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# A Mixed-method Approach for the Investigation of Riverine Nitrate Pollution at Catchment Scale

# A MIXED-METHOD APPROACH FOR THE INVESTIGATION OF RIVERINE NITRATE POLLUTION AT CATCHMENT SCALE

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*The more you know,*

*the more you know you don't know*

- *Aristotle –*

*For my family*

## Acknowledgements

This thesis is a book dissertation which consists of tasks developed at the Institute of Hydrology and Water Resources Management (IWW) of the Leibniz University of Hannover. The main focus of this research was to investigate the nitrate fate and transport at a river catchment scale, using a combination of different techniques or, in other words, a mixed-method approach. The investigation area was the Fuhse River Catchment in Northern Germany. The main parts of the research included field work, laboratory work, modelling and interpretation of the results. An important cooperation partner was the Federal Institute for Geosciences and Natural Resources (BGR).

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## Declaration

I, Ngoc Quynh Vu, hereby declare that:

a. I know the Regulations for doctoral candidates at the Faculty of Civil Engineering and Geodetic Science

b. I have completed the thesis independently; used materials by others shall be listed in the references

c. I did not pay any monetary benefits for regards to content

d. This dissertation has not been used as a M.Sc. or similar thesis before

e. I have previously not applied for any exam as a doctoral candidate at another academic institution

Hannover, October 2021

## Abstract

It is important to have an insight into the fate of riverine nitrate at the catchment level. The idea is to apply different methods for one same study site, in order to overcome their limitations and take advantage of their strong points for the research. An approach with necessary steps were proposed to be conducted: 1) evaluation of the current nitrogen status in the water bodies; then 2) identification of the major nitrogen input sources; and when possible 3) development of a model which is able to simulate the nitrogen dynamics within the river catchment.

A mixed-method approach, combining the experimental works (sampling campaigns and labs), statistical analysis (multivariate tool PCA, dual stable isotope tool), and modelling (isotope mixing model SIMMR, ecohydrological model SWAT) was proven to be an effective approach to investigate the fate of nitrogen, especially nitrate, at the river catchment level. In this dissertation, the Fuhse River catchment was chosen as the study site for investigating the status and dynamics of the riverine nitrate.

The results from hydrochemical statistical analyses showed that water of the Fuhse River was an evolved type with mix abundances of ionic concentrations. It was classified into the main hydrochemical group of Ca-Cl-SO4, which represented that the water was influenced by anthropogenic activities. After that, the dual isotope method and the mixing model SIMMR indicated the soil nitrogen, manure and sewage as the predominant nitrate sources in this river water, which might lead to the nitrate of the river exceeding the natural threshold concentration. Finally, the incorporation of isotope results into SWAT has improved the robustness and the creditability of model. The nitrate loads were successfully simulated by the model.

Keywords: Nitrate, river water quality, hydrochemistry, stable isotopes, SIMMR, nutrient model, SWAT

## Kurzfassung

Es ist wichtig einen Einblick in den Verbleib von Nitrat im Flusswasser auf Einzugsgebietsebene zu haben. Es sollen verschiedene Methoden für denselben Standort angewendet und verglichen werden, um so die Stärken der verschiedenen Methoden für die Forschung zu nutzen. Dabei soll wie folgt vorgegangen werden: 1) Bewertung des aktuellen Stickstoffzustands in den Gewässern; anschließend 2) Identifizierung der wichtigsten Stickstoffquellen; und wenn möglich 3) Entwicklung eines Modells, das die Stickstoffdynamik innerhalb des Flusseinzugsgebiets simulieren kann.

Ein Mixed-Method-Ansatz, der experimentelle Arbeiten (Probenahmen und Laborarbeiten), statistische Analysen (multivariate tool PCA, dual stable isotope tool) und Modellierung (Isotopenmischungsmodell SIMMR, ökohydrologisches Modell SWAT) kombiniert, hat sich als effektiver Ansatz erwiesen, um den Verbleib von Stickstoff, insbesondere Nitrat, auf der Ebene des Flusseinzugsgebiets zu untersuchen. In dieser Dissertation wurde das Einzugsgebiet der Fuhse als Untersuchungsgebiet für die Analyse des Zustands und der Dynamik des Flussnitrats ausgewählt.

Die Ergebnisse der hydrochemischen statistischen Analysen zeigen, dass das Wasser der Fuhse ein weiterentwickelter Typ mit gemischten Häufigkeiten von Ionenkonzentrationen ist. Es wird in die hydrochemische Hauptgruppe Ca-Cl-SO4 eingeordnet, was bedeutet, dass das Wasser durch anthropogene Aktivitäten beeinflusst ist. Die duale Isotopenmethode und das Mischungsmodell SIMMR zeigen, dass der Bodenstickstoff, Dünger und Abwasser die vorherrschenden Nitratquellen im Flusswasser sind, wodurch der Nitratgehalt des Flusses die natürliche Schwellenkonzentration überschreitet. Durch die Einbeziehung von Isotopenergebnissen in SWAT werden die Robustheit und

Glaubwürdigkeit des Modells verbessert. Die Nitratfrachten wurden durch das Modell erfolgreich simuliert.

Schlüsselwörter: Nitrat, Flusswasserqualität, Hydrochemie, stabile Isotope, SIMMR, Nährstoffmodell, SWAT

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## List of Abbreviations and Symbols

| | |
|---|---|
| % | percent |
| ‰ | per mil |
| AIR | Atmospheric Nitrogen |
| BGR | Bundesanstalt für Geowissenschaften und Rohstoffe / Federal Institute for Geosciences and Natural Resources |
| d | delta |
| DEM | Digital Elevation Model |
| DWD | Deutscher Wetterdienst / German Weather Services |
| e.g. | for example |
| et al. | and others |
| EU | European Union |
| HRU | Hydrologic Response Unit |
| i.e. | that is |
| IWW | Institute of Hydrology and Water Resources Management |
| NLWKN | Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz / Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency |

| | |
|---|---|
| NSE | Nash–Sutcliffe Efficiency |
| PBIAS | Percentage BIAS |
| SIMMR | Stable Isotope Mixing Model |
| SWAT | Soil and Water Assessment Tool |
| VSMOW | Vienna Standard Mean Ocean Water |
| WWTP | Waste Water Treatment Plant |

# *Chapter 1*

# Introduction

***

## 1.1 Research problems and motivation

Water plays an essential role in human societies and ecosystems, owing to the multiple services that it provides. Taking a closer look, surface water, particularly rivers, has benefited people with water supply for almost all daily activities, such as domestic uses, agriculture, and industry. Hydropower and navigation are also other services that rivers have been offering for years. In addition, rivers, since a long time, have carried and transported a variety of wastes containing organic matter and nutrients, such as nitrogen and phosphorus, which are discharged into them. Regarding the ecosystems, rivers have supported a large amount of wildlife, since many animals and plants live on the rivers for food and accommodation.

However, nowadays, many countries are facing with water quality issues. Water quality has been degraded, and thus has not met the sanitation standards to serve human uses and support ecosystems. This issue has resulted from different causes, mainly consisting of the excessive exploitation of rivers, the changes in water flow regimes, the point sources and non-point sources pollution from industry and agriculture to the water bodies, or the eutrophication from nutrient loadings, etc.

Nitrogen, besides phosphorus, is a vital nutrient for the growth of plants and animals. Nonetheless, a high concentration of this nutrient would lead to water quality degradation, which has severe impacts on both human and ecological health. Excess nitrogen together with phosphorus can cause eutrophication coming up with oxygen deficit, leading to an ecological change and possibly a decrease or increase in several animal and plant species. In addition, the overabundance of nitrogen also affects the water supply for human consumption purposes. Specifically, the infants may suffer from the “blue baby syndrome”, which is caused due to the restriction of oxygen circulation in blood, when the concentration of nitrate in drinking water is high.

Nitrogen is known to be naturally available in the environment; nevertheless, it is also attributed to the human products, such as fertilizers and sewage. Nitrate can directly enter the water bodies through the runoff which contains mineral fertilizers and manure. Furthermore, nitrogen can also get into the water in the form of nitrate, ammonium or organic nitrogen in the effluents from the wastewater treatment plants. As a result, rivers that flow by the areas of intense agriculture or a high population density generally have the high nitrate concentrations (EEA, 2015). Hence, it is of necessity to ensure the water supply with adequate quantity as well as quality for human and ecosystem.

The European Water Framework Directive 2000/60/EC (WFD) was introduced in the year 2000, in which thresholds have been set for water quality parameters including nitrogen. The ultimate aim is to achieve a good status of all waters of the European Union until 2015. Besides, in Germany, other important guidelines for reduction of nutrient concentrations in all waters are the Urban Waste Water Treatment Directive 91/271/EEC, the Groundwater Directive 2006/118/EC, the Drinking Water Directive 98/83/EC, the Nitrates Directive 91/676/EEC, and the Fertilizing Products Regulation (EU) 2019/1009. The pollution of the waters with nutrients such as nitrogen was identified and became an important question of the river management in all German river basins. The nutrients are diffused from agricultural areas and go into the surface water and groundwater via different paths. Beside diffuse sources, point source pollution results from municipal sewage treatment plants discharging into the surface water. In the end, nitrate may adversely affect the quality of water.

According to the European Environment Agency (EEA), Germany is observed to have high proportions of river stations with decreasing trends in nitrate during the time period from 1992 to 2015. However, more than 30% of rivers in Germany have nitrate concentrations exceeding 3.6 mg N/l between years 2013 – 2015 (EEA, 2015). This concentration is considered still higher than the background level of nitrate in natural water, which is about 1 mg N/l or approximately equivalent to 15 mg N-NO3/l (WHO, 2016). Therefore, although there has been considerable improvement in the quality of water, it is still needed to control the concentration of nitrogen in the surface water.

Water quality data have been collected through sampling and monitoring programs. The attention was paid on water quality sampling and monitoring since the 1950s, and the number of studies on this topic is observed to be in the rise since around 1980s. However, until now, developing countries are still having problems with lack of sampling and monitoring mechanisms, resulting in the poor availability in data of the water quality. On the contrary, developed countries, despite their quite abundant availability in data, often face the difficulty called “data rich but information poor syndrome”, in which data information has not met the expectation from users (Ward et al., 1986). In results, both developed and developing countries have to cope with the water quality sampling and monitoring problems. Therefore, it is necessary, besides testing the water samples, to analyze the result databases in order to obtain efficiently useful information from those analyses.

On the other hand, sampling costs would, in general, include sample collection and transport, materials for sample analysis, and labor associated with those works. In the end, the sampling might be of much cost-consumption. Perhaps, this is why current research on water quality monitoring network design usually covers large and very large rivers rather than small and medium rivers. Because the large and very large rivers play important parts in countries’ economy, they are often given more priority and attention in terms of research. Biggs et al. (2017) also point out this fact that small and medium rivers are not intensively sampled and monitored. Thus, there is a gap in studying the water quality at small to medium river catchment scale. This should be given more concern because a large percentage of the freshwater bodies are medium and small rivers.

Mixed-method research is defined to be a combined use of different quantitative and qualitative methods in the same study. This approach is commonly used in several fields in order to obtain more information effectively and efficiently. In the field of water resources management where there is always needs for addressing diverse issues, the researchers and environmentalists usually have to make decisions upon various methods, with the aim to find the most optimal approach. In order to deal with this problem, a mixed-method approach, in which multiple different research methods are integrated, has been recommended. This is apparently a promising solution to the current environmental issues, including water quality studies. However, the mixed-method approach has not been examined thoroughly in the water resources management field. Therefore, it is recommended to implement more studies in this specific field with the use of mixed-method research for verification.

In order to have efficient management measures to tackle the nitrogen issues, a mixed-method approach with necessary steps were proposed to be conducted: 1) evaluation of the current nitrogen status in the water bodies; then 2) identification of the major nitrogen input sources; and when possible 3) development of a model which is able to simulate the nitrogen dynamics within the river catchment.

## 1.2 Literature review

### 1.2.1 Hydrochemistry with regards to water quality

The study of hydrochemistry is commonly used while assessing the quality of water supply, because the hydrochemical results provide information for the characterization of the investigated water, geology, or geography. This characterizing information would enable the detection of the processes that may occur within the water bodies, identification of the temporal and spatial changes in the chemistry of water, and decision of the suitability of waters for use. There are several factors influencing the water chemistry; those can be listed as, for instance, geology, rock type, or recharge water (Berner & Berner, 1996).

The quality of the water can be evaluated and categorized using its chemical characteristics. The term hydrochemical facies is used to describe those categorical types of the water quality. Hydrochemical data analysis methods are regarded as a useful tool for the analysis and interpretation of environmental data sets. The multivariate analysis also provides the determination of the dependencies among parameters of the water. Principal component analysis, for example, is a multivariate statistical method which may detect the general relationship between measured variables. This method enables the explanation and classification of the original variables by introducing new uncorrelated components and reducing the dimension. By interpreting those new components, more understanding of the main occurring processes are gained. This in turns may enable the distribution of the hydrochemical variables to be described.

Multivariate statistical analysis has been successfully applied in hydrogeochemical studies as an effective tool to assess the water quality (Sandow et al., 2008), for example, to analyze the status of water quality parameters or to investigate the relationship between hydrochemical properties and geological origins (Lambrakis et al., 2004; Sojka et al., 2008). These methods offer the capability to assess datasets of large amounts, which is a typical character of environmental data. However, the number of hydrochemical studies on surface water seems to be outclassed by those on groundwater. Thus, this study would testify the ability of hydrochemical analysis methods for investigating the status of the water quality, with emphasis on nitrogen, of the river water.

### 1.2.2 Stable isotopes

Isotopes are different types of atoms of the same chemical element having a different number of neutrons. Therefore, the stable isotopes of an element have different mass number, but their numbers of protons are the same. Nitrogen has two stable isotopes, which are nitrogen-14 (d14N, approximately 99.6 %) and nitrogen-15 (d15N, nearly 0.4%). Different kinetic isotope effects can be attributed to different processes, i.e. assimilation, denitrification, nitrification and N-fixation. The two isotopes of nitrogen can be used in studies on the nitrogen cycle. However, a wide range of stable nitrogen isotope data of nitrate (d15N) in the nature enables it to be more useful in differentiation of nitrate inputs (Kendall et al., 1998). Therefore, identification of different nitrate sources can be detected by variations in d15N values.

Analysis of nitrogen isotopic composition is considered to be able to provide a direct, effective and accurate means of source identification by differentiating values of nitrogen isotopes in different sources. Due to the fact that different sources of nitrate, such as fertilizer, manure, soil, sewage and atmospheric sources, may contribute different fractions of nitrogen to the receiving bodies, the isotopic compositions of nitrate can be used as tracers to identify the nitrate sources (Mayer et al., 2002).

However, the mixing of waters which are impacted by different nitrate sources will also influence the stable isotope values of nitrate. There are some compounds having overlapping range of nitrogen isotopes, for example, soil nitrogen and mineral fertilizers. Thus, sometimes it is difficult to distinguish sources of nitrate just by only d15N because of the overlapping values. This difficulty has brought about the use of dual isotope approach. The two stable isotope d15N and d18O have been assessed from water nitrate samples. Isotopes are expressed in the delta notation, in which d15N is relative to atmospheric nitrogen (AIR) and d18O is relative to Vienna Standard Mean Ocean Water (VSMOW).

This dual isotope approach requires the use of both the nitrogen and oxygen isotope values of the samples. The additional measurement of d18O isotope in nitrate allows separating processes that overlap each other when using only d15N. For instance, dual analysis of d15N and d18O allows a better differentiation of nitrate sources between fertilizer-based and atmospheric nitrogen (Kendall, 1998). The dual isotope approach is known to be implemented in various environmental studies with a focus on nitrate (Pardo et al., 2004; Oelmann et al., 2007; etc). In summary, the nitrate dual isotope approach offers an additional tool to identify nitrogen sources and nitrogen cycle. Therefore, it is used in this study as a tool to investigate the nitrate input sources in the river water.

### 1.2.3 Ecohydrological water quality modelling

The introduction of the legislations on water quality, such as the Water Framework Directive 2000/60/EC or the Nitrates Directive 91/676/EEC has stimulated the development of tools to monitor and manage the quality of the water. As a result, the demand for proper models simulating the nutrients has been increasing (Wang et al., 2013). The reason is that modelling is considered a useful tool which supports the management and decision making (Abbaspour et al., 2015). There are a great number of models being developed for this purposes, out of which the commonly used ecohydrological models may include SWAT (Arnold et al., 1998), HYPE (Lindstrom et al., 2010), HSPF (Duda et al., 2012), or MIKE-SHE (Jaber & Shukla, 2012).

Ecohydrological models are able to properly depict the hydrology as well as the water quality of a catchment (Baffaut et al., 2015). Those models can represent the soil, landuse, topography and climate, so they can simulate the processes within the whole catchment. Therefore, ecohydrological models are usually implemented to assess the current management practices at the catchment, to predict the possible outputs under scenarios, or to evaluate the efficiency of the promising mitigation measures. The Soil and Water Assessment Tool (SWAT) (Arnold et al., 1998) has been widely used to predict long-term impacts on water quality as a continuous model (Abbaspour, 2008). There are a great number of SWAT model applied at different scales from local, regional to continental level for studying the hydrological and water quality conditions (Gassman et al., 2007, 2014; Haas et al., 2017; Huang et al., 2017).

Although valuable knowledge on water quantity and quality has been given by those case studies mentioned above, the ecohydrological model still has some drawbacks. For example, models may be calibrated with an aim to optimize some performance indicators, without noticing the realistic conditions of the catchment. The result is that, the models have very good performance values, but may have unrealistic values of some components. For instance, performance of a model can be good at the outlet when looking at its performing indicators. However, the nitrate loads from point sources are underestimated and those from agricultural lands are overestimated while compared with the actual conditions of the catchment. In addition, models may have uncertainties resulting from missing data, or during calibration procedure, etc. Therefore, further improvement should be made for more precise simulation of the hydrological and nutrient processes.

## 1.3 Research questions and objectives

Overall, the main objective of this dissertation was to have an insight into the fate of riverine nitrate at the catchment level by using a mixed-method approach, which includes hydrochemical statistical analysis, stable isotope technique, and ecohydrological modelling. The idea is to apply all of those methods for one same study site, in order to overcome their limits and take advantage of their strong points for the research.

This dissertation was performed to address the following questions

1. How good are the correlations of nitrate and other hydrochemical parameters of a river at a catchment scale evaluated by statistical approach? This is required as nitrate plays an important role in water chemistry. Thus, an understanding of the river's hydrochemistry would give a crucial background for the evaluation of the nitrate fate in the catchment, e.g. spatial and temporal characteristics of riverine nitrate.

2. How good is the nitrate source identification at a catchment scale by stable isotope approach? This is required as identification of nitrate sources is a vital step in the management of nitrate amount. Only when the pollution sources are determined, can remediation measures be proposed.

3. How good is nitrate load simulated by catchment model? This is required as nitrate should be quantified and evaluated in order to build management plans. The results of nitrogen input contribution from the stable isotope analysis in part 2 was used as a constraint to calibrate the model in this part.

### 1.4 Thesis structure

Corresponding to the research questions above, this dissertation included five chapters, consisting of one introductory chapter, three main chapters addressing the three research objectives, and a concluding chapter at the end.

Chapter 1 provided the general information of nitrogen and described the nitrogen cycle. Then, the chapter gave the state of the art in hydrochemistry, stable isotopes, and water quality modelling. Finally, research objectives and dissertation structure were shown.

Chapter 2 presented the Fuhse River catchment as the study area for the research, depicting the significant characteristics of this catchment. In addition, other scientific background was also described in this chapter.

Chapter 3 conducted the hydrochemical statistical analysis with multivariate tools, which were implemented to evaluate the current situation of the river water quality with regards to nitrate.

Chapter 4 implemented the dual isotope method to identify the major sources of nitrate in the river water. The results were compared with those from Chapter 3 to check the agreement of those two methods. After that, an isotope mixing model was used to quantify the proportion of each nitrogen sources contributing to the water body of interest.

Chapter 5 developed an ecohydrological model, specifically the SWAT model, in the Fuhse river catchment in order to simulate the discharge as well as the nitrate loading in this study site. The result of nitrogen source proportions from the isotope mixing model in Chapter 4 was used as a constraint for calibration of the SWAT in this chapter.

Finally, Chapter 6 was the concluding chapter. In other words, it provided a synopsis of the overall problem, in which all of the results of this dissertation were summarized and discussed. The advantages as well as drawbacks were presented. At the end of the chapter, some recommendations were given for further research on riverine nitrate pollution and management.

# *Chapter 2*

# Study Site and Scientific Background

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## 2.1 The nitrogen cycle

Despite its abundance in the atmosphere, nitrogen in its gaseous form dinitrogen $N_2$ is inert, in which the plants and animals cannot consume. Only when nitrogen undergoes some converting transformations, can it be accessible to organisms. Those transformations consist of major processes, namely nitrogen fixation, nitrification, denitrification, and ammonification. Therefore, the nitrogen cycle is considered a crucial nutrient cycle in the ecosystems (Hayatsu et al., 2008).

Nitrogen fixation is the process, in which dinitrogen is transformed into biologically available nitrogen such as ammonia. This process is usually conducted by the organisms; however, sometimes it can also be carried out abiotically by lightning. In the ecosystem, the nitrogen from the atmosphere is fixed owing to legume plants. Moreover, the combustion of fossil fuels during industrial processes may also trigger nitrogen fixation.

Nitrification is another important process of the nitrogen cycle. In this process, ammonia is first transformed into nitrite and then into nitrate. Thus, it can be considered a two-step process with different microorganisms required. The oxidation of ammonia to nitrite is the first step, and the oxidation of nitrite to nitrate is the second one. Most nitrification processes occur aerobically. As the nitrification process is faster than the ammonification, the concentration of the latter is usually low in comparison with the former.

Denitrification is the process in which nitrate is transformed into nitrogen gas. This dinitrogen gas then goes back to the atmosphere. Unlike nitrification, denitrification is an anaerobic process, or in other words, it often occur in soils, sediments, and anoxic zones of streams. It is observed that the denitrification occurs mainly at soil water content higher than 60% (Shelton et al., 2000). Denitrification is considered a vital process of the nitrogen cycle, due to the fact that it removes the mobile nitrogen from the ecosystem and returns it to the atmosphere in an inert form.

Ammonification is the process in which organic nitrogen is transformed into an inorganic form, i.e.: ammonia, by microorganisms. The generated ammonia then can be directly used by soil organisms or plants for growth. Sometimes, a part of this ammonia may be bounded to the soil particles and stored in the soils.

Many human activities have influenced the nitrogen cycle significantly. For instance, discharge of sewage or use of mineral fertilizers and manure, and other activities have significantly increased the amount of mobile nitrogen in the ecosystem. As a result, the nitrogen cycle is dramatically altered as these anthropogenic inputs increase.

Nitrogen-based fertilizers and manure are commonly used in the agricultural manufacture, in order to increase the plant yields. In fact, plant harvest takes nitrogen from the natural system; however, the intensive farming has led to excessive compensation of nitrogen losses by using fertilizers. The excess nitrogen, as nitrate, then may leach out of the soil. After that, it can get into the water bodies such as groundwater aquifers, streams, and rivers. In addition, effluents from industrial and municipal wastewater treatment, which still contain some amounts of nitrate, ammonium and organic nitrogen, are discharged directly into rivers. After that, the abundant nitrogen above may follow the rivers, flowing into the marine systems. In the end, if the anthropogenic impacts are not controlled properly, the water resources would continue to be in risks.

### *Nitrate nitrogen in the river water systems*

Increased nitrate concentration in river water systems has been becoming a thread to water supply and has been paid attention in recent years. Nitrate is a naturally-occurring nitrogen compound; other common forms can be listed as nitrite and ammonia. Out of those nitrogen forms, nitrate is essential for plant growth. However, an excess amount of nitrate may cause significant water quality problems of nitrogen (Sebilo et al., 2003).

Eutrophication may be accelerated by excessive amount of nitrate and phosphorus (Decrem et al., 2007). This can result in severe changes of the faunas and floras in and surroundings of the water bodies. Furthermore, water quality parameters, such as dissolved oxygen and temperature, etc., are also impacted. In fact, excess nitrates might lead to low levels of dissolved oxygen. In addition, nitrate is also a concern for drinking water supplies as high levels of nitrate can be toxic to human at high concentrations under certain conditions

(Johnson et al., 2010; Brindha et al., 2012). Inputs of nitrate into the surface water may come from different sources. Some of those may be the agricultural runoff containing fertilizer and manure, and the industrial and municipal wastewater (Zweimueller et al., 2008). Possible action options in term of the scope and location should be selected. This selection can be made based on the knowledge of nutrient sources, amount and types, as well as their paths into the waters.

## 2.2 Study area

The study site of this research is the Fuhse River Catchment with an area of more than 900 $km^2$, located in Lower Saxony, Northern Germany. It is a part of the WFD working area Fuhse/Wietze water bodies (Figure 2.1). This is an important agricultural catchment that later drains to the North Sea. The Fuhse River has a total length of 95 km, flowing to the North, ending in the Aller River. The biggest tributary flowing into the Fuse River is the Erse River. The Fuhse River is valued for many services it has been provided. For instance, it has supplied human and ecosystem with water for years. It has also received sewage from many wastewater treatment plants within the area. The catchment itself is an intensive agricultural production region in Lower Saxony. The urban population of the cities within and surroundings such as Peine, Braunschweig and Hannover is relatively high. There are 13 municipal WWTPs draining into the Fuhse River and 02 municipal WWTPs draining into the Erse River.

The geography of this area changes from mountains in the upper part, to geests in the middle, and finally lowlands in the lower part. Geest is a form of landscape which is commonly found in the Northern Germany. This area usually has a low location compared with sea level. Geest often contains glacial materials since it was formed during glacial processes. After the melt water from glacier washed away the fine soil layers on the surface, the remained areas were nutrient-poor sandy and gravelly soils. This geography-complex characteristic of the Fuhse River catchment may possibly have a vital influence on the flow regime of its region, which makes this landscape an interesting site for research. Therefore, the chosen monitoring sites in this study are located along the length of the Fuhse River with consideration to that geography difference. In some parts, surface water was sampled and analyzed in order to identify the impacts of both natural processes and anthropogenic activities to the nitrate fate of the river.

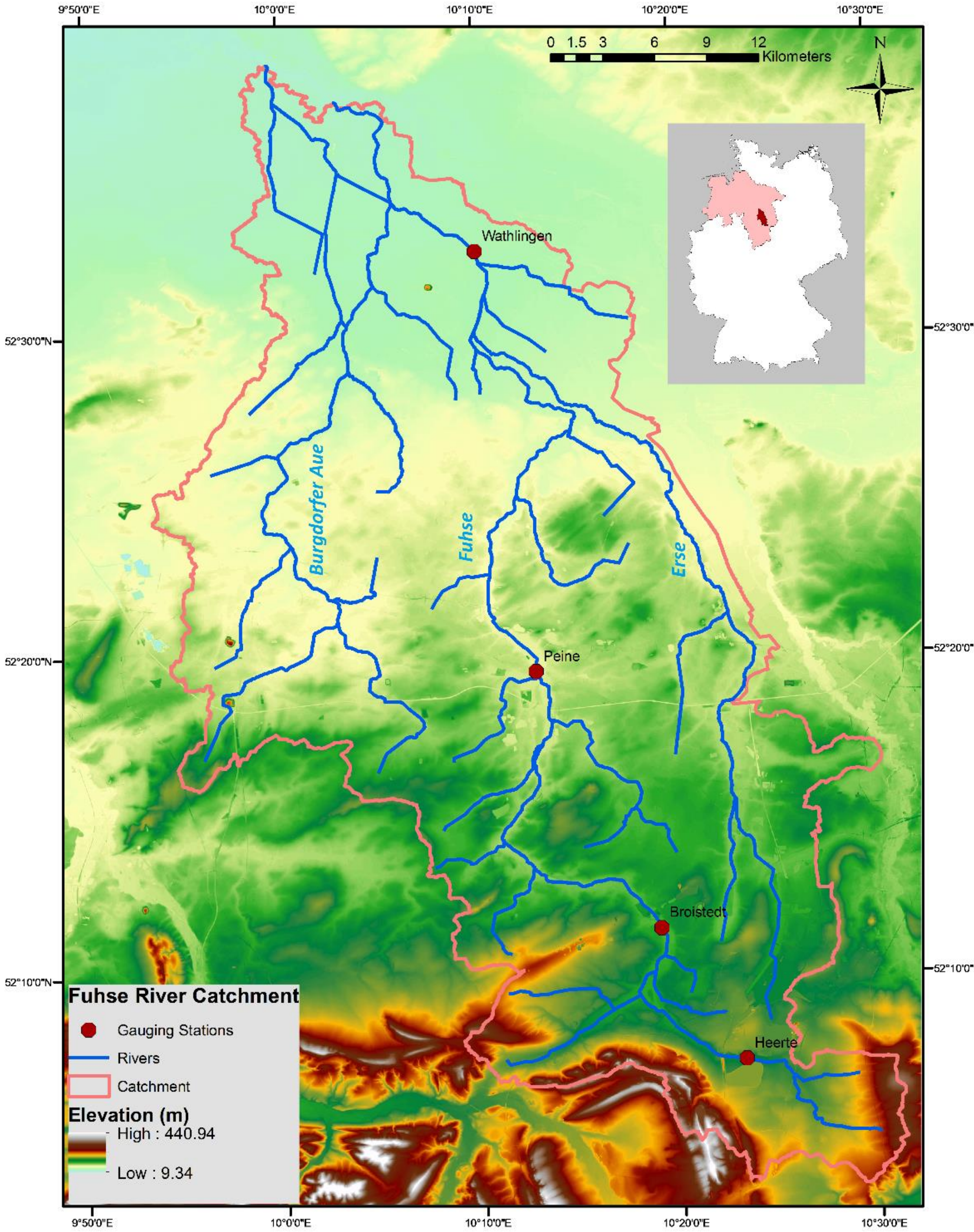

*Figure 2.1: Location of the Study Site: The Fuhse River Catchment*

## 2.3 Field work and laboratory work

*NLWKN sampling campaign*

The Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency (NLWKN) has dozens of water gauges on rivers at important locations throughout the Fuhse - Wietze watershed. The NLWKN operates the stations within the catchment to measure the flow discharges and water quality parameters including both physical and chemical parameters. Some of those water quality parameters can be named such as pH, water temperature, conductivity, dissolved oxygen, and chemical anions and cations, etc. The information from these stations is delivered to the NLWKN office and is updated to the system continuously. Maps and datasets are publicly available on the website of the NLWKN. From those data resources, the overall view on the current situation of the water quality of the river can be given. Moreover, the information is also useful in studying long-term water quality changes. These gauges are an important part for our analysis since they provide us with long-term data series in water quality and flow changes. However, one disadvantage of this dataset is its low frequency, as water quality indicators have usually been measured monthly.

*IWW sampling campaign*

In order to have more highly resolved data, the Institute of Hydrology and Water Resources Management (IWW) of the Leibniz University of Hannover (LUH) in cooperation with the Federal Institute for Geosciences and Natural Resources (BGR) have done sampling campaigns (Appendix – Figure A.1), in which stream water samples from an intensive investigation site was taken on a weekly basis over a period of nearly five year (2014 – 2019). This campaign dataset is expected to contribute to the investigation of the temporal variability of the nitrogen dynamics in the catchment. The sampling point is in Peine, locating in the region with relatively high nitrate concentration of the Fuhse River.

River water samples were taken in 500ml-plastic-bottles, 30ml-glass-bottles, and 100ml-plastic-bottles acidified with nitric acid to keep pH as low as 1-2. In-situ sensors were used to measure physical parameters such as dissolved oxygen, electric conductivity, pH, and water temperature.

The values were recorded once they stabilized. Then samples were extracted and chemically analyzed in the lab. Specific analysis methods for ion parameters are as followings: automatic titrator ($HCO_3$, $CO_3$, and OH); ion chromatography (F, Cl, $NO_2$, $NO_3$, and $SO_4$); and ICP-OES (K, Na, Mg, Ca, Br, $PO_4$, Fe, and Mn).

## 2.4 Model Literature Review

### *SWAT Model*

The Soil and Water Assessment Tool (SWAT) is a semi-distributed, time-continuous, eco-hydrological model that incorporated several modules to simulate the land and water processes for catchments. SWAT has been built based on a previous model SWRRB (Simulator for Water Sources in Rural Basins, Williams et al., 1985), which was developed by the USDA Agriculture Research Service. Other contributing models are CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management Systems, Knisel, 1980), GLEAMS (Groundwater Loading Effects on Agricultural Management Systems, Leonard et al., 1987), and EPIC (Erosion-Productivity Impact Calculator, Williams et al., 1989).

Water balance is considered the main principle behind all processes in the SWAT model. This also has significant impacts on the movement of nutrients (Arnold et al., 2012). Hydrological processes within a watershed that are simulated in the SWAT model can be seen from Figure 2.2. Main processes include evapotranspiration, surface runoff, infiltration, lateral flow, percolation, recharge, revap, and return flow, etc.

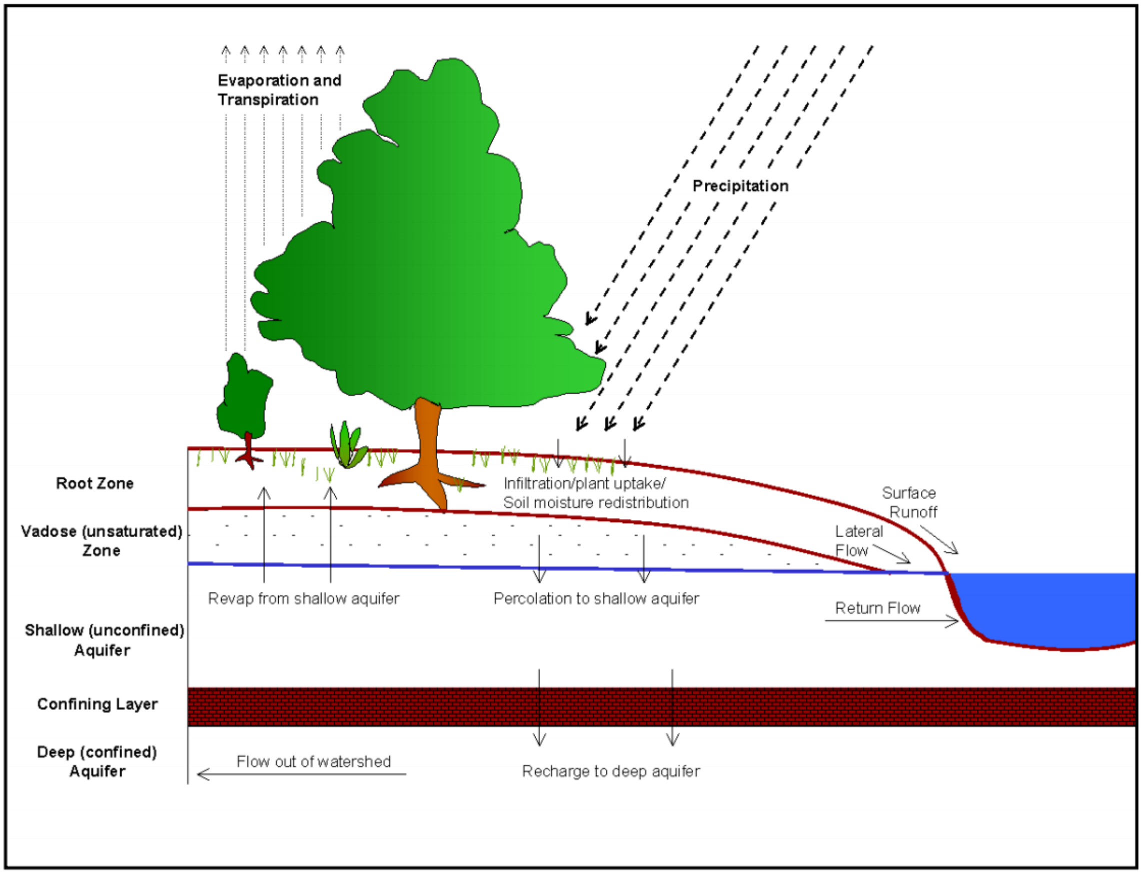

*Figure 2.2: Hydrologic processes simulated in the SWAT model (Neitsch et al., 2011)*

The SWAT model simulates the hydrological processes of the catchment in two phases: land phase and water (or routing) phase (Neitsch et al., 2011). The land phase is related to the land processes of the hydrologic cycle, by which the amount of water, sediment, and nutrient are controlled. In this phase, the water balance is the driving force, and its equation is implemented in order to model the hydrological cycle as following:

$$SW_t = SW_o + \Sigma\,(R_{day} - Q_{surf} - E_a - w_{seep} - Q_{gw})$$

In which:

$SW_t$ = final soil water content (mm H2O)
$SW_o$ = initial soil water content on day i (mm H2O)
$R_{day}$ = amount of precipitation on day i (mm H2O)
$Q_{surf}$ = amount of surface runoff on day i (mm H2O)
$E_a$ = amount of evapotranspiration on day i (mm H2O)
$w_{seep}$ = amount of water entering the vadose zone from soil on day i (mm H2O)
$Q_{gw}$ = amount of return flow on day i (mm H2O)

The loading outputs of the land phase are routed to the stream network in the water or routing phase. The water phase is related to the routing of the water cycle, which controls the movement of water, sediment, nutrient and organic chemicals. Firstly, flow routing is simulated using either variable storage method or Muskingum routing method. Then sediment transport is modeled using a function of peak channel velocity. In addition, QUAL2E (Brown & Barnwell, 1987) is the basis for the water quality module in SWAT, which is used to controls the nutrient routing in the catchment. Lastly, the organic chemical or pesticide is routed along with water.

As mentioned in the previous part, SWAT first divides the watershed into different subbasins, then further splits each subbasin into smaller units which are called Hydrological Response Units (HRUs). Subbasins are identified by the accumulation of flows on the digital elevation map (DEM), or in other words, based on the catchment topography. There is one reach in one subbasin, which passes the latter’s lowest elevation. Those reaches are assumed to be uniform in longitudinal dimensions, for instance, slopes, roughness, and cross section.

The use of subbasins is useful when areas dominated by different landuse and soil properties to the extent that the difference can impact the hydrology. Each HRU is said to be a unique combination of slope, soil type, and landuse. They are abstracted in the SWAT model as the fractions of the area of a subbasin. Then the water and load outputs of the HRUs are summed up from area weighted calculations to produce the inputs into reaches. In general, the SWAT model computes the calculations and simulates the hydrological and nutrient processes first at the HRU level, then at the subbasin level, and finally at the catchment's outlet.

### *Nitrogen Model Theory*

In SWAT, the nitrogen cycle is simulated in the soil and in the shallow aquifer (Neitsch et al., 2011). Nitrogen is extremely reactive and exists in various forms in the natural environment. On one hand, the addition of nitrogen to the soil occurs in the form of fertilizer, manure or rain. On the other hand, the removal of nitrogen from the soil is made through processes, such as denitrification, plant uptake, or leaching. Therefore, SWAT has categorized the nitrogen in the soil into five different pools in order to represent the activeness of nitrogen (Figure 2.3). Out of the five pools, two contain the mineral nitrogen, consisting of ammonia and nitrate. On the contrary, the remaining three pools consist of the organic nitrogen, labelling as active, stable and fresh respectively.

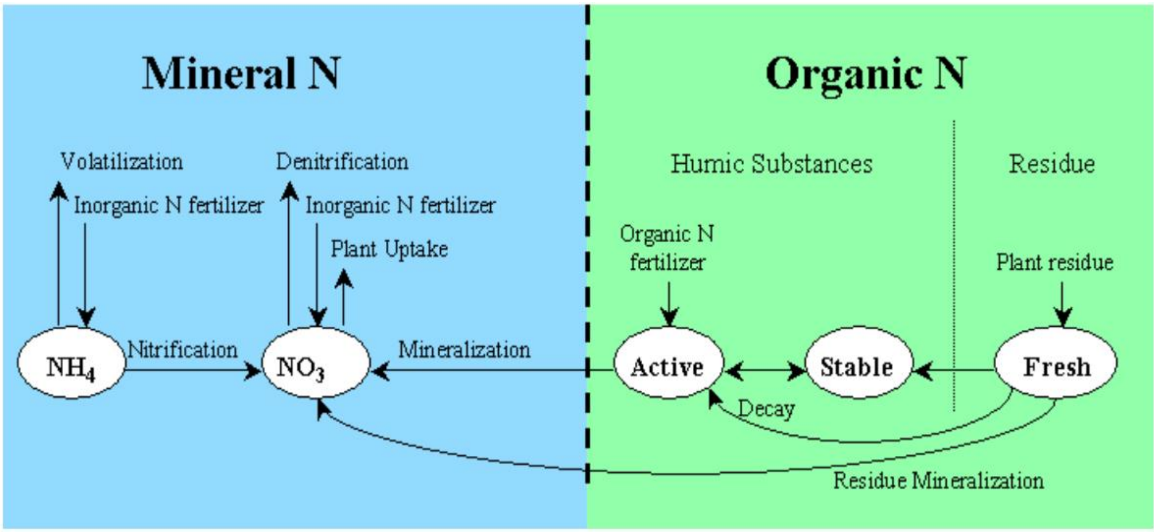

*Figure 2.3: Nitrogen pools in the soil in SWAT (Neitsch et al., 2011)*

In regard of three organic nitrogen pools, the first one is the active organic nitrogen, which results from organic nitrogen fertilizer, and is mineralized into nitrate. It can also transform from and to the second organic nitrogen pool - stable organic nitrogen. Unlike active organic nitrogen, stable organic nitrogen is not mineralized, instead, it plays as a storage for the organic nitrogen. The third organic nitrogen pool is the fresh organic nitrogen, which is the decomposition of the plant residues. It may decrease from decaying into active organic nitrogen, or from transferring into stable organic nitrogen. There are several factors and processes involving in the exchange among those three pools of organic nitrogen and their conversion into the mineral form nitrate, such as soil water content, soil temperature, mineralization, plant residue composition and decomposition, etc.

One of the two mineral nitrogen pools is the ammonium which increases with mineral nitrogen fertilizer and decreases from volatilization and nitrification. The result of the nitrification process is nitrate – the other pool of mineral nitrogen. Similar to ammonium, nitrate also increases via the mineral nitrogen fertilization. So in general, nitrate gains it amount through fertilization, nitrification, and mineralization processes. At the same time, its amount may be lost through processes such as plant uptake, denitrification, and probably leaching into the groundwater. Overall, nitrate might be transported through surface runoff, lateral flow, or percolation. Later, nitrate may enter or move out of the groundwater system, which occur due to the “revap” (the process where water in shallow aquifer returns to root zone) or the flowing to the main channel of the groundwater. Groundwater flow thus makes contribution to the in-stream nitrate. In addition, the revap also contributes to the nitrate pool in the soil, and then impacts the streams via surface runoff and lateral flow. Besides being a source of nitrate, aquifers act as sinks of the nitrate. Nitrate removal in the shallow aquifer due to microbial processes is modeled as a first order decay. More details of the SWAT model can be found in the theory document by Neitsch et al. (2011).

# *Chapter 3*

# Assessment of the hydrochemistry of the Fuhse River in Northern Germany

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## 3.1 Introduction

Rivers play an important role in the water cycle because they serve as the flowing agents which deliver the precipitation and transport the natural chemical solutes as well as additional anthropogenic components to the sea. River hydrochemistry is affected by natural processes, for instance, weathering or ion exchanges (Berner & Berner, 1996). In addition, the hydrochemical characteristics of rivers are also under changes due to anthropogenic activities, such as agricultural, municipal and industrial activities especially in the surroundings of the rivers, which have significant impacts on the water resources (Negrel et al., 2007; Kumar et al., 2015; Yu et al., 2015). Those changes in the water quality of rivers, which have mainly resulted from the significant rise in nutrients and chemicals, may cause harmful degradation to ecosystem and fatal risks for human health (Massoud, 2012). According to Vorosmarty et al. (2013), ecosystems can be harmed by climate changes and human activities.

Therefore, it is necessary to enhance the knowledge of the water quality of the rivers. Within this context, hydrochemical analyses of rivers are extremely useful to support hydrological studies. Major dissolved components in river water are closely connected with the weathering processes under the impacts of climatic conditions, as well as with human activities. In short, these analyses can contribute to the understanding of the ongoing hydrological processes and to the prediction of potential ecosystem scenarios.

Recent environmental studies have used multivariate statistical methods as an effective tool for analyses (Sandow et al., 2008). The statistical methods were successfully applied in the assessment of surface water quality (Liao et al., 2008), as well as groundwater quality (Papatheodorou et al., 2007). These studies provided an idea of the current situations, and enabled a prediction of the future trends when compared with historic data. However, it is difficult to conduct the studies of rivers because of the difficulty in sampling along river lengths of hundreds of kilometers, and at a high time resolution or high frequency.

Therefore, the aim of this chapter was to analyze the hydrochemical characteristics of water quality, especially the spatial and temporal variability of nitrate concentration, of the river system, taking advantage of various available data sources. In order to assess main processes that control the chemistry of the river water, multivariate statistical approach would be used. This study is conducted as a catchment-scale methodology. The hydrochemical behaviors of the river and the origins of the riverine nitrate were to be determined in this study.

## 3.2 Materials and methods

The study site of this research is the Fuhse River Catchment with an area of more than 900 km$^2$, located in Lower Saxony, Northern Germany. In this study, several sources of data were utilized and incorporated for the analyses, which are different in frequency and sampling dates, in order to take advantage of all available data sources. Main data sources include those from NLWKN, and those from BGR – IWW. While NLWKN data are on a monthly basis, those data from BGR-IWW are on a higher resolution, i.e., weekly basis. The procedure of sampling and lab analyzing was described above in Chapter 2.

First of all, an overall statistic summary of the river parameters was done using the NLWKN data during the time period from 1981 to 2017 for all four stations within the catchment, including Heerte, Broistedt, Peine and Wathlingen. NLWKN data, owing to its broad amount in both spatial and temporal aspects, enabled such a summarized investigation. This gave an overview of the water quality along the river. First ideas of the current water problems can be detected as well.

Then Piper's Diagram and Gibbs' Plot were implemented to give a more in-depth investigation into the hydrochemical characteristics of the Fuhse River. Similarly, NLWKN monthly data for years from 1981 to 2017 were selected for these analyses.

After that, Principal component analysis (PCA) of chemical data was performed using the R statistics tool. Prior to being analyzed, data were normalized to unit length. Regarding this analysis, the BGR-IWW data from 2014 – 2017 at Peine gauging station was used, because of its higher sampling frequency and greater number of water parameters when compared with those correspondences from NLWKN.

### 3.3 Results

Regarding the general hydrochemistry, the average concentrations of elements in the Fuhse River is summarized in the following table (Table 3.1).

Water of the Fuhse River could be considered slightly acidic or alkaline, as its pH ranged from 6.90 to 9.17, with an average value of 7.82. The electrical conductivity (EC) ranged from 367 to 3820 µS/cm. The average EC values were 1313, 1492, 1412 and 1154 µS/cm at Heerte, Broistedt, Peine and Wathlingen respectively. There were approximately 23% of the samples at Heerte (76 out of 331) being higher than the EC permissible limit of 1500 µS/cm, while this value was 43% (203/473) at Broistedt, 36% (198/548) at Peine, and 1% (7/525) at Wathlingen. The total dissolved solids (TDS) were measured by summing up all major ions concentrations (including Ca, Mg, Na, K, HCO3, SO4, and Cl), which range from 238 to 1887 mg/l. As per TDS classification, Broistedt and Peine can be regarded as brackish water type (TDS >1,000), whereas Heerte and Wathlingen can be considered fresh water (TDS <1,000).

Electricity conductivity is the whole reflection of total dissolved ion concentrations in water bodies, and to certain extent, EC value reflects the length of flow paths and residence times in water cycle. Usually during the water moving processes, the EC value of water body increases gradually with the extension of flow path and residence time while continually dissolving the dissolved minerals and generating ion exchange with adjoining rocks and soils. In this study, from the headwater sources, there is a wastewater treatment plant in between Heerte and Broistedt. The EC value increased when the Fuhse passed through these two points, which would be an impact from the WWTP effluents. However, downwards long the main river stream, the EC value of river water decreased from Broistedt to Peine and Wathlingen, indicating that surface water also received a recharge from a lower EC value source, or some processes such as dissolved solids subsidence or gas separation might occur.

*Table 3.1: General hydrochemistry of the Fuhse River*

| | Heerte | | | | Broistedt | | | | Peine | | | | Wathlingen | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Variable | Min | Max | Mean | Median | Min | Max | Mean | Median | Min | Max | Mean | Median | Min | Max | Mean | Median |
| Ca (mg/l) | 49 | 310 | 186 | 190 | 55 | 240 | 169 | 170 | 60 | 220 | 162 | 163 | 60 | 190 | 127 | 128 |
| EC (µS/cm) | 367 | 2790 | 1313 | 1340 | 470 | 3820 | 1492 | 1445 | 460 | 2600 | 1412 | 1401 | 537 | 1982 | 1154 | 1150 |
| NO3-N (mg/l) | 0.70 | 19.00 | 4.34 | 3.80 | 0.01 | 16.00 | 5.43 | 4.90 | 0.11 | 16.00 | 5.62 | 5.50 | 0.49 | 14.00 | 5.17 | 5.20 |
| SO4 (mg/l) | 43 | 586 | 176 | 174 | 51 | 590 | 211 | 210 | 50 | 340 | 225 | 230 | 19 | 349 | 205 | 206 |
| Mg (mg/l) | 4 | 70 | 19 | 19 | 6 | 30 | 18 | 18 | 5 | 34 | 17 | 17 | 6 | 32 | 13 | 13 |
| Na (mg/l) | 13 | 270 | 79 | 78 | 20 | 200 | 107 | 107 | 24 | 180 | 112 | 115 | 22 | 161 | 93 | 93 |
| K (mg/l) | 3 | 32 | 5 | 5 | 4 | 44 | 11 | 10 | 1 | 24 | 12 | 12 | 5 | 45 | 14 | 13 |
| Cl (mg/l) | 32 | 612 | 172 | 172 | 24 | 1050 | 213 | 189 | 33 | 1200 | 183 | 170 | 37 | 440 | 143 | 140 |
| HCO3 (mg/l) | 89 | 442 | 327 | 339 | 122 | 431 | 324 | 330 | 98 | 433 | 316 | 322 | 88 | 488 | 210 | 207 |
| Flow (cms) | 0.01 | 4.50 | 0.33 | 0.13 | 0.07 | 14.94 | 0.94 | 0.63 | 0.19 | 21.88 | 1.66 | 1.07 | 0.39 | 31.60 | 4.50 | 3.19 |
| WT (°C) | 0.00 | 23.10 | 10.57 | 9.30 | 0.00 | 22.50 | 11.29 | 10.90 | 0.00 | 24.40 | 11.18 | 10.55 | -0.10 | 24.50 | 11.14 | 10.85 |
| pH | 7.30 | 8.50 | 8.02 | 8.00 | 6.90 | 8.40 | 7.74 | 7.76 | 6.90 | 9.00 | 7.84 | 7.87 | 7.20 | 9.17 | 7.75 | 7.72 |
| DO (mg/l) | 4.50 | 20.60 | 12.51 | 12.40 | 1.80 | 18.80 | 9.90 | 10.20 | 3.80 | 19.30 | 9.33 | 9.50 | 5.10 | 18.60 | 9.65 | 9.70 |
| TDS (mg/l) | 238 | 1887 | 985 | 1004 | 517 | 1410 | 1040 | 1051 | 536 | 1301 | 1026 | 1051 | 422 | 1062 | 857 | 873 |

The distribution of major ions in the water (meq/l) was $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $Cl^{-} > HCO_3^{-} > SO_4^{2-}$. The concentration of $Ca^{2+}$ in the study area ranged from 49 to 310 mg/l with an average of 159 mg/l. According to the standards of WHO, 99% (1498/1510) of the samples in this study were crossing the maximum permissible limit of $Ca^{2+}$ (75 mg/l). The ion exchange of the minerals from rocks could be accounted for the major source of $Ca^{2+}$ in the river water in this catchment. Further, this may also be due to the presence of $CaCO_3$ and $CaSO_4$ minerals present in the soil horizon, gypsum anhydrides, dolomite, etc. The concentration of $Na^{+}$ showed a large variation from 13 to 270 mg/l, averaging 99 mg/l. Three (03) samples at Heerte, one (01) sample at Broistedt, and none of the water samples at Peine and Wathlingen have exceeded the maximum permissible limit of 200 mg/l of $Na^{+}$. The concentration of $Mg^{2+}$ ranged from 4 to 70 mg/l with an average value of 17 mg/l. All of the $Mg^{2+}$ concentrations were within the desirable limit of 50 mg/l, except for one sample at Heerte in 2002 (70 mg/l). The concentration of $K^{+}$ ranged from 1 to 45 mg/l with an average value of 11 mg/l.

The $Cl^{-}$ concentration ranged from 24 to 1200 mg/l, averaging 177 mg/l. Approximately 25% of the samples had the $Cl^{-}$ concentration more than the permissible limit of 200 mg/l, and most of them were samples taken before the year 2000 (83%). The $HCO_3^{-}$ concentration ranged from 88 to 488 mg/l with an average of 297 mg/l. The $SO_4^{2-}$ concentration ranged from 19 to 590 mg/l, with an average value of 206 mg/l. Overall, there were 58% of the samples having higher $SO4^{2-}$ concentrations than the maximum permissible limit of 200 mg/l. The $NO_3^{-}$-N concentration ranged from 0.01 to 19 with an average of 5.22 mg/l. About 3.5% of the samples had $NO_3^{-}$-N values higher than the permissible $NO_3^{-}$-N concentration of 10 mg/l.

## 3.4 Discussion

### 3.4.1 Hydrochemical classification

Major ions in water include $HCO_3^-$, $Ca^{2+}$, $Cl^-$, $Mg^{2+}$, $K^+$, $Na^+$, and $SO_4^{2-}$. Those ions are utilized in combination to determine the water types into categories. The composition of the water from study sites would be shown on a diagram called the Piper diagram. This diagram was described in a Piper's publication in 1944. It has two triangle-shaped plots showing the cations and anions of the water respectively. And in the middle, it has a diamond-shaped plot showing the overall composition of the water's ions. Each axis of the diagram represents a specific ion or a group of ions, ranging from 0 to 100%. A point shown on the diagram would have its coordinates summed up to 100%.

The classification of the Fuhse water facies was done using Piper's diagram (Figure 3.1). The plots show a Ca cation type and Cl - $SO_4$ mix-anion enriched trend. In other words, the Fuhse river water was mainly classified as a mixed type Ca-Cl-$SO_4$ as can be seen from the central diamond-shaped plot of the Piper diagram. Almost all of the water samples were located in this group, inferring an evolvement in the water type or a so-called chemical masking, where several hydrochemical processes were likely to occur at the same time, making it difficult to distinguish and identify them. Those processes may include the ion exchange, rock-water interaction, and anthropogenic impacts. Another noticeable point is that no water samples fell in Ca-$HCO_3$ group - the group represents the meteoric signatures or fresh water, which may indicate the pollution of the water.

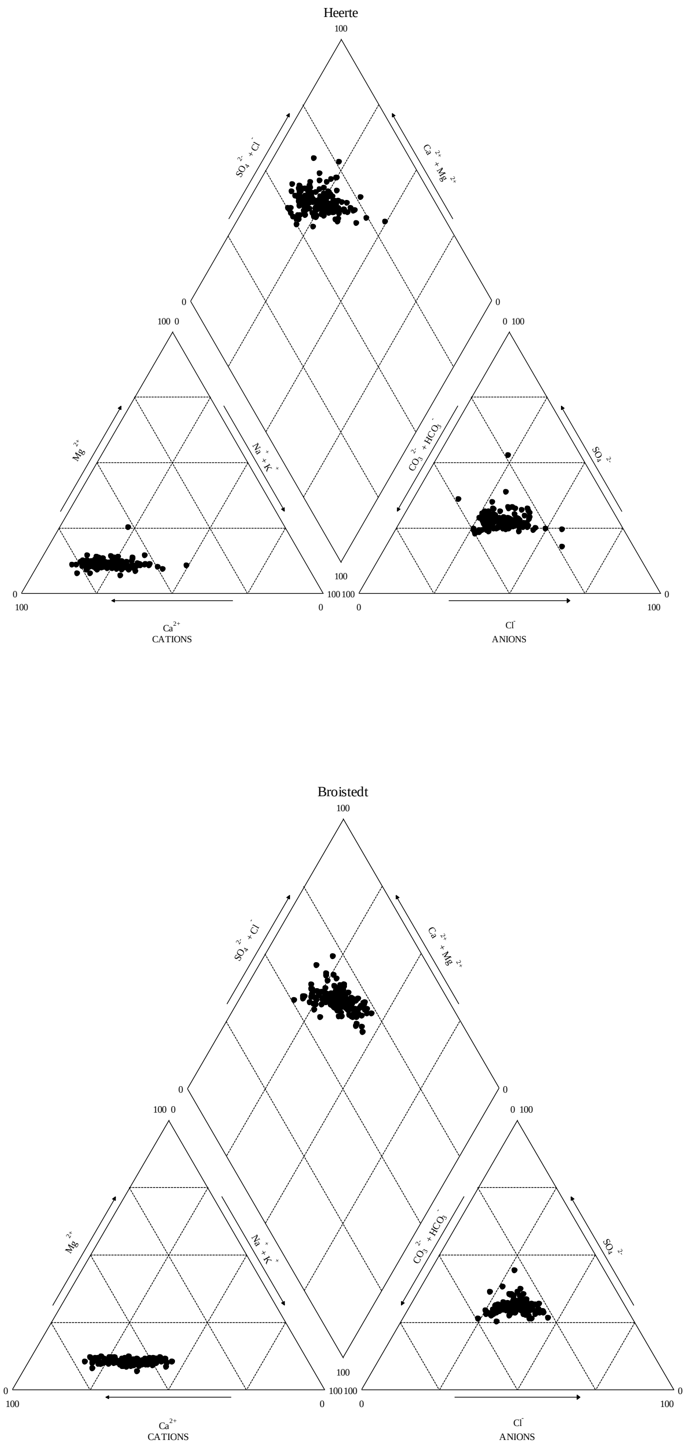
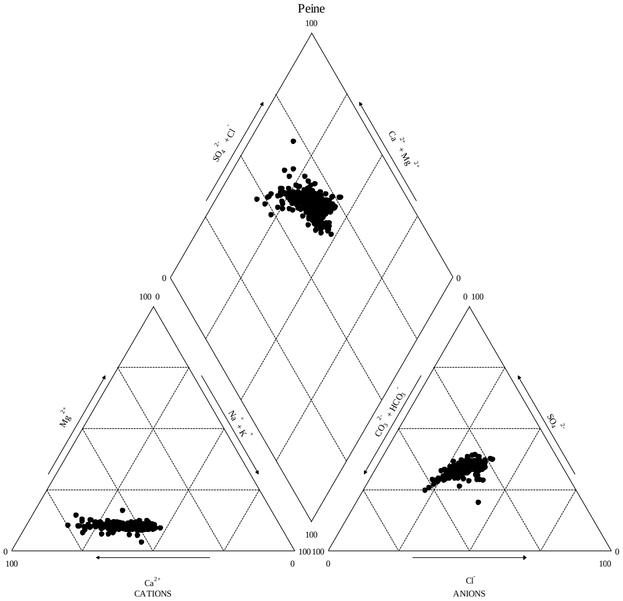


*Figure 3.1 (to be continued): Piper's Diagrams for the Fuhse River at different gauges. From up to down: Heerte, Broistedt, Peine and Wathlingen*



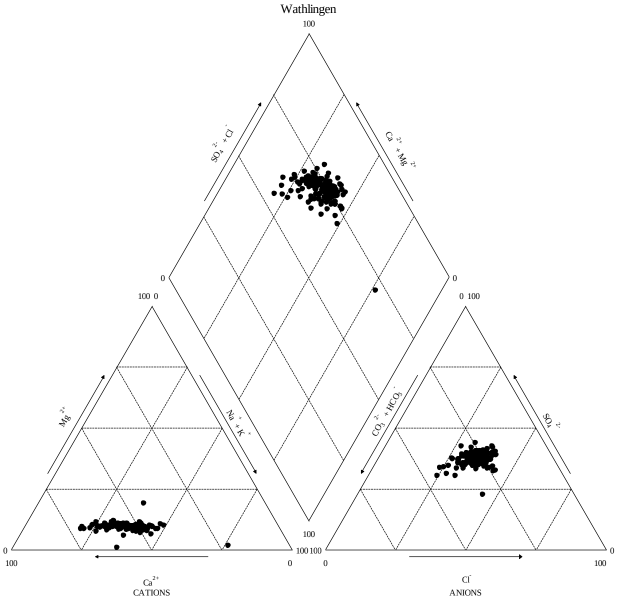


*Figure 3.1 (continued): Piper's Diagrams for the Fuhse River at different gauges. From up to down: Heerte, Broistedt, Peine and Wathlingen*

The ternary diagram of cations of the Fuhse River showed a line of samples in parallel with the calcium axis, while the ternary anion showed clustering of samples at the center. It was also observed that the river had higher proportion of $Ca^{2+}$ + $Mg^{2+}$ compared to $Na^{+}$ + $K^{+}$, which could be due to the presence of calcium rich minerals in the rocks, or due to the dominance of carbonate minerals in the catchment. In this study, the water samples also had a greater amount of $Cl^{-}$ + $SO4^{2-}$ compared to $HCO3^{-}$. This might be referred from an anthropogenic source of major ions. The ionic composition of water from Fuhse was similar to the composition at urban or agricultural sites. The four sites have similar proportion of major cations as well as of major anions, suggesting a similar in water chemical characteristics.

Because of the fertilization in agricultural production, the sulfate contained in the fertilizers may leach into the surface water via the return flow. As a result, the concentration of sulfate in the water within the agricultural land is usually high. Whereas, the water from urban areas usually contains high concentrations of chloride, sodium and potassium. Along the river, there is a slight tendency of anions shifting away from $HCO3^{-}$ towards $Cl^{-}$ and $SO4^{2-}$, as well as cations shifting from $Ca^{2+}$ towards $Na^{+}$ + $K^{+}$ from upstream to downstream, which indicates that the lower part of the catchment is more affected by human activities, e.g. agricultural practices and wastewater treatment, than the upper part. This maybe explained when looking into the topography and landuse map: the upper catchment is mainly mountainous area, whereas the lower part is lowland with more urban communities and agricultural lands.

### 3.4.2 Hydrochemical evolution

Usually the inputs carried by riverine waters are salts in rain water, materials from weathering and erosion in drainage basins, and anthropogenic matters in origin. Some rivers are linked with oceans, and the important indicator for world surface water is $Na^+$ for seawater and $Ca^{2+}$ for freshwater. Therefore, the analysis of surface water chemistry is often employed with a target to interpret any chemical alteration and to get insights into the characteristics of water. In order to identify the origin of water chemistry, the ions are plotted into one diagram which may show useful information on the controlling processes. The diagram expressing those processes was developed by Gibbs (1970).

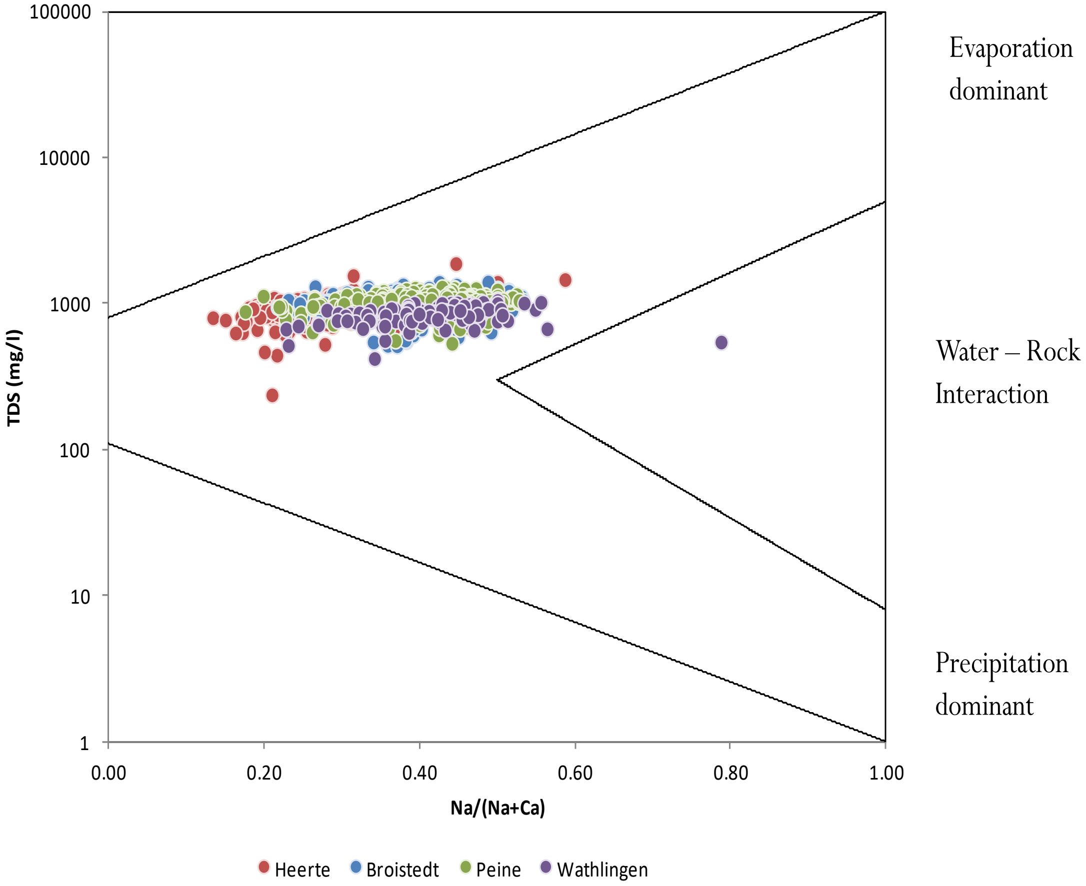


*Figure 3.2: Gibbs' Plot of the Fuhse River Water*

Gibbs plot was used in this study to determine the major processes controlling the river water chemistry, which include precipitation dominance, water-rock interaction, and evaporation/ crystallization dominance regions. The data points on the Gibbs diagram suggested that the Fuhse water chemistry was controlled principally by the rock weathering process. In addition, to some extent, the evaporation process was also an influencing factor which lead to the increased salinity and thus a poor quality of the water (Figure 3.2). This could be explained, because the concentration of ions, which were created during the rock weathering, would be risen due to the evaporation. As a result, the salinity would be increased following the ion concentrations.

### 3.4.3 Nitrate concentration of the river water

By combining the weekly data of BGR-IWW and the monthly data of NLWKN, the temporal trend in nitrate concentrations in this catchment could be assessed. The most commonly sampled sites are those along the River, and data for these sites from about 1981 are available from the NLWKN website. However, some sites have gaps in the records; thus, for this comparison, the period 1992-2017 was selected because during these years, there are available data for all stations.

Overall, nitrate concentrations at all sites have a tendency to be high in winter (Dec, Jan, Feb) and low in summer (Jun, Jul, Aug) (Figure 3.3). However, the differences can be observed in value ranges as the geography changes from mountains to geests to lowlands, which is from Heerte, Broistedt to Peine and to Wathlingen.

Nitrate concentration reduces as the Fuhse river flows from geests (Peine) and mountains (Broistedt) to lowlands (Wathlingen). Wathlingen is located in the lowlands downstream near the outlet point where the river Fuhse flows into the Aller. The concentration is likely to peak at Peine, then it starts to decrease until the Fuhse river flows to meet the Aller. Heerte, which can be considered headwater, has high nitrate concentration during winter time. However, its summer nitrate concentration was apparently much lower than the values of the other Fuhse stations. This may indicate an external nitrogen input source to the river in the downstream parts.

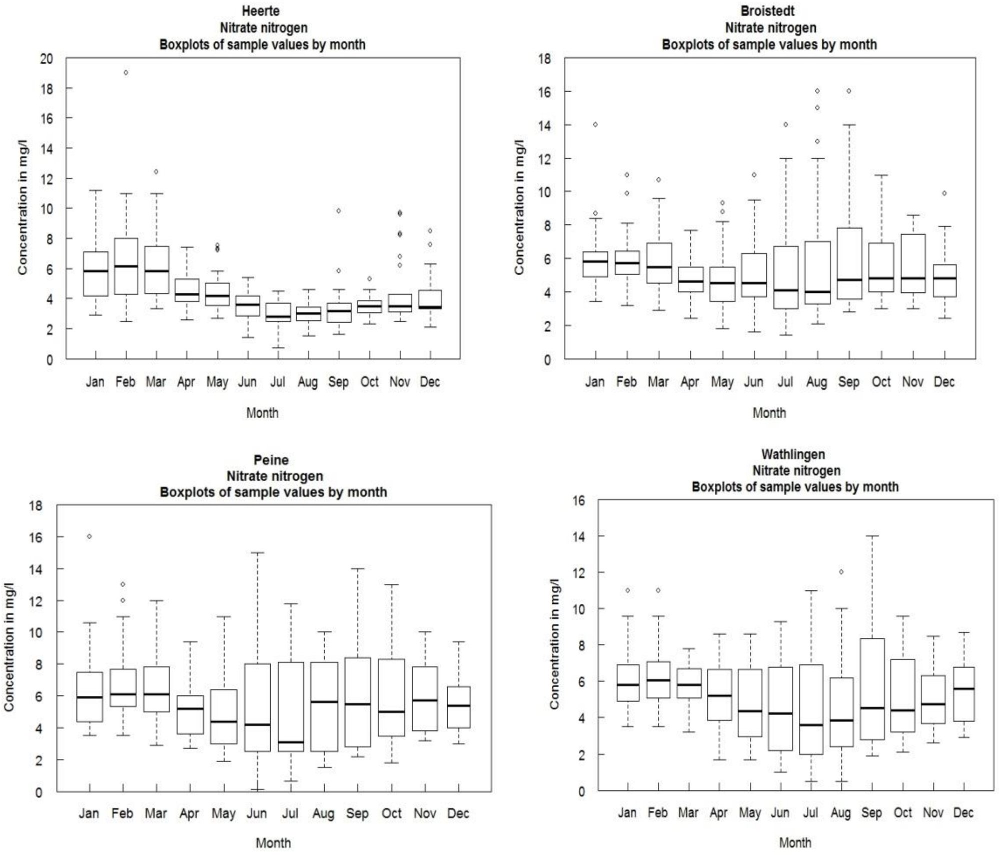


*Figure 3.3: Boxplots of monthly nitrate concentrations at Heerte, Broistedt, Peine, and Wathlingen*

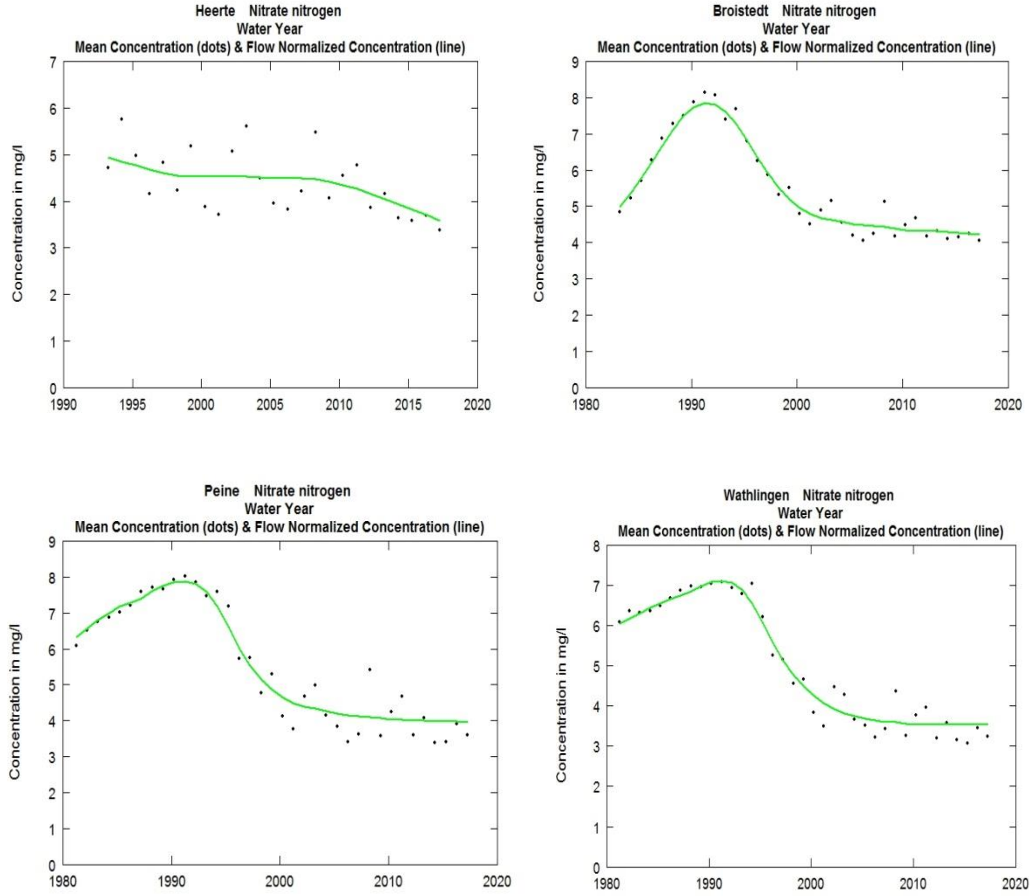


*Figure 3.4: Mean concentration (dots) and flow-normalized concentration (lines) of the riverine nitrate during 1992 to 2017*

As can be seen from the Figures 3.5, the relation between nitrate and discharge of the year 1997 has R-squared value of around 0.36; however, this value increases dramatically to 0.79 in the year 1998. This indicates a significant change in dynamics of nitrate concentrations, which can be confirmed in Figure 3.4. The concentration of nitrate during the period before 1998 is much higher than the later time.

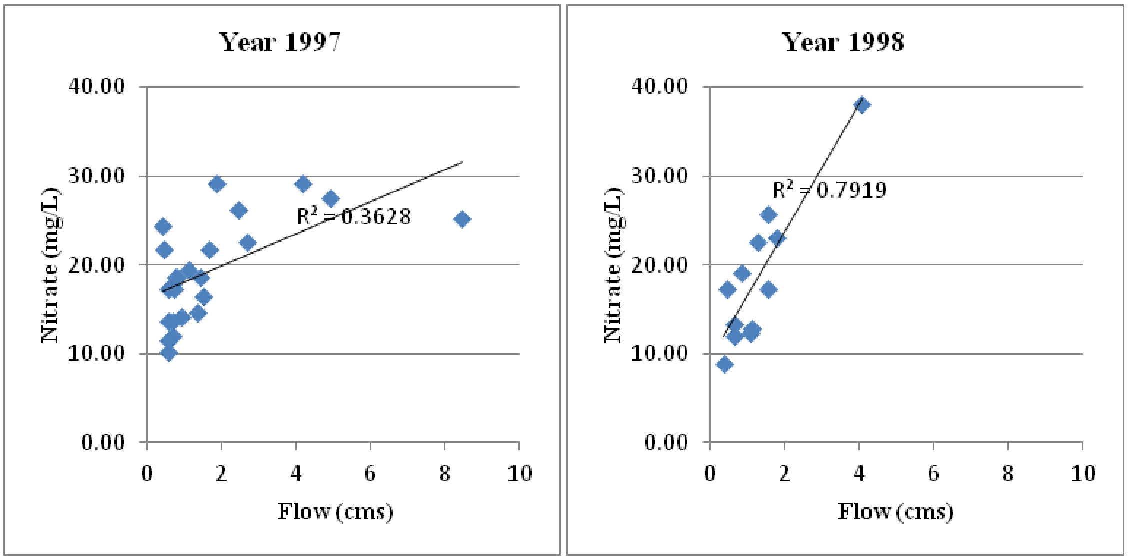


*Figure 3.5: Relationship between nitrate and flow (data collected at Peine) in year 1997 (left) and 1998 (right)*

After the year 1998, the relation between nitrate concentration and flow becomes strong, as their trends show much similarity. The concentration of nitrate has seasonality as the discharge: high values in winter and low values in summer. The relation has a R-squared value of nearly 0.80 (Figure 3.5). Nitrate concentration increases when flow increases. This behavior is also observed in other research (Mueller et al., 2016). High concentration of nitrate in streams might be accentuated by tile drainage of agricultural fields (Musolff et al., 2015).

In the Weser basin, the Fuhse River catchment might be considered to be a large agricultural area with its relatively extensive drainage network. This dense drainage network may perhaps be one of the causes of the increase in peak flow discharge and riverine nitrate concentration. The other causes could be concerned with the changes in land use, or the degradation of the soil.

The relation between nitrate and flow, however, is likely not to be in good agreement before the year 1998. During this time period, the concentration of nitrate is significantly high (Figure 3.4). In fact, there is a large-scaled wastewater treatment plant in Krähenriede, which is called Salzgitter-Nord. This WWTP is located downstream of the Heerte station, and right upstream of the Broistedt station. The WWTP was under a renovation in 1996 to improve its operation. Therefore, a possible explanation is that the operation of WWTP has affected the downstream of Fuhse, causing the elevated nitrate concentration. Then perhaps some improvement in wastewater treatment processes has been done in order to assure the required effluent standards before releasing the water to the rivers. As a result, there was a decrease in nitrate concentration, and the nitrate-flow was again clearly shown.

### 3.4.4 Principal Component Analysis

Principal Component Analysis (PCA) has quite commonly been applied in many research on the purpose of reducing the dimensionality of the datasets. It explains the correlation among a large set of variables in terms of a small number of underlying factors or PCs without losing much information, and allows assessing associations between variables. In this thesis, the PCA tool was implemented to investigate the water quality of the Fuhse River, to assess the influence that pollution and seasonality have on the quality of river water, and to discriminate the individual effects of natural conditions and human activities on the river hydrochemistry.

At first, all data parameters were normalized, having standard deviation of 1 and mean of 0. Then PCA was applied to those normalized data to assess the associations between variables. The PCA depends on an eigenvector of the correlation or covariance matrix. At the beginning, some clear hydrochemical relations can be readily inferred: High and positive correlation can be observed between HCO3, SO4, Cl, Ca, Mg, K, Na, and EC, which are responsible for water mineralization or natural process (Figure 3.6).

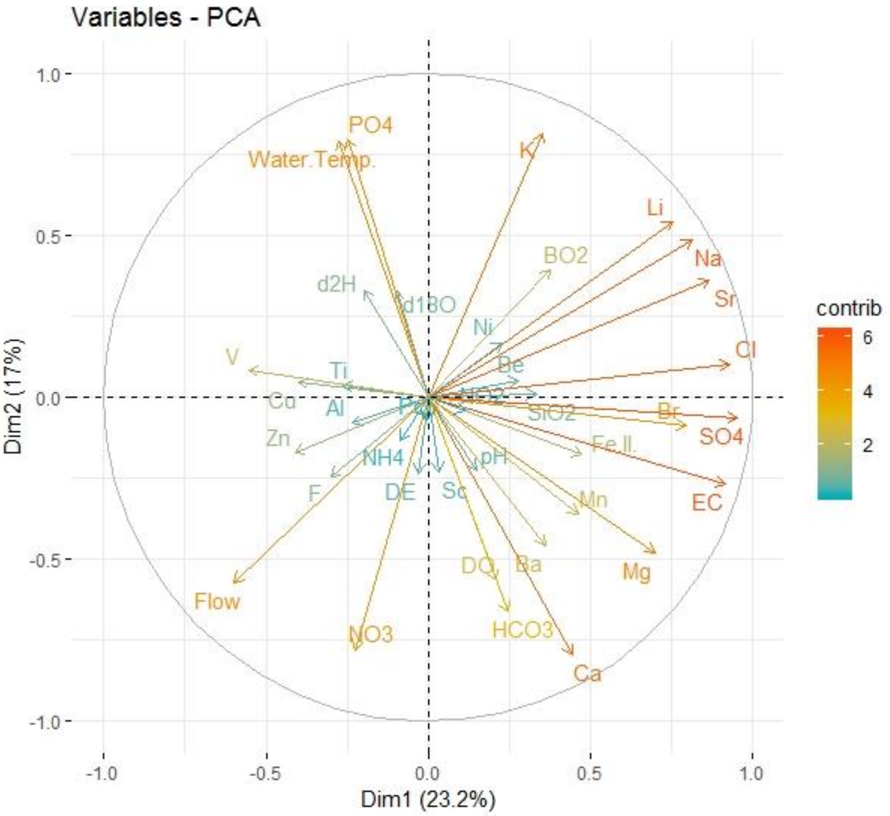


*Figure 3.6: Biplot of PCA for water quality parameters of the Fuhse River*

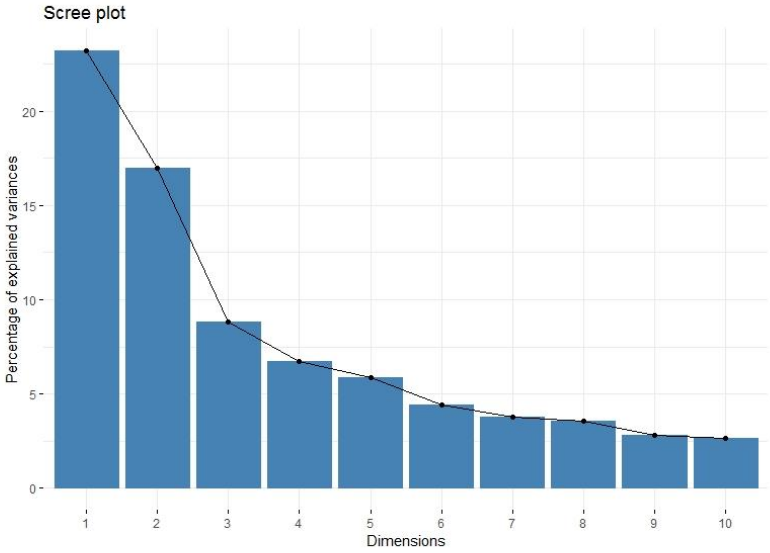


*Figure 3.7: Scree plot of the PCs*

*Table 3.2: First two PCs of the Principal Component Analysis for the Fuhse River*

| **Parameter** | **PC 1 (Dim.1)** | **PC 2 (Dim.2)** |
|---|---:|---:|
| pH | 0.148346 | -0.22523 |
| EC | 0.916628 | -0.26883 |
| DO | 0.209417 | -0.56581 |
| Water.Temp. | -0.27738 | 0.791132 |
| Pcp | -0.00654 | -0.07251 |
| Flow | -0.59796 | -0.5716 |
| K | 0.353143 | 0.813876 |
| Na | 0.813454 | 0.483548 |
| Cl | 0.93001 | 0.102015 |
| Mg | 0.700928 | -0.47943 |
| Ca | 0.4441 | -0.7949 |
| SO4 | 0.954947 | -0.06404 |
| HCO3 | 0.244978 | -0.66249 |
| Fe.II. | 0.474686 | -0.17711 |
| Mn | 0.462359 | -0.36096 |
| NO3 | -0.22408 | -0.77853 |
| Br | 0.796112 | -0.08872 |
| NH4 | -0.08682 | -0.13185 |
| NO2 | 0.115694 | -0.04347 |
| F | -0.30133 | -0.24641 |
| PO4 | -0.24808 | 0.794323 |
| Al | -0.2333 | -0.07937 |
| BO2 | 0.377592 | 0.395236 |
| Ba | 0.362071 | -0.45719 |
| Be | 0.277771 | 0.052488 |
| Cu | -0.40067 | 0.046942 |
| Li | 0.752753 | 0.542964 |

*Influencing factors with values equal or greater than 0.5 were highlighted in yellow

Flow rate was negatively correlated to most of the variables, since an increase in flow rate may cause the dilution of contaminants. This inverse correlation was highly significant for components like EC, Mg and SO4. Besides, the dissolved oxygen (DO) was observed to have a negative correlation with the water temperature. This could be explained, because when the water temperature increases, the solubility of the oxygen in water would decrease. In addition, DO was also inversely correlated with phosphate-phosphorous. This could be accounted from the partial oxidization of the phosphorous by the oxygen.

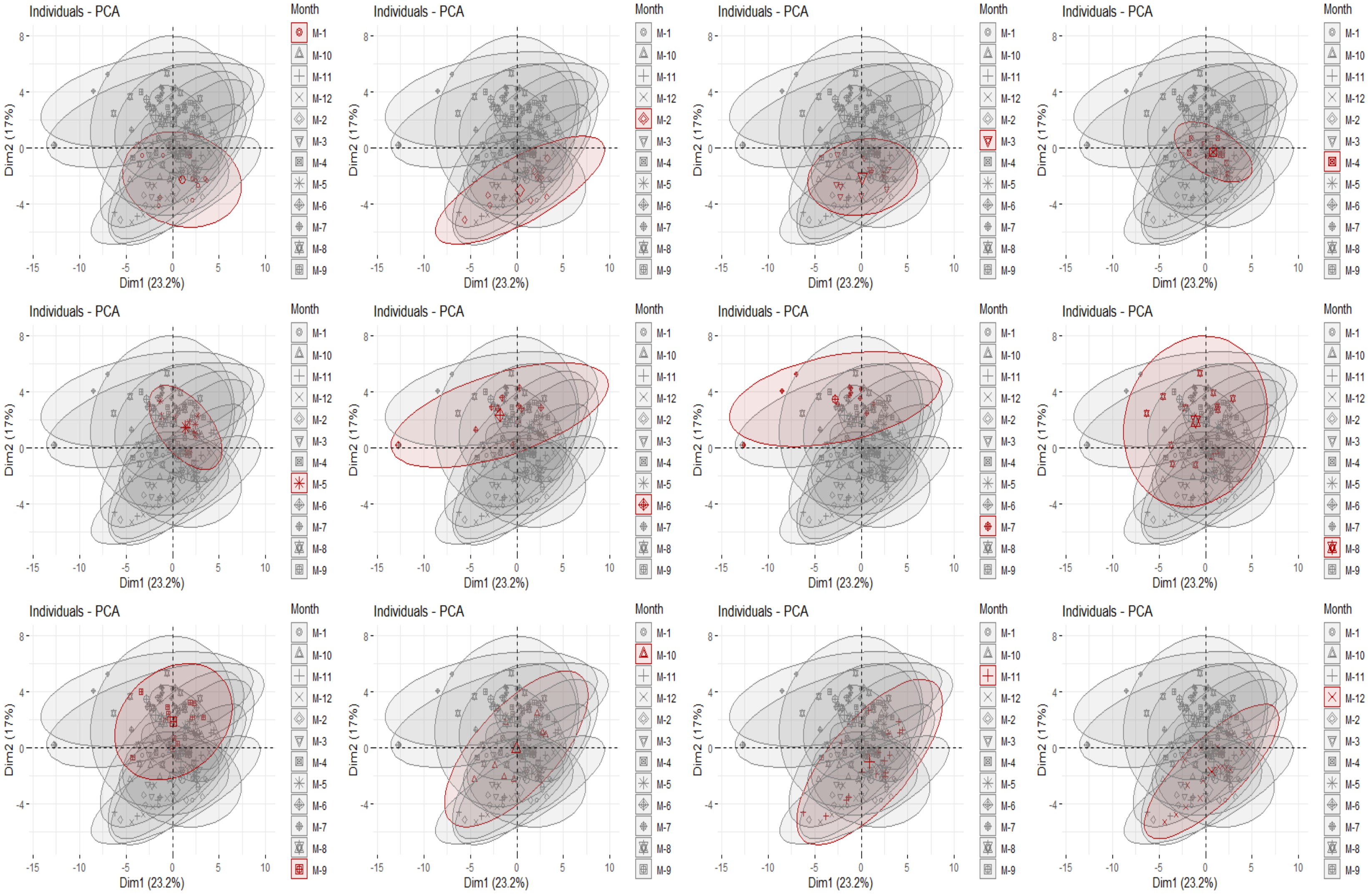


*Figure 3.8: Biplots of the PCA for the Fuhse River in a year*

The scree plot was used to identify the number of PCs to be retained in order to comprehend the underlying data structure. At the end, the first four PCs, which had the eigenvalues higher than unity, were kept. These PCs could explain approximately 76.5% of the variation of the original data (Figure 3.7). In other words, PCA has found a reduced number of variables which could give explanation to most of the information consisted in the initial water quality data.

Each PC is related to a small group of variables with a hydrochemical meaning, two of which are: natural processes for PC1, and anthropogenic impacts for PC2. The PC1 explains 23.2% of the variances, which is highly contribute by most variables such as EC, Na, Mg, Cl, SO4, and Br (Table 3.2). The PC2, which explains 17% may relate to the agricultural and municipal wastewater discharged into the river. In the meanwhile, temporal effects were associated to seasonal variations in flow rate which cause dilution of the pollutants and hence variations in water quality. As can be seen from Figure 3.8, the nitrate concentrations vary accordingly with the flow seasonality, with changing values between winter time and summer time. The application of PCA has achieved meaningful classification of hydrochemical variables of the river water.

To summarize, natural processes, i.e. weathering or mineralization processes, control the chemical composition of the Fuhse River. Nitrate concentrations are strongly dependent on the flow discharge. However, anthropogenic activities also have high impacts on the hydrochemistry of the river water in this catchment.

### 3.5 Conclusion

An integrated approach, combining the experimental works (sampling & labs), and statistical analysis (PCAs) is likely to be an effective method to investigate the hydrochemistry as well as the nitrate dynamics of the Fuhse River.

The distribution of major ions in the water is as follows: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $Cl^{-} > HCO3^{-} > SO4^{2-}$. Water of the Fuhse River is of evolved type with mix abundances of ionic concentrations. Using Piper's graph, water has been classified into the main hydrochemical group of Ca-Cl-SO4, as it chemically characterizes the water which is affected by anthropogenic activities.

The PCA study indicates that although natural factors controlling the water chemistry of the river, anthropogenic impacts in the form of agricultural activities and wastewater are also influencing the water chemistry. The fact is advocated by the presence of high concentrations of $NO3^{-}$, $Cl^{-}$, and $SO4^{2-}$ within the catchment.

Nitrate concentration is generally high during winter and is highest during significant runoff event (e.g.: winter runoff). Nitrate concentration tends to be highly correlated with discharge since year 1998 until now. Before 1998, the concentration is, however, affected by other external forces which are presumably the previous operation of WWTPs. Further in-depth study should be conducted to clarify this doubt.

The spatial dynamics of nitrate varies with changes in geography as shown in analyses: high nitrate levels in upper areas (Peine) and low nitrate levels in lowlands (Wathlingen). If the responses of nitrate to external forces such as discharge can be separated, then nitrate dynamics could be used perhaps to characterize different rivers or river sections.

Nitrate concentrations of the Fuhse River exceed the natural value. This issue is a major water concern in this catchment regarding the water supply sources. Therefore, further analysis and modeling of nitrate transport in water are recommended.

# *Chapter 4*

# Identification and partitioning of nitrate sources in a river catchment using dual isotope method and stable isotope mixing model

***

## 4.1 Introduction

Recently, nutrient pollution of surface water has become a worldwide issue, challenging the water resources management. Nutrient pollution, especially the nitrate contamination, of water poses a threat to both human and environmental health (Erisman et al., 2013). Nitrate occurs naturally in river water at low concentration as a result of rock weathering, in which the latter has brought about the decomposition of minerals and the release of the former in the soil. However, riverine nitrate may achieve abnormally high values due to overflow from the farming area together with discharge from human or livestock wastes (Laftouhi et al. 2003). Main anthropogenic nitrate sources namely include the sewage from industrial and municipal wastewater treatment plants, and the massive application of mineral nitrogen fertilizers and manure in agricultural activities. The excess nitrogen not uptaken by the crops, which is highly soluble and poorly bound to soils, will eventually enters the groundwater and surface water via leaching and surface runoff. As a result, the areas of agricultural production are having high risk of nutrient-contaminated water.

The ability of the ecosystem to temporarily retain or permanently remove nitrogen is referred as the nitrogen retention (Howarth et al., 2012). This natural retention of nitrogen occurs within systems including soils, groundwater, rivers and lakes, etc. on its pathway to reach the sea. Nitrogen can be stored temporarily in the sediment or organic matter. Nitrogen can also be removed from soils via denitrification under water saturation condition. Then within groundwater zone providing anoxic condition, nitrogen retention may result from both denitrification and nitrogen accumulation. After that, the nitrogen is released to surface water and can be further taken by crop uptake, sedimentation or transport loss within the river system. The retention processes are usually observed strongly at the interface between water and the river bed (Krause et al., 2011; Paern et al., 2012). Those nitrogen retention processes may temporarily retain or permanently remove the nitrogen on its pathway within the aquatic system, which thus leads to uncertainties and difficulties in quantifying the contribution of nitrogen inputs exposed to waters.

Identifying the nitrate sources is considered an effective method to combat with the nitrate pollution, as it enables man to target and reduce the nitrate inputs into the environment. As mentioned above, nitrate in surface water may results from various sources, such as precipitation, soil nitrogen, mineral fertilizer, and manure, domestic and industrial wastewater (Fogg et al., 1998). The sources of nitrate in surface water were once determined using different approaches, for instance, modelling approach (Wagner, 1992; Pohlert et al., 2005; Jiang et al., 2019), statistics approach (Sprulli et al., 2002; Sun, 2007, Ehrhardt et al., 2019), or stable isotope approach (Macko, 1994; Bryant Mason et al., 2013; Mueller et al., 2015). However, there has been rarely no studies applying different approaches separately to the same area, in order to investigate and compare how adequately those approaches may perform the source identification.

Of those methods mentioned above, analysis of nitrogen isotopic composition is considered to be able to provide a direct, effective and accurate means of source identification by differentiating values of nitrogen isotopes in different sources (Mayer et al; 2002). Due to the fact that different sources of nitrate may contribute different fractions of nitrogen to the receiving bodies, the isotopic compositions of nitrate can be used as tracers to identify the nitrate sources. Nitrogen (N) consists of two stable isotopes, which are nitrogen-14 and nitrogen-15. A wide range of stable nitrogen isotope data of nitrate (d15N) in the nature enables it to be useful in differentiation of nitrate inputs (Kendall et al., 1998). Therefore, identification of different nitrate sources can be detected by variations in d15N values. However, the mixing of waters which are impacted by different nitrate sources will also influence the stable isotope values of nitrate. There are some compounds having overlapping range of nitrogen isotopes, for example, soil nitrogen and mineral fertilizers. Thus, sometimes it is difficult to distinguish sources of nitrate just by only d15N because of the overlapping values. This difficulty has brought about the use of dual isotope approach. This approach requires the use of both the nitrogen and oxygen isotope values of the samples. The dual isotope approach was implemented in various environmental studies with a focus on nitrate, for instance, Deutsch et al., 2006; Oelmann et al., 2007; etc.

In the Fuhse catchment in Lower Saxony, northern Germany, the levels of nitrate measured by NLWKN are under the limit standard regulated in the German Ordinance of surface water. However, this level is still relatively high considering the ecological conditions. In addition, Fuhse catchment is a part of the focus pilot area Fuhse-Wietze introduced by the State of the Lower Saxony. The main target of that program is to enhance the nutrient efficiency by decreasing the inputs of phosphate and nitrate to the surface water bodies. It is necessary to investigate the current status of nitrate pollution in river water and propose relevant management measures to tackle with this nitrate issue. Thus, it is recommended that a precise method is applied for evaluating the nutrient contamination of water as well as its impacts on the environment, in order to support the decision makers in mitigation and investment planning. Possible action options in term of the scope and location are to be selected, based on the knowledge of nutrient sources and amount, as well as their paths into the waters. However, up to now, it still lacks of a proper approach to investigate the sources as well as the transport of the riverine nitrate within this catchment.

Therefore, the overall objectives of this study is to a) investigate the sources of nitrate-nitrogen of the surface water in the Fuhse catchment qualitatively; and b) to partition the contribution of each nitrogen inputs into the river water quantitatively. In order to achieve this target, the main nitrate sources were first identified using the dual isotope method. Then the partitioning of different nitrate inputs was conducted with the implementation of an isotope mixing model. Several graphs and tables are included for visualization of the results.

## 4.2 Materials and methods

Overall, the major steps of this study could be seen from Figure 4.1. First of all, the river water were sampled and delivered to the laboratory where they were analyzed for chemical properties and isotopic composition. Then the isotope values were evaluated, which consists of sources identification and partitioning. In details, main possible sources of nitrate were identified using the dual isotope approach. Finally, an isotope mixing model was applied to estimate the fraction of each source.

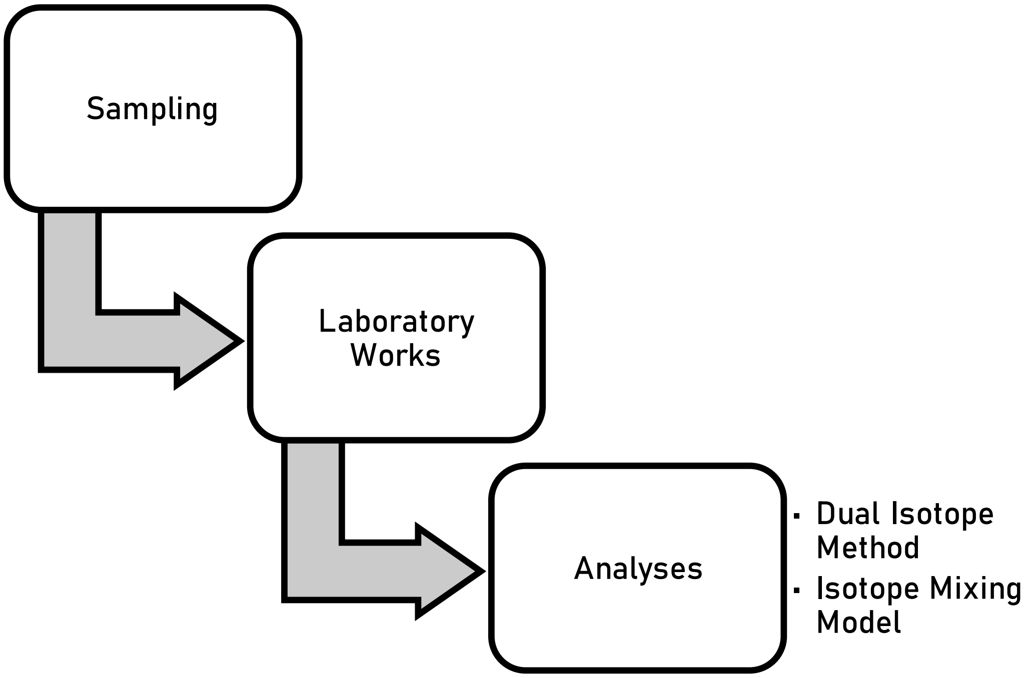


*Figure 4.1: Diagram describing the methodology steps*

### 4.2.1 Field sampling

The Institute of Hydrology and Water Resources Management (IWW) of the LUH in cooperation with the Federal Institute for Geosciences and Natural Resources (BGR) has conducted a water quality campaign along the Fuhse River in May 2019 in order to evaluate the fate of the nitrate in the river catchment. Description of the Fuhse River and its catchment were given in Chapter 2, Part *Study Site*.

The sampling points (Figure 4.2) were chosen by the following criteria: one sampling point was positioned at the source of the river (Flöthe) in order to determine the background concentration without WWTP impact; the other sampling points located along the Fuhse River and its main tributary Erse. The location of WWTPs and NLWKN's gauges was taken into consideration. Some samples were also taken from the Burgdorfer Aue and Fuhsekanal for comparison purposes.

River water samples were taken in 500ml-plastic-bottles, 30ml-glass-bottles, and 100ml-plastic-bottles acidified with nitric acid to keep the pH low. In-situ sensors were used to measure physical parameters such as dissolved oxygen, electric conductivity, pH, and water temperature. The values were recorded once they stabilized. The description of the sampling can also be seen in part 2.3 above.

### 4.2.2 Laboratory measurements

Then samples were extracted and chemically analyzed in the lab, as summarized in part 2.3 of the Chapter 2. Regarding the isotopic composition of nitrate, the method employed at the BGR laboratory uses the anion exchange resin technique which was originally developed by Silva et al. (2000), and later improved by Xing & Liu (2011). The method conducted the ion exchange separation of nitrate, followed by high temperature conversion to nitrogen gas using an elemental analyzer (Appendix – Figure A.2). This technique permits direct measurement of both nitrogen and oxygen isotopes in nitrate.

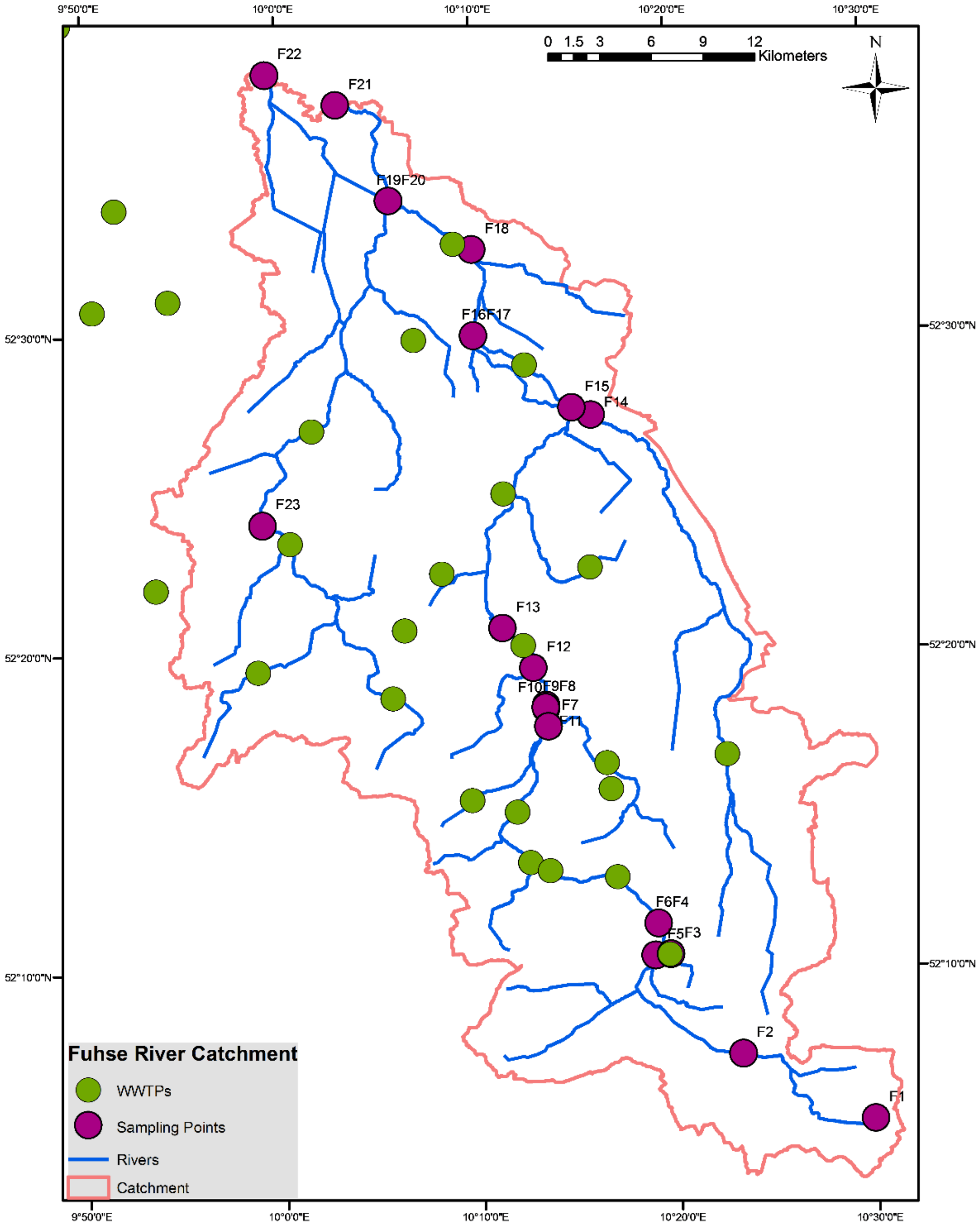


*Figure 4.2: The Fuhse River Catchment: sampling sites for isotopic analysis*

### 4.2.3 Analytical approach

The isotope results measured in the lab were, first of all, utilized for the identification of the main sources of nitrate at each of 22 sampling sites along the Fuhse River, using the dual isotope approach. The values of d15N and d18O were plotted in combination with potential ranges of isotopic compositions from different nitrate inputs. From this, main nitrate sources within the catchment were identified qualitatively.

Corresponding to the improvement in nitrate sources identification, the research direction is moving gradually from the step of being only qualitative to the next step of being quantitative. Recently, there have been a various mathematical models being developed with the aim of estimating the contribution proportions of different nitrate inputs in water. The most common models currently used can be listed as mixing model. In this study, the isotope mixing model SIMMR was chosen to address the question of performance of different approaches applied at the same catchment.

*SIMMR Model*

The SIMMR Model (Stable Isotope Mixing Model) is a Bayesian isotope mixing model based on mass balance, which was introduced as a package (2019) in the R Project for Statistical Computing (r-project.org). SIMMR was improved from SIAR package (Parnell et al., 2010) which was originally developed for ecological foodweb studies. Nevertheless, the SIAR model was applied widely in analyzing the contribution ratios of nitrate sources in water, including karstic spring (El Gaouzi, 2013), surface water (Xue et al., 2012), and sea water (Korth et al., 2014).

The stable isotopic compositions of nitrate d15N and d18O for the samples of the Fuhse, which were analyzed and obtained from the lab, were used as the input of the model. In total, there were 44 isotope values which were investigated for the 22 studied sites. The SIMMR, similar to SIAR in many features, applies a Bayesian mixing model to analyze those isotope data. The model is implemented to make an estimation of the possible fraction of each source, as well as the probability distribution of each source proportion to the water bodies. The updated version SIMMR has a relatively more sophisticated mixing model compared with the previous one SIAR. The model can be formulated as followings (Parnell et al., 2010)

$$X_{ij} = \sum_{k=1}^{K} p_k(S_{jk} + c_{jk}) + \varepsilon_{ij}$$

$$S_{jk} \sim N(\mu_{jk}, \omega^2{}_{jk})$$

$$c_{jk} \sim N(\lambda_{jk}, \tau^2{}_{jk})$$

$$\varepsilon_{jk} \sim N(0, \sigma^2{}_j)$$

in which

$X_{ij}$ = the isotope value of j of mixture i

$p_k$ = the proportion of source k

$S_{jk}$ = the source value k on isotope j from source i, having the normal distribution with mean μ and variance ω

$c_{jk}$ = the fractionation factor of isotope j from source i, having the normal distribution with mean λ and variance τ.

ε = the residual error which represents the variance of other compounds, having mean zero and standard deviation $\sigma$ under normal conditions

## 4.3 Results and discussion

### 4.3.1 Identification of nitrate sources using dual isotope approach

The isotopic composition of nitrate (d15N and d18O) in the Fuhse water was measured to identify the potential nitrate sources. There was no nitrate isotope result for the drainage in Klein Ilsede, probably due to the small amount of nitrate concentration at this site. Thus, there were 22 sites with results out of 23 samples. The results are shown in Figure 4.3 and Table 4.1. The common ranges of d15N and d18O for the main origins of nitrate which might have impacts on the water are also presented in Figure 4.3 (modified from Kendall et al., 1998, Kendall et al., 2015).

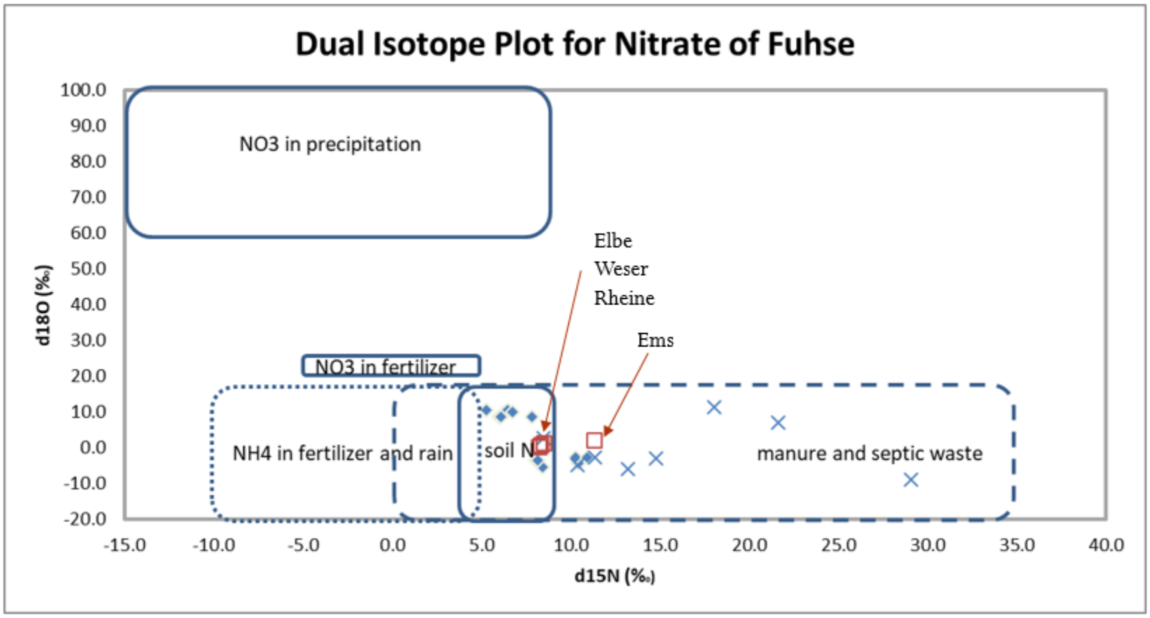


*Figure 4.3: Dual Isotope Plot (modified from Kendall et al., 1998; Kendall et al., 2015) for Nitrate in Fuhse River (blue dots: main stream, blue crosses: tributaries), in comparison with other German rivers (data from Johannsen et al., 2008; red rectangles)*

*Table 4.1: Isotopic composition of nitrate in the Fuhse River Catchment*

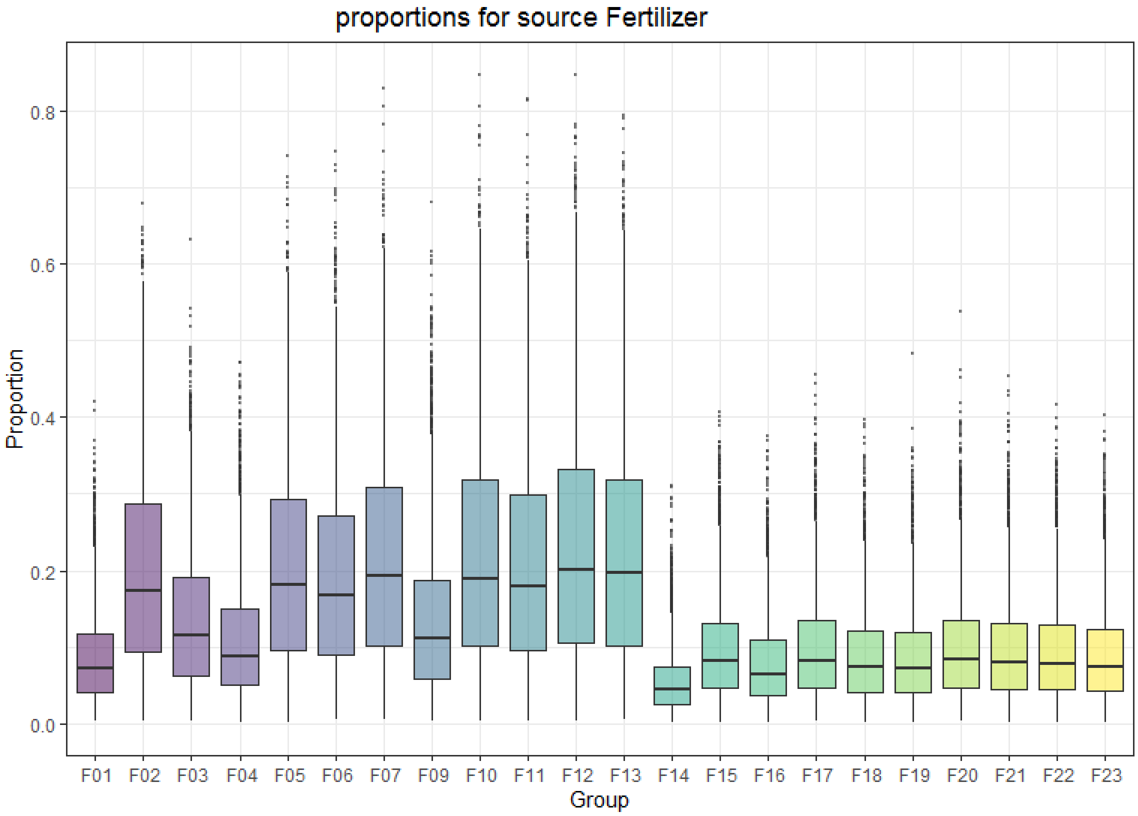
| Sample ID | Channel | Location | Date | d15N (%o) | d18O ((%o) |
|---|---|---|---|---|---|
| F01 | Main | Flöthe Quelle | 22.05.19 | 8.4 | -5.4 |
| F02 | Main | Heerte | 22.05.19 | 6.1 | 8.6 |
| F03 | Tributary | Krähenriede (oh KA) | 22.05.19 | 8.5 | 2.6 |
| F04 | Tributary | Krähenriede (uh KA) | 22.05.19 | 21.6 | 7.1 |
| F05 | Main | Reppner | 22.05.19 | 6.0 | 8.6 |
| F06 | Main | Broistedt | 22.05.19 | 7.8 | 8.7 |
| F07 | Main | Fuhse in der Nähe von Kl. Ilsede | 22.05.19 | 6.7 | 10.1 |
| F08 | No | Drainage (Kl. Ilsede) | 22.05.19 |  | 12.6 |
| F09 | Tributary | Pisserbach | 22.05.19 | 18.0 | 11.5 |
| F10 | Main | Fuhse beim Mittellandkanal stromaufwärts | 22.05.19 | 6.5 | 10.6 |
| F11 | Main | Fuhse beim Mittellandkanal stromabwärts | 22.05.19 | 6.3 | 10.1 |
| F12 | Main | Fuhse bei Peine | 22.05.19 | 5.3 | 10.7 |
| F13 | Main | Eixe | 22.05.19 | 6.4 | 10.3 |
| F14 | Tributary | Eltze | 23.05.19 | 29.1 | -8.8 |
| F15 | Main | Prangenhohl | 23.05.19 | 8.0 | -3.4 |
| F16 | Tributary | Erse (Fuhse i. d. N.) | 23.05.19 | 13.2 | -5.9 |
| F17 | Main | Fuhse (Erse i. d. N.) | 23.05.19 | 8.2 | -3.4 |
| F18 | Main | Wathlingen | 23.05.19 | 10.4 | -4.2 |
| F19 | Tributary | Aue | 23.05.19 | 10.4 | -4.9 |
| F20 | Main | Fuhsekreuz | 23.05.19 | 10.3 | -2.6 |
| F21 | Main | Fuhse Mündung | 23.05.19 | 10.9 | -2.6 |
| F22 | Tributary | Fuhsekanal Mündung | 23.05.19 | 11.4 | -2.7 |
| F23 | Tributary | Aligse Burgdorfer Aue | 23.05.19 | 14.8 | -2.9 |

In general, the upper part of the catchment has smaller d15N and higher d18O values than the lower part. This may result from the greater agricultural land areas as well as greater number of WWTPs locating in the downstream. Landuses also reveal that sites near WWTPs such as Eltze, Krähenriede, and Pisserbach have the highest value of d15N of all locations, which are 29.1%o, 21.6%o, and 18.0%o respectively.

The measured values of d15N of nitrate in water ranged between 5.3 %o at Peine and 29 %o at Eltze (Table 4.1). All of the study samples fell in the range of nitrogen originating from soil N, manure and septic waste as can be seen from Figure 4.3. In other words, major potential sources of nitrate in the Fuhse River Catchment include soil nitrogen, manure and sewage. Compared these outcomes to other rivers in Germany (Johannsen et al., 2008), it could be seen that there was a similarity in the signatures of the isotope components of nitrate of the current study with those signatures from other research. This agreement may indicate the same soil nitrogen-, sewage- and manure- derived sources for nitrate in the Fuhse and those other rivers.

### 4.3.2 Partitioning of nitrate source inputs using stable isotope mixing model

In this study, SIMMR was used to analyze the d15N and d18O values to estimate the contributions of five nitrate sources (nitrate in rainfall, soil nitrogen, fertilizer, manure, and sewage) in twenty two sampling points along the Fuhse river catchment. Isotope measurements of samples were arranged from upstream to downstream, in order to investigate the spatial source contributions. The dissolved oxygen concentrations of all sampling waters were relatively high which is not ideal for denitrification (Piña-Ochoa and Álvarez-Cobelas, 2006), indicating that no significant denitrification occurred during the sampling campaign. Hence, it is not necessary to determine the enrichment factors of denitrification. Finally, the results of the mixing model estimating the fractions of five nitrate sources at the sampling points in this study are illustrated in Figure 4.4.


proportions for source Fertilizer
Proportion
0.0
0.2
0.4
0.6
0.8
F01
F02
F03
F04
F05
F06
F07
F09
F10
F11
F12
F13
F14
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F16
F17
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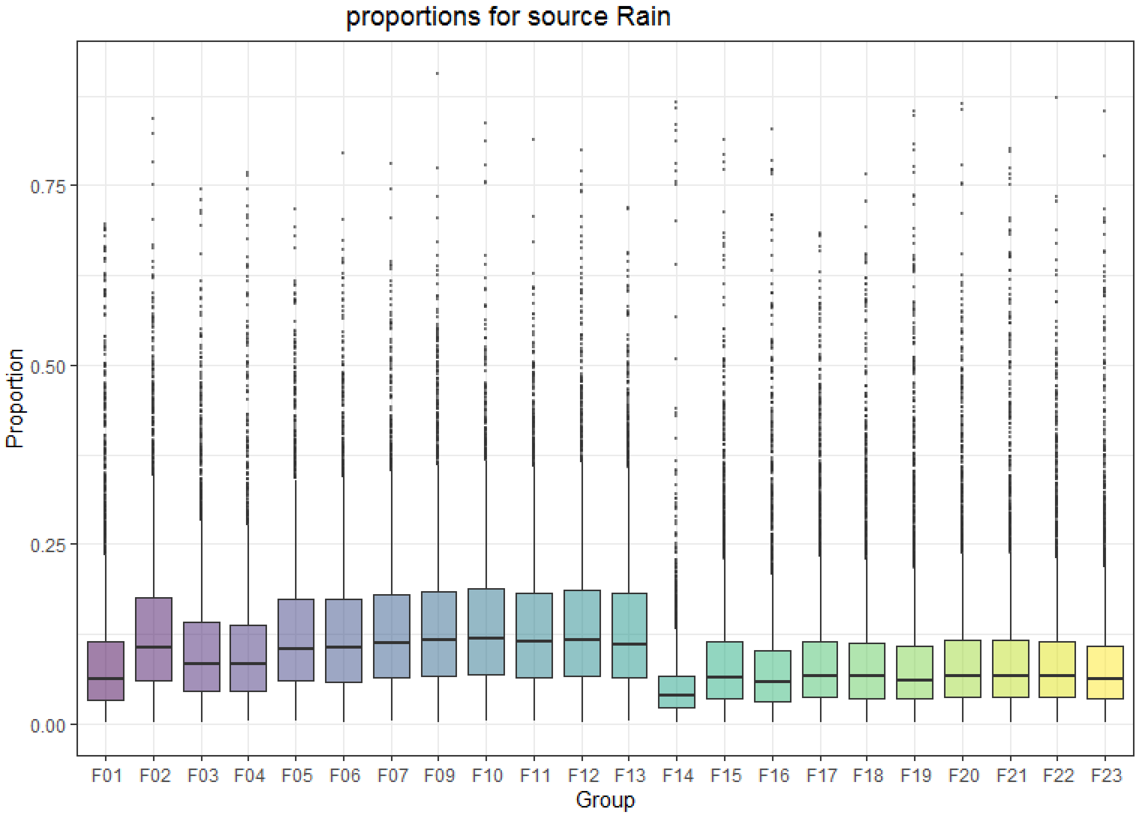
F20
F21
F22
F23
Group


proportions for source Rain
Proportion
0.00
0.25
0.50
0.75
F01
F02
F03
F04
F05
F06
F07
F09
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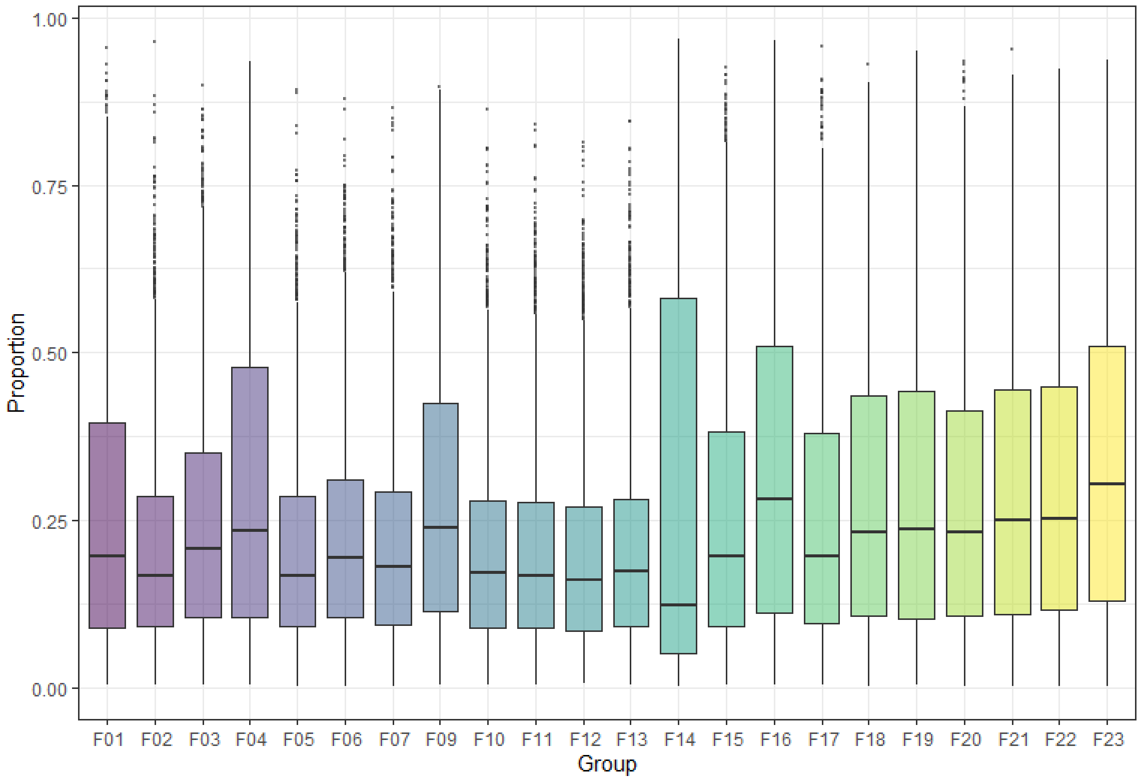
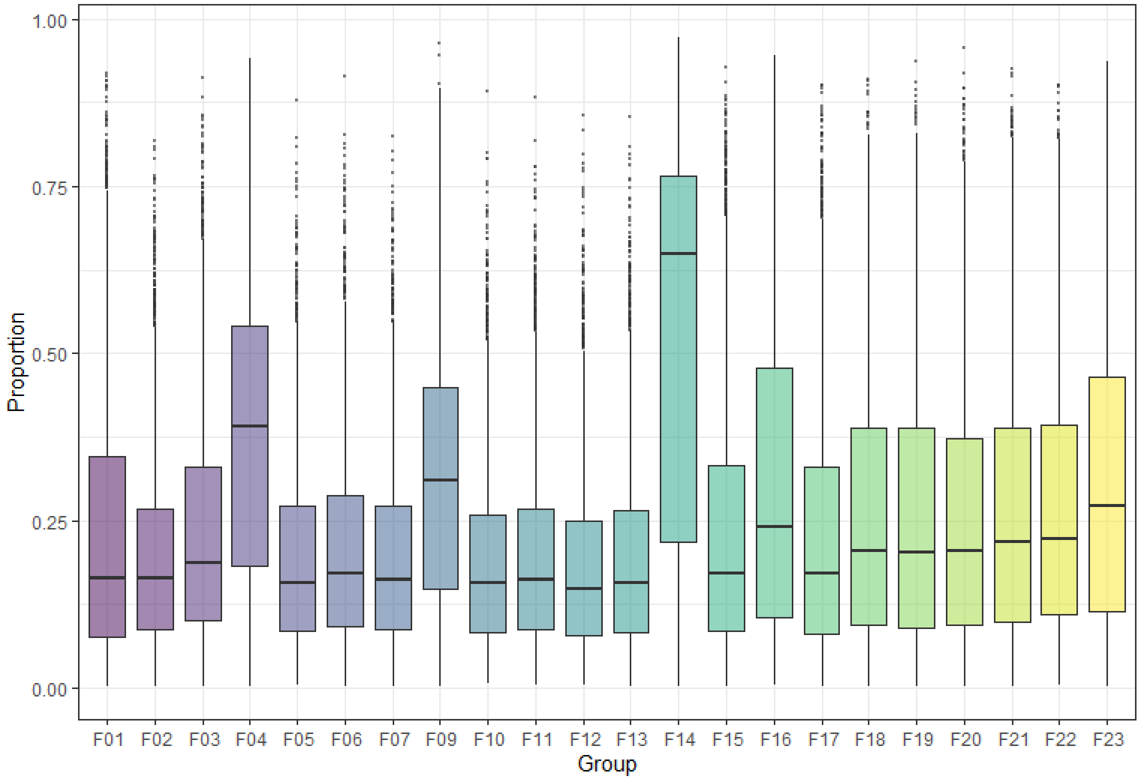
F22
F23
Group



proportions for source Manure



proportions for source Sewage

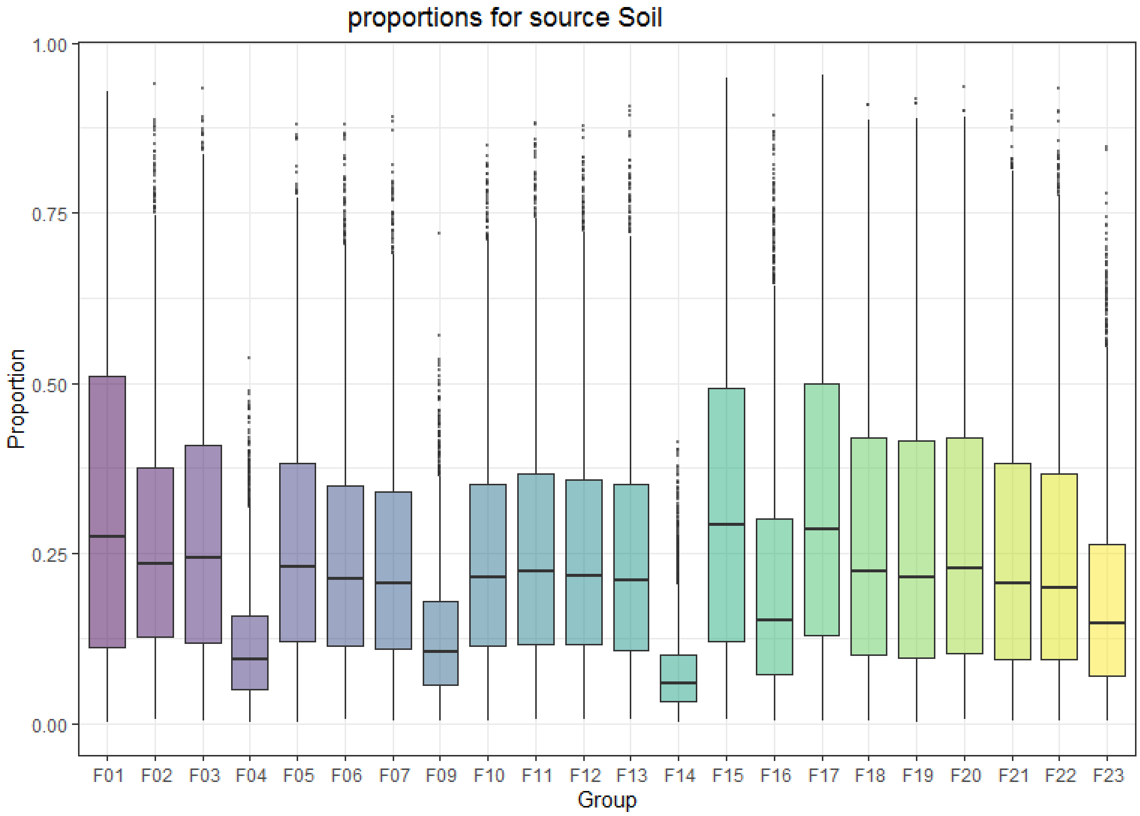


*Figure 4.4: Fractions of nitrate sources (Fertilizer, Rain, Sewage, Manure, and Soil) at sampling sites. The order of the sites are from upstream to downstream.*

The contribution of soil nitrogen was the highest, followed by sewage, manure, fertilizer, and rainfall to the Fuhse River, as can be seen from box plots in Figure 4.4. At three locations in Kraehenriede (WWTP), Eltze and Pisserbach, the nitrate from sewage constitutes the highest proportion, which is in good agreement with the finding from the dual isotope approach above.

Except for those three sites, in general, an increasing trend in sewage- and manure-based nitrate can be observed along the river from upper- to lower-part of the Fuhse catchment. This maybe because of the fact that the lower part of the catchment is mainly lowland where there are more livestock production than in the upper part comprising of mountainous areas. Together with the higher number of cattle, the use of manure in the downstream area is also higher than in the upstream area.

On the contrary, fertilizer appears to be more influencing in the upper part than in the lower one, which was shown clearly by the fraction gap in the first diagram of Figure 4.4. In the meanwhile, the rainfall-based nitrate seems to be relatively uniform with a proportion of about 10 – 12% throughout the catchment.

The nitrogen fractions for the sample taking at the Broistedt from SIMMR model was shown in Figure 4. 5 & Table 4.2 as an instance.

These findings indicated that soil nitrogen, manure and sewage were the dominant nitrate sources in this catchment, especially in the lower part, while fertilizer has certain impact on the nitrate level only in the upper part.

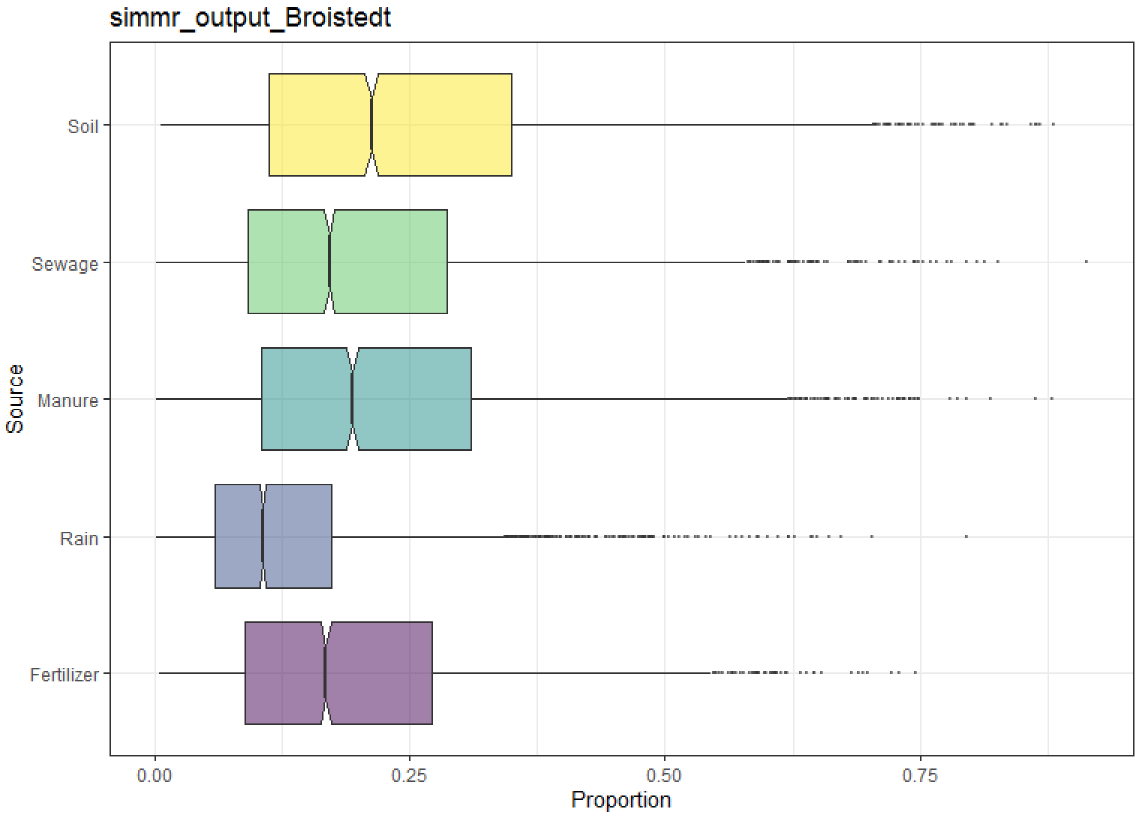


*Figure 4.5: Fractions of nitrate sources at Broistedt (using SIMMR model)*

*Table 4.2: Results from SIMMR model for the sample at Broistedt gauging point*

| **Sources** | **SIMMR (Range)** | **SIMMR (Normalized Mean)** |
|---|---|---|
| **Sewage** | ~ 8 – 27 % | ~ 19.2% |
| **Rainfall** | ~ 6 – 18 % | ~ 13.2 % |
| **Fertilization** | ~ 16 – 57 % (Fertilizer + Manure) | ~ 40.1 % |
| **Soil** | ~ 12 – 38 % | ~ 27.5 % |

## 4.4 Potential for differentiation of sewage- and manure- based nitrate inputs using potassium concentrations

During the sampling campaign, beside the isotope values, other water quality parameters were also determined, one of which is the potassium concentration (Table 4.3). Projecting the location of the sampling sites along the Fuhse River, and taking into consideration the results from the previous section together with the potassium concentrations, there seems to be a tendency as described followings. The points locate upstream of the wastewater treatment plants such as Floethe, Heerte, Kraehenriede oh KA (upstream of the WWTP) and Reppner, which can be considered having no impacts from WWTPs, have potassium concentrations ranged from 3.8 to 5.2 mg K/l. These values are relatively low when compared with potassium concentrations at other locations. On the contrary, the points right downstream of the WWTP (e.g.: Kraehenriede uh KA), or close to the WWTP (e.g.: Eltze and Aligse), which are supposed to be much influenced by the wastewater, have quite high values of potassium concentrations (36, 19.7, 19.8 mg K/l respectively).

Sewage from WWTPs is considered an important source of potassium for receiving rivers as potassium is not eliminated in the effluents. Noedler et al. (2011) has investigated and observed a good correlation of micro-contaminants from WWTPs and potassium in the Leine River, Germany. This result poses a possibility that potassium can be used as an indicator of wastewater inputs. In addition, in another study in Poland, potassium levels in river waters within agricultural areas were found out to be significantly lower than those under the influence of sewage (Skowron et al., 2018).

*Table 4.3: Measured potassium concentrations at sampling locations of the sampling campaign*

| **Sample ID** | **Location** | **K (mg/l)** |
|---|---|---|
| F01 | Flöthe Quelle | **3.7** |
| F02 | Heerte | **5.1** |
| F03 | Krähenriede (oh KA) | **3.8** |
| F04 | Krähenriede (uh KA) | *36.0* |
| F05 | Reppner | **5.2** |
| F06 | Broistedt | 11.1 |
| F07 | Fuhse in der Nähe von Kl. Ilsede | 11.2 |
| F09 | Pisserbach | 11.3 |
| F10 | Fuhse beim Mittellandkanal stromaufwärts | 9.3 |
| F11 | Fuhse beim Mittellandkanal stromabwärts | 9.4 |
| F12 | Fuhse bei Peine | 9.5 |
| F13 | Eixe | 11.1 |
| F14 | Eltze | *19.7* |
| F15 | Prangenhohl | 10.3 |
| F16 | Erse (Fuhse i. d. N.) | 13.7 |
| F17 | Fuhse (Erse i. d. N.) | 10.1 |
| F18 | Wathlingen | 11.3 |
| F19 | Aue | 10.7 |
| F20 | Fuhsekreuz | 11.0 |
| F21 | Fuhse Mündung | 10.7 |
| F22 | Fuhsekanal Mündung | 11.1 |
| F23 | Aligse Burgdorfer Aue | *19.8* |

*Relatively low values are bold, while relatively high values are italic

Based on the findings from the literatures and this study, a hypothesis is made that the potassium concentration in the river water can be an indicator of the contaminant sources. To be more specific, a high value of potassium may indicate a discharge of sewage into the river, while a low potassium value may be due to the occurrence of manure into the water. However, this prediction should only be given when taking into consideration other factors, such as landuse information or stable isotopes. Since this is just a case study, the proposed approach/ hypothesis should be verified with other catchments to see if it might also be applied generally for the identification of sources of nitrate in waters.

## 4.5 Conclusions

This study applied a dual-isotope methodology for identifying sources influencing the nitrate concentrations in the Fuhse River. The stable nitrogen d15N and oxygen isotopes d18O of nitrate indicated soil nitrogen, manure and sewage as the predominant nitrate sources in this river water, which leads to the nitrate of the river exceeding natural threshold concentrations. After that, the isotope mixing model SIMMR was applied to partition the proportion of potential nitrate inputs entering the Fuhse.

The results of the study also triggers a promising compatibility and feasibility to integrate the stable isotope approach with an ecohydrological model. The integration is highly recommended for the future research, so as to obtain the strong points of both methods. Stable isotope approach, without calibration parameters, provides relatively precise estimates of the source components' proportions. However, this method would be of much time- and cost-consumption when time series data are in need. On the contrary, modelling approach, once calibrated and validated, would be able to provide long-term data and even predictions under given scenarios. Nonetheless, this method also has disadvantages, e.g. various input requirements and calibration uncertainties. Therefore, the compilation of stable isotopes and hydrological modelling approaches would provide a reliable method not only to identify and quantify the nitrate sources, but also to simulate and predict the transport of nitrate within a catchment.

In addition, the study shows a potential approach of using potassium in combination with landuse and other analyses in order to differentiate the wastewater- and manure-based nitrate sources. However, this is still a hypothesis, which requires additional analyses and case studies to have it testified and to detect its limitations. If this approach can be validated and applied, it may contribute a simple yet effective way to further the source identification of nitrate diffused to waters.

All in all, this study proposed a feasibility of an approach that uses a combination of techniques, including dual-isotope analysis, isotope mixing model and hydrological model to identify sources of nitrate and estimate fractions of those inputs along a river system. The results of the study shall contribute to improve agricultural management practices and sewage disposal programs, so as to sustain water quality in the catchment. Since this is only a case study, further studies should be done at different sites (other river catchments), or different scales (field, regional, continental) for a more general view. Moreover, the recommendation of approach incorporation is made based on investigation of riverine nitrate data with specific tools (SIMMR and SWAT); nevertheless, it could also be applied for groundwater nitrate with different models.

# *Chapter 5*

# A constrained multi-objective calibration of nitrate loads with incorporation of nitrogen isotopic apportionment components

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## 5.1 Introduction

Ecohydrological models have been commonly used in environmental and hydrological research for the investigation of the hydrology and water quality (Santhi et al., 2001; Cerro et al., 2014). These models enable a greater understanding of hydrological processes occurring within the catchment. In addition, they also provide knowledge on how the hydrological processes would impact the nutrient loads in the river. It is recommended to take into consideration the environmental conditions during the calibration step of the model. In order to have the model be plausible and robust, various objective functions should be concerned. To meet that demand, there is a so-called multi-objective calibration, in which a variety types of objective functions can be applied for improving the simulation of nitrate.

Soil and Water Assessment Tool (SWAT) is a time-continuous, semi-distributed, eco-hydrological model (Arnold et al., 1998). Main focuses of the SWAT model are consisted of hydrology and agricultural management (Neitsch et al., 2011; Daniel et al., 2011). The SWAT model has been widely used for the simulation of flows and nutrients in various studies (Laurent & Ruelland, 2011; Liu et al., 2013; Cerro et al. 2014; Epelde et al., 2015; Rajib et al., 2018).

Nitrate nitrogen is usually calibrated in regard of fitting the overall dynamics. However, the components of nitrogen inputs have not been considered. This aspect should be paid attention, when a research focuses on investigating the nitrate loads of the catchment. The ability of determining how each nitrogen source would contribute to the final riverine nitrate is of much importance. This would in turn enable the water use planning and water quality management measures to be developed.

In this study, an innovation approach was to implement the isotopic components into the calibration of nitrate loads simulated by the SWAT model. As the apportionment of nitrogen inputs were known from the isotope analysis, these values played as a constraint during the calibration period of nitrate loads in the SWAT model. The results were expected to not only meeting the demand of fitting the dynamics in the nitrograph, but also reflecting the pathway of the major nitrogen sources in the catchment or their proportions in the riverine nitrate loads.

## 5.2 Methods and materials

A general overview of the new approach model calibration method for nitrate loads is provided step by step in Figures 5.1 a & b. The steps will be explained in the following parts. In step 1, model simulations were carried out with SWAT to provide discharge and nitrate load time series. Step 2 was the initial calibration of flow discharge. Step 3 focused on the calibration of nitrate loads. This was the core point of this study where the isotopic component results were incorporated into the calibration procedure of nitrate loads. Separate nitrate loads were calculated using four different model scenarios, which corresponded with four potential sources of nitrogen.

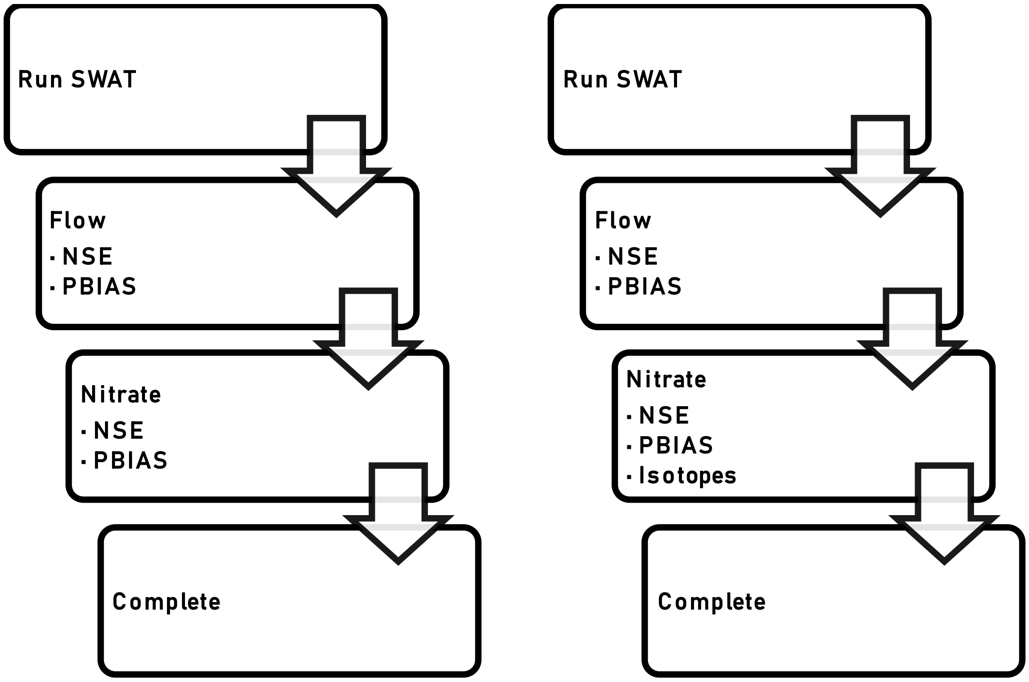

*Figure 5.1a: Overview of new calibration approach (right) in comparison with regular approach (left)*

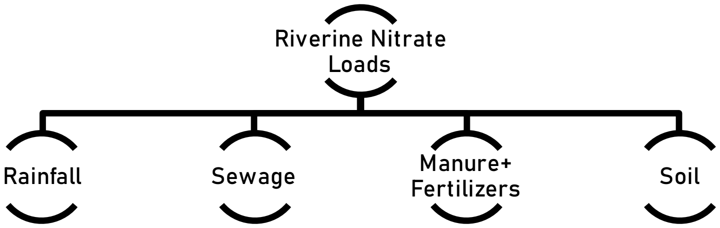

*Figure 5.1b: Four scenarios of the new calibration approach*

In this step 3, the objective functions including the NSE and PBIAS, as well as the comparison of N-components were estimated. All these performance efficiency values were calculated for each of the model simulation. Finally, step 4 refers to the selection of the best model simulation in a multi-objective calibration for flow and nitrate loads.

### 5.2.1 SWAT model

The Soil and Water Assessment Tool (SWAT) is a time-continuous, semi-distributed, eco-hydrological model (Arnold et al., 1998). SWAT is regarded as a compilation of several models specifying in different processes, for instance, rainfall runoff model (CREAMS), water quality model (QUAL2E), and crop growth model (EPIC). This enables SWAT to model the dynamics of flows and nutrients, making it a useful tool for studies on both water quantity and quality (Borah & Bera, 2003; Gassman et al., 2007; Gassman et al., 2014; Abbaspour et al., 2007; Abbaspour et al., 2015). All of those base models have been developed with focus on agriculture. Therefore, SWAT is expected to be an appropriate tool and was chosen for simulating the flows and nitrate loadings in an agricultural catchment like the Upper Fuhse River Catchment.

Main focuses of the SWAT model are consisted of hydrology and agricultural management (Neitsch et al., 2011; Daniel et al., 2011). The SWAT model has been widely used for the simulation of flows and nutrients in long-term resolution in various studies (Ferrant et al., 2013; Boithias et al., 2014; Abbaspour et al., 2015; Swain and Patra, 2017; Odusanya et al., 2019). The SWAT model divides the study watershed into subbasins, and further subdivides each subbasin into hydrologic response units (HRUs). These HRUs consist of unique combination of landuse, soil type and slope (Arnold et al., 2012). Beside topography, land cover, soil properties, SWAT requires other specific climate data including precipitation, temperature, radiation, wind speed, and humidity (Neitsch et al., 2011).

### 5.2.2 SWAT simulations

For the multi-objective model calibration approach, model simulations were carried out with the SWAT model. The procedure for developing a SWAT model include: watershed delineation, HRU definition, and detail editing. The details in the step of editing are specific land management operations such as timing of planting or tilling for crops, irrigation and fertilization, etc.

For daily stream discharges, the calibration period was 2008-2014 and the validation period 2015-2017. Similarly, for monthly nitrate loads, the calibration period was also 2008-2014 and the validation period 2015-2017.

The parameters which were shown in Table 1 were utilized for this calibration procedure. They were selected based on experiences. The detailed description for these parameters can be found in Neitsch et al. (2011).

*Table 5.1: Parameters used for the calibration procedure*

| **Parameter** | **Description** | **Value** |
|---|---|---|
| CN2* | Curve number for moisture condition II | 0.8 |
| SURLAG | Surface runoff lag coefficient | 0.1 |
| ALPHA_BF | Base flow alpha factor | 0.3 |
| GW_DELAY | Flow delay time for aquifer recharge | 300 |
| GWQMN | Flow threshold depth of water in shallow aquifer | 850 |
| REVAPMN | Threshold depth of water in the shallow aquifer | 780 |
| GW_REVAP | Groundwater re-evaporation coefficient | 0.1 |
| SOL_AWC* | Soil available water capacity | 1.25 |
| EPCO | Soil evaporation compensation factor | 1.0 |
| ESCO | Plant uptake compensation factor | 0.95 |
| CDN | Denitrification exponential rate coefficient | 0.01 |
| CMN | Rate factor for humus mineralization of active organic nitrogen | 0.001 |
| N_UPDIS | Nitrogen uptake distribution parameter | 10 |
| NPERCO | Nitrogen percolation coefficient | 0.5 |

*CN2 and SOL_AWC have relative changes, other parameters have absolute changes

### 5.2.3 Combined multi-objective calibration with nitrogen isotopic apportionment components

The multi-objective model calibration involved initially the apportionment of nitrogen components. This was given in the previous Chapter 4 as the results of the isotopic mixing model. For a specific gauging station, there were estimated proportions of major nitrogen inputs which include nitrogen from rainfall, soil, waste water, manure and fertilizers. Proportions of nitrogen originating from manure and fertilizer were combined, in order to be corresponding to the fertilization amount in the SWAT model.

The nitrogen isotopic apportionment components were applied for the model calibration with the aim not only to fit the dynamics but also to represent the pathways of nitrate loads. This concept, as far as the authors know, is the first time used in model calibration to simulate the nitrate loads.

As shown in the Figure above, there were four scenarios which were developed to calculate the contribution of each nitrogen input, i.e., nitrogen from rainfall, soil, waste water, and fertilization. Each model simulation would run all of these four scenarios. Thus, after each simulation, there would be a value set of nitrogen components calculated from SWAT, which were then compared with the value set from isotope mixing model SIMMR when considering the objective functions in the next step.

The objective functions, which were NSE, PBIAS, and N-component-comparison, were estimated model simulations seeking the best run. The evaluation of performance efficiency can be seen from the following Table. In the meanwhile, the optimal target of the N-component-comparison is to be as close as the SIMMR results. The best model simulation for nitrate loads was chosen, based on a combination of these three objective functions.

There are several criteria and statistic approaches to evaluate the performance of the model (Moriasi et al., 2007). Regarding this study, beside the N-component-comparison using the isotope results, the Nash-Sutcliffe coefficient (NSE) and percent bias (PBIAS) were chosen as the other two main objective functions for the procedure of calibration and validation. The equations below were implemented for the calculation of the performance efficiency:

$$NSE = 1 - \frac{\sum_i (Qo - Qs)_i^2}{\sum_i (Qo, i - Qo)^2}$$

$$PBIAS = 100 * \frac{\sum_{i-1}^{n} (Qo - Qs)_i}{\sum_{i=1}^{n} Qo, i}$$

In which

*NSE* = Nash-Sutcliffe coefficient
*PBIAS* = percent bias
*Q* = variable
*o* = observed variable
*s* = simulated variable
*i* = the $i^{th}$ value

Overall, the performance of the model is commonly ranked from unsatisfactory to very good (Table 5.2). For flow discharge, the optimal NSE value is 0.5, while this optimum is lower for nitrate loading with NSE aimed to be 0.35. Similarly, the optimal *PBIAS* percent for stream flow is 15%, whereas the percent bias for nitrate load can be up to 40%.

*Table 5.2: General performance efficiency for statistical methods (Adapted from Moriasi et al., 2007)*

| **Performance** | **NSE** | | **PBIAS** | |
|---|---|---|---|---|
| | **(Streamflow)** | **($NO_3$-N)** | **(Streamflow)** | **($NO_3$-N)** |
| Very good | $\text{NSE} > 0.8$ | $\text{NSE} > 0.65$ | $\text{PBIAS} < \pm 10$ | $\text{PBIAS} < \pm 25$ |
| Good | $0.7 < \text{NSE} < 0.8$ | $0.5 < \text{NSE} < 0.65$ | $\pm 10 \leq \text{PBIAS} < \pm 15$ | $\pm 25 \leq \text{PBIAS} < \pm 40$ |
| Satisfactory | $0.5 < \text{NSE} < 0.7$ | $0.35 < \text{NSE} < 0.5$ | $\pm 15 \leq \text{PBIAS} < \pm 25$ | $\pm 40 \leq \text{PBIAS} < \pm 70$ |
| Unsatisfactory | $\text{NSE} < 0.5$ | $\text{NSE} < 0.35$ | $\text{PBIAS} \geq \pm 25$ | $\text{PBIAS} \geq \pm 70$ |

The same parameter set, which was found in the calibration procedure, was applied in the validation period. In other words, the model performance during the validation was also assessed, using the efficiency criteria which were implemented in the calibration procedure. This step helps to evaluate if the model would provide consistent results when separate time series data were used.

## 5.3 Study area and model input data

To test the multi-objective calibration approach, the Upper Fuhse River Catchment was selected as the study site. This study catchment is located in Lower Saxony in the Northern of Germany. The Fuhse River has a total length of 95 km, flowing to the North, ending in the Aller River which later drains to the North Sea. The catchment is an intensive agricultural production region, with more than 70% of its area is arable land. Thus, nitrate is paid attention, regarding the water quality in the catchment. The simulation model in this study covered the area of approximately 181 km$^2$ from the source of the Fuhse River until Broistedt gauging station (Figure 5.2). The details about the location as well as further characteristics of the catchment can be found in the Chapter 2, part *Study Site* of this dissertation.

SWAT requires four general inputs: digital elevation model, soil types, landuse types, and climatic and meteorological data. The climatic data were downloaded from the German Weather Services (DWD) with the stations' geographic coordinates. Aside from the climate datasets, the inputs are in the form of digital maps and geodatabases.

The Digital Elevation Model (DEM) provided the information of the surface features. The DEM had a raster format with the grid size of 25 x 25. The raster map was accompanied by attribute tables of topography characteristics.

Soil data were developed from the map BÜK 200 of the BGR. The soil map contained irregular polygons whose attribute tables contained the soil and their layers' physical characteristics. Examples of these characteristics were number of soil layers, layer depths, soil texture, soil available water capacity, soil organic carbon content, and hydraulic conductivity, etc. Those soil data attributes were then incorporated into SWAT, via a look-up table, as one main input component. The main soil types in the catchment may correspond either to soils whose texture are mainly from loess or loam overlying several groups of rocks. The presence of these soils indicates that there are soils with an increase of clay amount in the subsoil. These soils may indicate moderate to high fertility in the soil.

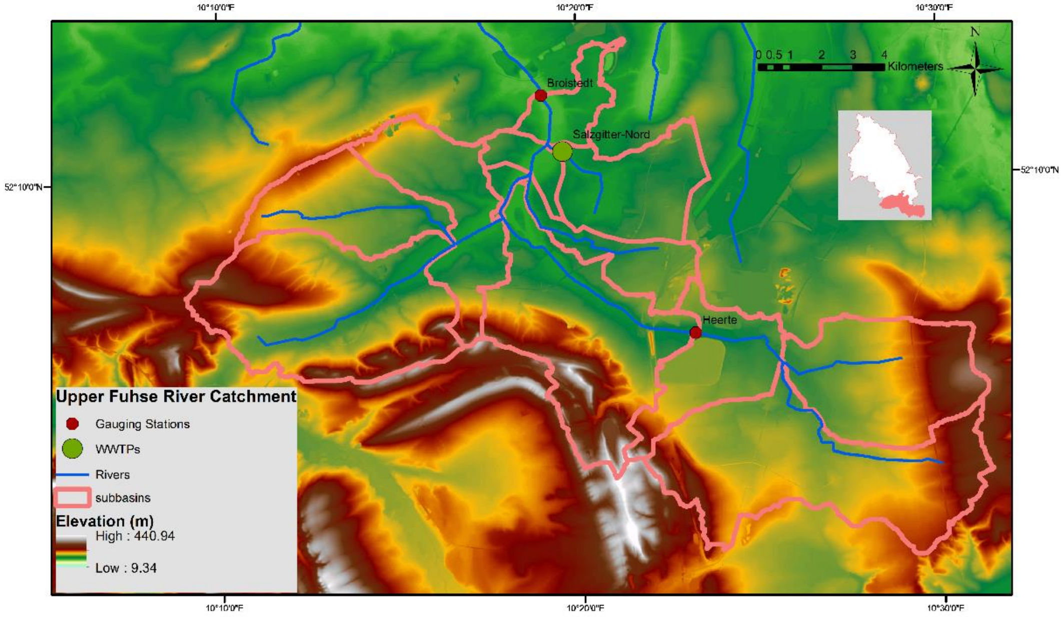

*Figure 5.2: Location of the Upper Fuhse River Catchment of the study. The model outlet is selected at Broistedt gauging station*

Beside DEM and soil data, the other component of the HRU definition was the landuse data. These data might give information on the urban areas, agricultural areas, and other purpose lands. In this study, the CORINE Land Cover map was used for setting up the SWAT model. Landuse change was ignored due to the lack of data availability. A look-up table, which was developed similarly as the one for soil data, was required in order to transform the landuse classes in the data source to a SWAT equivalent.

SWAT requires the following daily climate inputs for the simulation: precipitation, air temperature, relative humidity, wind speed, and solar radiation. Climatic data were obtained from the German Weather Services (DWD) which provides public online database. Interpolation using inverse distance weighting was applied to fill in missing records as well as to provide data for each subbasin of the catchment. This process was implemented for all climate inputs. The selected stations included the stations within the catchment and the near surrounding ones.

SWAT incorporated the ArcHydro extension for watershed delineation, which used DEM as the input data. In addition, a point source was added to the watershed for this study, representing the Salzgitter-Nord WWTP. In order to obtain the nitrate concentrations discharged from this source to the streams, it was necessary to consult the biannual reports available on the NLWKN website. Finally, the model configuration for this study contained 12 subbasins.

Each subbasin consisted of multiple HRUs, which were different combinations of landuse, soil type, and slope. Because there were many types of landuses and soils in the catchment, there were also a great number of HRUs in the catchment. However, out of these HRUs, there were several ones with small proportions of areas, which made their contribution to the model performance also very small, and thus could be ignored. In the end, after the HRU definition was completed, there were 219 HRUs in this studied catchment (Appendix – Figure A.3).

The next step for the SWAT model development was editing the format of the weather databases to a text form which can be used later by the SWAT executables. A database was produced within the SWAT model, in which parameters or management operations were adjusted. The management operations, which were made, were mainly listed as agricultural activities, for instance, planting, fertilizing, tilling, and harvest, etc.

In details, the following order of management was employed for all agricultural HRUs: tillage, planting, fertilization, irrigation, and harvesting. From which, auto-irrigation was chosen while developing the model. This added irrigation water whenever a crop undergoes water stress. Nitrogen stress and fertilizer application were concerned with crops, which were calculated from the integrated database in SWAT. In addition, the timing of all of these management practices was also set up with regard of some general base growing schedules. In the meanwhile, the default management operations of SWAT were applied for the other HRUs, including forest and urban areas. In fact, there were lawn and bushes in urban areas, which also require fertilization and irrigation. However, since this area is relatively small compared with the entire catchment, those operations could be ignored. After determining and editing the management operations, the simulation period was set and run.

The SWAT model was used to estimate the major processes controlling the nutrient losses. Firstly, all potential nitrate sources were removed, creating a baseline model. Then four sub-models were generated with four different scenarios. In each scenario, only one of the nitrogen sources, amongst rainfall, soil, fertilizer, and sewage, acted as the input. Then the average monthly nitrate loads were calculated. Therefore, the nitrate load from each source with their contribution to the total nitrate in the river can be estimated. The obtained estimations from SWAT model were compared with the fractions from SIMMR model (Figure 4.5 & Table 4.2). The calibration was made manually with the try-and-error approach, until the best option case was obtained.

SWAT was said to be a highly parameterized model with a plenty number of parameters and modules.  Calibration was the procedure for adjusting the model parameters to the values which provide a simulation that best fit the observation datasets. The calibration algorithm employed was one-at-a-time option (OAT) and executed manually with regard of the performance efficiency criteria. The calibration procedure first operated on a calibration period. Then the model was validated using the same parameters with a validation period. Table 5.1 shows the parameters used in this study.

## 5.4 Results

### 5.4.1 Simulation of flow discharges

During the calibration procedure, the calibration parameter set was optimized, aiming at the possible highest NSE, and then the PBIAS. During the validation period, the parameter set was fixed, in other word no further optimization was made, and NSE and PBIAS were computed once again. The calibration period NSE was 0.68, and that for the validation period was 0.67. The PBIAS were -5.88 and 11.73 for calibration and validation periods respectively. Generally, the model under predicted the discharge by approximately 6% during the calibration period. However, the validation PBIAS had the different trend: nearly 12% over prediction.

Figures 5.3 & 5.4 show the results for the calibration and validation during the years between 2008 and 2017 for the stream discharge as a time series with the observations. Overall, the model had the tendency to under predict the peak observations. This under prediction trend can be clearly seen with the floods in year 2013 and year 2017. In general, the validation performed almost similarly to the calibration. This trend could be seen numerically in efficiency statistics and graphically on the time series plots.

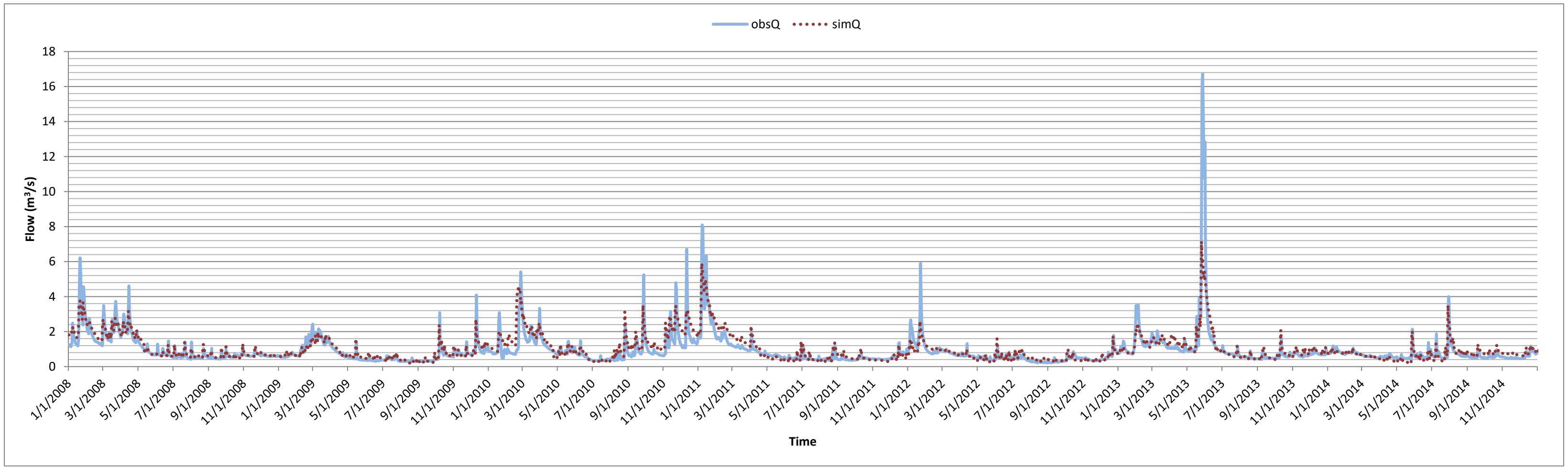

*Figure 5.3: Simulated and observed flows of the Fuhse River at Broistedt gauge at daily time steps (calibration period from 2008 to 2014)*

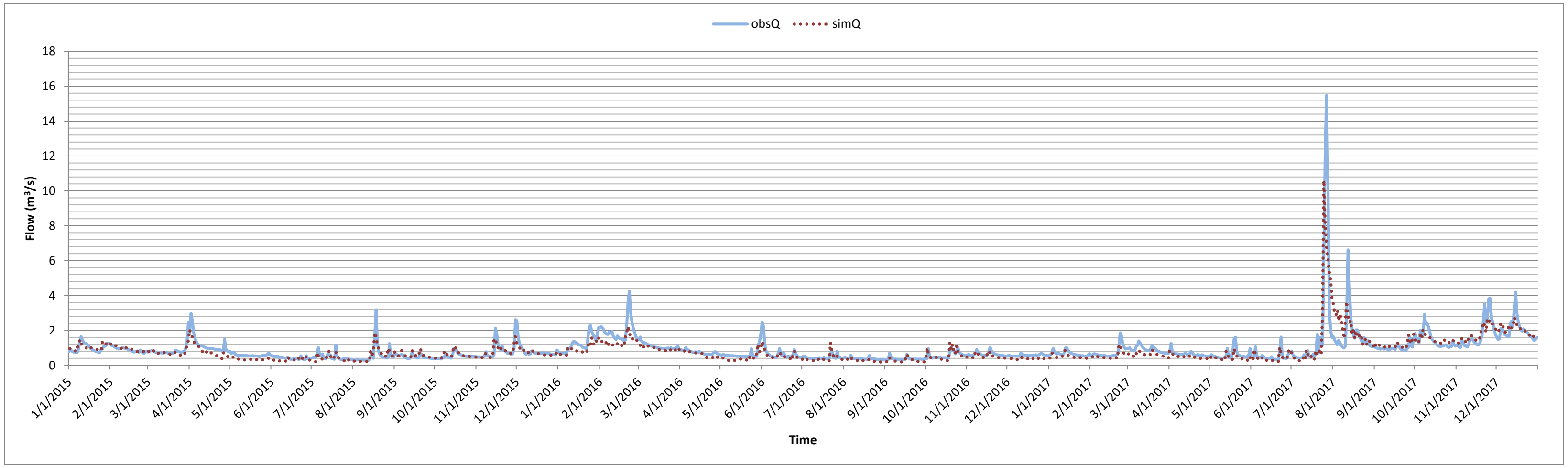

*Figure 5.4: Simulated and observed flows of the Fuhse River at Broistedt gauge at daily time steps (validation period from 2015 to 2017)*

### 5.4.2 Simulations of nitrate loads with the incorporation of nitrogen isotopic apportionment components

The calibration was successful in finding a simulation for nitrate loads that met the efficiency criteria. The NSEs for nitrate loads were 0.77 and 0.75 for calibration and validation respectively, which can be regarded as very good performance according to the efficiency ratings stated above in Table 5.2. Overall, the model tended to under predict the nitrate loads for calibration period (PBIAS = -6.34 %) and slightly over predicted those values for the validation period (PBIAS = 3.07 %). The values of nitrogen components calculated by SWAT were relatively close to those estimated by SIMMR.

Nitrate load is correlated with discharge, as the former is the product result of the latter and nitrate concentration. However, the flow has a higher variance compared with that of nitrate. Furthermore, when the model failed to simulated the peak flows in 2013 and 2017, an under prediction in nitrate loads were also seen in this two years. Figures 5.5 & 5.6 show the monthly nitrate loads during calibration and validation periods. These figures illustrate the performance calculations made above. In the meanwhile, Figures 5.7 & 5.8 show the nitrate loading in terms of daily basis, in order to provide a more detailed sight into the model performance.

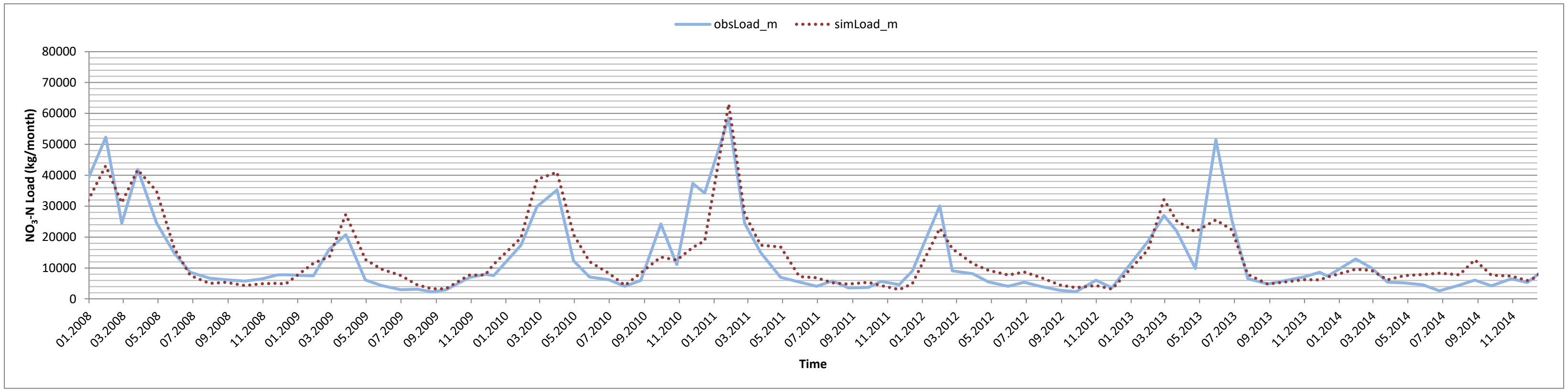

*Figure 5.5: Simulated and observed nitrate loads of the Fuhse River catchment at Broistedt gauge at monthly time steps (calibration period from 2008 to 2014)*

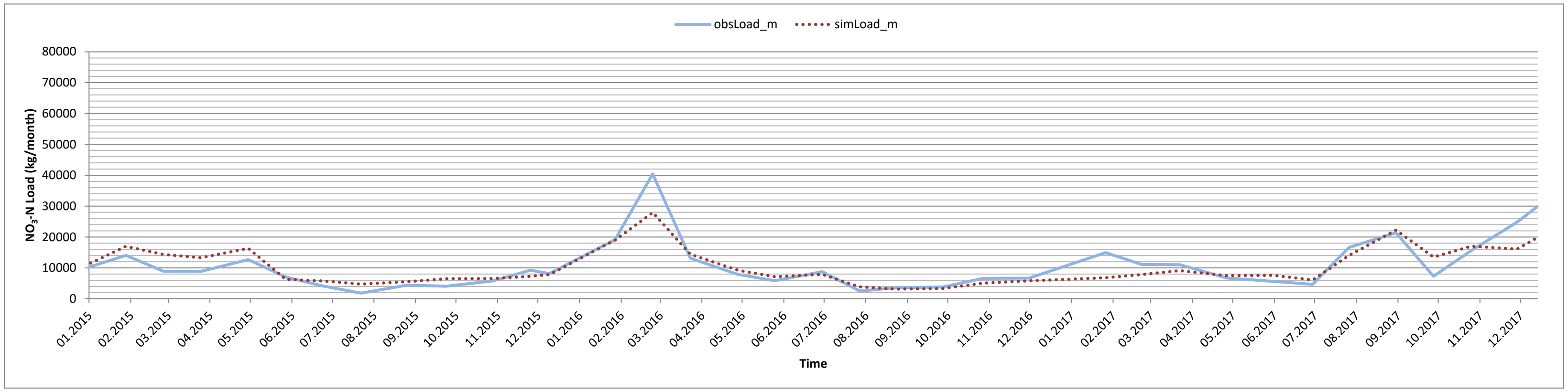

*Figure 5.6: Simulated and observed nitrate loads of the Fuhse River catchment at Broistedt gauge at monthly time steps (validation period from 2015 to 2017)*

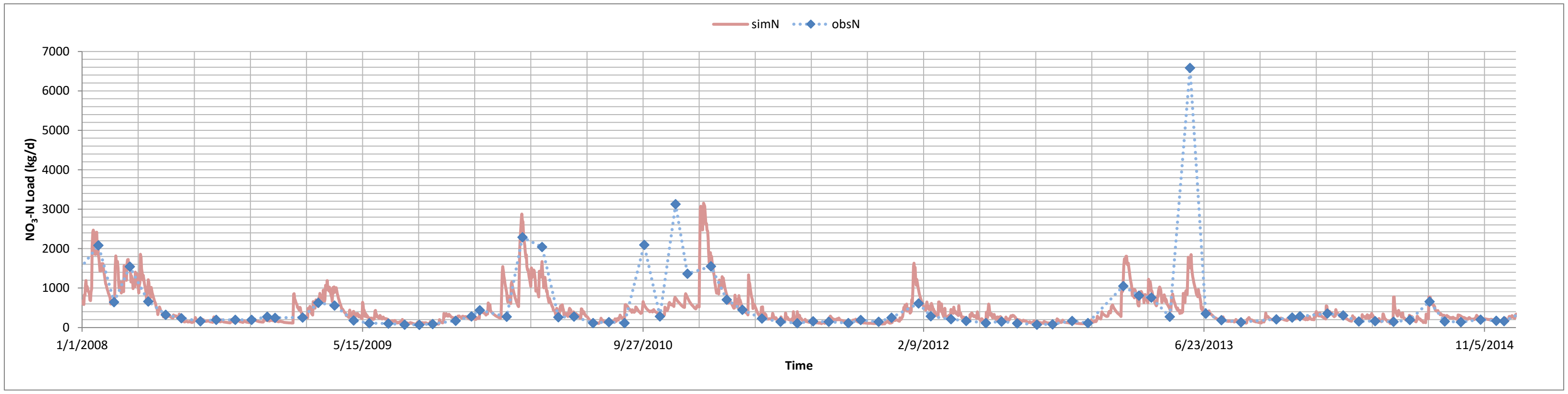

*Figure 5.7: Simulated and observed nitrate loads of the Fuhse River catchment at Broistedt gauge on sampling days (calibration period from 2008 to 2014)*

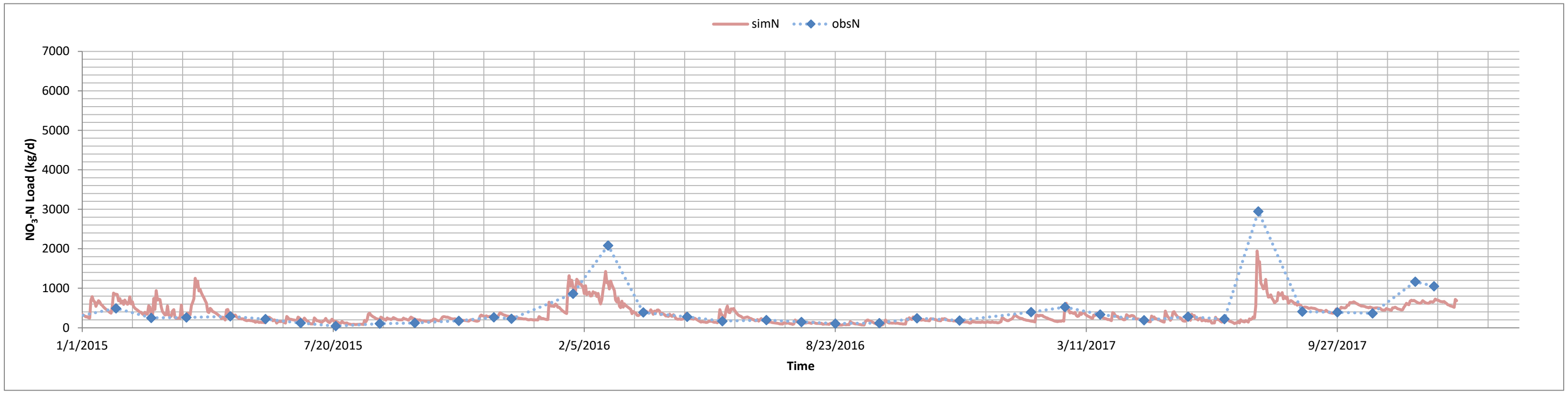

*Figure 5.8: Simulated and observed nitrate loads of the Fuhse River catchment at Broistedt gauge on sampling days (validation period from 2015 to 2017)*

Overall, the SWAT model successfully simulated daily stream discharge and monthly nitrate loads at the Upper Fuhse River Catchment for the period from 2008 to 2017. The model could depict quite well the dynamics of discharge as well as nitrate loads, except for some missed peaks. For daily stream discharge, the NSE statistic for Broistedt station met the value of NSE=0.68 and 0.67 during calibration and validation periods, respectively. Monthly nitrate loads showed good NSE values for both calibration and validation periods (NSE=0.77 & 0.75, respectively) at the Broistedt outlet. The validation period showed similar statistics as the calibration. This behavior could be attributed to either input data being accurate for those simulating years or the selected calibration parameter set was relatively good.

## 5.5 Usage of stable isotopes as a constraint for model calibration: Comparison with a regular calibration run

In this study, the nitrate source fractions in the previous *Chapter 4: Stable Isotopes* was used as a constraint during the calibration process. In other words, the proportions of nitrate from all sources, including atmosphere, soil, sewage, fertilizer and manure, were assumed to be true and used as the references for those corresponding components in the SWAT model.

In order to cross check the calibration results using the new approach, the model was also calibrated for nitrate loads using the regular approach which focused on only NSE and PBIAS values. The calibration parameter sets of these two models were kept the same for flow discharges, but there were some changes for nitrate loads (Table 5.3). Parameters concerning the mineralization of the active organic nutrients or N in this study (CMN), nitrogen uptake (N_UPDIS), nitrate percolation (NPERCO) played relatively important impacts on the results.

The performance efficiency values of the regularly calibrated model run were found in the Table 5.4. As can be seen from this table, overall, the results of both approaches were quite similar regarding the NSE values for the calibration period. However, regarding the validation period, the new approach provided better NSE as well as PBIAS values than the traditional approach. This can indicate an improvement in the robustness of the model. In other words, even though there were only N isotope data for one individual day, the results seemed promising, considering the enhancement of the SWAT model.

*Table 5.3: Comparison of parameters used for regular approach and new approach calibration procedures*

| **Parameter** | **Regular approach** | **New approach** |
|---|---|---|
| CN2* | 0.8 | 0.8 |
| SURLAG | 0.1 | 0.1 |
| ALPHA_BF | 0.3 | 0.3 |
| GW_DELAY | 300 | 300 |
| GWQMN | 850 | 850 |
| REVAPMN | 780 | 780 |
| GW_REVAP | 0.1 | 0.1 |
| SOL_AWC* | 1.25 | 1.25 |
| EPCO | 0.9 | 1.0 |
| ESCO | 0.95 | 0.95 |
| CDN | 0.05 | 0.01 |
| CMN | 0.002 | 0.001 |
| N_UPDIS | 12 | 10 |
| NPERCO | 0.8 | 0.5 |

*relative changes

*Table 5.4: Comparison of results for nitrate loads using regular approach and new approach calibration procedures*

| **Performance Efficiency** | **Regular approach** | **New approach** |
|---|---|---|
| NSE | Calibration: 0.75<br>Validation: 0.63 | Calibration: 0.77<br>Validation: 0.75 |
| PBIAS | Calibration: -2.74<br>Validation: 10.85 | Calibration: -6.34<br>Validation: 3.07 |

*Table 5.5: Comparison of results from SWAT models and SIMMR model*

| **Sources** | **SWAT (Regular calibration approach)** | **SWAT (New calibration approach)** | **SIMMR (Range)** | **SIMMR (Normalized Mean)** |
|---|---|---|---|---|
| Sewage | ~ 20 % | ~ 19 % | ~ 8 – 27 % | ~ 19.2% |
| Rainfall | ~ 18 % | ~ 13 % | ~ 6 – 18 % | ~ 13.2 % |
| Fertilization | ~ 30 % | ~ 43% | ~ 16 – 57 % (Fertilizer + Manure) | ~ 40.1 % |
| Soil | ~ 32 % | ~ 25% | ~ 12 – 38 % | ~ 27.5 % |

Regarding the nitrogen components simulated by the SWAT model. As can be seen from the Table 5.5, both the calibration approaches gave the results within the range resulted from the isotope mixing model SIMMR. However, the new calibration approach yielded a better results, considering the agreement with the normalized mean values. This indicated that the new calibration approach, with the incorporation of the isotopic component data, enabled the SWAT model to better describe the pathways of the nitrogen within the catchment, as well as to better estimate the contribution of each nitrogen input in the nitrate loads of the river. Therefore, the reliability of the model in simulating nitrate loads could be improved.

## 5.6 Conclusion

In this chapter, a SWAT model was set up to simulate the flow discharge and nitrate loads at a river catchment scale. The site of interest was the Upper Fuhse River Catchment, and Broistedt gauging station was chosen as the outlet of the SWAT model. The observed discharges and nitrate concentrations were available from the website of the Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency (NLWKN). In the meanwhile, the precipitation and climate data, such as temperature, humidity, and wind speed, etc., were downloaded from the German Weather Services (DWD). For the study site, the catchment size was determined, based on the digital elevation model DEM with a resolution of 25m. Subsequently, the percentage of main landuse types as well as soil types were calculated using the landuse CORINE and soil BÜK dataset. Salzgitter-Nord, the WWTP in the chosen area, was incorporated into the model as a point source. The SWAT model was setup and was calibrated for stream flow and nitrate load.

A noticeable point of this Chapter 5 is the implementation of stable isotope approach as the constraint to improve the calibration of the ecohydrological SWAT model. Those nitrate source fractions in the previous chapter were used for this purpose. In the previous Chapter, the dual isotope methodology was applied for identifying sources influencing the nitrate concentrations in the Fuhse River. The stable isotopic composition of nitrate indicated that the soil nitrogen, manure and sewage may be the predominant nitrate sources in this river water, which would lead to the nitrate concentrations of the river exceeding the natural thresholds. After that, the isotope mixing model SIMMR was set up and applied to partition the proportion of potential nitrate inputs entering the Fuhse.

It is usually challenging to adequately simulate the pathways of nutrients in the catchment. However, for a research with the focus on water quality, the understanding of the nutrient pathways as well as their proportions in the nutrient loads is of much interest. Thus, an innovation was made in this study, as the results of nitrate source fractions in the previous *Chapter 4: Stable Isotopes* was implemented as the constraint during the calibrating process of the SWAT model.

The SWAT model successfully simulated daily stream discharge and monthly nitrate loads at the Upper Fuhse River Catchment for the period from 2008 to 2017. For daily stream discharge, the NSE statistic for Broistedt station met the value of NSE=0.68 and 0.67 in calibration and validation periods respectively. Nitrate loads met the good NSE for the monthly time step (NSE=0.77 & 0.75 for calibration and validation periods, respectively) at the Broistedt outlet. The validation period showed quite similar statistics, almost nearly equal to those values of the calibration.

Nevertheless, it may be observed that the ability of the model to simulate nitrogen dynamics using loads depends much on the flow simulation. Thus, it perhaps is more appropriate to consider the nitrate concentrations instead of loads, which would require more detailed input data, for example, the exact dates of fertilization or the exact amount of mineral fertilizer and manure applied, etc. Therefore, it is recommended to further enhance the ability of the simulating model to represent the nitrate concentration.

Both mixing model and hydrological model have their advantages and disadvantages. For instance, SWAT requires a great amount of data as well as skills in model setup and calibration. Those factors may impact the accuracy of the model a lot. Whereas, the mixing model can be easily applied in any river catchment, provided that water samples for isotope analysis are available. However, SWAT may provide various outputs from flows to nutrients, which can in turn become inputs for other further research. The SWAT, in addition, is able to offer predictions of flow and nitrate loads in form of time series results under different scenarios. In the meanwhile, the SIMMR can only provide the results of past and present time.

From this study, it is recommended to combine those two models in other future studies, so that advantages of both models can be taken for the investigation of nitrate fates. Indeed, there were uncertainties of the combined model, due to the fact that the N could only be removed nearly almost all out of each N component in the SWAT model, the calculations then became approximates. However, this problem did not changed much the final proportions and thus could be ignored in this study. The expectation is that the results of mixing model may enable the increase in reliability and the robustness of the hydrological model similarly as shown in the Fuhse River catchment model. The results of the study shall contribute to improve agricultural management practices and sewage disposal programs, so as to sustain water quality in the catchment.

# *Chapter 6*

# Synopsis

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Surface water is a key component in the ecosystem as it provides the habitat to various species of flora and fauna. River, a major type of surface water, plays an important role in human daily practices, for instance, sources for irrigation and water supply, as well as sinks to overflows and wastewater. Therefore, it is highly essential to pay good attention to the water quality of the rivers.

A mixed-method approach, combining the experimental works (sampling campaigns and labs), statistical analysis (multivariate tool PCA, dual stable isotope tool), and modelling (isotope mixing model SIMMR, ecohydrological model SWAT) is proven to be an effective approach to investigate the fate of nitrogen, especially nitrate, at the river catchment level. In this dissertation, the Fuhse River catchment was chosen as the study site for investigating the status and dynamics of the riverine nitrate.

The results from hydrochemical statistical analyses showed that the distribution of major ions in the water is as follows: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $Cl^{-} > HCO3^{-} > SO4^{2-}$. Water of the Fuhse River is of evolved type with mix abundances of ionic concentrations. Using Piper's graph, water has been classified into the main hydrochemical group of Ca-Cl-SO4, as it chemically characterizes the water which is affected by anthropogenic activities. Nitrate concentration is generally high during winter and is highest during significant runoff event. In addition, nitrate concentration tends to be highly correlated with discharge since year 1998 until now.

Principal component analysis (PCA) is known as a multivariate statistical tool used to identify the important components which explain most of the variances of the original system. In general, the PCA would generate several linear combinations of the initial parameters. The linear combinations, which are produced by the PCA, represent a type of abstract measurements or factors that are better descriptors for the data-set structure than the original measurements. The PCA in this dissertation indicates that although natural factors controlling the water chemistry of the river, anthropogenic impacts in the form of agricultural activities and wastewater are also influencing the water chemistry. The fact is advocated by the presence of high concentrations of NO3, Cl, and SO4 within the catchment.

The results of the hydrochemical analyses provide a very first description of the water quality status in the catchment. This is of importance since it enables the environmentalists and authorities to determine the current conditions of water bodies as well as to identify the vulnerable spots to pollution risks. Thus, this hydrochemical statistical approach has a role as a prerequisite step for the further in-depth steps of the whole research.

In the next step, this dissertation applied a dual-isotope methodology for identifying sources influencing the nitrate concentrations in the Fuhse River. The stable isotopic composition of nitrate, i.e.: d18O and d15N, indicated the soil nitrogen, manure and sewage as the predominant nitrate sources in this river water, which leads to the nitrate of the river exceeding natural threshold concentrations. This finding was in good agreement with the hydrochemical analyses on the potential sources of nitrate within the catchment.

After that, the isotope mixing model SIMMR was applied to partition the proportion of potential nitrate inputs entering the Fuhse River. In addition, the study shows a potential approach of using potassium in combination with landuse and other analyses in order to differentiate the wastewater- and manure-based nitrate sources. However, this is still a hypothesis, which requires additional analyses and case studies to have it testified and to detect its limitations. If this approach can be validated and applied, it may contribute a simple yet effective way to further the source identification of nitrate diffused to waters.

The results of from the analysis of stable isotopes triggered a promising compatibility and feasibility to integrate the stable isotope tools with an ecohydrological model. The integration is highly recommended for future studies, so that the strong points of both methods could be taken advantage of. Stable isotope approach, without calibration parameters, provides relatively precise estimates of the source components' proportions. However, this method would be of much time- and cost- consumption when time series data are in need. On the contrary, modelling approach, once calibrated and validated, would be able to provide long-term data and even predictions under given scenarios. Nonetheless, this method also has disadvantages, e.g. various input requirements and calibration uncertainties. Therefore, the compilation of stable isotopes and hydrological modelling approaches would provide a reliable method not only to identify and quantify the nitrate sources, but also to simulate and predict the transport of nitrate within a catchment.

In general, ecohydrological models are regarded as an effective tool for the investigation of the hydrology and water quality of river catchments. Out of the several steps of establishing a model, calibration might be considered a very important one, since this step adjusts and makes the model get closer to the realistic condition of the study site. This, furthermore, enables a better performance of the model. There are a variety of objective functions and calibration parameters which should be taken into consideration while calibrating the model, with the aim to properly simulate both the hydrology and water quality of the catchment. This study presents a multi-objective calibration of nitrate loads simulated with the ecohydrological model SWAT. For this purpose, a calibration approach was introduced by incorporating with the nitrogen isotropic apportionment components.

The SWAT model, after the calibration process with proportion constraints of nitrate inputs, successfully simulated daily stream discharge and monthly nitrate loads at the Upper Fuhse River Catchment for the period from 2008 to 2017. For daily stream discharge, the NSE statistic for Broistedt station met the value of NSE=0.68 and 0.67 in calibration and validation periods respectively. Nitrate loads met the good NSE for the monthly time step (NSE=0.77 & 0.75 for calibration and validation periods, respectively) at the Broistedt outlet. The validation period showed quite similar statistics, almost nearly equal to those values of the calibration. This behavior might be accounted from a proper selection of the calibration parameter set.

Moreover, it can be observed from literature reviews, as well as from this study, that the modelling of water quality parameters, which in this case is nitrate, is more complex than hydrological modelling only. Seemingly, more improvements and modifications have been made for hydrological models than for water quality models. Even the performance indicators for evaluation of a hydrological model and a nitrate model have different levels. The possible reason for this issue perhaps is the limitation in input data for ecohydrological models which are usually rare and difficult to find, for instance the daily WWTP effluents, crop data, irrigation and fertilization schedule, etc.

The unavailability of those data may bring about uncertainties for the models, hence, impacting on their precision as well as applicability. Therefore, it is recommended to pay more attention to the input data preparation, in order to further improve the ability of the model to simulate the quality of the water. One possible solution may be paying more attention to monitoring, for example increase the number of stations or increase the sampling frequency, in order to have spatially and temporally high-dimension data.

Nevertheless, it may be observed that the ability of the model to simulate the nitrogen dynamics using loads depends much on the flow simulation. Thus, it perhaps is more appropriate to consider the nitrate concentrations instead of loads, which would require more detailed input data, for example, the exact dates of fertilization or the exact amount of mineral fertilizer and manure applied, etc.

Due to the limitations in the practical input data, for example, agricultural practices, groundwater parameters, or rates biological processes, etc., ecohydrological models are often simplified and set up with lots of information neglected. This actually results in many uncertainties of the models themselves, especially conceptual models. If those relevant data are available, together with proper set up and calibration processes, the modelling tool would become an effective tool in simulating the nutrients, particularly nitrate concentrations. This would contribute to the water quality management and support the nitrate-reduction measures.

In summary, in order to better manage the riverine nitrogen, it is necessary to increase the understanding of what has happened in the past, what is happening, and what might come up in the near future under changing scenarios within the ecosystem of the catchment. To deal with those issues, a mixed-method approach for water quality management might be a useful tool, which may optimize the benefits of each method individually and combine them in an integrated research for the sustainable development of the water resources. Last but not least, in this dissertation, a specific river catchment was selected as a study site to test the new calibration approach. This new approach of calibration was made with an aim to improve the reliability as well as the robustness of an ecohydrological model, in which the results of nitrogen input contributions from the stable isotope analysis would be used as a constraint to calibrate the ecohydrological model. It is, in the end, highly recommended to verify this new approach by applying it into other catchments and at other scales.

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# Appendix

*Figure A.1: Photos from different sampling campaigns for weekly water quality (at Peine gauge) and stable isotopes (at points along the Fuhse River)*

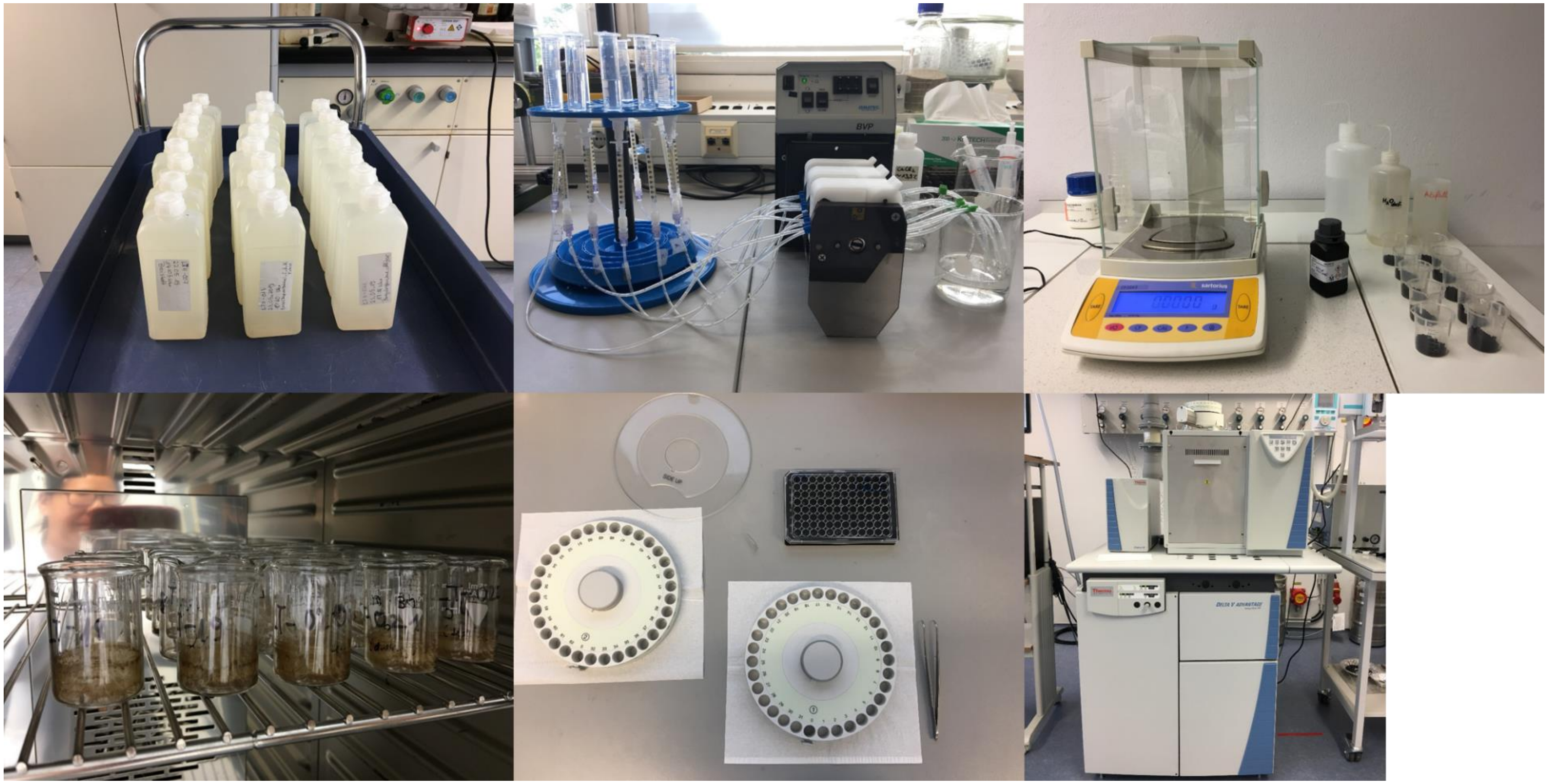

*Figure A.2: Photos from lab analysis for stable isotopic composition of nitrate*

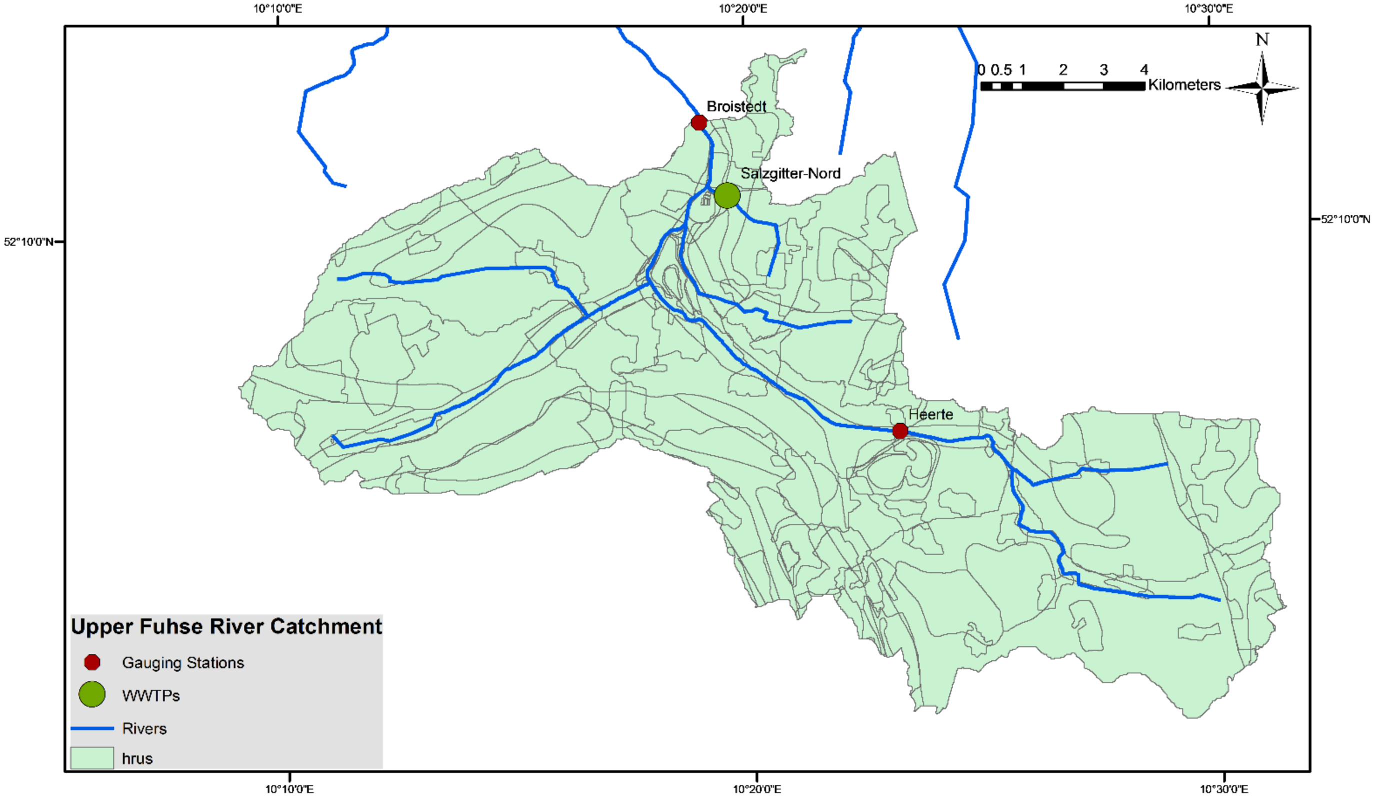

*Figure A.3: HRU definition step from SWAT model for the Upper Fuhse River Catchment*

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