Uppsala Universitet

Master's Programme in Environmental and Water Engineering

Modelling of aquatic ecosystems, 15 hp

The Fate of a Browning Swedish Lake

- Undermined by its mining history -

Author:
Hanna Pierrau

Supervisor
Thomas Grabs

March 19, 2022

Sammanfattning

Övre Skärsjön är en sjö belägen i Skinnskattebergs kommun i Västmanland. Detta projekt syftar till att undersöka sjöns status med avseende på brunifiering, försurning och effekter kopplade till en nerlagd gruva i närheten av sjön. Dessa undersökningar gjordes för att avgöra om sjön löper någon risk att klassas med en lägre status, något som skulle bryta mot rådande miljökvalitetsnormer. Ett flertal olika statistiska tester genomfördes för att avgöra sjöns status, bland annat Kendall-korrelationer, linjära regressioner och Mann-Kendalls test för tidstrender.

Resultaten visade att Övre Skärsjön hade den starkaste brunifieringstrenden av fyra jämförda svenska sjöar, och att sjöns vattenfärg kunde anses som bland de brunaste. När vidare undersökningar om brunifieringen gjordes framkom det att trenden hade slutat, och att ingen signifikant förbruning av sjön hade skett sedan 2010. Detta kopplades till en liknande trend för försurningsrelaterade variabler, då varken pH eller sulfatkoncentrationen i sjön heller hade ändrats sedan 2010. Kopplingen kunde göras eftersom dessa försurningsvariabler visades vara de enda statistisk signifikanta drivvariablerna för brunifieringen i Övre Skärsjön.

Från undersökningar av koppar- och arsenikkoncentrationerna i sjön framgick det att Övre Skärsjön fortfarande påverkas av den nu nedlagda gruvdriften, eftersom koncentrationerna av metallerna i sjöns ytvatten fortfarande sjunker och alltså inte hunnit återställas än. Denna minskning av toxiska metaller antas, tillsammans med ett ökat pH, ligga bakom att antalet individer av en sorts bottenlevande organism också ökar i de grunda delarna av sjön. I sjöns djupare delar ses dock en motsatt trend, där samma art hade ett minskande individantal i stället. Anledningen till detta tros vara att brunifieringen av sjön skapar en miljö med mindre syre och sämre tillgång till föda i de djupare delarna av sjön, tillsammans med potentiellt höga koncentrationer av koppar i sedimentet. Det sistnämnda kan dock inte påstås med säkerhet, då det inte fanns några mätvärden för koppar i de djupare delarna av sjön. Med detta i åtanke uppmanas framtida mätinsatser att även ta prover i Övre Skärsjöns djupa delar.

Bortsett från denna minskning av bottenfauna indikerade inga andra variabler att Över Skärsjöns status är på väg att försämras för tillfället, och således att rådande miljökvalitetsnormer inte kommer brytas.

Abstract

The aim of this project was to investigate the status of the Swedish lake Övre Skärsjön in regard to brownification, acidification and effects of a nearby closed down mine. Several statistical tests were performed, including Kendall correlations, linear regressions, and Mann-Kendall trend tests. The results showed that compared to three other Swedish lakes Övre Skärsjön had the strongest brownification trend and among the brownest water. Further investigations of the brownification revealed that the trend stopped in 2010. This was connected to a similar trend in acidification, as neither pH nor sulphate concentrations changed significantly since 2010 either. This connection was made as recovery from acidification emerged as the only statistically significant driver of brownification in the lake. Investigations of copper and arsenic concentrations showed that Övre Skärsjön still is affected by the mine, as the concentrations even now are decreasing in the surface layer of the lake. This decrease of toxic metals could be the partial explanation of the increasing numbers of an invertebrate found in the shallow parts of the lake. However, in the deep parts of the lake the same species was decreasing. The underlying reason is possibly the brownification causing a more hostile environment, together with high copper concentrations in the sediment. This could not be claimed for certain however, as copper was not sampled at the bottom of the lake; something future monitoring efforts are encouraged to do. Apart for this decrease of benthic fauna, no other variable indicated the status of Övre Skärsjön getting worse.

Acknowledgements

I want to thank Karin Lindström, from Riddarhyttans Hembygds- och Intresseförening, and Lars O. Ericsson, professor emeritus of geotechnics at Chalmers University of Technology and part of Geocentrums vänner i Riddarhyttan, for their help in finding information about the mines surrounding the studied lake, along with showing interest in the project.

Contents

1 Introduction

1.1 Purpose

In the year 2000 the European Union created The EU Water Framework Directive, a common set of rules made to ensure good surface- and ground water quality in all of Europe. The overarching goal was for all waters to achieve a good status by 2015, or at latest by 2027 (Vattenmyndigheterna 2010). This has been implemented in Sweden trough a number of environmental quality standards relating to different biological, chemical, and physical properties of water. An important main rule is that the status of a lake is not allowed to get worse (ibid.).

This project aims to investigate the status of a Swedish lake named Övre Skärsjön to see if there is a risk of a declining status. The focus of the study is acidification, the effects of an old closed mine, and in particular brownification. This is done through a combination of comparisons between Övre Skärsjön and three other Swedish lakes, in addition to individual investigations.

The questions considered in this project are:

- Is brownification a problem found in Swedish lakes regardless of their geographical location?
- Does the trend of brownification vary in time?
- Is Övre Skärsjön recovering from acidification?
- What is the main driving force of brownification in the studied lake?
- Does the mine still affect the water quality of Övre Skärsjön?

Examinations of these questions can serve as a base for further investigations into the lake's water quality, as well as a pointer toward what areas future monitoring efforts might want to focus on.

1.2 Background

Compared to other processes affecting lake water quality, like eutrophication and acidification, the concept of brownification is comparatively new and still surrounded by considerable interest and many uncertainties (Kritzberg et al. 2020). Due to this the browning of waters is the main focus of this study, followed by the effects of acidification and mining activities, as they are important processes for the lake in question.

1.2.1 Brownification

Brownification is a term that refers to the process of waters significantly increasing in colour, something that can happen due to increasing concentrations of iron, but is mainly attributed to rising amounts of dissolved organic carbon (DOC) in waters (ibid.). This trend has been observed in a vast amount of Nordic lakes and is the source of a number of different concerns, ranging from drinking water production to increasing stability of thermal stratification (De Wit et al. 2016).

There are several different factors that play part in if a lake is brown or not to begin with. Most of the organic matter (OM) found in northern lakes originates from the land surrounding it (Creed et al. 2018). Thus, the land cover of the catchment plays a major role in the colour of the lake; brown lakes are more frequently found in areas dominated by forests rather than areas where agriculture plays the bigger role (Kritzberg et al. 2020). This is because forests, especially coniferous ones, are where the thickest organic soil layers generally are found, their thickness allowing them to store and export more DOC (Bārdule et al. 2021). Due to their high amount of organic carbon, wetlands are a large contributing factor to the amount of DOC in lake waters similarly to the forests, possibly even more as they are considered to be the land type that exports most organic carbon per unit area (Freeman et al. 2001).

Other parameters have also been found to play a role when it comes to the brownness of surface waters. Although DOM mainly contains carbon, it is also made up out of nutrients like iron. Iron plays a role in water colour as it, among other things, contribute to changes in chromophoric properties of DOM, which creates an even browner colour (Creed et al. 2018). The geographical position of the lake also seem to matter: smaller amounts of DOC are exported from soils in the far north, due to permafrost in the soil combined with a shorter growing season (ibid.).

However, surface waters are not just remaining brown; they have been getting browner. Evidence from the UK Acid Waters Monitoring Network show statistically significant positive trends in DOC ever since the monitoring began in 1988 (Evans et al. 2006), and several different drivers have been suggested to contribute to this trend: climate change, changes in land cover and acid deposition are some of them (Kritzberg et al. 2020).

A study from Norway by Hongve et al. (2004) found statistically significant correlations between precipitation and watercolour. The study shows that changing water pathways, due to increasing frequencies of intensive rain as well as more rain overall, led to more leaching of coloured OM from upper soil layers of forests. Although this increased rain was due to climate change, they could find no apparent effect of increasing temperatures, another important part of the changing climate (ibid.). However, there are other articles claiming that rising temperatures do play a role in trends of rising DOC. There are two main arguments for this: firstly, higher temperatures lead to longer growing seasons and thus a higher terrestrial net primary production, that in turn leads to a larger accumulation of OM that can be exported to lakes (Creed et al. 2018). Secondly: increasing temperatures causes warming and drying of peat-soils, increasing OM decomposition rates and thus the amount of DOC that ends up in water. This is a process that is likely to keep increasing as global temperatures continue to rise according to Freeman et al. (2001).

Other studies have found concentrations of DOC to be strongly inversely correlated to changes of concentrations in both sulphate and chloride, where anthropogenic SO_4^{2-}-deposition accounted for more than 85% of the total effect on DOC in most studied cases (Monteith, Stoddard, et al. 2007). The suggested mechanisms behind this are the deposition affecting soil organic matter in two ways. One mechanism is decrease of the ionic strength of the soil solution, which have been shown to increase the flux of DOC. The other way is through increasing the pH. As OM consists largely of organic acid this also increases OM solubility, something that in turn offsets the decrease of acidity as more organic acids are found in the water (ibid.).

Although some studies conclude that trends of browning will continue (De Wit et al. 2016), others have shown the opposite. A recent study by Eklöf et al. (2021) observed that concentrations of TOC and CDOM were neither linear nor monotonic over the last three decades. Contrary to the conclusion of De Wit et al. (2016) the study found that an increasing trend of TOC was detected in fewer than 20% of the studied lakes after 2010. For CDOM the pattern was similar, but the trend ended a decade earlier around 2000, indicating a shift in OM quality over time (Eklöf et al. 2021). Even though a trend of brownification was common in most lakes before 2010, the situation has been more stable during the last decade. This study thus also calls into question that climate change is what is driving brownification, as there in that case would not exist a reason for the trend to cease (ibid.).

The potential consequences of browning waters are many. Brown waters are recreationally seen as less attractive: studies have found that only 1% of people prefer to swim in brown lakes over clear ones (Kritzberg et al. 2020). However, brownification affects far more than the aesthetics of the water as it also alters the conditions of the lake's ecosystem. Increasing colour means that the surface water absorbs more light, leading to a shallower thermocline as well as restricting the photic zone to shallow waters. This, in turn, leads to a suppression of autotrophs in the benthic parts of the lake, resulting in deep water anoxia and reducing the habitat of fauna living on the lake floor. The browner water also means less light penetrating deep into the lake, which does protect organisms form harmful UV-rays, but also makes it harder for predators to see prey (Creed et al. 2018). The effects of browning waters spread even further than previously mentioned effects: diversity and productivity of phytoplankton can decrease (Kritzberg et al. 2020) and risks of exposure to cyanobacteria toxins rise, among other things. However, many uncertainties and unknowns still remain (Creed et al. 2018).

1.2.2 Acidifiaction

Freshwater acidification is normally caused by deposition from the atmosphere, a problem affecting large geographical areas which emerged in the late 1960s as the result of emissions from industrial processes (Driscoll et al. 2001). The deposition reached its peak in early 1980s and thereafter decreased sharply as a result of international legislation (Kritzberg et al. 2020). Acidic deposition can consists of several different substances derived from emissions of e.g. nitrogen and sulphur compounds (Driscoll et al. 2001), but the anthropogenic acidification of freshwater is mainly attributed to deposition of sulphuric acid (Hongve et al. 2004).

The pH of most freshwater lakes usually ranges between 6 to 8 (Hasler et al. 2018), and a pH below 5.5 can result in conditions toxic to many life forms, leading to loss of biota (Gray et al. 2016). Although the reductions of sulphur deposition have led to chemical recovery of acid lakes, there is still much room for additional reductions of sulphates (Monteith, Evans, et al. 2014). However, despite clear signs of chemical recovery, biological signs are much less obvious, although they have been seen (Gray et al. 2016).

1.2.3 Mines

No matter the type of mine, some form of water pollution always arises due to the large-scale ground disturbance associated with mining (Johnston et al. 2008). One way mine activities can have adverse effects on the local environment is through acid mine drainage, which happens when sulphides, found in mines, react with oxygen and water which creates an acidic environment that can dissolve minerals and subsequently transport them out of the mine and into nearby environments (Larsson et al. 2018). One such mineral of significance is copper, as it is mined from ores containing sulphides as well as being a metal that can affect ecosystems greatly and cause problems that remain long after the mine has closed (Larsson et al. 2018).

Copper is not only found in the water itself, but also in lake sediments. A study by McDonald et al. (2010) found high concentrations of copper in the sediment of a mine affected lake, 40 years after the mine had closed. The highest amounts of copper remains were found at the deepest parts of the lake. This is thought to be due to finer sediment particles having a higher sorptive capacity for copper, while also being the particles that accumulate in deep water. The pore water in the sediments of the lake were found to have copper concentrations almost 20 times larger than the concentrations in the water column, and copper continuously releasing from the sediment is thought to maintain copper concentrations in the rest of the lake (ibid.).

Another element that is often found in higher concentrations around mining operations is arsenic. Even if the arsenic itself is not the goal of the mining, it is often released into the environment as it is a common impurity in metal ores, especially in sulphur-containing minerals where metals such as copper and gold often are found (SME 2015).

Benthic invertebrates, small animals living at the bottom of the lake floor, are a part of the lake ecosystem that can be impaired by mining activities. The toxic metals in acid mine drainage causes both chronic and acute problems that can reduce species diversity and abundance of the invertebrates (Anderson 2007). Due to benthic invertebrates having an ability to recolonise damaged ecosystems, coupled with their relative abundance, they are often used in studies monitoring the health of aquatic ecosystems. The study by Anderson (ibid.) found that the rate of recovery of benthic invertebrates in mining affected waters depended on the improvement of water quality, along with some other factors, such as the rate of relocation of the invertebrates.

1.2.4 Hypotheses

Based on the information presented in the background a number of hypotheses have been made relating to the questions considered in this project. These hypotheses are divided into "group hypotheses" and "individual hypotheses" depending on if they include all four lakes, or just Övre Skärsjön.

Group hypothesis

- Considering the number of studies having found trends of brownification, similar trends, in either TOC or absorbance, should be found in all lakes.

Individual hypotheses

- There is no trend of brownification in Övre Skärsjön after the year 2010 in accordance with the study by Eklöf et al. (2021).
- The lake is recovering from acidification due to a decrease of sulphate deposition.
- A decrease of sulphate deposition is the main driving variable of brownification in the lake, but other variables affect the brownification as well.
- As there currently are no active mines nearby Övre Skärsjön the concentration of mining-related contaminations, such as copper and arsenic, should be decreasing.

- Because of the ability of benthic invertebrates to recolonise impaired ecosystems an increasing abundance of organisms should be seen, assuming the aforementioned recoveries.

2 Data and methods

2.1 Description of study area

Övre Skärsjön (Figure 1) is a lake located in Skinskatteberg municipality in the county Västmanland (VISS 2021) about 5 km north of the town Riddarhyttan (Google Maps 2021). The lake is located 219 m over sea level and covers an area of 1.7 km^2, the maximum depth of the lake is 32 m, although the average depth is much shallower at 6.1 m (SLU 2009). The catchment of Övre Skärsjön has no other catchments above it and contains no other lakes than Övre Skärsjön, making it a head water lake (SMHI 2021c).

Dahlberg (2004) describes Övre Skärsjön as a nutrient poor, humic, woodland lake, affected by mining activities. The same report shows that pike and perch, species tolerant to acidic waters, are the only two types of fish found in the lake, despite there having been more than twice as many species before. The lake is not only acidic, but also have no alkalinity or buffering capacity (SLU 2009). Remains of benthic fauna known to be very sensitive to acidity have been found at the lake floor, showing that Övre Skärsjön has not always been acidic. However, Mossberg (2009) only found species resistant to acidity currently living in the lake. Although acidification is a longstanding problem of the surrounding area, Övre Skärsjön has never been limed, and thus works as a reference lake to other lakes in the area that have received the treatment (ibid.). The status of Övre Skärsjön is high in regard to Secchi depth and nutrients, and there are many types of aquatic vegetation (SLU 2009).

Figure 1. *A map of Övre Skärsjön and the surrounding area. Source: Lantmäteriet.*

Historically, much activity has surrounded Övre Skärsjön. There are records of mines in the vicinity of the lake as early as 1680, and some time before 1880 the mine Persgruvan was built right on the shore of Övre Skärsjön (Figure 2) (Geijer et al. 1923). The ore that was mined at Persgruvan contained copper and iron, as well as being rich in sulphur (ibid.). The last mine in the area was supposedly closed 1982 and Persgruvan a few years earlier in 1967 (Ekeving 2017), although no reliable sources can be found for this information.

Figure 2. *A picture of Persgruvan and Övre Skärsjön next to it. Photographer: Harald Carlborg/Tekniska Museet (1916).*

According to model data from SMHI (2021c) the catchment of Övre Skärsjön has an area of about 9 km^2 and consists of 77% forest, 3% wetland and $<$1% of agricultural land, heath land or other land. The remaining 19% of the catchment is made up out of Övre Skärsjön itself. The soil in the area is mainly till (47%) and peat (12%) soil, and about 22% of the area is covered in thin soil layers or exposed bedrock (ibid.).

As a part of this project Övre Skärsjön was compared with three other lakes: Spjutsjön, Täftesträsket and Jutsajaure. The four lakes are spread quite widely across Sweden with about 830 km between the two lakes that are furthest apart (Figure 3). Similarly to Övre Skärsjön both Spjutsjön and Jutsajaure are headwater lakes. Täftesträsket is not, but is also located quite high up in the catchment hierarchy with only two small catchments above it (ibid.).

Figure 3. *Geographical location of the four studied lakes.*

All four lakes are small ($<$2.5 km^2) woodland lakes with catchments that consist of around 70-90% forest. Spjutsjön is considerably smaller than the rest of the lakes, being less than half the size of the next smallest lake. The catchment of Jutsajaure has the largest areal percentage of both peat soil and wetland, while Spjutsjön's catchment has the least amount of both.

2.2 Data

Miljödata MVM **(SLU 2021a)**
This data supplied by The Swedish University of Agricultural Sciences (SLU) contains quality-controlled information about water chemistry, benthic fauna, phytoplankton and macrophytes from lakes part of ether national or regional environmental monitoring programs. All available data for Övre Skärsjön, spanning the years 1983-2021, was downloaded.

Modelldata per område **(SMHI 2021c)**
Through the product "modelldata per område" data for different sub-catchments of Sweden is supplied by The Swedish Meteorological and Hydrological Institute (SMHI), calculated using the hydrological model S-HYPE. The model calculates variables like runoff, water temperature and transport of nutrients. Other data concerning the catchment, like soil types and land cover, is also supplied. As the data is modelled some uncertainties follow, and although there are many decimals in the provided values, this does not reflect the actual accuracy of the calculations. Because of the large amount of data calculated by the model it is not possible to control its quality (SMHI 2020b). Data was downloaded

from the sub-catchment "Utloppet av Övre Skärsjön" which belongs to the main catchment Norrström (SMHI 2021c).

***Concentrations in precipitation* (SMHI 2021a)**
The data for concentrations in precipitation is collected either by municipalities or the Swedish Environmental Protection Agency due to demands in directives and conventions. The data is quality controlled and reported to SMHI on a yearly basis (SMHI 2020a). There is deposition data for a number of different compounds and elements, but only data for SO_4^{2-}-concentrations in rain was collected. Data was downloaded from three stations (Grimsö and Kindlahöjden in Örebro county, and Kvisterhult in Västmanland County) as there was no single station with a sufficiently long data series. Together the data spanned the years 1983-2020 and was measured on a monthly basis, but there was not data for every month (SMHI 2021a). The closest station (Grimsö) is located 11 km from Övre skärsjön, and the station that is furthest away (Kvisterhult) is about 50 km away (Google Maps 2021).

***Meteorological observations* (SMHI 2021b)**
This database offer data of several different variables at several different time resolutions. Only monthly values for precipitation and temperature were downloaded from a station called Kloten located around 16 km west of Övre Skärsjön. Although most of the data was quality controlled and approved, there were also some data classed as "suspicious, aggregated, roughly quality controlled or not controlled" (ibid.).

2.3 Methods

Due to lack of data in years earlier than 1987 analyses were limited to the years 1987-2021. To be able to compare the four lakes only samples taken from the surface layer (0.5-2.7 m) of the lakes were analysed. This demarcation was used for all other analyses as well, except for the one concerning benthic fauna.

2.3.1 Brownification

Trends in absorbance and TOC in the four different lakes was investigated with a Mann-Kendall trend test for time series using all available data between 1987-2021. To get a visualisation of the trends yearly mean values were plotted against time.

The brownification for Övre Skärsjön was then further investigated by examining whether the trend of brownification in the lake was consistent in time. This was done by dividing the data for TOC into two data sets of ten years around the year 2010 which was chosen as the "dividing year" due to the findings in the study by Eklöf et al. (2021). After the data was divided Mann-Kendall's method was used separately on the two data sets. For all individual analyses concerning brownification only TOC was studied as opposed to both TOC and absorbance. This was done as there was more data available for TOC and it would be too time consuming to preform and compare analyses of both absorbance and TOC. TOC has also been found to show the highest correlation with water colour of all water quality parameters (Klante et al. 2021). It can therefore be taken as a proxy for the brownness of water.

2.3.2 Acidification

To be able to investigate trends in acidification some conversions had to be made as the method for analysing SO_4^{2-}-concentrations in the water was changed in 2016. The older method produced concentrations in the unit *mg/l sulphur* (S), while data from the new method was reported in $mg/l\ SO_4^{2-}$. All values were converted into the unit $mg/l\ S$ (as this unit had the longest time series) using the molar mass of S in relation to the molar mass of SO_4^{2-}. As this conversion produced values consistent with the data from the older analysis method (Appendix 7.2), the conversion was deemed successful. Trends in time were then investigated using Mann-Kendall's method for pH and SO_4^{2-}-concentrations of the lake. This was first done for the whole time period, then by dividing it into two different time series in the same manner as for TOC. This was investigated as acidification was a suspected driver of changes in TOC-concentrations.

The next step of investigating acidification was looking into the relation between SO_4^{2-} deposition through precipitation ($SO_{4,\ rain}^{2-}$) and the concentration of SO_4^{2-} in the lake ($SO_{4,\ lake}^{2-}$). Since the $SO_{4,\ rain}^{2-}$ data had to be downloaded from three different stations to cover the years 1987-2020 (there was no data for 2021) it was first examined if the data from the three stations could be combined. This was done by plotting the data points in the same graph. The three time series were considered consistent enough to be combined (Appendix 7.3). Yearly mean values of $SO_{4,\ lake}^{2-}$ and $SO_{4,\ rain}^{2-}$ were calculated to get the same amount of data points for both variables. A linear regression was done between the two variables after transforming the SO_4^{2-}-concentration in rainwater using the natural logarithm, as this was required for a linear relation. The yearly mean of $SO_{4,\ rain}^{2-}$ was used as the driving variable in the regression and the yearly mean of $SO_{4,\ lake}^{2-}$ of the *following* year was used as the response variable. This shift in years was used because the majority of SO_4^{2-} that reaches the lake first has to pass through soil, which is expected to cause a delay. The residuals of the regression were analysed to determine if the regression could be used or not.

The final step of acidification investigations was to examine the relation between pH and $SO_{4,\ lake}^{2-}$. This was done through Kendall's correlation test as there was no linear relationship between the two variables.

2.3.3 Driving variables of brownification

The potential drivers of the brownification of Övre Skärsjön were tested using Kendall's correlation. This correlation test was used as it would be easier to compare the different potential drivers if the same test was used for all of them, together with the fact that not all variables showed a linear relationship to TOC. Yearly mean values were used to get the same amount of data points for each variable, which was deemed important as having more data can make weaker correlations significant.

2.3.4 Mining activities and benthic invertebrates

For all analyses related to investigations of the effect of the mine on the lake all available data was used, as long as there were corresponding values for all variables. In this case that meant data between 2000-2021. Mann-Kendall trend tests were performed for copper-concentrations (Cu) and arsenic-concentration (As) as well as a correlation between the two. A correlation test was also preformed between Cu and the pH of the water. The correlation tests were done as a significant relation between two variables could indicate a common source. All correlations were done using Kendall's correlation test as there were no obvious linear relations.

Lastly the status of benthic fauna was analysed. This was done for two species: diptera (a type of fly larvae) and oligochaeta (a type of aquatic worm). The reason for analysing these two was the fact they were the only species with sufficient amounts of data. All data points available were used and were divided into two sets for each species: one representing the profundal zone of the lake (>28 m deep) and one representing either the sub-littoral zone (6-9 m deep, used for diptera) or the littoral zone (<1 m deep, used for oligochaeta) depending on what data was available. Mann-Kendall's method was then used to find potential trends in time in each data set.

3 Results

3.1 Group Hypothesis

3.1.1 Brownification

When looking at a visual representation of the trends in TOC-concentration there seems to be a positive trend for both Övre Skärsjön and Täftesträstket between the years 1987-2021 (Figure 4). A similar pattern can be seen for absorbance (Appendix 7.1). The figures also make it clear that Övre Skärsjön has among the brownest water between the four lakes.

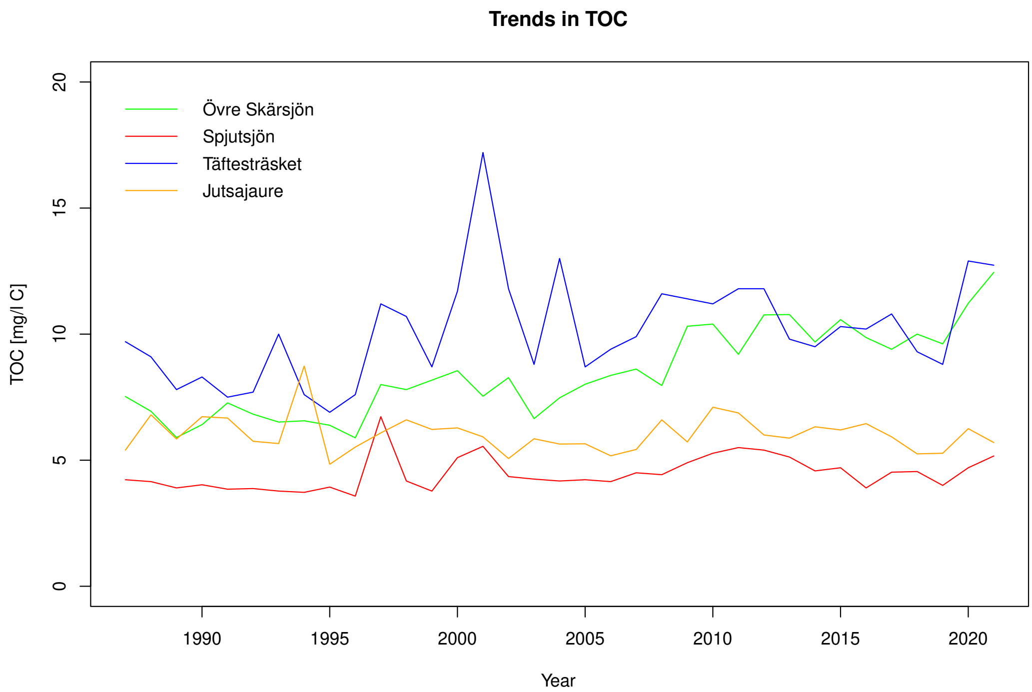

Figure 4. *The TOC trends of the studied lakes, based on yearly mean values.*

The Mann-Kendall trend test confirm the trends in Övre Skärsjön and Täftesträsket and reveals that Spjutsjön has a significant positive trend in TOC as well, although Övre

Skärsjön and Täftesträsket have much larger Theilslopes. When it comes to absorbance only Övre Skärsjön and Jutsajaure show significant positive trends, where the trend in Övre Skärsjön again is the largest (Table 3). Thus, all lakes show a significant trend in at least one variable connected to brownification, and Övre Skärsjön is the only lake to show a significant trend in both.

Table 3. Trends in abs and TOC, 1987-2021. The unit of the Theilslope is [mg/l C per year] for TOC and [/5 cm per year] for absorbance.

Variable	Lake	n	p-value	Theilslope
AbsF420 [/5cm]	Övre Skärsjön	267	0.00001	0.0034
	Spjutsjön	138	0.1	0.00017
	Täftesträsket	118	0.2	0.00075
	Jutsajaure	156	0.03	0.0005
TOC [mg/l C]	Övre Skärsjön	267	0.000002	0.15
	Spjutsjön	138	0.003	0.028
	Täftesträsket	118	0.001	0.072
	Jutsajaure	156	0.7	0.0

3.2 Individual Hypotheses

3.2.1 Consistency of the brownification trend

Over the whole time span (1987-2021) there is, as mentioned earlier, a significant increase of TOC (Table 3). If the data series is divided into two equally long sets of data before and after the year 2010 the result is different. For the time period 2000-2010 there is a significant positive trend for TOC (n=85, p=0.02, Theilslope=0.24 mg/l C per year), but for the later time period, 2011-2021, a significant trend cannot be found (n=84, p=0.4, Theilslope=0.05 mg/l C per year).

3.2.2 Driving forces of brownification

Examining the relationships between TOC and potential driving variables (n=35 in all cases) no significant relationship is found between TOC and either temperature (p=0.174, tau=0.16) or precipitation (p=0.89, tau=0.017). On the other hand the relation between TOC and acidity-related variables is significant, for SO_4^{2-} the p-value is $1.9 \cdot 10^{-9}$ (tau = -0.66) and for pH it is p = $1.4 \cdot 10^{-6}$ (tau=0.54).

3.2.3 Recovery from acidification

Similarly to brownification there are significant trends for both pH (n=266, p=0.000001, Theilslope=0.019 per year) and SO_4^{2-} (n=278, p=$3 \cdot 10^{-8}$, Theilslope=-0.058 mg/l S per year) when looking at the full time series. The yearly mean pH increases from 5.2 in 1987 to 6.0 in 2020.

When the data is divided as before there is no significant trend for pH either before 2010 (n=88, p=0.1, Theilslope=0.014 per year) or after (n=84, p=0.1, Theilslope=0.017 per year). For SO_4^{2-}, on the other hand, there is a trend during the time period 2000-2010 (n=88, p=0.0004, Theilslope=0.05 mg/l S per year), but not during 2011-2021 (n=85, p=0.8, Theilslope=0 mg/l S per year).

A significant relation is found between the concentration of SO_4^{2-} in the lake-water and in the rainwater of the previous year (Figure 5). The linear regression between the two variables has a p-value of $9.8 \cdot 10^{-15}$ and the equation

$$SO_{4,\ lake}^{2-} = 1.2 \times ln(SO_{4,\ rain}^{2-}) + 2.7. \tag{1}$$

The regression is based on 35 observations and its R^2-value is 0.83. The residual plot of the linear regression shows no obvious pattern, and a Shapiro-Wilk test of the residuals show that they can be assumed normally distributed (p=0.57).

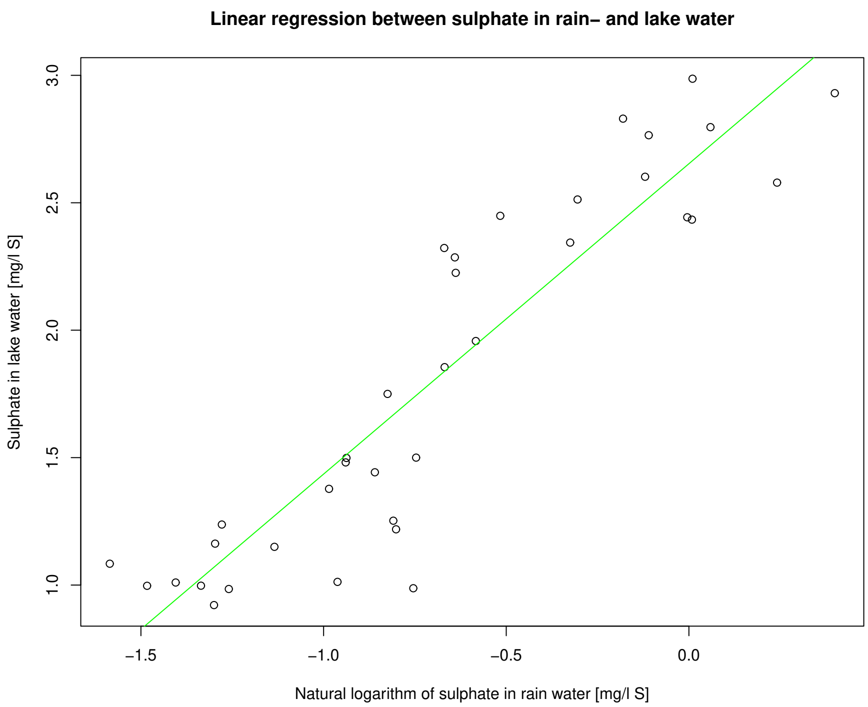

Figure 5. *Linear regression between the sulphate concentration in rain water ($SO_{4,\ rain}^{2-}$) and in the lake water the following year $SO_{4,\ lake}^{2-}$ of Övre Skärsjön between the years 1983 and 1996.*

The SO_4^{2-}-concentration of the lake water has in turn a significant relation to the pH of the lake water (p=$4.8 \cdot 10^{-10}$, tau=-0.67, n=35).

3.2.4 Mining activities

Both the amount of copper and arsenic in Övre Skärsjön is significantly decreasing. Cu with a p-value of 0.0002 an the Theilslope -0.155 μg/l per year, and arsenic with the p-value 0.047 and slope -0.0017 μg/l per year. The decrease of Cu and As is also correlated (n=39, p $=1.6 \cdot 10^{-5}$, tau=0.50), while no such relation can be found between Cu and pH (n=39, p=0.93, tau=0.0097).

3.2.5 Benthic invertebrates

When looking at the indicator organism Oligochaeta there is a significant increase of the organism in the shallow parts of the lake (n=35, p=0.0008, Theilslope=0.82 organisms/sample per year) while there is a significant decrease in the deep parts of the lake (n=40, p=0.0008, Theilslope=-4.5 organisms/m^2 per year). The species Diptera on the other hand shows no significant trends in the sub-littoral zone (n=38, p=0.4, Theilslope=5.6 organisms/m^2 per year) nor the profundal zone (n=40, p=0.3, Theilslope=-1.6 organisms/m^2 per year).

4 Discussion

4.1 Group Hypothesis

4.1.1 Brownification

Some type of significant brownification trend can be seen in each lake. What is interesting is that Övre Skärsjön is the only lake to have significant trends in both variables (Table 3). Similarly to what both Eklöf et al. (2021) and Worrall et al. (2010) found, this points to a change in quality of the carbon of the three other lakes, as TOC and absorbance indicate the presence of different types of carbon compounds (TOC represents mainly compounds of mainly low molecular weight, while absorbance indicate high molecular weight (Arvola et al. 2016)). This in turn point toward different processes being of importance for the four lakes: if the absorbance is changing significantly something is happening that affects the heavier molecules more and vice versa if there is only a significant trend for TOC. There only being a trend in absorbance, like for Jutsajaure, could also mean that maybe the concentration of iron in the lake is increasing, as that also affects the absorbance.

4.2 Individual Hypotheses

4.2.1 Trends and drivers of brownification

Like many other lakes in Sweden the brownification of Övre Skärsjön is on hold, showing that the trend of brownification has varied in time for the lake (Result 3.2.1). Considering the results of Eklöf et al. (2021), this result is not very surprising.

When studying the potential drivers of brownification a possible explanation for this pattern is found. The concentration of SO_4^{2-} is the driver with the strongest correlation to TOC, and similarly to TOC the SO_4^{2-}-concentration has no trend between 2010-2021 (Result 3.2.3). Thus, it seems likely that the decrease in sulphate concentration really is the most important driver for brownification in Övre Skärsjön, as the two variables both are significantly correlated and follow the same pattern.

The correlation that is seen between pH and brownification is most likely closely linked to the concentration of SO_4^{2-}. The reason this relation is weaker probably has to do with the fact that pH is affected by many other variables as well. For example the pH of water has been linked to the amounts of carbon dioxide in the atmosphere (Hasler et al. 2018), and is also known to decrease from higher amounts of TOC as it contains a lot of organic acids (Monteith, Stoddard, et al. 2007). These factors are both counteracting the increase in pH, most likely making the relation between pH and TOC weaker. In the case of Övre

Skärsjön in particular it is possible that the pH-situation is made even more complicated due to acidic mine drainage.

It is interesting that the only statistically significant drivers of brownification are related to acidification (Result 3.2.2), as there are studies finding connections to both increasing precipitation (Hongve et al. 2004) and temperature (Creed et al. 2018). Maybe the fact that acidification is such a longstanding problem in the greater area surrounding Övre Skärsjön (Mossberg 2009) is overshadowing the other processes, or maybe precipitation and temperature simply have not changed enough in the area to make a difference.

4.2.2 Recovery from acidification

Övre Skärsjön has been recovering from acidification, as shown by the significant trends for both pH and SO_4^{2-}-concentration over the whole time span. However, the recovery is currently on hold, as no significant trend exist for either variable during the last decade (Result 3.2.3). Hopefully, the chemical recovery that has happened is enough to allow fauna to recover as well, but as no fauna sensitive to acidic environments could be found in 2009 (ibid.), and no significant change has happened since, this is very uncertain.

As the concentration of SO_4^{2-} in the lake can be explained very well by the concentrations in rain water, which in turn is related to the pH of the lake, it is highly possible that the cause of the recovery being on hold also is connected to the deposition of sulphur. One possible explanation is that as the levels of deposition are getting closer to pre-industrial levels, it becomes harder to decrease the deposition further, which in turn hinders further recovery.

4.2.3 Mining activities

Considering that levels of Cu and As still are decreasing (Result 3.2.4), Övre Skärsjön is still affected by, and recovering from, the old mining activities in the area. The mechanisms behind the decreasing concentrations is probably a combination of uptake in organisms, turnover of the water and sedimentation (McDonald et al. 2010).

As the concentrations of As and Cu are correlated, it also seems likely that they are connected to the same source, which in this case would be the mine. For a similar reason the relation between pH and Cu was also examined, as acid drainage from the mine also could have affected the pH of the lake, but no relation could be found. This is most likely because the acidity of the lake is controlled by other factors than acid mine drainage, such as atmospheric deposition.

As sedimentation is a likely fate of copper it would have been interesting to look into the copper concentrations in the deep part of the lake, as it could be much higher there (ibid.). A similar pattern could likely be found for arsenic as well, as it also has been found in high concentrations in lake sediments (Azcue et al. 1993). Unfortunately, there existed no data that could be used to examine this.

4.2.4 Benthic invertebrates

Living organisms are affected by the conditions surrounding them. Analysing the trends of benthic fauna was thus done as a way to investigate what the actual biological effects were of all the studied trends, as well as of processes that were not studied.

Only one of the species (oligochaeta) showed significant trends (Result 3.2.5). This might be due to a difference in sensitivity between the species. It is also worth to point out that the shallower diptera samples were still taken at a deeper depths than the oligochaeta samples, so the conditions might differ somewhat.

The significant trends showed an increase of found organisms in the shallow areas of the lake, while there was a decrease in the deep parts of the lake. Although the trends for diptera were not significant, they did show the same pattern.

The cause of these trends is probably a combination of several different processes: the increase seen in the littoral zone might be due to the increase in pH in combination with lower concentrations of As and Cu. This effect might also be synergistic, as the bioavailability of copper decreases rapidly with increasing pH, particularly for pH values below 6 (Vattenmyndigheterna 2018), which Övre Skärsjön has.

Down at the bottom of the lake it is more plausible that other processes are governing the conditions. Although no analyses have been performed on the chemical conditions of the bottom of Övre Skärsjön it is quite safe to assume that the brownification has led to lower light conditions leading to less primary production. This in turn means both less oxygen and food available for the benthic fauna, on top of the darkness making it harder for them to see their prey (Creed et al. 2018). Considering copper's tendency to settle, with particularly large amounts ending up in the deep part of the lake (McDonald et al. 2010), it is also possible that these potentially high metal concentrations are adding to the hostile environment.

As benthic organisms are important food sources for other organisms such as fish and birds (Anderson 2007), and fish too use the sediments for parts of their life cycle (Johnston et al. 2008), it is plausible that the conditions of the lake are affecting larger parts of the ecosystem than just the invertebrates. This theory is supported by a study that examined seven toxic metals in a lake: although copper had the lowest concentration in the water itself out of the seven metals, the copper concentration was the third highest when looking at concentrations in the liver of fishes (Muneer et al. 2022).

4.3 Uncertanties

An effort was made to try and avoid analyses giving misleading results, for example by analysing the same number of years before and after 2010 instead of using all available years before 2010 which could have increased the chances of seeing a significant trend. Despite this it is impossible to assure that all analyses were done on "equal grounds" as the amount of data available differed greatly between different variables. This problem was mostly circumvented by using yearly mean values or only using data from occasions when all variables had values available, which led to some data being excluded or summarised.

There are several uncertainties in the data itself. For example the change in analysis method for SO_4^{2-} was done due to the tendency of the old method to overestimate the amount of sulphate in humic waters (SLU 2021b), which is relevant as Övre Skärsjön is a humic lake. Some of the used data used was modelled data (SMHI 2021c), which brings its own set of uncertainties.

Although Mann-Kendall is a robust non-parametric test to use for analysing trends in time it does summarise all trends that might exist over the available time period. It is thus possible that there were trends in the data that could not be detected by Mann-Kendall's method, or that several different trends were combined into one. It would probably have been possible to learn more about the dynamics of the system if a method that did not assume that there was only one trend was used.

Finally, it is important to note that aquatic ecosystems are very complicated and it is hard to grasp what processes might actually be at play when a change is seen, as there are so many things that are interacting. It could not be fit into the scope of the project to examine every available variable so it is very possible that some important trend that could have explained current conditions have been missed.

5 Conclusions

The main rule of the environmental quality standards implemented to follow The EU Water Framework Directive is that the status of a lake cannot get worse. In regard to this, the fate of Övre Skärsjön looks bright, at least if the chemical status is considered. All observed trends are currently moving towards values that would impact the lake positively, such as decreased amounts of copper and arsenic, or on hold, like brownification and acidification. Unless something alters the current trajectories of these trends, it seems like Övre Skärsjön will not break this most important rule.

When it comes to biological status it is not as certain. Although both positive and negative trends are found in the lake, the nature of the net change is unknown. There being a negative trend at all points toward the habitat in the profundal zone of the lake getting worse, although what exactly is causing this deterioration is uncertain.

It it evident that the mines surrounding Övre Skärsjön have undermined the status of the lake. Despite the last mine in the area having closed almost 40 years ago, the lake is still not done recovering. It is also possible that some parts of the lake are not recovering at all in regards to this; the situation at the bottom of the lake is completely unknown, but it seems plausible it would be filled with copper and arsenic-rich sediment.

To be able to determine the actual status of the deep part of Övre Skärsjön I would recommend future sampling efforts to also take water samples that will be analysed for copper and other metals at the deep part of the lake. It would likewise be interesting to study sediment cores of Övre Skärsjön, to see how metal concentrations differ with sediment depth. These tests would serve as a good base for further investigations into Övre Skärsjön's status, and would for example inform on whether the decrease of organisms on the bottom of the lake could be due to the toxic nature of metals in the sediment. If this is the case, it would also be interesting to investigate the fate of these metals: are they bio-accumulated in the benthic fauna? How does this affect the species feeding on these organisms? How far up in the food web can effects be seen?

6 References

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Image sources

Figure 1: Lantmäteriet (u.d.). "Min Karta". https://minkarta.lantmateriet.se/

Figure 2: Harald Carlborg, Tekniska museet (u.d.) "Persgruvan". https://digitaltmuseum.se/021016320955/persgruvan-riddarhyttan

7 Appendix

7.1 Trends in absorbance

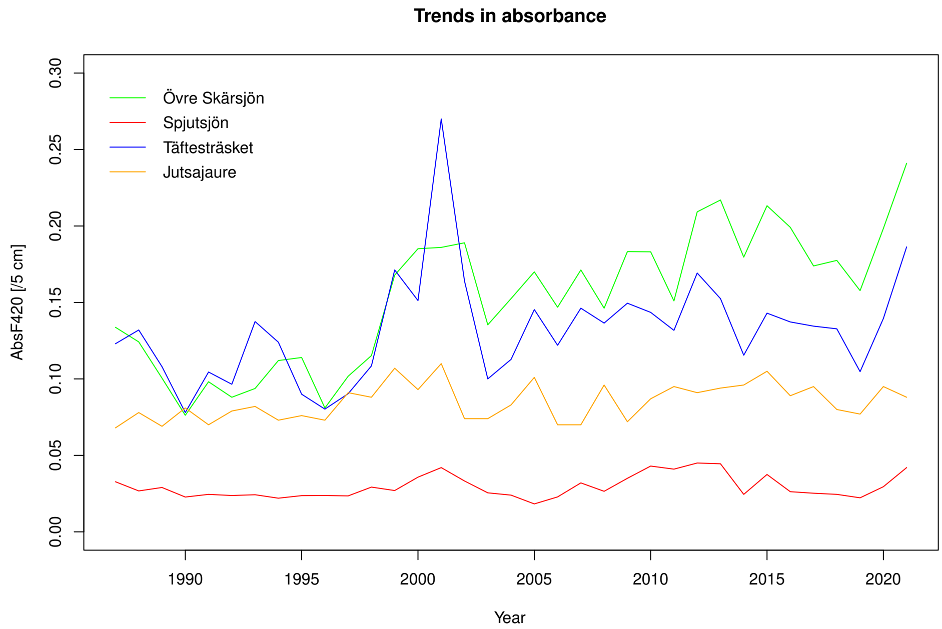

Figure 6. *The absorbance trends of the studied lakes*

7.2 SO4 Unit Conversion Test

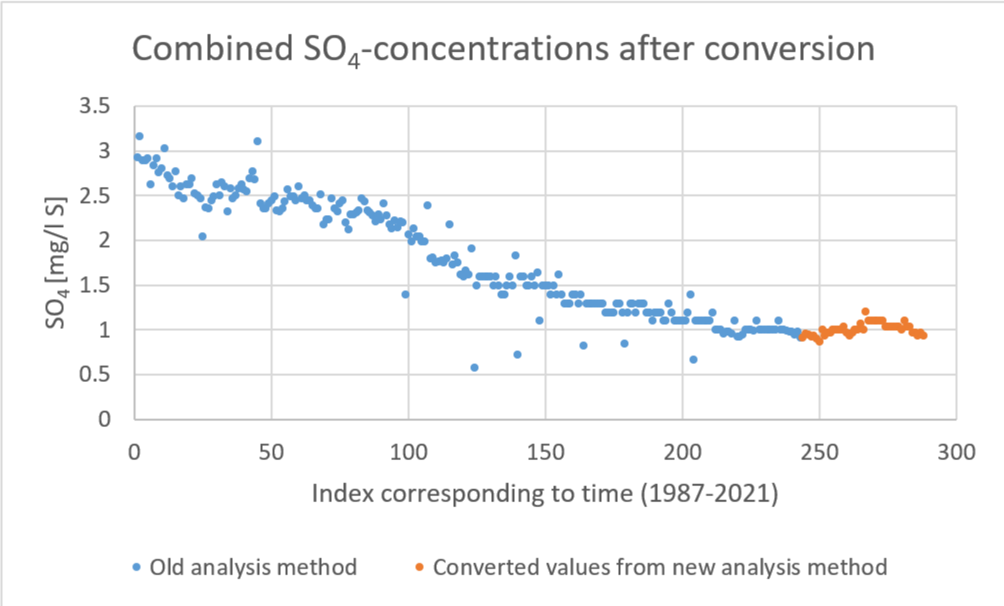

Figure 7. *A comparison between SO4 values from the old analysis method and converted values from the new method.*

7.3 SO4-deposition combination test

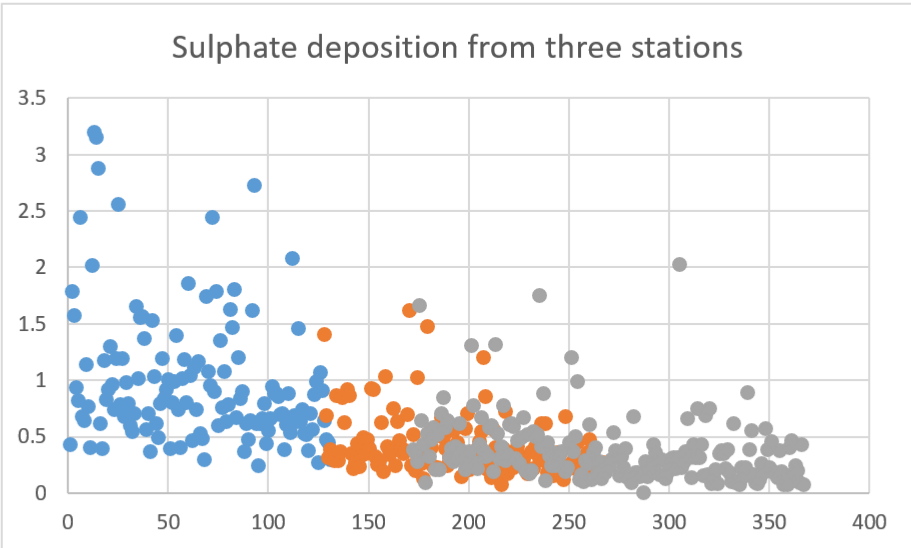

Figure 8. *A comparison between SO_4^{2-} deposition date of the three stations to see if they can be combined. The blue dots represent data from the station in Grimsö, the orange dots represents Kindlahöjden and the blue dots corresponds to data from the station in Kvisterhult.*