



HAL
open science

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, Rafael Ramon, J. Patrick Patrick Laceby, O. Evrard, Jean Paolo Gomes Minella

► To cite this version:

Tales Tiecher, Rafael Ramon, J. Patrick Patrick Laceby, O. Evrard, Jean Paolo Gomes Minella. Potential of phosphorus fractions to trace sediment sources in a rural catchment of Southern Brazil: Comparison with the conventional approach based on elemental geochemistry. *Geoderma*, 2019, 337, pp.1067-1076. 10.1016/j.geoderma.2018.11.011 . cea-02615743

HAL Id: cea-02615743

<https://cea.hal.science/cea-02615743>

Submitted on 25 May 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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.

46 1. Introduction

47 Soil erosion remains one of the main environmental problems caused by human society in their
48 search for food, fiber and energy production. The global annual estimates of soil erosion are about 2.87
49 Mg ha⁻¹ yr⁻¹ (**Borrelli et al., 2017**), and Southern Brazil stands out as one of the hotspots of soil erosion
50 in the world. Recently, **Didoné et al. (2017)** have estimated sediment yields ranging from 36 to 260 Mg
51 km² yr⁻¹ in rural catchments of Southern Brazil. This situation raises major concerns as projected climate
52 change impacts on rainfall erosivity across Brazil indicated that Southern Brazil will be one of the most
53 affected regions, with projected increases in rainfall erosivity reaching up to 109% in the period of 2007–
54 2040 (**Almagro et al., 2017**). In this context, it is important to identify the main sediment sources in
55 catchments in order to guide decision makers in the efficient allocation of limited public resources
56 available to mitigate sediment production.

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

66 Two of the main prerequisites for using physico-chemical properties as tracers of sediment
67 origin are that: (i) significant differences in property concentrations are found between the potential
68 sources and that (ii) they remain conservative during erosion and transport processes (**Owens and Xu,**
69 **2011**). Usually, non-parametric tests (such as the Kruskal-Wallis *H*-test or Mann-Whitney *U*-test) are
70 employed to identify physico-chemical properties that may be used as a sediment source tracer.

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

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

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

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

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

103 Another important point that is often overlooked in the literature is related to the digestion
104 method used to prepare the samples and estimate their elemental concentrations (Fig. 1b). Not all the
105 methods used in previous studies are able to estimate the total P content in soils and sediments. In order
106 to quantify the absolute total P content, the digestion must include the use of acids, including hydrogen
107 fluoride (15% of the studies included in the comparison – Fig. 1b), as this substance is needed to fully
108 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
109 (3% of the studies investigated – Fig. 1b). The use of sodium carbonate (Na_2CO_3) fusion (Bender and
110 Wood, 2000), or HClO_4 (Ostrofsky, 2012) (18% of those studies included in the review – Fig. 1b) provide
111 potential alternatives, as well as those spectroscopic methods analyzing solid powders as the X-ray
112 fluorescence (XRF) (13% of those previous studies – Fig. 1b). The other digestion methods provide
113 limited information related to a fraction of the total P only, as they do not assess the more recalcitrant
114 forms of P, and are usually considered as a pseudo-total content of P (Bender and Wood, 2000). This
115 means that the amount of P used to trace the contributions of potential sediment sources in several
116 previous studies was likely the fraction that was the most sensitive to environmental changes and the
117 less conservative during erosion and transportation processes, whereas the most stable fraction, which
118 should be targeted in sediment tracing studies, was neglected (Dabrin et al., 2014).

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

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

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

144

145 **2. Material and methods**

146 *2.1. Study catchment, source and sediment sampling*

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

154 by tobacco cultivated under minimum tillage (16%) or under conventional ploughing (10%), native forest
155 (47%), grain crops (17%), grassland (6%), unpaved roads (2%), and rural residential areas (2%). The
156 catchment does not have any urban development.

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

168 Thirty-one suspended sediment samples were collected during various stages (i.e. rising, peak,
169 and recession) of nine significant floods that occurred between October 2009 and July 2011 (**Maier,**
170 **2013**). A large volume of water (120 to 200 liters) was collected manually at the outlet. Each bulk water
171 sample was centrifuged using a continuous flow device (Alfie-500 Alfa Laval) to concentrate sediment
172 samples. All the source material and sediment samples were oven-dried at 50°C, gently disaggregated
173 using a pestle and mortar, and sieved to 63 μm prior to laboratory analyses. In a previous analysis of the
174 same set of sources and suspended sediment samples, the pseudo-total contents of 28 elements
175 (including total-P) were estimated by ICP-OES after microwave assisted digestion with HCl and HNO₃
176 (aqua-regia digestion). Further information on these analyzes can be found in **Tiecher et al. (2015)**. Grain
177 size distribution was analyzed with a laser granulometer for all suspended sediment and source samples
178 after oxidation of organic matter with H₂O₂ and chemical dispersion with NaOH.

179

180 *2.2. Phosphorus fractions analysis*

181 The P-fractions evaluated in the current study were obtained following two methods: (i) the
182 sequential extraction of different chemical reactivities to address the lability of P (**Hedley et al., 1982**),
183 and (ii) the separation of the organic and inorganic forms of P (**Olsen and Sommers, 1982**). The Hedley
184 fractionation was performed by the sequential extractions with: (i) anion exchange resin membrane
185 (P_{resin}); (ii) $0.5 \text{ mol L}^{-1} \text{ NaHCO}_3$ at pH 8.5 (P_{bic}); (iii) $0.1 \text{ mol L}^{-1} \text{ NaOH}$ ($P_{\text{NaOH}0.1}$); (iv) $1.0 \text{ mol L}^{-1} \text{ HCl}$ (P_{HCl}); (v)
186 $0.5 \text{ mol L}^{-1} \text{ NaOH}$ ($P_{\text{NaOH}0.5}$). After each extraction, the soil suspensions were centrifuged at $2,510 \times g$ for
187 15 min to collect supernatants. Then, the remaining sediment was dried at $\sim 50^\circ\text{C}$, ground and submitted
188 to digestion with H_2SO_4 and H_2O_2 in the presence of saturated MgCl_2 . Then, the residual Hedley-P-
189 fraction was determined (P_{residual}). In the acid extracts, P was directly determined according to the
190 **Murphy and Riley (1962)** method. For the NaHCO_3 and NaOH extractors, the extracts were first digested
191 with H_2SO_4 and ammonium persulphate in an autoclave at 121°C (**USEPA, 1971**), and then the P content
192 was determined by the **Murphy and Riley (1962)** method.

193 When separating the organic and inorganic forms of P, the total organic P (P_{org}) was estimated
194 by the ignition method proposed by **Olsen and Sommers (1982)**, as the difference between the amount
195 of P extracted with $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ from ignited (550°C , 2h) and non-ignited soil. Total P was estimated
196 by digestion with H_2SO_4 and H_2O_2 in the presence of saturated MgCl_2 , as proposed by **Olsen and**
197 **Sommers (1982)**. Then, total inorganic P (P_{inorg}) was estimated by the difference between total P and
198 total organic P.

199

200 2.3. Tracer selection

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

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

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

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

223

224 2.5. Sediment source apportionment

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

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

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

232 sum of all P_s estimations equalling 1. The GRG Non-Linear solving method was used with automatic
233 scaling in Solver, ignoring integer constraints, with a maximum run time of 5000 and allowing for 2500
234 iterations. A multi-start population size of 2500 was used along with the same random seed for each of
235 the model runs while requiring bounds on the variables. A constraint precision and convergence of
236 0.000001 were selected.

237

238 **3. Results and discussion**

239 *3.1. Total P content*

240 Phosphorus content estimated by aqua-regia digestion (HNO_3+HCl), which is the most widely
241 used digestion procedure in sediment fingerprinting studies using P as potential tracers, was on average
242 $48\pm 8\%$ of that estimated by the sulfuric acid digestion (**Fig. 3**). This comparison demonstrated that the
243 aqua-regia method is less effective in assessing the P content in soil and sediments, and that $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$
244 was more effective to evaluate the total P content (**Malá and Lagová, 2014**). The low capacity of the
245 aqua-regia digestion method to extract P from soil and sediment may be the cause of this tracer removal
246 in several previous sediment fingerprinting studies, indicating that this technique likely targets those P
247 fractions that are more loosely bound to the soil particles, which may be less conservative during erosion
248 and transportation processes.

249

250 *3.2. Phosphorus fractions*

251 All of the P-fractions evaluated in the current research passed the KW-H-test ($p<0.01$), except
252 the P_{residual} , which means that these fractions can be considered as potential tracers of sediment sources
253 in this catchment (**Fig. 4**). The results of the DFA using the individual P fractions showed that they were
254 able to correctly classify 48 ($P_{\text{NaOH}0.5}$) to 75% (P_{bic}) of the sediment source samples (**Fig. 4**). Concentrations
255 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
256 sampled in other sources (cropland>stream channels=unpaved roads, **Table 1, Supplementary**
257 **material**). Those higher values found in cropland are likely due to the frequent fertilization of agricultural

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

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

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

285 sources and suspended sediment were very similar, as can be seen in **Fig. 5**. In addition, although almost
286 all fractions of P showed a significant relationship with the specific surface area (estimated by the
287 particle size distribution), the correlation coefficient was very low (mean $R^2 = 0.18$, ranging from 0.04-
288 0.37) (**Table 2**). The same trend was observed for the relationship of P forms with the total organic
289 carbon content of the samples (mean $R^2 = 0.21$, ranging from 0.05-0.34). These results shows that for
290 the present study, the fractions of P were little influenced by the granulometry and organic carbon
291 content.

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

306

307 3.3. Discriminant analysis

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

312 The P-fractions that passed the KW *H*-test and were considered conservative (P_{resin} , P_{bic} , $P_{\text{NaOH}0.1}$,
313 P_{org}) were entered into a DFA, which selected only two of them (P_{resin} , P_{org}) (**Table 3**). The final value of
314 the Wilk's lambda parameter using P-fractions only was 0.2154 (**Table 3**). As this value is the proportion
315 of the total variance due to the error in the source discrimination, the two selected P-fractions were
316 associated with an error of 21.5%, *i.e.*, the combination of these two P-fractions explained
317 approximately 78.5% of the differences observed between the sources. The discrimination power of the
318 P-fractions was lower than that obtained with the geochemical approach, which explained 98.7% of the
319 difference between the sources (**Table 3 – data from Tiecher et al. 2015**). Moreover, the approach based
320 on the P-forms was able to correctly classify 87.5% of the samples, with an average uncertainty of 21.5%,
321 significantly separated by an average squared Mahalanobis distance of 7.3 (**Table 3**). The uncertainty of
322 classification was much higher and the squared Mahalanobis distance was much lower than those
323 obtained for the geochemical approach (average of 2.08E-03% and 48.1, respectively – **Tiecher et al.**
324 **2015**). The better discrimination of sediment sources obtained in the geochemical approach compared
325 to P-fractions can be well visualized comparing the **Fig. 7a** and **Fig. 7b**, which are two-dimensional
326 scatterplots of the first and second discriminant functions obtained when running stepwise DFA for
327 geochemical and P-fractions, respectively.

328 When the P-fractions were combined with geochemical tracers in the DFA, six variables were
329 selected, including the same two P-fractions as those selected in the previous approach (P_{resin} , P_{org}) and
330 four geochemical tracers (Mo, Fe, Ag, As) (**Table 3**). The final value of the Wilk's lambda parameter was
331 slightly reduced to 0.0122 when associating these parameters (**Table 3**) (*i.e.*, together, these six tracers
332 explained approximately 98.8% of the differences observed between the sources). This original
333 combination of parameters resulted in the correct classification of 100% of the samples in their
334 respective groups. More importantly, the discrimination power was higher than when using the
335 geochemical tracers alone. The Mahalanobis distance increased to an average of 52.2 (**Table 3**), which
336 was 9% higher than that observed when following the geochemical approach. The better discrimination
337 of sediment sources obtained when combining the geochemical elements and P-fractions can be well
338 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 $48\pm 16\%$ 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 $26\pm 16\%$ 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 $20\pm 15\%$
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 $25\pm 13\%$ 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

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

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

388

389 4. Conclusions

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

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

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

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

416

417

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

468 based on a quantitative composite fingerprinting technique. *CATENA* 29, 1–27. doi:10.1016/S0341-
469 8162(96)00064-1

470 Collins, A.L., Walling, D.E., Leeks, G.J.L., 1997b. Sediment sources in the Upper Severn catchment: a
471 fingerprinting approach. *Hydrol. Earth Syst. Sci.* 1, 509–521. doi:10.5194/hess-1-509-1997

472 Collins, A.L., Walling, D.E., Sickingabula, H.M., Leeks, G.J.L., 2001. Suspended sediment source
473 fingerprinting in a small tropical catchment and some management implications. *Appl. Geogr.* 21,
474 387–412. doi:10.1016/S0143-6228(01)00013-3

475 Collins, A.L., Zhang, Y., Walling, D.E., Grenfell, S.E., Smith, P., 2010. Tracing sediment loss from eroding
476 farm tracks using a geochemical fingerprinting procedure combining local and genetic algorithm
477 optimisation. *Sci. Total Environ.* 408, 5461–5471. doi:10.1016/j.scitotenv.2010.07.066

478 Cooper, R.J., Krueger, T., Hiscock, K.M., Rawlins, B.G., 2015. High-temporal resolution fluvial sediment
479 source fingerprinting with uncertainty: a Bayesian approach. *Earth Surf. Process. Landforms* 40,
480 78–92. doi:10.1002/esp.3621

481 Cross, A.F., Schlesinger, W.H., 1995. A literature review and evaluation of the Hedley fractionation:
482 Applications to the biogeochemical cycle of soil phosphorus in natural ecosystems. *Geoderma* 64,
483 197–214. doi:10.1016/0016-7061(94)00023-4

484 D'Haen, K., Verstraeten, G., Duser, B., Degryse, P., Haex, J., Waelkens, M., 2013. Unravelling changing
485 sediment sources in a Mediterranean mountain catchment: A Bayesian fingerprinting approach.
486 *Hydrol. Process.* 27, 896–910. doi:10.1002/hyp.9399

487 Dabrin, A., Schäfer, J., Bertrand, O., Masson, M., Blanc, G., 2014. Origin of suspended matter and
488 sediment inferred from the residual metal fraction: Application to the Marennes Oleron Bay,
489 France. *Cont. Shelf Res.* 72, 119–130. doi:10.1016/j.csr.2013.07.008

490 Deiss, L., de Moraes, A., Dieckow, J., Franzluebbbers, A.J., Gatiboni, L.C., Sasaki, G. Ianzi, Carvalho, P.C.F.,
491 2016. Soil phosphorus compounds in integrated crop-livestock systems of subtropical Brazil.
492 *Geoderma* 274, 88–96. doi:10.1016/j.geoderma.2016.03.028

493 Devereux, O.H., Prestegard, K.L., Needelman, B.A., Gellis, A.C., 2010. Suspended-sediment sources in
494 an urban watershed, Northeast Branch Anacostia River, Maryland. *Hydrol. Process.* 24, 1391–1403.
495 doi:10.1002/hyp.7604

496 Didoné, E.J., Minella, J.P.G., Evrard, O., 2017. Measuring and modelling soil erosion and sediment yields
497 in a large cultivated catchment under no-till of Southern Brazil. *Soil Tillage Res.* 174, 24–33.
498 doi:10.1016/j.still.2017.05.011

499 Dutton, C., Anisfeld, S.C., Ernstberger, H., 2013. A novel sediment fingerprinting method using filtration:
500 Application to the Mara River, East Africa. *J. Soils Sediments* 13, 1708–1723. doi:10.1007/s11368-
501 013-0725-z

502 Gellis, A.C., Noe, G.B., 2013. Sediment source analysis in the Linganore Creek watershed, Maryland, USA,
503 using the sediment fingerprinting approach: 2008 to 2010. *J. Soils Sediments* 13, 1735–1753.
504 doi:10.1007/s11368-013-0771-6

505 Gholami, H., Middleton, N., Nazari Samani, A.A., Wasson, R., 2017. Determining contribution of sand
506 dune potential sources using radionuclides, trace and major elements in central Iran. *Arab. J.*
507 *Geosci.* 10, 163. doi:10.1007/s12517-017-2917-0

508 Gardini, R., Comin, J.J., Schmitt, D.E., Tiecher, T., Bender, M.A., dos Santos, D.R., Mezzari, C.P., Oliveira,
509 B.S., Gatiboni, L.C., Brunetto, G., 2012. Accumulation of phosphorus fractions in typic Hapludalf
510 soil after long-term application of pig slurry and deep pig litter in a no-tillage system. *Nutr. Cycl.*
511 *Agroecosystems* 93. doi:10.1007/s10705-012-9511-3

512 Haddadchi, A., Nosrati, K., Ahmadi, F., 2014a. Differences between the source contribution of bed
513 material and suspended sediments in a mountainous agricultural catchment of western Iran.
514 *Catena* 116, 105–113. doi:10.1016/j.catena.2013.12.011

515 Haddadchi, A., Olley, J., Laceby, P., 2014b. Accuracy of mixing models in predicting sediment source
516 contributions. *Sci. Total Environ.* 497–498, 139–152. doi:10.1016/j.scitotenv.2014.07.105

517 Haddadchi, A., Ryder, D.S., Evrard, O., Olley, J., 2013. Sediment fingerprinting in fluvial systems: review
518 of tracers, sediment sources and mixing models. *Int. J. Sediment Res.* 28, 560–578.
519 doi:10.1016/S1001-6279(14)60013-5

520 Hedley, M.J., Stewart, J.W.B., Chauhan, B.S., 1982. Changes in inorganic and organic soil phosphorus
521 fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46,

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

523 Hughes, A.O., Olley, J.M., Croke, J.C., McKergow, L.A., 2009. Sediment source changes over the last
524 250 years in a dry-tropical catchment, central Queensland, Australia. *Geomorphology* 104, 262–
525 275. doi:10.1016/j.geomorph.2008.09.003

526 Huisman, N.L.H., Karthikeyan, K.G., Lamba, J., Thompson, A.M., Peaslee, G., 2013. Quantification of
527 seasonal sediment and phosphorus transport dynamics in an agricultural watershed using
528 radiometric fingerprinting techniques. *J. Soils Sediments* 13, 1724–1734. doi:10.1007/s11368-013-
529 0769-0

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

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

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

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

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

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

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

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

554 Laceby, J.P., Olley, J., 2015. An examination of geochemical modelling approaches to tracing sediment
555 sources incorporating distribution mixing and elemental correlations. *Hydrol. Process.* 29, 1669–
556 1685. doi:10.1002/hyp.10287

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

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

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

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

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

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

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

576 assessment in suspended sediment fingerprinting based on tracer mixing models : a case study
577 from Luxembourg. *Sediment Dyn. Chang. Environ. IAHS Publ.* 325 325, 94–105.

578 Martínez-Carreras, N., Krein, A., Udelhoven, T., Gallart, F., Iffly, J.F., Hoffmann, L., Pfister, L., Walling,
579 D.E., 2010a. A rapid spectral-reflectance-based fingerprinting approach for documenting
580 suspended sediment sources during storm runoff events. *J. Soils Sediments* 10, 400–413.
581 doi:10.1007/s11368-009-0162-1

582 Martínez-Carreras, N., Udelhoven, T., Krein, A., Gallart, F., Iffly, J.F., Ziebel, J., Hoffmann, L., Pfister, L.,
583 Walling, D.E., 2010b. The use of sediment colour measured by diffuse reflectance spectrometry to
584 determine sediment sources: Application to the Attert River catchment (Luxembourg). *J. Hydrol.*
585 382, 49–63. doi:10.1016/j.jhydrol.2009.12.017

586 Massoudieh, A., Gellis, A., Banks, W.S., Wieczorek, M.E., 2013. Suspended sediment source
587 apportionment in Chesapeake Bay watershed using Bayesian chemical mass balance receptor
588 modeling. *Hydrol. Process.* 27, 3363–3374. doi:10.1002/hyp.9429

589 Miguel, P., Dalmolin, R.S.D., Pedron, F. de A., Moura-Bueno, J.M., Tiecher, T., 2014. Identificação de
590 fontes de produção de sedimentos em uma bacia hidrográfica de encosta. *Rev. Bras. Ciência do*
591 *Solo* 38, 585–598. doi:10.1590/S0100-06832014000200023

592 Miller, J.R., Mackin, G., Lechler, P., Lord, M., Lorentz, S., 2013. Influence of basin connectivity on
593 sediment source, transport, and storage within the Mkabela Basin, South Africa. *Hydrol. Earth Syst.*
594 *Sci.* 17, 761–781. doi:10.5194/hess-17-761-2013

595 Minella, J.P.G., Merten, G.H., Reichert, J.M., Santos, D.R. dos, 2007. Identificação e implicações para a
596 conservação do solo das fontes de sedimentos em bacias hidrográficas. *Rev. Bras. Ciência do Solo*
597 31, 1637–1646. doi:10.1590/S0100-06832007000600039

598 Minella, J.P.G., Walling, D.E., Merten, G.H., 2008. Combining sediment source tracing techniques with
599 traditional monitoring to assess the impact of improved land management on catchment sediment
600 yields. *J. Hydrol.* 348, 546–563. doi:10.1016/j.jhydrol.2007.10.026

601 Motha, J.A., Wallbrink, P.J., Hairsine, P.B., Grayson, R.B., 2004. Unsealed roads as suspended sediment
602 sources in an agricultural catchment in south-eastern Australia. *J. Hydrol.* 286, 1–18.
603 doi:10.1016/j.jhydrol.2003.07.006

604 Motha, J.A., Wallbrink, P.J., Hairsine, P.B., Grayson, R.B., 2003. Determining the sources of suspended
605 sediment in a forested catchment in southeastern Australia. *Water Resour. Res.* 39, n/a-n/a.
606 doi:10.1029/2001WR000794

607 Mukundan, R., Radcliffe, D.E., Ritchie, J.C., Risse, L.M., McKinley, R.A., 2010. Sediment Fingerprinting to
608 Determine the Source of Suspended Sediment in a Southern Piedmont Stream. *J. Environ. Qual.*
609 39, 1328. doi:10.2134/jeq2009.0405

610 Murphy, J., Riley, J.P., 1962. A modified single solution method for the determination of phosphate in
611 natural waters. *Anal. Chim. Acta* 27, 31–36. doi:10.1016/S0003-2670(00)88444-5

612 Nosrati, K., Govers, G., Ahmadil, H., Sharifi, F., Amoozegar, M.A., Merckx, R., Vanmaercke, M., 2011. An
613 exploratory study on the use of enzyme activities as sediment tracers: biochemical fingerprints?
614 *Int. J. Sediment Res.* 26, 136–151. doi:10.1016/S1001-6279(11)60082-6

615 Nosrati, K., Govers, G., Semmens, B.X., Ward, E.J., 2014. A mixing model to incorporate uncertainty in
616 sediment fingerprinting. *Geoderma* 217–218, 173–180. doi:10.1016/j.geoderma.2013.12.002

617 Olsen, S.R., Sommers, L.E., 1982. Phosphorus Methods of Soil Analysis, in: Page, A.L., Miller, R.H.,
618 Keeney, Q.R. (Eds.), *Chemical and Microbiological Properties*. Soil Science Society of America,
619 Madison, pp. 403–430.

620 Ostrofsky, M.L., 2012. Determination of total phosphorus in lake sediments. *Hydrobiologia* 696, 199–
621 203. doi:10.1007/s10750-012-1208-8

622 Owens, P.N., Walling, D.E., Leeks, G.J.K. Use of floodplain sediment cores to investigate recent historical
623 changes in overbank sedimentation rates and sediment sources in the catchment of the River Ouse,
624 Yorkshire, UK. *Catena*, 36, 21–47. doi.org/10.1016/S0341-8162(99)00010-7

625 Owens, P.N., Walling, D.E., 2002. The phosphorus content of fluvial sediment in rural and industrialized
626 river basins. *Water Res.* 36, 685–701. doi:10.1016/S0043-1354(01)00247-0

627 Owens, P.N., Xu, Z., 2011. Recent advances and future directions in soils and sediments research. *J. Soils*
628 *Sediments* 11, 875–888. doi:10.1007/s11368-011-0406-8

629 Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2016. Combining catchment

630 modelling and sediment fingerprinting to assess sediment dynamics in a Spanish Pyrenean river
631 system. *Sci. Total Environ.* 569–570, 1136–1148. doi:10.1016/j.scitotenv.2016.06.189

632 Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2015. Comparing catchment
633 sediment fingerprinting procedures using an auto-evaluation approach with virtual sample
634 mixtures. *Sci. Total Environ.* 532, 456–466. doi:10.1016/j.scitotenv.2015.05.003

635 Palazón, L., Navas, A., 2017. Variability in source sediment contributions by applying different statistic
636 test for a Pyrenean catchment. *J. Environ. Manage.* 194, 42–53.
637 doi:10.1016/j.jenvman.2016.07.058

638 Pavinato, P.S., Merlin, A., Rosolem, C.A., 2009. Phosphorus fractions in Brazilian Cerrado soils as affected
639 by tillage. *Soil Tillage Res.* 105, 149–155. doi:10.1016/j.still.2009.07.001

640 Pulley, S., Foster, I., Antunes, P., 2015a. The uncertainties associated with sediment fingerprinting
641 suspended and recently deposited fluvial sediment in the Nene river basin. *Geomorphology* 228,
642 303–319. doi:10.1016/j.geomorph.2014.09.016

643 Pulley, S., Foster, I., Antunes, P., 2015b. The application of sediment fingerprinting to floodplain and lake
644 sediment cores: assumptions and uncertainties evaluated through case studies in the Nene Basin,
645 UK. *J. Soils Sediments* 15, 2132–2154. doi:10.1007/s11368-015-1136-0

646 Ramon, R., 2017. Kinetic energy measurement of rainfall and defining a pluvial index to estimate
647 erosivity in Arvorezinha/RS. Federal University of Santa Maria.

648 Rodrigues, M., Pavinato, P.S., Withers, P.J.A., Teles, A.P.B., Herrera, W.F.B., 2016. Legacy phosphorus
649 and no tillage agriculture in tropical oxisols of the Brazilian savanna. *Sci. Total Environ.* 542, 1050–
650 1061. doi:10.1016/j.scitotenv.2015.08.118

651 Rowan, J.S., Black, S., Franks, S.W., 2012. Sediment fingerprinting as an environmental forensics tool
652 explaining cyanobacteria blooms in lakes. *Appl. Geogr.* 32, 832–843.
653 doi:10.1016/j.apgeog.2011.07.004

654 Russell, M.A., Walling, D.E., Hodgkinson, R.A., 2001. Suspended sediment sources in two small lowland
655 agricultural catchments in the UK. *J. Hydrol.* 252, 1–24. doi:10.1016/S0022-1694(01)00388-2

656 Saavedra, C., Delgado, A., 2005. Iron-related phosphorus in eroded sediments from agricultural soils of
657 Mediterranean areas. *Geoderma* 125, 1–9. doi:10.1016/j.geoderma.2004.06.001

658 Schmitt, D.E., Brunetto, G., Santos, E. dos, Wagner, W. de L., Sete, P.B., Souza, M., Ambrosini, V.G.,
659 Santos, M.A. dos, Tiecher, T., Comin, J.J., Couto, R. da R., Gatiboni, L.C., Giachini, A., 2017.
660 Phosphorus fractions in apple orchards in southern Brazil. *Bragantia* 76, 422–432.
661 doi:10.1590/1678-4499.173

662 Sherriff, S.C., Franks, S.W., Rowan, J.S., Fenton, O., Ó'hUallacháin, D., 2015. Uncertainty-based
663 assessment of tracer selection, tracer non-conservativeness and multiple solutions in sediment
664 fingerprinting using synthetic and field data. *J. Soils Sediments* 15, 2101–2116.
665 doi:10.1007/s11368-015-1123-5

666 Smith, H.G., Blake, W.H., 2014. Sediment fingerprinting in agricultural catchments: A critical re-
667 examination of source discrimination and data corrections. *Geomorphology* 204, 177–191.
668 doi:10.1016/j.geomorph.2013.08.003

669 Teles, A.P.B., Rodrigues, M., Herrera, W.F.B., Soltangheisi, A., Sartor, L.R., Withers, P.J.A., Pavinato, P.S.,
670 2017. Do cover crops change the lability of phosphorus in a clayey subtropical soil under different
671 phosphate fertilizers ? *Soil Use Manag.* 1–11. doi:10.1111/sum.12327

672 Thompson, J., Cassidy, R., Doody, D.G., Flynn, R., 2013. Predicting critical source areas of sediment in
673 headwater catchments. *Agric. Ecosyst. Environ.* 179, 41–52. doi:10.1016/j.agee.2013.07.010

674 Tiecher, T., Caner, L., Minella, J.P.G., Bender, M.A., dos Santos, D.R., 2016. Tracing sediment sources in
675 a subtropical rural catchment of southern Brazil by using geochemical tracers and near-infrared
676 spectroscopy. *Soil Tillage Res.* 155, 478–491. doi:10.1016/j.still.2015.03.001

677 Tiecher, T., Caner, L., Minella, J.P.G., Pellegrini, A., Capoane, V., Rasche, J.W.A., Schaefer, G.L.,
678 Rheinheimer, D. dos S., 2017a. Tracing sediment sources in two paired agricultural catchments with
679 different riparian forest and wetland proportion in southern Brazil. *Geoderma* 285, 225–239.
680 doi:10.1016/j.geoderma.2016.10.008

681 Tiecher, T., Caner, L., Minella, J.P.G., Santos, D.R. dos, 2015. Combining visible-based-color parameters
682 and geochemical tracers to improve sediment source discrimination and apportionment. *Sci. Total*
683 *Environ.* 527–528, 135–149. doi:10.1016/j.scitotenv.2015.04.103

684 Tiecher, T., Gomes, M.V., Ambrosini, V.G., Amorim, M.B., Bayer, C., 2018. Assessing linkage between soil
685 phosphorus forms in contrasting tillage systems by path analysis. *Soil Tillage Res.* 175.
686 doi:10.1016/j.still.2017.09.015

687 Tiecher, T., Minella, J.P.G., Caner, L., Evrard, O., Zafar, M., Capoane, V., Le Gall, M., Santos, D.R. dos,
688 2017b. Quantifying land use contributions to suspended sediment in a large cultivated catchment
689 of Southern Brazil (Guaporé River, Rio Grande do Sul). *Agric. Ecosyst. Environ.* 237, 95–108.
690 doi:10.1016/j.agee.2016.12.004

691 Tiecher, T., Minella, J.P.G., Miguel, P., Alvarez, J.W.R., Pellegrini, A., Capoane, V., Ciotti, L.H., Schaefer,
692 G.L., dos Santos, D.R., 2014. Contribuição das fontes de sedimentos em uma bacia hidrográfica
693 agrícola sob plantio direto. *Rev. Bras. Cienc. do Solo* 38, 639–649. doi:10.1590/S0100-
694 06832014000200028

695 Tiecher, T., Schenato, R.B., Santanna, M.A., Caner, L., Santos, D.R. dos, 2017c. Phosphorus Forms in
696 Sediments as Indicators of Anthropic Pressures in an Agricultural Catchment in Southern Brazil.
697 *Rev. Bras. Ciência do Solo* 41, 1–17. doi:10.1590/18069657rbcs20160569

698 USEPA, 1971. *Methods of chemical analysis for water and wastes*. United States Environmental
699 Protection Agency, Cincinnati, US.

700 Walling, D.E., 2013. The evolution of sediment source fingerprinting investigations in fluvial systems. *J.*
701 *Soils Sediments* 13, 1658–1675. doi:10.1007/s11368-013-0767-2

702 Walling, D.E., Collins, A.L., Jones, P.A., Leeks, G.J.L., Old, G., 2006. Establishing fine-grained sediment
703 budgets for the Pang and Lambourn LOCAR catchments, UK. *J. Hydrol.* 330, 126–141.
704 doi:10.1016/j.jhydrol.2006.04.015

705 Walling, D.E., Collins, A.L., Stroud, R.W., 2008. Tracing suspended sediment and particulate phosphorus
706 sources in catchments. *J. Hydrol.* 350, 274–289. doi:10.1016/j.jhydrol.2007.10.047

707 Walling, D.E., Owens, P.N., Leeks, G.J.L., 1999. Fingerprinting suspended sediment sources in the
708 catchment of the River Ouse, Yorkshire, UK. *Hydrol. Process.* 13, 955–975. doi:10.1002/(SICI)1099-
709 1085(199905)13:7<955::AID-HYP784>3.0.CO;2-G

710 Wang, C., Zhang, Y., Li, H., Morrison, R.J., 2013. Sequential extraction procedures for the determination
711 of phosphorus forms in sediment 14, 147–157. doi:10.1007/s10201-012-0397-1

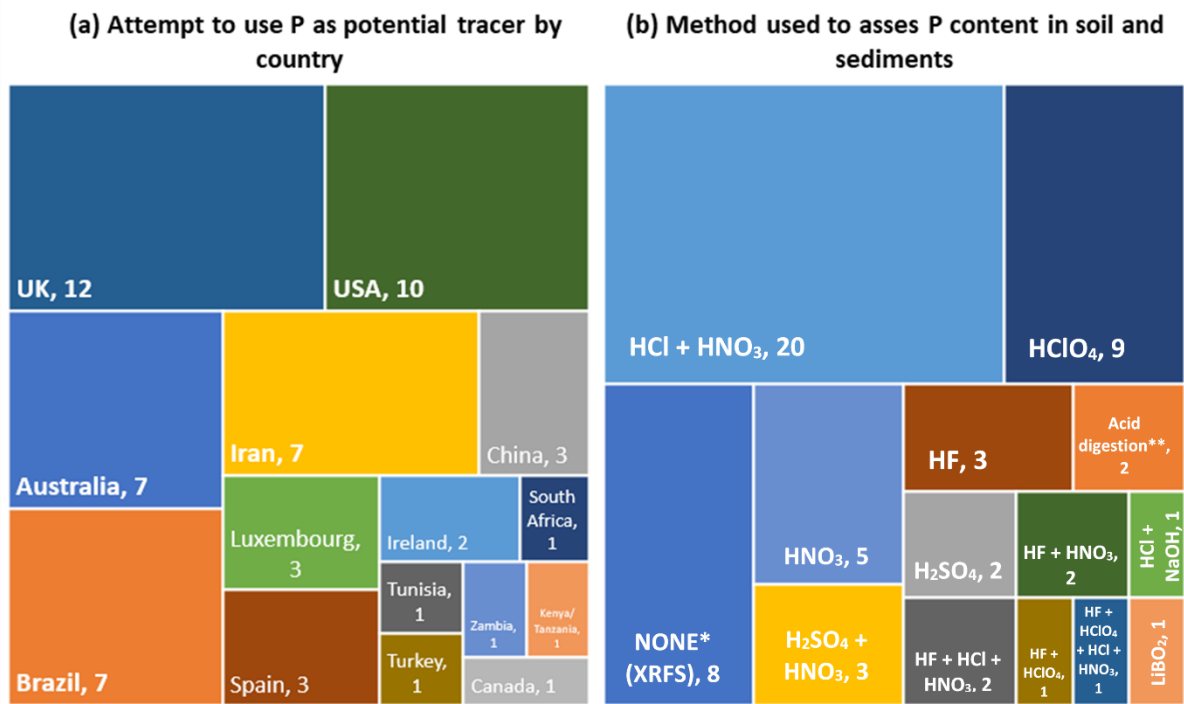
712 Wilkinson, S.N., Hancock, G.J., Bartley, R., Hawdon, A.A., Keen, R.J., 2013. Using sediment tracing to
713 assess processes and spatial patterns of erosion in grazed rangelands, Burdekin River basin,
714 Australia. *Agric. Ecosyst. Environ.* 180, 90–102. doi:10.1016/j.agee.2012.02.002

715 Yang, X., Post, W.M., 2011. Phosphorus transformations as a function of pedogenesis: A synthesis of soil
716 phosphorus data using Hedley fractionation method. *Biogeosciences* 8, 2907–2916.
717 doi:10.5194/bg-8-2907-2011

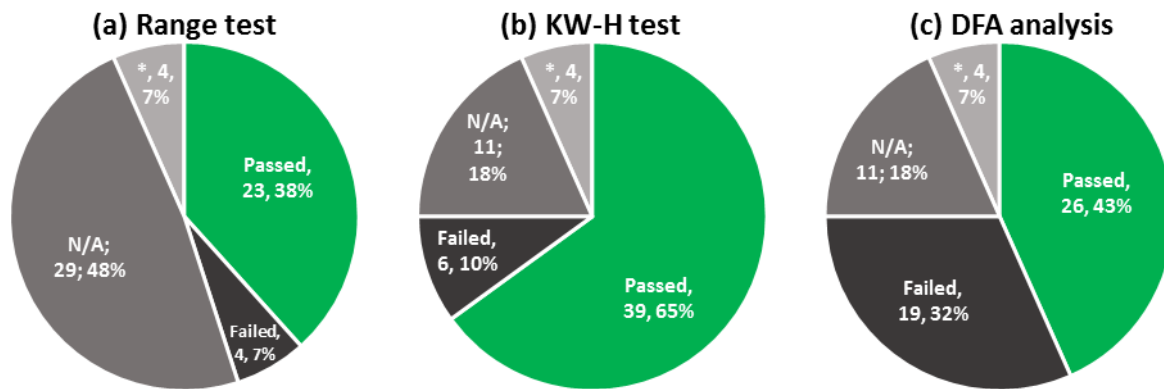
718 Zhang, X.C.J., Liu, B.L., 2016. Using multiple composite fingerprints to quantify fine sediment source
719 contributions: A new direction. *Geoderma* 268, 108–118. doi:10.1016/j.geoderma.2016.01.031

720 Zhang, Y.S., Collins, A.L., Horowitz, A.J., 2012. A preliminary assessment of the spatial sources of
721 contemporary suspended sediment in the Ohio River basin, United States, using water quality
722 data from the NASQAN 334, 326–334. doi:10.1002/hyp.8128

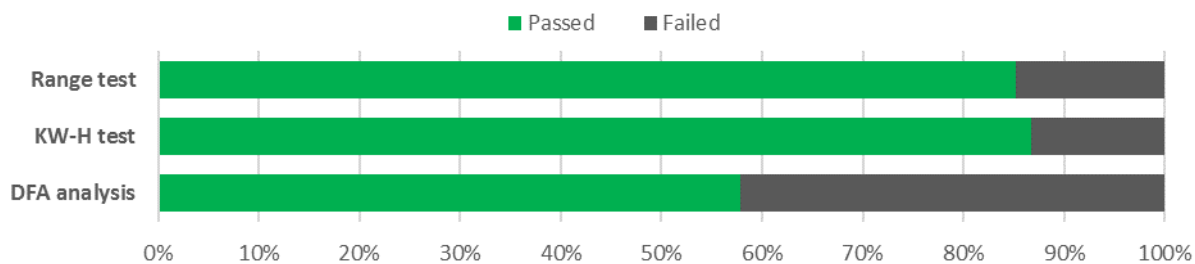
723



1
2 **Figure 1.** Distribution of the selection of 60 sediment fingerprinting studies found in the
3 literature and testing the use of P as a potential tracer depending on the country of the study
4 site (a) and the digestion method used to prepare soil and sediment material (b). *For X-ray
5 Fluorescence Spectroscopy (XRFS) no digestion is required. **No information about the acid
6 used for digestion.
7



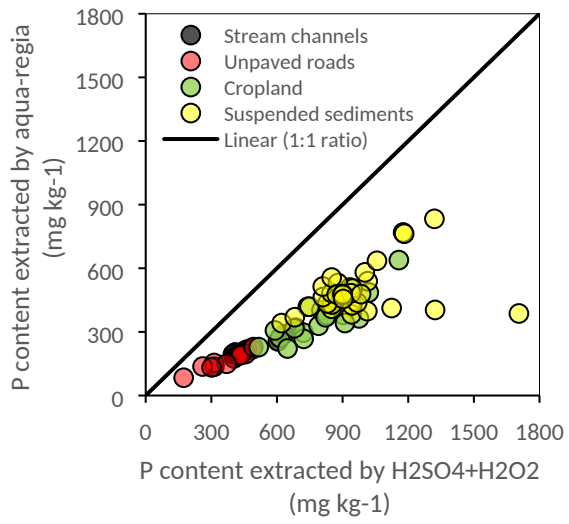
(d) Percentage of valid cases that have passed or failed the test



8

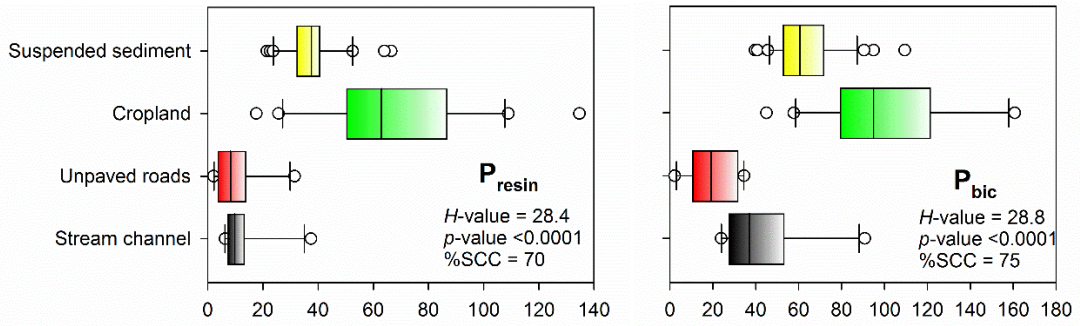
9

10 **Figure 2.** Summary of results obtained by the range test (a), Kruskal-Wallis H-test (KW-H, b),
 11 and discriminant function analysis (DFA, c) for the selection of 60 sediment fingerprinting
 12 studies that tested P as a potential tracer, and the percentage of studies that applied these tests
 13 in which P passed or failed the tests (d). This figure is based on results provided in Table 1. *P
 14 was excluded on the basis of the potential non-conservative behavior of P during downstream
 15 transport and it was not tested for KW-H, Range Test, and DFA. N/A = not available.
 16

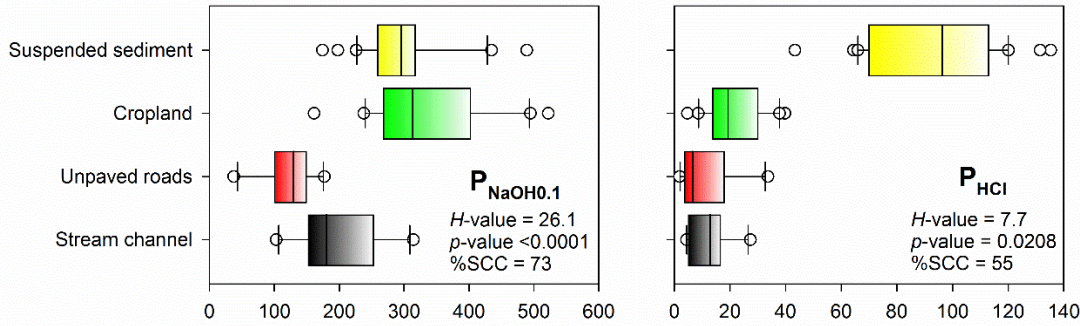


17
18 **Figure 3.** Comparison between P extracted by digestion methods using aqua-regia (HNO₃+HCl) and by
19 H₂SO₄+H₂O₂.
20

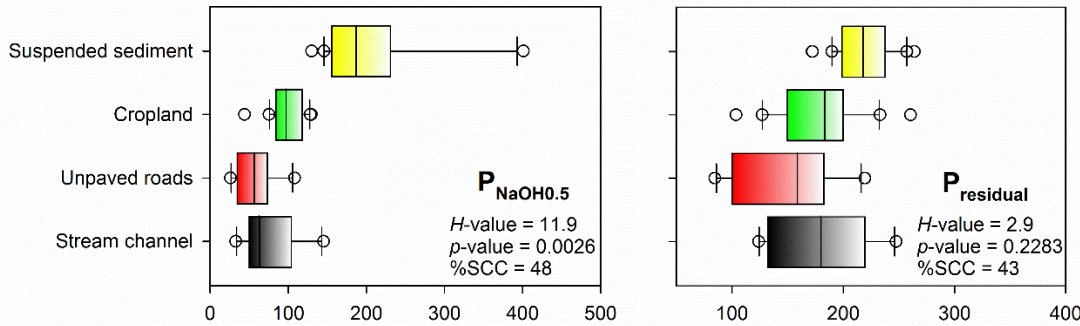
21



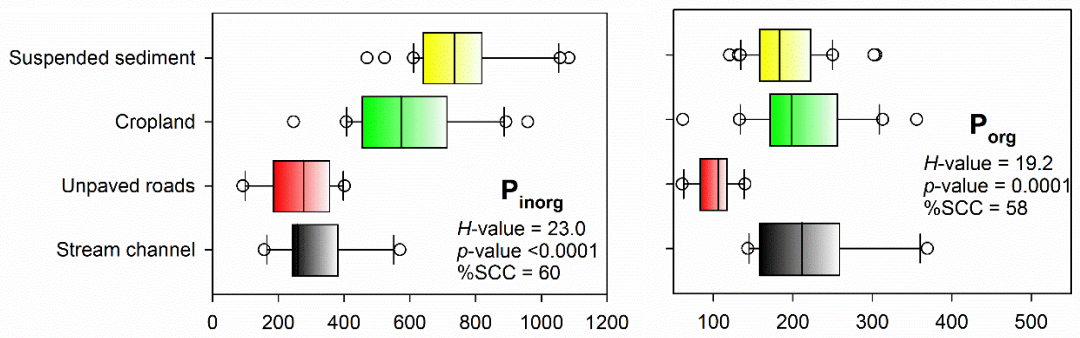
22



23

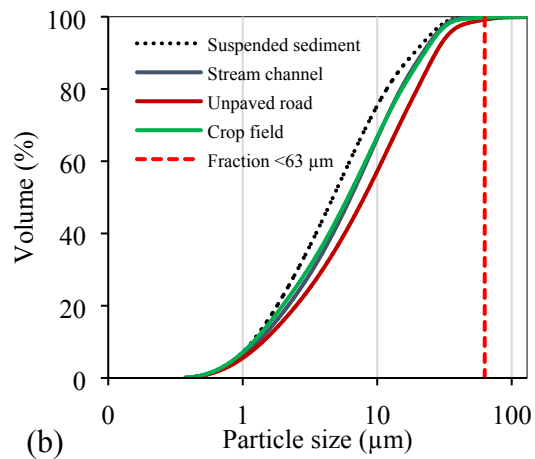
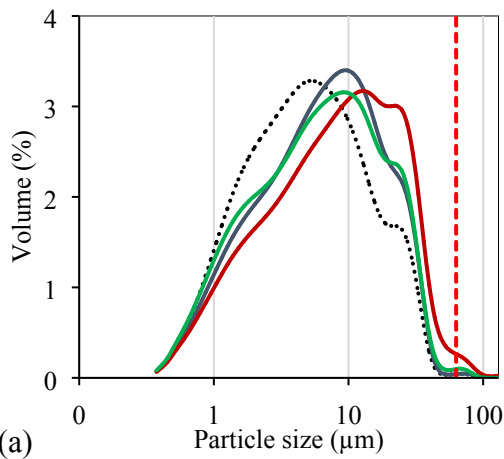


24



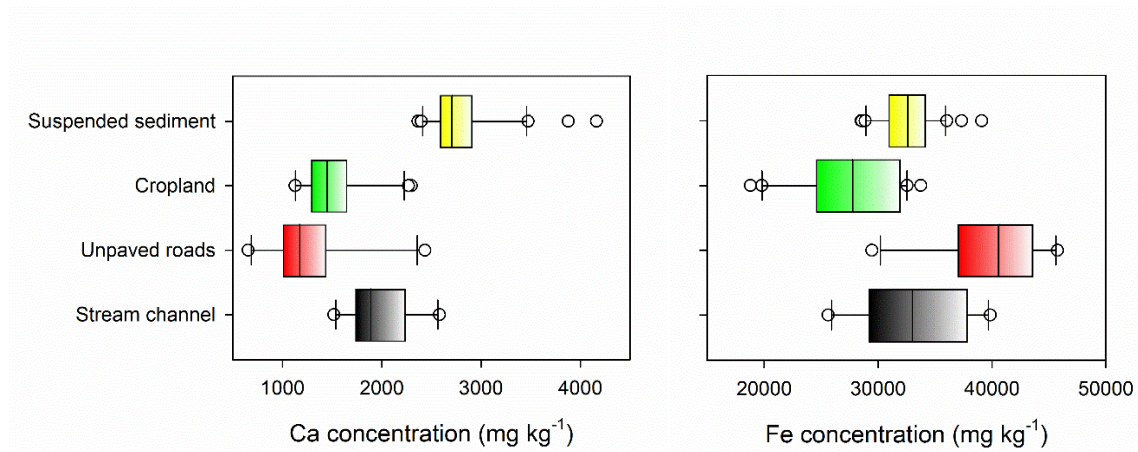
30

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 the range 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.



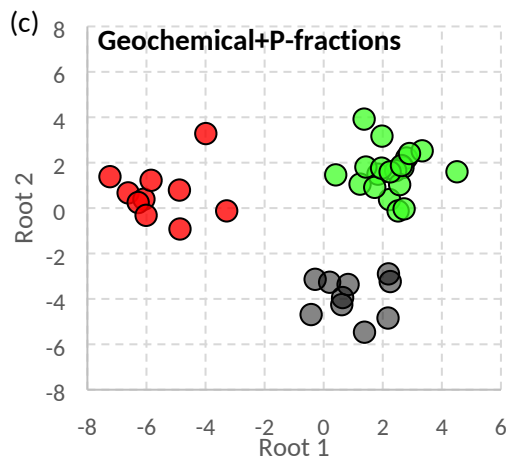
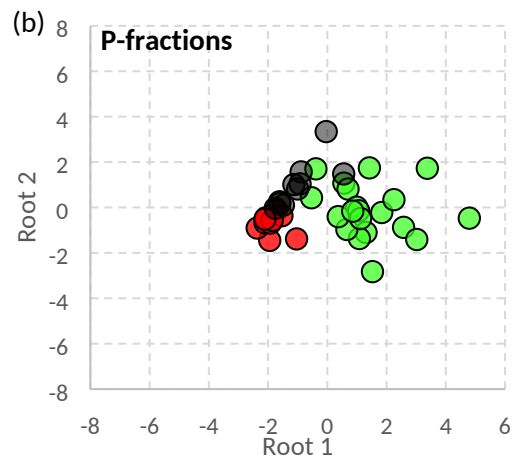
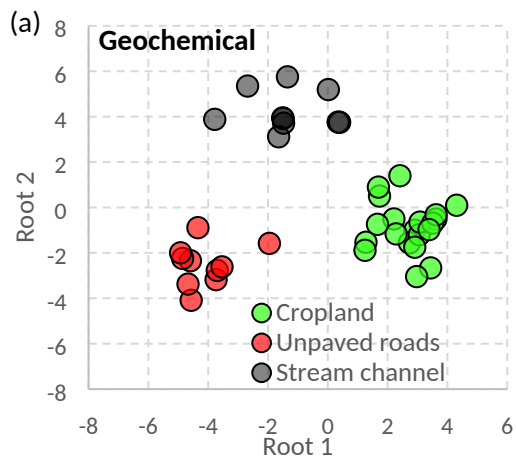
31
32
33
34
35

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 μm in Arvorezinha catchment.



36
37
38
39
40
41
42

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 $\pm 1SD$.



43

44

45

46

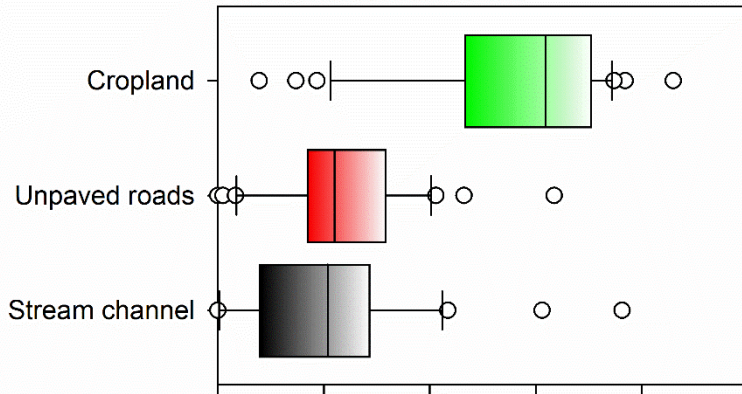
47

48

49

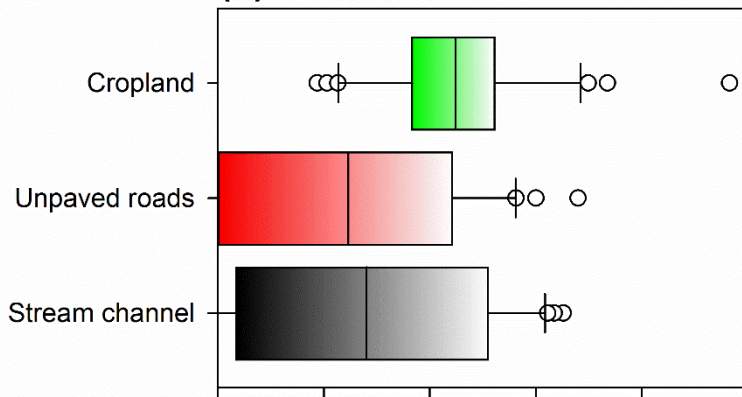
Figure 7. Two-dimensional scatterplots of the first and second discriminant functions provided by the stepwise discriminant function analysis (DFA) applied to selected sets of tracers using geochemical elements (a – data from Tiecher et al. 2015), P-forms (b), and the combination of geochemical elements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

(a) Geochemical



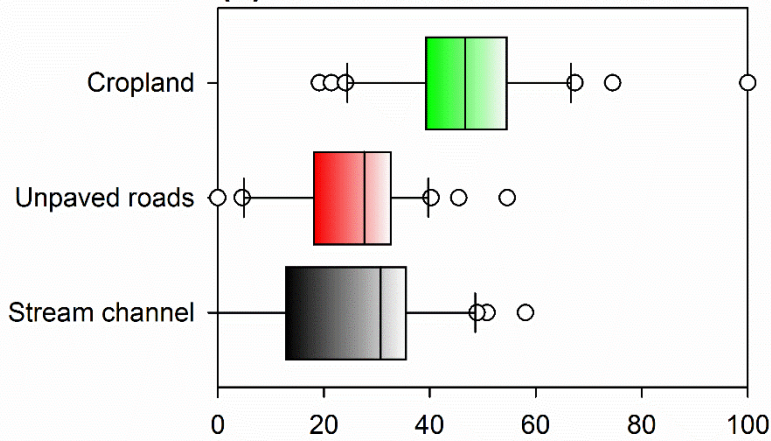
50

(b) P-fractions



51

(c) Geochemical + P-fractions



Sediment source contribution (%)

52
53 **Figure 8.** Box plot of the sediment source contributions to suspended sediment calculated using
54 different sets of tracing properties. The box indicates the first and the third quartiles; the line indicates
55 the median value; whiskers indicate the non-outlier range; circles indicate values outside of the range
56 of $\pm 1SD$.

57

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.

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

P-fractions	Specific surface area ($\text{m}^2 \text{g}^{-1}$)		Total organic carbon (g kg^{-1})	
	R^2	p -value	R^2	p -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
$P_{\text{NaOH}0.1}$	0.10	0.007	0.25	<0.001
P_{HCl}	0.22	<0.001	0.27	<0.001
$P_{\text{NaOH}0.5}$	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

16
 17
 18

19 **Table 3.** Results of the discriminant function analysis applied to different sets of tracing properties:
 20 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 _{bic}	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
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
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

