Examensarbete 30 hp Mars 2009



Sveriges lantbruksuniversitet

Water chemistry of the riparian zone in the forest landscape

Skogslandskapets inverkan på vattenkemin

i bäcknära zonen

Julia V. Paraskova

ABSTRACT

Water chemistry of the riparian zone in the forest landscape

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A riparian zone is the strip of land adjacent to the stream that plays an important role in the forest landscape. Its unique ecology supports a wide variety of life and serves as a boundary between the terrestrial and aquatic environments. An important function of the riparian zone is to serve as a chemical buffer, intercepting nutrients and preventing them from reaching the stream. It is hypothesized that yet another function of the zone is to shape the chemical composition of the runoff water, as it is the last soil that the water comes in contact with before it reaches the stream.

The aim of this thesis was to study the water chemistry in the forest landscape through water extracted from soil profiles in different riparian zones. The project was carried out in the Krycklan Riparian Observatory located in Svartberget Experimental Forest near Vindeln, in northern Sweden and was based on a previous study from the same area which used data from a single soil plot. The object of this work was to expand the study by including a variety of monitored riparian zones located in different landscape units. For this purpose soil chemistry was monitored for six months at thirteen sites. Analyses of the samples included measurements of absorbance and pH values as well as the determination of dissolved organic carbon (DOC) content. This was related to groundwater variations and stream discharge.

Results allowed the sites to be grouped into four types of riparian zones, based on topography and common characteristics – *forest*, *wetland*, *hillside* and *fluvial*. The most important factor determining the hydrological characteristics of the different riparian zones was topography, specifically the slope of the ground surface. The variations in the pH value were consistent with the presence and quantity of organic material. The lowest pH value was found in the top layers of all soil profiles with a subsequent rise with increasing depth. The DOC concentration in the *forest* and *wetland* profiles showed a clear seasonal dependency, whereas no seasonal variations could be observed for sites located in well-drained hillslope areas, represented by the group *hillside*.

Keywords: riparian zone, soil water, water chemistry, DOC, forest landscape

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REFERAT

Skogslandskapets inverkan på vattenkemin i bäcknära zonen

Julia Paraskova

Bäcknära zonen, *riparian zone* på engelska, innefattar bäckens omgivning och spelar en viktig roll i skogslandskapet. Den unika positioneringen gynnar den ekologiska mångfalden, där zonen fungerar som en gräns mellan de terrestra och akvatiska miljöerna. Bäcknära zonen har en viktig funktion som en kemisk buffert som fångar upp näringsämnen från genomströmmande vatten och hindrar dem från att nå bäcken. En hypotes är att zonen påverkar den kemiska sammansättningen av det avrinnande vattnet då den är den sista jordprofilen som vattnet kommer i kontakt med på sin väg mot bäcken.

Examensarbetets mål var att studera hur bäcknära zonens vattenkemi påverkas av skogslandskapet genom att undersöka markvatten som extraherats från olika provplatser. Projektet utfördes i Krycklan Riparian Observatory som ligger i Svartbergets försökspark i Vindeln i norra Sverige och baserades på en tidigare studie från samma område med data från enbart en markprofil. Målet med det nya arbetet var att utvidga undersökningen för att omfatta ett antal olika bäcknära zoner från olika delar av landskapet. Följaktligen övervakades mark- och vattenkemi i sex månader på tretton olika platser. Analysen av proverna inkluderade mätning av absorbans och pH-värde samt beräkning av halten löst organisk kol (DOC). Dessa värden relaterades sedan till variationer av grundvattennivå och flöde i bäcken.

En utvärdering av resultat möjliggjorde en indelning av bäcknära zonerna i fyra typer, utifrån topografi och gemensamma kännetecken: *skog*, *våtmark*, *sluttning* och *fluvial*. Topografin, speciellt markens lutning, var avgörande för läget på grundvattendjupet i de olika bäcknära zonerna. Variationerna i pH-värden överensstämde med förekomsten och mängden organiskt material. De lägsta värdena påträffades i det översta skiktet av samtliga studerade jordprofiler och därefter steg pH-värdet med ökat djup. Halterna DOC i typerna *skog* och *våtmark* visade ett tydligt säsongsbetonat beroende, medan inga variationer påvisades för typen *sluttning*.

Nyckelord: bäcknära zon, markvatten, vattenkemi, DOC, skogslandskap

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PREFACE

This thesis is submitted as a partial fulfilment of the requirements for the degree of Master of Science in Aquatic and Environmental Engineering at Uppsala University. The work was carried out at the Department of Aquatic Sciences and Assessment at the Swedish University of Agricultural Sciences (SLU), Uppsala. Thomas Grabs, Ph.D. student at Stockholm University has supervised the project. Professor Kevin Bishop from the Department of Environmental Assessment, SLU has reviewed it.

The project is part of an extensive study that started in 2002 in Vindeln Experimental Forest of SLU. In 2005 the Krycklan Riparian Observatory (KRO) was created in order to study the effects of the riparian zone on stream water chemistry. The KRO is a collaboration between SLU Umeå, SLU Uppsala and Stockholm University.

Many people have made this project possible. I would like to thank:

- Kevin Bishop for his incredible enthusiasm that made me so interested in this project and for always finding the time to answer my questions.
- Magdalena Nyberg and Rémi Masquelier for making field work easier and much more fun.
- Peder Blomkvist, Viktor Sjöblom, Maria Ingvarsson, Mahsa Haei and Ida Taber for helping me out in Umeå even though they didn't have to.
- Carolin Haglund, Linnéa Sparrman and André Spans for making life "at work" something to look forward to every day.
- Daniel Lundberg for being my trusted editor and for making everything look pretty.
- The Department of Chemistry at SLU for all the great Fridays they let me score on the innebandy field.

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UPTEC W 09 004, ISSN 1401-5765

Printed at the Department of Earth Sciences, Geotryckeriet, Uppsala University, Uppsala, 2009.

POPULÄRVETENSKAPLIG SAMMANFATTNING

Bäcknära zonen, *riparian zone* på engelska, innefattar bäckens omgivning och spelar en viktig roll i skogslandskapet. Definitionen för bäcknära zonen beror på den specifika studien och kan innefatta allt ifrån en smal markremsa nära bäcken till ett stort område som översvämmas då ett vattendrags vattennivå stiger över sin naturliga bädd. Zonens unika position i landskapet gynnar den ekologiska mångfalden vilket leder till att den fungerar som ett slags gräns mellan mark- och vattenmiljön. En viktig funktion av bäcknära zonen är att fungera som en kemisk buffertzon som fångar upp näringsämnen från genomströmmande vatten och hindrar dem från att nå bäcken. En hypotes är att zonen också påverkar den kemiska sammansättningen av det vatten som rinner igenom den, eftersom den är den sista jordprofilen som vattnet kommer i kontakt med på sin väg mot bäcken.

Examensarbetets mål var att studera hur bäcknära zonens vattenkemi påverkas av skogslandskapet genom att undersöka markvatten som extraherats från olika områden. Projektet har utförts vid Krycklan i Svartbergets försökspark i Vindeln. Arbetet är en del av ett större samarbetsprojekt mellan Sveriges lantbruksuniversitet och Stockholms universitet och är en fortsättning på en tidigare studie som undersökte en mindre del av samma avrinningsområde, Nyänget. Då den föregående studien grundades på resultat av endast en försöksplats, ville man med den nuvarande studien utvidga undersökningen för att omfatta ett antal olika bäcknära zoner från olika delar av landskapet. Därför studerades mark- och vattenkemi i sex månader på tretton olika platser som valdes ut på grund av sina olika topografiska egenskaper. Målet var att täcka in olika typer av bäcknära zoner såsom våtmarker, skogbeväxta områden eller platser med lite vegetation, plana och sluttande, samt ytor på olika höjder över havet.

Provtagning skedde en gång per månad med totalt sex olika provtagningstillfällen från maj till oktober 2008. Vattenprover samlades med hjälp av lysimetrar, apparater som med hjälp av undertryck suger upp vatten från jorden. Även platsernas grundvattendjup samt vattenflöde i en av bäckarna mättes kontinuerligt under försöksperioden. Grundvattennivåerna kontrollerades också manuellt för att kunna verifierade automatiskt uppmätta värdena. Flödesmätningar gjordes dock endast vid en bäck, Västrabäcken, vilket ledde till antagandet att flödet inom hela avrinningsområdet var detsamma per ytenhet. Analysen av proverna inkluderade mätning av absorbans och pH-värde samt beräkning av halten löst organisk kol (DOC).

Från fältobservationer och absorbansresultat kunde man gruppera bäcknärazonerna vid de olika provplatserna i fyra grupper. Utifrån topografi och gemensamma kännetecken klassificerades grupperna som *skog*, *våtmark*, *sluttning* och *fluvial*. Gruppen *skog* innehöll platser som karakteriserades av en relativt plan och skogsbevuxen mark med ett avsevärt lager av organiskt material i de översta skikten. Gruppen *våtmark* innehöll platser som ibland översvämmades och som innehöll mycket organiskt material i alla skikt i form av torv. Gruppen *sluttning* representerade områden som antingen befann sig i sluttningar eller angränsade till sluttningar och var därför väldränerade, där mängden organiskt material var begränsat. Här fanns det även stenar och grövre jordmaterial än på de andra platserna. Gruppen *fluvial* låg i den lägsta delen av försöksområdet ovanpå glaciofluvial sediment,

d.v.s. ett sedimentet som avsatts i ett vattendrag, bildat av smältvattenströmmar från glaciärer eller inlandsisar (NE 2009).

Variationerna i grundvattennivå under hela halvårsperioden kopplades till flödesmätningar i bäcken. Å ena sidan ville man veta om variationerna i flöde som orsakades av regntillfällen alternativt torka följdes också av en respons i grundvattenytan, å andra sidan ville man se hur bra relationen var och studerade den genom korrelationsgrafer. Resultaten visade att på alla utom tre provplatser fanns det ett tydligt samband mellan flöde i bäcken och variationen i grundvattennivå. På två av provplatserna där det inte hittades något samband var troligen instrumenten trasiga. Ett tredje område var en myr där grundvattenytan ofta låg ovanför markytan. Instrumentet var ej avsett att registrera vatten *ovanför* markytan och visade därför en nästan oförändrad nivå under hela försöksperioden.

Den ytligaste medelgrundvattennivån observerades hos gruppen *skog*, där även stora regntillfällen och torrperioder medförde små ändringar i grundvattendjupet. Hos gruppen *våtmark* fann man perioder då grundvattenytan steg kraftigt och resulterade i ytavrinning. Provplatserna blev då översvämmade, en av dem i över en månad. Responsen från grundvattnet var mycket kraftigare än den hos gruppen *skog*. I gruppen *sluttning* låg grundvattennivån djupast, vilket var en följd av att platserna var väldränerade. Inga specifika drag påvisades för gruppen *fluvial*, eftersom topografin var avgörande för läget på grundvattennivån.

Variationerna i pH-värde överensstämde med förekomsten av och mängden organiskt material på respektive plats. De lägsta värdena påträffades i det översta skiktet av samtliga jordprofiler och därefter steg pH-värdet med ökat djup. Vid elva av tretton av provtagningsplatser var pH-värdet väldigt nära pH = 7 på 75 cm djup.

DOC-halterna i grupperna *skog* och *våtmark* visade ett tydligt säsongsbetonat beroende, medan inga variationer påvisades för gruppen *sluttning*. Variationerna i DOC kunde hänföras till en rad faktorer. Den största ökningen observerades på platser där marken var plan, grundvattennivån låg ytligt och där det fanns mycket organiskt material.

För att kunna fortsätta studien av de olika bäcknära zonerna behövs det en mer detaljerad indelning inom grupperna där utöver de redan använda karakteristika, även jordmånstyp, en kvantifierad mängd organiskt material samt beräknad lutning av den studerade platsen skulle vara nödvändiga att ingå.

Förståelsen av hur DOC ändras inom den bäcknära zonen är viktigt då man vill hitta nya sätt att hantera olika miljöproblem. En viktig egenskap hos DOC är att binda olika joner av betydelsefulla metaller, däribland järn, koppar, kvicksilver och aluminium. Därmed möjliggörs metalljonernas transport från bäcknära zonen till bäcken. En säsongbetonad ökning av DOC skulle kunna resultera i ökade halter av metalljoner både i bäcknära zonerna och i vattendragen, vilket i sin tur kan påverka livet både i mark- och vattenmiljön, beroende på metaljon.

SYMBOLS AND ABBREVIATIONS

А	Area	
Abs	Absorbance	
DOC	Dissolved Organic Carbon	
GIS	Geographic Information System	
1	Length	
pН	- $\log_{10} [\text{H}^+]$	
Q	Flow	
R	Specific discharge	
SAGA	Simple API for Grid Applications	
SLU	Sveriges lantbruksuniversitet	Swedish University of Agricultural Sciences
TOC	Total Organic Carbon	
λ	Wavelength	

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1. INTRODUCTION

1.1 BACKGROUND

1.1.1 Aim of the project

The purpose of this thesis is to explore the nature of the riparian zone in the forest landscape from a chemical perspective. It has been proposed that water entering the stream receives its chemical signature from riparian soils (Bishop 2004). From the moment water falls on the ground as precipitation until the moment it emerges from the ground to enter the stream it undergoes many changes. Depending on soil residence times, flow pathways and the speed at which the water moves, those changes are more or less significant. It is then reasonable to assume that since the riparian soils are the last soils to come in contact with the water before it reaches the stream, they leave an imprint on the water's chemical composition. This assumption is supported by a study of the Nyänget catchment in Vindeln, northern Sweden which links the chemistry of the soil with stream chemistry (Bishop 2004). A shortcoming of that study is that it was based on data from only one stream and a single soil plot, although several soil profiles were monitored. The object of this work is to include a variety of monitored riparian zones located in different landscape units in an attempt to study what deciding factors in the landscape shape the riparian zone. Since organic matter in the forest plays a major role in deciding the chemical composition of soil water a closer look at dissolved organic carbon (DOC) was also taken.

1.1.2 The riparian zone

The definition of a riparian zone can be quite broad depending on the focus of the specific study and can be described in a variety of ways. In the broadest sense the riparian zone is the area around the stream. Depending on the size of the stream it can span from a narrow strip of land to a larger plane, and can be very different in character. One view of such a zone is the flood plane occurring along a river that has spilled over its natural confines (Britannica online, 2008). Yet, when the riparian zone was first described in the beginning of the nineteenth century, it only pertained to the vegetation in proximity the stream. Later, however, it has been expanded to include a wider strip of land (Burt et al. 2002). It is not always land area that constitutes the riparian zone. Some view them as "ecological boundaries, or ecotones, which physically separate terrestrial and aquatic ecosystems" (Burt et al. 2002). Regardless of the definition at hand, riparian zones are subject to great variability due to their nature since they either represent a type of wetland or are dependent on the shape and size of the adjacent stream. As a result of large scale geological and climatological influences and small scale topographic and hydrological effects the zones rarely look the same. In addition, their properties vary over the seasons and between years due to, among other things, variations in the groundwater table (Hatterman et al. 2006).

Defining the main purpose of the riparian zone is difficult, as the zone *de facto* fulfills two functions simultaneously. On one hand the zone acts as a template for the chemical composition of water that flows into the stream, and on the other hand it binds many elements within it, thus preventing them from getting into the stream. The duality of the riparian function can be seen in its ability to act both as a source and a sink for different chemical elements. For example, in agriculture, it acts as a sink for nutrients, specifically

nitrogen and phosphorus, which are washed from the fields and captured in the zone on their way to the stream. On the other hand, the zone which is rich on organic material, acts as a source of DOC. DOC is produced as a result of the dissolution of decomposing organic matter in the soil water that eventually leaches into the stream. The supposition that the riparian zone "links the terrestrial and aquatic environments, but also acts as a barrier between them" (Burt 2005, p. 2088) sums it up quite neatly. One explanation of this phenomenon is related to the time scale, i.e. if the water moves through the soil rapidly (time scale of hours to days), its chemistry will be influenced by the soil, but if instead it moves through the soil slowly (time scale of months or longer) it will itself have an effect on the chemistry of the soil (Bishop *et al.* 2004). Interestingly, the opposite can also be true! If the water constantly flows through the soils rapidly it will continuously export DOC from the soil. This could result in relatively low DOC concentrations in the soil water, which would in turn have an impact on the soil through a change of its microbiological composition.

In this project the riparian zone has been defined as the area contiguous to the stream, including soil and vegetation (Fig. 1). One important detail is that the width of the zone varies from site to site because it is defined by flow paths of the water and soil characteristics.



Figure 1: Project definition of the riparian zone

1.1.3 Why study riparian zones?

The significance of riparian zones has been discussed in many different studies, especially in the last couple of decades (Peterjohn & Correll 1984, Decamps *et al.* 1988, Gilliam 1994, Spruill 2000, Nieminen *et.al.* 2005, MacNally *et al.* 2008). Two areas in particular have interested scientists: biodiversity and eutrophication. Due to their unique ecology the zones support a wide variety of life and have therefore been of great interest to biologists (Toner & Keddy, 1997, Bretschko *et al.* 2001, Jiang *et al.* 2005). Additionally it has been shown that the zones serve as a buffer for the streams, intercepting nutrients from agricultural lands and that has facilitated interest in research of the riparian zone for environmentalists (Lowrance *et al.* 1983, Vought *et al.* 1994, Rosenblatt *et al.* 2001). In

Scandinavia the zones' importance has been explored in connection to the interception and retention of nitrogen from forests that have been clear-cut (Jacks & Norrström 2004, Kokkonen *et al.* 2006). In Sweden the riparian zone has been analyzed as the source of DOC and some metals, such as aluminum, iron and mercury, among others, and it has therefore been hypothesized to exert major control on the water chemistry (Cory *et al.* 2007). Understanding the processes that govern the chemistry and transport mechanisms of the soil near the streams can be crucial in developing new ways of dealing with pollution.

1.1.4 Study area

The results in this thesis are based on soil-water samples collected from the Krycklan catchment, located in the research park Svartberget in Vindeln, Sweden (Fig. 2). The catchment has an area of 68 km^2 and is a forested watershed, consisting of a network of streams. It represents a typical boreal catchment in northern Sweden. It is situated about 50 kilometers northwest of the city of Umeå and 30 kilometers from the coastal line of the Gulf of Bothnia.



Figure 2: Positioning of the Krycklan catchment, modeled in GIS, in Sweden and a view of the study area within it.

The landscape within the catchment is characterized by coniferous forests mixed with wetlands on podzol soils. The upland parts of the catchment are mainly forested, dominated

by mature Scots pine (*Pinus sylvestris*) in upslope drier areas and by Norway spruce (*Picea abies*) in low-lying wetter areas. Significant areas are covered by mires in the upper part of the catchment (Laudon *et. al* 2007). Wetlands and riparian zones are typically associated with deciduous species, mainly birches (*Betula spp.*).

The positioning of the sample sites within the study area can be seen in Figure 3. In an attempt to diversify the study and represent different types of riparian zones (such as forested areas or wetlands, higher and lower part of the catchment, flat or sloping surfaces, etc.) fifteen sites have been chosen. The selection process was based on visual inspection of the area, study of geological maps and various topographic indices as well as analysis of previously collected data on soil types.



0 400 800 1200 Meters

Figure 3: Positioning of the sampling sites within the study area.

A summary of the sites' characteristics is provided in Table 1 and a more detailed description can be found in Appendix 1. Observe that sites 3 and 13 were not included in the study. They were damaged soon after installation by an exceptionally high spring flood.

Table 1: Name of streams and characteristics of the study sites. * Denotes a site that was out of order.

Site	Stream name	Description
1	Fulbäcken	steep, slopes towards the stream, moraine
2	Fulbäcken	wetland, often flooded, moraine
3*	Fulbäcken	wetland, often flooded, moraine
4	Stortjärnsbäcken	steep, divergent, moraine
5	Västrabäcken	forest, flat, moraine
6	Västrabäcken	forest, flat, moraine
7	Västrabäcken	forest, flat, moraine
8	Kallkällmyren	wetland, stream outlet, peat, organic soil
9	Kallkällbäcken	steep, well-drained, moraine
10	Kallkällbäcken	wetland, moraine
11	Stormyrbäcken	wetland, wave-washed sediment, sand
12	Renberget	sloped, drained, moraine
13*	Åhedsbäcken	low in the catchment
14	Åhedsbäcken	wetland, coarse silt-fine sand, glacial sediment
15	Långbäcken	deep stream, drained hillside, glacial sediment

It is important to note that the landscape provides valuable information about the catchment and flow paths of water within it. With help of landscape analysis performed in ArcGIS and SAGA the catchment and the stream network could be visualized on a map, and allowed hillside area calculations to be completed. As proposed by Kokkonen (2006), hillslopes as basic landscape elements present a framework for observing interactions between landscape forms and processes that govern the transport of water and pollutants. Since the object of the study is to be able to generalize the riparian zone, it was important to have sites represent smaller and larger catchments, sloping and flat surfaces, wetlands with high content of organic material and drier areas with little peat content, as well as different bedrock and soil types.

A common practice in Sweden in the early twentieth century was to ditch headwater streams in order to improve drainage and forest productivity (Cory et al. 2007 and references therein). As a result, virtually all streams in the studied area have been deepened at some point in time, and it is believed that some of the streams in fact are not natural, but man-made. The impact of the ditching is lowering of the groundwater flow pathways, especially in the area near the stream.

1.1.5 Climate and hydrology

Mean annual air temperature in the area of the Krycklan catchment is $1.3 \,^{\circ}$ C, and the mean annual precipitation is 600 mm, 35% of which falls as snow (Löfvenius *et al.* 2003) and approximately 50 % becomes runoff (Ågren *et al.* 2007). The climate is characterized by short summers and long winters, with a snow cover from late October until early May (Laudon *et al.* 2007). The highest runoff peak can be observed in May during the spring flood and is due to extensive snowmelt (Ågren *et al.* 2007). Additional runoff peaks in summer and fall are caused by rainfall.

2. METHODS

2.1 FIELD WORK

 Table 2: Survey dates.

2.1.1 Sampling of soil water

Sampling was carried out on a monthly basis from May 2008 until October 2008 with a total of six surveys conducted (Tab 2).

Survey	Dates	Notes
1	2008-05-13 - 2008-05-17	
2	2008-06-20 - 2008-06-24	
3	2008-07-24 - 2008-07-28	
4	2008-08-22 - 2008-08-26	wetland sites flooded
5	2008-09-20 - 2008-09-24	
6	2008-10-21 - 2008-10-23	frost

Ceramic suction lysimeters were used to gather soil water samples at different depths approximately 1 to 2 meters away from the streams. A lysimeter is a device created for collecting pore water from soil. It consists of a porous suction cup and a tube that connects it to the ground level through which the sample can be retrieved, as shown in Figure 4.



Figure 4: Principle sketch of the measurement equipment and its placement in the field, a – suction lysimeter, b – temperature probe, c – groundwater capacitance probe, d – recording instrument, e – sampling bottle.

During collection of a sample, an evacuated bottle is attached to the tube using a syringe. As a result of the negative pressure, the pore water is drawn from the soil into the bottle (SMS 2008).

The collection of the samples took from 24 to 48 hours. In order to ensure that no old water was present in the tubing of the equipment at the beginning of sampling, every survey started with a rinse cycle, 48 hours during the summer months and 24 hours in the fall. This way, old water was discarded prior to each sampling. Duplicate lysimeters were used at each of the thirteen sites, and the water was collected at five depths, 15 cm, 30 cm, 45 cm, 60 cm and 75 cm, respectively, from the ground level. Replicate values were averaged for each sample date. No outliers were detected.

2.1.2 Installation

In the field, the bottles and lysimeter tubes were protected from heat and solar radiation by styrofoam boxes (Fig. 5). In the summer, ice packs were added to the boxes to prevent heating and to minimize evaporation from the samples. In the fall an additional styrofoam cover was placed atop the box to prevent the equipment from freezing (Fig. 5).



Figure 5: Installation of sampling equipment, summer (left) and fall (right).

2.1.3 Groundwater levels

Groundwater levels were automatically recorded from the beginning of the project in May 2008 until October 2008 using capacitance probes. A capacity probe consists of a metal tube fitted into a groundwater pipe with a connection to a memory device. It records the position of the groundwater at programmed regular time intervals and stores the information until it is downloaded to a computer. In order to exclude unintentional events

or accidents, manual measurements have been performed during the last three surveys from August until October 2008. To calculate the offsets for each site, manual and automated measurements from the same sample instances were plotted against each other and the equation for the linear regression was used to calculate the true positioning of the groundwater.

2.1.4 Stream discharge

The Västrabäcken stream flowing through site seven has been equipped with a V-notch weir where stage height was recorded continuously with a pressure transducer connected to a Campbell Scientific CR10 data logger (Cory *et al.* 2007). The discharge is calculated from the logged stage height based on a rating curve. Since the Krycklan catchment is not very large it has been assumed that the discharge from this particular site is representative of the overall discharge within the area. The discharge at each sampling site was calculated according to equation 1.

$$Q_{site} = Q_{stream} \frac{A_{site}}{A_{stream}}$$
(1)

Where Q_{site} is the discharge at the sampling site, Q_{stream} is the discharge at the stream Västrabäcken, A_{site} is the contributing area at the sampling site calculated in ArcGIS and A_{stream} is the area contributing to discharge at site seven, also calculated in ArcGIS.

Discharge measurements are expressed in liters per second. To reflect the actual flow within the different hillslopes, specific discharge for every sampling site was calculated (eq. 2).

$$R = \frac{Q}{A} \tag{2}$$

Where R is specific discharge, Q is the stream discharge and A is the hillslope area.

Additionally, the estimated discharge has been correlated to the fluctuations in the groundwater levels through plot graphs of the two against each other at the different sites.

2.2 LABORATORY ANALYSIS

Samples were transported from the field to the lab in isolated boxes and refrigerated after sub-sampling. Preliminary analysis subsequent to the field work, within a week of the sampling, included absorbance and air-equilibrated pH measurements and was performed in a laboratory at Umeå University. The samples for the preliminary analysis were stored at +4 °C. Additional samples were frozen for later analysis for selected anions, cations and DOC. The samples were used as such without further filtration. The ceramic cup of the lysimeter effectively acts as a filter of appropriate size, 45 µm.

2.2.1 Absorbance

The absorbance A at $\lambda = 254$ nm was measured with a HP 8452A diode array spectrophotometer at ambient room temperature in a quartz cuvette, l = 0,1 cm, with Millipore water as reference.

Because of the time constrains for this project it was chosen to base preliminary results on absorbance measurements and calculate total organic carbon (TOC) concentrations from them. An empirical linear relationship between absorbance and TOC, established in a previous study on seasonal TOC export from the same area (Laudon *et al.* 2003), presented here in Figure 6, was used.



Figure 6: The relationship between absorbance and total organic carbon (TOC) for seven streams, including two streams included in this study, Kallkällbäcken and Västrabäcken (after Laudon *et al.* 2003).

This method was thus chosen for the first analysis of this thesis. It serves as an indicator of TOC levels which can be calculated using the linear regression value from Figure 6, according to equation 3.

$$TOC = 23.5 \cdot A \tag{3}$$

Additionally, absorbance gives an indication of the character of TOC. Carbon-specific UV absorbance at $\lambda = 254$ nm is commonly interpreted as an index of aromaticity (Hernes *et al.*

2008), for example presence of some aromatic rings in the sample manifests itself in the darker color of the water.

2.2.2 pH

An indicator of the sample's acidity, pH, is a good way of assessing the water quality. There is a unique relation between pH value, DOC and the concentration of different anions in a sample, making a pH measurement an excellent tool in establishing a chemical base of the sample. In addition pH measurements are simple to perform. All measurements were performed with a Thermo Scientific Orion 720A double glass electrode pH meter.

2.2.3 DOC

DOC is a classification for organic carbon passing through a 0.45 μ m filter, which is comparable to the samples collected and filtered by the lysimeters. DOC accounts for 90% of the TOC in streams (Ågren *et al.* 2007) and serves as an indicator of how much carbon there is in the organic matter studied, in this case soil water. It plays a major role in many biogeochemical processes and has been used, among other things, to assess the quality of water. Seasonal variability of DOC in the soil is of particular interest, because there are distinct seasonal variations in the stream DOC and one riparian hypothesis suggests that this should be reflected in the soil water of the riparian zone. Dissolved organic carbon has an effect on other things, such as transport and solubility of heavy metals, pH levels and nutrient availability. In boreal regions, such as the one studied, wetlands and riparian soils are the main sources of DOC. If hydrologically connected to streams, the temporal variations in soil water DOC and flow pathways should be reflected in the variations of stream DOC concentrations.

3. **RESULTS**

To present the results the sampling sites have been grouped to reflect similarities. Four groups have been formed, representing different types of riparian zones, as can be seen in the map below (Fig. 7).



0 400 800 1200 Meters

Figure 7: The sampling locations in a topographical map. The color coding of the station marker corresponds to the classification: *forest* (yellow), *wetland* (green), *hillside* (red), *fluvial* (violet). White makers indicate sites that were not included in the study.

Group 1 classified as *forest* (yellow code) consisted of site 5, 6 and 7 and was representative of areas with relatively flat surface, wooded vegetation and with presence of substantial organic cover in the top layer of the soil. Group 2 classified as *wetland* (green code) consisted of sites 2, 8, 10, and 11 and represented areas that could be susceptible to

flooding and where the soil had high peat content. Group 3 classified as *hillside* (red code) consisted of site 1, 4, 9 and 12 and represented areas that were either situated on a hillside or adjacent to hillsides which resulted in good drainage of the soil. Additional characteristics of group 3 were the coarser soil, presence of larger rocks as well as lesser content of organic material. Group 4 classified as *fluvial* (violet code) represented the more unusual sites 14 and 15. Situated in the lowest part of the catchment these sites were set on glacial-fluvial sediment. Additionally site 14 was situated on a mire and 15 was placed next to a much deeper stream, both of which are very different from the rest of the sampling sites.

3.1 HYDROLOGY

3.1.1 Actual groundwater levels

A list of equations used for calculations of actual groundwater levels from automated and manual measurements can be found in Appendix 2.

3.1.2 Groundwater levels vs. stream discharge

Groundwater level variations from all sites have been plotted against discharge collected from the gauging station at the outlet of the stream Västrabäcken in order to examine the validity of the data. The gauging station is the only available one in the research area. Primary goal was to study whether major precipitation events were followed by a response in the groundwater table. An example of such an evaluation is presented in Figure 8. The plots for all the sampling sites can be found in Appendix 3.



Figure 8: Groundwater levels, including automatic and manual measurements, at site 1 and discharge variations from the gauging station at the stream Västrabäcken during the sampling period.

Additionally the relationship between groundwater levels and discharge were studied through correlation graphs. An example of such a graph can be seen in Figure 9. The graphs for all the sampling sites can be found in Appendix 3.



Figure 9: Correlation between groundwater level at site 10 and discharge measurements from gauging station at Västrabäcken.

For such a check a R^2 -value higher than 0.6 was deemed acceptable. The calculated R^2 values are presented in Table 3.

Table 3	$: \mathbb{R}^2$	values	for	correlati	on be	etween	ground	water	depth	variati	ons a	at the	sampli	ing	sites	and	flow	from
	the	e gaugii	ng st	ation at	the st	ream V	/ästrabä	cken.	* Den	otes a j	partia	al san	iple pe	riod	l.			

Site	R ² -value
1	0.84
2	0.75
4	0.01
5*	0.81
6	0.76
7	0.50
8	0.71
9	0.67
10	0.73
11	0.61
12	0.84
14	0.05
15	0.71

A summary of the findings on groundwater level variations is presented in Table 4.

Site	Group	Min	Mean	Max	Days with overland flow	Notes
5	forest	29.4	15.8	0.1	none	
6	forest	19.8	15.7	8.6	none	
7	forest	79.1	31.3	8.3	none	Inconsistent logger measurements
2 8 10 11	wetland wetland wetland wetland	71.7 27.3 44.2 8.6	16.2 10.4 23.3 4.0	0.0 0.0 0.0 0.0	35.8 9.2 1.9 2.7	Inconsistent logger measurements
1 4 9 12	hillside hillside hillside hillside	58.6 - 63.9 76.0	53.6 - 46.5 62.0	36.9 - 31.9 40.7	none none none	No available measurements
14 15	fluvial fluvial	13.0 57.6	3.9 49.4	0 20.4	0.4 none	Inconsistent logger measurements

Table 4: Automatically recorded groundwater level variations including minimum, mean and maximum groundwater depth in cm and presence of overland flow at the sample sites, sorted by group. All values indicate depth referenced to ground level.

Group 1 forest

Mean groundwater levels were quite shallow and fluctuated between 15 and 30 cm below ground level. Manual measurements reflected that. The groundwater table for site 5 and 6 showed very little change throughout the sampling period. Groundwater level variations followed major precipitation events as reflected by discharge measurements from the gauging station at the outlet of Västrabäcken. Good correlation could be observed for site 5 and 6. The logger for site 7 showed inconsistent readings and appeared to have been broken (see Table 3 and Appendix 3).

Group 2 wetland

Mean groundwater levels were comparative to that of group 1 and fluctuated between 4 and 24 cm below ground level. Extreme values, however, were subject to greater variability within this group. Groundwater level variations followed major precipitation events as reflected by discharge measurements from the gauging station. Correlation could be observed for all sites. Although the logger for site 8 showed a response from the groundwater level after rain, the peaks were smoothed out and the manual measurements did not agree with the automatic measurements. The inconsistent readings could be attributed to a problem with the logger. All sites were flooded for some time after large rainfalls, site 2 for an extensive period of time. Flooding was signified by groundwater level appearing as a positive value on the graph. Manual measurements reflected that.

Group 3 *hillside*

Mean groundwater levels lay deepest in comparison with the other groups, between 46 and 62 cm below ground surface, which is a reflection of the sites' topography. Groundwater

level variations followed major precipitation events as reflected by discharge measurements from the gauging station. Good correlation was found for sites 1, 9 and 12, and manual measurements also reflected that. The logger for site 4 appeared to have been clogged from the beginning of the sampling period and showed a fixed level which is inconsistent with the manual measurements. However, high discharge peaks caused by intense rain were registered as peaks in the groundwater table. The available manual measurements at site 4 put groundwater depth at approximately 50 cm below ground surface, which is consistent for this group.

Group 4 *fluvial*

Groundwater levels could not accurately be measured at site 14 due to its positioning in the middle of a mire. The location was wet throughout the sampling period. Manual measurements reflected that the groundwater level was above ground level, which could not be recorded by the automatic equipment. The readings from the logger indicated that the mean groundwater level was 4 cm below surface which was inconsistent with the manual measurements.

Groundwater level at site 15 lay deep with a mean around 50 cm below ground surface, which was comparable to group *hillside*. Groundwater level variations followed major precipitation events as reflected by discharge measurements from the gauging station. Groundwater depth and stream discharge were found to be reasonably well correlated.

3.2 CHEMISTRY

3.2.1 pH

The variations of pH value in the different levels of the soil profiles are presented in table 5 and are plotted separately for each site. In this section one graph is presented for each group. All graphs can be found in Appendix 4.

Site	Group	Min	Mean	Max
5	forest	5.0	5.9	6.8
6	forest	4.5	5.4	7.0
7	forest	4.0	5.0	5.9
2	wetland	5.3	5.7	6.9
8	wetland	4.1	4.5	5.2
10	wetland	4.8	5.8	6.8
11	wetland	6.1	6.7	7.4
1	hillside	4.8	6.1	6.9
4	hillside	5.2	6.1	6.5
9	hillside	4.6	5.8	6.4
12	hillside	5.2	6.1	6.9
14	fluvial	6.2	6.6	7.4
15	fluvial	5.5	6.0	7.0

Table 5: pH values including minimum, mean and maximum, at the sample sites, sorted by group.

Group 1 forest

All sites in the group *forest* exhibited similar trends. The lowest pH value was found in the top 15 cm of the soil profile. Subsequently, the pH value rose with increased depth and was approximately two units higher at the lowest sampled depth, 75 cm, compared to the top 15 cm. No considerable seasonal variations in pH could be observed (Fig. 10).



Figure 10: A sample pH profile representative of group *forest*, based on site 6, showing variations in pH values throughout the sampling period (left) and a vertical profile (right).

Group 2 wetland

Mean pH values for the group *wetland* were comparable to the mean pH values for group *forest*, although they were a subject to more variation within the group due to the different nature of the wetlands. As in the group *forest*, the lowest pH value could be found in the upper layer of the soil. However, pH varied little with depth (Fig. 11). Site 8 was more acidic then the other sites in the group, because of its positioning at an outlet of a low-pH mire. The highest pH value registered there was pH = 5.2. Highest pH values within the group *wetland* were found at site 11, where lowest value registered was pH = 6.1.



Figure 11: A sample pH profile representative of group *wetland*, based on site 10, showing variations in pH values throughout the sampling period (left) and a vertical profile (right).

Group 3 hillside

Because the sites in the group *hillside* were located in well-drained areas, it was in general harder to get results from the top layers of the soil. During drier periods there was not enough water in the soil to be collected by the lysimeters. Available pH measurements indicated that pH values were almost a unit lower in the top 15 cm of the soil than in the rest of the layers with higher values and little variation in the deeper profiles (Fig. 12).



Figure 12: A sample pH profile representative of group *hillside*, based on site 1, showing variations in pH values throughout the sampling period (left) and a vertical profile (right).

Group 4 fluvial

The two sites representing the group *fluvial* did not exhibit common characteristics. Site 14 showed less variability in pH within all the layers and had the highest pH values of all the studied sites (Fig. 13).



Figure 13: A pH profile for site 14, group *fluvial*, showing variations in pH values throughout the sampling period (left) and a vertical profile (right).

Site 15 behaved in a similar fashion to group *hillside*, with lowest pH value found in the upper 15 cm of the soil and little variation in pH values in the lower layers (Fig. 14).



Figure 14: A pH profile for site 15, group fluvial, showing variation in pH values throughout the sampling period (left) and a vertical profile (right).

3.2.2 DOC and Absorbance

The variations of DOC levels and absorbance in the different levels of the soil profiles have been plotted for each site. In this section one set of graphs is presented for each group. All graphs can be found in Appendix 5. Mean groundwater levels have been plotted on the absorbance graph as to give an indication of whether the groundwater level has an influence on the chemistry of the soil water. DOC values varied greatly from site to site, which is reflected in the different scale of the y-axis of the graphs.

The largest change in DOC levels was observed in the top 15 cm layer of the soil, therefore it is presented separately in Table 6.

Table 6: DOC values sampled at 15 cm depth at the beginning of the sampling period, May 2008, at the end of the sampling period, October 2008, and the change accrued over this period in mg/L, at the studied sample sites, sorted by group. * Denotes sites where the sample was taken at 30 cm depth.

Site	Group	DOC	DOC	DOC
		May	October	change
5	forest	15	32	17
6	forest	23	64	41
7	forest	44	77	33
2	wetland	25	39	14
8	wetland	20	31	11
10	wetland	10	36	26
11	wetland	57	62	5
1	hillside	17	-	-
4*	hillside	0.5	1	0.5
9	hillside	3	4.5	1.5
12	hillside	20	43	13
14	fluvial	3	-	3
15*	fluvial	3	12	9

Group 1 forest

Common for the sites in this group was the distinct rise of DOC levels across the entire soil profile throughout the sampling period. Highest DOC concentrations could be observed in the 15 cm closest to soil surface. On average the DOC levels doubled from spring to fall in the top layer (Fig. 15). The mean groundwater level indicated that most samples were taken from saturated soil.



Figure 15: An example of the DOC and absorbance profiles representative of group *forest*, based on site 6, showing DOC variations throughout the sampling period (left) and a vertical absorbance profile (right).

Group 2 wetland

The rising trend of DOC was not as apparent in this group across the entire soil profile. Most considerable increase could be observed in the upper 15 cm layer of the soil, where DOC levels rose approximately 50 % above the levels measured at the beginning of the sampling period (Fig. 16). Mean groundwater level indicated that only the samples at 15 cm depth were taken from unsaturated soil.



Figure 16: An example of the DOC and absorbance profiles representative of group *wetland*, based on site 10, showing DOC variations throughout the sampling period (left) and a vertical absorbance profile (right).

Group 3 hillside

The four sites in this group did not show any common tendencies in regards to DOC, except for the fact that DOC levels were lower than for the first two groups. No trends could be observed in the lower layers of the soil profiles in all sites (Fig. 17). The only exception was site 12 that showed a clear rise in DOC levels in the upper 15 cm layer (Appendix 5).



Figure 17: An example of the DOC and absorbance profiles representative of group *hillside*, based on site 1, showing DOC variations throughout the sampling period (left) and a vertical absorbance profile (right).

Group 4 fluvial

No particular patterns in the DOC levels could be attributed to the *fluvial* group. Site 14 was characterized by extremely low DOC levels in all the layers of the soil, which did not change throughout the sampling period (Fig 18). DOC levels were higher at site 15 and there was a trend towards increasing DOC levels, although with no particular dependency on the depth at which the samples were taken (Appendix 5).



Figure 18: DOC and absorbance profiles for site 14, group *fluvial*, showing DOC variations throughout the sampling period (left) and a vertical absorbance profile (right).

4. **DISCUSSION**

3.3 HYDROLOGY

The most important factor determining the hydrological characteristics of the different riparian zones was topography, specifically the slope of the ground surface. If the studied places were located in sloping, well-drained areas, the groundwater level lay deep. Flat surfaces were consistent with shallow groundwater level, while wetlands showed greater variability in the groundwater levels and at some point the groundwater level reached the surface. Underlying fluvial sediment did not appear to play a role in the depth of the groundwater level. Instead the extent of human activities, such as ditching of streams, factored in. Deeper streambed resulted in the lower groundwater level next to the sampling site, although how much the different streams have been ditched has not been evaluated in this study. Figure 19 summarizes the variations in the groundwater levels within the studied sites.



Figure 19: A summary of the groundwater level variations at the studied sites sorted by group.

During the evaluation of the groundwater level data it was observed that several sites showed inconsistent readings, which has been attributed to a problem with the data loggers. The groundwater data from site 7 in particular were of an anomalous character. Manual groundwater measurements, made during the last three surveys, showed groundwater levels to lie closer to the surface, very similar to the behavior of the groundwater table at site 5 and 6 with which site 7 was grouped. It was expected that the groundwater table would behave similarly in all three sites. However the logger registered a 60 cm recession in the groundwater table in the months of June and July. Although a recession was expected due to dry weather no other sites showed such a big change and it was therefore concluded that the logger was broken.

A different explanation could be given to the situation observed at site 14, positioned at the lowest part of the catchment, downstream of an ephemeral stream. The site's placement in

the middle of a mire made groundwater level measurements much harder to perform. Because groundwater level lay very close to the surface throughout the survey, it could not always be distinguished from the surface water. During dry seasons the up-welling of the groundwater results in large lateral flow and surface near water and makes it impossible to find a meaningful groundwater-discharge relation. This has resulted in an abnormal data log curve. According to the logger mean groundwater level lay approximately 3 cm below surface, while all manual measurements place groundwater table above surface.

A certain limitation for this study was the fact that discharge data was available from only one stream. Although the size of the catchment is not very large and allows for generalizations about flow within it, some uncertainties arise from measuring discharge from one location and extrapolating from it to make calculations for other parts of the catchment. Hillslope areas were calculated through GIS modeling, therefore the calculations of specific discharge were also subject to errors. Nevertheless, visual assessment of data showed good correlation between groundwater levels and discharge variations from the stream for nearly all of the sites. Major precipitation events resulted in both a peak of the stream discharge and an immediate response in the groundwater level, as would be expected.

3.4 CHEMISTRY

3.4.1 pH

The variations in the pH were consistent with the presence and quantity of organic material in the riparian zones. The upper layers of the soil profiles, especially in the groups *forest* and *wetland*, had a considerable organic cover, which contributed to the lower pH found in the upper 15 cm of the soil. As the amount of organic material subsided with depth, the pH value rose. The variations in pH values could not be attributed to any characteristics in the specific group as seen in Figure 20.



Figure 20: A summary of the pH value variations at the studied sites, sorted by group.

Common for all groups: in the lower 75 cm of the soil the pH value was on average very near pH = 7.0 in all but two of the sites.

The lowest pH profile could be observed at site 8, which was situated at the edge of a lowpH mire. Even the bottom layer measured a value no higher than pH = 5.2. This was to be expected because of the high peat deposits in the soil, which are acid in nature.

It is interesting to note that pH was considerably higher at site 11, with a mean a unit and a half to two units higher then the mean for the rest of the sites. Although it was grouped with the other wetland sites, it is the only site situated atop of wave-washed sediment and the wetland is thus of a different type. It had a very specific odor, possibly due to some sulfur compounds in the area, and the water was considerably darker than at the other sampling sites.

3.4.2 DOC

The seasonal variations in DOC in the riparian zones can be attributed to a set of factors. Largest changes were observed in the group *forest* and *wetland*, where the ground surface was flat, the groundwater table lay shallow and there was plenty of organic material. The greatest increase was found in the top layer of the soil, as presented in Figure 21. The group *hillside* where the groundwater lay deep showed very low DOC values with the exception of site 12 which could also be classified as *forest*.



Figure 21: A summary of the DOC levels in the top 15 cm of the soil profiles, minimum observed in the beginning of sampling period, maximum observed in the end of sampling period, at the studied sites, sorted by group.

In this study groups have been formed based on visual assessment and bedrock/sediment classification. A more detailed grouping would need to include soil type, quantified vegetation and specific slope of the studied area.

At site 11, extremely low concentrations of DOC were found in all but top layer. The underlying sediment may play a major role in the composition of the soil. Since the site is wet and substantial quantities of organic material can be found on the ground, the top layer behaves very much like group *forest*, showing a considerable rise (triple the spring value) in the DOC-levels throughout the summer with a peak before the fall. No such changes could be observed in the other layers of the soil.

Extremely low concentrations of DOC were found in all layers at site 14. Ideally this site should not be grouped with any other, because it represents a completely different groundwater situation compared with the other sites at Krycklan, because flow may be on surface or sub-surface and happen simultaneously.

Since true DOC measurements were not performed in this study, DOC concentrations were calculated from available absorbance data. It is noteworthy that the linear relationship of absorbance and DOC is empirical and has been developed based on stream DOC; therefore the results are subject to some uncertainties.

Understanding how DOC changes within the riparian zone is important for working on new ways in dealing with various environmental problems. DOC is a strong complexing agent for various metal ions, such as iron, copper, mercury and aluminum. If metals are leached from the forest into the riparian zone and bound to DOC within it, they can easily be transported and contaminate the groundwater and the stream water. Seasonal increase in DOC levels may result in higher concentrations of metal ions in the riparian zone as well as the stream water in the fall. That in turn may have an affect on the biota of both the riparian and the aquatic systems.

Suggestions for future studies

A natural step in continuation of this study would be to compare the chemistry of the riparian soil-water to that of stream water. Additionally the study of the partitioning of ions in the soil-water would complete the chemical picture of the riparian zone.

5. CONCLUSIONS

The *nature* of the riparian zone is a deciding factor in soil chemistry. Most important features of the riparian zone in the forest landscape are:

- Topography, specifically slope
- Soil type, in particular presence of organic material
- Groundwater level

Additional factors:

- Drainage
- Vegetation

Clearly defined forest types of riparian zones show a distinctive seasonal flux of DOC.

The seasonal increase in DOC should affect the chemistry of the runoff water.

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APPENDIX 1: Description of the sampling sites

Stream names, sites description, bedrock types, hillslope area (area pertaining to the contributing upstream area calculated in GIS) in hectares and elevation in meters.

Site	Stream name	Description	Bedrock	Hillslope	Elevation
1	Fulbäcken	steep, slopes towards the stream	moraine	18714	248.6
2	Fulbäcken	wetland, often flooded	moraine	21383	232.6
3*	Fulbäcken	wetland, often flooded	moraine	21383	232.6
4	Stortjärnsbäcken	steep, divergent	moraine	9202	249.4
5	Västrabäcken	forest, relatively flat	moraine	893	258.3
6	Västrabäcken	forest, relatively flat	moraine	634	255.4
7	Västrabäcken	forest, relatively flat	moraine	642	241.5
8	Kallkällmyren	wetland, stream outlet, peat	moraine	1782	278.0
9	Kallkällbäcken	steep, well-drained	moraine	1875	273.0
10	Kallkällbäcken	wetland	moraine	1748	268.9
11	Stormyrbäcken	wetland, sand	wave-washed sediment	31732	253.8
12	Renberget	sloping, drained	moraine	1853	238.2
13*	Åhedsbäcken	low in the catchment	glacio-fluvial sediment	138509	160.7
14	Åhedsbäcken	coarse silt - fine sand, low in the catchment	glacio-fluvial sediment	141656	158.3
15	Långbäcken	coarse silt – fine sand, low in the catchment	glacio-fluvial sediment	72187	169.4

Equations for determining actual groundwater depths from available automatic and manual measurements					
Site	Equation	R ² -value			
1	y = -0.5952x + 663.02	0.6904			
2	y = -2.4762x + 1174.3	0.4286			
3	site disabled				
4	no manual measurements available				
5	y = -0.9509x + 929.21	0.8928			
6	y = -0.6822x + 593.71	0.6164			
7	y = -1.2546x + 880.56	0.8108			
8	y = 0.3018x - 405.36	0.0206			
9	y = -1.0147x + 1154.6	0.9936			
10	y = 0.4775x - 193.26	0.0553			
11	y = -0.7509x + 728.19	0.7897			
12	y = -0.9554x + 899.9	0.8683			
13	site disabled				
14	y = -1.0833x + 1239.1	0.0827			
15	y = -0.897x + 816.09	0.9343			

APPENDIX 2: Automatic vs. manual groundwater level measurements

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APPENDIX 3: Groundwater level vs. stream discharge measurements

For all graphs, blue line represents groundwater level variations, pink line represents discharge variations, orange triangles show manual measurements.

Group 1 forest

Automatically recorded measurements for site 5 show that the logger was not working properly until the beginning of July. Therefore only values after July 1 2008 have been taken into account for analysis.



Figure A: Hydrological data evaluation for site 5, unrevised series.



Figure B: Hydrological data evaluation for site 5, revised series, only includes values from July 1 2008.



Figure C: Hydrological data evaluation for site 6.



Figure D: Hydrological data evaluation for site 7.



Group 2 wetland

Figure E: Hydrological data evaluation for site 2.





Figure F: Hydrological data evaluation for site 8.



Figure G: Hydrological data evaluation for site 10.



Figure H: Hydrological data evaluation for site 11.

Group 3 hillside





y = -1,5152Ln(x) - 13,898 $R^2 = 0,0119$

20

25

Figure H: Hydrological data evaluation for site 1



Figure I: Hydrological data evaluation for site 4



20

10

-10

-20

-30

-40

-50

-60

0

5

10

Discharge [L/s]

15

Groundwater level [cm]

Figure J: Hydrological data evaluation for site 9.



10

Figure K: Hydrological data evaluation for site 12

Group 4 *fluvial*



Figure L: Hydrological data evaluation for site 14.



Figure M: Hydrological data evaluation for site 15.



y = 0.6445 Ln(x) - 4.6077 $R^2 = 0.0463$



APPENDIX 4: pH variations in the soil profiles

Group 1 forest



Figure I: pH value variations at the different sampling depths for site 5.



Figure II: pH value variations at the different sampling depths for site 6.



Figure III: pH value variations at the different sampling depths for site 7.

Group 2 wetland



Figure IV: pH value variations at the different sampling depths for site 2.



Figure V: pH value variations at the different sampling depths for site 8.



Figure VI: pH value variations at the different sampling depths for site 10.



Figure VII: pH value variations at the different sampling depths for site 11.





Figure VIII: pH value variations at the different sampling depths for site 1.



Figure IX: pH value variations at the different sampling depths for site 4.



Figure X: pH value variations at the different sampling depths for site 9.



Figure XI: pH value variations at the different sampling depths for site 12.

Group 4 fluvial



Figure XII: pH value variations at the different sampling depths for site 14.



Figure XIII: pH value variations at the different sampling depths for site 15.







Figure i: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 5.



Figure ii: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 6.



Figure iii: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 7.





Figure iv: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 2.



Figure v: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 8.



Figure vi: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 10.



Figure vii: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 11.



Group 3 hillside

Figure viii: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 1.



Figure ix: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 4.



Figure x: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 9.



Figure xi: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 12.

Group 4 fluvial



Figure xii: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 14.



Figure xiii: Variations in DOC (left) and absorbance (right) at the different sampling depths for site 15.