Tracing Sediment Sources Using Mid-infrared Spectroscopy in Arvorezinha Catchment, Southern Brazil

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

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ABSTRACT

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

KEY WORDS: soil erosion, sediment fingerprinting, spectral properties, suspended sediment, 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

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

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

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

MATERIAL AND METHODS

Study catchment

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

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

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

Source material sampling

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

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

Suspended sediment sampling

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

Source material and sediment analysis

All the source material and sediment samples were oven-dried at 50^{o}C, gently disaggregated using a pestle and mortar, and passed through a 63 µm mesh prior to laboratory analyses to compare similar particle size fractions in all the samples. Mid-infrared (MIR) diffuse reflectance spectra were recorded in the 400–4000 cm^{-1} region using a Nicolet 510- FTIR spectrometer (Thermo Electron Scientific, Madison, WI, USA) in reflection mode with a 2 cm^{-1} resolution and 100 co-added scans per spectrum. The spectrometer was continuously purged with dry CO_2-depleted air. Care was taken when adding the samples into the sample port to avoid differences in sample packing and surface smoothness.

Sediment source discrimination based on MIR-spectroscopy

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

The band 2360–2325 cm^{-1} of MIR spectra corresponds to the CO_2 molecule vibrations. Even purging the entire analysis chamber with CO_2-free gas, it is possible that some CO_2 has been trapped between the soil particles. For this reason, in order to avoid any CO_2 (gas) interference in MIR spectra, the wavelengths from 2400–2300 cm^{-1} were removed, and statistical analyses were performed on wavelengths in the ranges of 3800–2400 cm^{-1} and 2300–650 cm^{-1}.

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

Sediment source quantification using the MIR-spectroscopy approach

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

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

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

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

RESULTS AND DISCUSSION

Source discrimination

MIR spectra of the <63 µm 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 cm^{-1}corresponds to OH stretching (ν_{1a}) of Kt. Spectral features 2, 12, 13, 14 and 16 at 3620, 1115, 1020, 915 and 698 cm^{-1} correspond to SCM (Table 1). Spectral features 3 and 4, measured at 2930 and 2850 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 cm^{-1} correspond to Si–O stretching bands of Qz. Spectral features 8 and 15 at 1630 and 808 cm^{-1} correspond to both SCM and Qz; features 9 and 10 at 1530 and 1340 cm^{-1} correspond to both OC and Qz; feature 11 at 1160 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 Λ^* 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<6.5E-09) (Table 2).

Partial last-square models based on MIR spectroscopy

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

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

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

Source contribution to sediment

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

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

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

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

Physicochemical basis of the source discrimination provided by MIR spectroscopy

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

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

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

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

In catchment characterized by soils with very distinct mineralogical properties, a simple qualitative comparison of mid-infrared spectra proved to provide a fast and efficient technique to identify the main sediment sources. In Mexico, Evrard *et al*. (2013) showed that the mid-infrared spectrum of Acrisols was characterized by the dominance of kaolinite in the clay fraction (bands at 3600–3700 cm^{-1}), whereas Andisol spectra were characterized by gibbsite. Similarly, in the French Alps, Poulenard *et al*. (2012) showed that soils developed on gypsum substrates were characterized by absorption bands at 3500 cm^{-1} and in the region between 2370 and 2060 cm^{-1}, corresponding to $CaSO_4$; whereas soils developed on molasses were characterized by absorption bands at 2430–2640 cm^{-1} corresponding to calcite ($CaCO_3$) and absorption bands at 3500–3700 cm^{-1} corresponding to aluminosilicates. However, Poulenard *et al*. (2012) warned against the application of MIR-PLSR models in catchments characterized by more complex sources of sediment, with variations in soil types and land uses. This may typically be the case in studies discriminating catchment compartments (surface vs. subsurface) as in the current research.

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

CONCLUSIONS

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

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

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

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

Spectral feature	Wavenumber (cm^{-1})	Wavenumber according to the literature (cm^{-1})	Soil constituent	Functional group	MIR mode
1	3695	3695[a]	Kt	O–H	ν_{1a}
2	3620	3620[a]	Kt	O–H	ν_{1b}
		3620[a]	Sm	O–H	ν_1
		3620[a]	Mc	O–H	ν_1
3	2930	2930[a]	OC (aromatic)	C–H	ν_3
4	2850	2850[a]	OC (aliphatic)	C–H	ν_1
5	1990	1975[b]	Qz	Si–O	ν
6	1870	1867[b]	Qz	Si–O	ν
7	1785	1790[b]	Qz	Si–O	ν
8	1630	1628[b]	Kt, Sm, Mc, HIV	O–H	δ
		1628[b]	Qz	Si–O	ν
9	1530	1527[b]	Qz	Si–O	ν
		1525[c]	OC (aromatic)	C=C	ν
10	1340	1527[b]	Qz	Si–O	ν
		1350[c]	OC (aliphatic)	C–H	ν
11	1160	1157[b]	OC (polysaccharide)	C–O	ν
		1157[b]	OC (aliphatic)	C–OH	ν
		1157[b]	Kt, Sm, Mc, HIV	O–Al–OH	δ
12	1115	1111[b]	Kt, Sm, Mc, HIV	Si–O–Si	ν
		1111[b]	Gb	Al–O–OH	δ
13	1020	1018[b]	Kt, Sm, Mc, HIV	Si–O–Si	ν_5
14	915	915[a]	Kt	Al–OH	δ
		915[a]	Sm	Al–OH	δ_a
15	808	814[b]	Qz	Si–O	ν
		814[b]	Kt, HIV, Gb	Al–OH	δ
16	698	702[b]	Kt, Sm, Mc, HIV	Si–O	ν

604 Kt, kaolinite; Sm, smectite; Mc, micas; HIV, hydroxy-interlayered vermiculite; Gb, gibbsite; Qz, quartz; OC, organic compounds.
605 [a] Viscarra Rossel and Behrens (2010)
606 [b] Terra (2011)
607 [c] Yang and Mouazen (2012)
608

Table 2. Results of the discriminant function analysis and prediction error for the MIR spectroscopy 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

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

Sediment source	NC	R_{adj}	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

NC, number of components used in the MIR-PLSR model; R_{adj}, coefficient of determination; RMSEC, root mean square error of calibration; RMSEP, root mean square error of prediction; RMSECV, root mean square error of cross-validation; RPD, ratio between the standard deviation and RMSECV.

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

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

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

[a] Tiecher *et al*. (2015)

[b] Tiecher *et al*. (2016)

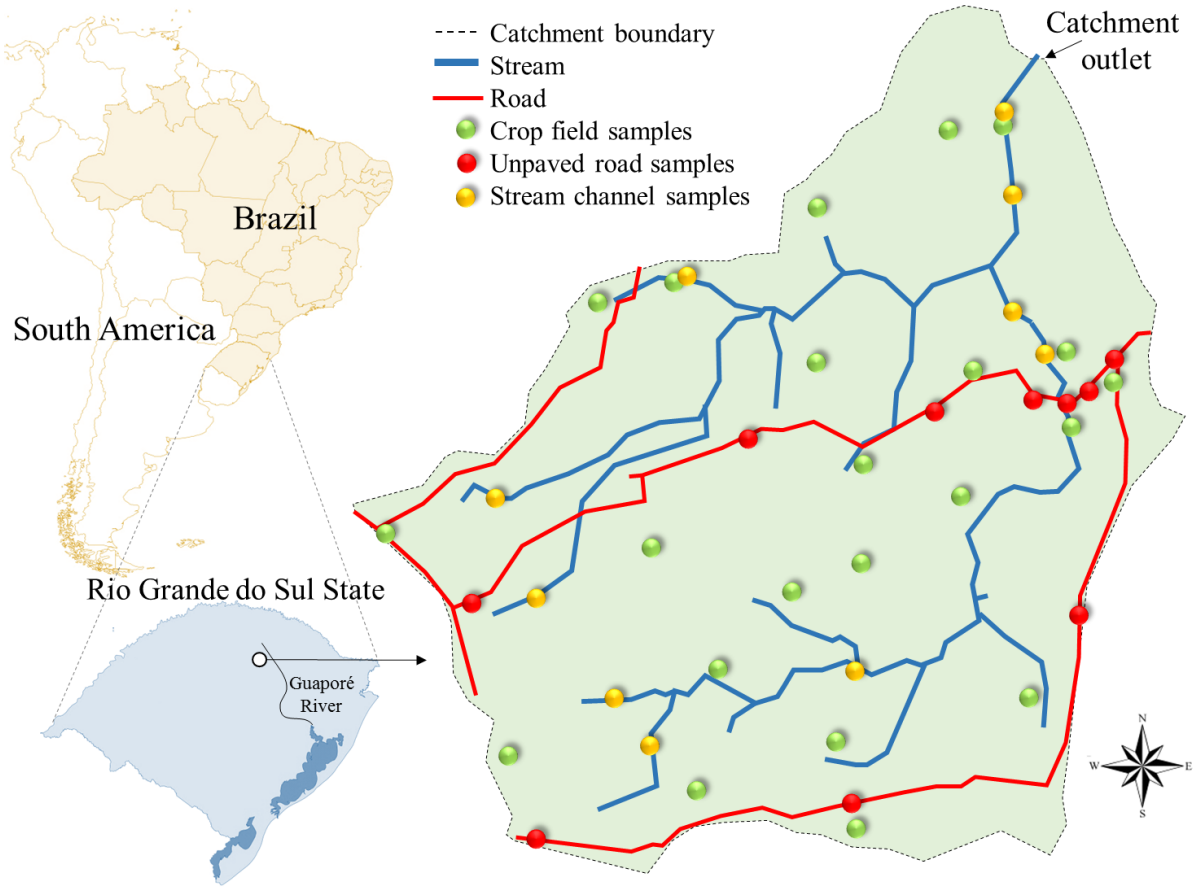


Fig. 1. Location of the Arvorezinha catchment in Southern Brazil, and location of the potential sediment source sampling sites.

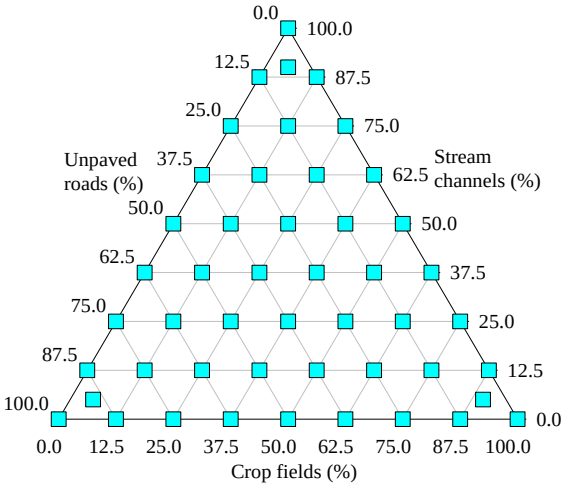


Fig. 2. Ternary diagram showing the composition of the experimental mixtures prepared in the laboratory for the MIR-PLSR model calibration.

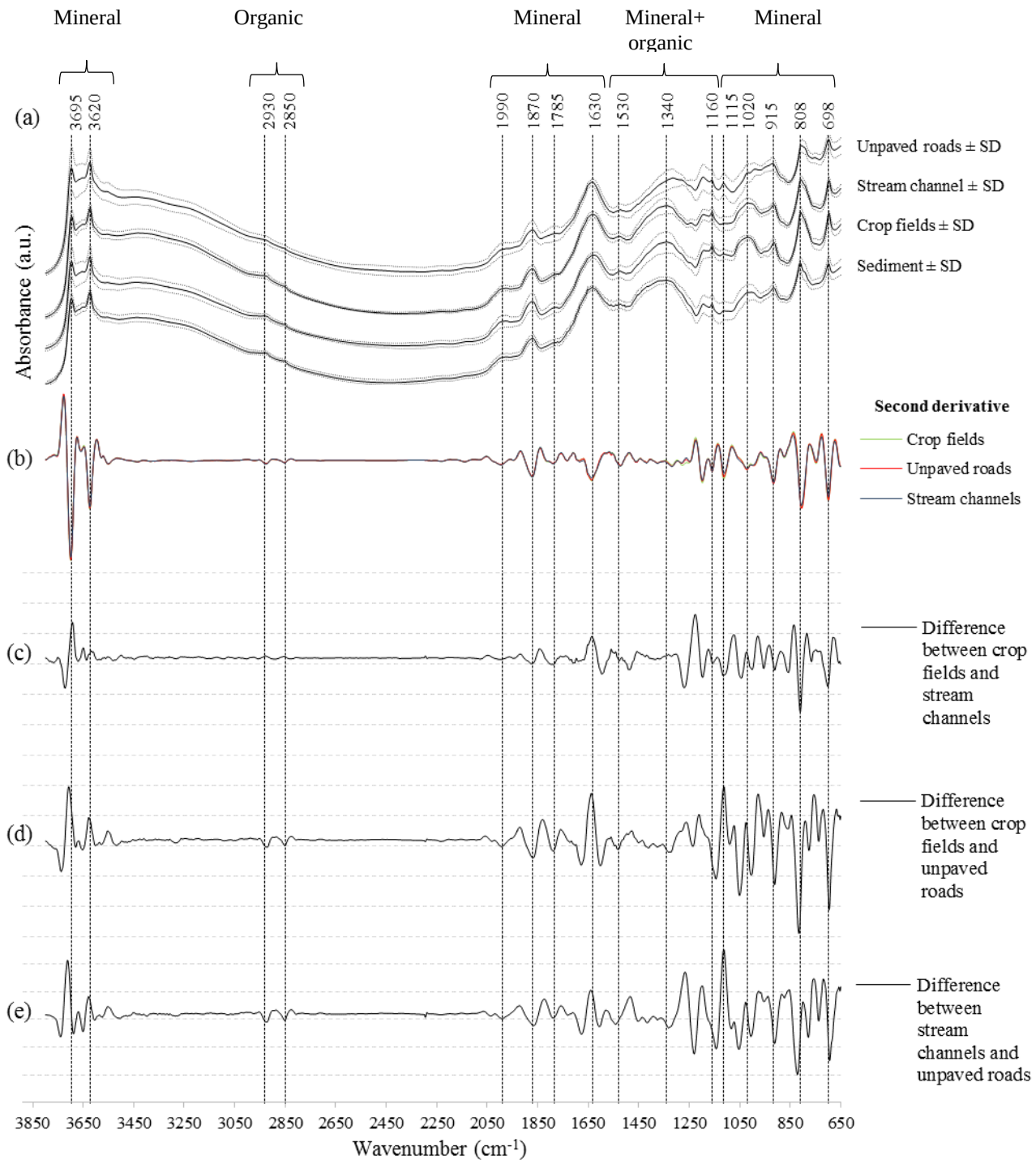


Fig. 3. Mean MIR spectra of the main sediment sources (unpaved road [UR], stream channel [SC], and crop field [CF]) and suspended sediment (a), second-derivative of the UR, SC, and CF (b), difference between CF and SC (c), difference between CF and UR (d), and difference between SC and UR (e).

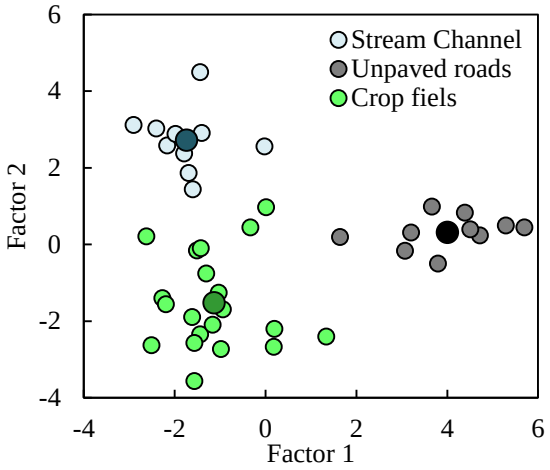


Fig. 4. Two-dimensional scatter plot of the first and second discriminant functions derived from stepwise discriminant function analysis (DFA) applied to MIR spectroscopy. Larger symbols represent the centroids of each source.

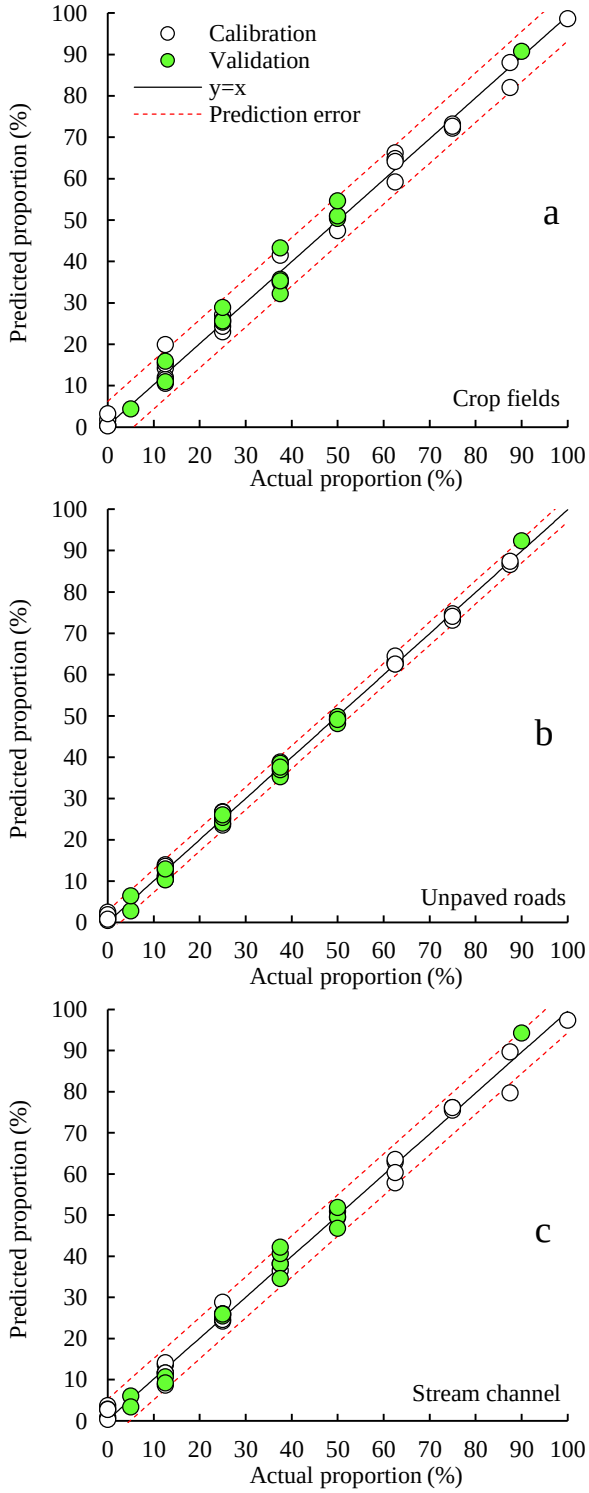


Fig. 5. Relationship between actual proportions of sediment sources and those calculated using MIR-PLSR models in experimental mixtures for crop fields (a), unpaved roads (b), and stream channels (c). Red dashed lines provide the 95-% confidence limits (95%).

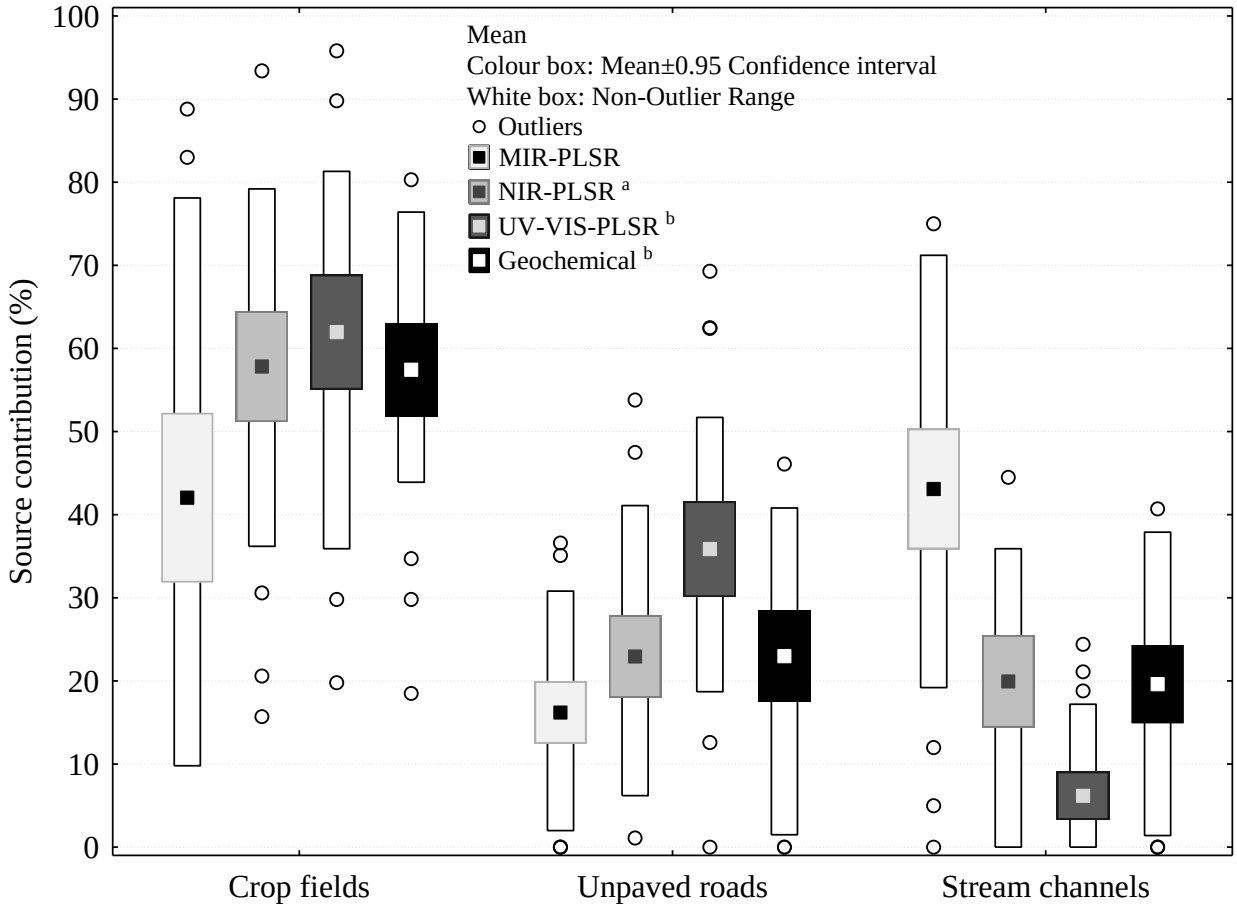


Fig. 6. Box plot of the sediment source contributions for the 29 suspended sediment samples collected at the Arvorezinha catchment outlet, estimated by MIR spectroscopy (this study), NIR-spectroscopy (a – Tiecher *et al*., 2016), UV-VIS spectroscopy and conventional sediment fingerprinting approach based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

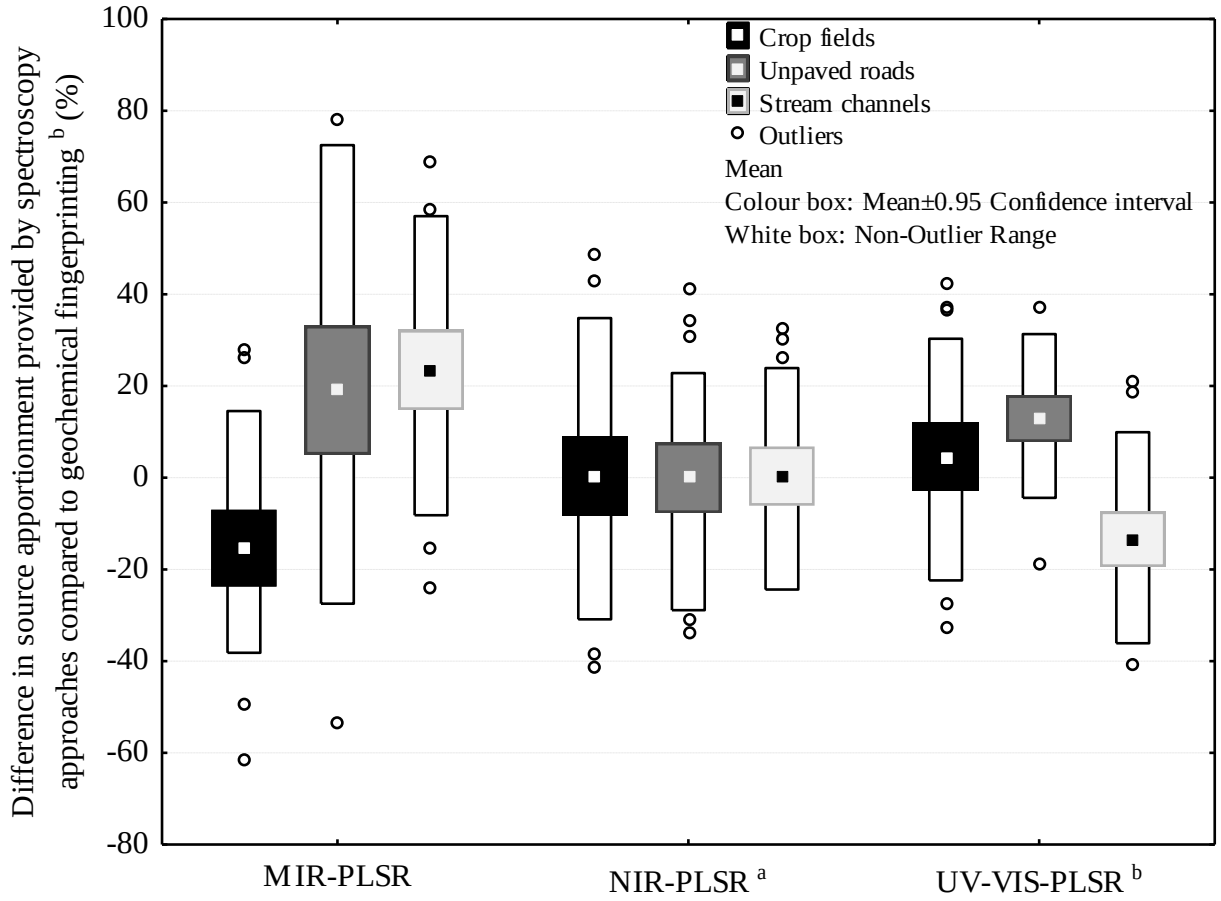
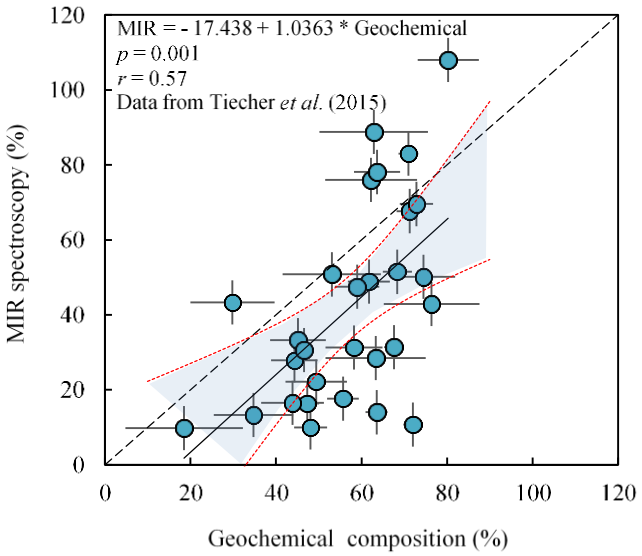


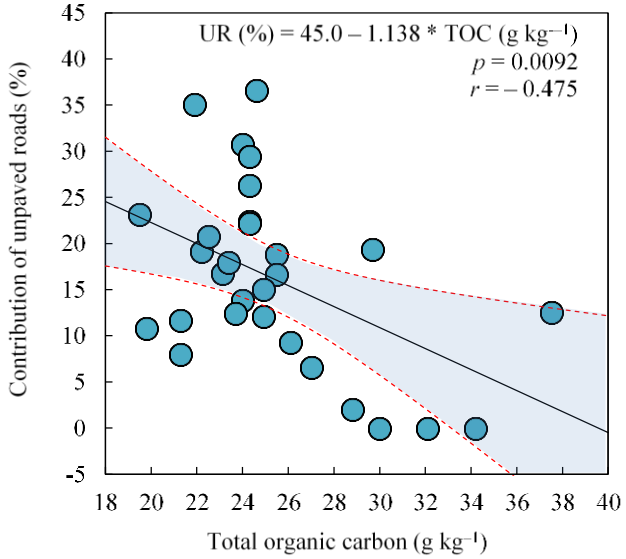
Fig. 7. Box plot of the difference in source apportionment provided by spectroscopy approaches compared to geochemical fingerprinting (Tiecher *et al.*, 2015) for the 29 suspended sediment samples collected at the Arvorezinha catchment.

[a] Tiecher *et al.* (2016)

[b] Tiecher *et al.* (2015)



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