Potential of phosphorus fractions to trace sediment sources in a rural catchment of Southern Brazil: comparison with the conventional approach based on elemental geochemistry

Tales Tiecher^{a,*}, Rafael Ramon^b, J. Patrick Laceby^c, Olivier Evrard^d, Jean Paolo Gomes Minella^e

^a Department of Soil Science, Federal University of Rio Grande do Sul, Bento Gonçalves Ave. 7712, 91540-000, Porto Alegre, RS, Brazil

^b Graduate Program in Soil Science, Federal University of Rio Grande do Sul, Bento Gonçalves Ave., 91540-000, Porto Alegre, RS, Brazil

^c Environmental Monitoring and Science Division, Alberta Environment and Parks, 3115 – 12 Street NE
Calgary, Alberta, Canada, T2K 2W6

^d Laboratoire des Sciences et de l'Environnement, UMR 8212 (CEA/CNRS/UVSQ), Université Paris-Saclay, Domaine du CNRS, Avenue de la Terrasse, Gif-sur-Yvette Cedex 91198, France

^e Department of Soil Science, Federal University of Santa Maria, Roraima Ave. 1000, 97105-900 Santa Maria, RS, Brazil

* Corresponding author. E-mail address: tales.tiecher@ufrgs.br (T. Tiecher).

Abstract

In areas with extensive soil erosion, there is a need to identify the sources supplying sediment to rivers in order to improve our understanding of erosion processes and to guide the implementation of effective soil management measures. Geochemical elements are often used as tracers in sediment fingerprinting studies. Among them, P has often been used as it may specifically trace sediment originating from cropland. Although P-fractions can provide more detailed information than the total P content, their potential to distinguish between different potential sources of sediments has rarely been tested. The objective of the current research was to evaluate the contribution of sediment sources in a rural catchment (Arvorezinha, 1.23 km²) of Southern Brazil, using different sets of tracers (i.e. P-fractions only, geochemical tracers only, and a combination of both tracers). Three potential sediment source types were identified in the catchment: (i) cropland, (ii) unpaved roads and (iii) stream channel banks. Thirty-one suspended sediment samples were collected in the river draining this catchment during 9 significant floods between 2009 and 2011. Estimates of P-fractions were obtained by Hedley fractionation using anion exchange resin membrane (P_{resin}); 0.5 mol L⁻¹ NaHCO₃ (pH 8.5) (P_{bic}); 0.1 mol L⁻¹ NaOH ($P_{\text{NaOH0.1}}$); 1.0 mol L⁻¹ HCl (P_{HCl}); 0.5 mol L⁻¹ NaOH ($P_{\text{NaOH0.5}}$); and residual P (P_{residual}). Total organic (P_{org}) and inorganic P (P_{inorg}) were obtained by the ignition method. The concentrations of P_{HCl} , $P_{\text{NaOH0.5}}$ and P_{inorg} in suspended sediments were higher than those found in the sources. Accordingly, these fractions were considered not to be conservative and were excluded from further analysis. With the exception of P_{residual} , all P-fractions passed the Kruskal-Wallis H -test and were considered as potential tracers of sediment sources. When the P-fractions were combined with geochemical tracers, the discrimination power was much higher than when using geochemical tracers only. The Mahalanobis distance was 9% higher than that observed in the geochemical approach. The calculated contribution of sediment sources using the three approaches was very similar, and cropland was the dominant source of sediment, with calculated contributions of 56±19, 46±16 and 48±16% for those approaches based on geochemical elements, P-fractions, and geochemical+P-fractions, respectively. These results demonstrate the effectiveness of some P-fractions to trace potential sediment sources in rural catchments, as they have a high discriminant power while remaining conservative during sediment transport in the catchment.

Key-words: Phosphorus fractionation, sediment source fingerprinting, sediment tracers.

1. Introduction

Soil erosion remains one of the main environmental problems caused by human society in their search for food, fiber and energy production. The global annual estimates of soil erosion are about 2.87 Mg ha⁻¹ yr⁻¹ (**Borrelli et al., 2017**), and Southern Brazil stands out as one of the hotspots of soil erosion in the world. Recently, **Didoné et al. (2017)** have estimated sediment yields ranging from 36 to 260 Mg km² yr⁻¹ in rural catchments of Southern Brazil. This situation raises major concerns as projected climate change impacts on rainfall erosivity across Brazil indicated that Southern Brazil will be one of the most affected regions, with projected increases in rainfall erosivity reaching up to 109% in the period of 2007–2040 (**Almagro et al., 2017**). In this context, it is important to identify the main sediment sources in catchments in order to guide decision makers in the efficient allocation of limited public resources available to mitigate sediment production.

One of the main techniques used to obtain this information is the sediment source fingerprinting approach, which is based on the measurement of physico-chemical properties in both sediments and in their potential sources to estimate their respective contribution to the material transiting river networks (**Koiter et al., 2013a; Walling, 2013**). The number of sediment fingerprinting studies has increased in recent decades and this technique has been successfully used worldwide. However, there is no universal recommendation or guideline for tracer pre-selection because successful fingerprint properties are highly site-specific, making parameter selection time-consuming and costly (**Collins and Walling, 2002**). Despite these difficulties, the most frequently and successfully set of tracers used are radionuclides and elemental geochemistry (**Haddadchi et al., 2013; Koiter et al., 2013a**).

Two of the main prerequisites for using physico-chemical properties as tracers of sediment origin are that: (i) significant differences in property concentrations are found between the potential sources and that (ii) they remain conservative during erosion and transport processes (**Owens and Xu, 2011**). Usually, non-parametric tests (such as the Kruskal-Wallis *H*-test or Mann-Whitney *U*-test) are employed to identify physico-chemical properties that may be used as a sediment source tracer.

The modification of sediment properties used in sediment fingerprinting studies may occur during their transport as a result of particle size sorting (**Laceby et al., 2017**), organic matter

enrichment/depletion, and biogeochemical transformations. Accordingly, the conservativeness of tracing properties is increasingly discussed in the literature (Sherriff et al., 2015). Many studies compare tracer concentrations between sources and sediments and conduct a range test as a way of assessing conservativeness. However, the conservative behavior of properties is highly site-specific and the conclusions of these previous studies cannot be directly extrapolated for other study areas.

Among the geochemical tracers, P often provides significant discrimination between agricultural soils and other land uses due to the higher concentrations of P found in cropland as a result of fertilization. A brief analysis of 60 fingerprinting studies that tested P as a potential tracer and that were conducted around the world (Table 1) shows that most studies were performed in the UK (20%), the United States (17%), Australia (12%), Brazil (12%) and Iran (12%) (Fig. 1). Four of these studies (Table 1) measured P although they did not perform any statistical test, excluding this element from further analysis because of the potential risk of non-conservative behavior during sediment transport in the catchment (Palazón et al., 2016, 2015; Palazón and Navas, 2017; Smith and Blake, 2014). Only 45% ($n = 27$) of these 60 studies (Table 1) applied statistical tests or criteria to evaluate the conservativeness of P during erosion and transportation processes (Fig. 2a) and among these, P passed the conservativeness test and was considered to have a conservative behavior in 85% of the publications ($n = 23$) (Fig. 2d). The non-conservative behavior of P in some of these studies can be attributed to the local soil characteristics (such as pH and clay mineralogy), which can decrease the sorption capacity of P by the solid phase, resulting in a higher mobility of this element in the soil-water system. Moreover, point-based sources can deliver significant amounts of dissolved P which can be subsequently adsorbed by sediment increasing the P concentration of sediment during its transport from the source to the sink (Owens and Walling, 2002).

About three quarters (Fig. 2b) of the studies included in the comparison (Table 1) used the Kruskal-Wallis H -test to compare P concentrations in the potential sources, and, P passed this test and was considered as a potential tracer in 87% of these studies (Fig. 2d). Finally, during the optimization step for selecting the final set of tracers used to model the source contributions (generally performed through the application of the discriminant function analysis - DFA), P was selected in 43% of the cases

(Fig. 2c). This analysis of the literature demonstrates that although P has been treated with some hesitancy by researchers in sediment fingerprinting studies, this property has often been incorporated into the final un-mixing models to estimate source contributions to sediment.

Another important point that is often overlooked in the literature is related to the digestion method used to prepare the samples and estimate their elemental concentrations (Fig. 1b). Not all the methods used in previous studies are able to estimate the total P content in soils and sediments. In order to quantify the absolute total P content, the digestion must include the use of acids, including hydrogen fluoride (15% of the studies included in the comparison – Fig. 1b), as this substance is needed to fully dissolve the silicate minerals, or $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ for the specific case of soils devoid of apatite-like minerals (3% of the studies investigated – Fig. 1b). The use of sodium carbonate (Na_2CO_3) fusion (Bender and Wood, 2000), or HClO_4 (Ostrofsky, 2012) (18% of those studies included in the review – Fig. 1b) provide potential alternatives, as well as those spectroscopic methods analyzing solid powders as the X-ray fluorescence (XRF) (13% of those previous studies – Fig. 1b). The other digestion methods provide limited information related to a fraction of the total P only, as they do not assess the more recalcitrant forms of P, and are usually considered as a pseudo-total content of P (Bender and Wood, 2000). This means that the amount of P used to trace the contributions of potential sediment sources in several previous studies was likely the fraction that was the most sensitive to environmental changes and the less conservative during erosion and transportation processes, whereas the most stable fraction, which should be targeted in sediment tracing studies, was neglected (Dabrin et al., 2014).

P accumulates differently in the soils, depending on their mineralogical and chemical properties, the land use and soil management, and total-P is less sensitive to these factors than P-fractions (Cade-Menun, 2017; Cherubin et al., 2016; Teles et al., 2017). Studies on the chemistry of P in soil and sediments are commonly based on its fractionation, and P compounds are subdivided into several pools according to their solubility or their reactivity with various chemical solutions (Lukkari et al., 2007; Wang et al., 2013). The P-fractions can be estimated based on the lability of P evaluated by sequential extractions involving different chemical substances (Hedley et al., 1982), or they can be estimated based on the separation of the organic and inorganic forms of P (Olsen and Sommers, 1982). Using these latter

methods, **Tiecher et al. (2017d)** demonstrated that the chemical fractionation of P provided an effective technique to distinguish sediments originating from sub-catchments characterized by different land uses and managed in different ways depending on the season, in a rural study site of Southern Brazil (Agudo catchment). This study demonstrated that P-fractions can provide more meaningful information than the simple total content of P and suggested that these P-fractions may be more sensitive to distinguish potential sources of sediments. In other regions of the world, very few studies conducted in the UK used P-fractions in sediment fingerprinting studies (**Walling et al., 2006, 1999**). In particular, it was shown that organic and inorganic P fractions may be more effective than the total P concentration to trace those contributions of different land use sources to sediment transiting rivers draining agricultural catchments (**Carter et al., 2003; Walling et al., 2008**).

The hypothesis of the current research is that the chemical fractionation of P can provide parameters that are very sensitive to soil use and management and that they therefore provide tracers that effectively predict sediment sources contributions in agricultural catchments. Accordingly, the current study evaluated the contribution of sediment sources in a rural catchment in Southern Brazil through the use of P-fractions only or their combination with conventional geochemical tracers. The implications of this comparison for the choice of potential tracers in future sediment tracing applications are then discussed.

2. Material and methods

2.1. Study catchment, source and sediment sampling

The Arvorezinha catchment covers a surface area of 1.23 km² in the southernmost state of Brazil (Rio Grande do Sul). The site is mainly underlain by extrusive igneous rocks (rhyodacite). Altitude ranges from 560 to 740 m. According to the Köppen classification, the climate is classified as subtropical super humid and mild (Cfb type) with warm summers and the absence of a dry season. Based on data measured in the catchment during 15 years (2002 to 2017), the mean annual rainfall is 1,938 mm and the rainfall erosivity index (EI30) is 9,344 MJ mm ha⁻¹ year⁻¹ (**Ramon, 2017**). The soil types found in the catchment are Acrisols (57%), Cambisols (33%) and Leptosols (10%). In 2009-2011, land use was covered

by tobacco cultivated under minimum tillage (16%) or under conventional ploughing (10%), native forest (47%), grain crops (17%), grassland (6%), unpaved roads (2%), and rural residential areas (2%). The catchment does not have any urban development.

Three main sediment sources were considered: (i) cropland, (ii) unpaved roads and (iii) stream channel banks. Samples of potential source material were collected in the uppermost layer (0–0.05 m) of the cropland soil surface ($n=20$) and unpaved roads ($n=10$) with a plastic trowel by taking 10 subsamples at each site into one sample. Unpaved roads and tracks provide an important sediment source and a significant transfer pathway. The channel network is characterized by steep step-pool channels with high roughness and turbulent flow. Stream channel bank samples were taken on exposed sites located along the main river channel network ($n=10$) by scraping the surface of river channel banks. Each river bank sample was composed of subsamples collected along approximately 5–10 m distance and 0.2–1.0 m of height. Care was taken to avoid sampling material recently deposited on the channel bank. Each sample was composed of 10 sub-samples collected in the vicinity of the sampling point in order to obtain representative source material.

Thirty-one suspended sediment samples were collected during various stages (i.e. rising, peak, and recession) of nine significant floods that occurred between October 2009 and July 2011 (**Maier, 2013**). A large volume of water (120 to 200 liters) was collected manually at the outlet. Each bulk water sample was centrifuged using a continuous flow device (Alfie-500 Alfa Laval) to concentrate sediment samples. All the source material and sediment samples were oven-dried at 50°C, gently disaggregated using a pestle and mortar, and sieved to 63 μm prior to laboratory analyses. In a previous analysis of the same set of sources and suspended sediment samples, the pseudo-total contents of 28 elements (including total-P) were estimated by ICP-OES after microwave assisted digestion with HCl and HNO_3 (aqua-regia digestion). Further information on these analyzes can be found in **Tiecher et al. (2015)**. Grain size distribution was analyzed with a laser granulometer for all suspended sediment and source samples after oxidation of organic matter with H_2O_2 and chemical dispersion with NaOH.

2.2. Phosphorus fractions analysis

The P-fractions evaluated in the current study were obtained following two methods: (i) the sequential extraction of different chemical reagents to address the lability of P (**Hedley et al., 1982**), and (ii) the separation of the organic and inorganic forms of P (**Olsen and Sommers, 1982**). The Hedley fractionation was performed by the sequential extractions with: (i) anion exchange resin membrane (P_{resin}); (ii) 0.5 mol L⁻¹ NaHCO₃ at pH 8.5 (P_{bic}); (iii) 0.1 mol L⁻¹ NaOH ($P_{\text{NaOH0.1}}$); (iv) 1.0 mol L⁻¹ HCl (P_{HCl}); (v) 0.5 mol L⁻¹ NaOH ($P_{\text{NaOH0.5}}$). After each extraction, the soil suspensions were centrifuged at 2,510 × g for 15 min to collect supernatants. Then, the remaining sediment was dried at ~50°C, ground and submitted to digestion with H₂SO₄ and H₂O₂ in the presence of saturated MgCl₂. Then, the residual Hedley-P-fraction was determined (P_{residual}). In the acid extracts, P was directly determined according to the **Murphy and Riley (1962)** method. For the NaHCO₃ and NaOH extractors, the extracts were first digested with H₂SO₄ and ammonium persulphate in an autoclave at 121°C (**USEPA, 1971**), and then the P content was determined by the **Murphy and Riley (1962)** method.

When separating the organic and inorganic forms of P, the total organic P (P_{org}) was estimated by the ignition method proposed by **Olsen and Sommers (1982)**, as the difference between the amount of P extracted with 0.5 mol L⁻¹ H₂SO₄ from ignited (550°C, 2h) and non-ignited soil. Total P was estimated by digestion with H₂SO₄ and H₂O₂ in the presence of saturated MgCl₂, as proposed by **Olsen and Sommers (1982)**. Then, total inorganic P (P_{inorg}) was estimated by the difference between total P and total organic P.

2.3. Tracer selection

The selection of tracers was performed following two steps: (i) a conservative range test and a Kruskal–Wallis *H* test (KW *H*-test), and (ii) discriminant function analysis (DFA). For the range test, the variables with sediment concentrations lying outside the range of sources ±1 standard deviation were excluded from further analysis, as recommended by **Smith and Blake (2014)**, and they were considered as non-conservative. Then, the KW-*H* test was performed to test the null hypothesis ($p < 0.1$) that the sources are belonging to the same population (**Collins et al., 1997a**). The KW-*H*-test defined which properties were statistically different among the sediment sources (i.e., whether they can be considered

as potential tracers). Tracers that did not pass the conservative test or the KW *H*-test were removed from the next analysis.

Subsequently, a multivariate DFA was performed to determine the minimum number of variables that maximizes the discrimination between the sources. DFA was performed only with the variable considered to be conservative by the range test and that passed the KW *H*-test. DFA is based on the Wilks' lambda (Λ^*) value from the analysis of variance, where the criterion used by the statistical model is the minimization of Λ^* . A Λ^* value of 1 is found when all the group means are the same whilst a low Λ^* value means that the variability within the groups is small compared to the total variability. The DFA was performed in the backward mode, with 0.01 as the maximum or minimum significance of *F* to include or remove a property.

In order to test the hypothesis that the P-fractions can be used as effective tracers of the sediment sources and/or that they may improve the predictions obtained with geochemical tracers, the DFA was performed using three different sets of variables: (i) geochemical variables only; (ii) P-fractions only; and (iii) the combination of geochemical elemental concentrations (with the exception of pseudo-total-P estimated by aqua-regia digestion) and P-fractions.

2.5. Sediment source apportionment

A modified version of the classical Solver-based mixing model determined the relative contribution of different sources to in-stream sediment through simultaneously minimizing mixing model difference (MMD):

$$MMD = \sum_{i=1}^n \left(\left(C_i - \left(\sum_{s=1}^m P_s S_{si} \right) \right) / C_i \right)^2 \quad (\text{Eq. 1})$$

where *n* is the number of parameters in the model chosen by the three-step selection process; *C_i* is the in-stream sample parameter (*i*); *m* is the number of sources; *P_s* is the contribution of source (*s*); *S_{si}* is the mean of parameter (*i*) in source (*s*). The proportional contribution from each source (*P_s*) is modelled by solving Equation 1 with the Solver Function in Microsoft Excel with *P_s* being between 0 and 1 and the

sum of all P_s estimations equalling 1. The GRG Non-Linear solving method was used with automatic scaling in Solver, ignoring integer constraints, with a maximum run time of 5000 and allowing for 2500 iterations. A multi-start population size of 2500 was used along with the same random seed for each of the model runs while requiring bounds on the variables. A constraint precision and convergence of 0.000001 were selected.

3. Results and discussion

3.1. Total P content

Phosphorus content estimated by aqua-regia digestion (HNO_3+HCl), which is the most widely used digestion procedure in sediment fingerprinting studies using P as potential tracers, was on average $48\pm 8\%$ of that estimated by the sulfuric acid digestion (**Fig. 3**). This comparison demonstrated that the aqua-regia method is less effective in assessing the P content in soil and sediments, and that $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$ was more effective to evaluate the total P content (**Malá and Lagová, 2014**). The low capacity of the aqua-regia digestion method to extract P from soil and sediment may be the cause of this tracer removal in several previous sediment fingerprinting studies, indicating that this technique likely targets those P fractions that are more loosely bound to the soil particles, which may be less conservative during erosion and transportation processes.

3.2. Phosphorus fractions

All of the P-fractions evaluated in the current research passed the KW-H-test ($p<0.01$), except the P_{residual} , which means that these fractions can be considered as potential tracers of sediment sources in this catchment (**Fig. 4**). The results of the DFA using the individual P fractions showed that they were able to correctly classify 48 ($P_{\text{NaOH}0.5}$) to 75% (P_{bic}) of the sediment source samples (**Fig. 4**). Concentrations of P_{resin} , P_{HCl} , $P_{\text{NaOH}0.5}$ and P_{inorg} were higher in those soil samples collected in cropland compared to those sampled in other sources (cropland>stream channels=unpaved roads, **Table 1, Supplementary material**). Those higher values found in cropland are likely due to the frequent fertilization of agricultural

land with fertilizers enriched in phosphates, which causes the accumulation of P in general and its inorganic and more labile forms in particular, in the soil (Guardini et al., 2012; Schmitt et al., 2017).

The P_{bic} and $P_{NaOH0.1}$ fractions were also higher in the cropland samples, although these forms were also able to discriminate the unpaved roads and the channel bank sources, with the unpaved road samples having the lowest values, and the stream channel samples reaching intermediate levels (cropland>stream channels>unpaved roads) (Fig. 4 and Table 1, Supplementary material). These P-fractions of intermediate lability were also higher in cropland because of their inputs with phosphate fertilizers. On the contrary, total organic P (P_{org}) did not provide discrimination between cropland and channel bank samples (Table 1, Supplementary material), although it was able to discriminate the unpaved road samples, which were systematically depleted in this fraction compared to other sources (cropland=stream channels>unpaved roads). The presence of organic P in soils is due to the absorption of inorganic P by plants and microorganisms, which incorporate this element into organic forms that accumulate in the soil (Tiecher et al., 2018). As there is almost no biological activity and organic residue inputs in unpaved roads, the P_{org} contents in this source are very low, and possibly restricted to those organic recalcitrant forms such as monoesters strongly adsorbed to the soil (Deiss et al., 2016), which may be inherited from the biological activity that occurred in these areas before the construction of roads.

Despite their great tracer potential, the P_{HCl} and $P_{NaOH0.5}$ fractions were not conservative (Fig. 4). Concentrations in these P-fractions measured in all sediment samples were higher than the highest concentration found in a source sample (Table 2 and 3, Supplementary material). The concentration of P_{inorg} was slightly higher in the sediment samples compared to that found in sediment sources. Only five suspended sediment samples showed a concentration of P_{inorg} higher than the highest concentration found in sediment sources (Table 2 and 3, Supplementary material). This result indicates a possible enrichment of these specific P-fractions during the erosion process, and they were therefore excluded from the following statistical treatment steps. The enrichment of P-forms in the sediment compared to the sources could be related to the enrichment of fine particles that are richer in P during the erosion and transport processes. However, this seems unlikely because the particle size distribution of the

sources and suspended sediment were very similar, as can be seen in **Fig. 5**. In addition, although almost all fractions of P showed a significant relationship with the specific surface area (estimated by the particle size distribution), the correlation coefficient was very low (mean $R^2 = 0.18$, ranging from 0.04-0.37) (**Table 2**). The same trend was observed for the relationship of P forms with the total organic carbon content of the samples (mean $R^2 = 0.21$, ranging from 0.05-0.34). These results shows that for the present study, the fractions of P were little influenced by the granulometry and organic carbon content.

When conducting the chemical fractionations of P, HCl is used to estimate the content of P bound to Ca (**Wang et al., 2013**). The current study showed that there was an enrichment in the content of total Ca in the sediment compared to the sources during the erosion and sediment transport processes (**Fig. 6**), and this may have resulted in the precipitation of Ca phosphates in sediments (**Hupfer et al., 2009**) and, consequently, in the enrichment of the P_{HCl} fraction. In contrast, NaOH is normally used to estimate the content of P bound to Fe oxides (**Wang et al., 2013**). However, contrary to Ca, no enrichment of total Fe was found in the suspended sediments (**Fig. 6**), and this process cannot explain the enrichment of P-fraction extracted by NaOH 0.5 mol L⁻¹. Although there was no enrichment in the content of total-Fe, it has been demonstrated that poorly crystalline oxides with low P contents are preferentially eroded (**Saavedra and Delgado, 2005**). Accordingly, it is possible that during transport these Fe-oxides adsorb soluble P increasing their concentration in $P_{NaOH0.5}$. However, it is important to note that chemical fractionation is an operational and likely non-specific approach to speciation of P in geochemical systems and, therefore, the causes of the enrichment of this particular P-fraction should be further investigated to confirm this process.

3.3. Discriminant analysis

The results of the discriminant function analysis (DFA) using the geochemical tracers only were presented and discussed in **Tiecher et al. (2015)**. In the current research, these results will only be compared with those obtained using the P-fractions alone and the combination of P-fractions with geochemical tracers.

The P-fractions that passed the KW *H*-test and were considered conservative (P_{resin} , P_{bic} , $P_{\text{NaOH0.1}}$, P_{org}) were entered into a DFA, which selected only two of them (P_{resin} , P_{org}) (**Table 3**). The final value of the Wilk's lambda parameter using P-fractions only was 0.2154 (**Table 3**). As this value is the proportion of the total variance due to the error in the source discrimination, the two selected P-fractions were associated with an error of 21.5%, *i.e.*, the combination of these two P-fractions explained approximately 78.5% of the differences observed between the sources. The discrimination power of the P-fractions was lower than that obtained with the geochemical approach, which explained 98.7% of the difference between the sources (**Table 3 – data from Tiecher et al. 2015**). Moreover, the approach based on the P-forms was able to correctly classify 87.5% of the samples, with an average uncertainty of 21.5%, significantly separated by an average squared Mahalanobis distance of 7.3 (**Table 3**). The uncertainty of classification was much higher and the squared Mahalanobis distance was much lower than those obtained for the geochemical approach (average of 2.08E-03% and 48.1, respectively – **Tiecher et al. 2015**). The better discrimination of sediment sources obtained in the geochemical approach compared to P-fractions can be well visualized comparing the **Fig. 7a** and **Fig. 7b**, which are two-dimensional scatterplots of the first and second discriminant functions obtained when running stepwise DFA for geochemical and P-fractions, respectively.

When the P-fractions were combined with geochemical tracers in the DFA, six variables were selected, including the same two P-fractions as those selected in the previous approach (P_{resin} , P_{org}) and four geochemical tracers (Mo, Fe, Ag, As) (**Table 3**). The final value of the Wilk's lambda parameter was slightly reduced to 0.0122 when associating these parameters (**Table 3**) (*i.e.*, together, these six tracers explained approximately 98.8% of the differences observed between the sources). This original combination of parameters resulted in the correct classification of 100% of the samples in their respective groups. More importantly, the discrimination power was higher than when using the geochemical tracers alone. The Mahalanobis distance increased to an average of 52.2 (**Table 3**), which was 9% higher than that observed when following the geochemical approach. The better discrimination of sediment sources obtained when combining the geochemical elements and P-fractions can be well visualized through the comparison of **Fig. 7c** with **Fig. 7a** and **7b**.

339

340 3.4. Sediment source apportionment

341 The predictions of the sediment source contribution obtained with the geochemical tracers were
342 considered as the reference values, and the results obtained with the P-fractions alone and the
343 combination of both sets of tracers (geochemical elements + P-fractions) were compared to this
344 reference. **Fig. 8** summarizes the sediment source contributions calculated with the three datasets for
345 the 31 suspended sediment samples analyzed in the current research. Sediment source contributions
346 obtained when following the three approaches were very similar (**Fig. 8**). For the three approaches, the
347 cropland was the dominant source of sediment (**Fig. 8**), with calculated contributions of 56 ± 19 , 46 ± 16
348 and $48\pm16\%$ for the geochemical, P-fraction, and geochemical+P-fractions approaches, respectively.
349 Calculated contributions of unpaved roads were very stable and varied between 23 ± 14 and 27 ± 13 for
350 geochemical and geochemical+P-fractions, respectively. Calculated contributions of stream channel
351 banks was 21 ± 18 , 29 ± 24 and $26\pm16\%$ for the three approaches. These results agreed well with those
352 obtained in previous studies conducted on the same suspended sediment samples collected in this
353 catchment using near infrared spectroscopy (58 ± 18 of cropland, 23 ± 13 of unpaved roads, and $20\pm15\%$
354 of stream channels – **Tiecher et al., 2016**) and the combination of geochemical elements and colour
355 parameters (48 ± 13 of cropland, 27 ± 13 of unpaved roads, and $25\pm13\%$ of stream channels – **Tiecher et**
356 **al., 2015**). The results of the current research showed that when conducting an approach with multiple
357 geochemical tracers, the replacement of total phosphorus by the P-fractions generated very similar
358 results. Moreover, the use of the P-fractions alone also generated consistent results, indicating their
359 potential use as tracers in rural catchments.

360 The results obtained here demonstrate that several fractions of P have the potential to
361 effectively discriminate sediment sources while remaining conservative during the erosion and transport
362 processes. However, it is important to highlight that our study catchment has characteristics that
363 potentiate the use of P fractions as tracers of sediment origin, such as its very small size (1.23 km^2), the
364 high connectivity between the sediment sources and the drainage network, and a very fast hydrological
365 response, with very little opportunity to store sediments in places with biogeochemical characteristics

where there could be transformation of the forms of P. Thus, although the results obtained in the present study were promising, the use of P-fractions to track the origin of sediments should still be cautious, especially in larger river basins (Koiter et al., 2013a) and in situations where sediment is stored in various landscape units for long periods of time, such as riparian, river channel and/or floodplain environments.

The P-fractions can distinguish between the sediment sources and their use to calculate sediment source contributions provided results that remained consistent with those obtained with the conventional method based on elemental geochemistry. However, discrimination of sources by P-fractionation is poorer than by geochemical element analysis (Fig. 7), and the uncertainties are greater (Fig. 8). On the other hand, the use of P-fractions combined with other geochemical elements did not improve the statistical discrimination nor the quantification of the source contributions. Accordingly, the use of P-fractions as potential tracers provides an excellent low-cost alternative, and although the analysis of these parameters may be more labour-intensive to obtain a relatively limited number of variables, it only requires a basic laboratory infrastructure (including a UV-visible spectrometer, an autoclave and a muffle furnace). This is very important for research groups that do not have access to sophisticated equipment (e.g. ICP-OES or ICP-MS, microwave oven) or sufficient resources to perform the geochemical analyses used in the conventional approach. In addition to the land use discrimination, P-fractions may be used to distinguish between contrasting soil management practices, such as conventional ploughing or no-tillage (Pavinato et al., 2009; Rodrigues et al., 2016; Tiecher et al., 2018). Moreover, as P-fractions were shown to be affected by soil weathering factors (Araújo et al., 2004; Cross and Schlesinger, 1995; Yang and Post, 2011) they could be used to trace the contributions of different soil types and lithologies to sediment transiting rivers in catchments.

4. Conclusions

In this current research, the potential use of P-fractions as tracers to identify the source of suspended sediments in a rural catchment in Southern Brazil was evaluated. With the exception of the residual-P fraction, all the other seven P-fractions evaluated passed the KW-H-test and were considered

as potential tracers of sediment origin. The P-fraction associated with Ca (extracted with HCl), Fe oxides (extracted with NaOH 0.5 mol L⁻¹) and the total inorganic P were not conservative, as these fractions were enriched in the suspended sediment compared to the sources. The use of P-fractions alone was able to discriminate 87.5% of the sediment source samples. Discriminant function analysis shows that the combination of the P-fractions with geochemical tracers improved the discrimination power compared to the use of geochemical tracers only. The Mahalanobis distance was 9% higher than that observed when following the geochemical approach.

Cropland was identified as the dominant source of sediment in the three approaches. The calculated contributions of sediment sources were very similar, with calculated cropland contributions of 56±19, 46±16 and 48±16% for the approaches based on geochemical elements, P-fractions, and the combination of both types of parameters, respectively. Although cropland was estimated to contribute for most of eroded sediments from the catchment studied, it also constituted 96% of the catchment land area. On the other hand, unpaved roads and stream banks contributed each to approximately one fourth of the sediment but represented a much smaller land area and, therefore, are hotspots with more intensive erosive activity in the basin and should be targeted as priority areas in management programs aiming to decrease the sediment yield of the catchment.

The results obtained in the current research confirmed the hypothesis that some P-fractions have a great discrimination potential that will be particularly useful in studies investigating the sources of sediments in rural catchments, as they demonstrated to provide a high discriminant potential while remaining conservative during erosion and transport processes. Future research should examine the non-conservative behavior of P_{inorg} and other fractions to understand how and why P is transformed during sediment transport in streams and improve our knowledge on the nature and the dynamics of P in riverine and lacustrine environments.

418 **Acknowledgements**

419 The research was funded by the Foundation for Research Support of the State of Rio Grande do
420 Sul (FAPERGS) project nº 10/0034-0, and the CAPES-COFECUB project nº 761/12 and project no Te870-
421 15.

422
423 **References**

- 424 Almagro, A., Oliveira, P.T.S., Nearing, M.A., Hagemann, S., 2017. Projected climate change impacts in
425 rainfall erosivity over Brazil. *Sci. Rep.* 7, 8130. doi:10.1038/s41598-017-08298-y
- 426 Araújo, M.S.B., Schaefer, C.E.R., Sampaio, E.V.S.B., 2004. Soil phosphorus fractions from toposequences
427 of semi-arid Latosols and Luvisols in northeastern Brazil. *Geoderma* 119, 309–321.
428 doi:10.1016/j.geoderma.2003.07.002
- 429 Banks, W.S., Gellis, A.C., Noe, G.B., 2010. Sources of fine-grained suspended sediment in Mill Stream
430 Branch watershed, Corsica River basin, a tributary to the Chesapeake Bay, Maryland, 2009, in: 2nd
431 Joint Federal INTERagency Conference. Las Vegas, NV.
- 432 Ben Slimane, A., Raclot, D., Evrard, O., Sanaa, M., Lefèvre, I., Ahmadi, M., Tounsi, M., Rumpel, C., Ben
433 Mammou, A., Le Bissonnais, Y., 2013. Fingerprinting sediment sources in the outlet reservoir of a
434 hilly cultivated catchment in Tunisia. *J. Soils Sediments* 13, 801–815. doi:10.1007/s11368-012-
435 0642-6
- 436 Bender, M., Wood, C., 2000. Total Phosphorous in Soil, in: Pierzynski, G.M. (Ed.), *Methods of Phosphorus*
437 *Analysis for Soils, Sediments, Residuals, and Waters*. pp. 45–49. doi:citeulike-article-id:7529961
- 438 Borrelli, P., Robinson, D.A., Fleischer, L.R., Lugato, E., Ballabio, C., Alewell, C., Meusburger, K., Modugno,
439 S., Schütt, B., Ferro, V., Bagarello, V., Oost, K. Van, Montanarella, L., Panagos, P., 2017. An
440 assessment of the global impact of 21st century land use change on soil erosion. *Nat. Commun.* 8,
441 2013. doi:10.1038/s41467-017-02142-7
- 442 Cade-Menun, B.J., 2017. Characterizing phosphorus forms in cropland soils with solution 31P-NMR: past
443 studies and future research needs. *Chem. Biol. Technol. Agric.* 4, 1–12. doi:10.1186/s40538-017-
444 0098-4
- 445 Carter, J., Owens, P., Walling, D., Leeks, G., 2003. Fingerprinting suspended sediment sources in a large
446 urban river system. *Sci. Total Environ.* 314–316, 513–534. doi:10.1016/S0048-9697(03)00071-8
- 447 Chen, F., Fang, N., Shi, Z., 2016a. Using biomarkers as fingerprint properties to identify sediment sources
448 in a small catchment. *Sci. Total Environ.* 557–558, 123–133. doi:10.1016/j.scitotenv.2016.03.028
- 449 Chen, F., Zhang, F., Fang, N., Shi, Z., 2016b. Sediment source analysis using the fingerprinting method in
450 a small catchment of the Loess Plateau, China. *J. Soils Sediments* 16, 1655–1669.
451 doi:10.1007/s11368-015-1336-7
- 452 Cherubin, M.R., Franco, A.L.C., Cerri, C.E.P., Karlen, D.L., Pavinato, P.S., Rodrigues, M., Davies, C. a., Cerri,
453 C.C., 2016. Phosphorus pools responses to land-use change for sugarcane expansion in weathered
454 Brazilian soils. *Geoderma* 265, 27–38. doi:10.1016/j.geoderma.2015.11.017
- 455 Collins, A., Walling, D., 2002. Selecting fingerprint properties for discriminating potential suspended
456 sediment sources in river basins. *J. Hydrol.* 261, 218–244. doi:10.1016/S0022-1694(02)00011-2
- 457 Collins, A.L., Walling, D., Leeks, G.J.L., 1996. Composite fingerprinting of the spatial source of fluvial
458 suspended sediment: a case study of the Exe and Severn river basins, United Kingdom.
459 *Géomorphologie Reli. Process. Environ.* 2, 41–53. doi:10.3406/morfo.1996.877
- 460 Collins, A.L., Walling, D.E., 2007. Sources of fine sediment recovered from the channel bed of lowland
461 groundwater-fed catchments in the UK. *Geomorphology* 88, 120–138.
462 doi:10.1016/j.geomorph.2006.10.018
- 463 Collins, A.L., Walling, D.E., Leeks, G.J.L., 1998. Use of composite fingerprints to determine the
464 provenance of the contemporary suspended sediment load transported by rivers. *Earth Surf.*
465 *Process. Landforms* 23, 31–52. doi:10.1002/(SICI)1096-9837(199801)23:1<31::AID-
466 ESP816>3.0.CO;2-Z
- 467 Collins, A.L., Walling, D.E., Leeks, G.J.L., 1997a. Source type ascription for fluvial suspended sediment

- based on a quantitative composite fingerprinting technique. *CATENA* 29, 1–27. doi:10.1016/S0341-8162(96)00064-1
- Collins, A.L., Walling, D.E., Leeks, G.J.L., 1997b. Sediment sources in the Upper Severn catchment: a fingerprinting approach. *Hydrol. Earth Syst. Sci.* 1, 509–521. doi:10.5194/hess-1-509-1997
- Collins, A.L., Walling, D.E., Sickingabula, H.M., Leeks, G.J.L., 2001. Suspended sediment source fingerprinting in a small tropical catchment and some management implications. *Appl. Geogr.* 21, 387–412. doi:10.1016/S0143-6228(01)00013-3
- Collins, A.L., Zhang, Y., Walling, D.E., Grenfell, S.E., Smith, P., 2010. Tracing sediment loss from eroding farm tracks using a geochemical fingerprinting procedure combining local and genetic algorithm optimisation. *Sci. Total Environ.* 408, 5461–5471. doi:10.1016/j.scitotenv.2010.07.066
- Cooper, R.J., Krueger, T., Hiscock, K.M., Rawlins, B.G., 2015. High-temporal resolution fluvial sediment source fingerprinting with uncertainty: a Bayesian approach. *Earth Surf. Process. Landforms* 40, 78–92. doi:10.1002/esp.3621
- Cross, A.F., Schlesinger, W.H., 1995. A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* 64, 197–214. doi:10.1016/0016-7061(94)00023-4
- D'Haen, K., Verstraeten, G., Duser, B., Degryse, P., Haex, J., Waelkens, M., 2013. Unravelling changing sediment sources in a Mediterranean mountain catchment: A Bayesian fingerprinting approach. *Hydrol. Process.* 27, 896–910. doi:10.1002/hyp.9399
- Dabrin, A., Schäfer, J., Bertrand, O., Masson, M., Blanc, G., 2014. Origin of suspended matter and sediment inferred from the residual metal fraction: Application to the Marennes Oleron Bay, France. *Cont. Shelf Res.* 72, 119–130. doi:10.1016/j.csr.2013.07.008
- Deiss, L., de Moraes, A., Dieckow, J., Franzluebbbers, A.J., Gatiboni, L.C., Sasaki, G., Ianzi, Carvalho, P.C.F., 2016. Soil phosphorus compounds in integrated crop-livestock systems of subtropical Brazil. *Geoderma* 274, 88–96. doi:10.1016/j.geoderma.2016.03.028
- Devereux, O.H., Prestegard, K.L., Needelman, B.A., Gellis, A.C., 2010. Suspended-sediment sources in an urban watershed, Northeast Branch Anacostia River, Maryland. *Hydrol. Process.* 24, 1391–1403. doi:10.1002/hyp.7604
- Didoné, E.J., Minella, J.P.G., Evrard, O., 2017. Measuring and modelling soil erosion and sediment yields in a large cultivated catchment under no-till of Southern Brazil. *Soil Tillage Res.* 174, 24–33. doi:10.1016/j.still.2017.05.011
- Dutton, C., Anisfeld, S.C., Ernstberger, H., 2013. A novel sediment fingerprinting method using filtration: Application to the Mara River, East Africa. *J. Soils Sediments* 13, 1708–1723. doi:10.1007/s11368-013-0725-z
- Gellis, A.C., Noe, G.B., 2013. Sediment source analysis in the Linganore Creek watershed, Maryland, USA, using the sediment fingerprinting approach: 2008 to 2010. *J. Soils Sediments* 13, 1735–1753. doi:10.1007/s11368-013-0771-6
- Gholami, H., Middleton, N., Nazari Samani, A.A., Wasson, R., 2017. Determining contribution of sand dune potential sources using radionuclides, trace and major elements in central Iran. *Arab. J. Geosci.* 10, 163. doi:10.1007/s12517-017-2917-0
- Guardini, R., Comin, J.J., Schmitt, D.E., Tiecher, T., Bender, M.A., dos Santos, D.R., Mezzari, C.P., Oliveira, B.S., Gatiboni, L.C., Brunetto, G., 2012. Accumulation of phosphorus fractions in typic Hapludalf soil after long-term application of pig slurry and deep pig litter in a no-tillage system. *Nutr. Cycl. Agroecosystems* 93. doi:10.1007/s10705-012-9511-3
- Haddadchi, A., Nosrati, K., Ahmadi, F., 2014a. Differences between the source contribution of bed material and suspended sediments in a mountainous agricultural catchment of western Iran. *Catena* 116, 105–113. doi:10.1016/j.catena.2013.12.011
- Haddadchi, A., Olley, J., Laceby, P., 2014b. Accuracy of mixing models in predicting sediment source contributions. *Sci. Total Environ.* 497–498, 139–152. doi:10.1016/j.scitotenv.2014.07.105
- Haddadchi, A., Ryder, D.S., Evrard, O., Olley, J., 2013. Sediment fingerprinting in fluvial systems: review of tracers, sediment sources and mixing models. *Int. J. Sediment Res.* 28, 560–578. doi:10.1016/S1001-6279(14)60013-5
- Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46,

970–976. doi:10.2136/sssaj1982.03615995004600050017x

Hughes, A.O., Olley, J.M., Croke, J.C., McKergow, L.A., 2009. Sediment source changes over the last 250 years in a dry-tropical catchment, central Queensland, Australia. *Geomorphology* 104, 262–275. doi:10.1016/j.geomorph.2008.09.003

Huisman, N.L.H., Karthikeyan, K.G., Lamba, J., Thompson, A.M., Peaslee, G., 2013. Quantification of seasonal sediment and phosphorus transport dynamics in an agricultural watershed using radiometric fingerprinting techniques. *J. Soils Sediments* 13, 1724–1734. doi:10.1007/s11368-013-0769-0

Hupfer, M., Zak, D., Roßberg, R., Herzog, C., Pöthig, R., 2009. Sequential Phosphorus Technique in Calcite Lakes 399–410.

Koiter, A.J., Owens, P.N., Petticrew, E.L., Lobb, D.A., 2013a. The behavioural characteristics of sediment properties and their implications for sediment fingerprinting as an approach for identifying sediment sources in river basins. *Earth-Science Rev.* 125, 24–42. doi:10.1016/j.earscirev.2013.05.009

Koiter, A.J., Lobb, D.A., Owens, P.N., Petticrew, E.L., Tiessen, K.H.D., Li, S., 2013b. Investigating the role of connectivity and scale in assessing the sources of sediment in an agricultural watershed in the Canadian prairies using sediment source fingerprinting. *J. Soils Sediments* 13, 1676–1691. doi:10.1007/s11368-013-0762-7

Kouhpeima, A., Feiznia, S., Ahmadi, H., Hashemi, S.A.A., 2012. An assessment of specific sediment yield of geological formations using investigated sedimentary deposits in reservoirs and fingerprinting. *J. Agric. Sci. Technol.* 14, 435–447.

Kouhpeima, A., Feiznia, S., Ahmadi, H., Hashemi, S.A., Zareiee, A.R., 2010. Application of quantitative composite fingerprinting technique to identify the main sediment sources in two small catchments of Iran. *Hydrol. Earth Syst. Sci. Discuss.* 7, 6677–6698. doi:10.5194/hessd-7-6677-2010

Kouhpeima, A., Shiri, H.G., 2013. Estimation of sediment sources using a fingerprinting procedure. *Pollution* 56, 13252–13259.

Lacey, J.P., Evrard, O., Smith, H.G., Blake, W.H., Olley, J.M., Minella, J.P.G., Owens, P.N., 2017. The challenges and opportunities of addressing particle size effects in sediment source fingerprinting: A review. *Earth-Science Rev.* 169, 85–103. doi:10.1016/j.earscirev.2017.04.009

Lacey, J.P., McMahon, J., Evrard, O., Olley, J., 2015. A comparison of geological and statistical approaches to element selection for sediment fingerprinting. *J. Soils Sediments* 15, 2117–2131. doi:10.1007/s11368-015-1111-9

Lacey, J.P., Olley, J., 2015. An examination of geochemical modelling approaches to tracing sediment sources incorporating distribution mixing and elemental correlations. *Hydrol. Process.* 29, 1669–1685. doi:10.1002/hyp.10287

Lamba, J., Karthikeyan, K.G., Thompson, A.M., 2015a. Apportionment of suspended sediment sources in an agricultural watershed using sediment fingerprinting. *Geoderma* 239, 25–33. doi:10.1016/j.geoderma.2014.09.024

Lamba, J., Thompson, A.M., Karthikeyan, K.G., Fitzpatrick, F.A., 2015b. Sources of fine sediment stored in agricultural lowland streams, Midwest, USA. *Geomorphology* 236, 44–53. doi:10.1016/j.geomorph.2015.02.001

Lin, J., Huang, Y., Wang, M., Kuang, J., Jiang, F., Zhang, X., Ge, H., 2015. Assessing the sources of sediment transported in gully systems using a fingerprinting approach: An example from South-east China. *Catena* 129, 9–17. doi:10.1016/j.catena.2015.02.012

Lukkari, K., Hartikainen, H., Leivuori, M., 2007. Fractionation of sediment phosphorus revisited. I: Fractionation steps and their biogeochemical basis. *Limnol. Oceanogr. Methods* 5, 433–444. doi:10.4319/lom.2007.5.433

Maier, C., 2013. Variabilidade intra-evento da origem das fontes de sedimentos em uma bacia hidrográfica rural (Intra-event variability of sources from sediment basin in a rural). 2013. 124 f. Thesis (PhD in Water Resources and Sanitation) – Universidade Federal do Rio Grande do Sul, Porto Alegre.

Malá, J., Lagová, M., 2014. Comparison of digestion methods for determination of total phosphorus in river sediments. *Chem. Pap.* 68, 1015–1021. doi:10.2478/s11696-014-0555-5

Martinez-Carreras, N., Gallart, F., Iffly, J.F., Pfister, L., Walling, D., Krein, A., 2008. Uncertainty

- assessment in suspended sediment fingerprinting based on tracer mixing models : a case study from Luxembourg. *Sediment Dyn. Chang. Environ. IAHS Publ.* 325 325, 94–105.
- Martínez-Carreras, N., Krein, A., Udelhoven, T., Gallart, F., Iffly, J.F., Hoffmann, L., Pfister, L., Walling, D.E., 2010a. A rapid spectral-reflectance-based fingerprinting approach for documenting suspended sediment sources during storm runoff events. *J. Soils Sediments* 10, 400–413. doi:10.1007/s11368-009-0162-1
- Martínez-Carreras, N., Udelhoven, T., Krein, A., Gallart, F., Iffly, J.F., Ziebel, J., Hoffmann, L., Pfister, L., Walling, D.E., 2010b. The use of sediment colour measured by diffuse reflectance spectrometry to determine sediment sources: Application to the Attert River catchment (Luxembourg). *J. Hydrol.* 382, 49–63. doi:10.1016/j.jhydrol.2009.12.017
- Massoudieh, A., Gellis, A., Banks, W.S., Wieczorek, M.E., 2013. Suspended sediment source apportionment in Chesapeake Bay watershed using Bayesian chemical mass balance receptor modeling. *Hydrol. Process.* 27, 3363–3374. doi:10.1002/hyp.9429
- Miguel, P., Dalmolin, R.S.D., Pedron, F. de A., Moura-Bueno, J.M., Tiecher, T., 2014. Identificação de fontes de produção de sedimentos em uma bacia hidrográfica de encosta. *Rev. Bras. Ciência do Solo* 38, 585–598. doi:10.1590/S0100-06832014000200023
- Miller, J.R., Mackin, G., Lechler, P., Lord, M., Lorentz, S., 2013. Influence of basin connectivity on sediment source, transport, and storage within the Mkabela Basin, South Africa. *Hydrol. Earth Syst. Sci.* 17, 761–781. doi:10.5194/hess-17-761-2013
- Minella, J.P.G., Merten, G.H., Reichert, J.M., Santos, D.R. dos, 2007. Identificação e implicações para a conservação do solo das fontes de sedimentos em bacias hidrográficas. *Rev. Bras. Ciência do Solo* 31, 1637–1646. doi:10.1590/S0100-06832007000600039
- Minella, J.P.G., Walling, D.E., Merten, G.H., 2008. Combining sediment source tracing techniques with traditional monitoring to assess the impact of improved land management on catchment sediment yields. *J. Hydrol.* 348, 546–563. doi:10.1016/j.jhydrol.2007.10.026
- Motha, J.A., Wallbrink, P.J., Hairsine, P.B., Grayson, R.B., 2004. Unsealed roads as suspended sediment sources in an agricultural catchment in south-eastern Australia. *J. Hydrol.* 286, 1–18. doi:10.1016/j.jhydrol.2003.07.006
- Motha, J.A., Wallbrink, P.J., Hairsine, P.B., Grayson, R.B., 2003. Determining the sources of suspended sediment in a forested catchment in southeastern Australia. *Water Resour. Res.* 39, n/a-n/a. doi:10.1029/2001WR000794
- Mukundan, R., Radcliffe, D.E., Ritchie, J.C., Risse, L.M., McKinley, R.A., 2010. Sediment Fingerprinting to Determine the Source of Suspended Sediment in a Southern Piedmont Stream. *J. Environ. Qual.* 39, 1328. doi:10.2134/jeq2009.0405
- Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27, 31–36. doi:10.1016/S0003-2670(00)88444-5
- Nosrati, K., Govers, G., Ahmadil, H., Sharifi, F., Amoozegar, M.A., Merckx, R., Vanmaercke, M., 2011. An exploratory study on the use of enzyme activities as sediment tracers: biochemical fingerprints? *Int. J. Sediment Res.* 26, 136–151. doi:10.1016/S1001-6279(11)60082-6
- Nosrati, K., Govers, G., Semmens, B.X., Ward, E.J., 2014. A mixing model to incorporate uncertainty in sediment fingerprinting. *Geoderma* 217–218, 173–180. doi:10.1016/j.geoderma.2013.12.002
- Olsen, S.R., Sommers, L.E., 1982. Phosphorus Methods of Soil Analysis, in: Page, A.L., Miller, R.H., Keeney, Q.R. (Eds.), *Chemical and Microbiological Properties*. Soil Science Society of America, Madison, pp. 403–430.
- Ostrofsky, M.L., 2012. Determination of total phosphorus in lake sediments. *Hydrobiologia* 696, 199–203. doi:10.1007/s10750-012-1208-8
- Owens, P.N., Walling, D.E., Leeks, G.J.K. Use of floodplain sediment cores to investigate recent historical changes in overbank sedimentation rates and sediment sources in the catchment of the River Ouse, Yorkshire, UK. *Catena*, 36, 21–47. doi.org/10.1016/S0341-8162(99)00010-7
- Owens, P.N., Walling, D.E., 2002. The phosphorus content of fluvial sediment in rural and industrialized river basins. *Water Res.* 36, 685–701. doi:10.1016/S0043-1354(01)00247-0
- Owens, P.N., Xu, Z., 2011. Recent advances and future directions in soils and sediments research. *J. Soils Sediments* 11, 875–888. doi:10.1007/s11368-011-0406-8
- Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2016. Combining catchment

- modelling and sediment fingerprinting to assess sediment dynamics in a Spanish Pyrenean river system. *Sci. Total Environ.* 569–570, 1136–1148. doi:10.1016/j.scitotenv.2016.06.189
- Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2015. Comparing catchment sediment fingerprinting procedures using an auto-evaluation approach with virtual sample mixtures. *Sci. Total Environ.* 532, 456–466. doi:10.1016/j.scitotenv.2015.05.003
- Palazón, L., Navas, A., 2017. Variability in source sediment contributions by applying different statistic test for a Pyrenean catchment. *J. Environ. Manage.* 194, 42–53. doi:10.1016/j.jenvman.2016.07.058
- Pavinato, P.S., Merlin, A., Rosolem, C.A., 2009. Phosphorus fractions in Brazilian Cerrado soils as affected by tillage. *Soil Tillage Res.* 105, 149–155. doi:10.1016/j.still.2009.07.001
- Pulley, S., Foster, I., Antunes, P., 2015a. The uncertainties associated with sediment fingerprinting suspended and recently deposited fluvial sediment in the Nene river basin. *Geomorphology* 228, 303–319. doi:10.1016/j.geomorph.2014.09.016
- Pulley, S., Foster, I., Antunes, P., 2015b. The application of sediment fingerprinting to floodplain and lake sediment cores: assumptions and uncertainties evaluated through case studies in the Nene Basin, UK. *J. Soils Sediments* 15, 2132–2154. doi:10.1007/s11368-015-1136-0
- Ramon, R., 2017. Kinetic energy measurement of rainfall and defining a pluvial index to estimate erosivity in Arvorezinha/RS. Federal University of Santa Maria.
- Rodrigues, M., Pavinato, P.S., Withers, P.J.A., Teles, A.P.B., Herrera, W.F.B., 2016. Legacy phosphorus and no tillage agriculture in tropical oxisols of the Brazilian savanna. *Sci. Total Environ.* 542, 1050–1061. doi:10.1016/j.scitotenv.2015.08.118
- Rowan, J.S., Black, S., Franks, S.W., 2012. Sediment fingerprinting as an environmental forensics tool explaining cyanobacteria blooms in lakes. *Appl. Geogr.* 32, 832–843. doi:10.1016/j.apgeog.2011.07.004
- Russell, M.A., Walling, D.E., Hodgkinson, R.A., 2001. Suspended sediment sources in two small lowland agricultural catchments in the UK. *J. Hydrol.* 252, 1–24. doi:10.1016/S0022-1694(01)00388-2
- Saavedra, C., Delgado, A., 2005. Iron-related phosphorus in eroded sediments from agricultural soils of Mediterranean areas. *Geoderma* 125, 1–9. doi:10.1016/j.geoderma.2004.06.001
- Schmitt, D.E., Brunetto, G., Santos, E. dos, Wagner, W. de L., Sete, P.B., Souza, M., Ambrosini, V.G., Santos, M.A. dos, Tiecher, T., Comin, J.J., Couto, R. da R., Gatiboni, L.C., Giachini, A., 2017. Phosphorus fractions in apple orchards in southern Brazil. *Bragantia* 76, 422–432. doi:10.1590/1678-4499.173
- Sherriff, S.C., Franks, S.W., Rowan, J.S., Fenton, O., Ó'hUallacháin, D., 2015. Uncertainty-based assessment of tracer selection, tracer non-conservativeness and multiple solutions in sediment fingerprinting using synthetic and field data. *J. Soils Sediments* 15, 2101–2116. doi:10.1007/s11368-015-1123-5
- Smith, H.G., Blake, W.H., 2014. Sediment fingerprinting in agricultural catchments: A critical re-examination of source discrimination and data corrections. *Geomorphology* 204, 177–191. doi:10.1016/j.geomorph.2013.08.003
- Teles, A.P.B., Rodrigues, M., Herrera, W.F.B., Soltangheisi, A., Sartor, L.R., Withers, P.J.A., Pavinato, P.S., 2017. Do cover crops change the lability of phosphorus in a clayey subtropical soil under different phosphate fertilizers ? *Soil Use Manag.* 1–11. doi:10.1111/sum.12327
- Thompson, J., Cassidy, R., Doody, D.G., Flynn, R., 2013. Predicting critical source areas of sediment in headwater catchments. *Agric. Ecosyst. Environ.* 179, 41–52. doi:10.1016/j.agee.2013.07.010
- Tiecher, T., Caner, L., Minella, J.P.G., Bender, M.A., dos Santos, D.R., 2016. Tracing sediment sources in a subtropical rural catchment of southern Brazil by using geochemical tracers and near-infrared spectroscopy. *Soil Tillage Res.* 155, 478–491. doi:10.1016/j.still.2015.03.001
- Tiecher, T., Caner, L., Minella, J.P.G., Pellegrini, A., Capoane, V., Rasche, J.W.A., Schaefer, G.L., Rheinheimer, D. dos S., 2017a. Tracing sediment sources in two paired agricultural catchments with different riparian forest and wetland proportion in southern Brazil. *Geoderma* 285, 225–239. doi:10.1016/j.geoderma.2016.10.008
- Tiecher, T., Caner, L., Minella, J.P.G., Santos, D.R. dos, 2015. Combining visible-based-color parameters and geochemical tracers to improve sediment source discrimination and apportionment. *Sci. Total Environ.* 527–528, 135–149. doi:10.1016/j.scitotenv.2015.04.103

- Tiecher, T., Gomes, M.V., Ambrosini, V.G., Amorim, M.B., Bayer, C., 2018. Assessing linkage between soil phosphorus forms in contrasting tillage systems by path analysis. *Soil Tillage Res.* 175. doi:10.1016/j.still.2017.09.015
- Tiecher, T., Minella, J.P.G., Caner, L., Evrard, O., Zafar, M., Capoane, V., Le Gall, M., Santos, D.R. dos, 2017b. Quantifying land use contributions to suspended sediment in a large cultivated catchment of Southern Brazil (Guaporé River, Rio Grande do Sul). *Agric. Ecosyst. Environ.* 237, 95–108. doi:10.1016/j.agee.2016.12.004
- Tiecher, T., Minella, J.P.G., Miguel, P., Alvarez, J.W.R., Pellegrini, A., Capoane, V., Ciotti, L.H., Schaefer, G.L., dos Santos, D.R., 2014. Contribuição das fontes de sedimentos em uma bacia hidrográfica agrícola sob plantio direto. *Rev. Bras. Cienc. do Solo* 38, 639–649. doi:10.1590/S0100-06832014000200028
- Tiecher, T., Schenato, R.B., Santanna, M.A., Caner, L., Santos, D.R. dos, 2017c. Phosphorus Forms in Sediments as Indicators of Anthropic Pressures in an Agricultural Catchment in Southern Brazil. *Rev. Bras. Ciência do Solo* 41, 1–17. doi:10.1590/18069657rbcs20160569
- USEPA, 1971. Methods of chemical analysis for water and wastes. United States Environmental Protection Agency, Cincinnati, US.
- Walling, D.E., 2013. The evolution of sediment source fingerprinting investigations in fluvial systems. *J. Soils Sediments* 13, 1658–1675. doi:10.1007/s11368-013-0767-2
- Walling, D.E., Collins, A.L., Jones, P.A., Leeks, G.J.L., Old, G., 2006. Establishing fine-grained sediment budgets for the Pang and Lambourn LOCAR catchments, UK. *J. Hydrol.* 330, 126–141. doi:10.1016/j.jhydrol.2006.04.015
- Walling, D.E., Collins, A.L., Stroud, R.W., 2008. Tracing suspended sediment and particulate phosphorus sources in catchments. *J. Hydrol.* 350, 274–289. doi:10.1016/j.jhydrol.2007.10.047
- Walling, D.E., Owens, P.N., Leeks, G.J.L., 1999. Fingerprinting suspended sediment sources in the catchment of the River Ouse, Yorkshire, UK. *Hydrol. Process.* 13, 955–975. doi:10.1002/(SICI)1099-1085(199905)13:7<955::AID-HYP784>3.0.CO;2-G
- Wang, C., Zhang, Y., Li, H., Morrison, R.J., 2013. Sequential extraction procedures for the determination of phosphorus forms in sediment 14, 147–157. doi:10.1007/s10201-012-0397-1
- Wilkinson, S.N., Hancock, G.J., Bartley, R., Hawdon, A.A., Keen, R.J., 2013. Using sediment tracing to assess processes and spatial patterns of erosion in grazed rangelands, Burdekin River basin, Australia. *Agric. Ecosyst. Environ.* 180, 90–102. doi:10.1016/j.agee.2012.02.002
- Yang, X., Post, W.M., 2011. Phosphorus transformations as a function of pedogenesis: A synthesis of soil phosphorus data using Hedley fractionation method. *Biogeosciences* 8, 2907–2916. doi:10.5194/bg-8-2907-2011
- Zhang, X.C.J., Liu, B.L., 2016. Using multiple composite fingerprints to quantify fine sediment source contributions: A new direction. *Geoderma* 268, 108–118. doi:10.1016/j.geoderma.2016.01.031
- Zhang, Y.S., Collins, A.L., Horowitz, A.J., 2012. A preliminary assessment of the spatial sources of contemporary suspended sediment in the Ohio River basin, United States, using water quality data from the NASQAN 334, 326–334. doi:10.1002/hyp.8128

Figure 1. Distribution of the selection of 60 sediment fingerprinting studies found in the literature and testing the use of P as a potential tracer depending on the country of the study site (a) and the digestion method used to prepare soil and sediment material (b). *For X-ray Fluorescence Spectroscopy (XRFs) no digestion is required. **No information about the acid used for digestion.

(d) Percentage of valid cases that have passed or failed the test

Figure 2. Summary of results obtained by the range test (a), Kruskal-Wallis H-test (KW-H, b), and discriminant function analysis (DFA, c) for the selection of 60 sediment fingerprinting studies that tested P as a potential tracer, and the percentage of studies that applied these tests in which P passed or failed the tests (d). This figure is based on results provided in Table 1. *P was excluded on the basis of the potential non-conservative behavior of P during downstream transport and it was not tested for KW-H, Range Test, and DFA. N/A = not available.

Figure 3. Comparison between P extracted by digestion methods using aqua-regia (HNO₃+HCl) and by H₂SO₄+H₂O₂.

Figure 4. Box-plots of concentration in P-fractions measured in the potential sources and in suspended sediment samples. The box indicates the location of the first and third quartiles; the line indicates the median value; whiskers indicate the non-outlier range; circles indicate values outside of $\pm 1SD$. %SCC = percentage of source samples (cropland, unpaved roads, and stream channel) correctly classified in their respective groups as a result of the DFA.

Figure 5. Average particle size distribution (a) and accumulated particle size distribution (b) of suspended sediment samples ($n = 31$) and sediment sources (10 samples of unpaved roads, 10 samples of stream channel, and 20 samples of crop field) sieved at $63\ \mu\text{m}$ in Arvorezinha catchment.

Figure 6. Box-plots of Ca (left) and Fe (right) concentrations in the potential sources and in suspended sediment samples (data from **Tiecher et al. (2015)**). The box indicates the first and the third quartiles; the line indicates the median value; whiskers indicate the non-outlier range; circles indicate values outside of the range of $\pm 1SD$.

Figure 7. Two-dimensional scatterplots of the first and second discriminant functions provided by the stepwise discriminant function analysis (DFA) applied to selected sets of tracers using geochemical elements (a – data from Tiecher et al. 2015), P-forms (b), and the combination of geochemical elements (excluding total-P) and P-forms (c) as potential tracing properties.

(a) Geochemical

(b) P-fractions

(c) Geochemical + P-fractions

Figure 8. Box plot of the sediment source contributions to suspended sediment calculated using different sets of tracing properties. The box indicates the first and the third quartiles; the line indicates the median value; whiskers indicate the non-outlier range; circles indicate values outside of the range of $\pm 1SD$.

Table 1. Summary of the statistical test results used for P selection as a potential tracer in a selection of 60 studies found in the literature including P in the list of the potential tracing properties; list of countries of the study sites, the selected solid digestion method and the equipment used to measure P.

Reference	Journal	Country	Digestion method	Equipment	Passed KW-H test	Range test	Passed DFA analysis	Agriculture source
Banks and Gellis (2010)	‡	USA	HF+HNO ₃	ICP-OES	N/A	Failed	N/A	✓
Chen et al. (2016)	JSS	China	HCl+HNO ₃	ICP-MS	✓	✓	✓	✓
Chen et al. (2016)	STOTEN	China	HCl+HNO ₃	ICP-MS	✓	✓	Failed	✓
Collins and Walling (2007)	GEOM	UK	Acid digestion***	UV/Vis	✓	N/A	Failed	✓
Collins et al. (1996)	Géomorphologie	UK	HClO ₄	UV/Vis	✓	N/A	Failed	✓
Collins et al. (1997a)	Catena	UK	HClO ₄	UV/Vis	✓	N/A	✓	✓
Collins et al. (1997b)	HESS	UK	HClO ₄	UV/Vis	✓	N/A	Failed	✓
Collins et al. (1998)	ESPL	UK	HClO ₄	UV/Vis	✓	N/A	✓	✓
Collins et al. (2001)	AG	Zambia	HClO ₄	UV/Vis	✓	N/A	✓	✓
Collins et al. (2010)	STOTEN	UK	HCl+NaOH	UV/Vis	✓	N/A	✓	✓
Cooper et al. (2014)	ESPL	UK	None	XRFS	N/A	Failed	N/A	✓
Devereux et al. (2010)	HP	USA	HNO ₃	ICP-MS	✓	✓	Failed	✓
D'Haen et al. (2013)	HP	Turkey	HCl+HNO ₃	ICP-OES	✓	N/A	Failed	
Dutton et al. (2013)	JSS	Kenya/Tanz	HF+HCl+HNO ₃	ICP-MS	✓	✓	✓	
Gellis et al. (2013)	JSS	USA	HF+HNO ₃	ICP-OES	✓	✓	Failed	✓
Gholami et al. (2017)	AJG	Iran	HCl+HNO ₃	ICP-MS	✓	N/A	Failed	
Haddadchi et al. (2014)	STOTEN	Australia	HCl+HNO ₃	ICP-OES	✓	N/A	Failed	
Haddadchi et al. (2014)	Catena	Iran	HCl+HNO ₃	ICP-OES	✓	N/A	Failed	✓
Hughes et al. (2009)	GEOM	Australia	None**	XRFS	N/A	N/A	✓	
Huisman et al. (2013)	JSS	USA	H ₂ SO ₄ +HNO ₃	FIA	N/A	N/A	✓	✓
Koiter et al. (2013b)	JSS	Canada	HNO ₃	ICP-MS	Failed	N/A	N/A	✓
Kouhpeima et al. (2010)	HESS	Iran	HClO ₄	UV/Vis	✓	✓	✓	
Kouhpeima et al. (2012)	JAST	Iran	HClO ₄	UV/Vis	✓	✓	Failed	
Kouhpeima et al. (2013)	Pollution	Iran	HClO ₄	UV/Vis	✓	✓	✓	
Lacey and Olley (2015)	HP	Australia	None	XRFS	✓	✓	Failed	
Lacey et al. (2015)	JSS	Australia	LiBO ₂	ICP-OES	✓	✓	✓	
Lamba et al. (2015)	GEOD	USA	H ₂ SO ₄ +HNO ₃	FIA	Failed	✓	N/A	✓
Lamba et al. (2015)	GEOM	USA	H ₂ SO ₄ +HNO ₃	FIA	✓	✓	Failed	✓
Lin et al. (2015)	CAT	China	HCl+HNO ₃	UV/Vis	✓	N/A	✓	
Martínez-Carrera et al. (2008)	IAHS	Luxembourg	HCl+HNO ₃	UV/Vis	✓	✓	✓	✓
Martínez-Carrera et al. (2010)	JH	Luxembourg	HCl+HNO ₃	UV/Vis	✓	✓	✓	✓
Martínez-Carrera et al. (2010)	JSS	Luxembourg	HCl+HNO ₃	UV/Vis	Failed	N/A	N/A	✓
Massoudieh et al. (2013)	HP	USA	HF+HClO ₄ +HCl+HNO ₃	ICP-MS	N/A	N/A	N/A	✓
Miguel et al. (2014)	RBCS	Brazil	HCl+HNO ₃	ICP-OES	✓	N/A	✓	✓
Miller et al. (2013)	HESS	South Africa	HCl+HNO ₃	ICP-MS	N/A	N/A	Failed	✓
Minella et al. (2007)	RBCS	Brazil	H ₂ SO ₄ +H ₂ O ₂	UV/Vis	✓	N/A	✓	✓
Minella et al. (2008)	JH	Brazil	H ₂ SO ₄ +H ₂ O ₂	UV/Vis	✓	N/A	✓	✓
Motha et al. (2003)	WRR	Australia	None	XRFS	N/A	✓	✓	✓
Motha et al. (2004)	JH	Australia	None	XRFS	N/A	✓	✓	✓
Mukundan et al. (2010)	JEQ	USA	HNO ₃	ICP-OES	Failed	N/A	N/A	✓
Nosrati et al. (2011)	IJSR	Iran	HCl+HNO ₃	ICP-OES	✓	N/A	Failed	
Nosrati et al. (2014)	GEOD	Iran	HCl+HNO ₃	ICP-OES	✓	N/A	Failed	
Palazón et al. (2015)	STOTEN	Spain	HF	ICP-OES	*	*	*	✓
Palazón et al. (2016)	STOTEN	Spain	HF	ICP-OES	*	*	*	✓
Palazón and Navas (2017)	JEM	Spain	HF	ICP-OES	*	*	*	✓
Pulley et al. (2015)	GEOM	UK	HCl+HNO ₃	ICP-OES	✓	✓	✓	✓
Pulley et al. (2015)	JSS	UK	HCl+HNO ₃	ICP-OES	✓	✓	✓	
Rowan et al. (2012)	AG	UK	None	XRFS	N/A	✓	✓	✓
Russel et al. (2001)	JH	UK	HClO ₄	UV/Vis	Failed	N/A	N/A	✓
Slimane et al. (2013)	JSS	Tunisia	HF+HClO ₄		Failed	✓	N/A	✓
Smith & Blake. (2014)	GEOM	UK	None	XRFS	*	*	*	✓
Thompson et al. (2013)	AEE	Ireland	HCl+HNO ₃	ICP-OES	✓	N/A	Failed	✓
Thompson et al. (2013)	AEE	Ireland	HNO ₃	ICP-OES	✓	N/A	Failed	✓
Tiecher et al. (2014)	RBCS	Brazil	HF+HCl+HNO ₃	UV/Vis	✓	N/A	✓	✓
Tiecher et al. (2015)	STR	Brazil	HCl+HNO ₃	ICP-OES	✓	✓	✓	✓
Tiecher et al. (2017)	AEE	Brazil	HCl+HNO ₃	ICP-OES	✓	✓	✓	✓
Tiecher et al. (2017)	GEOD	Brazil	HCl+HNO ₃	ICP-OES	✓	Failed	N/A	✓
Wilkinson et al. (2013)	AEE	Australia	None	XRFS	✓	✓	Failed	
Zhang and Liu (2016)	GEOD	USA	HNO ₃	ICP-MS	N/A	Failed	N/A	✓
Zhang et al. (2012)	HP	USA	Acid digestion	N/A	N/A	N/A	✓	

*P was excluded because of its potential non-conservative behavior during erosion and transport and was therefore not tested for KW-H, Range Test, and DFA.

For X-ray Fluorescence Spectroscopy (XRFS) no digestion is required. *No information about the acid used for digestion. N/A = not available. RBCS, Revista Brasileira de Ciência do Solo. GEOD, Geoderma. GEOM, Geomorphology. ESPL, Earth Surface Processes and Landforms. HESS, Hydrology and Earth System Sciences. HP, Hydrological Processes. IJSR, International Journal of Sediment Research. JEQ, Journal of Environmental Quality. JH, Journal of Hydrology. STR, Soil and Tillage Research. JSS, Journal of Soil and Sediments. STOTEN, The Science of Total Environment. AEE, Agriculture, Ecosystems & Environment. JEM, Journal of Environmental Management. LDD, Land Degradation and Development. AJG, Arabian Journal Geoscience. PPG, Progress in Physical Geography. WRR, Water Resources Research. AGG, Applied Geography. AGC, Applied Geochemistry. JAST, Journal of Agricultural Science and Technology. ‡ 2nd Joint Federal Interagency Conference, Las Vegas, NV.

Table 2. Pearson correlation between P-fractions concentration and specific surface area and total organic carbon for all data set, including source and suspended sediment samples ($n=71$). Bold numbers indicate significant correlation at $p<0.05$.

P-fractions	Specific surface area (m ² g ⁻¹)		Total organic carbon (g kg ⁻¹)	
	R ²	<i>p</i> -value	R ²	<i>p</i> -value
Total P (aqua-regia)	0.21	<0.001	0.34	<0.001
P _{resin}	0.04	0.111	0.05	0.056
P _{bic}	0.05	0.075	0.08	0.020
P _{NaOH0.1}	0.10	0.007	0.25	<0.001
P _{HCl}	0.22	<0.001	0.27	<0.001
P _{NaOH0.5}	0.21	<0.001	0.13	0.003
P _{residual}	0.37	<0.001	0.33	<0.001
P _{org}	0.12	0.004	0.14	0.002
P _{inorg}	0.29	<0.001	0.31	<0.001

Table 3. Results of the discriminant function analysis applied to different sets of tracing properties: geochemical elements, P-fractions and the combination of geochemical elements and P-fractions.

DFA parameters	Geochemical ^a	P-fractions	Geochemical +P-fractions
<i>Wilks' lambda</i>	0.0126	0.2154	0.0122
<i>Variance due to differences between sources (%)</i>	98.7	78.5	98.8
<i>Selected tracers</i>	Cr Fe As Ag Mo P	P _{resin} P _{org}	P _{org} Mo P _{resin} Fe Ag As
<i>Source type samples correctly classified (%)</i>			
Cropland	100	90	100
Unpaved roads	100	100	100
Stream channel	100	70	100
Total	100	87.5	100
<i>Squared Mahalanobis distances</i>			
Stream channels vs. unpaved roads	53.2	3.6	62.7
Stream channels vs. cropland	42.2	7.1	32.4
Unpaved roads vs. cropland	48.8	11.2	61.6
Average	48.1	9.0	52.2
<i>p-levels</i>			
Stream channels vs. unpaved roads	2.9E-13	7.7E-04	2.9E-14
Stream channels vs. cropland	1.3E-13	3.9E-07	5.1E-12
Unpaved roads vs. cropland	1.7E-14	2.3E-09	6.7E-16
<i>Uncertainty associated with the discrimination of the source (%)</i>			
Cropland	2.9E-03	18.6	1.6E-03
Unpaved roads	2.3E-03	16.5	2.3E-05
Stream channel	1.5E-04	32.0	8.6E-03
Average	2.1E-03	21.5	4.8E-04

^a Tiecher et al. (2015).

Supplementary material

Table 1. Result of the Mann-Whitney *U*-test for comparison of the contents of the P-fractions between each sediment sources. Bold values indicate $p < 0.1$.

Comparison	P _{resin}	P _{bic}	P _{NaOH0.1}	P _{HCl}	P _{NaOH0.5}	P _{residual}	P _{org}	P _{inorg}
Stream channel vs. Unpaved roads	0.257	0.003	0.007	0.364	0.290	0.257	1.6E-04	0.821
Stream channel vs. Cropland	1.6E-05	1.1E-04	4.3E-04	0.048	0.095	0.758	0.895	2.2E-04
Unpaved road vs. Cropland	1.6E-05	1.1E-05	1.6E-05	0.016	4.7E-04	0.086	7.5E-05	4.3E-05

Table 2. P-fractions content (mg kg⁻¹) in sediment sources samples. SD, standard deviation.

Sample	ID	P _{resin}	P _{pic}	P _{NaOH0.1}	P _{HCl}	P _{NaOH0.5}	P _{residual}	P _{org}	P _{inorg}
Stream channel	1	13.1	49.2	244.8	18.7	94.8	183.4	221.7	382.3
	2	9.3	37.8	259.5	12.7	97.4	214.5	251.8	379.4
	3	10.3	38.0	250.3	15.3	123.1	247.5	369.2	315.3
	4	37.4	90.8	314.2	27.4	145.2	233.6	278.8	569.8
	5	7.4	31.9	138.6	4.9	44.0	176.2	158.4	244.7
	6	9.3	28.8	171.3	5.2	66.7	184.1	215.3	250.2
	7	6.3	23.9	170.8	15.8	59.4	133.4	143.2	266.3
	8	6.6	24.8	157.1	13.0	59.1	138.7	162.4	236.8
	9	13.4	64.6	189.7	11.2	52.1	123.9	207.4	247.4
	10	10.3	36.0	102.9	4.4	32.7	127.8	157.1	157.1
	Mean	12.3	42.6	199.9	12.9	77.5	176.3	216.5	304.9
	SD	9.1	20.8	64.9	7.1	36.4	45.1	69.7	115.3
Unpaved road	1	14.8	22.4	122.5	33.6	35.0	84.6	60.6	252.3
	2	2.1	2.2	37.3	5.3	26.0	100.6	81.4	92.1
	3	5.3	11.3	94.2	15.7	34.0	99.4	99.9	159.9
	4	31.5	32.8	177.1	6.5	64.1	173.8	84.5	401.4
	5	8.7	19.9	162.4	6.7	82.1	177.2	103.7	353.2
	6	3.7	10.5	127.7	1.9	61.4	219.4	112.3	312.3
	7	7.8	18.3	144.2	9.2	70.1	185.8	139.7	295.7
	8	13.4	34.5	130.7	24.3	108.1	181.2	130.1	362.1
	9	8.9	31.2	133.7	4.0	48.7	143.8	111.4	258.9
	10	3.7	10.8	102.2	3.0	51.4	130.2	108.8	192.5
	Mean	10.0	19.4	123.2	11.0	58.1	149.6	103.2	268.0
	SD	8.6	10.9	39.1	10.4	24.8	44.8	23.3	97.3
Cropland	1	92.5	160.7	475.8	24.1	75.4	191.4	61.5	958.3
	2	73.7	114.6	297.4	26.1	82.1	127.2	152.6	568.4
	3	95.9	133.4	282.0	39.7	102.1	173.5	193.3	633.4
	4	40.9	79.8	263.6	15.3	122.1	200.3	256.5	465.5
	5	17.6	57.7	161.2	9.5	83.4	187.1	270.4	246.2
	6	45.8	65.9	320.5	9.5	128.1	220.7	245.1	545.4
	7	71.7	123.5	394.3	23.1	129.5	233.0	132.7	842.4
	8	58.2	84.3	237.8	19.4	84.1	129.9	207.4	406.3
	9	60.3	81.5	280.8	13.8	96.1	147.2	145.4	534.3
	10	25.6	45.0	257.9	4.7	87.4	227.5	196.3	451.8
	11	60.8	86.1	372.5	8.6	113.5	260.5	200.0	702.0
	12	51.6	94.2	302.2	14.7	90.1	188.3	313.0	428.2
	13	76.3	111.1	305.8	33.1	104.1	173.1	213.1	590.3
	14	49.9	79.4	264.2	15.0	44.0	138.3	170.3	420.5
	15	65.0	95.6	332.8	22.9	118.1	194.3	182.3	646.4
	16	134.7	185.5	522.1	37.3	98.1	179.5	265.3	891.9
	17	109.0	74.9	494.8	31.3	84.1	103.7	173.5	724.2
	18	89.0	124.4	404.9	37.8	120.1	157.6	355.7	578.1
	19	57.2	113.9	411.9	13.8	116.1	197.8	194.5	716.2
	20	79.3	112.3	365.5	19.1	85.4	160.8	253.7	568.7
	Mean	67.8	101.2	337.4	20.9	98.2	179.6	209.1	595.9
	SD	27.8	34.2	92.3	10.5	21.3	39.3	66.4	176.1
Hihest source sample content		134.7	185.5	522.1	39.7	145.2	260.5	369.2	958.3
Lowest source sample content		2.1	2.2	37.3	1.9	24.8	44.8	23.3	92.1

Table 3. P-fractions content (mg kg⁻¹) in suspended sediment samples. SD, standard deviation. Bold values indicate suspended sediment samples with P content higher than the highest value found in sediment source samples (Table 1).

Suspended sediment sample	ID	P _{resin}	P _{bic}	P _{NaOH0.1}	P _{HCl}	P _{NaOH0.5}	P _{residual}	P _{org}	P _{inorg}
	1	40.5	40.7	231.8	68.0	1103.6	221.2	209.9	1496.0
	2	32.6	53.4	289.6	66.2	663.3	217.7	239.0	1083.8
	3	39.6	54.5	264.7	68.5	401.1	263.9	250.1	874.0
	4	32.8	55.5	226.1	71.8	341.1	213.5	173.9	767.0
	5	32.0	51.6	260.4	70.0	361.9	237.6	196.2	816.8
	6	33.5	52.9	260.4	70.3	293.2	233.7	201.0	743.0
	7	37.6	52.9	231.1	96.4	230.9	200.6	133.6	716.1
	8	40.3	57.7	259.7	102.2	187.9	202.6	165.8	684.7
	9	32.4	54.0	336.6	98.4	226.6	219.8	179.7	787.2
	10	40.0	72.1	401.0	119.9	167.9	213.8	304.4	710.3
	11	37.7	69.4	309.6	116.6	186.5	226.1	140.9	804.9
	12	21.4	39.7	174.0	67.1	147.1	172.0	151.8	469.5
	13	22.6	45.6	197.7	72.5	151.4	191.5	158.2	523.3
	14	24.3	51.4	255.0	64.4	183.6	257.2	188.9	641.3
	15	52.5	74.3	282.5	104.5	231.6	256.2	183.3	818.3
	16	23.6	48.7	252.6	87.2	145.7	190.6	137.8	610.6
	17	31.8	55.4	288.9	88.4	146.3	198.8	173.9	635.9
	18	37.6	54.5	296.8	66.0	175.0	224.2	225.7	623.7
	19	36.5	67.0	313.2	104.4	129.9	172.4	181.4	627.9
	20	45.3	69.4	315.2	104.4	147.8	196.4	199.0	679.6
	21	46.0	73.5	378.9	112.9	196.5	249.4	184.6	872.5
	22	38.7	71.6	316.8	87.5	145.7	189.7	237.1	612.9
	23	64.0	109.4	434.9	114.3	215.1	244.4	120.3	1056.4
	24	52.5	90.5	489.0	135.3	215.1	199.1	144.1	1037.3
	25	66.5	95.0	655.1	131.6	172.9	198.7	302.0	1017.7
	26	31.7	60.6	295.3	114.0	165.7	205.4	222.5	650.2
	27	37.6	68.1	316.8	120.1	177.9	218.7	159.5	779.6
	28	34.9	73.7	321.0	111.1	155.7	203.3	131.3	768.5
	29	34.7	64.0	300.3	105.1	177.2	223.8	222.0	678.2
	30	33.3	67.2	311.0	95.1	220.4	257.1	248.9	735.4
	31	50.5	70.5	270.4	43.4	221.6	246.4	176.2	726.7
	Mean	38.2	63.4	307.6	92.8	248.0	217.6	191.7	775.8
	SD	10.6	15.4	91.4	23.2	190.4	25.1	46.5	199.4