

# Mineralogy and nutrient desorption of suspended sediments during a storm event

Edson Campanhola Bortoluzzi ·  
Danilo Rheinheimer dos Santos · Maria Alice Santanna ·  
Laurent Caner

Received: 2 August 2012 / Accepted: 27 March 2013 / Published online: 24 April 2013  
© Springer-Verlag Berlin Heidelberg 2013

## Abstract

**Purpose** This study investigated desorption of potassium (K) and phosphorus (P) from soil and river suspended sediments sampled during a storm event in a Brazilian watershed traditionally used for tobacco plantations.

**Material and methods** Suspended sediment samples were collected automatically at the outlet of the watershed and were grouped into three phases: beginning (phase *a*), middle (phase *b*) and final stages (phase *c*) of the storm event. Granulometric and mineralogical characterisation of soils (0 to 0.20 m depth) and suspended sediments was determined, and K and P extractions were performed using a cation and anion exchange resin (CAER) membrane. A kinetic modelling approach was used to estimate the amount of K and P desorbed.

**Results and discussion** Clay-sized (<2 µm) content of the soils were all <21 %. Kaolinite, smectite (partially with hydroxy-Al interlayer) and a small amount of illite were found

in the clay fraction of the different soils. The clay-sized fractions in sediments of phases *a*, *b* and *c* of the storm event were 49, 52 and 72 %, respectively. Smectite (>90 %) and kaolinite (<10 %) were the dominant clay minerals in the suspended sediments. The values of labile P and potentially available P of suspended sediments were higher than those for soils. In sediments, the highest values of labile P (325 mg kg<sup>-1</sup>) and labile K (4,458 mg kg<sup>-1</sup>) were found in phase *c* and in phase *a*, respectively.

**Conclusions** Particle size distribution and clay mineralogy of soils differed from those of suspended sediments collected during the storm event. By comparison with the watershed soils, suspended sediments collected during the storm event were enriched in fine particles composed mainly of smectite, and this may explain their P and K desorption behaviour. This suggests particle size and clay species selectivity processes during the transfer of sediment particles from soils to aquatic systems. The amounts of P and K desorbed from the suspended sediments in the three phases of the storm event were much larger than those desorbed from soils. This indicates that rainfall promoted the transfer of these nutrients to the watercourses.

---

Responsible editor: Brian Kronvang

---

E. C. Bortoluzzi (✉)  
Faculty of Agronomy and Veterinary Medicine,  
University of Passo Fundo, 99001-970 Passo Fundo,  
Rio Grande do Sul (RS), Brazil  
e-mail: edsonb@upf.br

D. R. dos Santos  
Department of Soils, Center of Rural Sciences, Federal University  
of Santa Maria, 97105-900 Santa Maria, RS, Brazil

M. A. Santanna  
Physics Department, Center of Natural and Exact Sciences,  
Federal University of Santa Maria, 97105-900 Santa Maria, RS,  
Brazil

L. Caner  
University of Poitiers, IC2MP-HydrASA UMR 7285,  
86022 Poitiers, France

**Keywords** Anthropogenic pressure · Ion desorption ·  
Smectite clay mineral · X-ray diffraction

## 1 Introduction

Soils in a given landscape are the result of long-term pedogenic processes and can be heterogeneous in composition, organisation or behaviour (Pédro 1979). Contribution of agricultural soils to river suspended sediment depends on soil type, vegetation, topographic and hydrologic aspects, land use and soil management practices (Owens et al. 2005, 2010; Minella et al. 2007, 2009; Verstraeten et al. 2009;

Bortoluzzi et al. 2010; Pellegrini et al. 2010; Salomons and Förstner 2010).

Fate of agricultural pollutants in soils depends on different adsorption capacities of ions and molecules on soil particles (Barrow 1983; Correll 1998; McDowell et al. 2001a, b). Therefore, the sorption phenomena of ions and molecules on sediments play an important role in the transfer pathways of pollutants in ecosystems (Barriuso et al. 1996; Kaiser and Guggenberger 2003; Owens et al. 2005, 2010; Pellegrini et al. 2010). In this sense, pollutant availability depends on the strength of the chemical bonds established between the ions and the chemical functional groups of the soil or sediment particles (Barrow 1983).

Soils, and the sediments that originate from them, presents heterogeneous mineralogical composition; it is likely that they also present different capacities of association with ions and molecules. A fast potassium (K) desorption rate has been observed for kaolinite that has only external planar surface sites to interact with cations (Selim et al. 1976; Sharpley 1987; Sparks 2001), while a strong K energy bond is observed for 2:1 clay minerals, particularly vermiculite, which has a permanent negative charge. Another aspect to note is that clay minerals (either 1:1 or 2:1 structures) are not expected to adsorb high amounts of anions. From an environmental point of view, one of the most important anions is phosphate. The most reactive surfaces for phosphate interaction are those of minerals such as iron (Fe) and aluminium (Al) oxyhydroxides, followed by edge sites of layer silicates (Rhue and Harris 1999). At these sites, surface hydroxyl groups can be exchanged by phosphate anions (Zhu et al. 2009). Therefore, variable charge minerals, such as kaolinite and Fe and Al oxides, are considered as the major mechanism responsible for phosphorus (P) fixation in highly weathered soils (Parfitt 1978; McLaughlin et al. 1981). However, in soils with 2:1 clay minerals, another P adsorption mechanism is likely to occur due to presence of surface coatings of Fe oxyhydroxides, in which adsorption of anions, such as phosphate, can occur (Golterman 2010).

In this sense, mineralogical characterisation is widely used in soil science to study ion sorption phenomena on clay minerals. Studies of suspended sediment commonly show detailed particle size analysis to specify processes of particle transfers. However, identification and quantification of clay minerals can be useful approaches to estimate nutrient transfers in rural watersheds (e.g., Bortoluzzi et al. 2010). Thus, it is plausible to suppose that variability of particle size distributions and clay mineral species between soils and sediments affects the sorption phenomena as well as the potential transfer of pollutants at the watershed scale. In addition, if there are changes in particle size distribution and mineralogy of suspended sediments during a storm event, the nutrient desorption behaviour will vary during the rainfall event. Here, we aim to investigate K and P desorption of soils and suspended sediment samples in a small rural sub-tropical watershed subject to a high rainfall and

erosion regime. The data are discussed in relation to the mineralogy of the soils and suspended sediments in the catchment. The suspended sediments were collected at the discharge point of the watershed during a storm event.

## 2 Material and methods

### 2.1 Catchment location and characteristics

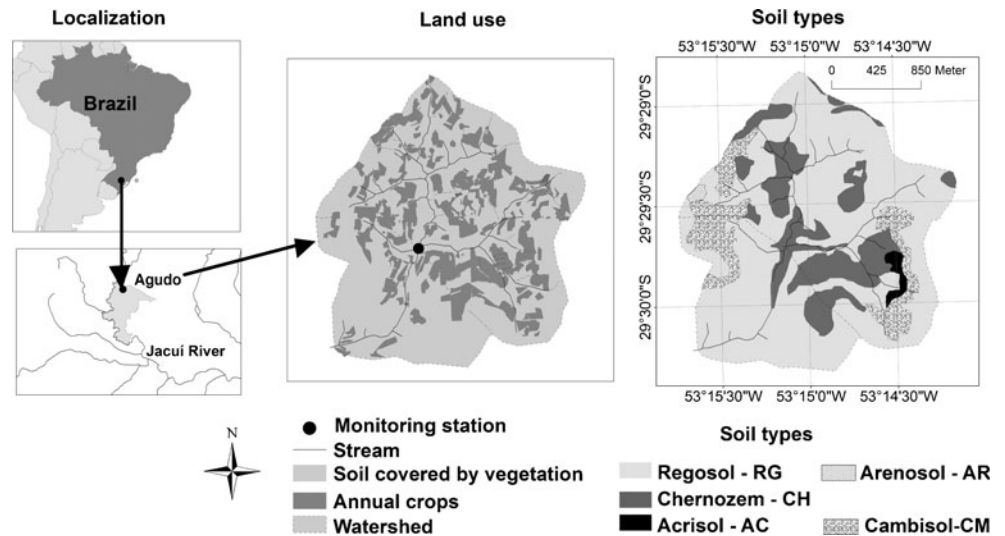
The rural Agudo watershed (total area of 0.48 km<sup>2</sup>), located in a sub-tropical climate in the Rio Grande do Sul State (Southern Brazil), was monitored from 2000 to 2004 as part of a comprehensive research programme (Rheinheimer 2003). Geology is dominated by the Serra Geral Formation, which parent materials are andesite–basalts from basic to intermediate lava flows. It also includes sandstone rocks from the Botucatu Formation. The original natural vegetation of the watershed was a deciduous sub-tropical forest, Mata Atlântica (Atlantic forest). Secondary forest represents >60 % of the remaining area. Soil types and main land uses in 2003 were identified by topographic maps, aerial photographs and a field survey using a global positioning system (GPS) device. The land uses were grouped as follows: annual crops, forest cover (forests and reforestation), perennial pasture and other land uses (fields cultivated, orchards, installations and roads) (Fig. 1 and Table 1). Watershed details can be found in earlier studies (e.g., Rheinheimer 2003; Dalmolin et al. 2004; Bortoluzzi et al. 2006, 2007; Sechinatto 2007; Minella et al. 2007, 2009; Pellegrini et al. 2010; Rheinheimer et al. 2010).

The watershed is composed of 36 farms. Eighty percent of the farmers produce tobacco crops under a conventional tillage system, which implies high and frequent pesticide and fertiliser applications (Bortoluzzi et al. 2006, 2007). The soil types in the watershed are Regosol, Chernozem, Cambisol, Acrisol and Arenosol (see Table 1) (Dalmolin et al. 2004). Chernozem and Regosol soils are located in the slopes of the watershed and are under intense human pressure, mainly due to agriculture (Pellegrini et al. 2010).

### 2.2 Soil sampling and analysis

Soil samples (0–0.20-m layer) were collected for five different cultivated soil types. To collect the soil samples, 50 trenches (0.20 m wide × 0.20 m thick) were dug at randomly chosen points in each area. These 50 sub-samples were mixed, air dried, sieved (<1 mm) and stored at room temperature. pH and total amounts of exchangeable P, K, Al, Ca and Mg were determined in the soil samples. Soil organic matter (SOM) was determined by wet digestion with H<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in a block digestion (Rheinheimer et al. 2008). Effective cation exchange capacity (CEC<sub>E</sub>) and the cation

**Fig. 1** Map showing the location, the land use and the main soil types in the Agudo watershed, Rio Grande do Sul state, Brazil. The monitoring station where the suspended sediment samples were collected during a rain storm event is also indicated. Adapted from Rheinheimer (2003) and Dalmolin et al. (2004)



exchange capacity at pH 7 (CEC<sub>7</sub>) were determined by the sum of the cations (K, Ca, Mg and Al) and (K, Ca, Mg and H+Al), respectively. Total surface area (TSA) of soil clay fraction was measured by adsorption of ethylene glycol monoethyl ether (EGME) according to Carter et al. (1965).

2.3 River suspended sediment sampling strategy

A stream monitoring station (Parshall flume) was installed at the outlet of the watershed, where tributaries flow into the main stream, to allow calculation of outflow discharge. Water

**Table 1** Land use and soil physicochemical characteristics in the Agudo watershed, Rio Grande do Sul state, southern Brazil

Land/soil parameters	Soil types				
	Chernozem CH	Regosol RG	Arenosol AR	Cambisol CM	Acrisol AC
Soil distribution and land uses					
Depth (m)	0–0.20	0–0.20	0–0.20	0–0.20	0–0.20
Total area (%)	24.1	61.8	0.6	11.0	1.5
Area cropped (%)	40.3	38.8	0.3	16.3	3.4
Soil chemical characteristics					
pH	5.4	5.1	5.3	6.1	5.6
P (mg kg <sup>-1</sup> )	17.1	11.8	6.0	18.9	31.2
K (mg kg <sup>-1</sup> )	120	176	44	188	220
Al (cmol <sub>c</sub> kg <sup>-1</sup> )	0.5	0.2	0.2	0	0
Ca (cmol <sub>c</sub> kg <sup>-1</sup> )	14.7	12.5	1.8	6.9	2.3
Mg (cmol <sub>c</sub> kg <sup>-1</sup> )	4.3	2.6	0.6	1.1	0.7
H+Al (cmol <sub>c</sub> kg <sup>-1</sup> )	2.8	4.4	2	1.7	2.2
Soil characteristics <sup>a</sup>					
Clay (%)	21	14	12	17	15
SOM (%)	2.0	3.4	0.7	2.9	1.0
TSA (m <sup>2</sup> g <sup>-1</sup> )	271.7	142.2	177.8	115.0	233.5
Cation exchange capacity <sup>b</sup>					
CEC <sub>E</sub> (cmol <sub>c</sub> kg <sup>-1</sup> )	19.8	15.8	2.7	8.5	3.6
CEC <sub>7</sub> (cmol <sub>c</sub> kg <sup>-1</sup> )	22.1	20	4.5	10.2	5.8
Soil clay mineralogy <sup>c</sup>					
Smectite+HIS	+	++	++	+	**
Illite	**	*	*	*	**
Kaolinite	*	***	*	+	***

<sup>a</sup>Clay is clay contents, TSA is total surface area and SOM is soil organic matter  
<sup>b</sup>CEC<sub>E</sub> and CEC<sub>7</sub> correspond, respectively, to the effective and at pH 7 cation exchange capacities  
<sup>c</sup>Semi-quantitative analysis relative proportion classification, following: \* 1–10 %, \*\* 11–25 %, \*\*\* 26–40 %, + 41–65 %, ++ 66–80 %; HIS is hydroxy-Al inter-layered smectite

flow ( $Q$ ) and river suspended sediment concentrations (SSC) were determined for all rain events between 2000 and 2004. The data for  $Q$  (cubic meters per second) at the stream monitoring station were estimated as a function of the height of the water layer in the Parshall flume ( $X$ ) using the equation:  $Q=10.544X^{1.2666}$  (Sechinatto 2007). The sampler employed to collect suspended sediments was a modified version of the model US U-59.

In the present study, a detailed investigation of a storm event that occurred on 8 October 2003 was performed, focusing on mineralogy and P and K desorption behaviour of soils and river suspended sediments. During this rainfall event, suspended sediment samples were collected at the stream monitoring point, in duplicate, according the following sampling strategy. From the onset of rainfall ( $t=0$  min) until 20 min, three suspended sediment samples were collected at intervals of 10 min. After that, during the high water flow period, five samples were taken at intervals of 4 min (the last one at  $t=40$  min). From that time up to  $t=100$  min, six samples were collected at intervals of 10 min. Finally, 20 min latter, a last sample ( $t=120$  min) was collected. This procedure gave rise to 15 suspended sediment samples.

To perform mineralogical characterisation as well as P and K desorption from suspended sediments, both requiring high sample amounts, the samples were grouped into three phases ( $a$ ,  $b$  and  $c$ ). Criteria used to establish the three phases of the rain event was based on the water flow (Fig. 2):

- Phase  $a$ : included the two samples collected at the beginning of the rainfall, when the water flow was  $<1,000 \text{ l s}^{-1}$ . This phase represents a low SSC and corresponds to the background water flow (regular stream flow);
- Phase  $b$ : comprises the 10 samples collected when the water flow was  $>1,000 \text{ l s}^{-1}$ . During this period ( $20 \text{ min} < t < 80 \text{ min}$ ), the water flow had a fast increase (up to  $2,299 \text{ l s}^{-1}$ ), followed by a slow decrease. This phase has high SSCs.
- Phase  $c$ : consisted of the last three samples, collected when the water flow was again  $<1,000 \text{ l s}^{-1}$ . This phase had low SSCs, corresponding to the more persistent fine particles in the water.

#### 2.4 Preparation of samples for particle size and mineralogical analyses

Soil samples were pre-treated with  $\text{H}_2\text{O}_2$  (30 % v/v) to remove organic matter and underwent chemical and mechanical dispersion. To enable comparisons, the same methodology for particle size analysis was adopted for soils and sediments. Suspended sediment samples underwent shaking and chemical dispersion only. Sand ( $>53 \mu\text{m}$ ) and silt ( $2\text{--}53 \mu\text{m}$ ) fractions were separated out by sieving and weighed. Clay fractions ( $<2 \mu\text{m}$ ) were extracted by centrifugation and

determined by the pipette method (sedimentation) according to the procedure described by Robert and Tessier (1974).

A sub-sample of the clay fractions from the soils and suspended sediments was saturated with  $\text{CaCl}_2$  ( $1 \text{ mol l}^{-1}$ , three times) and washed with distilled water to eliminate excess ion in order to perform x-ray diffraction (XRD) and TSA measurements (Robert and Tessier 1974). A second sub-sample (5 ml) of suspended sediment was taken to determine the SSC by weighting after drying at  $100 \text{ }^\circ\text{C}$ .

XRD patterns from soils and suspended particles of the three sampling phases ( $a$ ,  $b$  and  $c$ ) were determined on oriented specimens using a Siemens D5000 diffractometer equipped with a monochromator (Co  $\text{K}\alpha$  radiation) operating at 40 kV and 30 mA. Oriented specimens were prepared by depositing a clay suspension onto a glass slide. These samples were scanned after air drying at room temperature (AD), solvation with ethylene glycol (EG) and heating at 200 and  $550 \text{ }^\circ\text{C}$ , as described by Robert and Tessier (1974) and Bortoluzzi et al. (2010). The XRD patterns were interpreted using the DIFFRAC AT software (Socobim, France) according the procedures described in Brindley and Brown (1980). The XRD patterns were decomposed into their elementary component curves using the DecompXR software (Lanson 1997) in the  $4\text{--}16^\circ 2\theta$  angular range. A semi-quantitative phase analysis was performed using the relative surface peak areas of clay minerals, according to the intensity and full width at half maximum (FWHM) of each peak in XRD pattern (Hughes et al. 1994). The relative intensity of each peak does not correspond to the proportion of the respective mineral; however, the variations of relative intensities correspond to variations in mineral quantities (Lanson 1997).

#### 2.5 Soils and sediment P and K desorption

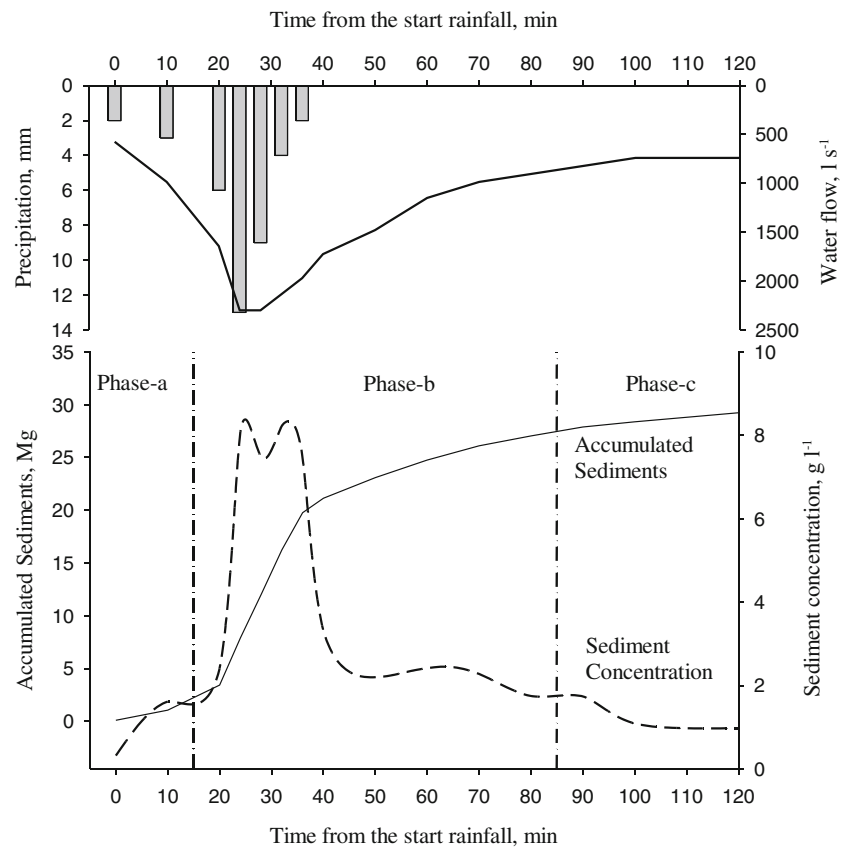
Soil P and K desorption capacities were estimated by nine successive extractions with a CAER membrane, while for the suspended sediment samples, they were estimated by four successive extractions. Details of the procedure are presented by Pellegrini et al. (2010). The results for each soil sample are presented as the mean of triplicate sub-samples submitted to this CAER extraction method. In addition, total P and K contents of the suspended sediments were solubilised by digestion using  $\text{HF}+\text{H}_2\text{SO}_4$  and they were estimated by UV-visible spectroscopy and flame emission spectroscopy.

#### 2.6 Desorption data analysis

Ion desorption from both soil and suspended sediment sample data were determined using the McKean and Warren's equation (McKean and Warren 1996):

$$Q_{\text{des}} = \beta - (\beta - \alpha)e^{-\lambda t} \quad (1)$$

**Fig. 2** Precipitation, water flow, suspended sediment concentration and amount of suspended sediment collected at the river monitoring station during a rain storm event that occurred on October 8th 2003 in the Agudo watershed. The vertical dashed lines in the bottom graph indicate the limits between the three phases of the rain storm event, established from the river flow data: phase *a* (start of rainfall event; water flow  $<1,000 \text{ l s}^{-1}$ ); phase *b* (middle of rainfall event; water flow  $>1,000 \text{ l s}^{-1}$ ) and phase *c* (end of rainfall event; water flow  $<1,000 \text{ l s}^{-1}$ )



where  $Q_{des}$  is the amount of ion desorbed after a given time  $t$  and  $\lambda$  is the constant desorption rate of the first-order desorption reaction. The amount extracted in the first extraction ( $t=0$ ) is equal to the parameter  $\alpha$  (labile ion), corresponding to the chemical element quantities readily desorbable from soil. Parameter  $\beta$  represents the ultimate amount of chemical element desorbable from each soil after successive extractions with the resin, which can be assumed to represent the potentially bioavailable amount of these elements in the soil. In the fitting,  $\beta$  and  $\lambda$  were treated as parameters to be optimised and were computed using an iterative technique. Higher values of  $\lambda$  indicate higher reaction rates.

### 3 Results

#### 3.1 Soil and river suspended sediment characterisation

Soil clay contents are presented in Table 1 and particle size distribution of suspended sediments are shown in Fig. 3. In soils, the clay fraction contents were  $<21\%$ . Organic matter contents ranged between 0.7 and 3.4%. The soils were slightly acidic, with  $\text{pH}_{\text{water}}$  values ranging between 5.1 and 6.1, and all had low values of  $\text{H+Al}$ .  $\text{CEC}_7$  ranged between 4.5 and  $22.1 \text{ cmol}_c \text{ kg}^{-1}$ . Low  $\text{CEC}_7$  values were found for Acrisol and Arenosol, and higher values were

found for Chernozem, Regosol and Cambisol soils. Exchangeable P and K are considered high in these soils; exchangeable P ranged from  $6.0 \text{ mg kg}^{-1}$  (Arenosol) to  $31.2 \text{ mg kg}^{-1}$  (Acrisol), while exchangeable K ranged from  $44 \text{ mg kg}^{-1}$  (Arenosol) to  $220 \text{ mg kg}^{-1}$  (Acrisol). The TSA of the soil clay fractions ranged between  $115 \text{ m}^2 \text{ g}^{-1}$  (Cambisol) and  $271 \text{ m}^2 \text{ g}^{-1}$  (Chernozem).

Mineralogy analysis of these soils (XRD patterns not shown) showed a peak at  $d=1.45 \text{ nm}$  (AD), which undergoes shifting after the EG solvation, indicating the presence of smectite. Part of these minerals may correspond to hydroxy-Al inter-layered smectite (HIS) because there was a collapse of incomplete layers to  $d=1.0 \text{ nm}$  after heating at  $550^\circ\text{C}$ . The peaks at  $d=1.0, 0.5$  and  $0.33 \text{ nm}$  correspond to illite (Moore and Reynolds 1997). Kaolinite is represented by the peaks at  $d=0.715$  and  $0.358 \text{ nm}$ , which disappeared after heating at  $550^\circ\text{C}$ . These clay minerals are ubiquitous in sub-tropical soils (Bortoluzzi et al. 2008). Relative proportion of clay contents was semi-quantified by XRD pattern decomposition. Clay mineral contents in soil clay fraction (2:1) are predominant in all soils ( $\sim 50\%$ ), except for Acrisol ( $\sim 25\%$ ). Illite was present in all soils in proportions  $<15\%$ . Kaolinite appears in large quantities in Regosol ( $\sim 30\%$ ), Cambisol ( $\sim 40\%$ ) and Acrisol ( $30\%$ ) and proportionally  $<10\%$  in Chernozem and Regosols (see Table 1).

In suspended sediments, the SSC was lower in phases *a* and *c* and higher in phase *b* (with approximately  $8 \text{ g l}^{-1}$ ) (see

**Fig. 3** Grain size distribution of suspended sediments collected at the river monitoring station during a rain storm event in the Agudo watershed. The vertical dashed lines indicate the limits between the three phases of the rain storm event: phase *a* (start of rainfall event; water flow  $<1,000 \text{ l s}^{-1}$ ); phase *b* (middle of rainfall event; water flow  $>1,000 \text{ l s}^{-1}$ ) and phase *c* (end of rainfall event; water flow  $<1,000 \text{ l s}^{-1}$ )

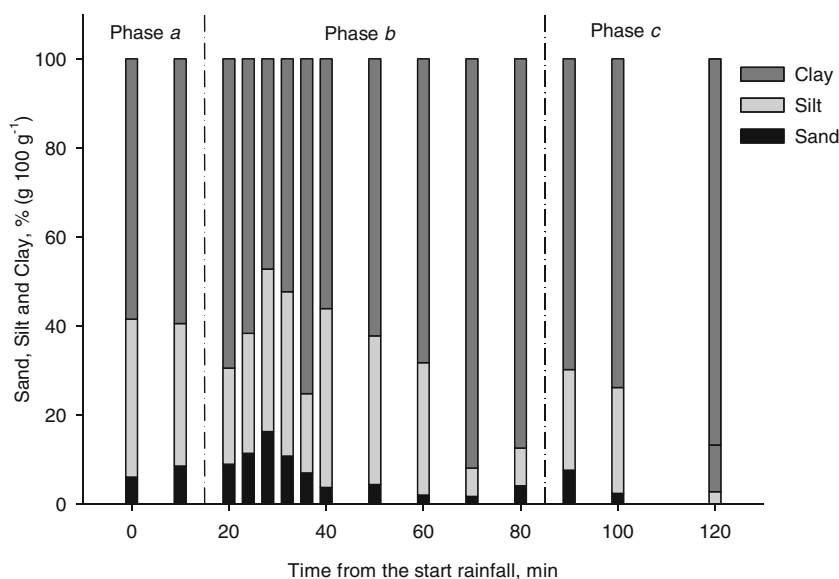


Fig. 2). In spite of the low total precipitation (39 mm) of this rain event, the maximum intensity of  $3.25 \text{ mm min}^{-1}$  ( $195 \text{ mm h}^{-1}$ ) indicates a high erosive potential (Mehl et al. 2001; Oliveira et al. 2012). This storm resulted in a  $Q$  as high as  $2,500 \text{ l s}^{-1}$ ; the transported sediment reached 29.2 Mg for the total catchment (480 ha). During the storm event, the contribution of the clay fraction in the river suspended sediment load increased, while the silt and sand fractions decreased (see Fig. 3). The clay fraction was the dominant particle size fraction in the suspended load during the rain event, representing 49, 53 and 72 % content in phases *a*, *b* and *c*, respectively. In phases *a*, *b* and *c*, silt represented 36, 34 and 19 % of the total particle load, respectively. The sand size fraction corresponded to 14, 13 and 8 % content in phases *a*, *b* and *c*, respectively.

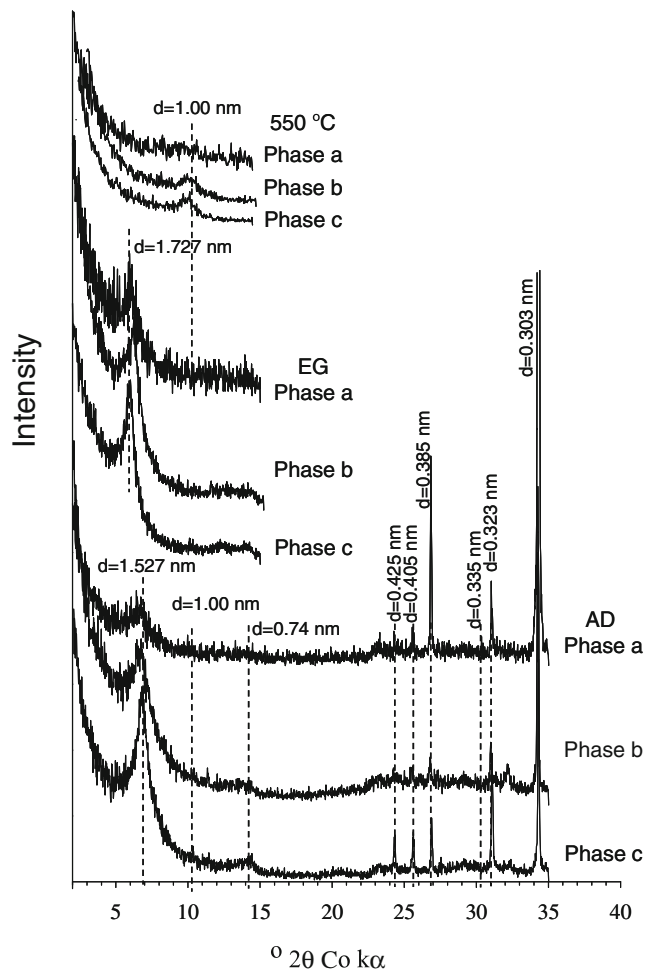
The amounts of total P and total K present in the suspended sediment samples collected during the rain event are shown in Table 3. The highest values of total P and total K correspond to samples collected at the beginning of the rain event when the water level at the stream monitoring station started to increase. A sharp decline of both ions is observed in the subsequent samples. The lowest values of total P and total K in suspended sediments were observed during phase *b* of the rainfall (maximum water flow), being 645 and  $4,210 \text{ mg kg}^{-1}$ , respectively.

The mineralogy of suspended sediment is shown in Fig. 4. In the XRD patterns of phase *a*, a peak at  $d=1.53 \text{ nm}$  (N), which displaces towards  $d=1.73 \text{ nm}$  after EG solvation, was observed. Following heating at 200 and  $550 \text{ }^\circ\text{C}$ , the  $d=1.53\text{-nm}$  peak collapses at  $d=1.0 \text{ nm}$ . These treatments allow for an expandable 2:1 clay mineral to be identified, most likely smectite (Moore and Reynolds 1997). The high intensity and the narrow FWHM of the peak at  $d=1.53 \text{ nm}$  indicate a high coherent scattering domain size, commonly attributed to high crystallinity. Peaks corresponding to illite ( $d=1.00$  and

$0.50 \text{ nm}$ ) were not found. The peaks at  $d\sim 0.72\text{--}0.75 \text{ nm}$  and  $d=0.358 \text{ nm}$ , which disappeared following heating at  $550 \text{ }^\circ\text{C}$ , indicate the presence of kaolinite (Brindley and Brown 1980). In phases *b* and *c*, the observed clay minerals were quite similar; however, the peaks of the 2:1 clay minerals were more intense. It is possible to see intense peaks in the suspended sediment XRD patterns, which correspond to the third order of peak at  $d=1.50 \text{ nm}$ . The peaks at  $d=0.425$  and  $0.334 \text{ nm}$  correspond to quartz. The narrow and intense peaks at  $d=0.385$  and  $0.303 \text{ nm}$  in all XRD patterns indicate the presence of calcite. The presence of this mineral can be explained by the high lime quantities applied to the soils for tobacco growing. Occurrence of feldspars was confirmed by the presence of peaks at  $d=0.405$  and  $0.323 \text{ nm}$  (Brindley and Brown 1980). Smectite, calcite and quartz were detected in all XRD patterns of the suspended sediments and the soils. Feldspars, illite and kaolinite were found only in the XRD patterns corresponding to phases *b* and *c* of suspended sediments.

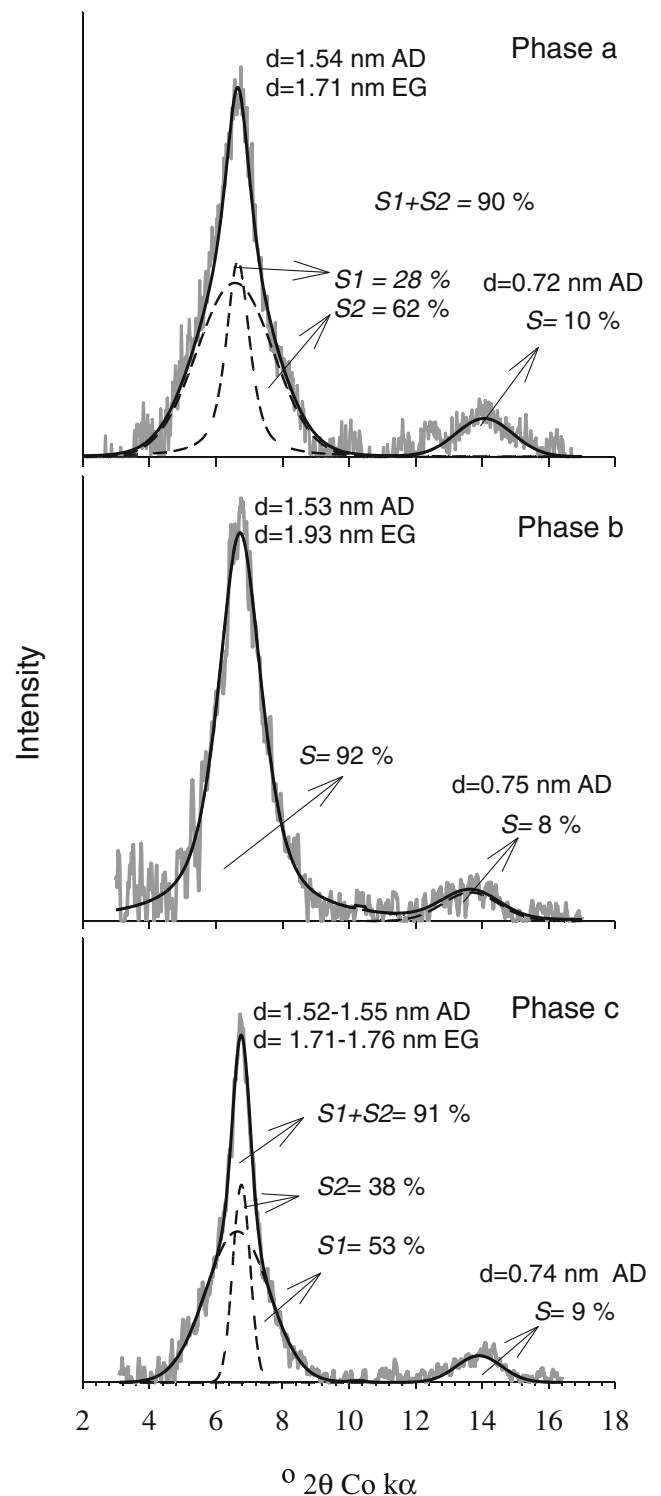
The XRD pattern for suspended sediment for phase *a* was adjusted with three Gaussian curves after decomposition (Fig. 5). Two curves (S1 and S2) with maximum intensity at  $d=1.54 \text{ nm}$  (AD), corresponding to smectite clay minerals, represent 90 % of the relative surface area. The S1 curve corresponds to a swelling/shrinking smectite because swelling after EG solvation, followed by collapse after  $550 \text{ }^\circ\text{C}$  treatment (see Fig. 4), was observed. The S2 peak probably corresponds to HIS, since there was an incomplete collapse of layers to  $d=1.00 \text{ nm}$  after  $550 \text{ }^\circ\text{C}$  (see Fig. 4). This is in accordance with the fact that this mineral is commonly found in regional soils (Bortoluzzi et al. 2008, 2012). The curve with maximum intensity at  $d=0.72 \text{ nm}$  (AD) corresponds to kaolinite and represents 10 % of the relative surface area (see Fig. 5).

The XRD pattern for suspended sediment for phase *b* was adjusted with two Gaussian curves after decomposition.



**Fig. 4** XRD patterns of the  $\text{Ca}^{2+}$ -saturated  $<2\text{-}\mu\text{m}$  fraction of suspended sediments after air-drying (AD), ethylene glycol solvation (EG) and heating at  $550\text{ }^\circ\text{C}$ . The suspended sediment samples were collected at the river monitoring station during a rain storm event in the Agudo watershed. The phases of the rain storm event were: phase *a* (start of rainfall event; water flow  $<1,000\text{ l s}^{-1}$ ), phase *b* (middle of rainfall event; water flow  $>1,000\text{ l s}^{-1}$ ) and phase *c* (end of rainfall event; water flow  $<1,000\text{ l s}^{-1}$ )

Smectite and kaolinite clay mineral peaks correspond, respectively, to 92 and 8 % of the relative surface area under the curve. For the phase *c*, the XRD pattern decomposition shows that the kaolinite peak at  $d=0.74\text{ nm}$  corresponds to 9 % of the relative surface area under the curve. The peak at  $d=1.52\text{--}1.55\text{ nm}$  (AD) was adjusted with two Gaussian curves (S1 and S2) that accounted for 91 % of the total relative area. The first peak was at  $d=1.52\text{ nm}$  (AD) and shifted to  $d=1.71\text{ nm}$  following EG solvation, and the second peak at  $d=1.55\text{ nm}$  shifted to  $d=1.76\text{ nm}$  after EG treatment (see Fig. 5). The smectite mineral found in the *b* and *c* phases represents a layer collapse after heat treatment at  $550\text{ }^\circ\text{C}$  (see Fig. 4), indicating low quantities of hydroxy-Al inter-layered. This behaviour suggests the presence of smectite clay minerals with different degrees of crystallinity (Moore and Reynolds 1997; Velde 2001). Smectite and kaolinite are, thus, the main clay minerals



**Fig. 5** Decomposition of XRD patterns, using the DecompXR programme, of the  $<2\text{-}\mu\text{m}$  fraction of suspended sediment samples collected at the river monitoring station during a rain storm event in the Agudo watershed. The phases of the rain storm event were: phase *a* (start of rainfall event; water flow  $<1,000\text{ l s}^{-1}$ ), phase *b* (middle of rainfall event; water flow  $>1,000\text{ l s}^{-1}$ ) and phase *c* (end of rainfall event; water flow  $<1,000\text{ l s}^{-1}$ ). AD air-dried, EG ethylene glycol treatment, *S* proportion of surface area of peak in the x-ray pattern. Grey line indicates experimental curve, black line is the best-fit curve and black dashed line corresponds to the computed elementary curve

dispersed during this rainfall event. This result indicates that there was a preferential leaching of smectites, which are usually of smaller size than kaolinites and illites. Illite was not present in suspended sediments.

### 3.2 Phosphorus and potassium desorption in soils and suspended sediments

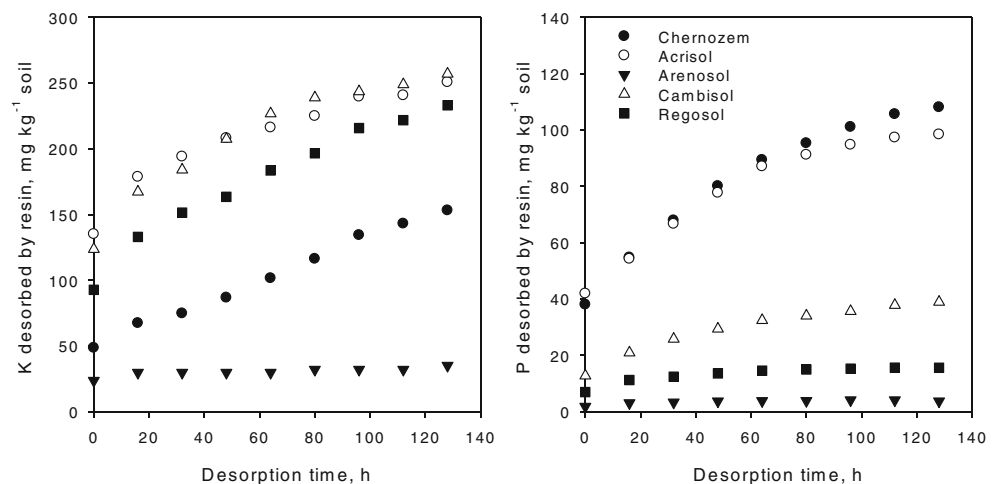
In soils, after nine extractions, most of the desorption curves reached a plateau, and afterwards, very little additional P or K was extracted (Fig. 6). For Arenosol, the K and P accumulations present very low increases along the extraction times, while for the other soils, a greater increase in K was observed during the time period. Chernozem and Arenosol present the lowest values of labile K ( $\alpha=49$  and  $24 \text{ mg kg}^{-1}$ , respectively; Table 2). Despite the low amount of labile K in soils, Chernozem plays an important role in the transport of K by sediment particles, as it presented the highest value of potentially desorbable K ( $\beta=1,029 \text{ mg kg}^{-1}$ ) and the lowest desorption constant of the desorption reaction ( $\lambda=8.96\text{E}-04 \text{ h}^{-1}$ ). Successive extractions procedure employed ( $\alpha$  and  $\beta$  parameters) reflect the behaviour of sediments originating from this soil. Therefore, it is expected that sediments coming from Chernozem soils transport significant quantities of K. However, due to the low K lability, delivery of K from the sediment to the watercourses is likely to occur slowly. Besides Chernozem, Cambisol and Regosol are also important soil types with a large spatial distribution and are used for agriculture in the watershed. Both presented a similar behaviour for K desorption, although Cambisol has a slightly higher amount of labile K ( $\alpha=124 \text{ mg kg}^{-1}$ ) compared to Regosol ( $\alpha=93 \text{ mg kg}^{-1}$ ). Quantities of potentially desorbable K (parameter  $\beta$ ) are quite similar for Cambisol and Regosol ( $269$  and  $272 \text{ mg kg}^{-1}$ , respectively). The values of the constant of desorption reaction are also similar for these soil types but are approximately one order of magnitude larger than the  $\lambda$  value obtained for Cambisol

(see Table 2). Sediments from Cambisol and Regosol are, therefore, likely to primarily carry labile K, which is then quickly delivered to the watercourses.

Chernozem and Regosol occupy 79 % of the total cultivated area of the watershed (see Table 1), but they presented a contrasting potential of P desorption. While Chernozem desorbed high amounts of labile P ( $\alpha=38 \text{ mg kg}^{-1}$ ) and it has high P supply (potentially available P,  $\beta=122 \text{ mg kg}^{-1}$ ), Regosol presents a smaller P pool ( $\alpha=7.0 \text{ mg kg}^{-1}$  and  $\beta=16 \text{ mg kg}^{-1}$ ). Although Acrisol presented high amounts of labile P and potentially available P ( $\alpha=42 \text{ mg kg}^{-1}$  and  $\beta=109 \text{ mg kg}^{-1}$ ), its contribution to water P contamination is low because this soil type is cultivated less, representing only 3.4 % of total cultivated area in the watershed. As related as the other soils that have low P availability, their influence on the P contamination of water is probably also low.

In suspended sediments, the highest amounts of desorbed K were observed for sediments sampled in phase *a* ( $\alpha=4,458 \text{ mg kg}^{-1}$ ;  $B=6,679 \text{ mg kg}^{-1}$ ) (Fig. 7 and Table 3). The lowest quantities of desorbed K obtained ( $\alpha=950 \text{ mg kg}^{-1}$ ;  $B=1,698 \text{ mg kg}^{-1}$ ) were in sediments collected during phase *b*. This feature can be explained by: (1) the presence of coarse particles due to the high water flux in the stream and (2) their consequent low area/volume ratio. Finally, in phase *c*, when the stream recovered its normal water level and carried high amounts of clay-sized particles in suspension, the values of desorbed K increased ( $\alpha=2,423 \text{ mg kg}^{-1}$ ;  $B=4,067 \text{ mg kg}^{-1}$ ). Sediments collected in the phase *a* of the rainfall event presented the highest values of labile K ( $\alpha=4,458 \text{ mg kg}^{-1}$ ) (Table 3). However, the  $\alpha$  value for K desorption from sediments in phase *a* was 36 times that obtained for Cambisol, which have the highest  $\alpha$  value among the three dominant soil types of the watershed. These data indicate that sediments in this initial phase of the rain event carried much more labile K than one would expect considering only the soil types of the watershed. The size-selective transport of particles as suspended sediments may be responsible for this result due to

**Fig. 6** Cumulative potassium (K) and phosphorus (P) desorbed by successive cation–anion exchange resin extractions from the main soil types present in the Agudo watershed





**Table 2** Parameters of the first-order rate equation for desorption of potassium (K) and phosphorus (P) from different soil types in the Agudo watershed

Soil types	K desorption parameters			P desorption parameters		
	$\alpha$ (mg kg <sup>-1</sup> )	$\beta$ (mg kg <sup>-1</sup> )	$\lambda$ (h <sup>-1</sup> )	$\alpha$ (mg kg <sup>-1</sup> )	$\beta$ (mg kg <sup>-1</sup> )	$\lambda$ (h <sup>-1</sup> )
Chernozem	49	1,029	8.96E-04	38	122	1.42E-02
Acrisol	135	253	2.07E-02	42	109	1.57E-02
Arenosol	24	33	3.07E-02	1.9	4	4.51E-02
Cambisol	124	269	1.86E-02	13	41	1.91E-02
Regosol	93	272	1.15E-02	7.0	16	3.40E-02

$\alpha$  is the readily desorbable chemical element (labile ion),

$\beta$  is the potentially available chemical element (potentially available ion),  $\lambda$  is the constant desorption rate of the first-order desorption reaction

the existence of large amounts of sites to adsorb K associated with the small particles of the suspended sediments. The highest amount of labile P ( $\alpha=325$  mg kg<sup>-1</sup>) was observed in suspended sediments collected in phase *c*, while the lowest ( $\alpha=176$  mg kg<sup>-1</sup>) was obtained in sediments collected during the higher flux of stream water (phase *b*).

Application of the kinetic model to the sediment samples gave rise to highly overestimated  $\beta$  values for P (phases *b* and *c*) as well as for K (phase *a*). For this reason, to compare the P and K desorption in soils with those sediments, we will use the direct ion extraction results of sediments and the potentially available P in sediment will be considered as the value of cumulated desorbed P obtained after four extractions with CAER (named *B* value). Thus, the obtained values of the potentially available P were 433, 249, and 445 mg kg<sup>-1</sup> for phase *a*, *b* and *c*, respectively (see Fig. 7 and Table 3). A similar approach was used in the analysis of K desorption behaviour in the sediments (see Fig. 7 and Table 3).

P and K desorption parameters ( $\alpha$ , *B* and total) from the sediments are given in Table 3. For phase *b* and *c*, the values of  $\alpha$ /total and *B*/total for K were similar to the analogous ones for P, despite the differences in the particle size distribution in suspended sediments of these phases. In phase *b*,  $\alpha$ /total=22 % for K and 27 % for P, while *B*/total=40 % for

K and 39 % for P. In phase *c*,  $\alpha$ /total=37 % for K and 38 % for P, while *B*/total=63 % for K and 51 % for P. However, there was a significant difference between K and P desorption behaviours for the suspended sediments of phase *a*, which are supposed to represent the background water stream flow. Total K was labile (65 %) and potentially (97 %) available, while for P, the analogous values were only 7 and 14 %, respectively (see Table 3).

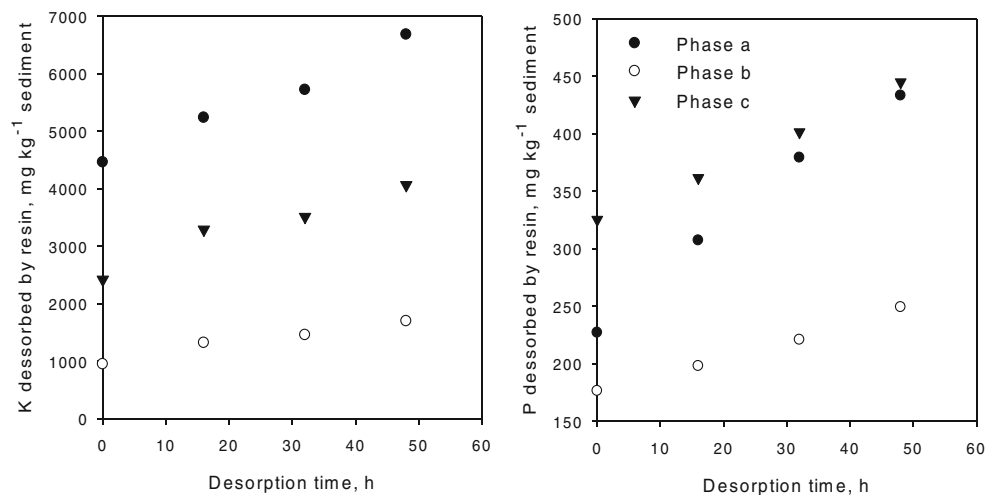
### 4 Discussion

#### 4.1 Soil mineralogy versus sediment mineralogy

High total sediment amount (29.2 Mg) was lost from the watershed during only one storm event. This implies that particles were suspended and eroded close to the watershed outlet. Bortoluzzi et al. (2006) and Pellegrini et al. (2010) studied this watershed and found good correlations between the distances between streams and pollutant sources and the amounts of P and pesticides in the stream waters.

SSC generally depend on precipitation intensity and water flow rate (Brassington and Richards 2000). The amount of suspended sediments typically increases as water flow

**Fig. 7** Potassium (K) and phosphorus (P) desorbed by successive cation–anion exchange resin extractions from suspended sediments collected at the river monitoring station during a rain storm event in the Agudo watershed. The three phases of the rain storm event were: phase *a* (start of rainfall event; water flow <1,000 l s<sup>-1</sup>), phase *b* (middle of rainfall event; water flow >1,000 l s<sup>-1</sup>) and phase *c* (end of rainfall event; water flow <1,000 l s<sup>-1</sup>)



**Table 3** Total ion concentrations and the parameters for potassium (K) and phosphorus (P) desorption from suspended sediments collected during the three phases of a storm event in the Agudo watershed

Phases of the rainfall	Total K (mg kg <sup>-1</sup> )	K parameters		Total P (mg kg <sup>-1</sup> )	P parameters	
		$\alpha$ (mg kg <sup>-1</sup> )	$B$ (mg kg <sup>-1</sup> )		$\alpha$ (mg kg <sup>-1</sup> )	$B$ (mg kg <sup>-1</sup> )
<i>a</i>	6,886	4,458 (65)	6,679 (97)	3,057	227 (7)	433 (14)
<i>b</i>	4,220	950 (22)	1,698 (40)	645	176 (27)	249 (39)
<i>c</i>	6,484	2,423 (37)	4,067 (63)	865	325 (38)	445 (51)

Parameter  $\alpha$  is the amount of ion desorbed in the first CAER resin extraction (labile ion). Parameter  $B$  is the accumulated amount of ion desorbed after four successive CAER resin extractions. The values between parentheses give the percentage of the total ion amount represented by  $\alpha$  or  $B$  parameters

increases (Owens et al. 2005) (see also Fig. 2). The clay contents of the suspended sediments were different from the clay contents of the soils from which these sediments were derived (see Table 1 and Fig. 3). The highest value of soil clay fraction was 21 % for Chernozem (see Table 1), while in suspended sediments collected at the watershed outlet, the clay fraction content was generally >49 % (see Fig. 3). The particle size distribution during the storm event shows that the proportion of sand, silt and clay contents were similar in phases *a* and *b*, which is related to the increase of water flow (see Figs. 2 and 3). In phase *c*, when the flow intensity decreased, the suspended silt and sand fractions decreased to 14 and 8 %, respectively. The clay fraction remained in suspension in water in phase *c* at 72 % (see Fig. 3). It is likely that the soil erosion processes associated with the main soil types of the watershed gave rise to size segregation during sediment transport; coarser fractions tend to be deposited on the streambed.

In addition, despite the wide variety of clay minerals found in the representative watershed soil types (see Table 1), the mineralogical diversity of the suspended sediment was lower (see Figs. 4 and 5). Smectite was the dominant mineral in fine sediments compared to soils, where it was the less abundant clay mineral, except in Chernozem soils, suggesting that this soil type contributes, to a large extent, to the sediment load. This agrees with Hsieh (1984), who suggested that clay minerals can be segregated by their size during the sediment transfer processes occurring in a watershed. In addition, the selective dispersion and smectite losses were also described in soils with clay illuviation (e.g., Mercier et al. 2000; Rousseau et al. 2004; Montagne et al. 2008).

Accordingly, the Chernozem soils, located in areas with high levels of anthropogenic activities (mainly agriculture), are sensitive to erosion and contribute, to a large extent, to the sediment load. Results also showed that Regosols, despite their location on hillslopes with high anthropogenic pressure, are unlikely to be important contributors to the suspended sediment load.

These findings highlight the role played by suspended particles, which must be taken into account in order to successfully address the transport and fate of colloid-associated

pollutants in agricultural watersheds. This paper outlines the differences between soil mineralogy and particle composition of suspended sediments in three distinct phases in an intensively cropped and vulnerable sub-tropical catchment with a rainfall regime of high erosion potential.

#### 4.2 P and K desorption from soils versus suspended sediments

High soil K supply was verified for the different soils, but they presented low K desorptivity due to the occurrence of specific K sorption on mineral surfaces. K desorption from soils is strongly dependent on the type of clay minerals present (Sharpley 1987). The high P quantities applied in tobacco crops promote P saturation on the exchange sites of particles and give rise to higher P desorption rates (Pellegrini et al. 2010).

High values of  $\alpha$  and  $\beta$  parameters were obtained for the first-order P desorption reaction equation for Chernozem. Regosol, compared with Chernozem and Cambisol, is likely to play a minor role in P transfer process in catchment, since it has low values of labile P ( $\alpha=7.0$  mg kg<sup>-1</sup>) and potentially desorbable P ( $\beta=16$  mg kg<sup>-1</sup>), and its desorbable P undergoes a fast desorption reaction ( $\lambda=0.0340$  h<sup>-1</sup>). Acrisol, Cambisol and Arenosol presented low contributions to P transfer to watercourses because they have low anthropogenic pressure and their position in the landscape is generally in upland areas and far away from watercourses.

In all soils, notably in Chernozem, 2:1 clay minerals were found, resulting in high soil CEC (see Table 1). Although low adsorption of anions is expected in 2:1 clay minerals, we observed high values of desorbed P from soils. The presence of surface coating of Fe oxyhydroxides on the 2:1 clay mineral surfaces can promote the adsorption of phosphate onto these clay minerals (Golterman 2010). Therefore, in the acidic soils of the Agudo watershed (see Table 1), we suppose that part of the phosphate desorption was related to Fe oxyhydroxide coatings on clay mineral surfaces.

Clay fraction contents of the suspended sediments did not match those of the soils (see Table 1 and Fig. 3). This suggests that there is both particle size and clay species selectivity in the

soil–sediment transfer process. In addition, the mineralogical composition of the suspended sediment was predominantly composed of smectite. Due to its crystalline radius and coordination number,  $K^+$  can be easily fixed in the interlayer space of smectites, forming an inner sphere complex that will reduce its exchangeability (Sharpley 1987). Thus, it can be inferred that sediments dominated by smectite are likely to carry K for long distances in a watershed. On the other hand, in kaolinite, only the planar external surface sites are available for K adsorption/desorption, as hydrogen bonds tightly hold the tetrahedral layers in adjacent clay sheets (Sparks 2001).

The K-desorbed behaviour of suspended sediments collected in phase *b* of the rain event had 22 and 40 % of the total K as labile and potentially available K, respectively. Phase *b* had the lowest amount of labile K ( $\alpha=950 \text{ mg kg}^{-1}$ ) among the phases of the rainfall event. This is related to the presence, in the suspended sediments of this phase, of coarse particles that are carried long distances due to the high water flow rates (see Table 3 and Fig. 3). These coarse particles have a low area-to-volume ratio and, consequently, are likely to have a low amount of available superficial sites. However, the labile K value measured for suspended sediments of phase *b* was approximately 19 times larger than that obtained for the Chernozem soil. This implies that even during the highest stream water flux, the amount of labile K transported is much higher than was expected if only the desorption characteristics of the soil types were taken into account. This is in accordance with the mineralogical analysis of sediments collected in phase *b*, which identified smectite as the major clay mineral.

For suspended sediments collected in phase *c*, which are composed mainly of fine particles, the K desorption study showed that 37 and 63 % of the total K was labile K and potentially available K, respectively (see Table 3). In absolute values, the  $\alpha$  value of phase *c* was approximately 50 times larger than that obtained for the Chernozem soil. These results are in accordance with the grain size distribution obtained for suspended sediments in phase *c* (see Fig. 3), since it is known that slight variations in the amount of smaller particles can cause a large increase in specific sediment surface area, thereby enhancing the sorption of ions or molecules.

The lowest value of labile P in suspended sediment was in phase *b* ( $176 \text{ mg kg}^{-1}$ , i.e., 27 % of total P) and the highest one in phase *c* ( $325 \text{ mg kg}^{-1}$ , i.e., 38 % of total P). The sediment labile P values were always higher than the similar ones of soils. Even the lowest value of labile P obtained in suspended sediments (phase *b*) is 4.6 times larger than the labile P estimated for Chernozem. This result can be attributed to the particle size selection occurring during sediment transportation, as phase *b* presents mainly coarse particles (meaning a lower number of available adsorption sites for P), while an increase in clay fraction was observed in phase *c*.

P in a sediment–water system is highly dependent on P sorption behaviour, which in turn, determines bioavailability and, therefore, the eutrophication potential of these particles (Sharpley et al. 1992). P lability and the potential capacity of P release are higher during phase *c* of the rain event. In the case of the Agudo watershed, where the main crop is tobacco cultivated under conventional tillage employing high amounts of P and K fertilisers (Rheinheimer 2003), our results have shown that cropping areas become sources of high amounts of sediments, which in turn, are likely to be quickly transferred to the stream as soon as rainfall starts (Minella et al. 2007, 2009).

## 5 Conclusions

This study demonstrated that there were both particle size and clay mineralogy selectivity in soil–sediment transfer processes in a small rural watershed in southern Brazil. The particle–mineralogy dynamics was also influenced by the soil types and the land uses of the watershed. By comparison with the soils occurring in the watershed, suspended sediments collected during the storm event were enriched in fine particles ( $<2 \mu\text{m}$ ). The clay-sized fraction constitutes the greatest portion of the suspended sediments and increased along the phases of the storm event. Smectite (partially with hydroxy-Al interlayer) was the dominant clay mineral in suspended sediments. In this study, the preferential leaching of smectites, which are usually of smaller size than kaolinites and illites, was evidenced at the watershed scale. Besides smectite, soils were composed of kaolinite and some illite clay minerals.

The amounts of P and K desorbed from the suspended sediments in the three phases of the storm event were much larger than those desorbed from the soils. This indicates that rainfall is promoting the transfer of these nutrients to the watercourses. P and K desorption from soil and sediments depended on three main factors: the chemical nature of the desorbed ion, the particle size content, and the mineralogy. The highest values of labile P were found in suspended sediment collected during the last phase of the storm event, which was dominated by clay-sized material. The suspended sediments collected in the first phase of the rainfall event (with low clay content) had the highest values of labile K.

Mineralogy characterisation is a powerful tool to explain the nutrient desorption phenomena associated with soils and suspended sediments. This approach may contribute to the improved understanding of pollution transfer processes at the watershed scale.

**Acknowledgements** The authors thank A. Copetti, J.B. Pellegrini and C. Gonçalves for the technical support in the sample collection and chemical analysis, as well as CAPES (CAPES-COFEUCUB program, Edital 009/2011, process number 3504-11-5) for the financial support. D.S. Rheinheimer and E.C. Bortoluzzi thank CNPq for their fellowships.

## References

- Barriuso E, Calvet R, Schiavon M, Soulas G (1996) Les pesticides et les polluants organiques des sols: transformations et dissipation. *Étude et Gestion Sols* 3:279–296
- Barrow NJ (1983) A mechanistic model for describing the sorption and desorption of phosphate by soil. *J Soil Sci* 34:733–750
- Bortoluzzi EC, Moterle DF, Rheinheimer DS, Cassali CA, Melo GW, Brunetto G (2012) Mineralogical changes caused by grape production in a regosol from subtropical Brazilian climate. *J Soils Sediments* 12:854–862
- Bortoluzzi EC, Rheinheimer DS, Gonçalves CS, Pellegrini JBR, Maroneze AM, Kurz MHS, Bacar NM, Zanella R (2007) Investigation of the occurrence of pesticide residues in rural wells and surface water following application to tobacco. *Quím Nova* 30:1872–1876
- Bortoluzzi EC, Rheinheimer DS, Gonçalves CS, Pellegrini JBR, Zanella R, Copetti ACC (2006) Contaminação de águas superficiais por agrotóxicos em função do uso do solo numa microbacia hidrográfica de Agudo, RS. *Rev Bras Eng Agric Ambient* 10:881–887
- Bortoluzzi EC, Santos MAS, Villetti MA (2010) Sediment characterization. In: Poletto C, Charlesworth S (eds) *Sedimentology of aqueous systems*. Wiley-Blackwell, Hoboken, pp 80–107
- Bortoluzzi EC, Velde B, Pernes M, Dur JC, Tessier D (2008) Vermiculite with hydroxy-aluminium interlayer and kaolinite formation in a subtropical sandy soil from south Brazil. *Clay Min* 43:155–163
- Brassington J, Richards K (2000) Turbidity and suspended sediment dynamics in small catchments in the Nepal Middle Hills. *Hydrol Process* 14:2559–2574
- Brindley GW, Brown G (1980) Crystal structures of clays minerals and their x-ray identification. Mineralogical Society, monograph no. 5, London, 495 pp
- Carter DL, Heiman R, Gonzales CL (1965) Ethylene glycol monoethyl ether for determining surface area of silicate minerals. *Soil Sci* 100:356–360
- Correll DL (1998) The role of phosphorus in the eutrophication of receiving waters: a review. *J Environ Qual* 27:261–266
- Dalmolin RSD, Pedron FA, Azevedo AC, Zago A (2004) Levantamento semidetalhado de solos da microbacia do arroio Lino-Município de Agudo (RS). Santa Maria – RS, 2004, 84 pp
- Golterman HL (2010) The chemistry of phosphate and nitrogen compounds in sediments. Kluwer, Dordrecht, p 251
- Hsieh YP (1984) Using clay mineralogy to infer sources of suspended clay and silt in a watershed: quantitative approach. *Soil Sci Soc Am J* 48:1446–1450
- Hughes RE, Moore DM, Glass HD (1994) Qualitative and quantitative analysis of clay minerals in soils. In: Baters JM (ed) *Quantitative methods in soil mineralogy*. Soil Science Society of America, Madison, pp 330–359
- Kaiser K, Guggenberger G (2003) Mineral surfaces and soil organic matter. *Eur J Soil Science* 53:219–236
- Lanson B (1997) Decomposition of experimental x-ray diffraction patterns (profile fitting): a convenient way to study clay minerals. *Clays Clay Miner* 45:132–146
- McDowell RW, Sharpley AN, Folmar G (2001a) Phosphorus export from an agricultural watershed: linking source and transport mechanisms. *J Environ Qual* 30:1587–1595
- McDowell RW, Sharpley AN, Condrón LM, Haygarth PM, Brookes PC (2001b) Processes controlling soil phosphorus release to runoff and implications for agricultural management. *Nutr Cycl Agroecosyst* 59:269–284
- McKean SJ, Warren GP (1996) Determination of phosphate desorption characteristics in soils using successive resin extractions. *Commun Soil Sci Plant Anal* 27:2397–2417
- McLaughlin JR, Ryden JC, Syers JK (1981) Sorption of inorganic phosphate by iron-, aluminium-containing components. *J Soil Sci* 32:365–377
- Mehl HU, Eltz FLF, Reichert JM, Didoné IA (2001) Caracterização de padrões de chuvas ocorrentes em Santa Maria (RS). *Rev Bras Ci Solo* 25:475–483
- Mercier P, Denaix L, Robert M (2000) Caractérisation des matières colloïdales évacuées au cours du drainage agricole: incidence sur l'évolution pédogénétique des sols. *CR Acad Sci Paris* 331:195–202
- Minella JPG, Merten GH, Reichert JM, Rheinheimer DS (2007) Identificação e implicações para a conservação do solo das fontes de sedimentos em bacias hidrográficas. *Rev Bras Ci Solo* 31:1637–1646
- Minella JPG, Merten GH, Walling DE, Reichert JM (2009) Changing sediment yield as an indicator of improved soil management practices in Southern Brazil. *Catena* 79:228–236
- Montagne D, Cornu S, Le Forestier L, Hardy M, Josière O, Caner L, Cousin I (2008) Impact of drainage on soil-forming mechanisms in a French Albeluvisol: input of mineralogical data in mass-balance modelling. *Geoderma* 145:426–438
- Moore DM, Reynolds RC (1997) X-ray diffraction and the identification and analysis of clay minerals. Oxford University Press, New York
- Oliveira PTS, Wendland E, Nearing MA (2012) Rainfall erosivity in Brazil: a review. *Catena* 100:139–147
- Owens PN, Batalla RJ, Collins AJ, Gomez B, Hicks DM, Horowitz AJ, Kondolf GM, Marden M, Page MJ, Peacock DH, Petticrew EL, Salomons W, Trustrum NA (2005) Fine-grained sediment in river systems: environmental significance and management issues. *River Res Appl* 21:693–717
- Owens PN, Petticrew EL, Van der Perk M (2010) Sediment response to catchment disturbances. *J Soils Sediments* 10:591–596
- Parfitt RL (1978) Anion adsorption by soils and soil materials. *Adv Agron* 30:1–50
- Pédro G (1979) Les conditions de formation des constituants secondaires. In: Bonneau M, Souchier B (eds) *Pédologie: Constituants et propriétés du sol*. Masson, Paris, pp 58–71
- Pellegrini JBR, Rheinheimer DS, Gonçalves CS, Copetti ACC, Bortoluzzi EC, Tessier D (2010) Impacts of anthropic pressures on soil phosphorus availability, concentration, and phosphorus forms in sediments in a Southern Brazilian watershed. *J Soils Sediments* 10:451–460
- Rheinheimer DS (2003) Caracterização física, química e biológica dos solos na microbacia hidrográfica do Arroio Lino, Nova Boemia, Agudo—RS. In: Rheinheimer DS (ed) *Relatório Técnico ano III*, Rio Grande do Sul. FATEC, Santa Maria
- Rheinheimer DS, Gonçalves CS, Bortoluzzi EC, Pellegrini JBR, Silva JLS, Petry C (2010) Qualidade de águas subterrâneas captadas em fontes em função da presença de proteção física e de sua posição na paisagem. *Eng Agric Jaboticabal* 30:948–957
- Rheinheimer DS, Campos BHC, Giacomini SJ, Conceição PC, Bortoluzzi EC (2008) Comparação de métodos de determinação de carbono orgânico total no solo. *Rev Bras Ci Solo* 32:435–440
- Rhue RD, Harris WG (1999) Phosphorus sorption/desorption reactions in soils and sediments. In: Reddy KR, O'Connor GA, Schelske CL (eds) *Phosphorus biogeochemistry in subtropical ecosystems*. CRC, Boca Raton, pp 187–206
- Robert M, Tessier D (1974) Méthode de préparation des argiles de sols pour les études minéralogiques. *Annales Agronomique* 25:859–882
- Rousseau M, Di Pietro L, Angulo-Jaramillo R, Tessier D, Cabibel B (2004) Preferential transport of soil colloidal particles: physico-chemical effects on particle mobilization. *Vadose Zone J* 3:247–261
- Salomons W, Förstner U (2010) Sediments and the “system”: from site-specific to regional-scale research. “A story of joy in researching dirt”. *J Soils Sediments* 10:1436–1439

- Sechinatto L (2007) A insustentabilidade do uso do solo com fumicultura em terras declivosas. Thesis Universidade federal de Santa Maria. 155 pp
- Sparks DL (2001) Dynamics of K in soils and their role in management of K nutrition. In: International Potash Institute PR II K in nutrient management for sustainable crop production in India, New Delhi, India, 03–05 Dec
- Selim HM, Mansell RS, Zelazny LW (1976) Modelling reaction and transport of potassium in soils. *Soil Sci* 122:77–84
- Sharpley AN (1987) The kinetics of soil potassium desorption. *Soil Sci Soc Amer J* 51(1987):912–917
- Sharpley AN, Smith SJ, Jones OR, Berg WA, Coleman GA (1992) The transport of bioavailable phosphorus in agricultural runoff. *J Environ Qual* 21:30–35
- Velde B (2001) Clay minerals in the agricultural horizon of loams and silt loams in the central United States. *Clay Miner* 36:277–294
- Verstraeten G, Lang A, Houben P (2009) Human impact on sediment dynamics—quantification and timing. *Catena* 77:77–80
- Zhu MX, Ding KY, Xu SH, Jiang X (2009) Adsorption of phosphate on hydroxyaluminum- and hydroxyiron-montmorillonite complexes. *J Hazard Mater* 165:645–651