The presence of heavy metals in the sediment of the Limfjord and the capture ability of the sediment.

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Abstract:

Through the ages has heavy metal been emitted into the environment due to various causes. This includes human action such as protective paints on ships and emissions from transport and its infrastructure. These heavy metals would then be found in the different environments. One such environment where heavy metal can be found is the marine sediment. But the concentrations found are known to vary between locations. This also apply to the Limfjord, as was found in a previous project on the subject of heavy metal in the fjord.

The scope of this project is to investigate the factors that govern these differences in concentration and find the correlations between the concentration of heavy metal and the local conditions.

This was done with a primary focus on the content of organic matter, which was found to be strongly correlated to the concentrations of heavy metal.

Depth and and placement of sample location that was studied and it was found to control organic matter and the stability of metal species was found to be inconsequential to the concentration of heavy metal.

Preface 1

This project was written by the 10. semester geography student Johannes Albeck Larsen.

The purpose of this study was to investigate the relation between the concentration of heavy metal in the sediment of the Limfjord and local factors that might affect the ability of the sediment to bind the heavy metal. This was done with a focus on organic content, water depth and the most stable species of heavy metal.

The references in this project is ordered as the following [Author;Title;Origin; Year].

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In the project Larsen [2021] the presence of heavy metals was found as a result of testing on samples taken along the southern coast of the Limfjord. These samples was of a visible variation in how coarse the particles was and the coarser particles also seemed to have lower concentrations than the rest of the samples. In addition was the samples from project Larsen [2021] all taken along the edge of the water thus limiting the data to samples from the bottom of the fjord in the shallow water near the coast. This however means that the areas exposed to ships whose antifouling paints could act as a theoretical source of heavy metal was limited to smaller boats and sailboats from the marina that was used as a pointsource.

The scope of the original project was to investigate if a single location like a marina could act like a source of heavy metal to the fjord around it. However it could not be concluded that the marina was the source of the heavy metal found in the samples and for some metals it seemed that the concentration was controlled by other factors than the pointsource. It is not known if this was due to the shallow water affecting the amount of heavy metal brought by the water. Alternatively could it be that the locations are simply not being supplied with a flow of heavy metals [Larsen, 2021].

Throughout the Larsen [2021] project the focus has mainly been on the ability of heavy metal to move from one point to other points and on what connections that might be between the concentrations found in the various point. However there has been little to no focus on what might cause heavy metals to bind them self to a given location. In this project there will be included a focus on what effect local condition have on the concentrations of heavy metal in a given location. In addition this focus will be used to estimate which locations are good or bad at binding heavy metals and use this knowledge to estimate if seemingly dissimilar concentrations have difference in heavy metals due to difference in the ability to bind heavy metals rather than the amount of heavy metals the area is exposed to.

2.1 Types of heavy metal

In the Larsen [2021] project several possible sources of different heavy metals was noted to exist in the project area. Historically ships used heavy metals like lead and copper to protect themself against fouling. Organism was prevented from growing on the ships by covering the bottom of the ship in a layer of paint containing toxic elements or components that collectively can be referred to as biocides [Bressy and Lejars, 2014]. Additionally could sacrificial anodes on ships also contribute to the emission of the heavy metals Zinc and cadmium [Lagerström et al., 2016; Hansen et al., 2013]. Further vectors in Aalborg that could have brought heavy metals into the Limfjord was the use of lead in gasoline before the practise was banned and the presence of train tracks that could cause emission of cadmium, lead, zinc and nickel [Illerup et al., 1999].

This resulted in a group of heavy metals of interest consisting of copper, cadmium, nickel, lead and zinc. These heavy metals are of interest from an environmental perspective due to their toxic effect on aquatic organism in the case of lead, cadmium and nickel. In addition can metals that are essential for living organisms still be toxic in high enough concentrations [Potters, 2013; Water Quality Australia, n.d.].

An additional heavy metal that might be worth studying might be chromium. This heavy metal is mainly released from combustion installations such as power-plants as well as wastewater plants. Chromium is of interest as a heavy metal due to it being toxic to humans, plants and animals and a potential to cause cancer [Tumolo et al., 2020]

2.2 Potential predictors of heavy metal

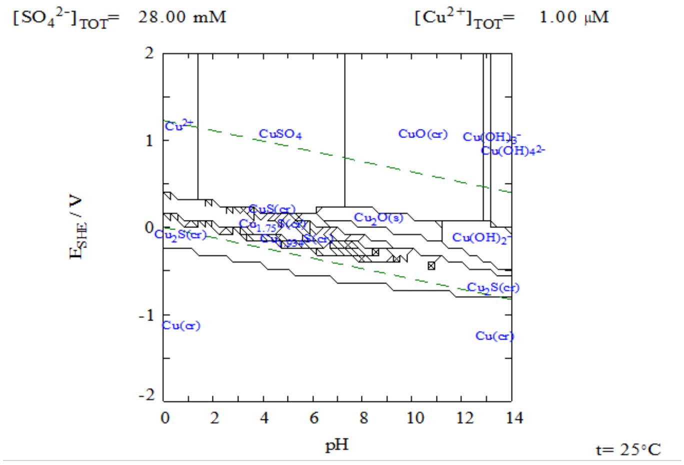
When measuring the content of heavy metals in a location, is it practical to be able to compare multiple different samples despite the differences in sample location. One step in such a process is being able to say if it is likely that heavy metals will bind to the sediments in a location.

The Pourbaix diagram

One potential method to find out about this is to investigate if the heavy metal is stable as disolved ions in the water. Or if the enviromental conditions in a given location will cause the ions to be more stable on a solid form and become a part of the local sediment. One way to see this is using what is known as a stability diagram or a Pourbaix diagram.

A Pourbaix diagram is a diagram showing the most stable form of an element for a given pH value and at a given oxydation-reduction potential. This works by the diagram being a plot of chemical redox potential, refereed to as Eh value and measured in volt, plotted against pH value. Inside this plot is the various forms the element can take plotted as areas of of Eh aginst pH. Additionally does the diagram also show the span of Eh and pH value where water is stable [Huang, 2016].

This allows the diagram to show what chemical form, refereed to as chemical species, the element takes at any given combination of Eh and pH values. As the diagram is made with the assumption that the reaction is in equilibrium the diagram can be used to tell not only what species the element takes at specific conditions but also what phase the element is most likely found in as due to the phase species [Huang, 2016]. This can be seen on the Pourbaix diagram illustrated in figure 2.1. In the diagram it can be seen that different combinations of Eh and pH create a number of different ranges for different species of copper. Inside these ranges the individual species are stable and the lines between them are where the one species stop being stable and another starts being stable. This depends on the pH if the line between species is vertical, redox potential if the line is horizontal and a mix of both redox potential and pH if the line is anything else [Ahmad, 2006].On the y-axis of figure 2.1 the potential is given as E_{she}/V meaning that the potential is defined using the standard hydrogen electrode (SHE) as a reference. However since this standard is impractical for laboratory use, it can be replaced with the normal hydrogen electrode (NHE) that is a the measurement corrected with a equipment and temperature specific constant [Xylem Analytics Germany, 2017; Popek, 2018].



Figur 2.1. Pourbaix diagram for a water solution with copper and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

When reading the figure it can be seen that the different phases of the copper species can be seen after the name of the species. In the given example is (cr) and (s) indicators of the species being solids with (cr) also indicating its is crystalline, while any copper species with no indicators of phase defaults to being in the aqueous phase. Finally can it be noted that according to Ahmad [2006] is the diagram calculated at conditions at 25° Celsius and the concentration of metals in a pourbaix diagram are always assumed to be 1 μmole metal per litre of solution.

In the context of this project would the use of Pourbaix diagrams allow the investigation of how likely the heavy metals are to precipitate at any location that samples are taken from.

It is necessary to include the presence of sulfide in the Pourbauix diagram. This is due to the ablity of sulfur to form complexes with heavy metals and the fact that sulfide is the second most common anion in seawater [RadwanAl-Farawati and den Berg, 1999; Canfield and Farquhar, 2009]. This concentration is acording to Canfield and Farquhar [2009] on 28 millimole sulfide per litre seawater.

Organic content

Another factor that can influence the presence of heavy metals in sediment is organic matter. Heavy metals does according to Beiras [2018] tend to bind to organic matter. This means that the sediment can act as a pool of heavy metals that allows the water bottom to both release heavy metals into the water and for the water to deposit heavy metals onto the water bottom [Ali et al., 2019]. This means that it would be of interest to study how the concentration of organic mater connect with the concentration of heavy metal. Since the concentrations of the different heavy metals should correlate with the concentration of organic matter it should be possible to use the organic mater to estimate how much organic material that is bound in the location as a function how polluted with heavy metals the area is rather than as a function of the sample sites ability to bind heavy metal [Henriksen1 et al., 2001].

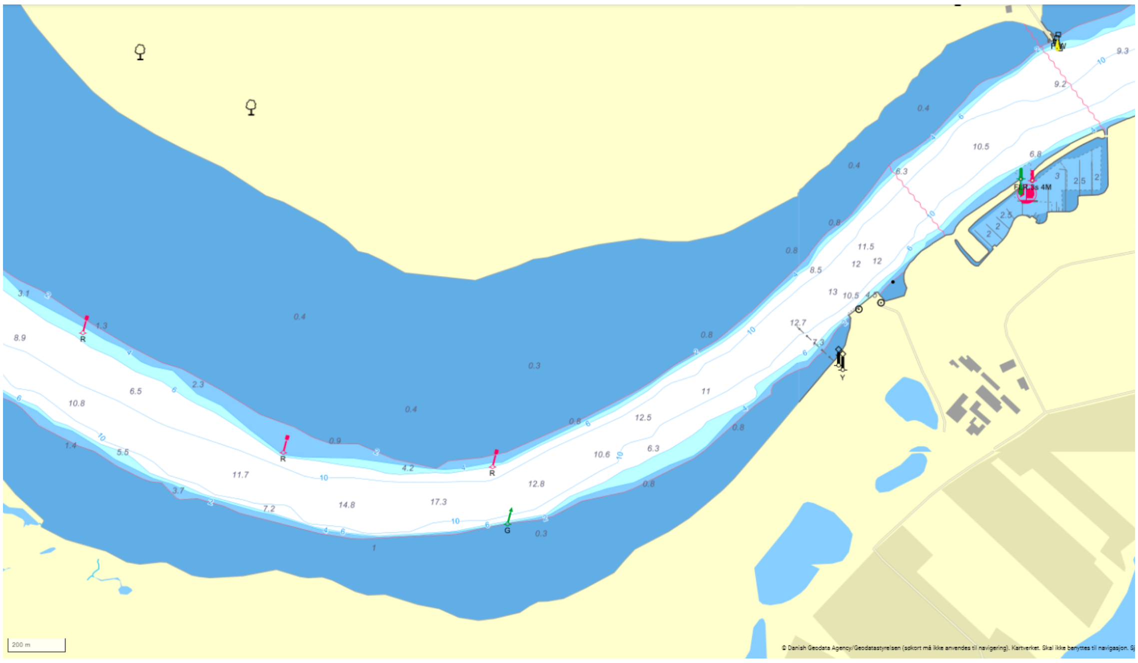
Waterdepth

Finally it would be desirable to investigate if there is a connection between the amount of heavy metals that can be found in a location and how large a waterflow the location are subject to. The primary idea behind this being that a greater flow of water would cause a large amount of water carried heavy metal ion to pass through the water column above the location and thus increase the chance of heavy metals being deposited into the sediment. In addition to this would a greater depth also mean a greater proximity to the main waterway and thus a greater proximity to ships which also might cause an increase in the concentration of heavy metal [krak.dk, n.d.]. This could be studied by taking several groups of samples at different depths but at the same location relative to the coast.

2.3 Area of interest

The investigation of the, in section 2.2 mentioned, factors required a location that could provide sample locations where all factors could be tested. To accomplish this the area had a number of requirements that it needed to fulfill. First and foremost did the area need both an area of shallow water near the shore and a deeper section, ideally as close the the actual waterway as possible. These areas needed both provide access to the shallow areas and to the deeper parts of the sections of the water. Due to the lack of a boat it was necessary to find an area that was accessible on foot as it otherwise wouldn't be possible to get samples from further out in the fjord. This meant that the sections of the fjord that are by the quay was unsuitable as a work area due to reducing access to the fjord to the parts of the Limfjord which are directly adjacent to the quay. In in addition was it was it prioritised to have an area where shallow and deep water was available on both sides of the fjord to introduce in the measuring areas.

These requirements resulted in the section of the fjord south of Egholm being chosen as a project area. This area was chosen due to it meeting all the requirements needed for a usable project area. The coast is accessible on both sides of the fjord due to consisting of either sandy beach or climbable coastal protection. In addition did the area also have a large shallow section neat the coasts on both the northern and southern sides of the fjord, as can be seen on the depth chart in figure 2.2.



Figur 2.2. Seachart of the project area showing water depth [krak.dk, n.d.].

The shallow area at both coasts can on figure 2.2 be seen to be between 30 and 40 centimeters and remains so most of the way out to the waterway where it tends towards being 80 centimeters deep. This made these coasts suitable as a locations for taking samples from shallow water. Afterwards it can be seen to quickly become deeper hinting at a strong slope. But the 80 centimeter area before the beginning of the strong slope was usable for taking samples at greater water depth. A final characteristic of the area is flow of water in the Limfjord. The flow of the fjord is not fixed but is instead determined by the strength and direction of the wind. This also means that there is chaotic currents when there is no strong wind to give it direction [Kristensen et al., 2018]. As for the wind driving the direction of the current can it in Cappelen and Jørgensen [1999] be seen that the wind mainly blows from the west and west-southwest meaning that when there is a current present in the water it most often flows to the east and towards Aalborg harbour [Kristensen et al., 2018].

Since the area is limited to mostly receiving currents from the west, it can be assumed that the heavy metals found in Aalborg harbour is somewhat limited in their influence of the concentration of heavy metals in the area. Therefore should the possible influence of local sources heavy metals be considered.

2.3.1 Heavy metal sources in the project area

When selecting a project area, it is important to know what factors that might act as sources of heavy metal to the project area.

A marina can be seen on the upper right side of figure 2.2, meaning that the presence of ships going to and from the marina as well as passing though the waterway might act as a source of heavy metal.

In addition does the eastern part of the project area contain a ferry route meaning that there might might be a long term contribution of heavy metals from any biocides used to protect the ferry against fouling. Finally does the area also contain several sewage related outlets, as can be seen on figure 2.3.

Figure 2.3 shows that the Aalborg treatment plant west has an outlet in the waterway. The figure also shows the existence of rain overflow outlets from the common sewage system and separate sewage systems. This means that during strong rain the area might be subject to heavy metals found in both sewage and on roads.

Figur 2.3. Shown are outlets and overflow of sewage in the project area [Geodatastyrelsen, n.d.].

Hypothesis of the study 3

In this project there will be a focus on the presence of heavy metals in the sediment of the bottom of the Limfjord. The research will take place in the part of the fjord located just south of the island Egholm. The metals that will be investigated is cadmium, copper, chromium, lead, nickel and zinc. The purpose of the project is to study the effect of local conditions on the ability of the heavy metal to bind it self to a location.

The Hypothesis of the study consists of several parts. The first hypothesis is that there is a correlation between the amount of organic content in a sampling point and how much heavy metal that can be found in this sampling point. In the second hypothesis is it theorised that the stable species caused by the redox potential and the pH value of a sample location are influencing how much of the individual heavy metals are bound to the sediment in the sample location, and that the metal concentrations can be partly predicted using the Pourbaix diagrams. Finally is it hypothesized that greater depth increases the amount of heavy metal found in a sample location due to access either more heavy metal being moved through the water column or closer proximity to passing ships.

Should the hypothesis be proven wrong in part or as a whole, is the null hypothesis for the correlation between organic matter and heavy metal that no correlation can be proven for all or any specific metal. For the second hypothesis is the null hypothesis that there is no provable influence of the stable species caused by the redox potential and pH and that the Pourbaix diagram cannot be used to predict trends for concentration in sample locations. For the third hypothesis is the null hypothesis that neither the proximity to the waterway nor the depth of the sampling location can be proven to have any correlation to the concentrations of heavy metals found in the sample sites.

The hypothesis can be summarised as following.

How is the concentration of heavy metals bound in the sediment of the Limfjord affected by local conditions, such as organic content, stable metal species and water depth, and can a correlation be found between any of these conditions and the concentrations of heavy metal.

To expand further upon this the following questions is asked.

- *What interactions are there between the content of organic matter and concentrations of heavy metal in a site?*
- *What effect, if any, does water depth and the proximity to the main waterway have on the concentration of heavy metals?*
- *What effect does the stability of different types of metal species have on the concentrations of heavy metals?*

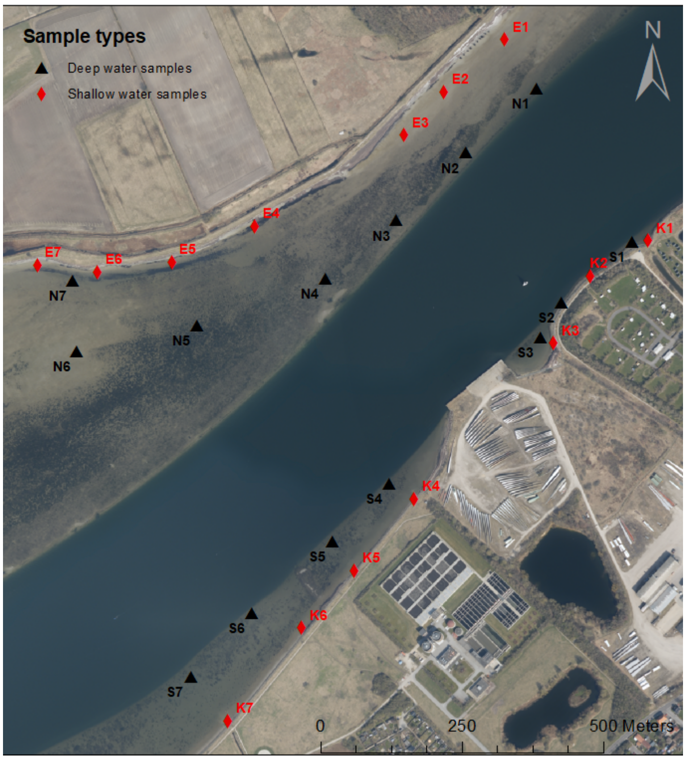
Soil sampling and heavy metal analysis

4

In this chapter the sites where samples was collected from, the collection of samples and the processing and analysis of the samples will be described.

4.1 The collection of Samples

To test the fjord for the presence of the heavy metals cadmium, copper, zinc, nickel and lead, samples was taken from 28 locations in the area south of Egholm. It was chosen to take samples on both sides of the fjord to increase the redundancy in the samples. To investigate the effect water flow it was chosen to takes samples in areas near the shores where the water was shallow and the location therefore had a limited flow of water across it. This was to be compared to a location with a larger flow through it. To accomplish this was locations with greater depths chosen although these were still located so that they would be located in the same general direction from the shore compared to their equivalent sample location at shallow water. This was done on both side of the deep center of the fjord and the measuring points were located right across each other as far as it was possible on both sides of the fjord. The purpose of this was go give an even spread of the location from where the samples would be taken as can be seen on figure 4.1.



Figur 4.1. Show are locations chosen as sample sites, divided into the categories of deep and shallow locations.

4.1.1 Sample locations

The area the samples were taken from was divided into four different groups of seven. These groups were each made up of a string of sample sites along the direction of the coastline.

Coast of Aalborg

The most southern group of samples was taken along the southern coast of the fjord. This set of samples named *K1* to *K7*, collectively called the K group, was taken at shallow water near the edge of the water. For this set of samples was it worth noting that the coast along sample sites *K1* to *K3* consisted of coastal protection made of big stone with a beach and water edge consisting of mud, stone and assorted pieces of masonry and the small bay that *K3* was taken from contained a small outlet pipe located in the side of the coastal protection and terminating above water level. In addition was a storage location for wings from windmills located between sampling location *K3* and *K4*. This potentially being a source of iron to the nearby area. Additionally was the area where *K4* to *7* was taken from an area that according to the warning sign shown in figure 4.2 was an old dumping area for waste from construction and production of fibre cement. As a result of this was all of the area marked with red on figure 4.2 potentially polluted with asbestos this especially applying to the beach. This meant that the samples could contain asbestos thus limiting the tests that could be performed on these four samples.

Renseanlæg Vest

Borgerinformation

Færdsel på området frarådes og sker på eget ansvar. Dele af området er tidligere fyldpladsområde (byggepladsaffald og affald fra eternitproduktion), og der ligger således synligt affald flere steder heriblandt asbestholdigt eternitaffald.

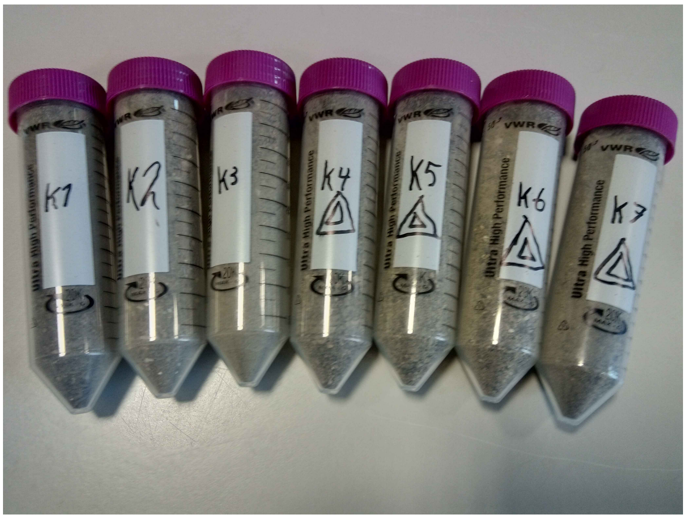
Dette gælder især stranden, arealerne nord for den øst-vestgående vej ved helikopterlandingspladsen og området omkring søen, der grænser op til kolonihaverne. Der sker en løbende fjernelse af synligt affald, indtil en varig løsning er fundet i samarbejde med Aalborg Kommune.

Desuden benyttes en del af arealerne til udlægning af slam fra spildevandsrensningen, hvorfra der kan være smitterisiko.

🟥 Areal tilhørende Renseanlæg Vest
🟩 Renseanlæg Vest
🟨 Miljøgodkendt areal til nedpløjning af sand og slam
🟦 Mellemlager til sand og slam

Figur 4.2. Local sign informing that parts of the area marked with red might contain asbestos containing building and eternit waste.

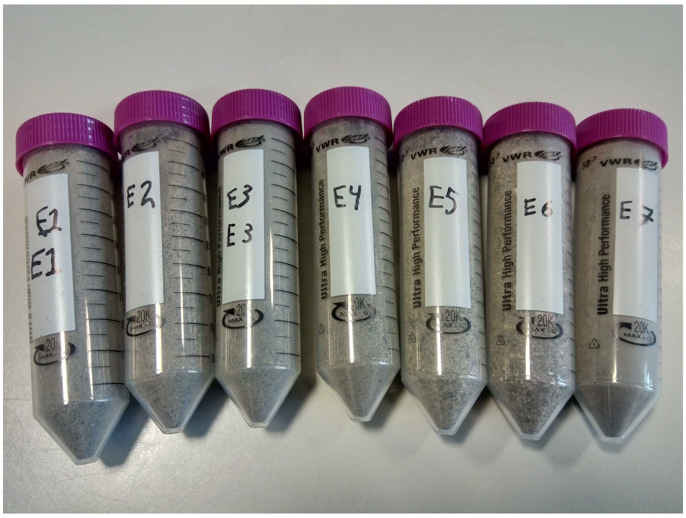
The samples were, as can be seen on figure 4.3, consisted of a sandy material with a mix of coarse impurities contained in it. The exception to this was sample *K3* and *K7* that can be seen to be of a finer sand with less impurities.



Figur 4.3. Samples taken at the coast of Aalborg near Rensningsanlæg Vest, the triangles indicating samples that might contain asbestos.

Egholm beach

The most northern group of samples was taken along the southern coast of the island Egholm. This set of samples are named as the samples *E1* to *E7* and collectively called the E group. Samples from these locations was taken in shallow water just at the edge of the shore. The samples taken from the beach of Egholm, shown on figure 4.4, can be seen to be a somewhat sandy texture with a small amount of what looked as dark particles mixed into it possibly grains of organic matter.

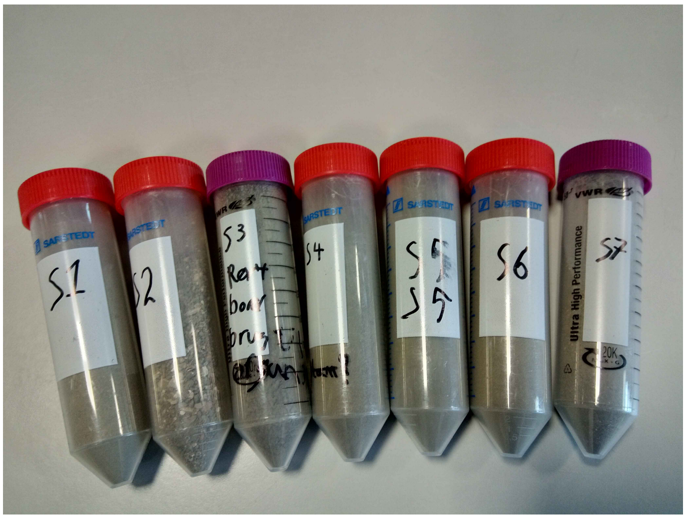


Figur 4.4. Sample taken at the south coast of the island Egholm

Deepwater south

The southern of sample groups taken in the deeper water are made made up of the samples *S1* to *S7* and collectively called the S group. These samples were taken as close as possible to the deeper waterway in the Limfjord. Of special note was sampling locations *S2* that due to the strong downward slope of the fjord bottom meant that it was taken a few meters from shore despite the sample being taken at one of deepest sampling locations. Additionally is the sampling location of *S4* later found to be taken near the overflow outlet from a combined sewage and rainwater system, a sewage outlet from rainwater sewage system as can be seen on figure 2.3 page 10.

Finaly can it be noted that the sample from *S6* was visually confirmed to have been taken about 2 to 3 meters from the edge of the deeper waterway used by ships to pass though section of the fjord.



Figur 4.5. Samples taken in deep water at the southern edge of the waterway.

The samples can be seen on figure 4.5. It can be seen that the samples, with the exception of sample *S2*, have fine texture consisting of small particles. Sample *S2* on the other hand consists of a coarse collection of sand and many large particles, even after having the stones removed due to testing requirements.

Deepwater North

The Northern sample group taken from the deeper water is refereed to as sample location *N1* to *N7* and collectively called the N group. These samples are taken as close to the northern side of the waterway as was possible. A thing that makes this set of samples stand out in comparison to the other samples is that they were taken from an area with large amounts of water plants but the samples them self were taken from plant less spots on the bottom of the fjord.

Figur 4.6. Samples taken in deep water at the northern side of the waterway.

The samples can be seen on figure 4.6 to be of a fine texture compared to the Egholm samples shown on figure 4.4. In addition there can be seen several picess of black matter in the samples that clearly isn't particles of sand, but appears to be plantmatter. These can possible be debris from nearby waterplants.

4.1.2 Sampling procedure

To avoid contaminating the samples with metal during sampling there was used sampling equipment made exclusively of plastic. The sampling in the locations *K1*, *K2* and *K3* was performed using a plexiglass pipe to extract the samples as a core sample but a small plastic shovel was used from location *K4* to *K7* and for the sample locations *E1* to *E7*. The samples from these locations was taken from the water in the immediate vicinity of the shore. And was therefore taken from a relative shallow depth of around 10 to 30 centimeters.

The samples consisted of the sediment taken from the upper 5 to 7 centimeters of the sediment of the fjord, and were taken from 3 spots in the sample location and mixed into a single plastic container to give a representative sample for the given sample location.

The *S* and *N* samples were taken as close to the edge of the waterway in the fjord as possible. However sample had to be taken using a pair of wader to walk to the location and the choice of location was therefore limited by how accessible the area was. The distance from the shore varied due to difference in the slope of the bottom of the fjord. Additionally did the soft bottom of the fjord make it infeasible to move further out in some locations due to risk of getting stuck in the mud.

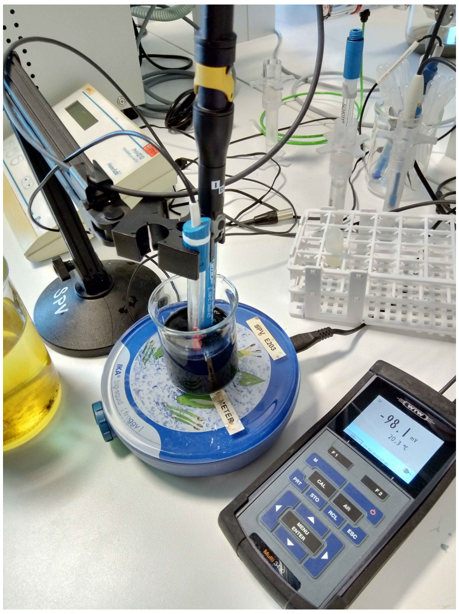
The samples taken form the edge of the waterway could, due to the waterdepth, not be taken using the hand shovel or the plexiglass pipe. These samples were taken using a feed shovel mounted on a long handle. This meant that the samples could be taken at greater depth than otherwise possible.

These samples were taken at a water depth varying between of 60 to 80 cm of water. A great part of the uncertainly in the depth was due to differences in the consistency of the fjord bottom with certain parts consisting of soft mud that effectively provided greater depth during sampling.

Theses samples were taken from a single point in the samplelocation due to the impracticality of having to find the same location point again due to lacking reference points during sampling. The samples were then taken from what is estemated to be the upper 10 centimeter of the soil and then stored into a platstic container.

4.2 Sample treatment

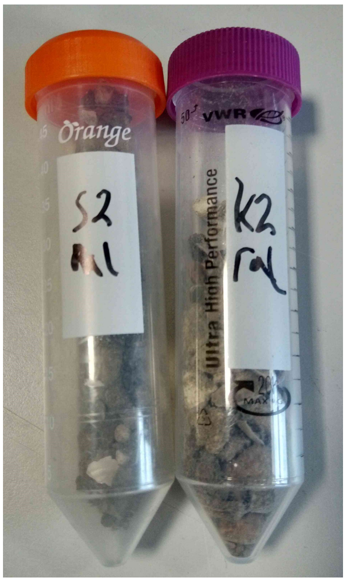
After the samples were collected they were brought back to the laboratory. The samples were subjected to a test of both pH value and redox potential. This was done before any treatment of the samples to get a result as close as possible to what would be found in the sample site itself. This procedure was performed by taking 20 g of sediment and suspend it in 80g of demineralized water. This ratio was chosen since the organic content still was unknown and according to Yu and Rinklebe [2013] can the test be performed with a ratio of 1:4 for very mineral soils while the test could work with a ratio of 1:10 for very organic soils. This was done by using a magnetic stirrer using a plastic covered magnet to suspend the solution. The pH was then measured using a pH-meter, and the redox potential was measured using an ORP-T 900P SenTix Electrode resulting in the setup that can be seen on figure 4.7.



Figur 4.7. The setup that was used to measure the pH and redox potential of the samples.

The measurements from the ORP-T900P electrode was given in millivolt and had to be converted by adding a temperature dependent constant to the measure result so the potential would be using the normal hydrogen electrode as a refrence. The measurements was performed at 22° Celsius meaning that the constant that was needed to convert the measurement to NHE was 211 [Xylem Analytics Germany, 2017]. As a side effect of this procedure it was discovered that several of the samples contained metal splinters. This was discovered due to the splinters being found on the magnet during cleaning and since the plastic cover of the magnet was intact it could not be the source. The splinters is believed to be iron due to being black and magnetic and they was found in sample *K1* to *K4* as well as in all *S*samples and *N*samples.

To prepare the samples for further analysis they were dried and ground down to individual particles. To do this the samples were subjected to two days in an oven at 105° Celsius to remove water and moisture. When the samples were dry they were crushed using mortar and pestle and stored for further use. Extra safety precautions had to be taken for samples *K4*, *K5*, *K6* and *K7* due to a potential presence of asbestos. In addition was small stones and gravel removed from sample *S2* and sample *K2*, as can be seen on figure 4.8, to make them usable for the heavy metal analysis.



Figur 4.8. Shown in collection of small stones removed during the crushing of sample *S2* and sample *K2*.

After the samples had been crushed a small amount of the samples was taken and used for the heavy metal analysis. The remaining sample was used to test for the amount of organic matter using the weight loss on ignition procedure.

The the weight loss on ignition was performed by using a furnace to remove the organic fraction of the samples by heating the samples to 550° Celsius and burning away the organic content. This was done by measuring between 40g to 50g of sediment, depending on the sample, in a small crucible of known weight. The samples were then heated in a furnace like the one shown on figure 4.9 for a time span of 23 hours to 23 hours and 25 minutes. The first hour of which was spent heating the furnace.

Figur 4.9. The furnace was used to remove all organic matter from the samples, so that the organic content could be found.

After almost a full day of 550° Celsius organic content had vanished from the sample, as can be seen on figure 4.10, and the samples was taken out of the furnace and their weight was measured. the difference between the before and after weight of the sediment in the crucible was the the loss of organic matter.

Figur 4.10. Sediment shown after being subjected to the loss of ignition procedure.

This was done to the E, N and S samples groups. However due to safety concerns only the *K1*, *K2* and *K3* samples was subjected to the loss on ignition procedure. This was due to the remaining four samples being taken from locations that made it possible that asbestos or other eternit waste would be present in the sample. To avoid the release of asbestos containing dust or other undesirable materials that might be contained in dumped building material on the site.

4.2.1 Heavy metal analysis

As mentioned were the samples dried and crushed. Afterwards there was taken from between 0.5g to 1g of sediment from the crushed sample. As gravel and stone already had been removed from sample *S2* and sample *K2*, along with uncrushable shells and organic debris, all samples had a texture suitable for the metal analysis. It was attempted to take an amount of sample closer to 1g sediment for the samples that visibly was estimated to have a coarser sand texture and looking like it contained less organic matter due to its brighter shade. For the rest of the samples it was attempted to take a subsample closer to 0.5g sediment.

The procedure for this was that each sample would be tested by having it triple determined to protect against measuring error and outliers. The triple determination resulted in three groups of sample that were referred to as their location and a, b or c. This resulted in a total of 84 subsamples that can be seen on table 4.1 with weight given in grams of sample.

	a	b	c
K1	0.5203g	0.8848g	0.7808g
K2	0.9858g	0.7949g	0.7520g
K3	0.7397g	0.9080g	0.7383g
K4	0.7413g	0.7261g	0.8658g
K5	0.7196g	0.7856g	0.8780g
K6	0.6341g	0.6838g	0.8044g
K7	0.7597g	0.7183g	0.6976g
E1	0.6813g	0.7407g	0.6914g
E2	0.6740g	0.7884g	0.8416g
E3	0.7260g	0.7470g	0.7444g
E4	0.6322g	0.7985g	0.5905g
E5	0.7916g	0.6088g	0.5662g
E6	0.9477g	0.8064g	0.7568g
E7	0.5113g	0.6064g	0.5634g
S1	0.6215g	0.6503g	0.6402g
S2	0.5965g	0.5616g	0.5882g
S3	0.5500g	0.5865g	0.5630g
S4	0.6567g	0.5929g	0.5740g
S5	0.5139g	0.5666g	0.5820g
S6	0.6186g	0.5227g	0.5551g
S7	0.6150g	0.5289g	0.5346g
N1	0.5733g	0.6650g	0.5603g
N2	0.5306g	0.5700g	0.5325g
N3	0.7051g	0.6784g	0.7324g
N4	0.5846g	0.5601g	0.9186g
N5	0.5348g	0.6559g	0.6451g
N6	0.5016g	0.6524g	0.5677g
N7	0.9045g	0.8132g	0.9213g

Tabel 4.1. Weight of the sediment content of each subsample.

After the subsamples had been measured they had to be processed to be usable for the metal analysis. To do this the subsamles had to have the organic material digested.

This was done by adding 5ml HNO_3 67-69% weight/weight to the subsamples. Then the samples was put in a multiwave 7000, as shown on figure 4.11 to digest at a temperature of 180° Celsius and a stating pressure of 40 bar. This was done to release the metal ions into the solution.

Figur 4.11. Multiwave 7000 used for digestion of organic content in subsamples.

After the subsamples had been digested in the multiwave 7000 they were diluted in pure water. Using a weight 20 gram of pure water was added to the solution so the sample was dissolved in 25ml liquid resulting in a total weight of about 28.5g. After this the subsamples were shaken and allowed to sediment again.

After this 10 ml worth of solution was taken from each subsample. This was then used to perform the metal analysis.

The metal analysis was performed using Inductively coupled plasma - optical emission spectrometry, shortened to ICP-OES, where the solution turned to aerosols and send into a 6000-7000 kelvin argon plasma where the sample is ionised. This makes the electron in the metal ions excited for a time.When the electrons return to their nonexcited state light is emitted and the intensity of light on differnet wavelengths of the emitted light can be measured to be determined. These measurements are then calculated into concentrations of different metal in the sample [Radboud University, n.d.].

From Larsen [2021] it was known that the sediment in the fjord could contain large amounts of iron and that this would need to be taken into account to perform the measurements. However during the measuring it was discovered that the amount of iron in the samples were so high that the metal analysis could not be done using a solution made of metal standards to calibrate the measurements with.

Data and data analysis 5

In this chapter will the results of the measurements performed on the samples of sediment be shown and analysed.

5.1 Measuring results

In this section the measuring result from the different experimental analytical procedure will be presented.

5.1.1 Redox potential and pH measurements

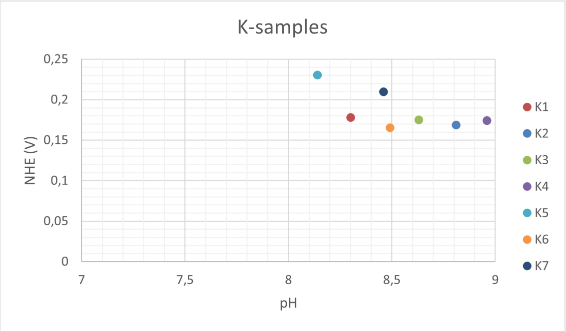
The potential and pH of the samples was measured to find the redox potential and pH values of the sample sites. After the potential had been measured using the ORP-T 900-P diode the results had 211 added to them to convert the results into the NHE values, given in milliVolt, for the sample locatons. To compare these values to the pourbaix diagrams they had to be converted from milliVolt to volt. This was done by dividing the NHE value in millivotl by a thousand, giving the NHE in volt as shown in table 5.1. Shown in the same table the values measured with the ORP-T 900-P diode and the pH value of the pH value of the sediment.

When reading table 5.1 it can be seen that all pH values reides within the interval of 7.39 pH to 8.96 pH and that the NHE value stays within the voltage interval of 0.1038 V to 0.3194 V meaning that this is the interval of interest for the pourbaix diagrams of the investigated metals. This however is only the total interval and the individual groups of samples have different pH and Voltage intervals.

	Measured mV	NHE (V)	pH
K1	-33.2	0.1778	8.3
K2	-42.2	0.1688	8.81
K3	-36	0.175	8.63
K4	-36.9	0.1741	8.96
K5	19.6	0.2306	8.14
K6	-45.7	0.1653	8.49
K7	-1.5	0.2095	8.46
E1	86	0.297	8.16
E2	108.4	0.3194	8.13
E3	83.1	0.2941	8.17
E4	45.9	0.2569	8.33
E5	8	0.219	8.2
E6	6.8	0.2178	8.34
E7	4.5	0.2155	8.41
S1	45.9	0.2569	7.63
S2	-79.5	0.1315	8.55
S3	-25.7	0.1853	7.39
S4	-107.2	0.1038	8.9
S5	-67.7	0.1433	7.55
S6	-104.5	0.1065	7.96
S7	-50.5	0.1605	8.37
N1	-15.6	0.1954	7.88
N2	-28	0.183	7.55
N3	57.6	0.2686	7.93
N4	48.4	0.2594	7.93
N5	54	0.265	7.99
N6	66.7	0.2777	8.17
N7	-12.2	0.1988	7.9

Tabel 5.1. The measured potential of the samplesites, the calculated NHE value for same and their pH vaules.

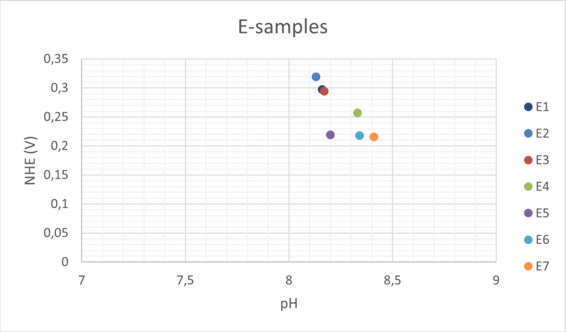
A consequence of the different groups having different value intervals of pH and NHE value, means that the stable species of metal complex might differ between the individual sample group and all sample groups as a whole.



Figur 5.1. Shown is the interval of pH and NHE values for the K sample group.

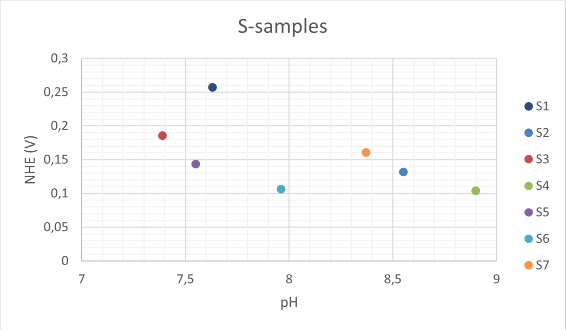
The K-samples can, on figure 5.1, be seen to have NHE values in an interval ranging from

0.1653 V to 0.2306 V. And pH values ranging from 8.14 pH to 8.96 pH.



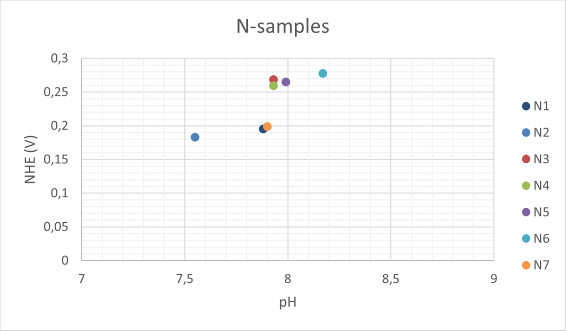
Figur 5.2. Shown is the interval of pH and NHE values for the E sample group.

The E-samples can, on figure 5.2, be seen to have NHE values in an interval ranging from 0.2155 V to 0.3194 V. And pH values ranging from 8.13 pH to 8.41 pH.



Figur 5.3. Shown is the interval of pH and NHE values for the S sample group.

The S-samples can, on figure 5.3, be seen to have NHE values in an interval ranging from 0.1038 V to 0.2569 V. And pH values ranging from 7.39 pH to 8.9 pH.

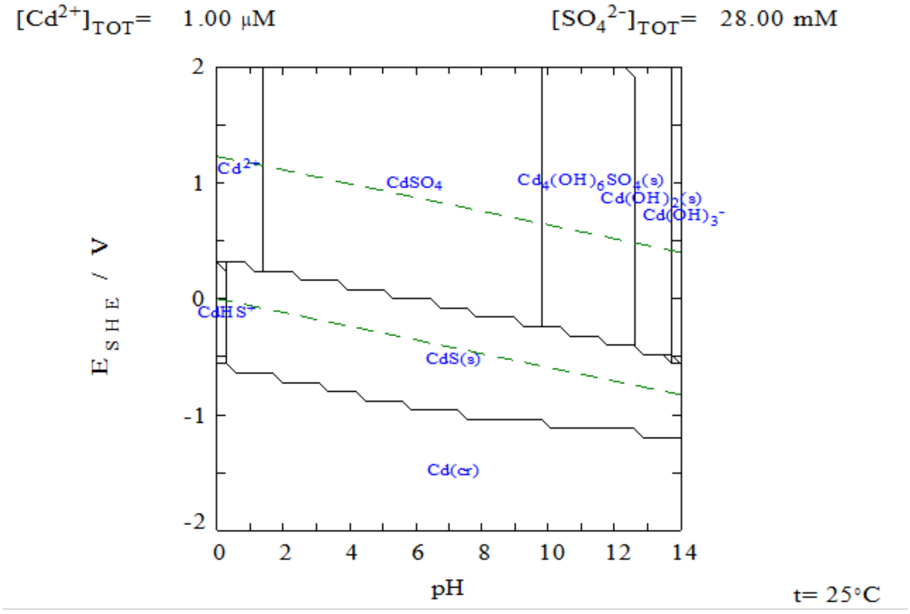


Figur 5.4. Shown is the interval of pH and NHE values for the N sample group.

Finally can the N-samples, on figure 5.4, be seen to have NHE values in an interval ranging from 0.1830 V to 0.2777 V. And pH values ranging from 7.55 pH to 8.17 pH.

Cadmium

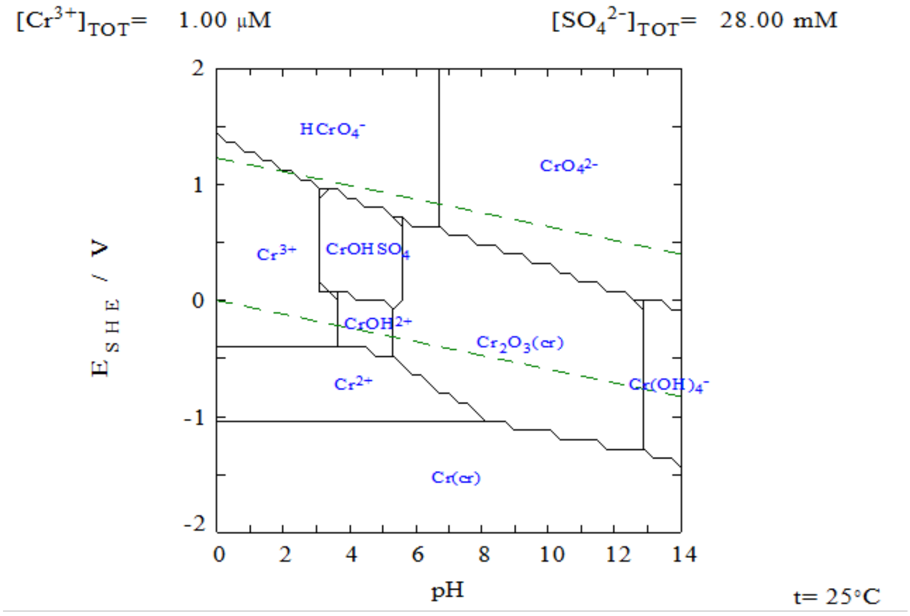
When comparing the NHE and pH values from table 5.1 with the Pourbaix diagram for cadmium, seen in figure 5.5, it can be noticed that the most stable species of cadmium is $CdSO_4$. It can on figure 5.5 be seen that there is no indicater of phase on $CdSO_4$ which, as mentioned in section 2.2, means that the phase of the species is it being aqueous and thus dissolved in the water. It can be seen that this applies to all the sample sites.



Figur 5.5. Pourbaix diagram for a water solution with cadmium and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

Chromium

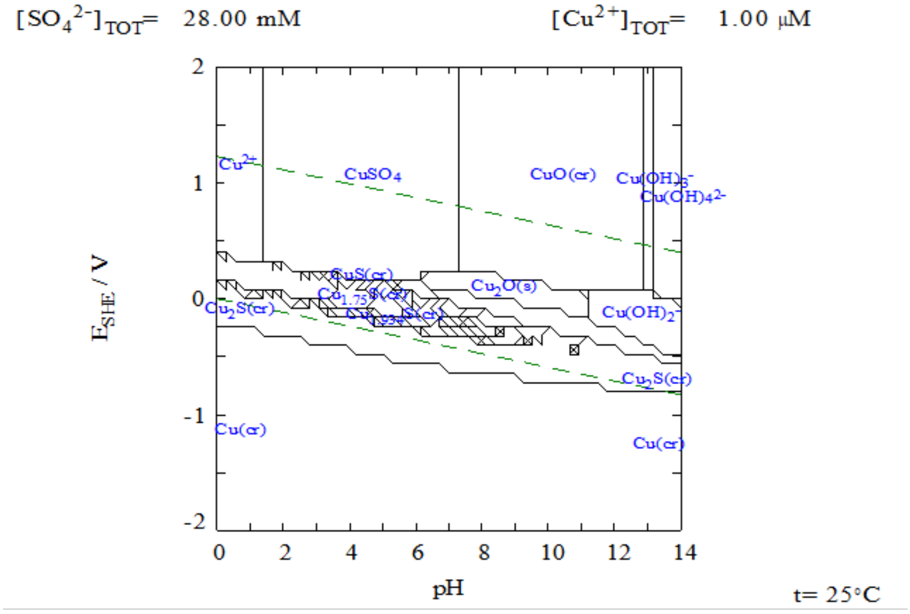
When comparing the NHE and pH values from table 5.1 with the Pourbaix diagram for chromium, seen in figure 5.6, it can be noticed that the most stable species of chromium is Cr_2O_3 (cr). Since Cr_2O_3 is marked with the phase indicator cr for crystal is the most stable form of chromium a solid. This applies to all the sample sites.



Figur 5.6. Pourbaix diagram for a water solution with chromium and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

Copper

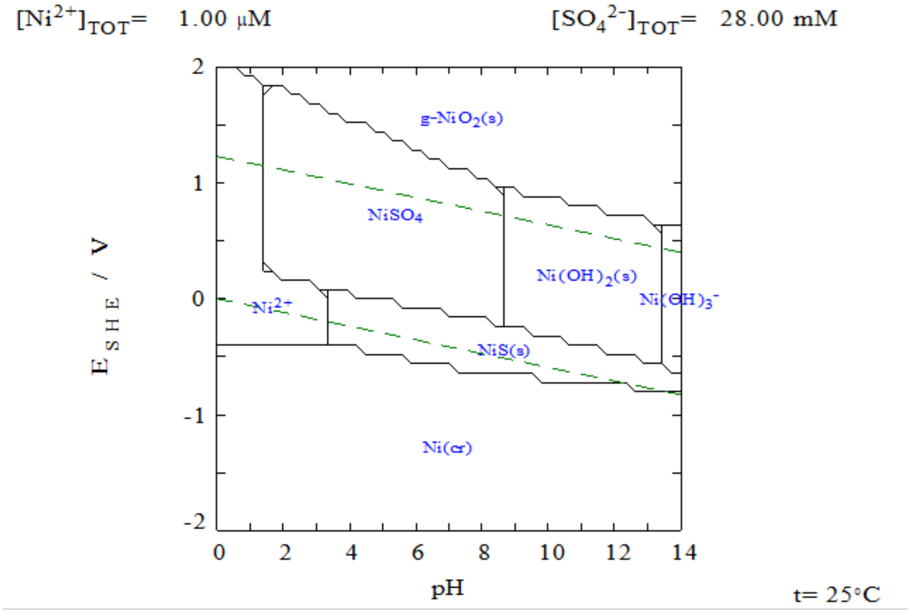
When comparing the NHE and pH values from table 5.1 with the Pourbaix diagram for copper, seen in figure 5.7, it can be seen that the two stable copper species in the project area. These two species is CuO (cr) and CU_2O (s) both of which is solids as indicated by the phase indicaters (cr) and (s).



Figur 5.7. Pourbaix diagram for a water solution with copper and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

Nickel

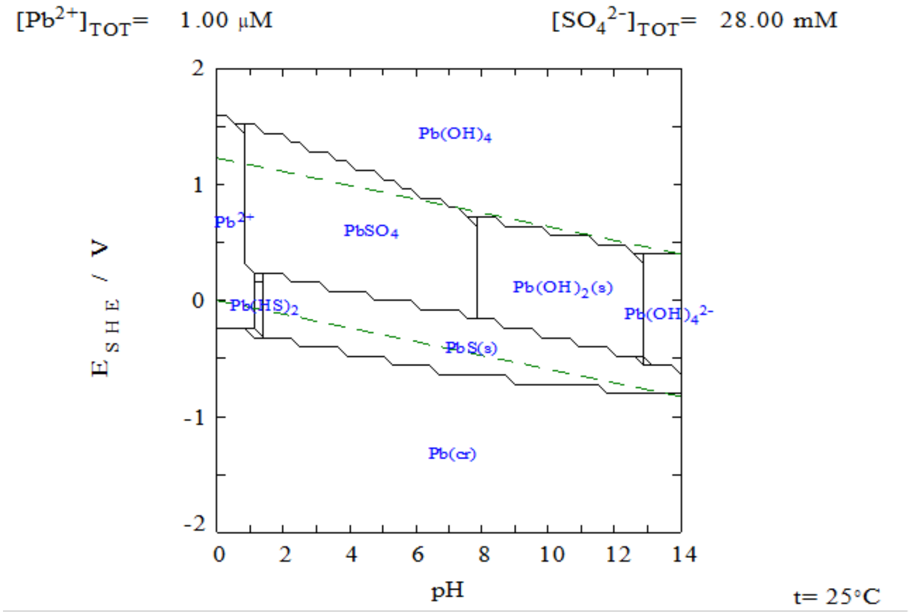
When comparing the NHE and pH values from table 5.1 with the Pourbaix diagram for nickel, seen in 5.8 it can be seen that the there are two stable species. these are NISO$_4$ that is aqueous and NI(OH)$_2$ (s) that is a solid. it can be seen that in most of the sample sites are NISO$_4$ the most stable species but in sample site *K2*, *K4* and *S4* is the stable species for nickel NI(OH)$_2$.



Figur 5.8. Pourbaix diagram for a water solution with nickel and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

Lead

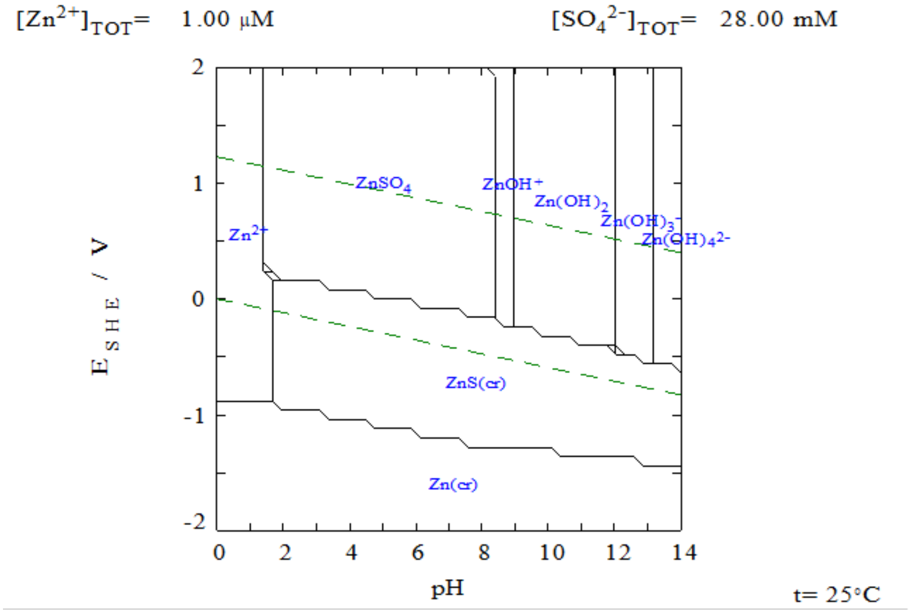
When comparing the NHE and pH values from table 5.1 with the Pourbaix diagram for lead, seen on figure 5.9, it can be seen that there are two different species of lead that can be the most stable in the project area. In the majority of the area is the most stable species of lead Pb(OH)$_2$ (s), a solid, while in sample location *S1*, *S3*, *S5* and *N3* is the most stable species of lead PbSO$_4$.



Figur 5.9. Pourbaix diagram for a water solution with lead and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

Zinc

When comparing the NHE and pH values from table 5.1 with the Pourbaix diagram for zinc, shown on figure 5.10, it can be seen that there are three species of zinc that can be the most stable species in the project area. These are $ZnSO_4$, $ZnOH^+$ and $Zn(OH)_2$ that all are aqueous species of zinc.



Figur 5.10. Pourbaix diagram for a water solution with zinc and sulfur made in Hydra-Medusa [KTH Royal Institute of Technology, 2020]

5.1.2 Soil loss on ignition

After the samples had been subjected to the soil loss on ignition procedure was the percentages of organic matter, shown in table 5.2, found. Here there was found concentrations of organic matter ranging from 0.82% to 7.7% organic matter. No measurements was made for *K4* to *K7* due to risk of asbestos content.

	organic matter %
K1	3.8625
K2	2.016
K3	1.6821
K4	Na
K5	Na
K6	Na
K7	Na
E1	1.1317
E2	0.8399
E3	2.0002
E4	1.3169
E5	0.8197
E6	0.9142
E7	2.702
S1	4.214
S2	5.3791
S3	7.6643
S4	5.4222
S5	4.8627
S6	5.1104
S7	3.4014
N1	4.2421
N2	3.2224
N3	1.0401
N4	2.1014
N5	3.8792
N6	2.0645
N7	0.9397

Tabel 5.2. Table for measured concentration of organic matter in sample sites. No measurements available for *K4* to *K7* due to potential risk of asbestos content.

5.1.3 ICP-OES metal analysis

After the metal analysis had been performed by the ICP-OES the resulting content of heavy metals contained in the samples were given as measurements taken at different wavelengths of light. However not all measured wavelengths gave usable results. This disruption was caused by a large concentration of iron in the samples. The iron content was also measured and found to be reach concentration as high as 8041 μg/g iron per gram sample and never go below 720 μg/g iron per gram sample.

The number of usable wavelengths would vary from metal to metal. The usable wavelengths are 214.4 nm and 228.8nm for cadmium, 359.3 nm for chromium, 324.7 nm and 327.3 nm for copper, 221.6 nm and 231.6 nm for nickel, 220.3 nm for lead and 202.5 nm, 206.2 nm and 213.8 nm for zinc.

The ICP-OES gives the results of the analysis as microgram heavy metal per litre solution. This can be processed to μgram metal per gram sample,shortened to μg/g sample, by calculating how many g sample was added per litre solution using the measured samples from figure 4.1 to calculate this. The measurements can be seen in appendix A.

Microgram metal per gram sample can be found once g sample per Litre solution is known. This can be done by dividing the measuring result with g sample pr litre solution but how to do this depends on how many usable wavelengths there were for the calculated metal. For zinc with 3 usable wavelengths the wavelength with the median values, 202.5 nm, was chosen. For copper, nickel and cadmium there were 2 usable wavelengths for each metal and therefore the mean of these wavelengths was used. For Chromium and lead the only usable wavelengths were used directly.

It should be noted the detection limit of cadmium is estimated to be 3 μg/L solution meaning that it cannot be guarantied that the measurements of cadmium is exact [Inorganic Ventures, n.d.].

The found concentrations are shown in tables on the following pages. The tables each gives the results for a single sample group and the results have been rounded to three decimal places.

Sample location	Cd μg/g sample	Cr μg/g sample	Cu μg/g sample	Ni μg/g sample	Pb μg/g sample	Zn μg/g sample
K1a	0.147	2.822	10.189	2.994	4.144	23.823
K1b	0.163	2.620	15.058	2.867	4.207	18.744
K1c	0.140	2.699	6.810	3.021	3.874	18.017
K2a	0.134	2.520	19.531	2.933	7.197	22.218
K2b	0.118	2.030	13.813	2.731	6.642	22.217
K2c	0.109	2.188	18.391	2.423	7.108	30.821
K3a	0.101	2.045	2.910	2.223	3.093	16.740
K3b	0.102	1.900	6.432	2.264	4.959	18.191
K3c	0.107	2.053	3.194	2.260	2.882	27.350
K4a	0.120	4.243	7.688	4.634	2.983	16.434
K4b	0.144	9.637	27.439	8.491	3.873	27.235
K4c	0.129	6.147	8.644	5.037	3.153	17.339
K5a	0.051	1.128	1.039	1.197	1.485	7.132
K5b	0.041	0.697	0.759	0.886	1.305	5.664
K5c	0.044	0.718	0.839	0.893	1.330	5.994
K6a	0.055	1.208	1.039	1.215	1.821	7.250
K6b	0.056	1.143	1.312	1.201	1.666	7.129
K6c	0.056	1.297	1.062	1.044	1.625	7.966
K7a	0.051	1.047	1.037	1.159	1.678	7.039
K7b	0.048	0.938	0.971	1.080	1.490	6.404
K7c	0.056	1.172	1.156	1.236	1.803	7.203

Tabel 5.3. Measured concentration of heavy metals for all subsamples in the K group.

In table 5.3 is shown the concentrations of heavy metal measured in each subsample in sample group *K*. In this group it is found that the measured concentration of copper in *K4b* is much higher than the other subsamples. It isn't possible to definitivly test if a sample is an outlier due to the lack of a reference during ICP-OES procedure. However due to the great disparity between the measured copper concentrations in sample *K4* is it assumed that the concentration of copper in *K4b* is an outlier and it will be removed under that assumption. In addition are the concentrations of zinc measured in *K2c* and *K3c* visibly higher that the other subsamples for their respective sample location. However these differences are not high enough that they with certainty can be declared as outliers and be removed.

Sample location	Cd μg/g sample	Cr μg/g sample	Cu μg/g sample	Ni μg/g sample	Pb μg/g sample	Zn μg/g sample
E1a	0.054	1.374	1.437	1.412	1.668	6.788
E1b	0.052	1.244	1.348	1.347	1.611	6.602
E1c	0.053	1.215	0.994	1.319	1.620	6.776
E2a	0.037	0.968	0.773	1.017	1.161	4.662
E2b	0.039	0.896	0.707	0.994	1.213	4.538
E2c	0.041	1.031	0.823	1.062	1.247	5.840
E3a	0.056	1.268	0.965	1.338	1.303	5.620
E3b	0.054	1.143	0.973	1.334	1.388	6.074
E3c	0.054	1.152	0.985	1.334	1.263	5.750
E4a	0.064	1.767	14.940	1.815	1.657	10.673
E4b	0.063	1.642	1.338	1.727	1.515	6.409
E4c	0.056	1.561	1.155	1.625	1.460	6.804
E5a	0.038	1.025	0.703	0.912	1.399	4.425
E5b	0.039	0.967	0.604	0.897	1.301	4.661
E5c	0.037	0.950	0.579	0.862	1.295	4.733
E6a	0.040	0.631	0.883	0.882	1.494	9.491
E6b	0.034	0.664	0.679	0.757	1.412	4.759
E6c	0.032	0.687	0.732	0.744	1.598	4.493
E7a	0.086	3.209	2.120	3.519	2.481	9.955
E7b	0.098	3.636	2.382	3.931	2.812	11.065
E7c	0.100	3.778	2.467	4.156	2.816	11.306

Tabel 5.4. Measured concentration of heavy metals for all subsamples in the E group.

In table 5.4 is shown the concentrations of heavy metal found in each subsample in sample group *E*. In this group is it found that the concentration of copper found in subsample *E4a* is more than ten times the concentration of copper found in the two other subsamples taken from sample *E4*. Because of this will the concentration of copper found in subsample *E4a* be assumed to be an outlier and not be used going forward.

Sample location	Cd μg/g sample	Cr μg/g sample	Cu μg/g sample	Ni μg/g sample	Pb μg/g sample	Zn μg/g sample
S1a	0.170	3.909	3.672	4.274	3.947	19.163
S1b	0.161	3.777	3.842	4.233	3.917	17.869
S1c	0.160	3.846	3.578	4.243	3.862	17.721
S2a	0.186	3.152	6.073	4.168	5.884	38.889
S2b	0.184	3.163	5.909	4.308	5.342	36.187
S2c	0.188	3.993	5.315	5.598	5.938	37.130
S3a	0.343	7.705	8.275	8.577	7.677	37.327
S3b	0.339	7.408	7.867	8.365	7.502	37.421
S3c	0.328	7.371	7.744	8.213	7.349	35.315
S4a	0.275	6.148	6.434	6.616	6.453	32.675
S4b	0.264	5.988	6.247	6.403	6.274	32.788
S4c	0.276	6.263	6.376	6.588	6.507	34.203
S5a	0.271	6.178	6.139	6.327	6.368	30.760
S5b	0.271	6.005	6.069	6.164	6.155	30.687
S5c	0.264	5.915	6.063	6.162	6.160	29.678
S6a	0.251	5.731	5.884	5.961	5.925	26.875
S6b	0.255	5.606	5.586	6.081	5.964	26.674
S6c	0.248	5.535	5.510	5.967	5.850	26.320
S7a	0.149	3.104	3.333	3.654	3.613	17.081
S7b	0.149	3.058	3.313	3.578	3.517	16.104
S7c	0.149	3.164	3.240	3.523	3.552	16.807

Tabel 5.5. Measured concentration of heavy metals for all subsamples in the S group.

In table 5.5 is shown the concentrations of heavy metal found in each subsample in sample group *S*. No meaningful differences are noticed between the subsamples of any sample site in this group of samples.

Sample location	Cd μg/g sample	Cr μg/g sample	Cu μg/g sample	Ni μg/g sample	Pb μg/g sample	Zn μg/g sample
N1a	0.172	4.535	4.085	4.952	4.242	19.462
N1b	0.174	4.628	3.985	4.925	4.188	18.605
N1c	0.175	4.805	4.100	5.073	4.392	19.378
N2a	0.151	4.024	3.400	4.057	3.749	16.924
N2b	0.158	4.019	3.429	4.196	3.859	17.882
N2c	0.158	4.375	3.454	4.241	3.844	17.427
N3a	0.052	1.319	0.930	1.255	1.853	5.705
N3b	0.051	1.264	0.980	1.276	1.945	5.671
N3c	0.049	1.496	0.915	1.232	1.886	5.410
N4a	0.089	2.308	2.018	2.671	2.406	10.195
N4b	0.088	2.406	2.244	2.741	2.460	10.730
N4c	0.089	2.358	2.111	2.683	2.387	10.464
N5a	0.127	3.077	2.890	3.625	2.859	13.426
N5b	0.127	3.058	2.832	3.625	2.766	13.238
N5c	0.133	3.061	2.849	3.656	2.805	15.843
N6a	0.073	2.361	1.771	2.638	2.320	9.096
N6b	0.079	2.283	1.775	2.624	2.371	9.224
N6c	0.077	2.374	1.835	2.703	2.331	9.332
N7a	0.033	1.045	0.980	1.135	1.077	4.342
N7b	0.034	1.154	0.663	1.170	1.083	4.267
N7c	0.035	1.196	0.674	1.189	1.073	4.306

Tabel 5.6. Measured concentration of heavy metals for all subsamples in the N group.

In table 5.6 is shown the concentrations of heavy metal found in each subsample in sample group *N*. No meaningful differences are noticed between the subsamples of any sample site in this group of samples.

Sample location	Cd μg/g sample	Cr μg/g sample	Cu μg/g sample	Ni μg/g sample	Pb μg/g sample	Zn μg/g sample
K1	0.150	2.714	10.686	2.961	4.075	20.195
K2	0.120	2.246	17.245	2.696	6.982	25.085
K3	0.103	1.999	4.179	2.249	3.644	20.760
K4	0.131	6.676	8.166	6.054	3.337	20.336
K5	0.045	0.847	0.879	0.992	1.373	6.264
K6	0.056	1.216	1.138	1.154	1.704	7.448
K7	0.051	1.052	1.054	1.158	1.657	6.882
E1	0.053	1.278	1.259	1.359	1.633	6.722
E2	0.039	0.965	0.768	1.024	1.207	5.013
E3	0.055	1.188	0.974	1.335	1.318	5.815
E4	0.061	1.657	0.831	1.722	1.544	7.962
E5	0.038	0.981	0.629	0.890	1.332	4.606
E6	0.035	0.661	0.765	0.794	1.501	6.248
E7	0.095	3.541	2.323	3.869	2.703	10.776
S1	0.164	3.844	3.697	4.250	3.909	18.251
S2	0.186	3.436	5.766	4.691	5.721	37.402
S3	0.337	7.495	7.962	8.385	7.509	36.688
S4	0.272	6.133	6.352	6.536	6.411	33.222
S5	0.269	6.033	6.091	6.218	6.228	30.375
S6	0.251	5.624	5.660	6.003	5.913	26.623
S7	0.149	3.108	3.295	3.585	3.561	16.664
N1	0.174	4.656	4.057	4.983	4.274	19.148
N2	0.156	4.139	3.428	4.165	3.817	17.411
N3	0.051	1.360	0.942	1.255	1.894	5.596
N4	0.089	2.358	2.124	2.699	2.418	10.463
N5	0.129	3.066	2.857	3.635	2.810	14.169
N6	0.076	2.339	1.793	2.655	2.341	9.217
N7	0.034	1.132	0.772	1.165	1.078	4.305

Tabel 5.7. Concentrations taken as mean of measured values with outliers removed.

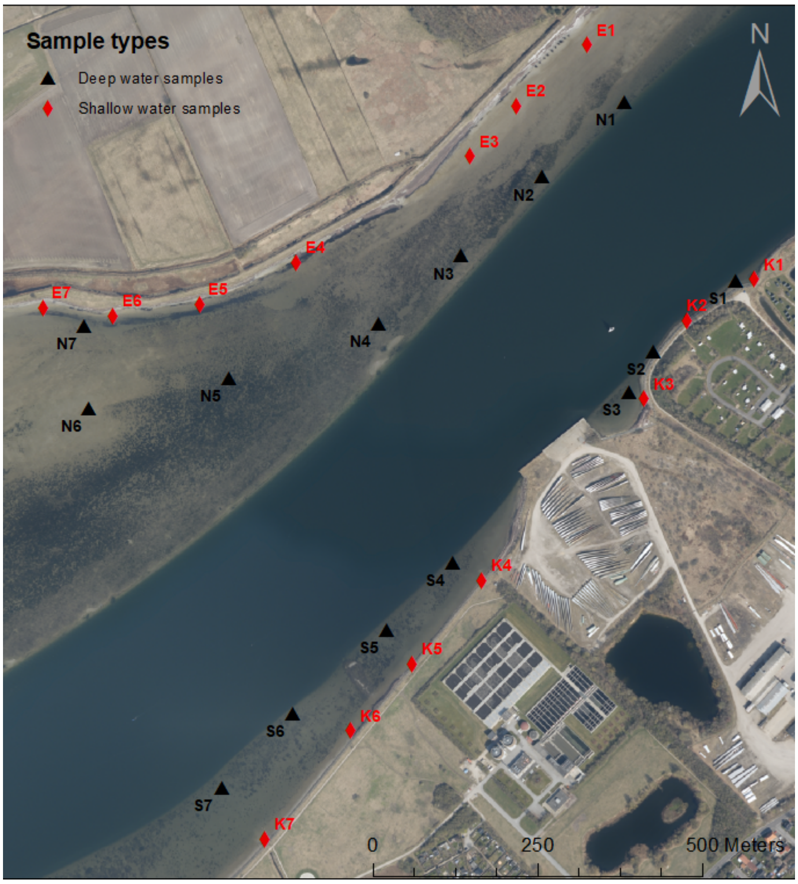
The concentrations for all sample locations was found by taking the mean of all subsamples. The exception to this being the copper concentration of subsample *K4b* and *E4a* that was removed for being outliers. The presence of these outliers were however mitigated by the use of triple testing as the mean instead could be taken of the remaining non outliers. The resulting concentrations are shown in table 5.7.

5.2 Data analysis

In this section will the acquired data be analysed and they will be compared to other types of data to find any correlation that might be between the the different types of data.

5.2.1 Concentrations by sample group

The concentration of heavy metal will be compared to each other as groups to see if any of the groups stand out among the others. This is done by comparing the measurements for each numbered point with the equivalent measuring point. To give an example will the measuring points *K1*, *S1*, *N1*, and *E1* be compared as being said equivalent samples. Additionally is the mean of the concentrations found in the sample groups compared. However due to the placements of the measure points, as can be seen on figure 5.11, sample *N7* is taken so close to shore in comparison to the rest of the *N* group that it makes most sense to remove this sample from the *N* group when comparing the means. Instead is the sample added to the *E* group due to its proximity the coast and the sample sites *E6* and *E7*.



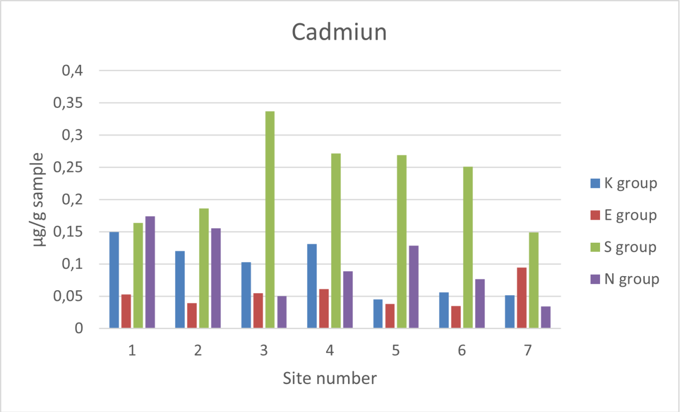
Figur 5.11. Placement of sample sites separated on types of sample.

Figure 5.11 show that sample sites *K1* to *K3* and sample sites *S1* to *S3* are close to each other. However none of these will be removed from their group due to the close proximity to each other. This is due to the small distance between the samples being caused by the proximity to the waterway therefore creating greater depths closer to the shore.

Cadmium

The concentrations of cadmium for each sample site are shown on figure 5.12. Site number is understood as the sample number in the group. This results in the concentration for the *K* group given as a bar in site 1 of the barplot equals the sample location *K1*.

When comparing the measured concentrations of cadmium in figure 5.12 it can be seen that the S group generally has higher concentrations of cadmium than the other sample groups. The exception to this is Site number 1 where the N group has the highest concentration but overall there is little difference between group K, S and N. Finally can it be noted that the E group has the lowest concentration of cadmium in all sites except for site *E7*. It can be seen that the concentration in site number 3 is especially high for group S compared to the other groups.



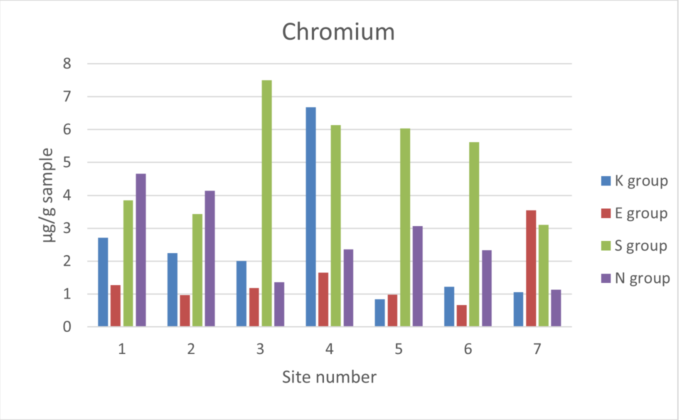
Figur 5.12. Figure shows the concentration of cadmium, given in μg/g sample, found in each sample site.

If the means of the concentrations are used to compare the samples the same result can be found with the S group having a mean concentration of 0.23 μg/g sample and the E group having a mean concentration of 0.05 μg/g sample. The K and N groups have mean concentrations of 0.09 and 0.11 μg/g sample respectively but as mentioned are several of the measured concentrations of cadmium near the detection limit or below it. This means that the accuracy of what can be said about the cadmium concentrations is limited to mainly saying that it looks like that the S group has the highest concentration of cadmium.

This gives the appearance that the average concentration of cadmium is bigger for the samples that are closer to the center of the fjord and the waterway compared to the samples sites that are closer to the coasts.

Chromium

The concentrations of chromium in the different groups are compared in figure 5.13. It can be seen that the highest concentrations of chromium is found in the S group except for Site number 7 where the highest concentration is found in the E group and thus sample site *E7*. It can be seen that the concentration in site number 3 is especially high for group S compared to the other groups. The K group has a concentration that is much higher *K4* than the concentrations found in the rest of the group.



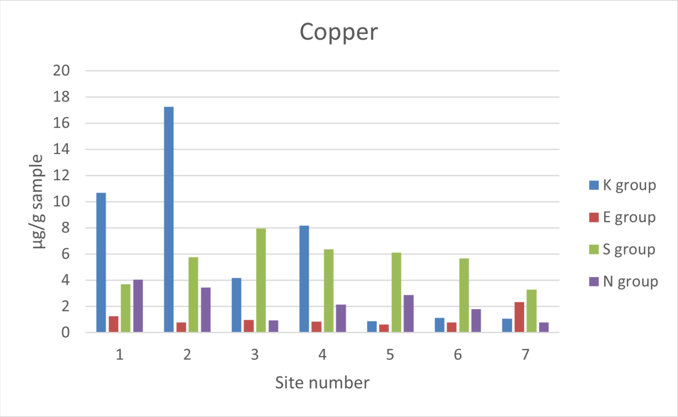
Figur 5.13. Figure shows the concentration of chromium, given in μg/g sample, found in each sample site.

When comparing the means of the chromium concentrations, it can be seen that there on the average is most chromium found on the southern side of the fjord with a mean concentration of 5.10 μg/g sample found in the deep water of the S group and a concentration of 2.39 μg/g sample in the shallow water where the K group is taken from. In comparison there is found a chromium concentration of 2.99 μg/g sample in the deeper water of the N group and 1.43 μg/g sample in the shallow water of the E group.

This gives the appearance that the average concentration of chromium is bigger for the samples that are closer to the center of the fjord and the waterway compared to the samples sites that are closer to the coasts.

Copper

The concentrations of copper in the different groups are compared in figure 5.14. The highest measured concentrations of copper are measured in the sample sites *K1* and *K2*. These concentrations are greater than any other found concentrations of copper and are found in the samples from near the coast. However it should be noticed that they are located at the point where the coast are at its closest to the waterway. It can also be noticed that the *K5*, *K6* and *K7* copper concentrations are very low in comparison the the other copper concentrations in the K group. The S group is more evenly split between sample sites and appear to have second highest concentration overall.



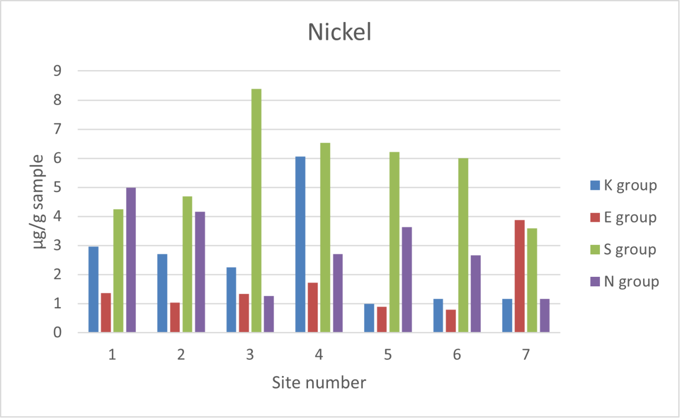
Figur 5.14. Figure shows the concentration of copper, given in μg/g sample, found in each sample site.

This can be confirmed when taking the mean of the copper concentration in the sample sites. The highest mean is found in the shallow water of the K group but this is heavily influenced by the Sample *K1* and *K2*. As a result of this is the mean concentration of copper for the K group 6.19 μg/g sample unless Sample *K1* and *K2* are omitted in which case it is 3.08 μg/g sample. This omission is the deciding factor on weather or not more heavy metals on average can be found near the coast or near the waterway on the south side of the fjord, due to the mean copper concentration of the S group being 5.55 μg/g sample.

On the north side of the fjord the average concentrations of copper are greatest in the deeper water of the N group at 2.53 μg/g sample compared to 1.04 μg/g sample for the shallow water of the E group.

Nickel

The concentrations of nickel in the sample sites can be seen in figure 5.15. When comparing the sample groups can it be seen that the samplegroup with the biggest overall amount of nickel is the S group. The two site number where the S group doesn't have the biggest concentration of nickel is due to *N1* having a larger concentration than *S1* and due to *E7* having a larger concentration than *S7*.



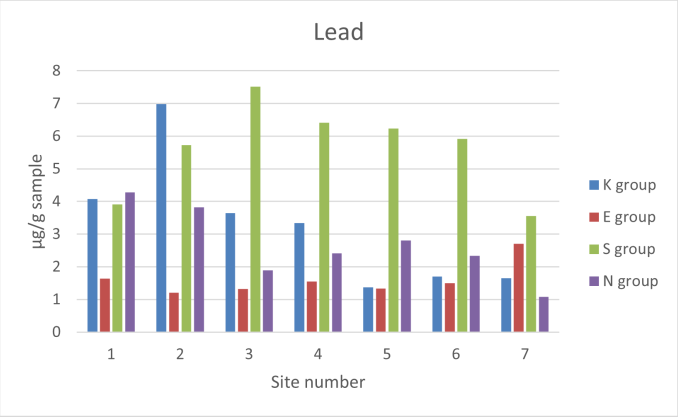
Figur 5.15. Figure shows the concentration of nickel, given in μg/g sample, found in each sample site.

When comparing the means of the nickel concentrations, it can be seen that there on the average is most nickel found on the southern side of the fjord with a mean concentration of 5.67 μg/g sample found in the deep water of the S group and a concentration of 2.47 μg/g sample in the shallow water where the K group is taken from. In comparison there is found a nickel concentration of 3.23 μg/g sample in the deeper water of the N group and 1.52 μg/g sample in the shallow water of the E group.

This gives the appearance that the average concentration of nickel is bigger for the samples that is closer to the center of the fjord and the waterway compared to the samples sites that are closer to the coasts.

Lead

In figure 5.16 it can be seen that the concentration of lead is relatively even in the values measured in the *K1*, *S1* and *N1* samples but lower in the *E1* sample. This is interesting because in figure 5.11 it can be seen that the sample sites for *K1*, *S1* and *N1* are taken close to the waterway while the *E1* is taken further away from the waterway hinting that there might be a connection there. Similarly is the largest concentration found in Site number 2, measured in sample *K2*. This sample is also taken in an area where the sampling location is closer to the waterway. Overall is the group with the highest amount of lead in most sample sites group S that with exception of the two mentioned sites contain most in any other equivalent sample.



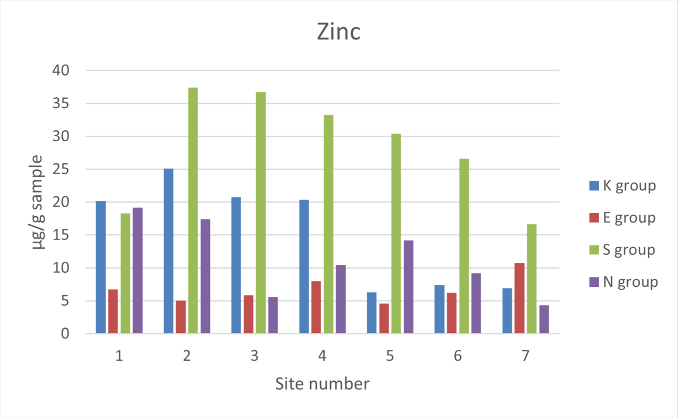
Figur 5.16. Figure shows the concentration of lead, given in μg/g sample, found in each sample site.

When comparing the means of the lead concentrations, can it be seen that there on the average is most lead found on the southern side of the fjord with a mean concentration of 5.61 μg/g sample found in the deep water of the S group and a concentration of 3.25 μg/g sample in the shallow water where the K group is taken from. In comparison there is found a lead concentration of 2.93 μg/g sample in the deeper water of the N group and 1.54 μg/g sample in the shallow water of the E group.

This gives the appearance that the average concentration of lead is bigger for the samples that is closer to the center of the fjord and the waterway compared to the samples sites that are closer to the coasts.

Zinc

When looking at figure 5.17 it can be seen that the group with the biggest concentration of zinc is the S group. Here it is only in site number 1 that higher concentrations can be found in the form of sample location *K1* and *N1*. It can also be noted that the group with the lowest concentration in most places is in the E group where the concentration is consistently low.



Figur 5.17. Figure shows the concentration of zinc, given in μg/g sample, found in each sample site.

When comparing the mean of the zinc concentrations, it can be seen that there on the average is most zinc found on the southern side of the fjord with a mean concentration of 28.46 μg/g sample found in the deep water of the S group and a zinc concentration of 15.28 μg/g sample in the shallow water where the K group is taken from. In comparison there is found a zinc concentration of 12.67 μg/g sample in the deeper water the N group is taken from and 6.43 μg/g sample in the shallow water of the E group.

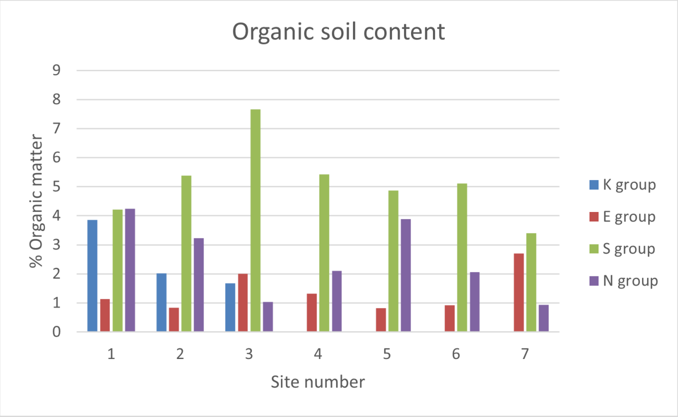
This gives the appearance that the average concentration of zinc is bigger for the samples that is closer to the center of the fjord and the waterway compared to the samples sites that are closer to the coasts.

5.2.2 Organic matter in the samples

Overall does it appear that there is a connection between how close the sample site is to the waterway and how big the concentration of heavy metals is. This means that more heavy metal are found at greater depth. However to be able to compare this there need to be some way to tell if its actually the case that there are more heavy metals at greater depths or if it is due to the limiting factors in the ability of the sediment to bind heavy metals. As such will it be investigated if there is any correlation between amount of heavy metals found in the sediment and the amount of organic matter measured in the samples.

For the analysis of the content of organic matter should it be noticed that there is no data for *K4* to *K7*, and that sample location *N7* still is treated as a part of group E due to its location.

When the content of organic matter is studied in the same way as the concentrations of heavy metal has been, it can be found that there are similarities between the percentage of organic matter and concentration of heavy metals. When studying figure 5.18 can it be seen that the biggest amount of organic matter is found in the S group. The group with the second highest amount in all sample is the N group. Both these groups can be noted to be deep water groups. This is also supported by finding the average percentage of organic matter in the sediment where the S group on a average has a content of organic matter on 5.2% while group N has 2.8%. Less accurate is the K group due to only having a known content of organic matter for 3 samples. It almost matches the content of the N group with a average content of 2.5% orgnic matter. Finally is the lowest amount of organic matter found in the E group where the organic matter is at 1.3 %.



Figur 5.18. Figure shows the percentage of organic matter found in each sample site.

When visually comparing figure 5.18 with the other bar charts is a noticeable similarity found. It can be seen that site number 3 for the the organic content has a high S group surrounded by comparatively small values for the other groups. This pattern is a repeat of a pattern seen on all the site number 3 concentrations, on the bar charts for the heavy metals, indicating a possible connection between the content of organic matter and the concentration of the heavy metals.

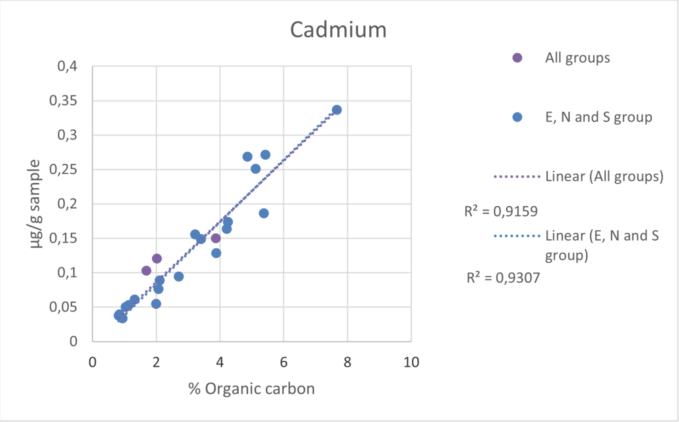
5.2.3 Correlation between organic matter and heavy metal

The correlation between heavy metal and organic content of a sample can be investigated by plotting the samples concentration of heavy metal against the content of organic matter. As shown on figure 5.18 is there no data for organic content for sample *K4* to *K7* and these will therefor have to be omitted from the comparison. These correlations, were using the definitions of LaMorte [2021], found to be very strong for cadmium, chromium and nickel while strong for zinc and lead but barely moderate for copper. In the case of copper, lead and zinc it was noticed that the samples from the K group were acting differently from the the other samples and therefor it was decided to investigate how this influenced the correlation. This along with the original correlation will be explained in the following sections.

Organic correlation with cadmium

When investigating the correlation between the concentrations of cadmium and organic material, the two set of data were plotted against each other.

When the organic content was plotted against the concentration of cadmium, it was found that the correlation was very strong. This can be seen on figure 5.19 where it is shown that the R^2=0.9159 for the correlation taken on all groups.



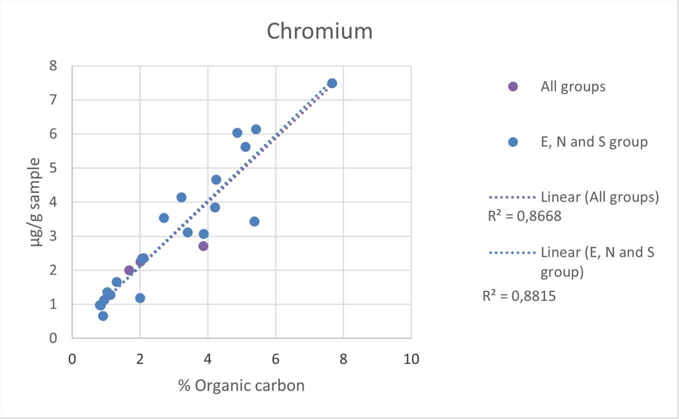
Figur 5.19. Shown are the correlations between cadmium and % organic content both with and without the K group.

However as mentioned it was seen that the K group was acting differently for some of the metals. It was therefore decided to remove the K group to see if their presence caused any change in the correlation between the metals and organic matter.

To do this was the organic matter and cadmium concentration plotted against each other for group E,N and S. In figure 5.19 can it be seen that the correlation value still is very strong with a R^2=0.9307 value. From this it can be seen that removing the K group doesn't seem to change the correlation between the concentration of cadmium and organic matter.

Organic correlation with chromium

When investigating the correlation between content of organic matter and the concentration of chromium the two sets of data were plotted against each other. First the plot was made including the K group. It can be seen on figure 5.20 that the correlation between the content of organic material and chromium was very strong with R^2=0.8668.

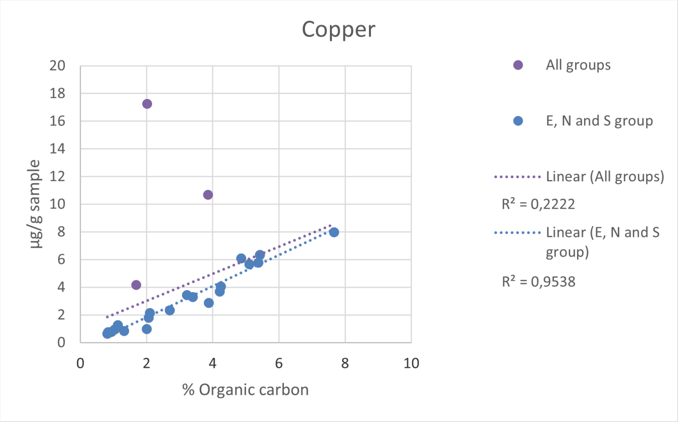


Figur 5.20. Shown are the correlations between chromium and % organic content both with and without the K group.

When checking if there is an effect from the K group, did figure 5.20 show that the R^2 value for the correlation between organic matter and chromium was R^2=0.8815. This meant the removal of the k group did little to change the correlation that still was strong and only increased marginally.

Organic correlation with copper

Figure 5.21 shows that the correlation between the concentration of copper and content of organic matter for all samples is weak. It can be seen that the correlation is weak due to the R^2 value being R^2=0.2222. On the figure it can be seen that 3 sample points has a much higher concentration of copper compared to other sample points of equal organic content. When comparing table 5.2 on page 32 and table 5.7 on page 36 it can be seen that the mentioned sample sites are *K1*, *K2* and *K3*.



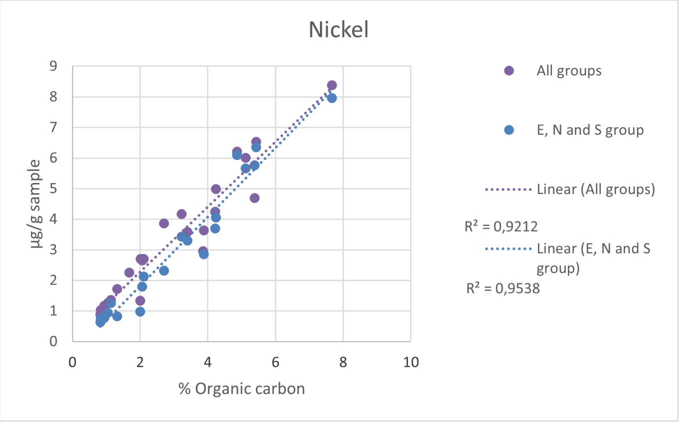
Figur 5.21. Shown are the correlations between copper and % organic content both with and without the K group.

To test if the three sample sites are influencing the correlation between the copper and organic matter is the K group removed and a correlation is taken using only the E, N and S group. This correlation can on figure 5.21 be seen to a strong correlation. From this can it be seen that the three sample sites in the K group are reducing the correlation between copper and organic matter.

The high correlation with the K group removed gives the appearance that the sample sites contains copper that is bound to the location without binding them self to the organic matter.

Organic correlation with nickel

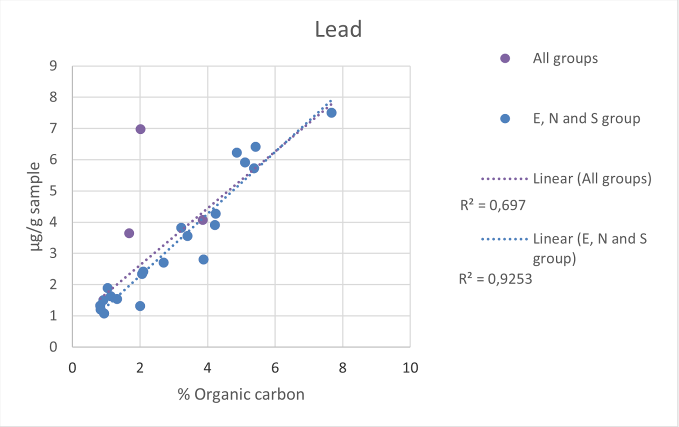
The correlation between the concentration of nickel and organic matter can be seen on figure 5.22. Similar to the correlations for cadmium and chromium are the correlations for nickel very strong both when calculated compared to all samples with R^2=0.9212 and without the K group with R^2=0.9538. However the correlation is still better without the K group even if marginally.



Figur 5.22. Shown are the correlations between nickel and % organic content both with and without the K group.

Organic correlation with lead

When looking at correlations between the concentration of lead in the samples and the concentration of organic matter using all samples can it on figure 5.23 be seen that the correlation between the two is strong despite the fact that one of the sample sites has a lead concentration that is noticeable higher than the other sample sites that also have 2% organic content.

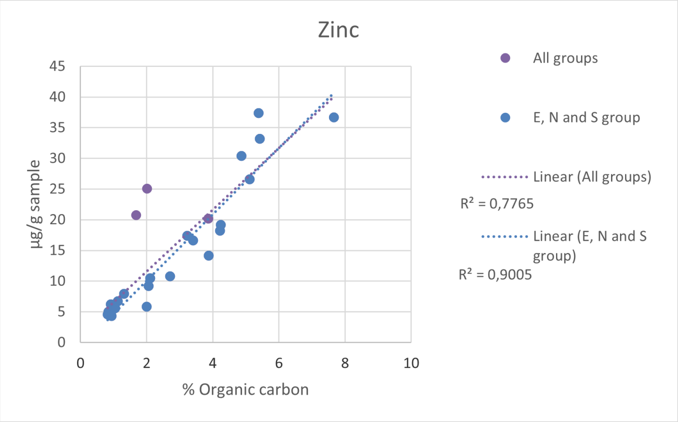


Figur 5.23. Shown are the correlations between lead and % organic content both with and without the K group.

A difference can be seen when this is compared to a correlation where the K group is removed. Once the K group has been removed from the sample can it be seen that the R^2 has increased from strong correlation of R^2=0.697 to a very strong correlation of R^2=0.9253.

Organic correlation with zinc

When looking at the correlation between the concentration of zinc and the content of organic matter, the correlation can be seen in figure 5.24 to be a strong correlation between the these two with R^2=0.7765. Like with lead can it be seen that there are samples that has concentrations well above what is expected.



Figur 5.24. Shown are the correlations between zinc and % organic content both with and without the K group.

When the K gruop is removed can it be seen that the correlation between zinc and organic matter turn from a strong to a very strong correlation with R^2=0.9005. This indicates that some of the samples in the K group aren't following the same rules for correlation between zinc and organic matter as the rest of the sample groups.

Correlations with organic matter

If the correlations where the K group has been removed are looked at as a whole it is clear that organic content is a important factor in the ability of the sediment to bind the investigated heavy metals. It was found that all heavy metals had a strong correlation with the content of organic matter. This also compare favorably with the findings that the highest concentrations of any given heavy metal was found in the groups located in the deep parts in the Limfjord. This was the same pattern found for organic matter.

As mentioned it was found that correlation between the organic content and concentrations of copper, lead and zinc were dependent on whether or not the K group was included. While the K group was included the correlations were significantly lower than when they were excluded. Given that only 3 sample sites act so differently from all other sample sites and only for 3 specific metals, it might be guessed that something is influencing these samples specifically. The fact that the samples *S1*, *S2* and *S3*, were taken near sample *K1*, *K2* and *K3*, didn't show same behavior as the K samples indicates that something in these K samples is influencing how much copper, lead and zinc that can be found in these locations.

5.2.4 Concentration per organic matter

Another factor that its worth investigating if it influences the concentration of heavy metal in the sample sites and possible influences the high amounts of copper lead and zinc found in the K group, can be caused by the most stable species being noticeable different from the other sample sites. To find this it would require knowing the concentration of heavy metal per unit of organic material. This can be found in table 5.8 that shows the concentration of heavy metal per gram of organic matter in each sample site.

Sample location	Cd μg/g OM	Cr μg/g OM	Cu μg/g OM	Ni μg/g OM	Pb μg/g OM	Zn μg/g OM
K1	3.88	70.26	276.66	76.65	105.51	522.84
K2	5.97	111.40	855.41	133.71	346.35	1244.32
K3	6.13	118.86	248.40	133.68	216.66	1234.16
E1	4.67	112.89	111.29	120.12	144.32	593.98
E2	4.68	114.89	91.38	121.95	143.74	596.91
E3	2.74	59.37	48.71	66.75	65.89	290.70
E4	4.65	125.80	63.10	130.77	117.23	604.57
E5	4.65	119.66	76.73	108.58	162.47	561.91
E6	3.84	72.28	83.65	86.85	164.21	683.41
E7	3.50	131.05	85.96	143.18	100.04	398.80
S1	3.89	91.22	87.74	100.85	92.76	433.10
S2	3.46	63.87	107.19	87.21	106.36	695.32
S3	4.40	97.79	103.88	109.40	97.98	478.69
S4	5.01	113.11	117.15	120.53	118.24	612.70
S5	5.53	124.06	125.25	127.86	128.07	624.66
S6	4.92	110.04	110.76	117.47	115.71	520.95
S7	4.37	91.39	96.88	105.40	104.69	489.93
N1	4.10	109.76	95.63	117.47	100.75	451.39
N2	4.83	128.46	106.37	129.24	118.46	540.31
N3	4.86	130.72	90.53	120.62	182.15	537.99
N4	4.22	112.19	101.09	128.42	115.05	497.91
N5	3.32	79.03	73.65	93.72	72.44	365.25
N6	3.70	113.31	86.87	128.61	113.38	446.46
N7	3.61	120.45	82.20	123.96	114.71	458.16

Tabel 5.8. Concentration of heavy metals per gram of organic matter (OM).

Any concentration of heavy metal per organic matter that is strongly influenced by another factor than the organic matter, through means unique to its sample site, should appear as a outlier in the data set.

Using the values from table 5.8 to find outliers can be done by finding the mean of the concentration per organic matter and then using the standard deviation (SD) to identify non-outliers with a 95% confidence interval.

	Cd μg/g OM	Cr μg/g OM	Cu μg/g OM	Ni μg/g OM	Pb μg/g OM	Zn μg/g OM
Mean	4.37	105.08	138.60	113.88	131.13	578.52
SD	0.83	21.79	160.97	19.62	56.87	225.19
SD*1.96	1.62	42.71	315.49	38.46	111.47	441.37
Mean + SD*1.96	5.99	147.78	454.10	152.34	242.60	1019.88
Mean - SD*1.96	2.75	62.37	-176.89	75.42	19.67	137.15

Tabel 5.9. Mean, standard deviation and 95% confidence interval for the concentation of heavy metal per gram of organic matter.

This is done using the mean value for each metal, shown in table 5.9, and the standard deviation for same. Any concentration from table 5.8 not present in the interval of Mean+SD*1.96 to Mean -SD*1.96, as shown on table 5.9, is an outlier. The way this should be understood is that if the outlier was above the interval there would be more of the heavy metal than expected using only carbon and if it was below then there would be less heavy metal than expected. It should be noted that it was not possible for an copper outlier to be less than expected due to the confidence interval ending in a negative concentration.

When comparing the found intervals in table 5.9 to the concentrations in table 5.8 it was found that there were several outliers. The Influence of these outliers could now be found by comparing them to what species was the most stable in a sample site which were shown in section 5.1.1. Should the outliers be caused by the stable species of the metal then they would be expected to match a sample location where the stable species were different for the rest of the sample sites. It might then explain why the sample site was an outlier. The two types of outliers would be expected to match to the two different types of phase that was found for the stable species. An outlier that is higher than expected would be expected to match an sample site where the stable species would be solid or crystalline, but the majority of the stable species for the other sample sites would be aqueous. On the contrary should a outlier with a value lower than expected the phase would be expected to be a sample site with an aqueous metal species among sites with solid species of metal.

Cadmium

The stable species for cadmium was the same aqueous metal species for all sample sites meaning that there is little connection to be found between the two outliers *K3* and *E3* that was respectively higher and lower than expected.

Chromium

The stable species for chromium was the same crystalline metal species for all sample sites meaning that there is little connection to be found between the phase of the species and the outlier that was found when the concentration of *E3* was lower than expected.

Copper

The stable species of copper was either on solid or crystal phase but there was no visible connection between the outlier that was higher than expected and the phase of *K2* where is was located. Nor was *K3*, that was on the line of being both solid and crystal, in any way different from the rest of the found concentrations.

Nickel

The majority of the sample sites had an aqueous species of nickel as the most stable species. Given that the outlier not only was lower than expected, but also was located in one of these sites, there was little connection to be seen between outlier and metal species.

Lead

The single outlier *K2* found for lead was located among the sample sites having a solid metal species as the most stable. These also made op the majority of the sites and thus no connection could be seen between the outlier and the phase of the stable metal.

Zinc

Stable species for zinc was the same aqueous metal species for all sample sites meaning that there is little connection to be found between the two outliers *K2* and *K3* both of which was higher than the upper border of the 95% confidence interval. Thus no connection between the stable species and the outlier was noticeable.

5.2.5 Site conditions and concentrations

As it was stated no connection was found between the species of metal and the outliers. This likely means that the variation in the concentration of heavy metal per organic matter cannot be explained by the stable species and therefore the concentration isn't heavily influenced by the pH and redox values of the sample site.

When comparing the average concentration of a metal in each group, as show on table 5.10, and comparing them to each other it can be found that there is no overall pattern in whether or not the highest concentration per organic matter is taken form samples at deeper water or not. It can however be noticed that the average concentration of copper, lead and zinc per gram of organic material is higher toward the edges of the fjord. For cadmium, chromium and nickel no such pattern can be found.

	Cd μg/g OM	Cr μg/g OM	Cu μg/g OM	Ni μg/g OM	Pb μg/g OM	Zn μg/g OM
E group	4.04	107.05	80.38	112.77	126.58	523.56
N group	4.17	112.24	92.36	119.68	117.04	473.22
S group	4.51	98.78	106.98	109.82	109.11	550.76
K group	5.33	100.17	460.16	114.68	222.84	1000.4

Tabel 5.10. Average value of concentration per g organic matter for each sample group. Groups is ordered by geographic order in north south direction and N7 is transferred to Group E due to proximity.

Discussion 6

The purpose of this project was to investigate the ability of local factors to govern the the ability of sediment in the Limfjord to bind heavy metals. The factors that the project would focus on were content of organic matter, stable metal species and water depth.

When the concentrations of heavy metals was examined was it found that, with the exception of copper, the highest concentration found on any side of the fjord would tend to be found in the group of samples found at deep water.

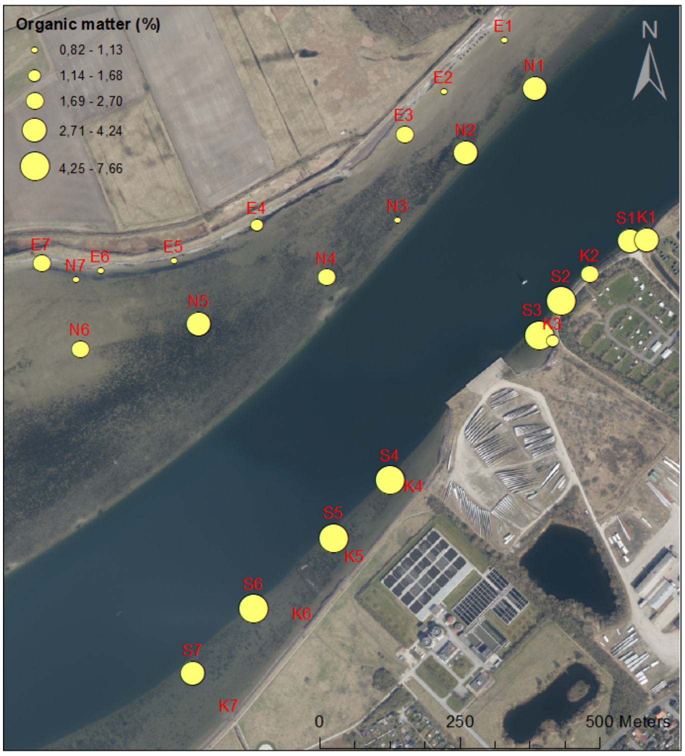
A similar phenomena would show it self for content of organic matter. When comparing the two groups found on one side of the Fjord, it would generally be found that the concentration of organic matter would be higher near the waterway and smaller closer to shore.

When the average content of organic matter and the average Concentrations of heavy metal were compared a pattern would reveal itself. The highest concentrations of either would always be found in the deep water followed by a lower concentration found in the shallow water sample sites. When comparing the two deep groups would it also always be visible that the biggest concentration of either heavy metals or organic concentration would be in the most southern group.

This seemed to indicate that the concentration of heavy metal was dictated by the concentration of the organic matter. While water depth didn't control the concentrations of heavy metals, it seem to have an influence on the content of organic matter. In most of the samples taken in shallow water the organic content would be less than the content taken in the deep water on the same side of the fjord.

This can be seen on figure 6.1 where the highest content of organic matter is found at the deeper water. It can also be noticed that the biggest concentration of organic matter was found on the southern side of the fjord. This could possibly be caused by the sewage overflow outlets found near sample site *S4*, but it does not seem to be the only cause since the organic matter isn't concentrated around this area. Alternatively is the organic content being moved in the waterway from west to east and this causes most of it to settle on the south side of the fjord.

It should however also be noted that he sample sites on the northern side is at a greater distance from the waterway than the ones the south side. It can in addition be seen on figure 6.1 that the N group sample sites with the highest content of organic matter is located in dark sections that show large patches of water foliage that the samples were taken among. Thus indicating a local source near these sample sites causing an increase in organic content for these locations.



Figur 6.1. Visual overview of the content of organic matter for each sample site and their proportional size in comparison to each other.

The organic material being moved in the deeper parts of the waterway is also being supported by how figure 6.1 shows that the smallest groups on their respective sides of the fjord are the E group on the north side and the K group. With the organic content of the K group, compared to the S group, being dependent on how sheltered the K site is compared to an equivalent S site. The best example is *K3* located in the inner parts of a small bay while *S3* is located near the outer edge of said bay. When these two are compared it is clearly seen that S1 has the greater organic content. While *K2* is lacking in shelter it is taken at much shallower water compared to *S2* again pointing at water depths influencing the content of organic matter. This can also be found to fit the difference in concentration between the samples from group E taken in shallow water at the coast and the samples from group N taken in deeper water near the waterway.

This would also fit with the correlations found in chapter 5 section 5.2.3 between the content of organic matter and concentration of heavy metals. Here it was found that all heavy metals, except copper had a strong to very strong correlation between the concentration of heavy metal and the content of organic matter. In addition it was found that this correlation would improve if the 3 used samples from the K group was removed. Removing the K group would also increase the correlation, from a weak correlation to a very strong correlation, indicating that the 3 samples were not acting like the samples in the other groups. This was additionally confirmed when it was found that whenever a sample would be an outlier with more of a heavy metal than expected then it would be either *K2* or *K3*.

The only samples to display much higher concentration expected according to the correlation with organic matter was *K2* and *K3*. This indicates the excess heavy metal could be caused by another source. While the other source cannot be identified with certainty some guesses can be made with basis in the local area.

The copper concentration per organic matter was at its highest in all sites from the K group even the ones that wasn't outliers. What is noticeable about this is that due to the shape of the the waterway and the slope of the fjord bottom was *S1* located more between *K1* and *K2* than away from the coast. Nonetheless was S1 not among the sites with high concentration per organic matter of copper but instead remained below the mean value for copper. The same could be seen for *S2* that also was located close to the coast and somewhat between the *K2* and *K3*. Finally was *S3* located in the only path between *K3* and a waterway as a whole but still didn't contain anything approaching the large concentration per organic matter of copper found in the K group. This seem to indicate that the copper concentration per organic matter isn't caused by something brought to the K group from the fjord. Instead it seems that the high concentration per organic matter follow the shoreline in the area of *K1* to *K3*. It is possible that the cost in the area contains copper from the masonry debris that was found on the stony semi beach in the area. It is possible that the copper found was small pieces of copper containing material and not bound in the sediment.

An alternative explanation might be the proximity to the nearby marina. For this to happen however it would most likely require that the copper containing material would have been drifting on the water surface before settling at the edge of the coast to avoid the deeper sample sites.

Disproportional high concentrations per organic matter of heavy metal in *K2* and *K3* were also found for zinc and high concentration per organic matter were found in both locations for cadmium and lead. This again points towards the marina due to both copper and lead having been used in anti fouling on ships and cadmium and zinc are in use in sacrificial anodes.

Finally was it found that no connection could be proven to exist between what species of metal were most stable in a location and the concentration of said metal in the location. The hypothesis was that locations where a metal would prefer to be a species on a solid or crystal phase would have a high concentration of said metal. When comparing the most stable metal species and their phase with the actual concentrations per organic matter found in in the sample sites no connection was found. This also meant that the most stable metal species didn't have any connection to the outliers for any of the metal.

When comparing the sample sites that had outlying values of heavy metal it was found that the species of metal would match the majority of species for that metal.

It was also found that in the case where sample *K2*, being the sample with the most outliers, had a stable species of nickel and solid phase that wasn't a part of the majority of stable nickel species, the concentration per organic matter of that metal was not an outlier. In addition there was a sample with a aqueous metal species with almost the exact concentration per organic matter of nickel per gram organic matter located near it.

This means that it it unlikely that the high concentration per gram of organic matter found in the K group is caused by the what the most stable species of cadmium, copper, lead or zinc were.

As a result of this it seems that the species of a metal in a location has no influence on the the ability of a metal to bind itself to that location, and that this instead is governed by other factors such a the content of organic matter.

Conclusion 7

Through out this project there has been focus on answering three hypotheses that was summarised in the following problem formulation.

How is the concentration of heavy metals bound in the sediment of the Limfjord affected by local conditions, such as organic content, stable metal species and water depth, and can a correlation be found between any of these conditions and the concentrations of heavy metal.

To answer this 28 samples was taken from the Limfjord. Tests were performed on the samples and this was used to test the three hypotheses of the project.

From studying the connection between the concentrations of the six heavy metals and the content of organic matter it was found that there was a strong correlation between organic matter and heavy metal. As such the first hypothesis that there is a correlation between organic content and heavy metal can be accepted.

While trying to test the second hypothesis the concentrations of heavy metal were used. No connection between the metal species found with the Pourbaix diagram and the concentration of heavy metal was found. For this reason is it not possible to accept the hypothesis and therefore the alternative null hypothesis, that there are no provable connection between concentration of heavy metals and stable metal species and that the Pourbaix cannot be used as a tool to predict if there is high or low concentrations of heavy metals in the area, had to be accepted.

When testing the third hypothesis it were found that the water depth and proximity to the waterway seemed to influence not the direct concentration of heavy metal but the content of organic matter in the area. Thus can the hypothesis be accepted as true on the condition that greater water depth and proximity to the waterway is increasing the heavy metal in the sample sites through the mechanism of increasing the content of organic matter in the sample sites.

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Appendix

A Raw ICP-OES measuring data

Subsample	Cd2144 μg/L	Cd2288 μg/L	Cr3593 μg/L	Cu3247 μg/L	Cu3273 μg/L
k1a	3.652	2.469	58.74	212.2	211.9
k1b	6.683	4.826	92.73	535.8	530.1
k1c	5.216	3.558	84.30	213.0	212.4
k2a	6.656	3.899	99.38	774.6	765.7
k2b	4.78	2.733	64.53	435.9	442.5
k2c	4.185	2.383	65.80	551.1	555.3
k3a	3.569	2.395	60.52	85.01	87.20
k3b	4.358	3.019	69.01	232.9	234.3
k3c	3.805	2.516	60.62	91.78	96.85
k4a	4.649	2.497	125.8	229.5	226.4
k4b	5.506	2.832	279.9	804.5	789.4
k4c	5.846	3.115	212.9	301.1	297.6
k5a	1.733	1.181	32.46	29.76	30.07
k5b	1.497	1.068	21.91	23.65	24.06
k5c	1.737	1.357	25.20	28.69	30.24
k6a	1.711	1.104	30.65	26.26	26.47
k6b	1.764	1.302	31.26	35.96	35.80
k6c	2.06	1.55	41.74	33.84	34.49
k7a	1.816	1.279	31.81	31.53	31.49
k7b	1.56	1.181	26.96	28.12	27.67
k7c	1.704	1.395	32.69	31.61	32.88
E1a	1.779	1.156	37.44	39.49	38.82
E1b	1.842	1.216	36.86	40.04	39.82
E1c	1.706	1.232	33.60	27.24	27.74
E2a	1.193	0.8103	26.09	21.08	20.61
E2b	1.443	1.042	28.26	22.82	21.75
E2c	1.628	1.163	34.71	28.12	27.27
E3a	1.866	1.408	36.81	27.93	28.13
E3b	1.905	1.342	34.16	29.00	29.14
E3c	1.868	1.326	34.30	29.26	29.37
E4a	2.002	1.251	44.68	381.9	373.7
E4b	2.384	1.654	52.45	42.95	42.54
E4c	1.599	1.057	36.87	27.38	27.17
E5a	1.449	0.9649	32.47	22.33	22.22
E5b	1.102	0.8056	23.55	14.90	14.54
E5c	0.9934	0.6809	21.52	13.01	13.22

Table 7.1 continued from previous page

	Cd2144	Cd2288	Cr3593	Cu3247	Cu3273
E6a	1.807	1.203	23.92	32.84	34.12
E6b	1.278	0.9093	21.41	20.38	23.41
E6c	1.116	0.7963	20.81	21.70	22.63
E7a	2.309	1.223	65.63	43.77	42.93
E7b	3.052	1.698	88.19	58.44	57.11
E7c	2.962	1.529	85.14	56.16	55.02
S1a	4.896	3.579	97.17	91.08	91.48
S1b	4.841	3.541	98.26	100.1	99.79
S1c	4.728	3.447	98.50	91.52	91.72
S2a	5.158	3.738	75.21	140.0	149.8
S2b	4.88	3.375	71.05	129.8	135.7
S2c	5.089	3.777	93.94	119.8	130.3
S3a	8.906	6.206	169.5	184.2	179.9
S3b	9.291	6.619	173.8	187.0	182.1
S3c	8.67	6.113	166.0	176.7	172.1
S4a	8.556	5.875	161.5	171.1	166.9
S4b	7.436	5.094	142.0	149.5	146.8
S4c	7.522	5.147	143.8	147.9	144.9
S5a	6.498	4.661	127.0	128.1	124.3
S5b	7.142	5.133	136.1	139.9	135.2
S5c	7.182	5.119	137.7	143.4	138.9
S6a	7.23	5.189	141.8	147.1	144.1
S6b	6.188	4.46	117.2	118.1	115.5
S6c	6.465	4.56	122.9	124.0	120.7
S7a	4.272	3.066	76.36	78.89	85.10
S7b	3.674	2.616	64.69	66.44	73.73
S7c	3.72	2.634	67.65	66.78	71.78
N1a	4.667	3.234	104.0	94.84	92.53
N1b	5.544	3.702	123.1	107.0	105.0
N1c	4.769	3.092	107.7	92.99	90.80
N2a	3.755	2.648	85.41	72.94	71.37
N2b	4.367	2.853	91.64	79.27	77.10
N2c	3.993	2.732	93.18	74.27	72.89
N3a	1.637	1.269	37.20	26.59	25.85
N3b	1.62	1.156	34.29	26.72	26.49
N3c	1.648	1.218	43.83	27.34	26.26
N4a	2.475	1.675	53.97	48.16	46.23
N4b	2.386	1.54	53.91	50.97	49.57
N4c	3.964	2.609	86.66	78.89	76.22
N5a	3.323	2.106	65.83	61.60	62.03
N5b	3.998	2.646	80.24	73.74	74.85
N5c	4.102	2.75	78.99	73.03	74.02
N6a	1.879	1.065	47.37	35.42	35.63
N6b	2.501	1.605	59.59	46.03	46.60

Table 7.1 continued from previous page

	Cd2144	Cd2288	Cr3593	Cu3247	Cu3273
N6c	2.168	1.347	53.90	41.33	42.00
N7a	1.527	0.8778	37.80	36.29	34.65
N7b	1.355	0.8301	37.55	22.15	20.99
N7c	1.593	0.9794	44.09	25.35	24.31

Tabel 7.1. Shown are the raw measurements of the concentrations of cadmium. chromium and copper. Data are given as microgram metal per liter solution.

Subsample	Ni2216 μg/L	Ni2316 μg/L	Pb2203 μg/L	Zn2025 μg/L	Zn2062 μg/L	Zn2138 μg/L
k1a	60.31	64.33	86.25	495.8	494.8	518.8
k1b	98.36	104.6	148.9	663.4	659.6	708.6
k1c	91.32	97.36	121.0	562.7	560.6	597.2
k2a	112.7	118.6	283.8	876.1	868.8	943.3
k2b	84.53	89.12	211.2	706.4	701.4	765.9
k2c	70.71	75.08	213.8	927.1	921.0	1002.
k3a	63.23	68.29	91.52	495.3	493.0	522.9
k3b	79.55	84.88	180.1	660.7	657.7	702.3
k3c	64.35	69.13	85.10	807.7	802.1	859.3
k4a	134.3	140.5	88.45	487.3	483.2	514.6
k4b	242.1	251.1	112.5	791.0	780.5	831.8
k4c	170.4	178.5	109.2	600.5	595.2	640.8
k5a	32.97	35.96	42.74	205.3	203.9	211.0
k5b	26.90	28.80	41.00	178.0	177.1	182.9
k5c	30.03	32.66	46.71	210.5	209.2	218.1
k6a	29.21	32.44	46.19	183.9	182.4	189.5
k6b	31.19	34.53	45.58	195.0	193.7	200.7
k6c	32.30	34.91	52.30	256.3	254.7	263.7
k7a	33.76	36.66	50.98	213.9	212.2	220.8
k7b	30.03	32.04	42.81	184.0	182.4	188.1
k7c	33.09	35.87	50.31	201.0	200.1	208.0
E1a	36.72	40.24	45.46	185.0	183.4	191.3
E1b	38.28	41.53	47.74	195.6	195.0	201.5
E1c	34.80	38.17	44.81	187.4	186.6	193.8
E2a	26.29	28.52	31.31	125.7	125.2	129.1
E2b	29.93	32.76	38.26	143.1	142.5	147.3
E2c	34.23	37.30	41.99	196.6	196.2	202.0
E3a	37.40	40.29	37.83	163.2	163.0	169.8
E3b	38.23	41.48	41.47	181.5	181.2	188.7
E3c	38.15	41.28	37.62	171.2	171.2	177.9
E4a	43.83	47.95	41.89	269.9	265.7	275.9
E4b	53.01	57.32	48.40	204.7	205.2	213.3
E4c	36.83	39.92	34.48	160.7	160.1	165.8
E5a	27.23	30.50	44.30	140.1	140.0	145.3

Table 7.2 continued from previous page

	Ni2216	Ni2316	Pb2203	Zn2025	Zn2062	Zn2138
E5b	20.76	22.93	31.68	113.5	113.2	116.5
E5c	18.23	20.80	29.34	107.2	106.8	110.0
E6a	31.89	34.96	56.62	359.8	358.6	372.6
E6b	23.13	25.68	45.54	153.5	153.9	159.2
E6c	21.45	23.57	48.38	136.0	135.0	140.5
E7a	69.84	74.10	50.75	203.6	203.1	213.6
E7b	92.68	98.04	68.20	268.4	267.1	283.6
E7c	90.99	96.33	63.46	254.8	254.9	268.2
S1a	103.4	109.1	98.12	476.4	476.0	506.4
S1b	107.1	113.1	101.9	464.8	462.2	495.3
S1c	105.6	111.7	98.90	453.8	453.4	483.5
S2a	96.38	102.5	140.4	927.9	925.4	1012.
S2b	93.45	100.1	120.0	812.9	808.9	877.3
S2c	128.4	135.0	139.7	873.6	870.2	955.6
S3a	183.3	194.1	168.9	821.2	818.1	885.3
S3b	190.9	201.6	176.0	877.9	875.6	948.2
S3c	180.0	189.9	165.5	795.3	794.1	857.5
S4a	168.5	179.1	169.5	858.3	855.6	918.6
S4b	147.6	156.1	148.8	777.6	775.9	827.1
S4c	146.8	155.7	149.4	785.3	785.6	835.4
S5a	126.3	133.8	130.9	632.3	630.5	662.4
S5b	135.7	143.7	139.5	695.5	694.0	730.7
S5c	139.3	147.6	143.4	690.9	688.7	726.5
S6a	143.3	151.7	146.6	665.0	667.0	708.4
S6b	123.6	130.7	124.7	557.7	557.1	590.7
S6c	128.7	136.3	129.9	584.4	583.4	620.9
S7a	87.11	92.66	88.89	420.2	419.1	451.8
S7b	73.40	77.99	74.40	340.7	341.2	365.2
S7c	73.09	77.59	75.96	359.4	359.3	382.8
N1a	110.2	116.9	97.27	446.3	445.7	471.9
N1b	127.2	134.8	111.4	494.9	496.2	526.3
N1c	110.4	117.0	98.44	434.3	433.9	458.8
N2a	83.35	88.87	79.56	359.2	359.4	375.2
N2b	92.63	98.71	87.98	407.7	406.0	427.3
N2c	87.35	93.30	81.88	371.2	372.1	388.3
N3a	33.92	36.88	52.25	160.9	161.3	165.8
N3b	33.02	36.25	52.77	153.9	154.4	158.7
N3c	34.73	37.47	55.26	158.5	158.6	163.2
N4a	60.54	64.40	56.27	238.4	238.9	247.7
N4b	59.60	63.23	55.11	240.4	240.9	249.2
N4c	95.36	101.8	87.71	384.5	384.6	404.2
N5a	75.12	79.97	61.15	287.2	287.5	303.2
N5b	92.34	97.88	72.58	347.3	347.8	369.0
N5c	91.63	97.05	72.39	408.8	409.1	433.4

Table 7.2 continued from previous page

	Ni2216	Ni2316	Pb2203	Zn2025	Zn2062	Zn2138
N6a	51.29	54.57	46.55	182.5	183.0	191.7
N6b	66.36	70.60	61.87	240.7	240.7	253.9
N6c	59.57	63.20	52.94	211.9	212.3	222.9
N7a	39.71	42.45	38.98	157.1	157.0	161.8
N7b	36.82	39.30	35.23	138.8	139.1	142.7
N7c	42.35	45.28	39.55	158.7	158.4	163.3

Tabel 7.2. Shown are the raw measurements of the concentrations of nickel. lead and zinc. Data are given as microgram metal per liter solution.