

The effects of high intensity precipitation and snowmelt events on the export of nitrogen and sulphur in stream water within the Wüstebach catchment

Master thesis



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Abstract

High intensity rainfall and snowmelt events cause a high discharge, resulting in loss of valuable nutrients for the ecosystem (Yusop et al., 2006; Inamdar et al., 2006; Gao et al., 2014). These events will occur more in the future due to climate change and should therefore be taken into account by making forest management strategies (Federal German Government, 2008) of the National Park Eifel in Germany, where foresters try to bring back the endemic beech by cutting spruce trees (Etmann, 2009). In this study, the effects of snowmelt and high intensity precipitation events on the Nitrogen (N) and Sulphur (S) export of different N and S species in the Wüstebach stream were analysed during five high intensity precipitation and two combined snowmelt and precipitation events. High resolution sampling was conducted in March and May 2018 to cover both limbs of the hydrograph better, and the concentrations of nitrate, sulphate, ammonium, total nitrogen, and total sulphur were measured by various chemical analytic methods. During all events, nitrate and sulphate showed a dilution effect on the rising limb of the hydrograph, which means that these anions are transported by groundwater. Ammonium and organic N and S showed an increase during peak discharge, as they are transported by surface water. Winter events had a larger effect on the export of N and S, because of their long duration, high discharge level and higher in stream concentrations of nitrate and sulphur. Organic N and ammonium concentrations were low, but due to the duration of the event and high discharge, the loss of ammonium and organic N was still higher in winter. Organic S concentrations were negligible and were not considered in the analysis winter event. Therefore, especially combined snowmelt and rainfall events at the end of the winter should be considered in forest management, as they export large amounts of inorganic nutrients and the vegetation cannot compensate the loss by shifting to organic nutrients, because the organic nutrient concentrations are low at the end of the winter.

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1. Introduction

The earth can be seen as a closed system with the sun as external energy source, which means that all matter and energy cycles within the system (Steffen et al., 2006). Humans interfere with the system earth and are the main drivers of global change and biodiversity loss since the industrial revolution (Vitousek et al., 1997; Steffen et al., 2007). Global change can be divided into three categories: land use change, alteration of the biogeochemical cycles, and biotic losses and additions, which are all drivers or results of climate change (Vitousek et al., 1997).

In Germany, climate change will increase the amount of precipitation and the precipitation intensity, and high intensity precipitation events will occur more often in winter than before (Federal German Government, 2008). The effects of these high intensity precipitation events are peaks in discharge in streams (Gao et al., 2014). Land use change can affect how the landscape buffers these high intensity precipitation events. Deforestation decreases the buffering capacity and causes more erosion and transfer sediment and nutrients downstream (Allan et al., 1997). In the second half of the 20th century industrial processes, traffic, industry and agriculture emitted large amounts of chemical compounds, which caused several problems as climate change, acid rain, acidification and eutrophication (Vitousek et al., 1997 a). All these processes have feedback on each other, so climate change, land use change and the emission of chemicals will also have a positive feedback on the changing biogeochemical cycles (Vitousek et al., 1997 a).

Two important biogeochemical cycles are the sulphur (S) and nitrogen (N) cycle. Both are nutrients for plants and are therefore necessary for the food security on earth (Botkin & Keller, 2003; Gruber & Galloway, 2008). The chemical forms that are easiest for plants to take up, SO_4^{2-} and NO_3^- , are highly mobile and can therefore be lost easily (McNeill et al., 2005). After NO_3^- and SO_4^{2-} , plant nutrition is driven by NH_4^+ and organic forms of N and S. These forms are less abundant and/or less mobile, but they can also be lost after high intensity rainfall events. Studies show that peak discharges in small streams also affect the whole biogeochemical cycles in their catchments (Oeurng et al., 2010). Furthermore, due to hydrological connectivity within a catchment, nutrient transport downstream is not only limited to nutrient release from the riparian zone, but to the whole catchment (Oeurng et al., 2011). Hence the peak discharges can alter the biogeochemical cycles upstream by loss of nutrients (Yusop et al. 2006). Indamar et al., (2006) reported that 20, 23, 48, and 49 % of the NO_3^- , SO_4^{2-} , NH_4^+ , and dissolved organic nitrogen (DON) budget was exported during storm events in a forested catchment. Increased concentrations of nutrients can also have detrimental effects on the ecology and water quality in the area (Kleinman et al., 2006; Park et al., 2010).

Capturing samples to measure the transport of nutrients during storms is difficult, because initial nutrient transport occurs rapidly after the start of the extreme precipitation event (Gao et al., 2014; Decker

& Weiler, 2015). The most feasible approach to measure the export of S and N during snowmelt and rainfall events is through the usage of automated samplers, as shown by multiple previous studies (Cánovas et al., 2008; Silins et al., 2009; Riscassi et al., 2010; Gao et al., 2014; Decker & Weiler, 2015). Constant maintenance and setting adjustments are necessary to ensure optimal automatic sampling and additional care should be taken during snowmelt events, because the samples can freeze or access to the machine can be limited (Silins et al., 2009). High resolution sampling with automated samplers has nevertheless been proven as a good method to provide more insight in fluxes of chemical compounds during high flow events (Cánovas et al., 2008; Silins et al., 2009; Riscassi et al., 2010). This study will take both events in summer and winter into account. Summer is defined by Stockinger et al., (2014) as from the 1st of May till the 1st of November based on its catchment response and the winter season from the 1st of November till the 1st of May. Therefore, this study will consider snowmelt events, combined snowmelt and high intensity precipitation events, and high intensity precipitation events.

1.1 Study Area

This study was carried out in the Wüstebach catchment, a small sub catchment of the river Rur in the Eifel National Park. The Eifel National Park is located in the west of Germany and has a national park status since 2004 (Job et al., 2009). It is located in between Cologne, Bonn, Aachen, and the Dutch and Belgian border. The area was established as national park to conserve the endemic beech forest (Job et al., 2009). It is a very popular national park among citizens of Germany, the Netherlands and Belgium and has a Natura 2000 protection status (Mayer et al., 2010). The Eifel National Park is also used as drinking water extraction area for North Rhine Westphalia and the area around Cologne (Vidaurre et al., 2016). The Wüstebach catchment in the Eifel National Park is home to the Eifel/Lower Rhine observatory of the Germany-wide climate change research network TERENO (Terrestrial Environmental Observatories; www.tereno.net). TERENO aims at examining the long-term climate change impacts on the terrestrial environment, landscape and society. The research that is conducted focusses on the hydrosphere, biosphere, pedosphere, atmosphere and anthroposphere (Zacharias et al., 2011; Bogena et al., 2016). There are four research areas in Germany in the framework of the TERENO project (see Figure 1), which represent the different landscapes in the country but also other central European countries (Bogena et al., 2016).

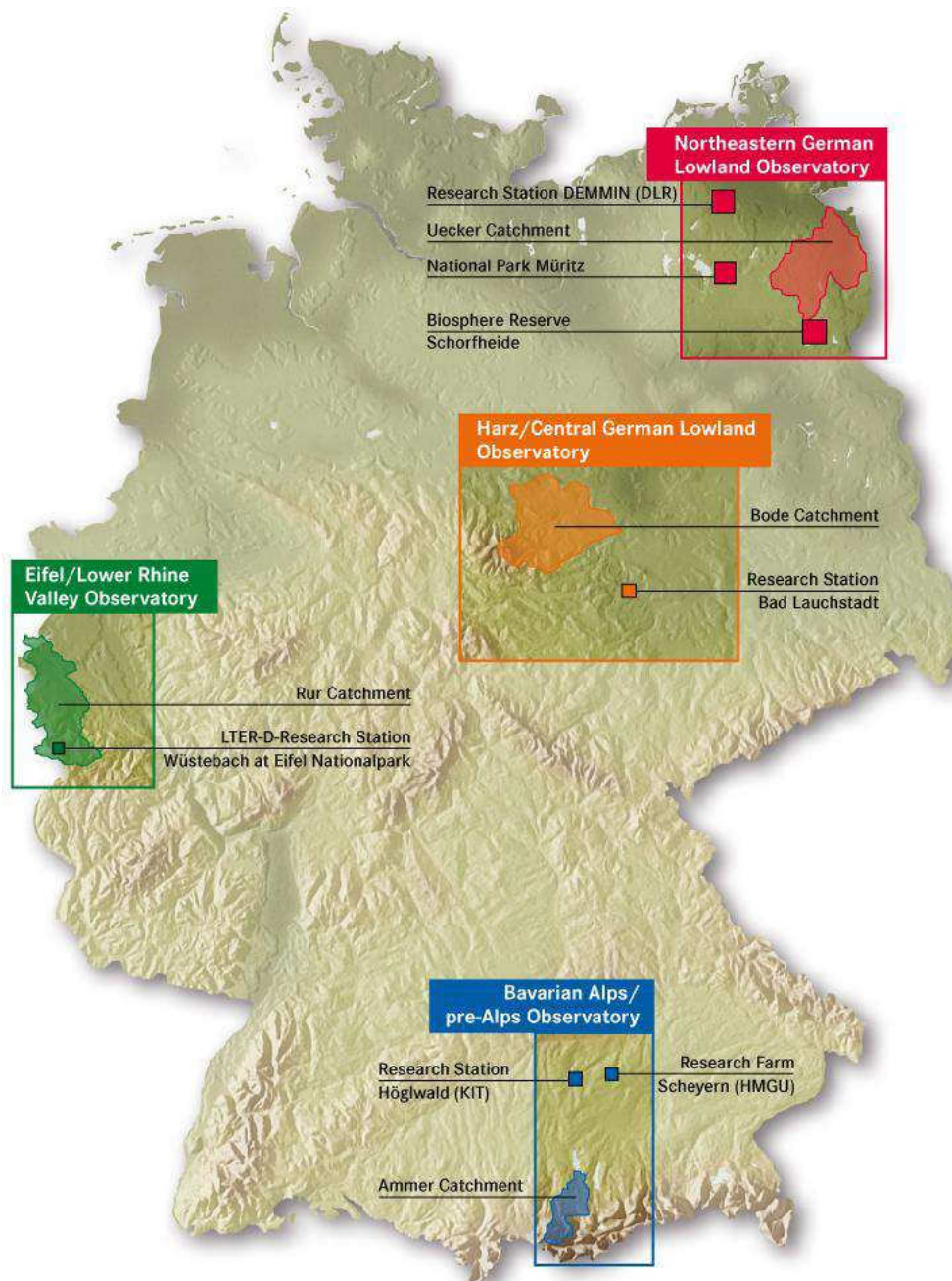


Figure 1. The TERENO network in Germany, the observatories and experimental catchments (Zacharias et al., 2011).

The Eifel/Lower Rhine observatory covers 2354 km² and has a large land use gradient. The south is part of the Eifel Mountains and includes some drinking water extraction sites, in the north (between the Rhine and the Dutch border) the land is used for intensive agriculture and many cities have developed (Bogena et al., 2006). The Wüstebach catchment is located close to the Belgian border in the Eifel National Park and covers 38.5 ha (Graf et al., 2014; Stockinger et al. 2014). After the Second World War, spruce trees were planted in the area for timber production, which predetermined the current dominant tree vegetation

(Etmann, 2009). In 2013, the spruce trees around the Wüstebach stream were removed to create space for the endemic beech trees (Bogena et al., 2015). The hydrology, climate, soils and geology of the site will be explained in more detail in the theoretical framework.

2. Research aim & questions

The aim of this study is to conduct high resolution sampling and continuous measurements to examine the effects of high intensity precipitation and snowmelt events on N and S and to compare the seasonal peculiarities between events. For this purpose, stream water sampling at the outlet of the Wüstebach catchment was modified for optimal time resolved capture of snowmelt and extreme precipitation events. These samples were prepared according to a filtration cascade protocol and analysed for N and S compounds through multiple detection techniques.

In the study area, three automated samplers (Ecotech, Germany) have been installed and are owned by the Helmholtz research centre in Jülich. However, hydrochemistry data of past events has never been fully researched and the sampler has not been used lately. For this study, separate programmes from the automated sampler have been used to collect event samples, more specific information can be found in the sampling strategy section.

The core research question for this study was:

What are the effects of extreme precipitation and snowmelt events on the export of different Nitrogen and Sulphur compounds in stream water within the Wüstebach catchment?

Sub questions

- How do the 5 different tributaries measured contribute to N and S export?
- What are the effects of extreme precipitation on the export of different Nitrogen compounds in the Wüstebach catchment?
- What are the effects of extreme precipitation on export of different Sulphur compounds in the Wüstebach catchment?
- What is the difference between the effects of peak discharge on the export and chemical speciation of N and S between events in winter and in summer?
- Which analytical method for nitrate or sulphate addresses the export of N and S compounds best during snowmelt or high intensity precipitation events?

3. Theoretical framework

3.1 The sulphur cycle

The largest pool of S is the Earth's core, which is around 90% of S on earth (Savage et al., 2015). It reaches the earth's surface by volcanic eruptions in gas or solid form, where it escapes or solidifies and is stored in minerals and rocks (Granat et al., 1976). After weathering of these rocks, mineral S is found in the soil S is transported by water in the form of sulphate and finally ends up in the ocean or atmosphere (Granat et al., 1976). S in the ocean can either cycle through the marine food chain, sink to the deep ocean, react with iron to ferrous sulphide, or it can be emitted to the atmosphere via sea spray (Bates et al., 1992). Sea spray is a process where bubbles formed by wave action are filled with sea salt particles and other chemicals, depending on the chemicals present, bursts and the particles get transported away by the wind (Blanchard, 1989). In the atmosphere, S reacts with oxygen and water vapour and get deposited via wet and dry deposition on the land. S can also be directly emitted by volcanic activity in the form of H_2S , SO_2 , elemental S in gas form, sulphate compounds, and SO_3 (Granat et al., 1976).

In terrestrial ecosystems, S can be either taken up by vegetation or micro-organisms as sulphate or organic S (Granat et al., 1976). According to the theory of bioavailability, the most readily available form of S for plants is inorganic Sulphur (i.e. sulphate), but this is only a small fraction of the total available S in the soil. 95 % of S in soils is present in the form of organic S (Eriksen et al., 1998), of which there are three main forms; sulphate esters, S in amino acids and sulphates and hetero-cyclic S (Kertesz & Mirleau, 2004). Organic S can also be taken up by plants, but this mainly occurs under S deficiencies (Eriksen et al., 1998). Taking up organic S uses more energy from the S mobilising microbes and is only possible under suitable environmental conditions. These include a certain moisture percentage, a defined temperature range, a set microbial community as well as the presence of degradable forms of organic S (Scherer, 2009).

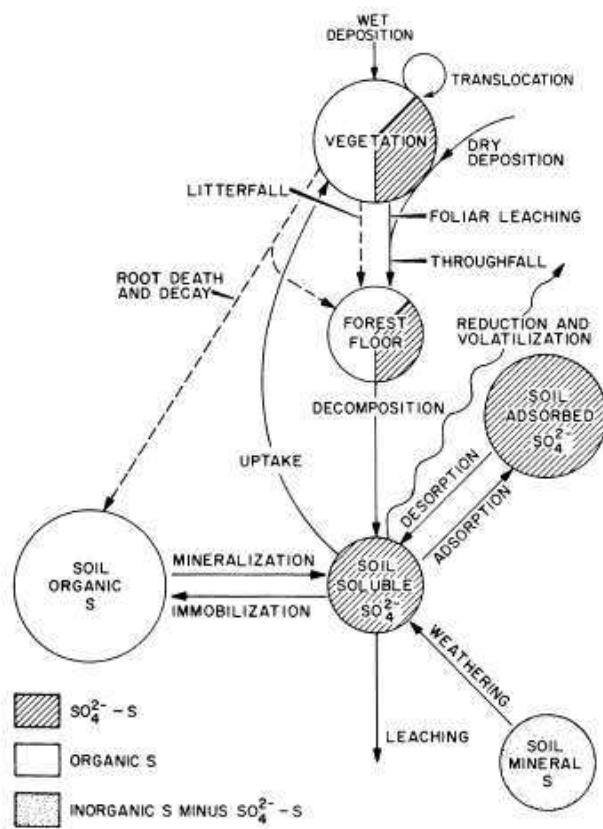


Figure 2. Schematic visualisation of the Sulphur cycle in forests (Johnson, 1984).

Organic S can be transformed to sulphate through mineralisation processes in the rhizosphere (Kertesz & Mirleau, 2004). In turn, immobilisation defines the transformation of inorganic S to organic S (Kertesz & Mirleau, 2004). Both processes are critical for the S cycle in soils and rely mainly on microbes (Ghani et al., 1993).

Plants that have acquired sulphate are then ingested by animals and S further moved through the food chain. When animals die and decompose, S is mineralised or ends up in tissues of micro-organisms, when the micro-organisms decompose the S compounds. After oxidation S can be emitted as SO_2 to the atmosphere again after oxidation (Granat et al., 1976).

In forest ecosystems, litter fall and processes in the forest soils should also be taken into account, as they are a sink for S (Scherer, 2009). Due to litter fall there is a lot of available organic carbon in the form of cellulose and glucose, which enhances microbial activity and thus drives immobilisation (Ghani et al., 1993; Eriksen, 1997; Vong et al., 2003). A moist forest environment additionally supports this (Ghani et al., 1993). Despite the role of N as a limiting nutrient for ecosystems, enhanced N levels only seem to slightly increase the immobilisation of sulphate (Vong et al., 2003). Immobilisation and mineralisation processes of S can take place at the same time (Ghani et al., 1993). Hence, microbes and plants need sulphate for those

processes at the same time and thus compete (Kertesz & Mirleau, 2004). Therefore, an excess of S deposition will increase mineralisation (Johnson, 1984).

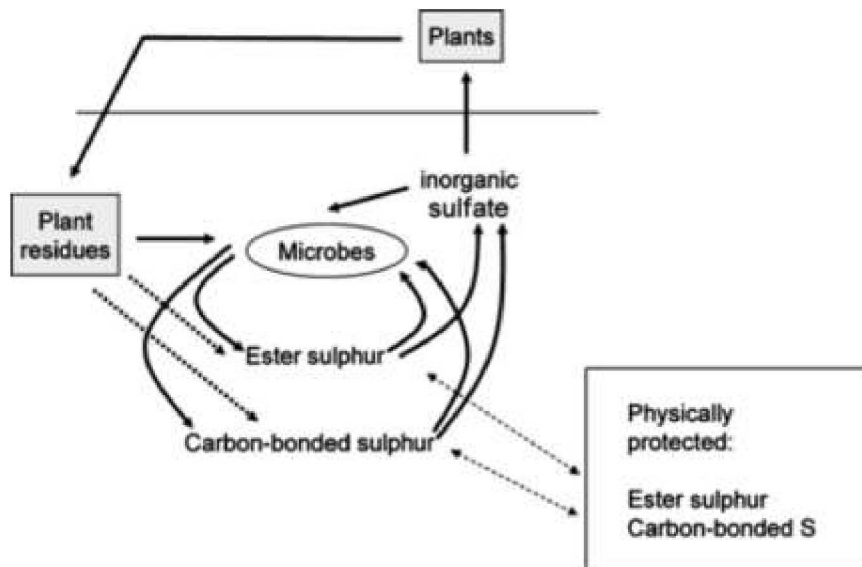


Figure 3. The Sulphur cycle in the soil (McGill & Cole, 1981).

Two main anthropogenic sources of S distribution in the form of sulphur dioxide are burning fossil fuels and adding S to the environment as fertiliser in the form of sulphate or elemental sulphur (Ivanov, 1981; Perraud et al., 2015). In populated areas, the S emissions are mostly dominated by fossil fuel burning for transport (Bates et al., 1992). This Sulphur reacts with oxygen and water (oxidation) and causes acid rain in the form of wet or dry deposition, which harms vegetation (Ivanov, 1981; Greaver et al., 2012). SO_2 deposits close to the source of emission, since the gas has limited mobility, therefore a higher part deposits on land than in the sea, because emissions are mostly land based (Ivanov, 1981). In addition, Sulphur can also act as a green-house gas, enhancing climate change.

Policies such as the clean air act in the United States and the UNECE convention on Long Range Transboundary Air Pollution (LRTAP) in the EU, caused a decrease in S emissions and thus depositions (Gottlicher et al., 2010). Nevertheless, there is a disadvantage to the decrease in S deposition: the amount of sulphate in soil also decreased and now S deficiencies can be a real problem for plants, as the problem of acid rain decreased (Kertesz & Mirleau, 2004; McNeill et al., 2005). S deficiencies do not reduce the growth of the plants but cause an accumulation of amino acids without Sulphur in the foliage of trees. These amino acids are a food source for foliar fungal pathogens, who then grow and can cause deformity or defoliation (Turner & Labert, 1980).

3.2 The nitrogen cycle

70 % of the atmosphere consists out of N in the form of N_2 , which is the N pool for life on earth (Vitousek et al.,1997 b). There are three ways of N fixation: the largest amount of N is fixed by micro-organisms in marine ecosystems, the second largest pool of N is fixed by micro-organisms in terrestrial ecosystems and another way of fixation of N from the atmosphere is by lightning (Galloway et al.,1995).

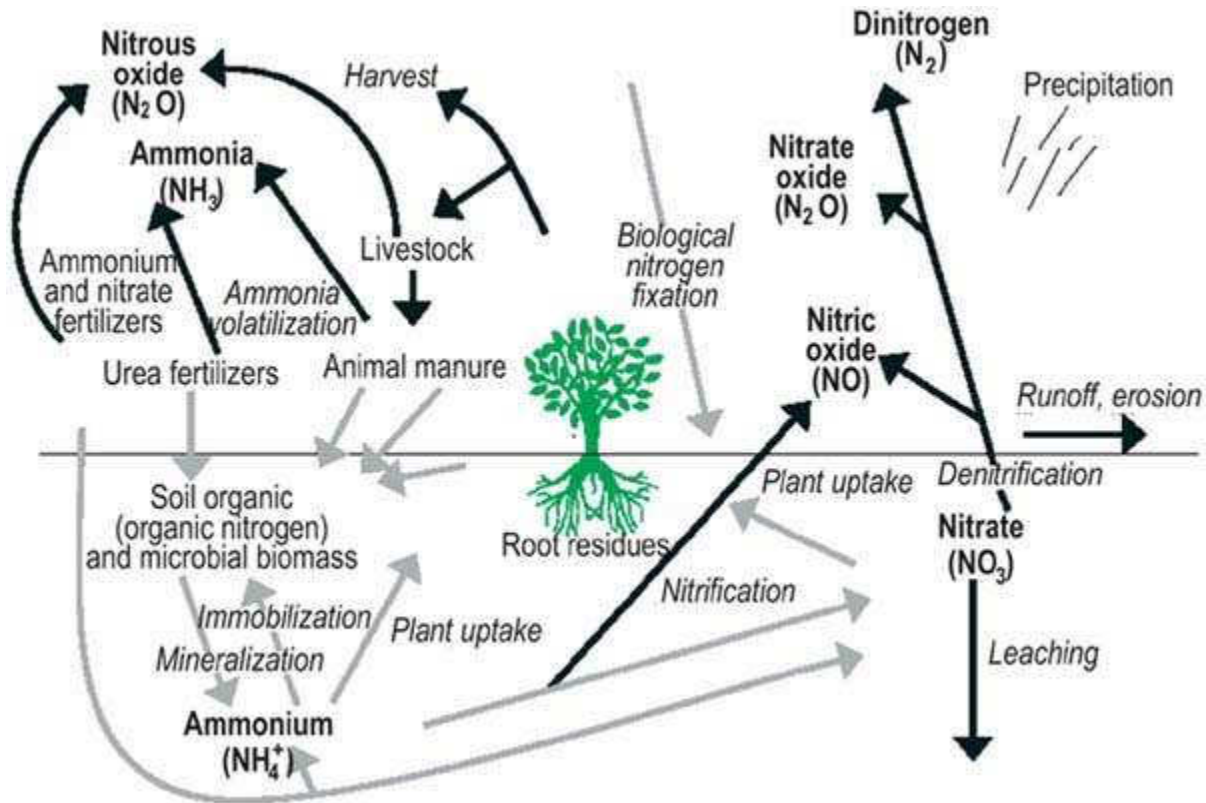


Figure 4. The Nitrogen cycle (OECD, 2001).

This study will focus on N cycling terrestrial ecosystems, a basic overview of the terrestrial N cycle is displayed in Figure 4. In terrestrial ecosystems, atmospheric N is fixed by legumes and nitrifying bacteria that transform it into NH_4^+ . Then, it can be immobilised to organic N by microbes or it can be nitrified by oxidation to NO_3^- by nitrifying microbes. Organic Nitrogen can also be reduced to inorganic Nitrogen by decomposition and mineralisation of organic material (Galloway et al.,1995). In forest soils, pH is a limiting factor for autotroph nitrifying bacteria. At pH levels lower than 5, the nitrification must be done by heterotroph nitrifying microbes (Zhang et al.,2011). In addition, decomposition and mineralisation of soil organic matter from litter fall is dependent on the type of vegetation (Zhang et al.,2011).

In the terrestrial ecosystems, both the inorganic and the organic N is taken up by plants as a nutrients and cycles through the food chain (Näsholm et al.,1998). Animals transform the organic N to inorganic N and add it to the environment again by urinating or decomposition after they die (Galloway et al.,1995).

Denitrifying micro-organisms transform nitrate back to N_2 , NO_2 and NO and emit it to the atmosphere (McNeill et al., 2005). Another important cause of losses of N in forests is wildfires, since they can also burn the forest floor (Johnson & Turner, 2014). Before the industrial age, this was the only way that N was emitted back to the atmosphere. Since the industrial revolution, the N cycle has altered (Galloway et al., 1995; Vitousek et al., 1997 b). Because N is a nutrient for plants, industrial N fixation to create inorganic fertilizer increased in the second half of the 20th century (Galloway et al., 1995). A smaller increase in N fixation is caused by the cultivation of more N fixating crops, such as soybeans and high temperature fossil fuel combustion (Galloway et al., 1995). The latter is also affecting other parts of the N cycle. Fossil fuel combustion also emits Nitrous oxide and nitric (di) oxide to the atmosphere, these gases can act as greenhouse gases and will form acidic compounds when they react with oxygen or water vapour in the atmosphere (Galloway et al., 1995). S can also form acidic compounds in the air and when the acidic N and S compounds reach the soil and vegetation as precipitation they can harm the environment and soil buffering capacity (Greaver et al., 2012).

Another effect of the increased amount of fixed N is an excess of N in the soil (Gruber & Galloway, 2008). Since N acts as a nutrient for plants excesses can limit ecosystem functioning (Hautier et al., 2009). This can cause eutrophication, which firstly increases primary production, but will later make other nutrients will become limiting factors (Tessier & Raynal, 2003). Not all plants and animals can handle this, and biodiversity will decrease (Hautier et al., 2009). A second effect of N excesses is acidification of the soil, which causes increased mobility of toxic metals in the soil, for example aluminium (Vitousek et al., 1997 b, Greaver et al., 2012).

3.3 Other forms than inorganic N and S

Besides sulphate and nitrate, there are also ammonium and organic forms of N and S present in the Wüstebach catchment. Sulphites and Nitrites are not considered in this study, because they hardly occur in the study area (teodoor.icg.kfa-juelich.de, 2018). Gao et al., (2014) for example distinguishes different types of Nitrogen compounds: $N-NO_3^-$, $N-NH_4^+$, Particulate N and Dissolved Organic N. They follow the operational definition of “dissolved”, which defines all nitrogen compounds passing a 450 nm filter as dissolved. Besides inorganic S, also Organic S is considered in this study (Scherer, 2009) can also be transported by clay minerals and iron and aluminium ions, loss of sulphur via those mechanisms also counts as loss of nutrients and is therefore considered in this study. Nitrogen occurs also in organic forms that are behaving differently in the environment than inorganic nitrogen compounds (Inamdar et al., 2006).

It is assumed that sulphate and nitrate are always occurring in a dissolved state, however, there is increasing knowledge in science about transport of nutrients on nanoparticles and colloids (Scherer, 2009; Gottselig et al., 2014; Bol et al., 2015). Studies such as Bol et al. (2015) and Gottselig et al. (2014) define truly dissolved as passing through a 1 k Da filter and everything between 1 nm under 0.1 μm as nanoparticles

(Hartland et al., 2013; Gottselig et al., 2014). Everything that is has a diameter between 1 nm and 1 μm and smaller than 1 μm is called colloid (Hartland et al., 2013; Gottselig et al., 2014). Nanoparticles are actually colloids, although they are a specific group due to their higher reactivity compared to colloids (Hartland et al., 2013). Everything larger than 1 μm will be called particulate (Hartland et al., 2013; Gottselig et al., 2014). Hence, filtration cascades will therefore be used in this study as well as total sulphur and total nitrogen measurements to give an estimate of the organic nitrogen and sulphur and which sizes and mechanisms cause leaching of these compounds.

3.4 The Hydrology of Wüstebach

3.4.1 Precipitation

Data used for this analysis originates from the Deutsche Wetter Dienst (DWD) weather station Kalterherberg- Monschau 8 kilometres from the Wüstebach catchment (Bogena et al., 2015). The data stretches from 2007 till 2018. According to analyses with larger datasets, the average yearly precipitation of the Wüstebach catchment is 1220 mm (1979-1999) (Bogena et al., 2010).

3.4.2 Hydrogeology

The average slope of the catchment is 3.6 % and the maximum slopes are 10.4 %, this causes shallow soils, of which cambisols and planosols are the most common. Histosols and gleysols can also be found, mostly in the riparian zone (Bogena et al., 2015). The soils are formed in a silty clay loam parent material with a large fraction of coarser material, in the category of 0.2 cm to several cm (Rosenbaum et al., 2013; Graf et al., 2014).

The geology of the Wüstebach catchment is mainly Devonian shale and has sandstone inclusions, the porosity and hydraulic conductivity are low (HK100, 2009). The bedrock is covered by two periglacial solifluction layers, the top layer has a lower bulk density and consists out of loess and local debris, the bottom layer has a higher bulk density and consists out of local debris and clay (Borchardt, 2013). Together these layers are 1 to 2 meters thick (Graf et al., 2014). Due to the low density of the upper layer, the water can infiltrate well in this part after precipitation events, and this layer has a higher soil moisture (Borchardt, 2013). Water infiltrates slower in the second layer, which results in a decreased vertical transportation, thus the water will flow over this layer to the stream (Borchardt, 2013). Water that is already in this second layer can flow through the layer to the river (Borchardt, 2013).

The bedrock is highly cemented and therefore water must move through the fractures in the bedrock and the unsaturated zone. Torres et al., (1998) found that when rain falls on a wet soil, a pressure wave is created that can create rapid runoff in the unsaturated zone. Within the Wüstebach catchment, soils are on average wet, i.e. having a soil moisture content of 35% or higher, from November till May and dry from May till November (Rosenbaum et al., 2012; Stockinger et al., 2014).

3.4.3 Groundwater and unsaturated zone response

Under normal circumstances, the fraction of young water in the Wüstebach catchment is 8.4% to 9.0%, this water is younger than 54 days, coming from rainfall (Stockinger et al., 2016).

Grayson et al (1997) described that soils can be in a wet and a dry state. In the wet state, water flows laterally through the unsaturated zone. In the dry state, water moves vertically through the soil. In the dry state local soil properties have an influence on spatial patterns. The wet state is also called, the nonlocal state, since local properties have less influence on spatial patterns (Grayson et al., 1997). In the wet state, also nutrients can be transported. Stockinger et al., (2014) found that during the dry state, hydrological connectivity with the slopes in the Wüstebach catchment is lost and the main catchment response is coming from the riparian zone.

A study by Wiekenkamp et al., (2016) discussed the occurrence of different types of preferential flow during different types of precipitation events. Preferential flow means that the hill slopes of the Wüstebach catchment are connected to the stream via flow paths. They found out that the occurrence of preferential flow is related to the intensity and duration of precipitation. The occurrence of preferential flow during high intensity precipitation events is negatively related to the soil moisture content before the event, which means that there is less preferential flow during high intensity precipitation events (Wiekenkamp et al., 2016). However, high and low intensity precipitation events cause more preferential flow than intermediate events (Wiekenkamp et al., 2016). Wiekenkamp et al., (2016) did not find a specific spatial relationship for the occurrence of preferential flow, although the differences in soil, the biological structures and small-scale flow paths might affect the occurrence of preferential flow.

3.4.4 Hydrochemistry

The groundwater fed streams (WU3, WU12, WU15) have a lower, less varying pH than the surface water fed streams (WU1, WU8 and WU9), but the difference was not significant (Bol et al., 2015). The sampling points in the histosol area (WU1) have the lowest pHs of the catchment, equalling 4.6 (Bol et al., 2015). This affects the microbial activity there and can cause anoxic conditions, which has an influence on the occurring of N and S compounds, especially ammonium. The pH of the riparian zone does not vary that much during the year (Bol et al., 2015).

When the pH and hydrological conditions are changing, the nutrients show the largest variability, this is during events (Rusjan & Mikoš, 2010). The factors that affect the temporal variation are the same as the factors affecting the spatial variations, such as pH, anoxic conditions, water availability (Rusjan & Mikoš, 2010). Nitrate and sulphate concentrations show a seasonal variation as well, as the concentrations are likely to be higher in winter, due to reduced uptake by plants for primary production (Clark et al., 2004). There are also studies that reported diurnal variations, caused by an increase in uptake by photoautotrophs and plants. The concentration of nitrate is largest in the morning and the lowest before sunset. This diurnal

variation is the largest in spring, at that time discharge is also largest (Roberts & Mulholland, 2007; Rusjan & Mikoš, 2010).

4. Methods

This study worked with the precipitation, discharge, and hydro chemical data from the TERENO data portal and data from event-based sampling during at least two precipitation events. According to the glossary of the Deutsche Wetter Dienst (DWD), there are different types of high intensity rainfall events. The first type is a warning for extreme weather (colour code: orange), there can be two types of rainfall events, short events (15-25 mm/h) or longer events (20-35 mm over 6 hours). The second type is the thunderstorm warning (colour code: red), this type also distinguishes two type of events: short events (>25 mm/h) and long events (>35 mm over 6 hours). The third and last type is the warning for extreme thunderstorms (colour code: burgundy), which includes short events (>40 mm/h) and longer events (>60 mm over 6 hours) (DWD, n.d.).

A database from all past high intensity precipitation events was created. Because the current data failed to describe the transport of soluble nutrients (of N and S) and organic compounds of N and S in the headwater stream in the Wüstebach during extreme precipitation events, sampling was carried out during these events. Ideally, sampling took place during the peak discharge over the whole range of the hydrograph (right before the extreme precipitation event, during and after). Water samples were taken in the Wüstebach stream at the outlet of the catchment at point W14 with an automatic sampler. The samples were analysed for nitrate, ammonium and sulphate, total nitrogen and total sulphur. The general overview of the methods of the study is displayed in Figure 5.

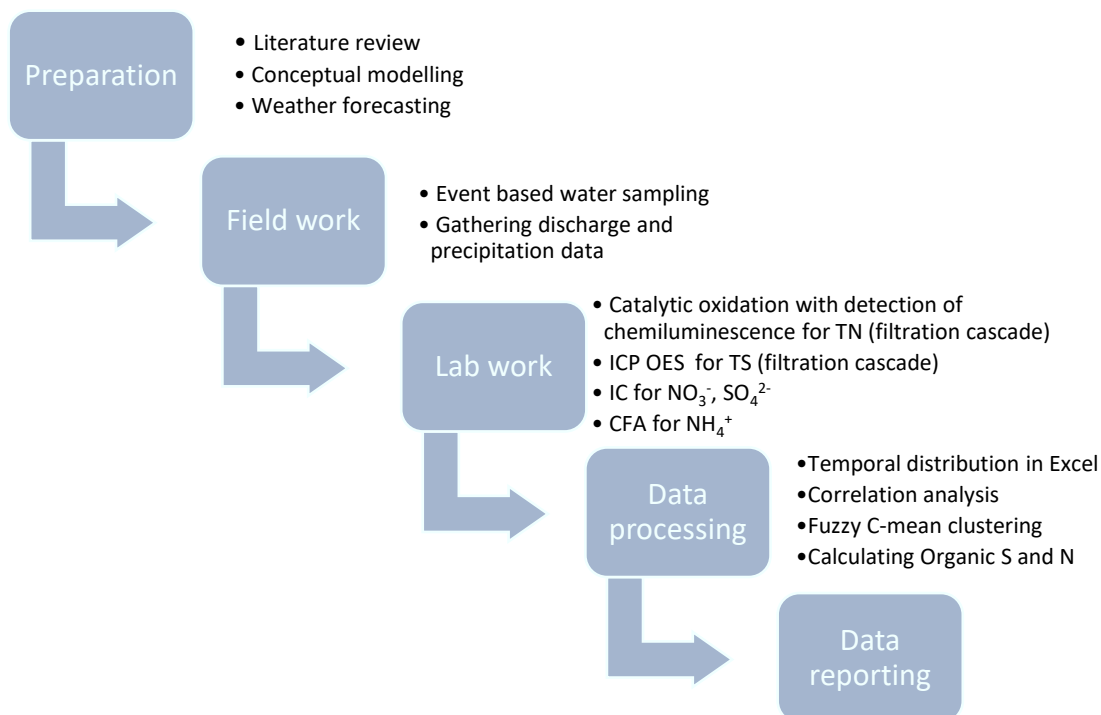


Figure 5. General workflow of this study

4.1 Data evaluation

Firstly, a desktop study was started to explore the current scientific literature about this topic. Secondly, conceptual modelling of existing data was done. The data were available on the theodoor TERENO website (teodoor.icg.kfa-juelich.de, 2018), the website of the German Weather Service (DWD) (ftp-cdc.dwd.de, 2018) and wetteronline.com (n.d.). The precipitation measured on the Wüstebach field site came from a pluviometer and temperature data used for this study was in the first place from a pluviometer and a 2.5 m high eddy covariance tower in the Wüstebach field site (Bogena et al., 2015). If this was lacking, the precipitation data is approximated by the precipitation measurements done 5 kilometres away at the meteorological station Kalterherberg (German Weather Service, 535 m above sea level), Kall-Sistig (German Weather Service, 505 m above sea level, 16 km away) or the meteorological station Elsenborn 10 kilometres away (Royal Meteorological Institute, 535 m above sea level), in one case, the pluviometer at Tereno weather station Schönesseiffen (609 m above sea level) 3.5 km away from the study area was used. This data was analysed for precipitation extremes and temperature changes.

The data has been compared to the discharge data, continuously measured at WU14 and WU10 by a V-notch weir for low flow discharge and a Parshall flume for normal to high flows (Bogena et al., 2015). Peak discharge was defined as an event where the discharge increased by at least a factor 3. The peak discharge could be caused by precipitation or snowmelt. According to these standards, there were 98 peak discharge events in the Wüstebach catchment. 15 of those events have been sampled with an automatic sampler, installed at WU14. Of those 15 events, 5 events were chosen that covered a both sides of the hydrograph and were analysed more in detail. According to the definition of summer and winter of Stockinger et al. (2014), 2 past winter events and 3 past summer events have been analysed to find out what could be expected for the export of the target elements in 2018. These events were examined for maximum 10 minute or hourly intensity, total amount of precipitation, air temperature, duration of the event, lag time, increase in discharge, and increase in discharge over time and duration of the peak flow.

The hydrochemistry data came from weekly grab samples from the reference stream and the Wüstebach and were analysed in the lab of the Helmholtz research centre in Jülich for NO_3^- , SO_4^{2-} and NH_4^+ , and TN. They were filtered with a 0.45 μm filter and NO_3^- and SO_4^{2-} were measured using IC, NH_4^+ by CFA, and TN by Catalytic oxidation with detection of chemiluminescence. Nevertheless, NH_4^+ concentrations were often below the detection limit (0.06 and 0.08 mg/L), although there are speculations that this will be above the detection limit during high precipitation events.

The data was examined in Microsoft Excel to create graphs, look for correlations between rainfall, discharge and the amount of NO_3^- , SO_4^{2-} and NH_4^+ , and TN. The TN has been divided by a factor 4.426124, which is the molecular mass of NO_3^- divided by the molecular mass of a single N atom, to find the N- NO_3^- concentration. Then, the N- NH_4^+ concentration has been calculated by dividing by 1.287794 (molecular

mass of NH_4^+ divided by the molecular mass of an N atom). Through subtraction of the N- NO_3^- and NH_4^+ concentration from the TN concentration, the N-organic N (ON) was found and graphs were created in Microsoft Excel.

4.2 Sampling Strategy

In 2018, one summer event and one winter event have been sampled, that took place from the 5th of March until the 12th of March 2018 and on the 16th of May 2018.

During these events, NO_3^- concentrations and discharge were measured every 10 minutes by TriOS-multi probes (YSI 6820, YSI Inc., USA) (Bogena et al., 2015). There were two auto samplers installed next to point W10 and point W14. The automatic sampler (ASW Ecotech, Germany) at station W14 was used for this study, every week it sampled 24 bottles of water with an 8-hour time interval and a faster programme with a sampling interval of 2 hours (winter) or 30 minutes (summer). This programme was set at a water level that is likely to belong to the start of a peak discharge event and started when the weir detected that certain water level. The automatic sampler would then take a sample of 600 mL in a 1 L PE bottle. Snowmelt events were also included in this study, as they caused peak discharges together with rainfall in winter. This was also realized through event-based sampling, the sampling strategy was the same.

Manual samples were taken at the 6th and 8th of March 2018, for both days at 12.00 h CET and at 15.00 h CET, at the points W1, W8, W12, W14 and W17 (see Figure 6.). These samples are mainly analysed to examine the contribution to nutrient export of the tributaries. At every point, two 1 L bottles were sampled and analysed for NO_3^- , SO_4^{2-} and NH_4^+ , and TN. At point W14, a TriOS probe

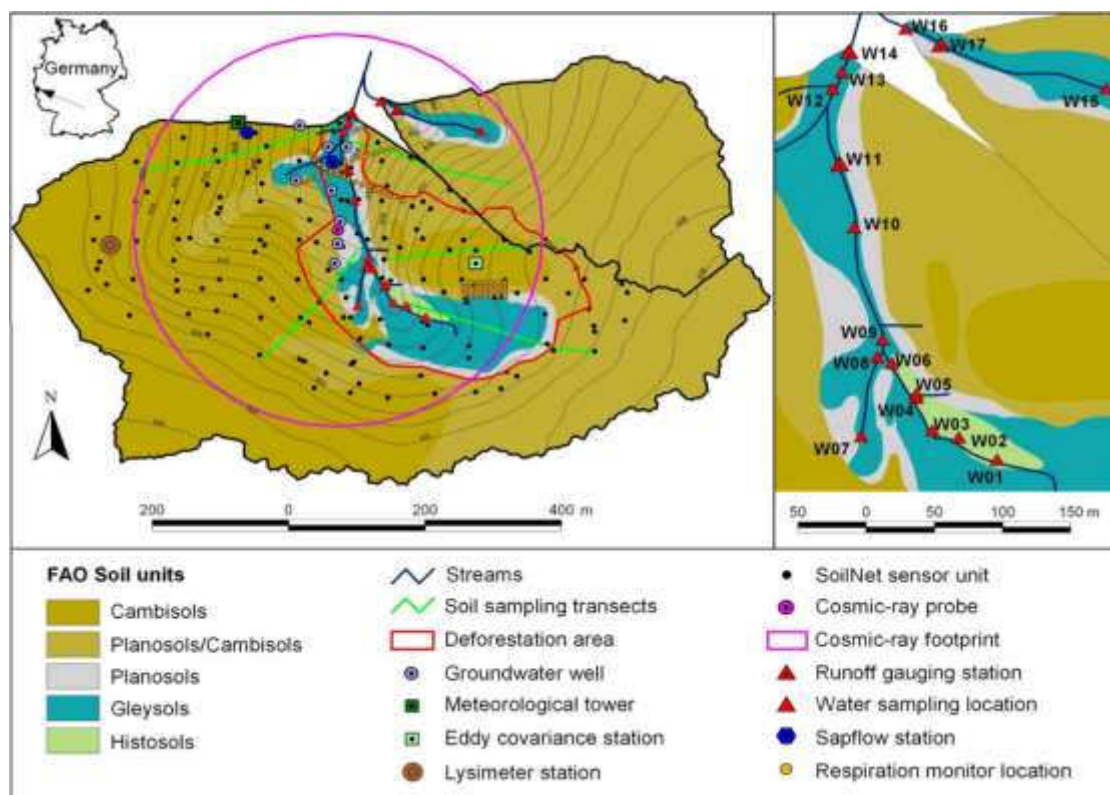


Figure 6. The Wüstebach field site (Golor, 2016 after Bogen et al., 2015)

4.3 Chemical analysis

The water samples in the PE bottles were stored at a low temperature (e.g. 4 °C) (Gao et al., 2014) and then analysed in the laboratory of the Forschungszentrum Jülich within a week. Firstly, the samples of the May event were split in four groups of 100 ml and were filtered with a 5 µm, 1 µm, 0.45 µm, and 0.22 or 0.1 µm PES filter (TH. Geyen, Lohmar, Germany), the rest remained unfiltered. The samples from the event in March were only filtered with a 0.45 µm PES filter. The Samples from the May event, prepared with all filtrations, the unfiltered samples, and the March event samples were analysed with ICP OES for TS (iCAP 6500 ICP-OES; Themofisher Scientific, Waltham, United States) and with Catalytic oxidation with detection of chemiluminescence for TOC and TN with a Shimadzu TOC-V_{CPH} analyser (Shimadzu Corp., Kyoto, Japan). Samples filtered with a 0.45 or smaller filtration step were analysed with IC with a Dionex ICS-3000 (Themofisher Scientific, Waltham, United States), CFA with a CFA Analysator FLOWSYS 3-Kanal (Alliance Instruments GmbH, Salzburg, Austria) and HPLC (Berthold Technologies GmbH & Co. KG, Bad Wilbad, Germany) for NO₃⁻, SO₄²⁻ and NH₄⁺ (only detected with CFA). During both HPLC and IC, molecules are separated the molecules based on their ionic exchange capacity and then detected with indirect UV adsorption or a conductivity meter. During HPLC, both anions were detected by indirect UV adsorption at a 320 nm wavelength. In the case of IC, NO₃⁻ was detected by indirect adsorption at a 210 nm wavelength and SO₄²⁻ with a conductivity meter. In order to evaluate the accuracy of HPLC and IC, NO₃⁻ standards were made with KNO₃⁻ with different concentrations that were calculated beforehand. To two

standards, a small NOM particle was added from the Aquatic NOM from Suwannee River standard (International Society on Humic Substances, IHSS, Denver, USA) in order to analyse whether HPLC and IC only detect nitrate. These standards have a standard organic nitrogen concentration on particles with different diameter sizes.

4.4 Data analysis

After the chemical analysis, data analysis was done in MS Excel. Concentrations were plotted together with the discharge to analyse the temporal distribution of the ions. Then, the loads of NO_3^- , SO_4^{2-} and NH_4^+ were calculated by multiplying the concentrations by the discharge, and these values were plotted as well with the discharge.

The TN concentration has been divided by a factor 4.426124, which is the molecular mass of NO_3^- divided by the molecular mass of a single N atom, to find the N- NO_3^- concentration. Then, the N- NH_4^+ concentration has been calculated by dividing by 1.287794 (molecular mass of NH_4^+ divided by the molecular mass of a N atom). Through subtraction of the N- NO_3^- and NH_4^+ concentration from the TN concentration, the N-organic N (ON) was found. Subsequently, loads were calculated and plotted together with the discharge.

A similar calculation has been performed on the results of the ICP OES analysis for TS. The TS concentration has been divided by 2.9993752, the molecular mass of SO_4^{2-} divided by the molecular mass of an S atom, to find the S- SO_4^{2-} concentration. By subtracting the S- SO_4^{2-} concentration from the TS concentration, the S-DOS concentration was found. From these data, loads were calculated as well and plotted with the discharge.

Then, from the TN and TS concentrations of the May event, three fractions have been calculated: diameter $<0.1 \mu\text{m}$ (nanoparticles), diameter $= 0.1 \mu\text{m} - 1 \mu\text{m}$ (fine colloids) and diameter $>1 \mu\text{m}$ (large particles) (Gottselig et al., 2014). The $<0.1 \mu\text{m}$ fraction equalled the TN concentration of the samples that have been filtered with a $0.1 \mu\text{m}$ filter. After that, the categories were made: $0.1 \mu\text{m} - 0.45 \mu\text{m}$, $0.45 \mu\text{m} - 1 \mu\text{m}$, $1 \mu\text{m} - 5 \mu\text{m}$ and $>5 \mu\text{m}$. The concentrations TN per category was derived by subtracting the smaller concentration TN of the smaller filter size by from the larger one (concentration TN ($0.45 \mu\text{m}$) – concentration TN ($0.1 \mu\text{m}$) = concentration TN (category $0.1 \mu\text{m} - 0.45 \mu\text{m}$)). If the result was negative, the concentration of that category equalled 0. The $0.1 \mu\text{m} - 1 \mu\text{m}$ fraction equalled the sum of the $0.1 \mu\text{m} - 0.45 \mu\text{m}$ category and the $0.45 \mu\text{m} - 1 \mu\text{m}$ category. The $> 1 \mu\text{m}$ fraction equalled the sum of the $1 \mu\text{m} - 5 \mu\text{m}$ category and the $> 5 \mu\text{m}$ fraction. The same calculation was used for TS.

Then, the data was investigated for correlations (95% confidence interval) with the amount of rainfall and discharge and whether there is or whether there is no anti-correlation during the high intensity rainfall events.

To investigate which analytical method for measuring nitrate or sulphate to addresses the export of -N and S compounds best during events, a linear regression analysis was carried out between the results of HPLC

and IC. F-tests were used to define whether the variance of the HPLC values was the same as the IC values in order to choose the right T-test. Subsequently, a T-test was performed to check whether there was a significant difference between the HPLC and IC values.

Of all N and S compounds, only NO_3^- was measured continuously (every 10 minutes) with a UV process photometric sensor in the Wüstebach stream at point W14 (TriOS Tribox system, ProPS, TriOS GmbH, Oldenburg, Germany), it was sampled with high resolution and analysed with HPLC, TOC/TN analysis and IC. To evaluate whether continuous measuring or high-resolution sampling was best, linear regression analyses have been performed between the TriOS probe and HPLC, IC, and TOC/TN. F-tests were used to define whether the variance of the continuously measured values was the same as the high-resolution sampled values to choose the right T-test. Subsequently, a T-test was performed to check whether there was a significant difference. Then, the values of HPLC and IC NO_3^- for the March event were interpolated so they had the same resolution as the continuously measured samples a load (mg per 10 minutes) were calculated by multiplying all the NO_3^- by the discharge. For every method, the loads were summed up and total loads in mg per second by multiplying the loads per 10 minutes by a factor 600. The assumption was made that W14, where the measurements were done, was the outlet of the catchment and therefore all the NO_3^- export was measured there. To calculate the load per hectare that was lost, the loads for the whole catchment were divided by a factor 38.5 and the loads in grams instead of milligrams were calculated. Lastly, the contribution of the tributaries was analysed by taking the average of the results for NO_3^- , SO_4^{2-} and NH_4^+ per tributary. The N-compounds were calculated in the method described earlier and the DOC/TN ration was found by dividing the DOC concentration by the TN concentration.

5. Results

5.1 Contribution of the different tributaries

Five tributaries of the Wüstebach have been sampled and were analysed for their TN, DOC, SO_4^{2-} , NO_3^- and NH_4^+ before the peak discharge event in March 2018. Figure 7 shows the ratio of DOC to NO_3^- and shows that the ratio is highest at tributary 1 and lowest at tributary 12. During the event in March, tributary 1 was classified as most influenced by surface water mixing processes, tributary 12 and 17 were classified as groundwater fed and 14 as influenced by both the surface water and groundwater. Tributary 8 had very little water due to frozen circumstances but has a ratio that induces both surface water fed, and surface water fed mixed with groundwater.

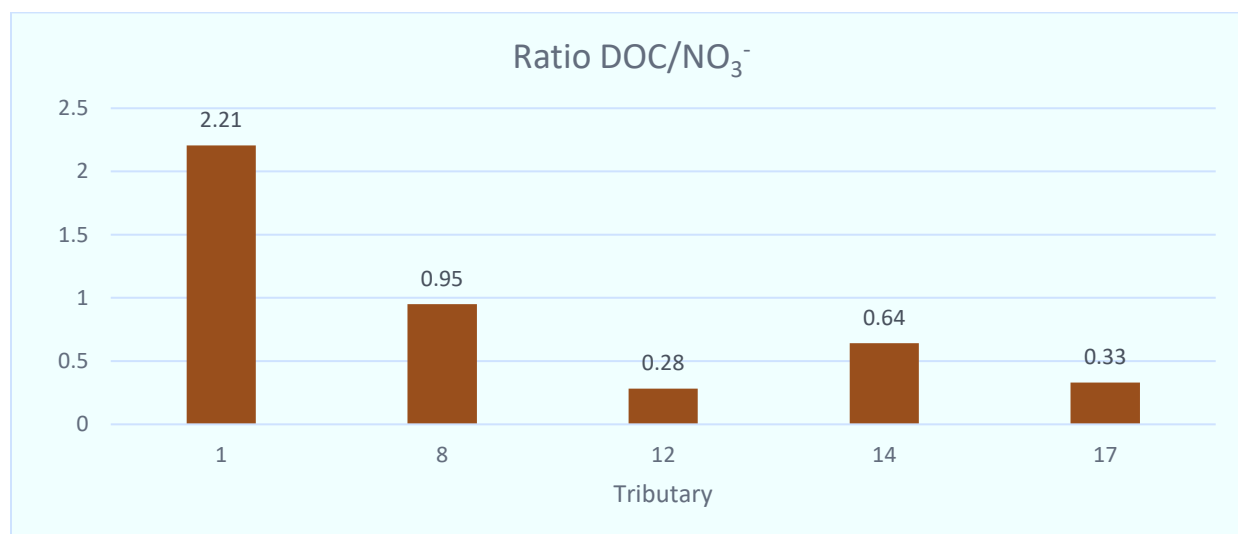


Figure 7. DOC/NO_3^- ratios of the 5 measured tributaries.

The sulphate and nitrate concentrations per sampling point are displayed in Figure 10. The concentration sulphate in the tributaries is higher than the concentration nitrate, except for in tributary 12. The sulphate concentrations are the highest at tributary 17 and the lowest in tributary 12. The nitrate concentrations are the highest in tributary 12 and the lowest in tributary 1. The difference between the nitrate and sulphate concentrations is the highest in tributary 1 and the lowest in tributary 12. Figure 9 shows that the ammonium concentrations are the highest in tributary 1 and 8, which are both surface waters dominated, in tributary 12 and 17, the groundwater dominated tributaries, is ammonium under the detection limit. Tributary 14, the catchment outlet, characterised by a mix of groundwater and surface water, the ammonium concentrations are slightly above the detection limit. The chemical speciation of N per tributary is displayed in Figure 8 in March 2018. The concentration TN is the highest at tributary 12 and the lowest at tributary 1. Tributary 12 and 17 Organic N concentrations at tributary 12 and 17 were negligible, while they were highest at tributary 1 and 8, where ammonium was highest as well. NO_3^- -N was highest at tributary 12 and lowest at tributary 1.

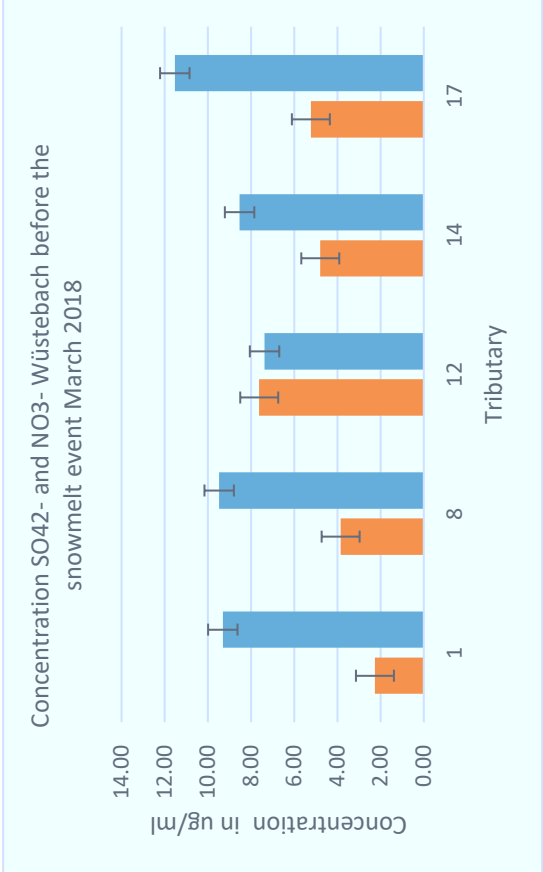
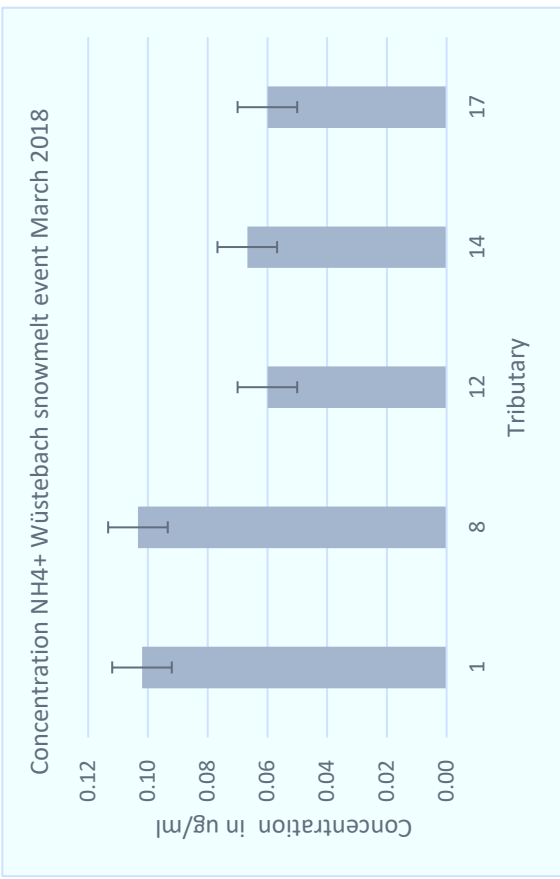


Figure 8. Chemical speciation of N in the sampled tributaries.
Figure 9. Ammonium concentrations per sampled tributary
Figure 10. Nitrate and Sulphate concentrations per sampled tributary

5.2 Past events

A storm database has been made of 98 storm events in the Wüstebach catchment from 2010 till 2017. The average amount of events per year was 12.3. Out of all high intensity precipitation events analysed, the highest precipitation intensity measured was 56.7 mm in 10 minutes. The second highest intensity is 30 mm per ten minutes has a one year return period. The highest precipitation intensity measured in winter season is 5.45 mm per 10 minutes, thus the intensities of the precipitation events are highest summer season. In winter, precipitation intensity is lower, but rain showers on average take longer, since the total amount of rainfall can be above 50 mm and cause an increase in discharge of a factor 3.5 or more. Before the events, baseflow was usually 4.46 L s^{-1} , with having baseflows larger than 5 L s^{-1} more common in winter. Baseflows increased after precipitation or snowmelt events on average with a factor 13.4. Events in winter caused a higher discharge than events in summer, although the highest discharges occurred in summer.

From 2011 till 2014, 20 peak discharge events out of 98 peak discharge events have been sampled by the auto sampler at WU_AW_14. The sampling interval was either 20 minutes (11), 10 minutes (2), 30 minutes (4), 60 minutes (2) or 4 hours (1). 7 of the 20 events were in winter, the rest was in summer.

A correlation analysis has been performed on the data from all the events, sulphate and nitrate are positively correlated with a correlation coefficient of 0.45. Sulphate and ammonium are negatively correlated with a correlation coefficient of -0.47 and nitrate and ammonium are negatively correlated with a correlation coefficient of -0.14. This means that the response of sulphate and nitrate are similar during peak discharge. A negative correlation means that ammonium is likely to respond in a different way than nitrate and sulphate during peak discharge.

The concentration of sulphate and nitrate is lower in summer than in winter. The highest concentration of sulphate that has been measured is 13.1 mg L^{-1} in winter and the lowest concentration was 3.05 mg L^{-1} , which was in summer. The highest concentration of nitrate that has been measured is 14.8 mg L^{-1} , which is in winter and the lowest concentration is 2.54 mg L^{-1} in summer. The concentration of ammonium is not fluctuating with the seasons. The highest concentration of ammonium measured is 0.3 mg/L , the lowest is below the detection limit.

Out of all the events, five events were chosen to analyse in further detail, their properties of the past events can be found in Table 1. Note that the event of the 23rd of July 2013 and the event of the 29th and 30th of July 2014 lacks some data. There was no rainfall recorded on the weather station of the Wüstebach station on the 23rd of July 2013, and only 1.5 mm at the weather station Monschau – Kalterherberg. However, an increase of 22.5 in discharge was measured at WU14, the nearest weather station that recorded a precipitation event was the Tereno weather station Schönesseiffen (609 m a.s.l., 3.5 km east from study area). These 5 events are events that were sampled by the automated sampler at WU14

and fulfilled the criteria of causing at least an increase in discharge of a factor 3 and having both limbs of the hydrograph sampled.

The event of the 4th and 5th of January 2012 does not fulfil both criteria, because it only causes an increase in discharge of a factor 2.3. Nevertheless, this event represents a winter event without snowmelt, because it belongs according to the DWD to an extreme weather event, taking more than 6 hours and causing more than 25 mm of precipitation (DWD, n.d.). The event of January 2011 is a snowmelt event combined with a winter precipitation event, characterised by having temperatures below zero before the event took place, and having snowmelt and rain during the event. The precipitation combined with snowmelt lasts the longest and causes a slow response in discharge. The winter event of 2012 is only a precipitation event and has a shorter duration, but still a longer duration than the summer events. Temperatures were not below zero before the event in 2012 and there were other precipitation events before the event of the 4th and 5th of January took place.

Table 1. Properties of past events

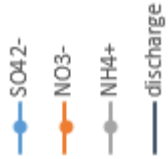
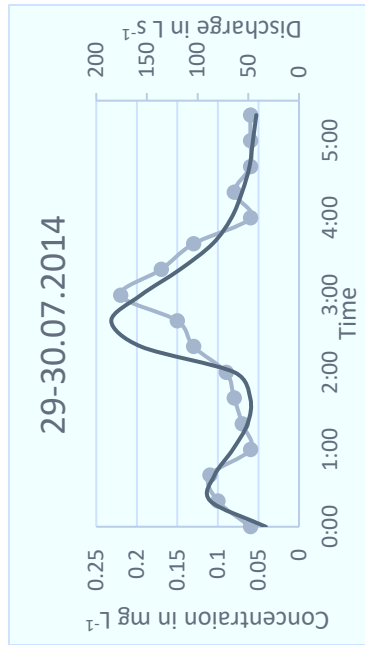
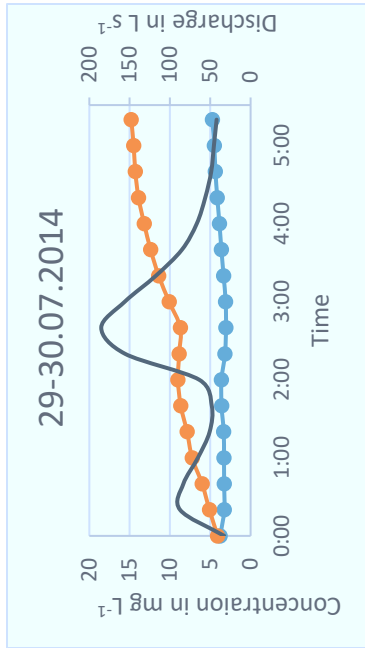
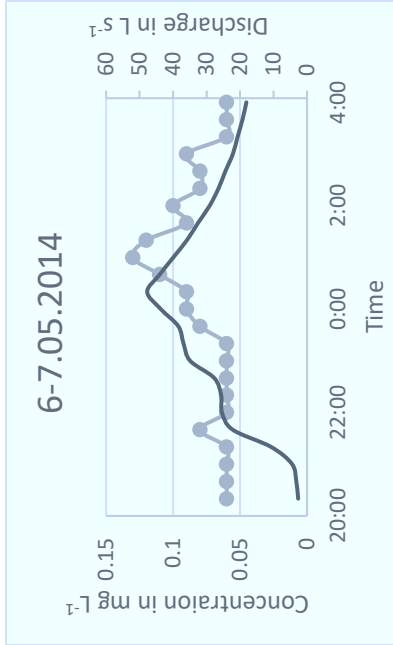
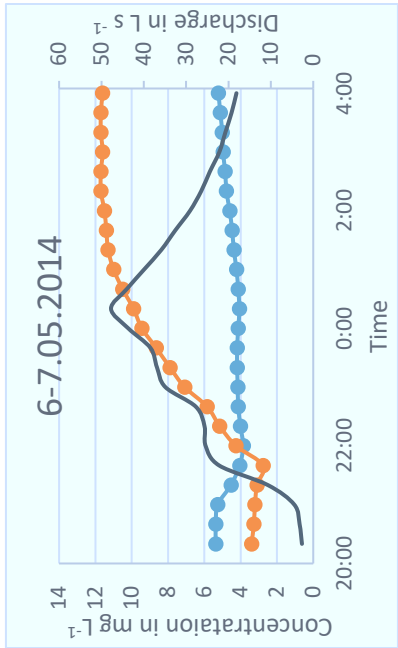
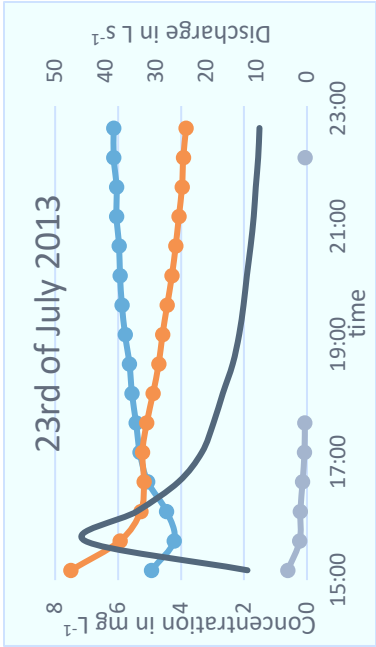
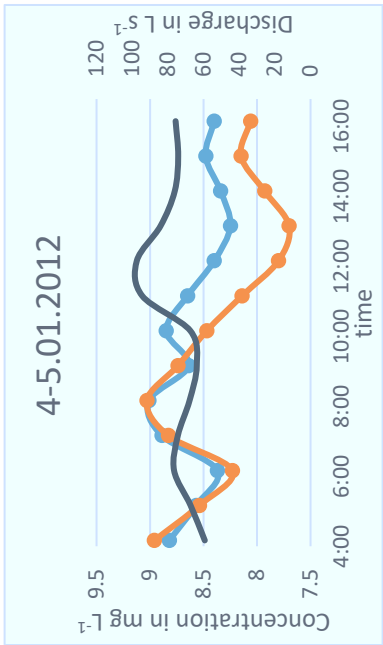
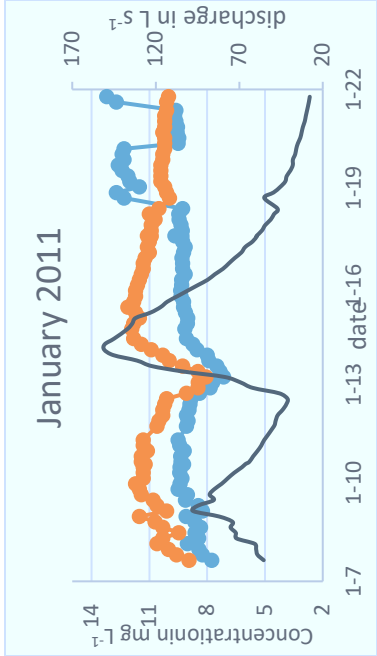
Date	January 2011	4-5.01.2012	23.07.2013	6-7.05.2014	29-30.07.2014
Season	Winter	Winter	Summer	Summer	Summer
T in °C before (winter event, T increase)	-7.9 (17.7) and -3.9 (14.3)	3.7	21.3	17.3	16.4
Total precipitation in mm	125 (41.6 and 67.8)	33.1	5.9	37.6	22.7
Maximum 10-minute precipitation intensity in mm	1.0 and 1.3	2.7	2.7	4.1	8.7
Duration climatic event	15 d	14 h and 50 m	2 h and 30 m	6 h and 10 m	5 h and 30 m
Discharge before in L s ⁻¹	6.7 and 40.2	43.0	2.0	1.5	5.8
Peak discharge in L s ⁻¹	102.0 and 154.1	98.4	45.0	47.7	185.2
Factor increase	15.2 and 3.8	2.3	22.5	31.8	31.9
Time for discharge increase until peak	2 d, 23 h, 48 m and 1 d, 9 h, and 12 m	15 h and 10 m	1 h	4 h and 40 m	4 h and 10 m
Duration hydrologic event	5 d, 19 h, and 36 m	18 h and 10 m	6 h and 10 m	10 h	9 h and 50 m
Lag time	1 day	30 minutes	No	No	No
Hydrological connectivity	Yes	Yes	No	No	Yes

The summer events are of shorter duration and have higher 10-minute intensities. The events also cause larger increases in discharge, of which the event of the 29th and 30th of July 2014 has the highest increase and the highest discharge. The event of the 23rd of July 2013 occurred on the warmest day, with temperatures just before the precipitation event at 21.3 ° C with a maximum of 29 ° C during midday. The event of the 5th and 6th of May has the highest total amount of precipitation of the summer events, but has the lowest temperature, being more a spring event. Prior to the event of the 29th and 30th of July 2014, there have been more precipitation events: on the 21st, 25th and 28th of July. These events also had high intensities and temperature was above 20 ° C the whole week, being highest on the 23rd with 25.9 ° C.

During the winter events, the stream responded after the precipitation fell, which was longer during the snowmelt event than during the rainfall event in 2012. The stream was connected hydrologically with the hillslopes in the catchment during both winter events and during the summer event of the 29th and 30th of July due to precedent precipitation events that week.

Figure 11 till 17 show the response of the concentrations of NO_3^- , SO_4^{2-} and NH_4^+ during peak discharge during the five events. Before the events, the concentrations of NO_3^- and SO_4^{2-} were highest during the snowmelt event in 2011 (Figure 11.) and lowest during the event in July 2014 (Figure 16.). When the discharge increases, the concentrations of NO_3^- and SO_4^{2-} decrease and show a sort of “dilution effect”. After that, the concentrations increase again, except for the NO_3^- concentrations during the event of the 23rd of July 2013 (Figure 13.) and the SO_4^{2-} concentrations of the two events in 2014 (Figure 14 and 16), which don’t show a large increase. NH_4^+ concentrations were negligible for the two winter events. For the two events in 2014 they show an increase (see Figure 15 and 17), lagging two hours in the event in May (Figure 15.). During the event in 2013, the concentrations of NH_4^+ decreased (Figure 13.). After the events, concentrations of NO_3^- and SO_4^{2-} were higher than before the event, except for the event of January 2012 (Figure 12.), the NO_3^- concentrations during the July event in 2013 (Figure 13.) and the SO_4^{2-} concentrations during the event of May 2014 (Figure 14.). The NO_3^- concentrations show more variance during the events than the other ions.

5.2.1 Response concentrations



Numbering of the figures goes from left to right, from above to down.

Figure 11. NO_3^- and SO_4^{2-} concentrations

Figure 12. NO_3^- and SO_4^{2-} concentrations

Figure 13. NO_3^- , NH_4^+ and SO_4^{2-} concentrations

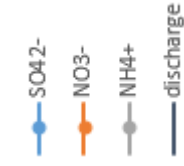
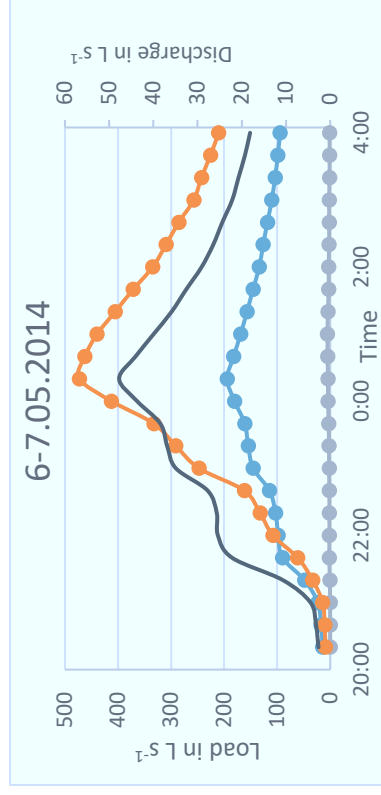
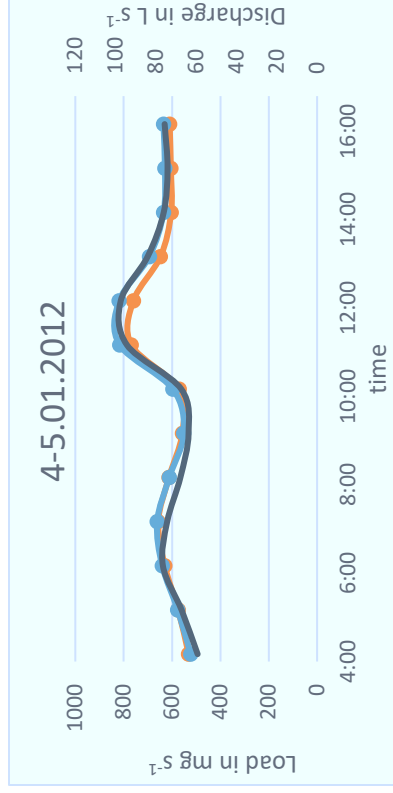
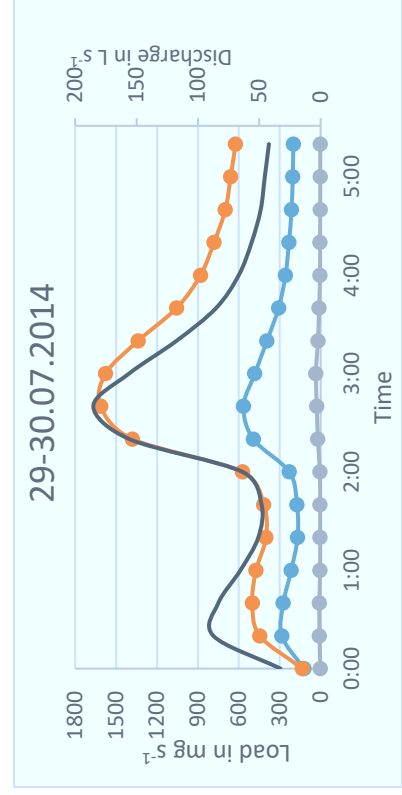
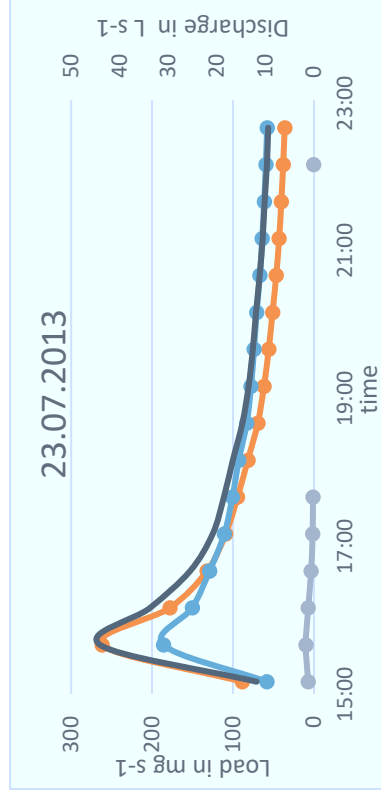
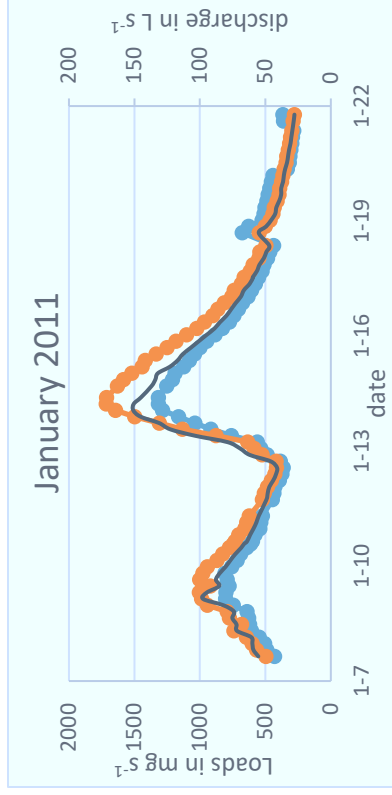
Figure 14. NO_3^- and SO_4^{2-} concentrations

Figure 15. NH_4^+ concentrations

Figure 16. NO_3^- and SO_4^{2-} concentrations

Figure 17. NH_4^+ concentrations

5.2.2 Response loads



Numbering of the figures goes from left to right, from above to down.

Figure 18. NO_3^- and SO_4^{2-} loads

Figure 19. NO_3^- and SO_4^{2-} loads

Figure 20. NO_3^- , NH_4^+ and SO_4^{2-} loads

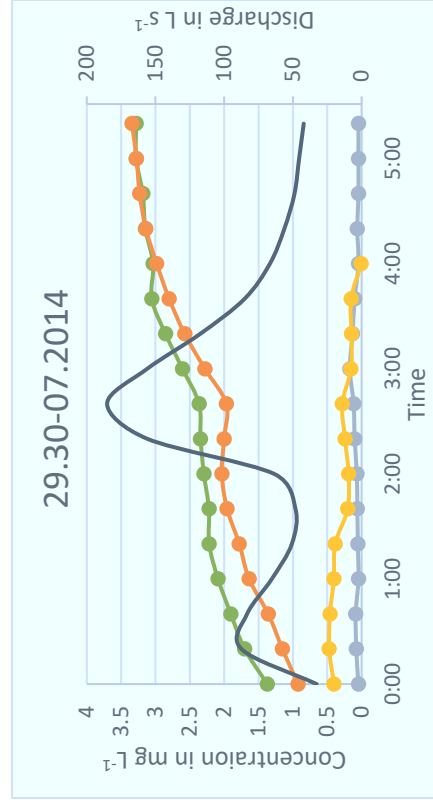
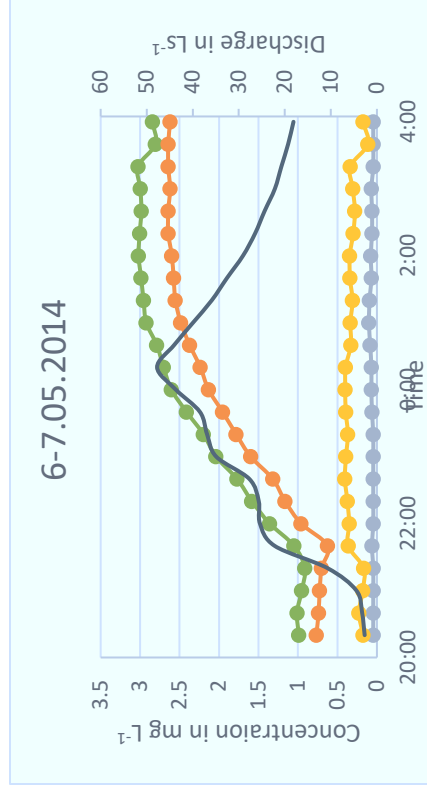
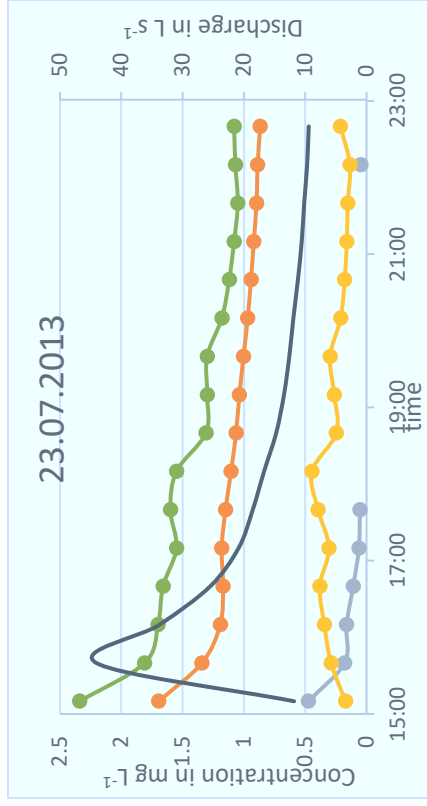
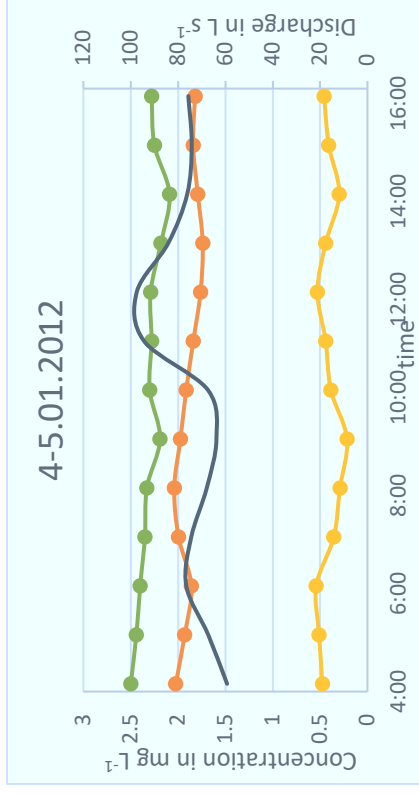
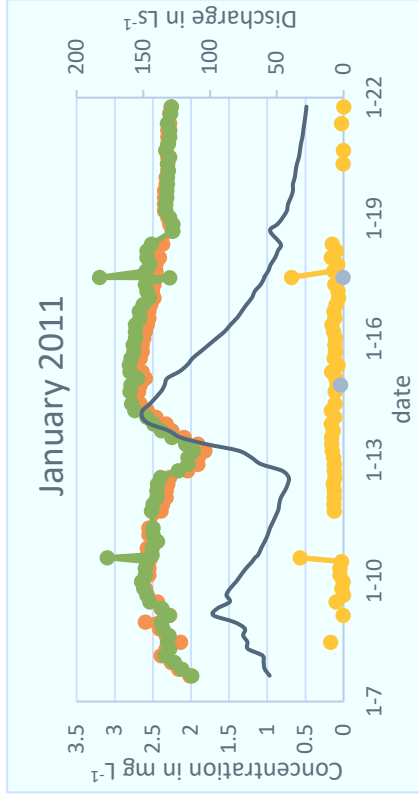
Figure 21. NO_3^- , NH_4^+ and SO_4^{2-} loads

Figure 22. NO_3^- , NH_4^+ and SO_4^{2-} loads

Figure 18 till 22 show the response of the loads of NO_3^- , SO_4^{2-} and NH_4^+ to peak discharge. NO_3^- has higher loads than SO_4^{2-} , but also had higher concentrations. Mostly, the nitrate loads, and sulphate loads increase with the same speed and have their peak at the same time, often together with the peak in discharge. However, during the event of January 2011, the SO_4^{2-} loads peak faster than the NO_3^- loads during the first peak discharge, which is 4 hours earlier (see Figure 18.). This also happens during the second time peak discharge during the event of the 29th and 30th of July 2014 (Figure 22.), where NO_3^- loads lag 20 minutes compared to the discharge and sulphate loads. During the event of the 6th and 7th of May in 2014, NO_3^- loads increase faster than the SO_4^{2-} loads, which can be seen in Figure 21. Nitrate and sulphate peak the second time both 4 hours later than the discharge. Ammonium was above detection limit during the summer events, and peaks at the same time as the other ions and discharge. However, ammonium shows a lag time of 30 minutes and 40 minutes during the first event of the 29th-30th of July 2014 (Figure 22.) and the 6th and 7th of May 2014 (Figure 21). In addition, a dilution effect can be noted during the event of the 6th and 7th of May 2014, as NO_3^- , SO_4^{2-} and NH_4^+ don't rise as fast as the discharge (Figure 21.). After the peak discharge in all events, the loads drop again.

5.2.3 Response N species

Figures 23 to 27 explain the distribution of different N species and show that during all events, NO_3^- -N is the most common N species during events in the Wüstebach stream. TN and NO_3^- -N show a dilution effect during peak discharge, while Organic N increases during peak discharge, having its peak at the same time. Most of the events have an Organic N concentration of about 0.5 mg L^{-1} , except for the winter event in 2011, which has lower concentrations. During the winter events NH_4^+ -N is mostly under the detection limit, it was not detected at all during the event of the 4th and 5th of January 2012 and was only at the detection limit during the event of January 2011.



29.30-07.2014

● TN
 ● N-NO3-
 ● N-NH4+
 ● N-ON
 — Discharge

Numbering of the figures goes from left to right, from above to down.

Figure 23. Snowmelt event January 2011

Figure 24. Event 4-5th of January 2012

Figure 25. Event of the 23rd of July 2013

Figure 26. Event of May 6-7th 2014

Figure 27. Event of July 29th-30th 2014

5.3 Differences measuring methods

5.3.1 HPLC and IC

For this study two methods were available for analysis of nitrate and sulphate: ion chromatography (IC) and high-performance liquid chromatography (HPLC). IC measures the concentration of nitrate and sulphate based on their ionic exchange capacity. Nitrate was detected with indirect UV adsorption at a wavelength of 210 nm, sulphate was detected by measuring the conductivity. At IBG-3 samples are analysed with HPLC with a method similar to ion chromatography. For the two events, both methods have been used to quantify the concentrations of nitrate and sulphate.

The concentrations measured with HPLC were on average 0.04 mg L^{-1} lower than the concentrations with IC, but it was not a significant difference at a 95% confidence interval (see Figure 24.). The concentrations measured by HPLC and IC showed also a high positive correlation, with an R^2 value of 0.98, and there was a significant regression with a slope of 0.97. The IC concentrations of sulphate were well explained by the sulphate concentrations measured by HPLC, having an R^2 value of 0.99, and there were no significant differences between the values (see Appendix A.1). The concentration of nitrate measured with HPLC explained the nitrate concentrations measured by IC for 96%, having an R^2 value of 0.96 and no significant differences (see Appendix A.1). However, it seemed that the correlation was not everywhere the same, as two chemicals during two seasons, including events and a normal situation were measured.

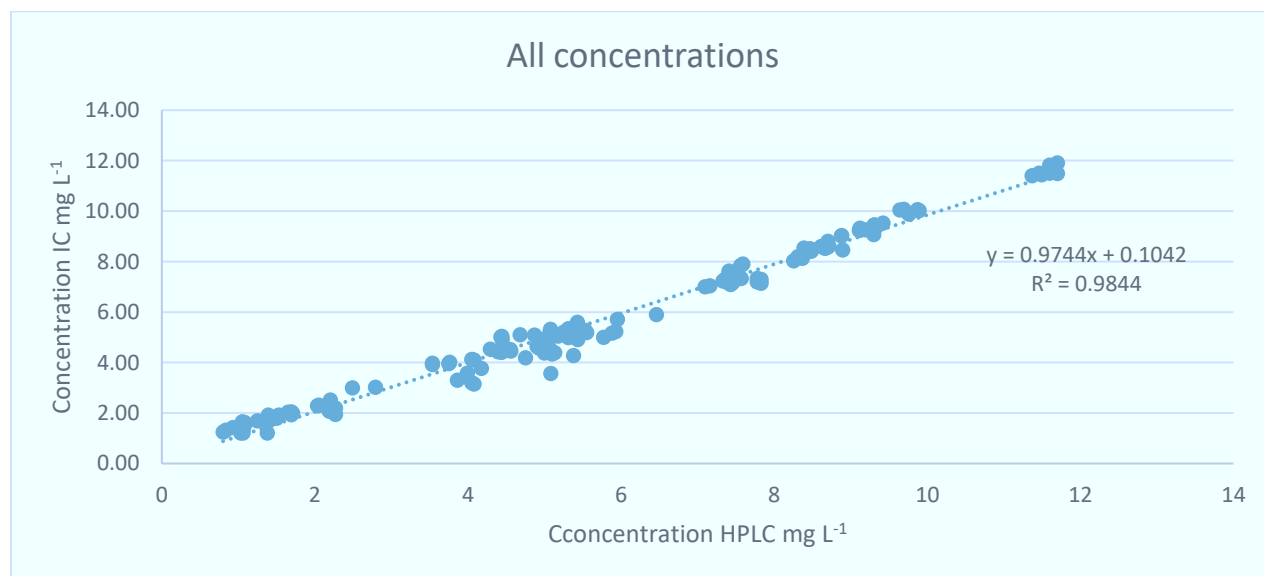


Figure 24. Comparison of HPLC and IC results for all concentrations measured.

Together with the regression analysis, the residuals were plotted against the predicted Y values, which can be seen in Figure 25. The predicted Y is very similar to the real Y values, having some higher values around the concentrations of 5 mg L^{-1} . In Figure 26 the residuals are plotted per HPLC concentration value and a 3rd order polynomial regression line has been drawn. The residuals were on average above zero until 2.5

mg L⁻¹ and were below zero between 2.5 and 8 mg L⁻¹. From 8 mg L⁻¹ the residuals were above zero again. The explanatory power of the HPLC concentration of the residuals was low, having an R² factor of 0.25.

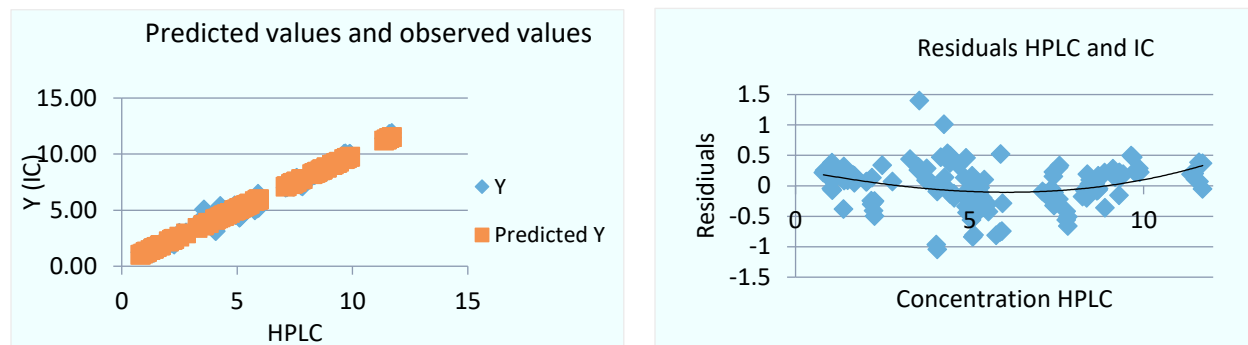


Figure 25 (left). Predicted IC values and observed IC values per HPLC value.

Figure 26 (right). Plotted residuals per HPLC value.

To identify the three different groups in the data, Fuzzy c-mean clustering has been performed in MATLAB on the all the data. The algorithm identified three different clusters, the centre point of the first cluster was (1.6603, 1.8975), the centre point of the second cluster was (4.9746, 4.9764), and the centre point of the third cluster was (9.0096, 9.0027). Then, every data point got appointed to a cluster using Euclidean distance, this resulted in Figure 27.

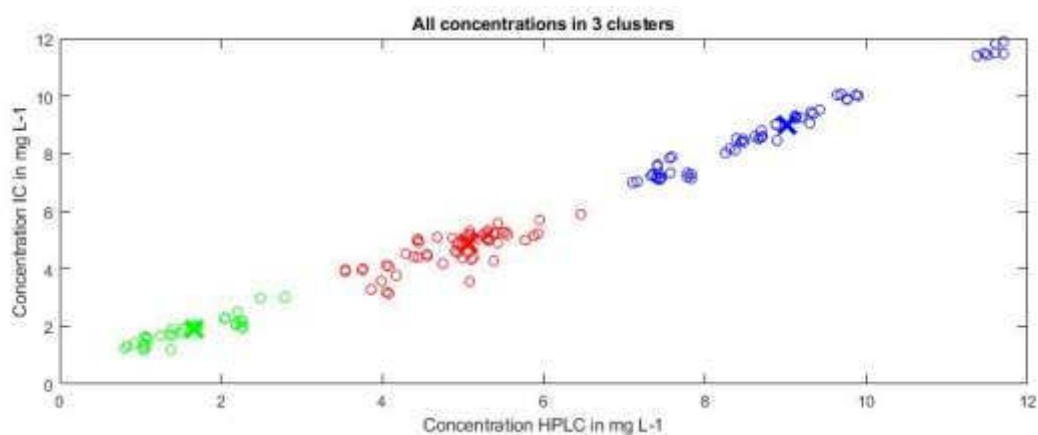


Figure 27. All measured values with HPLC and IC in three clusters with centre points.

Regression analyses were performed on the three different clusters, of which results can be found in Figure 28. data in first cluster had an R² value of 0.80, the data in the second cluster had a weaker correlation and had an R² value of 0.54 and the data in third cluster had a stronger correlation again, i.e. 0.98.

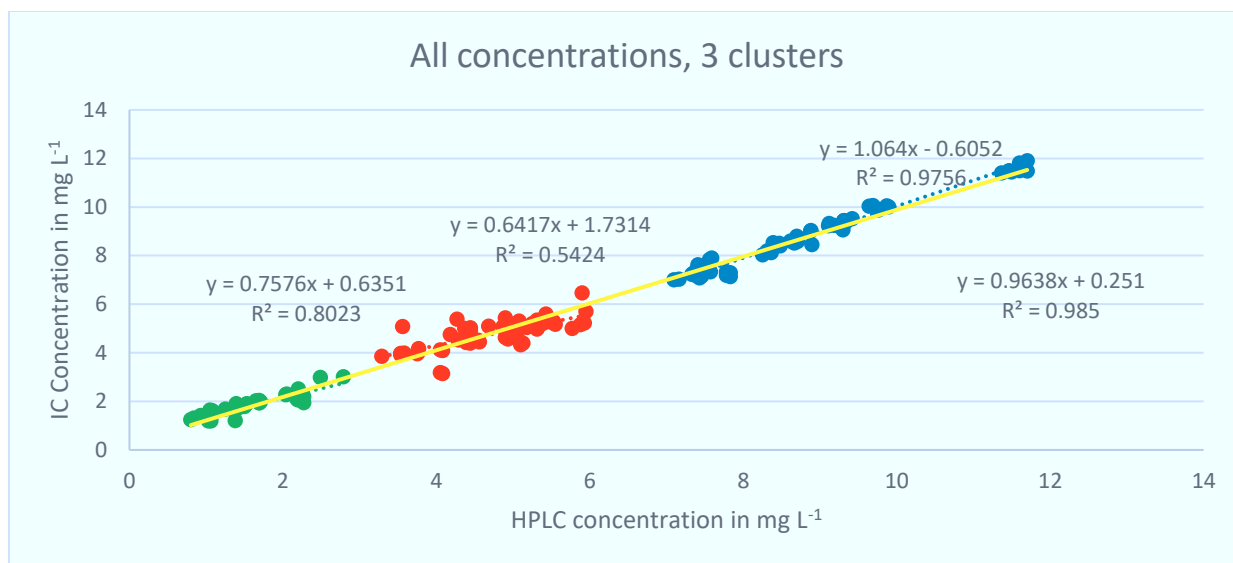


Figure 28. The 3 clusters of concentrations with regression analyses performed on all of them.

The first cluster represented the nitrate values of the summer event and the values of tributary WU1 at the beginning of the winter event, and has a higher correlation of than the second cluster. The second cluster is made of the nitrate values of the winter event, the sulphate values of the summer event and the values of tributary WU8, WU14 and WU17 at the beginning of the event. The third cluster represents the sulphate values of the winter event, the sulphate values of all tributaries measured at the beginning of the winter event and the values of nitrate of tributary WU12. The values measured by HPLC and IC in the first cluster had equal variances but were statistically significant at a 95% confidence level (p -value = 0.030). The values of the second and third cluster measured were not significantly different.

All the nitrate event values (see Figure 29.) together are not differing significantly, although having different variances. They are on average 0.04 mg L^{-1} higher when they are measured by IC than by HPLC. During the winter events they were on average 0.70 mg L^{-1} higher when they were measured by IC than when they were measured by HPLC, which was a significant difference on a 95 % confidence level (p -value = 0.043). During summer events, the IC values were on average 0.35 mg L^{-1} higher than the HPLC values, which was also significantly different at a 95 % confidence level (p -value = 0.011). For both events, the values from both methods had equal variances. The sulphate event concentrations of the two chemical analyses did not differ significantly and were highly correlated, having an R^2 value of 0.96.

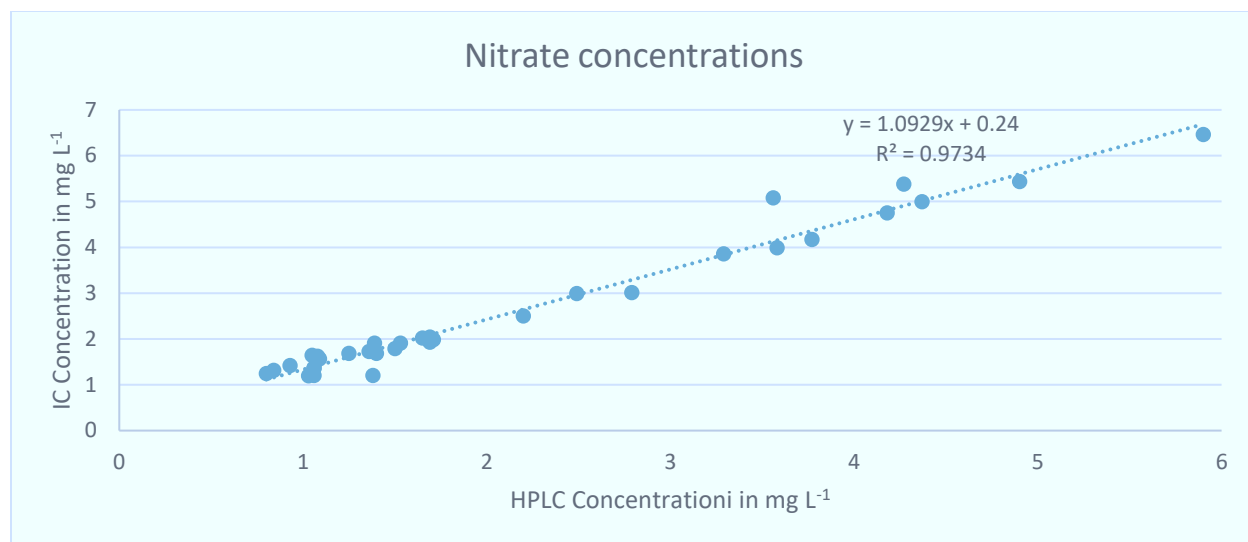


Figure 29. Comparison of HPLC and IC results for all nitrate concentrations measured during events.

To find out which method used in this project is most precise, standards were made and sent to the two labs, and results of the analyses can be found in Table 2. A one-way ANOVA test was used to determine whether the two outcomes differed from the beforehand calculated concentrations. It was found that the two methods did not differ significantly from the standards. However, it can be found that the IC results were more precise and the results of HPLC were lower than the IC results.

Table 2.. Nitrate standards made and analysed by IC and HPLC.

Tube	Molarity (mM)	Concentration standard (mg L ⁻¹)	Concentration IC (mg L ⁻¹)	Concentration HPLC (mg L ⁻¹)
1	0.1372	8.5043	8.22	7.9
2	0.0686	4.25215	4.12	3.9
3	0.1983	12.2948	3.29	3.0
4	0.01372	0.85043	0.84	0.6
5	0.00686	0.425215	0.45	0.3
6	0	0	0.11	0
7	0.15714	9.74268	0	0

Tube 3 and 7 also included the standard Aquatic NOM from Suwannee River (International Society on Humic Substances, IHSS, Denver, USA). This particle standard included N nanoparticles and humic acids but was not detected by HPLC nor IC. However, there was a little (0.1 mg L⁻¹) sulphate detected by IC. Therefore, neither HPLC or IC can detect organic N.

5.4 Events 2018

5.4.1 Snowmelt event March 2018

In February 2018, temperatures were on average -2.8°C) and there was a lot of snow in the study area. From the 4th of March 2018, temperatures increased and were above zero and there was 14.3 mm of precipitation (DWD, 2018). The maximum 10-minute precipitation intensity was higher than 1 mm on the 8th of March (see Figure 30).

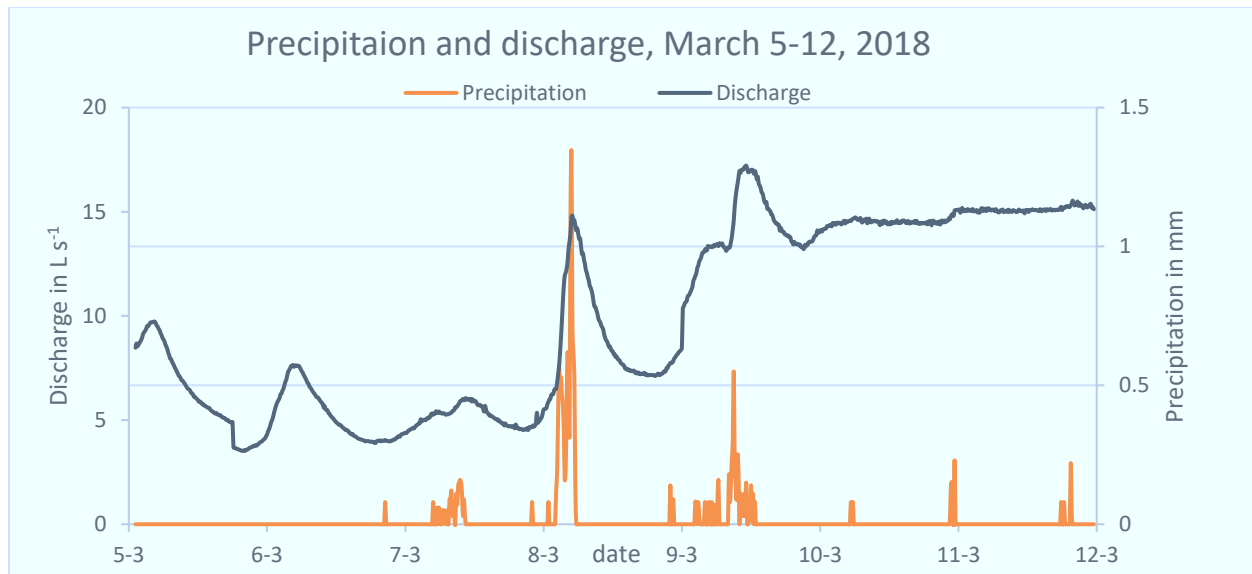


Figure 30. Precipitation and discharge during the snowmelt event of March 2018.

From the 5th of March, an automatic sampler was programmed at WU14 to take a sample every 8 hours for a week long, when the water level would reach 12 cm, a sample was taken every 2 hours. These samples were analysed for the temporal distribution of N and S compounds. Due to the different programming of the automatic sampler, storm and snowmelt events could be captured better and in higher resolution.

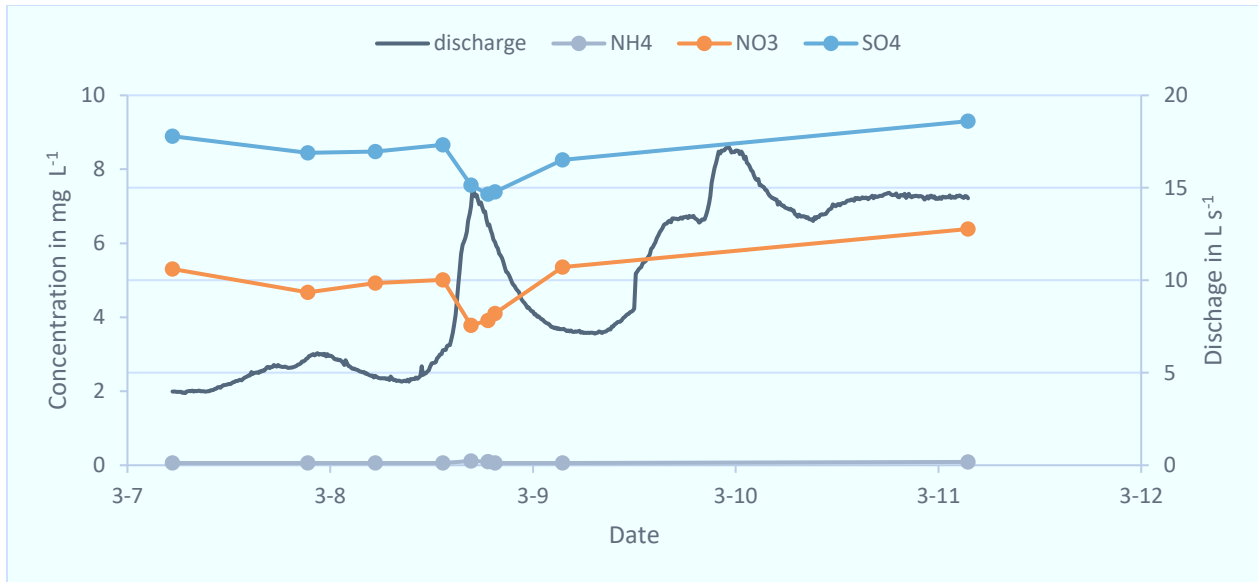


Figure 31. Response of the concentrations of the inorganic nutrients.

Figure 31 shows the concentrations of NO_3^- , SO_4^{2-} and NH_4^+ during the event of March 2018, the NO_3^- and SO_4^{2-} concentrations are increasing when the discharge starts increasing and then decrease, showing a dilution effect. On the falling limb of the hydrograph, the concentrations increase again until after the event. The NH_4^+ concentrations are under the detection limit before the event and increase to above the detection limit during peak discharge and then decrease again, being above the detection limit again on the 11th of March, after the event.

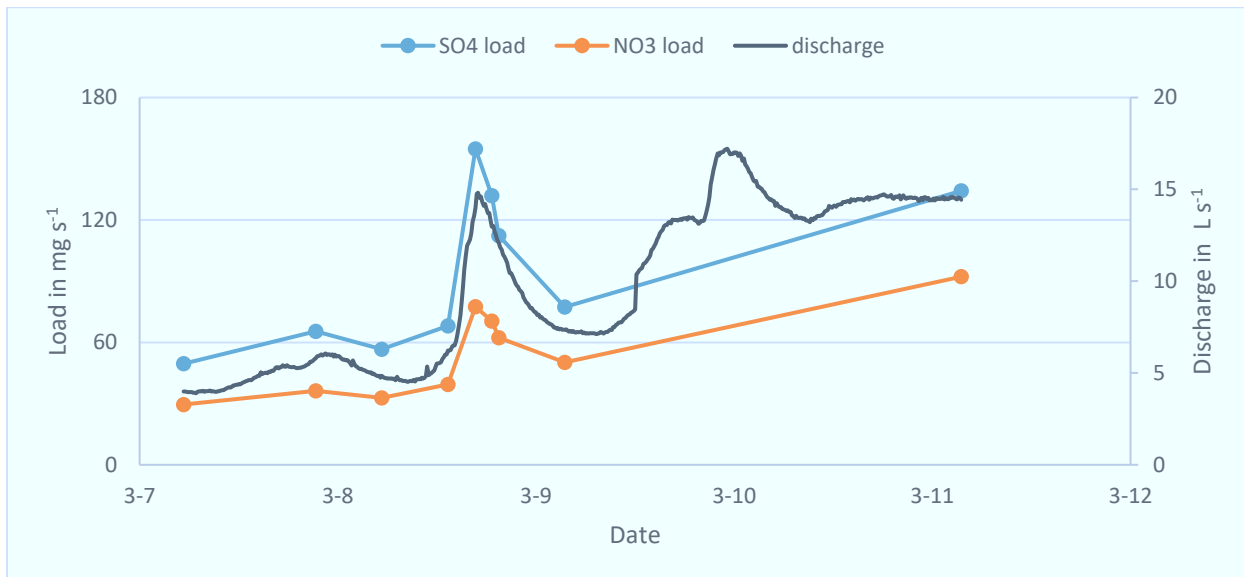


Figure 32. Response of the sulphate and nitrate load during the snowmelt event in March 2018.

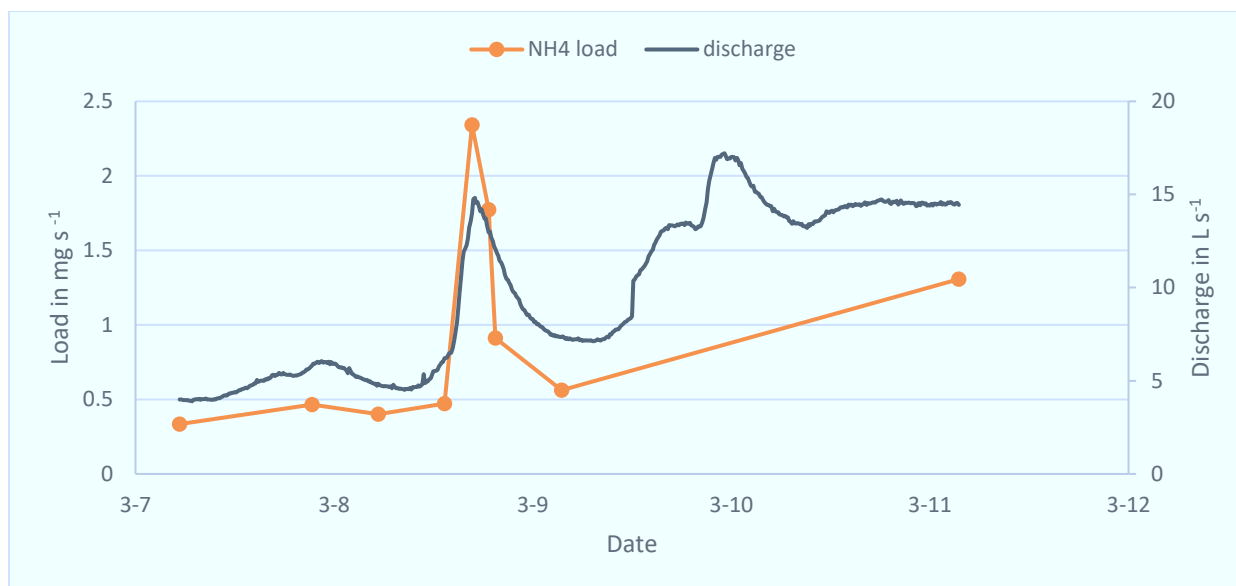


Figure 33. Response of the ammonium load during the snowmelt event in March 2018.

Figure 32 and 33 show the loads of NO_3^- , SO_4^{2-} and NH_4^+ during the peak discharge, all loads increase together with the discharge. The maximum NO_3^- load was 77.4 mg s^{-1} , the maximum SO_4^{2-} load was 154.9 mg s^{-1} and the maximum NH_4^+ load was 2.3 mg s^{-1} . The correlation between the SO_4^{2-} loads and the discharge is the strongest, having a correlation coefficient of 0.98 ($R^2=0.96$), followed by NH_4^+ (0.96 ($R^2=0.91$)), and are the weakest between NO_3^- and the discharge 0.87 ($R^2=0.75$). The SO_4^{2-} loads were also higher than the NO_3^- and NH_4^+ loads.

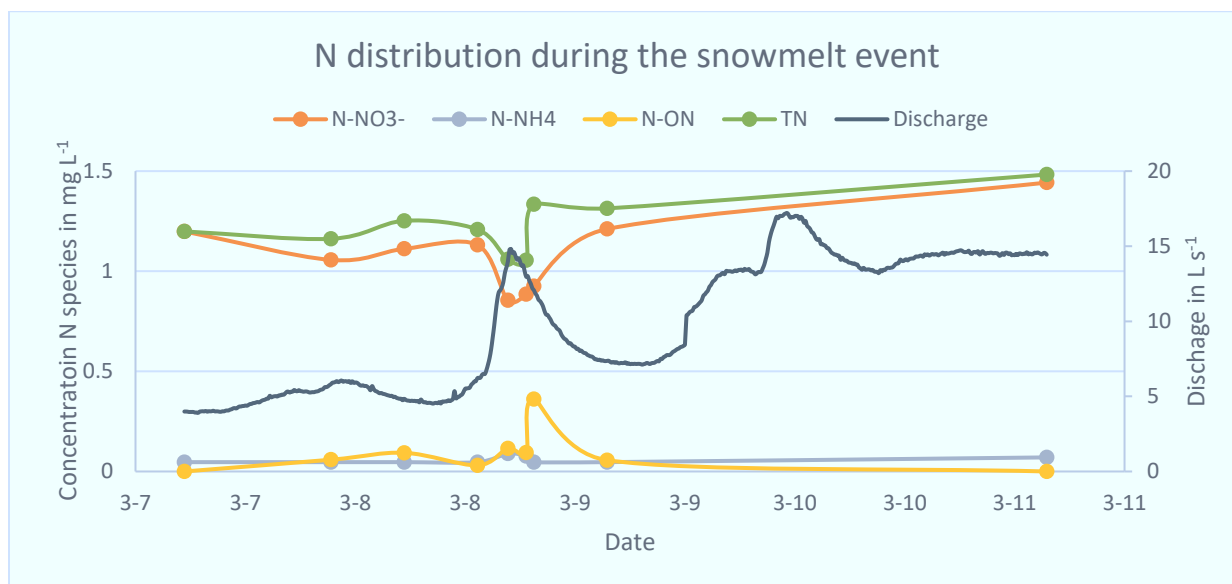


Figure 34. N species concentrations during the snowmelt event of March 2018

Figure 34 explains the N speciation in concentrations during the snowmelt event of March 2018. Both the N and nitrate concentrations are decreasing during the event (8th of March) and increase after the event (8th of March), showing a dilution effect. The lowest concentrations are at the same time as the highest discharge. The difference between the total N concentrations and the nitrate concentrations are smaller before the event and increasing 2 days before the event until the day after the event. The Ammonium and Organic N concentrations are highest during the event and have their highest value during peak discharge, they decrease after the peak discharge.

In Table 3 the relationships between the different N compounds and discharge and rainfall are displayed. Ammonium has the highest correlation with both discharge and rainfall, after N-NO₃⁻ with discharge and TN with rainfall. However, the correlation of ammonium and discharge and rainfall is positive and the correlation of rainfall and discharge with TN and N-NO₃⁻ is negative. The organic N has a relatively strong positive correlation with discharge and little correlation with rainfall.

Table 3. Correlations between the different N compounds and discharge and rainfall.

N compound	r discharge	R ² discharge	r rainfall	R ² rainfall
TN	-0.22	0.05	-0.50	0.25
N-NO ₃ ⁻	-0.50	0.25	-0.49	0.24
N-NH ₄ ⁺	0.86	0.75	0.69	0.47
N-ON	0.40	0.16	0.07	0.01

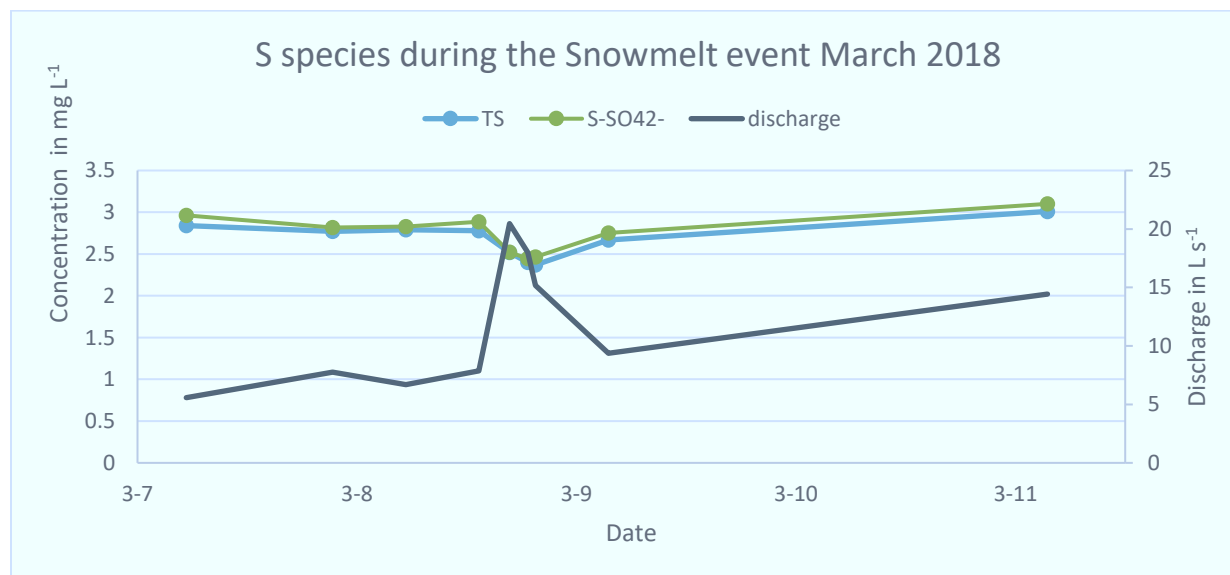


Figure 35. S compounds during the snowmelt event in March 2018, only the samples from the 7th till the 11th are chosen for analysis.

An ICP OES analysis was also performed with the samples (see figure 37). S-DOS could not be defined, because the SO₄²⁻-S values were higher than the TS values. It can be assumed that organic S concentrations must be very low during this event and that all the S detected by ICP OES was SO₄²⁻-S. The TS also shows

the same behaviour as the SO_4^{2-} -S, both decreasing during peak discharge and increasing again after the event.

5.4.2 Precipitation event 16th of May 2018

On the 16th of May, a shower, starting at 19.50 h CEST, having a maximum 10-minute intensity of 2.73 mm caused an increase of a factor 9 in discharge (see Figure 36). The discharge responded 10 minutes after the start of the shower and rose from 1.9 L s^{-1} to 18.1 L s^{-1} . Samples were taken by an automatic sampler that started sampling on the 16th of May on 17.40 h CEST. The second sample was taken at 20.10 h CEST, from that sample on every 30 minutes a sample was taken (until 07.10 h CEST on the 17th of May 2018).

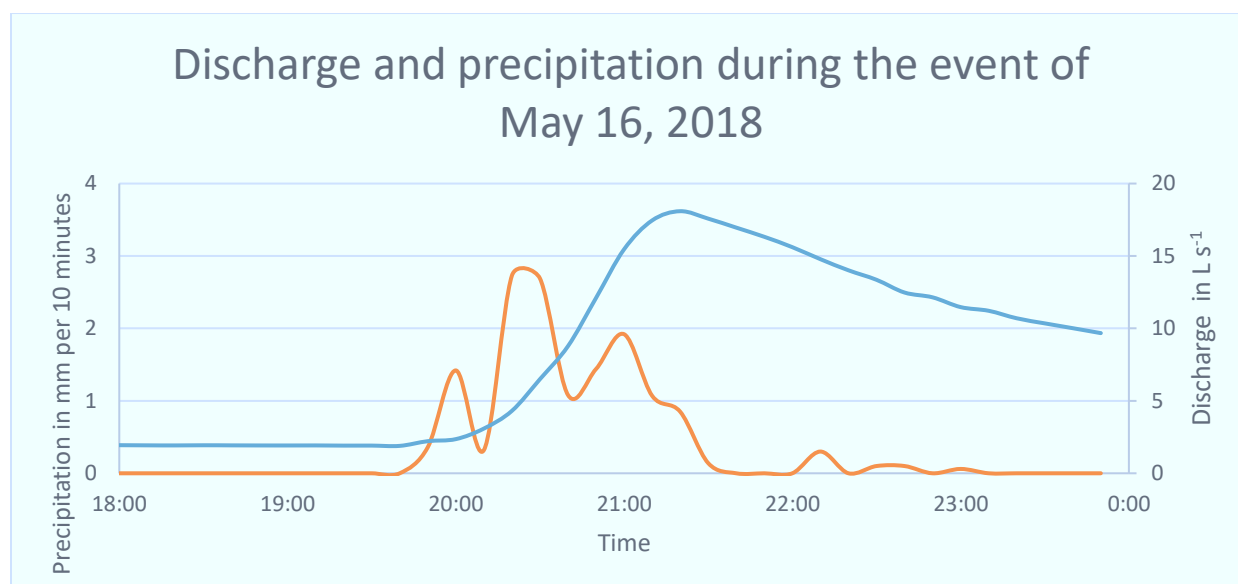


Figure 36. Discharge and precipitation during the event of the 16th of May 2018.

The samples were analysed with several analytical methods, Ammonium concentrations were analysed by CFA (filtered 0.45 μm) and Sulphate, Nitrite and Nitrate concentrations were analysed by both HPLC and IC (filtered 0.45 μm). Nitrite concentrations were below the detection limit or at the detection limit (0.01 $\mu\text{g/ml}$) and are therefore not considered in this section. Nitrate was also detected on higher resolution (10 minutes, instream, unfiltered) by the TriOS Probe, using UV detection. A filtration cascade was performed: the samples were analysed unfiltered, at 5 μm , 1 μm , 0.45 μm and 0.1 μm . The analyses that were performed on these were ICP OES for S and TOC/TN for N.

Figure 37 shows the concentrations of NO_3^- , SO_4^{2-} and NH_4^+ during the precipitation event in May 2018. The sulphate concentrations are the highest during the event, followed by the nitrate concentrations and the ammonium concentrations. The NO_3^- and SO_4^{2-} decrease when the discharge is increasing, showing a dilution effect. The NO_3^- concentrations decreases the most, relatively and absolutely. The SO_4^{2-} concentrations increase again when the discharge is decreasing, the NO_3^- concentrations increase after the

event. The NH_4^+ concentrations are under the detection limit, except for during the rising limb of the hydrograph, having a maximum in the middle of the rising limb of the hydrograph, at 20.40 h CEST.

Correlations between the concentrations and the discharge were strong and negative, having a correlation coefficient of -0.914 ($R^2 = 0.835$). If the concentrations are considered, all the samples and the discharge will give a correlation of 0.136 ($R^2 = 0.018$) and for the samples above detection limit the correlation is -0.244 ($R^2 = 0.060$). The correlation between the NO_3^- concentration and the discharge was equal to -0.633 ($R^2 = 0.400$), which is a relatively strong negative correlation.

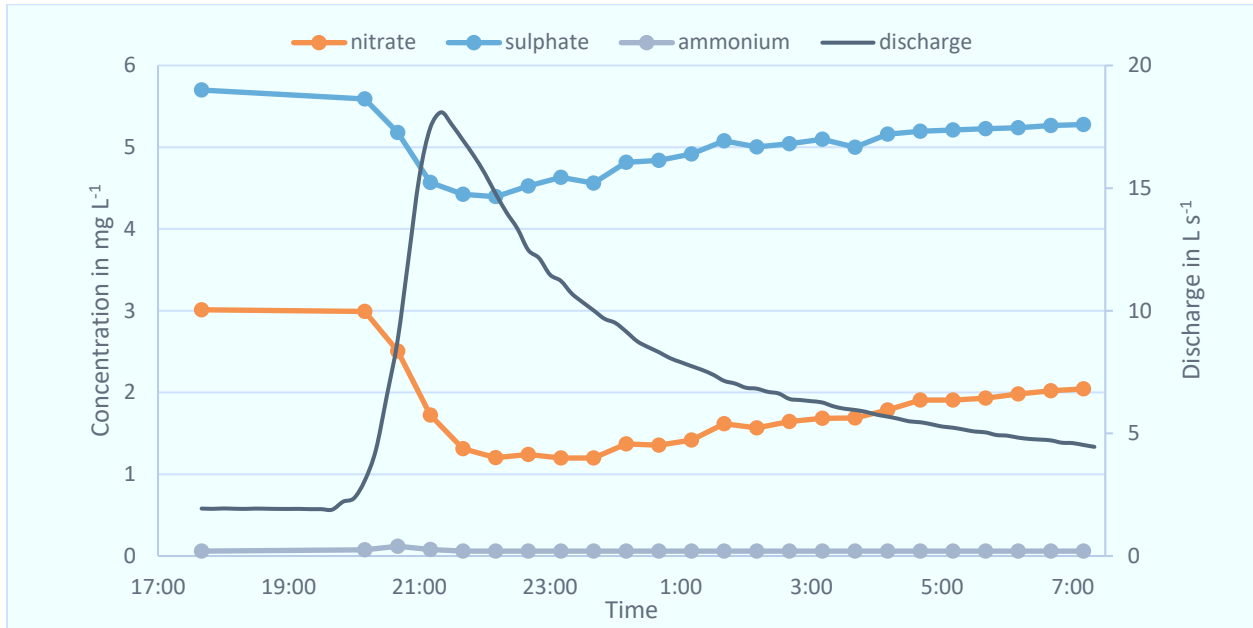


Figure 37. Response of the concentration of the inorganic nutrients to the event of May 2018.

In Figure 38 the loads of NO_3^- , SO_4^{2-} and NH_4^+ are displayed in figure 44, they all have their maximum at the same time as the discharge. The SO_4^{2-} loads are the highest, with a maximum of 79.8 mg s^{-1} , followed by the NO_3^- loads. The highest NO_3^- calculated was 30.1 mg s^{-1} . The NH_4^+ loads are the lowest, with a maximum of 1.4 mg s^{-1} . The SO_4^{2-} loads were strongly correlated to the changes in discharge during the event, as the correlation coefficient was 0.998 ($R^2 = 0.995$). The NO_3^- loads increase slower than the SO_4^{2-} loads, showing a dilution effect. The correlation between the NO_3^- loads and the discharge was equal to 0.872 ($R^2 = 0.760$), a strong positive correlation. If all samples of NH_4^+ were considered the correlation between ammonium loads and the discharge is 0.921 ($R^2 = 0.849$), if only the samples that were above detection limit were considered, the correlation is 0.437 ($R^2 = 0.191$). Figure 41 describes the NO_3^- loads during the peak discharge and shows that the loads rise faster than the discharge and decrease faster than the discharge.

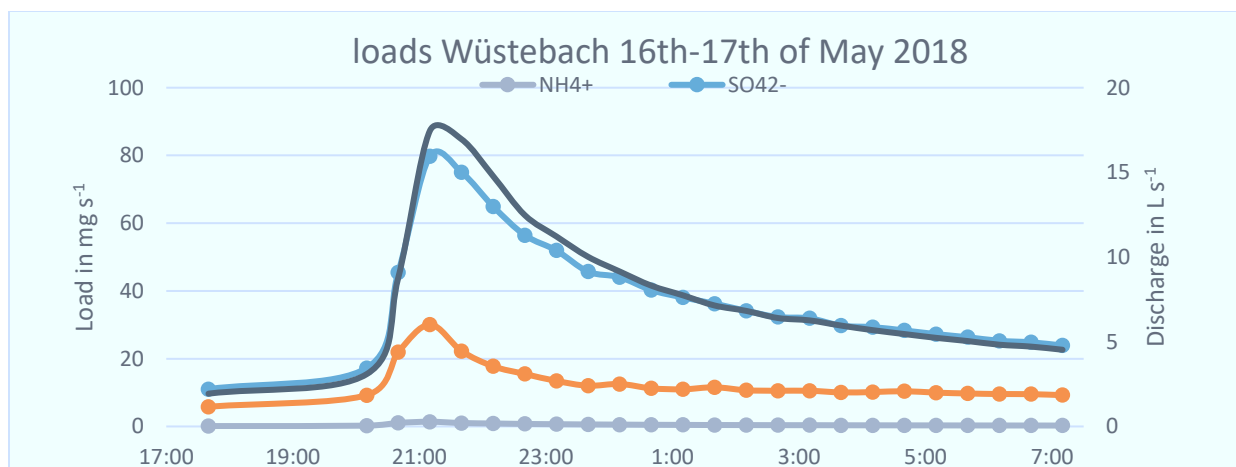


Figure 38. Response of the loads of the inorganic nutrients to the event of May 2018.

The chemical speciation of the N during the precipitation event of May 2018 is displayed in Figure 39. During the event, between 20.00 h CEST and 0.00 h CEST on the 16th of May, the N-NO_3^- concentrations decrease and increase after the event again. The lowest concentrations occur one hour later than the highest discharge. TN concentrations first peak and then decreases. The highest concentration is at the same time as the highest discharge. The difference between the total N concentrations and the nitrate concentrations are relatively constant until 21.10 CEST, increase is constant again at 4.10 CEST on the 17th, when peak discharge is over. The Ammonium and Organic N concentrations are highest during the event, Organic N is highest when discharge is the highest, and Ammonium is highest when the rainfall is highest.

Off all the N compounds, N-ON has the strongest correlation with discharge, and N-NO_3^- has the second strongest correlation with discharge (see Table 4). However, N-ON has a positive correlation and N-NO_3^- has a negative correlation. N-NH_4^+ has the highest correlation with both rainfalls, followed by N-NO_3^- with and TN. The correlation of N-NH_4^+ and TN with rainfall is positive and the correlation of rainfall with N-NO_3^- is negative. N-ON has a relatively strong positive correlation with rainfall and little correlation with rainfall.

Table 4. Relationships between rainfall, discharge, and different N species.

N compound	r discharge	R ² discharge	R rainfall	R ² rainfall
TN	0.06	0.003	0.63	0.39
N-NO_3^-	-0.63	0.40	-0.66	0.44
N-NH_4^+	0.13	0.02	0.87	0.76
N-ON	0.80	0.64	0.20	0.04

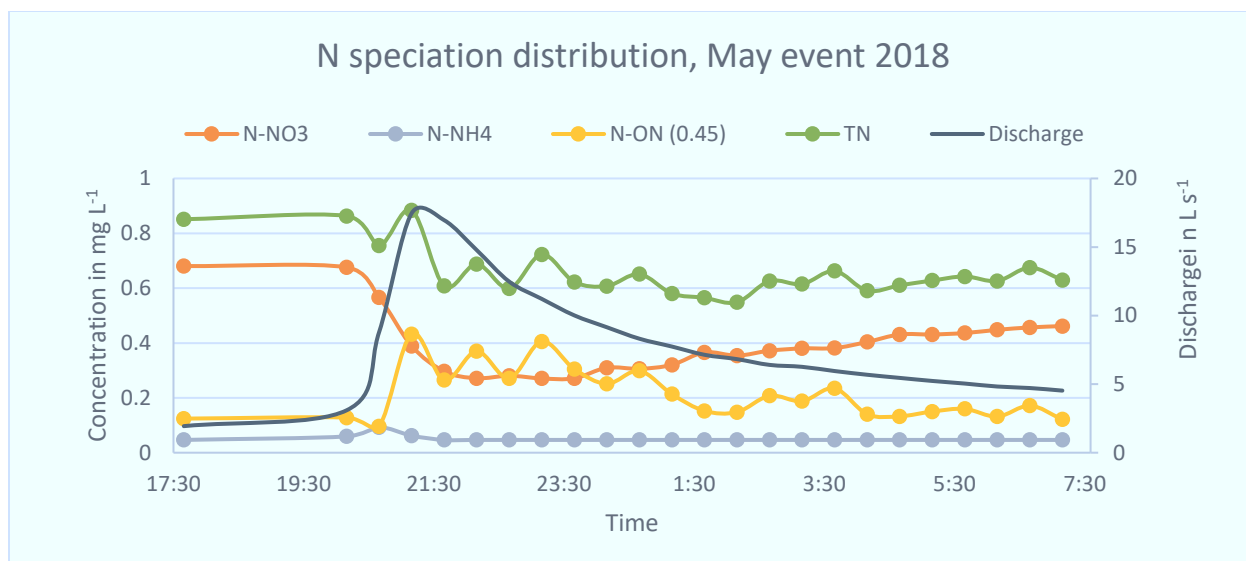


Figure 39. Different N species during the event of May 16-17, 2018.

Figure 40 displays the distribution per particle size, during the event in May 2018. The smallest filtration step, $<0.1 \mu\text{m}$, being the nanoparticles and “truly dissolved” particles, decrease during the peak discharge, showing a dilution effect. The larger particulates, being larger than $1 \mu\text{m}$ increase during peak discharge and decrease fast on the falling limb. The fine colloid fraction (with diameters between $0.1 \mu\text{m}$ and $1 \mu\text{m}$) are first decreasing with the rising limb, but later increasing and then decreasing again. Most of the N measured in the samples was of the smallest fraction. However, the during peak discharge the concentration of the smallest fraction was nearly equal to the concentration of the largest fraction. This was the moment where the distribution of N over the three fractions was most diverse.

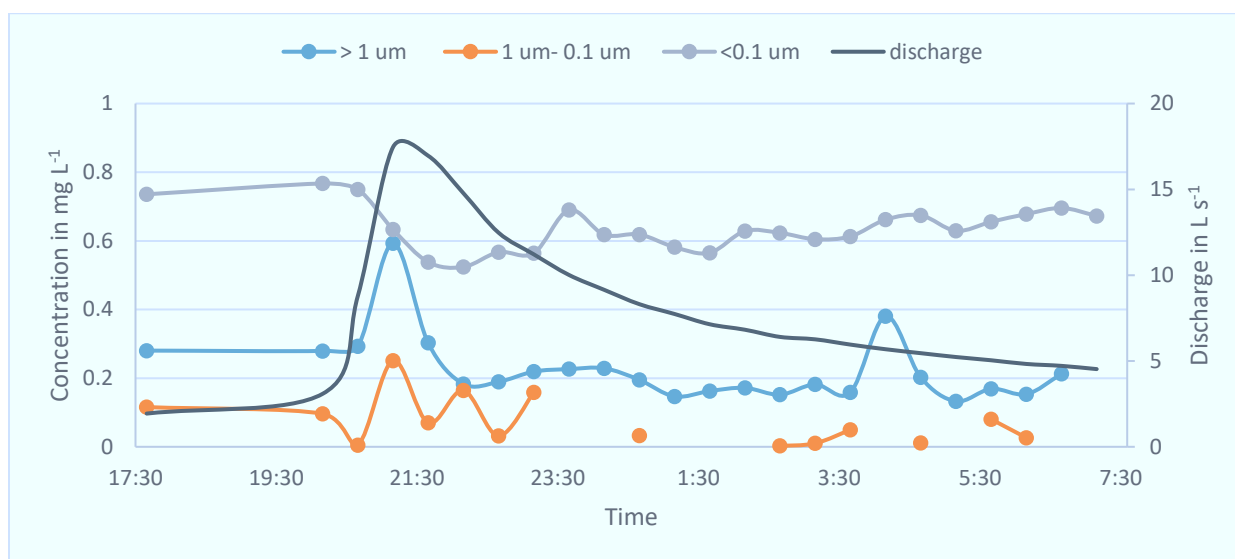


Figure 40. Distribution of N compounds per particle size during the event of May 2018.

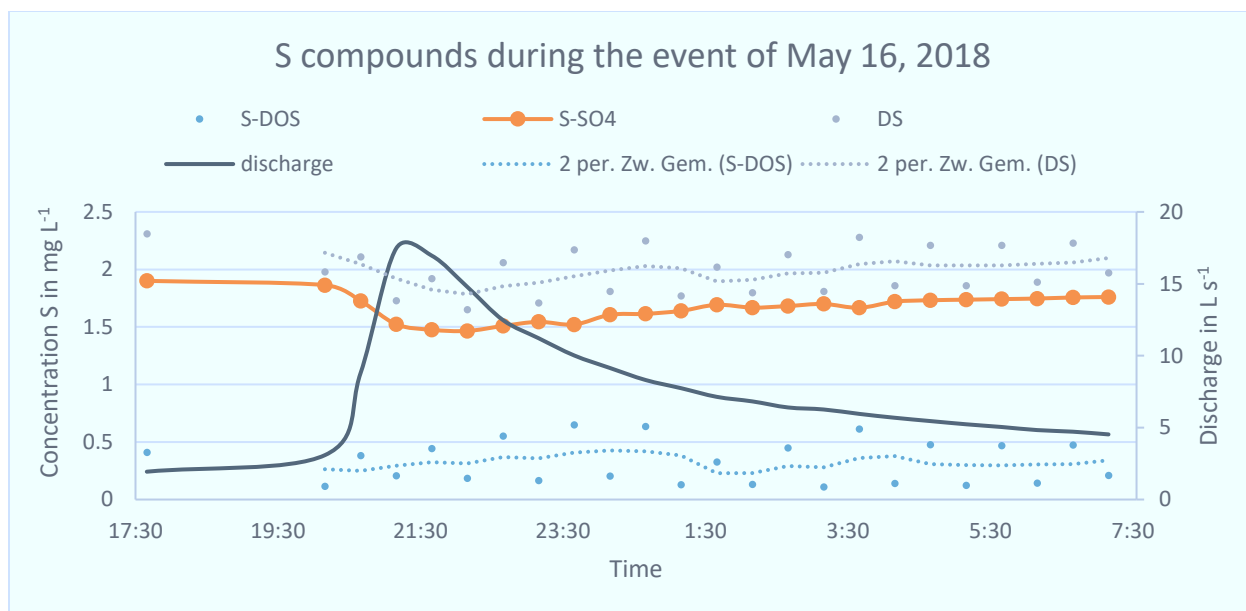


Figure 41. S compounds during the event of May 16th-17th, 2018. 2 per. Zw. Gem. Means “moving average, period of 2”.

Total S concentrations were detected by ICP OES analysis, measured at different filtration steps. The S-SO_4^{2-} and S-DOS (from 0.45 μm) were calculated in a similar way as the N compounds (see Figure 41). The TS and S-DOS have a fluctuation pattern. During the event, S-SO_4^{2-} concentration directly decrease when the discharge increases and increase after the event. TS concentrations decrease a little during the event and increase after. S-DOS concentration decreases when the rainfall increases and increases when the discharge increases. If moving averages with a power of 2 have been used, the S-DOS shows a small increase during peak discharge, while TS shows a small decrease. Most of the Sulphur measured is S-SO_4^{2-} .

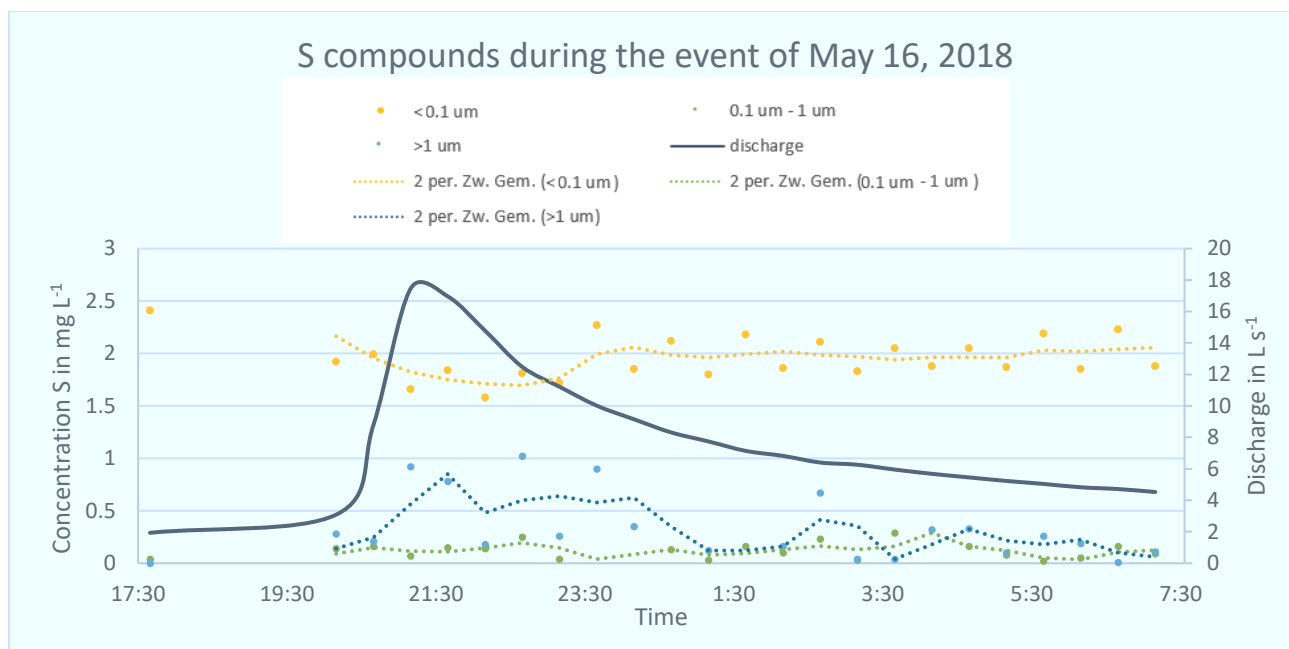


Figure 42. S compounds during the event of May 16th-17th, 2018. 2 per. Zw. Gem. Means “moving average, period of 2”.

Classes of filtration steps have been made according to the definitions of nanoparticles (see Figure 42) (smaller than 0.1 μm), fine colloids (1 μm -0.1 μm) and larger particulates (larger than 1 μm). The nanoparticles are most common and have a similar behaviour as the S-SO_4^{2-} . Fine colloids and coarser colloids have a more similar behaviour as the S-DOS and increase during peak discharge. Larger particulates are more common than fine colloids.

5.5 High resolution event based sampling and continuous measuring for nitrate detection

Nitrate (NO_3^-) was measured using four analytical methods and two temporal resolutions. A TriOS probe quantified in-stream NO_3^- using UV detection every 10 minutes (Sandford et al., 2013). IC and HPLC were used to quantify NO_3^- in a lower temporal resolution. The Trios Probe uses UV detection to measure the NO_3^- concentration and HPLC and IC are two ion chromatography methods, measuring the ion exchange capacity. In this subchapter, the techniques are compared for both events of 2018 by analysing the correlation and differences. The analysis was not performed with the TN concentrations, since the TN analysis only measures the N atom in the N compounds, which can also be other N compounds than Nitrate. The figures on the below (Figure 43 and Figure 44) describe the continuously measured runoff and nitrate concentrations and the analysed samples that were taken on a lower resolution of a snowmelt event in the winter of 2018 and a spring storm in May 2018. Both figures show that the results of the analytical methods are somewhat similar to the continuously measured values. However, they are mostly higher, of which the results of IC are the highest.

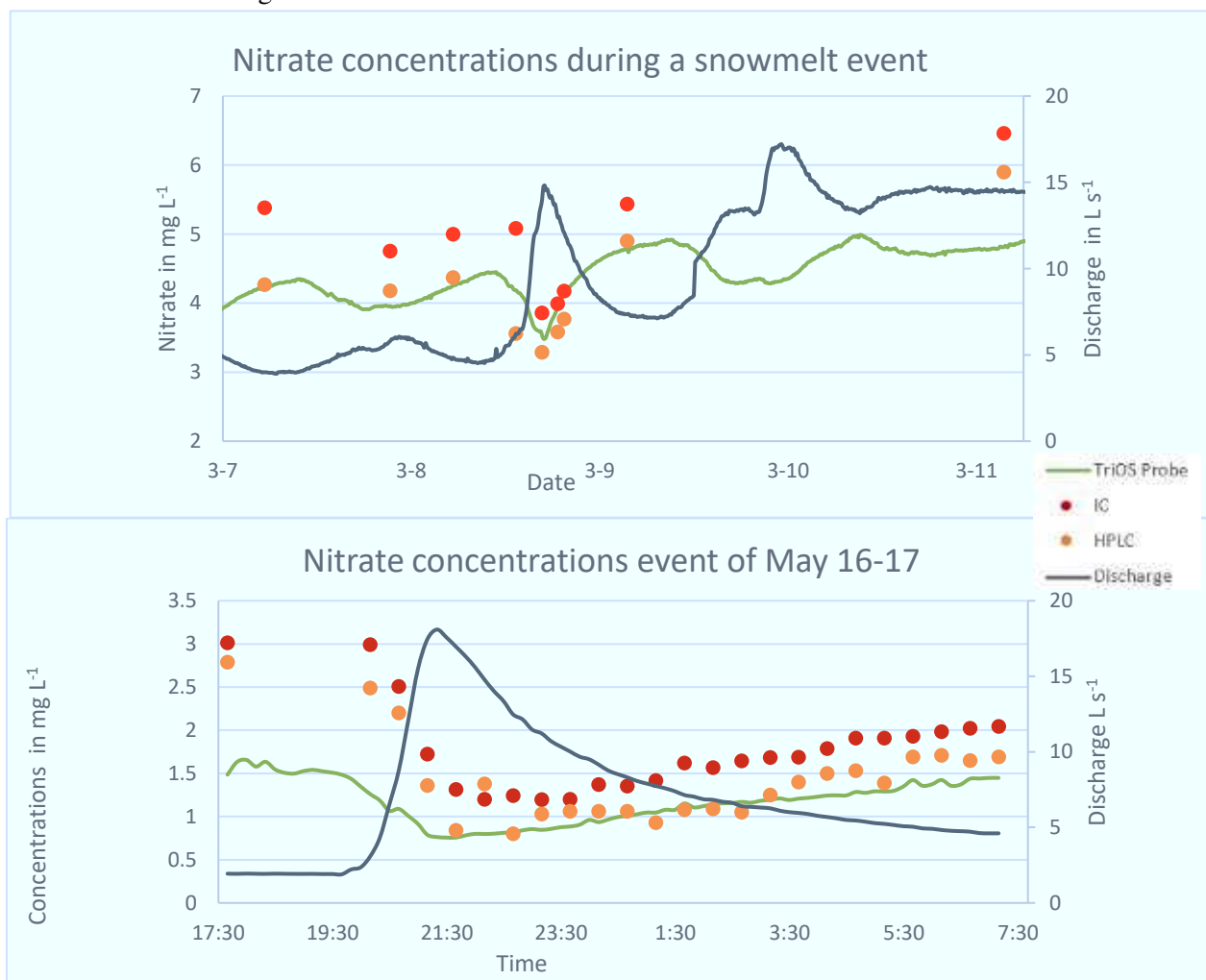


Figure 43 and 44. Nitrate concentrations, measured by three methods during the two events of 2018

The concentrations of the event in March measured by IC and the TriOS Probe are statistically significant at a 95% confidence level (p -value = 0.018), the values measured by HPLC and the TriOS Probe do not differ significantly. The concentrations are also relatively strongly correlated, having an R^2 value of 0.76 for IC and the TriOS Probe and an R^2 value of 0.74 for HPLC and the TriOS Probe. The TriOS Probe and HPLC and IC concentrations don't have different variances. More information can be found in Appendix A.2.

During the event in May, the IC and TriOS probe measurements have the highest R^2 value again, i.e. 0.48, but the concentrations measured by the TriOS Probe are significantly lower at a 95 % confidence level (p -value = 1.75E-06). The HPLC and TriOS probe measurements have a R^2 value of 0.39 the results for the event in May and the concentrations measured by the TriOS probe are significantly lower (p = 0.008). The TriOS Probe and HPLC and IC concentrations have significantly different variance as well. NO_3^- exports per method during the event of January 2018. More information can be found in appendix A.2.

Total NO_3^- exports were calculated by interpolating the IC and HPLC concentrations to create the same resolution as the TriOS Probe Resolutions. The exports are shown in Figure 45 and Figure 46 and can be found below. The total exports of nitrate per hectare during the winter event were 483.5 gram, 431.4 and 389.1 gram for IC, HPLC and the TriOS probe. The total export of nitrate per hectare during the event in May were 15.2-gram, 12.2 gram and 9.5 gram for IC, HPLC and the TriOS probe. All the exports were calculated assuming that the whole catchment contributed to nitrate export.

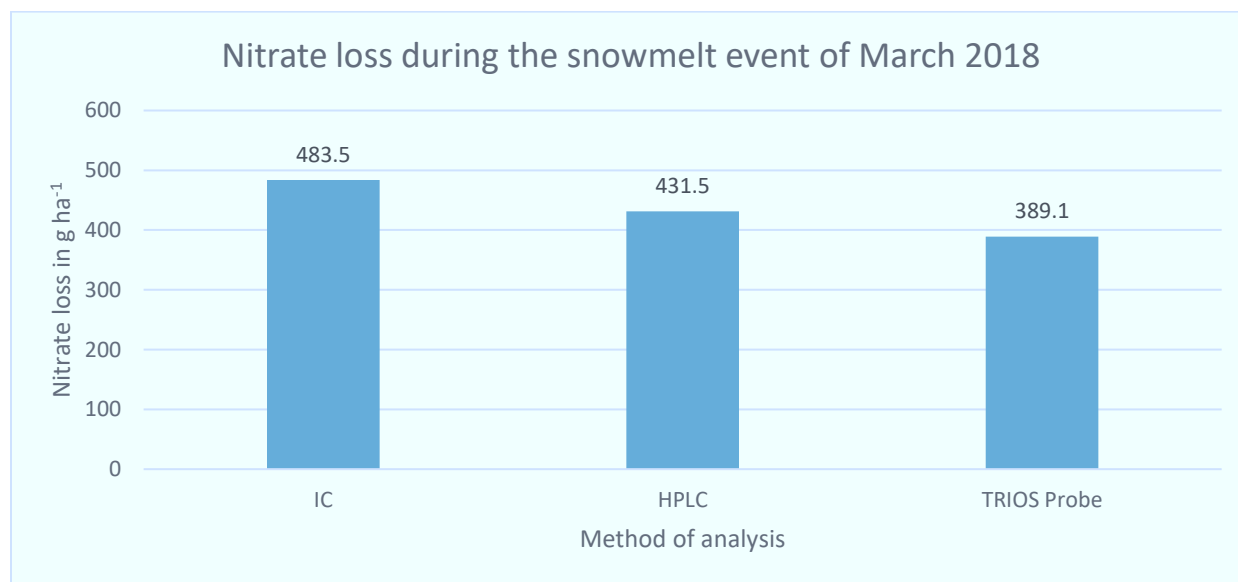


Figure 45. The total NO_3^- loss during peak discharge during the snowmelt event in March 2018 calculated with the results from IC, HPLC and the TriOS probe.

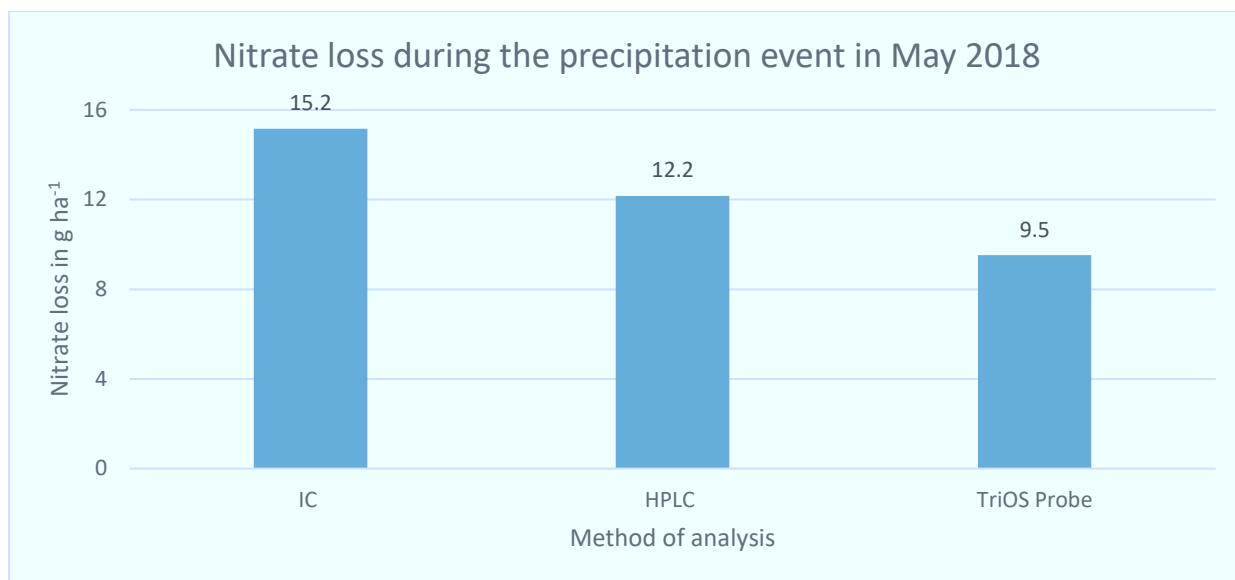


Figure 46. The total NO_3^- loss during peak discharge during the event in May 2018 calculated with the results from IC, HPLC and the TriOS probe.

6. Discussion

6.1 The contribution of the tributaries

In this study five tributaries have been measured at the beginning of the winter event of 2018, to measure the contribution of the tributaries during events. The WU1 and WU8 tributary was clearly surface water driven, having a very high DOC/NO₃⁻ ratio. WU 17 and 12 were groundwater driven and had a low DOC/NO₃⁻ ratio, and WU 14 showed to be a mix of surface water and groundwater. WU 8 was surface water driven with some groundwater influence. The contribution of the tributaries has also been studied by Weigand et al. (2017), showing similar values. However, Weigand et al. (2017) measured the tributaries during baseflow and measured the “average” DOC/NO₃⁻ ratio. This ratio was higher for WU1 and WU8 and lower for WU17, WU14, and WU12. This shows that the contribution of the tributaries is different during events. Only the DOC/NO₃⁻ ratio of WU8 is twice a standard deviation lower than in the study of Weigand et al. (2017). This could mean that during events the surface water dominated tributaries become more influenced by groundwater and the groundwater influenced tributaries will be more influenced by surface water processes.

Within the different types of tributaries, the chemical environment also differs. WU1 lies in an area of histosols and has the lowest pH, i.e. 4.6 and are more likely to have anoxic conditions (Bol et al., 2015). This causes a different environment for microbial activity than the groundwater fed tributaries, resulting in higher ammonium and DOC concentrations and lower nitrate concentrations. WU8 is also surface water driven (Bol et al., 2015; Weigand et al., 2017) but has a higher pH than the other tributaries, in between 5.9 and 6.3, it is still close to the histosol area and has therefore also a higher ammonium concentration. The groundwater influenced tributaries WU17 and WU12 have a more neutral environment, having a pH of around 5.7 (Bol et al. 2015), resulting in high NO₃⁻ concentrations, which has also been found in the study of Weigand et al., 2017. WU17 is the reference stream, which has not been deforested, therefore WU17 shows higher sulphate concentrations. WU14 is the outlet and is influenced by both groundwater and surface water and shows both high DOC, nitrate (Weigand et al., 2017) and sulphate concentrations, and ammonium concentrations above detection limit. In summer, microbial activity increases (Inamdar et al., 2006) and plants take up more nutrients, resulting in lower concentrations nitrate and sulphate and higher ammonium concentrations. However, data lacks to completely describe the spatial distribution, as the tributaries have only been sampled in winter and data on the Tereno website shows room for improvement.

6.2 N and S export during events

6.2.1 The response of inorganic N and S export during events

During all the analysed past events and the events in 2018, both the sulphate and nitrate concentrations show a dilution effect, decreasing during peak discharge, which is in line with the study of Inamdar et al., (2006). Nitrate has lower concentrations before the event and decreases the most, showing the strongest

dilution effect. Low nitrate concentrations are also found by other studies, for example by Gao et al., (2014). The sulphate concentrations recover faster but do not increase that much after as the nitrate concentrations. This is because the sulphate concentrations are higher in the soil than the nitrate concentrations and the nitrate is a more mobile ion than sulphate, which means that nitrate does not adsorb easily to other compounds in the soil (Johnson & Cole, 1980). Nitrate and sulphate peak on the falling limb, when the interflow increases, a groundwater driven process (Musy, 2001), which is displayed in Figure 47. Nitrate and sulphate also get pushed out by the old water effect, this effect is larger after dry periods, when export of nutrients was low due to low rate of leaching (Inamdar et al., 2006). High nitrate and sulphate concentrations are also common in situations when there is hydrological connectivity and groundwater flows from the hillslopes to the riparian zone, triggered by pressure waves from the precipitation. These pressure waves are stronger during high intensity rainfall events (Stockinger et al. 2014). Then not only has the riparian zone reacted, but the whole catchment (Rosenbaum et al., 2012; Stockinger et al., 2014). This condition occurs when the soil moisture level is 35 % or higher, which is during winter season, between November and May (Rosenbaum et al., 2012; Stockinger et al., 2014). This condition can also occur during high intensity rainfall events (Stockinger et al., 2014) or in situations in summer where a lot of precipitation falls within for example a week (Inamdar et al., 2006).

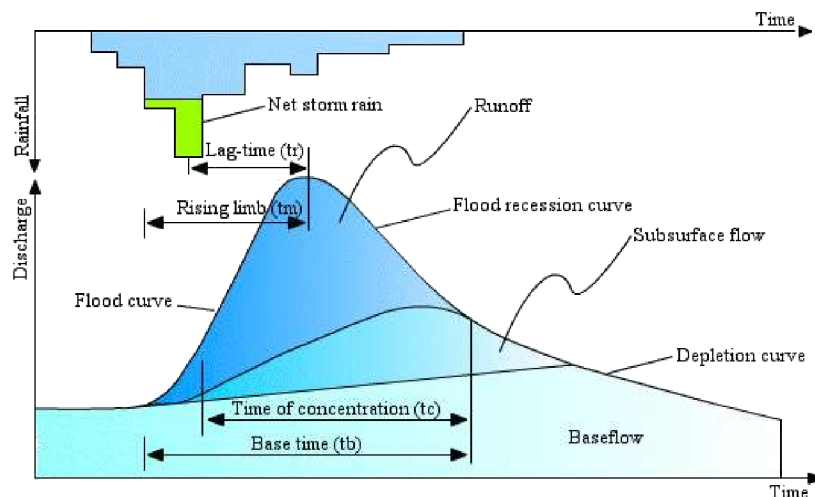


Figure 47. Catchment response after a high intensity rainfall event (Musy, 2001).

Another explanation for the export of N and S anions to the stream could be the occurrence of preferential flow in the unsaturated zone. This can occur when the hillslopes are not hydrologically connected to the riparian zone. Wiekenkamp et al., (2016) found that during rainfall events with more than 25 mm of precipitation, preferential flow occurred more when the soil was dryer. This could explain the increase of the nitrate concentration during the event of the 6th and 7th of May 2014, because there was no hydrological connectivity.

Ammonium is usually under the detection limit, but during the rising limb of the hydrograph the concentrations are above the detection limit and show a peak. Usually this peak is also at the same time as the highest intensity in rainfall and showed strong correlation with the amount of rainfall. This shows that ammonium export is a surface water driven process, which was also found by Butturini & Sabater (2002) and Inamdar et al., (2006). In other situations, ammonium is nitrified quickly by microbes in the water to nitrate or used up directly by plants as a nutrient, during high intensity rainfall events, this nitrification is disrupted by surface water mixing and ammonium will be exported (Cooper, 1983), therefore higher ammonium concentrations occur during events than during baseflow. Organic S in summer and organic N shows the same response as ammonium, being strongly correlated with rainfall and positively correlated with the discharged. Studies by Inamdar et al., (2006) found that (dissolved) organic matter, including organic N and S has increased export during high discharge events, caused by overland flow. However, overland flow has never been observed in Wüstebach, although the concentrations organic N and S could be explained by this process (Inamdar & Mitchel, 2007;). It is more likely that the driver behind the high concentration of could also be explained by preferential flow paths in the top soil that are active during the dry season (Wiekenkamp et al. 2016) and transporting organic N and S compounds to the Wüstebach stream from the top soil and surface.

6.2.2 The response of the inorganic N and S loads

The past events show larger loads for nitrate than for sulphate and ammonium, with the largest loads during winter events or the summer event of the 29th and 30th of July 2014. The event of March 2018 is similar the previously stated events, although the nitrate loads are lower than the sulphate loads. The high loads in winter and summer events with hydrological connectivity are caused by the high discharge due to the whole catchment responding and higher concentrations (Stockinger et al., 2014). In winter, the nutrients are taken up less by the vegetation, causing higher concentrations in the stream water (Inamdar et al., 2006). The event of May 2018 shows similar loads to the past events in summer (excluding the event of the 29th and 30th of July 2014), having high loads. However, the nitrate loads are during the summer events in 2013 and 2014 larger than the sulphate loads, while they are smaller than the sulphate loads during the May event in 2018. This could not have been caused by the deforestation, because then it should also be lower during both events in 2014 (Golor, 2016).

Deforestation causes a decrease in the sulphate concentrations, because sulphate originates from plant material and in lower amounts from the geology and air pollution (Scherer, 2009). This is not shown in the results of this study and the study does not have enough data analysed to make a statement about this. The total export of nitrate was 483.5 grams per hectare during the winter event and 15.2 grams per hectare, which is nearly 32 times less in summer as in winter. 483.5 grams per hectare is a very high loss for an event, Casson & Watsmough (2014) found that combined rain and snowmelt events are transporting up to

90% of the winter export of nitrate and 40 % of the total export of nitrate. Inamdar et al., (2006) found that events in general did not contribute to the total nitrate export as much as was found by Casson & Watsmough (2014). However, they also found that winter and spring events contributed more to the total budget than summer events (Inamdar et al., 2006). The values found by Inamdar et al., (2006) are more likely to be also representative for the Wüstebach study area, because the environment is similar to the study area by Inamdar et al., 2006). High nitrate losses in winter could have been caused by the fact that before the event in March, there was a period of low temperatures and low precipitation, the study area was covered by snow. The nitrate and sulphate within the soil could have been kept in the frozen soil before it was leached to the stream (Laudon et al., 2004).

6.2.3 Chemical speciation N and S during events

The organic N, ammonium, and organic S are showing the opposite behaviour of nitrate and sulphate, as they increase during peak discharge, having their maximum when the discharge is also at its maximum (David & Mitchel, 1987; Inamdar & Mitchel, 2007). Therefore, the export of organic N and organic S is similar to the export of DOM and is a surface water driven process and comes from overland flow (David & Mitchel, Inamdar & Mitchel, 2007). The concentrations organic N and organic S are both higher in summer than in winter, due to the decrease of vegetation in winter. Organic S concentrations were even negligible during winter. This can also be seen in the past events, during the snowmelt event in 2011, the organic N concentrations were smaller than during the summer events and the rainfall event in winter 2012. That event is an exception to general winter events, because it is not a snowmelt event. During this event the Organic N concentrations are similar to the summer events, indicating that there also occurred overland flow and N immobilisation. Laudon et al., (2004) found that overland flow is not occurring as often during snowmelt events as during rainfall events due to infiltrating snowmelt water and the higher groundwater table, which can also be on top of a frozen soil layer (Laudon et al. 2004). The study by Gao et al. (2014) shows also that during peak discharge the diversity of N species becomes larger, having more particulate N and organic N during peak discharge and less Nitrate. Gao et al., (2014) is only focusing on summer events, and therefore the events show large diversity of N species. During the two events with the highest intensity, 59.4 and 32.2 mm, the diversity was the largest and showed a peak in TN, due to large particulate N transport (Gao et al. 2014). These events can be compared with the summer event of May 2014, where the 37.6 mm precipitation fell, N diversity was high, and the TN concentration increases on the rising limb of the hydrograph. During the event with 19.8 mm precipitation, the TN and N species showed a dilution effect (Gao et al., 2014). Therefore, N diversity and probably S diversity, as they have similar drivers (Inamdar et al., 2006), increases with higher precipitation intensity causing a peak in TN, but a dilution effect in nitrate concentrations.

For the event of May 2018, the samples have also been filtered to analyse the different sizes of the compounds. Most of the S and N analysed was in the range of nanoparticles ($<0.1\text{ }\mu\text{m}$), the second largest fraction were the large colloids ($>1\text{ }\mu\text{m}$) and the smallest fraction were the fine colloids ($0.1 - 1\text{ }\mu\text{m}$). The nanoparticles fraction showed similar behaviour to the inorganic ions, decreasing during peak discharge and increasing after. The large colloids of N and S and the fine colloids of N showed similar behaviour to the organic N and S, having a maximum together with the discharge. The fine colloids of S showed little response to the increase in discharge, being slightly larger than during peak discharge than during baseflow.

Comparing the results of the filtration cascade, it shows that the nanoparticles are likely to be the nitrate and sulphate ions, as they are showing the same response to the changes in discharge and since nitrate and sulphate ions are smaller than $0.1\text{ }\mu\text{m}$. The fine colloids and large colloids could be the organic N and organic S, because they show the same response to peak discharge as the organic N and S. The organic N and S could be amino acids, sulphate esters and sulphate particles connected to iron and aluminium ions (Scherer, 2009; Gottselig et al., 2014).

6.3 Differences between summer and winter events

Events in winter are mostly characterised by a long duration, snowmelt and a high discharge. The discharge increases relatively slow. Concentrations of nitrate and sulphate high and more sulphate and nitrate is lost during winter, because the growing season has not started yet and immobilisation is going slow due to low temperatures. Organic N and S and ammonium showed low concentrations are and will not be lost as much as the inorganic nutrients because of the snow cover and possible frozen soil. These events have a larger effect on ecology, because snowmelt events take place just before the growing season. Especially the sulphate leaching was large during the snowmelt event in 2018, this can be a large problem and might make the young plants shift to take up the organic S. However, organic S was not measured in stream water, so it might be that there is a lack of S nutrients. A lack of N will also cause problems for the plants to grow, as they can not use organic N as a nutrient. Winter events will be more common, although they are likely to become rainfall events instead of snowmelt events. If winter events are still coupled snowmelt and rainfall events at the beginning of the growing season, or become rainfall events of long duration, this might cause problems for the regenerating forest to grow with a lack of nutrients at the start of the growing season. Measures should be taken to keep the nutrients within the catchment.

Summer events are generally shorter than winter events, more intense and show a fast increase in discharge. There are not as many nutrients lost, because of the shorter duration of the event, the fact that mostly only the riparian zone is active and there is no hydrological connectivity (Stockinger et al., 2014). In addition, there are higher concentrations of organic N and S and ammonium, which are then lost as well during high intensity precipitation events. This means that all possible nutrients are lost, but in lower

quantity. Summer events mostly occur after dry periods, only after several rainfall events or during an event with a very high precipitation intensity the whole catchment will respond, but that is rare (Stockinger et al., 2014). It is more likely that in the dry season the hill slopes are connected to the stream by preferential flow channels (Wiekenkamp et al., 2016). Lastly, events in early summer, May and June, are having a larger effect on the ecology than events happening at the end of summer, September and October, because the plants are still growing during the early summer months (Inamdar et al., 2006). Summer events are not likely either to affect the ecology of the whole catchment, due to the riparian zone that is reacting to the rainfall, and the riparian zone is smaller than the deforested area (Bogena et al., 2015). Of the events of 2018 we could not analyse whether the riparian zone and the rest of the catchment were hydrologically connected because the soil moisture data was only available until 2015.

6.4 Differences in measuring methods

6.4.1 The differences between HPLC and IC

HPLC and IC are both good ways to measure nitrate and sulphate, as they show similar values and have a large recovery of nitrate and they are not showing large significant differences for all the concentrations measured. However, HPLC and IC differ significantly when they measure nitrate in low concentrations. Low concentrations of nitrate occur during events in both summer and winter, the winter and summer events were both different at a confidence level of 95 %. A reason for this could be the high Cl^- concentrations in Wüstebach that were both above 50 mg L^{-1} during these events in 2018, because of road salt that was leaching from the federal highway B258. This leads to higher Cl^- concentrations in the Wüstebach stream.

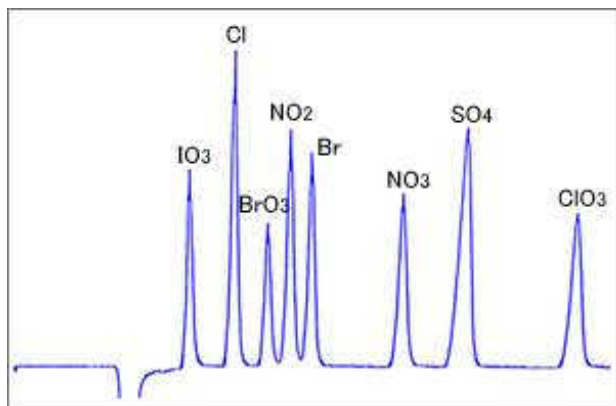


Figure 48. Example chromatograph after ion chromatography with indirect absorbance detection (www.shimadzu.com, n.d.).

On average, the Cl^- concentrations measured by IC are 51.3 mg L^{-1} (standard deviation: 9.06 mg L^{-1}) in winter and 52.3 mg L^{-1} (standard deviation: 12.43 mg L^{-1}) in summer, the concentrations in winter are not significantly different from the concentrations in summer. During the event in March, the Cl^- concentrations were on average 62.0 mg L^{-1} , which is relatively high compared to the average, but not statistically different. At the chromatograph response, the Cl^- peak comes directly before the NO_2^- , Br^- and NO_3^- peak

as can be seen in Figure 48 (www.shimadzu.com, n.d.). There was no NO_2^- and Br^- measured in the samples, thus during the performance of HPLC, the Cl^- concentrations caused a large peak at the chromatograph just before the nitrate peak, which it is hard to separate the peak of Cl^- and The technician performing HPLC adapted to this situation by changing the UV wavelength used for detection and made the Cl^- peak narrower. The technicians of IC did not see this and followed their standard procedure. Nevertheless, for NO_3^- the values still differed significantly from the NO_3^- concentrations measured with IC at the ZEA-3.

Similar observations were made by Ramaswami et al., (2017), who found that Cl^- concentrations higher than 50 mg L⁻¹ can cause a decrease in NO_3^- recovery during IC. On average the recovery was still relatively good, being 90% or larger (Ramaswami et al. 2017). It is better to use IC for studies in this study area, because all the data on the Tereno platform is measured with IC. The standards show high nitrate recovery in both methods that, IC a bit more accurate, but they are not significantly different. Ramaswami et al. 2017 found that nitrate can best be measured under high Cl^- circumstances with cuvette measurements. Both methods only detect NO_3^- , as they didn't respond to the NOM particle standard, there was only a little SO_4^{2-} detected with IC. The standard includes organic material and includes S compounds.

6.4.2 The differences between high resolution sampling and continuous measuring

The NO_3^- loss per hectare for the two events in 2018 were the highest measured by IC, followed by HPLC and the TriOS Probe. It was found that IC detects NO_3^- the most accurate, therefore IC will be the preferred method to detect NO_3^- . HPLC detected 89.2 and 80.3 % of the total NO_3^- export during the winter and summer event measured by IC, the TriOS Probe detected 80.5 and 62.5 % during the winter and summer event in 2018. The TriOS probe sampled several minor NO_3^- troughs which were not sampled by the autosampler which explains the lower NO_3^- export. However, the TriOS Probe is also measuring lower concentrations, as it measures lower concentrations than HPLC. The IC measurements are higher than HPLC and the TriOS Probe and the IC measurements most precise, as they show the highest recovery of nitrate from the standards. The TriOS Probe can be a way of estimating the total nitrate export and can be used for estimating the effects of peak discharge on the nitrate dynamics. However, it cannot be used for exact measurements as it measures very low concentrations compared to IC. In winter, the TriOS probe shows a better representation of the nitrate dynamics, as the correlation was higher and the p-value of the differences between IC and the Probe measurements was higher than during summer.

It would be the best to sample every 10 minutes and analyse the samples with IC. This brings practical difficulties, as there are only 24 bottles in the automated sampler. Therefore, this resolution sampling could only be used during short summer events. The TriOS probe is then a way of estimating, as it cannot give exact answer. TN is a way of estimating the nitrate concentrations, as most of the TN is nitrate. Although we found that the diversity of N species in the Wüstebach increases during peak discharge,

which was also found by Gao et al., (2014). Therefore, TN is not a trustworthy analysis to detect nitrate. It can still be used in combination with IC to calculate $N-NO_3^-$ and calculate the concentration organic N.

6.5 Recommendations for further research

Further research could focus on improving the sampling strategy and chemical analysis. There are difficulties with automated sampling approach, in the past the threshold water level for sampling has been proven to be too high, as the concentration of N and S compounds were already diluted when sampling started. The threshold cannot not be lowered either, which might cause the automated sampler to start sampling too soon. However, the events in 2018 are well captured, as they cover both the rising limb as the falling limb, therefore the study could be expanded with this sampling strategy.

The results also depend on the sampling location or locations within the Wüstebach, as the concentrations of inorganic and organic S and N compounds differ spatially. For this study, the outlet of the catchment has been chosen, as it is representative for the whole catchment. Although for measuring ammonium export it might would have been interesting to measure around the places where ammonium is more common, such as WU1. For nitrate dynamics, groundwater processes and hydrological connectivity, WU12 could be studied. Sulphate dynamics could have been measured at WU17, where there is more influence from the vegetation and therefore more sulphate dynamics between winter and summer.

Further research could also work in the direction of the organic N and S, for example by applying the filtration cascade to all samples or working on the organic nitrogen detector and combining this with AF4 techniques that are available in the FZJ. At the time of this study, the organic nitrogen detector was still under construction, but it could be used in further studies. Nevertheless, the TN measurement and calculating the Organic N also gave a good indication of the chemical speciation of N.

The study could be expanded to gain more data about events, snowmelt, combined snowmelt and rainfall, winter rainfall and spring and summer rainfall, to fully examine transport of nutrients during high intensity precipitation events. In this study, the weather has been checked every week. During weeks with possible snowmelt or high intensity rainfall events the water level has been monitored so the automatic sampler programme can be adjusted to the water level. After the event, the discharge data was evaluated whether it was worth to collect the samples to analyse the transport of Nitrogen and Sulphur compounds in a small mountainous headwater catchment.

7. Conclusion

During the two events in 2018, nitrate concentrations differed significantly due to the high chloride level, caused by road salt that was leached to the stream. Out of all the methods that were used for analysing the nitrate concentrations, IC was found to be the most accurate method, as it showed the highest recovery of nitrate in the standards. The TriOS probe showed a more detailed overview of the N dynamics, but IC is still a preferred measurement because nitrate recovery is the highest and always showed higher concentrations. Sulphate concentrations measured by HPLC and IC did not differ significantly and can therefore be measured by both methods. However, IC is preferred to keep consistency in the measurement methods for the Tereno data on the online platform.

In the Wüstebach stream, the nitrate and sulphate export is groundwater driven, as the concentrations of these ions were the highest in the groundwater driven tributaries WU12 and WU17. The concentrations of nitrate and sulphate are likely to show a dilution effect during peak discharge and the concentrations will increase on the falling limb of the hydrograph. Nitrate and sulphate showed similar behaviour to the N and S that was smaller than 0.1 μm , therefore most of this size range will be nitrate and sulphate. Ammonium and organic N and S export is a surface water driven process, because the concentrations of ammonium and organic N were the highest in the groundwater driven tributaries WU1 and WU8. Ammonium comes from the histosol area around WU1, where the pH is low and anoxic conditions are present. During rainfall events, it will be exported quickly and the concentrations will show a maximum on the rising limb of the hydrograph. Organic N and S will have their maximum concentration after Ammonium, during the maximum discharge. Organic N and S are mostly occurring as particulates ($>1 \mu\text{m}$), as they showed similar behaviour during events. Colloids showed this behaviour as well and are likely to also be organic N and S, but concentrations of N and S in the size range of 0.1 μm to 1 μm was low.

WU14 has been proven as being a good point to measure nutrient exports as it is the catchment outlet and is surface water driven as well as ground water driven. During winter events, the surface water driven tributaries showed more influence from groundwater and the groundwater driven tributaries showed more influence from surface water.

The highest nutrient export takes place in winter during combined rainfall and snowmelt events, when they show the highest loads. Winter nutrient losses are higher than summer nutrient losses due to their long duration, hydrological connectivity, high discharge level, and the high concentration of sulphate and nitrate. In summer, nutrient losses are smaller, because nutrient concentrations are low due to the nutrient uptake in the growing season. In addition, losses are larger in summer when the stream is hydrologically connected to the hillslope or when it occurs preferential flow than when there is no

hydrological connectivity or preferential flow occurring. In the future, winter precipitation will increase as well as precipitation intensity, this can cause more export of nutrients in winter in the future. The increased nutrient export can have negative effects on the forest regeneration, since nutrients are needed for vegetation growth. Organic N and S can also be used as a nutrient, but concentrations are low at the beginning of spring. This should be kept in mind by creating forest management strategies of the Eifel National Park.

8. Acknowledgements

I would like to thank my supervisors Nina Gottselig and Roland Bol for helping with this project, always having ideas to improve the quality of my thesis, my fellow students and co-workers Johnny Vogel and Xinlei Guo for helping with the field work and sample preparation, Sophie Baartman for reading my draft, and the IBG-3 staff: Ferdi Engels, Stephan Köppchen, Martina Krause, Andrea Ecker and ZEA-3 staff: Volker Nischwitz, Daniela Gesekus for the sample collection and chemical analyses. This study was also sponsored by the Amsterdams Universiteits Fonds.

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Appendix A.

A.1 Differences between HPLC and IC

If only the event samples were considered, the concentrations were on average 0.12 mg L⁻¹ higher when they were measured with HPLC than when they were measured with IC (see Figure 49). However, this difference was not statistically significant at a 95 % confidence interval. There was also a strong correlation between the values of the IC and HPLC, as the R² value was 0.97. The concentrations of sulphate during events, measured with HPLC, were 0.16 mg L⁻¹ lower when they were measured with HPLC than when they were measured with IC (see Figure 50). This was not significant at a confidence interval of 95 %, neither for the events together or on their own. The correlation decreases, but is still very high, having an R² value of 0.96.

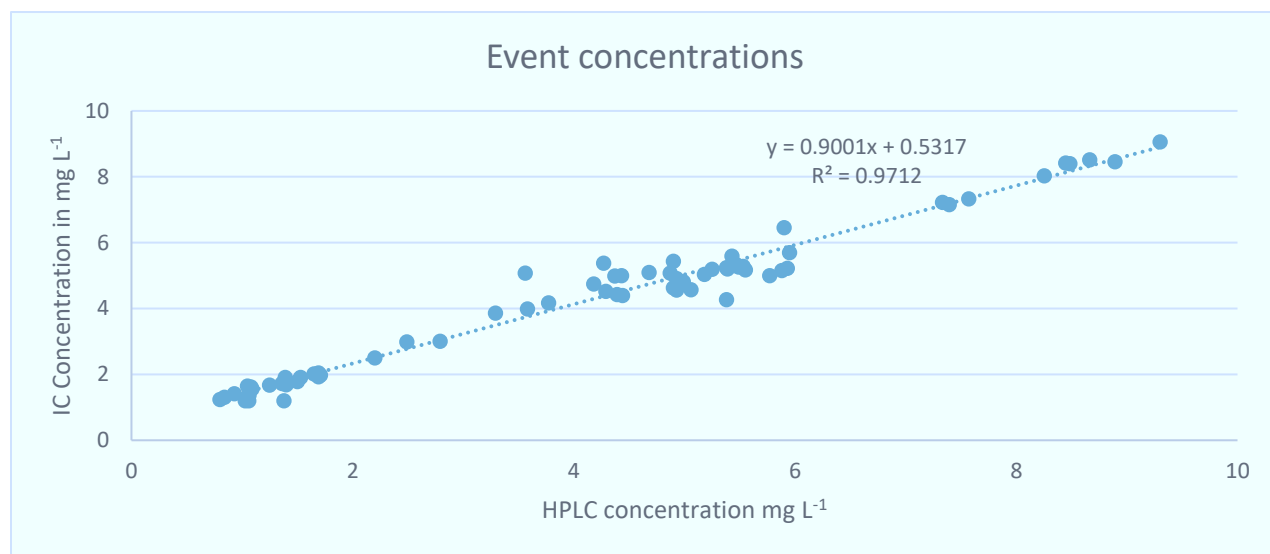


Figure 49. Only event concentrations compared for HPLC and IC

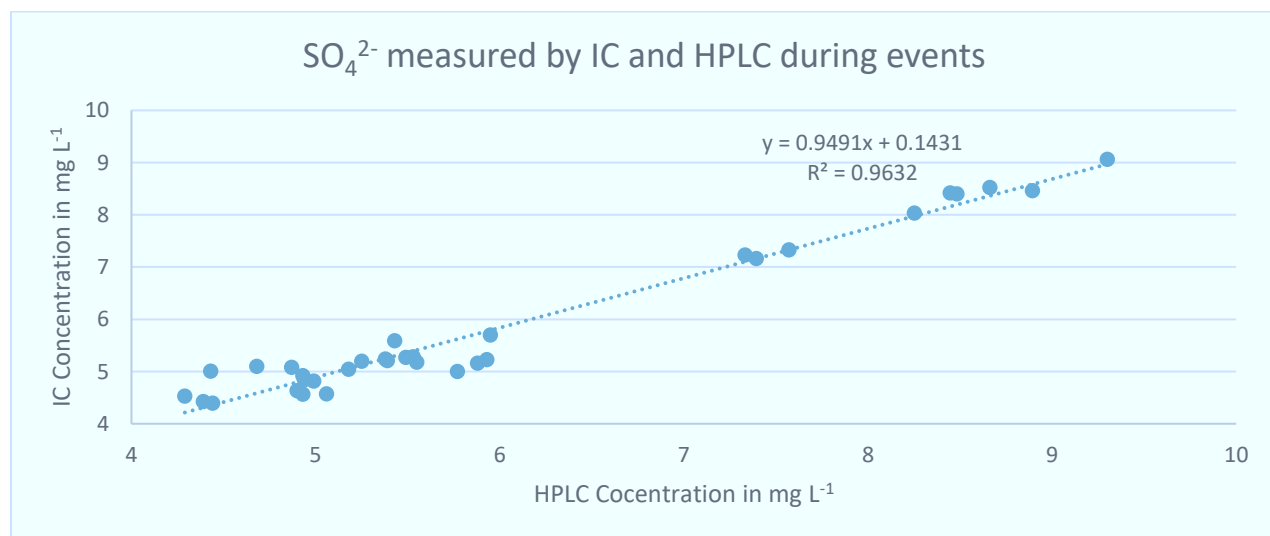


Figure 50. Comparison of the concentrations of SO₄²⁻ measured by IC and HPLC

A.2 Differences between high resolution sampling and continuous measuring

Figure 51 and 52 show the discharge plotted together with the nitrate loads, measured by automatic probes. The automatic probes measure nitrate based on optical properties, with UV detection. The nitrate loads increase together with the discharge and then stay high after the rainfall event.

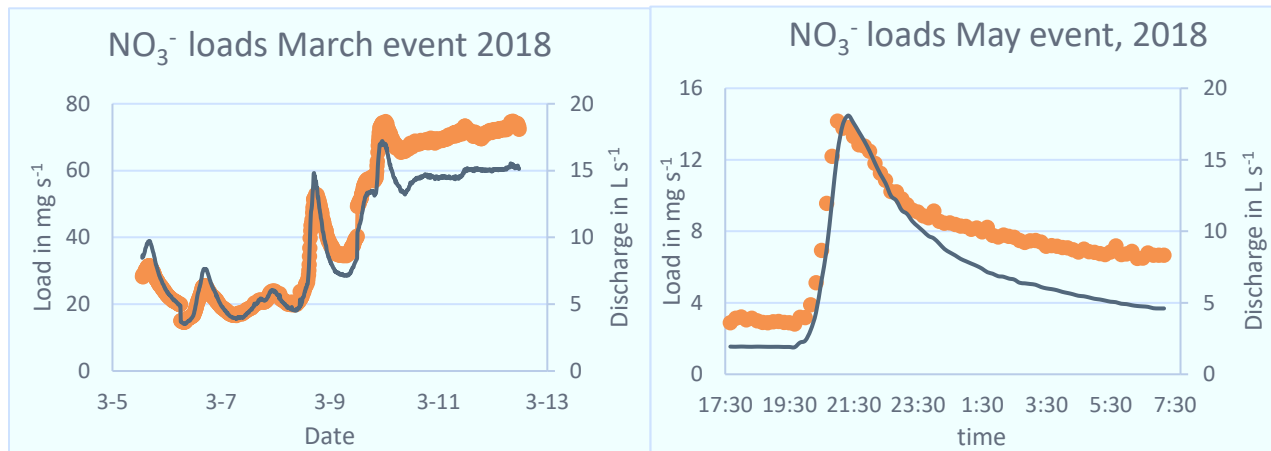


Figure 51. Nitrate loads measured by the TriOS probe during the snowmelt event of March 2018.

Figure 52. Nitrate loads measured by the TriOS probe during the event of May 2018.

● Nitrate load
— Discharge

On the next page the relationships between the three different measuring methods are shown.

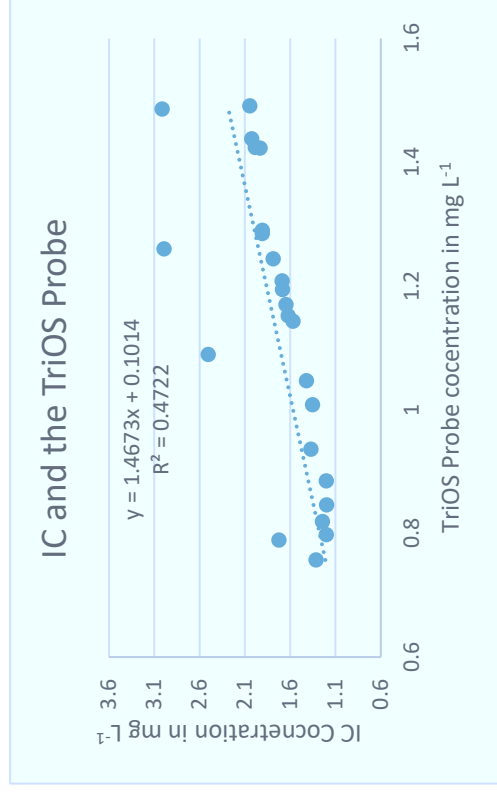
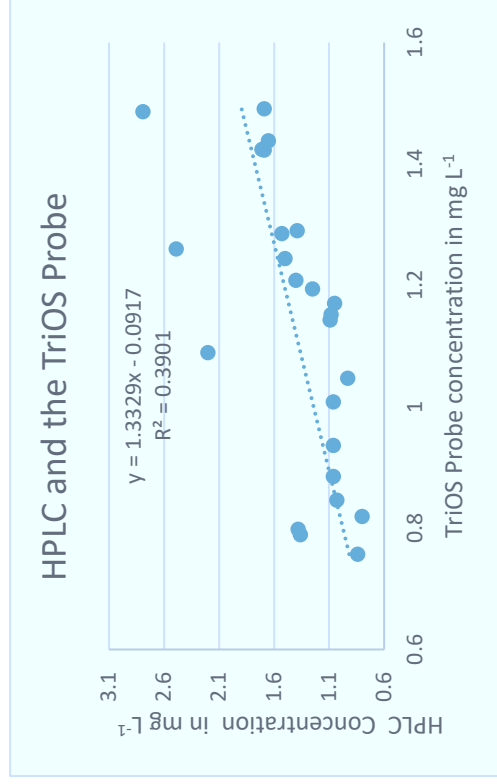
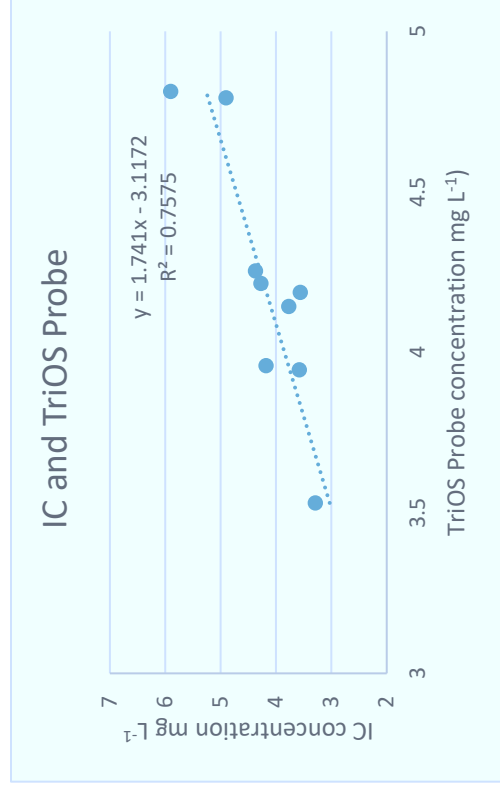
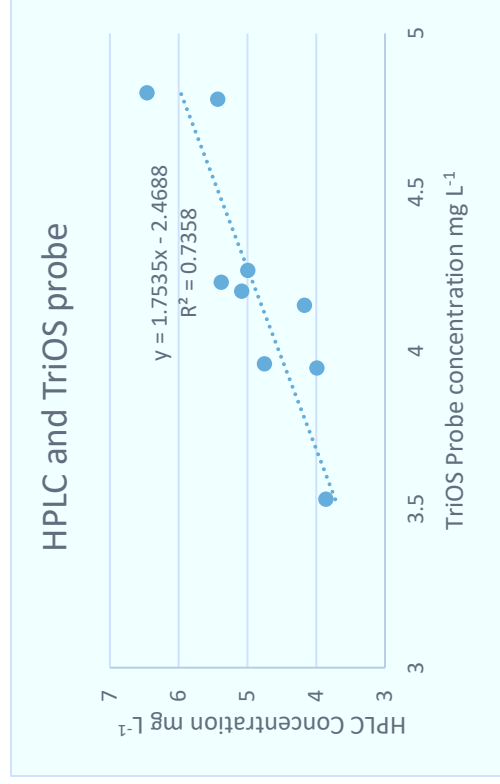


Figure 53. The relationship between the nitrate concentrations measured by HPLC and the TriOS probe during the March event in 2018.
 Figure 54. The relationship between the nitrate concentrations measured by IC and the TriOS probe during the March event in 2018.
 Figure 55. The relationship between the nitrate concentrations measured by HPLC and the TriOS probe during the May event in 2018.
 Figure 56. The relationship between the nitrate concentrations measured by IC and the TriOS probe during the May event in 2018.
 Figure numbering goes from left to right, from up till down

