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Exploring innovative techniques for identifying geochemical elements as fingerprints of sediment sources in an agricultural catchment of Argentina affected by soil erosion

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Abstract

Identification of hot spots of land degradation is strongly related with the selection of soil tracers for sediment pathways. This research proposes the complementary and integrated application of two analytical techniques to select the most suitable fingerprint tracers for identifying the main sources of sediments in an agricultural catchment located in Central Argentina with erosive loess soils. Diffuse reflectance Fourier transformed in the mid-infrared range (DRIFT-MIR) spectroscopy and energy-dispersive X-ray fluorescence (EDXRF) were used for a suitable fingerprint selection. For using DRIFT-MIR spectroscopy as fingerprinting technique, calibration through quantitative parameters is needed to link and correlate DRIFT-MIR spectra with soil tracers. EDXRF was used in this context for determining the concentrations of geochemical elements in soil samples. The selected tracers were confirmed using two artificial mixtures composed of known proportions of soil collected in different sites with distinctive soil uses. These fingerprint elements were used as parameters to build a predictive model with the whole set of DRIFT-MIR spectra. Fingerprint elements such as phosphorus, iron, calcium, barium, and titanium were identified for obtaining a suitable reconstruction of the source proportions in the artificial mixtures. Mid-infrared spectra produced successful prediction models ($R^2 = 0.91$) for Fe content and moderate useful prediction ($R^2 = 0.72$) for Ti content. For Ca, P, and Ba, the R^2 were 0.44, 0.58, and 0.59 respectively.

Keywords Energy-dispersive X-ray fluorescence (EDXRF) spectroscopy · Diffuse reflectance Fourier transformed mid-infrared (DRIFT-MIR) spectroscopy · Artificial mixtures · Fingerprints

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Introduction

Soil erosion is a naturally occurring soil degradation agent, which involves three specific processes: detachment, movement, and deposition of soil particles. Soil erosion reduces cropland productivity and contributes to the pollution of watercourses, wetlands, and lakes (Pimentel 2006). The excessive sediment input to a river-dam system produces loss of reservoir storage capacity due to siltation, damage to wetland and estuary ecosystems, floodplains, and negative impacts on infrastructure (Walling and Collins 2016). Therefore, information on soil loss and sediment delivery is essential to implement effective management practices to reduce the overall on-site and off-site impact of soil erosion (IAEA 2014).

Soil movement becomes even more critical in arid and semi-arid zones (Manyevere et al. 2016). This is also the case for the west-central region of Argentina, due to two main reasons: (i) agricultural area has been expanded at expenses of forest cover altering the hydrological balance (Giménez et al. 2016), and (ii) associated with climate change, in the last decades, the rains show tendency to sustained increase, with a higher frequency of extreme rainfall events (Penalba and Vargas 2004; de la Casa and Ovando 2014; Barros et al. 2015). Therefore, in order to implement effective strategies for controlling excessive flow of sediment, it is necessary to establish both the nature and location of the main sources of sediments at the watershed scale.

Recent studies have demonstrated that the sediment fingerprinting technique can be an effective approach for assembling information on suspended sediment sources (Collins and Walling 2002; Blake et al. 2012; Palazón et al. 2015; Owens et al. 2016). Fingerprinting techniques have been successfully applied in different ecosystems using stable and radioactive isotopes, biomarkers, soil properties, and/or trace elements (Walling and Woodward 1995; Collins et al. 1998; Walling 2005; Gibbs 2008; Guzmán et al. 2013; Schuller et al. 2013; IAEA 2014; Bravo-Linares et al. 2018). However, until now, there are no peer-reviewed studies of the application of these tracing techniques in arid or semi-arid agro-environments across Latin America.

Sediment geochemistry has been widely used to identify the spatial sources of sediments delivered to watercourses (Hardy et al. 2010). At the catchment scale, fingerprint techniques allow identification and quantification of transported sediment from different sources, measuring sediment properties that allow recognizing sediments originating from different areas or land uses (Collins et al. 1996, 1998). The geochemical concentrations of eroded sediments are mainly conditioned by the type of soils and the geological substratum from which they originate. Essential parts of this technique are the mixing models, as through them it is possible to infer the relative contributions of different sources to the sediment mixtures in the stream, river, or dam. However, before a

mixing modeling approach can be applied, it is necessary to select the tracer properties that perform the best as fingerprints of the land uses we would like to discriminate. This can be achieved by the composition of artificial soil mixtures based on existing sediment sources collected from the studied catchment. The proportion of these sources in the artificial mixtures is estimated by the mixing model, whose result is then compared with the true values of the apportionment. Using an artificial mixture, the most suitable fingerprints can then be determined. The selected elements are then the appropriate ones for studying the catchment.

Differences in the soil content of some geochemical elements could be an appropriate attribute to identify the proportions with which various sources form a mixed soil sample. These differences can be originated mainly by (a) the composition of the soil on site, (b) changes in the content of these elements due to previous spatial alterations (in depth or surface, e.g., grooves formation), and (c) distinctive soil uses.

Mass concentration of geochemical element in soil can be assessed by energy-dispersive X-ray fluorescence (EDXRF) spectroscopy, a technique barely used nowadays with this purpose (Fryirs and Gore 2013; Melquiades et al. 2013) and with several advantages: (i) this is a non-destructive analytical method; (ii) it allows fast measurement and involves simple sample preparation (i.e., pressed pellets); (iii) a wide range of elements from sodium to uranium can be measured simultaneously; (iv) analytical sensitivity of approximately $10 \mu\text{g g}^{-1}$ (depending on the element) is appropriate for determining most metal concentration. On the other hand, this technique may not be the cheapest one and may require sampling preparation skills, time, and specific equipment for making the soil pellets prior to measurement.

Due to the high costs for determining the elemental composition and other soil properties, in recent years, there has been a growing interest in the use of diffuse reflectance Fourier transform mid-infrared spectroscopy (DRIFT-MIRS) (Cobo et al. 2010; Demyan et al. 2012, 2013; Towett et al. 2015). This technique combined with chemometric multivariate statistical methods can produce accurate prediction of soil properties, as elemental composition, at low costs. Among the multivariate methods used, partial least squares regression (PLSR) analysis is the most widely used because of its ability to address multicollinearity of spectral data (Viscarra Rossel et al. 2006; Stenberg et al. 2010). The performance of this model relies on the ability to extract important spectral characteristic features (e.g., electron transitions, overtones, and combination of fundamental vibrations in the mid-infrared frequencies) relevant to the soil attributes of interest (Viscarra Rossel et al. 2006; Viscarra Rossel and Lark 2009). PLSR is based on the assumption of a linear relationship between the dependent variable of interest (e.g., soil concentration of chemical elements) and a predictor variable (e.g., absorbance peaks in the MIR spectra). Nevertheless, most models have been validated with traditional

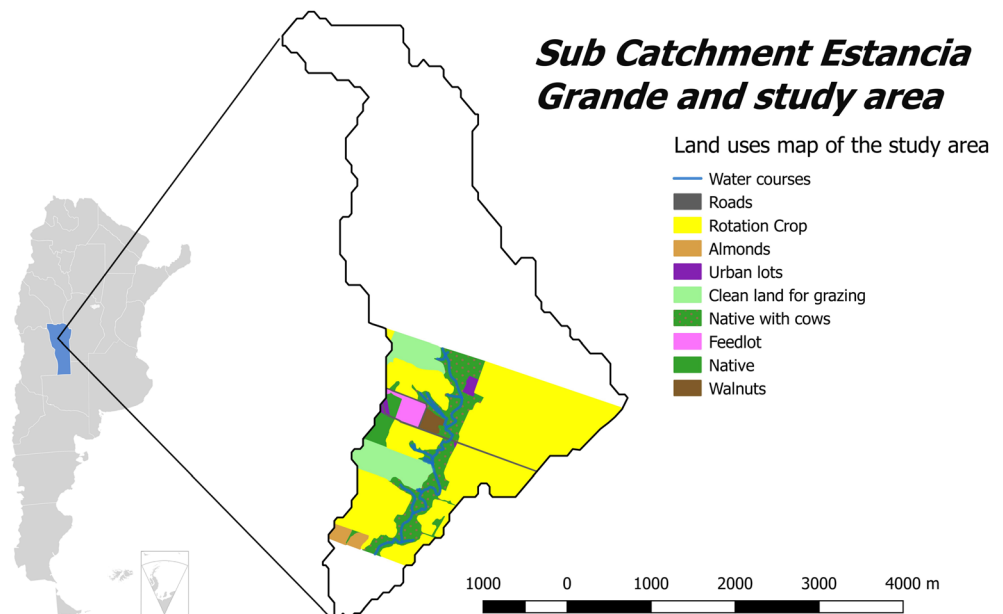
wet analytical techniques. In this study, we evaluate the capability of DRIFT-MIR spectroscopy to predict the selected fingerprint element contents measured by EDXRF. The main objective of this research work was to identify the more efficient set of fingerprint elements in order to use them in a subsequent study on the erosion-sedimentation process in the catchment. Summing up, the objectives were the following: (i) evaluate the fingerprint selection process for EDXRF measurement results, (ii) identify specific elemental tracers of land use with artificial mixtures, and (iii) find a predictor model for these elements using DRIFT-MIR spectroscopy.

Materials and methods

Study site

The Estancia Grande sub-catchment (Fig. 1) is located in central Argentina (S 33° 10'; W 66° 08'), 23 km northeast of San Luis City (province of San Luis) at 1100 m a.s.l. The studied area is about 4.7 km², and it is a portion of the Rio Volcán catchment. The average annual temperature is 17 °C, while in summer (December to March) the mean temperature is 23 °C. Annual rainfall ranges from 600 to 800 mm, with a tendency to increase and a rising frequency of extreme rainfall events during the last decades (Penalba and Vargas 2004; de la Casa and Ovando 2014) (Fig. 1 of Supporting Material). Rainfall varies seasonally, with a dry season from May to October and a rainy season from November to April. Rains in the dry season are scarce and sporadic, with occasional drizzles.

Fig. 1 Soil samples and location of the study area



San Luis, Argentina. S 33°10'; W 66°08'

Soils are dominated by haplic Kastanozems (IUSS Working Group WRB 2014). These soils originated from loamy loess material and possess a high level of organic matter in their upper 25 cm. The area is currently being used for agriculture (crop rotation), and livestock (free grazing and feedlots), and some fields are used for growing nut trees (walnuts and almonds) (Peña Zubieta et al. 2006).

The studied catchment belongs to the loess belt of North East Argentina (Teruggi 1957), and there is no rocky outcrop in the investigated watershed, being loess sediment. The soil is composed of silt-sandy materials of aeolian origin (Ojeda 2005).

Regarding cropping and soil management practices, for more than 10 years, direct seeding mulch-based systems have been adopted as the main practice for crop cultivation. This practice has increased crop yield and reduced soil erosion. The main cultivated crops are soybean, maize, and wheat. The used herbicides are atrazine and glyphosate. Fertilizers are not applied with the same regularity on the agricultural land. Farmers mainly use N-P-K-based fertilizers such as urea ammonium nitrate (UAN) 32-0-0, monoammonium phosphate (MAP) 11-52-0, triple superphosphate 0-46-0, and biological growth promoters depending on the crop. Feedlot cattle are fed with maize, oats, sunflower meal, and grazing hay. Mineral supplements of sodium chloride, calcium, phosphorus, and magnesium are also given to the cattle, which are necessary for growing young animals.

Sampling

Soil and sediment sampling were conducted in April 2015. Top 20 mm of surface soil samples (source samples) were collected from the different land uses following the

procedures proposed by Gibbs (2008, 2014). The sampling procedure involved removing the leaves and plant material that was found in the place before taking a soil layer 20 cm² and 20-mm thick of exposed soil using a stainless steel flat spatula. At each location, multiple subsamples from an area of about 100–200 m² were combined in a plastic bucket as a composite sample to ensure the sample was representative of that land use. Land uses included crops, grassland, feedlot, walnuts, stream banks, and fallow lands. Sediment samples (mixture samples in the water courses) were collected at the top 20 mm of the deposition zone of the watershed on little floodplains where deposition process was observed. In total, 29 samples were collected among sources and mixtures. Four of these samples (four different land uses) were used to create two artificial mixtures, for selection of the best suitable set of tracers. The number of selected samples was decided based on (a) the number of different sediment sources and land uses, which was in total eight (six for livestock and agriculture lands and two minimal areas intended for dirt roads and barns), and (b) the compound-specific stable isotope (CSSI) analyses (not reported in this study), applied to be further correlated in a later stage with EDXRF and MIRS analyses (the bottle neck for the number of samples is CSSI, with normally one composite sample per land use or sediment source and sediment deposition zones). In the future, a more complete study will aim at identifying the sedimentary sources and their destination with a more complete sampling plan and statistical validation.

Analytical methods

The samples were dried at 50 °C, disaggregated, and then sieved through a 2-mm sieve at the GEA-IMASL Laboratory. Two artificial mixed samples (MIX 1 and MIX 2) were then composed using identified source samples following the below proportions:

$$\text{MIX 1} = 10\%S1 + 25\%S2 + 40\%S3 + 25\%S4$$

$$\text{MIX 2} = 3\%S1 + 45\%S2 + 20\%S3 + 32\%S4$$

The soil source S1 originated from a riverbank.

The sources S2 and S4 were two soil samples collected in crop rotation commercial farms. During the sampling, one of these sources was under corn and the other one under soybean cultivation, respectively. These cultivations change between corn and soybean yearly.

The source S3 came from a feedlot.

The proportions were chosen in such a way that they represent the possible distributions of sediment origin, including the end-members of sediment contribution to make sure that the model testing gets results outside the uncertainty margins of the model. The two resulting artificial mixtures were homogenized prior to analysis.

For EDXRF spectrometry analysis, the samples were ground into fine powder, which was used to produce pressed pellets of 25-mm diameter and 2.5-g weight. The pellets were measured at the Nuclear Science and Instrumentation Laboratory (IAEA Laboratories, Seibersdorf, Austria), using a heavy-duty, fully software-controlled EDXRF spectrometer (Pd-anode X-ray tube) utilizing five secondary targets (SPECTRO X-LAB 2000).

DRIFT-MIRS analyses were carried out at the Applied Chemistry Research Laboratory of the Central University of Venezuela. The samples were milled for 45 s in a micromill. The spectral data were obtained in a Nicolet Si10 DRIFT-MIRS and finely ground dry KBr was used as background. The spectra were collected between 4000 and 400 cm⁻¹ with 4 cm⁻¹ of resolution and 64 scans; the analyses were run in triplicates. The TQ analyst 9.4.45 software of Nicolet was used to perform the PLSR of the EDXRF analysis in combination with the DRIFT-MIRS. The selection of calibration and validation samples was done through an algorithm included in the software, from the condition of covering the whole concentration range (for the five parameters involved) in the best possible way to obtain a robust model. No random selection of these groups was made due to the reduced number of samples. In this study, focusing on the identification of suitable geochemical fingerprints for tracing sediments in the investigated basin, 29 soil samples were collected over the entire catchment of 4.7 km². Additionally, two artificial mixtures, using four of these 29 samples, were composed, for validating mixing models. For building the prediction model using MIR spectra, we used the 29 collected samples and one of the artificial mixtures. In summary, the analysis carried out by MIR spectroscopy included 30 soil samples. Raw spectral data as well as first and second derivative of the spectral were applied for developing prediction models that provide insight into a rapid and inexpensive estimate of the fingerprint elements in soils and sediments compared to conventional chemical procedures.

Mixing models

The EDXRF provided the concentration of more than 40 elements for each sample. The interpretation of this significant amount of data required the use of mixing models (MM) to deconstruct sediment mixtures into their source components. An appropriate application of MM needs the identification of a subset of discriminating elements (fingerprints) whose concentrations are input parameters into this MM.

The two artificial mixed samples were used to select the suitable set of fingerprints to explain an accurate proportion of each source in the artificial samples composition. Following the methodology proposed by (Collins and Walling 2002) for the identification of fingerprints, the Kruskal–Wallis *H* test was used in this study as the first step to reject fingerprint

properties that are redundant. This procedure is a non-parametric method equivalent to analysis of variance (ANOVA). Through it, the differences between the sources of sediments according to each measured property are analyzed. Then, as a second step, discriminate function analysis (DFA) was used to test the ability of the parameters that passed Kruskal–Wallis H test to classify all the source samples from the catchment into the correct categories. DFA was performed in R software using the KLaR package (Roeber et al. 2014). A greedy Wilks' test was applied for the DFA. This test performs a stepwise forward variable selection using the Wilks' Lambda criterion: select the set of properties that minimizes the Wilks' lambda of the model including the variable if its p value still shows statistical significance.

The third and last step consists in a visual analysis of 2-D plots of the elements that were statistically selected. The 2-D plots were used to select the most appropriate elements for the mixing model run. Thus, all possible combinations of element pairs as bi-plots were created; if a mixture lies outside the source polygon, then one or both of the elements pair should not be used. After examining all of the 2-D plots, there will be a selection of elements that are valid, and these should be used in the mixing model run. Then, the CSSIAR v1.00 software (de los Santos-Villalobos et al. 2017) was used as MM to determine the contribution of the source samples to the mixtures. This software has a friendly environment and is written in R language (R Core Team 2014). This mixing model is based on SIAR (Stable Isotope Analysis in R) (Parnell et al. 2010; Jackson 2013). It runs a Bayesian mixing model with the given tracers to find the best solution for a specific problem. In addition, this software provides the analysis of larger sets of data and gives more detailed statistical information such as the uncertainty. It is possible to get the proportion of sediment contribution from different land uses in the catchment. Moreover, the simple isotopic MM IsoSource (Phillips and Gregg 2003) was used to compare its output with the result obtained by CSSIAR.

Results

As mentioned before, this study was carried out to properly select geochemical elements that are able to act as fingerprints of different land uses encountered in the Estancia Grande basin. At the same time, it was tested if the selected tracers can be predicted through DRIFT-MIR spectroscopy.

Elemental tracers' selection

Seven elements were selected after applying the Kruskal–Wallis H test and DFA with minimization of Wilks' lambda, such as phosphorus (P), iron (Fe), calcium (Ca), magnesium (Mg), barium (Ba), manganese (Mn), and titanium (Ti). From

analysis of the 2-D plots generated, it was concluded that most of these seven elements performed as expected. This means that taking each element content as vertical and horizontal axes, it is possible to draw a polygon (with the sources points as vertices) which encloses the mixtures' points. Some examples are depicted in Fig. 2a: Ca–Ba, P–Fe, and Ba–Ti plots show artificial mixtures' points enclosed by the polygon that was generated by their sources. These plots indicate that using these five elements (Ca, Ba, P, Fe, and Ti), it is possible to explain the mixtures' contents as a vector sum of their sources' contents.

In Fig. 2b, P–Mg, Ti–Mn, and Fe–Mn plots show some examples in which one or both artificial mixtures' points are outside the polygon created by the sources. In these combinations of elements, it is not possible to explain the mixture concentrations as a vector sum of sources' concentrations. Therefore, Mn and Mg were taken out of the set of fingerprinting elements.

Passing all tests, phosphorus, iron, calcium, barium, and titanium were selected as fingerprints for the study. Table 1 shows the mean and standard deviation of the selected fingerprint concentrations for the different land uses. Marked in italics are the land uses sediments that participate in the artificial mixtures.

The concentrations of these five elements were used in the CSSIAR v1.0 and IsoSource software, in order to reconstruct the two artificial mixtures into their soil sources. CSSIAR's outputs are the source proportions and the uncertainties of these proportions (given by the standard deviation). The calculated proportions by CSSIAR can be found in Fig. 3, for both mixtures. IsoSource calculated similar proportions as CSSIAR, although without uncertainty information. Both models found an accurate and realistic solution when using the set of P, Fe, Ca, Ba, and Ti, with a mean absolute error (MAE) of 5.1% for each of the two artificial mixtures using the CSSIAR software (Fig. 3), and a MAE of 7.5 and 4.5% for each respective mixture (MIX 1 and MIX 2) using IsoSource was found.

The error bars in the charts represent the associated uncertainty when preparing the artificial mixtures. For the calculated soil proportions, we used the standard deviation output provided by the tested mixing model. It can be noticed that for the artificial mixture MIX 1, the calculated decomposition is accurate as it identifies the main contributor and the source with less proportion in the mixture. The mean absolute error is 5.1%, which can be considered as a good result. For MIX 2, we obtained the same MAE, although this solution is not pinpointing the main contributor in the mixture, i.e., corn soil, proposing as the greatest proportion the soybean soil. The swap in these two sources is mainly due to the fact that these soil sources were under different crop rotations, one under corn and the other one under soybean when the sampling took place. But in previous years, the cropping system had the

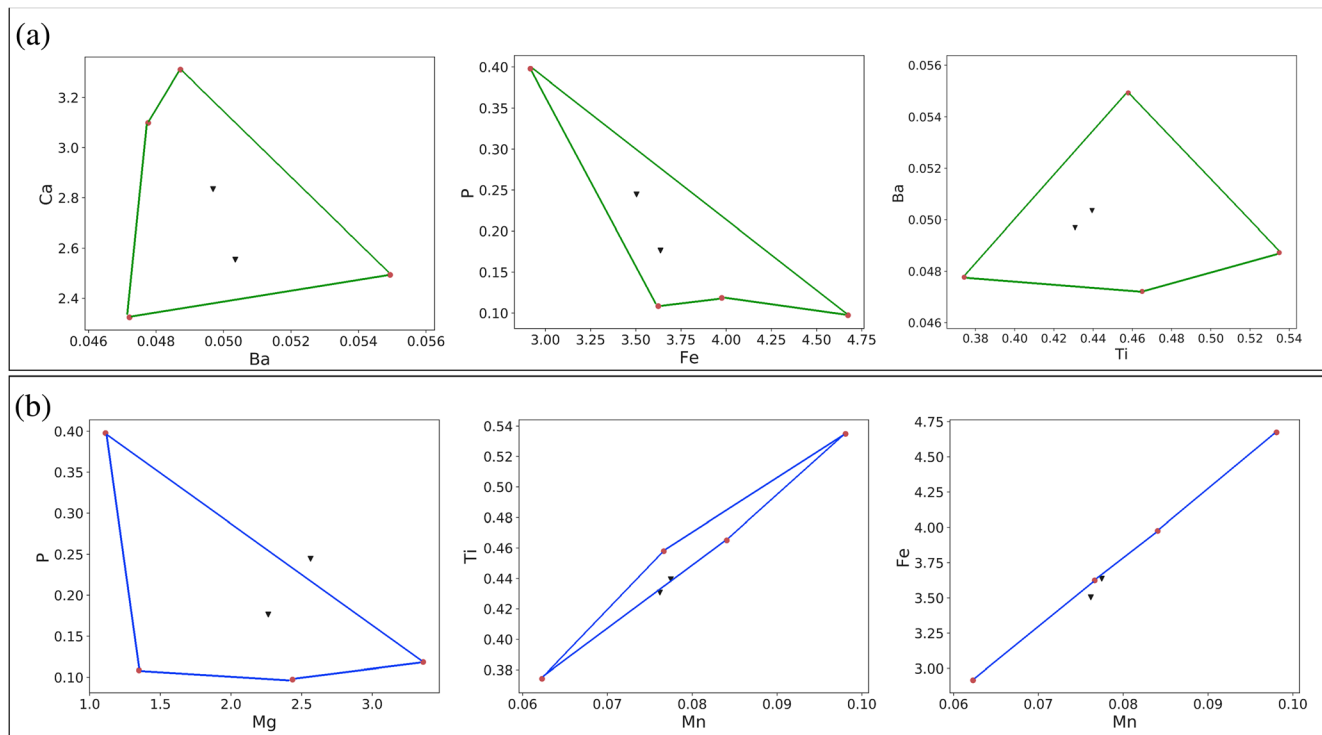


Fig. 2 **a** Examples of 2-D plots in which the polygon encloses the mixtures. These elements work properly. **b** Examples of 2-D plots in which the polygon does not enclose the mixtures. Mn and Mg do not work properly as fingerprints

crops in reverse location. This feature is clear when the concentrations of the selected tracers are inspected. Indeed, the mentioned sources have very similar concentration values for Ti, Fe, and Ca. This issue can be interpreted as a limitation of geochemical elements to accurately distinguish between two fields used for the same crop in different years. Nevertheless, it is important to highlight that if these sources are considered together (S2 + S4), the mixing model proposed a proportion of 76.5% in the MIX 2 for them, when the actual proportion is 77%. This is a very accurate result highlighting that the agricultural land uses are the main contributor versus bank and

feedlot soil, which were accurately predicted as shown in the chart. The bank's contribution to the mixture is in accordance with the actual proportions in both mixtures; in MIX 1, the difference between the calculated and the actual value is only 4%, while in MIX 2 this difference is 1.7%. Furthermore, for feedlot source apportion, the result is close to the actual value; in MIX 1, the absolute difference between the calculated and the actual proportion is 6%, and in MIX 2 it is only 2%. Thus, the selected elemental tracers work properly to identify the main soil sources: feedlot, rotation crops (as a whole), and bank.

Table 1 Descriptive statistics parameters for the selected five elements. In italics, land uses involved in the artificial mixtures

Sources	Number of samples	Elemental concentrations ($\% \times 10^{-2}$)									
		P		Ca		Fe		Ti		Ba	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
<i>Stream banks</i>	6	9.9	0.7	293	46	391	42	46.3	3.8	5.4	0.5
<i>Rotation crops</i>	3	11.1	0.8	239	9	370	26	45.2	2.0	5.3	0.5
Walnuts	1	13.5	–	214	–	332	–	41.4	–	5.2	–
Grassland	2	14.7	0.1	321	20	375	66	44.0	4.0	4.9	0.6
<i>Feedlot</i>	2	039.5	0.9	318	7	292	1	37.2	0.5	4.9	0.1
Fallow lands	3	9.3	0.4	306	14	418	33	45.9	1.7	5.0	0.2

Table 2 Spectral regions. Bibliography of functional soil properties associated with the regions selected by TQ analyst software

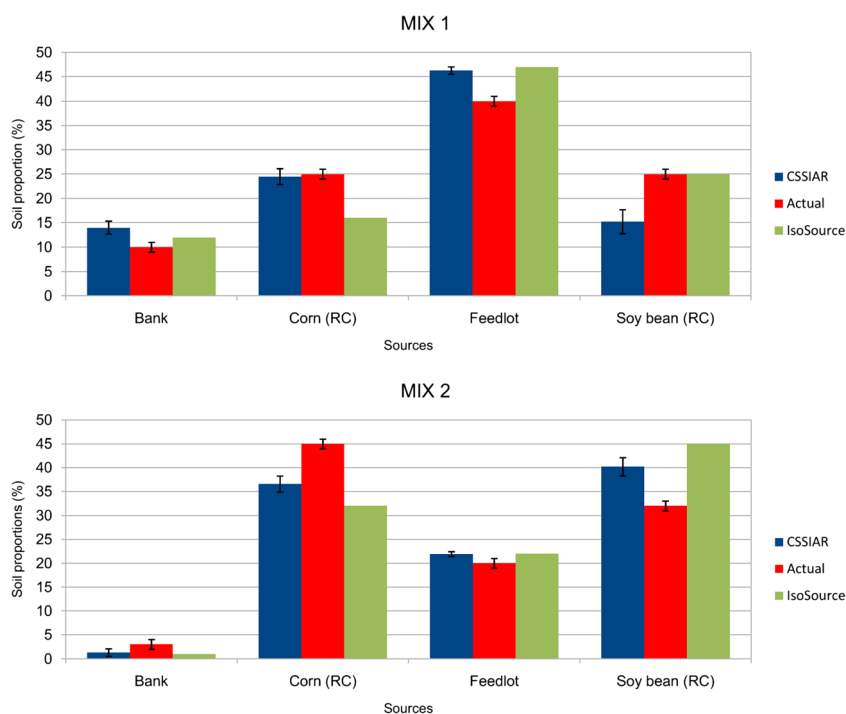
Soil component	Wavenumber (cm ⁻¹)	Related bonds	Reference
Clay minerals	3690–3620	–OH stretch band of Kaolinite	(Janik et al. 1998; Madejová et al. 2017; Nguyen et al. 1991)
	950–600	–OH stretch band of smactite	(Janik et al. 1998; Madejová et al. 2017; Nguyen et al. 1991)
	3630–3620	–OH stretch band of smactite	(Janik et al. 1998; Madejová et al. 2017; Nguyen et al. 1991)
Carbonates	1200–700	Si–O stretch bands	(Janik et al. 1998; Madejová et al. 2017; Nguyen et al. 1991)
	600–400	Si–O bending	(Janik et al. 1998; Madejová et al. 2017; Nguyen et al. 1991)
	2520–2513	CO ₃ ⁻²	(Bruckman and Wriessnig 2013; Van der Marel and Beutelspacher 1976)
Iron oxides	1798	Carbonates calcite dominated	(Bruckman and Wriessnig 2013; Van der Marel and Beutelspacher 1976)
	1445	Carbonates, carboxylates	(Bruckman and Wriessnig 2013; Van der Marel and Beutelspacher 1976)
Iron oxyhydroxides	600–700	Fe–O	(Van der Marel and Beutelspacher 1976)
Phosphorous compounds	3100, 900, 800	Fe–O–O–H	(Van der Marel and Beutelspacher 1976)
Aluminum and Fe phosphates	1250–750	P–O–H stretch bands and bending	(Janik et al. 1998; Kizewski et al. 2011)
Metal phytates	1090 and 1150	P–O–H stretch bands	(Kizewski et al. 2011)
	900–790 triplet	P–O–C stretch bands	(He et al. 2006a, b)

Prediction models using DRIFT-MIR spectroscopy

Once the most efficient set of fingerprint elements to trace sediment movement in the studied catchment was identified, DRIFT-MIR spectroscopy was used to predict the concentration of these fingerprint elements through the produced spectra, with a wave number range between 3851.15 and 2400 cm⁻¹, 2200 and 766.08 cm⁻¹, and 578.54 and 508.63 cm⁻¹, through partial least square modeling. This approach allowed increasing the number of data without the disadvantage of the major cost and intensive sample

preparation for XRF analysis. These spectral regions were selected to include functional soil properties such as clay minerals and phosphorus (P) soil compounds, as reported in the literature (Table 2), given that clay minerals are the main soil components responsible for the transport of fingerprint elements, such as the cations Ca²⁺, Ti⁴⁺ and Ba²⁺, Fe^{2+/3+}, and P in its various forms. DRIFT-MIR spectra combined with PLS (raw, first, and second derivative) is one of the most common techniques for spectral calibration and prediction modeling. Using the geochemical contents measured by EDXRF, it is possible to generate good prediction models of

Fig. 3 Artificial mixed samples. In blue, reconstruction using CSSIAR v1.0 mixing model. In green, reconstruction using IsoSource, and in red, the actual proportions. The source contributions are properly calculated using P, Fe, Ca, Ti, and Ba as tracers



the content of the identified fingerprint elements, through their different concentration ranges in all the soil/sediment samples. The first derivative spectra give the best prediction models compared with using second derivative and raw spectra. Furthermore, working with no smoothing on the spectra was more appropriate for obtaining better models given the parameters used for the quantification. The useful regions of the spectra were selected by TQ analyst software. Three regions were used: 3851.15–2400 cm^{-1} , 2200–766.08 cm^{-1} , and 578.54–508.63 cm^{-1} . The cross-validation plots for the PLS regression of the first derivative using the DRIFT-MIR spectra data for all samples (sources and mixed) are shown in Fig. 4. Regarding the calibrations, the five parameters were properly quantified as the calculated contents made by the model have a correlation coefficient higher than 0.85. When testing the model with the validation samples, iron ($R_{\text{pred}} = 0.95$) and titanium ($R_{\text{pred}} = 0.85$) showed a better correlation between the calculated and the actual contents. Phosphorus has $R_{\text{pred}} = 0.76$, despite it shows an excellent correlation coefficient in the calibration ($R_{\text{cal}} = 0.99$). Barium has a similar result, with an $R_{\text{pred}} = 0.77$ and a very good correlation coefficient in the calibration ($R_{\text{cal}} = 0.94$). Notwithstanding these good results, for the validation samples, calcium does not show a satisfactory correlation between the content calculated by the model and the actual one ($R_{\text{pred}} = 0.67$ and $R_{\text{cal}} = 0.87$). Following the guidelines proposed by (Malley et al. 2004), predictions for Fe was classified as successful prediction ($0.95 \leq R^2 < 0.90$) and for Ti moderate useful prediction ($0.8 \leq R^2 < 0.7$). Table 3 summarizes the results of the prediction model.

Discussion

The selected tracers are Ca, Ba, P, Fe, and Ti. Despite in this set of fingerprinting tracers Ca and Fe are major elements, they can be used as good fingerprint tracers due to the particular features the land uses have in the study area. Calcium content is lower in the topsoil of the agricultural fields as compared to the soil from the stream banks and fallow land without human intervention. Calcium carbonates in the lower subsoil could originate from the vertical, horizontal, or in situ resettlement of carbonates during pedogenesis in the soil-sedimentary environment. At the stream banks, this subsoil may appear at the surface, due to erosion. In the natural fallow land, erosion may let appear the subsoil at the surface as well. Further leaching through intensive agricultural practices may reduce the Ca in the topsoil. Calcium content is high also in the feedlot soil, which may be caused by enrichment through the cows' manure probably holding calcium from the animal feed (Edmeades 2003). Iron may show different concentrations as well. The lower content of Fe may be due to the constant application of fresh manure in the feedlot soils (Whalen et al. 2000). Besides, it is expected a lower Fe content

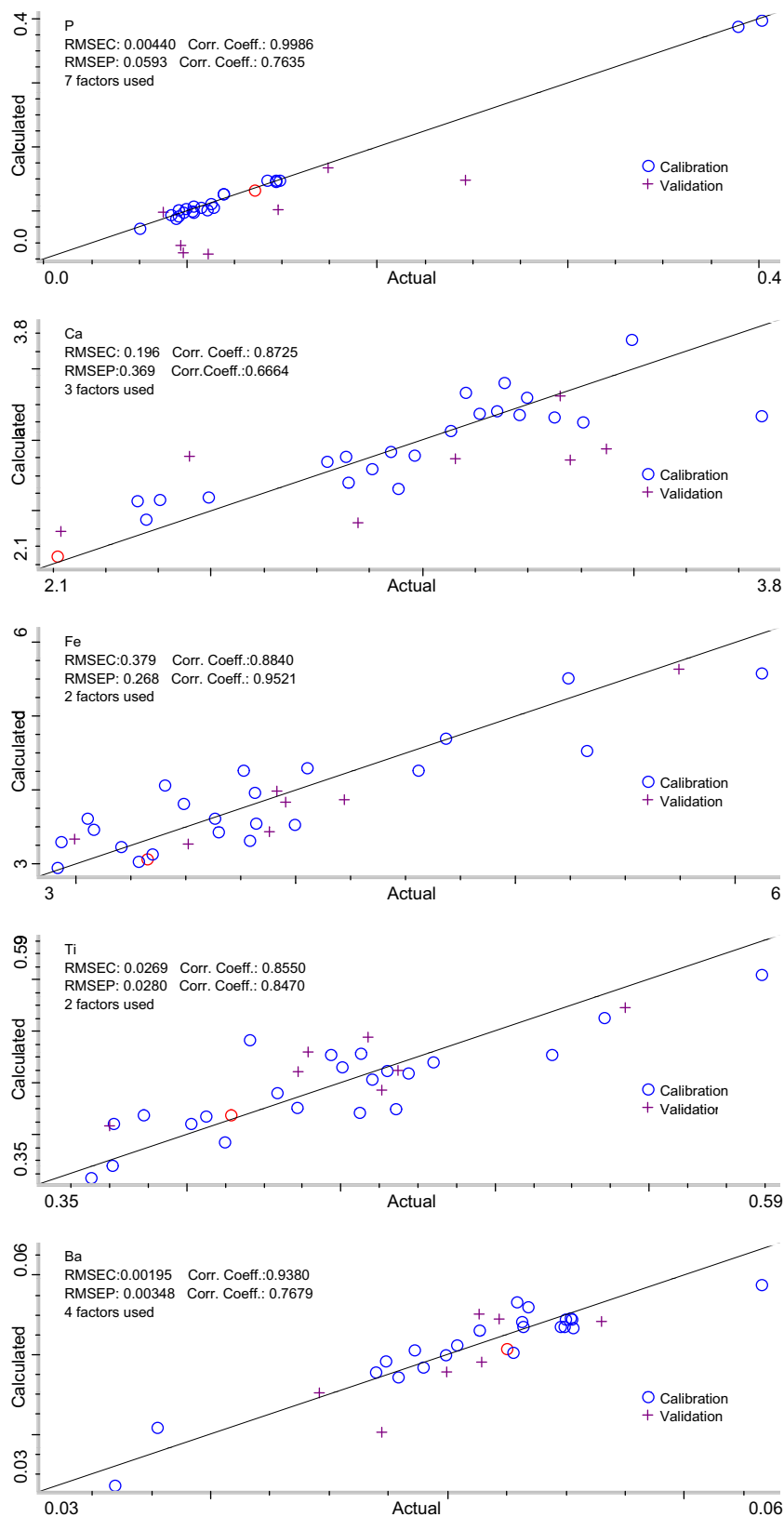
in the trees' topsoil (walnuts) than in the fallow and grassland top soils (Little and Bolger, 1995), as a higher content of organic matter can be found due to accumulation of humic substances caused by decomposition of dead plant residues and other organic (animal) materials on walnuts' soils. Regarding the use of phosphorus, it is expected to find the highest content of this element in the feedlot due to the cattle manure (Sharpley and Moyer 2000). For similar reasons, it is expected an increased concentration of P in the soil in grazing pasture areas (grassland). An increased P content in the agricultural fields might be due to the use of fertilizers (Roger et al. 2014) and to a lesser extent herbicides (Peruzzo et al. 2008). Titanium content may be inherited from the parent material and the variability in this element content may show differences due to the origin of the loess materials (Karathanasis A.D. 2009). This would explain the variability in Ti comparing cultivated and uncultivated areas, as banks and fallow lands.

Using this set of tracers, out of the 43 geochemical elements measured with X-ray fluorescence, the calculated soil proportions are very close to the real initial proportions. The artificial mixture MIX 2 is more complex including only 3% of the source bank. This was carried out to test the strength of the technique in difficult situations expected in the real sediment mixtures of our studied catchment. For the MIX 1, the mean absolute error (MAE) is 5.1% (7.5% using IsoSource); for the MIX 2, MAE is 5.1% (4.5% using IsoSource). It is a very good result considering the complexity of these mixtures. The results obtained by using CSSIAR and IsoSource are close to each other, which proves that the mixing model software used is not critical for the analysis of the mixtures. One important aspect to consider is that CSSIAR output includes the standard deviation of the calculated proportions. This key information allows establishing the uncertainty limits of the calculations.

Our findings highlight the importance of testing different tracers using artificial mixtures with known soil proportion sources from the study area prior to analyzing the whole set of field samples and sediment mixtures. The third and last step of the selection process (visual analysis of the bi-plots) ends up being a valuable step. Thanks to this, we move from having a solution with a MAE of 7 and 15%, for MIX1 and MIX2 (using the tracers selected by statistical tests), to get a MAE of 5% for each mixture (using P, Ca, Fe, Ti, and Ba). Then with this approach (three steps for the selection of tracers), the set of fingerprint elements is the one that provides the more precise results on the calculated proportions of the artificial mixtures. As previously reported by (Haddadchi et al. 2014), we consider as well this preliminary test an important calibration step for validating a fingerprinting technique.

The attempt to find a prediction model using DRIFT-MIR spectra through the PLS regression was partially successful. The study shows a good predictive model using the first derivative of the spectral data. The coefficients of determination

Fig. 4 PLS Regression using P, Ca, Fe, Ti, and Ba as parameters



for the predictions (R^2_{pred}) are similar and in some cases better than the ones reported before by other authors. The R^2 values for the validation of P and Fe are in agreement with the median

reported in a recent review on the performance of infrared reflectance spectroscopy for the prediction of soil properties (Soriano-Disla et al. 2014) and slightly above the values

Table 3 Results of root mean square error for calibration and prediction (RMSEC and RMSEP) as well as R^2 values for the calibration and the prediction of the developed model

Element (%)	Factors used	R^2_{cal}	RMSEC	R^2_{pred}	RMSEP
P	7	0.99	0.0044	0.58	0.0593
Ca	3	0.76	0.1960	0.44	0.3690
Fe	2	0.78	0.3790	0.91	0.2680
Ti	2	0.73	0.0269	0.72	0.0280
Ba	4	0.88	0.0020	0.59	0.0035

Note: R^2_{cal} is the square of the correlation coefficient of the calibration and R^2_{pred} is the square of the correlation coefficient of prediction

reported by Soriano-Disla et al. (2013) for agricultural and grazing European soils. The predictions made for Ba and Ti are in agreement and slightly above the values reported in the mentioned paper. The prediction made for Ca content ($R^2_{pred} = 0.44$) is not satisfactory as it is not in agreement with the median found in several other studies ($R^2 = 0.79$) (Soriano-Disla et al. 2014). The model is fairly correct, for predicting four of the five fingerprinting elements, considering the reduced number of samples used to build the model. Although, when these predicted contents were used in the mixing model as inputs, no expected results were found. The MAE of these proportions is 15%, which is three times the MAE calculated when using the measured contents with EDXRF. The model can predict realistically Fe and Ti contents from the spectra of the samples but the predictions on the rest of the fingerprint elements are not that accurate for being used as a replacement of these element contents when apportioning the mixture.

Conclusions

This study shows that a good predictive model using the first derivative of the spectral data can be built using EDXRF measurements of element contents as parameters in a PLS regression. It is possible to predict the parameters P, Ca, Fe, Ti, and Ba with relative accuracy, especially P which is difficult to predict using DRIFT-MIRS and PLS regression with wet analytical techniques. As a first approach, the results obtained in this study reveal the need for a larger number of samples in order to determine the quantitative potential of the prediction models using DRIFT-MIR spectra with EDXRF as a fingerprinting technique. However, these results are very encouraging since they show that geochemical tracers can be used in small areas where the geology is very homogeneous, an approach that has not been studied so far. Furthermore, the use of the element contents has the advantage over isotopic tracers (such as $\delta^{13}C$ of fatty acids) that it does not need conversion from the isotopic proportions (result of the MM) into soil

proportions, since mass concentrations are used as tracers, i.e., the conversion factor is 1 for all the sources.

The development of new analytical methods that can involve geochemical tracers in combination with land use, through the use of relatively economic analytical methods, opens a new perspective in erosion evaluation which in turn delivers essential information for effective and precise soil erosion management.

It is important to highlight that this study is a preliminary assessment, necessary to select and validate proper tracers; a more complete study aimed at identifying the contributions of major sources of sediments will demand a more extensive sampling strategy.

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