universität wien

MASTERARBEIT / MASTER'S THESIS

Titel der Masterarbeit / Title of the Master's Thesis

„Tracing discharge in the Southern Pyrenees – comparing fingerprinting approaches for tracer selection"

verfasst von / submitted by

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

Master of Science (MSc)

Wien, 2019 / Vienna 2019

Studienkennzahl lt. Studienblatt / degree programme code as it appears on the student record sheet:	A 066 855
Studienrichtung lt. Studienblatt / degree programme as it appears on the student record sheet:	Masterstudium Geographie UG2002
Betreut von / Supervisor:	Dr. Sabine Kraushaar

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Wien, am 28.01.2019

Jakob Heinzle, BSc

Acknowledgments

First of all, I thank my mentor and supervisor Dr. Sabine Kraushaar at the University of Vienna. Thank you for fascinating me for this project, taking your time to join us during the field campaign and for always being available for questions and discussions.

I also want to thank the University of Vienna to fund this study with a conveyor scholarship, which was necessary to be able to set up the field work.

Additionally, I want to thank Janika Kiep from the Freie Universität Berlin who helped during the field trip although she was working on her own master thesis.

I really appreciated the possibility to join the Department Of Catchment Hydrology at the UFZ in Halle for my two visits. Thank you Dr. habil. Christian Siebert for introducing me into your field of study, answering many of my questions and giving me a chance to work in the laboratory at the UFZ.

A special thanks goes to Cornelia Wilske at the UFZ, who took time off her PhD work to support me in the laboratory.

Moreover, I want to thank Silke Köhler at the UFZ, for giving me the chance to work individually at the laboratory in Halle and supporting me with my sample analysis.

I want to thank all of my friends at the University and additionally all members of the *Engage* working group for making be feel at home during my studies.

A special thank you to my dear friend Matthias Konzett. Without our countless project partnerships during our studies, I would not have been able to come this far.

From all of my heart I thank my dear parents Beate & Wilfried, who always stood behind me, supported me in my decisions and gave me the financial possibility to study in Vienna.

And finally, I thank you Johanna, for giving me so many reasons to step aside from work, but also for motivating me to finish my thesis just in time.

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a.s.l	Above sea level
CO	Conglomerate source area
CSIC	Consejo Superior de Investigacioness Cientificas
DEM	Digital elevation model
EC	Electrical conductivity
EMMA	End-member mixing analysis
EU	European Union
FP	Fingerprint
HCO_3	Hydrogencarbonate/bicarbonate
HDPE	High-density Polyethylen
IC	Ion chromatography
ICP-MS	Inductively coupled Plasma – mass spectrometry
KW	Kruskal-Wallis
LDA	Linear discriminant analysis
LD	Linear discriminant
LS	Limestone source area
NO_3	Nitrate
MA	Marl source area
REE	Rare Earth Elements
SO_4	Sulphate
SS	Sandstone source area
SWAT	Soil and Water Assessment Tool
UFZ	Helmholtz Zentrum für Umweltforschung (Halle, Germany)
USGS	United States Geology Survey
WFD	water framework directive
WHO	World Health Organisation

1. Introduction

1.1 The impact of dams on a river system

Semi-arid and Mediterranean regions all over the world suffer from increased water scarcity (BRONSTERT ET AL. 2014) To optimize water usage for agricultural, residential, industrial or commercial use as well as flood control, many countries decided to build dams and reservoirs at river catchment outlets (KONDOLF 1997).

Although reservoirs help to use water more efficiently, they also can lead to severe ecological problems within the river catchment. By disrupting ecological systems into nonconnected parts, the whole catchment area up- and downstream is affected (GRANT ET AL. 2003). Issues coming with this range from flow regime changes due to the altering of flood peaks (GRANT ET AL. 2003), to fishes being prevented from moving or the interruption of bedload and sediment movement, resulting in high incisive "hungry" rivers downstream of dams, as well as the siltation of reservoirs (KONDOLF 1997).

Due to climatic factors, areas such as the Spanish Pyrenees with lots of dams built, suffer from increased sensitivity to sediment mobilisation (VALERO-GARCÉS ET AL. 1999). This is due to the low vegetation cover as well as wide areas of bare soil, high intense rainfalls and high connectivity from slope to the river (LÓPEZ TARAZÓN ET AL. 2009). High rates of sediment movement from the catchment slopes downstream, lead to a rapid and ongoing siltation of reservoirs. This decreases their water storage capacity until the sediment gets removed, which requires large financial investments (VALERO-GARCÉS ET AL. 1999).

Therefore, the goal for many local governments is to decrease sediment yield and sediment transport into the river and downstream to the reservoir. Due to the fact that financial resources are often sparse, it is of interest to find low cost but highly effective ways to address the issue. Because the removal of dams is rarely an option, ways to tackle the fast siltation of reservoirs are in high demand. Therefore, information of sediment production and transport in a time- and spatial scale at a catchment level is needed (PALAZÓN AND NAVAS 2017).

1.2 Fingerprinting as a tool to trace sediment from source to sink

One way to address sediment and water provenance within a river catchment, the so-called 'fingerprinting technique', is getting increased attention within the scientific community (KOITER ET AL. 2013).

Fingerprinting is based on the idea that source areas within a river catchment can be attributed with distinct signals based on their lithological, soil or land use setting. These signals, called 'fingerprints', are reflected in the chemical characteristics of the sediment eroded on the slope, but also in the chemistry of the rivers draining these source areas (COLLINS ET AL. 1997). The assumption of fingerprinting studies is, that the mixture of information of all source fingerprints can be found in their combined sink. Therefore, by comparing fingerprints from different sources with each other and with a sink sample, it is possible to calculate the relative contribution of the input sources by using unmixing models (WALLING 2005). Although the aim of fingerprinting studies may be different, they all follow the same conceptual framework, which is given in *Fig. 1.1* modified after COLLINS AND WALLING (2002) and BROSINKSY ET AL. (2014).

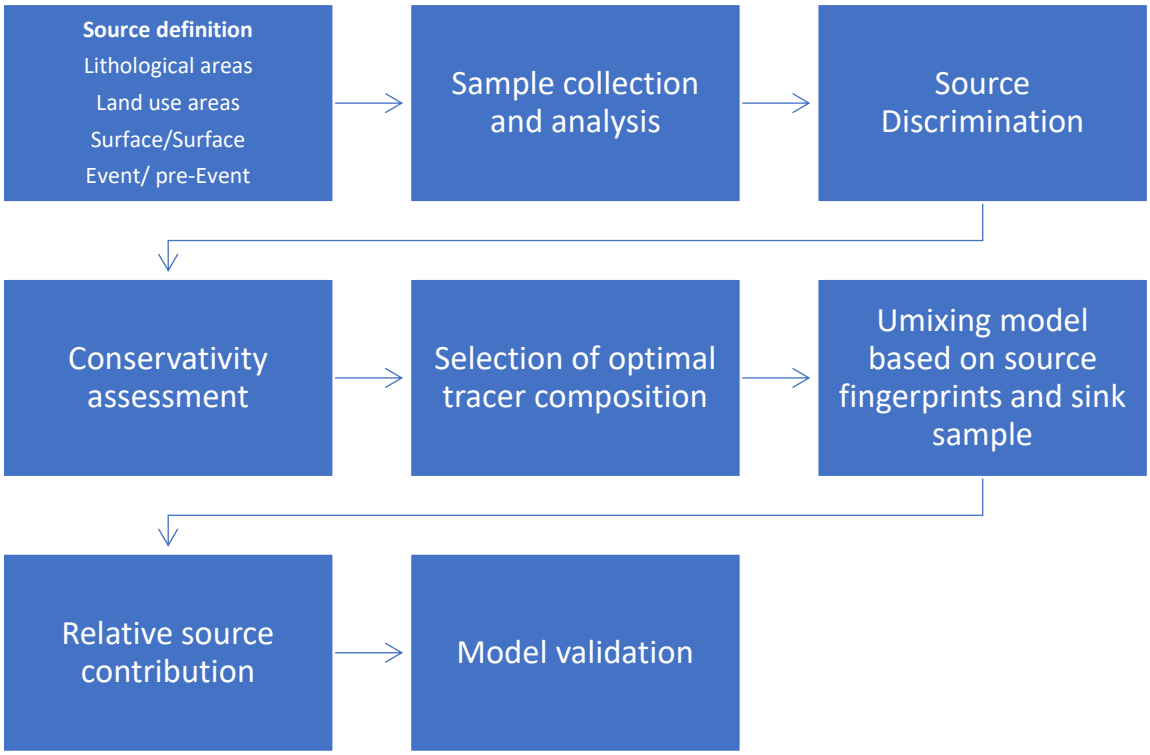


Fig 1.1 : Conceptual framework of fingerprinting studies, modified after COLLINS AND WALLING (2002) AND BROSINKSY ET AL. (2014).

Fingerprinting studies have been performed in a wide range of scientific fields, especially in geomorphology and hydrology or geochemistry. To show how these techniques developed, what their key principles, similarities and differences are, and how a combination of both could lead to new insights, will be presented in the following

1.2.1 Sediment fingerprinting

In the community of geomorphology, the fingerprinting tool was mainly developed by A.L. Collins and D.E. Walling from the University of Exeter. They addressed soil erosion and sediment transport since the 1990s. Their basic fingerprinting idea was to gather sediment properties (e.g. element concentrations, isotope ratios, biological parameters, etc.) from different possible sediment sources and compare them with the same properties of the sediment at the river catchment outlet, the so called sink (WALLING 2005).

They stated, that under the assumption, that the sink sample is a mixture of sediment from all relevant sources, it was essential that also the sediment properties in the sink reflected those of the sediment sources (COLLINS ET AL. 1997).

The goal therefore was to find those sediment properties of different sources which are unique for one source and could be used to discriminate between different sources. However, as already WALLING ET AL. (1993) described, no single property would be enough to use as reliable source discriminating tool as it may be reflected in multiple sources or its concentrations may change in a non-linear way within the river catchment. Because of this, later sediment fingerprinting studies analysed a large set of different possible discriminating properties, so through statistical analysis, a composition of the best properties, the so-called 'composite fingerprint' could be put together (e.g. WALLING 2005, PALAZÓN ET AL. 2016, KRAUSHAAR 2016).

1.2.2 Hydrological fingerprinting

In hydrology and geochemistry, the focus is not on sediment eroded from the slope but instead on the chemistry of river water within a catchment. Hydrological fingerprinting studies have been implemented under the assumption that river water chemistry varies between tributaries within a catchment due to different lithological and weathering

conditions (HELLMANN 1999). The idea to characterise flows throughout the catchment has been developed already in the 1970s (INAMDAR 2011). The concept is similar to the sediment fingerprinting performed by geomorphologists. However, instead of analysing sediment on the slope which might get eroded and then transported via the stream down to the sink, river water chemistry at different spring waters is used as source information. Additionally, it is important to notice, that in hydrological studies, the term 'property' for discriminating parameters between sources is exchanged for the term 'tracer' in hydrological studies.

By analysing the mixture off all tributaries in the catchment runoff on the one hand as well as characterizing possible sources within the catchment on the other hand, mixing models have been developed to determine the contributions from the different sources to the mixture at the catchment outlet (INAMDAR 2011). The aim of these models therefore was to determine the geographic sources of water (GENEREOUX AND HOOPER 1998). The principle of these mixing models require the base assumption, that waters coming from different areas of the catchment, gather distinct chemical information which is then transported downstream. These signatures, also called 'fingerprints', are the basis of source discrimination. Only if the fingerprints from the sources of interest are distinct, mixing models can produce a meaningful output. However, while initially it was assumed that waters take up chemical information of all areas which they flow through, recent publications claim that the last source interaction has the highest impact on water chemistry (INAMDAR 2011).

The first hydrological fingerprinting studies, developed during the 1970s mostly used stable isotopes ($\delta O^{18}/\delta D$) and major anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-) or cations (Mg^{2+}, Ca^{2+}, K^+, $Na^{+)}$ as tracers (INAMDAR 2011). While some of them only were interested in general watershed behaviour, many models were used to distinguish between water from base flow and water from flooding events. Stable isotopes ratios of oxygen (O^{18}/O^{16}) and hydrogen (H^2/H), given in relation to a standard, are still one of most common tracers used in hydrology, as they have several advantages (SKLASH AND FARVOLDEN 1979, KENDALL AND DOCTOR 2003):

- Stable isotope ratios have distinct signatures in base flow and flooding events

- Stable isotope ratios differ between locations at distinct elevations due to a Rayleigh fractionation
- Stable isotope ratios are considered conservative until mixing with other waters

In the past couple of decades, tracer selection and the statistical process to relate the sink to the sources have been constantly improved and several reviews (CHRISTOPHERSEN AND HOOPER 1992, HOOPER 2003, BARTHOLD ET AL. 2011) showed popular tracers or demonstrated pitfalls of the method. Especially the statistic assessment of data processing has been developed a lot. While earlier studies like SKLASH ET AL. (1976) only used one tracer to distinguish between water sources, the implementation of multivariate statistical analysis (HOOPER ET AL. 1992) required a set of tracers which allowed the choice to choose the ones which discriminate the sources with the best power. Since then, the term of 'end member mixing analysis' (EMMA) has been established in hydrological fingerprinting studies. Whereas the term 'hydrograph separation' is related to the separation of water sources in different time steps (e.g. pre-event vs. event water), EMMA targets the distinction of geographic water sources (BARTHOLD ET AL. 2011).

1.2.3 Comparison of sediment and hydrological fingerprinting

Comparing sediment and hydrological fingerprinting, most general principles of are similar, which is also shown in recent review and case study articles (e.g. INAMDAR 2011, BARTHOLD ET AL. 2011, KOITER ET AL. 2013, COLLINS ET AL. 2017). However, it is important to notice, that both methods have been developed uninfluenced by each other, as none of the major reviews seem to cite one another.

To sum up the presentation of the general fingerprinting idea, *Tab. 1.1* shows an overview and comparison of principles from hydrological and sediment fingerprinting regarding tracer selection and processing.

The first principle is regarding the conservativity of the used tracers or properties. Similar to each other, INAMDAR (2011) addresses that tracer concentrations must not change due to biogeochemical processes over the time scale considered, while KOITER ET

AL. (2013) state that properties must not change from source to sink or evolve due to anaerobic zones, changes in underlying geology or anthropogenic influences.

However, there seems to be a major difference in regarding conservativity of tracers between sediment and hydrological fingerprinting studies. While both communities regard conservativity of tracer as a major issue, hydrological fingerprintings often rely on simple correlations between tracers throughout the catchment to show conservativity, which his suggested by HOOPER (2003). In sediment fingerprinting studies, conservativity is given an increased focus, as shown in the review of COLLINS ET AL. (2017), who emphasise on conservativity related issues such as solubility, connectivity or organic matter induced changes.

However, INAMDAR (2011) additionally focusses on conservativity of the sources regarding their chemical composition . This means, that the chemical composition of sources must not change over the time that is considered by the mixing model (INAMDAR 2011). If differences between base flow and flooding events want to be addressed, a single fingerprinting study based on data from one of the states would not be sufficient, due to expected change of chemical composition between the two states. Similar issues are addressed by COLLINS (2013) and COLLINS ET AL. (2017) regarding sediment. Seasonal changes in climate, pollution or anthropogenic input might change property concentrations in sources, sinks and also affect the connectivity between them. Additionally, it is mentioned, that if sediment depositions are analysed during different timesteps, some tracers cannot be assumed to be conservative due to atmospheric pollution.

The second principle is regarding the representativity of the selected tracers. As BARTHOLD ET AL. (2011) and KOITER ET AL. (2013) state, it is essential that the selected tracers have different concentrations between the regarded sources. Only if the concentrations are somewhat extreme in regard to each other, they can be used as valuable discriminators between the sources.

In hydrological mixing studies, additionally the importance of linear mixing is emphasized (BARTHOLD ET AL. 2011). This means, that in order to assume conservative behaviour of soluble ions and elements like most major ions and salts, tests for linear

change between multiple ions within the river system are usually performed. Although relying on this aspect to ensure conservativity is far from exact, there is no better way to ensure soluble tracer conservativity available at the moment (BARTHOLD ET AL. 2011). Additionally, the importance of linear mixing is emphasising that streams joining together need a certain amount of time and space until mixing is completed and representative samples can be taken (FISCHER 2013).

Tab. 1.1 additionally shows examples of used tracer in hydrological and sediment fingerprinting studies. In hydrological studies, mostly a selection of major ions and stable isotopes is used (BARTHOLD ET AL. 2011). Some studies like BURNS ET AL. (2001) also used parameters which are regularly measured on site like *pH* and electrical conductivity, however the conservativity of these parameters is hardly ever reliable. Only few studies like LADOUCHE ET AL. (2001) or FRÖHLICH ET AL. (2008) successfully used trace elements like *Li, Rb, Sr* and *Ba.*

In contrast to hydrological fingerprinting, sediment fingerprinting has been applied with a broader set of trace properties (*Tab.. 1.1*). These range from physical properties like colour (BARTHOD ET AL. 2015) and grain size (WELTJE 2012) to many chemical properties like clay mineralogy (EBERL 2004), radionuclides (PERG ET AL. 2003), stable isotopes and isotope ratios (FOX AND PAPANICOLAOU ET AL. 2008) to biological properties like soil enzymes (NOSRATI ET AL. 2011) or pollen (BROWN 1985).

The wide spectrum of applied tracers or properties for mixing models shows that due to the uniqueness of each river catchment at a given timestep, it is not predictable in advance which tracers are the best to analyse and use for the modelling process. Therefore, the bigger the set of analysed properties, the better is the set of properties which then can be chosen for the source discrimination and mixing model. The absolute minimum to solve the mixing model thereby is one less than the amount of sources (BARTHOLD ET AL. 2011).

With the comparison of sediment and hydrological fingerprinting mentioned above, it can be concluded that it would be of interest to compare the methods with each other in an actual case study. To do that, a catchment with a broad spectrum of already performed fingerprinting studies would be optimal, as it would allow to compare results

with each other. The Isábena catchment in the Southern Pyrenees was found to be the optimal study area, as many studies have been performed in the past decades, which will be described in detail in the following.

Tab. 1.1 : Comparison of principles for hydrological and sediment fingerprinting from recent reviews

	Hydrology (Tracer)	*Sediment (Properties)*
CONSERVATIVITY	Tracer concentrations must behave conservative over time scale considered (INAMDAR 2011). The chemical composition of the sources must be similar within the source groups (INAMDAR 2011).	Properties must not change from source to sink (KOITER ET AL. 2013). Properties need to be measurable and comparable between source and sink (COLLINS ET AL. 2017). Seasonal patterns and possible changes need to be considered (COLLINS 2013). If properties evolve, they must to so in a predictable manner (KOITER ET AL. 2013).
REPRESENTATIVITY	The source solutions have extreme concentrations to be able to distinguish the sources (BARTHOLD ET AL. 2011).	Properties need to be representative, they need to be able to distinguish between at least two sources (KOITER ET AL. 2013, COLLINS ET AL. 2017).
LINEAR MIXING	Stream water is a mixture of source solutions with a fixed composition (BARTHOLD ET AL. 2011). Mixing process is linear and relies completely on hydrodynamic mixing (INAMDAR 2011, BARTHOLD ET AL. 2011).	
USED TRACER	Chemical tracers: Stable isotopes ($\delta^{18}O$, δD) (SKLASH AND FARVOLDEN 1979), major ions and (Ca, K, Mg, Na, Cl^-) pH and EC (BURNS ET AL. 2001), trace elements (Li, Rb, Sr, Ba (FRÖHLICH ET AL. 2008).	Physical properties: colour (BARTHOD ET AL. 2015), grain size (WELTJE 2012). Chemical properties: Clay mineralogy (EBERL 2004), geochemistry (COLLINS AND WALLING 2002), Radionuclides (PERG ET AL. 2003), stable isotopes and isotope ratios (Yang et al. 2008). Biological properties: soil enzymes (NOSRATI ET AL. 2011), pollen (BROWN 1985).

1.3 Fingerprinting studies in the Isábena catchment

Sediment mobilisation and transportation as well as river water discharge has been studied in various ways in the Isábena catchment, beginning in the 1990s. Most of the studies are related to the Barasona reservoir, which is located at the catchment outlet. The Barasona reservoir was first constructed in the 1930s with its capacity of 71hm³ which was enlarged in 1972 up to 92hm³ (LÓPEZ-TARAZÓN 2011).

Regardless of the enlargement, a survey in 1995 estimated that about one third of the reservoir has been filled with sediment in the first 65 years after construction (SALAS ET AL. 1997). Despite the other contributing catchment to the reservoir, the Ésera catchment, (1532km²) is larger than the Isábena catchment, the sediment input from Isábena contributes massively.

As siltation of reservoirs grew to become a major problem in several areas of Spain, especially in the Pyrenees, SALAS ET AL. (1997) addressed the sediment input of the Barasona reservoir at the outlet of the Isábena. Their showings of the high impact of reservoir siltation and enormous costs of removing sediment, made way for further studies in the area.

The first proper assessment of sediment movement in the Isábena catchment was carried out by VALERO-GARCÉS ET AL. 1999. They addressed the mineralogy of suspended and river channel sediments during floods and tried to relate them to different source areas. Although their assessment of sediment provenance was lacking additional data, they concluded that the appearance of floods increased in the past decades and there was a strong correlation between sediment movement and flooding events, while sediment production was closely related to anthropogenic influence in active or abandoned agricultural areas (VALERO-GARCÉS ET AL. 1999).

After some quiet years, the University of Potsdam in partnership with the University of Lleida and also the University of Zaragoza focussed again on the Isábena catchment. The setup of several discharge measuring stations (FRANCKE ET AL. 2008), the regular analysis of suspended sediments during different weather conditions (LÓPEZ TARAZÓN ET AL. 2009, ALATORRE ET AL. 2010) and the assessment of connectivity through in-channel

sediment storage (LÓPEZ TARAZÓN ET AL. 2011) allowed to create sediment and water budgets for the Isábena catchment. LÓPEZ TARAZÓN ET AL. (2012). Their findings included high variabilities in runoff and sediment transportation dynamics with relatively constant baseflow (LÓPEZ TARAZÓN ET AL. 2009), high in-channel connectivity with only about 5% of sediment being stored within streams, and a total sediment input into the Barasona reservoir of about 0.36 hm^3, which equals about 0.4% of the reservoir storage volume (LÓPEZ TARAZÓN 2012). One of their major findings also included the high importance of a small area of marls (<1% of catchment), which contributes heavily to the sediment production, especially during flooding events (FRANCKE AND LÓPEZ TARAZÓN 2014).

FIG. 1.2 shows the results of sediment and water budgets calculated by LÓPEZ TARAZÓN ET AL. (2012) based on continuous discharge and sediment yield measurements. The study was performed for two 1-year study periods (*Fig 1.2 (A,B))* and also the two-year average is shown (*Fig. 1.2 (C))* . As already mentioned, most of the sediment input was attributed to the badlands in the Villacarli sub-catchment and the agriculturally shaped Lasquarre sub-catchment in the south. The water mass balance shows the majority of input through the northern sub-catchment of Cabecera. Unfortunately, input from secondary streams within Cabecera or the unnamed southwestern part of the catchment was not addressed by LÓPEZ TARAZÓN ET AL. (2012). The large variation in sediment and water balance within the two 1-year study periods is notable and has to be addressed in discussing results based on one-time measurements.

The first fingerprint study in the area was carried out by BROSINSKY ET AL. (2014). By performing a sediment fingerprinting study based on spectral properties of suspended sediments coming from different land use areas, they managed to reproduce the findings of FRANCKE AND LÓPEZ TARAZÓN (2014), and contributed about 60-80% of sediment produced during flooding events to the marl areas, while most of the other sediment was associated with agricultural areas in the south of the catchment.

A more recent study by PALAZÓN ET AL. (2016) combined a sediment fingerprinting study with the Soil and Water Assessment Tool (SWAT) in order to track sediment provenance of sediment samples from different areas of the Barasona reservoir. Their

findings agree with those of BROSINKSY ET AL. (2014) and found the marl areas to be the most important sediment contributors. The latest study by PALAZÓN AND NAVAS (2017) focussed on implementing different statistical variations in the fingerprinting procedure and tracer selection.

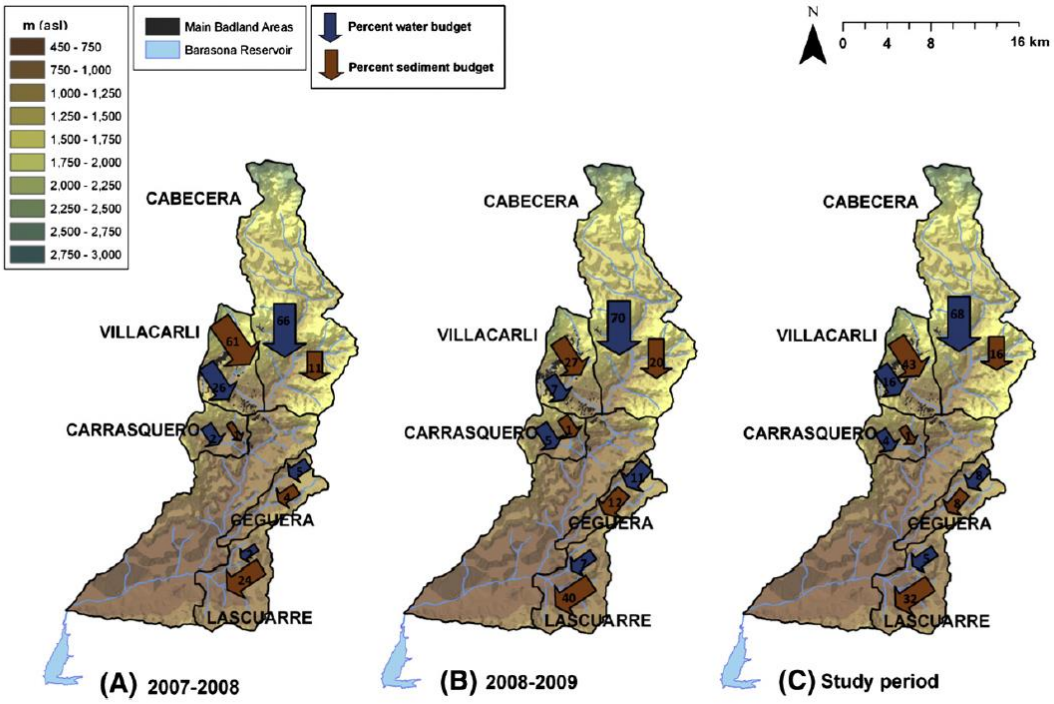


Fig 1.2 : Results from sediment and water budget calculated for the years 2007-2009 based on continuous discharge and sediment yield measurements (Source: LÓPEZ TARAZÓN ET AL. (2012)).

1.4 Aims and research questions of this study

Concluding the introduction, the following can be stated:

- Sediment and hydrological fingerprintings are based on similar principles, with major differences in regarding conservativity of tracers
- Comparisons of these principles and used models are sparse.
- The Isábena catchment has been studied intensively regarding sediment movement and therefore would be suited to compare sediment and hydrological fingerprintings (BROSINKSY ET AL. 2014).
- Water analysis in the catchment could provide additional information regarding water quality, which was not yet addressed in the catchment.

To combine all of the above, it was necessary to take a step back from the sediment analysis and focus on water analysis as this would open up a set of new possibilities. Therefore the aim of this study is to perform an assessment of water quality as well as a comparison of different hydrological fingerprinting models in the Isábena catchment.

In late 2016 a partnership was formed between the *Engage* working group within the Institute Of Geography And Regional Research at the University of Vienna, the Department Of Catchment Hydrology at the Helmholtz Zentrum für Umweltforschung (UFZ) in Halle (Saale) and the Institute Of Geography at the Freie Universität Berlin. Together a set of new methods and techniques in regard to sediment production and transportation as well as geochemical processes was gathered and discussed. The partnership additionally incorporated two more master thesis, which focus on a sediment fingerprinting based on phytoliths. In the following, an overview of final objects and aims, which form the research questions for this study will be given.

1.4.1 Assessment of water chemistry and quality

The first aim of this study is to assess water quality throughout the Isábena catchment. To do this, an assessment of river water chemistry throughout the catchment would allow a quantitative and qualitative observation of geochemical and hydrological processes and draw conclusions in comparison to previous studies. As the natural composition and quality of river water mainly depends on its geology (GRAY 2008), spring and river waters in the geologically heterogeneous Isábena catchment may differ greatly. These effects may be relevant for major anions (Cl^-, SO_4^{2-}, HCO_3^-, NO_3^-), cations (Mg^{2+}, Ca^{2+}, K^+, Na^+) or minor and trace elements. While HCO_3^- and Ca^{2+} are usually the dominant ions (MEYBECK 2003), expected differences include increased amounts of Ca^{2+} and HCO_3^- in limestone draining areas, increased Na^+, K^+ and SO_4^{2-} in sandstone areas and high amounts of Ca^{2+}, Mg^{2+} and HCO_3^- in marl areas (MEYBECK 2003). Minor and trace elements may also be distinct between different lithologies, however, as they are defined by concentrations below 1 mg/l, they are highly sensitive for anthropogenic pollution and may provide signals from agricultural or industrial usage which exceed the lithological information (GAILLARDET 2003). These insights on water chemistry not only allow to describe differences throughout the catchment, but also allow to address

water quality regarding drinking water guidelines from the World Health Organisation (WHO) or the European Union (EU).

1.4.2 Hydrological fingerprinting models based on different tracer sets

The second, and major aim of this study, is to addresses the discussed similarities and differences between sediment and hydrological fingerprintings. This will be done by incorporating the river water chemistry data and setting up multiple hydrological fingerprinting models. The models will differ regarding their tracer selection in context of tracer conservativity, but will be similar in set up to discriminate water from different lithological source areas. The results of models based on different conservativity approaches therefore would allow to:

- Compare results with discharge measurements and water balance calculations by previous studies to choose to most realistic model
- Address the possible errors that come with choosing tracers that do not behave conservatively.

1.4.3 Research questions

The above described aims and objects of the study allow to formulate the following research questions:

Question 1: Do river waters in the Isábena catchment exceed the WHO or EU drinking water guideline for certain elements or ions and if yes, is it possible to relate affected areas to human activities (e.g. agriculture, industry)?

Question 2: Can the lithological areas in the Isábena catchment be distinguished based on their spring water chemistry and if yes, is it possible to set up hydrological fingerprinting models to discriminate waters coming from different source areas?

Question 3: Are there differences in the results of hydrological fingerprinting models based on different tracers combinations and if yes, are they comparable to river discharge measurements and other studies in the Isábena catchment?

1.5 Structure of the thesis

The structure of this thesis will be presented in the following. The introduction (CHAPTER 1) included basics, similarities and differences of sediment and hydrological fingerprinting in general and in the Isábena catchment in particular, as well as the aims and research questions of this study. CHAPTER 2 will give a more detailed overview of the study area, including topography (*2.1*), climate and hydrology (*2.2*), geomorphology and geology (*2.3*), soils (*2.4*) as well as vegetation and land use (*2.5*). Additionally, the Barasona reservoir, will be described (*2.6*). CHAPTER 3 will cover the methods used in this study and will be subdivided into three major parts, including field work methods (*3.1*), laboratory analysis (*3.2*) and statistical analysis (*3.3*) respectively. Results will be presented in CHAPTER 4, which will be divided into two parts. Part one (*4.1*) will be containing the descriptive presentation of water chemistry and WHO/EU -guideline comparison, which will be used to answer the first research question. The second part (*4.2*) will cover the different fingerprinting models, while each model section will include the tracer selection process as well as the unmixing results. The second part will be concluded by the model validations, which will be described in CHAPTER 3.1 Finally, CHAPTER 5 will include a discussion of the above, ranging from a discussion of the applied methods up to the results. The thesis will be finalised with by drawing conclusions towards further studies (CHAPTER 6) and the list of the used literature (CHAPTER 7).

2. Study Area

2.1 Topography

The study area is the Isábena catchment, which lies in the Southern Pyrenees and covers an area of 445km². The wide spectrum of elevation ranging from 445m above sea level (a.s.l.) up to 2720m a.s.l. makes it one of several heterogeneous river catchments, which drain out of the Pyrenees into the Ebro and ultimately into the Mediterranean Sea.
Before flowing into the Ebro, the Isábena river joins the Ésera river near the city of Graus, where together they contributing into the Barasona reservoir. The Ésera River is the biggest tributary to the Cinca river, which is the second biggest tributary of the Ebro. In total, the Isábena comes up for 0.48% of the Ebro basin and makes up around 1.5% of the Ebro discharge, measured between 1945 and 2009 (LÓPEZ-TARAZÓN ET AL. 2009).

Delineating water flow, the Isábena catchment can be divided into five sub-catchments, which are named after local villages or valleys. *Fig. 2.1* gives an overview of the catchment area with its sub-catchments. *Tab. 3.1* shows the sub-catchments with their total and relative area after (FRANCKE ET AL. 2014). Several small creeks and streams in the southern area of the Isábena catchment make up the areas that do not drain into specific sub-catchments, called Capella and Con- Isábena. Many of those small streams flow only periodically after rainfall events or during snow melt (LÓPEZ-TARAZÓN 2011).

Tab. 2.1: Total and relative size of sub-catchments in the Isábena study area

Sub-catchment	**Area (km²)**	**Area (%)**
Cabecera	146	33
Villacarli	42	9
Carrasquero	25	6
Ceguera	28	6
Lasquarre	45	10
Sum	286	64
Capella	144	36
Con-Isábena	15	4
Total	445	100

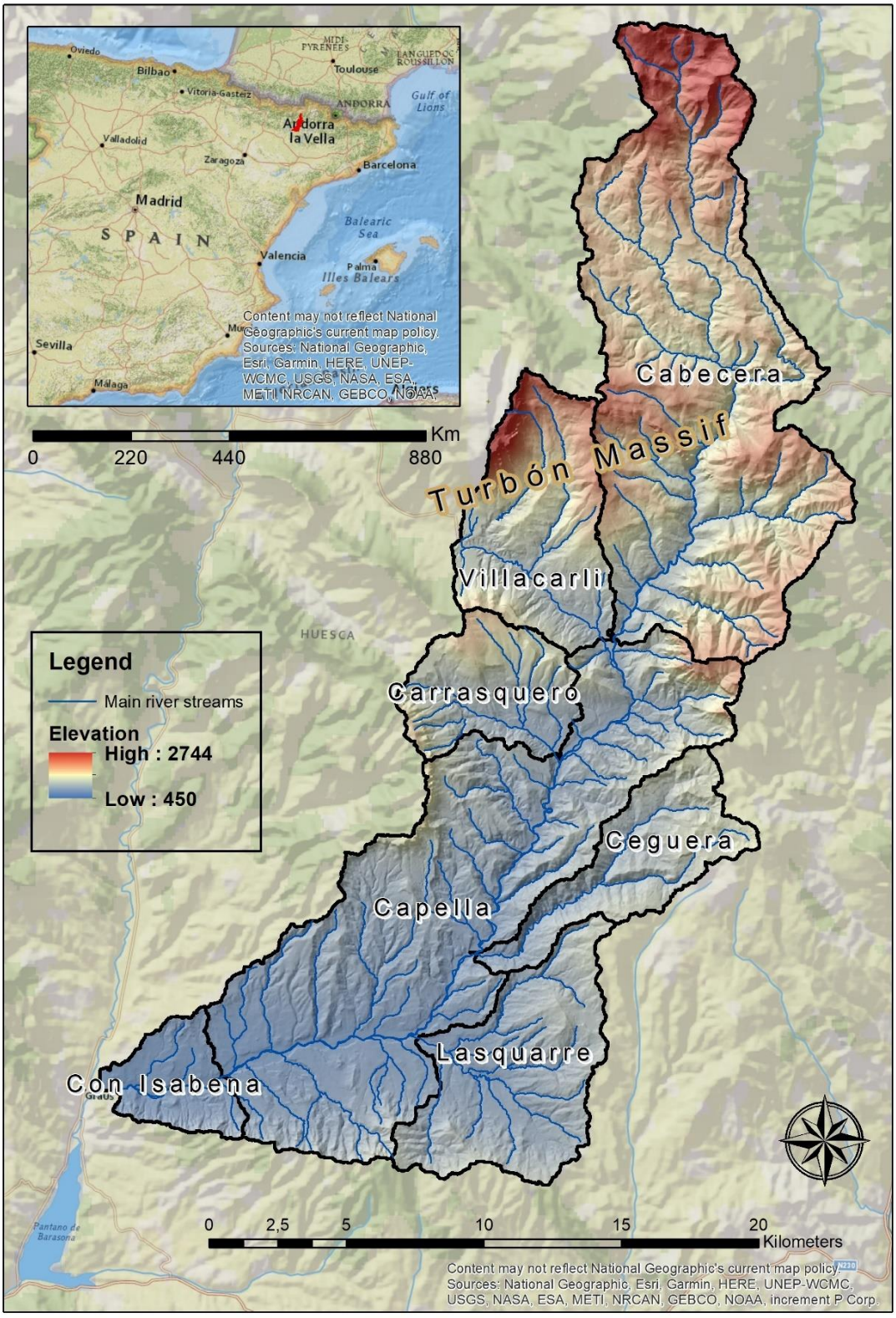


Fig. 2.1: Digital elevation model (DEM) of the Isábena catchment with its sub-catchments. Notice the steep elevation gradient from south to north, with the Turbón Massif between Villacarli and Cabecera. (DEM, river data source: University of Potsdam, Basemap: National Geographic, Map design: Heinzle 2018)

2.2 Climate and hydrology

The climate in the study area is of the Mediterranean mountainous type, being characterised by cold, dry winters and hot summers, with heavy storms occurring regularly (LÓPEZ-TARAZÓN 2011, BROSINSKY 2014). Besides these strong seasonal climatic variations, after (LÓPEZ-TARAZÓN 2011) the catchment can also be divided in two climatic zones, which is resulted by the elevation differences between southern and northern parts. The 'Turbón Massif' in the Villacarli and Cabecera sub-catchments (*Fig. 2.1*), thereby acts as a distinct border, cutting of the warmer and drier south from the more humid and colder north (LÓPEZ-TARAZÓN 2011). This results in mean annual temperatures ranging from 9°C to 11°C in the north and 11°C - 14°C in the south (VERDÚ 2003). The mean annual precipitation of the Isábena catchment is 767mm, which is also distributed heterogeneously throughout the year and the sub-catchments. Detailed analysis of precipitation by LÓPEZ-TARAZÓN (2010) also recorded a high interannual variability, indicated by mean annual precipitation values of 624mm and 792mm within three hydrological years, marking a variability of almost 20% between years. The high spatial variability within the catchment is reflected in mean annual precipitation rates of 450mm in the south and up to 1600mm in the summit areas (LÓPEZ-TARAZÓN 2011). Lowest precipitation rates are usually measured in summer months, although heavy rainstorms with up to 70mm per hour occur regularly, resulting in the activation of periodic streams, surface runoff, high sediment yield and flooding (LÓPEZ TARAZÓN ET AL. 2009).

This high variability in temperature and precipitation also results in variability in hydrological parameters. Discharge measurements at the Isábena outlet between 1945 and 2009 resulted in a mean annual discharge of 4.1 m^3/s with a large standard error of 2.2 m^3/s (FRANCKE ET AL. 2014). The mean annual water yield at the outlet is 177 hm^3, whereat a great portion of the discharge comes from stormy events in October and November, or snow melt in March and April (LÓPEZ-TARAZÓN 2011). Discharge measurements also recorded higher discharge peaks in the 1960s and 1970s, represented through the two largest floods happened in 1963 and 1966 with peak discharges of more than 300m^3/s.

Typical for river catchments with high variability in elevation, the Isábena river can be easily divided into three zones, wherein water flow and thereby sediment transport is distinct (SCHUMM 1977). The different fluvial dynamics are shown in *Fig. 2.2* from photographs within the study area. Flow patterns change heavily from steep and small streams in the headwaters (*Fig. 2.2. (A)),* towards transition zones (*Fig 2.2 (B))* and into deposition areas (*Fig 2.2. (C)).*

Fig 2.2: Photographs from the Isábena catchment along the river profile. A: Headwaters in Cabecera at around 1700m a.s.l; B: Isábena flowing through Turbón Massif in the southern part of Cabecara; C: Isábena stream close to entry into Barasona reservoir. (Photographs by Kiep/Heinzle 2018).

2.3 Geology and geomorphology

The Isábena catchment is part of the Tremp-Graus geological basin, a mostly wide depression settled in high mountains which follow the east-west aspect of the Pyrenees (LÓPEZ-TARAZÓN 2011). *Fig. 2.3* shows a geological map which was used for this study.

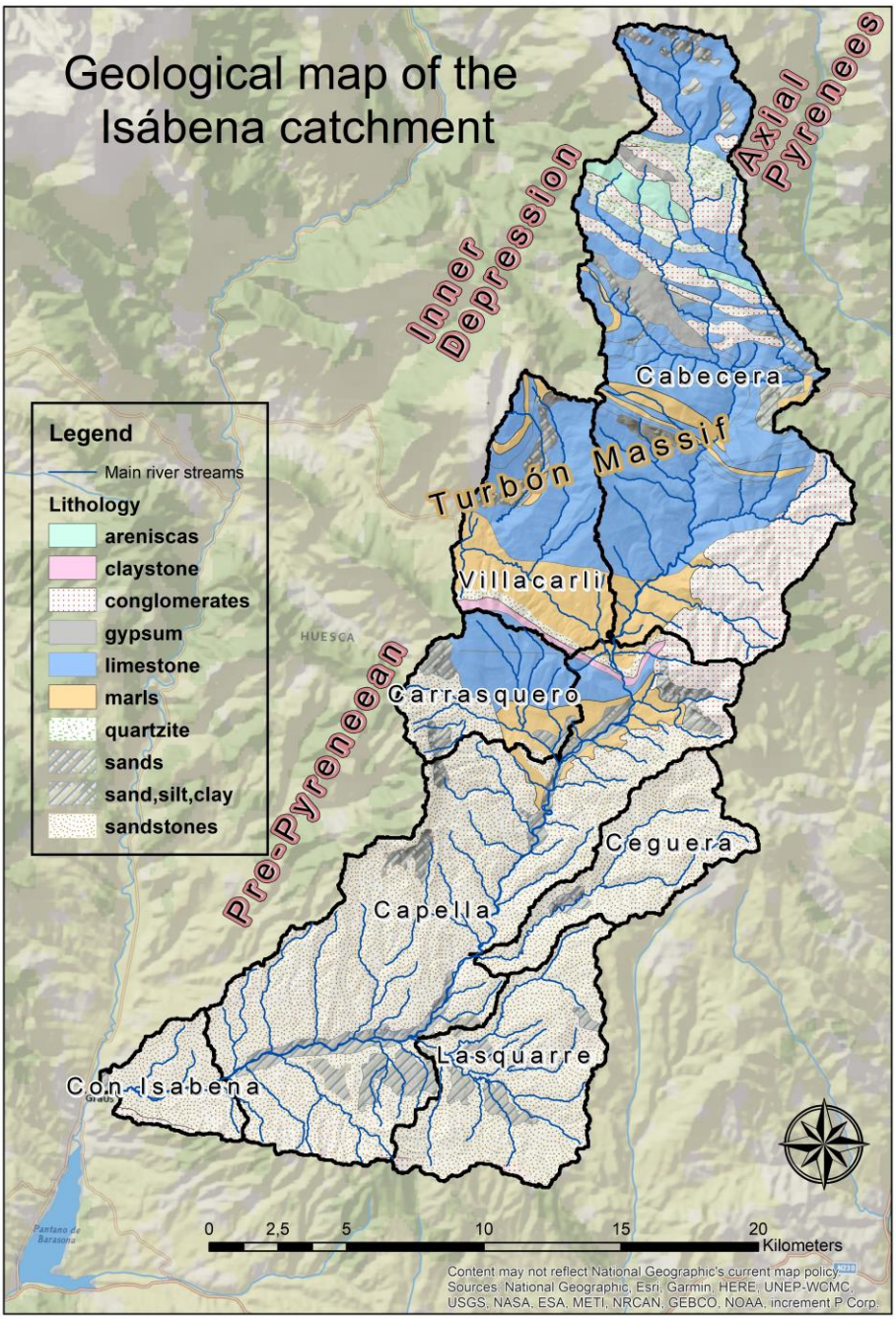


Fig. 2.3: Geological map of the Isábena catchment used for this study (Geological data: CSIC 2000, DEM, river data source: University of Potsdam, Basemap: National Geographic, Map design: Heinzle 2018)

VALERO-GARCÉS ET AL. 1999 distinguished three distinct geological units. In the first one, the Axial-Pyrenees in the northern part of the catchment, tectonic activity led to a very heterogeneous composition of party carstified Cretaceous limestones, local sandstones and slates ('areniscas"') in various colours, quartzites, conglomerates and even gypsums. This lithological heterogeneity of the northern catchment was difficult to validate during the field visit, as especially quarzite and conglomerate areas in the north could not be found where they were indicated in the geological map. The Turbón massif, where the Isábena river runs through narrow gorges with high intensity, marks the southern border of the northern geological unit after VALERO-GARCÉS ET AL. (1999).

South of the Tubon Massif, the second geological unit, the internal ranges continue, which are made up by Cretaceous and Paleogene sediments. Besides the eastern ridge which is composed of conglomerates, these areas are characterised by easily erodible marls, which cover large areas of the Villacarli and the Carrasquero sub-catchments VALERO-GARCÉS ET AL. (1999).

The most southern area of the catchment, the flatter lowlands where also most of the villages and the city Graus is located, is dominated by Neogene continental sediments, mostly sandstones (BROSINSKY ET AL. 2014). While geological maps only show sandstones and partly siltstones, also layers of conglomerates between sandstone layers have been observed during the field campaign. The southern border of the catchment is marked by external ranges which are mostly made up of conglomerates and belong to the same ridge as the conglomerates in the central part of the catchment.

Fig. 2.4 shows an overview of lithological units within the three geological zones of the catchment. It shows snow-covered peaks of massif limestones in the peak area of Cabecara and the Massif Turbón (*Fig. 2.4 A,C),* small scale changes in lithology shown by the red areniscas (*Fig. 2.4 B),* developed badlands in shrublands and forests, steep walls of conglomerates surrounding the catchment in the eastern and southern border (*Fig. 2.4 E)* and layers of sandstones, which are found in Capella, Ceguera and Lasquarre (*Fig. 2.4 F).*

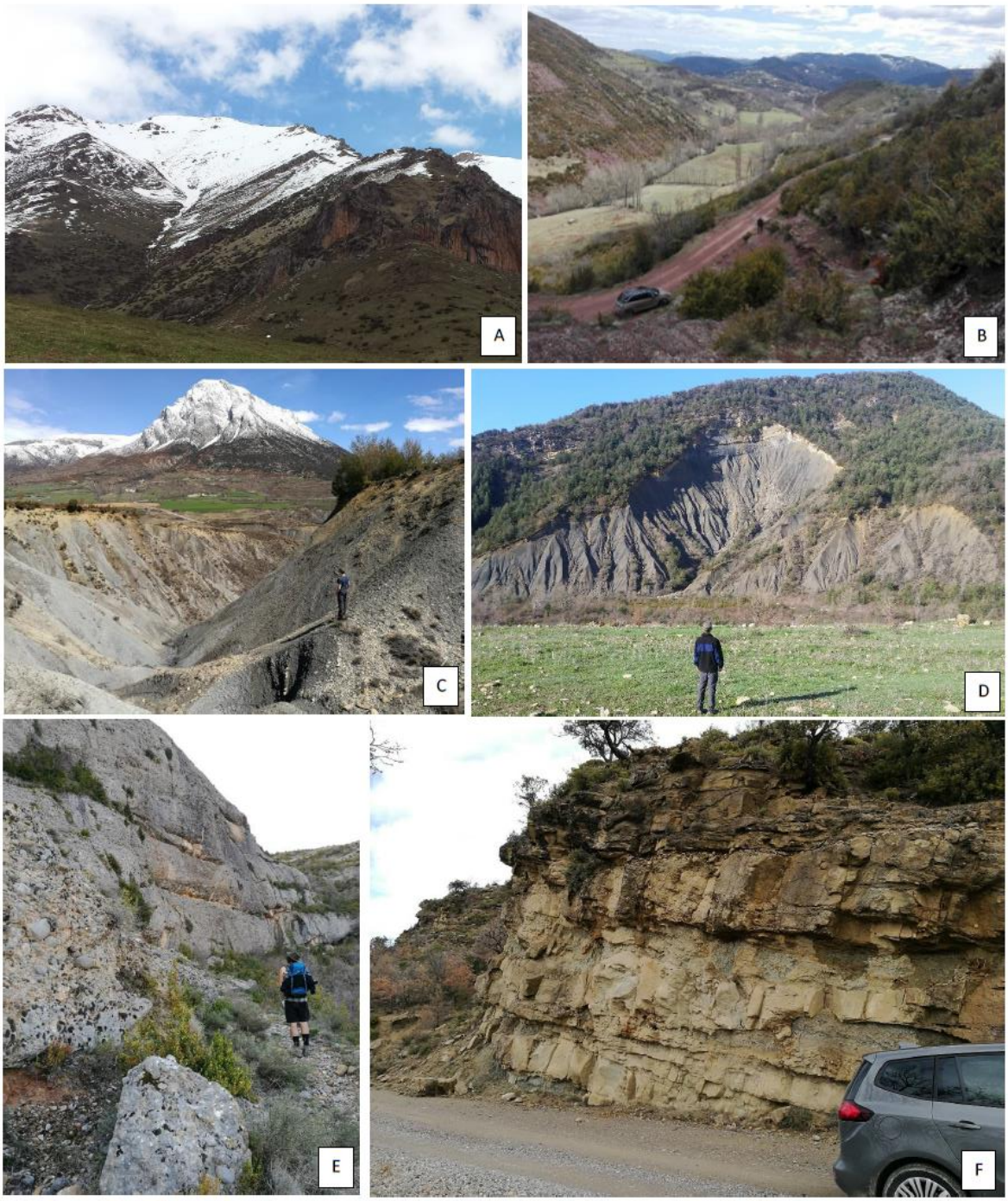


Fig 2.4 Photographs from different lithological units within Isábena catchment. A: Limestones in headwaters in Cabecera; B: Red areniscas in the northern catchment; C: Badlands over marls, snow-covered Massif Turbón in the background; D: Badlands in forest in Villacarli; E: Conglomerates in southern Cabecera; F: Sandstones in Capella. (Photographs by /Heinzle/Konzett/Kraushaar 2018).

2.4 Soils

Due to climatic and topographic limitations, the soils in the Isábena catchment are mostly shallow. Based on unpublished soil maps from the early 1990s, ALATORRE ET AL. 2010 described around 50% of the soils as mineral and shallow, with regosols, leptosols and fluvisols dominating. Other 30% of the area include kastanosems with high amount of organic matter. Despite no updated soil maps published, LÓPEZ-TARAZÓN ET AL. (2012) described the shallow mineral soils in more detail, with silty-loamy texture, low organic content (<2%) and low water retention capacity. Laboratory analysis by BROSINKSY (2014) showed high carbonate concentrations in most analysed soils throughout the catchment. Analysed soil texture is dominated by the silt fraction, with notable clay content of 19% on average. Soils in various land uses, geologies and slope angles show strong indices of regular sheet and rill erosion. Extreme cases are found in the marl zones in Villacarli and Carrasquero, where soils are completely eroded to the weathered surface *(Fig. 2.4*).

2.5 Land use and vegetation

The high variability in elevation, climate and topography also results in land use and vegetation differences within the catchment. The lowlands in the south are widely used for agricultural practises, whereas in the central and northern parts of the catchment, forests and shrublands dominate (LÓPEZ-TARAZÓN 2011). In the higher mountainous areas above the timberline at around 2100m a.s.l (CAMARERO ET AL. 2002), also alpine grasslands occur. *Fig. 2.5* shows a map of the catchment with its land use, details of land use classes are shown in *Tab. 2.2*, derived from PALAZÓN ET AL. 2017:

Tab. 2.2: Distribution of land use classes in the Isábena catchment

Land use class	**Area (km²)**	**Area (%)**
Agriculture	61	14
Forest	206	46
Shrubland	136	30
Grassland	36	9
Badland	4	<1
Total	445	100

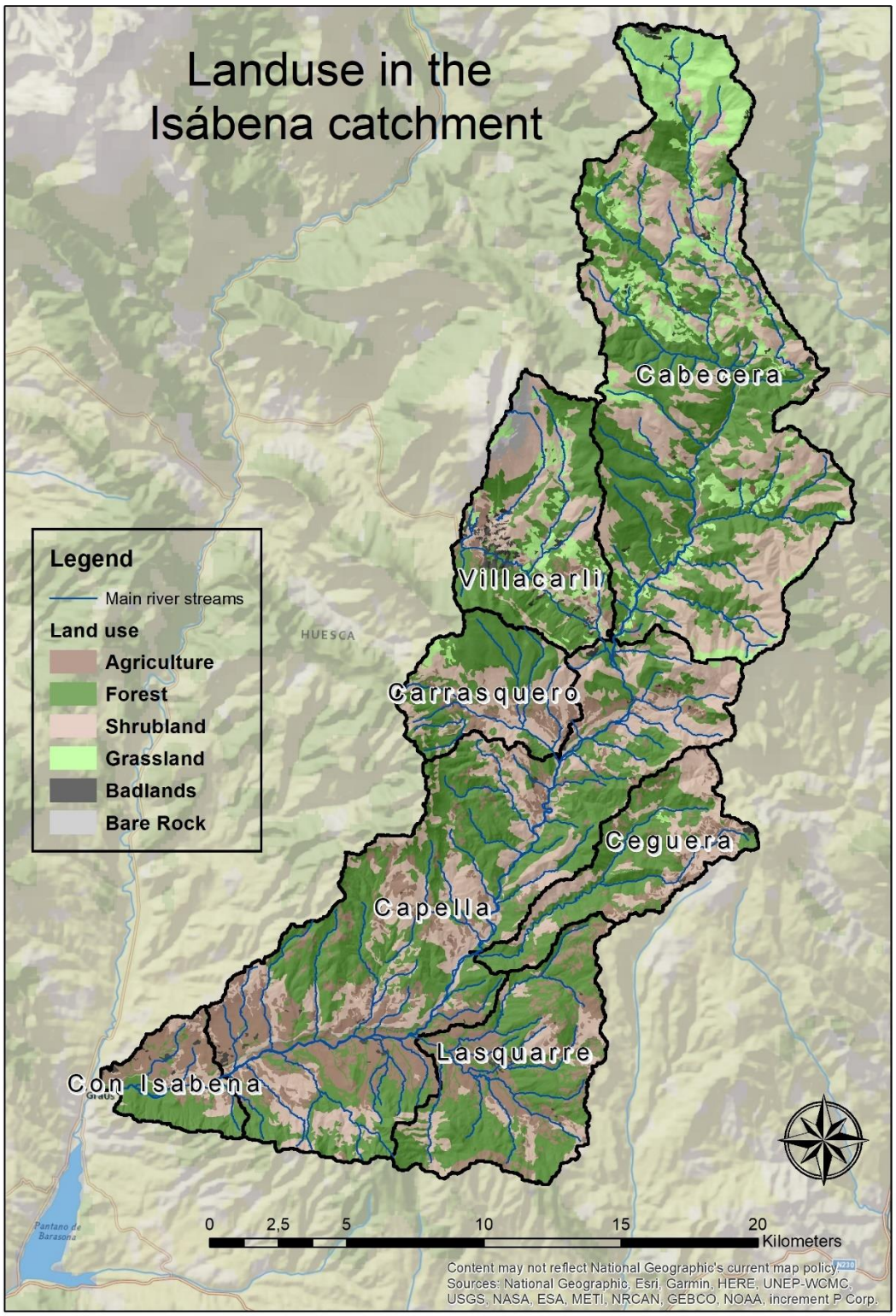


Fig. 2.5: Land use map of the Isábena catchment. (Land use, DEM, river data source: University of Potsdam, Basemap: National Geographic, Map design: Heinzle 2018)

Vegetation has been described in detail by LÓPEZ-TARAZÓN (2011): About half of the catchment area is covered by forests. Forestry, using different kinds of pines (*Pinus halepensis, Pinus nigra, Pinus sylvestris)* predominantly plays a role in the south of the catchment. The central of the catchment is dominated by mostly coniferous and mixed forests made up by pines (*Pinus halpensis)* and oaks (*Quercus ilex ballota, Quercus faginea).* In the north and the higher mountainous areas of the catchment, oaks are no longer present and pine forests dominate. (*Pinus sylvestris up to 1600m a.s.l, Pinus uncinate above*).

Being mostly abandoned cropland, shrublands are revegetated by different kinds of grasses and shrubs (*Buxus empervirens, Thymus vulgaris, Buxus empervirens)* with young oaks (*Quercus coccifera)* growing mostly isolated.

Grasslands and pastures are mostly covered by a combination of different grasses of the Festuca genus (*Festuca supina, Fustuca nigrescens, Festuca ovina, Festuca eskia).* Wet areas within slopes or areas close to springs are mostly accommodated by grasses of the Cares genus (e.g. *Cares sempervirens).*

While *Tab. 2.6* represents the current state of the catchment, LASANTO-MARTINEZ ET AL. (2005) reported a large two dimensional shift in land use in the Spanish Pyrenees during the last century. The first dimension involved a decrease in stocking rate, resulted from a change from sheep towards cattle usage. This led to an overall decrease of used land, leaving previously used areas abandoned. The second dimension was an overall decrease of agriculturally used areas, due to a decrease of population and an increase of amount of imported agricultural goods (NAVAS ET AL. 2008).

As for the nearby Borau valley which was looked at closely by LASANTO-MARTINEZ ET AL. (2005), more than half of agriculturally used land was left bare. Most of these former used areas went under the process of natural revegetation and shifted in to various forms of shrublands, leading to a heterogenous mosaic landscape of today, especially in the central and northern part of the catchment.

Fig. 2.6 gives an overview of this mosaic landscape as well as the ongoing succession of shrublands. Abandoned houses, built stonewalls and terraces are relicts of former agricultural usage.

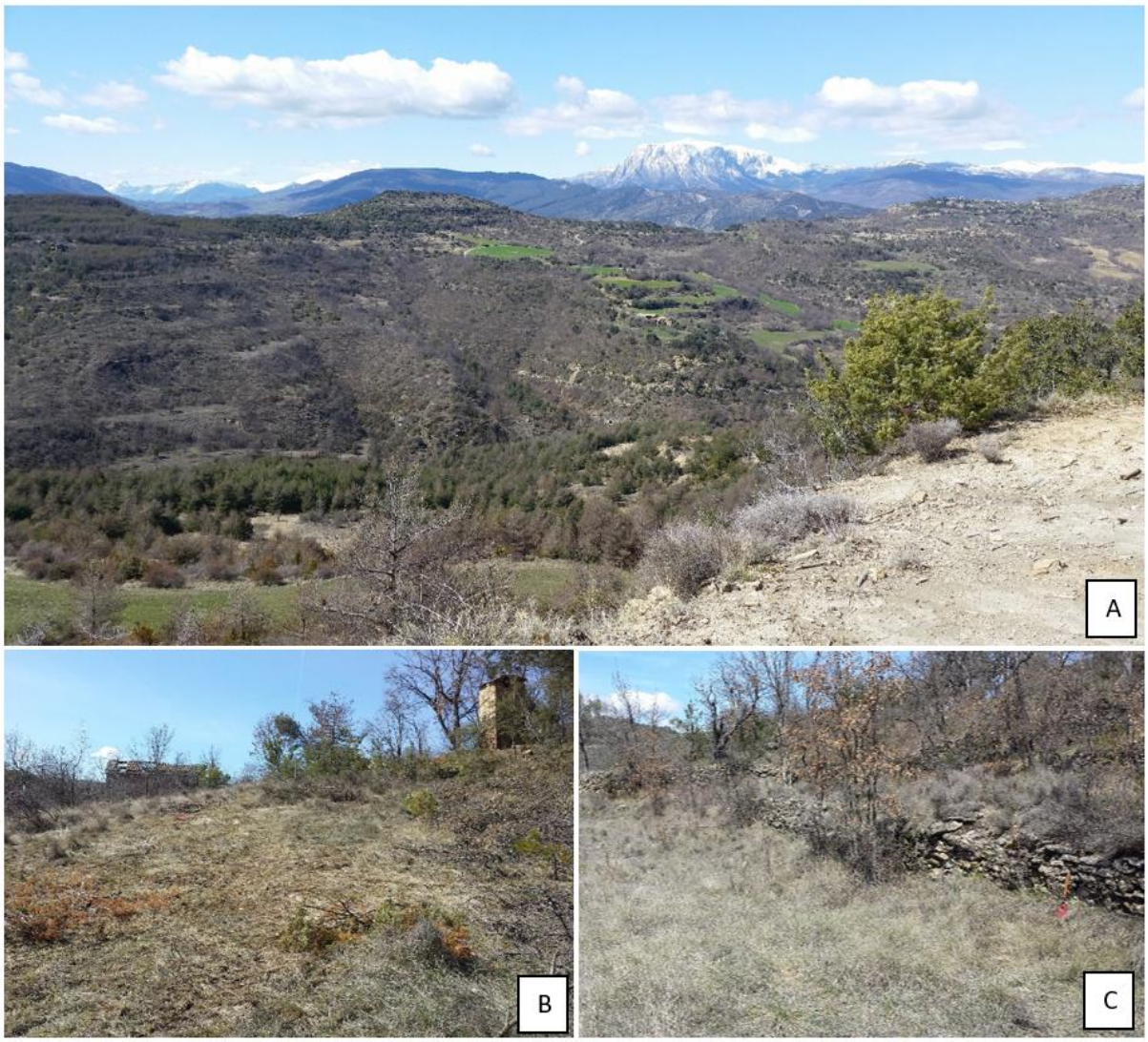


Fig. 2.6: (A): View from Cequera towards N-W. Various abandoned and still used agricultural areas visible. Note the snow covered "Turbón Massif" in Villacarli in the back. Distance approximately 15km. B&C: Abandoned agricultural fields revegetated by shrublands. Note ruined buildings (B) and stone walls (C). (Photographs by Kiep/Heinzle 2018.)

3. Methods

3.1 Field Work Methods

In order to address water chemistry throughout the catchment, a variety of different samples have been taken during a 14 days field campaign in April 2018. Additionally, river discharge was at all non-spring river sample locations. The sample strategy and methods as well as the on- site discharge measurements will be covered in the following.

3.1.1 Sample strategy

Sample locations were distinguished into three categories (*A-C*), which cover different locations within the stream network.

A: River spring samples: Samples were taken directly at or as close as possible to a river spring. Multiple river spring samples were taken in all major lithological units. Spring samples delivered source information for the hydrological fingerprinting.

B: Isábena tributary samples: River samples at tributaries to the Isábena river. Locations were ideally close to the river mouth into the Isábena and at tributaries where also spring samples had been taken. Tributary samples were used for validations and have been important for discharge measurements.

C: Isábena main stream samples. Samples were taken throughout the catchment along the Isábena river. Locations were chosen to be upstream of main tributaries joining the Isábena. Isábena main stream samples were used for source information in the headwaters, validation throughout the catchment and the important sink information at the catchment outlet.

Fig. 3.1 shows a map with the sample locations, divided into the three different sample types. In total, 15 river spring sample locations (A), 10 tributary sample locations (B) and 10 main stream sample locations have been covered. In addition to these water samples, river sediment and rock samples were taken. However, laboratory analysis are still ongoing so results from sediment or rock analysis will not be covered within this thesis.

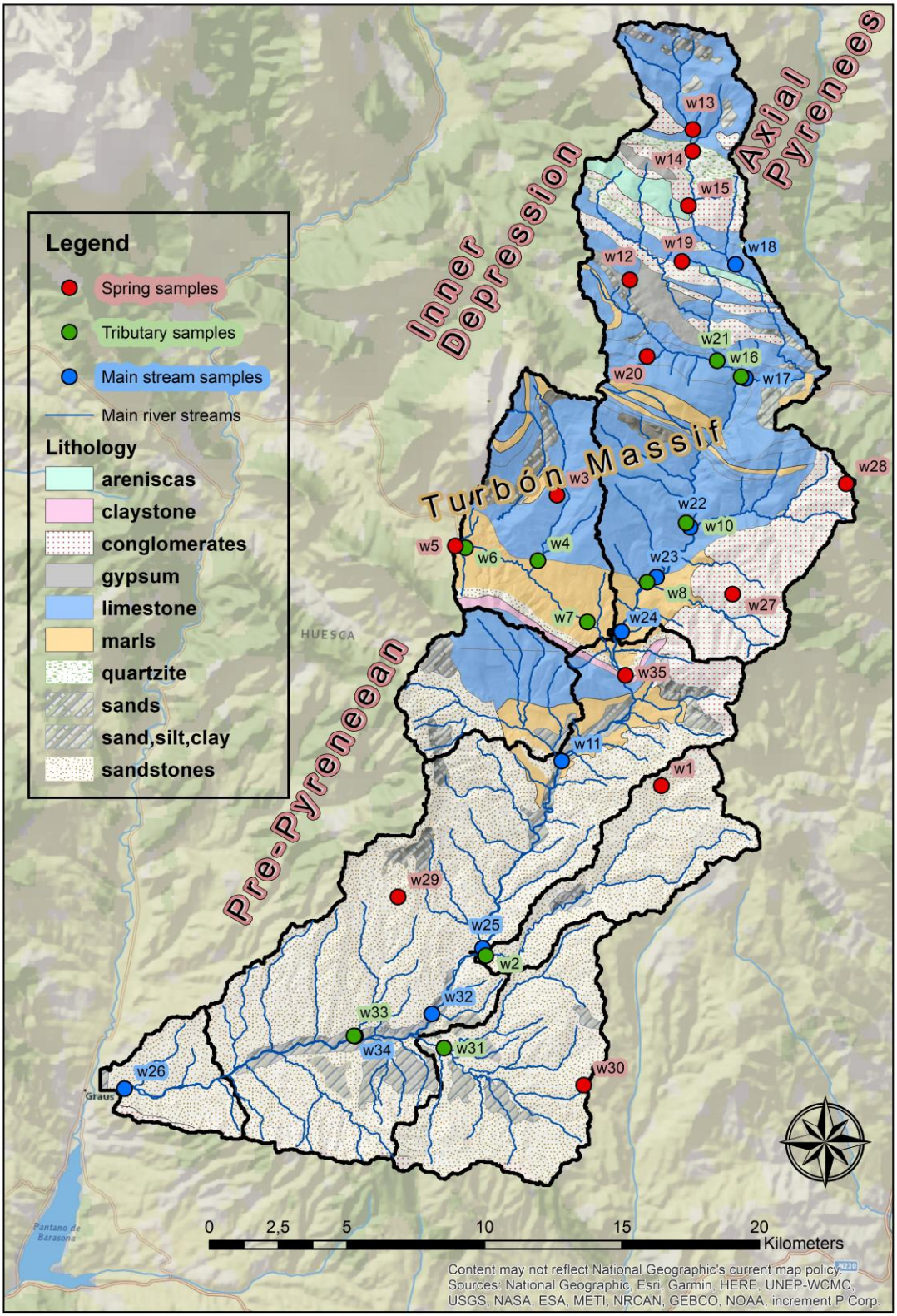


Fig. 3.1: Geological map of the Isábena catchment with sampling spots used for this study (Geological data: CSIC 2000, DEM, river data source: University of Potsdam, Basemap: National Geographic, Map design: Heinzle 2018)

3.1.2 Water sampling

Water sampling was performed following the practical guidebook of SELENT (1998). A sampling protocol, which is shown in the appendix, was set up which included general site information such as the weather, land use, geology, vegetation as well as on-site measurements. Sampling sites were documented with photographs and location coordinates were recorded with a hand-held GPS device.

Two samples were taken at each sampling site. These included:

- 30ml for anions and stable isotopes
- 30ml for cations

All samples were taken in HDPE (High Density Polyethylen) bottles which do not alter the chemical composition of the samples and can be used in extreme conditions. They were submitted to us by the UFZ Halle. Both samples were filtered with a 0.45µm SARTORIUS syringe filter holder before sampling. Four drops of HNO_3 were added to cation samples to minimize adsorption of bottle walls (HÜTTER 1996).

Samples were taken by hand and it was ensured that no air remained inside the bottles. Bottles were flushed twice with sampling water before samples were taken. In addition to the water sampling, important on-site measurements were taken. These included water temperature, electrical conductivity and pH-value. These parameters play an important role regarding solubility and stability of chemical components as well as ecological parameters such as increased pH-values due to photosynthesis of water plants (HÜTTER 1996). As they are expected to change shorty after sampling, it was important to take them on-site (SELENT 1998). On-site measurements were performed using a WTW Multi 3620 IDS portable device, submitted by the University of Vienna.
Samples have been kept as cool as possible during sampling sessions are were put in refrigerators (4°C – 6°C) until sent to the UFZ Halle via the Spanish Mail at the end of the field campaign. Sample cooling therefore was not given during transport from Spain to Germany. *Fig. 3.2* gives an overview of sampling procedure and on-site measurements.

Fig. 3.2: Overview of water sampling procedure at spring sampling sites (w3, w30). (Photographs by Kraushaar/Konzett/Heinzle 2018).

3.1.3 Water discharge measurements

In order to compare results from hydrological fingerprinting with actual discharge, on-site discharge measurements were taken at tributary and Isábena main stream sample sites. This was done using a propeller current meter (OTT Nautilus C2000) coupled with a reading device SENZA Z 300 from the University of Vienna. River discharge was derived by applying the mid-section method (SHAW 2014). Thereby the stream cross section was cut into regular intervals of 10 to 20cm (depending on total river width). Discharge measurements were then taken once in each subsection and multiplied with

the depth and width of each subsection. The sum of all subsections equals the total river discharge.

Fig. 3.3 shows a concept of the mid-section method, modified from the U.S. Geological Survey (USGS).

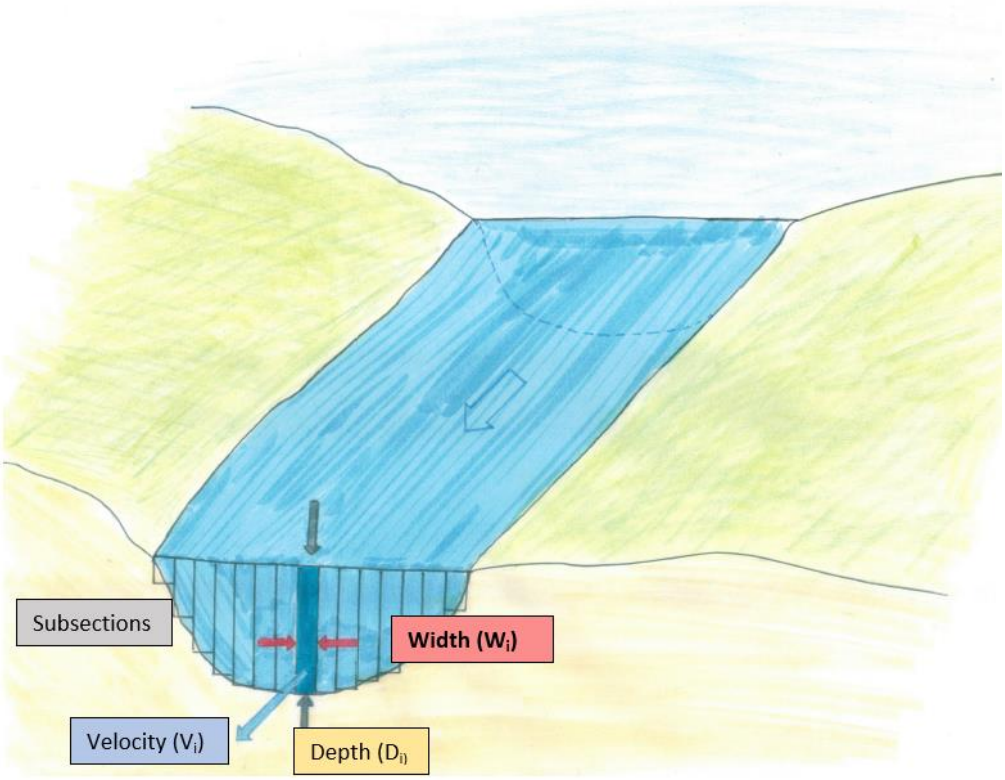


Fig. 3.3: Principle of river discharge measurements with subsections. Own design after: USGS.gov

Modified from SHAW (2014), discharge therefore is given as:

$$Q = \sum_i^n (D_i * W_i * V_i) \qquad (1)$$

with:
Q = Total river discharge
D_i= Measured depth for river section (i)
W_i = Measured width for river section (i)
V_i = Measured velocity for river section (i)
n = number of subsections

Due to intense discharge it was not possible to measure discharge using the mid-section method at all sample sites as entering the river was too dangerous. This was especially

the case for main stream sample sites. In cases where entering the river was not possible, river discharge was roughly estimated by comparing traveling time of multiple floating wood branches at different sections within the river. Travelling length of the wood branches was set to 30m and at least 10 equally large branches were tested. Although this is a highly unscientific method and especially river depth estimations had to be made additionally, it provided an overall sense of discharge change within the catchment. However, comparisons from fingerprinting results with estimated discharge have to be made very carefully. *Fig. 3.4* shows photographs of the OTT Nautilus C2000, successful discharge measurements (w7, w33) and the main Isábena stream in the background (w34) which was no longer possible to enter. *Tab. 3.1* gives an overview where discharge measurements were possible and where discharge had to be estimated.

Fig. 3.4: River discharge measurements with subsections. Top: Tributary sampling (w33) before entering the main Isábena stream. Bottom right: Tributary in marl area (w7). Bottom left: OTT Nautilus C2000. (Photographs by: Konzett/Heinzle).

Tab. 3.1: Overview of measured and estimated discharge sample sites.

	No discharge measured (spring samples)	**Discharge measured**	**Discharge estimated**
Sample ID	w1, w3, w5, w9, w12, w13, w14, w15, w19, w20, w27, w28, w29, w30	w2, w4, w6, w7, w10, w16, w21, w31, w33	w11, w17, w18, w22, w23, w24, w25, w26, w32, w34

3.2 Laboratory Analysis

In the following section, the analysis of water samples will be described. The first part will cover the titration for calculating the concentration of HCO_3 in anion samples, which was done during two of my visits at the UFZ in Halle in May and October of 2018. The second part will cover the analysis performed by the technical staff of the UFZ in Halle and their partners in Magdeburg.

In order to make a meaningful statement on water quality and be able to compile valid composite fingerprints, a wide range of ion and element concentrations have been analysed for each water, sediment and rock sample. Because of differences in ion and element composition, therefore a set of analytical methods have been used. These include titration, ion chromatography (IC) and inductively coupled plasma – mass spectrometry (ICP-MS). Analysis still worked on in the laboratories at the moment and not included within this thesis are the analysis of sediment and rock samples for a set of elements and the addition of rare earth elements (REE), experiments of REE-leaching to estimate water-rock interaction of samples for a given amount of time and the analysis of Li-isotopes, which could serve as an additional tracer for weathering and discharge. A selection of photographs from the ongoing analysis is shown in the Appendix.

Tab. 3.2 gives an overview of analysed ions, elements, used standards and involved facilities for analysis used in this study.

Tab. 3.2: Overview of analysed ions/element concentrations, related standards, used equipment and facility of analysis.

Method	Ions / Elements	Standard	Equipment	Facility
Titration	HCO_3	DIN 38409 – H7	RAININ E4 XLS Pipette	UFZ Halle
IC	Cl, SO_4, NO_3	DIN EN ISO 10304-1:2009-07	ICS 2000 (Dionex)	UFZ Halle
ICP-MS	Ca, Mg, Sr, Rb, Cs, Mn, U, As, Cr, Ti, V, Ni, Pb, Mo Na, K, Ba, Li, Fe, Sr	DIN EN ISO 17294-2:2017-01	Agilent 8800 Triple Quadrupole ICP-MS	UFZ Magdeburg

3.2.1 Titration for HCO_3 concentration

As there is no method to measure HCO_3 directly, it has to be either calculated by assuming mass-balance between ions or derived by titration (HÜTTER 1996). As shown *Fig. 3.5 (WILHELM 2008)*, at a pH-value of 4.3, all HCO_3 is converted into CO_2. Therefore, adding acid to the sample and reducing the pH value to 4.3 allows to calculate the HCO_3 concentration of the original sample.

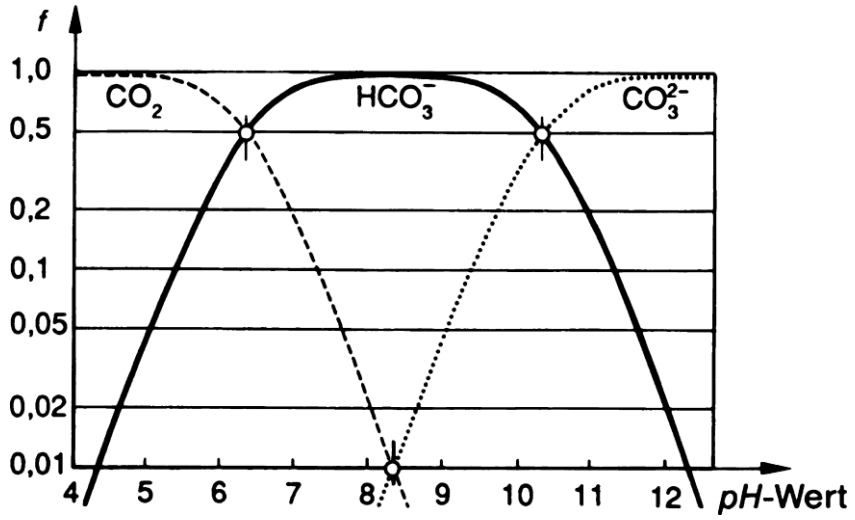


Fig. 3.5: Existence of CO_2, HCO_3^- and CO_3^{2-} at certain pH-values. Source: WILHELM (2008).

After (WILHELM 2008), the concentration of HCO^3 is then calculated by multiplying the volume of needed acid (to reduce the sample to pH-value of 4.3) with the concentration of the used acid divided by the sample volume (Eq.2). To get the concentration of HCO_3 in mg/l, it is finally multiplied by 1000. After WILHELM (2008), the formula therefore is:

$$HCO_3\ (\frac{mg}{l}) = \frac{V_a * c * 1000}{V_s} \qquad (2)$$

with:

HCO_3: Concentration of HCO3 in samples
V_a = Volume of needed acid
c = concentration of needed acid in mol/l
V_s = Volume of sample

Samples of this study were titrated with an automatic RAININ E4 XLS Pipette, using a 0.1M HCl acid and 10ml of each sample. During titration, samples were constantly mixed and pH was measured using a WTW pH-meter Multiline P4. *Fig. 3.6* shows an overview of the sampling titration setup at the UFZ in Halle.

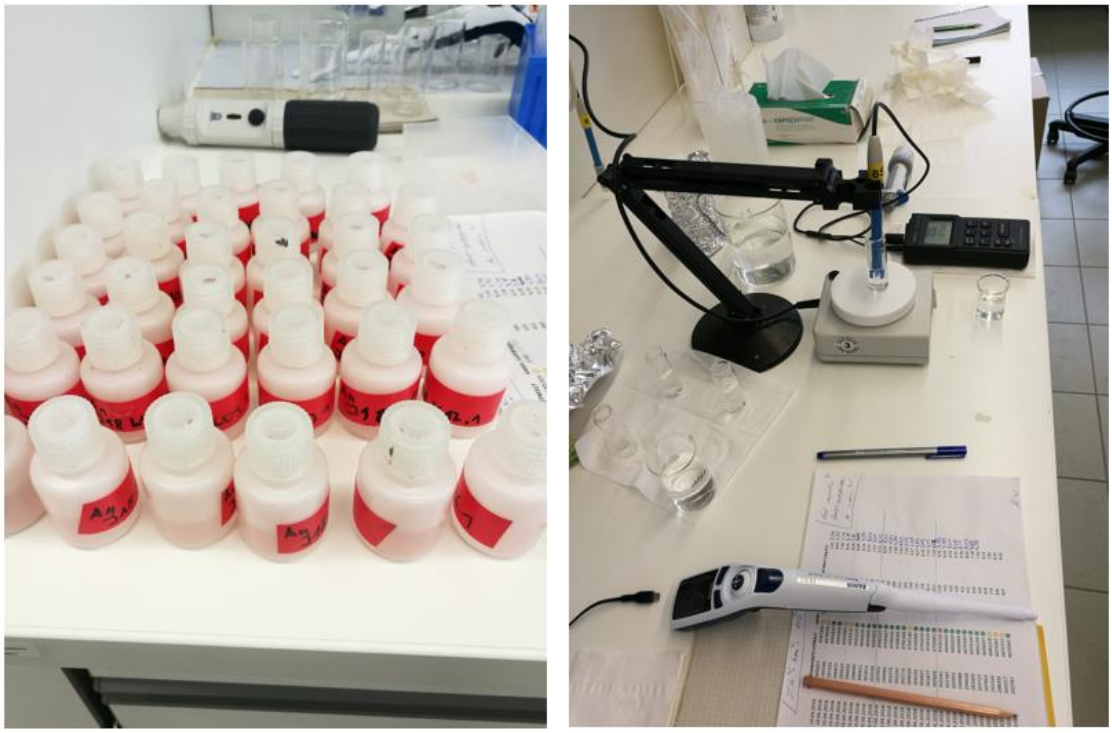


Fig. 3.6: Photographs of anion samples and titration setup for HCO_3 calculation at the UFZ in Halle. (Photographs: Heinzle 2018).

3.2.2 Analysis done by staff

The water analysis including all other ions and elements was performed by the UFZ staff in Halle and Magdeburg (*Tab. 3.2)*. As I was not involved in those analysis, only the principles of Ion chromatography (IC) and inductively coupled plasma – mass spectrometry (ICP-MS) will be presented in the following.

Ion chromatography (IC) is the chromatographic separation and measurements of ions (SMALL 2013). By combining principles of ion exchange and chromatography, IC is used regularly for analysing inorganic anions, cations or transition metals (JACKSON 2006). As IC can determine several ions at a time, results are easily reproduceable and is highly sensitive, it is one of the most commonly used methods (MICHALSKI AND KURZYCA 2006).

In the IC system, a filtered and diluted sample, referred as 'mobile phase', travels through a column which is packed with ion exchange solids or gels, which is called the 'solid phase' (SMALL 2013). In the column, ions get separated through ion exchange processes and then exit the column after different timesteps relative to their ionic composition.

By using a high accuracy pump, the mobile phase passing through the system can be held at a controlled rate and at constant pressure. After the column, electrical conductivity is detected. Changes in conductivity of the fluid passing through the columns are then drawn as curves relative to the impact of the given signal. By analysing the time the fluid took to run through the columns and the amplitude of the peak, ion types and concentrations can be determined. Therefore, the area under the drawn curves are compared with those of also measured standard samples with previously known concentrations. *Fig. 3.7* shows a scheme of an IC measurement with two different analysed ions after SMALL 2013.

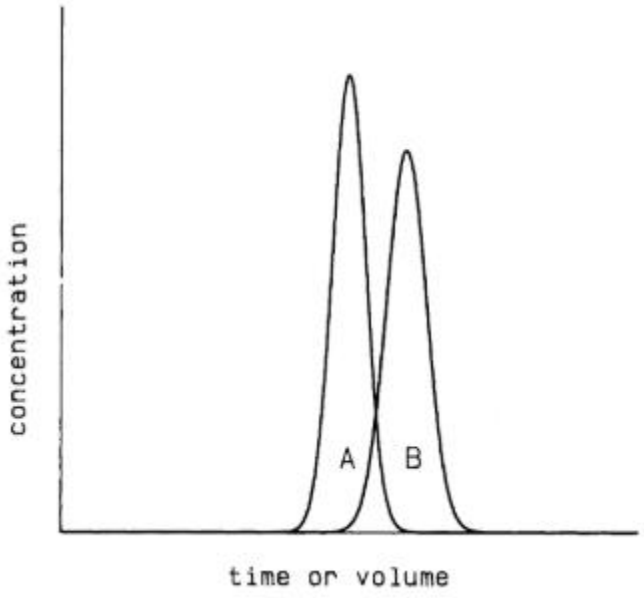


Fig. 3.7: Scheme of IC measurements. Peak of curves indicate concentrations while time of passing through solid phase indicates type of ion (Source: SMALL (2013)).

Inductively coupled plasma – mass spectrometry (ICP-MS) is a method for inorganic element analysis which is very robust and capable of detecting very low concentrations down to ng/l (GROSS 2012).

The system consists of the inductively couples plasma (ICP), a gas (usually Argon) which gets heated to a high temperature plasma at up to 10000°C. The sample passes through this inductively coupled plasma and due to the high temperature it gets ionised. These ions then are transferred into the second part of the system, the mass spectrometer (MS). There, in an electric field, they are separated according to their mass/charge (m/z) ratio and measured by the mass spectrometer. Measurements are shown in plots drawing the (m/z) ratio versus the signal strength. Whereas the (m/z) ratio indicates the element, the signal strength is directly proportional to the concentrations of the elements in the sample (GROSS 2012).

The wide spectrum of Elements analysed with ICP-MS for this study has been shown in *Tab. 3.2*.

3.3 Statistical Analysis

This section will cover two parts of statistical analysis of data. The first part will address the assessment of water chemistry and quality. The second part will give a stepwise description of the statistics used for the hydrological fingerprint with various data sets.

3.3.1 Descriptive statistic to address water quality

As stated already, the large amount of element concentrations analysed in water throughout the catchment, allows to address water quality. Therefore, analysed concentrations of ions and elements will be shown in the beginning of CHAPTER 4. Ecological guidelines such as the EU Water Framework Directive (WFD) are mostly qualitative (HERING ET AL. 2010), and will therefore not be covered in this study. On the other hand, thresholds for potentially health affecting concentrations of certain elements or ions have been formulated in quantitative guidelines such as the WHO-drinking water guideline or the EU drinking water directive. (WHO 2011, EUROPEAN COMISSION 1998). *Tab. 3.3* gives an overview of threshold values for elements or ions analysed in river water samples within this study as well as associated health issues listed by the WHO/EU guidelines. Elements or ions analysed but missing in the below table do not have assigned thresholds by the WHO or EU guidelines.

Tab. 3.3: Existing thresholds for analysed elements or ions regarding drinking water standards and associated health issues

element / ion	WHO	European Union	Associated health issues
Arsenic (As)	10 µg/l	10 µg/l	dermal lesions, skin cancer, lung cancer
Barium (Ba)	700 µg/l	-	potentially increased hypertension
Boron (B)	2400 µg/l	1000 µg/l	potentially increased damage of male reproductive tract
Chromium (Cr)	50 µg/l	50 µg/l	potentially carcinogenic (lung cancer)
Iron (Fe)	-	0.2 mg/l	noticeable taste and colour
Lead (Pb)	-	10 µg/l	toxic, harms liver, bones, hair, nervous system, kidney
Manganese (Mn)	-	50 µg/l	noticeable taste
Nickel (Ni)	-	20 µg/l	potentially carcinogenic
Nitrate (NO3)	50 mg/l	50 mg/l	cyanosis (children)
Sulphate (SO4)		250 mg/l	laxative

Besides the comparison with the health relating guidelines, the water chemistry will be used to identify distinct patters within the catchment. These include the geogenic differences between waters coming from various lithologies, their mixing in the main Isábena stream or the detection of certain influences that may be anthropogenic. Additionally, this will allow first assumptions regarding optimal tracers for the hydrological fingerprinting models.

3.3.2 Statistical process of hydrological fingerprinting

In the following, a detailed and step wise description of the data processing and statistical unmixing, already mentioned in *Fig. 1.1 (CHAPTER 1.1)*, will be given. Thereby, the principles of conservativity, representativity and linear mixing given in *Tab. 1.1* (*CHAPTER 1.2.3*) will be addressed regarding the tracer selection. Note that all statistical analysis were done using the free software "*R*".

As already stated, in order to address possible uncertainties using non-conservative tracers like major ions, the hydrological fingerprinting process will be split into two groups. As the sandstone area in the south is expected to be difficult to discriminate from the other lithologies, each model will be run once with and once without the sandstone area in the south. The first group will consist of popular tracers in hydrological fingerprinting studies like stable isotopes and major ions. To address its probable errors due to non-conservative behaviour of tracers, a second model using conservative minor and trace elements will be performed. The tracers used in the second model will be mostly non-soluble heavy metals.

To perform a hydrological fingerprinting, the following steps, derived by COLLINS ET AL. (2017) and INAMDAR (2011), will be performed to choose the most powerful tracers for source discrimination and unmixing of the sink sample. Note that as water samples are used for the fingerprinting, some relevant steps for sediment fingerprinting (e.g. particle size, organic matter) which are emphasize on by COLLINS ET AL. (2017), are not considered. The used combination of Kruskal-Wallis (KW) test and discriminant function analysis (DFA) was already focussed on by COLLINS ET AL. (1997) and will be

adapted by a series of further testing. The step-wise hydrological fingerprinting will include the following steps:

- Classification of water source groups
- Range test to assure mass conservation between sources and the sink
- Tracer selection for discrimination of sources via Kruskal-Wallis test
- Tracer conservativity assessment
- Determination of source discrimination power via Linear Discriminant analysis
- Unmixing model via Monte Carlo iteration to relate the mix sample to possible sources

3.3.2.1 Water source classification

As already presented in *Fig. 3.1*, several spring, tributary and main stream samples in various lithological units have been taken. In order to investigate the provenance of the water throughout the catchment, it is necessary to implement source groups which each inherit typical characteristics within the group and have maximal separation to other groups (SMALL ET AL. 2002). In regard to the aim of studies, source classification types (e.g. land use, lithology) are mostly determined before field work, as it commonly affects sample collection (COLLINS ET. AL. 2017). While source group classification based on land use units may be more advantageous in regard to management procedures, this study will rely on a source classification by lithological units. This is especially interesting, as most previous studies in the Isábena catchment focussed on land use units as sources areas (e.g. BROSINKSY ET AL. 2014, PALAZÓN ET AL. (2016). While this may also provide difficulties in comparing results with one another, it is also practical, as water spring samples are expected to be valid and precise indicators for their originating lithology (HELLMANN 1999) and large differences can be expected in such a heterogeneous catchment. As seen in *Fig. 3.1*, besides several small areas of lithologies, the catchment can be distinguished into four major lithological areas, which will represent the four source groups for the following tracer selection and source apportionment modelling. Smaller lithological areas such as gypsum or areniscas are excluded from the modelling process, as there were no representative samples taken from these areas.

However, to ensure each source lithology is represented through its geochemical and lithological characteristics, not all samples can be used as input for representing a source or sink. Therefore, several samples have been dismissed from the subsequent statistical processing.

In a first step, all main stream samples which are not the closest to the Isábena spring (w13) or the Isábena sink at the Barasona reservoir (w26) were removed, as they are expected to represent a mixture of different lithological signals and thereby would decrease separation between groups if used as source input for one lithology. The sink samples (w26 for including sandstones, w11 for excluding sandstones) are needed as references for the unmixing models. Additionally, tributary samples were removed if their flow path went through different lithological areas on their way to the Isábena, or if they are mixtures of secondary tributaries from different lithological units themselves. This ensures that no samples with mixed signals from various lithological units enter the modelling process. Additionally, samples w5 and w35 were removed from the following statistical analysis due to uncertainties in sampling procedure and classification.

After this, the source samples were grouped together, with every group only having samples from a distinct lithology. *Tab. 3.4* gives an overview of source groups with their representative samples, distinct locations can be derived from *Fig. 3.1*.

Tab. 3.4: Source group classification and representation through sample types

	Lithological source groups			
	Limestone (LS)	*Marls (MA)*	*Conglomerates (CO)*	*Sandstones (SS)*
Spring	w3, w12, w13, w19, w20		w27, w28	w1, w29, w30
Tributary	w4, w16, w21	w6, w7		w2, w31, w33
Main stream	w18			
Sink samples	w26 (with sandstones) / w11 (without sandstones)			

Note that distributions throughout lithological groups and sample types is far from equal, as limestone and sandstone areas outnumber marl and conglomerate samples. Additionally no usable spring samples for marl areas and no relevant tributary samples for conglomerate areas had been taken. As the Isábena spring is in limestone areas, only main stream samples from the upper limestone areas are suited to be included into the subsequent analysis, as samples further downstream may be affected by different lithologies. Therefore, it is not possible to include main stream samples representing marl, conglomerate or sandstone source areas.

3.3.2.2 Range test to assure mass conservation

As COLLINS ET AL. (2017) stated, it is necessary to ensure mass conservation of tracers. This can be done by validating if used tracer concentrations (elements/ions) or ratios (stable isotopes) of the sink are within the range of concentrations/ratios of all sources. If concentrations of a potential tracer in the sink samples would be below ore above all relevant sources, this would either indicate major flaws in its conservativity throughout the catchment or the influence of areas which were not sampled but have major influence on the sink mixture (FOSTER AND LEES 2000). In both of those cases, affected potential tracers should be dismissed from the further analysis. A range test will therefore be performed for all model setups at the start of the data processing.

3.3.2.3 Tracer selection via Kruskal-Wallis test

As already mentioned, it is necessary to ensure the maximal difference of tracer concentrations between source groups. To incorporate this, the Kruskal-Wallis H-test (KW), a non-parametric statistical test is performed. The KW tests the null hypothesis, that three or more samples have been drawn from the same population. (MCCARROLL 2016). Thereby, for each possible tracer, measured values of lithological units are replaced by ranks and ordered. The test then examines, if the sum of ranks for each group (e.g. lithology) are different from each other.

After MCCARROLL (2016), the test statistic is given as:

$$H = \frac{12}{N(N+1)} \sum_{i=1}^{k} \frac{R_i^2}{n_i} - 3(N+1) \quad (3)$$

with:

R_i *= Sum of ranks for each group*
N *= Total sample size*
n_i *= Size of each group*
k *= number of groups*

Differences between groups are indicated by the p-value of the test statistic. P-values below 0.05 indicate that based on the sum of ranks for each group, the null hypothesis can be discarded, and at least two groups have significant distinct values for the observed potential tracer (McCarroll 2016). In regard to the potential tracers, p-values above 0.05 of the KW test statistic would indicate that these tracers do not show significant differences between at least two sources at a 5% confidence interval, and therefore have to be dismissed from the further analysis (Collins and Walling 2004, Pulley et al. 2015).

3.3.2.4 Conservativity of tracers

As described in Chapter 1.2, sediment fingerprinting studies focus a lot on tracer conservativity (Collins et al. 2017), while hydrological fingerprinting studies mostly rely on correlations between tracer concentrations within the catchment to ensure conservativity (INAMDAR 2011). Therefore, after dismissing potential tracers based on the KW test, a subsequent assessment of conservativity will be performed. For the first group, including major ions and stable isotopes tracer conservativity will only be tested via correlation between potential tracers as proposed for hydrological fingerprinting models by INAMDAR (2011) and HOOPER (2003). While stable isotopes are considered conservative based on their evidence in literature (Chapter 1.2.2), major ions have to fulfil the following criteria to pass on to the subsequent tests:

- Correlation coefficient > 0.5 to δ^2H and $\delta^{18}O$.
- Correlation coefficient > 0.5 to at least one other major ion

For The second group, following the sediment fingerprinting principles, elements passing the KW-test will be tested regarding conservativity through a literature review process, similar to KRAUSHAAR (2016).

3.3.2.5 Linear discrimination analysis

After the statistical and literature based exclusion of non-fitting tracers, a linear discrimination function analysis (LDA) will be performed. The LDA is a statistical method to evaluate group differences, identify outliers or evaluate samples that may have been assigned to the wrong group (BAHRENBERG ET AL. 2008). This is done by plotting the variables (potential tracers) for all groups against each other. However, as each group (lithological source area) consist of multiple variables, the dimension of the plot has to be reduced. This is done by calculating a discriminant function for each group, which inherits a discriminant coefficient for each variable in this group. Each discriminant function is then given as:

$$Y_i = C_{ia} + C_{ib} + C_{ic} + \ldots\ldots\ldots \quad (4)$$

with:
Y_i = Discriminant function for each group
C_i = Discriminant coefficient for each variable in each group
a, b, c, = variables

While calculating the optimal discriminant coefficients for a two group analysis is rather simple, multiple group LDA requires the calculation of Eigenvalues for each group. After FAHRMEIR AND HAMERLE (1984) the Eigenvector which relates to the largest Eigenvalue for each group, inherits the discriminant coefficient which implements the most optimal separation between the groups (BAHRENBERG ET AL. 2008). Therefore the first Eigenvector for each group is used to calculate the first discriminant function, the second Eigenvectors to calculate the second function and so on. The explanatory power is the greatest for the first discriminant function decreases with the subsequent functions (BAHRENBERG ET AL. 2008).

In the case of this study, the LDA allows to reduce the dimensionality of the multivariable lithological groups to a two dimensional plot. Moreover, the discriminant coefficient for each variable is an indicator for strong discrimination power between groups. While many fingerprinting studies use the minimisation of Wilks' lambda to finalize the tracer selection (COLLINS ET AL. 1997), here reclassification accuracy of testing data and trial of different tracer combinations will be used, similar to KRAUSHAAR (2016).

The selected combination of tracers then will be put together and form the 'composite fingerprint' for each model, which will be used for the subsequent unmixing model.

It is important to notice that the LDA two dimensional plot also gives information about the quality of source classification. Large within group variation and especially overlapping of groups on the important first discriminant function may indicate poor source classification (COLLINS ET AL. 2017).

3.3.2.6 Unmixing model

The final part of the statistical analysis includes the input of the composite fingerprint into the unmixing model. Assuming a mass balance between source and sink, the model multiplies the values of the composite fingerprint of each source with an unknown factor representing this sources apportionment of the sink mixture, so that it equals the concentrations of the measured sink sample in the best possible way (PALAZÓN AND NAVAS 2017). Two constraints must be satisfied thereby (COLLINS ET AL. 1997):

- Each source must contribute between 0% and 100%
- The contributions of all sources must sum up to 100%

While sediment fingerprinting models often include specific weighting factors for particle size or organic carbon (COLLINS ET AL. 1997), this is not needed for hydrological unmixing models. The unmixing model, after WILKINSON ET AL. (2012) thereby aims to minimize the sum of squares of the weighted errors of the used tracers (SSE). It is given as:

$$SSE = \sum_{i=1}^{e} \left\{ \frac{C_i - \left(\sum_{s=1}^{m} P_s S_{si} SV_{si}\right)}{C_i} \right\}^2 W_i \qquad (5)$$

with:
SSE: sum of squares of weighted errors
e: number of tracers in the composite fingerprint
C_i: Concentration (or ratio for stable isotopes) of tracer (i) in sink sample
m: number of source categories (lithological groups)
P_s: optimised proportional contribution from the source category (S)
S_{si}: Weighting of within source variability of tracer (i) in source category (S)
W_i: Tracer specific discriminatory weighting

As a perfect discrimination of sources cannot be assumed, the above model will produce different optimised proportional contributions from each source category (P_s), if run multiple times. In order to address model uncertainty, models are therefore run via a Monte Carole iteration at least 1000 times (e.g. COLLINS ET AL. 2010, WILKINSON ET AL. 2012, KRAUSHAAR 2016). In this study, all models will be run 2000 times. Using the differences of relative proportional contributions from each category within the 2000 model runs, an error estimation, given as mean relative error (MRE) can be calculated (WILKINSON ET AL. 2012). The MRE is given as:

$$MRE = \frac{1}{r} \sum_{j=1}^{r} \left(\frac{SSE}{m} \right) \qquad (6)$$

with:
r: number of model runs (2000)
m: number of source categories (lithological groups)
SSE: sum of squares of weighted errors (given in Eq. (5))

3.3.2.7 Model validation

In order to make high quality statements based on the models results, they have to be validated. COLLINS ET AL. (2017) suggest the usage of so-called artificial mixtures for

fingerprinting studies, which are manually assembled samples with known compositions of all source groups. By replacing the artificial mixtures with the sink samples, models can be validated as their output should represent the know composition of the artificial mixture. In this study, instead of creating an artificial sample, the main Isábena stream sample (w17) will be used for model validation. As this sample is located in an area where only input from limestone sources should be present (*FIG. 3.1*), replacing it with the sink sample and running the model will allow to evaluate model performance. In an optimal way this would result in a relative source contribution of 100% from limestone areas, while other source groups are not represented.

The second part of the validation will implement the discharge measurements taken in the field. This allows to compare the qualitative model out (relative source contributions from lithological units) with the quantitative discharge measured. This however, has to be based on the assumption, that discharge measurements were accurate and representative, which cannot be assured (CHAPTER 3.1.3). However, as previous studies such as LÓPEZ TARAZÓN ET AL. (2012) set up a water balance for the catchment, these results can also be incorporated in the validation process.

4. Results

This chapter will at first cover the qualitative assessment of river quality based on the analysis of 35 water samples within the Isábena catchment. Thereby, the water chemistry will be first looked at for the whole catchment, before WHO and European drinking water guidelines will be addressed. The second and major part will cover the results and validation of the hydrological fingerprintings with different data sets.

4.1 River water chemistry

4.1.1 Ion and element concentrations

First of all, major ions in spring and river waters throughout the catchment will be looked at. *Fig. 4.1* shows the distributions of major anions and cations in two separate maps. Ion distributions for each sample are represented as bar plots with their size increasing with higher concentrations of ions. As there should be a equilibrium state between anions and cations (HELLMANN 1999), samples with similar sizes of bar plots are indicating low mass balance errors. Cations are mostly reperesented by Ca_2, especially in northern and central limestone areas, conglomerates and sandstone spring samples. Mg_2 also is represented in northern limestone and southern sandstone spring samples. Especially input from southern areas is reflected in the most southern sample close to the Barasona reservoir (w26). The high Ca_2 and Mg_2 percentages found in limestone and marl areas, can be related to geogenic input (HÜTTER 1994). High amount of *Na* is found in one particular tributary in the northern area as well as the spring sample within the marl area (w5). As *Na* is often enriched in highly weathered lithologies (HÜTTER 1994), this could be a reason for their occurrence in the badland marl area. As for the northern *Na* enriched samples (w21, w16), possibly small not mapped input of highly weathered areas are responsible. Southern Isábena main stream samples are dominated by Ca_2. *K* is underpresented in all samples as expected (HELLMANN 1999), but is slightly increased in the sandstone areas.

Major anions are dominated by HCO_3, which especially in the northern catchment makes up most of the anion percentage of water samples. HCO_3 concentrations of waters which are in contact with carbonatic minerals (e.g. limestones), increase over time (HELLMANN 1999). Additionally, HCO_3 usually reaches its maximum concentration in comparison to

CO_2 and H_2CO_3 at a pH-value of 8.2 (WILHELM 2008, *FIG. 3.5*). As the pH-value ranges between 7.1 and 8.6 within all water samples analysed, high HCO_3 concentrations are typical. This explains the high amount of HCO_3 in the limestone areas. *Cl* is enriched in the same samples as *Na* was enriched for anions, but is not enriched in the marl areas where *Na* was enriched as well. Therfore the *Na*/*Cl* enrichment could also result from an anthropogenic input such as a salt storage. NO_3 is only represeted in the southern areas and is most likeley related to the agricultural practise. SO_4 is enriched throughout the marl and sandstone areas. This could as well be explained by fertilizers used in agriculture, or waste water coming from industrial areas (HÜTTER 1994). There is also a reasonalble amount of SO_4 in the *Cl*/*Na* enriched samples (w16, w21). This could be indicating the impact of the gypsum area, which is geologically mapped above these sample sites and was also found during the field trip. However, note that the sample within the gypsum area (w12) does not inherit any SO_4 accumulation. Because of this, it was reclassified as a limestone spring sample.

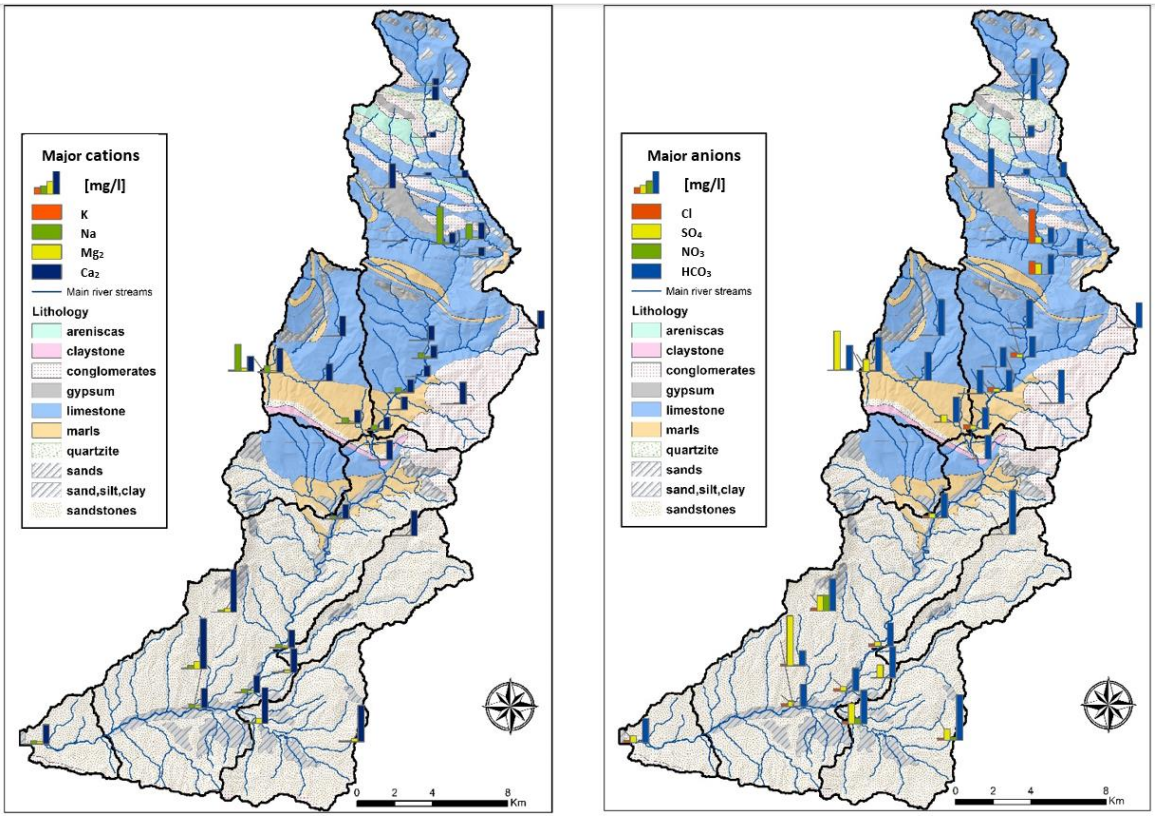


Fig. 4.1: Comparison of major cations and anions throughout the catchment. Size of bar chart representing amount of ions. (Source geological map: University Potsdam, Map design: Heinzle 2018)

Fig. 4.2 shows concentrations of all the other elements analysed, each represented by a distinct map. Circle sizes are increasing with element concentrations, however, note that concentrations are scaled differently between elements. There are several remarkable trends to be noticed. The northern area of limestones, which is hardly touched by human activities, has low concentrations of all elements analysed. *As, Ba, Cr, Fe, Pb, Mn, Ni, Ti* and *V* all follow a similar pattern. Their concentrations are enriched in conglomerate and sandstone spring samples as well as in the southern Isábena samples. As especially *Fe* and *Mn* are expected to have small concentrations in streams without human impact (HÜTTER 1996), these increased concentrations could point towards an anthropogenic pollution. As also other metals are enriched, these enrichments could come from old pipes, fences or tools which were left behind after the shift in land use.

Another pattern is shown in *B, Li*, and *Sr* concentrations. They each have their highest concentrations in the marl spring sample but are then drastically reduced towards the southern catchment. Sample (w21) which was represented by high amounts of *Cl* and *Na* also inherits the highest concentrations of *Rb* and *Cs* throughout the catchment, reinforcing its unordinary element composition. Analysis of ^{137}Cs could indicate whether this Cs enrichments are geogenic or human-induced, as ^{137}Cs is only found after the nuclear testing in the 1950s (WALLING ET AL. 1986).

As HÖLLER (1994) noted, enrichments in *Cr, Ni, Pb, Ti* and *V* are rarely derived from geogenic inputs and may point towards an anthropogenic waste influence. However, to clearly indicate whether these small concentrations are human-induced or based on geogenic, multitemporal measurements would be needed to describe the geogenic background information (HELLMANN 1999).

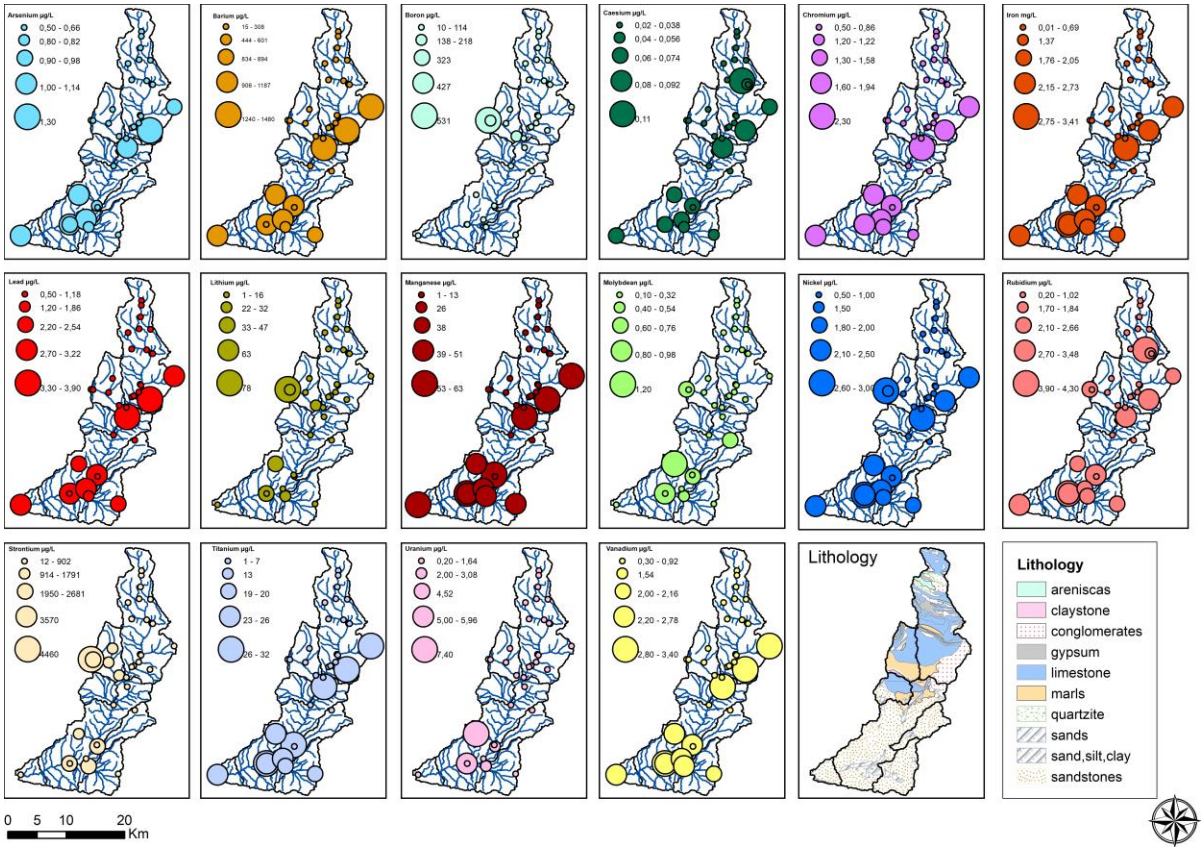


Fig. 4.2: Minor and trace element concentrations of spring, tributary and Isábena water samples throughout the catchment. (Source geological map: University of Potsdam, Map design: Heinzle 2018).

4.1.2 Assessing drinking water guidelines

After showing overall patterns of ion and element concentrations throughout the catchment, the drinking water guidelines will be addressed. As shown in CHAPTER 3.3.1, there exist only thresholds for a certain amount of ions or elements. *Fig* 4.3 shows a set of boxplots representing analysed parameters with existing thresholds. The thresholds are drawn as red lines. Note that scaling between parameters is varying. Thresholds were exceeded for at least one sample for *Ba, Fe, Mn, NO_3* and *SO_4*. Many samples did not show concentrations above the detection limit for several parameters, which is shown as the boxplots touch zero for most parameters.

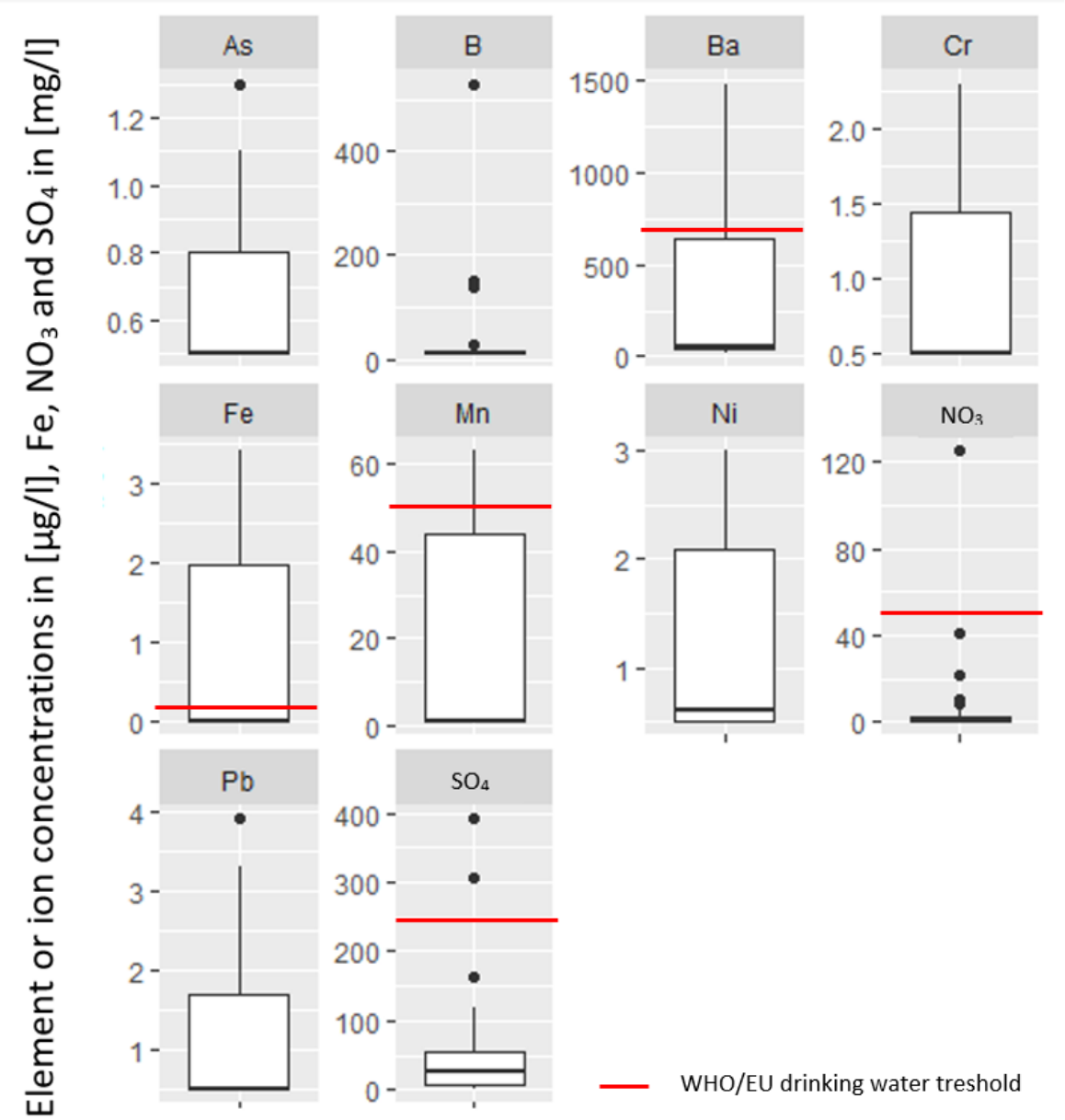


Fig. 4.3: Element or ion concentrations of parameters with existing WHO/EU drinking water guidelines.

Tab. 4.1 gives additional information towards the drinking water guidelines violation. Besides concentrations and sample spots (*Fig. 3.1*) , also lithology and land use is given. No samples of the northern limestone area is exceeding any of the thresholds.

The marl spring sample (w5) is exceeding the treshold for SO_4 (250mg/l) , same as one of the tributaries within the southern sandstone areas (w33), where SO_4 reaches its maximum at 392 mg/l.

Samples w25 to w35 all exceed one or multiple thresholds. They all exceed the *Fe* guideline of 0.2 mg/l considerably. While elsewhere in the catchment *Fe* concentrations

are at or around detection limit (0.01 mg/l), the southern areas have concentrations up to 3.41 mg/l at sample w35. Note that *Fe* exceeding sample spots come from different sample types, lithologies and land uses, thus making it difficult to account one of these parameters as main controlling factor.

Ba and *Mn* show similar behaviour for samples w25 to w35. While not all samples exceed the guideline, they all are enriched and have substantial higher concentrations in comparison to other catchment samples such as w5. As seen in CHAPTER 4.1.1, also some other elements follow this trend of having their highest concentrations in the conglomerate springs and in the southern sandstone areas.

W33 is the only sample which exceeds the guideline for NO_3 (50mg/l). As other samples in the area also have increased concentrations, none of the spring samples nor the Isábena sink sample at the catchment outlet is enriched by NO_3, indicating possible nitrification during transport.

Tab. 4.1: Samples exceeding WHO/EU guidelines for drinking water plus sample type, lithology and land use. Bold numbers indicate violation of the related threshold.

	Exceeded treshold							
		EU						
	WHO							
← *Sample ID*	Ba (µg/l)	NO_3 (mg/l)	Fe (mg/l)	Mn (µg/l)	SO_4 (mg/l)	***Sample type***	***Lithology***	***Land use***
	thresholds							
	700	***50***	***0.2***	***50***	***250***			
w5	10	0.92	0.02	< 1	**306.0**	Spring	Marl	Badlands
w25	**1180**	1.29	**2.47**	**54**	35.7	Isábena	Sandstone	Agriculture
w26	**1110**	5.17	**2.33**	**53**	51.6	Isábena	Sandstone	Agriculture
w27	**1280**	0.26	**2.65**	**56**	3.0	Spring	Conglomerate	Forest/Shrubs
w28	**1240**	0.25	**2.50**	**53**	2.5	Spring	Conglomerate	Forest/Shrubs
w29	**906**	**125.0**	**2.15**	49	120.0	Spring	Sandstone	Agriculture
w30	**834**	21.58	**1.76**	39	85.6	Spring	Sandstone	Agriculture
w31	444	41.35	**1.83**	41	162.0	Tributary	Sandstone	Agriculture
w32	**1060**	2.33	**2.21**	47	38.7	Isábena	Sandstone	Agriculture
w33	243	10.11	**2.75**	**61**	**392**	Tributary	Sandstone	Agriculture
w34	**1110**	3.04	**2.53**	48	43.1	Isábena	Sandstone	Agriculture
w35	**1480**	< 0,25	**3.41**	**63**	3.7	Spring	Limestone	Forest

Relating to *Tab. 3.3*, although a considerable amount of samples exceed guidelines, their potential harm to human is limited. *Fe* and *Mn* only are related to changes in water colour and taste. *Ba* has been connected to hypertension, but its dangerous limit is still in debate (WHO 2011). SO_4 may have a laxative effect and NO_3 may cause cyanosis for children, but is only increased in one spring sample and no tributary with increased discharge.

4.2 Hydrological Fingerprinting

The following part will show the results of the hydrological fingerprinting. As mentioned in CHAPTER 3.3, two different model combinations with each consisting of two distinct model setups have been performed. These model combinations are:

- Hydrological fingerprinting using *major ions and stable isotopes* for the *whole* Isábena catchment
- Hydrological fingerprinting using *major ions and stable isotopes* for the catchment *without the sandstone areas*
- Hydrological fingerprinting using *minor and trace elements* for the *whole* Isábena catchment
- Hydrological fingerprinting using *minor and trace elements* for the catchment *without the sandstone areas*

Each section will show an overview of the tracer selection and statistical processing, which will be summarized in a table for each model run. As in CHAPTER 3.3 described, the tests include a range test for mass conservation, a Kruskal-Wallis-H-test for source discrimination suitability of tracers, followed by a conservativity test and the linear discriminant analysis to test for discrimination power.

Based on LDA results, tracers for the unmixing model will be chosen. Additionally, for each model run a combination of figures will be presented, including a graph of the linear discriminant functions, boxplots of used tracers used in the mixing model as well as results of relative source distribution by the mixing model.

4.2.1 Major ions and stable isotopes for the whole catchment

Tab. 4.2 shows an overview of the statistical procedure described in CHAPTER 3.3. For major ions, all possible tracers passed the range test, as the sink values for each ion are between the minimum and maximum value of all sources.

For major ions and stable isotopes in the whole catchment, HCO_3 did not pass the Kruskal-Wallis test, indicated by p-values above 0.05. Therefore it is dismissed and no longer used in the subsequent analysis. All the other tracers with p-values above 0.05 are at least suitable to discriminate between two source groups. Based on INAMDAR (2011) and HOOPER (2003), possible tracers usually are then plotted against each other, to prove conservative behaviour within the catchment through positive correlations between the elements. As in (INAMDAR 2011) stated, at least one correlation factor above 0.5 should prove this. *Tab. 4.2* shows the correlation coefficients for stable isotopes and major ions for the whole catchment. δ^2H and $\delta^{18}O$ correlate very strong with each other and have correlation coefficients above 0.5 with all major ions. Additionally, they all have correlate with at least one other major ion at coefficient of above 0.5 Therefore, all possible tracers enter the linear discriminant analysis.

Tab. 4.2: Correlation matrix of stable isotopes and major ions for whole catchment.

δ^2H	$\delta^{18}O$	*Cl*	SO_4	NO_3	*K*	*Na*	Mg_2	Ca_2	
	0.989	**0.608**	**0.538**	**0.542**	**0.676**	**0.519**	**0.535**	**0.809**	$\delta^{18}O$
		0.662	**0.605**	**0.578**	**0.735**	**0.547**	**0.607**	**0.837**	$\delta^{18}O$
			0.566	**0.693**	**0.538**	0.375	**0.743**	**0.719**	*Cl*
				0.308	**0.759**	0.461	**0.936**	**0.773**	SO_4
					0.135	0.185	0.475	**0.566**	NO_3
						0.553	**0.712**	**0.718**	*K*
							0.370	0.298	*Na*
								0.795	Mg_2
									Ca_2

Tab. 4.3 shows the overview of the statistical processing including the linear discriminant analysis. For major ions and stable isotopes, the first linear discriminant function (LD1) is able to account for 98,73% of the data. The second linear discriminant function (LD2) accounts for 1,13%. The other 0,14% is explained by LD3 which is not shown here. δ^2H, $\delta^{18}O$, *K* and *Na* show the highest absolute values for linear discriminant functions and after testing make up the optimal composite fingerprint for the subsequent mixing model.

Tab. 4.3: Overview of statistical processing for major ions and stable isotopes in the whole catchment.

Major Ions and stable isotopes	Mass conservation (values in mg/l)			Kruskal-Wallis H-test		Conser-vativity	Linear Discriminant Analysis	
	Min	Max	Sink	Chi^2	p-value	Correlation	LD1 (98,73%)	LD2 (1,13%)
δ^2H	**-81.40**	**-60.00**	**-69.20**	**8.1**	**0.0442**	**+**	**-3.10**	**-0.80**
$\delta^{18}O$	-11.68	-7.99	-9.66	9.5	0.0224	+	**26.76**	**4.74**
Cl	0.17	22.17	18.78	10.5	0.0143	+	**1.55	-0.49
SO_4	2.52	392.00	51.64	12.5	0.0058	+	**-0.10	-0.03
NO_3	0.25	125.00	5.61	10,5	0.0141	+	**-0.70	0.09
K	**9,12**	**4.24**	**1.45**	**12.1**	**0.0069**	**+**	**-15.56**	**3.82**
Na	**0.30**	**30.00**	**15.00**	**12.4**	**0.0060**	**+**	**4.63**	**0.06**
Mg_2	0.88	34.10	11.80	8.6	0.0339	+	**-0.20	0.17
Ca_2	8,49	231.00	89.60	10.3	0.0160	+	**-0,05	0,02
HCO_3	20.46	355.36	188.24	2.9	*0.5650	/	/	/

*p-value > 0.05: not significant for discriminating at least two sources
** Dismissed by testing for model performance or weak relevance
"/ ": Dismissed by previous test
"bold": input into unmixing model

Fig. 4.4 shows the summary of results for major ions and stable isotopes in the whole catchment. It shows the linear discriminant functions, boxplots of used tracers and mixing model output.

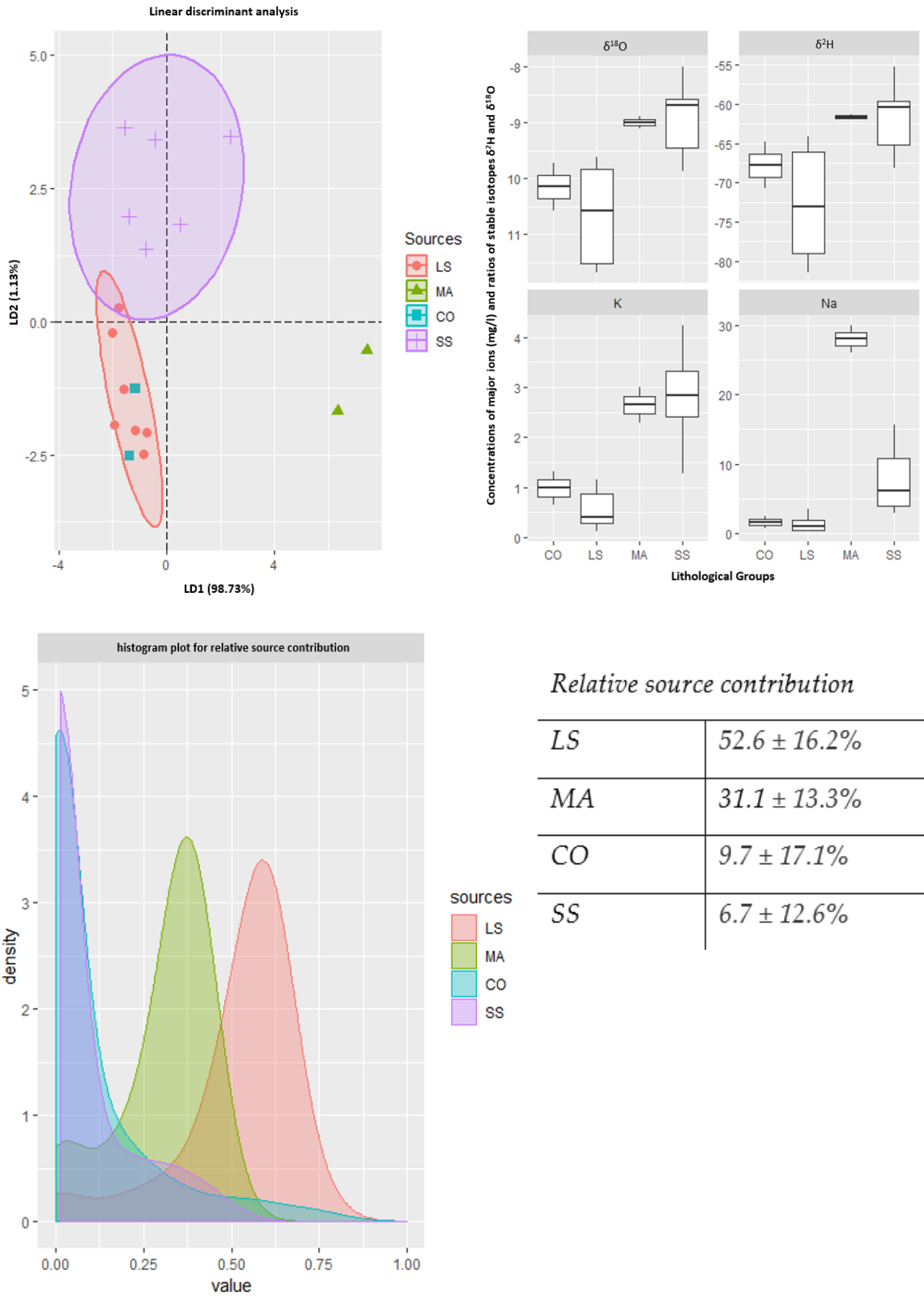
The LDA shows a strong overlapping of sources on both axis (LD1 and LD2) indicating a suboptimal source discrimination. While the marl areas (MA) can be discriminated well, the sandstone areas (SS) overlap the limestone (LS) and the conglomerate areas (CO). The conglomerate areas are hardly distinguishable from the limestone area as they are

overlaid by them on LD1 and LD2. Note that the X-axis (LD1) of the LDA explains 98.73% of the data, so only 1.13% are explained by the Y-axis (LD2). Hence the Y-Axis only has a very small impact on source discrimination. Due to the fact, that the overlapping sandstones only can be distinguished from limestones by the impact of LD2, the outcome of the discriminant analysis is rather unsuccessful.

The boxplots in *Fig. 4.4* show the distribution of the used tracers (δ^2H, $\delta^{18}O$, *K*, *Na*) for discriminating between certain sources. Plots not overlapping with each other indicate significant difference between the sources. δ^2H and $\delta^{18}O$ have similar behaviour, indicating discrimination power between SS/MA and CO/LS. The same accounts for *K*, which shows differences between SS/MA and CO/LS. Additionally, CO and LS can be distinguished well by *K*. *Na* is suited to discriminate between MA and other lithologies, while SS can also be distinguished from CO/LS.

The output of the mixing model, which was run 2000 times, is shown in the combined histogram in *Fig. 4.4* with the complementary table showing the results with error estimation, indicated by the variation within the 2000 model runs.

The marl areas in the south are responsible for 31.1 ± 13.3% of the sink concentration. The sandstones can be associated with 6.7 ± 12.6%, the limestone areas with 52.6 ± 16.2% and the conglomerates with 9.7 ± 17.1% of the sink mixture. Note that the error, which is derived from the standard deviation of the mixing model is high for all sources (12.6 – 17.1%), indicating the poor discrimination of sources by the linear discriminant function. Nevertheless, it is shown that the limestone areas are likely the most relevant source, followed by the marl areas. Due to the fact that the marls have been discriminated rather well, their value might provide a basis for comparison with the later results shown.



Relative source contribution

LS	*52.6 ± 16.2%*
MA	*31.1 ± 13.3%*
CO	*9.7 ± 17.1%*
SS	*6.7 ± 12.6%*

Fig 4.4: Summary of results for mixing model with major ions and stable isotopes in the whole catchment. LDA-plot, boxplots for used tracers and histogram of relative source contribution with complementary table.

4.2.2 Major ions and stable isotopes for catchment without sandstone source areas:

As mentioned already and shown in *Fig. 4.4*, discrimination of the sandstone source group is not optimal. Therefore another run with stable isotopes and major ions, excluding the sandstone sources in the south, was performed. Similar to the previous run, the following sections will show tables and combinations of figures for tracer selection and model results. Due to the dismissing of the sandstone sources and the change of the set sink source, also the statistic pre-processing has to be redone, as it is likely that different tracer elements or stable isotopes are best suited for the mixing model as in the previous models. *Tab. 4.4* gives an overview of the tracer selection and statistical processing.

All possible tracers pass the mass conservation test, as the sink concentrations are within the range of all source concentrations. However, although the difficult to discriminate sandstone sources are dismissed, only two tracers (SO_4, K) pass the Kruskal-Wallis test and are thereby eligible to discriminate at least two sources. *Tab. 4.3* shows the correlation matrix for the remaining two major ions. Again, they each have correlation coefficients > 0.5 with stable isotopes and each other, validation their conservativity under the given criteria.

Tab. 4.3: Correlation matrix of stable isotopes and major ions for catchment without sandstones

δ^2H	$\delta^{18}O$	SO_4	K	
	0.989	**0.537**	**0.738**	δ^2H
		0.608	**0.797**	$\delta^{18}O$
			0.902	SO_4
				K

The linear discriminant analysis is performed with the only two possible tracers left (SO_4, K). The linear discriminant LD1 describes 95.26% of the data distribution, LD2 describes 4.74%. Low concentrations of SO_4 and K lead to their low linear discriminant coefficients.

Table 4.4: Overview of statistical processing major ions and stable isotopes without sandstone source areas

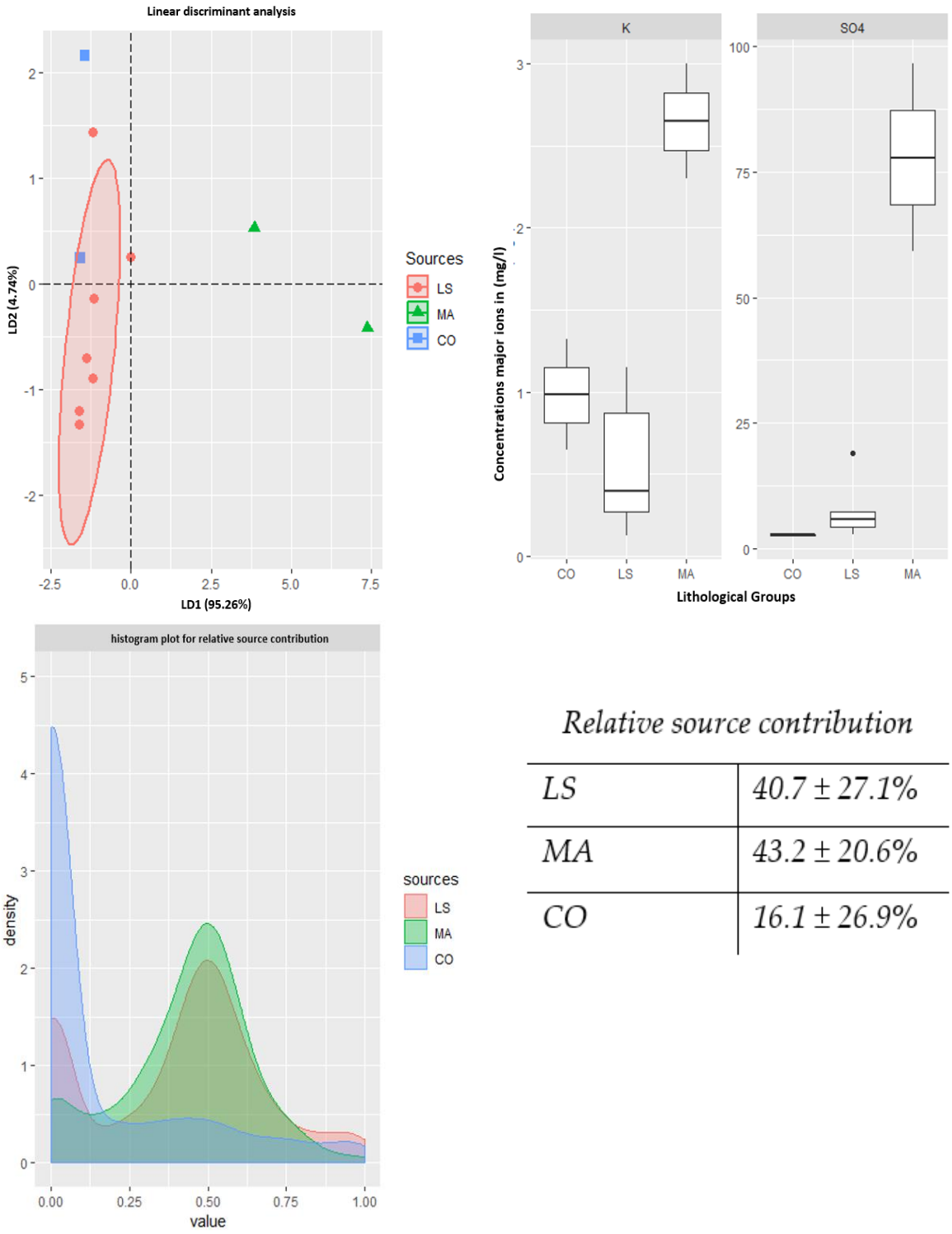
Major Ions and stable isotopes	Mass conservation (values in mg/l)			Kruskal-Wallis H-test		Conser-vativity	Linear Discriminant Analysis	
	Min	Max	Sink	Chi^2	p-value	Correlation	LD1 (95.26%)	LD2 (4.74%)
δ^2H	-81.40	-61.30	-70.00	5.0	*0.0810	/	/	/
$\delta^{18}O$	-11.68	-8.88	-10.37	4.6	*0.0976	/	/	/
Cl	0.17	7.45	15.59	3.6	*0.1687	/	/	/
SO_4	**2.83**	**96.56**	**34.64**	**6.6**	**0.0368**	**+**	**0.0916**	**-0.0796**
NO_3	0.25	8.90	0.938	5.1	*0.0782	/	/	/
K	**0.16**	**3.00**	**0.869**	**5.7**	**0.0475**	**+**	**0.1496**	**2.901**
Na	0.31	30.00	13.40	4.7	*0.0937	/	/	/
Mg_2	0.88	8.08	6.33	4.7	*0.0937	/	/	/
Ca_2	30.00	113.00	67.80	1.3	*0.5257	/	/	/
HCO_3	20.26	306.48	189.70	0.7	*0.7180	/	/	/

*p-value > 0.05: not significant for discriminating at least two sources
** Dismissed by testing for model performance or weak relevance
"/ ": Dismissed by previous test
"bold": input into unmixing model

Fig. 4.5 shows the combinations of plots for results of the mixing model derived from major ions and stable isotopes without the sandstone source areas. As expected, due to the poor element selection and only two reliable tracers, the linear discriminant analysis failed to distinguish all three remaining lithologies. While marl areas are distinguished well on LD1 which makes up 95.26% of the data distribution, they cannot be distinguished from limestones or conglomerates on LD2. Limestones and conglomerates can neither be distinguished on LD1 or LD2 from each other. The reason for these failed discrimination can be seen in the boxplots, showing the concentrations of *SO_4* and *K* within the source groups. Both tracers are suited well for the discrimination of marls, but fail to distinguish between conglomerates and limestones. As all other tracers, which possibly would have been able to distinguish those two groups failed to pass the Kruskal-Wallis-Test, the result of the given mixing model which was again run 2000 times, is rather unsuccessful and error margins of all source groups are very high.

Nevertheless, the results indicate that limestone (40.7 ± 27.1%) and marl areas (42.3 ± 20.6%) both contribute similar to the sink mixture. Conglomerates have a lower impact

on the sink mixture with 16.1 ± 26.9%. Due to the unsuccessful discrimination of limestone and marl areas, especially the results of these two source groups have to be considered heavily inaccurate.



Relative source contribution

LS	*40.7 ± 27.1%*
MA	*43.2 ± 20.6%*
CO	*16.1 ± 26.9%*

Fig 4.5: Summary of results for mixing model with major ions and stable isotopes without sandstone source areas. LDA-plot, boxplots for used tracers and histogram of relative source contribution with complementary table.

4.2.3 Minor and trace elements for whole catchment

The following section will cover the hydrological fingerprint for minor and trace elements in the whole catchment. *Tab. 4.5* shows the overview for statistical processing similar to the previous model setup.

Table 4.5 Overview of statistical processing for minor and trace elements in the whole catchment

Minor and trace elements	Mass conservation (values in µg/l)			Kruskal-Wallis H-test		Conser-vativity	Linear Discriminant Analysis	
	Min	Max	Sink	Chi^2	p-value	Literature	LD1 (87.19%)	LD2 (11.13%)
B	10.0	150.0	12.0	7.2	*0.0653	/	/	/
Ti	**1.0**	**29.0**	**25.0**	**11.1**	**0.0110**	**+**	**-6.2645**	**-3.5459**
U	**0.1**	**7.4**	**0.8**	**13.9**	**0.0035**	**+**	**3.0704**	**-3.4894**
V	**0.3**	**3.0**	**2.7**	**12.6**	**0.0056**	**+**	**4.2279**	**5.1646**
Sr	53.0	2370.0	641.0	10.0	0.0185	+	**-1.0214	-7.6340
As	0.5	1.3	1.0	10.6	0.0138	+	**1.3309	7.7040
Cr	**0.5**	**1.9**	**1.9**	**10.7**	**0.0136**	**+**	**-2.348**	**-3.8766**
Pb	**0.5**	**3.3**	**2.9**	**11.7**	**0.0086**	**+**	**3.9917**	**4.542**
Ni	**0.5**	**2.4**	**2.3**	**11.8**	**0.0080**	**+**	**2.3048**	**8.5534**
Mn	1.0	61.0	53.0	9.80	0.0203	+	**1.0635	-7.2399
Li	1.0	44.9	9.5	12.7	0.0054	-	/	/
Fe	10.0	2750.0	2330.0	12.0	0.0072	-	/	/
Ba	15	1280	1110	13.7	0.0080	-	/	/
Rb	0.2	4.3	2.9	13.7	0.0082	-	/	/
Mo	0.1	1.2	0.2	15.2	0.0042	+	**1.4548	1.9555

*p-value > 0.05: not significant for discriminating at least two sources
** Dismissed by testing for model performance or weak relevance
"/ ": Dismissed by previous test
"bold": input into unmixing model

For this model run, all minor and trace elements pass the range test, indicated by sink concentrations within the range of source concentrations. *B* does not pass the Kruskal-Wallis test (p-value >0.05), therefore is not suitable to distinguish at least two sources and for this reason dismissed. In contrast to the correlation assessment between potential tracers done for the previous models, for this model run a literature assessment of conservativity will follow.

Based on PENG ET AL. (2009), the metal species can be expected to leach at different pH-values from sediment into water, thereby altering the representativity. The stated pH-values are 5.0-6.0 for *Ni* and *As*, 4.0 for *Pb* and 2.5 *Fe*. As no measured pH-values from agricultural or riparian vegetation soils nor suspended sediments are available, it is difficult to address this. However, it can be expected that most areas do not fall into acid conditions below pH of 4.0, therefore declaring *Pb* and *Fe* as conservative in this regard. The same should account for *Ti* and *Cr* as they should not be leached from sediment under the given pH-values and are widely used in tracing studies (NEAL ET AL. 2011, BOYACIOGLU et al. 2011). *Li, Rb, B*a and *U* are expected to behave conservatively during mixing, although a certain amount (up to 30%) is expected to be lost during 0.45µg/l filtering (PAULSEN ET AL. 1997). While *U* will remain in the models due to ins conservativity regarding pH-value, *Li*, *Rb* and *Ba* will be dismissed. WANG ET AL. (2009) state that increased occurrence of phytoplankton within streams may increase the V concentration. Although this is difficult to address, high lateral connectivity in the Isábena catchment points towards low residence time and decreased interaction with phytoplankton. Therefore *V* will be considered conservative. Although *Fe* was considered conservative in regard to sediment leaching, it is oxidized by air at neutral pH and thereby also dismissed from further analysis (SLY ET AL. 1990). *Mn* is not oxidized and even stable during water treatment processes, thereby it is considered conservative (SLY ET AL. 1990). *Sr* and *Mo* finally are considered conservative as their concentrations should not get altered during mixing (PAULSEN ET AL. 1997).

Based on model performance and the power levels therefore the elements *Ti*, *U*, *V*, *Cr*, *Pb*, and *Ni* make up the composite fingerprint, while *Sr, As, Mo* and *Mn* are getting dismissed. *Fig. 4.6* shows the overview of results for this model run. Similar to *Fig. 4.5* a LDA-plot, boxplots of used tracers and mixing model result with a complementary table are shown.

The LDA showed that LD1 explains 87.19% of the data, while LD2 explains 11.13%. Therefore, also the Y-axis (LD2) is considerable. While LDA for major ions and stable isotopes for the whole catchment showed large overlapping between groups of SS, CO and LS, LDA for minor and trace elements only has overlap for LS and MA on LD1 but is able to distinguish the CO very well from the other groups. In contrast to that, LD2

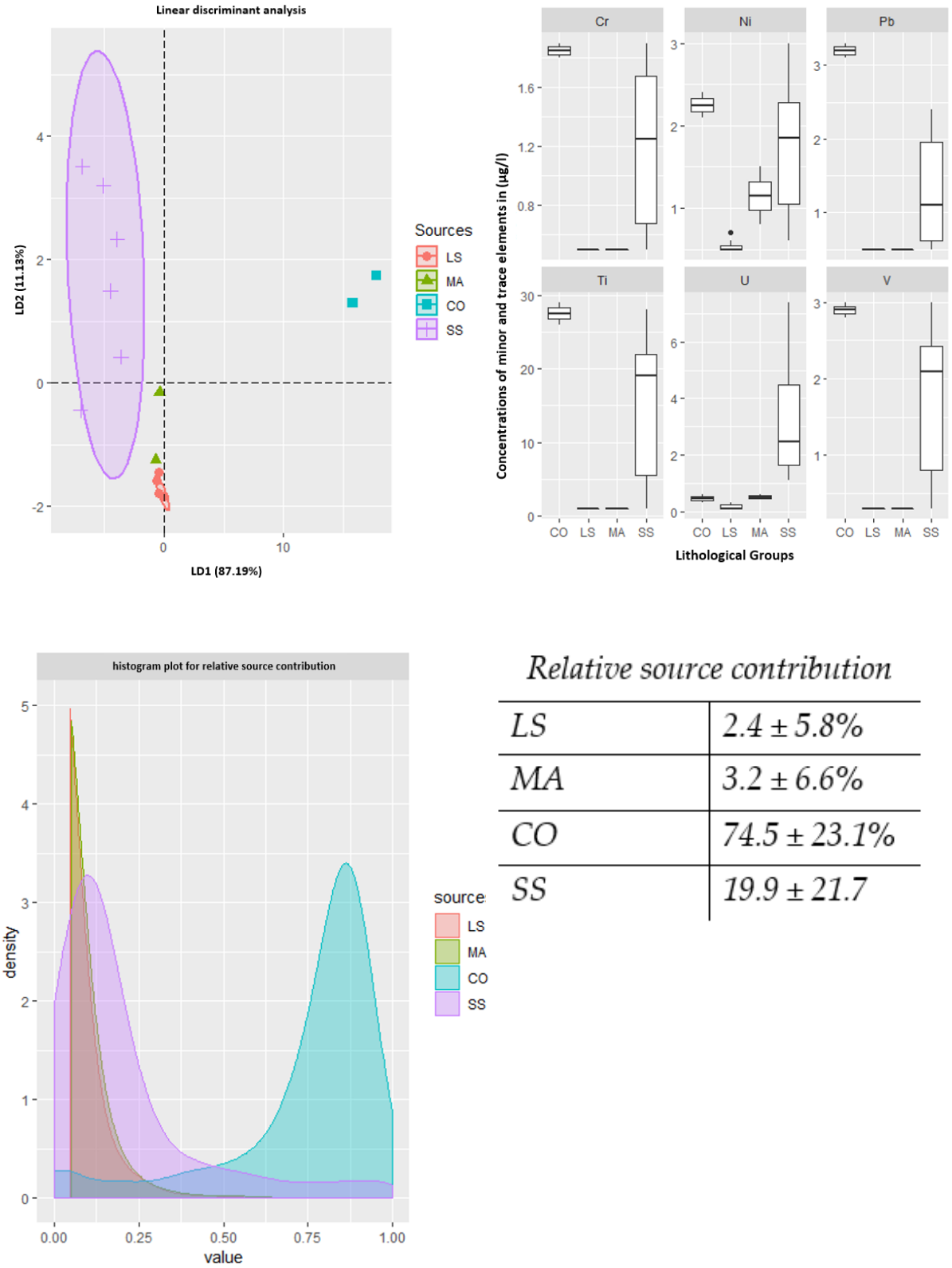
shows large overlapping of SS with CO and marls while CO and MA do not overlap each other.

Boxplots in *Fig. 4.6* show suitability of each used tracer to distinguish between certain sources. *Cr*, *Ti*, *Pb* and *V* all have similar behaviour. High values in the CO samples make them suitable to distinguish between CO and other groups, while concentrations in LS and MA samples are all below detection limit. SS values are widely spread and cover values between detection limit and the lower limit of CO values. *Ni* is suitable to discriminate between LS and MA, as MA values are measurable while LS also for *Ni* are not. However, *Ni* fails to discriminate between CO and SS. Finally, *U* is suitable to distinguish between SS and other lithologies as well as between LS and other lithologies but fails to distinguish between CO and MA.

The output of the mixing model, which was run 2000 times, is shown in the combined histogram in *Fig. 4.6* with the complementary table showing the results with error estimation.

Based on this model run, CO are reliable for 74.5 ± 23.1% of the sink information, while SS come up for 19.9 ± 21.7% of the sink. MA and LS can be associated with 3.2 ± 6.6% and 2.4 ± 5.8% respectively. Similar to the first group of models, error margins are high, even outreaching mean values for all but the sandstone groups. CO being classified as dominant source is likely due to *Cr*, *Ni*, *Pb*, *Ti* and *V* values above detection limit in the sink sample.

Note that the results are very different in comparison to the hydrological fingerprint based on major ions and stable isotopes for the whole catchment, as the tracers making up the composite fingerprints indicate different source distributions. As seen in the LDA plots of both hydrological fingerprints, one of the key factors leading to this, is the very poor discrimination of the sandstone sources in the southern catchment as well as the high concentrations of trace elements in conglomerate spring samples.



Relative source contribution

LS	*2.4 ± 5.8%*
MA	*3.2 ± 6.6%*
CO	*74.5 ± 23.1%*
SS	*19.9 ± 21.7*

Fig 4.6: Summary of results for mixing model with minor and trace elements in whole catchment. LDA-plot, boxplots for used tracers and histogram of relative source contribution with complementary table.

4.2.4 Minor and trace elements for catchment without sandstone source areas

The final model run includes minor and trace elements while dismissing the sandstone source areas. *Tab. 4.6* shows the statistical tracer selection and pre-processing similar to the model runs before.

As in the previous model run, all possible tracers successfully pass the range test, indicated by the sink concentrations within the range of the source concentrations. However, it should be noted that for an accountable number of possible tracers (*Ti*, *V*, *As*, *Cr*, *Pb*, *Ni*, *Fe, Mo*), the sink concentrations equals the minimum concentration within the source areas, which also equals the detection limit of these elements. *Sr*, *Li, Ba* and *Fe* do not pass the KW-test for source discrimination and are dismissed. *B* has not been tested for conservativity yet, but is not expected to change through filtering and is therefore considered conservative, although there might be slight inputs of *B* with the usage of fertilizers (PAULSEN ET AL. 1997, VOUTSA ET AL. 20009). All other elements are conservative, considered by the previous assessment. (CHAPTER 4.23). Therefore the elements *B*, *Ti*, *U*, *V*, *As*, *Cr*, *Pb*, *Ni*, *Mn* and *Mo* enter the linear discriminant analysis.

The results of the LDA show that *U* and *Ni* point in a similar direction on LD1. *Ni, V* and *Pb* point in the same direction but with lower power. *Mn* and *B* show in the opposite direction indicated by their negative prefix. *As* and Mo are dismissed from the composite fingerprint, as they negatively influenced reclassification. All remaining elements make up the composite fingerprint and results of the mixing model are shown in *Fig. 4.7*.

The LDA shows very good discrimination of sources on LD1 which is relevant for 97.68% of the data distribution, as there is no overlap on the X-Axis of any source groups. However, there is a large overlap of limestone and conglomerates on LD2, but as LD2 explains 2.32% of the data distribution, this is not much of a factor. *Cr*, *Mn*, *Pb*, *Ti* and *V* all have similar concentrations in source groups, making them suitable to distinguish between CO and the other two source groups of LS and MA. *B* is suitable to distinguish MA and *U* is suitable to distinguish LS from each of the other two source groups. *Ni* is suitable to distinguish between all three source groups, as CO have the

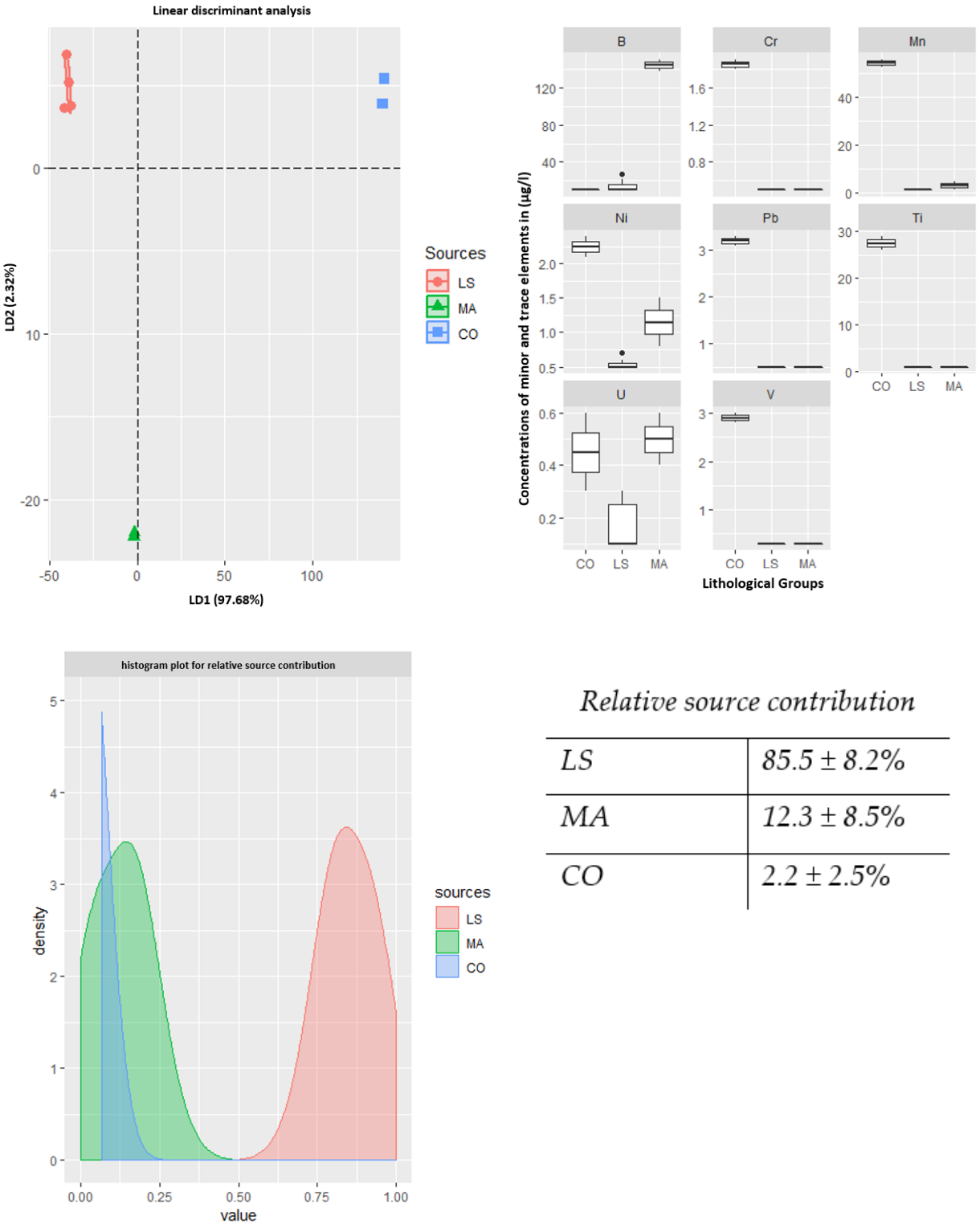
highest concentrations at around 2µg/l, marls at 1-1.2µg/l and limestone below the detection limit of 0.5µg/l.

Table 4.6: Overview of statistical processing for minor and trace elements without sandstone source areas

Minor and trace elements	Mass conservation (values in µg/l)			Kruskal-Wallis H-test		Conser-vativity	Linear Discriminant Analysis	
	Min	Max	Sink	Chi^2	p-value	Literature	LD1 (97.68%)	LD2 (2.32%)
B	**10.0**	**150.0**	**16.0**	**6.3**	**0.0417**	**+**	**-0,3242**	**0.1596**
Ti	**1.0**	**29.0**	**1.0**	**9.9**	**0.0071**	**+**	**-0.4329**	**-0.0359**
U	**0.1**	**7.4**	**0.3**	**6.5**	**0.0373**	**+**	**18.3180**	**-4.6492**
V	**0.3**	**3.0**	**0.3**	**9.9**	**0.0070**	**+**	**-6,4939**	**-0.5397**
Sr	53.0	2370.0	566.0	5.0	*0.0810	/	/	/
As	0.5	1.3	0.5	9.9	0.0070	+	**-3.2469	-0.2698
Cr	**0.5**	**1.9**	**0.5**	**9.9**	**0.0070**	**+**	**-12.9878**	**-1.0794**
Pb	**0.5**	**3.3**	**0.5**	**9.9**	**0.0070**	**+**	**-6.4939**	**-0.5397**
Ni	**0.5**	**2.4**	**0.5**	**8.1**	**0.0174**	**+**	**11.8347**	**3.2333**
Mn	**1.0**	**61.0**	**1.0**	**8.4**	**0.0147**	**+**	**-1.3536**	**0.0529**
Li	1.0	44.9	2.3	5.7	*0.0580	/	/	/
Fe	10.0	2750.0	10.0	5.9	*0.0504	/	/	/
Ba	15	1280	45	13.7	*0.1013	-	/	/
Rb	0.2	2.7	0.5	13.7	0.0207	/	/	/
Mo	0.1	0.7	0.1	15.2	0.0170	/	**-14.495	0.8247

*p-value > 0.05: not significant for discriminating at least two sources
** Dismissed by testing for model performance
"/ ": Dismissed by previous test
"bold": input into unmixing model

The unmixing model indicates that 85.5 ± 8.2% of the sink information can be accounted to the limestone sources, 12.3 ± 8.5% to marls and 2.2 ± 2.5% to conglomerates. Note the low error margins for all groups in comparison to the previous models, which can be accounted to the good discrimination of sources. The model was again run 2000 times.



Relative source contribution

LS	*85.5 ± 8.2%*
MA	*12.3 ± 8.5%*
CO	*2.2 ± 2.5%*

Fig 4.7: Summary of results for mixing model with minor and trace elements without sandstone source areas. LDA-plot, boxplots for used tracers and histogram of relative source contribution with complementary table.

4.2.5 Model comparison and validation

In the following, a comparison of the model run results and the model validation will be presented. *Tab. 4.7* shows a summary of the relative source contribution for all model runs. Note the substantial differences for each source group between the runs, indicated by different and mostly poor source discrimination based on the suitable tracers in comparison between the models.

The two models including sandstone areas resulted in opposite source contributions. While the model based on major ions/stable isotopes pointed towards a major influence of limestone (*52.6 ± 16.2%)* and marl areas (*31.1 ± 13.3%)*, the model based on minor/trace elements indicated a major influence from conglomerate areas (*74.5 ± 23.1%)* with sandstone areas also being relevant (*19.9 ± 21.7%)*.

By removing the sandstone area as possible source group due to difficulties with source discrimination, model results approached each other. While the model based on major ions/stable isotopes indicated similar input from limestone (*40.7 ± 27.1%)* and marl areas (*43.2 ± 20.6%)* with conglomerates being still relevant (*16.1 ± 26.6%)*, the model based on minor/trace elements accounts the vast majority of information to limestone sources (*85.5 ± 8.2%)*, while marl areas are accountable for most of the remaining input (12.3 ± 8.5%).

Tab. 4.7: Comparison of hydrological fingerprinting model results indicating relative source contribution from lithological source groups

	Model runs			
	with sandstone areas		*without sandstone areas*	
	major/isotopes	*minor/trace*	*major/isotopes*	*minor/trace*
Limestone (LS)	*52.6 ± 16.2%*	*2.4 ± 5.8%*	*40.7 ± 27.1%*	*85.5 ± 8.2%*
Marls (MA)	*31.1 ± 13.3%*	*3.2 ± 6.6%*	*43.2 ± 20.6%*	*12.3 ± 8.5%*
Conglomerates (CO)	*9.7 ± 17.1%*	*74.5 ± 23.1%*	*16.1 ± 26.6%*	*2.2 ± 2.5%*
Sandstones (SS)	*6.7 ± 12.6%*	*19.9 ± 21.7%*	/	/

To address model accuracy of the previously run models, all of them have been validated. As described in, this was done by setting the sink sample to sample spot w17 (*Fig. 3.1*), while input data from all source groups remained in the model setup. As w17 lies north of any conglomerate, marl or sandstone input based on the geological map used, it should only inherit information from limestone sources. Therefore model runs using w17 as sink sample should account all sink information to the limestone source. The composite fingerprint for each model validation run remained the same as in the original runs. *Fig. 4.8* shows an overview of the validation runs with complementary tables.

The validation of all models was successful, as the majority of relative source contribution points towards limestone in each validation. For major ions/stable isotopes limestone areas are assigned with 90.8 ± 20.0% (with sandstone sources) and 84.3 ± 28.8% (without sandstone sources). Due to the high error margins, also conglomerate areas are assigned with relevant source contributions of 8.5 ± 19.8% (with sandstone sources) and 14.6 ± 27.9% (without sandstone sources). Possible reasons for the notable influence of conglomerate source information into the validation sink mixture will be discussed in *CHAPTER 5.* Model validation for minor/trace elements pointed heavily towards limestone sources, which indicates good model performances. The sandstone including model for minor/trace elements accounted 97.8 ± 4.6% of sink information towards limestone sources, the model without sandstone sources assigned 98.5% ± 1.9% of information to limestone. Note that not only percentage values are higher but also error margins smaller than in the major ions/stable isotopes models.

Finally, a comparison of all available data and modelled parameters can be done. These include the discharge measurements which were taken during the field trip, the four previously shown model runs and the data from other studies. The comparing data will be the water budget, calculated by LÓPEZ TARAZÓN ET AL. (2012), which was presented in CHAPTER 1.2. *Tab. 4.8* shows the overview of data gathered in modelled in this study and the water mass balance from LÓPEZ TARAZÓN ET AL. (2012). Also used sample site discharge measurements to represent each lithological group are mentioned. W17 (4.49 m^3/s) is used for validation the limestone areas, the tributaries w8 and w10 (2.17 m^3/s)

are used for conglomerates. W7 (6.93 m³/s) is used for the marl areas although one of the springs from these tributaries comes from a limestone area. Sandstone discharge measurements are summed up from w2, w31 and w33 (3.50 m³/s). Note that the sum of each discharge groups exceeds the discharge measured at the catchment outlet by far.

Therefore, validations and comparisons based on the on-site discharge measurements have to be considered carefully.

It has to be noted, that the Carrasquero sub-catchment, which made up 2-5% of the water budget by LÓPEZ TARAZÓN ET AL. (2012), was not covered within this study.

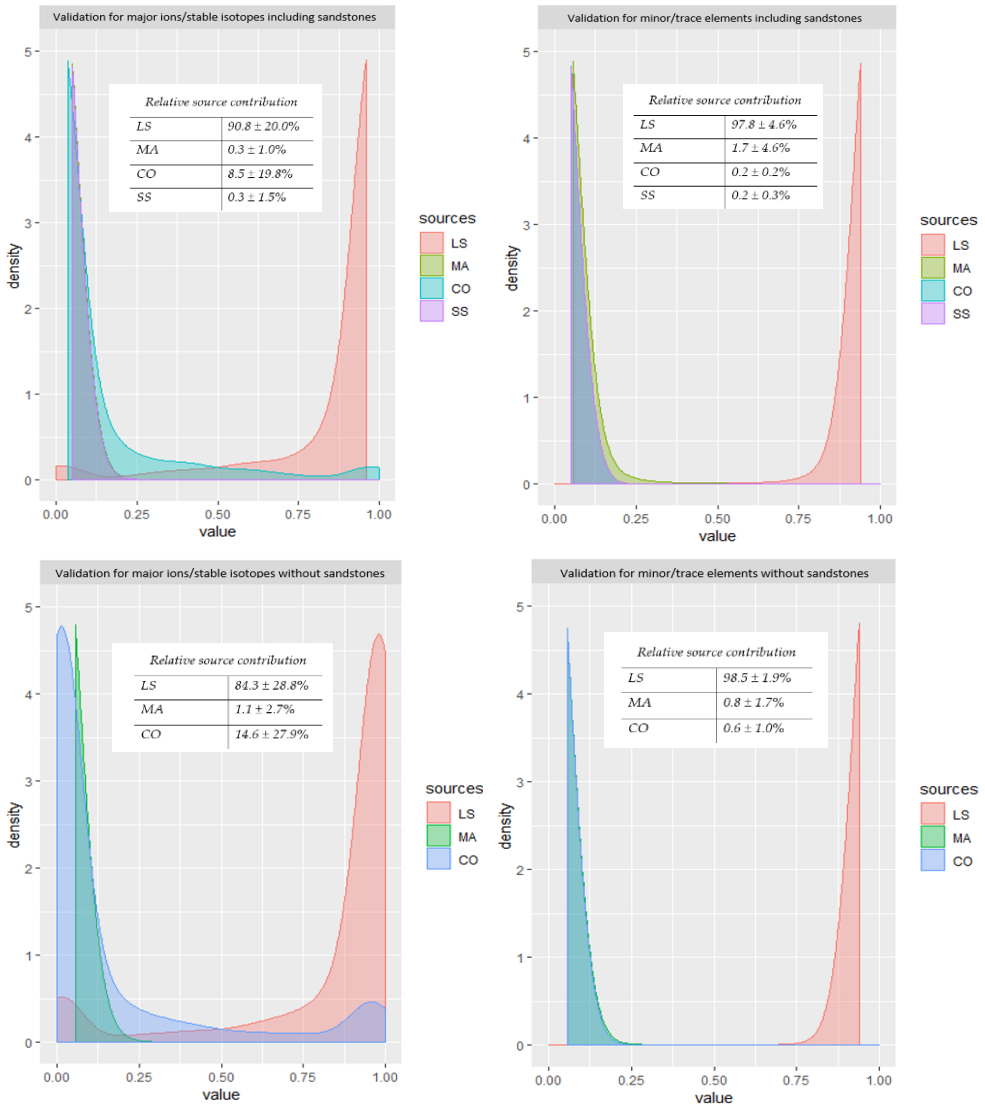


Fig. 4.2.5: Comparison of validation results for all models run. Histogram plots with complementary tables, showing relative source contributions for validation models.

Tab. 4.8: On-site discharge measurements, model results and water budget by LÓPEZ TARAZÓN ET AL. (2012).

	Discharge measurements/ estimations		***Model runs***				***López Tarazón et al. 2012***
			With sandstone		*Without sandstone*		
			Major/ isotopes	*Minor/ trace*	*Major/ isotopes*	*Minor/ trace*	
LS (w17)	4,49 m³/s	26.3%	52.6 ± 16.2%	2.4 ± 5.8%	40.7 ± 27.1%	85.5 ± 8.2%	60-70%
CO (w8 + w10)	2,17 m³/s	12.7%	9.7 ± 17.1%	74.5 ± 23.1%	16.1 ± 26.6%	2.2 ± 2.5%	
MA (w7)	6,93 m³/s	40.5%	31.1 ± 13.3%	3.2 ± 6.6%	43.2 ± 20.6%	12.3 ± 8.5%	7-26%
SS (w2 + w31 + w32)	3,50 m³/s	20.5%	6.7 ± 12.6%	19.9 ± 21.7%	/	/	7-18%
Carras-quero	/		/	/	/	/	2-5%

LÓPEZ TARAZÓN ET AL. (2012) accounted 60-70% to the northern part of the catchment, including the limestone and conglomerate areas. Discharge measurements performed within this study came up for only 39.0%, which is due to the high discharge from the Villacarli marl area. The models based on major ions and stable isotopes come close to the discharge measurements of LÓPEZ TARAZÓN ET AL. (2012) from the limestone and conglomerate areas (60-70%), while models on minor/trace elements overestimate the discharge from these areas. LÓPEZ TARAZÓN ET AL. (2012) measured between 7-26% of discharge coming from the marls in the Villacarli sub-catchment. Discharge measured for this study was at 6.93 m³/s and thereby exceeds this value at 40.5%. The high discharge of 6.93m³/s has to be accounted to the heavy rainfalls during and before the measurements. As also LÓPEZ TARAZÓN ET AL. (2012) stated, the Villacarli discharge is highly variable and extremely susceptible to heavy rainfalls. Due to the large error margins, all model results are within the 7-26% span. However, the mean value of the minor/trace elements model without sandstones at 12.3% is close to the mean of discharge measured by LÓPEZ TARAZÓN ET AL. (2012). Sandstone area contribution is indicated at 20.5% by discharge measurements from this study and 7-18% by LÓPEZ TARAZÓN ET AL. (2012). Both models including the sandstone areas provide relative source contributions close to those values. It has to be noted that mean discharge measurements from previous studies were highly variable, ranging from 1.88 m³/s (2005-2006) to 4.30 m³/s (2006-2007) LÓPEZ TARAZÓN ET AL. (2009).

5. Discussion

In the following the choice and performance of used methods and the results will be discussed. Based on the results the research questions will be addressed and perspectives for future studies in general and the Isábena catchment will be given.

5.1 Discussion of methods

The study area itself proved as very fitting. Most areas are easily accessible and sampling was never a problem. However, as this study was based on differences in lithology, the heterogeneous north of the catchment, may have caused some issues. Small scale areas of areniscas, conglomerates or quarzite were either not found or not put into the model due to the lack of representative sample spots. Hence, it cannot be excluded that those areas may have major influences on the river chemistry in the northern part and especially alter the fingerprint of the limestone areas. These uncertainties in lithology, also reflected in the used geological map was not addressed in any of the previous studies and therefore is still in debate.

As already mentioned briefly in CHAPTER 3.1, sample scheme was not optimal. While the total of 35 samples may be sufficient for assessing the aims of this study, sample locations should have covered the lithological areas equally. Marl and conglomerate areas were underrepresented. Only represented by two samples each, heavily increased the potential influence of external sample disturbance (e.g. weather, human-induced waste etc.) and thereby decreased the statistical robustness (COLLINS ET AL. 2017). Another minor issue regarding water sampling is concerning the sink samples. If assumed previously, that sandstone areas could be problematic for source discrimination, a more optimal sink sample spot than w11 for the northern lithologies could have been chosen.

Due to increasingly hot temperatures and the dependence on the Spanish Mail, it was not possible to ensure the cooling of the water samples from the study area to the laboratory at the UFZ in Halle. While samples were cooled during the stay at 4-6°C, possible issues regarding this problem are difficult to address.

As the fingerprinting models performed in this study are relevant for exactly one time spot, it has to be mentioned that there were major shifts in weather during the two-week field campaign. Heavy rainfalls at the beginning of the field work influenced the discharge coming from the marl (w7) and conglomerate areas (w8, w10). Additionally, heavy precipitation may have greatly altered the chemical composition of the water samples, as the precipitation influence acts diluting on the geochemical signal of the waters (HELLMANN 1999). On the other hand, increased overland flow and input from eroding soils may have increased the influx of certain elements leached through the eroding process.

It is notable that various analysed elements have low concentrations in the earlier samples taken, while their concentrations arise above the detection limit at the later taken samples. As precipitation stopped after the first days, this may have been a key factor for some of the analysed results. Elements featuring this characteristic especially include minor and trace elements (*Pb, U, Ba, Ti, V, Cr, Mn, Fe, Ni, As, Mo*). If increased concentrations of these elements would indeed be geochemical signs from the conglomerate and sandstone sources as indicated in the element analysis, w11 and w24 should also show increased concentrations, as they are below the conglomerate springs in the river network (*Fig. 3.1).*

The fact, that it is not possible to take all samples and measurements at the same moment in time, is also reflected in the discharge measurements, which pose another major problem regarding the field methods. First of all, discharge was only measured once within the two-week time span of the field work campaign. These measurements may provide a guideline when comparing discharge measurements between sub-catchments, but have to be regarded very sceptical when drawing conclusions over longer time periods. Moreover, as only about half of the discharge measurements have been taken with an actual accurate instrument, this get increasingly problematic. As also other studies faced major variabilities in discharge within short and long time study periods (FRANCK ET AL. 2014, LÓPEZ TARAZÓN ET AL. 2012), this gets increasingly difficult to address.

Another method relating topic that has to be covered is the change of perspective this study had after the field visit. The sampling strategy was mainly based around the idea of comparing rock and river sediment with the water chemistry. As rock and sediment samples are still being analysed, geochemical processes could not be fully assessed within this study. While some of the samples taken were not useful for the fingerprinting models set up in this study, they will provide useful information for addressing rock-water interactions and weather or human-induced alteration of water chemistry. Analysis still ongoing include the assessment of rare earth element (REE) concentrations in rock and river sediment samples (POLYAKOV AND NEARING 2004), REE-leaching experiments of rock samples and the analysis of Li-isotopes which is increasingly used as a geochemical tracer (TANG ET AL. 2007). Some photographs of the ongoing analysis is shown in the appendix.

5.2 Discussion of results

To discuss the results of this study, each of the formulated research questions, will be addressed individually.

Question 1: Do river waters in the Isábena catchment exceed the WHO or EU drinking water guidelines for certain elements or ions and if yes, is it possible to relate affected areas to human activities (e.g. agriculture, industry)?

As shown in CHAPTER 4.1.2, there are several violations of drinking water guidelines for samples analysed within this study. These include *Ba* and NO_3 treshold for the WHO guideline and NO_3, *Fe*, *Mn* and SO_4 threshold for the EU guideline. It is challenging to address whether these violations are related to human-induced change. As most of the affected samples are taken within agricultural land or the main stream in the southern catchment, this could well be the case. However, most of the violations also follow the previously described pattern with increased concentrations in sandstone and conglomerate spring samples. This is especially true for *Ba*, *Fe* and *Mn* violations. Moreover, as increased concentrations of these elements usually are related with industrial waste (HÜTTER 1996), the only explanation could be that leftovers from previously resident people are applying a constant pollution, as there is no industry near the conglomerate spring sample spots. For NO_3 and SO_4, the connection to the ongoing

agricultural practise is clearly visible. As only one sample for NO_3 and two samples for SO_4 violate the guidelines, the effect concerning the health of people who would drink the river water regularly is not dramatic but should be monitored, as these parameters also could be subjects of change. It has to be noticed, that as the assessment of water quality was not previously planned, important parameters such as nitrite and phosphate have not been analysed. As those are typical indicators of the excessive use of fertilisers (SAVCI ET AL. 2012), they could have increased the information value of the water quality assessment.

Question 2: Can the lithological areas in the Isábena catchment be distinguished based on their spring water chemistry and if yes, is it possible to set up hydrological fingerprinting models to discriminate waters coming from different source areas?

The major part of this study included the setting up of different hydrological fingerprinting models. Based on the water chemistry of spring samples from different lithological units, it was possible to distinguish between the lithological areas of limestones, marls and conglomerates. Sandstone areas were difficult do discriminate, which lead to the reclassification of the model setup excluding the southern areas. Especially minor and trace elements shown a broad spectrum of concentrations in the sandstone areas, while mostly being above the detection limit.

While some sandstone samples showed the expected increase in NO_3 due to agriculture, it was not enough to separate them from the other source groups. Although low in concentrations throughout the catchment, *K* concentrations were significantly higher in sandstone areas than in the rest of the catchment, making them valid for discriminating that source. Limestone areas were characteristic for low total concentrations of major ions, mostly made up by Ca_2 and HCO_3.

Two samples in the limestone area showed increased concentrations for *Cl*, but were not enough to use as discrimination, as the other limestone springs did not show this signal. Minor and trace elements were also characteristically low for limestone areas, being mostly below the detection limit. Stable isotopes ratios worked well for distinguishing between the sandstones/marls and conglomerates/limestones. However, it must be

assumed that this is mostly due to differences in elevation, not only due to the lithological composition. There was also an attempt for elevation correction, but similar to HUYGHE ET AL. (2018), it was not reasonable for this part of the Pyrenees, which may be due to the mostly narrow valleys in the catchment.

Marls were characterised by increased *Na*, *Sr*, *B*, and *U* which allowed to discriminate them well. Conglomerates showed high values for *Cr*, *V*, *Ti*, *Pb*, *Ni*, and *Mn* but no distinct signal in any major ion, which also made them difficult to discriminate. However, if assumed that these increased values in conglomerate sources are not due to a bias in sampling as discussed in CHAPTER 5.1, they are valid for source discrimination.

Based on these discriminating factors, it was possible to set up four distinct hydrological fingerprinting models while additionally focus on the conservativity of tracers. While this was done via correlation testing between tracers for major ions/stable isotopes and via literature research for minor/trace elements, there were still enough reliable tracers available for each model to run successfully.

Nevertheless, it has to be addressed that in both ways of assessing conservativity, there is still room for improvement. While correlation coefficients, as suggested by INAMDAR (2011) and HOOPER (2003) may be a valid tool, their threshold at 0.5 seems very low. Additionally, if only one correlation coefficient has to be above 0.5, the simple increase of analysed parameters could falsely increase the conservativity power of the single elements. On the other hand, if conservativity of tracers wants to be addressed via literature research and maximum care as proposed in COLLINS ET AL. (2017), it soon becomes apparent that many additional parameters such as organic matter, characteristics of suspended sediments or soil characteristics within the source groups need to be analysed. This is especially true for sediment fingerprinting studies, in which the solubility of possible tracers plays a major role.

Relying on insoluble tracers as performed within this study may solve one issue but seem to arise several new ones like detection limits or weather related change. The validation of models via the limestone sink sample worked well, especially due to the clear source discrimination from minor/trace elements, which lead to smaller error margins.

Question 3: Are there differences in the results of hydrological fingerprinting models based on different tracers combinations and if yes, are they comparable to river discharge measurements and other studies in the Isábena catchment?

As already shown in CHAPTER 4.2.5 there are several relevant differences between the four models run within this study. The model based on minor/trace elements with sandstone areas accounts 74.5 ± 23.1% of the relative source contribution to the conglomerate areas. The small size of the tributaries coming from the conglomerate areas in comparison to the main Isábena stream, indicate a flaw in the minor/trace model with sandstones. In comparison, all other models account only 2.2 ± 2.5% up to 16.1 ± 26.6% to the conglomerates, while source contribution is dominated by limestone areas.

As monitored by LÓPEZ TARAZÓN ET AL. (2012), in baseflow or over long time mean, most of the water seems to come from the northern limestone areas. This is also the outcome of the major ions/stable isotope models. Marl contribution is highly variable between the model results, which may results from tracer concentrations reacting differently to increased precipitation during marl area sampling. Sandstone areas were difficult to discriminate, resulting in high error margins for the models where they were included.

As already discussed, expected errors in on-site discharge measurements lead to an uncertainty regarding the comparison with the model results. However, as former studies conducted long-time discharge measurements and water budget calculations, those were used as comparison LÓPEZ TARAZÓN (2009, 2012). The only issue was the lack of distinguishing between limestone and conglomerate source areas and the missing measurements from the smaller tributaries in the south. Despite a comparison therefore was made possible, the large error margins for all models in combination with the variability of discharge, makes it difficult to rank the overall performance of the models. Nevertheless, it can be concluded that a sufficient amount of analysed parameters at multiple sample spots in all relevant source groups will allow an in-depth assessment of tracer conservativity and performance of hydrological fingerprintings. As many recent studies stated, also this study showed that the assessment of conservativity is a major issue and may change the model outcome drastically.

6. Conclusions

To address the hydrological processes in the Isábena catchment in the Southern Pyrenees, a comparison of hydrological fingerprinting models was performed. Models were different in regarding their selection of tracers, following key principles from sediment and hydrological fingerprinting studies relating to the conservativity of tracers (HOOPER 2003, COLLINS ET AL. 2017). Additionally, an assessment of water quality was performed, relating to drinking water guidelines (WHO 2011, EU 1998). The analysis and modelling was based on 35 water samples, which were sampled throughout the river catchment (445km²) during a two-week field campaign in April of 2018.

The results and discussion show, that a well set up sampling scheme and continuous weather conditions are crucial for applying a hydrological fingerprint for one point in time. While this may be difficult to predict for study areas as far away as the Isábena catchment, it should be addressed as good as possible. Additionally, catchments with high variability in discharge may not be suited perfectly for hydrological fingerprinting models based on one time measurements. As discharge monitoring showed (LÓPEZ TARAZÓN ET AL. (2012), a few stormy days within a year result in a considerable amount of discharge and sediment transportation change, which lead to considerable flaws in the hydrological models.

The fingerprinting models itself were highly sensitive regarding tracer selection. As tracer conservativity assessment is often performed imprecisely, this study showed, that this can lead to severe misunderstandings regarding hydrological processes. Hence, the results of this study stress the importance of tracer selection and the appropriate conservativity assessment. However, as each study area and project setup is different, universally valid statements regarding the best method to guarantee conservativity, cannot be made based on this study.

Finally, I hope that the ongoing analysis will deepen the understanding of the presented results from this study and may allow to discuss the arguments made here. Especially geochemical processes regarding rock-water interactions will be of great interest and may also be relevant for future sediment fingerprinting studies in the study area and in similar geological settings.

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IV. Appendix

Abstract

The Isábena catchment in the Southern Pyrenees (445km²) suffers from increased soil erosion, which leads to an ongoing siltation in the Barasona reservoir at the river catchment outlet. The area is characterized by limestone in the northern higher altitudes, marl and conglomerates in the foothills and sandstone in the agricultural used southern plains. Several sediment-fingerprint and erosion studies from that area showed, that the vast majority of sediment input results from marly badlands occupying less than one percent of the area.

To further deepen the understanding of the hydrological processes related to sediment export in the catchment, a comparison of hydrological fingerprinting models based on different tracer sets was conducted, to analyse the relative discharge contribution from the different geological units to the main Isábena river.

Therefore, 35 water samples from springs, all major tributaries and the Isábena river were taken throughout the catchment and afterwards analysed for major ions and trace elements, as well as their stable isotope signatures $\delta^{18}O$ and $\delta^{2}H$. Additionally, at all sample locations discharge measurements were conducted.

The study qualitatively evaluates the element concentrations of the waters regarding drinking water guidelines and addresses suitable elements to characterize the discharge from the different geological units. The model results are comparable to on-site and discharge monitoring from earlier studies in the area, but show partially large error margins. This is discussed in context of geochemical processes, tracer conservativity, sampling strategy and model setup before conclusions for further studies are drawn.

Kurzfassung

Das Isábena Einzugsgebiet in den Südlichen Pyrenäen (445km²) leidet unter hoher Bodenerosion, was zu einer anhaltenden Sedimentation des Barasona Reservoirs am Ende des Einzugsgebiets führt. Das Gebiet ist durch Kalkstein in den Bereichen großer Seehöhe im Norden, Mergel und Konglomerate an den Hängen und durch Sandsteine in den landwirtschaftlich genutzten Ebenen des Südens gekennzeichnet. Mehrere Sediment-Fingerprinting und Erosionsstudien im Gebiet haben gezeigt, dass der Großteil des Sediments von Badlands aus dem mergeligen Gebiet stammt, welche jedoch weniger als ein Prozent der Untersuchungsgebietsfläche einnehmen.

Um die hydrologischen Prozesse im Zusammenhang mit dem Sedimenttransport im Einzugsgebiet besser zu verstehen, wurde ein Vergleich hydrologischer Fingerprintingmodelle, basierend auf variierenden Tracerkombinationen durchgeführt, um den relativen Abfluss aus den unterschiedlichen geologischen Bereichen in den Isábena Hauptstrom abzuschätzen.

Dafür wurden 35 Wasserproben aus Quellen, Zuströmen und dem Isábena Hauptstrom genommen, auf Hauptionen, Spurenelemente und stabile Isotope $\delta^{18}O$ und $\delta^{2}H$ untersucht. An allen Probestandorten wurde zusätzlich eine Abflussmessung durchgeführt.

Die Ergebnisse umfassen eine qualitative Erhebung der Elementkonzentrationen des Wassers im Bezug auf Trinkwasserrichtlinien und zeigen geeignete Elemente zur Charakterisierung des Abflusses aus den unterschiedlichen geologischen Einheiten. Die Modellergebnisse sind mit den durchgeführten Abflussmessungen und dem Abflussmonitoring früherer Studien vergleichbar, zeigen aber teilweise große Fehlerbereiche. Dies wird im Kontext von geochemischen Prozessen, der Konservativität von Tracern, der Probenahmestrategie und der Modelkonfigurationen diskutiert bevor Rückschlüsse für zukünftige Studien gezogen werden.

Supplementary tables

Sample ID	X	Y	Elevation	Lithology	pH	Temp °C	EC (µS)	Discharge m³/s
w1	301128	4685262	1038,1	SS	7,58	8,9	435	0
w2	294746	4679079	601,6	SS	8,42	13,5	402	2,71
w3	297334	4695830	1278,1	LS	7,45	10,5	546	0
w4	296637	4693455	958	LS	8,4	10,7	584	0,82
w5	293637	4693985	1004,2	MA	8,28	14,9	949	0
w6	294002	4693919	1002,57	MA	8,44	15,5	653	6,93
w7	298440	4691225	853,5	MA_?	8,16	9,6	441	6,93
w8	300611	4692670	885,6	MIX	8,1	8,6	281	0,59
w9	301815	4693509	944,2	BR	7,55	9,5	242	0
w10	302034	4694825	1025,4	MIX	8,33	8,2	317	1,58
w11	297501	4686157	712,7	MIX	8,29	7,5	414	7,75
w12	299982	4703667	1477	LS	7,09	7,9	496	0
w13	302275	4709141	1640,5	LS	7,98	9,1	184	0
w14	302261	4708345	1586,1	MIX	7,43	8,9	313	0
w15	302114	4706368	1506,7	MIX	7,99	8,2	142	0
w16	304029	4700146	1215,4	LS_?	8,27	9,4	749	3,86
w17	304192	4700085	1156,8	LS_?	8,07	7,5	223	4,49
w18	303827	4704233	1381,9	LS	8,1	7,4	198	3,78
w19	301877	4704334	1347,8	LS_?	7,41	15,4	92,5	0
w20	300609	4700881	1386,2	LS	7,29	5,6	60,1	0
w21	303162	4700725	1178,5	LS	8,26	6,8	1160	2,51
w22	302183	4694669	973,4	MIX	8,25	10,9	432	4,95
w23	300952	4692850	891,7	MIX	8,36	11	420	5,15
w24	299686	4690869	840,1	MIX	8,55	13	410	5,58
w25	294628	4679344	604,5	MIX	8,59	15,7	416	7,89
w26	281605	4674240	457,3	MIX	8,52	16,2	471	9,59
w27	303723	4692234	1507,8	CO	7,38	10,9	410	0
w28	307855	4696247	1584,5	CO	7,95	8,2	300	0
w29	291554	4681218	821,3	SS	8,15	12,7	978	0
w30	298305	4674367	903	SS	7,66	14,6	779	0
w31	293217	4675713	579	SS	8,35	13,5	836	0,65
w32	292783	4676962	569	MIX	8,5	15,2	427	8,91
w33	289946	4676160	538,5	SS	8,19	18,1	1130	0,16
w34	290002	4676151	535,3	MIX	8,57	15,4	448	9,13
w35	299826	4689279	820,5	LS_?	7,72	10,1	305	0

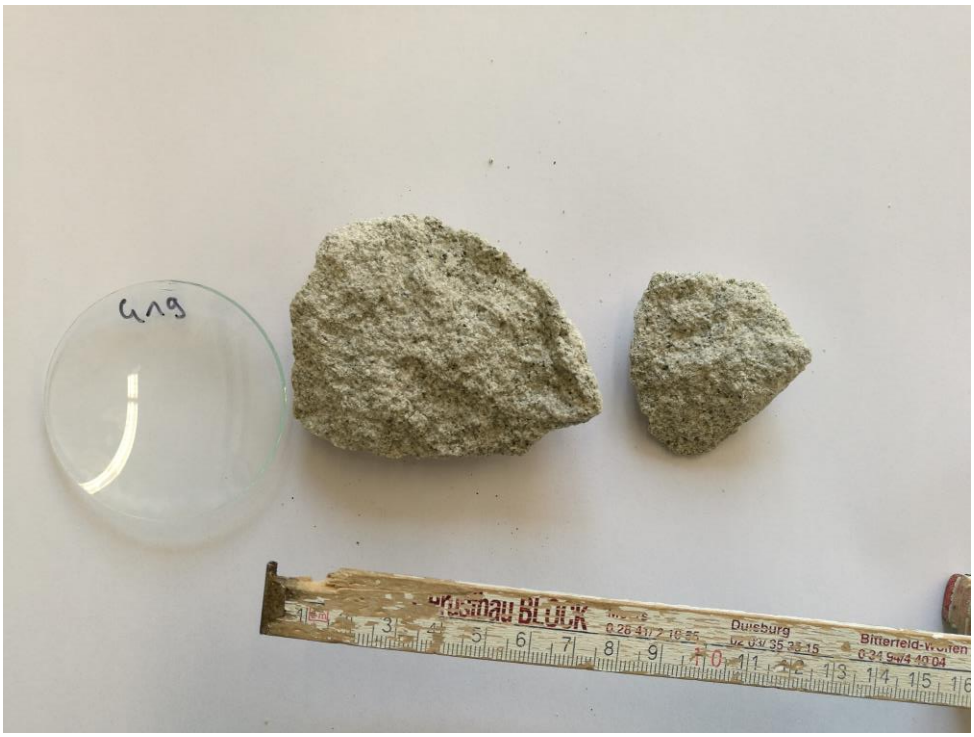
Sample ID	δ2H, in ‰	δ18O, in ‰	Excess	Sampling date
w1	-66,6	-9,66	10,7	14.04.2018
w2	-68,2	-9,87	10,8	14.04.2018
w3	-65,5	-9,61	11,4	15.04.2018
w4	-64,2	-9,71	13,5	15.04.2018
w5	-63,1	-8,87	7,9	15.04.2018
w6	-61,3	-8,88	9,7	15.04.2018
w7	-62,0	-9,11	10,9	16.04.2018
w8	-68,8	-10,28	13,4	16.04.2018
w9	-67,5	-10,29	14,8	16.04.2018
w10	-68,6	-10,30	13,8	16.04.2018
w11	-70,0	-10,37	13,0	17.04.2018
w12	-66,7	-9,96	13,0	18.04.2018
w13	-81,4	-11,68	12,0	18.04.2018
w14	-71,1	-10,49	12,8	18.04.2018
w15	-81,0	-11,66	12,3	18.04.2018
w16	-72,7	-10,69	12,8	18.04.2018
w17	-78,3	-11,45	13,3	19.04.2018
w18	-79,7	-11,58	12,9	19.04.2018
w19	-76,2	-10,97	11,6	19.04.2018
w20	-73,1	-10,58	11,5	19.04.2018
w21	-74,2	-10,69	11,3	20.04.2018
w22	-73,6	-10,74	12,3	20.04.2018
w23	-72,8	-10,68	12,6	20.04.2018
w24	-72,4	-10,64	12,7	20.04.2018
w25	-69,8	-10,27	12,4	20.04.2018
w26	-69,2	-10,15	12,0	20.04.2018
w27	-64,8	-9,72	13,0	21.04.2018
w28	-70,8	-10,58	13,8	21.04.2018
w29	-55,2	-7,99	8,7	22.04.2018
w30	-60,8	-8,80	9,6	22.04.2018
w31	-59,6	-8,57	9,0	22.04.2018
w32	-69,9	-10,38	13,1	22.04.2018
w33	-60,0	-8,59	8,7	22.04.2018
w34	-69,7	-10,20	11,9	22.04.2018
w35	-67,4	-10,00	12,6	22.04.2018

Sample ID	Cl- (mg/l)	Sulfat (mg/l)	Nitrat (mg/l)	HC03- mg/l	K+mg/l	Na+ mg/l	Mg2+ mg/l	Ca2+ mg/l
w1	2,674	7,552	<0,5	349,14	2,67	2,88	3,38	116
w2	2,972	101	2,914	245,41	2,33	4,58	11,7	109
w3	3,715	5,873	<0,25	282,39	1,15	1,91	2,92	92,8
w4	1,567	18,91	0,921	220,27	1,1	3,53	5,2	81
w5	3,066	306	10,46	195,99	5,03	124	14	69,2
w6	7,452	96,56	8,908	269,02	3	30	7,65	111
w7	2,343	59,19	1,619	197,33	2,3	26,1	8,08	61,5
w8	2,779	6,156	0,458	184,82	0,353	1,72	2,18	59,5
w9	2,621	2,596	<0,25	153,28	0,314	1,18	1,23	50,3
w10	3,029	5,851	0,355	224,79	0,565	1,61	2,54	67,4
w11	15,59	34,65	0,938	189,70	0,869	13,4	6,33	67,8
w12	0,393	3,24	0,454	306,49	0,124	0,439	0,884	113
w13	0,168	2,831	<0,25	128,26	0,158	0,311	6,86	30
w14	0,196	8,347	0,245	196,48	0,18	0,521	5,29	61,4
w15	0,157	1,111	<0,25	87,13	0,442	0,361	4,46	24
w16	103	86,83	0,545	155,90	1,51	67,5	8,38	76,9
w17	2,063	7,383	0,95	133,14	0,387	1,79	4,99	39,5
w18	1,043	5,3	1,217	115,63	0,395	0,966	5,1	34,5
w19	0,796	2,529	<0,25	49,85	0,816	1,16	2,03	15,5
w20	0,383	7,249	<0,25	20,26	0,646	0,302	2,06	8,49
w21	266	51,58	1,722	123,25	2,53	169	7,67	51,7
w22	37,98	28,13	0,668	164,44	0,712	24,4	7,06	59
w23	34,73	26,55	0,646	167,86	0,705	22,3	6,63	59,3
w24	33,42	26,65	0,683	166,76	0,72	21,7	6,65	59,8
w25	18,9	35,71	1,293	182,93	1,22	15,6	9,92	80,8
w26	18,78	51,64	5,168	188,24	1,45	15	11,8	89,6
w27	1,104	2,996	0,255	261,40	1,32	2,53	5,52	102
w28	0,424	2,528	<0,25	194,83	0,646	0,671	4,06	80,9
w29	21,17	120	125	253,28	1,28	11,9	18,8	197
w30	17,65	85,58	21,58	355,36	3,43	3,72	15,1	167
w31	18,62	162	41,35	266,16	3,02	7,77	24,8	166
w32	20,61	38,7	2,331	181,10	1,26	16,7	10	79,5
w33	12,69	392	10,11	118,50	4,24	15,7	34,1	231
w34	20,6	43,04	3,035	176,10	1,36	16,8	11,4	89,9
w35	0,88	3,724	<0,25	185,61	0,925	1,38	5,67	91,1

Sample ID	Titan µg/l	Vanadium µg/l	Chrom µg/l	Mangan µg/l	Eisen mg/l	Nickel µg/l	Arsen µg/l	Molybdean µg/l
w1	< 1,00	0,4	< 0,500	< 1,00	0,015	0,6	< 0,500	0,6
w2	< 1,00	< 0,300	< 0,500	< 1,00	0,0286	0,8	< 0,500	0,7
w3	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	0,7	< 0,500	< 0,100
w4	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	0,6	< 0,500	< 0,100
w5	< 1,00	< 0,300	< 0,500	< 1,00	0,0155	2,7	< 0,500	0,7
w6	< 1,00	< 0,300	< 0,500	4,7	< 0,010	1,5	< 0,500	0,2
w7	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	0,8	< 0,500	0,3
w8	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w9	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	0,5	< 0,500	< 0,100
w10	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w11	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	0,5	< 0,500	< 0,100
w12	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w13	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w14	< 1,00	< 0,300	< 0,500	< 1,00	0,0208	< 0,500	< 0,500	< 0,100
w15	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w16	< 1,00	< 0,300	< 0,500	< 1,00	0,0102	< 0,500	< 0,500	0,2
w17	< 1,00	< 0,300	< 0,500	< 1,00	0,0115	< 0,500	< 0,500	< 0,100
w18	< 1,00	< 0,300	< 0,500	< 1,00	0,0101	< 0,500	< 0,500	< 0,100
w19	< 1,00	< 0,300	< 0,500	1,7	0,0813	0,7	< 0,500	< 0,100
w20	< 1,00	< 0,300	< 0,500	< 1,00	0,0402	< 0,500	< 0,500	< 0,100
w21	< 1,00	< 0,300	< 0,500	< 1,00	0,0132	< 0,500	< 0,500	0,2
w22	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w23	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w24	< 1,00	< 0,300	< 0,500	< 1,00	< 0,010	< 0,500	< 0,500	< 0,100
w25	26	2,7	1,9	54	2,47	2,3	0,8	0,2
w26	25	2,7	1,8	53	2,33	2,3	1	0,2
w27	29	3	1,9	56	2,65	2,4	1,3	< 0,100
w28	26	2,8	1,8	53	2,5	2,1	0,9	< 0,100
w29	23	2,5	1,8	49	2,15	2,4	1	1,2
w30	19	2	1,2	39	1,76	1,8	0,6	0,2
w31	19	2,2	1,3	41	1,83	1,9	0,8	0,4
w32	23	2,4	1,6	47	2,21	2,2	1	0,2
w33	28	3	1,9	61	2,75	3	1,1	0,8
w34	25	2,5	1,6	48	2,53	2,1	0,9	0,2
w35	32	3,4	2,3	63	3,41	2,6	1,1	< 0,100

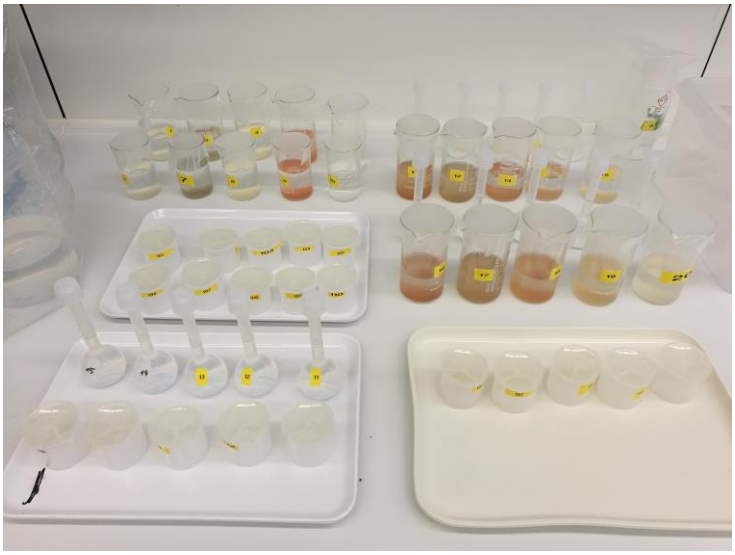
Sample ID	Blei µg/l	Uran µg/l	Lithium µg/l	Bor µg/l	Rubidium µg/l	Strontium µg/l	Cäsium µg/l	Barium µg/l
w1	< 0,500	1,1	10	< 10,0	0,6	435	< 0,020	174
w2	< 0,500	2	15,3	15	0,8	2170	< 0,020	62
w3	< 0,500	0,3	7,3	22	0,5	914	< 0,020	27
w4	< 0,500	0,3	9,5	27	0,5	1080	< 0,020	24
w5	< 0,500	0,9	78,4	531	2,1	4460	< 0,020	39
w6	< 0,500	0,6	24	138	1	2370	< 0,020	39
w7	< 0,500	0,4	23,3	150	0,9	1770	< 0,020	20
w8	< 0,500	0,2	2,2	< 10,0	< 0,200	182	< 0,020	36
w9	< 0,500	0,2	< 1,00	< 10,0	< 0,200	111	< 0,020	37
w10	< 0,500	0,3	2,3	< 10,0	< 0,200	326	< 0,020	40
w11	< 0,500	0,3	5,3	16	0,5	566	< 0,020	45
w12	< 0,500	0,2	< 1,00	< 10,0	< 0,200	93	< 0,020	34
w13	< 0,500	< 0,100	< 1,00	< 10,0	< 0,200	53	< 0,020	130
w14	< 0,500	< 0,100	2,8	< 10,0	0,6	193	0,03	22
w15	< 0,500	< 0,100	< 1,00	< 10,0	0,3	22	< 0,020	60
w16	< 0,500	0,3	4,3	< 10,0	1,7	588	0,04	57
w17	< 0,500	< 0,100	1	< 10,0	0,2	106	< 0,020	54
w18	< 0,500	< 0,100	1,3	< 10,0	0,2	87	< 0,020	60
w19	< 0,500	< 0,100	< 1,00	< 10,0	0,3	25	< 0,020	19
w20	< 0,500	< 0,100	< 1,00	< 10,0	0,4	12	< 0,020	15
w21	< 0,500	0,2	7,7	14	3,9	413	0,11	64
w22	< 0,500	0,2	2,6	< 10,0	0,7	289	< 0,020	41
w23	< 0,500	0,3	2,4	< 10,0	0,6	321	< 0,020	44
w24	< 0,500	0,2	3	< 10,0	0,6	336	< 0,020	41
w25	3	0,5	8,9	15	3	641	0,06	1180
w26	2,9	0,8	9,5	12	2,9	849	0,06	1110
w27	3,3	0,6	7,5	< 10,0	2,7	190	0,08	1280
w28	3,1	0,3	2,8	< 10,0	2,5	111	0,06	1240
w29	2,4	7,4	32,9	17	2,5	1610	0,06	906
w30	2,2	1,5	15,2	< 10,0	2,5	514	0,05	834
w31	1,2	2,9	21,8	16	2,5	1950	0,05	444
w32	2,7	0,5	8,6	13	2,6	682	0,07	1060
w33	1	5	44,9	15	4,3	2250	0,07	243
w34	2,9	0,7	9	13	3	739	0,06	1110
w35	3,9	0,5	4,4	< 10,0	3,3	151	0,09	1480

Supplementary photographs



Rock Sample preparation

Photographs by Heinzle (2018)



Preparation for REE- leaching experiment

Preparation for analysis of Li - isotopes

Photographs by Heinzle (2018)