universität wien

MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

„The importance of foreplay in sediment fingerprint studies"

verfasst von / submitted by

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angestrebter akademischer Grad / in partial fulfilment of the requirements for the degree of

Master of Science (MSc)

Wien, 2020 / Vienna 2020

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet:	A 066 855
Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:	Masterstudium Geographie / Master's degree programme Geography
Betreut von / Supervisor:	Dr. Sabine Kraushaar

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Vienna, April 2020

Konzett Matthias

Acknowledgements

First of all, I would like to thank Sabine Kraushaar at the University of Vienna. Thank you for inspiring me on geomorphology and soils, all your time, your help during the field campaign, encouraging me for this thesis and supervising it.

Further, I want to thank Julia Meister at the University of Würzburg for her advices, reviewing and the overall support for the thesis.

Big thanks to Janika Kiep from the Freie Universität Berlin for partnering up, the flawless work, showing me how to analyze and count Phytoliths, helping me to find a place and bars/Spätis in Berlin.

Additionally, I would like to thank Philipp Garbe of the University of Würzburg, who took time off his PhD in order to further analyze Phytoliths.

Moreover, I would like to thank Peter Nagl at the University of Vienna for giving me the possibility to learn how to prepare and analyze soil samples for their geochemical composition and analyzing the samples.

A special thank goes to all my friends at the University of Vienna, the Geography degree program and the Engage working group for this precious time, laughter and the countless beers.

I would also like to thank my friends outside the University without whom my studies would have been finished much faster, but my life would have been unpleasant and boring.

Jakob… My dear Jakob (Heinzle). You were the Samweis Gamdschie to my Frodo Baggins. Thank you for being my duo partner for so many years. Without you I would not be where I am now.

A heartfelt thanks goes to my mother, father and sister. Thank you for making all this even possible by giving me the opportunity to study in Vienna, always having my back but also – if needed – giving me a nudge in the right direction.

Last but not least, a very special thank goes to my beloved Lisa for your invaluable support, enduring my moods during the writing process, and the welcome diversions from work.

Abstract

A widely used tool in order to estimate relative source contributions to the overall eroded sediment of mid to large scale catchments is sediment fingerprinting. In order to do so, the deposited sediment in sinks as well as soil samples of the classified sources (e.g. land use, lithology, …) are analyzed on their tracer (e.g. geochemistry, pollen, …) composition. Before the estimated source contributions are calculated, it is common to apply (statistical) tests on the analyzed tracers to identify those – so called fingerprints – which have the highest discrimination potential between the sources of the catchment. Depending on the fingerprints applied – and therefore depending on the fingerprint selection procedure used – the results may vary. Therefore, there is a need to establish which selection procedure delivers the most reliable results. In order to achieve this aim, this study conducted a sediment fingerprinting approach in a subcatchment of the Isábena catchment.

Three optimum packages (OP) were generated using three different fingerprint selection procedures and used to calculate the estimated source contributions to the deposited sediment along the river using the R-package “fingerPro” by Lizaga et al. (2018). Validation of the optimum packages and the estimated contributions was conducted with a linear discriminant analysis (LDA), literature reviews, and artificial sink samples.

The results of the study suggest, that the most accurate contributions are produced with a fingerprint selection consisting of a range test, Kruskal-Wallis test, and a discriminant function analysis. The authors further recommend to validate sediment fingerprinting results with artificial sink samples as they have shown to be the most reliable validation tool.

Kurzfassung

Ein oft genutztes Mittel um die relativen Erosionsbeiträge verschiedener Quellen in einem mittelgroßem bis großem Einzugsgebiet abzuschätzen ist das sogenannte sediment fingerprinting. Dafür wird das in Senken abgelagerte Sediment sowie Bodenproben der Quellen (z.B. Landnutzung, Lithologie, usw.) auf ihre Tracer-Zusammensetzung (z.B. Geochemie, Pollen, usw.) analysiert. Bevor die Quellenbeiträge berechnet werden, werden üblicherweise (statistische) Tests an den analysierten Tracern durchgeführt, um diejenigen – sogenannte fingerprints (Fingerabdrücke) – zu identifizieren, die das höchste Diskriminierungspotential zwischen den Quellen des Einzugsgebiets aufweisen. Abhängig von den verwendeten fingerprints und daher von dem verwendeten fingerprint Auswahlverfahren können die Ergebnisse variieren. Deshalb sollte das Verfahren bestimmt werden, welches die zuverlässigsten Ergebnisse liefert. Um dieses Ziel zu erreichen, wurde in dieser Studie einen sediment fingerprinting Ansatz in einem Teileinzugsgebiet des Isábena Einzugsgebiets durchgeführt.

Drei Optimum Pakete (OP) wurden durch die Anwendung von drei verschiedenen Verfahren zur Auswahl von fingerprints erzeugt. Diese wurden dann zur Berechnung der relativen Beiträge der Quellen zum erodierten und abgelagerten Material in Senken entlang des Flusslaufes mithilfe des R-Pakets „fingerPro“ von Lizaga et al. (2018) verwendet. Die Validierung der OP‘s und der geschätzten Beiträge wurde mit einer linearen Diskriminanzanalyse (LDA), einem Literaturvergleich und Ergebnissen aus künstlichen Senken durchgeführt.

Die Ergebnisse der Studie legen nahe, dass die genauesten Beiträge mit einer fingerprint Auswahl erzielt werden, die aus einem range-Test, einem Kruskal-Wallis-Test und einer Diskriminanzfunktion besteht. Die Autoren empfehlen ferner, die Ergebnisse von sediment fingerprinting Untersuchungen mit künstlichen Senkenproben zu validieren, da sie sich als das zuverlässigste Validierungsinstrument erwiesen haben.

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Introduction

The Central Spanish Pyrenees suffer severely from soil erosion and sediment yield, due to the topographic and climatic heterogeneity and altitudinal gradient. An additional enhancing effect to soil erosion and sediment yield in this area is the ongoing land abandonment happening since the 1950's (Palazón & Navas 2014). Terraces initially played a substantial role on cultivated hillslopes due to the enhanced water infiltration and therefore reduced surface runoff. Due to the ceasing of maintenance, terraces collapse and increase the supply of sediment loads (Arnaez et al. 2010). As a consequence of that reservoirs of the region suffer severely from siltation.

In order to take countermeasures, information about the relative contribution of each source of a catchment to the total eroded sediment is valuable data to understand soil distribution processes and therefore for catchment management strategies (Gaspar et al. 2019). Sediment fingerprinting is a widely used technique through which this data can be gathered (Collins and Walling 2002, Walling 2005, Kraushaar et al. 2015, Palazón et al. 2015, Collins et al. 2017, Gaspar et al. 2019). Different source types (e.g. land use, geology) influence the properties – or fingerprints – of the sediment situated on the given source. These fingerprints can be of physical (colour or grain size), chemical (geochemistry, mineral-magnetism, fallout radionuclides, etc.), or biological (soil enzymes, pollen) nature (Collins et al. 2017). By linking the sources' fingerprint concentrations to the concentrations found in the deposited sediment, the origin as well as the relative contribution of each source can be identified (Owens et al. 2016).

The sediment fingerprinting workflow consists of two major steps (Collins et al. 2017). In the first step properties of the sediment are tested on their power to discriminate between the sources. Properties that pass the tests are further used in the second step, the endmember modelling. In this study, the properties – as individuals – are referred to as fingerprints while the combination of those are called optimum packages.

The endmember modelling typically generates an estimated mean source contribution to the sink – whereas the sum of estimated source contributions does not exceed 100% - and an associated standard deviation for each source type (Brosinsky et al. 2014, Kraushaar et al. 2015, Manjoro et al. 2017, Palazón & Navas 2017, Gaspar et al. 2019, Lizaga et al. 2019). As an additional step most studies validate the results using artificial sink samples (Brosinsky et al. 2014, Smith et al. 2018, Gaspar et al., 2019), literature (Manjoro et al. 2017), the goodness of fit – a parameter to measure the quality of each endmember model results – (Haddadchi et al. 2014, Gaspar et al. 2019), or suspended sediment load (Palazón et al. 2015, Vercruysse & Grabowski, 2019).

A pitfall in sediment fingerprinting is, that different tests or combinations of tests can be and are used to determine the fingerprints and therefore the optimum packages. This study aims to continue the work of Palazón & Navas (2017), Smith et al. (2018) and Gaspar et al. (2019) in order to identify one workflow, that generally produces the most reliable results.

Study site

The Ceguera catchment – a 22 km² subcatchment of the Isábena catchment – was chosen as study site, since it fulfilled three major criterias: (i) the study area had to be suited on a homogenous lithology, (ii) previous studies had to prove a high sediment yield from the catchment (López-Tarazón et al. 2012), and (iii) a high relief energy within the catchment had to be given.

The Mediterranean and Atlantic Ocean influence the study area in the southern, central Pyrenees (600 – 1355 m a.s.l.) on the Iberian Peninsula, resulting in a wet and cold mountain type climate (García Ruiz et al. 2001). The catchment is mainly situated on sandstone, while only small portions in the north-east are characterized by conglomerates.

As a result of lithology and climate, the dominant soil type of the catchment is Kastanozem on which mainly shrublands (53,9%) and forests (41,3%) occur, while agricultural land (4,7%) and badlands (0,1%) only cover a small portion.

Methods

For each land use unit of the Ceguera catchment (4) six sediment source samples were taken, resulting in a total source sample size of 24. Additionally, four sink samples of freshly deposited alluvial sediment were gathered along the river. Each of the 28 samples was a result of multiple samples per sampling site combined in one bulk sample of approximately 300 g. These samples were then oven dried (105°C), sieved (<63 µm) and analysed on their geochemical composition. Prior to the fingerprint selection potential non-conservative tracers (P2O5, Cu, Pb, and Zn) were excluded and a range test was conducted in order to eliminate further non-conservatively behaving tracers.

Three different optimum packages (OP) consisting of selected fingerprints were generated, each time using different selection methods. The first OP was generated using a Kruskal-Wallis test and a Discriminant function analysis, representing the most commonly used OP (Collins et al. 2017). OP2 was generated through a Kruskal-Wallis test and the selection of well discriminating fingerprints according to their boxplots. OP3 had no further tests or selection methods applied and consisted of all conservative behaving fingerprints. The latter two optimum packages are more frequently mentioned and tested in recent studies, since either a pure statistical selection method (Lizaga et al. 2019) or the importance of a fingerprint selection in general (Smith et al. 2018) is questioned, respectively.

The unmixing was done using the R package fingerPro by Lizaga et al. (2018). This package uses a linear multivariate unmixing model with a Monte Carlo uncertainty analysis in order to estimate the relative contributions of each sediment source to the total eroded and deposited material in the sink.

Since, the validation of the modelled results is one of the – if not the most – crucial part of a (sediment fingerprinting) study, three validation possibilities were applied and tested. (i) The discrimination potential of each optimum package was checked using a linear discriminant analysis. (ii) The estimated results for each OP were compared to the findings of six other erosion studies which were conducted in either the Isábena or the Ebro catchment, of which the Isábena is a subcatchment of. (iii) To validate the performance of each optimum package, five artificial sink samples were generated and unmixed. Since, the “true” relative contribution of each artificial sink sample is known, the OP performance was assessed by checking if the “true” contributions lie within the modelled mean values ± their standard deviation.

Publication

The importance of foreplay in sediment fingerprint studies

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Keywords: Sediment Fingerprinting, Geochemistry, Fingerprint Selection, FingerPro unmixing model, Artificial mixtures

Under review confirmation

The manuscript was submitted to the “Earth Surface Processes and Landforms” on the 30.03.2020 and is currently under review.

Submitted Manuscripts

STATUS	ID	TITLE	CREATED	SUBMITTED
ADM: Ravi, Harsha • Under review • Under Review	ESP-20-0101	The importance of foreplay in sediment fingerprint studies View Submission Cover Letter	27-Mar-2020	30-Mar-2020

Abstract

Sediment fingerprinting is a widely used method for estimating relative sediment contributions of given sources to the total sediment output at catchment scale. It is an important tool in sediment management in mid to large scale catchments. However, results may vary depending on the applied tracer selection and model used. Hence, there is a need to test the most reliable approach for the individual setting. In this study a sediment fingerprinting approach was conducted in a subcatchment of the Isábena River in the Spanish Pyrenees. As the Isábena catchment suffers from accelerated erosion it has been the focus of other erosion and fingerprinting studies and therefore serves well to test different methodological approaches.

Three different pre-test procedures were used to test which non-soluble element compositions deliver the most reliable results in comparison to the results of linear discriminant analyses (LDA), literature reviews, and artificial sink samples. The endmember modeling was conducted using the R-package “fingerPro” by Lizaga et al. (2018).

Results indicate that a combination of the Kruskal-Wallis test and discriminant analysis as a pre-test serve best. Furthermore, artificial sink samples prove to be the most accurate validation tool and are preferable to a simple literature comparison.

Introduction

Fingerprinting is a commonly used method to assess the relative source contributions of a sediment, pollen or any kind of material to a sink, which may be lake sediments (Palazón et al. 2016, Palazón & Navas 2017), channel banks (Haddadchi et al. 2014, Sherriff et al. 2018) or an archaeological finding (Pitblado et al. 2013, Zipkin et al. 2017). The information derived from the assessment displays the dynamics of a system and allocates the contributions to the final content. This information, as in the case of sediments, can be vital for further management plans for a catchment (e.g. Walling 2005, Navratil et al. 2012, Gholami et al. 2017).

The sediment fingerprinting method is based on the assumption that different source types (e.g. land use, geology) influence the physical (grain size, color), geochemical (major and trace elements), mineral magnetic (magnetic susceptibility) and/or organic (fatty acids, pollen) properties – or fingerprints – of the soils or sediments (Collins et al. 2017). These fingerprints are used to identify the origins of deposited sediments by linking their concentrations in sinks to those in source areas of the catchment (Owens et al. 2016).

The broad spectrum of applications, the high number of possible tracers as well as the many adjusting screws that influence the mixing models output have led to a large number of studies investigating the workflow of sediment fingerprinting. Customarily the workflow consists of the foreplay – through which properties are selected as fingerprints for the further steps –, the unmixing of the data, and the validation of the results. Recent studies have evaluated the spatial variability of source material properties (Du & Walling 2017), the effect of different mixing models (Laceby & Olley 2014, Palazón et al. 2015), uncertainty assessments of the modeled estimations (Martínez-Carreras et al. 2008), and the temporal and/or spatial variability of source sediments (Cooper et al. 2014, Sherriff et al. 2018, Lizaga et al. 2019, Vercruysse & Grabowski 2019). Regarding the selection of fingerprints, researchers have focused on the potential of new fingerprints (Gaspar & Navas 2013, Gellis & Noe 2013, Barthod et al. 2015, Alewell et al. 2016, Reiffarth et al. 2016), the conservative behavior of fingerprints (Koiter et al. 2013b, Sherriff et al. 2015) and the selection of optimum fingerprint packages (Collins et al. 2017, Palazón & Navas 2017, Gaspar et al. 2019a).

The selection of optimal fingerprints is a crucial requirement in sediment fingerprinting assessments (Lizaga et al. 2019). In this paper we designate the measured element concentration of each source as properties which, when selected, will then be referred to as fingerprints. Fingerprints need to provide a good discrimination between the potential sources and behave conservatively on their way from source to sink. The impact of weathering processes on a sediment fingerprint should be known and taken into account (Collins et al. 2017, Koiter et al.

2018), as should possible changes in the chemical milieu the sediments might be deposited in (Kraushaar et al. 2015).

The conservative behavior and the impact of weathering processes can be evaluated through the application of statistical tests and knowledge-based decisions. Common practice in assessing the conservative behavior of fingerprints involves performing a simple range test or excluding properties that are prone to be affected by weathering (Collins & Walling 2002, Koiter et al. 2013b, Miller et al. 2014, Collins et al. 2017, Palazón & Navas 2017, Lizaga et al. 2018, Gaspar et al. 2019b). Even though there are various statistical tests and knowledge-based methods for selecting fingerprints with the highest discriminatory power, there is no universal pre-mixing workflow (Collins et al. 2017). Nevertheless, fingerprint selection through the application of a range test, a Kruskall-Wallis test, and a discriminant function analysis can be considered as the most commonly used tracer set in various sediment fingerprinting studies (Collins et al. 1998, Collins & Walling 2002, Walling 2005, Evrard et al. 2011, Smith & Blake 2014, Palazón et al. 2015, Gholami et al. 2017, Palazón & Navas 2017, Boudreault et al. 2019). An increasing number of studies question the validity of a purely statistical foreplay and rather include expert-based knowledge (Koiter et al. 2013a, Collins et al. 2017, Lizaga et al. 2019), posing the question of which foreplay results in the most reliable results.

In this regard, this study aims to evaluate the performance of three different approaches to selecting the optimum fingerprint package (OP) for a given catchment and presents the most reliable pre-mixing workflow for the case study of the Isábena River in Spain. The three approaches evaluated include the selection of fingerprints through (i) range test, Kruskal-Wallis test (KW-test) and discriminant function analysis (DFA), (ii) range test, KW-test and boxplots, and (iii) applying no tests or expert decisions in order to test whether such steps are necessary. Validation of the mixing model results was performed using linear discriminant analysis, literature values from previous studies and artificial sink samples. In a further step, these validation tools will be assessed in terms of their implementation and soundness as a validation tool. The study was conducted in the Isábena catchment in the southern central Spanish Pyrenees. The area is highly affected by soil erosion compared to similar sized catchments in European Mediterranean regions (Vente et al. 2006, López-Tarazón et al. 2012), leading to severe siltation in the Barasona reservoir, as well as numerous research studies focusing on erosion and sediment yield (Francke et al. 2008, López-Tarazón et al. 2009, Brosinsky et al. 2014, Buendia et al. 2015, Palazón et al. 2015, Francke et al. 2018). This intensively investigated catchment is therefore most suitable for the testing of new tracers (Brosinsky et al. 2014) and better selection procedures.

Study Area

The Ceguera catchment is located in the southern central Pyrenees on the Iberian Peninsula (Figure 1) and encompasses an area of 22 km². Its drainage area is a tributary to the Isábena and downstream of the Èsera River. Two kilometers after the confluence of the Isábena and the Ésera River, the water flows into the Barasona Reservoir from where it enters the Ebro River. The elevation of the Ceguera catchment ranges from 600 to 1355 m a.s.l. (Figure 1a), leading to slight temperature and precipitation gradients from west to east (Verdú et al. 2006a). Both the Mediterranean and the Atlantic Ocean influence the catchment's climate, resulting in a wet and cold mountain type climate (García Ruiz et al. 2001). Measurements of mean annual precipitation between 2009 and 2014 varied from 620 mm to 671 mm depending on the measurement configuration (Francke et al. 2018).

The hydrology of the catchment is characterized by nival-pluvial precipitation. Periods of high water yield (max. 22.4 m³/s) typically occur in spring due to snowmelt and in late summer and autumn due to local thunderstorms (García Ruiz et al. 2001, Francke et al. 2018). From July until August the river typically has the least flow and is likely to dry out (López-Tarazón et al. 2012). Gauging stations at the outlet of the catchment measured a mean discharge of 0.21m³/s between 2009 and 2014 (Francke et al. 2018).

The homogenous lithology of the Ceguera catchment is characterized mainly by sandstone, with small areas in the north consisting of conglomerates. Kastanozems are the dominant soil type of the catchment, although there are small areas in the north where Rendzinas prevail (ESDB 2004). The mostly shallow soils (< 0.6 m) of the catchment are stony, overlie fractured bedrock and have textures ranging from loam to sandy loam. This leads to well-drained soils with limited average water content (Palazón & Navas 2014, Palazón & Navas 2016).

Both river branches – northern and southern – originate on the sandstone plateau before cutting through the steep, v-shaped valleys. After the merging of the two branches to the Ceguera River, the v-shaped morphology of the valley continues. Therefore, for most of the catchment area, the lateral connectivity from slope to river is ensured. A good longitudinal connectivity can be assumed, since the riverbed consists mainly of bedrock with few gravels.

During the last 60 years the Spanish Pyrenean region has suffered from agricultural land abandonment. The former agricultural land has gradually become overgrown, leading to natural reforestation (Gallart & Llorens 2004), which is currently in the successional stage of shrubs, as confirmed by Corine Satellite Land Cover observations (Figure 1d, CLC 2018) which show the catchment is currently predominantly covered by shrubland (53.99%) and forests (41.31%), while agricultural fields (4.67%) and badlands (0.03%) play a minor role. However, since only 11 (agriculture: 3, badlands: 0, forests: 5, shrublands: 3) out of 24 sampled sites correspond with the CLC 2018 data (Figure 1 d), the land use proportions of the CLC data are considered only as a rough estimate. The inconsistencies are most likely caused by misclassifications during the classification process of the CLC.

The Ceguera catchment was selected as the study area since it fulfilled three conditions: (i) the study area had to be characterized by a homogeneous lithology since the authors wanted to avoid varying geochemical concentrations of the soil being caused by changing lithology rather than by changes in land cover; (ii) the catchment had to be proven to be characterized by a high sediment yield by previous studies (López-Tarazón et al. 2012); and (iii) the study area had to have high relief energy as well as high connectivity in order to ensure that the eroded sediment reaches the river and is not deposited on its way downslope.

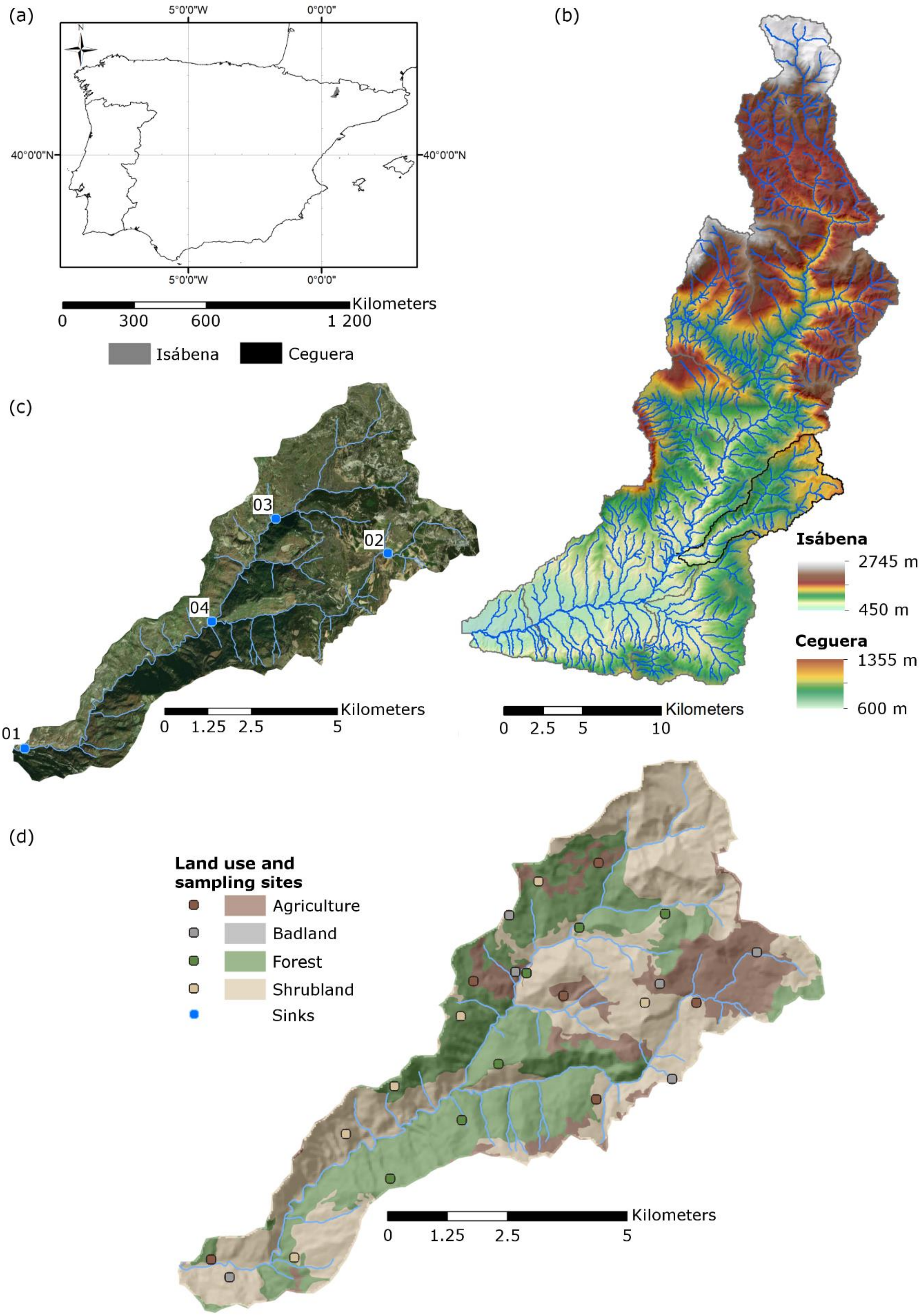

Figure 1: Maps showing (a) Digital Elevation Model of the Isábena catchment. (b) the location of the Ceguera and Isábena catchments on the Spanish Peninsula. (c) Orthoimage of the Ceguera catchment as well as positions of sampled sinks. (d) Land use distribution of the catchment and source sample locations.

Methods

Sediment source sampling and laboratory analyses

Six sediment source samples (n = 24) were collected in each land use unit (Fig. 1). The choice of sampling sites was based on (i) the occurrence of visible erosion features, such as rill or sheet erosion, (ii) characteristics of long-term land uses, such as tall trees or terraces, and (iii) equal distribution throughout the catchment. At each sampling site multiple samples were taken from the first three centimeters of topsoil, combining a mixed sample of around 300g using a plastic shovel. Additionally, four sink samples were gathered from recently deposited alluvial sediment banks along the river (Fig. 1). Sediments were only retrieved from vegetation-free areas and showed no signs of longer deposition in the form of initial pedogenesis, for example.

In the laboratory, the source and sink samples were oven dried at 105°C and sieved to <63 µm to generate a comparable grain size fraction between source and sediment materials, following the sample preparation procedure of Walling (2005) and Collins et al. (2017). Finally, all samples were finely ground in a swing mill before analysis of their major and trace elements (Table 1).
Ten major element concentrations were determined by applying a X-Ray fluorescence spectrometry (XRFS) analysis on a sequential X-Ray spectrometer PANalytical PW2404 (4kW and Rh anode) using fused beads. The fused beads were produced by pouring the homogenized mixture of 0.8000 g of calcined powder and 8.0000 g of a TB/MB-Mixture (Fluxana FX-X65-2; Di-Lithiumtetraborate:Di-Lithiummetaborate = 66:34) in the automatic fusion machine PANalytical EAGON 2 (Duboc et al. 2019 – supporting information).

To measure the trace element composition of the samples, about 0.5 ml of an aqueous polyvinyl alcohol solution were added to approx. 10 grams of non-ignited rock powder, which was then well mixed with a glass rod for 10 minutes. The mixture was then filled into a press tool with a diameter of 40 mm and compacted with a hydraulic press applying a pressure of 16 tons per cm². The pressed pellets were then analyzed in the X-Ray spectrometer (Nagl & Mader 2019).
Scandium, Tantal and Wolfram contained values below the detection limit, and thus were excluded for further tracer exploration. Potential non-conservative tracers, such as P_2O_5, Cu, Pb, and Zn, were eliminated following the literature (Koiter et al. 2013b, Miller et al. 2014, Lizaga et al. 2018).

Table 1: Analyzed property groups with their measured properties and the amount of properties per group

Property Group	Measured Properties	n
Major Elements	SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5	10
Trace Elements	As, Ba, Ce, Co, Cr, Cu, Ga, La, Mo, Nb, Nd, Ni, Pb, Rb, Sc, Sn, Sr, Ta, Th, U, V, Y, Zn, Zr	24

Furthermore, a range test was applied for the remaining properties to ensure that sink values were within the range of the source values and that therefore the properties behaved conservatively (Collins & Walling 2002, Palazón & Navas 2017, Lizaga et al. 2018, Gaspar et al. 2019). However, no further properties were eliminated through this test.

Optimum Packages

Three different types of optimum package selection were used in this study (Table 2). The first optimum package (OP1) is compiled of fingerprints that were solely selected through statistical tests (KW-test and DFA). This optimum package can be considered as the most commonly used tracer set in various sediment fingerprinting studies (Collins et al. 1998, Collins & Walling 2002, Walling 2005, Evrard et al. 2011, Smith & Blake 2014, Palazón et al. 2015, Gholami et al. 2017, Palazón & Navas 2017, Boudreault et al. 2019). OP2 was generated using a mixture of statistical tests and expert knowledge (KW-test and evaluation of boxplots). The selection procedure of OP2 has recently gained attention in fingerprinting studies due to the involvement of expert knowledge (Lizaga et al. 2019). Since OP3 is intended as a control package to assess whether any pre-tests are necessary, no further in- or exclusion of properties was conducted. A rule of thumb in sediment fingerprinting studies is to use at least m = n – 1 fingerprints, where m equals the amount of fingerprints and n is defined by the amount of source types (Alewell et al. 2016).

For OP1 & 2 a Kruskal-Wallis H-Test (p-value = 0.05) was conducted in order to exclude tracers that do not significantly differentiate between at least two of the sediment sources at a 95% confidence level (Walling 2005, Pulley et al. 2015, Lizaga et al. 2018). The last step of tracer selection for OP1 was a discriminant function analysis (DFA) in combination with a multivariate stepwise selection algorithm, based on the minimization of Wilks' lambda (niveau = 0.01). This determines a combination of properties that has the smallest number of tracers but the highest discrimination potential between the sources (Collins & Walling 2002, Gaspar et al. 2019a).

Table 2: Applied selection method and resulting fingerprints per optimum package

Optimum Package	Selection method	Selected fingerprints
1	(1) Range Test, (2) KW, (3) DFA	SiO_2, CaO, As, Ga, Rb
2	(1) Range Test, (2) KW, (3) Boxplot selection	Al_2O_3, CaO, Sr
3	(1) Range Test	SiO_2, TiO_2, Al_2O_3, MnO, MgO, CaO, Na_2O, K_2O, As, Ba, Ce, Co, Cr, Ga, La, Mo, Nb, Nd, Ni, Rb, Sn, Sr, Th, U, V, Y, Zr

Unmixing Model

The selection of optimum properties and the unmixing were undertaken using the R package fingerPro by Lizaga et al. (2018). The unmixing model of fingerPro relies on two premises regarding the fingerprints used: (i) selected fingerprint concentrations in sediment samples have to be in the range of the concentrations in source samples (have to be conservative), and (ii) the proportions of fingerprints in sediment samples reflect the relative contributions of sediment out of source samples (Gaspar et al. 2019a, Gaspar et al. 2019b). The standard linear multivariate unmixing model with Monte Carlo uncertainty analysis within fingerPro estimates the relative contributions of each sediment source per optimum package (Lizaga et al. 2018) according to the following equation (Eq1):

$$b_i = \sum_{j=1}^{m} a_{i,j} \times \omega_j \qquad \text{(Eq1)}$$

which meets the following constraints:

$$1 = \sum_{j=1}^{m} \omega_j$$

$$0 \leq \omega_j \leq 1$$

where b_i is the tracer property i (i = 1 to n) of the sink sample, $a_{i,j}$ represents the tracer property i in the source type j (j = 1 to m), ω_j is the unknown relative contribution of the source type j, m represents the number of sediment sources and n is the number of selected tracer properties (Palazón et al. 2015, Gaspar et al. 2019a, Gaspar et al. 2019b).

The package also calculates the goodness of fit (GOF), which can be used to assess the quality of each iteration based on the sum of the squares of the relative error (Motha et al. 2003, Eq2). With an increasing GOF (0 – 100%) the unmixing model should perform better and therefore estimate more accurate results. Yet, studies have shown that a high GOF does not always produce true results (Manjoro et al. 2017, Gaspar et al. 2019b); Pulley et al. (2015) further argue that different models with a high GOF result in a wide range of source contributions. As a result Gaspar et al. (2019b) and Manjoro et al. (2017) discourage the sole use of the GOF as a validation tool in sediment fingerprinting studies.

$$GOF = 1 - \frac{1}{n} \times \left(\sum_{i=1}^{n} \frac{\left|b_i - \sum_{j=1}^{m} \omega_j a_{i,j}\right|}{\Delta_i}\right) \qquad \text{(Eq2)}$$

Where n is the number of tracers used in the optimum package, Δ_i is a correction factor to normalize the tracer properties ranges, and b_i, ω_j and $a_{i,j}$ are the same as in Equation 1 (Gaspar et al., 2019b).

The model was set to perform 2000 iterations following Kraushaar et al. (2015), reaching a homogenous distribution of possible source contributions as mean values and standard deviation, and the respective GOFs. Manjoro et al. (2017) show that an increasing number of iterations neither decreases the modeled ranges of contributions nor increases the GOF.

Validation

The optimum tracer compositions were validated using three different quality criteria: (i) evaluation of the Linear Discriminant Analysis (LDA), (ii) comparison of the modeled results with other fingerprinting and model studies from the area, and (iii) checking of the performance of the results with five artificial sink samples.

The linear discriminant analysis was performed using the LDAPlot function implemented in the fingerPro package (Lizaga et al. 2018). Figure 2 shows the discriminatory power of each optimum package for the four sources. The fewer the intersections of the different colored source planes, the higher the potential of the OP to discriminate between the sources.

A literature review identified six research studies that focused on soil erosion in the Ebro basin (85,362 km^2), of which the Ceguera catchment (22 km^2) is a part (Table 3, López-Vicente et al. 2013, Brosinsky et al. 2014, Palazón et al. 2015, Palazón & Navas 2016, Palazón et al. 2016, Palazón & Navas 2017). Palazón et al. (2015) and Palazón & Navas (2017) used chemical sediment fingerprinting to estimate the relative contribution of each land use unit in the Ebro basin, while Brosinsky et al. (2014) implemented a spectral fingerprint. The studies investigated the relative contribution to more than just one sink, hence the sink closest to the mouthing point of each river was chosen. The other three studies examined the soil erosion through (semi-)physically based models. López-Vicente et al. (2013) used the semi-physically based Revised Morgan, Morgan and Finney (RMMF) model, while Palazón et al. (2016) and Palazón & Navas (2016) used the continuous and physically based Soil and Water Assessment Tool (SWAT).

	Catchment	Type	Fingerprints	Selection method	Mixing Model	Sink
Brosinsky et al 2014†	Isabená	Fingerprinting	Spectral	KW	Multivariat	unknown
Palazon et al. 2015	Isabená	Fingerprinting	Geochemistry	KW + DFA	linear	first delta sample (D1)
Palazon & Navas 2017	Barasona	Fingerprinting	Geochemistry	KW + DFA	linear	first lake sample (D)

	Catchment	Type	Values taken from	Comment
López-Vicente et. al 2013	Estanque de Arriba	RMMF	table 2	contribution values were converted to percentages
Palazon et al. 2016	Barasona	SWAT	table 9	did not state standard deviations for their estimations
Palazon & Navas 2016	Barasona	SWAT	table 2	contribution values were converted to percentages

Table 3: Overview of the literature used to validate the estimated contributions of sink 1. The top three studies were conducted with sediment fingerprinting studies, while (semi-) physically based models were used for the lower three studies. † only stated that between 60 and 80% of the total eroded sediment originated from badlands and <10% from forests; a more specific breakdown was not possible.

Three parameters are used to validate the performance of the optimum packages with artificial sink samples (Table 5). The first one is the number of sources wrongly estimated by the model (Table 5, Figure AS; red crosses). A source is classified as wrongly estimated if the artificially generated contribution does not lie within the modeled mean ± standard deviation. In this case the highest minimal deviation of the modeled and generated contributions is used as the second parameter. The minimal deviation is defined as the closest deviation of the modeled contribution range to the generated value (e.g. modeled value = 60% ± 20% [mean ± sd], generated value = 20%: minimal deviation = 20%, maximum deviation = 60%).

Additionally, the GOF was used to support the prior two parameters. There is no universal threshold to determine whether a GOF is considered to be high or low, thus the authors implemented the commonly used threshold of 80% following Martínez-Carreras et al. (2008), Evrard et al. (2011), and Pulley et al. (2015).

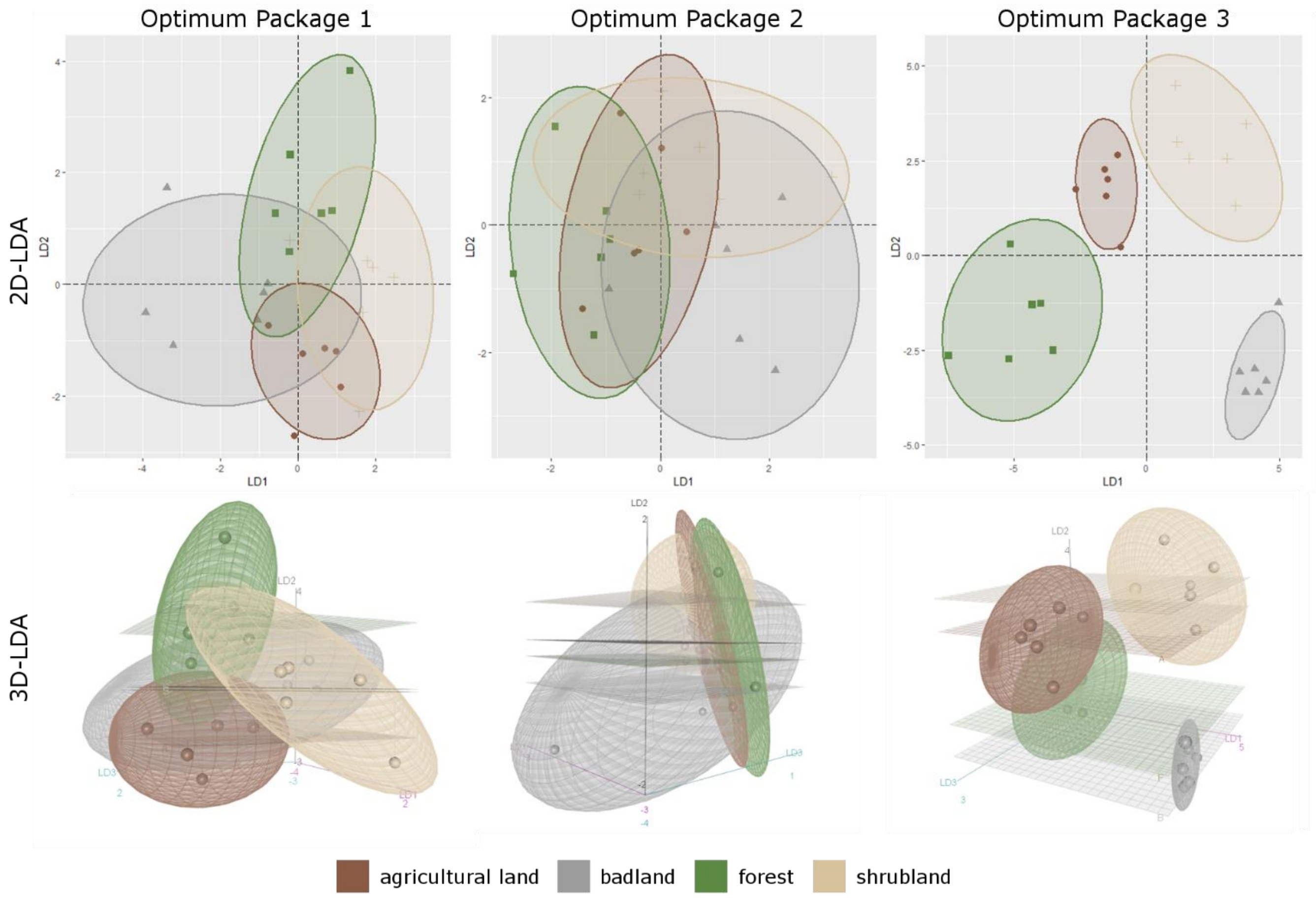

Figure 2: 2D and 3D scatterplots of the linear discriminant analysis results with the area for each source. Both versions show the LD1 on the x-axis and the LD2 on the y-axis.The 3D version additionally provides the LD3 on the z-axis.

Results

For all three optimum packages, the model computed consistently that the two main contributors to the total erosion in sink 1 are shrublands and badlands. While for OP1 and OP3 shrublands were the main contributor (76.39% ± 30.79% and 60.29% ± 19.29%, respectively), for OP2 it was badlands (57.47% ± 32.66%). Agricultural lands produced results varying between 0% and 18.58% of the total contribution. The sources contributions in OP1 and OP2 are rather low with 1.86% ± 6.29% and 0.82% ± 4.41%, respectively. OP3 computed the highest contribution range from agricultural land with a mean value of 7.52% and a standard deviation of 11.06%. Forests are considered to have a low impact on the total eroded material with mean values ranging from 0.09% to 0.67%. All three optimum packages have a low GOF ranging from 59.83% to 72.89% (Table 4).

In contrast to the modeled results of the Ceguera catchment, selected literature results from the Ebro basin showed that the two most productive land use areas are badlands and agricultural land (Fig. 4). Badlands stand out with mean contributions ranging between 25% (Palazón et al. 2015) and 95.40% (Palazón & Navas 2016). Estimated mean contributions for agricultural land vary from 3.92% (Palazón & Navas 2016) to 43% (Palazón et al. 2015). Only Palazón et al. (2015) estimated forests as the second highest contributor, whereas the rest of the studies modeled rather low mean value contributions of forests to the overall eroded sediment, ranging between 0.11% (Palazón & Navas 2016) and 5.4% (López-Vicente et al. 2013). According to the literature, shrublands also indicate low mean values ranging from 0.57% (Palazón and Navas 2016) to 6.9% (Palazón and Navas 2017).

Figure 5 shows the calculated contributions per optimum package for each of the four sampled sinks across the Ceguera River. Especially sink 3 has fundamentally different source contributions than the other sink samples. It shows relatively high proportions of sedimentary input from forests and comparatively low proportions from bad- and shrublands. These contributions are lost after the merging with the southern branch of the Ceguera. Generally, OP1 and OP3 correspond in the contribution patterns, whereas OP2 always shows a different distribution of sediment sources.

Table 4: GOF and estimated source contributions for sink 1 per optimum package. Values are given in %. Contributions per source are stated as mean ± sd.

	GOF	A	B	F	S
OP1	66.46	1.86 ± 6.29	21.65 ± 29.5	0.09 ± 0.2	76.39 ± 30.79
OP2	72.89	0.82 ± 4.41	57.47 ± 32.66	0.1 ± 0.25	41.6 ± 32.99
OP3	59.83	7.52 ± 11.06	31.52 ± 16.74	0.67 ± 3.43	60.29 ± 19.29

		GOF	A			B			F			S			wrongly estimated sources	highest minimal deviation
			cont.	mean	sd	**cont.**	mean	sd	**cont.**	mean	sd	**cont.**	mean	sd		
OP1	AS1	94.01	**30**	39.12	23.26	**10**	10.35	10.23	**40**	27.69	16.11	**20**	22.84	14.77	0	
	AS2	90.93	**30**	12.99†	16.52	**40**	46.29	16.97	**10**	20.41	12.52	**20**	20.31	18.75	1	0.49
	AS3	85.62	**40**	22.4	17.76	**10**	20.88	19.27	**15**	6.37	9.59	**35**	50.34	25.8	0	
	AS4	91.19	**15**	18.62	18.36	**15**	30.69	16.89	**30**	15.97†	12.66	**40**	34.71	21.04	1	1.37
	AS5	92.35	**25**	33.29	20.06	**25**	17.83	14.43	**25**	11.88†	12.86	**25**	36.99	19.38	1	0.26
OP2	AS1	97.48	**30**	41.08	32.1	**10**	8.81	10.39	**40**	27.29	19.6	**20**	22.82	17.53	0	
	AS2	94.76	**30**	22	21.24	**40**	30.81	20.86	**10**	9.04	11.35	**20**	38.15	25.73	0	
	AS3	90.87	**40**	18.78†	20.35	**10**	14.29	18.98	**15**	4.62†	8.45	**35**	62.31†	26.4	3	1.93
	AS4	95.65	**15**	30.72	25.98	**15**	15.6	15.64	**30**	11.69†	13.84	**40**	41.99	23.31	1	4.47
	AS5	96.15	**25**	29.6	25.89	**25**	22.55	17	**25**	14.58	14.69	**25**	33.26	22.92	0	
OP3	AS1	81.9	**30**	36.17	18.15	**10**	10.39	8.44	**40**	29.46	13.28	**20**	23.97	11.38	0	
	AS2	73.8	**30**	37	16.45	**40**	26.91†	10.64	**10**	12.42	10.75	**20**	23.67	12.23	1	2.45
	AS3	70.87	**40**	37.21	14.27	**10**	16.47	10.35	**15**	5.22†	7.66	**35**	41.1	13.07	1	2.12
	AS4	75.84	**15**	24.88	16	**15**	20.55	10.04	**30**	16.77†	10.77	**40**	37.8	12.24	1	2.46
	AS5	76.77	**25**	32.29	16.51	**25**	18.88	8.89	**25**	21.7	11.44	**25**	27.12	10.84	0	

Table 5: Goodness of fit (GOF) [%], estimated contributions [%], amount of wrongly estimated sources and the highest minimal deviation [percentage point; p.p.] for each artificial sink sample per optimum package. (i) cont. stands for the generated proportions of each land use unit per artificial sink sample, (ii) mean is the modeled mean value of 2000 iterations, and (iii) sd stands for the modeled standard deviation. † at mean value indicate sources that were wrongly estimated by the model.

The unmxing of the artificial sink samples (Figure 3) showed that standard deviations of each modeled source contribution ranged between 7.66% and 32.09% of its respective mean value and therefore defined a broad window corresponding to 85% of the cases in OP1 and OP3. OP2 produces the most wrongly (4) identified source contributions. However, three of the four mismodeled sources originate from one artificial sink sample (AS3). The lowest sum of minimal deviation was generated in OP1 (2.12), while OP2 and 3 have more than three times higher summed minimal deviations reaching 6.4 and 7.03, respectively. The GOF results range in average above 90% for OP1 and OP2, whereas OP3 shows GOF values below the threshold (70.87% - 81.9%).

All GOFs for sink 1 are lower than 80% (Table 4), which indicates the modeled contributions are incorrect. However, Table 6 shows that a selection of model outputs with a GOF ≥ 80% would not have had a major impact on the estimated contributions and therefore would not have produced results that corresponded better with the literature. This supports the statements of (Pulley, Foster, & Antunes, 2015), (Manjoro, Rowntree, Kakembo, Foster, & Collins, 2017), and (Gaspar et al., 2019b), who state that using just one GOF for validation is not recommended. The fact that for OP3 none of the 2000 iterations had a GOF ≥ 80% indicates interference in the performance of the model through the inclusion of tracers that are not able to differentiate between sources.

Table 6: Comparison of estimated mean contributions per land use unit for sink 1, if only models with a GOF ≥ 80% were used or no limitations on GOF inclusion were made. The number stated in brackets in the Condition column indicates the amount of models with a GOF ≥ 80%. Only mean values are stated for each source. All values are in %

		GOF	A	B	F	S
OP1	GOF ≥ 80	82.76 (69)	0.70	10.51	0.11	88.68
	all GOF's	66.46	1.86	21.65	0.09	76.39
OP2	GOF ≥ 80	84.01 (433)	0.23	64.10	0.13	35.54
	all GOF's	72.9	0.82	57.47	0.10	41.60
OP3	GOF ≥ 80	NA (0)	NA	NA	NA	NA
	all GOF's	59.83	7.52	31.52	0.67	60.29

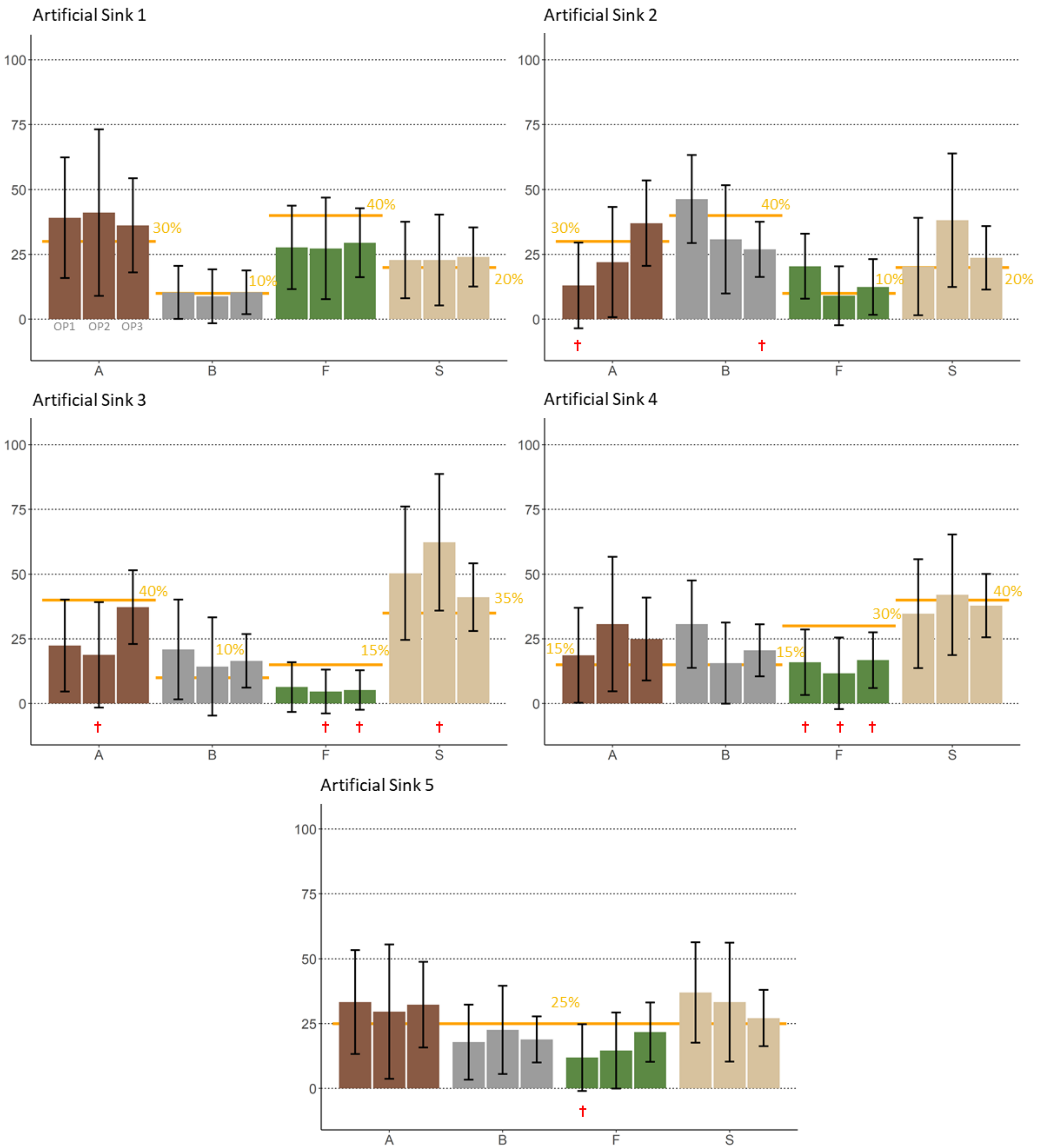

Figure 3: Modeled source contribution in percentage of each of the optimum packages 1, 2 and 3 (from left to right; see Artificial Sink 1 A) per artificial sink sample. The real proportion of each source is shown as a solid, orange line. Red crosses below the bars indicate wrongly estimated source contributions.

Discussion

Various sediment fingerprinting studies use the statistical foreplay approach of OP1 through the application of a range test, KW-test and DFA to select the optimum fingerprint composition (Collins et al. 1998, Collins & Walling 2002, Walling 2005, Evrard et al. 2011, Smith & Blake 2014, Palazón et al. 2015, Gholami et al. 2017, Palazón & Navas 2017, Boudreault et al. 2019). Yet, recent studies by Koiter et al. (2013), Collins et al. (2017), and Lizaga et al. (2019) have criticized pure statistical fingerprint selection due to its high statistical reliability and lack of expert knowledge, leading to fingerprint compositions which are selected like OP2. In order to test whether any type of foreplay is necessary to achieve sediment fingerprinting, this study – following others (Smith et al. 2018) – evaluates the performance of optimum packages consisting of all measured properties (OP3).

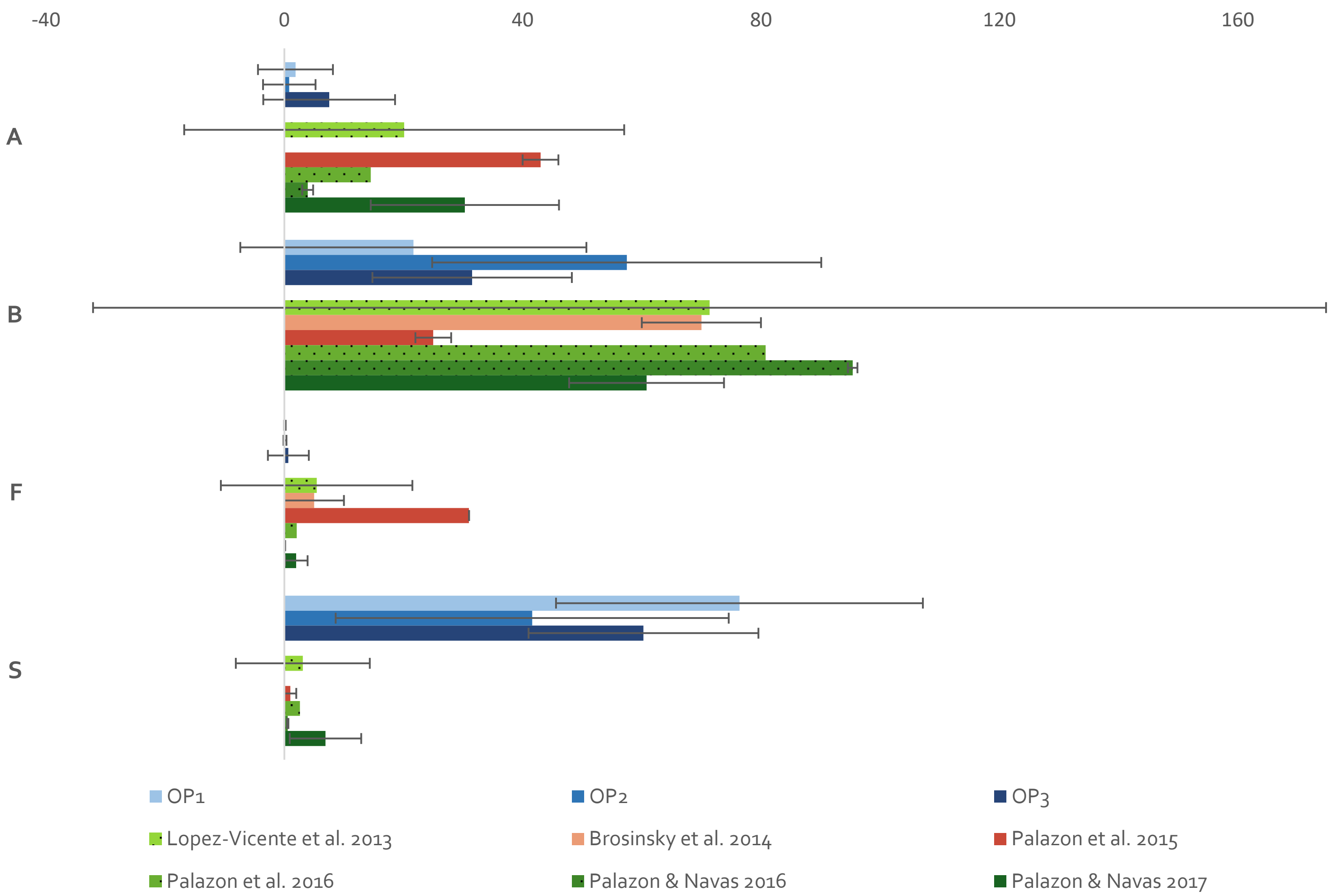

Figure 4: Source contributions [%] of each OP (in blue colors) and the results of literature. Dotted bars represent studies that were conducted using SWAT or RMMF, and non-dotted bars represent sediment fingerprinting studies. Green bars were used in the discussion to validate the results. Red bars were excluded of the validation.

This study explores the variation of results caused by different statistical foreplay procedures. The results show variations of between 0.82% and 7.52% for agricultural land, 21.65% - 57.47% for badland, 0.09% - 0.67% for forest, and 41.60% - 76.39% for shrubland. To evaluate a suitable pre-treatment of the data three validation criteria were implemented and their potential as validation tools tested: (i) analysis of LDA plots, (ii) comparison with the literature, (iii) accordance with artificial sink samples.

Variation of results between optimum packages

The results of the three optimum packages are displayed in Figure 5 and prove that statistical pre-selection methods have a great impact on the results of the models. OP1 and OP3 correspond in terms of contribution, depicting sink samples 1, 2 and 4 as having the highest sediment contributions from shrublands, followed by badlands. However, OP2 estimated the proportions of the two top erosive sources differently, with badlands being the main contributor.

Firstly, these results match with the findings of Francke et al. (2008), Alatorre et al. (2010), and López-Tarazón et al. (2012), who show that badlands are one of the main contributors to the overall eroded sediment. Secondly, the results also correspond to the findings of Arnaez et al. (2010), who demonstrate that abandoned agricultural lands (shrublands) are commonly the main sediment contributors, due to the breaking of terraces. Nevertheless, based on field observations for sinks 1, 2, and especially 4 (where the major part of the subcatchment is in agricultural use), it was anticipated that the contributions of agricultural land would be higher. The cause of this discrepancy is still unclear but could be linked to misclassifications of agricultural land and shrublands, overshadowing by badlands or disruptions in the connectivity of agricultural land. Following the estimated contributions downstream from sink 4, the proportions of badlands decrease while those of shrublands increase, independently of the optimum package used. This reflects the observed relative land use distribution, with increasing shrubland and decreasing badland land coverage downstream. The root cause of the differences in the estimated contributions of sink 3 compared to the others has not yet been determined, but of course might be linked to the land use distribution. Nevertheless, this information is lost downstream as soon as the two major branches unite right before sink 2.

Validation using LDA

Out of the four sources badlands are less intersected by the variations of other sources, and thus they are best distinguishable with the selected fingerprint. However, they also show to have the highest scatter on the two, respective three axis (Fig. 2). Optimum package 3 shows no overlapping variations of the sources due to the high number of tracers used in this package. OP1 and OP2 show to have low variations, since sources overlap as visible in figure 2d&e. Yet, the higher adjusted R^2 of OP1 (0.5079) compared to the one of OP2 (0.1561) indicate higher variations through the tracers used in OP1. While the 2D LDA plot of OP2 (Fig. 2 b) implies big overlapping areas of all the sources, the 3D versions clarifies, that in fact there is only a small overlapping space of all four source types. This is especially the case for forests and agricultural lands, where Fig. 2e clarifies, that they in fact run parallel to each other and only have a small space of intersection.

One of the flaws using a linear discriminant analysis to evaluate the performance of the optimum packages is, that the discrimination performance of the LDA will rise with the number of tracers used. Since, the three optimum packages used in this study all use a different amount of fingerprints (OP1: n = 5; OP2: n = 3; OP3: n = 27), it is obvious that OP3 will discriminate better than the others.

Therefore, the authors suggest to only use linear discriminant analysis as a validation tool, if the optimum packages consist of the same amount of fingerprints.

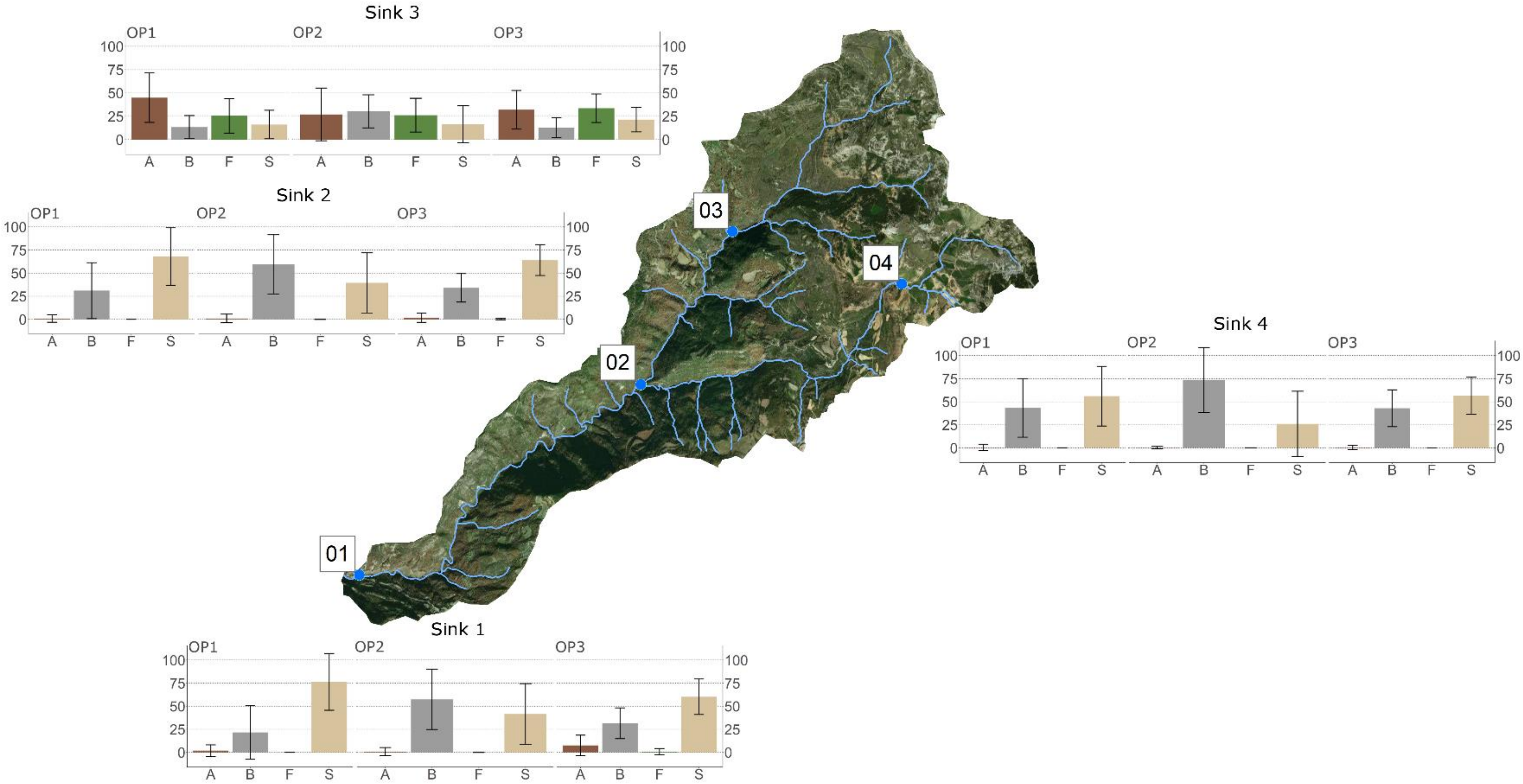

Figure 5: Source contributions per optimum package for each of the four sampled sinks of the catchment.

Validation using literature comparison

In many studies (Vente et al. 2006, Palazón et al. 2015, Manjoro et al., 2017) a literature review serves as the baseline for a comparison and validation of the final results. However, even in a well-researched area like the Isábena catchment, comparing literature values is hampered by multiple difficulties. These are:

(1) Selection of sources and samples: All consulted studies showed the same classification of land use units for the sampling sheme. Nevertheless, the modelled shrubland contributions of the present study are significantly higher and the agricultural land contributions significantly lower than those of the studies by López-Vicente et al. (2013), Palazón et al. (2015), Palazón et al. (2016), and Palazón & Navas (2017). This could be linked (i) either to the abandonment of former agricultural fields, which are now classified as shrubland, (ii) to a missclassifications by the fingerprint procedure, or (iii) simply due to the sampling timing and capturing a different system dynamic or cascading effect.

(2) Scale dependency: Revised literature considered the whole Isábena catchment of which Ceguera is a part. Hence, crucial erosion parameters and features, such as slope gradient, cover percentage of land use classes, lateral and longitudinal connectivity, precipitation and erosion processes or discharges, are considered on a smaller scale which alters results.

(3) Sampling timing: According to Collins et al. (2017) and Lizaga et al. (2019) timing is a crucial factor for the model performances. The studies considered either have long term (Brosinsky et al. 2014), short term (López-Vicente et al. 2013, Palazón et al. 2016, Palazón & Navas 2016), or unknown (Palazón et al. 2015, Palazón & Navas 2017) sampling periods. In the present study samples were collected in the two weeks after a storm event in April 2018. This issue – as well as problem (2) – can also be considered as inescapable, since it is impossible to find two catchments that are identical and/or two sampling periods that have identical conditions regarding climatic parameters.

(4) The three fingerprinting studies (Brosinsky et al. 2014, Palazón et al. 2015, Palazón & Navas 2017) use different foreplay procedures to determine the optimal fingerprints, and two kinds of mixing models. While (Brosinsky et al. 2014) only deploy a KW-test and use a multivariate mixing model, the other two studies single out the optimal fingerprints by applying a KW-test and a DFA, and later use a linear mixing model to estimate the sources' contributions.

(5) Congruency between studies: For the Isábena catchment the selected studies show no congruent findings concerning erosion patterns and contribution percentages per source. Studies by López-Vicente et al. (2013), Palazón et al. (2016), Palazón & Navas (2016), and Palazón & Navas (2017) show a similar pattern of source contributions with badlands and agricultural land being the main contributors, while forests and shrublands only contribute a small portion. However, differences in the ranges of contributions between these studies still reach up to 26.39% for agricultural land, 34.6% for badlands, 5.31% for forests, and 6.33% for shrublands. The study by Palazón et al. (2015) displays a different pattern for the same

sources with agricultural land being the main contributor, followed by forests, badlands, and shrublands. Hence, in this study the validation is undertaken by concentrating on the four studies by López-Vicente et al. (2013), Palazón et al. (2016), Palazón & Navas (2016), and Palazón & Navas (2017), since the study by Palazón et al. (2015) shows a different contribution pattern and Brosinsky et al. (2014) lacks data for agricultural land and shrublands.

(6) Contribution ranges: Lopez-Vicente (2013) published erosion contributions ranges for the Isábena catchment with standard deviations exceeding 100% of their modeled mean values, which allows for interpretation leeways that prohibit a true validation.

Overall, the results of OP2 correspond best in terms of source patterns and contribution ranges to the literature of López-Vicente et al. (2013), Palazón et al. (2016), Palazón & Navas (2016), and Palazón & Navas (2017)(Fig. 4). Estimating the highest badland as well as the lowest shrubland contributions of the three tested OPs, the results of this optimum package are most comparable with the ones observed in the Isábena, Barasona and Estanque de Arriba catchments.

Although literature comparison is a common tool for justifying model results (Vente et al. 2006, Palazón et al. 2015, Manjoro et al. 2017) the above-mentioned controversial points illustrate the difficulties of comparing study results. In this regard a greater focus was put on the artificial sink samples as an objective method to validate differing results.

Validation with artificial sinks

The variety of results per optimum package in each artificial sink proves that there is a need to include more than just one artificial sink as a validation tool. Artificial sink 1, for example, suggests that all optimum packages are equally good in predicting the sources' contributions, while AS 3 suggests a contrary conclusion.

The mean values of GOFs per OP (OP1 = 91.19%, OP2 = 95.65%, OP3 = 75.84%) indicate a worse performance of OP3 compared to OP1 and OP2. Yet, as seen before, a low GOF might also produce similar results to a high GOF even though there may be interference in the model's performance.

The number of wrongly estimated sources per optimum package ranges from 3 (OP1 and OP3) to 4 (OP2) and therefore provides little evidence on the performances of each OP. The highest minimal deviation indicates the best performance of OP1 (0.49 - 1.37 p.p.) across all artificial sinks. The rather high deviations of OP3 point to interference in the performance. Even though AS3 of OP2 has three wrongly estimated sources, the highest minimal deviation is lower (1.93) than that of AS4 (4.47), which only had one wrongly estimated source. The best performance was produced using optimal package 1, while determining whether OP2 or OP3 were more accurate is rather difficult.

In conclusion, the literature validation points to OP2 as providing the most reliable results, while validation through artificial sinks indicates OP1 is the most reliable. OP1 generally involves a minimized workload and would therefore be a preferable outcome. Additionally, the authors believe that due to the aforementioned difficulties of literature validation the artificial sink samples should be given higher weighting. Another positive aspect of artificial sink samples is that they are generated manually and the setup is therefore more controllable than through literature reviews.

Generally, the contributions and uncertainties generated through the application of OP2 (RT + KW + boxplot selection) and OP3 (no pre-tests) do not differ from the results of OP1 as much as expected. This raises the question of whether a foreplay in sediment fingerprinting is needed or whether similar results can be produced without the application of statistical tests or expert knowledge to select optimal fingerprints. This matches with the findings of (Smith et al. 2018), who could even generate more reliable results by using as many conservative tracers as possible than with the standard procedure applying a KW-test and a DFA.

This study points out the difficulties of foreplay in sediment fingerprinting studies and their validation. Each validation tool proved that a different optimum package was the most reliable one. LDA showed the superior discrimination of OP3, the results of OP2 corresponded best with those in the literature, and artificial sink samples showed that OP1 produced the most reliable results. The authors of this study chose to weight the validation with artificial sink samples more highly than the other tools, and therefore concluded that OP1 produced the most accurate results. The authors therefore advise testing different optimum packages for each study individually and validating the OPs through artificial sinks.

Additionally, these findings, paired with those of Smith et al. (2018), indicate that foreplay in sediment fingerprinting studies can be narrowed down to eliminating non-conservative tracers. This quick and dirty foreplay procedure produces results that are almost as good as or even better than the statistical/expert selection procedures.

Conclusions

With the continuous increase in sediment fingerprinting studies aiming to estimate the relative source contributions of eroded sediment in a catchment, there is a need to determine the most reliable method of selecting the best suited fingerprints. This study goes some way to filling this gap by evaluating the performance of three optimum tracer packages. Our investigations show varying source contributions and accuracy levels depending on the optimum package. Supporting the findings of Palazón & Navas (2017) and, Gaspar et al. (2019a) the most consistent results were produced by using a range test, Kruskal Wallis test and a discriminant function analysis.

This study also shows that the validation potential of GOF is inconsistent, since it is neither the case that a high GOF produces accurate source predictions nor the case that a low GOF produces wrong results. Additionally, it has to be questioned whether validation through LDA is advisable, as the discrimination potential increases with an increasing amount of tracers. Therefore, this method should at best only be applied if the number of tracers in different optimum packages is (close to) equal. Validating modeled results with those found in the literature has also proved difficult, due to changing catchment conditions and the high ranges of results. Assessing performance with artificial sink samples, on the other hand, has been shown to be promising. Artificial sink samples are generated manually under controlled circumstances and deliver an overview of the plausibility of the data.

Continued research is needed, either to fill the gap by determining one universal workflow for fingerprint selection or to build a shortcut around the gap and perform no pre-tests at all. A universal workflow would increase the reliability of sediment fingerprinting studies, since the comparability of results would improve.

Acknowledgements

The authors would like to thank Dr. José M. García Ruiz for posting his book, Mag. Peter Nagl for analyzing the samples, Dr. José A. López-Tarazón for the provision of data and advice, and Katharine Thomas for prove reading and corrections. Last but not least, thanks go to the Austrian tax payer for funding the thesis through the University of Vienna.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author.

Literature

Alatorre, L. C., Beguería, S., & García-Ruiz, J. M. (2010, 9). Regional scale modeling of hillslope sediment delivery: A case study in the Barasona Reservoir watershed (Spain) using WATEM/SEDEM. *Journal of Hydrology, 391*, 109-123. doi:10.1016/j.jhydrol.2010.07.010

Alewell, C., Birkholz, A., Meusburger, K., Wildhaber, Y. S., & Mabit, L. (2016, 3). Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland). *Biogeosciences, 13*, 1587-1596. doi:10.5194/bg-13-1587-2016

Arnaez, J., Lasanta, T., Errea, M. P., & Ortigosa, L. (2010, 8). Land abandonment, landscape evolution, and soil erosion in a Spanish Mediterranean mountain region: The case of Camero Viejo. *Land Degradation & Development, 22*, 537-550. doi:10.1002/ldr.1032

Barthod, L. R., Liu, K., Lobb, D. A., Owens, P. N., Martínez-Carreras, N., Koiter, A. J., . . . Gaspar, L. (2015, 9). Selecting Color-based Tracers and Classifying Sediment Sources in the Assessment of Sediment Dynamics Using Sediment Source Fingerprinting. *Journal of Environmental Quality, 44*, 1605-1616. doi:10.2134/jeq2015.01.0043

Boudreault, M., Koiter, A. J., Lobb, D. A., Liu, K., Benoy, G., Owens, P. N., & Li, S. (2019, 4). Comparison of sampling designs for sediment source fingerprinting in an agricultural watershed in Atlantic Canada. *Journal of Soils and Sediments, 19*, 3302-3318. doi:10.1007/s11368-019-02306-6

Brosinsky, A., Foerster, S., Segl, K., López-Tarazón, J. A., Piqué, G., & Bronstert, A. (2014, 6). Spectral fingerprinting: characterizing suspended sediment sources by the use of VNIR-SWIR spectral information. *Journal of Soils and Sediments, 14*, 1965-1981. doi:10.1007/s11368-014-0927-z

Buendia, C., Vericat, D., Batalla, R. J., & Gibbins, C. N. (2015, 3). Temporal Dynamics of Sediment Transport and Transient In-channel Storage in a Highly Erodible Catchment. *Land Degradation & Development, 27*, 1045-1063. doi:10.1002/ldr.2348

Bull, P. A., Parker, A., & Morgan, R. M. (2006, 10). The forensic analysis of soils and sediment taken from the cast of a footprint. *Forensic Science International, 162*, 6-12. doi:10.1016/j.forsciint.2006.06.075

Collins, A. L., & Walling, D. E. (2002, 4). Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins. *Journal of Hydrology, 261*, 218-244. doi:10.1016/s0022-1694(02)00011-2

Collins, A. L., Pulley, S., Foster, I. D., Gellis, A., Porto, P., & Horowitz, A. J. (2017, 6). Sediment source fingerprinting as an aid to catchment management: A review of the current state of knowledge and a methodological decision-tree for end-users. *Journal of Environmental Management, 194*, 86-108. doi:10.1016/j.jenvman.2016.09.075

Collins, A. L., Walling, D. E., & Leeks, G. J. (1998). Use of composite fingerprints to determine the provenance of the contemporary suspended sediment load transported by rivers. *Earth Surface Processes and Landforms, 23*, 31-52. doi:10.1002/(SICI)1096-9837(199801)23:1<31::AID-ESP816>3.0.CO;2-Z

Cooper, R. J., Krueger, T., Hiscock, K. M., & Rawlins, B. G. (2014, 7). High-temporal resolution fluvial sediment source fingerprinting with uncertainty: a Bayesian approach. *Earth Surface Processes and Landforms, 40*, 78-92. doi:10.1002/esp.3621

Cover, C. L. (2018). Available at: https://land.copernicus.eu/pan-european/corine-land-cover/clc2018.

Du, P., & Walling, D. E. (2017, 6). Fingerprinting surficial sediment sources: Exploring some potential problems associated with the spatial variability of source material properties. *Journal of Environmental Management, 194*, 4-15. doi:10.1016/j.jenvman.2016.05.066

Duboc, O., Robbe, A., Santner, J., Folegnani, G., Gallais, P., Lecanuet, C., . . . Wenzel, W. W. (2019, 4). Silicon Availability from Chemically Diverse Fertilizers and Secondary Raw Materials. *Environmental Science & Technology, 53*, 5359-5368. doi:10.1021/acs.est.8b06597

Evrard, O., Navratil, O., Ayrault, S., Ahmadi, M., Némery, J., Legout, C., . . . Esteves, M. (2011, 2). Combining suspended sediment monitoring and fingerprinting to determine the spatial origin of fine sediment in a mountainous river catchment. *Earth Surface Processes and Landforms, 36*, 1072-1089. doi:10.1002/esp.2133

Francke, T., Baroni, G., Brosinsky, A., Foerster, S., López-Tarazón, J. A., Sommerer, E., & Bronstert, A. (2018, 11). What Did Really Improve Our Mesoscale Hydrological Model? A Multidimensional Analysis Based on Real Observations. *Water Resources Research, 54*, 8594-8612. doi:10.1029/2018wr022813

Francke, T., López-Tarazón, J. A., Vericat, D., Bronstert, A., & Batalla, R. J. (2008, 11). Flood-based analysis of high-magnitude sediment transport using a non-parametric method. *Earth Surface Processes and Landforms, 33*, 2064-2077. doi:10.1002/esp.1654

Franz, C., Makeschin, F., Weiß, H., & Lorz, C. (2014, 1). Sediments in urban river basins: Identification of sediment sources within the Lago Paranoá catchment, Brasilia DF, Brazil – using the fingerprint approach. *Science of The Total Environment, 466-467*, 513-523. doi:10.1016/j.scitotenv.2013.07.056

Gallart, F., & Llorens, P. (2004). Observations on land cover changes and water resources in the headwaters of the Ebro catchment, Iberian Peninsula. *Physics and Chemistry of the Earth, 29*, 769-773.

García Ruiz, J. M., Beguería Portugués, S., López Moreno, J. I., Lorente Grima, A., & Seeger, M. (2001). *Los recursos hídricos superficiales del Pirineo aragonés y su evolución reciente.* Geoforma Ediciones. Retrieved from https://www.amazon.com/Cartografi-x301-geomorfolo-gica-aplicada/dp/848777931X?SubscriptionId=AKIAIOBINVZYXZQZ2U3A&tag=chimbori05-20&linkCode=xm2&camp=2025&creative=165953&creativeASIN=848777931X

Gaspar, L., & Navas, A. (2013, 10). Vertical and lateral distributions of 137Cs in cultivated and uncultivated soils on Mediterranean hillslopes. *Geoderma, 207-208*, 131-143. doi:10.1016/j.geoderma.2013.04.034

Gaspar, L., Blake, W. H., Smith, H. G., Lizaga, I., & Navas, A. (2019, 3). Testing the sensitivity of a multivariate mixing model using geochemical fingerprints with artificial mixtures. *Geoderma, 337*, 498-510. doi:10.1016/j.geoderma.2018.10.005

Gaspar, L., Lizaga, I., Blake, W. H., Latorre, B., Quijano, L., & Navas, A. (2019, 6). Fingerprinting changes in source contribution for evaluating soil response during an exceptional rainfall in Spanish pre-pyrenees. *Journal of Environmental Management, 240*, 136-148. doi:10.1016/j.jenvman.2019.03.109

Gellis, A. C., & Noe, G. B. (2013, 9). Sediment source analysis in the Linganore Creek watershed, Maryland, USA, using the sediment fingerprinting approach: 2008 to

2010. *Journal of Soils and Sediments, 13*, 1735-1753. doi:10.1007/s11368-013-0771-6

Gholami, H., Telfer, M. W., Blake, W. H., & Fathabadi, A. (2017, 8). Aeolian sediment fingerprinting using a Bayesian mixing model. *Earth Surface Processes and Landforms, 42*, 2365-2376. doi:10.1002/esp.4189

Haddadchi, A., Nosrati, K., & Ahmadi, F. (2014, 5). Differences between the source contribution of bed material and suspended sediments in a mountainous agricultural catchment of western Iran. *CATENA, 116*, 105-113. doi:10.1016/j.catena.2013.12.011

Koiter, A. J., Lobb, D. A., Owens, P. N., Petticrew, E. L., Tiessen, K. H., & Li, S. (2013, 8). Investigating the role of connectivity and scale in assessing the sources of sediment in an agricultural watershed in the Canadian prairies using sediment source fingerprinting. *Journal of Soils and Sediments, 13*, 1676-1691. doi:10.1007/s11368-013-0762-7

Koiter, A. J., Owens, P. N., Petticrew, E. L., & Lobb, D. A. (2013, 10). The behavioural characteristics of sediment properties and their implications for sediment fingerprinting as an approach for identifying sediment sources in river basins. *Earth-Science Reviews, 125*, 24-42. doi:10.1016/j.earscirev.2013.05.009

Koiter, A. J., Owens, P. N., Petticrew, E. L., & Lobb, D. A. (2018, 9). Assessment of particle size and organic matter correction factors in sediment source fingerprinting investigations: An example of two contrasting watersheds in Canada. *Geoderma, 325*, 195-207. doi:10.1016/j.geoderma.2018.02.044

Kraushaar, S., Schumann, T., Ollesch, G., Schubert, M., Vogel, H.-J., & Siebert, C. (2015, 7). Sediment fingerprinting in northern Jordan: element-specific correction factors in a carbonatic setting. *Journal of Soils and Sediments, 15*, 2155-2173. doi:10.1007/s11368-015-1179-2

Laceby, J. P., & Olley, J. (2014, 8). An examination of geochemical modelling approaches to tracing sediment sources incorporating distribution mixing and elemental correlations. *Hydrological Processes, 29*, 1669-1685. doi:10.1002/hyp.10287

Lamba, J., Karthikeyan, K. G., & Thompson, A. M. (2015, 2). Apportionment of suspended sediment sources in an agricultural watershed using sediment fingerprinting. *Geoderma, 239-240*, 25-33. doi:10.1016/j.geoderma.2014.09.024

Lexartza-Artza, I., & Wainwright, J. (2011, 3). Making connections: changing sediment sources and sinks in an upland catchment. *Earth Surface Processes and Landforms, 36*, 1090-1104. doi:10.1002/esp.2134

Lizaga, I., Gaspar, L., Blake, W. H., Latorre, B., & Navas, A. (2019, 9). Fingerprinting changes of source apportionments from mixed land uses in stream sediments before and after an exceptional rainstorm event. *Geomorphology, 341*, 216-229. doi:10.1016/j.geomorph.2019.05.015

Lizaga, I., Latorre, B., Gaspar, L., & Navas, A. (2018). fingerPro: an R Package for Sediment Source Tracing. Zenodo. doi:10.5281/ZENODO.1402029

López-Tarazón, J. A., Batalla, R. J., Vericat, D., & Francke, T. (2009, 8). Suspended sediment transport in a highly erodible catchment: The River Isábena (Southern Pyrenees). *Geomorphology, 109*, 210-221. doi:10.1016/j.geomorph.2009.03.003

López-Tarazón, J. A., Batalla, R. J., Vericat, D., & Francke, T. (2012, 2). The sediment budget of a highly dynamic mesoscale catchment: The River Isábena. *Geomorphology, 138*, 15-28. doi:10.1016/j.geomorph.2011.08.020

López-Vicente, M., Poesen, J., Navas, A., & Gaspar, L. (2013, 3). Predicting runoff and sediment connectivity and soil erosion by water for different land use scenarios in the Spanish Pre-Pyrenees. *CATENA, 102*, 62-73. doi:10.1016/j.catena.2011.01.001

Manjoro, M., Rowntree, K., Kakembo, V., Foster, I., & Collins, A. L. (2017, 6). Use of sediment source fingerprinting to assess the role of subsurface erosion in the supply of fine sediment in a degraded catchment in the Eastern Cape, South Africa. *Journal of Environmental Management, 194*, 27-41. doi:10.1016/j.jenvman.2016.07.019

Martínez-Carreras, N., Gallart, F., Iffly, J. F., Pfister, L., Walling, D., & Krein, A. (2008, 12). Uncertainty assessment in suspended sediment fingerprinting based on tracer mixing models: a case study from Luxembourg. *Proceedings of of a symposium held at Christchurch, NewZealand, 325*.

Miller, J. R., Mackin, G., & Miller, S. M. (2014, 12). Geochemical Fingerprinting. In *SpringerBriefs in Earth Sciences* (pp. 11-51). Springer International Publishing. doi:10.1007/978-3-319-13221-1_2

Motha, J. A., Wallbrink, P. J., Hairsine, P. B., & Grayson, R. B. (2003, 3). Determining the sources of suspended sediment in a forested catchment in southeastern Australia. *Water Resources Research, 39*. doi:10.1029/2001wr000794

Nagl, P., & Mader, D. (2019, 9 5). X-ray fluorescence (XRF) and instrumental neutron activation analysis (INAA) for the geochemical analysis of rocks, presented on in-house control samples. *Biennial Meeting of the Austrian Mineralogical Society, Graz, Österreich.*

Nakai, I., Furuya, S., Bong, W., Abe, Y., Osaka, K., Matsumoto, T., . . . Ninomiya, T. (2013, 6). Quantitative analysis of heavy elements and semi-quantitative evaluation of heavy mineral compositions of sediments in Japan for construction of a forensic soil database using synchrotron radiation X-ray analyses. *X-Ray Spectrometry, 43*, 38-48. doi:10.1002/xrs.2496

Navratil, O., Evrard, O., Esteves, M., Legout, C., Ayrault, S., Némery, J., . . . Bonté, P. (2012, 1). Temporal variability of suspended sediment sources in an alpine catchment combining river/rainfall monitoring and sediment fingerprinting. *Earth Surface Processes and Landforms, 37*, 828-846. doi:10.1002/esp.3201

Owens, P. N., Blake, W. H., Gaspar, L., Gateuille, D., Koiter, A. J., Lobb, D. A., . . . Woodward, J. C. (2016, 11). Fingerprinting and tracing the sources of soils and sediments: Earth and ocean science, geoarchaeological, forensic, and human health applications. *Earth-Science Reviews, 162*, 1-23. doi:10.1016/j.earscirev.2016.08.012

Palazón, L., & Navas, A. (2014, 5). Modeling sediment sources and yields in a Pyrenean catchment draining to a large reservoir (Ésera River, Ebro Basin). *Journal of Soils and Sediments, 14*, 1612-1625. doi:10.1007/s11368-014-0911-7

Palazón, L., & Navas, A. (2016, 2). Land use sediment production response under different climatic conditions in an alpine–prealpine catchment. *CATENA, 137*, 244-255. doi:10.1016/j.catena.2015.09.025

Palazón, L., & Navas, A. (2017, 6). Variability in source sediment contributions by applying different statistic test for a Pyrenean catchment. *Journal of Environmental Management, 194*, 42-53. doi:10.1016/j.jenvman.2016.07.058

Palazón, L., Gaspar, L., Latorre, B., Blake, W. H., & Navas, A. (2015, 6). Identifying sediment sources by applying a fingerprinting mixing model in a Pyrenean drainage catchment. *Journal of Soils and Sediments, 15*, 2067-2085. doi:10.1007/s11368-015-1175-6

Palazón, L., Latorre, B., Gaspar, L., Blake, W. H., Smith, H. G., & Navas, A. (2016, 11). Combining catchment modelling and sediment fingerprinting to assess sediment dynamics in a Spanish Pyrenean river system. *Science of The Total Environment, 569-570*, 1136-1148. doi:10.1016/j.scitotenv.2016.06.189

Pitblado, B. L., Cannon, M. B., Bloxham, M., Janetski, J., Adovasio, J. M., Anderson, K. R., & Nelson, S. T. (2013, 8). Archaeological Fingerprinting and Fremont Figurines. *Advances in Archaeological Practice, 1*, 3-12. doi:10.7183/2326-3768.1.1.3

Pulley, S., Foster, I., & Antunes, P. (2015, 1). The uncertainties associated with sediment fingerprinting suspended and recently deposited fluvial sediment in the Nene river basin. *Geomorphology, 228*, 303-319. doi:10.1016/j.geomorph.2014.09.016

Reiffarth, D. G., Petticrew, E. L., Owens, P. N., & Lobb, D. A. (2016, 9). Sources of variability in fatty acid (FA) biomarkers in the application of compound-specific stable isotopes (CSSIs) to soil and sediment fingerprinting and tracing: A review. *Science of The Total Environment, 565*, 8-27. doi:10.1016/j.scitotenv.2016.04.137

Sherriff, S. C., Franks, S. W., Rowan, J. S., Fenton, O., & Ó'hUallacháin, D. (2015, 4). Uncertainty-based assessment of tracer selection, tracer non-conservativeness and multiple solutions in sediment fingerprinting using synthetic and field data. *Journal of Soils and Sediments, 15*, 2101-2116. doi:10.1007/s11368-015-1123-5

Sherriff, S. C., Rowan, J. S., Fenton, O., Jordan, P., & D. Ó. (2018, 11). Sediment fingerprinting as a tool to identify temporal and spatial variability of sediment sources and transport pathways in agricultural catchments. *Agriculture, Ecosystems & Environment, 267*, 188-200. doi:10.1016/j.agee.2018.08.023

Smith, H. G., & Blake, W. H. (2014, 1). Sediment fingerprinting in agricultural catchments: A critical re-examination of source discrimination and data corrections. *Geomorphology, 204*, 177-191. doi:10.1016/j.geomorph.2013.08.003

Smith, H. G., Karam, D. S., & Lennard, A. T. (2018, 4). Evaluating tracer selection for catchment sediment fingerprinting. *Journal of Soils and Sediments, 18*, 3005-3019. doi:10.1007/s11368-018-1990-7

Vente, J., Poesen, J., Bazzoffi, P., Rompaey, A. V., & Verstraeten, G. (2006). Predicting catchment sediment yield in Mediterranean environments: the importance of sediment sources and connectivity in Italian drainage basins. *Earth Surface Processes and Landforms, 31*, 1017-1034. doi:10.1002/esp.1305

Vercruysse, K., & Grabowski, R. C. (2019, 7). Temporal variation in suspended sediment transport: linking sediment sources and hydro-meteorological drivers. *Earth Surface Processes and Landforms, 44*, 2587-2599. doi:10.1002/esp.4682

Verdú, J. M., Batalla, R. J., & Martínez Casasnovas, J. A. (2006). Estudio hidrológico de la cuenca del río Isábena (Pirineos, España). II: respuesta hidrológica. *Ingeniería del agua, 13*, 331.

Verdú, J. M., Batalla, R. J., & Martínez Casasnovas, J. A. (2006(a)). Estudio hidrológico de la cuenca del río Isábena (cuenca del Ebro). I: variabilidad de la precipitación. *Ingeniería del agua, 13*, 321.

Walling, D. E. (2005, 5). Tracing suspended sediment sources in catchments and river systems. *Science of The Total Environment, 344*, 159-184. doi:10.1016/j.scitotenv.2005.02.011

Zipkin, A. M., Ambrose, S. H., Hanchar, J. M., Piccoli, P. M., Brooks, A. S., & Anthony, E. Y. (2017, 2). Elemental fingerprinting of Kenya Rift Valley ochre deposits for provenance studies of rock art and archaeological pigments. *Quaternary International, 430*, 42-59. doi:10.1016/j.quaint.2016.08.032

Summary of the results

For sink 1 the unmixing model estimated the two main contributing sources to be shrublands and badlands, independent on the optimum package used. Yet, for OP1 and OP3 shrublands were the main contributing source (76.39% ± 30.79% and 60.29% ± 19.29%, respectively), while it was badlands for OP2 (57.47% ± 32.66%). The contributing proportions of both, agricultural land and forests, were estimated to be low with mean values ranging from 0.82% - 7.52% for agricultural land and 0.09% - 0.67% for forests.

The review literature in this study consistently estimated badlands and agricultural land to be the main contributing sources. In five of the six studies (López-Vicente et al. 2013, Brosinsky et al. 2014, Palazón et al. 2016, Palazón & Navas 2016, Palazón & Navas 2017) badlands were modelled to have the highest proportions (60.8% - 95.4%), while only in the study of Palazón et al. (2015) agricultural land is the main contributor (43%). According to the literature forests and shrublands have a low impact on the overall eroded sediment. Except for the study of Palazón et al. (2015) - in which the contribution of forests was estimated at 31% - both sources only contributed between 0.1% - 6.9%.

The results of the artificial sink samples show that OP1 and OP3 both have 3 and OP2 has 4 out of 20 sources wrongly estimated. The lowest highest minimal deviations were reached in OP1, while OP2 and OP3 had overall higher highest minimal deviations.

Discussion

Dependent on the optimum package used to estimate the sources' contributions to sink 1, the results vary between 0.82% and 7.52% for agricultural land, 21.65% - 57.47% for badland, 0.09% - 0.67% for forest, and 41.60% - 76.39% for shrubland. Eventhough these results show that the predominant origins of the deposited sediment in sink 1 are badlands and shrublands, the range of contribution for both sources – 35.82 p.p. and 34.79 p.p., respectively - can be considered as high.

Results of the LDA indicate, that OP3 is the optimum package consisting of the most distinguishable fingerprints – yet this is mainly the effect of the high number of fingerprints (n = 27) in this OP. The overlapping areas of OP1 and OP2 in figure 2d&e, show low variations within these OP's and therefore should produce less accurate results according to this method. Nevertheless, since the performance of the LDA enhances with an increasing number of fingerprints this derivation is not legitimate in this setting. Therefore, the authors advise to only apply this method, if the used optimum packages consist of the same number of fingerprints.

Comparison with literature showed to have multiple pitfalls which need to be considered. The selection of sources and samples, scale dependency, and sampling timing are examples for potential pitfalls, which should be considered before or during the field campaign. If the comparing results were also produced with sediment fingerprinting, the choice of mixing model can also lead to differing results and obviously the procedure to select optimum fingerprints is crucial in this matter (Haddadchi et al. 2014, Collins et al. 2017, Palazón & Navas 2017, Gaspar et al. 2019). Literature comparison in this study showed, that OP2 produced the most corresponding results to the ones found in literature of López-Vicente et al. (2013), Palazón et al. (2016), Palazón & Navas (2016), and Palazón & Navas (2017). This is mainly the effect of the high badland and low shrubland contributions estimated by the model.

Validation with artificial sink samples indicate that optimum package 1 is the most promising one to produce the most accurate results. While the number of wrongly estimated sources for OP1 (3) is the same for OP3 and close to the one for OP2 (4), the highest minimal deviations of this optimum package (0.49, 1.37, and 0.26) are lower than the ones of OP2 (1.93, and 4.47) and OP3 (2.45, 2.12, and 2.46).

Conclusions

Sediment fingerprinting is a useful (management) tool in order to estimate the catchment's source contributions to a sink. Yet, to enhance the performance, the reproducibility, and the comparability of the method it is important to determine the most reliable fingerprint selection method. This study aimed to continue the research of earlier studies (e.g. Palazón & Navas 2017, Smith et al. 2018, Gaspar et al. 2019a), in order to fill this knowledge gap.

To validate each optimum package, three different methods were applied and again tested on their suitability as a validation method. Linear discriminant analysis was found only to be a suitable validation method, if the comparing optimum packages consist of the same number of fingerprints. Literature review showed to be suitable but there are pitfalls, which have to be considered if being applied. Artificial sink samples showed the best potential as a validation method, since they are generated under controlled circumstances and deliver an overview on the plausibility of the data. Yet, in this study each validation method assessed a different optimum package as the most promising one.

Because artificial sink samples were found to be the most reliable validation method and OP1 was found to produce the most suiting results with artificial sink samples, this study supports the findings of Palazón & Navas (2017) and Gaspar et al. (2019) and suggests the selection method of OP1 – range test, Kruskal Wallis test and discriminant analysis – to be applied in further sediment fingerprinting studies.

Nevertheless, the authors would also like to point out, that the differences between the applied optimum packages are not that high in order to produce completely different results. All three optimum packages estimated that badlands and shrublands are the major contributors and that the impact of agricultural land and forests can be neglected for three of the four tested sinks in the Ceguera catchment. This is especially the case for OP3 – where except for a range test no further tests were applied – and therefore produced promising results with the least effort, supporting the results of Smith et al. (2018).

Bibliography

Arnaez, J., Lasanta, T., Errea, M.P. and Ortigosa, L. (2010) 'Land abandonment, landscape evolution, and soil erosion in a Spanish Mediterranean mountain region: The case of Camero Viejo', Land Degradation & Development, vol. 22, pp. 537-550.

Brosinsky, A., Foerster, S., Segl, K., López-Tarazón, J.A., Piqué, G. and Bronstert, A. (2014) 'Spectral fingerprinting: characterizing suspended sediment sources by the use of VNIR-SWIR spectral information', Journal of Soils and Sediments, vol. 14, pp. 1965-1981.

Collins, A.L., Pulley, S., Foster, I.D.L., Gellis, A., Porto, P. and Horowitz, A.J. (2017) 'Sediment source fingerprinting as an aid to catchment management: A review of the current state of knowledge and a methodological decision-tree for end-users', Journal of Environmental Management, vol. 194, pp. 86-108.

Collins, A.L. and Walling, D.E. (2002) 'Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins', Journal of Hydrology, vol. 261, pp. 218-244.

García Ruiz, J.M., Beguería Portugués, S., López Moreno, J.I., Lorente Grima, A. and Seeger, M. (2001) 'Los recursos hídricos superficiales del Pirineo aragonés y su evolución reciente', Geoforma Ediciones,

Gaspar, L., Blake, W.H., Smith, H.G., Lizaga, I. and Navas, A. (2019a) 'Testing the sensitivity of a multivariate mixing model using geochemical fingerprints with artificial mixtures', Geoderma, vol. 337, pp. 498-510.

Haddadchi, A., Nosrati, K. and Ahmadi, F. (2014) 'Differences between the source contribution of bed material and suspended sediments in a mountainous agricultural catchment of western Iran', CATENA, vol. 116, pp. 105-113.

Kraushaar, S., Schumann, T., Ollesch, G., Schubert, M., Vogel, H.-J. and Siebert, C. (2015) 'Sediment fingerprinting in northern Jordan: element-specific correction factors in a carbonatic setting', Journal of Soils and Sediments, vol. 15, pp. 2155-2173.

Lizaga, I., Gaspar, L., Blake, W.H., Latorre, B. and Navas, A. (2019) 'Fingerprinting changes of source apportionments from mixed land uses in stream sediments before and after an exceptional rainstorm event', Geomorphology, vol. 341, pp. 216-229.

Lizaga, I., Latorre, B., Gaspar, L. and Navas, A. (2018) 'fingerPro: an R Package for Sediment Source Tracing' Zenodo.

López-Tarazón, J.A., Batalla, R.J., Vericat, D. and Francke, T. (2012) 'The sediment budget of a highly dynamic mesoscale catchment: The River Isábena', Geomorphology, vol. 138, pp. 15-28.

López-Vicente, M., Poesen, J., Navas, A. and Gaspar, L. (2013) 'Predicting runoff and sediment connectivity and soil erosion by water for different land use scenarios in the Spanish Pre-Pyrenees', CATENA, vol. 102, pp. 62-73.

Manjoro, M., Rowntree, K., Kakembo, V., Foster, I. and Collins, A.L. (2017) 'Use of sediment source fingerprinting to assess the role of subsurface erosion in the supply of fine sediment in a degraded catchment in the Eastern Cape, South Africa', Journal of Environmental Management, vol. 194, pp. 27-41.

Owens, P.N., Blake, W.H., Gaspar, L., Gateuille, D., Koiter, A.J., Lobb, D.A., Petticrew, E.L., Reiffarth, D.G., Smith, H.G. and Woodward, J.C. (2016) 'Fingerprinting and tracing the sources of soils and sediments: Earth and ocean science, geoarchaeological, forensic, and human health applications', Earth-Science Reviews, vol. 162, pp. 1-23.

Palazón, L., Gaspar, L., Latorre, B., Blake, W.H. and Navas, A. (2015) 'Identifying sediment sources by applying a fingerprinting mixing model in a Pyrenean drainage catchment', Journal of Soils and Sediments, vol. 15, pp. 2067-2085.

Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G. and Navas, A. (2016) 'Combining catchment modelling and sediment fingerprinting to assess sediment dynamics in a Spanish Pyrenean river system', Science of The Total Environment, vol. 569-570, pp. 1136-1148.

Palazón, L. and Navas, A. (2014) 'Modeling sediment sources and yields in a Pyrenean catchment draining to a large reservoir (Ésera River, Ebro Basin)', Journal of Soils and Sediments, vol. 14, pp. 1612-1625.

Palazón, L. and Navas, A. (2016) 'Land use sediment production response under different climatic conditions in an alpine–prealpine catchment', CATENA, vol. 137, pp. 244-255.

Palazón, L. and Navas, A. (2017) 'Variability in source sediment contributions by applying different statistic test for a Pyrenean catchment', Journal of Environmental Management, vol. 194, pp. 42-53.

Smith, H.G., Karam, D.S. and Lennard, A.T. (2018) 'Evaluating tracer selection for catchment sediment fingerprinting', Journal of Soils and Sediments, vol. 18, pp. 3005-3019.

Vercruysse, K. and Grabowski, R.C. (2019) 'Temporal variation in suspended sediment transport: linking sediment sources and hydro-meteorological drivers', Earth Surface Processes and Landforms, vol. 44, pp. 2587-2599.

Walling, D.E. (2005) 'Tracing suspended sediment sources in catchments and river systems', Science of The Total Environment, vol. 344, pp. 159-184.