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Master Thesis

THE EFFICIENCY OF IN-STREAM AMMONIUM UPTAKE ALONG A GRADIENT OF AMMONIUM LOADING

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Abstract

Due to increased anthropogenic influences on watercourses and their alterations, the natural functions of many Austrian streams are already strongly affected in manifold ways. Apart from channelization and straightening, one of the main anthropogenic influences is the input of nutrients (especially nitrogen and phosphorous) through agriculture, which in the long term may impair the ecosystem functions. In this thesis the context between background ammonium concentration, season and ammonium uptake/ retention ability of streams was determined within the frame of the project “PowerStreams”.

Consecutive short-term nutrient addition experiments - with NH_4Cl as nutrient and NaCl as conservative tracer - were conducted in spring and summer of the year 2015 at 9 low- order streams located in Lower Austria. This region was chosen because of the presence of different land use intensities and therefore varying ammonium loading. To assess the in-stream NH_4-N demand, nutrient spiraling metrics were calculated from the longitudinal decline in NH_4-N concentration during the experiments. Hydrologic retention and whole-stream metabolism were calculated, hydromorphology was recorded and water and sediment samples were taken and analysed for NH_4-N, NO_3-N and NO_2-N concentration. Biofilm samples were analysed for chlorophyll-a concentration and sediments for microbial abundance. Regression approaches were used to search for statistical relationships between uptake and hydromorphological, biological and chemical parameters. The sampling at two seasons enabled comparisons of nutrient uptake and influencing factors during spring and summer.

A close connection between surrounding land use and ammonium concentration in the water was found, as well as a connection between ammonium load and ammonium uptake performance: mass transfer coefficients significantly decreased with increasing ammonium loading level, while uptake lengths generally increased. At the same time highly loaded streams saturated earlier (regarding relative increase in ammonium concentration), showed higher uptake lengths and faster dropping uptake rates than less loaded ones.

There was no significant difference between uptake parameters in spring and summer. Both, the stream wetted perimeter and the width, were positively correlated with mass transfer coefficient and negatively with uptake length, underlining the importance of streambed heterogeneity for ammonium uptake. No significant correlations could be found for any other hydromorphological parameter or hydrologic retention. Uptake length decreased and mass transfer coefficient increased with increasing community respiration. In spring the uptake rate increased with increasing community respiration, while mass transfer coefficient de- and uptake length increased with increasing gross primary production/ community respiration ratio, indicating higher uptake with increasing microbial abundance. Neither microbial abundances nor chlorophyll-a concentration alone did prove to be a good predictor for ammonium uptake.

In summary, the findings confirm a negative impact of in-stream and sedimentary nitrogen concentration and the lack of channel heterogeneity (mostly resulting from agricultural land use and other anthropogenic influences) on the self-purification ability of the surveyed stream systems. The aim should therefore be to mitigate the effects of land use and the input of nutrients in order to protect the streams and their natural functions.

Zusammenfassung

Die natürlichen Funktionen vieler österreichischer Fließgewässer sind durch wachsende anthropogene Einflüsse sowie bauliche Änderungen an Bächen und Flüssen (z.B. Landwirtschaft, Kanalisierung, Begradigung) bereits auf verschiedene Weisen eingeschränkt. Abgesehen von Begradigung und Kanalisierung der Gewässer, stellt der anthropogene - größtenteils durch landwirtschaftliche Aktivitäten verursachte - Eintrag von Nährstoffen (insbesondere Stickstoff und Phosphor) einen der größten menschlichen Einflüsse dar. Auf lange Sicht kann dieser die Funktionen des Ökosystems negativ beeinflussen.

In dieser Arbeit wurden im Rahmen des Projekts „PowerStreams“ die Auswirkungen unterschiedlicher Ammoniumhintergrundbelastungen, sowie der Jahreszeit, auf die Ammoniumaufnahme- bzw. Retentionsfähigkeit von Fließgewässern untersucht. Im Frühling und Sommer des Jahres 2015 wurden an 9 niederösterreichischen Flüssen jeweils 3 aufeinanderfolgende Kurzzeiteinspeisungen mit NH_4Cl in Kombination mit einem konservativen Tracer (NaCl) durchgeführt. Diese Region wurde aufgrund ihrer verschiedenen Intensitäten in Bezug auf die Landnutzung im Einzugsgebiet - und in Folge auch der unterschiedlichen Ammoniumbelastung - gewählt. Der Ammoniumbedarf im Gewässer wurde auf Basis des „Nutrient Spiraling“-Konzeptes mit seinen zugehörigen Aufnahmeparametern aus der longitudinalen Abnahme der NH_4-N - Konzentration während der Experimente berechnet. Hydrologische Retention und Metabolismus wurden berechnet, hydromorphologische Parameter erfasst und Wasser-, Biofilm- und Sedimentproben genommen und analysiert. Unter Verwendung einer statistischen Regressionsanalyse wurden mögliche Zusammenhänge zwischen der Aufnahme und hydromorphologischen, biologischen sowie chemischen Parametern identifiziert. Die Probennahme über zwei Jahreszeiten hinweg ermöglichte zudem einen Vergleich von Nährstoffaufnahme sowie deren Einflussfaktoren, für Frühling und Sommer.

Zwischen Landnutzungsintensität und Ammoniumkonzentration im Wasser wurde eine positive Korrelation gefunden, ebenso ein Zusammenhang zwischen Ammoniumbelastung und Aufnahme- bzw. Retentionsleistung: Der Massentransferkoeffizient fiel signifikant mit wachsender Gewässerbelastung, die Aufnahmelänge hingegen nahm generell zu. Stark belastete Flüsse zeigten eine schnellere Sättigung (bei niedrigeren relativen Erhöhungen), höhere Aufnahmelängen und schneller fallende Aufnahmeraten als saubere. Zwischen den Aufnahmeparametern bestand kein signifikanter saisonaler Unterschied. Sowohl der benetzte Umfang als auch die Bachbreite waren positiv mit dem Massentransferkoeffizienten, und negativ mit der Aufnahmelänge korreliert (und verdeutlichten somit die Wichtigkeit der Flussbettheterogenität), jedoch mit keinem der anderen hydrologischen Parameter oder der hydrologischen Retention. Die Aufnahmelänge fiel und der Massentransferkoeffizient stieg

signifikant mit steigender Gesamtrespiration. Im Frühling fiel der Massentransferkoeffizient und die Aufnahmelänge stieg mit ansteigendem Verhältnis von Gesamtprimärproduktion zu Gesamtrespirationsrate. Die Resultate weisen auf erhöhte Aufnahmeleistung bei höherer Bakterienabundanz hin, wobei jedoch weder Bakterienabundanz noch Chlorophyll-a-Konzentration direkt mit der Ammoniumaufnahme korrelierten.

Die gefundenen Zusammenhänge bestätigen einen negativen Einfluss von Stickstoffverschmutzung und fehlender Flussbettheterogenität in Fließgewässern (und damit auch landwirtschaftlicher Flächennutzung auf angrenzenden Flächen) auf die Selbstreinigungskapazität der untersuchten Gewässer. Ziel sollte also sein, die negativen Auswirkungen der Landnutzung zu mildern und die Flüsse und deren Fähigkeit zur Selbstreinigung zu erhalten.

Key words and abbreviations

Key words

Agriculture, ammonium uptake, in-stream nutrient uptake, nutrient loading gradient, nutrient spiraling, land use gradient, self-purification capacity, transient storage

Abbreviations

CR	Community respiration
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
GPP	Gross primary production
OM	Organic matter
S_w	Uptake length
U_t	Uptake rate
V_f	Uptake velocity
FE	Feichsen
GAM	Gamingbach
GMB	Gmoosbach
GRB	Grestenbach
KB	Kothbergbach
RB	Rußbach
SB	Schweinzbach
SI	Sierning
ZB	Zettelbach

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1. Introduction

Apart from downwards transport of water and the function as a habitat for various plants and animals, stream ecosystems also provide many other important functions to the environment and human society. These ecosystem services include uptake, retention and removal of nutrients – for example nitrogen or phosphorus – as well as uptake and degradation of pesticides and processing of organic matter (OM). Especially low-order streams, within the context of bigger river networks, can have a disproportionately large impact on the rate of nitrogen retention and extenuation and therefore downstream transport within streams (Alexander et al., 2000; O’Brien et al., 2007).

In many Austrian rivers these aquatic functions, though, are already strongly influenced by anthropogenic impacts, such as agricultural activities and wastewater disposal, leading to a reduction of water quality. This trend has been observed more and more in the last century. One problem is, that an increase in nitrogen concentration due to anthropogenic impacts can cause strong changes in the nutrient uptake ability (Bernot & Dodds, 2005; Bernot et al., 2006; Bunch & Bernot, 2012; Johnson et al., 2009). In this thesis, uptake is defined as the “gross removal of dissolved inorganic N from the water column” (Hall & Tank, 2003). In addition, the anthropogenic alteration of the stream morphology (through channelization, establishment of uniform stream profiles with the intention of efficient flood removal, vegetation clearance, alteration of in-stream structures etc.) can lead to shifts in abundance and diversity of stream biota and a change of the cycling of nutrients (Payn et al., 2005). Shorter contact times with biogeochemical reactive surfaces and therefore a decrease in natural functions, such as self-purification capacity, can occur as well. As a result, the amount of nutrients transported downstream is raised (Dodds et al., 2004; Earl et al., 2006; Weigelhofer et al., 2013).

In many regions of the world, agriculture has been identified to be the main single source of N for aquatic environments (Birgand et al., 2007), nutrient cycles have been modified through the production of P- and N-based fertilizers (Sheibley et al., 2014). In consequence of the human alteration, many channelized and morphologically modified streams lack buffer zones as well as appropriate vegetation. Therefore, nutrients in form of eroded soil particles can enter the water through overland flow (Teufl et al., 2013; Weigelhofer et al., 2013) without passing a barrier. In addition, diffuse sources, such as agriculture (fertilizer use), but also atmospheric decompositions or point pollution sources (e.g. wastewater treatment plants or leaky sewers) contribute to increased N input (Craig et al., 2008; Johnson et al., 2009; Wollheim et al., 2005) through many different modes of transmission (Craig et al., 2008). Once in the surface water, the agricultural streams then “[…] serve as conduits rather than nutrient processors” (Sheibley et al., 2014). These increased, non-natural accumulations not only do alter the quality of water, but also can lead to significant changes in the sediment structure, as well as hyporheic water exchange. They can therefore cause oxygen depletion in the sediments, and also affect habitat diversity and stream metabolism negatively. In turn, these alterations can lead to changes in the nitrogen cycling and reduce the natural stream functions (Bhattarai et al., 2009; Teufl et al., 2013; Weigelhofer et al., 2013; Wood & Armitage, 1997). Additionally, nutrient-loaded stream sediments can also cause an increasing saturation of the aquatic system, as they might act as an internal eutrophication source (Hancock, 2002; Weigelhofer et al., 2013). According to Sheibley et al. (2014) the increased amount of reactive N in the hydrosphere may represent an even bigger ecological problem than climate change.

Agriculture represents the most important anthropogenic in-stream nutrient source in Austria. With an area of about 1,36 million ha, the cropland in Austria accounts for almost 50% of the total agricultural area of 2,76 million ha (BMLFUW, 2013). The main nutrients ending up in streams are nitrogen, phosphorus and dissolved organic carbon (DOC) (Piscart et al., 2009). In this study ammonium uptake and retention ability of different streams are compared, under the special consideration of a gradient of ammonium concentration in water and sediments in streams. The gradient covers the range from forested catchments over intensive grassland with manure application to intensive cropland with artificial fertilizer use and occurrence of erosion. The change in ambient ammonium concentration, resulting from application of manure and fertilizer, can affect the efficiency of nutrient uptake in different ways: one possible effect of increasing ambient concentrations is the reduction - or even the saturation - of the demand of nutrients when the organisms saturate or the abiotic adsorption sites become filled (Bernot et al., 2005). These changes in turn lead to declining uptake velocities and uptakes rates increasing in a curvilinear way, often following the Michaelis- Menten equation (Earl et al., 2006; Gibson et al., 2015; Kemp & Dodds, 2002; O'Brien et al., 2007). Another effect is the possible dependency of the uptake of a certain nutrient on the availability of another nutrient component. High nitrogen availability for example could cause phosphorous limitation and stimulate its uptake, or vice versa (Earl et al., 2006; Gibson et al., 2015). Apart from the aspect of ambient nutrient concentration, land use may also influence and impair the uptake ability of a stream indirectly by having an impact on whole-stream metabolism, discharge, light availability (through clearing of riparian vegetation) and elevated sediment inputs (Gibson et al., 2015; Lovett et al., 2000). In addition to the NH_4-N concentrations in the stream water and the sediments, also two other forms of nitrogen, namely NO_3-N (nitrate) and NO_2-N (nitrite), will be examined to study possible interdependencies between the different nitrogen forms.

There are several factors which might affect the uptake and retention capacity, velocity and rate of in-stream ecosystems. The factors - amongst others - include canopy cover, water temperature, algal mass, ambient ammonium load, microbial abundance (stoichiometry in streams can be influenced by bacteria in terms of dissolved nutrients (Cross et al., 2005)), biofilm amount, hydrologic retention capacity and discharge. The uptake parameters introduced by the Stream Solute Workshop (1990) are interdependent; uptake length (S_w) usually increases with decreasing uptake rate (U_t) and decreasing nutrient demand relative to supply (V_f). Literature research (Arango et al., 2008; Birgand et al., 2007; Chen et al., 2013; Hall et al., 2002; Hines & Hershey, 2011; Johnson et al., 2009; Weigelhofer et al., 2013) led to an expected influence as following in Table 1:

Table 1: Expected influence of different factors on ammonium uptake parameters. The “+” indicates an increase, the “–“ a decrease in demand, uptake rate or uptake length, respectively.

	Demand relative to supply	Uptake rate (sufficient supply)	Uptake length
Influencing factor	**V_f**	**U_t**	**S_w**
Algal biomass	+	+	-
Canopy cover	-	-	+
Water temperature	+	+	-
Ambient NH_4	-	+	+
Retention capacity	+	+	-
Discharge, Depth, Flow velocity	-	-	+
Microbial abundance	+	+	-

It seems clear that many of the points listed above, such as water temperature, canopy cover, chlorophyll-a or discharge, usually strongly depend on the season, hence seasonality is in turn expected to show an influence on the uptake parameters. In summer, e.g. water temperature mostly is higher than in spring, but at the same time chlorophyll-a concentration is supposed to be lower due to increased shading caused by denser riparian vegetation. Also the ambient ammonium concentration in agriculturally affected catchments usually changes with changing season and therefore cultivation management. This should lead to a visible seasonal pattern.

In addition, discharge and also flow velocity, wetted perimeter and in consequence of that also hydrologic retention capacity are influenced by changing season. The topic of seasonality is a very complex one, and the season with all its influence on the uptake mechanisms has to be considered throughout the whole study. For the exploration of seasonality and its effects on biotic, physical, hydraulic and morphologic conditions on in-stream nutrient uptake, sample taking and measurements across different times of the year became necessary.

To fully understand the retention capacity of a stream, it is essential to know the mechanisms of nitrogen retention and removal in an ecosystem. Nutrient uptake is a central ecosystem function of streams (Payn et al., 2005), uptake rates generally decrease with increasing discharge and stream order (Craig et al., 2008). The whole process of nutrient uptake starts with the import of nutrients into the stream system - mainly from agricultural activities or sewers discharging into the stream - causing the different stream components to begin with the nutrient uptake. Nitrogen may be retained temporarily or removed permanently; the retention capacity is composed of burial in sediment and organic matter, adsorption and biotic uptake, while the permanent removal includes ammonia volatilization, biomass removal or the process of nitrification with subsequent denitrification. The mechanisms relevant for this thesis are explained below.

1.1 Mechanisms relevant for ammonium retention

Biotic uptake (Assimilation into biomass)

Nutrients can temporarily be removed from the water column via uptake through biofilms (microbial matrices on the surfaces of substrata). The retention through biofilm uptake can be very high - because of an intense recycling within benthic communities - but there are many factors limiting the total amount of N retainable in biofilms (e.g. sloughing, disturbance through floods, light limitation…) (Bernot et al., 2005; Burns, 1998). The biofilms release the nutrients to the water column at some point via mineralization and alter biogeochemical conditions that influence microbial transformation rates (Bernot et al., 2005). According to Peterson et al. (2001), assimilation by photosynthetic and heterotrophic organisms – together with sorption to sediments – is the main ammonium removal mechanism. Photosynthetic organisms include filamentous algae, unicellular algae and bryophytes, while heterotrophic organisms are represented by fungi and bacteria. Tank et al. (2000), Gibson et al. (2015) and Bunch et al. (2012) attested a preferential uptake of NH_4-N over NO_3-N, resulting in larger uptake values and faster uptake velocity for this nitrogen species. This is probably caused by the fact that “NH_4-N does not have to be reduced by organisms prior to incorporation and consequently requires less energy to assimilate” (Kemp et al., 2002). Bunch et al. (2012) state that “[…] organisms, particularly fast-growing microbial species, may also be capable of adapting to different conditions and changing uptake rates over time”.

One method of quantifying biotic activities is the measurement of whole-stream metabolism. According to Bernot et al. (2010), the rates of whole-system metabolism represent “fundamental indicators of ecosystem structure and function” and can be used to specify whether a stream is heterotrophic of autotrophic. The cycling of carbon is closely linked to other nutrient cycles, and factors controlling stream metabolism might therefore also regulate nutrient processing.

Figure 1 (after Bernot et al. (2010)) shows the primary factors hypothesised to influence the metabolism parameters gross primary production (GPP) and community respiration (CR), with larger arrows indicating greater influence.

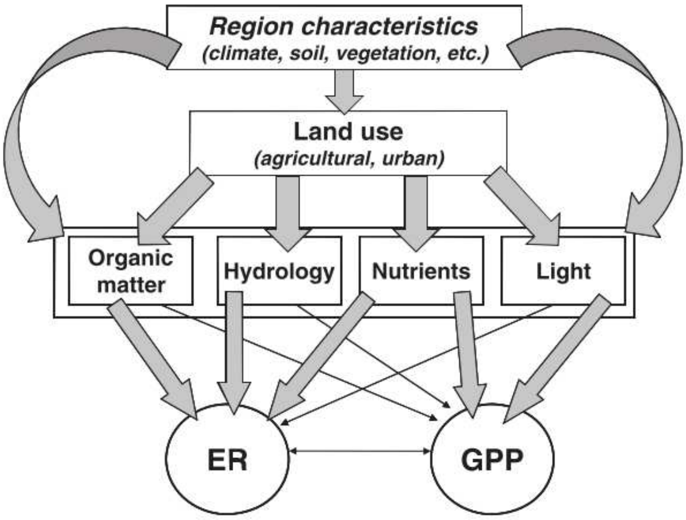

Figure 1: Factors influencing ecosystem metabolism (Bernot et al., 2010)

While stream metabolism is said to provide an integrative measure of stream function and structure, and therefore is an important indicator of nutrient and organic matter cycling (Izagirre et al., 2008), the knowledge about the possible influence of land use on ecosystem metabolism is limited. Until now most studies concentrate on stream metabolism in one single stream ore one single region.

Another measure of biotic uptake is represented by concentration of chlorophyll-a in the epilithic biofilms. According to Marti et al. (1997), a higher amount of algal biomass is one of the factors increasing the nutrient demand in streams, and therefore it decreases the nutrient uptake lengths. Chlorophyll-a is a general photosynthetic pigment used by plants to perform oxygenic photosynthesis (Björn et al. 2009). In this thesis it is used as an indicator to estimate the amount of algae in the stream biofilm, based on the approximation that a higher amount of algae leads to an increase in chlorophyll-a concentration.

In addition to chlorophyll-a and stream metabolism, also the abundance of microbes in the stream sediments can be used to draw conclusions to biotic uptake. As microbes have higher metabolic rates in comparison to larger organisms, the microbial abundance is likely to influence the uptake velocity in stream ecosystems. It is well known that an increase in nutrient availability leads to higher sedimentary microbial abundances, which can influence nitrogen movement and degradation in the ecosystem significantly (Mathooko et al. 2002; Piscart et al., 2009). Bunch & Bernot (2012) conducted laboratory experiments, regarding the intensity of ammonium uptake under differing levels of ammonium enrichment. They found out that sediment microbial communities were able to adapt to long-term changes in nutrient availability. In this thesis the dependence of ammonium uptake on microbial community was tested directly in the stream.

Abiotic uptake (Sorption)

Sorption describes the process in which a dissolved substance “becomes associated with a solid surface” (Runkel & Bencala, 1995), in this case the binding of ammonium to the surface of organic and inorganic particles via ion exchange. The dissolved substance is called “sorbate” while the solid substance (e.g. clay minerals or organic matter) is called “sorbent”. As a result of adsorption the diffusion of the sorbate is slowed and the mobility decreased. For that reason it is an important feature of nitrogen retention in streams (Runkel et al., 1995). The abiotic uptake is a function of contact area and contact time. Therefore, the stream parameters discharge and flow velocity, as well as width and wetted perimeter might have an influence on the uptake parameters. Apart from the hydromorphological parameters, also the measurement of transient storage can be relevant and interesting for research questions concerning nutrient retention.

Transient storage, especially noted in small streams, can be defined as the temporary hydrologic retention of stream water moving downstream much slower than the average flow velocity in the main channel (Runkel, 1998). This leads to a residence time longer than those of the main channel. It has become critical in biogeochemical studies aiming to examine nutrient uptake factors to quantify the transient storage zone, as the transient storage may have an influence on the nutrient uptake (Argerich et al., 2011). Due to the slower flow velocity and the longer travel time, the contact time between the solute and active surfaces is increased, which can lead to higher nutrient uptake and hence higher removal rates. These zones of transient storage can be found either in surface (e.g. stagnant water pockets or small eddies) or subsurface areas, such as the coarse streambed gravel or the porous stream bank areas, known as hyporheic zones (Argerich et al., 2011; Roberts et al., 2007; Runkel et al., 1995; Runkel, 1998). According to Argerich et al. (2011), even woody debris and leaf packs can cause longer water residence time along the stream reach. Different results already exist in the literature; some authors are stating no or only a weak positive correlation between the relative size of transient storage and the ammonium uptake velocity (Bukaveckas, 2007; Pander & Geist, 2013), others found a significantly positive correlation for one or even more nutrients (Bernot et al., 2010; Ensign & Doyle, 2005; Weigelhofer et al., 2012).

Permanent removal of nitrogen generally is more desirable, but also a temporary retention and storage can already help to increase the contact time with denitrifying bacteria and organic matter, and therefore lead to a permanent removal in the end (Craig et al., 2008; Kemp et al., 2002). Most of the retention and removal mechanisms, with exception of N transport, ammonia volatilization and biomass removal, saturate at some point. This means that the involved components, such as the sediments or the stream biota, cannot take up or bind any more of the ammonium after reaching a certain level of saturation (depending on many factors, such as temperature, sediment composition etc.). Loaded waters might produce more algal biomass due to nutrient availability, which probably increases uptake velocity and shortens uptake length, but this can compensate for the higher nutrient background only up to a certain, unknown point (Niyogi et al., 2004). Therefore, the stream components will saturate sooner or later with increased N loading (Bernot et al., 2005).

Even though the understanding of nitrogen fate in streams is steadily increasing, it is still difficult to apportion the removal/uptake of nitrogen measured from the water column to the various uptake compartments (Bernhardt et al., 2002).

1.2 Nutrient spiraling parameters

Nutrients in streams are continually transformed - from dissolved inorganic to particulate organic forms and eventually back to dissolved inorganic forms - as they are transported downstream. These processes of nutrient cycling and downstream transport were described as “spiraling” by Webster and Patten (1979). According to the Stream Solute Workshop (1990) there are three interrelated parameters that will be used in this thesis to describe nutrient spiraling, in particular the elements involving nutrient retention:

1. The average distance a molecule travels downstream in dissolved inorganic form before it is taken up. It is indicated by the **uptake length (S_w)** [in m] (Newbold et al., 1981).

2. The mass of nutrient retained/ immobilized per time unit and area of stream bottom, which is indicated by the **uptake rate (U_t)** [in mg m^{-2} s^{-1}].

3. **The mass transfer coefficient (V_f)**, which represents the rate of vertical movement of molecules out of the water column into the sediments and evaluates the intrinsic nitrogen removal ability of a stream, as well as the benthic nutrient demand relative to supply (Birgand et al., 2007; Hall et al., 2002). It is often also called uptake velocity [in m s^{-1}].

U_t is expected to rise and then saturate - following the Michaelis-Menten kinetics - with increasing nutrient concentration. At the same time the uptake velocity V_f decreases rapidly because of decreasing demand, while the uptake length S_w increases linearly (Bernot et al.; Dodds et al., 2002; Earl et al., 2006; Niyogi et al., 2004; O’Brien et al., 2007).

These parameters can be used to quantify the nutrient retention in the selected streams and to compare the retention capacities and mechanisms of different streams. Apart from that, nutrient uptake length has already been used to measure e.g. stream response to wastewater treatment plant effluent, forest and riparian management and dam removal (Payn et al., 2005). The uptake length is directly measured from the experiments and therefore represents the stream length needed until all the dissolved nutrients are taken up by the biofilm or sediments. The information gained is especially relevant for restoration measures and stream management. The uptake length can be a function of discharge and water depth and may therefore not be very suitable to describe uptake behaviour across streams with differing sizes and discharges. This is why the uptake rate and the mass transfer coefficients also were included in the analysis, as these two variables are supposed to be independent of discharge and depth (Dodds et al., 2002).

2. Objectives, hypotheses and rationale

2.1 Objectives

This master thesis was written as part of a larger research project called “PowerStreams”, which is a research-education-cooperation with four schools located in Lower Austria. In the frame of this project, the impact of nutrient loading of streams on their natural functions was investigated. The project spans different approaches, such as measurement of greenhouse gases in the streams, conduction of experiments in order to investigate sedimentary nutrient/ greenhouse gas uptake or release ability, as well as a long-term experiment to test the effects of long-term DOC (dissolved organic carbon) addition on the stream metabolism and water quality.

The aim of this thesis was to gather particular knowledge about the capacity and sustainability of the self-purification, specifically nitrogen retention, of streams along a gradient of land use and therefore ammonium load. The effects of seasonality and hydromorphology on the uptake behaviour were explored, as well as the context between uptake and microbial and algal abundance in the sediments and in-stream metabolism. The measured uptake parameters for each stream were searched for saturation patterns and it was tried to assign the different uptake behaviour /saturation patterns to the respective state of ammonium loading. With this knowledge, and by quantification of the interaction of land use and self-purification capacity, it was aimed to identify options for a future sustainable management of stream ecosystems.

For this purpose, short-term ammonium addition experiments were conducted at nine different streams in spring 2015 and repeated at nine of the streams in summer. In addition, sediment and biofilm samples were taken from each of the nine streams, to investigate possible interactions between the nutrient uptake and the stream biota. Statistical analyses of the gained parameters were performed, including a comparison between spring and summer, and the findings then were discussed in detail.

2.2 Hypotheses

Hypothesis A

An increased background load of ammonium in water and sediments leads to a reduction of the in-stream ammonium uptake due to reduced nitrogen demand

The background concentration of ammonium positively correlates with the uptake rate (Weigelhofer et al., 2013). The uptake lengths of non-polluted streams are shorter and the mass transfer coefficient is higher than those of highly polluted streams.

Hypothesis B

If exposed to pulses with increasing ammonium concentrations, streams with lower in-stream ammonium load tend to saturate earlier than streams with moderate or high ammonium load

As the microorganisms in the stream are adapted to high loads of ammonium, streams with a higher concentration of ammonium in the water saturate later than lowly loaded streams.

Hypothesis C

The ammonium uptake velocity V_f is higher in spring than in summer

This is due to lower shading (less canopy cover) leading to higher chlorophyll-a concentration and benthic organic matter standing stocks (Johnson et al., 2009) and therefore an increased autotrophic N demand.

Hypothesis D

The longer the contact time and the higher the wetted perimeter of the stream, the higher the mass transfer coefficient becomes. Higher water retention equals a longer contact time between water and sediments and therefore leads to higher nutrient uptake rates and lower uptake lengths.

Slower flow velocity equals shorter uptake length up to a certain point. Stagnant water sections in turn can lead to anoxic conditions in the sediment and therefore decrease the uptake through aerobic nitrification. The uptake length is negatively correlated to the wetted perimeter and positively correlated to stream size and discharge (Niyogi et al., 2004; Webster et al., 2003).

Hypothesis E

The mass transfer coefficient is higher in streams with a GPP/CR ratio >1 (autotrophic) and positively correlated to algal and microbial abundance

Increased GPP/CR ratio leads to higher stoichiometric requirement of N, leading to increased uptake velocities (Hall et al., 2003). Higher concentrations of chlorophyll-a in the stream biofilm equal higher amounts of algae; the ammonium uptake velocity increases with algal abundance (Hall et al., 2003; Marti et al., 1997). As microbes have higher metabolic rates in comparison to larger organisms, microbial abundance is positively correlated to the uptake velocity in stream ecosystems (Bunch et al., 2012).

2.3 Rationale

Ammonium is considered to be one of the two major dissolved inorganic nitrogen (DIN) species available in running waters (Ribot et al., 2015). In addition, NH_4-N is said to be taken up preferentially over NO_3-N (Tank et al. 2000; Bunch et al. 2012), which is the reason why it is examined here. An aim is to figure out at which conditions streams show a tendency of saturation and if a linkage with ambient ammonium concentration exists. This will be studied with the help of the consecutive additions featuring steadily increasing NH_4 concentrations. This aspect has not yet been examined sufficiently in highly productive and nutrient rich streams yet (except Bernot et al. 2006).

There are already some studies focusing on the impacts of eutrophication caused by agricultural land use or morphological alterations on the self-purification and nutrient retention ability (Bernot et al., 2005; Johnson et al., 2009; Roberts et al., 2007). The aspect of a gradient of nitrogen loading (from pristine to heavily loaded streams) has also been addressed by some other studies (Bernot et al., 2006; Dodds et al., 2002; Gibson et al., 2015; Kemp et al., 2002; Niyogi et al., 2004). However, there is a scientific gap when it comes to combining the uptake measurements across the gradient of nutrient loading with the induction and exploration of in-stream nutrient saturation. In addition, most of the studies have been conducted at only one stream, or in regions differing significantly from Austrian catchments in terms of climate (e.g. Birgand et al., 2007; M. Kemp et al., 2002; O’Brien & Dodds, 2008). According to Niyogi, Simon, and Townsend (2004) also seasonality in context with agriculturally modified and urban influenced streams has not been studied sufficiently, particularly not in catchments placed in temperate regions strongly subjected to seasonality. The nutrient uptake experiments were conducted in April/ May and July/August, so a comparison of spring and summer conditions and therefore also a quantification of seasonality became possible. The streams were selected to be as similar to each other in hydromorphology as possible, in order to avoid influences apart from the land use gradient. While the hydrological functions and mechanisms in context with nutrient export have been studied thoroughly and their importance is known, the biotically induced nutrient retention in streams has not fully been explored and understood yet (Bernot et al., 2006). Low order streams were chosen, because due to their spatial proximity to the sources, they are known to be especially sensitive to nutrient loading, in addition they are said to have a higher efficiency in N removal relative to their size (Hill & Bolgrien, 2011; Withers & Jarvie, 2008).

The overall objective of the thesis is to improve understanding of stream functions and self-purification mechanisms and to gain an in-depth knowledge of nutrient processing, states of saturation and influencing parameters within the streams in context with background ammonium concentration and season. This thesis covers a broad range of influencing factors and does not only consider physical, but also chemical and biological factors. It therefore represents a multilateral approach, illuminating the many different mechanisms probably influencing and inhibiting the uptake of nutrients. The thesis may become the basis for arguing for specific restoration measures, such as rehabilitation of forested riparian buffers, with the aims of raising the habitat heterogeneity and retaining diffuse particle inputs from the catchment and surrounding crop fields more efficiently (Teufl et al., 2013; Weigelhofer et al., 2012).

3. Material and methods

In this chapter the sampling design and the measurement methods are explained. The choice and description of the study area were argued, afterwards the methods applied, as well as the preparation of the experiments and the needed materials were illustrated. In addition, the formulas used for the calculation of the parameters were listed and explained.

3.1 Measurement methods

To measure the overall nutrient retention in streams, one option is the conduction of short-term nutrient addition experiments, where an inorganic nutrient compound - such as NH_4^+, NO_3^- or PO_4^- - is released into the stream at a constant rate, using e.g. a peristaltic pump or a Mariott'sche bottle (Bernhardt et al., 2002; Bernot et al., 2005, 2006; Johnson et al., 2009; O'Brien et al., 2008; Payn et al., 2005; Roberts et al., 2007; Stream Solute Workshop, 1990). The uptake of the nutrient is then measured through the longitudinal decline in concentration over time. The additions are used to give an insight into biogeochemical (like adsorption), as well as hydrologic processes (transient storage, advection and dispersion) relevant for the transport and retention of nutrients (Weigelhofer et al., 2012). Alternatives use e.g. isotope enrichment for the determination of the uptake parameters. Advantages of short-term additions lie in the minor costs and the better practicability. While the short-term addition experiments usually are less complex than isotopic methods, typically the ambient uptake rates are underestimated (and therefore the uptake length S_w is overestimated). The reason for that is that the S_w at increased experimental concentrations is longer than the S_w at ambient concentrations. According to Mulholland et al. (2002) the degree of overestimation during nutrient additions is positively correlated to the increase in nutrient concentration. To limit this problem, low levels of enrichment should be used and they should also be similar between time periods within a given stream and among streams. This should enable a useful comparison of the nutrient uptake (Mulholland et al., 2002; Roberts et al., 2007). As the gained data will only be used to compare the uptake parameters of the different streams rather than getting absolute rates, the nutrient addition method is an excellent option.

In addition to the short-term ammonium addition experiments, it is necessary to take sediment and biofilm samples to analyse them for N-concentrations, dissolved organic carbon (DOC) and microbial abundances as well as chlorophyll-a concentration. These samples have the advantage of being easy to collect and the analyses can be conducted and replicated under laboratory conditions. On the other hand a disadvantage may be the difficulty in scaling up the results to the whole stream system (O'Brien et al., 2008).

3.2 Study area

For the conduction of the experiments for this master thesis, 9 different headwater streams were selected. The reason for choosing headwater streams lies in their high relevance in nutrient retention, as they spatially dominate the landscape and show a high ratio of benthic surface area to water volume (Cross et al., 2005). The most important selection criterion was the type and increasing intensity of surrounding land use and hence the expected ammonium loading.

The selection according to this criterion was done with the intention to gain a broad range of streams with differing nutrient loading levels. When a stream was suitable in terms of land use gradient, some other factors had to be considered:

- First the stream had to be small enough to enable a sufficient increase in ammonium concentration above ambient level, but also to manage a measurement of transects and to walk into the stream wearing rubber boots.

- To ensure a quick and efficient sampling, the good accessibility of the stream was an important factor.

- Another important point was the absence of visible tributaries or drainage pipes in the chosen section, as these could become sources for additional amounts of unwanted ammonium.

- Then, for reasons of comparability, the variations in size, flow characteristics (Schade et al., 2011), vegetation and ecological status had to be as small as possible. For the most polluted stream (the Gmoosbach) it was not possible to meet this criterion, because due to intensive anthropogenic alterations the hydromorphology of this stream significantly differed from the other streams.

All of the nine streams chosen were located in Lower Austria, because this federal state shows a wide range of different agricultural land use intensities in its catchments.

There were 3 different land use categories that were applied to the streams in order to estimate their nutrient loading:

1. Forested catchment with expected lowest nitrogen loading: In the south-western region of the Mostviertel (blue zone in Figure 2) the streams are relatively unaffected by nitrogen loading; few agricultural influences are possible. Grestenbach and Kothbergbach form this category together with Gamingbach. Along the Gamingbach a few meadows are situated, which may be intensively cultivated. Soil erosion is expected to be low, as meadows and forests are not ploughed. Very low nutrient loading is expected for these streams.

2. Moderately cultivated grass- and cropland: The streams are located in the central region of the Mostviertel and include Feichsen, Zettelbach, Schweinzbach and Sierning, whereas the last two already show a very low percentage of forest in the catchment (compare Table 5) and erosion is increased in the Sierning. The area is dominated by small villages and intensively cultivated meadows with occasional cropland (maize). Soil erosion is expected to be moderate due to the mixture of meadows and croplands. Usage of fertilizers and therefore nutrient loading can hardly be estimated, but is expected to be moderate.

3. Intensively cultivated cropland with high soil erosion: The Rußbach and Gmoosbach are situated in the north-eastern region of Lower Austria, called Weinviertel (yellow zone in Figure 2), which is affected by heavy agricultural land use. The Gmoosbach shows a uniform channel shape (trapezoid-shaped) and vegetation clearance and in that it differs from the other streams. High nutrient loading is expected for these streams.

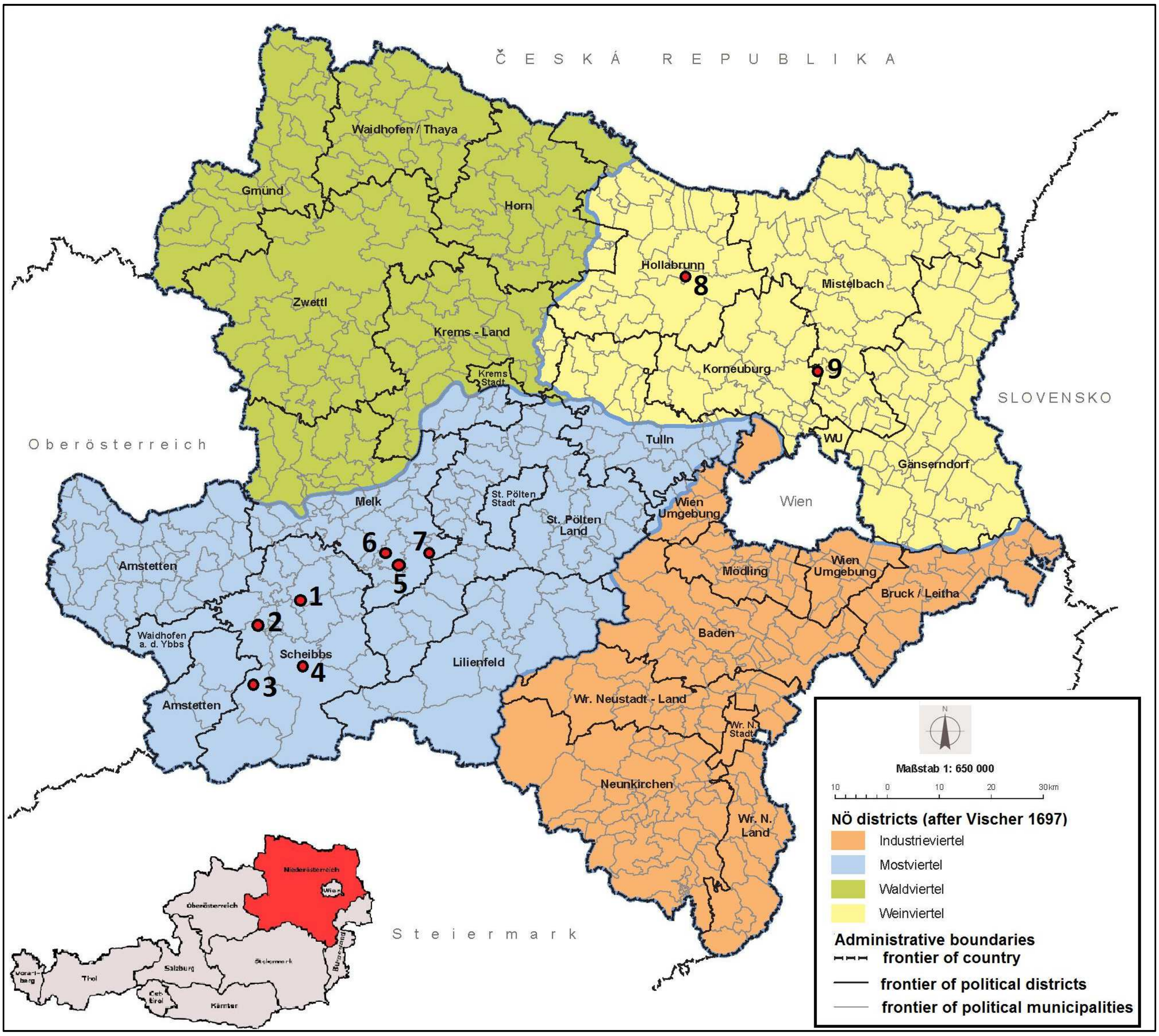

Figure 2: The 4 districts of Lower Austria (Industrieviertel marked orange, Mostviertel blue, Waldviertel green and Weinviertel yellow) with the positions of the stream reaches. 1…Feichsen, 2…Grestenbach, 3…Kothbergbach, 4…Gamingbach, 5…Zettelbach, 6…Schweinzbach, 7…Sierning, 8…Gmoosbach, 9…Rußbach. Source: [http://noe.gv.at/bilder/d17/BD5noe31-Viertelsgrenzen.png?7150, 21.08.2015]

3.3 Preparation of nutrient additions

In order to measure the stream ammonium demand and uptake parameters, 2 sets of short-term addition experiments with adjacent sample taking were performed. The experiments were performed following the protocol of the Stream Solute Workshop (1990). For this purpose, different stream stretches (ten in spring, eight in summer) with a total length of about 300-350m were chosen based on considerations stated in chapter 3.2. Three consecutive short-term additions of ammonium chloride (NH_4Cl^-) with increasing ammonium concentration (target enrichment was the 2, 6 and 12-fold background concentration) were released into each stream, using a peristaltic pump with a flow rate of $6mls^{-1}$. The experiments also included additions of phosphate in the form of NaH_2PO_4 in order not to change the proportion of N:P in the stream, as this could affect the uptake of ammonium. The first addition per reach and season was always performed in combination with sodium chloride (NaCl), acting as a conservative tracer. A conservative tracer is a substance exclusively subject to the physical processes of advection, dispersion, transient storage and lateral inflow (Runkel, 1998). Hence it is not reacting chemically or biologically and not competing for exchange sites with other ions. It usually is injected into the stream together with the reactive solute (i.e. NH_4Cl in this experiment) and can be used to calculate dilution caused by groundwater influx and dispersion. It is also useful to confirm whether the distance between the addition point and the first sampling station was chosen big enough to ensure a complete mixing (Dodds et al., 2002). There are various types of conservative tracers available, including radioactive materials, fluorescent dyes or chemical salts, such as sodium, chloride, magnesium, potassium and lithium. Generally, chloride is considered to be the most conservative of the available solutes and it can be followed in-situ by using a conductivity meter (e.g. Hach Lange HQ 40D) (Stream Solute Workshop, 1990). Even though a conservative tracer is not supposed to react chemically or biologically, in practice there are some factors which can alter the conservative behaviour of the tracer ion. Chloride, for instance, may be sorbed by soils if the pH becomes <7, as the water becomes more acidic (Jackman et al., 1984).

The NH_4Cl^- addition was necessary in order to increase the stream ammonium concentrations to the 2-12-fold of the ambient background concentration and hence assess the degree of saturation of the stream components. While the addition of a nutrient plus a conservative tracer provides information on biogeochemical processes, such as saturation and retention of nutrients along a reach, the addition of the conservative tracer is necessary to gather information about hydraulic as well as hydrologic properties at reach scale (Weigelhofer et al., 2012). Therefore with the addition of a conservative tracer, information about transient storage, flow velocity etc. can be gained. In addition, the NaCl was used to survey the mixture of water by observation of changes in conductivity.

The amount of NH_4Cl needed for the increase of concentration to the 2-, 6 and 12-fold of the background concentration was calculated according to the equations summarized in chapter 3.6.1.

3.4 Sampling procedure

The sampling process incorporated the gathering of water and sediment samples, as well as collection of biofilm samples and measurement of transects, in-stream oxygen concentration and water temperature.

The first set of experiments was done from March to April 2015, the second set between July and August 2015. The experimental design and approach were the same for both sets; the exact sampling procedures are described in the chapters below.

3.4.1 Hydromorphology

For each stream reach and sampling date, at least 2-3 characteristic cross-sectional profiles (transects) were recorded after the sampling to measure average depth, flow velocity and width of the stream reach. The measurements were performed with a tape measure or foot rule. The width was measured at a position representing the typical stream reach. The depth was recorded - along the same transect as the width - in 0.3m intervals. The flow velocity, used for calculation of discharge, was estimated by a quick floating experiment (recording of time needed for a small branch or leaf to travel 4m, repeated at least 3 times per transect to calculate a mean value). In addition, the whole reach flow velocities (v_{min}, v_{mean}, v_{max}) were retrieved from the conductivity curve measured with the Hach Lange HQ40 multiparameter meter. It was intended to also calculate transient storage parameters, but they could not be calculated for some streams due to fluctuations in the conductivity. The parameters d/w and v_{min}/v_{mean} were therefore used as a surrogate: d/w represents the proportion between size of uptake area and water volume, while v_{min}/v_{mean} describes the decline of the conductivity curve and therefore the retention of salt in the stream.

3.4.2 Water samples

As a first step, the location of the pump and container used for the ammonium addition was chosen to ensure a quick and complete mixing of the solution within the stream water. For that reason, the first sampling point had to be at least 100m away from the addition point and stagnant water sections right downstream the addition device had to be avoided. Then a stretch of 200-250m was measured with the tape measure. This minimum length was chosen to ensure a travel time between the addition point and the reach end of at least half an hour, the maximum length was limited by lateral tributaries. The measured stretch then was divided into 9-11 evenly spaced longitudinal stations with an interval of 20-25m. A schematic representation of the experimental setting can be seen below in Figure 3.

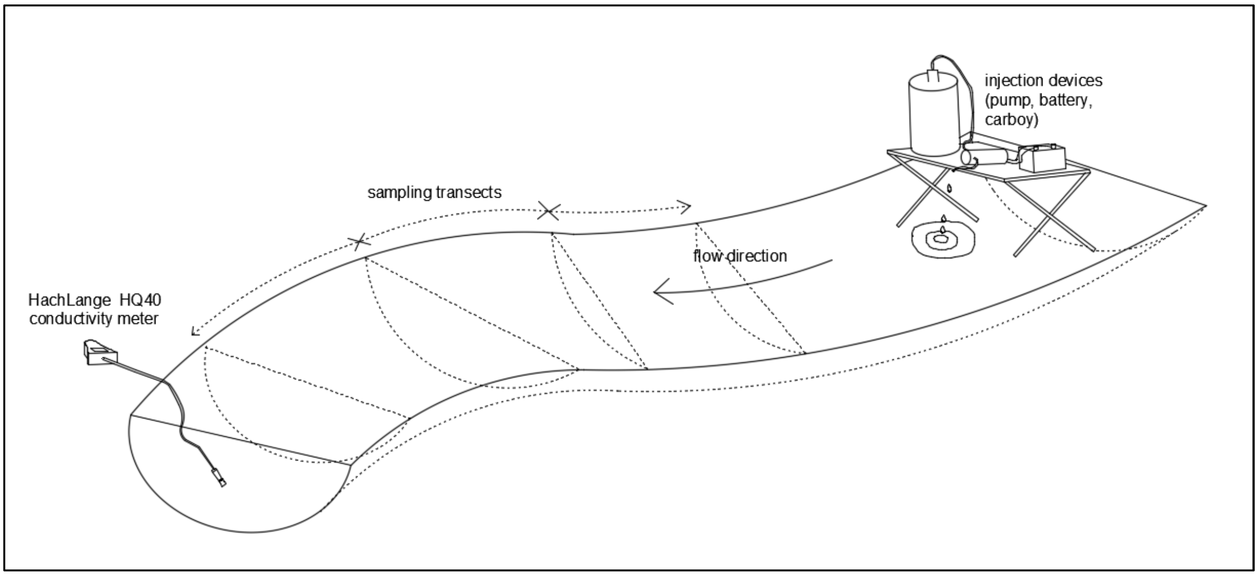

Figure 3: Scheme of addition device, conductivity meter and transect positioning

Each of these stations then was marked and labelled with duct tape in order to easily find the location again during the sampling process and also in summer. The presence of culverts, gauging weirs or pipes delivering water was avoided as much as possible, as these installations could have led to a falsification of the data due to undesired nutrient input from fields or similar.

Before starting the additions, in every second marked transect of the study reach a background sample was collected to determine the ambient NH_4-N, NO_3-N and NO_2-N concentrations, as well as the background conductivity, making altogether 5-6 background samples. An electric multiparameter meter (HQ40d; Hach Lange, Düsseldorf, Germany) was placed at the very last transect of the reach to monitor the downstream changes in the electric conductivity over time and was therefore used to identify a stable (not changing for several minutes) plateau of conductivity, indicating a complete mixture of the ammonium with the stream water. The conductivity meter at the end of the test track was also used to record any changes in context with NaCl addition and to generate a time-conductivity curve with a resolution of 30 seconds.

The first addition with a solution consisting of the tracer NaCl and the NH_4Cl^- was then started with a constant flow rate of $6mls^{-1}$ and the starting time was noted. To achieve the constant rate, either a peristaltic pump (e.g. Watson-Marlow) or a Mariott'sche bottle was used. When the stable plateau of conductivity was reached, one water sample per transect point (9-11 per addition) was taken with a 250ml plastic water bottle, trying to consider the flow velocity and to follow the "cloud" of injected ammonium as well as possible. Prior to that, the electric conductivity in each transect was measured with the help of a second Hach Lange HQ40 multiparameter meter in order to verify stable plateau conditions. The containers were then closed with a plastic lid, the water was filtered through GF/F filters (using a 50ml syringe) immediately afterwards, stored in a cooling box and analysed for NH_4-N concentration within 24 hours of sampling.

It was necessary to note the time needed for reaching stable plateau conditions after the NaCl addition to estimate the mixing time for the second and the third addition, as no NaCl tracer was used during these additions. After all samples of the first addition were taken, the injection container was emptied and the time was noted. By noting the ending time of the first addition and also measuring and recording the decline in electric conductivity, a complete curve of conductivity could be generated. With the help of this conductivity curve the flow velocity of the stretch could be calculated. The next solution with a higher NH_4Cl concentration was poured into the container (this time to achieve the 6-fold of background concentration) and the second addition was started, using the same pumping rate as before. When the time needed for reaching the plateau in the first addition was elapsed, the second set of samples was taken in each transect. Directly after that, the third addition (12-fold of the background concentration) was started and samples were taken again after sufficient mixing time.

Furthermore, during each addition three additional samples were taken upstream of the test track. This enabled the registration of possible changes in nutrient- and substance concentration during the experiments (e.g. point source pollution from wastewater plants). All the water samples were taken carefully (in order to not disturb the addition), always with a fresh container mounted on an extendable stick. The container was flushed with stream water 3 times before taking the actual sample. Altogether a total of ca. 38 water samples per stretch was taken: 5 for the background ammonium concentration (in every second transect, before the addition) and 9 - 11 per addition to measure the ammonium retention, resulting in a total of 90 background and 486-594 plateau water samples for nine streams and both seasons. The background samples were analysed for NH_4-N, NO_3-N, NO_2-N and DOC, while the samples taken during the addition plateaus were only analysed for NH_4–N concentration. On the basis of the decline of the added substance in the longitudinal direction under plateau conditions, the parameters of ammonium uptake were then calculated considering a correction of the conservative tracer (Weigelhofer et al., 2012).

Figure 4: On the left: Nutrient injection device with pump, battery and carboy. On the right: sampling

3.4.3 Sediment samples

In addition to the water samples, 10 sediment samples from a pre-defined area (sieve frame as a reference area) were taken upstream the addition place and sieved in-situ through a 4mm diameter sieve. The sediment samples were collected randomly at each study site, digging up to approximately 3 cm depth of the sediment surface. The samples (about 250g of sediments each) were placed in plastic bags and stored in the stream for cooling purposes. After the sampling the bags were removed from the stream, transported home in a cooling box and frozen at -20℃ for later analysis. Only the amount needed for analysis of microbial abundances was removed before freezing. The sediments were used for the analysis of ammonium, nitrite & nitrate, microbial abundance and organic matter content as well as for the calculation of the dry weight of each sample. For the determination of the microbial abundances, 1.5g of the sediment were fixed with 3ml stream water and 0.75ml fixing solution (2.5% formaldehyde) as soon as possible in order not to falsify the results. All in all, 180 sediment samples were taken.

3.4.4 Biofilm samples

The epilithic biomass (biofilm) was sampled either before or during additions (upstreams) by scraping off the biofilm from rocks/ stones located in the stream and noting the scraped area. For this purpose, a Stanley knife was used. 10 replicates were taken for each stream, using either a sieve frame as a reference area or estimating the scraped area afterwards. The samples were put in 15ml tubes and shock-frozen with the help of liquid nitrogen. They were stored in the laboratory freezer at -20℃ until later analysis. The biofilm samples (180 samples altogether) then were analysed for chlorophyll-a concentration.

3.4.5 Stream metabolism

Three parameters were used to quantify the whole-stream metabolism: gross primary production (GPP), community respiration (CR) and the ratio between these two parameters (P/R). Bott (2007) defines primary production as „the rate of formation of organic matter from inorganic carbon by photosynthesizing organisms and [it] thus represents the conversion of solar energy to reduced chemical energy“. The gross primary production is the sum of the fixed energy lost through plant respiration (Ra) plus the portion stored in biomass (net primary production NPP) and therefore represents the whole amount of carbon fixed.

$$\mathrm{GPP} = \mathrm{NPP} + \mathrm{Ra} \qquad \text{[Eq. 1]}$$

At the end of the sampling and measuring procedure, an YSI 600 OMS V2 oxygen probe was fixed and left in the stream in combination with a light-sensitive sensor for a minimum of two days in order to record in-stream oxygen changes, as well as light and temperature with an interval of 30 minutes. The weather conditions always were sunny or partly cloudy at most, no storms occurring during the measurements. A diurnal dissolved oxygen (DO), light and temperature curve over a period of at least 48 hours could then be generated for each stream and each of the two seasons. It was assumed that changes in the O_2 concentration were identical throughout the reach, therefore the single station method with only one probe, after Lamberti & Steinman (1997), was used. GPP and CR then were calculated following the protocol of Bott (2007); GPP was calculated as the area under the DO change curves corrected for gas exchange, while CR was determined via multiplying the average hourly night-time respiration rate by 24 (Weigelhofer et al., 2013).

3.5 Laboratory methods

Here the methods used for water, sediment, biofilm and enzyme sample analysis are listed and explained.

3.5.1 Water sample analysis

The following analyses were performed within 24 hours of sampling:

NH_4-N: All water samples were analysed for ammonium concentration, using colorimetric methods after APHA (1998). For this purpose, two different reagents (dichlorisocyanuric acid, as well as a mixed solution containing sodium nitroprusside, NaOH and water) were produced, added to the samples and then adsorbance was measured at a wavelength of 690nm using a Hach DR2800 portable spectrophotometer. The detection limit for this analysis lies at 4µgl^{-1}.

NO_3-N: The background samples were analysed for nitrate concentration using continuous flow analysis (CFA) (ISO 13395, 1996).The detection limit for this analysis lies at 100µgl^{-1}.

NO_2-N: The background samples were analysed for nitrite concentration using the CFA (ISO 13395, 1996). The detection limit for this analysis lies at 1µgl^{-1}.

DOC: The background samples were analysed for dissolved organic carbon (DOC) via Sievers*900 portable Total Organic Carbon Analyzer. The published instrument detection limit is 0.030 ppb (General Electric Company, 2005).

3.5.2 Sediment sample analysis

If not analysed within the maximum of a day after sampling, the sediments were frozen and stored in the freezer at -20℃ until the later analysis.

NH_4-N: All sediments were analysed for NH_4-N after extraction with potassium chloride (KCl) after the method of Mulvaney (1996). For this purpose about 1.5g of sediments were put in a beaker, enriched with 25ml potassium chloride and the closed beakers left on the shaker for 16 hours. The extract then was poured into glass tubes, put in the centrifuge and the supernatant was analysed for NH_4-N (procedure see water analysis). The exact weight of the sediment was noted to correct for the dry weight and calculate the concentration of ammonium per gram dry sediment. The detection limit for this analysis lies at 4µgl^{-1}.

NO_3-N: All sediments were analysed for NO_3-N after extraction with H_2O according to Mulvaney (1996) using the CFA method (ISO 13395, 1996). The approach of sediment treatment was the same as described before for NH_4-N, but with the difference that distilled water was used instead of KCl. The detection limit for this analysis lies at 20µgl^{-1}.

NO_2-N: All sediments were analysed for NO_2-N after extraction with H_2O (treatment procedure see above) according to Mulvaney (1996) using the CFA method (ISO 13395, 1996). The detection limit for this analysis lies at 1µgl^{-1}.

Water content: The water content of each sediment sample was determined following ÖNORM B 4410 (2009). About 20g of sediments (wet weight) were dried in the oven at 80℃ until constant weight (dry weight) and then the mass difference between the wet and the dry weight was calculated. This mass difference represented the absolute water content, which was transformed into the water content relative to the wet weight (relative water content).

Microbial abundances: About 1.5g of each sediment sample were weighed into a tube within a few hours after sampling and then fixed with 3ml stream water and 0.75ml fixing solution (2.5%

formaldehyde). All sediments were then analysed for microbial abundance after the protocol of Duhamel & Jacquet (2006), using a Cytoflex flow cytometer from Beckman Coulter. The abundances (bacteria per ml) were then divided by the dry weight of the sediment to calculate the amount of bacteria per g dry weight.

3.5.3 Biofilm sample analysis

Chlorophyll-a: 10ml of 90% acetone were added to each biofilm sample and the tube contents then were homogenized with an ultrasonic device to extract the chlorophyll-a. The samples were shaken and afterwards stored in the dark at 4℃ for 24 hours. Afterwards the samples were centrifuged and the supernatants were analysed fluorometrically for chlorophyll-a content, following the directions of Steinman, Lamberti & Leavitt (2007).

3.6 Calculations

In this chapter the formulas used for the calculation of needed NH_4Cl, physical stream parameters as well as the computation of the uptake parameters are summarized.

3.6.1 Calculation of needed NH4Cl

The following equations, based on the mass balance approach after Stream Solute Workshop (1990), were used to calculate the amount of NH_4Cl needed for the increase of concentration to the 2-, 6 and 12-fold of the background ammonium concentration:

First the desired NH_4-N concentration at plateau (during state of complete mixture of solution with stream water) was calculated:

$$C_{Plateau} = C_{Background} * f \qquad \text{[Eq.2]}$$

Then the concentration of ammonium in the carboy was determined:

$$C_{Ammonium} = \frac{\left(\left((Q+p)*C_{Plateau}\right)-\left(Q*C_{Background}\right)\right)}{p} \qquad \text{[Eq.3]}$$

The next step was to calculate the concentration of reagent (NH_4Cl^-) in the carboy:

$$C_{Reagent} = C_{Ammonium} * \left(\frac{M_r}{M_N}\right) \qquad \text{[Eq.4]}$$

The amount of reagent (in g) - needed to increase the in-stream ammonium concentration to the desired $C_{Plateau}$ - then was calculated as:

$$m_{Reagent} = \frac{V_{Water} * C_{Reagent}}{1000} \qquad \text{[Eq.5]}$$

where

$$V_{Water} = p * 3600 * t \qquad \text{[Eq.6]}$$

With:

$C_{Plateau}$... desired resulting in-stream ammonium concentration at plateau [mgl^{-1}]
$C_{Background}$...background ammonium concentration [mgl^{-1}]
f...multiplication factor to calculate 2-, 6- and 12-fold nutrient increase (2,6,12) [-]
Q…stream discharge [Ls^{-1}]
p...pump rate [Ls^{-1}]
$C_{Reagent}$...reagent (NH_4Cl^-) concentration in carboy [mg/l]
$C_{Ammonium}$...NH_4-N concentration in carboy [mg/l]
M_r...molar mass of reagent (NH_4Cl) in the water [g]
M_n...molar mass of nitrogen (N) in the water [g]
$m_{reagent}$...amount of reagent (NH_4Cl) needed [g]
V_{water}...volume of water in carboy [l]
t… time of addition [h]

The ambient NH_4-N background concentration was determined by collection of samples and analysis a few days/ weeks before the sampling.

3.6.2 Calculation of physical parameters

The average cross-sectional area (A) was calculated as the product of the average measured streambed width (w) and depth (d). The discharge (Q) then was calculated by multiplying the cross-sectional area with the surface velocity and a correction factor of 0.85 after Gordon et al. (1993).

$$Q\ [m^3/s] = A * v_{surface} * 0{,}85 \qquad \text{[Eq.7]}$$

Due to the fact that a stream, having structures such as pools, riffles or log jams, usually is a very heterogeneous system, a mean flow velocity suitable to represent the whole stream reach was determined. This was done via the electric conductivity curve measured in-stream with the conductivity meter during the addition experiments. For this purpose, the reach length l was divided through t_n (for better understanding see Figure 5).

$$v_{mean}[m/s] = {}^{l}/_{t_n} \qquad \text{[Eq.8]}$$

With:

l...reach length [m]
tn...time needed to reach half steady state conductivity plateau [s]

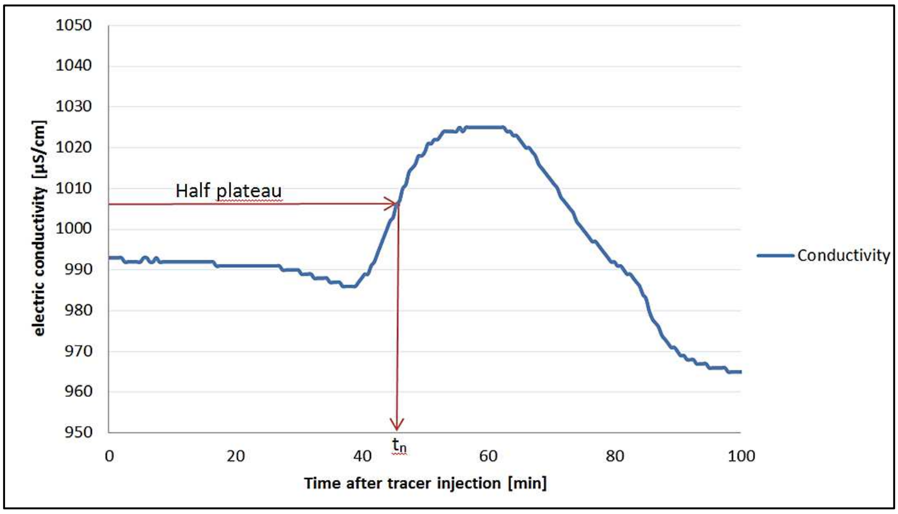

Figure 5: Electric conductivity curve over time, measured at Rußbach in summer. The red arrows show the point where half the plateau of conductivity is reached and also mark the time (t_n).

In addition, the minimum and maximum flow velocity [ms^{-1}] were determined by dividing the reach length through the time needed to reach the whole plateau and the time needed until the first increase in conductivity was visible, respectively.

An average depth, better suitable for the whole stream reach, was calculated by dividing the calculated discharge through the width and the mean flow velocity.

$$d[m] = \frac{Q}{w * v_{mean}} \qquad \text{[Eq.9]}$$

The wetted perimeter was calculated as well, using the following formula:

$$Pw\ [m] = w + 2 * d \qquad \text{[Eq. 10]}$$

Q …discharge [m^3s^{-1}]
A…mean cross-sectional area [m^2]
$v_{surface}$…mean surface flow velocity [ms^{-1}]
d… average depth [m]
w…mean width [m]
v_{mean}…mean flow velocity [m^{-1}]
P_w…mean wetted perimeter [m]

3.6.3 Calculation of ammonium uptake and uptake parameters

As a first step, the background NH_4-N concentration was subtracted from the plateau concentration of each transect in order to calculate the net concentration increase. This procedure was repeated with the electric conductivity values, representing the NaCl concentration.

Correction for background concentration:

$$Cnet_{N_x}[\mu g/l] = CPlateau_{N_x}[\mu g/l] - CBackground_{N_x}\ [\mu g/l] \qquad \text{[Eq. 11]}$$

$$Cnet_{cond_x}[\mu S/cm] = CPlateau_{cond_x}[\mu S/cm] - CBackground_{cond_x}[\mu S/cm] \qquad \text{[Eq. 12]}$$

With:

$Cnet_{Nx.}$... net NH_4-N concentration at transect x [$\mu g l^{-1}$]
$CPlateau_{Nx}$…plateau NH_4-N concentration at transect x [$\mu g l^{-1}$]
$CBackground_{Nx}$…background NH_4-N concentration at transect x [$\mu g l^{-1}$]
$Cnet_{condx.}$...net conductivity at transect x [$\mu S cm^{-1}$]
$CPlateau_{condx}$…plateau conductivity at transect x [$\mu S cm^{-1}$]
$CBackground_{condx}$…background conductivity at transect x [$\mu S cm^{-1}$]

To calculate the decrease in NH_4-N concentration relative to the start concentration, the net NH_4-N concentration of each transect then was divided by the net NH_4-N concentration of the first transect. The same was done with the electric conductivity in order to calculate the percentage of decrease in the salt concentration across the stream reach, but in this case the plateau conductivity was used, because using the percentage decrease of the net conductivity would have falsified the result.

Concentration in percent:

$$Cnet_{N_x}\ [\%] = \frac{Cnet_{N_x}[\mu g/l]}{Cnet_{N_1}[\mu g/l]} \qquad \text{[Eq. 13]}$$

$$Ccond_x\ [\%] = \frac{Ccond_x[\mu S/cm]}{Ccond_1[\mu S/cm]} \qquad \text{[Eq. 14]}$$

With:

$Cnet_{Nx}$… net NH_4-N concentration at transect x [$\mu g l^{-1}$]
$Cnet_{N1}$… net NH_4-N concentration at transect 1 [$\mu g l^{-1}$]
$C_{cond\ x}$… plateau conductivity at transect x [$\mu S cm^{-1}$]
$C_{cond\ 1}$… plateau conductivity at transect 1 [$\mu S cm^{-1}$]

Afterwards the concentrations in percent were used to correct the NH_4-N value in terms of possible losses. Losses can be caused by dilution with groundwater, dispersion or advection and have to be considered in the calculation as they can alter the results. To correct for groundwater-input induced dilutions, the logarithmic ratio of net ammonium concentrations (in %) measured during plateau conditions of each transect over the net Cl concentrations (in %) of the respective transect was calculated.

Correction for losses:

$$\ln(Ccorr_{N_x})[-] = ln\left(\frac{Cnet_{N_x}[\%]}{Cnet_{cond_x}\ [\%]}\right) \qquad \text{[Eq. 15]}$$

This was repeated for each transect, the nutrient uptake parameters then were calculated “from the longitudinal decline of the corrected nutrient concentrations during plateau conditions” with the help of a first-order regression curve (Weigelhofer et al., 2012) according to the Stream Solute Workshop (1990):

Nutrient uptake length S_w

To determine the uptake length, the change in the natural logarithm of the ratio nutrient/tracer concentration versus distance downstream was plotted (Sheibley et al., 2014). The ammonium uptake length for each addition then was calculated as the negative inverse of the uptake regression curve slope *k*

$$Sw\ [m] = -{}^{1}/_{k} \qquad \text{[Eq.16]}$$

With:

k... slope of uptake regression curve

Nutrient uptake rate U_t

The nutrient uptake rate (in $\mu g m^{-2} s^{-1}$) was calculated according to equation 17:

$$Ut\ [\frac{\mu g}{m^2} * s] = \frac{Cp*Q}{Sw*Pw} \qquad \text{[Eq. 17]}$$

With *C* being the ammonium background concentration [mgL^{-1}], Q the stream discharge [Ls^{-1}], S_w representing the uptake length [m] and P_w the average stream wetted perimeter [m].

Mass transfer coefficient V_f

As the mass transfer coefficient is related to the uptake length S_w, it is calculated using equation 18:

$$Vf\ [\frac{m}{s}] = \frac{d*v}{Sw} \qquad \text{[Eq. 18]}$$

Where *d* represents the mean water depth [m] and *v* the mean current velocity [$m\ s^{-1}$] calculated from the conductivity curve. It is a measure of the biotic uptake rate in the stream relative to the nutrients available.

3.7 Statistical analyses

All the data were recorded digitally and organised with the program MS Excel. The statistical analyses were performed using the program IBM SPSS Statistics Version 21 for Windows (Armonk, NY: IBM Corp., released 2012). All data were tested for normality using the Kolmogorov-Smirnov test. The uptake regression of each addition was tested for significance, for this purpose a null hypothesis, stating that the regression coefficient equals zero, was tested.

In order to test if the uptake regressions of the individual ammonium additions significantly differed from each other, an ANCOVA (analysis of covariance) was performed. To examine the relationships between ambient ammonium concentrations and the ammonium uptake, as well as possible correlations among hydromorphology, ammonium uptake, biotic and sedimentary characteristics, Spearman‘s rank correlation was used. Spearman’s correlation was useful due to low sample size, lack of normality and possible outliers.

Differences between the reaches grouped into “nutrient loading groups” in terms of in-stream ammonium uptake were analysed using Kruskal-Wallis-Test. This test was also applied to determine whether hydrological and morphological, as well as physical and chemical parameters, differed between the groups. In addition, all the parameters were tested across spring and summer to detect significant differences between the two seasons. For this purpose, the Mann-Whitney-U-Test was used because of the lack of normal distribution concerning the data.

To calculate an uptake length at ambient ammonium concentration, at first an attempt after Payn et al. (2005) was tried. But the extrapolation following the Payn-method was not successful, as it requires an almost linear positive correlation between the NH_4-N concentration and the uptake length, which could only be found in very few of the addition experiments. For group comparisons, as well as for correlations with influencing parameters, only the uptake results of the first additions were taken from each stream, because these data best resembled “ambient” conditions and did not aim at saturation; if the first addition did not achieve a plateau of at least 2.5 fold the background, the uptake results of the next highest addition were taken.

An alpha level of 0.05 was applied throughout the analyses.

4. Results

4.1 Water chemistry

In spring the NH_4-N concentration ranged between 4 and 193µgl^{-1}, in summer between 4 and 175µgl^{-1} (compare Table 12, appendix). Figure 6 shows a comparison and ranking of the ammonium concentration in the stream water in spring and summer. For further details concerning NO_3-N, NO_2-N and DOC concentrations see Table 12 (appendix).

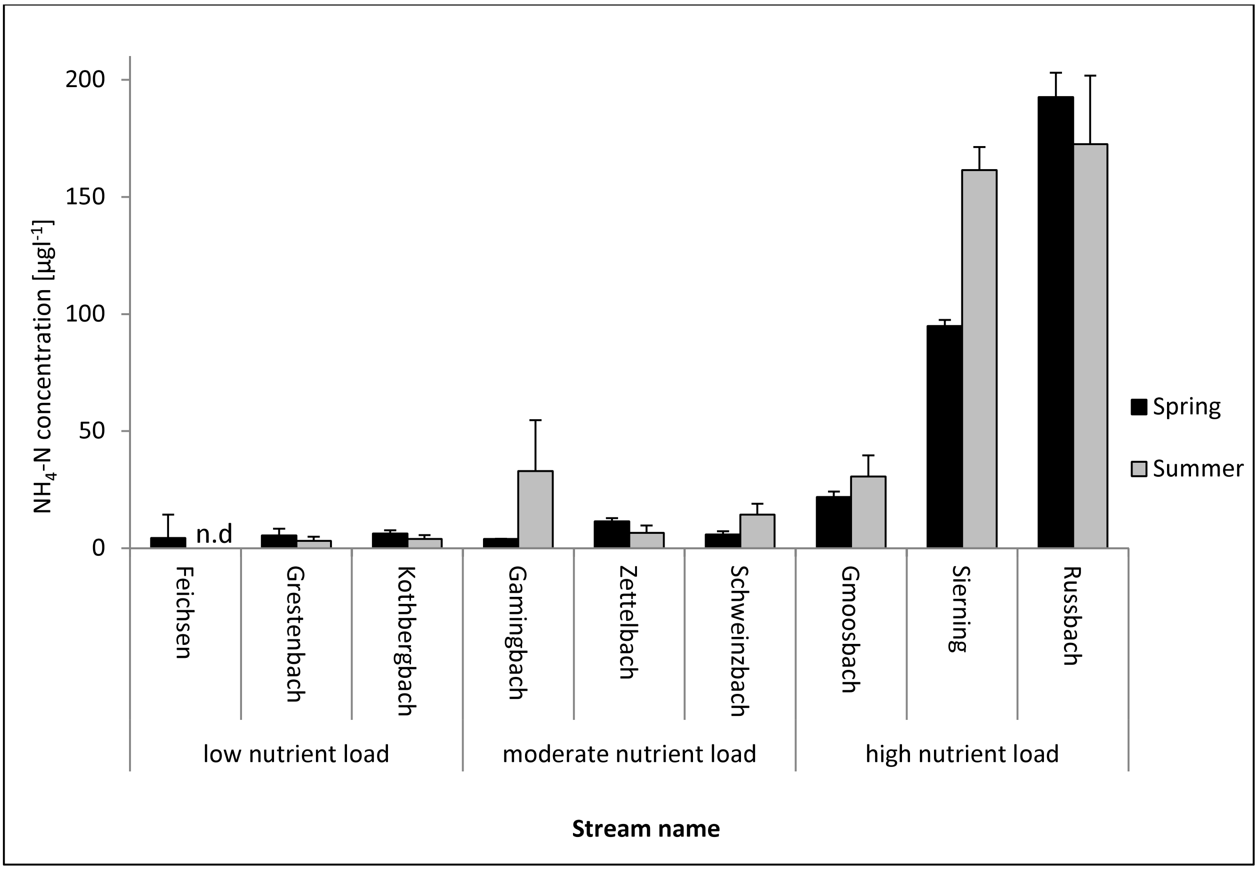

Figure 6: Comparison of ammonium concentrations in water [µgl^{-1}] between spring and summer (mean plus/ minus standard deviation, n=3-6, n.d....no data)

The stream sequence, ranked according to increasing ammonium concentrations, did not exactly match the expectations derived from the land use gradient. Because this thesis focuses on NH_4-N, and also out of statistical reasons, the streams were finally classified according to their average in-stream NH_4-N concentration (calculated as the mean from spring and summer) with additional consideration of sedimentary NH_4-N concentration in order to affirm or argue for or against the classification (see e.g. Gmoosbach, chapter 4.2, Table 13).

The Sierning in general was much higher loaded than expected and was therefore classified as “high” nutrient loading group. The Gamingbach showed unexpected increases in NH_4-N concentration in summer, which might be due to manure application or release from sediments. It was therefore not considered as “lowly loaded”, as an adaptation to ammonium pulses could not be ruled out. Sierning and Gmoosbach showed significantly higher NH_4-N concentrations in summer than in spring, while the NH_4-N concentration in the Rußbach decreased in summer.

The final classes derived from the ambient ammonium concentrations (see also Figure 6) therefore are:

- **“Low” nutrient loading:** Feichsen, Grestenbach, Kothbergbach
- **“Moderate” nutrient loading:** Gamingbach, Zettelbach, Schweinzbach
- **“High” nutrient loading:** Gmoosbach, Sierning, Rußbach. Gmoosbach however ranges in group “moderate” according to the NH_4-N concentration in the water.

4.1.1 Comparison of “nutrient loading” groups and seasons – water compartment

In order to identify statistically significant differences between hydromorphology as well as physical, chemical and uptake parameters of the nutrient loading groups “low”, “moderate” and “high” (defined in chapter 4.1), the groups were tested against each other. In addition, a comparison of the values from spring and summer was performed to identify significant differences between seasons.

Group comparison

Regarding the water chemistry, significant differences among the groups could be found for NH_4-N (Kruskal-Wallis-Test, p=0.000, n=86), NO_2-N (Kruskal-Wallis-Test, p=0.000, n=89), NO_3-N (Kruskal-Wallis-Test, p=0.000, n=86) and also the DOC content (Kruskal-Wallis-Test, p=0.000, n=92), all parameters showing the highest values in the group of “high” nutrient loading (compare Figure 7).

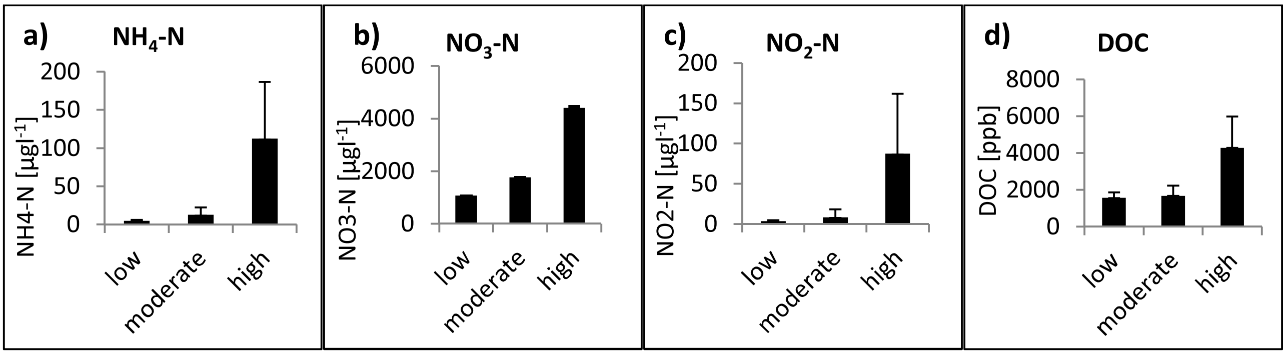

Figure 7: Mean NH_4-N (a), NO_3-N (b), NO_2-N (c) concentration and DOC content (d) according to level of pollution (mean plus standard deviation, n=23-31).

Seasonal comparison

The NH_4-N concentration in the water of all streams tested together did not differ significantly between the seasons (Mann-Whitney-U-Test, p=0.234, n=106), neither did NO_3-N (Mann-Whitney-U-Test, p=0.610, n=87). NO_2-N concentration in the water however differed significantly (Mann-Whitney-U-Test p=0.010, n=85). As can be seen in Figure 8, the average concentration of all different nitrogen forms in water was higher in summer than in spring. The DOC content in the water was significantly higher in summer than in spring (Mann-Whitney-U-Test, p=0.000, n=96) (see Table 12). If testing differences between spring and summer while grouping the streams into the different pollution groups, in the “low pollution” group significantly lower NH_4-N (Mann-Whitney-U-Test, p=0.001, n=24) and NO_2-N concentrations (Mann-Whitney-U-Test, p=0.031, n=28) were found for summer. DOC values were found to be significantly higher in summer in the “highly polluted” group (Mann-Whitney-U-Test, p=0.004, n=35).

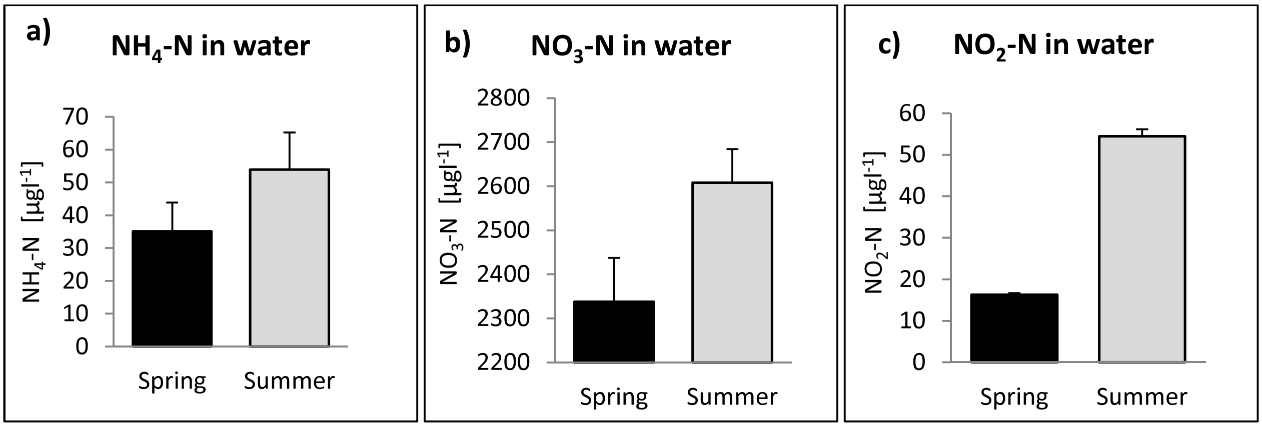

Figure 8: Differences in mean water N content [µgl^{-1}] between spring and summer (mean plus standard deviation, n=9-10), a) NO_3-N-concentration, b) NO_2-N concentration, c) NH_4-N concentration

4.2 Sediment chemistry

Figure 9 shows the NH_4-N concentration in the stream sediments. It is evident that the Sierning generally showed a very low NH_4-N concentration in the sediments in spring and summer, while having a very high NH_4-N concentration in the water. At the same time the Gmoosbach and Rußbach both showed high NH_4-N concentrations in the sediments. Even though the Gmoosbach did show moderate nutrient loading in the water, the high sedimentary NH_4-N concentration in the sediments supports the decision of the classification to the “high” nutrient loading group. For the different loading groups a seasonal pattern could be found: In the “low” and “moderately” loaded streams the sedimentary NH4-N concentration was higher in summer than in spring, while in the “high” loading group it was the other way round. For further details, concerning the NO_3-N and NO_2-N concentrations, refer to Table 13 (appendix).

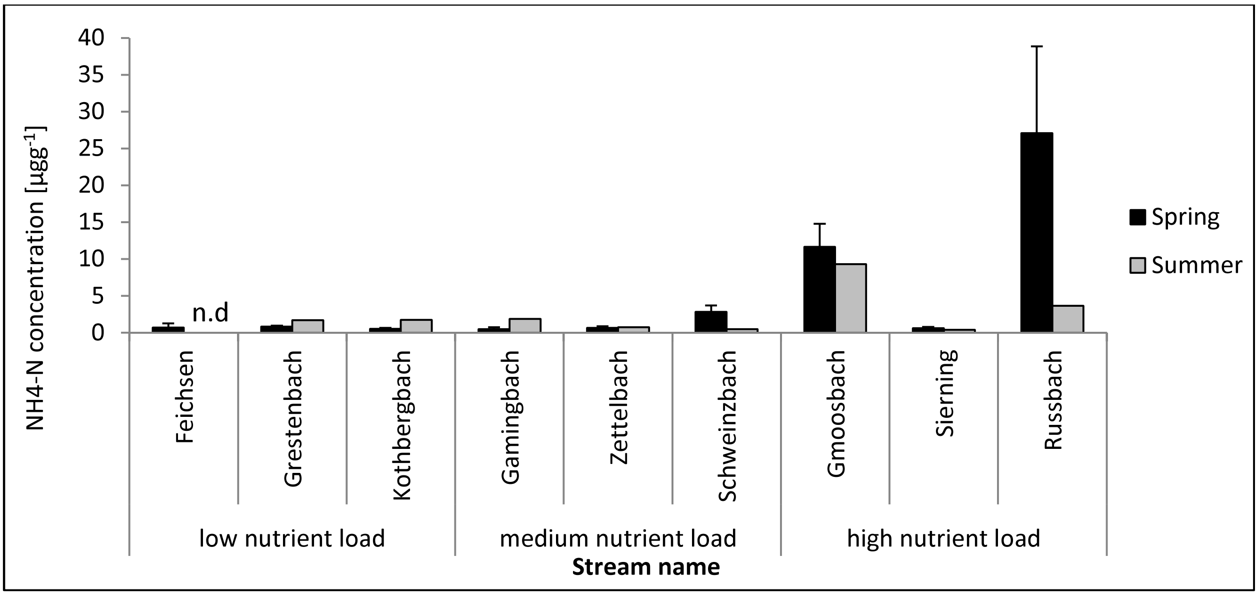

Figure 9: Comparison of ammonium concentrations in the sediments [µgg^{-1}] between spring and summer, (mean plus standard deviation, n=5, n.d...no data)

4.2.1 Comparison of “nutrient loading” groups and seasons - sediments

Group comparison

In terms of sediments, the “high” nutrient loading group showed significantly higher NH_4-N (Kruskal-Wallis-Test, p=0.000, n=190), NO_3-N (Kruskal-Wallis-Test, p=0.000, n=130) and NO_2-N concentrations (Kruskal-Wallis-Test, p=0.000, n=130) than the other two groups (see Table 13, Figure 9). The organic matter (OM) content of the sediments differed significantly between the groups as well, and was highest in the group with “high” nutrient loading (Kruskal-Wallis-Test p=0.000, n=132) (Table 13).

Seasonal comparison

No significant difference between NH_4-N in the sediments across the two seasons could be found. The sedimentary NO_3-N however differed significantly (Mann-Whitney-U-Test, p=0.000, n=133), as well as the sedimentary NO_2-N concentration (Mann-Whitney-U-Test, p=0.000, n=135) (Table 13), with the average concentration of all nitrogen species in the sediments being higher in spring than in summer if all streams were taken together (as can be seen in Figure 10). The OM content in the sediments also was significantly higher in spring than in summer (Mann-Whitney-U, p=0.002).

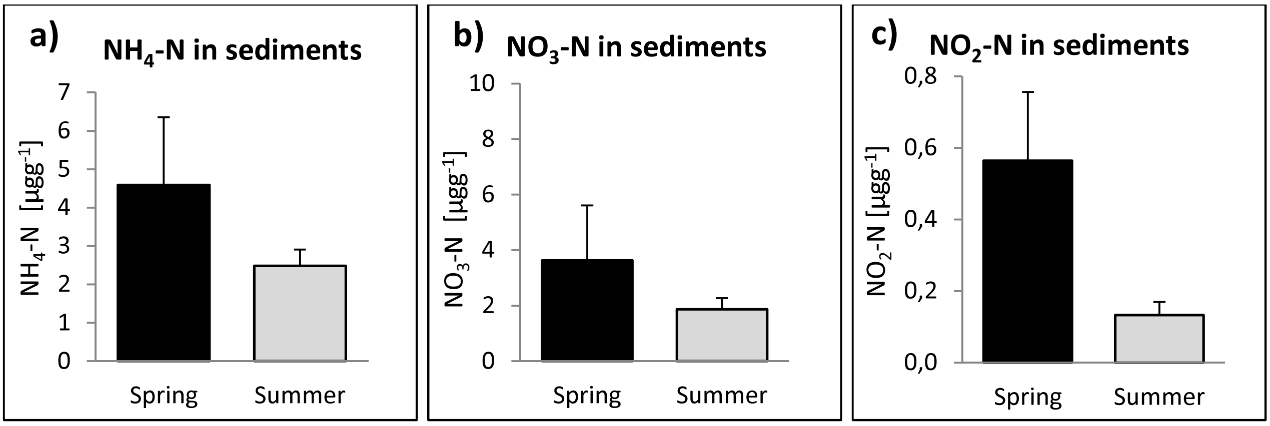

Figure 10: Differences in mean sedimentary N- content [µgg^{-1}] between spring and summer (mean plus standard deviation, n=50, a) NO_3-N-concentration, b) NO_2-N concentration, c) NH_4-N concentration

4.3 Ammonium uptake

In spring 30 short-term nutrient addition experiments were performed at 9 streams, resulting in 23 significant regression curves. Of the 24 additions performed in summer, 19 showed a significant NH_4-N uptake.

It was not easy to produce an exact increase of the 2-, 6- and 12-fold background concentration, as it was originally intended. The background samples taken for calculation of needed NH_4Cl amount (see 3.6.1) only represented a short-time picture of the actual ammonium concentration; changes due to fertilizer application or heavy rainfalls washing the nutrients into the stream could happen very quickly. In addition, the usually decreased discharge in summer increased the ammonium concentration (due to less dilution). Thus, final plateau conditions ranged between the 1 and 86-fold of the ammonium background concentrations, depending on how well the background and the discharge were estimated. The results of the uptake parameter calculations for the relevant additions in spring and summer are summarized in Table 2.

*Table 2: Results of nutrient addition experiments in spring and summer 2015. The table shows the background NH_4-N concentrations as well as plateau NH_4-N concentrations, the increase factors, uptake lengths, mass transfer coefficients and uptake rates. The * indicates non-significant uptake which was still used as an estimation value*

Stream Name	Spring NH_4 at plateau [µgl^{-1}]	Summer NH_4 at plateau [µgl^{-1}]	Spring Uptake length [m]	Summer Uptake length [m]	Spring Mass transfer coefficient [mm min^{-1}]	Summer Mass transfer coefficient [mm min^{-1}]	Spring Uptake rate [µgm^{-2}s]	Summer Uptake rate [µgm^{-2}s]	Spring Increase factor [-]	Summer Increase factor [-]
Feichsen	10.42	-	94	-	13.06	-	0.90	-	2.4	-
Feichsen	25.58	-	n.s.	-	n.s.	-	n.s.	-	5.8	-
Feichsen	96.00	-	714	-	1.73	-	0.12	-	21.8	-
Grestenbach	23.27	25.56	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	4.4	6.5
Grestenbach	92.73	138.84	1667	238	2.26	4.94	0.17	0.28	16.5	35.0
Grestenbach	189.64	337.85	667	435	5.65	2.71	0.43	0.16	33.6	86.4
Kothbergbach	5.38	12.36	n.s.	192	n.s.	16.52	n.s.	0.99	0.8	3.09
Kothbergbach	25.00	23.60	119	238	38.68	13.34	3.70	0.80	4	5.90
Kothbergbach	50.67	84.43	333	263	13.81	12.07	1.30	0.73	8.1	21.11
Gamingbach 1	16.00	99.00	29	102	570.52	11.19	10.20	6.16	5.3	3.0
Gamingbach1	210.17	166.61	263	400	62.84	2.86	2.70	1.43	52.5	5.0
Gmingbach1	-	711.98	-	370	-	3.08	-	1.70	-	24.0
Gamingbach 2	18.73	-	35	-	438.71	-	18.50	-	4.7	-
Gamingbach 2	90.63	-	385	-	40.31	-	1.70	-	22.7	-
Zettelbach	43.28	29.36	n.s.	49	n.s.	18.33	n.s.	1.72	3.8	4.1
Zettelbach	136.06	134.45	625	161	2.11	5.52	0.37	0.50	11.8	20.5
Zettelbach	306.52	175.02	526	357	2.51	2.49	0.44	0.23	26.7	27.3
Schweinzbach	28.08	53.45	217	588	10.14	2.10	0.85	0.33	4.7	3.7
Schweinzbach	61.50	154.64	385	345	5.73	3.58	0.48	0.56	10.3	10.8
Schweinzbach	159.25	343.00	667	769	3.31	1.60	0.28	0.25	26.8	23.9
Gmoosbach	78.40	171.00	10000*	909	0.62*	2.67	0.2*	1.09	3.5	5.4
Gmoosbach	228.48	363.87	5000	2000*	1.25	1.21*	0.36	0.5*	10.9	11.7
Gmoosbach	344.76	745.87	2500	10000*	2.49	0.24*	0.70	0.01*	16.8	23.9
Sierning	113.18	180.57	1667	76	1.70	16.39	2.10	37.20	1.2	1.1
Sierning	136.64	444.36	833	556	3.42	2.25	4.30	5.11	1.4	2.8
Sierning	277.73	992.44	769	556	3.70	2.25	4.60	5.11	2.9	6.1
Rußbach	378.33	142.80	217	769	14.65	1.79	42.49	5.11	1.4	0.8
Rußbach	617.50	444.24	1111	2500*	2.87	0.55*	8.31	1.49*	3.8	2.57*
Rußbach	1861.1	1229.78	3333	10000*	0.96	0.14*	2.77	0.3*	8.0	7.00*

4.3.1 Comparison of “nutrient loading” groups and seasons - uptake parameters

Group comparison

For this comparison always the first uptake parameter per addition and stream, which was gained at an ammonium plateau ≥ 2.5-fold ambient concentration, was used. Spring and summer data were tested together. Using this approach, significant differences in terms of the mass transfer coefficient V_f could be found between the groups of “low” and “high” nutrient loading, with the V_f being significantly lower in the “high” nutrient loading group (Mann-Whitney-U p= 0.030, n=12, see Table 3) and in terms of uptake length S_w for the groups “moderate” and “high” nutrient loading, with significantly higher lengths for the “high” nutrient loading group (Mann-Whitney-U p= 0.026, n=12, Table 3). No other significant differences between the groups were found. If excluding the Gamingbach with its exceptionally high V_f from the analysis, a clear decrease in V_f with increasing ammonium concentration can be observed (see Figure 11). The pattern in U_t illustrates the increase in uptake rate in moderately polluted streams, probably due to adaption to short-term nutrient pulses.

Table 3: Mann-Whitney-U-Test p results, n=2-4, S_w…uptake length, U_t…uptake rate, V_f…mass transfer coefficient, 1…group “low pollution”, 2…group “moderate pollution”, 3…group “high pollution”

	1&2	2&3	1&3
S_w [m]	n.s.	**0.026**	n.s.
U_t [$\mu g m^{-2} s^{-1}$]	n.s.	n.s.	n.s.
V_f [$mm min^{-1}$]	n.s.	n.s.	**0.030**

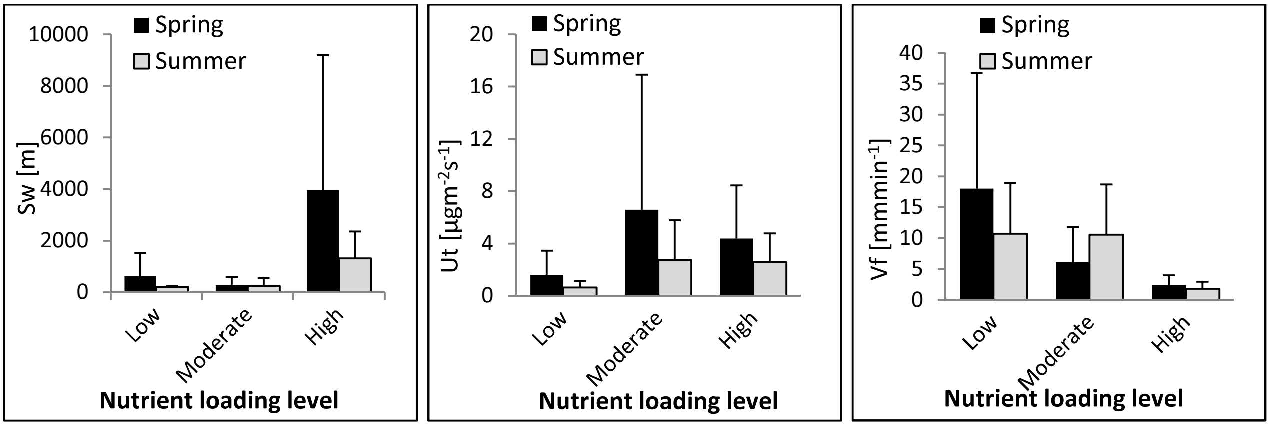

Figure 11: Uptake parameters grouped according to level of nutrient loading; mean plus standard deviation, n=2-3) S_w…Uptake length [m], U_t…Uptake rate [$\mu g m^{-2} s^{-1}$], V_f…Mass transfer coefficient [$mm min^{-1}$].

Seasonal comparison

No significant difference between the seasons could be found, neither for the uptake length, nor for the uptake rate or the mass transfer coefficient (Mann-Whitney-U-Test, $p>0.05$, n=45-47, compare Figure 12 or Table 2).

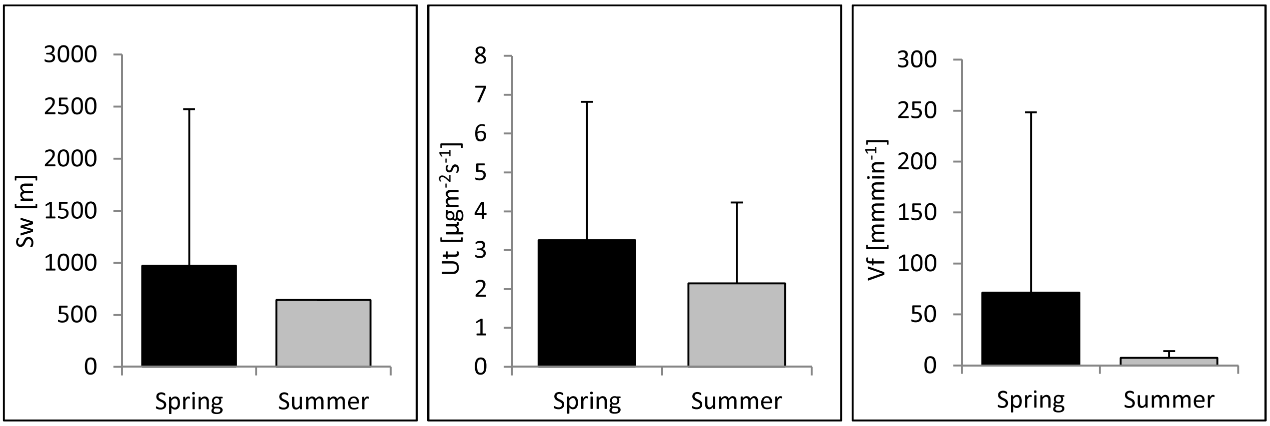

Figure 12: Average S_w (uptake length), U_t (uptake rate) and V_f (mass transfer coefficient), comparison between spring and summer (Mean plus standard deviation, n=8-9)

4.3.2 Comparison of uptake lengths across season and nutrient loading gradient

In order to directly compare the uptake lengths of lowly and moderately loaded with those of heavily loaded streams, the uptake lengths at similar plateau concentrations were compared, regardless of season and pollution gradient. The analysis showed the following: The highly loaded Rußbach showed a much higher uptake length (S_w=769m) compared to the lowly loaded Grestenbach (S_w=238m) under similar plateau conditions (142µgl^{-1} Rußbach, 139µgl^{-1} Grestenbach), probably due to the ammonium background loading. A comparison of the Sierning with Zettelbach (both with plateau of 136µgl^{-1}) showed a higher uptake length for the Sierning (833m vs. 633m). The Gmoosbach showed an uptake length of 10000m at a plateau concentration of 78µgl^{-1}, while the Kothbergbach under similar plateau conditions (84µgl^{-1}) only needed 263m to take up the nutrients. When comparing the Schweinzbach in summer at a plateau of 343µgl^{-1} with the Gmoosbach in spring (background of 345µgl^{-1}), the S_w of the Schweinzbach was only 769m, while the S_w of the Gmoosbach was 2500m. The same applied if comparing the Gmoosbach to the Grestenbach, which at a plateau of 338µgl^{-1} had a S_w of 435m in summer. Even though in summer the Gamingbach showed a higher background concentration than the Gmoosbach (33µgl^{-1} vs. 20µgl^{-1}), the Gamingbach still showed a much lower uptake length (S_w= 370m) than the Gmoosbach (S_w=10.000m) at a comparable plateau concentration (712 vs. 746µgl^{-1}). The results are summarised in Table 4.

Table 4: Comparison of uptake lengths of lowly, moderately and highly loaded streams at similar NH_4-N plateau (Sw…Uptake length [m], low and moderate loading= green, high loading= red)

	Rußbach	**Grestenbach**
Plateau [$\mu g l^{-1}$]	142	139
Sw [m]	769	238

	Sierning	**Zettelbach**
Plateau [$\mu g l^{-1}$]	136	136
Sw [m]	833	625

	Gmoosbach	**Kothbergbach**
Plateau [$\mu g l^{-1}$]	79	84
Sw [m]	10000	263

	Gmoosbach	**Schweinzbach**
Plateau [$\mu g l^{-1}$]	345	343
Sw [m]	2500	769

	Gmoosbach	**Grestenbach**
Plateau [$\mu g l^{-1}$]	345	338
Sw [m]	2500	435

	Gmoosbach	**Gamingbach**
Plateau [$\mu g l^{-1}$]	746	712
Sw [m]	10000	370

4.4 Hydromorphology

During the study period, the discharges ranged between 84-1042Ls^{-1} in spring and 43-267Ls^{-1} in summer. Overall the average water depths varied between 0.11 and 1.05m and the flow velocity between 0.04 and 0.33ms^{-1} at the time of the release experiments. For further details see Table 5, holding a summary of the morphological and physical characteristics, a short description of surrounding and catchment land use and also the percentage of forest in the catchment.

4.4.1 Comparison of “nutrient loading” groups and seasons - hydromorphology

Group comparison

No significant differences could be found in the hydromorphological and physical parameters discharge, flow velocity, depth, wetted perimeter and water temperature among the groups (Kruskal-Wallis-Test, p>0.05, n=17-18).

Seasonal comparison

The discharge between summer and spring differed significantly (Mann-Whitney-U, p=0.000, n=55), with discharge being higher in spring. The widths also differed significantly between spring and summer (p=0.010, n=53), as well as wetted perimeter (Mann-Whitney-U-Test, p=0.034, n=18) and flow velocity (Mann-Whitney-U-Test, p=0.003, n=18), all of them being higher in spring than in summer. No significant differences were found for the depths (Mann-Whitney-U-Test, p> 0.05). For detailed results see Table 5.

Table 5: *Summary of morphological, hydrological and physical stream properties as well as particularities and land use classification (mean, n = 5-96)*

Stream Name	Surrounding land use	Forest in the catchment [%]	Discharge [Ls^{-1}]		Flow velocity [ms^{-1}]		Mean depth [m]		Mean width [m]		Bankful width [m]		Particularities	
			Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
Feichsen	**Meadows & crop fields**	54	86	-	0.15	-	0.16	-	4.17	-	4.49	-	-	-
Grestenbach	**Forest & meadows**	54	193	50	0.19	0.09	0.25	0.22	3.07	2.53	3.57	2.97	-	-
Kothbergbach	**Forest**	100	391	267	0.33	0.19	0.24	0.28	5.10	5.05	5.57	5.60	-	-
Gamingbach 1	**Forest & meadows**	100	873	70	0.26	0.10	0.98	0.19	3.38	3.70	5.34	4.07	GW inflow	Wastewater treatment plant (WWTP)
Gamingbach 2	**Forest & meadows**	100	1042	-	0.26	-	1.05	-	3.78	-	5.88	-	-	-
Zettelbach	**Meadows & fields**	58	84	43	0.12	0.04	0.18	0.34	3.83	2.90	4.20	3.57	-	-
Schweinzbach	**Meadows & fields**	<1%	133	44	0.11	0.04	0.33	0.53	3.63	2.12	4.30	3.17	-	Very low flow velocity because of beaver dams
Gmoosbach	**crop fields**	3	260	93	0.31	0.11	0.33	0.37	2.50	2.30	3.17	3.03	trapezoid profile	Strong fluctuations in NH_4-N and water level due to WWTP, trapezoid profile, logging in stream
Sierning	**Meadow & crop fields**	21	133	54	0.13	0.08	0.37	0.26	2.80	2.60	3.54	3.12	-	-
Rußbach	**crop fields**	10	181	80	0.29	0.20	0.18	0.12	3.41	3.50	3.78	3.73	-	WWTP effluent upstream

4.5 Benthic communities and stream metabolism

4.5.1 Stream metabolism

During the two seasons, GPP ranged between 0.9 and 7.2gCm^{-2}d. CR values ranged between 2.4 and 23.0gCm^{-2}d, while the ratio GPP/CR took values from 0.1 to 0.8 [-], indicating that all streams were heterotrophic (GPP/CR <1). Oxygen values varied from 4.7 to 13.4mgl^{-1} and the temperature ranged from a minimum of 5.8 to a maximum of 37.6℃. For further details refer to Table 6.

Table 6: Metabolic parameters of the sampled streams in spring and summer (GPP…gross primary production [gCm^{-2}d], CR…community respiration [gCm^{-2}d], P/R...ratio between GPP and CR [-], Omin, Omax…minimum/maximum oxygen concentration [mgl^{-1}], Tmin, Tmax…minimum/maximum water temperature [℃], spr…spring, sum…summer, data with „-“ were not measured, n=1)

	GPP		**CR**		**P/R**		**Omin**		**Omax**		**Tmin**		**Tmax**	
Stream name	**spr**	**sum**	**spr**	**sum**	**spr**	**sum**	**spr**	**sum**	**spr**	**sum**	**spr**	**sum**	**spr**	**sum**
Feichsen	6.7	-	11.6	-	0.6	-	10.0	-	11.9	-	7.7	-	16.9	-
Grestenbach	1.1	-	1.5	-	0.7	-	10.0	-	11.5	-	5.8	-	13.8	-
Kothbergbach	3.1	3.2	23.0	20.5	0.1	0.2	9.1	8.3	10.4	9.8	8.6	10.6	13.8	14.1
Gamingbach	4.1	1.5	17.0	4.9	0.2	0.3	10.4	8.7	11.4	9.9	6.0	12.9	14.0	18.7
Zettelbach	1.8	4.5	2.4	11.7	0.8	0.4	8.0	7.5	11.8	9.6	9.8	16.5	14.7	19.8
Schweinzbach	3.9	6.7	6.7	11.6	0.6	0.6	9.7	9.9	10.5	11.9	10.2	7.7	16.9	11.9
Gmoosbach	6.5	2.7	8.2	5.0	0.8	0.5	8.0	4.7	13.4	11.3	8.0	17.6	18.4	37.6
Sierning	5.4	4.3	9.9	6.1	0.6	0.7	8.6	7.6	11.6	10.7	9.4	15.2	14.5	17.8
Russbach	7.2	0.9	10.8	7.2	0.7	0.1	9.1	6.8	12.5	8.1	6.9	19.2	12.6	23.2

Figure 13 shows the results grouped after increasing level of nutrient load (“low”, “moderate” and “high”). In spring, GPP was highest in the loaded streams, while in summer the lowest values were found in this group. CR in summer decreased with increasing load, while the spring value was quite stable over all three categories. P/R increased with nutrient loading level in both spring and summer, whereas the average P/R was generally higher in spring.

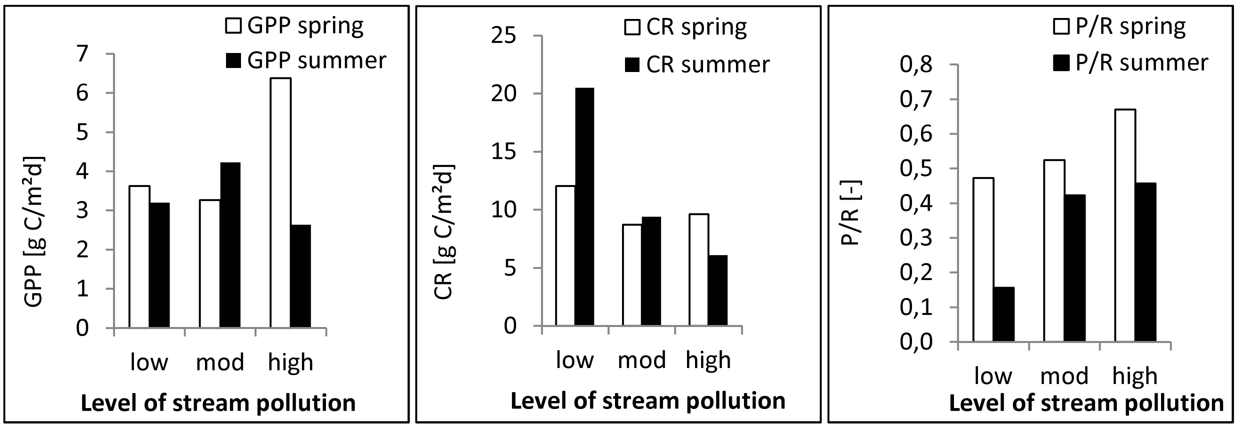

Figure 13: Metabolism results grouped after level of nutrient loading (mean, n=2-3, GPP…gross primary production, CR…community respiration, P/R…GPP/CR)

No significant differences in metabolism parameters could be found between the nutrient loading groups, a seasonal comparison revealed significantly higher O_{min} (Mann-Whitney-U-Test p=0.031) and O_{max} (Mann-Whitney-U-Test p=0.023) concentrations in spring. No other differences could be observed.

4.5.2 Chlorophyll-a

Average chlorophyll-a concentration ranged from 13.6 to 507.9µgcm^{-2} in spring and from 5.9 to 100.5µgcm^{-2} in summer, with the highest overall concentrations found in the Rußbach. For further details see Table 7. No significant differences between the nutrient loading groups or between the seasons could be found.

4.5.3 Microbial abundance

The amount of microbial abundances in the sediments in summer ranged between 1.74 and 24.93 billion bacteria per g dry weight, with the highest value found for the Rußbach (compare Table 7). No significant differences between the nutrient loading groups could be found.

Table 7: Microbial abundance in sediment in summer [in billion bacteria per g dry weight], spring and summer chlorophyll-a content in biofilm, algae and fine sediments [µgcm^{-2}] (mean plus standard deviation, n=10)

	Benthic chlorophyll-a		**Microbial abundances**
Stream name	**spring**	**summer**	**summer**
Feichsen	37.1 ± 23.33	-	-
Grestenbach	168.1 ± 138.54	22.62 ± 24.09	1.74 ± 1.4
Kothbergbach	13.57 ± 6.72	5.87 ± 2.19	8.96 ± 3.5
Gamingbach	18.87 ± 7.62	16.53 ± 2.34	3.8 ± 1.9
Zettelbach	63.2 ± 39.49	7.18 ± 3.19	2.11 ± 1.1
Schweinzbach	74.74 ± 31.5	100.45 ± 113.33	4.49 ± 2.0
Gmoosbach	15.15 ± 14.84	5.6 ± 2.17	9.81 ± 2.4
Sierning	32.14 ± 15.62	2.83 ± 2.09	3.58 ± 2.2
Russbach	507.85 ± 445.36	49.99 ± 24.61	24.93 ± 11.0

4.6 Correlations

4.6.1 Correlations of uptake parameters with water chemistry

For the uptake lengths of both seasons, significant positive correlations with NO_2-N were found (compare Table 8). Summer data held both significantly positive relationships with NO_3-N (Spearman, r_S =0.714*, n=7) and NO_2-N (Spearman, r_S=0.857*, n=7). No correlations between uptake rate and in-stream nitrogen concentration could be found, neither for all data together nor grouped into spring and summer. A significantly negative correlation with the mass transfer coefficient V_f could be found for all N species (Table 8). For summer only, a significant decrease in V_f could be found in context with increasing NO_3-N concentration (Spearman, r_S =-0.714*, n=7), but also for NO_2-N (Spearman, r_S =-0.833*, n=7). A good correlation between uptake length S_w and DOC (Spearman, r_S= 0.704**), as well as between V_f and DOC (Spearman, r_S=-0.792**) was found (Table 8).

The analysis showed that the uptake lengths in general became higher with increasing NH_4-N concentration, while uptake rates and mass transfer coefficients decreased.

Table 8: Spearman's rank correlation between uptake parameters and ambient N concentrations in water, with significance level (S_w…Uptake length [m], U_t… Uptake rate [$\mu gm^{-2}s^{-1}$], V_f…Mass transfer coefficient [$mmmin^{-1}$]), n=18

	NH_4-N [μgl^{-1}]	NO_3-N [μgl^{-1}]	NO_2-N [μgl^{-1}]	DOC [ppb]
S_w [m]	n.s.	n.s.	**0.662****	**0.704****
U_t [$\mu gm^{-2}s^{-1}$]	n.s.	n.s.	n.s.	n.s.
V_f [$mmmin^{-1}$]	**-0.556***	**-0.525***	**-0.743****	**-0.792****

* $p < 0.5$

** $p < 0.01$

4.6.2 Correlations of sediment chemistry with water chemistry and uptake parameters

Water chemistry

Table 9 shows the correlations between the different chemical parameters in the water and the sediments. There was a significant positive correlation between all nitrogen species among themselves, as well as between all nitrogen species and the DOC content in the water column. Of the nitrogen forms in the sediment however, none was found to be significantly positive correlated to the DOC in the water. No correlation of the sediment parameters among themselves or between the sediment and water parameters could be found.

Table 9: Summary of Spearman's correlations between in-stream and sedimentary chemical parameters (spring and summer together), with significance level (DOC...dissolved organic carbon [ppb]), n=18

	Water NO_3-N [μgl^{-1}]	Water NO_2-N [μgl^{-1}]	Sediment NH_4-N [μgg^{-1}]	Sediment NO_3-N [μgg^{-1}]	Sediment NO_2-N [μgg^{-1}]	DOC [ppb]
Water NH_4-N [μgl^{-1}]	**0.661****	**0.650****	n.s.	n.s.	n.s.	**0.626****
Water NO_3-N [μgl^{-1}]		**0.895****	n.s.	n.s.	n.s.	**0.822****
Water NO_2-N [μgl^{-1}]			n.s.	n.s.	n.s.	**0.946****
Sediment NH_4-N [μgg^{-1}]				n.s.	n.s.	n.s.
Sediment NO_3-N [μgg^{-1}]					n.s.	n.s.
Sediment NO_2-N [μgg^{-1}]						n.s.

* $p < 0.05$

** $p < 0.01$

Uptake parameters

If regarding only the additions above 2.5-fold increase, no positive correlations between any of the three uptake parameters $S_{w,}$ U_t or V_f and the sedimentary N concentration could be found (Spearman, p>0.05, n=17). If regarding the seasons separately, only one positive correlation between S_w and NO_2-N was found (Spearman, r_S= 0.711*, n=9).

4.6.3 Correlations of uptake parameters with hydromorphology

A significant negative correlation between uptake length S_w and wetted perimeter P_w could be found, as well as a positive correlation between mass transfer coefficient V_f and P_w. The same pattern could be found for the average stream width. No correlations with any other hydromorphological parameter or the simplified transient storage parameters v_{min}/v_{mean} and d/w. were found (compare Table 10).

Table 10: Spearman's rank correlation between hydromorphological and uptake parameters, with significance level (Q…discharge, v…flow velocity, vmin,max…minimum/maximum flow velocity, d…average streambed depth, w…average streambed width, P_w…wetted perimeter, S_w…Uptake length [m], U_t… Uptake rate [$\mu gm^{-2}s^{-1}$], V_f…Mass transfer coefficient [$mmmin^{-1}$]), n=18

	Q [m^3s^{-1}]	**v [ms^{-1}]**	**vmin [ms^{-1}]**	**vmax [ms^{-1}]**	**vmin/vmean [ms^{-1}]**	**d [m]**	**w [m]**	**d/w [-]**	**P_w [m]**
S_w [m]	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	**-0.549***	n.s.	**-0.622****
U_t [$\mu gm^{-2}s^{-1}$]	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
V_f [$mmmin^{-1}$]	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	**0.571***	n.s.	**0.608****

* p < 0.05

** p < 0.01

4.6.4 Correlations of benthic communities and stream metabolism with water chemistry and uptake parameters

Water chemistry

The only correlations found between water chemistry and metabolism were a negative correlation of NH_4-N with the minimum concentration of oxygen in the water (Spearman, r_s= -0.526*, n=17), as well as a correlation between NO_2-N in the water with the minimum concentration of oxygen in the water (Spearman, r_s= -0.597*, n=17). No correlations between any of the water chemistry parameters and chlorophyll or microbial abundances were found.

Uptake parameters

No significant correlations between uptake parameters and GPP could be found, but V_f showed significantly positive correlations with CR (Spearman, p<0.05, n=16), while S_w was negatively correlated with CR (Spearman, p<0.05, n=16). If considering only spring values, significant negative correlations between S_w and CR (Spearman, r_S= -0.745*, n=9) and V_f and GPP/CR (Spearman, r_S= -0.964**, n=9), as well as positive correlations between U_t and CR (Spearman, r_S=0.767*, n=9), respectively S_w and GPP/CR (Spearman, r_S=0.734*, n=9) could be found. No correlation between any uptake parameter and chlorophyll-a concentration in the biofilm could be found; the same applied for the microbial abundances.

4.7 Patterns of ammonium uptake

In this chapter the different uptake parameters were analysed visually, under consideration of the plateau concentration as well as the ambient in-stream ammonium concentration. For each nutrient loading group and season the uptake parameters of the streams were summarized into a graph (compare Figure 14, Figure 15 and Figure 16) and the patterns were described. From the combined knowledge of all three uptake parameters, conclusions were then drawn to possible states of saturation in chapter 5.2. Due to lacking of data in summer, and therefore also the possibility of a comparison between the two seasons, the Feichsen was excluded from this analysis. Table 11 holds a summary of the initial uptake parameter values and their changes with advancing nutrient injection.

4.7.1 Streams of low nutrient load

In spring the uptake length of the **Grestenbach** was negatively correlated to the NH_4-N concentration and dropped from 1666 to 666m, while U_t increased from 0.17 to 0.43µgm^{-2}s^{-1} and V_f slightly increased from 2.3 to 5.7mmmin^{-1}. In summer the S_w increased from 238 to 435m, although the increase was very shallow. A slight decrease in U_t from 0.28 to 0.16µgm^{-2}s^{-1} was observed, corresponding to the slight increase in S_w. Analysis of V_f showed slight decreases for Grestenbach from 4.9 to 2.3mmmin^{-1}.

The **Kothbergbach** in spring showed an increase in uptake length (from 120 to 333m) with increasing ammonium concentration, while at the same time the uptake rate dropped steeply from 3.7 to 1.3µgm^{-2}s^{-1} and the V_f steeply decreased from 38.7 to 13.8mmmin^{-1}. Unfortunately, only two additions gained significant uptake, otherwise probably a clearer pattern could have been observed, as the change between the first and second addition already was quite steep. For the summer additions in Kothbergbach a very low increase in uptake length S_w from 192 to 263m was observed, as well as a quite stable U_t (drop from 0.99 to 0.733µgm^{-2}s^{-1}) and a slight decrease in V_f from 16.5 to 12.1mmmin^{-1}.

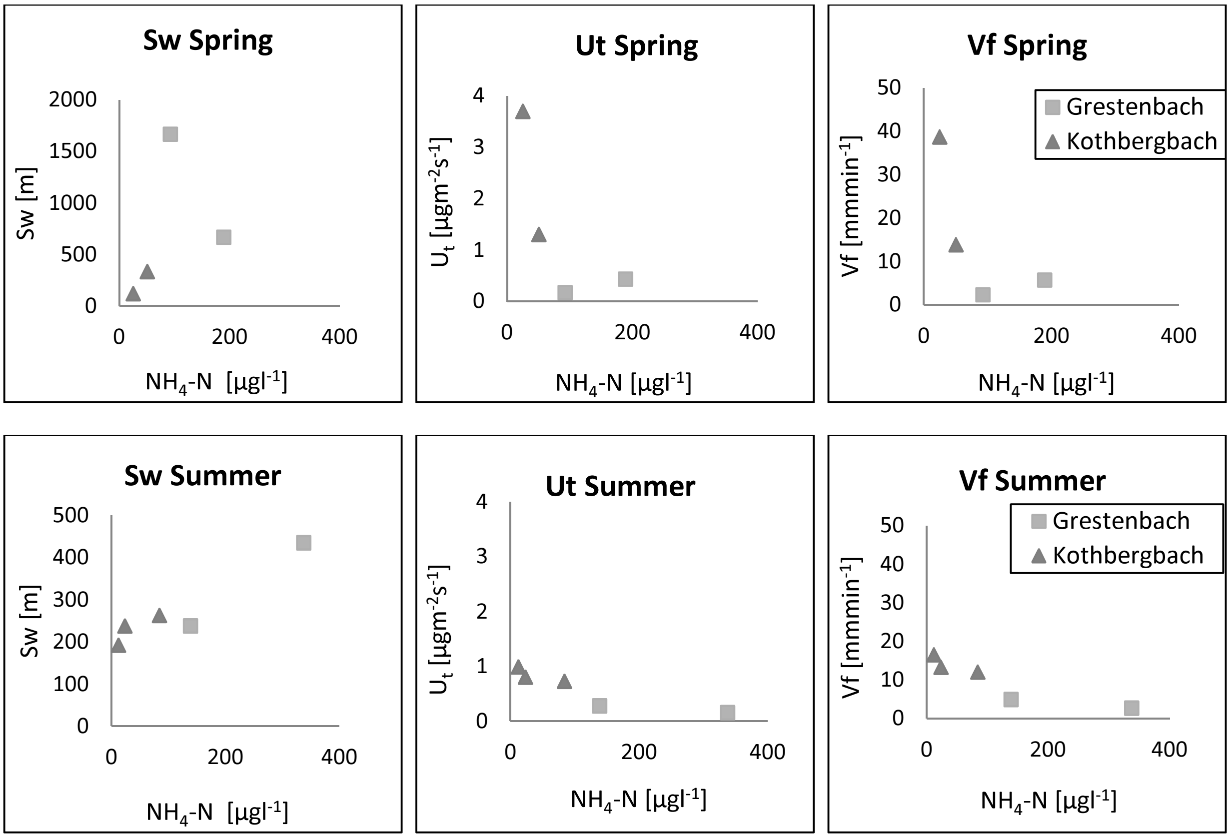

Figure 14: Uptake lengths (S_w), uptake rates (U_t) and mass transfer coefficients (V_f) of the lowly loaded streams, dependent upon NH_4-N concentration at plateau. Upper row: spring, lower row: summer (n=1)

4.7.2 Streams of moderate nutrient load

The **Gamingbach** reaches in spring showed very low uptake lengths at the beginning (29-35m) which then steeply increased with increasing ammonium concentration (up to 385m). A decrease in U_t (from 18.5 to 2.7µgm^{-2}s^{-1}) was observed, while V_f for the first reach dropped from very high 570.5mmmin^{-1} to 62.84mmmin^{-1} and from 438 to 40.3mmmin^{-1} for the second reach. In summer the pattern looked similar, even though the NH_4-N background was much higher than in spring (33µgl^{-1} vs. 4µgl^{-1}). The Gamingbach first showed an S_w of 100m, which rose up to 400m steeply and then stayed very stable (370m) considering the fact that the plateau concentration between the second and third addition was quite large (from 167 to 712µgl^{-1}). A decrease in U_t (6.2 to 1.7 µgm^{-2}s^{-1}) was observed, while V_f dropped from 11 to 3.08mmmin^{-1}.

The **Zettelbach** in spring showed a decrease in uptake length with increasing plateau concentration. The uptake length was relatively high at the beginning (909m) and then steeply decreased to 526m. U_t of the Zettelbach slightly increased from very low 0.37 to 0.44µgm^{-2}s^{-1} while V_f also slightly increased from 2.11 to 2.51mmmin^{-1}. In summer the Zettelbach showed a totally different behaviour: the start uptake length was lower (49m) and steeply increased to 357m with increasing ammonium concentration, while U_t slightly decreased from 1.72 to very low 0.23 µgm^{-2}s^{-1}, with V_f steeply dropping from 18.3 to 3.6mmmin^{-1} during the experiment.

The **Schweinzbach** showed a very steep increase in uptake length from 217 to 667m in spring, with a shallow drop in U_t from 0.85 to 0.28mmmin^{-1} and a rapid decrease in V_f (from 10.1 to 3.3mmmin^{-1}). In summer the uptake length first decreased from 588 to 345m and then increased to 769m. The uptake rate first increased from 0.33 to 0.56µgm^{-2}s^{-1} and then dropped to 0.25µgm^{-2}s^{-1}, while V_f increased from 2.1 to 3.6 mmmin^{-1} and then decreased to 1.6mmmin^{-1}.

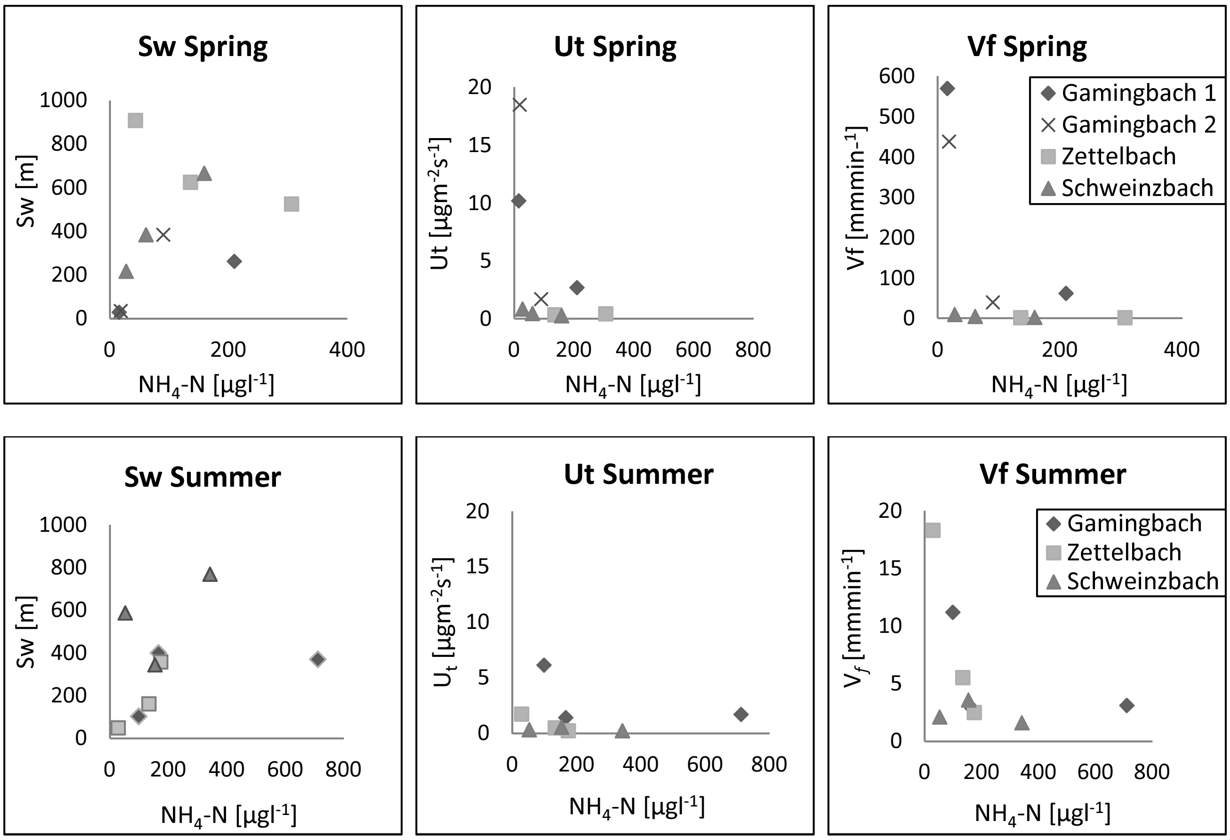

Figure 15: Uptake lengths (S_w), uptake rates (U_t) and mass transfer coefficients (V_f) of the moderately loaded streams, dependent upon NH_4-N concentration at plateau. Upper row: spring, lower row: summer (n=1)

4.7.3 Streams of high nutrient load

The **Gmoosbach** showed patterns differing across the seasons. In spring the S_w steeply decreased with increasing plateau concentration (from 10000 to 2500m), while U_t slightly increased from 0.2 to 0.7µgm^{-2}s^{-1} and V_f increased from 0.62 to 2.49mmmin^{-1}. In summer, in turn, S_w increased with increasing NH_4-N concentration (from 909 to 10000m) while U_t decreased from 1.1 to 0.01µgm^{-2}s^{-1} and V_f from 2.67 to 0.24mmmin^{-1}. Overall, the average S_w of the Gmoosbach were the highest ones observed during the whole experiments, ranging from 900 to 10000m.

The **Sierning** showed the following patterns: In spring the first addition led to a very high uptake length of 1666m which then dropped to 833m and stayed very stable. An increase in U_t could be found for the Sierning (2.10 to 4.60µgm^{-2}s^{-1}), with the steepest decrease occurring between the first and second addition. V_f increased from 1.7 to 3.7mmmin^{-1}. In summer the first uptake length was very low (76m), but it increased to 555m and then stayed stable again. U_t clearly dropped from 37.2 to 5.11µgm^{-2}s^{-1} while at the same time V_f steeply dropped from 16.39 to 2.25mmmin^{-1}.

The **Rußbach** showed a positive correlation between S_w and ambient concentration in spring, the uptake lengths steeply increasing from 217 to 3333m. U_t rapidly decreased with increasing nutrient concentration from 42.5 to 2.77 µgm^{-2}s^{-1}, while V_f rapidly decreased from 14.6 to 0.7mmmin^{-1} after the first addition. In summer S_w increased from 769 to 10000m, with U_t decreasing from 5.11 to 0.30µgm^{-2}s^{-1} and V_f decreasing from already very low 1.8 to 0.14mmmin^{-1}.

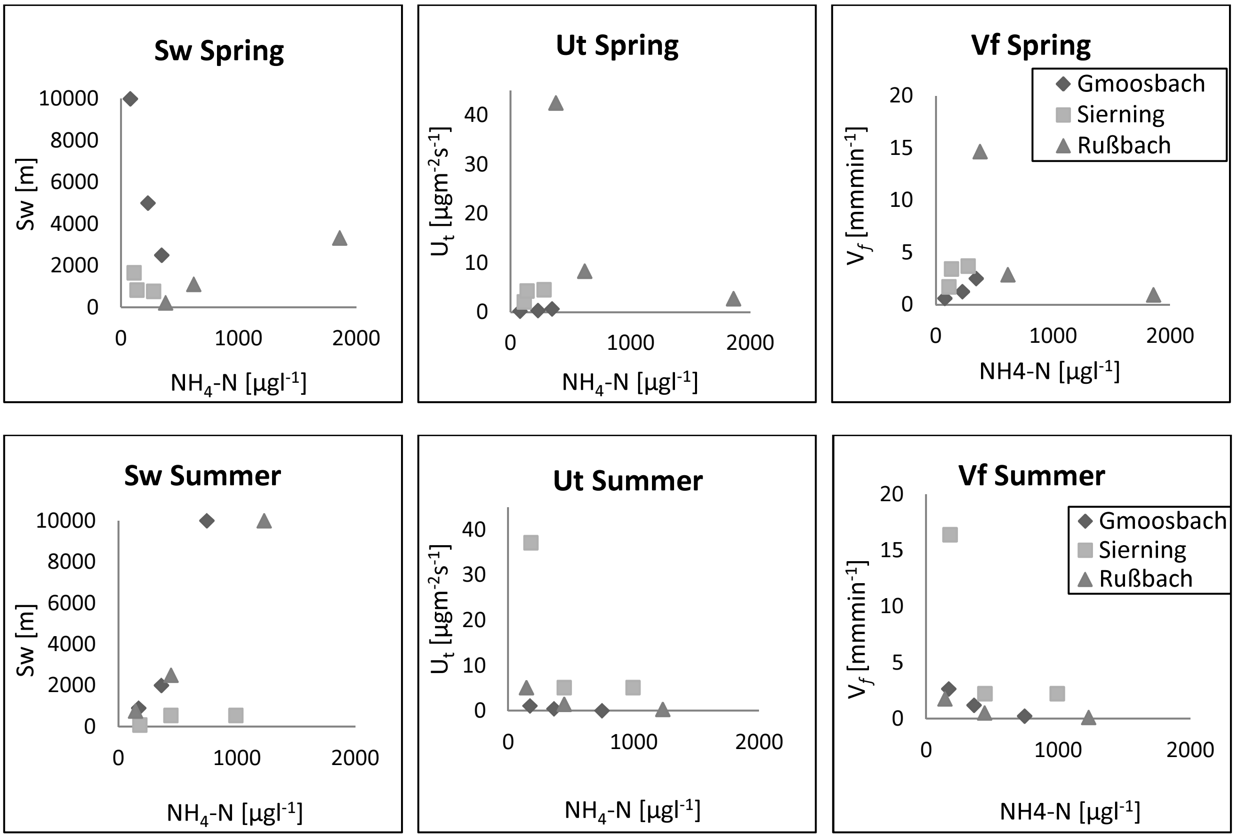

Figure 16: Uptake lengths (S_w), uptake rates (U_t) and mass transfer coefficients (V_f) of the highly loaded streams, dependent upon NH_4-N concentration at plateau. Upper low: spring values, lower low: summer values (n=1)

Table 11: Summary of uptake parameter start values and their further development during the additions (S_w…uptake length, U_t…Uptake rate, V_f…mass transfer coefficient) Fe…Feichsen, GRB…Grestenbach, KB…Kothbergbach, GAMB…Gamingbach, ZB…Zettelbach, SB…Schweinzbach, GMB…Gmoosbach, SI…Sierning, RB…Rußbach)

		S_w		**U_t**		**V_f**	
		Start value [m]	**behaviour**	**Start value [$\mu gg^{-2}s^{-1}$]**	**behaviour**	**Start value [mmmin^{-1}]**	**behaviour**
GRB	spring	1666	moderate, steep decrease	0.17	low, slight increase	2.3	very low, increase
	summer	238	low, slight increase	0.28	low, stable	4.9	low, stable
KB	spring	120	low, steep increase	3.7	low, steep decrease	38.7	high, steep decrease
	summer	192	low, slight increase	0.99	low, stable	16.5	moderate, stable
GAMB	spring	29	very low, steep increase	18.5	moderate, steep decrease	570.5	very high, very steep decrease
	summer	100	low, steep increase, then stable	6.2	low, moderate decrease	11	moderate, steep decrease
ZB	spring	909	moderate, steep decrease	0.37	very low, stable	2.11	very low, stable
	summer	49	very low, steep increase	1.72	low, decrease	18.3	moderate, steep decrease
SB	spring	217	low, steep increase	0.85	very low, stable	10.1	moderate, stable
	summer	588	moderate, first de-than increase	0.33	very low, first in-, then decrease	0.25	very low, first in-, then decrease
GMB	spring	10000	very high, steep decrease	0.2	very low, slight increase	0.62	very low, increase
	summer	909	high, very steep increase	1.1	low, slight decrease	2.67	low, slight decrease
SI	spring	1666	high, first decrease, then stable	2.1	low, increase	1.7	low, increase
	summer	76	very low, increase, then stable	37.2	very high, steep decrease, then stable	16.39	moderate, steep decrease, then stable
RB	spring	217m	low, steep increase, then stable	42.5	very high, steep decrease, then stable	14.6	moderate, steep decrease, then stable
	summer	769	moderate, very steep increase	5.11	low, decrease	1.8	very low, decrease

5. Discussion

5.1 Stream chemistry and ammonium uptake

Hypothesis A: An increased background load of ammonium in water and sediments leads to a reduction of the in-stream ammonium uptake due to reduced nitrogen demand.

Within the study streams a clear gradient in ammonium concentration in the stream water was observed, which was partly reflected in the sediments, too. The assumed pollution gradient was also reflected in the DOC concentration in the water, with significant differences in in-stream DOC content across the nutrient loading levels (highest DOC content in “high” group).

The differences in the N concentrations and the DOC content in the water (both higher in summer than in spring) across the two seasons possibly can be explained by the lower discharge and therefore less dilution. According to Teufl et al. (2013), NO_3-N and NH_4-N concentrations in the sediments usually follow fertilizer applications on the field, where nitrate is washed out from the soil and enters the stream predominantly via subsurface flow, while ammonium adsorbs to soil particles and follows soil inputs, which usually are higher in spring where vegetation is lower. The overall higher sedimentary N concentrations in spring therefore most likely are the result of decomposition and accumulation at the beginning of spring, whereas during spring and summer this N is then taken up and incorporated again into biomass, explaining the lower concentrations in summer.

Of the 54 additions performed in spring and summer, 12 led to a non-significant uptake. There are different reasons potentially leading to a non-significant uptake:

1. The difference between background NH_4-N concentration and the concentration increased through the addition is too low. The signal gets covered by the background ammonium noise and a clear uptake in not present. This was most likely the case for Kothbergbach in spring.

2. It is assumed that microbial communities need a certain time to adapt and react to the nutrient addition (Bunch et al., 2012), which might be the reason why the first addition did not lead to a clear uptake in some cases. In spring this was the case for the Zettelbach (3.8–fold increase) as well as the Gmoosbach (2.8-fold increase) and the Grestenbach (4.4-fold). In summer only the Grestenbach was affected (6.5-fold) by this problem. These data were excluded from the analysis, as a reliable calculation of uptake parameters was not possible under these circumstances.

3. The stream is already saturated or close to NH_4-N saturation. In spring this can be seen for example at the Rußbach, where the first uptake was significant, but then became non-significant for the second and third addition. The mass transfer coefficient became very low and the uptake lengths very high, which is a sign for saturation (Dodds et al., 2002; Earl et al., 2006; Niyogi et al., 2004; O'Brien et al., 2007). These data were used for the further analysis, even though the uptake length was much longer than the actual reach length and therefore only represented an estimation of the actual uptake length.

While Bernot et al. (2006), Johnson et al. (2009) and Gibson et al. (2015) could not find any significant relationships, in this thesis the mass transfer coefficient – as stated in chapter 4.6.1-did show a significantly negative correlation with in-stream ammonium concentration, meaning that the ammonium demand and therefore the uptake velocity decreased with increasing ammonium background concentration. This was also confirmed by Newbold et al. (2006).

Even though no significant correlation between S_w and the ambient NH_4-N concentration in the stream water was found, the lowly loaded streams generally showed much lower uptake lengths when compared to highly loaded streams (cp.4.3.1 or 4.3.2). This finding was confirmed by Bernot et al. (2006), who also found S_w to be positively correlated to the background NH_4-N concentration.

U_t was found to be significantly positive correlated to NH_4-N background concentration by Bernot et al. (2006). This, however, could not be verified in this thesis. In fact, U_t was not correlated to any of the N species analysed. Even though the uptake rates of the highly loaded streams Rußbach (in spring) and Sierning (in summer) were the highest found throughout the experiments, they quickly dropped after the first addition and then ranged at the same level as the lowly loaded streams. The other highly loaded streams even started with a very low U_t and high S_w. High ambient ammonium nutrient loading therefore can be said to cause an increase in uptake length and uptake rate and a decrease in nutrient demand, confirming that highly loaded streams do possess the hypothesized reduced uptake capacity in comparison with lowly loaded streams. While the S_w in moderately loaded streams were similar to those of lowly loaded ones, the U_t and V_f ranged just between those of the two categories "low" and "high". The comparison between the different nutrient loading groups further affirmed the assumption, showing that S_w and U_t increased with the nutrient loading level, while V_f decreased.

For the other two nitrogen species in the stream water, the negative correlations between NO_2-N, S_w and V_f, respectively, as well as between NO_3-N and V_f showed a similar pattern. The correlation between NH_4-N V_f and stream water NO_3-N concentration can also be confirmed by

Bernhardt et al. (2002) and may be a result of NO_3-N and NO_2-N being transformed to NH_4-N through nitrate ammonification processes (Balk et al., 2015; Cruz-Garci et al., 2007).

In terms of nitrogen in the sediments, S_w held significant negative correlations with both, NO_2-N and NO_3-N. The results showed that an increased NH_4-N concentration in the sediments generally led to an increase in uptake length and also to a decrease in V_f, - these results however were not significant. Apart from that, the NH_4-N concentration in the sediments even seemed to be less important in terms of ammonium uptake than the other two nitrogen species.

Hypothesis A therefore can partly be confirmed, as the results show longer uptake lengths and slower mass transfer coefficients with increasing NH_4-N concentration, as well as a quicker dropping uptake rate in those streams with a higher background NH_4-N concentration. Some of the highly polluted streams even showed clear signs of saturation (non-significant uptake, see point 3 above), which could not be observed in lowly or moderately polluted streams. Overall, the analysis didn’t show an exclusive influence of ammonium on the uptake, but rather proved that the sum of nitrogen species loadings in a stream – very likely caused by agriculture - has a negative impact on the uptake capacity of a stream.

5.2 Water chemistry and saturation effects

Hypothesis B: If exposed to pulses with increasing ammonium concentrations, streams with lower in-stream ammonium load tend to saturate earlier than streams with moderate or high ammonium load.

As already mentioned in the introduction, when a stream ecosystem approaches saturation, the uptake length increases linearly with increasing nutrient concentration, while the mass transfer coefficient decreases dramatically along the same gradient and the uptake rate either increases linearly (Stream Solute Workshop, 1990) or reaches an asymptote with increasing N concentration, following the Michaelis-Menten kinetics (Dodds et al., 2002; Earl et al., 2006; Niyogi et al., 2004; O'Brien et al., 2007). Long uptake lengths and exponentially or nonlinearly declining V_f indicate a saturation of the biological demand (Dodds et al., 2002; Gibson et al., 2015), while an increasing and then stable U_t with increasing nutrient concentration (exhibiting Michaelis- Menten dynamics), indicates saturation of biological uptake (Arango et al., 2008).

A decrease in uptake rate with increasing nutrient concentration cannot be explained by any of the mentioned models but was observed in some of the streams, the same counts for uptake lengths decreasing with ammonium concentration. A rapid drop in initially high mass transfer coefficient during nutrient addition indicates a low saturation point and no adaptation to short-term nutrient pulses, while a low but unchanging or even increasing mass transfer coefficient rather points to an adaptation of the stream system to short-term nutrient pulses. Because of the mass transfer coefficient being the most reliable of the uptake parameters, it was used to identify saturation patterns in the first place. The other two parameters then were used to improve the assumptions and to identify contradicting patterns.

The streams were grouped according to their uptake behaviour into the following groups:

1) Approaching saturation, adapted to short-term nutrient pulses:

Grestenbach and Kothbergbach showed saturation signs and decreasing uptake capacities during the summer additions (very low uptake rates and steadily increasing uptake lengths). Uptake rates and mass transfer coefficients stayed quite stable during the additions, indicating adaptation to the pulses. Schweinzbach in spring showed moderate but stable V_f and very low but stable U_t, indicating an adaptation, Sw however pointed towards a saturation. Findings at the Schweinzbach in summer first indicated an adaptation to the pulses (increasing V_f and U_t, decreasing S_w), then increasing S_w and decreasing U_t and V_f indicated upcoming saturation.

2) Approaching saturation, not adapted to short-term nutrient pulses:

Kothbergbach in spring, Gamingbach (in both seasons) and Zettelbach (in summer) seemed not to be adapted to short-term nutrient addition; they showed a steep decrease in V_f with addition of nutrients, a steep increase in their initially low S_w and a decrease in U_t. A similar pattern could be observed for the Rußbach in spring, albeit of course the differences in added amount of ammonium were big between the “moderate” and “high” nutrient loading group. While Kothbergbach and Gamingbach in spring were not yet quite saturated (moderate V_f), the very low V_f in Gamingbach and Zettelbach in summer, as well as in Rußbach in summer, pointed to an approaching saturation. Saturation patterns were also observed at the Sierning in summer (rapid drop in mass transfer coefficient and uptake rate, increase in uptake length.

3) Already saturated:

Saturation was observed at the Gmoosbach in summer (overall low mass transfer coefficient, very high and further increasing uptake lengths and decreasing uptake rates), but also at the Rußbach in summer (drops in mass transfer coefficient at the second addition). At the same time the overall high uptake lengths increased even further. The low uptake rates decreased, the uptake became non-significant.

4) Decreasing uptake length:

The Grestenbach in spring showed a very low mass transfer coefficient and therefore signs of saturation. The drop in uptake length (which then flattens with further addition) and the increase in V_f and U_t with increasing concentration however hint to an adaptation to short-term nutrient pulses and some kind of delayed “activation” of uptake mechanisms. The Zettelbach in spring showed a similar pattern. The Gmoosbach in spring showed an adaptation to short-term nutrient pulses as well (rapidly decreasing uptake lengths). In the Sierning in spring the uptake lengths dropped and then stayed stable, while the low uptake rate and mass transfer coefficient increased and then stayed stable as well, indicating first an activation of nutrient uptake mechanisms and then an adaptation to the nutrient addition with further nutrient addition.

The observed decrease in uptake length cannot be explained by any of the established models, which predict increasing uptake length with increase in concentration, but might be connected to water temperature if considering the fact that all of the four streams showed the effect in spring.

While Niyogi et al. (2004) found no clear evidence of saturation in streams showing elevated background concentrations, the findings of this thesis allow the conclusion that an elevated background concentration - contrary to Hypothesis B - can indeed promote a saturation of the stream components, and therefore an undesired downstream transport of nutrients. This was supported by Arango et al. (2008), who also found that in agricultural and urban (but not in forested) streams the whole-stream NH_4-N removal (expressed as areal uptake, U_t) approached saturation at higher inorganic N concentrations. In addition, V_f was also found to be negatively correlated to NH4-N concentration. Earl et al. (2006) also stated a positive correlation between ambient N concentration and proximity to saturation.

In this thesis in general the lowly polluted streams were rather adapted to addition of nutrients, could buffer the increase up to a certain point and showed overall much lower uptake lengths (maximum 1667m) than the highly loaded ones (maximum 10000m), even when aiming towards saturation. They were able to compensate the ammonium addition until a manifold of their background concentration and significantly took up the ammonium until a much higher increase relative to the ambient concentration (5.9 to 35-fold) than the highly polluted ones, where even slight increases in concentration (0.8 to 5.4-fold) already led to saturation. The highly loaded streams in general did not show any signs of adaptation to the pulses, but either were already saturated or saturated soon during the additions. Nevertheless, the lowly loaded streams saturated - or aimed towards saturation - at much lower absolute ammonium concentrations (23.6 to 138µgl^{-1}) when compared to the highly loaded ones (76-617µgl^{-1}). The moderately loaded streams partly were and partly were not adapted to short-term nutrient inputs; they showed very low to moderate uptake lengths and in terms of saturation point ranged in the middle, with saturation signs occurring at 4.7 to 27-fold increase and 53 to 343µgl^{-1}.

The sensitivity of lowly loaded streams to absolute increases in ammonium concentration clearly illustrates the importance of lowly loaded streams to be protected and kept clean in terms of nutrient input.

5.3 Seasonal patterns

Hypothesis C: The ammonium uptake velocity V_f is higher in spring than in summer.

Arango et al. (2008); Hoellein et al. (2007), Simon et al. (2005) and also Johnson et al. (2009) found the NH_4-N mass transfer coefficient to be highest in spring. They underlined the importance of autotrophy in the spring in temperate forested streams just before leaf-out, when high light availability levels cause a peak in assimilatory N demand by primary producers. They found chlorophyll-a concentrations to be significantly higher in spring, supporting their assumption and Johnson et al. (2009) further affirmed the observations by attesting a significantly negative relation of NH_4-N V_f to percent canopy cover.

None of these findings, however, could be verified by our observations. Statistical analysis showed, that although the average V_f indeed was higher in spring than in summer (compare Figure 12), no significant differences could be found (see chapter 4.3.1). Arango et al. (2008) explain the lower seasonality of nutrient demand in agriculturally influenced streams with the year-round open canopies and the higher light levels in comparison to forested streams. The non-significant differences between the chlorophyll-a concentrations found among the seasons, which indicate a low variability in algal abundance in the streams, might also play a role.

A direct comparison of the stream mass transfer coefficients at similar plateau NH_4-N concentrations showed that for some streams (Grestenbach, Kothbergbach, Gamingbach, Gmoosbach and Rußbach) the V_f indeed was higher in spring. For Zettelbach, Sierning and Schweinzbach, though, the mass transfer coefficient was higher in summer. It seems that for the streams chosen in this study, V_f did not only depend on the season but rather on other factors, such as in-stream ammonium concentration or proximity to stream saturation.

Hypothesis C, stating that the mass transfer coefficient is generally higher in spring than in summer, therefore was rejected.

5.4 Influence of hydromorphology on ammonium uptake

Hypothesis D: The longer the contact time and the higher the wetted perimeter of the stream, the higher the mass transfer coefficient becomes. Higher water retention equals a longer contact time between water and sediments and therefore also leads to higher nutrient uptake rates and lower uptake lengths.

According to Bukaveckas (2007), Ensign et al. (2005) and Roberts et al., (2007) the size of contact area between the reactive surface of the streambed and the water, as well as residence time - and in consequence of that wetted perimeter and streambed width, flow velocity (Weigelhofer et al., 2013) and (sometimes) transient storage (Hall et al., 2009; Webster et al., 2003; Weigelhofer et al., 2013) might play an important role in ammonium uptake. A longer residence time (slower flow velocity/ higher hydrologic retention) and bigger surface area (higher wetted perimeter and streambed width) increase the contact of the nutrients with the biologically, physically and chemically reactive streambed surface and the stream conenoses (especially benthic algae and biofilm). The nutrients can therefore be processed more intensely (Weigelhofer et al., 2011), leading to lower S_w (Klocker et al., 2009; Weigelhofer et al., 2013) and higher U_t (Baker et al., 2012; Roberts et al., 2007) in the streams.

The negative correlation between wetted perimeter and uptake length (compare 4.6.3) verifies hypothesis D, stating that an increased wetted perimeter leads to a decrease in S_w. The positive correlation between P_w and V_f further supports the hypothesis. The same patterns could be found for the average stream width, the expected negative correlation between flow velocity and uptake length on the other hand could not be found.

Additionally, none of the nutrient spiraling parameters was correlated to the simplified transient storage parameters (v_{min}/v_{mean} and d/w). Even though Weigelhofer et al. (2012) found significant relationships between transient storage and NH_4-N uptake parameters, this was not the case in this thesis. A reason for this might lie in the low differences in hydrologic retention; while Weigelhofer et al. (2012) compared pristine with incised reaches, the reaches chosen in this study were similar to each other in terms of hydromorphology (see chapter 4.4). It might also be that the stronger influence of ammonium background concentration interfered with that of the hydrologic retention, or that the simplified parameters for measuring hydrologic retention were not suitable for finding a correlation. Further research is recommended on that topic.

It seemed that at the Gmoosbach the impaired uptake ability resulted rather from the lack of flow- and streambed variability than from the ambient ammonium concentration, because the Sierning showed much lower uptake lengths, at ambient ammonium concentrations which were manifold higher. The Gmoosbach with its very low retention capability - due to trapezoid shaped channel alteration - showed very low (but still significant) uptake with lengths between 2500 and

10000m in spring, and a rapid saturation in summer, with uptake lengths between 900 and 10000m. These (together with the Rußbach) represented the highest uptake lengths of the whole experiment.

The correlations between V_f, S_w and the wetted perimeter (respectively the stream depth) indicate that the uptake capacity of a stream does not only depend on the grade of nutrient loading, but also on the presence of streambed heterogeneity and natural flow variability. Usually the degradation of a stream in terms of hydromorphology, however, is tightly connected to the degree of surrounding agricultural activity, as channelization and river straightening often are a consequence of agricultural land use. The results underline the role of streambed heterogeneity in nutrient uptake efficiency and reflect the findings of e.g. Bukaveckas (2007) and Weigelhofer et al. (2013) who state that stream channel restoration can support nutrient retention and thus mitigate downstream nutrient transport.

It is, though, very difficult to directly connect the uptake parameters singly to the hydromorphological parameters, as they strongly depend on other factors. A stream showing a very heterogeneous streambed might therefore still have very long uptake lengths because it is already near saturation, not because of flow conditions. An experimental set-up under controlled flow conditions (e.g. with a flume) might be better suitable to answer these questions.

Hypothesis D therefore can be confirmed in terms of wetted perimeter (contact area), but only partly in terms of flow velocity or water retention (contact time).

5.5 Biotic factors and their influence on uptake

Hypothesis E: The mass transfer coefficient is higher in streams with a GPP/CR ratio >1 (autotrophic) and positively correlated to algal and microbial abundance.

According to Bernot et al. (2010, 2006) nutrients are supposed to represent an important influencing factor in stream metabolism. In this thesis, though, no correlation between metabolism and any of the nitrogen concentrations in water or sediments was found, suggesting that DIN concentration was not driving variation in metabolism in the chosen streams. The findings are supported by Hall et al. (2003), who also did not find a significant correlation between metabolism and NH_4-N concentration in his study. Bernot et al. (2006) also found no significant relationships between nutrient concentration and CR, neither did they find a significant relationship between nutrient uptake parameters and GPP or CR, "...likely due to the multiple controls on gross estimates of whole-stream metabolism (i.e. light, temperature, pH as well as nutrient uptake)".

The positive correlation between V_f and CR, as well as the negative correlation between S_w and CR in this thesis, however, indicated a significant influence of metabolism on the uptake. This was also observed by Webster et al. (2003) and also Hall et al. (2003), who found 50% of the variability in NH_4-N V_f explained by CR. Hall et al. (2003) found 78% of the variability in V_f also explained by GPP, which could not be confirmed by our findings. The findings in spring, with negative correlations between V_f and GPP/CR as well as positive correlation between S_w and GPP/CR, further indicate a higher uptake velocity in heterotrophic streams in comparison to autotrophic streams. According to Hall et al. (2003) the overall low GPP/CR ratios found in the streams might "suggest a strong heterotrophic (bacterial or fungal) component to stream metabolism that contributes to NH_4 removal from the water column". The higher importance of heterotrophic over autotrophic components in the observed streams possibly can be explained by the earlier saturation of autotrophic components, as stated by Bernot et al. (2005)

A positive correlation between the algal biomass and the ammonium uptake velocity was expected, as assimilation by photosynthetic (and heterotrophic) organisms and therefore biotic demand by algae is supposed to be – together with sorption to sediments – the main ammonium removal mechanism. It should therefore represent one of the ultimate factors for nutrient uptake and transformation in a stream (Hall et al., 2003; Peterson et al., 2001; Webster et al., 2003). Marti et al. (1997) attests a higher demand for nutrients and lower uptake lengths for streams with higher algal abundance, Arango et al. (2008) found evidence for autotrophy playing a significant role in NH_4-N V_f – directly through assimilatory demand and indirectly by influencing nitrification. However, no such correlation could be found for any of the three spiraling metrics uptake length, uptake rate or mass transfer coefficient.

The results probably can be explained with the low biomass variability found across the seasons and nutrient loading levels, and the rather high standard deviations. Weigelhofer et al., (2013) did also not find any linkage between V_f and chlorophyll-a concentration, Gibson & Meyer (2003) propose that the high background concentrations of ammonium might cover the uptake effect in highly loaded streams. Further research is recommended.

No direct correlation at all could be found between any of the three uptake parameters and the microbial abundances. Again, this finding was unexpected, as - together with algal biomass - C uptake by heterotrophic organisms (leading to an increased N demand) is supposed to be the main ammonium removal mechanism besides sorption to sediments (Arnon et al., 2013; Hall et al., 2003; Peterson et al., 2001; Sweeney et al., 2004) and – as mentioned before – a positive correlation between V_f and CR, as well as a negative between S_w and CR was found. The correlations of uptake parameters with GPP/CR indicate an importance of heterotrophic organisms as well. A possible explanation for not finding a direct correlation in this case might be the low amount of samples (summer only).

Summing up the results discussed in chapter 5.5, even though a correlation between uptake parameters and metabolism - indicating a linkage between community respiration and uptake velocity/ uptake length - could be found, the findings could not be confirmed by direct statistical analysis of the respective parameters and Hypothesis E therefore can only partly be confirmed.

6. Conclusion and outlook

With this thesis it was attested that the capacity of self-purification of a stream ecosystem in terms of ammonium does indeed strongly depend on its grade of agricultural influence and resulting nitrogen nutrient loading (in stream water as well as in the sediments). Also it was found out, that not the concentration of ammonium is the main influencing factor for uptake of ammonium, but rather all nitrogen species together, respectively the overall grade of nutrient loading (maybe even including other nutrients) resulting from land use in the catchment.

The lowly loaded streams showed lower overall uptake lengths in comparison to the highly loaded ones, and were able to compensate nitrogen input above ambient ammonium concentration up to a multiple of the background concentration, until a certain point after which they showed saturation patterns. The highly loaded streams in contrast mostly only showed uptake at ambient ammonium concentration (with exception of the Sierning showing very high uptake lengths), but rapidly saturated when experiencing further input and then completely lost the ability of efficient uptake. This - and the correlations found between nitrogen concentrations and the uptake parameters - showed, that in comparison to lowly loaded streams, highly loaded streams are hindered in their capability of performing an efficient uptake of ammonium. The lowly loaded streams however are not adapted to high inputs of nutrients and must therefore be protected from future nutrient loading and the influence of agricultural activities in order to keep the ambient nitrogen concentrations low and preserve their natural self-purification capacity. Further, the correlations found between hydromorphology and ammonium uptake underlined the importance of stream conservation and enhancing of channel heterogeneity (Weigelhofer et al., 2013).

In future, with population numbers growing worldwide and plants like e.g. canola being used as a renewable fuel, agricultural production will become even more important. Tilman et al. (2001) state that if there is no change in cultivation, fertilization and irrigation practices, the mean forecast for global N fertilization will be increased by 1.6-fold in 2020 and by the 2.7-fold in 2050 (compared to 2001). This equates to an annual addition of $236*10^6$ MT of N in 2050, solely through fertilization, while the natural annual rate is $140*10^6 MTa^{-1}$.

The future focus should therefore lie on protecting still rather unimpacted streams from future degradation and nutrient loading, in order to preserve the natural self-cleaning and retention capacity of these waterbodies. For streams which are already strongly affected, we should concentrate on developing measures, as well as on the implementation of best management practices, for mitigating the already existent negative effects of land use on the in-stream nutrient uptake ability.

To effectively reduce the amount of nutrients in the stream, several measures can be taken, either in the catchment (or stream surrounding area) or at the stream borders. Regarding the catchment, raising awareness among the farmers for the problems caused by nutrients in stream water might be one important measure on the way to the reduction of exceeding application of fertilizer. This might for example be combined with financial aid, e.g for introduction of organic farming, or for the practice of extensive instead of conventional tillage in order to reduce soil erosion and therefore the deportation and washing of nutrients into the stream in the first place. An alternative would be the implementation of crop rotation or the planting of cover crops on the fields.

Measures along the stream borders might include the compulsory installation of buffer zones – for example riparian forest or grass buffers. These buffers seem to be an effective possibility to hinder nutrients of getting into the stream, even if they have already been applied to the field; additionally the installation of riparian vegetation also might hinder eutrophication by shading the algae. Unfortunately these natural buffers are often bypassed by drainage pipes- the bypass then leading to a direct nutrient transport into the stream (Weigelhofer et al., 2012); many of these drainage pipes were spotted throughout the nutrient addition experiments.

In case the nutrients already have reached the water, the implementation of slow- flowing sections or zones of high heterogeneity might help enhance and accelerate the uptake and removal of nutrients (Klocker et al., 2009) in order to hinder them from being transported downwards. Craig et al. (2008) suggest "[...] approaches that increase in-stream carbon availability, contact between the water and benthos, and connections between streams and adjacent terrestrial environments".

If mitigating the effects and eliminating the causes of nutrient input into stream ecosystems, the services provided by streams - such as the capacity for assimilation and recycling of wastes, but also the provision of food, clean air and water, a living space for animals and plants and the representation of a local recreation area for humans can be secured.

Apart from the factors tested in this thesis, there exist also other factors which influence the uptake capacity of streams, such as shading through riparian vegetation or the time of the day. The conclusions drawn in this thesis about saturation patterns and the negative influence of nitrogen pollution on the N uptake velocity and uptake length however provide an insight into the mechanisms and should help to sensitize to the set of problems caused by agriculture. With purposeful measures it could be possible to enhance the protection of sensitive stream waterbodies, especially in regions like big parts of Lower Austria, which are used intensively for agricultural production and therefore are heavily affected by nutrient pollution.

Further research could focus on controllable experiments in identically constructed flumes with changing nutrient loading gradient, in order to have no differences in hydromorphology and sediment composition between the streams and therefore solely concentrate on the influence of differing nutrient concentration on the uptake. This could be useful to test if only the nitrogen pollution, or rather the sum of alterations (erosion, uniform streambed shape) usually following the agricultural land use have an effect on the uptake performance and to further isolate the problem to develop more targeted mitigation measures. Also the uptake behaviour under long-term nutrient additions could be performed to explore the effects of different mitigation measures, such as enhancing of transient storage or streambed heterogeneity.

Repeating the experiments also in autumn and winter might help closing the seasonal gaps and provide a better understanding of a full-year cycle and respective measures. The values for the microbial abundances were limited to summer and therefore not very meaningful; it would be advantageous to gather more information and also samples for spring to enable further research in terms of the importance of microbial abundances in the uptake and removal of ammonium in streams. The role of chlorophyll-a in the uptake of ammonium should be investigated more detailed, maybe also in combination with the shading through riparian vegetation, as the biotic uptake (together with microbial abundance) is supposed to be one of the most important factors in the processing of nutrients.

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8. Tables and figures

8.1 List of tables

8.2 List of figures

9. Appendix

Table 12: Summary of water chemistry results (DOC… dissolved organic carbon, Fe…Feichsen, GRB…Grestenbach, KB…Kothbergbach, GAM… lower (l) and upper (u) Gamingbach, ZB…Zettelbach, SB…Schweinzbach, GMB…Gmoosbach, SI…Sierning, RB…Rußbach)

Stream name	NH_4-N [µgl^{-1}]		NO_3-N [µgl^{-1}]		NO_2-N [µgl^{-1}]		DOC [ppb]	
	Spring	Summer	Spring	Summer	Spring	Summer	Spring	Summer
FE	4.4 ± 10	-	1156.2 ± 15.4	-	4 ± 0.1	-	1874.7 ± 149.9	-
GRB	5.5 ± 2.9	3.6 ± 1.9	976.0 ± 10.1	1275 ± 256.7	3.1 ± 0.2	6 ± 0.5	1708.3 ± 82.7	1720.7 ± 31.1
KB	6.3 ± 1.4	4.0 ± 0.0	1017.4 ± 26.9	961.3 ±19.4	1,3 ± 0.2	2.5 ± 1.1	1154 ± 96.3	1327.3 ± 24.3
GAM (l)	4.4 ± 45.8	-	1056.8 ± 9.3	-	1.3 ± 0.3	-	1028.9 ± 93.2	-
GAM (u)	12.4 ± 9-4	33.0 ± 21.7	1056.8 ± 9.3	837.4 ± 9.0	1.3 ± 0.3	2.3 ± 0.4	1028.9 ± 93.2	1305 ± 184.1
ZB	11.5 ± 1.4	6.4 ± 3.2	1492.2 ± 430.2	1609.6 ± 19.0	6 ± 0.1	4.9 ± 0.2	2028 ± 148.5	1830.7 ± 38.0
SB	5.9 ± 1.3	14.4 ± 4.7	3308.2 ± 130.2	3020.7 ± 99.0	19.5 ± 1.2	22.5 ±1.5	1984 ± 292.4	2483.3 ± 214.6
GMB	21.9 ± 2.4	30.6 ± 9.0	2306.9 ± 196.6	3497.3 ± 91.5	28.1 ± 0.3	58 ± 1.4	5683.7 ± 91.6	6385 ± 199.6
SI	94.9 ± 2.6	163.7 ± 9.9	4151.6 ± 50.1	5604.6 ± 34.6	45.8 ± 0.2	142 ± 3.9	2366.7 ± 168.7	3293.3 ± 257.7
RB	192.7±10.4	175.6±29.3	6857.2 ± 138.4	4059.2 ± 81.7	52.8 ± 0.5	197 ± 4.9	2717.3 ± 559.4	5253.3 ± 340.0

Table 13: Summary of sedimentary nutrient, water and organic matter content (Fe…Feichsen, GRB…Grestenbach, KB…Kothbergbach, GAM…lower (l) and upper (u) Gamingbach, ZB…Zettelbach, SB…Schweinzbach, GMB…Gmoosbach, SI…Sierning, RB…Rußbach)

Stream name	NH_4-N [µgg^{-1}]		NO_3-N [µgg^{-1}]		NO_2-N [µgg^{-1}]		organic matter [%]		water in sediment [%]	
	Spring	Summer	Spring		Spring	Summer	Spring	Summer	Spring	Summer
FE	0.7 ± 0.6	-	1.6 ± 0.6	-	0.5 ± 0.1	-	2.1 ± 0.2	-	23.2 ± 2.1	-
GRB	0.8 ± 0.2	1.7 ± 0.9	6.8 ± 1.7	2.3 ± 1.5	0.9 ± 0.3	0.13± 0.1	1.9 ± 0.1	1.3 ± 0.1	23.9 ± 2.7	22.1 ± 3.0
KB	0.5 ± 0.1	1.7 ± 0.3	1.7 ± 0.4	1.23 ± 0	0.1 ± 0.0	0.03± 0.0	0.4 ± 0.1	0.6 ± 0.1	23.3 ± 1.1	19.9 ± 1.8
GAM (l)	0.5 ± 0.2	-	2.4 ± 0.4	-	0.6 ± 0.2	-	2.7 ± 0.2	-	21.8 ± 1.3	-
GAM (u)	0.5 ± 0.3	1.9 ± 0.5	2.9 ± 0.9	1.5 ± 0.2	0.1 ± 0.0	0.03± 0.0	3.0 ± 0.2	0.4 ± 0.1	21.9 ± 2.7	17.9 ± 2.7
ZB	0.7 ± 0.2	0.7 ± 0.5	2.4 ± 0.7	2.2 ± 0.4	0.1 ± 0.0	0.2 ± 0.0	1.5 ± 0.0	1.0 ± 0.1	23.3 ± 1.1	19.9 ± 1.8
SB	2.8 ± 0.9	0.5 ± 0.1	1.1 ± 1.0	2.1 ± 0.2	0.3 ± 0.2	0.05± 0.0	1.1 ± 0.1	1.3 ± 0.1	20.8 ± 1.1	17.8 ± 1.7
GMB	11.6 ±3.2	9.3 ± 0.4	9.9 ±11.3	0.5 ± 0.2	1.7 ± 0.5	0.4 ± 0.1	6.7 ± 1.5	6.7 ± 1.0	48.9 ± 7.5	52.1 ± 4.7
SI	0.6 ± 0.2	0.4 ± 0.2	4.1 ± 1.2	1.6 ± 0.7	0.1 ± 0.0	0.1 ± 0.1	1.0 ± 0.2	1.5 ± 0.3	22.0 ± 2.2	24.1 ± 1.6
RB	27 ± 11.8	3.7 ± 0.5	3.5 ± 1.6	3.4 ± 0.8	1.5 ± 0.5	0.2 ± 0.0	4.9 ± 0.7	1.3 ± 0.2	40.4 ± 7.1	22.7 ± 0.5

10. Affirmation

I certify that this master thesis was written by me, not using sources and tools other than quoted and without use of any other illegitimate support.

Furthermore, I confirm that I have not submitted this master thesis - nationally or internationally - in any form.

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Place, date	*name surname*	*signature*