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Hydrology and surface water chemistry in a small forested catchment –Which factors influence surface water acidity?

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Hydrologi och ytvattenkemi i ett mindre skogbeklätt avrinningsområde – Vilka faktorer påverkar ytvattenförsurning

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Master thesis, 30 credits, in *Physical geography and ecosystem analysis*

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Abstract

Water chemistry alterations such as acidification and eutrophication represent major threats to the running waters of the world, and Swedish waters are among the most vulnerable. In this study the small forested catchment Storskogen, part of the SWETHRO monitoring network, was analysed to examine the links between deposition, catchment hydrological properties and surface water chemistry. Storskogen was characterised in terms of physical and chemical hydrology, and compared to the well-studied catchment Gårdsjön. Both catchments were inventoried to document the distribution of wetlands in order to examine to what extent they influence surface water chemistry. The water balance model FyrisQ was used to model discharge from Storskogen and was validated using measurement data collected by IVL from 2014 to 2017.

The stream in Storskogen had an observed median discharge of 0.7 $l\ s^{-1}$ and responded quickly to precipitation, which could cause a tenfold increase in discharge. For this reason, the model FyrisQ, was found to be inappropriate because it could not adequately recreate the dynamics of the discharge. Surface water was found to be acidic (pH< 5) with significantly lower acid neutralising capacity and pH upstream in Storskogen than downstream. Surface water in Gårdsjön was more acidic than in Storskogen. Even though the surface waters' acid neutralising capacity was found to be significantly correlated with deposition, none of the examined factors (deposition, mineralogy and wetland extent) could account for the observed differences in acidity between the upper and lower dam in Storskogen, or between Storskogen and Gårdsjön. The pH of both catchments was correlated with deposition of sea salt however, the amounts did not differ significantly between sites. It is likely that the difference in acidity between the upper and lower part of the catchment in Storskogen can be explained by different transit times but to prove this, further monitoring is encouraged.

Sammanfattning

Vattenkemiska förändringar som försurning och övergödning utgör betydande hot mot ytvatten och svenska vatten är bland de mest utsatta. I den här undersökningen analyserades skogsområdet Storskogen som är en del av krondroppsnätet, för att undersöka sambandet mellan atmosfäriskt nedfall, hydrologi och ytvattenkemi. Storskogen jämfördes också med det väl undersökta avrinningsområdet Gårdsjön. Båda avrinningsområdena besöktes för att dokumentera fördelningen av våtmarker för att undersöka i vilken utsträckning de påverkar ytvattenkemi. Vattenbalansmodellen FyrisQ användes för att modellera avrinning från Storskogen och validerades med hjälp av mätdata som samlats in av IVL från 2014 till 2017.

Skogsbäcken i Storskogen hade en observerad medianavrinning på 0,7 $l\ s^{-1}$ som svarade snabbt på nederbörd. Kraftigt regn kunde orsaka en tiofaldig ökning av avrinningen. På grund av avrinningens snabba svar på nederbörd visade sig modellen FyrisQ vara olämplig eftersom den inte på ett tillfredsställande sätt kunde återskapa avrinningens dynamik. Ytvattnet i Storkogen visade sig vara surt (pH <5) med signifikant lägre syraneutraliserande kapacitet och pH uppströms än nedströms. Ytvattnet i Gårdsjön var surare än i Storskogen. Ytvattnets syraneutraliserande kapacitet var signifikant korrelerad med atmosfäriskt nedfall, men ingen av de undersökta faktorerna (nedfall, mineralogi och våtmark) kunde ensamt förklara de observerade skillnaderna i surhet mellan den övre och nedre dammen i Storskogen eller mellan Storskogen och Gårdsjön. pH-värdet för båda avrinningsområdena var korrelerat med nedfall av havssalt, men mängden deponerat havssalt skilde sig inte signifikant mellan områdena. Det är troligt att skillnaden i surhet mellan övre och nedre delen av avloppet i Storskogen kan förklaras av olika transittider, men för att bevisa detta krävs ytterligare studier.

Contents

1 Introduction

Water chemistry alterations have been identified as major threats to the running waters of the world, and the driving factors behind them can be summarised to: climate change, urbanisation, industry, land-use change and water-course alterations (Meybeck and Helmer 1989; Malmqvist and Rundle 2002; Whitehead et al. 2009). Therefore, scientists have recognised the need for long-term monitoring of water quality to assess future, and on-going, water chemistry alterations (Foster and Charlesworth 1996; Evans et al. 2005; Burt et al. 2010; Löfgren et al. 2011; Löfgren 2012; de Jong et al. 2017). Scandinavian soils are typically poorly buffered and particularly prone to acidification due to a thin soil layer and silica-rich bedrock with a slow weathering rate which directly affects the quality of surface waters as they too become particularly vulnerable (Reuss et al. 1987). The issue of surface water degradation is reflected in several of the 16 environmental objectives adopted by the Swedish parliament, four of which are related to the research presented in this thesis, namely 'Flourishing lakes and streams', 'Good-quality groundwater', 'Natural acidification only' and 'Zero eutrophication' (Liljenström et al. 2008).

In the late 1970s, airborne pollution due to industrial emissions of mainly sulphur and nitrogen reached its maximum in Europe. Since then, research on the causes of acidification and on the recovery process has led to the passing of several national and international regulations of industrial sulphur emissions which, in turn, has led to reductions in the atmospheric deposition of these regulated compounds, and to a slow recovery of many ecosystems (Warfvinge and Bertills 2000; Malmqvist and Rundle 2002; Skjelkvale et al. 2005; Löfgren et al. 2011). The recovery rate from acidification is, however, complicated and much slower than the reduction rate of acid deposition (Reuss et al. 1987; Warfvinge and Bertills 2000; Akselsson et al. 2013). Furthermore, the deposition of nitrogen, which can lead to both eutrophication and acidification, has not decreased at the same rate as sulphur and is, by some, projected to increase in the future(Warfvinge and Bertills 2000; Galloway et al. 2004).

In 2016, the Swedish government proposed a Climate and air conservation strategy (Prop. 2016/17:146) that will come into force in January 2018. The goal is that, by 2045, Sweden will have zero net emissions of greenhouse gases and to achieve this, an increased biomass output is advocated. Final harvest, and the associated land preparation, has been proven to constitute the phase of forest generation that causes the greatest impact on the water quality of forest streams (Ring 2008). This can lead to increased discharge, increased transportation of nutrients and increased acidification (Löfgren 2012; de Jong et al. 2017).

In 2013, IVL (the Swedish Environmental Research Institute) established a new study site within the SWETHRO monitoring network, a network where atmospheric deposition and soil water chemistry is monitored on more than 60 forest sites all over Sweden (Pihl Karlsson et al. 2011). The site, called Storskogen, is located in one of the most severely acidified areas of Sweden. In addition to the SWETHRO measurements, groundwater and surface water chemistry is measured in the Storskogen catchment area. The purpose of the extended SWETHRO measurements is to study the links between atmospheric deposition, soil water and discharge. In addition, parts of the forest within the catchment will be harvested during 2018 and this thesis will serve as a preliminary study and as a reference for future research (Karlsson, pers. comm.).

1.1 Aim

The overall aim of this thesis is to characterise the hydrology of the catchment in Storskogen and assess the suitability of using the water balance model FyrisQ to simulate its discharge. Furthermore, the aim is to study surface water acidity and to investigate the main driving factors behind it. The study will address the following research questions:

Q1 What does the hydrology of Storskogen look like in terms of volume?

Q2 Can the hydrological model FyrisQ be used to adequately simulate discharge from Storskogen?

Q3 What does the chemical hydrology of Storskogen look like and does it differ from the nearby Integrated monitoring (IM) catchment Gårdsjön?

Q4 Which factors determine the surface water acidity in these catchments?

2 Background

2.1 Acidification

An acidic ecosystem, such as a catchment or a forest, can either be at a steady acidic state or suffer from on-going acidification whereby the total buffer capacity of the system is reduced (Warfvinge 2011). The acidity of water determines a multitude of soil chemical and biological properties, and excessive acidity can cause long term damage to the ecosystem (Brady and Weil 2002).

It is difficult to differentiate between natural and anthropogenic acidification. Anthropogenic acidification is primarily caused by the release of acidifying compounds such as sulphate through the combustion of fossil fuels. Modern intensive forestry can also contribute to anthropogenic acidification through the removal of basic nutrients from the ecosystem. Overall, anthropogenic acidification causes a fast acidifying process. Natural acidification, on the other hand, is a slow process. Swedish soils have undergone natural acidification since the retreat of the last ice age. This is partially due to the naturally occurring dissolved carbonic acid in precipitation (Bertills and Lövblad 2002), but also to vegetation. As plants take up basic nutrients they release hydrogen ions (H^+) to the soil solution, and when the plants die and start to decompose, there is a release of organic acids which can dissolve in the soil solution to form DOC (dissolved organic carbon). Both of these processes lower the pH of the soil solution and, as a consequence, lower the pH of surface water (Warfvinge 2011).

During heavy rainfall, when the rate of precipitation exceeds the infiltration capacity of the soil, or when soils are impervious or naturally saturated areas such as wetlands, precipitation will produce surface runoff. Surface runoff limits the interaction between precipitation and soil, and reduces the soils' capacity to neutralize the acidity. When surface runoff enters a stream directly it can cause a sharp decline in pH, known as an acid surge (Grip and Rodhe 2000; Dingman 2015). During low levels of precipitation, wetlands can also influence the acidity of the surface water through inputs of DOC. The anaerobic conditions in a wetland limit decomposition and cause the formation of peat. Peat consists of partly decomposed material that is high in DOC. A higher proportional wetland cover of a catchment generally increases the amount of DOC observed in the discharge. (Grip and Rodhe 2000; Xenopoulos et al. 2003).

Lightning storms and sea-water salt spray are two further causes of natural acidification. Lightning storms create a reaction between the nitrogen and oxygen in the atmosphere to form nitric oxide which can contribute to acidification as discussed below, and the ions in sea salt increase the net charge of the soil solution, which can lead to a release of H^+ (Brady and Weil 2002; Akselsson et al. 2013; Pihl Karlsson et al. 2016).

Since low pH can have natural causes it is necessary to also examine other factors when analysing acidification. An improved measure of acidification is the acid neutralising capacity (ANC) which estimates the buffer capacity of a system and does not take pH into consideration. The buffer capacity of most soils depends on the abundance of exchangeable base cations. Cations are common positively charged ions loosely held by the negatively charged soil colloids. Calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium ions (Na^+) are the dominant non-acid cations and all, apart from Na^+, are important nutrients. In simple terms ANC is the relative difference between concentrations of base cations and strong acid anions, and is calculated as in equation (1) (Warfvinge and Bertills 2000; Warfvinge 2011).

$$ANC = [Na^+] + [K^+] + [Ca^{2+}] + [Mg^{2+}] - ([Cl^-] + [NO_3^-] + [SO_4^{2-}]) \qquad (1)$$

All cations have different relative strengths of attraction between the positive ion and the negative soil colloids. Both Al^{3+} and H^+ are strongly attracted to the soil colloids and a release of them can dissolve bound cations into solution, after which the cations can be utilized by vegetation. However, if they are released too rapidly, or precipitation has been high, they may be lost through leaching (Ashman and Puri 2002). The rate of acidification is determined by the rate of base cation leaching or removal, the resupply rate of base cations through mineral weathering and the total sum of exchangeable base cations in the catchment (Kirchner and Lydersen 1995).

The main anions that enter an ecosystem via deposition are sulphuric and inorganic nitric acids. They primarily originate from the combustion of fossil fuels where they are released as sulphur dioxide (SO_2) and nitrogen oxides (NO_x), Bertills and Lövblad 2002). As these gases react with water in the precipitation they form sulphuric acid (H_2SO_4) and nitric acid (HNO_3) that, in turn, dissociates and form sulphate (SO_4^{2-}) or nitrate (NO_3^-). This disassociation causes a release of hydrogen ions (H^+) to the soil solution, which increases its acidity. The sulphuric and nitric acids can also disassociate aluminium ions (Al^{3+}) from the soil minerals which are directly toxic to e.g. fish and can cause negative growth effects on forests (Reuss et al. 1987; Schaedle et al. 1989; Brady and Weil 2002; Malmqvist and Rundle 2002). Chloride (Cl^-) mainly enters the ecosystem dissolved in precipitation, or as dry deposited salt particles (Grip and Rodhe 2000).

Inorganic nitrogen can also enter an ecosystem via deposition of reduced nitrogen (NH_x), such as ammonia gas (NH_3) or ammonium (NH_4), which comes mainly from agricultural sources (Asman et al. 1998). If reduced nitrogen is oxidised to NO_3^- through the process of nitrification it releases H^+ to the soil solution and increases the acidity (Brady and Weil 2002). However, if the NO_3^- ion is then used by a plant, the plant will release a hydroxide (OH^-) ion to maintain electrical balance. That OH^- ion can combine with the formerly released H^+ to form water. Thus, acidification by nitrification will only occur if the NO_3^- is not taken up by plants and is leached from the system (Brady and Weil 2002).

The acidity of soil and surface water does not only depend on deposition, but also on the inherent properties of the soil and the interactions between soil and water. The pH value and the aluminium concentration of water are determined by the total amount of other dissolved substances through equilibrium relationships (Warfvinge and Bertills 2000). The equilibrium relationship between pH, ANC and DOC is shown in Figure 1. It shows how an increased concentration of DOC results in higher ANC given that pH stays the same, or the opposite: that a higher concentration of DOC results in a lower pH if ANC stays the same.

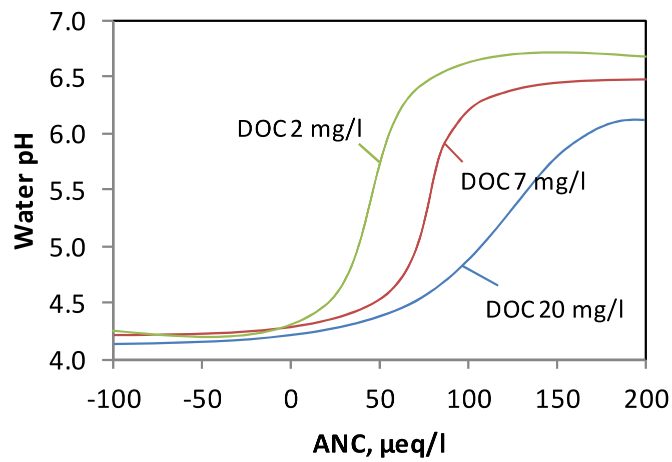

Figure 1. pH of water as a function of ANC for three different concentrations of DOC. Based on model calculations from Warfvinge and Bertills 2000.

2.2 Catchment hydrology

A catchment is defined as the area that contributes to the flow of water in a specified outlet point (Dingman 2015). The boundary of a catchment is called a water divide (Figure 2). All precipitation that falls within the divide can contribute to the outlet flow unless it is lost through water abstraction or evapotranspiration (ET). It should be noted that surface water- and groundwater divide are not the same thing, but that for typical thin Swedish till soils they usually coincide to a great extent. Thus, it can be assumed that the groundwater that makes up part of the flow through the outlet originates from precipitation within the catchment (Grip and Rodhe 2000).

The position of the outlet can be at any chosen location and therefore the catchment is not a fixed spatial entity. Every catchment consists of an innumerable number of smaller catchments or sub catchments. Often, however, the position of the outlet is set to a defined point where the stream or river meets the ocean, or at a dam or stream gauging station.

This conceptual landscape unit is very useful for making quantitative budgets for fluxes of substances and for understanding the processes that affect these fluxes. Simply measuring the input from the atmosphere and the output via the outlet can give an idea of the combined result of the biogeochemical processes that occur within the soil and vegetation of the catchment, how much is stored in the ground and how much is lost through the soil and bedrock or to the atmosphere (Bernes et al. 1986; Warfvinge 2011).

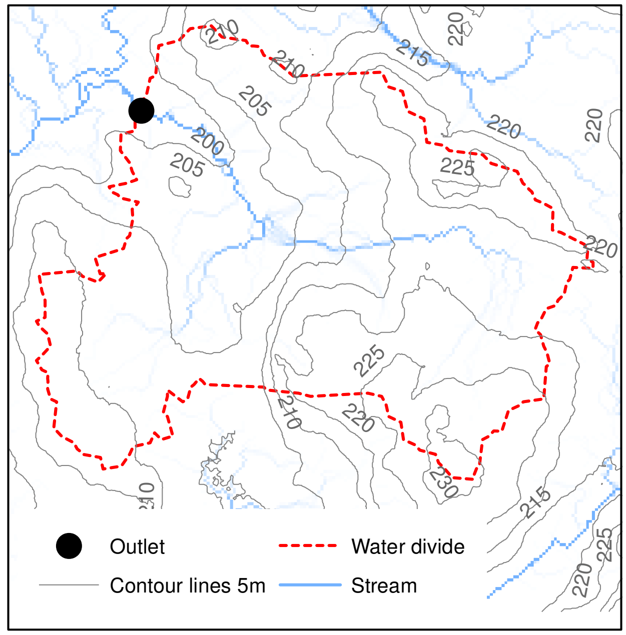

Figure 2. The catchment at Storskogen. The area within the water divide (dashed line) is the catchment, which means that all precipitation that falls within this area can contribute to the flow at the outlet point unless it is lost through water abstraction or evapotranspiration.

2.2.1 Hydrological monitoring

Precipitation

Precipitation is often measured as bulk precipitation to an open field, which will contain substances dissolved in the precipitation, i.e. wet deposition. It can also be a measure of the so called throughfall. Throughfall is the part of deposition that is not lost through interception by vegetation and further evaporation, it is what falls through the vegetation and actually reaches the ground. Throughfall contains both wet and dry deposition, where dry deposition consists of particles and gases that are intercepted by the canopy and transported down to the surface with the precipitation, and wet deposition consists of dissolved substances in the precipitation (Grip and Rodhe 2000; IVL 2017b). It is measured under the canopy and, depending on tree type and specific leaf area, the amount can be up to 40% of the open field precipitation (Grip and Rodhe 2000). The interaction between canopy and precipitation water can affect not only the amount of water, but also its chemical composition which is known as internal circulation (Warfvinge 2011; Pihl Karlsson et al. 2016).

The measurement technique used to sample precipitation can be very detailed or very simple depending on the precision required. In many cases the equipment utilised simply involves a bucket and funnel for water collection. The funnel prevents the water from evaporating and the bucket is weighed, or the water level recorded, at regular intervals. In this thesis these simple techniques are used for both open field and throughfall precipitation measurements.

Soil water

Water that enters the soil percolates through the pore spaces of the unsaturated zone. From here, it can either be used by the vegetation or by soil microbes, evaporate or enter the saturated zone where it is known as groundwater. Soil water is sampled using suction lysimeters. These are pipes with fine permeable ceramic filters to which a suction pressure is added so that water can be extracted from the pore spaces for analysis (IVL 2017a). The depth of 50 cm is assumed to be under the root zone where roots play an active role (Akselsson, pers. comm.).

Roots release organic exudates which lower the pH of the soil solution and increase the weathering rate of minerals. Roots also respire and release carbon dioxide (CO_2) which forms carbonic acid (H_2CO_3) as it comes into contact with the soil water. This also increases the acidity of the soil water and causes mineral weathering. Furthermore, the root zone is an area of high microbial activity due to the amounts of decomposing material left from the roots (Brady and Weil 2002). Therefore, the chemical composition of soil water is different from the precipitation. This is both because of the above mentioned root activity and because of the contact of the percolating water with the mineral soil and the organic rich topsoil. The topsoil contains high amounts of partly decomposed material with large amounts of exchangeable H^+ and cations that can dissolve in the soil solution. As the flow of water continues through the mineral soil, further weathering takes place and the concentration of several ions increase successively (Grip and Rodhe 2000).

Evapotranspiration

Evapotranspiration (ET) is the combined loss of water through evaporation from surfaces and via transpiration through the vascular system of plants. Empirical methods of measuring both evaporation and transpiration are available for short time periods, small areas or singular units such as a tree. One such technique is the evaporation pan method, where the rate of weight loss from the open pan filled with water is measured to determine evaporation rate. Another technique uses sap-flow measurements by applying heat to the stem of a tree and measuring the rate at which the heat moves through the trunk to determine its transpiration (Dingman 2015). However, actual ET (AET) from a large area cannot be directly measured, which presents a major challenge for hydrological monitoring. While potential ET, where endless water resources are assumed, can be calculated using e.g. Penman's equation

(Penman 1948), actual ET is more complex. There is an indirect way to calculate the actual ET for an area over a longer time period using the water mass balance equation, described in section 2.3 below. Other methods include models using a mass-transfer equation such as the widely used Penman-Monteith equation (Monteith 1965). It is worth noting, however, that several input variables (canopy conductance, wind speed and vegetation roughness etc.) are required in order to achieve an accurate estimation using this method, some of which are almost as difficult to measure as AET. In this thesis the indirect mass balance equation technique is used to calculate ET for a full hydrological year.

Discharge

Several stream-gauging methods may be used to determine the discharge (Q), i.e. the volume rate of flow, from a catchment. Some approximate the flow at a certain point in time (such as the velocity area method or the dilution method), whereas others, that are used for continuous discharge monitoring, make use of known stage-discharge relations (Dingman 2015). One such method is the sharp crested V-notch weir, also known as the Thomson weir, which is the method used in this thesis.

The weir, or dam, is constructed so that all water flows through the V-notch. The notch has a sharp edge to let the water spill freely over the edge of the V-notch and not seep down along the edge of the dam (Figure 3). Discharge through a V-notch can be calculated as in equation (2) (Shen 1981).

$$Q = C \frac{8}{15} \sqrt{2g} \tan\frac{\theta}{2} h^{5/2} \qquad (2)$$

Q = volume rate of flow
C = dimensionless discharge coefficient (determined by calibration)
g = the gravitational acceleration
θ = angle of weir
h = Weir head

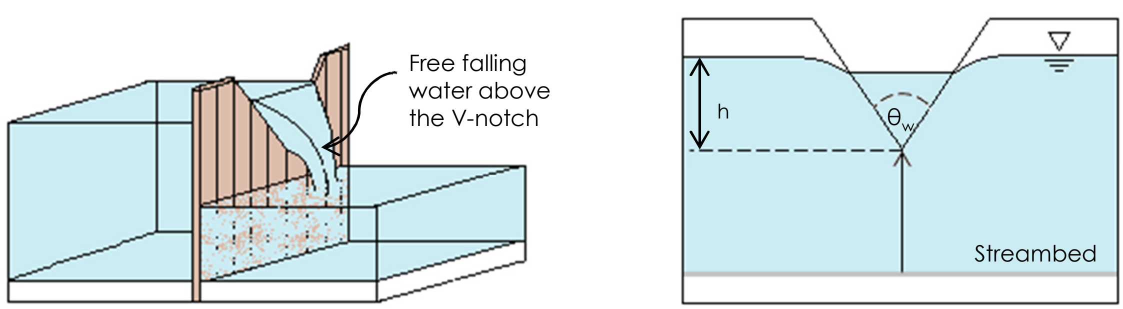

Figure 3. Schematic illustration of a V-notch weir and its cross section showing the variables used in the discharge equation (2) (Modified from Shen 1981).

Dividing discharge by the area of the catchment gives the specific discharge (q) which is expressed in volume per time per area, often l $s^{-1}m^{-2}$. This is a useful unit because it normalises discharge and thus, allows for the comparison of catchments of different sizes. Furthermore the unit l $s^{-1}m^{-2}$ can also be expressed as mm s^{-1} which is how precipitation is commonly measured, thus making the precipitation and discharge easily comparable.

2.3 Water balance calculations

In simple terms, the water balance of a catchment can be described as the difference in quantity between the water that enters a catchment as precipitation and the water that leaves the catchment via discharge or ET. If the two quantities are not equal there is a change in storage within the catchment. This balance can be expressed by the mass balance equation (3).

$$P=ET+Q+\Delta S \tag{3}$$

P =Precipitation
ET =Evaporation from surfaces and transpiration from vegetation via the stomata
Q =Discharge
ΔS =Change in storage

Over large periods of time undisturbed catchments generally do not show substantial changes in storage (unless the time scale is large enough to cover changes in climate or vegetation cover) and so the term ΔS can be left out from the equation (3) (Grip and Rodhe 2000; Dingman 2015). With this method, ET can be calculated simply as the difference between precipitation and discharge. In Sweden, the water balance is commonly calculated in this way for a hydrological year, which refers to a period from October until next September. The hydrological new-year occurs at a time when storage within the catchment is relatively constant between years. Should the common new year, 31 December, be used instead, the storage would change substantially from year to year due to variations in snow cover depth (Grip and Rodhe 2000).

As previously mentioned, some quantities that are difficult to measure are often modelled rather than measured. Hydrological models can be used for several purposes: to study catchment dynamics, catchment sensitivity to inputs and to project future conditions to mention a few. This thesis uses the model FyrisQ in an attempt to determine its suitability for modelling discharge at Storskogen (Djodjic and Nilsson 2016). It was chosen for its simplicity in terms of input requirements and user friendliness. A well suited model could potentially be more efficient than collecting actual measurements, or to inter- or extrapolate measurement.

FyrisQ is a deterministic descriptive water balance model that models discharge from a catchment on a monthly, weekly or daily basis. It was developed at the Department of Water and Environment at the Swedish University of Agricultural Sciences in Uppsala and contains the same equations and processes as used in the conceptual lumped Water And Snow balance MODeling system (WASMOD) developed at Oslo University (Xu 2002), and can thus be seen as a graphical user interface to WASMOD. The conceptual model is shown in Figure 4.

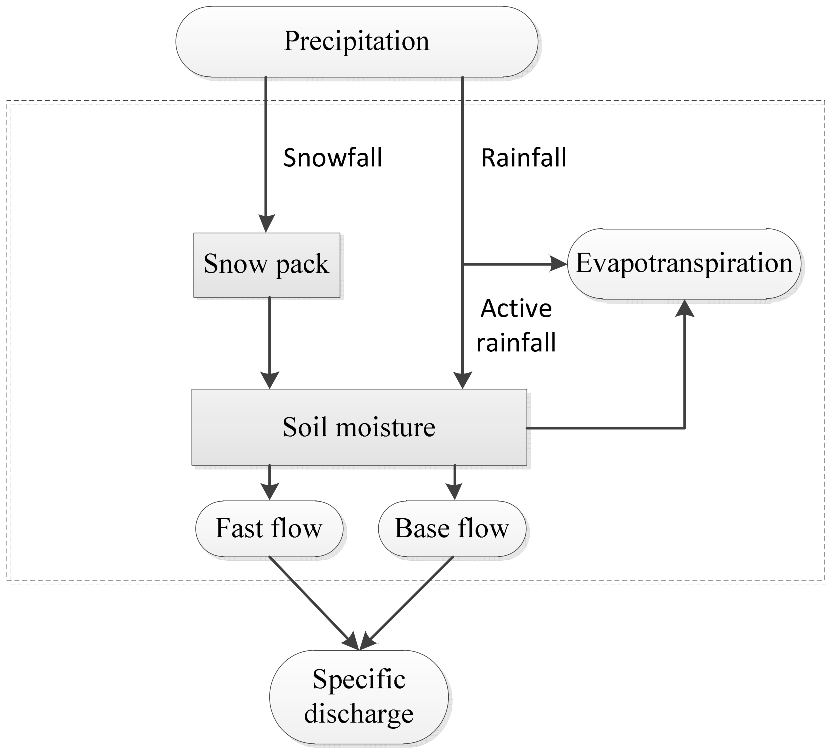

Figure 4. Conceptual model of the water balance model FyrisQ (Modified from Xu 2002).

Precipitation is separated into snow or rain by a temperature index function. After each time step, snow is added to the first state variable ‘snow pack’. Part of the rainfall will be lost through evaporation depending on temperature and only the ‘active rainfall’ fraction will add to the second state variable ‘soil moisture’. When the snow pack melts, depending on temperature, the melt water will be added to the ‘soil moisture’. Soil moisture in its turn contributes to the ET, which depends on the potential ET as well as the available water. It also contributes to both fast and slow flow components of discharge. Slow flow is made up of stored soil moisture, whereas fast flow consists of both storm flow and slow flow. FyrisQ only requires precipitation and temperature as input variables and discharge for calibration and validation. However, it can also take long term climatic averages of temperature and potential ET (PET) as optional input variables for subcomponents of the model. For a detailed description on the equations used see Xu (2002) and Widen-Nilsson et al. (2007).

3 Materials and methods

The workflow used to answer the four research questions is described in Figure 5. In general terms, the questions concerned the hydrology of the catchment in Storskogen, the suitability of using the water balance model FyrisQ to simulate its discharge, the driving factors behind observed differences in acidity within Storskogen and between Storskogen and Gårdsjön.

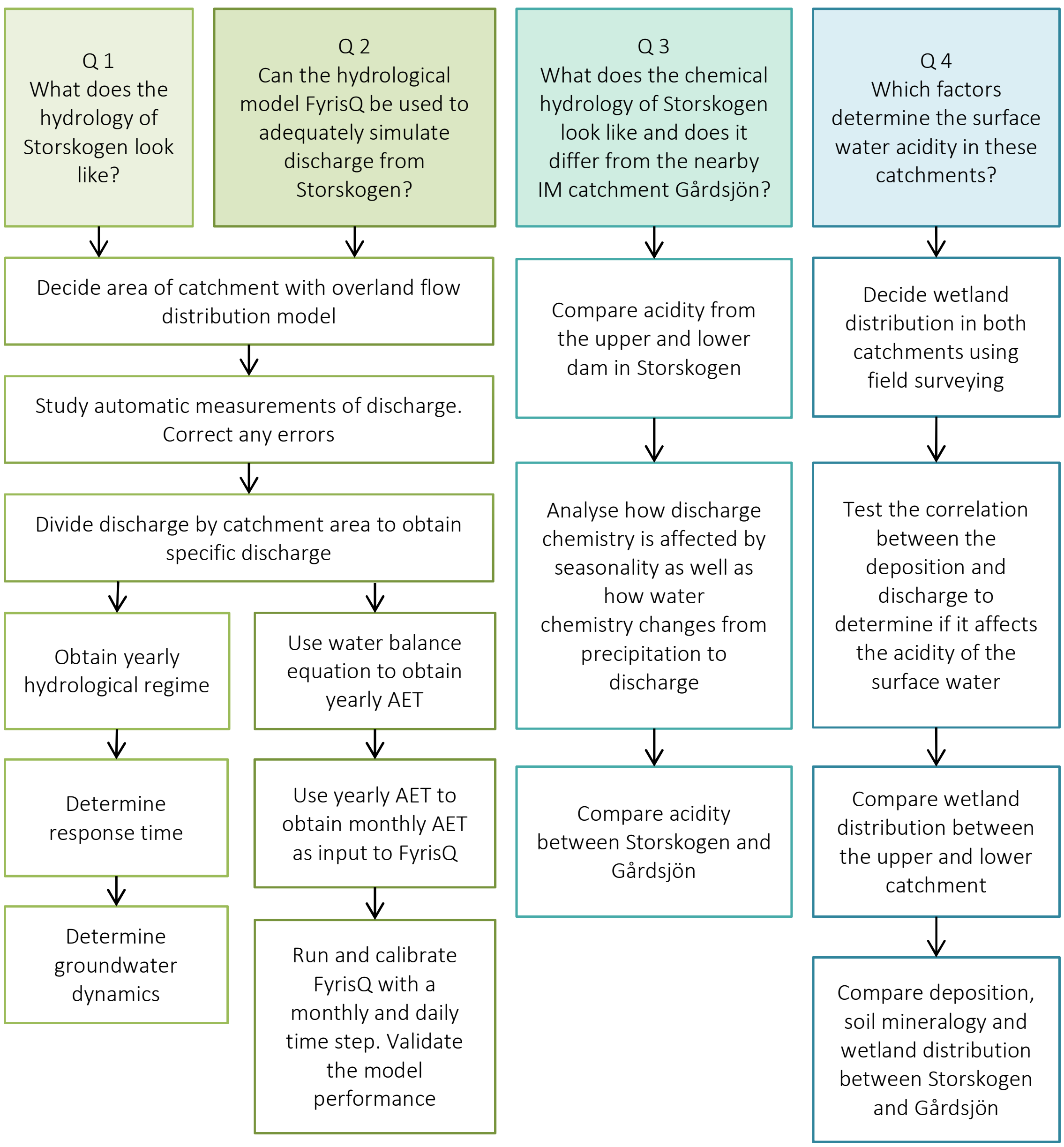

Figure 5. Workflow used to answer the four research questions. Some steps, i.e step 1, 2 and 3 of questions Q1 and 2, were used to answer more than one question and are indicated by broader boxes.

3.1 Site descriptions

The main study site was the catchment at Storskogen (57°51'3" N 12°40'1" E), a site in the SWETHRO monitoring network developed and run by IVL since 2013 (Figure 6; Pihl Karlsson et al. 2011, 2016). The catchment which dewaters a small head-water stream, is located in the Swedish county of Västra Götaland between the cities of Alingsås and Borås and constitutes a part of the river Sågebäcken catchment.

The second study site, Gårdsjön (58°3'19" N 12°1'15" E), is an Integrated Monitoring (IM) site and comprises several catchments. It is located 35 km north of Göteborg and 44 km NW of Storskogen (Figure 6). The sub catchment named F1 (Gårdsjöstiftelsen 2017), hereafter referred to simply as Gårdsjön, was used in this thesis as a reference plot.

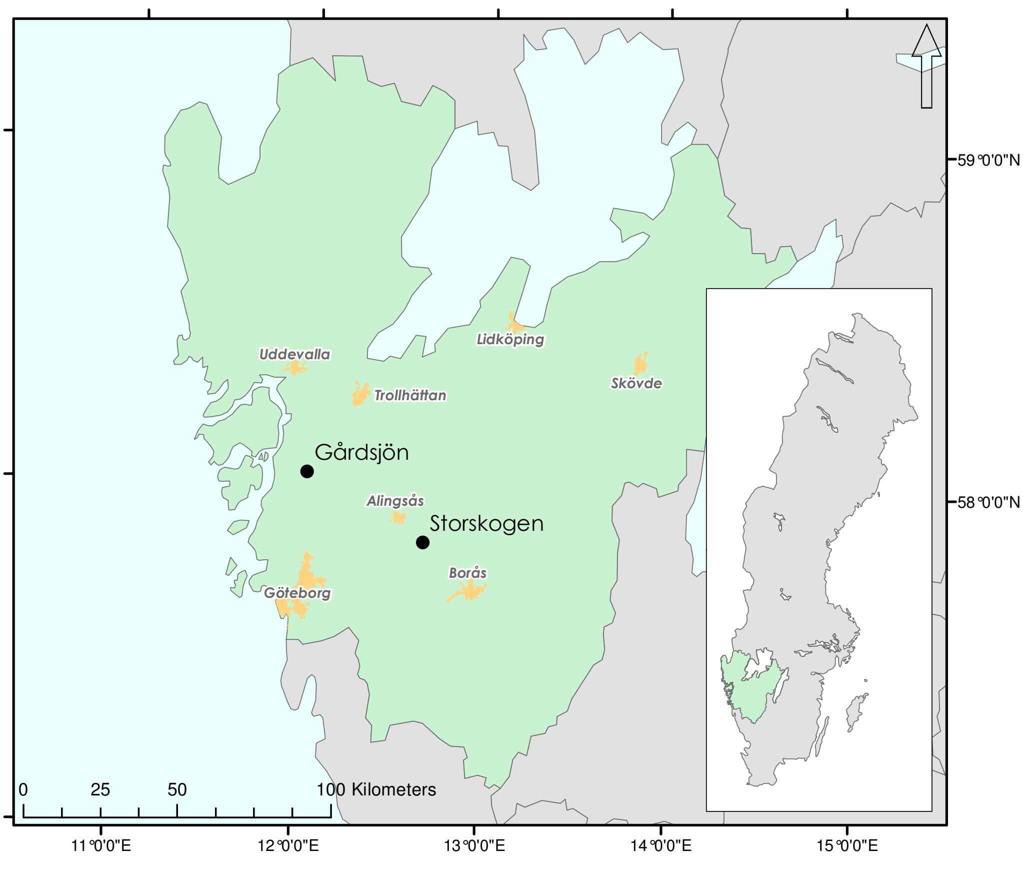

Figure 6. Location of the study sites Gårdsjön and Storskogen. Both sites are located within the Swedish county of Västra Götaland. Base map: GSD-Topographic map © Swedish National Land Survey

Both sites are located in the Boreo-Nemoral zone and are dominated by conifer forests, mainly Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris).* The forest in Storskogen is roughly 90 years old and in Gårdsjön it is around 100 years old (Gradén, pers.

comm; Olsson et al. 1985). Both catchments are in a Cs2 climate according to the Köppen classification, i.e. a temperate climate with precipitation maximum during summer and a mild winter climate (Påhlsson et al. 1984). The mean annual temperature for the climate normal 1961-1990 is 6.1°C and the annual precipitation is approximately 900 mm (SMHI 2017a, b). The two catchments have thin till soils with considerable amounts of exposed outcrops (Olsson et al. 1985). The average soil depth has not been measured at Storskogen but is estimated to be approximately 0.5 m (Jonshagen, pers. comm.), and at Gårdsjön it is estimated to be on average 0.63 m (Sverdrup et al. 1998). The bedrock at both sites is composed of granite-tonalite which, at Storskogen, is older (1700—1670 million years) than at Gårdsjön (1600—1560 million years), (Wastenson et al. 2003). Storskogen is located on average 215 m.a.s.l. and Gårdsjön 128 m.a.s.l.

Storskogen was established as a monitoring site in 2013 on behalf of the county administrative board of Västra Götaland. The throughfall, open field and soil water measurements are part of the Swedish Throughfall Monitoring (SWETHRO) network, and are financed by the regional air quality protection association and local county administrative board (Pihl Karlsson et al. 2011). The discharge and groundwater measurements are financed by the Swedish Agency for Marine and Water Management as well as the Swedish Forest Agency and the local county administrative board (Pihl Karlsson et al. 2016). All measurements were analysed for chemical compounds by IVL according to standardised methods described further by Akselsson et al. (2013). Table 1 gives an overview of the measurements and sampling frequencies at Storskogen.

Table 1. Measurement periods for the sampling locations at Storskogen. Simultaneous measurements for all stations are available for 17 months from May 2015 to September 2016.

Measurement	Measurement period	Sampling frequency
Groundwater	2014-06 to 2017-01	Monthly
Stream lower dam	2014-04 to 2017-01	Monthly/ Automatically every 10 min
Stream upper dam	2015-05 to 2017-01	Monthly/ Automatically every 10 min
Soil water	2014-04 to 2016-09	2—5 times/year
Throughfall deposition	2014-01 to 2016-09	Monthly
Open field deposition	2014-10 to 2016-09	Monthly

The location of the measurement stations within the two catchments is illustrated in Figure 7. This section will focus on the hydrological monitoring and collection methods at Storskogen, which are the same as were used at Gårdsjön. For a detailed description of the collection methods at Gårdsjön, see e.g. Löfgren et al. (2011) and Andersson and Olsson (1985).

The results of the chemical components analysis were delivered in mg l^{-1}. For calculations of ANC the results were recalculated to µeq l^{-1}. To calculate yearly wet and dry deposition, the deposition values were multiplied by the total yearly precipitation and recalculated to kg ha^{-1}.

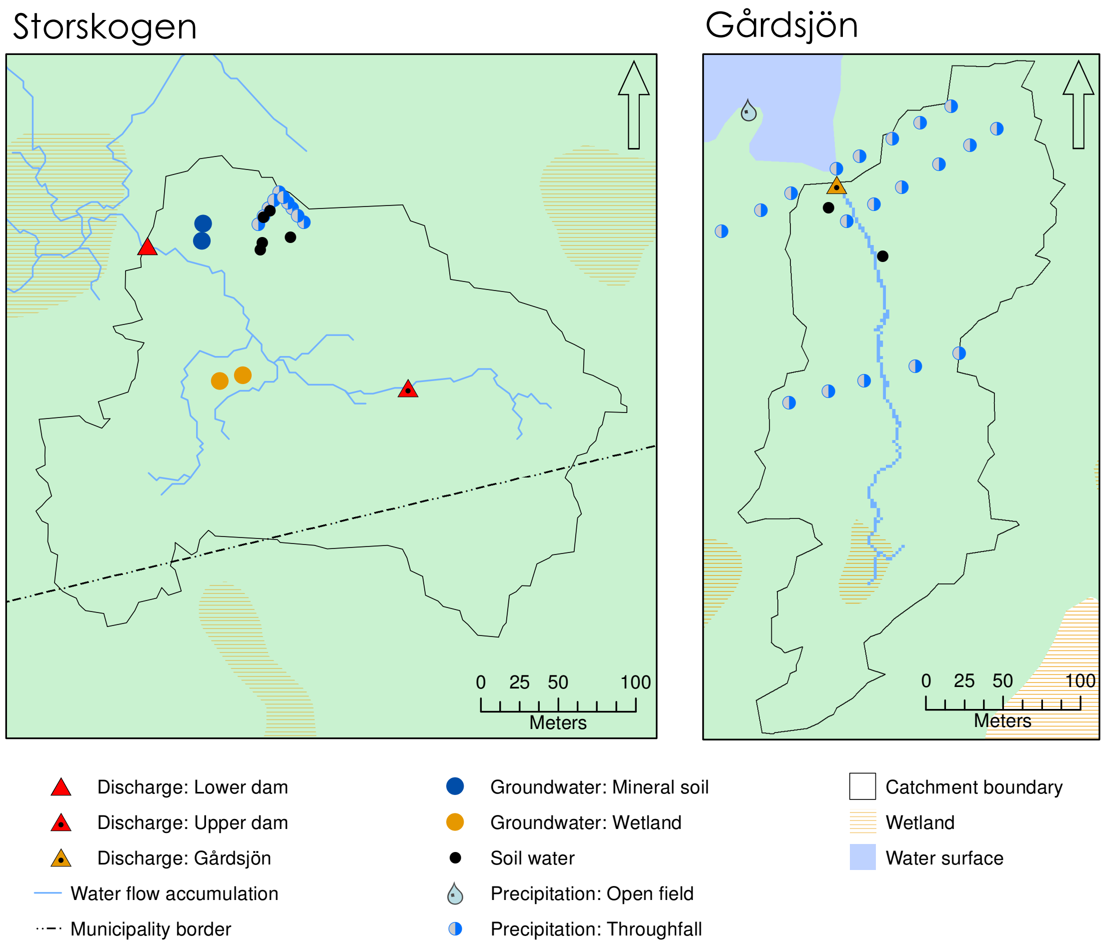

Figure 7. Locations of measurement stations within Storskogen and Gårdsjön. The catchments are monitored using suction lysimeters for sampling soil water, piezometers for groundwater and precipitation is measured as both open field and throughfall. In Storskogen there are two V-notch dams for discharge monitoring, whereas Gårdsjön only has one. Base map: GSD-Topographic map © Swedish National Land Survey

Precipitation was measured at two locations, as throughfall and as open field. Throughfall was measured along two transects in the northern part of the catchment and collected via funnels into ten plastic containers. During winter, the throughfall was collected directly in the plastic containers. The open field measurements were collected from a meadow roughly 300 metres south of the catchment.

Soil water chemistry was monitored using five suction lysimeters that sampled water from a depth of 50 cm. Two 100 cm piezometers were installed to monitor groundwater level and chemistry in the mineral and a further two piezometers monitor the wetland.

A Thomson weir, or a V-notch dam, with a notch-angle of 120 degrees was constructed in April 2014 (Figure 8 a). A pressure sensor connected to an automatic data logger (DL/N70.

Sensor Technik Sirnach AG, Switzerland) was installed to register the water height above the V-notch, with measurements taken at 10-minute intervals from June 3 2014. This dam is referred to as the lower dam. A second dam, with a notch-angle of 90°, was constructed further up in the catchment a year later, in April 2015 (Figure 8 b). This dam is referred to as the upper dam. Both dams were fitted with stainless steel netting in October 2015 to prevent dirt from accumulating in the notch. Manual discharge measurements were taken at monthly intervals to validate the automatic measurements.

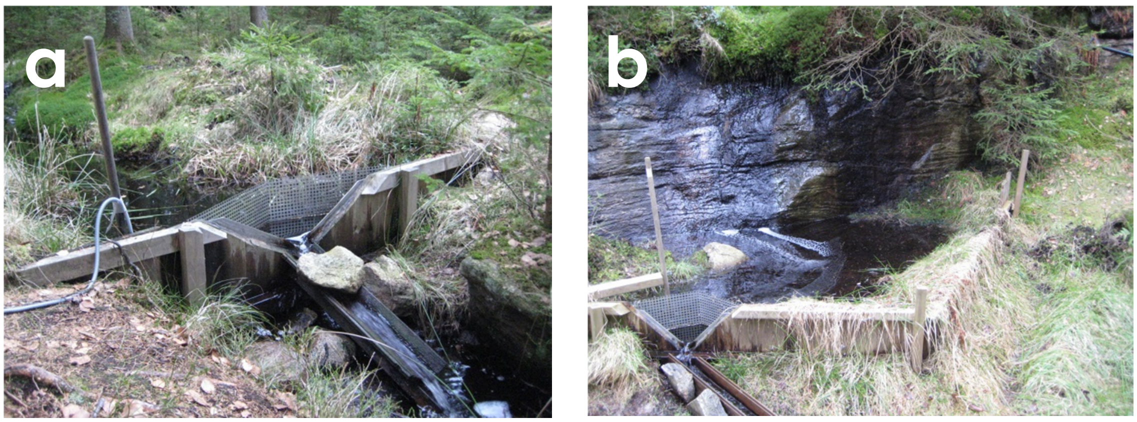

Figure 8. Discharge measurement setup at the a) lower dam, and b) upper dam in Storskogen. The V-notch at the lower dam has an angle of 120° and 90° at the upper dam. Installed in both dams are pressure sensors connected to automatic data loggers that register the water table height above the V-notch every 10 minutes.

3.2 Hydrology in Storskogen

The first aim of this study was to characterise the hydrology of Storskogen (research question 1). This was done using the automatic discharge measurements from the lower dam, and the groundwater level measurements from the wetland and the mineral soil. To be able to calculate specific discharge, the size of each sub-catchment had to be decided.

3.2.1 Catchment delineation

All spatial hydrologic modelling was based on a digital elevation model (DEM) of the catchments with a two metre resolution. The GIS data used in this study are listed in table 2. The DEM was used as input to a Triangular Form-based multiple flow algorithm (TFM) developed by Pilesjö and Hasan (2014). TFM calculates flow paths from each cell of the DEM and distributes it to one or more of the eight surrounding cells based on their relative elevation. TFM will also calculate the total number of cells that drain into the single cell entered as the pour point, or outlet, of the catchment, i.e. determine the area of the catchment.

Furthermore, it can decide the flow accumulation by calculating the number of cells that drain into every cell within the DEM (Pilesjö and Hasan 2014).

For Storskogen two GPS coordinates, one from the upper and one from the lower dam, were used as pour points for modelling the flow at Storskogen. Upon inspection, the catchments produced by the model were smaller than 100 m^2 each and not connected. Since this was known to be incorrect, each GPS-sampled pour point was automatically repositioned to the closest cell with the highest flow accumulation within the 7 metre position accuracy of the GPS-receiver (Thales Navigation 2002). For Gårdsjön the same procedure was used with just one pour point at the position of the gauging station.

Table 2. Topographic data used in this thesis. The elevation model was used for overland flow distribution while the topographic map was used as a base map.

Product name	GSD-Elevation data, Grid 2+	GSD-Topographic map
Format	Raster	Vector
Resolution	2 m	-
Projection	Plane: SWEREF 99TM Height: RH 2000	Plane: SWEREF 99TM Height: RH 2000
Govt. agency	Swedish National Land Survey	Swedish National Land Survey
Accuracy	Plane: 0.25 m Height: 0.05 m	Plane: 10 m
Data collection	March 2012	-

3.2.2 Hydrological characteristics

Upon inspection of the automatic discharge measurements, it became clear that certain values were incorrect. In order to correct these for modelling purposes, the following discharge data processing was performed.

Discharge data processing

Firstly, all negative discharge values present in the data were replaced with 0. The negative values were due to the pressure sensor registering a water table height below the notch. The stream in Storskogen is small and it is possible that the flow of water could not reach above the notch during certain times. However, this should be registered as no flow, i.e. 0, and not as negative values. The resultant negative values were simply due to limitation of the equation (2) used to calculate discharge (Persson, pers. comm.).

The 10-minute measurements were subsequently summed to daily values and further divided by the catchment area, as given by the flow distribution model, to obtain the specific discharge (q) in unit mm d^{-1}. It was noted that there were outliers in the high values with measurements of as much as 146 mm d^{-1} (Figure 9). Considering that the average yearly specific discharge in this area is approximately 500 mm, these measurements were assumed to be wrong and were further edited as described below (SMHI 2009).

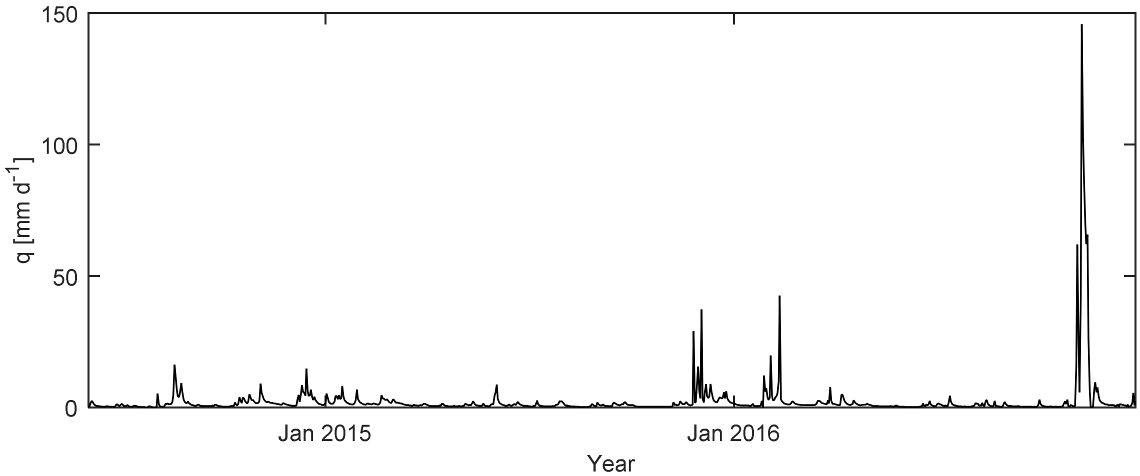

Figure 9. Original specific discharge from Storskogen after negative values had been removed. The logger seems to have functioned correctly until the end of 2015. During 2016 some abnormally high storm peaks, reaching as high as 146 mm day^{-1}, were present in the data.

The specific discharge was subsequently analysed together with the three closest quality controlled Swedish meteorological and hydrological institute (SMHI) hydrometric stations: Tvärsjön2, Hällered and Bosgården (Table 3).

Table 3. Location of the three hydrometric stations: Tvärsjön2, Hällered and Bosgården, of which the specific discharge were compared to Storskogen (SMHI 2017d).

Hydrometric station	Location	Distance (km) and direction from Storskogen	Catchment size (km^2)
Tvärsjön2	57°76' N 12°4' E	20.5 WSW	5.2
Hällered	57°79' N 12°74' E	9.1 SSE	42.2
Bosgården	57°81' N 13°06' E	23.3 ESE	354.7

The discharge from Storskogen followed the dynamics of the other stations closely but with higher peaks and what appeared to be faster response to precipitation, which would be logic considering that the catchment at Storskogen is considerably smaller than the others. The data were subsequently tested for linear dependence. Pearson's correlation coefficient suggested that the correlation between Storskogen and all three SMHI stations were strongly significant ($p<0.001$), and that the strongest positive relationship was between Storskogen and Hällered (R: 0.19**). The low R value was due to the previously mentioned outliers in the Storskogen data. Hällered was thus further used in order to adjust the Storskogen data.

After careful analysis it was concluded that the logger mainly gave unreasonable discharge values during high flow events and that, during periods when the logger functioned correctly, Storskogen would display higher peaks than Hällered. For these reasons, only dates when Hällered registered a specific discharge of 5 mm d^{-1} or more (assumed to represent high flow events) were used for further editing.

When discharge from Storskogen exceeded that of Hällered, it had a median value of 4.2 mm day^{-1} higher than Hällered. This information was used in order to remove the outliers from the Storskogen data using a conditional statement: If discharge from Storskogen exceeded that from Hällered with more than 4.2 mm day^{-1} it was replaced with the value from Hällered plus 4.2 mm. This brought down the maximum discharge value from 146 to 13 mm day^{-1}. There were, however, still some values that appeared to be wrong in November 2016 (Persson, pers. comm.). When a further comparison between these values and daily precipitation measures from the SMHI weather station in Alingsås, failed to explain the dynamics of the discharge (not shown), it was decided that these values should be linearly interpolated between the dates October 31st and November 25th 2016 (Figure 10 dashed box; Persson, pers. comm.).

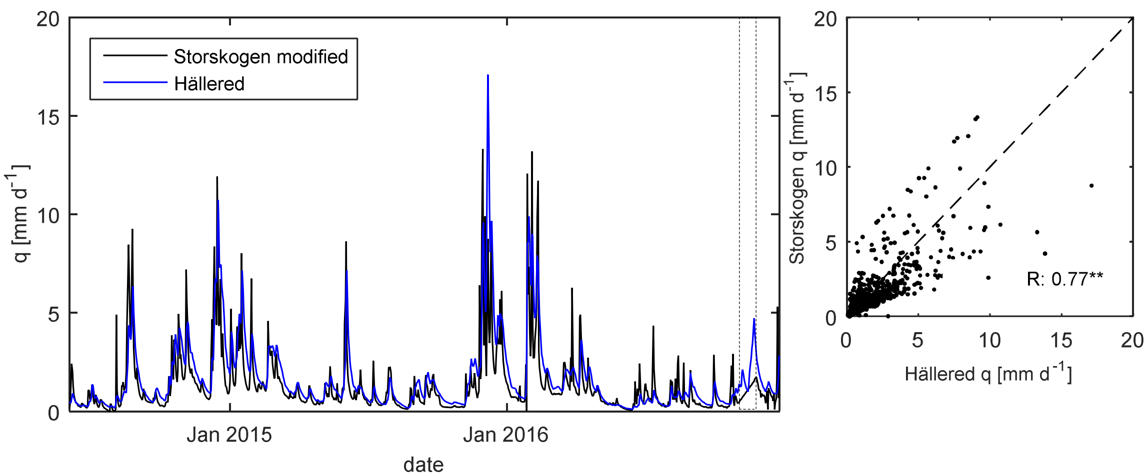

Figure 10. Comparison between the modified discharge data from Storskogen and Hällered. The dashed box indicates where Storskogen specific discharge could be explained neither by Hällered nor by precipitation and was linearly interpolated. The interpolation was done from October 31st 2016 to November 25th 2016. The scatter plot shows the correlation between Hällered and the modified Storskogen data (R: 0.77**).

Hydrological regime and response time

The following characteristics were examined to describe the hydrology of Storskogen: hydrological regime, response time and groundwater level. Hydrological regime is a term that refers to the discharge dynamics, averaged over a longer period of time, and observations of its fluctuations. For Storskogen the specific discharge for the full measurement period (April 2014 to January 2017) was averaged to discharge per month.

Since the precipitation sampling frequency at Storskogen was too low, the response time, i.e. the time lag between peak precipitation and peak runoff, was analysed using daily precipitation data from the SMHI weather station in Alingsås. The month of January 2015 was chosen for further inspection since the monthly precipitation was measured to exactly 121.3 mm at both locations (Figure 11).

Precipitation from Alingsås does not necessarily represent the conditions in Storskogen, mainly because of an important orographic effect in south western Sweden, but the monthly values were well correlated between sites (R 0.76**, Johansson and Nilsson 1985).

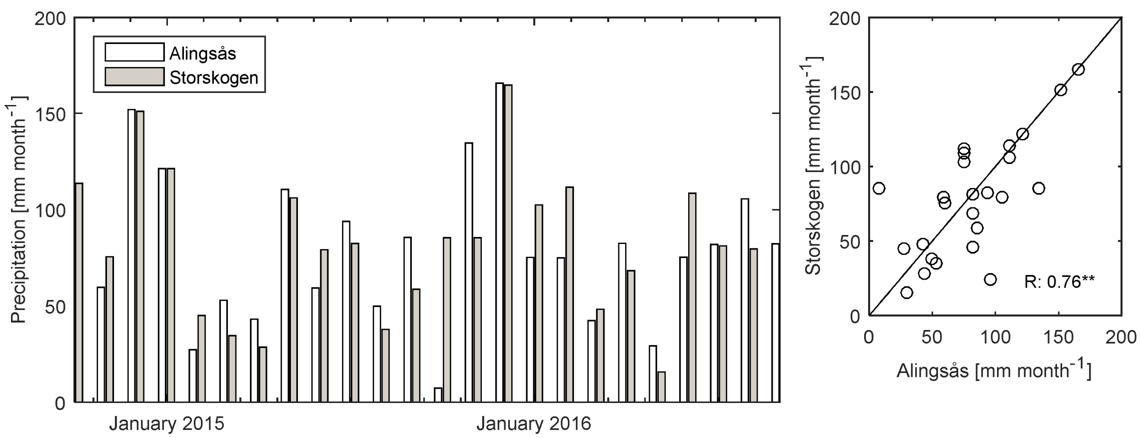

Figure 11. Monthly precipitation from Alingsås and Storskogen (open field measurements). The scatter plot indicates that there was a strong positive correlation between Alingsås and Storskogen (R: 0.76**).

3.3 Modelled discharge

3.3.1 Water mass balance equation

The water mass balance equation (3) was used to determine yearly actual evapotranspiration (AET) from Storskogen. The yearly AET was further divided into monthly values, used as input to the water balance model FyrisQ to answer research question two.

Two full hydrological years of open field precipitation measurements (October 1st 2014 to September 30th 2016) were available and used to calculate yearly precipitation values (P). The modified discharge measurements from the lower dam were used to obtain yearly specific discharge values for the same time-period (R). P and R were subsequently used as input variables to calculate the yearly ET as per equation (3).

In Eriksson (1981) the average monthly potential ET (PET) for Borås was calculated for the period 1961-1978, using Penman's equation. As previously mentioned, PET assumes unlimited water resources. To get from PET to AET, the difference between the yearly PET, i.e. the sum of all months, and the yearly AET was calculated. The mean of the two differences was 89.6 mm year^{-1}.

The difference between PET and AET for each month was then subtracted by assigning each month a weight depending on its contribution to the total yearly PET (Figure 12). As an example, the PET in June was 117 mm which constituted 21.5% of the yearly total PET. 21.5% of the average yearly difference between PET and AET, in this case 19.3 mm, was removed from the PET to get the AET of 97.7 mm. These values were further used in the water balance model FyrisQ described in section 3.3.2.

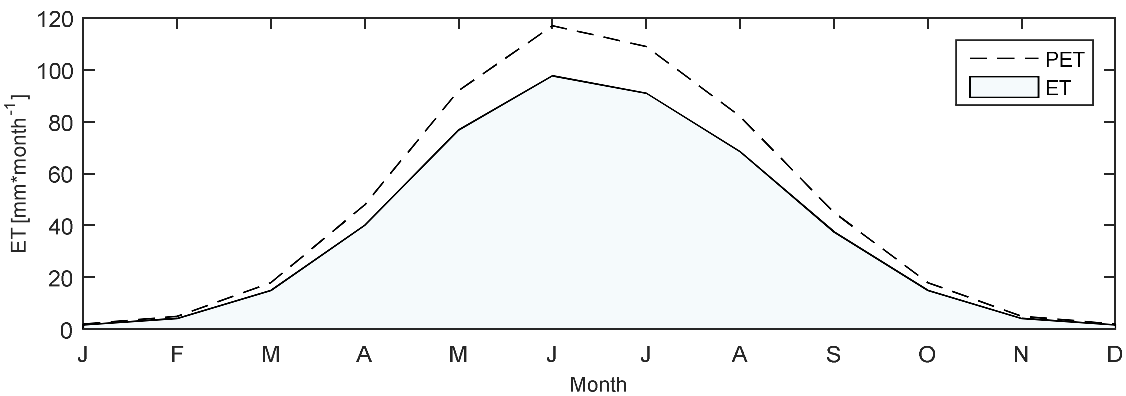

Figure 12. The monthly evaporation at Storskogen as ET and PET. The values for each month were obtained by subtracting the proportion of the yearly difference between PET and ET for each month from the PET.

3.3.2 Discharge modelling with FyrisQ

The water balance model FyrisQ was initially run using a daily time step to capture the dynamic discharge pattern of the catchment. However, the models daily time step is at the limit of its performance and the monthly time step often leads to better results (Widén Nilsson, pers. comm.). Therefore, a second run with a monthly time step was performed.

The input variable specific discharge was based on data from the lower dam in Storskogen. Temperature data was taken from the recorded daily average temperature data from the SMHI weather station Rångedala A (57°78'N 13°17'E), approximately 30 km east of Storskogen (SMHI 2017c). Rångedala weather station was chosen for its proximity to Storskogen and because it is located in an area that closely resembles Storskogen in terms of vegetation and remoteness.

Some of the sub components of the model required further input in the form of monthly average AET (named ET in the model) and temperature (Table 4). Here, the previously presented monthly ET was used. The average temperature in this case was based on temperature data from the SMHI weather station in Borås (57°76'N 12°95'E) for the period 1961—1990 (SMHI 2017c). In this case Rångedala was not used because of its lack of long-term data.

Table 4. Input parameters to FyrisQ of monthly average temperature and ET for Borås and Storskogen respectively.

Input variable	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Temp (°C)	-2.9	-3.0	0.0	4.3	10.3	14.4	15.5	14.7	11.0	7.3	2.6	-0.9
ET (mm)	2.0	4.0	15.0	40.0	77.0	98.0	91.0	68.0	38.0	15.0	4.0	2.0

The model was run with a start-up period of 1 year (June 3rd 2014 – June 2nd 2015) to stabilise land moisture and snow pack values. Because of the short available time series, and to preserve data for validation, the calibration was performed on that same first year. The calibration was run using 10 000 Monte Carlo simulations with combinations of random parameter settings between the parameter interval boundaries specified in table 5. The model was set to use all 6 available tunable parameters. The resultant best parameter combination based on RMSE was subsequently used for validation on the period June 2015 to December 2016 for the monthly time step, and June 2015 to January 2017 for the daily time step (Table 5). To answer research question 2 the model fit was evaluated using the coefficient of determination as well as the root mean square error (RMSE).

Table 5. Summary of parameters used FyrisQ and the model processes they govern. Here presented together with suggested values and restrictions, and finally the calibrated values used in the validation

Parameter	Governing	Interval boundary	Restrictions	Value (Monthly)	Value (Daily)
a1	Snowfall	1— 3	-	1.32	2.72
a2	Snowmelt	-3— -1	-	-2.90	-2.50
a3	PET	0— 0.2	$a3 \geq 0$	0.04	0.19
a4	ET	0— 1	$0 \leq a4 \leq 1$	0.86	0.99
a5	Slow runoff	0— 0.1	$a5 \geq 0$	0.06	0.09
a6	Fast runoff	0— 0.01	$a6 \geq 0$	0.0012	0.0053

3.4 Surface water chemistry

The third research question was answered by analysing the chemical composition of water in the form of open field precipitation, throughfall and discharge. Statistical tests were performed to analyse the difference in acidity between the upper and lower dam in Storskogen, as well as the difference between Storskogen and Gårdsjön.

All statistical tests were performed in the statistical analysis software SPSS with a significance level of 0.05 (IBM SPSS Statistics for Windows, version 20, IBM Corp., Armonk, N.Y., USA). Significant results are indicated by one, two or three asterisks for $p \leq 0.05$, $p \leq 0.01$ and $p \leq 0.001$ respectively. All variables were tested for normal probability distribution using the Shapiro-Wilks test. Data that failed to reach a significant normal probability distribution were transformed using logarithmic and square root transformations but since, for several of the variables, the transformations failed to achieve normal distribution, non-parametric tests were chosen. Non-parametric tests make no assumptions about probability distribution and are often a better choice when sample sizes are small which was the case with this three year time-series (McCarroll 2016).

Measurements of discharge chemistry from the upper and lower dam were assumed to be paired because of the short, less than 200-metre distance between the two dams. Therefore the difference in acidity between the dams in Storskogen was tested using Wilcoxon's matched-pairs signed-ranks test for all variables and with Student's paired t-test for the variables that had a normal probability distribution.

Differences in acidity between Storskogen and Gårdsjön were assumed to be independent. These were tested using a Mann-Whitney's U test.

3.5 Drivers of acidity

To determine the driving factors behind the acidity of the surface water, research question four, a number of variables were considered, namely: deposition of acidifying substances, mineralogy of the soil and the wetland-affected fraction of surface water that reached each dam.

Deposition

At first it was determined whether or not the deposition influenced the acidity of discharge by use of Spearman's rank correlation-test. It was used to statistically test if the pH and ANC of discharge water were correlated with the deposition values. All variables were inspected for outliers using box plots, and the results from the test were used to partly determine which factors determine the acidity of discharge. Secondly, it was determined if there was any significant difference in deposition between Storskogen and Gårdsjön using a Mann-Whitney's U test.

Mineralogy

Data on the soil mineralogy of Storskogen and Gårdsjön was collected with a short literature review, using both published and unpublished work regarding the total element content of the catchments.

Delineation and influence of wetlands

Each study site was geographically surveyed using a handheld GPS receiver (Magellan SporTrak Pro) in order to determine the wetland coverage, and to map the locations of measurement stations. Storskogen and Gårdsjön were surveyed on 16th and 17th March 2017 together with environmental consultant Anders Jonshagen in Storskogen, and with Hans Hultberg from IVL at Gårdsjön.

The definition of wetland was based on available descriptions by Påhlsson (1998) and by Gunnarsson and Löfroth (2009), as well as by the Swedish Forest Agency (Skogsstyrelsen 2017). A forested wetland is a wetland with a canopy cover of at least 30% consisting of trees with an average height of a minimum of 3 m. Wetland soil should be highly organic and the peat cover should be at least 30 cm. It should have a field cover consisting of at least 50% hydrophilic species such as peat moss (*Sphagnum*), haircap moss (*Polytrichum*) or sedge (*Carex*), and the groundwater table should be near or at the surface during most of the year.

In most cases the separation between soil types was easily identifiable. The wetlands were also typically low-lying which made the delineation straight forward. All indicators used to define wetlands were present at both sites, as illustrated in Figure 13. The border of each wetland was noted using GPS waypoints approximately every 10 m or more if needed to capture the details. After adding the waypoints into ArcMap (ArcGIS, release 10.2.2, Environmental Systems Research Institute (ESRI), Redlands, CA., USA) and calculating the area of the wetlands, the point within each wetland with the highest flow accumulation, the lowest position of the wetland, was selected. The positions of those points were used as pour points in TFM to determine the size of the catchment surface that drain to the wetland and thus, the fraction of surface water affected by wetlands.

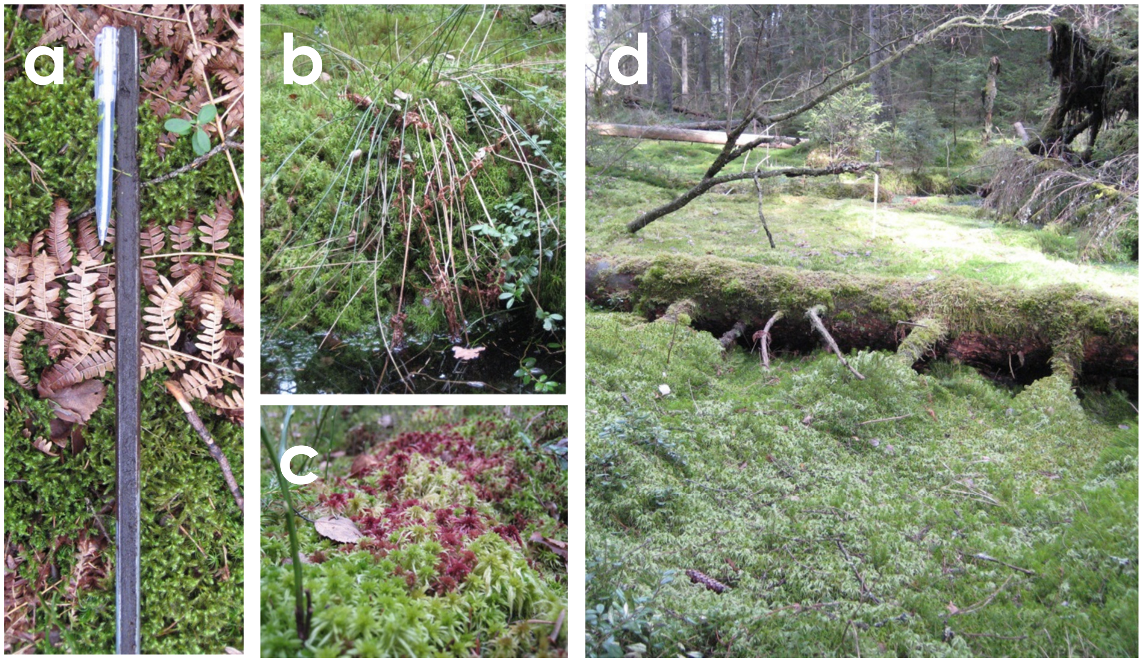

Figure 13. Four photos from Storskogen and Gårdsjön that display indicators used to define a wetland. A) A soil core from the upper wetland at Gårdsjön that shows how the depth of the peat layer was sampled using a soil core sampler. The peat was often deeper than the actual sampler. B) *Carex* C) *Sphagnum* D) A fallen tree in the lower wetland and Gårdsjön covered by *Sphagnum*.

4 Results

4.1 Hydrology in Storskogen

4.1.1 Catchment delineation

The overland flow distribution model TFM generated the catchment boundaries presented in e.g. Figure 7. The entire catchment at Storskogen measured 7.1 hectares and the sub catchment that drains to the upper dam measured 1.9 hectares. The catchment at Gårdsjön measured 4.9 hectares.

4.1.2 Hydrological characteristics

Discharge during the observed period ranged from 0 to 10.9 (σ 1.4) l s^{-1}, with a median discharge of 0.7 l s^{-1}. Figure 14 illustrates the hydrological regime of Storskogen with specific discharge averaged per month based on the period April 2014 to January 2017. Storskogen displayed only one discharge maximum which occurred during winter. The discharge rate is at its lowest during summer even though precipitation does not decrease in the same manner. Increased evaporation, due to higher temperature, and increased uptake by plants most likely account for these dynamics.

Figure 15 shows the hydrograph of the lower dam together with a hyetograph for Alingsås from January 2015 as an example of the response time of the catchment. The headwater stream at Storskogen responded quickly to precipitation and the response time appears to have been approximately one day. The 10-minute discharge data revealed minor variability during the course of 24 hours (not shown) indicating that, although it is possible that the response time is faster than one day, a time-resolution of one day captures the major dynamics of the catchment and is thus suitable for modelling-purposes.

The groundwater levels in the mineral soil and in the wetland are displayed in Figure 16. Groundwater levels in the wetland were only measured for a short period: August 2016 – February 2017, but for the measured period, the water table reached its highest level during winter and its lowest during summer which followed the pattern of the longer time-series of groundwater level measurements in the mineral soil.

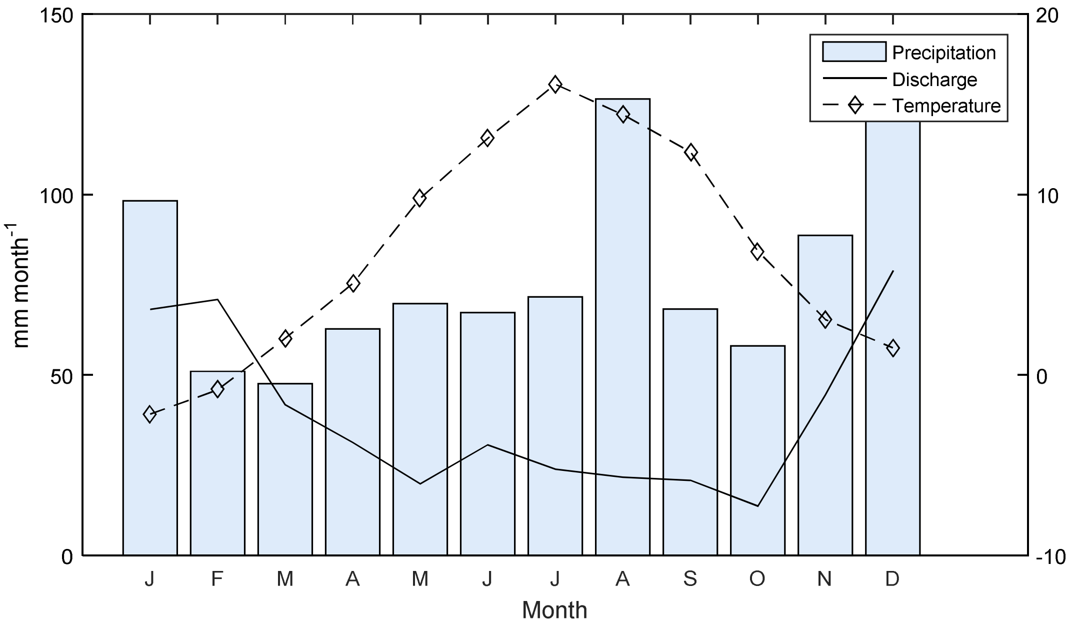

Figure 14. Hydrological regime at Storskogen. Climate graph and specific discharge (mm month^{-1}) from Storskogen shows the yearly hydrological regime for the period April 2014 to January 2017. Storskogen displayed a single discharge maximum during winter and a significant decrease during the summer months.

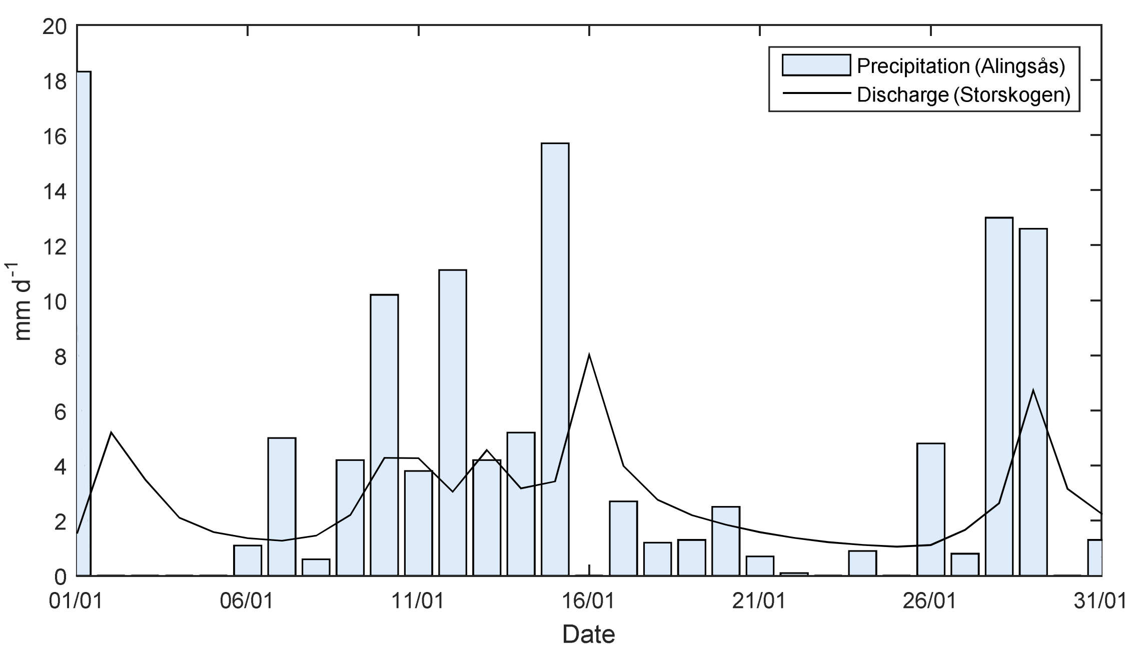

Figure 15. Response time at Storskogen. Hydrograph of the lower dam in Storskogen and hyetograph of Alingsås for January 2015. Storskogen had a response lag of approximately one day, meaning that the discharge maximum occurred one day after the precipitation maximum.

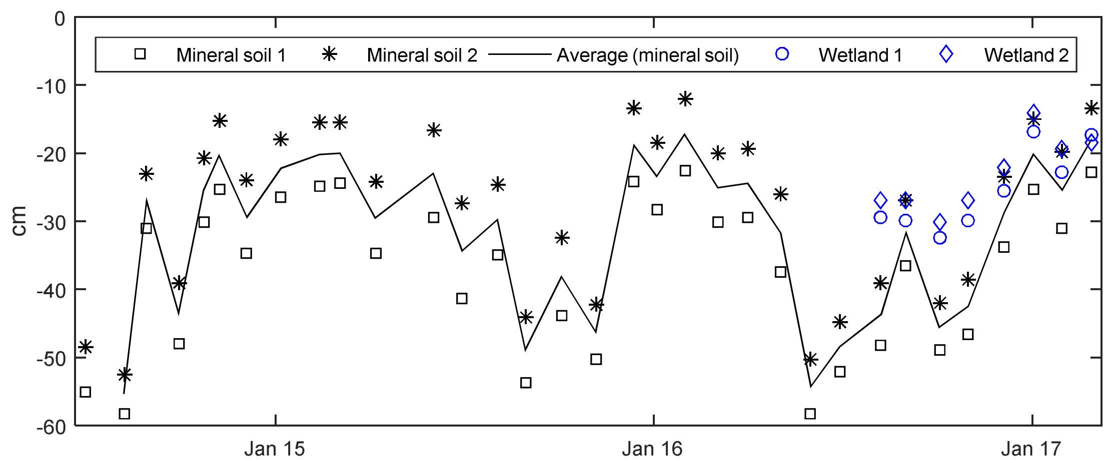

Figure 16. Groundwater level in the lower wetland and in the mineral soil at Storskogen from July 2014 to February 2017. The water table was high during winter and low during summer.

4.2 Modelled discharge

4.2.1 Water mass balance equation

The water mass balance was calculated for the two available full hydrological years (October to September) 2014—15 and 2015—16. Total yearly AET was calculated as the difference between the open field precipitation (P) and the cumulative specific discharge (Q) as per the water balance equation (4), and it equalled 401 mm for the first year and 505 mm the second.

Table 6. Water balance variables for Storskogen for the hydrological years 2014—15 and 2015—16. All units are in mm. Precipitation (P) and discharge (Q) are measured variables. ET is the calculated yearly AET based on the water balance equation (4). The difference between the potential ET (PET_E) for Borås and the calculated ET is presented as ΔET.

Hydrological year	P	Q	ET	PET_E	Δ ET
2014—15	934	533	401	543	142
2015—16	997	492	505	543	38

The resulting ET was compared with the average yearly potential ET for Borås (PET_E) as calculated by Eriksson (1981). The difference between the PET_E and actual ET was 142 mm the first year and 38 mm the second. The actual ET thus constituted 74% of PET_E the first year and 93% the second.

4.2.2 Discharge modelling with FyrisQ

The model validation was run using independent data from Storskogen from June 2015 to January 2017 for the daily time step, and from June 2015 to December 2016 for the monthly time step. The results are shown in Figure 17.

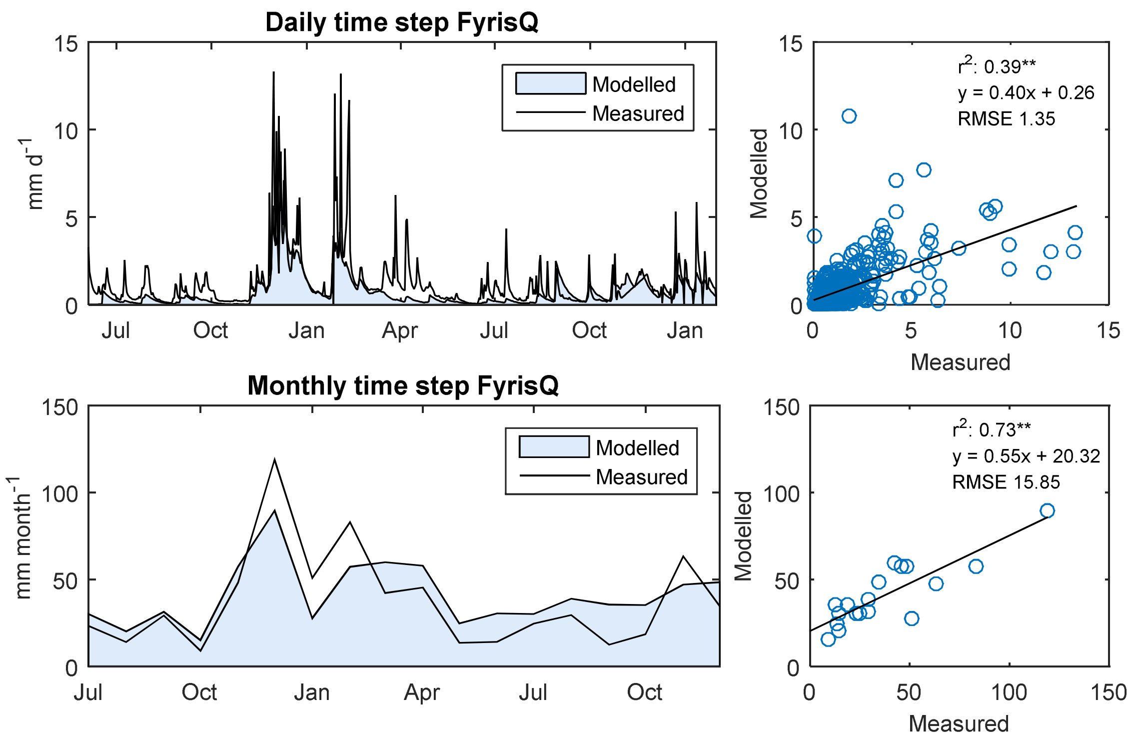

Figure 17. Validation of the model performance of FyrisQ for discharge simulation in Storskogen. The model performance was higher when the model was run with a monthly rather than a daily time step. The daily time step resulted in an overall model underestimation of the storm peaks and the monthly time step resulted in a model overestimation except during winter months.

The coefficients of determination gives that 39% of the discharge variation was explained by the daily time step model (r^2 0.39), and that 73% of the variation was explained by the monthly time step model (r^2 0.73). A further indication of the superiority of the monthly time step was the root mean squared error (RMSE). RMSE for the daily time step was 1.35 mm d^{-1} whereas for the monthly time step it was 15.85 mm $month^{-1}$. A daily error of 1.35 mm would result in a monthly error (30 days) of 40.5 mm.

The daily model was unable to recreate the amplitude of the measured peaks and generally underestimated discharge from the catchment, whereas the monthly model mostly overestimated discharge. However, during the winter months November to February, the monthly model also underestimated the discharge because precipitation was added to the snow pack in the model (not shown).

4.3 Surface water chemistry

4.3.1 Differences between the upper and lower dam in Storskogen

The discharge chemistry measured at the upper dam in Storskogen differed significantly from that from the lower dam during the observed period (Table 7). The results of the Wilcoxon's matched-pairs signed-ranks test indicate that concentrations of all measured variables (with the exception of DOC) were significantly ($p<0.05$) higher in the lower dam. The results of Student's t-test, used to test the normally distributed variables, further reinforced the significance of this difference (Table 7). Both pH and ANC were lower in the upper dam during the observed period. The average concentration of DOC was higher in the lower dam (near significance p 0.08).

Table 7. Difference in discharge chemistry between the upper and the lower dam in Storskogen using Wilcoxon's matched-pairs signed-ranks test (Wilcoxon's) and Student's t-test assuming paired samples (Student's). The mean values are in unit mg l^{-1} apart from ANC which is given as µeq l^{-1} and pH which is unitless.

Wilcoxon's	**µ Upper dam (mg/l)**	**µ Lower dam(mg/l)**	**T**	**One tail significance (p)**
pH	4.30	4.51	153	<0.001***
ANC	0.01	0.04	153	<0.001***
DOC	18.93	19.30	47	0.082
SO_4^{2-}	0.65	0.93	117	0.006**
NO_3^-	0.01	0.03	66	0.002**
Cl^-	7.72	10.27	153	<0.001***
NH_4^+	0.04	0.05	45	0.037*
Na^+	4.52	6.40	153	<0.001***
K^+	0.19	0.25	136	<0.001***
Mg^{2+}	0.46	0.69	153	<0.001***
Ca^{2+}	0.54	1.03	153	<0.001***

Student's	**µ Upper dam (mg/l)**	**µ Lower dam (mg/l)**	**t**	**One tail significance (p)**
pH	4.30	4.51	-9.323	<0.001***
ANC	0.01	0.04	-3.319	0.003**
SO_4^{2-}	0.65	0.93	-2.643	0.011*

Seasonal dynamics

The pH level of the discharge in both dams, as shown in Figure 18, is relatively steady throughout the year, whereas the DOC concentrations and ANC show a marked increase during the summer months. The seasonal dynamics of the ions concentrations that make up ANC were also analysed in order to determine what decided this dynamic (Figure 18). For ANC to increase either the concentration of anions must decrease or the concentration of cations must increase. The anions sulphate (SO_4^{2-}) and nitrate (NO_3^-) did decrease markedly during the growing season, while Cl^- showed a less strong decline. The cations Ca^{2+} and Mg^{2+} increased during the growing season. Concentrations of Na^+ were steady throughout the year and K^+ showed an early spring peak.

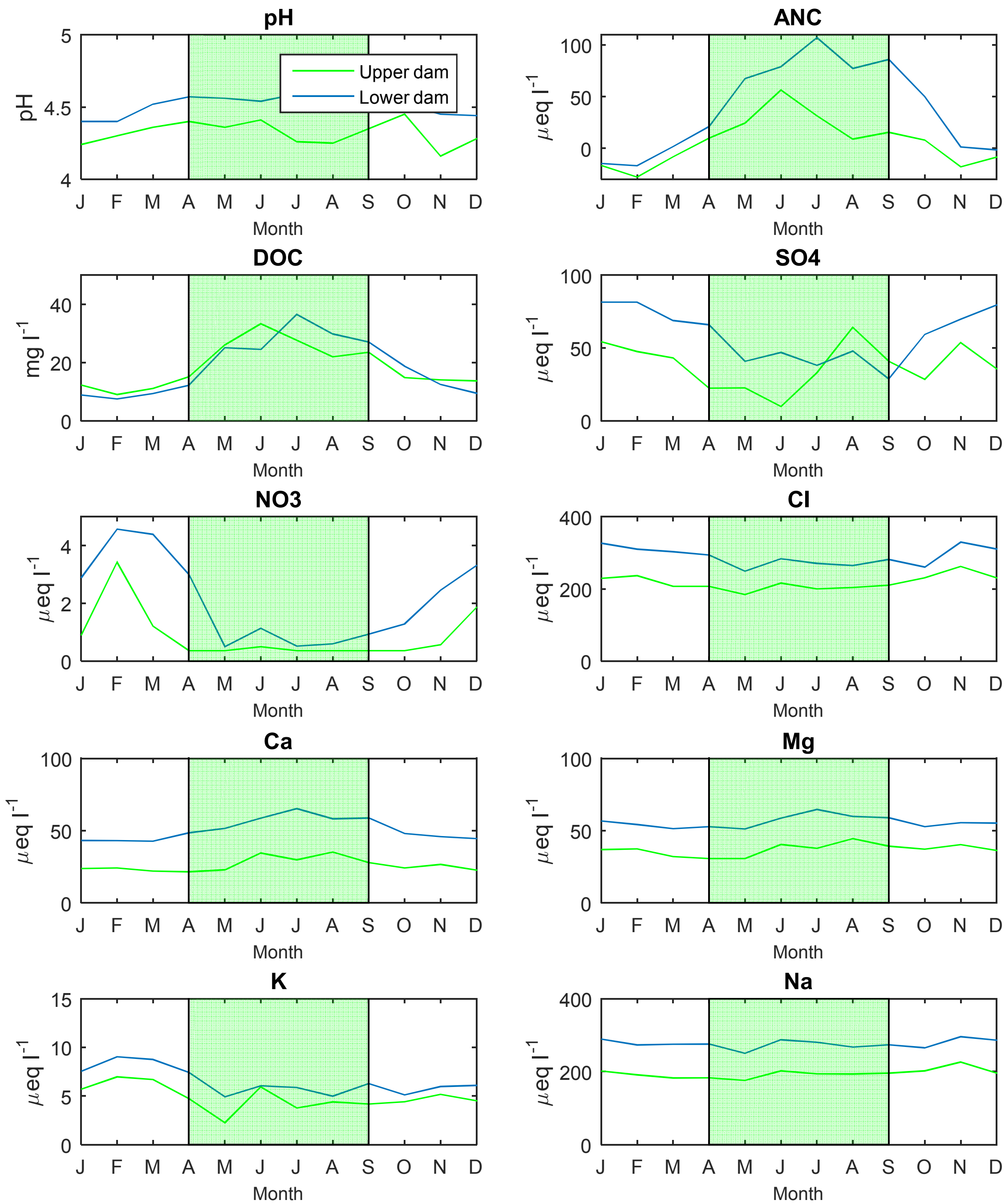

Figure 18. Seasonal dynamics of the pH, ANC, DOC and ion concentration of the discharge water from the upper and lower dam at Storskogen. Growing season (April –September) is indicated by a green background.

From precipitation to discharge

In order to study the chemical composition of water as it moves through the catchment, the average yearly ion concentration of water from four measurement stations in Storskogen: Open field precipitation, throughfall and discharge from the upper and lower dam were examined (Figure 19). The examined ions, separated into cations and anions, are those included in measurements of ANC plus ammonium (NH_4^+). The values were based on precipitation measurements from January 2015 (throughfall) and October 2014 (open field) to September 2016, and discharge measurements from April 2014 (lower dam) and May 2015 (upper dam) to January 2017.

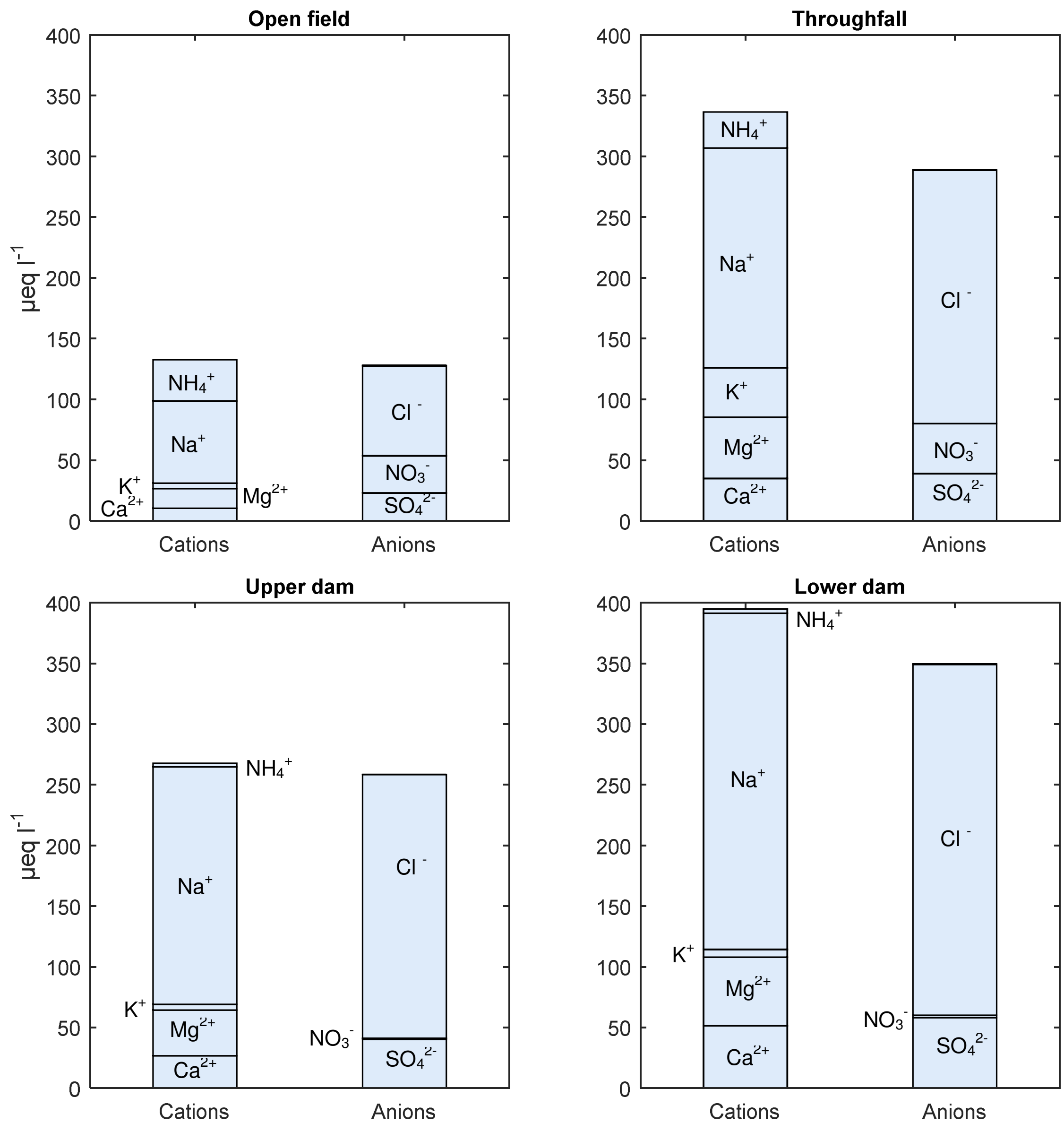

Figure 19. Changes in measured ion concentration as water moved through the catchment. Presented here are the yearly average values of the precipitation, as well as the discharge from the upper and lower dam in Storskogen.

The open field precipitation contained wet deposition of both sulphur and inorganic nitrogen. For hydrological years 2014—15 and 2015—16 the wet deposition of SO_4^{2-} amounted to 3.4 and 2.8 kg S ha^{-1}, and inorganic nitrogen (NO_3^- and NH_4^+) to 8.2 and 5.4 kg N ha^{-1}.

Throughfall is assumed to be a measure of the total deposition, i.e. the wet and dry deposition minus internal circulation, and Figure 17 shows that the concentration of all measured ions increased in the throughfall. This increase can be partly explained by the loss of water through interception. The K^+ and Ca^{2+} concentrations, however, increased by 923% for K^+ and 337% for Ca^{2+} from open field to throughfall, which is not only due to interception loss, but also to active foliage leaching and internal circulation (Warfvinge 2011; Akselsson et al. 2013; Pihl Karlsson et al. 2016). For SO_4^{2-} there is no internal circulation and the total deposition amounted to 6.9 and 3.8 kg ha^{-1} per year. Throughfall is, however, not a reliable measure of the total deposition of inorganic nitrogen because the nitrogen can be utilized by the canopy directly through the foliage (Karlsson et al. 2011).

Practically all available inorganic nitrogen in the precipitation was used by the time the water left the catchment which can be seen in the reduction of NH_4^+ and NO_3^- between open field precipitation and the discharge from the lower dam. In the upper dam the concentrations of cation and anions were nearly equal. As water moved from the upper to the lower dam, the total concentration of ions increased, but the concentration of cations increased more than that of anions. This increase accounted for the higher ANC measured in the lower dam.

4.3.2 Difference between Storskogen and Gårdsjön

A Mann-Whitney U-test revealed that there were also important differences in discharge chemistry between Storskogen and Gårdsjön. The concentration of all measured variables (with the exception of DOC and SO_4^{2-}) differed significantly ($p<0.05$) between the catchments (Table 8). The ion concentration analysis (Appendix) revealed that ANC, pH and DOC were higher in Storskogen during the majority of months. Gårdsjön had a higher concentration of Cl^-, Na^+, K^+ and Mg^{2+} and Storskogen had a higher concentration of NO_3^-, NH_4^+ and Ca^{2+} (Table 8).

Table 8. Difference in discharge chemistry between Storskogen and Gårdsjön F1 using Mann-Whitney's U test.

Mann-Whitney's	**µ Storskogen (mg/l)**	**µ Gårdsjön (mg/l)**	**U**	**One tail significance (p)**
pH	4.51	4.41	202.0	<0.001***
ANC	0.04	0.02	310.0	0.03*
DOC	19.30	14.55	340.5	0.078
SO_4^{2-}	0.93	1.07	520.5	0.0945
NO_3^-	0.03	0.02	316.5	0.0365*
Cl^-	10.27	14.98	758.0	<0.001***
NH_4^+	0.05	0.03	216.5	<0.001***
Na^+	6.40	8.84	860.0	<0.001***
K^+	0.25	0.56	868.0	<0.001***
Mg^{2+}	0.69	0.98	747.5	<0.001***
Ca^{2+}	1.03	0.57	0.0	<0.001***

4.4 Drivers of acidity

So far, differences in discharge chemistry within Storskogen, and between Storskogen and Gårdsjön, have been confirmed. The analysis of the measured components also revealed within-year variations in concentration of several variables. The following sections outline to what extent the investigated factors contribute to the observed differences. The investigated factors include: depositional differences to the two catchments, difference in mineralogy of the soil and difference in wetland distribution within each catchment.

Deposition

In order to test if the chemical composition of the throughfall correlated with the discharge from both Storskogen and Gårdsjön a Spearman's rank correlation-test was run.

The results of Spearman's rank correlation test (table 9) between discharge water and throughfall chemistry in Storskogen indicated that the ANC of discharge water was significantly (ρ <0.05) correlated with five of the nine examined variables in the throughfall. The strongest correlations (all negative) were observed between the ANC of the discharge water and the SO_4^{2-}, Cl^-, Na^+ and Mg^{2+} concentrations, which might seem contradictory since an increase in Na^+ and Mg^{2+} would increase ANC rather than decrease it. This would be true if all other variables remain stable, but in a dynamic system such as Storskogen this is not the case. The correlation with throughfall pH was positive (ρ 0.43).

Table 9. Correlation between monthly throughfall and monthly discharge acidity from Storskogen and Gårdsjön. The values, ranging from -1 to 1, indicate the strength and direction of correlation expressed as Spearman's rank correlation coefficient (ρ).

Variable Throughfall	*Variable discharge* ANC Storskogen	pH Storskogen	ANC Gårdsjön	pH Gårdsjön
pH	0.43*	0.18	0.53**	0.29
SO_4^{2-}	-0.51**	-0.16	-0.42*	-0.17
NO_3^-	-0.36	-0.02	-0.34	0.22
Cl^-	-0.57**	-0.50**	-0.55**	-0.46*
NH_4^+	0.04	0.34	-0.12	0.22
Na^+	-0.66**	-0.51**	-0.61**	-0.52**
K^+	0.35	0.18	0.22	0.07
Mg^{2+}	-0.51**	-0.37	-0.49**	-0.31
Ca^{2+}	-0.31	-0.22	-0.38*	-0.18

The analysis of correlation between throughfall and discharge ANC at Gårdsjön showed similar results as Storskogen, the only exception being that also Ca^{2+} concentration was correlated with ANC. Here too, the correlations were negative for all significant results apart from the correlation between throughfall pH and ANC (ρ 0.53)

The pH of discharge from both Storskogen and Gårdsjön was significantly correlated only with Na^+ and Cl^-, the two major components of sea salt.

It is thus safe to conclude that discharge ANC was correlated with throughfall chemistry at both sites. However, a Mann-Whitney U-test of differences between the deposition to each catchment revealed that there was no significant difference in throughfall chemistry between Storskogen and Gårdsjön (Table 10). Therefore, differences in precipitation chemistry cannot account for the difference in acidity between Storskogen and Gårdsjön. The limited spatial resolution of the precipitation data unfortunately made a similar comparison between the upper and lower dam in Storskogen impossible.

Table 10. Difference in precipitation chemistry of the throughfall between Storskogen and Gårdsjön using Mann-Whitney's U test.

	µ Storskogen	**µ Gårdsjön**	**Mann-Whitney U**	**Two tail significance (p)**
pH	5.27	5.22	478.0	0.52
SO_4^{2-}	0.68	0.76	611.0	0.27
NO_3^-	0.63	0.57	554.0	0.72
Cl^-	8.12	10.48	570.5	0.57
NH_4^+	0.46	0.37	422.0	0.17
Na^+	4.56	5.84	583.5	0.46
K^+	1.74	1.91	466.0	0.423
Mg^{2+}	0.67	0.83	593.0	0.39
Ca^{2+}	0.77	0.75	489.0	0.62

Mineralogy

The mineralogy of the soil, and the rate of chemical weathering, determines the rate at which ions are released to the soil water. Mineralogy is therefore a major factor governing the acidity of a catchment (Kirchner and Lydersen 1995). Previous studies of the total element contents of the soils at the two catchments showed that Gårdsjön has a slightly higher total concentration of base cations compared to Storskogen. Table 11 demonstrates the different concentrations as a quota of base cation to silicate content, silicate being the dominant mineral in both soils (Melkerud 1983; Pihl Karlsson et al. 2011).

Table 11. Element content of the mineral soil presented as a quota at the two study sites. Gårdsjön has a higher concentration of all measured elements. Based on data from Melkerud (1983) and Karlsson et al. (2011a).

Element	Storskogen	Gårdsjön
CaO/SiO2	0.024	0.029
MgO/SiO2	0.010	0.012
K2O/SiO2	0.030	0.038
Na2O/SiO2	0.037	0.038

The ion concentration analysis of discharge (Table 8) showed that Gårdsjön had a higher concentration of Na^+, K^+ and Mg^{2+} compared to Storskogen. The mineralogy of the soil could thus account for the different concentrations of these ions in discharge. The Ca^{2+} concentration, however, was higher in the discharge from Storskogen which is not consistent with the differences in mineralogy. Furthermore, discharge ANC was lower at Gårdsjön, which cannot be explained by the results of the mineralogy analysis.

Wetland distribution

The areal extent of wetlands in Storskogen was 8 642 m^2 which corresponds to 12% of the entire catchment. 1 963 m^2 of these were located in the sub catchment that drains to the upper dam and 6 680 m^2 were located in the sub catchment that drains to the lower dam (Figure 20, Table 12).

Table 12. Areal extent of wetlands in both catchments as well as the total area draining to wetlands.

Storskogen	Wetland (m^2)	Sub catchment (m^2)	Wetland %	Wetland affected (m^2)	Affected %
Upper	1 963	19 024	10	17 008	89
Lower	6 680	51 944	13	65 693	-
Total catchment	*8 642*	*70 969*	*12*	-	*93*
Gårdsjön					
Upper	3 595	-	-	16 931	-
Lower	694	-	-	33 830	-
Total catchment	*4 289*	*48 536*	*9*	-	*70*

In Gårdsjön, the areal extent of wetlands was 4 289 m^2 which corresponds to 9% of the catchment. Here, there were also two wetlands, 3 595 m^2 and 694 m^2 each. However, there was only one dam where the discharge chemistry was measured (Figure 21, Table 12).

The total fraction of wetlands did not differ considerably between neither the upper and lower dam in Storskogen (12% and 13%, respectively), nor between Storskogen and Gårdsjön (12% and 9%, respectively). Thus, the fraction alone could not account for the differences in acidity.

A further analysis was performed in order to determine the size of the catchment surface that drain to a wetland (indicated by the pale blue colour in Figure 20 and 21). This measure was used to decide the fraction of surface water reaching each dam that was affected by wetlands. In Storskogen the majority, 93%, of surface water that reached the lower dam was affected by wetland, whereas in Gårdsjön 70% of surface water that reached the dam was wetland-affected (Table 12). This difference in wetland-affected surface water could potentially account for differences in discharge acidity. However, Gårdsjön had a lower proportion of wetland-affected surface water which, in theory, would lead to a higher chance for the mineral soil to neutralise the acidity of the precipitation, and the discharge from Gårdsjön was more acidic than Storskogen (Table 8). Furthermore, the presence of wetlands increase the DOC content of discharge water during normal conditions, but can also, during high flow events, limit the DOC transport because surface water runs over the wetland (Xenopoulos et al. 2003). There was no significant difference in DOC between Storskogen and Gårdsjön (Table 8).

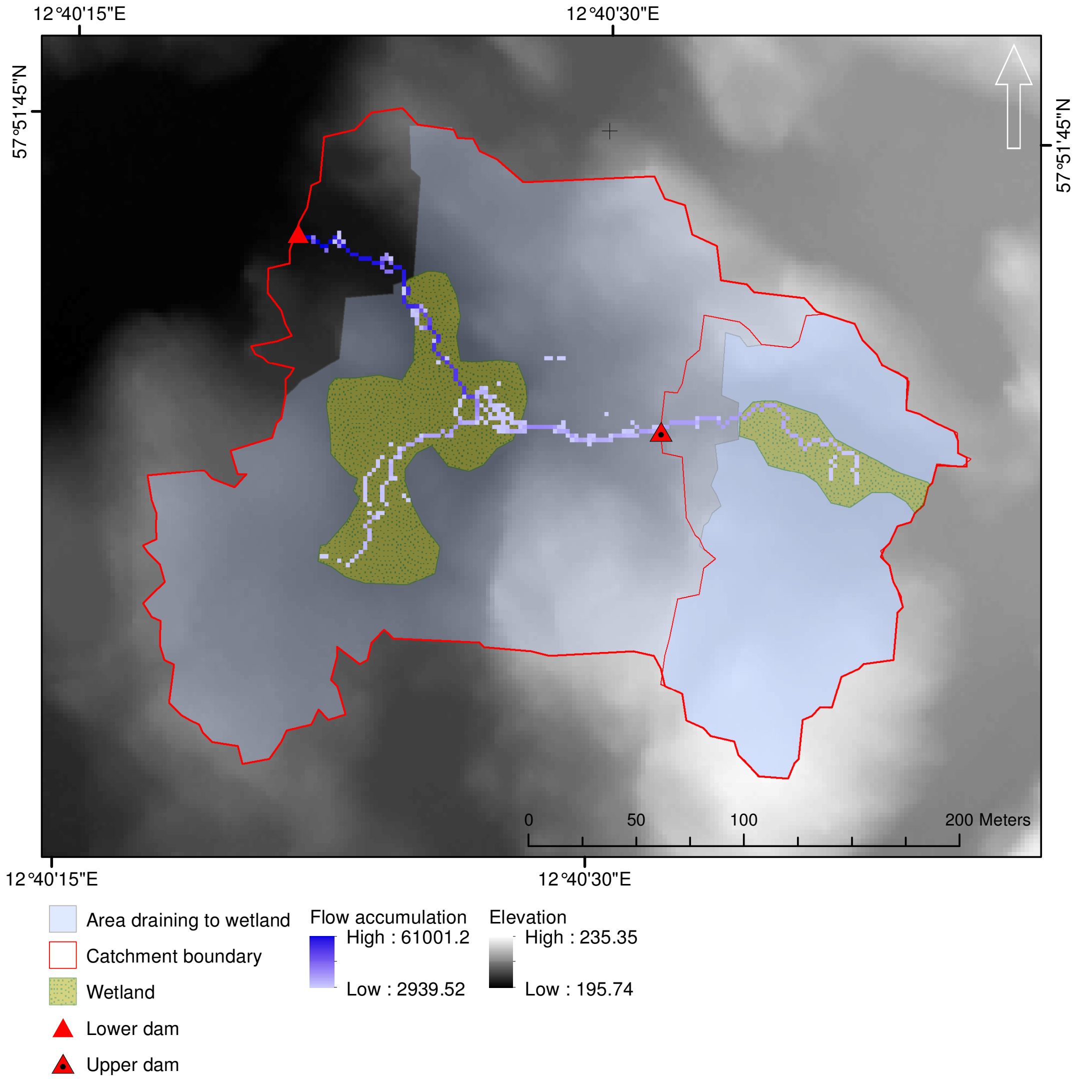

Figure 20. Wetland distribution in Storskogen. The wetlands covered 12.2% of the total catchment. 89% of the water that reaches the upper dam has run through wetland. 93% of the water that reaches the lower dam has run through the upper and/or lower wetland.

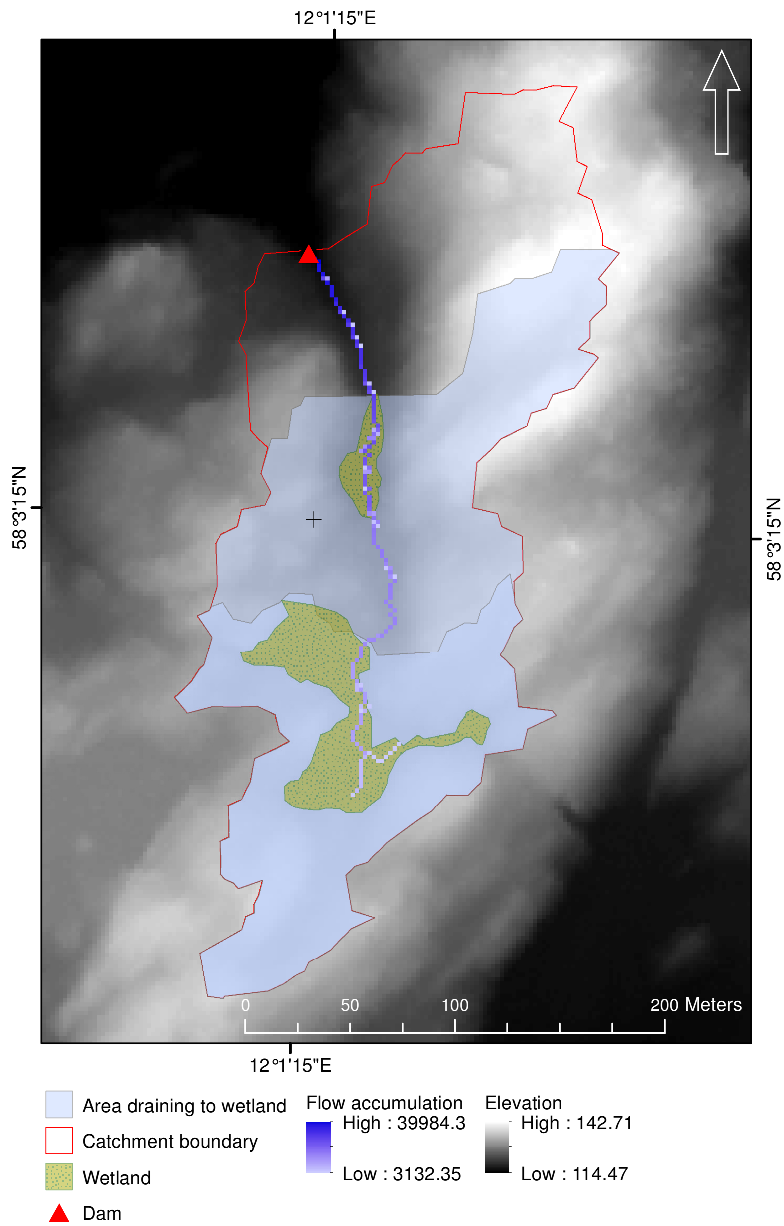

Figure 21. Wetland distribution in Gårdsjön. The wetlands cover 8.8% of the total catchment. 69% of the water that reaches the dam has run through the upper and/or lower wetland.

5 Discussion

5.1 Results

5.1.1 Hydrology in Storskogen

The observed median discharge in Storskogen was 0.7 $l\ s^{-1}$ which is higher than the median discharge that was manually measured each month for comparison with the automatic measurements (0.45 $l\ s^{-1}$). Because the peak discharge was revised to fit discharge values from Hällered, and the minimum flow was manually set to zero, there are substantial uncertainties in the range (0 to 10.9 $l\ s^{-1}$).

Many watercourses in southern Sweden show two discharge maxima in connection with high precipitation during autumn and spring snowmelt (Melin 1970). The hydrologic regime at Storskogen showed only one discharge maximum. This could be due to an absence of snow cover at Storskogen during the observed period. The mean annual temperature for the same period was 6.8°C which is 0.7°C warmer than the long-time average (SMHI 2017c). It is worth remembering however, that the results were based on measurements sampled during only two and a half year. A proper assessment of the hydrologic regime would require a substantially longer monitoring period, typically 30 years. A simple comparison of the hydrological regime and the groundwater level suggests that these are correlated in that discharge is high when groundwater levels are high. This implies that the discharge is primarily made up of groundwater rather than direct rainfall or surface flow, which is consistent with previous research (Rodhe 1987).

The response time was estimated to one day simply by observing the dynamics of the discharge and precipitation. A more thorough analysis of the response time could have been performed using a correlation analysis with different time lags of the automatic discharge data. This would, however, require higher temporal resolution of the precipitation measurements. The current monthly precipitation data from Storskogen was not enough to capture the response time, and even the daily data from Alingsås, which was used in this study, would have been unsuitable for a correlation analysis. A tipping bucket rain gauge with an automatic logger could be installed to get a higher temporal resolution to improve the estimation of the response time, or hourly data from weather stations located further away could be used.

5.1.2 Modelled discharge

The model performance of FyrisQ was high when using the monthly time step and it was low using the daily time step, which was indicated by the coefficient of determination as well as by the RMSE. If the model were to be used instead of collecting actual measurements it would thus seem most appropriate to use the monthly time step. However, considering that the response time was estimated to one day, a better option would be to use a model that can capture the dynamics of Storskogen, or use a longer calibration period, which requires further measurements. A longer calibration period is likely to improve the performance of the model since it was only based on a single year's measurements and the interannual variability can be important. A further improvement would, as previously mentioned, be to collect precipitation data more often. Input precipitation to FyrisQ with a daily time step was from Rångedala, a weather station that is similar to Storskogen in many respects but is close to 300 m.a.s.l., whereas Storskogen is located at 215 m.a.s.l. This difference in elevation might have had a big effect on the precipitation (Johansson and Nilsson 1985). In addition to this, the temperature data used as input was based on daily averages over 24 hours. This means that maximum and, in particular, minimum values are smoothed out which could result in a lower model performance during freeze-thaw events.

5.1.3 Surface water chemistry

The Wilcoxon's matched-pairs signed-ranks test revealed significant differences in surface water acidity between the upper and lower dam in Storskogen, with the lower being less acidic than the upper. The most notable result regarding how water chemistry changed as it moved through the catchment was that the total concentration of ions increased from the upper to the lower dam, and that the cations increased more than the anions. First of all it should be noted that parts of the total increase could be due to a concentration effect, i.e. that water is evapotranspired along the way to the lower dam, leading to higher overall concentrations. However, the increase in ion concentrations varied between compounds. The amounts of cations that dissolve in the soil solution largely depend on the soils cation exchange capacity, the residence time and the chemistry of the soil solution (Warfvinge and Bertills 2000). The longer the residence time, i.e. the amount of time each water particle has spent in the different soil layers and the more acidic the water, the more cations can be exchanged. The anions (NO_3^-, Cl^- and SO_4^{2-}) did not increase in the same way. Nitrogen is a limiting factor for the Swedish forests, which means that any available NO_3^- is more or less immediately immobilised by vegetation or soil microbes, which explains why it does not increase. Cl^- mainly arrives to the catchment dissolved in precipitation or dry deposited as salt particles (Grip and Rodhe 2000). In Storskogen Cl^- did increase in the lower dam but this could be due to the previously mentioned concentration effect. As for SO_4^{2-}, it is not common in the soil but it would have been adsorbed during the acidification phase and is now desorbed from the soil particles. This explains the increase in SO_4^{2-} and is one of the reasons why the recovery from acidification is slower than the decrease rate of acid deposition (Warfvinge and Bertills 2000). In conclusion, the anions are not naturally present in the soil in the same way as the cations and this explains why the concentration of cations increased more.

The yearly dynamics of ANC, measured in the discharge from Storskogen, showed that it was low during winter when the groundwater level was high. The higher acidity during winter could thus be a natural consequence of the fact that the soil was nearly saturated. A saturated soil would cause precipitation to enter the stream directly as overland flow, and the soils' acid neutralizing capacity would be lost. The dynamics shown, where a higher concentration of DOC during summer resulted in a higher ANC with a stable pH, could also be explained by the chemical equilibrium relationships discussed in the background section (Figure 1).

The Mann-U Whitney test revealed that there were significant differences in surface water acidity between Storskogen and Gårdsjön. Of the base cations, Gårdsjön had a higher concentration of Na^+, K^+ and Mg^{2+} throughout the year and Storskogen had a higher concentration of Ca^{2+}. However, Gårdsjön also had higher concentrations of SO_4^{2-} (non-significant) and Cl^- (significant), which resulted in Gårdsjön having a significantly lower ANC than Storskogen.

5.1.4 Drivers of acidity

The difference in acidity between the upper and lower dam in Storskogen could not be explained by a difference in wetland cover. It is likely that the difference in acidity can be explained by the transit time, i.e. the amount of time it takes from when a water particle enters the catchment until it reaches the outlet. A higher fraction of the water will have spent a longer time in the soil at the lower dam, and the soil will have had a longer time to neutralise the acidity of the water (Rodhe 1987; Grip and Rodhe 2000). This hypothesis regarding transit time could be studied further by the use of tracers such as the stable oxygen isotope or the salt content.

There were, as mentioned, significant differences in surface water acidity between Storskogen and Gårdsjön. In fact, all measured variables differed apart from DOC and SO_4^{2-}. This suggests that the differences in pH and ANC were not due to naturally occurring differences in organic acids, but rather to something else. However, neither the difference in wetland cover, nor the atmospheric deposition could explain the difference in surface water acidity between Storskogen and Gårdsjön. The wetland cover was similar between sites (12%

in Storskogen and 9% at Gårdsjön) and the deposition did not show any significant difference. The mineralogy of the soils in each catchment would in fact, suggest that Gårdsjön had a larger potential supply of base cations that could be weathered and reach the soil solution. Thus, the mineralogy was also a factor that was unable to explain the difference in surface water acidity.

The pH of discharge from both Storskogen and Gårdsjön was significantly correlated only with Na^+ and Cl^-, the two major components of sea salt. Sea salt increases the net charge of the soil solution and causes an increased ion exchange where particularly Na^+ exchanges with H^+. This lowers the pH of the water and can cause an acid surge (Akselsson et al. 2013; Pihl Karlsson et al. 2016). The concentration of both Cl^- and Na^+ deposited differed between sites, with Gårdsjön receiving higher concentrations than Storskogen. This difference, however not significant, could account for part of the difference in acidity observed between the catchments.

The wet deposition to Storskogen contained 8.2 and 5.4 kg ha^{-1} of inorganic nitrogen during the two observed years. The critical load of inorganic nitrogen to Swedish spruce and pine forests is 5 kg ha^{-1} yr^{-1} and was thus, even when only considering wet deposition, exceeded for both years (Pihl Karlsson et al. 2016). However, practically all available inorganic nitrogen in the precipitation was used by the time the water left the catchment, which can be seen in the reduction of NH_4^+ and NO_3^- between open field and the lower dam. Because inorganic nitrogen only acts acidifying if it is lost via leaching, this indicates that the deposition of inorganic nitrogen was not a significant contributing factor to the acidity of Storskogen.

According to Pihl Karlsson et al. (2015) the area receives, on average 2 to 4 kg of anthropogenic sulphur per year but the total deposition of sulphur measured at Storskogen was 6.9 and 3.8 kg ha-1 during the two observed years. During 2014—15 there was a volcanic eruption in Iceland that released triple the amount of sulphur produced by all European industries together, which perhaps could explain the high deposition during 2014—15 (Schmidt et al. 2015).

5.2 Uncertainties

5.2.1 Catchment delineation

The overland flow distribution model TFM generated the catchment divides at Storskogen and Gårdsjön. During the surveying it was noted that the actual extent of the upper wetland at Storskogen extended beyond the limit of the catchment as modelled by TFM. It is unlikely that the divide should separate a wetland in two and more likely that the actual catchment was larger than modelled. This could be due to a problem with how TFM handles flat surfaces (Hasan et al. 2012), or it could be due to the DEM itself. The Gårdsjön catchment was modelled to 4.9 ha whereas it has been stated in several sources to be 3.7 ha (Andersson and Olsson 1985; SLU 2017). The quality description of the DEM Grid 2+ does mention that in hilly terrain with sharp differences in elevation the model might produce a smoothed out surface, which could have affected the catchments modelled (Lantmäteriet 2016). However, there is no mention of difficulties regarding the elevation classification of flat surfaces, and, at least at Storskogen, this is where the error seems to be. This uncertainty as to the actual area of the catchment has affected the specific discharge calculations at Storskogen, which might thus be overestimated if the area is larger in reality. However, the uncertainty regarding the size at Gårdsjön will probably not have affected the results of this study.

During the surveying in Storskogen, the ground around the upper dam was found to be water saturated. The construction of the dam did not manage to make all surface water pass through the V-notch. Therefore measurements of discharge from the upper dam contain an error margin. This was confirmed by comparing the specific discharge from the upper and lower dam. If the measurements were correct they should show a correlation of almost 1, but in reality it was much lower. This would, however, not have had an effect of the chemical analysis of the discharge which was the only measurement from the upper dam used in this study. The discharge rate from the upper dam was left uncorrected and for further studies this needs to be addressed.

5.2.2 Discharge data processing

The discharge data processing increased the strength of correlation between Storskogen and Hällered. However, the higher correlation does not suggest that the modified Storskogen data are correct, only that they are more similar to Hällered which has been quality controlled by SMHI. Discharge is dependent on precipitation, and since precipitation is strongly dependent on location and altitude there is a risk in assuming that it should have been the same over the two catchments. Furthermore, the response lag depends on the size of the catchment. A small catchment responds quickly to input and will show clear peaks in discharge following precipitation. A large catchment on the other hand will show less pronounced storm peaks, and the rate at which discharge drops to base flow after a storm peak is slower because water will be retained within the soil. Comparing the substantially larger Hällered catchment to Storskogen and using it as an editing reference could result in some of the true peak dynamics being edited away.

5.2.3 Water balance calculations

The results from the water balance equation gave that the actual ET constituted 74% of PET the first hydrological year and 93% the second. The normal fraction for longer observation series is usually 80% (Johansson and Nilsson 1985). The average fraction, which was the one used to obtain monthly ET, therefore seems reasonable. However, the PET might also be subject to error since it was calculated using Penman's equation. A study by Vörösmarty et al. (1998) tested nine different methods of calculating PET and found that Penman's equation overestimated PET by, on average, 117 mm yr^{-1}. Furthermore, the precipitation measurements used in the water balance equation also contain some uncertainty. The measurements are subject to errors such as e.g. wind, splashing or evaporation (Dingman 2015), and precipitation measurements have been shown to underestimate amounts by as much as 15-20% (Grip and Rodhe 2000).

5.2.4 Soil depth

During the field surveying it was observed that the soil at Gårdsjön, although reported to be of an average depth of 0.63 m, appeared shallower than the soil at Storskogen which was estimated to be of around 0.5 m. This requires further investigation to be confirmed, but if it is true it could also be a reason for the higher acidity at Gårdsjön since, as previously discussed, more soil-water interaction leads to a higher acid neutralising capacity.

6 Conclusions

The results of this study suggest that the headwater stream in Storskogen had a low median discharge of only 0.7 l s^{-1} but that it responded quickly to precipitation inputs, which could result in a tenfold increase in rate of flow. The yearly hydrological regime displayed one discharge maximum during winter which coincided with the winter precipitation maximum.

The hydrological model FyrisQ was found to be unsuitable for modelling discharge from Storskogen even though the accuracy of the monthly time step was high. The monthly time step is unlikely to capture the dynamics of the catchment, and the accuracy of the daily time step was too low.

Differences in surface water chemistry were found both within Storskogen, and between Storskogen and Gårdsjön. It can be concluded that the total concentration of ions increased in the discharge from the upper to the lower dam in Storskogen, and that cations increased more than anions. This increase in cations accounted for the higher ANC measured at the lower dam. Gårdsjön was more acidic than Storskogen and had a higher concentration of all ions included in the calculations of ANC, apart from NO_3^- and Ca^{2+}. The pH of discharge from both Storskogen and Gårdsjön was found to be significantly correlated with the two major components of sea salt, Na^+ and Cl^-.

Neither the difference in acidity between the upper and lower dam, nor the difference between Storskogen and Gårdsjön, could be explained by a difference in wetland cover. Precipitation chemistry and mineralogy were also unable to account for the differences in acidity between the catchments. It is likely that these differences can be explained by the residence time and flow path of the water in different parts of the catchments, i.e. the amount of time each water particle has spent in the different soil layers. To test this would however, require a more advanced hydrological model

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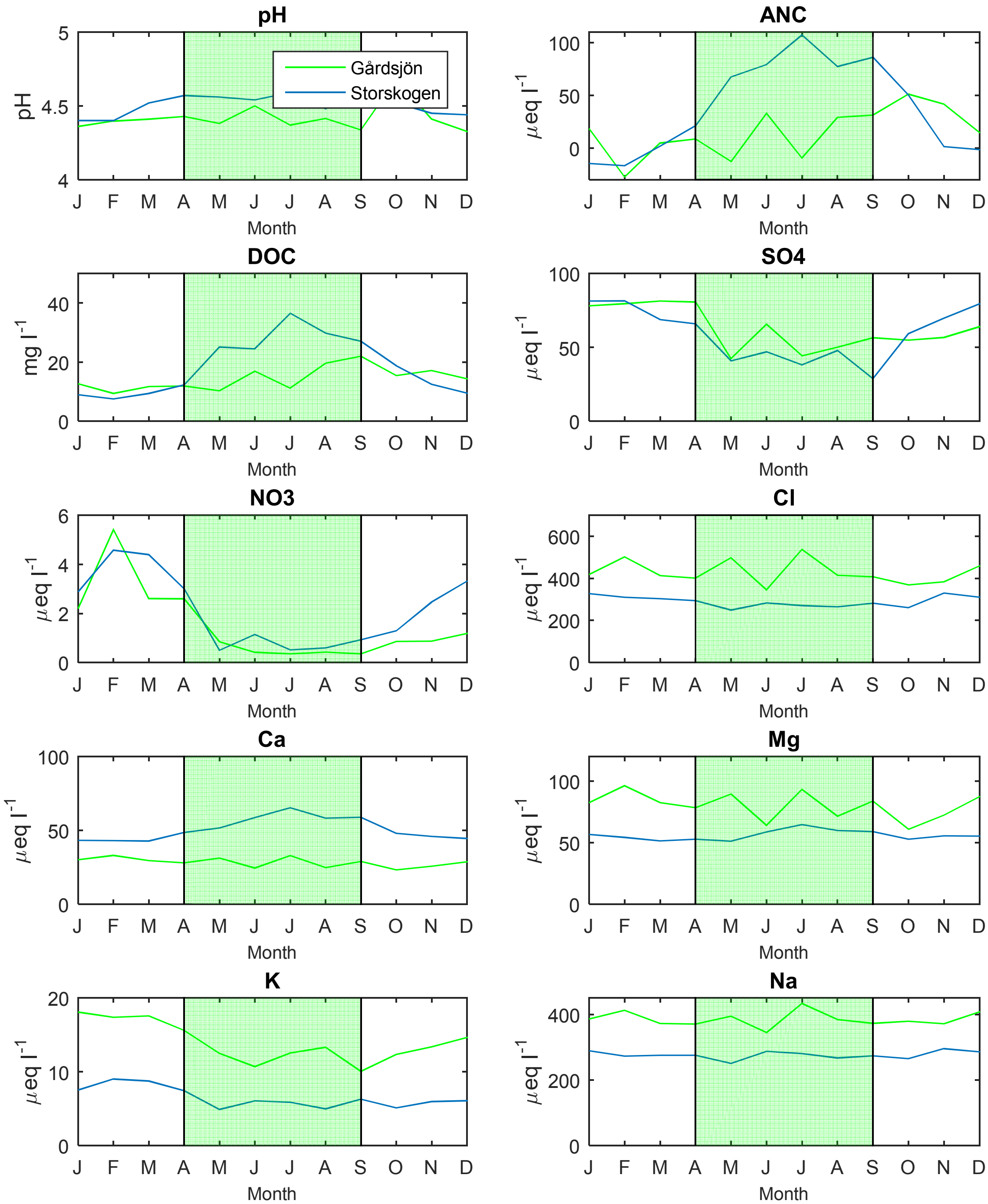
Appendix



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