Sveriges lantbruksuniversitet
Swedish University of Agricultural Sciences

**Faculty of Natural Resources and Agricultural Science**

# pH-sensitivity in boreal streams – the influence of landscape characteristics

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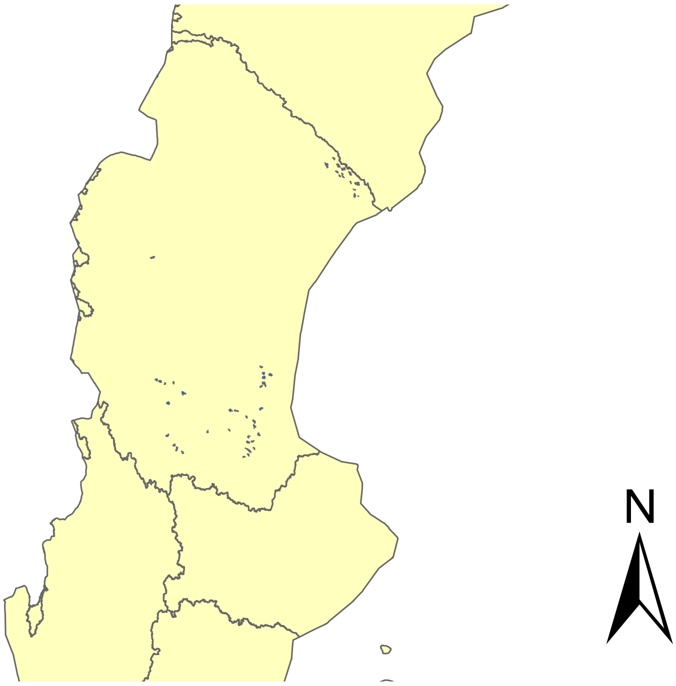
## Abstract

The goal of the society to increase the proportion of renewable energy has led to an increased demand of bioenergy e.g. forest biomass. However, there are concerns that removal of biomass will lead to decreased base cation concentrations in the soils and acidification of streams. In order to find in which types of landscape removal of branches and tops could have such negative effects, this study aims to analyse the relations between pH-sensitivity and landscape variables in the Bothnia Bay water district. GIS and digital geographical data were used to analyse the landscape in subcatchments. This data were analysed together with stream water chemistry data by using principal component analysis. The results indicate differences between the north and south parts of the district. In the northern subcatchments, pH-sensitivity was positively correlated to water surfaces and coarse quaternary deposits with Scots pine forests. In the south, pH-sensitive streams were positively correlated to till soils and the concentrations of total organic matter (TOC). In both areas, alkalinity and ANC were the most important factors indicating that the buffering capacity primarily was due to weathering.

## Sammanfattning

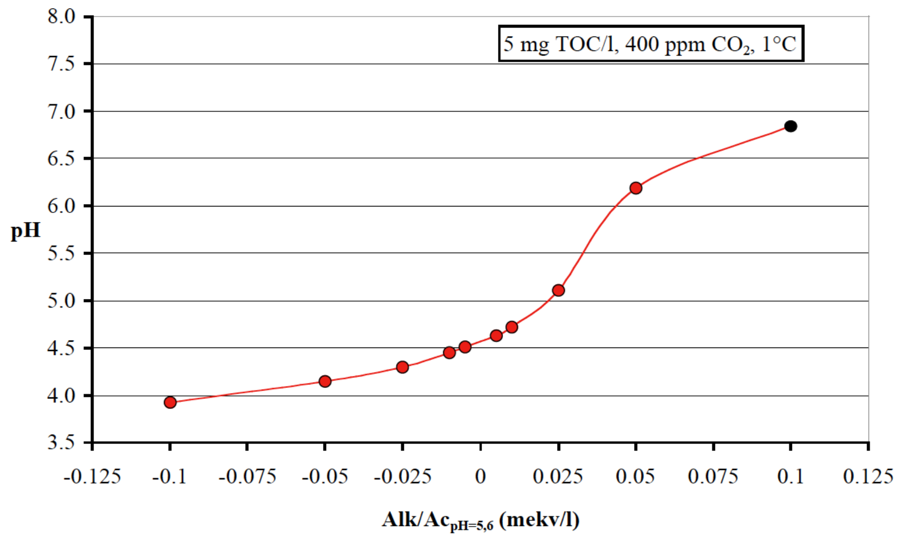
Politiska mål och ökad medvetenhet om klimatförändringarna har ökat efterfrågan på förnybara energikällor. I Sverige är skogsbiomassa en lättillgänglig energiresurs och uttaget av GROT (grenar och toppar) efter avverkning ökar. Det finns dock en oro för att uttag av GROT kan leda till försurning av mark och vattendrag eftersom basiska katjoner forslas bort från skogen tillsammans med hyggesavfallet.

Olika landskapstyper är mer eller mindre känsliga för förändringar i pH och tidigare studier har visat att det finns regionala variationer i vilka egenskaper som har betydelse för pH. Jag har undersökt delavrinningsområden i Bottenhavets vattendistrikt (figur 1) för att avgöra i vilka slags bestånd GROT-uttag innebär en större risk för försurning.




**Figur 1: Karta över Vattendistrikten med delavrinningsområdena som ingår i studien inkluderade**

De två kemiska ämnesgrupperna som har störst inverkan på pH-värdet i vattendrag är vittringsprodukter och organiskt material. Karbonat, kolsyra och svaga organiska syror utgör tillsammans alkaliniteten i systemet. När pH är högt (över ~6,5) så buffrar vätekarbonat så att pH håller sig stabilt även om tillförseln av vätejoner skulle öka. Vid lågt pH (under ~4,5) agerar anjonerna till svaga organiska syror som baser och håller pH på en stabil nivå. I pH-intervallet där emellan förändras pH fort om sammansättningen av joner i vattnet ändras och pH är därför känsligt (se figur 2).




**Figur 2: Sambandet mellan pH och alkalinitet, när pH är högt eller lågt är pH mer stabilt p.g.a. ämnen som buffrar (från Löfgren & Laudon, 2004. Surstötar i norra Dalarna 1994-2002. Länsstyrelsen Dalarna rapport 2004:7).**

Vittringshastigheten, produktionen av organiska syror och delavrinningsområdets hydrologi kommer tillsammans att påverka den kemiska sammansättningen i det dränerande vattendraget och därmed också dess pH. De metoder som finns för att bedöma vittringshastigheten är osäkra, och kunskapen om hur vittringsprodukter och organiska syror transporteras i marken är inte heller fullständig. Därför går det inte att dra slutsatser om pH-känslighet i en bäck genom teoretiska beräkningar. Genom att istället undersöka sambandet mellan pH-känslighet och olika landskapstyper kan det statistiskt gå att dra generella slutsatser om vart det innebär större risk för försurning om GROT-uttag görs.

I den här studien användes ArcGIS för att ta reda på hur delavrinningsområdena som var med i analysen såg ut och göra en sammanställning över hur stor andel av arealen olika landskapselement utgjorde av delavrinningsområdena. De variabler som analyserades presenteras i tabell 1.

**Tabell 1: landskapsvariabler och kemiska variabler som inkluderades i studien**

| Variabel | Enhet |
|---|---|
| Jordbruksmark | % |
| Lövskog | % |
| Barrskog | % |
| Blandskog | % |
| Land i föränring mellan buskar och träd | % |
| Vatten | % |
| Tallskog | % |
| Granskog | % |
| Volym | m3sk/ha |
| Totalt avverkat | % |
| Medelaltitud | m över havet |
| Under Högsta Kustlinjen | % |
| Lera-silt | % |
| Grovkornig jordart | % |
| Torv | % |
| Berg i dagen | % |
| Morän | % |
| Alkalinitet | meqv/l |
| ANC | meqv/l |
| Kalcium | meqv/l |
| TOC | mg/l |
| pH-känslighet | klass |

Geografiska data analyserades statistiskt tillsammans med vattenkemidata och pH-känslighet med hjälp av principalkomponentanalys (PCA) för att undersöka sambandet mellan pH-känslighet och övriga variabler i analysen.

När alla delavrinningsområden inkluderades i analysen var det svårt att se ett samband mellan pH-känslighet och andra variabler, antagligen för att området var för stort för att det skulle finnas klara samband. Datat delades därför upp i två delar, en för de norra delavrinningsområdena och en för de södra. Den norra delen inkluderade totalt 19 delavrinningsområden; 17 i Västerbotten och ett vardera i Jämtland och Västernorrland. Den södra delen inkluderade totalt 34 delavrinningsområdena varav 13 i Dalarnas län och 21 i Gästriklands län. Resultaten för den norra delen visade att bäckar med känsligt pH återfinns i delavrinningsområden som domineras av tallskogar och grova jordarter eller har en stor andel vattenyta. Väl pH-buffrade bäckar i norra delen visade sig vara kopplat till delavrinningsområden dominerade av granskogar med hög biomassa på finkorniga jordar samt en vattenkemi med hög ANC, alkalinitet och koncentration av kalcium (tabell 2). Karbonaterna som innefattas i alkaliniteten, och kalcium är vittringsprodukter som buffrar pH, därför blir pH mindre känsligt när dessa variabler är höga. Grovkorniga jordar är ofta mer svårvittrade än finkorniga jordar och bidrar därför i mindre utsträckning med buffrande ämnen. Att områden med hög ANC är okänsliga indikerar att pH är högt när pH-känsligheten är låg och därmed att pH i området domineras av värden över 5,6 (se figur 2).

**Tabell 2: Sammanfattning över vilka variabler som påverkar pH-känsligheten i de norra respektive södra avrinningsområdena**

| | Norra delen | Södra delen |
|---|---|---|
| Variabler som korrelerar med känsligt pH | Tallskog<br>Grovkorniga jordarter<br>Vattenytor | Moränjordar<br>TOC |
| Variabler som korrelerar med okänsligt pH | Granskog<br>Finkorniga jordar<br>Alkalinitet<br>Kalciumkoncentration<br>ANC | Alkalinitet<br>ANC |

För de södra delavrinningsområdena är samband mellan landskapsvariabler och pH-känslighet mindre tydligt. pH-känsliga bäckar är kopplade till delavrinningsområden med hög andel moränjordar och höga halter av totalt organiskt kol (TOC). Delavrinningsområden med låg pH-känslighet korrelerade till vattendrag som hade hög ANC och alkalinitet (tabell 2). En anledning till det mer otydliga sambandet i den södra delen kan bero på att delavrinningsområdena var utspridda över en större yta i jämförelse med de norra områdena och vilka variabler som styr pH-känsligheten inom området varierar i en utsträckning som gör att det inte går att dra några generella slutsatser för den södra delen av distriktet.

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## Introduction

In the endeavour to reach a sustainable exploitation of the natural resources several environmental aspects need to be taken into consideration. While searching for new sources of energy in order to decrease the impact of fossil fuels on climate, this is a challenge. The need for a reformation of the energy sector in order to reduce the climatic impact is recognized on political level. EU has set a goal that 20% of the energy used in the union should be renewable by the year 2020 in order to decrease greenhouse gas emission by 20% (European commission, 2012). In Sweden, forest biomass is a potential source of renewable energy, which is not fully utilized (Thorsén *et al.* 2012). The area used for intense forest production is increasing (Swedish Forest Agency 2012), thereby enhancing the potential for bioenergy harvest. Since 1980, the market for forest biofuel has increased with about 3 TWh per year and rest products from the forest industry are now fully utilized as energy source (Thorsén *et al.* 2012). Additionally, the removal of branches and tops from harvesting sites for use as fuel is becoming more and more common (Swedish Forest Agency 2012). The development of a more efficient forest production, where more bioenergy could be harvested, is considered a part of the solution to increase the renewable energy fraction (Thorsén *et al.* 2012). However, the scientific knowledge is not enough to fully understand what environmental consequences this increase in forest intensity will have on streams and lakes (Laudon et al 2011). Concern has been raised that the increased removal of biomass from harvesting sites could cause surface water acidification (Thorsén *et al.* 2012; Kreutzweiser *et al.* 2008).

The Water Authority of the Bothnia Bay has pointed out acidification and physical impacts as the main environmental disturbances of surface waters in the district (Water authority Bothnia Bay 2013). The Swedish environmental objective of zero acidification is not expected reached in any of the counties of the Bothnia Bay catchment (SEPA 2012:2). The anthropogenic acid deposition of sulfur (S) in the area has varied within the range 0.5-7 kg S $ha^{-1}$ $yr^{-1}$ for the period 1998-2011 (SMHI 2013). During this period, the deposition has been higher in the eastern, coast near parts (SMHI 2013). The acid deposition gradient have an impact on the acidification status in soil water, groundwater and stream water (Löfgren *et al.* 2011), but since the deposition has decreased since the 1980’s (SMHI 2013) other factors have become relatively more important. Factors such as catchment characteristics are also important (Ågren & Löfgren, 2012). One of the mentioned strategies in order to reach the objective of zero acidification is to adjust the forestry practices by considering the pH-sensitivity of the site (SEPA 2012:1), which is dependent on the catchment characteristics (Ågren & Löfgren, 2012).

Acid neutralizing capacity (ANC) is an important variable defining the acid-base chemistry in natural systems. The concentration of base cations (BC), including calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), potassium ($K^+$) and sodium ($Na^+$), and strong acid anions are determining ANC (see below). At harvest, BC in biomass are removed from the forest. Based on weathering estimates and long-term steady-state mass balances for Ca, Mg and K in Norwegian spruce (*Pinus sylvestris*) and Scots pine (*Picea abies*) stands, Akselsson *et al.* (2007) found net losses of BC at WTH (Whole Tree Harvest) in Norwegian spruce stands. The estimated BC losses were at rates that would cause low base saturation in the soils in the long-term, potentially affecting soil fertility and run off water quality (Akselsson *et al.* 2007).

According to data compiled by Iwald *et al.* (2013) the concentrations of BC in branches are about double the concentration in stems for Scots pine and about seven times higher in Norwegian spruce. Comparing needles and stems the concentration of BC are about nine times higher in needles for Scots pine and about ten times higher for Norwegian spruce. These differences indicate less removed BC at stem only harvest compared to (WTH) (Iwald *et al.* 2013).

Zetterberg *et al.* (2013) evaluated the long-term effects on $Ca^{2+}$ concentrations in soil and soil solution and concluded that there was a depletion of $Ca^{2+}$ in soils and soil solution after WTH compared with conventional harvest 27-30 years after treatment. However 32-53 years after harvest these effects were no longer significant. The changes were most obvious larger at the more well buffered site, where the change in $Ca^{2+}$ concentrations would not likely lead to any acidification.

Several studies have evaluated the impact of WTH on soil chemistry (Duchesne and Houle 2005; Olsson *et al.* 1996; Brandtberg and Olsson 2012) and site production (Walmsley *et al.* 2009; Thiffault et al 2011). In a review of logging impacts on the biogeochemistry of forest soils and waters, Kreutzweiser *et al.* (2008) concluded that the effects depend on site specific properties such as soil type, hydrological connectivity, type and time of harvest and water flow patterns after harvest. They also concluded that there is a lack in long-term assessments of WTH impacts on surface water. Aherne et al (2008 and 2011) used the MAGIC model to estimate the long-term impact of WTH on water chemistry in scenarios assuming varying acid deposition levels (Aherne *et al.* 2008) and climate (Aherne *et al.* 2011). The results indicate an increased risk of stream water acidification after WTH.

### Aim

Acid sensitive areas, where a decrease in stream BC concentration would cause acidification, can to some extent be identified from landscape properties (Ågren and Löfgren 2012). Such knowledge can be used to limit the risk of acidifying effects after biofuel harvest by identifying areas not suitable for WTH or where BC compensation e.g. ash recycling should be recommended (SEPA 2007). The aim of this thesis is to establish relationships between catchment properties and pH-sensitivity in streams within sub-catchments of the Bothnia Bay water district.

## Background

### Water chemistry in boreal streams

In natural systems the bicarbonate system, organic acids and inorganic aluminium ($Al^{n+}$) control pH. The bicarbonate system includes $CO_2$, $CO_3^{2-}$, $HCO_3^-$ and $H_2CO_3$, where the dominating form in surface waters depends on the pH and $CO_2$-pressure. Below pH 5.6 $H_2CO_3$ is the dominating form and the bicarbonate system will not buffer against acid inputs, instead the anions to weak organic acids ($RCOO^-$) will determine the buffer capacity of the system. Together the bicarbonate system and presence of organic acids are determining the $alkalinity_{tot}$ (equation 1) of the system. When pH is below 5 also $Al^{n+}$ will influence the buffer capacity.

$$Alkalinity_{tot} = [OH^-] + [RCOO^-] + [HCO_3^-] + [CO_3^{2-}] - [H^+] \qquad \text{Eq. 1}$$

Alkalinity is in Swedish environmental monitoring determined by titrating to pH 5.6 ($alkalinity_{pH-5.6}$) and only the bicarbonate system is reflected by the parameter. ANC (equation 2) is equal to the $alkalinity_{tot}$ (equation 1) when pH is above 5 and Al is not influencing the buffering capacity. The parameters in ANC (equation 2) are independent of the $CO_2$-pressure and pH and more easily measured.

$$ANC\ (\mu eq/l) = ([Ca^{2+}] + [Mg^{2+}] + [Na^{+}] + [K^{+}]) - ([SO_4^{2-}] + [Cl^{-}] + [NO_3^{-}]) \text{ Eq. 2}$$

With increasing TOC pH is decreasing because organic matter includes strong organic acids. This may occur without changes in $alkalinity_{tot}$ and ANC. When pH is low the system is not sensitive to changes in pH because of the buffering of organic acids and $Al^{n+}$. When pH is high, the concentrations of BC are high and the streams will be buffered by bicarbonate. A decrease in BC concentrations in stream water would have largest effect on pH in the range 5 and 6 (Ågren *et al.* 2010). Streams with higher or lower pH were not as affected by the change in BC concentration (Ågren *et al.* 2010).

A combination of the transport and properties of TOC, the weathering rates and the transportation of ions from soils to water will influence the effect different landscape features have on stream water chemistry. How these factors interact depend on the catchment properties, and results in different pH with different sensitivity to changes.

## Importance of flow paths

The groundwater pathways in the soil-profile affect the chemical composition of the discharge water (Vestin *et al.* 2008:I), and will therefore be an important factor influencing the stream water chemistry. "Old water" is an expression used for soil water that is resting in the unsaturated zone. The chemistry of this water will depend on the soil properties (Bishop *et al.* 2004). When melt water is percolating through the soil the ion concentration will increase, this is why the concentration of BC in the soil solution increase with depth and varies over the year (Land and Öhlander 2000; Olsson and Melkerud 2000). At one meter depth the concentration of BC is rather stable (Ingri *et al.* 2005). When the water table rise the old water will be transported. In soil layers closer to the soil surface the hydraulic conductivity is usually higher why this water will transport faster and have a larger impact on the mixed water entering the stream (Bishop *et al.* 2004). As a consequence, the water chemistry will depend on the groundwater table and the soil properties. Bishop *et al.* (2004) state that the soil in the riparian zone has the most important chemical influence on the stream water and that the concentration of DOC in streams depends on the properties of the riparian zone and wetlands rather than the mor-layers in recharge areas. The stream TOC concentrations are dependent on the soil properties in the riparian zone (Grabs *et al.* 2012). In the discharge area the concentrations of exchangeable cations are higher than in the recharge area, this is explained by a higher carbon and soil water content in the riparian zones (Vestin *et al.* 2008:b).

## Organic acids

DOC (dissolved organic carbon) and TOC contain weak and strong organic acids and play an important role for the acid-base chemistry of streams. The transport of organic carbon to streams is related to the catchment hydrology and precipitation (Nordström *et al.* 2010). DOC is an important transporter of cations from soil to water because of the negative charge of carboxylic groups in DOC (Vestin *et al.* 2008:II). Depending on the molecular size, the DOC mobilization seems to be different. The large mass fraction is more common in discharge areas while the low mass molecule fraction is more important for the local transport within the soil profile (Vestin *et al.* 2008:II). Under base flow conditions; DOC in watercourses mainly has its origin in wetlands (Laudon *et al.* 2011). There are also results indicating that the DOC concentration in streams is higher in areas largely influenced by forestry, mainly due to mobilization after soil disturbances (Schenker *et al.* 2012). However, forest composition and ecosystem acidification seems to have a minor influence on mobilization of DOC (Ohno *et al.* 2007).

### Weathering

Weathering is neutralizing acidity by releasing buffering ions to the soil solution (Thomas *et al.* 1999). Therefore, the sensitivity to acidification (Thomas *et al.* 1999) and surface water pH patterns (Lauerwald *et al.* 2013) are dependent on the weathering of soils and bedrock. The process of weathering is hard to estimate, as there are a lot of different sub-processes involved that is not fully understood (Laudon *et al.* 2011; Futter *et al.* 2012). Biological, chemical and physical processes affect the weathering of minerals. Plants are regulating the carbonic acid in the soil by root respiration and decaying organic matter is resulting in organic acids, which acidify the soil solution and increase the weathering. Additionally, mycorrhizae fungi may mine minerals to gain nutrients (Finley *et al.* 2009). Chemical weathering is dependent on the mineralogy and increase with temperature and soil moisture content. Larger surface areas of the soil particles increase the contact between minerals and soil solution and increase the weathering rate (Olivia *et al.* 2003). For the same reason the proportion of big stones will influence the total weathering rate of a soil (Klaminder *et al.* 2011). More shallow soils seem to have a higher weathering rate than deep ones (Olivia *et al.* 2003). The hydrology in a catchment and the residence time of water in the soil will differ according to the topography and this relationship will also influence the weathering rates (Klaminder *et al.* 2011; Olivia *et al.* 2003). All these factors interact and a change influencing one factor can potentially have an effect on other processes as well.

## pH-sensitivity and landscape variables

Langan and Wilson (1992) were predicting acid surface waters in Scotland by classifying streams according to mineralogy in the bedrock and soil type. Ye *et al.* (2002) did a similar survey for China and included land use in the analysis. In the land use classification, areas dominated by coniferous forest were classified as most sensitive followed by shrubbery/grassland, deciduous forest and agriculture/deserts as least sensitive (Ye *et al.* 2002). Dunford et al (2012) found a connection between forest cover and low pH in Scotland freshwaters even though acid deposition was decreasing.

Ågren and Löfgren (2012) show that the pH sensitivity in stream water is controlled by different factors in different parts of Sweden. They concluded that in Västerbotten and the highlands of Småland the pH sensitive streams were influenced by catchments with wetlands resulting in high TOC concentrations, and low concentrations of BC. However, in Småland the insensitive areas were characterized by high altitude and large proportion of rock outcrops while in Västerbotten it was lowland areas with sedimentary soils that was correlating negatively to pH-sensitivity. In Bergslagen and at the west coast, Ågren and Löfgren (2012) suggested TOC to be buffering pH. At the west coast, TOC seemed to act as a base and the pH sensitivity was high in streams with low

TOC concentrations. In Bergslagen, the pH sensitive streams were associated with till soils at a pH around 5.6, a pH that was high for the area.

In a study from northern Sweden, Ågren *et al.* (2010) found that catchments of the first order, with steep slope, high forest cover or forested wetlands, tend to be pH-sensitive to changes in BC concentrations in contrast to downstream, in subcatchments with agricultural fields. Driscoll *et al.* (2006) suggested that the reason for this is that the downstream water has a longer soil transit time where the concentration of alkaline weathering products will increase in the water. Additionally, the conditions for weathering are usually better in the lower parts of a catchment due to finer soil texture and better mineralogy (Ågren *et al.* 2010). Neff *et al.* (2012) also found a negative correlation between elevation and the water chemistry variables ANC and pH in north eastern USA.

# Methods

## Literature review

Mainly three databases were used for finding articles and reports for background knowledge. Primo is a search tool delivered by SLU library that contains the library catalogue and web based articles available via the library. Scopus and Web of knowledge were also used for search and to find references to articles of interest. Search-words used were "watershed", "catchment", "basin" and "land-use" together with "pH", "sensitive", "acidification", "stream water chemistry" and "characteristics" in different combinations. It was hard to find articles dealing with the relationship between pH-sensitivity and landscape variables. Therefore, I choose to also look for articles about the relationship between specific landscape variables and stream water chemistry using the search-words "wetland", "altitude", "vegetation cover" and "soil" in combination with "water chemistry", "pH" and "acidification". In order to find articles at chemical level I used the search words "DOC transport" and "weathering process" and refined my searches to articles in the category "hydrology". Some articles I found by searching literature in order to find sources that confirm knowledge I had from before. My supervisors have recommended some of the articles and the official websites from the Swedish Forest Agency and the Swedish Environmental Protection Agency have been used to find reports and information about measurements against biological acidification proposed by the authorities and of the current Swedish environmental status, respectively.

## Site description

The Bothnia Bay water district (Figure 1) covers 145 000 $km^2$ and include the counties of Gävleborg, Jämtland, Västernorrland, large parts of the county Dalarna, and small parts of the Västerbotten, Uppland and Västmanland counties. The catchment also includes some parts of Norway (Water authority 2013). The water divide, defining the water district, is found in the mountains between Norway and Sweden and follow altitude ridges down to the Bothnia Sea. 3 723 lakes and 7 379 streams are defined as water bodies in the district. The area is dominated by till soils and slowly weathered bedrock (Water authority Bothnia Bay 2013).

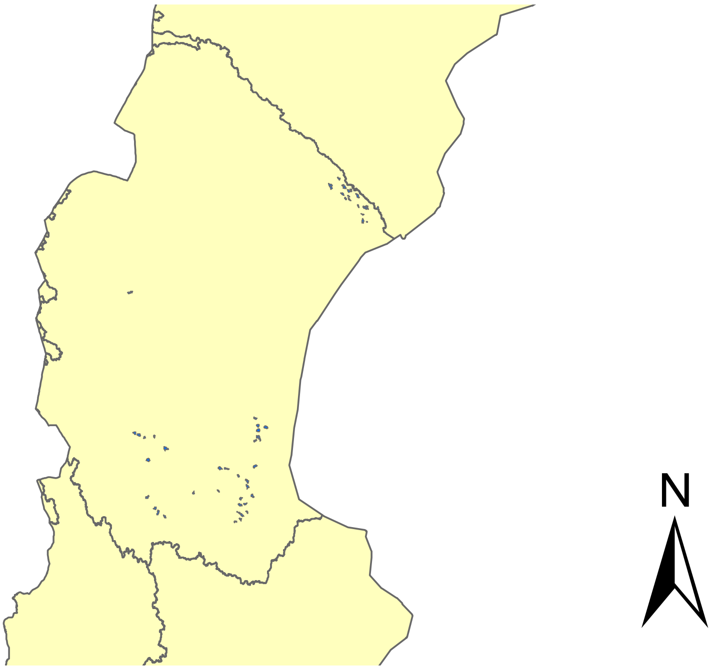


**Figure 1: Map over Bothnia Bay water district and the subcatchments included in the study**

Just over 70% of the area is covered by mainly managed forest that is the base for the dominating industry in the area producing products in wood, paper pulp and paper (Water authority Bothnia Bay 2013). Around 920 000 people are living in the area (Water authority Bothnia Bay 2013) corresponding to about 10% of the Swedish population.

## Data

Stream water chemistry data was collected from KEU, a project analysing the effects of liming hosted by SLU. Samples were collected with help from the county boards and analysed at the SLU geochemical laboratory in Uppsala (Fölster and Djursäter 2013). The pH measurements were made on aerated samples (Fölster and Djursäter 2013). The analytical precisions for the parameters are presented in table 1 (From 2013). Alkalinity was titrated to pH 5.6 (From 2013). The definition of ANC is presented in equation 2. The catchments were defined by the KEU project and handed to me as shape files together with the water chemistry data. The catchments where defined by the watershed tool in ArcGIS by using the VIVAN elevation model and with manual corrections (Fölster and Djursäter 2013).

**Table 1: Analytical precision in the SLU geochemical laboratory for the parameters used in the study**

| Parameter | Analytical precision |
|---|---|
| pH | 0.24 units |
| $Ca^{2+}$ | 9% |
| $Mg^{2+}$ | 12% |
| $Na^{+}$ | 6% |
| $K^{+}$ | 9% |
| Alkalinity | 3-5% |
| TOC | 8-11% |

Temnerud (2007) showed that stream water flow and chemistry stabilize in catchment areas exceeding 5 $km^2$ and the connection between catchment properties and water chemistry will not be clear. Small catchments were therefore chosen in order to detect landscape influence. When collecting data for this thesis it was not possible to get enough data points when limiting the catchment size to 5 $km^2$. The maximum catchment size was instead set to be 10 $km^2$ and collected from the watersheds sampled by the KEU project. All the data used were sampled in streams not limed.

In total, 53 catchments were included in the analysis distributed on the counties in Bothnia Bay watershed according to table 2. The majority of the subcatchments are located either in the south or in the north of the district because only a few subcatchments small enough were sampled in the counties of Västernorrland and Jämtland. Therefore, the dataset was divided into two subgroups of north and south catchments, respectively. The southern catchments were located in the counties of Dalarna and Gävleborg while those in Jämtland, Västernorrland and Västerbotten were defined as northern catchments. The splitting into two subgroups was done because different factors may affect the pH-sensitivity in different regions (Ågren and Löfgren 2012).

**Table 2: Number of analysed catchments in each county of Bothnia Bay water district**

| County | Number of catchments |
|---|---|
| Dalarna | 13 |
| Gävleborg | 21 |
| Västernorrland | 1 |
| Jämtland | 1 |
| Västerbotten | 17 |

Data from base flow conditions were used because the water chemistry is more stable. In addition, base flow stream water has a longer residence time in the soils and the landscape control on pH-sensitivity may be easier to detect.

Water discharge from SMHI (2013) was used to determine the flow at each sampling occasion. The data include the mean value of the lowest modelled daily flow every year (MQL) and the mean value of the daily flow over the entire period (MQ). For each watershed, the water chemical data was used from the sampling occasion at the lowest modelled flow. Two streams were lacking data sampled at occasions with lower flow than MQ why they were excluded from the analysis. The chosen sampling months and flow data for each watershed are presented in table 3.

**Table 3: Names of the sampling points together with flow data statistics, the flow at the chosen sampling occasion and the month of sampling, MQ is the mean flow for the modelled period and MLQ is the mean of every modelled year's lowest flow value (KAU; SMHI Water web)**

| Catchment | MQ [m3/s] | MLQ [m3/s] | Median flow [m3/s] | Flow when sampling [m3/s] | Month |
|---|---|---|---|---|---|
| Vinan | 0,05 | 0,01 | 0,02 | 0,02 | 11 |
| Bråtabäcken | 0,16 | 0,02 | 0,08 | 0,06 | 11 |
| Surmyrdalsbäcken | 0,07 | 0,01 | 0,03 | 0,02 | 11 |
| Kvarnbäcken (Stennäs) | 17,10 | 3,77 | 18,60 | 8,42 | 7 |
| Hällvasslan | 0,36 | 0,04 | 0,19 | 0,02 | 3 |
| Kölån | 0,43 | 0,02 | 0,21 | 0,02 | 3 |
| Tenningån | 0,15 | 0,01 | 0,07 | 0,01 | 3 |
| Bäck från Hälltjärnen | 0,05 | 0,00 | 0,03 | 0,01 | 3 |
| Bäck från Högsjön | 0,61 | 0,10 | 0,36 | 0,09 | 3 |
| Laxbäcken | 0,08 | 0,01 | 0,03 | 0,02 | 6 |
| Laxtjärnsbäcken | 0,22 | 0,02 | 0,12 | 0,03 | 3 |
| Pengerbäcken | 0,08 | 0,01 | 0,03 | 0,02 | 6 |
| Pysslabäcken | 0,17 | 0,02 | 0,05 | 0,01 | 11 |
| Släthedsbäcken | 0,13 | 0,02 | 0,09 | 0,03 | 3 |
| Smed-Larsbäcken | 0,13 | 0,01 | 0,06 | 0,03 | 11 |
| Tollsbäcken | 0,23 | 0,02 | 0,11 | 0,04 | 11 |
| Råstensbäcken | 0,51 | 0,03 | 0,25 | 0,02 | 3 |
| Hässjebäcken | 0,62 | 0,08 | 0,32 | 0,15 | 11 |
| Bäcken från Vådtjärn | 1,33 | 0,23 | 0,81 | 0,40 | 11 |
| Smalviksbäcken | 0,73 | 0,22 | 0,53 | 0,38 | 3 |
| Gåsån | 0,10 | 0,01 | 0,04 | 0,01 | 11 |
| Örtjärnsbäcken | 0,05 | 0,01 | 0,02 | 0,01 | 11 |
| Nedströms Sör Järnässjön | 0,06 | 0,01 | 0,02 | 0,01 | 11 |
| Bäck från Skitigsjön | 0,14 | 0,01 | 0,07 | 0,01 | 11 |
| Karlsmyrbäcken | 0,11 | 0,02 | 0,05 | 0,01 | 11 |
| Mössbobäcken | 0,11 | 0,01 | 0,04 | 0,01 | 11 |
| Svartvallstjärnsbäcken | 0,32 | 0,03 | 0,13 | 0,03 | 11 |
| Ottjärnbäcken | 0,04 | 0,01 | 0,02 | 0,02 | 11 |
| Svartbäcken Brattsbacka | 1,07 | 0,19 | 0,61 | 0,78 | 9 |
| Djupmyrbäcken | 0,13 | 0,01 | 0,05 | 0,04 | 11 |
| Ottjärnbäcken | 0,36 | 0,07 | 0,21 | 0,16 | 9 |
| Ljusacksbäcken | 0,23 | 0,03 | 0,10 | 0,04 | 11 |
| Bergmyrbäcken | 17,80 | 3,47 | 12,00 | 9,54 | 7 |
| Björntjärnbäcken | 0,57 | 0,12 | 0,34 | 0,19 | 7 |
| Fågelmyrbäcken | 1,70 | 0,27 | 1,08 | 0,54 | 7 |
| Kvarnbäcken (Nordmalingstjärnen) | 0,20 | 0,02 | 0,10 | 0,23 | 11 |
| Smaltjärnbäcken | 1,63 | 0,26 | 1,03 | 0,53 | 7 |
| Sprängstjärnbäcken | 1,63 | 0,26 | 1,03 | 0,53 | 7 |
| Bäcken från Männikumäckmyren | 0,66 | 0,05 | 0,32 | 0,03 | 3 |
| Källsjöbäcken | 0,13 | 0,01 | 0,06 | 0,01 | 3 |
| Tobacksbäcken | 0,51 | 0,03 | 0,25 | 0,02 | 3 |
| Bäck i Hässäljan | 0,18 | 0,02 | 0,08 | 0,05 | 3 |
| Granmyrbäcken | 0,13 | 0,01 | 0,06 | 0,03 | 3 |
| Björntjärnen | 0,07 | 0,01 | 0,03 | 0,02 | 7 |
| Djupbäcken | 0,05 | 0,00 | 0,02 | 0,01 | 7 |
| Lerbäcken | 16,00 | 2,56 | 10,60 | 8,91 | 7 |
| Låtilampbäcken | 0,07 | 0,01 | 0,03 | 0,02 | 6 |
| Halvstensån | 0,04 | 0,00 | 0,02 | 0,01 | 11 |
| Sallaporosbäcken | 0,04 | 0,00 | 0,02 | 0,01 | 3 |
| Lappkåtabäck | 0,17 | 0,02 | 0,09 | 0,07 | 11 |
| Hedtjärnsbäcken | 0,12 | 0,01 | 0,06 | 0,01 | 3 |
| Mörkån | 0,10 | 0,01 | 0,04 | 0,04 | 11 |
| Gesundaån | 0,03 | 0,00 | 0,01 | 0,01 | 11 |

pH-sensitivity was defined as the deviation from pH 5.6 according to the method described by Ågren and Löfgren (2012) (Table 4).

**Table 4: Classification of pH-sensitivity (Ågren and Löfgren 2012)**

| Class | pH | |
|---|---|---|
| 1 | <4.2 | Insensitive |
| 2 | 4.2-4.6 | |
| 3 | 4.6-5 | |
| 4 | 5-5.4 | |
| 5 | 5.4-5.8 | Most sensitive |
| 4 | 5.8-6.2 | |
| 3 | 6.2-6.6 | |
| 2 | 6.6-7 | |
| 1 | >7 | Insensitive |

In the pH-range where neither the carbonate system nor the weak organic acids act as a buffer pH will change fast if there are changes in the chemical composition (Figure 2).

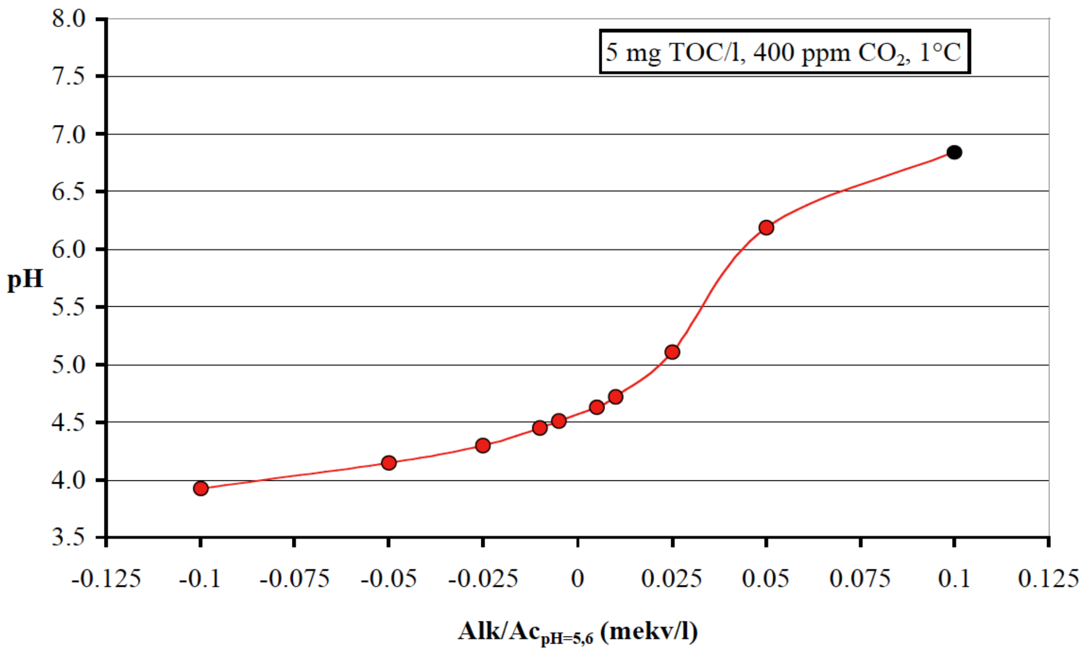


**Figure 2: The relationship between pH and ANC (=Alk/AcpH=5.6) show that the buffering capacity is low around pH 5.6 (Löfgren and Laudon 2004)**

Map layers used to analyse the catchments properties are presented in table 5 together with the source, scale and variables used in each map. In order to decrease the number of variables, highly covariate variables were aggregated to one. “Pastures” and “land occupied by agriculture” were added together and named “agriculture land”. The same was done with “postglacial sedimentary sand to stones” and “galcofluvial sedimentary sand to stones” and this new variable was named “coarse quaternary deposits”.

**Table 5: Geographical data used listed together with its properties and the parameters used in the analysis from each map**

| Map name | Parameters used | Provider | Scale | Geographical data type |
|---|---|---|---|---|
| Corine | Pastures | Commission of the European Communities 2006 | 100x100m | Raster |
| | Land occupied by agriculture | | | |
| | Broad leaved forest | | | |
| | Coniferous forest | | | |
| | Mixed forest | | | |
| | Transitional woodland-shrubs | | | |
| Skogens källa | Total harvested | The Swedish forest authority 2013 | | Polygon |
| kNN | Scots pine | SLU 2010 | 25x25 m | Raster |
| | Norwegian spruce | | | |
| | Volume | | | |
| National geological soil map | Clay-silt | Swedish Geological Institute | 1:50 000 | Polygon |
| | Rock outcrops | | | |
| | Till | | | |
| | Sand-stones postglacial | | | |
| | Sand-stones glacofluvial sediments | | | |
| | Peat | | | |
| Road map | Water surfaces | Swedish ordnance survey | 1:50 000 | Polygon |
| Highest coastline map | Highest coastline | | | |
| Elevation model | Altitude | | 50x50 m | Raster |
| Catchment areas | Catchment borders | The KEU project | | Polygon |

## Geographical analyses

The map layers were analysed using ArcGIS. The watersheds were defined by the KEU project in ArcGIS and checked manually by comparing with gridlines in the road map (Fölster and Djursäter 2013).

All raster layers were cut out based on the water divides by using extract by mask. For the Corine layer and elevation model the raster data were transformed to polygons. The land cover was according to Corine (table 5) and altitude was classified in 100 m intervals. The resulting polygons were intersected with the watershed polygons in order to join the information of the attribute tables. For the new layer the area was calculated for all polygons and the attribute table was exported for further analyses. Corine and elevation raster layers were covering all land area and the sum of the new polygons differed somewhat from the catchment area. The raster layers are in the form of squares and the boarders of created polygons were not smooth. This caused loss or gain of some areas in the intersect action (table 6).

In order to define areas dominated by Scots pine or Norwegian spruce, the layers with volumes of deciduous and coniferous trees were added to total volume. The volumes of Norwegian spruce and Scots pine were divided with total volume to estimate the tree species fraction in the catchments. These new raster layers were limited to 4 classes, representing the proportion of Norwegian spruce and Scots pine in each raster cell. The raster data were transformed to polygons based on tree species classes. The areas dominated by each tree species were calculated for each catchment.

**Table 6: The difference in area between the initial catchment area and the area after intersecting it with the Corine and altitude raster respectively**

| | Corine data | | Altitude | |
|---|---|---|---|---|
| Statistics all catchments | Difference km2 | Difference % | Difference km2 | Difference % |
| Max | 0.3 | 6.7 | 0.2 | 3.7 |
| Min | 0.1 | 1.6 | 0.0 | 0.9 |
| Mean | 0.1 | 2.9 | 0.1 | 1.6 |
| Median | 0.1 | 2.7 | 0.1 | 1.5 |

For the polygon layers the clip tool in ArcGIS was used to extract the data inside the watersheds. The watershed layer and the new polygon layer where intersected to join the information of the layers. For the new layer the area was calculated for all the polygons. The attribute table was then exported for further analyses.

## Data properties

The properties of geographical and water chemistry data are presented in table 7. In order to have normal distributed data for the statistical analysis some parameters were transformed due to skewness. Arcsine of the square root was used as transformation method for geographical parameters described as the fraction of land cover. For parameters described in absolute values, the third square root was used to transform the data. In cases where the distribution did not get an improved normal distribution by transformation the original figures where used. The transformation methods for each parameter are shown in table 7.

**Table 7: Properties and transformation method for the generated geographical and water chemistry data used in the principal component analysis**

| Property | Min | Max | Mean | Median | Unit | Transformation |
|---|---|---|---|---|---|---|
| Agriculture land | 0.0 | 6.8 | 0.2 | 0.0 | % | - |
| Broad leaved forest | 0.0 | 8.2 | 0.2 | 0.0 | % | - |
| Coniferous forest | 8.1 | 100.0 | 72.6 | 74.6 | % | Arcsine |
| Mixed forest | 0.0 | 31.1 | 1.6 | 0.0 | % | Arcsine |
| Transitional land woodland - shrubs | 0.0 | 71.7 | 19.5 | 16.7 | % | - |
| Water | 0.0 | 7.0 | 1.3 | 0.69 | % | Arcsine |
| Dominated by Scots pine | 0.0 | 62.5 | 25.5 | 25.0 | % | - |
| Dominated by Norwegian spruce | 0.0 | 15.2 | 2.2 | 1.5 | % | Arcsine |
| Volume | 0.1 | 73.7 | 22.0 | 19.6 | m3sk/ha | 3 root |
| Total harvested | 0.0 | 40.1 | 8.5 | 7.1 | % | Arcsine |
| Mean altitude | 103.1 | 664.8 | 294.7 | 250 | m above sea level | Arcsine |
| Under Highest Coastline | 0.0 | 100.0 | 42.0 | 28.0 | % | Arcsine |
| Clay-silt | 0.0 | 15.8 | 1.4 | 0.0 | % | 3 root |
| Coarse soil | 0.0 | 99.8 | 5.8 | 0.0 | % | - |
| Peat | 0.0 | 41.4 | 5.7 | 0.0 | % | 3 root |
| Rock outcrops | 0.0 | 86.6 | 16.8 | 9.1 | % | - |
| Till | 0.0 | 100.0 | 70.3 | 80.6 | % | - |
| Alkalinity | -0.1 | 0.2 | 0.05 | 0.04 | meqv/l | - |
| ANC | 0.1 | 0.4 | 0.2 | 0.20 | meqv/l | - |
| Calcium | 0.0 | 0.2 | 0.1 | 0.11 | meqv/l | - |
| TOC | 2.8 | 37.2 | 15.2 | 14.80 | mg/l | Arcsine |
| pH | 4.3 | 7.0 | 6.3 | 6.4 |  | - |
| pH-sensitivity | 1,0 | 5,0 | 3,0 | 3,000 | class | - |

## Statistical analyses

The correlations between pH-sensitivity and geographical parameters were analysed with principal components analysis (PCA) using the software JMP 10. In the PCA the variance in the data is analysed for each variable, uncorrelated to each other. The analysis results in the same number of components, as there are variables. The first two components explain most of the variance in the data. Components with low variance are assumed to be noise. The first two components are shown and used for making conclusions on how pH-sensitivity correlates to landscape and water chemistry variables.

Two variations of analyses were made; one including all geographical parameters and one excluding variables with a median of 0,0 (table 7). The analyses where all variables were included cover variables uncommon in the data landscape found only in a few catchments. Variables with a median of zero were excluded in order to avoided that a few observations could have a significant influence on the result. These two analyses were performed both with and without water chemistry data. The correlations between pH-sensitivity and landscape properties were analysed when water chemistry data were excluded. The latter were added to the analyses in order to get a picture of how alkalinity and calcium, indicating weathering and TOC correlate with the pH-sensitivity. In order to examine if there were geographical differences, the analyses were performed on the entire database as well as for the northern and southern regions, respectively. In total, 12 principal component analyses were performed.

## Results

The number of catchments classified in each pH-sensitivity class is presented in Figure 3. All pH-sensitivity classes are represented in the southern subcatchments, however, only one subcatchment was found in class 1, representing the lowest pH-sensitivity. In the northern subcatchments sensitivity class 1 is not represented.

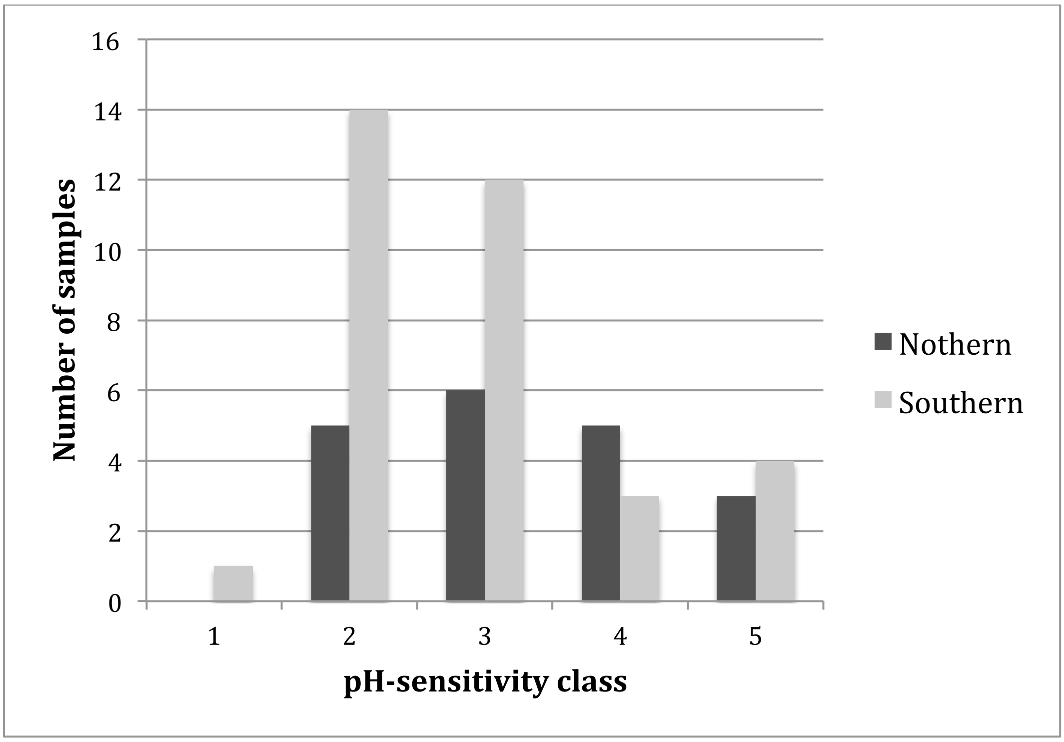


**Figure 3: Number of catchments classified in each pH-sensitivity class for the North and South subcatchments, respectively**

### PCA results

Each analysis results in a graph where all variables included in the analysis are related to the two components that explain most of the variation in the data. In order to get an indication for how the variables are correlated to each other the relation between the placement of the variables are of greater interest than the relation to the components. If the variables are placed close to each other and have a similar correlation to the principal components, they are positively correlated to each other. Variables with an opposite correlation to the principal components are negatively correlated to each other.

**PCA with all catchments**

Based on all catchments and all geographical variables (Figure 4), the two first components (pc1 and pc2) are explaining 34.8% of the variation in the data. Both principal components are weakly correlated to pH-sensitivity and they do not give any valuable information about how pH-sensitivity correlates to the landscape features. The result indicates that pc1 corresponds to an altitude gradient.

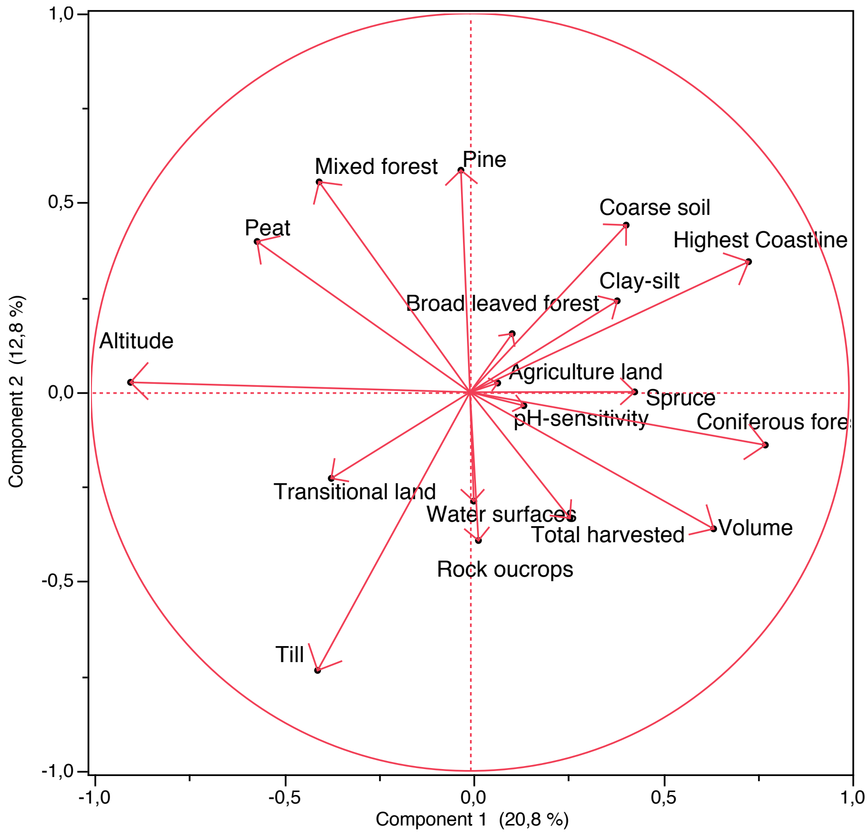


**Figure 4: PCA including all subcatchments and all geographical variables**

However, the pH-sensitivity was positively correlated to pc4 (Figure 5). Areas dominated by Scots pine and agriculture land were positively and rock outcrops negatively correlated to pc4, although these correlations were weak. Pc4 explains only 9.6% of the variation in the dataset.

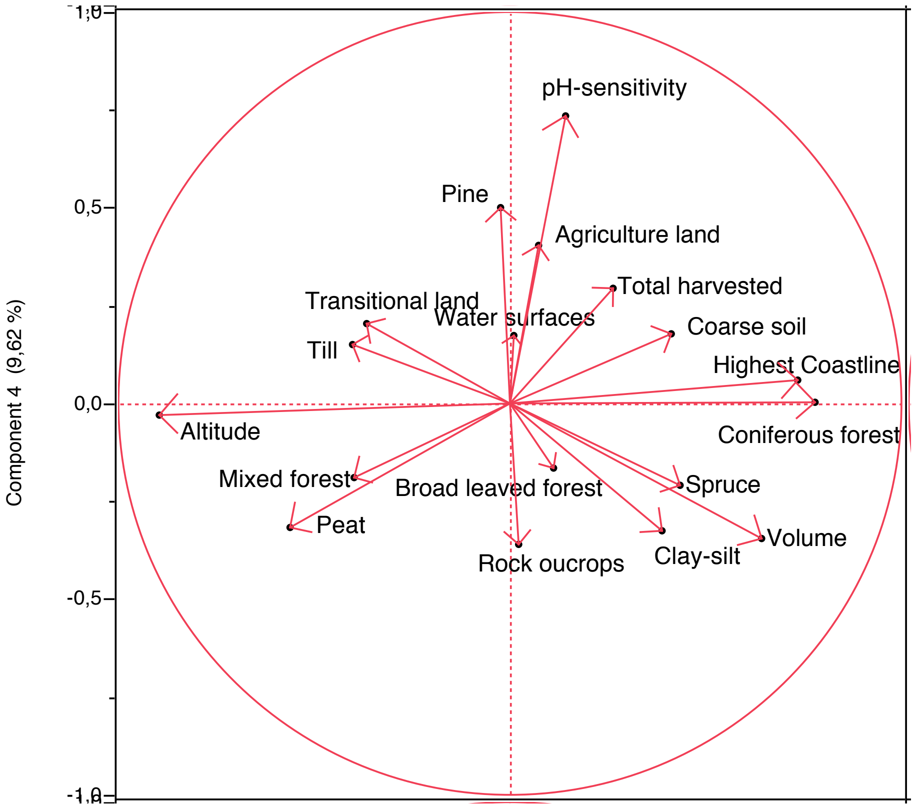


**Figure 5: The first and the fourth principal component including all geographical variables**

**PCA with all catchments and all geographical and chemistry variables**

Adding the water chemistry properties ANC, TOC, alkalinity and calcium to the PCA (Figure 6), the first two components explained 35% of the variation in the dataset.

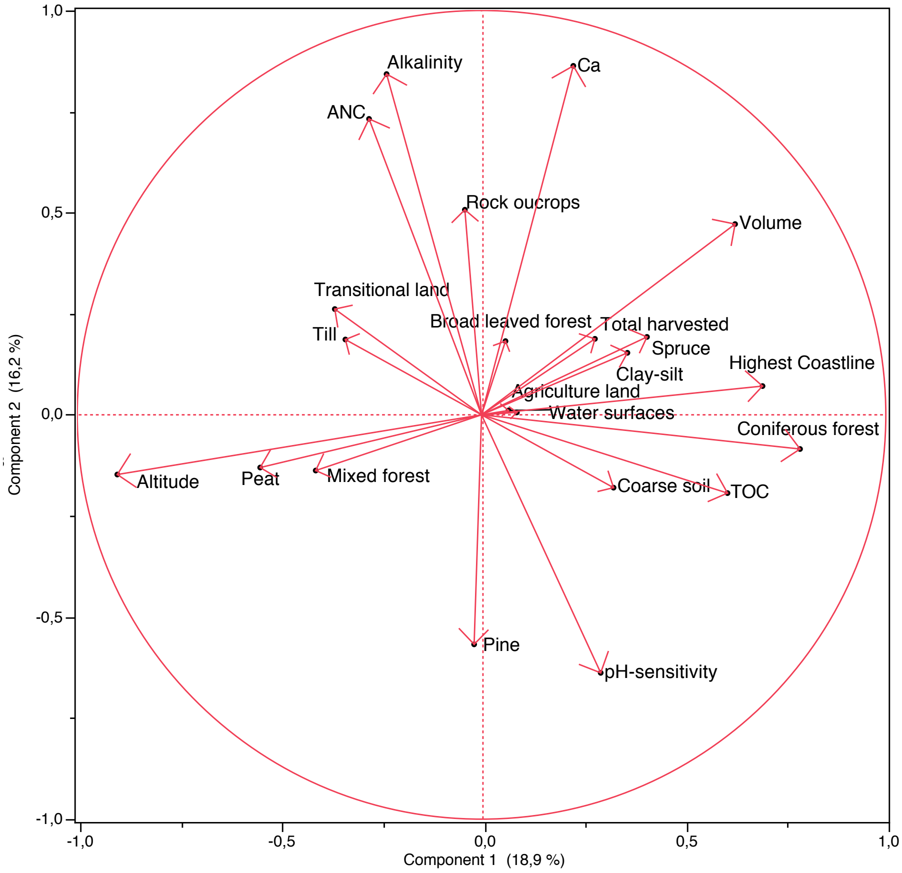


**Figure 6: PCA including all subcatchments with all geographical and chemical variables**

Pc1 indicates an altitude gradient, while Pc2 indicates a chemical gradient with negative correlations between pH-sensitivity and the variables ANC, alkalinity and calcium. The PCA (Figure 6) also indicates that pH-sensitivity is positively correlated to areas dominated by Scots pine and negatively correlated with rock outcrops.

#### PCA limited to variables with many observations

The geographical variables that only occurred in a few subcatchments could have a relatively large impact in the analysis and skew the results. Therefore, the PCA was also performed when variables with a median of zero (Figure 7) were excluded. In the PCA with all catchments, limited to the variables with median over zero, pc1 and pc2 explained 41% of the variation.

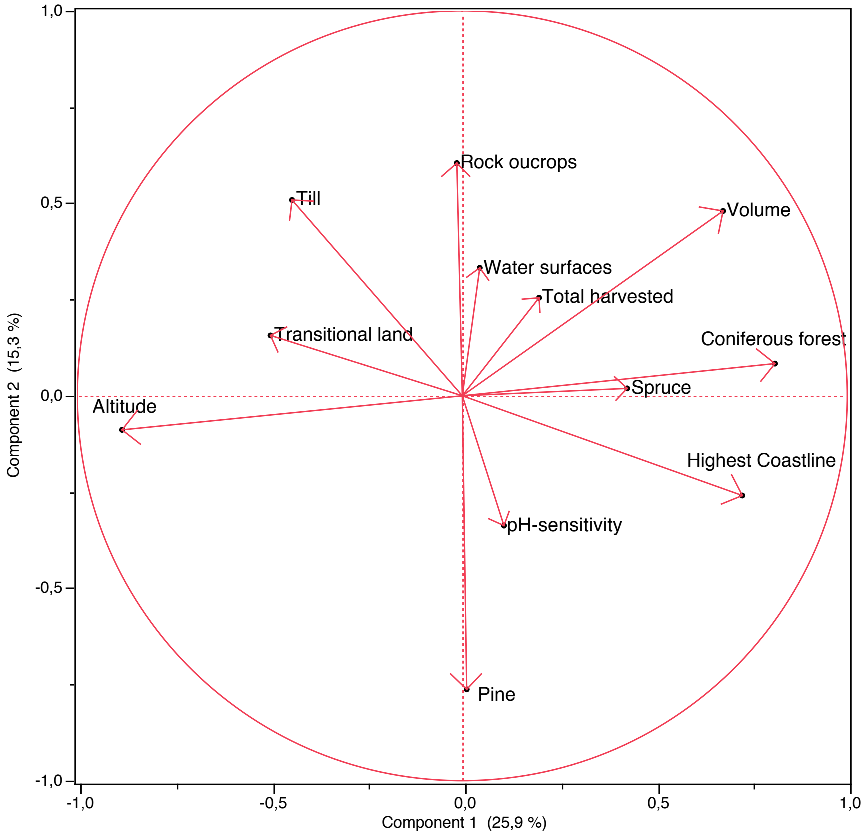


**Figure 7: PCA based on geographical variables with median values above zero**

Also in this analysis there is an altitude gradient along the first component. pH-sensitivity was weakly correlated to both principal components. There is an indication that pH-sensitivity is positively correlated to Scots pine and negatively correlated to rock outcrops.

**PCA limited to variables with many observations, chemistry variables included**

When water chemistry variables are included and the geographical variables that occurred in only a few subcatchments were excluded (Figure 8), the variation explained by the two first components was 44%.

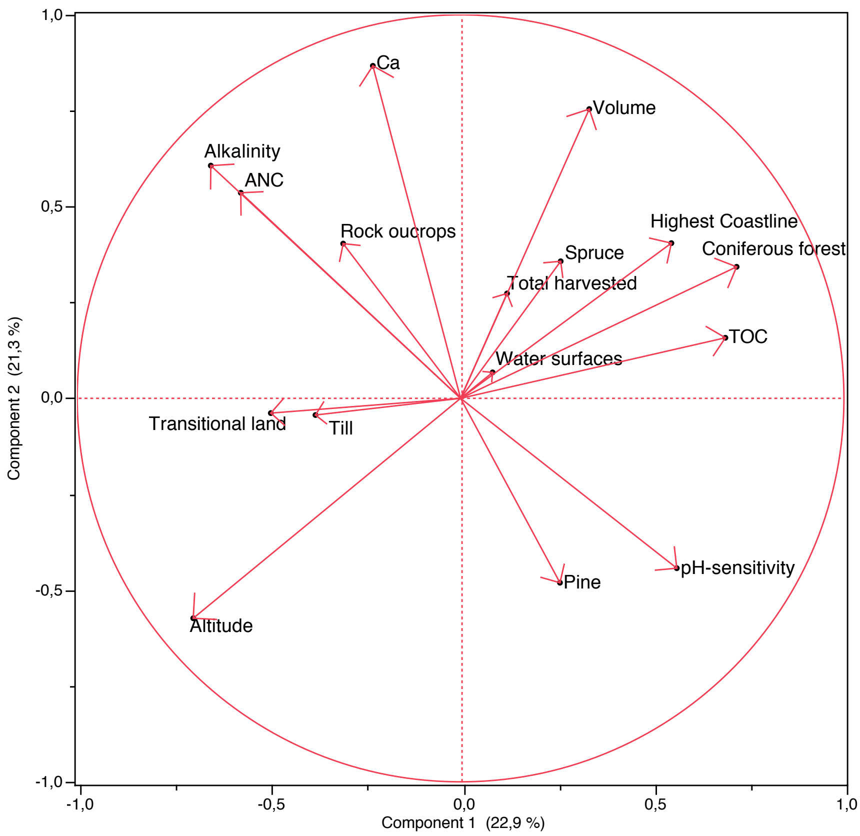


**Figure 8: PCA including geographical components with a median above zero and water chemical variables**

When chemistry is added to the analysis the pH-sensitivity correlation to pc1 and pc2 becomes close to 0.5 and -0.5, respectively. The pH-sensitivity is positively correlated with Scots pine dominated areas and negatively correlated to rock outcrops, ANC, alkalinity and calcium (Figure 8).

Based on the above results it is shown that pH-sensitivity has no clear relation to any landscape variable when including all subcatchmens in the PCA's. Therefore separate PCA's were made for the northern and southern regions, respectively.

## Northern subcatchments

The northern division includes subcatchments in the counties Västerbotten, Västernorrland and Jämtland. The samples have a mean pH 6 and there are no subcatchments with pH-sensitivity class 1 in the samples (table 6).

**Table 6: Properties of the data in the northern subcatchments**

| Property | Mean | Min | Max | Median | Unit |
|---|---|---|---|---|---|
| Agriculture land | 0.6 | 0.0 | 6.8 | 0.0 | % |
| Broad leaved forest | 0.0 | 0.0 | 0.0 | 0.0 | % |
| Coniferous forest | 1.0 | 0.3 | 1.6 | 1.0 | % |
| Mixed forest | 1.2 | 0.0 | 13.8 | 0.0 | % |
| Transitional land woodland - shrubs | 0.5 | 0.0 | 1.0 | 0.5 | % |
| Water | 0.1 | 0.0 | 0.2 | 0.1 | % |
| Dominated by Scots pine | 0.5 | 0.2 | 0.9 | 0.5 | % |
| Dominated by Norwegian spruce | 0.2 | 0.1 | 0.4 | 0.2 | % |
| Volume | 2.4 | 1.6 | 3.7 | 2.3 | m3sk/ha |
| Total harvested | 0.3 | 0.1 | 0.7 | 0.3 | % |
| Mean altitude | 6.3 | 4.9 | 8.6 | 6.2 | m above sea level |
| Under Highest Coastline | 67.2 | 0.0 | 100.0 | 93.8 | % |
| Clay-silt | 2.9 | 0.0 | 15.8 | 0.0 | % |
| Coarse soil | 7.4 | 0.0 | 99.8 | 0.0 | % |
| Peat | 2.2 | 0.0 | 29.4 | 0.0 | % |
| Rock outcrops | 0.6 | 0.0 | 1.2 | 0.6 | % |
| Till | 0.8 | 0.0 | 1.3 | 1.0 | % |
| Alkalinity | 0.0 | -0.1 | 0.2 | 0.0 | meqv/l |
| ANC | 0.2 | 0.1 | 0.3 | 0.2 | meqv/l |
| Calcium | 0.5 | 0.4 | 0.5 | 0.5 | meqv/l |
| TOC | 16.7 | 2.8 | 37.2 | 15.7 | mg/l |
| pH | 6.0 | 4.3 | 6.9 | 6.0 | |
| pH-sensitivity | 3.3 | 2.0 | 5.0 | 3.0 | class |

#### PCA northern subcatchments

The first PCA performed with the northern catchments includes all geographical variables (Figure 9), and the two first principal components explained 44.5% of the variation in the dataset.

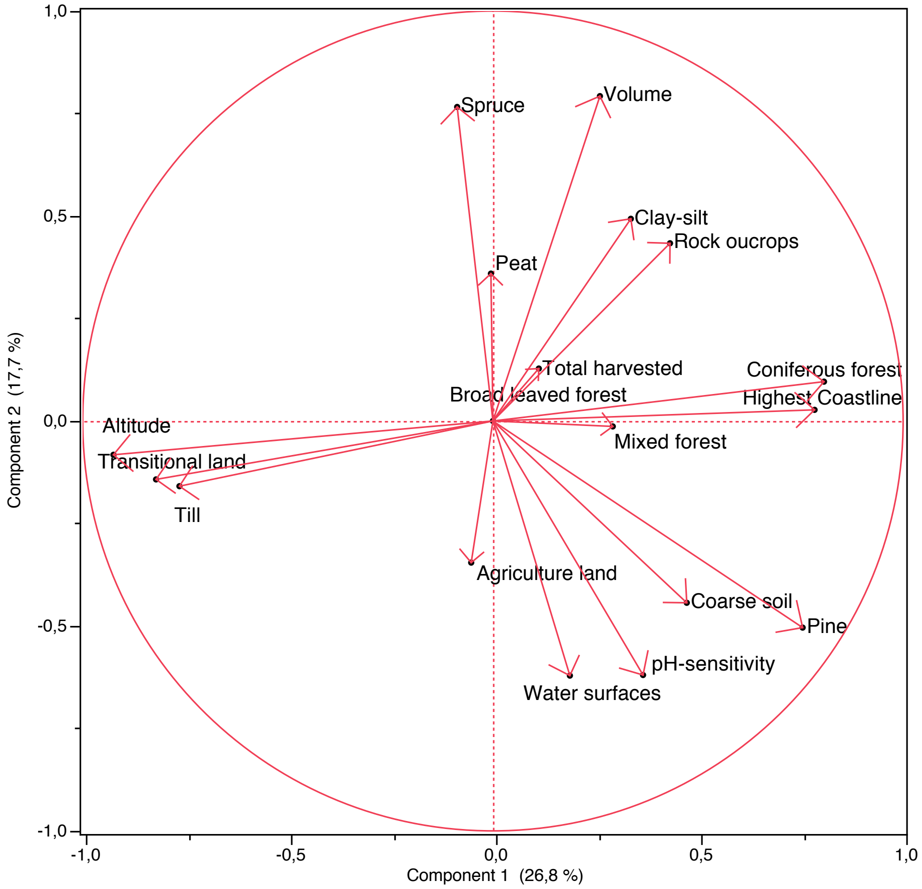


**Figure 9: PCA of the geographical variables of the northern catchments**

Along pc1 there is an indication of an altitude gradient. pH-sensitivity is better correlated to pc2, indicating a positive relation water surfaces, Scots pine dominated areas and coarse quaternary deposits, and a negative correlation with areas dominated by Norwegian spruce.

**All geographical and chemistry variables**

When chemistry variables are included in the PCA, the two principal components explain 46% of the variation in the dataset (Figure 10). The indication of an altitude gradient along pc1 is still present.

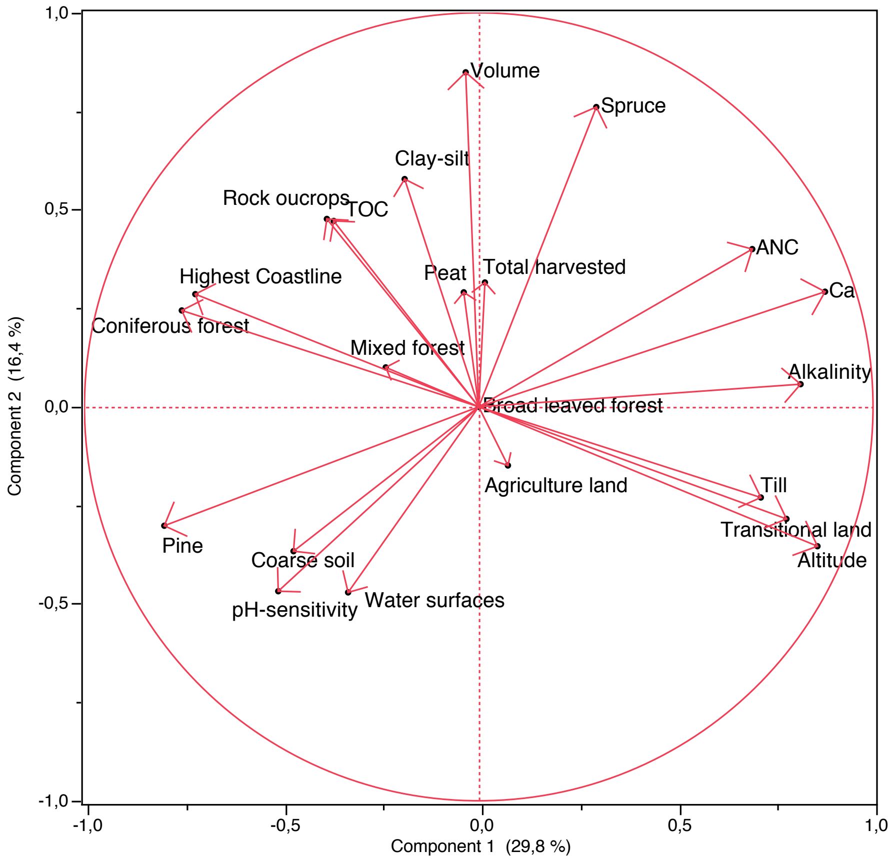


**Figure 10: PCA of the geographical and chemical variables in the northern catchments**

The result indicates that pH-sensitivity has a positive correlation to Scots pine, coarse quaternary deposits and water surfaces. ANC and Norwegian spruce dominated areas seems to be negatively correlated to pH-sensitivity.

**PCA limited to variables with many observations in northern catchments, with and without chemistry**

Analysing the data for the northern subcatchments, with the geographical variables only present in a few subcatchments excluded, result in Figure 11. The two first principal components are explaining 59.8% of the variation in the dataset.

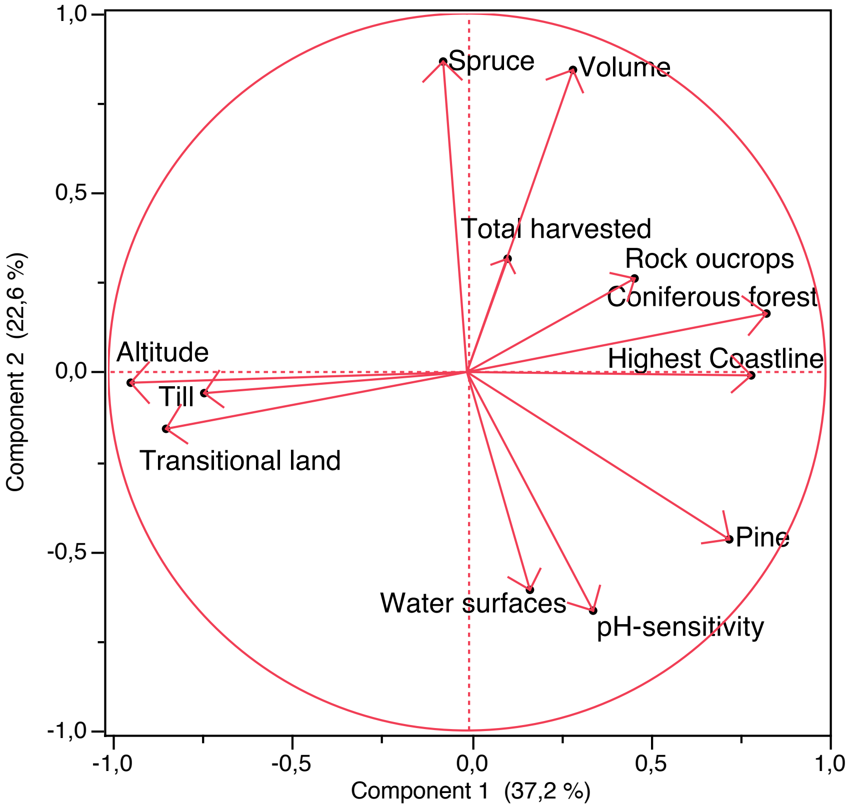


**Figure 11: PCA of the geographical variables with a median over zero in the northern catchments**

When also chemical variables are included in the PCA (Figure 12), the components explain 59.4% of the variation.

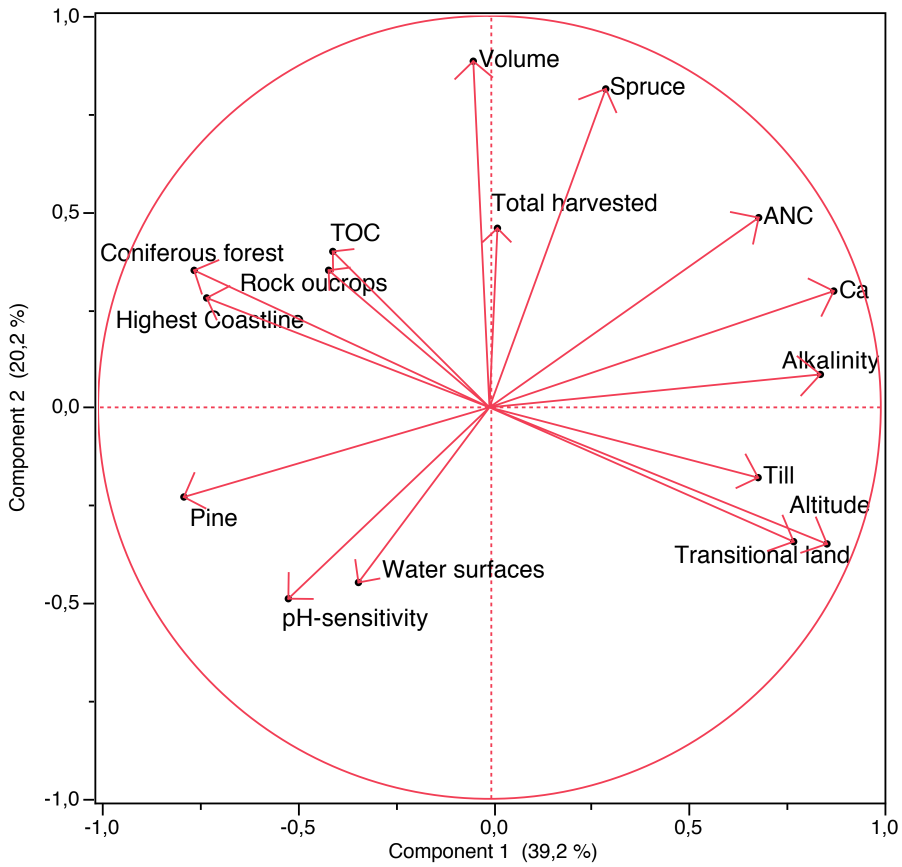


**Figure 12: PCA limited to geographical variables with a median over zero and chemical properties in the northern catchments**

In both these analyses done for the northern catchments there is an indication of an altitude gradient. The PCA based on landscape variables (Figure 11), indicates that pH-sensitivity has a positive correlation to water surfaces and areas dominated by Scots pine, and a negative correlation to areas dominated by Norwegian spruce and biomass volume. The pH-sensitivity correlation to water surfaces and areas dominated by Scots pine, remains when adding water chemistry to the analysis (Figure 12). Additionally, the PCA indicates that ANC, alkalinity, calcium and areas dominated by Norwegian spruce have a negative correlation to the pH-sensitivity.

## Southern subcatchments

The south division includes subcatchments in Dalarna and Gävleborg counties. Compared to the north part the pH is generally higer with mean pH 6.4 and all pH-sensitivity classes are represented (table 7).

**Table 7: Properties of the data in the southern subcatchments**

| Property | Mean | Min | Max | Median | Unit |
|---|---|---|---|---|---|
| Agriculture land | 0.0 | 0.0 | 0.0 | 0.0 | % |
| Broad leaved forest | 0.2 | 0.0 | 8.2 | 0.0 | % |
| Coniferous forest | 1.1 | 0.3 | 1.6 | 1.1 | % |
| Mixed forest | 1.8 | 0.0 | 31.1 | 0.0 | % |
| Transitional land woodland - shrubs | 0.4 | 0.0 | 0.8 | 0.4 | % |
| Water | 0.1 | 0.0 | 0.3 | 0.1 | % |
| Dominated by Scots pine | 0.5 | 0.0 | 0.7 | 0.5 | % |
| Dominated by Norwegian spruce | 0.1 | 0.0 | 0.3 | 0.1 | % |
| Volume | 2.7 | 0.5 | 4.2 | 3.0 | m3sk/ha |
| Total harvested | 0.3 | 0.0 | 0.5 | 0.3 | % |
| Mean altitude | 6.7 | 4.7 | 8.7 | 6.5 | m above sea level |
| Under Highest Coastline | 27.9 | 0.0 | 99.1 | 0.5 | % |
| Clay-silt | 0.7 | 0.0 | 7.9 | 0.0 | % |
| Coarse soil | 4.9 | 0.0 | 46.0 | 0.0 | % |
| Peat | 7.6 | 0.0 | 41.4 | 0.0 | % |
| Rock outcrops | 0.2 | 0.0 | 0.6 | 0.2 | % |
| Till | 1.1 | 0.7 | 1.6 | 1.2 | % |
| Alkalinity | 0.1 | -0.1 | 0.2 | 0.1 | meqv/l |
| ANC | 0.2 | 0.1 | 0.4 | 0.2 | meqv/l |
| Calcium | 0.5 | 0.4 | 0.6 | 0.5 | meqv/l |
| TOC | 14.4 | 3.9 | 30.8 | 13.8 | mg/l |
| pH | 6.4 | 7.0 | 5.7 | 6.5 | |
| pH-sensitivity | 2.9 | 1.0 | 5.0 | 3.0 | class |

#### PCA southern subcatchments

For the southern catchments the principal components explained 39.8% when only geographical variables were included and 43.3% when also chemical variables were taken into account (Figure 13 and 14).

pH-sensitivity has a positive correlation to till (Figure 13) and a negative correlation to broad leaved forest. When water chemistry is included (Figure 14) the result implies that pH-sensitivity has a positive correlation to TOC and till. Additionally, ANC and alkalinity were negatively correlated to pH-sensitivity (Figure 14).

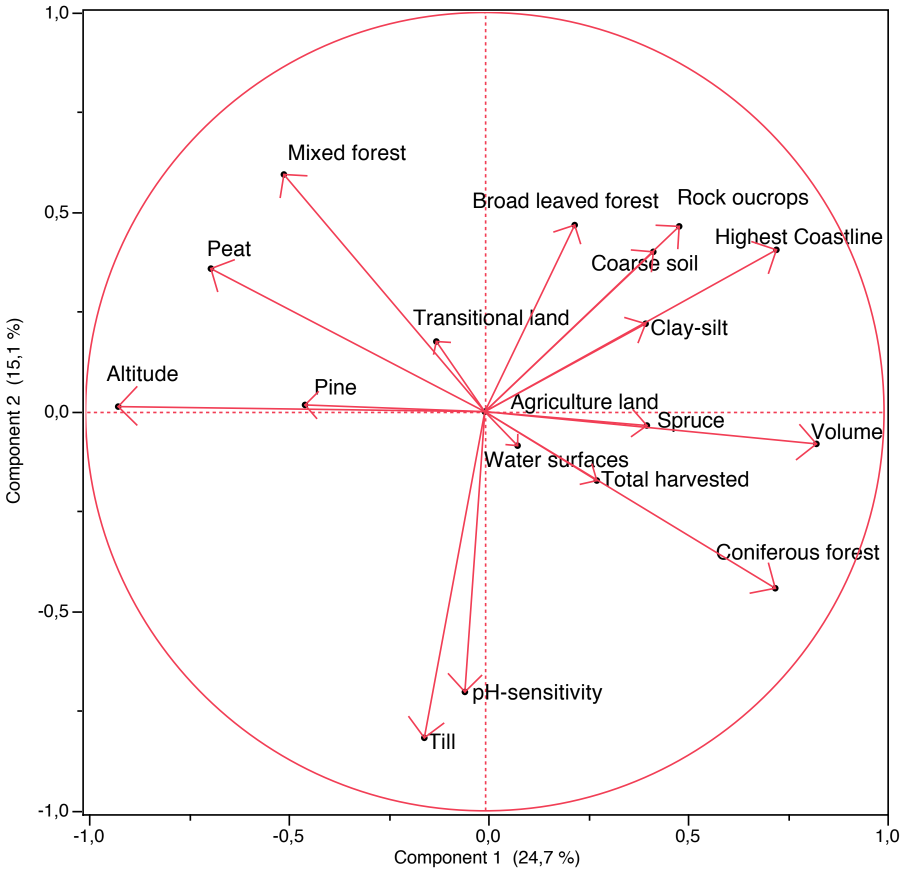


**Figure 13: PCA of the geographical variables of the southern catchments**

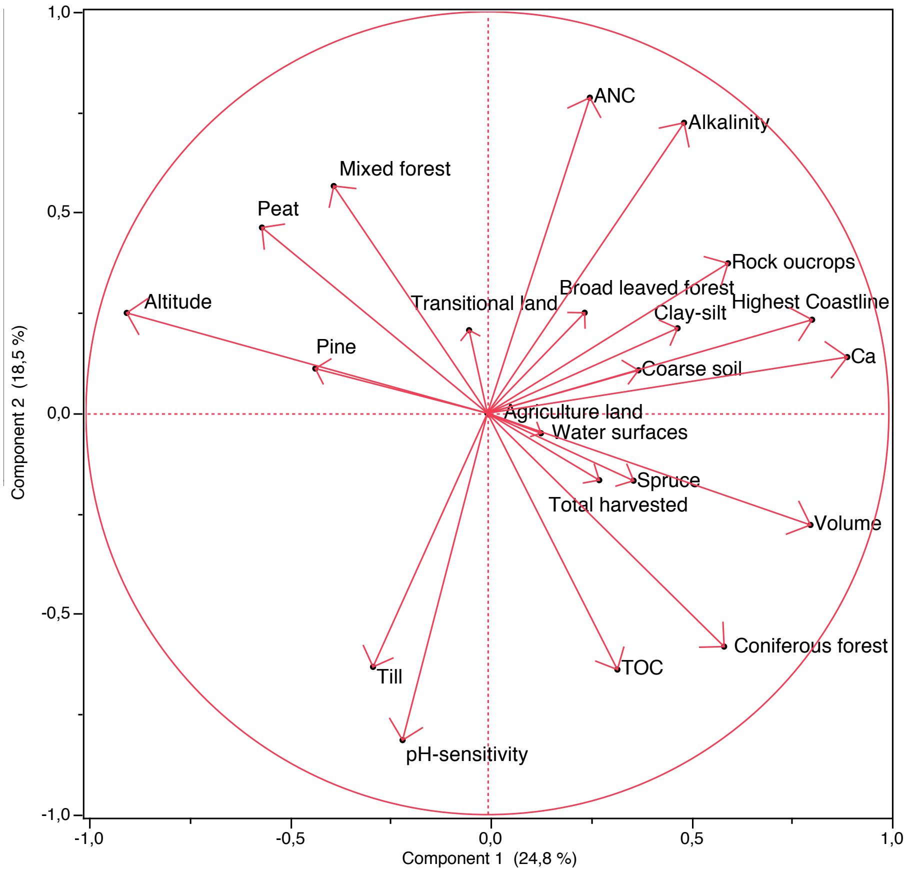


**Figure 14: PCA including geographical and chemical variables in the southern catchments**

**PCA limited to variables with many observations, without and with chemical vaiables**

Excluding the geographical variables only occurring in a few subcatchments from the PCA gives the results shown in Figure 15 and 16. When only geographical variables were included 59.7% of the variation was explained by the two first principal components. When chemical variables were included in the PCA 59.4% of the variation was explained by the two first components.

The PCA including geographical variables for the southern subcatchments indicates that pH-sensitivity is positively correlated to till and negatively correlated to rock outcrops and land in transition between scrubs and woodland (Figure 15).

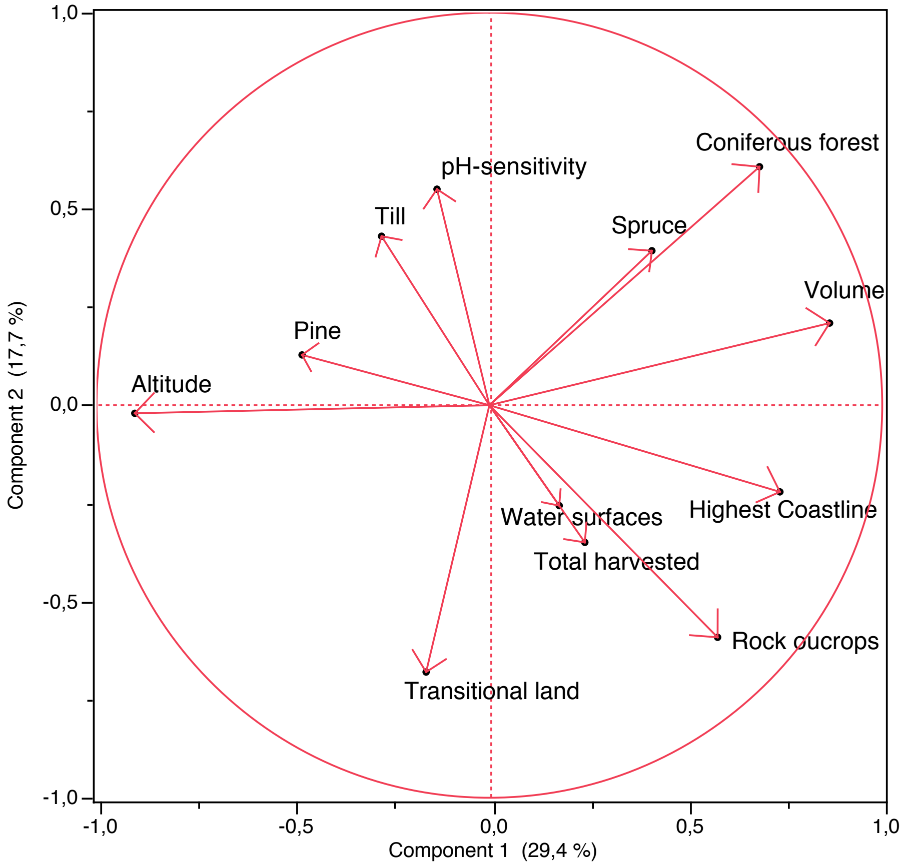


**Figure 15: PCA including geographical variables with a median over zero in the southern catchments**

When water chemistry is added to the analysis, the pH-sensitivity correlation to pc2 is larger, about 0.75 (Figure 16). The result indicates that TOC and till correlates positively to pH-sensitivity and that ANC, alkalinity and rock outcrops have a negative correlation to pH-sensitivity.

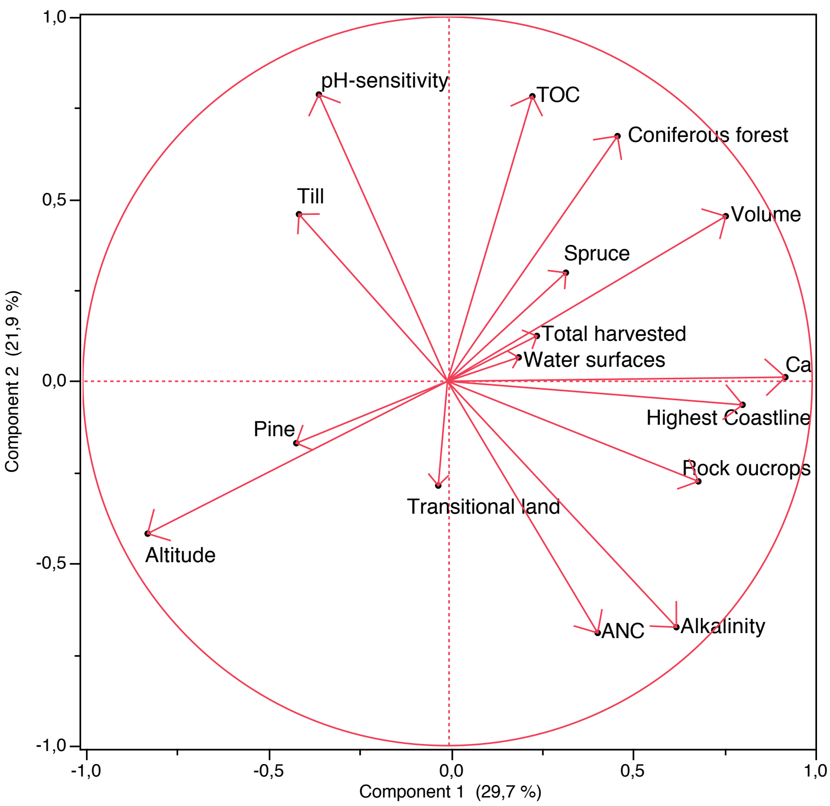


**Figure 16: PCA including geographical variables with a median over zero and chemical properties in the southern catchments**

In summary, different variables are correlated to pH-sensitivity in the north and south subcatchments respectively (table 8). The PCA's limited to common variables and with water chemistry included resulted in principal components with higher explanation of variation in the dataset compared to the other analyses. For the northern part, the components in the analyses explained a higher proportion of the variation in the dataset compared to the south region (table 8).

**Table 8: Summary of the results including the percentages of variation explained by the PCA when limited to common variables and water chemistry, and the variables correlated to pH-sensitivity**

| | Northern subcatchments | Southern subcatchments |
|---|---|---|
| Variation explained by pc1 | 39.2% | 29.7% |
| Variation explained by pc2 | 20.2% | 21.9% |
| Variables with positive correlation to pH-sensitivity | Dominated by Scots pine<br>Coarse textured soils<br>Water surfaces | Till<br>TOC |
| Variables with negative correlation to pH-sensitivity | Norwegian spruce<br>Fine textures soils<br>Alkalinity<br>Calcium concentration<br>ANC | Alkalinity<br>ANC |

# Discussion

## Restrictions in water chemical and geographical data

For this study, it was difficult to find data sampled in small catchments. Therefore, it is a large area of the Bothnia Bay water district that is not covered by the study. It was most difficult to find data from streams draining small catchments in the counties of Jämtland and Västerbotten. The geographical gap in suitable data makes it impossible to evaluate the whole water district. The dataset was divided and analysed separately in a north and south part, but the division resulted in few catchments in each analysis, which reduce the reliability of the results. In order to increase the number of observations, catchments up to 10 $km^2$ were included in the study even though the catchment influence on water chemistry seems to level out in catchments exceeding 5 $km^2$ (Temnerud 2007). In the south there are 34 catchments and in the north there are 19 catchments. The limitations caused by the catchment size and the exclusion of limed watercourses potentially influence the result by a loss of some of the variation in the landscape.

It is important to use data sampled at the same flow intensity because flow intensities affects the water chemistry. In this study, the ambition was to include data only from samples taken during base flow. However, base flow is a relative term and it is possible that deviations in flow rates between catchments are a source of uncertainty.

The maps used to analyse the geographical data were generally at relatively large scales (Table 5) adding additional uncertainties to the results. A new national elevation model (DEM) is under development, but the data for the Bothnia Bay water district is not yet released. Therefore, the old DEM with higher uncertainties were used. The kNN data is not recommended for analyses at catchment scales used in this study (SLU, 2013), but in lack of other options this is the best data available on forest status.

## Geographical differences in pH-sensitivity

When all catchments were included in the PCA, there were only weak correlations between pH-sensitivity and landscape variables and no conclusions could be drawn. When the analyses were limited to the northern and southern catchments separately, the results indicate that there are geographical differences in the variables, influencing pH-sensitivity. Ågren and Löfgren (2012) found that pH-sensitivity seems to depend on different factors in different regions. Therefore, the discussion will focus on the separate results from the northern and southern parts, respectively. Additionally, the discussions are primarily based on the results from the PCA-analyses where the median for the geographical variables exceeds zero, which gave the best models. It should also be kept in mind that the water chemical data primarily represents base flow conditions.

ANC had a negative relation to pH-sensitivity in all analyses. This indicates that the non-sensitive streams mainly have a relatively high pH, most probably well above pH=6.2 (c.f. Tables 4 and 7). In both the northern and southern catchments, alkalinity was positively correlated to ANC. Alkalinity mainly reflects the bicarbonate system, which implies that bicarbonate rather than weak organic acids dominates ANC.

In the northern catchments, the stream water calcium concentrations positively correlated with ANC and alkalinity (Figure 12). This indicates that weathering is an important process, creating buffer capacity. However, the positive relation for the variables with altitude indicates that streams at high elevations were more well buffered than those found in the lowlands. This is generally not the case, indicating a non-representative sub-sample of streams. Hence, in the northern region pH-sensitive streams were more common at low altitude (Figure 11).

The results from the northern region also indicate that the catchments with pH-sensitive streams are characterized by a high share of water surfaces (lakes and streams), coarse quaternary deposits and Scots pine dominated forests (Figures 10 and 11). The weathering rates for coarse base poor soils are generally low and the supply of buffering capacity in the form of bicarbonate (alkalinity) is usually low. Additionally, a large share of water surfaces reduces the area of soils supplying the watercourse with buffering compounds. Scots pine prefers coarse quaternary deposits textures and will therefore be correlated to pH-sensitivity in the same way as coarse quaternary deposits. Streams with low pH-sensitivity tend to correlate to areas with high volumes of Norwegian spruce (Figure 11). At sites with more fine textured soils (clay-silt), the biomass (volume) tends to be higher compared to more coarse quaternary deposits (Figure 9). Norwegian spruce is more adapted to fine textured soils and will therefore also indicate more alkaline soil properties. In summary, it seems as if pH-sensitive streams in the northern region are primarily found on course sediments with Scots pine at low altitude.

The northern catchments in this study are located relatively close to the Västerbotten sites included in Ågren and Löfgren (2012). When comparing the results, the relations between pH-sensitivity and ANC are similar. In the Ågren and Löfgren (2012) study, however, the pH-sensitivity was positively related to TOC, while in this study the pH-sensitivity does not have a clear relation to TOC (Figure 12).

In the southern catchments, the relation between calcium concentration and alkalinity was less pronounced and calcium was negatively related to altitude (Figure 16). This shows that pH-sensitivity, ANC and alkalinity is only weakly related to altitude and that you can find pH-sensitive streams at most elevations and calcium concentrations in the southern region, but generally in streams with low alkalinity and ANC. The relations between ANC and TOC also tend to differ between the geographical areas. In the southern catchments TOC and ANC seem to be negatively correlated (Figure 16) indicating that TOC in these areas performs as organic acids, titrating alkalinity (bicarbonate) and lowering pH. In the northern catchments, TOC is less related to ANC and therefore poorly related to pH-sensitivity (Figure 12).

Ågren and Löfgren (2012) performed similar analyses in Bergslagen, which is relatively close to the southern region in this study. They also found a positive correlation between till and pH-sensitivity. However, regarding other factors the results do not resemble. In the study by Ågren and Löfgren (2012), TOC was acting as a base, while in this study TOC seems to be an acid, positively correlated to the pH-sensitivity. The most probable explanation for this is that the ANC and pH is much higher in this study (Table 9); perhaps as a consequence of base flow conditions.

The southern subcatchments are distributed over a larger area compared to the northern subcatchments (see Figure 1). This could potentially be a reason why there were fewer variables that could be related to pH-sensitivity and that the principal components are explaining a smaller part of the variation in the dataset over the south subcatchments.

Both this and the Ågren and Löfgren (2012) studies show that there are geographical differences regarding factors influencing the pH-sensitivity. This may be an important reason why the results from the two studies are slightly different even thought the areas studied are located relatively close to each other. Langan and Wilson (1992) and Ye et al. (2002) defined weathering rate as an important factor influencing the risk of acidification of streams. The results of this study also show an important relationship between weathering related chemical constituents and pH-sensitivity, but also acknowledge the importance of organic acids.

## Conclusions

This study indicates, that different landscape elements determine the pH-sensitivity of streams in northern respective southern parts of the Bothnia Bay water district. In the north, pH-sensitivity seems to be positively correlated to areas with Scots pine on coarse textured soils and water surfaces, while areas with fine textured soils and high volumes of Norwegian spruce where associated with low pH-sensitivity. In the south, till soils were related to high pH-sensitivity, while the influence of other landscape elements were poor. Weathering, influencing alkalinity and ANC, seems to be an important buffering factor in both regions, while TOC has an important role by contributing with acidity in the south catchments.

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