# Acid sulphate soils and its influence on metal concentrations in adjacent water bodies

- A case study from Halland, SW Sweden

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# Abstract

Acid sulphate soils have been referred to as being among the most harmful soils in the world due to their ability to severely decrease the pH of the water, consequently enabling an increased metal load to recipient water streams, lakes, groundwater reservoirs and estuaries. The presence of acid sulphate soils has triggered several fish kill episodes in northern Scandinavia and the soils are today threatening many of the national environmental goals of Sweden. Their widespread coverage in northern Sweden and western Finland have endorsed these regions to be the focal point for previous investigations. However, in early 2019, acid sulphate soils were discovered in Halland, SW Sweden and this study therefore aimed to investigate the impact from these non-investigated soils on the surface water chemistry of an affected area. This was conducted through in situ surface water sampling from two areas, in order to cover both smaller ditches (area 1) and a larger canal (area 2), located adjacent to a confirmed acid sulphate soil. Sampling was conducted during three separate occasions; autumn, winter and spring with the purpose of investigating differences in discharge depending on season. Water pH and electric conductivity was determined in situ, and the total metal compositions of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn was analysed with an ICP-MS instrument. Additionally, groundwater data was collected to determine potential impact on the drinking water of the region. The results provide strong indications of leakage from the acid sulphate soils into the surface water, visible through elevated metal concentrations along with pH values between 3.8 and 6.6. Additionally, high electric conductivity values were measured in the water (32-129 mS/m) implying high SO<sub>4</sub><sup>2-</sup> composition in the water. Higher metal concentrations and lower pH values were measured in area 1 compared to area 2, hence assumed to be more influenced by the adjacent sulphuric soil layer. The metal concentrations in the water decreased from autumn to spring, likely reflecting the high temperatures and prolonged precipitation in Halland 2019/2020, further implying the importance of considering climatic parameters when investigating acid sulphate soil leaching. No indications of contaminated groundwater were seen in the results; however, no definite conclusions could be drawn due to limitations in the dataset. The study site was further compared to other sites in Sweden and Finland, where indications of slightly lower discharge were seen in Halland.

Keywords: Acid sulphate soils, physicochemistry, metal distribution, surface water, climate

# SAMMANFATTNING

Sura sulfatjordar är kända för att vara bland de mest skadliga jordtyperna i världen på grund av deras förmåga att minska pH nivån i vattendrag och därigenom möjliggöra för metaller att utlaka till närliggande floder, sjöar, grundvattensmagasin och/eller estuarier. Förekomsten av sura sulfatjordar har dessutom orsakat många episoder av fiskdöd i norra Skandinavien, och idag hotas ett flertal av Sveriges nationella miljömål av deras närvaro. Den betydande utbredningen av sura sulfatjordar i norra Sverige och västra Finland har historiskt sett möjliggjort för omfattande utredningar i dessa områden, men under 2019 bekräftades även befintliga sura sulfatjordar i Halland, SV Sverige. Denna studie syftar därför till att undersöka möjlig påverkan av dessa tidigare oupptäckta jordar på ytvattenskemin i området. Studien utfördes genom ytvattenprovtagning från två närliggande områden, båda angränsande till den bekräftade sura sulfatjorden, och där både mindre diken (area 1) och en större kanal (area 2) inkluderades. Provtagningarna utfördes under tre separata tillfällen; under hösten, vintern och våren för att kunna fastställa möjliga utsläppsskillnader beroende på säsong. Vattnets pH och elektriska konduktivitet undersöktes i fält, och den totala koncentrationen av Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V och Zn fastställdes genom ICP-MS analys. Dessutom samlades tillgänglig data över grundvattenkemi in för att kunna undersöka möjlig påverkan på dricksvattnets kvalité i regionen. Resultaten visade starka indikationer på läckage från de sura sulfatjordarna till ytvattnet, genom förhöjda metallhalter och pH värden mellan 3.8 och 6.6. Dessutom hade vattnet en hög elektrisk konduktivitet (32–129 mS/m) vilket tyder på en hög halt SO<sub>4</sub><sup>2-</sup> i ytvattnet. Area 1 innehöll generellt högre metallhalter och lägre pH värden än area 2 och antogs således vara mer påverkat av den omkringliggande sulfatjorden. Skillnader i metallhalter mellan säsonger observerades även, där resultatet visade minskande metallhalt från höst till vår. Detta är troligen orsakat av de höga temperaturer och ihållande regn i Halland under 2019/2020, vilket belyser klimatets betydande roll för metalläckaget. Ingen indikation av kontaminering återfanns i grundvattensdatan, men på grund av stora begränsningar i datasetet kunde inga slutsatser dras gällande dricksvattnets kvalité. Slutligen jämfördes studiens resultat mot likvärdiga studier från norra Sverige och västra Finland, varvid en något lägre kontamineringsgrad påträffades i Halland jämfört med de andra områdena.

Nyckelord: Sura sulfatjordar, hydrokemi, metallutbredning, ytvatten, klimat

I would first and foremost like to extend my appreciations to my supervisor and mentor, Markus Giese at the Department of Earth Sciences, Gothenburg University for his unlimited support throughout this project, and for un-doubtfully believing in my abilities. A special thanks to Christian Öhrling (SGU Gothenburg) for initiating this project and for helping me out whenever needed. Thank you Marina Becher (SGU Uppsala) and Mats Åström (Linnaeus University, Kalmar) for allowing me to always put forward questions, even the most stupid ones. I would moreover like to acknowledge Aila Schachinger (Department of Earth Sciences) and Sebastien Rauch (Chalmers University of Technology) for the assistance received in the analysis of both metals and DOC. A special thanks to my fellow classmates as well as co-workers in this project; Ida Kling Jonasson and Johanna Bergström, for being as interested in this subject as I am, and for proving a well needed assistance in field. Last but not least, I would like to thank my examiner Thomas Zack at the Department of Earth Sciences for helping me out when needed and for giving me constructive feedback throughout this thesis.

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## 1. INTRODUCTION

Acid sulphate soils are a common issue in many places around the world, such as Australia (Wu et al., 2013), Asia, Africa and Latin America (Fältmarsch et al., 2009). These soils have in the literature been described as the "nastiest soils in the world" (Dent & Pons, 1995, pg. 1) due to their ability to decrease the pH down to 2, allowing for toxic metals such as aluminium, to be leached out of the ground, harming the surrounding vegetation and to pollute drinking water reservoirs (Dent & Pons, 1995). They are also a well-discussed topic in Sweden (Becher et al., 2019; Lax, 2005; Sohlenius, 2011; Myrstener, 2012; Thomas, 2016) and Finland (Åström & Björklund, 1995; Boman et al., 2010; Fältmarsch et al., 2009; Joukainen & Yli-Halla, 2003; Mattbäck et al., 2017; Saarinen & Kløve, 2012) due to the recorded damaging effect these soils have on the surrounding environment. It thus becomes clear that sulphate soils are an enormous environmental concern in both Sweden and other areas around the world.

## 1.1 MOTIVATION

In the fall of 2006, a fish kill event was reported in Larsmosjön, western Finland. The cause of the event was a combination of several factors regarding weather changes and soil characteristic. The dry summer of 2006 was followed by a wet autumn allowing for comprehensive changes in water level. The climatic fluctuations together with the presence of acid sulphate soils in the catchment area favoured extensive leaching of acidic water into the recipient lake, resulting in the documented fish kills (Västra Finlands Miljötillståndsverk, 2009). The first recorded fish kills related to acid sulphate soils in Finland, however, occurred in Kyrönjoki River more than 170 years earlier, in 1834 (Bärlund et al., 2004). Since then, episodes of fish kills have been a reoccurring event, for instance in Uusikaupunki in 1968 (Bärlund et al., 2004), again in Kyrönjoki River in the 1970s (Åström & Björklund, 1995) and as late as in the fall of 2019 in Larsmosjön (Kyheröinen, 2019, 27<sup>th</sup> of November). Fish kills have also been noted in Sweden as a consequence of leaching acids from active sulphate soils (Erixsson, 2009). Since the episode of fish kills in Finland in 2006, the concern regarding the effect of leaching acid sulphate soils on stream water quality have increased in both Finland and Sweden (Länsstyrelsen Västerbotten, 2017).

Sweden is today actively working to ensure a good and healthy environment for future generations (1 kap 1§ Miljöbalken (1998:808), which is distinctive through the 16 environmental goals established in 1995 (Sveriges miljömål, 2019). As many as 10 of these goals are affected by the presence of acid sulphate soils (Länsstyrelensen Västerbotten, 2017). One example is goal number three; "*natural acidification only*" (Naturvårdsverket, 2018), intended to ensure that all environmental acidification occurs as a response to natural causes rather than anthropogenic. Still, 10% of all Swedish lakes are acidified by human activities

(Sveriges miljömål, N.D), and continuous ditching of sulphide rich soils could increase this number further in the future. Other goals being affected by the presence of acid sulphate soils are goal number eight "flourishing lakes and streams" and number ten "a balanced marine environment, flourishing coastal areas and archipelagos" (Naturvårdsverket, 2018). The aforementioned fish kills is one example of the negative effect of acid sulphate soils to the surrounding aquatic life, where several studies have explicitly shown that fish population are negatively affected by the presence of acid sulphate soils, due to the increasing acidity of the surrounding water (Hudd & Kjellman, 2002; Urho et al., 1990; Erixon, 2009). Additionally, studies have also shown that acid sulphate soils in a drainage basin are, in fact, the leading cause for increased metal concentrations in stream waters (Åström, & Björklund, 1995). The environmental consequences from acid sulphate soils on surface water quality have allowed these soils to be important subjects in previous Swedish investigations (Wennerström, 2017; Åström, 2001b; Åbjörnsson et al., 2018). Many of these investigations have however been focused along the north-eastern coast of the country, in for instance Mälardalen (Bayard & Karlsson Mood, 2014; Lax, 2005), Norrbotten (Wennström, 2017; Filppa, 2012) and Gumbodafjärden (Thomas, 2016). Only a few studies have been focused on regions southwards, stressing a strong demand for additional investigations regarding acid sulphate soils and their consequences in the southern part of the country.

#### 1.2 BACKGROUND

#### 1.2.1 Formation and characteristics of acid sulphate soils

Acid sulphate soils are usually divided up into two types; "*potential acid sulphate soil*" and "*active acid sulphate soil*". Potential acid sulphate soils are formed due to the process of bacterial decomposition in a waterlogged anoxic environment. During decomposition, oxygen will be used as a primary source, but as oxygen is depleting, other elements will be consumed as substitutes. Sulphates  $[SO_4^{2-}]$ , being one of the most common ions in marine waters (Bydén et al., 2003), is accordingly reduced into sulphides  $[S^{2-}]$  as a result of the depleting oxygen, while iron in the sediment is reduces from the oxidized state of Fe<sup>3+</sup> to the reduced state of Fe<sup>2+</sup>. The final product is iron sulphide  $[FeS_2]$ , more commonly known as "*pyrite*". As long as these soils are kept under reducing conditions, they remain chemically stable and are referred to as potential acid sulphate soils due to their inability to leach acids to the adjacent environment (Dent & Pons, 1995; Becher et al., 2019). The chemical reaction forming potential acid sulphate soils is described as (Becher et al., 2019):

$$SO_4^{2-} + Fe^{3+} \rightarrow H_2S + Fe^{2+} \rightarrow FeS_2$$
 (eq.1)

A potential acid sulphate soil may however turn into an active acid sulphate soil, through the process of oxidation. This commonly occurs as a result of different anthropogenic processes,

such as ditching of a former waterlogged area or in other ways lowering the groundwater table substantially. The increased void space of the soil allows oxygen to enter and oxidize the compounds below (Becher et al., 2019). The chemical reaction between the sulphides in the soil and oxygen forms sulphuric acid [H<sub>2</sub>SO<sub>4</sub>], which severely increases the acidity of the soil. Additionally,  $Fe^{2+}$  will oxidize back to  $Fe^{3+}$ , enabling a higher mobility of the iron with the draining water (Sohlenius et al., 2015). The acid environment created by the formation of sulphuric acid also allows for other elements to be mobilised and consequently increase in concentrations in adjacent water paths (Åström, 2001a; Åström, 2001b). The chemical reaction forming active acid sulphate soil is (Hulisz et al., 2017):

$$\operatorname{FeS}_2 + \operatorname{O}_2 + \operatorname{H}_2\operatorname{O} \xrightarrow{} \operatorname{Fe}(\operatorname{OH})_3 + \operatorname{SO}_4^{2-} + \operatorname{H}^+$$
 (eq.2)

The appearance of potential or active acid sulphate soils also differs. Potential acid sulphate soils are commonly recognized through a black soil-colour along with a more neutral pH and are often located below the groundwater surface, where reduced conditions predominate. To the contrary, an active acid sulphate soil is instead lighter in colour, may include precipitated rust [Fe<sub>2</sub>O<sub>3</sub>], and have a pH value below 4.5 (Boman, 2018). These soils are commonly located above the groundwater table, in the vadose zone where oxygen occurs (Länsstyrelsen Västerbotten, 2017). Active acid sulphate soils therefore typically follow a specific curve of pH change with depth (Figure 1).

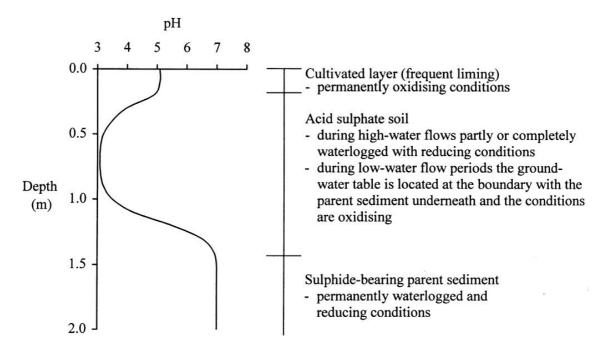


Figure 1: pH profile with depth for a typical acid sulphate soil. Figure retrieved from Åström, 2001b.

#### 1.2.2 The environmental effect of sulphate soils on water chemistry

Studies have shown that several potentially harmful metals such as Cobalt [Co], Nickel [Ni], Cadmium [Cd], Manganese [Mn], Zink [Zn], Cupper [Cu], Beryllium [Be], Lithium [Li], Strontium [Sr] and Aluminium [Al] are commonly leached out from areas containing acid sulphate soils (Wennström, 2017; Åström & Björklund, 1995). Some of these metals, such as Cu, Mn, Fe and Zn are toxic in certain concentrations since they accumulate in fish and other aquatic organisms (Augustsson et al., 2017). One of the most environmentally significant metal is Al, being able to comprehensively reduce fish species if the concentration exceeds 0.5 mg/l (Nystrand & Österholm, 2013). In Fennoscandian streams however, the concentration of Al is typically lower than this critical value (Table 1). In order to fully comprehend the potential leakage from acid sulphate soils, it is therefore useful to compare metal concentrations in the surface water to given reference values for similar water streams (Table 1).

Table 1: Table presenting background values for large and small streams in Sweden (Naturvårdsverket, 2008), along with
background values on Fennoscandian streams (Edén & Björklund, 1993 (cited by Wennström, 2017). Values used in this
study are marked bold.

	Large stream S. Sweden	Natural levels, large streams*	Small stream S. Sweden**	Natural levels, small streams*	Fennoscandia streams (M)
Al [mg/1]	-	-	-	_	0.03
As [μg/l]	0.40	0.20	0.03	0.06	0.22
Cd [µg/1]	0.014	0.003	0.016	0.002	-
Co [µg/l]	0.13	0.05	0.06	0.03	0.07
Cr [µg/l]	0.40	0.20	0.20	0.10	0.40
Cu [µg/l]	1.30	1.00	0.50	0.30	-
Fe [mg/1]	-	-	-	-	0.10
Mn [µg/l]	-	-	-	-	14.00
Ni [µg/l]	1.00	0.50	0.40	0.30	1.20
Pb [µg/l]	0.32	0.05	0.24	0.02	0.20
V [µg/l]	0.40	0.10	0.20	0.06	0.16
Zn [µg/l]	4.30	3.00	2.00	1.00	7.20
Source:	a	a	a	a	b

\* Natural levels based on streams in Northern Sweden

**\*\*** Values are hence based on lakes in Southern Sweden, due to a lack of data over non-acidified streams in this area.

a: Naturvårdsverket, 2008

b: Edén & Björklund (1993), found in Wennström (2007).

The concentration of metals is therefore of major importance for thriving water streams, but of equal importance are several physicochemical parameters such as pH of the water, metal-size, metal distribution and seasonal variations. A pH value below 5.5 is stated as a critical point for various aquatic organisms (Nystrand & Österholm, 2013). The pH value further controls the mobility of several metals, as low pH values allow many metals to stay suspended in the water (Nystrand & Österholm, 2013; Andersson et al., 2014). Additionally, decreasing pH values does not have to occur over a long period of time in order to mobilise metals. Instead, studies have shown that mobilisation may occur through only a short-term acidification event (Claff et al., 2011). The pH is therefore one of the most important factors for the mobility and suspension of metals in water environments (Nystrand & Österholm, 2013; Havs- och vattenmyndighetsen, 2016). Another important aspect for the toxicity of metals is the size of the particles. Metals in water can be divided into three categories based on their size; particles (>0,45 µm), colloid  $(0,45 \,\mu\text{m} - 1\text{kDa})$  and dissolved (<1 kDa). The most mobile and toxic of these are the dissolved metals, given that this size is most accessible for aquatic biota. Colloids also play an important role for the water chemistry due to their high adsorption capacity, which therefore may decrease the concentration of dissolved metals, consequently decreasing the toxicity for aquatic life (Nystrand & Österholm, 2013). Additionally, the concentration of metals also varies depending on the season, i.e. differences in flood conditions. One example is presented by Åström, 2001b, who found that SO<sub>4</sub><sup>2-</sup> along with several elements such as Al, Cd, Cu, Ni, Co, and Zn increased in concentration downstream during heavy flooding events in autumn.

#### 1.2.3 Prerequisite of sulphate soils in Sweden

Acid sulphate soils are prone to occur in Sweden, due to the glaciated history of the country. The retreat of the Weichselian ice sheet allowed four distinct phases to occur; the Baltic ice lake, the Yoldia Sea, the Ancylus Lake and finally, the Littorina Sea. The different conditions regarding salinity and oxygen-supply in these phases permitted the deposited sediment to be of distinctive characteristics (Boman, 2010). Previous studies by e.g. Bayard et al. (2014), Öborn, (1993), Sohlenius, et al. (1996), Dent & Pons (1995) and Åbjörnsson et al. (2018) have established that the acid sulphate soils found in Sweden today was deposited during the salty and anoxic Littorina stage. During this phase, the sea-level was strongly fluctuating in the southern parts of Sweden due to the balancing conditions between water exchange from the surrounding oceans and the isostatic rebound, occurring in response to the retreating ice sheet. The nutritious water entering the Baltic Sea contained high levels of salt, enabling algae and other organisms to flourish. As these organisms died and accumulated on the seabed, the decomposition consumed all oxygen, allowing the bottom sediment to become anoxic (Boman et al., 2010; Havet.nu, 2004). The upper limit for acid sulphate soils is therefore often defined by the limits of the Littorina Sea (Figure 2; Becher et al., 2019). As the isostatic rebound continued, much of the black coloured sediment deposited below sea level became exposed to oxygen on land. A much later growing population and increased agricultural expansion, allowed much of the land to be drained, the soil to be oxidized and the active acid sulphate soils to develop (Becher et al., 2019). Sulphate soils are also very good soils for many commonly grown crops in Sweden, such as rye (*Secale cereal*), oats (*Avena sativa*) and potatoes (*Solanum tuberosum*) (Öborn, 1993) which could explain the extensive drainage of these soils in Sweden as agricultural interests increased.

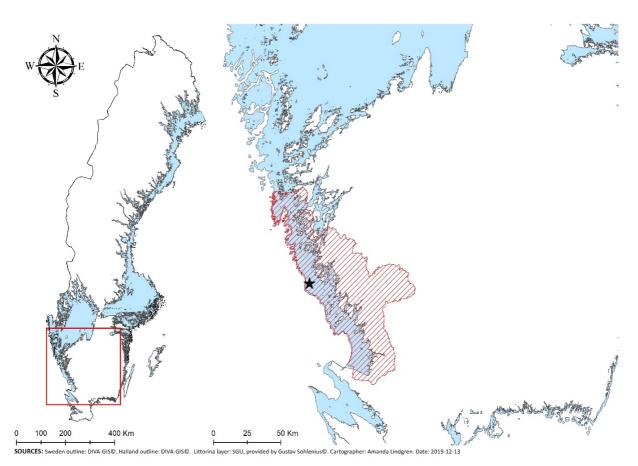


Figure 2: Map of the extend from the highest coastline, focused on the south-western coast of Sweden. Black star in the map indicates the focus area for this study.

Apart from ditching and drainage activities in sulphide rich soils, acid sulphate soils are also highly subjected to climate change, in particular changes in precipitation patterns which alters the water level in the unsaturated zone. Longer periods of low precipitation in combination with increased temperatures may result in lowering of the groundwater table, which accordingly allows for more soil to be exposed to the air and oxidize. Succeeding rainfall events may consequently drain the soil and flush the newly formed acids into the recipient streams (Wennström, 2007). It is therefore understandable that the highest discharge of acidic water from sulphuric soils occur in autumn, due to high amounts of precipitation, and in spring during snowmelt (Becher et al., 2019; Åström, 2001b). Increased average temperatures also affect the leaching directly, since no discharge of acidic occurs when the ground is frozen. Increased temperatures therefore prolong the season of acidic leaching to the adjacent streams (Lindström, 2017). Furthermore, land use changes such as removal of peat covers may also affect the

development and drainage of sulphate soils, since peat commonly enables the sulphuric soil to remain saturated. It is therefore important that land use changes are planned carefully in areas of existing sulphate soils (Dens & Pons, 1995).

Today, acid sulphate soils in Sweden most commonly occur along the north-eastern coast, and issues related to these soils have been most prominent around the Bothnian Sea and the Bothnian Bay. Nevertheless, acid sulphate soils may arise wherever isostatic rebound has occurred and may therefore be found in a much larger part of Sweden than only along the north-eastern coast (Becher et al., 2019). For instance, Geological Survey of Sweden (SGU) found strong indications of existing acid sulphate soils in early 2019 during a construction of a new building in Falkenberg, south-western Sweden (Gustavsson, 2019, 6<sup>th</sup> of March; Christian Öhrling, personal communication 2019-06-04), which may also be explained by the extent of the Littorina sea on the south-western coast.

# 1.3 AIM OF STUDY

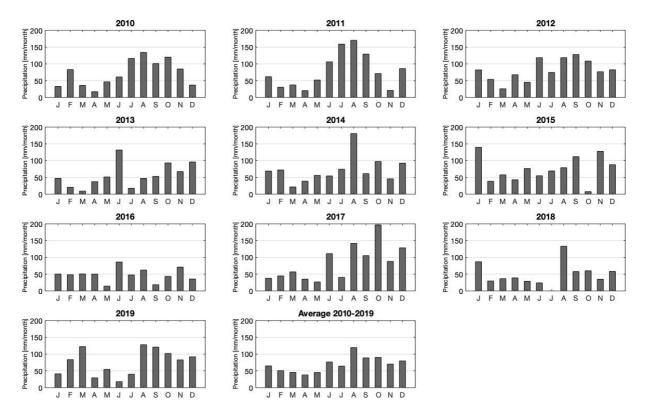
Due to the aforementioned problematics related to acid sulphate soils concerning the Swedish legislation and the observed environmental effect on the surrounding marine environment, this study aims to investigate the physicochemical connection between leaching acid sulphate soils and the distribution of metals in the waters that surround them. The study will be focused on the county of Halland, located on the south-western coast of Sweden, where previous studies are sparse. This study site was selected in order to contribute in decreasing the discrepancy of information about the effect of acid sulphate soils in the south-western part of Sweden.

The research questions used as guidance in this report are:

- 1. What are the metal distributions and concentrations in the study area?
- 2. What are the clear signs of impacts from acid sulphate soils in the water?
- 3. How does the study area compare to other areas in Sweden and Finland, being affected by acid sulphate soil drainage?

# 2 SITE DESCRIPTION

Given the lack of information regarding the effects of sulphate soils in the southern parts of Sweden, Halland was selected as the investigation area of this study. Halland is located on the south-western coast of Sweden, below the limit of the highest coastline (Figure 2) and was submerged by ocean approximately 5200 years BC (Christensen & Nielsen, 2008). The coastal location allows the county to be strongly impacted by Kattegatt to the west. According to Köppen-Geiger climate classification system, Halland has a Cfb climate (Climate-data.org, N.D), implicating fluctuating seasonal temperatures with evenly distributed precipitation throughout the year (Encyclopædia brittanica, 2019). The precipitation of Halland has been measured to around 600-1200 mm/year on average for the climate normal of 1961-1990 (SMHI, 2019). The seasonal precipitation pattern between 2010-2019 (Figure 3) indicate high amounts of rainfall during the summertime (July-August), most prominently seen between 2010-2012. Precipitation in July 2018. The autumn season (September-November) is also shown to be wet in the area, most evident in 2010, 2012, 2017 and 2019 (Figure 3).



**Figure 3:** Graphs of the monthly cumulative precipitation from Varberg's meteorological station 2010-2019, located approximately 18 km north of the study area. Last graph represents average precipitation between 2010-2019. All data retrieved from SMHI, 2020.

The average temperatures are between -1°C and -3°C on average for January, and around 15-16°C for July (SMHI, 2019). Given the relatively high temperatures, it is expected that the ground remains unfrozen throughout most of the year. Regarding the geological settings, the coastal area of Halland is dominated by a highly permeable postglacial fine sand (SGU, N.Da), being susceptible to infiltrating precipitation. The soil depth varies between 10-20 m towards the coast and 5-10 m inland (SGU, N.Dc) with an underlying bedrock of mainly granite and gneiss, dating back to the Sveconorwegian orogeny around 1.7-1.6 billion years ago (SGU, N.Dd). In total, Halland consists of six municipalities and five cities, but a large part of the county is still composed of forested land (52%), agricultural properties (22%), farmland (19%) and pasture (3%) (SCB, 2019). The predominating agricultural activity enables the formation of active acid sulphate soils, since ditching is a natural part in developing good arable land (Needelman, 2007).

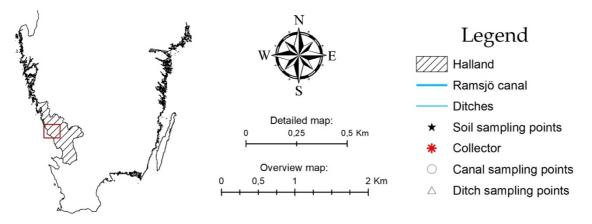
#### 2.1 STUDY AREA FOR WATER SAMPLING

The area selected for water sampling is located south of Varberg and north of Falkenberg, between the smaller districts Vinberg and Glommen (Figure 4). Several requirements were predecided before the project started, with the first requirement being the existence of an active acid sulphate soil layer. Simultaneously as this report was conducted, parts of Halland was investigated by a fellow student at the Department of Earth Sciences in Gothenburg with regard to mapping acid sulphate soils in the county (Kling Jonasson, 2020). The soil mapping was conducted by using an Edelmann auger corer to drill down around 3 meters (if possible) into the soil and note pH variations, colour and soil type each 10 cm along the core. Four sites (H19001, H19016, H19030 and H19032) were located within the study area, all of which followed the typical pH profile of an active acid sulphate soil (Figure 1, Appendix 2), validating the suitability of the selected study site and consequently meeting the first requirement. The two sites mainly used in this report (H19030 and H19032) are presented in Figure 4. Another requirement was the existence of a water stream in contact with the acid sulphate soil layer. The chosen area is crosscut by a large manmade canal, Ramsjö canal (onwards mainly referred to as "area 2"), connected to the acid sulphate soil by several smaller ditches (referred to as "area 1"). Given the relatively large catchment size of Ramsjö canal, being approximately 60 km<sup>2</sup> (SMHI, N.D) along with the additional anthropogenic influences into the canal, the ditches of area 1 were selected as the primary focus site for this investigation.

Ramsjö canal is crossing a large area of postglacial silt and peat, both with a lower permeability, than the typically occurring fine sands of Halland (SGU, N.Da; SGU, N.Db). The canal was dug by hand between 1852-1858 with the purpose of draining a larger marsh land and lake, called Ramsjön (Figure 5). Digging the canal was intended to increase the proportion of cultivated land, which resulted in an additional 12.8 km<sup>2</sup> of cropland, 2 km<sup>2</sup> of meadow and an

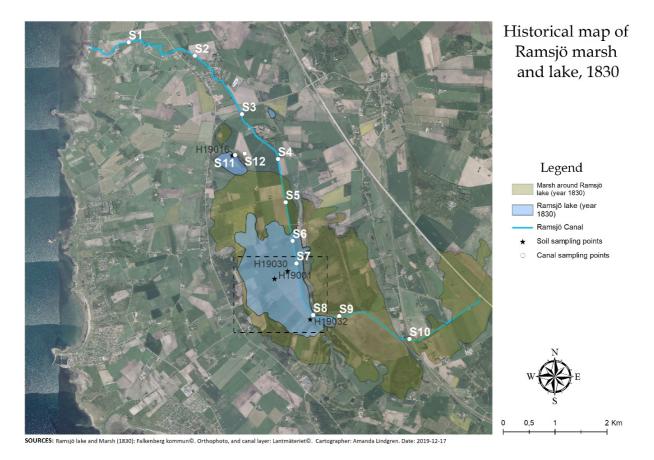


SOURCES: Sweden and Halland outline:DIVA-GIS©. Ortophoto, canal and ditches: Lantmäteriet©. Cartographer: Amanda Lindgren. Date: 2019-12-13



**Figure 4:** Map of the study area in Halland. Overview map presents area 2 while the detailed map (*bottom left corner*) presents area 1. All sampling points are indicated with red asterisk or white circles/ triangles. Soil samplings conducted by Kling Jonasson, 2020 are marked with black stars in both maps. GIS layers provided by Lantmäteriet (N.D) and SGU (N.De).

additional 2.9 km<sup>2</sup> of peat moss (Sveriges hembygdförening, N.D). The canal has since then been decluttered (Sveriges hembygdförening, N.D), and is today a 12 km long canal, with its outlet in the ocean. The estuary of Ramsjö canal is classified as a "Natura2000" area (Länsstyrelsen Hallands län, N.D) allowing for a special national protection status for both aquatic and terrestrial species. Given that the ecological status of the canal was "*moderate*" in 2009 and the chemical status was "*failing to achieve good*" (VISS, N.D) a pilot project of investigating the estuary of Ramsjö canal was initiated in 2019, with the aim to take action against the problem of over fertilization in the estuary (Havs- och vattenmyndigheten, 2019). This project does not, however, incorporate the problematics of potential metal leakage from acid soils in the catchment areas.



**Figure 5:** Map of the study area in Halland, including both areas 1 and 2, with dashed line marking area 1. Ramsjö lake is displayed in blue while the marsh around Ramsjö canal is displayed in brown. All soil sample spots; H19016, H19030, H19001 and H19032 conducted by Kling Jonasson, 2020 are displayed as black stars in the figure. GIS layers provided by Lantmäteriet (N.D) and SGU (N.De)

# 3 Method

In order to fulfil the aim of this study, the selected methodology involved a two-step process. As a first step, surface water was analysed in regard to determine the composition of metals and define the physicochemical status of the water. The results were onwards compared to given reference values for similar streams of southern Sweden. The focus area (area 1) were accompanied by samples from area 2 to determine possible environmental effects of the water draining from the canal into the estuary in Kattegat. To further investigate potential seasonal differences, samples were collected from area 1 during three occasions in (1) October/November, (2) January and (3) March, representing autumn, winter and spring respectively. Two additional samples were conducted during winter and spring in a nearby collector of drainage pipes located in area 1 (marked as a red asterisk in Figure 4) to find potential impacts from the surrounding fields slightly outside the study area. As a second step of this study, concentration levels from other studies focused on sulphate soil affected areas of northern Europe (north-western Sweden and western Finland) were collected and compared to the data received from Halland, where similarities and differences were investigated.

#### 3.1 SAMPLING PROCEDURE

Initial surface water samples were collected from both area 1 (D1-D7), area 2 (S1-S10) and by a waterlogged area near the canal (S11-S12) during two separate events in October and November 2019. For sites D3, D5 and D6, double samples were collected (up- and downstream the ditch) with the purpose of investigating internal differences in metal concentrations within the sites. Two sites, S9 and S10, were designated as reference points, based on their location being positioned upstream the acid sulphate soil and therefore presumable not affected by the discharging acids. As aforementioned, additional samples from area 1 were conducted in January and March (Table 2) in order to distinguish seasonal distributions of acid and metal leakage throughout more than one season. No additional samples were collected in winter or spring from area 2. The water was collected directly from the stream into 60- and 250-ml high density polyethylene bottles. All bottles were labelled prior to sampling with corresponding sample ID and filled completely to ensure that no air would affect the sample during storage. After sampling, the bottles were stored cool and dark to assure a good quality of the metal analysis. Measurements of pH, electric conductivity (EC) [mS/m] and dissolved oxygen (DO) [%] was conducted using a Hannah instrument (HI 98194) in situ. In addition to these parameters, redox potential [mV/orp], temperature [°C], atmospheric pressure [mBar] and total dissolved solids (Tds) [mg/L] was measured and are presented in Appendixes 4 and 6. Earlier studies have highlighted the importance of measuring the physicochemical parameters simultaneously as water is collected, in order to accurately measure the bioavailable concentration of metals in the water (Havs- och vattenmyndigheten, 2016), and this advice was followed. The sampling time, date, weather conditions and air temperature [°C] was noted in situ, together with other relevant information, such as high or low water flow, colour and smell of water, visible organic content and surrounding features such as animals and agriculture (Appendixes 4 and 6). In addition to sampling the surface water of areas 1 and 2, the quality of the groundwater from surrounding wells was investigated to find potential signs of contaminated groundwater near the acid sulphate soil layers. This was done through data collection from SGU. The dataset provided values of several parameters and elements, such as pH, EC, SO4<sup>2-</sup>, Cu and Fe, sampled from private wells in the area between 2007- 2016. The depth and type of each well along with cause of analysis and possible water filters was also retrieved by SGU. Water from the collector was sampled during two occasions, and both physicochemical parameters and metal concentration was tested.

	Autumn			Winter			Spring		
	PA	MA	DOC	PA	MA	DOC	PA	MA	DOC
S1-S10	$\checkmark$	$\checkmark$	-	-	-	-	-	-	-
S11-S12	$\checkmark$	$\checkmark$	-	-	-	-	-	-	-
D1-D7	$\checkmark$	$\checkmark$	√*	√*	√*	-	√*	√*	-
Collector	-	-	-	$\checkmark$	$\checkmark$	-	$\checkmark$	$\checkmark$	-
No. of samples		30		1	7		1	7	

 Table 2: Summary of the measurements conducted in area 1 and 2. PA: Physicochemical analysis conducted. MA: Metal analysis conducted. DOC: DOC analysis conducted. \*D2 was excluded from the measurements.

## 3.2 ANALYSIS OF METALS AND DOC

The initial 30 water samples collected in the autumn were analysed using a Thermo Scientific ICAP Q ICP-MS (inductively coupled plasma mass spectrometry) instrument at Chalmers University of Technology, Gothenburg. The concentrations of DOC in the water was analysed by a TOC-L CPH at the Department of Earth Sciences, Gothenburg. Prior to the analysis, all water samples were filtered through 0.45µm filters using a syringe and transferred into individual test tube marked with the corresponding sample ID. To limit potential risks of cross contamination between the samples, new syringes and filters were used for each individual sample. A total of 8 ml of each water sample was extracted for the ICP-MS analysis and 20 ml for DOC analysis. After the filtration procedure was conducted, 0.1 ml of 65% nitric acid [HNO<sub>3</sub>] was added to the test tubes analysed in the ICP-MS, in order to mobilise as much of the metals as possible, and to decrease the pH of the water. The dilution resulted in a HNO<sub>3</sub> concentration of 1.0%. The samples were analysed using ICP multi-element standard solution IV, with the concentration of 1000 mg/l and the data reduction for the concentrations was

calculated by the instrument technician. The water to be tested for DOC was instead transferred into glass bottles and acidified automatically by the instrument during analysis. The additional 14 samples collected in the winter and spring were sent to the accredited lab ALS in Luleå and analysed using ICP-AES and ICP-SFMS instruments. These samples were sent unfiltered and unacidified as these procedures were conducted by the lab technicians. The metals investigated in all 44 water samples were Al, (Ti), V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, (Mo), Cd, (Sb), Pb and (U), where brackets indicate metals not further discussed in this report.

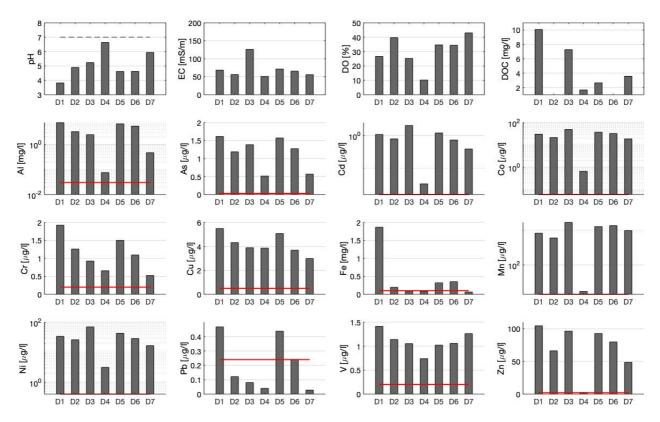
# 3.3 COMPARISON STUDY

The lack of information from the area selected as study site specified the need for a comparison to other acid sulphate soil affected areas, which was done through a literature study. The selected studies used for comparison were based on several aspects, such as location, catchment size, known coverage of acid sulphate soils in the catchment area, size of water stream and availability of data in the published reports. In total, four studies were selected for the comparison, all of which were based on studies conducted along the Swedish and Finnish coasts of the Baltic Sea. These studies were selected given that the Baltic Sea is an extensively studied coast due to the comprehensive problematics related to leaching acids from adjacent sulphuric soils. Out of the four studies selected, two were conducted in Finland (Petalax å and Bläckträskbäcken) being different in catchment size and acid sulphate soil coverage in the drainage basin, and two were conducted in Sweden (Norrbotten and Västerbotten).

## 4.1 AREA 1 (D1-D7)

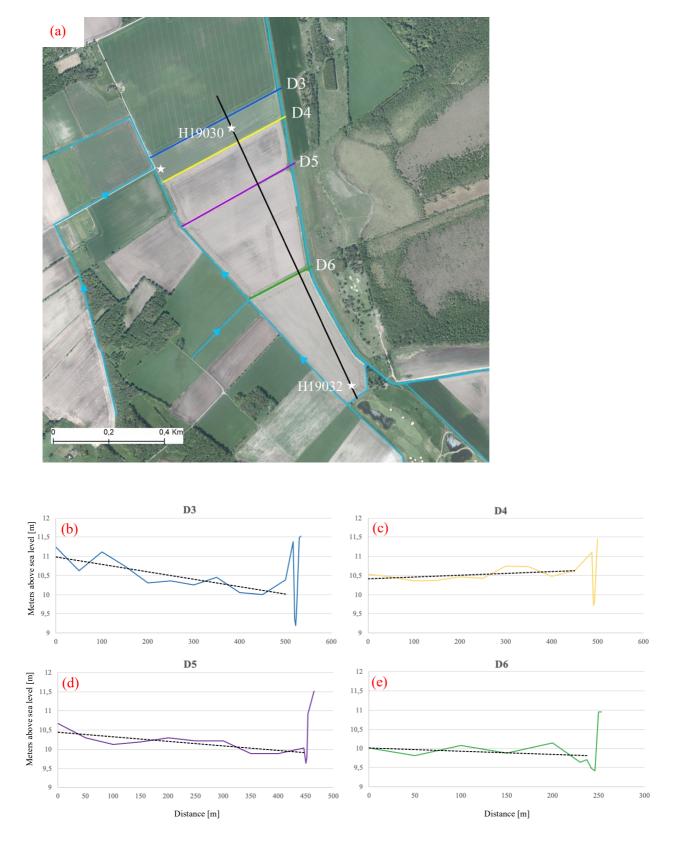
Given the increased leaching from acid sulphate soils during autumn, Figure 6 presents the physicochemical parameters, DOC and metal results retrieved from area 1 during the sampling conducted in October/November 2019. The physicochemical parameters reveal an average pH value of 5.11, with site D1 being most acidified (pH 3.82) and opposing D4 being most alkaline (pH 6.64). High electric conductivity is also noticeable in the area, with an average value of 72 mS/m and with a clear peak at site D3 with a value of 126 mS/m. The DO measurements, with an average of 31% show a clear decline at site D4, with a DO value of 10%. The highest DOC concentration is observed at site D1, while the lowest is seen at site D4, hence the opposite pattern of the pH values. Elevated concentrations of DOC are also visible at site D3, associated with the peak in electric conductivity. No measurement of the DOC concentrations was pursued at sites D2 and D6, thus information regarding the concentrations at these sites cannot be established.

The metal concentrations retrieved from area 1, presented mainly as averages between upstream and downstream ditches, show elevated concentrations of Al, As, Cd, Co, Cr, Cu, Mn, Ni, V and Zn, all exceeding the reference values to different degrees. The only metals deviating from this trend are Fe and Pb, only exceeding the reference values at sites D1, D5 and D6. A strong association between increased Cr concentrations and decreased pH values is further observed throughout the area. High metal concentrations are perceived at site D1, visible for e.g. Cr, Pb, Zn and particularly distinguished in the Fe concentration, where D1 is around 10 times higher than the remaining sites. A few exceptions to the predominately increased levels at D1 are observed in the Cd, Co, Mn and Ni concentrations, all instead presenting peaks at site D3. To the opposite of site D1, a pattern of low concentrations is recognized at site D4, evident in the concentrations of e.g. Al, Cd, Co, Mn and Zn. Moreover, a tendency of decreasing metal concentrations from site D5 towards site D7 is visible regarding several metals, such as e.g. As, Cd, Cr, Cu and Zn.



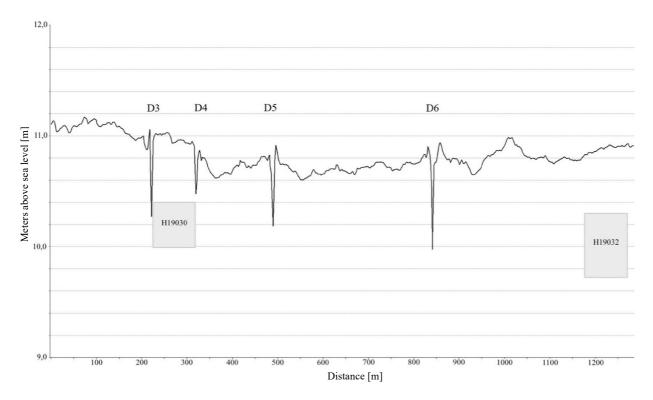
**Figure 6:** Graphs of the physicochemical parameters, DOC and metal concentrations retrieved from area 1 (D1-D7) in October/November 2019. No DOC analysis was conducted for sited D2 or D6. Since two samples were conducted from sites D3, D5 and D6, these sites are presenting through average concentrations. Red lines indicate reference values retrieved from Naturvårdsverket, 2008 and Edén & Björklund, 1993 (cited by Wennström, 2017). The concentrations of Al, Cd, Co, Mn and Ni are displayed with log/lin scales.

In order to better understand the physical settings of the area draining acid sulphate soil into the surface water, slope estimations of the ditches are presented in Figure 7. A vertical transect, including the soil measurements conducted by Kling Jonasson, 2020, is further presented in Figure 8. As visible, the slopes of each individual site vary, seen clearest between sites D3 and D4. Site D4 presents a minor positive inclination in an easterly direction, while site D3 is instead presenting a more distinctive negative slope towards the canal. Slight negative slopes are also seen for sites D5 and D6. The length of each ditch is observed along the x-axis of the graphs, indicating that D3 and D4 are the longest ditches, being both approximately 500 meters in length. Sites D5 and D6 are shorter, only reaching approximately 450 meters and 240 meters respectively.



**Figure 7:** Inclination graphs and over-view map of transects conducted. Figure 7(a) presents area 1, where each ditch is colorcoded to the inclination graphs in figures 7b-e. D3 is displayed in blue (7b), D4 in yellow (7c), D5 in purple (7d) and D6 in green (7e). The black line in figure 7(a) represents the transect displayed in figure 8, where the white stars are indicating the soil samples H19030 and H19032, both conducted by Kling Jonasson, 2020. Elevation data retrieved from Lantmäteriet (N.D).

Figure 8 represents a transect of sites D3-D6 relative to the acid sulphate soil layers measured in area 1 (displayed as grey cubes), mapped by Kling Jonasson, 2020. Some differences between the sample sites are evident in the figure, where for instance sites D3, D5 and D6 are all deep enough to reach the acid sulphate soil below, most prominent at site D6. To the contrary, site D4 is shallow and seemingly not in contact with the underlying sulphuric soil. Moreover, the upper limit of the acid sulphate soil layers is approximately 0.6 metres below ground level at both sampling sites. Some variations in total depths of the soils are however visible. Similarities in the soil types of H19030 and H19032 were recognized in situ, where sand, topsoil and a vast clayish layer was noted in both profiles (Kling Jonasson, 2020). These horizons did however differ slightly in total depth and re-occurrence. The largest difference was seen regarding the number of different soil types, where H19032 presented a higher variance than H19030, e.g. including a layer of peat and gravel, not observed at H19030 (Kling Jonasson, 2020). Metal concentrations for both soil profiles are displayed in Appendix 3.



**Figure 8:** Horizontal transect based on the black line seen in figure 7. Soil types for each site can be found in Kling Jonasson, 2020. Gray area represents the active acid sulphate soil layer measured in situ by Kling Jonasson, 2020.

Given the differences in length and slope of each individual ditch, a comparison between upstream and downstream water quality was conducted for sites D3, D5 and D6 and is presented in Table 3. The results show clear differences in the internal distribution of metals, with a general tendency of decreasing concentration of metals and DOC downstream at site D3 and a simultaneous increase in pH. Neither D5 nor D6 follows the same trend as D3, instead presenting an accumulative pattern towards the outlet of the ditch and a simultaneous decrease in pH. For site D5, the highest difference between inlet and outlet is seen in the Mn and Zn concentrations, increased by 290  $\mu$ g/l (~25%) and 12,4  $\mu$ g/l (~14%) respectively, while no difference is observed in the inflow and outflow concentrations of Cu and V. Also evident is a slight decreasing pH value and a more prominent increase in electric conductivity downstream of site D5. At site D6, an accumulative pattern is correspondingly visible downstream regarding most metal concentrations, with the highest increases likewise visible for Mn and Zn, increased by 252  $\mu$ g/l (~20%) and 13  $\mu$ g/l (~18%) respectively. Similar to site D5, a slight decrease in pH is also prominent, along with unaltered concentrations of V.

	D3 (US)	D3 ( <i>DS</i> )	D5 ( <i>US</i> )	D5 ( <i>DS</i> )	D6 (US)	D6 ( <i>DS</i> )
pН	4.9	5.6	4.7	4.6	4.7	4.6
DO [%]	25.6	25.0	33.0	36.3	42.3	26.5
EC [mS/m]	129.4	123.4	68.5	74.6	64.7	66.8
DOC [mg/l]	6.9	7.6	8.8	9.2	-	-
Al [mg/l]	4.4	0.5	5.7	7.5	4.3	6.4
As [µg/l]	1.7	1.1	1.5	1.7	1.1	1.4
Cd [µg/l]	2.6	1.5	1.1	1.3	0.7	0.8
Co [µg/l]	61.3	37.9	34.0	40.1	29.2	36.0
Cr [µg/l]	1.1	0.8	1.4	1.6	1.0	1.2
Cu [µg/l]	4.0	3.7	5.1	5.1	3.5	3.9
Fe [mg/l]	0.12	0.05	0.3	0.4	0.3	0.4
Mn [µg/l]	1656.4	1742.3	1144.9	1435.7	1248.7	1500.9
Ni [µg/l]	85.9	53.2	39.4	46.1	25.6	31.4
Pb [µg/l]	0.1	0.0	0.4	0.5	0.2	0.3
V [µg/l]	0.9	1.2	1.0	1.0	1.1	1.1
Zn [µg/l]	119.3	73.4	86.4	98.8	73.4	86.4

**Table 3:** Physicochemical parameters, DOC and metal concentrations for both upstream (*US*) and downstream (*DS*) of sites D3, D5 and D6. All samples were conducted in October/November 2019.

To further investigate if a potential correlation between increased metal concentrations and decreased pH values exists in the surface water of area 1, Figure 9 displays the pH values alongside the metals seemingly affected by the pH changes in table 3. Notice that the pH scale (right) is inverted in the figure for more observable trends. The results demonstrate a seemingly close connection between pH values and the concentrations of Fe, Al, Zn and Cu, as the concentrations decrease with an increasing pH and vice versa regarding all measuring points. To the contrary, the concentrations of Mn and Ni do not follow the pH variabilities to the same degree, seen clearest regarding Mn downstream of site D3 and for Ni upstream of site D5.

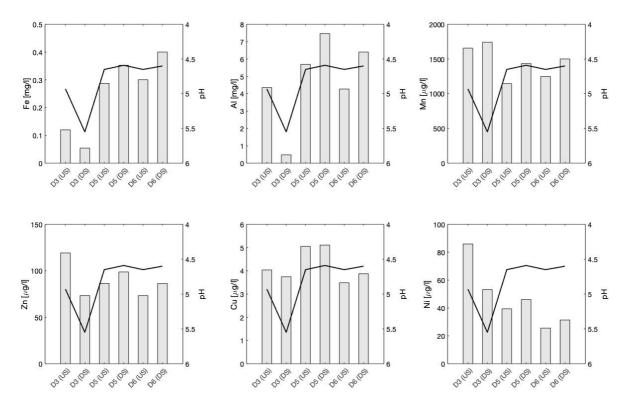
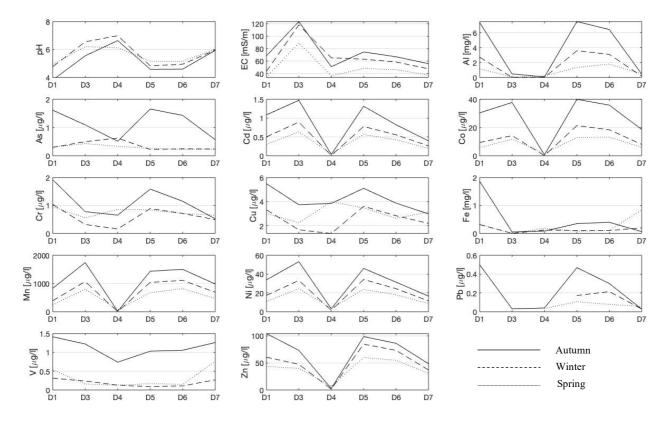


Figure 9: Graph of pH (line) and metal concentrations (bars) for sites D3, D5 and D6. US: Upstream, DS: Downstream. All samples were conducted in October/November 2019. Notice that pH scale (right) is inverted.

Furthermore, given the close relationship between metal and acid leakage from acid sulphate soils and different seasons, a comparison between the three different sampling periods; (1) autumn (October/November), (2) winter (January) and (3) spring (March) was conducted. These results, displayed in Figure 10, reveal a trend of generally lower electric conductivity in the spring compared to the autumn, along with a slight increase in pH during the same periods, most prominently seen for sites D5-D7. Some deviations to this pattern are however observed, for instance at site D4, presenting an overall increase of both pH and electric conductivity during winter, followed by a decrease of both parameters during the spring. A trend of seasonally dependent leakage is seen through high concentrations in the autumn followed by

decreasing concentration onwards, visible for e.g. Al, Co, Mn and Zn. A clear deviation to this pattern is seen at site D4 regarding Cr and Cu, where the highest concentrations are instead observed during spring, and the lowest in winter. Another exception is seen for Fe, not showing any seasonal pattern except for a slight consistency in the winter and spring sampling for several of the sites. The previously observed high V concentrations are strongly decreasing after the autumn samples, instead presenting fairly low concentrations in both winter and spring.



**Figure 10:** Graphs of seasonal distribution regarding the physicochemical parameters and metal concentrations for sites D1-D7. Autumn sampling (October/November) presented as solid lines, winter (January) presented as dashed lines and spring (March) presented as dotted lines. No sampling was conducted at site D2 in winter or spring and this site is therefore excluded from the graphs.

Further seasonal differences are observed in the results from the collector in area 1, provided in Table 4. The results present some variations between winter and spring, where pH is increased while the electric conductivity is declining in the spring relative to the winter. Additionally, most metal concentrations follow the same pattern as seen for pH, being increased in the spring relative to the winter, with exceptions seen for Cd, Cr, Cu and Zn. Most metals further exceed the reference values for surface water (provided in Table 1), with the only exception visible in the Pb concentrations, being somewhat lower than the reference value.

	Collector	Collector
	(Winter)	(Spring)
pH	6.03	6.10
EC [mS/m]	30.00	26.30
Al [mg/l]	0.31	0.36
As [µg/l]	0.46	0.61
Cd [µg/l]	0.05	0.04
Co [µg/l]	0.87	0.92
Cr [µg/l]	1.15	0.96
Cu [µg/l]	3.50	3.06
Fe [mg/l]	1.07	1.11
Mn [μg/l]	69.80	77.50
Ni [µg/l]	1.51	1.73
Pb [µg/l]	0.06	0.07
V [µg/l]	1.48	2.25
Zn [µg/l]	8.87	8.11

**Table 4:** Result of pH, EC and metal concentrations for small collector in area 1. Sampling conducted in January (winter) and March (spring)

# 4.2 AREA 2 (S1-S12)

A separate investigation was conducted in area 2, given that Ramsjö canal has its outflow in a Natura2000 area in the estuary of Kattegatt, and the results are presented in Figure 11. The physicochemical parameters measured in area 2 varies to some extent between the different sites, for instance visible in the pH values. Slightly acidic conditions predominate throughout the area, with pH values between 5.42 and 6.90 and with an average pH of 6.15. Exceptions are however visible at sites S9 and S10, presenting pH values closer to neutral conditions. Observing the pH from the reference points (S9 and S10) towards the outlet (S1) provides an indication of decreasing pH from S10 towards S6, being the most acidic site. A trend of more alkaline condition from site S6 towards the outlet at site S1 is furthermore evident in the results. Regarding the remaining physicochemical parameters such as electric conductivity and DO, all values are seemingly well-distributed without any apparent trends of increased or decreased values at any specific sample site.

The metal concentrations between sites S1-S10 reveal no evident pattern of increased metal concentrations from the reference point towards the outlet. To the contrary, slightly lower concentration are seen at site S1 compared to site S10 regarding e.g. Al, Cd, Co, Mn and Zn. The concentrations of Co, Ni and Cd vary substantially depending on site, while As, Fe, Pb and V are evenly distributed throughout the canal. Site S6 is distinguished from the surrounding sites, presenting the lowest overall concentration regarding most metals. Oppositely, the highest metal concentrations are perceived at S7, visible for e.g. Mn, Co, Ni and Cd. Additionally, most metals except for Pb and Fe are exceeding the reference limits at essentially all sites. The highest exceedance is displayed for Mn, presenting a peak at site S7 and a conflicting decrease at S6. Other metals such as Cd and Ni instead exceed the reference values by a factor 10, while As and Co exceed the limits by a factor 100.

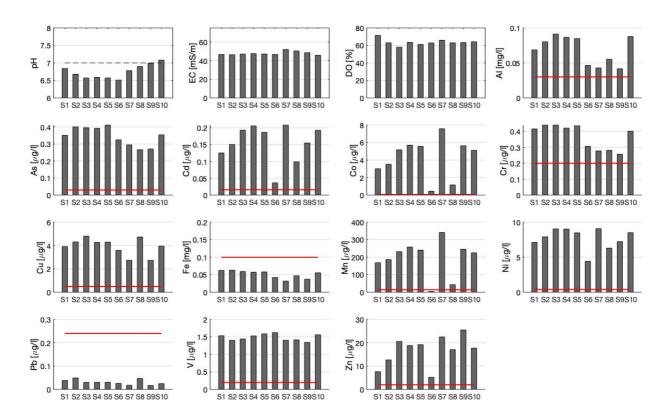
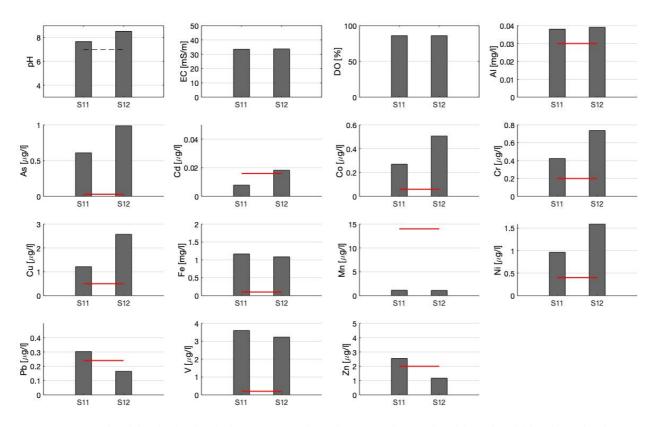


Figure 11: Graphs of the physicochemical parameters and metal concentrations retrieved from area 2 (S1-S10) in October/November 2019. Red lines indicate reference values retrieved from Naturvårdsverket, 2008 and Edén & Björklund, 1993 (cited by Wennström, 2017)

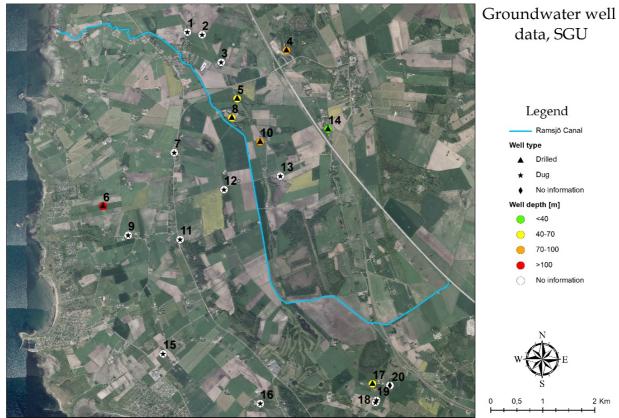
Due to the difference in settings of sites S11 and S12, the results gathered from these sites are presented separately in Figure 12. The pH values of sites S11 and S12 are higher than for sites S1-S10, with an average pH value of 8.1, and a maximum pH of 8.5 visible at site S12. Furthermore, lower values of electric conductivity are presented compared to the other sites in areas 2, along with higher DO. Regarding the metal concentrations, a slight dominating pattern of higher concentrations at site S12 compared to S11 is seen, visible for As, Cd, Co, Cr, Cu and Ni. Only Fe, Pb, V and Zn present exceeding metal concentrations at site S11. Additionally, the concentrations of several metals such as Al, Co, Cu, Mn and Ni are lower at sites S11 and S12 compared to any other site, with the greatest difference visible for Mn. Regardless of the overall low metal concentrations in sites S11-S12, most concentrations still exceed the reference values, with the only exception seen for Mn, not exceeded in neither S11 nor S12.



**Figure 12:** Graphs of the physicochemical parameters and metal concentrations retrieved from the additional two sites in area 2 (S11 and S12) in October/November 2019. Red lines indicate reference value retrieved from Naturvårdsverket, 2008 and Edén & Björklund, 1993 (cited by Wennström, 2017)

#### 4.3 GROUNDWATER QUALITY

Regarding a first indicative examination of the potential effects of acid sulphate soils on the groundwater quality, data was retrieved from SGU and the wells are displayed in Figure 13, presenting both the types and depths of wells investigated. Table 5 further presents the concentration of metals and ions measured in the wells, including limit values for "suitable water with remarks" (marked "R" in table) and "unsuitable water" (marked "U" in table).



SOURCES: Canal: Lantmäteriet®. Orthophoto: Lantmäteriet®. Well depth and type: SGU®. Cartographer: Amanda Lindgren. Date: 2019-12-17

**Figure 13:** Map of the groundwater wells where data was retrieved from SGU. Legend indicates both type of well (*drilled*, *dug* or *no information*) and depth of the well (*0-100 m*).

Wells 3 and 10 do unfortunately lack information concerning the metals and ions of interest, and the quality of these wells is therefore not further analysed. Most values are within the acceptance limits for suitable drinking water in Sweden, visible for all elements in e.g. wells 2, 5, 9 and 13. Some exceptions are however found, e.g. regarding Fe and Mn in well 4 and pH and  $NO_3^{2-}$  in well 18. The results further reveal that the metal most often exceeding the acceptance limits are Fe, exceeded in wells 1, 4, 15 and 17, none of which are located within the study area. Higher concentrations of Fe are instead observed in the wells located north and south of the study area relative to the ones located near Ramsjö canal in area 2. Moreover, well number 19 is the only well with a parameter within the limit of unsuitable drinking water, as

NO<sub>3</sub><sup>2-</sup> is exceeded by 47 mg/l. This dug well is located south of the study area, but no additional information regarding the depth of the well is available in the dataset. Concerning the pH values, most wells present neutral pH condition, with the only exceptions visible at wells 7, 16 and 18. A slight difference in pH is further observed between wells 6-8, crossing through the area of sample sites S11 and S12. Well number 7 presents a lower pH value (6.4) than wells 6 and 8, instead with pH values of 8.7 and 8.4 respectively. A difference in geological settings of these wells is also visible, as wells 6 and 8 are drilled into bedrock, but with different drilling depths. No information about the depth of well 7 could be retrieved from the dataset.

**Table 5:** Table of pH,  $SO_4^{2^\circ}$ ,  $NO_3^{2^\circ}$  and several metals obtained from private well measurements between 2007-2017. The well numbers on each row represents wells in figure 12. Values for "suitable drinking water with remarks" (*R*) and "unsuitable drinking water" (*U*) are retrieved from Livsmedelsverket, 2006.

	Sample year	pН	SO4 <sup>2-</sup> [mg/l]	NO3 <sup>2-</sup> [mg/l]	Al [mg/l]	As [µg/l]	Cu [µg/l]	Fe [mg/l]	Mn [mg/l]	Pb [µg/l]
1*	2008	7.44	15	1.1	-	-	0.034	0.64	0.017	_
2	2016	6.9	6.3	19	0.12	0.22	0.089	0.12	0.011	0.83
3	2007	-	-	-	-	-	-	-	-	-
4	2014	7	14	< 0.001	-	0.20	< 0.001	3.7	0.61	0.43
5	2015	8.7	58	< 0.001	0.002	0.17	< 0.001	0.2	< 0.001	0.034
6	2008	8.7	95	< 0.001	-	-	< 0.001	0.12	0.027	-
7	2007	6.4	28	3.7	-	-	0.054	0.15	0.069	-
8	2007	8.4	71	< 0.001	-	-	< 0.001	0.15	0.15	-
9	2016	6.9	< 0.001	< 0.001	0.061	0.38	< 0.001	0.24	< 0.001	0.93
10	2012	-	-	-	-	-	-	-	-	-
11	2007	6.6	13	3.5	-	-	0.054	0.17	0.024	-
12	2007	7.7	54	6.6	-	-	0.067	0.058	0.1	-
13	2014	7.8	56	< 0.001	0.0026	0.23	0.030	0.18	0.05	0.46
14	2008	8.1	64	0.44	-	-	< 0.001	< 0.001	0.024	-
15	2007	6.7	14	3.1	-	-	0.17	1.00	0.26	-
16	2007	5.9	24	6.2	-	-	0.44	0.15	0.039	-
17*	2015+2016	8.16	39	< 0.001	-	-	< 0.001	0.68	0.04	-
18	2008	6.24	29	31	-	-	0.029	0.07	0.01	-
19	2008	7.34	16	97	-	-	0.027	0.03	0.078	-
20	2008	7.68	25	11	-	-	0.026	0.025	< 0.001	-
R		<6.5	100	20	0.5	-	2000	0.5	0.3	-
U		-	-	50	-	10	-	-	-	10

\* Indicates that several measurements were taken at the well, hence the value stated is calculated as an average value.

#### 4.4 COMPARISON TO OTHER STUDIES

As this study was conducted in a formerly non-investigated site, a comparison to other studies was conducted as part of this study and is presented in Table 6. These studies were selected based on incorporating different stream sizes, draining different acid sulphate soil areas and located in different parts of northern Europe, i.e. Sweden and Finland. Given the differences in catchment size between the studies, area 1 which is smaller in size, is compared to studies conducted on smaller water streams in Finland and Sweden. Area 2 is for the same reason compared to Petalax å in Finland, being somewhat similar in catchment size (approx. 60 km<sup>2</sup> (SMHI, N.D) and 96 km<sup>2</sup> respectively).

The investigation shows that the results from Halland deviate, being both higher and lower than the other sites. This is for instance evident in the pH values, where area 1 presents lower pH than the studies conducted in Finland, and relatively equal or slightly higher than the other areas in Sweden. The pH values of area 2 are instead slightly higher than the other studies used for comparison. The lack of DOC results from several studies only allow a comparison of DOC with one Finnish site to be conducted, presenting values slightly elevated to those received from area 1. The electric conductivity from area 2 is somewhat higher but relatively equivalent to other measurements conducted in Finland, where instead a clear difference is seen for area 1, being higher than all studies with the only exception visible for the study conducted in Norrbotten. Since no measurement of  $SO_4^{2-}$  could be conducted in Halland, no comparison can be conducted for this parameter. The differences in metal concentrations observed between area 1 and 2 in Halland are also visible in the comparison, where area 1 more commonly exceed the other studies than area 2. Some exceptions are however visible, for instance in the Vconcentration, being elevated at both areas, indicating higher concentrations of V in Halland. The comparison further reveals that area 1 presents somewhat equal to slightly elevated metal concentrations compared to those in Finland and instead slightly decreased compared to the Swedish site, visible for e.g. Mn, Fe, Zn, Al, Ni and As. Furthermore, most metals are consistently decreased in area 2 of Halland compared to Petalax å, most evident regarding Al, Cu, Mn, Ni and Zn, were only As and V deviate slightly from this pattern.

		Aı	rea 1	Area 2			
Subarea:	Halland	BB	NB	VB	Halland	PA	Petalax å
pH	3.8-6.6	4.6	3.1-7.1	3.8-5.7	5.42-7.08	4.5	4.6-5.0
EC [mS/m]	32.7-129.4	14	2.4-226	1.72-30.39	35.5-51.9	41	13.2-90.0
SO42- [mg/l]	-	48*	0.91-939	0.06-2.55	-	160*	26-375
DOC [mg/l]	6.9-12.4	40	-	-	-	14	-
Al [mg/l]	0.07-7.5	2.3*	0.021-44*	-	0.04-0.63	5.5*	1.1-11*
As [µg/l]	0.5-1.7	0.87*	0.27-3.9*	-	0.25-1.26	0.79*	0.75-1.1*
Cd [µg/l]	0.03-2.6	0.26*	0.003-2.1*	-	0.04-0.34	0.68*	0.14-1.3*
Co [µg/l]	0.7-61.3	9.9*	0.03-88*	-	0.45-8.97	29*	6.2-78*
Cr [µg/l]	0.5-1.9	2.5*	0.25-4.9*	-	0.25-1.15	3.4*	2.1-2.7*
Cu [µg/l]	3-5.5	7.7*	0.31-32*	-	2.74–10.43	18*	4.3-21*
Fe [mg/l]	0.05-1.9	2.0*	1.1-77*	-	0.03-0.18	1.8*	0.624-1.74*
Mn [µg/l]	17-1742	360*	0.25-9900*	-	4.42-389	1280*	165-3550*
Ni [µg/l]	2.7-85.9	22*	0.43-130*	-	4.42-13.22	65*	13-182*
V [µg/l]	0.7-3.4	2.5*	0.05-0.68*	-	1.25-10.20	1.6*	0.85-2.8*
Zn [µg/l]	2.7-119.3	43*	0.25-320*	-	5.07–29.94	134*	40-334*
Country:	Swe	Fin	Swe	Swe	Swe	Fin	Fin
Sources:	а	b	с	d	а	b	е

**Table 6:** Table presenting the physicochemical parameters,  $SO_4^{2-}$ , DOC and metal concentrations of 5 different studies (including Halland), divided into Finland and Sweden along with the respective subarea.

\*Indicates unfiltered metal analysis

a: Halland (This study)

*b*: Åström & Corin, 2002. PA: Petalax å (catchment size: 96 km<sup>2</sup>). BB: Bläckträskbäcken (catchment size: 1.5 km<sup>2</sup>)

c: Wennström, 2007. NB: Norrbotten

d: Myrstener, 2012. VB: Västerbotten

e: Åström & Åström, 1997 (catchment size: 96 km<sup>2</sup>)

# 5 DISCUSSION

Both major and minor patterns in metal distribution and physicochemical factors observed in Halland will be discussed, with area 1 being the primary focus due to its small catchment size and adjacent location to the acid sulphate soil layer. The results will further be connected to indicators of acid sulphate soil drainage to assess the potential influence from these soils on the overall water quality in the study area, and seasonal variations will be assessed. The data and results collected will onwards be evaluated in relation to other studies conducted in northern Sweden and western Finland, where differences and similarities will be highlighted. Lastly, limitations of the study will be evaluated, along with suggested future studies and implications.

#### 5.1 GENERAL DISCUSSION

#### 5.1.1 Metal distribution and physicochemical parameters in areas 1 and 2

The results from the autumn sampling of area 1 showed increased metal load along with low pH values in the surface water of the ditches, as the results were compared to the given reference values for smaller streams of southern Sweden. Moreover, the results from area 1 also revealed several internal differences between the sites, for instance through relatively high pH levels and low metal concentrations at site D4 compared to the other ditches in the area. The transactional analysis did, however, reveal that site D4 is not in contact with the acid sulphate soil layer beneath, explaining the low metal content and neutral pH at the site. It is therefore expected that site D4 is not affected by acid sulphate soil drainage, as discharge from the soil to the surface water is unlikely to occur and the site does therefore not contribute to the overall negative environmental consequences of sulphate soils in the drainage basin. The results from site D4 could instead act as an additional reference site for the area. Such comparison validates the assumption of a generally high metal load in the surface water of area 1, as higher metal concentrations and lower pH values are established in all remaining sites of area 1 compared to site D4. The only metal deviating from this pattern is Cu, presenting equal concentrations at site D4 compared to the remainder sites. Similar observations have been detected in a study by Sohlenius & Oborn, 2004, who found that the concentrations of Cu were similar between sulphuric and non-sulphuric clays of Sweden and Finland, as this metal is commonly bound to oxides and is hence not as easily leached from the soil. It is therefore possible that the elevated Cu concentrations of area 1 are not necessarily a consequence of acid sulphate soil drainage, as indicated by Sohlenius & Öborn, 2004. Additionally, the metal concentrations at site D4 was slightly elevated compared to the given reference values used in the results, with exceptions seen for Fe and Pb. These results imply that the metal content in the surface water of Halland is slightly higher than in other surface water environments of southern Sweden.

Another commonly seen feature in area 1 is frequently higher concentrations of several metals in the northernmost sites D3 and D5, along with a visible decline in concentrations from D5 onwards to site D7. The acid sulphate soil layer at the two soil profiles H19030 and H19032 are approximately 0.6 meters below the ground surface, and the differences in metal concentrations within these profiles could explain the differences observed in the adjacent surface waters. As stated by Sohlenius & Öborn, 2002, soils containing iron sulphates commonly retain lower metal concentrations since the low pH of the soil allows most metals to leach downwards to the underlying layers. This feature is observed in the acid sulphate soil depth at site H19030, being decreased in all metals compared to the layer below, while increased in sulphur [S] (Kling Jonasson, 2020; Appendix 3). To the contrary, the soil profile at H19032 is not presenting this pattern, instead revealing somewhat elevated values at the depth of the acid sulphate soil layer compared to the layers below. As discussed by Kling Jonasson, 2020, these variations could be explained by development differences between the two soil profiles, affecting their leaching abilities to the recipient surface water. Furthermore, the author considers the possibility of a more ripe and developed soil at site H19032 and explains the lack of metal leakage from this profile to be a consequence of a longer period of leaching, allowing for less metals and acids to be retained in the soil column. The fact that the water sampling of sites D6 and D7, being adjacent to profile H19032, is a momentary examination of the water quality, the possibility of historically elevated concentrations compared to present values cannot be discarded. Furthermore, a less developed sulphuric soil at site H19030 could consequently explain the elevated metal concentrations and low pH values at the adjacent sites D3 and D5, as leaching would be greater from this soil profile. These results therefore indicate that the differences in metal concentrations between the northern and southern parts of area 1 are strongly controlled by the development difference and leaching abilities of the adjacent soil profiles, allowing for increased metal concentrations at sites D3-D5 compared to sites D6-D7.

The results retrieved from area 1 also revealed several differences in both metal concentrations and pH values up- and downstream of the sites, where the metal concentrations commonly increased with decreased pH and vice versa. These results indicate a strong pH dependency for the mobility and solubility of the metals, something previously discussed by e.g. Nystrand & Österholm, 2013. One example of a strong influence of pH for the metal solubility was visually seen in situ at site D3, through red and white precipitate in the water (Appendixes 1A and 1B), being indicative of Fe and Al complexes (Becher et al., 2019). The solubility of Al and Fe are highly dependent on the prevailing pH conditions, where Al and oxidized Fe is commonly most insoluble in waters with a pH range of 5-10 and 3-10 respectively. Additionally, Fe commonly precipitates into Fe(OH)<sub>3</sub> when O<sub>2</sub> is available in the water column (Tipping et al., 1988; Appelo & Postma, 2004; Åbjörnsson & Stenberg, 2017; Berger et al., 2015). Since the water at site D3 increased in pH towards the outlet, Al and Fe are more likely to have precipitated as the water became more alkaline downstream, resulting in the discoloured water observed in situ. These results therefore exemplify a strong correspondence between water acidity and metal solubility in the water column. Such circumstances would furthermore imply that the total amount of Al and Fe is likely not encountered for in the surface water, as the metals might have accumulated in the bottom sediment of the ditch, resulting in decreased concentrations downstream. To validate such assumption, the bottom sediment of the site D3 would have to be sampled and analysed for the total amount of Al and Fe. Other examples of strong pH dependency for metal mobility and solubility are perceived in the Co and Ni concentrations, as these metals consistently increased with a decreasing pH values when the in- and outlets of the ditches were compared. The results further indicate that the mobility of Mn and Zn are likely affected by additional factors, as these metals do not follow the pH fluctuations. A strong relationship was furthermore recognized between decreasing pH values and simultaneous increases in Cr concentrations in area 1, a feature not visible in area 2. This relationship is anticipated given that the most likely state of Cr in oxidized environments are Cr(III), being more soluble in acidic waters (Åström, 2001b), and the lack of such connection in area 2 would thus be explained by the generally more alkaline surface water of area 2. Additional factors are however essential for the distribution and solubility of Cr in stream water, such as the adsorption mechanisms from Fe-oxyhydroxides (Åström, 2001b). Since no speciation of neither Cr nor Fe were conducted in this report, such causes cannot be established. However, given that the variations in metal concentrations within the sites are seemingly connected to the simultaneous changes in pH, this study proposes a strong correlation between water acidity and metal distribution.

Elevated metal concentrations and decreased pH values were also perceived from area 2, being a secondary study area of this investigation. This was most prominently seen in the Mn, As and Co concentrations, being 10 to 100 times higher than the reference values. Moreover, area 2 did not present any clear accumulative pattern from the reference point of S10 towards the outlet at site S1, a feature previously observed by Åström, 2001b during two high water flow events in the autumn. The total cover of acid sulphate soils in the drainage basin in the study by Åström, 2001b did however increase from 0-31% towards the estuary, allowing for the outlet point to be more influenced by the sulphuric soil than further upstream. It is therefore likely that this feature is not occurring in area 2, given the relatively well-distributed metal concentration throughout all sites along Ramsjö canal. Sites S6 and S7 did however deviate from this pattern, presenting clear increases in metal concentrations at site S7, along with a visible decrease at site S6, most prominent for the concentrations of Mn, Co, Ni and Cd. These variations are presumably explained by the location of these two sites along with the pH sensitivity of the metals. Site S7 is located at the outlet of the ditches in area 1, enabling much of the metal rich water to be transported from the ditches into the canal, consequently increasing the concentrations at site S7. Furthermore, the ability of these metals to form iron and manganese precipitates and accumulate with clay particles as the pH changes (Andersson et al., 2014) could henceforth explain the decreased concentrations at site S6, being located downstream of site S7. It is therefore expected that the complexes formed downstream of site S7 have either (1) been accumulated on the bottom of the canal and was therefore unavailable in the water column during sampling or (2) were removed during the filtration process prior to analysis and cannot be accounted for.

A comparison between areas 1 and 2 reveal commonly higher metal concentrations in addition to lower pH values in area 1, with average pH values of 5.11 and 6.15 for area 1 and 2 respectively, both indicating acidic conditions. Furthermore, elevated electric conductivity values were also retrieved from both areas 1 and 2, averages of 72 and 46 mS/m respectively, and with a maximum value of 129 mS/m, measured at site D3. These values are high compared to several previous studies (e.g. Myrstener, 2012; Nystrand & Österholm, 2013), which may only partly be explained by the  $SO_4^{2-}$  composition of the water. It is also likely that these values are reflecting the coastal location of Halland, being highly influenced by saltwater spray particles, increasing the electric conductivity values further. Even though no ion analysis could be conducted in this study, electric conductivity levels of roughly 20-200 mS/m for fine-grained sulphuric soils have previously been measured in acid sulphate soil affected areas (Åström & Åström, 1997). Considering that the values of area 1 are within this range, it is presumed that the electric conductivity could provide a strong indicator for the  $SO_4^{2-}$  composition of the water. Furthermore, a sharp distinction between the two areas is visible in the electric conductivity and pH results, where area 1 presents generally higher electric conductivity and lower pH values than area 2. Aside from the influence of acid sulphate soil coverage between the two areas, additional factors are likely also explaining these differences, such as the size of the watercourses and their surroundings. Area 1 constitutes of smaller and more narrow ditches while Ramsjö canal in area 2 is larger, further draining water from a larger catchment area. These factors would thus allow the water of area 2 to be more diluted, resulting in increased pH and decreased electric conductivity. Area 2 is also influenced by several anthropogenic inputs, such as roads, building and railways whereas the surface water of area 1 is mostly influenced by the adjacent cultivated area, where active acid sulphate soils was detected by Kling Jonasson, 2020. Additional anthropogenic influences have likely also affected the results from sites S11 and S12, presenting higher pH values than both areas 1 and 2, being 7.67 and 8.53 respectively in the autumn of 2019. At these sites, distinctive indications were found in situ of liming activity, visible through white spots on the surrounding vegetation (Appendix 1F). This aspect allows for the assumption that the water at these sites was under a great influence of CaCO<sub>3</sub> leakage from the surrounding agriculture during times of water sampling, and these sites may consequently not be good representatives for the acid sulphate soil leakage of area 2. Given the time limitation and lack of ion analysis, site S11 and S12 will not be further discussed in this study.

Lastly, even though the impact on biotic life is unknown for several of the metals investigated, the negative effects of Al on aquatic biota have been addressed in previous Swedish studies (e.g. Åbjörnsson & Stenberg, 2017; Nystrand & Österholm, 2013) where an accumulative effect leading to fish deaths have been established (Slaninova et al., 2014). Nystrand & Österholm, 2013 declared 0.5 mg/l of dissolved (<1kDa) Al to be a limit for the elimination of several fish species in acidic waters. Even though this limit is not exceeded in the surface water of areas 2, being connected to the Natura2000 classified estuary, this limit is commonly exceeded in the ditches of area 1, evidently connected to the canal. This would thus mean that the levels of metals to the canal are likely to increase as a consequence of additional metal input from the ditches. Even though the size of the individual metal complexes was not determined through

this study, the toxic effect of Al along with the elevated concentrations in area 1 therefore emphasizes that the surface water is potentially harmful to several aquatic species in the estuary.

# 5.1.2 Acid sulphate soil impact on the water quality

As aforementioned, electric conductivity and water acidity are commonly used parameters when evaluating potential influence on water being adjacent to acid sulphate soils. Given that the surface water of areas 1 and 2 were acidic and presented high electric conductivity, it may thus be concluded that both areas are impacted by acid sulphate soil drainage. Site D1 presented the absolute lowest pH regarding both study areas and was thus initially assumed to be the single most affected site. However, the relatively high DOC concentration at site D1 combined with its near-forest location suggests an additional presence of organic acids which may alter the pH of the water (Åström & Corin, 2000; Åström, 2001b). The effect of organic acids on waterbodies being influenced by sulphuric soils seem to be a controversy in earlier studies (Weppling, 1993; Nyberg, 2012), implying that the pH alone might be an inadequate parameter for determining sulphuric impact on the surface water. Myrstener, 2012 instead presented a strong relationship between high electric conductivity and acid sulphate soil coverage, concluding that electric conductivity is a good indicator for determining the extent of the acid sulphate soil. This aspect was also highlighted by Saarinen et al., 2013 who suggested a combined approach of incorporating both water acidity and electric conductivity when investigating the potential influence from acid sulphate soils in a catchment area. Combining pH and electric conductivity measurements may therefore serve as the best indicator for sulphuric soil impact to the surface water, something also previously addressed in the study by Weppling, 1993. Considering this aspect, the results instead indicate that sites D1, D3 and D5, all of which present comparatively low pH values in combination with moderately high electric conductivity are assumed to be under greatest influences from the surrounding sulphuric soils. It should however be highlighted that the potential influence from organic acids in the surface water of site D1 cannot be accounted for in this study, hence no certain conclusion can be drawn for this site in particular. Furthermore, the consistently lower pH values and increased electric conductivity measured in area 1 compared to area 2 accordingly suggests that area 1 is more strongly affected by drainage from the adjacent sulphate soils. This assumption is also supported by the metal analysis, as higher concentrations was measured in area 1 compared to area 2. The discrepancy between the areas is most prominently seen in the concentrations of Al, Ni, Mn and Zn, all of which are strongly associated with water drainage from active acid sulphate soils (Wennström, 2017; Åström & Björklund, 1995). Combining the physicochemical results with the metal analysis from the two areas therefore suggests that even though both areas are affected by the adjacent sulphuric soil layer, a generally stronger influence is anticipated in area 1 compared to Ramsjö canal in area 2.

To the contrary of many of the investigated metals, neither Fe nor Pb were elevated substantially except for few clear peaks visible at site D1 for Fe and sites D1, D3 and D6 for

Pb. Considering that Pb has a generally low mobilisation capacity, while the mobilisation of Fe is determined by additional factors such as redox state and organic content (Andersson et al., 2014; Nystrand & Österholm, 2013), none of these metals are commonly leached from acid sulphate soils (Wennström, 2017; Åström & Corin, 2000; Lax, 2005), and lower concentrations should therefore be anticipated in the results. Increased levels of Fe in sulphuric waters have however been observed by Cook et al., 2000, who further connected increased concentrations to a longer period of acid sulphate soil drainage. The peak in Fe observed at site D1 could therefore indicate more prolonged leaching from the adjacent soil to the surface water compared to the other sites in area 1. This does not explain the few increases seen for Pb at sites D1 and D5, but it is expected that additional factors are controlling the distribution of Pb to the surface water at these sites. Aside from Pb and Fe, the concentrations of V was elevated in all samples, a metal not more frequently leached out from sulphuric soils than from other soils (Wennström, 2017). V is however a common metal in the soils of Halland compared to other counties of Sweden (Andersson et al., 2014) and the elevated concentrations in the water column might therefore be a natural occurrence, rather than a consequence of discharge from the adjacent acid sulphate soils. This assumption is also verified by the high concentrations of V at site D4, where little to no acid sulphate soil drainage is anticipated. Additionally, the increased concentrations of V measured in the surface water of area 2, assumed to be less affected by the adjacent sulphuric soil, further validates a natural abundance of V in the drainage basin of the study site.

As e.g. Åström, 2001b; Becher et al., 2019; Åström & Corin, 2000; Åström, & Björklund, 1996 has emphasized, acid sulphate soils commonly form during times of low groundwater levels, while leaching is increased during (1) autumn, where the amount of rainfall is increased, and (2) during spring, when the snow melts. Additionally, leakage during winter is commonly inhibited since low temperatures allow the soil to freeze (Lindström, 2017; Toivonen et al., 2013). These aspects therefore highlight the importance of incorporating a climatic perspective to the drainage pattern from the soil column to the surface water, as discharges may fluctuate depending on the season. The seasonal distribution of area 1 showed declining metal concentrations along with decreasing electric conductivity and increased pH from autumn to spring. This pattern is most likely explained by the surpassing temperatures in Halland from the autumn of 2019 to the spring of 2020, along with prolonged rainfall during the same period. The weather conditions would therefore allow for continuous leaching, leaving decreasing levels of acids and metals retained in the soil, thus resulting in declining metal concentrations and increased pH levels in the surface water over time. The elevated temperatures are likely also explaining the continuous leaching during winter as the soil was inhibited to freeze. The results from Halland therefore confirms the importance of temperature fluctuations to the overall metal and acid load from sulphuric soil layers into nearby surface water. Furthermore, considering that both temperature and precipitation patterns vary substantially between in different parts of Scandinavia (SMHI, 2017a; SMHI 2017b), variances in leakage pattern should be highlighted when investigating new areas of acid sulphate soils in the southernmost regions of Scandinavia. Seen to a future perspective, a changing climate with dryer summers and with warmer and wetter winters might therefore prolong the leaching for most parts of the year, hence enlarge the pre-existing issue of increased metal concentrations and decreased pH into the recipient water.

Aside from sampling surface water in the ditches of area 1, a collector in the area was sampled in the winter and spring to further assess the sulphate soil impact of the area. Given that the collector was seemingly not connected to the groundwater reservoir of area 1, but rather used for the accumulation of drainage water from adjacent agricultural fields before discharge into the recipient ditches, the result could not be used for interpreting the groundwater quality in the region. An accumulation of water in the collector is also validated by the increased metal concentrations in the spring compared to the winter sampling, a feature not commonly seen in other surface watercourses of area 1. The results from the collector could thus act as an additional representation of the surface water of the area and further present some indications of the soil outside the sampling sites of Kling Jonasson, 2020. A comparison between the sites of area 1 and the collector reveals that various metal concentrations in the collector surpassed those of the adjacent ditches during both the winter and spring sampling, seen clearest e.g. Al, Cr, As, Fe and V. Nevertheless, several metals commonly associated with acid sulphate soil drainage, e.g. Mn, Co, Ni and Zn (Wennström, 2007) are instead increased in the surface water of the ditches compared to the collector, implying either that the soils most adjacent to the collector are not of sulphuric character, or that the drainage pipes of the collector are elevated above the sulphuric soil layer (Appendix 1H). It is therefore suggested that even though metals are continuously leached from the agricultural fields into the collector, this water is likely not an additional contributor to the acid sulphate load of area 1. No mapping of the soil layers closest to the collector has yet been conducted, being outside the study area for Kling Jonasson, 2020, and it is therefore suggested that future studies further examines the soil of area 1, including the field where the collector is located.

Instead of using the collector for groundwater quality interpretation, several private wells were examined within and outside the study area. Investigations of groundwater reservoirs nearby sulphuric soils are important since previous studies have associated decreased drinking water quality with acid sulphate soil drainage, (Länsstyrelensen Västerbotten, 2017). This problem has for instance been recognized by Mattbäck et al., 2017, investigating groundwater regarding acidification and metal concentration in a boreal Holocene landscape in Finland. The authors found at least ten times higher concentrations of several metals, such as Al, Co, Fe and Mn when compared to median values of Finland, along with near-neutral pH values. Although the pH values from the private wells in Halland provided by SGU were within the same range as those measured by Mattbäck et al., 2017, the metal concentrations were substantially lower and does not seem to pose any considerable threat to the drinking water quality. Several of these wells are drilled deep into the bedrock, possibly explaining the overall low concentrations of metals in the water, given that the acid sulphate soil layers are located 0.6 meters below the ground surface. This would hence mean a non-existing contact between the well and the sulphuric soil, restricting the negative impact on the drinking water quality of the wells. It should however be highlighted that the data used for this analysis cannot be used for any deeper investigation, given the point-based character of the data set provided by SGU, being sampled sporadically between 2006-2016. These results should instead initiate future investigations which may establish a potentially negative effects on groundwater quality, a problem not supported by this study.

5.1.3 Comparison between Halland and other Scandinavian sites affected by acid sulphate soil drainage

A comparison to related studies was conducted as a part of this investigation, given the sparse amount of previous investigations on acid sulphate soils along the south-western coast of Sweden. The importance of stream size previously highlighted allowed for a comparison between area 1 and other smaller streams and ditches, and the results presented slightly lower pH values in Halland compared to the Finnish site (Åström & Corin, 2000) while moderately equal pH values compared to the sites of northern Sweden (Myrstener, 2012; Wennström, 2017). The electric conductivity values were likewise higher in Halland compared to Finland and slightly lower in comparison to the northern Swedish sites. The electric conductivity should, as previously mentioned, be used with caution given that it is controlled by the total ionic composition in the water rather than only reflecting the amount of SO4<sup>2-</sup> (Bydén et al., 2003). The near-shore location of Halland and the lack of ionic analysis in this report can therefore not fully determine the exclusive influence of  $SO_4^{2-}$  ions. However, the electric conductivity measurements combined with the pH values, implies that area 1 is less affected by the drainage of sulphuric soils than the northern parts of Sweden, whereas instead slightly more affected than the Finnish site used for comparison. The metal concentrations were also following the physicochemical parameters, showing relative equal concentrations of several metals compared to the Finnish site, while slightly lower concentrations were measured in Halland relative to the other Swedish site. Some of the metals most commonly associated with leakage from acid sulphate soils, such as Al, Zn, Mn, Co and Ni (Wennström, 2007; Åström & Björklund, 1995) are similarly elevated in Halland compared to the small ditches of Finland.

Considering the vast sulphuric soil problematics detected through other studies in Finland (Roos & Åström, 2005; Saarinen et al., 2013; Wallin et al., 2015; Weppling, 1993; Palko & Weppling, 1995) along with the reported fish kills in larger Finnish estuaries (Bärlund et al., 2004; Åström & Björklund, 1995; Kyheröinen, 2019, 27<sup>th</sup> of November), greater leaching in Halland seems unlikely. The deviations in the results are instead likely explained by the low amount of acid sulphate soil in the drainage basin of the particular Finnish study examined, only covering 6% of the total catchment area (Åström & Corin, 2000). To the contrary, acid sulphate soils are common in the site of northern Sweden (Wennström, 2007), explaining the increased levels of metals and decreased pH levels compared to Halland. This assumption is also reflected in the comparison conducted for area 2, being generally less influenced by the adjacent sulphuric soils than area 1. Area 2 was instead compared to two separate studies from Petalax å in Finland (Åström & Åström, 1997; Åström & Corin, 2000), being somewhat equal

in catchment size. The results revealed increased pH levels and decreased electric conductivity of area 2 compared to both studies of Petalax å, indicating that area 2 is less affected by the adjacent sulphuric soils than the Finnish sites. This is further verified by the metal concentrations, being decreased in relation to the Petalax å regarding most metals, including those most commonly associated with acid sulphate soil drainage. The levels of V deviated from this pattern, as it was increased in both areas 1 and 2 of Halland compared to all other studies used for comparison. The relatively high concentration of V has previously been discussed in this report, where it has been suggested that a naturally high abundance of V does not depend on the presence of acid sulphate soils in the catchment area.

There are however additional factors likely contributing to the differences in metal concentrations, such as the dissimilarities in filtration procedures prior to the metal analysis between the studies. This matter was addressed by Åström & Björklund, 1995, who noticed a high ratio ( $\geq 0.69$ ) between unfiltered and filtered samples, concluding that acidic conditions allow for most elements to be associated with smaller sized particles, <0.45 µm. Nevertheless, the same study also showed an increase in Al concentration by a factor of 50 when compared to filtered water samples collected nationally, implying that the potential removal of metal composition through filtration should not be completely discarded. Moreover, a study by Åbjörnsson, 2018 where filtrated and unfiltered Al and Fe were investigated instead revealed levels up to 100 times higher in the unfiltered samples compared to the ones being filtered. It should therefore be emphasized that the difference in methodology between the studies could be of high importance and that these aspects cannot be discarded in the evaluation. To fully determine the total amount of metals in the surface water of Halland, and further validate the potential effect of the filtration procedure, a comparison of metal concentrations between filtered and unfiltered samples should be conducted. Another factor omitted from the comparative analysis is the soil types of the different studies, affecting the capacity of the soil to resist acidification. This feature has previously been highlighted by Bayard & Karlsson Mood, 2014 who considered the potential for the silty soils of northern Sweden to be more susceptible to acidification. As no soil type comparison was conducted through this report, it cannot be determined whether the buffer capacity of Halland is greater, consequently limiting acidic leaching to the surface water. Therefore, even though the results suggest a slightly reduced sulphuric soil leaching in Halland compared to other parts of northern Europe, no validations can be drawn given the significance of the abovementioned factors. Instead, the comparative study should be considered as a first indication of the differences in soil leaching between the different areas, initiating the need for future studies to be conducted.

# 5.2 LIMITATIONS OF STUDY

Given that this study was conducted as a master thesis report of 45 credits, several aspects unfortunately provided some limitations to the study, all of which are discussed below. Firstly, one prominent limitation was the analysis of the groundwater wells provided by SGU, given the long timespan and seasonal variation of samples conducted from the wells. Most of the wells were only samples ones and no information regarding usage were provided in the dataset. Moreover, the water samples were conducted throughout January 2007 – December 2016, limiting the possibility for annual and seasonal patterns to be drawn based on the dataset alone. The groundwater quality data was instead used in this report as a first indicator of potential groundwater impacts from the adjacent acid sulphate soils and were hence not sufficient for any deeper analysis. Additionally, some differences in methodology compared to other studies have previously been highlighted in the discussion, especially in the preparation of the water samples prior to analysis. All water samples conducted through this study were filtered through a 0.45 µm filter with the purpose of removing any particles from the samples larger than that fraction, prior to the analysis in the ICP-MS. The other studies used in the comparison to Halland instead analysed unfiltered samples, and the discrepancy in methodology therefore only allowed for a general comparison to be conducted. A comparison between filtered and unfiltered samples could not be conducted within the frame of this study. Moreover, it has been established that the size of the metal complexes has a large impact on the chemical properties and toxicity of element (Nystrand & Österholm, 2013) but since no size determination could be conducted, no deeper conclusions on the toxicity of the metals on aquatic environment could be drawn. Lastly, the values used as reference values for both areas 1 and 2 were based on smaller streams in southern Sweden (Naturvårdsverket, 2008). Given that these values are somewhat generalized, these values should be used with caution as a comparison.

## 5.3 FUTURE STUDIES

As mentioned in section 1.2.3 the focal point for prior investigations regarding acid sulphate soils in northern Europe have been along the north-eastern part of Sweden and the coastal part of Finland. However, earlier studies (e.g. Åbjörnsson & Stenberg, 2017) have highlighted the need for additional investigations elsewhere in Sweden, and this study therefore aimed to assess sulphuric soil drainage in a previously non-investigated area. The results provided through this study confirmed a negative environmental impact from the adjacent acid sulphate soil on the recipient surface water of Halland, stressing the demand for this region to be examined further. These investigations should include a vaster assessment of the surface water in the county, along with a deeper examination of the sites S11 and S12, being omitted from this report. It is further desired that water from both areas 1 and 2 are investigated in regard to the total ion composition, in order to validate or discard the assumptions drawn regarding the electric conductivity in the area. Onwards, no directly negative effect on the surrounding groundwater wells provided by SGU was established, however, given the limitations of the dataset, no deeper

investigation of groundwater quality could be pursued through this study. This further implies that an impact from the sulphuric drainage on the groundwater quality cannot be rejected, but rather that future studies are needed to ascertain possible consequences from the acid sulphate soil drainage. Moreover, the results of this study emphasized the importance of climate variations for the duration and timing of acidic leaching from the soils. With a changing climate, it is likely that annual leaching variations will shift in the future, as precipitation and temperature patterns changes. Additionally, periods of low groundwater levels will likely allow for more potential sulphate soils to oxidize, and given the extensive time required for these soils to be completely leached out of metals (Åbjörnsson & Stenberg, 2017), the environmental effect might intensify in the future. This study therefore highlights the need to further investigate annual variations of the surface water quality in Halland, with a focus set on the potential consequences resulting from climate change.

Finally, several studies have highlighted the negative impact of acid sulphate soil drainage on the recipient estuaries (Wallin et al., 2015; Nystrand & Österholm, 2013; Nordmyr et al., 2008), and in several occasions, negative effects on fish-species and biotic life have been observed or anticipated as a consequence of the leaching acids and metals into the ocean (Urho et al., 1990; Nystrand & Österholm, 2013; Hudd & Kjellman, 2002). Even though some research on metal distributions in Kattegat and Skagerrak have been conducted (e.g. Dave & Dennegård, 1994), no such investigation has focused on metal leakage from acid sulphate soils at the outlet estuary of Ramsjö canal. The results of this study showed that some metals such as Ni and Co, commonly more available in ecosystems influenced by acid drainage from sulphuric soils are elevated in the surface waters of both study areas. Additionally, increased levels of several potentially toxic metals, such as Al were observed in the surface waters, posing a large threat to the safety of several fish species outside the estuary. Several species, such as eels, crustaceans, salmon and molluscs are likely to habit in the estuary (Trafikverket, 2015; Länsstyrelsen Hallands län, 2017), some of which are sensitive to changes in water acidity (Åbjörnsson & Stenberg, 2017; Havs- och vattenmyndigheten, 2014). The estuary of Ramsjö canal is further classified as a Natura 2000 area (Länsstyrelsen Hallands län, N.D), allowing it to be specifically pointed out as an area of special environmental interest (Naturvårdsverket, 2019). This specifies that even though fish kill episodes have not been reported as frequently on the south-western coast of Sweden, the inadequate chemical status of Ramsjö canal, combined with the sensitive species living by the outlet of the canal, highlights the need for future investigations of the estuary. It is therefore requested that the estuary of Ramsjö canal is examined further, in regard to assessing the chemical status of both sediment and water column. Moreover, as mentioned by e.g. Nystrand & Österholm, 2013, speciation and size of metals is a key factor in determining the overall toxicity of the elements to aquatic flora and fauna, and it is therefore desired that overall concentrations, speciation's and sizes of the metals leached from the ditches in area 1 and Ramsjö canal into the estuary of Kattegat is examined further.

# 6 CONCLUSIONS

This study aimed to investigate the surface water chemistry adjacent to a newly discovered area hosting acid sulphate soil in Halland, in order to assess the potential damage of the leakage. The research questions to be answered in this report was; (1) what are the metal distributions and concentrations in the study area, (2) what are the clear signs of impacts from acid sulphate soils in the water, and (3) how does the study area compare to other areas in Sweden and Finland being affected by acid sulphate soil drainage? The main finding of this study was:

- 1. The surface water of both areas 1 and 2 showed elevated metal concentrations, high electric conductivity and decreased pH levels. Distinct variations were furthermore seen at the different sites in both areas, assumed to be highly reflected by (1) differences in water acidity, implying a strong correlation between pH and metal solubility, and (2) the leaching ability of the adjacent soil profiles.
- 2. These results strongly indicated that both areas are affected by drainage from the adjacent acid sulphate soil. Differences between the areas were however established, where area 1 presented generally higher metal concentrations and lower pH values and was thus assumed to be more strongly affected by the leaching. Moreover, despite the fact that groundwater problematics are common in areas containing acid sulphate soils, no such consequence could be established from the available data in Halland. However, due to several limitations in the dataset, no conclusions can be established regarding the groundwater quality in the region.
- 3. The comparison between Halland and other sites in northern Europe revealed generally lower leaching in Halland compared to other established acid sulphate soil affected areas. This was assumed to be partly due to differences in total acid sulphate soil coverage in the catchment areas, but other factors such as methodology differences and soil types likely also affected the results.
- 4. The study also highlighted the need for future studies to be conducted in the region, suggesting a deeper investigation of the surface water chemistry, preferably including an analysis of the total ion composition of the water. Moreover, the groundwater quality should be examined further, in order to determine the potential risk for decreased drinking water quality. Lastly, it is also suggested that the estuary of area 2 is investigated, given the negative effect of acid water and increased metal leakage on aquatic living organisms.

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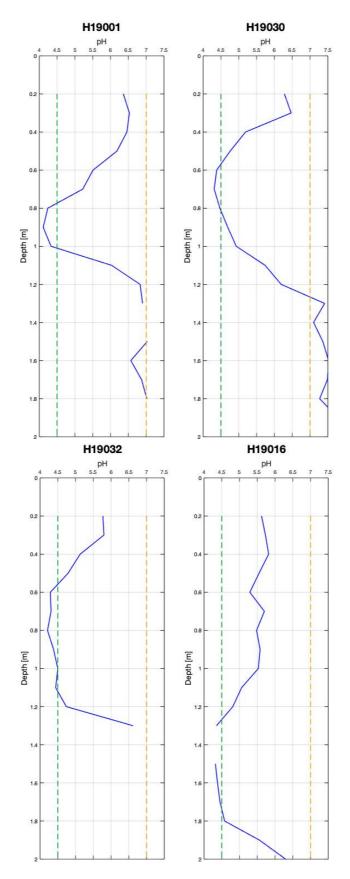
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**Appendix 1 (A-D):** Field pictures taken at the field sites where (A) is the taken upstream D3, showing the iron precipitates, (B) shows the aluminum precipitated downstream of D3, (C) is taken downstream of D1, with forested area seen in the background and (D) is taken by Ramsjö canal taken at site S5



**Appendix 1 (E-H):** Field pictures taken at the field sites where (E) is showing the smaller lake by S11, (F) shows the CaCO<sub>3</sub> spots on vegetation by S11 and S12, (G) shows iron precipitation on ground by S12 and (H) is taken down the well in area 1, showing the inflow and outflow pipes



**Appendix 2:** Graphs of pH with depth from sites H19001, H19030, H19032 and H19016. Data collected by Kling Jonasson, 2020.

Site: H19030			
	0.7 [m]	1.0 [m]	1.3 [m]
As [mg/kg TS]	<3	4.75	<3
Ba [mg/kg TS]	22.5	114	51.3
Be [mg/kg TS]	0.125	1.33	0.736
Cd [mg/kg TS]	<0.1	<0.1	<0.1
Co [mg/kg TS]	1.41	13.0	7.13
Cr [mg/kg TS]	6.50	27.5	17.0
Cu [mg/kg TS]	2.31	21.8	16.1
Fe [mg/kg TS]	12600	32000	19300
Hg [mg/kg TS]	<1	<1	<1
Mn [mg/kg TS]	71.8	1080	187
Ni [mg/kg TS]	2.82	25.5	13.4
P [mg/kg TS]	459	748	589
Pb [mg/kg TS]	2.76	12.4	7.19
S [mg/kg TS]	2390	335	381
Sr [mg/kg TS]	20.5	56.3	14.1
V [mg/kg TS]	21.2	61.1	44.7
Zn [mg/kg TS]	9.45	76.2	45.8
Site: H19032			
	0.6 [m]	1.3 [m]	
As [mg/kg TS]	5.10	<3	
Ba [mg/kg TS]	36.8	35.5	
Be [mg/kg TS]	0.330	0.355	
Cd [mg/kg TS]	<0.1	< 0.1	
Co [mg/kg TS]	2.71	3.70	
Cr [mg/kg TS]	21.1	10.7	
Cu [mg/kg TS]	15.2	8.10	
Fe [mg/kg TS]	15800	11700	
Hg [mg/kg TS]	<1	<1	
Mn [mg/kg TS]	112	147	
Ni [mg/kg TS]	6.16	6.36	
P [mg/kg TS]	558	485	
Pb [mg/kg TS]	4.27	3.24	
S [mg/kg TS]	1840	4980	
Sr [mg/kg TS]	11.8	28.6	
V [mg/kg TS]	32.2	27.4	
Zn [mg/kg TS]	23.8	23.0	

Appendix 3: Metal concentrations from soil sites H19030 and H19032. Data collected by Kling Jonasson,

Most likely chalked area. A smaller pond by the lake of SW_11. Precipitation of iron on the sides. Pond was around 20 cm deep. Sandy and high organic content.	Cloudy	168	1009,4	11,49	33,7	86	68,1 (?)	8,53	7,00	1	17:15	2019-10-25 17:15	S12
Most likely chalked area. "White spots" on vegetations around. Low water level. Something which looked like oil-spill on the sides. High organic content ("dv"). Brown water, no smell.	Cloudy	168	1009,1	12,38	33,5	86	173,5	7,67	7,00	1	17:37	2019-10-25 17:37	S11
Calm waters, lots of "vass". Located in between train tracks. Relatively clear waters. Sed sample taken above the waterline. Water level approx. 2 meter below ground.	Cloudy	229	1009,8	11,55	45,7	64,2	192,5	7,08	7,00	13°C	15:31 13°C	2019-10-25	S10
Taken in the middle of the stream to be able to see differences between edge of stream and middle of stream.	Sunny	241	1010,2	11,59	48,2	65,3	136,3	6,95	7,00	13°C	13:18	2019-10-25 13:18	S9:2
By farm, uses chalk on field. More clear water than other locations. Sed sample taken above waterline.	Sunny	242	1010,6	11,57	48,4	63,3	133,8	6,99	7,00	13°C	13:18	2019-10-25 13:18	S9:1
Waterlevel is around 2,5 meter below field. Brownish color of water, calm. Lots of "vass". Not as clear water as SW 09. Took only on side of stream, access issues. Sed sample taken above the water line.	Drizzle rain	252	1008,3	11,6	50,4	63	132,6	6,9	7,00	13°C	14:14	2019-10-25 14:14 13°C	S8
Strong current. Higher water in the stream than during first sampling. Rainy weather on the weekend, but no rain as the sample was taken.	Clody	210	1004,6	7,7	42	58,4	190	6,46	7,00	9°C	10:44	2019-11-18 10:44 9°C	S7:2
Had to change location a bit. Calm water, browning color. Dark outside while sampling, so no picture was taken. Very steep sides	Cloudy	259	1009,8	11,45	51,9	66	157,5	6,78	7,00	14°C	18:20	2019-10-25 18:20 14°C	S7:1
More rapid water. Lots of grass and animals around (ducks etc). Brown water. Had to adjust the spot a bit due to accesslimitations.	Rainy		1016,7	11,13	46,6	62,9	184	6,51	7,00	11,00	16:14	2019-10-21 16:14 11,00	S6
Some error source on pH, had to move the instrument around a bit (took an average). More rapid wher but still quite calm. Brown color of water.	Rainy		1017	11,12	47	61,1	177,6	6,57	7,00	12,00	15:29	2019-10-21 15:29	S2
Had to move point a bit due to accesslimitations. Location is next to agricultural farm. Calm waters, high particle matter. Brown color, no smell.	Sunny		1017,2	11,12	47,5	63,5	180	6,59	7,00	13,00		2019-10-21 14:47	S4
Day after heavy rain, higher water! This sample was taken around 1 meter upstream of SW_03_001 (2) and was only taken to be able to compare the upstream water from the water coming out from the outlet.	Cloudy	177	1006,9	10,73	35,5	55,6	202,4	6,43	7,00	10°C	13:10	2019-10-27 13:10 10°C	S3:4
Higher water than last time this point was sampled.	Cloudy and rainy	231	1000	8,11	46,3	61,3	216,6	6,24	7,00	9°C	16:15	2019-11-18 16:15	S3:3
Day after heavy rain, higher water! Around 20 meter upstream from SW_03_001 (1), on same side	Cloudy	212	1005,7	11,52	42,4	66,2	284,7	6,03	7,00	10°C	13:10	2019-10-27 13:10 10°C	S3:2
Had to change location due to a lack of road. Close to large trafficked road, under a bridge. Calm water 1 Brown color and very muddy.	Cloudy, fog. No rain		1018,9	11,04	47	58	186	6,57	7,00	11,00	13:08	2019-10-21 13:08	S3:1
Cloudy, fog. No rain Calm water, low water levels. By agricultural field	Cloudy, fog. No rai		1019	10,97	46,3	63	184	6,68	7,00	11,00	12:30	2019-10-21 12:30 11,00	S2
Had to redo measurements (measurements and sampling was conducted at seperate times). Rapid water! By large acre field, plowing done for the season. High particle matter, brown water.	Clody		1019	10,99	46,5	71,4	190,2	6,84	7,00	12,00	13:50	2019-10-21 13:50 12,00	S1
Fieldnotes	Weather	Tds [mg/l]	Pressure [mbar]	Temp [°C]	EC [mS/m]	DO [%]	Redox [mVorp]	PH	Neutral ph	Air temp [°C]	Time	Sampling- date	Site:

**Appendix 4:** Collection of fieldnotes from sites S1-S12, including fieldnotes of observations done in situ and physiochemical parameters

Site:	AI [mg/I]	V [ug/l]	Cr [ug/l]	Mn [ug/l]	Fe [mg/l]	Co [ug/l]	Ni [ug/l]	Cu [ug/l]	Zn [ug/l]	As [ug/l]	Cd [ug/l]	Pb [ug/l]
S1	0,0686	1,53	0,42	168,60	0,0624	3,01	7,13	3,91	7,61	0,35	0,13	0,04
S2	0,0802	1,40	0,44	186,49	0,0633	3 <i>,</i> 52	7,92	4,32	12,65	0,40	0,15	0,05
S3:1	0,0912	1,44	0,44	232,00	0,0594	5,18	9,04	4,81	20,55	0,40	0,19	0,03
\$3:2	0,3976	10,24	1,15	60,46	0,1805	2,71	12,57	10,43	20,26	1,26	0,26	0,22
S3:3	0,1341	1,27	0,55	292,13	0,0774	8,25	10,42	2,95	23,11	0,41	0,25	0,03
\$3:4	0,1392	1,75	0,49	52,04	0,1154	1,16	5,37	4,56	5,07	0,42	0,09	0,05
S4	0,0866	1,53	0,42	258,47	0,0574	5,71	9,03	4,28	18,81	0,39	0,21	0,03
S5	0,0847	1,59	0,44	240,97	0,0581	5,57	8,49	4,30	19,18	0,41	0,19	0,03
S6	0,0465	1,62	0,31	4,42	0,0422	0,45	4,42	3,60	5,21	0,32	0,04	0,03
S7:1	0,0428	1,40	0,28	341,72	0,0319	7,59	9,09	2,74	22,51	0,29	0,21	0,02
S7:2	0,1169	1,59	0,43	388,90	0,0699	8,97	11,48	3,23	19,64	0,36	0,30	0,03
S8	0,0553	1,42	0,28	43,29	0,0470	1,17	6,31	4,74	17,07	0,27	0,10	0,05
S9:1	0,0417	1,35	0,26	245,99	0,0373	5,64	7,24	2,74	25,50	0,27	0,15	0,02
S9:2	0,0504	1,51	0,25	176,77	0,0452	3,92	6,11	2,79	14,02	0,25	0,12	0,02
S10	0,0877	1,56	0,40	225,35	0,0555	5,11	8,52	3,95	17,70	0 <i>,</i> 35	0,19	0,02
S11	0,0381	3,60	0,42	1,13	1,1665	0,27	0,96	1,21	2,55	0,61	0,01	0,30
S12	0,0391	3,23	0,74	1,10	1,0865	0,51	1,59	2,57	1,17	0,99	0,02	0,16

**Appendix 5:** Raw data of metal concentrations for sites S1-S12 retrieved from Chalmers University of Technology.

Site:	Samplingdate Time		Air temp [°C]	먼	Redox [mVorp]	DO [%]	EC [mS/m]	Temp [°C]	Pressure [mbar]	Tds	DOC [mg/l]	Weather	Fieldnotes
D1 (Autumn)	2019-11-18	13:31	9°C	3,82	503,2	26,7	68,4	8,3	1001,0	342,0	10,9	Cloudy, no rain	Lots of grass, reddish colored water. Took a grass sample back to the department. The low pH value is indicating that the drainage path might be different than originally thought. LOTS of particles in the water.
D2 (Autumn)	2019-11-18	14:49	10°C	4,90	373,6	39,7	56,1	8 6,8	1000,6	280,0		Cloudy, drizzling rain	Oily water and very low water. No movement visible in the water at all, but the water seems to be draining Cloudy, drizzling rain towards the canal, indicated by plants. Brownish color and high organic content in the water.
D3:1 (Autumn)	2019-11-18	11:30	9°C	4,93	317,4	25,6	129,4	8,7	1002,5	674,0	7,697	Cloudy, no rain	Very brown/orange looking water. Perhaps iron
D3:2 (Autumn)		10:58	9°C	5,55	272,6	25,0	123,4	7,7	1003,4	617,0	8,4		Milky looking water, possibly aluminium. No connected to Ramsjö canal. Water is not moving at all in this ditch, since it has no exchange with surrounding water.
D4 (Autumn)	2019-11-18	12:01	9°C	6,64	53,0	10,2	50,9	7,6	1001,7	258,0	13,2		This measurement with Hannah might have a larger error source, since the instruemt sank into the sediment when measuring. The Redox showed negative values from time to time. A lot smaller ditch than ditch 3, also
D5:1 (Autumn)		12:43	9°C	4,65	9,965	33,0	68,5	8,0	1001,2	342,0	9,6		Ollspill in the water, not clear where this came from. Otherwise, very similar to the other ditch 5 site. Water connected to Ramsjö canal, but the gate to the canal was closed when measuring
D5:2 (Autumn)	2019-11-18	12:25	9°C	4,59	411,9	36,3	74,6	8,0	1001,6	373,0	10,0	Cloudy, no rain	Clear water, not very indicative of SSJ. No clear movement of water. Higher waterlevel than in Ditch 4. Grassy
D6:1 (Autumn)		14:20	10°C	4,65	382.4	42.3	64.7	8.1	1000.6	323.0		Cloudy, drizz ling rain	
D6:2 (Autumn)		14:00	10°C	4,60	423,4	26,5	66,8	8,0	1000,8	334,0		Cloudy, drizz ling rain	Very red, precipitated iron (2) stuck on vegetation in ditch. The depth of the ditch was around 70 cm, similar Cloudy, drizzing rain to ditch 3 and 5. Seems to be the accumulating area of the ditch, based on visual features. Higher waterflow
D7 (Autumn)		14:32		5,94	14,8	43,0	55,8	7,7	992,1	279,0	12,3	Driz zle rain	Looked like iron precipitations in the water. Smaller ditch, calm conditions. Lots of vegetation "vass". A LOT of organic content in the water.
D1 (Winter)	2020-01-24	•		4,77	314,80	22,80	43,40	6,34	1004,50	217,00			
D3:2 (Winter)	2020-01-24	•		6,55	231,30	31,60	118,20	5,91	1008,90	591,00			
D4 (Winter)	2020-01-24	•		6,99	-26,20	6,10	65,20	5,81	1006,70	326,00			
D5:2 (Winter)	2020-01-24	•		4,83	348,00	27,40	63,00	6,11	1006,00	315,00			
D6:2 (Winter)	2020-01-24	•		4,95	327,50	32,00	58,50	6,12	1005,80	292,00			
D7 (Winter)	2020-01-24	•		5,96	196,10	31,70	47,50	6,22	1005,40	238,00			
Well area 1 (Winter)	2020-01-24	•		6,03	123,40	8,30	30,00	5,88	1004,90	150,00			
D1 (Spring)	2020-03-03	•	5°C	4,93	290,90	9,80	33,60	4,79	993,30	168		Cloudy, no rain	
D3:2 (Spring)	2020-03-03	•	5°C	6,20	264,00	24,60	89,40	4,74	992,00	447,00		Cloudy, no rain	
D4 (Spring)	2020-03-03	•	5°C	6,13	78,00	3,30	36,10	4,81	992,30	180,0		Cloudy, no rain	
D5:2 (Spring)	2020-03-03	•	5°C	5,17	298,60	16,40	48,10	4,82	992,10	241,00		Cloudy, no rain	
D6:2 (Spring)	2020-03-03	•	5°C	5,15	275,90	22,50	46,10	5,09	992,40	231,00		Cloudy, no rain	
D7 (Spring)	2020-03-03	•	5°C	6,02	173,80	24,30	37,50	5,36	992,60	376		Cloudy, no rain	
Well area 1 (Spring)	2020-03-03		5°C	6,1	119,2	8,3	26,3	5,08	991,1	132		Cloudy, no rain	

**Appendix 6:** Collection of fieldnotes from sites D1-D7 (autumn, winter and spring). Table also includes fieldnotes of observations done in situ and physiochemical parameters.

Site:	AI [mg/I]	V [ug/l]	Cr [ug/l]	Mn [ug/l]	Fe [mg/l]	Co [ug/l]	Ni [ug/l]	Cu [ug/l]	Zn [ug/l]	As [ug/l]	Cd [ug/l]	Pb [ug/l]
D1 (Autumn)	7,33	1,4	1,9	828,3	1,9	30,5	33,9	5,5	104,4	1,6	1,1	0,5
D2 (Autumn)	3,21	1,1	1,3	601,9	0,2	21,5	25,9	4,3	66,3	1,2	0,8	0,1
D3:1 (Autumn)	4,36	0,9	1,1	1656,4	0,1	61,3	85,9	4,0	119,3	1,7	2,6	0,1
D3:2 (Autumn)	0,48	1,2	0,8	1742,3	0,1	37,9	53,2	3,7	73,4	1,1	1,5	0,0
D4 (Autumn)	0,07	0,7	0,7	17,0	0,1	0,7	3,1	3,9	2,7	0,5	0,0	0,0
D5:1 (Autumn)	5,70	1,0	1,4	1144,9	0,3	34,0	39,4	5,1	86,4	1,5	1,1	0,4
D5:2 (Autumn)	7,47	1,0	1,6	1435,7	0,4	40,1	46,1	5,1	98,8	1,7	1,3	0,5
D6:1 (Autumn)	4,27	1,1	1,0	1248,7	0,3	29,2	25,6	3,5	73,4	1,1	0,7	0,2
D6:2 (Autumn)	6,40	1,1	1,2	1500,9	0,4	36,0	31,4	3,9	86,4	1,4	0,8	0,3
D7 (Autumn)	0,47	1,3	0,5	982,5	0,1	18,7	16,6	3,0	48,6	0,6	0,4	0,0
D1 (Winter)	2,710	0,312	1,040	390,000	0,316	9,410	17,400	3,320	60,700	0,297	0,502	0,067
D3:2 (Winter)	0,015	0,238	0,321	1070,000	0,005	14,300	33,300	1,660	47,500	0,499	0,895	<0.01
D4 (Winter)	0,013	0,129	0,163	0,656	0,119	0,094	1,420	1,360	1,720	0,623	0,007	<0.01
D5:2 (Winter)	3,570	0,088	0,889	1040,000	0,104	21,400	34,300	3,610	84,800	0,221	0,777	0,172
D6:2 (Winter)	3,090	0,109	0,717	1110,000	0,104	18,500	24,500	2,830	73,300	0,247	0,555	0,214
D7 (Winter)	0,178	0,270	0,495	689,000	0,198	8 <i>,</i> 050	11,500	2,200	37,100	0,240	0,261	0,029
Well area 1 (Winter)	0,309	1,480	1,150	69,800	1,070	0,867	1,510	3,500	8,870	0,456	0,051	0,056
D1 (Spring)	1,160	0,538	0,951	245,000	0,328	5,900	10,800	3,000	43,700	0,303	0,300	0,036
D3:2 (Spring)	0,060	0,159	0,556	803,000	0,004	11,700	24,600	2,250	39,900	0,430	0,634	<0.01
D4 (Spring)	0,190	0,126	0,866	70,600	0,187	1,610	3,610	4,000	6,830	0,333	0,054	0,034
D5:2 (Spring)	1,340	0,170	0,840	676,000	0,079	13,000	23,700	3,480	60,100	0,261	0,564	0,107
D6:2 (Spring)	1,790	0,150	0,714	816,000	0,110	13,300	18,000	2,620	54,900	0,222	0,425	0,078
D7 (Spring)	0,477	0,760	0,653	472,000	0,843	5,960	8,810	3,140	30,700	0,231	0,196	0,059
Well area 1 (Spring)	0,359	2,250	0,958	77,500	1,110	0,916	1,730	3,060	8,110	0,605	0,043	0,067

**Appendix 7:** Raw data of metal concentrations for sites D1 - D7 (autumn, winter and spring) retrieved from ALS. Table also includes raw data from the collector in area 1 (named "well area 1)"

D7	D6 (Average)	D5 (Aver	D4	D3 (Average)	D2	D1	Site:
σ		age) 4,	6,		<b>4</b>	3,	
5,940	625	620	6,640	240	900	820	рн
14,800 43,000	4,625 402,900 34,400	D5 (Average) 4,620 405,900 34,650	53,000 10,200	5,240 295,000 25,300	4,900 373,600 39,700	3,820 503,200 26,700	Redox
43,000	34,400	34,650	10,200	25,300	39,700	26,700	Do
55,800	65,750	71,550	50,900	126,400	56,100	68,400	EC [mS/m]
3,6	NaN	2,65	1,66	7,28	NaN	10,08	DOC (corrected)
0,4658	5,33677	6,5805	0,0748	2,4193	3,2127	7,3302	Al [mg/l]
1,2609	1,0592	1,0216	0,0748 0,7399	1,0541	3,2127 1,1388 1,2591	1,4139	V [ug/l]
0,5242	1,0946	1,5022	0,6560	0,9249	1,2591	1,9241	Cr [ug/l]
982,4701	1,0592 1,0946 1374,7897	6,5805 1,0216 1,5022 1290,3211 0,3200	16,9507	1699,3343	601,9075	7,3302 1,4139 1,9241 828,3352	DOC (corrected) AI [mg/I] V [ug/I] Cr [ug/I] Mn [ug/I] Fe [mg/I] Co [ug/I] Ni [ug/I]
0,0641	0,3503	0,3200	0,0848	0,0872	0,1944	1,8657	Fe [mg/l]
18,6794 16,6043	32,5732 28,5008	37,0692 42,7271	0,6556	49,5755	21,4876 25,9271	30,4897 33,9064	Co [ug/l]
16,6043	28,5008	42,7271	3,1289	69,5949	25,9271	33,9064	Ni [ug/l]
2,9864	3,6825	5,0793	3,8538	3,8910	4,3166	5,4925	Cu [ug/l]
48,6307	79,8738	92,6116	2,7189	96,3155	66,2995	5,4925 104,4294 1,6152 1,0870	Cu [ug/l] Zn [ug/l] As [ug/l] Cd [ug/l] Pb [ug/l]
0,5674	1,2739	1,5720	0,5141	1,3867	1,1880	1,6152	As [ug/I]
0,3931	0,7388	1,5720 1,2083	0,0339	2,04225	0,8004	1,0870	Cd [ug/l]
0,0282	0,2385	0,4374	0,0400	0,0803	0,1212	0,4671	Pb [ug/I]

**Appendix 8:** Table of the average values used in figure 6.

Well number	Sampling year	Usage	Total depth [m]	Soil/Bedrock
1(1)	2008-04-29	-	-	Soil
1 (2)	2008-04-29	-	-	Soil
2	2016-04-06	Holiday house	-	Soil
3	2007-06-26	Permanent	-	Soil
4	2014-06-10	Other	82	Bedrock
5	2015-11-24	Permanent	64	Bedrock
6	2008-02-05	-	127	Bedrock
7	2007-08-28	-	-	Soil
8	2007-11-20	-	55	Bedrock
9	2016-05-16	Holiday house	-	Soil
10	2012-11-14	Permanent	82	Soil
11	2007-07-17	-	-	Soil
12	2007-12-18	-	-	Soil
13	2014-03-25	Permanent	-	Soil
14	2008-01-29	-	21	Bedrock
15	2007-11-06	-	-	Soil
16	2007-12-11	-	-	Soil
17 (1)	2015-01-12	Permanent	-	Bedrock
17 (2)	2015-09-15	Permanent	43	Bedrock
17 (3)	2016-08-31	Permanent	-	Bedrock
18	2008-04-15	-	-	Soil
19	2008-05-06	-	-	Soil
20	2008-05-20	-	-	-

Appendix 9: Table of private well information, retrieved from SGU.

#### Entire sampling period 1 (autumn)

Element	STD	Data retrieved from:
V [%]	±1.86 (0.37-3.91)	Chalmers University of Technology
Cr [%]	± 2.57 (0.30-9.68)	Chalmers University of Technology
Mn [%]	$\pm 1.54 (0.25 - 3.74)$	Chalmers University of Technology
Fe [%]	± 2.35 (0.76-6.33)	Chalmers University of Technology
Co [%]	± 1.57 (0.23-6.49)	Chalmers University of Technology
Ni [%]	± 1.37 (0.17-6.56)	Chalmers University of Technology
Cu [%]	± 1.36 (0.26-15.98)	Chalmers University of Technology
As [%]	± 8.05 (2.75-16.01)	Chalmers University of Technology
Cd [%]	$\pm 2.35(0.28-28.30)$	Chalmers University of Technology
Pb [%]	± 3.97 (0.48-18.05)	Chalmers University of Technology
Al [%]	-	Chalmers University of Technology
Zn [%]	±1.41 (0.29-10.11)	Chalmers University of Technology

Appendix 10(A): Standard deviation of results retrieved from Chalmers University of Technology

#### Site D3 (Winter)

Element	STD	Data retrieved from:
V [µg/l]	$\pm 0.044$	ALS (Luleå)
Cr [µg/l]	$\pm 0.090$	ALS (Luleå)
Mn [µg/l]	$\pm 66$	ALS (Luleå)
Fe [mg/l]	$\pm 0.00124$	ALS (Luleå)
Co [µg/l]	$\pm 2.5$	ALS (Luleå)
Ni [µg/l]	$\pm 6.1$	ALS (Luleå)
Cu [µg/l]	$\pm 0.29$	ALS (Luleå)
As [µg/l]	$\pm 0.127$	ALS (Luleå)
Cd [µg/l]	$\pm 0.137$	ALS (Luleå)
Pb [µg/l]	-	ALS (Luleå)
Al [μg/l]	$\pm 3.0$	ALS (Luleå)
Zn [µg/l]	$\pm 3.6$	ALS (Luleå)

Appendix 10(B): Standard deviation of results retrieved from ALS

		Site D4 (Winter)	
Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.026$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.032$	ALS (Luleå)	
Mn [µg/l]	$\pm 0.238$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.008$	ALS (Luleå)	
Co [µg/l]	$\pm 0.0227$	ALS (Luleå)	
Ni [µg/l]	$\pm 0.29$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.33$	ALS (Luleå)	
As [µg/l]	$\pm 0.113$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.00155$	ALS (Luleå)	
Pb [µg/l]	-	ALS (Luleå)	
Al [µg/l]	$\pm 2.5$	ALS (Luleå)	
Zn [µg/l]	$\pm 0.54$	ALS (Luleå)	

Appendix 10(C): Standard deviation of results retrieved from ALS

#### Site D5 (Winter)

Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.0190$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.168$	ALS (Luleå)	
Mn [µg/l]	$\pm 74$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.007$	ALS (Luleå)	
Co [µg/l]	$\pm 2.0$	ALS (Luleå)	
Ni [µg/l]	$\pm 6.6$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.70$	ALS (Luleå)	
As [μg/l]	$\pm 0.046$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.118$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.033$	ALS (Luleå)	
Al [µg/l]	$\pm 422$	ALS (Luleå)	
Zn [µg/l]	$\pm 5.9$	ALS (Luleå)	

Appendix 10(D): Standard deviation of results retrieved from ALS

#### Site D6 (Winter) Element STD Data retrieved from: V [µg/l] $\pm 0.022$ ALS (Luleå) Cr [µg/l] $\pm 0.137$ ALS (Luleå) Mn [µg/l] $\pm 75$ ALS (Luleå) Fe [mg/l] $\pm 0.007$ ALS (Luleå) Co [µg/l] $\pm 3.2$ ALS (Luleå) Ni [µg/l] $\pm 4.6$ ALS (Luleå) $\pm 0.61$ ALS (Luleå) Cu [µg/l] $\pm 0.069$ As [µg/l] ALS (Luleå) $\pm 0.084$ Cd [µg/l] ALS (Luleå) $\pm \ 0.040$ Pb [µg/l] ALS (Luleå) Al [µg/l] $\pm 364$ ALS (Luleå) $\pm 5.4$ ALS (Luleå) Zn [µg/l]

Appendix 10(E): Standard deviation of results retrieved from ALS

		Site D7 (Winter)	
Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.052$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.107$	ALS (Luleå)	
Mn [µg/l]	$\pm 44$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.014$	ALS (Luleå)	
Co [µg/l]	$\pm 1.41$	ALS (Luleå)	
Ni [µg/l]	$\pm 2.1$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.44$	ALS (Luleå)	
As [µg/l]	$\pm 0.061$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.040$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.0063$	ALS (Luleå)	
Al [µg/l]	$\pm 24$	ALS (Luleå)	
Zn [µg/l]	$\pm 2.9$	ALS (Luleå)	

Appendix 10(F): Standard deviation of results retrieved from ALS

Site D1 (Winter)			
Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.062$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.21$	ALS (Luleå)	
Mn [µg/l]	$\pm 25$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.022$	ALS (Luleå)	
Co [µg/l]	$\pm 1.65$	ALS (Luleå)	
Ni [µg/l]	$\pm 3.2$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.61$	ALS (Luleå)	
As [µg/l]	$\pm 0.118$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.077$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.0154$	ALS (Luleå)	
Al [µg/l]	$\pm 318$	ALS (Luleå)	
Zn [µg/l]	$\pm 4.4$	ALS (Luleå)	

Appendix 10(G): Standard deviation of results retrieved from ALS

Collector area 1 (Winter)			
Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.28$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.22$	ALS (Luleå)	
Mn [µg/l]	$\pm 4.4$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.07$	ALS (Luleå)	
Co [µg/l]	$\pm 0.152$	ALS (Luleå)	
Ni [µg/l]	$\pm 0.29$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.61$	ALS (Luleå)	
As [µg/l]	$\pm 0.125$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.0087$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.0169$	ALS (Luleå)	
Al [µg/l]	$\pm 57$	ALS (Luleå)	
Zn [µg/l]	$\pm 1.85$	ALS (Luleå)	

Appendix 10(H): Standard deviation of results retrieved from ALS

Site D3 (Spring)			
Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.046$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.107$	ALS (Luleå)	
Mn [µg/l]	$\pm 53$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.00087$	ALS (Luleå)	
Co [µg/l]	$\pm 2.1$	ALS (Luleå)	
Ni [µg/l]	$\pm 4.8$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.44$	ALS (Luleå)	
As [µg/l]	$\pm 0.080$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.096$	ALS (Luleå)	
Pb [µg/l]	-	ALS (Luleå)	
Al [µg/l]	$\pm 11.1$	ALS (Luleå)	
Zn [µg/l]	$\pm 3.7$	ALS (Luleå)	

Appendix 10(I): Standard deviation of results retrieved from ALS

#### Site D4 (Spring)

Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.033$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.169$	ALS (Luleå)	
Mn [µg/l]	$\pm 4.4$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.013$	ALS (Luleå)	
Co [µg/l]	$\pm 0.29$	ALS (Luleå)	
Ni [µg/l]	$\pm 0.81$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.75$	ALS (Luleå)	
As [µg/l]	$\pm 0.092$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.0086$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.0070$	ALS (Luleå)	
Al [µg/l]	$\pm 25$	ALS (Luleå)	
Zn [µg/l]	$\pm 1.47$	ALS (Luleå)	

Appendix 10(J): Standard deviation of results retrieved from ALS

#### Site D5 (Spring) Element STD Data retrieved from: $\pm 0.051$ V [µg/l] ALS (Luleå) Cr [µg/l] $\pm 0.161$ ALS (Luleå) Mn [µg/l] $\pm\,42$ ALS (Luleå) $\pm 0.0054$ ALS (Luleå) Fe [mg/l] Co [µg/l] ALS (Luleå) $\pm 2.3$ Ni [µg/l] $\pm 4.3$ ALS (Luleå) Cu [µg/l] $\pm 0.61$ ALS (Luleå) As [µg/l] $\pm 0.055$ ALS (Luleå) Cd [µg/l] $\pm 0.085$ ALS (Luleå) Pb [µg/l] $\pm 0.021$ ALS (Luleå) Al [µg/l] $\pm 159$ ALS (Luleå) Zn [µg/l] $\pm 4.3$ ALS (Luleå)

Appendix 10(K): Standard deviation of results retrieved from ALS

# Site D6 (Spring)

Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.032$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.137$	ALS (Luleå)	
Mn [µg/l]	$\pm 55$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.008$	ALS (Luleå)	
Co [µg/l]	$\pm 2.3$	ALS (Luleå)	
Ni [µg/l]	$\pm 3.3$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.50$	ALS (Luleå)	
As [µg/l]	$\pm 0.047$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.064$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.0147$	ALS (Luleå)	
Al [µg/l]	$\pm 214$	ALS (Luleå)	
Zn [µg/l]	$\pm 4.1$	ALS (Luleå)	

Appendix 10(L): Standard deviation of results retrieved from ALS

## Site D7 (Spring)

Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.155$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.121$	ALS (Luleå)	
Mn [µg/l]	$\pm 29$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.058$	ALS (Luleå)	
Co [µg/l]	$\pm 1.05$	ALS (Luleå)	
Ni [µg/l]	$\pm 1.67$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.63$	ALS (Luleå)	
As [μg/l]	$\pm 0.054$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.030$	ALS (Luleå)	
Pb [µg/l]	$\pm 0.0116$	ALS (Luleå)	
Al [µg/l]	$\pm 72$	ALS (Luleå)	
Zn [µg/l]	$\pm 2.6$	ALS (Luleå)	

Appendix 10(M): Standard deviation of results retrieved from ALS

#### Site D1 (Spring) Element STD Data retrieved from: $\pm 0.113$ ALS (Luleå) V [µg/l] $\pm \ 0.177$ Cr [µg/l] ALS (Luleå) Mn [µg/l] $\pm\,17$ ALS (Luleå) Fe [mg/l] $\pm \ 0.023$ ALS (Luleå) Co [µg/l] $\pm \ 1.04$ ALS (Luleå) Ni [µg/l] $\pm 2.0$ ALS (Luleå) Cu [µg/l] $\pm 0.56$ ALS (Luleå) $\pm \ 0.086$ ALS (Luleå) As [µg/l] Cd [µg/l] $\pm \ 0.045$ ALS (Luleå) $\pm \ 0.0074$ ALS (Luleå) Pb [µg/l] Al [µg/l] $\pm 137$ ALS (Luleå) Zn [µg/l] $\pm 3.3$ ALS (Luleå)

Appendix 10(N): Standard deviation of results retrieved from ALS

#### Collector area 1 (Spring)

Element	STD	Data retrieved from:	
V [µg/l]	$\pm 0.41$	ALS (Luleå)	
Cr [µg/l]	$\pm 0.180$	ALS (Luleå)	
Mn [µg/l]	$\pm 4.9$	ALS (Luleå)	
Fe [mg/l]	$\pm 0.08$	ALS (Luleå)	
Co [µg/l]	$\pm 0.163$	ALS (Luleå)	
Ni [µg/l]	$\pm 0.37$	ALS (Luleå)	
Cu [µg/l]	$\pm 0.56$	ALS (Luleå)	
As [µg/l]	$\pm 0.165$	ALS (Luleå)	
Cd [µg/l]	$\pm 0.0072$	ALS (Luleå)	
Pb [µg/1]	$\pm 0.0129$	ALS (Luleå)	
Al [µg/l]	$\pm 60$	ALS (Luleå)	
Zn [µg/l]	$\pm 1.63$	ALS (Luleå)	

Appendix 10(O): Standard deviation of results retrieved from ALS