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

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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} , $P_{\text{NaOH0.1}}$,
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

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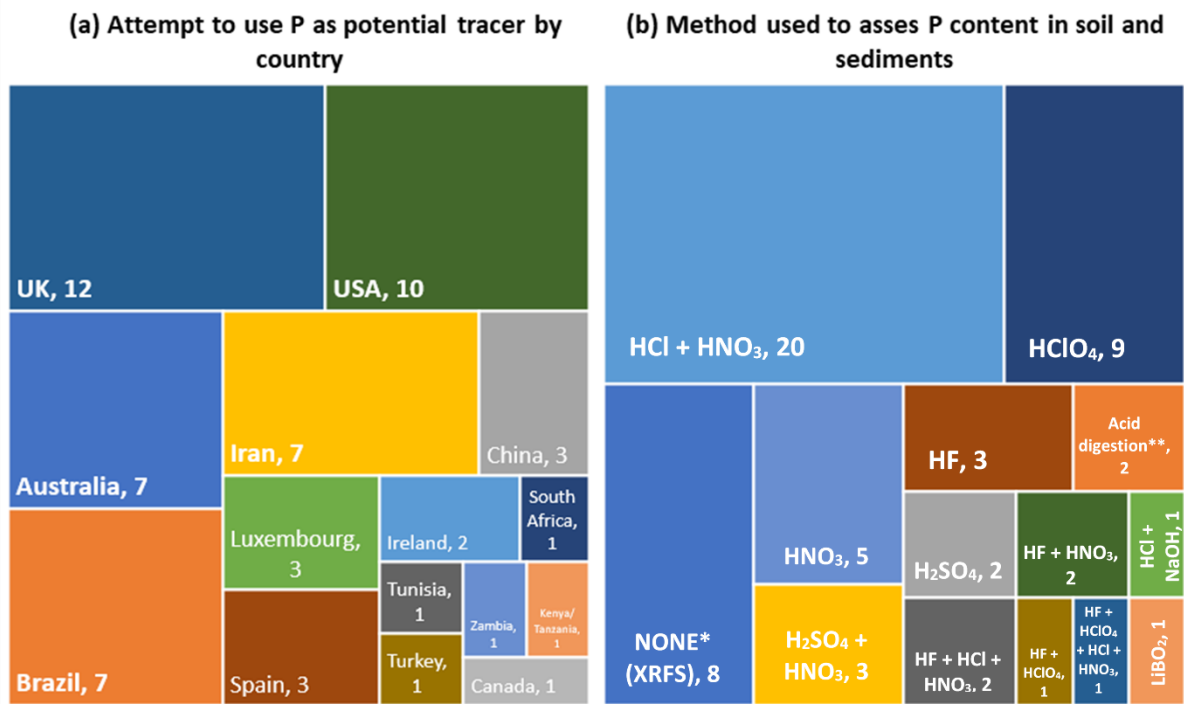
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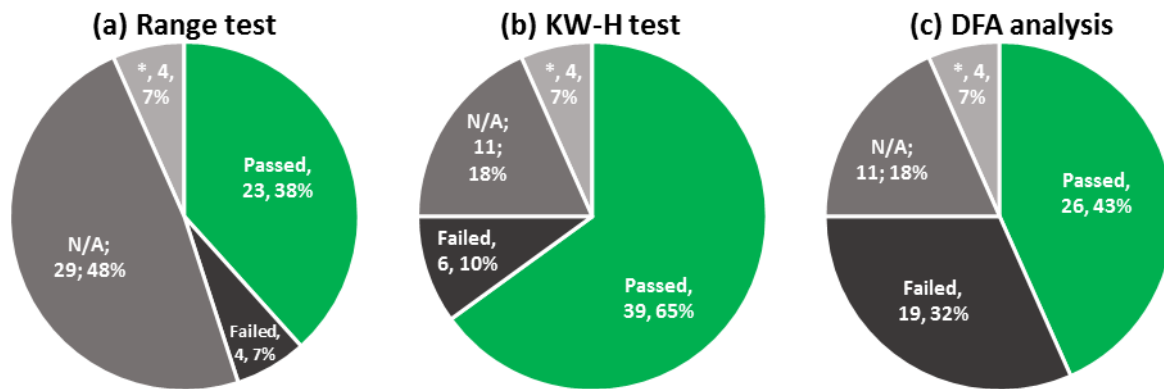
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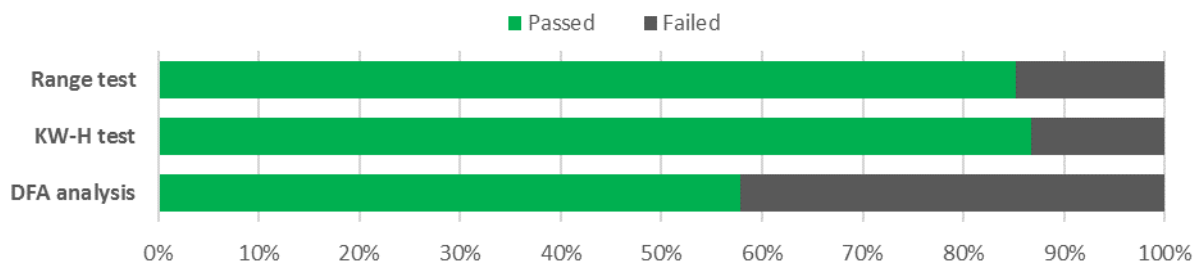
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2 **Figure 1.** Distribution of the selection of 60 sediment fingerprinting studies found in the
3 literature and testing the use of P as a potential tracer depending on the country of the study
4 site (a) and the digestion method used to prepare soil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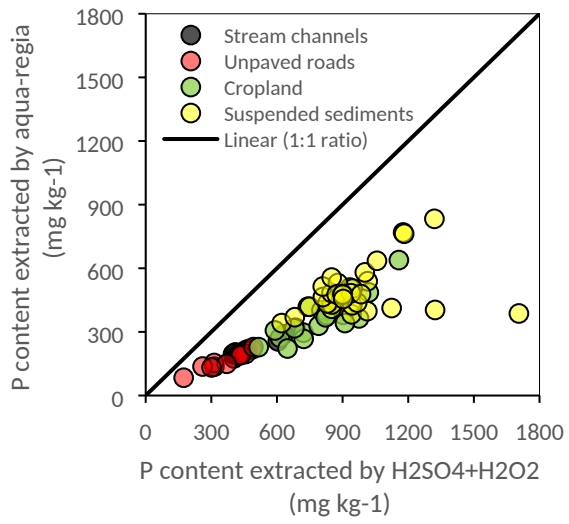
(d) Percentage of valid cases that have passed or failed the test



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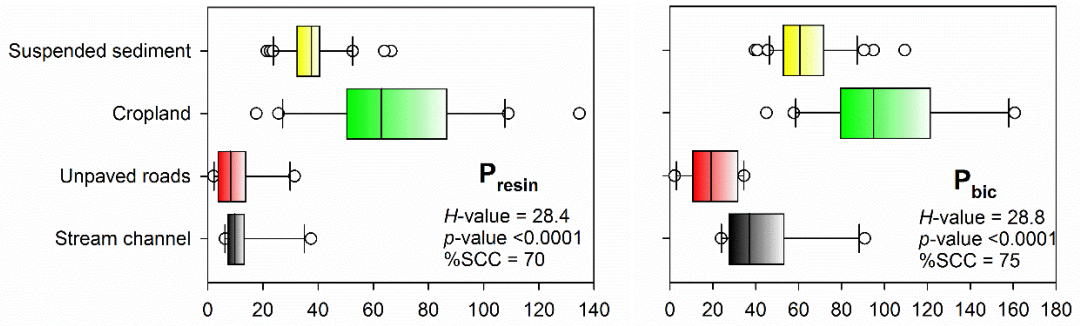
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10 **Figure 2.** Summary of results obtained by the range test (a), Kruskal-Wallis H-test (KW-H, b),
 11 and discriminant function analysis (DFA, c) for the selection of 60 sediment fingerprinting
 12 studies that tested P as a potential tracer, and 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.
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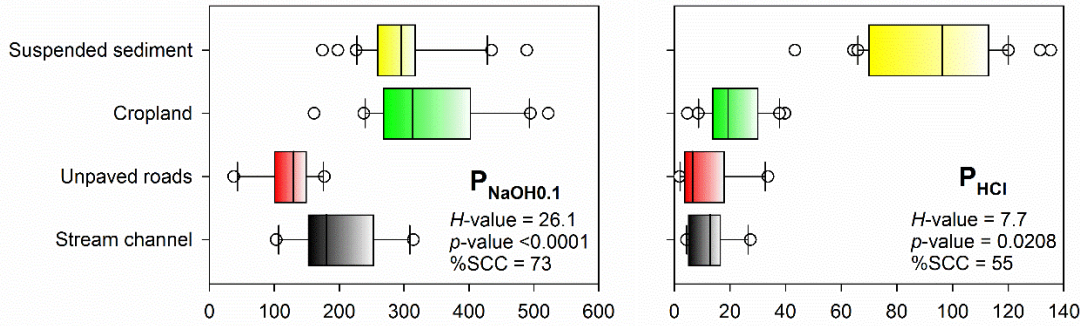


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 18 **Figure 3.** Comparison between P extracted by digestion methods using aqua-regia (HNO₃+HCl) and by
 19 H₂SO₄+H₂O₂.
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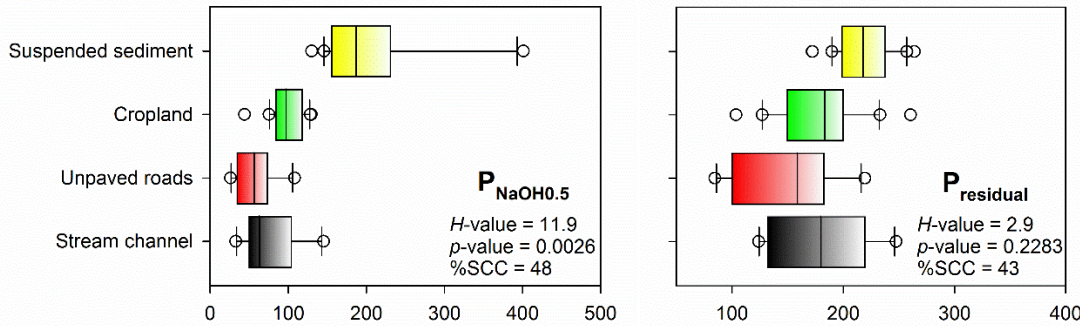
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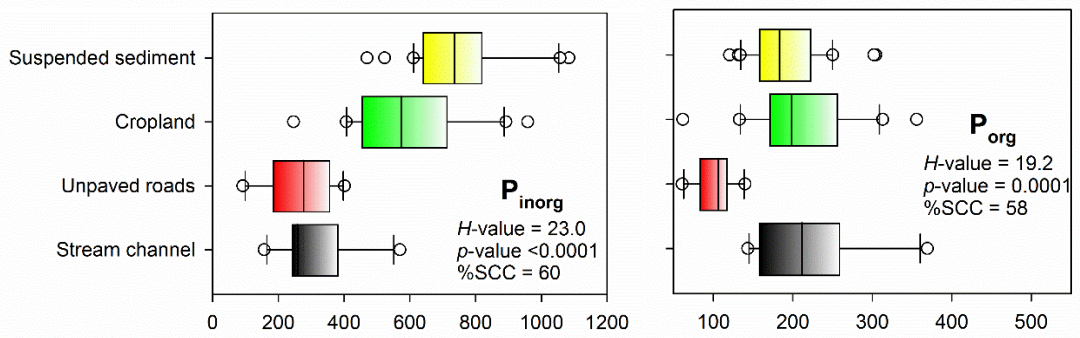
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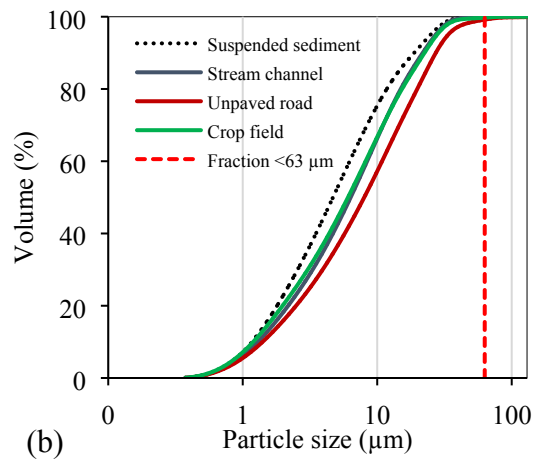
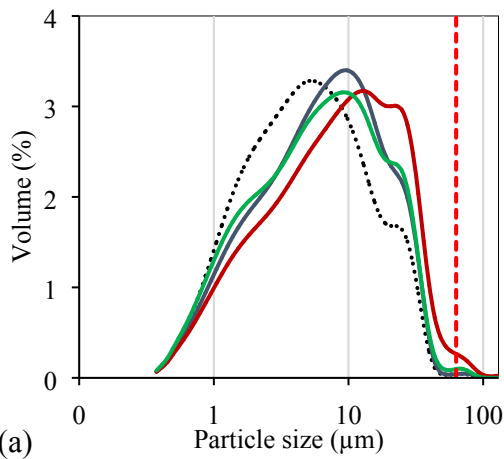


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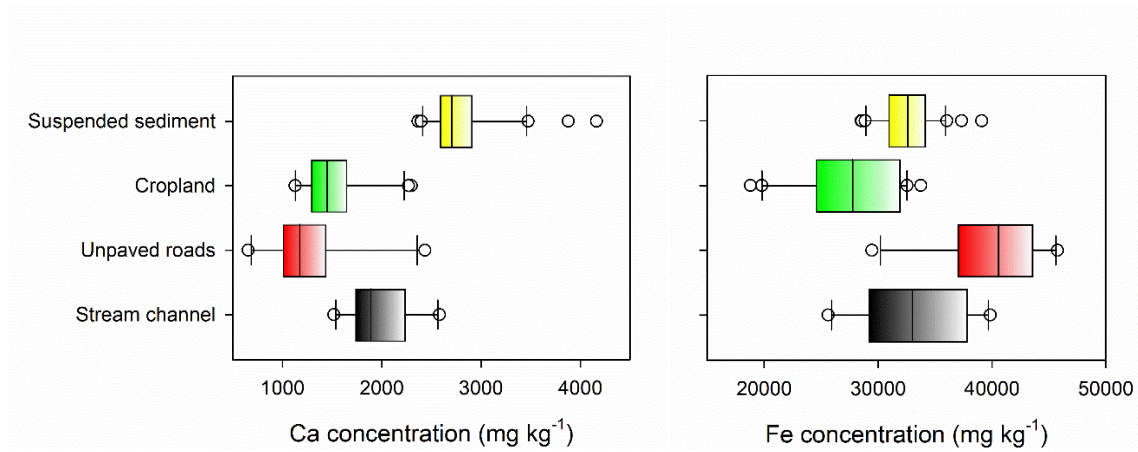
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Figure 4. Box-plots of concentration in P-fractions measured in the potential sources and in suspended sediment samples. The box indicates the location of the first and third quartiles; the line indicates the median value; whiskers indicate the non-outlier 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.



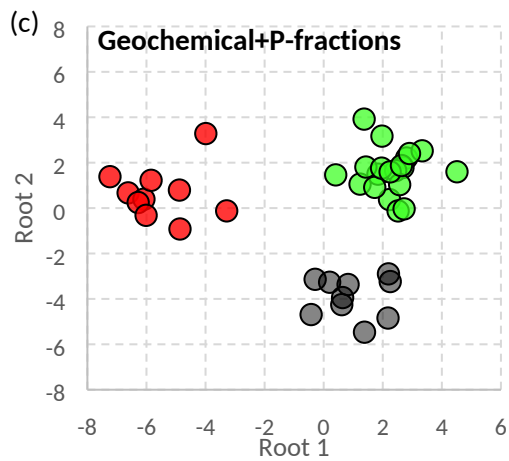
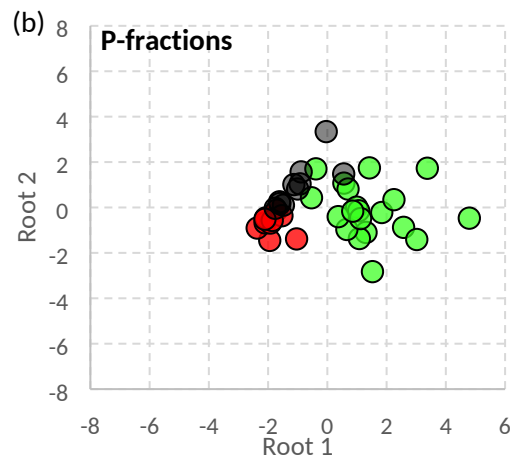
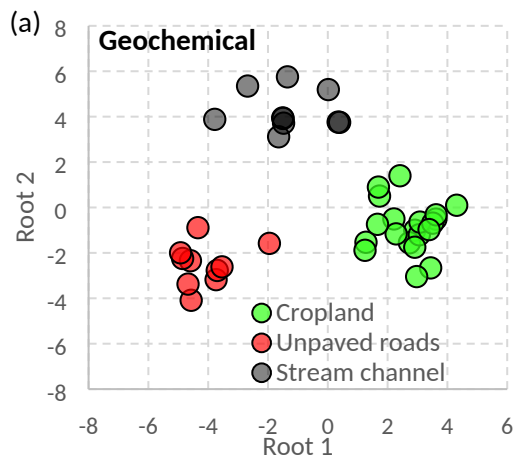
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Figure 5. Average particle size distribution (a) and accumulated particle size distribution (b) of suspended sediment samples ($n = 31$) and sediment sources (10 samples of unpaved roads, 10 samples of stream channel, and 20 samples of crop field)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



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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 $\pm 1SD$.



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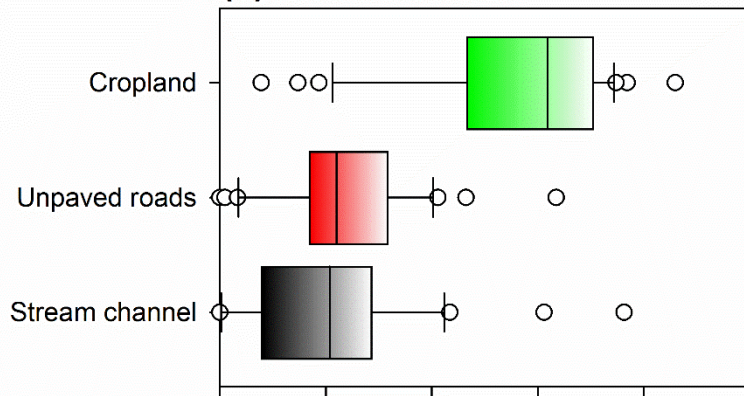
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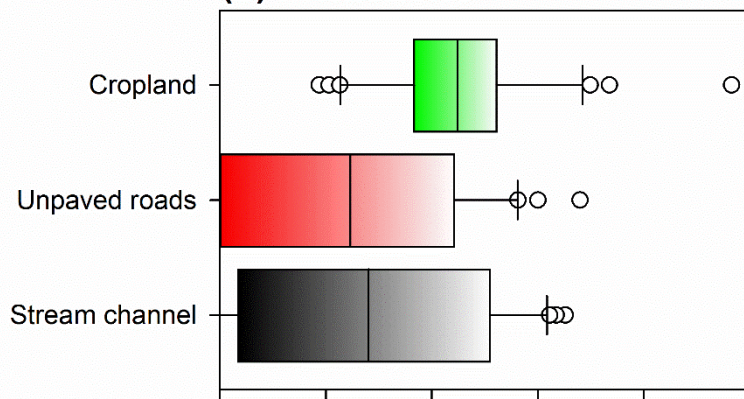
Figure 7. Two-dimensional scatterplots of the first and second discriminant functions provided by the stepwise discriminant function analysis (DFA) applied to selected sets of tracers using geochemical elements (a - data from Tiecher et al. 2015), P-forms (b), and the combination of geochemical elements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

(a) Geochemical



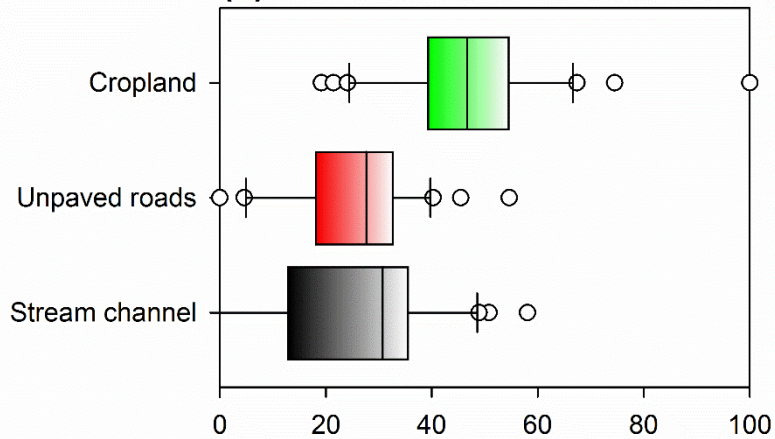
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(b) P-fractions



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(c) Geochemical + P-fractions



Sediment source contribution (%)

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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	UV/Vis	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

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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

