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Combining visible-based-color parameters and geochemical tracers to improve sediment source discrimination and apportionment

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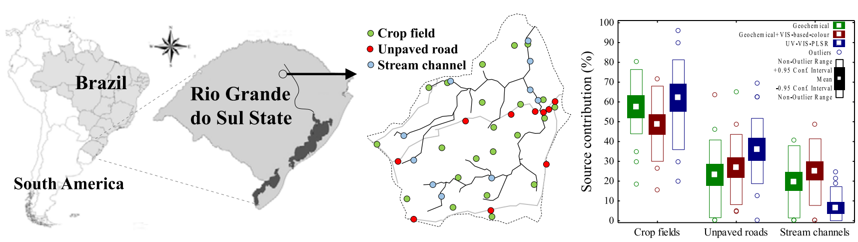
HIGHLIGHTS

- This is the first attempt to combine geochemical tracers and VIS-color parameters.
- Geochemical and VIS-color properties together improved source discrimination.
- Prediction error decreased using both geochemical and color tracers.

GRAPHICAL ABSTRACT



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ABSTRACT

Parameter selection in fingerprinting studies are often time-consuming and costly because successful fingerprint properties are generally highly site-specific. Recently, spectroscopy has been applied to trace sediment origin as a rapid, less expensive, non-destructive and straightforward alternative. We show in this study the first attempt to combine both geochemical tracers and color parameters derived from the visible (VIS) spectrum in a single estimate of sediment source contribution. Moreover, we compared the discrimination power and source apportionment using VIS-based-color parameters and using the whole ultra-violet–visible (UV–VIS) spectrum in partial last square regression (PLSR) models. This study was carried out in a small (1.19 km^2) rural catchment from southern Brazil. The sediment sources evaluated were crop fields, unpaved roads, and stream channels. Color parameters were only able to discriminate unpaved roads from the other sources, disabling its use to fingerprint sediment sources itself. Nonetheless, there was a great improvement in source discrimination combining geochemical tracers and color parameters. Unlike VIS-based-color parameters, the distances between sediment sources were always significantly different using the whole UV–VIS-spectrum. It indicates a loss of information and, consequently, loss of discriminating power when using VIS-based-color parameters instead of the whole UV–VIS spectrum. Overall, there was good agreement in source ascription obtained with geochemical tracers alone, geochemical tracers coupled with color parameters, and UV–VIS-PLSR models, and all of them indicate clearly that the main sediment source was the crop fields, corresponding to 57 ± 14, 48 ± 13, and 62 ± 18%, respectively. Prediction errors for UV–VIS-PLSR models (6.6 ± 1.1%) were very similar to those generated in a mixed linear model using geochemical tracers alone (6.4 ± 3.6%), but the combination of color parameters and geochemical tracers decreases the prediction error (5.4 ± 2.0%). Therefore, the use of VIS-based-color parameters combined to geochemical tracers can be a rapid and inexpensive way to improve source discrimination and precision of sediment source apportionment.

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1. Introduction

Soil erosion is the main cause of soil degradation in Brazil. The fast expansion of agriculture in Brazil has increased erosion rates and sediment yields (Minella et al., 2015), causing many negative environmental and economic impacts, both on- and off-site. A major limitation of most studies of sediment transfer, whether quantitative or qualitative, is the lack of information about the sediment origin (Walling et al., 2013). Information on sediment sources is required for effective sediment control strategies, to understand nutrient and pollutant transport, and for developing soil erosion models (Nosrati et al., 2014), for example in regions with land use conflicts (Pacheco et al., 2014; Valle Junior et al., 2014). Thereby, over the past three decades the approach known as "fingerprinting" has been developed, applied, and improved by researchers worldwide to address the sediment origin (Davis and Fox, 2009; D'Haen et al., 2012; Mukundan et al., 2012; Haddadchi et al., 2013; Walling, 2013).

Fingerprinting approach is based on the fact that the physical and biogeochemical properties (*i.e.*, "sediment fingerprints") of eroded sediments are related to those from potential sediment sources, and therefore, can be used to trace sediment provenance. However, to date, very few sediment source investigations using fingerprinting approaches have been carried out in Brazil (Minella et al., 2007, 2008, 2009a,b; Poleto et al., 2009; Franz et al., 2014; Miguel et al., 2014; Tiecher et al., 2014). One of the reasons for this is that there is no universal recommendation or guidelines for tracer pre-selection because successful fingerprint properties are highly site-specific, making parameter selection time-consuming and costly (Collins and Walling, 2002). Although fingerprinting methods are often of great help in larger watersheds, we applied this approach in a small catchment (1.19 km^2) from Southern Brazil because it presents a highly complex dynamics that hampers the understating of the processes linking the catchment surface to the stream network, making sediment sources unclear.

Spectroscopy in the visible (VIS), near infrared (NIR) and mid-infrared (MIR) ranges has been largely employed during the last decade to quantify physicochemical soil properties as a rapid, timely, less expensive, non-destructive, and straightforward alternative (Viscarra Rossel et al., 2006a). More recently, MIR (Poulenard et al., 2009, 2012; Evrard et al., 2013) and VIS–NIR (Martínez-Carreras et al., 2010a,b; Legout et al., 2013; Brosinsky et al., 2014a,b; Verheyen et al. 2014; Tiecher et al., 2015) spectroscopy has also been applied to trace suspended sediment origin. The prerequisites for use of tracer properties in sediment fingerprinting studies are the conservativeness and the linear additive behavior. Martínez-Carreras et al. (2010a) conducted an experiment using laboratory mixtures and confirmed that linearity for VIS-based-color parameters was achieved. Poulenard et al. (2009, 2012) have demonstrated that MIR spectra remain at least temporarily (*i.e.*, min. 1 month) conservative in the river. Legout et al. (2013) have demonstrated the same for VIS-based color parameters (*i.e.*, min. 2 month).

Overall, source-fingerprinting studies using diffuse reflectance measurements have been conducted in four different ways. Firstly, there are several attempts using VIS-based-color parameters and spectral features to trace sediment origin directly in an optimized mixing model. Briefly, Martínez-Carreras et al. (2010a,c) have shown the potential of color parameters as fingerprint properties for discriminating sediment origin in small catchments from Luxemburg with areas ranging from 0.7 to 4.4 km^2, as well as in larger ones with areas ranging from 19.4 to 247 km^2. In the same way, Brosinsky et al. (2014a,b) used both VIS-based-color parameters and additional 77 spectral features from VIS, shortwave-infrared (SWIR), and NIR diffuse reflectance spectroscopy in a 445 km^2 catchment in the central Spanish Pyrenees. Secondly, Martínez-Carreras et al. (2010b) combined VIS–NIR spectra with partial last-squares regression (PLSR) models to predict the concentrations of geochemical tracers that were then used in an optimized mixing model to trace sediment provenance. A third method consists of using directly the whole spectra to estimate the proportion of the different source materials in suspended sediment samples after conducting a PLSR model calibrated using artificial source material mixtures (French Alps — Poulenard et al., 2009, 2012; Mexico — Evrard et al., 2013; Ethiopia — Verheyen et al. 2014). The fourth attempt used by Legout et al. (2013) combine both VIS spectra and deduced colorimetric parameters in PLSR models calibrated using artificial source material mixtures.

Because the energy of the UV–VIS radiation is high, electronic excitations are the main processes in this spectral region, and generally, due to the broad and overlapping bands, UV–VIS spectra contain fewer absorption features than the MIR region, which may hinder interpretation (Stenberg et al., 2010). Nevertheless, this region contains useful information on organic and inorganic soil constituents, such as the absorptions at 400–780 nm associated to iron oxides (*e.g.*, haematite, goethite), and broad absorption bands assigned to chromophores of organic matter (Stenberg et al., 2010). Although spectroscopic-based fingerprinting have been applied successfully as tracer properties whatever the region used (VIS, NIR, SWIR, and MIR), there are still some points that deserve to be further studied. There is a recognized need to compare the results obtained from VIS-based-color parameters and those from classical fingerprinting based on geochemical tracers and/or radionuclides. However, among all of the above-mentioned studies, only Martínez-Carreras et al. (2010a) made a direct comparison of these methods. Besides, so far, to our knowledge, there has not been any attempt to combine VIS-based-color parameters and geochemical tracers in a single mixed linear model, nor any attempt to compare the use of VIS-based-color parameters and the whole spectra in PLSR for discriminating sediment sources.

In this sense, the present study was carried out aiming to evaluate and to compare the discrimination power and sediment source ascription by using (i) a conventional method based on geochemical composition, (ii) VIS-based-color parameters, (iii) geochemical tracers coupled with VIS-based-color parameters, and (iv) PLSR models based on UV–VIS spectrum, in a small subtropical rural catchment from southern Brazil.

2. Materials and methods

2.1. Study catchment

The study catchment, referred hereafter as the Arvorezinha catchment, is located in the Central-North region of the State of Rio Grande do Sul (RS) (28°52′S and 52°05′W) in Southern Brazil (Fig. 1). The Arvorezinha catchment covers an area of 1.19 km^2 and represents the headwaters of the Taquari River, a tributary of the Jacuí River, which is a major river from RS that supplies the metropolitan region of the RS state which features over 2 million people. The 10 year recorded average sediment yield in the Arvorezinha catchment (from 2002 to 2011), is about 156 t km^{-2} years^{-1} (Minella et al., 2014).

The climate is subtropical super-humid meso-thermic (*i.e.*, Cfb) according to the Köppen classification (Rossato, 2011). There are four relatively well-marked seasons and the mean annual precipitation ranges from 1250 to 2000 mm year^{-1} well distributed throughout the year. The elevation ranges between 560 and 740 m a.s.l. The relief on top of the catchment is wavy (7% slope), and in the middle and lower third is strongly undulating (>15%) with short and steep hillslopes. The time to peak for storm runoff hydrographs typically ranges from 20 to 50 min. The area is underlain predominantly by rhyodacite. The soils are moderately to highly weathered with average depths of about 50 cm (Embrapa, 1999). The soil types in the catchment according to the World Reference Base for Soil Resources (WRB) (IUSS Working Group WRB, 2006) determined from a detailed soil classification survey (1:5000) are Acrisols (57%), Cambisols (33%) and Leptosols (10%). The use and soil management are characterized by the cultivation of tobacco in minimum cultivation (23%), the cultivation of tobacco in the conventional system with plowing (17%), the native forest (20%), afforestation