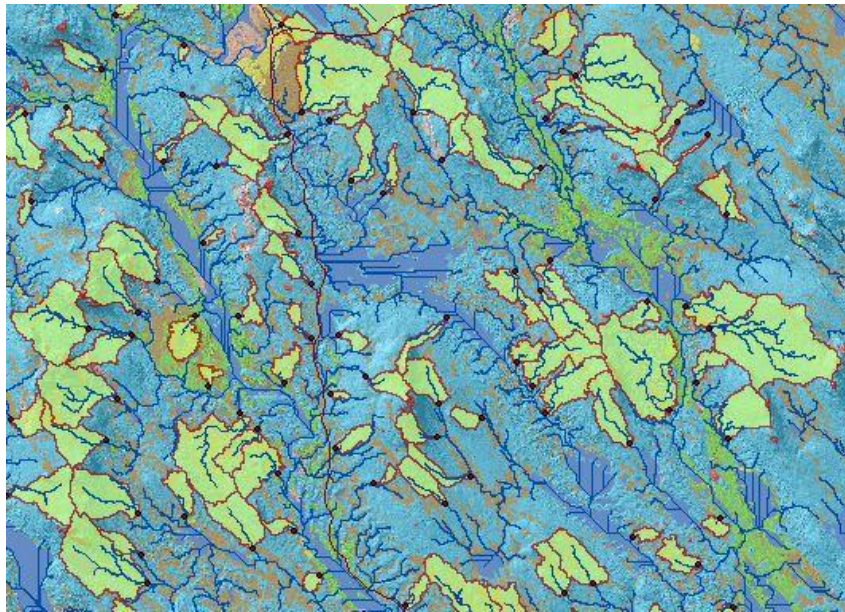# Geochemistry of stream plants and its statistical relations to soil- and bedrock geology, slope directions and till geochemistry

A GIS-analysis of small catchments in northern Sweden

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Master degree thesis, 30 credits in Master in Geographical Information Sciences
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Abstract

Subaquatic mosses and stream plants have been recognized as suitable sample media for detection of geochemical variations in their surrounding environments. These plants were originally used in search for mineral deposits but later on also for detection of environmental pollution. In this study it is investigated if statistically significant correlations could be detected between element content in subaquatic stream plant roots and some spatial parameters related to their catchments, which not necessarily contain mineral deposits or are polluted. Many small accurately outlined catchments and geological data therein from SGU were compared for a 2500 km^2 large area in the inland of Västerbotten, northern Sweden.

Research questions:
(1) Is there a statistical difference in geochemistry between subaquatic stream plant samples from catchments with different types of bedrock?
(2) Is there a statistical difference in geochemistry between subaquatic stream plant samples from catchments with different types of quaternary deposits?
(3) Is there a statistical difference in geochemistry between subaquatic stream plant samples from catchments with different dominating down slope directions, north or south?
(4) Is there a statistical correlation between the geochemistry of sub aquatic stream plants and the geochemistry of the till soils in their catchments?

The main results:
(1) For most elements there were no significant correlations between geochemistry, in plant samples and bedrock types. However, some trace elements (Cu, Ni, Rb and Zn) correlated positively with meta-sediments (negatively with granites) and some other (As, Mo, S, U, V, W, Y and Zr) correlated positively with granitic rocks (negatively with meta-sediments).
(2) For 6 of 27 elements (Al, Cu, Rb, Sr, U and Y) there were significant decreases in plant samples when percentage of peat cover increased in the catchments. Decrease of detrital particles and trapping of elements in the peat could be possible explanations. The areas of the other cover types (bare rocks and sediments) were too small to be interpreted.
(3) No differences in element contents of stream plants were detected related to percentage of down slope directions in the catchments.
(4) For 10 of 23 elements (Mn, Ba, Cu, Ni, Rb, Sr, U, Y, Zn and Zr) there were significant positive correlations between geochemistry, in stream plants and till soils in their catchments.

Generally, strong correlations between geochemistry of subaquatic stream plant samples and investigated landscape parameters are not found in this study.

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Contents

1 Introduction

The pioneering work in the field of biogeochemistry was done during the decades of 1930 up to 2000 by important researchers as: A. Kovalevsky (USSR), H. Warren (Canada) and R. Brook (New Zealand). Their work established valuable knowledge of the variation of element content in different plants depending on mineralogical variations in bedrocks and soils, from climate zones all over the world (Dunn, 2007a). In Sweden, N. Brundin investigated relationships between plants and mineralized areas (accumulations of economic important metals or minerals) and he also patented a method for such investigations (Brundin, 1939).

From investigations in Sweden during the 1970's and the 1980's it was suggested that subaquatic mosses and stream plant roots were the most suitable sample media for detection of geochemical variations in their surrounding environments, e.g. bedrocks and soils (Lax & Selinus, 2005). These mosses and roots were regarded as barrier free, i.e. they adsorb elements proportionally to the content in the surrounding media, which aerial parts of plants generally did not do. These conclusions were made after tests of plants and several other media types, e.g. inorganic stream sediments, stream peat and stream water (Brundin & Nairis, 1972 and Brundin et al. 1987).

The investigations made by Brundin and others laid the basis for the regional geochemical mapping programme of two sample media (aquatic stream plants and C-horizon till) started by the Geological Survey of Sweden (SGU) in the early 1980's. Up to date large parts of Sweden have been covered by the programme. The intention with the programme was to map and distinguish between natural and anthropogenic geochemical signatures in the landscape and to provide background data for mineral exploration programmes (Lax & Selinus, 2005).

In recent years The Swedish Mapping, Cadastral and Land Registration Authority (Lantmäteriet) has performed a laser scanning of the country. The intention was to construct a new high resolution digital elevation model (DEM) to be used in consequence analysis of climate change, e.g. flood mapping. With the new high resolution DEM and a GIS program, it is possible to evaluate properties and boundaries of catchments in a much more accurate way than before.

The overall aim with this study is to investigate if there are statistically significant connections/correlations between the geochemistry of subaquatic stream plants and some spatially differing landscape- and geological parameters over a quite large area. The idea is to accurately outline small catchment areas, as many as possible, based on the new high resolution DEM. The calculation of the catchment boundaries (with GIS software) is based on the locations of the subaquatic stream plants from the biogeochemical mapping program (SGU) in the area. The spatial parameters inside the catchments will then be evaluated in relation to the stream plants with different statistical tools. The purpose is to study normal landscapes not dominated by mineralized areas, although such could exist in some parts.

Four research questions (RQ's) were formulated and investigated:

RQ1. Is there a statistical difference in geochemistry between subaquatic stream plant samples from catchments with different types of bedrock?

Normally elements like Ca, Fe, Mg, Cr and V are more abundant in mafic rock minerals than in felsic rock minerals. Felsic rock minerals normally have higher content of e.g. Ba, Cl, Cu Mo, Pb, Rb, Zn and Zr than mafic minerals (Lax, 2005 & Anderson et al., 2014). Thus, there is potentially a difference in the geochemistry of plant samples located at stream outlets of catchments with different dominating bedrocks.

RQ2. Is there a statistical difference in geochemistry between subaquatic stream plant samples from catchments with different types of quaternary deposits? If there is, how does the element content vary?

The water drained from a catchment reflects the different types of quaternary deposits in the area, which can be of all possible kinds of sediment- and till types plus peat. Studies have shown that catchments with different amounts of peat/wetland areas differ a lot regarding water chemistry (Björkvald et al., 2008 and references there in). Plant samples from catchments with large areas of peat may e.g. have higher contents of Fe and Mn from organic and oxy/hydroxide complexes, plus elevated amounts of associated trace elements (Ingri & Widerlund, 1994). Also, much less amounts of detrital particles (reflected in lower Al and Ti content) are found in waters from catchments with lots of peat/wetland compared to more pure forest catchments (Björkvald et al., 2008). Lower S content could also be expected from mire/peat catchments due to more reduced soil water conditions with precipitation of sulfides (Ingri et al., 1997). All these differing environmental factors may potentially cause differences in the geochemistry of stream plants.

RQ3. Is there a statistical difference in geochemistry between subaquatic stream plant samples in streams from catchments with different dominating down slope directions?

Soil profiles from different parts of a landscape look very different. For example podzol profiles from down slopes pointing to the south are dryer and usually have more distinct horizons than profiles from down slopes pointing northward. The ground water level is often located very near the surface in north sloping profiles (field experience by the author). On top there usually is a much thicker humus or peat layer compared to the better drained profiles from down slopes on southern hillsides (Siebert et al. 2007).

Less solar radiation energy is absorbed on north pointing down slopes, resulting in cooler soils with less biologic activity, lower weathering rates and peat formation on some surfaces. Lower evapotranspiration will raise groundwater level and the formation of normal Fe-podzols are limited (Lundström et al., 2000). The release and adsorption of elements in the B-horizon may be different from dryer podzol types (Geisler et al., 2000). Thus, there is potentially a statistical difference in the geochemistry between plant samples from catchments dominated by south- or north pointing down slopes.

RQ4. Is there a statistical correlation between the geochemistry of sub aquatic plant samples and the geochemistry of till soils in an area? If there is, is it stronger if the till samples represent exactly the same catchment area as the plant samples compared to if they represent a circular area around the plant samples, near in space but not necessarily covering the catchment area?

Elevated content of trace elements in different types of vegetation in an area have from the beginning of the 20th century been used as indicators of underlying mineral deposits (Dune, 2007a). Brundin et al. (1987) found that plant roots and aquatic mosses gave geochemical patterns that reflect bedrock variations and were closely related to mineralizations. The approach in this study is more inclined to investigate if there is any detectable correlation between elements in sub aquatic stream plants and the till geochemistry, in regional areas that are not necessary mineralized.

The location of a plant sample in a stream defines a catchment area, where the runoff water flows through the sample point. Therefor there might be positive statistical correlation between the geochemistry of plant samples and the average till geochemistry in their catchments, calculated from interpolation of the surrounding till samples in the areas. It is possible to define other areas centered at the plant sample location, e.g. circles and investigate the correlation between plant- and till geochemistry for those areas. Theoretically the correlation with the catchments should be highest since they are the correct area that the plant samples adsorb elements from (compared to the circles).

2 Background

There is a huge amount of more or less complicated biological- and chemical processes involved in the part of the hydrological cycle which starts with precipitation and ends up as runoff discharged to the sea. The landscape type which the water runs through, on its way to the streams, influence the stream water properties, and thus potentially also the element uptake into the stream plants. In the following subsections a short review is given of: history of biogeochemistry, the background of the biogeochemical mapping programme at SGU, how elements are transported in river waters, how the concentration of some elements are related to landscape properties and the influence of water pH on adsorption of elements in the plants. In the review there is some focus on Al, Fe, and Mn because these elements are reported as carrier particles of other head- and trace elements in river water and thus adsorbed on the stream plants together with truly dissolved elements.

2.1 History of biogeochemistry

Not much research in the field of plant geochemistry associated with environmental issues or exploration was published before the end of the 19th century (Dune, 2007a). In the 1920's, work in biogeochemical exploration for mineral deposits began in the USSR, where it i.e. was discovered that elevated amounts of V, Ra and U in plant ash occur in the vicinity of an ore zone compared to areas outside the zone (Kovalevsky, 1987). During the 1930's the first biogeochemical methodology was published, it was described how a deposit of arsenopyrite in Siberia could be traced by the iron content in the vegetation above the ore body (Tkalish, 1938). In Sweden Nils Brundin discovered relationships between biogeochemical data and vanadium- and tungsten deposits and he also filed a patent on the use of vegetation data in mineral exploration (Brundin, 1939).

In the 1940's work was started in Canada by Harry Warren and he produced, among other data, analysis of elements in trees above sites that thereafter have been developed as mines (e.g. the Endako Mo mine and the Sullivan Pb-Zn mine, both in British Columbia). Warren also raised the credibility of biogeochemical methods for mineral prospecting purpose which at the time was quite low (Dunn, 2007a). In the 1950's and the 1960's there were pressure on finding uranium ores in the US, and lots of effort was devoted by USGS to establish biogeochemical signatures for U deposits (Dunn, 2007a).

In1960 Robert Brooks, New Zealand, initiated his over 40 years of fundamental work in biogeochemistry and geobotany from which important knowledge was gathered e.g. about flora connected to ultra-mafic rock associations around the world. Brooks also published several important books and reviews of biogeochemical methods for exploration in the1980's up to the late1990's (Dunn, 2007a). A shift of interest from mineral exploration towards more general reconnaissance studies for environmental and medical purposes was noted during these years (e.g. Selinus, 1988).

During the late 1990's and the first decade of the 21th century development of new methods for analysis (i.e. ICP-MS) enable more precis determinations of trace

elements with very low concentrations in plant tissues. Also partial leaching of tissues provides further insights into, i.e. labile phases of elements in plants (Dunn, 2007b).

2.2 The biogeochemical mapping programme at SGU

Before the 1980's inorganic stream sediments were sampled with a mineral prospecting purpose at SGU. Not all parts of the streams, especially in northern Sweden, contain enough inorganic sediment to sample. Other methods were tested, by Brundin & Nairis (1972), like water sampling and sampling of dead organic stream peat. Water was not very suitable for large sampling programmes, because of large volumes/weights to transport to the lab and risk of contamination due to very low element content in the media (ppb levels). Stream peat was better with high adsorption factors for trace elements to organic matter and Fe- and Mn-oxide/hydroxides. However the levels of element content in stream peat differed a lot during seasons, with high increase during storms and snow melt due to increased content of eroded material from surrounding top soil layers.

Then different living plants, with their roots in the streambank peat or water channel (sedge and mosses), where investigated by Brundin et al. (1987), and they found a strong linear relation between elements in stream peat and plant samples. Also the seasonal variations were much less in the root samples than in the stream peat. The authors concluded that aquatic mosses and stream plants would be the most suitable multi element sample type, which reflect the geochemistry in their growing environments and in the surrounding bedrocks and soils.

With the above experiences as a base, SGU started the large biogeochemical sampling programme of subaquatic plants in the early 1980's. The purpose was to detect natural as well as anthropogenic amount of metals in the environment (Lax & Selinus, 2005). The database now contains above 35 000 stream plant samples covering large parts of Sweden.

2.3 Element transport in boreal rivers

Originally not much attention was paid to the processes of element transport in the river waters feeding the aquatic plants, an important link between the biogeochemistry and the terrestrial environment. During the years lots of research has been devoted solely to the transportation of elements in boreal river systems. Result from that research is important for the understanding of what kind of substances that is adsorbed on the plants, with implications for the interpretation.

Researchers of sediment transport in boreal rivers often divide the transported particles into a suspended and dissolved mode, with the divide at 0.2 or 0.4 um (i.e. 1/10 of the clay/silt border). Further, the suspended mode is divided into a detrital (eroded mineral particles) and a non-detrital (authigenic precipitates) phase. The elements have different speciation among the modes and phases depending on several environmental factors (e.g. pH, snowmelt season, storm events, soil types, peat areas etc.).

Studies of boreal river waters show that most of the elements are transported in dissolved mode, indicating chemical weathering as the dominating source (Öhlander et al., 2014; Land and Öhlander, 2000). However for some elements (Al, Fe, Mn, P, Si and Ti) the suspended fraction could be quite large, above 30 % of total element transport. For Al, Si and Ti, this suspended fraction consists mostly of detrital particles, but for Fe, Mn and P, the non-detrital mode dominates, sometimes above 90%, especially at low flow regimes (summer, autumn and winter).

According to several studies, e.g. Ponter et al. (1992) and Ingri et al. (1994) none-detrital Fe- and Mn-oxy/hydroxides in combination with organic matter in suspension, act as very active adsorbents of dissolved trace elements in river systems. Detrital particles on the contrary do not adsorb elements to a great extent because of their (compared to none detrital particles) much smaller specific surface. The element / Al (or Ti) ratio is often used as a tool for evaluating the amount of detrital particles in the suspended load.

2.4 Element content in river waters and catchment properties.

There are studies that try to put the element contents in rivers in relation to catchment properties. Studies by e.g. Björkvald et al. (2008) and Cory et al. (2009) concluded that wetland and peat areas are of great importance for transport of Fe and dissolved organic carbon (DOC) in combination with associated trace elements. The transport of DOC and Fe was much higher from wetland dominated catchments compared to forest dominated ones, but they found no correlation for Mn with wetlands. They suggested that Mn was mostly bounded into mineral particles whereas most of Fe occurs in none detrital form. They also found much less Al and total suspended solids (detrital particles) in water from wetlands than from forest catchments. Andersson and Nyberg (2009) detected positive correlations, between wetland area in catchments and topographical wetness index (TWI) and between wetland area and the stream water parameters DOC and Fe. On the contrary, both Fe and DOC showed negative correlations with higher slope index (steeper slope).

Soil properties influence the geochemistry of soil water drained to the streams and several researchers have investigated the topographical factors influencing soil forming processes. Siebert et al. (2007) found that the thickness of organic layers in podzols correlated positively with TWI and that the leached E-horizon became thicker with larger upslope areas. They also reported lower pH in soils lying in north pointing down slopes compared to south pointing ones. Several kinds of organic acids from the humus layer play an important role in dissolving and extracting Al and Fe from the eluvial E-horizon, which in well drained profiles are precipitated into the deeper lying B-horizon (Geisler et al., 2000). However the illuvial horizon in podzols where the groundwater is high does not enrich Fe probably because Fe is in reduced form (Lundström et al., 2000).

2.5 Element uptake into sub aquatic plants and pH in the river water

There are some studies that directly relate the element content in river water to the uptake in aquatic plants, especially willow moss (*Fontinalis antipyretica*). In a study by Öhlander et al. (2014) of differences in river chemistry between landscapes with acid surface soils (drained postglacial clays with sulphides) and ordinary till soils with forest, in northern Sweden, much higher contents of most elements was observed in stream water from the acid soils. The oxidation of the sulphides lowered the pH which enhanced metal leaching. The increased metal content released by sulphide oxidation was only partly reflected in the willow moss due to low pH in the river water, according to the authors.

In another study from Spain, transplants of *Fontinalis antipyretica* were set out in a river draining a sulphide mine at different distances from the source. The metal content in the water was well reflected in the plant samples with lower values at increased distance from the mine. However, the highest metal content in the river near the mine was not reflected in the plant samples. It was concluded that the plant samples do not adsorb elements if the pH is too low due to strong competition of binding sites from the hydrogen ions (Fernández et al., 2006).

3 Materials & Methods

3.1 Study area

The criteria used when choosing study area was:
1. It must be covered by both plant- and till samples.
2. It should cover a landscape area of about 50*50 kilometres. An area of this size had about 350 - 400 samples from each sample category which was assessed enough for achieving reliable statistics, even after removal of some samples.
3. It should be located above the highest shoreline so influence from postglacial sediments with high metal leaching from acid sulphate soils was avoided (Lax, 2009).
4. It should be located in a sparsely populated area to decrease the risk of anthropogenic pollution in the stream waters.

The chosen area was located in the inland of Västerbotten, between Sorsele and Stor-Uman, representing a cold climate with long winters and relatively low weathering rates. The river Vindelälven flew through the area and two larger lakes, Storjuktan and Storuman occupied areas in the west and south west. Characteristic for the area was also a hilly landscape covered by coniferous forests with lots of smaller lakes and bogs. It was situated well above the highest shore line, approximately between 280 – 790 m.a.sl. The bedrock consisted mainly of old (1700 - 2000 my) felsic intrusive rocks and meta-sediments, with minor spots of mafic intrusive rocks. In the west there were some minor areas with sedimentary rocks belonging to the Caledonian orogen with an age of about 500 my. Most of the bedrock was covered by quaternary deposits. Glacial till was the dominating soil type, but a few south east trending esker ridges also existed in the area. Mires and bogs occupied significant areas in the lower parts of the landscape. The area was well covered by both plant- and till geochemistry samples. See Figure 1 below for an overview of the area.

3.2 Data sources

Elevation data: The new laser scanned digital elevation model (DEM) with a resolution of 2 metres horizontally and a vertical accuracy of +- 0.2 metres, from the Swedish mapping authority, was used for delineation of catchment borders (Lantmäteriet, 2015). The higher resolution enabled a more accurate outlining and restriction of catchment areas than the old DEM with only 50 metres horizontal resolution.

Plant geochemistry: This point source dataset (obtained from SGU) consisted of metal content in aquatic mosses and roots of aquatic higher plants, sampled inside first or second order streams in Sweden. The sampled plants/roots should have been in contact with the flowing water in the streams. After sampling the plants were thoroughly washed in the stream waters to minimise the amount of coating Fe/Mn-oxy/hydroxides, mineral- and organic particles. Most samples consisted of roots of sedge (*Carex species*) and some meadowsweet (*Filipendula ulmaria*) and whole plants of willow moss (*Fontinalis antipyretica*). These plant types respond closely to chemical variations in their environment, related to different bedrock and soil types and also to anthropogenic pollution. The exchange of elements between water and plant is a slow process, thus time variations of metals in a stream (from storm events

etc.) is unimportant in the short range. Therefore these plants provide a time integrated information about the metal contents in a stream. The samples have been analysed for more than 30 elements, by X-ray fluorescense (XRF) technique, after drying and combustion (Lax & Selinus, 2005).

The plant samples in the study area were collected during the summers of 1997 and 1998, meaning that the sampling was done before the time of usable GPS systems. Therefor it sometimes was difficult to locate (on a map) exactly were in a stream course a sample was taken. The sampler marked the likely sample location with a pen on a terrain map in scale 1:50 000 or 1:100 000, and the error in marked position could thereby be up to 50 metres. Sampling density was 1 per 7 square kilometres.

It appeared that sedge roots were the dominant sample type in the investigation area (there were relatively few samples of the other species, less than 10 %). Initial investigations of the chemistry data also revealed, in some cases quite large, differences in element absorption between species. To avoid errors in analysis introduced by species dependent element uptake it was decided to only use the sedge samples in the analysis.
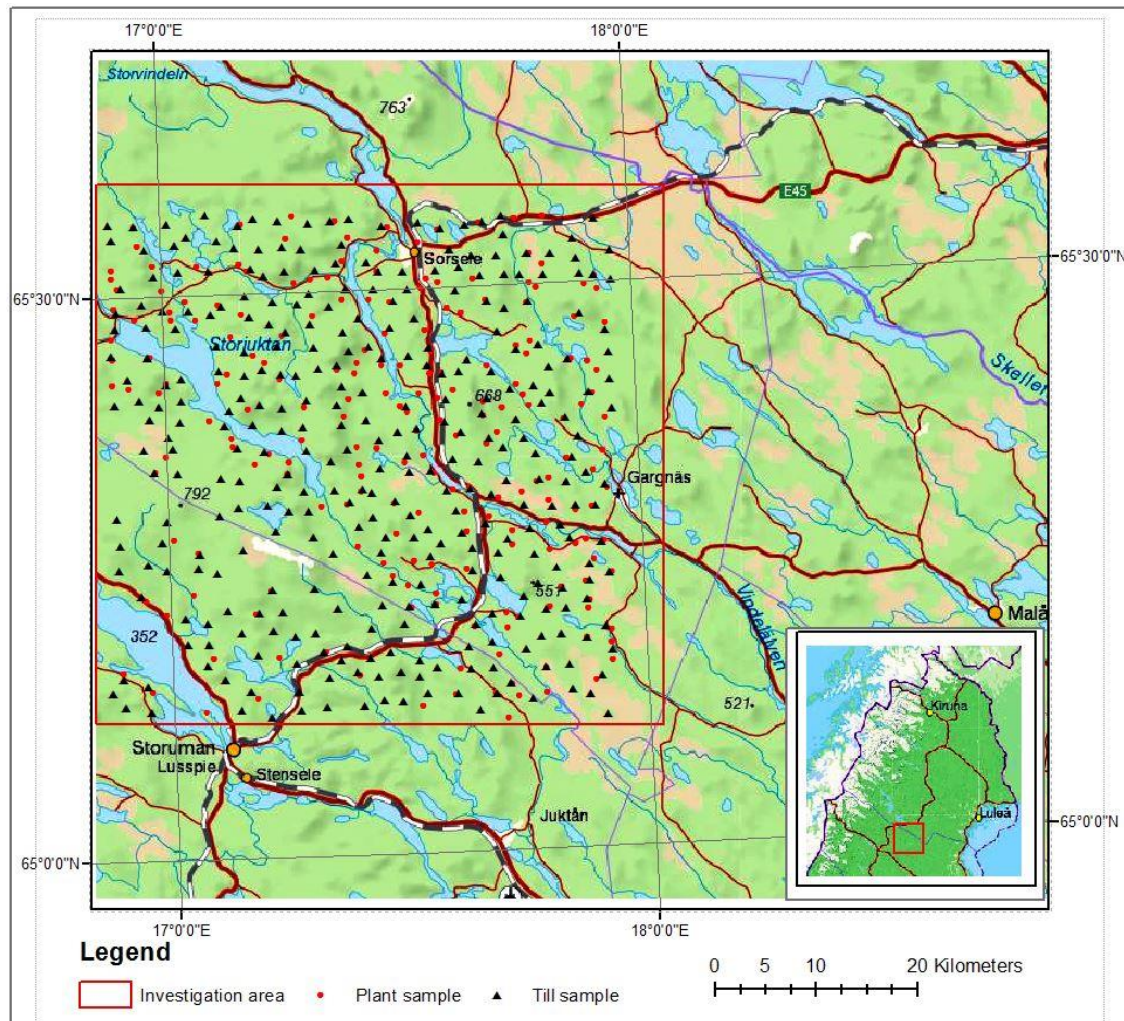
Figure 1: The investigation area with locations of plant- and till samples (background map © Lantmäteriet, Dnr: I2014/00579).

Till geochemistry: This point source dataset (compiled by SGU) was extracted from a database of glacial till samples, collected from all over Sweden. The 400 samples from the investigation area have been collected during the field seasons of 1997 and 1998. The error in position and the sample density was the same as for the plant data, i.e. 50 metres and about 1 sample per 7 square kilometres. The samples came from hand dug pits, usually 0.7–1 metres in depth, which in most Sweden is well into the C-horizon of a soil profile. The dried (< 0.063 mm) fine fraction has been analysed for more than 30 elements. The total content of elements in the till sample has been analysed by X-ray fluorescense (XRF) technique on pellets from the fine fraction. For the acid-leached element content in the samples, several techniques have been used through the years. Up to 1995 inductively coupled plasma emission spectroscopy (ICP-AES) was used with aqua regia leaching. Due to low accuracy for some elements, inductively coupled plasma mass spectrometry (ICP-MS) was introduced from 1995. This technique has been used on combinations of aqua regia and 7M nitric acid leached samples.

A rigorous quality control has been applied for both plant- and till geochemistry data. The measurement uncertainty is for most elements, in both data sets, between 5–10 percent, (Lax & Selinus, 2005).

Bedrock- and soil maps: Most parts of the bedrock- and soil covers in Sweden have been mapped by SGU, from which the raster and vector maps used were obtained. Mapping scale varied from 1:50 000 to 1:200 000. Soil maps have been constructed from images taken by satellites and aircrafts, accompanied by field controls. Bedrock maps have been constructed from field observations combined by interpretation of geophysical measurements, especially where the bedrock was covered by soil layers.

3.3 Pre-processing of data

3.3.1 Construction of catchment areas from plant sample locations

The following section describes in detail how the DEM-raster was manipulated for calculation of catchment areas from the plant sample locations. For readers who are familiar with the GIS operations involved, a condensed work flow scheme is presented at the end of this section.

Stream networks: The original DEM raster surface was first made continuous, which means that all depressions were filled up to their lowest pour point. Comparing the original and filled DEM with each other showed that most depressions were less than 25 centimetres deep and that the total area with deeper depressions was small and will not affect further analysis. The filling step was necessary to get a continuous stream network otherwise a stream may end up some place in the terrain model within a single cell lying lower than the surroundings. From the continuous raster layer, stream networks of different scales were calculated, i.e. how many cells were drained to a cell before it was recognized as a cell within a stream (10 000 raster cells was set as a lower limit for a stream course, i.e. 0.04 km^2 of drainage area).

Road culverts: When scrutinizing the calculated stream networks it appeared that streams generally did not cross the roads where they should, i.e. through a road

culvert. Instead the stream lines usually followed the road sides to a lower lying place where an overflow occurred. The original DEM is built from laser scanning, where emitted laser pulses are returned and measured from the top of a surface, e.g. a road. By that method water culverts located under the roads are not detected. Lantmäteriet have adjusted the measured levels over the largest culverts/streams to conform to the bottom levels of passing streams on the DEM. However, there are several hundred or even thousands of small road culverts in a landscape with the size of the project area and these are not accounted for in the original DEM. Stream networks calculated from the unadjusted DEM deviated a lot from reality, which resulted in incorrect outlining of drainage area boundaries. This problem had to be handled.

First a vector layer from Lantmäteriet, containing the roads in the area was superimposed on the DEM grid. Unfortunately the road layer was not very exact regarding positions, so the roads had to be manually adjusted to coincide with the locations of the roads on the DEM. Thereafter buffer zones with a radius of about 7-10 metres were constructed along the road lines. This was necessary because the road vector lines (thin in a GIS) located in the middle of the raster roads (on the DEM), were not reached by the vector lines (also thin) of the stream networks, since the roads on the DEM were too broad (several raster cells of 2 m each). Contact between the two network types was necessary for GIS-calculation of intersection points, and the extension of the thin road lines with buffer areas enabled that.

Circular buffers were then constructed from the intersection points. The circles got a quite large radius (20 m) so they reached across all kinds of roads, both narrow and wide. The (vector) circles were then transformed to raster format and the circle cells got a negative depth value (-5 m). The circle raster was then added to the original DEM grid. The result was a new DEM raster with circular 40 metres wide and 5 metres deep pits at the crossings of roads with streams. The created circular depressions in the DEM were then filled up to the level for continuous contact between the stream channels of both sides of the road. New stream networks were then constructed.

Evaluation of the corrected stream networks: The new stream networks were first visually compared to the old ones. In areas with roads stretched perpendicular to hill slopes the differences were largest, i.e. more road crossing streamlines (RCS) in the new network (see Figure 2). In more flat and low lying areas the differences were smaller. A visual evaluation of 50 road sections chosen by a stratified random sampling technique was done. The investigation area (50*50 km) was divided into 25 squares of 100 square kilometres each. In every such square two road sections 1 – 5 kilometres in length were randomly chosen. It turned out that there was about one RCS per 600 metres in the original raster whereas one RCS in every 300 metres in the new. From many years of field experience in such landscapes the author could conclude that this was a better model of the real situation.

Red line: Road   Blue line: Stream
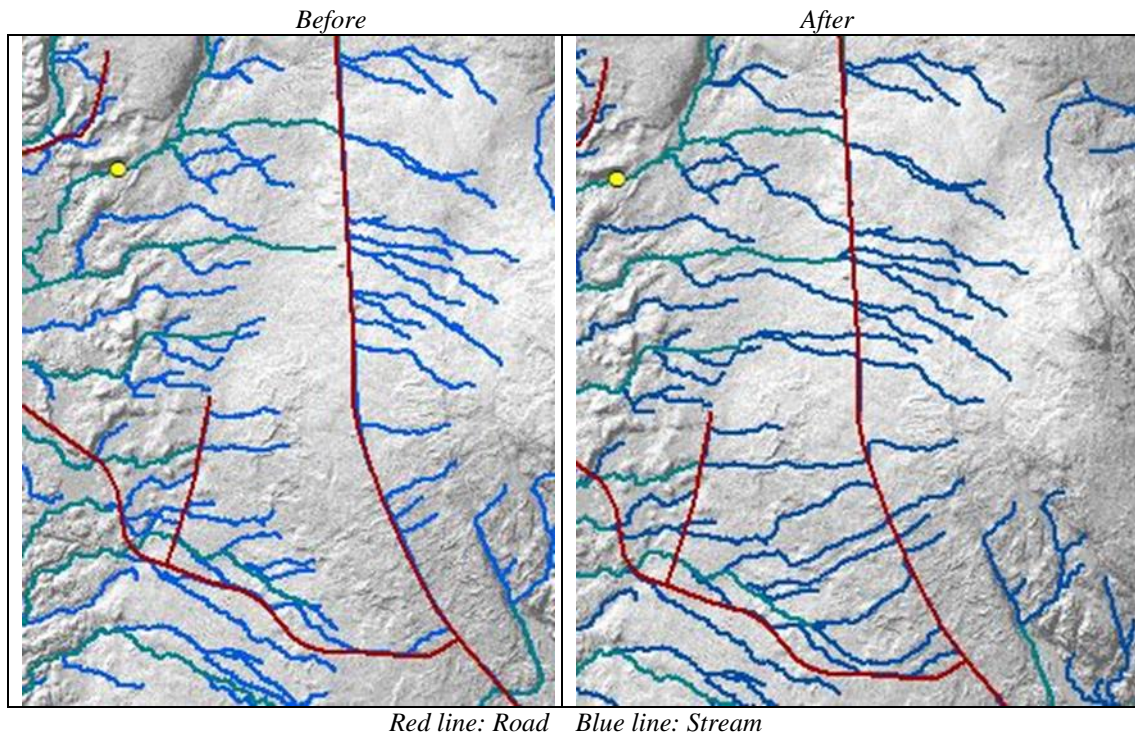
Figure 2: Example of stream networks before and after construction of artificial culverts (background data © Lantmäteriet, Dnr: I2014/00579).

Coupling of plant sample locations to their related stream courses: Before calculation of drainage areas for the plant sample sites could be done, the samples had to be connected to the corresponding stream course on the DEM. The coordinate points for the samples had an error in position of about 50 metres (points are digitalized from pencil crosses on field maps in scale 1:100 000, there were no available GPS technic at sampling time), so they were very seldom located exactly where the stream courses lay on the DEM. The calculation of drainage areas and borders required that every sample must be located exactly on a stream course raster cell. The plant sample locations were moved with a tool in the GIS program.

The tool searches for the cell with the highest flow-accumulation grid value, lying at a specified distance from the plant sample location, and marked it as a pour point. The tool was run three times with the largest search distances of: 25, 50 and 75 metres. If no stream course were reached with the distance set to 25 m the tool was run with 50 m distance and at last (for remaining points) with the distance set to 75 m. After that most location points were snapped to a stream course. Points lying more than 75 metres away from a stream were moved manually to the most likely stream course, deduced from the DEM in combination with a terrain map and some knowledge of sampling. About 85 % of the samples were moved less than 50 metres and 8 % were moved 50 - 75 metres. The rest 7 % (23 samples) were moved manually, a distance between 75 - 240 metres (12 samples more than 100 m). In a few cases, a sample point lay in between two stream courses and it was not possible to deduce to which stream it belonged to, the sample point was moved down to the stream divide so both streams lay above the sample point. In the few cases this method was used it did not change the drainage area to large amount.

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All snapped points were also manually checked afterwards to see that they corresponded as well as possible with the locations of the streams printed on the terrain map and with the streams on the DEM calculated by the GIS software. All in all, a number of 325 sample points were connected to stream courses in this way.

Construction of watersheds: A tool in the GIS-program was applied for the construction of drainage areas upstream of the plant samples. Afterwards all sample points lying far down in the stream networks, representing very large drainage areas with other plant samples higher up in the stream system, were removed. Also very small catchments inside other slightly larger catchments were removed. After that there were a number of 210 single catchments left, a reduction with 35 percent. This reduced dataset was used in the statistical analysis. The removed samples were regarded as not interesting to analyse, since they represented a mixture of the values from the samples higher up in the stream networks. See Figure 3 for some statistics and Figure 4 for the location of the plant samples and the catchment areas.

N	Valid	210
		Area (km^2)
Mean		2.18
Std. Error of Mean		0.15
Median		1.35
Std. Deviation		2.19
Skewness		2.26
Kurtosis		6.03
Minimum		0.10
Maximum		12.9
Percentiles	25	0.80
	50	1.35
	75	3.00
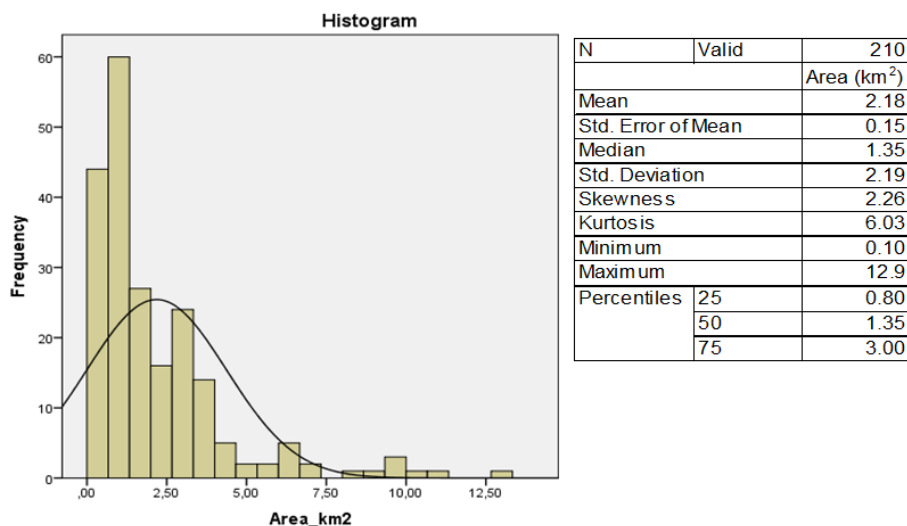
Figure 3: Histogram with statistics for the catchment areas (km^2).

Work flow for construction of new road culverts and watersheds:

o Add a vector layer with roads on top of the original DEM. Check/adjust the road lines so they coincide with the raster roads on the DEM.
o Add buffer zones along the vector roads wide enough to cover all kind of roads.
o Calculate intersection points between vector roads and vector streams.
o Construct circular buffers around the intersection points between roads and streams, large enough to reach across all kinds of roads.
o Convert the vector circles to raster and set a negative cell value (e.g. -5m).
o Add the raster with the circles to the original DEM raster.
o Make the new DEM raster continuous and calculate new stream networks.
o Define pour points, i.e. couple the plant sample sites to nearest stream course cell.
o Calculate the watersheds.
o Remove large watersheds representing large drainage areas with smaller watersheds inside their area.
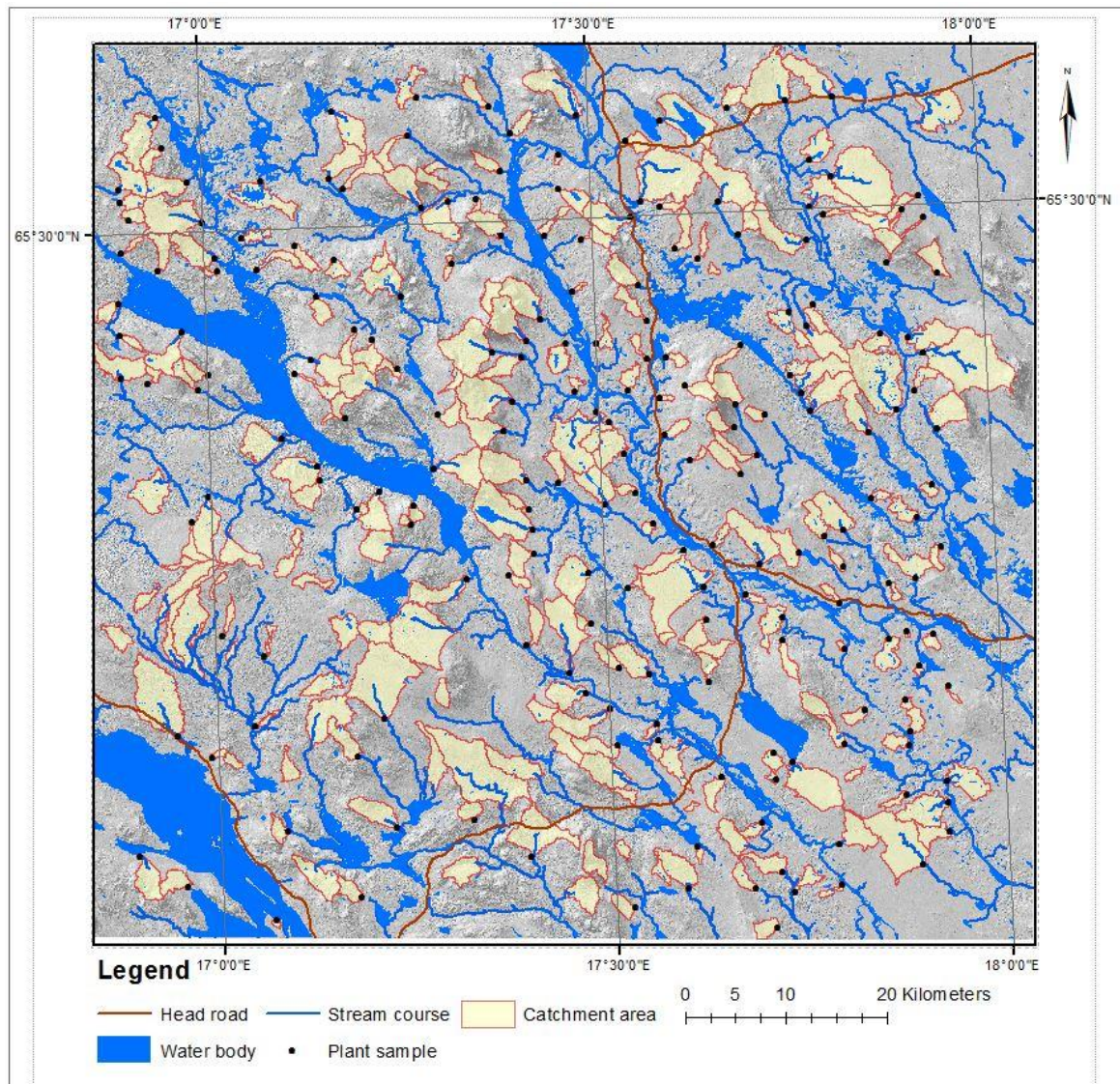
Figure 4: Locations of plant samples and their drainage areas (background map ©
Lantmäteriet, Dnr: I2014/00579).

3.3.2 Bedrock- and soil maps

The bedrock map and especially the soil map contained many different classes so
some simplifying was necessary before analysis. The soil types were aggregated into
five classes: outcropping bedrock, till, peat, coarse and fine sediments. The bedrock
types were aggregated into three classes: granitic-, mafic rocks and meta-sediments.
The simplified bedrock- and soil maps are shown in Figure 5 and Figure 6 below.
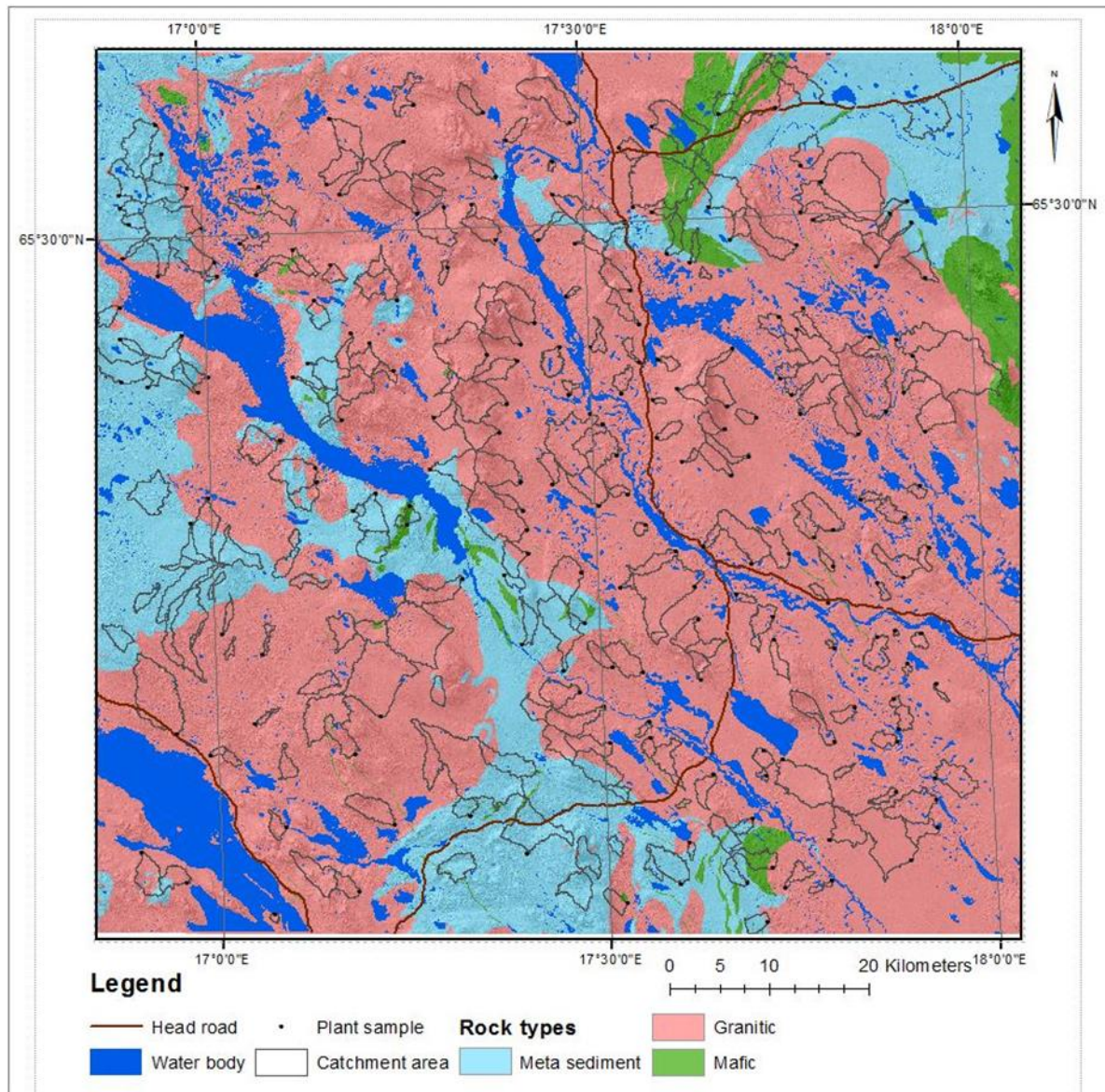
Figure 5: Simplified bedrock map with catchment areas for the plant samples (background data © SGU & © Lantmäteriet, Dnr: I2014/00579).

3.4 Methods for analysis

3.4.1 Overall statistics

This section describes how the original plant- and till datasets were analysed statistically, which led to the decision of using only non-parametric methods in further statistical analysis.

Summary statistics was calculated for all elements in the till- and plant datasets, and tests for normal distribution were performed with both the Shapiro-Wilks and the Kolmogorov-Smirnov methods, which both yielded equal results. Most of the elements in the two data sets had positive skewness, and as expected did not conform

to normal distribution in untransformed states (Riemann et al., 2000). When transformations were applied (logarithmic, square root) the situations were
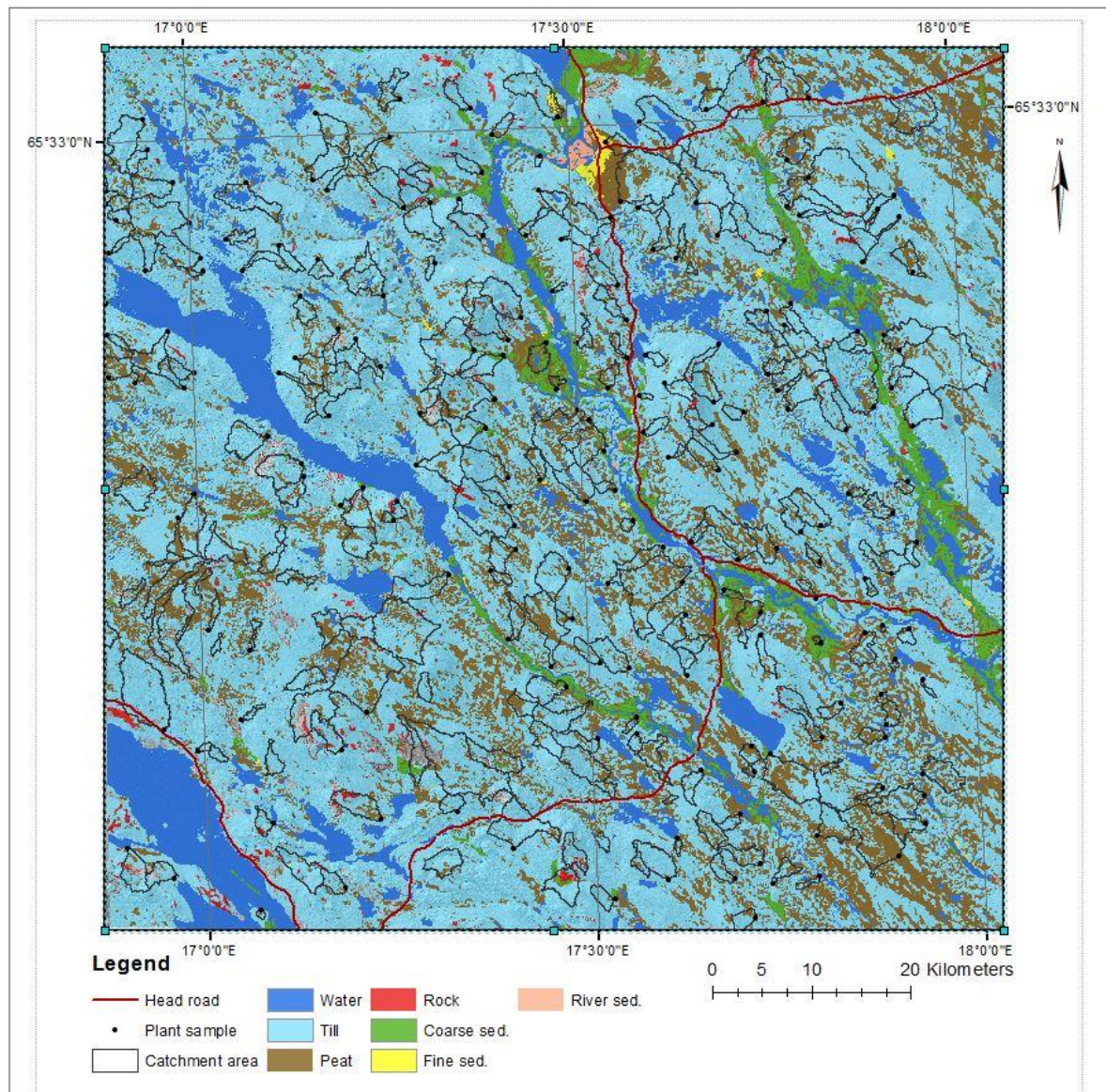
Figure 6: Simplified soil map including localisation of the plant samples and their drainage areas (background data © SGU & © Lantmäteriet, Dnr: I2014/00579).

somewhat improved, but no more than at best 13 out of 28 elements in each transformation achieved normal distribution. There were also lots of outliers in the datasets. According to Riemann et al. (2000) these circumstances excluded the use of parametric methods, multivariate techniques included, e.g. principal component analysis (PCA) and partial least square regression (PLSR). As a result only bivariate nonparametric methods, not sensitive to skewed distributions and robust to outliers, were used in further analysis. Used methods were:

- o **Spearman rank (r_s)** for correlation analysis. The method assesses how well the relationship between two ranked statistical variables can be described using a monotonic function (Daniel, 2000).

- o **Mann-Whitney-U** for two sample tests. A nonparametric test of the null hypothesis that two samples come from the same population against an alternative hypothesis (Hettmansperger and McKean, 1998).

Significant p-values that could appear by random processes in multiple comparisons were in this work treated with the false discovery rate method (FDR). A false discovery rate of 5% was used (q=0.05, i.e. 5% of the rejected null hypothesis or significant correlations in a test may be false). For details see Benjamini & Hochberg (1995).
All statistical calculations were done with the IBM-SPSS software.

3.4.2 RQ1 (Plant samples and bedrocks)

A tool in the GIS software was used for calculation of areas for the different bedrock classes inside the catchments. The element content, was then correlated (r_s) with percentage of bedrock types in the catchments.

3.4.3 RQ2 (Plant samples and soil cover)

This section describes the methods used for detecting differences in element content between plant samples from the outlets of the catchments related to different soil types with focus on peat areas.

A tool in the GIS software was used for calculation of the areas occupied by each soil type in the different catchments. Different types of statistical investigations were then performed on the dataset:

1: A correlation analysis (r_s) between percentage of soil type area in the catchments and element content in the plant samples. In this analysis 205 plant samples were included. Five samples were removed because their catchments reached outside the soil map cover in the western border.

2: A statistical test (type: two independent samples) was performed, to investigate if the element content in plant samples from till dominated catchments (with minor peat areas) represented a statistically different group (environment) compared to catchments with high amount of peat (with minor till areas). In this analysis not all samples were included (middle sections excluded) with the purpose to get clearly different groups regarding peat content. The null hypothesis (H_0) was: no difference between the groups and the alternative hypothesis (H_A) was: there is a difference.

The grouping needed to be somewhat asymmetric regarding percentage of soil cover, since catchments with dominating till cover were in excess compared to catchments with large peat areas. To get reasonably the same amount of samples in each group the areal divide between groups became:
- o Peat < 10% (i.e. Till > 90%), 37 samples
- o Peat > 40% (i.e. Till < 60%), 26 samples

3: Median value, interquartile range (quartil_75 – quartil_25) and relative variability (here calculated as: (quartil_75 - quartil_25) / median * 100) were evaluated for the elements in the plant samples from the different peat cover groups. The purpose was to see, if and how these parameters varied when the peat cover increased in the catchments.

3.4.4 RQ3 (Plant samples and down slope directions)

This section describes the methods used for detecting differences in element content between plant samples from the outlets of catchments with dominating down slopes pointing to the south compared to those with dominating north pointing down slopes.

For this question the down slope directions of the catchment cells had to be grouped. First, the slope directions (aspect values) were calculated for the DEM raster cells. The resulting raster values were then reclassified into a new raster with two classes, north and south. The divider between the classes was a line in east west direction. The number of cells pointing to the north and to the south in each catchment was then calculated. In Figure 7 below some catchment areas with classified down sloping cells are shown. Different types of statistical investigations were then performed on the dataset:
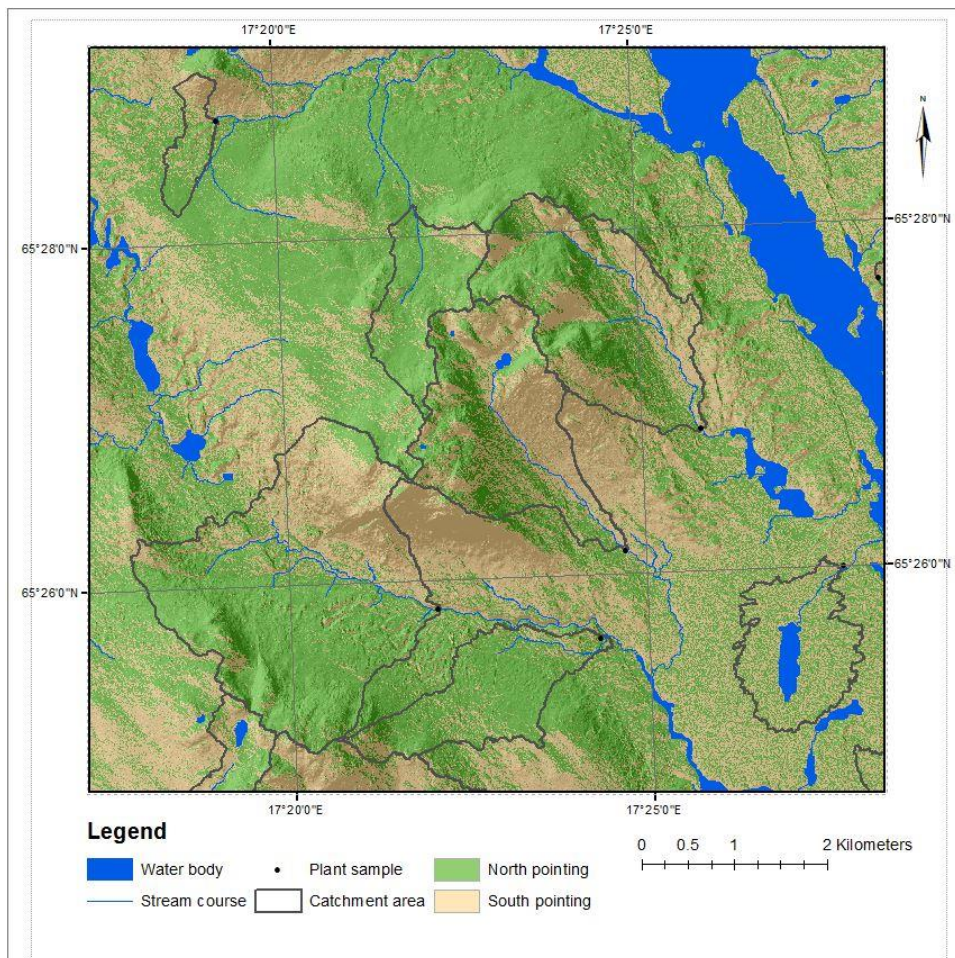
Figure 7: Classified down slope directions for cells in some catchments in the investigation area (background data © Lantmäteriet, Dnr: I2014/00579).

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1: A correlation analysis (r_s) was performed between percentage of north- and south pointing cells in the catchments and element content in the plant samples. In this analysis all the 210 samples were included.

2: A statistical test (two independent samples) was performed, to investigate if the element content in plant samples from catchments with high amount of north pointing cell slopes (minor south pointing) represented a statistically different group (environment) compared to catchments with high amount of south pointing cell slopes (minor north pointing). In this analysis not all samples were included (middle sections excluded) with the purpose to get clearly different groups regarding down slope directions. The null hypothesis (H_0) was: no difference between the groups and the alternative hypothesis (H_A) was: there is a difference.

In this case the grouping was symmetric, regarding percentage of down slope directions and the groups became:
- North $> 70\%$, (i.e. South $< 30\%$), 31 samples
- South $> 70\%$ (i.e. North $< 30\%$), 23 samples

3: Median value, interquartile range (quartil_75 – quartil_25) and relative variability (here calculated as: (quartil_75 - quartil_25) / median * 100) were evaluated for the elements in the plant samples from the different down slope direction groups. The purpose was to see, if and how these parameters varies among the groups.

4: A Correlation analysis (r_s) between percentage of cell slope directions (north and south) and percentage of soil cover (peat and till) was done. The intention was to investigate if there was more peat cover in catchments with large amount of north pointing down slopes (compared to those with more south pointing ones).

3.4.5 RQ4 (Plant samples and till geochemistry)

In this section it is first described how the two till datasets (total content and acid-leached) were evaluated before interpolation to element maps. Circle areas were then constructed around each plant sample location. The interpolated mean value of each till element inside the circle areas and the catchments respectively, were then correlated (r_s) against the corresponding element content in the plant samples.

1: The geochemistry of the till samples from the investigation area was evaluated. The till samples were collected quite closely in time (1997 and 1998), so the same laboratories and methods were used for the samples. This was good because no levelling of element values (caused by different analysis methods) was needed. The not leached till (total content) samples were all analysed by the Analytica lab in Täby with an XRF-technique, and the nitric acid leached samples were all analysed by SGU in Uppsala with an ICP-MS technique (SGU data documentation).
From the two till data sets, interpolated maps for each element were constructed with the inverse distance weighted method (IDW). First, about 50 samples were randomly removed from each data set to be used in accuracy determinations of some test interpolations, for some elements. The test interpolations were performed for weighting factors: 1, 1.5, 2 and 3, with 50 m cell size. It turned out that a weighting factor of one yielded the best results regarding deviation (mean error and standard

deviation) from the control samples. Then all elements (removed control samples included) were interpolated with a weighting factor of one.

2: Circular areas were drawn around each plant sample. The area of each circle was set equal to that of the related catchment. The location of circle areas and catchments placed on a background map of interpolated Cu-values (acid leached till) is visualized in Figure 8.

3: Statistics of the element values from the interpolated till geochemistry maps was calculated, inside the circle areas and the catchment areas. The mean values of the till elements inside each specific area were then coupled to the plant data table.

4: The relative variability of the elements in the different till analysis (total- and leached) was calculated and compared with the values for the plant samples in a diagram. The purpose was to see if the parameter differs among the sample types.

5: A correlation analysis (r_s) between the element content in the two till datasets and the plant samples were then performed for both the circle areas and the catchments.
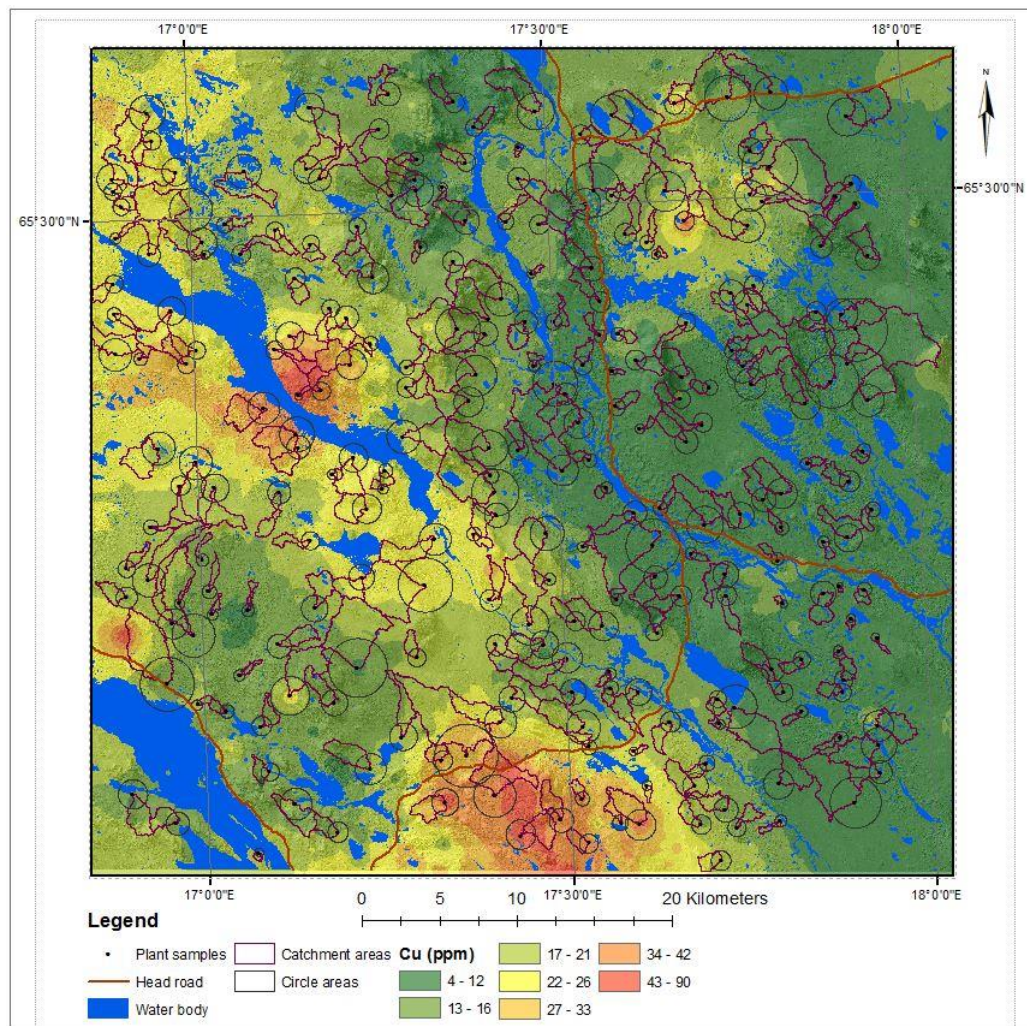
Figure 8: Circle areas and catchments located on a map of interpolated Cu-values for acid leached till (background data © SGU & © Lantmäteriet, Dnr: I2014/00579).

4 Results

4.1 RQ1 (Plant samples and bedrocks)

The spatial relationships between catchments and rock types can be viewed in Figure 5, section 3.3.2. The major part of the catchments was situated in areas dominated by granitic rocks. Of the 210 catchments there were:
- o   160 with more than 50% granitic rocks (121 with 100%).
- o   40 with more than 50% metasedimentary rocks (10 with 100%).
- o   15 with more than 10% mafic rocks (in the most extreme case 86%).

4.1.1 Correlation between plant elements and bedrock types

Most of the head elements showed no significant correlation with the different bedrock types, see Table 1(A).The only exception was Ca, which had negative (-0.22) correlation with granitic rocks (and was positive with meta-sediments, but not reaching significance, at the 5% FDR-level).

The correlation figures for the trace elements could be divided into two groups, one with positive figures for meta-sediments (negative with granitic rocks): Cu, Ni, Rb, Zn, see Table 1(B) and a second with positive figures for granitic rocks (negative with meta-sediments): As, Mo, S, U, (V), (W), Y and Zr, see Table 1(C).

There was no element that showed significant correlation with mafic rocks.

Table 1: Correlation coefficients (Spearman rank) related to bedrock types versus plant geochemistry.

A	Head elements								
N = 210	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti
Meta-sed.	-.100	.158	-.082	-.009	.038	.101	.112	-.166	-.026
Granitic	.097	**-.223**	.083	.060	-.013	-.083	-.088	.160	.054
Mafiic	-.079	.115	-.031	-.082	-.012	-.051	-.016	-.059	-.065

B	Trace elements: positive with sed % and negative with granitic %							
N = 210	Ba	Cl	Co	Cu	Ni	Rb	Sr	Zn
Meta sed.	.086	.147	.091	**.242**	**.533**	**.334**	.147	**.366**
Granitic	-.059	-0.16	-.089	**-.271**	**-.520**	**-.314**	-.153	**-.366**
Mafiic	-.077	0.064	-.009	,137	,146	.022	-.056	.114

C	Trace elements: negative with sed % and positive with granitic %									
N = 210	As	Cr	Mo	Pb	S	U	V	W	Y	Zr
Meta-sed.	**-.349**	-.025	**-.388**	-.135	**-.207**	**-.197**	**-.182**	**-.201**	**-.186**	**-.183**
Granitic	**.310**	.020	**.350**	.099	**.210**	**.170**	.163	.167	**.169**	**.192**
Mafiic	.007	.001	-.122	-.058	-.096	-.131	-.052	-.121	-.152	-.095
Black bold figures = significant, Red figures = not significant.										
Correction for multicomparisons are made by the FDR-method.										
Cut off significance: q = 0.014 (less than 5 % of the significant correlations are false discoveries).										

4.2 RQ2 (Plant samples and soil cover)

The content of some trace elements in the plant samples was lower in catchments with large peat areas compared to catchments with small peat areas.

The percentage distribution of soil types in a mean catchment was 76% for till and 22% for peat. Bare rock and sediments were quite uncommon with about 1% each. More precisely, of the 205 catchments there were:
- 190 catchments with more than 50% till (11 with more than 95%)
- 7 catchments with more than 50% peat (65% was maximum)
- 10 catchments with more than 5% bare rock (18% was maximum)
- 10 catchments with more than 10% coarse sediments (67% was maximum)
- 2 catchments with more than 9% fine sediments (14% was maximum)

The spatial relationships between catchments and soil types can be viewed in Figure 6, section 3.3.2.

4.2.1 Correlation between plant elements and soil types

The correlation coefficients between percentage of soil/rock surface cover in the catchments and sample site pH, ash content and plant sample element content is presented in Table 2 below. Since the areas of outcropping rocks and sediments were small compared to peat- and till areas, the correlation figures for the former surface covers were not investigated further.

Table 2: Correlation coefficients (Spearman rank) for soil cover types versus pH, ash and plant elements in the catchments (Gr/S=Gravel/sand, Si/Cl=Silt/clay).

Spearman rank correlation for starr-biodata & soil types

N=205	pH	Ash	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti	As	Ba	Cl	Co
			Head elements									**Trace elements**			
Till %	.044	-.083	**.202**	.158	-.145	.066	.171	.024	.071	.041	.059	-.080	-.137	.098	-.025
Peat %	-0.53	.113	**-.223**	-.152	.175	-.045	-.146	.012	-.039	-.027	-.061	.103	.140	-.060	.027
Rock %		.047	.173	.125	.090	-.110	-.073	**.279**	-.138	-.083	-.014	-.048	.119	.029	**.199**
Gr/S %		.022	.042	**-.194**	-.002	.081	-.069	-.098	-.047	.002	.075	.081	.062	-.166	.038
Si/Cl %		.109	-.020	.079	.138	-.091	-.084	.046	-.012	-.007	-.001	.090	.099	-.046	.025

N=205	Cr	Cu	Mo	Ni	Pb	Rb	S	Sr	U	V	W	Y	Zn	Zr
						Trace elements								
Till %	.009	**.264**	.062	.068	.096	**.282**	-.123	**.204**	**.304**	.018	.142	**.237**	.155	.002
Peat %	.000	**-.287**	-.076	-.081	-.101	**-.264**	.113	-.176	**-.345**	-.021	-.186	**-.274**	-.120	-.009
Rock %	.083	.116	.052	**.222**	-.018	**.211**	**-.199**	.035	**.249**	-.015	.103	.151	**.257**	-.088
Gr/S %	.046	.059	.132	-.061	.096	-.133	**.203**	-.106	.024	.109	.062	.075	-.131	.132
Si/Cl %	.049	-.007	.112	.036	.082	-.080	.004	-.018	.048	.007	-.039	.025	-.027	.016
Black bold figures = significant, Red figures = not significant.														
Correction for multicomparisons are made by the FDR-method.														
Cut off significance: q = 0.00714 (less than 5 % of the significant correlations are false discoveries).														

Six elements, one head- (Al) and five trace elements (Cu, Rb, Sr, U and Y) showed significant correlation figures with the dominant soil types (till and peat). The correlations for these elements were positive with till and negative with peat. No significant correlations were detected between the cover types for pH and ash content.

4.2.2 Two sample tests for different peat cover groups

The result from the statistical test (two independent samples, peat < 10% versus peat > 40%) is presented in Table 3 below. The null hypothesis of no difference between groups was in general rejected for the same elements that had significant correlations in Table 2 above (although p(Al) > FDR-limit here). The null hypothesis was not rejected for elements (pH and ash included) that did not correlate with the cover types (exception for Zn, with different groups in the 2-sample test). The result suggested that low peat- respective high peat cover groups, for some trace elements and Al (no other head element), could be regarded as representing (at least statistically) different environments.

Table 3: Significance figures from a two samples statistical test (Mann-Whitney-U) of plant element content in catchments with different percentage of peat cover. Test groups: peat cover < 10% (Pt<10) versus peat cover > 40 % (Pt>40). Direction of significant differences can be deduced from Table 2 above.

2-sample test: Peat < 10 % & Peat > 40 % (Mann-Whitney-U)

Pt <10 & Pt >40			Head elements									Trace elements			
N=(37 & 26)	pH	Ash	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti	As	Ba	Cl	Co
Sig. (2-tailed)	.188	.130	.013	.249	.076	.216	.175	.379	.753	.955	.978	.498	.141	.328	.906

Pt <10 & Pt >40						Trace elements								
N=(37 & 26)	Cr	Cu	Mo	Ni	Pb	Rb	S	Sr	U	V	W	Y	Zn	Zr
Sig. (2-tailed)	.775	**.003**	.430	.160	.701	**.0005**	.261	.123	**.001**	.878	.182	**.002**	**.004**	.867

Black bold figures = significant, Red figures = not significant.
Correction for multicomparisons are made by the FDR-method.
Cut off significance: q = 0.00893 (less than 5 % of the significant correlations are false discoveries).

Although only a few elements showed statistically verified differences between the peat cover groups, most elements (21 of 28) had lower median values in the group with high percentage of peat cover compared to that with less peat cover. This is illustrated in the table in Appendix 1, page 38.

4.3 RQ3 (Plant samples and down slope directions)

The result from this section was that different dominating down slope directions (north or south) in the catchments did not influence the geochemistry of the plant samples. Further, no correlation between percentage of north pointing down slopes and peat soils was detected in this area.

4.3.1 Correlation between plant elements and down slope directions

The correlation coefficients between down slope directions and element content in plant samples were not significant, see Table 4 below.

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Table 4: Correlation coefficients (Spearman rank) related to percentage of down slopes (north pointing and south pointing) in the catchments versus element content in plants.

N=210		Head elements										Trace elements			
Slopes	Ash	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti	As	Ba	Cl	Co
North %	-.124	-.067	-.093	-.128	.037	.022	-.171	.129	-.044	.031	-.127	-.115	-.013	-.088
South %	.124	.067	.093	.128	-.037	-.022	.171	-.129	.044	-.031	.127	.115	.013	.088

N=210	Trace elements													
Slopes	Cr	Cu	Mo	Ni	Pb	Rb	S	Sr	U	V	W	Y	Zn	Zr
North %	-.079	-.082	-.157	-.107	.070	.090	-.038	.059	-.112	.049	-.109	-.194	-.021	-.050
South %	.079	.082	.157	.107	-.070	-.090	.038	-.059	.112	-.049	.109	.194	.021	.050
Black bold figures = significant, Red figures = not significant.														
Correction for multicomparisons are made by the FDR-method.														

4.3.2 Two sample tests for different down slope direction groups

The result from the statistical test (two independent samples: North >70% versus South > 70%) is presented in Table 5. The null hypothesis was retained for all elements.

Table 5: Significance figures from a two samples statistical test (Mann-Whitney-U) of element content in plant samples from catchments with different percentage of down slope directions. Test groups, north pointing cells > 70% (31 samples) versus south pointing cells > 70 % (23 samples).

N >70, S >70		Head elements										Trace elements			
Nr=(31 & 23)	Ash	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti	As	Ba	Cl	Co
Sig. (2-tailed)	.058	.656	.868	.011	.612	.668	.037	.630	.972	.882	.010	.212	.759	.175

N >70, S >70	Trace elements													
Nr=(31 & 23)	Cr	Cu	Mo	Ni	Pb	Rb	S	Sr	U	V	W	Y	Zn	Zr
Sig. (2-tailed)	.278	.944	.172	.600	.340	.349	.098	.189	.479	.930	.365	.178	.310	.786
Black bold figures = significant, Red figures = not significant.														
Correction for multicomparisons are made by the FDR-method.														

Although none of the parameters showed a statistically verified difference between the slope groups, quite many of them (13 of 29, Ash and pH included) had a lower median value in the group with high percentage of north pointing down slopes compared to that with most south pointing down slopes. This is illustrated in the table in Appendix 2, page 39.

4.3.3 Correlation between down slope directions and soil cover

The correlation coefficients between percentage of catchment cells pointing to the north (or south) versus percentage of soil cover (peat and till) in the catchments are presented in Table 6. In this area no significant correlations were found between the variables.

Table 6: Correlation coefficients (Spearman rank) for percentage of down slope directions (North and South) versus percentage of soil cover (peat and till) in the catchments.

N=205	Till %	Peat %
North %	-.023	-.005
South %	.023	.005

Black bold figures = significant, Red figures = not significant.

4.4 RQ4 (Plant samples and till geochemistry)

For about 8 of 23 elements there were statistically significant positive correlations between the content in plant samples and interpolated mean values of the till samples, in both circle- and catchment areas. There were essentially no differences in correlation figures between the two area types. The large differences in relative variabilities between plants and till for some elements may reduce the correlation.

4.4.1 Relative variabilities for the different sample media

The differences in relative variability (RV) between the sample media elements are visualised in Figure 13.
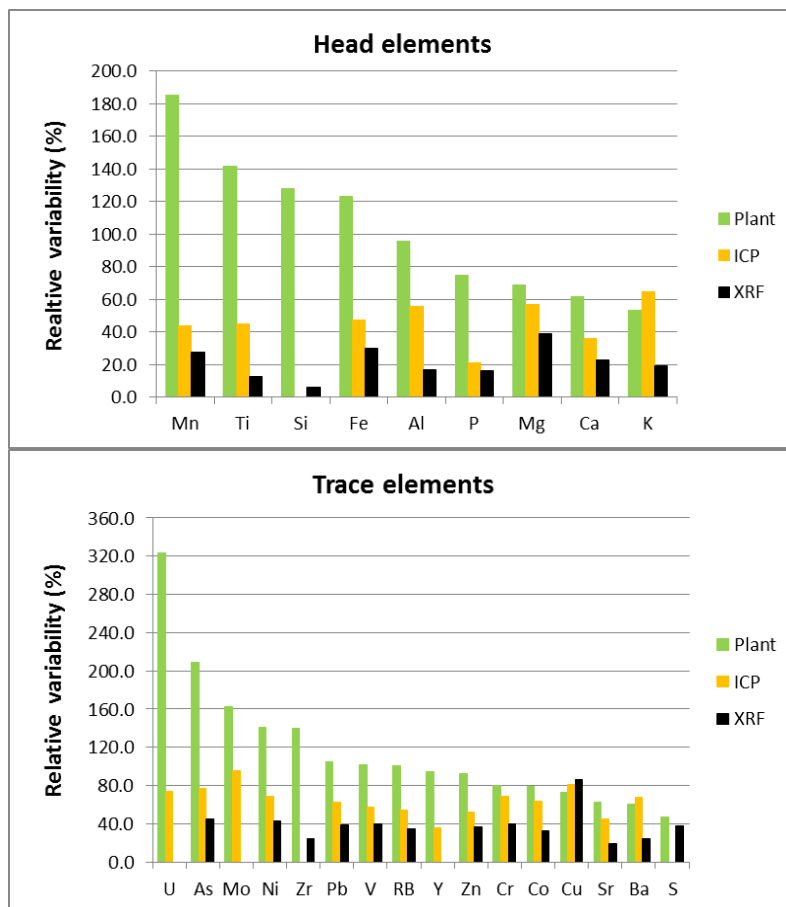
Figure 13: Comparison of relative variability values between plant- and till elements (total-(XRF) and leached (ICP) content). The columns are ordered after decreasing plant values.

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The plant elements generally had larger RV (in most cases much larger) than both the leached- and total content till elements. The RV for the till elements was generally lower for total content (XRF) compared to leached (ICP) data. The smallest differences in RV between plant and leached till elements were noted for Mg, K (head elements), and for Ba, Co, Cr and Cu among the trace elements. The largest differences were obtained for U and As. It should be noted that the large variabilities for As and Mo could arise from uncertainties in the chemical analysis (see 5.5).

4.4.2 Correlations between plant- and till elements in the sub-areas

In Table 7, the results from the correlation analysis between element content in plant samples and mean values from the interpolated till geochemistry maps are shown. There were no significant correlations detected for about 2/3 of the elements. However, for some elements significant positive values existed: Mn, Ba, Cu, Ni, Rb, Zn, and Zr, in the till total content case and for: Mn, Cu, Ni, Rb, Sr, U, Y and Zn in the leached till case. The highest correlation figures (> 0.45) were detected for Ni and U in leached till. Two elements, Mo and S, showed negative correlations between plant- and till content. The differences between the significant correlation figures for the catchment- respective circle areas were small and in most cases less than 5% (max 12% for Mn).

Table 7: Results from correlation analysis (Spearman rank) between plant element content and mean till element content from interpolated till maps (A: total- and B: leached) in circle- and catchment areas.

Correlation figures, plant elements versus total element contents in till.

A	Head elements									Trace elem.	
N=210	Al	Ca	Fe	K	Mg	Mn	P	Si	Ti	As	Ba
Catchments	.113	.000	-.045	-.019	.006	**.252**	.127	.128	.034	.138	**.232**
Circles	.138	-.006	-.043	-.024	.021	**.245**	.132	.111	.046	.152	**.246**
	Trace elements										
	Co	Cr	Cu	Ni	Pb	Rb	S	Sr	V	Zn	Zr
Catchments	.065	-.091	**.281**	**.462**	.122	**.304**	-.267	.156	-.153	**.270**	**.329**
Circles	.062	-.079	**.294**	**.472**	.089	**.277**	-.266	.148	-.133	**.269**	**.305**
Black bold figures = significant, Red figures = not significant.											
Correction for multicomparisons are made by the FDR-method. Cut off significance: q = 0.0182											
(less than 5 % of the significant correlations in each area group are false discoveries).											

Correlation figures, plant elements versus acid leached elements in till.

B	Head elements								Trace elements		
N=210	Al	Ca	Fe	K	Mg	Mn	P	Ti	As	Ba	Co
Catchments	-.053	.153	-.074	-.056	-.028	**.264**	.070	-.139	.083	.100	.044
Circle areas	-.019	.116	-.075	-.081	-.017	**.233**	.037	-.128	.076	.113	.024
	Trace elements										
	Cr	Cu	Mo	Ni	Pb	Rb	Sr	U	V	Y	Zn
Catchments	-.110	**.278**	-.239	**.477**	.086	**.244**	**.285**	**.492**	-.123	**.375**	**.278**
Circle areas	-.096	**.287**	-.245	**.490**	.066	**.232**	**.279**	**.490**	-.116	**.412**	**.273**
Black bold figures = significant, Red figures = not significant.											
Correction for multicomparisons are made by the FDR-method. Cut off significance: q = 0.0205											
(less than 5 % of the significant correlations in each area group are false discoveries).											

5 Discussion

5.1 RQ1 (Plant samples and bedrocks)

The source of most elements reaching the stream plants are the minerals in bedrocks and soils which are weathered, dissolved and transported by surface- and groundwater flows. The surface soil cover in the area is far more dominant than the area of outcropping bedrocks, but the soil cover is quite thin (< 0.5 m) in many catchments. However, a much larger specific area of small soil particles compared to areas exposed by solid bedrock (for weathering), imply that the soil is the dominant source of elements transported to the sedge plants. It is also worth noting, that the till material overlying the bedrock is not only representing the rock immediately beneath the soil, but is also derived from an area in opposite direction of the ice flow, which in some cases could be other bedrock types (here northwest lying areas with Caledonian sediments). All together these facts imply that high correlation figures between bedrock types and plant elements in the catchments could not be expected.

The significant figures (Table 1, section 4.1.1) can mainly be divided into two groups:
1) Elements having negative correlation with granitic rocks and positive with meta-sediments (Ca, Cu, Ni, Rb, Zn).

2) Elements with opposite signs, i.e. positive correlation with granitic rocks and negative with meta-sediments (As, Mo, S, U, V, W, Y, Zr).

From the first group, all elements except Rb, have a higher content naturally in sedimentary rocks compared to granitic rocks (Lax, 2005, p10), which is supported by the correlation figures. These elements also normally occur with higher percentage in mafic rocks than in granitic rocks. This fact is (somewhat) detected by the correlation figures, clearly positive although not reaching the FDR-significance level. Rubidium is, on the contrary, normally more associated with granitic rocks than sediments. However, high Rb contents are detected in meta-sedimentary rocks from the Caledonian mountains in the west (Anderson et al., 2014) a circumstance that to some extent (deposited till materials from the Caledonides) may explain the positive correlation with the meta-sedimentary rocks.

In the second group the elements: Mo, U, W, Y and Zr are naturally more associated with granitic rocks than meta-sedimentary or mafic rocks, which the correlation figures also imply. Three elements: As, S and V do not fit into that picture. Arsenic is normally associated with sulfidic mineralization in meta-sediments and V is associated with mafic rocks (Anderson et al., 2014), so these deviating correlations are difficult to explain. Regarding S, the element is (in not mineralized areas) normally derived from precipitation and not from weathering (Andersson, 2006; Ingri et al, 1997), so this correlation figure is probably irrelevant in a bedrock context. (It is also wise to keep in mind that one or two of the significant correlations can be random (see chapter 3.4.1).

There are several sources for errors in the analysis. One is related to the plant samples (applies for all RQ's), which will be discussed in section 5.6 and another is the uncertainty in the distribution of the bedrock types in the area. Most of the investigation area is covered by soils so much of the bedrocks distributions have been

outlined by indirect methods (by SGU). Also some simplification of bedrock types in this work may have added some errors. However, about 80 % of the catchments lie more or less completely inside areas of granitic- or sedimentary rocks. The rest (20%) of the catchments have a mix of granitic, sedimentary and sometimes also small amount of mafic rocks inside their areas. It is only in the latter catchments the uncertainties in rock border delineations could have influenced the results. Probably, rock border errors are not influencing the results for RQ1 in any serious way.

5.2 RQ2 (Plant samples and soil cover)

The results from the correlation analysis between soil type and plant elements (Table 2, chapter 4.2) and the statistical 2-sample test (low peat- coverage versus high peat coverage, Table 3, chapter 4.2) show that for most of the elements there were no differences in element adsorptions in sedge plants related to different amounts of peat cover in the catchments. Nevertheless a few exceptions, with clear statistical significance exist, and these elements are: Al (correlation), Rb, U, Y and Zn (2-sample test). For these five elements the uptake by sedge plant roots in stream water was reduced in catchments with high percentage of peat cover (compared to those with low peat coverage).

Several important factors can be involved:

1. Decreasing amount of detrital particles in stream water when peat cover increase.

2. Fe and P in authigenic (non-detrital) particles.

3. Trapping of elements in the peat.

4. Reduction of uptake due to more acid stream water from larger peat areas.

1. Normally two elements, Al (at normal pH) and Ti in stream water are transported bound into detrital particles, with small dissolved amounts in solution (Ingri & Widerlund, 1994). In the Sorsele study area there were no plant sample sites with enough low pH to cause Al-dissolution (pH<5, lowest was pH 5.3 and mean pH was 6.3) and there was a strong correlation between Al and Ti (0.74). Therefore the detected Al in the samples is mainly from adsorbed detrital particles and these particles decrease in river water from catchments with larger peat areas which is also found in other studies (e.g. Björkvald et al., 2008 and Cory et al., 2009).

The trace elements (Cu, Rb, Sr, U and Y) which also decrease in plants from catchments with high percentage of peat cover are probably also transported in detrital form associated with/within Al-particles. Positive correlation figures between these elements and Al support that interpretation. These five trace elements also show negative or no significant correlation with Fe (usually in suspended non detrital oxy/hydroxide form) the other major head element responsible for transport and adsorption of trace elements. See point *2* and Table 8 below.

A possible explanation at landscape level is that physically weathered detrital particles decrease in stream waters from catchments with large areas of peat since a larger part of the precipitation fall on peat or peat covered till. This reduces a direct physical erosion of mineral particles from the till. Rain water from peat areas dilutes the runoff water from more till dominated areas in the catchments, resulting in lower content of detrital particles in the stream water, to be adsorbed on the plant roots.

Table 8: Correlation figures (Spearman rank) between the transport/carrier elements: Al and Fe, versus the trace elements that differ in content between low and high peat catchments.

Transport elem.	Trace elements				
	Cu	Rb	Sr	U	Y
Al	**.376**	**.349**	**.362**	**.494**	**.593**
Fe	**-.226**	*-.139*	**-.227**	*-.200*	**-.012**

Black bold figures = significant, Red figures = not significant.
Cut off significance: q = 0.0005 (less than 5 % of the significant correlations are false discoveries).

2. For Fe there was no statistical difference detected between low and high peat cover catchments at the 5% FDR-level. However, if the requirement is lowered to a 10% FDR-level, then a positive correlation between Fe and high peat content in the catchments is observed (negative correlation with low peat coverage). Further Fe showed no correlation with Al (and Ti). This indicates that Fe is not transported (and adsorbed on the plants) in detrital form but in other phases, e.g. non-detrital form (authigenic) or/and dissolved matter. Authigenic Fe is often aggregated with organic particles which constitute the dominant carrier of particulate none detrital matter in streams and these particles can also scavenge lots of dissolved trace elements from river waters (Ingri & Widerlund, 1994). The importance of none detrital, Fe and organic based carriers, increase in runoff from areas with high content of mire and peat (Björkvald et al. 2008). In the Sorsele area Fe correlates best with As (0.72), and Co (0.71) but these two trace elements show no statistical difference between low and high peat cover catchments regarding uptake into sedge roots.

Authigenic Fe is also strongly associated with P in river water (Dahlqvist et al., 2007). However the plant sample case can be more difficult to interpret since P also is an essential nutrition compound. In the Sorsele area there is no statistically significant correlation detected between Fe and P in the sedge plants, and there is no difference in P-content detected between the peat cover groups.

3. An element that is trapped and normally enriched in peat and depleted in the water is U, where it is scavenged from the groundwater into organic- acids and colloids (Porcelli et al., 1997). In the Sorsele area a statistically significant decrease of U in the sedge plants is noted for catchments with large areas of peat compared to areas with little or no peat. This is probably related to both the decrease of detrital particles in the peat areas (U correlates quite strong with Al, see Table 8) and to high amount of organic substances in the peat areas (U has stronger negative correlation with peat areas than Al, see Table 2). Another element that is normally trapped in peat is S (from SO_4^{2-}), due to reduced condition in this soil type (Ingri et. al., 1997). However, in this study no difference was detected between the cover groups for this element.

4. It is possible that a lower pH in stream waters from peat dominated catchments reduce the adsorption of elements to plant samples. Acid river water contain relatively larger concentrations of hydronium ions (H_3O^+) compared to trace elements than not acidified waters and these hydronium ions compete with the positively charged trace element ions for anionic sites on the plants (Fernandez et al. 2006). In this study no statistical difference in sample site water pH between low- and high peat cover catchments is detected, so this factor is probably not important here.

There are several sources for errors in the analysis. One is related to the plant samples (applies for all RQ's) which will be discussed in section 5.6, and another is some uncertainty in the distribution (area and thickness) of the peat layers in the area. The uncertainty in the peat area distributions is probably not very high since on the whole, during mapping, these areas are relatively easy to distinguish from pure mineral soils, at least in open areas.

5.3 RQ3 (Plant samples and down slope directions)

The results show that in the Sorsele study area, there are no significant statistical differences detected in element uptake by sedge roots, between catchments dominated by north pointing down slopes compared to those dominated by south pointing down slopes (Tables 4 and 5, chapter 4.3). Also no differences in percentage of peat cover in the catchments are detected between the slope categories (see Tables 6, chapter 4.3). At least the last result is unexpected since normally there is more peat in north pointing down slopes compared to south pointing ones (field experience by the author).

The direction of slope influence the solar radiation energy which is lower on north pointing down slopes (compared to south pointing) and that causes higher soil moisture and higher near surface groundwater levels. Decomposition of dead organic matter is decreased, enhancing thicker humus layers, peat formation and lower soil water pH (Siebert et al. 2007). Together, these factors decrease the illuvial precipitation of Fe into the B-horizons of humic-podzols (Lundström et al., 2000) compared to better drained soil profiles at south pointing down slopes. Instead, larger portions of the element may be transported directly to the streams aggregated to different kinds of organic particles and organic acids or in a dissolved form, which potentially can be reflected in higher absorption into the plants.

However, no significant increase of Fe (or any other element) or decrease of pH is detected for plant sample sites in catchments dominated by north pointing down slopes (compared to south pointing) in the study area. Perhaps another result could be achieved in an analysis based not only on down slope aspects, but in combination with some sort of topographical wetness index as described by other authors (e.g. Siebert et al., 2007; Andersson and Nyberg 2009).

The errors in this section are mainly associated with the plant samples and will be described in section 5.6. The mapping of down slope directions is probably accurately calculated with the high resolution DEM.

5.4 RQ4 (Plant samples and till geochemistry)

The elements in the plant samples distinguish themselves from their corresponding till elements with much higher relative variabilities, with U as the most extreme example (Figure 13, chapter 4.4.1). This is probably caused by different kinds of biological- and hydrological processes during weathering, soil formation and transportation of elements through the catchments. The environment in the soils C-horizon where the till samples are taken is much more stable and the relative variability of these elements is lower.

The correlation coefficients for the elements in the two media (if significant) lie in the interval: 0.23 – 0.49 (Table 7, chapter 4.4.2), implying that the geochemical connection between the plants and their surrounding till soils in general is not very strong. The highest positive correlation figures are noted for: Ni, U and Y. The two negative correlation figures for Mo and S are difficult to explain and they may be artefacts. Especially S (in not mineralized areas) is an element which in Swedish river waters mainly is derived from precipitation and not from weathering (Andersson, 2006; Ingri et al, 1997).

The result also shows no large differences in correlation coefficients between the catchment and the circle approaches. Principally, the correlation should be better between plant samples and catchments because the water that flow through the plant sample locations comes from the uptake area inside the catchments borders. A big part of the circle areas are often located outside the areas that drains to the plant samples and the correlation may be lower.

There can be several explanations to why the result does not yield stronger correlation for the catchments compared to the circle areas. Firstly, the interpolation of till samples based on the relatively coarse sampling density (1 sample per 7 km^2) will miss smaller anomalies on the catchment scale which median size is only about 1.35 km^2. This means that the variability detected by the plant samples does not correlate with the element distribution on the oversimplified interpolated till element maps. Secondly, the element content in the soils may reflect the quite homogenous bedrock basement (mostly granites and meta-sediments) in the area. The element variability may be too low to be detected by the plant samples with their larger element variabilities caused by biological processes in the surrounding ecosystem.

Perhaps stronger correlation can be achieved if an investigation area with higher percentage of mafic rocks compared to felsic rocks can be found, which should enhance differences in soil geochemistry. Also a more dense net of till samples could improve another investigation. Incorporation of land cover types into the analysis could perhaps resolve some of the high element variabilities in the stream plants.

The errors in this part are related to the geochemical analysis of the plant- and till data which are discussed in section 5.6, and to the interpolation of till maps and the mean element values extracted from these maps. The interpolation with the IDW algorithm (evaluated in 3.4.5) is probably good enough for the quite low density of till data points at hand. The low density of till data points implies a risk of missing local anomalies (as discussed above) but also a risk of regionalising local anomalies. These risks are difficult to evaluate, without a denser net of till samples.

5.5 General conclusions from the results

Correlation studies between small high resolution catchments and geological datasets (bedrock- , soil maps and till geochemistry) probably also require very high resolution of the latter datasets (i.e. geological maps more detailed than the scale 1:50 000 - 1:200 000 available for this study and a denser net of till samples) for utilizing the performance and possibilities with the new DEM. Although some significant statistical results are found, maybe the geological variability in an ordinary (not mineralized) landscape generally is too small to be discovered by the used methods. Different processes in the connection between plant roots and stream water (result in high relative variability) which possibly mask the smaller variations in the geochemistry of these landscapes. Perhaps robust multivariate statistical methods, e.g. robust partial least square (rPLSR) or robust principal component analysis (rPCA) could be valuable and informative in another study, but these methods are beyond the scope of this thesis.

5.6 Errors

The uncertainties in the location of the plant samples (+-50m) could contribute to errors in the delineation of the catchment boundaries and areas. Analysis show that these uncertainties in most cases contribute to error in catchment areas with less than1%, and in worst cases for some very small catchments (a few) with up to 10%.

The analytical errors from measurements of the plant geochemistry are within 5% for most of the head elements, exceptions are Fe with only 2% and P with 6%. Most of the trace elements have uncertainties within 5%, but for some elements (Ni, Pb and S) the errors can be larger, within 7-11%. The uncertainties can be above 50% for As and Mo at low levels under the detection limits (SGU data documentation).
The error figures are the same for the total content till data, but are usually a little bit higher for the leached till samples, with errors around 9-12% for most elements (SGU data documentation).

The relative variabilities of the elements in the sedge samples are at least one order (except S with 0.7) of magnitude larger than the analytical errors, and the relative variabilities of the elements in the till samples are about 0.7 to 1 order of magnitude larger than the analytical errors. Possibly, the analytical errors do not affect the results in a decisive way.

Differences in rate of element absorption between the plant species *(Carex, F. antipyretica and F. ulmaria)* are avoided in the study since only data from the sedge plants (*Carex*) are used.

6 Conclusions

Spatial environmental variations in small catchments are for some parameters detectable in the geochemistry of sub aquatic plant samples at the stream outlets, although the relations are very complex. The geochemistry of the plants represent a time integrated mean value of biological and geological parameters in the catchments.

RQ1 (Plant samples and bedrocks):

For about 50% (13 of 27) of the elements in the plant samples statistically significant correlations with bedrock types in the catchments were detected. One group of elements correlated positively with meta-sediments (negatively with granite): Cu, Ni, Rb and Zn and another correlated positively with granite (negatively with meta-sed.): As, Mo, S, U, Y and Zr. For most elements (except As, Rb and S) this picture is what could be expected regarding element content in the different rock associations of the study area.

RQ2 (Plant samples and soil cover):

For most elements, 78%, (21 of 27) there were no differences in element content in the plant samples related to different amount of peat coverage in the catchments. However, for one head- (Al) and five trace elements (Cu, Rb, Sr, U and Y) significant differences were detected. The content of these elements were lowered in catchments with high percentage of peat cover compared to catchments with low or no peat cover. The decrease of these elements is probably related to lower amount of detrital particles in the stream waters from catchments with high peat content. Another process, important for U may be trapping/adsorption of the element by organic compounds in the peat layers.

RQ3 (Plant samples and down slope directions):

In the study area, there were no differences in element content detected between catchments dominated by north pointing down slopes compared to those dominated by south pointing down slopes.

RQ4 (Plant samples and till geochemistry):

The correlations between elements in plant- and till samples were investigated for two different area types related to the plant samples. The first and natural one was the area that drains to each plant sample, i.e. the catchment area. The second was a circle centered at the plant sample point with equal area as the corresponding catchment. The mean value of each till element was calculated from interpolated till maps for respective area type and plant sample. For about 45 % (10 of 22) of the elements (Mn, Ba, Cu, Ni, Rb, Sr, U, Y, Zn, Zr), there were significant and positive correlations between the content in the plant samples and the mean till geochemistry. Generally the correlation figures for both catchments and circle areas were quite equal in size. Perhaps a too coarse net of till samples (masking variabilities), or very homogenous soil chemistry over large areas, can explain why the differences were so small (strongest correlations with catchments was expected).

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Appendices

1: Median, ratios of median and relative variability for the plant elements in the different soil cover groups (P10 = Peat < 10 % and P40 = Peat > 40 %, in the catchments, there were 37 samples in P10 and 26 samples in P40). Table is sorted after ratios P40/P10, from small to large figures. Black bold elements showed different groups in the 2-sample test (Mann-Whitney-U).

	Median		Ratios	Rel. Var %	
	P10	P40	P40/P10	P10	P40
U	1.94	0.42	0.22	514.43	294.64
Rb	17.1	7.25	0.42	94.74	172.41
Y	9.80	5.35	0.55	104.08	104.21
Al2O3	0.65	0.39	0.60	95.28	75.49
Cu	7.20	4.35	0.60	64.58	87.36
MnO	0.06	0.04	0.64	151.69	202.67
Ni	3.30	2.30	0.70	116.67	171.74
Zn	62.0	43.8	0.71	106.21	50.74
Sr	20.7	16.7	0.81	50.24	83.68
MgO	0.17	0.14	0.82	52.94	58.93
K2O	0.59	0.49	0.83	61.86	81.63
W	0.60	0.50	0.83	175.00	85.00
SiO2	2.20	1.88	0.85	99.77	168.75
Mo	4.22	3.66	0.87	159.36	86.53
V	7.70	6.70	0.87	91.56	125.75
CaO	0.47	0.41	0.87	63.83	75.61
TiO2	0.02	0.02	0.92	182.42	159.87
Zr	9.70	9.10	0.94	140.21	146.70
pH	6.40	6.10	0.95	12.50	11.89
Cl	294	282	0.96	118.71	110.20
Pb	10.1	9.85	0.98	123.27	79.70
P2O5	0.17	0.17	1.00	82.35	107.35
BaO	0.01	0.01	1.00	68.75	106.25
Cr	3.50	3.50	1.00	111.43	93.57
Co	9.00	9.55	1.06	82.78	86.39
S	1766	1894	1.07	67.36	47.58
Ash	8.70	9.95	1.14	90.23	82.91
As	40.5	54.2	1.34	230.47	294.59
Fe2O3	1.96	3.01	1.54	105.10	229.07
Element-oxides in %, others in ppm (median values)					

2: Median, ratios of median and relative variability for the plant elements in the different down slope direction groups (S70 = South > 70 % and N70 = North > 70 %, in the catchments, there were 23 samples in S70 and 31 samples in N70). Table is sorted after ratios N70/S70, from small to large figures. There were no statistically significant differences between the slope groups according to the 2-sample test (Mann-Whitney-U), after correction for multi comparisons.

	Median		Ratio	Rel. Var. %	
Element	S70	N70	N70/S70	S70	N70
As	86.17	28.47	0.33	346.54	248.47
Mn	0.13	0.05	0.41	111.28	142.59
Fe2O3	3.65	1.93	0.53	133.70	142.49
Mo	4.85	3.15	0.65	218.97	132.70
Ash	12.70	8.80	0.69	55.12	82.95
Y	7.70	6.10	0.79	102.60	78.69
Cr	4.60	3.70	0.80	78.26	105.41
BaO	0.01	0.01	0.82	36.36	77.78
W	0.60	0.50	0.83	100.00	120.00
U	1.40	1.17	0.84	356.43	215.38
Co	11.80	10.00	0.85	87.29	91.00
S	1910.00	1680.00	0.88	71.31	74.88
K2O	0.60	0.55	0.92	63.33	50.91
CaO	0.44	0.42	0.95	47.73	90.48
Zr	10.50	10.30	0.98	159.05	143.69
Al2O3	0.58	0.57	0.98	125.13	121.85
Cu	5.90	6.10	1.03	72.88	88.52
TiO2	0.02	0.02	1.05	173.04	136.92
MgO	0.15	0.16	1.07	60.00	81.25
P2O5	0.15	0.16	1.07	86.67	93.75
Pb	9.20	10.40	1.13	109.78	87.50
V	9.40	10.70	1.14	101.06	93.46
Ni	3.30	3.80	1.15	81.82	163.16
Cl	278.00	322.00	1.16	70.14	83.23
Rb	17.80	20.90	1.17	77.53	81.82
Sr	17.80	21.40	1.20	60.11	50.93
SiO2	1.65	2.02	1.22	195.76	134.65
Zn	47.50	58.90	1.24	164.42	73.51
pH	6.20	6.00	0.97	9.68	13.33
Element-oxides in %, others in ppm (median values)					

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