Institute of Earth and Environmental Sciences

Spectral fingerprinting: The potential of VNIR-SWIR spectral characteristics for tracing suspended sediment sources

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Abstract

Current research on runoff and erosion processes, as well as an increasing demand for sustainable watershed management emphasize the need for an improved understanding of sediment dynamics. This involves the accurate assessment of erosion rates and sediment transfer, yield and origin. A variety of methods exist to capture these processes at the catchment scale. Among these, sediment fingerprinting, a technique to trace back the origin of sediment, has attracted increasing attention by the scientific community in recent years. It is a two-step procedure, based on the fundamental assumptions that potential sources of sediment can be reliably discriminated based on a set of characteristic 'fingerprint' properties, and that a comparison of source and sediment fingerprints allows to quantify the relative contribution of each source.

This thesis aims at further assessing the potential of spectroscopy to assist and improve the sediment fingerprinting technique. Specifically, this work focuses on (1) whether potential sediment sources can be reliably identified based on spectral features ('fingerprints'), whether (2) these spectral fingerprints permit the quantification of relative source contribution, and whether (3) in situ derived source information is sufficient for this purpose. Furthermore, sediment fingerprinting using spectral information is applied in a study catchment to (4) identify major sources and observe how relative source contributions change between and within individual flood events. And finally, (5) spectral fingerprinting results are compared and combined with simultaneous sediment flux measurements to study sediment origin, transport and storage behaviour.

For the sediment fingerprinting approach, soil samples were collected from potential sediment sources within the Isábena catchment, a meso-scale basin in the central Spanish Pyrenees. Undisturbed samples of the upper soil layer were measured in situ using an ASD spectroradiometer and subsequently sampled for measurements in the laboratory. Suspended sediment was sampled automatically by means of ISCO samplers at the catchment as well as at the five major subcatchment outlets during flood events, and stored fine sediment from the channel bed was collected from 14 cross-sections along the main river. Artificial mixtures of known contributions were produced from source soil samples. Then, all source, sediment and mixture samples were dried and spectrally measured in the laboratory. Subsequently, colour coefficients and physically based features with relation to organic carbon, iron oxide, clay content and carbonate, were calculated from all in situ and laboratory spectra. Spectral parameters passing a number of prerequisite tests were submitted to principal component analyses to study natural clustering of samples, discriminant function analyses to observe source differentiation accuracy, and a mixing model for source contribution assessment. In addition, annual as well as flood event based suspended sediment fluxes from the catchment and its subcatchments were calculated from rainfall, water discharge and suspended sediment concentration measurements using rating curves and Quantile Regression Forests. Results of sediment flux monitoring were interpreted individually with respect to storage behaviour, compared to fingerprinting source ascriptions and combined with fingerprinting to assess their joint explanatory potential.

In response to the key questions of this work, (1) three *source types* (land use) and five *spatial sources* (subcatchments) could be reliably discriminated based on spectral fingerprints. The artificial mixture experiment revealed that while (2) laboratory parameters permitted source contribution assessment, (3) the use of in situ derived information was insufficient. Apparently, high discrimination accuracy does not necessarily imply good quantification results. When applied to suspended sediment samples of the catchment outlet, the spectral fingerprinting approach was able to (4) quantify the major sediment sources: badlands and the Villacarli subcatchment, respectively, were identified as main contributors, which is consistent with field observations and previous studies. Thereby, source contribution was found to vary both, within and between individual flood events. Also sediment flux was found to vary considerably, annually as well as seasonally and on flood event base. Storage was confirmed to play an important role in the sediment dynamics of the studied catchment, whereas floods with lower total sediment yield tend to deposit and floods with higher yield rather remove material from the channel bed. Finally, a comparison of flux measurements with fingerprinting results highlighted the fact that (5) immediate transport from sources to the catchment outlet cannot be assumed. A combination of the two methods revealed different aspects of sediment dynamics that none of the techniques could have uncovered individually.

In summary, spectral properties provide a fast, non-destructive, and cost-efficient means to discriminate and quantify sediment sources, whereas, unfortunately, straight-forward in situ collected source information is insufficient for the approach. Mixture modelling using artificial mixtures permits valuable insights into the capabilities and limitations of the method and similar experiments are strongly recommended to be performed in the future. Furthermore, a combination of techniques such as e.g. (spectral) sediment fingerprinting and sediment flux monitoring can provide comprehensive understanding of sediment dynamics.

Zusammenfassung

Aktuelle Forschung zu Abfluss- und Erosionsprozessen und die steigende Nachfrage nach nachhaltiger Wasserbewirtschaftung unterstreichen die Notwendigkeit für ein verbessertes Verständnis von Sedimentdynamik. Dazu gehören die genaue Bewertung von Erosionsraten sowie die Abschätzung von Sedimenttransfer, -ertrag und -herkunft. Es existiert eine Vielzahl von Verfahren, um diese Prozesse auf Einzugsgebietsskala zu erfassen. Unter diesen hat das Sediment-Fingerprinting, eine Technik zur Bestimmung der Sedimentherkunft, in den letzten Jahren zunehmend die Aufmerksamkeit der wissenschaftlichen Gemeinschaft auf sich gezogen. Es ist ein zweiteiliges Verfahren auf Grundlage der Annahmen, dass mögliche Sedimentquellen unter Verwendung charakteristischer "Fingerabdrücke" zuverlässig unterschieden und dass ein Vergleich der Quell- und Sedimentfingerabdrücke es ermöglicht, den relativen Beitrag jeder Quelle zu quantifizieren.

Die vorliegende Arbeit untersucht die Möglichkeit, Spektroskopie zur Unterstützung und Verbesserung der Sediment-Fingerprinting Technik einzusetzen. Der Schwerpunkt liegt dabei auf den Fragen, ob (1) potenzielle Sedimentquellen basierend auf spektralen Merkmalen ("Fingerabdrücken") zuverlässig unterschieden werden können, ob (2) diese spektralen Fingerabdrücke die relative Quantifizierung von Quellbeiträgen erlauben und ob (3) in situ gemessene Quellinformationen für diesen Zweck ausreichend sind. Darüber hinaus wird spektrales Sediment-Fingerprinting in einem Untersuchungsgebiet angewandt, um (4) die wichtigsten Quellen zu identifizieren und um zu beobachten, wie sich relative Beiträge zwischen und innerhalb einzelner Hochwasserereignisse verändern. Außerdem werden (5) spektrale Sediment-Fingerprinting Ergebnisse mit gleichzeitig erhobenen Abfluss- und Sedimentflussdaten verglichen und kombiniert um Sedimentherkunft, -transport und -ablagerung zu untersuchen.

Für den Sediment-Fingerprinting Ansatz wurden Bodenproben potenzieller Sedimentquellen im Isábenabecken, einem mesoskaligen Einzugsgebiet in den zentralen spanischen Pyrenäen, gesammelt. Ungestörte Proben der Bodenoberfläche wurden in situ unter Verwendung eines ASD Spektroradiometers gemessen und anschließend für Labormessungen beprobt. Sedimentpartikel (Schwebfracht) wurden während Hochwasserereignissen automatisch mit Hilfe von ISCO Samplern am Gebietsauslass sowie an den fünf wichtigsten Teileinzugsbietsauslässen beprobt. Zusätzlich wurde im Flussbett abgelagertes Feinsediment an 14 Querschnitten entlang des Hauptflusses gesammelt. Aus den Bodenproben wurden zusätzlich künstliche Mischungen bekannter Zusammensetzung hergestellt. Alle Boden-, Sediment- und Gemischproben wurden getrocknet und im Labor spektral gemessen. Anschließend wurden aus allen Spektren (in situ und Labor) Farbkoeffizienten und physikalisch basierte features mit Bezug zu organischem Kohlenstoff, Eisenoxid, Tongehalt und Carbonat berechnet. Die spektralen Parameter wurden auf eine Reihe von Voraussetzungen getested. Auf Grundlage von Parametern, die die vorgegebenen Voraussetungen erfüllten, wurden die Proben anschließend mittels Hauptkomponenten-analyse auf natürliche Gruppierung getested. Die Differenzierungsgenauigkeit einzelner Parameter bzw. von Parameterkombinationen wurde mittels Diskriminanzfunktionsanalyse beurteilt und zur Quantifizierung der Beiträge verschiedener Quellen wurde ein Mischungs-

modell entwickelt. Darüber hinaus wurden mittels Eichkurven und Quantile Regression Forests aus Niederschlags-, Abfluss- und Sedimentkonzentrationsmessungen jährliche sowie hochwasserbasierte Sedimentflüsse aus dem Einzugsgebiet und seinen Teileinzugsgebieten berechnet. Ergebnisse des Sedimentfluss Monitorings wurden einzeln in Bezug auf Speicherverhalten interpretiert, mit Quellquantifizierungen aus dem Sediment-Fingerprinting verglichen und mit dem Fingerprinting kombiniert, um das gemeinsame Erklärungspotential der beiden Methoden zu bewerten.

Als Antwort auf die Schlüsselfragen dieser Arbeit konnten (1) drei Quelltypen (Landnutzung) bzw. fünf räumliche Quellen (Teileinzugsgebiete) basierend auf spektralen Fingerabdrücken zuverlässig unterschieden werden. Das Experiment mit den künstlichen Mischungen ergab, dass während (2) Laborparameter die Beitragsabschätzung erlauben, (3) die Verwendung von in situ abgeleiteten Informationen nicht ausreicht. Offenbar bedeutet eine hohe Diskriminierungsgenauigkeit nicht unbedingt gute Quantifizierungsergebnisse. Auf Sedimentproben des Gebietsauslasses angewandt war der spektrale Sediment-Fingerprinting Ansatz in der Lage, (4) die Hauptsedimentquellen zu quantifizieren: Badlands und das Villacarli Teileinzugsgebiet wurden jeweils als Hauptquellen identifiziert. Dies ist im Einklang mit Beobachtungen früherer Studien. Dabei wurde festgestellt, dass Quellbeiträge sowohl innerhalb als auch zwischen den einzelnen Hochwasserereignissen variieren. Außerdem wurden starke Schwankungen der Sedimentflüsse, auf jährlicher sowie saisonaler- und Hochwasserereignis-Basis gefunden. Die wichtige Rolle des Flusses als Speicher in der Sedimentdynamik des untersuchten Einzugsgebietes wurde bestätigt, wobei Hochwasser mit niedrigerer Gesamtsedimentausbeute in der Regel Material ablagern und Hochwasser mit höherer Ausbeute eher Material aus dem Flussbett entfernen. Schließlich zeigte ein Vergleich der Sedimentflussmessungen mit Sediment-Fingerprinting Ergebnissen, dass (5) nicht von unmittelbarem Materialtransport von den Quellen zum Gebietsauslass ausgegangen werden kann. Die Kombination der zwei Verfahren offenbarte verschiedene Aspekte der Sedimentdynamik, die keine der beiden Techniken einzeln hätte aufdecken können.

Zusammenfassend lässt sich festhalten, dass spektrale Messungen ein schnelles, zerstörungsfreies und kosteneffizientes Mittel zur Unterscheidung und Quantifizierung von Sedimentquellen bieten, wobei in situ gesammelte Quellinformationen leider nicht ausreichend für die Vorgehensweise sind. Experimente mit künstlichen Mischungen ermöglichten wertvolle Einblicke in die Möglichkeiten und Grenzen der Methode und ähnliche Versuche werden dringend für zukünftige Studien empfohlen. Eine Kombination von Techniken, wie z. B. (spektralem) Sediment-Fingerprinting und Sedimentfluss Monitoring können das Verständnis der Sedimentdynamik verbessern und vertiefen.

Chapter I
Introduction, objectives and overview

1.1 The impact of high suspended sediment loads

“Fine grained sediment is a natural and essential component of river systems and plays a major role in the hydrological, geomorphological and ecological functioning of rivers“ (Owens et al. 2005). Nevertheless, high sediment loads, frequently caused by anthropogenic activity, may have fundamental and often negative impacts on water quality and quantity. As such, fine sediments (particles < 63 µm mainly transported in suspension) were found to increase eutrophication and turbidity (e.g. review by Bilotta and Brazier 2008), leading to degradation of aquatic habitats and resulting in community changes and likely loss of biodiversity (Rabení et al. 2005). Furthermore, suspended particles are a key vector in the transport and storage of nutrients and contaminants (e.g. Owens and Walling 2002, Walling 2005) and were identified as a major source of nonpoint source water pollution (Davis and Fox 2009). High sediment loads can also affect water availability, e.g. due to changes in river morphology or reservoir siltation. These effects are related to a range of environmental but also to economic consequences, for example by increasing drinking water treatment costs or by reducing channel navigability, operational capabilities of hydroelectric power plants, water storage capacities of reservoirs or simply attractiveness for recreational use (e.g. review by Owens et al. 2005, Navratil et al. 2010, Evrard et al. 2011, Francke et al. 2014).

Though well documented, these impacts continue in representing a widespread problem (e.g. USEPA 2010). A prerequisite in the design of sustainable mitigation strategies is the understanding of complex sediment dynamics (Walling 2005, Davis and Fox 2009). Such strategies must target the primary sources of sediment (Mukundan et al. 2012), making sediment provenance a key factor in the adaptation of (expensive) watershed management practices (e.g. Walling 2005, Davis and Fox 2009, Mukundan et al. 2012, Navratil et al. 2012). Collins and Walling (2004) provide a detailed review of a wide variety of techniques to capture sediment origin. They describe traditional methods of sediment source assessment, involving for example the semi-quantitative mapping of erosion areas in the field or by the use of photogrammetry and remote sensing, surveying to evaluate sediment mobilisation using profilometers, erosion pins, and / or GPS, observation of erosion plots as well as direct measurement of suspended sediment fluxes. Thereby, each measurement procedure has its individual advantages and limitations and often several techniques have to be combined in order to provide a comprehensive assessment of sediment provenance. However, many of the methods are considered labour-intense, costly, spatially limited, and/or logistically difficult to implement, thus constraining coverage and duration of monitoring campaigns.

1.2 Fingerprinting to assess sediment provenance

One approach described by Collins and Walling (2004) that has attracted increasing attention in recent years is a technique called *sediment fingerprinting* (e.g. review by Koiter et al. 2013). It employs unique natural tracers termed ‘fingerprints’ collected from potential source areas as well as from (suspended) sediment samples, which are considered to represent mixtures of source material (Walling 2005). A wide variety of natural soil and sediment properties has been employed as fingerprints in the past, ranging from mineralogy over geochemistry, mineral magnetism, radionuclides, rare earth elements, organic substances,

and colour to particle size (e.g. reviews by Davis and Fox 2009, Collins and Walling 2002). Thereby, the combination of several diagnostic properties to ‚composite fingerprints' has proven most reliable in providing quantitative sediment source estimates (e.g. Peart and Walling 1986, Collins et al. 1997).
The method is founded on the principal assumptions that (1) potential sediment sources can be reliably discriminated based on these fingerprints, and that (2) a comparison of sources and sediments fingerprints permits the relative source contribution to be quantified (Collins and Walling 2002). The first assumption, the identification of sources based on fingerprint properties, is generally assessed by means of discriminant function analysis (DFA) (Collins and Walling 2002), but also principal component analysis (PCA) (e.g. Poulenard et al. 2009) or factor analyses (FA)(e.g. Walden et al. 1997) have been applied. Quantification of relative source contribution is commonly associated with multivariate mixture modelling (Collins and Walling 2002), though recent studies employ e.g. Partial Least Squares Regression (PLSR) as alternative means (e.g. Poulenard et al. 2009 and 2012, Evrard et al. 2013, Legout et al. 2013). A conceptual model of the sediment fingerprinting procedure is provided in Fig. 1.1.

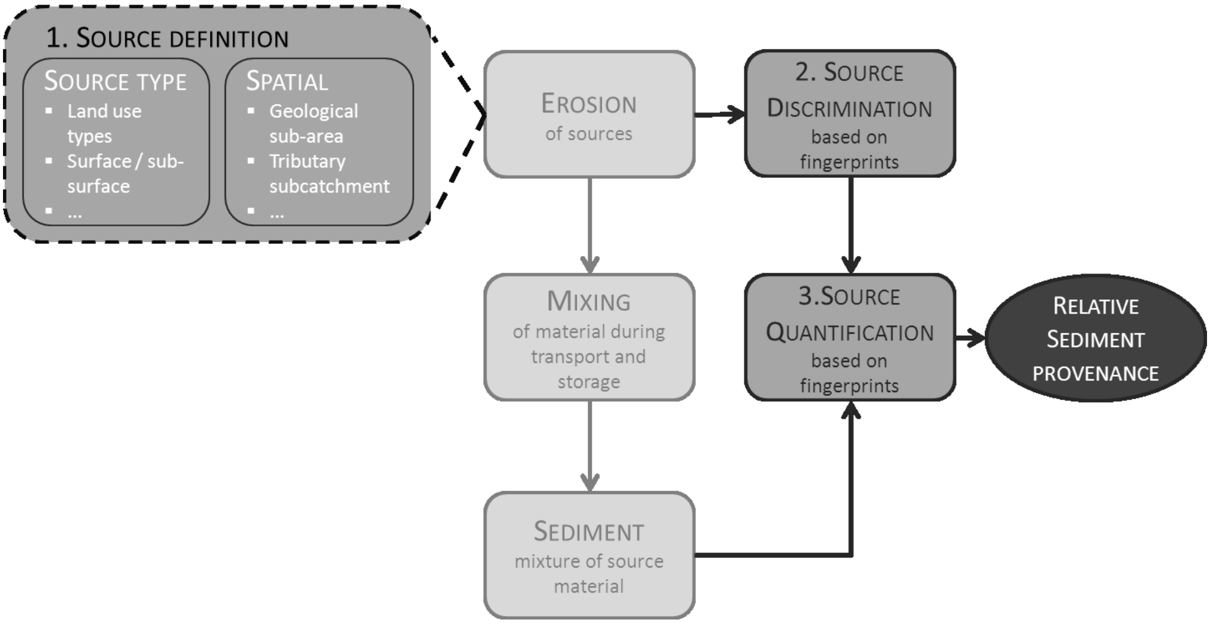

Fig. 1.1: Conceptual model of the sediment fingerprinting approach (modified after Collins and Walling 2002)

The major advantage of the sediment fingerprinting approach is probably its wide range of source definition possibilities, i.e. temporal (intra-storm to geological records), spatial (e.g. small tributary subcatchments to large river basins), and source type (e.g. land use types). Thus, it has been applied on a large range of temporal and spatial scales in a variety of environments and in various ecoregions around the world over the past decades (e.g. Walling 2005, Davis and Fox 2009, Koiter et al. 2013).
However, the approach is also facing a number of uncertainties requiring investigation. At present, one of its major limitations is seen in the potentially non-conservative behaviour of fingerprint properties (e.g. Davis and Fox 2009) resulting in spurious source ascriptions. This may include selective transport and consequently enrichment e.g. in fine particles

and/or organic matter, as well as physical or biogeochemical transformation of tracers (Koiter et al. 2013, Smith and Blake 2014). In addition, Collins and Walling 2004 remark a lack of general guidelines for parameter pre-selection or for the optimum number of samples to characterise sediment sources. Thus, the renewed analyses and testing of a variety of potential parameter can make the approach very time-consuming and costly. Finally, a wide variety of mixing models (and recently alternative methods, such as partial least squares regression (PLSR)) have evolved over the past decades, including sophisticated correction and weighting factors, constraints and possibilities to incorporate uncertainty (Rowan et al. 2000, Poulenard 2009 and 2012, Martínez-Carreras et al. 2010b, Motha et al. 2003, Collins et al. 2010). However, these modelling approaches are hardly ever verified using e.g. artificial mixtures of known contributions (e.g. Small et al. 2004, Franks and Rowan 2000), which may at least partly be explained by the high labour-intensity of retrieving most fingerprint properties. As a result, the sediment fingerprinting technique has been widely applied in scientific studies, whereas its anticipated use as management tool is still being hampered (Mukundan et al. 2012).

1.3 Spectral fingerprinting

In addition to the conservativeness issue of tracers, recent studies have mainly focused on the investigation of inexpensive yet robust properties (e.g. Poulenard et al. 2009 and 2012, Martínez-Carreras et al. 2010a and 2010b and 2010c, Evrard et al. 2013, Legout et al. 2013). Thereby, spectral reflectance measurements (see chapter III) were found to offer a rapid, low-cost, accurate and non-destructive alternative for the assessment of various soil properties (e.g. Viscarra Rossel et al. 2006a and 2006b, Ben Dor et al. 2009, Richter 2010, Bayer 2013) that allow source discrimination and quantification. For example, Martínez-Carreras et al. (2010a,c) tested the ability of colour parameters derived from visible (VIS) spectra to discriminate and quantify source types (land use) and spatial sources (geology) in catchments ranging from 0.7 to 247 km² in size (Luxembourg). They also used visible – near infrared (VNIR) and shortwave infrared (SWIR) spectra in combination with PLSR to quantify geochemical source and sediment properties and used the resulting parameters to estimate source contribution (Martínez-Carreras et al. 2010b). Poulenard et al. (2009, 2012) successfully used mid infrared (MIR) spectra and PLSR models trained on artificial source mixtures to predict source contribution in two small catchments (9.9 to 20 km²), while Legout et al. (2013) used PLSR models on VIS spectra in a 22 km² basin. In addition, these three studies assessed the conservativeness of spectra in submersion experiments for periods of up to 63 days. Only Martínez-Carreras et al. (2010a) published a direct comparisons of spectral and ‘classic’ fingerprinting based on geochemistry, whereas Evrard et al. (2013) made a similar comparison though without considering the effect of using a mixing model (classic approach) vs. PLSR model (spectral approach) to quantify the input from different sources.

In addition to being less labour-intense than many conventional analyses, spectroscopy can be applied to very small amounts of material (up from 60 mg, Krein et al. 2003, Martínez-Carreras et al. 2010a) which increases the number of potentially applicable sediment sampling strategies and enables the analysis of intra-event source variability. Furthermore, the rapidity of spectral measurements facilitates the inclusion of artificial mixtures to test mixture modelling accuracy. And finally, modern spectroradiometers offer the possibility to measure source properties in situ, making parameter retrieval even more efficient as proposed e.g. by Martínez-Carreras et al. (2010a) and Poulenard et al. (2012). Actually, a successful application of in situ source information might encourage the testing of airborne or satellite imaging spectroscopy data for even less labour intense while spatially more representative retrieval of source information.

1.4 Objectives of the thesis

Though spectroscopy has been a focus of recent fingerprinting studies, comparably few results have been published and many questions remain unanswered. For example, the usability of the SWIR spectral range has hardly been assessed, physically-based spectral features have not yet been tested and neither has the application of in situ source information been attempted nor has the examination of mixing model accuracy been incorporated into the fingerprinting process. Thus, this thesis aims at further investigating the potential of soil spectroscopy in providing innovative sediment fingerprint properties. Thereby, the focus is on the exploration of spectral parameters derived from the VIS, NIR and SWIR portion of the electromagnetic spectrum (0.35 – 2.5 µm). Specifically, the key questions addressed in the following chapters are:

1) Can potential sediment sources be reliably identified based on VNIR-SWIR spectral fingerprints?
2) Do these spectral fingerprints permit the quantification of relative source contribution?
3) Is in situ derived source information sufficient for spectral sediment fingerprinting?
4) What does the spectral fingerprinting approach reveal when applied to sediment and how do relative contributions from different sources vary?
5) How do spectral fingerprinting results compare with sediment flux measurements and what does a combination of methods reveal about sediment origin, transport and storage?

In the literature, the definitions of a “fingerprint” may differ. In this work, fingerprints are derived from the parameterization of spectral properties, which is achieved by means of feature calculation, and the calculation of colour coefficients and spectral indices. Therefore, in addition to describing spectral properties, spectral parameters and spectral features, these three terms all represent “spectral fingerprints”. A further synonym frequently used in the literature as well as in the following chapters is the term tracer.

1.5 Outline and structure of the thesis

The structure of this thesis is illustrated in Fig. 1.2. The first **chapter (I)** provides a short introduction to the ecologic and economic impact of high sediment loads and to the sediment fingerprinting approach as a first step in the design of mitigation strategies. An overview of the catchment investigated in this thesis is presented in **chapter II**. **Chapter III** describes the general principles of spectroscopy, reflectance properties of soils and the derivation of information from spectra by means of feature calculation.

The key questions expressed above are answered in **chapter IV to VI**. Therefore, soil samples were collected from potential sediment sources in the Isábena catchment (eastern Spanish Pyrenees). These samples were measured in situ as well as in the laboratory using an Analytical Spectral Device (ASD) field spectroradiometer. In addition to source soil samples, suspended sediment was collected from the catchment outlet and the five major subcatchment outlets during storm events by means of automatic sediment samplers. Fine sediment stored in the river channel was collected manually at different cross sections along the main channel. All sediment samples were spectrally measured in the laboratory. Then, colour coefficients and spectral features with relation to organic carbon, iron oxide, clay minerals and carbonate were calculated from all source soil and sediment spectra. These parameters were used as spectral fingerprint properties in subsequent analyses.

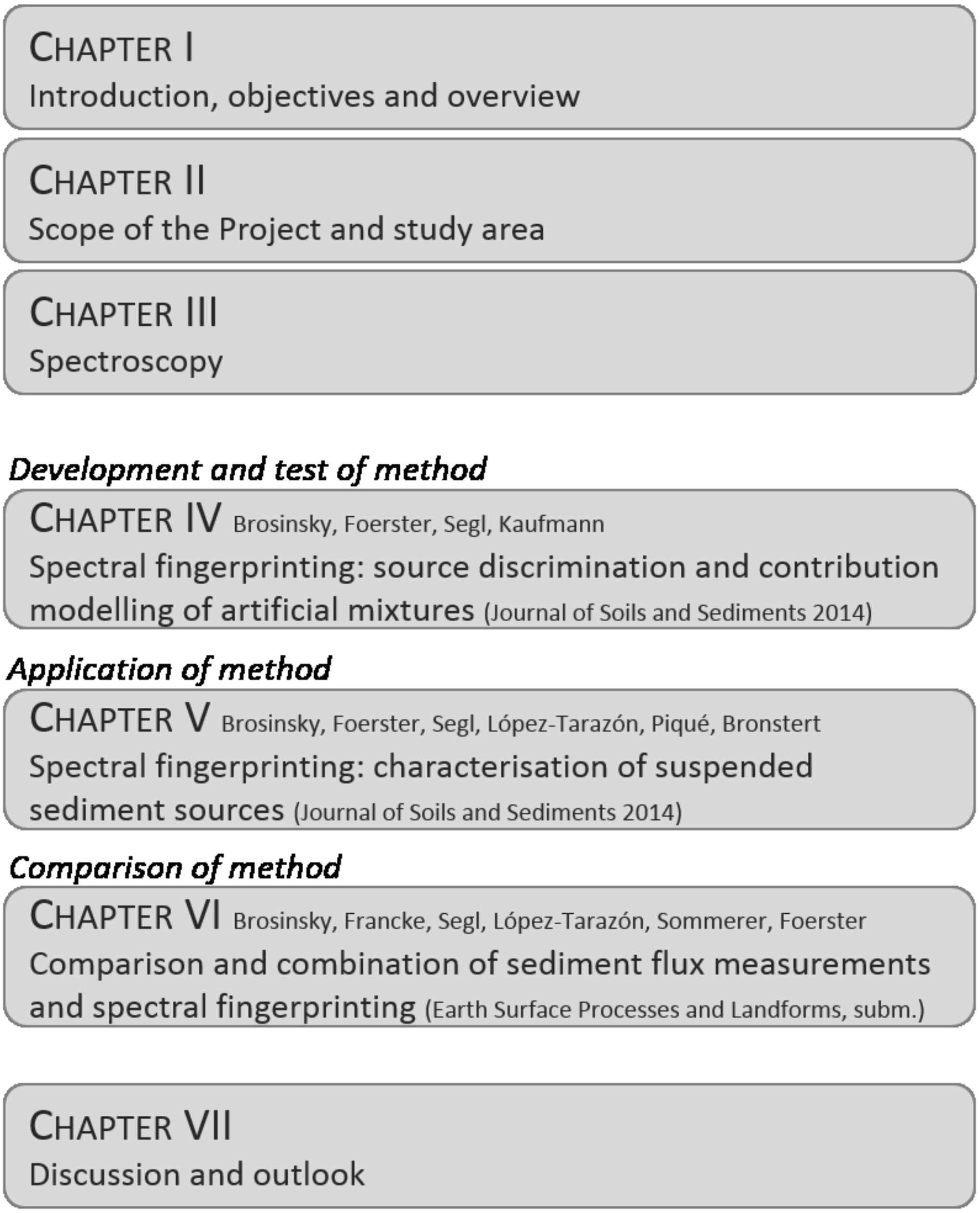

Fig. 1.2: Structure of this thesis. The chapter titles have been modified for clarity; for full titles see front pages of the respective chapters

The first three key questions, all related to the **development of the method**, are addressed in **chapter IV**: Source discrimination potential (1) was assessed by means of Discriminant Function Analysis (DFA) for a variety of different source definitions. In order to examine the extent and accuracy to which spectral fingerprints permit the quantification of relative source contribution (2), artificial mixtures of known proportions were produced from source sample material. This allowed application of a mixing model and observation of changes in contribution estimates due to changes in source definition and input parameters under controlled conditions. In addition, the use of these artificial mixtures enabled an assessment of the success to which in situ derived source information could be applied in sediment fingerprinting studies (3).

Chapter V describes the **application of the spectral fingerprinting approach** developed and tested in chapter IV to suspended sediment samples collected at the catchment outlet and to fine sediment collected from the channel bed. Major sediment sources were identified and changes in their relative contributions between and within individual storm events explained (4).

A **comparison of spectral fingerprinting** with direct sediment flux measurements (5) is presented in **chapter VI**. Therefore, sediment sources are defined not by source type (i.e. land use as in chapter IV and V) but spatially by subcatchment. Thus, fingerprinting is based exclusively on suspended sediment samples collected at the subcatchment (source material) and the catchment outlet (sediment material).

The study is summarized in **chapter VII**, where main results are discussed and an outlook to suggested further investigations is given.

1.6 Author’s contribution

This thesis is organized cumulatively, whereas chapters IV to VI were written as stand-alone manuscripts and published in (chapter IV and V) or submitted to (chapter VI) international peer-reviewed journals (full references given at front pages of respective chapters). The work described in these chapters has essentially been performed by the author. Co-authors have contributed significantly in terms of data collection (all sediment samples), calculation of sediment fluxes, and programming of the mixing model. Furthermore, they supported the author by means of valuable discussions and proof-reading of manuscripts.

The papers are reproduced largely unmodified with the exception of cross-references that have been replaced by chapter number, numbering of figures and tables, and references that can be found at the end of this thesis.

Chapter II
Study area

Scope of the project

The work presented in this thesis was conducted within the larger framework of the project *“Generation, transport and retention of water and suspended sediments in large dryland catchments: Monitoring and integrated modelling of fluxes and connectivity phenomena”* funded by DFG (Deutsche Forschungsgemeinschaft, 2010 - 2013). The overall objective of the project was the analysis of “connectivity processes between water and sediment delivering, accepting and transporting compartments, including the analysis of transfer routes and storage capabilities” (WASESAC 2009) in dryland regions. Extended field monitoring by various means and at multiple scales from hillslopes to the catchment (Sommerer et al. 2014, Francke et al. 2014), the identification of major sources, stores and paths of sediments through remotely sensed data (Foerster et al. 2014), and the application of innovative spectral sediment fingerprinting techniques (chapter V and VI), were used to understand and quantify water and suspended sediment fluxes in dryland regions. Currently, an existing modelling framework for water and sediment transport (WASA-SED) is re-parameterised to evaluate the effects of such spatially and temporally high resolution input data.
The work presented in this thesis further benefitted from data acquired and knowledge gained during a previous project conducted in the same study area. The SESAM project (*“Sediment Export from large Semi-Arid catchments: Measurements and Modelling”,* funded by DFG 2005-2008) aimed at monitoring and modelling water and sediment fluxes from their sources to the deposition areas.
Together, these results are expected to improve the knowledge and modelling capability of connectivity processes of water and sediment fluxes in dryland areas at spatial scales relevant for management decisions.

Some characteristics of the study area are directly linked to the success of the application of sediment fingerprinting, since in one way or another they may influence (spectral) fingerprint properties, (e.g., size, soil / lithology, land use, tributary structure, climate and runoff regime). Therefore, though the catchment investigated in this thesis is characterized in detail in chapter IV to VI, a short overview and some further aspects will be presented in the following section.

Location

All studies presented in this thesis were conducted in the Isábena catchment, a mesoscale watershed in the eastern Spanish Pyrenees. The Isábena River joins the river Ésera just before entering the Barasona reservoir. Together, they constitute some of the major tributaries of the River Cinca, in turn one of the largest tributaries to the Ebro basin (Fig 2.1). The Isábena drains an area of 445 km² (0.48 % of the Ebro basin) and produced an average of ~ 1.5 % of the Ebro basin’s total annual runoff in the period 1945 – 2009 (López-Tarazón et al. 2009).The Isábena mainstream has a length of approximately 50 km and its catchment is composed of five major subcatchments: Cabecera in the North (146 km², representing 33 % of the total catchment area), Villacarli (42 km², 9 %) and Carrasquero (25 km², 6%) in the NW, and Ceguera (28 km², 6 %) and Lascuarre (45 km², 10 %) in the SE. The remaining area (156 km², 34 %) drains directly into the Isábena River (Fig. 2.1a).

Geology

Overall, the Isábena catchment is characterized by a heterogeneous lithology and a rough terrain, ranging from 450 m a.s.l. in the southern lowlands to 2700 m a.s.l. in the headwaters (Fig. 2.1a and 2.1b). The catchment is part of the Tremp-Graus geological basin, a wide depression with generally WNW–ESE trending geological units (López-Tarazón 2011). Valero-Garcés et al. (1999) describe several geological units: (1) the Axial Pyrenees in the North, where quartzites and partially karstified Paleozoic limestones form peaks above 3000 m a.s.l.. Here, the Isábena River runs in a narrow gorge. To the South follow (2) the Internal Ranges composed of Cretaceous and Paleogene sediments. Some of these are easily erodible, resulting in steep and fractionated slopes. Especially on the marly substrates in the Villacarli and Carrasquero subcatchments, badlands have evolved. Despite representing less than one percent of the catchment area, these badlands are considered the major suspended sediment sources (e.g. Fargas et al. 1997, Valero-Garcés et al. 1999, Francke et al. 2008a, Alatorre and Beguería 2009, chapter V). Further south extends (3) the Intermediate Depression, an area of relatively low altiutude (450 – 750 m a.s.l) that is composed of Neogene continental sediment. The southern limit of the catchment is formed by the External ranges with elevations up to 1700 m a.s.l. (Valero-Garcés et al. 1999).

Soils

The soils developed on these substrates can be classified as shallow mineral soils (including regosols, leptosols and fluvisols) and soils with a considerable accumulation of organic matter, including kastanosems (Alatorre et al. 2010). Laboratory analyses of soil samples collected for this study revealed high carbonate concentrations in all but very few samples, and grain size in the < 63 µm fraction to be dominated by middle and fine silt (particles of the size 6 - 20 µm and 2 - 6 µm, respectively) while the average clay-sized content (particles < 2 µm) is 19 % (6.5 – 30 %).

Climate

The rough terrain results in a pronounced climatic and land cover gradient. The climate is of Mediterranean mountainous type, with generally cold, dry winters and hot summers featuring frequent storms. Thereby, the Turbón massif in the North of the Villacarli sub-catchment can be defined as a “climatic border” between the cooler and more humid North and the dryer and warmer South of the catchment (López-Tarazón 2011). Mean annual temperatures vary between 9 °C in the North and 14 °C in the South (Verdú 2003), whereas maximum mean values are registered in July and August (21 °C and 22 °C, respectively) and minima in January and December (2°C and 4 °C, respectively). December to February are also the months with highest freezing probabilities, though frost can appear from September throughout May (López-Tarazón 2011). Average precipitation ranges from 1600 mm (North) to 450 mm (South) (Verdú 2003), whereas precipitation is of high spatial and temporal variability and distributed irregularly over the catchment. Rainfall maxima generally occur in summer and autumn due to storms (López-Tarazón et al. 2010 and 2012).

Hydrology

These summer storms and late autumn heavy rains, together with late spring–early summer snow melt are responsible for the major floods in the Ésera–Isábena basins (pluvial–nival runoff regime, Valero-Garcés et al. 1999). Despite occasional gravel mining, the Isábena is an entirely unregulated river with a mean annual discharge of 4.1 m^3 s^{-1} for the period 1945 - 2009 (López-Tarazón 2011). However, inter-annual variation is considerable (Francke et al. 2014) and peak discharges exceed 50 m^3 s^{-1}.

Landuse

The higher altitudes of the Isábena catchment are mainly covered by forests (46 % of total catchment area, Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) 2008) (see Fig. 2.1c). Thereby, coniferous woodlands are dominated by *Pinus sylvestris* and *Pinus unicata* (from 1600 m a.s.l.), while broadleaved species *Quercus faginea, Quercus ilex, Betula pendula* and *Fraxinus sp.* form deciduous woodlands as well as mixed stands with coniferous species (Appel 2006). Major land use changes that occurred over the past 50 years resulted in the abandonment of cultivated areas and subsequent revegetation, initiated by shrub species and followed by forest regrowth (e.g. Lasanta and Vicente-Serrano 2012). Today, shrublands (Matorral) cover 30 % of the study area (MARM 2008) whereas many transition stages can be found. Common species are *Buxus sempervirens*, *Thymus vulgaris, Rosmarinus officinalis, Genista sp*. and *Juniperus communis*, partly intermixed with trees and grassland. Grassland accounts for 8 % of the catchment area (MARM 2008) and both, shrubland and grassland are mainly used for sheep and goat grazing. Lowlands and valley bottoms are largely used for agriculture (14 % of total catchment area) (MARM 2008). Dominant crops are wheat, barley, alfalfa and sunflowers (Appel 2006, López-Tarazón 2011).

Altogether, these catchment properties – steep slopes, shallow soils on highly erodible substrates, heavy storms, degraded vegetation cover and partly intense agriculture - result in high erosion rates (e.g. López-Tarazón et al. 2009, Francke et al. 2014), with instantaneous suspended sediment concentrations occasionally attaining 350 g l^{-1} (López-Tarazón et al. 2009). The high sediment loads cause severe siltation problems in the downstream Barasona reservoir and subsequently considerable loss of storage capacity (e.g. Valero-Garcés et al. 1999, Mamede 2008). Therefore, and because of its heterogeneous and high magnitude sediment response, the basin has been studied intensively over the past decade (Bronstert et al. 2014), resulting in a favourable instrumentation situation and data availability, making it an ideal test site for innovative techniques such as spectral sediment fingerprinting.

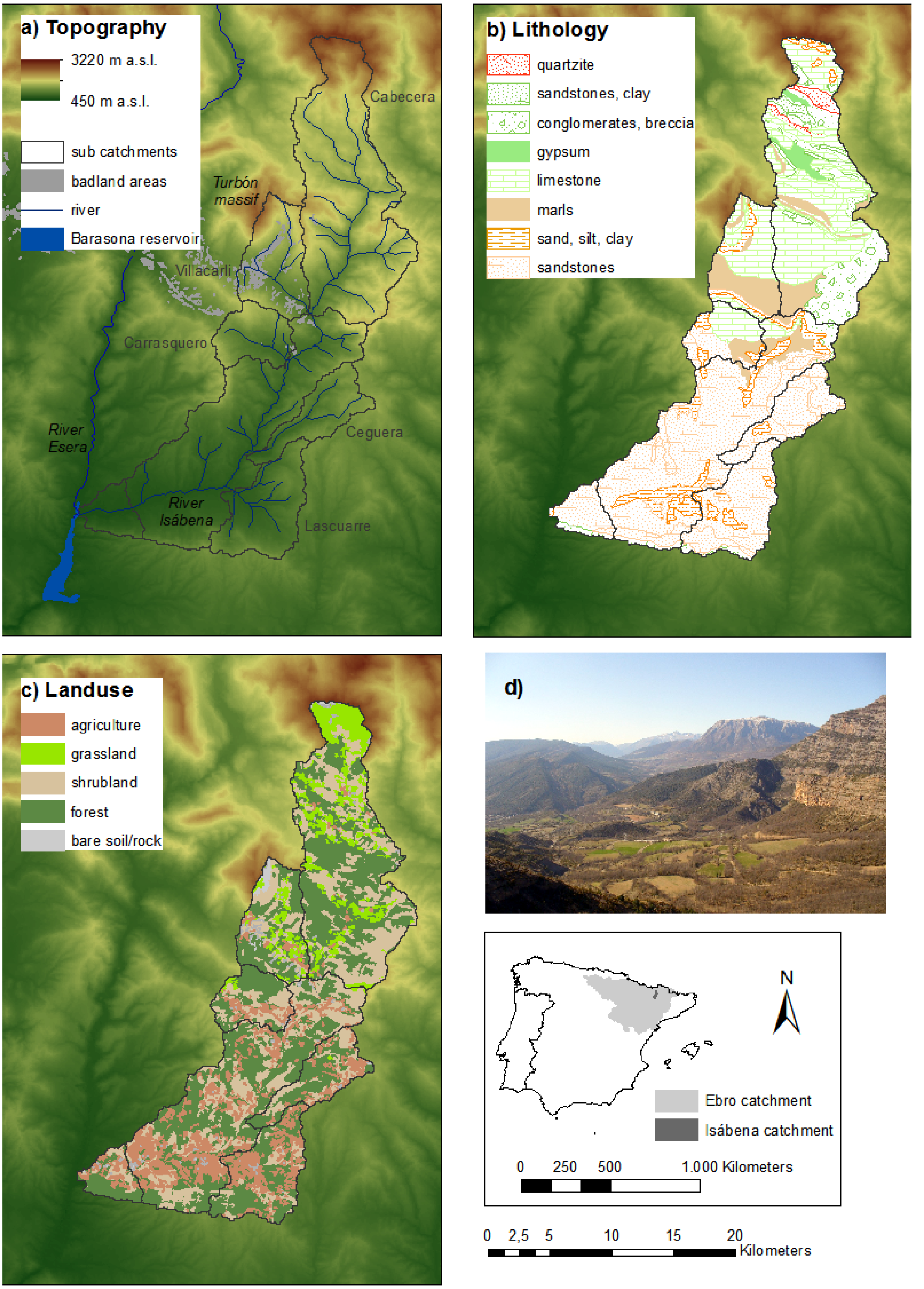

Fig. 2.1: Map of the Isábena catchment displaying a) topography (ASTER GDEM) and structure of subcatchments, b) lithology (CSIC), c) landuse (MARM 2008), and d) view of the Villacarli valley with Turbón massif

Chapter III
Spectroscopy

Spectroscopy is defined as “the study of light as a function of wavelength that has been emitted, reflected or scattered from a solid, liquid or gas” (Clark 1999). It can be used to identify and to characterise surface material qualitatively or quantitatively (Bayer 2013). The fundamental principles and basic mechanism of interaction between incident light and surface materials in general and the resulting spectral characteristics of soils will be explained briefly in the following sections. Thereby, this review is limited to the 0.35 - 2.5 µm portion of the electromagnetic spectrum because this is the range that was used for the measurements presented in the following chapters. In remote sensing studies, this spectral range is often separated into the regions 0.4 – 0.7 µm (visible (VIS) to the human eye), 0.7 – 1.1 µm (near-infrared (NIR)) and 1.1 - 2.5 µm (shortwave infrared (SWIR)).

Irradiance (E) is defined as the optical radiative power falling on a surface by unit area [W/m²] (Baumgardner et al. 1985). When irradiance (e.g. sunlight) interacts with a surface, parts may be absorbed (E_a), transmitted (E_t), and/or reflected (E_r). The sum of these three processes equals one (principle of conservation of energy) whereas their magnitude varies with wavelength (λ) (e.g. Lillesand et al. 2008).
In this study, the focus is on the *reflectance* of surfaces, which is defined as the ratio of reflected radiation to the total radiation incident on a surface ($E_{r,\lambda}$ / E_λ) as a function of wavelength (e.g. Baumgardner et al. 1985). It is commonly measured as the ratio of energy reflected by a target surface to the energy reflected by an ideal reference surface (assumed 100 % diffuse reflectance). The resulting reflectance spectrum is displayed as a graph providing the relative intensity of reflected radiation as a function of wavelength (Fig. 3.1a).

3.1 Mechanisms of absorption

There are a number of processes that determine how radiation interacts with surface materials. These processes are wavelength dependent and thus the proportions of energy reflected permit the derivation of information about certain surface characteristics (Clark 1999), e.g. soil chemistry. As such, a typical reflectance spectrum shows various minima and maxima that are caused by strong absorption bands. Differences in position, shape and depth of these features may allow materials to be identified in their quality or even quantity. The absorption bands are caused by two general processes: electronic and vibrational processes. A brief overview of these processes is given in the following sections, detailed descriptions can be found e.g. in Hunt (1977) and Clark (1999).

Electronic processes

When radiation interacts with a surface, the characteristics of electromagnetic radiation change. This change is caused by the transition of electrons between energy states (Hunt 1977). Since atoms or molecules can only possess certain discrete energy states, the energy of an emitted or absorbed photon equals the difference between these discrete energy levels (Ben-Dor et al. 1999). Absorption due to electronic transition is wavelength specific and usually produces broad bands in the ultraviolet (UV) range that extend to the VIS.

The absorptions referred to as **crystal field effects** are the most common electronic processes revealed in the spectra of minerals (Clark 1999). They are caused by unfilled electron shells of transition elements such as Ni, Cr, Co, Fe, etc., enabling the movement of electrons stimulated by absorption of energy (Clark 1999). Thereby, the resulting absorption features mainly depend on the valence state (e.g. Fe^{2+}, Fe^{3+}) of the ion as well as the crystal structure (Hunt 1977).

Charge transfer bands produce features due to inter-element electron transitions, where the absorbed energy causes electrons to migrate between ions or between ions and ligands (Clark 1999). The charge transfer may also occur between adjacent ions of the same metal in different valence states. Since such transfer requires high levels of energy, the absorption features are usually up to thousand times more intense than those produced by crystal field effects (Hunt 1977). Thus, they appear mostly in the UV and VIS wavelength region (Ben-Dor et al. 1999).

Other electronic processes, such as colour centres and conduction bands, are of minor importance for the observation of soil reflectance properties.

Vibrational processes

Features produced by vibrational processes result from the vibration of ions or molecules in a crystal lattice. Thereby, the frequency of vibration depends on the number and mass of a molecule's atoms, and the strength of the ion bonds (Clark 1999). A molecule composed of n ions has $3n$-6 normal modes of vibration (Hunt 1977). These are called fundamentals. The fundamental bands of most materials occur at wavelengths greater than 2.5 µm (Ben-Dor et al. 1999), which is out of the spectral range investigated in this study. This restricts the detection of features produced by vibrational processes to overtone bands (roughly multiples of single fundamental modes), and combination bands (combinations of different vibrational modes) of molecules with very high fundamental frequencies (Hunt 1977). Features usually get weaker with each higher overtone or combination. In contrast to the generally broad UV and VIS bands associated with electronic transitions, vibrational processes produce sharp features that are stronger in the SWIR and decrease in intensity and frequency of occurrence towards the NIR (Hunt 1977). Molecules providing high frequency fundamentals and hence producing particularly diagnostic vibrational absorption bands in in the SWIR are H_2O and OH^- (e.g. in clays) and CO_3^{2-} (e.g. in carbonates) (Clark 1999).

Analysis of absorption features

The mapping of specific absorption features and their characteristics is a very suitable method to analyse the chemical composition of materials (Clark 1999). Thereby, a technique called *continuum removal* or *hull normalisation* is frequently applied, where the spectrum is separated into a continuum and individual absorption features (Fig.3.1). This isolates the spectral absorption bands resulting from electronic or vibrational processes from the continuum representing background or overall reflectance, thus allowing analysis and intercomparison of the features. This analysis usually involves calculation of position and depth of maximum absorption relative to the continuum as well as parameters such as feature width (length between shoulders), area and asymmetry. A mathematical definition of the continuum is given by Clark and Roush (1984).

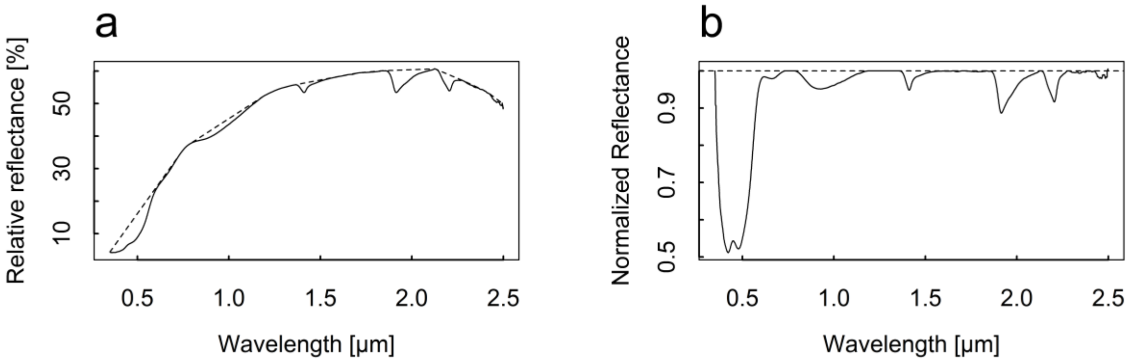

Fig. 3.1: Analysis of absorption features by continuum removal. Reflectance spectrum of a soil spectrum (solid line) measured in the laboratory and its derived hull (dashed line) as (a) relative reflectance and as (b) continuum removed reflectance plot

Atmospheric considerations

Measurements of a surface's spectral reflectance properties must consider the absorption of the Earth's atmosphere (Clark 1999). Generally, atmospheric transmittance is highest between 0.4 and 2.5 µm, whereas there are some distinct wavelength ranges of high absorption and scattering due to atmospheric gases. Thereby, water causes most of the absorption with two pronounced features near 1.4 and 1.9 µm. Oxygen absorbs in a narrow feature at 0.76 µm, and CO_2 at 1.6, 2.01 and 2.06 µm (Clark 1999). However, these issues are of minor importance for measurements with a contact probe (in situ) or under laboratory conditions as conducted in this study because of the reduced atmospheric path length.

Geometric considerations

Lillesand et al. (2008) describe two general ways in which incident radiation is reflected that are not only influenced by the absorption properties but also by surface characteristics (mainly roughness): Flat surfaces act like a mirror, where incident light is reflected at the same angle as the angle of incidence (*specular reflection*). In contrast, a rough surface ideally reflects incident light uniformly in all directions (*diffuse* or *Lambertian reflection*). In reality, reflectance characteristics of natural surfaces are usually between these two extremes.

In addition to these surface reflectance considerations, in situ field or airborne observations may be influenced by geometrical variations in viewing angle and illumination changes (Ben-Dor et al. 1999). Unlike field observations, measurements in laboratory situations are usually very controlled. As such, soil samples are prepared to contain little surface roughness, sensor zenith as well as illumination angle are fixed and illumination conditions are constant (Baumgardner et al. 1985). However, several measurements should be performed on each sample to consider shadowing effects due to minimal surface variations.

Mixtures

Spectroscopic observations are mainly limited to the top few µm of soil surfaces (Ben-Dor et al. 1999). Thereby, incident energy may not only be reflected from the surface but may also penetrate into the upper soil particles where it is absorbed or scattered (Jensen 2007). This (multiple) scattering is a non-linear process, making extraction of quantitative information more difficult (Clark 1999). Furthermore, the composition of grains in a soil, where "different materials are in intimate contact in a scattering surface", are defined as intimate mixtures that may cause further non-linearity of the spectral signal (Clark 1999). However, to allow for a mathematical description of the spectra, linear mixing is assumed in this study.

3.2 Reflectance properties of soils

Soil is the weathered material that has developed at the Earth's surface between atmosphere and lithosphere to a depth ranging from few centimetres to several meters (Scheffer and Schachtschabel 2010). It is a complex material of extremely variable physical and chemical composition (Ben-Dor et al. 1999). The major constituents of soil minerals (O, Si, Al, and Mg) do not have absorption features in the VIS to SWIR range (Hunt 1977). Thus, spectral reflectance characteristics of soils are mainly influenced by organic matter content, clay mineral composition, iron-oxide content, moisture content, salinity, texture and surface roughness (Jensen 2007). These characteristics are variable and interrelated (Lillesand et al. 2008) and thus may not be easy to delineate (Ben Dor 1999). The following section provides a brief overview of the spectral characteristics of soil components, whereas the descriptions apply to soils as well as to sediments, which are considered mixtures of soil particles. Examples of soil and sediment spectra from the Isábena catchment with relation to soil components spectral characteristics can be found in chapter IV (Fig. 4.2). A detailed review with cross-references to many fundamental as well as recent state of the art studies can be found in Bayer (2013).

Moisture

In general, the higher the moisture content of soil, the greater the absorption of incident radiation and the lower the reflectance (Jensen 2007). Water in soils can be present as (1) hydration water incorporated in the mineral lattice (e.g. gypsum), (2) hygroscopic water adsorbed on the surface of clay minerals and organic matter, and (3) free water in soil pores (Ben Dor et al. 1999). An increase in moisture results in a decrease of spectral response throughout the entire VNIR-SWIR wavelength interval, a deepening of the strong water absorption bands around 1.4 and 1.9 µm and occasionally the development of weaker absorption bands near 0.97, 1.2 and 1.77 µm (Baumgardner 1985, Jensen 2007).

Organic matter

Soil organic matter consists of any dead biomass (i.e., vegetation and animal litter) and all its conversion products (Scheffer and Schachtschabel 2010). As such, its chemistry is very complex and variable, resulting in a wide range of (small) spectral features across the 0.4 - 2.5 µm wavelength region (Ben-Dor et al. 1999). In general, as organic matter content increases, soil reflectance decreases throughout the entire VNIR-SWIR range, and absorption effects of other soil constituent may become masked, at least when organic matter contents exceed 2 % (Baumgardner et al. 1985).

Clay minerals

Clay minerals are the weathering products of primary minerals and are dominating the clay sized fraction of soils (< 2 µm) (Scheffer and Schachtschabel 2010). They consist of layered silicates of varying chemical composition and electrical charge. In general, mixed-clay mineralogies in which the layers overlap spectrally are more common than individual clay types (Baumgardner et al. 1985). Basically, the spectral features of clay minerals are associated with the presence of water (lattice and hygroscopic), producing strong absorption bands around 1.4 and 1.9 µm, and hydroxyl bands centred near 1.4 and 2.2 µm (Baumgardner et al. 1985, Ben-Dor et al. 1999).
Since a soil's grain size additionally affects its overall reflectance, a high clay-sized fraction of soil particles leads to a general increase in soil reflectance throughout the VNIR portion of the spectrum (e.g. Jensen 2007).

Iron

Iron oxides are among the major pigmenting agents of soils, producing yellowish-brown (goethite) to reddish (hematite) colours (Baumgardner et al. 1985). Thereby, even small amounts of iron can alter soil colour significantly (Ben Dor et al. 1999) up to the point where other soil features get masked. The iron's absorption features result from electronic transitions in the iron cations (Hunt 1977) and are mainly visible in the VNIR portion of the spectrum. Major features are located near 0.4, 0.7, and 0.87 µm (due to Fe^{3+}), and near 0.43, 0.45, 0.51, 0.55, and 1.0 µm (due to Fe^{2+}) (Ben Dor et al. 1999). In addition, a charge transfer band with maximum absorption in the UV region that extends to the VIS results in a strong decrease of reflectance intensity towards the UV (Clark 1999).

Carbonate

The most common carbonates are calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$). They are inherited from carbonic parent material or may result from precipitation during soil formation (Scheffer and Schachtschabel 2010). Carbonate minerals mainly cause a diagnostic absorption peak between 2.3 and 2.35 µm due to CO_3^- overtone vibrations, whereas the band centre is shifted towards shorter wavelength with increasing Mg^{2+} content (Richter 2010).

Soil Colour

The human eye is sensitive to reflectance in the VIS range, which is perceived as colour. Thereby, the colour blue is ascribed to the range of approximately 0.4 - 0.5 µm, green to 0.5 – 0.6 µm and red to 0.6 - 0.7 µm (Lillesand et al. 2008). Colour is one of the most useful attributes for describing differences between soils and an essential component in all modern soil classification systems (Baumgardner et al. 1985). It is influenced by the environmental conditions of soil formation and related to the quantity and quality of the soil components that absorb radiation at different wavelength and with differing intensities. The major components affecting soil colour are soil organic carbon (SOC), water, iron oxides and the chemical composition of clay minerals (Ben-Dor et al. 1999). In general, reddish and yellowish colours are related to the presence of hematite and goethite, respectively, whereas soil darkness is largely influenced by SOC, soil moisture and grain size. In soil science, soil colour is most commonly described visually by the use of Munsell soil colour charts (Ben-Dor et al. 1999). However, spectroradiometers provide a more physically based assessment of soil reflectance from which a range of colour parameters can be delineated more precisely and objectively.

Soil physical factors

Physical factors such as soil texture and surface roughness mainly influence the soil's albedo. In general, an increase in particle size causes a decrease in overall reflectance, thus coarse-grained soils show lower reflectance than fine-grained soils. Regarding in situ measurements, aggregate size (or surface roughness) rather than particle size may alter the shape of reflectance spectra (Ben-Dor et al. 1999). In addition, the formation of physical soil crusts e.g. resulting from raindrop impact may cause an increase in finer particles at the soil surface and thus an increase in soil reflectance.

In the following chapters, spectrally derived soil colour coefficients as well as spectral absorption features related to organic carbon, clay minerals, iron oxide and carbonate will be used as 'fingerprints' for the discrimination and quantification of potential sediment sources.

Chapter IV
Spectral fingerprinting: Sediment source discrimination and contribution modelling of artificial mixtures based on VNIR-SWIR spectral properties

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Abstract

Purpose: Knowledge of the origin of suspended sediment is important for improving our understanding of sediment dynamics and thereupon support of sustainable watershed management. A direct approach to trace the origin of sediments is the fingerprinting technique. It is based on the assumption that potential sediment sources can be discriminated and that the contribution of these sources to the sediment can be determined on the basis of distinctive characteristics (fingerprints). Recent studies indicate that visible–near-infrared (VNIR) and shortwave-infrared (SWIR) reflectance characteristics of soil may be a rapid, inexpensive alternative to traditional fingerprint properties (e.g. geochemistry or mineral magnetism).

Materials and methods: To further explore the applicability of VNIR-SWIR spectral data for sediment tracing purposes, source samples were collected in the Isábena watershed, a 445 km² dryland catchment in the central Spanish Pyrenees. Grab samples of the upper soil layer were collected from the main potential sediment source types along with *in-situ* reflectance spectra. Samples were dried, sieved, and artificial mixtures of known proportions were produced for algorithm validation. Then, spectral readings of potential source and artificial mixture samples were taken in the laboratory. Colour coefficients and physically based parameters were calculated from *in-situ* and laboratory measured spectra. All parameters passing a number of prerequisite tests were subsequently applied in discriminant function analysis for source discrimination and mixing model analyses for source contribution assessment.

Results and discussion: The three source types (i.e. badlands, forest/grassland and an aggregation of other sources, including agricultural land, shrubland, unpaved roads and open slopes) could be reliably identified based on spectral parameters. Laboratory-measured spectral fingerprints permitted the quantification of source contribution to artificial mixtures, and introduction of source heterogeneity into the mixing model decreased accuracies for some source types. Aggregation of source types that could not be discriminated did not improve mixing model results. Despite providing similar discrimination accuracies as laboratory source parameters, in-situ derived source information was found to be insufficient for contribution modelling.

Conclusions: The laboratory mixture experiment provides valuable insights into the capabilities and limitations of spectral fingerprint properties. From this study, we conclude that combinations of spectral properties can be used for mixing model analyses of a restricted number of source groups, whereas more straightforward *in-situ* measured source parameters do not seem suitable. However, modelling results based on laboratory parameters also need to be interpreted with care and should not rely on the estimates of mean values only but should consider uncertainty intervals as well.

4.1 Introduction

Suspended sediment entering surface waterways can have a range of negative impacts on water quality, e.g. by eutrophication, increased turbidity, and habitat degradation (e.g. review by Owens et al. 2005). Fine sediments were identified as one of the main sources of nonpoint source pollution (Davis and Fox 2009) due to their importance in the transport and storage of nutrients (e.g. phosphorus) and contaminants (e.g. Owens and Walling 2002, Walling 2005). In addition, sediment transported by rivers can adversely affect water quantity due to siltation and thus changes in river morphology or reduction in operational capacities of water supply facilities (e.g. reservoirs) (Owens et al. 2005). Therefore, knowledge of sediment sources is of fundamental importance in understanding complex suspended sediment dynamics and is a prerequisite for sustainable management practices (Walling 2005, Davis and Fox 2009).

Traditional methods of sediment provenance assessment (e.g. erosion mapping, surveying using profilometers or erosion pins, erosion vulnerability indices or erosion plots) are commonly constrained by problems of representativeness and high costs, limiting spatial coverage and monitoring duration of many methods (Peart and Walling 1986, Collins and Walling 2004). Thus, fingerprinting as an alternative direct measure that has been developed over the past three decades has attracted increasing attention (e.g. Davis and Fox 2009, Collins et al. 2010, Mukundan et al. 2012, Koiter et al. 2013). Sediment fingerprinting usually employs a combination of unique natural tracers (‘fingerprints’) collected from both potential source areas and (suspended) sediment samples that commonly represent mixtures of sources (Walling 2005). It is founded upon two principal assumptions: (1) that the selected fingerprints allow discrimination of potential sources; and (2) that comparison of source and sediment material using these fingerprints permits determination of relative source contribution (Collins and Walling 2004). Thereby, sources are commonly defined either spatially (e.g. tributary subcatchments, geological sub-areas) or typologically (e.g. land use types, surface vs. sub surface sources) (Collins and Walling 2002).

Investigations have shown that a range of characteristic soil properties can be used as fingerprints to trace back the sources of suspended river sediments, including mineral magnetism (e.g. Yu and Oldfield 1989, Walden et al. 1997), colour (e.g. Grimshaw and Lewin 1980, Krein et al. 2003, Martínez-Carreras et al. 2010a, c), geochemical composition and/or environmental radionuclides (e.g. Motha et al. 2003, Minella et al. 2008, Navratil et al. 2012). Thereby, the use of composite fingerprints, employing several diagnostic properties, has proven most reliable (e.g. Collins et al. 1997). However, there is no universal recommendation on which properties to include, making parameter retrieval often time-consuming and costly (e.g. Collins and Walling 2002).

Recent investigations have shown that visible (VIS), near-infrared (NIR) and shortwave-infrared (SWIR) diffuse reflectance spectroscopy allow determination of several physical and chemical soil properties (e.g. Kooistra et al. 2003, Viscarra Rossel et al. 2006a, 2006b, Ben-Dor et al. 2009, Richter 2010, Viscarra Rossel and Behrens 2010, Bayer 2013) and that these spectral soil properties can be applied to discriminate and trace-back sediment sources (Martínez-Carreras et al. 2010a, b, c). In addition to being less labour intense than, for example, geochemical analyses, spectroscopy also offers the potential to measure source parameters *in-situ*. Furthermore, it allows measurements of very small amounts of sediment material; for example, Martínez-Carreras et al. (2010a) found 60 mg retained on filters was sufficient to obtain reliable spectral readings, thus enabling inexpensive analyses even of intra-event variability.

In this study, we aim to further assess the potential of this innovative sediment tracing technique, specifically whether:

(1) potential sediment sources can be reliably identified based on VNIR-SWIR spectral features;
(2) spectral fingerprints permit the quantification of source contribution to artificial mixtures; and
(3) field-derived source information (i.e. more rapid) is sufficient for spectral fingerprinting or whether the approach requires laboratory-derived data (i.e. more controlled).

A total of 152 samples of potential sediment sources were collected in the Isábena watershed, a 445 km² dryland catchment in the central Spanish Pyrenees. Spectral reflectance readings were taken in the field as well as in the laboratory from dried and sieved samples using an Analytical Spectral Device (ASD) field spectroradiometer. Then, artificial mixtures of known proportions were produced from dried and sieved samples. Colour coefficients and physically based parameters were calculated from all source and mixture spectra. All parameters passing a number of prerequisite tests were subsequently applied in discriminant function analysis for source discrimination and mixing model analyses for source contribution assessment under controlled conditions.

4.2 Study area

The Isábena catchment (445 km²) is located in the northeast of Spain, in the southern Pyrenees (Fig. 4.1). The climate of the area can be described as typical Mediterranean mountainous with mean annual temperatures between 9 and 14 °C, and annual precipitation totals of ~770 mm (Verdú 2003). Overall, heterogeneous relief, lithology (Paleogene, Cretaceous, and Quaternary) and land use (agriculture in the valley bottoms, and shrubland, woodland and grasslands in the higher elevations) create a diverse landscape (Müller et al. 2010). The dominance of carbonate rocks and marls in the centre of the catchment lead to the development of badlands, with very high erosion rates and thus are considered to be the major sediment sources (e.g. Fargas et al. 1997, Valero-Garcés et al. 1999, Francke et al. 2008a, Alatorre and Beguería 2009).

4.3 Material and methods

4.3.1 Source sampling and data overview

Source material sampling sites were chosen based on previous analyses of land use distribution (Ministerio de Medio Ambiente y Medio Rural y Marino (MARM) 2008), erosion susceptibility (Fargas et al. 1997) and accessibility. Source soil samples were taken during two field campaigns in October 2010 and June 2011, covering the main land use types – shrubland (matorral), woodland, agricultural land and grassland – as well as potential sources, such as badland, unpaved roads and open slopes exposing soil next to roads or channels (Table 4.1). Sampling sites were chosen in close vicinity (< 100 m) to stream or river reaches to ensure the material will be easily transported to the river. At each site, five grab samples of easily erodible material (top 1 - 3 cm) were collected from a representative area of approximately 5 m x 5 m. The number of samples collected per land use was approximately proportional to the spatial representation of each source. Sampling locations are shown in Fig. 4.1.

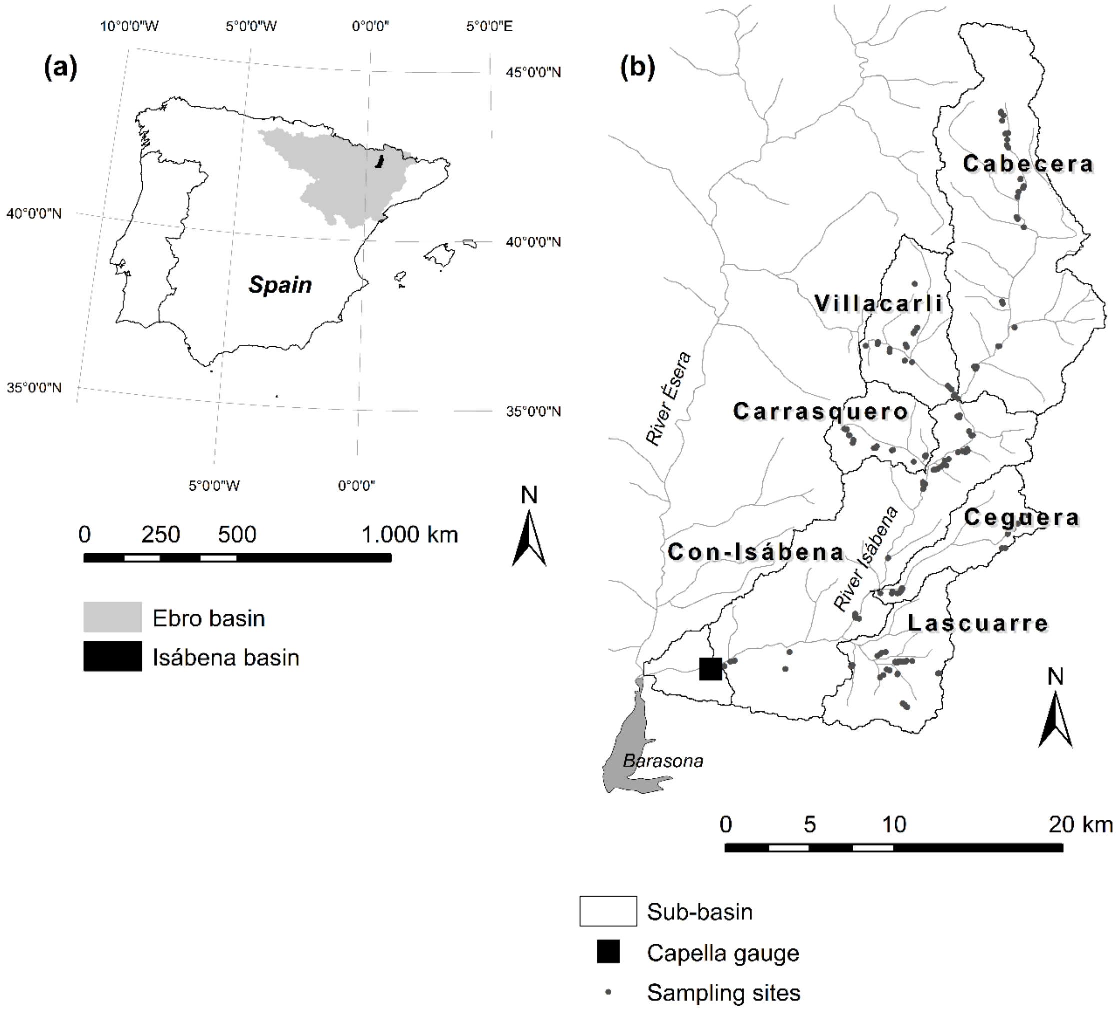

Fig. 4.1: Overview and location of the Isábena catchment study area (Spain) and sampling sites

To verify the assumption of linearly additive behaviour of tracers and to test the performance of the unmixing model, 33 artificial mixtures were produced from up to five source groups in the laboratory. Therefore, known proportions of up to five potential source type samples (forest, agricultural land, shrubland, unpaved road and badland soil material) were mixed in various ratios (5 – 90%).

Suspended sediment samples were collected using ISCO automatic samplers at the catchment outlet (44 samples) and near the main subcatchment outlets (46 samples) from

September 2011 to June 2012. The sampling procedure is described in detail in chapter V. For this study, sediment material was only used for assumption testing (section 3.4).

Table 4.1: Number of samples collected from each potential suspended sediment source by subcatchment

	Villacarli	Cabecera	Carrasquero	Con-Isábena	Ceguera	Lascuarre	**Total**
Agricultural land topsoil	3	1	3	8	4	8	**27**
Grassland topsoil	1	10	1	3	-	1	**16**
Shrubland topsoil	5	7	4	7	3	10	**36**
Forest topsoil	4	6	2	7	6	5	**30**
Badland	6	-	4	3	1	-	**14**
Open slope	1	-	1	5	4	8	**19**
Unpaved road	1	3	-	1	2	3	**10**
Total	**21**	**27**	**15**	**34**	**20**	**35**	**152**

4.3.2 Spectral measurements

Spectroscopy can be defined as the study of irradiation as a function of wavelength that is reflected from a surface (Clark 1999). Thereby, a spectrum displaying the quantities of reflected light can be used to identify and characterise material in its quality or quantity (Bayer 2013). Various soil components, such as soil organic carbon content, iron content and texture, exhibit spectral responses in the VIS range of the electromagnetic spectrum (0.4 – 0.7 µm) and thus influence soil colour (Viscarra Rossel et al. 2006a). In addition, some soil constituents produce spectral features in the VIS to SWIR spectral range that can be distinguished by their location in the spectrum and based on parameters describing their shape (Bayer 2013). Mean spectra and the influence of dominant soil constituent are described in Fig. 4.2.

In this study, an ASD FieldSpec3 High-Res portable spectroradiometer (Analytical Spectral Device Inc., Boulder, Colorado, USA) was used to measure relative reflectance spectra using a white reference (95 % Zenith Alucore Reflectance Target, SphereOptics GmbH, Uhldingen, Germany) as the standard. The ASD spectroradiometer acquires 2151 channels in the 0.35 – 2.5 µm spectral range at a sampling interval of 1.4 nm in the VNIR region (0.35 – 1.0 µm) and 2 nm in the SWIR region (1.0 – 2.5 µm).

Field reflectance spectra of source samples were collected *in-situ* just before grab sampling at the corresponding location using the ASD spectroradiometer with an accessory light source mounted on the light-collecting head of the instrument, thus keeping illumination conditions stable and excluding atmospheric influence for all measurements. Spectral readings were taken at five site-representative locations within 5 m x 5 m where soil was dry and least covered by vegetation/rocks/organic material, and subsequently averaged. The ASD instrument was optimized and white reference readings were taken before every measurement.

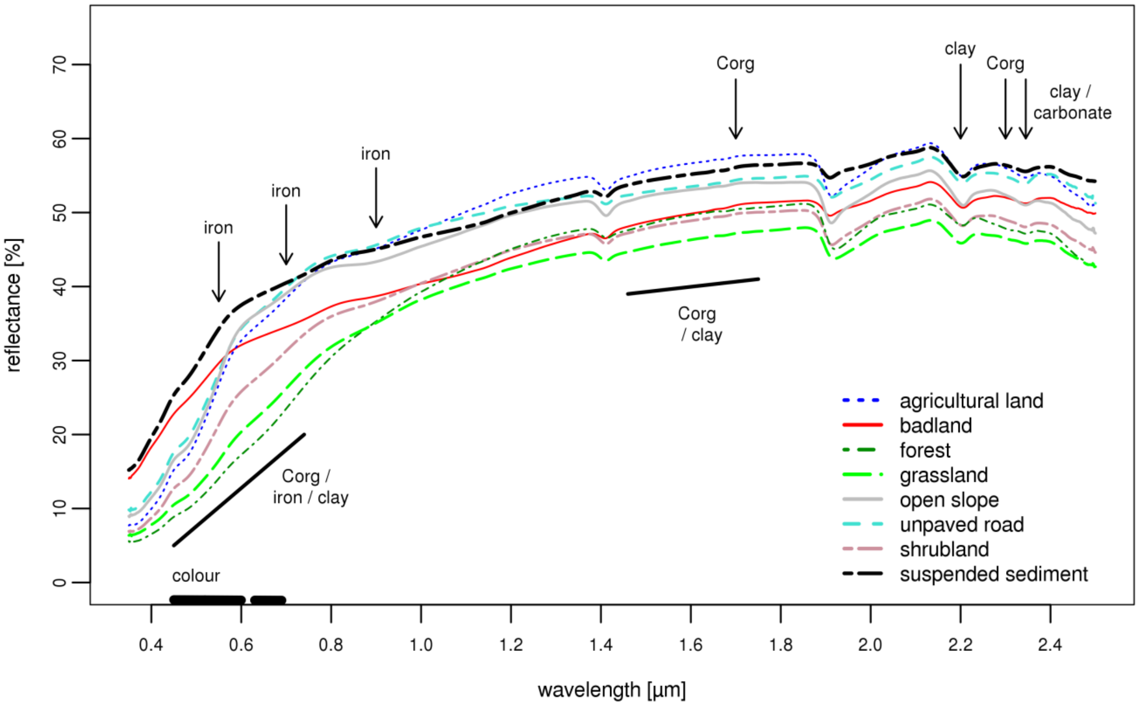

Fig. 4.2: Average spectra of soils per source type and sediment from the catchment outlet (Capella) and indication of location of features and influencing components (adapted from Bayer et al. 2012)

For laboratory measurements, source material collected from the five locations per site was thoroughly mixed to provide homogeneous samples. Sediment material was found to be predominantly < 63 µm. Thus, the samples were dry sieved to 63 µm to minimize differences in particle size composition between source and sediment material (Peart and Walling 1986, Smith and Blake 2014). Source material and the 33 artificial mixtures produced from homogenized, sieved source samples were placed in a shallow 5 cm x 5 cm plastic container and oven dried at 60 °C for 24 hours prior to spectral measurements. Spectral readings were taken in a dark room facility using the ASD spectroradiometer previously used in the field. Illumination was provided by a 2000 W lamp installed at approximately 80 cm from the sample at a zenith angle of 45° and the optical head of the ASD was mounted perpendicular to the sample at a distance of 4 cm, resulting in an effective target area of 1.7 cm. Measurement and instrument conditions were assumed to be constant, however, white reference readings and instrument optimization were performed prior to every measurement. Four readings per sample were taken and subsequently averaged, with the sample rotated 90° after every reading to reduce illumination effects.

4.3.3 Preprocessing of the spectra and parameter calculation

Mean spectra were calculated for each sample and detector jumps at 1.0 and 1.83 µm that occurred on rare occasions were corrected by adaptation to the first detector. All spectra were then smoothed using a Savitzky-Golay filter (Savitzky and Golay 1964) with a Kernel size of 7, meaning that smoothing was applied over seven adjacent spectral channels.

The spectra were averaged to Landsat RGB bands (blue, green and red, 0.45 – 0.52 µm, 0.52 – 0.6 µm, and 0.63 – 0.69 µm, respectively) and multiplied by 255 to get 8-bit colour encoding (Viscarra Rossel et al. 2006a). The derived RGB values were then transformed to eight other colour space models (i.e. Munsell HVC, decorrelated RGB, CIE xyY, CIE XYZ, CIELAB, CIELUV, CIELHC and Helmholtz chromaticity coordinates) using ColoSol software developed by Viscarra Rossel et al. (2006a). The colour gamut of the RGB system forms a cube comprising orthogonal red (R), green (G) and blue (B) axes. Every colour can be produced by a mixture of these three primary colours and represented by a coordinate on or in the cube. The Munsell HVC system commonly used in soil science describes the soil colour qualitatively by the use of hue (H), value (V) and chroma (C) that can be expressed on a numerical scale. Viscarra Rossel et al. (2006a) refer to the decorrelated RGB as a transformation of highly correlated RGB values into three statistically independent components. The CIE models were proposed by the Commission Internationale de l'Eclairage (CIE) (1931) to standardize colour models and facilitate visualization. In the XYZ system introduced first, Y represents brightness while X and Z are virtual components of the primary spectra. Since visualization of these values was difficult, the CIE xyY system was introduced, where Y represents luminance and x and y represent colour variations from blue to red and blue to green, respectively. The CIELAB and CIELUV models were introduced subsequently as an attempt to overcome the non-linearity of the two previous colour models; L represents brightness or luminance, and a* and b* and u* and v* represent chromaticity coordinates as opponent red –green and blue–yellow scales. The CIELHC model represents a transformation of the CIELAB spherical colour space into cylindrical coordinates, resulting in CIE hue (h*) and chroma (c*) values. Helmholtz chromaticity coordinates describe luminescence (L), dominant wavelength (λ_d), and purity of excication (P_e). All transformation algorithms are described in detail by Viscarra Rossel et al. (2006a) and details of colour models are explained by Wyszecki and Stiles (1982). A summary of the colour parameters applied in this study can be found in Table 4.2.

Table 4.2: Colour parameters derived from different colour space models calculated using ColoSol software (Viscarra Rossel et al. 2006a)

Colour space model	Parameter	Abbreviation
Munsell HVC	Hue	H
	Value	V [a]
	Chroma	C [a,b]
Decorrelated RGB	Hue	H_{RGB} [a,b]
	Light intensity	I_{RGB} [a]
	Chromatic information	S_{RGB} [a,b]
CIE xyY	Chromatic coordinate x	x [a,b]
	Chromatic coordinate y	y [a,b]
	Brightness	Y [a]
CIE XYZ	Virtual component X	X [a]
	Virtual component Z	Z [a]

Table 4.2(continued from page 30)

Colour space model	Parameter	Abbreviation
CIELUV	Metric lightness function	L [a]
	CC opponent red-green scales	u* [a,b]
	CC opponent blue-yellow scales	v* [a,b]
CIELAB	CC opponent red-green scales	a* [a,b]
	CC opponent blue-yellow scales	b* [a,b]
CIELCH	CIE hue	CIE.C [a,b]
	CIE chroma	CIE.H [a,b]
Helmholtz chromaticity	Dominant wavelength	λ_d (nm) [a,b]
	Purity of excitation	P_e [a,b]
Index	Redness index	RI [a]

[a] marks all parameters that passed prerequisite testing of laboratory measured samples
[b] represents all parameters that passed prerequisite testing of *in-situ* measured samples

Visual inspection of source spectra, laboratory analyses and preceding studies of the catchment area (e.g. Valero-Garcés et al. 1999) suggest that the occurrence of iron oxides, carbonates, organic carbon and different clay minerals differ between various source groups (i.e. land uses). Thus, a set of 77 VNIR and SWIR features found in the literature to be diagnostic of physically based information was calculated following descriptions by Chabrillat et al. (2011) and Bayer et al. (2012). The selected spectral parameters can be divided into spectral indices and three feature types: curve features; hull features; and absorption features. Curve features describe reflectance changes in specific wavelength ranges and were characterized by the mean slope (s) of the spectral curve (Fig. 4.3a). Hull features describe broader effects on spectra and were characterized by mean slope (s) and reflectance (r) of a convex hull fitted to a defined wavelength range (Fig. 4.3b).

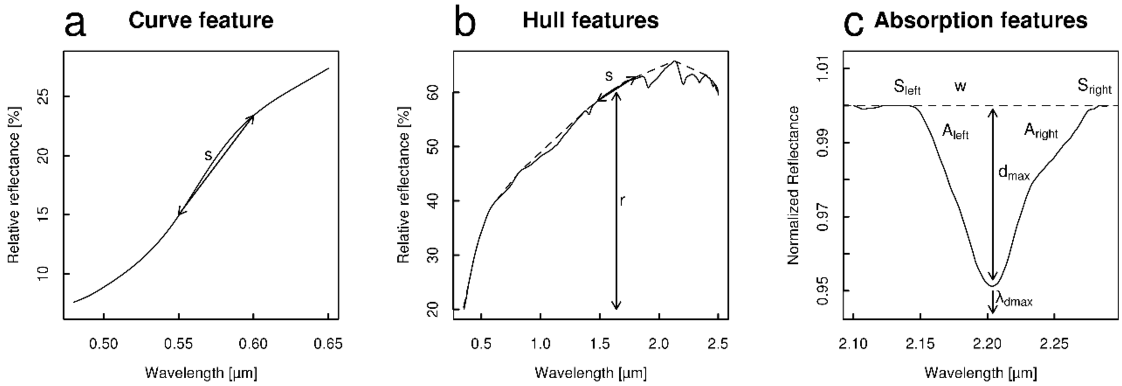

Fig. 4.3: Parameterization of variables for the spectral features used for the determination of soil organic carbon, iron oxides, clay and carbonate: a) curve features, b) hull features, and c) absorption features. Solid lines represent the reflectance curve and dotted lines represent the continuum of the reflectance curve (adapted from Bayer et al. 2012)

Distinct absorption features were calculated from continuum removed wavelength ranges, i.e. wavelength ranges of which the convex hull was subtracted in order to exclude overall reflectance trends and to allow for intercomparison. Following Bayer at al. (2012), absorption features were analysed for depth (d_{max}) and wavelength (λ_{dmax}) of maximal absorption, wavelength of maximal absorption according to literature values ($d_{\lambda lit}$), feature width (w) as the distance between feature shoulders ($S_{left/right}$), the area between normalized continuum and spectral curve (A) and its asymmetry ($AS = A_{left}/A_{right}$) (Fig. 4.3c). For parameterization of these feature types, reflectance spectra were analysed for the selected characteristics which were then transformed to numerical parameters. A list of these features can be found in Table 4.3. Detailed references to previous studies assessing absorption features and their foundations can be found in Bayer et al. (2012).

In total, a set of 98 colour and physical soil reflectance parameters was calculated. Due to similarity of some colour space models and/or calculation of physically based parameters from nearby spectral wavelength, some of these parameters are highly correlated (Viscarra Rossel et al. 2006a, Martínez-Carreras et al. 2010c). However, since colour coefficients may be easily converted and all parameters may potentially be used in spectroscopy and soil science, they will all be considered in the subsequent analyses.

Table 4.3: Physically based spectral features that are calculated for discrimination and unmixing of sediment sources. Feature types that can be ascribed to specific soil constituents may be absorption features (AF), hull features (HF), curve features (CF), or spectral indices. The spectral region describes the wavelength (range) from which the feature was calculated (for AF, the wavelength of $d_{\lambda lit}$ is given in brackets, if available). Parameters calculated are given in column parameterization whereas R represents individual wavelength channels used for the calculation of indices and CR represents the continuum removal described in text. The original sources can be found in Chabrillat et al. (2011) and Bayer et al. (2012). Bold entries passed prerequisite testing

Soil constituents	Feature type	Spectral region [µm]	Parameterization	Reference
Soil organic carbon	AF1	1.6-1.815 (1.73)	d_{max}, λ_{dmax}, w, A, AS	Bayer et al. 2012
	AF2	2.24-2.41 (2.33)	d_{max}, λ_{dmax}, $d_{\lambda lit}$, w, A, AS	Bayer et al. 2012
	HF1	0.45-0.74	$s^{a,b}$, $r^{a,b}$	Bayer et al. 2012
	HF2	1.46-1.75	$s^{a,b}$, $r^{a,b}$	Bayer et al. 2012
	SOC1	0.4-0.7	$1/(\Sigma R_{0.4} - R_{0.799} (CR-R))^{a,b}$	Chabrillat et al. 2011
	SOC2	0.4-0.6	$1/(slope(R_{0.4} - R_{0.6})^{a,b}$	Chabrillat et al. 2011
	SOC3	2.138-2.209	$1/(slope(R_{2.138} - R_{2.209})^{a,b}$	Chabrillat et al. 2011
Iron	AF3	0.45-0.68 (0.55)	$\mathbf{d_{max}}^{a,b}$, λ_{dmax}, $d_{\lambda lit}$, w, $\mathbf{A}^{a,b}$, AS	Bayer et al. 2012
	AF4	0.58-0.8 (0.7)	d_{max}, λ_{dmax}, $d_{\lambda lit}$, w, A, AS	Bayer et al. 2012
	AF5	0.75-1.3 (0.9)	$\mathbf{d_{max}}^{a,b}$, λ_{dmax}, $\mathbf{d_{\lambda lit}}^{a,b}$, w, A, AS	Bayer et al. 2012
	AF11	0.45-0.63	$\mathbf{d_{max}}^{a,b}$, λ_{dmax}, w, $\mathbf{A}^{a,b}$, AS	Chabrillat et al. 2011
	AF12	0.75-1.04	d_{max}, λ_{dmax}, w, $\mathbf{A}^{a,b}$, AS	Chabrillat et al. 2011
	CF	0.55-0.59	$s^{a,b}$	Bayer et al. 2012
	HF3	0.45-0.75	$s^{a,b}$, $r^{a,b}$	Bayer et al. 2012
	RI	0.477-0.693	$(R_{0.693})^2/((R_{0.477})*(R_{0.556})^3)^{a}$	Chabrillat et al. 2011

[a] marks all parameters that passed prerequisite testing of laboratory measured samples,
[b] represents all parameters that passed prerequisite testing of in-situ measured samples.

Table 4.3 (continued from page 32)

Soil constituents	Feature type	Spectral region [µm]	Parameterization	Reference
Clay minerals (Al-OH content)	AF6	2.1-2.29 (2.2)	d_{max} [a,b], λ_{dmax}, $d_{\lambda lit}$ [a,b], w, A [a,b], AS	Bayer et al. 2012
	AF7	2.27-2.41(2.34)	d_{max}, λ_{dmax}, $d_{\lambda lit}$, w, A, AS	Bayer et al. 2012
	AF10	2.12-2.25	**d_{max} [a,b]**, λ_{dmax}, w, **A [a,b]**, AS	Chabrillat et al. 2011
	HF4	0.45-0.7	s [a,b], r [a,b]	Bayer et al. 2012
	HF5	1.46-1.75	s [a,b], r [a,b]	Bayer et al. 2012
	SWIR FI	2.209-2.225	$(R_{2.133})^2/((R_{2.225})*(R_{2.2209})^3)$ [a]	Chabrillat et al. 2011
Carbonate (Mg-OH content)	AF13	2.3-2.4	d_{max}, λ_{dmax}, w, A, AS	Chabrillat et al. 2011

[a] marks all parameters that passed prerequisite testing of laboratory measured samples,
[b] represents all parameters that passed prerequisite testing of in-situ measured samples.

4.3.4 Test of assumptions

Small et al. (2004) summarize a number of principal sources of uncertainty within the established fingerprinting approach. Despite uncertainty in problem formulation (definition of source groups), tracer's discriminating power and source contribution estimation by the use of mixing models, source group variability, analytical errors, and tracer bias, transformation, enrichment and non-linearly additive behaviour may contribute to spurious source quantification results. The potential non-conservative behaviour of tracer properties, with a focus on enrichment and tracer transformation, has recently received attention (Koiter et al. 2013).

While some studies have applied particle size and/or organic matter correction mechanisms in model formulation (e.g. Collins et al. 1997, Motha et al. 2003), Smith and Blake (2014) strongly recommend not to use total organic carbon (TOC) correction factors and to carefully consider correcting for particle size since their studies showed that the use of a correction factor may result in large changes in source apportionment or even spurious results. Thus, in this study the problem of size selective transport was addressed by sieving all sampling materials to < 63 µm (e.g. Peart and Walling 1986, Collins and Walling 2002, Walling 2005, Martínez-Carreras et al. 2010a, Smith and Blake 2014).

Tracer transformation cannot be excluded either. However, Smith and Blake (2014) recommend to select tracer properties based on knowledge of their geochemical behaviour and to exclude tracers with sediment concentrations lying outside the range of sources. The majority of spectral properties (92 out of 98 for laboratory data and 79 out of 98 for field data) determined from sediment collected at the catchment outlet lie wholly in the range of source materials, indicating that alteration effects may have been relatively small (Walden et al. 1997).

Linear additivity of spectral properties was explicitly tested by comparing properties calculated from artificial mixture spectra to properties calculated from mixture spectra that were produced by a linear mixing algorithm using the five source spectra described previously. Spectral parameters were scaled from 0 to 1 and only parameters differing by a

root mean square error (RMSE) of < 0.1 were applied in the tracing procedure (48 out of 92 for laboratory data and 39 out of 79 for field data). Thereby, the number of sources (2 – 5) used to produce the mixture did not seem to have an effect on linearity (results not shown). Following Walling (2005), all remaining parameter values were scaled from 0 to 1 to ensure equal consideration of individual properties in statistical and mixing model analyses, and thus minimize the problem of tracer bias.
Finally, a non-parametric Kruskal-Wallis H-test was conducted, indicating the existence of any interclass contrasts (Collins and Walling 2002). All parameters were able to detect contrasts between the seven source types at the 5 % confidence level.
Thus, in summary, 48 out of 98 parameters calculated from laboratory measured source samples met the prerequisites applied to limit uncertainty to a minimum and were used for subsequent discrimination and unmixing analyses. When tested on field measured source data, an additional seven colour parameters and two physically based parameters failed the range tests, resulting in a dataset of 39 parameters. This dataset was used for independent assessment of *in-situ* derived parameters.

4.3.5 Statistical analyses to assess discrimination potential

A Principal Component Analysis (PCA) was performed on the 48 laboratory and 39 *in-situ* parameter sources using The Unscrambler® X 10.2 software (CAMO Software AS., Oslo, Norway). Its major principle can be described as linear transformation of the original data into a new coordinate system, whereas the first coordinate (first principal component (PC)) contains the maximum variability, the second PC (perpendicular to the first PC) contains the maximum share of the remaining variability, and so on. Its major aim is dimension reduction (Reimann et al. 2008). Following Poulenard et al. (2009) the PCA was conducted in order to assess natural clustering of samples and to evaluate overall variability and potential overlap between classes.
Following Collins and Walling (2002) a discriminant function analysis (DFA) was then performed on the two source datasets to test the discriminatory power of (1) individual spectral properties, and (2) a combination of properties drawn by a stepwise selection algorithm. Discriminant function analysis can be used as a classification procedure where a categorical grouping variable known *a priori* is predicted by one or more continuous predictor variables (Reimann et al. 2008). Therefore, it is useful in determining whether a set of variables is effective in discriminating between categories or source groups. The DFA analyses were performed using R packages (MASS and klaR). Discrimination potential was tested for seven source types (forest, grassland, shrubland, agricultural land, badland, unpaved road, open slopes) and the five source types used for production of mixtures (forest, agricultural land, shrubland, badland, road).
Based on a review of a number of fingerprinting studies, Mukundan et al. (2012) found that most of the investigations were carried out in catchments < 250 km², and concluded that this may represent a threshold at which sediment fingerprinting is feasible. In larger basins (> 500 km²), the expected greater heterogeneity in source type material could exacerbate accurate source determination and thus ascription by increasing intra-class variability. Thus – and since PCA plots and DFA matrices suggest confusion in discrimination between forest and grassland, as well as between shrubland and arable land, road and open slopes – samples

of seven source classes were aggregated into three source groups: badland; forest/grassland; and others. Discrimination potential was recalculated for those three source groups using only parameters that passed the Kruskal-Wallis H-test for the defined number of groups (all 48 and 39 parameters for five source groups, and 45 and 39 parameters for three source groups).

4.3.6 Mixing model analyses

Relative contributions of potential sources were estimated by comparing the fingerprint properties of the artificial mixtures with those of the potential sources using a mixing model adapted from other spectroscopic applications. The application of such models is widely adopted in fingerprinting studies (e.g. Yu and Oldfield 1989, Collins et al. 1997, Walden et al. 1997, Motha et al. 2003, Walling 2005, Minella et al. 2008, Martínez-Carreras et al. 2010a and 2010b). Since the model is mathematically over-determined (i.e. has infinite solutions due to the number of tracer properties exceeding the number of potential sources) it must be approximated by minimizing the errors between measured and estimated values. In this study, we used the non-negative least squares algorithm introduced by Lawson and Hanson (1974), where the best approximation is defined as that which minimizes the sum of squared differences between the measured data values and their corresponding modelled values:

$$min\left\| \sum_{i=1}^{n} \left(\sum_{j=1}^{m} a_{ij}\, x_j - b_i \right)^2 \right\| \quad ; \quad x_j \geq 0 \quad ; \quad \sum_{j=1}^{m} x_j = 1 \qquad \text{Eqn (1)}$$

Where, $a_{i,j}$ is the value of the tracer property i in source type j, x_j is the unknown contribution of source type j to the mixture sample, m is the number of source types, n is the number of tracers and b_i is the value of the tracer property in the mixture sample.

Uncertainty associated with modelled contribution results was assessed based on a concept outlined by Beven and Binley (1992) and successfully introduced to fingerprinting studies (e.g. Franks and Rowan 2000, Rowan et al. 2000, Motha et al. 2003, Small et al. 2004, Martínez-Carreras et al. 2010a). This method attempts to include modelling uncertainty related to source heterogeneity by means of Bayesian modelling. Following Martínez-Carreras et al. (2010a), a Gaussian distribution function was produced from mean and standard deviation calculated from each tracer property per source type. The 100 property values per source group produced this way were limited not to exceed threefold standard deviation (99 %) and all values were scaled from 0 to 1 after distribution modelling. This distribution was assumed to approximate its population mean and to represent spatial and temporal tracer variability as well as measurement error.

The model described above was then solved 10,000 times, choosing source information randomly from the Gaussian distributions representing different source groups for each run. Thereby, the model was restricted by the constraints that the source type contributions must all be non-negative and sum to 100 %. An additional tolerance criterion was introduced, accepting only those model runs with a RMSE ≤ 0.1 between a mixture's measured and its corresponding modelled tracer values. The replicate random sampling permitted the

calculation of percentiles, thus providing confidence estimates for the modelled contribution results.
To assess performance of the mixing model using spectral information, it was applied to the 33 artificial mixtures. The contribution of individual source types to the mixture is known and thus allows direct assessment of model performance and potential problems. The model was run therefore using different source type input sets, namely: (a) data from the up to five individual source samples that were used to produce the mixtures (without Monte-Carlo simulation); (b) all data simulated for each source type from Gaussian distribution functions (using laboratory parameters) and (c) all data simulated for each source type from Gaussian distribution functions (using in situ parameters). Input datasets consisted either of a selection of parameters based on stepwise DFA results or combinations of all parameters passing the assumption tests.

4.4 Results

4.4.1 Discrimination potential

Figure 4.4 shows a two-dimensional scatter plot of scores for the first two principal components (PC1 and PC2) from the PCA performed on source information. These two components summarize most variation in the datasets, where the more similar samples are closer in the plot. Thus, the plots give information on patterns in the samples. No distinct clustering can be observed in Fig. 4.4 for laboratory and *in-situ* source data. However, the data do group by land use, and is most pronounced for badland and forest soils and soils from arable land (Fig. 4.4a). Soils sampled from grassland largely overlap with forest samples and shrubland soils overlap with forest/grassland and arable land. Intra-class heterogeneity seems lowest for badland and largest for shrubland and agricultural soils, while unpaved roads and open slopes seem to originate from two separate groups, that in addition overlap with the four other land use groups. These findings are generally very similar for field source data (Fig. 4.4b).
The first two component plots show a large portion of the information in the data (sum of explained variance 72 - 82 %), so the relationships can be interpreted with a high degree of certainty. Seven PCs explain 98 % of the variance. On the other hand, Walden et al. (1997) conclude that very high explained variance in the first two components may result from low dimensionality of (mineral magnetic) datasets and suggest that only a small number (three to four) source types should be used for realistic source modelling.
Discriminant function analysis was used to assess the percentage of source material samples correctly classified by individual spectral properties that passed the assumption tests. For laboratory measured parameters, the accuracy varied between 20 – 45 % for seven source classes, 30 – 59 % for five source classes and 59 – 77 % for the aggregated three source classes. Hence, the performance of colour parameters and physically based parameters was well mixed, meaning that there were colour parameters as well as physically based parameters with high discrimination potential. However, for a higher number of source classes there was a higher number of colour coefficients with high discrimination accuracies, and the best performing parameter was always a colour parameter. No individual parameter

successfully discriminated all samples from three, five or seven source classes. For *in-situ* measured parameters, the accuracy was very similar to that achieved using laboratory parameters, namely 24 – 46 % for seven source classes, 31 – 58 % for five source classes and 59 – 81 % for the aggregated three source classes. Again, there were colour parameters as well as physically based parameters with high discrimination potential. However, although colour parameters were generally among those parameters with a higher discrimination potential, the best performing were always physically based parameters.

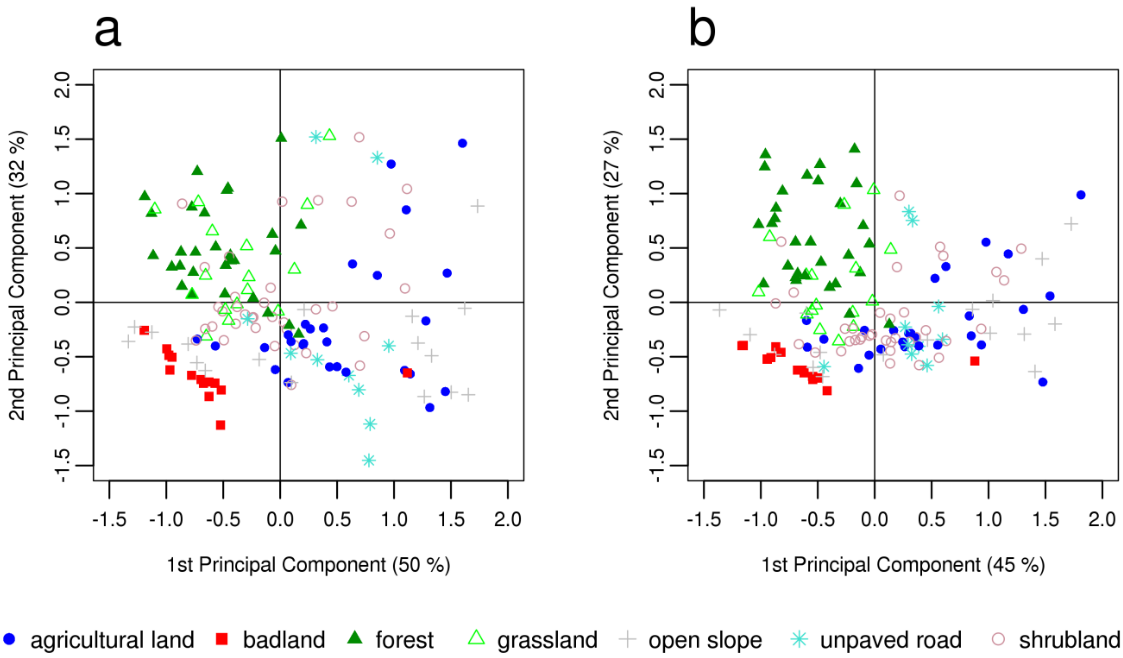

Fig. 4.4: Two-dimensional scatter plot of scores for the first and second principal component (PC) from the principal components analysis (PCA) for: a) laboratory source data by land use; and b) field source data by land use

A stepwise DFA was also performed to assess the discrimination potential of composite fingerprints. For laboratory source material samples, a combination of six parameters (*y, b*, AF6 A, AF6* d_{max}*, AF5* $d_{\lambda lit}$*, HF3 s)* correctly classified 60 % of the samples for seven source classes, a combination of four parameters (*y, X, AF6 A, a**) correctly classified 70 % for five source classes and a combination of five parameters (*X,* S_{RGB}*, CIE.H, AF11* d_{max}*, ri)* correctly classified 91 % for the aggregated three source classes. For *in-situ* source material samples, a combination of four parameters (*AF6 A, x, AF12 A, CF*) correctly classified 60 % for seven source groups, a combination of three parameters (*AF6 A, AF10* d_{max}*, a*)* correctly classified 73 % for five source groups, and a combination of three parameters (*AF10 A, x, AF6* $d_{\lambda lit}$) correctly classified 88 % for the aggregated three source classes. Hence, the performance of laboratory and field composites was very similar. However, although composite fingerprints always included colour and physically based parameters, for laboratory measured source samples colour parameters were always included first, while for *in-situ* samples physically based parameters were always included first. A summary of accuracies achieved and properties selected by stepwise DFA can be found in Table 4.4; the first two discriminant functions calculated by a DFA from stepwise selected properties for three source classes are depicted in Fig. 4.5.

Table 4.4: Summary of discriminant function analysis (DFA) results for laboratory and in-situ samples and discrimination between different numbers of source classes. The DFA accuracy ranges describe the range of accuracies achieved by each individual property, DFA accuracies for stepwise selected property represents the accuracy met by a composition of tracers selected by stepwise DFA. The properties given in brackets are the properties selected by the stepwise algorithm

	DFA accuracy ranges		DFA accuracies for stepwise selected properties	
	laboratory	in-situ	laboratory	in-situ
7 source classes	20 – 45 %	24 – 46 %	60 % (y, b*, AF6 A, AF6 d_{max}, AF5 $d_{\lambda lit}$,HF3 s)	60 % (AF6 A, x, AF12, A, CF)
5 source classes	30 – 59 %	31 – 58 %	70 % (y, X, AF6 A, a*)	73 % (AF6 A, AF10, d_{max}, a*)
3 source classes	59 – 77 %	59 – 81 %	91 % (X, S_{RGB}, CIE.H, AF11 d_{max}, ri)	88 % (AF10 A, x, AF6, $d_{\lambda lit}$)

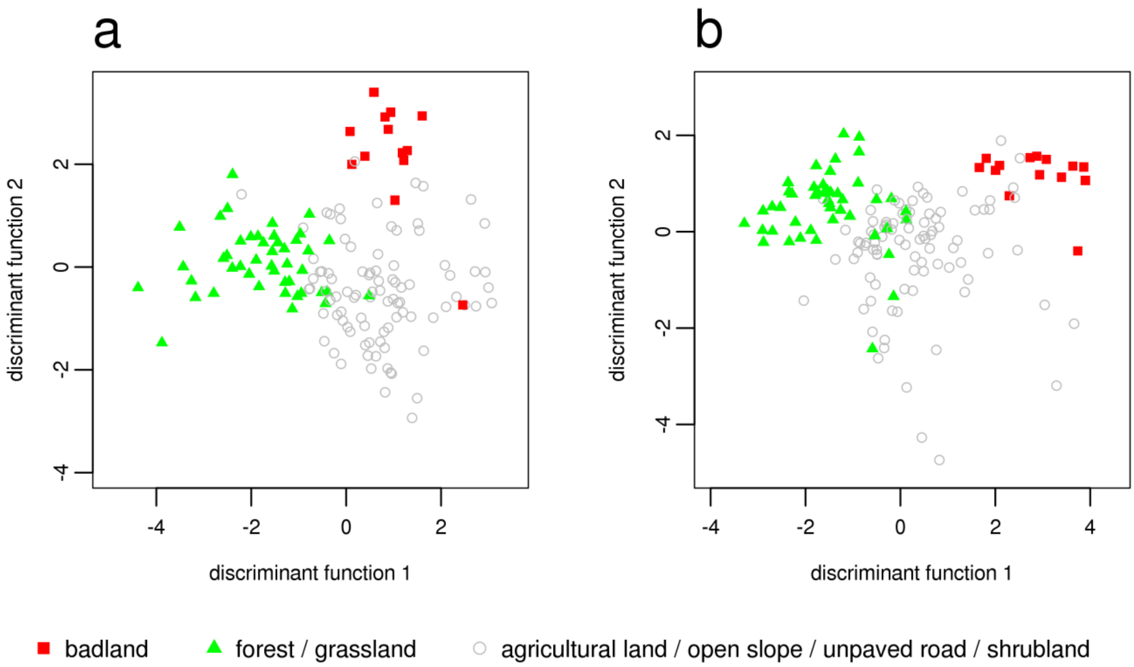

Fig. 4.5: Two-dimensional scatter plot of the first and second discriminant functions from stepwise discriminant function analysis (DFA) with selected parameters for: a) laboratory source data by land use; and b) field source data by land use

4.4.2 Mixing model analyses

Figure 4.6 shows the results of unmixing the 33 artificial mixtures produced for algorithm validation. Thus Fig. 4.6a shows the unmixing results based on the five individual source samples used for mixture production (one sample from badland, shrubland, agricultural land, forest, and road). Independent of the number of sources used to produce the mixtures (two to five), estimated contributions are very similar to the known contributions per source type with few exemptions. Errors are mainly < 10 %.

In Fig. 4.6b and 4.6c, source variability is introduced by means of Monte Carlo modelling. Instead of just one potential source sample, the modelling algorithm draws source type information from a pool of 100 Gauss distributed samples calculated based on all samples per source type. This methodology is thought to represent uncertainty intervals by providing estimates on the scatter of mixing model results. However, knowledge of the true contribution of each source reveals that for several source types, mean estimates (including corresponding uncertainty ranges) fail to represent the true contribution correctly.

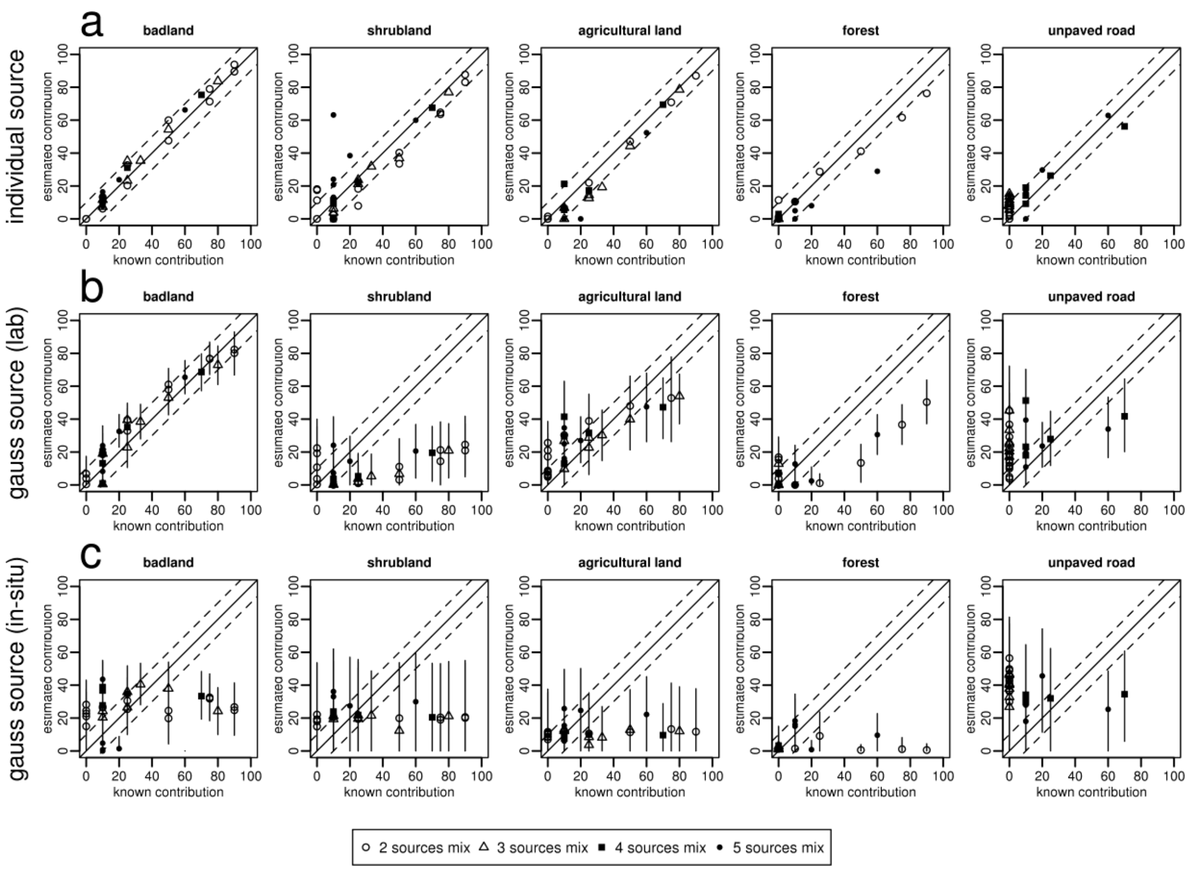

Fig. 4.6: Results of mixing model analyses per source type for the 33 artificial mixtures using all parameters passing the assumption tests: a) based on the five individual source samples used for mixture production; b) based on Gaussian distributed samples calculated from laboratory source information; and c) based on Gaussian distributed samples calculated from in-situ information. True contributions per source type are shown on the X, estimated contributions on the Y axes. Symbols represent mean values and error bars represent 90 % percentile

Using gauss distributions of laboratory source information for unmixing (Fig. 4.6b), badland sources can be modelled well while low contributions from agricultural land and unpaved road tend to be overestimated, and higher contributions from forest and unpaved roads tend to be underestimated. Shrubland sources cannot be modelled correctly. Using *in-situ* source information (Fig. 4.6c), results are similar for agricultural land, forest and unpaved road sources with the addition of higher uncertainty ranges. Shrubland and badland sources cannot be modelled by the use of *in-situ* data. The restriction of fingerprint parameters used for mixing model analyses to those selected by stepwise DFA as generally executed in fingerprinting studies does not improve the results but seems only to increases uncertainty ranges (results not shown).

Aggregation of the five source types used for mixture production to three classes as suggested by PCA and DFA results (badland, forest and agricultural land/unpaved road/shrubland) did not greatly improve mixing model results, as can be seen from Fig. 4.7. For laboratory source information (Fig. 4.7a), aggregation negatively affects the estimation of badland sources by introducing a trend to overestimation especially for lower contributions. Forest sources remain overestimated for low contributions and underestimated (though less) for higher contributions, while the aggregated source group is especially underestimated for higher contributions. Thereby, estimated uncertainty ranges are rather low.

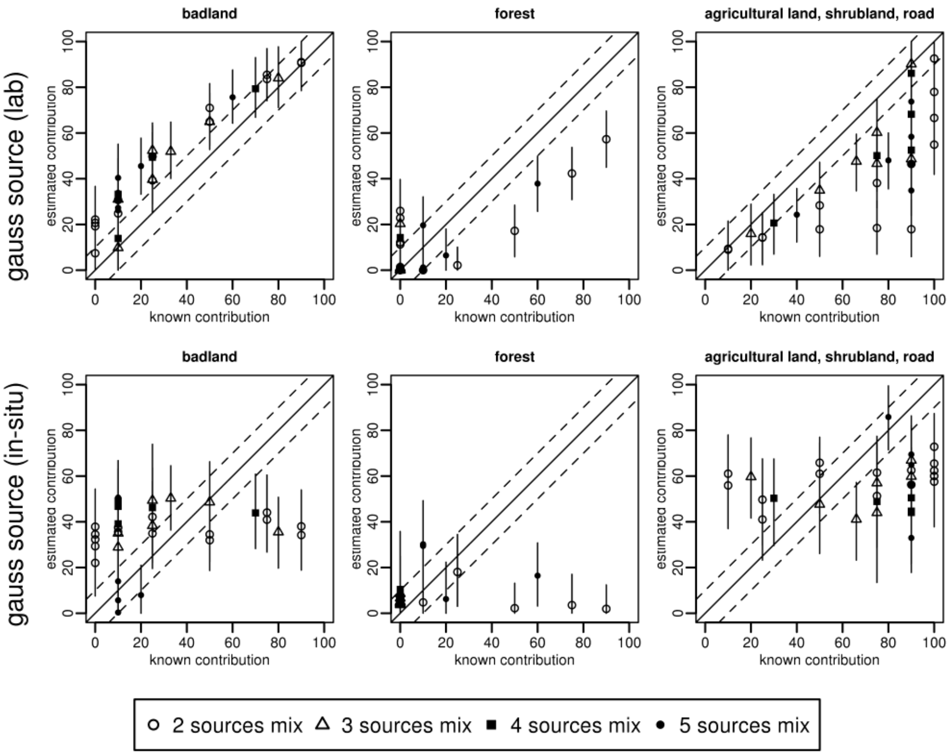

Fig. 4.7: Results of mixture modelling per source type for the 33 artificial mixtures produced for algorithm validation aggregated to three source types: a) based on gauss distributed samples calculated from laboratory source information; and b) based on gauss distributed samples calculated from in-situ information. True contributions per source type are shown on the X, estimated contributions on the Y axes

Using in situ information, none of the three source types can be modelled accurately (Fig. 4.7b): badland and forest source contributions are largely underestimated for contributions > 20 %, while the contributions of the aggregated source types seem to be estimated randomly.

4.5 Discussion

4.5.1 Discrimination

Although PCA results indicate grouping of source samples by land use, overlapping of certain classes is evident from the PC plot. Source soil samples from the forest and grassland classes seem indistinguishable which may be due to the higher organic carbon content of these two land use types as compared to all other classes. Source soil samples from shrublands were found to overlap especially with the agricultural land and the forest/grassland groups. This is most likely due to shrublands forming succession states between former agricultural areas that are partly reverting to natural forests after land abandonment (e.g. Lasanta and Vicente-Serrano 2012). In addition, shrublands are very heterogeneous: While some areas are characterized by a variable number of shrubs (mainly *Buxus sempervirens, Genista scorpius* and *Juniperus communis*) on otherwise rather bare soil, other areas may be much more grassy (partly used for sheep and goat grazing), or interspersed with trees. Different transition stages are thus found close-by. There is no conclusive explanation for the arrangement of unpaved road, open slope and badland samples in the PCA plot. Though the material is likely to be pedogenically less developed than material from forest, grassland, shrubland or agricultural land, it does not seem to cluster as separate group(s). Only badland samples form a distinct cluster that is distinguishable from most other samples, while unpaved road and open slope samples intermix with samples from other land uses, presumably with lower soil organic carbon contents. Contrary to expectation, there seems to be no influence of bedrock or area of origin on the distribution of road and open slope samples. No explanation was found for the obvious separation of samples collected from open slopes.

Overall, within-group variation is clearly evident while between-group variation of spectral properties may lack some dimensionality. Walden et al. (1997) presume that this "may influence the effectiveness with which certain suspended sediment samples can be unmixed".

Results obtained by DFA for classification of seven and five source types support the impression of overlapping classes suggested by PCA plots. However, results for three aggregated classes are well within the range of results obtained in other studies. Using colour coefficients from VNIR reflectance spectra in a 247 km² catchment in Luxembourg, Martínez-Carreras et al. (2010c) report percentages of correctly classified samples of 21 – 48 % (four source groups) and 57 - 74 % (two source groups) for individual tracer properties. In the same study, stepwise DFA yielded maximum percentage of 48.7 % (three properties), and 74.3 % (one property), respectively. However, no mixing model analysis was performed based on this property selection. Using geochemical tracers and radionuclides, for example, Collins and Walling (2002) report classification correctness rates of 29 – 87.5 % for individual fingerprint properties and cumulative values of 94 – 100 % for stepwise selected combinations of five to 12 properties (four source types in 63 - 852 km² basins in Zambia and UK). Walling (2005) describes individual 8 – 62 % and cumulative 100 % (seven parameters, four source types), and cumulative 90 % (seven parameters, two source types) based on geochemical and radionuclide analyses for two catchments (258 km² and 3315 km²) in the UK, respectively. Thus, it was concluded that the source groups should be aggregated and that the cumulative values of 91 % and 88 % achieved by spectral laboratory and *in-situ* parameters, respectively, are sufficient for subsequent mixing model analyses.

4.5.2 Model

The low error rates achieved for contribution assessment using one individual sample per source type suggest that the use of spectral parameters in general is appropriate for mixing model analyses. However, the introduction of source variability by means of Monte Carlo modelling results in a decrease in modelling accuracy. Estimated mean contributions, including estimated uncertainty, were found not to represent true percentages correctly for several source types. This may be due to large intra-class heterogeneity of some source types. As observed from the PCA plots, badland samples seem to be more homogeneous than all other source classes, and badland contribution can be modelled with high accuracies even under the influence of source variability. However, coefficients of variance calculated for each property of each source type revealed no major differences in variability. Overall, uncertainty was found to generally decrease with higher numbers of tracing properties included in the modelling approach, which is consistent with findings of Franks and Rowan (2000) and Martínez-Carreras et al. (2010a).

Again, contrary to expectations, aggregation of the five source types into three classes was found not to greatly improve mixing model results but possibly to even decrease accuracy. With regard to DFA results, this implies that high discrimination potential does not necessarily result in successful mixing model analyses. No conclusive explanation was found for this effect but it may be related to increased intra-class variability of the new, aggregated group. Overall, mixing model results are in the range generally observed in spectral unmixing studies. For example, Somers et al. (2009) report best mixing model accuracies of R^2 of 0.35 – 0.94 when including source or endmember (EM) variability, and Bachmann (2007) found average accuracies of R^2 of 0.64 - 0.96. In remote sensing, where spectral mixture analyses are commonly applied, results may be confounded due to a number of reasons. Of these, high intra- and low inter-class variability of EM (potential sources) were found to potentially cause high error rates (e.g. Bachmann 2007, Somers et al. 2011), which is suspected to be the main difficulty in this analysis.

The effects described above are comparable for laboratory and *in-situ* measured spectral parameters. However, while discrimination yields similar results, estimates of source contributions based on *in-situ* parameters are less successful than estimates based on parameters calculated from laboratory measured spectra. This is most likely due to the differences in the treatment of *in-situ* measured source and laboratory measured mixture samples. While measurement conditions were kept constant during field sampling (use of artificial light source), other factors such as soil moisture and grain size were subject to variability. Both factors exert a key control and may alter spectral reflectance significantly. In addition, averaged spectral measurements collected from the surface topsoil of five individual locations may differ from spectral measurements taken from a mixture of material collected from the top 1-3 cm of these points and further alter reflectance spectra.

Since laboratory analyses for geochemistry or mineral magnetic properties, for example, are much more labour intensive and more expensive than spectral measurements, there are few fingerprinting studies working with artificial mixtures. Results obtained in this study seem to contradict findings by Franks and Rowan (2000), who successfully modelled the contribution of five artificial mixtures consisting of five source types based on major chemical groups. On the contrary, Lees (1997) found that certain source type components, as well as four or more sources or sources with similar characteristics, could not be unmixed successfully using mineral magnetic properties of 78 artificial mixtures. This was attributed to magnetic variability, calibration inaccuracies and complex grain interactions found in mixtures. Reasons for variability other than source type heterogeneity in spectral parameters may include scattering effects of soil particles that can be different in mixtures than in pure components or measurement inaccuracies due to minimal sample inhomogeneities that could not be assessed by averaging of point measurements. Lees (1997) stressed the necessity for such laboratory mixture experiments as they provide estimates of capabilities and limitation of the properties and methods applied.

Martínez-Carreras et al. (2010a) found a good consistency between both approaches when comparing suspended sediment source ascriptions based on spectral colour parameters to ascriptions based on classical fingerprinting parameters (geochemistry and radionuclides) for three small catchments. Thus, the difficulties described above may be site-specific problems of the fingerprinting method in general.

From this experiment, we conclude that spectral parameters can be used for mixing model analyses of a restricted number of source types (3 to 4), that a higher number of parameters to characterize samples results in lower uncertainty estimates, and, although providing good discrimination potential, *in-situ* measured source parameters do not seem suitable for mixing model analyses. However, modelling results based on laboratory-measured parameters also need to be interpreted with care and should not rely on mean estimates only.

4.6 Conclusions

In this study, we aimed to further assess the potential of spectral parameters as innovative sediment tracing properties, with emphasis on the questions of whether:

(1) potential sediment sources can be reliably identified based on VNIR/SWIR spectral features;
(2) spectral fingerprints permit the quantification of source contributions to artificial mixtures; and
(3) field-derived source information is sufficient for spectral fingerprinting.

We found that:

(1) Three aggregated source types can be reliably identified based on spectral parameters. However, discrimination relies on intra- and inter-source variability, thus these findings may differ when transferred to other catchments and/or other source (type) formulation, as is the case for other fingerprint properties.
(2) Spectral fingerprints permit the quantification of source contribution to artificial mixtures, whereas introduction of source heterogeneity decreases modelling accuracies for some source types. Aggregation of source types does not improve mixture modelling results but, however, the results do provide valuable insight on how to interpret sediment source ascriptions, where the true contribution is unknown.
(3) Despite providing similar discrimination accuracies as laboratory source parameters, in-situ derived source information was found to be insufficient for contribution modelling. This is most likely due to differences in soil moisture and grain size in the field. A similar treatment of source and sediment samples (drying, sieving) seems necessary.

In summary, spectral measurements provide a rapid, non-destructive and cost efficient means to characterize potential sources and analyse mixture samples qualitatively and, with restrictions, quantitatively. In the future, a combination of spectral with more established properties in composite fingerprints, as suggested by Martínez-Carreras et al. (2010a), might increase the dimensionality of the datasets and thus improve tracing reliability. In addition, inclusion of spectral features with no physical basis but high classification potential that pass the assumptions tests may improve modelling reliability. Furthermore, the efficiency of source ascription based on Partial Least Squares Regression (PLSR) models calibrated on artificial mixtures, as proposed by Poulenard et al. (2009, 2012), Evrard et al. (2013) and Legout et al. (2013), could be tested for VNIR-SWIR spectroscopy.

4.7 Acknowledgments

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Chapter V
Spectral fingerprinting: Characterising suspended sediment sources by the use of VNIR-SWIR spectral information

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Abstract

Purpose: Knowledge of sediment sources is a prerequisite for sustainable management practices and may furthermore improve our understanding of water and sediment fluxes. Investigations have shown that a number of characteristic soil properties can be used as "fingerprints" to trace back the sources of river sediments. Spectral properties have recently been successfully used as such characteristics in fingerprinting studies. Despite being less labour-intensive than geochemical analyses, for example, spectroscopy allows measurements of small amounts of sediment material (> 60 mg), thus enabling inexpensive analyses even of intra-event variability. The focus of this study is on the examination of spectral properties of fluvial sediment samples to detect changes in source contributions, both between and within individual flood events.

Materials and methods: Sediment samples from three different origins were collected in the Isábena catchment (445 km^2) in the central Spanish Pyrenees: 1) soil samples from the main potential source areas; 2) stored fine sediment from the channel bed once each season in 2011; and 3) suspended sediment samples during four flood events in autumn 2011 and spring 2012 at the catchment outlet as well as at several subcatchment outlets. All samples were dried and measured for spectral properties in the laboratory using an ASD spectroradiometer. Colour parameters and physically based features (e.g. organic carbon, iron oxide and clay content) were calculated from the spectra. Principal component analyses (PCA) were applied to all three types of samples to determine natural clustering of samples, and a mixing model was applied to determine source contributions.

Results and discussion: We found that fine sediment stored in the river bed seems to be mainly influenced by grain size and seasonal variability, while sampling location – and thus the effect of individual tributaries or subcatchments – seem to be of minor importance. Suspended sediment sources were found to vary between, as well as within, flood events; although badlands were always the major source. Forests and grasslands contributed little (< 10 %) and other sources (not further determinable) contributed up to 40 %. The analyses further suggested that sediment sources differ among the subcatchments and that sub-catchments comprising relatively large proportions of badlands contributed most to the four flood events analysed.

Conclusions: Spectral fingerprints provide a rapid and cost-efficient alternative to conventional fingerprint properties. However, a combination of spectral and conventional fingerprint properties could potentially permit discrimination of a larger number of source types.

5.1 Introduction

In addition to negative impacts that suspended sediments can have on water quality, as described by numerous studies (e.g. Owens et al. 2005, Walling 2005, Davis and Fox 2009, Poulenard et al. 2009), large amounts of suspended sediments also affect water quantity, as is the case in the Isábena catchment (Spain) investigated in this study. Suspended sediment concentrations at the Isábena outlet can exceed 350 g l^{-1} during flood events (López-Tarazón et al. 2009). Such high concentrations result in severe siltation problems in the Barasona reservoir, located at the catchment outlet below the confluence with the River Ésera. The reservoir was built in 1932 and enlarged in the 1970s to a capacity of 92 x 10^6 m^3 (López-Tarazón 2011). Despite sluicing in the late 1990s, the initial capacity has been reduced considerably, adversely affecting the mid-term reliability of water supply (Mamede 2008).

Knowledge of sediment provenance is a key factor in understanding sediment transport and delivery processes and thus a first step in the design of sustainable watershed management strategies (e.g. Walling 2005, Davis and Fox 2009, Navratil et al. 2012). Such strategies must target the primary sources in order to control sediment fluxes within the watershed (Mukundan et al. 2012). In the study catchment, field observations as well as modelling have indicated badlands to be the major sediment source (e.g. Fargas et al. 1997, Francke et al. 2008a, Alatorre et al. 2010, López-Tarazón et al. 2012). Badlands are defined as "areas of unconsolidated sediments or poorly consolidated bedrock, with little or no vegetation […] in an intensely dissected landscape" (Gallart et al. 2002a). Lithology is a major factor for badland development and though they are commonly considered characteristic of dryland regions they also occur in more humid climates with high topographic gradients and intense rainstorms (Gallart et al. 2002a). Despite badlands being considered as major sediment sources, significant changes in the colour of the suspended sediments have been observed between, and even within, runoff events, suggesting the influence of varying sources.

A direct approach to trace the origin of sediment is a method called fingerprinting. It is founded on the principal assumptions that: (1) potential sediment sources can be discriminated based on a set of characteristic properties ("fingerprints"); and (2) the comparison of these source characteristics with those of (suspended) sediment allow for determination of relative source contribution (Collins and Walling 2004). In the past 30 years, the source fingerprinting approach has been successfully applied as a research tool in many ecoregions around the world (e.g. Walling 2005, Davis and Fox 2009). However, the adaptation of the technique as a management tool is hampered due to several reasons. Most importantly, the choice of successful fingerprint properties is highly site-specific and the lack of general guidelines for pre-selection of parameters capable of tracing back sources can make the approach very time consuming and costly (e.g. Collins and Walling 2002). Thus, recent studies have focused on the testing of robust and inexpensive methods for the derivation of such properties (e.g. Gibbs 2008, Poulenard et al. 2009, Martínez-Carreras et al. 2010b). Consequently, spectroscopy was found to offer considerable potential for time-efficient and cost-effective measurements (Poulenard et al. 2009 and 2012, Martínez-Carreras et al. 2010a, b, c, Evrard et al. 2013, Legout et al. 2013, chapter IV). In addition to being less labour intensive regarding laboratory analyses, spectroscopy offers the advantage of small sample size requirements (Martínez-Carreras et al. 2010a).

The aim of the current study is the interpretation of visible (VIS) to shortwave infrared (SWIR) spectroscopic data (0.35 – 2.5 µm) to examine the relative contributions from different sources and how these contributions change both between and within individual storm events. Therefore, potential source areas (1), as well as suspended sediments (2), and fine sediment stored in the channel bed (3) were collected and spectrally measured. Colour parameters and spectral features with relation to organic carbon, iron oxide and clay content were calculated from spectra and subsequently tested to meet a number of assumptions. Parameters meeting the assumptions were used in principal component analyses (PCA) for all three sample types (1-3) to determine natural clustering, and a mixing model was applied to suspended sediment samples to determine source contributions.

5.2 Study area

The Isábena River drains a 445 km² basin in the southern Pyrenees (Ebro catchment, NE Spain, just before entering the Barasona reservoir together with the Ésera River (Fig. 5.1). The Isábena catchment comprises five main subcatchments: the Cabecera sub-catchment in the North (146 km², representing 33 % of the total catchment area), the Villacarli (42 km², 9 %) and Carrasquero (25 km², 6%) subcatchments in the NW and Ceguera (28 km², 6 %) and the Lascuarre subcatchment (45 km², 10 %) in the SE (Fig. 5.1). The remaining area drains directly into the Isábena River. Overall, the area is characterized by a rough terrain (450 m a.s.l. in the southern lowlands to 2700 m a.s.l. in the headwaters), resulting in a pronounced climatic and land cover gradient. The climate is of Mediterranean mountainous type with mean annual temperatures ranging between 14 °C (south) to 9 °C (north) and a mean annual precipitation of 450 mm (south) to 1600 mm (north) (Verdú 2003). Precipitation is of high spatial and temporal variability with maxima generally occurring in spring and autumn (López-Tarazón et al. 2010). Despite occasional gravel mining, the Isábena is an entirely unregulated river with a pluvial–nival runoff regime. Valero-Garcés et al. (1999) found that the major floods in the Ésera–Isábena basins are caused by late spring–early summer snow melt in combination with heavy rains, summer thunderstorms, and late autumn heavy rains. Frequent floods keep sediment transport rates at relatively high levels, with instantaneous suspended sediment concentrations occasionally attaining 350 g l^{-1} (López-Tarazón et al. 2009).

While valley bottoms are mainly used for agriculture, higher altitudes are dominated by shrubland (matorral), grassland, woodland (*Quercus* and *Pinus*) and bare soil and rock. Major land use changes that occurred over the past 50 years resulted in the abandonment of cultivated areas and subsequent revegetation, initiated by shrub species and followed by forest regrowth (e.g. Lasanta and Vicente-Serrano 2012).

The catchment is characterized by a heterogeneous lithology. Valero-Garcés et al. (1999) describe several WNW–ESE trending geologic units, i.e.: (1) the Axial Pyrenees composed of Paleozoic rocks (quartzites, limestone) with peaks above 3000 m a.s.l. in the north; (2) the Internal Ranges composed of Cretaceous and Paleocene sediments in the centre; and (3) the Intermediate Depression, a relatively lowland area in the south of the catchment that is composed of Miocene continental sediment. The most important soil types developed in this area can be classified as shallow mineral soils (including regosols, leptosols and fluvisols) and soils with a considerable accumulation of organic matter, including kastanosems (Alatorre et al. 2010). There is high variability in soil colour that is most obvious in the agricultural fields, ranging from reddish brown to greyish and dark brown.

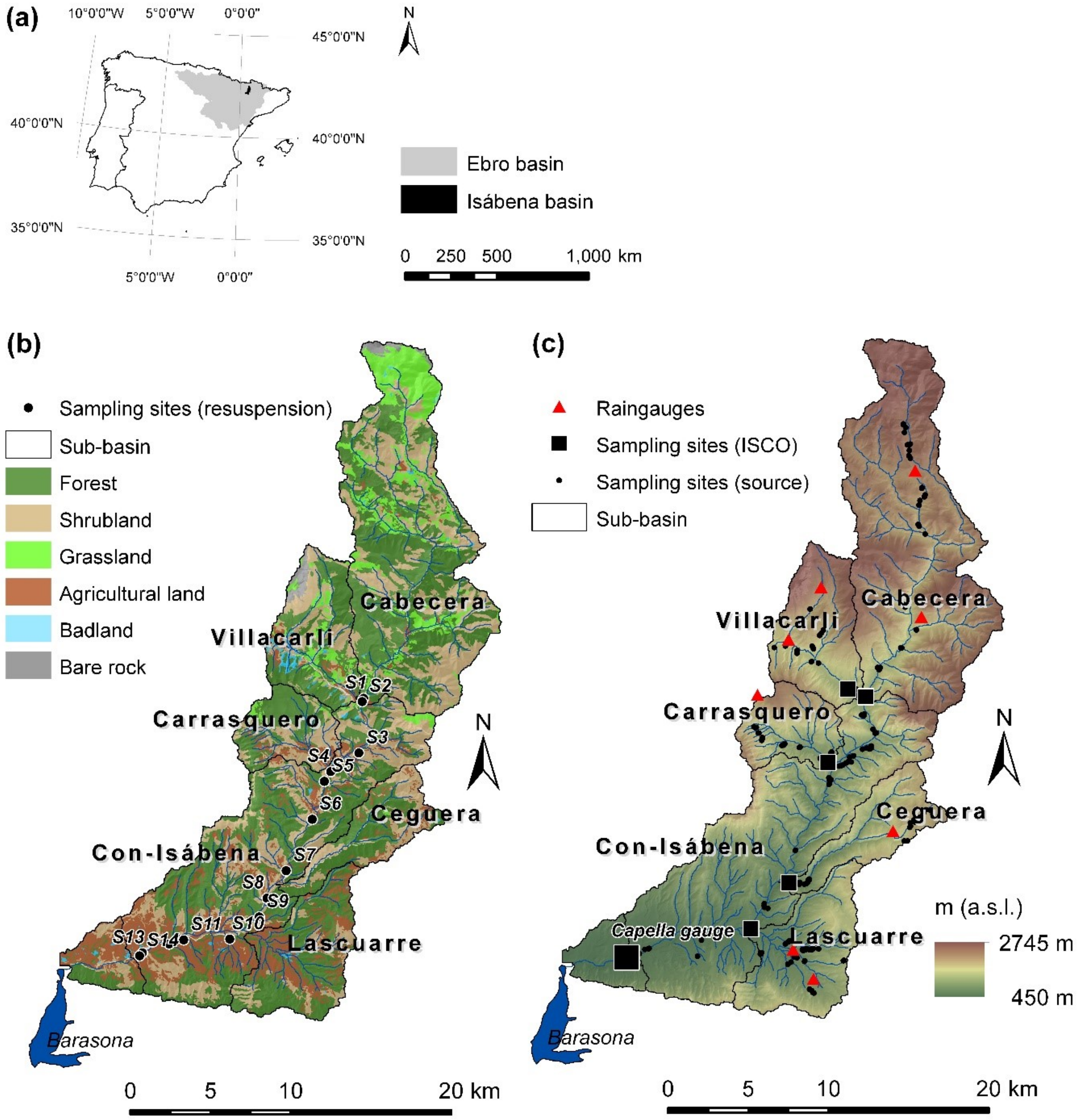


Fig. 5.1: Study area (Isábena basin) including location in Spain, land use, topography, main river network, subcatchments, and sampling locations (source sampling, ISCOs for suspended sediment, channel bed resuspension sampling, rain gauges)

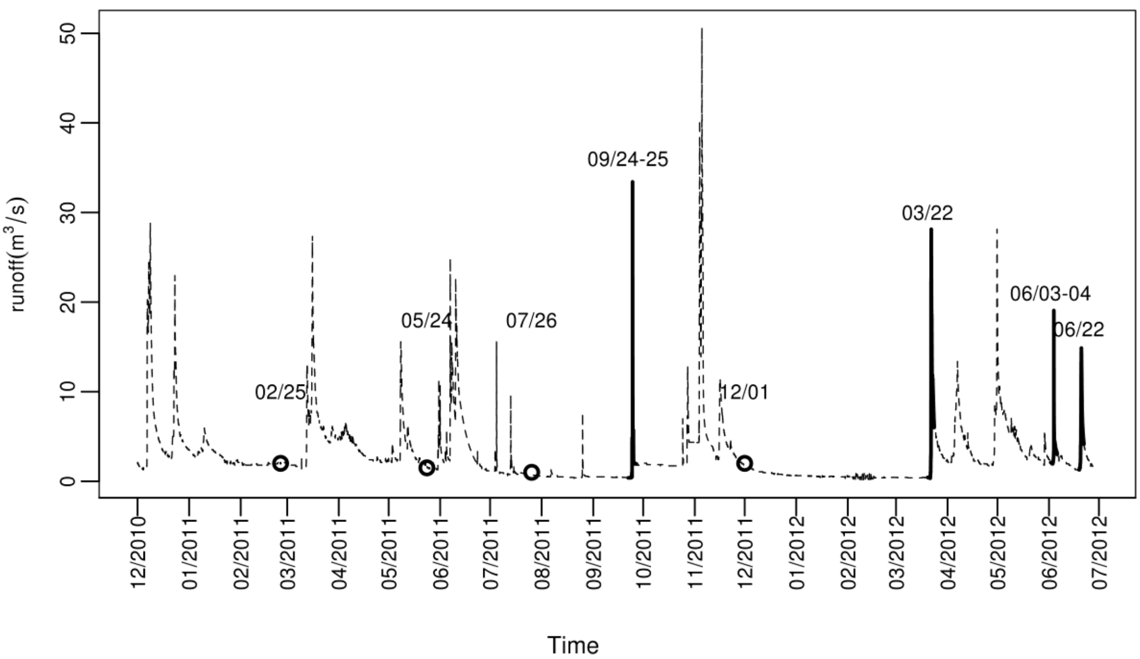
Valero-Garcés et al. (1999) describe several internal depressions formed upon highly erodible materials (marls, sandstones, and carbonates) that are located in the central part of the watershed. These areas with relatively high topographic gradients and moderate vegetation cover lead to the development of badlands. Despite representing < 1 % of the total basin area (mainly in the Villacarli and Carrasquero subcatchments), badlands are considered the most important sediment source in the catchment (e.g. Fargas et al. 1997, Francke et al. 2008a, Alatorre and Beguería 2009, López-Tarazón et al. 2012) with erosion rates estimated to exceed 550 t ha^{-1} yr^{-1} (Appel 2006). Although the topographic gradient is higher in the northern areas, lithology as well as higher vegetation cover (grassland, forest) reduce sediment production. In the southern areas, cultivated land predominates. While Valero-Garcés et al. (1999) suggest that the smaller topographic gradient seems to be reducing erosion, Alatorre et al. (2010) identify dryland crop areas as important contributors of suspended sediment yield.

The catchment has been subject to intensive hydrological studies over the past decade (e.g. Bronstert et al. 2014), resulting in a detailed understanding of hydrological and geomorphological processes and a favourable instrumentation situation, thus making it an ideal test site for innovative techniques.

5.3 Material and methods

5.3.1 Sampling and data overview

Field campaigns were conducted to collect samples from three different origins: 1) 152 soil samples were collected from the main potential source areas within the Isábena catchment; 2) a total of 48 samples of fine sediment stored in the main channel bed were collected at 14 cross sections once each season in 2011; and 3) suspended sediment samples from the river were collected during four flood events in autumn 2011 and spring 2012 at the catchment outlet (44 samples) as well as at several subcatchment outlets (46 samples selected for analyses).



Online Supplementary Material 1: Discharge at Capella weir over the study period including sampling dates for resuspension samples (circle) and suspended sediments during storms (thick lines)

The spatial location of sampling sites is shown in Fig.5.1, the temporal allocation of sediment samples (channel bed and suspended) with respect to discharge at the Capella gauge can be seen in Online Supplementary Material 1. In addition, potential sources covering only small areas (< 1 %) but possibly contributing a high proportion of material were sampled, including badlands, unpaved roads and open slopes. Thereby, the distribution of sampling locations were considered to be spatially representative of all subcatchments. The number and details of samples collected are listed in Table 5.2.

Table 5.2: Number of samples collected from potential suspended sediment sources per sub-catchment

Catchment	Area [km²]	Number of samples cultivated	grassland	shrubland	forest	badland	open slope	road	**Total**
Cabecera	145	1	10	7	6	-	-	3	**27**
Villacarli	41	3	1	5	4	6	1	1	**21**
Carrasquero	25	3	1	4	2	4	1		**15**
Ceguera	29	4	-	3	6	1	4	2	**20**
Lascuarre	44	8	1	10	5	-	8	3	**35**
Con-Isábena	160	8	3	7	7	3	5	1	**34**
Total		**27**	**16**	**36**	**30**	**14**	**19**	**10**	**152**

Since soils in the study area are shallow with poorly developed diagnostic horizons (López-Tarazón 2011), and lithology is not very distinct and overall rather homogeneous in large parts of the catchment, emphasis was placed on a land use-based sampling strategy. However, care was taken to ensure that the distribution of sampling locations were spatially representative over all lithological units (Ministerio de Agricultura, Alimentación y Medio Ambiente). Sampling sites were chosen in close vicinity (< 100 m) to stream or river reaches to make sure the material will be easily transported to the river. From each site, five grab samples of easily erodible material (top 1 - 3 cm) were collected from a 5 m x 5 m area and well mixed. The location of sampling sites is shown in Fig. 5.1.

River sediment sampling

Suspended sediment samples were collected hourly during flood events by an ISCO automatic sampler (ISCO 3700, Teledyne, Lincoln, Nebraska, USA) at the Capella gauging station near the catchment outlet. The sampler was triggered by flow conditions (i.e., start sampling from a certain water level). Four of the events sampled were chosen to be analysed and discussed in more detail in the present work, namely from (i) 24th/25th September 2011 (event A), (ii) 22nd March 2012 (event B), (iii) 3rd/4th June 2012 (event C) and (iv) 20th June 2012 (event D) (Table 5.3).

Table 5.3: Number of suspended sediment samples collected during different events at the outlet of the main channel and at four subcatchment outlets, along with information on suspended sediment concentration (SSC)

Date	Catchment	number of samples*	SSC [g l-1] min	mean	max
24 Sept 2011	Villacarli	5 (16)	11.08	151.08	332.62
24 Oct 2011	Villacarli	5 (15)	4.55	63.09	215.33
27 Oct 2011	Villacarli	5 (16)	2.13	32.54	99.94
03 Nov 2011	Villacarli	3 (12)	3.68	22.57	101.60
24 Sept 2011	Carrasquero	3 (03)	40.20	71.00	116.57
24 Oct 2011	Carrasquero	5 (16)	1.06	6.19	22.05
27 Oct 2011	Carrasquero	3 (11)	2.03	5.72	10.81
03 Nov 2011	Carrasquero	4 (10)	3.02	8.23	40.22
24 Sept 2011	Ceguera	3 (16)	9.87	25.86	54.25
03 Nov 2011	Ceguera	3 (24)	3.09	12.48	30.79
24 Sept 2011	Lascuarre	3 (14)	3.55	7.00	11.32
03 Nov 2011	Lascuarre	4 (23)	0.98	11.82	42.25
24-25 Sep 2011	Capella	24 (24)	3.28	10.36	35.72
22 Mar 2012	Capella	5 (05)	4.71	11.73	19.88
03-04 Jun 2012	Capella	8 (08)	2.54	34.23	65.25
20 Jun 2012	Capella	7 (07)	1.78	3.60	5.47

*number of samples measured with the spectrometer, with the total number of samples collected during the event in parentheses

In addition, suspended sediment samples were collected near the outlets of the five main subcatchments described above, by means of ISCO samplers (ISCO 3700C, Teledyne). Again, the samplers were triggered by flow conditions and samples were collected in 15 minute to hourly intervals depending on the runoff behaviour prevailing in the individual subcatchment (Table 5.3).

Furthermore, fine sediment stored within the bed of the Isábena main channel was sampled using the methodology developed by Lambert and Walling (1988). At 14 different cross-sections along the main channel, a metal cylinder of 50 cm in diameter and 60 cm height was carefully placed on the channel bed and slowly rotated to create a seal with the underlying gravel. The sampling area thus created was manually disturbed using a rod, resulting in re-suspension of stored fine sediment (for details see López-Tarazón et al. 2011). This procedure was repeated four times, once per season (namely, 25th February, 24th May, 26th July, and 1st December) in 2011; sampling was performed at exactly the same locations during all campaigns. The number and details of samples analysed are listed in Table 5.4, and sampling locations are shown in Fig 5.1.

Table 5.4: Number of channel bed resuspension samples collected on four dates, once each season, in 2011. Sampling site location can be seen in Fig. 5.1

25.02.2011 (I)	24.05.2011 (II)	26.07.2011 (III)	01.12.2011 (IV)
*	*	S01	S01
*	S02	S02	S02
S03	S03	S03	S03
*	*	S04	S04
S05	S05	S05	S05
*	S06	*	S06
S07	S07	S07	S07
S08	S08	S08	S08
S09	S09	S09	S09
S10	S10	S10	S10
S11	S11	S11	S11
S12	S12	S12	S12
S13	S13	S13	S13
*	S14	S14	S14

* amount of material was not enough for measurement or filters were damaged

Sediment concentration of all samples was determined by settling of known volumes of higher concentration samples (approx. > 2 g l^{-1}) and filtering of lower concentration samples using 1.2 µm FILTER-LAB glass microfiber filters. Loose material was dried at 60 °C for > 24 hours or air dried for over one week and weighed; filters were weighed prior to material application, then dried at 60 °C for two to three hours or air dried for > 24 hours and reweighed.

Water discharge and rainfall measurements

Water stage was recorded in 15 minute intervals at the Capella gauging station by the Ebro Water Authorities (CHE) and later transformed into discharge using the calibrated stage – discharge rating curve developed by López-Tarazón et al. (2010). Rainfall was measured by tipping-bucket gauges operated by the University of Potsdam / GFZ Potsdam. There are one or two rain gauges installed per subcatchment, resulting in a total number of eight rain gauges representing rainfall distribution over the catchment area. Sampling locations are shown in Fig. 5.1.

5.3.2 Spectral measurements of source and sediment samples

Spectral reflectance data were collected using an Analytical Spectral Device (ASD) FieldSpec3 High-Res portable spectroradiometer (Analytical Spectral Device, INC., Boulder, Colorado, USA), acquiring 2151 bands in the 0.35 – 2.5 µm range of the electromagnetic spectrum at a true sampling interval of 1.4 nm in the VIS-NIR region (0.35 – 1.0 µm) and 2 nm in the SWIR region (1.0 – 2.5 µm). Relative reflectance was calculated automatically by using a white reference panel as standard (100 %).

Loose material was thoroughly mixed to provide homogeneous samples. Since suspended sediment samples were mainly < 63 μm, source material was sieved to 63 μm to minimize spectral variations resulting from differences in particle size composition between source and suspended sediment material (e.g. Walling 2005). Source and suspended sediment material was placed in shallow 5 cm x 5 cm plastic containers and oven dried at 60 °C for 24 hours prior to spectral measurements. Spectral readings were taken in a dark room facility (for details see chapter IV). Four readings per sample were taken, with the sample rotated 90° after each reading to reduce illumination effects.
We detected spectral differences between loose material and material on filters that can partly be attributed to a loss in fine material (filter pore size 1.2 μm) and partly to alignment of sediment particles resulting in changes in reflectance behaviour. Thus, loose material and material retained on filters can both be used but the measurements should not be compared directly. While all soil and suspended sediment analyses were based on loose samples, there was not always enough material from resuspension samples. Thus, all resuspension samples were applied to glass fibre filters as described above for spectral measurements. In addition, some of the resuspension samples were much coarser than suspended samples collected by ISCOs; the resuspension samples were not sieved prior to spectral measurements.

5.3.3 Preprocessing and parameter calculation

Spectral readings per sample were averaged and smoothed using a Savitzky-Golay filter (Savitzky and Golay 1964). Then, red, green and blue (RGB) colour parameters were calculated from spectra by averaging values of spectral reflectance ranges corresponding to the blue, green and red Landsat bands (0.45 – 0.52 μm, 0.52 – 0.6 μm, and 0.63 – 0.69 μm, respectively) and multiplication with 255 to get 8-bit colour encoding (Viscarra Rossel et al. 2006a). These RGB values were transformed to other colour space models using ColoSol software developed by Viscarra Rossel et al. (2006a). All transformation algorithms are described in detail by Viscarra Rossel et al. (2006a) and details on colour models are explained by Wyszecki and Stiles (1982).
Following the description by Bayer et al. (2012), features found in the previous literature to be diagnostic of physically based information on soil organic carbon, clay, iron and carbonate content were calculated. The selected spectral parameters can be divided into spectral indices and three feature types, namely curve features, hull features, and absorption features. Details on the calculation of parameters can be found in Chabrillat et al. (2011), Bayer et al. (2012) and chapter IV.
In total, a set of 98 colour and physically based soil reflectance parameters was calculated (see chapter IV). Since colour coefficients may be easily converted and all spectral features are potentially used in spectroscopy and soil science, they were all considered in subsequent analyses, although some of these parameters may be highly correlated (Viscarra Rossel et al. 2006a, Martínez-Carreras et al. 2010c). In the following, the term "spectral parameter(s)" is used as a synonym for spectral fingerprint property, describing colour parameters and/or physically based reflectance features calculated as outlined above.

5.3.4 Test of assumptions

A number of fundamental assumptions of the fingerprinting procedure were tested in an attempt to limit uncertainty of sediment provenance assessment to a minimum. In recent studies, the potential non-conservativeness of tracer properties has been identified as a major concern, with key issues being particle size selective transport and tracer transformation (e.g. Koiter et al. 2013). For example, Smith and Blake (2014) found the relationships between these processes to be highly complex and discourage the use of correction factors. Thus, the problem of size selective transport was addressed by sieving all soil and suspended sediment material to < 63 µm (e.g. Martínez-Carreras 2010a, Mukundan et al. 2012, Smith and Blake 2014). Grain size analyses of a selection of sieved samples pointed to no enrichment or depletion effects. Secondly, although tracer transformation cannot be entirely excluded, it was addressed by limiting the analyses to spectral parameters whose values calculated from suspended sediment lie wholly in the range of those calculated from potential source samples (92 out of 98) (Smith and Blake 2014). The high number of parameters meeting this prerequisite indicates that any alteration effects may have been relatively small (Walden et al. 1997). Though spectroscopic measurements are sensitive to alterations during transport, such as reduction of iron or decomposition of organic matter, Legout et al. (2013) found changes in VIS spectra and colour parameters to remain < 10 % when comparing original samples to samples immersed in a river for a maximum period of 63 days. Linear additivity of spectral properties was explicitly tested by comparing properties calculated from artificial mixture spectra to properties calculated from mixture spectra produced by a linear mixing algorithm (chapter IV). Only 48 out of 92 parameters met this assumption and were used in subsequent procedures. Following Walling (2005), all remaining parameter values were scaled between 0 and 1 to ensure equal consideration of individual properties. A non-parametric Kruskal-Wallis H-test used to assess the existence of any significant interclass contrasts (Collins and Walling 2002) revealed that all 48 parameters were able to detect contrasts between the seven source types at the 95 % confidence level.

5.3.5 Statistical analyses to assess natural clustering of samples

Principal component analyses (PCA) were performed on the 48 parameter source and sediment datasets to determine natural clustering of samples and to evaluate overall variability and potential overlap between classes (Poulenard et al. 2009). The PCA was applied on source and suspended sediment samples (Capella) together, providing an indication of how successful subsequent quantitative mixing modelling is likely to be (Walden et al. 1997). In addition, PCA was applied on suspended sediment from river samples only (Capella and subcatchments) in order to get an impression of sample clustering between and within individual runoff events.

Furthermore, a PCA was performed on the resuspended material data only, since, unlike all other samples, the resuspended material was retained on glass fibre filters. Therefore these data could not be directly compared to the suspended sediment or source samples which were not filtered. Thus, this analysis will provide only qualitative results on general changes or resemblances within the stored sediment and will not allow us to draw conclusions on source contributions or similarities with the suspended load collected during individual flood events. All PCA analyses were performed using The Unscrambler® X 10.2 software (CAMO Software AS., Oslo, Norway).

5.3.6 Mixing model analyses

Since previous PCA and discriminant function analyses (DFA) results calculated from source samples suggested confusion between forest and grassland samples, as well as between shrubland and arable land, road and open slopes (chapter IV), the seven source types were aggregated into three source types for input to the mixing model; namely: badland; forest/grassland; and others. Only 45 parameters passed the Kruskal-Wallis H-test for the three groups and were used for subsequent unmixing analyses.

Relative contributions of potential sources were estimated by comparing the fingerprint properties of the sediment samples with those of the potential sources using a multivariate mixing model; a detailed description of the model can be found in chapter IV. Errors between measured and estimated values were approximated using the non-negative least squares algorithm introduced by Lawson and Hanson (1974), where the best approximation is defined as the one minimizing the sum of squared differences between the measured data values and their corresponding modelled values. The model was restricted by the constraints that the source type contributions must all be non-negative and sum to 100 %. Uncertainty associated with modelling results due to source heterogeneity was assessed by producing Gaussian distribution functions from the mean and standard deviation of each tracer property per source type (Martínez-Carreras et al. 2010a). The mixing model was run 10,000 times, choosing source information randomly from the Gaussian distribution functions, thus allowing source describing properties to vary in each solution. This replicate random sampling provides confidence estimates for the modelled contribution results by permitting the calculation of percentiles. The model was implemented using in-house software (ANSI - C).

5.4 Results

5.4.1 Principal component analyses – natural clustering of samples

Resuspension samples

Figure 5.2 shows PCA score plots of all samples of resuspended channel bed sediment (first three components). Generally, the heterogeneity of the samples reflected in the first three components is rather high. The first three components together explain 88 % of the variance (44 %, 35 % and 9 %, respectively), and seven components explain 98 % of the total variance.

A scatterplot of the first two components (Fig. 5.2a), in general, seems mainly influenced by grain size. Though grain size distribution was not analysed in particular, visual inspection revealed that some filters contained very fine material while other filters contained coarser material and/or sand grains. The majority of finer samples cluster in the upper right corner of the scatter plot while the coarser samples are mainly distributed to the lower left. Samples

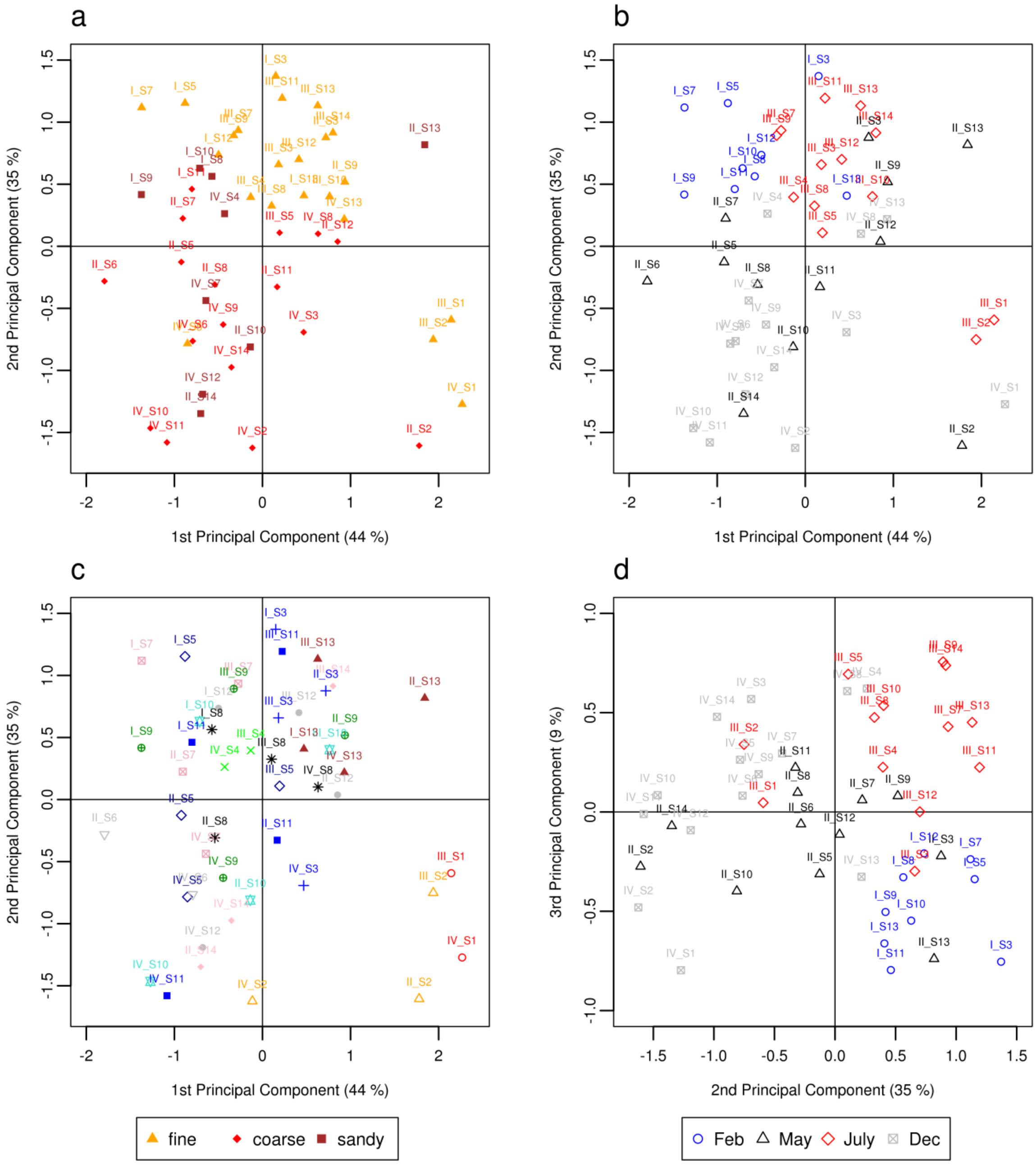


Fig. 5.2: Two-dimensional scatter plot of scores for the first three principal components (PC) from the PCA of channel bed resuspension samples: a) first two PCs by grain size; b) first two PCs by season; c) first two PCs by sampling location; and d) second and third PC by season

from February (I) and July (III) seem generally finer than samples from May (II) and December (IV) but this is inconsistent and not true for all sections sampled (Fig. 5.2b).

Fig. 5.2c again depicts the first two components, where the samples are identified by the 14 sections they were collected from. Both samples S1 and two of the three S2 samples cluster well away from the other samples and rather close together. Then, a rough zonation trend can be observed for the upstream sections with samples from S3 situated to the right of the plot and samples from S4, S5, and S6 distributed further to the left. Samples from S7

and S8 are again distributed further to the right. With the exception of S13, samples S9 to S14 are very heterogeneous. The observed "zonation trend" is not consistent with either season or grain size variation.
Figure 5.2d shows the second and third PC that mainly seem to reflect seasonal variation. Thus, samples collected in May (II) cluster between the samples from February (I) and December (IV) while samples collected in July (III) are separate. As in the first two component plots, samples from S1 and S2 are somewhat separate. Apart from that, the sampling section does not seem to have a detectable influence on any of the first seven components.

Suspended sediment samples

Figure 5.3 shows several PCA score plots of source and suspended sediment samples (first two components). Overlap between samples from different land use classes is evident from Fig. 5.3a, whereas badland and forest/meadow samples form somewhat separate clusters and all other land uses seem not to differentiate. The Capella suspended sediment samples plot within the catchment source materials, between badland and road, agricultural and shrubland samples. Compared to source material samples, sediment material is very homogeneous. However, a distinction between individual events is clearly evident.

No grouping is visible with respect to the source samples' subcatchment of origin (see Fig. 5.3b), with the exception of the northernmost subcatchment (Cabecera), which is underlain by different substrates than the more southern subcatchments. However, no grouping by lithology is evident from the PCA scatter plots (results not shown).
Although Fig. 5.3b does not reveal clustering of source samples by subcatchment, Fig. 5.3c shows a clear distinction of all suspended sediment samples by subcatchment (Capella and subcatchment samples). A distinct clustering of most samples into the four subcatchments of their origin is evident. Due to a lack of sampling material, the northernmost subcatchment (Cabecera) is missing from this analysis. Samples collected near the basin outlet (Capella) plot completely in the centre, with a shift towards the Villacarli and Carrasquero sub-catchments.
Figure 5.3d shows the first and second PC of a PCA performed on Capella sediment samples only. Despite being generally much more homogeneous than source samples, the distinction between individual events evident from Fig. 5.3a is even more pronounced when looking at the sediment samples separately. While events B and C plot closely together, most samples from event D are clearly different. Intra-event variability is mainly visible from PC2. Event A contains most samples and is most heterogeneous, with large variability along both first PCs, with some samples resembling events B, C and D and other samples being obviously of different composition. Therefore, it is the early (samples A1 - A4) and later (samples A15 - A22) stages of the event that more closely resemble the other events sampled at Capella while, the middle (samples A7-A14) and end (samples A23 and A24) stages seem most different.

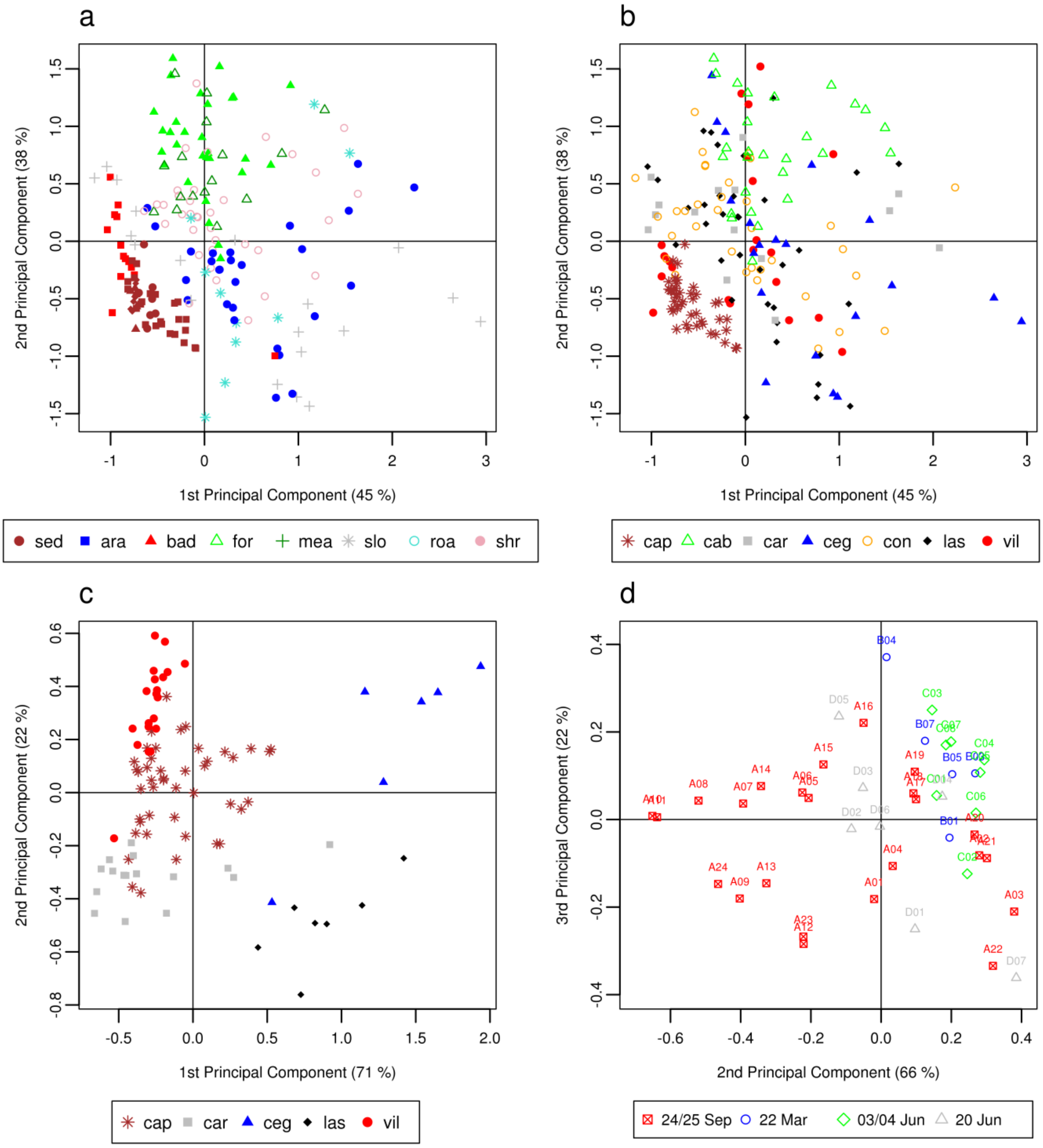


Fig. 5.3: Two-dimensional scatter plot of scores for the first and second principal component (PC) from the PCA for: a) source data by land use with suspended sediment sampled at the basin outlet (Capella); b) source data by subcatchment with suspended sediment sampled at the basin outlet (Capella); c) suspended sediment samples from the basin outlet (cap) and four subcatchments; and d) suspended sediment samples from the basin outlet by flood event. Acronyms describe Capella suspended sediment (sed) and source sample land use classes (ara = agricultural land, bad = badland, for = forest, mea = grassland, slo = open slope, roa = unpaved road, shr = shrubland) and subcatchment/location of ISCO sampler (cap = Capella, cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre, vil = Villacarli)

5.4.2 Application of mixing model to suspended sediment samples

Source tracing results of four events sampled at Capella from September 2011 to June 2012 including information on runoff and suspended sediment concentration (SSC) are shown in Fig. 5.4 to Fig. 5.7. Details on precipitation (sum, average, intensity, duration) and a rough characterization of distribution over the subcatchments can be found in Table 5.5.

Table 5.5: Characterization of precipitation events that caused the runoff sampled for suspended sediment at Capella. Av gives the average amount of precipitation interpolated over the study area from information measured at the subcatchment gauges. Events per sub-catchment are summaries of events that occurred in the period given in column date, whereas an event was defined as continuous rainfall with interruptions < 1 hr. The numbers in brackets represent the number of rain gauges per subcatchment. Maximum intensity was calculated for 15 minute intervals

		Precipitation (mm)		Duration (h)			Max. intensity
Date	Catchment	mean	sum	min	mean	max	($mm\ h^{-1}$)
18-24 Sep 2011	Cabecera (2)	7.28	118.30	1.40	2.24	3.37	20.27
Av 39.86 mm	Villacarli (2)	5.93	63.98	0.23	1.74	2.82	31.79
	Carrasquero (1)	10.55	57.96	2.68	2.75	2.82	68.04
	Ceguera (1)	4.86	28.14	0.35	1.13	3.15	9.22
	Lascuarre (2)	5.46	31.36	0.43	1.78	2.88	40.37
18-22 Mar 2012	Cabecera (2)	2.45	162.45	0.20	8.48	19.85	12.00
Av 67.99 mm	Villacarli (2)	1.93	142.42	0.22	4.77	19.13	20.95
	Carrasquero (1)	2.57	72.66	0.68	5.55	19.38	16.38
	Ceguera (1)	2.65	91.01	1.43	6.41	19.25	20.09
	Lascuarre (2)	2.26	110.03	0.43	3.18	10.08	16.46
28 May 2012 -	Cabecera (2)	5.34	58.10	0.27	1.17	2.10	28.80
03 Jun 2012	Villacarli (2)	10.24	170.32	0.73	1.99	6.02	102.51
Av 25.46 mm	Carrasquero (1)	9.37	44.46	1.25	1.70	2.20	37.62
	Ceguera (1)	4.20	16.94	0.25	0.92	1.63	8.27
	Lascuarre (2)	8.61	38.40	0.63	1.23	1.70	42.55
18-23 Jun 2012	Cabecera (2)	1.90	40.48	0.62	4.25	12.97	18.48
Av 40.22 mm	Villacarli (2)	2.62	99.48	0.40	4.50	13.73	15.68
	Carrasquero (1)	2.53	92.04	0.50	4.35	12.42	15.96
	Ceguera (1)	2.29	44.13	1.00	4.19	12.32	13.97
	Lascuarre (2)	1.62	45.92	0.47	2.98	12.30	9.21

Figure 5.4 provides evidence of the high intra-event variability from 24th to 25th September 2011. Runoff shows a pronounced peak with steep rising and falling limbs and a much smaller second peak about 12 hours after the first peak. The peak runoff was 33 $m^3\ s^{-1}$, and maximum SSC was 35 $g\ l^{-1}$ at the peak and decreased quickly. Precipitation during the event was of short duration (< 3 hours) and high intensity (up to 40 $mm\ h^{-1}$) while the average amount of rainfall was moderate (40 mm). Overall, the samples comprise high proportions of badland material (mean 58 to 80 %). During the fallings limbs, other sources became more

dominant (on average up to mean 42 %) while the contribution of forest/grassland was generally low (mean 0 to 11 %).

For the three events sampled in 2012, sample availability as well as intra-event variability, were lower (Fig. 5.5-5.7). The event from 22nd March 2012 is characterized by a much broader runoff peak with a steep rising and a shallow falling limb (Fig. 5.5). Peak runoff was 28 m^3 s^{-1} and maximum SSC was 19 g l^{-1} at the peak and decreased quickly. Precipitation during the event was of longer duration (> 15 hours) and of lower intensity (< 20 mm h^{-1}) than the September event while the average amount of rainfall was higher (70 mm). The contribution of badland material to suspended sediment was estimated to exceed 80 % for all but the first sample and forest/grassland contribution was low (< 4 %) for all samples.

The event from 3rd to 4th June, 2012 is again characterized by a steep runoff peak (Fig. 5.6) yielding a maximum of only 19 m^3 s^{-1}. However, SSC was high, with a maximum of 68 g l^{-1} during the peak. Precipitation during the event was again of short duration (< 3 hours) and partly of very high intensity (10-40 mm h^{-1}, in the Villacarli subcatchment up to 105 mm h^{-1}) while the average amount of rainfall was low (25 mm). Mean estimated contribution of badland material to suspended sediment varied between 78 and 85 %, and forest/grassland contribution was again low (< 5 %) for all samples.

As for the event sampled in March 2012, the event from 20th June 2012 was characterized by a broad runoff peak with shallow rising and falling limbs (Fig. 5.7). Runoff and SSC were low yielding maxima of 15 m^3 s^{-1} and 5.5 g l^{-1}, respectively. Precipitation during the event was characterized by several short low intensity – low amount events followed by a longer (> 12 hours) event of low intensity (< 20 mm h^{-1}), while the average amount of rainfall was moderate (40 mm). The mean estimated contribution of badland material to suspended sediment varies between 68 and 81 %, and the contribution increased with the rising and decreased with the falling limb. The forest/grassland contribution was estimated to be low (< 5 %) for all but the last sample, where this source was estimated to account for 20 %. Other sources were estimated to contribute 12 to 26 %.

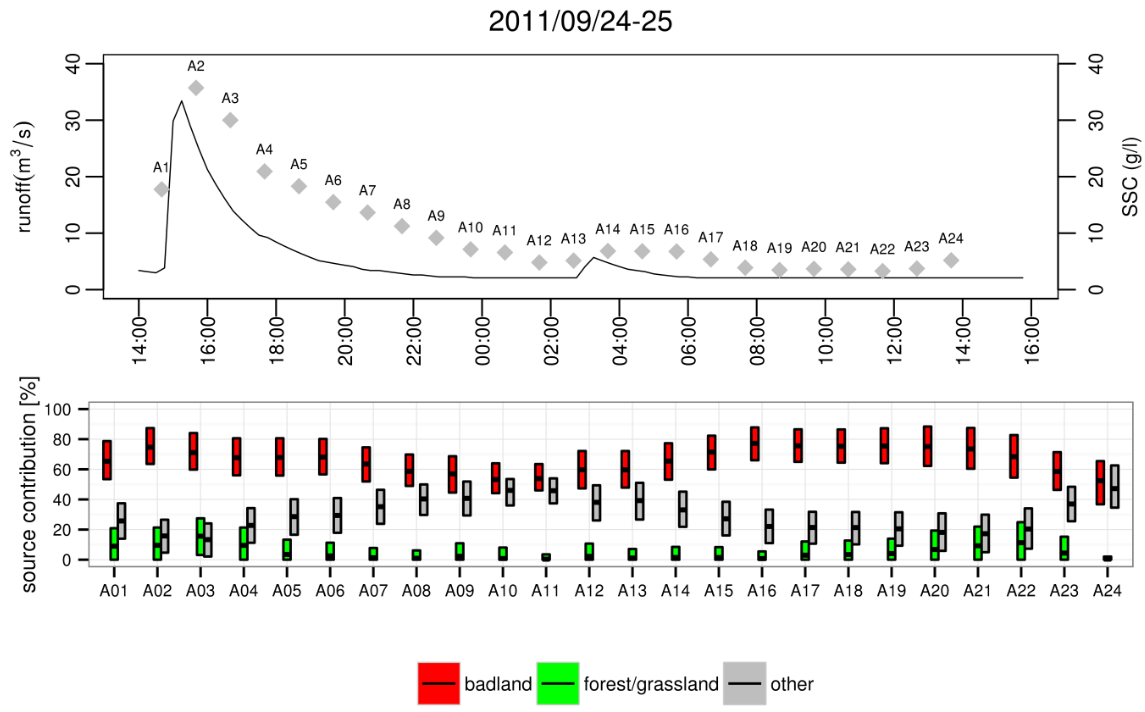


Fig. 5.4: Discharge, suspended sediment concentration (SSC) and estimated suspended sediment source contribution for the event that occurred on 24th/25th September 2011. Black bars indicate mean estimates, confidence intervals are at the 90 % level

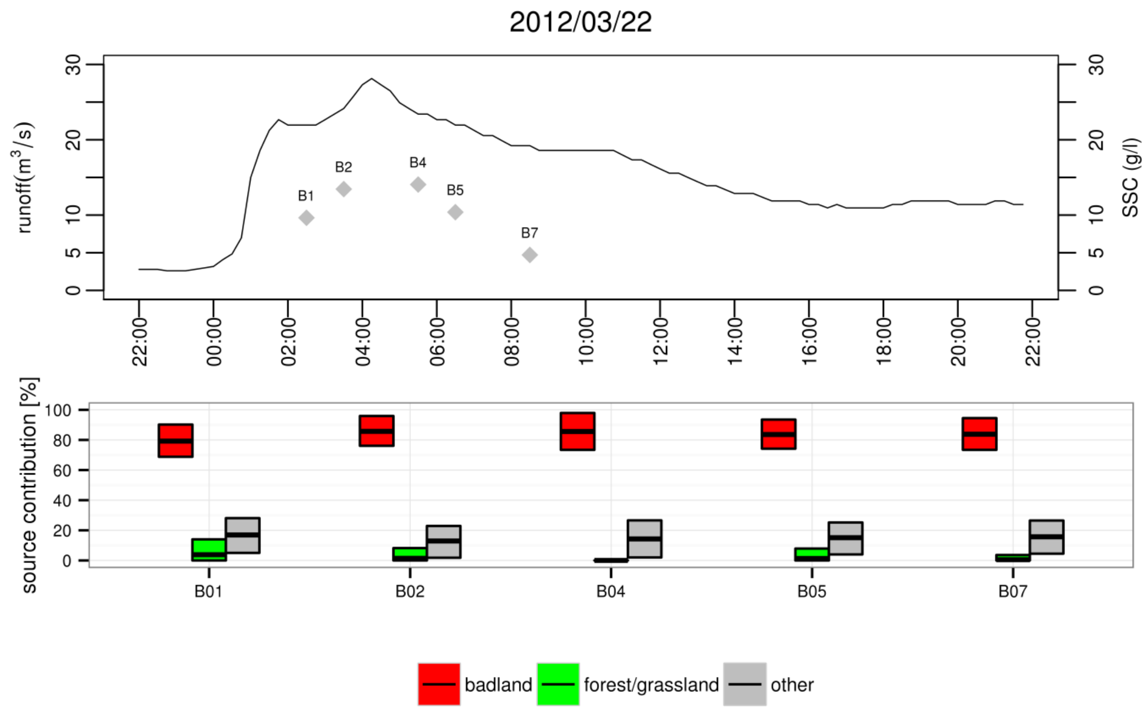


Fig. 5.5: Discharge, suspended sediment concentration (SSC) and estimated suspended sediment source contribution for the event that occurred on 22th March 2012. Black bars indicate mean estimates, confidence intervals are at the 90 % level

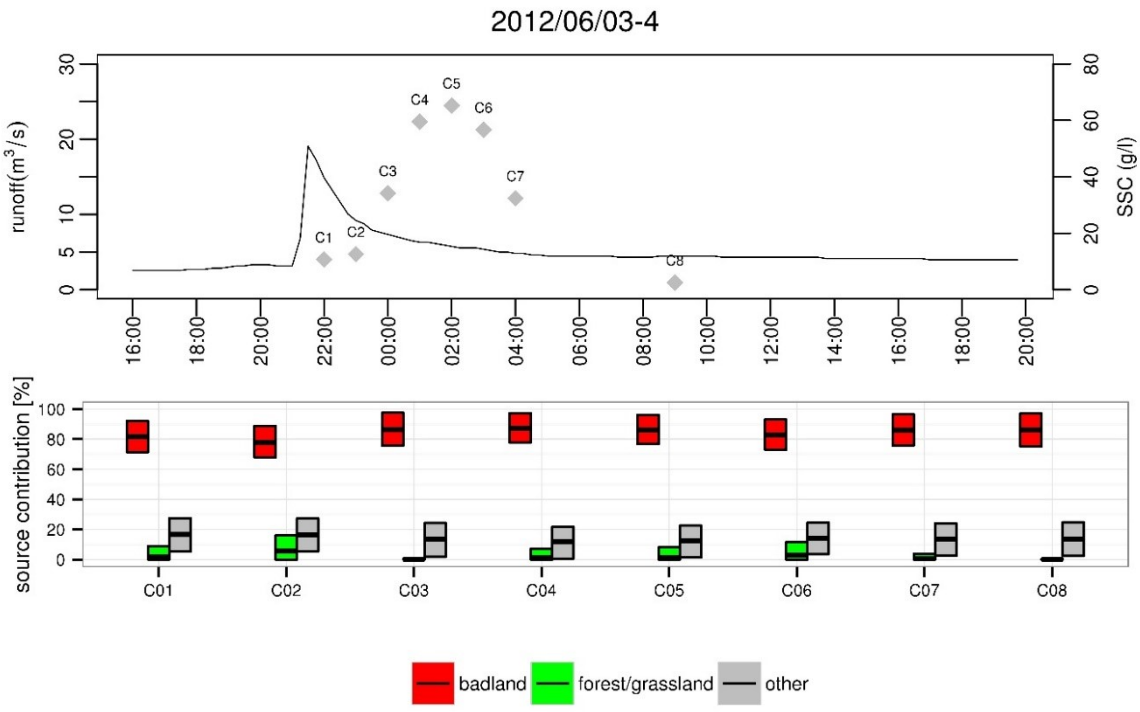


Fig. 5.6: Discharge, suspended sediment concentration (SSC) and estimated suspended sediment source contribution for the event that occurred on 3rd/4th June 2012. Black bars indicate mean estimates, confidence intervals are at the 90 % level

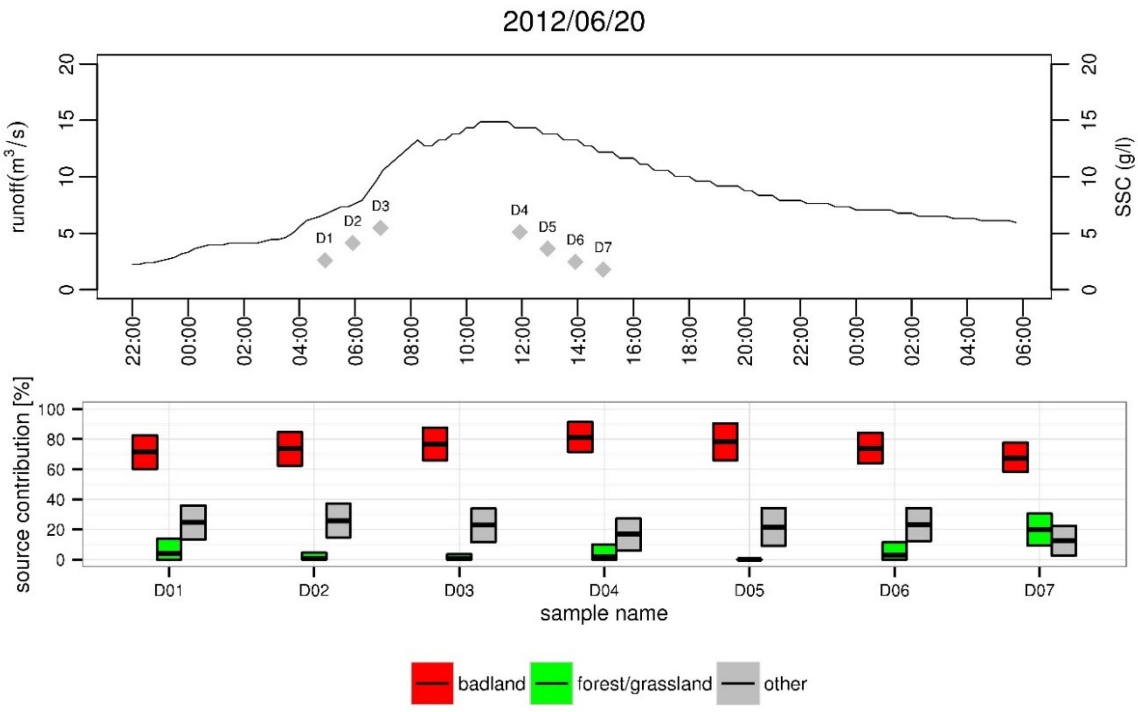


Fig. 5.7: Discharge, suspended sediment concentration (SSC) and estimated suspended sediment source contribution for the event that occurred on 20th June 2012. Black bars indicate mean estimates, confidence intervals are at the 90 % level

5.5 Discussion

5.5.1 Principal components analyses – natural clustering of samples

Resuspension samples

The PCA performed on resuspended sediment samples indicates that spectral reflectance of the samples was mainly influenced by variations in grain size as well as seasonal variations. Since seasonal variations are not completely identical with grain size variations there must be other/further influencing factors such as source contribution variations or variations in storage and transition behaviour of the River Isábena (Piqué et al. 2014). Samples collected at sections S1 and S2, upstream of the Cabecera outlet, were found to differ from most other samples. Apart from that, a lot of heterogeneity was found in the samples within, as well as between, sampling sections, indicating that if there is a pattern at all it is superimposed on other factors. This is consistent with results of López-Tarazón et al. (2011) and Piqué et al. (2014) who analysed the amount of stored sediment in the lower Isábena reaches (S11 - S14) for the periods 2007 - 2008 and 2011 - 2012, respectively. They found considerable variations in sediment storage along the main channel, identifying an annual cycle of sediment production and transfer downstream. However, it is difficult to capture this pattern since sediment accumulation is not linear in time and space, but is largely influenced by spatial and temporal (i.e. seasonal) heterogeneity in the catchment's hydrology and sediment production in the badlands.

Suspended sediment samples

Results of the source and suspended sediment PCAs can be interpreted as indicators of the feasibility of the spectral fingerprinting approach (Walden et al. 1997). The fact that all suspended sediment samples plot within the margins of potential source samples may be seen as an indicator that all major sources have been sampled and that changes in suspended sediments which may have occurred during transport and storage have been relatively small (Walden et al. 1997).

A distinct pattern of source samples by land use was found, however, no clustering was evident by lithological units, indicating that (in this catchment) land use practices may supersede soil type or lithological differences. The plotting of suspended sediment samples close to badland and unpaved road, agricultural and shrubland source samples, and further away from forest and grassland source samples, confirm the mixing model results, which suggest: a high contribution of badland materials in all samples; a medium to high contribution of other materials; and a low contribution from forest/grassland materials. Compared to source material samples, the heterogeneity of sediment material is very limited. However, a distinction between individual events is evident, confirming changes in source contributions between the events as suggested by the mixing model. Samples estimated to contain a higher proportion of badland materials (events B and C, some samples of events A and D) plot closer to badland source samples, while samples containing higher shares of other materials (event A) plot closer to unpaved road, open slope, agricultural and shrubland source samples.

There is no clustering of source samples by subcatchment but there is a clear distinction in the suspended sediment samples from the subcatchments by origin, indicating major differences of source contributions in individual subcatchments. Unfortunately, the number of source samples per subcatchment is limited, constraining a subcatchment-based fingerprinting approach. Samples collected near the basin outlet (Capella) plot in the centre of the subcatchment sediment samples and thus seem to represent mixtures of the subcatchment's materials, with higher contributions from the Villacarli and Carrasquero subcatchments. This is consistent with the results of other studies undertaken in the area, which identified Villacarli as a major contributor for the same (Francke et al. 2014) and other study periods (Francke et al. 2008a and 2008b, López-Tarazón et al. 2012). However, López-Tarazón et al. (2012) identified Lascuarre as the second most important sediment source, indicating that there may be major changes in spatial source contribution between different years/study periods. In addition, analyses of resuspension samples indicate that tributaries not attributed to any subcatchment (i.e. S6, S7, S9, S11 - S14) may cause substantial heterogeneity and thus contribute to sediment collected at the catchment outlet.

5.5.2 Mixing model

The mixing model results are consistent with the PCA results in terms of source ascription, suggesting that contribution estimates are reliable (Walden et al. 1997). Previous experiments on artificial laboratory mixtures where source contributions were known revealed high levels of uncertainty (chapter IV), thus suggesting reliance on the general ascription of source contributions but not on exact values. However, when comparing the suspended sediment mixing model results to artificial laboratory unmixing results it is evident that unmixing results obtained in the present study fall within the ranges that seemed reliable in the previous, controlled study (i.e. chapter IV) using artificial mixtures (> 60 % badland, < 40 % others, < 20 % forest/grassland).

Overall, although badlands were found to be the major contributing sources to all samples analysed, there are differences between, as well as within, events. Rainfall is distributed irregularly over the catchment and runoff response was found to be highly variable (e.g. López-Tarazón et al. 2010), resulting in differences in the occurrence of floods at the subcatchment level and in the production of secondary SSC peaks (López-Tarazón et al. 2012). Differences in precipitation (short duration / high intensity around 24th/25th September and 3rd/4th June vs. long duration / low intensity around 22nd March and 20th June) caused differences in runoff behaviour. Whereas the runoff peak was very pronounced with steep limbs in September and early June, it was a lot broader in March and late June. The SSC was found to be generally lower in the two broad peak events, whereas it was found to be extremely low in the 20th June event. This is likely due to material depletion after the event from 3rd/4th June, where SSC exceeded 60 g l^{-1}. Material availability may also be the explanation for the differences between events B and D which, due to similar rainfall and runoff characteristics, were expected to be of more similar composition. However, mixing model as well as PCA analyses suggest a greater similarity between events B and C, whereas samples from event D resemble first peak / early falling limb and the later samples of event A. No concurrent explanation was found on the changes within the very long event A. Samples from the late stages of the first falling limb of event A

are unique in their low badland / high other sources contribution as compared to the other events sampled, which again may be due to the long duration of the event and thus sediment exhaustion. Samples taken during the second, smaller peak largely resemble events B and C. Together with the occurrence of the second runoff and SSC peak, this indicates that a local rainburst may have led to the delayed contribution of a source, tributary or subcatchment.
This leads to the limitations of the fingerprinting technique, which is capable only of providing information on the ultimate sediment source and not the proximal one; sediment stored from previous events will be identical to sediment arriving at the sampling location at the same time from the ultimate source (Parsons 2012). Furthermore, mixing models do not consider the travel time of sediment from source to sampling point. Thus, differences in travel time arising, for example, from differences in particle size or source distance in larger catchments, can invalidate the analysis of spatial origin (Parsons 2012) and impede interpretation of changes in source type contribution.
However, the overall suggestion of badland sources being the main contributors meets the general expectation for this catchment (e.g. Valéro-Garcés et al. 1999, Alatorre et al. 2010). There are no analyses specifying the proportion of badland material in suspended sediment. Nevertheless, previous studies found badland erosion rates to be very high with specific sediment yields exceeding 6200 t km^{-2} for a three month study period (Francke et al. 2008a). In addition, Francke et al. (2008a and 2008b) calculated suspended sediment yield of the Villacarli subcatchment – the subcatchment with highest portion in badlands (6 % of the area) – to account for about 45 % of the yield measured at the catchment outlet from September to December 2006. López-Tarazón et al. (2012) estimated Villacarlis' suspended sediment contributions to vary between 61 % and 27 % for the study periods 2007-2008 and 2008-2009, respectively. Forest and grassland sources contributed little to the samples analysed in the current study, which was also expected since the soil is predominantly well protected by high vegetation cover. Unfortunately, the aggregated "other" sources could not be analysed in more detail. Mukundan et al. (2012) discuss a catchment size of < 250 km² as the maximum scale at which fingerprinting is likely to be meaningful. Collins et al. (1998) state < 500 km² appropriate for source type fingerprinting, while increasing source heterogeneity in larger catchments could make source type fingerprinting less successful. A combination of spectral with classic fingerprinting properties such as geochemistry, mineral magnetism or radionuclides, as proposed by Martínez-Carreras et al. (2010a), could potentially provide a deeper understanding of the contribution of sources classified as "others" in this study.
Though differences between source contributions to different events were detected, no obvious seasonal variation was found. Instead, sediment availability seems to play a major role in the Isábena catchment. This is consistent with findings of López-Tarazón et al. (2010), who found that while there was no correlation between rainfall intensity and SSC, sediment availability in badlands and sediment storage in the channels influence the river's sedimentary response. López-Tarazón et al. (2012) found sediment delivery ratios of 90 %, indicating that large parts of the sediment mobilized in the catchment is easily transported to the outlet. However, sediment storage values in the Isábena main channel were estimated by López-Tarazón et al. (2011, 2012) to range from an average of 5 % of the annual total load to up to 55 % during certain periods Thus, they conclude that the fine-grained sediment

stored in the channel can represent an important factor in controlling the suspended sediment dynamics.

5.6 Conclusions

The focus of this study was on the examination of spectral parameters for changes in sediment source in stored and suspended sediment, over the seasons as well as within and between flood events. Results suggest that variability in stored fine sediment is most likely due to grain size and seasonal variation. Apart from the two uppermost sampling sections, no clear trends by sampling location were observed. Overall, the influence of inter-storm and/or seasonal variation on storage and transition behaviour of the Isábena seems to be much greater than the influence of sampling location and thus, for example, the influence of individual tributaries or subcatchments.

However, regarding suspended sediment, considerable variability was detected between subcatchments as well as in source type contribution, both between and within individual runoff events. Badlands, with a total aerial fraction cover of < 1 %, were found to be the major contributing sources with values of 60 – 80 %. Other sources, covering 45 % of the study catchment, contributed up to ~ 40 % and forest/grasslands usually contributed < 10 % despite covering 54 % of the study area. This is consistent with expectations based on field observations and previous studies. Unfortunately, it was not feasible to trace the aggregated "other sources" in more detail by this spectral approach. The PCA further suggests that the Villacarli and Carrasquero subcatchments contribute most material to the flood events sampled, and that suspended sediment sources are very different in the subcatchments.

The results of this study point to badlands as the major sources of suspended sediment, thus management actions should focus on controlling sediment production from these areas. While García-Ruiz et al. (2013) think that more studies are needed to understand the evolution and functioning of badland ecosystems and that little can be done to prevent sediment export, Lee et al. (2013) demonstrate successful application of erosion control measures on previously bare badland structures developed on steep mudstone slopes in Taiwan. On studying Italian badlands that have become overgrown in recent years, Bierbaß et al. (2014) found that vegetation plays a key role in altering soil properties, resulting in more stable slope conditions. However, considering that reservoir siltation rather than loss of surface soil is the main problem in the study catchment, trapping material in or near the outlet of badlands, at the place of production, might be a more economically feasible option. Morgan (2005) describes measures such as siltation fences and artificial sedimentation ponds – capturing suspended sediment and allowing clearer runoff to flow – as suitable (temporary) measures. These might be adapted for use in badland areas. Nevertheless, for sustainable management, other sources of suspended sediment – which were found to contribute up to 40% – should not be neglected.

Overall, spectral fingerprints were found to provide a rapid, cost-efficient and non-destructive alternative to classic fingerprint properties. In the future, it is planned to compare the results of this spectral fingerprinting approach with "classic" fingerprinting based on geochemistry/radionuclides using the same samples. Thereby, a composite of spectral and classic properties may enable discrimination of other sources which could not be determined in this study. In addition, it would be of interest to study in more detail the sediment sources within the various subcatchments.

5.7 Acknowledgments

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Chapter VI
Sediment source variability: Comparison and combination of sediment flux measurements and spectral fingerprinting

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Abstract

Current research on runoff and erosion processes and an increasing demand for sustainable watershed management emphasises the need for a better understanding of sediment transport and storage dynamics. In the present study, results of sediment flux measurements and spectral sediment fingerprinting techniques were compared to observe different aspects of source contribution, and combined to characterise overall spatial and temporal variability of sediment sources in a highly erosive mountainous catchment.

Rainfall, water discharge and suspended sediment transport were measured at the outlet of the Isábena basin (445 km²) and its five subcatchment outlets from July 2011 to October 2013. Annual and event-based suspended sediment fluxes were analysed to assess transport and storage behaviour. Furthermore, colour parameters and spectral features calculated from sediment VNIR-SWIR spectra were analysed by means of Principal Component Analysis to assess clustering of samples, Discriminant Function Analysis to determine their discrimination potential, and a mixing model to identify the subcatchments' contribution to sediment collected at the outlet.

We found considerable variation in annual, seasonal and event-based discharge and sediment flux dynamics, whereas discharge was roughly proportional to subcatchment size and sediment yield related to the spatial proportion of badlands. Furthermore, the results confirm the substantial storage of sediment in the riverbed as identified by previous studies. Thereby, floods with lower total sediment yield tend to deposit, while floods with higher sediment yield remove material from the river channel. This behaviour is related to runoff characteristics and material input from subcatchments, but not to preceding events or the season of flood occurrence. The Villacarli subcatchment was identified as the major sediment source.

Though the two methods may not be easily compared, they do complement each other. In the future, hydrological modelling may provide further insights into sediment dynamics and its connection to environmental variables and flood characteristics.

6.1 Introduction

A great number of soil erosion and sediment transport studies describe the fundamental environmental and economic consequences arising from high erosion and siltation rates. Environmental consequences include for example adverse effects on water quality, aquatic habitats and related biodiversity (e.g. Owens et al. 2005). Economic aspects are related to land degradation and resulting losses in agricultural productivity (e.g. Rhoton et al. 2008), channel navigability, attractiveness for recreational use and water storage reliability of reservoirs (e.g. Navratil et al. 2010, Evrard et al. 2011, Francke et al. 2014). Most of these studies identify a need to accurately assess erosion rates and sediment yields and origin to improve understanding of the corresponding dynamics and adapt (expensive) watershed management practices (e.g. Navratil et al. 2012, Collins and Walling 2004, Merritt et al. 2003). This need is of special importance in arid and semiarid regions, such as the Mediterranean, where soils are generally shallow and often with inadequate vegetative cover (e.g. Rhoton et al. 2008).

A variety of methods exists to capture sediment dynamics at varying labour intensity, cost and accuracy. For understanding sediment dynamics of a catchment, two main methodologies can be distinguished (e.g. Rhoton et al. 2008):

Sediment fingerprinting as a means to assess catchment suspended sediment sources has attracted increasing attention in recent years (e.g. Koiter et al. 2013) with a range of innovative tracing properties (e.g. Martínez-Carreras et al. 2010a,b,c, Legout et al. 2013) and modelling approaches (e.g. Franks and Rowan 2000, Poulenard et al. 2009) being tested. The method is founded on the principal assumptions that 1) potential sources can be reliably identified based on their selected fingerprints, and that 2) a comparison of the source's and sediment's fingerprint properties allows determination of relative source importance (e.g. Collins and Walling 2004). It is associated with numerous advantages, most importantly the wide range of temporal (intra-storm to seasonal) and spatial source definition possibilities, i.e. spatial sources such as geological sub-areas or tributaries and sources types such as land use or surface vs. sub-surface (Collins and Walling 2002). On the other hand, "transformation from a research to management tool" (Mukundan et al. 2012) has been hampered by a number of currently unsolved problems. Collins and Walling (2004) criticise that generic guidelines for the pre-selection of fingerprint properties or the optimum number of samples required to characterise sediment sources do not exist, which may increase sampling and analysing intensity and thus costs involved. Furthermore, the potential of property transformation and/or enrichment during transport and storage (e.g. Smith and Blake 2014, Koiter et al. 2013) may introduce uncertainty to source estimates. Finally, the method reveals information on relative source importance only, i.e. it allows estimation of a source's percentage contribution to individual samples which cannot be easily transferred to absolute source contribution (e.g. in tons per events).

On the other hand, **flux monitoring** involves the measurement of suspended sediment fluxes from several tributary basins. Hence, a later comparison with the total sediment flux measured at the catchment outlet allows evaluation of the contribution from individual spatial sources (i.e. subcatchments) (Collins and Walling 2004). Among the advantages of such sediment flux estimates is the reduction of spatial sampling constraints in larger catchments. In addition, careful observation can reveal transport and storage behaviour. However, there are also numerous disadvantages related with this technique: it is not useful for distinguishing between source *types (*Rhoton et al. 2008) unless these are tributary-specific (Collins and Walling 2004) or for the quantification of erosion processes occurring within the catchment (Evrard et al. 2011). The required field sampling intensity and thus logistic constraints and costs involved may be high. In addition, the sampling of discharge and suspended sediment concentration is subject to numerous insecurities, ranging from data gaps due to e.g. logger failure, over-selective sampling of automated samplers and contamination of intake hoses to issues of rating curve estimation and reconstruction of continuous sedigraphs (e.g. Mano et al. 2009, Francke et al. 2014).

It is evident that the methods described above differ in their labour intensity, data requirements and output. They are both associated with individual sources and levels of uncertainties. This study aims at analysing results of the two methods, namely

- sediment fingerprinting techniques (based on spectral properties of sediment samples),
- flux monitoring techniques (installation of river gauges, turbidimeters and sediment samplers at several subcatchments),

in understanding sediment provenance and fate at different spatial and temporal scales. On one hand, the comparison of source estimates may provide a means of validating results of the individual approaches. On the other hand, the techniques may reveal different aspects of source contribution and their combination may allow further conclusions on sediment transfer and storage behaviour.

6.2 Study area

The study was conducted in the Isábena catchment, a 445 km² watershed in the Spanish Pyrenees (Fig. 6.1). Overall, the catchment experiences high erosion rates (e.g. López-Tarazón et al. 2009, Francke et al. 2014), causing severe siltation problems in the downstream Barasona reservoir and subsequently considerable loss of storage capacity (e.g. Valero-Garcés et al. 1999, Mamede 2008). Because of its heterogeneous and high magnitude sediment response, the basin has been studied intensively in the past (Bronstert et al. 2014).

The areas' altitude ranges from 2700 m a.s.l. in the North to 450 m a.s.l. in the South, resulting in a pronounced climatic and land cover gradient. The climate is of Mediterranean mountainous type, with mean annual temperatures between 9 °C in the North and 14 °C in the South (Verdú 2003). Rainfall is of high spatial and temporal variability and distributed irregularly over the catchment (e.g. López-Tarazón et al. 2010 and 2012) with annual averages of 1600 mm (North) and 450 mm (South) (Verdú 2003). The River Isábena shows a pluvial-nival runoff regime with considerable inter-annual irregularity and remarkable discharge variations (Francke et al. 2014). Major floods were found to occur following snowmelt in spring, thunderstorms in summer and heavy rains in autumn (Valero-Garcés et al. 1999). While higher altitudes are mainly covered by forests (46 % of total catchment area), shrubland (30 %) and grassland (8 %), lowlands and valley bottoms are largely used for agriculture (14 %) (Ministerio de Medio Ambiente y Medio Rural y Marino 2008). The

basin is characterized by a heterogeneous lithology with Paleozoic rocks in the North, Cretaceous and Paleocene sediments in the centre and Miocene continental sediments in the Southern lowlands (Valero-Garcés et al. 1999). A special feature is the formation of badlands on marly substrates, which are defined as “areas of unconsolidated sediments or poorly consolidated bedrock, intensely dissected and with little or no vegetation“ (Gallart et al. 2002a). Despite representing less than one percent of the catchment area, these badlands are considered the major suspended sediment sources (e.g. Fargas et al. 1997, Valero-Garcés et al. 1999, Francke et al. 2008a, Alatorre and Beguería 2009, chapter V).
The Isábena catchment is composed of five major subcatchments, namely Cabecera in the North, Villacarli and Carrasquero in the NW and Ceguera and Lascuarre in the SE (Fig. 6.1 and Table 6.1). The majority of badlands is located in the Villacarli and Carrasquero subcatchments (6 % and 2 % of their area, respectively (López-Tarazón et al. 2012)). About one-third of the catchment cannot be attributed to a subcatchment and drains directly into the Isábena River (Con-Isábena).

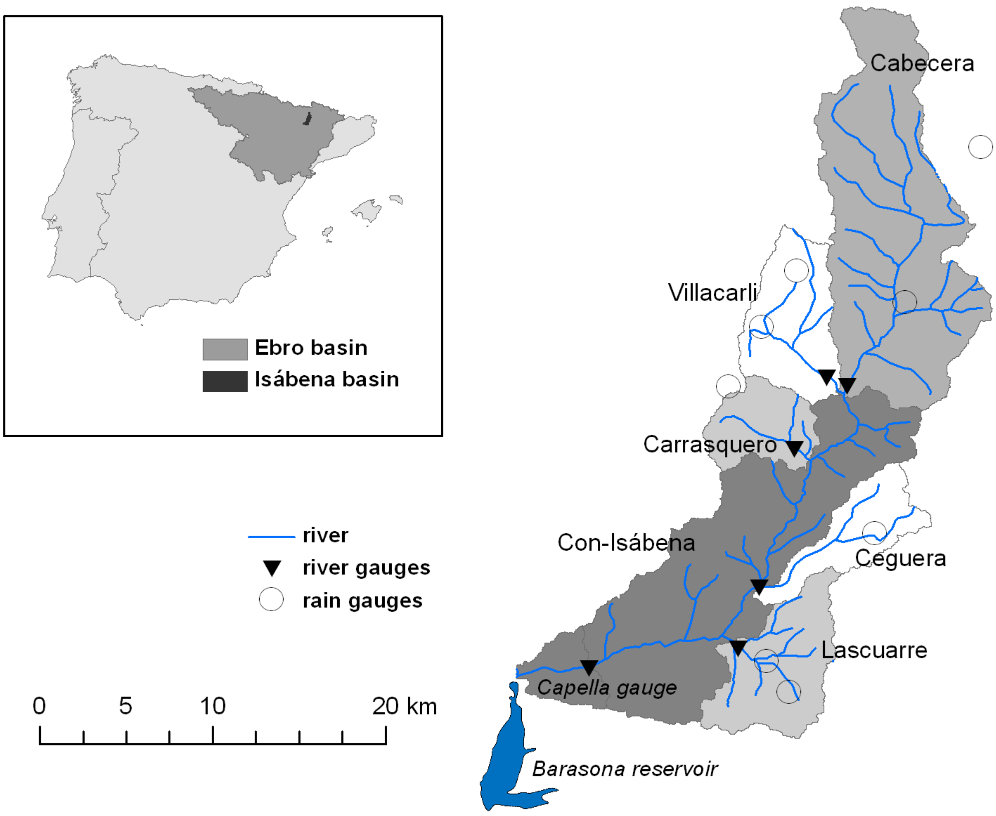

Fig. 6.1: Overview of the Isábena catchment and its subcatchments including sampling sites (river and rain gauges). Top left: Location of study area on the Iberian peninsula

6.3 Material and methods

If not specified otherwise, all data and samples were collected in the period July 2011 to October 2013. The first section (5.3.1) provides an overview of sampling methods and data availability (rainfall, discharge (Q) and suspended sediment concentration (SSC)). The following sections describe the processing of the data with regard to calculation of sediment flux (6.3.2) and spectral fingerprinting (6.3.3).

6.3.1 Sampling methods and data overview

Water

Rainfall was measured using nine tipping-bucket rain gauges distributed over all sub-catchments (see Fig. 6.1).
Water stage was recorded near the catchment outlet (Capella gauging station) by the Ebro Water Authorities (CHE) in 15-minute intervals and near the subcatchments' outlets by own installations at quasi-natural cross-sections (i.e. bridges) in 5-minute intervals. Automatic measurements with capacitive waterstage sensors (TruTrack WT-HR, Intech Instruments Ltd., New Zealand) and a microwave stage recorder (RQ 24, Sommer Messtechnik, Koblach, Austria, gauge Villacarli only) were complemented by manual meterings for a wide range of flow conditions (C2 current meter and ADC, OTT Hydromet, Kempten, Germany, salt dilution). For details on instrumentation and calibration see Francke et al. (2014).

Sediment

At the catchment outlet (Capella gauging station), turbidimeter records (Turbimax W CUS41, Endress+Hauser, Reinach Switzerland) were collected at 15-minute intervals. In addition, suspended sediment samples of river flow were collected at the catchment and sub-catchments' outlets manually and automatically using ISCO samplers (ISCO 3700, Teledyne, Lincoln, NE) on event basis. Regarding Capella, ISCO samples were only available from January 2011 to June 2012. The samplers were triggered by flow conditions to collect up to 24 samples in 15- to 180-minute intervals. Suspended sediment concentration (SSC) was subsequently determined by decanting (concentration approx. > 2 g l^{-1}) or filtering (1.2 µm FILTER-LAB glass microfiber filters), oven-drying (60 °C) and weighing of all samples. The total number of samples collected per (sub)catchment is listed in Table 6.1.

6.3.2 Sediment flux

Water stages measured at Capella gauging station were transformed to discharge (Q) using rating curves developed by López-Tarazón et al. (2010). Turbidimeter readings were transformed into suspended sediment concentration (SSC) using an updated rating curve of the original developed by López-Tarazón et al. (2009).
For calculation of the subcatchments' discharge, manual readings were used to correct logger stage records for sensor drift. Then, power-law rating curves were applied using HYDRASUB software, resulting in time series which were subsequently linearly interpolated to fill data gaps and to remove artefacts. Field observations as well as previous studies (e.g. López-Tarazón et al. 2012, Pique et al. 2014) identified other drivers apart from discharge to influence SSC, such as sediment exhaustion or temporary in-channel storage, seasonality and weathering dynamics. Thus, non-parametric, tree-based Quantile Regression Forests (QRF, Meinshausen 2006) which have proven efficient for sediment prediction

under such circumstances (e.g. Francke et al. 2008a) were used to reconstruct sedigraphs (see Francke et al. 2014 for details on predictors). A separate QRF model for each sub-catchment was calibrated with measured SSC concentrations and validated using cross-validation techniques, whereas 250 Monte-Carlo replicates allowed the estimation of suspended sediment distributions including uncertainty estimates. A detailed description of data processing at sub scale can be found in Francke et al. (2014).

Table 6.1: Summary of subcatchment geographic, discharge and suspended sediment flux properties, and number of ISCO samples used for the present study. Mean, min and max values refer to the entire study period. No. of ISCO samples represent the number of samples collected and used for calibration/validation of sediment flux, the number given in brackets represents the number of samples included in the fingerprinting approach

catchment	area [km²]	min. altitude [m]	max. altitude [m]	discharge [m³] mean	min	max	susp. sediment flux [kg/s] mean	min	max	No. of ISCO samples
Cabecera	145	827	2,671	1.61	0.22	18.96	0.14	0.00	17	259(33)
Villacarli	41	836	2,366	0.33	0.02	14.38	4.82	0.05	1,536	319(38)
Carrasquero	25	728	1,539	0.19	0.00	13.70	0.49	0.00	503	369(38)
Ceguera	29	606	1,314	0.15	0.00	25.70	0.32	0.00	96	324(35)
Lascuarre	44	552	1,139	0.07	0.00	12.40	0.12	0.00	187	375(37)
Con-Isábena	153	436	1,739	x	x	x	x	x	x	x
Isábena	445	436	2,671	3.57	0.04	123.8	6.96	0.00	6,892	254(138)

Event based

Individual events were identified based on sediment flux (Q * SSC). Event delineation was performed semi-automatically using an algorithm based on peak detection and relative changes in a moving window. The respective code has been added to the RHydro-package (Reusser et al. 2014).

6.3.3 Spectral fingerprinting

The use of spectral properties in fingerprinting applications was found to be a rapid, inexpensive alternative to classic properties such as geochemistry or mineral magnetism (e.g. Martínez-Carreras et al. 2010a, Legout et al. 2013, chapter IV). In addition, it offers the advantage of very small sampling sizes (mg) being sufficient for analyses, thus even filters from SSC assessment can be measured. Samples of ten concomitant events were available to be analysed in more detail. Events that occurred after June 2012 were excluded due to the beginning of massive road construction works in combination with changes of sampling scheme, both in the Villacarli subcatchment, and the resulting probability of changes in source characteristics. Since differences in reflectance behaviour were detected between loose sediment and material retained on filters during previous experiments (chapter V), only material retained on filters was used in this study. Filters were selected to expose no visible damage or “cracks” and prepared to contain approx. 0.2 g of material. The total number of filters measured per (sub)catchment is listed in Table 6.1.

Spectral measurements

Spectral readings were acquired using an ASD FieldSpec3 High-Res spectroradiometer (2151 bands, 0.35 – 2.5 µm) (Analytical Spectral Device, Inc., Boulder, CO) in a dark room facility. Illumination was provided by a 2000 W lamp installed approximately 70 cm from the sample at a zenith angle of 45 °. Four readings were averaged per sample, with the filter rotated 90° after every reading to reduce illumination effects. Relative reflectance was calculated automatically using a white reference panel and white reference calibration was repeated every ten measurements. More details on the experimental setup can be found in chapter IV.

Calculation of spectral fingerprint properties and tracer selection

Spectral measurements per sample were averaged, smoothed using a Savitzky-Golay filter (Savitzky and Golay 1964) and detector jumps were routinely corrected using in-house software (chapter IV). Then, spectral features related to soil organic carbon, iron oxides, clay minerals and carbonates were calculated. These physically based features were found to be characteristic of reflectance changes induced by the varying content of those soil properties. They can be described by parameterizing (a) the spectral curve, (b) a convex hull of the spectra, and (c) absorption features (from continuum normalized spectral intervals). In total, 77 physically based parameters were calculated from each sample’s spectrum. Details on relationships and calculation can be found in Table 6.2 and in chapter IV, Bayer et al. (2012) and Chabrillat et al. (2011). In addition, 21 colour parameters were calculated. Initially, R, G and B parameters were derived by averaging spectral ranges corresponding to the red, green and blue Landsat bands (0.63 – 0.69 µm, 0.52 – 0.6 µm, and 0.45 – 0.52 µm, respectively) and multiplying the values with 255 to get 8-bit encoding (Viscarra Rossel et al. 2006a). These RGB parameters were then transformed to eight other colour space models using ColoSol software developed by Viscarra Rossel et al. (2006a). In total, 98 spectral parameters were calculated.
Effects of *tracer transformation* and *enrichment* were limited by excluding spectral properties with sediment concentrations outside the range of sources values (e.g. Walden et al. 1997, Martínez-Carreras et al 2010a, Smith and Blake 2014). *Linear additivity* of spectral properties was explicitly tested in an artificial mixture experiment (chapter IV), keeping only properties meeting the linearity assumption with a root mean squared error (RMSE) of < 0.1. Finally a Kruskal-Wallis H-test was performed to remove parameters unable to *detect significant interclass contrasts* between sources (5 % confidence level) from the parameter set (Collins and Walling 2002). Following Walling (2005), parameter values were scaled to range between 0 and 1 to ensure equal consideration in subsequent statistical analyses and mixture modelling.

Table 6.2: Summary of 47 parameters that passed prerequisite testing including mean and standard deviation and percentage of correctly classified samples with discriminant function analysis (DFA %). Parameters marked with [aa] did not pass prerequisite testing when all Capella samples were included. Regarding physically-based soil properties, HF = Hull feature, AF = Absorption feature, CF = Curve feature; s = slope, r = mean reflectance, d_{max} = depth of maximum absorption, Ad_{max} = wavelength of maximum absorption, A = area between normalized continuum and spectral curve.

			Capella		subcatchments		
Colour space model / soil property	Parameter	name	mean	stdev	mean	stdev	DFA %
Decorrelated RGB	Hue	H_{RGB}	1.67	0.61	2.30	1.56	75
	Light intensity	I_{RGB}	91.37	6.48	94.49	13.22	53
	chromatic inf.	S_{RGB}	13.01	2.96	17.78	7.85	67
CIE xyY	Chromatic coordinate x	x	0.35	0.01	0.37	0.02	60
	Chromatic coordinate y	y	0.37	0.01	0.38	0.02	64
	Brightness	Y	11.45	1.76	12.89	3.94	54
CIE XYZ	Virtual component X	X	11.02	1.68	12.50	3.83	51
	Virtual component Z	Z	8.75	1.33	8.71	2.51	53
CIELUV	Metric lightness funct.	L	40.19	2.86	41.98	6.05	55
	CC red-green scale	u*	6.78	1.79	9.55	4.54	58
	CC blue-yellow scale	v*	12.85	2.83	17.04	7.44	58
CIELAB	CC red-green scale	a*	1.00	0.71	1.68	1.54	44
CIELAB	CC blue-yellow scale	b*	10.78	2.41	14.59	6.43	63
CIELCH	chroma	h*	10.84	2.44	14.75	6.47	65
Redness index	$(R)^2/(B)*(G)^3$	RI	1.64	0.61	1.76	1.63	52
Munsell HVC	Value	V	3.91	0.28	4.09	0.59	55
	Chroma	C	1.99	0.32	2.51	0.87	60
Helmholtz -	dominant wavelength	Λ_d (nm)	579.79	1.38	581.55	1.98	43
chromaticity	purity of excitation	P_e	18.67	4.62	25.13	10.94	62
Soil Organic	0.45-0.74 µm	HF1 s	0.50	0.09	0.61	0.21	62
Carbon	0.45-0.74 µm	HF1 r	0.35	0.02	0.37	0.05	48
	1.46-1.75 µm	HF2 s	0.06	0.03	0.06	0.05	53
	1.46-1.75 µm	HF2 r	0.51	0.05	0.55	0.10	41
	1/(Σ400-799 (CR-R))	SOC1	0.01	0.00	0.01	0.00	54
	1/(slope(R 400-600)	SOC2	30.42	4.78	27.19	9.84	59
	1/(slope(R 2138-2209)	SOC3	-327.39	45.40	-317.11	93.00	61

*Table 6.2**(continued from page 77)*

			Capella		subcatchments		
Colour space model / soil property	Parameter	name	mean	stdev	mean	stdev	DFA %
Iron	0.45-0.68 µm	AF3 d_{max}	0.02	0.02	0.05	0.04	64
	0.45-0.68 µm	AF3 A	0.00	0.00	0.00	0.00	56
	0.75-1.30 µm	AF5 d_{max}	0.01	0.00	0.02	0.01	55
	0.75-1.30 µm	AF5 Λd_{max}	1.00	0.00	0.99	0.01	57
	0.45-0.63 µm	AF11 d_{max}	0.02	0.02	0.05	0.04	64
	0.45-0.63 µm	AF11 A	0.00	0.00	0.00	0.00	56
	0.75-1.04 µm	AF12 A	0.00	0.00	0.00	0.00	57
	0.55-0.59 µm	CF	0.64	0.18	0.98	0.53	66
	0.45-0.75 µm	HF3 s	0.49	0.09	0.60	0.20	61
	0.45-0.75 µm	HF3 r	0.07	0.01	0.09	0.03	61
	R693)^2/(R477)*(556)^3	RI	11.91	2.31	13.72	6.18	49
Clay Minerals	2.10-2.29 µm	[aa]AF6 d_{max}	0.06	0.01	0.06	0.02	51
	2.10-2.29 µm	[aa]AF6Λd_{max}	0.94	0.01	0.94	0.02	51
	2.10-2.29 µm	[aa]AF6 A	0.00	0.00	0.00	0.00	46
	2.12-2.25 µm	[aa]AF10 d_{max}	0.05	0.01	0.06	0.01	51
	2.12-2.25 µm	[aa]AF10 A	0.00	0.00	0.00	0.00	51
	0.45-0.70 µm	HF4 s	0.54	0.10	0.67	0.23	62
	0.45-0.70 µm	HF4 r	0.07	0.01	0.08	0.03	62
	1.46-1.75 µm	HF5 s	0.06	0.03	0.06	0.05	53
	1.46-1.75 µm	HF5 r	0.01	0.00	0.01	0.01	53
	(R2133)^2/(R2225)*(R2209)^3	[aa]SWIR FI	5.06	1.06	4.89	1.91	47

Discrimination potential

Principal component analysis (PCA) was applied on source sediment and Capella sediment samples together to assess natural clustering (Poulenard et al. 2009) and overall feasibility of the fingerprinting approach (Walden et al. 1997).

The first principal assumption, i.e. that potential sources can be reliably identified based on their selected fingerprints, was then tested for sediment from the five subcatchments (sources dataset) with the discriminatory power of individual spectral properties thus tested using discriminant function analysis (DFA). Previous work found combinations of parameters (composite fingerprints) most successful in source discrimination (Collins and Walling 2002). Such composites are commonly selected by the use of stepwise DFA algorithms. However, since we found a higher number of fingerprint properties to generally decrease mixing model uncertainty (chapter IV), we tested the discrimination potential of a combination of 15 properties (correlation $R^2 < 0.9$). DFA analyses were performed using R package MASS (Venables and Ripley 2002).

Mixing model analyses (event based)

We constructed a Monte Carlo mixing model using inhouse software (ANSI-C) as detailed in chapter IV to quantify the relative contribution of each subcatchment (source) to the suspended sediment samples collected at the outlet gauging station. Given that collected source samples are subject to measurement error and may furthermore not represent the complete spatial and temporal tracer variability, each source was characterised by a Gaussian distribution function calculated from mean and standard deviation of each tracer property per source type (Martínez-Carreras et al 2010a). Since a restriction of properties as generally performed in fingerprinting studies did not improve mixture modelling results but rather increased uncertainty ranges (chapter IV), all properties that passed prerequisite testing were used in the mixing model. In total, 10,000 assessments per sediment sample were generated, thus providing mean contribution as well as uncertainty estimates.
These contribution estimates were compared with observed suspended sediment fluxes from the subcatchments on an event-base.

6.4 Results

6.4.1 Suspended sediment flux

Long-term averages

Fig. 6.2 shows the flood activity recorded at Capella gauge during the study period, with considerable variation in discharge and suspended sediment flux dynamics. This is also reflected in Table 6.3, which summarizes annual discharge and suspended sediment yield at the catchment outlet and the five subcatchments: At Capella, cumulative discharge of the ten-month period monitored in 2013 is more than twice as high as for the entire year 2012, which in turn is about twice as high as for the six-month period monitored in 2011.

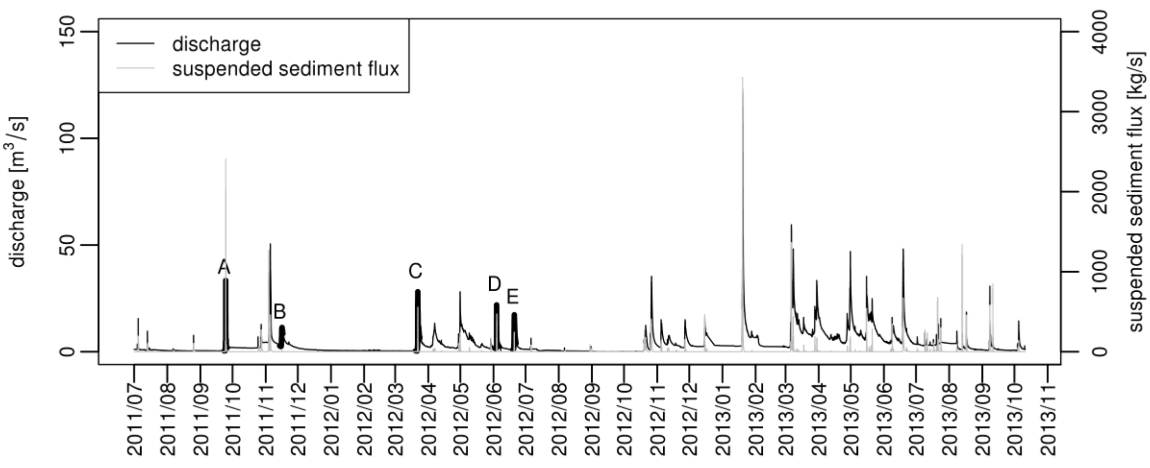

Fig. 6.2: Flood activity recorded at Capella gauge during the study period. Events analysed in detail are marked by fat line and name, their details are given in the text and Table 6.4

For all three periods, total water yield at Capella (output) is about one- third higher than the combined total yield from the five subcatchments (input). This corresponds to the area of the monitored subcatchments (two-thirds) to the unmonitored Con-Isábena (one-third). For all periods, Cabecera, being the largest and most humid subcatchment, contributes the largest share to the total water yield, followed by Villacarli, while the contribution of Carrasquero, Ceguera and Lascuarre is of minor importance.

Table 6.3: Total yield (discharge and suspended sediment) in Capella and the five subcatchments incl. sum of all subcatchment values

		2011 (6 months)	2012 (12 months)	2013 (10 months)
discharge [hm³]	Capella	30.92	70.55	156.76
	Σ subcatchments	20.48	54.13	95.53
	Cabecera	12.84	38.20	65.42
	Villacarli	5.65	8.34	9.70
	Carrasquero	1.01	2.54	10.45
	Ceguera	0.58	3.32	7.05
	Lascuarre	0.39	1.74	2.91
sediment yield [t]	Capella	90,328	98,844	266,454
	Σ subcatchments	98,202	146,783	181,801
	Cabecera	1,571	3,639	5,244
	Villacarli	89,725	126,702	132,768
	Carrasquero	4,359	5,533	25,803
	Ceguera	1,790	8,830	12,552
	Lascuarre	757	2,078	5,434

However, similar relationships cannot be observed for suspended sediment yield: While in the monitoring periods 2011 and 2012 more sediment is released from the subcatchments than exported at the outlet, sediment export in 2013 exceeds input by about one-third. In terms of suspended sediment yield, Villacarli dominates the subcatchments' contributions (Table 6.3), reflecting its high proportion of badlands. Unlike for the other subcatchments, suspended sediment flux from Villacarli is high not only during floods but also during low flow.

Event based

Fig. 6.2 shows considerable variation in discharge and suspended sediment flux dynamics, whereas high peak discharge does not necessarily imply high suspended sediment fluxes. In total, 76 flood events were recorded in the catchment during the 28 month study period considering all gauges. Of these, only 57 were observed at Capella gauging station, indicating deposition of sediment material in the channel during smaller events that did not reach the outlet. The relationship between sediment input from subcatchments and output at Capella gauge at the event base is depicted in Fig. 6.3: There is a clear tendency for events with lower total sediment yield ($Y_{sed\ Capella}$) to deposit material, while events with higher sediment yield ($Y_{sed\ Capella}$) remove more material from the catchment than is supplied by the subcatchments.

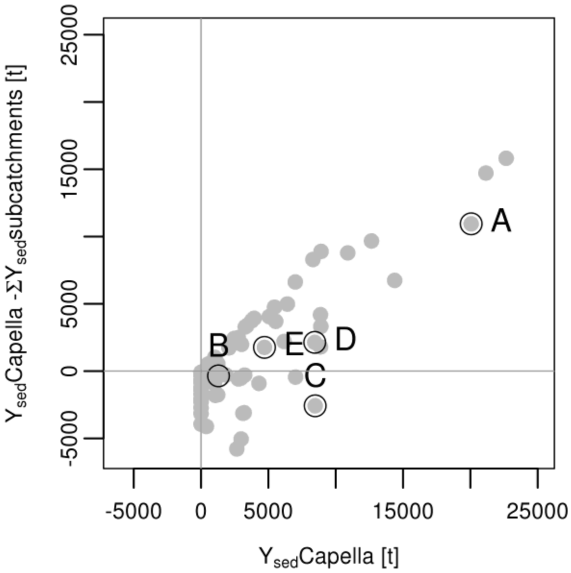

Fig. 6.3: Relationship of sediment yield Capella to sediment balance (difference yield outlet to yield subcatchments) per event. Events analysed in detail are marked by circles and event name, their details are given in the text and Table 6.4

Table 6.4: Summary of correlation of sediment balance ($Y_{bal} = Y_{sed\ Capella} - \Sigma\ Y_{sed\ subcatchments}$) with several variables of current and previous events. Events from the period January to March 2013 were excluded from analyses due to compromised data in some subcatchments during this period

	variable	R^2
event	$Y_{sed\ Capella}$	0.88
	$\Sigma\ Y_{sed\ subcatchments}$	0.33
	$Q_{max\ Capella}$	0.70
	$Y_{Q\ Capella}$	0.75
	Nr of contributing subcatchments	0.43
	Duration of event [h]	0.44
	Month of event	0.20*
previous event	Y_{bal}	-0.04
	$\Sigma\ Y_{sed\ subcatchments}$	-0.12
	$Y_{sed\ Capella}$	-0.09
	$Q_{max\ Capella}$	-0.22
	Nr of days since previous event	-0.23

* indicates Spearman rank correlation (n=67)

Thereby, total sediment yield ($Y_{sed\ Capella}$) is highly correlated with the combined sub-catchment's sediment contribution ($\Sigma\ Y_{sed\ subcatchments}$, $R^2 = 0.73$). In addition, the observed sediment balance ($Y_{bal} = Y_{sed\ Capella} - \Sigma\ Y_{sed\ subcatchments}$) is correlated with several variables describing the event (Table 6.4), such as catchment sediment yield ($Y_{sed\ Capella}$, $R^2 = 0.88$), total water yield of the event at Capella gauge ($Y_{Q\ Capella}$, $R^2 = 0.75$), and peak discharge at Capella gauge ($Q_{max\ Capella}$, $R^2 = 0.70$). Medium correlation was observed with duration of the event ($R^2 = 0.44$) and number of subcatchments contributing to the event ($R^2 = 0.43$), and only low correlation with the combined subcatchment's sediment contribution ($\Sigma\ Y_{sed\ subcatchments}$, $R^2 = 0.33$) and month of the event's occurrence ($R^2 = 0.20$). Also, variables describing conditions of the previous event (balance of previous event, sub-catchments' sediment yield of previous event, total water yield of the previous event at Capella gauge, peak discharge of previous event at Capella gauge, number of days since previous event) are not correlated with sediment balance (Y_{bal}) (Table 6.4). Events from the period January to March 2013 were excluded from these analyses due to technical difficulties in some subcatchments that resulted in compromised data quality (see Francke et al. 2014).

6.4.2 Spectral fingerprinting

Overall, spectral differences in the source materials are already apparent to the human eye, mainly in terms of colour differences between suspended sediment collected from the five subcatchment outlets: While material from Lascuarre is mostly yellowish, suspended sediment from Ceguera is mainly ochery. Material released from Carrasquero displayed the greatest heterogeneity, with colours ranging from grey over ochre and yellowish to reddish brown: noticeable colour changes occurred between as well as within events. In contrast, suspended sediment from Villacarli is mostly homogeneous and of grey colour only. Material collected at Cabecera is mostly of brownish to dark brownish colour and may contain coarser grains and/or organic particles.

Discrimination

Figure 6.4 shows a scatter plot of the first and second principal component of a PCA including all samples from subcatchments (n=181) and Capella (n=138). This analysis was performed using 41 parameters passing the prerequisite tests (Table 6.2). A clear clustering of samples by subcatchment origin becomes evident, whereas samples from Lascuarre and Ceguera show some overlap. Carrasquero displays the greatest heterogeneity as expected from previously observed colour variations. Most samples collected at Capella plot near Villacarli, Carrasquero and Cabecera samples, indicating that they are likely to consist of a combination of material from these subcatchments. However, a few samples collected at Capella plot outside the range set by subcatchment samples. These samples were collected during events in January and June 2011, before sediment sampling in the subcatchments started. Since we had to assume that these Capella samples could not be described adequately by subcatchment source material collected at later periods, and that they were also found not to meet root mean square error (RMSE) constraints set during subsequent mixture model analyses, all Capella samples collected previous to July 2011 were excluded from further analyses (78 out of 138). Re-performance of prerequisite testing on the reduced sampling set (five floods) resulted in selecting 47 properties. A summary of these properties is presented in Table 6.5.

Analyses of PCA plots further revealed that subcatchment of sediment origin and respective observed sediment colour seem to be the main reasons for clustering, while other variables such as month or year of sampling or the total sediment yield of a sample seem to be without influence.

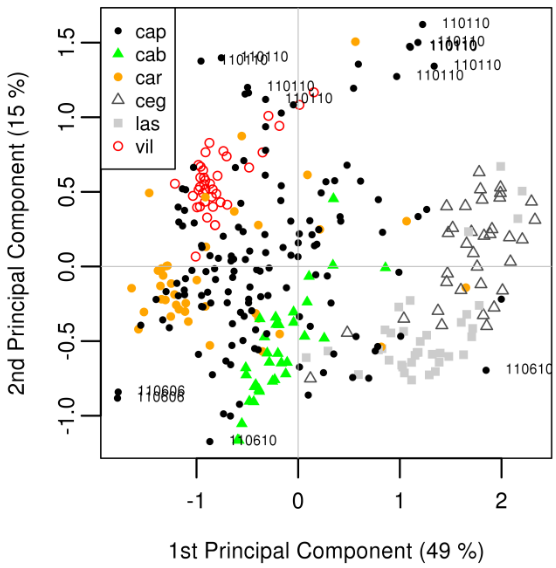

Fig 6.4: Two-dimensional scatter plot of the first and second principal component from PCA using 41 properties of all measured subcatchment and Capella sediment samples. Numbers indicate sampling dates (YYMMDD), cap = Capella, cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli

Table 6.5: Duration, total yield Q, total yield suspended sediment and max Q per event analysed in detail

				Capella (outlet)			Σ subcatchments	
event	date and time		duration [h]	Yield Q [m³]	max Q [m³]	Yield sed [t]	Yield Q [m³]	Yield sed [t]
A	09/24/2011 06:40	- 09/24/2011 21:20	14:40	452,843	33.4	20,060	112,699	9114
B	11/15/2011 15:35	- 11/16/2011 21:00	29:25	1,022,028	11.4	1,296	708,253	1,649
C	03/21/2012 20:40	- 03/23/2012 01:35	28:55	1,401,601	28.1	8,475	995,390	11,052
D	06/03/2012 19:05	- 06/04/2012 07:35	12:30	365,027	22.0	8,443	102,350	6,306
E	06/19/2012 22:10	- 06/20/2012 21:20	23:10	1,095,242	17.3	4,710	689,050	2,945

DFA was performed to assess the percentage of subcatchment source samples correctly classified (1) by each of the 47 selected properties individually. The accuracy achieved (percentage of correctly classified samples) varied between 41 and 75 % (Table 6.2). A colour parameter (H_{RGB}) was found to have the highest discrimination potential, though overall there were both colour and physically-based properties achieving high discrimination accuracies (Table 6.2). (2) A second DFA was performed using a combination of 15 properties ($R^2 < 0.9$) that were drawn from a set of properties with high individual discrimination accuracy. This combination of properties resulted in a discrimination accuracy of 98 %. Fig. 6.5 shows the clustering of source sediment samples in a scatter plot of the first two discriminant functions.

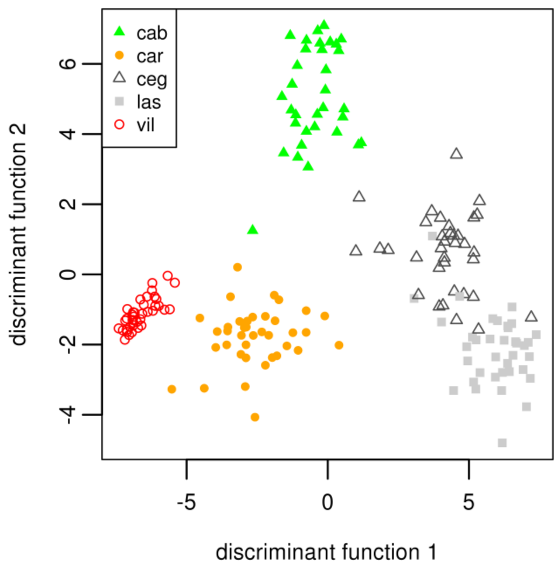

Fig. 6.5: Two-dimensional scatter plot of the first and second discriminant functions from DFA using a selection of 15 properties (percentage of correctly classified samples = 98 %) (cap = Capella, cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli)

Mixing model analyses

Fig. 6.6 to 6.10 show events A – E recorded at Capella gauge between September 2011 and June 2012. The five events display different discharge behaviour, with steep and fast receding peaks of event A (2011/09/24-25) and D (2012/06/03-04) and broader and slower receding limbs of events B (2011/011/15-16), C (2012/03/21-22), and E (2012/06/20). A summary of event characteristics can be found in Table 6.5: Duration of events A and D was shorter and total water yield was lower than for events B, C and E. However, maximum discharge was highest for event A, followed by event C and D, while peak discharge of event B and E were lowest. Suspended sediment yield was highest for event A, followed by event C and D, while yields for E and B were lower. However, suspended sediment yield from the subcatchments was highest for event C, followed by event A, D, E and B.

Considering ISCO sampling gaps for some events, the calculation of absolute mean source contribution and source variability per event from fingerprinting results is not feasible.

Furthermore, we were unable to discern characteristic time lags between sediment release from the subcatchments and sediment arrival at the outlet. This prevented a more detailed comparison between flux measurements and fingerprinting. However, general or dominant patterns can be recognized (Fig. 6.6 to 6.10): Villacarli (and Carrasquero) are the major sources in all events, while other subcatchments contribute little and usually only during low flow / flux. Also the two peaks of sediment material released from Villacarli and Carrasquero in event A are clearly visible in the mixing model result (i.e. sample A01 to A06 and sample A15 to A23) (Fig. 6.6). The mixing model generally tends to overestimate the contribution from Cabecera as compared to the measurements – both on event scale as well as on annual scale. Contribution from Ceguera and Lascuarre is overestimated by the model for some samples (e.g. A08 – A13 and B09 – B15 for Ceguera, B01 – B06 for Lascuarre) while underestimated for others (event C).

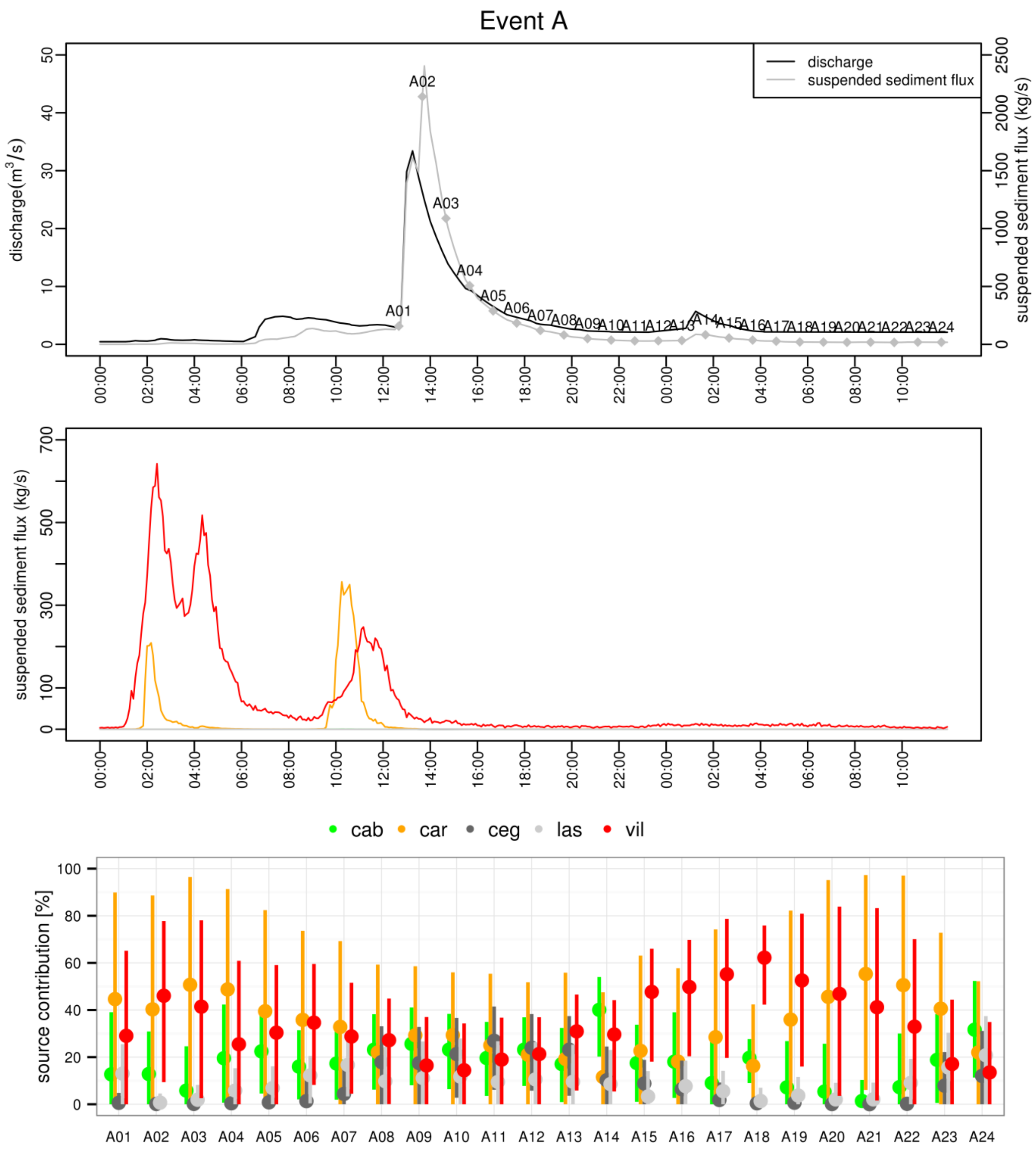

Fig. 6.6: Discharge, suspended sediment flux and ISCO samples for Capella (top), suspended sediment flux recorded simultaneously at subcatchments (centre) and estimated suspended source contribution for each ISCO sample (bottom) for event A (September 24th /25th 2011). Dots indicate mean estimates, bars indicate confidence intervals at 90 % level. (cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli)

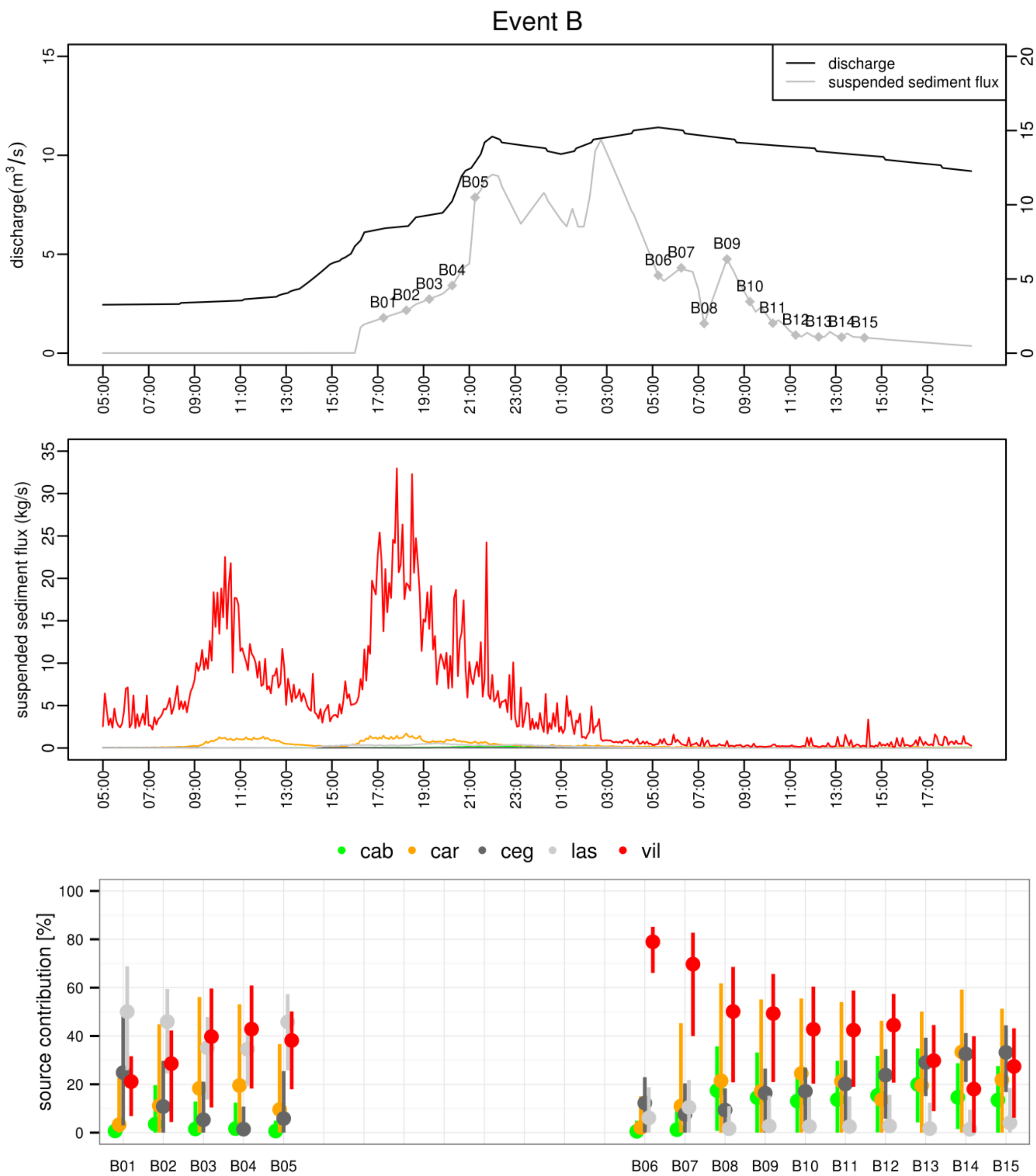

Fig. 6.7: Discharge, suspended sediment flux and ISCO samples for Capella (top), suspended sediment flux recorded simultaneously at subcatchments (centre) and estimated suspended source contribution for each ISCO sample (bottom) for event B (November 15th /16th 2011). Dots indicate mean estimates, bars indicate confidence intervals at 90 % level. (cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli)

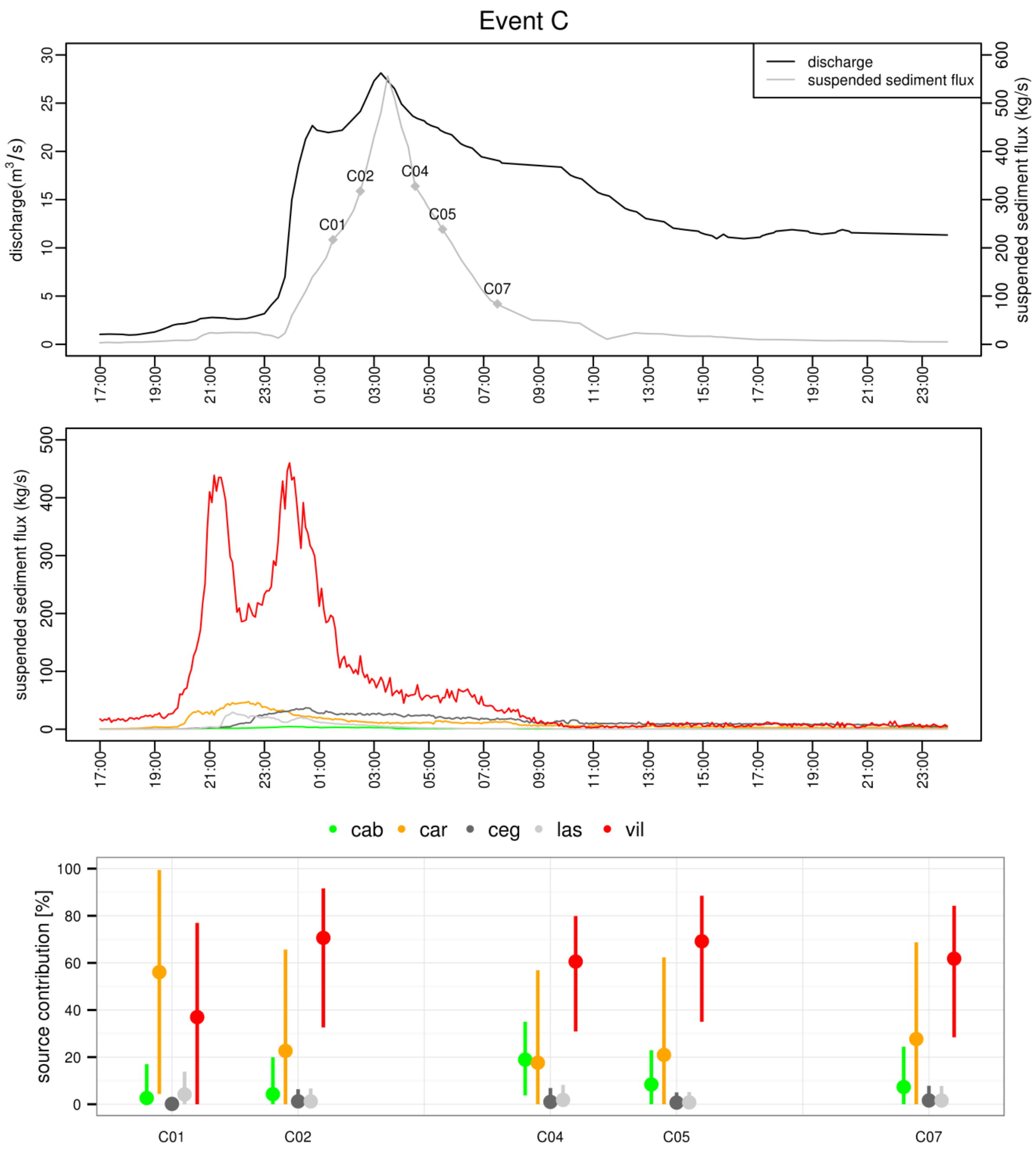

Fig. 6.8: Discharge, suspended sediment flux and ISCO samples for Capella (top), suspended sediment flux recorded simultaneously at subcatchments (centre) and estimated suspended source contribution for each ISCO sample (bottom) for event C (March 22nd 2012). Dots indicate mean estimates, bars indicate confidence intervals at 90 % level. (cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli)

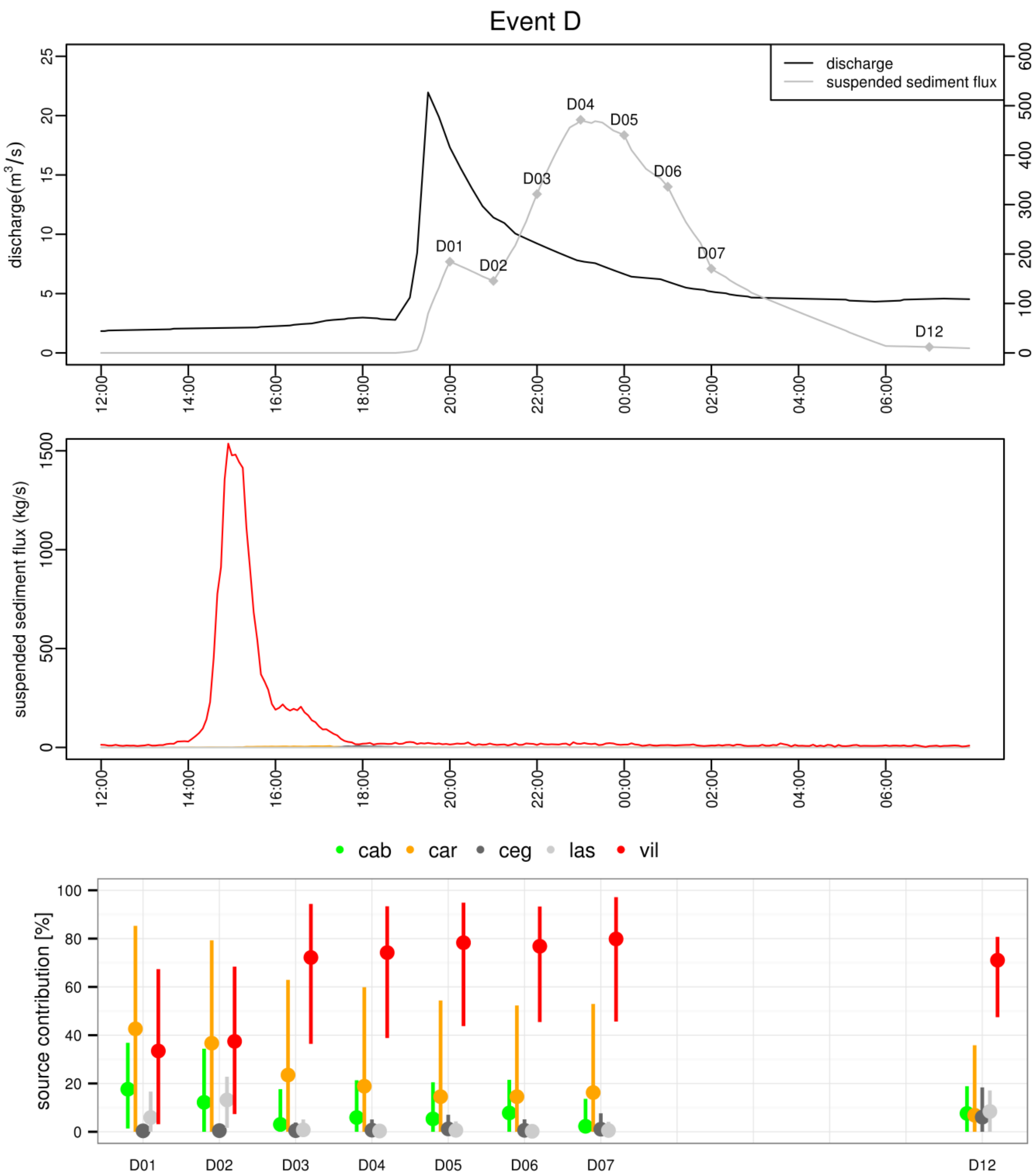

Fig. 6.9: Discharge, suspended sediment flux and ISCO samples for Capella (top), suspended sediment flux recorded simultaneously at subcatchments (centre) and estimated suspended source contribution for each ISCO sample (bottom) for event D (June 3rd/4th 2012). Dots indicate mean estimates, bars indicate confidence intervals at 90 % level. (cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli)

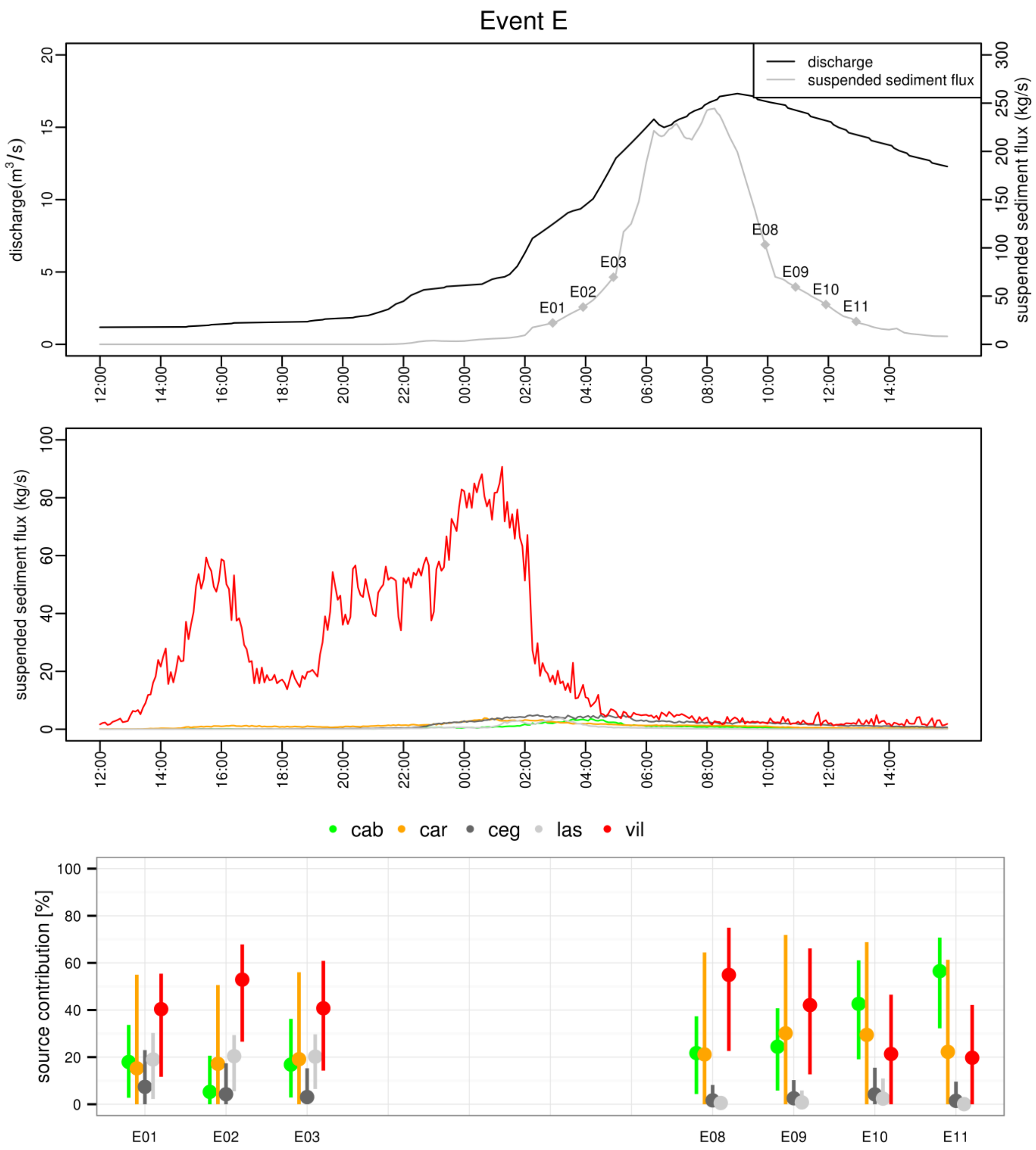

Fig. 6.10: Discharge, suspended sediment flux and ISCO samples for Capella (top), suspended sediment flux recorded simultaneously at subcatchments (centre) and estimated suspended source contribution for each ISCO sample (bottom) for event E (June 20th 2012). Dots indicate mean estimates, bars indicate confidence intervals at 90 % level. (cab = Cabecera, car = Carrasquero, ceg = Ceguera, las = Lascuarre and vil = Villacarli)

6.5 Discussion

6.5.1 Suspended sediment flux and conveyance

Discharge behaviour of the years 2011 and 2012 is closer to observed long-term averages, while 2013 shows both a higher flood activity in general as well as peak discharges above average (Francke et al. 2014).

The observed discrepancies between subcatchment input and catchment output (Y_{bal}) are considerable on event- and annual scales. While excess sediment at the outlet ($Y_{bal} > 0$) could also be attributed to input from the unmonitored Con-Isábena, sediment deficit ($Y_{bal} < 0$) can only be explained by deposition in the river channel. Thus, as long-term budgets also indicate low sediment inputs from Con-Isábena (Francke et al. 2014), storage effects appear to be the most probable explanation. Analyses of long-term averages in sediment yield suggest a considerable storage potential for the River Isábena. López-Tarazón et al. (2011) reported estimated sediment storage values of up to 55 % of the annual load during certain periods. They also identified a roughly annual cycle of sediment production and downstream transfer, which was confirmed by Piqué et al. (2014), with the sediment being produced in badlands during winter, transferred to the main channel during spring, stored in the river during summer and, finally, exported out of the basin by the autumn floods. This cycle could not be confirmed by the present study. However, the pattern may be difficult to capture due to the highly irregular precipitation (López-Tarazón et al. 2011), the non-linear character of the runoff and sediment response relationship (Gallart et al. 2002b, Mathys et al. 2005) and its connection with seasonal heterogeneity of weathering dynamics in badlands as the major sediment source (e.g. Gallart et al. 2002b, Regües et al. 2004).

A detailed analysis of sediment fluxes at the subcatchments and Capella allowed general conclusions to be drawn on deposition/export relationships on an event base. A high correlation between sediment balance (Y_{bal}) and material exported at the catchment outlet ($Y_{sed\ Capella}$) was observed: whereas events with lower total sediment yield generally tend to deposit, events with higher total yield seem rather to remove material from the river channel (Fig. 6.3). This relationship was found to be somewhat independent of subcatchments' sediment input and more connected to current than to previous event characteristics, which contradicts the findings by López-Tarazón et al. (2010) on the effect of flood succession generating an 'exhaustion effect' for subsequent floods and seasons. Previous research in Mediterranean basins identified soil moisture, total precipitation and storm size as the most important factors in runoff generation (Gallart et al 2002b, Seeger et al. 2006). In addition, site-specific and temporally variable erodibility conditions (Mathys et al. 2005, Evrard et al. 2011), may result in strong seasonalities of runoff generating and, subsequently, sediment transport and accumulation processes. However, neither of these factors nor their possible interrelations could be considered in our rather simple correlation approach to explain the evident deposition/export_relationship. Hence, to understand these relations in more detail, the application of a hydrological model in combination with a hydraulic and channel-storage module (e.g. Mueller et al. 2006) may be useful to (1) include variables not considered in the present approach, like rainfall characteristics and antecedent moisture conditions, as well as (2) potentially complex feedback relationships between variables. However, such a modelling approach may be complicated due to the large data requirements and complex nature of processes and interactions at catchment scale (e.g. Merrit 2003, de Vente et al. 2006) and thus was beyond scope of this study.

6.5.2 Sediment sources

PCA and DFA revealed high discrimination accuracy between the subcatchments' suspended sediment sources. A previous study on a reduced number of samples revealed that while there are little subcatchment specific differences in source *soils*, *suspended sediment* released from the individual subcatchments differs greatly (chapter V). This suggests that there are major differences in source type (i.e. soil originating from different land use) among the subcatchments. In the present study, the PCA further revealed that Capella sediment samples from certain events (generally before June 2011, especially January 2011) were different from all subcatchment sediment samples collected after July 2011. The same events also caused difficulties in mixing model analyses. According to Walden et al. (1997), this may indicate either that not all sources have been sampled appropriately and/or that major changes have occurred during transport. This led us to conclude that before July 2011, different erosion processes may have been active and/or different sediment sources may have been connected to the channel in one, several or all of the subcatchments. The month of January in particular has not been sampled for suspended sediment in any subcatchment due to technical constraints, suggesting that ice- and snow-related processes may have played a role in sediment generation and/or alteration. This is in agreement with Valero-Garcés et al. (1999) who state that the flood producing mechanism may affect its sedimentological characteristics. When analysing changes in riverbed sediment over a period of two years, Evrard et al. (2011) found temporal variations in the contributions of different (geological) sources. However, Capella samples also collected in June 2011, a month sampled at all gauges during the following years, were found to be outside the range other subcatchment material collected later.

The Villacarli subcatchment was found to be the major source of suspended sediment in all focus events, which is in agreement with flux measurement. This dominant contribution was also detected by previous studies. Francke et al. (2014) found more than 80 % of suspended sediment to originate from Villacarli in the study period 2011 - 2013 and López-Tarazón et al. (2012) determined up to 61 % for the study period 2007 - 2009. Except for the large contribution of Carrasquero to event A, identified by both fingerprinting and flux measurement, none of the other four subcatchments revealed such dominant contribution characteristics for any other event. In fact, the other catchments contribute little to the total yield of the events considering that their large contribution identified by the mixing model is usually limited to the low flux stages. This points less to an increased contribution from these subcatchments but rather to a decrease in contribution from Villacarli. The especially large contribution of Lascuarre and Ceguera during the rising limb (e.g. event B) may be attributed to the closeness of these subcatchments sources to the Capella outlet. No stringent explanation was found for the comparably large contribution of Cabecera identified by fingerprinting but not by flux measurements. While errors in the flux measurements cannot be ruled out completely, the consistent disagreement between these and the results from the mixing model for all events do not qualify them as an explanation regarding the contribution of Cabecera. The mixing model may have confounded heterogeneous Carrasquero material with sediment supplied from Cabecera. Also, the obviously high organic content characterising Cabecera sediment (brownish colour, organic particles) may result in confusion of organic material supplied by other sources with sediment originating from Cabecera. Furthermore, darker materials spectrally dominate intimate mixtures such as sediment particles since the photons have a higher probability of being absorbed by darker grains (Clark 1999) which may also result in overestimation of organics as in the Cabecera material. Finally, though alteration of spectral properties cannot be excluded, we do consider them to be of minor importance with regard to (a) the absence of evidence of particle size selective transport and (b) results of submersion experiments performed by Legout et al. (2013). Due to its similar lithological and landscape characteristics with Lascuarre, the outlet catchment itself (Con-Isábena) is not expected to act as having caused this signal. However, despite overall agreement between flux measurements and mixing model analyses, its omission as a source in the fingerprinting study may add additional uncertainty to the mixing model results.

In addition to the assessment of spatial sediment origin (i.e. subcatchments), the fingerprinting offers the advantage of source-type based assessment (e.g. land use) if source sampling is performed accordingly. A comparison between the presented subcatchment-based fingerprinting and a former land use-based fingerprinting (chapter V) for four of the five focus events revealed similar patterns: The contribution of Villacarli and Carrasquero subcatchments corresponds to the contribution of badland sources (< 10 % difference). This is in agreement with the high proportion of badland areas in these two subcatchments that were identified as major sediment sources by previous research in the Isábena (e.g. Valero-Garcés et al. 1999, Francke et al. 2008a, Alatorre and Beguería 2009, Piqué et al. 2014) and similar catchments (e.g. Navratil et al. 2012). The only exception is event E, where the combined contribution from Villacarli and Carrasquero exceeds the contribution of badlands, indicating that sediment sources other than badlands must have been active during this event – most likely in Carrasquero, displaying the greatest heterogeneity in sediment colour and thus expected to expose greatest heterogeneity in sediment source type. Other land uses traced in the preceding study (chapter V) cannot be attributed to individual sub-catchments that directly.

6.5.3 Sediment fluxes and comparison with fingerprinting

It turned out to be difficult to compare the results of sediment flux measurements and the fingerprinting approach. Not only may estimates by both methods be subject to considerable uncertainty (e.g. Navratil 2011, Francke et al. 2014, chapter IV, Smith and Blake 2014, Koiter et al. 2013) but also the time lag between sediment release from subcatchment and sediment arrival at the catchment outlet, in combination with differences in travel time due to source distance and event characteristics, can confound source ascription. In addition, Fig. 6.3 as well as Tables 6.3 and 6.5 point to substantial storage in the river channel playing a major role in the Isábena catchment, which is in agreement with findings for the Isábena (López-Tarazón et al. 2011) and similar catchments (Navratil et al. 2010). Though López-Tarazón et al. (2012) report a sediment delivery ratio of 90 % from slopes to the catchment outlet, material released from a subcatchment during an event may not reach the outlet or may be mixed with material deposited in the channel from previous events during transport.

Following hysteretic analyses, López-Tarazón et al. (2009) hypothesize that “at the flood scale, the river channel controls the transport of sediment, occasionally acting as the main source of sediment and other times as a sink”, which was later confirmed by Piqué et al. (2014).
Hence, there is not necessarily a connection between measurement of suspended sediment released from subcatchments and fingerprinting results at the basin outlet, neither on an event base nor during longer periods. In fingerprinting terms, this storage behaviour masks source contribution. This is in agreement with Evrard et al. (2011), who detected rather different trends when comparing mixing model results and measurements of suspended sediment yield on four occasions within two years. Nevertheless, general patterns seem to be transferred to the outlet, such as Villacarli being the major source for the two sediment flux peaks from Villacarli and Carrasquero during event A.
There were major differences between the five events analysed in detail, from B and C where deposition occurred and not all material released actually reached the outlet, to events A, D and E where (much) more material was exported from the catchment than was supplied by the subcatchments. For the reasons described above, a detailed assessment of what was released from subcatchments and what was recorded at Capella during the same flood was not feasible for any of the focus events, neither by means of fingerprinting nor by flux measurements. However, the event-based analysis of flux measurements from the five sub-catchments and Capella revealed not only the importance of sediment storage but also a relationship between event characteristics and sediment deposition/export. It has been argued previously that fingerprinting can only provide information on the ultimate sediment source and does not consider storage and travelling time (e.g. Parsons 2012). The analysis of sediment flux in the present case demonstrates very clearly that a direct transport of source material to the catchment outlet as assumed by the fingerprinting approach cannot be generally expected. For the 450 km² Isábena catchment, sediment does not seem to be transferred from the subcatchments to the outlet immediately, not during individual flood-events and potentially not even during longer inter-storm periods, making source ascriptions somewhat less meaningful. As has been discussed by other authors (e.g. Collins et al. 1998, Mukundan et al. 2012), there may be a catchment size-dependency from which scale source (type) fingerprinting could be less successful. Here, we propose to consider not only catchment size but also the catchments sediment transfer and storage behaviour in assessing the feasibility of source contribution estimates by means of fingerprinting.

6.6 Conclusion

Our results showed that both methods have their advantages and drawbacks and though their outcomes may not be easily compared, they do complement each other. Among others, Evrard et al. (2011) and Navratil et al. (2012) strongly recommend the combination of such different techniques to improve our understanding of sediment origin and dynamics. The monitoring of the subcatchments and the catchments suspended sediment fluxes revealed general sediment export and deposition behaviour on an event-basis and its connection with discharge characteristics and sediment supply. Though intense storage in the river channel rendered proximal source ascriptions by means of fingerprinting impossible, spectral properties were found to be very suitable for (spatial) source ascriptions. Furthermore, the fingerprinting approach revealed potential changes in erosion processes and/or source connectivity that could not have been detected by means of flux measurements only. However, considering catchment size and storage behaviour, inter-event, monthly, seasonal and/or annual sampling approach (or a combination thereof) using sediment traps in the river channel or reservoir deposits may be more appropriate for effective source assessment. In the future, incorporation of the results into a hydrological and sediment transport model may provide further insights into erosion processes, sediment accumulation in and removal from the channel and along-channel connectivity for sediment transfer.

6.7 Acknowledgements

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Chapter VII
Discussion and conclusion

7.1 Discussion of main results

The overall goal of this thesis was a comprehensive assessment of the potential of soil spectroscopy in providing innovative properties for sediment fingerprinting. In the previous chapters, this potential was thoroughly investigated by a detailed test of methods under controlled conditions (chapter IV), application of these methods (chapter V) as well as a comparison with other methods of sediment provenance evaluation (chapter VI). This integrated approach of method development and application provided numerous scientific outcomes that will be discussed in the following sections with respect to the key questions defined in chapter I.

(1) *Can potential sediment sources be reliably identified based on VNIR-SWIR spectral fingerprints?*

Source discrimination is site as well as source specific. Whether a parameter can differentiate between source types largely depends on how these sources differ, as well as on intra- and inter- source variability. Thus, a fingerprint property, or selection of properties may be applied successful in one catchment or for a specific source definition, while it may be even better suited or fail completely in a different setting. Discrimination results for different source definitions are presented and discussed in chapter IV and VI.

In case of the Isábena catchment, selections of VNIR-SWIR spectral properties could reliably identify three source types, namely badlands, soils from forests and grassland, and an aggregation of soils from agricultural land, shrubland, open slopes and unpaved roads ('other sources'). Especially within this aggregated source type, intra-source variability was very high. Unfortunately, these 'other sources' could not be further discriminated by means of spectral fingerprinting. A fingerprinting study conducted by Palazón et al. (2014) in the Isábena catchment showed that agricultural soils could be discriminated using geochemical, radionuclide, and magnetic susceptibility properties. Though they worked with different samples and with different focus, this indicates that a combination of spectral with classic properties might offer a cost-effective and timesaving, yet very efficient solution in cases were spectral properties cannot discriminate all sources considered important.

In terms of spatial source definition, selections of VNIR-SWIR spectral properties were unable to discriminate different lithologies, with exception of the northernmost subcatchment (Cabecera), were the bedrock differs most in terms of lithology and geological evolution from the rest of the catchment. These differences between Cabecera and the southern subcatchments were found for soil as well as for resuspended sediment samples. Thereby, lithology in the south consists mainly of sediments rich in carbonates (limestone, marl, calcrete) that can be considered (spectrally) rather homogeneous. However, spectral fingerprints were able to differentiate between suspended sediment material from all five subcatchments with very high accuracy. Obviously, intra-source variability was much lower and inter-source contrasts were higher when regarding sediment from individual subcatchments than soil from the entire catchment area. This implies that the major source types may differ greatly between the individual subcatchments.

Overall, discrimination results are well within range of results obtained by other studies, using spectral (Martínez-Carreras 2010c) as well as classic properties (Collins and Walling 2002, Walling 2005), and regarding number of sources as well as accuracy.

(2) *Do these spectral fingerprints permit the quantification of relative source contribution?*

Results of the artificial mixture experiment, where source contributions were modelled under controlled conditions, are presented and discussed in chapter IV. This experiment provides valuable insights into the unmixing process and on factors influencing quantification accuracy:

In general, the use of spectral parameters is appropriate, whereas the introduction of source heterogeneity decreases modelling accuracy, especially when intra-source variability is high. This advises a choice of parameters with little intra-source heterogeneity. However, a suitable variability measure has yet to be found, as it turned out that e.g. the commonly applied coefficient of variance was inappropriate (results not shown).

Surprisingly, aggregation of source types that could not be reliably differentiated did not improve mixture modelling results – apparently, accurate source discrimination does not necessarily imply successful mixture modelling, as is generally assumed in fingerprinting studies. Nevertheless, the results of the mixture experiment provide valuable insight on the interpretation of sediment source ascriptions, where the true contribution is unknown.

The experiment further revealed a decrease of estimated uncertainty with increasing number of properties included in the modelling procedure. This is consistent with findings of Franks and Rowan (2000) and Martínez-Carreras et al. (2010a) and suggests rethinking of the conservative selection procedure to create composite fingerprints consisting of a minimum of available properties. Instead, the choice of suitable properties should be left to the mixing model itself, as proposed by Franks and Rowan (2000). Again, a suitable measure, this time for model improvement, has yet to be detected.

As outlined in chapter I, there are very few (published) studies working with artificial mixtures, which is most likely due to the labour intense and expensive retrieval of many classic fingerprint properties. Some studies work with computed artificial mixtures (e.g. Laceby and Olley 2014) but there may be complex interactions within mixtures (Lees 1997) not correctly represented by such simulated mixtures. We agree with Lees (1997) in stressing the importance of artificial mixture experiments to test capabilities and limitations of fingerprint properties as well as of modelling procedures. This includes for example the rigorous testing of property suitability as outlined in the next section. In addition, e.g. the effects of weighting factors (e.g. for tracer homogeneity), property normalization, and model-inclusive property selection procedure could be easily assessed.

(3) *Is in situ derived source information sufficient for spectral sediment fingerprinting?*
In addition to providing insight on the interpretation of unmixing results, the artificial mixture experiment revealed that in situ source information is insufficient for source contribution modelling (chapter IV). This is most likely due to differences in grain size and soil moisture between undisturbed field samples and processed sediment samples. In addition, while lab samples consisted of the top 1 - 3 cm of soil, in situ measurements were performed on the soil surface, which may not have been perfectly representative of the sample e.g. due to soil crusts. Thus, a similar treatment of source and sediment samples is strongly recommended. However, since in situ source information provided comparable discrimination accuracies as laboratory derived source parameters, this is another indication that successful source discrimination does not guarantee successful mixture modelling. That is despite the fact that the selection of fingerprint properties was limited to those parameters where all sediment properties were within the range of soil properties, a measure that should reduce the effect of possible tracer transformation (e.g. Walden et al. 1997, Smith and Blake 2014). As such, spectral in situ measurements, proposed to be tested by several authors (Martínez-Carreras 2010a, Poulenard 2012), are not suitable for fingerprinting assessments - at least not in the VNIR SWIR range. A further implication following from that discovery is the need to carefully assess not only the discrimination potential of fingerprint but also their quantification potential. Of course, it also discourages the use of airborne or satellite imaging spectroscopy data for an anticipated even less labour intense while spatially more representative retrieval of source information.

(4) *What does the spectral fingerprinting approach reveal when applied to sediment and how do relative contributions from different sources vary?*
Chapter V describes a detailed assessment of sediment source ascriptions by source type (i.e. land use) by applying the methods developed in chapter IV. Results indicate that soil from all major sources has been sampled, and that if any property transformation occurred, it may have been rather small (Walden et al. 1997).
Thereby, source attributions meet the general expectations for this catchment based on field observations and previous studies (e.g. Valero-Garcés et al. 1999, Alatorre et al. 2010, Francke et al. 2008a,b, 2014): Despite covering 54 % of the catchment area, forest and grassland sources contribute little (usually < 10 %), while badlands, representing less than 1 % of the catchment area, were identified as main contributors (60 – 80 %) to all samples analysed. All other sources (i.e. agricultural land, shrubland, open slopes and unpaved roads) cover 45 % of the study catchment and were found to contribute up to ~ 20 - 40 % to suspended sediment material during flood events. This general pattern in source contribution (badland > other >

forest/grassland) is very stable, though minor differences can be observed between as well as within individual storm events. These cannot be attributed to differences in rainfall only, which, being distributed irregularly over the catchment, causes differences in runoff response. In addition, similar rainfall-runoff characteristics resulting in different source ascriptions point to the role of material stored in the river channel. López- Tarazón et al. (2010) identified an 'exhaustion effect' of material accumulated in the channel bed, indicating that depletion of these secondary sources may represent an important factor in controlling sediment response. However, a seasonal pattern in sediment availability from primary as well as secondary sources as described by López-Tarazón et al. (2011) and Piqué et al. (2014) could not be observed, neither from analysis of suspended river flow nor from resuspended channel bed material.

When interpreting changes in source contribution, one should keep in mind that the fingerprinting approach only provides information on the relative source contribution. Thus, the observation of higher contributions from one source may simply result from lower contribution of another source at the same time, e.g. during the falling limb when suspended sediment concentration generally decreases. Therefore, estimated relative contributions could be transferred to absolute values. However, depending on the sampling setup, such a transformation may be difficult and highly inaccurate.

(5) *How do spectral fingerprinting results compare with sediment flux measurements and what does a combination of methods reveal about sediment origin, transport and storage?*

The two methods used to assess spatial sediment origin as presented in chapter VI revealed different aspects of sediment provenance and were found rather unfeasible to be combined.

In summary, flux measurements exposed considerable discrepancies between sediment input from the five major subcatchments and sediment output at the catchment outlet, both at flood and annual scale. In-channel storage effects appear as the most probable explanation, which is consistent with previous observations (López-Tarazón et al. (2011) and Piqué et al. (2014)). However, their described annual cycle could again not be confirmed. A more detailed analysis of the deposition/export relationship on a flood event-basis suggested that events with low total sediment yield generally tend to deposit while events with higher total yield rather remove material from the river channel. A simple correlation approach of this behaviour indicates a connection to current but not to previous event characteristics, which contradicts the source depletion effect that was described by López-Tarazón et al. (2010) and considered likely in the explanation of source contribution changes in chapter IV.

The fingerprinting results presented in chapter V profit from the enormous advantage of spectral fingerprinting to rely on small amounts of material only. Whereas results discussed in chapter IV and V were mostly derived from measurements of loose source soil and sediment material (> 2 g), all measurements presented in this chapter were taken from glass fibre filters, enabling consideration of samples even of minor events with low SSC. Spectral fingerprinting revealed the Villacarli subcatchment to be the major suspended sediment source, which is in agreement with flux measurements for the same period (Francke et al. 2014) as well as with previous observations López-Tarazón et al. (2012). It is also in good agreement with the high contribution of badland sources identified in chapter V and by Valero-Garcés et al. (1999), Alatorre et al. (2010) or Francke et al. (2008a,b). However, there were also major differences between flux and fingerprinting contribution identification, e.g. regarding the contribution of the Cabecera subcatchment, for which no stringent explanation was found.

Overall, a comparison of sediment flux monitoring and sediment fingerprinting was found difficult due to the substantial in-channel storage potentially masking source contribution, and lags in travelling time from subcatchments to the outlet that differ with source distance and event characteristics. General patterns, such as Villacarli with its high percentage of badlands being the main sediment source, were uncovered by both methods. However, sediment flux monitoring clearly demonstrated that a direct transport of source material to the outlet as assumed by the fingerprinting approach is wrong, at least in case of the studied Isábena catchment. This highlights the major criticism on the fingerprinting approach in general: It can only provide information on the primary (ultimate) sources of sediment, whereas the effects of travel time and storage cannot be considered, potentially revoking the entire provenance analysis (Parsons 2012).

However, the fingerprinting approach was also found to have its justification, since the combination of methods revealed findings that no method could have revealed individually: the flux monitoring identified the general export/deposition relationship and its connection with discharge behaviour and sediment supply, and thereby pinpointed the immense storage potential controlling sediment dynamics and hampering the fingerprinting approach. On the other hand, fingerprinting revealed potential changes in erosion processes and/or source connectivity that could not have been detected otherwise.

Future provenance assessments are strongly recommended to consider sediment transfer and storage behaviour of the studied catchment in the design of sampling schemes and keep in mind that the sampled sediment may not originate directly from the primary source(s). As stressed by Evrard et al (2011) and Navratil et al. (2012), complementary methods such as flux measurements and fingerprinting should continue to be combined to improve our understanding of sediment origin and dynamics.

7.2 Directions of future research

The discussion of main results presented in the section above has already highlighted a number of potential directions of future research. These, as well as additional research questions unanswered or uncovered by this work will be outlined in the following section.

Fingerprint properties

Discrimination potential of the spectral fingerprint properties applied in this thesis has been carefully tested for various source definitions. Thereby, it was found that in the studied catchment, three *source types* could be reliably identified, whereas one of these source types comprised actually an aggregation of four different types (i.e., shrubland, agricultural land, open slope, unpaved road) that could not be further discriminated.

Using a different set of samples, Palazòn et al. (2014) showed that agricultural sources could be discriminated by a combination of geochemical, radionuclide and magnetic susceptibility properties in the Isábena catchment. Thus, the potential of a fingerprinting approach using a combination of classic properties (e.g. geochemistry, radionuclides, and mineral magnetism) should be attempted, at least where sample material is sufficient. Since both classic and spectral fingerprinting use the same fundamental approach and involve numerous uncertainties, neither technique can serve as independent validation of the other (Martínez-Carreras et al. 2010a). However, as the classic properties are more established, results of classic and spectral fingerprinting should be compared to evaluate the potential of each technique. Also, a possible improvement of the approach by combining classic and spectral properties should be assessed.

However, though thoroughly assessed, the potential of VNIR-SWIR spectroscopy to provide fingerprint properties has not been fully exhausted by the present study. Preliminary tests of spectral features with no exact physical basis demonstrated high discrimination accuracies of individual properties. Based on a moving window for a defined maximum wavelength interval, seven spectral parameters were calculated as described by Schodlok (2004) (i.e., mean, standard deviation, ratio of first and last band of chosen interval, area of spectral curve between first and last band, minimum band depth within interval, and 1st and 2nd order polynomial). Depending on spectral resolution and choice of wavelength interval, thousands of variables can be generated automatically using this algorithm. For testing purposes, 180,156 spectral features were calculated, scaled and submitted to Discriminant Function Analysis to assess the discrimination potential of each variable individually (for three *source types*). All variables reached discrimination accuracies > 50 %, 134,438 (75 %) variables reached accuracies > 60 %, 49161 (27 %) variables reached > 70 % and 5386 (0.03 %) variables reached > 80 % discrimination accuracy. A maximum accuracy of 84.9 % was yielded by a number of 18 variables individually. For comparison, the highest accuracy achieved by a colour parameter was 77 %, and 76 % for a physically based property. However, a potential drawback of the 'artificial feature' approach may be that handling of such amounts of data can be complicated, and property selection procedures might have to be adapted.

In addition, absorbance spectra or derivatives of VNIR-SWIR spectra could be further explored in the future. Furthermore, Viscarra-Rossel et al. (2006b) demonstrated the potential of MIR spectra for the assessment of soil properties in general, and Poulenard et al. (2009, 2012) and Evrard et al. (2013) for fingerprinting purposes in particular.

Mixing models

The mixing model is a central element in the confident quantification of sediment sources (Laceby and Olley 2014). Therefore, a vast number of slightly different modelling approaches have evolved over the past decades of fingerprinting research, starting from simple algorithms relying on one mean value to represent each source (e.g. Walling et al. 1999) to complex models incorporating parameter selection procedures (e.g. Franks and Rowan 2000) source heterogeneity (e.g. Martínez-Carreras 2010a,b), uncertainty estimates (e.g. Martínez-Carreras 2010a, Rowan and Franks 2000, Small et al. 2002, Motha et al. 2003), and / or weighting and correction procedures (e.g. Motha et al. 2003, Collins et al. 1997). Constraints can be set, and output accuracies are assessed by various means. However, due to the unknown nature of true source contribution, the success of many of these options remains somewhat unclear. Recent studies suggest that integration of some options may be rather harmful than helpful in source ascription, mainly increasing uncertainty or worse, blurring results (e.g. Smith and Blake 2014, Laceby and Olley 2014). Therefore, we recommend a rigorous testing of available modelling options using artificial mixtures as presented in chapter VI of this thesis. The long term overall goal could be a generic mixing model applicable by scientists as well as managers interested in sediment provenance.

Tracer conservativeness

An issue in the focus of current fingerprinting studies but beyond the scope of this work is the conservativeness of fingerprint properties (e.g. Koiter et al. 2013, Smith and Blake 2014). Particle size selective transport, enrichment of organic carbon and (e.g. geochemical) transformation of tracers are of great concern to the community. Though concerns have been expressed in the past (e.g. Peart and Walling 1986), conservativeness has been naturally assumed by most studies. Some authors have tried to incorporate correction factors in their model (e.g. Motha et al. 2003, Collins et al. 1997) but considering that enrichment and transformation processes are complex, poorly understood and furthermore probably highly site-specific, other authors fear that this may only increase uncertainty (e.g. Martínez-Carreras et al. 2010a). Smith and Blake 2014 present a test of several correction factors and strongly discourage their application. Instead, they recommend to limit the selection of tracers to those where sediment properties fall within the range of source properties, as has previously been suggested by Walden et al. (1997) and Martínez-Carreras et al. (2010a). In addition, considering the vast number of possible transformation processes given the complexity of a river basin, Koiter et al. (2014) suggest to focus on the selection of fingerprint properties that are less likely to be subject to transformations. This could be attempted e.g. by submersion experiments as performed by Poulenard et al. (2012) and Legout et al. (2013). However, though general conclusions may be drawn on tracer transformation from such experiments, size selective transport and enrichment are highly site-specific and thus would have to be assessed for each study catchment individually.

Therefore, it appears that finding a means to investigate and account for tracer conservativeness will remain in the focus of fingerprinting studies.

7.3 Conclusion

Considering the general site-specifity of the fingerprinting approach, spectral properties are very suitable for sediment source discrimination. They do allow source quantification by the use of mixture models. However, artificial mixture experiments indicated constraints most likely attributable to intra-source variability that may also apply to 'classic' properties not yet tested in similar approaches. These experiments further revealed that, despite providing similar discrimination accuracies, in situ source information is insufficient for source contribution modelling. When applied to sediment samples of a 445 km² study catchment, the spectral fingerprinting approach was able to discriminate and quantify the major sediment sources, by *source type* as well as *spatially* by subcatchment. Nevertheless, a comparison with flux measurements of the same sampling period highlighted the fact that immediate transport from sources to the catchment outlet cannot be assumed in the Isábena basin and thus in-channel storage may mask details in the behaviour of primary source contribution.

In summary, spectral properties were found to provide a fast, non-destructive, cost-efficient approach to trace back sediment sources, offering an alternative or possible supplement to classic properties. In case of the Isábena, a combination of spectral and classic properties might allow a more detailed *source type* discrimination. This thesis answered many questions, but as the section 'directions of future research' shows, many more questions are still open or were raised by this study, especially regarding the potential of further spectral properties, the rigorous testing of mixing models, and tracer conservativeness.

Besides the academic motivation of this research, the understanding of sediment provenance is a prerequisite for sound and sustainable management decisions. In order to serve as a management tool, the procedure of fingerprinting including all the methodological steps should be concisely and, if possible, simply defined. Properties - such as spectral parameters - that are cheap and fast to derive, and whose conservativeness should become ascertained, in combination with the availability of a reliable mixing model would greatly facilitate the transfer of fingerprinting from a mere research to a management tool. Thereby, researchers as well as water resource managers should keep in mind the major limitation of the fingerprinting method highlighted by this study, namely that it only provides information on primary sources but does neither consider storage behaviour nor travelling time. However, sediment fingerprinting, especially using spectral properties, can provide a cheap and fast idea of general sediment origin, and in combination with other monitoring techniques a sound base for management decisions.

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