Soil & Tillage Research 155 (2016) 478–491

Contents lists available at ScienceDirect

Soil & Tillage Research

journal homepage: www.elsevier.com/locate/still

Tracing sediment sources in a subtropical rural catchment of southern Brazil by using geochemical tracers and near-infrared spectroscopy

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ARTICLE INFO

Article history:
Received 6 November 2014
Received in revised form 28 February 2015
Accepted 2 March 2015

Keywords:
Erosion
Modeling
Suspended sediment
Fingerprinting approach

ABSTRACT

Conventional fingerprinting methods based on geochemical composition still require a time-consuming and critical preliminary sample preparation. Thus, fingerprinting characteristics that can be measured in a rapid and cheap way requiring a minimal sample preparation, such as spectroscopy methods, can be a good choice for this purpose. The present study aimed to evaluate the sediment sources contribution in a rural catchment by using conventional method based on geochemical composition and an alternative method based on near-infrared diffuse reflectance (NIR) spectroscopy. This study was carried out in a rural catchment with an area of 1.19 km^2 located in southern Brazil. The sediment sources evaluated were crop fields, unpaved roads and stream channels. Twenty nine suspended sediment samples were collected from nine significant storm runoff events between October 2009 and July 2011. NIR spectra of the sources and the suspended sediment samples were very similar. Nevertheless, the alternative method used to trace suspended sediment based on NIR spectroscopy was sensitive enough to detect differences in mineralogical composition of the sources materials, which were confirmed by X-ray diffraction analyses. Both conventional and alternative methods were able to discriminate the sediment sources and, despite the lack of correlation between the two methods, provided very close source ascription. The differences in the final results obtained by conventional and alternative methods are due to the nature of the variables used in each case, which are not mandatorily correlated. Efforts should be taken to try to combine both geochemical composition and near-infrared spectroscopy information on a single estimative of the sediment sources contribution in order to provide results with an even higher accuracy.

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1. Introduction

Soil erosion is a well-known problem that generates both on-site and off-site effects. On-sites problems are related to the decrease of soil fertility and water holding capacity which have direct effects on crops productivity. Off-sites problems are related to the dams, reservoirs and canals siltation, as well as the degradation of aquatic environments caused by the transport of nutrients and pollutants to the water bodies. The connectivity between the origin of soil erosion and its impacts on the watercourses is not straightforward, as it is governed by complex mechanisms resulting from hydrosedimentological behavior of each river catchment (Minella and Merten, 2011). Therefore, a major limitation of most studies of sediment transfer, whether quantitative or qualitative, is the lack of information about the origin of the sediments (Walling et al., 2013). The knowledge of the spatial pattern of the main diffuse sources of pollution, such as sediment, can increase the efficiency of use of resources invested in management strategies aiming to mitigate the transfer of sediment and adsorbed pollutant to the watercourses. Recently there has been a growing interest in studies aiming to understand spatial patterns of suspended sediment sources in order to have a better description of the connection processes between sediment source and sink as well as the planning of natural resources (Walling, 2013).

The contribution of sediment sources can be estimated by direct and indirect methods. The most common methods are indirect, involving either visual observations (e.g., analysis of aerial photos, Day et al., 2013) or measures of erosive activity (e.g., plots of erosion, Anh et al., 2014). Direct methods for estimating the

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http://dx.doi.org/10.1016/j.still.2015.03.001
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contribution of sediment sources based on the fact that the physical and chemical characteristics of eroded sediments are related to the characteristics of the potential sediment sources. In this case, 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). Even though, the most frequently and successfully used tracers are radionuclides (^{137}Cs, ^{210}Pb, ^{7}Be), and the geochemical composition (Walling and Woodward 1995; Davis and Fox, 2009; D'Haen et al., 2012; Haddadchi et al., 2013). However, traditional analysis such as loss-on-ignition, colorimetry, and total chemical analysis, tend to be expensive, time consuming, and destructive. In addition, these techniques demand high quantities of samples, hindering comparison with suspended sediment samples that are often obtained in low quantities (Cooper et al., 2014). Thus, there is a challenge to develop methods easily applicable to a large number of samples involving minimal sample preparation and also efficient in detecting potential sediment sources.

In order to meet this demand, many studies have been recently developed worldwide using spectroscopic methods to trace sediment sources origin, by using visible reflectance (Legout et al., 2013,b; Martínez-Carreras et al., 2010a,b), visible–near-infrared (VNIR) and shortwave-infrared (SWIR) (Martínez-Carreras et al., 2010c,b; Brosinsky et al., 2014a,b) and by using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in the mid-infrared (MIR) range (Poulenard et al., 2009, 2012; Evrard et al., 2013), as an alternative to the classical geochemical and radionuclides tracers. Tracing primary source materials (geological sub-areas) in a headwater catchment from the French Alps, Legout et al. (2013) found a general good agreement between PLSR models based on visible reflectance and those obtained from a conventional geochemical fingerprinting method (Navratil et al., 2012). Martínez-Carreras et al. (2010a) found a good consistency comparing suspended sediment source ascriptions based on color parameters obtained from visible reflectance and ascriptions based on classical fingerprinting parameters based on geochemistry and radionuclides in three small catchments from Luxemburg. Moreover, Evrard et al. (2013) made a direct comparison of the classical fingerprinting approach, based on the use of geochemical and radionuclides tracers, and an alternative method using partial least-squares regression (PLSR) based on MIR spectroscopy, in rural catchments from Mexico. They found similar results from both methods in two of the three catchments studied. In one of the three catchments, however, the results were quite different because MIR spectroscopy was very sensitive to the organic matter content in sediment samples. On the other hand, Verheyen et al. (2014) found that fingerprinting based on VNIR spectra offers great potential for tracing sediment provenance and the values obtained are comparable to more established techniques such as those based on geochemical fingerprints.

The NIR region is characterized by broad, superimposed, and weak vibrational modes, giving soil NIR spectra few broad absorption features, which makes the NIR spectra difficult to interpret (Stenberg et al., 2010). Nevertheless, this region contains useful information on organic and inorganic composition in the soil. Although the results clearly demonstrate the potential for using spectroscopy to identify the origin of sediments in catchments, the method must be applied in other geological and land-use settings in order to test its general applicability to sediment fingerprinting. Moreover, the results should also be compared with those provided by classic geochemical fingerprinting methods. Besides, so far, to our knowledge, there was one attempt to directly compare results from NIR spectroscopy and geochemical

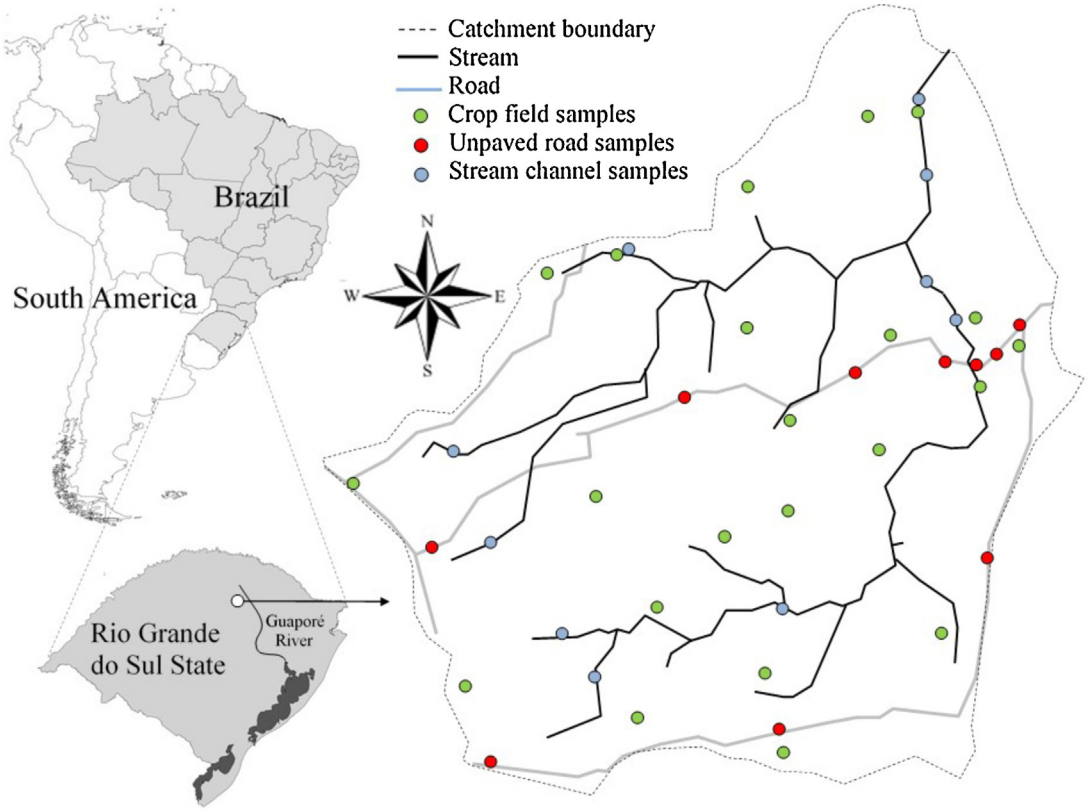

Fig. 1. The location of the Arvorezinha catchment and sampling sites.

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