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Monitoring land use impacts on sediment production: a case study of the pilot catchment from the Brazilian program of payment for environmental services

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ABSTRACT: Through the lack or non-use of conservationist criteria for adequate land use and management, the scarcity of natural resources becomes ever more evident. This study aimed to analyze the origin of the sediments in the Posses catchment, municipality of Extrema, state of Minas Gerais, Brazil, throughout the fingerprinting technique and portable X-ray fluorescence. Samples from soils under agriculture, pasture, and roads; and from the subsoil of theses land uses were taken in a widespread and representative manner from the entire Posses catchment. Lag deposits and river bed sediment samples were collected downstream from the catchment outlet. A total of 45 geochemical elements were analyzed in the samples by a portable X-ray fluorescence device (pXRF). The outlier test, Kruskal-Wallis test, multivariate discriminant analysis, and a mixing model were used to estimate the contribution of each source in relation to the sediments that arrive at the mouth of the catchment. The elements selected as geochemical tracers were Sr, Al_2O_3, Ba, Rb, Ti, Fe, and Zn, which combined correctly discriminated 81 % of the sediment sources. The largest and smallest proportion of sediment from the Posses catchment outlet comes from rural roads and agriculture, respectively. The contribution of the subsoil was higher for lag deposits or lower for river bed sediments, than the pasture. There was a low degree of uncertainty (<8 %) for predictions made by the model employed. The types of use, selected as potential sediment sources in the Posses catchment, are adequately discriminated through the geochemical tracers quantified through the pXRF. The fingerprinting technique estimates that the contributions to outlet sediments are dominated by rural roads, following by subsoil or pasture (depending on the type of sediment evaluated) and by agriculture. The sediment sampling strategies used in this study provided similar results for the period studied. Our results showed the potential of the fingerprinting technique and the pXRF for use as tools by the program of Payment for Environmental Services in the monitoring of catchment areas.

Keywords: fingerprinting, soil erosion, rural roads, ecosystem service.

INTRODUCTION

The scarcity of natural resources becomes ever more evident to the extent that catchments are exploited without the adoption of adequate conservationist criteria. In this context, one of the phenomena that has intensified is water erosion and, along with it, a series of problems, such as siltation and pollution of streams and rivers. They not only receive sediments from erosion, but also transport them, compromising the quality of locations even though distant from the areas that gave rise to the process. Thus, knowing the sources, the mechanisms, and the agents involved in the transfer of sediments that arrive at the mouth of watercourses becomes a crucial step in the management of catchments.

Faced with water deficit crises that have occurred in recent years in various regions of Brazil, affecting large metropolitan areas such as the city of São Paulo (Richards et al., 2015), the National Water Agency (ANA - acronym in Portuguese) developed the Payment for Environmental Services (PES) program and then selected Posses as the pilot catchment. Located in the municipality of Extrema, state of Minas Gerais, Brazil, Posses is within the Jaguari River catchment – an important contributor to the reservoir that provides water to more than 10 million people in the metropolitan region of São Paulo city, the Cantareira System (Pereira et al., 2010). Through the PES, rural producers received a financial incentive to adapt their properties to reduce erosion, silting, and pollution of water sources in the rural area. This stimulus has been implemented based only on the "opportunity cost" and is still in a refinement stage. For that reason, knowing and discriminating the contribution of each one of the sediment sources produced may be a good option for the lack of quantitative criteria applicable to evaluation and monitoring of impacts, positive or negative, of the management practices adopted on the rural properties monitored by the PES (Saad et al., 2018).

The identification of the origin of sediments may improve understanding of their dynamics in the environment, which is an essential step in the strategic process of control of the processes through which they were generated (Merten and Minela, 2011). In general, the techniques of tracing these sediments involve direct measurements of, for example, erosion (Laubel et al., 1999). The traditional fingerprinting methods have also often been used through properties inherent to the soil (geochemical, mineralogical, and magnetic), radionuclides, stable isotopes (Nosrati, 2017), and sediment markers, such as rare earth elements (Stevens and Quinton, 2008). Recent advances in sediment tracing techniques have been described in various studies, as in Batista et al. (2019).

Fingerprinting uses a statistical approach, applied to the variables measured in samples of the sources and of the sediments coming from them to discriminate the relative contribution of each one of these sources to the sediment produced in a catchment. It is a technique that has been successfully used in a wide variety of contexts. For example, it has been used to verify the contribution of potential sediment sources based on land use (Tiecher et al., 2017), on geology (Laceby et al., 2015), and soil types (Le Gall et al., 2017) within a catchment, or even in types of contaminants associated with human health (Owens et al., 2016). It has also been successfully used in distinguishing spatially distributed sources, including individual tributary catchments (Walling et al., 1999). In large catchments, the diversity of geology, which is usually considerable, makes it easier to obtain good tracers. In smaller catchments, differences in tracers generally result from the type of land use and the intensity of the erosive phenomenon (Merten and Minela, 2011).

The fingerprinting technique uses the qualitative dimension of samples from source areas and from sediments through a detailed examination of various attributes analyzed in these samples (Collins et al., 1996). Therefore, a larger number of tracers can reduce the uncertainty and increase the discrimination ability of the sediment sources. Nevertheless, the high cost and time spent to obtain many of these tracers may make the use of this method unfeasible. In that regard, equipment able to analyze and generate a large amount of data in a fast and practical manner, such as the portable X-ray fluorescence scanner (pXRF), maybe a good alternative, even though it is little used in studies of this nature.

The pXRF is a class of sensors able to identify and quantify a wide diversity of chemical elements and compounds present in the soil and sediments in real-time, *ex situ* or *in situ* (Hseu et al., 2016). This quantification occurs through the fluorescence energy that is characteristic of each element present in the soil or sediment analyzed. The pXRF sensors provide good analytic precision (Stockmann et al., 2016) and have been successfully used in pedological studies, in soil and water contamination studies, and for diverse environmental studies (Silva et al., 2016; Wu et al., 2016). Despite the wide applicability of this sensor, it has not been explored by PSE programs in the management of sediment source areas, making it of practical and scientific interest to combine the fingerprint technique with the pXRF sensor.

An international debate continues regarding the need for continued refinement of the fingerprinting technique for tracing sediments in an attempt to resolve specific questions (Koiter et al., 2013; Walling, 2013). Nevertheless, although this technique is increasingly used throughout the world, its potential has not yet been explored in Brazil outside of the South of country, and even less in the context of programs such as PES. For example, PES managers can use the fingerprinting technique to monitor the contribution of each rural property for the total sediments produced in the catchment and thus decide how much each farmer will receive for contributing to reduce sediment yield over time. Thus, the aims of this study were to analyze the origin of the sediments in the Posses catchment, municipality of Extrema, state of Minas Gerais, Brazil, throughout the fingerprinting technique and portable X-ray fluorescence, and to provide scientific subsidies for improvement of the PES and incentives for its application in other catchments in Brazil.

MATERIALS AND METHODS

Study area

The Posses catchment covers an area of 1,200 ha, with altitudes from 1,144 to 1,739 m, in the municipality of Extrema, in the South of Minas Gerais (Figure 1). The climate is Cfb (Köppen classification system), humid subtropical with mild summers. The mean annual temperature is 18 °C and the mean rainfall is 1,477 mm yr^{-1}, concentrated in October to March.

Posses is a catchment of the Jaguari River, one of the important rivers that contribute to the complex of reservoirs of the Cantareira System. The geology is characterized by two distinct geological formations composed of gneissic granite and migmatite (CPRM, 2015), with the latter occupying the greater area of the catchment (Figure 2). According to the Brazilian Soil Classification System (Santos et al., 2018) and US Soil Taxonomy (Soil Survey Staff, 2014), respectively, the soils in the area were classified as *Argissolo Vermelho* (Typic Rhodudult), *Argissolo Vermelho-Amarelo* [Typic Hapludult* (red-yellow)], *Cambissolo Háplico* (Typic Dystrudept), *Gleissolo Háplico* + *Cambissolo Flúvico* (Typic Endoaquent + Fluventic Dystrudept), *Argissolo Amarelo* [Typic Hapludult (yellow)], and *Latossolo Vermelho* + *Latossolo Vermelho-Amarelo* (Rhodic Hapludox + Typic Hapludox). They cover about 56, 13, 10, 10, 9, and 2 % of the area, respectively (Silva et al., 2019). The main relief classes are steep and very steep.

About 78 % of the area of the catchment is under old, degraded pastures, 7 % is under agricultural crops (corn, dry edible bean, potato, vegetable crops, eucalyptus, etc.), 14 % is under forests, and the rest under roads that are unpaved or devoid of vegetation. It is an area characterized by only a small proportion of riparian forests. In addition, the roads were built without adequate planning, many of them placed in positions prone to receive water flow, making them important sediment sources.

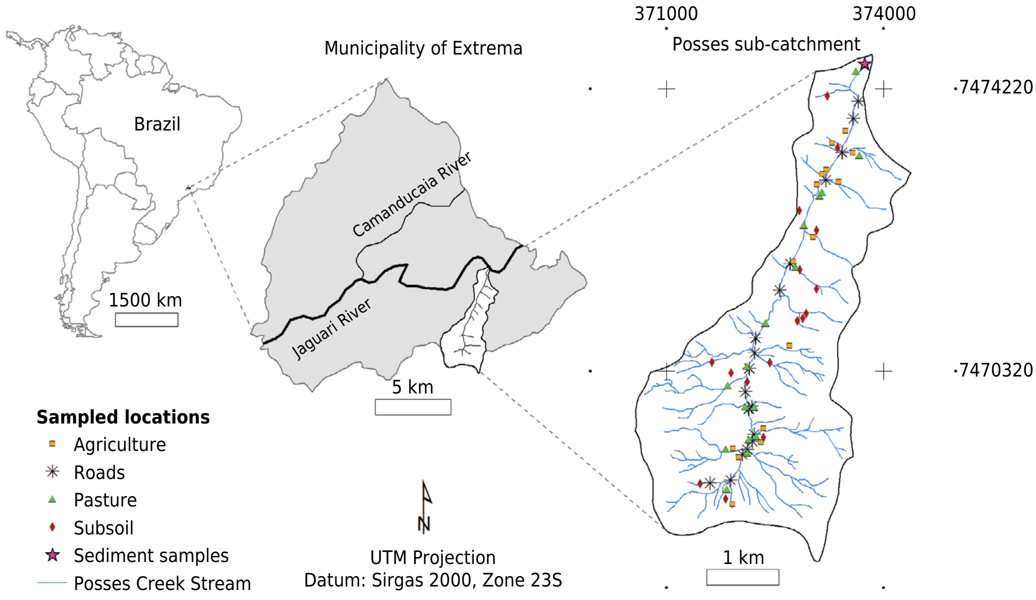

Figure 1. Geographic location of the Posses catchment and the collection points of samples of sources and sediments used in the fingerprinting study.

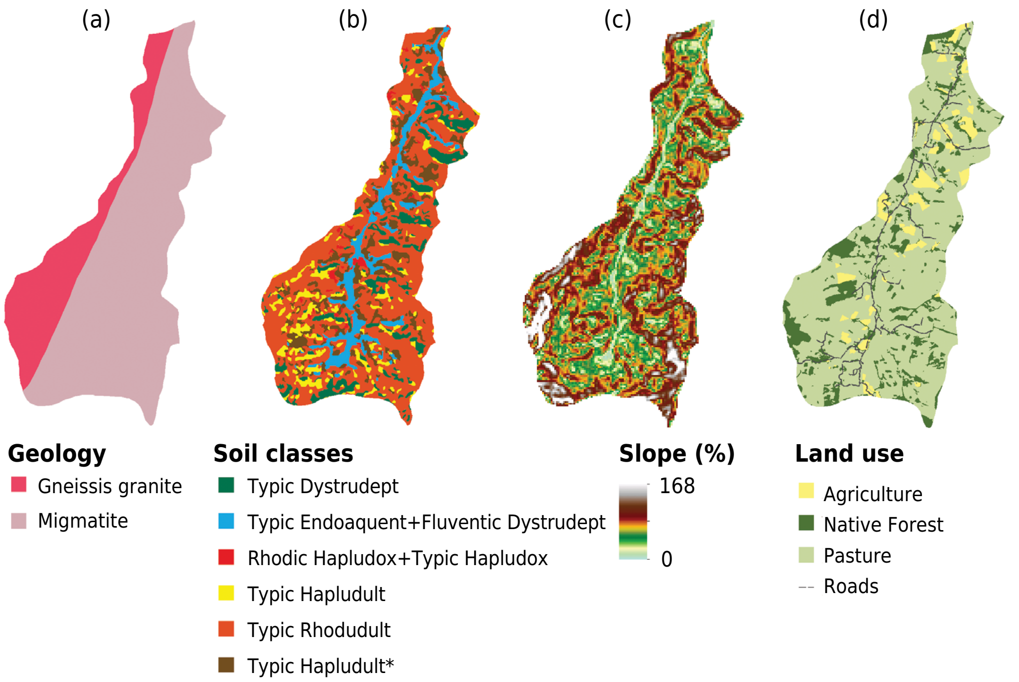

Figure 2. Geology (a), soil types (b), slope (c), and land use (d) that predominate in the Posses catchment. Source: adapted from CPRM (2015), Bispo et al. (2017), and Silva et al. (2019).

Sampling

The selection of collection locations and the potential sediment sources was based on orbital images freely available from Google Earth and on observations of the process of removal, transport, and mobilization of sediments through field visits. A sampling of sources was carried out in September 2017, at the end of an extended dry period (Figure 3), and therefore the best time to access collection points, since the relief of the hydrographic basin is very steep.

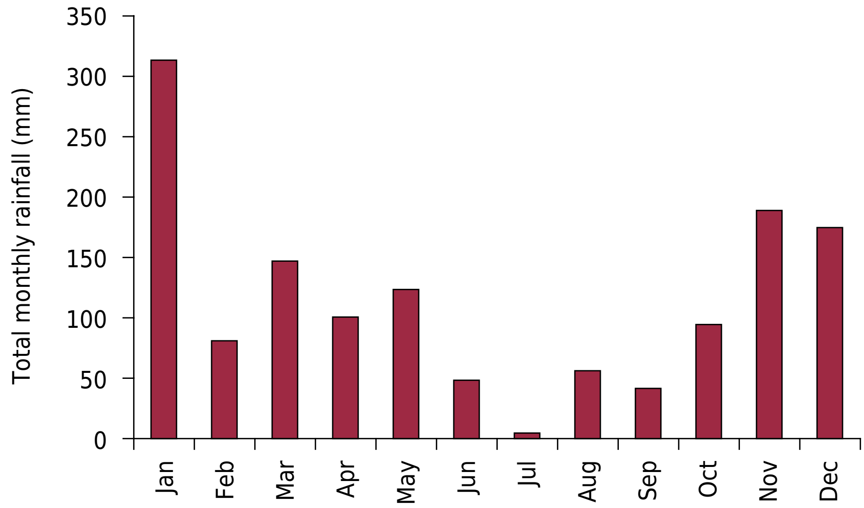

Figure 3. Distribution of total monthly rainfall (mean of the values obtained from the stations, codes 2246168, 2246169, 2246167, 2246171, 2246170, and 2246175, distributed across the Posses catchment) for the year 2017.

Sampling was stratified to cover the four main potential sediment sources that arrive at the mouth of the Posses catchment. These sources included areas under agriculture (Figure 4a), degraded pasture (Figure 4b), unpaved rural roads (Figure 4c), and subsoil (furrows, gullies, and cattle paths that cut the underlying subsoil and regolith) (Figure 4d). Inclusion of subsoil as a source aimed to clarify the effect of severe erosion, which has been a consequence of intense cattle traffic in a large part of the study area, as well as deforestation followed by the abandonment of areas that are sloped and highly susceptible to the erosion process. Figure 1 provides a detailed view of the distribution of the sampling points of both the sediment sources along the catchment and the deposited sediments at the outlet of the catchment under study.

Samples of soils under agriculture (n = 15), pasture (n = 16), and roads (n = 18) were collected in the upper 0.02 m of the soil profile, a depth that is, therefore, more susceptible to mobilization by water erosion and subsequent transport to and within fluvial channels. The subsoil (n = 16) was sampled through scraping across the entire vertical extension of the exposed soil profile, thus avoiding over-representation of the soil surface layers (Collins et al., 2013), taking care not to allow sample contamination from displaced surface material or sediments deposited over the subsoil.

Each sample (~500 g) was composed of 10 combined sub-samples, which were collected in a radius of approximately 20 m from each central sampling point with a polyethylene spatula that was repeatedly cleaned to avoid contamination among samples. The samples were placed in plastic bags before being taken to the laboratory.

To obtain the relative importance of agriculture, pasture, rural roads, and subsoil material as sediment sources, lag deposits and river bed sediment samples were collected downstream from the Posses catchment outlet (Figure 1). The lag deposits are referred to as contemporary drapes sediments located on riverbanks and formed after recent floods (Batista et al., 2019). They may be more linked to the changes that have occurred within a short recent period of time, whereas the river bed sediments may reflect the mean production of sediments over a relatively long time (Nosrati, 2017). A sampling of these materials was also performed with a polyethylene spatula, and the samples were then placed in plastic bags. To ensure representativeness, samples composed of a combination of ten subsamples were collected across a length of approximately 20 m in the drainage channel of the stream. To better reflect the relationship between recent production (lag deposits) and "old" production (river bed) of sediments and their

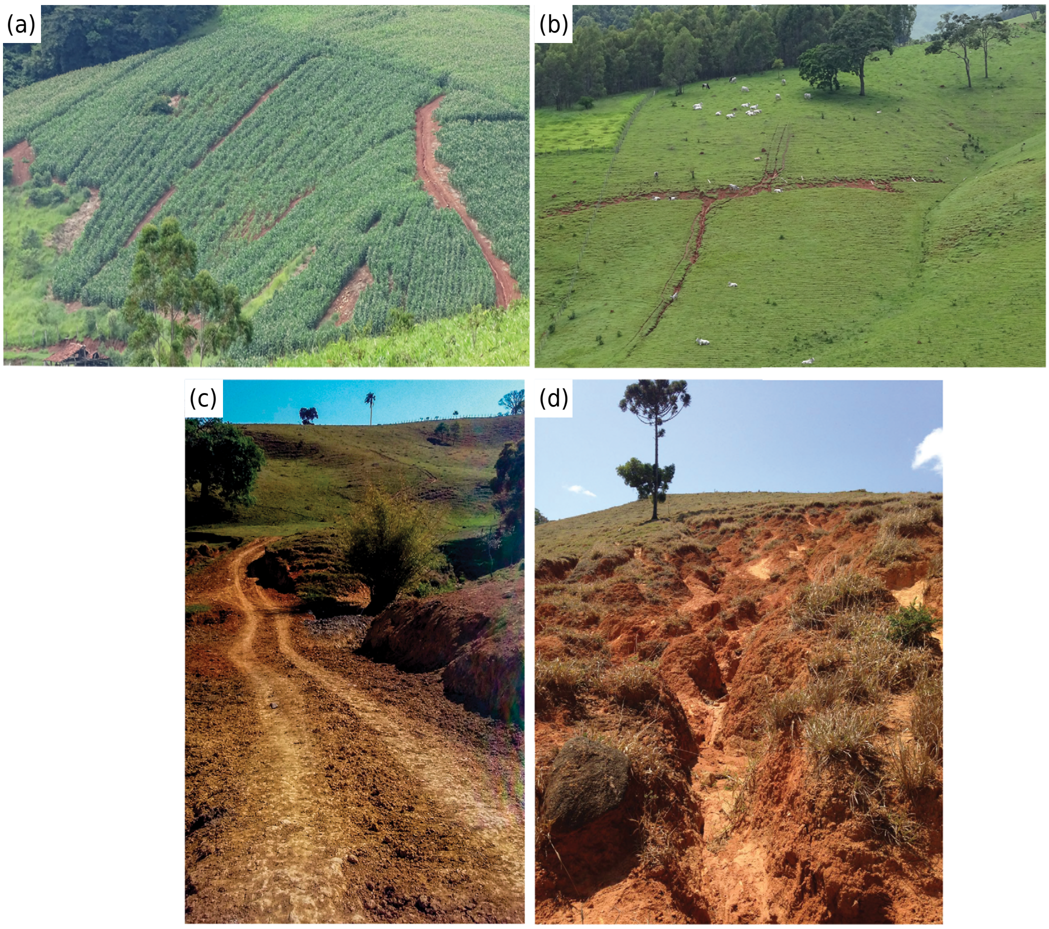

Figure 4. Downslope cultivated cornfield (a), eroded cattle trails (b), steep rural roads with no conservation planning (c), deep rills, and small gullies found at degraded pastures (d) in the Posses catchment, Extrema-MG.

source areas, sediments were collected at 0.00-0.01 m layer and 0.00-0.05 m layer in the bed and at the bottom of the Posses creek, respectively.

Laboratory analyses

All the samples were dried in a laboratory oven at 40 °C, broken up manually with a mortar and pestle, and dry sieved through a 63-µm mesh to allow direct comparison between the samples from the sources and the sediments. This standardization reduces uncertainties related to dilution in the concentration of chemical elements due to the presence of coarse particles, taking into consideration that finer materials are more susceptible to transport through erosion processes (Tiecher et al., 2017). This choice is also justifiable due to the predominance of more clayey soils in the study area (Figure 2).

A group of geochemical properties was selected for analysis to allow the acquisition of a set of tracers more efficient in discrimination of sources but that have individual properties responsive to environmental changes. A total of 45 geochemical properties were included in the analytical program. Concentrations (in ppm) of Ag, Al_2O_3, As, Au, Ba, Bi, CaO, Cd, Ce, Cl, Co, Cr, Cu, Fe, Hf, Hg, K_2O, La, Mg, Mn, Mo, Nb, Ni, P_2O_5, Pb, Pd, Pt, Rb, Rh, S, Sb, Se, SiO_2, Sn, Sr, Ta, Th, Ti, Tl, U, V, W, Y, Zn, and Zr were determined through a portable X-ray fluorescence device, the pXRF Bruker® (S1 Titan LE). This piece of equipment contains a Rh tube (4 W, 15-50 KeV, and 5-100 µA) and SSD with resolution <145 eV.

Each sample was placed in a polyethylene bag and was scanned in triplicate on the pXRF in the "Trace" operational mode for 60 s for determination of the concentrations of the geochemical elements cited above. The concentrations of Al, Ca, K, P, and Si were expressed in terms of specified oxides of these elements.

Quality control (precision and bias) of the chemical analyses was monitored using four certified reference materials (NIST - National Institute of Standards and Technology, San Joaquin Soil 2709a, Montana I Soil 2710a, and Montana II Soil 2711a). The results obtained from these analyses were within the ranges certified for these materials, which showed the consistency of the analytical procedures (recovery >85 %).

Selection of the geochemical tracers and discrimination of sediment sources

One of the main requirements for the success of the fingerprinting technique is obtaining a set of tracers that can efficiently discriminate the sediment sources. In this respect, the following elements with concentrations lower than the detection limit of the pXRF were excluded: Ag (<10 ppm), As (<3 ppm), Au (<7 ppm), Bi (<12 ppm), Cd (<19 ppm), Ce (<35 ppm), Co (<5 ppm), Cr (<19 ppm), Hf (<6 ppm), Hg (<6 ppm), La (<166 ppm), Mg (<7000 ppm), Pd (<29 ppm), Pt (<7 ppm), Rh (<15 ppm), S (<80 ppm), Sb (<30 ppm), Se (<3 ppm), Sn (<20 ppm), Ta (<4 ppm), Th (<17 ppm), Tl (<5 ppm), U (<53 ppm), and W (<6 ppm).

In each source group, each tracer was tested for normality (Shapiro-Wilk test at 0.05 significance), and those that did not follow normality were log-transformed. The discrepant values (outliers) were excluded through exploratory evaluation of the data. After that, the variables with values in the samples of the sources outside of the interval of the values obtained for the sediments were excluded, as recommended by Zhang and Liu (2016). This procedure is known as the "bracket test" or "range test".

The geochemical tracers that passed in the aforementioned tests advanced to the non-parametric Kruskal-Wallis test or H test to select the elements able to individually discriminate at least two different types of sources sampled. The null hypothesis of the test is that all the sediments originate from the same population (source). Tracers with p-value ≤0.05 can discriminate sources and be used in the next steps.

In the second stage, linear discriminant analysis (niveau = 0.1) was performed to select an optimal subset of tracers, those that passed the Kruskal-Wallis test, capable of minimizing the probability of incorrect classification (classification error) of the samples within each one of the groups (sources) sampled. This analysis was based on the minimization of the Wilks' lambda and carried out by the "stepwise" procedure.

Estimation of the relative contribution of the sediment sources

After defining the ideal set of discriminant variables (tracers), a mixing model, described in Walling (2005), was used to estimate the contribution of each source in relation to the sediments that arrived at the mouth of the catchment studied. The function used (Equation 1) in the multivariate mixing model was:

$$Y_i = \sum a_{is} P_s \qquad \text{Eq. 1}$$

in which Y_i is the concentration of the tracer i in the sediment; a_{is} is the mean concentration of the tracer i in source s; and P_s is the relative contribution of the sources in relation to the sediment.

The model assumes that the sediment has the same characteristics as its source and that this sediment comes only from the material of the sources identified. It was solved through an iterative process (5,000 interactions) with 10,000 random samples obtained from the distributions constructed with the original values. In this process, the contribution of each potential source is obtained when the sum of squares of the relative errors of the algorithm (Equation 2) is minimal.

$$\sum_{i=1}^{m} \left\{ \frac{Y_i - (\sum_{s=1}^{n} a_{is} P_s)}{Y_i} \right\}^2 \qquad \text{Eq. 2}$$

in which m is the number of tracers used and n represents the number of sources.

During the minimization process, the P_s values were under the following restrictions: (i) P_s must be a non-negative value, but at most 1 ($0< P_s \leq 1$); and (ii) the sum of the P_s of all the sources must be equal to 1 (100 %). The robustness of the optimized solutions provided by the multivariate mixing model was evaluated by comparison of the results obtained by the model with the values observed in the samples, a procedure known as “goodness of fit” (GOF), described by equation 3. The results of a mixing model are generally acceptable when the GOF >0.8.

$$GOF = 1 - \left\{ \frac{1}{n} \sum_{i=1}^{n} \left(\left| Y_i - \sum_{s=1}^{m} a_{is} P_s \right| / Y_i \right) \right\} \qquad \text{Eq. 3}$$

RESULTS

The mean concentrations of the 21 geochemical tracers analyzed and with concentrations higher than the detection limit of the pXRF can be seen in table 1. The concentrations of Cu, Mn, Mo, and Zr in most of the sediment samples, especially river bed sediments, were higher than the highest concentrations in the source samples (Table 1). In contrast, the concentrations of P_2O_5 and Pb were lower in most of the sediment samples compared to the source samples. These elements were then considered as non-conservative and, therefore, were not included in the later steps.

Even passing the bracket test, CaO and K_2O were also excluded because exhibiting non-conservative characteristics during the erosion process (Tiecher et al., 2017). They are found in soils with a high degree of weathering, as it is the case of the Posses catchment, normally associated with clay and organic matter in outer-sphere complexes (Sparks, 2003). Therefore, they are highly soluble and for that reason, are less conservative during the process of erosion and transport in fluvial channels. Chlorine was also removed, as it has much less conservative behavior than Ca and K, due to the predominant negative charges in Brazilian soils.

Table 2 shows the results of the Kruskal-Wallis test applied to the 12 tracer elements associated with the sediments and that passed previous steps. Five of them (Al_2O_3, Fe, Rb, Sr, and Y) were selected as tracers able to individually differentiate at least two sources ($p \leq 0.05$).

The discriminant capacity of the geochemical elements in relation to the sediment sources was then re-evaluated using Wilks’ Lambda test (Table 3). Although Ba, Ti, and Zn did not pass the Kruskal Wallis test, they were included in the discriminant analysis because they considerably increased the accuracy of the model. Without these elements, only 56 % of the samples of the sources selected were correctly classified. Thus, the final set of elements selected as geochemical tracers of sediments in the Posses catchment was composed of Sr, Al_2O_3, Ba, Rb, Ti, Fe, and Zn.

As the Wilks’ Lambda value represents the proportion of the total variability of the sources because of error, the set of the seven variables selected provided an error of 14 %; in other words, the set of variables selected explains approximately 86 % of the differences among the sources (Table 3). Nevertheless, the percentage of samples correctly classified in their respective groups (sources) was 81 %.

Table 1. Mean and standard deviation (SD) of the concentrations of geochemical tracers analyzed in sediment samples (Bed – river bed sediments; Lag – lag deposits) and in their potential sources in the Posses catchment

Tracer		Bed (n=1)	Lag (n=1)	Agriculture (n=15)		Pasture (n=16)		Roads (n=18)		Subsoil (n=16)		LOD
		Mean	Mean	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Al_2O_3	g kg^{-1}	107	115	105	25	123	19	122	22	140	20	1.8
Ba	mg kg^{-1}	769	771	628	282	725	261	700	127	583	229	188
CaO	g kg^{-1}	4.9	5.2	3.2	1.6	4.2	2.9	8.8	3.5	1.4	0.9	0.05
Cl	mg kg^{-1}	553	748	689	199	779	304	600	150	510	90	135
Cu	mg kg^{-1}	39	20	25	3.5	21	4.7	22	5.1	17	3.5	5.0
Fe	g kg^{-1}	51	53	44	14	47	12	46	9.5	62	13	0.01
K_2O	g kg^{-1}	17	17	13	7.1	15	6.4	20	5.6	8.6	4.1	0.05
Mn	g kg^{-1}	0.9	1.2	0.5	0.2	0.6	0.2	0.5	0.1	0.5	0.3	0.02
Mo	mg kg^{-1}	23	12	9.1	3.5	9.2	4.0	13	5.1	7.9	3.5	6.0
Nb	mg kg^{-1}	16	16	17	7.6	16	4.6	17	3.3	15	6.4	2.0
Ni	mg kg^{-1}	17	12	15	5.7	16	5.3	11	7.7	19	9	5.0
P_2O_5	mg kg^{-1}	211	1158	1497	481	1261	347	1030	241	1035	237	206
Pb	mg kg^{-1}	16	32	28	8	31	6	29	6.3	30	7.6	11.0
Rb	mg kg^{-1}	79	82	64	32	74	35	102	26	46	24	3.0
SiO_2	g kg^{-1}	411	394	343	51	352	49	365	49	327	48	1.1
Sr	mg kg^{-1}	131	141	127	34	133	49	176	41	92	29	4.0
Ti	g kg^{-1}	11	8.9	10	3.5	10	2.4	9.5	1.5	10	1.3	0.02
V	mg kg^{-1}	95	72	78	29	95	33	96	22	82	42	8.0
Y	mg kg^{-1}	21	19	18	5.9	21	7.6	25	5.7	21	6.7	4.0
Zn	mg kg^{-1}	61	59	55	9.0	63	18	57	12	52	13	3.0
Zr	mg kg^{-1}	1813	827	449	92	573	283	725	193	417	158	3.0

LOD: lower than the limit of detection for each element determined by pXRF sensor.

Table 2. Efficacy of the individual geochemical tracer elements in distinguishing the sediment sources in relation to land use in the Posses catchment, evaluated through the H test of Kruskal-Wallis. Acceptance requires a p-value≤0.05

Tracer	H-value	p-value
Al_2O_3	16.5	0.00
Ba	4.4	0.22
Fe	14.0	0.00
Nb	2.2	0.53
Ni	7.9	0.05
Rb	22.6	0.00
SiO_2	6.7	0.08
Sr	26.2	0.00
Ti	1.5	0.69
V	4.5	0.21
Y	9.1	0.03
Zn	3.6	0.31

The relative contributions of the sediment sources are displayed in figure 5. In general, the source contribution for lag deposits and river bed sediment collected downstream from the Posses catchment outlet were rural roads > subsoil > pasture > agriculture

Table 3. Set of tracers able to discriminate the sediment sources in relation to land use in the Posses catchment, selected through a discriminant function using Wilks' Lambda in a stepwise procedure

Tracer	Step	Wilks' Lambda	Samples of correctly classified sources
			% accumulated
Sr	1	0.607	44
Al_2O_3	2	0.453	62
Ba	3	0.364	66
Rb	4	0.300	69
Ti	5	0.232	75
Fe	6	0.197	75
Zn	7	0.144	81

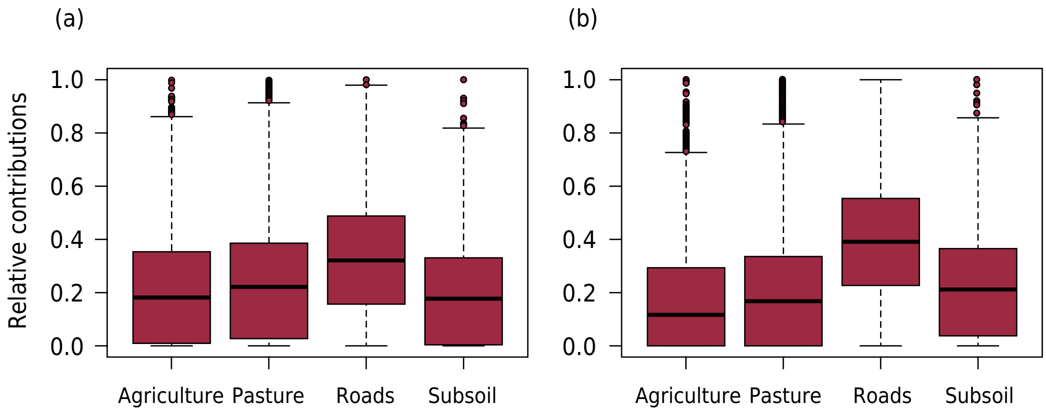

Figure 5. Box plots of relative contributions from each one of the sources of river bed sediment (a) and lag deposits (b) collected downstream from the Posses catchment outlet.

and rural roads > pasture > subsoil > agriculture, respectively. The model fit was also very good (GOF = 93 % for both the lag deposits and river bed sediments), showing that the method was effective in determination of the contributions of the sources for both types of sediments analyzed.

DISCUSSION

Source discrimination

The selected variables can be used as good fingerprint tracers due to the pedogenesis or land use that may have somehow marked the soil with these tracers. For example, Al_2O_3 and Fe are inherited from the parent material (Gneissic granite and Migmatite – Figure 2) of the soils widely found in Posses catchment. This justifies the highest Al_2O_3 and Fe contents in subsoil samples (Table 1).

Titanium content may also be inherited from the parent material, but in this study, the variability in this element content was closely related to land use influence. Erosion of highlands may progressively enrich rock-derived Ti surface soil, which would explain the highest content of titanium in pasture samples comparing to other sources. In the agriculture land, preparation of soil before sowing the crop seeds increasing the Ti contents in the topsoil by mixing the soil layers. The low content of Ti in the roads can be explained by the modification of the original composition of the soil (increase in coarser particles) carried out in these areas to improve trafficability.

On the other hand, higher contents of Rb and Sr were found on the roads and so little in the subsoil (Table 1). The highest levels of these elements on the roads result from fertilizers used for several years in farming areas which may have fallen in these places when being transported by agricultural machines. In addition to these elements, Ba and Zn are in appreciable amounts in straight and compound fertilizers originated from natural rocks (Senesi et al., 1983; Avelar et al., 2011), which may explain the higher concentrations of these elements in agriculture, pasture, and roads compared to subsoil samples.

Ascribing sediment sources

The rural roads were the main sources of both lag deposits (median = 40 %) and river bed (median = 33 %) sediments (Figure 5). Differences in these median values reveal, not a smaller contribution from this source over a relatively longer time, but a delay in other sources inputs (mainly from pasture and agriculture), which may be being controlled by other factors such as storm events, in addition to agricultural practices. However, these results contrast with the results obtained by Tiecher et al. (2017), who found low contributions (2-6 %) from unpaved roads to the sediment produced in a rural catchment of 2,032 km^2 in the South of Brazil. However, the dimension of the Posses catchment (12 km^2) is much smaller than in that study and, for that reason, the contribution of the roads to the sediments that arrive at the mouth was more evident. The impacts of roads on the production of sediments are closely related to the scale of evaluation, and it is more perceptible in small catchments (Thomaz et al., 2014).

Although they occupy less than 1 % of the total area studied, the roads are concentrated parallel to the main drainage route, the Posses Stream, which is nearly totally devoid of riparian forest (Figure 2d). Positive effects of riparian forest on reducing the amount of sediments and the content of phosphorus transferred to water bodies have been reported by Massoudieh et al. (2013) and Bispo et al. (2017). In this respect, the reconstitution of riparian forests may be a good option for adoption by the PSE program in mitigation of the sediments produced in the Posses catchment. Despite that, the need for relocation of the already constructed roads is not excluded, just as is good planning regarding the opening of new roads. Similar results were observed by Saad et al. (2018) related to the conservation of roads and recomposition of riparian forest.

The large number of deep furrows and gullies with a direct connection to the fluvial channels together with the large areas under degraded pasture (78 % of the catchment), associated with high erosivity values and with very hilly relief in the region of study (Pontes et al., 2017), may explain the significant contributions of these sources to the sediments produced in the catchment (Figure 4). Silva et al. (2013) stated that pasture is the most adequate use for the region to prevent water erosion. However, our research has shown that having a pasture cover alone is worthless, in conservationist terms, if it is not properly managed. The results further emphasize the negative impacts arising from inadequate soil management in most of the area studied and alert to the need for immediate intervention directed at these locations, as well as the rural roads, as previously mentioned. It is important to emphasize that most of the models routinely used in monitoring erosion in catchments do not take deep furrows and gullies sources into account, which validates, even more, the applicability of the fingerprinting techniques in Payment for Environmental Services programs.

The small contribution of agriculture to the sediments produced can be explained by the small area (7 %) under agriculture in the catchment studied (Figure 2d). However, the contribution of this source for river bed was greater than to lag deposits sediments (Figure 5), which generates a concern that contributions from agriculture may increase in rainy periods. Lima et al. (2016) reported the erosion as a response from the preparation of soil, when the topsoil of fields is loosened and overturned, before sowing the crop seeds, which usually occurs at the beginning of the rainy season (between September and October).The situation may be even more complicated, because the region is very hilly

(Figure 2c) and that tillage (plowing and tilling) and cropping are traditionally performed up and down the slope, without adoption of any conservationist practice.

Studies developed by Tiecher et al. (2017), investigating the effect of land use on production of sediments in a catchment in the South of Brazil using the fingerprinting technique, observed low contribution from cropped land during drier periods and that these contributions tend to increase with an increase in rainfall. In the same study, an inverse behavior was obtained for unpaved roads. These studies emphasize the importance of collecting data for longer periods of time, seeking to include the different ranges of rainfall in the study area. Evaluations over a greater period will assist in increasing the consistency of the inferences about changes in land use and cropping practices adopted throughout the year, which are closely related to the rainfall regime of the region. Also, that may increase the reliability of the results of the fingerprinting technique and the spread of its use as a tool for guiding decision-making in the PSE program in this region.

It is important to emphasize the wide usefulness of the fingerprinting technique based on the chemical elements quantified through the pXRF in programs for monitoring point sediment sources, confirmed through the present study, as well as of pollutants for rivers. These sources are normally neglected by the models used in the process of predicting losses by water erosion, especially those based on the Universal Soil Loss Equation (USLE), which was constructed to predict rill and interrill erosion. In addition, most regions of Brazil have a severe lack of monitoring stations to feed the large database required by more complex models, which makes them unfeasible to use. In this respect, the fingerprinting technique can reduce the distance between areas related to planning, monitoring, and performance of conservationist practices in catchments in Brazil because it is a technique of easily carried out, and with good accuracy in indicating critical locations that require intervention.

CONCLUSIONS

The types of land use selected as potential sediment sources in the Posses catchment are adequately discriminated, with 81 % accuracy, through the elements Sr, Al_2O_3, Ba, Rb, Ti, Fe, and Zn, quantified through the portable X-ray fluorescence. The fingerprinting technique estimates that the contributions to outlet sediments are dominated by rural roads, following by subsoil or pasture (depending on the type of sediment evaluated) and by agriculture. The results of this report showed the potential of the fingerprinting technique and the portable X-ray fluorescence for use as tools in the Payment for Environmental Services program in the monitoring of catchments.

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