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# Combining EDXRF and DRIFT-MIRS to distinguish sedimentary sources in an agricultural catchment of Argentina: Identification of suitable fingerprint elements

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**Abstract**

Sediment transport and the associated deposition process are key environmental problems in the semi-arid center of Argentina where the agricultural frontier and new land uses grow at the expense of native vegetation. Using sediment source fingerprinting techniques could be a way of identifying hot spots critiques of land degradation. In this research we explore the use of natural elements in soil to identify sedimentary sources in a small basin in the province of San Luis, Argentina. Soil samples were collected in different points of the basin, representing different land use (source samples) and sediments samples were taken along the stream (mixed samples). Concentrations of possible fingerprint elements were measured using EDXRF technique. Additionally, multivariate PLS analysis was applied to the infrared spectral data of the samples. With the aim of validate the procedure, two artificial mixtures were made up with known proportions of source samples. Fingerprints elements were identified obtaining with them a very good reconstruction of the source proportions in the artificial mixtures. DRIFT-MIRS PLS analysis shows a good correlation between MIRS spectra and the identified fingerprint elements.

**Keywords:** Soil Sediment•Fingerprints•EDXFR•MIRS•Mixing Models

**Introduction**

Soil erosion is recognized as one of the most critical environmental issues. This problem becomes even more critical in arid and semiarid zones, such as the west-central region of Argentina, primarily for two reasons: *i)* natural forest area declined at expenses of agricultural expansion and *ii)* the increased rainfall events in the region (in frequency and intensity) associated with the climate change (Barros *et al*., 2015). In order to implement strategies to control the flow of sediment, it is necessary to establish both the nature and location of the main sources of sediments within the watershed. Thus, recent research shows that sediment fingerprinting can be an effective approach for assembling information on suspended sediment sources (Blake *et al*., 2012; Collins and Walling, 2002). This technique has been successfully applied in different ecosystems using as fingerprints stable and radioactive isotopes (Schuller *et al.,* 2013), biomarkers, soil properties or trace elements (Gibbs, 2007; Walling, 2005). In addition, in recent years there has been growing interest in the use of Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT-MIRS) combined with chemometrics multivariate statistical methods for the accurate prediction of soil properties at low costs. Among the multivariate methods used, PLS analysis is the most widely used because of its ability to address multicollinearity of spectral data (Stenberg *et al*., 2010; Viscarra Rossel *et al*., 2006). 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 and Lark, 2009; Viscarra Rossel *et al*., 2006. PLS 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 MIRS spectra). Nevertheless, most models have been validated with traditional wet analytical techniques. This study presents preliminary results on the feasibility of using natural elements in soil as fingerprint to identify sedimentary sources in a small basin in the province of San Luis, Argentina. In addition, we have used a non destructive technique such as Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) to calibrate and validate partial least square (PLS) analysis of DRIFT-MIRS spectral data.

**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 north-east of San Luis City (Province of San Luis) at 1100 meters above sea level. The explored area is about 6 km$^2$, being part of the Rio Volcán catchment. The average annual temperature is 17 ºC, while in summer (December–March) the mean temperature is 23 ºC. Annual rainfall ranges from 600 mm to 800 mm, increasing in the last few years 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.

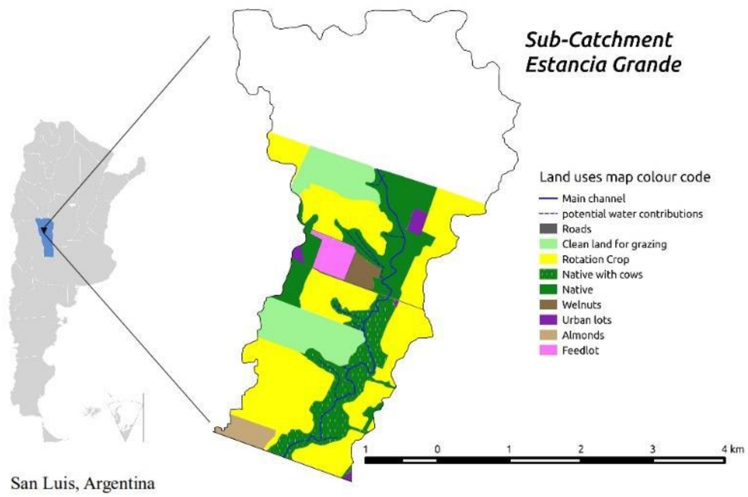


Figure 1: Sub-catchment Estancia Grande (San Luis, Argentina) with the land uses map.

The sub-catchment soils are mainly Xerosols Calcic with Solonetz inclusions, can also be formed by Lithosols. Soils in this series have as originating material a loamy loess, they are well supplied with organic matter in the upper 25 cm. The area is currently being used mostly for agriculture (rotation crop) and livestock (free grazing and feedlots), nevertheless there are some plots intended for growing nuts trees (walnuts and almonds).

*Sampling.* Soil and sediment sampling were conducted in April 2015. Source samples from surface soil layers (about 2 kg each one) were collected from the different land uses following standard procedures. Sediment samples (mixture samples) were collected from the deposition zone for the watershed sources (top 20 mm) on river banks or little flood plains where deposition has occurred. In laboratory, two artificial mixed samples were composed, using identified source samples.

*Analytical methods.* All the 29 collected soil and sediment samples and the two artificial mixed samples were initially prepared at the GEA-IMASL Laboratory. The sample preparation consisted of drying at 50° C and sieved to 2 mm. For Energy Dispersive X-Ray Spectrometry (EDXRF) analysis were the samples were ground to a fine powder which was used to make pellets of 25 mm diameter and 2.5 g weight. The pellets were measured in SPECTRO X-LAB 2000, a heavy-duty, fully software controlled EDXRF spectrometer (Pd-anode X-ray tube) utilizing 5 secondary targets, with the technical support of the Nuclear Science and Instrumentation Laboratory (IAEA Laboratories, Seibersdorf, Austria. Mid-Infrared Spectrometry -diffuse reflectance mode- (MIRS-DRIFT) were carried out at the Applied Chemistry Research Laboratory of the Central University of Venezuela. The samples were milled for 45 secs in a micromill. The spectral data was obtained in a Nicolet Si10 DRIFT-MIRS, finely grinded 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 PLS of the EDFRX analysis in combination with the DRIFT-MIRS.

Normal spectral data as well as first and second derivative of the spectral were applied for developing prediction models that provides insight into a rapid and inexpensive estimate of the fingerprint elements in soils and sediments compared to conventional chemical procedures.

*Mixing model.* The CSSIAR v2.00 software (de los Santos-Villalobos *et al*., 2015) was used to study our catchment. The software has a friendly environment and is written in R language (free programming language). It provides the analysis of larger sets of data and gives more detailed statistical information (i.e. uncertainty).

**Results and discussions**

The CSSIAR v2.00 software was applied considering as input the concentration of the elements obtained from EDXRF analysis of the four soil sources forming part of the artificial mixed samples (MIX 1 and MIX 2). As it is known the real source proportions in the artificial mixtures, it is possible to find those tracers (constituent elements in this case) that can rebuild the mixture acceptably. Analyzing the X-Y plots of the elements concentrations it is possible to find which tracers can generate a polygon of sources that contain the 2 mixture's signatures. Once chosen an accurate sub set of elements, using the software, the model is executed using these fingerprints. The following 5 elements behave as effective tracers: Fe, Ca, Na, P and V. Figure 2 shows comparatively real and calculated proportion for MIX 1 and MIX 2.

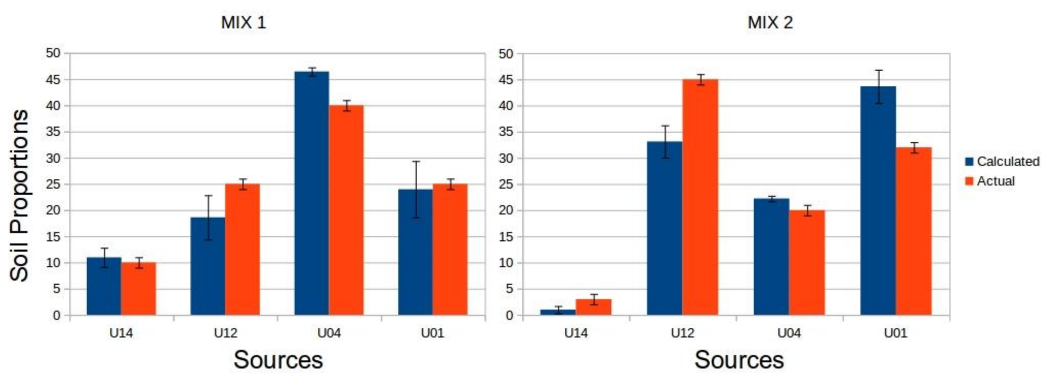


Figure 2. Comparision between actual and calculated soil proportion in the studied (mixed) samples.

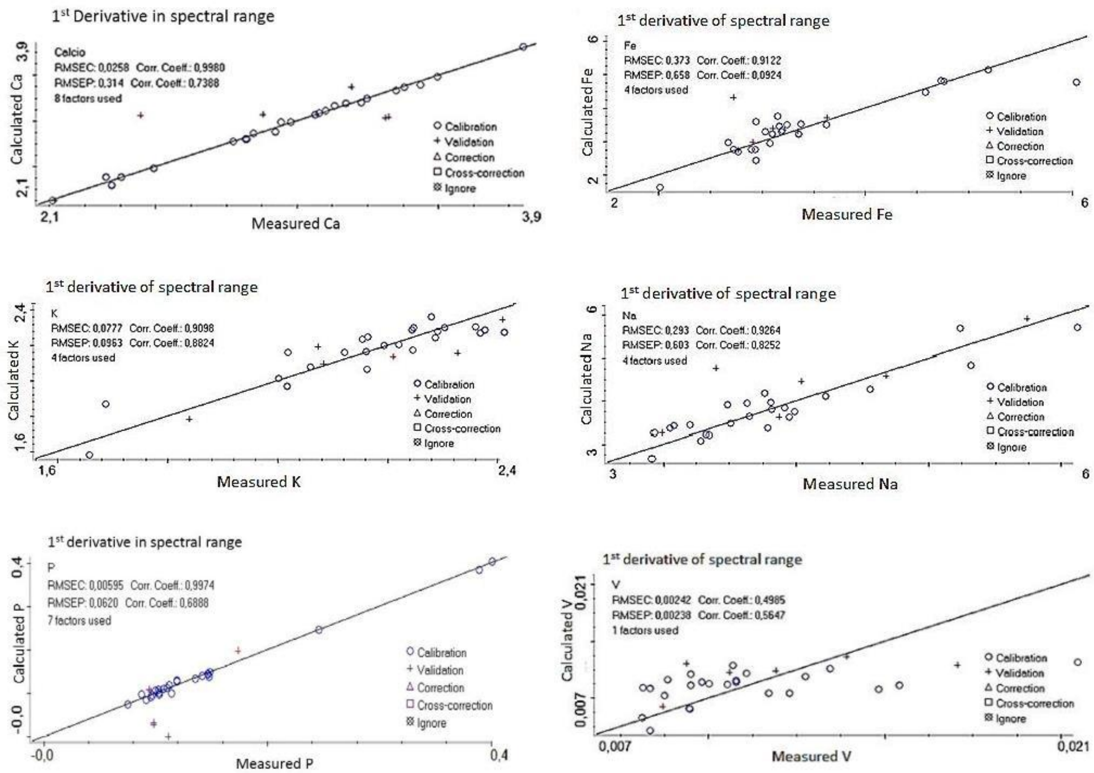


Figure 3. PLS Analysis. Predictive models using the 1st derivative of the spectral data.

A second point of this research was focused in determining if DRIFT-MIRS spectra combined with PLS (normal, first and second derivative) could generate good prediction models of the content of the identified fingerprint elements, across the different concentration ranges of them in all the soil/sediment samples. The cross-validation plots for the PLS of the 1st derivative using the DRIFT-MIRS spectra data for all samples (sources and mixed) are shown in Figure 3. The results for the model were obtained using P, Ca, Na, V, Fe and K to build the model (Table 1).

## Conclusions

Fe, Ca, Na, P and V were suitable fingerprints for the deconstruction of mixed samples. In addition, the DRIFT-MIRS PLS analysis shows a good predictive model using the 1st derivative of the spectral data. This study demonstrated that it is possible to predict the parameters of the quality of P, Ca, K and Na as fingerprint elements, especially P which has been difficult to predict using DRIFT-MIRS PLS analysis with wet analytical techniques.

**Table 1.** Results of root mean square error for calibration and prediction of predictive model using the 1st derivative of the spectral data.

| Results | Ca | K | P | Fe | V | Na |
|---|---|---|---|---|---|---|
| N° factors used | 8 | 4 | 7 | 4 | 1 | 4 |
| RMSEC | 0.0258 | 0.0777 | 0.00595 | 0.373 | 0.00242 | 0.293 |
| Correlation Coeff RMSEC | 0.998 | 0.9098 | 0.9974 | 0.9122 | 0.4985 | 0.9264 |
| RMSEP | 0.314 | 0.0963 | 0.062 | 0.658 | 0.00238 | 0.603 |
| Correlation Coeff RMSEC | 0.7388 | 0.8824 | 0.6888 | 0.0924 | 0.5647 | 0.8252 |
| % RMSEC | 0.87 | 3.59 | 4.33 | 11.05 | 0.003 | 7.54 |

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