 15% and short, steep slopes. This steep terrain favors rapid water runoff, with flood hydrographs recording peak times between 1 and 3 hours (Helfer et al., 2024; Bender et al., 2018).

The region's climate is classified as Cfb (superhumid subtropical, with no defined dry season) according to the Köppen classification, with an average annual rainfall of 1,938 mm, recorded between 2002 and 2016. Rainfall is evenly distributed throughout the year, but runoff rates are higher in spring (September to November) due to the greater rainfall intensity during this period (Menella et al., 2022; Bastos et al., 2021).

The basin's soils are diverse, with a predominance of Ultisols (60%), occurring mainly in the upper portion; Litholic Neosols (33%), located in the lower portion; and Cambisols (7%), scattered among the other two soil types.

Litholic Neosols and Cambisols are shallow soils with a sandy surface layer and no subsoil layer, lying directly on rock. This characteristic results in a high infiltration potential but limited water storage capacity, which contributes to the rapid formation of surface runoff. Ultisols, in turn, present an abrupt change in texture between the surface soil and the subsoil, with the latter having a higher clay content and lower infiltration capacity, which also favors surface runoff (Helfer et al., 2024; Bastos et al., 2021; Minella, 2007).

The basin is predominantly rural, with a highly dynamic land use distribution that fluctuates in response to changes in agricultural commodity prices. Rural properties, with areas ranging from 5 to 20 hectares, have low technological levels and diverse land uses. The main crops and land uses in the basin include tobacco cultivation 13.1%, soybeans and corn 24%, eucalyptus forests 34.8%, pastures and fields 5.2%, native forests 15.5% and other miscellaneous uses 7.4% (Helfer et al., 2024; Minella et al., 2022; Barros et al., 2021).

The Guaporé River Basin, Figure 2, with an area of 2,032 km², is located in the northeast of the state of Rio Grande do Sul. The region's climate is classified as Cfa (humid subtropical), with annual rainfall between 1,400 and 2,000 mm. The basin's altitude ranges from 207 to 830 meters, and the soils are derived primarily from basalt and rhyodacite volcanic rocks. The predominant soils in the region are Argisols, Alisols, Latosols, Luvisols, Nitosols, and Regosols, which exhibit wide variation in pedological and mineralogical characteristics (Troian et al., 2024; Naibo et al., 2022).

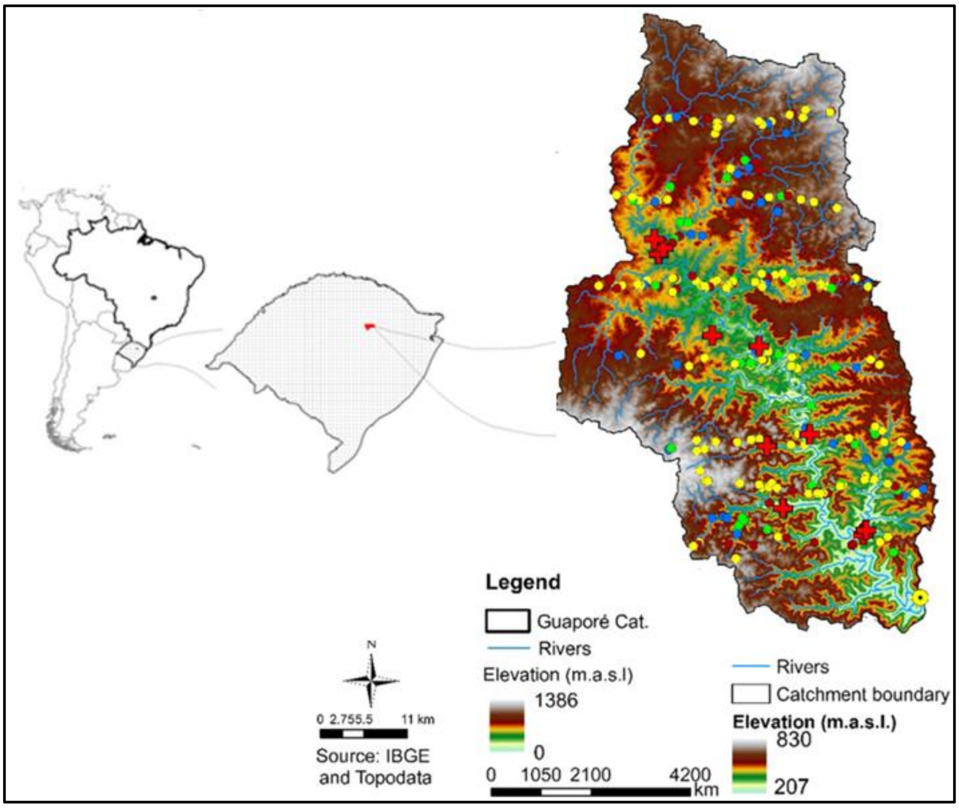

Figure 2. Guaporé River Basin: soil and altimetry. Adapted of Naibo et al. (2022).

The land use in the Guaporé River Basin is heterogeneous, with 9.7% pastureland, 56.6% forested areas, and 32.5% cropland. In the upper third of the basin, the terrain is characterized by gentle slopes, with predominantly soybean and corn crops in the summer and wheat and other cover crops in the winter, under a no-till system. In the other two-thirds of the basin (middle and lower parts), the main crops are tobacco, corn, yerba mate, eucalyptus reforestation, and perennial and annual pastures for dairy farming (Naibo et al., 2022).

The Conceição River Basin, Figure 3, with an area of 804 km², is located in the northwest of the state of Rio Grande do Sul. The region's climate is classified as Cfa (humid subtropical, with no defined dry season), with an average annual rainfall of between 1,750 and 2,000 mm and an average temperature of 18.6°C. The basin is representative of the basaltic plateau region of the Serra Geral Formation, where the main soil classes are Latosols

(80%), Nitosols (18%), and Argisols (2%), with a mineralogy dominated by iron oxides and kaolinite (Ramon et al., 2024; Didoné et al., 2021).

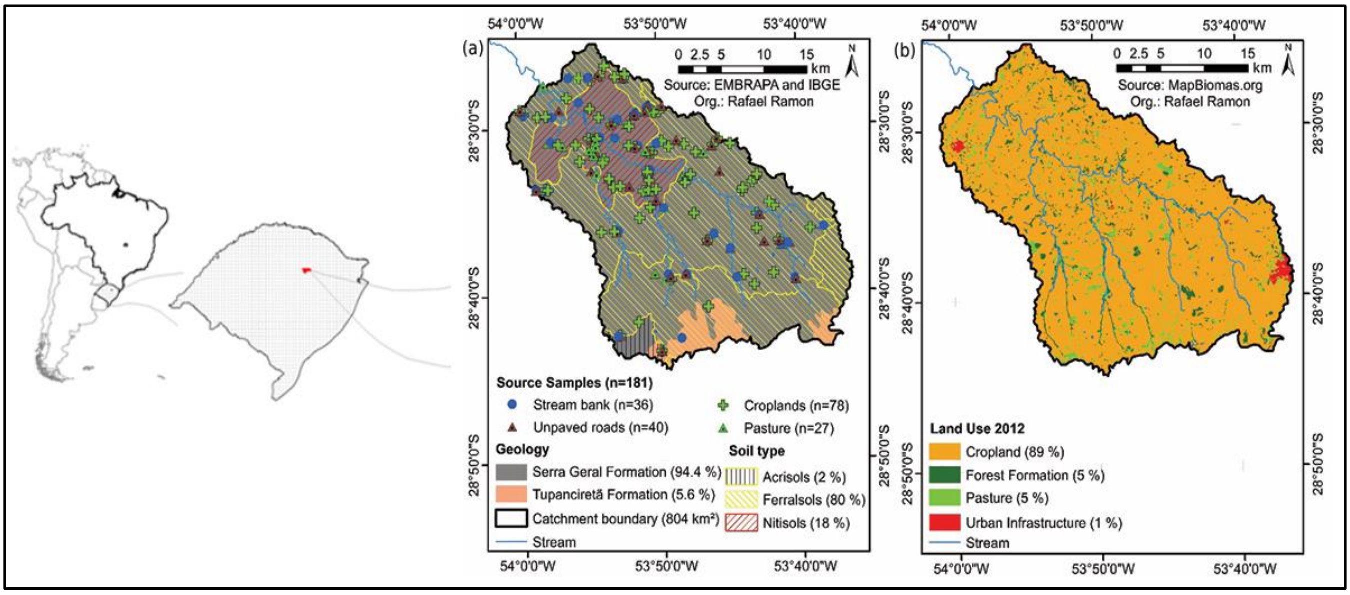

Figure 3. Conceição River Basin: Lithological formations, soil types (a); and land-use map. Adapted of Ramon et al. (2024).

The main land use in the basin is agriculture (89%), mainly with soybean cultivation in the summer and wheat, oats, and ryegrass in the winter, under the no-tillage system. Despite advances in soil management practices, the region still experiences high erosion rates due to the poor quality of the no-tillage system adopted. The basin's relief is characterized by gentle slopes (6-9%) in the higher areas and steeper slopes (10-14%) near the drainage channels, with altitudes ranging from 270 to 480 meters. The mouth of the basin is located in the municipality of Ijuí (Brum et al., 2022; Didoné et al, 2021).

3.2 *Monitoring, Sampling, and Preparation of Hydro-Sedimentological Samples*

The rainfall-runoff-sediment events monitored in this study occurred during 2012 and 2013 at several times of the year, reflecting different soil cover conditions and varying precipitation magnitudes. This dataset represents key anthropogenic and climatic controlling factors (Utzig et al., 2023; Dambroz et al., 2022; Peart, 2003). Monitoring was conducted using the following instruments: a rain gauge (Solar brand, Ville de Paris IPL002 model) and a limnigraph (Solar brand, pressure sensor model). The mean suspended sediment load (CSSméd) was assessed using turbidimetry (Solar brand) and manual wading sampling during intense rainfall events using a DH-48 suspended sediment sampler with a 1/4" nozzle (Hidromec), at points corresponding to the rising limb, peak, and falling limb of the hydrograph. The collection interval depended on the speed and pattern of the flood wave.

In Arroio Lajeado Ferreira, Rio Guaporé, and Rio Conceição, 32, 17, and 40 samples were collected, respectively. In the Arroio Lajeado Ferreira watershed, seven precipitation events (30 to 111 mm) were monitored, with observed average and peak flow rates of 0.21 $m^3 s^{-1}$ and 1.47 $m^3 s^{-1}$, respectively. In the Rio Conceição watershed, nine rainfall events (48 to 201 mm) were monitored, with observed average and peak flow rates of 54.6 and 177.7 $m^3 s^{-1}$, respectively. In the Rio Guaporé watershed, four events were monitored, with a maximum flow rate of 945.2 $m^3 s^{-1}$ and an average flow rate of 198.4 $m^3 s^{-1}$. The event data are presented in Supplementary Table 1 (Supplementary Material).

Smaller watersheds have greater hydrological connectivity between the slope and the channel. The physical proximity between sediment sources (agricultural areas, roads) and the outlet results in faster transport, with less opportunity for the deposition of larger particles. In contrast, larger watersheds may have intermediate deposition zones (such as floodplains), which act as "disconnectors," retaining part of the sediment load (Conceição et al., 2024;

Minella et al., 2022). This difference in connectivity helps explain variations in nutrient loads and concentrations between watersheds, which is the central objective of comparing them (Rollet et al., 2024; Conceição, Bonotto, 2000).

Water and sediment samples were stored in 20-liter containers and sent to the Surface Erosion and Hydrology Research Laboratory (LAPEHS) at the Federal University of Santa Maria. Samples were prepared following a decantation and drying protocol in a forced-air oven at 50°C. The sediments were then sieved using a 63 μm nylon mesh. The fine fractions (< 63 μm) and coarse fractions (> 63-500 μm) were subsequently analyzed for granulometry, total carbon, total nitrogen, total phosphorus, organic phosphorus, and bioavailable phosphorus.
The hydrological connectivity of river basins allows materials from distant sources to reach the outlet, altering the chemical signature of the suspended sediment (Peart, 2003; Salgado, Valadão, 2003; Conceição, Bonotto, 2000). Assessing this dynamic for phosphorus, nitrogen, and total organic carbon supports the hypothesis that the form of transported nutrients varies significantly with intense precipitation events. Furthermore, assessing particle size homogeneity, even in basins of different scales and land uses (from 1.19 km² to 1,980 km²), may suggest the existence of a selective and efficient transport process (Felippe et al., 2024; Silva et al., 2017; Braziera et al., 2005).
The analytical data were included in the database of the experimental hydrological basins monitored by LAPEHS, where hydrological and sedimentological understanding has been described and supported by other studies (Utzig et al., 2023; Barros et al., 2020; Minella et al., 2022; Dambroz et al., 2022).

3.3 Granulometric and Chemical Analyses of TOC, TN, TP, POrg, and Pd in Suspended Sediments

Granulometric analysis was conducted using a laser granulometer (CILAS, model 1064) with 0.2 g of material. The fractions were sonicated using ultrasound for 30 seconds, and a scanning range of 0.04-500 μm was used to classify 100 particle size classes (Rollet et al., 2024). Characteristic diameters in the granulometric distribution curve D(25), D(50), and D(75) were calculated from these results.

TP content was estimated through digestion with H_2SO_4 and H_2O_2 in the presence of saturated $MgCl_2$ (Olsen, Sommers, 1982). POrg concentration was estimated as the difference between P extracted with 0.5 mol. L^{-1} H_2SO_4 from ignited (550 ºC, 2 hours) and non-ignited soil samples (Olsen, Sommers, 1982). Pd content was determined using an anion exchange resin method. The phosphate in different extracts was quantified using the Murphy and Riley (1962) method.

TOC and TN contents were determined using dry combustion in an elemental analyzer (Flash EA 1112, Thermo Finnigan). Samples were ground to achieve homogeneity and placed in tin capsules for combustion in a chamber at approximately 975°C.

3.4 Total Loss of C, N, and P Associated with Suspended Sediments and Geochemical Denudation

The quantities of C, N, and P were estimated based on liquid and solid discharge, along with their dissolved concentrations in suspended sediments. Geochemical denudation was estimated as the ratio between the mass (kg) of chemical elements transferred in suspended sediments and the drainage area (km²).

3.5 Statistical Methods and Graphical Construction

The free software PAST - PAleontological STatistics (Version 4.17), by Hammer (2024), was used for Boxplot analysis (graphical representation of the distribution of a data set), the Jarque-Bera normality test (checks whether a data set follows a Gaussian distribution, enabling the use of parametric statistics), and the Kruskal-Wallis (compare independent groups and determine if there is a difference in their medians) test on granulometric distribution data and also employed for Discriminant Analysis to compare watersheds using granulometric fractions and phosphorus, nitrogen, and carbon concentrations.

4. Results and discussion

The boxplots of suspended sediment particle-size distribution across all monitored intense rainfall events in the three watersheds are presented in Figure 4.

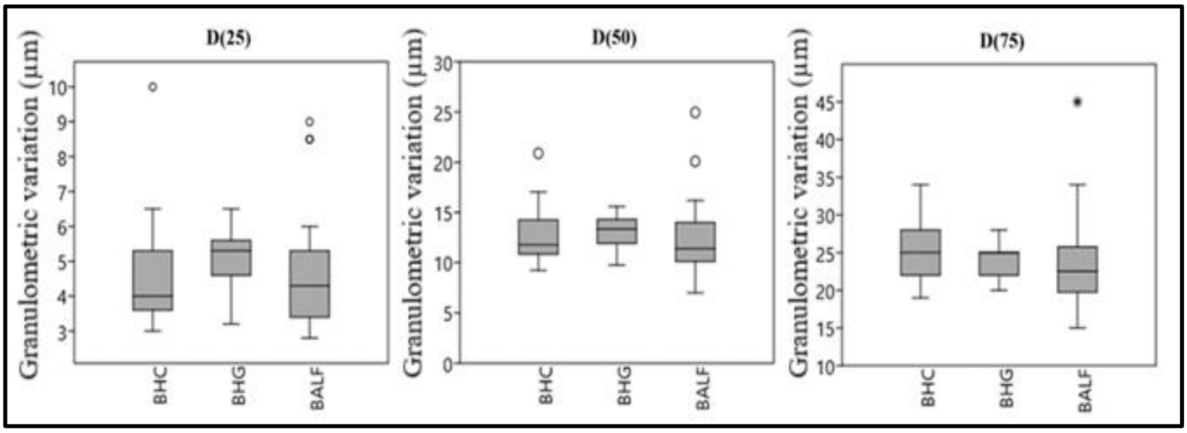

Figure 4. Boxplot graph of the grain size variation range in suspended sediment samples from the Conceição River Watershed (BHC), the Guaporé River Watershed (BHG), and the Lajeado Ferreira Stream Micro-watershed (BALF). D(25)= particle diameter (25%); D(50)= particle diameter (50%); D(75) particle diameter (75%).

In this case, granulometric variation among the watersheds no are significant differences (Grubbs, Jarque-Bera, and Kruskal-Wallis tests, see Supplementary Table 2 - Supplementary Material). Median values differ due to high dataset variance, but these differences are not statistically significant. In all watersheds, the predominant particle size class is medium silt (6 to 20 µm) (see Supplementary Table 3 - Supplementary Material).

In Figure 2, it was observed that the particle size (D25, D50, D75) of the suspended sediments did not vary significantly between the basins, with medium silt (6-20 µm) being the predominant class. Fine particles (silt and clay), which form stable microaggregates, are preferentially eroded and connected to the channel without undergoing significant deposition along the way.

This suggests that the presence of microaggregates composed of clay-sized silt particles is the predominant transport mechanism of these elements (Minella et al., 2022; Pellegrini et al., 2009; Droppo et al., 2005). The maximum characteristic diameters observed in the sample particles are inversely proportional to the areas of the drainage basins; that is, drainage basins with large drainage areas tend to produce greater quantities of fine particulate matter. This result is consistent, as smaller watersheds tend to have better connectivity between the source and the hydrological system, with lower sediment deposition rates (Zafar et al., 2017; Ramos et al., 2016; Braziera et al., 2005; Peart, 2003).

The study documented that phosphorus exhibits dynamic behavior, being predominantly inorganic at basal flow but becoming predominantly organic (>50%) during rainfall events. This change is a strong indicator of high hydrosedimentological connectivity (Conceição et al., 2024; Conceição, Bonotto, 2000). In Figure 5 considers intra-event rainfall variability. In this case, it is assumed that variations occur within events and that these may be related to the hydrological pattern of the events.

Likewise, no strongly correlated patterns were observed with the measured hydrograph. The results in Figure 5 demonstrate variability in TP, POrg, and Pd concentrations during different phases of the hydrograph (rising, peak, and falling stages). In the small Arroio Lajeado Ferreira watershed, TP and POrg levels increased with increasing flow.

The first two samples showed significant variation in POrg concentration, which can be explained by the increase in the total volume of surface runoff between the two samples (76.79 m^3 - 200.20 m^3) and, consequently, the increase in CSSméd, which ranged from 0.06 g L^{-1} to 0.16 g L^{-1}. The amounts of desorbed P from suspended sediments (Pd) remained constant throughout the event, except for a slight decrease in the final phase of the hydrograph. The greatest variation in the Rio Conceição watershed occurred in sample 5, where POrg concentrations increased compared to previous samples.

During heavy rainfall events, rapid runoff generation in source areas (such as agricultural soils with high organic matter and crop residue content) mobilizes and transports soil aggregates enriched with organic phosphorus to rivers. As this watershed is larger than the others considered in the study, there may have been a delay in the arrival of sediment loads at the outlet, meaning sediments with high organic P content may have originated from distant sources within the watershed. In the Rio Guaporé, the first two samples showed low POrg values (21.57 mg kg^{-1} and 117.26 mg kg^{-1}), with concentrations varying according to flow variation in the hydrological system. In the last three samples, CSSméd stabilized for TP, POrg, and Pd concentrations; however, slight variations in measured flow were still observed in the hydrological system.

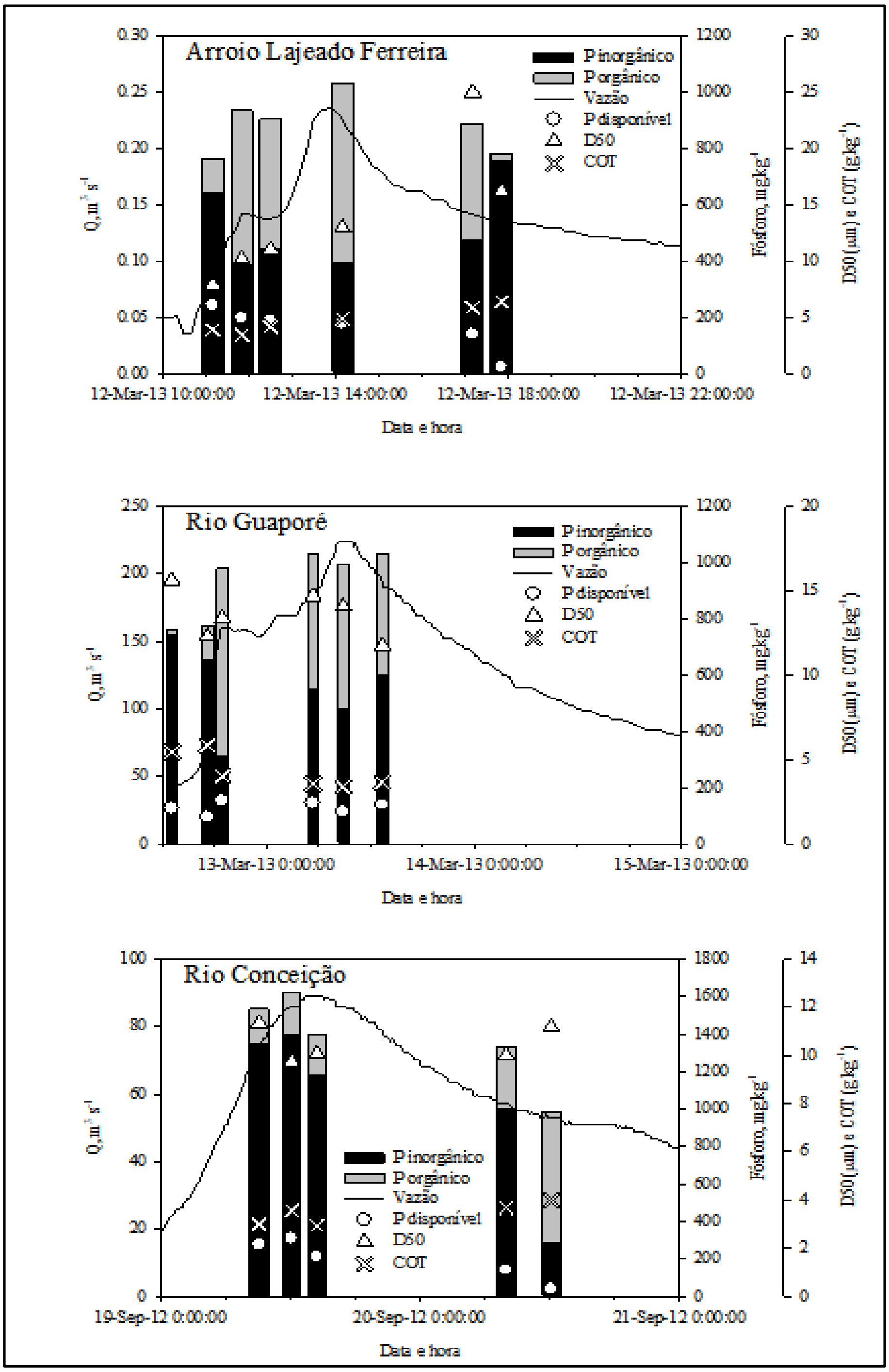

Figure 5. Temporal variability between flow rate and TP (< 63µm), Org-P (< 63µm), d-P (< 63µm), D50, and TOC (< 63µm) during rainfall events in three watersheds of different scales.

Regarding TP levels in fine sediment fractions (< 63 µm), the Rio Conceição watershed exhibited the highest concentrations, significantly exceeding those of the Arroio Lajeado Ferreira and Rio Guaporé watersheds (table 1).

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The naturally high TP content in soils, combined with decades of phosphate fertilizer additions, intensive and constant soil disturbance, and the adoption of no-till farming (where phosphates are added at a depth of up to 6 cm), results in phosphate enrichment at the residue/soil surface interface, facilitating the transfer of sediments enriched in this nutrient (Brenna, Surian, 2023).

Even when compared to the small Arroio Lajeado Ferreira watershed, which has intensive agricultural activity, high erosion rates, and strong hydrological connectivity leading to the transfer of TP-rich sediments into the drainage network, the Rio Conceição watershed still showed approximately 30% higher TP concentrations. In the small Arroio Lajeado Ferreira watershed, in the fine fraction (< 63 μm), it was demonstrated that POrg levels in farmland and channels are very similar, while POrg levels in roads are significantly lower.

However, Pd was found to be 6-8 times higher in farmland soils compared to channels and roads. Using only Pd and POrg, 87.5% of source samples (farmland, channel, and road) were correctly classified (Brenna, Surian, 2023; Conceição, Bonotto, 2000). NT concentrations in the fine fractions (< 63 μm) of suspended sediment samples from the three watersheds ranged from a maximum of 18 g kg^{-1} to a minimum of 2 g kg^{-1}. The average TOC concentrations in the fine fractions (< 63 μm) of suspended sediment samples in the three watersheds were similar, at approximately 33 g kg^{-1}.

Regarding TP levels in fine sediment fractions (< 63 μm), the Rio Conceição watershed exhibited the highest concentrations, significantly exceeding those of the Arroio Lajeado Ferreira and Rio Guaporé watersheds. Soil management in the Conceição River basin impacts the soil and creates an enriched source of nutrients that are mobilized and transported in enriched sediments during rainfall events, resulting in geochemical loss.

The high natural TP content in soils, combined with decades of phosphate fertilizer additions, intensive and constant soil disturbance, and the adoption of no-till farming (where phosphates are added to a depth of up to 6 cm), results in phosphate enrichment at the residue/soil surface interface, facilitating the transfer of nutrient-enriched sediments (Brenna, Surian, 2023).

Even when compared to the small Arroio Lajeado Ferreira watershed, which has intensive agricultural activity, high erosion rates, and strong hydrological connectivity leading to the transfer of TP-rich sediments into the drainage network, the Rio Conceição watershed still showed approximately 30% higher TP concentrations. This result, dialogue with those found by Pellegrini et al. (2009) and Conceição and Bonotto (2000), may be associated with the fact that roads, with different chemical signatures and lower average concentrations of POrg, for example, act as preferential conduits for runoff, and are elements of high structural connectivity within the river basin.

In the small Arroio Lajeado Ferreira watershed, in the fine fraction (< 63 μm), it was demonstrated that POrg levels in farmland and channels are very similar, while POrg levels in roads are significantly lower. However, Pd was found to be 6-8 times higher in farmland soils compared to channels and roads. Using only Pd and POrg, 87.5% of source samples (farmland, channel, and road) were correctly classified (Brenna and Surian, 2023).

NT concentrations in the fine fractions (< 63 μm) of suspended sediment samples from the three watersheds ranged from a maximum of 18 g kg^{-1} to a minimum of 2 g kg^{-1}. The average TOC concentrations in the fine fractions (< 63 μm) of suspended sediment samples in the three watersheds were similar, at approximately 33 g kg^{-1}.

This confirms that water erosion in the studied watersheds is not only a selective process concerning granulometry (favoring silt-sized particles) but also in exporting substantial TOC loads. TOC concentrations in fine fractions (< 63 μm) of suspended sediment samples ranged from 49 to 64 g kg^{-1}, consistent with values reported by Müller et al. (2024) and other rural watershed studies (Peart, 2003).

The TOC/NT ratio in suspended sediment samples (< 63 μm) may indicate eroded material from agricultural areas. On average, the Rio Conceição watershed had a TOC/NT ratio of 7.2, higher than the Rio Guaporé watershed (5.2) and the small Arroio Lajeado Ferreira watershed (6.8). These elements directly influence microbial activity, potentially prolonging the mineralization of toxic compounds such as ammonia and nitrite, while also promoting the proliferation of algae and bacteria that contribute to eutrophication processes (Müller et al., 2024; Dalke et al., 2022; Silva et al., 2017).

The relative importance of Pd in the fine fractions (< 63 μm) of suspended sediment samples is demonstrated by the Pd/POrg ratio, which increases from (Pd/POrg = 0.3) in the Rio Conceição and Rio Guaporé watersheds to

(Pd/POrg = 0.5) in the small Arroio Lajeado Ferreira watershed. The elemental ratios between POrg and Pd help elucidate phosphorus sources in watersheds.

Table 1. Variation range of chemical element concentrations in suspended sediment samples from the three monitored watersheds during the period 2012-2013.

Fine (< 63μm)	**P_T (mg.kg^{-1})**	**P_{Org} (mg.kg^{-1})**	**P_d(mg.kg^{-1})**	**C_{OT} (mg.kg^{-1})**	**N_T (mg.kg^{-1})**
Arroio Lajeado Ferreira					
Minimum	510.7	26.5	22.3	18	2
Maximum	1052.3	909.2	242.0	64	15
Mean	859.2	360.7	156.8	33	5
Median	887.0	323.4	158.2	33	5
Rio Conceição					
Minimum	985.4	177.7	13.8	24	3
Maximum	1629.7	829.9	287.7	49	18
Mean	1359.1	530.3	134.6	34	5
Median	1338.3	534.2	126.8	33	4
Rio Guaporé					
Minimum	631.6	101.3	18.1	28	4
Maximum	1250.9	784.0	224.7	58	11
Mean	1012.9	560.0	129.0	36	7
Median	1058.2	584.5	136.0	33	7
Grosseiros (>63-500 μm)	**P_T (mg.kg^{-1})**	**P_{Org} (mg.kg^{-1})**	**P_d(mg.kg^{-1})**	**C_{OT} (mg.kg^{-1})**	**N_T (mg.kg^{-1})**
Arroio Lajeado Ferreira					
Minimum	521.2	19.6	5.4	3	24
Maximum	2783.7	851.2	272.7	17	49
Mean	905.3	393.3	127.3	5	34
Median	820.9	374.4	133.5	4	33
Rio Conceição					
Minimum	761.5	21.6	4.7	0.5	29
Maximum	1463.1	878.3	187.1	1.2	61
Mean	1042.2	612.5	116.7	0.8	40
Median	1030.1	667.3	125.1	0.7	39
Rio Guaporé					
Minimum	273.2	93.0	8.9	2	19
Maximum	750.2	658.0	285.1	13	58
Mean	531.1	361.1	156.0	6	35
Median	550.5	394.8	151.1	5	35

Statistical criteria were used to identify trends in relationships between hydrological, physical, and chemical variables in suspended sediment samples during intense rainfall events. The results of the statistical techniques employed are presented in Table 2 and Figure 6.

Table 2. Discriminant Analysis Table summarizing the process and the percentage of explanation related to sediments from the Arroio Lajeado Ferreira micro-watershed (BALF), the Rio Conceição watershed (BHC), and the Rio Guaporé watershed (BHG).

	Clay	Silt	Sand	PT*	PORG*	Pd*	NT*	COT*	PT**	PORG**	Pd**	NT**	COT**
A1	0.58	-0.70	0.23	129.6	33.33	-5.32	-0.02	-0.004	65.43	-26.62	-5.32	-0.044	-0.10
A2	-0.49	0.82	-0.15	-5.43	56.04	-3.19	0.07	0.11	206.73	85.39	-16.11	0.070	0.19

Forces of approach/retreat (dimensionless), *Fine Particles, **Coarse Particles

Discriminant analysis was implemented to track the relationships between chemical element concentrations in different particle size fractions and identify potential sediment sources. The data matrix consists of four groups, each with 13 components, where the first two component axes are significant.

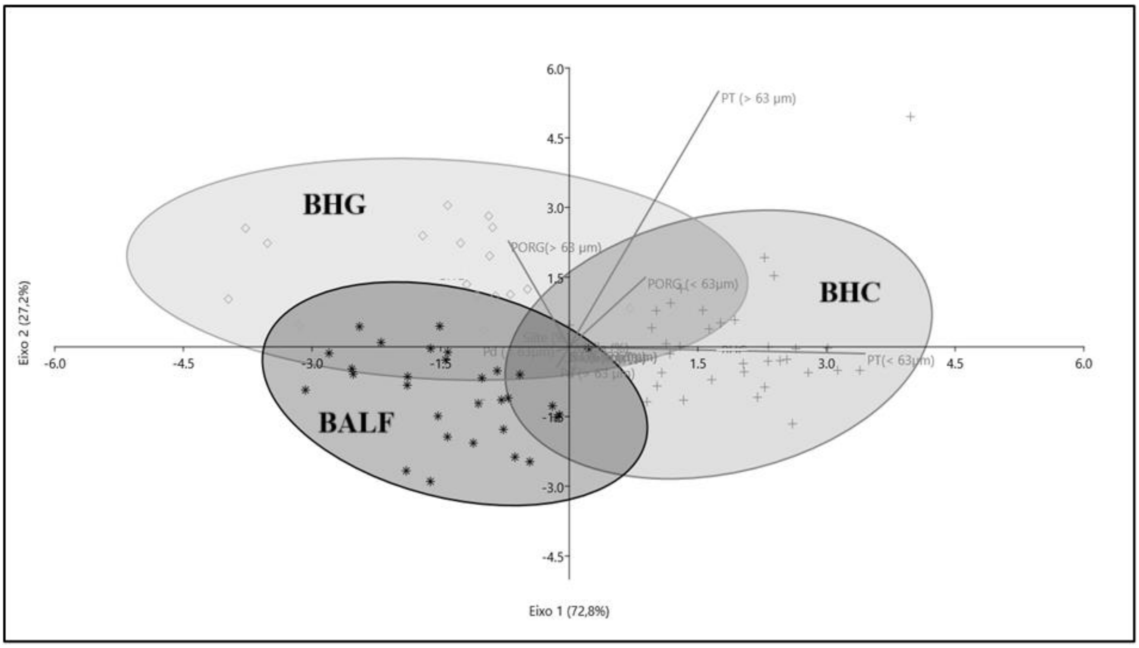

Figure 6. Discriminant Analysis graph of suspended sediment samples from the Conceição River Watershed (BHC), the Guaporé River Watershed (BHG), and the Lajeado Ferreira Stream Micro-watershed (BALF).

Thus, the elements were organized into distinct groups corresponding to each of the studied river basins. Discriminant analysis demonstrates the distinction between the areas into three large groups (water basins) based on the constituent elements of the samples. It is important to note that they behave differently geochemically, with a group strongly linked to clay (%), PT (mg kg-1, > 63-500 µm), PORG (mg kg-1, < 63 µm), PT (mg kg-1, > 63-500 µm), and PORG (mg kg-1, > 63-500 µm). This result highlights the importance of investigating the geochemical denudation of elements not only in the fine fractions transported or locally collected from the bottom, as suggested by the work of Conceição et al. (2024). It is important to note that we used simple linear regressions between dependent and independent variables, but none of them showed a clear pattern of statistical dependence. Figure 4 presents some correlations that express the pattern found for all other variables presented.

Table 3. Estimate of variables for each sampling segment of the event, based on the concentrations of suspended sediment sampled.

Nº	Event	Time	Precipitation(mm)	Sediment Production	P_T	C_{OT}	N_T
Arroio Lajeado Ferreira Micro-Watershed (Area de 1,19 km²)							
1	26/08/2012	10:00	30	78.25	0.04	6.25	1.12
	26/08/2012	15:30		*	*	*	*
	26/08/2012	19:30		43.40	0.02	3.40	0.75
	Total	**10:00**		**121.65**	**0.05**	**9.66**	**1.88**
2	09/09/2012	16:52	73	178.83	0.16	7.10	1.19
	09/09/2012	17:39		267.19	0.08	13.24	2.24
	Total	**0:51**		**446.02**	**0.24**	**20.34**	**3.43**
3	17/09/2012	22:55	111	226.38	0.06	14.50	3.40
	18/09/2012	12:55		165.53	0.14	7.38	1.25
	18/09/2012	13:40		246.36	0.20	14.35	1.50
	Total	**14:45**		**638.27**	**0.41**	**36.23**	**6.15**
4	12/03/2013	11:10	*	12.28	0.01	0.91	0.20
	12/03/2013	11:49		52.97	0.01	3.46	0.53
	12/03/2013	12:35		88.03	0.12	7.11	1.25
	12/03/2013	14:10		224.46	0.36	20.80	2.42
	12/03/2013	17:14		71.98	0.10	8.01	1.67
	12/03/2013	17:53		19.86	0.03	2.41	0.56
	Total	**07:54**		**469.58**	**0.69**	**42.71**	**6.62**
Conceição River Watershed (Area de 800 km²)							
1	06/07/2012	*	84	39.69	0.07	3.49	0.77
	06/07/2012			53.19	0.09	4.38	0.76
	06/07/2012			102.31	0.12	8.76	1.57
	07/07/2012			138.50	0.28	12.11	3.01
	08/07/2012			80.12	0.06	6.06	2.76
	Total			**413.81**	**0.64**	**34.80**	**8.87**
2	19/09/2012	*	125	1026.45	2.44	66.59	10.76
	19/09/2012			1021.82	2.77	36.36	9.44
	19/09/2012			1953.34	5.18	119.68	15.27
	20/09/2012			260.07	0.52	19.85	3.07
	20/09/2012			53.85	0.10	3.99	0.73
	Total			**4315.53**	**11.01**	**246.46**	**39.28**
3	02/10/2012	*	121	2543.60	5.54	148.99	26.82
	03/10/2012			3567.55	7.63	227.11	29.43
	03/10/2012			516.57	1.12	31.58	4.68
	04/10/2021			180.31	0.23	12.00	1.75
	04/102012			87.90	0.17	6.00	0.91
	Total			**9895.93**	**14.69**	**425.68**	**63.59**
4	22/10/2012	*	47	290.47	0.73	14.67	1.85
	23/10/2012			203.12	0.52	11.04	1.29
	23/10/2012			121.09	0.26	7.67	1.04
	23/10/2012			73.64	0.16	5.81	0.68
	23/10/2012			102.75	0.24	6.89	0.87
	24/10//2012			67.83	0.19	6.21	0.70
	Total			**858.89**	**2.10**	**52.29**	**6.42**

5	24/08/2013	*	124	60.78	0.14	3.84	0.61
	24/08/2013			147.41	0.32	10.07	1.64
	25/08/2013			112.05	0.28	6.81	0.93
	25/08/2013			215.53	0.50	15.63	2.90
	26/08/2013			186.93	0.47	13.05	2.28
	Total			**722.69**	**1.72**	**49.40**	**8.36**
6	20/09/2013	*	73	90.95	0.22	4.72	0.48
	21/09/2013			161.03	0.48	9.60	1.25
	22/09/2013			134.22	0.25	7.59	0.95
	Total			**386.20**	**0.95**	**21.90**	**2.69**
7	24/10/2013	*	122	14.13	0.03	0.73	0.10
	24/10/2013			30.57	0.06	1.48	0.18
	25/10/2013			57.80	0.13	3.04	0.39
	25/10/2013			57.06	0.04	2.00	0.26
	Total			**159.56**	**0.25**	**7.25**	**0.94**
Guaporé River Watershed (Area de 2.000 km²)							
1	06/07/2012	13:11	*	354.53	0.83	29.41	4.78
	06/07/2012	17:02		1561.42	0.00	111.37	26.26
	07/07/2012	01:30		1632.65	3.45	120.53	24.63
	07/07/2012	08:29		1055.67	2.42	71.11	22.19
	07/07/2012	13:11		479.17	1.10	32.57	10.84
	Total	**24:00**		**5083.44**	**7.80**	**364.99**	**88.70**
2	18/09/2012	01:55	*	109.05	0.23	9.34	2.50
	19/09/2012	14:20		20421.54	42.56	1908.04	264.44
	Total	**12:25**		**20530.60**	**42.78**	**1917.38**	**266.94**
3	12/03/2013	13:07	*	36.27	0.05	3.51	0.60
	12/03/2013	17:10		62.84	0.05	6.93	1.33
	12/03/2013	18:53		657.45	1.21	54.98	9.63
	13/03/2013	05:25		953.84	1.86	68.75	12.29
	13/03/2013	08:50		587.89	1.09	36.76	7.79
	13/03/2013	13:23		917.96	1.81	60.26	12.15
	Total	**24:16**		**3216.25**	**6.07**	**231.20**	**43.80**
4	20/09/2013	22:51	*	293.62	0.60	17.78	3.20
	21/09/2013	08:38		619.66	1.23	40.07	5.61
	21/09/2013	10:58		1399.59	3.27	103.07	13.28
	21/09/2013	23:19		3050.45	7.69	191.34	26.87
	Total	**24:13**		**5363.1**	**12.80**	**352.26**	**48.96**

Units: Sediment production, P_T, Co_T, and N_T in kg

Table 3 presents the number of events considered in the study for each river basin and their total loads. Observing the data reveals the different intensities and transports present in each event.

In this case, the variability between rainfall events is explored, as it includes all sampled events. These graphs present all samples collected from all monitored events in each of the three monitored basins. In this case, an independent variable was chosen that theoretically reflects the intensity and magnitude of the erosion process: maximum discharge.

The maximum discharge of the sampled section was correlated with the characteristic diameter and the concentration of PT in the fraction smaller than 63 μm. Note that the variability in the characteristic diameter for the Lajeado Ferreira Stream basin is greater, which is natural for a basin with greater connectivity and less capacity to absorb flood waves. For the Conceição and Guaporé River basins, there was no difference between the observed values. In the case of PT concentration, a distinct position on the Cartesian axis with higher PT concentrations is

observed for the Conceição River basin. As shown in Table 1, a greater difference is noted for the chemical variables than the physical variables of the suspended sediments monitored in the watersheds between 2012 and 2013.
The estimate of material losses in the three watersheds considered the loads of mass variables for each sampling section of the heavy rainfall event, based on the sampled suspended sediment concentrations. Table 3 presents these values.

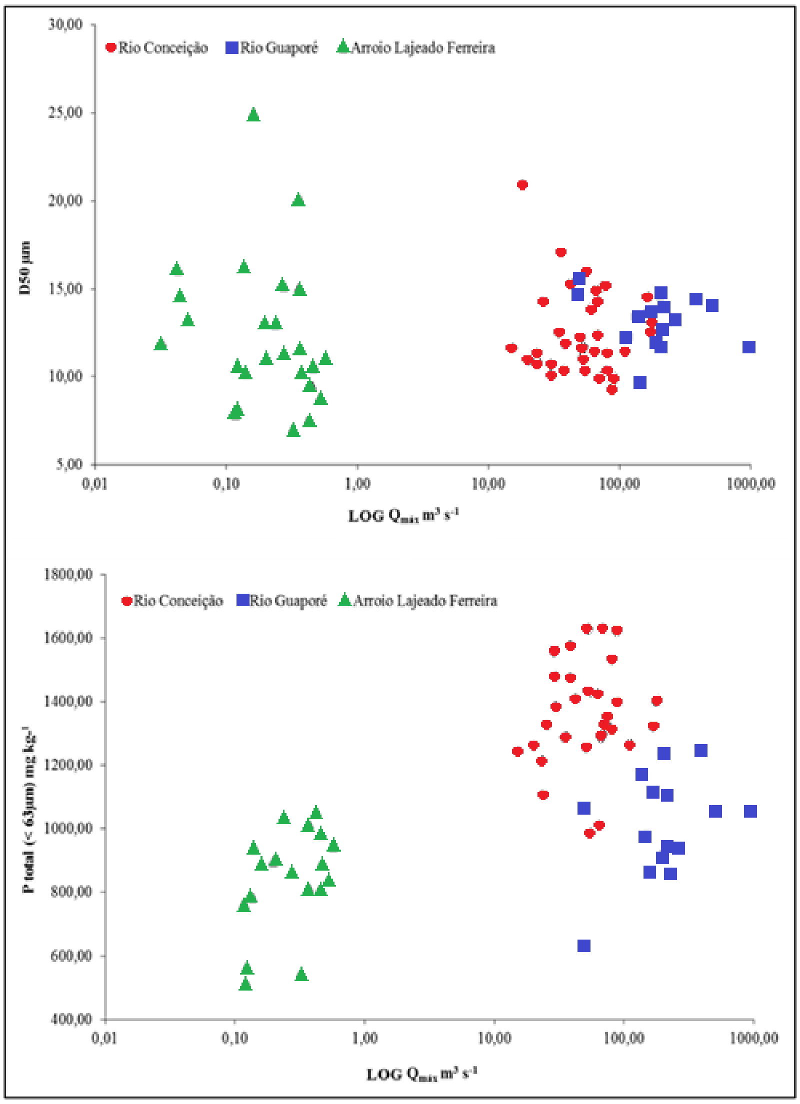

Figure 7. Correlation between the hydrological variable (Qmax), physical variable (D50), and chemical variable (Total P) in three watersheds of different scales.

Table 3 presents the number of events considered in the study for each river basin and their total loads. Observing the data, it is possible to verify the different intensities and transports existing in each event. The calculation of Geochemical Denudation of elements for the three river basins considered the data presented in Table 3 and is presented graphically in Figure 8.

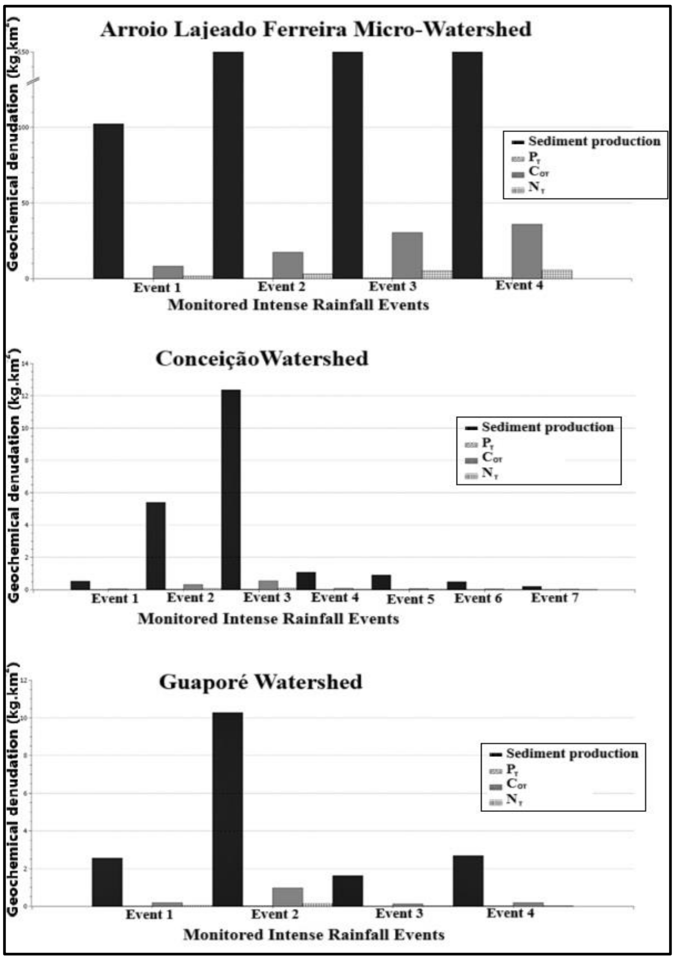

Figure 8. Geochemical denudation due to the loss of local elements as a result of erosional processes and rainfall transport.

Figure 8 shows the pronounced behavior of Geochemical Denudation in the small Lajeado Ferreira Stream basin compared to the other river basins studied. The intense denudation values are associated with the high production of sediments rich in TOC and P. It is located in a headwater area at the transition between the Southern Plateau and the Central Depression, a region known as the ledge, formed by steep walls and enclosed valleys that favor erosion (Utzg et al., 2023; Minella et al., 2022). Soil erosion in agricultural areas of river basins contributes to the process of geochemical denudation of elements, enabling the input of PT, NT, and TOC loads that reach aquatic systems through surface runoff. Excess TOC and PT in rivers induce eutrophication by stimulating increased primary productivity of algae and microorganisms, which can lead to hypoxia in the water system and species mortality. Contamination due to excess NT occurs due to its conversion into ammonia in water bodies, causing oxygen unavailability (interaction with blood hemoglobin) and histological changes in fish gills (Zafar et al., 2017; Sharpley, 2016; Pellegrini et al., 2009).

5. Conclusion

This study investigated geochemical erosion during intense rainfall events in river basins in southern Brazil, aiming to analyze the hydrometric characteristics, physical attributes, and chemical properties associated with the loss of suspended sediment load. Erosion in agricultural areas during intense rainfall events manifests itself through a geochemical erosion process with selective characteristics, preferentially transporting fine sediments (<63 μm) enriched with nutrients. During these intense rainfall events, more than 50% of the phosphorus in suspended sediments (< 63 μm) can assume an organic form, contrasting with the inorganic predominance observed in the basal flow. Furthermore, it was found that geochemical erosion is selective, exporting significant loads of organic carbon (average of 33 g kg^{-1}) and phosphorus, with the Conceição River basin showing P concentrations ~30% higher than the others, reflecting the impact of agricultural management. The granulometry of the sediments did not vary significantly between basins of different scales, indicating a similar transport mechanism based on silt microaggregates.

The Conceição River basin stood out for the greatest nutrient loss per area, demonstrating that local agricultural practices intensify this impact, contributing to eutrophication and water resource degradation. Although the number of events and the study period are consistent in this study, they may not capture long-term climate cycles (such as more severe El Niño or La Niña events), which drastically influence erosion and nutrient transport and can be explored in new studies.

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Author Contributions: PRBS: methodology, software, writing - revision and editing. MLK: Data curation, Writing - initial version, Investigation. JPGM: Investigation, Supervision, Writing - initial version. TT: Writing – revision, Investigation. DRS.: Writing – revision, resources. VC: methodology, software. CAPB: Investigation, Supervision. ED: Investigation, Supervision. LD: Investigation, Supervision.

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