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1 TRACING SEDIMENT SOURCES USING MID-INFRARED SPECTROSCOPY IN  
2 ARVOREZINHA CATCHMENT, SOUTHERN BRAZIL

3  
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17  
18 ABSTRACT

19 The widespread adoption of the sediment fingerprinting approach to guide catchment management  
20 has been limited by the cost and the difficulty to prepare and process samples for geochemical and  
21 radionuclide analyses. Spectral properties have recently been shown to provide a rapid and cost-  
22 efficient alternative for this purpose. The current research objective was (i) to quantify the  
23 sediment source contributions in a 1.19-km<sup>2</sup> rural catchment of Southern Brazil by using mid-  
24 infrared (MIR) spectroscopy, and (ii) to compare these results with those obtained with  
25 geochemical approach and near-infrared (NIR) and ultraviolet-visible (UV-VIS) spectroscopy  
26 methods. The sediment sources to discriminate were cropland surface ( $n=20$ ), unpaved roads  
27 ( $n=10$ ) and stream channel banks ( $n=10$ ). Twenty-nine suspended sediment samples were  
28 collected at the catchment outlet during nine significant flood events. The sources could be  
29 distinguished by MIR spectroscopy. Cropland and channel bank sources mainly differed in their  
30 clay mineral contents, but their similar organic matter content complicated the MIR-model  
31 predictions. Unpaved road contributions were discriminated from the other sources by their lower  
32 organic carbon content. When the results of the current research based on MIR spectroscopy are  
33 compared to those obtained using other sediment fingerprinting approaches, based on  
34 geochemistry and NIR and UV-VIS spectroscopy, an overestimation of channel banks contribution  
35 and an underestimation of cropland and unpaved road contributions is found. These results suggest  
36 that MIR spectroscopy can provide a useful tool that is non-destructive, rapid and cheap for tracing  
37 sediment sources in rural catchments and for guiding the implementation of soil and water  
38 conservation measures.

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40 KEY WORDS: soil erosion, sediment fingerprinting, spectral properties, suspended sediment,  
41 rapid and cost-efficient tracers.

## INTRODUCTION

Intensification of agriculture for increasing food production has led to the degradation of soil and water resources during the last several decades (Comino *et al.*, 2015; Erkossa *et al.*, 2015; Seutloali and Beckedahl, 2015; Taguas *et al.*, 2015). Modern and intensive agricultural practices expose the soil to the erosion and accelerate the transfer of sediment to the lower parts of landscape (Minella *et al.*, 2014) and into water bodies, along with contaminants such as pesticides (Magnusson *et al.*, 2013; Yahia and Elsharkawy, 2014) and phosphorus (Poulenard *et al.*, 2008; Dodd *et al.*, 2014; Dodd and Sharpley, 2015). In agricultural catchments with high runoff coefficients and sediment yields, as in Southern Brazil, erosion process needs to be controlled to prevent an irreversible degradation of soil and water quality (Didoné *et al.*, 2015; Merten *et al.*, 2015). In order to mitigate these problems at the catchment scale, it is first required to have information on the respective contributions of the potential sources of sediment to the river.

Accordingly, the sediment fingerprinting approach quantifies the contribution of non-point sediment sources through the use of a range of natural tracers combined with rigorous statistical modeling techniques. This tool is very useful to assist local managers in developing strategies for remediating river siltation and pollution in catchments (Walling and Woodward, 1995; Davis and Fox, 2009; D'Haen *et al.*, 2012; Haddadchi *et al.*, 2013; Koiter *et al.*, 2013). However, the wider application of this technique by local managers is complicated by the difficulty accessing the conventional physicochemical analysis techniques, their cost, and the necessity to collect sufficient material in the rivers to conduct these (generally) destructive measurements (Cooper *et al.*, 2014).

Spectroscopic reflectance is a low-cost and non-destructive alternative methods that can be carried out very quickly on dried sieved samples to assess various physical, chemical and biological properties of soils (McBratney *et al.*, 2006; Viscarra Rossel *et al.*, 2006). In this sense, Poulenard *et al.* (2009) developed a first attempt to use Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) to fingerprint sediment sources in catchments. The method was successfully used to discriminate and predict the contributions of topsoil and channel sources (Poulenard *et al.*, 2009) and soils developed on different substrates to sediment (Poulenard *et al.*, 2012). In addition, both studies confirmed that these properties remained conservative during a time period consistent with the duration of the study (i.e., min. 1 month), and this is a prerequisite for a property to be used as a tracer.

In the last years, several studies using spectroscopic method have been developed worldwide to trace sediment sources. Visible (VIS) and near-infrared (NIR) reflectance was tested in the French Alps (Legout *et al.*, 2013), Luxemburg (Martínez-Carreras *et al.*, 2010a, 2010b, 2010c), Spain (Brosinsky *et al.*, 2014a, 2014b), Ethiopia (Verheyen *et al.*, 2014), the Eastern Cape

76 of South Africa (Pulley and Rowntree, 2015), United Kingdom (Collins *et al.*, 2014), and southern  
77 Brazil (Tiecher *et al.*, 2015, 2016). Besides, some of these studies showed a good agreement  
78 between the results obtained with the spectroscopic method and those provided by the  
79 conventional fingerprinting approach based on geochemical properties (Martínez-Carreras *et al.*,  
80 2010c; Legout *et al.*, 2013; Verheyen *et al.*, 2014; Tiecher *et al.*, 2015, 2016). Near-infrared  
81 spectroscopy have proved to be a valuable tool to trace sediment originating from different land  
82 uses [e.g. badland, forest/grassland, others – Brosinsky *et al.* (2014a, 2014b); landslide, cropland,  
83 grazing land – Verheyen *et al.* (2014); cropland, unpaved road, stream channels – Tiecher *et al.*  
84 (2016)], parent material [black marls, limestones, molasses – Legout *et al.* (2013)]. However, some  
85 of these studies warned that these technique may not necessarily work in all catchments because  
86 of the risks of significant non-conservative tracer behaviour of organic molecular structures  
87 (Collins *et al.*, 2014) or high-soluble minerals, such as gypsum (Legout *et al.*, 2013).

88 To the best of our knowledge, there are very few studies using spectroscopic measurements  
89 in the mid-infrared (MIR) region for sediment tracing (Poulenard *et al.*, 2009, 2012; Evrard *et al.*,  
90 2013). Nevertheless, several studies have proved that the MIR is more suitable than the VIS or  
91 NIR due to the higher incidence of spectral bands in this region as well as the higher intensity and  
92 specificity of the signal (Viscarra Rossel *et al.*, 2006; Reeves, 2010; Xie *et al.*, 2011; Soriano-  
93 Disla *et al.*, 2014) Although Evrard *et al.* (2013) found similar results with conventional and  
94 alternative tracing methods, it showed that the MIR spectroscopy, like NIR spectroscopy, is very  
95 sensitive to the organic matter content in sediment. This technique should therefore be applied in  
96 other environmental contexts in order to test the general applicability of MIR spectroscopy  
97 methods for sediment fingerprinting. Moreover, to date, there has been no attempt to compare the  
98 use of spectroscopy for tracing sediment sources in the different ranges of the electromagnetic  
99 spectrum, such as MIR, NIR, and ultraviolet-VIS (UV-VIS) infrared.

100 To this end, the objectives of the current research were (i) to evaluate the sediment source  
101 contributions in a subtropical rural catchment of southern Brazil using this alternative MIR  
102 spectroscopy-based method, and (ii) to compare these results with those obtained by the  
103 conventional fingerprinting approach based on geochemical properties, and those obtained by  
104 NIR- and UV-VIS-spectroscopy based methods (data published in Tiecher *et al.* 2015, 2016).  
105 Then, the physicochemical basis of the source discrimination provided by MIR spectroscopy  
106 properties was discussed.

107

108

## MATERIAL AND METHODS

109 *Study catchment*

110 The Arvorezinha catchment (Fig. 1) covers a surface area of 1.19 km<sup>2</sup> and it is located on  
111 the upper north-eastern edge of the Rio Grande plateau, in Rio Grande do Sul, the southernmost  
112 state of Brazil (Fig. 1). The Arvorezinha catchment is located in the headwaters of the Taquari  
113 River, a tributary of the Jacuí River, which is one of the major water bodies in the region. The  
114 average channel slope is 9%. The time to peak for flood hydrographs recorded at the outlet  
115 typically ranges from 20 to 50 min. The area is mainly underlain by extrusive igneous rocks  
116 (rhyodacite). The altitude ranges from 560 to 740 m. Hillslopes on top of the catchment have an  
117 undulating topography (7% slope), whereas they may be classified as rolling (>15%) and short in  
118 the middle and lower parts of the catchment (Soil Survey Division Staff, 1993). According to the  
119 Köppen classification, the climate is classified as subtropical super humid mild (Cfb type) with  
120 warm summer and the absence of dry season. Mean annual rainfall is 1605 mm. The erosivity  
121 index (EI30) calculated from 40 years of historical data is 6540 MJ mm ha<sup>-1</sup> year<sup>-1</sup>, which can be  
122 considered as moderate to strong (Argenta *et al.*, 2001).

123 Soil types in the catchment according to World Reference Base for soil Resources (WRB)  
124 (IUSS Working Group WRB, 2007) and determined from a detailed soil classification survey  
125 (1:5000) are Acrisols (57%), Cambisols (33%) and Leptosols (10%). Acrisols are mainly found in  
126 upper parts of the catchment, and they are characterized by an abrupt texture change between  
127 horizons A and B, leading to a reduction of infiltration in the low permeable argic B horizon  
128 because of its higher clay content. Isolated spots of Cambisols are found in areas dominated by  
129 Acrisols and/or Leptosols. The Leptosols occur in the lower parts of the catchment, where the  
130 relief is the steepest. Land uses are not related to the soil types. Therefore, samples of potential  
131 sediment sources were collected on soils representative of all soil types found in the catchment,  
132 respecting the proportion of the surface area covered by each soil type.

133 There is no urban area in Arvorezinha catchment. It is inhabited by a local rural community  
134 (Cândido Brum) including 16 families growing tobacco in small farms (7–10 ha). Tobacco is  
135 cultivated under minimum tillage (31.2% of the catchment surface area) or under conventional  
136 ploughing (13.5%). Other land uses in the catchment (55.3%) are native forest, fallow, areas  
137 afforested with eucalyptus and grassland (Barros *et al.*, 2014).

### 138 139 *Source material sampling*

140 Three main sediment sources types were identified during previous research (Minella *et*  
141 *al.*, 2008, 2009b), namely: (i) surface of cropland, (ii) unpaved roads and (iii) stream channel  
142 banks. Areas under pasture, fallow and forest were not included as a potential source because  
143 previous research showed their low sensitivity to erosion (Minella *et al.*, 2009a). The samples of

144 potential source material were collected using non-metallic trowels in the uppermost layer (0–0.05  
145 m) of the cropland surface ( $n=20$ ) and unpaved roads ( $n=10$ ), and on exposed sites located along  
146 the main river channel network ( $n=10$ ) by scraping the surface of river banks. Care was taken to  
147 avoid sampling material recently deposited on the channel bank. Each sample was composed of  
148 10 sub-samples collected in the vicinity of the sampling point in order to obtain representative  
149 source material. Sampling points were concentrated in sites sensitive to erosion and potentially  
150 connected to the river network. Sediment source sampling was performed to cover the entire range  
151 of soil types found in the catchment.

152

### 153 *Suspended sediment sampling*

154 Twenty-nine suspended sediment samples were collected at various stages (rising,  
155 recession limbs) during nine significant floods between October 2009 and July 2011 (Maier,  
156 2013). A large volume of water (120 to 200 liters) was collected manually on a footbridge built at  
157 the outlet. Each bulk water sample was centrifuged in a continuous flow centrifuge (Alfie-500 Alfa  
158 Laval) to concentrate sediment samples for subsequent spectroscopy analysis.

159

### 160 *Source material and sediment analysis*

161 All the source material and sediment samples were oven-dried at 50°C, gently  
162 disaggregated using a pestle and mortar, and passed through a 63  $\mu\text{m}$  mesh prior to laboratory  
163 analyses to compare similar particle size fractions in all the samples. Mid-infrared (MIR) diffuse  
164 reflectance spectra were recorded in the 400–4000  $\text{cm}^{-1}$  region using a Nicolet 510- FTIR  
165 spectrometer (Thermo Electron Scientific, Madison, WI, USA) in reflection mode with a 2  $\text{cm}^{-1}$   
166 resolution and 100 co-added scans per spectrum. The spectrometer was continuously purged with  
167 dry  $\text{CO}_2$ -depleted air. Care was taken when adding the samples into the sample port to avoid  
168 differences in sample packing and surface smoothness.

169

### 170 *Sediment source discrimination based on MIR-spectroscopy*

171 Sediment source discrimination was performed using the second-derivative of MIR spectra  
172 of the source samples. Using the second-derivative avoids differences in baseline positions and  
173 removing the small differences that may arise from uncontrolled sources of variation (e.g. sample  
174 packaging). Derivative treatment not only reduces scattering effects but also increases the  
175 resolution of spectral peaks of both mineral (Scheinost *et al.*, 1998) and organic (Fernández-Getino  
176 *et al.*, 2010) components.

177 The band 2360–2325  $\text{cm}^{-1}$  of MIR spectra corresponds to the  $\text{CO}_2$  molecule vibrations.  
178 Even purging the entire analysis chamber with  $\text{CO}_2$ -free gas, it is possible that some  $\text{CO}_2$  has been  
179 trapped between the soil particles. For this reason, in order to avoid any  $\text{CO}_2$  (gas) interference in  
180 MIR spectra, the wavelengths from 2400–2300  $\text{cm}^{-1}$  were removed, and statistical analyses were  
181 performed on wavelengths in the ranges of 3800–2400  $\text{cm}^{-1}$  and 2300–650  $\text{cm}^{-1}$ .

182 Data obtained from the MIR spectroscopy consists of a continuous spectrum with a large  
183 number of variables (intervals of 2  $\text{cm}^{-1}$  = 1583 wavenumbers) for a set of 40 sediment source  
184 samples. A Principal Component Analysis (PCA) was performed to reduce the number of variables  
185 without losing significant information. PCA was performed using the R package “ade4” (R-  
186 project.org). Then, a Discriminant Function Analysis (DFA) in backwards mode was conducted  
187 on the scores obtained from the PCA. At each step, the principal component (PC) which minimized  
188 the overall Wilks' Lambda was entered. Maximum significance of F to enter a principal component  
189 (PC) was 0.01. Minimum significance of F to remove a PC was 0.01. DFA was performed using  
190 STATISTICA software.

191

#### 192 *Sediment source quantification using the MIR-spectroscopy approach*

193 The individual samples representative of each sediment source (i.e. 20 samples of cropland  
194 surface, 10 samples of unpaved roads, and 10 samples of stream channel banks) were mixed in  
195 equal proportions at the laboratory to prepare a unique reference sample for each source. Then, the  
196 three reference source samples were mixed in different weight proportions to obtain 48 composites  
197 with different source material ratios as displayed in Fig. 2. MIR spectra were obtained for each  
198 mixture.

199 Relationships between MIR spectra ( $x$  variate) and the corresponding weight contribution  
200 of each sediment source ( $y$  variate) were analyzed using partial least squares regressions (PLSR).  
201 The composites samples were randomly chosen to build the model. Thirty-six mixed samples were  
202 used to develop the calibration models and the remaining 12 mixed samples were used for model  
203 validation. The number of components providing the lowest predictive standard error was used.  
204 PLSR was performed using STATISTICA software.

205 The predictive performance of the models was evaluated by calculating several standard  
206 indicators such as the root mean square error of calibration (RMSEC), the root mean square error  
207 of cross-validation (RMSECV), the root mean square error of prediction (RMSEP), the ratio  
208 RMSECV to standard deviation (RPD) and the coefficient of determination  $R^2$  obtained when  
209 comparing predicted values with reference data. The uncertainty associated with the prediction  
210 was estimated by the confidence interval (95%) of prediction calculated by the regression of

211 predicted values against reference data. Three independent MIR-PLSR models were constructed  
212 to estimate the proportion of sediment supplied by the three sources. MIR spectra of suspended  
213 sediment were then introduced into these MIR-PLSR models to estimate the contribution of each  
214 sediment source and the associated uncertainty.

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## RESULTS AND DISCUSSION

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### *Source discrimination*

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MIR spectra of the <63  $\mu\text{m}$  fractions of suspended sediment and sediment source samples were very similar, and 16 spectral features were observed in all spectra (Fig. 3a and Table 1). In order to simplify the interpretation, the spectral features were grouped according to the main soil constituents, namely Soil Clay Minerals (SCM – kaolinite [Kt], smectite [Sm], mica [Mc], hydroxy-interlayered vermiculite [HIV], gibbsite [Gb]), quartz (Qz), and organic compounds (OC) (Viscarra Rossel and Behrens, 2010; Madejová *et al.*, 2011; Terra, 2011; Yang and Mouazen, 2012). Spectral feature 1 at 3695  $\text{cm}^{-1}$  corresponds to OH stretching ( $\nu_{1a}$ ) of Kt. Spectral features 2, 12, 13, 14 and 16 at 3620, 1115, 1020, 915 and 698  $\text{cm}^{-1}$  correspond to SCM (Table 1). Spectral features 3 and 4, measured at 2930 and 2850  $\text{cm}^{-1}$ , correspond to C–H stretching of aromatic and aliphatic organic compounds, respectively. Spectral features 5, 6, and 7 at 1990, 1870 and 1785  $\text{cm}^{-1}$  correspond to Si–O stretching bands of Qz. Spectral features 8 and 15 at 1630 and 808  $\text{cm}^{-1}$  correspond to both SCM and Qz; features 9 and 10 at 1530 and 1340  $\text{cm}^{-1}$  correspond to both OC and Qz; feature 11 at 1160  $\text{cm}^{-1}$  correspond to both OC and SCM (Table 1).

The potential of the spectroscopy method to discriminate sediment sources was analyzed based on the scores obtained from the PCA. The scores of 39 principal components (PC) obtained in the PCA were then entered in the DFA (PC-DFA model) where six PCs were selected. These six PCs together explained 70.8% of the total variation obtained from the 39 PCs. In the DFA, the final  $\Lambda^*$  value was 0.0342 (Table 2), meaning that 96.6% of variation included in these six PCs was due to differences between sediment sources, and only 3.4% of the variation was due to intra-source differences. The PC-DFA model correctly classified 97.5% of the sediment source samples with an average uncertainty of 3.426% (Table 2). The square Mahalanobis distance between channel banks and cropland surface was smaller (18.4) than the distance between these sources and unpaved roads (channel banks vs. unpaved roads = 38.7, cropland surface vs. unpaved roads = 29.7) (Fig. 4). Nonetheless, the distances between sediment sources remained systematically significant ( $P < 6.5\text{E-}09$ ) (Table 2).

### *Partial last-square models based on MIR spectroscopy*

245 MIR-PLSR model performance is given in Table 3. Four components were used to  
246 construct MIR-PLSR models. Correlations between actual and predicted proportions were very  
247 high, with  $R^2$  values close to 1 for the three independent MIR-PLSR models (Fig. 5). RPD values  
248 higher than 2 indicate robust models of high quality (Chang *et al.*, 2001). In the current research,  
249 all the independent MIR-PLSR models showed RPD values higher than 10, indicating a good  
250 predictability. Moreover, the average difference between predicted and actual values on the  
251 calibration dataset measured by the RMSEP parameter was always lower than 4.7%.

252 Regions of the MIR spectra providing the best discrimination between the sediment sources  
253 are shown in Fig. 3. Fig. 3b display the second-derivative of MIR spectra of all the three sediment  
254 sources. To facilitate the visualization of differences in the spectral features, the differences  
255 between the second-derivatives of each source are shown in Fig. 3c, d, e. These figures show a  
256 greater variation between the unpaved roads vs. cropland surface (Fig. 3d) and unpaved roads vs.  
257 channel banks (Fig. 3e) than between cropland surface vs. channel banks (Fig. 3c).

258 Spectral features at 2930 and 2850  $\text{cm}^{-1}$  corresponding to C–H stretching of aromatic and  
259 aliphatic functional compounds, respectively, provided a better discrimination of unpaved roads  
260 (Fig. 3d, e). In contrast, they did not vary between cropland surface and channel banks (Fig. 3c).  
261 The same interpretation can be made for the spectral features found at 1160  $\text{cm}^{-1}$  (OC + SCM) and  
262 at 1530 and 1340  $\text{cm}^{-1}$  (OC + Qz). This difference is likely due to the lower content of TOC in  
263 unpaved roads ( $12.0 \pm 5.5 \text{ g C kg}^{-1}$ , data not shown) compared to cropland surface and channel  
264 banks ( $20.5 \pm 6.6$  and  $21.3 \pm 3.1 \text{ g C kg}^{-1}$ , respectively, data not shown). Moreover, a higher  
265 abundance of 2:1 clay minerals and a lower quantity of Qz in the unpaved roads compared to the  
266 cropland and channel banks may have contributed to the better discrimination of unpaved roads  
267 with the spectral features 1, 2, 12, 13, 14 and 16 (SCM), and the spectral features 5, 6 and 7 (Qz).  
268 Thus, the combined effect of differences in mineral composition and organic matter content  
269 resulted in the lowest predictive error ( $\pm 2.8\%$ ) for the MIR-PLSR models built for unpaved roads  
270 (Fig. 5b and Table 3), and in the correct classification of 100% of the road samples (Table 2). As  
271 a result of the much more similar mineral and organic compositions of cropland and channel bank  
272 sources, the predictive errors were higher (5.9 for cropland and 5.1% and channel banks) than  
273 those obtained for unpaved roads (2.8%) (Table 3). However, errors associated with all MIR-PLSR  
274 models remained far below the 15%-threshold, which was considered as ‘acceptable’ in previous  
275 sediment fingerprinting studies (Collins and Walling, 2002).

276

277 *Source contribution to sediment*

278 The uncertainty of MIR-PLSR model predictions remained very low (see the 95%  
279 confidence intervals on Fig. 5, with a mean of 4.6% for the three sediment sources) (Table 3).  
280 Source contributions were very variable from one event to the next, with a dominance in similar  
281 proportions of cropland surface (mean:  $42 \pm 27\%$ ; Fig. 6) and channel banks (mean:  $43 \pm 19\%$ ; Fig.  
282 6), and a much lower contribution of unpaved roads (mean:  $16 \pm 10\%$ ; Fig. 6). When these results  
283 are compared to those obtained by Tiecher *et al.* (2015) using conventional sediment fingerprinting  
284 based on geochemical properties, the cropland contribution was clearly underestimated by the  
285 spectroscopic method, whereas channel bank contribution was overestimated (Fig. 6). In contrast,  
286 the contribution of unpaved roads calculated by both methods remained very similar (Fig. 6.).

287 When compared to the results obtained with other sediment fingerprinting approaches, such  
288 as those based on elemental geochemistry (Tiecher *et al.*, 2015), ultraviolet-visible (UV-VIS)  
289 (Tiecher *et al.*, 2015), and near-infrared (NIR) properties (Tiecher *et al.*, 2016), the results found  
290 with MIR spectroscopy showed an overestimation of channel bank contribution and an  
291 underestimation of cropland and unpaved road contributions (Fig. 6). Moreover, MIR-PLSR  
292 model predictions showed the highest difference in source contributions compared to those  
293 obtained with geochemical properties (Fig. 7). Although NIR-PLSR predictions were the closest  
294 to those obtained with the geochemical approach, there was no significant correlation between the  
295 methods (Table 4). UV-VIS-PLSR showed an intermediate behaviour, with slight variations in  
296 source contributions compared to those obtained with the geochemical approach. In addition, UV-  
297 VIS predictions were well correlated to MIR predictions for all sediment sources and showed a  
298 significant correlation with results of the geochemical approach for cropland and unpaved roads  
299 (Table 4).

300 A strong positive correlation ( $p = 0.001$ ,  $r = 0.57$ ) was found between the cropland surface  
301 contributions calculated by both approaches (Table 4 and Fig. 7). The contribution of unpaved  
302 road estimated by MIR-PLSR models was poorly correlated to the contribution obtained by  
303 geochemical approach ( $p = 0.108$ ,  $r = 0.30$ , Table 4). This type of relationship was not observed  
304 for channel banks. Moreover, the unpaved road contribution predicted by the spectroscopic method  
305 was found to be negatively correlated with the total organic carbon content in suspended sediment  
306 (Fig. 8). This result demonstrates that the mid-infrared signature and the results of MIR-PLSR  
307 models were impacted by the low organic carbon content found in deep soil horizons  
308 corresponding to unpaved road material, which may explain why unpaved road predictions were  
309 very similar for both methods (Fig. 6). When assuming that the sediment source contributions  
310 provided by the conventional fingerprinting method based on geochemistry are correct and  
311 reflecting the ground truth, results of the current research demonstrate that the analysis of the MIR

312 region of the electromagnetic spectrum provided less accurate results than the NIR and UV-VIS  
313 regions. This is likely due to the higher sensitivity of MIR to organic matter, as observed in several  
314 other studies (Viscarra Rossel *et al.*, 2006; Reeves, 2010; Xie *et al.*, 2011; Soriano-Disla *et al.*,  
315 2014).

316  
317 *Physicochemical basis of the source discrimination provided by MIR spectroscopy*

318 In the Arvorezinha catchment, the discrimination between sediment sources by using MIR  
319 spectroscopy was possible due to differences in both organic carbon content and in mineralogical  
320 composition between sources. It has been demonstrated that the signatures of different organic  
321 compounds in the mid-infrared region can be very useful to discriminate topsoils (relatively rich  
322 in organic matter) and deeper horizons and gully material depleted in organic matter (Poulenard  
323 *et al.* 2009; Evrard *et al.* 2013). However, in certain conditions, the high sensitivity of mid-infrared  
324 spectra to the organic carbon content can become problematic. In one of the Mexican catchments  
325 investigated by Evrard *et al.* (2013), the source predictions based on the spectroscopic method  
326 greatly differed from those provided by the classical sediment fingerprinting method based on  
327 geochemical properties because one source of soluble organic matter delivered by anthropogenic  
328 activities (excess of cow dung) caused an enrichment of carbon in sediments, leading to an  
329 overestimation of the contribution of surface soil.

330 In Arvorezinha, unpaved roads are composed of subsurface material as these areas have  
331 been severely eroded during the last several decades. This process explains the lower organic  
332 carbon content found in unpaved roads compared to that measured in cropland surface and channel  
333 bank samples, leading to a better discrimination of the former source (see Mahalanobis distances  
334 in Table 2). The higher abundance of 2:1 clay minerals in the unpaved road samples is likely due  
335 to the fact that most of the soils in Arvorezinha catchment are Acrisols (~57% of the total area).  
336 These soils are characterized by the migration of clays in depth, forming a clay-enriched textural  
337 B subsurface horizon. The higher abundance of 2:1 clay minerals in unpaved roads is due to the  
338 selective eluviation of smectite compared to other sources, which also contributed to the better  
339 discrimination of unpaved roads samples. In contrast, the discrimination between cropland surface  
340 and channel banks, was complicated by their similar contents and composition in organic carbon.  
341 They only differed by their different proportions in mineral components, such as the higher  
342 proportion of Qz and the lower content of 2:1 clay minerals in cropland compared to channel  
343 banks.

344 It is well known that unpaved rural roads contribute significantly to soil loss in agricultural  
345 catchments despite representing a small fraction of watershed-occupied areas (Cao *et al.*, 2015).

346 Despite the low contribution of unpaved roads to sediment obtained in this study ( $16\pm 10\%$ ), they  
347 represent perennial landscape features, and their construction should therefore be planned in the  
348 framework of integrated soil erosion control programs. The high soil erosion and sediment yield  
349 rates in unpaved roads should be take into account when designing and constructing road and  
350 railway cuts, because it is very important for infrastructure maintenance, as well as for soil  
351 formation, water protection, vegetation establishment and controlling land degradation (Seutloali  
352 and Beckedahl, 2015; Navarro-Hevia *et al.*, 2016). Moreover, unpaved road material can also  
353 contain considerable amounts of heavy metals like Pb, Cu, Cd, and Zn, which are present in  
354 gasoline type fuels, tire and brake pad wear, oils, lubricants, and grease transport (Trujillo-  
355 González *et al.*, 2016).

356 In catchment characterized by soils with very distinct mineralogical properties, a simple  
357 qualitative comparison of mid-infrared spectra proved to provide a fast and efficient technique to  
358 identify the main sediment sources. In Mexico, Evrard *et al.* (2013) showed that the mid-infrared  
359 spectrum of Acrisols was characterized by the dominance of kaolinite in the clay fraction (bands  
360 at  $3600\text{--}3700\text{ cm}^{-1}$ ), whereas Andisol spectra were characterized by gibbsite. Similarly, in the  
361 French Alps, Poulenard *et al.* (2012) showed that soils developed on gypsum substrates were  
362 characterized by absorption bands at  $3500\text{ cm}^{-1}$  and in the region between  $2370$  and  $2060\text{ cm}^{-1}$ ,  
363 corresponding to  $\text{CaSO}_4$ ; whereas soils developed on molasses were characterized by absorption  
364 bands at  $2430\text{--}2640\text{ cm}^{-1}$  corresponding to calcite ( $\text{CaCO}_3$ ) and absorption bands at  $3500\text{--}3700$   
365  $\text{cm}^{-1}$  corresponding to aluminosilicates. However, Poulenard *et al.* (2012) warned against the  
366 application of MIR-PLSR models in catchments characterized by more complex sources of  
367 sediment, with variations in soil types and land uses. This may typically be the case in studies  
368 discriminating catchment compartments (surface vs. subsurface) as in the current research.

369 As MIR is very sensitive to organic matter, the discrimination of sediment sources with  
370 similar organic carbon contents can be difficult if there are no additional differences in mineral  
371 composition. Further efforts should be made to combine the information provided by both methods  
372 in order to provide estimations of sediment source contributions with a higher precision.

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## CONCLUSIONS

375 This study showed the potential of using an alternative sediment fingerprinting method  
376 based on mid-infrared (MIR) spectroscopy to quantify sediment source contributions in a  
377 subtropical rural catchment of southern Brazil. MIR spectra were comparable in both suspended  
378 sediment and potential sources, and 16 spectral features could be identified in all spectra to  
379 differentiate them. Sources could be distinguished with this method, although the discrimination

380 between these sources could not be attributed to the detection of specific minerals. The model  
381 based on MIR spectra correctly classified  $97.5\pm 2.5\%$  of the source samples. The discrimination of  
382 cropland and channel banks was possible given their differences in clay mineral contents. In  
383 contrast, the similar organic matter content found in both sources complicated their discrimination  
384 by the spectroscopic method.

385 When the results of the current research based on MIR spectroscopy are compared to those  
386 obtained using other approaches based on geochemistry (Tiecher *et al.*, 2015), ultraviolet-visible  
387 (UV-VIS) (Tiecher *et al.*, 2015), and near-infrared (NIR) spectroscopy (Tiecher *et al.*, 2016),  
388 results of the current research focusing on MIR spectroscopy showed an overestimation of channel  
389 bank contribution and an underestimation of cropland and unpaved road contributions. Moreover,  
390 among the spectroscopic approaches, predictions based on the analysis of the MIR region showed  
391 the highest difference in source contributions compared to those obtained with the geochemical  
392 conventional approach which is considered to provide the ‘ground truth’. Mid-infrared  
393 spectroscopy signatures were clearly impacted by the low organic carbon content of deep soil  
394 horizons, as that found in unpaved road material, resulting in a better discrimination of this source  
395 and similar contributions to sediment calculated by geochemical approach. In the future, additional  
396 tracers could be used, e.g. fallout radionuclides including  $^{137}\text{Cs}$ , to provide further discrimination  
397 between surface and subsurface material in order to validate the relevance of the low-cost MIR  
398 spectroscopy approach for tracing sediment sources in rural catchments.

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**Table 1.** Characteristics of the absorption features detected by MIR spectroscopy.

Spectral feature	Wavenumber (cm <sup>-1</sup> )	Wavenumber according to the literature (cm <sup>-1</sup> )	Soil constituent	Functional group	MIR mode
1	3695	3695 <sup>a</sup>	Kt	O–H	v <sub>1a</sub>
2	3620	3620 <sup>a</sup>	Kt	O–H	v <sub>1b</sub>
		3620 <sup>a</sup>	Sm	O–H	v <sub>1</sub>
		3620 <sup>a</sup>	Mc	O–H	v <sub>1</sub>
3	2930	2930 <sup>a</sup>	OC (aromatic)	C–H	v <sub>3</sub>
4	2850	2850 <sup>a</sup>	OC (aliphatic)	C–H	v <sub>1</sub>
5	1990	1975 <sup>b</sup>	Qz	Si–O	v
6	1870	1867 <sup>b</sup>	Qz	Si–O	v
7	1785	1790 <sup>b</sup>	Qz	Si–O	v
8	1630	1628 <sup>b</sup>	Kt, Sm, Mc, HIV	O–H	δ
		1628 <sup>b</sup>	Qz	Si–O	v
9	1530	1527 <sup>b</sup>	Qz	Si–O	v
		1525 <sup>c</sup>	OC (aromatic)	C=C	v
10	1340	1527 <sup>b</sup>	Qz	Si–O	v
		1350 <sup>c</sup>	OC (aliphatic)	C–H	v
11	1160	1157 <sup>b</sup>	OC (polysaccharide)	C–O	v
		1157 <sup>b</sup>	OC (aliphatic)	C–OH	v
		1157 <sup>b</sup>	Kt, Sm, Mc, HIV	O–Al–OH	δ
12	1115	1111 <sup>b</sup>	Kt, Sm, Mc, HIV	Si–O–Si	v
		1111 <sup>b</sup>	Gb	Al–O–OH	δ
13	1020	1018 <sup>b</sup>	Kt, Sm, Mc, HIV	Si–O–Si	v <sub>5</sub>
14	915	915 <sup>a</sup>	Kt	Al–OH	δ
		915 <sup>a</sup>	Sm	Al–OH	δ <sub>a</sub>
15	808	814 <sup>b</sup>	Qz	Si–O	v
		814 <sup>b</sup>	Kt, HIV, Gb	Al–OH	δ
16	698	702 <sup>b</sup>	Kt, Sm, Mc, HIV	Si–O	v

604 Kt, kaolinite; Sm, smectite; Mc, micas; HIV, hydroxy-interlayered vermiculite; Gb, gibbsite; Qz, quartz; OC, organic compounds.

605 <sup>a</sup> Viscarra Rossel and Behrens (2010)606 <sup>b</sup> Terra (2011)607 <sup>c</sup> Yang and Mouazen (2012)

608

609 **Table 2.** Results of the discriminant function analysis and prediction error for the MIR spectroscopy  
 610 approach.

DFA parameters	Source	Value
F-values (F critical = 2.4)	SC vs. UR	27.9
	SC vs. CF	17.7
	UR vs. CF	28.6
p-levels	SC vs. UR	2.2E-11
	SC vs. CF	6.5E-09
	UR vs. CF	1.6E-11
Squared Mahalanobis distances	SC vs. UR	38.7
	SC vs. CF	18.4
	UR vs. CF	29.7
	Average	28.9
Source samples correctly classified (%)	SC	100
	UR	100
	CF	95
	Average	97.5
Uncertainty associated with source discrimination (%)	SC	0.311
	UR	0.751
	CF	6.322
	Average	3.426
Prediction error (%)	SC	5.1
	UR	2.8
	CF	5.9
	Average	4.6

612  
 613 **Table 3.** Predictive performance of the MIR-PLSR models based on MIR spectroscopy.

Sediment source	NC	R <sub>adj</sub>	RMSEC	RMSEP	RMSECV	RPD
Crop fields	4	0.9903	2.1	4.7	2.9	10.0
Unpaved roads	4	0.9978	1.2	2.1	1.5	19.8
Stream channels	4	0.9929	1.6	3.9	2.3	12.4

614 NC, number of components used in the MIR-PLSR model; R<sub>adj</sub>, coefficient of determination; RMSEC, root mean square error of  
 615 calibration; RMSEP, root mean square error of prediction; RMSECV, root mean square error of cross-validation; RPD, ratio  
 616 between the standard deviation and RMSECV.  
 617

618 **Table 4.** Linear correlation between the sediment source contributions predicted by sediment fingerprinting  
 619 techniques based on MIR spectroscopy, NIR spectroscopy (Tiecher *et al.*, 2016), UV-VIS spectroscopy  
 620 and elemental geochemistry (Tiecher *et al.*, 2015).

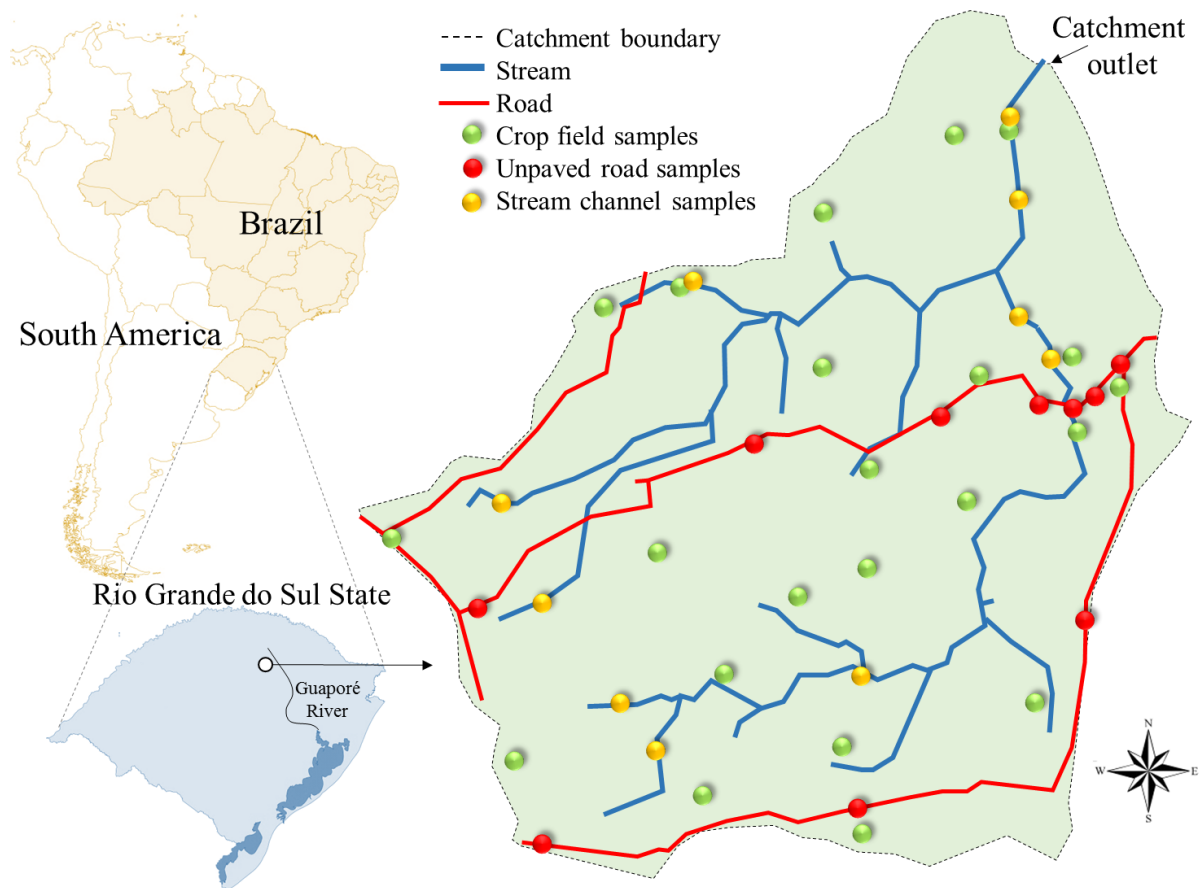
Sediment source/method	MIR-spectroscopy		Geochemistry <sup>a</sup>		UV-VIS-spectroscopy <sup>a</sup>	
	<i>r</i>	<i>p</i> -value	<i>r</i>	<i>p</i> -value	<i>r</i>	<i>p</i> -value
<i>Cropland</i>						
Geochemistry <sup>a</sup>	0.57	<b>0.001</b>				
UV-VIS-spectroscopy <sup>a</sup>	0.43	<b>0.019</b>	0.31	<b>0.098</b>		
NIR-spectroscopy <sup>b</sup>	0.04	0.826	0.01	0.962	-0.44	<b>0.018</b>
<i>Channel bank</i>						
Geochemistry <sup>a</sup>	-0.01	0.939				
UV-VIS-spectroscopy <sup>a</sup>	0.31	<b>0.098</b>	-0.22	0.253		
NIR-spectroscopy <sup>b</sup>	0.07	0.701	0.22	0.251	0.37	<b>0.049</b>
<i>Unpaved road</i>						
Geochemistry <sup>a</sup>	0.30	0.108				
UV-VIS-spectroscopy <sup>a</sup>	0.61	<b>0.001</b>	0.59	<b>0.001</b>		
NIR-spectroscopy <sup>b</sup>	0.54	<b>0.003</b>	-0.07	0.718	0.23	0.230

621 Values in **bold** indicate significant correlation between source contributions estimated by both methods at  $P < 0.05$

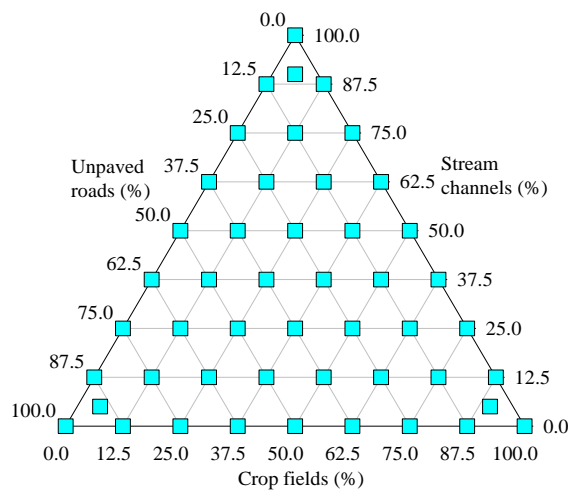
622 <sup>a</sup> Tiecher *et al.* (2015)

623 <sup>b</sup> Tiecher *et al.* (2016)

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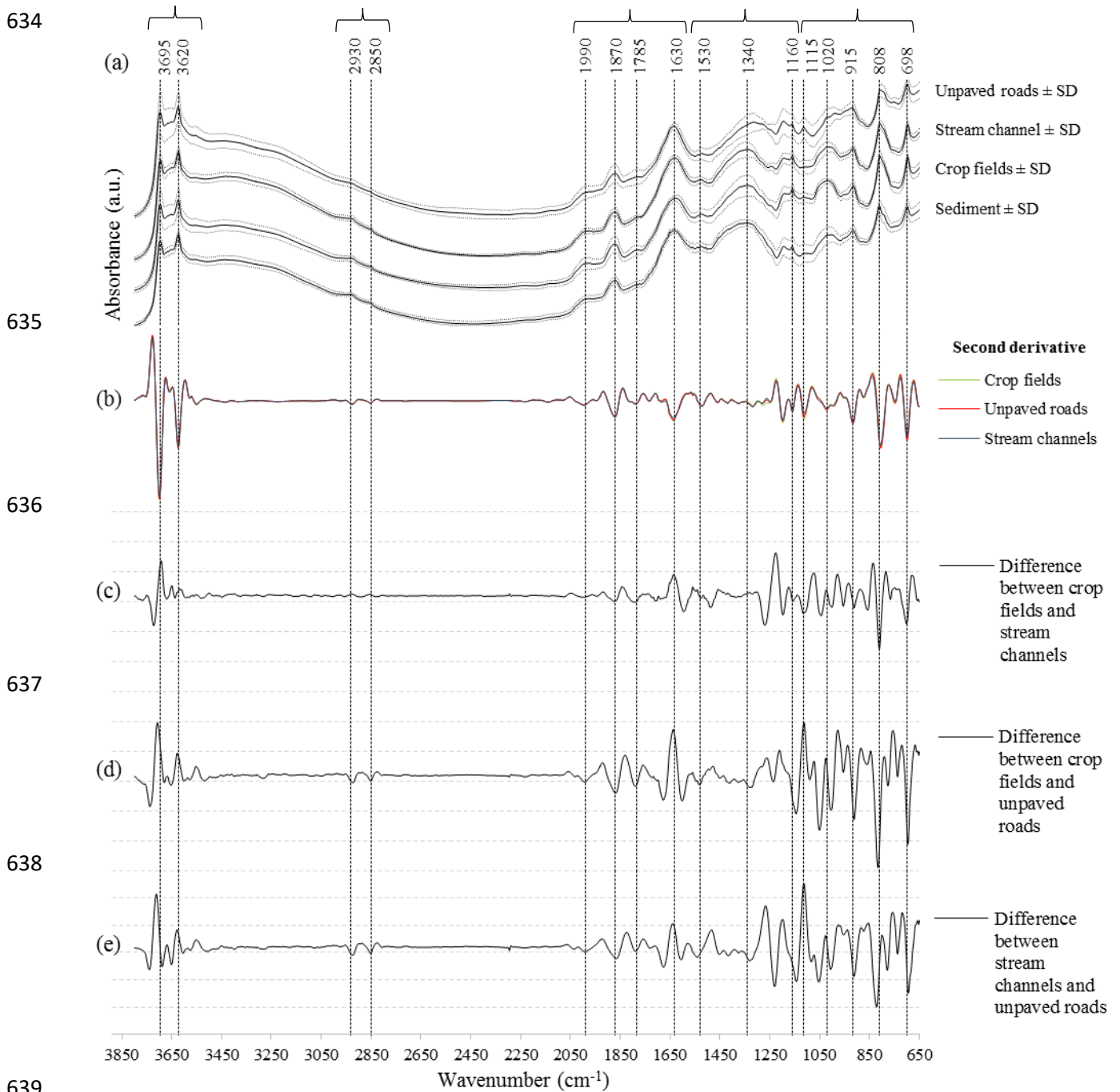


625  
 626 **Fig. 1.** Location of the Arvorezinha catchment in Southern Brazil, and location of the potential  
 627 sediment source sampling sites.  
 628



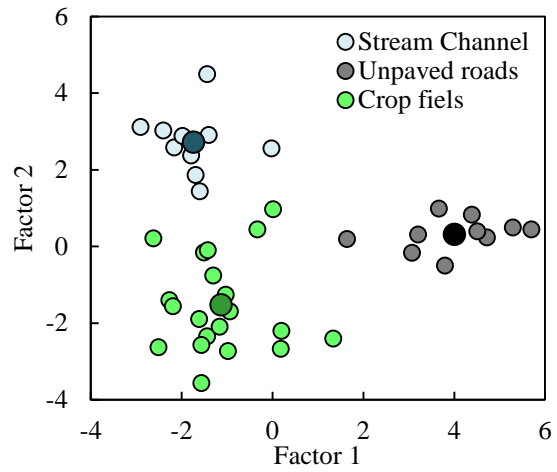
629  
 630 **Fig. 2.** Ternary diagram showing the composition of the experimental mixtures prepared in the  
 631 laboratory for the MIR-PLSR model calibration.

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633  
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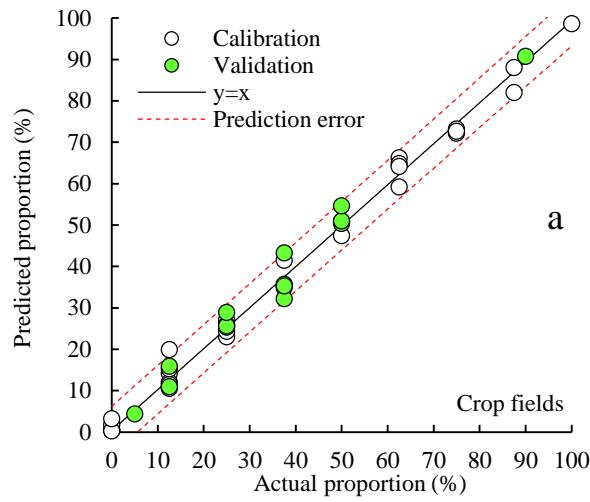
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**Fig. 3.** Mean MIR spectra of the main sediment sources (unpaved road [UR], stream channel [SC], and crop field [CF]) and suspended sediment (a), second-derivative of the UR, SC, and CF (b), difference between CF and SC (c), difference between CF and UR (d), and difference between SC and UR (e).

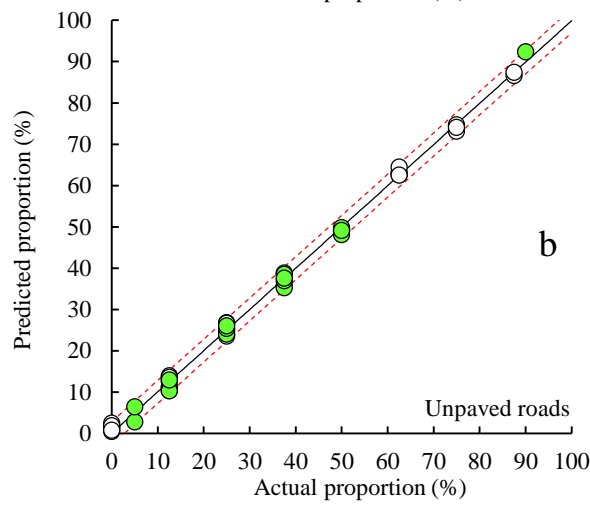


644  
645 **Fig. 4.** Two-dimensional scatter plot of the first and second discriminant functions derived from  
646 stepwise discriminant function analysis (DFA) applied to MIR spectroscopy. Larger symbols  
647 represent the centroids of each source.  
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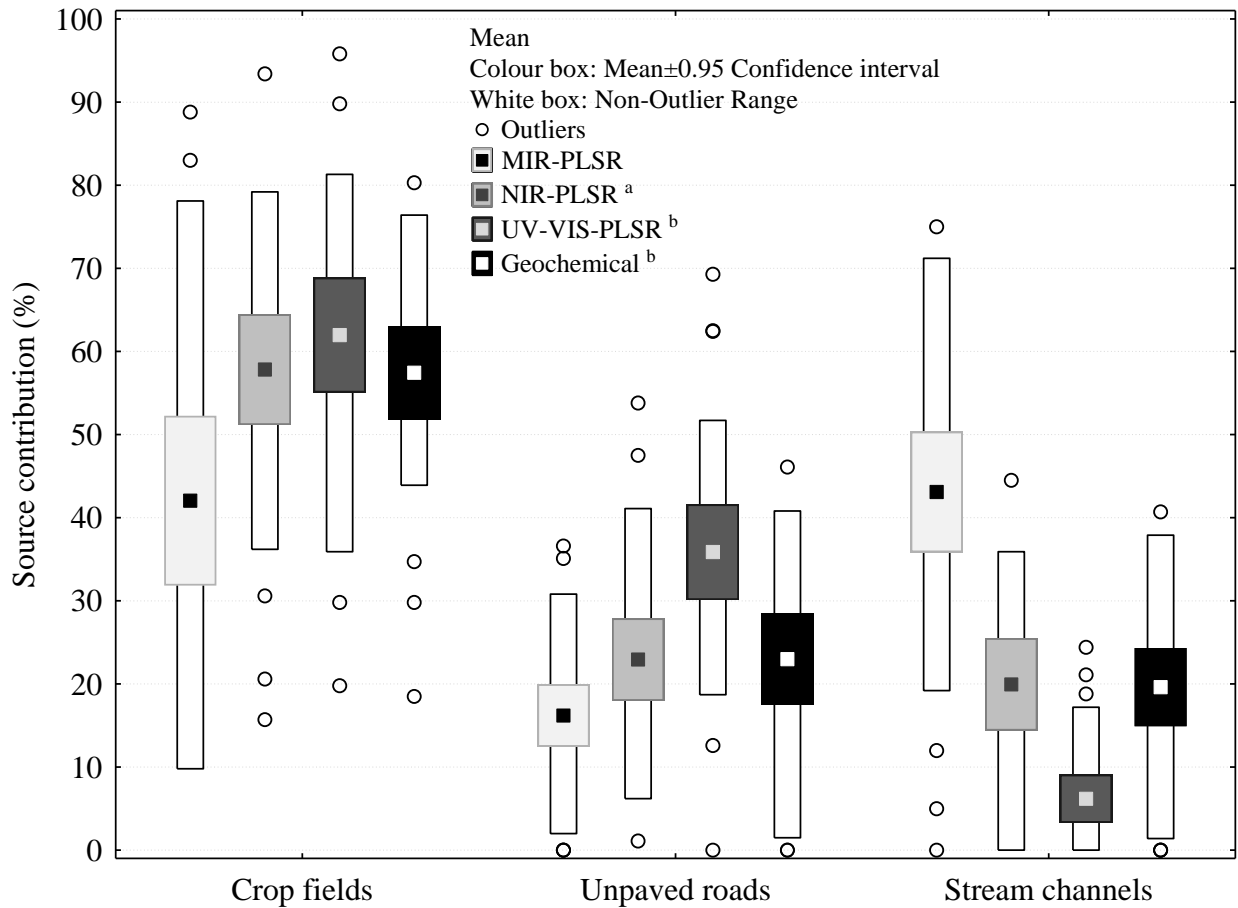
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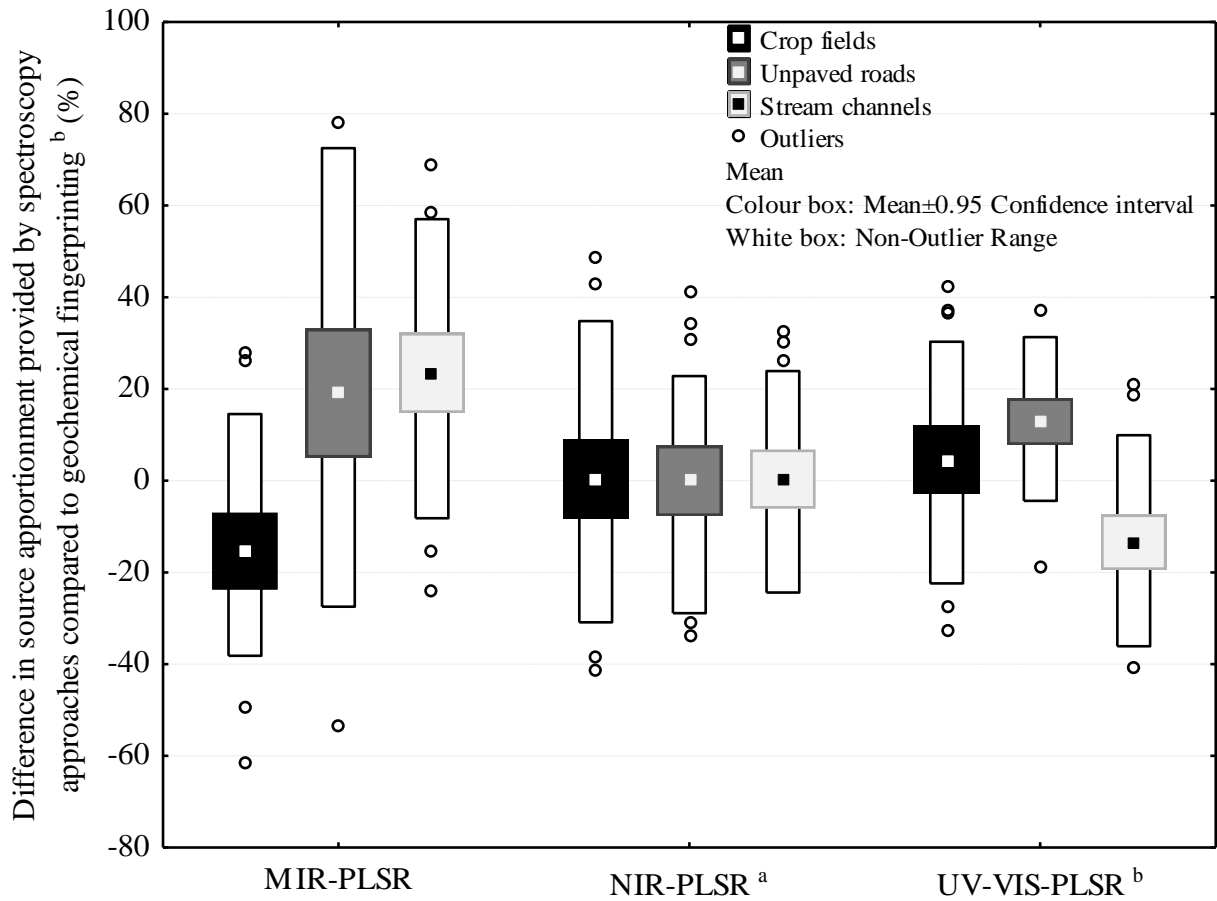
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655

**Fig. 5.** Relationship between actual proportions of sediment sources and those calculated using MIR-PLSR models in experimental mixtures for crop fields (a), unpaved roads (b), and stream channels (c). Red dashed lines provide the 95%-confidence limits (95%).



656  
 657 **Fig. 6.** Box plot of the sediment source contributions for the 29 suspended sediment samples  
 658 collected at the Arvorezinha catchment outlet, estimated by MIR spectroscopy (this study), NIR-  
 659 spectroscopy (a – Tiecher *et al.*, 2016), UV-VIS spectroscopy and conventional sediment  
 660 fingerprinting approach based on elemental geochemistry (b – Tiecher *et al.*, 2015).  
 661  
 662



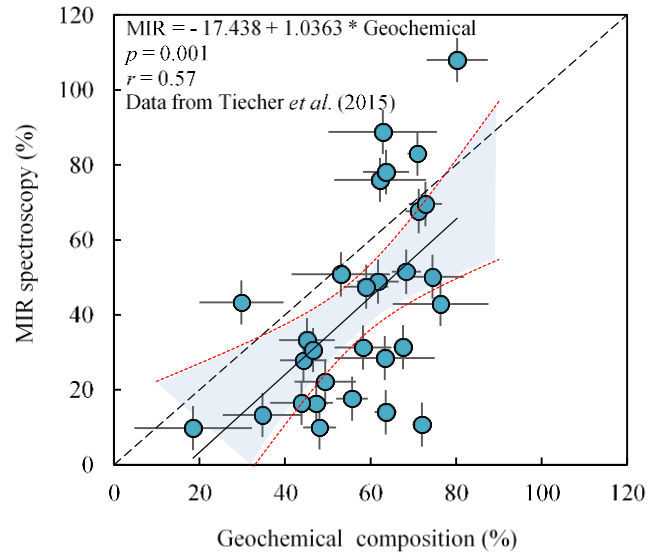
663  
 664 **Fig. 7.** Box plot of the difference in source apportionment provided by spectroscopy approaches  
 665 compared to geochemical fingerprinting (Tiecher *et al.*, 2015) for the 29 suspended sediment  
 666 samples collected at the Arvorezinha catchment.

667 <sup>a</sup> Tiecher *et al.* (2016)

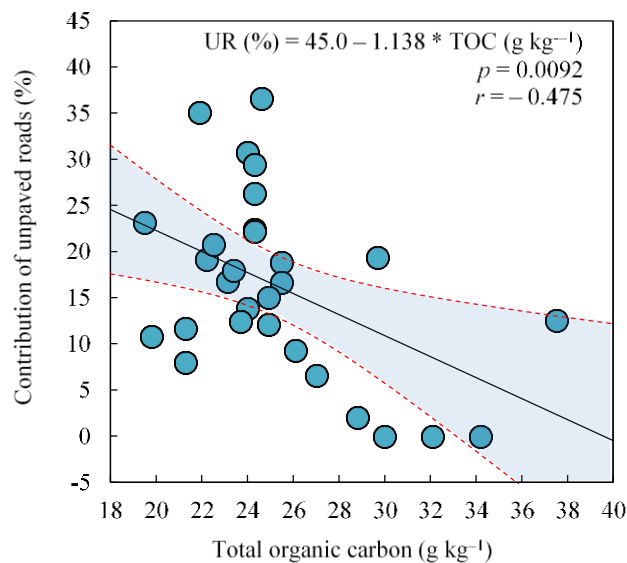
668 <sup>b</sup> Tiecher *et al.* (2015)

669

670



671  
 672 **Fig. 8.** Comparison of the crop field contributions to sediment predicted by the conventional  
 673 sediment fingerprinting method based on elemental geochemistry (Tiecher *et al.*, 2015) and those  
 674 predicted by the partial least-squares regression model based on MIR spectroscopy. Error bars  
 675 correspond to the estimated error of prediction for each method. The dashed line represents the 1:1  
 676 line. Red dotted lines provide the 95-% confidence limits.  
 677



678  
 679 **Fig. 9.** Relationship between the unpaved roads contributions to sediment predicted by the partial  
 680 least-squares regression model based on MIR spectroscopy and the total organic carbon content in  
 681 sediment. The red dashed lines provide the 95-% confidence limits.  
 682