Nitrogen deposition in a riparian zone

Bachelor Thesis in Environmental Sciences

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Abstract

Assessing the effect of river restoration on ground water quality, especially on nitrate concentration, is one of the goals of the project RECORD (Restored Corridor Dynamics). In line with that goal, nitrogen input in a restored riparian zone of the Swiss River Thur was quantified as a preliminary work for an assessment of its nitrogen status.

Total nitrogen deposition was estimated for one year, between April 2009 and March 2010. Atmospheric nitrogen deposition was estimated using a throughfall method that allows precipitation sampling under a canopy. Either reference sticks or synthetic turf mats were used to estimate the alluvial nitrogen deposition.

The total deposition of nitrogen in the test site at the River Thur was between 40 and 252 kg N ha⁻¹ y⁻¹, differing significantly for and within the different functional process zones (FPZ). Atmospheric nitrogen deposition was 8 kg N ha⁻¹ y⁻¹ for the FPZ Grass and 17 kg N ha⁻¹ y⁻¹ for the FPZ Mixed Forest. The dominant nitrogen source was sedimentation, being responsible for 97% and 89% of the total nitrogen deposition in the two lower elevated and dynamic FPZ Grass and Willow Bush. For the more elevated and stable FPZ Mixed Forest, sedimentation still accounted for 58%. Alluvial deposition varied strongly with topography. It could be shown that given a certain flood event, the relief of the riparian zone was the most dominant factor for the amount of nitrogen deposited.

The large amount of deposited nitrogen (up to 406 kg N ha⁻¹ y⁻¹ per sampling plot) raises attention to the question of a critical load for the ecosystem and to the groundwater quality. Considering the actual nitrogen deposition rate, extensive leaching of nitrogen to the groundwater must be assumed. This asks for further research, e.g. modelling of a mass balance with the deposition results of this thesis as an important input factor.

Keywords: riparian zone, nitrogen, river restoration, atmospheric nitrogen deposition, alluvial nitrogen deposition
1. Introduction

1.1. River restoration and the project RECORD

Riparian zones act as buffers that reduce pollution from agricultural land to streams (Hefting et al. 2006). Specifically, riparian zones are able to attenuate nitrate by plant uptake, denitrification and dilution (Pfeiffer et al. 2006).

Due to ongoing canalization of rivers in order to avoid flooding and to gain arable land, natural riparian zones have diminished and river restoration is widely regarded as an improvement of the ecological status of a water course. Although many restorations have been realized in recent years, the understanding of the effects a restoration has on the hydrology and ecology remains limited. The Competence Center of Environment and Sustainability (CCES) of the ETH domain launched therefore the project RECORD (Restored Corridor Dynamics) to conduct research in a restored and channelized section of the Swiss River Thur (CCES 2009).

Assessing the effect of river corridor restoration on ground water quality, especially on nitrate concentration, is one of the goals of RECORD. To quantify the input of nitrogen in the test site as a preliminary work for an assessment of its nitrogen status is an important part of the ground water assessment and is the objective of this thesis.

1.2. Nitrogen cycle

Nitrogen is an essential macronutrient for organisms and is assimilated into the biomass as proteins. For some organisms nitrogen also provides energy (as an energy carrier or electron acceptor). The following Figure 1 shows schematically the anthropogenic-bio-geological cycle of nitrogen.

![Figure 1: Schematic nitrogen cycle
(Pidwirny 2010)](image)

Although nitrogen is very abundant in its elementary form in the atmosphere, its availability for the ecosystem may remain limited because the elementary nitrogen is inert and the oxidation is rather complex and energy intense for microorganism. Assimilation of nitrogen by microorganism and plants generally can only take place in form of nitrate (NO$_3^-$), nitrite (NO$_2^-$) and ammonium (NH$_4^+$). From this perspective nitrogen is rather scarce and limiting the growth of biomass. On the other hand these species are soluble in water and especially nitrate can be leached out into groundwater as a pollutant.
that endangers human health. Additionally, when biological available nitrogen is too abundant in an ecosystem, it can contribute to its eutrophication with effects such as loss of biodiversity. This means, that a low biologically available nitrogen input and a high nitrate removal capacity of the ecosystem is appreciated with respect to (drinking) water quality and ecosystem resilience.

1.3. Nitrogen deposition

One important source of nitrogen is atmospheric deposition, which follows two different pathways: (1) Wet deposition (WD), as nitrogen gases and particles are washed out from the atmosphere during rain/snowfall. (2) Dry deposition (DD), where nitrogen particles adsorb to a surface (e.g. ground or foliage).

In open field, WD and DD are sampled with open bulk collectors and according to the sampled precipitation amount and concentration, total atmospheric nitrogen deposition can be derived. Such a sampling in an area covered with higher vegetation (e.g. forest) is not directly applicable, because some of the nitrogen will be taken up by the plants (e.g. in the canopy) before the precipitation will reach the collectors on the ground. A further possible effect of the vegetation is, that the augmented surface, roughness and physiological properties of the foliage can lead to a higher dry deposition, which then will be washed to the ground with subsequent rain (Thimonier et al. 2005).

To quantify the total nitrogen deposition in a forest, a canopy exchange model has to be used that accounts for the canopy exchange (primarily uptake) and that is linked to the throughfall that can be sampled with collectors. According to equation (1) throughfall nitrogen deposition (TF) can be described as the sum of total nitrogen deposition (TD) and canopy nitrogen exchange (CE), when stem flow is neglected. TD is the sum of (incident) bulk precipitation of nitrogen (BP), which means the direct WD and DD onto bulk collectors, and DD onto the canopy, which is indirectly deposed onto the bulk collectors by subsequent rain (Lovett et al. 1996).

\[ TF = TD + CE = BP + DD + CE \]  

(1)

For forested habitats many studies have been conducted in order to quantify atmospheric nitrogen deposition. The Pan-European forest monitoring program (ICP Forests) reports a total atmospheric nitrogen deposition of 1.4-42 kg N ha\(^{-1}\) y\(^{-1}\), being at the upper end of the range for plots in Central and Western Europe (De Vries et al. 2003). For Switzerland in particular, Thimonier et al. (2005) report an average nitrogen deposition of 18-29 kg N ha\(^{-1}\) y\(^{-1}\) for the Central Plateau (mainly habituated by the tree species *Quercus robur*, *Fagus sylvatica* and *Abies alba*). The study was conducted in the framework of the Swiss Long-term Forest Ecosystem Research (LWF) which meets the aim of the ICP Forests program.

But atmospheric deposition is not the only important nitrogen source in a riparian zone. According to research on the River Adour floodplain in France, large river systems should not be considered only as export systems because riparian zones can retain a significant amount of suspended organic and mineral matter during floods, including organic nitrogen (Brunet et al. 1994). The deposition of nitrogen by sedimentation on a riparian zone might therefore be considerable.

The quantity of sediment stored in a riparian zone results from the local balance between erosion and sedimentation. According to Steiger and Gurnell (2003), observed sedimentation in a riparian zone of the River Garonne in France varied significantly with river discharge at flood peak, landform type and associated vegetation cover and, in some cases, with sample location within the landform. A general quantification of nitrogen deposition by sedimentation is difficult due to high variability in land use, discharge rate, geomorphology, topography and vegetation and specific research for Swiss rivers is scarce. But in general, total organic nitrogen increases according to the quantity of deposited sedi-
ments and the concentration of organic nitrogen increases significantly with an increase in the percentage of silt and clay (Steiger and Gurnell 2003).

1.4. Research questions

Three main questions are addressed in this thesis: (1) How much is the total deposition of nitrogen in the test site at the River Thur? (2) Does the amount of deposited nitrogen differ in different parts of the floodplain? (3) Is the composition of the freshly deposited sediments, including physico-chemical soil properties and organic nitrogen concentration, dependent on the relief of the riparian zone? Additionally, the hypothesis that sedimentation is the main nitrogen input for soils in the riparian zone shall be tested.
2. Methodology

2.1. Test site

The test site of the RECORD project is located at the (partly) renaturalized section of the Swiss River Thur near Altikon, where the width of the main river channel has been doubled over a length of two kilometres. River Thur is 127 kilometres long, has a catchment area of about 1750 km², no natural or artificial reservoir and a hydrological regime with the characteristic presence of flash floods (Pasquale et al. 2011).

The boundaries of the test site of RECORD are given by a hill slope in the north, a levee in the south, a bridge in the east (upstream) and by the point where the river starts to cut into solid bedrock in the west (downstream) (CCES 2009). Homogeneous carbonate rich sediments of silty sand overlay the semi-confined aquifer of glaciofluvial gravel and sand (Hoehn and Sholtis 2011 and Samaritani et al. 2011). An overview of the test site were sampling took place is given in Figure 2.

![Figure 2: Ariel view of the test site](image)

*Four sampling plots per each functional process zone (FPZ) Grass, Willow Bush and Mixed Forest*

2.2. The concept of Functional Process Zones

A river corridor can be seen as an array of hydro-geomorphic patches that are hierarchically scaled and formed by factors such as geomorphology, hydrologic pattern, riparian condition and climate. These patches that can be defined in four dimensions (longitudinal, lateral, vertical and temporal) can differ significantly among and within patch types. In order to close the gap for intermediate scale patches between valleys and reaches, the term Functional Process Zone (FPZ) was introduced. The term “function” refers here to the physical function of geomorphologic and hydrologic forces that shape the river and therefore the structure and function of the ecosystems (Thorp et al. 2008).

For this study, the FPZ concept was applied at a smaller scale to hydro-geomorphic patches within a single reach (restored section of the river corridor). And the term “functional” was not restricted to physical functions but rather extended to ecological processes (Samaritani et al. 2011).
This study was carried out in four FPZ: Grass, Willow Bush, Mixed Forest and Willow Forest as described by Samaritani et al. (2011). Grass consists of a gravel strip which is covered by fine sediments with a depth of up to one meter. The dominant species is the grass *Phalaris arundinacea*. Willow Bush consists of banks of older sediments with shrubs, mainly *Salix viminalis*, planted during restoration. This strip has a width of five to ten meters. Mixed Forest and Willow Forest are characteristic mature floodplain forests, which are dominated by *Acer pseudoplatanus* and *Fraxinus excelsior* trees for the former and by mature *Salix alba* trees for the latter (Samaritani et al. 2011). Figure 3 gives a view over Grass, Willow Bush and Mixed Forest from the river bed along the sampling transect.

The minimum and maximum elevation of FPZ Grass is 372.5 m and 373.4 m above sea level. FPZ Willow Bush has a minimum and maximum elevation of 372.5 m and 373.6 m above sea level. And the minimum and maximum elevation of FPZ Mixed Forest is 373.6 and 374.9 m above sea level. Flooding in Grass begins at a river discharge of 125 m³ per second and it is completely flooded above a discharge of 250 m³ per second. Flooding in Willow Bush starts at a discharge of 150 m³ per second and it is completely flooded above a discharge of 270 m³ per second. And the flooding in Mixed Forest begins at a discharge of 650 m³ per second and it is completely covered with water at a discharge greater than 800 m³ per second. These values refer to May 2010 and are subject to ongoing sedimentation and erosion processes (Samaritani et al. 2011).

According to historical discharge data, mean yearly discharge from 2007 to 2010 was around 50 m³ per second and the statistical frequency of peak discharges over the last 106 years was 822 m³ per second every tenth year, 730 m³ per second every fifth year and 573 m³ per second every second year (FOEN 2011). From 2007 to 2009, at least half of the area of Grass was flooded more than ten times a year with an inundation period of one to 14 days. Half of Willow Bush or more was flooded four to six times with an inundation period of shorter than a day. And at least half of the area of Mixed Forest was inundated one to two times a year for less than a day (Samaritani et al. 2011).
2.3. Quantification of atmospheric nitrogen deposition

2.3.1. Throughfall method

Atmospheric nitrogen deposition onto open field, referred to as bulk precipitation, was measured by continuously collecting the dry and wet precipitation onto open bulk collectors over a given period and analysing the nitrogen concentration (NO$_2^-$, NO$_3^-$, NH$_4^+$) of the collected solution. With those values, fluxes of nitrogen were scaled to a reference surface and period (kg N ha$^{-1}$ year$^{-1}$).

For forested areas covered with a canopy, the throughfall method of Thimonier et al. (2005) was applied and adapted to quantify nitrogen deposition only:

Total deposition of nitrogen (TD) was throughfall of nitrogen (TF) plus canopy uptake of nitrogen (CU), neglecting stem flow and canopy nitrogen leaching. This resulted in the following equation:

\[ TD = TF + CU \]  \hspace{1cm} (2)

Whereas TF was quantified directly by sampling precipitation under the canopy and analysing dissolved nitrogen species, CU had to be measured with proxies. CU was modelled based on the ion exchange principle. Therefore the mass concentration of all relevant species (e.g. mg/L) was transformed to a charge concentration (e.g. micro mol equivalent charge/L).

In exchange for the uptake of NH$_4^+$ and H$^+$ and as counterions of weak acids, plants leach base cat ions (Ca$^2+$, Mg$^{2+}$, K$^+$). Corrected for a certain throughfall ratio of NO$_3^-$ (TFNO3) and NH$_4^+$ (TFNH4), CU can thus be defined as canopy leaching of base cations (Clebc), minus canopy leaching of weak acids (Clewa) and canopy uptake of H$^+$ (CUH). It was assumed from empirical results that ion exchange efficiency of NH$_4^+$ is six times larger than NO$_3^-$ (Thimonier et al. 2005).

\[ CU = (Clebc - Clewa - CUH) \times (1 + TFNO3 / 6TFNH4) \]  \hspace{1cm} (3)

Clebc is the difference between the throughfall of base cations (TFbc) and the total deposition of base cations. The latter was estimated from bulk precipitation of base cations (BPbc) times the ratio of throughfall to bulk precipitation of Na-ions (TFNa and BPNa), assuming that the particles containing Na-ions have a similar diameter as particles containing the leached base cations (Thimonier et al. 2005).

\[ Clebc = TFbc - BPbc \times TFNa / BPNa \]  \hspace{1cm} (4)

Clewa was calculated as the throughfall of weak acids (TFwa) minus two times bulk precipitation of weak acids (BPwa), where weak acids are derived from the difference of the cations (base cations, H$^+$ and NH$_4^+$) and the strong acid anions SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ (Thimonier et al. 2005).

\[ Clewa = TFwa - 2BPwa \]  \hspace{1cm} (5)

Finally, CUH was modelled as the difference of Clebc and Clewa, corrected with an empirical factor gained from the ratio of the throughfall of H$^+$ (TFH) and TFNH4 (Thimonier et al. 2005).

\[ CUH = (Clebc - Clewa) \times 6TFH / (TFNH4 + 6TFH) \]  \hspace{1cm} (6)

CU and TD were derived with applying equations (2) to (6) to the measured throughfall and bulk fluxes of NH$_4^+$, NO$_3^-$, Na$^+$, Ca$^2+$, Mg$^{2+}$, K$^+$, H$^+$ and SO$_4^{2-}$.

Total deposition (TD) was then separated into WD and DD according to equation (7). For simplicity, WD was assumed to be equal to BP, although a correction factor should have been applied to account for direct DD onto the collector.

\[ TD = WD + DD = BP + DD \]  \hspace{1cm} (7)
NO$_2$ as a further nitrogen species is neglected in the model because its concentration is rather low and used to be under the limit of detection in the past (personal information by Anne Thimonier).

2.3.2. Atmospheric deposition sampling

Atmospheric deposition was sampled from beginning of April 2009 to end of March 2010 in a biweekly modus by Benjamin Huber (WSL), according to standard methods of Thimonier (1998) and Thimonier et al. (2005). Additionally, precipitation volume, temperature and humidity data were recorded in real-time by a nearby meteorological station of RECORD. Open funnel-type rainwater collectors were mounted 1.5 m above ground, as shown in Figure 4. To avoid bird droppings, a ring that exceeded the diameter of the funnel by ten centimetres was installed horizontally some centimetres above the top of the funnel.

![Figure 4: Open bulk collector used for precipitation sampling](image)

Throughfall precipitation was sampled in the mature mixed forest, representing the FPZ *Mixed Forest* and additionally in a nearby mature willow forest representing the FPZ *Willow Forest*. There was no sampling representing the FPZ *Willow Bush*. In *Mixed Forest*, ten open collectors were distributed randomly along the transect F2, F5 and F9. In the FPZ *Willow Forest*, ten collectors were distributed randomly.

Simultaneously, bulk precipitation was sampled in a nearby unrestored pasture within the test site of RECORD, representing FPZ *Grass*. In the pasture, three open collectors were arranged along a straight line with a distance of one meter between.

2.3.3. Sample preparation and chemical analysis

All precipitation samples were visually checked for contamination (e.g. bird droppings) before they were pooled per FPZ, filtered (0.45 micrometer) and stored at 4$^\circ$ C until analysis. Beside the chemical species NH$_4^+$, NO$_3^-$, Na$^+$, Ca$^+$, Mg$^{2+}$, K$^+$, H$^+$, SO$_4^{2-}$ relevant for the throughfall method, the conductivity and the concentration of the following bulk parameters/species were quantified: total nitrogen, dissolved organic carbon, NO$_2^-$, Al$^3+$, Fe$^{2+}$, Mn$^{2+}$, Si$^{4+}$, P, S.

In total, samples of 14 time periods were collected and analyzed, representing about two third of the time and precipitation of the whole year. One of the sampling periods comprised of four instead of
two weeks. Three quarters of the samples were collected between April and October in order to account for the more intense precipitation and canopy exchange during the growing season.

2.3.4. Estimation of missing precipitation samples and concentrations

In order to complete the data set, precipitation and concentration of the relevant species were interpolated for all FPZ for the time periods not covered by samples. Simple linear regressions (least square estimator) were conducted in R and log-transformations were applied where they improved the distribution of residuals and the coefficient of determination ($R^2$).

For the regression of the precipitation volumes, the value from the meteorological station was the explanatory variable and sampled volume was the dependent variable. For every FPZ a single regression was performed. $R^2$ for Grass amounts to 0.99, for Mixed Forest to 0.97 and for Willow Forest to 0.95 (n=14 for all FPZ).

For the regression of the hydro-chemical concentrations, the measured amount of precipitation volume was the explanatory variable and hydro-chemical concentration was the dependent variable. This linear model was motivated by the assumption that the amount of washed out chemical species (concentration) is diminishing with ongoing rain in a biweekly period (rain intensity). For every FPZ a single regression was performed with sample size of 14. Where $R^2$ was too low or the distribution of the residuals was insufficient, mean values over all periods were used as predictions instead.

After replacing all values below the detection limit by zero and filling the data gaps of precipitation and chemical data, for every FPZ and chemical species, the average of the concentration over all intervals was calculated, weighted by their respective share of whole-year precipitation volume. The averaged values were then used in the throughfall method to calculate TD for each FPZ.

2.3.5. Statistical analysis

To evaluate whether there is a connection between precipitation intensity and the concentration of the nitrogen species in the precipitation, for each species a simple linear regression in R was performed. The concentration of the species of every sample period was the dependent variable, whereas the sampled precipitation volume for each sample period was the independent variable.

In order to infer a dependency between precipitation intensity and the mass flow of the nitrogen species, for each species a simple linear regression in R was conducted. The concentration of the species times the precipitation volume of every sample period was the dependent variable and the precipitation volume on its own was the independent variable.
2.4. Quantification of alluvial nitrogen deposition

2.4.1. Alluvial deposition sampling

During the sampling period, five significant flood events took place. They had a peak discharge of roughly 400-600 m³ per second and occurred around the following dates, where the daily average discharge per second reached their maximum (in brackets): 03.06.2010 (229 m³), 19.06.2010 (326 m³), 06.08.2010 (373 m³), 28.08.2010 (235 m³) and 26.09.2010 (369 m³). The values are taken from the “Hydrological foundations and data” of the Federal Department of the Environment, Transport, Energy and Communication (FOEN) and are measured at Andelfingen, about five kilometres downstream of the test site (FOEN 2011). The recording station may show a systematically lower discharge rate during floods due to existing floodplains between the test site and the station.

In the low-lying FPZ Grass and Willow Bush that are exposed to frequent flooding, high flow velocity and heavy erosion, elevation changes were tracked with sediment sticks. The solid sticks, with a length of about one meter and a diameter of about three centimetres, were piled vertically into ground. The net change of the depth of the sediment could be derived from the change of the distance from the ground to the top of the stick. According to Steiger et al. (2003), sediment sticks are inexpensive and reliable but they can have an impact on the local flow pattern and thus on local sediment rate.

In the more elevated FPZ Mixed Forest with rare flooding, lower flow velocity and temporary puddles, sediment traps were used. Patches of synthetic turf with an edge length of 30 times 40 centimetres were nailed to the ground. Particles were then trapped by the augmented capillary surface that simulates covered ground (e.g. litter). Research indicates that although the turf mats hardly trap particles smaller than six micrometers, a substantial proportion of larger particle were trapped (Steiger et al. 2003). Sediment traps were also installed in Willow Bush to gain sampling material for nitrogen analysis. Examples of an installed sediment trap and sediment stick are shown in Figure 5.

![Figure 5: Sediment trap and stick used for sediment sampling. Synthetic turf mat as a trap (left), massive stick as elevation reference (right)](image)

Measurements with sticks took place in four plots in each of the following FPZ: Grass (PH1-4) and Willow Bush (SB1-4). Per plot, nine sticks with a distance of about five meters were arrayed to a 3x3-square with a side length of about ten meters. As shown in the Figure 6, the square was parallel to the
river flow direction and the sticks were continuously numbered from top-left to down-right, starting with stick one as the most remote and downstream located stick.

![Figure 6: Array of the stick within the sampling plots](image)

The plots where monitored over a period of one year, beginning in April 2010. During the water intense summer half year from mid of April 2010 to mid of October 2010, the sediment elevations were recorded four times. Mid of April 2011 was a final review, where no significant changes of the levels could be detected.

Sampling with traps was done using synthetic turf mats. There were two plots in Willow Bush (SB2-3) and four plots in Mixed Forest (F2-3, F5, F9) with three traps per plot. The traps within a plot were arrayed along a transect orthogonal to the river flow direction. Sedimentation on the traps was sampled from mid of April 2010 to mid of October 2010. Sampling period can be regarded as a whole year, because there was no flood after October 2010. The exact positions of all plots (sticks and traps) are shown in Figure 2 in the chapter "Introduction".

2.4.2. Sample preparation and analysis

The total volume of sedimentation in Grass and Willow Bush was calculated per stick from the net change of sediment depth over one year times the reference area of one hectare. The resulting volumes were then multiplied with a representative bulk density of 840 kg/m³ for Grass and 1130 kg/m³ for Willow Bush. Bulk density values were taken from volumetric top soil samplings in 2008. An average mass-weighted nitrogen content derived from the measured nitrogen content of SB2-3 (traps) was then applied to all sticks. Converting the values to a mass basis and scaling them up to a hectare, a stick specific total nitrogen deposition (kg N ha⁻¹ y⁻¹) resulted. Average values per stick, per plot, per FPZ and for all sticks together (both FPZ) were calculated.

The sediment was washed off the traps just after each flood event. After drying the suspension, the mass of the net sedimentation per trap was measured. The total nitrogen and organic carbon content of finely ground, dried soils were determined as described by Walthert et al. (2010). Furthermore the particle size distribution (fraction of sand, silt and clay) was determined by the pipette method of Gee and Bauder (1986).

For the FPZ Mixed Forest the measured nitrogen content per trap and flood event was applied to the respective measured sedimentation mass. The area of one trap was then scaled up to a hectare and the sum over all events resulted in the amount of deposited nitrogen per one trap. The mean values of each plot, of all plots per FPZ and of all plots together (both FPZ) were then calculated. During one large flood (19.06.2010) no traps were installed in plot SB2-3. The sedimentation rate and nitrogen content for this event was estimated by using the values of the same plot from a flood event with a very similar discharge rate (06.08.2010). During the flood of 06.08.2010 some sedimentation took place in plot F9 but the amount per trap was too small to analyse. The three samples were pooled to
one sample. The measured average nitrogen content of the whole plot was then applied to all three traps and the total mass of sediment was allocated to the traps according to the fractions of other flood events.

2.4.3. Statistical analysis

In order to identify whether there are significant differences in alluvial nitrogen deposition with respect to FPZ, plot and within-plot position, a simultaneous multi-way analysis of variances was performed in R. Total kilogram nitrogen deposited per hectare and flood event is the dependent variable, whereas FPZ, plot and the relative position within the plot are the explanatory variables (all variables are blocking variables, except the relative position). The within-plot position is relative to the river and determined by “left”, “centre”, “right”, “up”, “mid” and “down”, with “left” as most down stream and “up” as most remote, and therefore most elevated by trend. Additionally, Tukey’s post-hoc tests were performed in order to infer significant differences between pairs of FPZ and plots.

The relation between different sediment fractions, namely sand, silt and clay, and the nitrogen content of the sediment was inferred by a linear regression in R. In order to avoid singularity due to the multicollinearity of the explanatory variables (they always sum up to 100%) simple regressions were performed instead of multiple ones.
3. Results

3.1. Atmospheric nitrogen deposition

Bulk precipitation measured in the pasture from April 2009 to March 2010 amounted to 854 mm. The meteorological station recorded 898 mm, close to the long-term average (Samaritani et al. 2011). Total atmospheric inorganic nitrogen deposition in the open FPZ (e.g. Grass) was 8.0 kg N ha⁻¹ y⁻¹. It was composed of 2.5 kg N ha⁻¹ y⁻¹ from NO₃⁻ and 5.4 kg N ha⁻¹ y⁻¹ from NH₄⁺. Furthermore, the rain samples contained dissolved organic nitrogen (3.0 kg N ha⁻¹ y⁻¹) and NO₂⁻ (0.1 kg N ha⁻¹ y⁻¹).

In the FPZ Mixed Forest, the throughfall precipitation from April 2009 to March 2010 amounted to 683 mm. Analysis of precipitation samples of Mixed Forest and application of the throughfall method resulted in a total atmospheric inorganic nitrogen deposition of 16.7 kg N ha⁻¹ y⁻¹, neglecting NO₃⁻ (0.7 kg N ha⁻¹ y⁻¹). TF is 7.2 kg N ha⁻¹ y⁻¹, WD is 7.9 kg N ha⁻¹ y⁻¹, DD is 8.8 kg N ha⁻¹ y⁻¹ and CU is 9.6 kg N ha⁻¹ y⁻¹. Furthermore, the throughfall samples contained dissolved organic nitrogen (4.6 kg N ha⁻¹ y⁻¹).

Applying the throughfall method to the nearby FPZ Willow Forest resulted in a total nitrogen deposition of 22.9 kg N ha⁻¹ y⁻¹. TF is 11.0 kg N ha⁻¹ y⁻¹, WD is 7.9 kg N ha⁻¹ y⁻¹, DD is 15.0 kg N ha⁻¹ y⁻¹ and CU is 11.9 kg N ha⁻¹ y⁻¹. NO₂⁻ is neglected (0.8 kg N ha⁻¹ y⁻¹). Furthermore, the throughfall samples contained dissolved organic nitrogen (3.1 kg N ha⁻¹ y⁻¹). Table 1 gives an overview of the results for Mixed Forest and Willow Forest, showing also the results on the chemical species level.

<table>
<thead>
<tr>
<th>Table 1: Atmospheric nitrogen deposition by precipitation type and canopy uptake</th>
</tr>
</thead>
<tbody>
<tr>
<td>TD=Total deposition, TF=Throughfall, WD=Wet deposition, DD=Dry deposition, CU=Canopy uptake</td>
</tr>
</tbody>
</table>

### Atmospheric Deposition

<table>
<thead>
<tr>
<th>Species</th>
<th>Unit</th>
<th>Mixed Forest</th>
<th>Unit</th>
<th>TBD</th>
<th>TF</th>
<th>WD</th>
<th>DD</th>
<th>CU</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>13.5</td>
<td>4.7</td>
<td>5.4</td>
<td>8.1</td>
<td>8.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>3.2</td>
<td>2.5</td>
<td>2.5</td>
<td>0.7</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOT</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>16.7</td>
<td>7.2</td>
<td>7.9</td>
<td>8.6</td>
<td>9.6</td>
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<table>
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<th>Species</th>
<th>Unit</th>
<th>Willow Forest</th>
<th>Unit</th>
<th>TBD</th>
<th>TF</th>
<th>WD</th>
<th>DD</th>
<th>CU</th>
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<tr>
<td>NH₄⁺</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>19.4</td>
<td>8.2</td>
<td>5.4</td>
<td>14.0</td>
<td>11.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>3.5</td>
<td>2.9</td>
<td>2.5</td>
<td>1.0</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TOT</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>22.9</td>
<td>11.0</td>
<td>7.9</td>
<td>15.0</td>
<td>11.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

An important factor for the amount of atmospheric deposition in open field is the amount of precipitation (WD). A linear regression reveals a significant positive relation between the mass flow of the species and precipitation intensity (volume per biweekly sampling period). This effect for an additional millimetre of rain is estimated 0.121 mol/ha for NO₃⁻ (p-value=0.021, adj. R²=0.344, n=13), 0.276 mol/ha for NH₄⁺ (p-value=0.088, adj. R²=0.173, n=13) and 0.006 mol/ha for NO₂⁻ (p-value=0.007, adj. R²=0.451, n=13). There is no indication for a diminishing concentration of nitrogen species with increasing precipitation volume in a sample period (wash-out effect), except for NO₃⁻. This dilution effect amounts to -0.586 micromol/L for an additional millimetre of rain (p-value=0.012, adj. R²=0.402, n=13). *Figure 7* gives an overview over the regression results.
3.2. Alluvial nitrogen deposition

In the FPZ Grass net sediment deposited in one year yields 17.9 mm. Applying an average nitrogen mass-weighted content of 0.162 % derived from SB2-3, the sediment represents a total alluvial nitrogen deposition of 244 kg N ha\(^{-1}\) y\(^{-1}\) in the FPZ Grass. The standard deviation of all plots in this FPZ is 110 kg N ha\(^{-1}\) y\(^{-1}\). Minimum and maximum average deposition per plot is 167 kg N ha\(^{-1}\) y\(^{-1}\) and 406 kg N ha\(^{-1}\) y\(^{-1}\). Lowest and highest within plot standard deviation is 93 kg N ha\(^{-1}\) y\(^{-1}\) and 277 kg N ha\(^{-1}\) y\(^{-1}\).

Mean net sedimentation in the FPZ Willow Bush in the observed year amounts to 5.9 mm, reflecting a total alluvial nitrogen deposition of 107 kg N ha\(^{-1}\) y\(^{-1}\). The standard deviation of all plots in this FPZ is 46 kg N ha\(^{-1}\) y\(^{-1}\). Minimum and maximum average deposition per plot is 62 kg N ha\(^{-1}\) y\(^{-1}\) and 171 kg N ha\(^{-1}\) y\(^{-1}\). Lowest and highest within plot standard deviation is 77 kg N ha\(^{-1}\) y\(^{-1}\) and 162 kg N ha\(^{-1}\) y\(^{-1}\).

On average, 23 kg N ha\(^{-1}\) y\(^{-1}\) were deposited by floods in the FPZ Mixed Forest. Smallest deposition per plot was zero in F2 (no flood) and the highest deposition was 50 kg N ha\(^{-1}\) y\(^{-1}\). The mass-weighted average nitrogen content over all plots in Mixed Forest was 0.23%, ranging from 0.19 % to 0.32 % per plot.

Figure 8 shows the total alluvial nitrogen deposition per flood event for all plots, once for the sticks (s) and once for the traps (t). There is a visual trend of decreasing nitrogen deposition with increasing elevation of the FPZ (PH<SB<MF). The difference between Grass (PH) and Willow Bush (SB) measured
with sticks is highly significant (p-value <0.001, n=360) and also the difference between SB and Mixed Forest (MF) measured with traps shows a strong significance (p-value<0.001, n=72). A Tukey’s post-hoc test on a confidence level of 95% shows for the stick samples four significant differences out of all 28 possible two-plot combinations: PH1-PH2, PH1-PH3, PH1-PH4 and PH1-SB2. For the trap samples, nine of 15 trap sample pairs are significantly different: SB2-MF2, SB2-MF3, SB2-MF5, SB2-MF9, SB2-SB3, SB3-MF2, SB3-MF3, SB3-MF5, SB3-MF9.

The two sample series (stick and traps) overlap in the plots SB2-3. By comparing the nitrogen deposition as done in the Figure 9, the results seem to be similar for SB2 but very different for SB3. This perception can be confirmed with a Wilcoxon-Mann-Whitney test, showing that there is no significant difference between the two SB2 samples (n1=45, n2=12) but a highly significant difference between the SB3 samples (p-value <0.001, n1=45, n2=12).

Figure 8: Nitrogen deposition (sticks and traps) for all plots and flood events

Figure 9: Comparison of nitrogen deposition measured by two different sampling methods
For plots SB2 and SB3 (s=stick, t=trap)
Although there are no exact elevation values for the plots available, the relative positions within a plot are given for the stick samples. These positions of the subplot measurements can give an indication for the relative elevation. The empirical distribution of nitrogen deposition per relative elevation is indicated in the box plot of Figure 10. The difference of nitrogen deposition between the relative elevations (sticks) is highly significant (p-value <0.001, n=360) and the Tukey’s post-hoc test shows that all relative elevations are significantly different to each other on a confidence level of 95%.

![Nitrogen per relative elevation (sticks)](image)

Figure 10: Comparison of nitrogen deposition (sticks) between different within-plot elevations

The results for the new sedimentation per event in millimetre are in general very similar to the results of nitrogen deposition. Therefore and because absolute amount of sedimentation is not in focus of this thesis, these results are not presented.

With regard to the grain size distribution, the statistics exhibit no significant effects for sand, but a weak significant effect of decreasing nitrogen content with increasing silt content (p-value = 0.097, adj. R²=0.074, n=26). For clay, this effect is stronger, very significant and able to explain more of the variation (p-value = 0.006, adj. R²=0.247, n=26). An increase of one percent clay leads to an increase in nitrogen concentration of 0.007 percent.

In order to clarify whether the composition of the three fractions sand, silt and clay varies between the FPZ and the plots, a simultaneous multi-way analysis of variance was performed. The box plots in Figure 11 give a visual indication of the difference in nitrogen content between the FPZ and plots for the different fractions. There is no significant difference in nitrogen content for sand between Mixed Forest and Willow Bush. For silt there is a significant FPZ effect of 1.0 percentage point between the two FPZ (p-value = 0.012, n=26), with higher levels of silt in Willow Bush. And for clay, the effect of FPZ is calculated as 5.5 percentage point with the share of clay in Mixed Forest being higher than in Willow Bush. This effect is strongly significant (p-value <0.001, n=26). When the effect of the plot within a FPZ on the distribution of the soil fractions is analyzed, a more heterogeneous picture with high inter-plot variation is visible. The only significant plot effect is related to the fraction of silt (p-value = 0.024, n=26) but there is no significant difference anymore when the differences between all two-plot combinations are tested pairwise with the Tukey’s post hoc test.
Total Nitrogen deposition, nitrogen concentration, net new sediment, grain size distribution and C-N ratio are summarized per FPZ and plot in Table 2. C-N ratios are provided by Benjamin Huber (unpublished data).

Table 2: Characterization of the alluvial deposition for all FPZ and plots
(Total nitrogen deposition and content, net new sediment, grain size distribution and C-N ratio)

<table>
<thead>
<tr>
<th>FPZ/Plot</th>
<th>Unit</th>
<th>Grass</th>
<th>PH1</th>
<th>PH2</th>
<th>PH3</th>
<th>PH4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>245.7 ± 197.2</td>
<td>406.3 ± 277.2</td>
<td>208.3 ± 181.3</td>
<td>193.6 ± 92.5</td>
<td>166.6 ± 166.6</td>
</tr>
<tr>
<td>N Content</td>
<td>%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Net New Sediment</td>
<td>mm y⁻¹</td>
<td>17.9</td>
<td>29.8</td>
<td>15.3</td>
<td>14.2</td>
<td>12.2</td>
</tr>
<tr>
<td>Fraction of sand</td>
<td>%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fraction of silt</td>
<td>%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fraction of clay</td>
<td>%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>C-N ratio</td>
<td>-</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
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</table>

<table>
<thead>
<tr>
<th>FPZ/Plot</th>
<th>Unit</th>
<th>Willow Bush</th>
<th>SB1</th>
<th>SB2</th>
<th>SB3</th>
<th>SB4</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>107.4 ± 125.8</td>
<td>170.6 ± 181.7</td>
<td>62.2 ± 77.1</td>
<td>108.0 ± 145.2</td>
<td>90.7 ± 93.4</td>
</tr>
<tr>
<td>N Content</td>
<td>%</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.17</td>
<td>0.16</td>
<td>n.a.</td>
</tr>
<tr>
<td>Net New Sediment</td>
<td>mm y⁻¹</td>
<td>5.9</td>
<td>9.3</td>
<td>3.4</td>
<td>5.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Fraction of sand</td>
<td>%</td>
<td>15.8</td>
<td>n.a.</td>
<td>8.4</td>
<td>17.4</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fraction of silt</td>
<td>%</td>
<td>67.5</td>
<td>n.a.</td>
<td>74.0</td>
<td>68.0</td>
<td>n.a.</td>
</tr>
<tr>
<td>Fraction of clay</td>
<td>%</td>
<td>16.7</td>
<td>n.a.</td>
<td>17.5</td>
<td>18.5</td>
<td>n.a.</td>
</tr>
<tr>
<td>C-N ratio</td>
<td>-</td>
<td>11.91</td>
<td>n.a.</td>
<td>11.20</td>
<td>12.06</td>
<td>n.a.</td>
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<table>
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<th>FPZ/Plot</th>
<th>Unit</th>
<th>Mixed Forest</th>
<th>F2</th>
<th>F3</th>
<th>F5</th>
<th>F9</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>kg ha⁻¹ y⁻¹</td>
<td>23.2 ± 19.9</td>
<td>0.0 ± 0.0</td>
<td>20.4 ± 11.1</td>
<td>20.7 ± 8.2</td>
<td>49.7 ± 11.7</td>
</tr>
<tr>
<td>N Content</td>
<td>%</td>
<td>0.23</td>
<td>n.a.</td>
<td>0.25</td>
<td>0.27</td>
<td>0.20</td>
</tr>
<tr>
<td>Net New Sediment</td>
<td>mm y⁻¹</td>
<td>1.1</td>
<td>0.0</td>
<td>0.9</td>
<td>0.9</td>
<td>2.5</td>
</tr>
<tr>
<td>Fraction of sand</td>
<td>%</td>
<td>12.9</td>
<td>n.a.</td>
<td>11.4</td>
<td>13.9</td>
<td>3.4</td>
</tr>
<tr>
<td>Fraction of silt</td>
<td>%</td>
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<td>n.a.</td>
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<tr>
<td>Fraction of clay</td>
<td>%</td>
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<td>n.a.</td>
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<td>25.5</td>
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<td>C-N ratio</td>
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<td>10.57</td>
<td>n.a.</td>
<td>10.72</td>
<td>10.81</td>
<td>10.50</td>
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</table>
3.3. Total nitrogen deposition

Total nitrogen deposition as the sum of atmospheric and alluvial deposition amounts for the sample year to 252 kg N ha\(^{-1}\) y\(^{-1}\) for FPZ Grass, 120 kg N ha\(^{-1}\) y\(^{-1}\) for FPZ Willow Bush and 40 kg N ha\(^{-1}\) y\(^{-1}\) for FPZ Mixed Forest. In FPZ Grass, alluvial deposition is responsible for 97% of the total nitrogen input, in FPZ Willow Bush for 90% and in FPZ Mixed Forest still for 58%. The results are summarised in Table 3.

Table 3: Contribution of atmospheric and alluvial to total nitrogen deposition

<table>
<thead>
<tr>
<th>FPZ/Plot</th>
<th>Unit</th>
<th>Grass</th>
<th>PH1</th>
<th>PH2</th>
<th>PH3</th>
<th>PH4</th>
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<tbody>
<tr>
<td>Atmospheric N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>8.0 (3%)</td>
<td>8.0 (2%)</td>
<td>8.0 (4%)</td>
<td>8.0 (4%)</td>
<td>8.0 (5%)</td>
</tr>
<tr>
<td>Alluvial N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>243.7 (97%)</td>
<td>406 (98%)</td>
<td>208.3 (96%)</td>
<td>193.9 (96%)</td>
<td>166.6 (55%)</td>
</tr>
<tr>
<td>Total N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>251.7 (100%)</td>
<td>414.0 (100%)</td>
<td>216.3 (100%)</td>
<td>251.9 (100%)</td>
<td>174.6 (100%)</td>
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<th>FPZ/Plot</th>
<th>Unit</th>
<th>Willow Bush</th>
<th>SB1</th>
<th>SB2</th>
<th>SB3</th>
<th>SB4</th>
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<tbody>
<tr>
<td>Atmospheric N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>12.4 (10%)</td>
<td>12.4 (7%)</td>
<td>12.4 (14%)</td>
<td>12.4 (10%)</td>
<td>12.4 (11%)</td>
</tr>
<tr>
<td>Alluvial N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>107.4 (90%)</td>
<td>170.6 (93%)</td>
<td>74.6 (96%)</td>
<td>106.0 (90%)</td>
<td>90.7 (39%)</td>
</tr>
<tr>
<td>Total N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>119.8 (100%)</td>
<td>183.0 (100%)</td>
<td>87.0 (100%)</td>
<td>118.4 (100%)</td>
<td>103.1 (100%)</td>
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</table>

<table>
<thead>
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<th>FPZ/Plot</th>
<th>Unit</th>
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<th>F2</th>
<th>F3</th>
<th>F5</th>
<th>F9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>16.7 (42%)</td>
<td>16.7 (100%)</td>
<td>16.7 (45%)</td>
<td>16.7 (45%)</td>
<td>16.7 (25%)</td>
</tr>
<tr>
<td>Alluvial N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>23.2 (58%)</td>
<td>0.0 (0%)</td>
<td>20.4 (55%)</td>
<td>20.7 (55%)</td>
<td>49.7 (75%)</td>
</tr>
<tr>
<td>Total N Deposition</td>
<td>kg ha(^{-1}) y(^{-1})</td>
<td>39.9 (100%)</td>
<td>16.7 (100%)</td>
<td>37.1 (100%)</td>
<td>37.4 (100%)</td>
<td>66.4 (100%)</td>
</tr>
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</table>
4. Discussion

4.1. Atmospheric deposition

As assumed in the applied throughfall method, it could be shown that the precipitation intensity over a medium term period (e.g. a fortnight) has a positive effect on the amount of deposited nitrogen. And for NO₃⁻ a significant dilution effect with the precipitation intensity was found. Therefore not only the total precipitation but also the pattern over the whole year may influence TD.

Considering the differences between the FPZ, it is noticeable that the amount of deposited nitrogen in the forested FPZ (17 kg N ha⁻¹ y⁻¹ and 23 kg N ha⁻¹ y⁻¹) is two to three times higher than in the open FPZ Grass (8 kg N ha⁻¹ y⁻¹). Although the FPZ differ in location, different surface properties of the vegetation in the FPZ are more likely to explain the differences. A canopy has a much higher relative surface than a pasture and different tree species and stands have different surface properties (e.g. adsorption rate). Many related studies are able to confirm a canopy retention effect in a similar range of 30-60% of TD (personal information by Anne Thimonier, see appendix).

The CU of 10-12 kg N ha⁻¹ y⁻¹ is high and represents slightly more than half of the total deposition. Although the total amount of nitrogen is in agreement with the study of Thimonier et al. (2005), they derived a much lower CU of about 25% for the Central Plateau in Switzerland. Nevertheless the result underlines the importance of the direct plant uptake of nitrogen via the canopy and of the compartment atmosphere as an important direct source of nitrogen for plants in general.

Differentiating between the various nitrogen species reveals that the amount of NH₄⁺ deposited is about five times higher than the amount of deposited NO₃⁻. This result is similar to the study of Thimonier et al. (2005) that finds an approximate factor of three. The higher ratio in the experimental site of project RECORD may stem from the use of slurry as fertilizer in the nearby arable farmland.

Although there is no possibility of quantifying the uncertainties concerning the model (personal information by Anne Thimonier) the numerous applications of the model in line with the European ICP forest program assures its adequacy. A lack of the model is the exclusion of NO₃⁻. Including it would increase the total atmospheric deposition by 1-4 %. This is not negligible and would justify further research in a model extension.

Thimonier et al. (2005) reports an organic nitrogen deposition between 0.8 and 4.2 kg N ha⁻¹ y⁻¹ in throughfall fluxes and a much lower value for open areas (<1 kg N ha⁻¹ y⁻¹). The fact that the deposition is systematically higher under the canopy than in open areas indicates that the deposition primarily stems from the vegetation above the collectors. The deposition of organic nitrogen can therefore be regarded as an intra-system turnover of nitrogen. Accordingly it was not included in the calculation of the total nitrogen deposition for this study. The deposition in the FPZ Grass (3.0 kg N ha⁻¹ y⁻¹) may was influenced by the proximity of a mature forest.

In order to validate the results, the calculated total atmospheric nitrogen deposition was compared to the results of a different model that can be applied without in-situ precipitation samples. This model is based on the work of Rihm (1996) and was developed further by the FOEN in cooperation with the Coordination Centre on Effects (CCE). CCE is responsible for the development of modelling and mapping methodologies for the integrated assessment of European air pollution effects.

For the model of FOEN (2008), nitrogen deposition was calculated with a combined approach for the reference year 2000 according to the throughfall method. For all subsequent years, WD is estimated by combining the concentration of nitrate and ammonium in precipitation samples of the year 2000 with a precipitation map. And a similar approach was used to determine the dry deposition (gas and aerosols). The concentration fields for these species are derived from emission inventories (200 m
resolution respectively 100 m for NH$_3$) by applying statistical dispersion models. The concentration field for HNO$_3$ is calculated as a function of altitude only. The concentration fields are multiplied by deposition velocities, which are dependent on the reactivity of the species, the surface properties and climatic parameters. The latest specific nitrogen deposition values for the experimental site (coordinates of the federal office of topography: 700300/272100) have been calculated by Beat Rihm by courtesy of the FOEN and refer to the year 2007. They amount to 20.3 kg N ha$^{-1}$ y$^{-1}$, excluding a NO$_x$ deposition of 3.6 kg N ha$^{-1}$ y$^{-1}$. Accordingly, the results from the throughfall method (16.7-23.9 kg N ha$^{-1}$ y$^{-1}$) are not only in line with the general findings from the ICP Forests for Switzerland but also with the more specific estimation of the FOEN model.

Beside atmospheric deposition, atmospheric nitrogen fixation by plants may be another source of nitrogen. Considering the experimental site, no abundant plant species that inhabit the Grass, Willow Bush or Mixed Forest is known to build symbiosis with diazotrophic microorganism. Soil samples show a rather high mean nitrogen concentration of 1.0 to 1.6 g N kg$^{-1}$ and a rather low mean C:N ratio from 13.4-16.2 (Samaritani et al. 2011). These values indicate favourable conditions for biologic activity which revokes the major competitive advantage of symbiotic and free living diazotrophs to establish abundantly in the ecosystem. Therefore nitrogen input by fixation of elementary nitrogen can be regarded as minor and it is not considered in the nitrogen deposition quantification.

Although there was no visual indication of bird droppings in the precipitation samples, most mixed samples exceed the threshold of 0.25 mg PO$_4$$^{3-}$ L$^{-1}$ suggested by Erisman et al. (2003). For more in depth insight to quality assurance of precipitation samples refer to the manual of quality assurance of ICP Forests (2010). An in-situ measurement of the conductivity of each sample before pooling and the use of a fine net on the top of the funnel are recommended for future sampling.

4.2. Alluvial deposition

The expected high variability in the amount of alluvial nitrogen deposition was confirmed. The deposition in the FPZ Grass with an average value of 244 kg N ha$^{-1}$ y$^{-1}$ is about an order of magnitude higher than the deposition in the FPZ Mixed Forest. And it is still roughly five times higher than the deposition in the FPZ Willow Bush. Also the variability within FPZ and even within individual plots is considerably high. It is plausible that given a specific flooding regime (discharge rate, nitrogen load, flow velocity, duration of inundation, surface and flow properties etc.) the elevation is the main determining factor of alluvial nitrogen deposition. Although the exact elevation per sample spot was not defined, the relative position within a plot that tends to follow elevation in the direction of the sampling transect supports this assumption.

A further finding is that the nitrogen content increases significantly with the clay content of the sediment. This effect is probably driven by the high ion exchange capacity and relative surface of the clay particles that results in a strong binding of nitrogen. The different FPZ with different average elevations show a significant difference in clay content with a positive link to the elevation. This effect is probably due to the decreased flow velocity with increased elevation, which allows fine particles such as clay to sediment whereas the larger particles such a sand and silt tend to have already precipitated at lower elevations. Nevertheless this effect on the relative amount of deposited nitrogen content is over-compensated by the much stronger and negative effect of elevation on the absolute amount of nitrogen (sediment mass).

The elevation of a sampling spot is not an exogenous factor but is changing as a result of past sedimentation. Therefore it can be assumed that in the medium term (months to years) the sedimentation reaches a temporary equilibrium where erosion equals sedimentation respectively where net sedimentation tends to be zero until the next extreme flood occurs. It is therefore unclear how far the FPZ are from a temporary steady state and whether the deposition rate is overestimated. In the long run
there is no such equilibrium, because the riparian zone may be exposed to a strong change in the flow regime (e.g. the respective riparian zone is completely eroded and becomes part of the river bed).

Although it seems plausible that traps with its enhanced capillary surface tend to retain more sediment than the surrounding soil, the measured amounts in one plot are very similar to the results of the stick, whereas they differ significantly in another plot. More overlapping sampling should be performed in the future in order to be able to statistically reveal whether there is a systematic difference between traps and sticks and how big this difference is.
5. Conclusions and recommendations

The study is able to answer the addressed research questions: (1) The total deposition of nitrogen in the test site at the River Thur amounts to 40-252 kg N ha\textsuperscript{-1} y\textsuperscript{-1}. (2) The different FPZ differ significantly in the amount of deposited nitrogen and show also a high variability within the FPZ. (3) The amount and content of nitrogen and the fraction of clay in the sediments depends on the elevation; both the fraction of clay and the nitrogen content increase with elevation, whereas the total amount of deposited nitrogen decreases.

The hypothesis that sedimentation is the dominant nitrogen input holds true. Sedimentation is responsible for 97% and 89% of the total nitrogen input into the two lower and more dynamic FPZ Grass and Willow Bush. For the mature and more elevated FPZ Mixed Forest sedimentation still accounts for 58%.

Nitrogen deposition is dependent on the nitrogen sources (emissions and transmission), precipitation and altitude. On a local scale (e.g. around hundred metres) the type of vegetation becomes a very prominent factor which cannot be neglected and has to be accounted for in a canopy model.

The significant amount of deposited nitrogen (up to 406 kg N ha\textsuperscript{-1} y\textsuperscript{-1} per sampling plot) raises attention to the question of a critical load for the ecosystem and to the groundwater quality. Although the young and dynamic FPZ Willow Bush may be able to assimilate a significant amount of nitrogen for the production of its biomass, which is not in a steady state yet, the high nitrogen deposition values are an indication for an oversupply of nitrogen to the ecosystem and extensive nitrogen leaching to the groundwater must be assumed. This raised suspicion asks for further research, e.g. modelling of a mass balance with the deposition results of this thesis as an important input factor.

Alluvial deposition varies heavily with the topography of the location. It could be shown that given a certain flood event, the relief of the riparian zone is the most dominant factor for the deposition rate. In order to quantify the deposition more precisely in the future, sampling should cover the whole profile orthogonal to the river flow direction rather than the parallel one. The recorded data including amount of sediment deposited, flood properties (number of days, daily average discharge, etc.) can then be applied to the whole surface area of the riparian zone which before needs to be assigned to elevation class (e.g. vertical resolution of ten centimetres). In order to obtain reliable estimations of the future alluvial nitrogen deposition in the medium term, statistical data of the discharge rates must be included into an autoregressive time series model.

The alluvial deposition is dominant for the total nitrogen deposition. In order to allocate research resources more efficient, it is suggested to limit the sampling and the modelling to the alluvial deposition only. Given the uncertainties and the minor role of atmospheric deposition, the model of FOEN seems to estimate the atmospheric deposition adequately enough. This was also confirmed by Thimonier et al. (2005), where the results of the throughfall method were close to the modelled values by Rihm (1996).
References


Erisman, J.W. et al. (2003). Field intercomparison of precipitation measurements performed within the framework of the Pan European Intensive Monitoring Program of EU/ICP Forest. In: Environmental Pollution, 125, 139-155.


Appendix

Sampled, recorded and interpolated (coloured) precipitation data:

<table>
<thead>
<tr>
<th>Date</th>
<th>Precipitation (mm)</th>
<th>Mean Value</th>
<th>Max Value</th>
<th>Min Value</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>01.01.2010</td>
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<td>21.2</td>
<td>22.4</td>
<td>19.0</td>
<td>1.3</td>
</tr>
<tr>
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<td>16.8</td>
<td>17.9</td>
<td>14.5</td>
<td>1.2</td>
</tr>
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<td>1.1</td>
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<td>14.8</td>
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</tr>
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<td>1.5</td>
</tr>
<tr>
<td>08.01.2010</td>
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<td>19.5</td>
<td>20.6</td>
<td>15.9</td>
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</tr>
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<td>22.6</td>
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<tr>
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<td>18.9</td>
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<td>1.3</td>
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<td>21.3</td>
<td>22.4</td>
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<td>1.4</td>
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<td>13.01.2010</td>
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<td>16.2</td>
<td>17.3</td>
<td>12.5</td>
<td>1.3</td>
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Chemical analysis of precipitation samples (coloured: interpolations):

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<tr>
<th>Sampling Date</th>
<th>pH</th>
<th>Conductivity</th>
<th>Cl (μS/cm)</th>
<th>NO((3)</th>
<th>SO(2) (μg/L)</th>
<th>NH(4) (μg/L)</th>
<th>Ca (μg/L)</th>
<th>Mg (μg/L)</th>
<th>Na (μg/L)</th>
<th>Total (mg/L)</th>
</tr>
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<tr>
<td>01.01.2010</td>
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<td>0.58</td>
<td>54.7</td>
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<td>13.2</td>
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<td>4.51</td>
<td>18.9</td>
<td>5.2</td>
<td>34.5</td>
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<tr>
<td>02.01.2010</td>
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<td>0.58</td>
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<td>4.51</td>
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<td>5.2</td>
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<td>18.9</td>
<td>5.2</td>
</tr>
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<td>03.01.2010</td>
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<td>0.58</td>
<td>74.4</td>
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<td>13.2</td>
<td>24.0</td>
<td>4.51</td>
<td>18.9</td>
<td>5.2</td>
<td>34.5</td>
</tr>
<tr>
<td>04.01.2010</td>
<td>7.0</td>
<td>0.58</td>
<td>12.4</td>
<td>24.0</td>
<td>4.51</td>
<td>18.9</td>
<td>5.2</td>
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<td>18.9</td>
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<td>5.2</td>
<td>34.5</td>
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<tr>
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<td>74.4</td>
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<tr>
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<tr>
<td>09.01.2010</td>
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<tr>
<td>10.01.2010</td>
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<td>0.58</td>
<td>12.4</td>
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<td>5.2</td>
<td>34.5</td>
<td>18.9</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Note: Interpolation values are in italics.
Estimated canopy uptake by several studies (Anne Thimonier, unpublished):

<table>
<thead>
<tr>
<th>species</th>
<th>site</th>
<th>estimated canopy retention (kg/ha/yr)</th>
<th>% of total deposition</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Picea abies</td>
<td>Zuna (760 m), Switzerland</td>
<td>0 - 2.5</td>
<td></td>
<td>Fluckiger et al. 1997</td>
</tr>
<tr>
<td>Picea abies</td>
<td>Lauen (1600 m), Switzerland</td>
<td>~ 10</td>
<td>~ 55%</td>
<td>Hor et al. 1989</td>
</tr>
<tr>
<td>Picea abies</td>
<td>Fichtelgebirge, Germany</td>
<td>12.5</td>
<td>42.5%</td>
<td>Ignatova &amp; Dambroe 2000</td>
</tr>
<tr>
<td>Picea abies</td>
<td>Strengbach, France</td>
<td>~ 4 (over 8.5 months)</td>
<td>~ 30 - 50%</td>
<td></td>
</tr>
<tr>
<td>Pseudotsuga menziesii</td>
<td>Spauldor, Netherlands</td>
<td>12</td>
<td>Draaijer &amp; Ermans 1985</td>
<td></td>
</tr>
<tr>
<td>Picea rubens + Abies balsamea</td>
<td>Whiteface Mountain, New York, United States</td>
<td>5.1</td>
<td>31%</td>
<td>Friedland et al. 1991</td>
</tr>
<tr>
<td>Pinus taeda</td>
<td>Georgia Piedmont, United States</td>
<td>4.5</td>
<td>47%</td>
<td>Cappellato et al., 1993</td>
</tr>
<tr>
<td>Carya sp, Quercus sp, Liriodendron</td>
<td>various stands, United States and Norway</td>
<td>4.1</td>
<td>47%</td>
<td>Lovett &amp; Lindberg 1993</td>
</tr>
<tr>
<td>Acer saccharum, Quercus sp, Fagus grandifolia</td>
<td>various stands, New York, NY, United States</td>
<td>1 - 2</td>
<td>40%</td>
<td>Butt &amp; Likens, 1995</td>
</tr>
<tr>
<td>Quercus sp</td>
<td>NC Aurora</td>
<td>11</td>
<td>45%</td>
<td>Puxbaumberg &amp; Gregori 1998</td>
</tr>
</tbody>
</table>
Sampling data from stick measurement (FPZ Grass and Willow Bush):
Sampling data from trap measurement (FPZ Mixed Forest and Willow Bush (partially)):

<table>
<thead>
<tr>
<th>Date</th>
<th>16.06.10</th>
<th>06.06.10</th>
<th>29.05.10</th>
<th>26.09.10</th>
<th>All Events</th>
</tr>
</thead>
<tbody>
<tr>
<td>Event date</td>
<td>16.06.10</td>
<td>06.06.10</td>
<td>29.05.10</td>
<td>26.09.10</td>
<td>All Events</td>
</tr>
<tr>
<td>Discharge m³/s</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrogen in kg/ha per flood event</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrogen per FPZ (sticks)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Nitrogen per FPZ (traps)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Distribution of alluvial nitrogen deposition per FPZ:

<table>
<thead>
<tr>
<th>FPZ (sticks)</th>
<th>Nitrogen per FPZ (sticks)</th>
<th>Nitrogen per FPZ (traps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB</td>
<td>120.0</td>
<td>120.0</td>
</tr>
<tr>
<td>PH</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>FPZ (traps)</th>
<th>Nitrogen per FPZ (sticks)</th>
<th>Nitrogen per FPZ (traps)</th>
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</thead>
<tbody>
<tr>
<td>SB</td>
<td>120.0</td>
<td>120.0</td>
</tr>
<tr>
<td>MF</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Distribution of grain size fractions (sand, silt, clay) per FPZ:

Relation between share of grain size fraction and nitrogen content:

Distribution of nitrogen content per FPZ, plot and relative horizontal position: