Tracing sediment sources in a tropical highland catchment of central Mexico by using conventional and alternative fingerprinting methods

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Abstract (max. 250 words)

Land degradation is intense in tropical regions where it causes for instance a decline in soil fertility and reservoir siltation. Two fingerprinting approaches (i.e., the conventional approach based on radionuclide and geochemical concentrations and the alternative Diffuse Reflectance Infrared Fourier Transform Spectroscopy method) were conducted independently to outline the sources delivering sediment to the river network draining into the Cointzio reservoir, in Mexican tropical highlands. This study was conducted between May and October in 2009 in subcatchments representative of the different environments supplying sediment to the river network. Overall, Cointzio catchment is characterised by very altered soils and the dominance of Andisols and Acrisols. Both fingerprinting methods provided very similar results regarding the origin of sediment in Huertitas subcatchment (dominated by Acrisols) where the bulk of sediment was supplied by gullies. In contrast, in La Cortina subcatchment dominated by Andisols, the bulk of sediment was supplied by cropland. Sediment originating from Potrerillos subcatchment characterised by a mix of Acrisols and Andisols was supplied in variable proportions by both gullies and rangeland/cropland. In this latter subcatchment, results provided by both fingerprinting methods were very variable. Our results outline the need to take the organic carbon content of soils into account and the difficulty to use geochemical properties to fingerprint sediment in very altered volcanic catchments. However, combining our fingerprinting results with sediment export data provided a way to prioritise the implementation of erosion control measures to mitigate sediment supply to the Cointzio reservoir supplying drinking water to Morelia city.

Keywords

Sediment; fingerprinting; soil types; Mexico; tropical catchment.

1. Introduction

Land degradation is particularly severe in tropical regions, such as in Mexico (Descroix et al., 2008), in southern China (Barton et al., 2004) or in eastern Africa (Nyssen et al., 2004). In Mexico, overgrazing, deforestation, and the intensification of food crop cultivation have led to severe erosion and to a decline in soil fertility (Roldán et al., 2003). Furthermore, once it reaches the river, sediment leads to numerous problems in downstream areas (Owens et al., 2005). It causes for instance an increase in water turbidity and a rapid filling of reservoirs (Syvitski et al., 2005). Sediment is also associated with numerous contaminants (e.g., metals, organic compounds, antibiotics, radionuclides; e.g., Tamtam et al., 2011; Le Cloarec et al., 2011). Their integration into the food chain can lead to public health problems after the consumption of contaminated fish (Sánchez-Chardi et al., 2009; Urban et al., 2009). Sediment also conveys nutrients, and soil erosion and deposition play therefore a significant role in global biogeochemical cycles (Quinton et al., 2010). Furthermore, in mountainous environments, the problems associated with erosion and sedimentation are exacerbated by the large quantities of sediment produced within very short periods (Meybeck et al., 2003; Mano et al., 2009).

Sediment supply to the river needs to be controlled to prevent these problems. However, there is a preliminary need to determine the main erosion sources to implement appropriate and effective erosion mitigation measures. In tropical areas such as the highlands of central Mexico where hydrology is controlled by the succession of a dry and a rainy season, it is generally assumed that the increase in discharge at the beginning of the rainy season can lead to an important resuspension of sediment accumulated in the river channel (e.g. Susperregui et al., 2009). Evrard et al. (2010) showed that the first storms of the year exported the bulk of the sediment stock accumulated in the river channel during the previous rainy season. However, this study also outlined that sediment can also be directly eroded from hillslopes and exported from small (3–12 km²) catchments during individual heavy storms. Furthermore, the contribution of different sediment source areas (e.g., historical gullies vs. cropland) was suspected, but it remained to be quantified in order to prioritise the implementation of erosion control measures.

We propose to use two different sediment fingerprinting techniques to outline the main sources of sediment within those catchments. The fingerprinting method consists in tracing conservative sediment properties or characteristics that can be identified in both catchment sources and sediment delivered downstream (Walling, 2005). So far, very few fingerprinting

studies have been conducted in tropical regions (see for instance Collins et al., 2001, in a catchment of Zambia). Fingerprinting generally requires a multi-tracer approach. Besides ‘conventional’ fingerprinting based on the measurement of radionuclides and geochemical elements, alternative fingerprints have been recently used such as sediment colour properties (Martínez-Carreras et al., 2010a, b) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS; Poulenard et al., 2009; Poulenard et al., in press) to trace the origin of suspended sediment transported by rivers.

In this context, we conduct two independent fingerprinting exercises (i.e., the conventional approach based on radionuclide and geochemical concentrations, and the alternative DRIFTS method) to quantify sediment sources in three small tropical catchments of the Mexican Central Highlands. Those three areas cover the range of land use, topographic gradients and soil conditions of the potential areas delivering sediment to a reservoir providing 25% of the water distributed in the region of Morelia city (ca. 1,000,000 inhabitants). The implications of the sediment fingerprinting results to control reservoir siltation will also be discussed. Factors controlling sediment fluxes exported from those catchments and sediment transfer times within those areas are discussed elsewhere (Duvert et al., 2010, 2011; Evrard et al., 2010).

2. Materials and methods

2.1 Study area

The Cointzio catchment covers an area of 630 km² located in the transverse volcanic belt of central Mexico (Fig. 1). The catchment bedrock consists of igneous rocks generated by Quaternary volcanic activities. Soils within the catchment are mainly Acrisols on the hillsides, Andisols in headwater areas and Luvisols in the plains (FAO, 2006). The river network is dominated by the Grande de Morelia River. A dam is located at the outlet of the catchment, 13 km upstream of Morelia city (ca. 1,000,000 inhabitants). This dam was built in 1940 to supply water for domestic consumption as well as for industrial and agricultural activities. The Cointzio reservoir (4 km²; 65×10⁶ m³) undergoes significant sedimentation, which has led to a severe deterioration of environmental conditions in the lake (Ramírez-Olvera et al., 2004) and to a 20% loss of its water storage capacity since its construction (Susperregui et al., 2009).

Three subcatchments representative of the various land use, slope gradients and soil conditions found in the Cointzio catchment were monitored in the framework of this study:

Huertitas (3 km²), La Cortina (9 km²) and Potrerillos (12 km²; Fig. 1). Their characteristics are described in Table 1. In addition, we monitored the river discharge and sediment fluxes in Santiago Undameo, at the outlet of the entire catchment, just upstream of Cointzio reservoir (Gratiot et al., 2010; Duvert et al., 2011). It is important to note that villages located within the catchment are not equipped with sanitation systems and that they directly discharge their wastewater into the river network.

2.2. Field measurements

Rainfall and discharge

Rain gauges and river monitoring stations were installed in the three subcatchments (Fig. 1). They provided continuous precipitation and water discharge data derived from continuous water level measurements (with a 5-min time step) obtained with a Thalimedde OTT water-level gauge, and discharge calculated using stage-discharge rating curves (see Duvert et al., 2010, for details on this method).

Measurement of SSC

At the outlet of each subcatchment, data on Suspended Sediment Concentration (SSC; g L⁻¹) were obtained using an automatic water sampler (ISCO 3700) triggered by water level variations. During floods, water samples were collected after each 5-cm water level variation. This sampling frequency was selected based on the mean characteristics (i.e., flood duration, shape of rising and falling limbs) of the floods recorded previously (i.e., between 2006 – 2008; Duvert and Gratiot, unpublished data) in the subcatchments to obtain a trade-off between a satisfactory flood coverage and a reasonable amount of samples to collect in the field (see Duvert et al., 2010 and Duvert et al., 2011 for details).

SSC (generally ≥ 2 g L⁻¹) was estimated at the laboratory after drying the entire sample for 24 hours at 60°C. For each flood, a composite sample was prepared by mixing all the available individual samples. This provided a mean representative sample of each individual flood with a sufficient quantity of fine sediment (2–50 g) to conduct radionuclide and DRIFTS analyses. Details on the calculation of sediment fluxes at the outlet of the different subcatchments can be found in Duvert et al. (2010). In total, 40 events that occurred between May and November 2009 were sampled throughout the rainy season at the outlet of the three subcatchments.

Soil collection

Soil representative of the different land uses (i.e., gullies, cropland, woodland) observed in the three subcatchments was collected. Sampling was concentrated in potential sediment source areas (i.e., sites sensitive to erosion, and potentially connected to the river network). For each potential source (i.e., gullies, cropland, woodland), we collected five samples of surface material potentially submitted to erosion processes and connected to the river (top 0–5 cm; i.e. 0–2 cm at most locations and 0–5 cm where the erosion extent warranted a deeper sampling depth) and mixed them well to provide a homogeneous sample. In total, 17 representative composite samples were collected in the field between June and November 2009 (Fig. 1). This number of sources samples is rather limited, mainly due to practical and logistical reasons, but stress was laid in the field on providing representative samples of each land use class. In ideal conditions, more samples could have been collected. If we were aiming to discriminate the contribution of different lithological sources to suspended sediment, it would not have been enough to capture the within-source variability of fingerprint properties. However, this study aims to discriminate land use sources. We will therefore add a step to the conventional fingerprinting procedure by selecting the most relevant tracers from a physiochemical point of view to achieve this specific objective.

Furthermore, riverbed sediment was collected on exposed sites located along the main river channel network, using non-metallic trowels in order to avoid sample contamination. Several subsamples (~ 10) were collected in January 2008 and in June 2009 at each of the 18 locations selected along the river network. They were used to prepare composite samples representative of the sediment deposited on the riverbed.

2.3 Soil and sediment analysis

Radionuclide measurements

All suspended sediment and soil samples were dried and sieved (< 250 μm) before analysis. To check that grain size of particles remained similar between soil and sediment samples, grain size distribution was determined with a Malvern® particle size analyzer after being submitted to a 10-min ultrasonic agitation.

Fallout and geogenic radionuclides were measured in all the collected samples ($n=55$ with 17 composite soil samples, 18 composite riverbed samples and 20 composite suspended sediment samples), whereas the analyses of elemental geochemistry were carried out on a selection of samples ($n=37$, i.e. 17 composite soil samples and 20 composite suspended

sediment samples). For the measurement of radionuclides in each sample, soil and sediment were placed in a counting box. Fallout (Am-241, Be-7, Cs-137, Pb-210) and geogenic (K-40, Ra-226, Ra-228, Th-228, Th-234) radionuclide concentrations were determined by gamma-spectrometry using the very low-background coaxial N- and P-types GeHP detectors (Canberra / Ortec) available at the *Laboratoire des Sciences du Climat et de l'Environnement* (Gif-sur-Yvette, France). “Excess” ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$) was calculated by subtracting the supported activity (determined using two ^{238}U daughters, i.e. ^{214}Pb , by taking the average count number at 295.2 and 351.9 keV, and ^{214}Bi at 609.3 keV) from the total activity of ^{210}Pb (measured at 46.5 keV). Efficiencies and background levels of the detectors were periodically controlled with internal and IAEA soil and sediment standards. Radionuclide activities were systematically corrected taking account of the decay after the sampling period.

Geochemical measurements

For the measurement of elemental geochemistry, Rare Earth Elements (REE; i.e., Ce, Eu, La, Lu, Sm, Tb, Yb), three major elements (Fe, K, Na) and ten trace elements (As, Ba, Co, Cr, Cs, Hf, Sc, Ta, Th, Zn) were analysed by Instrumental Neutron Activation Analysis (INAA). Dried subsamples (ca. 40–80 mg) were packed into tightly closed plastic bags, without any preliminary digestion. The subsamples were exposed to irradiation at the experimental nuclear reactor Orphée of the *Commissariat à l'Energie Atomique* (CEA; Saclay, France). The subsamples underwent a flux of thermal neutrons of $2.13 \times 10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ during 30 minutes. After a 4-days cooling, four successive measurements of gamma activities were carried out using HPGe detectors. Two reference materials (i.e., IAEA SL-1 and Soil-7) were systematically used to cross-check the results. Uncertainty on these measurements is $\leq 5\%$.

Carbon and Nitrogen content measurements

Soil and suspended sediment content in bulk Carbon (C) and Nitrogen (N) was measured by CHN analysis using a CN-analyzer FlashEA 1112 (Thermo Fisher Sci., MA, USA) at the *Laboratoire d'Ecologie Alpine* (LECA; Grenoble, France). About 20 mg of each sample were burnt at high temperature with a catalyser under helium flux, to transform total C into carbon dioxide and total N into N_2 . Obtained CO_2 and N_2 were separated using a gas chromatography column and analysed by thermal conductivity detector. Results are expressed in %C and %N. Soil content in carbonates was analysed at the INRA soil analysis laboratory in Arras (France) using classical calcimetric method (Robertson et al, 1999) according to the normative procedure NF ISO 10693. Results are expressed in %C (CaCO_3).

Isotopic analyses

Furthermore, $\delta^{13}\text{C}$ measurements were conducted to outline potentially different contributions of avocado fields and maize fields, based on the difference in the stable carbon isotope signatures between C3 and C4 plants (Balesdent and Wagner, 1988). $\delta^{13}\text{C}$ analyses were conducted on representative samples from (i) maize fields and (ii) avocado fields from La Cortina subcatchment to test the potential discrimination between both sources. Analyses were conducted at LSCE on an EA-IRMS devoted to organic samples (Thermo Fischer Delta+XP).

Spectroscopic measurements

A ThermoNicolet 380 spectrometer equipped with a liquid-nitrogen cooled MCT (Mercury – Cadmium – Telluride) detector was used to perform the Fourier Transform Infrared (FT-IR) analysis of soil and suspended sediment. Spectra were obtained using the diffuse reflectance (DRIFTS) measurement technique. The spectra scan range was 4000 –650 cm^{-1} at a resolution of 2 cm^{-1} with 32 co-added scans per spectrum. Results were then compiled using the OMNIC© (version 7.3) software provided by the spectrometer manufacturer (ThermoNicolet, USA). This software facilitated measurement of the peak areas that were relevant to determine the DRIFTS signatures.

2.4. Statistical analyses and sediment tracing

Conventional mixing model

The different sediment source types were characterised by their mean concentration and by the standard deviation of each of the 29 radionuclide and geochemical properties measured in the samples. The ability of the 29 potential fingerprinting properties to discriminate between the potential sediment sources was investigated by conducting a Kruskal-Wallis H -test as initially proposed by Collins and Walling (2002). Based on the set of discriminating properties retained, an optimum ‘composite fingerprint’ was identified by performing a stepwise selection procedure. This procedure consisted in minimising Wilk’s lambda, as suggested by Collins and Walling (2002). Then, we constructed a Monte Carlo mixing model to quantify the range of contribution of each sediment source to the sediment samples collected at the different stations. Details on this model can be found in Evrard et al. (2011).

DRIFTS-PLS model for source determination

In each subcatchment, two main types of potential sediment sources were considered (see the land use classes mentioned in Table 2). Two to six soil samples of each source were mixed in equal proportions to constitute a unique reference sample for the corresponding source type. In subsequent steps, those reference samples were mixed in various weight proportions. A DRIFTS spectrum was obtained for each mixture. The number of mixtures prepared in each case varied between 20 and 30. This choice was dictated by (i) the previous experiments showing that the chemometric models can be built based on the analyses of 20 to 30 mixtures (Poulenard et al., 2009 ; Poulenard et al., in press) and (ii) the willingness not to over complicate the procedure when applying the DRIFTS-PLS method to several subcatchments. Relationships between DRIFTS spectra ('x' variate) and the corresponding weight contribution of the sediment source datasets ('y' variate) were analysed using Partial Least Square (PLS) analyses. Approximately 75% of samples were used to develop the calibration models, whereas the remaining 25% were used for validation. In order to get rid of the small differences due to uncontrolled sources of variation, data pre-processing methods were applied to the spectra, such as baseline correction, Savitzky–Golay smoothing, mean centering, variable scaling, multiplicative signal correction (MSC) and standard normal variate (SNV). The procedure followed by Poulenard et al. (2009; in press) was used to determine the number of components providing the best compromise between the description of the calibration set and the model predictive power, i.e. the lowest predictive standard error (PRESS).

The predictive performance of the models was evaluated by calculating several standard indicators such as the root-mean-square error of calibration (RMSEC), the root-mean-square error of cross-validation (RMSECV), the root-mean-square error of prediction (RMSEP), and coefficient of determination R^2 of predicted values against reference data. Model validation was performed by both cross-validation and validation. RMSECV and RMSEP values provided the average uncertainty that can be expected for predictions of future samples. This uncertainty is only associated with the use of PLS models. Additional uncertainty associated with the application of this model to suspended sediment could not be taken into account.

Two independent PLS models were constructed to estimate the proportion of sediment originating from the main potential sources in each subcatchment. DRIFTS spectra of suspended sediment were then introduced into these PLS models to estimate the contribution of each sediment source and the associated uncertainty (Poulenard et al., in press).

3. Results

3.1. Quantifying the contribution of sources delivering sediment to the river

Overall, soils of the catchment are characterized by very low concentrations in geochemical elements and carbonates ($< 0.01\%$) (Table 2). These low levels reflect the strongly weathered character of soils in this highland volcanic region of central Mexico. This strong alteration is confirmed by the low content of soils in elements such as K, C and N in degraded soils and gullies (Table 2) as already reported by Bravo-Espinoza et al. (2009). Furthermore, the bulk of C content in soils is mainly under organic form as previously observed in the same study area (Cavolea et al, 2011). In this context and to provide a strong physiochemical basis to our conventional fingerprinting exercise, we decided to restrict our fingerprint property selection to the fallout radionuclides and the biogenic elements. Fallout radionuclides such as ^{137}Cs and $^{210}\text{Pb}_{\text{xs}}$ can indeed provide a powerful tracer to discriminate between surface and subsurface (i.e., gully) sources (Wallbrink and Murray, 1993). Biogenic elements (e.g., C, N) can also provide this information, provided they are used to quantify the sources of suspended sediment to ensure that the conservation of those properties is achieved during the rapid transfer of particles to and within the river (Collins and Walling, 2002).

Conservation of particle grain size during their transfer between the sources and the river constitutes another prerequisite of the fingerprinting method to verify. Particle size was constant in 2009 at the outlet of each subcatchment, as demonstrated by the median particle size (d_{50}) of sediment collected in Huertitas ($10\pm 1\ \mu\text{m}$), Potrerillos ($12\pm 4\ \mu\text{m}$) and La Cortina ($26\pm 6\ \mu\text{m}$). Furthermore, those values are very close to the median sizes of particles measured in the soil samples (Tables 2 and 3).

Conventional fingerprint properties retained to discriminate sediment sources in the three subcatchments are provided in Table 4. Performance of predictive models used for the DRIFTS approach are given in Table 5. The PLS model, based on soil mixture analyses, was robust despite the limited number of samples analysed (Table 5). The correlations between actual and predicted proportions are excellent with R^2 close to 1 for all the models. The RMSEP (average difference between prediction and actual value on the set of calibration – i.e., not used to build the model) remains close to 10%. This is acceptable given that our study only aimed at obtaining an order of magnitude of the contribution of different sources delivering sediment to the river.

Huertitas

This subcatchment exported large quantities of sediment ($900 - 1500 \text{ t km}^{-2} \text{ y}^{-1}$; Duvert et al., 2010). Active gully networks provided a constant source of sediment. Our fingerprinting analyses showed that sediment collected at the outlet during the 2009 rainy season was mostly supplied by the extended gully network of this subcatchment. This contribution varied between $72 \pm 10\%$ and $100 \pm 12\%$ according to the model based on spectroscopic properties, and between $88 - 98\%$ according to the conventional mixing model (Figure 2). The low content in %C (about 1%) and in %N (about 0.08%) of sediment during floods illustrates that most of the sediment originated from gully soils poor in C and N. Sediment supply by cropland slightly decreased throughout the rainy season, which probably reflects the effect of vegetation growth that protected the soil against rainfall splash effect and erosion. During the most erosive storms (e.g., on 3 September), sediment was almost only supplied by gullies. Results provided by both spectroscopic and “conventional” fingerprinting techniques are consistent.

La Cortina

This subcatchment exported low quantities of sediment (ca. $30 \text{ t km}^{-2} \text{ y}^{-1}$; Duvert et al., 2010). An attempt was made to differentiate the contribution of different vegetation types based on their stable carbon isotopic signature but we could not outline any different contribution of maize and avocado fields. However, test analyses showed that $\delta^{13}\text{C}$ value in river sediment ($-22.22 \pm 0.15\text{‰}$) was close to cropland value (between $-22.31 \pm 0.10\text{‰}$ and $-21.86 \pm 0.10\text{‰}$) and significantly different from the woodland value ($-26.60 \pm 0.10\text{‰}$). DRIFT-PLS model showed that 70 to $80 \pm 20\%$ of the suspended sediment was provided by cropland without significant differences all throughout the season (Figure 3). The mixing model based on conventional fingerprinting properties similarly showed that $50 - 85\%$ of sediment was supplied from cropland area. This result is consistent with the mean content in carbon (6.5 %) and nitrogen (0.4 %) of sediment during flood that is very close to the mean content measured in soils (%C = 6.31 and %N = 0.43) (Table 2). Sediment export was higher during the first months of the rainy season because vegetation growth has progressively protected the soil against erosion and because the first storm of the rainy season flushed the sediment stock accumulated on the riverbed as demonstrated by Evrard et al. (2010).

Potrerosillos

Sediment source contributions varied strongly throughout the rainy season. This subcatchment was characterized by large sediment exports ($600 - 800 \text{ t km}^{-2} \text{ y}^{-1}$; Duvert et al., 2010). A rapid succession of several storms was observed in this catchment in 2009 that was characterized by a strong reactivity and a “sawtooth behaviour”. Sediment was delivered by both gullies and rangeland, in variable proportions (Figure 4).

Results provided by both fingerprinting techniques differ, mainly for 3 to 4 events (Figure 4). Conventional fingerprinting showed a strongly variable supply of sediment by gullies (5–86%) and rangeland (14–95%) all throughout the season. A very variable sediment supply by gullies (36–97%) was also outlined by the DRIFTS approach. This bias is partially explained by the relationships observed between the contribution of the topsoils in rangeland determined by DRIFTS-PLS model and the organic carbon content of suspended sediment (Figure 5). The mid-infrared signature and thereby the results of DRIFTS-PLS were clearly influenced by the organic carbon content originating from the topsoil horizons. The DRIFTS-PLS model provided in this case discrimination between the relative contribution of topsoils (relatively rich in organic matter; Table 2) and the deep horizons of gullies depleted in organic matter. During the first flood of the season, river sediment sample was characterized by a very high C content (2% vs. 0.3–0.8% during the rest of the season; Fig. 5). This is probably due to the export of cow dung stored on the soil surface by the first heavy storm of the season. This indicates that, at the beginning of the rainy season, an important stock of sediment and organic matter can be easily mobilized. This stock is probably accumulated during the dry season due to the combined effect of cattle grazing and trampling of the soil.

3.2. Origin of sediment along the river network

Overall, concentrations in geochemical elements and activities in radionuclides are very low in all the riverbed sediment collected along the river network of the entire catchment (data not shown). Various ratios between geochemical elements and radionuclides were calculated but they did not provide a way to outline specific sediment contributions within the catchment. However, farming practices such as application of fertilizers and pesticides can affect the composition of agricultural soils and sediment (Bravo-Espinoza et al., 2009). Phosphate fertilizers contain indeed 10 – 200 times more U than soils, whereas they have a lower Th content than soils (Takeda et al., 2004). The U/Th ratio can therefore provide a way to outline the supply of sediment by agricultural soils along the river network. Figure 6 illustrates that U/Th ratio gradually increased from headwaters to the Cointzio reservoir. We

hypothesize that this observation reflects the increase in sediment supply by agricultural areas along the river network. This hypothesis is consistent with the more detailed fingerprinting results available for the three subcatchments (Fig. 6): (i) U/Th ratio is high in sediment collected at the outlet of La Cortina where the bulk of material was supplied by cropland; (ii) U/Th ratio was lower at the outlet of Potrerillos where a mixed contribution of gullies and rangeland was outlined and (iii) U/Th ratio was the lowest at the outlet of Huertitas where sediment was almost exclusively provided by the gully network.

3.3. Origin of sediment at the catchment outlet

Based on the previous work conducted in the subcatchments, we wanted to outline the origin of suspended sediment collected at the river station draining the entire catchment and located just upstream of Cointzio reservoir. We chose to discriminate the sediment delivered by Acrisols (i.e., dominant type in Huertitas and Potrerillos) from sediment supplied by Andisols (i.e., dominant type in La Cortina). Reference Acrisols were taken from Huertitas gullies, whereas reference Andisols consisted of cropland soil (i.e., corn and avocado fields) from La Cortina. Infrared spectrum of Acrisols was characterized by the dominance of kaolinite in the clay fraction with three classical bands in the 3600–3700 cm⁻¹ area. In contrast, Andisol spectrum was associated with gibbsite characteristic bands (Figure 7).

When compared to those source spectra, the infrared spectra of suspended sediment collected at Santiago Undameo station were very similar to the Acrisol spectra. The PLS-DRIFTS model confirmed the dominance of the contribution of Acrisols delivering more than 70% of the suspended sediment conveyed by the river at that location. This proportion can even reach 90% during most of the rainy season during which 99% of sediment are exported to the lake (Figure 8). In contrast, during the dry season, the PLS-DRIFT model indicates that the sediment delivery from cultivated Andisols is higher and can reach up to 30% of total sediment, but this sediment corresponds to only 1% of the annual export from the entire catchment, which is negligible. Furthermore, those low water periods also coincide with the highest organic carbon concentrations measured in river sediment (Figure 8). This carbon is likely to originate from local villages that are not equipped with sanitation systems. In contrast, during high flow periods, river sediment is characterised by very low carbon contents, which is consistent with a dominant sediment supply by Huertitas or Potrerillos-like gully soils (Table 2). Apparent increase of sediment supply by cultivated Andisols to the river

could then reflect a bias of the DRIFT-PLS approach induced by this strong increase in the organic carbon content of sediment during the dry season.

4. Discussion

4.1 Sediment tracing methods

The low concentrations in geochemical elements made it difficult to outline significant composition differences between different types of sources (e.g., soil types). In contrast, low activities in fallout radionuclides provided an efficient way to discriminate between different types of sources (typically gullies vs. cropland surface sheet erosion) when low-background and efficient gamma spectrometry detectors are available to conduct measurements. The results obtained in this study confirmed the preliminary observations made by Evrard et al. (2010) on potential sediment sources based on the Cs-137 activities in soils and sediment.

The DRIFT-PLS method provided results that are very consistent with the conventional geochemical approach in the context where minerals provide a dominant signal to the soil. In these contexts, with very distinct mineralogy, a simple qualitative comparison of infrared spectra provided a fast way to identify the dominant sediment sources. The dependence of the infrared method to the soil content in organic matter has facilitated sediment source apportionment in Potrerillos catchment, where it outlined the relative important contribution of surface (cropland) and depth (gullies) material, which was consistent with the carbon content of exported sediment. However, during the low stage period, the introduction of one source of soluble organic matter delivered by anthropogenic activities that is likely to have sorbed onto suspended sediment led to an overestimation of the contribution of surface soil to river sediment, given that they were the only sources included into the model and containing a large organic carbon content.

4.2 Soil conservation in highland tropical catchments of central Mexico

Our results have clear and significant management implications to control erosion and reservoir siltation in this Mexican catchment. It is important to highlight that high turbidity levels are observed at a regional scale in lakes and reservoirs of the Mexican central plateau (Merino-Ibarra et al., 2007; Bravo-Inclan et al., 2008 ; Severo et al., 2002). However, none of them attenuates light penetration to such a degree as in Cointzio reservoir, where Secchi disk depths rarely exceed 0.2m (Susperregui et al., 2009). Our results showed that gullies

developed in Acrisols provide the bulk of fine particles to the reservoir, even if they occupy less than 0.5% of the catchment area (Mendoza and Lopez, 2007). In this context, it is clear that mitigation efforts concentrated in areas sensitive to soil erosion could lead to a rapid improvement of water quality in the catchment and, more importantly, in the Cointzio reservoir.

In future, the expected decrease in rain and the increase in temperature should result in an increase in aridity and in surface runoff (Gratiot et al., 2010), which will certainly complicate the implementation of soil conservation measures already tested in the area such as the introduction of a crop rotation and the use of a crop residue cover on the soil (Bravo-Espinoza et al, 2009). In this context, it is urgent to test some complementary mitigating strategies to stabilize specific gullies and to evaluate their effectiveness, before generalizing their installation across the entire Cointzio catchment (Martinez-Palacios et al., 2011).

5. Conclusions

Land degradation is intense in tropical regions, such as in volcanic highlands of central Mexico. Two fingerprinting approaches were conducted to outline the main sources delivering sediment leading to the siltation of Cointzio reservoir draining a 630-km² catchment. This study was conducted in three subcatchments (3 – 12 km²) representative of the different environments observed in this area. Both fingerprinting methods provided similar results in Huertitas catchment, covered with Acrisols, where sediment was almost exclusively delivered by gullies. In La Cortina, characterized by Andisols, sediment was supplied by cropland. However, results provided by both methods in Potrerillos, covered with a mix of Andisols and Acrisols, strongly differed. Furthermore, massive export of sediment rich in organic matter produced by cattle activity and trampling during the dry season by the first heavy storm of the year is suspected in this subcatchment. This study thereby outlined several difficulties encountered when conducting fingerprinting studies in this type of volcanic catchments. First, soils are very altered in this region, complicating the choice of relevant geochemical fingerprint properties. Second, the DRIFTS-PLS method proved to be very sensitive to the soil content in organic matter. Nevertheless, in a second step, our study could demonstrate the dominant contribution of Acrisols to the sediment delivered from the entire 630-km² catchment to the Cointzio reservoir. Soil conservation measures should therefore focus on stabilizing gully networks as the ones observed in Huertitas catchment as well as on implementing alternative farming practices in Potrerillos-like areas. In the future,

both fingerprinting methods could usefully be applied to trace sediment in different environments, and solutions to decrease the potential DRIFTS-PLS method sensitivity to soil organic matter content should be investigated.

Acknowledgements

This is the LSCE contribution No. X. This work is a part of the STREAMS (*Sediment Transport and Erosion Across Mountains*) project, funded by the French National Research Agency (ANR/ BLAN06-1_139157) and DESIRE (Desertification, mitigation and land Restoration) project funded by European Union. The authors are also very grateful to Dr. Christine Hatté for conducting the test $\delta^{13}\text{C}$ measurements.

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Figure captions

Figure 1. Location of the monitored subcatchments (Huertitas, Potrerillos, La Cortina) and the Santiago Undameo station within the Cointzio catchment in the tropical highlands of central Mexico. Areas characterized by different soil types are also delineated, and locations where composite soil samples were collected are indicated. This study focused on the samples collected within the boundaries of the monitored subcatchments.

Figure 2. Sediment sources in Huertitas catchment as defined by conventional and alternative fingerprinting techniques. Please note that, because of logistical problems to conduct the sample irradiations, results derived from the conventional mixing model are only available for the five first composite river sediment samples of the season.

Figure 3. Sediment sources in La Cortina catchment as defined by conventional and alternative fingerprinting techniques.

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Figure 4. Sediment sources in Potrerillos catchment as defined by conventional and alternative fingerprinting techniques.

Figure 5. Relationship between contribution of rangeland topsoil and suspended sediment organic carbon content at the outlet of Potrerillos subcatchment. Carbon content of sediment collected during the 1/7/2009 flood constitutes an outlier (probably explained by the massive export of cow dung stored on the soil surface by the first heavy storm of the season).

Figure 6. Values of U/Th ratio measured in riverbed sediment samples collected along the river network within the entire catchment (U corresponds to activities in Ra-226, and Th to activities in Ra-228).

Figure 7. Typical spectra of Andisols, Acrisols and suspended sediment collected at Santiago Undameo station.

Figure 8. Contribution of Acrisols to sediment monitored at Santiago Undameo station. Discharge values correspond to mean discharges measured during the sediment collection period by the trap.

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Tables

Table 1
Altitude, soil, slope, and erosion characteristics of the study sites

Subcatchment	Area (km ²)	Altitude range (m)	Soil types ^a	Severely eroded areas ^b (% of the catchment surface)
Huertitas	3	2150 – 2450	Acrisols (100%)	6
La Cortina	9	2250 – 2700	Andisols (100%)	0
Potrerosillos	12	2200 – 2700	Acrisols (60%) Andisols (40%)	1
Undameo	630	2000 – 3440	Andisols (37%) Luvisols Acrisols (33%)	0.5

^a According to FAO (2006).
^b Derived from the analysis of aerial photographs.

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Table 2
Geochemical (g kg⁻¹), radionuclide (Bq kg⁻¹), organic matter (%) and grain size properties of the sediment source samples.

Huertitas		n	K	Na	As	Th	Yb	Hf	Fe	Tb	Sc	Ta	Cs	Co	Eu	xs-Pb-210	Pb-210	Th-234	Ra-226	Ra-228	Th-228	Cs-137	%C	%N	%C (CaCO ₃)	% <63µm	d50 (µm)
Gullies	mean	6	0.0	0.0	2.3	6.2	2.5	6.2	6.8	0.5	23.7	1.0	0.9	20.7	0.9	0.0	17.0	23.4	23.7	24.2	24.2	0.0	0.34	0.03	< 0,01	95	12
	variance		0.0	0.0	1.5	1.9	0.2	1.1	0.1	0.1	1.5	0.5	0.8	9.9	0.0	0.0	20.0	23.3	31.3	38.1	34.6	0.0	0.28	0.03		1	2
Cropland	mean	3	0.4	0.2	2.0	7.1	2.9	7.1	6.4	0.9	20.0	0.8	1.8	30.1	1.0	8.0	34.0	32.5	26.1	27.2	27.7	1.3	2.73	0.21	< 0,01	88	17
	variance		0.0	0.0	5.7	3.9	0.0	0.4	0.1	0.0	0.3	0.8	4.3	43.2	0.0	5.1	63.2	19.3	36.7	48.1	65.8	0.9	0.75	0.06		3	2
La Cortina																											
Cropland	Mean	2	0.1	0.1	6.4	9.4	3.0	8.7	7.2	1.0	22.3	2.1	5.0	21.5	1.4	16.2	49.8	38.1	33.7	36.8	37.4	3.7	6.31	0.43	0.02	89	19
	Variance		0.0	0.0	1.1	3.7	0.1	1.3	0.2	0.0	0.2	0.9	0.2	16.2	0.1	5.3	6.6	14.0	23.9	10.8	10.8	0.3	0.14	0.03	0.01	11	10
Woodland	Mean	2	0.2	0.1	5.5	9	2	7.7	7.2	1.2	23.7	1.3	5.1	25	1.6	81.0	37.1	37.8	32.8	36.1	36.8	6.6	9.94	0.50	0.01	81	26
	Variance		0.0	0.0	0.3	0.4	0.1	0.4	0.4	0.1	1.2	0.1	0.3	1.3	0.1	62.0	1.9	1.9	1.6	1.8	1.8	0.3	5.6	0.1	0.01	6	2
Potrerosillos																											
Gullies	Mean	2	0.7	0.9	0.0	8.0	2.4	8.2	6.2	1.6	17.3	1.8	4.5	29.2	1.3	0.0	17.2	32.0	23.1	32.2	32.8	1.3	0.13	0.01	< 0,01	83	25
	Variance		0.0	0.1	0.0	0.0	0.0	1.0	0.1	0.4	1.6	0.0	6.8	15.4	0.0	0.0	4.0	6.3	8.5	1.9	3.5	2.1	0.12	0.02		11	8
Cropland	Mean	2	0.4	0.4	3.2	6.8	2.5	6.0	6.1	0.5	17.3	2.2	1.6	27.0	0.9	7.0	30.0	33.7	23.8	31.6	32.1	1.4	1.43	0.11	< 0,01	82	22
	Variance		0.0	0.0	0.3	0.0	0.0	0.1	2.8	0.4	3.3	0.4	3.4	37.0	0.0	10.0	53.3	3.2	13.2	0.1	0.3	0.9	0.74	0.07		11	12

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Table 3
Geochemical (g kg⁻¹), radionuclide (Bq kg⁻¹), organic matter (%) and grain size properties of the river sediment samples.

Huertitas	Date	K	Na	As	Th	Yb	Hf	Fe	Tb	Sc	Ta	Cs	Co	Eu	xs-Pb-210	Pb-210	Th-234	Ra-226	Ra-228	Th-228	Cs-137	%C	%N	% <63µm	d50 (µm)
	26/06/09	0.2	0.1	2.8	6	2	6.0	6.1	0.0	20.1	0.0	3.3	18	0.7	15.0	34.1	31.4	19.3	29.2	26.4	0.5	1.2	0.08	97	10
	12/07/09	0.2	0.1	3.3	7	3	6.9	6.3	0.0	21.5	1.3	0.0	19	0.9	11.0	33.5	32.3	22.1	28.3	27.5	0.5	1.1	0.08	99	9
	25/07/09	0.1	0.1	0.0	5	2	7.1	6.3	0.0	19.4	0.0	0.0	21	0.6	13.0	34	26.2	21.0	26	27	0.0	1.2	0.08	92	11
	25/07/09	0.2	0.1	2.5	6	3	6.1	6.6	0.7	21.5	1.0	2.4	22	0.8	14.0	34	29.6	20.0	26	27	0.0	1.2	0.08	96	10
	04/08/09	0.2	0.1	3.3	6	2	6.4	6.5	0.0	20.4	0.0	2.4	24	0.6	10.0	25.6	23.8	15.5	24.5	22.9	0.4	0.9	0.05	91	11
La Cortina	Date	K	Na	As	Th	Yb	Hf	Fe	Tb	Sc	Ta	Cs	Co	Eu	xs-Pb-210	Pb-210	Th-234	Ra-226	Ra-228	Th-228	Cs-137	%C	%N	% <63µm	d50 (µm)
	14/07/09	0.3	0.2	3.8	7	3	6.2	6.5	2.3	23.8	1.5	4.2	23	1.9	40.0	65.3	38.1	25.8	29.4	30.9	2.8	7.1	0.48	88	18
	25/07/09	0.2	0.1	4.2	6	3	5.6	6.3	1.0	22.8	1.2	2.6	22	1.4	50.0	68.0	23.1	18.6	21.3	25.4	2.5	6.9	0.45	n/a	n/a
	06/08/09	0.2	0.1	3.4	6	3	5.6	6.5	0.8	21.6	1.1	2.1	25	1.1	24.0	42.0	28.4	17.6	23.1	24.1	2.4	5.4	0.32	76	29
	14/08/09	0.2	0.2	3.3	6	3	5.7	6.4	0.7	22.1	0.0	2.5	22	1.4	48.0	61.2	22.9	13.0	25.5	24.9	2.0	6.1	0.39	81	29
	26/08/09	0.2	0.1	0.0	6	3	6.0	6.4	0.9	21.5	0.0	2.6	23	1.1	39.0	59.3	34.0	20.5	27.8	28.6	2.0	7.1	0.42	75	30
Potrerosillos	Date	K	Na	As	Th	Yb	Hf	Fe	Tb	Sc	Ta	Cs	Co	Eu	xs-Pb-210	Pb-210	Th-234	Ra-226	Ra-228	Th-228	Cs-137	%C	%N	% <63µm	d50 (µm)
	01/07/09	0.6	0.4	0.0	9	5	8.1	6.4	1.4	22.6	1.6	3.5	28	1.9	5.0	29.7	38.3	24.7	37.8	36.4	0.5	2.0	0.12	n/a	n/a
	12/07/09	0.5	0.4	0.0	7	3	7.0	5.6	1.1	18.0	0.0	5.6	22	1.3	8.0	29.8	32.1	21.7	35.8	35.4	0.0	0.4	0.02	97	10
	15/07/09	0.6	0.3	2.8	8	3	6.8	6.2	0.0	20.6	0.0	4.2	25	1.4	1.0	25.5	34.9	24.5	32.4	32.2	0.3	0.8	0.05	95	10
	16/07/09	0.6	0.5	3.0	8	4	7.2	6.0	0.0	19.7	1.3	4.6	26	1.3	15.0	29.4	30.1	14.0	31.9	26.8	0.0	0.3	0.01	88	16
	17/07/09	0.6	0.6	3.3	6	3	6.5	5.7	0.0	16.8	0.0	5.6	29	1.2	6.0	19.8	27.4	13.6	27.7	24.3	0.3	0.4	0.02	n/a	n/a
	19/07/09	0.6	0.6	0.0	7	3	6.7	6.5	1.1	19.0	1.5	3.4	36	1.2	5.0	17.9	27.3	12.9	26.0	25.1	0.3	0.6	0.02	88	16
	26/07/09	0.6	0.5	3.3	8	3	5.9	5.6	0.7	17.8	1.3	6.2	22	1.1	14.0	28.0	29.0	15.0	33	33.0	0.0	0.4	0.02	99	7
	28/07/09	0.6	0.4	2.6	8	3	6.8	6.3	0.7	20.2	2.0	6.1	23	1.2	17.0	20.0	32.0	13.0	33	28.0	0.0	0.5	0.03	99	8
	18/08/09	0.6	0.7	0.0	7	3	6.8	6.6	0.9	18.4	1.5	4.9	41	1.1	1.0	26.8	33.5	24.7	31.9	33.1	0.2	0.5	0.02	87	16
	22/08/09	0.5	0.4	2.4	8	3	8.5	6.9	0.8	20.7	1.3	5.9	31	1.0	1.0	23.2	35.9	24.2	33.1	33.7	0.4	0.5	0.03	86	19

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776 Table 4
 777 Discriminant properties in the three study sites (Wilk's lambda and percentage of correctly classified samples)
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780	Fingerprint property	Wilk's lambda	Cumulative % of
781	added		samples classified
782			correctly
783	<hr/>		
784			
785	(a) Huertitas subcatchment		
786	C	0.0192	96
787	xs-Pb-210	0.0096	98
788	Cs-137	0.0048	100
789			
790	(b) La Cortina subcatchment		
791	xs-Pb-210	5.88 E-15	100
792	Cs-137	9.81 E-17	100
793			
794	(c) Potrerillos subcatchment		
795	C	1.07 E-16	100
796	xs-Pb-210	2.18 E-17	100
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808 Table 5
 809 Predictive performance of the PLS (Partial Least Squares) models in the different Mexican subcatchments
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Sub-catchment	Number of mixture samples	Considered sources of sediments	R ²	RMSEC	RMSEP	RMSECV
Huertitas	20	Gullies	0.99	2.38	4.49	6.13
		Cropland	0.99	1.1	4.41	5.88
La Cortina	32	Forest Road	0.99	1.18	2.43	6.64
		Cropland	0.99	2.96	8.66	6.67
Potrerillos	22	Gullies	0.99	0.321	11.1	11.1
		Cropland	0.98	5.04	7.46	6.73
Undameo	22	Acrisols	0.99	4.08	2.24	13.2
		Andisols	0.99	5.21	3.41	13.6

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 812 R²: coefficient of determination; RMSEC: Root-Mean-Square Error of Calibration; RMSEP: Root-Mean-Square Error of Prediction; RMSECV:
 813 Root-Mean-Square Error of Cross-Validation.
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[S180] Tracing sediment sources in a tropical highland catchment of central Mexico by using conventional and alternative fingerprinting methods

Journal:	<i>Hydrological Processes</i>
Manuscript ID:	HYP-11-0762.R1
Wiley - Manuscript type:	Special Issue Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Evrard, Olivier; CEA, LSCE Poulenard, Jerome Nemery, Julien; G-INP, LTHE Ayrault, Sophie; CEA, LSCE Gratiot, Nicolas; IRD, LTHE Duvert, Clement; IRD, LTHE Prat, Christian; IRD, LTHE Lefèvre, Irène; CEA, LSCE Bonté, Philippe; CEA, LSCE Esteves, Michel; IRD, LTHE
Keywords:	sediment, fingerprinting, soil types, Mexico, tropical catchment

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Figure 1

Figure 5.

Figure 6. Values of U/Th ratio measured in riverbed sediment samples collected along the river network within the entire catchment (U corresponds to activities in Ra-226, and Th to activities in Ra-228).

Figure 7.

Figure 8.