UNIVERSIDADE FEDERAL DE SANTA MARIA
CENTERE OF RURAL SCIENCES
GRADUATE PROGRAM IN SOIL SCIENCE

# PHOSPHORUS DYNAMICS IN SEDIMENTS FROM A SUBTROPICAL CATCHMENT WITH RURAL AND URBAN POLLUTION

**DOCTORAL THESIS**

by

**Mohsin Zafar**

**Santa Maria, RS, Brasil.**

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# PHOSPHORUS DYNAMICS IN SEDIMENTS FROM A SUBTROPICAL CATCHMENT WITH RURAL AND URBAN POLLUTION

by

**Mohsin Zafar**

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**Centre of Rural Sciences**
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a thesis submitted in partial fulfillment of
the requirements for the degree of
**Doctor in Soil Science**

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**Santa Maria, 23 November, 2015**

# DEDICATION

Throughout my life two person has always been there during those difficult and trying times. I would like to dedicate this thesis and 'all that I am, or hope to be' to my parents, especially to my angel mother, Razzia Begum (mãe Tu és o ❤ da minha vida), and endless efforts of my great father, Zafar Iqbal who raised me and taught me to give priority to the quest for knowledge in my life.

&

to

THE LADY

*"All my love to her, for finding me the light, whenever it was away"*

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Santa Maria, November 23, 2015

Mohsin Zafar

# RESUMO

Tese de Doutorado
Programa de Pós-Graduação em Ciência do Solo
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# DINÂMICA DO FÓSFORO DE SEDIMENTOS ORIUNDOS DE BACIA HIDROGRÁFICA SUBTROPICAL COMPOLUIÇÃO RURAL E URBANA

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ORIENTADOR: DANILO RHEINHEIMER DOS SANTOS
Local e Data de Defesa: Santa Maria, 23 de novembro de 2015.

As áreas de bacias hidrográficas declivosas e densamente ocupadas pela agricultura familiar no Sul do Brasil, apesar de apresentarem grande superfície com florestas regeneradas, caracterizam-se pela persistência de fontes de poluição rurais e urbanas que vêm comprometendo a qualidade dos sistemas aquáticos. O uso do solo fora de sua aptidão, a adoção de sistemas de manejo inadequados, o sistema integrado de produção animal (aves e suínos) em quantidades ambientalmente intoleráveis e o não tratamento dos esgotos domésticos das pequenas cidades são fatores responsáveis pelo aporte de grandes quantidades de fósforo aos cursos d'água. Nesse contexto, a presente tese de doutorado visa (i) monitorar a variação temporal do fósforo ligado aos sedimentos em sub-bacias com diferentes usos e manejo do solo e (ii) avaliar o potencial dos sedimentos de fontes rurais e urbana em atuarem como fonte ou dreno de fósforo aos sistemas aquáticos.Na Bacia Hidrográfica do Rio Guaporé – RS/Brasil foram monitoradas seis sub-bacias de cabeceira representativas de uso da terra e de sistemas de manejo do solo contrastantes. As sub-bacias selecionadas caracterizavam-se por:i) predomínio demata nativa (controle); (ii) predomínio de áreas transformadas em agricultura recentemente, mas sob sistema de cultivo convencional – SCC (sub1); (iii) áreas emSCC, mas com predomínio de produção de erva-mate (sub2); (iv) predomínio de áreas emSCC há longa data para cultivo do tabaco (sub3 ); (v) predomínio de agricultura intensiva, mas sob o sistema plantio direto– SPD (sub4); e (vi) predomínio de agricultura intensiva sobSPD e recebendo esgoto não tratada de uma cidade com 20 mil habitantes (sub5). Adicionalmente, monitoraram-se cinco pontos no rio principal (P1 a P5), sendo que o primeiro está localizado na junção das sub-bacias 4 e 5 e o último é o exutório da bacia.Coletaram-se sedimentos de fundo e em suspensão, em dez campanhas de campo, durante 24 meses (10/2012 a 10/2014). Foram analisadas as diferentes frações de fósforo no sedimento, de acordo com a biodisponibilidade e estimaram-se os parâmetros de adsortividade e dessortividade do fósforo no sedimento. A conversão da mata nativa para implantação de culturas anuais induz a produção de sedimentos com maiores teores de fósforo total, fósforo inorgânico e fósforo lábil. Os valores da capacidade máxima de adsorção, fósforo instantaneamente disponível, fósforo potencialmente disponível, taxa de dessorção e índice de mobilidade de fósforo dos sedimentos coletados nas diferentes sub-bacias aumentaram na seguinte ordem: mata nativa < SCC < SCC intenso com produção de tabaco < SPD < SPD no meio rural mais esgoto urbano. Foram observadas correlações positivas dasdiferentes frações de fósforo (em especial aquela relacionada ao P lábil), bem como dos diferentes parâmetros de sorção/dessorção, com os teores de ferro e alumínio do sedimento.Foi encontrado maior teor de fósforo lábil nos sedimentos coletados no final do inverno e início da primavera,particularmente naqueles correspondentes aos locais onde se cultiva tabaco em SCC.

**Palavras-chave:** Bacia hidrográfica. Uso e manejo do solo. Sedimentos de fundo. Biodisponibilidade de fósforo. Pressão antrópica. Fontes de poluição pontual e difusa.

# ABSTRACT

Doctoral Thesis
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# PHOSPHORUS DYNAMICS IN SEDIMENTS FROM A SUBTROPICAL CATCHMENT WITH RURAL AND URBAN POLLUTION

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Areas at steep slopes in the catchments with high occupation by family farmers in Southern Brazil, even with a high surface covered with regenerated forests, are characterized by the persistence of sources of rural and urban pollution that are undermining the quality of aquatic systems. The unfair use of soil outside its capability, the adoption of inadequate soil tillage systems, the integrated system of animal production (poultry and swine) in quantities environmentally intolerable and the untreated domestic sewage from small villages are the main factors responsible for the input of high amounts of phosphorus into watercourses. In this context, the present doctoral thesis aims (i) monitoring the temporal variation in sediment-bound phosphorus in sub-catchments under different land-use and soil tillage systems and (ii) assessment of the potential of sediments from rural and urban sources to behave as source or sink of phosphorus for aquatic systems. In the Guaporé River catchment, six representative headwater sub-catchments with contrasting land-use and soil management were monitored. The selected sub-catchments were characterized by: (i) predominance of native forest (control); (ii) predominance of areas transformed to agriculture recently, but under conventional tillage – CT (sub1); (iii) areas under CT, but with predominance of *Ilex* plantations (sub2); (iv) predominance of tobacco cultivation of long term under CT (sub3); (v) intensive agriculture under no-tillage – NT (sub4); and (vi) intensive agriculture under NT and receiving untreated sewage of a twenty thousand inhabitant town (sub5). In addition, five points of the main river (P1 to P5) were monitored: the first one is located near to the junction of the sub-catchments 4 and 5, and the last one at the outlet of the watershed. Suspended and bed sediments were collected, comprising ten field campaigns performed in the monitoring period of 24 months (October 2012 to October 2014). The different fractions of phosphorus (P) of sediment were analyzed considering the bioavailability. The P sorption-desorption parameters in the sediments were estimated. The conversion of native forest for annual crops production areas promotes the production of sediments with higher amounts of total, inorganic and labile phosphorus. The values of maxima phosphorus adsorption capacity, instantaneous available and potentially available phosphorus forms, desorption rate and mobility index of phosphorus in sediments collected in the different sub-catchments in the following order: native forest < CT < CT with the intensive production of tobacco < NT < NT in the rural area plus urban sewage. A highly positive correlation was observed between different phosphorus fractions (especially the labile phosphorus), as well as different parameters of sorption/desorption, and amounts of iron and aluminum in sediments. It was found the highest amount of labile phosphorus in sediments collected at the end of winter and beginning of spring, particularly in the areas where tobacco is cultivated under CT.

**Keywords:** Catchment. Soil use and management. Bed sediments. Phosphorus bioavailability. Anthropic pressure. Point and diffuse pollution.

# LIST OF FIGURES

## STUDY BACKGROUND

## ARTICLE - I

## ARTICLE - II

## ARTICLE - III

# LIST OF TABLES

## ARTICLE - I

## ARTICLE - II

## ARTICLE - III

## GENERAL DISCUSSION - III

# TABLE OF APPENDIX

# TABLE OF CONTENTS

# 1 GENERAL INTRODUCTION

## 1.1 Phosphorus in agriculture

In our world, with an approximate population of nine billion people by 2050, maintaining food security without hampering ecological sustainability is a real challenge for humanity. However, under current agriculture production systems, phosphorus (P) and water recourses are declining both in quantitative as well as qualitative aspects (ALCOTT et al., 2012; CORDELL et al., 2014).

Agricultural intensification and urbanization have led to widespread enrichment of water resources resulting in a range of environmental, economic and social problems both at regional and global scale under the eutrophication phenomena. Agricultural discharge is proven P contributor that reaches to riverine waters, however, concentration vary globally depending upon the national and regional soils, and farm scale P fertilization observed in Asia (SUN et al., 2012; WU et al., 2013; LI et al., 2015; LIU et al., 2015); Australia and New Zealand (MCDOWELL; NASH, 2012); Europe (BALLANTINE et al., 2008; WITHERS; JARVIE, 2008; RODRIGUEZ-BLANCO et al., 2013a; BORDA et al., 2014; COOPER et al., 2015); South America (SHIGAKI et al., 2006; PELLEGRINI et al., 2010; OVALLE et al., 2013; GATIBONI et al., 2015); and USA (DUBROVSKY et al., 2010; ULEN et al., 2010; SHARPLEY et al., 2009, 2013).

Similarly, worldwide, increased ecological problems are associated with the high anthropogenic pressure, urban and industrial settlements, particularly generating untreated sewage and city effluent which are ultimately deposited into nearby water resources (PIETERSE et al., 2003; JARVIE et al., 2006; NEMERY et al., 2007; RUSSELL et al., 2008; WITHERS et al., 2009; HOROWITZ et al., 2012; CAREY et al., 2013; SMITH et al., 2013; MCDOWELL; MONAGHAN, 2014).

In Brazil, agro-industry is an important sector in national economy (30%) and Southern Brazil, specifically, which contributes two-thirds of national share, has immense agricultural potential due to favorable soil and climatic resources. Similarly, dairy and swine production (18.2 million heads) has expanded in the region producing approximately 155 million liter slurry per day during 2013 (IBGE, 2013) and is continuously applied to same farmland over the years (GUARDINI et al., 2012; COUTO et al., 2015). The use of chemical P fertilizer is also routine practice and national consumptions indicate an average application rate of 69 kg $P_2O_5$ $ha^{-1}$ $year^{-1}$ (ANDA, 2011; RODRIGUES et al., 2015).

Several studies have shown as the animal production within a catchment increase, soil P levels increase due to surface application of manure, and the overall risk of P loss increase (WITHERS et al., 2003; DJODJIC et al., 2005; SVANBACK et al., 2013).

## 1.2 Phosphorus from field to river water

It is very important to identify the upstream P sources because catchment scale P export is function of land-use, population density of area, soil and crop management practices, and urban and industrial development. Therefore, the effective management aiming to reduce P loads to river is highly dependent on the fact that *from where* and *when* P is lost in the landscape (USEPA, 2010; SHARPLY et al., 2013).

Phosphorus can be transported in either soluble or particulate form (adsorbed on inorganic colloids or as component of organic substances), and its transport is dependent on various agronomic, geomorphic and hydraulic characteristics of the studied area varying while taking into account the spatial and temporal considerations together (SHARPLEY et al., 1995; REYNOLDS; DAVIES, 2001). Several studies across the globe have evidenced that the most of total P (TP) is lost in particulate form (PP) and accounts for 60 to 90% such as in rural UK catchments (WALLING et al., 1997; JAVRIE; WITHERS, 2008), Sweden (BERGSTROM et al., 2015), Spain (RODRÍGUEZ-BLANCO et al., 2013a, b, c), USA (HORWARTIZ et al., 2012). However, a dynamic equilibrium exists between the amount of labile sediment-bound P and the dissolved P (DP) concentration present both in soil solution and river water (PALMER-FELGATE et al., 2009).

Sediment-bound can be lost from agricultural fields through several ways but mostly reported either via fast surface runoff, and slow leaching through or subsurface drains (PELLEGRINI et al., 2010; JAVARI et al., 2015). A systematic illustration is presented in Figure 1 as explained by the MCDOWELL (2004).

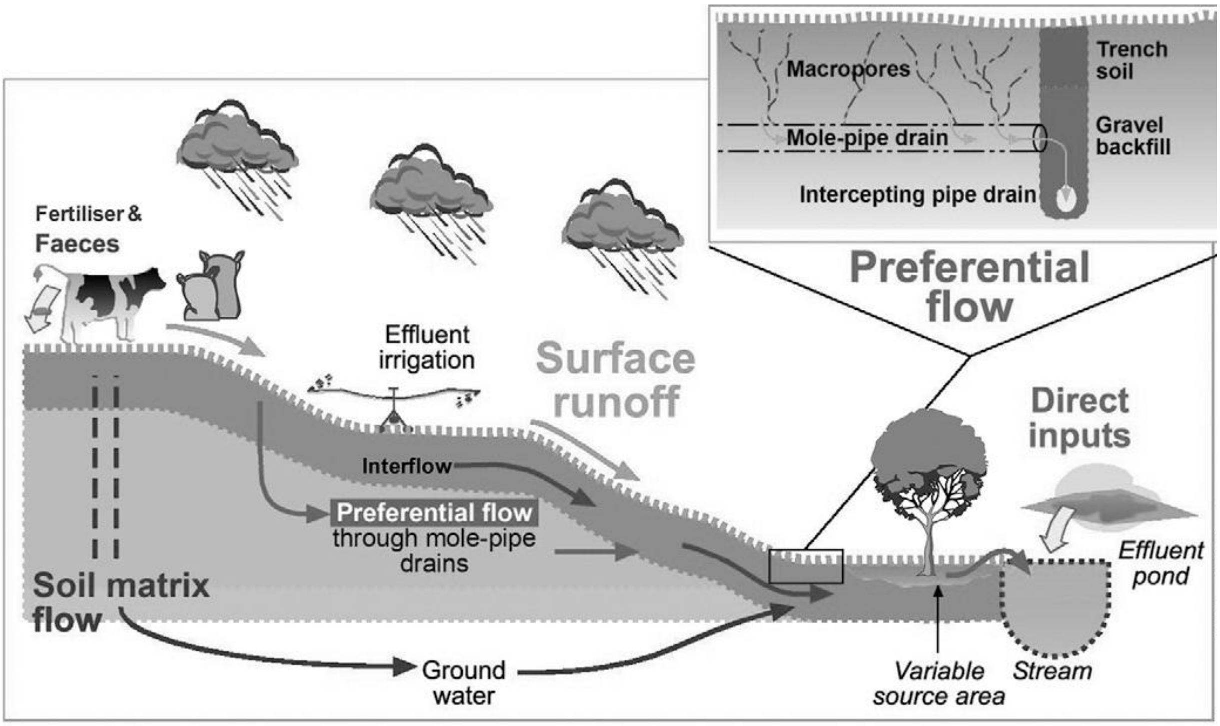

**Figure 1 –** Conceptual diagram showing the major process involved in P transport from land to river waters (modified from MCDOWELL et al., 2004).

In Southern Brazil, especially in the state of Rio Grande do Sul, the physiographic and climatic feature indicate that areas are more vulnerable to water erosion and high sediment concentration. This facilitates P transport in higher PP form yet, a clear study explaining quantitative loads at catchment scale is lacking. However, these studies are mainly focused on estimating sediment production (MINELLA et al., 2015). This aspect is partially documented by Tiecher (2015) who explained that 60% of sediment sources originate from agricultural fields depending upon the catchment size and land-use.

### 1.2.1 Landscape factors affecting phosphorus transport and system response

The spatial distribution of potential P "hotspots" within catchment varies and the hydrological, geomorphological and land management factors collectively control P fluxes. The landscape physical factors primarily control the water movement while sediment drives the biogeochemical P cycling as it moves along land–river downstream (MANZONI; PORPORATO, 2011). Various mechanisms involved in P exchange while its transportation along land-river continuum have been reported across a variety of soils and landscape characteristics (WITHERS et al., 2002; HAYGARTH et al., 2006; BALLANTINE et al., 2009; BERGSTRÖM et al., 2015) and streams and rivers (HAGGARD; SHARPLEY, 2007; WITHERS; JARVIE, 2008; EDWARDS; WITHERS, 2008; RODRIGUEZ-BLANCO et al., 2013b; SU et al., 2014; CAPOANE et al., 2015).

The biogeochemical processes that regulate the sediment-bound P movement from field to river include: mineral precipitation and dissolution (PARFITT, 1989; PIERZYNSKI et al., 2005); sorption and desorption (HOUSE et al., 1998; REDDY et al., 1999; SHARPLEY et al., 2012; GATIBONI et al., 2015); organic P mineralization (CONDRON et al., 2005; RHEINHEIMER et al., 2008), microbial activity (GACHTER; MEYER, 1993); and molecular diffusion (FROSSARD et al., 2000).

Many studies from Southern Brazil indicate that the physiographic features of the region are more vulnerable to water erosion and sediment production due to high annual rainfall (1200 to 2000 mm), rainfall intensity sometime approaching to annual rainfall erosivity ($EI_{30}$) of 6540 MJ mm $ha^{-1}$ $h^{-1}$ $year^{-1}$ during winter months (MINELLA et al., 2009). The most of soils developed from basalt and relatively have high soil silt and clay proportions and thus high risk of nutrient losses. The relief is highly variable and is often characterized by long and steep slopes near the river waters. As a result, high sediment production is recorded in many studies (DIDONÉ et al., 2014; MINELLA et al., 2009; 2015).

The land-use in Southern Brazil is highly divers and vary across the landscape with different farm size but majority are small land holders. No-tillage (NT) with soybean/wheat/maize is preferentially practiced on nearly 70% of the area since late 1970s (DERPSCH et al., 2014; MERTEN et al., 2015), yet, tobacco cultivation under conventional tillage (CT) is also key land-use in some parts mainly in the steep slope areas. The most soils of the region are highly weathered and dominated by Ferralsol types (Oxisols) with presence of higher amounts of Fe and Al metal oxides, kaolinite, and 2:1 type clays with interlayer fixed hydroxy-Al (BORTOLUZZI et al., 2015; FINK et al., 2016). The pH is acidic and P is preferentially sorbed by Fe and Al oxides (RHEINHEIMER et al., 2008).

Therefore, under such condition, apparently, there is high risk of sediment-bound P loss due to high clay contents P (BORTOLUZZI et al., 2015). Most soils in the region are well drained and a major portion of the detached particles along with P is reaching to the rivers (TIECHER et al., 2014; MINELLA et al., 2015). Pacini; Gachter, (1999) have reported that the clay particles can hold 12 times higher P than sand when compared at equal proportions. Recently, Gatiboni et al. (2015) found a linear relationship between clay percentage and P retention in a variety of regional soils from Southern Brazil.

When eroded particles carrying this PP enters river waters, a significant part of this P becomes potentially bioavailable as reported by the Maynard et al. (2009) and Pellegrini et al. (2010). In contrast, Uusitalo et al. (2000) have reported that only 10% of the P bound as PP was directly bioavailable. Nevertheless, the knowledge of the soil type in a catchment area is key to identify the vulnerability of sediment-bound P transport, as well as its potential bioavailability of the river P. The following illustration comprehensively summarizes the catchments scale natural, managed, soil, and management practice influences on the systems P legacy (SHARPLEY et al., 2013).

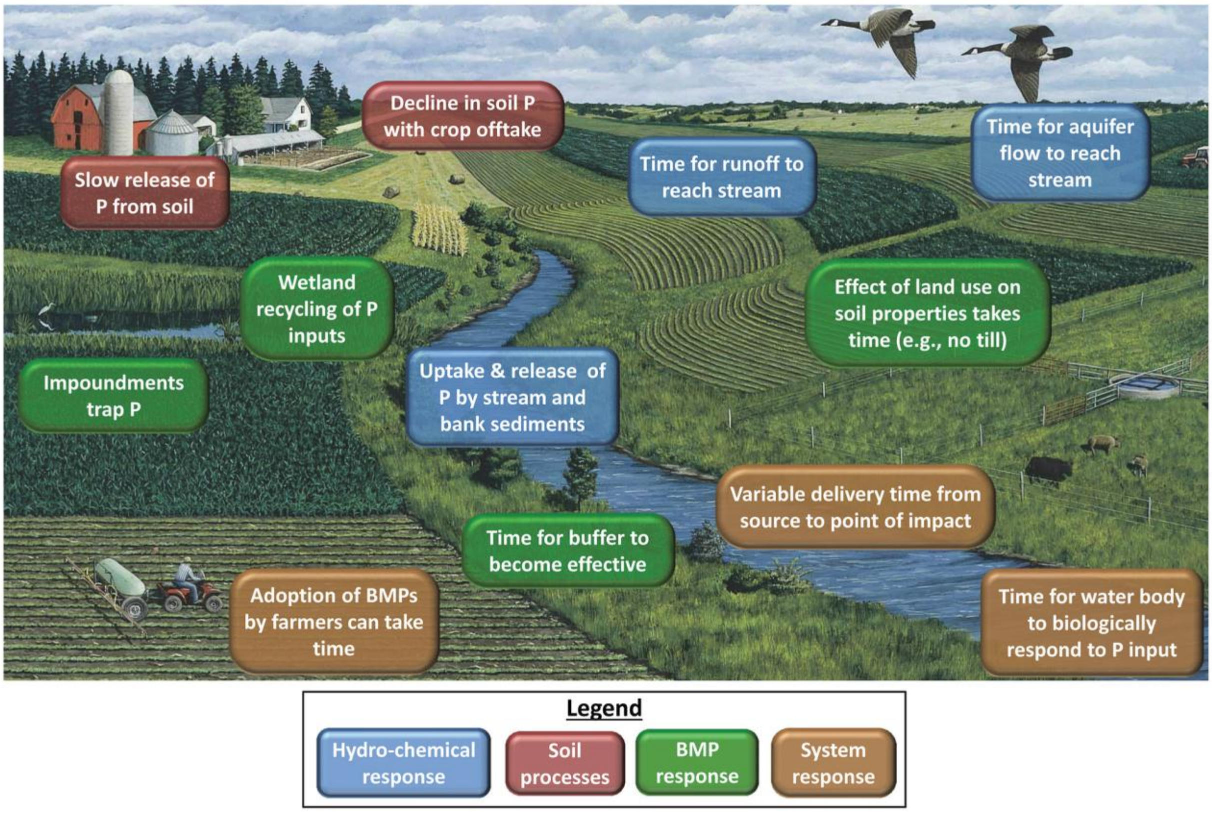

**Figure 2 –** Conceptual representation of natural, managed, soil, and best management practice (BMP) processes influencing the lag time for system response to P (adapted from SHARPLEY et al., 2013).

### 1.2.2 Seasonal P transport

In agricultural catchments, P transport is complex and greatly influenced by rainfall-runoff patterns. The higher amounts of sediment load and P are exported during storm events and can reach as high as 80% of total P export (BIEROZA et al., 2014). Many studies reported this pattern for P concentrations in agricultural rivers i.e., Pionke et al. (2000)

estimated that 90% of the P export from agricultural watershed in the USA occurred during storm event; KRONVANG et al. (2003) in Denmark showed most of P transported during high runoff; EKSTRAND et al. (2010) observed 76% TP transport during 18 days; and RODRÍGUEZ-BLANCO et al. (2013c) recorded 68% of the annual TP transport during runoff events during only 2% of total study period. In contrast, during low river condition, runoff is reduced, and water in ditches and small rivers becomes stagnant, this situation can change sediment biogeochemical behavior thus by releasing bioavailable P into water (SHARPLEY et al., 2007; WITHERS et al., 2009).

In Southern Brazil, the most of catchment monitoring studies have focused principally on soil erosion, runoff, suspended sediment concentration, sediment yield and nutrient losses at various scale sunder different soil management systems. Most of the studies on steep slope landscapes have revealed that the highest sediment production and nutrient losses occur during the Winter and Spring (August to November) and high intensity small storm event (BARROS et al., 2014; DIDONÉ et al., 2014; MERTEN et al., 2015; MINELLA et al., 2008, 2009, 2015). These insights reflect that, since, most of P loss occurs during winter runoff events and is often episodic, management strategies must focus these events to reduce surface P losses from these hydrologically active, high erosion risk and high surface accumulated P agricultural soils.

## 1.3 Particulate phosphorus in river: suspended versus bed sediments

Excessive sedimentation is a major threat to stream and river sustainability. Phosphorus moves along river continuum either as suspended sediment or deposited and temporarily stored as bed sediment. Particulate P in both cases has a specific influence on river water P concentration, i.e., it can act as a sink or source of P for the overlying water. A number of research studies based on suspended sediment P loads around the globe has been documented, which is a major driver of river ecosystem (SIMS; SHARPLEY, 2005; BALLANTINE et al., 2008; PELLEGRINI et al., 2010; WANG et al., 2010; CHEN et al., 2011; RODRIGUEZ-BLANCO et al., 2013a; BORDA et al., 2014; PERKS et al., 2015).

A number of sediment and P load oriented studies reveal that the P from diffuse sources are directly responsible for standing water reservoirs quality deterioration. Nevertheless, a great difference in P flux entering into rivers and at catchment outlet has been recorded. It clearly indicates that a portion of P is retained and temporarily deposited on the river bottom as bed sediments.

During the low flow conditions, bed sediments can act as sinks for excessive P in rivers receiving high discharges of sewage and untreated city effluent (JARVIE et al., 2006; DUDLEY; MAY, 2007; WITHERS et al., 2008). In contrast, bed sediment can act as P source particularly under low flow conditions during summer, which can accelerate eutrophication by hydraulic resuspension (BUKAVECKAS et al., 2007; JARVIE et al., 2008; NÉMERY; GARNIER, 2007). Redox conditions, overlying water composition, particle size, oxide content, sediment chemical composition regulate the bed sediments P sorption/desorption (FROELICH, 1988; FOX, 1993; STONE et al., 1995). The different processes occurring on the sediment surface when sediment enters to a river are illustrated in Figure 3 as described by WITHERS et al. (2008).

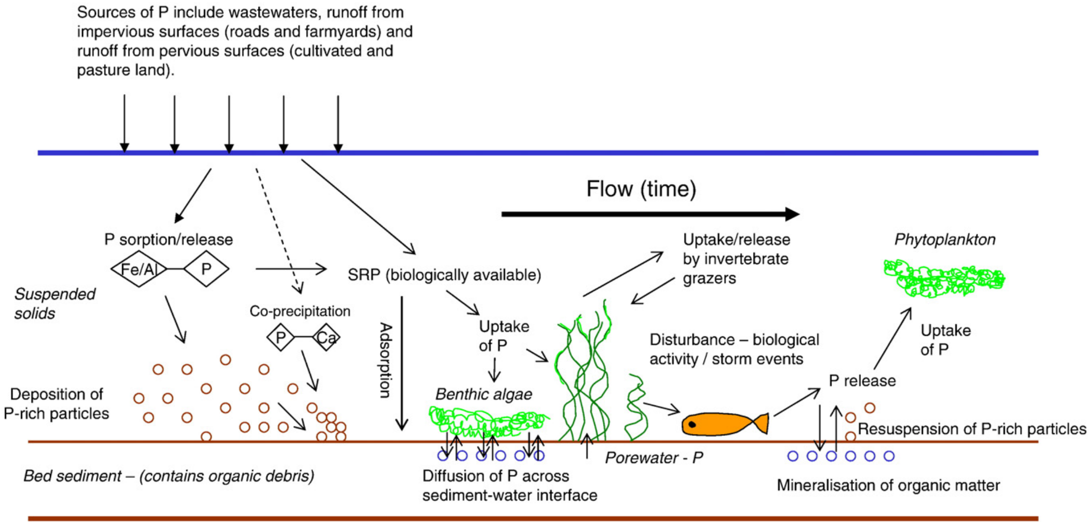

**Figure 3** – In-stream processes influencing P concentrations in flowing water (modified from WITHERS et al., 2008).

## 1.4 Characterization of sediment-bound phosphorus

The widespread application of fertilizers and manure in modern agriculture leads to high sediment P fluxes towards aquatic systems which can cause serious environmental impacts (RHEINHEIMER et al., 2008; PELLEGRINI et al., 2010; GUARDINI et al., 2012; TIECHER et al., 2012; GATIBONI et al., 2015).

Characterization of P interactions at sediment-water interface is a valuable tool while investigating P retention mechanisms within the catchment. It is evident that most of P entering and cycled within river systems is present as suspended or bed sediment in PP form. A range of analytic approaches from simple TP or IP/OP measurement (OLSEN; SOMMERS, 1982), organic and inorganic fractionation (HEDLEY et al., 1982), sorption-desorption kinetics (MEAD, 1981), P desorption under different redox conditions(SHENKER et al., 2005)nuclear magnetic resonance spectroscopy ($^{31}$P NMR - CADE-MENUN et al., 2015) has been established.

### 1.4.1 Fractionation as tool to predict phosphorus lability

The sediment-bound P can desorb P and act as a long-term source within water systems, sediment TP measurement does not reveal its environmental behavior. Therefore, a detailed identification and separation of P chemical forms is necessary to unfold its bioavailability (PETTERSSON et al., 1988; TIESSEN; MOIR, 1993; CONDRON et al., 2011).

Phosphorus fractionation with sequential extraction provides an estimation of soil and sediment P bioavailability to aquatic systems. So far, many P fractionation schemes have been developed to assess different P forms, such as for inorganic P pool (CHANG; JACKSON, 1957; HIELTJES; LIJKLEMA, 1980) or organic P (SOMMERS et al., 1972; BOWMAN; COLE, 1978; IVANOFF et al., 1998, including microbial P); bioavailable P pools (VAN ECK, 1982, PSENNER et al., 1988; RUTTENBERG, 1992; GOLTERMAN et al., 1998, CHEN et al., 2000; PARDO et al., 2003; TIESSEN; MOIR, 2008; HEDLEY et al., 1982).

As under standing water systems, sediment P is already deposited and therefore most of P fractionation studies conducted was focused to access its chemical speciation. However, in running waters, estimation of P lability is more important to assess P bioavailability for river biota. The Hedley's fractionation scheme with modifications suggested by the TIESSEN; MOIR, (1993), is one of the most widely adopted and preferentially used for range of soils and sediments (RHEINHEIMER; ANGHINONI, 2001; NEGASSA; LEINWEBER, 2009; HUND et al., 2013).

### 1.4.2 Effectiveness of P sorption-desorption and equilibrium phosphorus concentration (EPC) approach as indicator of sediment phosphorus behavior

At the sediment-water interface, sorption-desorption balance is regulated by a dynamic equilibrium between the amount of labile P present in sediment and DP (SIMS et al., 2002; NAIR et al., 2004; PALMER-FELGATE et al., 2009) and it is controlled by a number of biogeochemical processes.

To understand either sediment is P sink or source in river water, measuring equilibrium phosphorus concentration (EPC) and parameterized models describing P sorption has been developed (SPOSITO, 2008; BOLSTER et al., 2012). These sorption experiments are simple where a known sediment quantity is added to known P concentration solution and P sorbed is calculated as the difference from initial to final concentration (FROELICH, 1988; CUCARELLA; RENMAN, 2009). The sorption parameters for the sediment are then calculated by fitting the data to a selected model. In soil and sediment research, many studies have shown the suitability of the Langmuir and Freundlich isotherm equations to estimate environmental P thresholds (AN; LI, 2009; GUARDINI et al., 2012; SHAFQAT; PIERZYNSKI, 2014; ABDALA et al., 2015; GATIBONI et al., 2015).

Similarly, when focus is to determine sediment potential instant P availability and mobility, desorption kinetics studies have been used as a tool in predicating the potentially available sediment associated P. Several studies based on the MCKEAN; WARREN, (1996) equation have described the reliable assessment of sediment P release potential (P buffering capacity) on sediment-water interface (RHEINHEIMER et al., 2001; PELLEGRINI et al., 2010; TIECHER et al., 2012).

## 1.5 Hypothesis

There is high intra-catchment variability in geomorphological features of the Guaporé catchment, which have significant control on the hydrosedimentological flux. Therefore, each monitoring station can greatly vary in terms of erosivity (R), erodibility (K), topographic (LS), land use and soil management (C), and conservation practice (P), all factors that generate variable magnitude of surface runoff and suspended sediments. The upstream Northern one third of basin area is gently hilly, while lower two third have steep slopes with rocky patches. This steepness is higher in sub-catchment with tobacco under conventional tillage. The Guaporé catchment presents high annual rainfall during winter months mostly recorded as intense rain events.

Due to high landscape variation and different parent materials, many soil classes exist. In the upstream one-third Oxisols predominates while the lower two third contains less developed soils (Ultisols, Entisols, and Alfisols). Therefore, the sediments that are reaching water bodies present different and variable amounts of clay and oxides, which leads to different P sorption capacity. As suspended colloid, these particles even with similar P content can act as source or sink of P for water systems.

As the anthropic pressure and landscape land-use determine its ecological impacts, the catchment is heterogeneous in land-use and could therefore show variable impact in terms of sediment-bound P transport. The upper one-third of the catchment have soybean under no-tillage. The two upstream tributaries of Guaporé river lies in this area and one of them have urban population near the stream, which receives untreated sewage and industrial effluent containing high P. In the middle part of landscape there is somewhat mixture of soil management and high concentration of animal production, generating high amounts of manure. Whereas, the downstream one-third have typically fragmented areas with tobacco cultivation under conventional tillage, but it is mainly covered by natural forest along the river and steep slopes.

By keeping the above considerations in mind, the main hypothesis includes:

*i.* The sediments from the natural forest catchment will have minimum potential of phosphorus release to water.

*ii.* The sediments from tobacco cultivation under conventional till even with the high application of chemical fertilizers still will behave as phosphorus sink when reached into the water.

*iii.* The sediment from the sub-catchment where no-tillage predominates will show high phosphorus saturation, behaving as phosphorus source when enters into the water.

*iv.* The untreated urban sewage, when disposed in the river, will enrich the sediments in organic phosphorus and will reduce sediment phosphorus adsorption capacity.

*v.* The seasonal land-use will reflect and regulate the river phosphorus legacy.

## 1.6 Aims and objectives

The overall aims of this thesis were i) monitoring the temporal variation in sediment-bound phosphorus in sub-catchments under different land-use and soil tillage systems and (ii) assessment of the potential of sediments from rural and urban sources to act as source or sink of phosphorus for aquatic systems inorder to counter P export and improve mitigation practices in Guaporé catchment, Southern Brazil.

While, the specific objective includes:

*i.* To determine the temporal dynamics of PP sediment concentration reaching to the six sub-catchments and five sediment station along the river continuum.

*ii.* To determine the sediment chemical P forms to quantify their potential river P legacies under different soil management and anthropic pressure.

*iii.* To evaluate either the surface sediments act as sink or source for river water on the basis of equilibrium phosphorus concentration, instant desorbed P (bioavailable) and P buffering capacity in relation to sediment geochemical composition.

*iv.* To analyze the seasonal variation in P transformation between suspended and bed sediment and to evaluate the importance of bed sediment in regulating running water P concentration and pattern of internal loading across different land-use and catchment heterogeneity.

## 1.7 Thesis organization

This thesis is submitted to the Graduate Program of Soil Science, Centre of Rural Sciences, Federal University of Santa Maria (UFSM). It represents my work from 2012-2015 at Guaporé catchment, all chemical analysis was done at Soil Chemistry, the Federal University of Santa Maria under the supervision of Professor Danilo Rheinheimer dos Santos.

This study was financed by three resources: i) the first includes the doctoral scholarship jointly financed by the Academy of Sciences for the Developing World (TWAS) and the Brazilian National Council for Scientific and Technological Development (CNPq) under process number 190334/2011-8. The second resource includesa projectentitled "Qualidade da água na bacia do rio Guaporé (RS-Brasil): avaliação preliminar da contaminação por pesticidas, drogas veterinárias e fósforo" (Water quality in the Guaporé river catchment (RS-Brazil): Preliminary assessment of contamination by pesticides, veterinary drugs and phosphorus)" that was approved by MCTI/CNPQ/Universal 14/2014 via CNPq. The third financial assitance includes a sub project from "Água e poluentes, das lavouras às cidades: avaliação e tecnologias melhoradas de manejo em rede de bacias hidrográficas no. (10/0034-0)- recursos da FINEP (MCTI) com contrapartida do Governo do Estado (FEPAGRO) através do subprojeto monitora do Projeto Mais Água" (Water and pollutants, Agricultural crops to cities: evaluation and improved technology management in river basins drainage network (10/0034-0).

The current study catchment, Guaporé is an important agricultural and hydrographical unit in the State of Rio Grande do Sul. Earlier studies conducted were limited to the hydro sedimentology (DIDONÉ, 2014; KOCHMEM, 2014; SCOTTO, 2014) by Professor Jean Paolo Gomes Minella research group. However, soil and water chemistry group started comprehensive research including a doctoral study (TIECHER, 2015) aiming to track sediment source by fingerprinting approach, and two more doctoral students are still working on biofilms bound investigation of agricultural pesticides (LIMA, 2016), and human pharmaceuticals/veterinary medicine (BASTOS, 2017) all under the supervision of Professor Danilo Rheinheimer dos Santos.

This thesis is divided into following 5 chapters as:

1. **Chapter 1**, presents a comprehensive overview of anthropogenic and agricultural phosphorus pollution of river system including biogeochemical and physical factor, landscape and topographic features, sediment transport and delivery and in last section some insight into the sediment chemical phosphorus characterization aiming to describe phosphorus bioavailability in running water systems.

2. **Chapter 2**, article I entitled "*Assessing the lability and distribution of phosphorus in suspended sediments from a subtropical catchment under diverse anthropic pressure in Southern Brazil*" describes the preliminary characteristics of total particulate phosphorus and its relative forms reaching to the river waters across different origins sediments.

3. **Chapter 3**, Article II entitled "*Phosphorus seasonal sorption–desorption kinetics in suspended sediment in response to land use and management in a subtropical South Brazilian catchment*" deals with the seasonal measurement of phosphorus sorption-desorption in relation to land-use.

4. **Chapter 4**, Article III entitled "*Relating bed sediments P legacy and desorption kinetics to landscape land use in the Guaporé catchment Southern Brazil*" gives an insight to the river bed sediment P fractions and their desorption patterns.

5. **Chapter 5**, includes general discussion, elaborates our findings with some global studies and a worldwide comparison of sediment-P interactions, conclusions, future perspectives, bibliography and few landscape photos and figures from the catchment.

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# 2 ARTICLE I – Assessing the lability and distribution of phosphorus in suspended sediments from a sub-tropical catchment under diverse anthropic pressure in Southern Brazil[1]

## 2.1 Abstract

Measuring release of anthropogenically enriched sediment-boundP to water is a useful tool in ecological monitoring and planning mitigation options for future agriculture. The identification and chemical characterization of diffuse P sources is critical to minimize the surface P losses to surface waters. Therefore, catchment-scale monitoring is an effective strategy that links the spatial and temporal aspects of sediment-associated total P, P fractions, and P lability and can help to differentiate and understand P distribution in these sources. In this study, six representative headwater sub-catchments differing in land-use and management i.e., reference forest, recently turned low agriculture under conventional tillage-CT, low agriculture under CT dominated with *Ilex paraguariensis* plantations, intense agriculture under CT, intense agriculture under no-tillage - NT, and highly anthropic urban receiving untreated sewage; and five monitoring station on the main river, receiving both agricultural and animal P exports, along river continuum in Guaporé catchment, from October 2012 to October 2014 comprising 10 catchment campaigns were carried. Total P and individual P fractions in 63-µm particle size were determined with slight modifications in the Hedley fractionation. Results indicated that average over the monitoring period, the TP concentration lied between 752 mg kg$^{-1}$ in reference forest to as high as 1738 mg kg$^{-1}$ in highly anthropic sediments. Overall, there was 20 to 131% increase in TP contents between low agriculture land use and highly anthropic over reference forest. Across monitored sites, individual P fraction when pooled for different P lability indicated 10, 35, and 55% of TP as labile, moderately labile and non-labile P, respectively. It was obvious that land use has astrong

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impact on sediment P lability. With a land use shift from forest to highly anthropic urban, an increase in labile P (172%), moderately labile P (705%) and non-labile P (874%) was observed. Among agricultural sub-catchments, intensive agriculture under CT relatively retained higher algal bioavailable P ($P_{AER}$) and lower bicarbonate organic P ($Po_{BIC}$) than under NT. The consistent higher values of non-labile ($Pi + Po_{HID-0.5}$) and residual P in urban, high agriculture and main river sediment indicates the high P affinity due to thepresence of high Fe/Al oxides. Temporal analysis revealed that regardless of P lability, higher concentration was found in winter months (July to November) particularly under CT sub-catchment showing high sediment production and increased transport of added P during tobacco cultivation period. The results provided a baseline to revisit the current fertilization, soil management and policy measures to minimize the pressure on the water resources for sustainable ecological management.

**Keywords:** Phosphorus, Suspended sediment, Lability, No-tillage, Diffuse pollution, Land use

## 2.2 Introduction

While the developed countries are debating about the global P stewardship and its wise use for well-being of the society and environment, the developing regions still need a great research to identify the potential P hot spots for suitable P management (Withers et al., 2015). The presence of P rich suspended sediments (SS) is a significant risk to the fresh water and have raised serious concerns on the functional integrity of whole lito-hidrosphere across the globe (Jarvie et al., 2006; Shigaki et al., 2006; Rowe et al., 2015). Therefore, increased understanding of the catchment scale interactions between the freshwater river system and P dynamics of headwater resources and/or rivers function as corridor of the watershed to facilitate P delivery to lake or ocean via transportation is of great importance for ecological environment. It is a well-established fact that the excessive P inputs driven by the over application of P fertilizers, manure and untreated sewage wastewater often lead to the eutrophication (Withers and Jarvie, 2008; Sharpley et al., 2013). The adverse effects of eutrophication may range from significant decline in the chemical and ecological quality of water bodies to whole human society and economy of particular region (Withers et al., 2015).

Over the last three decades, in Southern Brazil, the anthropogenic modification of the landscape has been accelerated and the animal production has emerged as one of the most promising revenue generating sector in Brazilian agro-economy. Brazil is among the major competitor in international trade and export of agro-products like soybeans, poultry, swine, beef, corn and rice. As a result of expansion in poultry and dairy demands, the Brazilian livestock industry has expanded quickly to around 1741 × $10^6$ animals (IBGE, 2010). The poultry industry alone with over 15 million MT poultry meat export is contributing approximately US$ 10 billion (USDA, 2013). Pig farming is practiced on relatively small farms (area between 15 and 30 ha), but with high slurry production (3600 $m^3$ $yr^{-1}$) with hilly topography. These huge amounts of pig slurry has been applied to the soil successively on small area without taking into account plant nutritional requirement and environmental concerns (Gatiboni et al., 2014; Couto et al., 2015). Therefore, the environmental hazards caused by this commercial activity primarily on water quality are much detrimental as result of their land application or either due to water consumption, with an eutrophication potential of 372 g TKN $m^{-3}$ and a $BOD_5$ pollution load of 0.14-0.18 kg $BOD_5$ $kg^{-1}$ per fowl (Kist and Moutaqi, 2009) in the region. Similar growth trend in cereal production and cattle population is predicted to 20 and 40 % increase respectively by year 2021-22 from the current number with an approximate addition of 4107 × $10^3$ Mg P $yr^{-1}$ to the environment (AGE, 2012; Tiecher et al., 2014). Resultantly, the consumption of agro-industrial P-containing compounds is expected to further increase due to dietary preferences both for human and animal feed along with increased inflow of untreated effluent and sewage into the environment (Qu and Kroeze, 2010).

The South Brazilian agriculture has adopted to no-tillage system (NT) since early 1980s (Bollinger et al., 2007, Merten et al., 2015). Due to increased soil erosion control, enhance water retention and improve soil health. Currently, there is about 30 M ha$^{-1}$ of farmland under NT in Brazil (FEBRAPDP, 2013). The farming community has being convinced and confident that NT characterized by minimal soil disturbance and profile mixing is the best to control soil and surface runoff losses, increase biological activity, high crop growth and yields than conventional tillage (Olson and Ebelhar, 2009; Lafond et al., 2011). Nevertheless, the farmers removed the terraces from their field and with an insufficient topsoil crop residues have resulted in accelerated water erosion even under NT (Pellegrini et al., 2010; Streck, 2012; Didoné et al., 2014; Minella et al., 2015; Tiecher et al., 2015). Additionally, recent studies on long-term NT and surface P fertilization experiments have shown the nutrient stratification particularly of P in the soil surface (0-5 cm) layer (Tiecher et al., 2012; Ferreira et al., 2013). Repeated application of P in the soil surface contribute to environmental contamination (Sharpley, 2003; Guardini et al., 2012). The annual high rainfall erosivity and sloping topography turned this area as P hot spot. There is high environmental and eutrophication risk of anthropogenically mobilized sediment associated P from Guaporé watersheds to enter into Jacui river and ultimately reaches in the Guaíba lake, which is the only water source for 2 million metropolitan population of RS and Porto Alegre city, as well as potential contaminant to whole costal line of South Atlantic Ocean.

Conversely, recent studies carried on four soil types in A horizons occurring in Guaporé watersheds has demonstrated high content of crystallized iron i.e., hematite, goethite, goethite–ferrihydrite and gibbsite. Mostly adsorbed P was found associated with the goethite and clay content (Bortoluzzi et al., 2015; Fink et al., 2016). Therefore, the average P application is at higher rates when compared to other regions of world due to compensate rapid immobilization of soil solution P by the presence of high secondary presence of high Fe and Al contents in these soils (Novais et al., 2007; Sattari et al., 2012). During soil saturated conditions and or the dry season in river, the reducing conditions accelerate the reduction of Fe(III) to the more soluble Fe(II) with subsequent release of the strongly fixed P. This phenomenon significantly enhances the soluble P fraction in soil and sediments and the soluble reactive P in the river water.

Several P sequential fractionation schemes have been developed to characterize lability of soil, sediment and manure P based on susceptibility to extraction (Tiessen and Moir, 1993; Condron and Newman, 2011). However, the simplest and fairly standardized scheme which separate different P fraction into various pools on the basis of lability i.e., labile-P ($H_2O$, resin, and 0.5 M $NaHCO_3$-Pi and Po), moderately labile-P (0.1 M NaOH-Pi and Po), and stable-P (HCl and residual) fractions is by Hedley et al. (1982). It is worldwide adopted and accepted for diverse type of land-use and management systems (Negassa and Leinweber, 2009; Hund et al., 2013).

Several studies have been conducted on soil P fractionation to assess the P lability in response to tillage (Fink et al., 2016), cropping pattern (Tiecher et al., 2012), manure and fertilizer management (Rheinheimer and Anghinoni, 2001; Pavinato et al., 2010; Rodrigues et al., 2015) in the region. A few studies have also been focused on particulate and dissolved P characterization in runoff from field and or small catchment scale (Pellegrini et al., 2010; Lourenzi et al., 2015). There is, though, a lack of research on the regional scale monitoring of suspended sediment P fractionation and pattern of P lability within such sediments and also to link this information to the land use and its implication for ecological P management.

In this context, this study aims to provide a basis for understanding the characteristics and distribution of P compounds in suspended sediments of Guaporé catchment by Hedley P fractionation. We hypothesized that (i) the availability of a specific sediment P fraction extracted will vary in response to land use and anthropic activity, (ii) either P lability will differ or is exchangeable to some extent depending on sediment characteristics.

## 2.3 Materials and methods

### 2.3.1 Catchment location and geomorphic characteristics

This study was carried out in Guaporé catchment situated in the northeastern part of the Rio Grande do Sul state, the most Southern  Brazilian State (Fig. 1). The catchment with a basin area of 2,030 km$^2$ was chosen to monitor and characterize for the sediment bound P behavior, sediment load and hydrological processes with representative land use, soil and landscape conditions, as well as the fact that it offers a wide heterogeneity at sub-catchment scale with varying anthropic and conservation agricultural practices. The catchment is located on the plateau slopes with steep hilly slopes and highly vulernarable to ecological fragility. It covers part of the physiographic regions of the middle plateau (upper third of the basin) and the lower northeastern slope (intermediate and lower thirds of the basin). The Guaporé river is a tributary of river Taquari, and Taquari river is part of the Regional Hydrographic Guaíba estuary.

The altitude of the basin varies widely, from 40 m near its confluence with the river Taquari to 800 m in north at the starting part of the right portion of the basin. Climate is classified as Cfa according to the Koppen climate classification. Mean annual rainfall varies between 1,400 and 2,000 mm with well distributed over the year, however heavy rain occurs during Winter and Spring months (August - October) and relatively less rainfall during summer (February - March). The mean annual temperature is 17.4 °C. Geology is diverse but predominated by volcanic lava flows and basalt with undulating to hilly type relief as presented in supplementary Figure 1b. Due to high variations in pedo-climatic conditions, various soil classes i.e., Entisols, Luvisol, Cambisol, Oxisol, Ultisol, Chernosol are present but dominated by Oxisol, as shown in supplementary Figure 1a.

### 2.3.2 Agriculture and land use patterns

The anthropic impact in the catchment is very distinct with 0.5 million people out of which 50 % is living in the upper half of the catchment near headwater region around Capingui and Marau stream before their confluence. The most of domestic and industrial untreated sewage is directly discharged into the river. The catchment have over 1800 pig and poultry houses, whose manure and slurry are applied to relatively small farm size ranging from 10 to 100 ha (IBGE, 2013). The land use is highly heterogenious and can be subdivided into the upper one-third and lower two-third. The upper one-third has gentle slope and a little hilly train with soybean (*Glycine max* (L.) Merr) as major crop under no-tillage (NT). The middle to lower two-third of the catchment exhibits a mixed land use pattern specifically the lower part under tobacco (*Nicotiana tabacum* L.) cultivation on steep slopes under conventional tillage (CT - supplementary Figure 2b). The patches of maize (*Zea mays* L.) and areas with afforested Eucalyptus (*Eucalyptus* spp.), along with fair proportion of cultivated or natural pastures are also maintained. In this part, different types of soil management, principally conventional and minimum tillage can be identified. The high sloppy areas, especially riversides, dense native forest cover with the presence of small towns and urban areas are present as shown in supplementary Figure 2a. The data regarding hydro-sedimentologicalparameters of the catchment ispresented in supplementary data Table 1.

### 2.3.3 Identification and selection of representative monitoring stations

The land use and land cover maps were generated by using the images from RapidEye system with spatial resolution of 5m multispectral sensor type, and radiometric resolution of 12 bits and five spectral bands. Later, the images were georeferenced by using the coordinate system in UTM zone 22S and were imported into a database in SPRING software, version 5.2 provided by DPI/INPE. The geological map of the study area was obtained by using the Mineral Resources Research Company's repository (CPRM).The soil classification map at the scale 1: 1,200,000, is a cartographic generalization of Soil Recognition Survey of the State of Rio Grande do Sul at the scale 1: 750,000 (Brazil, 1973) and was prepared by Streck et al. (2008). The slope maps were extracted from a digital elevation model originating in mapping mission of Earth relief - SRTM (Shuttle Radar Topography Mission) by using the software ArcGIS 10 (ESRI, 2011).

The six monitoring stations were identified and installed at sub-catchment scale and five monitoring station were identified on the main river (Fig. 1). The detail of variation in land use and management system is summarized in Table 1. Briefly, the sub-catchments include: (i) native forest, as reference site;  (ii) sub1, recently converted low intensity arable with few tobacco and maize under CT; (iii) sub2,  low arable with tobacco cultivation under CT and erva-mate (*Ilex paraguariensis* Saint - Hilaire) plantations; (iv) sub3, high agriculture with predominance of tobacco cultivation under CT; (v) sub4, intensive agriculture dominated by soybean/corn cultivation under NT, and (vi) sub5, similar to sub4 and with high anthropic urban source (Marau city) receiving city and industrial untreated  sewage.

On the main river five monitoring station include, P1, installed after the confluence of sub5 and sub6 tributaries; P2 and P3 monitoring station in middle reaches with an area showing maximum pig/poultry production and high landscape heterogeneity; while P4 receiving relatively high P inputs from tobacco cultivation region in lower reach and catchment outlet (P5) receiving all upstream P input with high forest and river straightening. The P5 also contains principal hydrological and sedimentological monitoring station (Fig. 1; Table 1).

### 2.3.4 Sediment collection and preparation

At each monitoring station the suspended sediments samples were collected from a period of December, 2012 to October, 2014. During the first week of October 2012, the first field campaign was started and two time-integrated suspended sediment samplers as described by Maier (2013) were installed at each of 11 monitoring stations. Over the whole study period, a total of 10 field campaigns during (Dec-12, Feb-13, April-13, Jul-13, Sep-13, Nov-13, Feb-14, May-14, July-14, and Sep-14) were carried out and samples were collected after each 75 day generally depending upon the water level and river flow conditions. After each sampling period, the samplers were taken out and all sediments was transferred into acid-washed 20 L plastic gallon and transfer to laboratory and then oven-dried at 50 °C, gently disaggregated using a rubber head pestle and mortar, and sieved through a 63-µm mesh prior to chemical analysis. A set of original oven dried was passed through 2 mm mesh and kept for particle size analysis.

### 2.3.5 Phosphorus fractionation scheme

During whole analysis, dried and 63-µm size sediment sample were used. Keeping in view the objective to assess the sediment bound P lability, sequential P fractionation scheme proposed by Hedley et al. (1982) with little modifications as suggested by Condron et al. (1985) was chosen. At each step, 10 mL of extractant was added to 0.5 g sediment in a 15 mL centrifuge tubes (1:20 ratio) and the tubes were vertically shaken on end-over-end at 60 rpm for 16 h at 25 °C. The order and forms of P removed by each sequential extraction as explained in literature is summarized in Fig. 2. The anion exchange membrane strips (AMI-7001S;

Membranes International Inc, New Jersey) were used in the first extraction during fractionation prior to saturation with $NaHCO_3$ as described by Gatiboni et al. (2005). To insure the extraction efficiency both OP and TP were measured by the method of Olsen and Sommers (1982). The OP was estimated by ignition method and was calculated by the difference between the amount of P extracted with 0.5 M $H_2SO_4$ from ignited (550 °C, 4 h) and non-ignited sediment samples, while TP was estimated by digestion with $H_2SO_4$ and $H_2O_2$ in the presence of saturated $MgCl_2$ and both were subsequently determined colorimetrically by the method of Murphy and Riley (1962).

### 2.3.6 Complementary analysis of sediments

To insight into the P fractionation, key physicochemical characteristics were also determined with three replications. The total organic carbon (TOC) was determined by wet oxidation with $K_2Cr_2O_7$ and $H_2SO_4$ according to Walkley and Black (1934). The iron ($Fe_{\mathbf{ox}}$) and aluminum($Al_{ox}$) were extracted with $0.2\ \mathrm{mol\ L^{-1}}$ ammonium oxalate at pH 3 in dark (Schwertmann, 1964) and with dithionite–citrate–bicarbonate ($Fe_{\mathbf{dcb}}$ and $Al_{dcb}$) as explained by Mehra and Jackson (1960) and extracted concentrations were determined on an atomic absorption spectrophotometer.

To determine particle size distribution, 2 g of the 2 mm sieved sediment material was taken in a 200 mL glass snap cap bottle. The sample was oxidized with $H_2O_2$ to eliminate organic material and subsequently dispersed with 6 % NaOH solution and thereafter shaken for 12 h on back and forth shaker. Then the sample was filtered with 63 µm sieve to separate silt and clay from sand. The retained sand in the sieve was oven dried at 105 °C and weight was recorded. The particle size of silt + clay samples was determined using a laser particle size analyzer (Muggler et al., 1997). The values obtained with the particle size analyzer to 2-µm have been assigned as clay fraction, and those between 2 and 63 µm were attributed to silt fraction.

### 2.3.7 Statistic alanalysis

The statistical analysis was carried out using Statistica software. The comparisons among sampling sites and seasons at each collection sampling site was performed using the non-parametric test of Kruskal-Wallis (*H*). The *H* test allows to test the null hypothesis that the means values of samples sites or seasons at each collection sampling site are the same. The testwasappliedaccordingtoEquation 1:

$$H = \frac{12}{n(n+1)} \sum_{s=1}^{k} \frac{R_s^2}{n_1} - 3(n+1) \qquad (1)$$

where, $R_s$ is the sum of the "ranks" occupied by each sampling site or seasons, $n_1$ is the number of observations; $n$, is the sum of $n_1$'s; and $k$ is the number of sampling sites or seasons.

Due to high number of data set, box and whisker plots were chosen to facilitate the interpretation of results. In each plot value represents n = 30 (10 collection timings and 3 laboratory replication). The correlation co-efficient between pair of means of different P fractions over the whole sampling period and related chemical characteristics was also performed. Finally, cluster analysis was performed to determine variability between the monitoring stations for different P lability. Euclidean distance and Ward's method were used as dissimilarity matrix and linkage method, respectively.

## 2.4 Results

### 2.4.1 Sediment chemical characteristics and textural behavior

Results related to changes in sediment chemical behavior induced by land use patterns and or environmental factors as described by the Kruskal–Wallis *H*-test and significance level are presented in Table 2. Average across sampling locations and timings, the sediment TOC ranged (20.3 to 39 g $kg^{-1}$), $Fe_{ox}$ (4.1 to 7.8 g $kg^{-1}$), $Fe_{dcb}$ (33.9 to 51.2 g $kg^{-1}$), $Al_{ox}$ (1.2 to 2.2 g $kg^{-1}$), $Al_{dcb}$ (3.1 to 5.6 g $kg^{-1}$), clay (43.8 to 128.3 g $kg^{-1}$), and sand (274.8 to 327.3 g $kg^{-1}$). Within monitoring locations, among agricultural sub-catchments, sub3 showed highest 34.9 g $kg^{-1}$ and forest lowest 20.3 g $kg^{-1}$ TOC while, among main river points, P2 showed maximum 39.0 g $kg^{-1}$ and P5 minimum 32.2 g $kg^{-1}$ TOC content, respectively. The poorly absorbed $Fe_{ox}$ was highest 7.4 g $kg^{-1}$ in sub5 sediments and lowest 4.1 g $kg^{-1}$ at forest site whereas on main river, both P1 and P2 have highest 7.8 g $kg^{-1}$ and lowest 7.1 g $kg^{-1}$ $Fe_{ox}$ in P4 sediments. Similarly, highest (51.2 g $kg^{-1}$) contents of crystalline bound $Fe_{dcb}$ was recorded for sub5 and lowest (33.9 g $kg^{-1}$) in forest sediments. However, P1 retained maximum 46.2 and P5 lowest 43.0 g $kg^{-1}$ $Fe_{dcb}$ content among main river sites. A slight change within all monitoring locations was recorded for amorphous $Al_{ox,}$ but, higher values in sub-catchment sediments were observed as compared to the main river sediments. The results regarding $Al_{dcb}$ demonstrated that maximum 5.6 g $kg^{-1}$ $Al_{dcb}$ was present in urban sediment when compared to native forest with lowest 3.1 g $kg^{-1}$.Among main river sites, higher $Al_{dcb}$ contents at P5 over rest of monitored locations was also recorded (Table 2).

A substantial difference in the clay size distribution was recorded, among sub3 (insensitivity CT tobacco production) showed highest 128.3 g $kg^{-1}$clay content, followed by sub2 with 105.9 g $kg^{-1}$clay and least in native forest 43.8 g $kg^{-1}$. The main river points did not exhibited statistically variation in clay contents. The sand fraction was relatively less in sub-catchments than main river sediments, while, the silt fraction dominated and often exhibited over 60% of the soil particle size (Table 2).

The monthly hydrosedimentological attributes i.e., water discharge (Q), sediment yield (SY), erosivity index ($EI_{30}$), and rainfall (R) during the study period between October 2012 and October 2014 is presented in supplementary Table 1. In general, maximum rainfall occurred in winter months during August to October in both years, consequently generating highest amount of Q, SY and $EI_{30}$.

### 2.4.2 Inorganic P fractions

The concentration and relative distribution of the various inorganic P fractions pooled over sampling period in sediment for different sites are summarized in Table 2. The details description of each fraction is given in the following sections.

#### 2.4.2.1 Labile P fractions ($P_{AER}$ and $Pi_{BIC}$)

Among sub-catchments, the highest $P_{AER}$ concentration 61 mg kg$^{-1}$ was found in sub5 (point source receiving city effluent), followed by the sub3 (tobacco under CT) 57.9 mgkg$^{-1}$ when compared to reference forest sub-catchment with 29.4 mg kg$^{-1}$ $P_{AER}$. However, the sub4 (NT) also showed 28% more P when compared to forest. The downstream P4 showed highest 47.4 mg kg$^{-1}$, and P5 lowest 39.5 mg kg$^{-1}$$P_{AER}$ on main river. Similarly, highest 75.4 mg kg$^{-1}$ $Pi_{BIC}$ was recorded in sub5 among all sub-catchments while less pronounced difference was observed among main river sediments (Fig. 3, 4a, Table 2). The largest difference in both labile fractions was noted among sub-catchments and followed the sequence as sub5 >sub3 > sub4 > sub2 ≈ sub1 > forest. Average across land-uses, the relative increase in anthropically influenced sediments was high (i.e., 21.9 to 107.6%) for $P_{AER}$ and (1.7 to 57.9%) for $Pi_{BIC}$ over forest.

#### 2.4.2.2 Moderately labile P fractions ($Pi_{HID-0.1}$ and $P_{HCl}$)

The results showed that moderately labile $Pi_{HID-0.1}$ was highest (343.4 mg kg$^{-1}$) in urban sediments (sub5), followed by intensive agriculture sediment under CT- sub3 (202.1 mg kg$^{-1}$), and by sub4 (183.6 mg kg$^{-1}$) in comparison to forest 127.3 mg kg$^{-1}$. Among sediments on main river, P1 showed highest 298.1 mg kg$^{-1}$, whereas, the rest of sediments exhibited reducing trend in moderately labile concentration while moving downstream untill catchment outlet (Fig 5a, Table 2). At sub-catchment scale, the moderately labile $P_{HCl}$ content was also highest in urban sediments (249.9 mg $kg^{-1}$), followed by low agriculture sub1 (159.9 mg $kg^{-1}$) and then by intensive agriculture sub3 (145.3 mg $kg^{-1}$). The NT and CT sites showed a similar concentration for moderately labile $P_{HCl}$ content in their sediments and the difference between two was non-significant. On the other hand, main river the upstream site P1 showed maximum (261.8 mg $kg^{-1}$) moderately labile $P_{HCl}$, while downstream sediments showed inconsistent pattern for moderately labile $P_{HCl}$(Fig. 7a, Table 2). In general, the concentration of Fe/Al bound P ($Pi_{HID-0.1}$) was higher when compared to the Ca-precipitated P ($P_{HCl}$) in most of sediments sites, however, the Ca-precipitated P was highest in the high anthropically influenced sediments (sub3, sub4 and sub5) and all main river sediment (P1 to P5) when compared to the relatively less anthropic site (sub1 and sub2) and native forest (Fig. 7a).

### 2.4.2.3 Non-labile P fractions ($Pi_{HID-0.5}$ and $P_{Residual}$)

The Fig 6a and 7b showed the average concentration of non-labile ($Pi_{HID-0.5}$ and $P_{Residual}$) for all 11 monitored sites. In sub-catchment 5 (urban), both, non-labile $Pi_{HID-0.5}$ and $P_{Residual}$ showed highest contents 272.7 and 497.6 mg $kg^{-1}$, followed by sub3 (tobacco under CT) 268.6 and 486.2 mg $kg^{-1}$ and then by sub4 (NT) with 259.2 and 481.7 mg $kg^{-1}$, respectively. The reference forest sub-catchment showed lowest non-labile $Pi_{HID-0.5}$ and $P_{Residual}$, whereas, sub1 and sub2 showed little variance between them (Table 2).

The sediments on main river showed high concentration for both non-labile at upstream P1 and lowest concentrations at downstream catchment outlet P5. The intermediate monitoring sediments between P1 and P5 (i.e., P2, P3 and P4) showed inconsistent trend for both non-labile. Within non-labile P pool, $P_{Residual}$ showed clear dominance over $Pi_{HID-0.5}$ and on an average across different land uses, alone contributed over 60% to total non-labile P.

### 2.4.3 Organic P fractions

Significant difference in Po fraction was detected among the sampled location as shown by the Kruskal-Wallis H-test and *p*-values (Table 2). Generally, the $NaHCO_3$ 0.5 mol $L^{-1}$ ($Po_{BIC}$) extractable labile organic P concentrations were lower when compared to either 0.1 mol $L^{-1}$ NaOH ($Po_{HID-0.1}$) or 0.5 mol $L^{-1}$ NaOH ($Po_{HID-0.5}$) extractable non-labile organic P fractions. The results indicated that the highest $Po_{BIC}$ concentration (40.8 and 39.2 mg $kg^{-1}$), corresponding to the 137% and 128% relative increase over forest was found in the urban (sub5) and NT (sub4) sediments, respectively (Fig. 4b). The sub-catchments sub1, sub2 and sub3 showed 26.1, 18.7 and 25.9 mg $kg^{-1}$ $Po_{BIC}$, respectively. On the other hand, the sediments from the main river sites did not showed much variation among them and ranged from 27.2 to 33.7 mg $kg^{-1}$ for$Po_{BIC}$.

The concentration of moderately labile organic P ($Po_{HID-0.1}$) in sediment of the sub3 was significantly ($p < 0.05$) higher (55.2%) than those of the sub5 (40.4%) and sub2 (36.5%) when compared to reference forest sub-catchment and the difference between the latter two was non-significant. The main river sediments showed relatively higher $Po_{HID-0.1}$ than the sub-catchments and an increasing trend in $Po_{HID-0.1}$ concentration was observed along the river continuum, except river outlet P5 sediments (Fig. 5b, Table 2).

Among the sub-catchments, the Fig. 7b indicates that the non-labile organic P fraction ($Po_{HID-0.5}$) was highest (123.5 ± 49.8 mg $kg^{-1}$; $p < 0.01$) in sub3 (tobacco under CT), followed by urban sub5 (109.0 ± 55.6 mg $kg^{-1}$; $p < 0.01$) and then by NT sub4 sediments (96.2 ± 47.1 mg $kg^{-1}$; $p < 0.01$). The sub1 and sub2 did not show much variation in $Po_{HID-0.5}$ with 52.1 and 45.8 mg $kg^{-1}$. However, the sediments from main river showed higher non-labile organic P fraction ($Po_{HID-0.5}$) then the sub-catchments. There was non-significant difference between upstream P1 and outlet P5, however, the intermediate sites showed slightly higher concentration of $Po_{HID-0.5}$ (Table 2).

### 2.4.4 Average spatial and temporal P lability (accounting for legacy river P)

To differentiate the overall P pools associated with P lability, the individual fraction of Pi and Po were grouped as labile P ($P_{AER}$, $Pi_{BIC}$ + $Po_{BIC}$), moderately labile ($P_{HID}$-0.1 Pi + Po and $P_{HCl}$), and non-labile P ($P_{HID}$-$_{0.5}$ Pi + Po and residual P) Figure 8. The highest 172.3 mg $kg^{-1}$ labile P was detected in highly anthropic urban (sub5) sediments, followed by intensive agriculture under CT (sub3) 140.5 mg $kg^{-1}$ and then by NT agriculture (sub4) 127.1 mg $kg^{-1}$, when compared to 97.5 mg $kg^{-1}$ in reference forest sediments. The sediment on main river showed 122.3 to 130.6 mg $kg^{-1}$ labile P along the river continuum. Overall, the total labile pool accounted for < 10% of total P in all main river and sub-catchments except low agriculture sub1 and sub2, and forest sediments. Based on the hierarchical aligned cluster analysis (HACA) and the spatial similarities of P liability recorded, the highest labile P was also identified in order, highly anthropic urban sub5 > intensive agriculture CT sub3 > intensive agriculture sub4 > main river points > lowest in sub1 and sub2, and forest sediments (Fig. 9a).

The moderately labile pool was a sizeable pool when calculated in proportional basis in TP and there was 31.4 to 167.2% increase in anthropically impacted sediments over forest. Maximum moderately labile P was recorded in urban sub5 sediments (704.8 mg $kg^{-1}$), followed by CT sub3 (457 mg $kg^{-1}$) and then by NT sub4 (374.3 mg $kg^{-1}$) when compared to in native forest (263.8 mg $kg^{-1}$). The relatively less influenced sub1 and sub2 sediments showed lower amount of moderately labile pool than highly influenced ones (i.e., sub3, sub4 and sub5). Among main river sediments, P1 showed highest 686.7 mg $kg^{-1}$ moderately labile P over rest of the sediments (Fig. 8b) showing the effect of high anthropic and agriculture intensification. The cluster analysis demonstrated that highest value for moderately labile P was found in urban sub5, CT sub3 and main river points receiving highly P inputs (Fig. 9b).

The relative contribution of moderately labile pool in TP ranged between 30 to 40% for all monitored locations except sub5 and P1, where it was > 40% (Fig. 8b).

When averaged over the full sampling period, the non-labile pool proved the largest portion of TP and approximately ranged from 50 to 60% for all sampling locations except sub4 (NT), where it accounts for 62.5%. Within non-labile P pool, the residual P alone was a major contributor and showed > 30% proportion (Fig. 8b). Again, the urban sub5 showed highest 873.6 mg $kg^{-1}$ non-labile P followed by the intensively cultivated CT (sub3) and then by NT (sub4). The sediments from highly disturbed site showed 2 fold high non-labile P than the reference forest sediments. The cluster analysis regarding non-labile P clearly indicated that highly enriched sediment (sub3, sub4, sub5 and P1 to P5) have higher values than the less disturbed (sub1 and sub2) and least in forest (Fig. 9c).

The temporal variations associated with labile, moderately labile and non-labile P for each sampling period and each of 11 monitored locations are presented in Fig. 10. The labile P pool was relatively high in winter months (July to November) and in January and February for sub-catchments under CT (Fig. 10a). Unlike labile P, moderately labile P showed a very clear pattern across the timings and highest values were recorded between July and September in 2013 for most of sediments except NT and forest. However, in May 2014, sizeable moderately labile P was also recorded in urban sub5, P1 and sub2 sediments (Fig. 10b). The non-labile P was higher between February and May in both 2013 and 2014 for most of the anthropically enriched sediments whereas less apparent difference was recorded in sub1, sub2 and forest site (Fig. 10c).

### 2.4.5 Correlations between P fractions and sediment chemical properties

Many P fraction and soil chemical characteristics showed significant correlation among them (Table 3). The highest significant correlation coefficients ($p < 0.001$) were shown between $P_{AER}$ and $Pi_{BIC}$ ($r = 0.87$), between $Pi_{HID\text{-}0.1}$ and P-HCl, TP ($r = 0.85, 0.88$), between $Pi_{HID\text{-}0.5}$

and residual P, TP, $Fe_{ox}$ ($r$ = 0.97, 0.95, 0.92), between $Po_{HID\text{-}0.5}$ and residual P, TP ($r$ = 0.94, 0.91), between residual P and TP, $Fe_{ox}$ ($r$ = 0.95, 0.90), between TP and $Fe_{ox}$ ($r$ = 0.91), between TOC and $Fe_{ox}$ ($r$ = 0.89), between $Fe_{dcb}$ and $Al_{dcb}$ ($r$ = 0.87).

The higher significant correlation coefficients ($p < 0.01$) were shown between $Po_{BIC}$ and $Pi_{HID\text{-}0.5}$, residual P, TP, $Fe_{ox}$ ($r$ = 0.82, 0.76, 0.78, 0.75), between $Pi_{HID\text{-}0.1}$ and $Pi_{HID\text{-}0.5}$,residual P ($r$ = 0.75, 0.72), between $Pi_{HID\text{-}0.1}$ and TOC ($r$ = 0.83), between P HCl and $Pi_{HID\text{-}0.5}$, residual P, TP, TOC, $Fe_{ox}$, $Fe_{dcb}$ ($r$ = 0.66, 0.62, 0.80, 0.61, 0.76, 0.65), between $Pi_{HID\text{-}0.5}$ and TOC, $Fe_{ox}$ ($r$ = 0.82, 0.83), between residual Pand TOC, $Fe_{dcb}$ ($r$ = 0.84, 0.66), between TP and TOC, $Fe_{dcb}$ ($r$ = 0.83, 0.74), and between $Fe_{dcb}$ and $Al_{dcb}$ ($r$ = 0.87). The rest of P fraction, chemical properties and clay content also showed high significant correlation coefficients ($p < 0.05$) between them as shown in Table 3.

## 2.5 Discussion

### 2.5.1 Effect of land use and anthropic modification on sediment P lability

It is evident from the results that a change in land use from minor anthropogenic disturbance to intensive agriculture practices and fertilizer input along with untreated urban sewage and industrial discharges has affected both total P concentrations and P lability in suspended sediments, which in turn may stimulate the eutrophication process. The comparison of individual P fractions at sub-catchment scale and in sediment along Guaporé river continuum and native forest indicated this impact more pronounced. Being the highly productive soils of the region, maintaining adequate soil solution P concentration is difficult in these soils due to the presence of high Fe/Al oxy-hydroxides and high affinity clay fraction (Bortoluzzi et al., 2015; Fink et al., 2016). Therefore, in these soils the mean annual P addition as external P source have been relatively high (80 kg P $ha^{-1}$) to counteract the P immobilization effects into inorganic and organic P forms (Rheinheimer and Anghinoni, 2001, 2003; Rheinheimer et al., 2008; Rodrigues et al., 2015). This have increased the top soil bioavailable P ($P_{AER}$) as much as 70 mg kg$^{-1}$ (i.e.,, Pellegrini et al., 2010) to 118.2 mg kg$^{-1}$ (this study) in the regional soils.

In most of sediments measured, the bioavailable P ($P_{AER}$) was increased between 22 to 108% over the native forest soil, showing the high external P inputs in intensive agriculture sediments over forest. In the sediments from urban area, the highest labile P contents was due to addition of high volume of untreated sewage from Marau city into river and similar findings were recorded by the Pagliosa et al. (2005) who noted significant higher bioavailable P in sediments from urban areas than the non-urbanized area. The similar pattern of available P in sediments due to sewage addition was recorded by the Jarvie et al. (2006) and Filho et al. (2015). The higher concentration of bioavailable P in sub-catchments under CT may be directly attributed to the high input of external P fertilizers with tobacco cultivation, as evidenced in other studies (Pellegrini et al., 2010; Wang, 2012; Bortoluzzi et al., 2013). The relatively high valuesof $P_{AER}$ in sub4 than the forest may also be attributed to legacy P as resultof P accumulation in soil surface due to successive manure and chemical fertilizer application(Guardini et al., 2012; Couto et al., 2015). The high $P_{AER}$ in the river sediments show a continuum input along the river.

Several other studies have confirmed the overall increase in soil labile P ($P_{BIC}$) pool due to P fertilization (Couto et al., 2015; Cade-Menun et al., 2015), soil and crop management (Saavedra et al., 2007; Guardini et al., 2012; Tiecher et al., 2012; Fink et al., 2016), which resultantly control the subsequent transfer of sediment bound P from these land uses to river waters.

Among the soil chemical properties, high concentrations of labile P fraction in sediments were accompanied by high $Fe_{ox}$ and $Fe_{dcb}$ ($p < 0.01 = 0.75$ and 0.69) indicating that Fe oxide directly control the bioavailable sediment P (Fig. 3, 4; Table 3) and these results are in agreement to those of Pellegrini et al. (2010).

At all monitored stations, most of the sediment P (> 90%) was found as moderately labile and non-labile forms. The highest concentration of $Pi_{HID-0.1}$ present in the NT (sub4), urban (sub5), and main river sediments receiving high diffuse P sources might be attributed to the presence of high iron oxides when compared to the sub-catchments under CT (Table 3) although a significant coorelation with TOC was also observed. The P-HCl showed a clear influence of anthropic activity and presence of significantly higher HCl bound P in urban, intensive agriculture (both CT and NT), and main river sediments is a result from the largeamount of sewage carrying contaminants from sewage, phosphogypsum from household or industry and calcite from farm land as drainage area increases towards outlet. These results are in accordance with the findings of Negassa and Leinweber (2009); Hund et al. (2013) and Lehtoranta et al. (2015) which explains the relative inefficiency of land use on the added P in soil, and carbon regulation on P pools.

The results about the non-labile pool indicate that it was the exceptionally high (> 50% of TP) in the sediments studied, however the relative proportion was a little higher for downstream sediments. The intensive agriculture and highly anthropic sediments (i.e., sub3, sub4 and sub5; and main river sediments) showed high fraction of $Pi_{HID-0.5}$ and residual P than the less anthropic catchments (sub1, sub 2 and forest). This increase in $Pi_{HID-0.5}$ is result of intensive agriculture and high P inputs. None of the land use affected the residual P and it showed approximately 30% of TP in either sediment. It is evident that, this residual P shows permanently occluded with Fe/Al oxy-hydroxides or as stable Po within inositol. This highly recalcitrant P can be attributed to the typical pedo-climatic nature of these highly weathered soils and sediments (Bortoluzzi et al., 2013; Fink et al., 2016).

Organic P forms also represented an important proportion of total P (7 to 13%) across different land use sediments. Nonetheless, the increase in amount of organic P was more obvious in NaOH both in moderately and non-labile P pools. Similar results were observed by

Rheinheimer et al. (2002); Tiecher et al. (2012) and Cade-Menun et al. (2015) and are explained by the formation of Fe/Al-P complexes with humic substances under similar geomorphological and soil management systems.

### 2.5.2 Temporal trends of P lability

The temporal P lability pattern indicated that the urban sub5 though showed highest labile P than any other land use, however, there was no clear distribution pattern with labile P which reflects the similar rate of annual P inputs to river. Similar results in higher bioavailable P concentration was recorded by the Pagliosa et al. (2005); Jarvie et al. (2006); and Filho et al. (2015) in urban environment sediments which receive untreated city effluent. The high labile P in winter months (July to October) in intensive agriculture sediments under CT (sub3) with tobacco cultivation in same season can be related to addition of high P fertilizer on these high slope areas accompanied by high rainfall and surface runoff generating erosion with increased colloidal size transport (Pellegrini et al., 2010; Didoné et al., 2014). A similar trend in low agriculture CT sediments (i.e.,, sub1 and sub2) was also noticed though impact was less pronounced. The NT sediments showed a relatively higher labile P concentration at the end of summer months (January to April) which can be contributed to the P mineralization and high turnover of crops residues (Vu et al., 2010; Ferreira et al., 2013; Lehtoranta et al., 2015).

In the main river sediments, the P1 showed high labile P in winter months as its received the two highly P enriched headwater sediments from sub4 and sub5. The similar trends was observed along the river continuum though less pronounced except P5, who exhibited relatively lower concentration than upstream sediments. Similar observations was in P losses were recorded by the Villa et al. (2015) from a mix land use catchment.

The moderately labile P concentration in the suspended sediments was variable and significant trends was recorded (Fig. 10b) among sub-catchments as well as main river sediments. Generally, high concentrations during winter (July to October) in 2013 were recorded than those in 2014. The urban sediments (sub5) showed a continuous highest concentration of moderately labile P than any other land use throughout the sampling period, but increased concentration during high rainfall winter months are indicative of a seasonal upstream agricultural input as well. The sub-catchment under CT showed 3 fold increases during winter months when compared to reference forest sediments in both 2013 and 2014. The NT sub-catchment (sub4) did not showed a seasonal trend although higher concentration was present than forest site. These results are comparable  and in agreement with the findings of Tiessen et al. (1984) and Abdala et al. (2015) for highly weathered acidic soils and sediments where Fe and Al strongly bind inorganic P but a significant increase in organic P occurs as a result of management and adoption to NT, continuous manures or lime application thereby increasing pH. Among main river sediments, a comparable seasonal change in moderately labile P was found in upper two-third (P1, P2 and P3) sites and then a gradual decrease was recorded downstream. This trend clearly indicates the high influence of sewage P and transportation of enriched sediments with increasing drainage area (Didoné et al., 2014), and intra river P immobilization and river dilution effect to some extent while moving towards outlet.

Over the entire study period, except the slight seasonal variation in non-labile P (0.5 M NaOH and residual P) in urban (sub5) and highly input agriculture (sub3 and sub4) was indicative of recalcitrant  nature of the permanent occluded Fe or Al oxy-hydroxides P due to the geology of soils and sediments in the region (Bortoluzzi et al., 2013; Jan et al., 2015).

## 2.6 Conclusions

Catchment scale sediments studies had been used as ecological and environmental indicators due to their capacity to bind anthropically enriched P entering into freshwater rivers. The TP, individual P fraction and pooled P lability varied both spatially and temporally among land use and main river stations under varying anthropic pressure. The land use and management, sediment chemical constituent and catchment geomorphic feature appeared as akey driver of P lability. The inter sub-catchments comparison for TP and P lability indicated a sequence as sub5 (urban) > sub3 (intensive agriculture under CT) > sub4 (intensive agriculture under NT) > both sub1 and sub2 (low agriculture under CT) > forest. These spatial variations between the sub-catchments are attributed mainly to characteristics land use patterns, intensive agriculture, soil management system, sediment chemical composition and particle size distribution. The slope, drainage characteristics, and high rainfall were also key factors contributing to these changes. Among sub-catchment, three most impaired sediments viz. sub5, sub3, and sub4 were identified as critical P contributing areas with high proportions of both P lability and higher variability in individual P fractions. Due to the upstream presence of two highly headwater polluted sub-catchments, the first monitoring station (P1) showed highest concentrations of the P lability and P fractions and a gradually decreasing trend along river continuum was observed with few high episodic P lability. The higher bioavailable P concentration in winter months also provide a useful insight that how organic carbon regulated sediment P biogeochemistry in the presence of high Fe/Al affinity to bind P. This study provides primary results on continuous monitoring of river sediment P lability and can provide useful information on identification of potential of land use, management system and fertilization strategies to the regional scale catchment P management perspective to minimize urban and agricultural based inputs of P-enriched sediment to the river systems.

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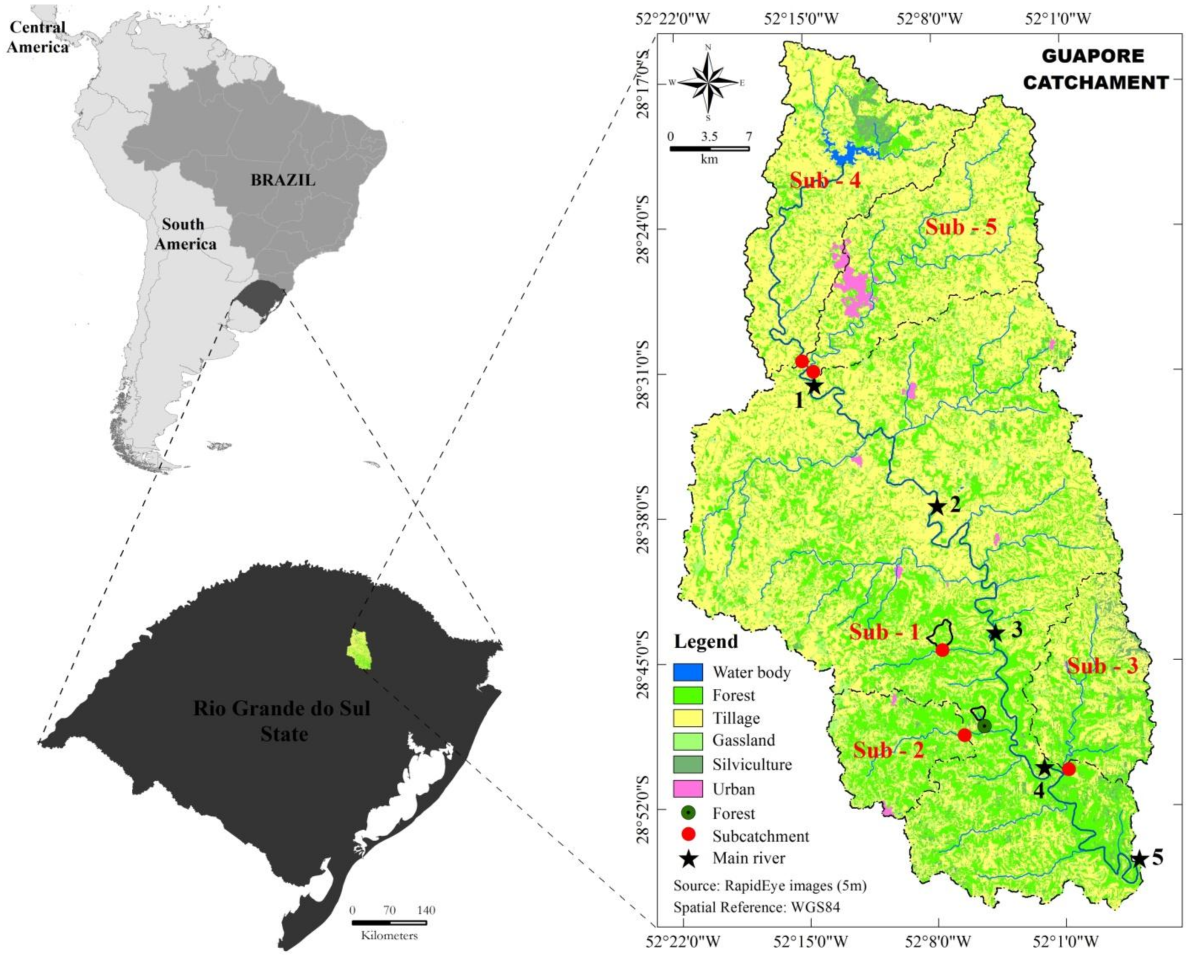

Source: RapidEye images (5m)
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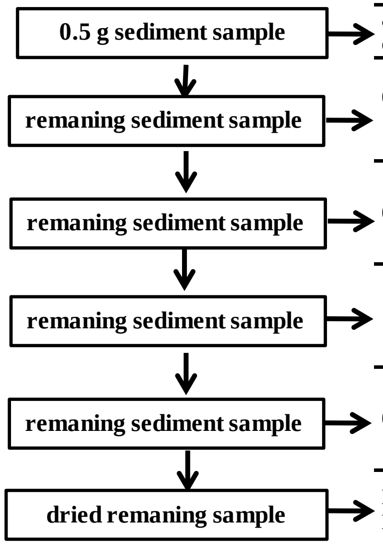
**Fig. 1.** Geographical location of the study catchment Guaporé in the Rio Grande do Sul State, Southern Brazil. The right-side map summarizes the location and land use of monitoring points.



| ¶Extractant | Equilibration | Fraction | Targeted P forms |
|---|---|---|---|
| anion exchange resin- $P_{AER}$ (2.0 $cm^2$ area) in deionized water | 16 h | Bioavailable P | It extracts labile inorganic P readily diffusing into solution using a resin membrane. |
| 0.5 mol $L^{-1}$ $NaHCO_3$ at pH 8.5 ($P_{Bic}$)* | 16 h | Labile P | It extracts labile inorganic P ($Pi_{Bic}$) weakly adsorbed on the surface of crystalline compounds and labile organic P ($Po_{Bic}$) compounds with low recalcitrance like ribonucleic acid and glycerophosphate (Tiessen and Moir, 1993). |
| 0.1 mol NaOH $L^{-1}$ ($P_{HID\text{-}0.1}$)* | 16 h | Moderately labile P | It removes moderately labile inorganic P ($Pi_{HID\text{-}0.1}$) strongly adsorbed onto Fe and Al and clay minerals (Hedley et al., 1982), and moderately labile organic P ($Po_{HID\text{-}0.1}$) mainly associated with fulvic and humic acids adsorbed on to mineral and SOM surfaces (Linquist et al., 1997). |
| 1.0 mol HCl $L^{-1}$ ($P_{HCl}$) | 16 h | Moderately labile inorganic P (principally Ca associated) | The moderately labile inorganic P associated with apatite and other sparingly-soluble Ca-P compounds or negatively charged oxide surfaces was extracted as shown by Gatiboni et al. (2007). |
| 0.5 mol NaOH $L^{-1}$ ($P_{HID\text{-}0.5}$)* | 16 h | Recalcitrant P | The more recalcitrant forms of inorganic P ($Pi_{HID\text{-}0.5}$) associated with Fe. Al and clay minerals and non-labile forms of organic P ($Po_{HID\text{-}0.5}$) associated with fulvic and humic acids inside aggregates were quantified (Condron et al., 1985). |
| $H_2SO_4$ + $H_2O_2$ with saturated $MgCl_2$ | 2 h at 250 °C | Residual P | The residual P was obtained after the remaining sediment was dried at 50 °C, milled and digested with $H_2SO_4$+$H_2O_2$ in the presence of saturated $MgCl_2$ as described by Olsen and Sommers (1982). |

¶The P fractions presented are a result of extracting sediment sample with solutions of increasing strength in order to solubilize P from more labile to more stable as mentioned by Hedley et al. (1982) with modifications suggested by Condron et al. (1985).

*To determine total P (Pt) in alkaline extracts ($NaHCO_3$ and HaOH) were digested according to USEPA (1971) and then solution concentration was determined colorimetrically (Murphy and Riley, 1962). The inorganic P ($P_i$ in the alkaline extracts was determined by method of Dick and Tabatabai (1977) and organic P ($P_o$) was calculated as the difference of $P_t - P_i$.

**Fig. 2.** Modified Hedley sequential P fraction scheme and extracted target P forms released during the chemical P fractionation procedure of suspended sediments.

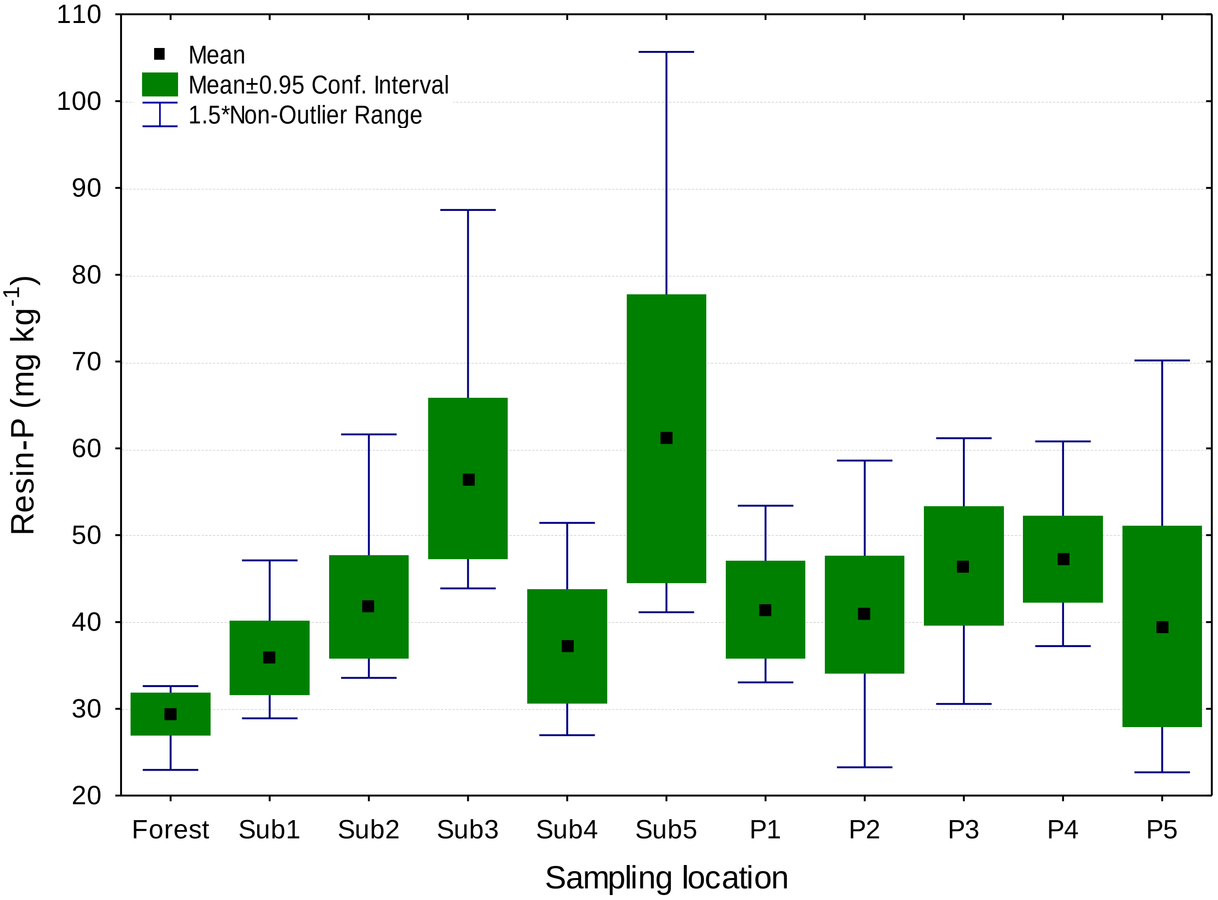


**Fig. 3.** Changes in anion exchange resin extractable P contents of suspended sediments collected across eleven different sampling locations in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (*n* = 30).

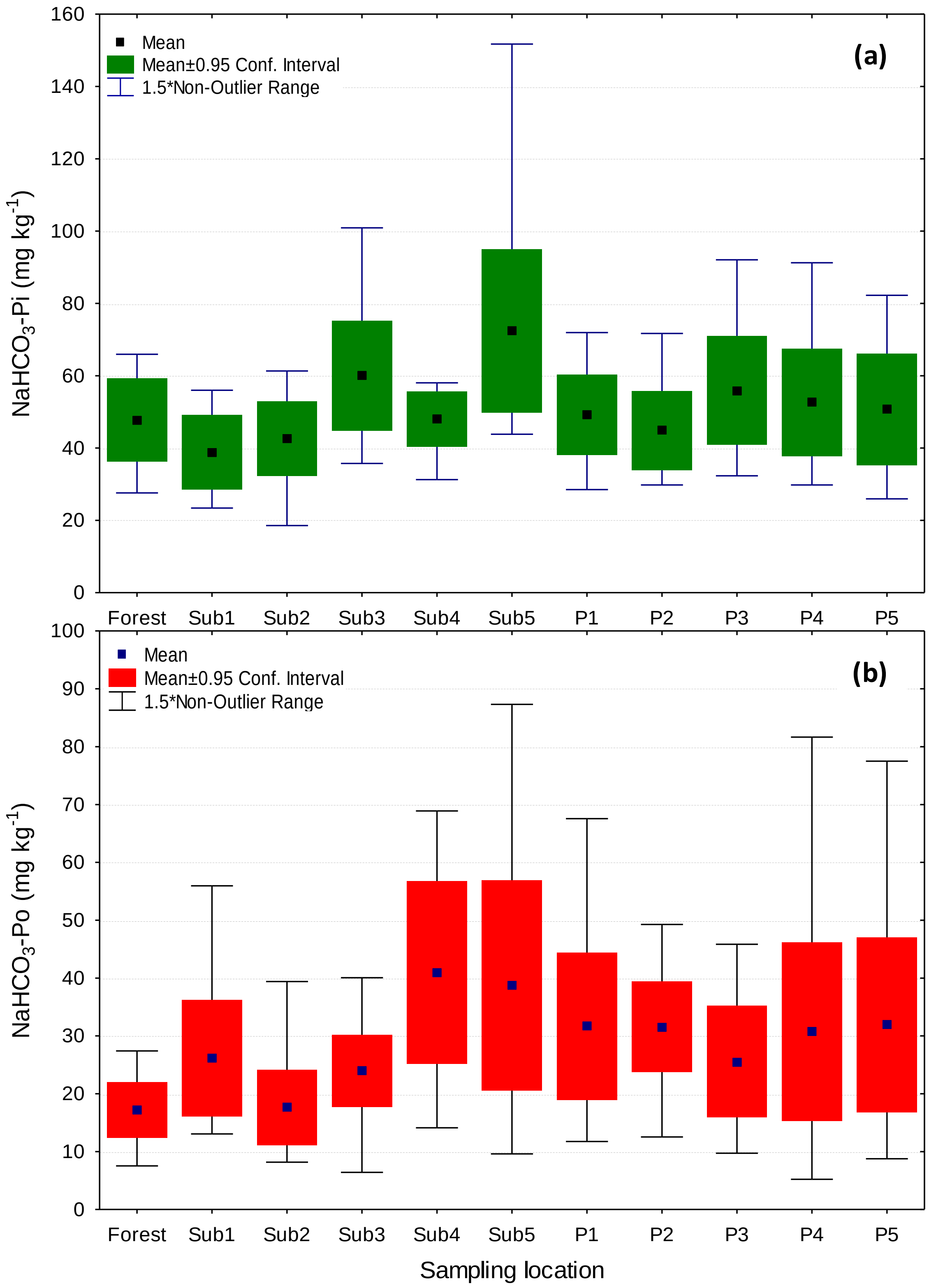


**Fig. 4.** Changes in sodium bicarbonate extractable inorganic P (a) and organic P (b) contents of suspended sediments collected across eleven different sampling locations in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (n = 30)

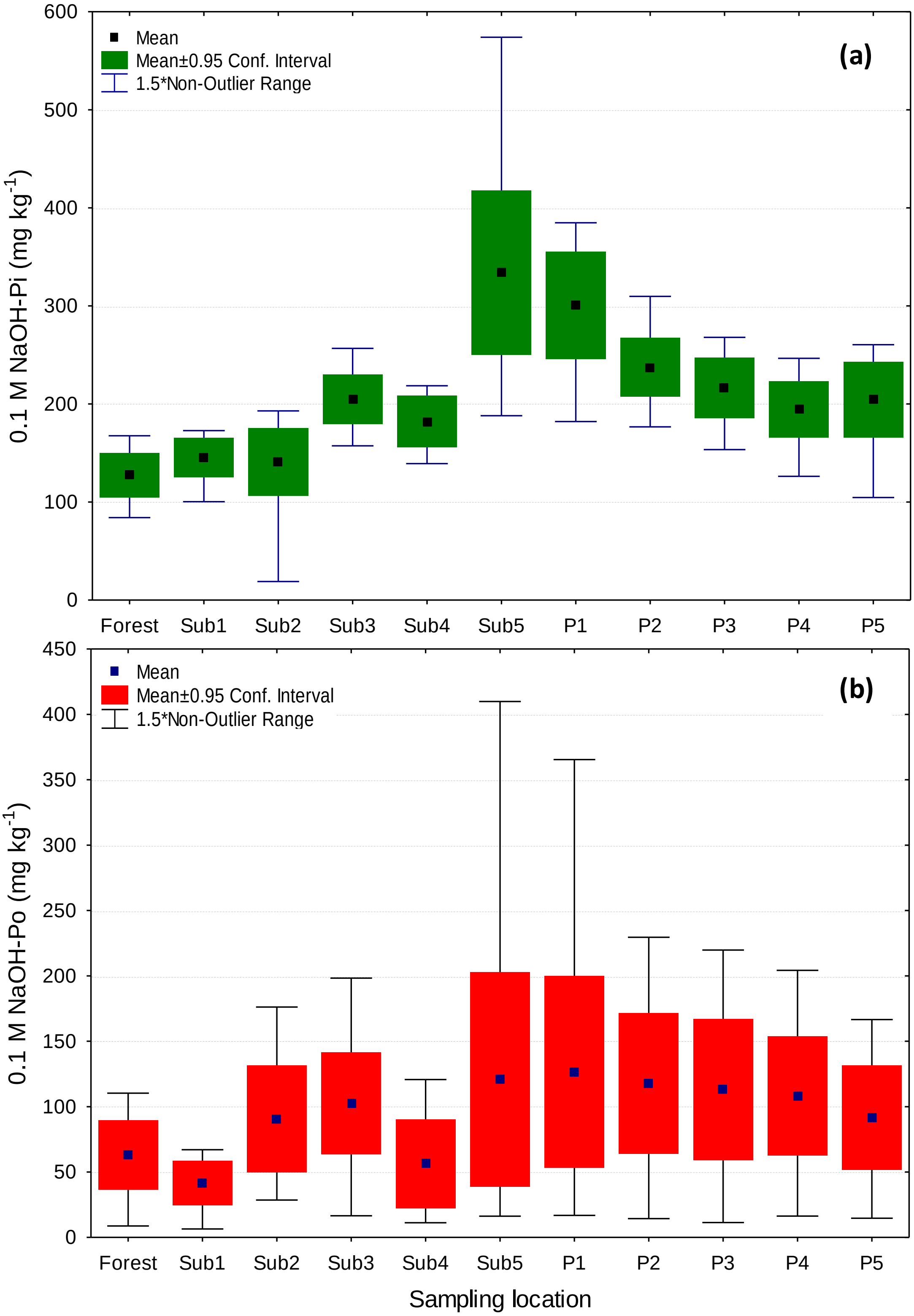


**Fig. 5.** Changes in 0.1 molar sodium hydroxide extractable inorganic P (a) and organic P (b) contents of suspended sediments collected across eleven different monitoring locations in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (n = 30).

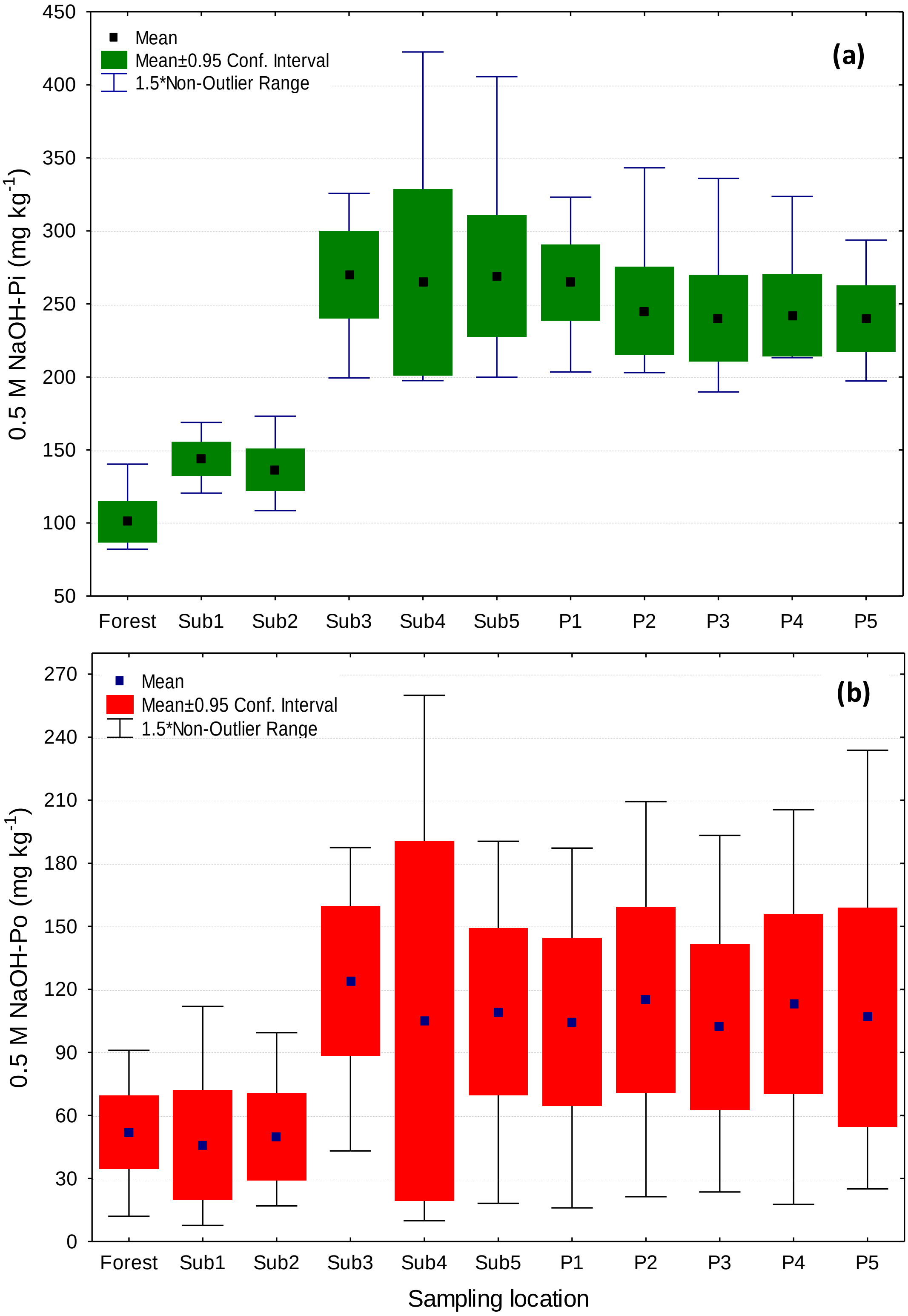


**Fig. 6.** Changes in 0.5 molar sodium hydroxide extractable inorganic P (a) and organic P (b)contents of suspended sediments collected across eleven different monitoring locations in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (n = 30).

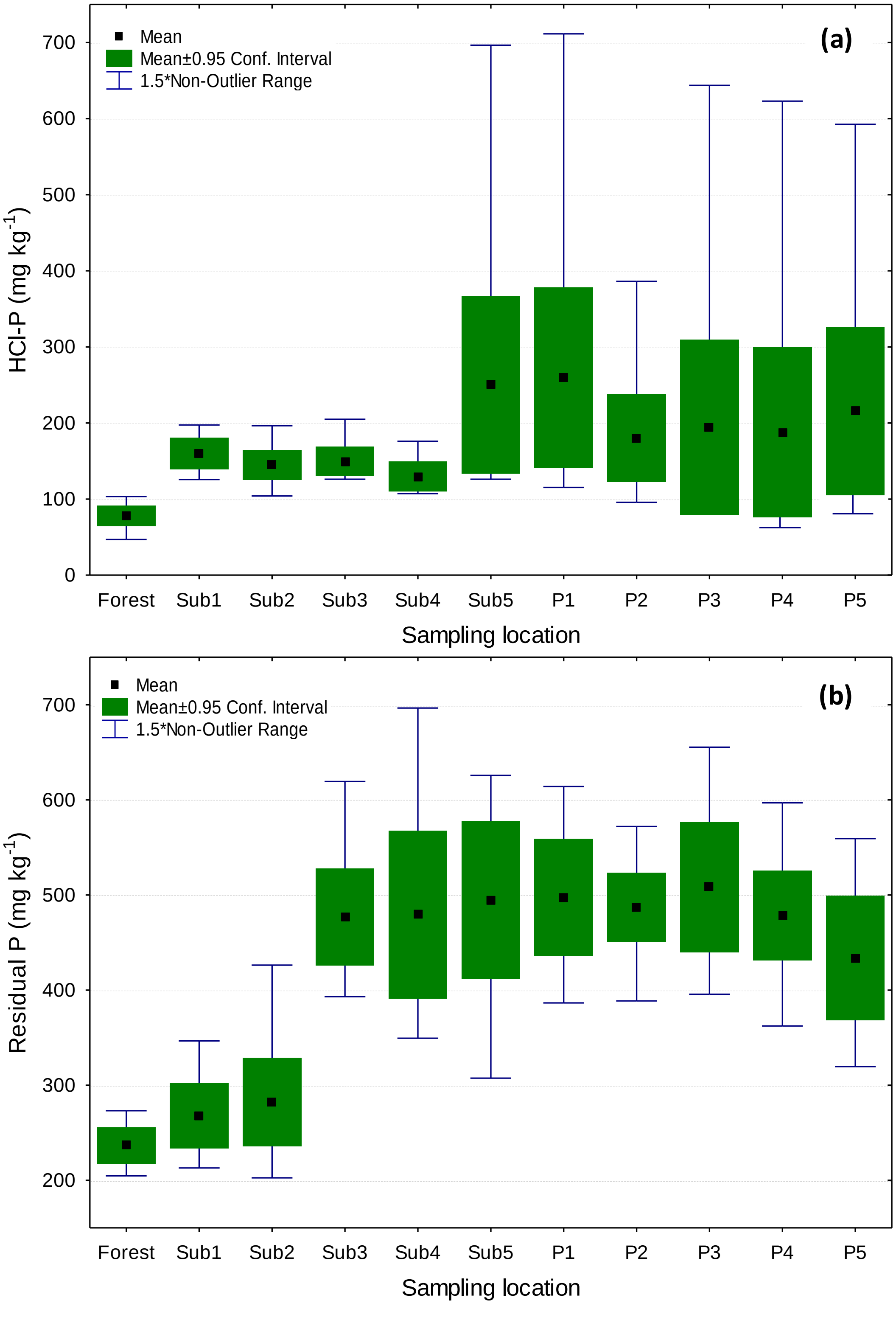


**Fig. 7.** Changes in hydrochloric acid extractable (a) and residual P (b) contents of suspended sediments collected across eleven different monitoring locations in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (n = 30).

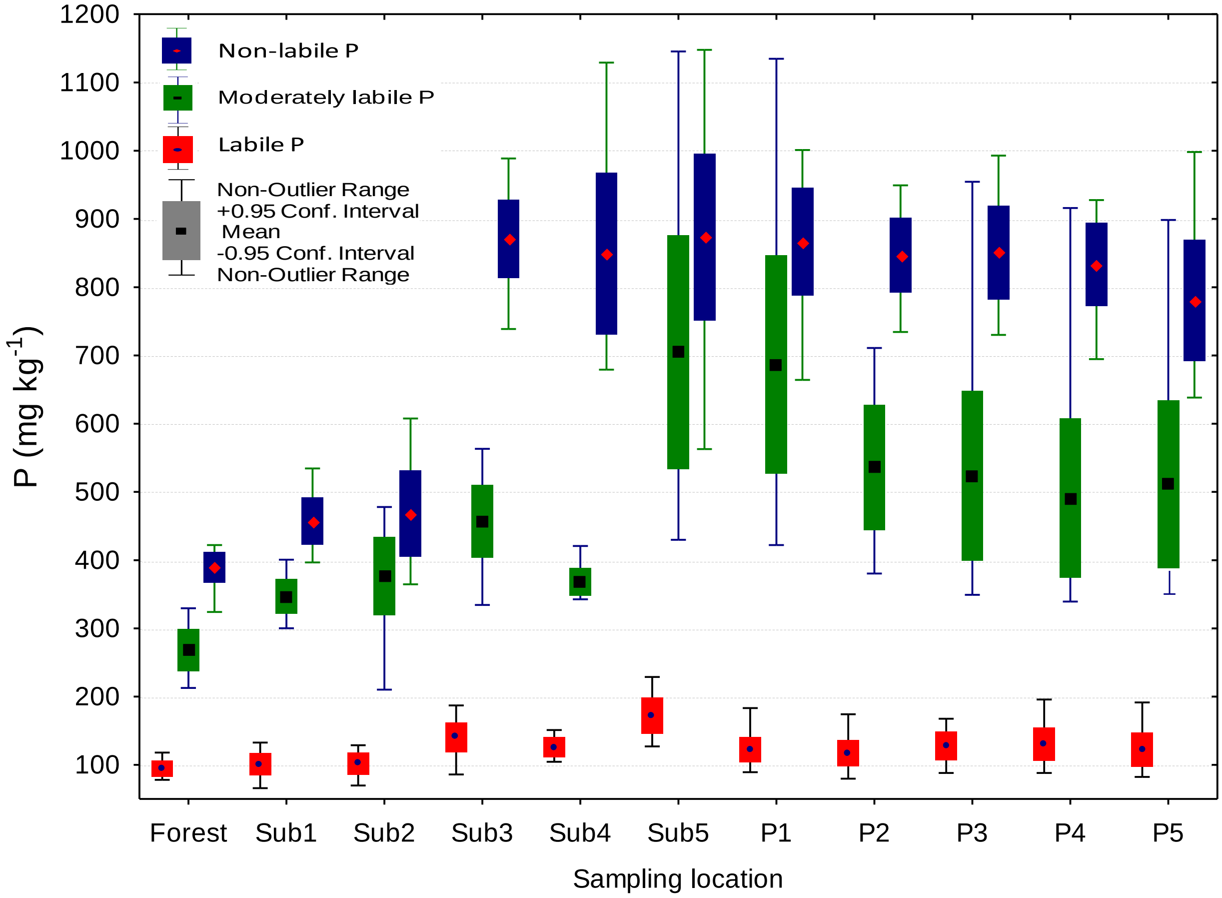


**Fig. 8.** The cumulative pattern of changes in labile P, moderately labile P and non- labile P pools in suspended sediments collected across eleven different monitoring locations in Guaporé catchment Southern Brazil, between October 2012 to October 2014 (n = 30).

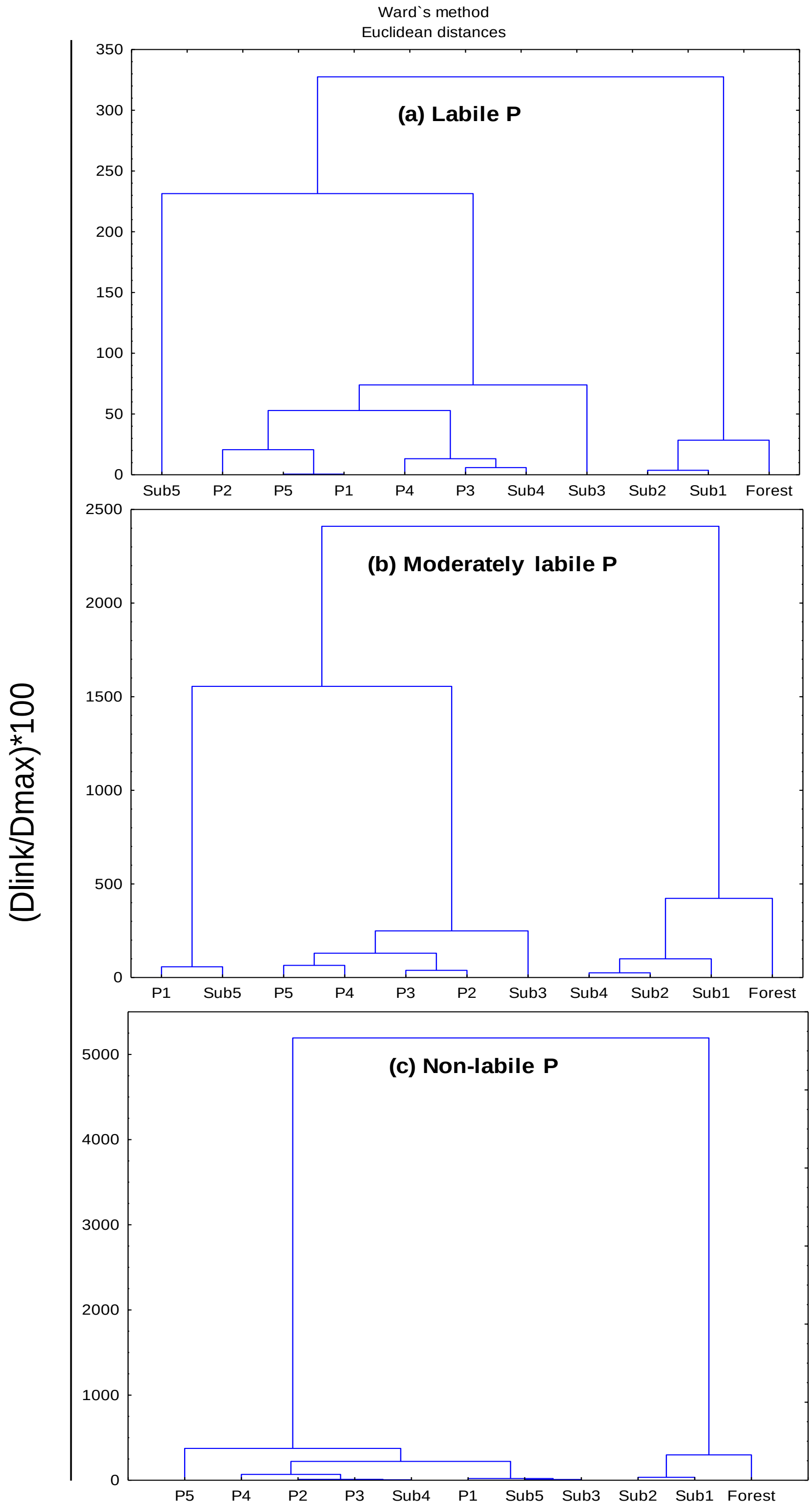


**Fig. 9.** Hierarchical cluster diagram of monitoring sites by Wards method as linkage method and Euclidean distance matrix (the distances reflect the degree of association between different monitoring locations based on the dissimilarity) of labile P (a), moderately labile P (b) and non- labile P (c) of suspended sediments.

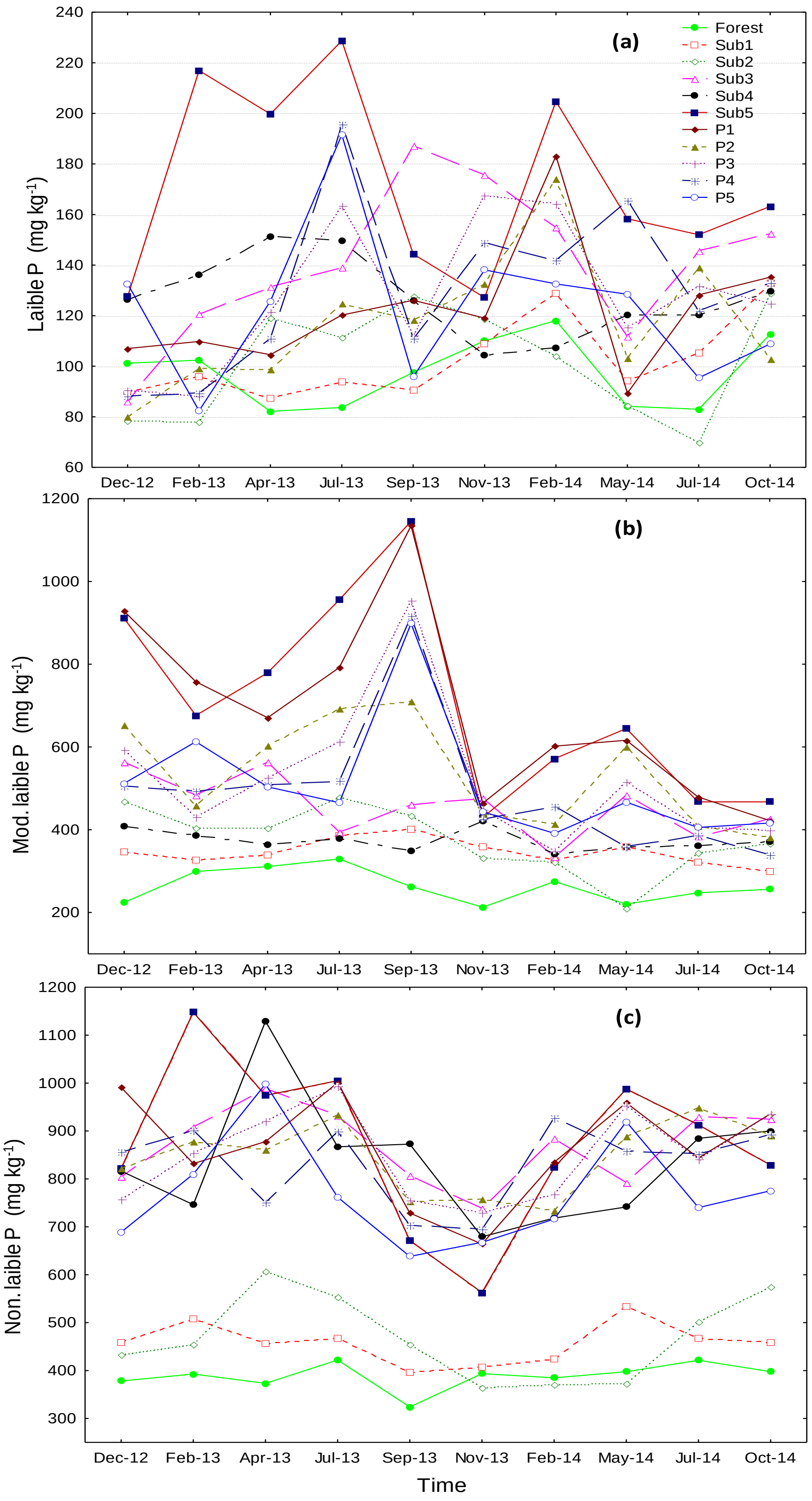
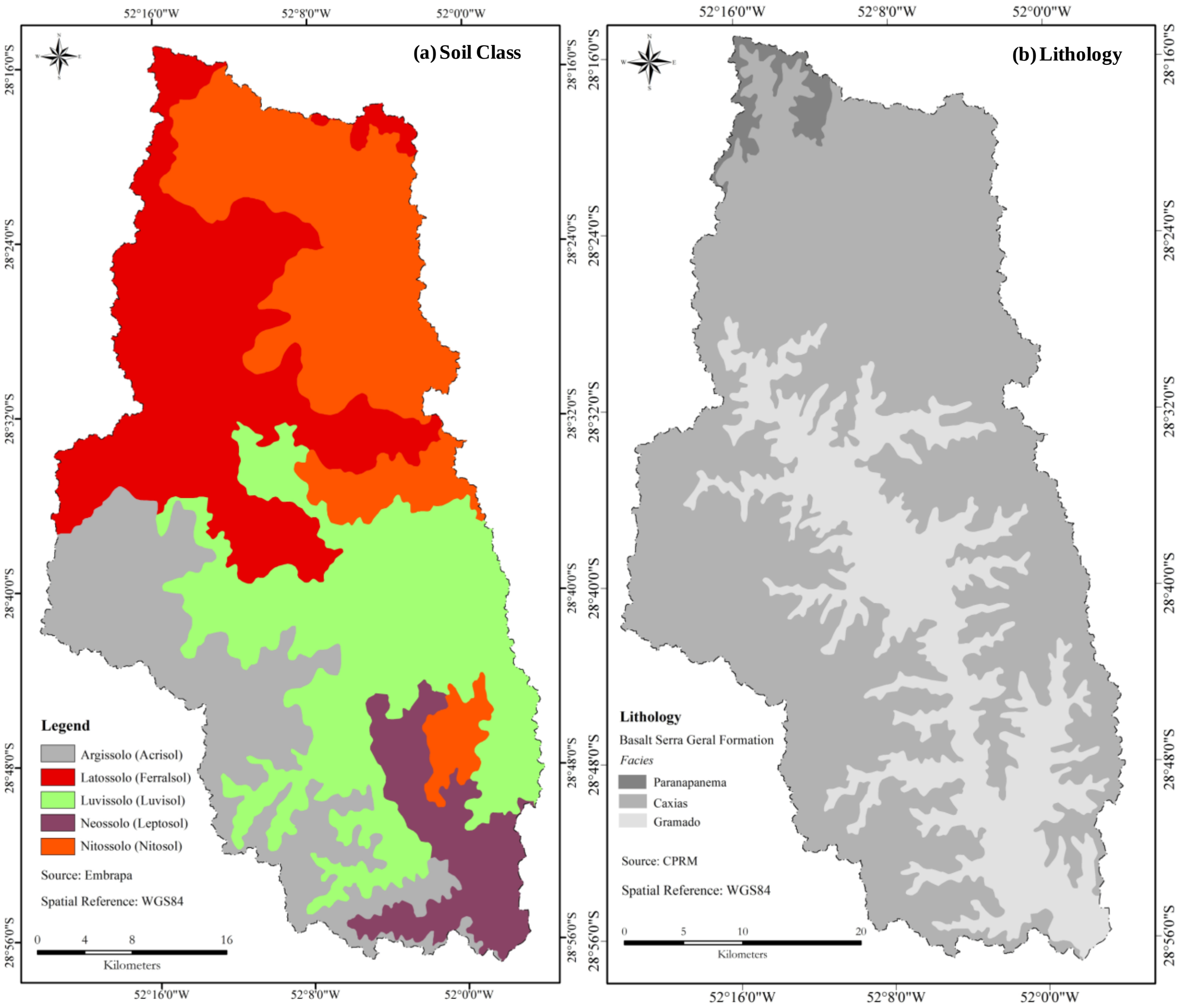
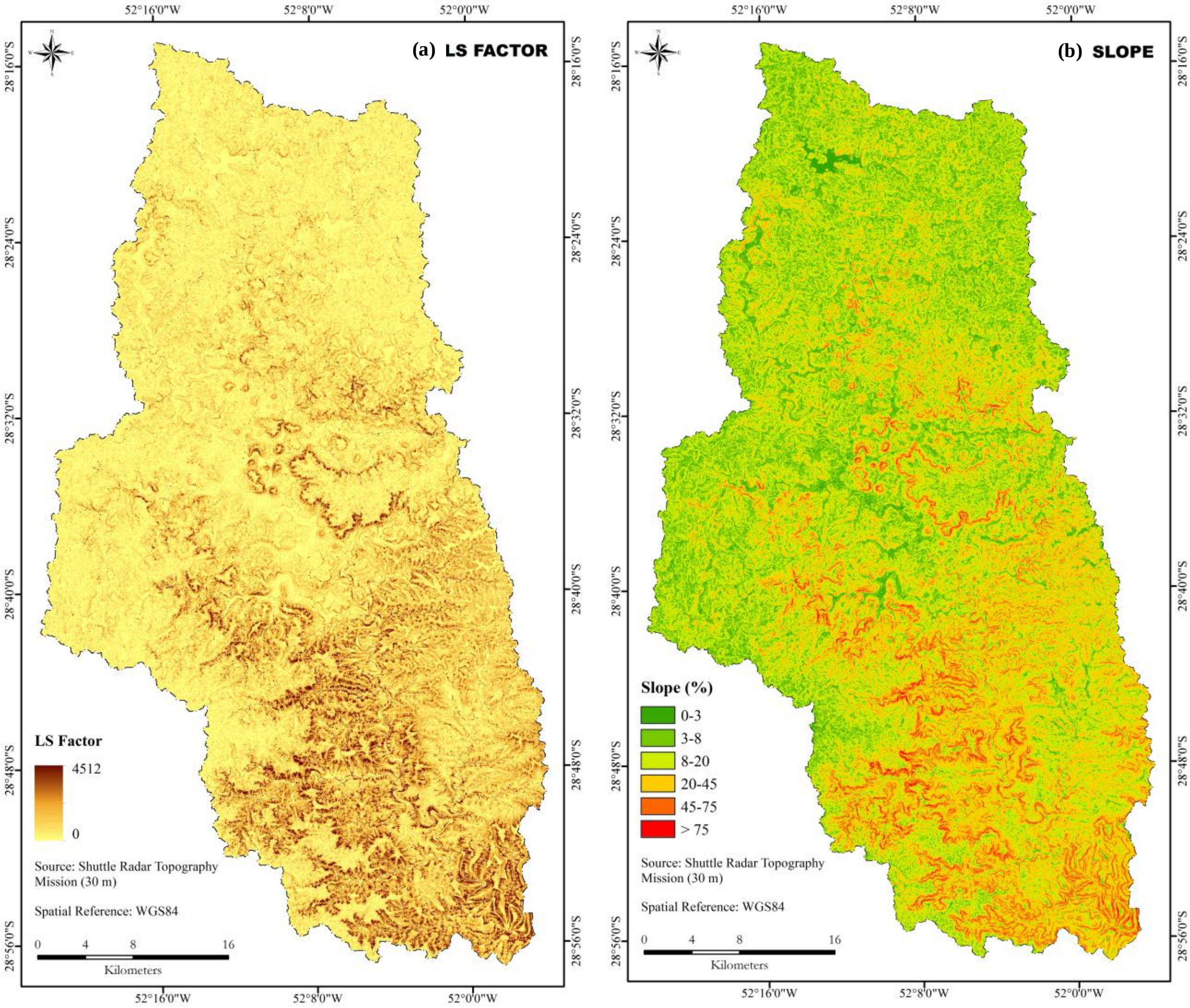


**Fig. 10.** Temporal changes in labile P (a), moderately labile P (b), and non- labile P (c) pools of suspended sediments (*n* = 3).



**Supplementary Fig. 1.** Major soil classes (a) and lithology (b) distribution of the study catchment Guaporé in the Rio Grande do Sul State, Southern Brazil.



**Supplementary Fig. 2.** The LS factor (a) and slope (b) variation in the study catchment Guaporé in the Rio Grande do Sul State, Southern Brazil.

**Table 1.** General characteristics of the monitoring locations in the Guaporé catchment, Southern Brazil.

| **Monitoring location** | **Area ($km^2$)** | **Coordinates** | | **Dominant soil type**[b] | **Farming system and land-use** [c] | **Land use (%)** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **E** | **S** | | | **Waterbodies** | **Arable** | **Forest** | **Pasture** | **Silviculture** | **Urban** |
| Forest | 0.998 | 393475 | 6814063 | Luvissolo | Forest, with few pasture and minimum anthropic disturbance | 0.0 | 0.0 | 68.4 | 29.5 | 2.2 | 0.0 |
| Sub1 [a] | 3.29 | 389998 | 6820260 | Argiossolo | Newly established low arable with maize under CTS, no swine/poultry | 0.0 | 34.5 | 57.9 | 7.0 | 0.7 | 0.0 |
| Sub2 | 99.04 | 391861 | 6812458 | Luvissolo | 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 | 401071 | 6809790 | Nitossolo | Intensive arable with tobacco and CTS, low poultry + beef | 0.1 | 49.6 | 37.0 | 4.6 | 8.7 | 0.0 |
| Sub4 | 269.39 | 377260 | 6846103 | Latossolo | 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 | 378257 | 6845049 | Argiossolo | 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 | 377786 | 6844236 | Latossolo | 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 | 389008 | 6832785 | Latossolo | Diffuse with intense swine production areas | 0.6 | 68.7 | 21.3 | 5.6 | 2.6 | 1.2 |
| P3 | 1441.38 | 394744 | 6821782 | Luvissolo | Diffuse with mix land-use and dairy + poultry | 0.5 | 66.2 | 24.2 | 5.8 | 2.3 | 0.9 |
| P4 | 1697.67 | 400749 | 6809187 | Neossolo | Diffuse with tobacco under CTS | 0.5 | 61.5 | 28.5 | 6.2 | 2.4 | 0.9 |
| P5 | 2029.91 | 407170 | 6801390 | Neossolo | 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] World Reference Base for Soil Resources (IUSS Working Group, 2006) .

[c] CTS= conventional tillage system; NTS= no-tillage system.

**Table 2.** The difference in average phosphorus fractions of suspended sediments and chemical properties from different land uses over monitoring period in Guaporé catchment by the Kruskal–Wallis *H*-test ($n = 30$).

| **P fraction**[s] (mg kg$^{-1}$) | **Monitoring locations** | | | | | | | | | | | **Kruskal–Wallis test** | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Forest | Sub1 | Sub2 | Sub3 | Sub4 | Sub5 | P1 | P2 | P3 | P4 | P5 | *p*-value[c] | *H*-value | Significance[d] |
| $P_{AER}$ | 29.4 ± 3.0 | 35.8 ± 5.2 | 41.7 ± 8.3 | 57.9 ± 12.9 | 37.6 ± 6.9 | 61.0 ± 23.2 | 40.1 ± 7.9 | 41.4 ± 9.4 | 46.9 ± 9.6 | 47.4 ± 7.0 | 39.5 ± 14.2 | **0.0001** | 47.6 | **** |
| $Pi_{BIC}$ | 47.8 ± 14.1 | 38.8 ± 12.4 | 44.2 ± 149.1 | 62.7 ± 21.2 | 48.6 ± 8.0 | 75.4 ± 31.6 | 50.7 ± 15.4 | 46.3 ± 15.3 | 58.1 ± 21.0 | 54.4 ± 20.7 | 50.7 ± 18.9 | **0.0849** | 16.5 | * |
| $Po_{BIC}$ | 17.2 ± 5.9 | 26.1 ± 12.4 | 18.7 ± 9.1 | 25.9 ± 6.8 | 39.2 ± 16.6 | 40.8 ± 25.4 | 33.2 ± 17.8 | 33.7 ± 10.9 | 27.2 ± 13.4 | 33.6 ± 21.6 | 31.9 ± 18.6 | **0.0301** | 19.9 | ** |
| $Pi_{HID-0.1}$ | 127.3 ± 27.7 | 145.4 ± 24.6 | 138.0 ± 48.0 | 202.1 ± 35.2 | 183.6 ± 27.8 | 343.4 ± 117.0 | 298.1 ± 76.4 | 236.4 ± 41.8 | 215.9 ± 43.2 | 189.9 ± 40.0 | 204.3 ± 47.3 | **0.0001** | 62.6 | **** |
| $Po_{HID-0.1}$ | 63.1 ± 32.4 | 41.4 ± 20.7 | 86.1 ± 56.9 | 97.9 ± 54.2 | 51.2 ± 35.7 | 88.5 ± 114.6 | 100.0 ± 102.3 | 105.3 ± 75.0 | 104.1 ± 75.6 | 109.3 ± 63.6 | 91.5 ± 48.9 | 0.1304 | 15..1 | ns |
| Pi-HCl | 77.7 ± 16.4 | 159.9 ± 25.6 | 142.2 ± 27.6 | 145.3 ± 26.4 | 132.5 ±20.7 | 249.9 ± 162.8 | 261.8 ± 165.7 | 181.2 ± 80.1 | 196.1 ± 160.9 | 190.0 ± 156.2 | 215.5 ± 135.2 | **0.0001** | 46.8 | **** |
| $Pi_{HID-0.5}$ | 101.0 ± 17.3 | 143.9 ± 14.3 | 136.3 ± 20.2 | 268.6 ± 41.7 | 259.2 ± 67.3 | 272.7 ± 58.1 | 263.4 ± 36.4 | 244.2 ± 42.2 | 238.2 ± 41.4 | 241.5 ± 39.1 | 240.0 ± 27.7 | **0.0001** | 65.8 | **** |
| $Po_{HID-0.5}$ | 52.1 ± 21.4 | 45.8 ± 32.0 | 50.5 ± 29.1 | 123.5 ± 49.8 | 96.2 ± 49.1 | 109.0 ± 55.6 | 104.9 ± 55.7 | 119.3 ± 61.8 | 105.6 ± 55.2 | 114.4 ± 59.7 | 106.8 ± 68.8 | **0.0057** | 24.8 | *** |
| Residual-P | 236.6 ± 23.4 | 267.7 ± 41.7 | 285.7 ± 65.0 | 486.2 ± 71.2 | 481.7 ± 92.9 | 497.7 ± 115.8 | 484.7 ± 85.9 | 486.2 ± 50.6 | 517.4 ± 95.7 | 475.3 ± 65.7 | 433.9 ± 80.2 | **0.0001** | 60.8 | **** |
| TP | 752.2 ± 43.1 | 905.1 ± 35.4 | 943.3 ± 153.6 | 1470.1 ± 89.1 | 1329.9 ± 134.6 | 1738.5 ± 321.3 | 1636.8 ± 247.1 | 1494.0 ± 135.6 | 1509.5 ± 180.9 | 1455.7 ±137.6 | 1414.2 ± 153.5 | **0.0001** | 72.8 | **** |
| **Chemical attributes**[b] (g kg$^{-1}$) | | | | | | | | | | | | | | |
| TOC | 20.3 ± 4.2 | 21.0 ± 3.5 | 31.8 ± 10.5 | 34.9 ± 7.9 | 30.5 ± 6.4 | 33.5 ± 7.4 | 36.5 ± 7.1 | 39.0 ± 12.7 | 35.8 ± 13.4 | 32.7 ± 4.4 | 32.9 ± 7.8 | **0.0001** | 45.8 | **** |
| $Fe_{ox}$ | 4.1 ± 1.1 | 5.8 ± 0.9 | 6.1 ± 1.0 | 7.2 ± 0.9 | 7.2 ± 0.6 | 7.4 ± 0.9 | 7.8 ± 0.7 | 7.8 ± 0.5 | 7.3 ± 0.7 | 7.1 ± 0.8 | 7.4 ± 1.2 | **0.0001** | 56.6 | **** |
| $Fe_{dcb}$ | 33.9 ± 1.4 | 41.4 ± 3.8 | 45.4 ± 7.1 | 45.7 ± 6.1 | 46.6 ± 3.3 | 51.2 ± 12.2 | 46.2 ± 5.3 | 43.9 ± 1.4 | 43.6 ± 2.2 | 43.1 ± 1.2 | 43.0 ± 1.3 | **0.0001** | 46.9 | **** |
| $Al_{ox}$ | 1.2 ± 0.3 | 1.4 ± 0.3 | 2.0 ± 0.7 | 1.6 ± 0.5 | 1.7 ± 0.3 | 2.2 ± 0.6 | 1.4 ± 0.6 | 1.5 ± 0.4 | 1.5 ± 0.4 | 1.4 ± 0.5 | 1.5 ± 0.4 | **0.0035** | 26.2 | *** |
| $Al_{dcb}$ | 3.1 ± 0.5 | 3.9 ± 0.8 | 5.2 ± 1.6 | 4.5 ± 1.2 | 4.7 ± 0.8 | 5.6 ± 1.3 | 3.9 ± 1.4 | 4.3 ± 0.9 | 4.2 ± 1.0 | 4.0 ± 1.0 | 4.3 ± 0.9 | **0.0008** | 30.3 | **** |
| Clay | 43.8 ± 6.3 | 103.4 ± 33.8 | 105.9 ± 27.6 | 128.3 ± 38.6 | 86.1 ± 16.6 | 97.9 ± 35.0 | 94.6 ± 25.5 | 98.3 ± 23.4 | 92.1 ±19.2 | 91.6 ± 23.1 | 95.8 ± 23.6 | **0.0001** | 36.2 | **** |
| Sand | 289.9 ± 75.8 | 239.4 ± 69.8 | 277.7 ± 77.7 | 274.8 ± 71.4 | 322.6 ± 56.7 | 327.3 ± 78.6 | 280.8 ± 69.6 | 304.6 ± 68.1 | 324.0 ± 86.8 | 302.3 ± 79.6 | 310.6 ± 72.6 | 0.2996 | 11.8 | ns |

[a] $P_{AER}$; anion exchange resin extractable P; $Pi_{BIC}$, 0.5 M sodium bicarbonate extractable inorganic P; $Po_{BIC}$, 0.5 M sodium bicarbonate extractable organic P; $Pi_{HID-0.1}$, 0.1 M sodiumhy droxide-extractable inorganic P; $Po_{HID-0.1}$, 0.1 M sodium hydroxide-extractable organic P; Pi-HCl. 1.0 M hydrochloric acid-extractable P; $Pi_{HID-0.5}$, 0.5 M sodium hydroxide-extractable inorganic P; $Po_{HID-0.5}$, 0.5 M sodium hydroxide-extractable organic P; and TP, total P.

[b] 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.

[c] Bold values indicate significant differences between the monitoring stations by the Kruskal–Wallis *H*-test at $p < 0.05$.

[d] ns, not significant; *$p < 0.1$; **$p < 0.05$; ***$p < 0.01$; ****$p < 0.001$.

**Table 3.** Pearson correlation coefficient (*r*-value) and significance (*) among sediment P fractions and soil variables in Guaporé catchment (*n* = 30).

| Parameters[a] | P$_{\mathrm{AER}}$ | Pi$_{\mathrm{BIC}}$ | Po$_{\mathrm{BIC}}$ | Pi$_{\mathrm{HID\text{-}0.1}}$ | Po$_{\mathrm{HID\text{-}0.1}}$ | Pi-HCl | Pi$_{\mathrm{HID\text{-}0.5}}$ | Po$_{\mathrm{HID\text{-}0.5}}$ | Residual-P | TP | TOC | Fe$_{\mathrm{ox}}$ | Fe$_{\mathrm{dcb}}$ | Al$_{\mathrm{ox}}$ | Al$_{\mathrm{dcb}}$ | Clay |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Pi$_{\mathrm{BIC}}$ | 0.87*** | | | | | | | | | | | | | | | |
| Po$_{\mathrm{BIC}}$ | 0.40 | 0.44 | | | | | | | | | | | | | | |
| Pi$_{\mathrm{HID\text{-}0.1}}$ | 0.61* | 0.70* | 0.73* | | | | | | | | | | | | | |
| Po$_{\mathrm{HID\text{-}0.1}}$ | 0.52 | 0.44 | 0.16 | 0.48 | | | | | | | | | | | | |
| Pi-HCl | 0.47 | 0.44 | 0.64* | 0.85*** | 0.53 | | | | | | | | | | | |
| Pi$_{\mathrm{HID\text{-}0.5}}$ | 0.65* | 0.61* | 0.82** | 0.75** | 0.53 | 0.66* | | | | | | | | | | |
| Po$_{\mathrm{HID\text{-}0.5}}$ | 0.62* | 0.60 | 0.66* | 0.65* | 0.71 | 0.55 | 0.93*** | | | | | | | | | |
| Residual-P | 0.62* | 0.61* | 0.76** | 0.72* | 0.62 | 0.62* | 0.97*** | 0.94*** | | | | | | | | |
| TP | 0.69* | 0.69* | 0.78** | 0.88*** | 0.66 | 0.80** | 0.95*** | 0.91*** | 0.95*** | | | | | | | |
| TOC | 0.56 | 0.41 | 0.48 | 0.63* | 0.83** | 0.61* | 0.79** | 0.82** | 0.84** | 0.83** | | | | | | |
| Fe$_{\mathrm{ox}}$ | 0.53 | 0.38 | 0.75** | 0.70* | 0.59 | 0.76** | 0.92*** | 0.83** | 0.90*** | 0.91*** | 0.89*** | | | | | |
| Fe$_{\mathrm{dcb}}$ | 0.73* | 0.57 | 0.69* | 0.72* | 0.30 | 0.65* | 0.73* | 0.52 | 0.66* | 0.74** | 0.65* | 0.77** | | | | |
| Al$_{\mathrm{ox}}$ | 0.60* | 0.50 | 0.32 | 0.39 | 0.03 | 0.25 | 0.26 | 0.08 | 0.20 | 0.29 | 0.30 | 0.29 | 0.78** | | | |
| Al$_{\mathrm{dcb}}$ | 0.68* | 0.52 | 0.41 | 0.45 | 0.16 | 0.36 | 0.41 | 0.23 | 0.35 | 0.42 | 0.45 | 0.46 | 0.87*** | 0.98*** | | |
| Clay | 0.64* | 0.22 | 0.21 | 0.25 | 0.31 | 0.37 | 0.48 | 0.38 | 0.39 | 0.42 | 0.52 | 0.60 | 0.67* | 0.44 | 0.57 | |
| Sand | 0.30 | 0.55 | 0.56 | 0.45 | 0.37 | 0.27 | 0.54 | 0.56 | 0.64* | 0.57 | 0.48 | 0.43 | 0.34 | 0.31 | 0.34 | -0.24 |

[a] P$_{\mathrm{AER}}$; anion exchange resin extractable P; Pi$_{\mathrm{BIC}}$, 0.5 M sodium bicarbonate extractable inorganic P; Po$_{\mathrm{BIC}}$, 0.5 M sodium bicarbonate extractable organic P; Pi$_{\mathrm{HID\text{-}0.1}}$, 0.1 M sodium hydroxide-extractable inorganic P; Po$_{\mathrm{HID\text{-}0.1}}$, 0.1 M sodiumh ydroxide-extractable organic P; Pi-HCl. 1.0 M hydrochloric acid-extractable P; Pi$_{\mathrm{HID\text{-}0.5}}$, 0.5 M sodium hydroxide-extractable inorganic P; Po$_{\mathrm{HID\text{-}0.5}}$, 0.5 M sodium hydroxide-extractable organic P; and TP, total P; TOC, total organic carbon; Fe$_{\mathrm{ox}}$, extracted with ammonium oxalate; Fe$_{\mathrm{dcb}}$, extracted with dithionite–citrate–bicarbonate; Al$_{\mathrm{ox}}$, extracted with ammonium oxalate and Al$_{\mathrm{dcb}}$, extracted with dithionite–citrate–bicarbonate.

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

**Supplementary Table 1.** Monthly hydro sedimentological summary for the Guaporé catchment outlet (P5) between October 2012 and October 2014.

| **2012** | **Month** | **Q** **($m^3 s^{-1}$)** | **SY** **(ton $km^{-2}$)** | **EI30** **(MJ mm $ha^{-1} h^{-1}$)** | **R** **(mm)** |
|---|---|---|---|---|---|
| | 10 | 63.18 | 9.91 | 943.18 | 161.73 |
| | 11 | 13.49 | 0.02 | 200.06 | 58.31 |
| | 12 | 39.98 | 15.88 | 2024.38 | 267.32 |
| | **Total** | 27.89 | 57.42 | 9013.79 | 1541.30 |
| **2013** | 1 | 23.38 | 0.72 | 335.55 | 87.11 |
| | 2 | 19.97 | 2.68 | 933.92 | 170.83 |
| | 3 | 65.03 | 17.21 | 1145.24 | 195.36 |
| | 4 | 35.83 | 2.44 | 375.62 | 93.82 |
| | 5 | 27.73 | 3.26 | 573.36 | 123.93 |
| | 6 | 49.88 | 13.01 | 452.74 | 106.09 |
| | 7 | 34.95 | 4.62 | 256.96 | 73.09 |
| | 8 | 147.74 | 43.45 | 2256.89 | 305.25 |
| | 9 | 88.78 | 10.41 | 1198.74 | 201.32 |
| | 10 | 47.26 | 15.17 | 614.66 | 129.73 |
| | 11 | 49.82 | 13.10 | 1030.70 | 182.28 |
| | 12 | 17.11 | 0.89 | 257.21 | 73.13 |
| | **Total** | 50.81 | 126.96 | 9431.59 | 1741.94 |
| **2014** | 1 | 25.43 | 1.03 | 1008.44 | 204.34 |
| | 2 | 22.98 | 1.08 | 1084.57 | 214.36 |
| | 3 | 53.78 | 9.99 | 674.04 | 156.76 |
| | 4 | 73.53 | 27.62 | 746.41 | 167.64 |
| | 5 | 67.68 | 15.97 | 778.46 | 172.34 |
| | 6 | 192.61 | 49.47 | 2081.57 | 329.17 |
| | 7 | 100.13 | 16.29 | 591.31 | 143.82 |
| | 8 | 45.99 | 7.51 | 344.59 | 100.82 |
| | 9 | 124.90 | 50.32 | 1269.41 | 237.74 |
| | 10 | 146.95 | 35.04 | 1075.59 | 213.19 |
| | 11 | 28.54 | 1.13 | 281.22 | 88.20 |
| | 12 | 56.87 | 5.71 | 1163.89 | 224.55 |
| | Total | 78.44 | 221.14 | 11099.51 | 2252.94 |

Q - water discharge, SY- sediment yield, EI$_{30}$ - erosivity index, R- rainfall mm.

## Phosphorus storage capacity and adsorption characteristics in relation to sediment compositions

The P fractionation separates sediment P into operational fractions (labile, moderately labile and non or very reduced labile) which show variable bioavailability to the aquatic biota i.e., with varying from readily available exchangeable P, to less available aluminum P (Al-P) and organic P, to more recalcitrant calcium (Ca) and apatite P and residual P (HUND et al., 2013). However, when the river is receiving multiple P loads from the various origin, P lability does not reveal much about the source or sink behavior of sediments to the water.

The physicochemical characteristics of sediments are very important to regulate sediment P bioavailability to algae, and P release potential has been documented already at the sediment–water interfaces (PAN; REDDY, 2003; SONDERGAARD et al., 2003). P adsorption and desorption on sediments are influenced by the initial P, particle size, organic matter, ionic strength, Fe- and Al-oxides and the cation exchange capacity (CEC) (WANG et al., 2006)

Our initial results from the fractionation showed elevated TP concentration in the fluvial suspended sediments, and the IP showed over 70% of the TP, it was evident that the much of P is transported as IP. The IP have a strong association with highly charged particles under high Fe and Al oxide contents. Despite the sediment have high total P little is known if the sediments would retain P from or release P to the surrounding water and to what extent they could release algal available P after entering the receiving waters.

The P sorption-desorption experiment clearly differentiates sediment as P sink or source and, therefore, are used in many ecological studies. If there are higher external P enters into the river than the equilibrium P concentration ($EPC_0$) for the sediment, P will be adsorbed by the sediment and subsequently will be drained to downstream while moving with sediment, while If the P concentration are lower than the $EPC_0$ or if the redox potential abruptly change, P will be desorbed from the sediment surface resulting in the high P internal loading (KERR et al., 2011). We conducted the P sorption and desorption experiments to link this aquatic sediment P with the upstream land-based sources of P in order to assess the landscape drivers of sediment P contents and forms.

# 3 ARTICLE II – Phosphorus seasonal sorption–desorption kinetics in suspended sediment in response to land use and management in a subtropical South Brazilian catchment [2]

## 3.1 Abstract

Catchment scale assessment of diffuse phosphorus (P) behavior in suspended sediment originating either from intensive agriculture or urban discharges is desirable to estimate the river P legacy to the downstream receptors. Since total P estimation does not reveal its bioavailability, determination of P sorption-desorption parameters like maximum P adsorption capacity ($P_{max}$), equilibrium P concentration (EPC), water desorbable P (α), potentially bioavailable P (β), desorption rate constant (λ), and mobility index *(*α/β ratio) are helpful for effective comparison and implement management decisions.In current study, the modified Langmuir equation for P adsorption and McKean and Warren model for P desorption kinetics were tested in suspended sediments from 11 different land uses types (forest, low and high intensity agriculture under conventional and no-till, urban point source and mixed-use) in Guaporé, Southern Brazil during summer and winter 2013 and 2014.The result showed a significant ($\alpha$ = 0.05) variation across sediment site or seasons and revealed that 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 specifically metal bound stable P in intensive agriculture sediments. These findings clearly indicate that agricultural practices, sediment characteristics,

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[2] Article is prepared in accordance with the format of Journal **Chemosphere**

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.

**Keywords**: Sediment phosphorus, Seasonal P release, Catchment characteristics, Anthropic activity

## 3.2 Introduction

Eutrophication of fresh waters is mainly linked to increased anthropogenic activities in the catchment, over fertilization, and untreated urban or industrial sewage discharge is containing high P amounts, altogether are posing a serious threat to the ecological environment (Sharpley et al., 2013; Withers et al., 2015). Non-point P reaching to fresh water rivers and streams is more difficult to manage as it is bound to the highly charged sediment and organic materials. However, with change in the land use and catchment geographical features, rainfall and runoff fluxes, seasonal pH and dissolved oxygen (DO), and sediment chemical composition, this sediment-bound P could be released into surrounding water by ion exchange and or molecular diffusion to a small extent (Withers and Jarvie, 2008; Upreti et al., 2015). This sorption-desorption P balance considerably contributes to the final tropic level of water bodies (Jarvie et al., 2008; Zhang et al., 2014).

Based on the fact that the P adsorption capacity to a larger extent is dependent on the sediment composition, the specific pedo-climatic induced variation in soil and sediment sesquioxide contents regulate P adsorption. 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 (Caner et al., 2014; Bortoluzzi et al., 2015; Fink et al., 2016). Their results have shown that these soils are predominant in Fe and Al sesquioxides, kaolinite clay and to a small proportion of 2:1 clay type with interlayer hydroxy-Al.

Furthermore, particle physical characteristics like size distribution are associated with 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, facilitate 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 P adsorption capacity ($P_{max}$) and equilibrium phosphorus concentration (EPC) have been used to estimate river - sediment P dynamics. Several mathematics models has 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 has already been reported in many studies to describe best P adsorption (House and Denison, 2000; Bibba et al., 2003; Guardini et al., 2012). However, when the sediment have 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 participate in the adsorption equilibrium and, therefore, it must be accounted. To overcome this situation, several modifications in Langmuir model has been proposed depending on the sediment type (Zhu et al., 2011), however, the modification introduced by Koski-Vahala and Hartikainem (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, the McKean and Warren (1996) proposed first-order kinetics equation which allows to estimate the instantaneous particulate bioavailable P ($\alpha$), potential particulate bioavailable P or P buffering capacity ($\beta$) and desorption rate constant ($\lambda$) sediment-water interface and is used in many recent studies (Rheinheimer et al., 2001, 2008; Pellegrini et al., 2010; Tiecher et al., 2012; Bortoluzzi et al., 2013).

So far, few studies focusing on water and sediment-bound P transportation has 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., 2015), and sediment source finger printing (Tiecher et al., 2015), yet, a comprehensive catchment scale temporal study integrating all these aspect 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, (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.

## 3.3 Materials and methods

### 3.3.1 Description of Guaporé catchment

The study area Guaporé catchment is located in the southern Brazil. The region is characterized with intensive agriculture and high anthropic activities including rapid expansion in dairy and poultry industry over past 30 years. It has a total basin area of over 2000 km$^2$ with areas under representative land uses for cropping pattern and fertilization management. 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). The basin altitude varies from 40 to 800 m from south to north. The climate of the region is Cfa type as per Koppen climate classification with average annual rainfall from 1,400 and 2,000 mm well distributed throughout the year, but high winter rain events are frequent from August to October, and average annual temperature is 17.4 °C. 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 Taquari River, and a key contributor to the regional hydrographic of Guaíba Lake, the high sediment production and associated P draining to the Atlantic Ocean near Porto Alegre city, the capital of Rio Grande do Sul Brazil. The Guaporé catchment thus has a great importance both for regional and international water resource 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).

### 3.3.2 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) by using the software ArcGIS 10 (ESRI, 2011) and maps developments. 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, 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-µm mesh before chemical analysis. A set of the original oven-dried sample was passed through 2 mm mesh and kept for particle size analysis.

### 3.3.3 Sediment characterization

Sediment (< 63-µm) TP was determined with $H_2SO_4$ and $H_2O_2$ digestion in the presence of saturated $MgCl_2$, while the organic P (OP) was estimated by ignition at 550 °C for six h (Olsen and Sommers, 1982) and subsequently determined colorimetrically (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 $K_2Cr_2O_7$ and $H_2SO_4$ following theWalkley and Black (1934). The sediment (< 63-µm) amorphous Fe and Al were extracted with 0.2 mol $L^{-1}$ ammonium oxalate at pH 3 in dark ($Fe_{\mathbf{ox}}$ and $Al_{ox}$), as described by Schwertmann (1964). The crystalline forms of Fe oxyhydroxides ($Fe_{dcb}$) and Al ($Al_{dcb}$) were performed in dithionite–citrate–bicarbonate (DCB) extraction as explained by Mehra and Jackson (1960). The particle size distribution was determined in 2 mm sediment by the laser particle size analyzer (Muggler et al., 1997) after oxidation with $H_2O_2$ and subsequent dispersion with 6% NaOH solution.

### 3.3.4 Phosphorus sorption study

To determine the P adsorption behavior, only summer sediments 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. Briefly, 0.5 g of powdered suspended sediment (< 63μm) 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 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 colorimetric 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 Hartikainem (2001) and given as follow:

$$\mathrm{Psorbed} = \frac{\mathrm{Pmax} \times \mathrm{Psolution}}{1 + \mathrm{km} \times \mathrm{Psolution}} - Q_0 \qquad (1)$$

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 as by the expression:

$$\mathrm{EPC} = \frac{\mathrm{Qo} \times \mathrm{km}}{\mathrm{Pmax} \times \mathrm{Qo}} \qquad (2)$$

### 3.3.5 Desorption kinetics study

Bioavailable particulate phosphorus in suspended sediments was estimated by a single extraction with anion-exchange resin strips (AMI-7001S; Membranes International Inc, New Jersey) as described by Rheinheimer et al. (2000). Briefly, 0.5 g of powdered suspended sediment (< 6-µm) and 10 mL of distilled water was taken in 15 mL falcon tube following a 0.5 mol $L^{-1}$ $NaHCO_3$ saturated anion-exchange resin strip (Gatiboni et al., 2005). 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 by Murphy and Riley (1962) method. 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 to zero.

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

$$\mathrm{Pdes} = \beta(\beta - \alpha)e^{-\lambda t} \qquad (3)$$

Where, *Pdes*, is the amount of P desorbed; $\beta$, potentially bioavailable particulate P; $\alpha$, instantaneous bioavailable particulate P; $\lambda$, desorption rate constant, and $t$, extraction time in minutes. The P mobility index was calculated as = ($\alpha \times 100/\beta$).

### 3.3.6 Statistics

One-way analysis of variance (ANOVA) followed by Scott-Knott test ($p < 0.05$) was conducted by using Sisvar statistical software (version 5.3) to determine significant differences between seasons and sampling stations (Ferreira, 2011). The correlation coefficient and principal component analysis between a pair of means of P sorption-desorption parameters and sediment characteristics were also performed.

## 3.4 Results

### 3.4.1 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 chemical characteristics is presented in Table 1 and two while particle size distribution is shown in Fig. 1. The rank order of the metal 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 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 eleven monitored locations, the sediment $Fe_{ox}$ ranged (4.40 to 7.35 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 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 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 rest of 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 to 2 g $kg^{-1}Al_{ox}$ for most of the sediments except highly anthropic (sub5) which showed as much as 3.37 g $kg^{-1}$ $Al_{ox}$. However, $Al_{dcb}$ 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 (Table 2).

The particle size distribution of different sediments collected over four seasons is presented in Fig. 1. 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 high clay and the sand proportion was recorded for intensive sub-catchment under CT (sub3) during winter period in both 2013-14.

### 3.4.2 Sediment organic, inorganic and total phosphorus fractions

The seasonal variations in OP, IP, and TP concentration showed significant differences according to Scott-Knott test ($p < 0.05$) for eleven monitored sites and four seasons and were summarized in Table 2. 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 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 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 (Table 2). 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 2013while 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% and 15.8 to 99.8% (summer and winter 2014) over the forest sediments (Table 2).

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.

### 3.4.3 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 results are presented in Table 3. 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 Pmax, km, and $Q_0$; followed by the highly urban sub5, then by the NT (sub4), and least in sub1 and forest, respectively (Table 3).

The sediments have finite P retention capacity and when get 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 (2013-14) 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 three points (Table 3).

### 3.4.4 Phosphorus desorption kinetics

Results regarding seasonal P desorption kinetics from different land uses in Guaporé region are presented in Fig. 2–6. Individually, across the four season, 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. The main river points (P1 to P5), a descending trend in α content along river continuum 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. 2).

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) due to receiving high diffuse P inputs showed relatively higher amount than agriculture treatments but followed the descending order along river continuum (Fig. 3). The relative increase in potentially 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 main river sediments was observed.

The results of the desorption rate constant (λ) revealed that highest values were recorded for downstream main river sediments (P3 and P4) during winter 2013. The less anthropic sediments (forest, sub1, and sub2) showed lower λvalues when compared to the intense agriculture and highly anthropic sediments (Fig. 4). To estimate the sediment eutrophication hazard, the ratios between $\alpha$ and β has been used as a useful tool to describe the P mobility index. Average across seasons, among the monitored sites, the sediments from low anthropic sub-catchments have higher values for $\alpha/\beta$ ratios (forest = 26.4%, sub1 = 29% and sub2 = 25%) than the highly anthropic sub5 (23.9%). The main river sediment though the high value of P mobility index than native forest but did not follow the upstream-downstream or dilution effect on P (Fig. 5).

The cumulative P release revealed that the different sediment showed a clear desorption behavior for all four seasons during the 2013 and 2014 (Fig. 6). To attain the nearly complete removal of sediment-bound P from all sediment, thirteen successive (192 h) AER extraction 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 extraction. Figure 8 indicates that in each season, the successive resin extraction resulted in a maximum of cumulative P in highly anthropic urban sub5 sediments while lowest in the native forest sediments.

### 3.4.5 Principal component analysis (PCA) and correlations

The PCA analysis 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. 7). The factor 1 showed 53.1% of total variance and was mainly related with $Fe_{dcb}$, $Fe_{ox}$, $\alpha$, $\beta$, IP, and $Al_{dcb}$. As $\alpha$ and $\beta$ 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 is strongly controlled by the $Fe_{dcb}$ and $Fe_{ox}$. The factor 2 accounting for 17.6% of total variability and EPC and $P_{max}$ were strongly correlated to clay and TOC contents. The PCA further reveled 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 among them. 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 4).

## 3.5 Discussion

### 3.5.1 Variation in sediment phosphorus and chemical characteristics

Phosphorus mainly reaches to river system through domestic wastes and agricultural runoff. However, several biogeochemical factors and landscape hydrological parameters control this phenomenon. Firstly, the land use and soil managements play a key role. The studied 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 sewage into the river. The recent studies in the region 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 et al., 2015). Similarly, Blanc et al. (2012) 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 describe that with increasing area under NT can enhance the P export 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. This is because the CT catchments have tobacco cultivation during the winter months, and soil is thoroughly tilled, which is highly vulnerable to water erosion and thus transports higher amounts of suspended colloids. Similar, results were found by the Kroger et al. (2012) with changing land use and geography while Zhang and Huang (2007) and Cooper et al. (2015) has reported that even a small (16-20%) of the total weight, the clay fraction can account up to 70% of the total surface area.

The mineralogical heterogeneity, geochemical composition particularly Fe/Al content in the landscape is another key feature that regulate the form and fate of P along the river continuum. In the 1:1 type clays, specially kaolinite, the aluminum groups strongly attracts proton that is generally protonated ($Al\text{-}OH_2^+$) and it can be easily displaced by phosphate causing strong bonded specific adsorption and with low equilibrium concentration (Chen et al., 1973). The ion phosphate and many types or organic phosphorus can be attached to the iron and aluminum in the hydroxides (Parfit, 1978; Sposito, 2008).

The most of the parent material is originated from Basalt lithology, and dominant soil type is Oxisols/Ultisols and show a high content of iron oxides. The intensive site under CT (sub3, sub2) lies in Ultisols while that under NT and urban are located under Oxisols. Earlier studies in the region on a variety of soil and sediment have shown similar geochemical behavior with rich fine clay types and high Fe and Al (hydro) oxides (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 creating a high risk to water quality. Similarly, the highest OP concentration in NT sediment explains the evidence of soil OP in the top carbon stratified layer in the area. 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 coincidently accelerated by the high rainfall during the same period (July to October) as observed in an earlier study (Pellegrini et al., 2010).

### 3.5.2 Phosphorus sorption

The land based P entering 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 (Nemery and Garnier, 2007; Withers and Jarvie, 2008; Jing et al., 20011; Meng et al., 2014).

In this study, we used paired forest (natural) sediments as a reference for the comparison with anthropogenically impacted sediments. The relatively lower values of $P_{max}$, Km, $Q_0$ and EPCin 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.

(2012), and the later authors found less seasonal variability in P release from forest sediments as they are nearly under balanced equilibrium.

On the other hand, the sediments from intensive site under CT (sub3 = 50% arable) located on steep slope with high rainfall facilitating increased erosion (Didoné et al., 2014) with a more 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 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 $P_{max}$, Qo, and EPC (Table 3). These findings indicate the importance of native vegetation and emphasize the importance of the distribution of forest vegetation in the landscape ecology (Table 4). 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 Qo and especially much smaller value of EPC in comparison of 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 have raised concerns 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, 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 (20,000 inhabitants). This induces a high physicochemical variation in sediments behavior and affects the sediment P dynamics over time. The adsorption results reported here reflect this effect and many authors have shown that urban P pollution in sediment with higher $P_{max}$, Km, Qo and $EPC_0$ with lower clay content. Therefore, these sediments easily can act as a P source in river system (Pieterse et al., 2003; Jarvie et al., 2012; Blanc et al., 2012).

The particle size distribution overall 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., $P_{max}$, km, $Q_0$, and $EPC_{0.}$ The 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 invariable related to the land use, agriculture, animal production; and therefore, there are several individual sources that 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 $P_{max}$.

### 3.5.3 Phosphorus desorption

The significant variability in AER extracted P in the different sediments is 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). The low values of α and $\beta$ in the forest and low anthropic effect (sub1) were detected when compared to the intensive agriculture sub2 and sub3. This indicates that P is highly 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 4); and between $\beta$ and $Fe_{ox}$, $Fe_{dcb}$; and $Al_{ox}$, $Al_{dcb}$ ($r$ = 0.74, 0.83; 0.75, 0.78 — Fig. 7, Table 4). 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 is a combined function of both background agricultural loads and intensity of urban P discharge. This trend is very obvious in sub5 as indicated by the continuous higher β values (i.e., 396 mg $kg^{-1}$ vs. 96 mg $kg^{-1}$) than in forest during winter 2013 as well as overall sub5 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 $\beta$ 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) have specifically sediment-bound P which is stable and can act as P source and also 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 the forest. The similar results for P desorption parameters were found in earlier studies (Tiessen et al. 1984; Favre et al. 2004; Agudelo et al. 2011).

The relatively higher desorption rate constants (*λ*) values in downstream sediment are indicative of higher organic carbon in these sediment 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 sediment. Our results are in accordance with the Pellegrini et al. (2010), Guardini et al. (2012) and Fink et al. (2016) and these authors observed a similar trend for P desorption parameters under low and high P conditions.

### 3.6 Conclusions

This intra-catchment comparison study has reflected the seasonal P sorption-desorption potential of sediments in relation to landscape controls by 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 between and seasonal sub-catchment changes 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 environment 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 (main river) showed higher bioavailable P ($\alpha$) and total desorbed P ($\beta$), which demonstrate that this sediment are P source and can pose a greater threat to stream waters during seasonal shifts and oxic-anoxic variations on sediment-water interface in the presence of high Fe, Al and Mn ions. Finally, desorption rate ($\lambda$) and the P mobility index ($\alpha \times 100/\beta$) were highest in intensive agriculture sediment (sub3) as well as in highly anthropic (sub5) indicating these two sites higher potential to river internal P loading during ecologically sensitive periods. 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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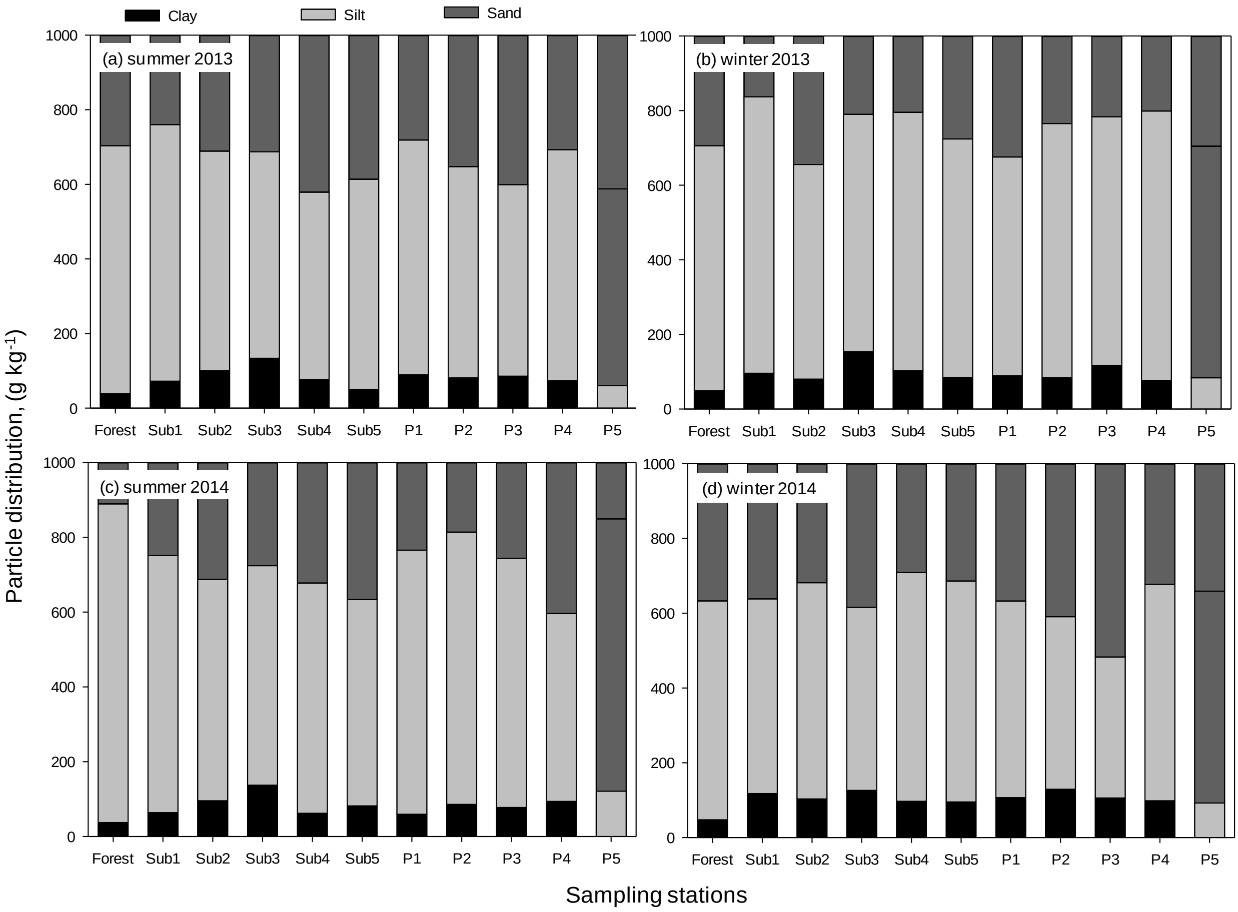

**Fig. 1.** Particle size distribution of suspended sediment samples during summer 2013 (a), winter 2013 (b), summer 2014, and winter 2014 (d) across eleven different monitoring sites in Guaporé catchment, Southern Brazil.

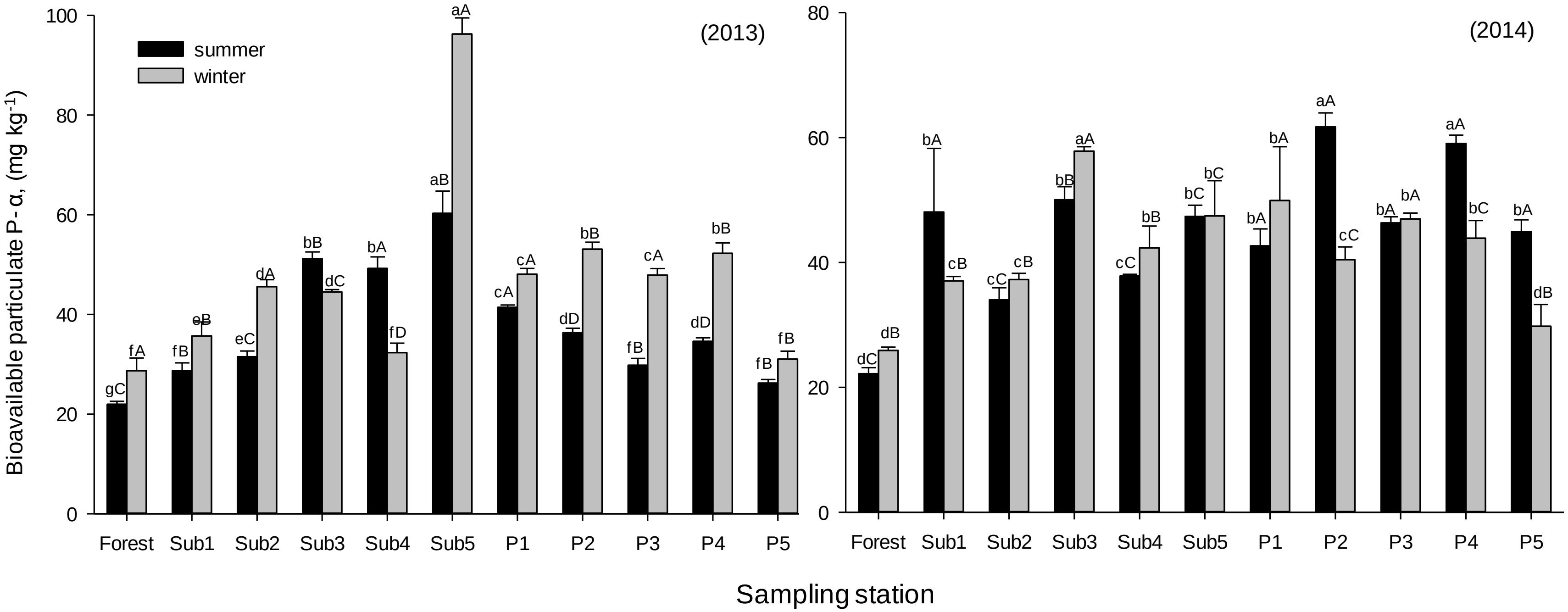

**Fig. 2.** Changes in the readily desorbable P (α, bioavailable P) of suspended sediment samples during summer-winter of 2013 and 2014 across eleven different monitoring sites in Guaporé catchment, Southern Brazil. Lowercase letters on each bar show seasonal variation among different land-use while uppercase letters indicate annual variation within monitoring site and the values followed by the same letter are not significant *p* < 0.05 according to the Scott-Knott test.

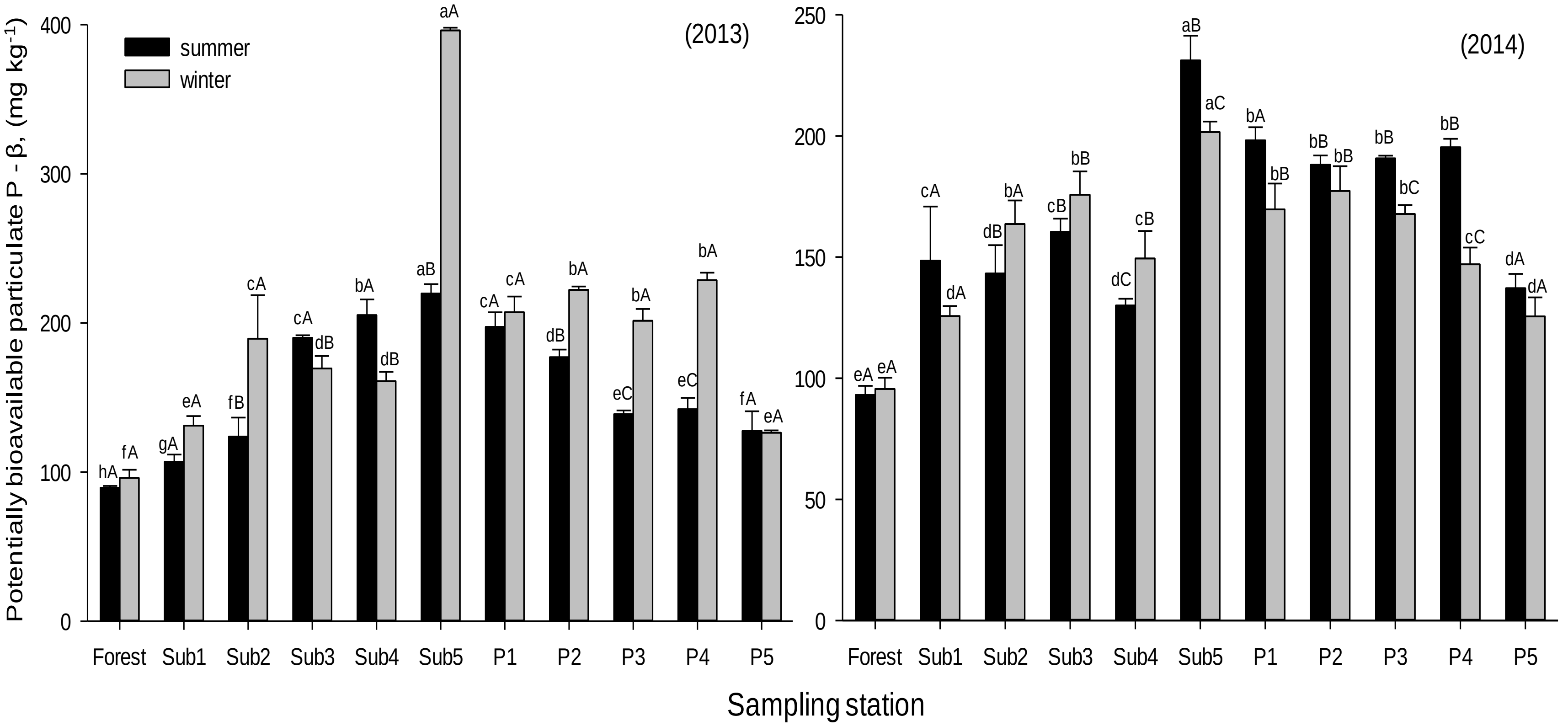

**Fig. 3.** Changes in the potentially available P (β, potentially available P) of suspended sediment samples during summer-winter of 2013 and 2014 across eleven different monitoring sites in Guaporé catchment, Southern Brazil. Lowercase letters on each bar show seasonal variation among different land-use 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.

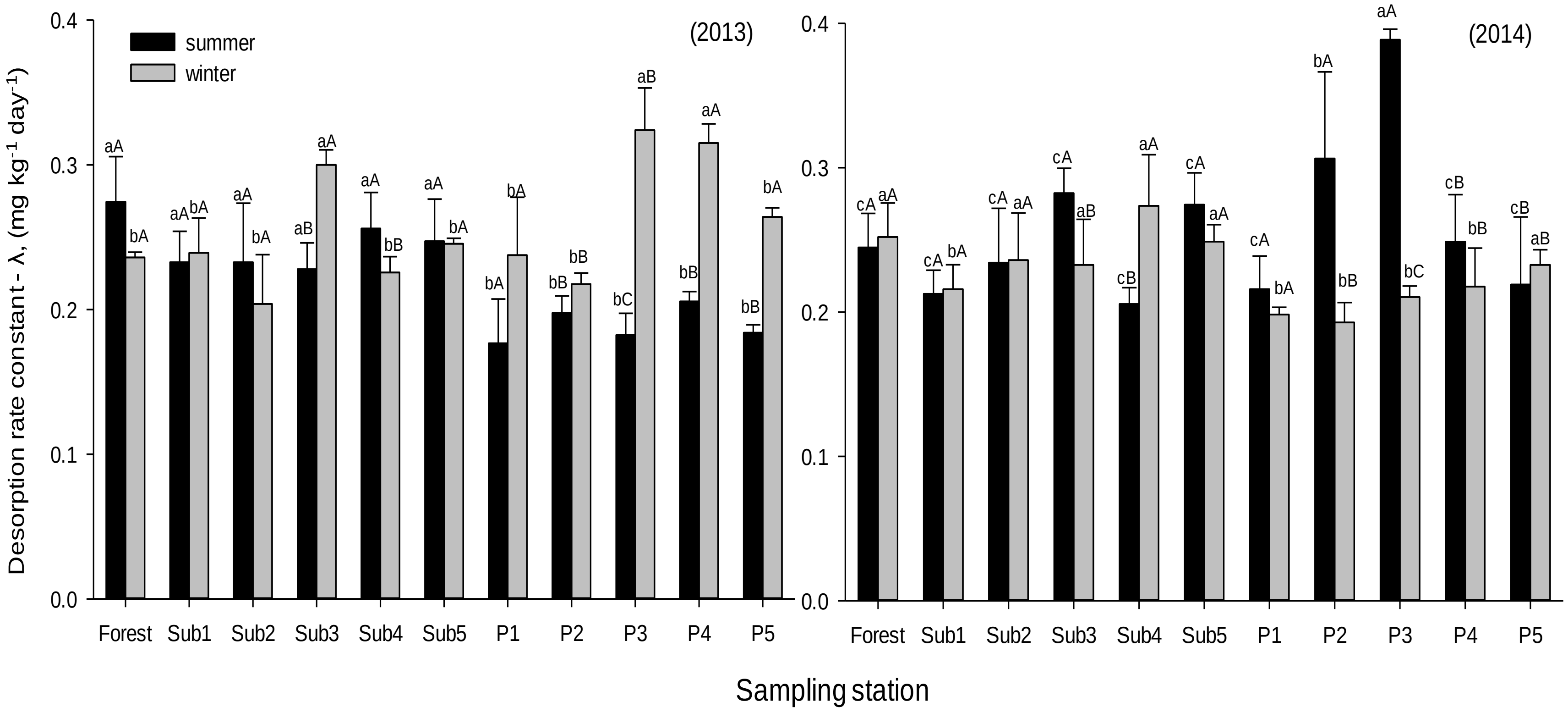

**Fig. 4.** Changes in the desorption rate constant (λ) of the first-order desorption reaction of suspended sediment samples during summer-winter of 2013 and 2014 across eleven different monitoring sites in Guaporé catchment, Southern Brazil. Lowercase letters on each bar show seasonal variation among 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.

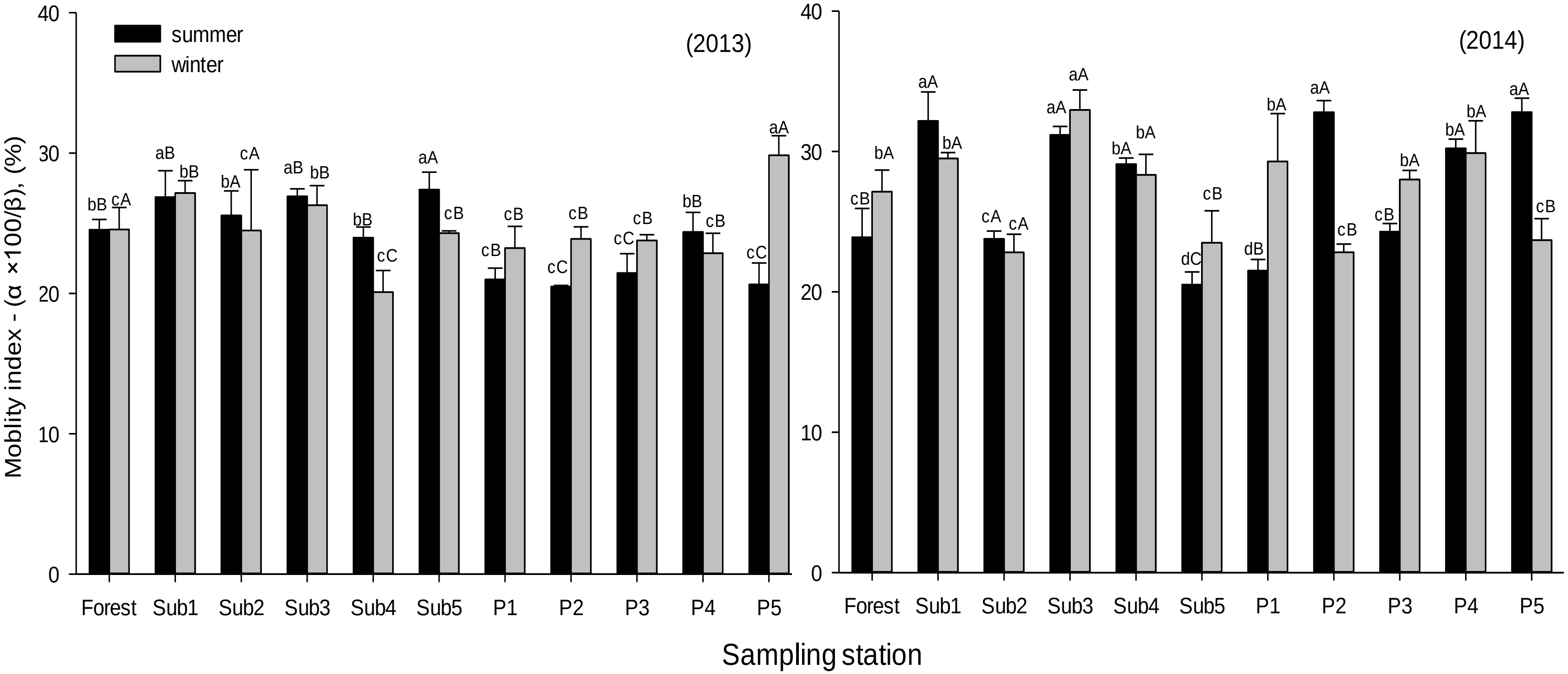

**Fig. 5.** Variation in the mobility index (α × 100/β) of suspended sediment samples during summer-winter of 2013 and 2014 across eleven different monitoring sites in Guaporé catchment, Southern Brazil. Lowercase letters on each bar show seasonal variation among different land-use while uppercase letters indicate annual variation within monitoring site and the values followed by the same letter are not significant $p < 0.05$ according to the Scott-Knott test.

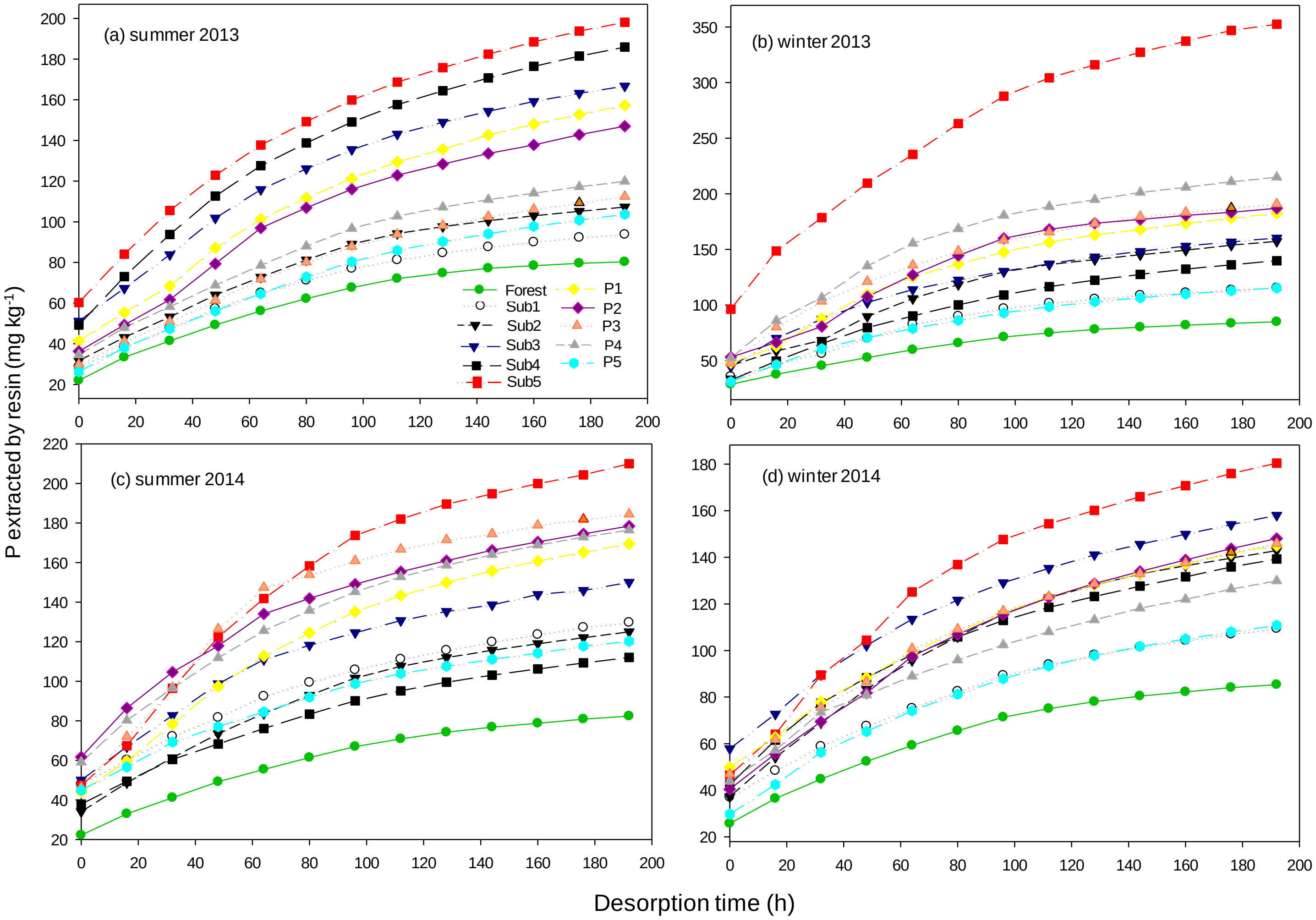

**Fig. 6.** Cumulative phosphorus desorbed by successive anion exchange resin extractions in suspended sediment samples during summer 2013 (a), winter 2013 (b), summer 2014, and winter 2014 (d) across eleven different monitoring sites in Guaporé catchment, Southern Brazil.

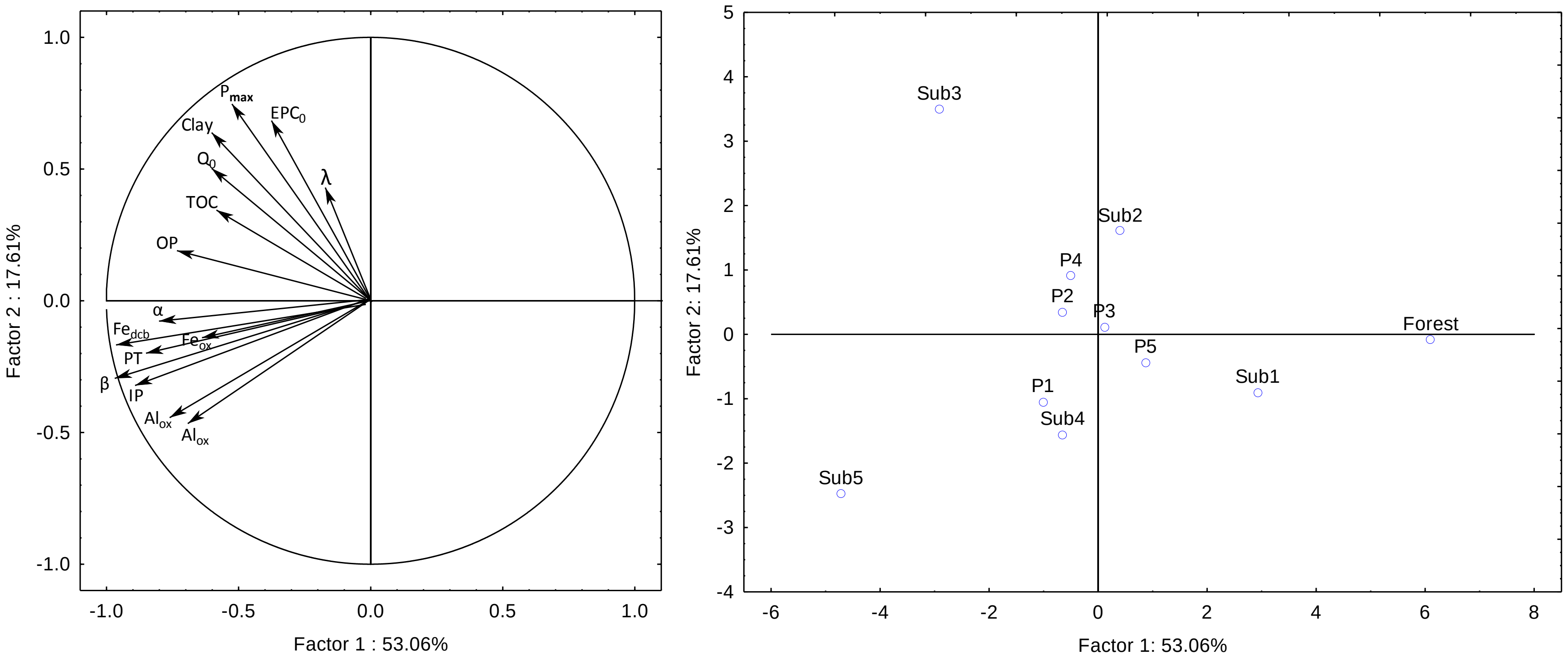

**Fig. 7.** Principal component analysis of the sediment adsorption-desorption parameters and related physicochemical characteristics.

**Table 1.** Seasonal changes in $\mathrm{Fe_{ox}}$, $\mathrm{Fe_{dcb}}$, $\mathrm{Al_{ox}}$, and $\mathrm{Al_{dcb}}$ of suspended sediments from different land uses in Guaporé catchment, Southern Brazil.

| Stations | $\mathrm{Fe_{ox}}$(g kg$^{-1}$) | | | | | | $\mathrm{Fe_{dcb}}$(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** |

| Stations | $\mathrm{Al_{ox}}$(g kg$^{-1}$) | | | | | | $\mathrm{Al_{dcb}}$(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** |

$\mathrm{Fe_{ox}}$, extracted with ammonium oxalate; $\mathrm{Fe_{dcb}}$, extracted with dithionite–citrate–bicarbonate; $\mathrm{Al_{ox}}$, extracted with ammonium oxalate and $\mathrm{Al_{dcb}}$, extracted with dithionite–citrate–bicarbonate.

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.

**Table 2.** Seasonal changes in organic P, inorganic P, total P and total organic C of suspended sediments from different land uses in Guaporé 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 | 872.5g | 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** |

| 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 the same letter in a column are not significantat $p < 0.05$ by the Scott-Knott test.

**Table 3.** Phosphorus adsorption parameters of suspended sediments collected during summer 2013 and 2014 from Guaporé 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 that allows half of the maximum P adsorption, $Q_0$ is water desorbed P (mg L$^{-1}$), and $EPC_{0.}$ 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 significantat $p < 0.05$ by the Scott-Knott test.

**Table 4.** Pearson correlation coefficient (*r*-value) and significance between P sorption-desorption parameters and sediment characteristics.

| Variables | $P_{max}$ | $Q_0$ | $EPC_0$ | $\alpha$ | $\beta$ | $\lambda$ | OP | IP | TP | TOC | $Fe_{ox}$ | $Fe_{dcb}$ | $Al_{ox}$ | $Al_{dcb}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Q_0$ | 0.59 | | | | | | | | | | | | | |
| $EPC_0$ | 0.78** | 0.85*** | | | | | | | | | | | | |
| $\alpha$ | 0.45 | 0.47 | 0.39 | | | | | | | | | | | |
| $\beta$ | 0.39 | 0.32 | 0.21 | 0.96*** | | | | | | | | | | |
| $\lambda$ | 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 $p < 0.001$.

**Supplementary Table 1.** Summary of descriptive statistics of total ions concentration in sediment (n = 4).

| Stations | Ca | | | | Cr | | | | Cu | | | | K | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$) | | | | | | | | | | | | | | | |
| | Mean | SD | Min. | Max. | Mean | SD | Min. | Max. | Mean | SD | Min. | Max. | Mean | SD | Min. | Max. |
| Forest | 1576.9 | 207.5 | 1271.1 | 1721.4 | 8.5 | 1.3 | 7.4 | 10.2 | 32.6 | 6.5 | 25.0 | 38.4 | 1201.3 | 152.2 | 1008.2 | 1356.8 |
| Sub1 | 3005.9 | 313.2 | 2726.3 | 3454.9 | 13.4 | 3.1 | 10.2 | 16.8 | 98.7 | 14.3 | 87.4 | 119.7 | 2174.4 | 685.2 | 1352.2 | 2846.5 |
| Sub2 | 2727.8 | 401.2 | 2274.4 | 3252.0 | 14.7 | 4.4 | 10.2 | 19.8 | 81.8 | 22.2 | 66.0 | 114.2 | 1287.9 | 822.6 | 176.4 | 2142.9 |
| Sub3 | 3360.7 | 920.5 | 2745.9 | 4726.9 | 26.0 | 5.7 | 18.8 | 32.8 | 152.0 | 53.9 | 110.1 | 230.9 | 1503.0 | 499.6 | 779.0 | 1926.7 |
| Sub4 | 2662.1 | 1774.2 | 1727.6 | 5321.5 | 23.6 | 8.1 | 17.2 | 33.8 | 112.6 | 31.5 | 89.2 | 155.7 | 1546.7 | 1233.7 | 918.1 | 3397.1 |
| Sub5 | 2994.9 | 1860.8 | 1486.9 | 5459.9 | 47.6 | 26.6 | 24.8 | 82.1 | 98.8 | 48.7 | 50.1 | 155.3 | 2531.6 | 2239.9 | 975.0 | 5746.3 |
| P1 | 2192.3 | 585.9 | 1468.9 | 2728.2 | 35.5 | 13.5 | 19.5 | 47.9 | 114.9 | 42.2 | 64.3 | 162.2 | 948.2 | 617.8 | 187.5 | 1691.6 |
| P2 | 2302.4 | 575.5 | 1755.3 | 2843.6 | 23.6 | 4.8 | 19.5 | 29.0 | 139.6 | 40.4 | 103.2 | 186.5 | 1072.3 | 638.1 | 284.2 | 1845.4 |
| P3 | 2545.3 | 535.4 | 1824.8 | 3010.0 | 23.5 | 5.6 | 15.4 | 28.4 | 160.6 | 46.4 | 99.7 | 209.5 | 976.5 | 560.8 | 348.9 | 1661.8 |
| P4 | 3029.4 | 308.1 | 2705.5 | 3386.3 | 26.4 | 3.4 | 23.0 | 30.6 | 166.5 | 37.9 | 114.6 | 201.9 | 1909.9 | 284.4 | 1634.0 | 2171.2 |
| P5 | 3281.5 | 681.4 | 2661.4 | 4252.2 | 28.3 | 4.7 | 21.5 | 32.5 | 146.7 | 27.4 | 122.3 | 183.9 | 2237.6 | 738.2 | 1580.5 | 3086.3 |

| Stations | Mg | | | | Mn | | | | Pb | | | | Zn | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | (mg kg$^{-1}$) | | | | | | | | | | | | | | | |
| | Mean | SD | Min. | Max. | Mean | SD | Min. | Max. | Mean | SD | Min. | Max. | Mean | SD | Min. | Max. |
| Forest | 2825.8 | 606.2 | 2300.4 | 3677.5 | 858.8 | 303.2 | 535.7 | 1246.8 | 19.6 | 6.4 | 12.2 | 25.1 | 18.8 | 10.9 | 8.5 | 29.3 |
| Sub1 | 4871.9 | 1727.2 | 2452.8 | 6536.5 | 1370.3 | 306.6 | 976.4 | 1708.6 | 12.9 | 2.7 | 10.6 | 16.7 | 21.3 | 16.6 | 10.4 | 46.0 |
| Sub2 | 4176.1 | 534.5 | 3789.7 | 4965.5 | 1292.1 | 324.2 | 1043.9 | 1738.0 | 16.7 | 4.7 | 11.3 | 21.5 | 26.4 | 19.8 | 7.9 | 48.6 |
| Sub3 | 4280.8 | 709.2 | 3749.8 | 5302.1 | 2072.1 | 432.2 | 1663.7 | 2658.4 | 14.4 | 5.4 | 8.4 | 19.5 | 22.6 | 11.1 | 9.7 | 34.6 |
| Sub4 | 3039.6 | 1188.8 | 2302.4 | 4793.2 | 1993.2 | 666.5 | 1480.6 | 288.1 | 18.1 | 4.7 | 15.4 | 25.0 | 20.8 | 5.5 | 10.6 | 27.8 |
| Sub5 | 3410.6 | 1336.9 | 2035.9 | 4663.8 | 1645.5 | 620.9 | 1051.4 | 2190.1 | 22.5 | 10.5 | 12.7 | 37.2 | 60.6 | 86.5 | 10.0 | 189.8 |
| P1 | 3191.5 | 888.7 | 2008.0 | 4129.5 | 2014.9 | 877.4 | 1221.0 | 2824.1 | 22.3 | 6.3 | 16.5 | 30.5 | 29.4 | 21.6 | 11.2 | 59.7 |
| P2 | 3285.2 | 717.2 | 2529.0 | 7019.2 | 1917.9 | 566.2 | 1396.7 | 2646.9 | 17.9 | 3.2 | 14.3 | 21.5 | 29.2 | 17.1 | 10.3 | 51.4 |
| P3 | 3794.6 | 650.6 | 2834.7 | 4279.2 | 1758.5 | 258.6 | 1410.1 | 2023.9 | 16.8 | 4.6 | 11.8 | 22.5 | 23.6 | 14.7 | 9.2 | 43.7 |
| P4 | 4192.6 | 221.8 | 3882.5 | 4409.6 | 1958.4 | 188.9 | 1801.6 | 2184.1 | 18.2 | 3.7 | 13.6 | 21.6 | 31.5 | 20.8 | 9.6 | 52.0 |
| P5 | 4075.7 | 168.1 | 3939.6 | 4321.1 | 1681.8 | 91.9 | 1605.2 | 1799.7 | 18.1 | 6.8 | 9.4 | 26.1 | 46.4 | 45.8 | 11.8 | 109.1 |

## Significance of river bed sediments on river P storage and bioavaliability

Although diffuse P loads reaching to the river via suspended sediment are considered responsible for the river P distribution and bioavailability in downstream recipient waters, little evidence supports this phenomenon that of diffuse agricultural inputs are main agents of running waters eutrophic nature (EDWARDS et al., 2000; BALLATINE et al., 2009).The sensitive time within the aquatic system of great ecological vulnerability is during low flow conditions and mostly during late spring and summer (November to March) in Guaporé catchment. There is clearly evident from P mass balance studies that the total P load entering into the river is not reaching at river outlet, and a considerable portion is retained and deposited within the river bed.

WITHERS et al. (2007) and BALLATINE et al. (2009) have showed that the bed sediment can hold a considerable part of external P loads and, therefore, are very important for instream P cycling and storage. Furthermore, these sediments on resuspension again can act as a P source and remobilize higher amounts of bound P to overlying river water. Several other studies have indicated the significance of bed sediment to act as P sink or source under urban, rural and agriculturally impacted, mixed land use environments (MCDOWELL; SHARPLEY, 2001; JARVIE et al., 2006).

Another key aspect that necessitated to explore the bed sediment P dynamics is the complex chemical nature and particle size of the eroded suspended sediments. As explained in article 1 and 2, the suspended sediment showed a great variation in mineralogy, particularly high concentration of amorphous Fe oxides, high TOC, and varied particle size distribution from different sediment origins. Therefore, the bed sediments from all monitoring sites except outlet (P5) was examined to make a comparison between suspended and bed sediment P speciation and bioavailability under in the context of different hydrological, geomorphological, land use and management variations.

# 4 ARTICLE III – Relating bed sediments P legacy and desorption kinetics to landscape land-use in the Guaporé catchment Southern Brazil[3]

## 4.1 Abstract

A quantitative temporal understanding of river phosphorus (P) dynamics in response to changes in anthropogenic P inputs, land use and climate is critical for developing effective watershed P control measures. In this study, river bed sediments from six headwater sub-catchments varying in land use and management i.e.,, (i) native forest, (ii) low agriculture under conventional tillage-CT (sub1), (iii) low agriculture under CT and natural mate plantations (sub2), (iv) intense agriculture under CT (sub3), (v) intense agriculture under no-till-NT (sub4), (vi) urban receiving sewage (sub5) and four monitoring station on main river (P1 to P4) along river continuum in Guaporé catchment from October 2012 to October 2014 comprising 10 sampling timing were analyzed for (a) bed sediment chemical nature and size distribution, (b) sediment P fractionation and season P lability, and (c) phosphorus desorption kinetics.The results reveal that when averaged across monitoring period, the TP concentration lied between 777.5 mg kg$^{-1}$ in the native forest to as high as 1916.8 mg kg$^{-1}$ in urban (sub5) sediments. Overall, there was 26 to 147% increase in TP contents between low agriculture land use (sub1) and highly anthropic (sub5) over the forest. Across monitored sites, individual P fraction when pooled for different P lability indicated 10, 35 and 55% of TP for labile, moderately labile and non-labile P, respectively. It was obvious that land use has a strong impact on sediment P lability. With a land use change from forest to more anthropic and intensive agriculture (sub1 to sub5), results showed an increase in labile P (38 to 127%), moderately labile P (29 to 199%) and non-labile P (23 to 117%), respectively. Among, different land use, both sub-5 (Urban P source) and sub4 (NT agriculture) relatively retained

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[3] Article is prepared in accordance with the format of Journal **Water, Air, & Soil Pollution**

high bioavailable P than sub3 (tobacco under CT), and the NT sediment also showed superiority for hydroxide organic P ($\mathrm{Po}_{\mathrm{HID\ 0.5}}$). Similarly, the highly anthropic sediments from sub5 and sub4 showed high concentrations for P desorption, i.e., bioavailable particulate P (α); potentially bioavailable particulate P (β); desorption rate constant (λ), and P mobility index. The high correlation of bed sediment IP, α, and β with Fe/Al proves that bed sediment from the highly weathered subtropical environment is principally controlled by the Fe/Al contents and that these bed sediment had the capacity to take up P in a strongly bound form. It can be inferred from the results that both urban and agricultural practices (intensive arable production) have a higher risk of P loss, and it can lead either directly or indirectly to increased river water P concentrations. This study further illustrated the importance of geochemical and physical controls on the bed sediments’ capacity to mitigate high P inputs in headwater rivers for sustainable ecological management.

**Keywords:** Phosphorus lability, Sediment-water interface, Anthropic intensification, Water quality

## 4.2 Introduction

In the agricultural landscapes, anthropogenic P is transported by the runoff water and can impair freshwater river quality regarding ecological effects. The P mass balance studies have indicated that only 1 to 38% of anthropogenic-added P is exported by the river to lakes or end receivers and over 60% is retained within the landscape and is often termed as legacy P (i.e., surplus P accumulated in watershed by anthropogenic P additions over years). This legacy P can be remobilized and can act as a P source to the downstream water ranging from years to centuries even after land base P transport is controlled. Many long-term catchment scale studies evidenced that legacy P is responsible for failure to achieve successful water quality and catchment nutrient management goals (Sharpley et al. 2013; Haygarthet al. 2014; Chen et al. 2015).

The most of the external legacy P is transported as sediment associated particulate phosphorus (PP) and often exceeds 85% of the total P. Therefore, the suspended sediment delivery and their deposition are key factors in river P dynamics. While on reaching the river, a portion of suspended solids is deposited in the river bed and hereafter called as bed sediments. The bed sediments can hold a considerable portion of PP, and their remobilization can influence the bioavailability of P particularly and river low flow (House 2003; Haggard and Sharpley 2007). Many studies have reported that when bed sediment-water interface have fluctuations in P concentration, they can act as P sink or source depending upon the equilibrium P concentration (Palmer-Felgate et al. 2009; Machesky et al. 2010).

Despite diffuse agricultural P losses, several other factors may also influence the bed sediment P concentrations. During low flow conditions, bed sediments can act as P sinks in water channels receiving untreated sewage effluent discharges (Jarvie et al. 2005; Withers et al. 2007). The in situ overlying river water composition, redox conditions, and sediment physicochemical nature can also influence its P sorption-desorption. The important sediment properties that control P exchange across sediment–water interface include; particle size distribution (Stone et al. 1995); metal oxide content particularly amorphous Fe/Al oxides including P precipitation as hydroxide (Fox 1993); P associated with organic carbon (Gachter et al. 1988)and the concentration of exchangeable P already sorbed to the particle surface (Zhang and Huang 2007). Therefore, it is important to consider these properties while accounting the impact of anthropogenic P sources on sediment P dynamics.

The ability of riverbed sediments to buffer P and to act as a sink or source of P depends on the bioavailability of sedimentP forms. The bioavailability of sedimentP forms which vary from readily available forms, to moderately available forms, to highly recalcitrant mineral associated P and this phenomenon of P bioavailability is collectively regulated by the hydrologic, geographic, and biochemical nature of the soil and landscape interactions (Bedore et al. 2008; Chen et al. 2015; McDowell and Hill 2015).

The release of P from bed sediment is a vital nutrient source that can induce continuous eutrophication in water systems even if external inputs are reduced (Ulen et al. 2014). Bed sediment P recycling depends to a large extent on the forms of P in sediments (Rogers et al. 2013; Son et al. 2015). Sediment P includes inorganic P (Pi) and organic P (Po); and transformation and releasing of both in the sediment can accelerate eutrophication. Many P fractionation schemes have been reported to characterize soil and sediment P lability (i.e., Hund et al. 2013; Condron et al. 2014). However, the Hedley et al. (1982) fractionation scheme is widely acceptable and differentiates the TP into different P fraction on the P lability basis i.e., labile-P (Presin, and 0.5 M $NaHCO_3$-Pi and Po), moderately labile-P (0.1 M NaOH-Pi and Po, and HCl-P), and stable-P (0.5 M NaOH-Pi and Po, and residual-P). The worldwide acceptability and of this method is reported for diverse type of land-use and management systems (Negassa and Leinweber, 2009; Hund et al., 2013).

In the Southern Brazil, the anthropogenic intensification of the landscape has been accelerated over last three decades and the animal and grain production areas are expanding to contribute in the national economy (AGE 2012; IBGE 2013). Furthermore, the surface application of large amounts of pig slurry and inorganic fertilizer over small land units, intensive cultivation of soils for tobacco during erosion-risk periods (winter months), disposal of untreated city sewage and industrial discharges into river, sloppy relief which increases the connectivity between the field and the water course, all are contributing to the increased P loss. Therefore, this situation is of many environmental concerns regarding hydrological sources and eutrophication (Gatiboni et al. 2014; Couto et al. 2015).

Under subtropical conditions of Southern Brazil, earlier studies have focused on suspended sediment OP, IP, TP, and P bioavailability. However, temporal investigations of the P liability and seasonal internal P release from bed sediment have been lacking. We hypothesized that the P flux on sediment-water interface is principally related to the sediment's chemical P behavior that, in turn, is influenced by upstream land use to points of drainage water entry.The specific objectives of this study were to detect the temporal P lability in river bed sediment and P desorption kinetics and study the relationship between P in bed sediment. This study provides useful information about the compounds and dynamics of P in Guaporé river and management of freshwater eutrophication.

## 4.3 Materials and methods

### 4.3.1 Catchment areas and sediment collection

This study area Guaporé catchment situated in the northeastern part of the Rio Grande do Sul, the most Southern Brazilian State. The details of the study site have already been discussed in article 1 and 2. Here, we collected the bed sediment in all six sub-catchments and but only from four monitoring sites on the main river without including catchment outlet (Fig. 1). To evaluate the seasonal variability of land-use and management, sampling was conducted under base flow conditions every 2.5 months over a 2-year period (i.e., during Dec-2012, Feb-2013, April-2013, Jul-2013, Sep-2013, Nov-2013, Feb-2014, May-2014, July-2014 and Sep-2014). After each sampling period, the samplers were manually collected based on the re-suspension technique (Ballantine et al. 2009) with a plastic bottle and subsequently sieved through < 2 mm stainless steel sieve. All sediments were transferred into acid-washed 20 L plastic gallon and transfer to the laboratory and then oven-dried at 50 °C, gently disaggregated using a rubber head pestle and mortar and sieved through a 63-µm mesh before chemical analysis. A set of original oven dried was passed through 2 mm mesh and kept for particle size analysis.

### 4.3.2 Bed sediment P fractionation

During whole analysis, dried and 63 µm size sediment sample were used. Keeping in view the objective to assess the sediment-bound P lability, sequential P fractionation scheme proposed by Hedley et al. (1982) with little modifications as suggested by Condron et al. (1985) was chosen and details methodology is already presented in article 1.

### 4.3.3 Desorption kinetics study

The desorption parameters of bed sediments were estimated by successive extraction with anion-exchange resin strips (AMI-7001S; Membranes International Inc, New Jersey) as described in Article 2. To estimate P desorption parameters, the first-order kinetic model proposed by the McKean and Warren (1996) in equation 3 was employed.

$$\mathrm{Pdes} = \beta(\beta - \alpha)e^{-\lambda t} \qquad (1)$$

Where, (Pdes), is amount of P desorbed; (β), potentially bioavailable particulate P; ($\alpha$), instantaneous bioavailable particulate P; ($\lambda$), desorption rate constant, and (t), extraction time in minutes. The P mobility index was calculated as = (α ×100/β).

### 4.3.4 Complementary analysis of sediments

The basic physicochemical characteristics including particle size distribution, TOC, $\mathrm{Fe_{ox}}$, $\mathrm{Fe_{dcb}}$, $\mathrm{Al_{ox}}$ and $\mathrm{Al_{dcb}}$ of bed sediment were also determined as described in the previous article.

### 4.3.5 Statistical analysis

The comparisons among sampling sites and seasons at each collection sampling site were performed using the non-parametric test of Kruskal-Wallis (*H*) as described in the article 1. Due to a high number of data set, box and whisker plots were chosen to facilitate the interpretation of results. In each plot value represents $n$ = 30 (10 collection timings and 3 laboratory replication).

For the P desorption parameters, one-way analysis of variance (ANOVA) followed by Scott-Knott test ($p < 0.05$) was conducted by using Sisvar statistical software (version 5.3) to determine significant differences between seasons and sampling sites. The Pearson's correlation co-efficient was also determined among the P labilities, P desorption parameters and sediment characteristics.

## 4.4 Results and Discussion

To explore the P behavior the bed sediment chemistry of different land use was compared between native forest sub-catchment (control) and impacted sites (urban, agricultural and main river site) over the whole study period and results are presented in the following sections.

### 4.4.1 Sediment chemical and textural behaviour

The Figure 2 and 3 presents the summary of mean values of the bed sediment chemical behavior in response to different land-uses and or environmental factors in Guaporé catchment. Average across sampling timings and land uses, the bed sediment $Fe_{ox}$ ranged (3.9 to 8.1 g $kg^{-1}$), $Fe_{dcb}$ (34.5 to 46.9 g $kg^{-1}$), $Al_{ox}$ (1.0 to 1.9 g $kg^{-1}$), $Al_{dcb}$ (3.0 to 5.1 g $kg^{-1}$), TOC (16.9 to 33.2 g $kg^{-1}$), clay (41.7 to 75.7 g $kg^{-1}$), and sand (428.3 to 642.8 g $kg^{-1}$).

Among sub-catchments, the comparison of the values showed that mean $Fe_{ox}$ contentswas highest (105% increase) in the NT sub-catchment over the forest. The $Fe_{ox}$ content showed a sequence: sub4 > sub5 > sub3 > sub2 > sub1 > forest. The main river sites (P1 to P4) showed relatively higher values when compared to the individual sub-catchments. Specifically the main river points showed a descending trend along the river continuum (Fig. 2a). The highest 46.9 g $kg^{-1}$ (i.e., 36% increase over forest) crystalline bound $Fe_{dcb}$ was recorded in urban bed sediments followed by the NT bed sediment with 45.1 g $kg^{-1}$ $Fe_{dcb}$

content. The main river sites did not showed much variation in $Fe_{dcb}$ contents but showed a 20 to 29 % relative increase over the forest bed sediments (Fig. 2b).

Across the full dataset, the highest 1.8 g $kg^{-1}$ (with 82% increase over forest) amorphous $Al_{ox}$ content was determined in urban bed sediments followed by the NT (i.e., 74% increase over forest) sediment among sub-catchments. The less impacted agricultural sites (sub1 and sub2) showed less variation in $Al_{ox}$ when compared to the native forest. However, among the main river bed sediment, P1 showed highest values of 1.9 g $kg^{-1}$ $Al_{ox}$ over rest of three main rivers monitored sites (Fig. 2c). The maximum $Al_{dcb}$ were recorded for urban sub-catchment with a (4.7 g $kg^{-1}$), i.e., 56% increase over the native forest. The intensive agriculture under CT also showed a higher $Al_{dcb}$contents over the NT and relatively less impacted sub 1. Among the main river points, the P1 with the highest (5.1 g $kg^{-1}$ with 56% increase over native forest) while the rest of three sampling site showed an inconsistent pattern in $Al_{dcb}$ along the river continuum (Fig. 2d).

The TOC contents varied between different sediments as presented in Fig.3a, and are mainly reflecting the contrasts in land use and inputs from individual anthropogenic sources. Among sub-catchments, urban sub5 showed largest 33.2 g $kg^{-1}$ and sub1 lowest 16.9 g $kg^{-1}$ TOC while intensive agriculture NT and CT (sub4 and sub3) showed 24.1 and 23.1 g $kg^{-1}$ TOC contents, respectively.On main river points, P1 showed maximum 27.3 g $kg^{-1}$ and then a descending trend along river continuum was recorded.

The clay fraction in the bed sediment increased significantly in agriculture sub-catchments over the whole study period especially in sediment from the sub-catchment 2 (75.7 g $kg^{-1}$). The urban sediments also showed the second higher clay contents (60.9 g $kg^{-1}$) among the sub-catchments. The main river sediment did not show much variation and followed a decreasing pattern in clay content along the river downstream (Fig. 3b). The sand fraction also showed great variation and there 14 to 50% relative increase in impacted sites over the native forest site and sand fraction individually showed over 60% proportion in particle size under the intensive agriculture sediment. Similarly, high sand proportions were also found in the main river site (Fig. 3c).

The difference in the P adsorption capacities among soils is principally associated with the chemical composition and geology of their parent material (Lopez et al. 1996).The high content of Fe and Al oxy-hydroxides have already been reported in the fine fluvial sediments of the region (Pellegrini et al. 2010; Bortoluzzi et al. 2013). Therefore, Fe/Al contents are a key regulator of the river bed sediment P immobilization between inorganic and organic P forms (Gao et al. 2014; Peryer-Fursdon et al. 2015).

### 4.4.2 Sediment organic, inorganic and total phosphorus distribution

The highest mean OP concentrations (254.9 mg $kg^{-1}$) were found in the NT sub-catchment (Fig. 4a) followed by the urban sub5 with 249.1 mg P $kg^{-1}$. Among the different sub-catchment, the OP followed an order: intense agriculture under NT (sub4) > sub5 > sub2 > sub3 > sub1 > forest. The main river sediments (P1 to P4) showed descending trend along river downstream.The relative increase in OP contents of disturbed bed sediment over native forest ranged from 2 to 86% over the whole study period (Fig.4a).

The maximum IP content 1663.2 mg $kg^{-1}$ in urban sub-catchment in comparison to native forest 640.3 mg $kg^{-1}$ was found among all six sub-catchments (Fig. 4b). The NT sub-catchment showed the second largest IP contents (1268.8 mg $kg^{-1}$) followed by the CT- sub3 intensive agriculture site with 1130.3 mg $kg^{-1}$. The low agriculture sub-catchments (sub1 and sub2) showed a relatively small difference over the forest catchment for IP contents. On the main river, the sediment from the upstream site (P1) showed highest (1498.5 mg $kg^{-1}$) IP values. Across different sediment locations, the relative increase in IP contents varied from32 to 160% over the forest bed sediments (Fig. 4b).

A high TP contents in the urban sediments was observed, and sediments showed 147% (1961.8mg $kg^{-1}$) increase in TP concentration when compared to the reference forest sediment (777.5 mg $kg^{-1}$). The intensive agriculture sediment from NT (sub4) and CT (sub3) also showed the higher 1523.7 and 1280.9 mg $kg^{-1}$when compared to the low agriculture and forest sediments. The upstream main river sediments (P1) showed highest TP (1732.4 mg $kg^{-1}$) and the concentration decreased while moving downstream. The percent relative increase in TP over forest site varied from 26 to 147%.

The results indicate that the TP, IP, and OP have high correlation ($p < 0.05$) with TOC, $Fe_{ox}$, $Fe_{dcb}$, $Al_{ox}$, and $Al_{dcb}$ contents (Table 1). The high correlation of TOC even with IPis just a coincidence and has no chemical significance. In fact, there was a strong correlation between oxalate and dithionite extracted Fe/Al with both IP and its fractions as well as with organic carbon. Thus, the phenomenon of adsorption is the same for both anions: phosphate or organic anions. Therefore, the storage of P as carbon associated in the river bed sediment is controlled by the Fe and that it is the preferential sediment-bound P form under these environments.

Comparison of the mean OP, IP, and TP concentrations shows that bed sediment also showed the similar pattern as shown by the suspended sediments and land use was major factor contributing to stream bed P. Land use contributes to the elevated TP levels and the highest TP contents observed in the urban site (sub5), although a similar soil management and arable area is present in sub4 are an evidence that the economic growth and the city population discharged large amounts of untreated wastewater and sludge have been directly disposed to river consequently contributing to a large loading of P into river. The similar increase in the urban and non-urban sediments was observed by Tang et al. (2010). The higher OP content in the NT sediment may be attributed to the long-term NT adoption and high surface fertilizers and manure application that increases the P export to the river. Furthermore, the relatively high TOC content can also facilitate the P release from the highly nutrient saturated top layer from these soils (Gatiboni et al. 2015).

### 4.4.3 Inorganic P fractions

The concentrations and relative distributions of the various inorganic P fraction pooled over the whole sample period in the bed sediments for different land uses are summarized in Fig. 5, 6, 7. Among most of theP fractions, the rank order of different land use was sub5 > sub4 > sub3 > sub2 > sub1 > forest, while the among main river P1 showed highest values for a different fraction. The detailed description of each fraction is presented as follow.

#### 4.4.3.1 Labile P fractions ($P_{AER}$ and $Pi_{BIC}$)

The highest $P_{AER}$ concentration of 64.8mgkg$^{-1}$ was found in sub5 (urban), followed by the sub4 (NT) 47.5 mgkg$^{-1}$ when compared to reference forest sub-catchment with 31.5 mg kg$^{-1}$ $P_{AER}$. However, the CT sub-catchments (sub1 to sub3) did not show much variation among them (Fig. 5a). Among main river sediments, the P1 showed maximum (53.8 mg kg$^{-1}$) $P_{AER}$ and a descending trend were observed along river continuum while moving downstream. Similarly, the $Pi_{BIC}$showed highest values (72.0 mg kg$^{-1}$) in the sub5 followed by the two intensive agriculture NT and CT (sub4 and sub3) sites, however, a non-significant difference was found between the later two.  Average across land-uses, high variation (33 to 106%) for $P_{AER}$ and (32 to 138%) for $Pi_{BIC}$ were recorded between forest and rest of land use depending upon the amount of P reaching to the river sediments from specific land use (Fig. 5c).

The above results showed the impact of high external P either from intensive agriculture and anthropic activity. The similar increase in the bioavailable P was recorded by the Balantine et al. (2009). The sediments as urban area (point source) showed highest labile P due to the addition of a high volume of untreated sewage from Marau city into the river and similar findings were recorded by Pagliosa et al. (2005) who noted significantly higher bioavailable P in sediments from urban areas than the non-urbanized area. The similar pattern of available P in stream bottom sediments due to sewage addition was recorded by the Jarvie et al. (2006) and Smith and Own (2013).

The relatively high values of $P_{AER}$and $P_{BIC}$ in sub-4 (NT) than the forest may also be attributed to legacy P as a result of P accumulation in the surface due to the successive slurry and manure applications (Sharpley et al. 2014; Couto et al. 2015). The high concentrations of labile P fraction in bed sediments were accompanied by high $Fe_{ox}$ and $Fe_{dcb}$ and higher ($p < 0.05$) correlations even in the presence of high TOC content indicate that iron oxide directly regulate the bioavailable sediment P (Fig. 5; Table 1), and these results are in agreement to those of Tuszynska et al. (2013).

#### 4.4.3.2 Moderately labile P fractions ($Pi_{HID-0.1}$ and $P_{HCl}$)

The results revealed that both moderately labile $Pi_{HID-0.1}$ and $P_{HCl}$ were highest (295.5 and 371.9 mg $kg^{-1}$) in sub5. The intensive sites (sub 3 and sub4) showed the second highest $Pi_{HID-0.1}$valuesamong the sub-catchments (184.5and 179.1 mg $kg^{-1}$), followed by low agriculture sub2 (146.3 mg $kg^{-1}$) in comparison to forest 88.5 mg $kg^{-1}$. Among main river sites, P1 showed highest values (218.7 and 317.1 mg $kg^{-1}$) moderately labile $Pi_{HID-0.1}$ and $P_{HCl}$ (Fig. 6a, c). Average among different land-uses, the concentration of Ca-precipitated P ($P_{HCl}$) in bed sediment was higher than the Fe/Al bound P ($Pi_{HID-0.1}$).

As explained in results, the most of the sediment showed > 35% of TP as moderately labile forms. The highest concentration of $Pi_{HID-0.1}$ urban (sub5) and NT (sub4) bed sediments might be attributed to the presence of high TOC and Fe/Al-P when compared to the sub-catchments under CT. These results are in accordance with the findings of Tuszynska et al. (2013) and Budha et al. (2014) which explains that the organic carbon and Fe oxide have a high control on the slightly available P, and NaOH fraction can present up to 79% of bed sediment TP.The similar observation by the Gao et al. (2014) and Jan et al. (2015) was reported for moderately labile P pool.

### 4.4.3.3 Non-labile P fractions ($Pi_{HID\text{-}0.5}$ and $P_{Residual}$)

The Fig 7a and 7c demonstrated the average concentration of non-labile $Pi_{HID\text{-}0.5}$ and $P_{Residual}$ for the 10 monitored sites. Among sub-catchments, the urban sub-catchment, both non-labile $Pi_{HID\text{-}0.5}$, and $P_{Residual}$ showed highest contents 382.5 and 480.9 mg kg$^{-1}$.The sediment from the intensive tobacco CT (sub3) and NT (sub4) showed second highest (337.1 and 333.9 mg kg$^{-1}$) and least in the less impacted (sub 2 and sub3) sediments. However, $P_{Residual}$ was higher (466.4 mg kg$^{-1}$) in NT sediment than the CT sediments (408.2 mg kg$^{-1}$). The sediments on the main river showed high concentration for both non-labile $Pi_{HID\text{-}0.5}$ and $P_{Residual}$ at upstream P1 and a decreasing trend downstream catchment outlet P4. Within non-labile P pool, $P_{Residual}$ showed clear dominance over $Pi_{HID\text{-}0.5}$ and on an average across different land uses, alone contributed over 55% to total non-labile P.

The results about the non-labile pool indicate that it was the exceptionally high (> 55% of TP) in the bed sediments studied. The urban site (sub5) and intensive agriculture bed sediments (i.e., sub3 and sub4 including the main river sediments) showed a high fraction of $Pi_{HID\text{-}0.5}$ and residual P than the less anthropic catchments (sub1, sub 2 and forest). This increase in $Pi_{HID\text{-}0.5}$ can be attributed to the excessive land P exports and stored in bed sediments in the river. The high proportion of residual P indicates the high stability and occluded nature with Fe/Al oxy-hydroxides. Therefore, this P can be attributed to the typical pedo-climatic nature of these highly weathered soils and sediments deposited along the river continuum (Bortoluzzi et al. 2013; Son et al. 2015).

### 4.4.4 Organic P fractions

Comparison of the mean$P_o$ fraction among the land-use is presented in Fig. 5c, 6b, and 7b. The $NaHCO_3$ 0.5 M ($Po_{BIC}$) extractable labile organic P concentrations were lower when compared to either 0.1 M NaOH ($Po_{HID-0.1}$) extractable moderately labile organic P or 0.5 M NaOH ($Po_{HID-0.5}$) extractable non-labile organic P fractions. Briefly, the highest $Po_{BIC}$ concentration (51.1 and 43.6 mg $kg^{-1}$), corresponding to the 142 and 103% relative increase over the forest, was found in the urban sediment (sub5) and intensive CT (sub2), respectively (Fig. 5c). The sub-catchments sub1, sub3 and sub4 showed 32.8, 37.2 and 43.0mg $kg^{-1}$ $Po_{BIC}$, respectively. The main river sediments did not show much variation among themselves, and $Po_{BIC}$ ranged from 39.1 to 55.9 mg $kg^{-1}$ for$Po_{BIC}$.

Similarly, the moderately labile organic P ($Po_{HID-0.1}$) concentration was highest in the urban sediments (103%), followed by the sub4 (52%), and then in sub2 (31%) when compared to reference forest site.Among the main river sediments, P1 showed the highest (113.1mg $kg^{-1}$) $Po_{HID-0.1}$ contents over the downstream sediments (Fig. 6b).

The Fig. 7b shows that the non-labile organic P fraction ($Po_{HID-0.5}$) was highest (111.4 mg $kg^{-1}$) in sub4 (NT), followed by sub5 (64.0 mg $kg^{-1}$), and then by the sub3 (58.5 mg $kg^{-1}$). The low agriculture sub-catchments sub1 and sub2 showed lower values that the reference forest bed sediments. The bed sediments from the main river showed higher non-labile organic P fraction ($Po_{HID-0.5}$) than the sub-catchments (Fig.7b).

The OP forms also represented an important proportion of total P (9 to 12%) among different bed sediments. Nonetheless, the increase in the organic P was more obvious in NaOH extracts both in moderately, and non-labile P pools. Similar results were observed by Rheinheimer et al. (2002); Tiecher et al. (2012) and Cade-Menun et al. (2015), and explained by the formation of Fe/Al-P complexes with humic substances under similar geomorphological and soil management systems.

### 4.4.5 Average P lability and distribution of river P legacy

To determine the extent of P legacy lability from the river bed sediments, the individual P fraction were grouped as labile P ($P_{AER}$, $Pi_{BIC}$ + $Po_{BIC}$), moderately labile ($P_{HID}$-0.1 Pi + Po and $P_{HCl}$), and non-labile P ($P_{HID}$-0.5 Pi + Po and residual P) Fig. 8. The temporal P lability trends indicated that among sub-catchments, the labile P, moderately labile and non-labile P showed an order: sub5 > sub4 > sub3 > sub2 > sub1 > forest. The relative increase in the labile P among the anthropically impacted environments ranged from 38 to 127%, moderately labile P from 29 to 199%, and non-labile P from 23 to 117% over the reference forest site. Furthermore, the results showed that the labile, moderately labile and non-labile P accounted for 10, 35 and 55% of TP of bed sediments. The highest significant correlation coefficients ($p < 0.05$) was observed among three P lability (labile, moderately-labile, and non-labile) withTOC, $Fe_{ox}$, $Fe_{dcb}$, $Al_{ox}$, and $Al_{dcb}$ (Table 1).

The high lability of the urban anthropic sub5 though showed over rest of the sediments is due to the continuous higher P inputs from the urban point source. Furtheremore, the higher labile P during low flow summer can accelerate the mineralization and increased turnover of OC and precipitated Fe-P can hold greater P. Therefore, the high chemical nature of the particles and reactions causing P precipitation could increase the transient storage potential for P. On the other hand, the anthropic sediment also contain high Ca amounts and therefore can also contribute to bind P. The relatively higher P labilitiy was observed by the Blanc et al. (2013) and Su et al. (2014) in urban and non-urban bed sediments.

The NT bed sediments high P labilities can be attributed to the higher rate of sediment settling in the river bed and some extent to the high fertilizer P losses to the river. However, the highest TP correlation with $Fe_{ox}$ describe the chemical nature of these particles and are the main factor regulating P lability.These findings are comparable to the findings of the earlier studies (Tiessen et al. 1984; Bortoluzzi et al., 2015; Abdala et al., 2015) who showed that under high OC condition, metal oxides were the main driver of P particle dynamics.

Alike suspended sediments, the tobacco cultivation, showed high P values during winter (tobacco cultivation season) which can either be contributed to the chemical fertilizer additions or due to high hydrological resuspension effect on the bed sediments under these high slope areas. The main river upstream P1 showed high P concentration because it was receiving the two highly polluted headwater tributaries, i.e., urban and NT.

The higher non-labile P (0.5 M NaOH and residual P) in highly anthropic sub-catchments (sub3 to sub5) also was the largest P pool in main river sediments, indicating the highly complex nature of these sediments from diffuse sources (Fig. 8c). This recalcitrant pool thus can permanent occluded Fe or Al oxy-hydroxides and can be exported with resuspension to larger distances in the landscape (Reddy et al., 1998; Dunne and Reddy, 2005).

### 4.4.6 Phosphorus desorption kinetics

To evaluate the bed sediment potential for eutrophication hazard, the desorption parameters including bioavailable particulate P (α); potentially bioavailable particulate P (β); desorption rate constant (λ); and P mobility index were determined and the results are shown in Figure 9. The α varied from 29.4 to 100.3, and 27.4 to 117.6 mg $kg^{-1}$ was recorded during 2013 and 2014, respectively (Fig. 8a).Individually, across the sub-catchments, the highest αvalues was recorded for urban sediments. The intensive agriculture site under NT showed the second highest α (63.4 and 72.7 mg $kg^{-1}$); followed by the relatively low agriculture (sub1 and sub2) during both study years. Among the main river sites, P1 showed the highest α (60.2 and 61.8 mg $kg^{-1}$) during summer 2013, and 2014 and a descending trend in α content along river continuum were observed. The relative increase in α values of anthropically impacted sediment over native forest ranged from 20 to 241% in summer 2013 and 17 to 330% during summer 2014 (Fig. 9a).

The similar trend for $\beta$ values were found among different sub-catchment and showed an order in land-use as urban sediments > intense agriculture under NT > low agriculture under CT (sub1 and sub2) > intense agriculture under CT (sub3) > native forest. The main river points (P1) showed relatively higher $\beta$ values over downstream sites and followed the descending order along river continuum. The relative increase in potentially bioavailable P varied from 20 to 186% and 14 to 127% during 2013 and 2014 respectively (Fig. 9b).

The results of the desorption rate constant ($\lambda$) revealed that among intensive agriculture sub-catchments, the NT site showed higher (0.37 and 0.26 mg $kg^{-1}$ $day^{-1}$) values than the CT sediments (0.18 and 0.20 mg $kg^{-1}$ $day^{-1}$) in both years. Similarly, between NT site sub4 and sub5 although both sites have a similar proportion of arable area, the urban contribution in sub5 increased the P desorption rate constant values in both years sediments. The less anthropic sediments (forest, sub1, and sub2) showed lower $\lambda$ values when compared to the intense agriculture and highly anthropic sediments (Fig. 9c).

The ratios between $\alpha$ and $\beta$ have been used as a useful tool to describe the P mobility index. Average across the monitoring sites, the sediments from the high anthropic site showed highest values for $\alpha/\beta$ ratios for sub5 = 34.6 and 42.3% during both summer 2013 and 2014, however, the less seasonal impact was observed on P mobility index. When averaged across over two years, the mobility was in order sub5 > sub4 > low agriculture sub-catchments (both sub1 and sub2) > forest.

The cumulative P release revealed that the different sediment showed a clear desorption behavior for all ten sites and both sampling years (Fig. 10). To attain the nearly complete removal of sediment-bound P from all sediment, thirteen successive (192 h) AER extraction 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 extraction. Figure 9 indicates that during both years, the successive resin extraction P was maximums in highly anthropic urban (sub5) sediments while lowest values were recorded for the native forest sediments (Fig. 10).

The significant correlation coefficients between labile αand TOC, $Fe_{dcb}$, $Al_{ox}$ ($r = 0.75$, 0.69, 0.57); between β and TOC, $Fe_{ox}$, $Fe_{dcb}$, $Al_{ox}$, $Al_{dcb}$ ($r = 0.83$, 0.55, 0.72, 0.78, 0.75); and λ and TOC ($r = 0.75$) were also determined and presented in Table 1.

The prediction of bioavailable P and P buffering capacity is critical in the sediment-water P relations. However, this phenomenon is even of more importance while determining the bed sediment P release potential. The low values of α and $\beta$ in less impacted bed sediment was determined when compared to the intensive agriculture NT and urban sediments. This reflects that the P is poorly retained in the forest and sub1 bed sediment than sub4 and sub5. This situation indicates that the highly impacted have strong mineralogical control on the P and to the high content of the amorphous and crystalline Fe or Al in these sediments. This is also indicated by the higher correlation between α and $Fe_{dcb}$; and $Al_{ox}$, ($r = 0.69$, 0.57 — Table 1); and between $\beta$ and $Fe_{ox}$, $Fe_{dcb}$ ($r = 0.72$, 0.78 — Table 1).

Similarly, the high concentration 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).

Similarly, both of these sites (sub4 and sub5) have specifically bound particle P that is stable and can be released over resuspension and or when overlying river water have fluctuations in the EPC concentration (Tiessen et al. 1984; Favre et al. 2004; Agudelo et al., 2011). The relatively higher desorption rate constants ($\lambda$) values in NT sediment also reveal the high P release risk from continuously NT and heavily fertilized soils. Our results are in accordance with the Pellegrini et al. (2010), Lehtoranta et al. (2015) and authors observed a similar trend for P desorption parameters for low and high soil P conditions.

## 4.5 Conclusions

The river bed sediments studies are a useful tool in the river system ecological assessment in response to high P loads. The TP, individual P fraction and pooled P liability varied both spatially and temporally at all sub-catchment and main river monitored sites in Guaporé, Southern Brazil.The land use and management, sediment chemical constituent and catchment geomorphic feature appeared as a key driver of P lability. The inter sub-catchments comparison for TP, P lability and P desorption kinetics followed order: urban source > intensive agriculture under NT > intensive agriculture under CT > low agriculture under CT > forest. These spatial variations between the sub-catchments are attributed mainly to typical land use patterns, intensive agriculture, soil management system, sediment chemical composition and particle size distribution. Among sub-catchment, three most impaired viz. sub5, sub4, and sub3 were identified as critical P sources with high proportions of either P lability and higher variability in individual P fractions. On the main river monitoring sites, P1 showed highest concentrations of the P bioavailability and mobility index reflecting that upstream P loss reduction is critical in the river quality management. The results further emphasized that higher bioavailable P concentration in bed sediment are associated with Fe/Al have high affinity to bind P, and they are the key driver of instream cycling and P release. This study provides primary results on temporal monitoring of P lability in fresh water bed sediments and can provide useful information while planing to reduce the land and agricultural based P loads to the river and that the share of bed sediment to P release should be accounted in developing watershed P management strategies.

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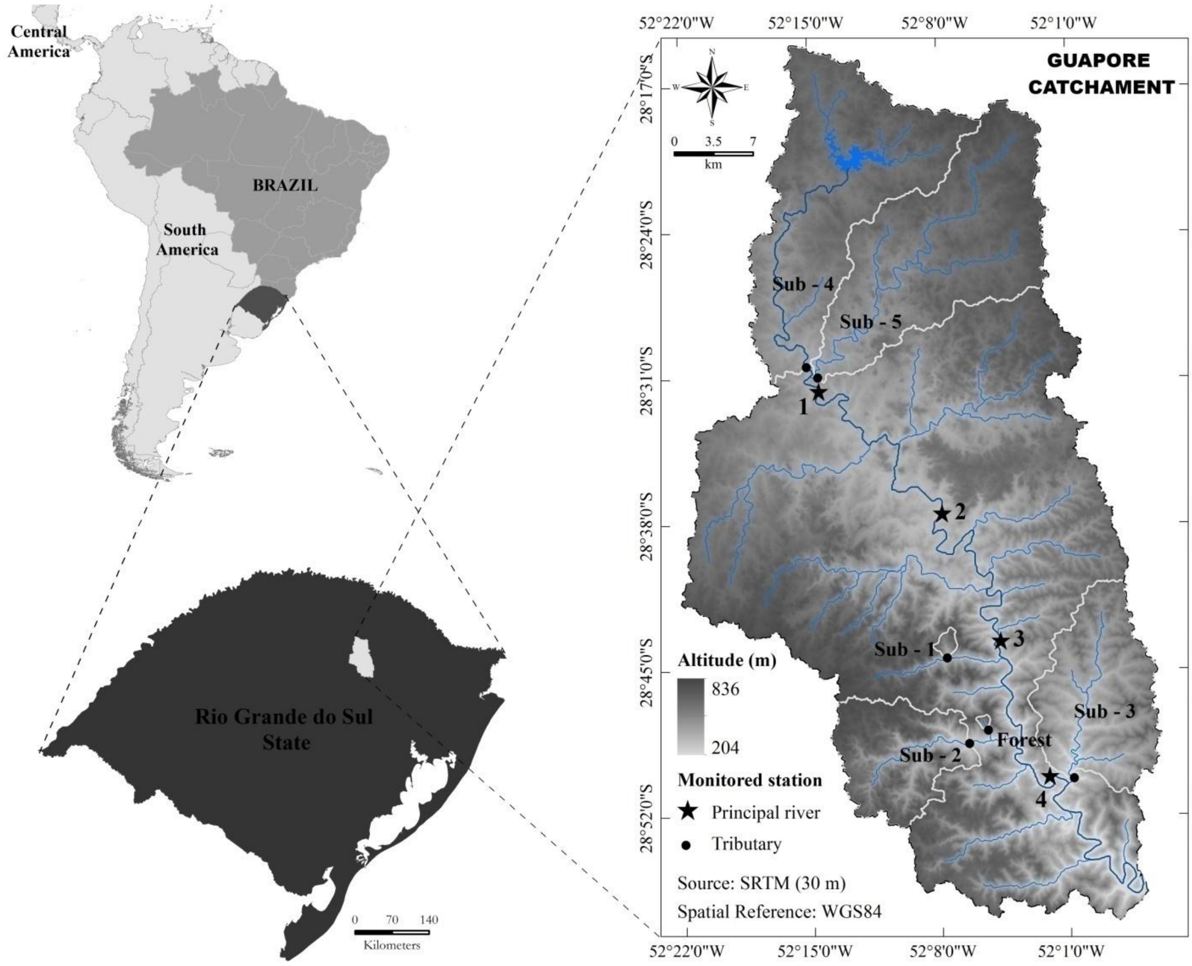

**Fig. 1.** Geographical location of the study catchment Guaporé in the Rio Grande do Sul State, Southern Brazil. The right-side map summarizes the location of six sub-catchment and four monitoring sites on the main river within the main catchment.

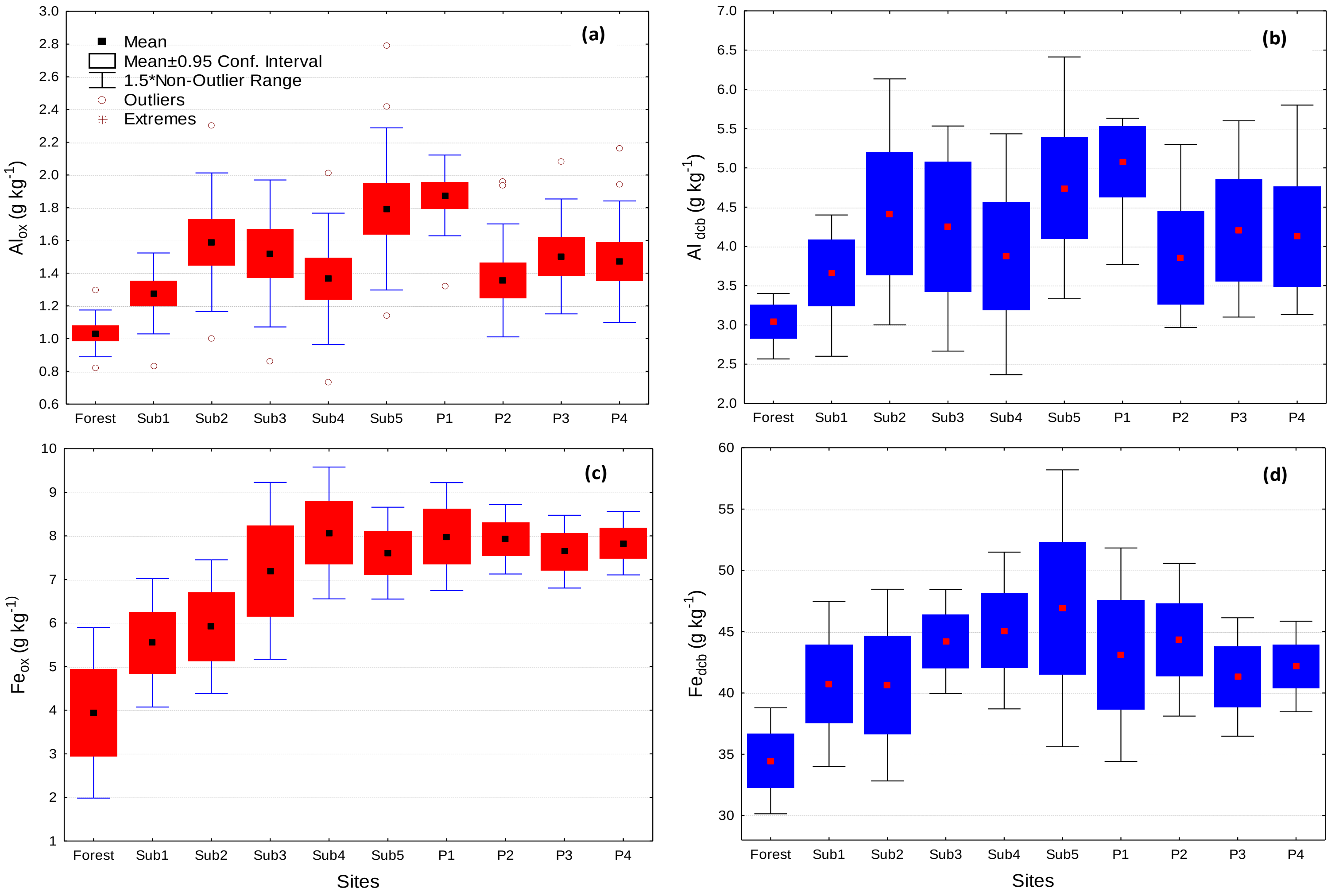

**Fig. 2.** Changes in ammonium oxalate extractable Al (a), dithionite–citrate–bicarbonate extractable Al (b), ammonium oxalate extractable Fe (c) and dithionite–citrate–bicarbonate extractable Fe (d) contents of bed sediments collected across ten different monitoring sites in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (*n*=30).

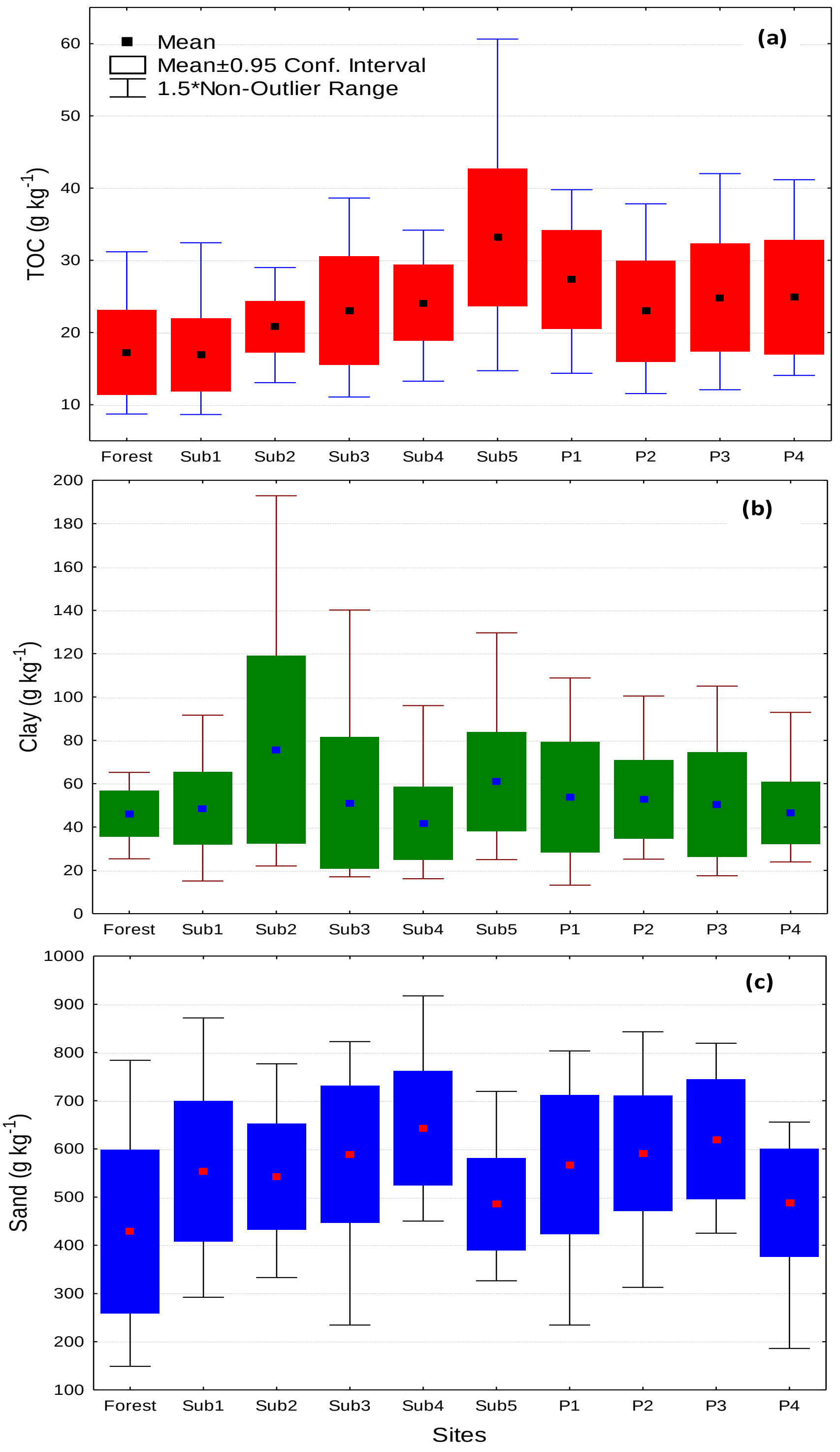

**Fig. 3.** Changes in total organic carbon (a), clay (b) and sand (c) contents of bed sediments collected across ten different monitoring sites in the Guaporé catchment Southern Brazil, between October 2012 to 2014 (*n*=30).

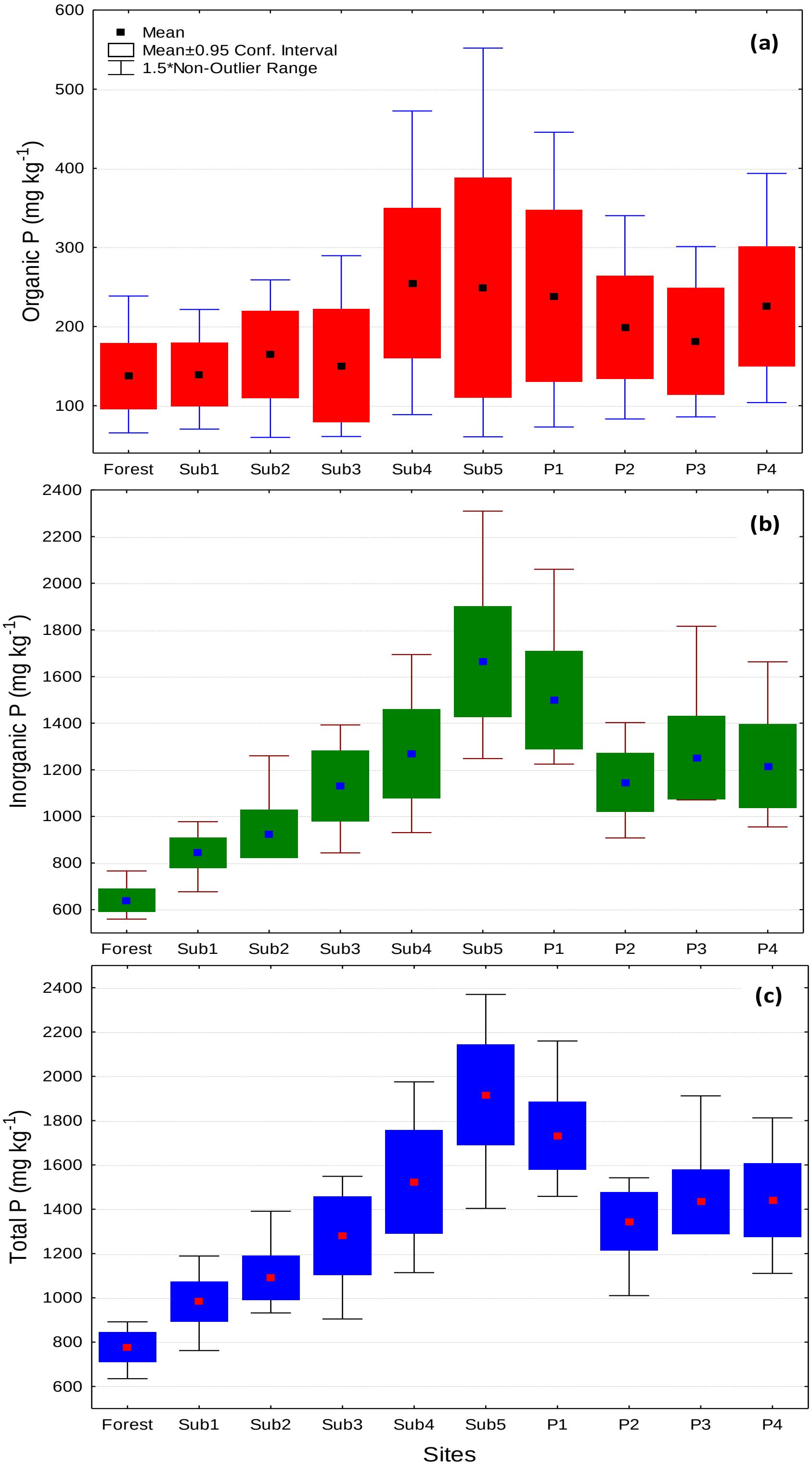

**Fig. 4.** Changes in organic P (a), inorganic P (b) and total P (c) contents of bed sediments collected across ten different monitoring sites in the Guaporé catchment Southern Brazil, between October 2012 to 2014 (*n*=30).

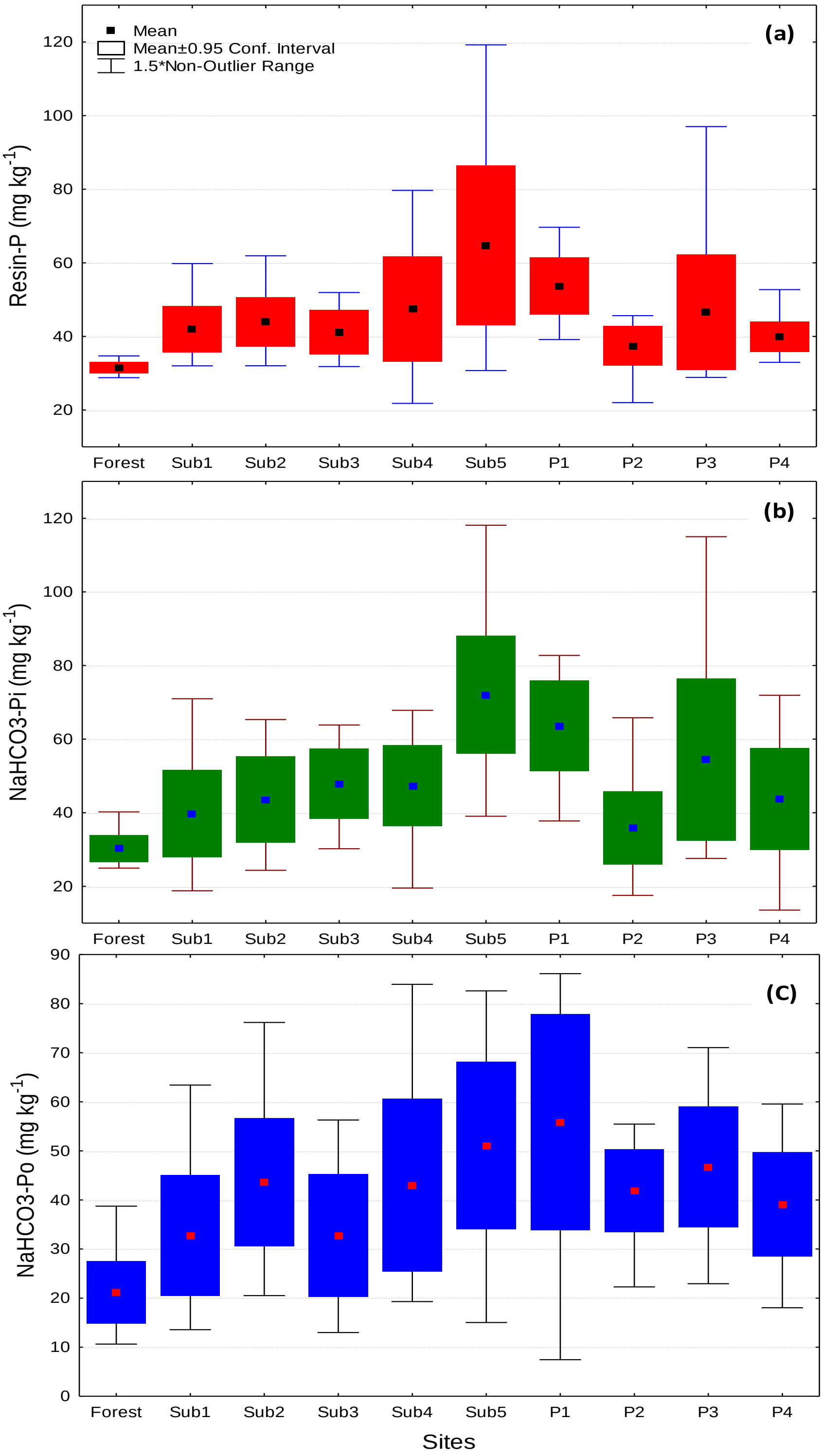

**Fig. 5.** Changes in resin extractable P (a), sodium bicarbonate extractable inorganic P (b) and sodium bicarbonate extractable organic P (c) contents of bed sediments collected across ten different monitoring sites in the Guaporé catchment Southern Brazil, between October 2012 to 2014 (*n*=30).

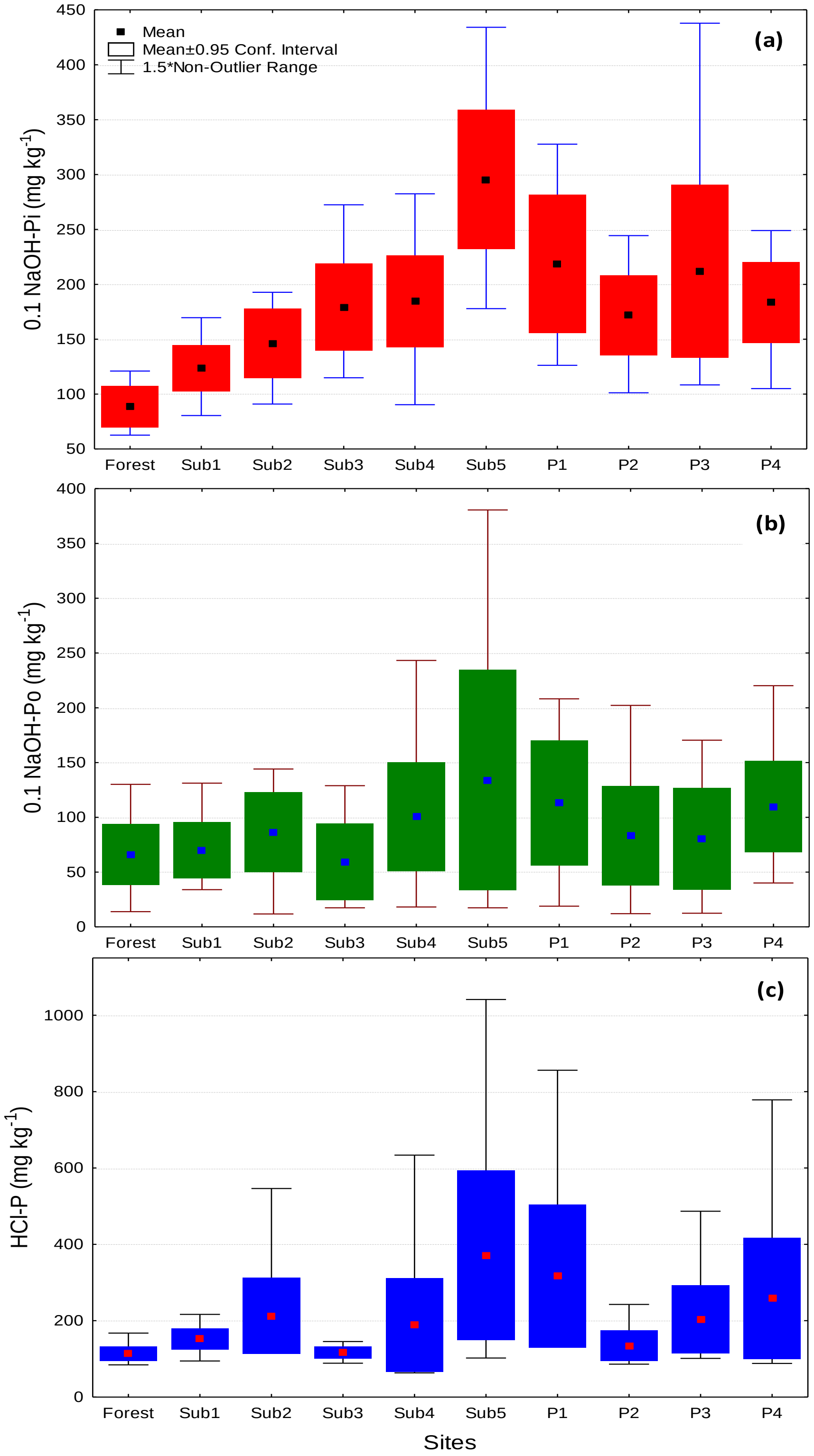

**Fig. 6.** Changes in 0.1 molar sodium hydroxide extractable inorganic P (a), 0.1 molar sodium hydroxide organic P (b) and hydrochloric acid extractable P (c) contents of bed sediments collected across ten different monitoring sites in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (*n*=30).

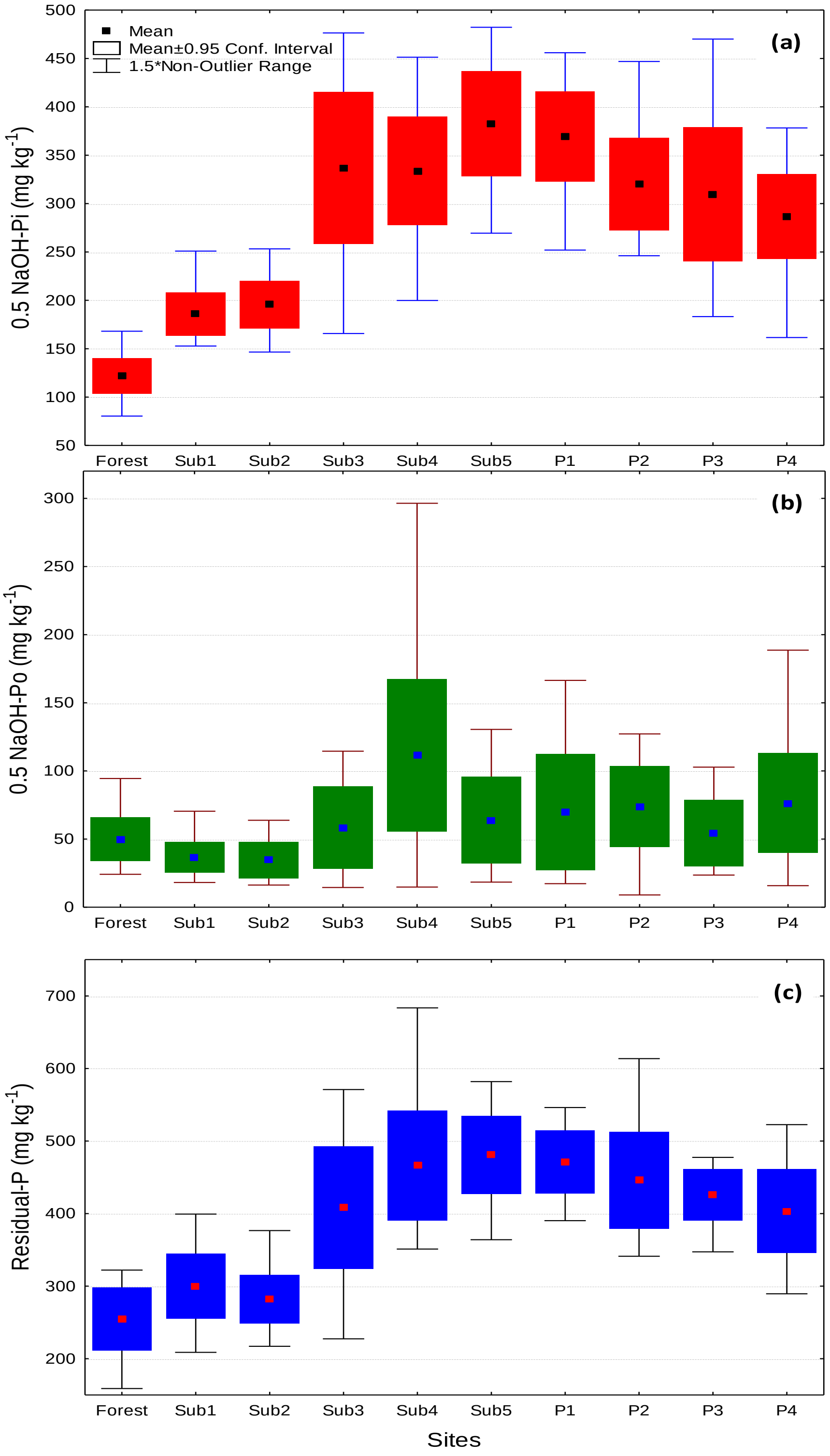

**Fig. 7.** Changes in 0.5 molar sodium hydroxide extractable inorganic P (a), 0.5 molar sodium hydroxide extractable organic P (b) and residual P (c) contents of bed sediments collected across ten different monitoring sites in the Guaporé catchment Southern Brazil, between October 2012 to October 2014 (*n*=30).

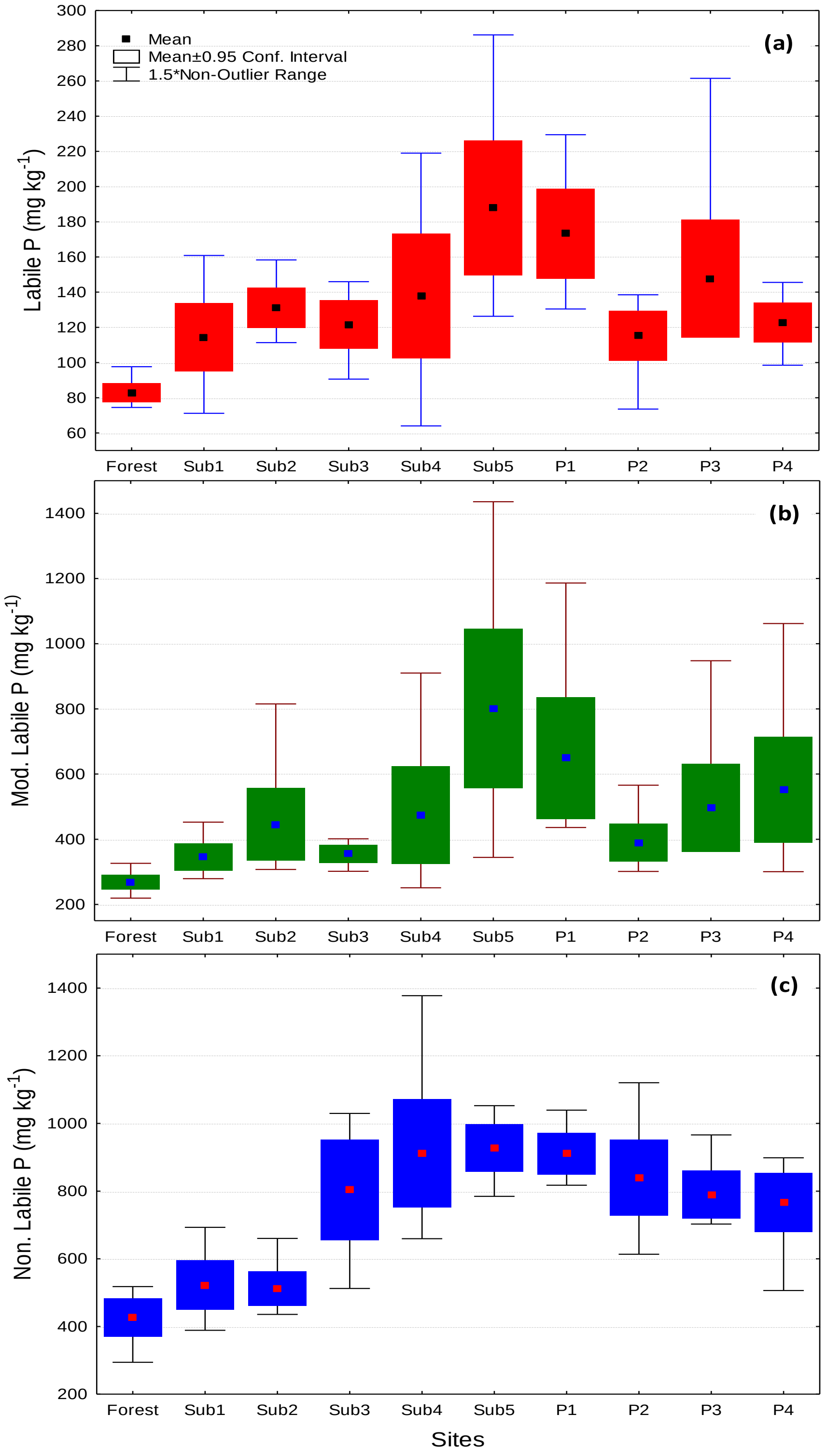

**Fig. 8.** Cumulative pattern of changes in labile P (a), moderately labile P (b) and non- labile P (c) pools of bed sediments across ten different monitoring sites in Guaporé catchment Southern Brazil, between October 2012 to October 2014 (*n*=30).

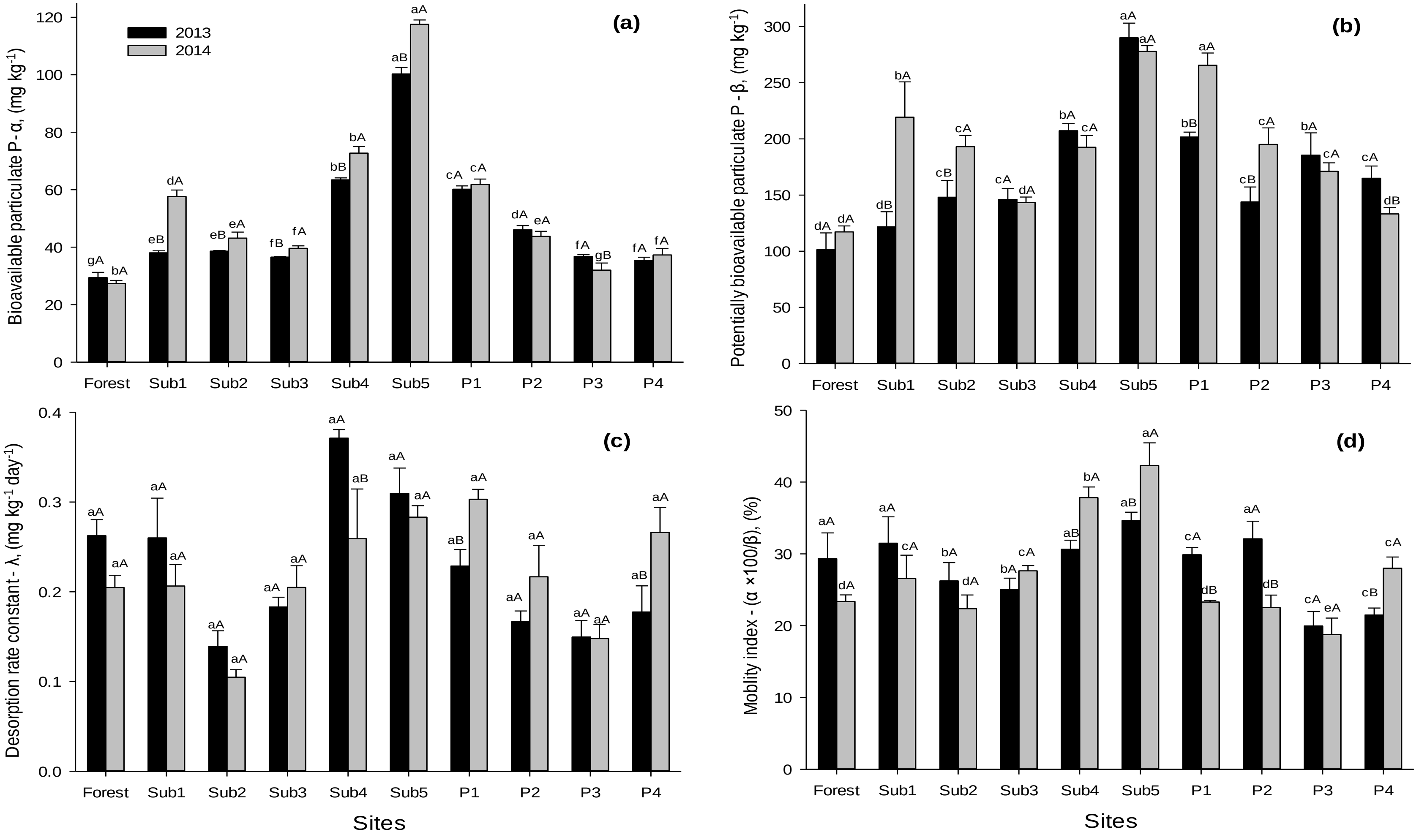

**Fig. 9.** Changes in the readily desorbable P - α (a), potentially available P - β (b), P desorption rate constant - λ (c), and mobility index - (α × 100/β) (d) of bed sediments across ten different monitoring sites in the Guaporé catchment Southern Brazil, during summer 2013 and 2014 (n=3). Lowercase letters on each bar show seasonal variation among different land uses while uppercase letters indicate annual variation within land use and the values followed by the same letter are not significant at $p < 0.05$ by the Scott-Knott test.

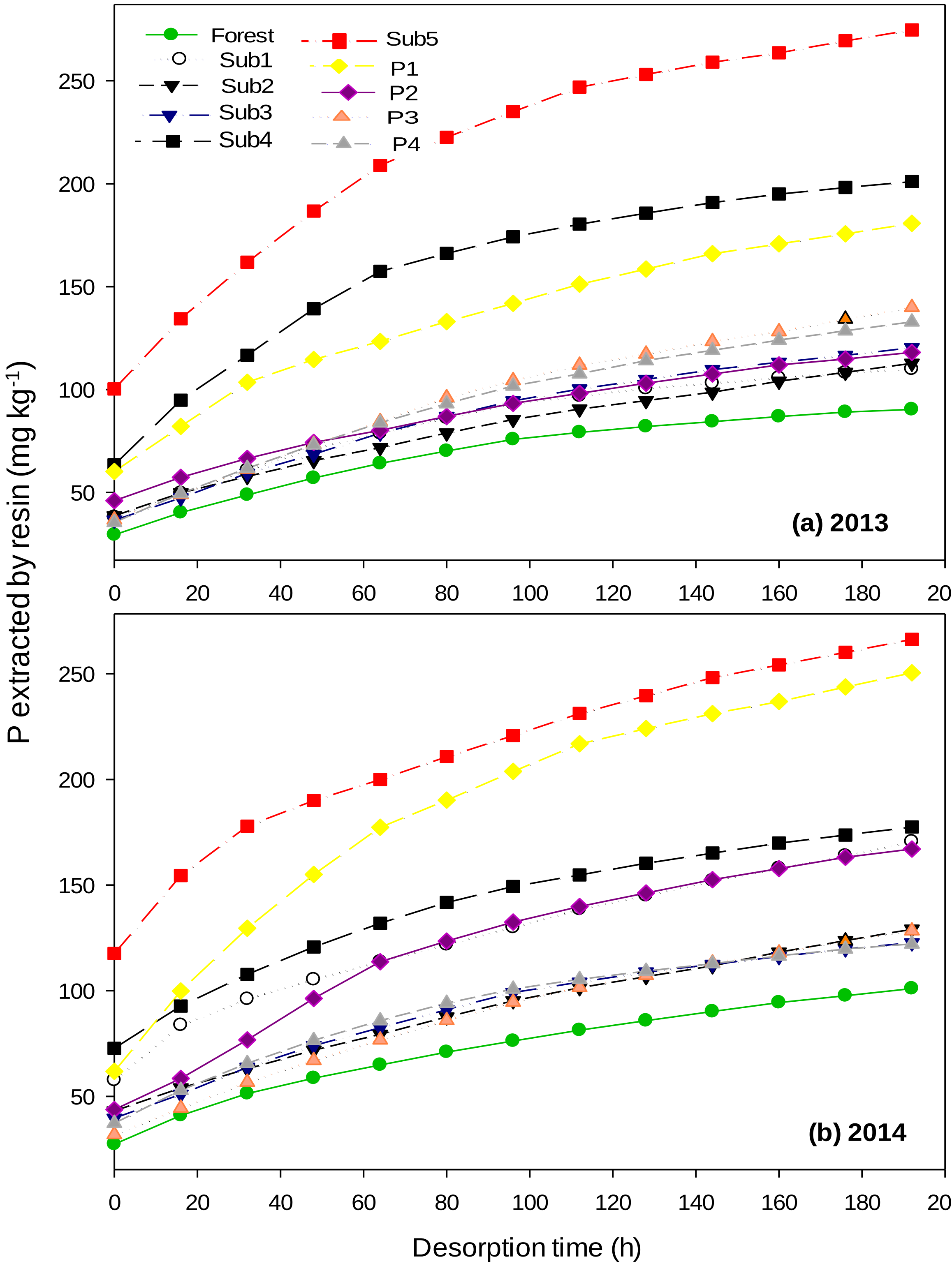

**Fig. 10.** Cumulative phosphorus desorbed by successive anion exchange resin extractions of bed sediments during summer 2013 (a) and summer 2014 (b) across ten different monitoring sites in theGuaporé catchment, Southern Brazil.

**Table 1.** Pearson correlation coefficient (*r*-value) and significance among bed sediment P pools, P lability, desorption parameters and soil variables in Guaporé catchment.

| Parameters | Resin-P | TP | OP | IP | Labile P | Mod. Labile P | Non-LabileP | α | β | λ | Mobility index | TOC | $Fe_{ox}$ | $Fe_{dcb}$ | $Al_{ox}$ | $Al_{dcb}$ | Clay |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TP | **0.85** | | | | | | | | | | | | | | | | |
| OP | **0.67** | **0.88** | | | | | | | | | | | | | | | |
| IP | **0.86** | **0.99** | **0.85** | | | | | | | | | | | | | | |
| Labile P | **0.97** | **0.91** | **0.71** | **0.92** | | | | | | | | | | | | | |
| Mod. Labile P | **0.91** | **0.91** | **0.80** | **0.91** | **0.93** | | | | | | | | | | | | |
| Non-labile P | **0.63** | **0.92** | **0.82** | **0.91** | **0.71** | **0.67** | | | | | | | | | | | |
| α | **0.89** | **0.75** | **0.69** | **0.74** | **0.78** | **0.79** | 0.58 | | | | | | | | | | |
| β | **0.97** | **0.86** | **0.73** | **0.86** | **0.94** | **0.89** | **0.67** | **0.92** | | | | | | | | | |
| λ | 0.36 | 0.41 | 0.59 | 0.37 | 0.26 | 0.33 | 0.42 | **0.60** | 0.42 | | | | | | | | |
| Mobility index | 0.56 | 0.43 | 0.51 | 0.41 | 0.38 | 0.44 | 0.36 | **0.87** | **0.62** | **0.75** | | | | | | | |
| TOC | **0.85** | **0.96** | **0.81** | **0.97** | **0.89** | **0.93** | **0.84** | **0.75** | **0.83** | 0.31 | 0.43 | | | | | | |
| $Fe_{ox}$ | 0.52 | **0.85** | **0.78** | **0.84** | **0.65** | **0.61** | **0.93** | 0.40 | 0.55 | 0.21 | 0.15 | **0.74** | | | | | |
| $Fe_{dcb}$ | **0.68** | **0.83** | **0.69** | **0.83** | **0.70** | **0.63** | **0.87** | **0.69** | **0.72** | 0.30 | 0.53 | **0.75** | **0.85** | | | | |
| $Al_{ox}$ | **0.83** | **0.81** | 0.58 | **0.83** | **0.91** | **0.84** | **0.63** | **0.57** | **0.78** | 0.04 | 0.17 | **0.80** | **0.63** | **0.65** | | | |
| $Al_{dcb}$ | **0.79** | **0.79** | 0.56 | **0.81** | **0.89** | **0.81** | **0.63** | 0.52 | **0.75** | 0.01 | 0.11 | **0.77** | **0.64** | **0.64** | **0.99** | | |
| Clay | 0.32 | 0.06 | -0.09 | 0.08 | 0.32 | 0.27 | -0.18 | 0.18 | 0.29 | -0.56 | -0.04 | 0.17 | -0.10 | 0.09 | 0.49 | 0.49 | |
| Sand | 0.13 | 0.26 | 0.20 | 0.27 | 0.23 | -0.05 | 0.49 | -0.01 | 0.16 | -0.05 | -0.12 | 0.08 | **0.60** | 0.51 | 0.19 | 0.24 | -0.13 |

Resin-P, resin extractable P; TP, total P; OP, organic P; IP, inorganic P; α, bioavailable particulate P; β, Potentially bioavailable particulate P; λ,desorption rate constant;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.

Bold values are significant at $p < 0.05$.

# 5 GENERAL DISCUSSION

## 5.1 Factors affecting sediment TP, P lability, and sorption-desorption kinetics

### 5.1.1 Landform features and hydrology as driver of sediment and PP export

The Guaporé catchment has a characteristics variation in the topographical features, and altitude gradually increases from the South (200 m) to North (850 m) with a hilly topography in the North to undulating in the South. Therefore, the upper one-third of the catchment (lies sub4 and sub5) have a gentle slope and likely to show lower runoff coefficient and sediment yield as compared to the lower one-third (lies forest, sub1, sub2, and sub3) which have a steep slope. Hence, it is logical that the-the increased water erosion in the lower part of the catchment is eroding the higher amount of coarse particle and high amount of soil nutrients. The results in our studies reveal this pattern more clearly during the high rainfall winter months, and thus the sediment eroded during this period contribute to the higher concentration of TP and it a fraction. Our results are in accordance with the recent studies conducted in the region by Didoné et al. (2014) and Minella et al. (2015), who observed the water erosion as a main factor for the soil and water quality deterioration.

### 5.1.2 Geology and spatial variation influence on the sediment P contents

The soil geology and particle chemical composition are very important while investigating sediment P interactions and can help to understand the variations among different sediments sites. The most of the soils are originated from Basalt lithology, and dominant soil classes are Oxisols/Ultisols and show a high content of Fe and Al oxides. The intensive CT site (sub3, sub2) lies in Ultisols while that under NT and urban are located under Oxisols. Therefore, its is obvious that the soil having high Fe and Al oxides are likely to retain high P and a similar trend in most of suspended and bed sediment for sub4 and sub5 sediments for TP, IP, P fractions and P sorption-desorption parameters justifies this relationship. Earlier studies in the region on a variety of soil and sediment have shown similar geochemical behavior with rich fine clay types and high Fe and Al (hydro) oxides (BORTOLUZZI et al., 2013, 2015; FINK et al., 2014, 2016).

### 5.1.3 Effect of urban sources on the sediment P content and its lability

The consistent higher TP and P fractions over the whole monitoring period, both in suspended and bed sediment highlight the significance of the point Resources and urban untreated sewage disposal to the river. It is worth mentioning here, that the both sub-catchments in the start (north) of the catchment (i.e., sub 4 and sub5) have similar land use and management (70% arable under NT), however, the sediments from urban settlement showed high amounts of TP, P lability, biological available P, potentially bioavailable P, and P mobility index. The similar increase in TP and its fractions is observed on the main river (P3) which receives the P flux from the high pig and poultry production drainage area. The similar results have been reported by the WITHERS and JARVIE (2008) and BLANC et al. (2014) in urban sediments and receiving untreated sewage.

### 5.1.4 Land use and soil managment influence on the P characteristics of sediment

The land use variation appeared as a most important factor in regulating the suspended sediment-bed sediment-water interface P dynamic in the river. The gradual increase in arable area linearly increased the sediment TP, P lability and P sorption-desorption kinetics parameters and a typical inter sub-catchment ranking order: urban source > intensive agriculture under NT > intensive agriculture under CT > low agriculture under CT > native forest was observed.

Similarly, the NT and CT also showed a clear difference and the higher sediment P was observed during the winter months of tobacco cultivation under CT. This indicates higher loss of the applied P fertilizer and it was the mostly indicative higher proportion of IP and labile P can during this period. On the other hand, the relatively higher concentration of TOC and OP ($Po_{BIC}$) indicate the increased risk of the P from the areas receiving the high dose of manure/slurry and P chemical fertilizers. Many studies have highlighted the contribution of legacy P as a result of P accumulation in the surface due to the successive slurry and manure applications (COUTO et al., 2015; GUARDINI et al., 2012; SHARPLEY et al., 2014).

### 5.1.5 Temporal variation in sediment TP and P lability and its fractions

The temporal pattern of the suspended and bed sediment clearly showed four distinct groups of monitored sites in terms of sediment P cycling. They include: (group-1) urban site appeared a single highest P containing sediment and over whole sampling period showed higher P values; (group-2) the intensive agriculture sites either under CT or NT; (group-3) the main river (P1 to P5) sediments in descending order along the river continuum; (group-4) low agriculture sub1 and sub2 over the forest.

The seasonal variation in TP, P lability and sorption-desorption concentrations highlighted that the winter months showed more higher sediment P concentration and consequently contributed to the high bioavailable P, high P mobility and Pmax values for the urban and high-intensity agriculture sediments, particularly under CT. Although the results were statistically significant, the inconsistent pattern is associated with the seasonal trends in PP concentrations as documented by the other authors, i.e., EVANS et al. (2004) and PERKS et al. (2015). Another constraint to specifically attribute this variation to a specific process is ambiguous due to the complex heterogeneity of landscape in hydrometeorological conditions, highly varied sediment chemical interactions and the lack of any definite record of nature of these seasonal changes.

## 5.2 Comparison of sediment-P interactions in current and some global studies

As described in the previous sections the P is mainly transported through rivers as PP, and account as much as 90% of total P (TP) load in freshwater catchments (i.e., BOWES et al., 2003; PALMER-FELGATE et al., 2009). The TP concentration gives an estimation of the loss of TP to the water systems and provides a base for the catchment P loads. A comparison of the TP concentrations in various types of freshwater sediments is summarized in Table 1.

The comparison of different land use indicated that the shift from the forest to the increasing anthropic activity there was 50% increase in TP under low agriculture (sub 1 and sub2), > 100 % in intensive agriculture ( sub3 and sub4), and almost two-fold increase in urban sediments. The reported TP concentration is higher from most the reported studies under similar land uses from the various parts of the world (Table 1). Similarly, the main river points indicated the > 130% increase in mean TP. The values reported here are almost two times as higher as reported in different environments except PERYER-FURSDON et al. (2015) who showed higher values than our results.

**Table 1.** The comparison of sediment TP from this study with some global studies.

| **Country** | **Sediment type** | **Land use** | **Total P (mg Kg$^{-1}$)** | **References** |
|---|---|---|---|---|
| UK | Bed Sediments | Mixed/dairy | 1440–1758 | EVANS et al. (2004) |
| UK | Bed Sediments | Mixed/Arable | 155–2678 | PALMER-FELGATE et al. (2009) |
| UK | Suspended | Mixed/Arable | 773–3093 | BALLANTINE et al. (2006) |
| UK | Bed Sediments | Arable | 0.076–0.133 | STUTTER et al. (2008) |
| USA | Suspended | Anthropic | 1163 | BERRETTA; SANSALONE (2011) |
| USA | Suspended | Anthropic/Agriculture | 0.06–0.09 | SMITH et al. (2005) |
| USA | Suspended | Agriculture/Froest | 0.03–0.313 | ELLISON; BRETT (2006) |
| Russia | Suspended | Agricultural | 567 | YAKUTINA (2011) |
| China | Ditch Sediments | Anthropic/Agriculture | 427–717 | ZHUet al. (2012) |
| Argentina | Bed Sediments | Livestock farming | 604 | GARCIA; DE LORIO (2003) |
| China | Suspended | Costal drained | 278–786 | HONG et al. (2010) |
| China | Ditch Sediments | Agriculture | 122.72–293.23 | ZHUAN-XI et al. (2009) |
| Spain | Bed Sediments | Anthropic/Alphine | 69–625.5 | AVILES et al. (2006) |
| Honh Kong | Suspended | Natural vegetation | 789–2463 | LAI; LAM (2008) |
| Australia | Suspended | Agriculture/Forest | 9.09 | KERR et al. (2011) |
| Brazil | Suspended | Agriculture | 0.87–5.51 | PELLEGRINI et al. (2010) |
| USA | Bed Sediments | Mixed/Agricultural | 340 | WANG; HE (2007) |
| China | Suspended | Agriculture | 374 – 537 | TANG et al. (2010) |
| New Zealand | Bed Sedimentary | Anthropic | 477 | COOPER et al.(2015) |
| Poland | Suspended | Agriculture/Diffuse | 1.13 to 1.35 | KATARZYNA et al. (2013) |
| Brazil | Bed Sediment | Urban/Anthropic | 38.59–1760.87 | BLANC et al. (2014) |
| Spain | Suspended | Agriculture/Diffuse | 973.9 | MARÍA et al. (2011) |
| China | Suspended | Agriculture/Diffuse | 396 | GAO et al. (2014) |
| USA | Bed Sediment | Wetland | 338 | DUNNE et al. (2006) |
| New Zealand | Suspended | Agriculture/Diffuse | 2157 | PERYER-FURSDON et al. (2015) |

***This study**

| Sediment type | Forest | sub1 | sub2 | sub3 | sub4 | sub5 | P1 | P2 | P3 | P4 | P5 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Suspended | 752.2 | 905.1 | 943.3 | 1470.1 | 1329.9 | 1738.5 | 1636.8 | 1494.0 | 1509.5 | 1455.7 | 1414.2 |
| Bed | 777.5 | 982.7 | 1089.4 | 1280.9 | 1523.7 | 1916.8 | 1732.4 | 1344.3 | 1433.7 | 1440.8 | -- |

* Each value represents the10 field and 3 laboratory replications.

## 5.3 Conclusions

This study investigated the P bioavailability, river P legacy and sorption-desorption characteristics of sediment-bound P in six representative sub-catchments, in a larger landscape scale a range of sediment properties and landform characteristics to improve our understanding of processes relating to P loss from land to water.

The TP, IP, OP, individual P fraction, either form of P liability and sorption-desorption varied both spatially and temporally among different land uses and the land use and management, sediment chemical constituent and catchment geomorphic feature appeared as a key driver of P mobility. The inter sub-catchments comparison for TP and P lability indicated an order: urban > intensive agriculture CT > intensive agriculture under NT > low agriculture under CT with natural mate plantation>low agriculture under CT > forest. The bed sediment also showed a similar trend for most of P fractions and bioavailability. However, NT sediments showed high P labilities when compared toCT. The most of impacted sediments showed 60% of TP as labile or moderately labile showing high pollution potential.

This indicated that urban untreated sewage is a major source of P pollution and is currently contributing a higher load to water systems, and there is need of immediate municipal wastewater treatments before discharging to the freshwater resources. Furthermore, the comparison of NT and urban sediment reflected that even with similar percentage of cultivated area and soil management system, urban pollution is a major contributor to sediment P, and if the upstream tributary is already affected, the management practices are not much effective in reducing the eutrophic state of the water body. Another key aspect that clearly reveals the high impact of urban and diffuses sources to P lability is the higher concentration of HCl-P (Ca-P) in the impacted sediments that the low agriculture and forest sediments.

The temporal pattern also revealed that the intensive agriculture sub-catchment under CT with tobacco release higher P loads river waters and the geographic factors i.e., slope, drainage connectivity, high rainfall are the key factors contributing to high sediment-bound P loss.

The sediment further revealed that within the same landscape aquatic system (i.e., intensive NT and urban sites), suspended sediment showed greater Prevention and higher P liability and lower degree of P saturation when compared to the river bed sediments. This indicated that bed sediments are equally susceptible to reach sediment P environment threshold and subsequently release P to the surrounding aquatic environments. Furthermore, the higher values of bioavailable P (α) and total desorbed P (β) also confirm this trend principally in suspended sediments.

Among highly intensity NT and CT sites, CT sediments hold high P and showed more capacity to absorb P during high rainfall winter months and will likely be transported over larger distances to the downstream receiving aquatic systems. This variation is likely due to the variation in particle size distribution between the two sediment types.

The chemical composition comparison between the sub-catchments showed that the Fe and Al oxides were the major factors regulating sediment-bound P. TheP sorption-desorption experiment observed high correlation P parameters and Fe/Al oxides. The TOC rather showed a fair correlation with P retention, but it was more significant in the forest and low agriculture catchments.

Surprisingly, the bed sediments, on an average showed almost equal amounts of TP, IP, OP, P fractions and desorption kinetics. As bed sediment are main deposited and stay over time in the river bottom, They can also pose a major threat during low flow summer periods. However, the Fe and Al content also showed their superior role on the sediment behavior.

Finally, the time integrated assessment of sediment-bound P dynamic from different land uses will be useful to draw a baseline to respond wisely to the high-risk agricultural practices, urban pollution and physical control of water erosion to reduce the fine sediment and P losses. The results further open a debate to argue on the suitability of widely practiced cultural practices on a highly heterogeneous landscape in the region to ensure water quality and catchment ecological sustainability.

## 5.4 Broader perspective and future outlook

While the developed countries and environments are talking about the stewardship of finite global P resource, much in environment research in relation to site and crop specific P management and urban planing is needed under the subtropical soil and environment conditions. The 5R strategic stewardship (Re-align P inputs, Reduce P losses, Recycle P in bioresources, Recover P in wastes, and Redefine P in food systems) proposed by the WITHERS et al. (2015) is highly appealing under high agriculture systems like those of Southern Brazil.

To achieve the later three goals in 5R equation at the regional and nation scale ecological P management; first two, i.e., *Re-align P inputs* and *Reduce* P losses are mandatory. Therefore, the temporal monitoring of catchment scale transport and delivery pattern of sediment-bound P are an effective tool.

To this part, the P lability and P fraction in the different sized particle can also reveal important tendencies of different land uses and spatial variations among different land uses.

Our results give us the insight to take the initiative regarding guiding the key manger i.e., local community and farmers to make them convinced to opt best management practices and also for the regional agriculture/urban planners to achieve ecosystem sustainability.

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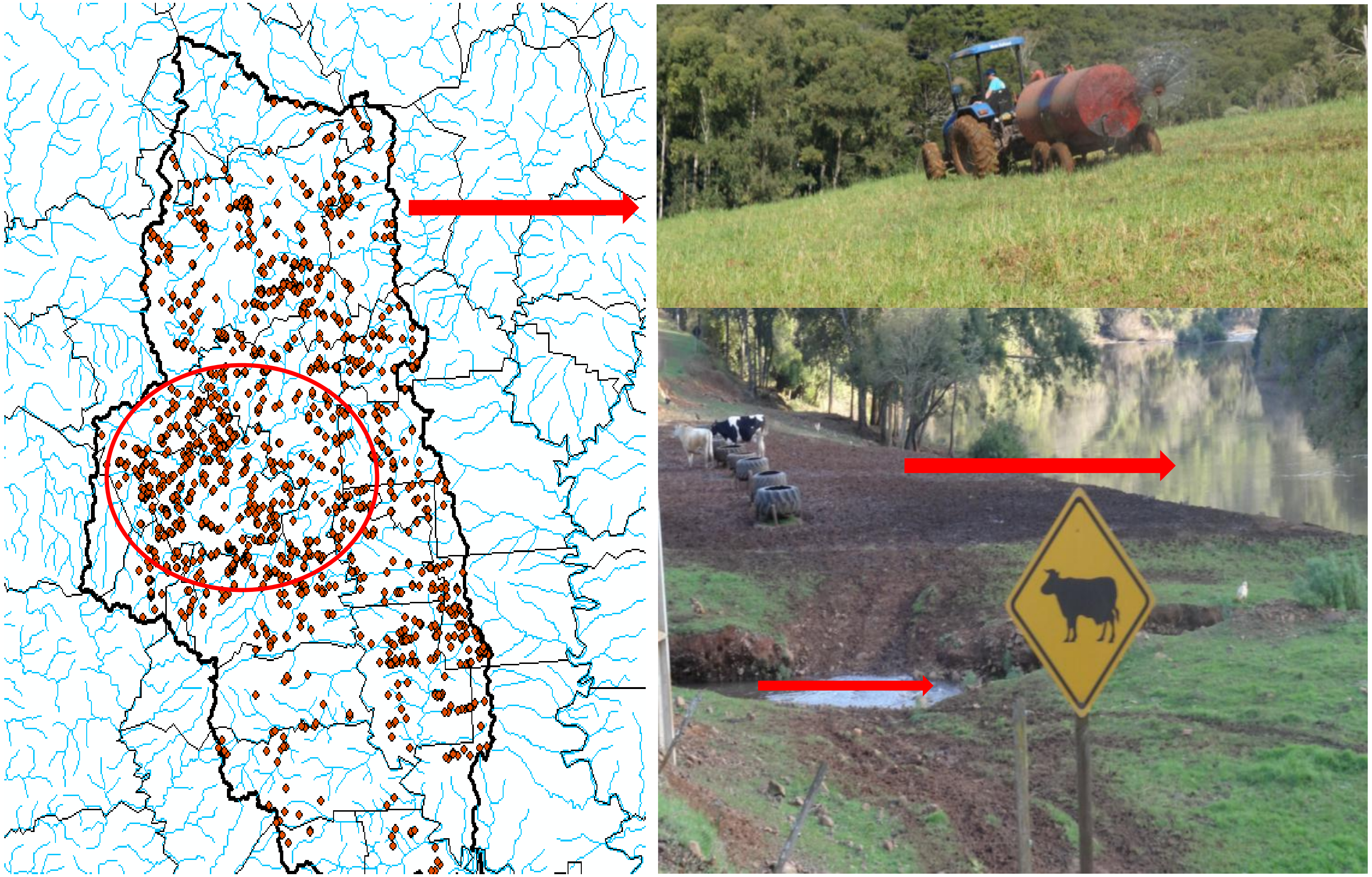
# APPENDIX

**Appendix 1.** The specifications of the time integrated suspended sediment sampler used in the study in the Guaporé in the Rio Grande do Sul State, Southern Brazil.

**Appendix 2.** Photographs of the untreated city sewage and industrial discharges in the upper Northern part (sub5) of the Guaporé catchment in the Rio Grande do Sul State, Southern Brazil.

**Appendix 3.** Photographs showing soybean fields under NT (sub4), in the upper Northern part of the Guaporé catchment in the Rio Grande do Sul State, Southern Brazil.



**Appendix 4.** Georeferenced photographs (left-hand image > 1800 production houses) showing dense pig/poultry farming, and pig slurry and direct disposal of animal wastes (right-hand images) into the river in the middle part of the Guaporé catchment in the Rio Grande do Sul State, Southern Brazil.

**Appendix 5.** Photographs showing steep slopes and water erosion in the lower part of the Guaporé catchment in the Rio Grande do Sul State, Southern Brazil.

**Appendix 6.** Photographs showing tobacco cultivation under CT (sub3), and pig slurry surface application in the lower part of the Guaporé catchment in the Rio Grande do Sul State, Southern Brazil.