

Master thesis

**Longitudinal effects of seep water on stream water discharge and chemistry
in a headwater catchment in Hubbard Brook Experimental Forest,
New Hampshire**



Suzanne Kok
Student number: 0448214
Faculty of Geosciences, Department Sustainable Development
University of Utrecht, The Netherlands, October 2013



Universiteit Utrecht

Supervisor Utrecht University: Dr. Karin T. Rebel



VirginiaTech
Invent the Future

Supervisor Virginia Tech: Dr. Kevin J. McGuire

Preface

This research was performed as part of the international research master program Sustainable Development (SD) at Utrecht University. Within the SD master the track 'Global change and ecosystems' addresses themes like the influence and response of land use, water and nutrient cycling, climate change, habitat fragmentation and species extinctions. These topics affect global changes and will need to be understood for sustainability in ecosystem services to humans. With this research I focus on the theme water and nutrient cycles in ecosystems and it concentrates on discharge and chemical composition of water in a headwater catchment. I find it important to gain knowledge on these hydrological and biogeochemical processes, and to understand what influence global changes have on water quality and biodiversity.

The aim of this research is to determine the influence of seep water on stream water. This research was conducted in the Hubbard Brook Experimental Forest in New Hampshire, in collaboration with Virginia Tech in Blacksburg, Virginia, USA. The research included several months of fieldwork conducted in early spring with the sampling of water during snowmelt, and a summer fieldwork with water sampling and discharge measurements. I learned a lot on all aspects of doing research, discovering another country and writing this thesis.

For all this I want to thank my supervisors Dr. Karin Rebel and Dr. Kevin McGuire for their support, patience, empathy and the feedback in this last part of my master program. I also want to thank the second reader Dr. Paul Schot for his time and flexibility. Many thanks to JP Gannon, Ph.D. student at Virginia Tech, who was stuck with me for the whole period of 5 months that I spend in the USA. Also, I want to thank Dr. Janaki Alavalapati for his hospitality and making me a part of the department of Forest Resources and Environmental Conservation at Virginia Tech, and also many thanks to all the hard-working people at the Forest Service Station at Hubbard Brook for the opportunity for me to perform this research in their catchment and the many interesting and educational field trips. And thanks to many others who were there for me in any kind of way.

Suzanne Kok
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Spring and summer fieldwork at Hubbard Brook Experimental Forest, NH, USA.

Summary

This research was conducted in the Hubbard Brook Experimental Forest in New Hampshire, USA, and focuses on water chemistry and discharge of stream water. The aim of this research is to find out if there is an effect of seep water on stream water. A seep is a groundwater upwelling area that is perennial wet. Seep water has a distinct chemical composition that leads to typical vegetation in that specific area. This research uses two methods to look at the influence of seep water on stream water. One method is the tracer injection method to measure discharge. With this method sodiumchloride (NaCl) was injected into the stream with a near-instantaneous 'slug' and the electrical conductivity (EC) was measured downstream of this injection point. To see if the stream had a gain or loss of water the EC was measured at several reaches whereby the change in discharge (ΔQ) could be calculated. The discharge results did not show a significant change that could be caused by the input of seep water. The second method in this research consisted of collecting water samples in spring and summer to see if the distinct chemistry of seep water had an influence on the water chemistry of a stream. Supplementary data from Zimmer et al. (2012) was used to show changes in chemistry over time and making this research complete. Also the chemical composition of stream water was not significantly influenced by the chemistry of seep water indicating that there is no connection.

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1. Introduction

1.1 Background

Investigating the effect of global changes on ecosystems is important, especially at high latitudes where headwater catchments play a significant part in the hydrological and biogeochemical cycle (Murdoch et al., 1998). Hydrological and biogeochemical processes in these headwater catchments control the recharge, discharge and transient storage of stream water to the hyporheic zone and therefore affect the chemical form, timing and longitudinal distances of solute transport to downstream water systems (Alexander et al., 2007; Wolock et al., 1997). Understanding how these catchments function is important for improving the protection of downstream water bodies that provide vital resources for people and ecosystems around the world (Alexander et al., 2007; Gomi et al., 2002; Likens et al., 1977).

A lot of research has already been performed in the hydrological and biogeochemical field, but there are still many uncertainties. With the increase in more intense rainfall events as a consequence of global changes (Knapp et al., 2008), it is of great importance to gain knowledge on how headwater catchments function and how they influence downstream water quality (Alexander et al., 2007). In headwater catchments there are different water sources that provide input to the streams. These different sources originate in different areas and flow through different soils in different periods of time. This water has therefore specific characteristics for example in chemical composition. The input of water from a source with high concentrated water can affect stream water significantly. It is therefore important to perform research on these water sources and see how they might influence stream water.

1.1.1 Water flow in the environment near a stream

Natural water flow in streams can be described along three axis. A first axis considers longitudinal flow; where water, and dissolved particulate matter, move from upstream in a downstream direction. Second, there are lateral flow connections between a stream to the riparian zone. And last, a vertical axis is described by surface water which is connected with the hyporheic zone and groundwater (Lake, 2003) (figure 1).

The riparian zone is described by the interface between the upland area and the stream (Naiman et al., 2005; Vidon et al., 2010). The hyporheic zone refers to the shallow subsurface area beneath and adjacent to the stream. In this zone the subsurface water is a mixture of at least 10% stream water, and 90% groundwater (Triska et al., 1989; Wondzell and Swanson, 1996). It is argued that the spatial configuration of the hyporheic zone changes depending on flow conditions. Several studies show that the zone shrinks with an increase in groundwater and discharge to the stream during high flow conditions, hence with low flow conditions and decreasing stream discharge the zone broadens (Boulton et al., 1998; Legrand-Marcq and Laudelout, 1985; Wondzell et al., 2006). However, other studies demonstrate that extension of the hyporheic zone is not strongly related to base flow conditions (Ward et al., 2012), or that the zone does not change in size at all, and being independent of discharge (Hart et al., 1999).

Water exchanges between the stream channel and the hyporheic zone are induced by the structure of the stream and valley (Payn et al., 2009). This exchange of water between these components is called hyporheic exchange flow and causes apparent loss/gain of water from the stream channel that returns as a gain/loss downstream (Bencala et al., 2011; Mulholland and Webster, 2010; Payn et al., 2009). Hyporheic flowpaths vary longitudinally, laterally and vertically in path length and flow rate which affects residence times, and therefore multiscaled exchanges with surface water occurs (Cardenas, 2008; Covino and McGlynn, 2007; Payn et al., 2009; Ruehl et al., 2006; Wondzell et al., 2006). On small scales the hyporheic exchange between the stream and subsurface is called the transient storage (Bencala et al., 2011). Exchange flows, as well as transient storage, increases with increasing discharge (Hart et al., 1999; Wondzell et al., 2011).

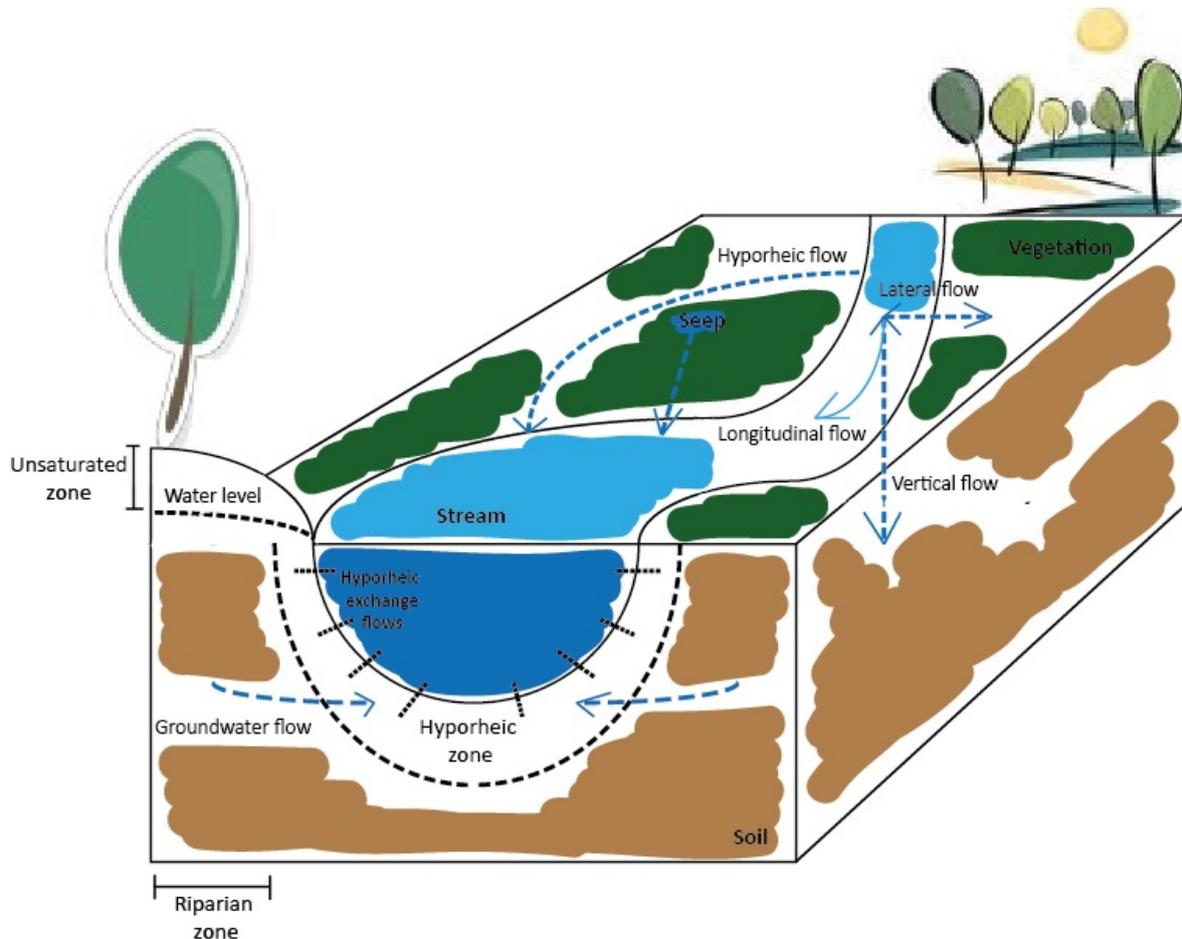


Figure 1. Schematic view of a stream and the location of its hyporheic zone, riparian zone and unsaturated zone with the different flowpaths. The three axis of stream water flow are shown (longitudinal, vertical and lateral). Hyporheic exchange flows between the stream and the hyporheic zone are visible, as well as groundwater flow from the soil through the hyporheic zone to the stream. Also a seep with its subsurface, or surface, flowpath downstream is shown. This figure is not to scale.

Stream channel flow can increase along a certain reach (gross gain), it can decrease (gross loss) or retention of water may take place (transient storage). The net change in water is explained by the difference in gross gains and gross losses of channel flow along a stream reach. The channel water balance is defined by the net gain or net loss of water in the stream channel, or the difference between downstream and upstream stream channel flow (Payn et al., 2009). The channel water balance is important for identifying stream discharge and fine scale chemical variations (Payn et al., 2009). Discharge regulates many aspects of stream functioning, for example, rates of nutrient export and habitat diversity (Moore, 2004; Ward et al., 2004). It is therefore an important variable for streams. The area of land that drains to a specific location in the landscape, for example in the stream channel, is the upslope accumulated area (UAA) or local contributing area (Jencso et al., 2009; Seibert and McGlynn, 2007). UAA is a topographic index and a proxy for local water flow. Surface topography is assumed to be in control of the direction of flow (Seibert and McGlynn, 2007).

Stream discharge changes temporally over a range of flow conditions (Gomi et al., 2002; Wolock et al., 1997), for instance due to riparian characteristics such as vegetation and soils (Dodds and Oakes, 2008). Low flow conditions possibly influence the broadness of the hyporheic zone, and the hyporheic flow declines (Dahm et al., 2003; Lake, 2003). Longitudinal disconnection of streams due to drought causes a disruption in water flow within a stream channel, but also between the stream and the subsurface flows (Lake, 2003). The disruption in connectivity of exchange flows can occur along the three axis described above. As surface flow ceases, fine sediments, detritus and nutrients are no longer transported and stay in so-called pools (the latter is further explained in

paragraph 1.1.2). Hyporheic exchange flow however still may occur (Lake, 2003; Stanley et al., 1997). When a drought period continues a stream can dry up what causes complete disconnection with the subsurface. The changes that occur in spatial configuration of the hyporheic zone due to this disconnection of water flow influences the biogeochemical processes in that zone (Dent et al., 2001; Lake, 2003). In contrast to low flow conditions, for example, during summer periods, snowmelt increases stream discharge and therefore exchange flows with the subsurface (Kuhn, 2001).

1.1.2 Water chemistry

The hydrological processes are coupled with biogeochemical processes. The apparent loss of stream water upstream could return from the hyporheic zone as a gain downstream. Within the hyporheic zone the stream water may undergo reactions that could possibly change the biogeochemical composition of the water (Bencala et al., 2011; Mulholland and Webster, 2010). In this zone, different water sources provide a complex flow network where stream water is affected by biogeochemical processes (Wondzell and Swanson, 1996).

Several studies explained temporal variations in stream water chemistry by the division in 'old' or pre event water as water stored in a catchment before an event, and 'new' or event water as water entering by precipitation or melt water (Hooper and Shoemaker, 1986; Zimmer et al., 2012). Hooper and Shoemaker (1986) state that chemistry of the groundwater is primarily determined by its residence time within the soil. Event water or water with a short residence time is more acidic and has a relatively high aluminum concentration. This is because of acid rain or snow that is stored seasonally and releases high concentrations of nutrients and acids in relatively short peaks to the stream with the first snowmelt (Kuhn, 2001; Meyer et al., 2009; Wellington and Driscoll, 2004). A longer residence time will be defined by water with a relatively high pH and low aluminum concentrations, because of the neutralization process with base cations like sodium and calcium. However, research also noted that high concentrations of silica are an indicator of deep water contributions because it is correlated to weathering rates that indicate a long residence time. Therefore, silicon can also be used as a tracer to separate new and old water contributions to different portions of the stream network (Hooper and Shoemaker, 1986; Zimmer et al., 2012).

Soils play an important role in water chemistry, because interactions of groundwater and soils are controlling chemical transformations in stream water (Zimmer et al., 2012). The presence of groundwater in different soil types can explain the variation in solute composition seen across a catchment (Zimmer et al., 2012). It was hypothesized by Lawrence and Driscoll (1990) that during low flow conditions the groundwater flow to the stream is 'old' water and is enriched with silicon and sodium concentrations, while these dilute during high flow conditions and neutralize the input of event water to the stream (Lawrence and Driscoll, 1990). Recent research in the Hubbard Brook Experimental Forest focusses on the field of hydrogeology where they investigate how different soil types are of influence on water flowpaths to the stream by determining, amongst others, the chemistry of soil water (McGuire et al., ongoing research).

Hot spots are isolated zones that show relatively high biogeochemical reaction rates in comparison to the surrounding oxic area due to spatially restricted anoxic conditions. Denitrification takes place in these hot spots that are found at anoxic-oxic interfaces, that often occur at the boundary between two features in a landscape for example at the upland to stream interfaces (McClain et al., 2003). The hyporheic zone is also an ideal site for the convergence of chemically distinct flowpaths and the development of hot spots (McClain et al., 2003). Burt and Pinay (2005) state that hot spots can affect the quality of stream water significantly.

Seeps represent natural groundwater discharge points located outside the stream channel (O'Driscoll and DeWalle, 2010; Zimmer et al., 2012). They act as local perennial biogeochemical hot spots where shallow anoxic groundwater with a relatively high concentration of DOC, CH_4 and NH_4^+ merges with upwelling groundwater that carries NO_3^- and N_2O . A hot spot along Smith Creek in Michigan was studied by Hedin et al. (1998) and shows signs of a zone with high denitrification (McClain et al., 2003). These zones could influence the chemical signature of stream water significantly (McClain et al., 2003; Zimmer et al., 2012). Seeps can be connected to streams through

the hyporheic zone by subsurface flows, or surface flows, depending on the flow conditions (Gold et al., 2001; O'Driscoll and DeWalle, 2010). A higher input of event water by rainfall or snowmelt could induce surface flow from a seep to a stream, whereas low flow conditions are dominated by subsurface flows (O'Driscoll and DeWalle, 2010).

The Hubbard Brook Experimental Forest (HBEF) is an area where a lot of research has been conducted, for example the variation in biogeochemical processes within the valley have been well-studied by Johnson et al. (2000). Whereas Likens and Buso (2006) surveyed stream chemistry across the entire valley. Groffman et al. (2009) found that the most important substrate variation within the HBEF landscape is depth to bedrock. This depth depends on the variation in accumulation of glacial till or other glacial features. Zimmer et al. (2012) concluded that water flowing through deeper flowpaths in deep glacial till or fractured bedrock may influence the chemistry in stream water by perennial seeps within the catchment that act as local hot spots.

Several seeps have been discovered in one of the watersheds (WS3) located in HBEF. Zimmer et al. (2012) confirmed with observations of flow direction in the field that the perceived input of water to a seep located near a stream was coming from upslope and not from riparian exchange flows from that near-by stream. Several studies at the Baldwin Creek watershed in Pennsylvania (USA) and Hubbard Brook suggest that the occurrence of seeps may coincide with the presence of bedrock fracture zones and flowpaths through deep glacial till (respectively, O'Driscoll and DeWalle, 2010; Zimmer et al., 2012). The latter however has not been confirmed. One possible verification is that seep water in watershed 3 had a two to five times higher pH, Na, Si and Ca and a relative low Al in comparison with stream water samples which suggests water from deeper flowpaths (Zimmer et al., 2012). Research by Likens and Buso (2006) shows higher concentrations of NO_3^- in these groundwater upwelling areas compared to stream water concentrations. These relative high concentrations indicate a contribution from weathered minerals and long residence times in the soils, therefore suggesting that seeps are upwelling zones of deeper groundwater (Zimmer et al., 2012). This research is based on the existing uncertainty of possible influence of seeps on stream water in the Hubbard Brook Experimental Forest.

1.2 Problem definition and aims

The overall aim of this research is to determine if seep water has an influence on stream water discharge and chemistry in a headwater catchment and if its influence varies over time. This is important because downstream water quality and ecosystems are affected by the stream water input from upstream watersheds.

We can separate this aim into two parts. First, we will look at seeps, that have a possible connections of water flow with a near-by stream, have an influence on its water discharge. Second, we will determine the effect of seep water chemistry on stream water chemistry.

Overall, this research contributes to ongoing spatial and temporal research in HBEF to describe the complex interactions of multiple systems in catchments and help better understand how headwater regions influence downstream hydroecological processes and water quality (Alexander et al., 2007; Bishop et al., 2008; Temnerud et al., 2010).

1.3 Research questions and hypotheses

The following research questions and hypotheses were formulated on the basis of the problem definition and the aims outlined above. The main research question is:
What is the effect of seep water on stream water discharge and chemistry in a headwater catchment over space and time?

Hypothesis: Depending on the season and the intensity of events (rain and/or snowmelt) that occur, the stream water quantity and chemistry will be influenced by seeps. The temporal component will have a significant influence on both discharge and chemistry due to different flow

conditions. The chemical composition of seep water will influence stream water chemistry by surface (high flow conditions) and subsurface flows (low flow conditions). The spatial component is of significance, because the location with reference to the seeps will be of importance for the extent in which these affect the stream.

The following sub-questions are addressed to answer the main research question.

- 1) Is there a measurable effect of seep water on stream water discharge in summer?

H1: The presence or absence of rain events will determine the influence of seep water on stream water discharge. With the absence of rainfall, seep water will not have a surface or subsurface flow to the stream and therefore will not have an influence on stream water discharge. While at high flow conditions caused by rain events, there is subsurface, or surface flow from the seeps to the stream therefore inducing the influence of seep water on stream water discharge.

- 2) What is the chemical composition of seep water during snowmelt?

H2: Seep water has a distinct chemical composition in comparison with stream water with relatively high concentrations of nutrients. The input of water by snowmelt will change the chemical composition of the seep water, due to the relatively high concentrated first input of water from snowmelt. If snowmelt progresses, the seep water will eventually be diluted, because the first meltwater input has the highest concentration in nutrients, which decreases over time.

- 3) What is the effect of the chemical input from seep water on the chemical composition of stream water during a snowmelt period?

H3: There will be a significant effect on stream water chemistry by seep water during a snowmelt event. However, there is also the first input flux of water from snowmelt directly to the stream what will also influence the chemistry of the stream water. The input of seep water to the stream will be detected downstream of the seep, because of its surface or subsurface flowpaths that are also depending on the input of event water by snowmelt.

- 4) Is there a measurable influence of seep water chemistry on stream water chemistry longitudinally?

H4: The chemical composition of seep water will have a measurable influence on the chemistry of the stream water and will show an increase in pH, Ca, Si and Na, and a decrease in Al, NO₃ and DOC in the stream reaches close to, and below, the seeps.

- 5) Is there a measurable effect of seep water on stream water chemistry temporally?

H5: There will be a difference in influence of seep water on stream water for different seasons. Seep water flows to the stream during a snowmelt event will have a significant effect on stream water chemistry, as well as rain events causing subsurface or surface flows from seeps to the stream. In between events however, the influence of seep water will be less significant because of the disconnection of flowpaths from the seeps to the stream.

H6: There will also be changes in the influence of seep water on stream water chemistry over longer periods in time. Due to the increase in rain events caused by global changes the water

flow from seeps to the stream will increase and therefore there will be an increasing effect of seep water chemistry on stream water chemistry.

1.4 Social and scientific relevance

This study adds to the research conducted in headwater catchments by focussing on seep water that might influence stream water discharge and chemistry. This research contributes to a better quantification of different sources of water to a first-order stream and the effect of upstream water of a headwater catchment influencing downstream water bodies (Alexander et al., 2007). For a more complete picture of the first order controls of runoff generation and stream water chemistry also the effect of event water, including a snowmelt event, will be taken into account.

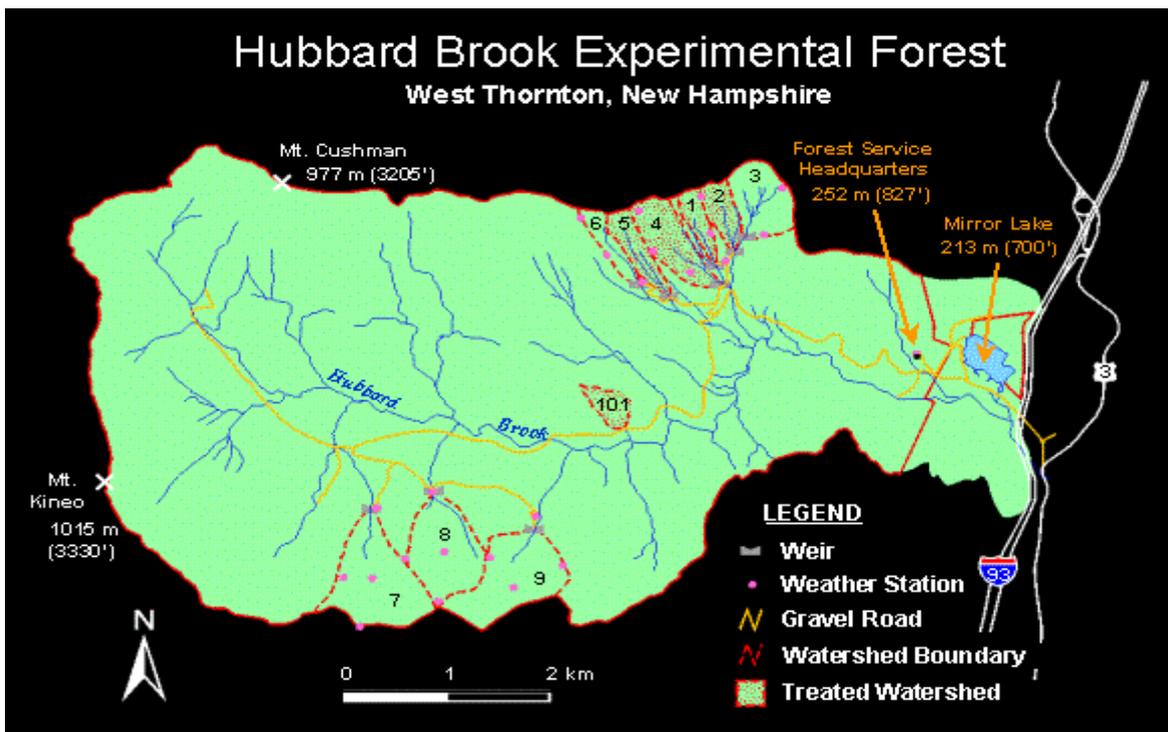


Figure 2. A map of the whole Hubbard Brook Experimental Forest (3.160 ha) in New Hampshire, USA. This figure includes the main stream Hubbard Brook and all experimental watersheds including watershed 3 (42,4 ha) in the northeast of the valley that was used for this research.

2. Material and methods

2.1 Site description

This research was conducted in the Hubbard Brook Experimental Forest (HBEF) which is a valley of 3160 ha in the White Mountain National Forest, New Hampshire, USA (43° 56' N, 71° 45' W) (figure 2). It was established in 1955 for the study of hydrology in forests (Soil Survey Staff, 2006). HBEF is a location for climate gradient studies because of long term ecological research (LTER) with significant variation in climate and relatively little variation in vegetation and soils with elevation (more in-depth described in the following paragraphs) (Campbell et al., 2007; Schwarz et al., 2003). The valley consists of several watersheds (figure 2) that fulfill different purposes for a series of paired watershed studies. For example, this research focusses on watershed 3 (WS3) that is used as a hydrologic reference watershed (Detty and McGuire, 2010a; 2010b; Zimmer et al., 2012).

Watershed 3 is a 42,4 ha southwest-facing catchment that consists of the headwaters of Paradise Brook (figure 3), which is a first-order stream within WS3 and a second-order tributary of Hubbard Brook (Zimmer et al., 2012). The watershed has an elevation range of 527-732 m, and is

entirely forested with second-growth even-aged stands of typical northern hardwood species (Detty and McGuire, 2010a; 2010b).

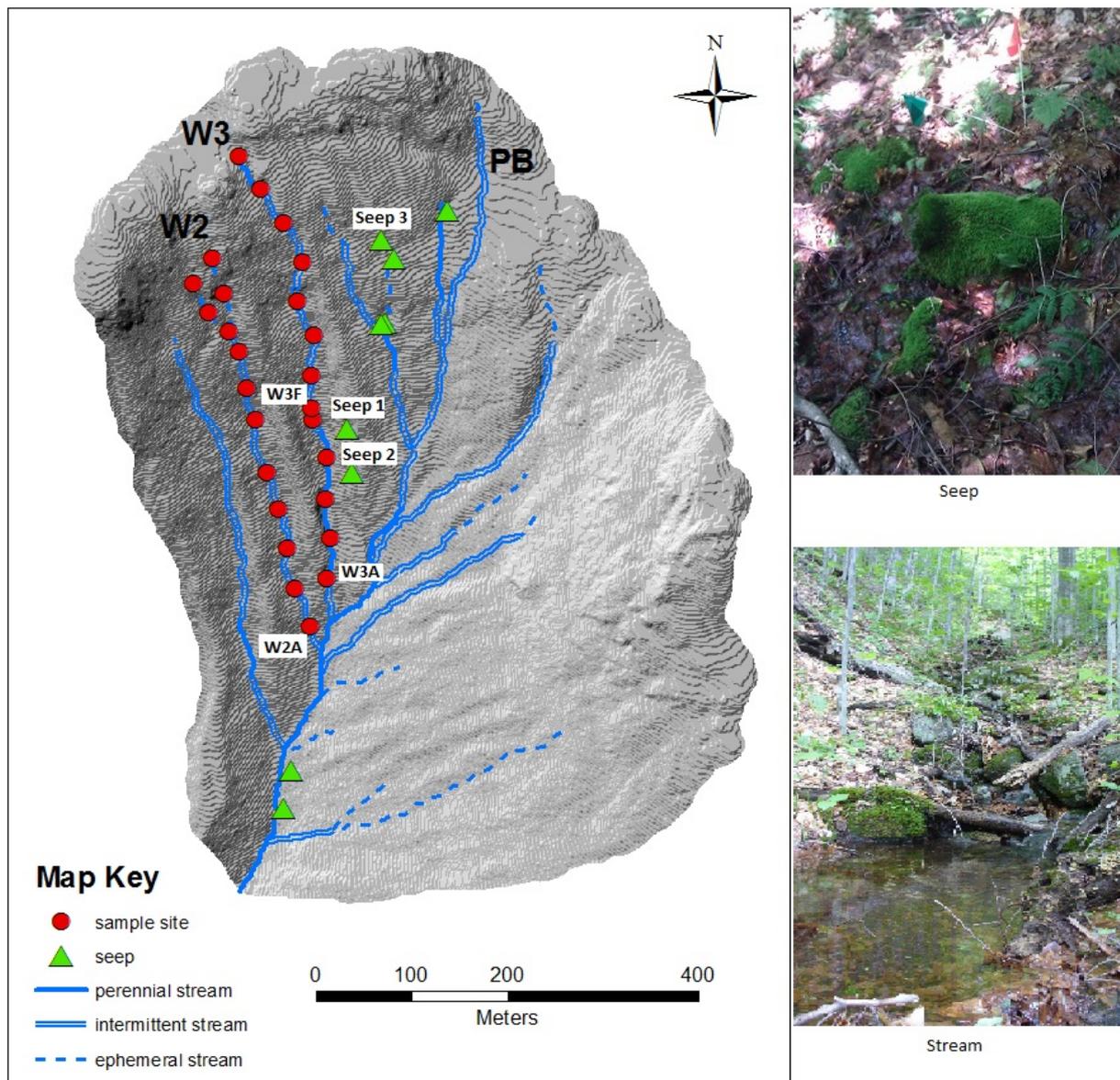


Figure 3. Map of the research area, watershed 3, with the main Paradise Brook (PB). The two sampled tributaries W2 and W3 are given with the specific sample sites W3A and W3F highlighted. Also the seeps 1, 2 and 3 that were sampled are shown. Note that seep 1 and seep 2 are located along tributary W3, whereas seep 3 is situated further north in the watershed.

2.1.1 Geology, geomorphology and soils

The soils in watershed 3 have been studied very well by the ongoing research in the relatively new field of hypopedology. This field aims on making predictions about the specific soils that could be correlated with specific hydrological processes in a watershed. The base of watershed 3 consists of a pelitic schist from the upper and lower Rangeley Formation. On top of this base, a sequence of Pleistocene glaciations, with the latest Wisconsinan glacial period, deposited layers of basal and ablation tills of varying thickness (Johnson et al., 2000). The soils mainly consist of Spodosols that have well-developed horizons, a typical eluviated layer and a predominant B horizon with sesquioxide coatings. The rest of the soils are Inceptisols with no, or poorly developed, spodic horizons. Soils in watershed 3 have a thick organic horizon (O/A) on top of a mineral horizon derived

from basal till parent material with a large proportion of boulders and rock fragments found at all depths in the soil profile. A large part of the soils have a very tight densipan C horizon (Cd) found at about 70 cm, which is composed of compacted silt loam tills (Detty and McGuire, 2010a; 2010b).

2.1.2 Climate

The climate at HBEF is humid continental with average temperatures of -9 °C in January and 18 °C in July. Precipitation is monitored by several stations spread over the whole Hubbard Brook Valley. The distribution of precipitation is uniformly spread throughout the year with an average of approximately 1400 mm, of which 30% falls as snow. Nearly half of the annual runoff of 870 mm occurs during the spring snowmelt period in the months March, April and May (Bailey et al., 2003; Johnson et al., 2000). The first part of this research started at the beginning of the spring snowmelt period in March 2013. The latter part of this study was conducted during the months June and July in the year 2013.

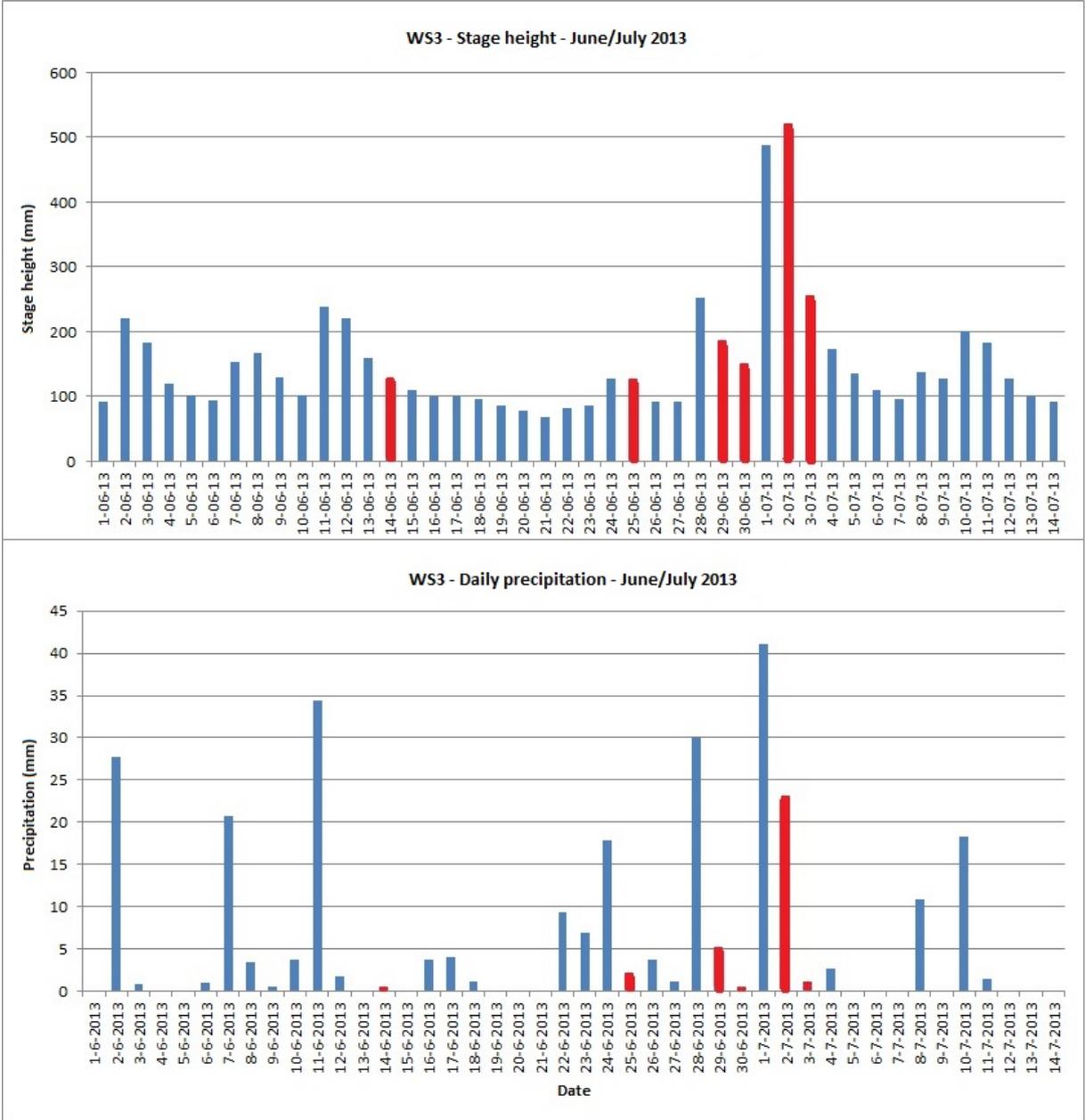


Figure 4. Measured stage height at the weir at the outlet of watershed 3 for the summer sample months June and July, 2013. This graph shows the fluctuations in stage height over time after a precipitation event. The sample dates for this research are marked with red: 14-06, 25-06, 29-06, 30-06, 02-07, 03-07.

2.1.3 Hydrology

Hydrology is the primary research area in Hubbard Brook. Watershed 3 is the hydrologic reference watershed and represents typical northeastern headwater catchments. A permanent weir installed at the base of this watershed records the stage height over time at the outlet (figure 4). A network of multiple shallow to deeper wells monitor the water level throughout the catchment. The annual water balance in this watershed based on long-term (1958-2000) measurements of streamflow, evapotranspiration and precipitation is: Precipitation (1326 mm) = Streamflow (833 mm) + Evapotranspiration (493 mm). This means that 63% of the precipitation that enters the watershed goes out as streamflow while the rest is returned to the atmosphere by evapotranspiration. Bedrock has been assumed to be water tight, therefore neglecting seepage through bedrock fractures, or laterally through the soil to adjacent watersheds (Bailey et al., 2003). More recent research at HBEF however, questions if these bedrock fractures should be neglected or that they might play an important role in subsurface flowpaths, and seeps in this watershed.

2.2 Sample sites and periods of sampling

2.2.1 Spring field measurements

The spring fieldwork was part of ongoing research done by Ph.D. student JP Gannon in the field of hydrogeology whereby soil development is linked with hydrological processes and used for predictions in chemistry of stream water. The fieldwork related to this research consisted of taking water samples from a network of several groundwater wells, stream water, seep water and soil water for the chemical composition. The soil water was collected with Prenart Super Quartz lysimeters that were installed to collect soil water at different depths. Next to these water samples, data from 10 minute dataloggers, that were connected to tensiometers measuring soil water tension (UMS T4 tensiometers) and soil moisture sensors (Decagon EC-5 capacitance moisture sensors), were gathered. These data were taken at eight sites with a combination of a groundwater well and one, two or three lysimeters. Three sites were monitored intensively and consisted of several groundwater wells at different depths, lysimeters and dataloggers for soil water tension and soil moisture.

The spring fieldwork took place in the months March and April of the year 2013. The start date coincided with the first signs of snowmelt in the period of March 10th to the 13th. This snowmelt however turned into a rain-on-snow event and stopped after 2 days thereby not all snow had melted. A second snowmelt event started around the 27th of March and continued through the month April making it a slow melting period.

This thesis uses a small amount of the data that was collected, mainly due to time constraint of analyzing the data in the laboratory. We used the data of two sample sites in one tributary (W3) of the Paradise Brook. W3 is located on the west-facing slope of the watershed. W3A and W3F were the only two sites sampled during this fieldwork and have a different elevation of respectively 580,2 m and 628,1 m. One seep (seep 3) was also sampled during this snowmelt period that is located northwest of W3 (figure 3). Seep 3 has no direct connection with W3, but it was the only seep that was sampled during the spring fieldwork.

2.2.2 Summer field measurements

The summer fieldwork started on the 14th of June and several measurements were done at the end of the month and the beginning of July. Discharge measurements were done on the following dates subdividing them by the two tributaries as follows: measurements in W3 were done on June 14, 25, 29 and July 3, whereas measurements in W2 were performed on the 30th of June and the 2nd of July, 2013. Water samples for chemical analyses were taken for both tributaries and both seeps on the same days that is to say on the 14th and the 29th of June, and the 2nd of July, 2013.

During the summer fieldwork we studied both tributary W3 as well as tributary W2. Both are tributaries of Paradise Brook, on the west-facing slope of the watershed. W2 and W3 are parallel to each other (figure 3) and the flow conditions are mostly influenced by events, making them zero-order ephemeral and intermittent streams in the headwater catchment (Zimmer et al., 2012). It was assumed that both tributaries have similar flow conditions. Along each tributary several sample locations were identified by former studies (e.g. Zimmer et al., 2012). Both tributaries have 13 sample sites that are 50 meters apart and go from about 50 meters from the intersection with Paradise Brook upstream to the origin of the tributary. The sample sites are named after the tributary followed by A to M in the case for W3, for W2 the sites are numbered A to I, but the tributary splits in two streams that are named 1A and 1B, and 2A and 2B. The two tributaries were chosen based on the location of identified seeps in its subcatchment. W3 is located along two visible seeps, seep 1 and seep 2, whereas W2 has no visible or identified seeps. The flowpath of both seeps is from its origin to lower elevations by subsurface or surface flows. This means that it is likely that if seep water has a significant influence on stream water this will be observed downstream from the elevation of the seeps. The elevations of seep 1 and seep 2 are respectively 628,9 m and 617,4 m (Appendix 1).

One set of water samples from the 2nd of July, 2013, was selected for chemical analysis. This date was based on having a useable set of discharge measurements gathered in the same time period, and to have comparable field conditions like stage height and amount of precipitation. The discharge datasets of the 29th of June and the 3rd of July for W3 and the 2nd of July for W2 had sufficient water flow for the analysis.

2.2.3 Supplementary data

The earlier mentioned limitations in time and staff to perform all chemical analyses caused the use of supplementary data from the research done by Zimmer et al. (2012). A selection of this data, based on the three most complete datasets, was used to support the temporal results and give data of the cations that were not obtained from the analyzed dataset from the 2nd of July, 2013. The dates of sampling by Zimmer et al. (2012) were the 10th of July 2009, April 1st 2010 and the 1st of October, 2010.

The research locations of Zimmer et al. (2012) were used for this research. This includes W2 and W3 and the seeps 1 and 2. Due to laboratory constraints, not all data were analyzed by the deadline of this thesis. Especially the cations were not analyzed yet. Therefore we used the data by Zimmer et al. (2012) to substitute for this lack of data. To be able to compare the datasets that were taken in this study (2013), and by Zimmer et al. (2012), we analyzed the anions of both studies and looked for differences. Next, the cations of Zimmer et al. (2012) were used to substitute for the lack of cations in this study.

2.3 Field measurements

2.3.1 Discharge

To determine the input effect of water from seep zones, the stream water discharge was measured. Discharge can be defined as the amount of water passing through a certain cross-sectional area with a certain velocity. This is shown by the formula below also known as the continuity equation where A is the cross-sectional area (m²), V is the average flow velocity (m/s) and Q is the discharge (m³/s):

$$Q = A * V \quad [1]$$

Discharge can be measured in several ways for example with the tracer injection procedure or a cross-section area procedure. This latter method however is not suitable for the more shallow streams, because of the difficulty to measure the cross-sectional area in a shallow stream and the

relatively low stream discharge. Therefore, this study used the tracer injection method to study the occurrence of stream water gain and loss from and to the hyporheic zone (Wondzell and Swanson, 1996). This tracer method is explained in the next paragraph.

2.3.2 Tracer injection method

Tracer injection methods are based on measuring a rise in electrical conductivity (EC ($\mu\text{S cm}^{-1}$)), which is the ease with which an electrical current can travel through water, in a stream over an elapsed time. For this thesis, two methods have been studied: 1) injection to the stream at a constant rate as described by the study of e.g. Wondzell (2006), 2) injection of the tracer as a near-instantaneous 'slug' as described by e.g. Payn et al. (2009). Both methods have advantages and disadvantages whereas the most important advantage of a slug injection is that you do not need special equipment for the constant-rate injection. However, discharge measurements done by a constant-rate injection are less affected by pools and the stream bed morphology, which is an important disadvantage for the slug injection method (Day, 1977). However, for this research the second method was chosen, because the slug injection is easier to execute in the field, and no special equipment is needed. Besides the two injection methods there are also several tracers that can be used for dilution gauging. Sodium chloride (NaCl) is the most ideal tracer, because it is inexpensive, easy to obtain, accurate to measure in the field and most important NaCl is not harmful to the environment in the used concentrations and exposure times that are typical for discharge measurements (Day, 1977; Payn et al., 2009).

In this study, in-channel electrical conductivity was recorded by using two temperature-conductivity probes and the software of In-Situ Inc. Aqua TROLL 100. The electrical conductivity is expressed in specific conductivity (SC) calculated from the actual conductivity and a standard reference temperature of 25 °C. For the greatest accuracy of the measurements a calibration has been performed before the slug injection of the tracer, to determine the calibration constant (k) that depends primarily on the salt concentration in the injection solution and secondarily on the chemical characteristics of the stream water (Payn et al., 2009). In this study 'k' is determined each time a series of slug injections is performed. The calibration constant 'k' can be specified using standards made from known masses of NaCl dissolved in known volumes of stream water, or by adding several known volumes of salt solution subsequently to 1000 mL stream water and measure SC values that correspond to the different values of relative concentration, and use these for the calculation of the slope of the linear relation between relative concentration and SC values (Ward et al., 2013). In this research the latter was used, because it was easier to perform this method in the field.

Before each salt injection the specific conductivity (SC) of the stream water is measured to obtain a background value (SC_{bg}) that is used to subtract from SC over time (SC(t)) for correction (Payn et al., 2009). One of the two conductivity probes is placed downstream of the salt injection location and measures SC over time, and within a certain reach (see 2.3.1). The salt passes the probe in a wave visually shown in a so-called breakthrough curve. The SC is measured until it returns to the background value. The total area under the breakthrough curve is calculated by a summation of all SC values above the background SC over a certain time period (dt). This is described in equation [2], with B representing the area under the curve ($\text{mg L}^{-1} \text{s}$).

$$B = \int (SC - SC_{bg}) dt \quad [2]$$

It should be mentioned that if the SC did not return to the background SC due to, for example, the limitation in time, the curve was linearly extended until the background SC was reached.

Subsequently, to calculate the discharge Q (L s^{-1}), equation [3] was used, where C is the concentration of salt solution (mg L^{-1}) and V is volume of slug injected salt solution added to the stream (L).

$$Q = C * V / B \quad [3]$$

With the calculated discharge values, the change in discharge (ΔQ) can be calculated per stream reach, which is the 50 meter distance between two sample sites. The change in discharge is calculated by subtracting the upstream discharge value (Q_U) from the downstream discharge (Q_D), shown in equation [4].

$$\Delta Q = Q_D - Q_U \quad [4]$$

This change in discharge per reach was calculated for every reach with available data and for both W2 and W3. With these results the gain (positive ΔQ) or loss (negative ΔQ) of water from a stream can be identified (Payn et al., 2009).

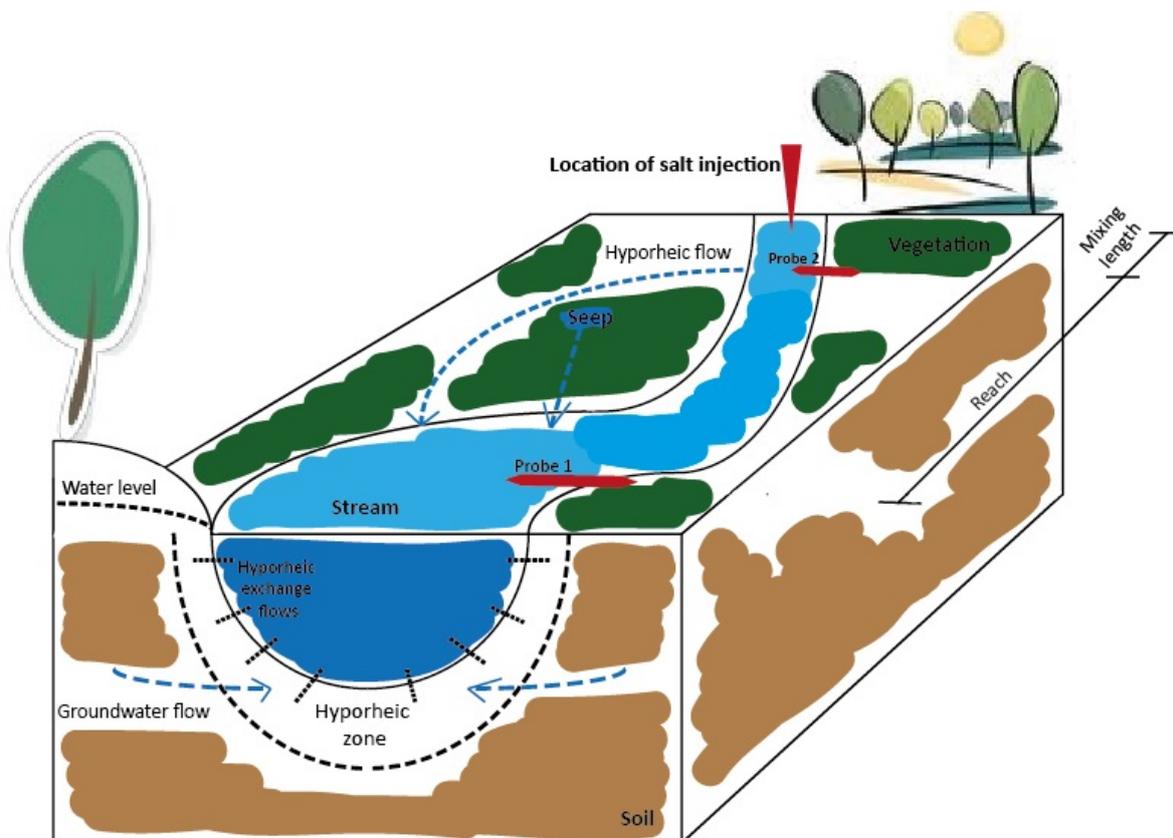


Figure 5. This figure also shows a certain reach of the stream and the placement of two conductivity probes in the stream, where probe 1 represents the downstream measure location (Q_D) and probe 2 corresponds with the upstream sample site (Q_U). The red arrow at the top of the figure represents the location of a salt injection, and the distance from this injection point to probe 2 is the mixing length. This figure is not to scale; for example the mixing length is not proportionate to the reach distance.

2.3.3 Stream reach, mixing length, salt concentration, UAA

A stream reach is defined by the distance between two sample sites, which is 50 meters in this research. The reaches are used for defining the quantity of water over a fixed distance of the stream. To measure the salt wave pass after an injection of salt in the stream a conductivity probe is placed at one sample site. To be able to calculate the channel water balance (see paragraph 1.1.1) another conductivity probe is placed at a sample site downstream of the former sample site (figure 5). With these measurements of specific conductivity (SC) the amount of water that is lost or gained from the stream can be determined (equation [4]) (Payn et al., 2009).

The mixing length is the distance in a stream channel that is necessary to attain well-mixed conditions of tracer solution with stream water (Ward et al., 2013). Predictions on the mixing length to reach uniform conditions based on theory about stream morphology are not reliable in headwater streams (Day, 1977; Ward et al., 2013). During relative high flow conditions mixing length is more dependent on stream morphology whereas this is less with low flow conditions where mixing length depends more on flow rates, and can therefore be shorter (Payn et al., 2009).

Therefore, to determine the best fitting values for stream reach and mixing length for multiple volumes of salt solution, the tracer injection method was performed in a preliminary study by O'Neill in the summer of 2012 (unpublished). This research was conducted in the same area as this research mainly to ensure that the method has a minor impact on the environment and other possible research performed in this specific area. The ideal mixing length was set to approximately 20 m. The reach distances of approximately 50 meters were used from the study done by Zimmer et al. (2012) who determined the distances with a GPS along all tributaries in WS3, including W2 and W3 that were used in this research (figure 3).

The slug injections were done with a solution of common table salt (sodium chloride, NaCl) and distilled water, as this is most inexpensive and least affecting on the environment (Day, 1977). Salt concentration of 17% was considered to provide an adequate compromise between strength and ease of dilution (Payn et al., 2009). The ideal volume of salt solution added to the stream was conceived to be 50 mL for a 20 meters mixing length.

For each sampling site, the upslope accumulated area (UAA) was determined. The geo-referenced sites were placed on a 5m DEM where UAA was calculated using a triangular multiple flow direction algorithm (Seibert and McGlynn, 2007). Seeps have a relative small UAA due to the upwelling of groundwater at those locations (Zimmer et al., 2012).

2.3.4 Water chemistry

Chemistry is, next to discharge, an important variable in stream water. As shown in paragraph 1.1.2 seeps have a distinct chemistry that might influence stream water through surface or subsurface flows. To determine the input of seep water chemistry on stream water multiple water samples were collected during two snowmelt events and during the summer fieldwork (see paragraph 2.2).

Samples were taken with 125 mL or 60 mL HDPE bottles at small cascades, or from fast moving water. All of these samples were eventually sent to the laboratory for chemical analyses. pH is measured potentiometrically for all collected samples within a day with a Broadley James rain probe and then refrigerated until they would be transferred to the analytical lab in Durham, NH, for chemical analysis. The anions including Cl, NO₃ and SO₄ were analyzed on a Metrohm-Peak 761 compact ion chromatograph. DOC was analyzed on a Shimadzu TO-5000A, and total dissolved nitrogen on an Antek nitrogen detector. The cations including Ca, Al, Na, Mg, Si and K, from the data from Zimmer et al. (2012) were analyzed on a Varian Vista axial inductively coupled plasma spectrometer.

3. Results

3.1 Stream discharge results

The discharge in both tributaries W2 and W3 increases moving downstream (figure 6). The correlation between the data points and the decreasing trend is significant, because for W3 the calculated R² values are 0,59 for the 29th of June and 0,60 for the 3rd of July, W2 shows a R² of 0,51 for the 2nd of July, 2013. The horizontal red lines in figure 11 represent seep 1 and seep 2 at an elevation of respectively 622,0 m and 609,3 m. The results show that below the elevation of the seeps the discharge data points are widely spread and show larger discharge velocities; with the highest discharge of 0,45 L s⁻¹ at an elevation of 566 m at reach W2A. Figure 7 shows data from the weir at the outlet of watershed 3 for the same dates as the discharge measurement dates. A

decrease in stage height is visible during the day. To see if there is a correlation between the increase in discharge per sample day and the amount of precipitation, the slope of the three trend lines was plotted against the amount of precipitation per day. The results however, did not show any correlation.

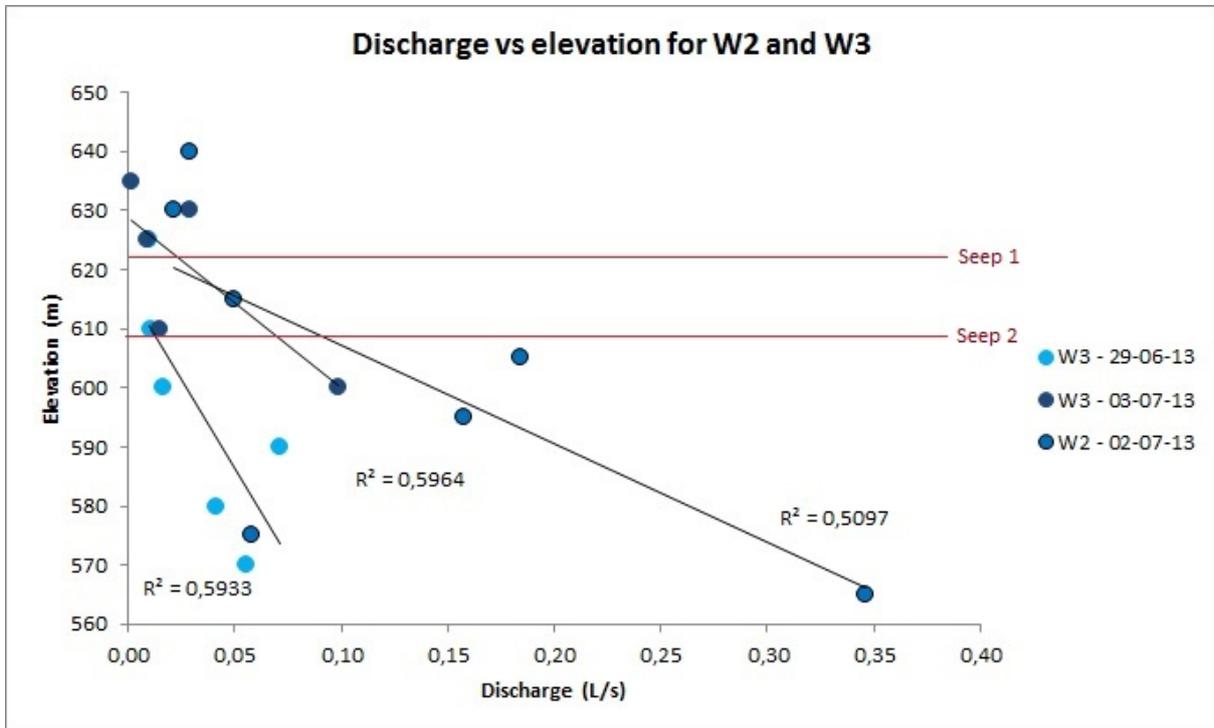


Figure 6. On the vertical axis the elevation is shown against the discharge on the horizontal axis. W3 is represented by 2 sample dates (light blue and dark blue circles), whereas W2 has one dataset (dark blue circle with contour). The horizontal red lines represent the elevation of seep 1 and seep 2.

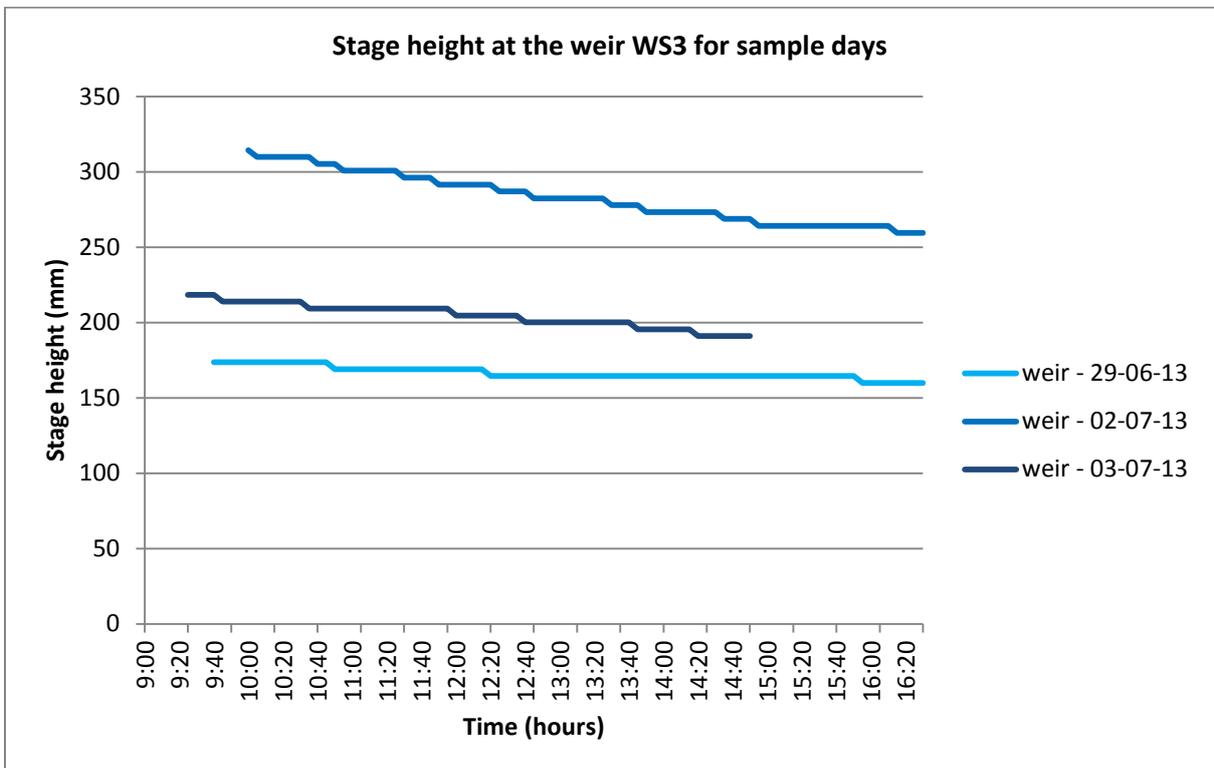


Figure 7. The time in hours is plotted on the horizontal axis and the stage height on the vertical axis for the 3 specific sample days with data taken at the weir located at the outlet of watershed 3 (WS3).

The results for the change in discharge (ΔQ) per reach show diverging results for W2 and W3. Figure 8 shows the results for W3 that show a positive change in discharge at reach DC which can be interpreted as a gain of water to the stream. The two reaches below show large negative value for ΔQ and represent a loss of water from the stream. Reach B shows a positive ΔQ correlated to a gain of water to the stream. The other reaches show a minor change in discharge at W3. These relatively high gains and losses of water to the stream occur at the reaches located below seep 1 and seep 2 that are located at the same elevations of respectively W3E and W3D. Figure 9 shows the results of the change in discharge calculated for W2. These results show a gain and loss of water to the stream. The changes in discharge in W2 are however less in comparison to the changes in W3. At the outlet of W2, at reach B and BA, a positive ΔQ is followed by a negative ΔQ .

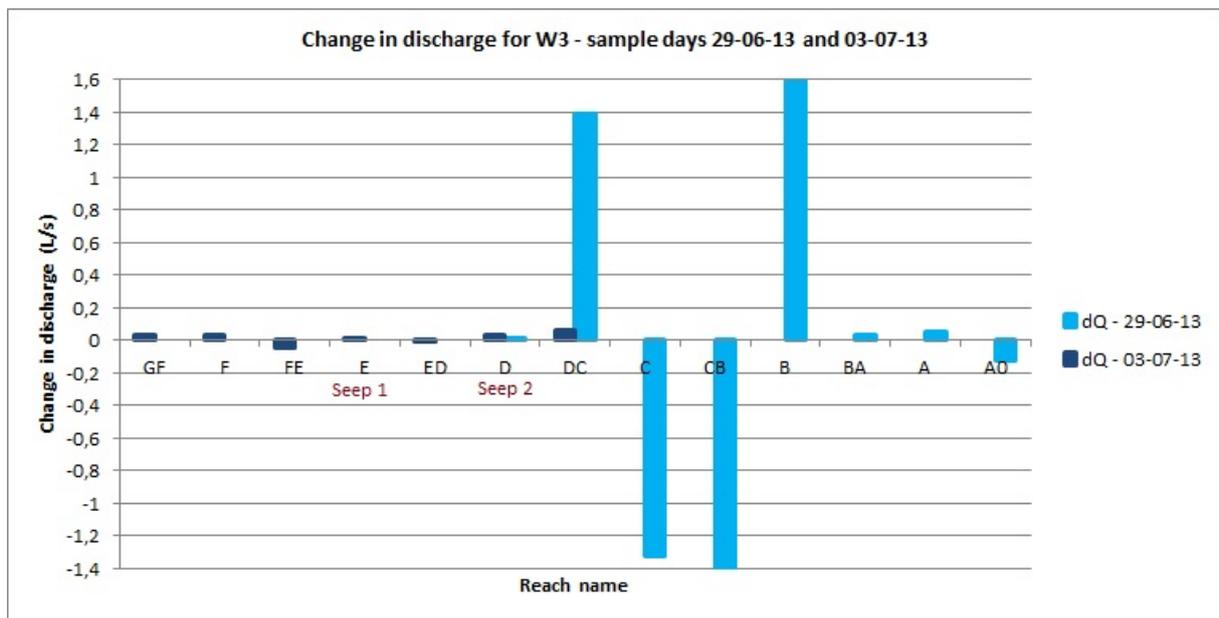


Figure 8. This figure shows the change in discharge, ΔQ , on the vertical axis and the different reaches on the horizontal axis. Two sample days are shown for W3. Also the location of seep 1 and seep 2 is shown.

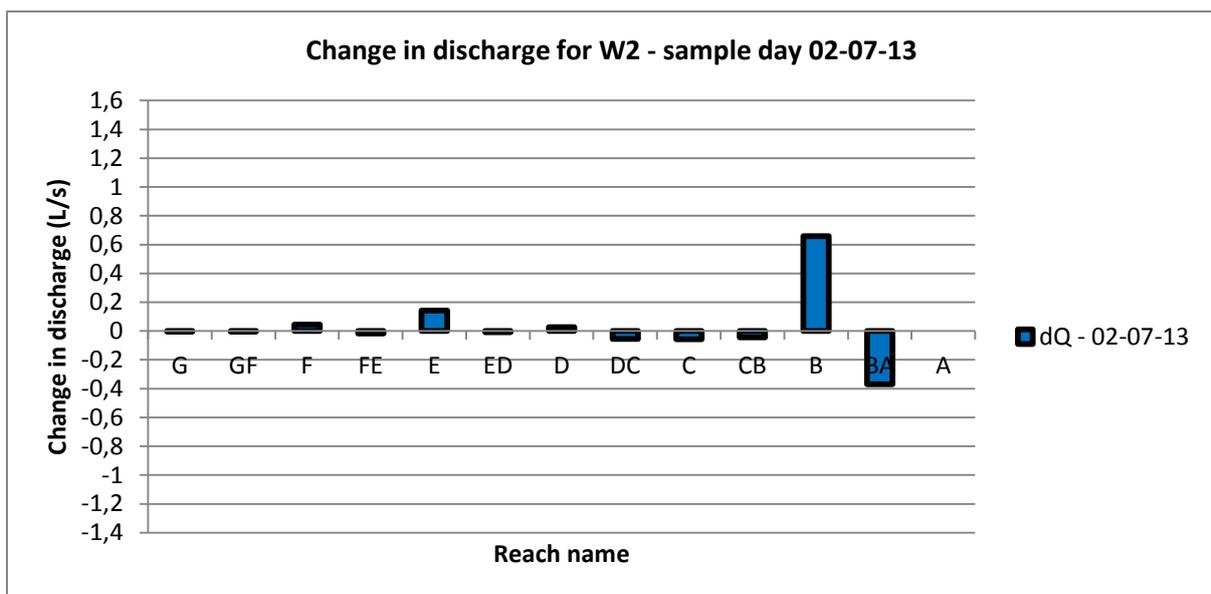


Figure 9. This figure shows the change in discharge, ΔQ , on the vertical axis and the different reaches on the horizontal axis.

3.2 Chemistry of seep water during snowmelt

The chemical composition of seep water does not seem to change during the two snowmelt events that were sampled. Figure 10 shows the pH of the seep water from seep 3 that fluctuates between 5,63 and 5,99. The anions that are shown in figure 11 are also stable during this snowmelt. There is a peak observed in DOC, TDN and NO_3^- concentrations at the 5th of April, 2013. The DOC doubles in concentration within 6 days. It shows an increase from an average of $1,3 \text{ mg L}^{-1}$ to $2,9 \text{ mg L}^{-1}$ DOC concentration and decreases back to $1,6 \text{ mg L}^{-1}$. The TDN concentration increases almost 4 times from the average concentration of $0,3 \text{ mg L}^{-1}$ to $1,1 \text{ mg L}^{-1}$. The increase in NO_3^- concentration is larger than 4 times and peaks from about $0,9 \text{ mg L}^{-1}$ to $4,3 \text{ mg L}^{-1}$.

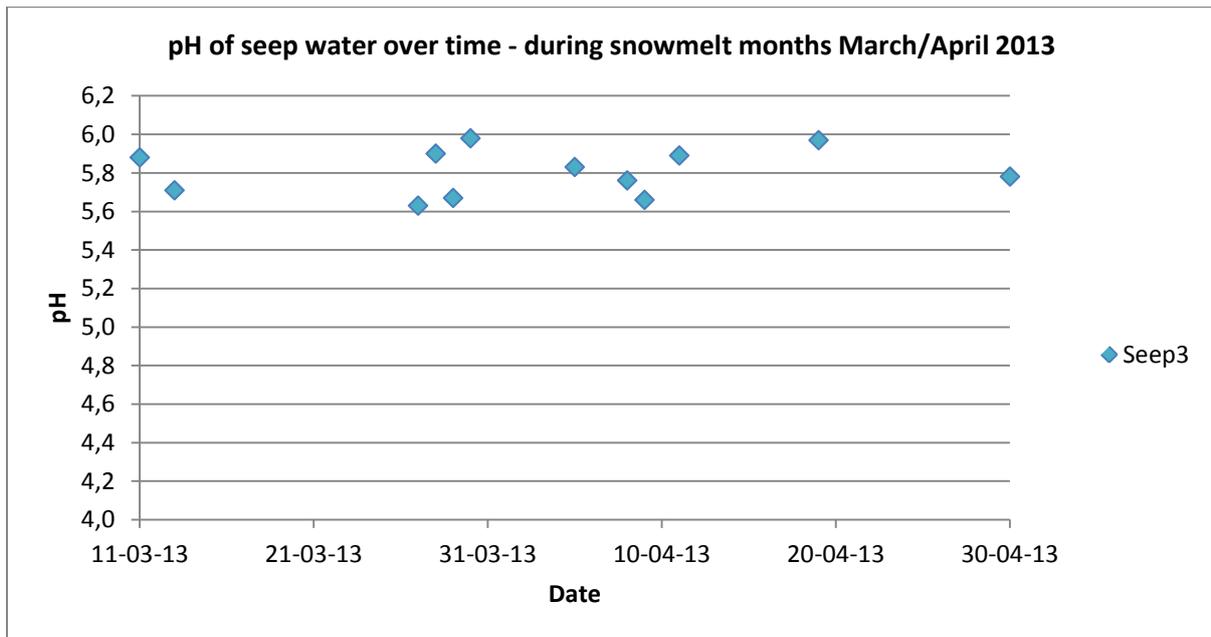


Figure 10. The horizontal axis shows time by means of dates. The vertical axis shows the pH of the seep water samples taken from seep 3. pH values fluctuate between 5,63 and 5,99.

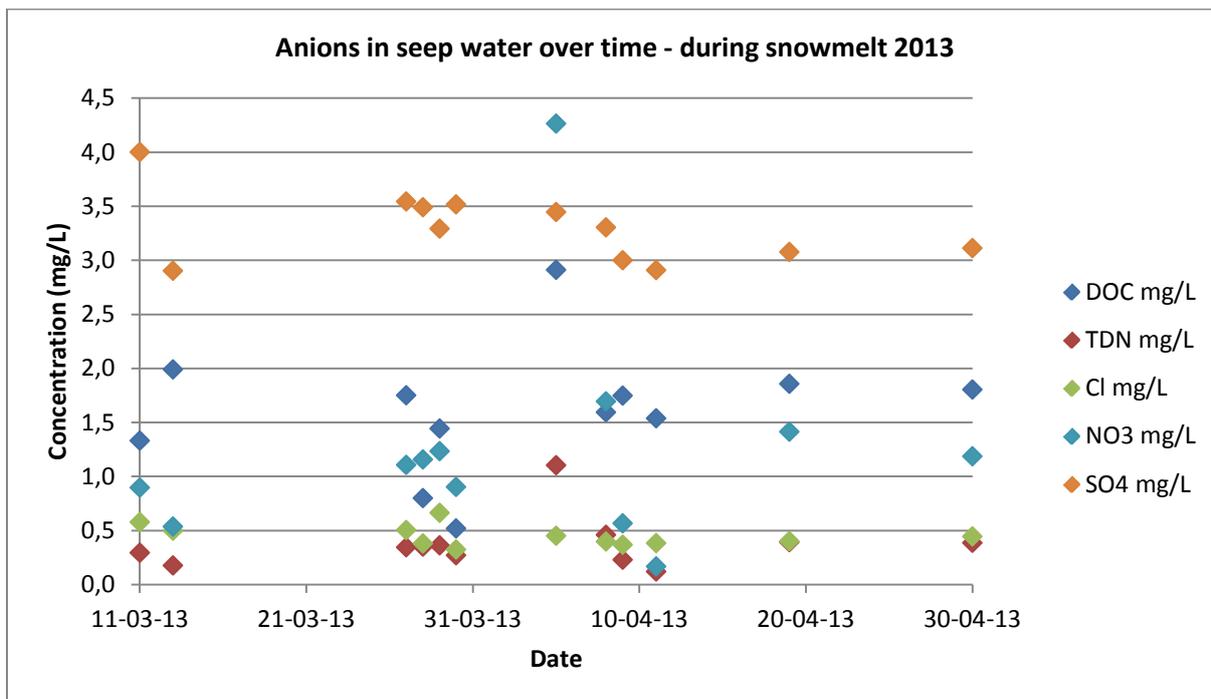


Figure 11. The horizontal axis shows time by means of date and the vertical axis represents the concentration of the anions in mg/L for seep 3. The different colors represent the different anions.

3.3 Chemistry of seep water and stream water during snowmelt

The results for the chemical analyses from stream water show stable concentrations during snowmelt. This is equal to the results from the chemical composition from seep water. Figure 12 shows the constant pH that is relatively higher in seep water than in the stream water samples. The stream water samples W3A and W3F have an elevation of respectively 580,2 m and 628,1 m. The pH at W3A is constantly higher than W3F that is higher in elevation. This means that the pH increases going downstream in W3. The DOC in figure 13 shows also constant values, however the concentrations in seep water fluctuate more than in stream water. This figure also shows the earlier mentioned peak in DOC concentration on the 5th of April, 2013 in seep water. This peak is not visible in the results from stream water. The results for SO₄ concentrations are given in figure 14, with a relatively higher SO₄ concentration in seep water in comparison with the stream water samples. The W3F water samples show the lowest SO₄ concentrations. There is no peak visible in neither seep nor stream water. Figure 15 shows the NO₃⁻ concentrations that fluctuate in seep water between 0,17 and 1,69 mg L⁻¹, excluding the peak concentration of 4,26 mg L⁻¹. For the stream sites the concentrations of NO₃⁻ fluctuate between 0,15 and 2,31 mg L⁻¹. The peak in seep water is not detectable in stream water. The NO₃⁻ concentrations from W3F are higher in comparison with W3A downstream.

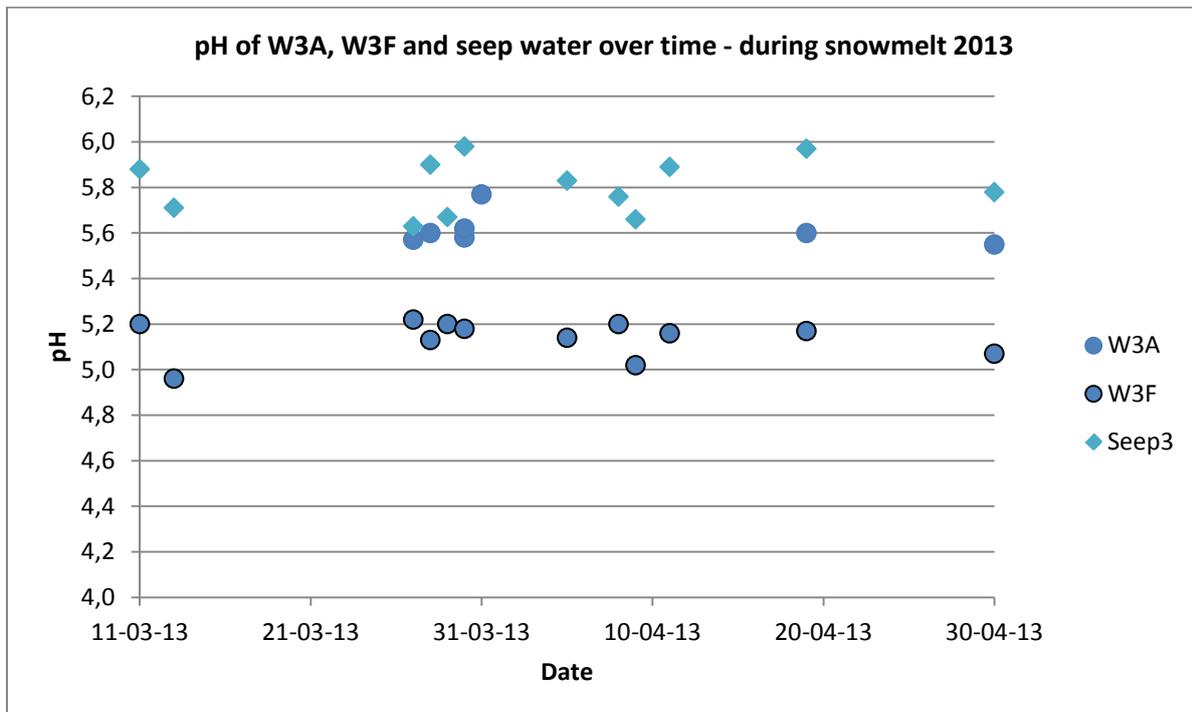


Figure 12. The pH on the vertical axis is plotted against the time (date) on the horizontal axis. Shown are sites W3A (blue circles), W3F (dark blue circles) located in W3 and seep 3 (blue diamonds).

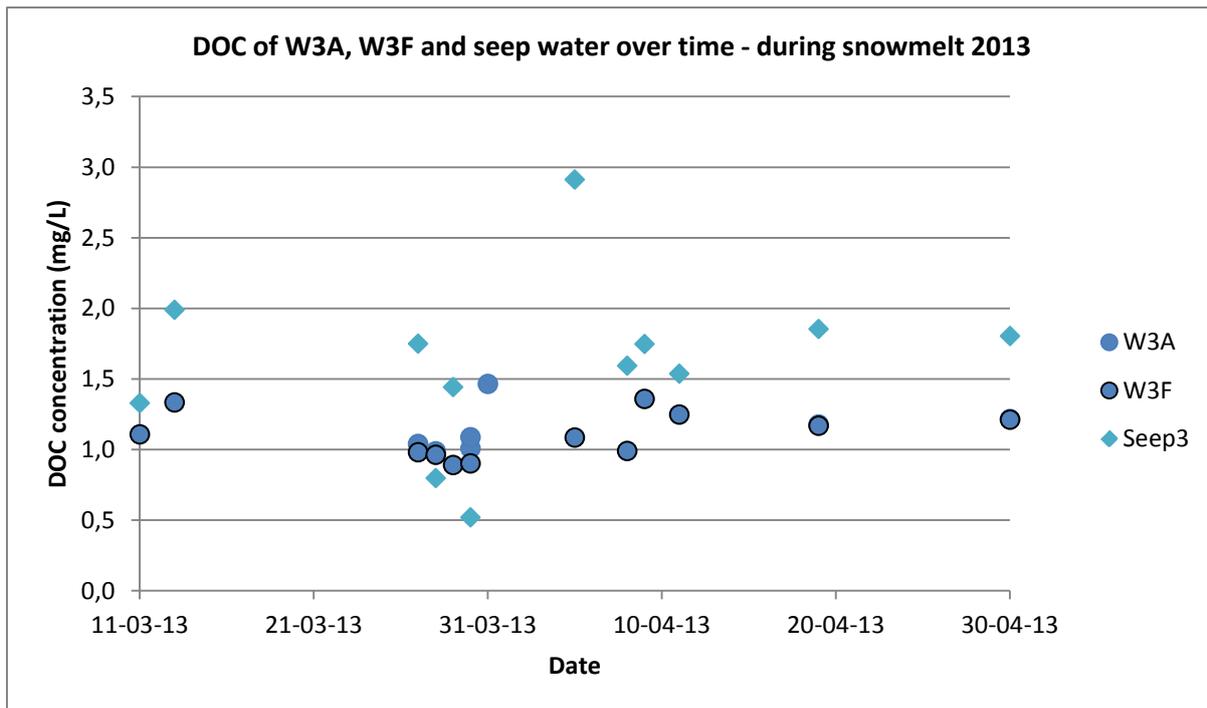


Figure 13. On the horizontal axis time (date) is shown, and on the vertical axis the concentration DOC.

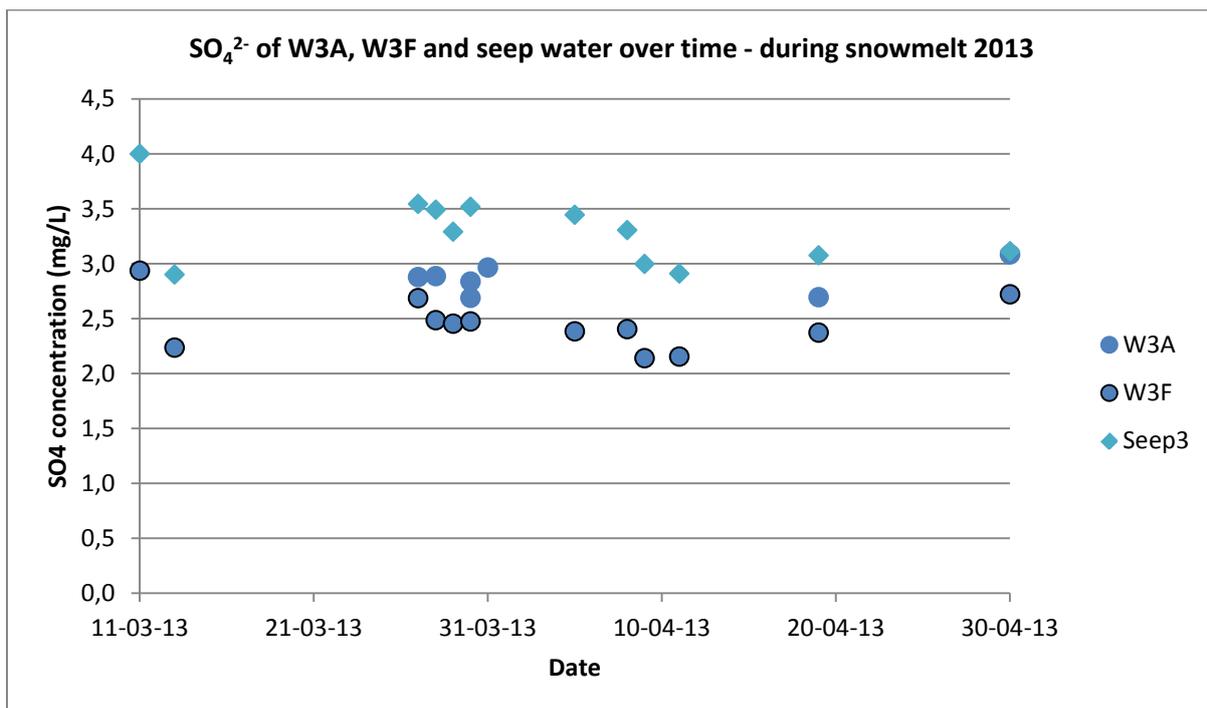


Figure 14. The horizontal axis represents the time (date), with SO₄ concentration on the vertical axis.

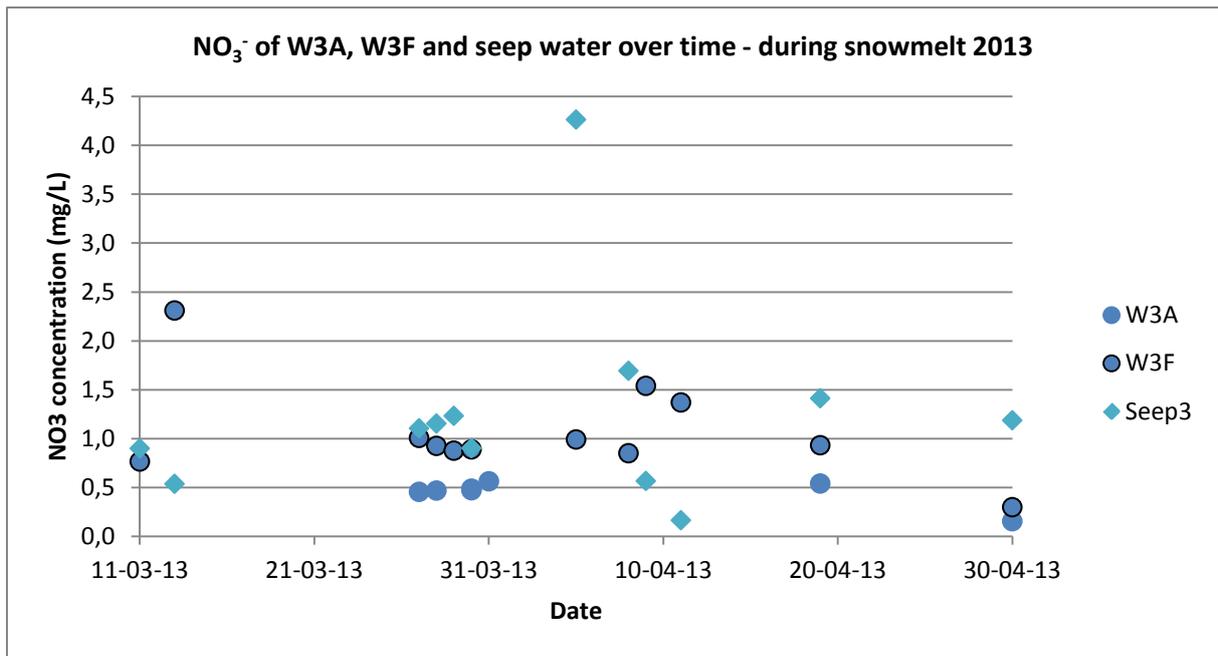


Figure 15. The horizontal axis shows time (date), against NO₃ concentration on the vertical axis.

3.4 Chemistry of stream water and seep water over elevation

The chemistry results from W2 show overall stable concentrations, in contrast to the results for W3 that fluctuate over elevation. The seeps show relatively high concentrations in chemical composition in comparison to W2 and W3. Figure 16 gives the pH results of stream water that show an overall increase going downstream. A steeper increase in W3 is visible in comparison with W2. The correlation in W3 is stronger than in W2 what is shown by R^2 values of 0,97 for W3 and 0,73 for W2. Both seeps have a higher pH in comparison to W3 and W2. The seep at an elevation of 622,0 has a pH of 5,4, whereas the seep that is located at a lower elevation (609,3 m) has a higher pH of 6,0. The DOC concentration in figure 17 shows stable results for W2 and similar concentrations for the seeps with a range between 1,48 and 3,08 mg L⁻¹ DOC concentration. W3 shows an exponential increase with increasing elevation and a R^2 of 0,83. The highest DOC concentration at an elevation of 705,3 m is 13,01 mg L⁻¹.

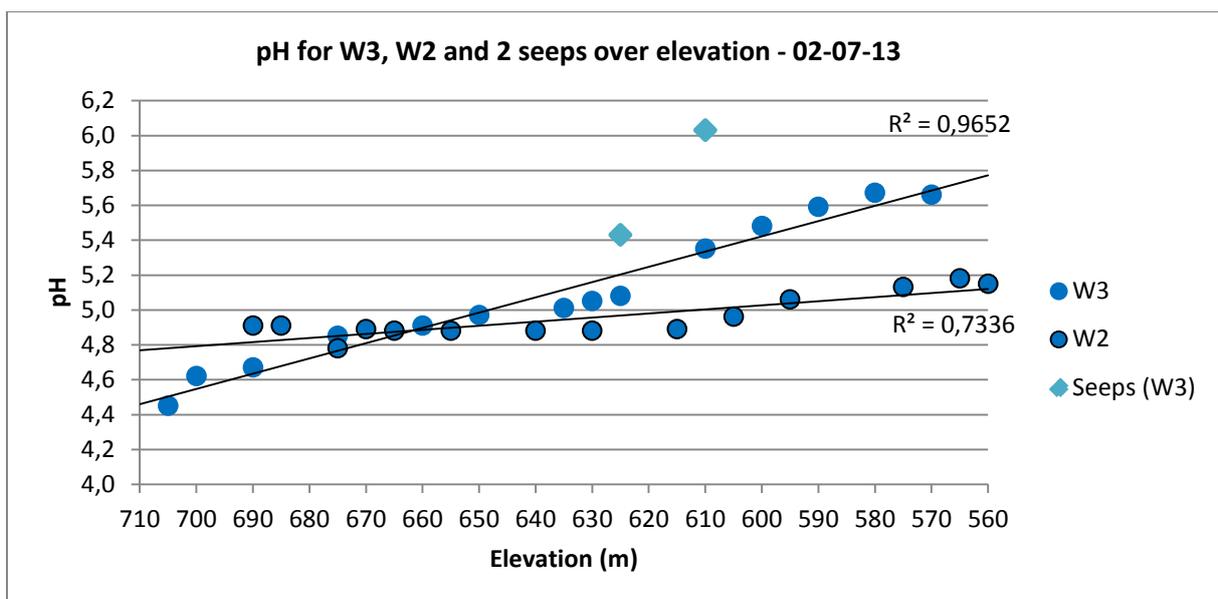


Figure 16. pH is shown on the vertical axis with elevation on the horizontal axis. W3 and W2 (respectively blue circle and blue circle with contour line) and two seeps (blue diamonds) are shown for the sample day of the 2nd of July, 2013.

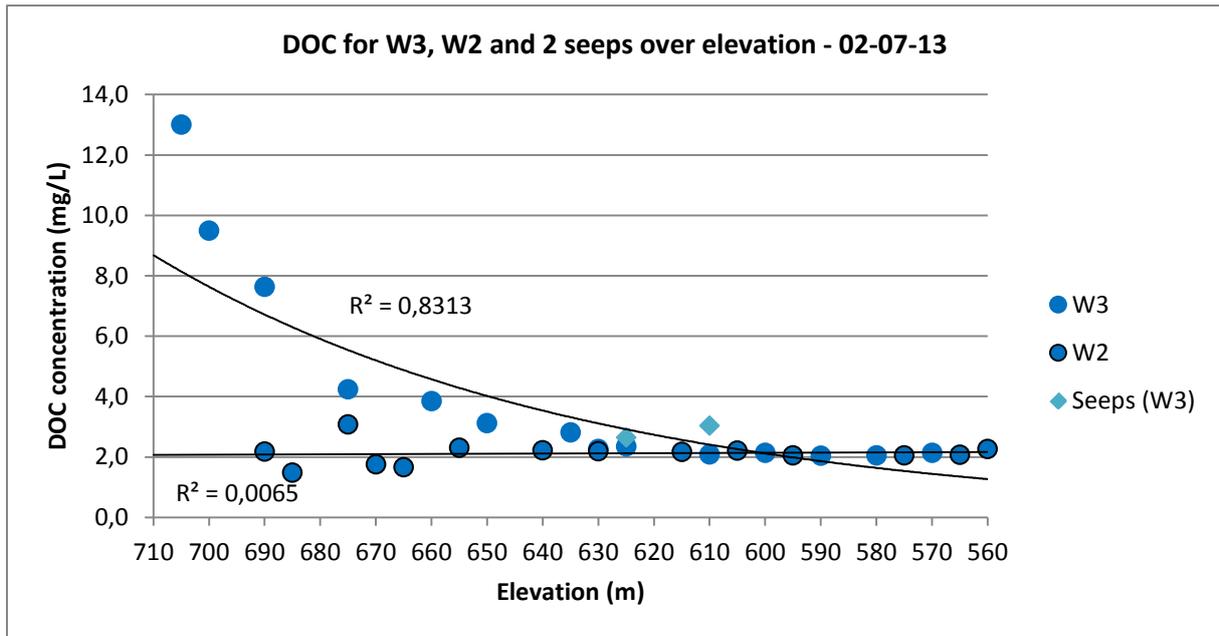


Figure 17. The vertical axis represents the concentration of DOC, over elevation on the horizontal axis.

Figure 18 shows higher SO_4^{2-} concentrations in the two seeps as in W2 and W3. The seep at 622,0 m elevation has a SO_4^{2-} concentration of $3,20 \text{ mg L}^{-1}$, and is higher than the concentration of the seep with an elevation of 609,3 m which is $2,85 \text{ mg L}^{-1}$. W2 shows constant SO_4^{2-} concentrations fluctuating between $1,71 \text{ mg L}^{-1}$ and $2,37 \text{ mg L}^{-1}$. W3 shows an increasing trend going from a SO_4^{2-} concentration of $1,19$ to $2,18 \text{ mg L}^{-1}$ moving downstream. The R^2 value of $0,94$ at the W3 results is significant high. The NO_3^- concentrations shown in figure 19 are also stable for W2 ranging between $0,00 \text{ mg L}^{-1}$ and $0,32 \text{ mg L}^{-1}$. The seeps have a relatively high NO_3^- concentration of $0,39 \text{ mg L}^{-1}$ for the seep at 622,0 m and $0,70 \text{ mg L}^{-1}$ for the seep at an elevation of 609,3 m. In W3 there is also a high concentration of NO_3^- visible of $0,53 \text{ mg L}^{-1}$ at an elevation of 705,3 m. This outlier causes an overall decreasing trend, the R^2 however does not changes and stays $> 0,35$. Without this data point the NO_3^- ranges between $0,00 \text{ mg L}^{-1}$ and $0,15 \text{ mg L}^{-1}$, what means that W3 fluctuates less in comparison with the NO_3^- concentrations in W2.

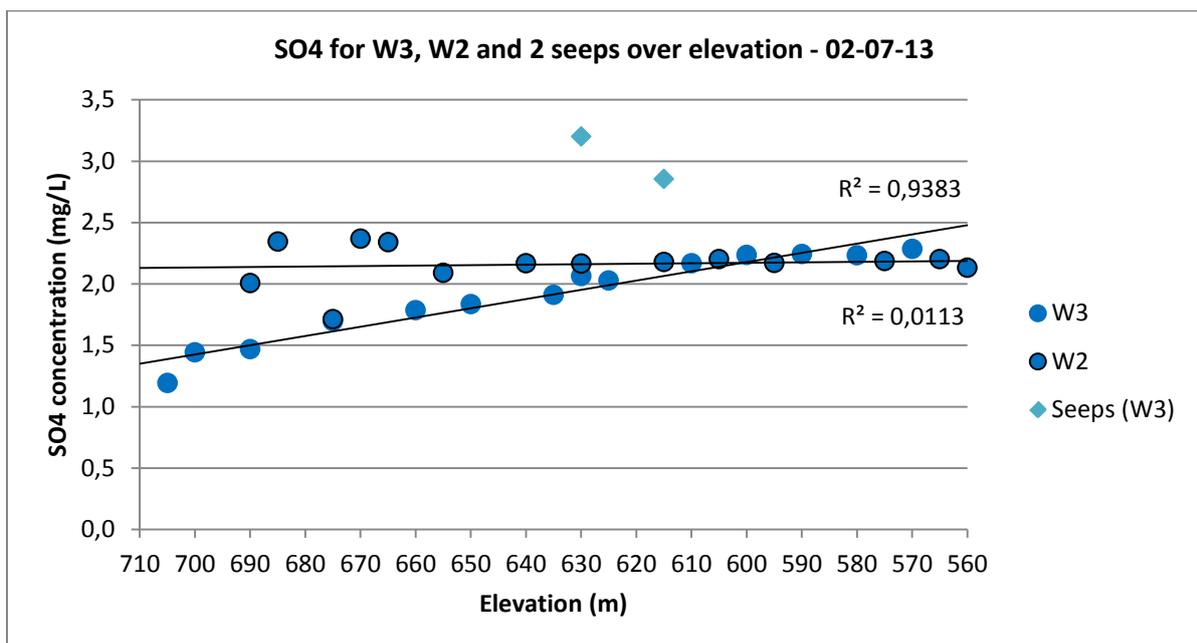


Figure 18. On the vertical axis SO_4^{2-} concentrations are plotted against elevation on the horizontal axis.

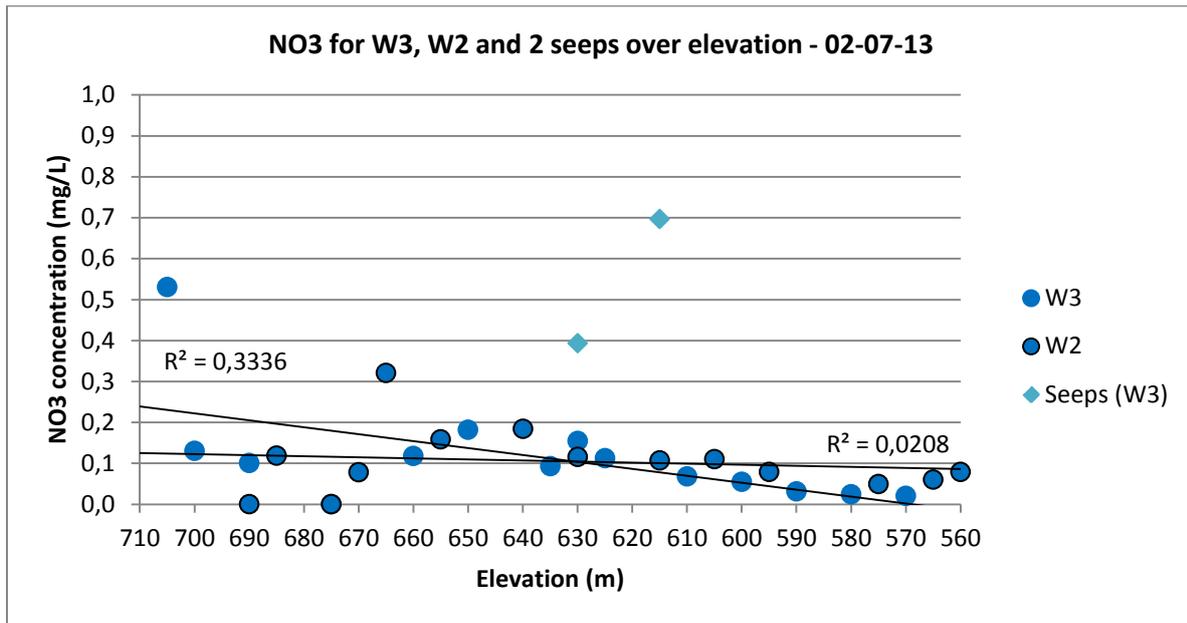


Figure 19. NO₃⁻ concentrations on the vertical axis over elevation on the horizontal axis for W2, W3 and both seeps.

3.5 Chemistry of seep water and stream water from spring to summer

Different seasons do not show large fluctuations in chemistry for both seep water and stream water. Figure 20 shows stable results in pH for W3A, W3F and seep 3. The pH in the seep is overall higher than that of W3 with an average of 5,82, whereas W3A has an average of 5,62 and W3F of 5,14. In figure 21 an increase in DOC concentration in W3F is visible over time. The DOC concentration increases from an average of 1,10 mg L⁻¹ in spring to 1,69 mg L⁻¹ in summer. This is an increase of 0,59 mg L⁻¹ which is more than half of the original value of 1,10 mg L⁻¹. Next to this, the trend line has a R² value 0,60 what makes this increase in DOC concentration in W3F significant. It can also be observed that the data point representing W3A in summer is higher in concentration than the results from spring. The seep shows stable DOC concentrations that fluctuate at 1,62 mg L⁻¹ with two outliers observed; one in spring on the 5th of April of 2,91 mg L⁻¹ and the other on June, 29th of 2,78 mg L⁻¹.

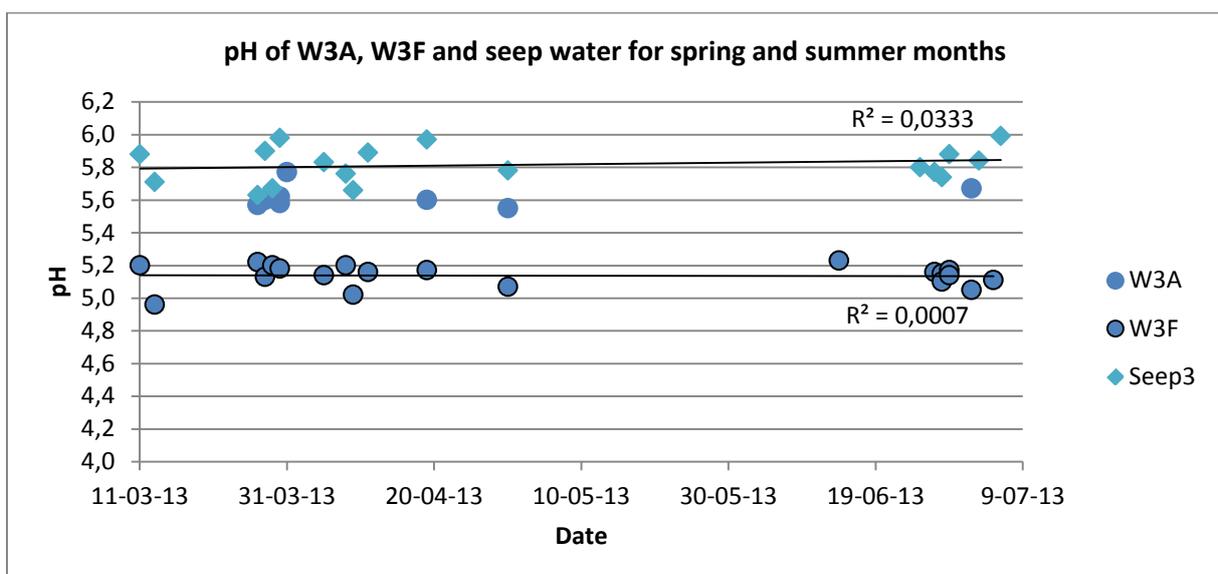


Figure 20. pH on the vertical axis against time (date) on the horizontal axis for the two sample sites in tributary W3, W3A (blue circle) and W3F (blue circle with contour line), and seep 3 (light blue diamond). The trend lines are shown for W3F and seep 3, because at W3A it would only depend on one sample point in summer what is not reliable.

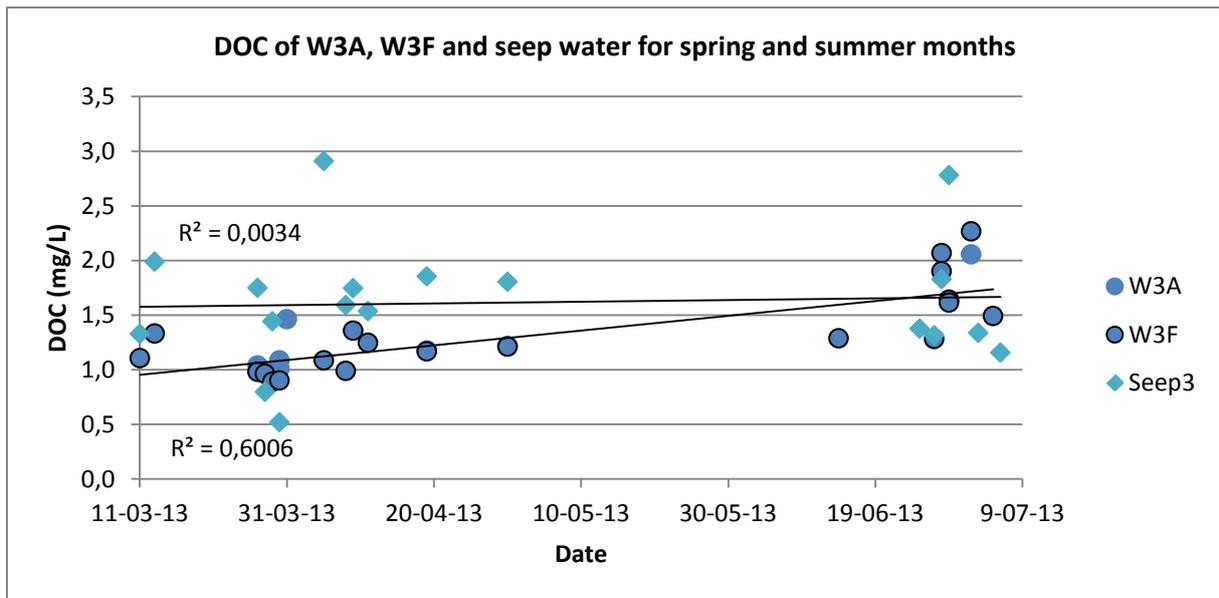


Figure 21. DOC concentrations are on the vertical axis over time (date) on the horizontal axis.

Figure 22 shows a minor decrease in SO_4^{2-} concentrations in both stream and seep water from spring to summer. The seep water reduces in SO_4^{2-} concentration from an average of $3,30 \text{ mg L}^{-1}$ in spring to an average of $3,20 \text{ mg L}^{-1}$ in summer. For the concentrations of SO_4^{2-} in W3F this decrease is from $2,45 \text{ mg L}^{-1}$ to $2,31 \text{ mg L}^{-1}$. The decreases are however not significant with R^2 values of 0,09 from seep 3 and 0,11 for W3F. The results for NO_3^- concentrations shown in figure 23 are fluctuating within a range in spring from $0,00 \text{ mg L}^{-1}$ to $2,31 \text{ mg L}^{-1}$, with the outlier in seep water on the 5th of April of $4,26 \text{ mg L}^{-1}$. The NO_3^- concentrations decrease in summer; for the seep water the decrease is less steep and reduces from an average of $1,26 \text{ mg L}^{-1}$ to $0,57 \text{ mg L}^{-1}$. W3F shows a decrease from an average NO_3^- concentration of $1,06 \text{ mg L}^{-1}$ to $0,07 \text{ mg L}^{-1}$. The R^2 value for W3F is 0,70 and is significant, in contrast with the R^2 of the seep of 0,10.

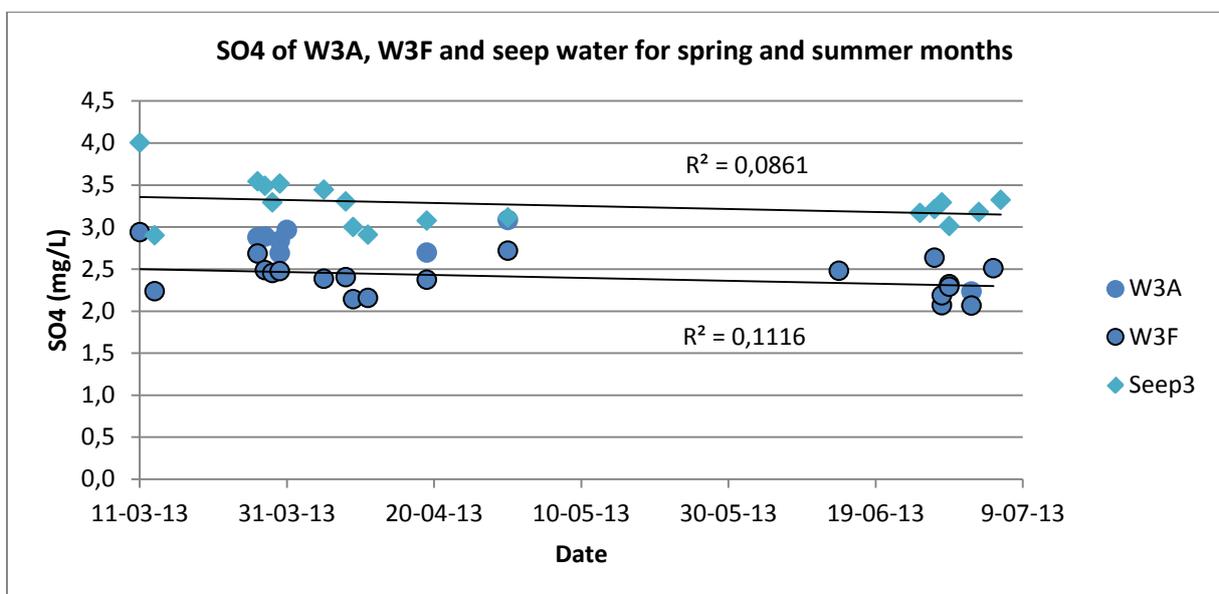


Figure 22. The SO_4 concentration on the vertical axis is plotted against the time.

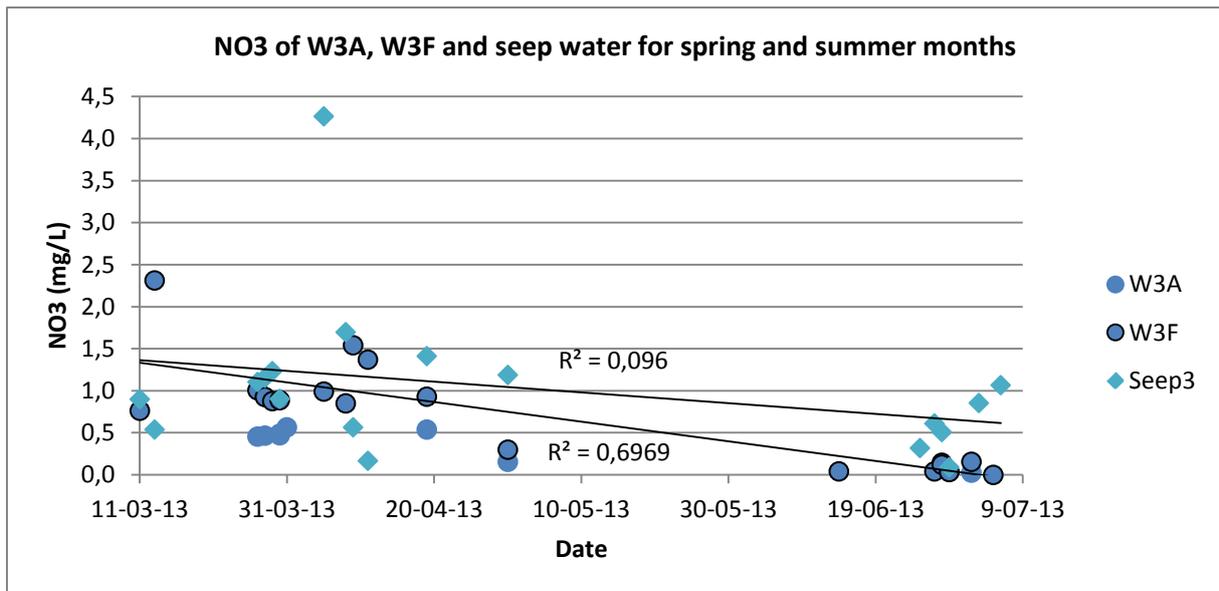


Figure 23. On the horizontal axis time is displayed against NO₃ concentration on the vertical axis.

3.6 Chemistry of seep water and stream water from 2009 to 2013

With the use of supplementary data from Zimmer et al. (2012) trends from 2009 and 2010 are compared with trends from 2013 for pH, SO₄²⁻ and NO₃⁻ concentrations. Figure 24 shows an increasing trend in pH going downstream in W3. The pH of W3 ranges between 4,35 and 5,85. The data from Zimmer et al. (2012) shows overall lower pH values than the data from 2013. The pH values from the 29th of June, 2013 show the steepest increase, whereas the data from the 10th of July, 2009 has the less steep increase in pH. The seeps show an overall higher pH value than the stream water with 6,12 as the highest value and 5,41 as the lowest pH value.

The pH values of W2 in figure 25 show an increase going downstream that is less steep in comparison with W3 looking at the trend lines in this figure. The pH values range between the 4,46 and 5,42 which is less diverse than the pH range in W3. There is not an increase in pH visible from 2009 to 2013. The data from the 10th of July, 2009, shows the lowest pH values with an average of 4,65, and April 1st, 2010, shows the highest values of pH 5,17.

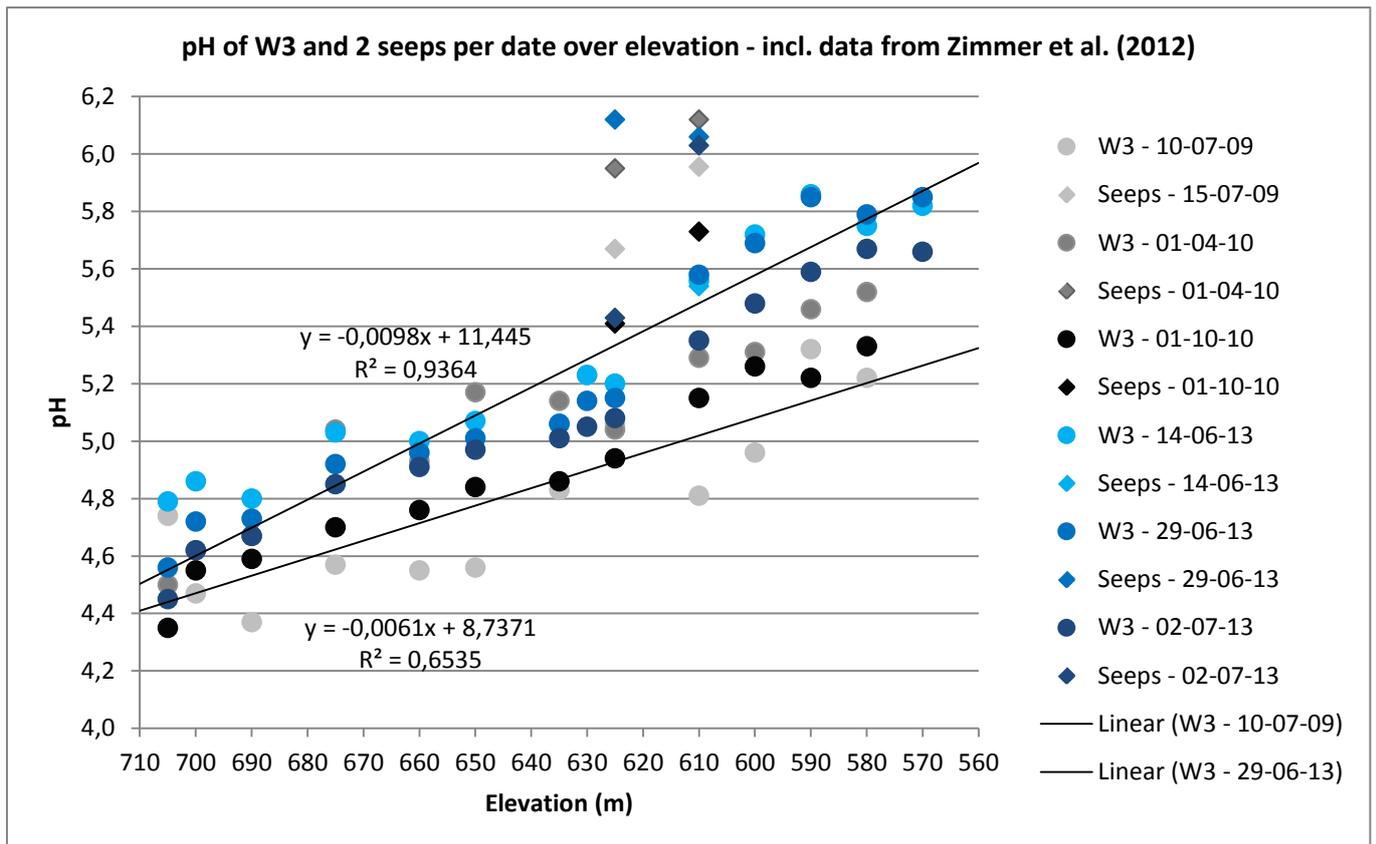


Figure 24. On the horizontal axis elevation is displayed with pH on the vertical axis. W3 (circles) and the seeps (diamonds) are represented by grey and blue gradient colors. Data from Zimmer et al. (2012) is corresponding with grey colors; the oldest date is represented by the lightest color of grey and the data from the 1th of October by the darkest grey. Also for the data from 2013 the gradient moves from light to dark blue for the oldest to the youngest data. Two trend lines are visible for the steepest increase at June 29th, 2013, and the less steepest increase at the 10th of July, 2009.

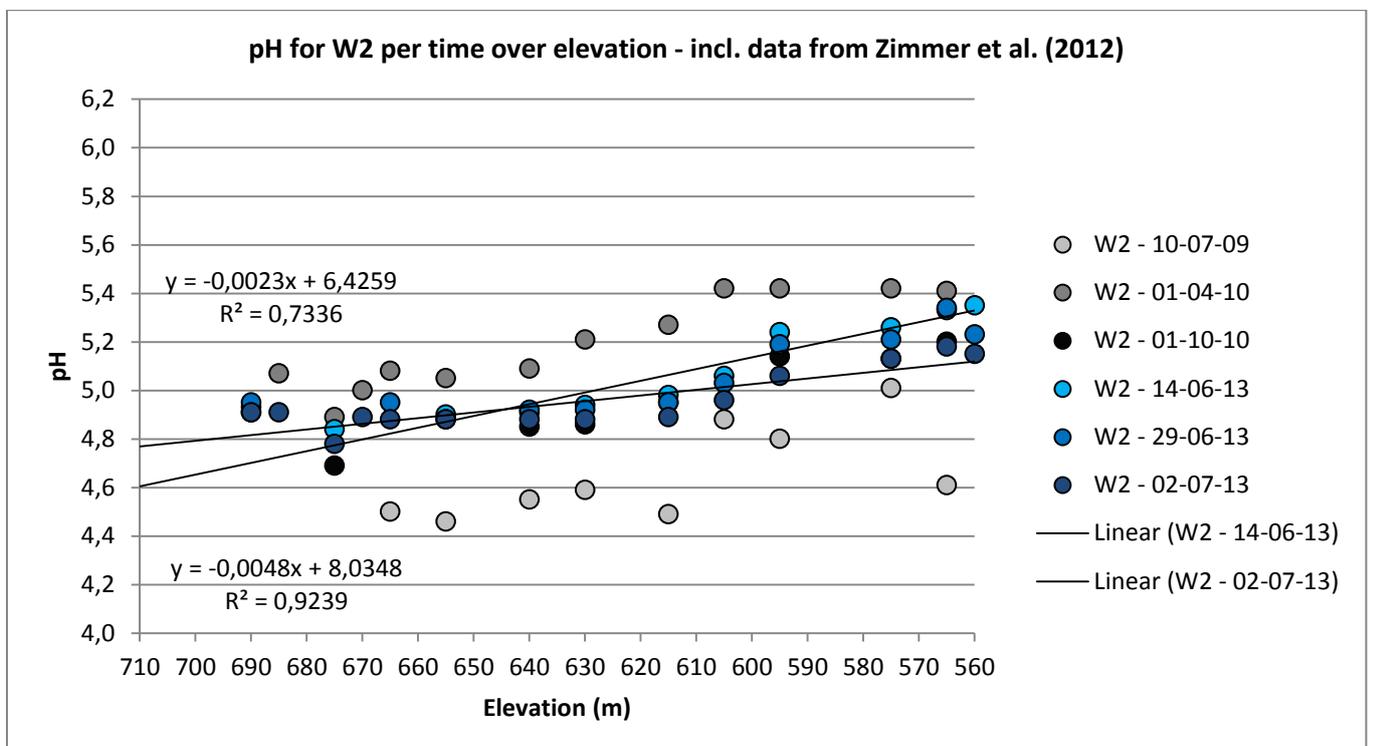


Figure 25. Elevation is on the horizontal axis, and pH on the vertical axis. W2 is represented with data from Zimmer et al. (2012) in grey gradients and data from 2013 measurements in blue gradients. Two trend lines are shown for the steepest increase at the 14th of June, 2013 and the less steepest increase in pH at the 2nd of July, 2013.

Figure 26 gives the SO_4^{2-} concentrations of W3 and the seeps for several dates including the data from Zimmer et al. (2012). There is an overall increase visible going downstream. The data from Zimmer et al. (2012) shows overall higher concentrations of SO_4^{2-} in W3, with the highest SO_4^{2-} concentrations for the 10th of July, 2009 with an average of $2,27 \text{ mg L}^{-1}$, in comparison with the data from the 2nd of July, 2013 with an average SO_4^{2-} concentration of $1,87 \text{ mg L}^{-1}$. All SO_4^{2-} concentrations measured range between $1,19 \text{ mg L}^{-1}$ and $2,97 \text{ mg L}^{-1}$. The seeps show in general higher SO_4^{2-} concentrations than W3; with the highest concentration of $3,69 \text{ mg L}^{-1}$ and the lowest of $2,85 \text{ mg L}^{-1}$.

Comparing these results from W3 with the SO_4^{2-} concentrations in W2, figure 27 shows that the SO_4^{2-} concentrations are relatively higher, with a range between $1,71 \text{ mg L}^{-1}$ and $3,23 \text{ mg L}^{-1}$. The increase in SO_4^{2-} concentrations is less steep in W2 in comparison to W3. Also in W2 the SO_4^{2-} concentrations on the 10th of July, 2009 are highest with an average of $2,51 \text{ mg L}^{-1}$, and the SO_4^{2-} concentrations from the 2nd of July, 2013 are lowest with an average of $2,16 \text{ mg L}^{-1}$.

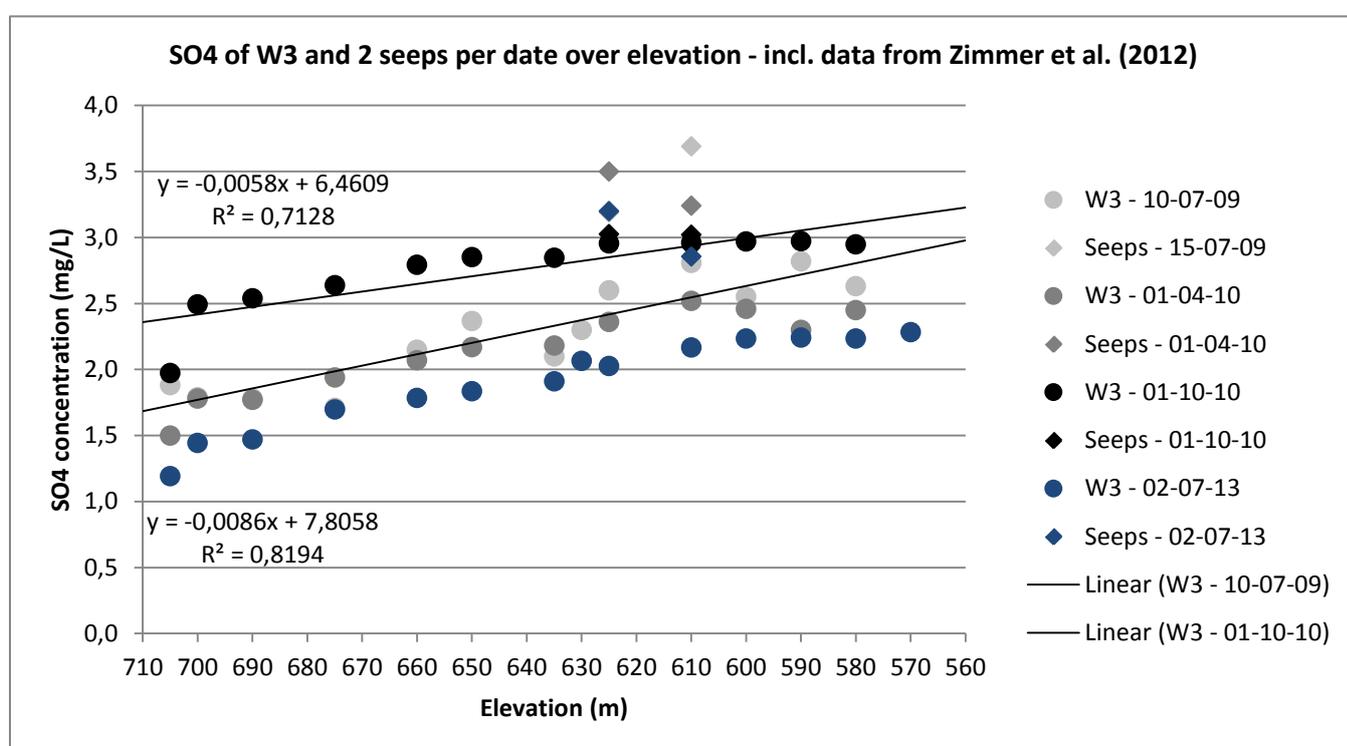


Figure 26. The horizontal axis shows elevation, and the vertical axis represents the SO_4 concentration. W3 (circles) and seeps (diamonds) are shown for different dates. Two trend lines are given as a representation of the steepest and less steep increase in SO_4 concentration.

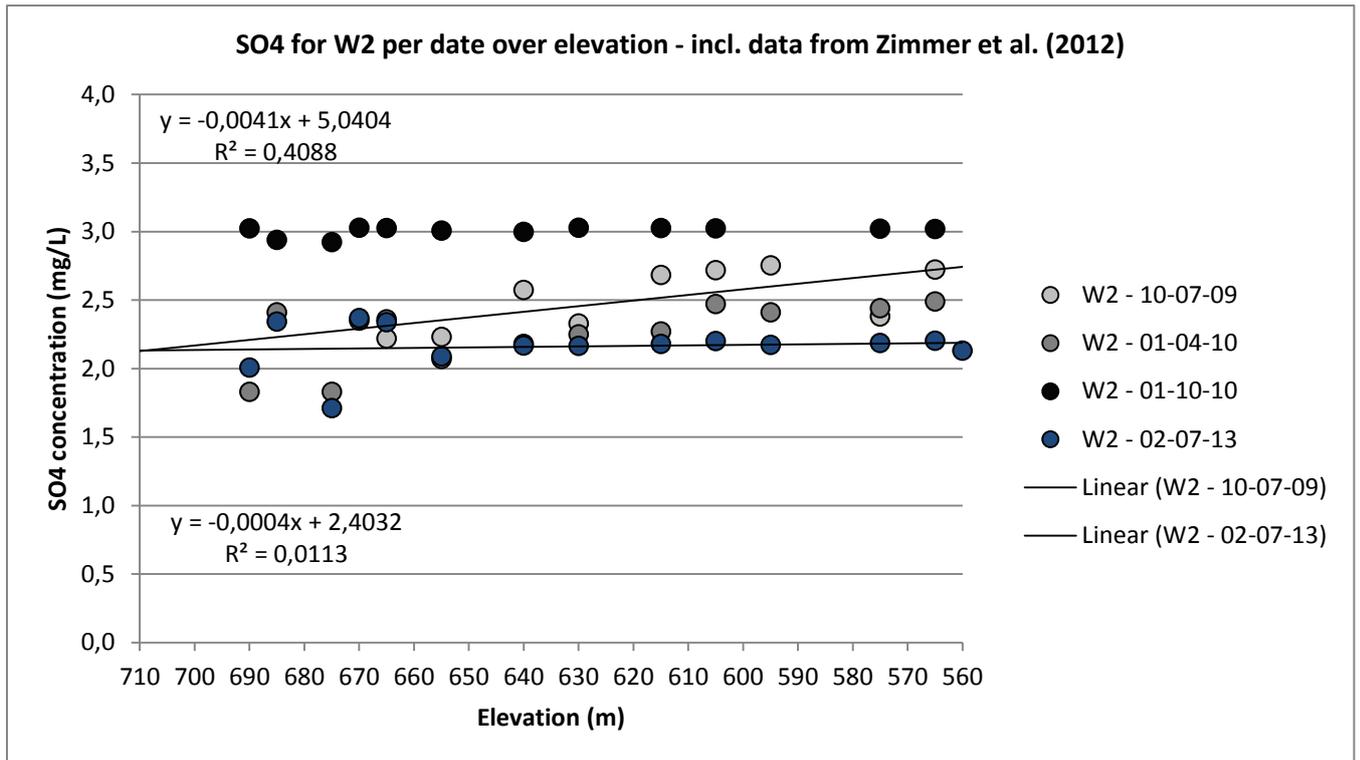


Figure 27. The horizontal axis shows elevation, and the vertical axis the SO₄ concentration in W2 for different dates. Two trend lines are shown of the steepest and less steep increasing lines.

NO₃⁻ concentrations are shown in figure 28 for W3 and the two seeps. The seep water from the 2nd of July, 2013 shows higher concentrations of NO₃⁻ of 0,39 mg L⁻¹ for seep 1 and 0,70 mg L⁻¹ for seep 2. The other dates show a concentration for seep 1 of 0,00 mg L⁻¹ and for seep 2 at the 1st of April, 2010, 0,22 mg L⁻¹ and the 1st of October, 2010, 0,05 mg L⁻¹. W3 shows higher NO₃⁻ concentrations upstream with the highest concentration of 0,91 mg L⁻¹ on the 1st of April, 2010. W2 shows in figure 29 an exponential decrease on the 1st of April, 2010 in NO₃⁻ concentration from the highest value of 1,28 mg L⁻¹ upstream. This is in contrast with the NO₃⁻ concentrations of other dates in W2 that show stable concentrations over elevation.

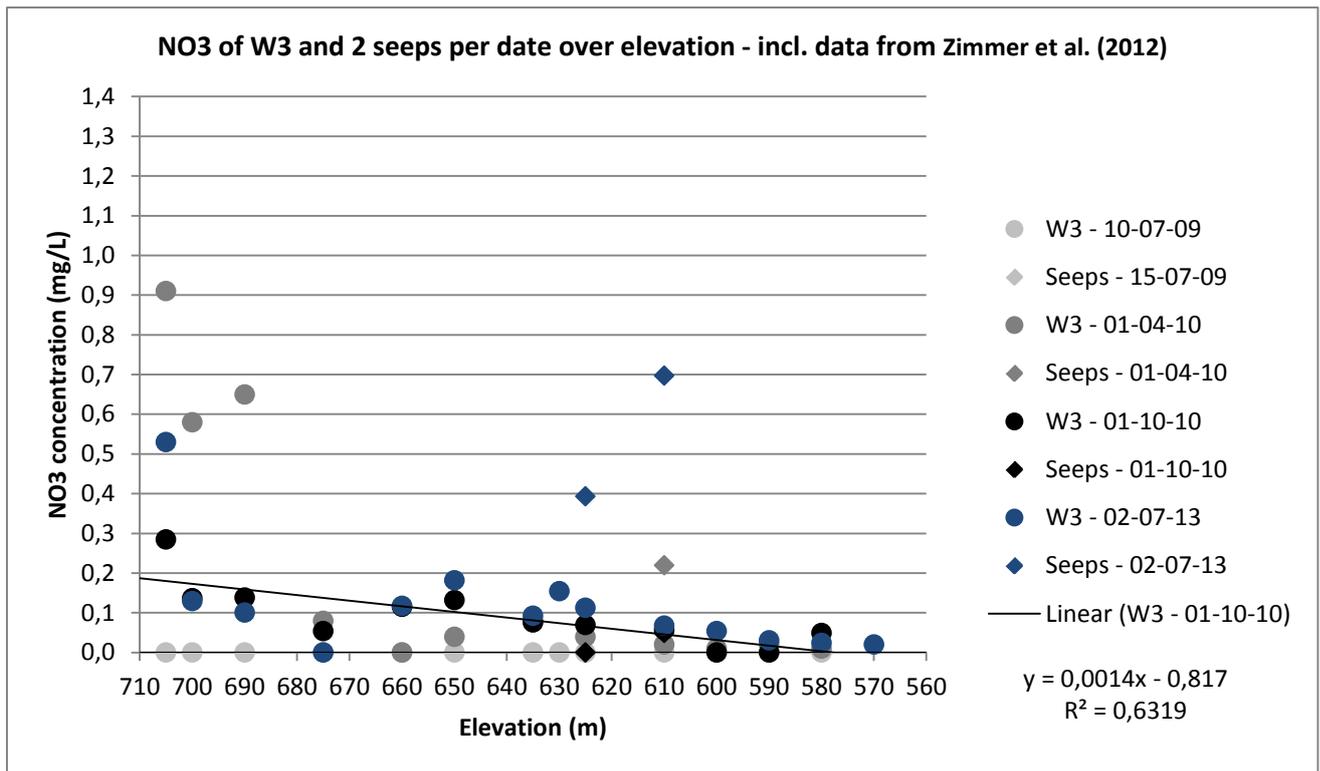


Figure 28. Elevation on the horizontal axis, and NO₃ concentration on the vertical axis. Data from Zimmer et al. (2012) is included and shown in grey scales, as well as the results from the chemical analyses of the 2nd of July, 2013 in dark blue. This is done for all results from W3 (circles) and the seeps (diamonds).

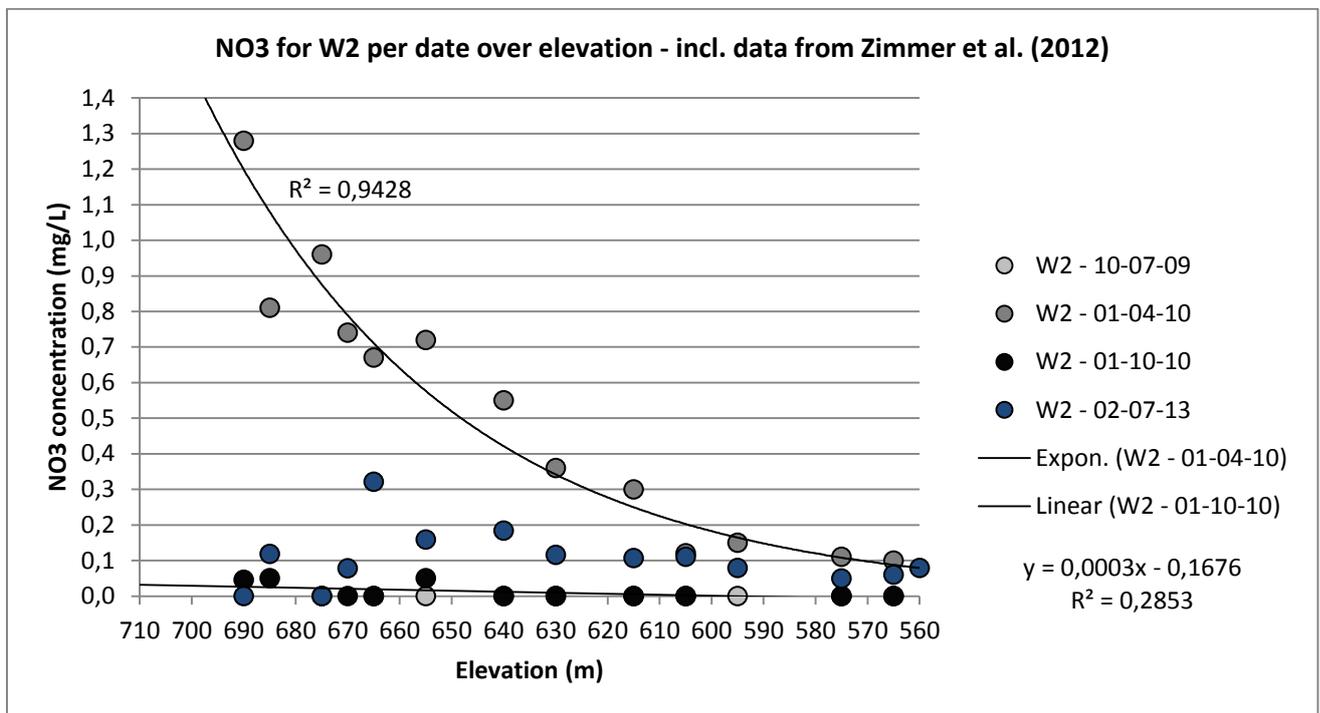


Figure 29. On the horizontal axis elevation is shown, on the vertical axis NO₃ concentrations for W2.

3.7 Cations in stream water and seep water from 2009 and 2010

The cation data from Zimmer et al. (2012) in the figures 30 to 33 show for W3 an increase moving downstream, and relatively high concentrations in both seeps. Al³⁺ concentrations however are an exception and show in figure 30 a decrease going downstream. The decrease is significant with R² values of 0,74 and higher. The Al³⁺ concentrations decrease within the range of a maximum

concentration of $0,47 \text{ mg g}^{-1}$ and a minimum concentration of $0,01 \text{ mg g}^{-1}$. The Al^{3+} concentration of seep water ranges between $0,02 \text{ mg g}^{-1}$ and $0,18 \text{ mg g}^{-1}$. Over time, there is an increase in Al^{3+} concentrations visible.

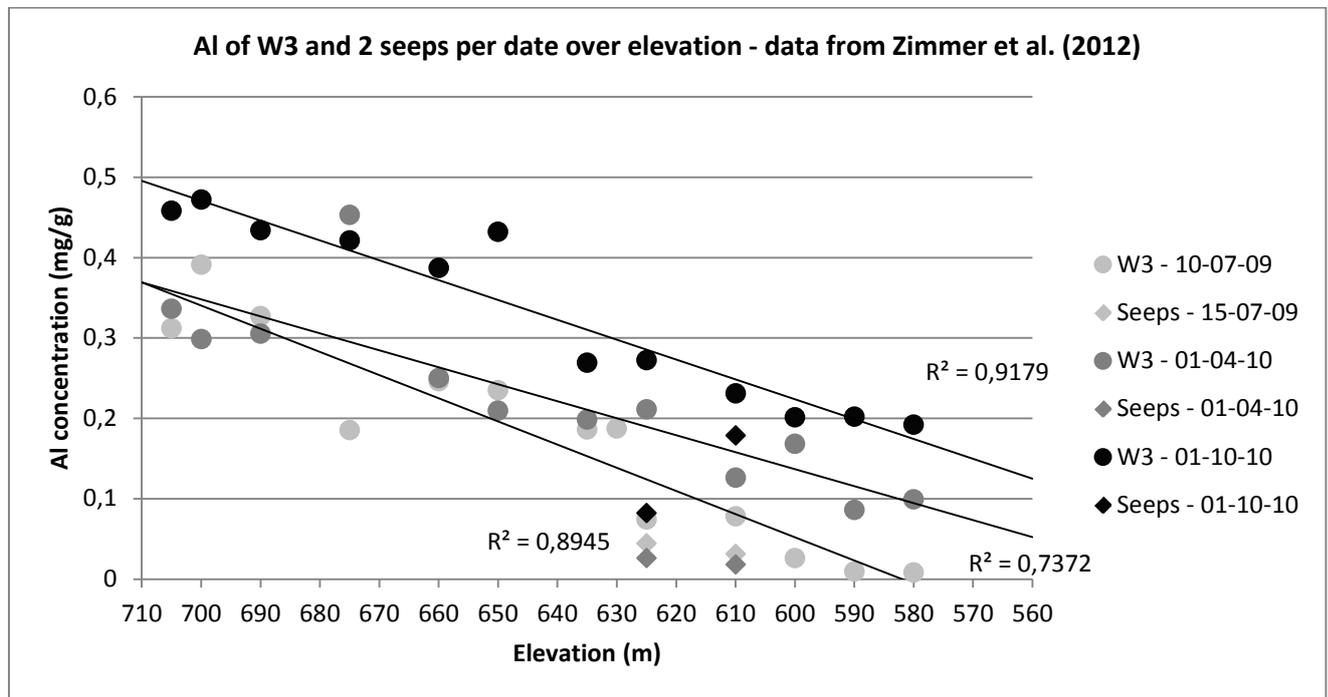


Figure 30. Elevation is shown on the horizontal axis and Al concentrations on the vertical axis. This is done with data from Zimmer et al. (2012) for W3 (circles) and the two seeps (diamonds).

Figure 31 shows increasing Na^+ concentrations going downstream in W3. There is an increase visible for all datasets, but the increase is steeper on the 10th of July, 2009, and less steep on the 1st of April, 2010. The Na^+ concentrations range between $0,27 \text{ mg g}^{-1}$ and $1,14 \text{ mg g}^{-1}$. The seeps show overall higher Na^+ concentrations with the highest concentrations of $2,05 \text{ mg g}^{-1}$ and the lowest concentration of $1,18 \text{ mg g}^{-1}$. When the different sample dates are compared there is a decrease in average Na^+ concentrations visible over time. The Si concentration for W3 in figure 32 ranges between $0,00 \text{ mg g}^{-1}$ and $2,30 \text{ mg g}^{-1}$, and shows an increase for the sample dates of the 1st of April, 2010 and the 1st of October, 2010, going downstream. The Si concentrations for the 10th of July show the lowest and highest concentrations of W3 and a decreasing trend line with a corresponding R^2 value of 0,02 that is not significant. This highest concentration of Si measured in W3 corresponds with the elevation of seep 2 at 609,3 m. All three sample dates show a peak Si concentration at this elevation, whereas below this point the Si concentrations show a decreasing trend going downstream instead of continuing the increasing trend line. The seeps show the highest Si concentrations of $4,61 \text{ mg g}^{-1}$. The lowest Si concentration is $1,90 \text{ mg g}^{-1}$. Figure 33 shows the Ca^{2+} concentrations that are within a range of $0,27 \text{ mg g}^{-1}$ and $0,75 \text{ mg g}^{-1}$. The trend for all sample dates is increasing going downstream. The Ca^{2+} concentration in the seep water is overall higher than in stream water with a lowest concentration of $1,13 \text{ mg g}^{-1}$ and the highest concentration of $2,52 \text{ mg g}^{-1}$.

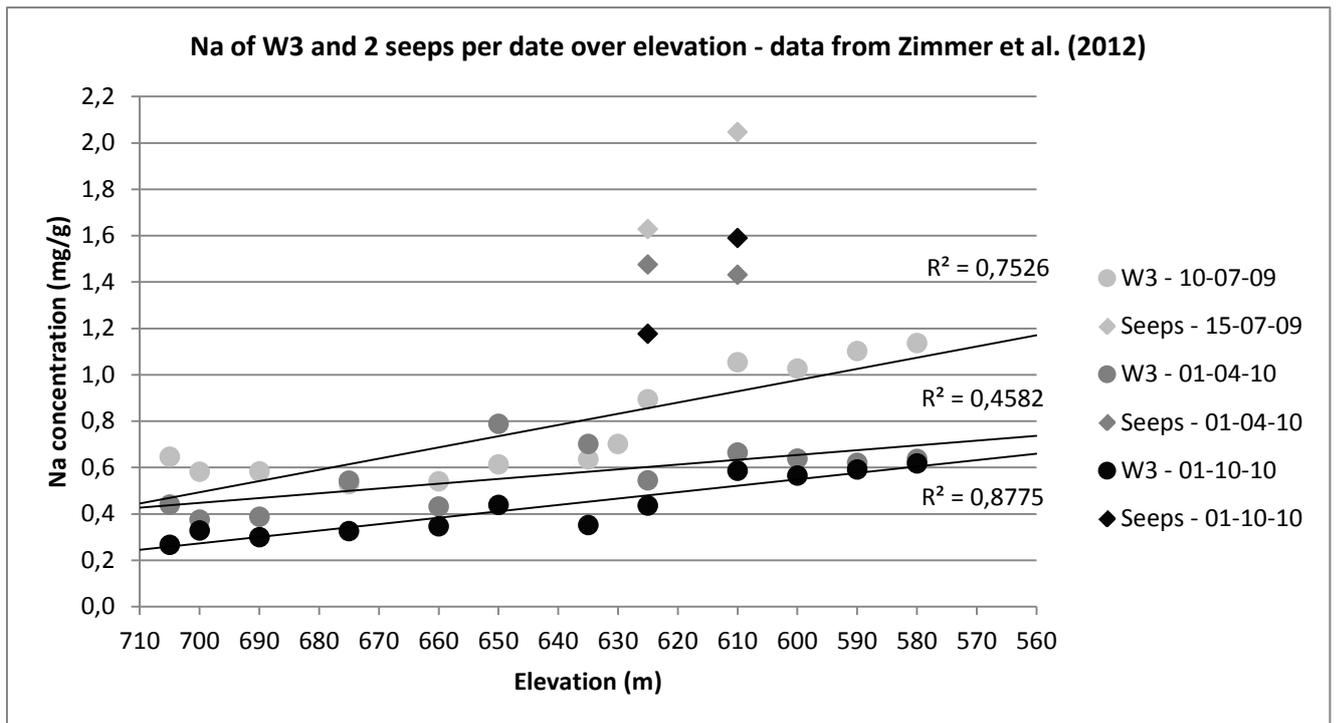


Figure 31. Shows elevation on the horizontal axis and the Na concentration on the vertical axis.

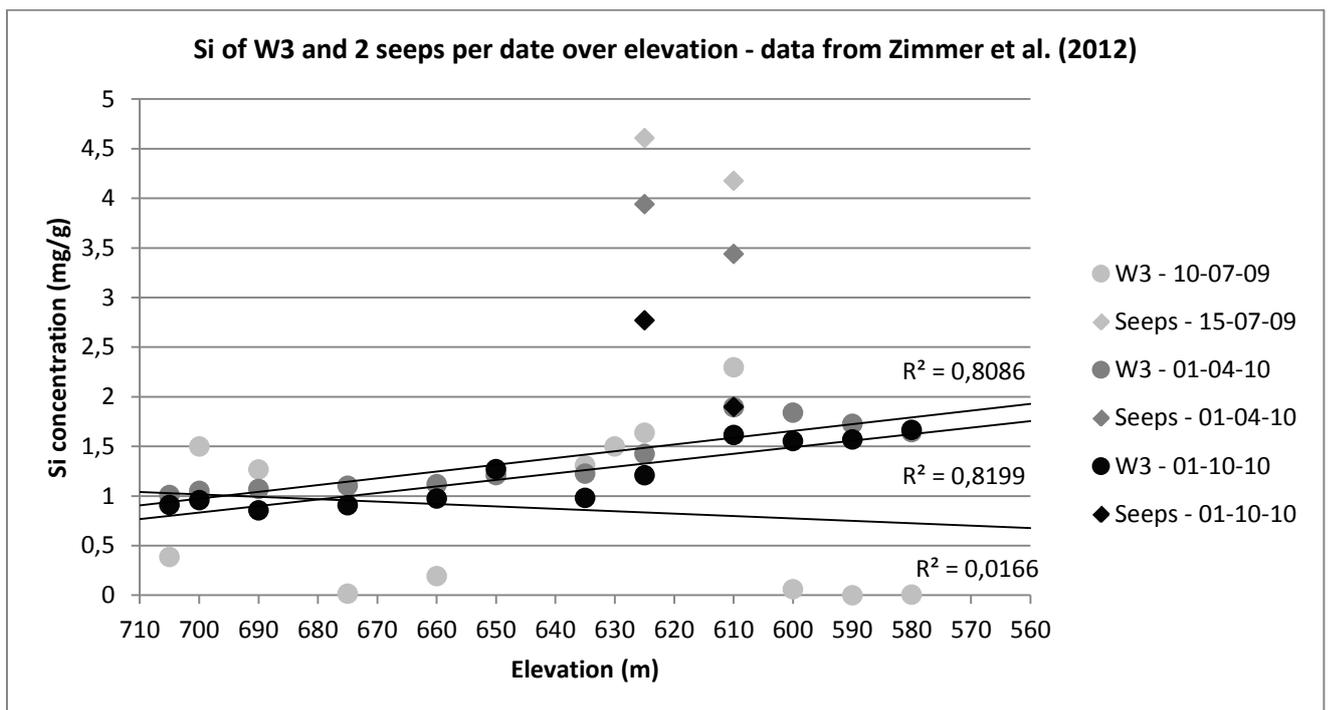


Figure 32. The horizontal axis shows the elevation, and the vertical axis the Si concentration.

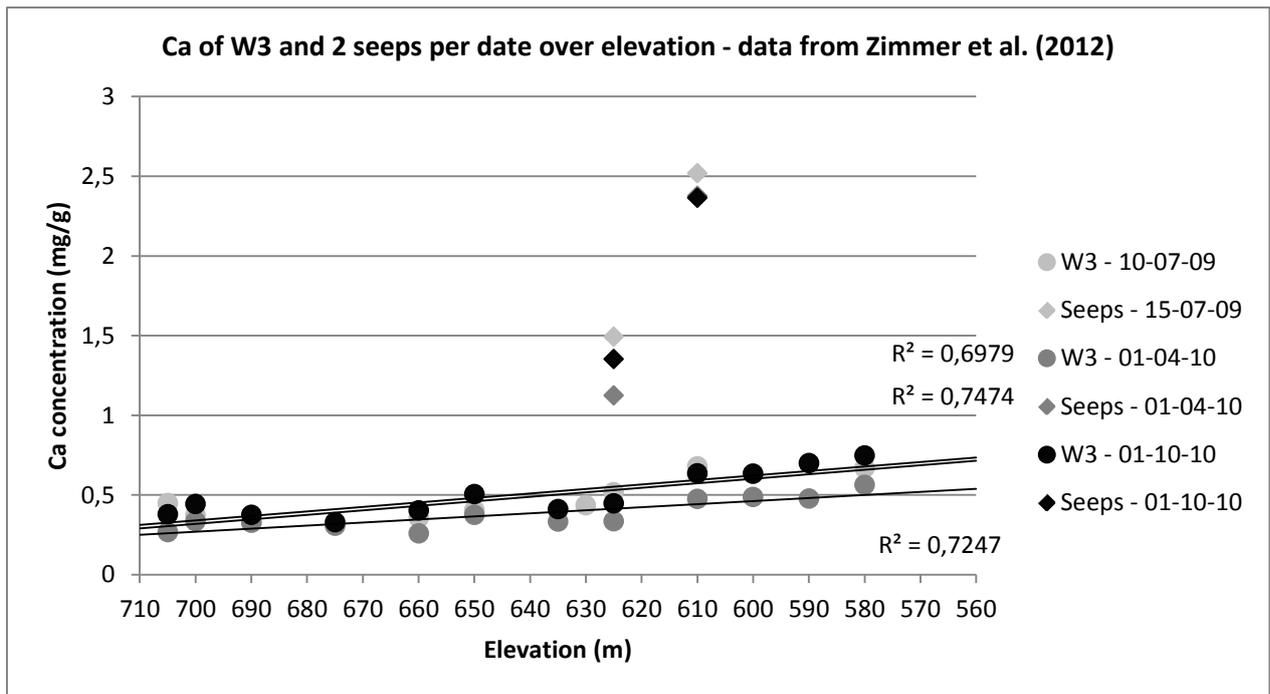


Figure 33. On the horizontal axis elevation is plotted against Ca concentration on the vertical axis.

4. Discussion

4.1 Interpretations

4.1.1 Increase in discharge going downstream

An overall increase in discharge is shown moving downstream for both tributaries, W2 and W3, what could be explained in multiple ways. One is that there could be an increase due to the seeps located along W3 at an elevation of 609,3 m and 622,0 meters (horizontal red lines in figure 6). It is assumed that if seep water has an influence on stream water this is likely to be downslope of the seep locations (Zimmer et al., 2012). This means that these results show that there is an input of seep water to the stream water downstream. When we look at the change in discharge of W3 and W2 per reach, in both a gain of water is followed by a downstream water loss. In W3 however this loss is followed by a reach where water gain is measured again. This could also be in favor of an input from seep water as it is not observed in the results from W2.

A second explanation of the increase in stream discharge going downstream has to do with the electrical conductivity (EC) of the stream that fluctuates throughout the day. These fluctuations account for the lack of exact return of EC to background values after a salt wave passage. O'Neill (2012 – unpublished) also reported minor fluctuations in EC in the stream that were even observed within the 10 minute intervals of data recording. These fluctuations could be due to instrument sensitivities (Ward et al., 2013); for this research this means the used temperature - conductivity probes.

A third point to consider here is time. The discharge decreases while moving upstream, but the measurements are also later in time. The water flow decreases throughout the day (Payn et al., 2009). This decrease in discharge is clarified with the recession analysis and explains the process of drainage or recession rate in periods with little or no new input of event water by rainfall to a stream (Tallaksen, 1995). This is supported by the data from the weir at the outlet of watershed 3 (figure 7) that also shows a decrease as the day progresses. This decrease induces an overestimation of water gain and an underestimation of water loss to the stream (Payn et al., 2009). This is however not relevant for this research as the downstream reaches are of most importance for detection of seep water input.

4.1.2 Chemistry of seep water and stream water during snowmelt

The seep water from the seep (seep 3) that was sampled during the snowmelt period in the months March and April, 2013, was assumed to be representative for the seeps that were used for the summer fieldwork (seep 1 and seep 2). Nevertheless, this seep does not have a surface or subsurface flow connection to the tributaries W3, or W2, that were used in the summer fieldwork to determine the chemical composition of stream water.

The results from the chemical analyses from the water samples taken during the spring fieldwork are showing very constant values for pH and the anions during snowmelt. This is in contrast with the findings from Kuhn (2001) that state that the first releases of water from snowmelt have relatively high concentrations of nutrients and acids, and therefore as well as the hypothesis stated, the first flux of snowmelt will show a change in chemical composition and an decrease in influence with an ongoing snowmelt event. Even this last point must be refuted as the composition of the seep water stays constant over time.

There is a peak noticeable at the 5th of April, 2013 in DOC, TDN and NO₃ concentrations. This peak can be caused by contamination of the water sample. This peak is not apparent in the stream water samples taken at the two sample sites (W3A and W3F) at tributary W3. This peak also does not show up at the 5th of April, 2013, in the stage height and precipitation data from the weir at the outlet of watershed 3. It is therefore reasonable to say that this peak was caused by contamination and should be disregarded in the results. When we erase this data point from the graphs it can be stated that also the seep stays constant in DOC, TDN and NO₃ during a snowmelt event.

When comparing the chemical composition of stream water with the seep water during a snowmelt period, it can be confirmed that seep water in general, with a few exceptions, shows higher concentrations in pH and anions than the stream water. If this seep water actually has an influence on the chemical composition of stream water it cannot be supported with this specific dataset, because this seep is not connected with the tributary W3.

4.1.3 Chemistry of two tributaries compared

The results from summer on the chemical composition of seep water also shows overall higher pH values than those results from stream water. We can see an increase in pH values moving downstream in both W2 and W3 for the two sample dates. The increase in pH in W2 however is less steep than that in the water samples taken from W3, this is also seen in the data from Zimmer et al. (2012). This could indicate an influence of the two seeps that is significant and causes a steeper increase in pH downstream of the seeps in W3.

However, it can also be discussed to what extent W2 and W3 are comparable. This is further endorsed by the results from the DOC, SO₄²⁻ and NO₃⁻ concentrations from the samples collected at the 2nd of July, 2013. There is an exponential decrease in concentration with decreasing elevation in W3, this is however not seen in W2, where the DOC concentrations stay stable over elevation. This same trend in W2 is visible for the SO₄²⁻ and NO₃⁻ concentrations that are stable over elevation, this validates for the incorrect assumption to compare these tributaries.

The relative high DOC concentrations measured upstream in W3 could be caused by high amounts of organic matter that are in contact with the tributary due to local shallow surface flowpaths (Zimmer et al., 2012). There is no visible influence of the seeps on the stream water DOC concentration, because the seeps have similar DOC concentrations as W3. In the results for the SO₄²⁻ concentrations there is an increase shown in W3 going downstream that is quite significant. This rising concentration of SO₄²⁻ has however already started above the two seeps. It is therefore not plausible to state that the SO₄²⁻ concentration in seep water has an influence on stream water. The NO₃⁻ concentration in the seeps is again relatively high, due to denitrification in this anoxic zone (McClain et al, 2003). In W3 there is no increase detected downstream of the seeps, this could mean that there is not an influence of seep water on stream water.

When we look at the cations Na, Si and Ca from former data by Zimmer et al. (2012) (respectively figure 30, 31 and 32) we see comparable results of relatively higher concentrations in

Na^+ , Si and Ca^{2+} in the seeps, this indicates that this seep water consists of 'old' or pre event water and could originate from deeper groundwater. Also the diverging trend in Al^{3+} concentrations showing a decrease in concentration going downstream suggests that seep water consists of 'old' water. Focusing on the significant decrease of Al^{3+} concentration in W3 going downstream is related to the the observed increase in discharge going downstream (see paragraph 4.1.2). This is however in contrast with the statement of Lawrence and Driscoll (1990) that says that Al^{3+} concentrations increase with increasing discharge. The Al^{3+} concentrations of the seeps are relatively low in comparison with the stream water and it can therefore be stated that there is no influence on W3 by Al^{3+} concentrations. The increasing trend in Si concentrations down to the elevation of seep 2 of 609,3 m followed by a decrease going further downstream could suggest an influence of the seeps on W3. This same trend however is observed in the Si concentrations in W2. It is therefore not valid to say that seep water effects the stream water in W3. What can be discussed is the possibility to compare W2 and W3 as the results for the cations in W2 showed similar trends as W3. This last point is in contrast with the statement made above that W2 and W3 could possibly not be compared.

Next to this, it was assumed that there was no seep located along W2 as it was not visible and detected. It can however not be ignored that there could still be seeps that are not discovered yet, as it is difficult to presume as watershed 3 has been well-studied.

4.1.4 Chemistry of seep water and stream water in time

When we add time to the analyses we can see that based on the data from the spring and summer fieldwork there are only significant changes in chemical composition in both stream and seep water for DOC and NO_3^- concentrations. Going from spring to summer DOC concentrations, there is a minor increase shown in stream water, this is due to the earlier mentioned higher interaction with organic matter as the stream becomes more shallow in summer in comparison with spring (Zimmer et al., 2012). The decrease in NO_3^- concentrations from spring to summer is explained by the seasonal variability in stream water. The demand for NO_3^- during the growing season is relatively large, what leads to lower concentrations of NO_3^- in the stream in summer and a higher concentration in spring during the non-growing season (O'Driscoll and DeWalle, 2010).

The results including data from Zimmer et al. (2012) show the same trend lines as the data collected in this research. Outstanding are the results for SO_4^{2-} concentration that show an increase from July 2009 to October 2010, what could be due to the season of the sampling. However, the results for SO_4^{2-} concentrations in July 2013 are relatively low again. Na^+ concentrations decrease over time, and Al^{3+} concentrations show an increase, due to the increase in discharge of the stream when we look at the dates from the analyzed samples.

4.2 Limitations

This research experienced some limitations that are mentioned shortly below. The tracer dilution method highly depends on the flow conditions. Even though this method is suitable to perform in relatively smaller streams, disconnection of flow and development of pools created areas of transient storage whereby the time period of passage of the salt wave prolonged. Because it was known that the two tributaries that were used in this research, W2 and W3, would desiccate in the course of the summer; the right conditions were needed to conduct a series of salt injections in the stream. This mainly meant that the tributaries had enough flow after precipitation events. It must be noted however that it is preferable not to perform this method during an event, because of the dilution of the injected salt with the rain water what could influence the breakthrough curve by making it more stretched (Ward et al, 2013). This research experienced relatively dry months in summer (figure 4), therefore making it difficult to obtain multiple datasets of discharge measurements.

Also depending on the flow conditions is the electrical conductivity (EC) that is introduced in the previous paragraph. The conductivity in a stream fluctuates during the day. This makes it impossible to determine a correct background EC, and the impossibility for the EC to return to the

exact same background EC after the salt wave has passed. These fluctuations in EC can be ascribed to the sensitivity of the probes, but also to the changing stream conditions with temperature as a factor influencing the EC values (Payn et al., 2009).

The mixing length that was based on the former study done by O'Neill (2012 - unpublished) was adjusted for the specific flow conditions. Where a lower flow depended more on the flow rate in the stream whereas with high flow the mixing length depended more on stream morphology. The mixing length in the field was determined by the flow conditions and the amount of pools present, therefore this deviated from the 20 meters mixing length that was previously established with the research performed by O'Neill (2012) (paragraph 2.3.3).

Considering the large number of water samples that were collected for chemical analyses, the selection that was made excluded important and possible decisive results. Next to this reduction in sample size, not all selected water samples were yet analyzed while writing this report due to the limit in time and dependence on the labor availability of the laboratory where the samples were to be analyzed.

4.3 Future research

As this tracer injection method was new to the Hubbard Brook Experimental Forest it is recommended to repeat this method several times to get a more reliable dataset, it is even suggested to extend it to other watersheds to emphasize the spatial component. For a better insight in the temporal aspect it would be interesting to perform discharge measurements during a period of snowmelt in combination with longitudinal sampling of water along the tributary.

It was discussed that W2 and W3 were possibly compared incorrectly as it was assumed that they had comparable flow characteristics. Due to this uncertain assumption it is worth comparing discharge measurements and chemistry of more tributaries in the same watershed.

Also more research still needs to be done on seeps as they are an important component in headwater catchments. Because their complexity in general and the influence they have on the environment, more research is needed to be able to determine the importance of the seeps on their environment and on stream water.

5. Conclusions

The measured discharges in the two tributaries in watershed 3 do not show a significant change that could be caused by the input of seep water. Both tributaries show an increase in discharge going downstream. It can therefore not be concluded that the increase in the tributary along the seep is caused by the input of seep water to the tributary. Also due to the limited number of datasets the influence of seep water could not be determined. More discharge measurements are needed from different water flow conditions.

Seep water has a distinct chemical composition that does not influence stream water during a snowmelt event. The results stay constant over time. Also in summer the overall higher concentrations of SO_4^{2-} and NO_3^- in seep water do not influence the stream water as there are no significant changes measured. Also the cations show constant and similar trends in both tributaries, without a visible influence of the higher concentrations in seep water on one of the tributaries.

It can be stated that stream water chemistry is not influenced by seep water chemistry downstream of the seeps. This stays the same over time when data from Zimmer et al. (2012) is included from 2009 and 2010.

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Appendix 1.

Sample site ID (Reach name)	Elevation_DEM (m)	Approximate distance from outlet to PB (m)	UAA (m ²)
Seep 1	621,96	-	6,93
Seep 2	609,32	-	5,53
Seep 3	672,02	-	8,32
W2A	565,97	50	694,09
W2B	578,29	100	692,38
W2C	590,60	150	504,62
W2D	602,00	200	105,38
W2E	613,58	250	577,64
W2F	629,02	300	16,10
W2G	642,35	350	116,36
W2H	655,86	400	277,53
W2I	662,11	450	126,05
W2.1A	670,78	500	131,91
W2.2A	674,66	500	67,12
W2.1B	684,33	550	99,48
W2.2B	690,74	550	88,54
W30	569,17	0	806,43
W3A	580,16	50	7,52
W3B	590,21	100	708,06
W3C	600,67	150	144,51
W3D	611,33	200	829,24
W3E	624,89	250	82,20
W3F	628,12	275	280,79
W3G	636,93	325	511,01
W3H	649,29	375	108,02
W3I	658,88	425	185,18
W3J	673,77	475	18,04
W3K	688,18	525	161,81
W3L	697,47	575	56,38
W3M	705,33	625	101,72

Table 1. The names of the sample sites are correlated with their elevation based on DEM values, the distance from the outlet of the tributary to the main stream, Paradise Brook (PB), and the Upslope Accumulated Area (UAA).