HYDROGEOCHEMICAL CHARACTERIZATION OF THE SAKATTI MINE PROSPECTING AREA, SODANKYLÄ, FINNISH LAPLAND

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Master's thesis

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Tiivistelmä – Referat – Abstract

In 2011, Anglo American Sakatti Mining Oy published an ore discovery in Sodankylä, Finnish Lapland. The rich Ni-Cu-PGE orebody, named Sakatti ore, is partially underlying Viiankiaapa-mire’s Natura 2000 protection area. This sets additional challenges for the utilization of the resource without compromising the fragile nature of the area. To estimate the impacts of possible future mining operations, the complex hydrochemical and hydrogeochemical conditions at Viiankiaapa must be well understood.

Most water samples from the research area show a chemical composition close to the natural Finnish groundwater composition Ca–HCO_3. However, in four groundwater observation wells, located south from Kiimakuusikko, Na–HCO_3 type waters were detected. These sites were GA300 (8.26 ppm of Na), GA202 (17.34 ppm of Na), GA202 deep (15.23 ppm of Na) and GA201 (7.92 ppm of Na). Source for the anomaly is likely lithological due to lack of chloride in the samples. One possible source could be weathering of albite to kaolinite. Albite is hosted in the breccia unit, located close to the site. Albite-kaolinite weathering could release Na^+ ions into the surrounding soil solution, which would provide a source for the high sodium concentrations.

Kitinen river shows slightly higher Al, Li and Cu contents compared to other waters from the research area. This could possibly be used to distinguish river water from groundwater at sites where river water infiltrates the groundwater system. On the other side, Na, K and DSi have higher concentrations in groundwaters compared to surface waters. This could make them useful groundwater indicators. Sakattioja and the other smaller streams draining the mire, are characterized by very high isotope values, low amounts of DSi and low EC. These characteristics likely reflect the hydrogeochemistry of the water on the surface of the mire. The hydrogeochemical similarity of these streams is also highlighted by the hierarchical cluster analysis, where the samples from these sites form a clear cluster of their own.

Stable isotope results are mixed and difficult to interpret. The most striking features are the low values observed at the mire near Kiimakuusikko and the high values observed in Sakattioja. Many groundwater samples show signs of evaporated source water component or re-infiltration of surface waters. This could be due to water from the mire infiltrating the groundwater system and then re-emerging in the observation wells and springs close to Kitinen.

Overall, based on the results, the hydrogeochemistry at the research area can be considered to be very complex. The samples represent multiple different water compositions residing in poorly connected groundwater and surface water systems. This makes interpreting the results particularly difficult and is also reflected in the statistical analyzes which produce somewhat mixed results.

Avainsanat – Nyckelord – Keywords

Hydrogeology, hydrogeochemistry, hydrochemistry

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Tiivistelmä – Referat – Abstract

Vuonna 2011 Anglo American Mining Oy julkisti tehneensä merkittävän malmilöydöksen Sodankylästä, Suomen Lapista. Rikas Ni-Cu-PGE -esiintymä, joka nimettiin Sakatiksi, sijaitsee osittain Viiankiaapa -suon Natura 2000 -luonnonsuojelualueen alla. Malmion haastava sijainti herkän suoympäristön alla asettaa malmin ekologisesti kestävälle hyödyntämiselle suuria lisähaasteita. Jotta mahdollisen kaivostoiminnan ympäristövaikutuksia voitaisiin arvioida, tulee alueen monimuotoiset hydrologiset ja hydrogeokemialliset olosuhteet tuntea erinomaisesti.

Suurin osa alueelta kerätyistä vesinäytteistä seuraa Suomen pohjavesien tyypillistä luonnollista $Ca–HCO_3$ koostumusta. Tästä poiketen, neljässä pohjaveden tarkkailuputkessa Kiimakuusikon eteläpuolella havaittiin $Na–HCO_3$ tyypin vesiä. Näihin tutkimuspisteisiin kuuluivat näytteet GA300 (8,26 ppm Na), GA202 (17,34 ppm Na), GA202 deep (15,23 ppm Na) ja GA201 (7,92 ppm Na). Anomalian alkuperä on todennäköisesti litologinen, sillä samoissa näytteissä ei havaittu merkittäviä määriä kloridia. Albiitin rapautuminen kaoliniitiksi on yksi mahdollinen lähde anomalialle. Albiittia on havaittu mainittujen näytepisteiden lähellä sijaitsevissa breksioissa. Albiitin rapautuminen kaoliniitiksi voisi vapauttaa veteen Na^+ ioneja, jotka selittäisivät korkeita natrium pitoisuuksia.

Kitinen joessa voidaan havaita hieman muista näytteistä kohollaan olevia Al, Li ja Cu pitoisuuksia. Tätä havaintoa voitaisiin mahdollisesti hyödyntää pintavesien tunnistamiseen kohteissa joissa jokivesi imeytyy pohjavesisysteemiin. Na, K ja DSi taas puolestaan ovat hieman yleisempiä pohjavesissä pintavesiin verrattuna. Tämä tekee niistä potentiaalisia pohjavesi indikaattoreita. Sakattiojaa ja muita suolta laskevia ojia karakterisoivat erittäin haihtuneet isotooppiarvot, pienet DSi pitoisuudet ja alhaiset sähkönjohtavuudet. Nämä ominaisuudet todennäköisesti viittaavat suon omiin pintavesiin. Ojien samankaltaisuus korostuu myös hierarkkisessa klusterianalyysissa, jossa ojista kerätyt näytteet muodostavat oman selkeän ryhmänsä.

Näytteistä saadut veden stabiilien isotooppien koostumukset ovat sekavia ja haastavia tulkita. Selkeimmät havainnot liittyvät Kiimakuusikon alueen vesien alhaisiin isotooppilukemiin ja Sakattiojan haihtumista osoittaviin korkeisiin arvoihin. Suuri osa pohjavesinäytteistä ilmentää joko haihtunutta lähtövettä tai pintavesien imeytymistä pohjavesisysteemiin. Yksi mahdollinen syy havainnolle voisi olla suon pintavesien imeytyminen pohjavesikiertoon. Suon alta ja reunoilta imeytynyt pintavesi selittäisi myös joen läheisyydessä olevien lähteiden haihtuneita isotooppiarvoja.

Yleisesti tulosten pohjalta voidaan todeta että tutkimusalue on hydrogeokemiallisesti tarkasteltuna erittäin monimutkainen. Kerätyt näytteet edustavat lukuisia erilaisia kemiallisia koostumuksia jotka tavataan useissa heikosti toisiinsa yhteydessä olevissa pohjavesi- ja pintavesi ympäristöissä. Tämä tekee tuloksista erityisen haastavia tulkita ja heijastuu myös tilastollisiin analyyseihin joiden tulokset ovat sekavahkoja.

Avainsanat – Nyckelord – Keywords

Hydrogeologia, hydrogeokemia, vesikemia

Säilytyspaikka – Förvaringställe – Where deposited

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1 INTRODUCTION

Mines are one of the largest sources of waste water in Europe (Wolkersdorfer 2005). Sustaining good water quality during and post-mining is one of the biggest challenges of modern mining (Lottermoser 2003). A well thought, comprehensive mine closure plan (MCP) starts considering mine closure and possible water quality related issues during the pre-feasibility, feasibility and design phases of a mining project (e.g. Heikkinen et al. 2008, International council on mining and metals (ICMM) 2008, Robertson and Shaw 2009). Environmental impacts of mining operations and the possible need and goals for post-mining remediation cannot be accurately estimated or modelled without information of the natural, pre-mining water conditions (Runnells et al. 1992). Collecting this data before mining operations is much easier and more accurate that trying to estimate the conditions later on via modelling (e.g. Runnells et al. 1992, Runkel et al. 2007).

In 2011, Anglo American Sakatti Mining Oy published an ore discovery in Sodankylä, Finnish Lapland (Brownscombe et al. 2015). The rich Ni-Cu-PGE orebody, named Sakatti ore, is partially underlying Viiankiaapa-mire’s Natura 2000 protection area. This sets additional challenges for the utilization of the resource without compromising the fragile nature of the area. To estimate the impacts of possible future mining operations, the complex sedimentological, hydrological, hydrogeochemical and paleohydrological conditions at Viiankiaapa must be well understood. To achieve this, the mining company launched Sakatti geoenvironments -project in collaboration with the University of Helsinki. In a series of thesis’ and publications the past and the present conditions at Viiankiaapa are studied.

The main goal of this this study is to produce accurate hydrogeochemical data and to describe and characterize the natural water quality at the area before any possible mining operations. After different water types present at the site have been identified, their chemical characteristics are further analyzed with statistical analysis. This is done to form a general picture of the western-Viiankiaapa’s hydrogeochemical conditions while also trying to identify possible hydrogeochemical anomalies. The anomalies, and their potential sources are then discussed further.

2 STUDY SITE

The main research area, consisting of the eastern banks of Kitinen river and western edges Viiankiaapa mire, is located approximately 15 kilometers northeast of the municipality of Sodankylä in the Finnish Lapland (Figure 1, Figure 2). Kitinen, which is a tributary of Kemijoki river, flows through the research area. Kitinen's headwater is the Porttipahta reservoir located 50 km upstream from the research site.

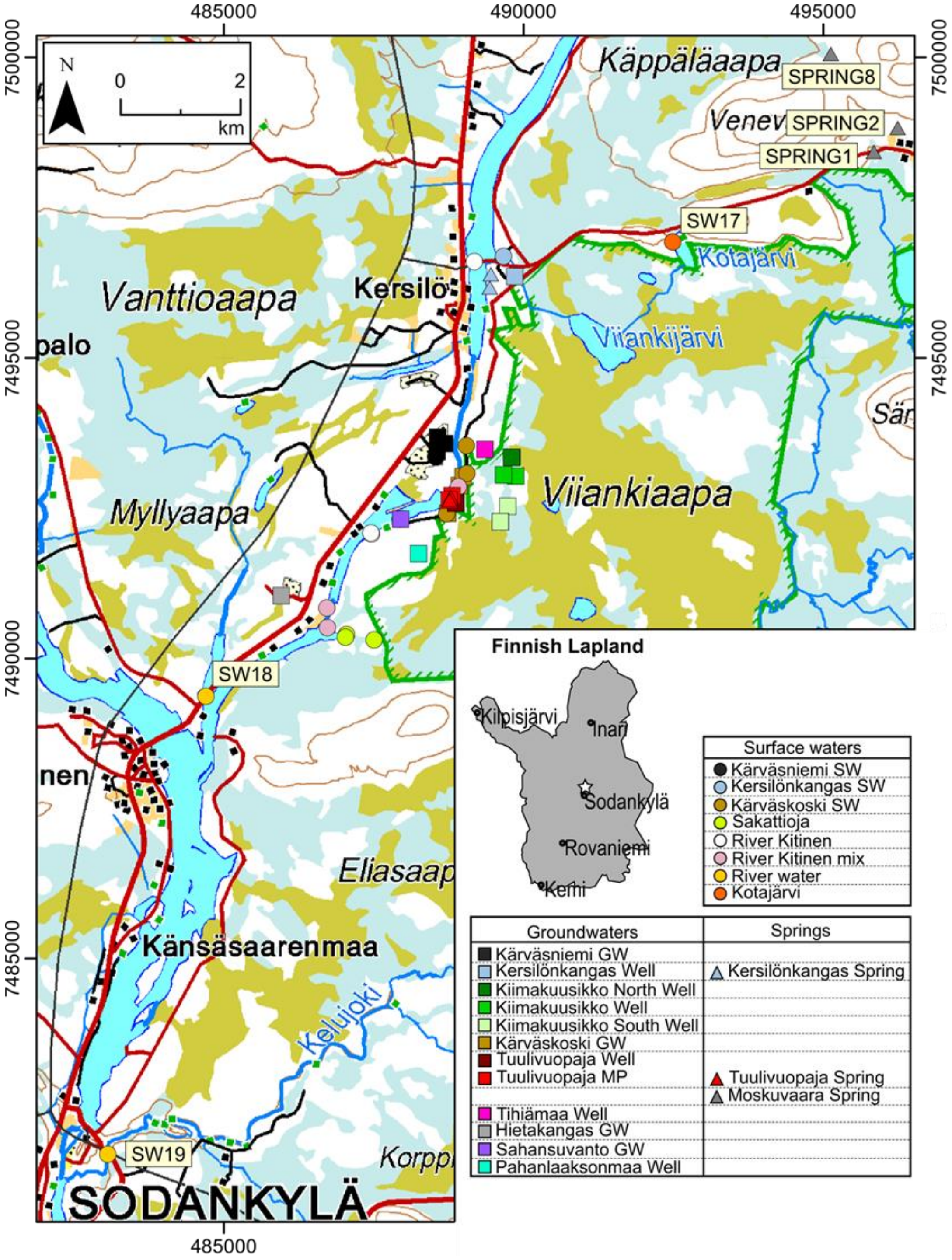

Figure 1. Location of the study area. Sampling sites of the main study area (western side of Viiankiaapa) are labeled in Figure 2. Base map (base map database @ National Land survey of Finland (NLS) 2010).

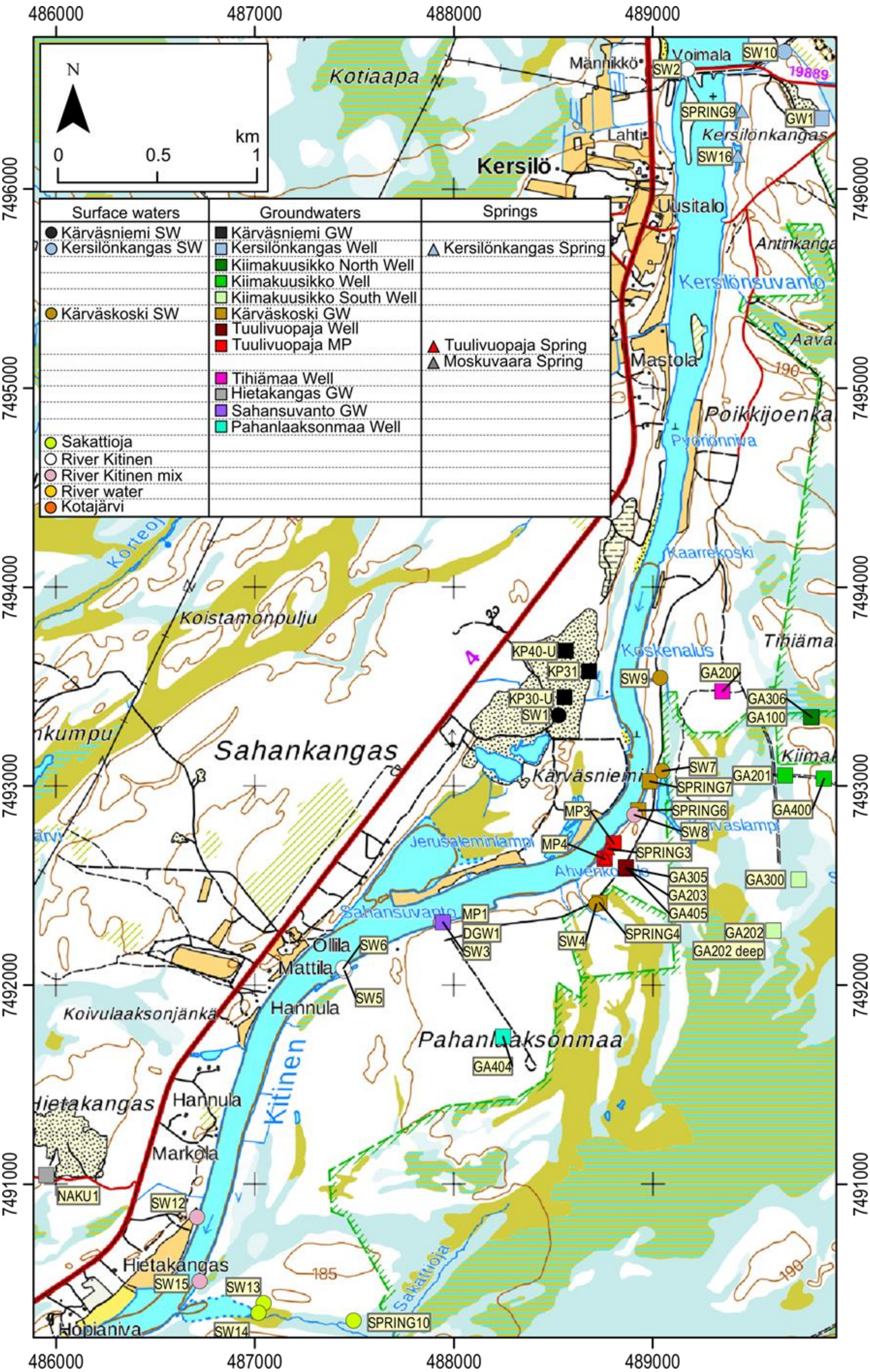

Figure 2. Sampling locations at the main study site at the western parts of Viiankiaapa mire. Base map (base map database @ NLS 2010).

2.1 Viiankiaapa mire

Viiankiaapa mire is a typical aapa mire being very wet and mostly treeless, apart from few higher and drier spots in the middle where pine and spruce grows (Figure 3) (Maunu and Virtanen 2005). Aapamires are minerotrophic peatlands that typically gain much of their needed nutrients from groundwater or surface water inflow (Charman 2002). Therefore, the water in the mires often strongly reflects the geology of the underlying bedrock or mineral soil (Rydin and Jeglum 2006). Water flow through the mire happens usually on the surface of the peat or very close to it (Bleutens et al. 2006). Even if majority of the outflow takes place through surface water runoff, aapamires are also drained by evaporation and seepage to groundwater reserves beneath the peat layer (Charman 2002). Overall, hydrology of aapamires can be consider to be very complex and different parts of the mire system have unique hydrological characteristics.

Figure 3. View from the edge of the mire. A typical higher spot for the otherwise treeless mire is seen on the right side of the image. The higher spot is called Kiimakuusikko and can also be seen on the right edge of Figure 2.

Western parts of Viiankiaapa are protected by both European union’s Natura 2000 conservation network and National mire conservation program issued by the Finnish government. Total size of the Natura protected area is 6594.84 hectares (European Environment Agency (EEA) 2017). The mire is part of both the Birds and the Habitats directive and houses 11 different protected habitat types, 21 protected bird- and 2 protected plant species along with the near threatened European otter (*Lutra lutra*) (EEA

2017). The protected habitats and species are listed in Appendice 1. Also, in total, 91 different bird species have been observed in the area, making it an especially diverse bird habitat (Metsähallitus 2006). Further, the mire has been noted of being an important recreational area for the local communities, which adds to its protection value (ELY 2013).

2.2 Hydrogeological settings

Because the research site is located close to the ice divide of the latest Weichselian glaciation, there's a lack of eskers and other major glaciofluvial formations near the area (Johansson 1995, Åberg et al. 2017). This also makes the aquifers of the ice divide area rather unique, as majority of larger aquifers in the Finnish Lapland are hosted in eskers, deltas and sandurs composed from glaciofluvial sediment (Lahermo 1970).

Aquifers of the research area are mostly small in volume and often restricted by interlaying layers of low permeability (Salonen et al. 2015, Åberg et al. 2017). Groundwater formations on the banks of Kitinen are housed in fluvial sediments. These fluvial sediments are more abundant on the western side of the river and include channels, bar systems and dunes as morphological features (Salonen et al. 2015, Åberg et al. 2017). Springs are common at the foot of the riverbank, which is typical for sites where fluvial sediments are underlain by a poor permeability till and groundwater from higher ground flows towards a river (Lahermo 1970). Åberg et al. (2017) observed perched groundwater tables at the area due to poorly permeable till units.

Bedrock in Lapland commonly includes cracks and fissures, which can hold significant amounts of groundwater. Lahermo (1970) observed mean yield from over 200 bedrock groundwater observation wells to be 2000 liters per hour. Bedrock fractures of the area have a very dominant west-east lineation (Räsänen 2008, Åberg et al. 2017).

There are four classified groundwater areas near the study site, housed on the previously mentioned fluvial sediments. Finnish Environment Institute (SYKE) (2017a) describes that the material in the aquifers consists of weakly sorted sands and gravels that are commonly overlain by dunes and other aeolian sediments. Thickness of the sand and gravel layers varies, but the aquifers themselves are commonly from two to eight meters thick. None of the aquifers are actively monitored or used for municipal or industrial water supply (SYKE 2017a). Ahvenjärvenkangas is the only Class II groundwater area near the site, making it suitable for water supply use (Appendice 2). The three other groundwater areas in the close vicinity (Kersilönkangas, Pahanlaaksonmaa and Hietakangas) have been classified as Class III - other groundwater areas (Appendice 2). Further, approximately three kilometers downstream from Viiankiaapa there is a Class II groundwater area called Myllymaa (Appendice 2) and near Moskuvaara there is one more Class III area called Moskuvaara. Åberg et al. (2017) describes the Pahanlaaksonmaa and Kersilönkangas aquifers to be consisting of alternating till and sorted sediment units, which makes their hydraulic conductivity heterogeneous. However, according to them, Ahvenjärvenkangas might form a uniform groundwater reservoir due to its thickness and better continuity.

Groundwater tables rise rapidly during spring in mid-April due to snowmelt. During the summer groundwater tables get lower again, but reach another highpoint in October with the falls rainy season (Salonen et al. 2015). During winter groundwater tables steadily regress (Lahermo 1970). In the AA Sakatti Oy monitoring data, groundwater surface on the eastern side of the river has been observed to vary between +182 and +187 meters above the sea level. The main groundwater flow directions are from Kärväsniemi, and from Viiankiaapa, towards Kitinen (Salonen et al. 2015, Åberg et al. 2017).

During the field campaign, groundwater level was about 20cm above long term average in Sodankylä area (Appendice 3) (SYKE 2016). The groundwater table remained above average for most of the summer. Similar trend can be observed in other groundwater observation wells around Lapland (SYKE 2016). Natural groundwater in the surrounding area has been observed to mainly be of type Ca-HCO_3 and to have a temperature around 4 degrees Celsius around the year (Lahermo et al. 2002). Natural seasonal variation in the oxygen isotopic concentration is common in the northern and eastern Finland and $\delta^{18}O$ values in groundwater can be expected to be below -14.5 ‰ VSMOW (Lahermo et al. 2002, Kortelainen and Karhu 2004).

2.3 Climate of central Lapland

Central Lapland belongs to the continental, subarctic climate which in Finland is only common for this area and some eastern parts of the country. The climate is characterized by long, cold winters and mild summers. On average at Sodankylä, thermal summer (daily average temperature is over 10 °C) begins on 9.–14.6 and lasts a less than three months until 23.–28.8. (Finnish meteorological institute (FMI) 2017a). Winter lasts approximately 7 months. First snow falls on average between 7.–17.10. and finally melts between 10.–20.5. (FMI 2016). January is the coldest month of the year with temperatures ranging between -13 and -14 °C. The warmest month is July when temperatures are on average between +13 and +14 °C (Kersalo and Pirinen 2009).

The average yearly rainfall in the area is 450–550 mm and almost half of it is accounted as snow (Kersalo and Pirinen 2009). The driest season lasts from February to April having on average 25–30 mm of rain per month. The rainiest months are July and August that have on average 60–70 mm of rain per month (Kersalo and Pirinen 2009).

2.4 Petrology of Sakatti ore and western Viiankiaapa area

Viiankiaapa is located within the paleoproterozoic central Lapland greenstone belt. In 2009, Anglo American Ltd. found a rich Cu-Ni-PGE deposit in the mafic-ultramafic igneous extrusions and intrusions of the belt. The Sakatti deposit consists of three bodies of olivine cumulate (Figure 4). According to Brownscombe et al. (2015), the ore bodies are surrounded by volcanoclastics and breccia unit on the northern side and by aphanitic unit and mafic- and ultramafic rocks on the southern side (Figure 4). The volcanoclastics consist of phyllite with biotite porphyroblasts and forms the uppermost unit in the hanging wall of the Sakatti deposit (Brownscombe et al. 2015). The hematite-dolomite-albite-talc altered breccia unit is highly heterogenous and located above the main ore body (Brownscombe et al. 2015). The aphanitic unit surrounds the main ore body closely and consists of plagioclase rich picrate with olivine phenocrysts. In addition to the aphanitic unit, a chlorite-amphibole altered mafic unit surrounds the southernmost body of the deposit (Brownscombe et al. 2015). The orebody is partially underlying the Natura 2000 protection area (the western edge of the protection area is seen in the background map of Figure 4, marked with a green, hashed line).

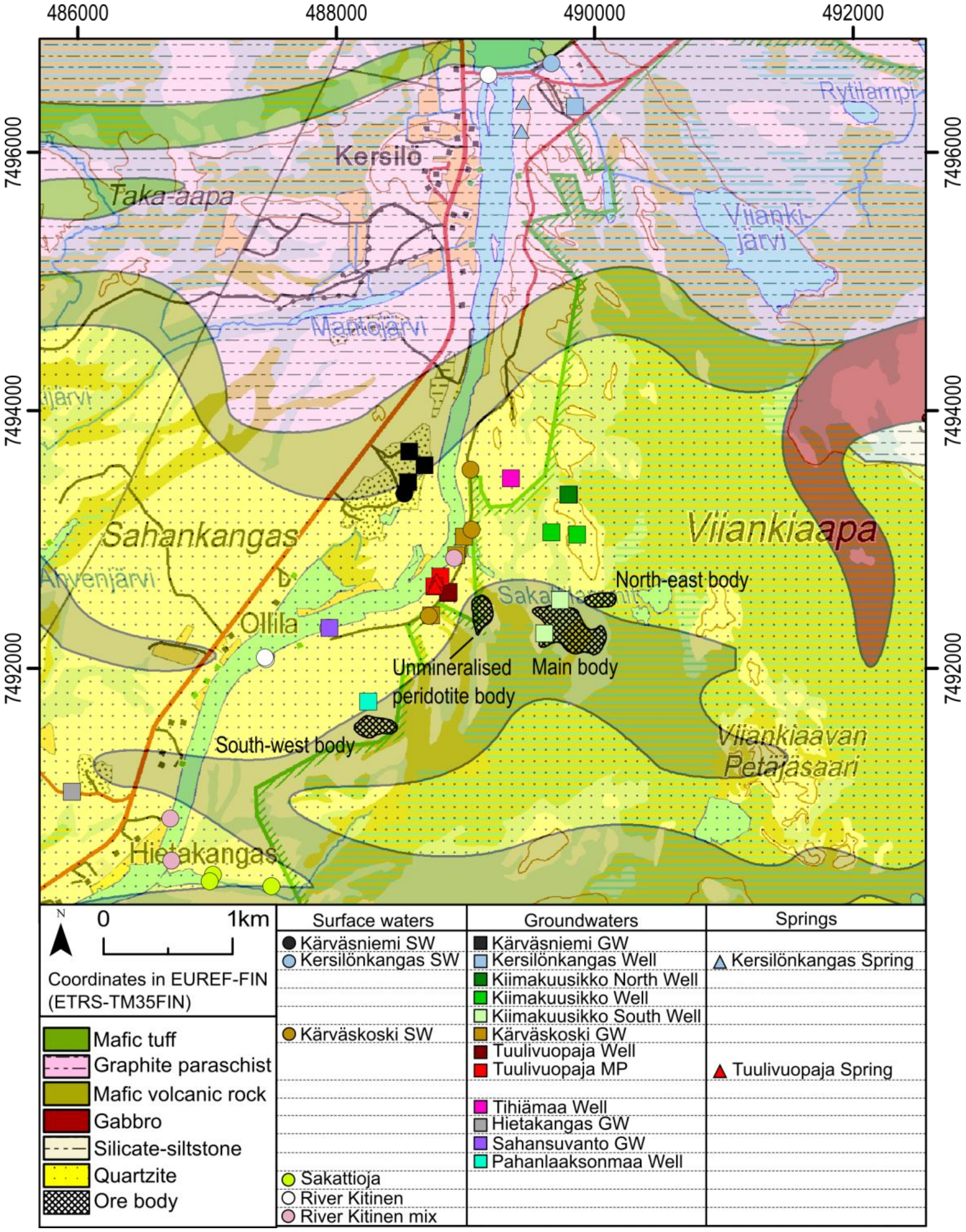

Figure 4. Bedrock map of the main research area. Scale for the bedrock map is 1:200000. Location of the ore bodies is approximated from Brownscombe et al. (2015). Location of the sampling sites is provided as a point of reference. Bedrock data (Bedrock data base @ Geological survey of Finland (2014)). Base map (base map database @ NLS 2010).

2.5 Anthropogenic impacts

Identifying possible sources of anthropogenic pollution and contaminants is important while characterizing hydrogeochemical composition of water, especially when trying to identify sources for possible anomalies. Knowledge about the previous anthropogenic sources of contaminants could possibly also be useful in the future, if the mining project commences. Without information about the pre-mining conditions, differentiating mining related contaminants from other and older contaminant sources is hard (Runnells et al. 1992).

Viiankiaapa has a long history of human presence. Hay was collected from drier parts of the mire until the 1950’s and the oldest barns in the area are more than hundred years old (Pääkkö 2004). However, the research area can be considered fairly pristine and major sources for anthropogenic impacts and pollution are scarce. Population around the main site is sparse and there are only few houses on the western side of Kitinen. There is minor industrial activity, located mostly on the western side of the river, focusing on gravel and sand extraction. The gravel pits are visible in Figure 2 as dotted sand colored areas. Reindeers are hoarded in the area between the river and Viiankiaapa. Finnish national road 4 (also known as European route E75) runs along the western banks of the river.

Kevitsa mine, located approximately 20km north from Viiankiaapa discharges its treated process waters into Kitinen. The mine produces copper and nickel. In 2007, it was estimated that the mine would discharge waste water at a rate of 25 l/s during summer, and 95 l/s during winter time and floods (Regional state administrative agency for Northern Finland (AVI) 2009). Estimated chemical quality of the treated waste waters is presented in Appendice 4.

There are seven hydroelectric power plants on Kitinen, the closest one (Matarakoski power plant) to the study area locating near sampling sites SW2 and SW10. The power plant is marked in to Figure 2 by a label “Voimala”. Water level of the river is regulated to prevent flooding during spring and to enable the operation of the hydroelectric plants. The damming has likely altered the hydrological conditions of the Viiankiaapa mire (Suonperä 2016). Pääkkö (2004) noted that also ditching and installation of culverts to local road 19889 from Kersilö to Moskuvaara (visible in Figure 1) has affected the natural flow of water in the area, but the exact hydrological changes were not specified.

On the western side of the river, at the Sahankangas area, there was a wood impregnation plant that was closed down in 1982. Despite minor chrome-, copper- and arsenic preservative leaks, groundwater quality is still noted to be good at the area (SYKE 2017a). Also, airborne nickel pollution originating from the Norilsk nickel smelter at Nikel, Russia has been observed in previous surface soil geochemistry surveys (Brownscombe et al. 2015). Elevated SO_4, Cu and Ni concentrations, originating from the smelters, have also been observed in small lakes close to the Russian border (Lappalainen et al. 2007).

3 MATERIALS AND METHODS

3.1 Sampling and sample preparation

To observe the chemical differences in different water types, a set of 49 stable isotope (oxygen, hydrogen), 41 dissolved silica (DSi), 38 major ion and 40 trace element samples were collected from 53 different ground- and surface water sampling sites during a field campaign between 5.8.2015–19.8.2015 (Figure 1, Figure 2, Table 1). The sampling was conducted per sampling strategy, which was to collect samples from locations possibly representing varying but distinct isotopic- and chemical water compositions. All accessible and known groundwater observation wells were included into the sampling strategy. Springs marked into large-scale topographical maps were also included into the strategy. Surface water samples were mainly collected from ponds and streams marked into small-scale topographical maps with emphasis on sites located between Kitinen and Viiankiaapa. Mini-piezometers were also installed to the same area. Surface water sampling sites were further evaluated on the field and locations that showed signs of groundwater–surface water mixing (low water temperature compared to average surface water temperatures) were favored.

Locations of the sampling sites, apart from the groundwater observation wells, were logged with Garmin Oregon 650t handheld GPS unit. The accuracy of the device can be expected to vary ±20m due to poor GPS signal in the Finnish Lapland. Locations of the groundwater observation wells were taken from the original well-logs by Golder Associates (2012).

Table 1. Location and background information about the sampling sites. Coordinates in EUREF-FIN (ETRS-TM35FIN).

ID	Date	Y	X	Water type	Soil type	Well bottom	Bedrock
NAKU1	7.8.	7491045	485953	Hietakangas GW^1	Sand		Quartzite
KP40-U	7.8.	7493680	488565	Kärväsniemi GW^1	Gravel		Mafic volcanic rock
KP31	7.8.	7493577	488682	Kärväsniemi GW^1	Gravel		Mafic volcanic rock/Quartzite
KP30-U	7.8.	7493445	488556	Kärväsniemi GW^1	Gravel		Quartzite/Mafic volcanic rock
SW1	7.8.	7493356	488527	Kärväsniemi SW^2	Gravel		Quartzite
SPRING1	7.8.	7498829	496238	Moskuvaara Spring	Bedrock		Peridotite
SPRING2	7.8.	7498427	495842	Moskuvaara Spring	Till		Graphite paraschist
SW2	7.8.	7496604	489176	River Kitinen	Till		Graphite paraschist/Mafic tuff
SADE1	8.8.	7477558	482352	Rainwater	Till		Biotite paraschist
SADE2	8.8.	7449309	497585	Rainwater			
SW3	8.8.	7492315	487946	River Kitinen	Gravel		Quartzite
MP1	8.8.	7492315	487946	Sahansuvanto GW^1	Gravel		Quartzite
GA200	8.8.	7493474	489350	Tihiämaa Well	Gravel	Till	Quartzite
GA305	8.8.	7492588	488865	Tuulivuopaja Well	Gravel	Till	Quartzite
GA203	8.8.	7492584	488865	Tuulivuopaja Well	Gravel	Gravel	Quartzite
GA405	8.8.	7492591	488867	Tuulivuopaja Well	Gravel	Bedrock	Quartzite
GA306	9.8.	7493346	489800	Kiimakuusikko North Well	C-peat	Sandy till	Quartzite
GA100	9.8.	7493346	489797	Kiimakuusikko North Well	C-peat	Peat	Quartzite
GA300	9.8.	7492530	489733	Kiimakuusikko South Well	Till	Bedrock	Mafic volcanic rock
GA202	9.8.	7492271	489607	Kiimakuusikko South Well	Till	Till	Mafic volcanic rock
GA202 deep	9.8.	7492271	489607	Kiimakuusikko South Well	Till	Till	Mafic volcanic rock
GA400	9.8.	7493036	489862	Kiimakuusikko Well	Till	Bedrock	Quartzite
GA201	9.8.	7493053	489666	Kiimakuusikko Well	C-peat^4	Bedrock	Quartzite
SPRING4	10.8.	7492413	488732	Kärvaskoski GW^1	Gravel		Quartzite
SW4	10.8.	7492407	488715	Kärväskoski SW^2	Gravel		Quartzite
GA404	10.8.	7491740	488247	Pahanlaaksonmaa Well	Gravel	Bedrock	Quartzite/Mafic volcanic rock
SW5	10.8.	7492072	487453	River Kitinen	Fine sand		Quartzite
SW6	10.8.	7492085	487444	River Kitinen	Fine sand		Quartzite
DGW1	10.8.	7492314	487937	River Kitinen mix	Gravel		Quartzite
SPRING3	10.8.	7492684	488776	Tuulivuopaja Spring	Gravel		Quartzite
SPRING9	11.8.	7496390	489447	Kersilönkangas Spring	Gravel		Graphite paraschist
GW1	11.8.	7496357	489847	Kersilönkangas Well	Gravel		Graphite paraschist
SPRING6	11.8.	7492878	488926	Kärväskoski GW^1	Gravel		Quartzite
SPRING7	11.8.	7493022	488985	Kärväskoski GW^1	Gravel		Quartzite
SW7	11.8.	7493076	489047	Kärväskoski SW^2	Gravel		Quartzite
SW9	11.8.	7493542	489039	Kärväskoski SW^2	Gravel		Quartzite
SW8	11.8.	7492856	488909	River Kitinen mix	Gravel		Quartzite
SPRING5	11.8.	7492635	488762	Tuulivuopaja Spring	Gravel		Quartzite
SW10	12.8.	7496690	489662	Kersilönkangas SW^2	Gravel		Graphite paraschist/Mafic tuff
SPRING8	12.8.	7500057	495127	Moskuvaara Spring	Till/gravel		Graphite paraschist
SW12	14.8.	7490834	486712	River Kitinen mix	Fine sand		Quartzite
SW16	15.8.	7496166	489429	Kersilönkangas Spring	Gravel		Graphite paraschist
SW15	15.8.	7490512	486722	River Kitinen mix	Fine sand		Quartzite
SW13	15.8.	7490399	487045	Sakattioja	Sand		Quartzite/Mafic volcanic rock
SW14	15.8.	7490350	487019	Sakattioja	C-peat^4/Sand		Quartzite/Mafic volcanic rock
SPRING10	15.8.	7490311	487498	Sakattioja	C-peat^4/Till		Mafic volcanic rock/Quartzite
MP3	15.8.	7492710	488805	Tuulivuopaja MP^3	Gravel		Quartzite
MP4	15.8.	7492634	488757	Tuulivuopaja MP^3	Gravel		Quartzite
SW17	17.8.	7496930	492483	Kotajärvi	Till		Graphite paraschist/Mafic tuff
SW18	17.8.	7489364	484693	River water	C-peat^4		Quartzite
SW19	17.8.	7481741	483060	River water	Till		Quartzite

[1] GW = groundwater [3] MP = mini piezomenet

[2] SW = surface water [4] C-peat = carex peat

Samples were collected into new high density polyethylene bottles (HDPE) that were washed beforehand with ion exchanged water. Before collecting the samples, the bottles were rinsed twice with the water from the sampling site. Groundwater samples from observation wells were primarily collected with inertia pumps. On few sites that had narrower older observation wells, or the pipe specific inertia pump was missing, minipiezometers were used to draw water from the wells (Figure 5). Minipiezometers were installed into three locations by the bolt-method first introduced by Lee and Cherry (1979). With both the regular groundwater observation wells and minipiezometers water was pumped out for at least several minutes, or as long as it took for the water to turn completely clear. All sample bottles were fully filled to minimize the airspace inside the bottle. This was done to limit isotope fractionation and chemical reactions. River water samples were taken from midstream and/or flowing parts of the stream to avoid sites where stagnant water could have altered the isotopic composition of the surface water (IAEA 2001). If sampling was done from a riverbank, samples were collected close to the bottom of the river while taking care that the bottom sediment of the river wasn't disturbed. On deeper parts of the river, where accurate sampling close to the bottom would've been more challenging, samples were collected from the depth of 1 meter to avoid the immediate surface water.

Figure 5. Groundwater sampling from a groundwater observation well using a minipiezometer and a syringe. Photo: Kirsti Korkka-Niemi.

Water samples for metal and cation analyses were prefiltered through VWR International 25mm syringe filters with 0.45 µm polypropylene membranes. New polypropylene syringes and filters were used for every sample. The syringes and filters were also rinsed with the sampling water before the actual sampling. HNO_3-acidified syringes and filters (0.45 µm) were used for samples for metal analyses. These samples were collected into 10ml polyethylene tubes with added 0.1 ml HNO_3 to prevent the precipitation of metals.

During the field work samples were stored in coolers with several icepacks for a maximum time of 10 hours. After returning from the field, samples for anion analysis were preserved in a freezer. Samples for stable isotope, DSi, cation and metal analysis were preserved in a refrigerator. Some samples for the anion analysis had to be stored in a refrigerator due to freezer space limitations. Samples were transported to University of Helsinki in coolers. Frozen samples stayed solid throughout the transportation.

All samples intended for stable isotope analysis were pipetted into 2 ml glass vials. The vials were filled completely, sealed and stored in a refrigerator. This was done to limit the fractionation of water isotopes happening when samples are stored for longer periods in HDPE bottles. According to IAEA (2001), HDPE –bottles with narrow necks can be expected to store the original isotopic signature only for few months. The glass vials stored in cool space with relatively low airspace, however, can maintain the original isotopic composition of water for several years without substantial fractioning (IAEA 2001).

3.2 Stable isotope composition of water

Through decades, isotopic composition of water (oxygen (^{18}O) and hydrogen (^{2}H or D)) has been utilized in numerous different applications dealing with natural- and contaminated waters (e.g. Fritz et al. 1976, Thorburn et al. 1993, Ladouche and Weng 2005). This is partly due to the stable isotope composition being very intrinsic parameter, which, in most cases, can be used to analyze groundwater samples from shallow aquifers independently from their chemical composition. However, in studies focusing on wetlands the method has been used quite rarely and was, for example, used for wetland mass balance calculations as late as 1996 by Hunt et al. (1996). This might be partially due to challenging temporal variations in wetlands caused by changes in temperature and peatland water balance conditions (meaning that the site should be monitored for long periods before solid conclusions can be formed) (Hunt et al. 1996) and the overall poor scalability of results from one peatland to other (e.g. Ladouche and Weng 2005, Ferlatte et al. 2015).

The method itself is based on the observation that higher isotopic mass of a $^{2}H^{2}H^{18}O$ molecule causes the molecules vapor pressure to be lower compared to other lighter molecules (Friedman 1953). Lower vapor pressure results in enrichment of heavier isotope in the liquid phase, while the lighter isotope is more ready to evaporate and exist in vapor form. In rainwater, the effect is reversed causing the heavier molecule to condense first leaving the water vapor in the cloud depleted of the heavier isotope

(Friedman 1953). The depletion progresses further towards the poles of the earth and inland from large water bodies like seas (Friedman 1953, Dansgaard 1964).

During the summer rainwater is more depleted of heavier elements in comparison to precipitation during the winter (Rozanski et al. 1982). During snowmelt, waters tend to become progressively more enriched with the heavier isotopes (Stichler 1987). In groundwater, the seasonal variation in stable isotope composition, typical for surface waters, is highly attenuated. Normally, in the shallow aquifers of the temperate region, the isotope composition follows the isotope composition of local rainfall (e.g. Clark and Fritz 1997, Kortelainen and Karhu 2004). The contrast in isotopic composition between surface- and groundwaters can also be used to distinguishing the water types from each other (Clark and Fritz 1997).

The samples were analyzed at the Department of Geosciences and Geography, University of Helsinki in August 2016 using Picarro L1115-i isotopic water analyzer that uses the cavity ring-down spectroscopy (CRDS) -method. Standard laboratory protocol was followed while analyzing all the samples, meaning that the results were standardized against three different water isotope quality standards. The isotope results are presented as per mill (‰) difference to Vienna Standard Mean Ocean Water (VSMOW) -standard (Equation 1).

$$\delta^{18}O \text{ or } \delta D = \frac{R_{sample} - R_{VSMOW}}{R_{VSMOW}} * 1000 \qquad \text{(Eq. 1)}$$

The isotope results are commonly compared against Global Meteoric Water Line (GMWL), which is based on the isotopic composition of precipitation from locations all around the globe (Craig 1961). A Local Meteoric Water Line (LMWL), composed by Kortelainen (2007) and based on Finnish precipitation values, is also used for comparison.

Deuterium excess (d-excess) can be calculated from the $\delta^{18}O$ and δD values (Equation 2) (Dansgaard 1964). The result can be used as to identify if evaporation has affected the isotopic signal after precipitation. Deuterium excess values that are clearly below global precipitation average of 10‰ indicate that the isotopic signal has been affected by evaporation processes (Kendall and Coplen 2001).

$$d\text{-}excess = \delta D - 8\delta^{18}O \qquad \text{(Eq. 2)}$$

3.3 Dissolved silica and trace elements

Dissolved silica and trace elements were analyzed using Agilent 7500ce/c inductively coupled plasma mass spectrometer (ICP-MS). The method is commonly used for analyzing similar water samples. All analysis were done by laboratory personnel, following the standard laboratory protocol of the University of Helsinki's geoscience laboratories. The standard protocol includes e.g. analyzing reference materials, doubles and blanks along with the samples (Virkanen et al. 2014).

3.4 Major ions in water

Ion chromatography (IC) was used to analyze anion (F-, Cl-, NO^{2-}, Br^{-}, NO^{3-}, PO_4^{3-}, SO_4^{2-}) and cation (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations in the samples. Analysis was carried out following standards from Finnish Standards Association (SFS) and using MIC-12 ion chromatograph. Standard SFS EN-ISO 14911 was used while analyzing cations and standard SFS EN-ISO 10304 was followed while analyzing anions. Alkalinity was analyzed in the laboratory with a potentiometric automatic titrator following method SFS EN-ISO 9963-1.

3.4.1 Ionic balance (IB)

Water in its natural state has a neutral charge. Therefore, the positive charge induced by the cations should be close to equal to the negative charge caused by the anions. The difference in anion and cation sums can be observed as ionic balance (IB), which shows the difference in positive and negative charges as a percentage. Ionic balance can be calculated with Equation 3 after the equivalent weights of the positive and negative ions have been added (Freeze and Cherry 1979).

$$IB\ (\%) = 100 * \frac{\sum cation - \sum anion}{\sum cation + \sum anion} \qquad \text{(Eq. 3)}$$

In optimal conditions IB should be equal to 0%. However, slight ion imbalances are quite common in water analytics. With water samples, a threshold of 10% is commonly used (Appelo and Postma 2004). Basically, if the imbalance exceeds 10% it means that there may be some source of error that could've happened during sampling, analysis or calculations. Ionic balance that exceeds 10% doesn't automatically mean that the results get discarded. If the source of the imbalance can be reliably identified, the results can still be used.

3.5 Electrical conductivity, temperature and pH

Electrical conductivity, temperature and pH are among the most measured variables in water quality analysis. The variables were all analyzed both in the laboratory from bottled samples and on the field using a YSI 600XLM-V2-M multiparameter water quality instrument. The sensors of the device were calibrated in a laboratory before the field campaign using standard calibration liquids. Unfortunately, at the field the temperature sensor of the device was observed to be inaccurate, and for the most part the water temperature readings can only be considered as indicative measurements. Along with the YSI, a Therma Plus stainless steel sediment temperature probe (Electronic Temperature instruments Ltd., accuracy 0.10 °C) was used. Electrical conductivity and pH were analyzed using the same YSI device. Due to old pH sensor, the measurements took a lot longer to complete than usual. Still, it was attended that the values in the device stabilized before taking up any readings. Electrical conductivity was analyzed in laboratory following standard SFS EN-ISO 5794 and using CON6/TDS6 conductivity meter.

3.6 Statistical methods and visualization

Results were further analyzed by means of statistical analysis and different visualization methods. All statistical analyses were performed in IBM SPSS Statistics version 24. The Piper diagram was generated in AquaChem version 2014.2. Maps were produced with ESRI ArcGIS 10.3 and tables in Microsoft Excel 2016. Maps, plots, tables and diagrams were further enhanced in Inkscape version 0.91, which is an open sourced vector editing software. All other software licenses were provided by the University of Helsinki.

3.6.1 Preparing data for multivariate data analysis: Shapiro-Wilk test for distribution, log_{10} transformation and data normalization.

All statistical methods used in this study expect the data to be normally or log-normally distributed. However, hydrogeochemical data rarely has a normal distribution and failing to take this into account will lead to biased or faulty results (Reimann and Filzmoser 2000). To ensure that the data would be as well suited as possible for the analyses, each of the variables' distributions was individually analyzed for normality using the Shapiro-Wilk test (first described by Shapiro and Wilk (1965)). Significance level for the test was chosen to be 5 percent ($\alpha = 0.05$), which is a commonly used significance level for the test while analyzing geochemical data (Reimann et al. 2011). Our null hypothesis was that *the hydrogeochemical and -logical data from Viiankiaapa is normally distributed* and our alternative hypothesis was that the *data isn't normally distributed.* Basically, if the Shapiro-Wilk test estimates a p-value higher than the chosen significance level, a distribution fulfills the null hypothesis, if the p-value is less than the chosen significance level the alternative hypothesis is correct (Shapiro and Wilk 1965).

If a tested variable didn't fulfill the null hypothesis, a base 10 logarithmic transformation (log-transformation) was applied to the results. The log-transformation is a very commonly used method, which helps especially with high skewness and kurtosis often present in geochemical data (Reimann et al. 2011). The transformation also tends to lessen the impact of data outliers, which have a very negative impact on the accuracy of multivariate data analysis, but are also many times the most interesting part of a geochemical data set (Reimann et al. 2011).

After the previous steps the data was normalized to make all variables comparable to each other. This was done with Equation 5, where x is the value being normalized, mu (μ) is the mean and sigma (σ) is the standard deviation of the variable.

$$x_{normalized} = \frac{x-\mu}{\sigma} \tag{Eq. 5}$$

The other, maybe even more commonly used option is to standardize the data. Problem with standardization is that while it neatly bounds all the values into the same scale (e.g. between 0 and 1), it also tends to diminish outliers and data variation by squeezing the values inside the chosen scale. Normalization on the other hand preserves the outliers better than standardization, but doesn't bound the data to any scale. Un-bounded data can cause problems with some multivariate methods like principle component analysis, because these methods tend to give higher emphasis on variables with high values (Reimann et al. 2011). In our case however, the variation in the results was quite small after normalization, and thus normalization was chosen over standardization.

Most of our trace elements contained so called censored values, which are values that do not represent real concentrations found in the samples. In our case, all censored values were values below the detection limit of the ICP-MS used for trace element analysis. This kind of censored values are very common in hydrogeochemical datasets (Güler et al. 2002). Censored values aren't appropriate for multivariate analysis, and have to be transformed into unqualified values before such methods are used (e.g. Farnham et al. 2002, Güler et al. 2002). Many different approaches exists for dealing with censored values. One common method, for example, is to replace values below detection limits with ¾ of the detection limit value (Güler et al. 2002). However, for example that particular method is not recommended if over 10% of the values are censored (which is the case with most of our trace elements) as it can lead to inaccurate analyzes (Sanford et al. 1993). An expectation–maximization algorithm (EM) was used to impute the censored values. The EM is a mathematically complicated iterative algorithm, which background theory is well outside the scope of this thesis. Basically, the EM is one method to attempt to find a maximum likelihood estimate (MLE). The MLE is commonly used in statistical analysis and for example Sanford et al. (1993) and Güler et al. (2002) recommend MLE to be used for imputing values in cases where large number of values exist below detection limits. EM was chosen to estimate the MLA because it is readily available via SPSS through the Missing Value Analysis –tool. Maximum number of iterations was set to be 100. The same method was used to estimate trace element concentrations and other results for the 11 sites that didn't have all analyses done from them. This brought the total number of valid cases in SPSS up to 49. Without the imputed values the case number would've been limited to 36 (i.e. sites where samples to all water analyses were collected from).

The data processing flow before multivariate analysis is shown in Figure 6. Major elements, DSi, isotopes, pH and EC were allowed to have non-normal distributions and still enter the multivariate analysis (results from the Shapiro-Wilk test after data transformations are shown in Appendice 10). All of these variables were also included into the analyzes, even though some of them (particularly pH, F and SO_4) had only very weak correlations with other variables. These concessions were made partially to keep the number of variables sufficient and partially because the aforementioned variables usually have the greatest impact on water geochemistry.

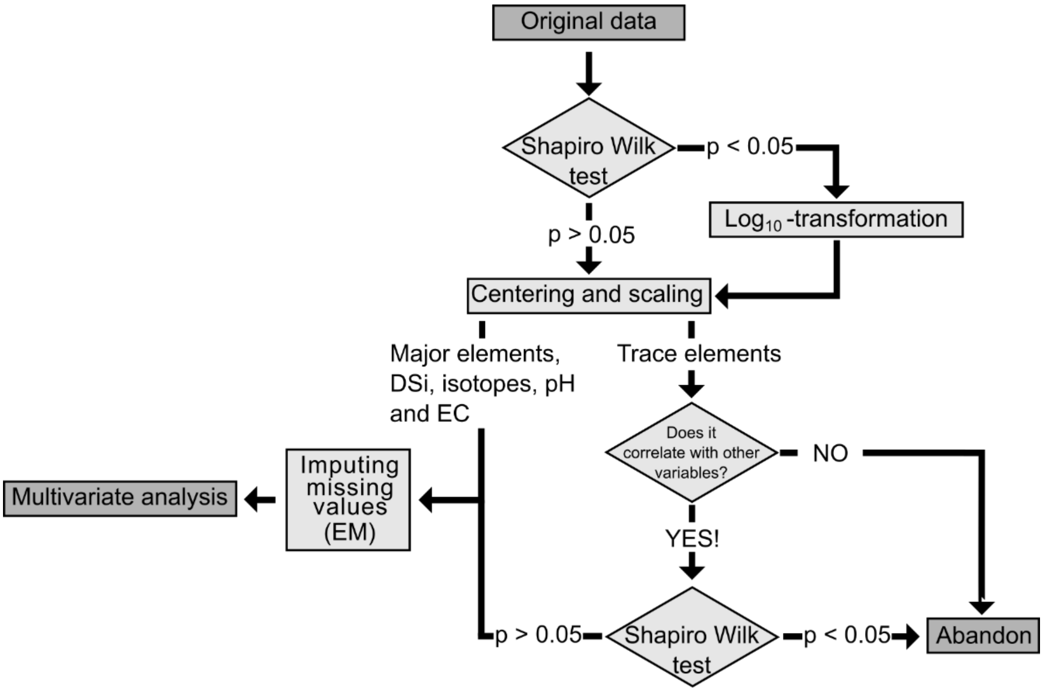

Figure 6. Process flow chart of the data preparation procedure used before multivariate analyzes.

3.6.2 *Bivariate correlation*

Variables were compared to each other via bivariate correlation using Pearson and Spearman correlation methods. A high Pearson coefficient (r) indicates linear correlation in the values of two variables, while a Spearman correlation (ρ) only shows if the two variables have a monotonic relationship. In text, significant correlations (two-tailed, significant at the 0.01 level ($p < 0.01$)) are marked with two asterisks (**), correlations that are single-tailed and significant only at level 0.05 are marked with one asterisk (*) and correlations that are otherwise worth mentioning, but do not reach either significance level are presented without asterisks'. In our data, most analysis are done with quite small sample size for bivariate analysis (from 36 to 49, depending on the variables chosen).

Bivariate correlation requires that a linear connection must exist between the variables. Connections between tested variables in our data were not always even close to linear. In some cases, the connection could be improved by carrying out logarithmic transformation to one or both variables. This step helped especially with variables that had multiple clear outliers and/or were right-skewed (i.e. the distribution had a long tail on the right-hand side). A scatterplot matrix of all correlations between major ions, isotopes and DSi are shown in Appendice 5. This scatterplot matrix was also used as a basis while analyzing the linearity of correlation for principle component analysis. Unfortunately trace elements had to be left out of the matrix for purely technical reasons – the resulting matrix would have been too large for SPSS to generate.

3.6.3 Principal component analysis

The goal of the principal component analysis (PCA) is to take a large amount of data and simplify it into as few comprehensive principal components (i.e. factors or 'groups of variables') as possible to make the interpretation of the results easier (Rock 1988). The first principal component (PC) explains as much of the variation in the original data as possible, the second tries to explain all the variation that the first PC couldn't explain and so forth until all input variables can be explained by the principal components (Rock 1988).

Modern computers and software have made PCA easily accessible. It is to be noted however, that PCA is an error-prone procedure even with large datasets and optimal data. The accuracy and viability of PCA compared to true factor analysis is often debated (Costello and Osborne 2005). On the other hand, PCA is also a fairly robust method, meaning that it can cope with inconsistencies (like non-normal distributions and non-linear correlations) in the inputs fairly well without compromising the results (Ranta et al. 1989). This, along with the facts that PCA has less input variables and that results from PCA and true factor analysis are often strikingly similar (Costello and Osborne 2005), made PCA the dimension reduction method of choice for this study.

Principal component analysis can be considered to be a method for analyzing large datasets. With smaller datasets, like the one used for this study, a risk exists that PCA will only show random variation from the original data without being able to identify real connections between variables (Ranta et al. 1989). However, the method is suitable for analyzing smaller datasets as long as the quality of the data is high enough to produce at least moderate (.50 or better) loadings in multiple components (Costello and Osborne 2005).

Before the analysis it needs to be ensured that sufficient relations between different variables exist. This was done with a correlation matrix which was also used as a basis for the analysis itself. The other option is to use a covariance matrix, but this choice isn't rational with samples that have different units (e.g. EC and pH). When a correlation matrix is used, the data needs to be normalized, but this also makes the analysis of variables with different units possible.

The number of resulting principle components was limited with Kaiser criterion. This means that all factors with eigenvalues greater than one were retained. Eigenvalue arguably isn’t the best choice for limiting factor size as it often tends to produce too many principal components (Velicer and Jackson 1990). On the other hand, Eigenvalue is the most commonly used method and includes minimal manual calculation making it very simple to use (Costello and Osborne 2005). Varimax was chosen for the rotation method. It is the most commonly used rotation in PCA and differences caused by between different rotation methods are often minor (Costello and Osborne 2005).

3.6.4 Hierarchical cluster analysis

Hierarchical cluster analysis compares variables of individual samples in pairs and forms clusters of samples possessing the least dissimilar values (Bridges 1966). The method combines similar samples into smaller number of groups that are easier to handle than large quantities of data. The method is best suited for datasets having less than 200 samples, which makes it suited for this study. The method is largely used in different applications of statistical analysis, being also a common tool in water sample analysis (see for example Vega et al. 1998, Suk and Lee 1999, Alberto et al. 2001 and Shrestha and Kazama 2007).

Ward’s method was chosen as the cluster method. The method starts by comparing individual samples to each other, pairs them based on their similarity and continues further pairing these small groups until it reaches one large cluster that includes the whole dataset (Ward 1963). This minimizes the increase in the within-cluster distances and thus tends to produce clusters that are small sized. The method is well suited for water samples as the variables tend to be quantitative and the variance in the results tends to be small (chemical quality of natural water can be considered to still vary by only relatively small scale). In other words, this means that small numerical differences can have big impact on water composition while interpreting the results. These small differences are emphasized by the Ward’s method which favors small cluster sizes.

With Ward’s method, a measuring interval proportional to Euclidean distance is recommendable as the method uses squared Euclidean distance to form the clusters. Thus, Euclidean distance was set as the distance measure. Euclidean distance requires quantitative variables, and is a relatively simple and widely used distance measurement method, but unfortunately doesn’t always work well with standardized or normalized values (Reimann et al. 2011).

Results from the cluster analysis were arranged to a dendrogram. This visualization step was done as it provides an easy way to see the similarities and dissimilarities in the data.

3.7 Previous water quality data

Overall, good and comprehensive water quality data with sufficient sampling resolution was fairly hard to find from the research area. Hydrological and especially hydrogeological studies in Lapland have traditionally been very locale or have had low sample resolution – likely due to the regions large size and remoteness. Further, hydrological conditions between different peatlands vary vastly, which makes drawing conclusions from other sites difficult and error prone (e.g. Ladouche and Weng 2005, Ferlatte et al. 2015). In the end, the results are compared mainly with results from Lahermo et al. (1996a, 1996b) and Lahermo et al. (2002), which are highly respected nationwide groundwater, stream water and well water studies, yet have few samples from our immediate research area. To a smaller degree, the results were also compared with surface water data from SYKE and groundwater monitoring data from Anglo American Sakatti Oy (both described below).

3.7.1 Surface- and groundwater databases by the Finnish environmental institute.

Water quality database by SYKE (2017b) provides some basic information and water quality data from Kitinen and the lakes in the area. For Kotajärvi, Viiankijärvi, Kokkolampi and Rytilampi -lakes data is available from only one sampling done in 1996, focusing mainly on the most basic parameters (such as pH and temperature) and nutrient loads (Appendice 6). However, for Kitinen, data is available from different parts of the river and for longer time periods. One of the most comprehensive datasets is available from Matarakoski dam, where samples have been collected since 1967 and more or less systematically since 1994. In this dataset, along with the basic parameters such as pH, temperature and alkalinity, also some chemical elements have been analyzed. From the dataset, the closest samples before and after our field campaign (10.8.2015 and 7.9.2015) were mainly used and are shown in Appendice 7. The samples were originally collected by Ramboll Finland Oy, and are presumably related to the river water monitoring program required from the damn operators.

As for groundwater, data is available less comprehensively. SYKE (2017a) shows some basic information of the groundwater areas near the site, such as soil material and an estimation about the amount of forming groundwater. Only one actual groundwater sample with analysis results is publicly given. The sample has been collected on 10.10.2016 from a pond of exposed groundwater in the gravel pits on the western side of Kitinen. According to coordinates, the sample is from the south-west orientated pond on the southernmost edge of the gravel pit, south-west from sample site SW1. The pond can be seen in Figure 2. The results contain basic information such as temperature, pH and electrical conductivity (Appendice 8).

3.7.2 Groundwater monitoring data of AA Sakatti Mining Oy.

Some previously collected water quality data from the groundwater observation wells in the research area was available for study. The data has been used with a permission from AA Sakatti Mining Oy, which holds the rights for the use of the database. The data has been collected between 4.4.2012–7.10.2013. Sampling interval has been irregular, but most sites have been sampled once every two or three months.

The older data was mainly used to compare it to the current data. Unfortunately, several issues and challenges made the full utilization of this resource difficult. One drawback is that the older data lacks some key variables like chloride. Another inconvenience is that most of the measured values represent total values, not filtered dissolved values. Before 23.5.2013 only total concentrations have been analyzed. Both total- and dissolved concentrations have been measured 27.–28.8.2013 and only dissolved values have been analyzed from those two days onwards. This makes a significant portion of the older data not readily comparable with the current results.

However, a more serious issue is that the older data has errors that make reliability of the data questionable. For example, dissolved concentrations of magnesium are labeled to be in unit µg/l, while the actual values very strongly suggest that the unit should be mg/l. Another irrationality is that dissolved concentrations commonly have higher values than total concentrations. For example, from groundwater observation well GA402 on 27.8.2013 a total concentration 1.97 mg/l of potassium has been measured, yet at the same time the amount of dissolved potassium has been analyzed to be 2.21 mg/l. Similar issues are present with many other variables (e.g. Mg, Mn and Na) and in samples from many other observation wells. Identifying and fixing all the problems in the old data is nearly impossible due to random nature of the errors and the sheer size of the database.

4 RESULTS AND DISCUSSION

The research material collected from the area is fairly comprehensive, especially when the difficulties with the location of the study site are considered. The research area is located approximately 1000km north from the University of Helsinki, the area is very large and the time of the field period was limited to two weeks. Some of the groundwater observation well samples meant to be collected from the mire had to be abandoned due to the extremely wet mire being too hard to transverse.

4.1 Water type and general chemical composition of the waters

As can be seen from the piper diagram (Figure 7), most water samples from the research area have composition close to the natural Finnish groundwater composition Ca–HCO_3, which is dominated by alkaline earths Ca and Mg and weak acids. However, on four locations Na–HCO_3 type waters were detected. Generally, groundwater samples from Kiimakuusikko area show a clear drift towards the alkali – carbonate (Na + K and HCO_3) corner of the diagram. Cation triangle shows a very spread out distribution without Mg or Ca neither clearly dominating, while in the anion diagram samples plot along the HCO_3 side of the triangle. Here, samples from Kärväsniemi gravel pit and spring water samples from Moskuvaara slightly shift towards sulphate dominated corner of the diagram.

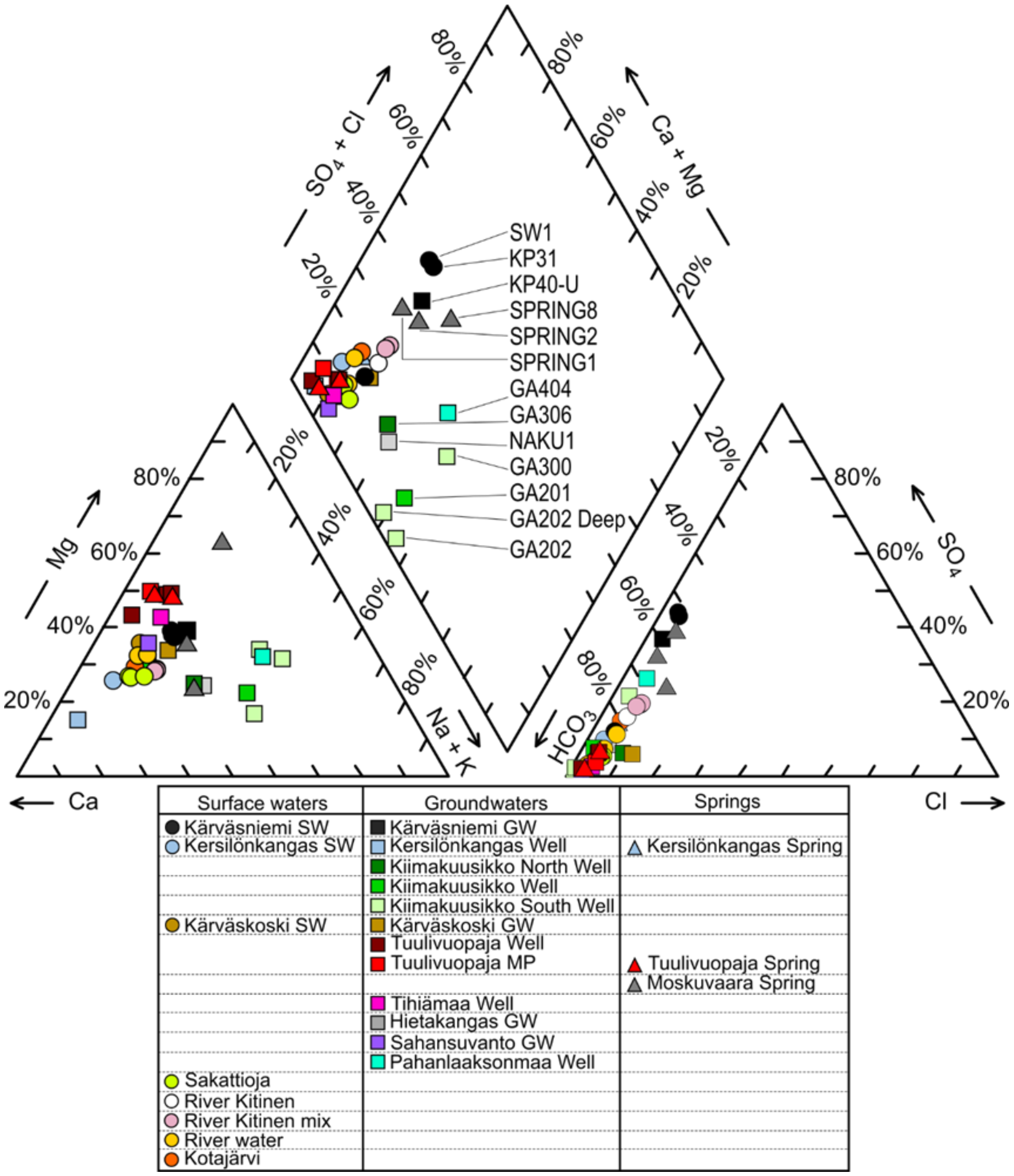

Figure 7. A piper diagram drawn based on the water samples from the research area. Most samples have the general Finnish groundwater composition of Ca-HCO_3, yet groundwater from the Kiimakuusikko area (green squares) drift towards the alkali corner of the main diagram.

4.2 Results from the analysis of pH, EC and major ions

Results from the analysis of major ions along with pH measured in the laboratory and field measured EC are presented in Table 2.

Table 2. Results from analysis of major ions and water quality indicators.

		pH	Cond	Na	K	Ca	Mg	F	Cl	NO_3	SO_4	HCO_3	$\sum$Cat	$\sum$An	IB
ID	**Date**	**lab**	(uS/m)	(ppm)								(mmolL^{-1})	(meqL^{-1})		(%)
KP40-U	7.8.	6.56	63.3	2.52	0.52	5.08	2.93	0.02	0.65	2.63	8.39	0.46	0.62	0.69	5.70
KP31	7.8.	6.22	35.2	0.74	1.05	2.95	1.50	0.01	0.40	0.83	6.23	0.37	0.33	0.52	22.76
KP30-U	7.8.	6.56	63.9	2.02	0.99	6.03	3.08	0.02	0.93	0.06	2.86	0.67	0.67	0.76	6.26
NAKU1	7.8.	6.91	24.8	1.63	0.23	2.20	0.73	0.02	0.64	1.54	1.34	0.36	0.25	0.43	27.45
SW1	7.8.	7.47	57.5	1.76	0.50	4.95	2.63	0.02	1.10	0.06	13.23	0.36	0.55	0.67	9.54
SW2	7.8.	7.23	35.7	1.37	0.46	4.19	1.38	0.05	0.88	0.09	3.04	0.27	0.39	0.36	4.41
SPRING1	7.8.	6.33	34.6	0.98	0.11	1.17	2.08	0.01	0.66	0.07	1.82	0.22	0.28	0.28	0.08
SPRING2	7.8.	6.67	43.6	1.79	0.70	3.76	1.86	0.07	0.63	0.05	5.36	0.33	0.44	0.46	2.42
GA305	8.8.	7.13	69.3	1.48	0.51	6.01	4.34	0.02	1.01	0.47	1.94	0.69	0.73	0.77	2.07
SW3	8.8.	7.13	34.6	1.31	0.44	3.99	1.31	0.05	0.83	0.09	2.86	0.34	0.38	0.43	6.57
GA203	8.8.	7.24	63.6	1.42	0.45	5.20	3.90	0.03	0.95	0.40	1.95	0.63	0.65	0.70	3.67
GA405	8.8.	7.05	191.9	1.88	0.83	21.17	10.72	0.05	1.64	0.11	1.93	2.19	2.04	2.28	5.49
GA200	8.8.	6.56	79.1	1.92	0.64	7.57	4.30	0.04	0.92	0.06	0.73	0.84	0.83	0.88	2.88
MP1	8.8.	7.15	88.5	2.44	0.58	9.79	4.11	0.05	0.79	0.06	0.78	0.94	0.95	0.98	1.59
GA306	9.8.	6.19	32.5	1.71	0.16	2.56	0.83	0.01	0.60	0.04	0.52	0.36	0.28	0.39	17.33
GA400	9.8.	7.24	57.2	1.73	0.56	6.52	2.24	0.03	0.83	0.13	2.04	0.66	0.60	0.73	9.84
GA300	9.8.	6.65	79.7	8.26	1.17	6.13	1.71	0.04	0.83	0.15	6.15	0.67	0.84	0.83	0.45
GA202	9.8.	7.77	169.5	17.34	1.60	7.93	6.62	0.08	0.65	0.02	1.59	1.85	1.74	1.90	4.54
GA202 deep	9.8.	7.83	161.5	15.23	1.83	9.66	7.50	0.08	0.68	0.03	1.97	1.79	1.81	1.85	1.15
GA201	9.8.	7.19	73.5	7.92	1.48	6.44	2.45	0.07	0.71	0.15	2.82	0.79	0.90	0.88	1.27
SW4	10.8.	7.00	23.9	0.58	0.05	2.69	1.09	0.02	0.31	0.02	0.39	0.30	0.25	0.32	11.66
SPRING4	10.8.	6.40	42.3	1.11	1.16	4.15	1.76	0.02	1.14	0.05	0.74	0.41	0.43	0.46	3.37
GA404	10.8.	7.08	40.2	2.28	2.15	2.04	1.47	0.05	0.75	0.12	4.78	0.31	0.38	0.44	7.62
SPRING3	10.8.	6.87	64.0	1.60	0.46	5.51	4.03	0.03	1.07	0.60	1.86	0.74	0.69	0.82	8.84
SPRING5	11.8.	7.19	88.9	1.45	0.46	8.34	5.53	0.03	1.06	0.04	0.68	0.96	0.95	1.01	3.23
GW1	11.8.	6.92	223.0	2.50	0.93	31.90	3.74	0.05	1.64	0.16	1.92	2.37	2.03	2.47	9.64
SW10	12.8.	7.07	36.3	0.77	0.19	5.30	1.28	0.03	0.46	0.07	1.58	0.34	0.41	0.39	2.55
SPRING8	12.8.	6.72	39.0	1.81	1.24	3.57	1.06	0.08	0.76	0.25	6.25	0.27	0.38	0.42	6.06
SW12	14.8.	7.09	44.1	1.59	0.53	4.81	1.55	0.06	1.13	0.09	3.94	0.36	0.45	0.48	3.07
SW13	15.8.	6.85	22.0	0.67	0.07	2.99	0.80	0.02	0.32	0.05	0.41	0.23	0.25	0.25	0.90
SW14	15.8.	6.49	23.4	0.76	0.05	3.19	0.85	0.02	0.32	0.02	0.39	0.24	0.26	0.26	0.33
SPRING10	15.8.	6.60	20.5	0.72	0.06	2.32	0.66	0.02	0.30	0.03	0.38	0.22	0.20	0.23	7.10
SW15	15.8.	7.15	42.0	1.57	0.59	5.09	1.61	0.06	1.08	0.10	3.84	0.37	0.47	0.49	1.55
MP4	15.8.	6.89	116.0	1.57	0.54	11.90	8.05	0.04	2.01	0.13	1.92	1.30	1.34	1.40	2.26
SW16	15.8.	7.25	56.6	1.56	0.34	6.65	1.85	0.03	0.98	0.04	3.45	0.48	0.56	0.58	1.96
SW17	17.8.	8.22	43.7	1.17	0.51	5.82	1.79	0.03	0.74	0.03	2.82	0.32	0.50	0.40	11.66
SW18	17.8.	7.08	43.0	1.19	0.34	5.67	2.00	0.04	0.84	0.05	2.15	0.39	0.51	0.46	4.72
SW19	17.8.	7.09	37.0	1.18	0.38	4.66	1.73	0.04	0.63	0.05	1.21	0.36	0.44	0.41	3.50

IB = ionic balance

4.2.1 pH

Mean value for pH at the research area was 6.97. This can be considered higher than expected as earlier studies by Lahermo et al. (1996a) and Lahermo et al. (1996b) show that the values should be closer to 6.5 despite the water type. Also, variation in the results is quite large (range was 2.02). The variation is probably at least partially explained by the fact that the results represent pH values measured at the laboratory, and not actual in-situ measurements. The in-situ pH measurements had to be discarded due to measurement instrument malfunction.

River water samples from Kitinen seem to be slightly more acidic compared to other surface water samples (Figure 8), simply meaning that the environment is more acidifying upstream from the study site. However, our pH results from the river were actually slightly more alkaline than those presented by SYKE (2017b). In their results pH was 7.00 before and 7.10 after our sampling date, while our results were 7.23 and 7.13 from sites SW2 and SW3 respectively. The difference, however, is very small and can easily come from e.g. different sampling sites and different sampling dates as SYKE (2017b) results have been collected by the damn and our samples represent water from further downstream. Further, also in the SYKE (2017b) database pH seems to vary from about 6.9 to 7.2 between different measurements. Overall it can be observed that the mean pH for all river water samples is very close to mean value of groundwater samples, yet this could be a mere coincidence.

In the sample from lake Kotajärvi, the very high pH (8.22) could possibly be explained by an unknown source of high alkalinity, but more likely than that, the result is a measurement error. SYKE (2017b) contains previous sample results from Kotajärvi on 28.2.1996. The results are quite old, meaning that the conditions at the lake could've changed substantially in past 20 years. The samples have been taken from three depths and the pH in each was 6.9 (1m), 6.8 (7m) and 6.7 (13m). Also, pH of the lake is likely somewhat higher during the summer due to biological activity, but our results can still be considered questionable. The Kotajärvi sample was originally mainly intended to act as a background sample, but the highly out of the ordinary pH along with its unbalanced IB makes it unsuitable for that purpose. Repeated measurements should be done in order to verify the results.

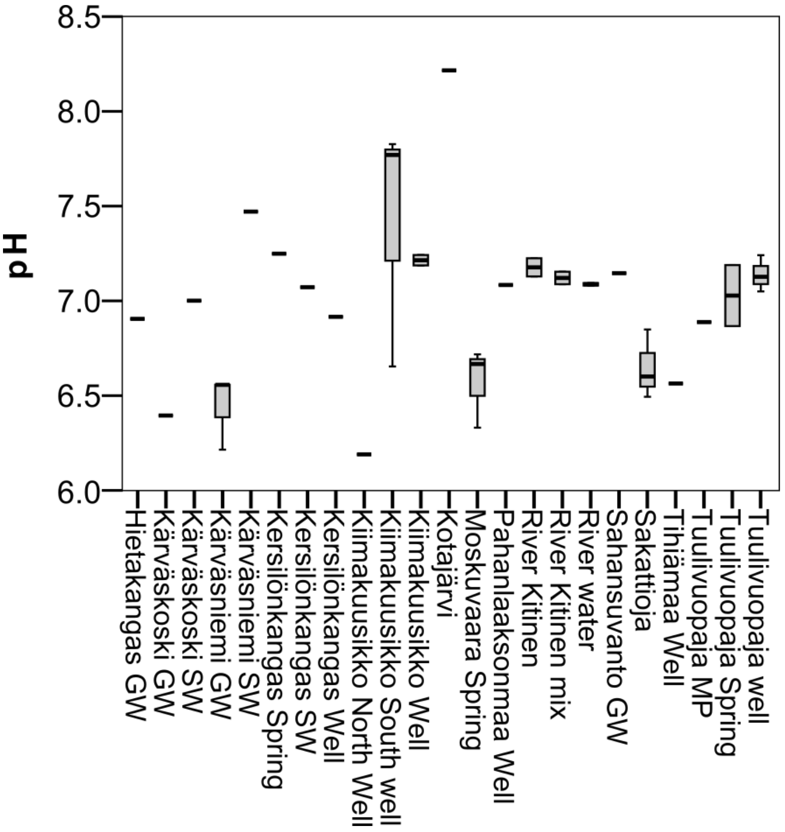

Figure 8. Distribution of laboratory measured pH values from the study site. Distribution is show in relation to water type.

Laboratory measured pH correlates poorly with almost all variables. Most of the connections are weak and non-significant. The only significant two tailed Pearson correlation is seen with fluoride, but the correlation is still quite weak (r = .497**). In a scatter diagram, no clear correlation is seen between the two variables, which likely indicates that the correlation coefficient is exaggerated by the analysis. Weaker single tailed correlations are seen with EC (r = .348*), Ca (r = .681*), Mg (r = .345*) and U (r = .412*). The nonparametric Spearman correlation shows significant correlations with Ca (ρ = .453**) and U (ρ = .476**), in addition to the fluoride (ρ = .474**). Commonly pH correlates well at least with alkalinity (e.g. Drever 1988, Lahermo et al. 2002), but in our case no such correlation is seen (r = .301 and ρ = .260, both nonsignificant). The unusual correlations are possibly at least partially explained by the fact that the measurements reflect laboratory results, measured from bottled samples, not in-situ measurements. Lahermo et al. (2002) noted that in their results laboratory measured pH values were up to 0.39 units higher (in samples from dug wells) compared to field measurements, and explained this by dissolved carbon dioxide (CO_2) being released from the samples during sampling, transportation and storing. They further explained that the shift in the results was largely dictated by amount of dissolved CO_2 in a water sample, which also varied by water type. This means that it is hard to estimate how much the pH of the individual water samples has been affected by the handling and storing, which might also add random, nonsystematic error to the results.

4.2.2 Electrical conductivity

Similarly to Lahermo et al. (1996a, 1996b) results, most samples show low EC values indicating low amounts of dissolved solids (mean value in our data is 64.9 µS/m) (Figure 9). Also, samples from Kitinen line up very nicely with the previous data from SYKE (2017b) with differences smaller than 4 µS/m.

In our data electrical conductivities over 70 µS/m are only seen in groundwater samples. However, also groundwater samples with very low EC do exist (like the GA306 of Kiimakuusikko North Well with a conductance of 32.5 µS/m). On a few locations clearly higher than average EC values were observed. These were Kersilönkangas Well (223.0 µS/m), Kiimakuusikko South Well (169.5 µS/m), Tuulivuopaja MP (116.0 µS/m) and sample GA405 from Tuulivuopaja Well (191.9 µS/m). The same sites also commonly act as outliers with other variables.

In the data, EC seems to correlate strongly with all major ions apart from NO_3 and SO_4. This is of course very natural as the EC of water is largely dictated by those ions. The variable also correlates with many trace elements (Mn, Rb, Sr, Y, Cs, Ba, La, Ce, Pr, Nd, Dy, Pb and Y), of which it clearly has a linear correlation at least with Y (r = .648**), Sr (r = .835**) and Rb (r = .720).

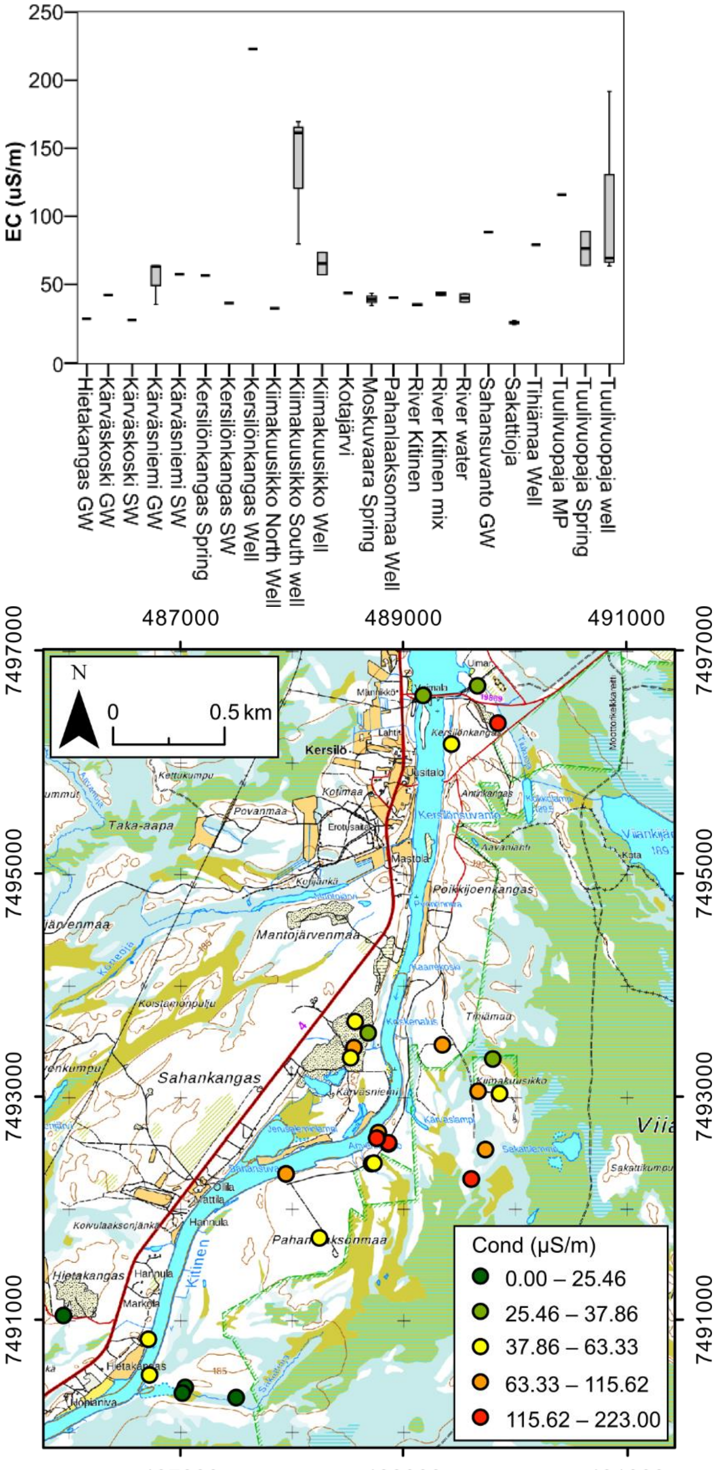

Figure 9. Distribution of electrical conductivity measurements. In the map, results have been classified into four intervals based on geometrical interval. Base map (base map database @ NLS 2010).

4.2.3 Sodium – high concentrations at four sites

Average sodium concentration in our data is 2.62mg/l and the values are spatially quite heterogeneously spread out (Figure 10). Overall, the amount of sodium in our samples can be considered slightly low when compared with Lahermo et al. (1996a, 1996b) results. On the other hand, the low concentrations from Kitinen match very well with data from SYKE (2017b) with differences less than ±0.2 mg/l.

Interestingly, however, our results are heavily affected by four outlying samples. These are GA300 (8.26 mg/l), GA202 (17.34 mg/l), GA202 deep (15.23 mg/l) and GA201 (7.92 mg/l). The sites are located fairly close to each other at the southern side of Kiimakuusikko (Figure 10). All samples are from groundwater observation wells. Even the 7.92 mg/l in the sample GA201 can be considered to be highly elevated, as the median amount of sodium in the rest of the samples (n = 34) is 1.57 mg/l. Chloride values in the outlier-samples are on natural levels, which rules out anthropogenic and other sources at least in the form of sodium chloride (NaCl). Lahermo et al. (1996a) observed slightly elevated sodium values in the area of Lapland’s schist belts, but on the other hand Lahermo et al. (2002) noted that rock type doesn’t seem to affect sodium values substantially in Finland. Other variables to show at least slightly elevated levels at the four sites are potassium, alkalinity and molybdenum.

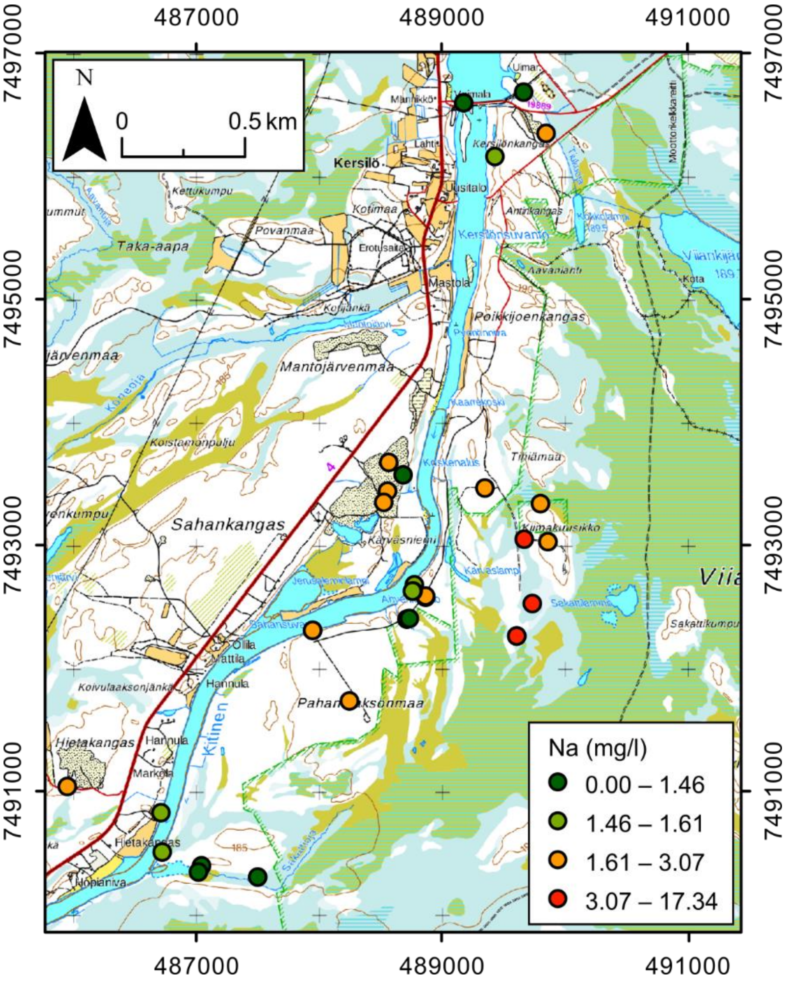

Figure 10. Distribution of sodium results. Note the wide range in the interval containing the highest values. Still, this interval contains only the samples GA300, GA202, GA202 deep and GA201, as other samples show far smaller concentrations. The results have been classified into four intervals based on geometrical interval. Base map (base map database @ NLS 2010).

Interestingly, the high sodium values are present also in the older AA Sakatti Mining’s monitoring data from 2012–2013. In the older samples sodium values as high as above 130 mg/l are present and high sodium values have also been observed in other groundwater observation wells in the close vicinity. A slight overall decrease in the sodium values can be observed over time, but the decline hasn’t been occurring linearly (Figure 11).

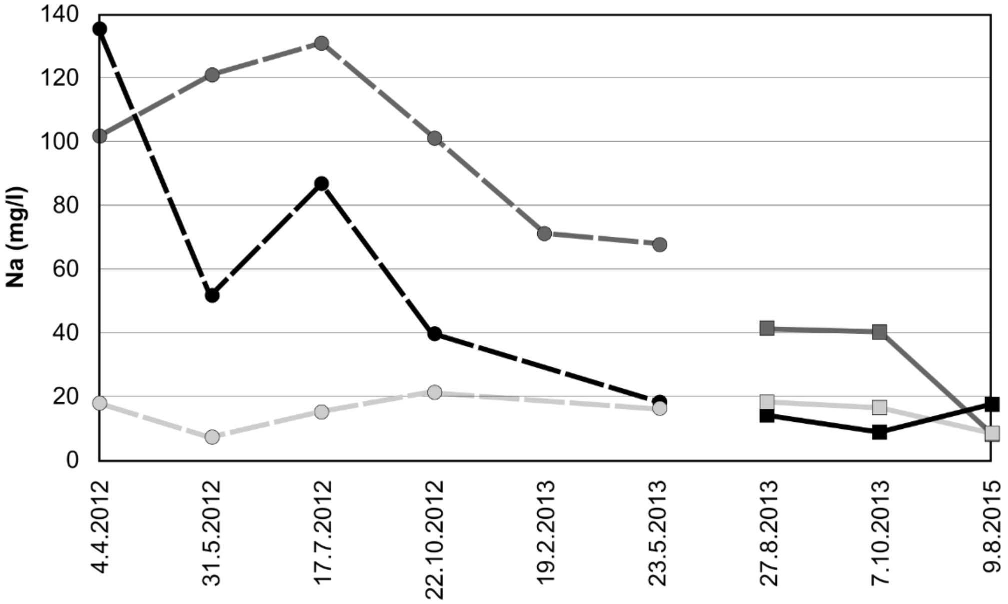

Figure 11. Change in sodium concentration over time. Light gray markers represent site GA201, dark gray is GA300 and black is GA202. Samples until 23.5.2013 are total values (dashed line and circle symbols), while values from 27.8.2013 onwards are dissolved values (solid line with square symbols). 9.8.2015 -data was collected for this study. Earlier measurements are AA Sakatti Mining Oy's monitoring data.

In our data sodium correlates well with multiple variables, including $\delta^{18}O$ (r = -.627**), δD (r = -.653**), DSi (r = .706**), EC (r = .688**), K (r = .680**), Ca (r = .422**), Mg (r = . 509**), F (r = .581**) and HCO_3 (r = .642**). It also correlates moderately (r ~ .5**) with most trace element including Sr, Y, La, Ce, Pr, Nd and Dy. In the current study, values of dissolved oxygen were not measured. However, in the older data from AA Sakatti mining Oy it has been monitored, from which it seems that the locations having unusually high sodium values also have relatively high dissolved oxygen contents compared to other groundwater sampling sites.

The distribution of sodium values is poor and doesn't follow normal distribution (Figure 12). This is largely due to the four outlying Na samples. The correlations and the estimated correlation coefficients between Na and other variables are also affected by these outliers. In strict interpretation, and in interpretation focusing on generalizing the data, these outliers should be removed (IBM 2017). If this is done, all correlation coefficients are generally slightly improved, but with Cl this improvement is drastic (Figure 13). Sodium and chloride usually have a very strong linear correlation (Lahermo et al. 1996a), which is not present if the outliers are not removed from the data. Unfortunately, if the few sites that show high sodium are separated into an independent dataset, the resulting sample size of four is too small to show any correlations between variables. The sample size of four is also too small for a reliable bivariate correlation.

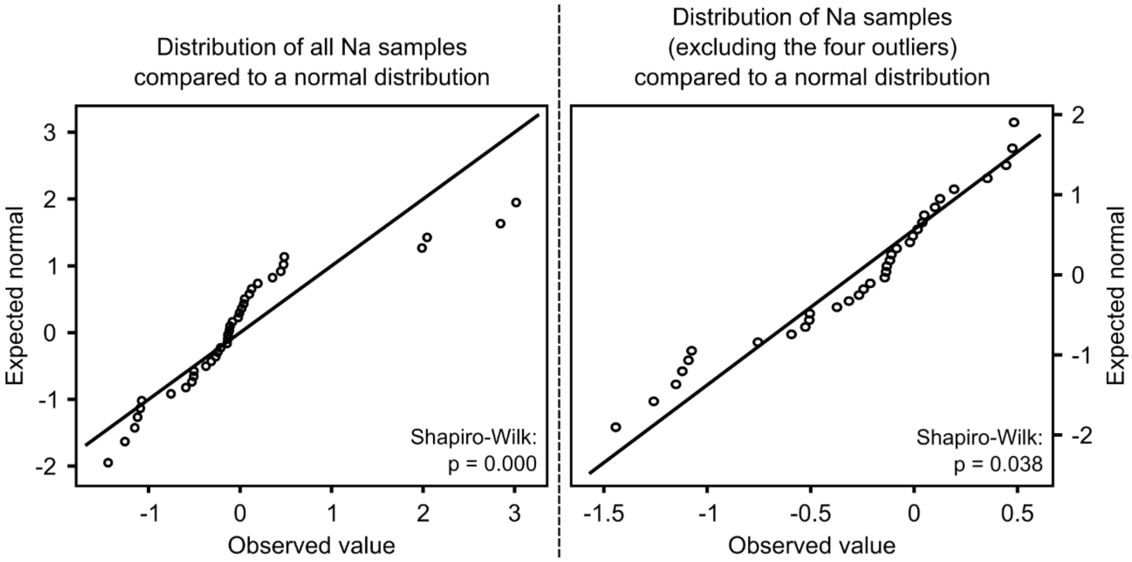

Figure 12. Distribution of Na samples compared to normal distribution required for many of the statistical analyzes. The distribution of the data is much improved if the four outliers in the data are removed, but on the other hand these outliers are of particular interest while interpreting the results.

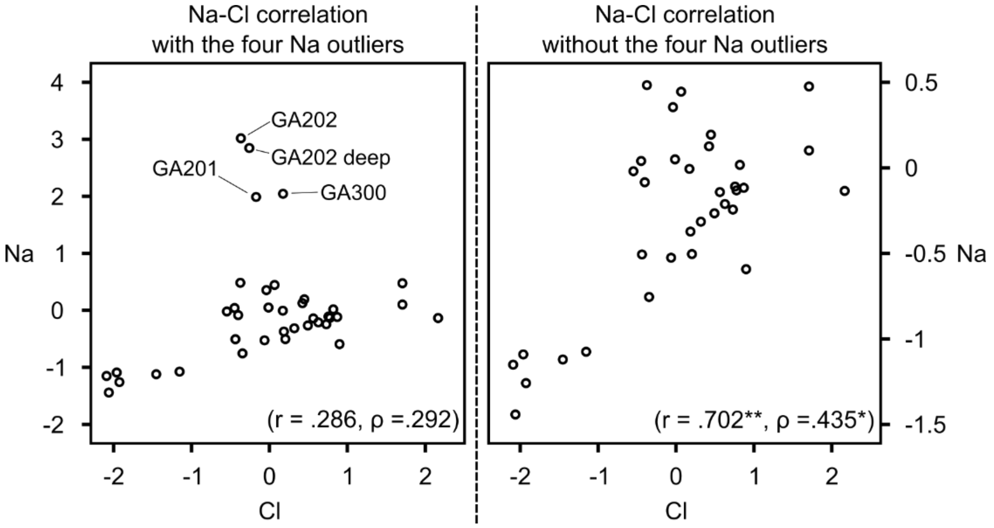

Figure 13. Correlation between sodium and chloride. The correlation coefficient is drastically hindered by the four Na outliers in the data (left graph). If the outliers are removed a clear correlation between the variables is seen on the right graph. Note the different vertical scale in Na values. All values have been log-transformed and normalized.

One possible source for the high sodium concentrations could be the albite hosted in the breccia unit around the ore body quite close to the sites with high concentrations. Albite ($NaAlSi_3O_8$) is the Na-rich end member of the albite-anorthite series. It weathers down to kaolinite ($Al_2Si_2O_5(OH)_4$) through reaction shown in Equation 6. Kaolinite is common in groundwater systems that exist in igneous rocks, as the other albite weathering products, like Na-montromillonite, are not stable in regular groundwater pH, pressure and temperature conditions (Freeze and Cherry 1979, Hiscock 2009). The reaction releases Na^+ ions into the surrounding soil solution thus providing a source for the high sodium concentrations. The reaction also releases silica as can be seen from Equation 6. The H+ ions required for the reaction could be provided by the mire in ample quantitates in the form of different organic acids – like carbonic acid (H_2CO_3).

$$NaAlSi_3O_8 + 4½\, H_2O + H^+ \leftrightarrow Na^+ + 2Si(OH)_4 + ½Al_2Si_2O_5(OH)_4 \qquad \text{(Eq. 6)}$$

Other source considered as an explanation for the high sodium values was shield brines. Shield brines are relatively common Ca-Na-Cl brines that occur at shield areas in deep crystalline rocks and have high salinity (Clark and Fritz 1997). Mixing of shield brines and regular groundwater has been observed before (Frape and Fritz 1982). Shield brines, however, have a tendency to alter δD signal by showing extreme enrichment and rising the values often by tens of per milles above the GMWL (Clark and Fritz 1997). All samples from Sakatti plot below the GMWL making substantial interactions with shield brines unlikely.

Further, Ladouche and Weng (2005) observed high salinities in groundwater below Rochefort marsh in France. The high salinity was caused by seawater trapped into clay sediments. The seawater evolved over time by rock-water interactions and mixing with the surrounding groundwater, but the high salinity was preserved. However, in their case the high salinity was observed with high Cl values even above >110 mg/l, which are not present at our site.

4.2.4 Potassium

Potassium content usually varies substantially depending on if the water is surface- or groundwater (Lahermo et al. 1996a, 1996b). At the research area, natural potassium concentrations for springs and dug wells should be slightly below 3.0 mg/l, for boreholes below 1.5 mg/l and for stream waters below 0.5mg/l (Lahermo et al. 1996a, 1996b). Generally, samples from the research area follow these background values, yet the results vary by quite a large scale. Smallest values are below 0.1 mg/l while the highest concentration was 2.51 mg/l (GA404 from Pahanlaaksonmaa). Also, high or low potassium concentration does not seem to be tied to any particular water type and high and low values seem to exist in almost all parts of the research area, apart from mire water from Sakattioja, which seems to be characterized by low potassium concentrations.

By default potassium results show a very non-normal distribution ($p = 0.001$) and the base 10 logarithm transformation doesn't improve the score by much ($p = 0.005$). Also, like with sodium, the poor results seem to be caused by outliers. Overall, potassium does seem to have some sort of connection with sodium, because the strongest correlation coefficient of K is seen between the two (r = .680**, ρ = .723**). This connection is indicated by the PCA where potassium is loading fairly strongly in principal component 3, mostly due to its connection to Na. Linear correlation between Na and K is slightly improved if the outlying Na values are removed (r = .703**), yet the non-parametric correlation is weakened (ρ = .623**). This means that the high K concentrations are connected to sites with high Na values, but the change in K concentration isn't proportional to changes in Na concentration (Figure 14). The correlation of sodium and potassium is very interesting as in the nationwide geochemistry mapping by Lahermo et al. (1996a) it was noted that high potassium and sodium concentrations don't generally appear together. The earlier hypothesis about albite–kaolinite weathering can be considered as a potential source for the areas potassium as albite can include up to 10% of potassium. This would explain the unusual correlation between the elements. Other thing to consider is that potassium and sodium are both alkali metals, which means they tend to favor similar chemical reactions and so might act and react similarly in the subsoil, even if they are from different lithological origins.

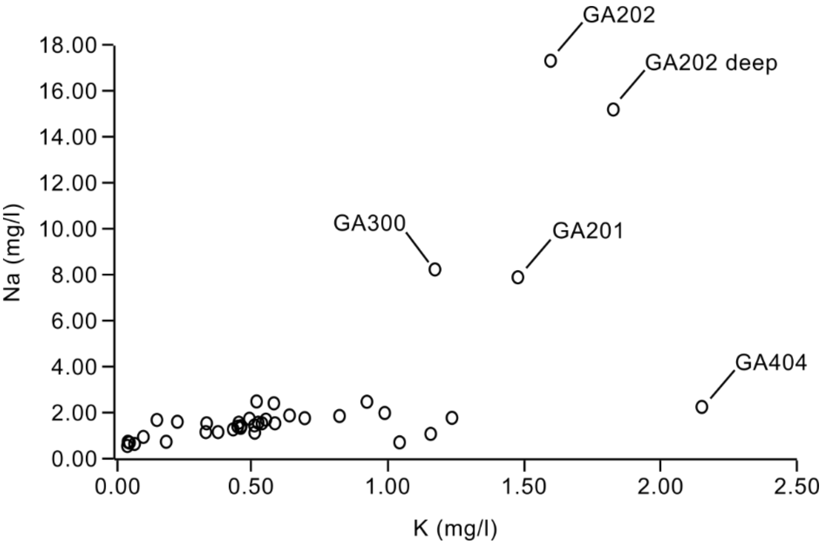

Figure 14. Correlation between sodium and potassium. Change in Na concentration isn't proportional to changes in K concentration. Na outliers also hinder the correlation clearly. Still, a linear correlation between the two variables can be seen.

Potassium also has moderate correlations with other major constituents, including δ^{18}O (r = -657**), δD (r = -.569**), DSi (r = .594**), EC (r = .648**), Ca (r = .473**), Mg (r = .540**), F (r = .545**), Cl (r = .587**), SO_4 (r = .615**) and HCO_3 (r = .642**). Connection to all of these variables shows at least small signs of linearity on a scatter plot. Potassium shows correlation to few trace-elements as well (Dy (r = .498**), Sr (r = .624**), Y (r = .554**), La (r = .495**), Pr (r = .486**) and Nd (r = .509**)). However, if observed on a scatter diagram, these connections do not appear very linear, which means that the correlation coefficients could be over exaggerated.

4.2.5 Calcium, magnesium and water hardness

In the Sodankylä –area, calcium concentrations can be expected to be below 10 mg/l in surface waters (Lahermo et al. 1996b) and below 20 mg/l in groundwater (Lahermo et al. 1996a). The only real exception to this rule is sample GW1, which contains 31.9 mg/l of Ca. Mafic- and ultramafic rocks of the greenstone belt have been observed to increase Ca values of water along with local deposit of carbonate rocks (Lahermo et al. 1996a). However, the sampling site is located on graphite paraschist on 1:200000 petrological map. Other samples collected from the area of the same rock type don’t show unusual values. The sampling site is located at the bottom of a gravel pit and the groundwater observation well where the sample was taken from seemed improperly installed, perhaps introducing some anthropogenic effect.

With magnesium, results are on par with Lahermo et al. (1996a, 1996b) observations. The concentrations, however, are slightly high compared to surrounding Lapland. One possible source for this are the mafic rocks in the area (Salminen 1995). Till in the middle Lapland greenstone belt also contains fairly high loadings of magnesium naturally (Lintinen 1995). A clearly elevated concentration of 10.72 mg/l was seen in the sample GA405, which is from a bedrock well in the Tuulivuopaja area, possibly further highlighting the lithological effect.

Water hardness can be calculated based on the calcium and magnesium results. Water hardness is the concentration of calcium and magnesium ions expressed as an equivalent of calcium carbonate ($CaCO_3$), and can be calculated using Equation 7.

$$Water\ hardness\ as\ CaCO_3\ equivivalent = 2.5 * [Ca\,] + 4.1 * [Mg] \qquad \text{(Eq. 7)}$$

The research area has a mean water hardness of 0.27 mmol/L (1.53 German degrees (°dH)) making the water medium hard. This is quite high considering that the water supply company of Inari and Sodankylä area reports that its intake water has hardness ranging from 0–1 °dH, meaning that the water is soft or very soft (Inergia 2017).

Calcium and magnesium concentrations correlate very strongly to each other (r = .745**, ρ = .806**) and they seem to behave similarly in the samples and appear at the same locations in similar concentrations (Figure 15). This is not surprising as Ca and Mg are by far the most common alkali-earth metals and cations in our samples and act similarly due to their similar chemical composition. In addition to each other, both variables correlate very strongly (r > .7**) to EC, HCO_3 and Sr, which are all logical connections as EC is largely defined by Ca and Mg, HCO_3 is the most common anion that balances the positive charge that the Ca and Mg induce and the trace element Sr is an alkali-earth metal like Ca and Mg, and so behaves similarly, even though it is present only in very small quantaties.

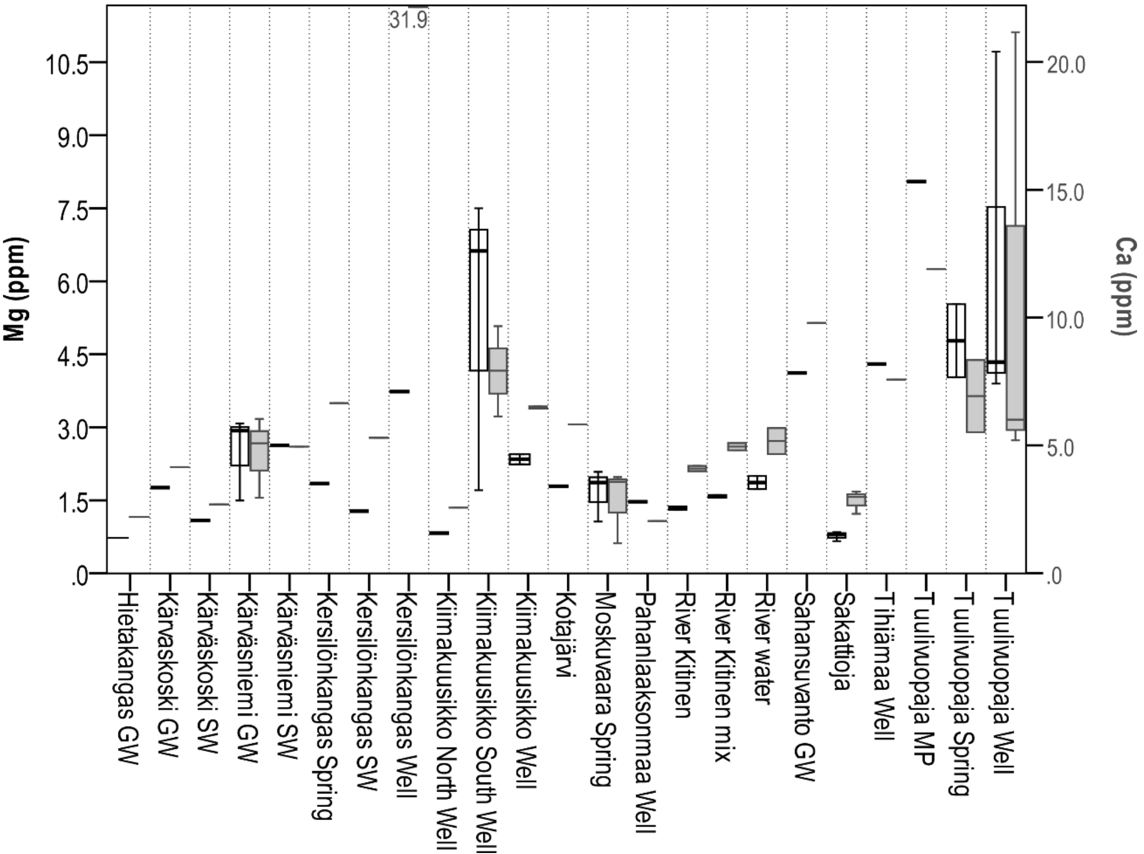

Figure 15. Spatial distribution of magnesium and calcium results. Samples with high magnesium concentration also tend to have higher amounts of calcium and vice versa.

4.2.6 Fluoride

Fluoride shows very low concentrations in all samples and the highest value measured was 0.08 mg/l –present at Moskuvaara Spring. The low concentrations were expected as the area doesn't contain K-rich granites, which are the usual source for higher concentrations of fluoride in the Finnish Lapland (Lahermo et al. 1996a). Fluoride does however show many significant connections to other variables, including pH (r = .497**), EC (r = .471**), Na (r = .581**), K (r = .545**) and Ca (r = .484**), yet when observed at the scatter plot the connections seem fairly random. Thus, the connections might be partially explained by the fact that there are a relatively low number of F samples with relatively low amount of variation, which increases the chance for random variation affecting the correlations and other statistical analyzes.

4.2.7 Chloride

Chloride results show natural background levels on all samples when compared with results from Lahermo et al. (1996a, 1996b). Tuulivuopaja area and Kersilönkangas well show slightly elevated values compared to other samples, but still have chloride concentrations below 2 mg/l. Other samples have chloride concentrations around or below 1 mg/l. This kind of value is to be expected with uncontaminated surface waters, but can be considered to be slightly low compared to groundwater background levels which could be expected to range between 5−10 mg/l (Lahermo et al. 1996a).

Correlation is seen mostly with other major ions including EC (r = .673**), K (r = .587**), Ca (r = .646**), Mg (r = .653**) and HCO_3 (r = .586**) along with the trace-element strontium (r = .650**). On a scatter diagram it can be seen that the correlation to any of these variables isn't particularly linear, but still clearly exists.

4.2.8 Nitrate

As is commonly known, significant amounts of nitrogen in natural water almost always reflect anthropogenic sources. As expected beforehand, nitrate values are generally very low at the research site as there is no remarkable human population, farming or industrial sites in the vicinity.

The highest NO_3 concentrations were 2.63 mg/l measured from KP40-U in Kärväsniemi GW and 1.54 mg/l from NAKU1 in group Hietakangas GW. All other samples had concentrations lower than 0.20 mg/l. Both the Kärväsniemi and Hietakangas site are groundwater observation wells on the bottom of active or recently active large gravel pits. Thus, the source of higher than average values has probably something to do with the gravel extraction, possibly due to the fact that by extracting the soil acting as a water filter, the groundwater in the area has become much more vulnerable to pollution (Wilson 1984).

4.2.9 Alkalinity (HCO_3^-)

Here, the term *bicarbonate (HCO_3^-)* is used synonymously with the term *alkalinity*. This is because carbonates (CO_3), hydroxyl ions (OH^-) or other potential bases like borates, phospates or silicates usually have negligible impacts on the total alkalinity in the neutral or slightly acidic Finnish groundwaters.

According to Lahermo et al. (1996a), alkalinity should have values around 0.5 mmol/L in groundwater near the study site. Most of water samples show alkalinity values close to this as the median value is only slightly lower at 0.38 mmol/L. The range of measured values is quite high (2.16 mmol/L) and standard deviation is 0.549. Again, samples from Kersilönkangas well (GW1 2.37 mmol/L), Tuulivuopaja (GA405 2.19 mmol/L, MP4 1.30 mmol/L) and groundwater samples from Kiimakuusikko South Well (GA202 1.85 mmol/L and a deeper sample from the same well at 1.79 mmol/L) stand out with their unusually high results. Elevated alkalinity, along with increased pH and Ca concentrations, have been found to be common characteristics for minerotrophic peatlands (Bendell-Young and Pick 1997, Bragazza and Gerdol 2002). The five samples also have pH and Ca results that can be considered to be on the higher end when compared to the rest of our results, but not elevated when compared to studies by Lahermo et al. (1996a, 1996b). The unusual water composition in the five samples could reflect water from the Viiankiaapa mire.

Statistically, alkalinity correlates well with a large number of different variables including DSi, EC, Na, K, Ca, Mg and Cl. There is a strong correlation between alkalinity and EC (r = .956**), calcium (r = .867**) and magnesium (r = .866**). Correlation with these variables was expected as HCO_3 exists mostly in the forms of calcium bicarbonate ($Ca(HCO_3)_2$) and magnesium bicarbonate ($Mg(HCO_3)_2$). Correlation with EC is explained simply by the higher number of other ions in the same samples with the high alkalinity.

Out of trace elements, alkalinity seems to correlate strongly with strontium (r = .839**), moderately with yttrium (r = .577**) and weakly, but significantly, with a large number of different element including Nd (r = .432**) and Dy (r = .492**).

4.2.10 Sulphate

Average sulphate concentration in our samples was 2.79 mg/l. Similarly low, but still slightly higher (about 5 mg/l) values were observed by Lahermo et al. (1996a, 1996b, 2002). Overall, sulphate results are rather mixed and unclear. Distribution of the results is quite right-skewed and possesses high kurtosis. The variable also shows a very large spectrum of values from 0.39 mg/l to 13.2 mg/l. Similar large variance was observed by Lahermo et al. (1996b) in Finnish stream water samples.

Samples from Kärväsniemi area seem to have above average SO_4 concentrations (Figure 16). Surface water sample SW1 has 13.2 mg/l of sulphate, but also groundwater samples from the area show elevated levels compared to research area average (KP40-U 8.39 mg/l and KP31 6.23 mg/l). However, the results are somewhat inconsistent as groundwater sample KP30-U from the same gravel pit, located in between SW1 and KP40-U only contains 2.86 mg/l of SO_4. The Kärväsniemi site is at the bottom of a recently active gravel pit on the western bank of Kitinen, and so the above average values could be of anthropogenic origin. Slightly elevated sulphate values are also seen in two samples from Kersilönkangas area (SPRING2 and SPRING 8) along with groundwater sample GA300 from Kiimakuusikko South.

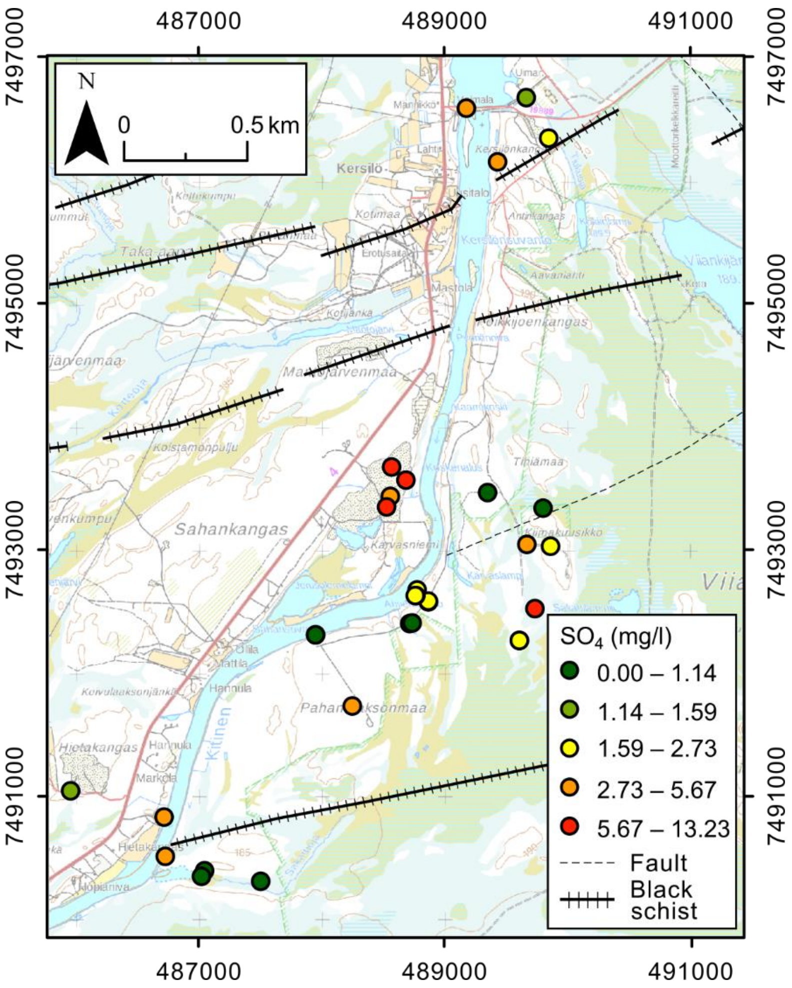

Figure 16. Distribution of sulphate. Bedrock data (Bedrock data base @ Geological survey of Finland (2014)). Base map (base map database @ NLS 2010).

According to Lahermo et al. (1996b), high sulphate results could also reflect the chemical composition of the Central-Lapland's schist belt. In our case sulphate does not correlate very well with other variables. The only significant correlations are seen with δ^{18}O (r = -.586**), K (r = .615**), NO_3 (r = .457**), Ni (r = .570**) and Rb (r = .580**). Lahermo et al. (1996a, 2002) also observed a similar connection with potassium and estimated that the connection could be due to clays. Connection to nickel could reflect lithological origin in the form of black schist. The black schist, however, do not seem to match the spatial location of high concentration samples in Figure 16. On the other hand, accuracy of the old 1:100000 bedrock map can be considered far too low for a solid conclusion and the SO_4 could also possibly migrate with groundwater flow. The connection to nickel might also be at least partially explained by emissions. Airborne nickel pollution originating from the metallurgic industry in the northwestern Kola Peninsula has been observed in a previous surface soil geochemistry survey (Brownscombe et al. 2015). Also, Lappalainen et al. (2007) noted that in the lakes near the Finnish – Russian border, elevated SO_4 and nickel concentration were common due to the metallurgic industry. On a scatter diagram the connection between SO_4 and nickel seems quite random, so the bivariate correlation might also overestimate the connection between the variables (Figure 17).

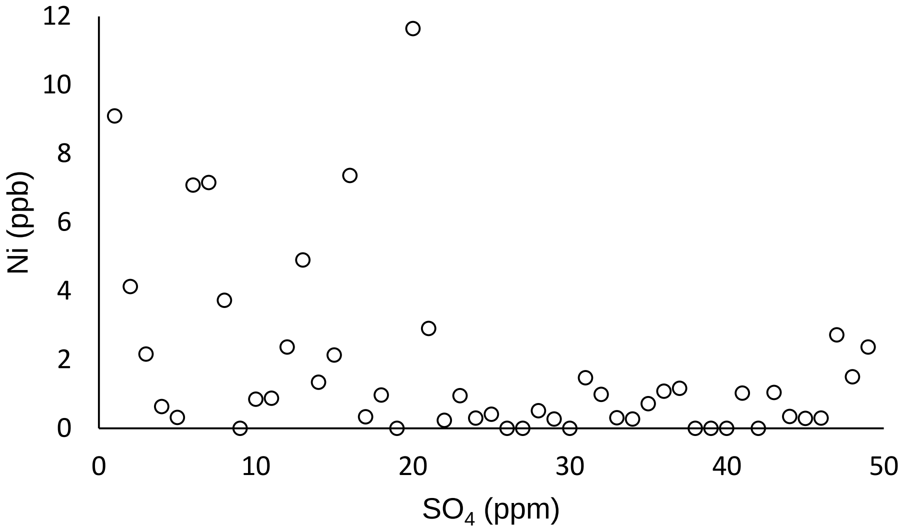

Figure 17. Scatter diagram between Ni and SO_4. No clear linear correlation between the variables can be seen, but high sulphate concentrations seem to be related to low amounts of nickel.

4.2.11 Ionic balance

Slight ionic imbalances were observed in all samples, but on majority of the samples show IB below 5%. Five samples showed high ion imbalances (IB >10%). These were KP31 (22.76%), NAKU1 (27.45%), GA306 (17.33%), SW4 (11.66 %) and SW17 (11.66%). In 29 samples out of the total 38 the ion imbalance was caused by excess amount of anions. The most likely source for such an error would be the laboratory analysis of alkalinity. This is also supported by the fact that HCO_3^- contributes by far the most to the anion sum of a water sample as it is the most common out of the major anions. Alkalinity was analyzed by titrating the samples with 0.1 mol/L hydrochloric acid solution. The results were calculated based on the amount of acid that was needed to reach a pH of 4.5. The method is fairly error prone, especially with samples that have low acid neutralization capacities. During the titration one additional unintended drop of acid could impact the results drastically. All of the samples with ion balance issues show alkalinities between 0.30 and 0.36 mmol/L and overall, samples that had alkalinities close to this range tended to have slightly higher than average IB. It might be that there has been a minor threshold value around this point which has made the titration difficult and thus has affected the results. Also, the ion chromatograph used to analyze rest of the major ions can be considered far more reliable than alkalinity titration.

In case of a larger sample set, it would be likely that imbalanced samples would simply be discarded from the statistical analysis or even from the results altogether. Two of the samples are from old gravel pits (KP31 and NAKU1) and one is a river water sample from the outside of the study area (SW17). Losing those samples wouldn’t have a big impact on the statistical analyzes or the whole interpretation of the results. However, losing the groundwater sample GA306 from the very interesting Kiimakuusikko area along with sample SW4 from the stretch of land between the mire and the river would be unfortunate with the already relatively small sample set (n = 49). As the source of the ion imbalance can be fairly reliably narrowed down to alkalinity titration, all values were included into the statistical analyzes.

4.3 Dissolved silica and the stable isotopes of water

The isotope- and d-excess values along with the amount of DSi are presented in Table 3.

Table 3. Results of the stable isotope and dissolved silica analysis.

ID	**Date**	**Water type**	**$\delta^{18}O$**	**δD**	**D-excess**	**DSi**
			(VSMOW, ‰)		(‰)	(ppm)
KP40-U	7.8.	Kärväsniemi GW	-13.29	-99.21	7.11	6.22
KP31	7.8.	Kärväsniemi GW	-12.00	-89.77	6.23	4.37
KP30-U	7.8.	Kärväsniemi GW	-13.62	-103.07	5.89	6.58
SW1	7.8.	Kärväsniemi SW	-12.25	-95.90	2.1	0.99
NAKU1	7.8.	Hietakangas GW	-14.26	-104.88	9.2	4.06
SPRING1	7.8.	Moskuvaara Spring	-14.04	-102.86	9.46	4.25
SPRING2	7.8.	Moskuvaara Spring	-14.10	-102.65	10.15	6.48
SW2	7.8.	River Kitinen	-12.15	-91.12	6.08	2.14
GA200	8.8.	Tihiämaa Well	-12.74	-98.05	3.87	7.4
MP1	8.8.	Sahansuvanto GW	-14.20	-106.90	6.7	4.4
GA305	8.8.	Tuulivuopaja well	-13.74	-103.14	6.78	4.54
GA203	8.8.	Tuulivuopaja well	-13.80	-103.68	6.72	4.57
GA405	8.8.	Tuulivuopaja well	-12.50	-96.17	3.83	7.95
SW3	8.8.	River Kitinen	-12.01	-90.18	5.9	2.10
GA300	9.8.	Kiimakuusikko South well	-14.01	-102.99	9.09	7.14
GA202	9.8.	Kiimakuusikko South well	-14.30	-107.04	7.36	7.7
GA202 deep	9.8.	Kiimakuusikko South well	-14.30	-107.07	7.33	
GA201	9.8.	Kiimakuusikko Well	-13.98	-103.39	8.45	8.68
GA400	9.8.	Kiimakuusikko Well	-14.61	-108.12	8.76	4.64
GA100	9.8.	Kiimakuusikko North Well	-14.23	-105.68	8.16	2.31
GA306	9.8.	Kiimakuusikko North Well	-10.26	-83.67	-1.59	7.45
GA404	10.8.	Pahanlaaksonmaa Well	-14.25	-105.23	8.77	5.45
SPRING4	10.8.	Kärvaskoski GW	-10.53	-83.58	0.66	2.96
SW4	10.8.	Kärväskoski SW	-9.16	-73.46	-0.18	1.19
SPRING3	10.8.	Tuulivuopaja Spring	-13.64	-102.87	6.25	4.40
SW5	10.8.	River Kitinen	-12.14	-91.62	5.5	
SW6	10.8.	River Kitinen	-12.05	-91.05	5.35	
DGW1	10.8.	River Kitinen mix	-12.28	-92.32	5.92	
SPRING9	11.8.	Kersilönkangas Spring	-13.60	-99.16	9.64	
GW1	11.8.	Kersilönkangas Well	-12.97	-97.18	6.58	7.66
SPRING6	11.8.	Kärväskoski GW	-10.40	-84.30	-1.1	2.96
SPRING7	11.8.	Kärväskoski GW	-9.88	-78.40	0.64	
SW7	11.8.	Kärväskoski SW	-9.62	-75.31	1.65	
SW9	11.8.	Kärväskoski SW	-9.63	-75.30	1.74	1.32
SPRING5	11.8.	Tuulivuopaja Spring	-12.78	-97.63	4.61	4.62
SW8	11.8.	River Kitinen mix	-12.24	-91.93	5.99	
SPRING8	12.8.	Moskuvaara Spring	-14.50	-106.02	9.98	6.20
SW10	12.8.	Kersilönkangas SW	-10.47	-80.42	3.34	2.00
SW12	14.8.	River Kitinen mix	-12.24	-92.48	5.44	2.56
SW16	15.8.	Kersilönkangas Spring	-13.58	-101.20	7.44	3.50
MP3	15.8.	Tuulivuopaja MP	-13.00	-99.44	4.56	3.40
MP4	15.8.	Tuulivuopaja MP	-11.94	-92.45	3.07	5.76
SW15	15.8.	River Kitinen mix	-12.12	-91.28	5.68	2.23
SW13	15.8.	Sakattioja	-10.09	-76.31	4.41	1.83
SW14	15.8.	Sakattioja	-9.76	-75.01	3.07	1.77
SPRING10	15.8.	Sakattioja	-9.56	-74.03	2.45	1.52
SW18	17.8.	River water	-11.41	-86.58	4.7	2.34
SW19	17.8.	River water	-11.37	-85.84	5.12	3.26
SW17	17.8.	Kotajärvi	-11.92	-92.42	2.94	2.95

4.3.1 Dissolved silica (DSi)

The biggest reason for measuring DSi content of natural water is the fact that DSi content, like the isotopes of water, is very self-sufficient and doesn't easily vary with changes in pH, salinity or concentrations of ions (Davis 1964). High concentrations can also indicate long residence times (Davis 1964). In our case DSi works fairly well as an indicator for groundwater and spring water, as concentrations in them are in most cases higher (>3 mg/l) than for example in surface waters (<3 mg/l). The difference is caused by the fact that DSi is mostly lithological in origin and thus more common in groundwater (Davis 1964). Overall, groundwater samples seem to contain the highest values, while surface water samples from Kärväskoski and -niemi have the lowest DSi concentrations. Kitinen seems to have a very distinct DSi concentration of about 2.1 mg/l (Figure 18).

The concentration of DSi varies vastly/significantly in the results. Smallest concentration was 0.99 mg/l while maximum was 8.68 mg/l, giving a wide range of 7.69. Considering this, mean and median values are quite close to each other (4.27 mg/l and 4.32 mg/l respectively), while standard deviation is 2.20. This shows that the data didn't have extreme outliers that would've caused the wide range, but a large and even distribution of all kinds of values. Distribution of results is quite normal, and skewness and kurtosis are within acceptable range (0.38 and -1.02, respectively). Normal distribution is also confirmed by the Shapiro-Wilk test for normality, where DSi was the only variable along with pH to pass the test without $\log_{10}$-transformation.

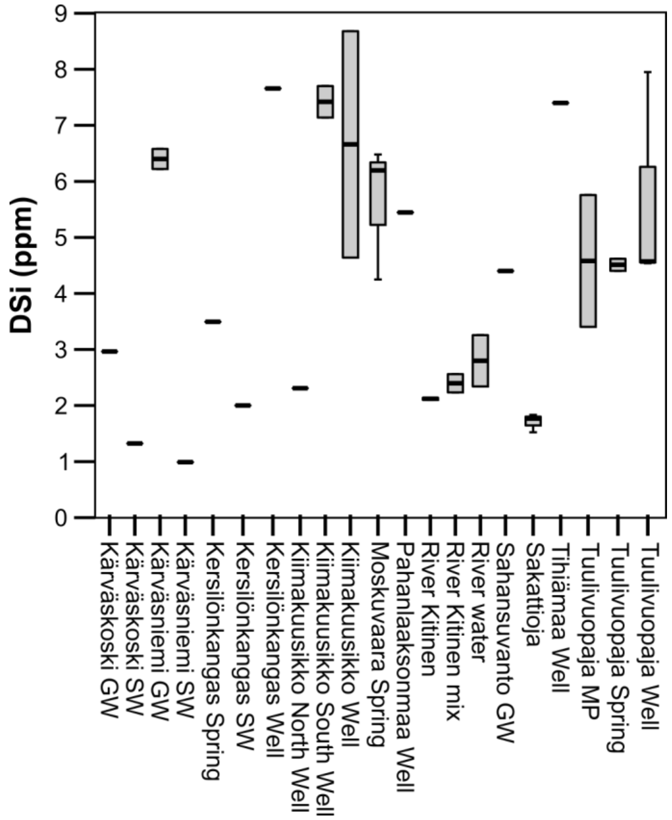

Figure 18. Distribution of DSi values. Ground- and surface waters can be roughly identified based on the values (Groundwater > 3 mg/l > surface water).

In our data DSi has significant, but modest correlations with many variables. (Table 4).

Table 4. Strongest bivariate correlations of dissolved silica. Correlations have been done on $\log_{10}$-transformed and normalized values.

		$\delta^{18}O$	δD	EC	Na	K	Ca	Mg	HCO3	Cr	Co	Ni	Rb	Sr	Y	Ba	La	Pr	Nd	Dy
DSi	r	-.570**	-.495**	.671**	.706**	.594**	.424**	.512**	.660**	.429**	.534**	.424**	.689**	.611**	.596**	.541**	.421**	.465**	.497**	.530**
	ρ	-.599**	-.607**	.667**	.777**	.661**	.477**	.550**	.655**	.265	.461**	.367*	.742**	.612**	.545**	.467**	.406*	.432**	.456**	.469**

Similar correlations were observed by Lahermo et al. (1996a). They observed that DSi correlated moderately well with Mg, Na and HCO_3 in diluted spring waters, and that the correlations got weaker with increasing depth and salinity. The last observation, however, doesn't line up well with our results as in many groundwater observation wells the correlation seems to be greater than for example in springs.

DSi has its strongest correlation to sodium values and it also connects fairly strongly with potassium values. The correlation would be explained by the hypothesis of albite-kaolinite weathering (introduced in Chapter 4.2.3) as the weathering reaction releases silica into the soil solution. Even if the hypothesis isn't true, the idea of DSi correlating with Na and K isn't completely out of line as all these variables likely reflect multiple different lithological origins. Further, the increased DSi concentrations might also indicate longer residence time for the samples with increased Na.

4.3.2 Stable water isotopes (δD, $\delta^{18}O$ and d-excess)

Majority of our stable water isotope results plot clearly below the LMWL defined by Kortelainen (2007) (Figure 19). Such behavior is typical for waters that have evaporated or have mixed with evaporated waters at some point after precipitation. According to Hunt (1996), an observation that water influenced by a mire tends to shift from the LMWL, indicates that evaporation has a larger part in removal of water than transpiration. However, Kellner (2001) comments that Swedish mires with a lot of open water area tend to be evaporation driven, while mires with extensive vascular vegetation tend to be transpiration dominated. At Viiankiaapa, on the main study area, both vegetation and open water areas seem to be quite common (Figure 3), which makes it difficult (solely based on the isotope values) to estimate whether the mire is evaporation or transpiration dominated.

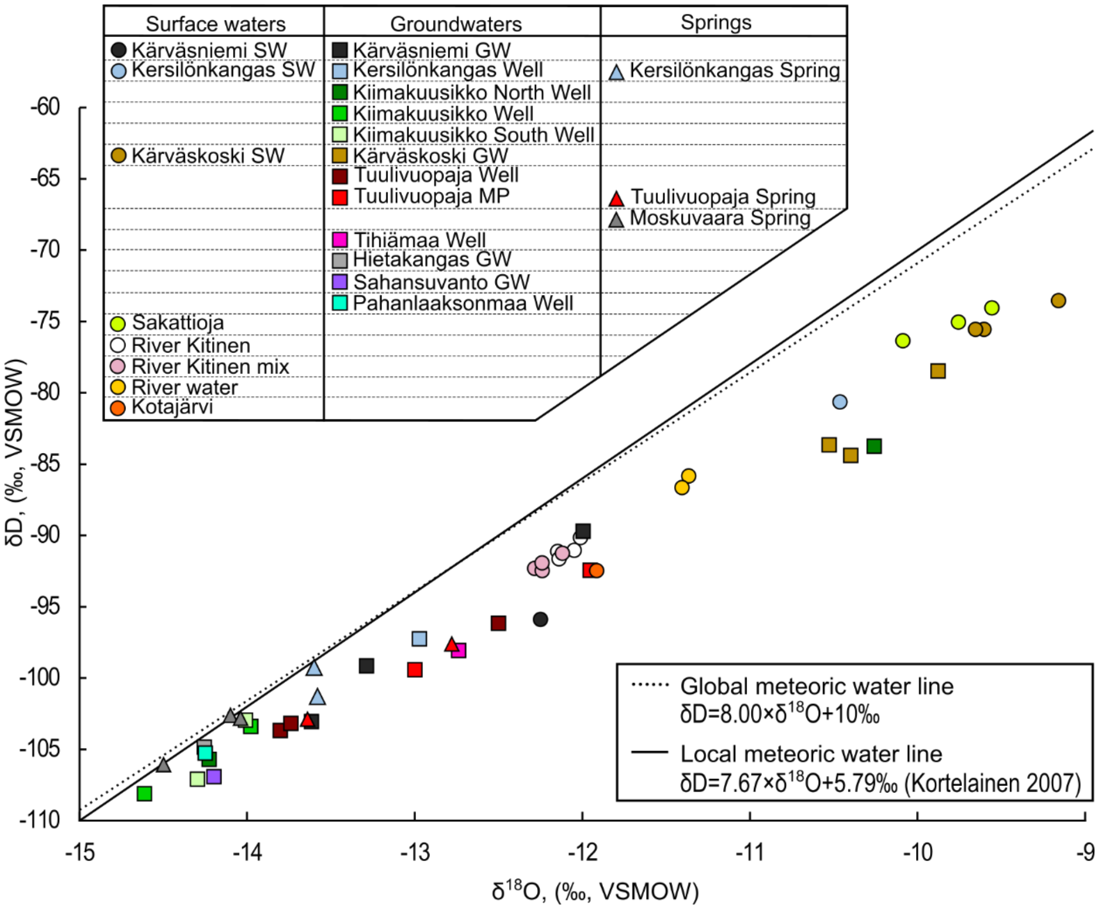

Figure 19. A plot of δD against $\delta^{18}O$.

According to Lahermo et al. (2002) and Kortelainen and Karhu (2004), $\delta^{18}O$ values in groundwater are usually below -14.5 ‰ VSMOW in Central-Lapland. Thus, generally the $\delta^{18}O$ values in groundwater samples, having an average of -12.99‰, can be considered to be modestly/slightly enriched with heavier isotopes. Only two samples have values at or below -14.5‰ (SPRING8 of Moskuvaara Spring (-14.50‰), GA400 of Kiimakuusikko Well (-14.61‰)). Overall, it is hard to draw clear spatial patterns from the stable isotope results. The most striking features are the low values observed at the mire near Kiimakuusikko (with an exception of GA306 of Kiimakuusikko North Well) and the high values observed near Sakattioja, which drains water from the mire (Figure 20). Dubiously, sample GA100, collected next to GA306 is supposed to have much less evaporated water isotope composition compared to the GA306. This is unusual because the GA306 –well is a much deeper observation well drawing water from the till layer below the mire (total length 6m, with a 1m long screen on the bottom). GA100 on the other hand is just 4m long in total and draws water straight from the peat layer itself. The mineral soil below the mire should show less evaporated values compared to the surface water layer. Thus it is possible that these samples have gotten switched at some point after the sampling. It would make sense for the GA306 to show less evaporated isotope composition, similar to the other groundwater observation wells near Kiimakuusikko. This would also make the GA100 to appear more similar with the samples from Sakattioja, which likely represent evaporated surface water from the mire. However, as the possible mix-up cannot be verified, the results are treated as is.

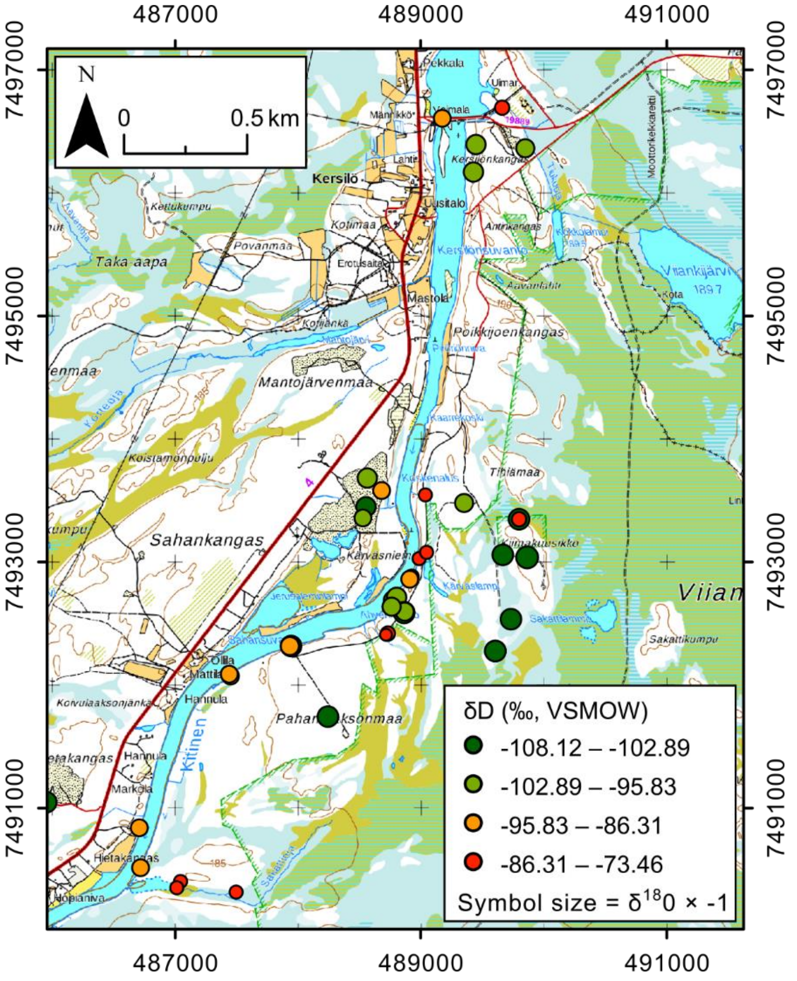

Figure 20. Stable isotope distribution over the main study area. The results have been classified under four symbols based on geometrical interval.

Hunt et al. (1996) concluded that at wetlands containing standing water, stable isotope values cannot be considered un-fractioned. Ferlatte et al. (2015) observed that vertical connections between peatlands and underlying aquifers seem to be very common, and that downwards flow from the peat layer to the aquifer is more common than other way around. Thus, the groundwater samples that contained evaporated δ^{18}O values could be re-infiltrated water from the mire, and so at least partially reflect the evaporated isotopic composition of the mire water. For example, samples grouped as Kärväskoski GW were considered representing the pure groundwater from springs during the field campaign.

However, the highly evaporated isotope ($\delta^{18}O$) readings of all three samples (SPRING7, -9.88‰; SPRING6, -10.40‰; SPRING4, -10.53‰) suggest that the waters are not purely groundwater and have been influenced by either or both re-infiltration of surface water and evaporated source water component. These three samples also have d-excess values very close to zero (0.54, -1.1 and 0.66, respectively) indicating high evaporation, which supports the previous conclusion. Also the general groundwater and surface water flow direction from the mire towards Kitinen (Åberg et al. 2017) supports the idea. The hypothesis is questioned by groundwater samples from Tuulivuopaja and Sahansuvanto, which show values much closer to typical groundwater of area described by Kortelainen and Karhu (2004), despite being located at the same stretch of land between Kitinen and the mire. However, Åberg et al. (2017) also notes that the sedimentary units in the area are very heterogeneous and poorly hydraulically connected, which might mean that despite being spatially close to one another Tuulivuopaja, Sahansuvanto and Kärväskoski represent different groundwater systems.

At the study site, Kitinen has isotopic composition of $\delta^{18}O$ -12.09‰ ±0.08‰ and δD -90.99‰ ±0.63‰. Samples collected from sites potentially showing groundwater-surface water mixing, show isotopic compositions very similar to the river, yet are very slightly more negative (average value for $\delta^{18}O$ in these samples is -12.22‰) indicating some groundwater component being present in them. The four samples containing mixed water also have a slightly higher mean d-excess value (5.76) compared to SW samples from Kitinen (5.71). The difference is mainly caused by slightly lower δD values in water samples containing groundwater-surface water exchange/mixing. The difference, however, is extremely small. Rautio (2015) observed low d-excess values in Keravanjoki and Tuusulanjoki rivers, located in Southern-Finland, and judged them to be caused by evaporated water from headwater lakes, supplementary water, artificial groundwater plants and damns along the rivers. Thus, similarly in our case the low d-excess value of river water might be due to e.g. evaporated source water from Porttipahta reservoir, catchments and low-flow areas induced by the several dams. However, the conditions between Keravanjoki, Tuusulanjoki and Kitinen are very different and so direct conclusions cannot be drawn.

Stream water samples have a clearly different isotopic composition compared to Kitinen. Interestingly, the highest isotope values out of all samples were seen in streams. It was observed that the streams where high values occur, collect their water straight from the mire. Sampling was done during late summer when amount of rain and flow rates of streams can be expected to be low. Thus, the highly evaporated isotope values in streams of the area might actually reflect the water standing still on the surface of the mire. This water has had a lot of time to evaporate from the lighter isotopes during its slow passage through the mire and into the streams. The idea is supported by Sprenger et al. (2017) who similarly observed very depleted isotope values in streams draining a peatland, while streams originating outside the area showed values closer to the LMWL.

At few sites, negative values for d-excess were observed. These were GA306 (Kiimakuusikko North Well, -1.59‰), SW4 (Kärväskoski SW, -0.18‰) and SPRING6 (Kärväskoski GW, -1.1‰). Generally, negative and close to zero values are connected to sites with more evaporated waters (Figure 21).

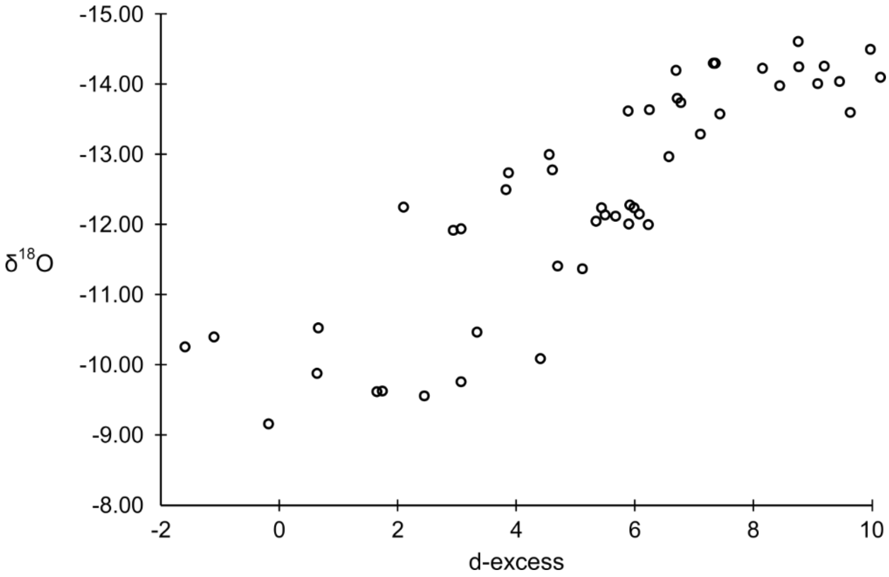

Figure 21. Deuterium excess vs δ¹⁸O. It can be clearly observed that more evaporated samples have lower d-excess values.

At first glance, ground material seems to correlate slightly with the isotope values. Sites where the ground material has been marked to be mainly till (GA400, GA300, GA202 and SPRING8), seem to systematically have lower values (δD < 96‰) compared to samples from areas with sand or gravel. On closer inspection, this observation can be labeled mostly false, once more highlighting the complexity and high difficulty of forming correct interpretations from the study site. First of all, the number of samples where the soil bottom has been marked to consist from till is low (n = 5, including two samples from GA202). Second, as mentioned before, Åberg et al. (2017) note that the sedimentary units in the area are very heterogeneous and poorly hydraulically connected. Thirdly, according to the original well-logs by Golder Associates (2012) GA400 has its screen installed into sheared bedrock with unsaturated till on top of the bedrock and GA300 actually has its screen installed into a gravel/sand layer. GA202 is the only observation well out of the three that truly has its screen on a till layer, but even there the source of the water could be speculated to be the four meters of sand observed above the till layer and not the poorly conducting till layer itself. Groundwater level which reaches to the top of the sand layers supports this idea.

One thing to consider is that the samples collected for this study represent the stable isotopic composition of the area during late summer. Clay et al. (2004) found major monthly variation in the stable isotope composition of a British wetland and concluded that the isotopic signal varied as the major water source of the wetland (e.g. precipitation, ground- and surface water inflow) varied throughout the year. Hunt et al. (1996), on the other hand, found very little temporal variation in isotope values over their yearlong study of wetlands in Wisconsin, USA. Results and observations based on other sites should be applied to Viiankiaapa with extreme caution, as it has been observed before by e.g. Ladouche and Weng (2005) and Ferlatte et al. (2015) that conclusion drawn from one peatland often scale poorly to others. Thus, monthly or by-monthly samples are needed if the temporal variation in groundwater flow conditions is to be studied via stable isotopes of water.

Overall it can be concluded that drawing solid conclusions from stable isotope data is very difficult at the study area. This seems to be the common case at similar wetlands as Hunt et al. (1996) notes that if a wetland has standing surface water along with major points of surface water in- and/or outflow (as is the case at the study area), understanding and modelling the hydrological system is often very complicated.

4.4 Interpreting trace element results.

The large pool of trace elements that were analyzed add a huge amount of new data and possibilities for interpretation (the results are show in Tables 5a and 5b). However, care was taken that the results weren’t over interpreted as the trace elements are often present in very low quantitates (down to parts per trillion). Because of this, especially in graphical presentations differences between samples might seem more significant than they actually are in nature. Of course, also more sensitive analytics and strict sampling procedures are needed in order to analyze samples at these levels, increasing also the risk for errors and sample contamination. Many of the trace elements show concentrations that are equal or below the detection limit of the ICP-MS. These samples are problematic in many ways and can for example alter the results from statistical analysis as the values do not actually represent real concentrations (Reimann et al. 2011).

Among the trace elements, the most interesting results were seen with aluminum and rubidium along with some of the elements associated with the Sakatti ore.

Table 5a. First table containing results from the trace element analysis. Results with gray background were below the detection limit and are shown as half of the limit value.

ID	Date	Li (ppb)	Al (ppb)	P (ppb)	Sc (ppb)	Cr (ppb)	Mn (ppb)	Fe (ppb)	Co (ppb)	Ni (ppb)	Cu (ppb)	Zn (ppb)	As (ppb)	Rb (ppb)	Sr (ppb)	Y (ppb)	Zr (ppb)	Mo (ppb)	Ag (ppb)	Cd (ppb)
KP40-U	7.8.	0.10	11.08	8.32	0.016	0.52	88.69	49.58	2.11	9.09	0.70	7.43	0.080	1.57	21.61	0.07	0.19	0.019	0.002	0.07
KP31	7.8.	0.06	18.08	10.30	0.016	0.49	3.90	9.90	0.12	4.13	0.84	9.70	0.080	4.56	16.10	0.21	0.19	0.05	0.014	0.05
KP30-U	7.8.	0.08	22.25	37.65	0.05	0.51	993.36	8350.68	5.49	2.16	0.38	4.47	2.13	3.69	36.07	0.27	0.26	0.06	0.002	0.05
NAKU1	7.8.	0.016	18.08	312.60	0.016	0.55	0.53	4.98	0.10	0.32	0.52	2.86	0.080	0.51	18.70	0.01	0.63	0.06	0.002	0.06
SW1	7.8.	0.06	16.18	6.94	0.016	0.36	4.93	4.07	0.08	0.64	0.62	1.86	0.16	1.55	22.32	0.01	0.08	0.07	0.002	0.013
SW2	7.8.	0.39	51.12	7.30	0.016	0.71	23.41	508.24	0.08	1.08	0.76	1.73	0.22	0.79	14.28	0.07	0.26	0.26	0.002	0.013
SPRING1	7.8.	0.12	157.44	1.525	0.21	1.96	14.76	100.47	0.50	7.08	1.43	6.28	0.080	0.83	5.60	0.22	0.39	0.019	0.002	0.04
SPRING2	7.8.	0.63	35.16	1.525	0.07	0.54	0.40	35.31	0.06	7.16	1.23	1.76	0.080	1.89	11.29	0.20	0.46	0.019	0.002	0.013
GA305	8.8.	0.08	14.45	7.92	0.05	0.50	14.27	16.63	0.32	0.99	0.62	1.91	0.080	1.99	17.85	0.04	0.40	0.04	0.002	0.07
SW3	8.8.	0.39	52.28	11.76	0.016	1.29	26.26	514.11	0.11	1.16	0.70	3.58	0.25	0.78	14.37	0.07	0.37	0.26	0.004	0.29
GA203	8.8.	0.016	12.40	9.12	0.03	0.30	12.67	10.62	0.19	0.31	0.24	4.13	0.080	2.23	18.54	0.12	0.13	0.05	0.002	0.013
GA405	8.8.	0.26	12.26	112.63	0.12	1.04	274.41	11271.60	0.35	0.27	0.14	1.41	1.96	3.25	32.78	0.12	0.59	0.22	0.002	0.013
GA200	8.8.	0.07	26.09	188.36	0.08	1.66	313.57	20800.12	3.04	2.91	0.66	5.98	3.76	2.35	20.68	0.29	0.39	0.17	0.005	0.03
MP1	8.8.	0.016	25.97	11.38	0.04	0.22	15.88	81.32	0.37	0.23	0.25	2.69	0.080	1.47	33.86	0.13	0.22	0.15	0.002	0.04
GA100	9.8.	0.14	49.24	13.63	0.07	0.73	71.31	3049.41	1.22	0.97	3.23	15.07	0.79	0.61	8.21	0.26	0.17	0.13	0.002	0.04
GA400	9.8.	0.32	23.98	17.50	0.016	0.44	15.77	5.24	0.05	0.34	0.55	1.79	0.080	1.54	16.20	0.02	0.07	0.04	0.002	0.03
GA300	9.8.	0.22	41.25	22.24	0.27	1.18	723.82	1447.79	5.24	4.90	1.25	58.70	0.75	3.75	31.96	3.01	1.02	0.21	0.002	0.10
GA202	9.8.	0.42	48.80	24.01	0.16	2.19	223.58	717.76	0.52	1.34	0.41	2.52	0.92	2.64	32.11	0.69	0.72	0.31	0.002	0.03
GA202 deep	9.8.	0.39	34.95	21.05	0.08	1.39	214.56	86.04	0.51	2.13	0.47	7.88	0.67	2.50	33.61	0.60	0.42	0.38	0.002	0.05
GA201	9.8.	0.60	21.31	36.84	0.05	1.90	117.92	2.76	2.77	7.37	0.31	3.77	0.23	0.69	26.96	0.06	0.12	0.18	0.002	0.06
SW4	10.8.	0.11	27.44	18.49	0.016	0.33	30.84	428.23	0.11	0.30	0.13	1.69	0.25	0.27	8.26	0.01	0.18	0.04	0.002	0.03
SPRING4	10.8.	0.11	62.11	16.09	0.016	0.56	8.88	13.52	0.05	0.95	0.39	1.41	0.080	0.68	11.91	0.07	0.34	0.04	0.023	0.013
GA404	10.8.	0.83	19.10	34.23	0.04	1.55	6.85	34.13	0.18	11.65	1.52	91.11	0.30	2.34	7.85	0.06	0.10	0.26	0.006	0.07
SPRING3	10.8.	0.016	19.34	13.80	0.016	0.23	0.41	2.12	0.03	0.28	0.22	1.37	0.080	2.29	20.11	0.10	0.21	0.07	0.002	0.03
SPRING5	11.8.	0.17	10.54	7.21	0.05	0.81	316.75	9322.58	0.90	0.72	0.39	2.30	0.59	1.99	25.32	0.10	0.33	0.06	0.002	0.03
GW1	11.8.	0.56	26.62	128.65	0.22	4.40	831.15	16365.02	0.55	0.87	0.16	1.15	0.96	2.32	45.46	0.64	1.51	0.21	0.003	0.013
SPRING6	11.8.	0.04	23.55	16.93	0.09	0.61	1.27	5.85	0.04	0.42	0.54	1.14	0.080	0.87	9.98	0.12	4.52	0.05	0.007	0.013
SW9	11.8.	0.11	30.13	17.42	0.016	0.59	10.95	423.37	0.10	0.51	0.64	3.87	0.23	0.45	7.92	0.01	0.16	0.04	0.002	0.025
SW10	12.8.	0.32	77.10	17.31	0.04	0.72	51.04	837.75	0.93	2.37	3.91	1.51	0.30	0.40	11.84	0.12	0.18	0.05	0.002	0.05
SPRING8	12.8.	0.47	24.09	15.96	0.016	0.52	0.29	3.41	0.67	3.73	0.24	2.17	0.080	1.43	12.61	0.04	0.12	0.14	0.002	0.03
SW12	14.8.	0.42	62.81	26.27	0.016	0.58	47.08	535.02	0.13	1.03	0.43	1.40	0.27	1.04	17.69	0.06	0.13	0.40	0.002	0.013
SW13	15.8.	0.11	13.87	8.54	0.016	0.59	42.00	453.56	0.30	0.35	0.19	2.02	0.36	0.18	8.09	0.03	0.17	0.019	0.002	0.03
SW14	15.8.	0.13	35.46	68.94	0.016	0.56	35.87	776.18	0.35	0.30	0.36	1.93	0.40	0.14	7.66	0.03	0.44	0.06	0.002	0.013
SPRING10	15.8.	0.09	33.82	28.22	0.016	0.53	11.37	506.29	0.17	0.30	0.32	3.09	0.35	0.13	5.84	0.01	0.17	0.04	0.002	0.03
SW15	15.8.	0.45	62.61	27.04	0.016	0.92	37.44	597.92	0.09	1.04	0.58	1.40	0.29	1.07	17.41	0.06	0.43	0.37	0.002	0.013
MP4	15.8.	0.15	41.27	28.87	0.12	2.07	673.09	19824.85	1.77	1.48	0.48	6.95	1.13	2.50	35.09	0.49	0.60	0.10	0.002	0.013
SW16	15.8.	0.21	23.02	9.59	0.04	0.66	13.62	190.97	0.05	0.85	0.28	1.54	0.40	0.89	17.21	0.04	0.13	0.07	0.002	0.013
SW17	17.8.	0.51	45.36	16.42	0.04	0.94	5.35	167.62	0.03	2.37	1.25	1.62	0.21	0.99	13.90	0.07	0.18	0.06	0.002	0.013
SW18	17.8.	0.28	66.53	34.86	0.05	1.35	36.91	1737.76	0.19	2.72	1.72	4.91	0.72	0.79	24.53	0.13	0.26	0.22	0.002	0.05
SW19	17.8.	0.33	76.73	34.95	0.06	1.10	207.56	2702.46	0.94	1.51	0.82	2.75	0.43	0.71	16.05	0.13	0.32	0.20	0.002	0.06
Detection limit		<0.0323	<0.6272	<3.0490	<0.0328	<0.0605	<0.0132	<0.3143	<0.0079	<0.0060	<0.0386	<0.1943	<0.1598	<0.0124	<0.0448	<0.0043	<0.0043	<0.0380	<0.0032	<0.0257

Table 5b. Second table containing results from the trace element analysis. Results with gray background were below the detection limit and are shown as half of the limit value.

ID	Date	Cs (ppb)	Ba (ppb)	La (ppb)	Ce (ppb)	Pr (ppb)	Nd (ppb)	Sm (ppb)	Eu (ppb)	Gd (ppb)	Tb (ppb)	Dy (ppb)	Ho (ppb)	Er (ppb)	Tm (ppb)	Yb (ppb)	Lu (ppb)	Pb (ppb)	U (ppb)
KP40-U	7.8.	0.05	4.40	0.03	0.06	0.010	0.042	0.004	0.004	0.009	0.001	0.008	0.002	0.006	0.001	0.003	0.001	0.266	0.005
KP31	7.8.	0.03	6.73	0.08	0.07	0.027	0.129	0.031	0.009	0.032	0.005	0.029	0.007	0.021	0.003	0.026	0.004	0.110	0.005
KP30-U	7.8.	0.01	7.14	0.20	0.76	0.052	0.231	0.042	0.012	0.052	0.006	0.033	0.009	0.025	0.003	0.022	0.004	0.115	0.004
NAKU1	7.8.	9.15	2.10	0.01	0.02	0.002	0.005	0.004	0.001	0.003	0.001	0.001	0.001	0.002	0.000	0.003	0.001	0.077	0.001
SW1	7.8.	0.00	2.11	0.01	0.01	0.001	0.005	0.004	0.001	0.003	0.001	0.001	0.001	0.002	0.000	0.003	0.001	0.041	0.010
SW2	7.8.	0.02	2.88	0.05	0.09	0.013	0.048	0.004	0.004	0.011	0.002	0.010	0.002	0.006	0.001	0.003	0.001	0.139	0.069
SPRING1	7.8.	0.08	2.37	0.19	0.39	0.055	0.213	0.044	0.012	0.045	0.007	0.039	0.008	0.022	0.004	0.020	0.003	0.125	0.010
SPRING2	7.8.	0.04	1.10	0.15	0.10	0.045	0.185	0.038	0.010	0.041	0.005	0.031	0.007	0.020	0.003	0.019	0.003	0.025	0.005
GA305	8.8.	0.19	5.33	0.01	0.03	0.004	0.014	0.004	0.003	0.003	0.001	0.004	0.002	0.005	0.001	0.003	0.001	0.033	0.011
SW3	8.8.	0.54	3.26	0.05	0.09	0.014	0.048	0.010	0.004	0.012	0.002	0.010	0.003	0.008	0.001	0.006	0.001	0.099	0.066
GA203	8.8.	0.02	1.67	0.05	0.06	0.015	0.065	0.011	0.003	0.014	0.002	0.013	0.004	0.012	0.002	0.013	0.002	0.031	0.020
GA405	8.8.	0.15	17.83	0.04	0.07	0.010	0.055	0.011	0.012	0.017	0.002	0.013	0.004	0.010	0.002	0.008	0.001	0.093	0.008
GA200	8.8.	0.03	3.85	0.14	0.41	0.043	0.191	0.041	0.012	0.043	0.007	0.041	0.010	0.030	0.004	0.031	0.006	0.076	0.027
MP1	8.8.	0.02	4.01	0.16	0.09	0.040	0.162	0.026	0.008	0.025	0.003	0.018	0.005	0.012	0.002	0.010	0.001	0.045	0.022
GA100	9.8.	0.07	5.44	0.18	0.50	0.055	0.237	0.047	0.015	0.057	0.007	0.044	0.010	0.026	0.004	0.026	0.004	0.024	0.059
GA400	9.8.	0.03	1.89	0.01	0.01	0.002	0.005	0.004	0.001	0.003	0.001	0.002	0.001	0.002	0.000	0.003	0.001	0.107	0.025
GA300	9.8.	0.02	9.05	1.01	2.90	0.402	1.837	0.395	0.100	0.437	0.062	0.384	0.092	0.298	0.045	0.313	0.056	0.096	0.084
GA202	9.8.	0.10	11.65	0.37	1.08	0.110	0.507	0.114	0.032	0.132	0.018	0.110	0.024	0.066	0.009	0.058	0.009	0.239	0.245
GA202 deep	9.8.	0.27	12.28	0.31	0.78	0.084	0.392	0.083	0.027	0.103	0.014	0.084	0.018	0.051	0.007	0.045	0.007	1.299	0.271
GA201	9.8.	0.01	5.84	0.01	0.03	0.005	0.026	0.004	0.004	0.008	0.001	0.006	0.002	0.005	0.001	0.006	0.001	0.163	0.019
SW4	10.8.	0.01	1.80	0.00	0.01	0.001	0.005	0.004	0.001	0.003	0.001	0.001	0.001	0.002	0.000	0.003	0.001	0.049	0.001
SPRING4	10.8.	0.83	1.86	0.07	0.14	0.017	0.064	0.015	0.004	0.015	0.002	0.013	0.003	0.008	0.001	0.007	0.001	0.029	0.006
GA404	10.8.	0.02	2.68	0.12	0.17	0.020	0.070	0.014	0.003	0.014	0.002	0.008	0.002	0.005	0.000	0.003	0.001	23.294	0.058
SPRING3	10.8.	0.01	2.31	0.03	0.01	0.008	0.042	0.004	0.003	0.011	0.001	0.010	0.003	0.009	0.002	0.011	0.001	0.031	0.001
SPRING5	11.8.	0.24	5.91	0.02	0.04	0.006	0.029	0.010	0.004	0.011	0.002	0.011	0.003	0.010	0.002	0.011	0.002	0.077	0.003
GW1	11.8.	0.03	16.75	0.12	0.28	0.036	0.200	0.051	0.023	0.074	0.012	0.078	0.019	0.065	0.011	0.077	0.015	0.044	0.020
SPRING6	11.8.	0.35	1.43	0.06	0.02	0.018	0.076	0.016	0.004	0.017	0.003	0.015	0.004	0.015	0.002	0.018	0.003	0.115	0.004
SW9	11.8.	0.09	1.69	0.01	0.02	0.002	0.008	0.004	0.001	0.003	0.001	0.002	0.001	0.002	0.000	0.003	0.001	0.057	0.001
SW10	12.8.	0.02	2.57	0.14	0.29	0.037	0.140	0.029	0.009	0.030	0.003	0.019	0.004	0.011	0.002	0.008	0.001	0.050	0.007
SPRING8	12.8.	0.01	1.24	0.01	0.01	0.005	0.026	0.004	0.001	0.008	0.001	0.006	0.002	0.005	0.001	0.006	0.001	0.026	0.001
SW12	14.8.	0.01	2.82	0.04	0.07	0.011	0.043	0.010	0.004	0.010	0.001	0.009	0.003	0.006	0.001	0.008	0.001	0.056	0.058
SW13	15.8.	0.01	3.26	0.01	0.03	0.004	0.014	0.004	0.003	0.003	0.001	0.004	0.001	0.002	0.000	0.003	0.001	0.111	0.001
SW14	15.8.	3.67	3.20	0.02	0.04	0.005	0.019	0.004	0.001	0.008	0.001	0.004	0.001	0.002	0.000	0.003	0.001	0.029	0.004
SPRING10	15.8.	0.05	2.27	0.01	0.02	0.002	0.005	0.004	0.001	0.003	0.001	0.002	0.001	0.002	0.000	0.003	0.001	0.054	0.001
SW15	15.8.	0.03	2.65	0.05	0.10	0.014	0.052	0.011	0.003	0.014	0.002	0.010	0.003	0.006	0.001	0.006	0.001	0.203	0.061
MP4	15.8.	0.02	13.19	0.23	0.54	0.066	0.281	0.065	0.018	0.071	0.010	0.058	0.014	0.042	0.006	0.041	0.007	0.059	0.053
SW16	15.8.	0.08	2.71	0.02	0.03	0.005	0.022	0.004	0.003	0.003	0.001	0.005	0.001	0.004	0.000	0.003	0.001	0.057	0.016
SW17	17.8.	0.09	0.87	0.03	0.06	0.010	0.046	0.011	0.004	0.010	0.001	0.009	0.002	0.006	0.001	0.006	0.001	0.051	0.006
SW18	17.8.	0.04	3.46	0.06	0.11	0.016	0.069	0.016	0.005	0.018	0.003	0.016	0.004	0.012	0.002	0.013	0.001	0.113	0.029
SW19	17.8.	0.10	3.80	0.10	0.19	0.025	0.099	0.021	0.007	0.025	0.003	0.020	0.005	0.013	0.002	0.013	0.001	0.130	0.033
Detection limit		<0.0010	<0.0182	<0.0020	<0.0024	<0.0016	<0.0096	<0.0088	<0.0026	<0.0068	<0.0015	<0.0016	<0.0016	<0.0040	<0.0009	<0.0054	<0.0024	<0.0090	<0.0018

4.4.1 Aluminium and rubidium

Aluminium is one of the least soluble metals (e.g. Huang and Keller 1972, Lahermo et al. 1996b, Lahermo et al. 2002). The amount of inorganic aluminium compounds in water are known to increase with lower pH values (Driscoll 1985). In our case, no correlation between Al and pH was observed ($r = -.004$, $\rho = -.017$). The poor correlation might be affected by the rather high pH results.

Generally, aluminum contents seem to be slightly higher in Kitinen compared to surrounding surface and groundwater. Exceptions to this observation do exist (Kärväskoski GW, Kersilönkangas SW and SPRING1 in Moskuvaara), but generally aluminum concentrations above 50 ppb are only seen in river water samples. This means that Al might be one potential chemical indicator if infiltration of river water to groundwater system in the area is to be studied later. The source for the higher aluminum concentration in the river can be only speculated. It could for example be related to the large river transporting more fine fractions from upstream, or the river might contain more colloidal Al. Some of the aluminum could be from anthropogenic sources like Kevitsa mines waste waters (which contain 0.4 mg/l of Al according to AVI (2009)).

Rubidium is an alkali metal and so it belongs to the same group of elements as sodium and potassium. In nationwide well water survey by Lahermo et al. (2002) rubidium was observed to correlate with potassium. At Sakatti similar effect can be observed as Rb correlates very well to K ($r = .809^{**}$, $\rho = .683^{**}$). The correlation between Rb –and K and Na can be expected to be related to the chemical similarities of the elements (i.e. they are alkali metals) (Lahermo et al. 2002). Rubidium also seems to be slightly more common in groundwater compared to surficial waters, likely due to its lithological origin.

4.4.2 Trace elements related to Sakatti ore: copper and nickel.

The Sakatti ore has been found to contain 3.40 wt% Cu, 3.54 wt% Ni, 1.81 g/t Pt, 2.09 g/t Pd, and 0.45 g/t Au in depths groundwater can easily reach to (39.95 m below ground surface) (Brownscombe et al. 2015). Out of these metals only copper and nickel were measured, while other elements associated with the ore (platinum, palladium and gold) were not analyzed.

Only a fraction of copper in soils exists as free, ionic copper (Cu^{2+}), and most of the metal is tightly bound to soil and minerals and is not easily soluble (Minnich and McBride 1987). In our samples, copper values are generally higher in surface waters than in groundwaters. Even if copper values on surface water samples are generally higher, copper cannot be recommended to be used as an indicator of water origin due to the few groundwater samples having high copper concentrations. Groundwater from Kiimakuusikko North Well (GA 306) shows the second highest amount of copper among the samples (3.23 µg/L). This well penetrates the peat layer and collects water from the sandy till layer underneath (Golder Associates Oy 2012). The same site has also had unique copper values previously, often being over ten times higher compared to other groundwater wells in the area. In the older groundwater monitoring data by AA Sakatti Mining Oy all copper values are staggeringly higher than in our current data and do not fit well with estimates from national monitoring done by Lahermo et al. (1996a). Source for the high amounts of copper in the older samples cannot reliably identified, but a lithogenic origin related to Sakatti ore is possible.

Copper in the surface waters, on the other hand, could be at least partially anthropogenic in origin. Lappalainen et al (2007) observer elevated copper concentrations in small lakes of Eastern Lapland due to airborne emissions from the smelters in the northwestern Kola Penisula, Russia. Another potential source could be the Finnish national road 4 which runs alongside the river all the way up to Porttipahta lake. According to Hjortenkrans (2008) traffic is a source of copper emissions and could possibly affect the geochemistry of recipient waters especially in the long term. Small amounts of copper (0.40 mg/l) and nickel (1.6 mg/l) are also released in treated waste waters from Kevitsa mine (AVI 2009).

With nickel, the highest values seem to be present in groundwater samples. Pahanlaaksonmaa well (GA404) has the highest nickel value among the samples (11.645 µg/L). Some groundwater samples from Kiimakuusikko Well and –South Well also show clearly elevated concentrations. High values are also present at the western side of Kitinen at the groundwater samples from the gravel pit of Kärväsniemi. At Kärväsniemi values seem to somewhat weakly correlate with sulphate values, but elsewhere the connection seems even more random. Samples with high nickel concentrations do not seem to match the black schists on the area either. Lahermo et al. (1996b) notes that there are high amounts of nickel in tills and stream sediments of the area. Thus the naturally high amount of nickel in tills is a likely source for the nickel in some groundwater samples. This is also logical as the groundwater wells having high nickel concentrations are generally installed to draw water from these till layers. However, GA404 has its screen installed straight into bedrock (Golder Associates Oy 2012) which means that the high nickel values could also result from water directly weathering the nickel rich bedrock.

4.5 Discussing the results of the statistical analyzes.

With statistical analyzes no "right answer" exists with correct choice of data pre-treatment steps, variables and method parameters. For example, Güler et al. (2002) lists three different proven ways to remove censored values (e.g. non-detected, less-than or greater-than) from a dataset. Choosing one over the other will affect the results. Thus, also the results here can be considered to be only one statistical interpretation over the contents of our dataset.

4.5.1 Distributions of variables and data handling

By default, many of the variables show non-normal, right-skewed distributions that are poorly suited for multivariate methods (descriptive statistics for all variables are shown in Appendice 9). This is usually the case with geochemical data (e.g. Miesch 1976 and Güler et al. 2002). According to George and Mallery (2010) values for skewness and kurtosis between -2 and +2 are considered acceptable in order to prove normal univariate distribution needed for the analyzes. From the major constituents four exceed this guideline for skewness. These were NO_3 (3.893), Ca (3.378), Na (3.245) and SO_4 (2.191) (Appendice 9). The high skewness is likely resulting from the few samples acting as outliers (Ca and Na), or from the overall very mixed results (NO_3 and SO_4). Kurtosis shows more variables closer to exceeding the aforementioned limits, which is due to the fat tails and/or shallowness of the bell curves. Eight major constituents had kurtosis over the guidelines. These were NO_3 (16.555), Ca (13.501), Na (10.38), EC (3.504), Mg (3.301), HCO_3 (3.252) and Cl (2.263). Another way to test the normality of the variables distribution is the Shapiro-Wilk test, according to which only DSi and pH distributions show univariate normality by default (DSi $p = 0.080$ and pH $p = 0.103$). Thus, a base 10 logarithmic transformation was applied to other variables (apart from the stable isotopes of water) and the normality was checked again. Logarithmic transformation normalized the distributions of for example EC, Ca, Mg, F, Cl and SO_4 and lessened the skewness and improved the distribution of basically all variables (e.g. Na, K, NO_3 and HCO_3). Stable water isotopes were left out from the log-transformation due to the fact that the values do not reflect actual measured concentrations, but instead are presented as difference to the international VSMOW standard. The stable isotope values are also negative by default, which means that in order to log-transform them, the values would have to be first scaled into positive values by adding an arbitrary constant into the results (Wicklin, 2011). This is not desirable as it will for example shift the mean of the values (Wicklin, 2011). Leaving the values un-transformed is also supported by the results' acceptable skewness and kurtosis (δD skewness was 0.536 and δ^{18}O was 0.475. Kurtosis was -0.826 and -0.935, respectively), even if the results from the Shapiro-Wilk test were poor ($p = 0.003$ with both variables). Results from the Shapiro-Wilk test are shown in Appendice 10.

Many of the trace elements were ruled out of the statistical analysis. Elements that didn't pass the Shapiro-Wilk test after the log-transformation were left out of the statistical analyzes (meaning Li, Sc, As, Mo, Ag, Cd and Sm). The trace elements were also correlated to each other and to other variables using scatter plots and those that showed at least slightly linear connections to some other variable were included into the analysis. This left Sr, Y, La, Ce, Pr, Nd, Dy, Er, Ho, Tb, Gd, Eu, Tm and Yb, which apart from Sr that correlates with Ca and Mg, correlate very strongly to one another (Pearson and Spearman correlations between all chosen variables are shown in Appendices 11a and 11b).

Excluding some of the major constituents was also considered. Nitrate had a strongly right-skewed distribution along with a very bad kurtosis value before the log-transformation (Appendice 9). Thus, the transformation wasn't able to fix the distribution of the variable and it still doesn't pass the Shapiro-Wilk test. Also fluoride was considered for exclusion as its concentrations are generally very low and so they might be partially unreliable. Further on, neither NO_3 nor F correlates particularly well with any other variables, which on strict interpretation would already make them unsuited for multivariate analysis. However, also many other major elements and variables suffer from poor correlations (especially pH and SO_4), and excluding all of them would lower the number of input variables unjustly and thus have a negative impact on the coverage of the analysis. The negative impacts of the poor correlations are, in our case, also pretty easy to observe and take into account, especially in the case of PCA.

Also imputing the missing values might induce at least some noise into the results, or in worse case alter them completely. As a simple example, the EM-algorithm doesn't take spatial variation into account. This leads to some estimates that are very likely not true in the real world. Sample GA202 from Kiimakuusikko South Well has a measured DSi concentration of 7.7 ppm. Sample GA202 deep, which is a sample from the same well and contains very similar concentrations to GA202 in all variables, doesn't have a measured DSi concentration. The EM-algorithm estimates that this value should be 9.1 ppm, which makes it the highest DSi concentration in the whole dataset and 1 ppm higher than the highest measured value in any Kiimakuusikko sample. Still, some sort of imputation method has to be used in order to include all samples into the analyzes.

4.5.2 Principal component analysis

The principal component analysis was conducted with the variables described in the previous chapter, using settings from the 'Statistical methods' chapter. Numerical indicators like the Kaiser-Meyer-Olkin test (KMO) show that the variables chosen are for the analysis have enough correlations to form realistic PCs' (KMO = 0.619) (Cerny and Kaiser 1977). With an eigenvalue of 1 the analysis forms 4 PCs'. If a scree plot is analyzed it can be seen that the eigenvalue is still declining quite steeply while the number of components stays below five (Appendice 12). Thus, a scree plot suggests that the number of components should be slightly higher – maybe even 7. This on the other hand would very likely generate components that would have less than 3 variables. A PC with fewer than three items is generally considered weak and unstable; five or more strongly loading items (.50 or better) are desirable and indicate a solid factor (Costello and Osborne 2005).

As can be seen in Figure 22, the first component explains 43.46% of the variance in the data. Principal component 1 is rather interesting as it's strongly loading trace-elements, or more exactly, rare earth elements (REE) (loadings between .874 – .954 were observed). Other variables have only low loadings. The component could form at least partially because of PCAs' weakness to data enhancement methods like centering and scaling. While these methods are helpful when trying to make the data as suitable as possible for the analysis, they also make the trace elements seem equal to other variables in the eyes of the analysis and thus give high emphasis on elements that are present only in extremely small quantities. On the other hand the REE's also correlate to each other very strongly on a scatter matrix with very clear linear correlations. Thus the elements might also represent common lithological origin in the form of REE bearing minerals (such as monazite, allanite or apatite). The groundwater sample GA300 belonging to Kiimakuusikko South Well group can be considered to be an outlier in REEs as it is the only sample to exceed 1 ppb in any of the elements.

The second component, which explains 20.86% of the total variance, is defined mainly by the main ions of natural water. This means strongly loading and correlating Ca, Mg and HCO_3 along with EC, which is largely defined by the former ions. The component could also at least partially reflect local-scale dissolution of carbonate minerals. As a beautiful little detail strontium belongs to the same PC. Strontium is an alkaline earth metal and so it is natural that it correlates well with the other more common alkaline earth metals –Mg and Ca. Similar effect was also noted by Lahermo et al. (2002) in their nationwide well water survey. Strontium concentrations are generally very low in all samples. The highest measured amount was approximately 45 ppb in sample GW1. For example, the average strontium concentration in Finnish dug wells is 79 ppb (Lahermo et al. 2002). Of the other variables, chloride is loading quite strongly in this component (.689). This is harder to explain as Cl generally isn't related to carbonate mineral dissolution like the other elements. On a scatter matrix its correlation to the other elements seems to be clearly weaker than the correlations between those elements. Chloride concentrations are generally very low and it loading into the PC might come down to the fact that it effects EC even in very low amounts. Overall it could be said that from the components, PC2 best reflects the natural background water quality of the research site.

The third component (15.36% of the variance) includes the water isotopes and SO_4. Also sodium and potassium are fairly strongly loading at .580 and .686, respectively. The connection between isotopes and SO_4 seems to exist also on scatter diagram, albeit it being fairly spread out (likely due to the mixed SO_4 results). Low sulphate concentrations seem to be more common with high isotope values, but on the other end the connections seems very vague. Sodium would be loading into this component far more strongly without its four outliers. This shows that the outlying samples aren't related to specific isotopic composition of water. In addition to its connection with Na, potassium seems to correlate with isotope values. The correlation seems to be quite strong on samples showing low K concentrations, but high isotope values. In cases where the K concentration rises higher, but isotope values get lower (i.e. more typical for groundwater), the correlation seems to get lost. This could mirror the mixed isotope results found in groundwater samples. On the other hand, this kind of behavior seems to be common for both K and SO_4 and some sort of weak, but linear, correlation does also seem to exits also between them.

The fourth and final component (7.08% of variation) includes pH and NO_3, being likely a sort of a left-over component consisting of the elements that do not fit to any other components. As explained in the previous chapter these elements do not correlate particularly well with any elements and neither do they correlate with each other. Also the similarly problematic F is loading quite strongly into this component. It could be very well argued that they should have been left out of the analysis in the first place. If the three variables are removed from the analysis, the fourth component is completely omitted and the three other components exist with very similar or slightly stronger loadings.

Interestingly, DSi isn't strongly associated with any of the components. As explained earlier, the variable seems to have quite clear correlation especially with Na, which also doesn't load very strongly to any components. With slightly different test parameters and data treatment steps, the correlation between DSi, Na and K can be seen more clearly.

Rotated Component Matrix[a]

PC	1	2	3	4
% of variance explained	43.46	20.86	15.36	7.08
$\delta^{18}O$	-0.226	-0.241	-0.870	-0.113
δD	-0.204	-0.321	-0.845	-0.104
DSi*	0.317	0.544	0.446	-0.033
pH	-0.026	0.175	0.308	0.812
EC*	0.366	0.854	0.268	0.174
Na*	0.320	0.363	0.580	0.465
K*	0.344	0.445	0.686	0.086
Ca*	0.177	0.910	-0.015	0.156
Mg*	0.328	0.798	0.132	0.024
F*	0.210	0.275	0.412	0.582
Cl*	0.132	0.689	0.303	-0.093
NO_3*	-0.170	0.167	0.463	-0.735
SO_4*	0.195	0.003	0.814	0.006
HCO_3*	0.274	0.919	0.118	0.115
Sr*	0.248	0.804	0.317	0.093
Y*	0.918	0.316	0.215	0.025
La*	0.939	0.107	0.193	0.074
Ce*	0.874	0.092	0.085	0.231
Pr*	0.954	0.119	0.203	0.058
Nd*	0.948	0.171	0.222	0.062
Dy*	0.951	0.219	0.145	0.061
Eu*	0.917	0.296	0.091	0.139
Gd*	0.954	0.214	0.179	0.091
Tb*	0.950	0.192	0.159	0.087
Ho*	0.933	0.279	0.184	0.049
Er*	0.931	0.298	0.170	0.009
Tm*	0.911	0.311	0.156	0.010
Yb*	0.892	0.337	0.173	-0.032

***** Values have been log-transformed and normalized before the analysis.

[a] Rotation converged in 5 iterations.

Figure 22. Principal component analysis with Varimax rotation and Kaiser normalization. Strong loadings that exceed 0.70 are highlighted.

If the PCA is done on un-normalized and un-transformed values (Appendice 13), the results differ slightly from those shown above. The two first PC's stay essentially the same as in the version discussed above. On the third PC, however, potassium is loading strongly along with sodium and the connection between them is thus better preserved. Fluoride is also present in the same PC, which is hard to explain as no clear connection are seen in bivariate correlation to any of the other PC's Both, the fourth and fifth component are quite weak, with only SO_4 loading strongly in the fourth and NO_3 in the fifth. Sulphate moving alone into the fourth component is quite interesting as in bivariate correlations connections should exist with for example with $\delta^{18}O$ and K from PC2, as seen also on the version presented above.

4.5.3 Hierarchical cluster analysis

As shown in Figure 23, cluster 1 contains only surface water samples, which apart from Kotajärvi, are all water samples from Kitinen. Samples from cluster I locate the furthest away from groundwater samples in the dendrogram highlighting their difference to groundwater samples.

Cluster 2 is another clearly surface water dominated, yet a slightly more mixed cluster. It contains either pure surface water (SW10, SW18 and SW19) samples, or samples from sites which show isotope results that are highly questionable for groundwater samples (e.g. GA306 -10.26‰ δ^{18}O, VSMOW and SPRING4 -10.53‰ δ^{18}O, VSMOW). The sample GA306 from Kiimakuusikko North well connects to the cluster via longer distance, which might be due to its overall lower concentrations in especially Ca, Mg and EC.

The third cluster reflects the characteristics of different surface waters discharging from the mire. SW4 is a sample from Ruosteoja which is a small ditch draining the mire. SW9 is from another small ditch draining the wet part of the Kärväskoski, which is connected to the mire (Figure 2). Further, SW7 is from Kärväslampi, which is very likely connected to both the ditch of SW9 and the mire. SPRING10, SW14 and SW14 are from Sakattioja, which is the biggest natural surface water drainage from Viiankiaapa to Kitinen at the research area. SPRING7 is probably the most controversial sample in the otherwise very clear cluster as it is supposed to represent spring water. The sample is made questionable by the fact the spring is located close, downhill and towards the river from Kärväslampi. The chemical characteristics of SPRING7 are also strikingly similar to those of SW7, and even their stable isotope composition are practically the same (SPRING7 -9.88 δ^{18}O, VSMOW and SW7 -9.62 δ^{18}O, VSMOW). Thus, SPRING7 is actually very likely composed of re-infiltrated surface water from Kärväslampi –area. The fact that these samples form their own cluster, which is then connected to the other clusters by a relatively long distance, shows the uniqueness of the mire water in comparison to regular surface waters in the area. Overall, waters in the third cluster are characterized by evaporated isotope values (SW4 -9.16‰ δ^{18}O, VSMOW), low amount of DSi (SW4 1.19 ppm) and low EC (SW4 23.9 µS/m).

Cluster 4 seems to be the first cluster containing mainly groundwater. This observation is based on the generally more negative isotope values and the fact that the cluster connects via very long distance to the surface water clusters before it. Still, the cluster is also clearly different from the two groundwater clusters below it. The cluster also contains two sub clusters. The lower sub cluster is differentiated from the upper mainly by slightly lower isotope values (mean value for $\delta^{18}O$ is -12.57 in the upper and -13.14 ‰, VSMOW in the lower sub cluster). Samples in this cluster are from Tuulivuopaja, Kersilönkangas, Tihiämaa and Kärväsniemi areas and represent waters from groundwater observation wells, springs, minipiezometers and surface waters. Geochemically the waters seem to be close to average in almost all variables, and so represent some sort of geochemical middle-ground, but show the slightly evaporated isotope values typical for groundwater from the research area.

Cluster 5 is one of the two clusters clearly containing pure groundwater. The highest $\delta^{18}O$ value was -13.64 ‰, VSMOW in sample SPRING3 from Tuulivuopaja Spring, but majority of the $\delta^{18}O$ values fall even below -14 %, VSMOW. Otherwise, as with the previous cluster, the samples do not seem to particularly stand out with any other variables. Thus, this cluster likely further reflects the average groundwater composition of the research area, but without the signs of surface water re-infiltration or evaporated source water component.

The final and slightly smaller cluster consists of groundwater samples from springs and observation wells. The cluster contains two sub-clusters. The upper sub-cluster consists of two similar spring water samples from Moskuvaara, but also interestingly KP30-U from Kärväsniemi GW resides in the top of the same sub-cluster. KP30-U has likely fallen into this cluster due to its overall higher trace element concentrations, compared to waters in cluster 5. The same is true for GA100 (in reality likely GA306, as GA100 should be a short observation well installed into the peat layer), which also contains slightly higher trace element levels. Spatially speaking the GA100 and KP30-U are very far from Moskuvaara, and so the geochemical similarity of the samples is probably just a coincidence, which gets picked up by the analysis. Finally, the lower sub-cluster includes three unusual samples from Kiimakuusikko South Well. These are the samples that contained for example most of the outlying Na concentrations. Interestingly, GA201 which also contains an outlying, albeit clearly lower Na concentration, is located quite far from these samples in the middle of cluster 5. This difference is likely due to smaller trace element concentrations in GA201 compared to the samples in the final sub-cluster.

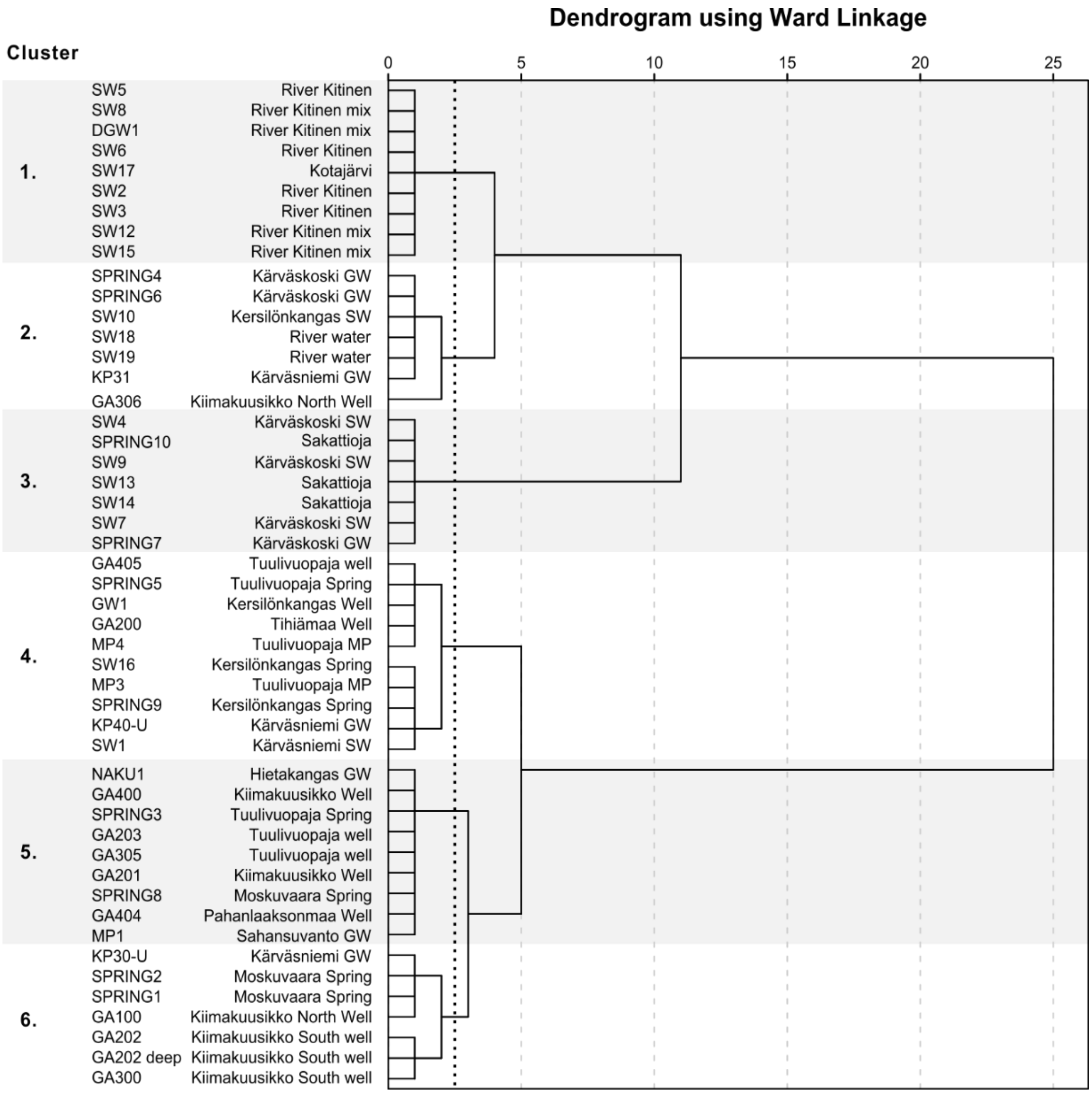

Figure 23. Dendrogram resulting from the hierarchical clustering of samples. The distance measurement was Euclidean distance and the clustering was done using the Ward's method. Number of groups was defined by the analyst and is based on the so called phenon line (dotted line in the figure).

5 CONCLUSIONS

Most water samples from the research area show a chemical composition close to the natural Finnish groundwater composition Ca–HCO_3, dominated by alkaline earths Ca and Mg along with weak acids. However, in four groundwater observation wells, located south from Kiimakuusikko, Na–HCO_3 type waters were detected. These sites were GA300 (8.26 ppm of Na), GA202 (17.34 ppm of Na), GA202 deep (15.23 ppm of Na) and GA201 (7.92 ppm of Na). Also slightly elevated concentration of potassium, alkalinity and molybdenum are seen in the same samples. In the older water quality monitoring data of AA Sakatti Mining Oy even higher Na concentrations, exceeding 130 ppm, have been observed at the same site. Source for the anomaly is likely lithological due to lack of chloride in the samples. One possible source could be weathering of albite to kaolinite. Albite is hosted in the breccia unit, located close to the site. Albite-kaolinite weathering could release Na^+ ions into the surrounding soil solution, which would provide a source for the high sodium concentrations. At the current state albite-kaolinite weathering can only be considered a hypothesis for the high concentrations. More study is needed to reliably identify the source of the anomaly.

Further, samples MP4 and GA405 from Tuulivuopaja and sample GW1 from Kersilönkangas act as outliers with elevated concentrations on most major ions and some trace-elements. Sample GA300 from Kiimakuusikko interestingly shows higher than usual trace element concentrations, but unusual values are not seen in major ions or other variables.

Kitinen shows slightly higher Al, Li and Cu contents compared to other waters from the research area. This could possibly be used to distinguish river water from groundwater at sites where river water infiltrates the groundwater system. On the other side, Na, K and DSi have higher concentrations in groundwaters compared to surface waters. This could make them useful as groundwater indicators. Sakattioja and the other smaller streams draining the mire, are characterized by very high isotope values, low amounts of DSi and low EC. These characteristics likely reflect the hydrogeochemistry of the water on the surface of the mire. The hydrogeochemical similarity of these streams is also highlighted by the hierarchical cluster analysis, where the samples from these sites form a clear cluster of their own.

Stable isotope results are mixed and difficult to interpret. Many groundwater samples show signs of either or both re-infiltration of surface water and evaporated source water component. The least fractioned waters are seen in groundwater wells near Kiimakuusikko and Pahanlaaksonmaa. Similar results were also observed at the springs of Moskuvaara and Kersilönkangas. The most fractioned waters were seen in surface water and spring water samples from Kärväskoski. This could be explained by water from the mire infiltrating the groundwater system underneath the peat layer and then re-emerging at the springs near Kärväskoski which are located quite close to the river. This hypothesis is questioned by groundwater samples from Tuulivuopaja and Sahansuvanto, which show values much closer to regular groundwater compared to the close by Kärväskoski.

Overall, based on the results, the hydrogeochemistry at the research area can be considered to be very complex. The samples represent multiple different water compositions residing in poorly connected groundwater and surface water systems. This makes interpreting the results particularly difficult and is also reflected in the statistical analyzes which produce somewhat mixed results.

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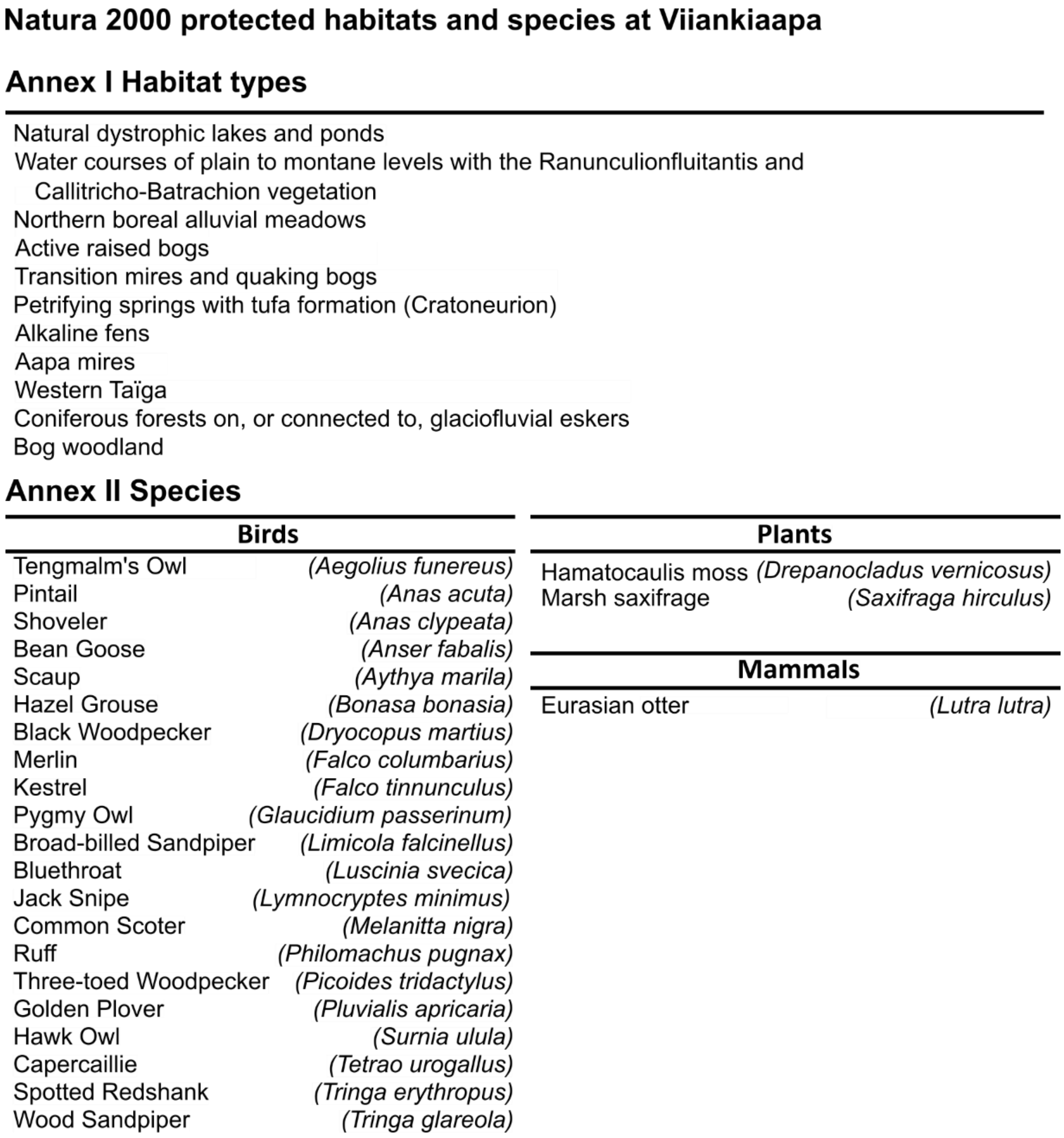
8 APPENDICES

Appendice 1. Natura 2000 protected habitat types and species at Viiankiaapa -mire (EEA 2016).



Natura 2000 protected habitats and species at Viiankiaapa

Annex I Habitat types

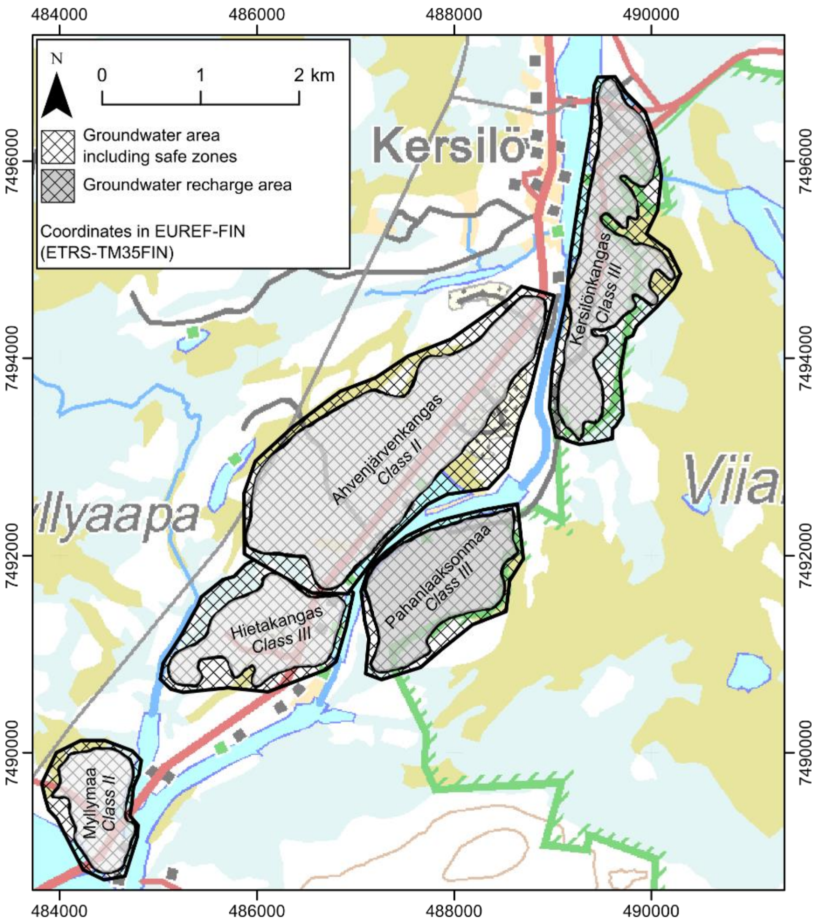
Natural dystrophic lakes and ponds
Water courses of plain to montane levels with the Ranunculionfluitantis and Callitricho-Batrachion vegetation
Northern boreal alluvial meadows
Active raised bogs
Transition mires and quaking bogs
Petrifying springs with tufa formation (Cratoneurion)
Alkaline fens
Aapa mires
Western Taïga
Coniferous forests on, or connected to, glaciofluvial eskers
Bog woodland

Annex II Species

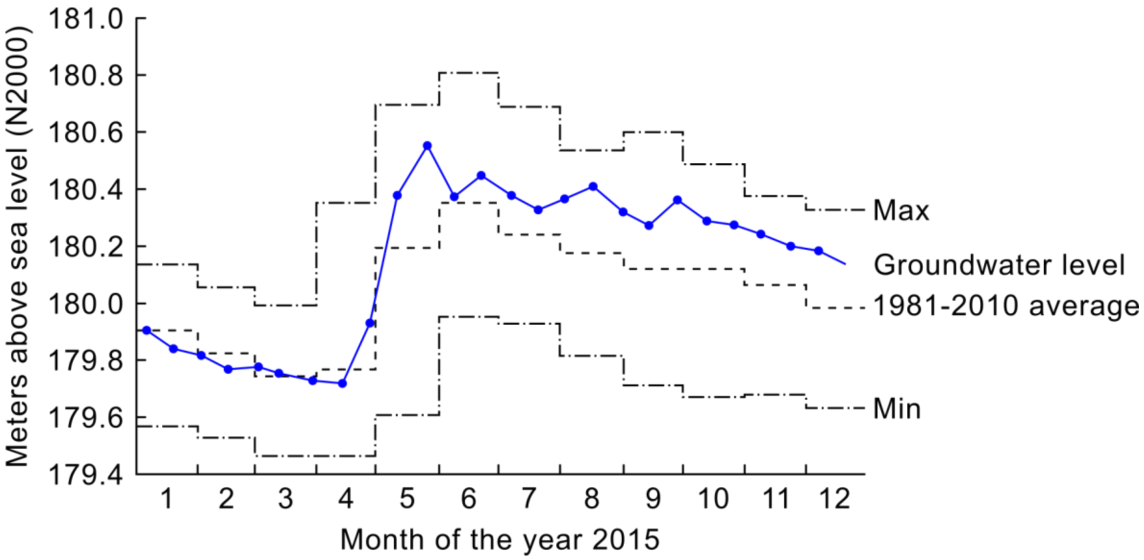
Birds	
Tengmalm's Owl	*(Aegolius funereus)*
Pintail	*(Anas acuta)*
Shoveler	*(Anas clypeata)*
Bean Goose	*(Anser fabalis)*
Scaup	*(Aythya marila)*
Hazel Grouse	*(Bonasa bonasia)*
Black Woodpecker	*(Dryocopus martius)*
Merlin	*(Falco columbarius)*
Kestrel	*(Falco tinnunculus)*
Pygmy Owl	*(Glaucidium passerinum)*
Broad-billed Sandpiper	*(Limicola falcinellus)*
Bluethroat	*(Luscinia svecica)*
Jack Snipe	*(Lymnocryptes minimus)*
Common Scoter	*(Melanitta nigra)*
Ruff	*(Philomachus pugnax)*
Three-toed Woodpecker	*(Picoides tridactylus)*
Golden Plover	*(Pluvialis apricaria)*
Hawk Owl	*(Surnia ulula)*
Capercaillie	*(Tetrao urogallus)*
Spotted Redshank	*(Tringa erythropus)*
Wood Sandpiper	*(Tringa glareola)*

Plants	
Hamatocaulis moss	*(Drepanocladus vernicosus)*
Marsh saxifrage	*(Saxifraga hirculus)*

Mammals	
Eurasian otter	*(Lutra lutra)*

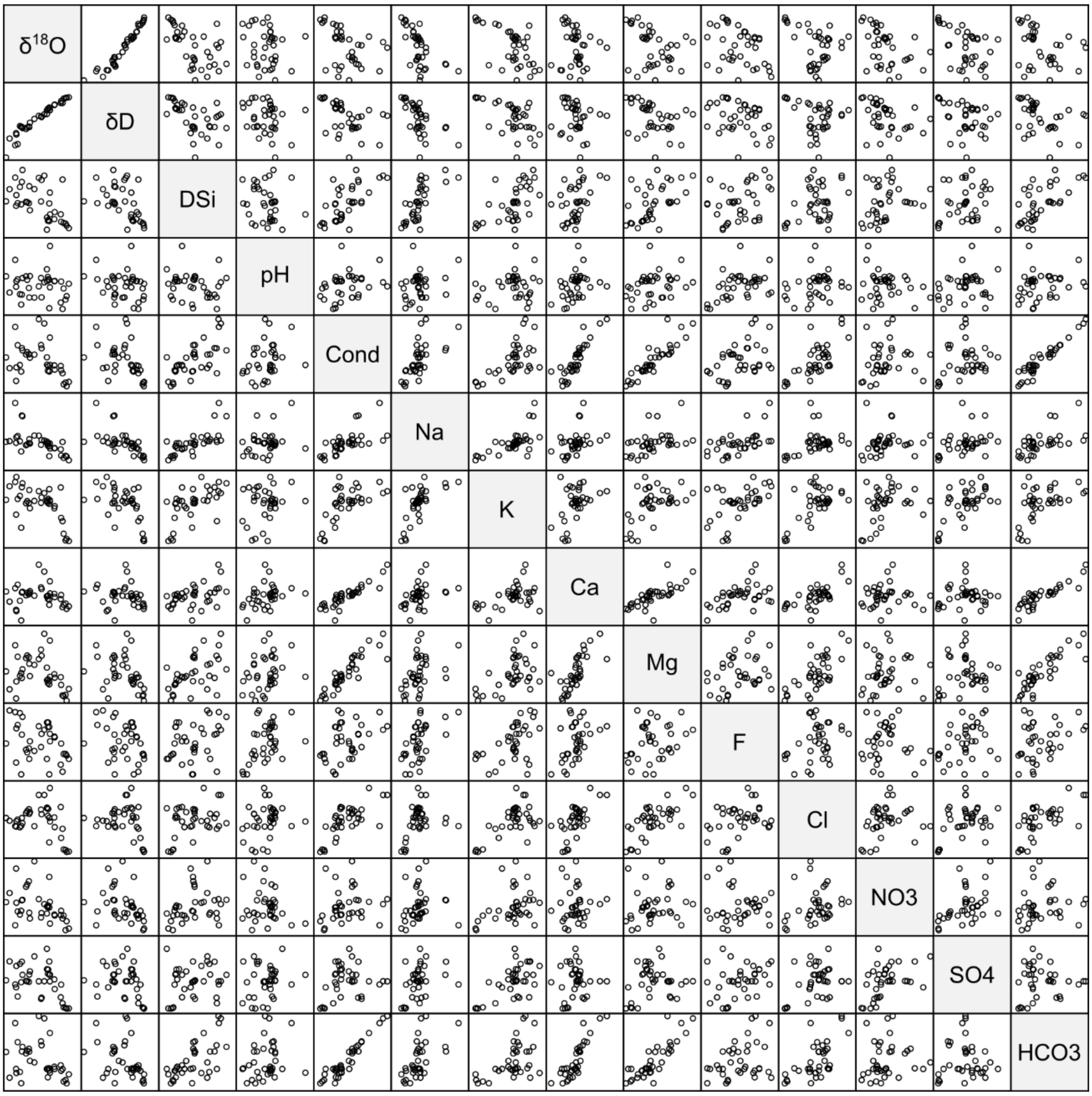


Appendice 2. Classified groundwater areas near the study area. Location and classification of the areas (SYKE 2017a). Base map (base map database @ NLS 2010).



Appendice 3. Variance in groundwater level at Sodankylä in the year 2015 (SYKE 2016). During the field campaign in August, groundwater level was about 20cm above the long term average.

Appendice 4. Estimated chemical quality of treated waste waters from Kevitsa mine. The treated waters are discharged into Kitinen approximately 20km north from the study area (AVI 2009)

	summer	**winter**	**during floods**	
Suspended solids	20	20	20	mg/l
EC	240	300	210	mS/m
Total-P	0.18	0.22	0.16	mg/l
NO_3-N	3.0	8.0	5.6	mg/l
NH_4-N	0.2	1.0	0.7	mg/l
SO_4	800	1000	700	mg/l
Total-Ca	403	500	352	mg/l
Total-Mg	202	253	177	mg/l
Total-Na	80	100	70	mg/l
Total-K	40	50	35	mg/l
Total-Mn	6.7	8.4	5.9	mg/l
Total-Ni	1.6	2.0	1.4	mg/l
Total-Al	0.40	0.50	0.35	mg/l
Total-Cu	0.06	0.07	0.05	mg/l
Total-Co	0.03	0.04	0.03	mg/l
Total-Zn	0.02	0.03	0.02	mg/l
Total-Cr	0.004	0.005	0.004	mg/l

Appendice 5. A scatterplot matrix of all correlations between major ions, isotopes and DSi. All values except for pH and Dsi have been log10-transformed.

Appendice 6. Water quality in the lakes of the research site in 1996 (SYKE 2017b).

Lake	Viiankijärvi	Kotajärvi	Kotajärvi	Kotajärvi	Rytilampi	Rytilampi	Kokkolampi	Kokkolampi	
Date	28.2.1996	28.2.1996	28.2.1996	28.2.1996	28.2.1996	28.2.1996	24.9.1996	24.9.1996	
Total depth	1.1	14	14	14	3.5	3.5	2.8	2.8	***(m)***
Sample depth	0.7	1	7	13	1	1.7	1	2.5	***(m)***
Temp.	1.1	1.2	3.4	3.7	1.3	2.4	5.8	5.7	***(°C)***
Diss. Oxy.	0.1	10.4	8.3	3.2	6.3	0	11.1	11.1	***(mg/l)***
Oxy. Saturation	0	73	62	24	45	0	89	89	***(sat. %)***
Turbidity	4.7	0.46	0.57	2.5	7.6	8.9	3.4	3.8	***(FNU)***
Cond	8.8	5.5	5.6	8	9.7	11.6	3.5	3.5	***(mS/m)***
Alkalinity	0.75	0.35	0.36	0.59	0.84	1.09	0.28	0.28	***(mmol/l)***
pH	6.5	6.9	6.8	6.7	6.8	6.6	6.9	7	
Color	120	50	50	60	120	300	100	100	***(mg/l Pt)***
Tot-N	1200	300	300	300	580	750	500	490	***(µg/l)***
NH_4-N	750	< 5	< 5	< 5	8	400	< 5	< 5	***(µg/l)***
Tot-P	22	7	5	6	22	62	27	22	***(µg/l)***
PO_4^{3-}-P	2	< 2	< 2	< 2	11	39	3	3	***(µg/l)***
Fe	5000	250	270	750	2300	14000	1400	1400	***(µg/l)***
Chemical oxygen demand	11	9.3	7.8	5.6	9.2	11	7.2	7.4	***(mg/l)***
Nitrite as NO_3-N	< 5	70	74	160	240	5	< 5	< 5	***(µg/l)***

Appendice 7. Water quality of Kitinen before and after the field work session. Samples have been collected from the downstream side of Matarakoski dam. Data from SYKE (2017b), but originally samples have been collected by Ramboll Finland Oy.

Site: Kitinen, Matarakoski dam
Coordinates: 7499650-3489310 (ETRS-TM35FIN)

Date	10.8.2015	7.9.2015	
Sample depth	0.5	0.5	**(m)**
Temp.	14.7	11.5	**(°C)**
Diss.Oxy.	8.8	9.8	***(mg/l)***
Oxy. Saturation	87	90	***(sat. %)***
Turbidity	1.3	1.2	***(FNU)***
TDS	<2.0	<2.0	***(mg/l)***
Cond	3.8	3.7	***(mS/m)***
Alkalinity	0.23	0.23	***(mmol/l)***
pH	7	7.1	
Color	80	60	***(mg/l Pt)***
Tot-N	260	270	***(µg/l)***
Nitrite-N	<2	<2	***(µg/l)***
Nitrate-N	15	27	***(µg/l)***
NH_4-N	9	6	***(µg/l)***
Tot-P	10	10	***(µg/l)***

	10.8.2015	7.9.2015	
PO_4^{3-}-P	<2.0	<2.0	***(µg/l)***
Fe	610	600	***(µg/l)***
Mn	35	30	***(µg/l)***
SO_{4-}	3.5	3.3	***(mg/l)***
K	0.45	0.5	***(mg/l)***
Ca+Mg	0.15	0.13	***(mmol/l)***
Chemical oxygen demand	12	8.5	***(mg/l)***
Cl	1.7	1	***(mg/l)***
Cr	<1.00	<1.00	***(µg/l)***
Cu	<1.00	<1.00	***(µg/l)***
Na	1.4	1.3	***(mg/l)***
Ni	<1.00	<1.00	***(µg/l)***
Odor	Odorless	Odorless	

Appendice 8. Groundwater quality in a pond at the Kärväsniemi area (SYKE 2017a).

Site: Nakuranta gravel pit
Coordinates: 7496219-3488435 (ETRS-TM35FIN)

Date	10.10.2016	
Cl	1	***(mg/l)***
Temp.	5.4	**(°C)**
Mn	19.2	***(µg/l)***
Nitrite-N	5.2	***(µg/l)***
Nitrate-N	<2	***(µg/l)***
Nitrite as NO_3-N	6.8	***(µg/l)***
pH	7.22	
Fe	35.1	***(µg/l)***
Cond	5	***(mS/m)***
Color	<5	***(mg/l Pt)***
Chemical oxygen demand	0.91	***(mg/l)***

Appendice 9 Desciptive statistics of different variables. Note that skewness and kurtosis have been calculated via SPSS.

	$\delta^{18}O$	**δD**	**DSi**	**pH lab**	**Cond**	**Na**	**K**	**Ca**	**Mg**
n	49	49	41	38	38	38	38	38	38
Max	-9.160	-73.460	8.680	8.216	223.000	17.343	2.152	31.900	10.715
Min	-14.610	-108.120	0.990	6.190	20.500	0.580	0.048	1.167	0.663
Mean	-12.398	-93.844	4.240	6.974	64.879	2.619	0.653	6.314	2.817
Median	-12.280	-95.900	4.250	7.061	43.900	1.583	0.518	5.144	1.855
Range	5.450	34.660	7.690	2.026	202.500	16.763	2.104	30.733	10.052
Std. Dev.	1.605	10.412	2.188	2.964	50.192	3.374	0.521	5.511	2.325
Skewness	0.475	0.536	0.380	0.520	1.960	3.245	1.232	3.378	1.805
Kurtosis	-0.935	-0.826	-1.020	1.011	3.504	10.308	1.306	13.501	3.301
	F	**Cl**	**NO_3**	**SO_4**	**HCO_3**	**∑Cations**	**∑Anions**	**IB**	**Li**
n	38	38	38	38	38	38	38	38	40
Max	0.080	2.005	2.634	13.226	2.374	2.041	2.465	27.447	0.835
Min	0.012	0.301	0.016	0.381	0.216	0.203	0.235	0.078	0.016
Mean	0.037	0.838	0.234	2.795	0.651	0.678	0.739	5.935	0.245
Median	0.032	0.806	0.067	1.947	0.380	0.505	0.505	4.041	0.161
Range	0.068	1.704	2.618	12.845	2.158	1.838	2.231	27.369	0.818
Std. Dev.	0.023	0.477	0.442	2.563	0.554	0.518	0.573	5.804	0.206
Skewness	0.773	1.139	3.893	2.191	1.967	1.721	1.923	2.062	0.950
Kurtosis	-0.295	2.263	16.555	6.276	3.252	2.265	3.241	4.791	0.329
	Al	**P**	**Sc**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**
n	40	40	40	40	40	40	40	40	40
Max	157.437	312.602	0.274	4.399	993.357	20800.115	5.492	11.645	3.908
Min	10.538	1.525	0.016	0.216	0.295	2.118	0.030	0.231	0.132
Mean	36.847	35.810	0.057	0.953	138.068	2549.881	0.770	2.209	0.747
Median	27.028	17.368	0.038	0.634	28.554	425.796	0.245	1.037	0.532
Range	146.899	311.078	0.257	4.183	993.062	20797.997	5.462	11.414	3.776
Std. Dev.	28.290	53.982	0.060	0.786	227.602	4980.154	1.200	2.596	0.753
Skewness	2.506	3.581	2.110	2.629	2.337	2.493	2.662	1.975	2.788
Kurtosis	9.236	14.215	4.311	9.522	4.804	5.337	7.025	3.517	8.766
	Zn	**As**	**Rb**	**Sr**	**Y**	**Zr**	**Mo**	**Ag**	**Cd**
n	40	40	40	40	40	40	40	40	40
Max	91.111	3.756	4.556	45.463	3.014	4.521	0.396	0.023	0.289
Min	1.144	0.080	0.134	5.601	0.007	0.068	0.019	0.002	0.013
Mean	7.022	0.502	1.518	18.946	0.220	0.439	0.130	0.003	0.040
Median	2.413	0.263	1.252	17.309	0.084	0.260	0.068	0.002	0.031
Range	89.967	3.676	4.422	39.862	3.007	4.453	0.377	0.022	0.277
Std. Dev.	15.068	0.666	1.144	11.612	0.445	0.669	0.111	0.004	0.044
Skewness	4.435	3.148	0.905	0.759	5.198	5.054	0.993	4.122	4.397
Kurtosis	20.180	11.674	0.374	-0.116	29.837	28.374	-0.079	18.442	23.541
	Cs	**Ba**	**La**	**Ce**	**Pr**	**Nd**	**Sm**	**Eu**	**Gd**
n	40	40	40	40	40	40	40	40	40
Max	9.154	17.833	1.006	2.898	0.402	1.837	0.395	0.100	0.437
Min	0.003	0.869	0.003	0.005	0.001	0.005	0.004	0.001	0.003
Mean	0.413	4.685	0.105	0.243	0.032	0.143	0.031	0.009	0.035
Median	0.033	3.037	0.051	0.074	0.014	0.053	0.011	0.004	0.014
Range	9.151	16.964	1.003	2.893	0.402	1.832	0.390	0.098	0.433
Std. Dev.	1.393	4.199	0.159	0.457	0.060	0.273	0.059	0.015	0.066
Skewness	5.235	1.869	4.124	4.294	5.021	5.060	5.063	4.634	4.917
Kurtosis	28.856	2.927	20.722	21.619	28.395	28.672	28.613	24.849	27.263
	Tb	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**	**Pb**	**U**
n	40	40	40	40	40	40	40	40	40
Max	0.062	0.384	0.092	0.298	0.045	0.313	0.056	23.294	0.271
Min	0.001	0.001	0.001	0.002	0.000	0.003	0.001	0.024	0.001
Mean	0.005	0.030	0.007	0.021	0.003	0.022	0.004	0.696	0.033
Median	0.002	0.010	0.003	0.008	0.001	0.008	0.001	0.076	0.010
Range	0.061	0.383	0.091	0.296	0.045	0.310	0.055	23.271	0.270
Std. Dev.	0.009	0.057	0.014	0.044	0.007	0.046	0.008	3.319	0.053
Skewness	4.926	4.984	5.136	5.290	5.325	5.358	5.427	6.296	3.261
Kurtosis	27.355	27.865	29.282	30.667	30.933	31.234	31.688	39.744	11.310

Appendice 10. Results from the Shapiro-Wilk test for distribution. W is the correlation between the data and an ideal normal distribution, n is the number of samples per variable and p is the significance level of the test. If $p > 0.05$, the distribution can be deemed to be normal. Variables marked with an asterix have had their values base 10 log-transformed.

Shapiro-Wilk test of normality

	W	n	p
$\delta^{18}O$ (VSMOW, ‰)	.920	49	.003
δD (VSMOW, ‰)	.922	49	.003
pH	.952	38	.103
DSi (ppm)	.947	37	.080
Cond (uS/m)*	.948	37	.085
Na (ppm)*	.829	37	.000
K (ppm)*	.899	37	.003
Ca (ppm)*	.959	37	.189
Mg (ppm)*	.972	37	.458
F (ppm)*	.971	37	.447
Cl (ppm)*	.942	37	.055
NO_3 (ppm)*	.921	37	.012
SO_4 (ppm)*	.962	37	.241
HCO_3 (mmolL-1)*	.909	37	.005
Li (ppb)*	.912	37	.007
Al (ppb)*	.973	37	.508
P (ppb)*	.951	37	.104
Sc (ppb)*	.847	37	.000
Cr (ppb)*	.970	37	.415
Mn (ppb)*	.953	37	.119
Fe (ppb)*	.952	37	.110
Co (ppb)*	.963	37	.243
Ni (ppb)*	.943	37	.058
Cu (ppb)*	.981	37	.762
Zn (ppb)*	.787	37	.000
As (ppb)*	.905	37	.004
Rb (ppb)*	.927	37	.018
Sr (ppb)*	.967	37	.333
Y (ppb)*	.978	37	.646
Zr (ppb)*	.985	37	.899
Mo (ppb)*	.929	37	.020
Ag (ppb)*	.456	37	.000
Cd (ppb)*	.881	37	.001
Cs (ppb)*	.907	37	.005
Ba (ppb)*	.959	37	.182
La (ppb)*	.982	37	.807
Ce (ppb)*	.983	37	.837
Pr (ppb)*	.986	37	.921
Nd (ppb)*	.965	37	.283
Sm (ppb)*	.871	37	.001
Eu (ppb)*	.931	37	.024
Gd (ppb)*	.936	37	.035
Tb (ppb)*	.853	37	.000
Dy (ppb)*	.975	37	.543
Ho (ppb)*	.929	37	.021
Er (ppb)*	.934	37	.030
Tm (ppb)*	.908	37	.005
Yb (ppb)*	.888	37	.001
Lu (ppb)*	.640	37	.000
Pb (ppb)*	.731	37	.000
U (ppb)*	.953	37	.122

* $\log_{10}$ transformed values

Appendice 11a. Pearson correlation coefficients between all variables chosen for the statistical analyses. Two-tailed correlations that are significant at the 0.01 level have been marked with double asterisks (**) and gray background. Significant two-tailed correlations at the 0.05 level have been marked with a single asterisk (*).

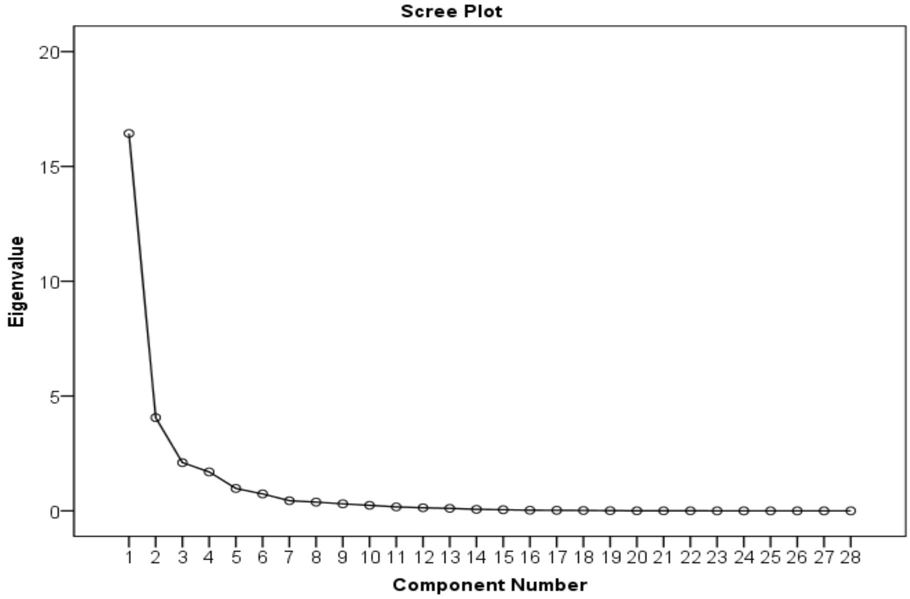
		$\delta^{18}O$	δD	DSi	pH	EC	Na	K	Ca	Mg	F	Cl	NO_3	SO_4	HCO_3	Sr	Y	La	Ce	Pr	Nd	Dy
$\delta^{18}O$	Pearson Corr.	1	.892**	-.570**	-.2	-.510**	-.627**	-.657**	-.224	-.466**	-.377*	-.408*	-.511**	-.586**	-.406*	-.451**	-.397*	-.327*	-.258	-.337*	-.339*	-.317*
	Sig. (2-tailed)		9E-18	1E-04	.229	.001	2E-05	8E-06	.177	.003	.02	.011	.001	1E-04	.011	.003	.011	.04	.108	.034	.032	.046
	N	49	49	41	38	38	38	38	38	38	38	38	38	38	38	40	40	40	40	40	40	40
δD	Pearson Corr.	.892**	1	-.495**	-.299	-.476**	-.653**	-.569**	-.196	-.425**	-.376*	-.258	-.266	-.328*	-.440**	-.361*	-.297	-.254	-.192	-.255	-.244	-.233
	Sig. (2-tailed)	9E-18		1E-03	.069	.003	9E-06	2E-04	.237	.008	.02	.118	.107	.045	.006	.022	.063	.114	.236	.113	.13	.148
	N	49	49	41	38	38	38	38	38	38	38	38	38	38	38	40	40	40	40	40	40	40
DSi	Pearson Corr.	-.570**	-.495**	1	-.176	.671**	.706**	.594**	.424**	.512**	.31	.363*	.274	.187	.660**	.611**	.596**	.421**	.397*	.465**	.497**	.530**
	Sig. (2-tailed)	1E-04	1E-03		.297	5E-06	1E-06	1E-04	.009	.001	.062	.027	.1	.267	9E-06	4E-05	6E-05	.008	.012	.003	.001	5E-04
	N	41	41	41	37	37	37	37	37	37	37	37	37	37	37	39	39	39	39	39	39	39
pH	Pearson Corr.	-.2	-.299	-.176	1	.348*	.371*	.271	.381*	.345*	.497**	.213	-.245	.175	.301	.296	-.035	-.063	-.022	-.09	-.068	-.075
	Sig. (2-tailed)	.229	.069	.297		.032	.022	.1	.018	.034	.001	.199	.139	.294	.066	.075	.839	.71	.899	.595	.69	.659
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
EC	Pearson Corr.	-.510**	-.476**	.671**	.348*	1	.688**	.648**	.868**	.904**	.471**	.673**	.07	.219	.956**	.835**	.648**	.463**	.444**	.464**	.517**	.566**
	Sig. (2-tailed)	.001	.003	5E-06	.032		2E-06	1E-05	2E-12	7E-15	.003	4E-06	.675	.187	8E-21	1E-10	1E-05	.004	.006	.004	.001	3E-04
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Na	Pearson Corr.	-.627**	-.653**	.706**	.371*	.688**	1	.680**	.422**	.509**	.581**	.286	.026	.313	.642**	.630**	.571**	.478**	.478**	.479**	.499**	.508**
	Sig. (2-tailed)	2E-05	9E-06	1E-06	.022	2E-06		3E-06	.008	.001	1E-04	.081	.876	.056	1E-05	3E-05	2E-04	.003	.003	.003	.002	.001
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
K	Pearson Corr.	-.657**	-.569**	.594**	.271	.648**	.680**	1	.473**	.540**	.545**	.587**	.276	.615**	.550**	.624**	.554**	.495**	.396*	.486**	.509**	.498**
	Sig. (2-tailed)	8E-06	2E-04	1E-04	.1	1E-05	3E-06		.003	5E-04	4E-04	1E-04	.093	4E-05	3E-04	4E-05	4E-04	.002	.015	.002	.001	.002
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Ca	Pearson Corr.	-.224	-.196	.424**	.381*	.868**	.422**	.473**	1	.745**	.484**	.646**	-.005	.093	.867**	.833**	.470**	.266	.277	.282	.334*	.403*
	Sig. (2-tailed)	.177	.237	.009	.018	2E-12	.008	.003		8E-08	.002	1E-05	.977	.578	2E-12	2E-10	.003	.112	.097	.091	.043	.013
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Mg	Pearson Corr.	-.466**	-.425**	.512**	.345*	.904**	.509**	.540**	.745**	1	.329*	.653**	.077	.154	.866**	.726**	.550**	.399*	.361*	.392*	.444**	.468**
	Sig. (2-tailed)	.003	.008	.001	.034	7E-15	.001	5E-04	8E-08		.044	9E-06	.648	.357	2E-12	4E-07	4E-04	.014	.028	.016	.006	.003
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
F	Pearson Corr.	-.377*	-.376*	.31	.497**	.471**	.581**	.545**	.484**	.329*	1	.313	-.137	.297	.392*	.381*	.351*	.321	.258	.342*	.357*	.366*
	Sig. (2-tailed)	.02	.02	.062	.001	.003	1E-04	4E-04	.002	.044		.056	.414	.071	.015	.02	.033	.052	.123	.038	.03	.026
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Cl	Pearson Corr.	-.408*	-.258	.363*	.213	.673**	.286	.587**	.646**	.653**	.313	1	.225	.386*	.586**	.650**	.374*	.273	.217	.25	.274	.293
	Sig. (2-tailed)	.011	.118	.027	.199	4E-06	.081	1E-04	1E-05	9E-06	.056		.175	.017	1E-04	1E-05	.022	.102	.197	.136	.101	.078
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
NO_3	Pearson Corr.	-.511**	-.266	.274	-.245	.07	.026	.276	-.005	.077	-.137	.225	1	.457**	.072	.206	.008	-.086	-.206	-.058	-.073	-.084
	Sig. (2-tailed)	.001	.107	.1	.139	.675	.876	.093	.977	.648	.414	.175		.004	.669	.221	.962	.611	.221	.732	.666	.622
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
SO_4	Pearson Corr.	-.586**	-.328*	.187	.175	.219	.313	.615**	.093	.154	.297	.386*	.457**	1	.016	.282	.231	.212	.097	.186	.213	.164
	Sig. (2-tailed)	1E-04	.045	.267	.294	.187	.056	4E-05	.578	.357	.071	.017	.004		.924	.091	.169	.208	.567	.27	.205	.333
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
HCO_3	Pearson Corr.	-.406*	-.440**	.660**	.301	.956**	.642**	.550**	.867**	.866**	.392*	.586**	.072	.016	1	.839**	.577**	.381*	.386*	.390*	.432**	.492**
	Sig. (2-tailed)	.011	.006	9E-06	.066	8E-21	1E-05	3E-04	2E-12	2E-12	.015	1E-04	.669	.924		9E-11	2E-04	.02	.018	.017	.008	.002
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Sr	Pearson Corr.	-.451**	-.361*	.611**	.296	.835**	.630**	.624**	.833**	.726**	.381*	.650**	.206	.282	.839**	1	.536**	.351*	.352*	.355*	.400*	.419**
	Sig. (2-tailed)	.003	.022	4E-05	.075	1E-10	3E-05	4E-05	2E-10	4E-07	.02	1E-05	.221	.091	9E-11		4E-04	.026	.026	.025	.011	.007
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Y	Pearson Corr.	-.397*	-.297	.596**	-.035	.648**	.571**	.554**	.470**	.550**	.351*	.374*	.008	.231	.577**	.536**	1	.922**	.841**	.948**	.964**	.981**
	Sig. (2-tailed)	.011	.063	6E-05	.839	1E-05	2E-04	4E-04	.003	4E-04	.033	.022	.962	.169	2E-04	4E-04		3E-17	1E-11	2E-20	1E-23	9E-29

	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
La	Pearson Corr.	-.327*	-.254	.421**	-.063	.463**	.478**	.495**	.266	.399*	.321	.273	-.086	.212	.381*	.351*	.922**	1	.914**	.987**	.974**	.938**
	Sig. (2-tailed)	.04	.114	.008	.71	.004	.003	.002	.112	.014	.052	.102	.611	.208	.02	.026	3E-17		2E-16	1E-31	4E-26	5E-19
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Ce	Pearson Corr.	-.258	-.192	.397*	-.022	.444**	.478**	.396*	.277	.361*	.258	.217	-.206	.097	.386*	.352*	.841**	.914**	1	.897**	.879**	.861**
	Sig. (2-tailed)	.108	.236	.012	.899	.006	.003	.015	.097	.028	.123	.197	.221	.567	.018	.026	1E-11	2E-16		5E-15	9E-14	1E-12
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Pr	Pearson Corr.	-.337*	-.255	.465**	-.09	.464**	.479**	.486**	.282	.392*	.342*	.25	-.058	.186	.390*	.355*	.948**	.987**	.897**	1	.990**	.970**
	Sig. (2-tailed)	.034	.113	.003	.595	.004	.003	.002	.091	.016	.038	.136	.732	.27	.017	.025	2E-20	1E-31	5E-15		5E-34	8E-25
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Nd	Pearson Corr.	-.339*	-.244	.497**	-.068	.517**	.499**	.509**	.334*	.444**	.357*	.274	-.073	.213	.432**	.400*	.964**	.974**	.879**	.990**	1	.977**
	Sig. (2-tailed)	.032	.13	.001	.69	.001	.002	.001	.043	.006	.03	.101	.666	.205	.008	.011	1E-23	4E-26	9E-14	5E-34		4E-27
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Dy	Pearson Corr.	-.317*	-.233	.530**	-.075	.566**	.508**	.498**	.403*	.468**	.366*	.293	-.084	.164	.492**	.419**	.981**	.938**	.861**	.970**	.977**	1
	Sig. (2-tailed)	.046	.148	5E-04	.659	3E-04	.001	.002	.013	.003	.026	.078	.622	.333	.002	.007	9E-29	5E-19	1E-12	8E-25	4E-27	
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40

Appendice 11b. Spearman correlation coefficients between all variables chosen for the statistical analyses. Two-tailed correlations that are significant at the .01 level have been marked with double asterisks (**) and gray background. Significant two-tailed correlations at the .05 level have been marked with a single asterisk (*).

		d^{18}O	**δD**	**DSi**	**pH**	**EC**	**Na**	**K**	**Ca**	**Mg**	**F**	**Cl**	**NO$_3$**	**SO$_4$**	**HCO$_3$**	**Sr**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Dy**
δ^{18}O	Spearman Corr.	1	.963**	-.599**	-.222	-.499**	-.751**	-.562**	-.273	-.439**	-.374*	-.147	-.470**	-.455**	-.384*	-.378*	-.264	-.246	-.183	-.260	-.242	-.196
	Sig. (2-tailed)		.000	.000	.180	.001	.000	.000	.098	.006	.021	.379	.003	.004	.017	.016	.100	.127	.259	.106	.132	.226
	N	49	49	41	38	38	38	38	38	38	38	38	38	38	38	40	40	40	40	40	40	40
δD	Spearman Corr.	.963**	1	-.607**	-.337*	-.576**	-.747**	-.583**	-.379*	-.512**	-.388*	-.223	-.399*	-.355*	-.476**	-.440**	-.295	-.270	-.190	-.282	-.277	-.225
	Sig. (2-tailed)	.000		.000	.038	.000	.000	.000	.019	.001	.016	.179	.013	.029	.003	.004	.065	.092	.241	.077	.083	.162
	N	49	49	41	38	38	38	38	38	38	38	38	38	38	38	40	40	40	40	40	40	40
DSi	Spearman Corr.	-.599**	-.607**	1	-.134	.667**	.777**	.661**	.477**	.550**	.332*	.224	.365*	.170	.655**	.612**	.545**	.406*	.353*	.432**	.456**	.469**
	Sig. (2-tailed)	.000	.000		.429	.000	.000	.000	.003	.000	.045	.182	.027	.316	.000	.000	.000	.010	.027	.006	.004	.003
	N	41	41	41	37	37	37	37	37	37	37	37	37	37	37	39	39	39	39	39	39	39
pH	Spearman Corr.	-.222	-.337*	-.134	1	.359*	.183	.131	.453**	.325*	.474**	.273	-.143	.198	.260	.257	-.136	-.138	-.106	-.146	-.138	-.147
	Sig. (2-tailed)	.180	.038	.429		.027	.271	.432	.004	.047	.003	.097	.390	.234	.115	.124	.422	.415	.531	.387	.416	.386
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
EC	Spearman Corr.	-.499**	-.576**	.667**	.359*	1	.711**	.626**	.902**	.905**	.464**	.625**	.213	.192	.913**	.860**	.565**	.390*	.341*	.396*	.442**	.483**
	Sig. (2-tailed)	.001	.000	.000	.027		.000	.000	.000	.000	.003	.000	.200	.247	.000	.000	.000	.017	.039	.015	.006	.002
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Na	Spearman Corr.	-.751**	-.747**	.777**	.183	.711**	1	.723**	.517**	.512**	.549**	.292	.288	.388*	.623**	.692**	.386*	.362*	.313	.353*	.370*	.318
	Sig. (2-tailed)	.000	.000	.000	.271	.000		.000	.001	.001	.000	.075	.080	.016	.000	.000	.018	.028	.059	.032	.024	.055
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
K	Spearman Corr.	-.562**	-.583**	.661**	.131	.626**	.723**	1	.429**	.450**	.552**	.346*	.297	.503**	.529**	.460**	.458**	.468**	.414*	.477**	.497**	.448**
	Sig. (2-tailed)	.000	.000	.000	.432	.000	.000		.007	.005	.000	.033	.070	.001	.001	.004	.004	.003	.011	.003	.002	.005
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Ca	Spearman Corr.	-.273	-.379*	.477**	.453**	.902**	.517**	.429**	1	.806**	.467**	.570**	.048	.043	.873**	.820**	.493**	.309	.310	.322	.362*	.435**
	Sig. (2-tailed)	.098	.019	.003	.004	.000	.001	.007		.000	.003	.000	.774	.796	.000	.000	.002	.062	.062	.052	.027	.007
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Mg	Spearman Corr.	-.439**	-.512**	.550**	.325*	.905**	.512**	.450**	.806**	1	.278	.575**	.136	.081	.837**	.744**	.561**	.376*	.315	.382*	.421**	.470**
	Sig. (2-tailed)	.006	.001	.000	.047	.000	.001	.005	.000		.091	.000	.414	.631	.000	.000	.000	.022	.058	.020	.009	.003
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
F	Spearman Corr.	-.374*	-.388*	.332*	.474**	.464**	.549**	.552**	.467**	.278	1	.245	.048	.333*	.309	.311	.304	.338*	.310	.346*	.354*	.327*

	Sig. (2-tailed)	.021	.016	.045	.003	.003	.000	.000	.003	.091		.138	.773	.041	.059	.061	.068	.041	.062	.036	.032	.048
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Cl	Spearman Corr.	-.147	-.223	.224	.273	.625**	.292	.346*	.570**	.575**	.245	1	.325*	.279	.565**	.539**	.197	.117	.125	.108	.143	.176
	Sig. (2-tailed)	.379	.179	.182	.097	.000	.075	.033	.000	.000	.138		.046	.090	.000	.001	.243	.492	.460	.526	.400	.296
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
NO_3	Spearman Corr.	-.470**	-.399*	.365*	-.143	.213	.288	.297	.048	.136	.048	.325*	1	.467**	.235	.257	.059	-.031	-.116	-.010	.000	-.026
	Sig. (2-tailed)	.003	.013	.027	.390	.200	.080	.070	.774	.414	.773	.046		.003	.156	.125	.728	.855	.493	.953	.998	.877
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
SO_4	Spearman Corr.	-.455**	-.355*	.170	.198	.192	.388*	.503**	.043	.081	.333*	.279	.467**	1	.012	.142	.056	.106	.041	.112	.105	.022
	Sig. (2-tailed)	.004	.029	.316	.234	.247	.016	.001	.796	.631	.041	.090	.003		.944	.402	.743	.532	.808	.510	.536	.896
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
HCO_3	Spearman Corr.	-.384*	-.476**	.655**	.260	.913**	.623**	.529**	.873**	.837**	.309	.565**	.235	.012	1	.890**	.550**	.353*	.322	.364*	.401*	.469**
	Sig. (2-tailed)	.017	.003	.000	.115	.000	.000	.001	.000	.000	.059	.000	.156	.944		.000	.000	.032	.052	.027	.014	.003
	N	38	38	37	38	38	38	38	38	38	38	38	38	38	38	37	37	37	37	37	37	37
Sr	Spearman Corr.	-.378*	-.440**	.612**	.257	.860**	.692**	.460**	.820**	.744**	.311	.539**	.257	.142	.890**	1	.475**	.303	.308	.292	.331*	.381*
	Sig. (2-tailed)	.016	.004	.000	.124	.000	.000	.004	.000	.000	.061	.001	.125	.402	.000		.002	.057	.053	.067	.037	.015
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Y	Spearman Corr.	-.264	-.295	.545**	-.136	.565**	.386*	.458**	.493**	.561**	.304	.197	.059	.056	.550**	.475**	1	.917**	.817**	.936**	.955**	.985**
	Sig. (2-tailed)	.100	.065	.000	.000	.000	.018	.004	.002	.000	.068	.243	.728	.743	.000	.002		.000	.000	.000	.000	.000
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
La	Spearman Corr.	-.246	-.270	.406*	-.138	.390*	.362*	.468**	.309	.376*	.338*	.117	-.031	.106	.353*	.303	.917**	1	.919**	.993**	.984**	.940**
	Sig. (2-tailed)	.127	.092	.010	.415	.017	.028	.003	.062	.022	.041	.492	.855	.532	.032	.057	.000		.000	.000	.000	.000
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Ce	Spearman Corr.	-.183	-.190	.353*	-.106	.341*	.313	.414*	.310	.315	.310	.125	-.116	.041	.322	.308	.817**	.919**	1	.902**	.890**	.856**
	Sig. (2-tailed)	.259	.241	.027	.531	.039	.059	.011	.062	.058	.062	.460	.493	.808	.052	.053	.000	.000		.000	.000	.000
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Pr	Spearman Corr.	-.260	-.282	.432**	-.146	.396*	.353*	.477**	.322	.382*	.346*	.108	-.010	.112	.364*	.292	.936**	.993**	.902**	1	.992**	.960**
	Sig. (2-tailed)	.106	.077	.006	.387	.015	.032	.003	.052	.020	.036	.526	.953	.510	.027	.067	.000	.000	.000		.000	.000
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Nd	Spearman Corr.	-.242	-.277	.456**	-.138	.442**	.370*	.497**	.362*	.421**	.354*	.143	.000	.105	.401*	.331*	.955**	.984**	.890**	.992**	1	.973**
	Sig. (2-tailed)	.132	.083	.004	.416	.006	.024	.002	.027	.009	.032	.400	.998	.536	.014	.037	.000	.000	.000	.000		.000
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40
Dy	Spearman Corr.	-.196	-.225	.469**	-.147	.483**	.318	.448**	.435**	.470**	.327*	.176	-.026	.022	.469**	.381*	.985**	.940**	.856**	.960**	.973**	1
	Sig. (2-tailed)	.226	.162	.003	.386	.002	.055	.005	.007	.003	.048	.296	.877	.896	.003	.015	.000	.000	.000	.000	.000	
	N	40	40	39	37	37	37	37	37	37	37	37	37	37	37	40	40	40	40	40	40	40



Appendice 12. A scree plot. Eigenvalues associated with a component versus number of components. With the Eigenvalue > 1 criteria, number of components gets to be 4. However, the scree plot shows that the Eigenvalue is still declining quite steeply at this point, which would suggest a slightly higher number of components (the optimal number of components can be seen at the point where the curve levels out). On the other hand a higher number of components would lead to weak components with less than three variables each. Thus, 4 components were chosen for the final analysis.

	Component				
	1	2	3	4	5
δ^{18}O	-0.124	-0.210	-0.735	-0.456	0.174
δD	-0.114	-0.271	-0.718	-0.461	0.158
Dsi	0.300	0.481	0.625	-0.122	-0.382
pH	-0.146	0.180	0.422	0.203	0.693
Cond	0.188	0.877	0.367	-0.088	0.062
Na	0.400	0.161	0.780	-0.200	0.135
K	0.228	0.192	0.771	0.104	0.022
Ca	0.075	0.923	0.021	-0.044	0.055
Mg	0.010	0.814	0.297	-0.081	0.033
F	0.069	0.189	0.728	-0.010	0.274
Cl	0.003	0.827	-0.103	0.346	0.091
NO3	-0.109	-0.035	0.105	0.281	-0.782
SO4	0.122	-0.104	0.145	0.830	-0.075
HCO3	0.149	0.885	0.349	-0.191	0.043
Sr	0.291	0.789	0.303	0.083	-0.067
Y	0.985	0.119	0.089	0.039	-0.019
La	0.954	0.063	0.218	0.014	0.032
Ce	0.960	0.059	0.186	-0.016	0.017
Pr	0.983	0.028	0.141	0.042	0.006
Nd	0.985	0.045	0.142	0.037	0.002
Eu	0.971	0.159	0.159	0.006	0.012
Gd	0.985	0.086	0.146	0.017	0.005
Tb	0.987	0.092	0.127	0.011	-0.003
Dy	0.986	0.100	0.124	0.017	-0.004
Ho	0.987	0.107	0.101	0.032	-0.018
Er	0.987	0.107	0.068	0.041	-0.027
Tm	0.984	0.111	0.052	0.044	-0.032
Yb	0.984	0.110	0.031	0.045	-0.038

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Appendice 13. An alternative version of the principal component analysis. The missing and censored values have been imputed, but the values have not been log-transformed or normalized.