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Salt induced stratification and accumulation of heavy metals in the roadside lake, Kutjern

Erik Brækken
Environmental Science

Acknowledgments

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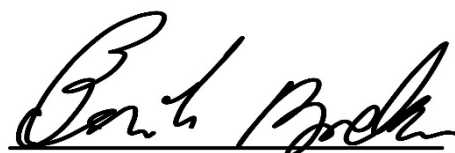
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Thank you.

A handwritten signature in black ink, appearing to read 'Erik Brækken', written over a horizontal line.

Erik Brækken

Ås, 15th of May 2024

Abstract

Road salt, commonly comprised of sodium chloride, is utilized to mitigate winter road icing by augmenting friction between car tires and asphalt (Norrström, 2005). Upon dissolution in water, NaCl dissociates into free Na⁺ and Cl⁻ ions, which are subsequently mobilized by rainfall and replace naturally occurring ions within soils and aquatic environments. Concurrently, heavy metals originating from vehicle abrasion are adsorbed to diluted salts and colloids, subsequently entering nearby aquatic systems during precipitation events. The principal objective of this study was to ascertain the stratification status of Kutjern and evaluate the extent of heavy metal accumulation within its water column.

Throughout this master's thesis, monitoring in Kutjern was conducted from May 25th to August 31st, 2023. Measurements were taken at one-meter intervals to assess parameters including oxygen concentration, pH, redox conditions, specific conductivity, and temperature. Additionally, weekly water sampling was performed to analyze nutrient and heavy metal content by using techniques such as filtration, color reactions, chromatography, and spectrometry. Comparative analysis with previous studies was undertaken, revealing if congruent metal concentrations and stratification patterns were present.

The findings unequivocally indicated meromixis in lake Kutjern, with a discernible chemocline forming around a depth of 4 meters. The lake retained a distinct temperature and saline stratification, impeding seasonal mixing during spring and fall. Notable deviations in physical parameters were observed, due to variations in precipitation and air temperature, during the summer of 2023. Anoxic conditions prevailing in the hypolimnion fostered reducing environments, facilitating release of heavy metals from the sediment surface, with elevated concentrations of Fe, S, and Zn in epilimnion. Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb had admittedly concentrations below toxic levels.

This research serves to elucidate the repercussions of road salt application on proximate water bodies, elucidating salt stratification dynamics and the accumulation of heavy metals. Moreover, it furnishes a foundational framework for subsequent investigations concerning the ecological ramifications of salt intrusion in roadside lakes.

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1. Introduction

Sodium Chloride or salt is a substance frequently used all over the world, due to its large quantities, chemical properties, and cost. As most substances extracted and used by man, the salt is eventually discharged back into nature. NaCl is not broken down in nature, and therefore a substance that severely damages ecological processes when led to land and water. Some of this salt is sedimented, but the remaining particles is spread into water and soils, where it affects natural processes through pollution and disturbance (Lazur 2020).

Salt is used to increase friction on roads, by removing ice and snow which prevents and lowers the risk of accidents (Statens vegvesen 2023). Salts should be applied according to each individual road's maintenance needs and winter classification. Roads classified as bare ground, like E18 - Ørje is applied with greater amounts of salt (Norconsult 2023). Since salt harms the environment, it is crucial that the application is not exaggerated, but sufficiently covers necessary requirements (Bjørnskau 2011).

E18 bypasses Kutjern and was expanded in 2021. The everyday traffic past Kutjern through the year (YDT) 2023 was 5750. A slight increase from the pandemic, according to Statens vegvesen's roadmap. Traffic data from Statens vegvesen, showed that in 2016 the YDT was estimated to 6730 (Dedikova 2023). Statens vegvesen have also listed their salt application for several years back for the part of E18 that bypasses Kutjern, which indicates that there has been a decrease in the total mass of applied salt. From 2012 until 2017, the average was 70,2 tons per km/season, (Wåhlin 2017) while the period from 2017 until 2022 was 10,8 ton per kilometer/season (Isaksen 2021). The amount of salt applied when the new road was built was 10.1 tons per kilometer/season in the first year (Statens vegvesen 2023). Salt application data and YDT from season 2023/24 has not yet been published, and according to personal communication with Ola Rosing Eide from Statens Vegvesen there are probabilities of reporting failure on behalf of Statens vegvesen.

Historical monitoring of salt application has shown that Statens Vegvesen has reduced their overall use of salt, considering geographical position and weather (Wåhlin 2017). Even though climate change is giving winter variation, more extreme weather in terms of wind, precipitation and higher temperatures, the application of salt on E18 Ørje should have decreased (Uleberg et al. 2014). Which is an important aspect in preventing amounts of salt discharging into Kutjern. When rain comes, the remains of salt get washed away into the nearest recipient (Bue 2013). In colder climates, rainy events occur under snowmelt in the spring (Norconsult 2023). By considering heavy metal accumulation by salt intrusion, this study and ongoing research, will hopefully provide evidence and results sufficient to indicate the sustainability of the life in lake Kutjern.

1.1 Properties of salt

Salinity is the total concentration of ions dissolved in water, either in aquatic or solid environments. In lakes with river systems, the salinity increases by evaporation and reduces by precipitation. Nutrient and mineral characteristics of inflow determines the total concentration of ions and its effect on water. There are multiple ways these ions can enter the basin. Either by physical or chemical weathering, oxidation and reduction reactions between soil and water or by exchange sites of minerals in soil water which is often dominated by Ca^{2+} and Mg^{2+} . By example the water that is saturated with Na^+ , Ca^{2+} and Mg^{2+} can gradually replace Na^+ . This Na^+ can be released as a free cation during periods of rain. With that said, there are several physical parameters that affect the exchange of ions in the basin. Such as depth, alkalinity, and groundwater exchange (Wetzel 2001).

Sodium Chloride is the most commonly used chemical to prevent icing on roads. Due to its environmental impacts, by corrosion and damage on cars and road constructions, more environmentally friendly alternatives are now desired. Statens vegvesen researched ways to replace sodium chloride as a friction medium during their project saltSMART in 2012 and are still trying to reduce amounts of salt applied to Norwegian roads (Amundsen 2008). So, this study will therefore elaborate how the salt is affecting lake Kutjern. Hence to heavy metals and salt intrusion. Since the stratification in Kutjern has been ongoing for several years (Wetzel 2001), the results of this study will be compared to previous years and relatable studies.

Without reducing friction between rubber tires and asphalt, physical and chemical properties multiplied with operational qualities like storage, handling and spreading, were compared to NaCl before evaluating if some salts of other kinds, was able to replace NaCl. Their research from 2008 concluded that CaCl_2 , MgCl_2 and K_2CO_3 among other salts and compounds, had the best qualities for replacing NaCl. CaCl_2 and MgCl_2 could even be applied together with NaCl as a subsidy to maintain the same traffic safety (Amundsen 2008).

In terms of ecological impacts, Ca and K can reduce the negative impacts of Cl by being better buffer elements. Otherwise, there is still needs to reduce the amounts of salt applied, even though this study does not give any recommendation of what's best or even what the better alternative for the environment is (Holen 2010).

1.2 Chemical composition- and mobility of heavy metals

Application of NaCl may interrupt the natural composition of cations in soil. If the cation exchange sites are dominated by Na^+ instead of Ca^+ , Mg^+ , Zn^+ or K^+ , the soil may experience temporarily decrease in pH and thereby increase the mobility of heavy metals. Over several years, lakes like Kutjern may accumulate metals like Fe, Cu, Pb and Zn from worn of parts of bypassing cars (Saunes & Værøy 2017). Their distribution of mass and concentration towards the basin is dependent on time and space. Temperature, chemical structure, O_2 concentration, pH and other physical factors are crucial. Depending on how the soil is suited for natural remediation, most of the pollutants from road will eventually be transported into the nearest basin. As explained metal compounds have different lag times (Amundsen 2008).

Metals from combustion and vehicle wear-off comes off the road in multiple ways like adsorption to soil, organic matter or clay minerals. Therefore, suspended solids and retention ponds allow metals to settle in highway environments. The soil fraction, metal properties and chemical composition of soil and water determine their mobility (Norrström 2005). Zn and Cd are especially movable in acidic environments and in soils with frequent ion exchange processes. Pb is harder to solve due to strong bounding to colloids. Zn and Cu are more soluble in water than by example Pb and Cd, which means easier transport into the nearest basin during periods of rain and runoff (Bäckström et al. 2004; Appelo & Postma, 1996).

Leaching of Pb and Cu is most likely to water transport of colloids. This happens when applied salt is followed by heavy rain (Amundsen 2008). Most heavy metals will be sorbed and eventually sedimented, while some stay free and soluble in the aquatic phase (Norconsult 2023). Cl and metals form metal complexes, according to a study done by Boekhold et. Al (1993). The study showed that 48% of Cd occurs as Cd^{2+} in 0.02 M Cl solutions with ionic strength of 0.03 M. Na may replace metals in soil exchange sites (Norrström and Bergstedt, 2001) and these two processes improve the leaching of metals (Norrström 2005).

Inflow of salts from other sources than roads is reflected by elevation of the lake. Increasing elevation means decreasing salinity. Ionic compounds and particles solved in rainwater are deposited at lower elevations. The salt's ability to fluctuate with evaporation from sea or land will also determine the amount precipitated into the basin (Wetzel 2001). Kutjern has minimal water flux and circulation throughout the basin, most of the salts in this lake are related to runoff from the nearby road of E18. According to Statens vegvesen's annual report of salts by *Isaksen* (2023) the climatic conditions were similar to earlier years, except for the amount of rain precipitated in the area. 20% above average values were found during spring. Since water is solvent to salts, the number of salts solved in rainwater increases by precipitation, and the nearest basin receives increased amounts of salts (Statens vegvesen 2023).

1.3 Stratification

Salty water has higher density than low ionic water and will sink towards the bottom of the lake. This layer requires more energy to be moved, and wind or turbulence

must be increased to help circulate the entire water column. Salt- or temperature stratification will therefore inhibit the process of circulation. Because when salt intrudes a lake over many years, the circulation of water does not proceed naturally. When saltwater falls through the water column and forms a layer in hypolimnion, it is isolating lower parts of the lake together with its nutrients, metals, and organic material (Norconsult 2023).

Diffusion of oxygen into water takes time, and to saturate water with oxygen from the atmosphere, the water must circulate. Ideal saturation is based on control of diffusion, mixing and saturation. Deviation in form of dissolved oxygen from photosynthesis or biochemical oxidations, can slightly impact the saturation (Wetzel 2001). Lake Kutjern has limited circulation due to stratification and limited primary production mostly in epilimnion, which is the reason to believe the lake is undersaturated (Bækken 2012). Extreme clinograde oxygen profiles can occur in meromictic lakes with a clear chemocline. When monimolimnion receives organic material or even sulfates from saline water, the oxygen intrusion depletes (Wetzel 2001).

Oxygen concentration is relative to content of salts in the water. Solubility declines exponentially with increasing salt content, which means seawater has 20% oxygen depletion compared to fresh water (Wetzel 2001). Kutjern is located in a climatic zone with seasonal variability. That means the physical, chemical, and biological processes are fundamentally driven by circulation in the lake and a great circulation of temperature through the water column (Figure 1). Stratification limits the distribution of nutrients as well as oxygen (Boehrer & Schultze 2008).

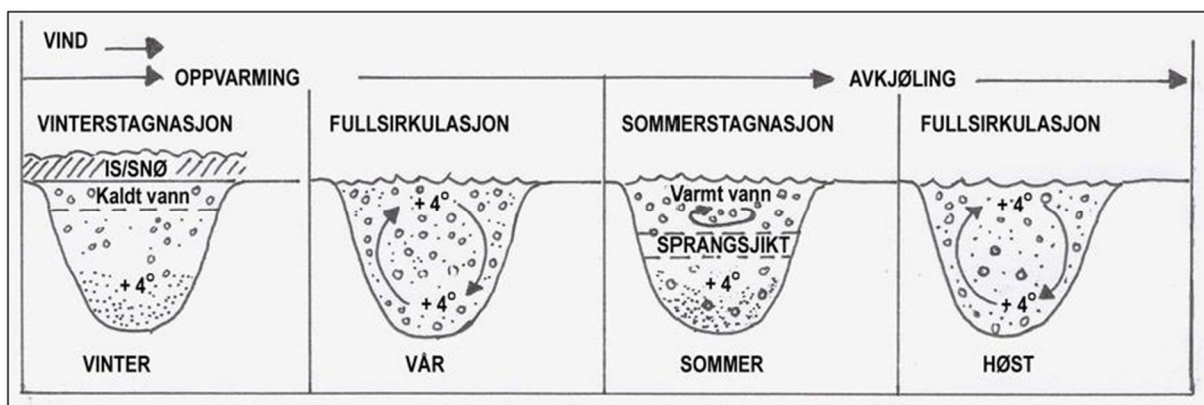


Figure 1 - Natural circulation of a lake (Norconsult 2023)

Over longer periods of stratification, respiration will decrease levels of O₂, due to consumption. Since there are little to no nutrients available for photosynthesis to proceed O₂ production in epilimnion, the lake will become anoxic with reducing conditions in the lower parts of the water column. The respiration of organic material in lakes recycles energy by turning organic matter into inorganic carbon. The relation between respiration and production determines the trophic levels of the lake and can

be related to whether the lake is net positive or negative in oxygen concentration. Rapid degradation of sediment or water without the supply of oxygen, might lead to oxygen depletion or anoxia. This is an important aspect of the ecological processes in the lake (Pace & Prairie 2005).

Microorganisms, plants and animals will mostly die during anoxia, because ecologically sustainable lakes have a yearly circulation and exchange water density with oxygen. Wind causes turbulence that eventually upwells water from deeper aquifers, making oxygen flux into rates substantial for respiration (Saunes & Værøy 2017). Anaerobic conditions happen because of the lack of sunlight for photosynthesis due to absorption in the upper parts of the epilimnion. With the respirational consumption of already produced O₂, some primary producers may be able to adapt and replace O₂ by using other electron acceptors. Nitrate, Iron, Manganese and Sulfate are examples which may produce H₂S and other toxins as biproducts, preliminary harmful to plant tissue when used as electron acceptors. Several unbeneficial ecological processes are likely to occur as well (Wetzel 2001).

A study done by Mattson & Likens in 1992, showed how different electron acceptors would suit decomposition of organic material in anoxic waters. 72% of carbon decomposition in the early summer happened in aerobic water. In the late summer when oxygen depleted, decomposition decreased by 26%, even with alternative electron acceptors available like sulfate, iron and methane. They would reduce efficiency and some organic material would even accumulate (Mattson & Likens 1992).

Thermal stratification occurs when there is different temperature in the vertical zones of a lake. Cold water with high density stays in the bottom layer, while the top layer is heated by sunlight. Due to algae or organic material, the sunlight may not be able to shine through the whole water column. Leaving absorption of heat to the upper parts of the lake. Only a few degrees difference is surficial to prevent mixing and create a thermal stratification of the lake (Yu et. al 2010).

By example in Kutjern, where depths from 2 - 3m and down towards the bottom, overall consists of a specter of lower temperatures from 6 °C and down to below 4°C. While there is temperature above 15 °C all the way to 20 °C in the first meter from the water mirror. This means sunlight and heat are absorbed in epilimnion and isolating the high-density water in hypolimnion. The turbulence created by wind is not sufficient to circulate heat and energy through the water column, due to large differences in density, the lake becomes meromictic with a temperature stratification (Wetzel 2001).

Salt stratification is represented by increased conductivity towards the bottom (Norconsult 2023). Low concentrations of oxygen can change redox potential and dissolve nutrients or metals from the sediment surface into the water column (Saunes & Værøy 2017). This chemocline is the reason why Kutjern is categorized as a meromictic lake because the circulation does not include the entire water column, nor

happens seasonally. Stormy events may bring turbulence into the water, by changing the mixing patterns and chemical composition (Meteorological data of Ørje 2024).

If the chemical composition of hypolimnion has been affected by anthropogenic activity over a longer period, the lake becomes anoxic, polluted or sedimented. These types of lakes are also called meromictic (Boehrer & Schultze 2008). We will now dive into how Kutjern is affected by road runoff and therefore make greater understanding of the chemical processes behind.

1.4 Reduction-oxidation reactions in deep waters

When prompted with “What affects redox conditions in lakes?” the Microsoft Copilot generated information indicating that reduction-oxidation (redox) reactions are a type of chemical reaction where the oxidation states of reactants change. In an oxidation, a substance loses its electrons or experiences an increase in oxidation state. For example, when iron rusts ($4 \text{ Fe(s)} + 3 \text{ O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3 \text{ (s)}$), iron atoms lose electrons to form Fe^{3+} ions. In a reduction, a substance gains electrons or experiences a decrease in its oxidation state. In the same rusting reaction, oxygen gains electrons to form O^{2-} ions (Microsoft 2023).

There are two main classes of redox reactions: Electron-transfer is when only one electron flows from the species being oxidized to the one being reduced. This reaction is related to redox couples and electrode potentials. Atom transfer is when atoms transfer from one substance to another. By example in rusting, iron atoms oxidize, and oxygen reduce (Boehrer & Schultze 2008).

The redox conditions in lakes are influenced by multiple factors:

Oxygen availability and the presence of dissolved oxygen (O_2) significantly impacts redox conditions, because in aerobic (oxygen-rich) environments, redox reactions tend to favor oxidation, when conversely, in anaerobic (low oxygen) conditions, reduction reactions dominate. Organic matter decomposition, because the breakdown of organic matter by microbial activity plays a crucial role for oxygen consumption. During decomposition, electron acceptors (such as O_2 , nitrate and sulfate) are consumed, leading to reducing conditions. In the absence of oxygen, anaerobic respiration take place and involves alternative electron acceptors like nitrate or sulfate. Nutrient cycling like nitrogen and sulfur cycles impact redox conditions because denitrification (conversion of nitrate into nitrogen gas) occurs under anaerobic conditions. Sulfate reduction leads to hydrogen sulfide release in sediments.

The different chemical properties of sediments (e.g., clay, sand, organic matter) affects redox reactions. Reducing sediments (rich in organic matter) promote anaerobic conditions, while oxidized sediments (with iron or manganese oxides) favor aerobic conditions. Water depth and stratification impacts thermocline formation in deeper lakes and leads to stratification, in which the oxygen depletion occurs in hypolimnion (bottom layer), resulting in anaerobic conditions. Human activities and pollution from agriculture, industry, and road runoff can affect redox conditions by

nutrient loading (e.g., excess nitrogen and phosphorus) which can alter the balance between aerobic and anaerobic zones.

Climate and seasonal variability like temperature, sunlight, and seasonal changes influence redox reactions by example through winter stratification that leads to oxygen depletion in deeper aquatic layers. In a summary, redox conditions in lakes is controlled by a complex interplay of biological, chemical, and physical factors, impacting nutrient cycling, heavy metal mobility, and overall ecosystem functionality (Microsoft 2023).

1.5 Release of heavy metals from sediment

Redox conditions affect heavy metals in lakes by determining their availability, mobility and toxicity. Various solid inputs in lakes like clay minerals, organic matter and oxides/hydroxides of Fe, Mn, and Al control the fixation. Heavy metals can be sorbed onto these solid surfaces thereby reducing their mobility. Low soluble minerals (e.g., sulfides, carbonates, phosphates) can precipitate heavy metals and thereby immobilizing them. Complexation can happen when organic matter is present (Microsoft 2023)

When it comes to redox conditions and metal release in lakes, there are a few parameters worth noticing. Oxidizing conditions (high redox potential) tend to increase heavy metal mobility. Dissolved oxygen also promotes the release of heavy metals from sediment into the water column. In terms of metal composition in aquatic systems, reducing conditions increase metal mobility. The redox gradient at the sediment-water interface controls mobility as well, while the changes in redox conditions may influence the persistence of heavy metals over time (Manahan 1994). We will now look further into these processes.

A study done by Dent et. Al 2014 indicates a clear relationship between oxygen concentration in the hypolimnion, and metal presence. By oxygenating hypolimnion in North Twin Lake - Washington, with a mean depth of 9.7m, the accumulation of mercury, iron and manganese nearly depleted into zero within a month. The flux of iron happens when Mn(IV) reaches Fe(II). Mn(IV) can be reduced abiotically to Mn(II) by accepting an electron from Fe(II). The result is oxidized Fe(III), which in its new particulate form settles out of the water column. Another loss mechanism for Fe(II) in hypolimnetic waters is through sulfide (FeS) precipitation. If sulfide concentration increases, hydrogen sulfide (HS^-) can bound to Fe(II), and form particulate FeS (Dent Et. Al 2014). Because Mn(IV) requires higher redox potential than Fe(II) to be reduced, particulate Mn(IV) can be reduced into soluble species, such as Mn(III) and Mn(II), in the upper parts of hypolimnion, where it accumulates in a relatively stable reduced form (Dent Et. Al 2014).

A drop in Cu concentration in the hypolimnetic water column, could be a result of coprecipitation with Fe(III) or even sedimentation. Early research has shown that Fe and Mn oxides could behave as sinks for dissolved Cu (Chadwick et al. 2006, Merritt & Amirbahman 2008). Fe(III) and Mn(IV) metal oxides can provide exchange sites for

the adsorption of numerous metals including Hg, arsenic, copper, zinc, and nickel (Davison 1993). In lake Kutjern, this process is also related to the concentration of Cadmium. Even though some heavy metals are nutrients for plants and animals in smaller concentrations, they are extremely toxic in larger quantities. How mobile and present they are for uptake, depends on the speciation and redox conditions. By example mercury, which is more toxic when methylated by anaerobic bacteria. Lead and cadmium are also significantly harmful, when made mobile and bioavailable (Manahan 1994).

A study done by Echeverria et al. 2003 showed that higher temperatures increased the sorption of metals by minerals. Simultaneously, increased temperature increases microbial activity, respiration and redox reaction rates, which may help release metals from sediment (Huang 2017). Salinization of aquatic ecosystems may relieve heavy metals by several mechanisms. Reduced pH leads to higher concentration of H^+ which increases the solubility of metals. Increased solubility can increase mobility and transport.

Changes in redox conditions due to salinization can increase the mobility, speciation, and complexation of metals. By example Manganese can change oxides into sulfides and thereby increase solubility. The formation of organic complexes or electrostatic forces also affect the mobility of heavy metals in sediments (Almaas Å. R., personal communication, 06th of March 2024). But first and foremost, the interest of this study is to see how pH and redox conditions can influence the release of heavy metals from the sediment surface into the water column.

Gao et. Al. 2023 researched the ecological effects of pH change in sediments, due to ocean acidification. The study enriched the sediments with CO_2 to increase acidification. Since the CO_2 levels in the atmosphere are rising, water basins are getting more acidic and results in low carbonate concentration, decreased pH and overall acidic environments. Water pH correlates to migration and retention of heavy metals, by directly determining the adsorption and desorption surface reactions and ion exchange processes on active surfaces. Water pH indirectly influences the dissolution and precipitation of organic matter, carbonate and sulfide as well as hydroxides. There might be significant change in metal concentrations by several orders of magnitude by changing pH even though metals behave differently, through their individual chemical and physical properties (Gao et. Al. 2023).

By example, cadmium is released in oxidizing conditions, as Cd^{2+} . It's considered more soluble than Zn^{2+} in acidic oxidizing solutions and adsorbed weakly to organic matter, silicates, or oxides unless pH rises over 6. Nickel on the other hand, is comparable to copper in stability, and forms bonds to softer organic ligands that contains nitrogen and sulfur. Under reducing conditions, Ni^{2+} incorporates sulfides that limits mobility. Under water saturation, oxygen depletion may cause series of redox reactions to buffer pH in sediments. These reactions influence metal solubility and the chemical forms of their ions. As some minerals dissolve or precipitate from the sediment surface, the redistribution of elements changes the chemical properties

of the soil. Particularly Fe and Mn oxides provide reoxidized soils with new reaction surfaces for heavy metal sorption (Balistrieri 1992).

The hypothesis of this master's thesis is therefore based on two statements:

H₀: The salt stratification shown in earlier research is permanent and still a problem.

H₁: Heavy metals from E18 – Ørje is solved and accumulated in Kutjern.

2. Method

2.1 Study site

Kutjern is located 68m east of E18 - Ørje (NVE 2023), with an area of 0,0148 km² 224 m above sea level. The lake and the nearby highway have formally been in the same catchment since 1959 (Wiik & Johansen, 2015). The lake, along with most of its catchment, lies above the marine boundary according to the Geological Survey of Norway (n.d.). The road has been upgraded multiple times, from being maintained with sand and gravel, to being extended into multiple highway lanes. The E18 was built and paved in the 1960's (Wiik & Johansen 2015). Notably, Kutjern was situated near the historical E18 Riksgrensen – Ørje highway, now known as Svenskeveien during the restoration. In 2017, the new section of the E18 highway was inaugurated at a more distant location from the lake (Amundsen, 2017). In proximity to the lake, there are several structures, including a skiing facility, an old gas station and a house (Google maps 2024). Most of these structures are linked to municipal wastewater treatment systems where Kutjern is unidentified as a recipient. However, one of the buildings features a sludge separator (Amundsen 2017).

The soil is mainly moraine deposition, and contains calcareous, humic water (Saunes & Værøy, 2017). The lake has a maximum depth of 8 meters but is generally shallow on average. Even though the area is connected to a larger bog, (NADAG 2024) surface deposits primarily consist of exposed rock and scant marine sediments. The lake is remote with a forest backline and a mountain of several windmills, which indicates an area filled with wind. It's connected to Holbekken/Upperudsälven catchment (NVE 2023). Water flow in the lake is determined mainly by precipitation and temperature. That is why Kutjern keeps a low turnover rate, due to its modest catchment size and considerable depth (Steiro 2022).

2.2 Water sampling

Water samples were made every week, in the period from 25th of May till 31st of August 2023. Samples were taken from each meter through the entire water column (1 - 8m) using a modified Ruttner water sampler (*Picture 1*). When using the water sampler, the container was connected to a measuring rope and lowered into the water. When preferred depth was reached, a solder that ran alongside the rope, was released from the water surface and thereby locking the sampler filled with

water. For each sample, 0,5 L of lake water was transferred into pre-washed plastic bottles.



Picture 1 - Showing a full water fetcher, where 0,5 L was transferred into pre-washed plastic bottles.

2.3 Multi probe

Depth profiles of oxygen concentration, pH, redox, specific conductivity, temperature and Chlorophyll a in depth were taken using an automatic vertical profiler with a YSI 6920 multiprobe. A new profile was taken every two hours. Resolution in depth was 4 cm. To make sure our data was collected properly, the probe was checked every week during the season, making sure it held its position in the water. Batteries were changed weekly to ensure that the coil was moving properly and sufficiently obtaining the data.



Picture 2 - Automatic vertical profiler with a YSI 6920 multiprobe

To minimize negative impacts of the samples, we went to the lab directly from the study site. We measured 200 mL of every sample in a measuring cup and then running it into an Erlenmeyer flask through a filter. This 200mL was poured into a funnel and by using a vacuum hose the water was simply pulled through. We will go through the exact details of methods used in the following.

2.4 Ammonium, total phosphorus, and orthophosphate

Ammonium-N, Tot-P, and PO₄-P were assessed by inducing color reactions in the samples. This resulted in color complexes from the absorbances measured, which reflecting the substance's concentration. Ammonium-N was determined using a modified Norwegian standard (NS 4746) with salicylic acid instead of phenol. Salicylate and hypochlorite were added to filtered water samples and diluted ammonium standards (QC3198) before a one-hour reaction period. Total phosphorous and orthophosphate were analyzed as per NS-EN 1189. Ascorbic acid and molybdate were added to samples, and reactions were allowed to proceed before measurement in 2 cm cuvettes using a Hitachi UH5300 spectrophotometer at 655 nm for NH₄-N and 880 nm for Tot-P and PO₄-P. The LOQs were 0.02 mg/L for NH₄-N, 0.0005 mg/L for PO₄-P, and 0.01 mg/L for P.

2.5 Nitrate, sulfate, chloride and total nitrogen.

The water samples underwent filtration using a 0.45 µm cellulose acetate membrane and GF/C fiberglass filters. They were then stored in a freezer until ion analysis. GF/C filters were placed in sealed 15 mL plastic containers and stored at - 21°C for future pigment analysis. 50 mL of untreated water samples were retained for metal and sulfur analysis. For Tot-P and Tot-N analyses, 10 mL of unfiltered water samples

were combined with potassium persulfate solution ($K_2S_2O_8$) and autoclaved at 121 °C for 25 minutes. Subsequently, 5 mL and 2 mL of the oxidized solution were added to Tot-N and Tot-P samples, respectively.

Ion concentrations of nitrate, sulfate, chloride, and total nitrogen were measured using ion chromatography. Filtrate samples were passed through an Lachat IC5000 ion chromatograph from Zellweger Analytics with an ASX-500 series autosampler, adhering to the Norwegian Standard NS-EN ISO 10304-1. Diluted certified standard samples, ION-96.4 and REF-IC was used as templates. Limits of quantification (LOQ) were set at 0.02 mg/L for NO_3-N , 0.12 mg/L for SO_4 , and 0.08 mg/L for Cl^- . Total nitrogen (Tot-N) was determined using the same instrument and the Norwegian Standard NS 4743, with an LOQ of 0.02 mg/L.



Picture 3 - Weekly set up of labwork.

2.6 Metals

Metal concentrations were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) following the Norwegian Standard NS-EN ISO 11885. The analysis was conducted by trained personnel on an Agilent 8800 ICP Triple Quad after nitric acid digestion using an UltraClave. The LOQ for Fe and Mn was 0.000 mg/L, with standard 1643H used as a control.

2.7 Dissolved Organic Carbon

Dissolved organic carbon (DOC) in filtrated samples was quantified based on the Norwegian Standard NS-EN 1484 using a Shimadzu Total Organic Carbon Analyzer

(TOC-VCPN) with an ASI-V autosampler. Inorganic carbon was removed by acidifying samples with HCl and purging with purified air. Non-purgeable organic carbon (NPOC) underwent oxidative combustion at 680 °C, and DOC was detected as CO₂(g) using a non-destructive infrared analyzer. The LOQ for DOC was 0.3 mg/L (Steiro 2022).

2.8 Statistical analysis

We categorized our data in an excel spreadsheet before we transferred them to Minitab for a PCA (Principal Component Analysis). The analysis was based on how the metals correlated in 0 - 4 m depth and 4 – 8 m depth. The PCA included a linear two-dimensional reduction technique applied for visualizing correlating data. The data is visualized in a coordinate system, where the direction of each parameter, by example pH, O₂, redox, Cu, Fe, Cd equals their variation (Wikipedia 2024). Furthermore, we analyzed the same dataset through a SPCR-analysis (Spearman's rank correlation coefficient), in which the relationship between two variables is valued in a monotonic function. Because the Spearman method is either linear or not, the perfect value of correlation is 1 or -1 (Wikipedia 2024).

3. Results

3.1 Meteorology

According to meteorological data from the Norsk klimaservicesenter, there was deviation in air temperature and rain, from the average in Østfold in the sampling period. The Median temperature varied between 10 °C to 15 °C, but some days had changes from 27 °C in the daytime and 10 °C in the night. Amounts of precipitation was low in the end of May and start of June. May was the driest month, with only four days with precipitation and 9,5 mm/day at most. June had precipitation in four days as well, but with 12,8 mm/day at most. Without any specific pattern, some days included large quantities of rain, possibly eroding soil- and road deposited materials to the lake and increasing the water level. 25th of July had 36,5 mm precipitation, while 27th of August had 96,3 mm in Ørje, Østfold.

In terms of air temperature, the coldest day was 29th of May with 9.2 °C in average. The hottest day was the 17th of June, with 21.8 °C in average. May was indeed the coldest month, while June was the hottest month. Overall temperatures were over 10°C throughout the sampling period according to Norsk Meteorological data of Kutjern (2024)

3.2 Water temperature in Kutjern

There was a definite correlation between stratification and temperature at the beginning of the sampling period. From 20 °C in the first centimeters of epilimnion and down to 12 °C from 1 m and beyond. After 2 m, the temperature sank rapidly down to 4 °C. Figure 2 shows that 25th of May had 20 °C the first meter, while 27th of May had 14°C. There was deviation within each day as well, but it only affected the first two meters (*Figure 2*). 14th of May to 22nd of May had increased temperatures in the first meter, reaching 25 °C at most.

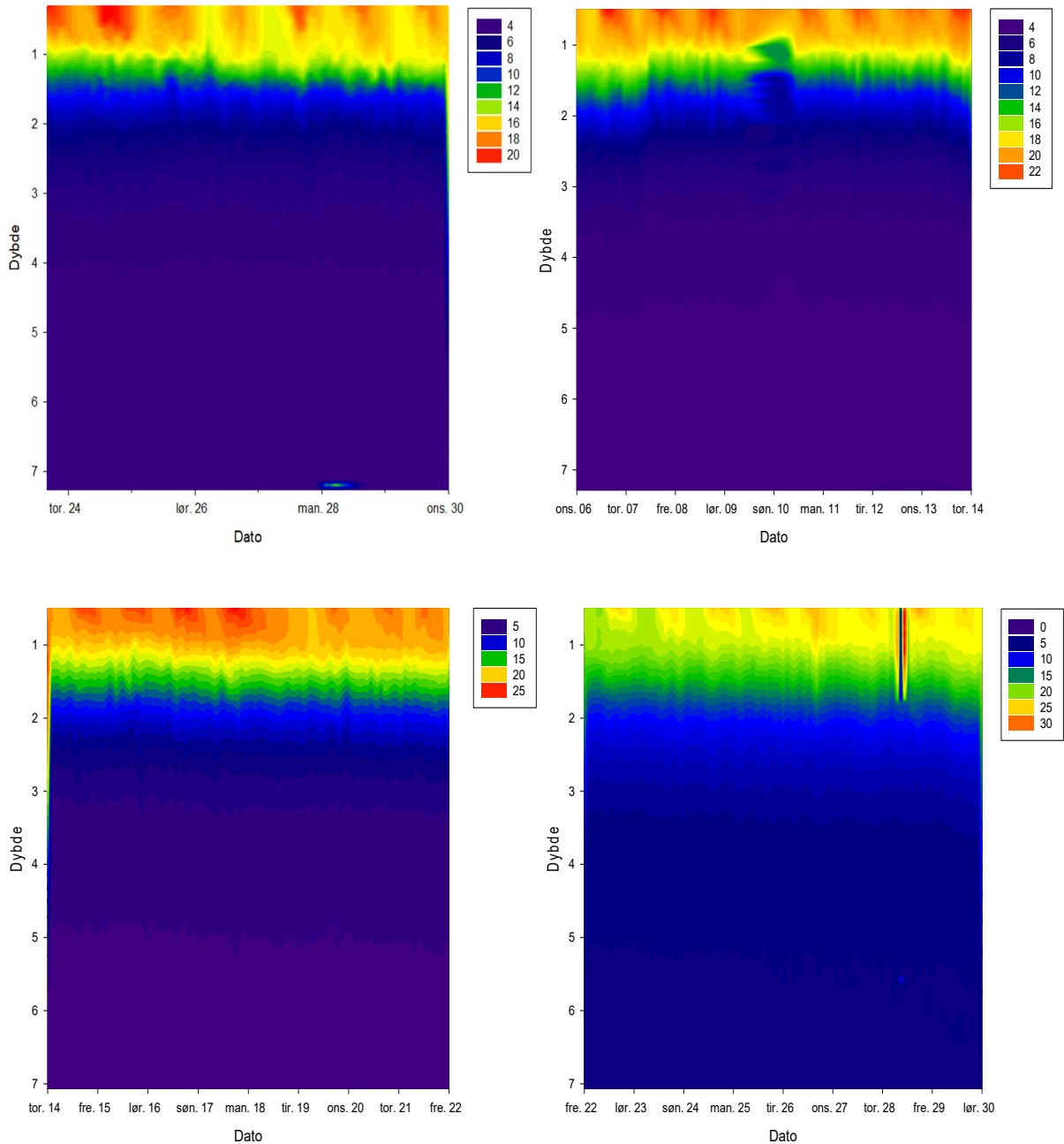


Figure 2 - Depth profile of temperature collected with the sensor from 24th of May to 30th of June distributed over four diagrams.

30th of June till 16th of July had elevated temperatures had extended down the water column. Making 10 °C approaching 3 m of depth. The first 8 days of this period the temperatures were between 15 °C and 20 °C and the first meter had temperatures from 15 °C to 25 °C. The distribution of heat in the first meter varied from 20 °C to 15°C. The temperature distribution gradually dipped further into the water, indicating that the temperature stratification was migrating deeper into the water column. More heat was registered in the first meter the last week of this period. In the period from 16th of July to 02nd of August (*Figure 3*), the temperature continued to reach further down in the water column.

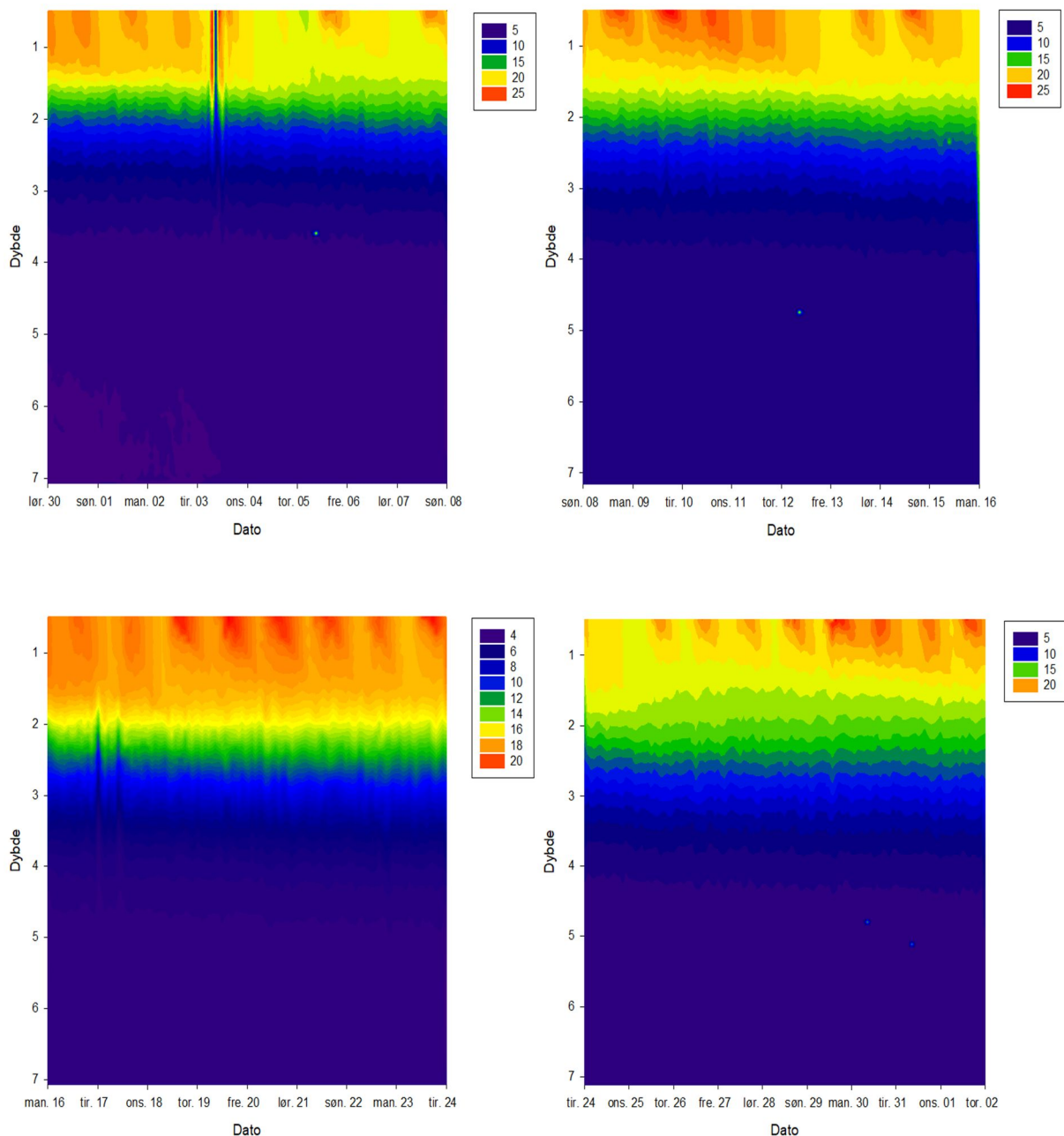


Figure 3 - Depth profile of temperature collected with the sensor from 30th of June to 02nd of August distributed over four diagrams.

The period from 02nd of August to 18th of August had decreased temperature. From increased temperature the first week of the period to decreased temperature the second week of this period. The second week temperatures of 14 °C reached 2.5 m. Both weeks had temperature stratification, and the first week had more rapid decrease in temperature from 2 m to 4 m, while the second week had already decreased temperature down from the water mirror followed by decrease from 2 m to 4 m of depth. The last two weeks of the sampling period, most of epilimnion had been heated. The first week had increased temperature in the first meter compared to the previous week. The 27th of August, (*Figure 4*) temperatures had lowered the depth but decreased in the first two meters. The temperatures slightly changed from day to day, with some days increasing or decreasing temperature.

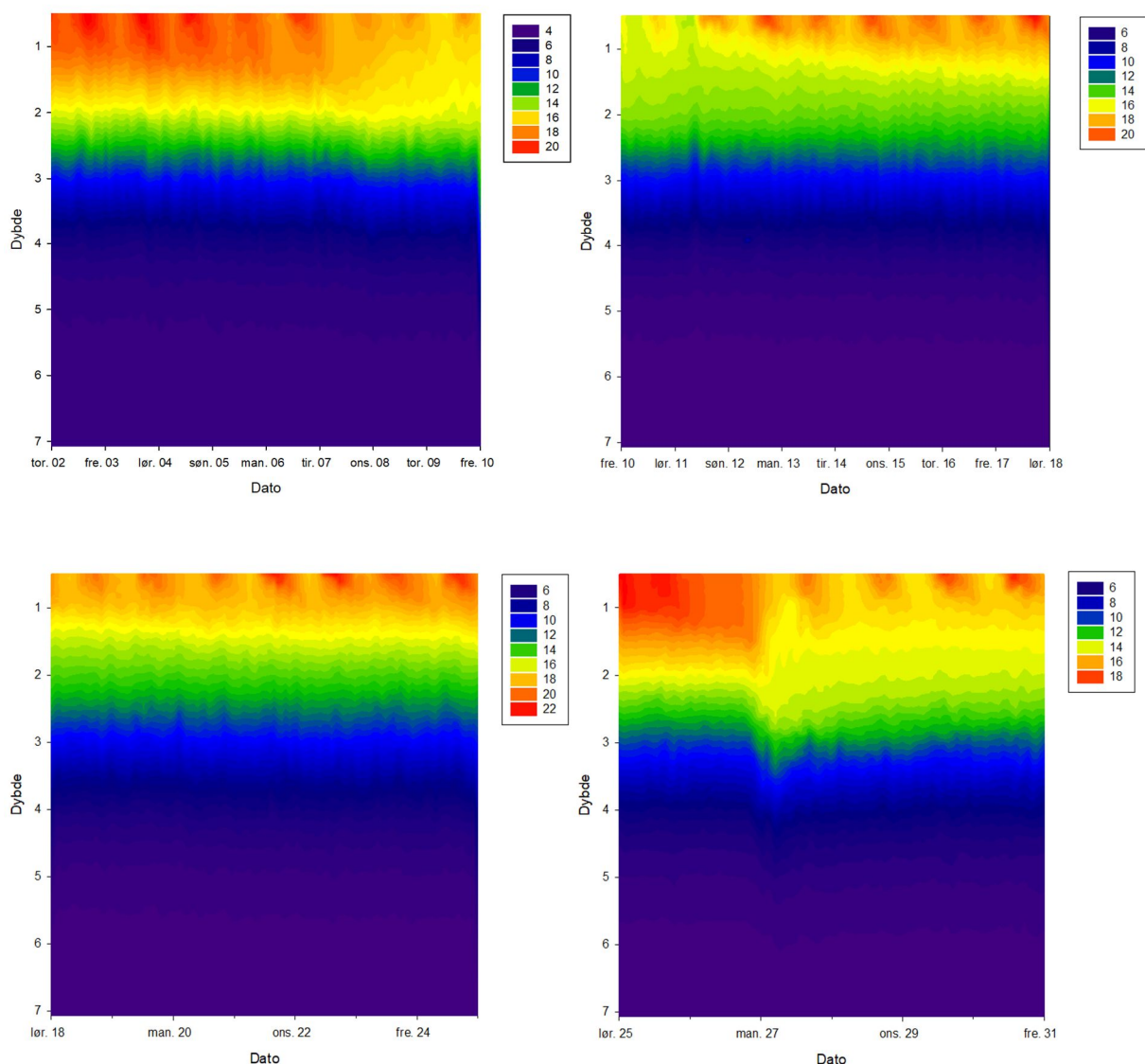


Figure 4 - Depth profile of temperature collected with the sensor from 02nd of August to 31st of August distributed over four diagrams.

3.3 Oxygen

Kutjern had an oxygen surplus in the first two meters from the surface. While there was an oxygen deficit in most of the water column from 4 m and down. The range 2 – 3 m varied, and the oxygen distribution in metalimnion stretched down to 3 - 3,5m in the end of May, as we see in figure 5. The following two weeks from date 14th of June to 30th of June had somewhat equal distribution of oxygen. The first meter consisted of 8 mg/l to 10 mg/l, while there were 5 mg/l distributed down to 1,5 m (Figure 5).

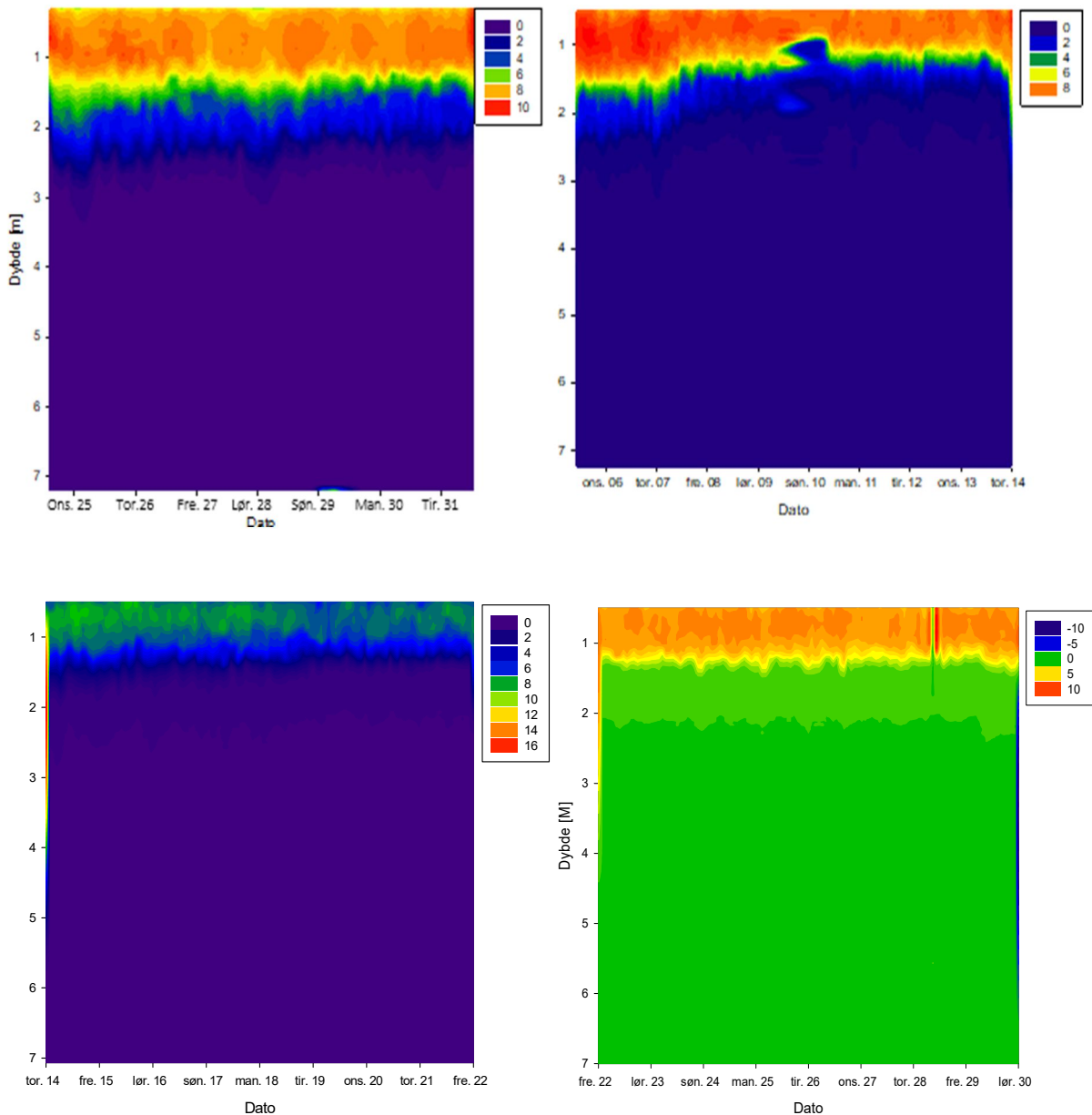


Figure 5 - Depth profile of oxygen concentrations collected with the sensor from 25th of May to 30th of June distributed over four diagrams.

In the first two weeks of July, more oxygen was distributed down towards 2 m of depth. The first two meters especially in the second week of this period, was evenly distributed with oxygen within each depth. Deeper down in the water column there was a sudden drop resulting in undersaturated water below 2 m of depth. The first two weeks of July had similar oxygen levels as the previous weeks, but there was uneven distribution in some depths. By example 10th of July, oxygen distribution only reached through the first 2 meters, while days like 14th of July the distribution was lowered by centimeters (Figure 6). From 8th of July to 16th of July, the oxygen depleted from 8 mg/l to 0 mg/l from below 2 m of depth. Oxygen was distributed further down the column in the last week of this period because the layer of stratification moved further down.

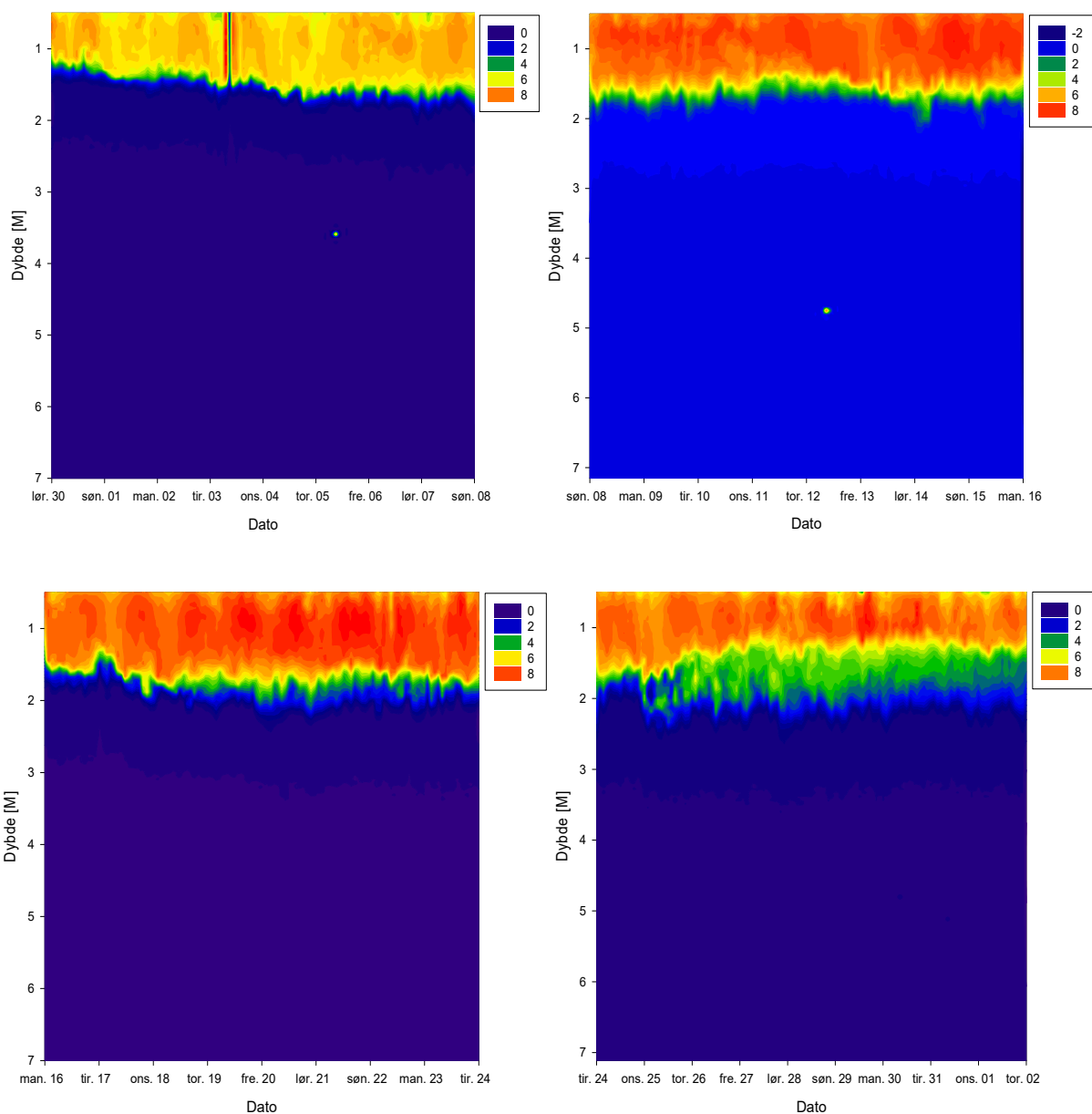


Figure 6 - Depth profile of oxygen concentrations collected with the sensor from 30th of June to 02nd of August distributed over four diagrams.

02nd of August till 18th of August had decrease in oxygen concentration below the first meter. From 02nd to 8th of August O₂ concentrations were measured to 8 mg/l in the first 1.5 meter. The concentrations went from 8 mg/l towards 8th of August and dropped down to 6 mg/l towards the 18th at 1,5 m of depth. From 10th till 18th of august there were measured higher concentrations of oxygen per depth down towards hypolimnion. Distribution of oxygen was inconsistent from day to day in epilimnion, where the stratification layer divided oxygen concentrations below 1,5 m during the period of Figure 7. Decreasing concentration was found in the two first meters for the last two weeks, even though the stratification layer moved down towards 3 m the last days of sampling.

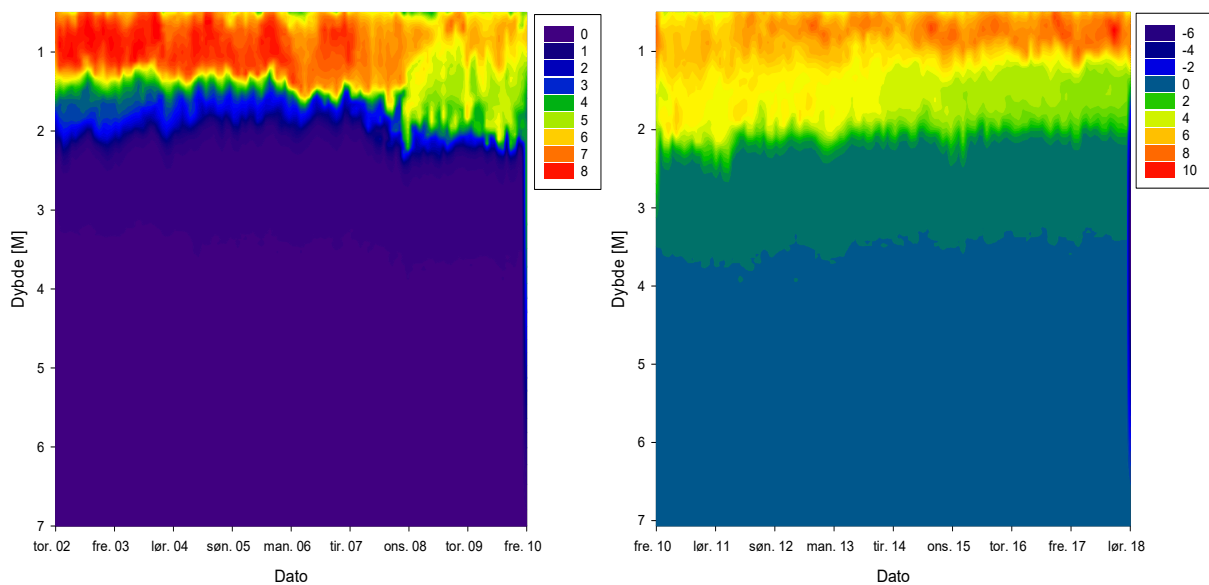


Figure 7 - Depth profile of oxygen concentrations collected with the sensor from 02nd August to 18th of August distributed over two diagrams.

In the period of figure 8, depth varied O₂ concentration. The first week of this period had lower concentrations than the previous between 1 m and 2 m. In the second week of this period, the oxygen levels increased from 1,5 m to 2,5 m. 27th of August till 31st of August had oxygen distributed down towards 3 m from 1,5 m. 2 mg/l of oxygen was found at the same depth 8 days before. 27th of august had an increase in oxygen at 8mg/l towards 3m. That was the highest measurement in oxygen concentration at 3m of depth during the whole sampling period. From 4 m and down there was lack of oxygen through the whole season (Figure 8).

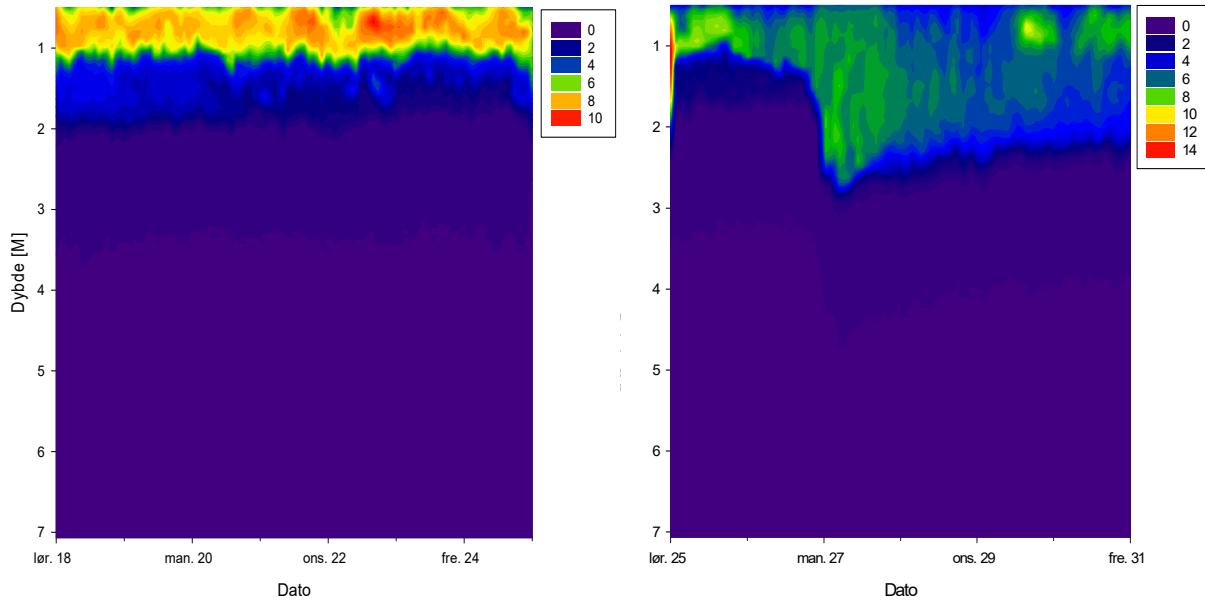


Figure 8 - Depth profile of oxygen concentrations collected with the sensor from 18th of August to 31st of August distributed over two diagrams.

3.4 pH

pH was measured between 5 - 6 across the entire water column with smaller deviations. Stable values was often measured within in each depth. There was a clear decrease in pH values between 1 m and 2 m for most days of the sampling period, but with smaller deviations in hypolimnion. Sunday 10th of June had a drop in pH down towards 4 m, temporarily increasing acidity in this area. 22nd to 30th of June varied between 5.8 and 6.0 at 4 – 5 m of depth (Figure 9).

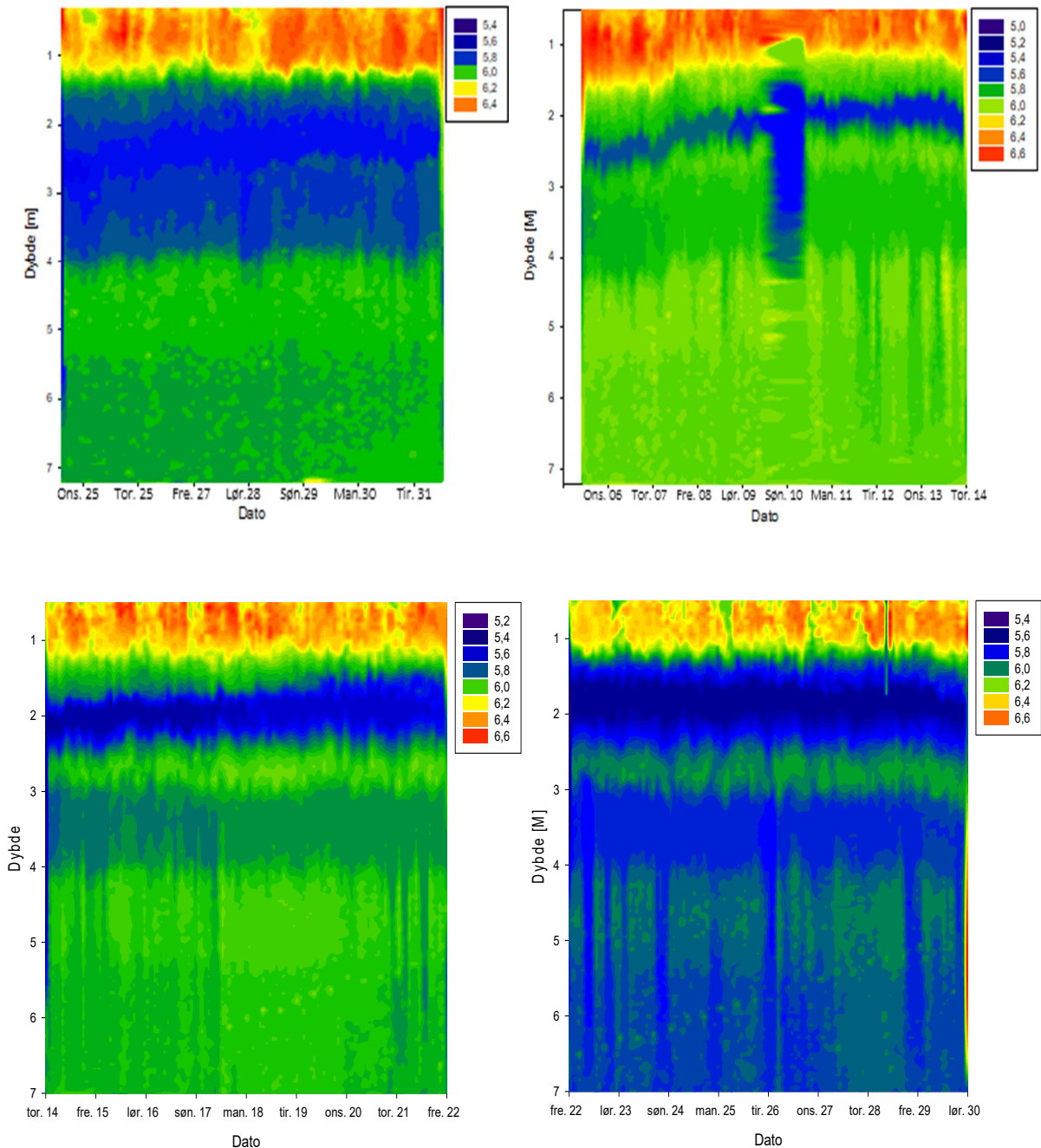


Figure 9 - Depth profile of pH collected with the sensor from 25th of May to 30th of June distributed over four diagrams.

From 30th of June to 02nd of August, there were smaller changes in pH in majorities of the water column, with different pH across the entire water column. The following week had more stable levels from 2 m and down, but also with a sudden decrease from 1.5 m to 2.5 m. Hypolimnion had variations of 6.0 to 6.2 in the last week in *figure 10*.

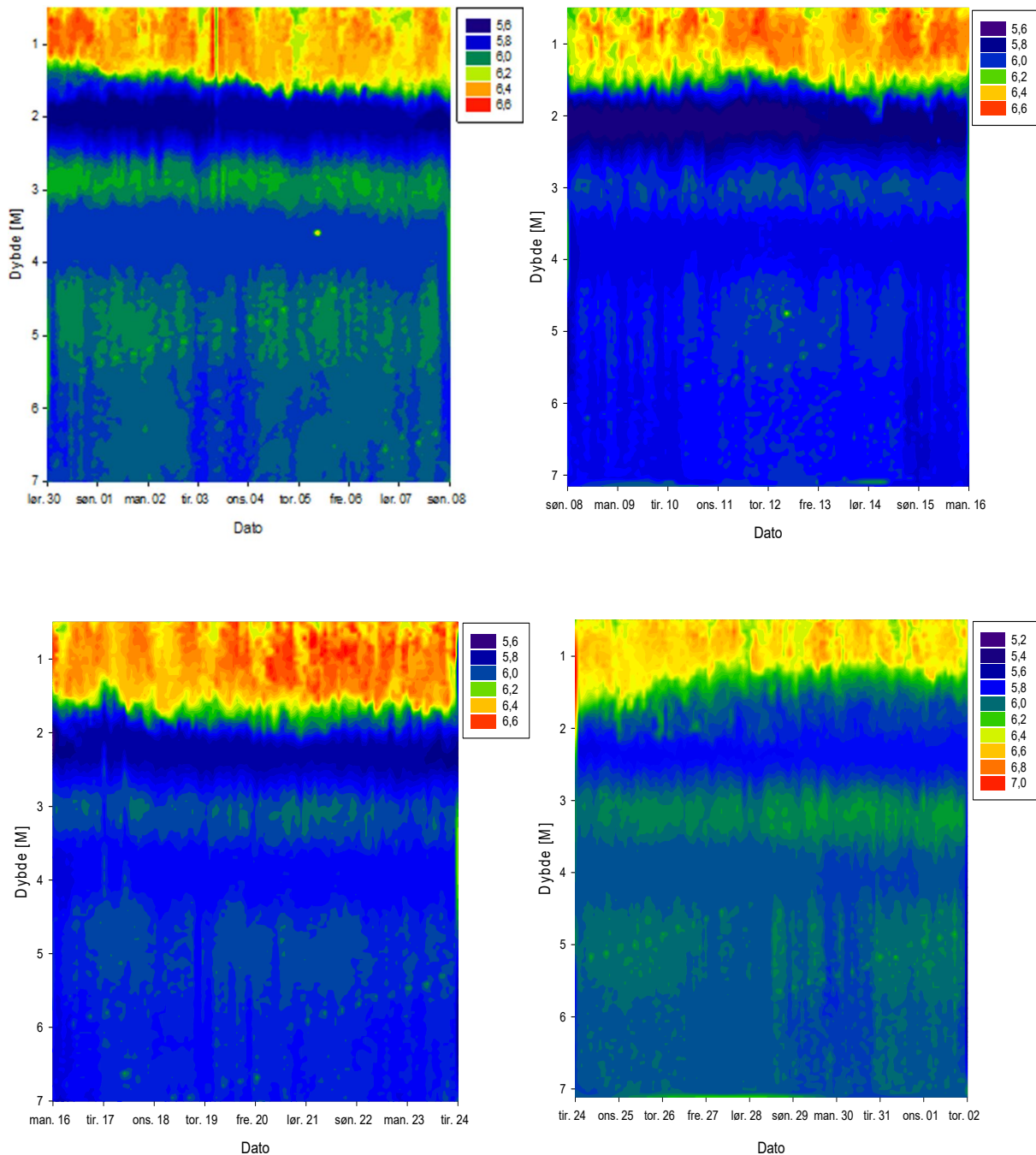


Figure 10 - Depth profile of pH collected with the sensor from 30th of June to 02nd of August distributed over four diagrams.

pH ranged from 5,8 to 6,2 all the way down to the bottom first week of the following period, which had pH of 6,6 in the first meter (*Figure 11*). Metalimnion had pH around 6,0 the first week, and there was generally higher pH between 3 – 4 m than the rest of hypolimnion. In the following week there was more acidity in the first two meters, and more basic conditions in hypolimnion. 27th of august had a sudden change in pH, from 6,0 to 5,0. The three last week of the sampling period, had overall lower pH in the first meter than the weeks before.

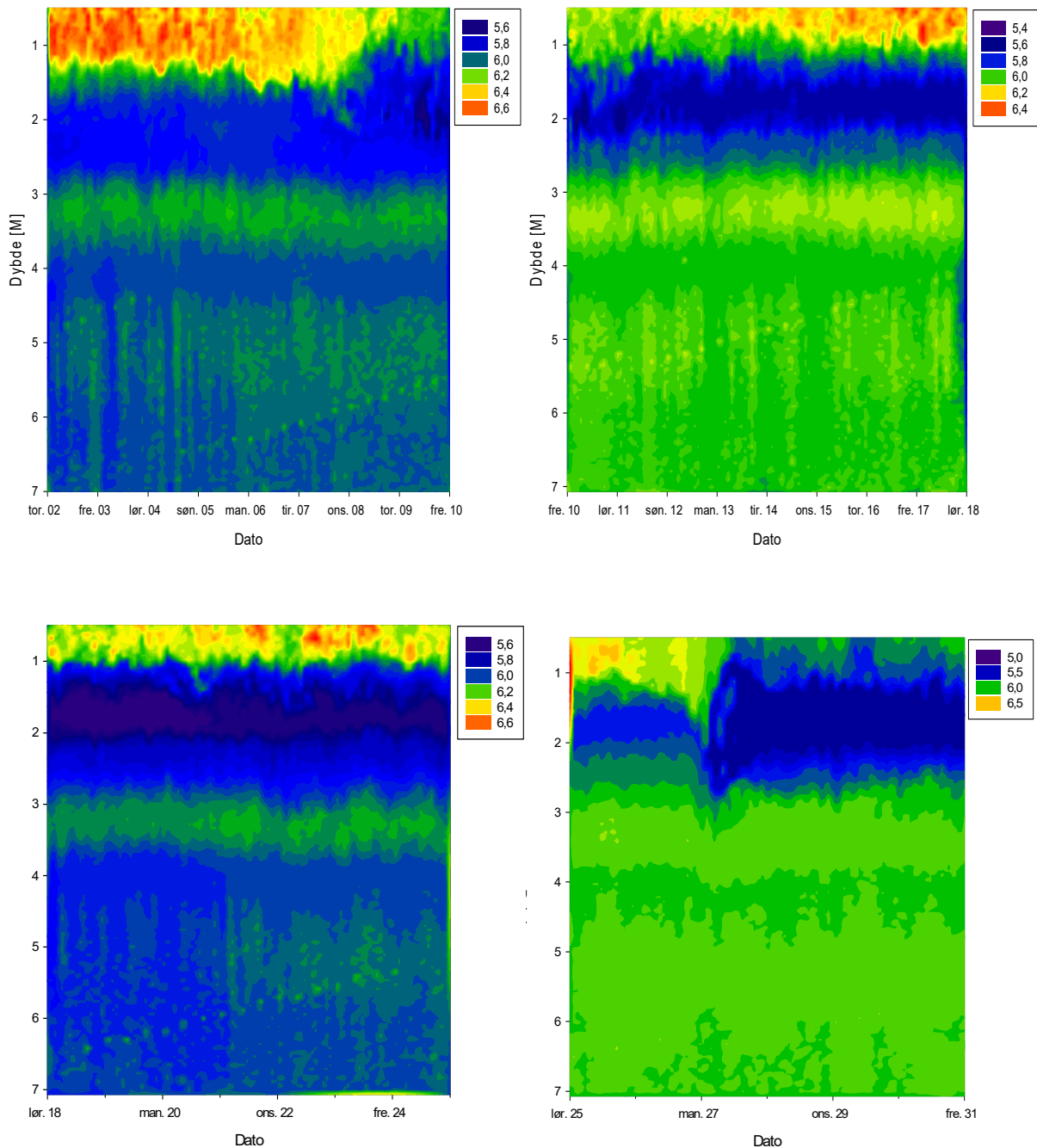


Figure 11 - Depth profile of pH collected with the sensor from 02nd of august to 31st of August distributed over four diagrams.

3.5 Redox

The redox potential had variation across the entire water column. Ranging from about 100 mV to – 195 mV. The variation somehow follows a pattern in changing from positive to negative values at 3.2 m of depth. Some minutes after the O₂ concentration went below zero, the redox potential went in a negative direction. Sunday 10th of June had higher redox potential than average from 0 – 3 m of depth, while the third week of June had redox potential of 50 mV in the first three meters. The following week had between 50 mV and 0 mV in the same range (*Figure 12*).

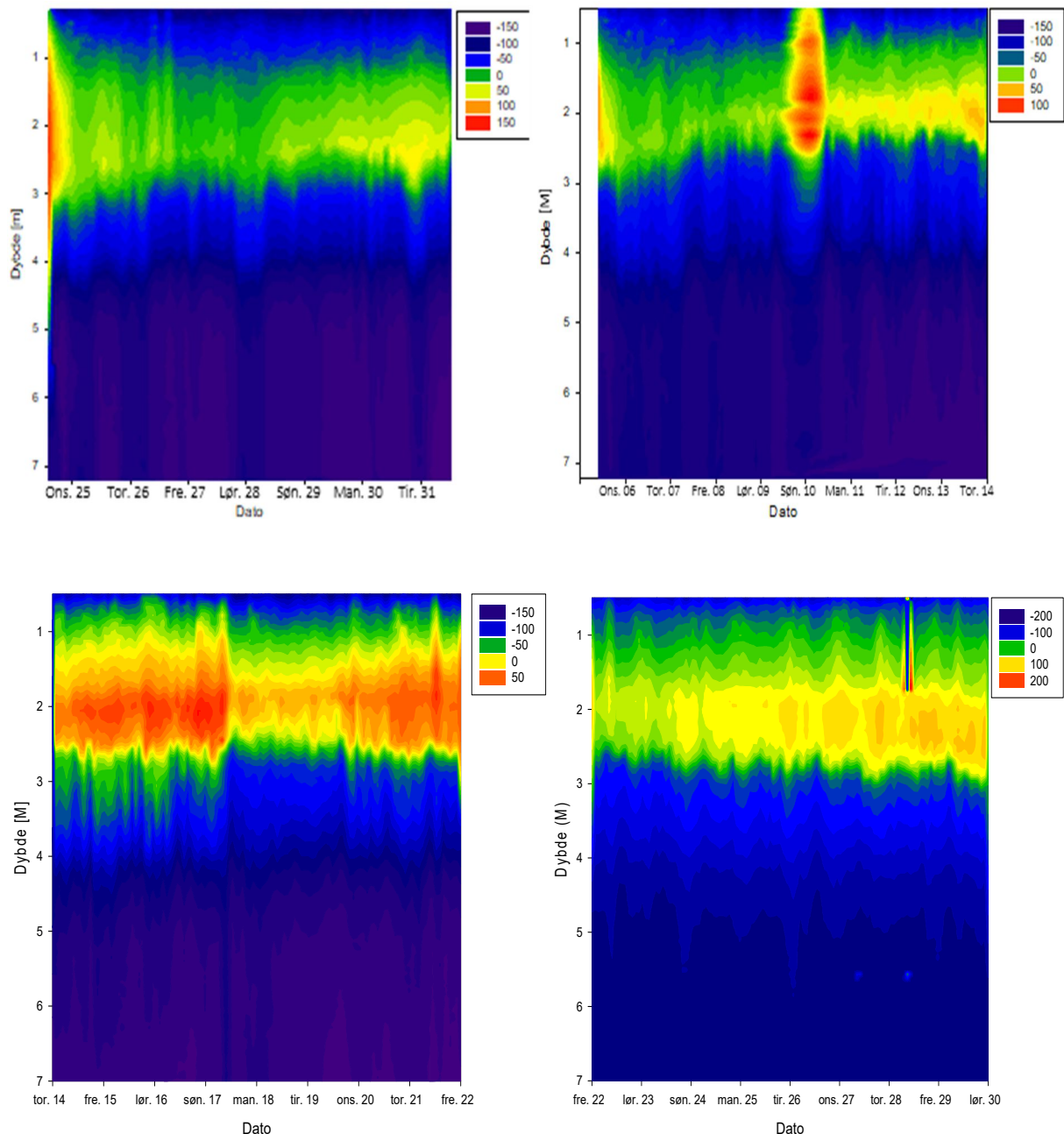


Figure 12 - Depth profile of redox potential collected with the sensor from 25th of May to 30th of June distributed over four diagrams.

The first two weeks of July the redox potential was positive down to 3 m of depth and below zero deeper than this point. Third week of July had high oxidation potential all the way down towards 4 m of depth. From 16th to 20th of July, and 28th of July to 2nd of August higher redox potential dominated epilimnion, while days in between had redox potential closer to zero, visualized by the two last diagrams of *figure 13*. Hypolimnion had negative redox potential through this period, but increased potential from 3 – 4 m from the first to the last week.

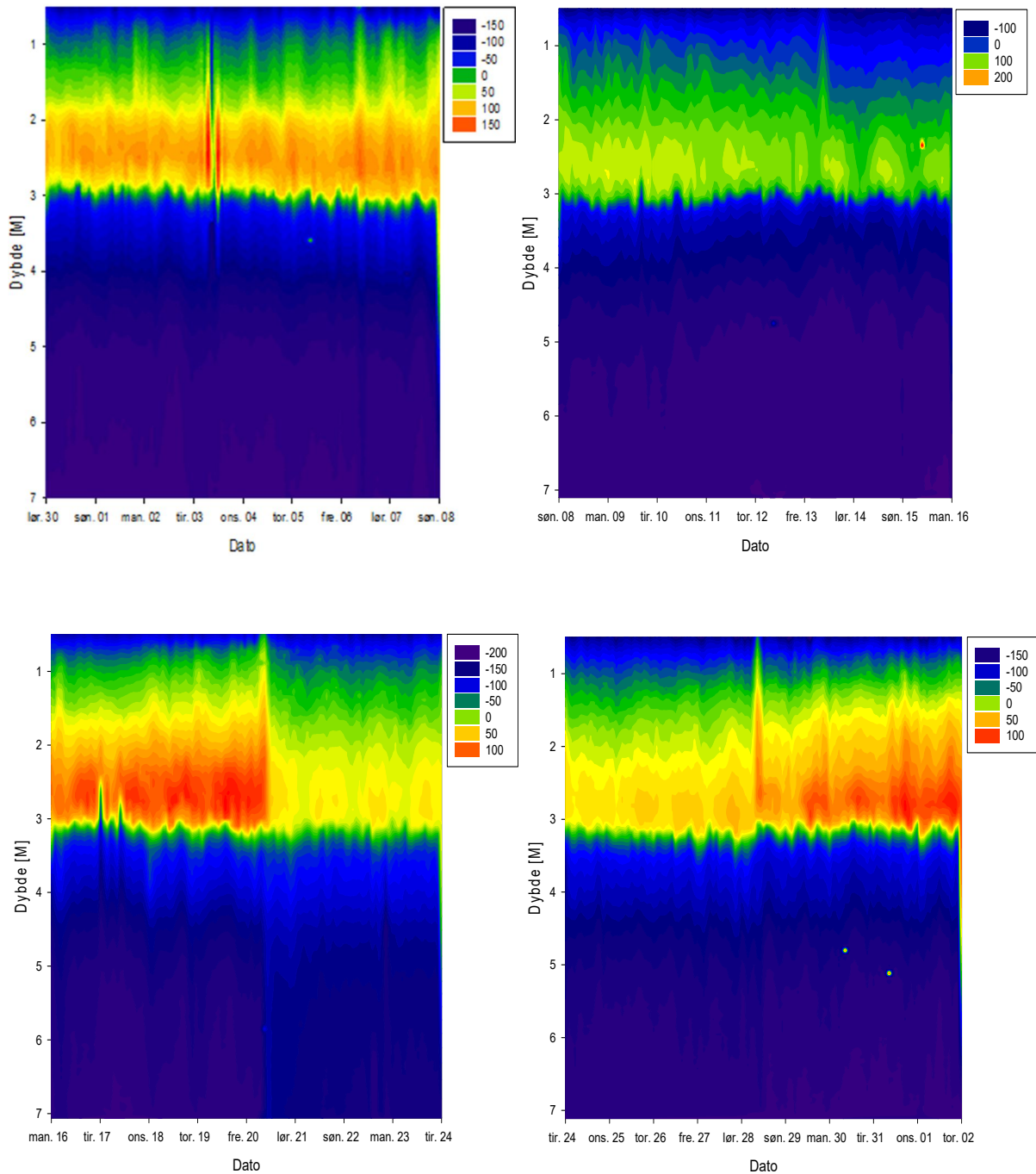


Figure 13 - Depth profile of redox potential collected with the sensor from 30th of June to 02nd of August distributed over four diagrams.

The last two weeks of August had oxidising conditions, ranging from 50 – 100 mg/L in epilimnion. In hypolimnion there were reducing conditions, with negative redox potential. Symbolized with the blue patterns in *figure 14*. August had higher redox potential in epilimnion than July. Especially the third week of August which had potential from 150 – 200 mV in 1 – 3 m of depth. From 25th to 27th of August there were a sudden drop in redox concentrations in the first three meters, before the redox potential slightly increased again towards the end of the sampling periode. Hypolimnion still remained it's negative redox potential.

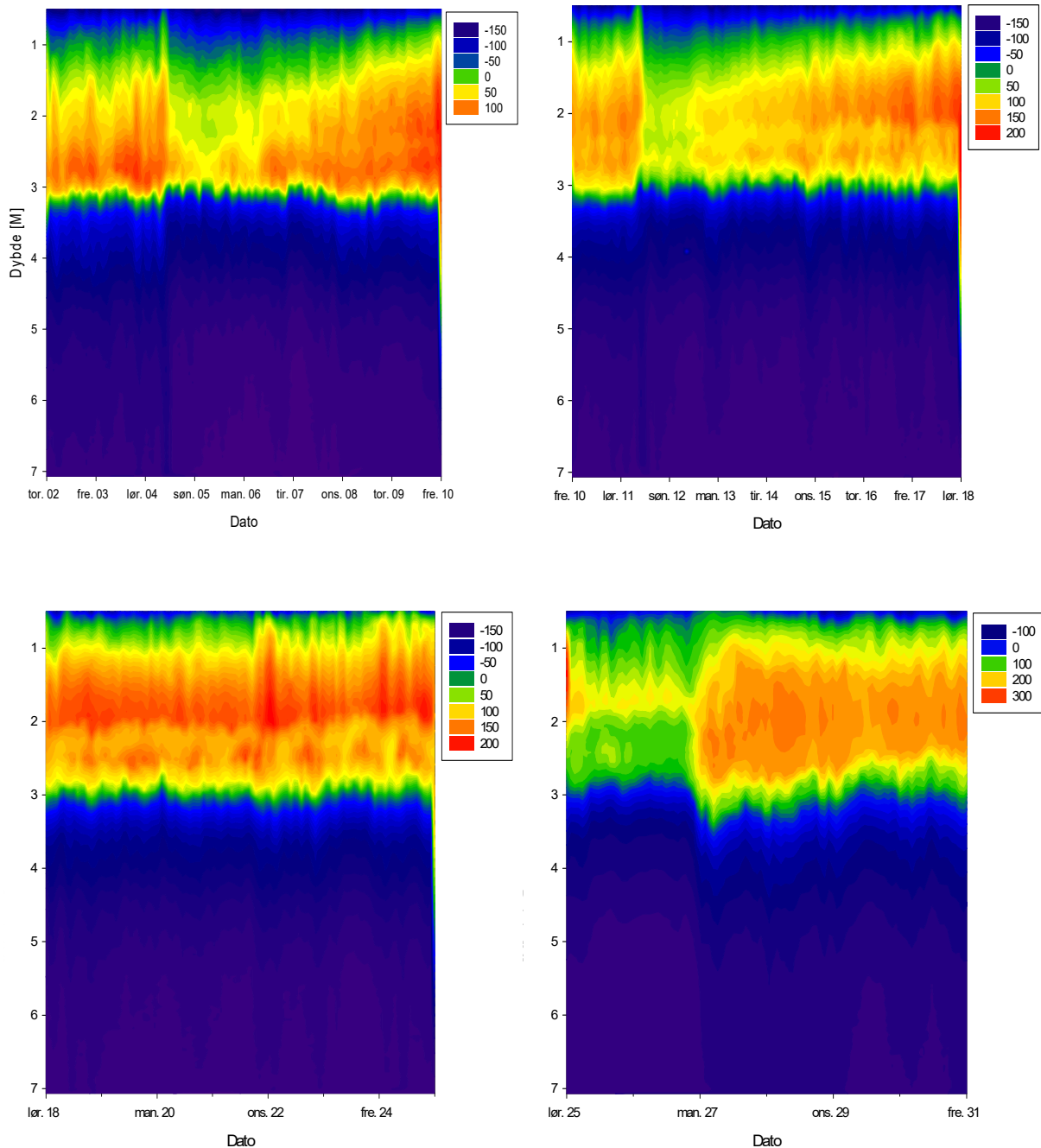


Figure 14 - Depth profile of redox potential collected with the sensor from 02nd of august to 31st of August distributed over four diagrams.

3.6 Salts and nutrients

Chloride

As the salt consist of NaCl, we can see a significant amount of chloride increasing down through the water column. The lake had a stratification layer from 5 – 8 m, through the season. In the start of July, the stratification layer fell from 5 m to 6 m. At the end of august the stratification raised again to original dept (*Figure 15*). The layer was persistent through the season, even though it was moving across the water column.

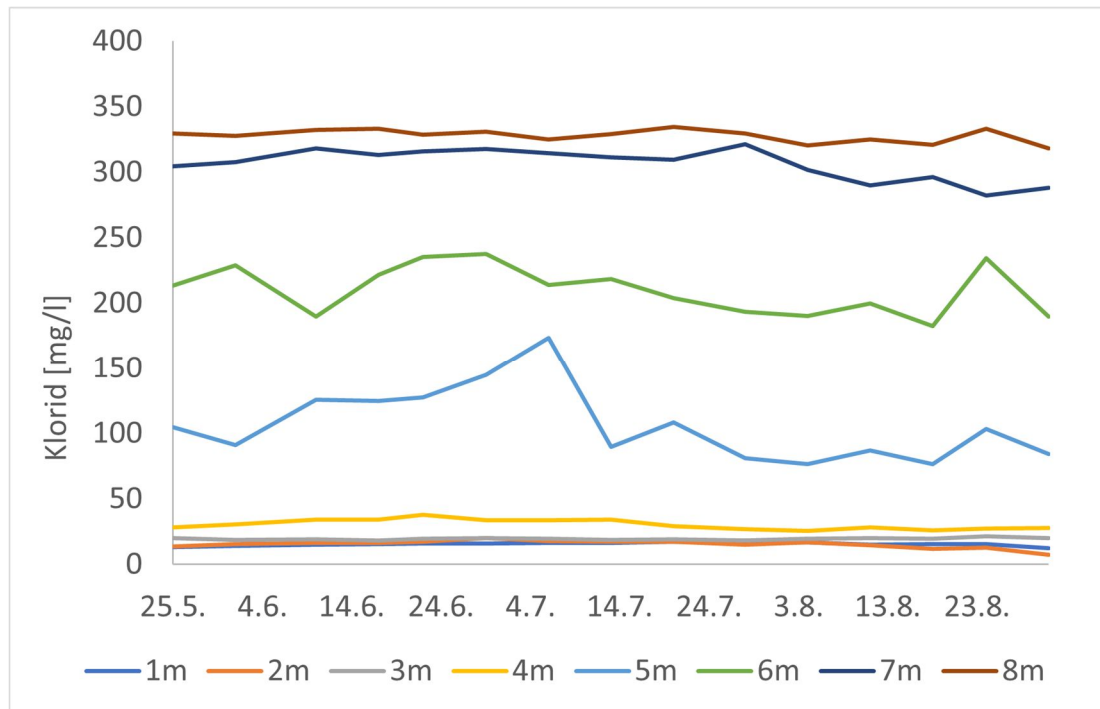


Figure 15 – Chloride concentrations measured for every meter of depth in lake Kutjern.

DOC

This substance was more evenly distributed through the water column. There was less mg/l difference in between depths, even though the quantities overall were high compared to the other elements. Total amount of DOC increased in epilimnion and decreased in hypolimnion through the season. DOC increased the most at 1 m and 2 m in august (*Figure 17*).

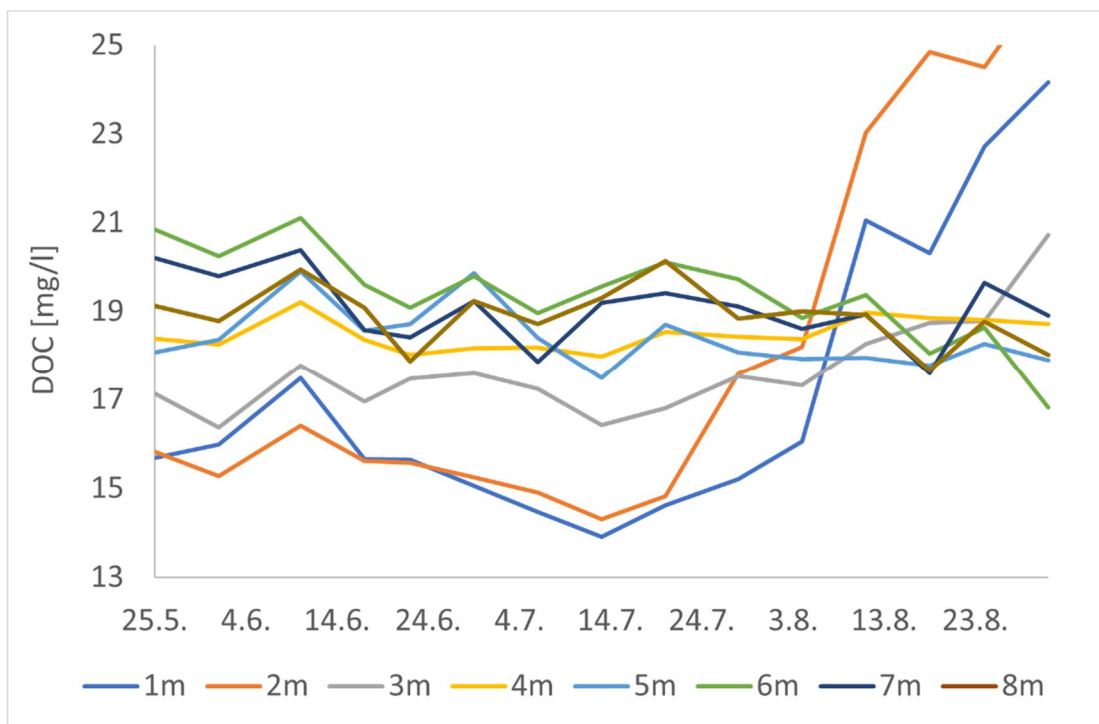


Figure 17 – DOC concentrations measured for every meter of depth in lake Kutjern.

NH₄-N

This molecule had great variation in concentration from day to day, and the concentration in 4 – 8 m decreased through the season. The concentration was relatively stable between 1 – 4 m. Measured to $32,5 \mu\text{g/l} \pm 12,5 \mu\text{g/l}$ (Figure 16). NH₄-N tested positive for high absorbance.

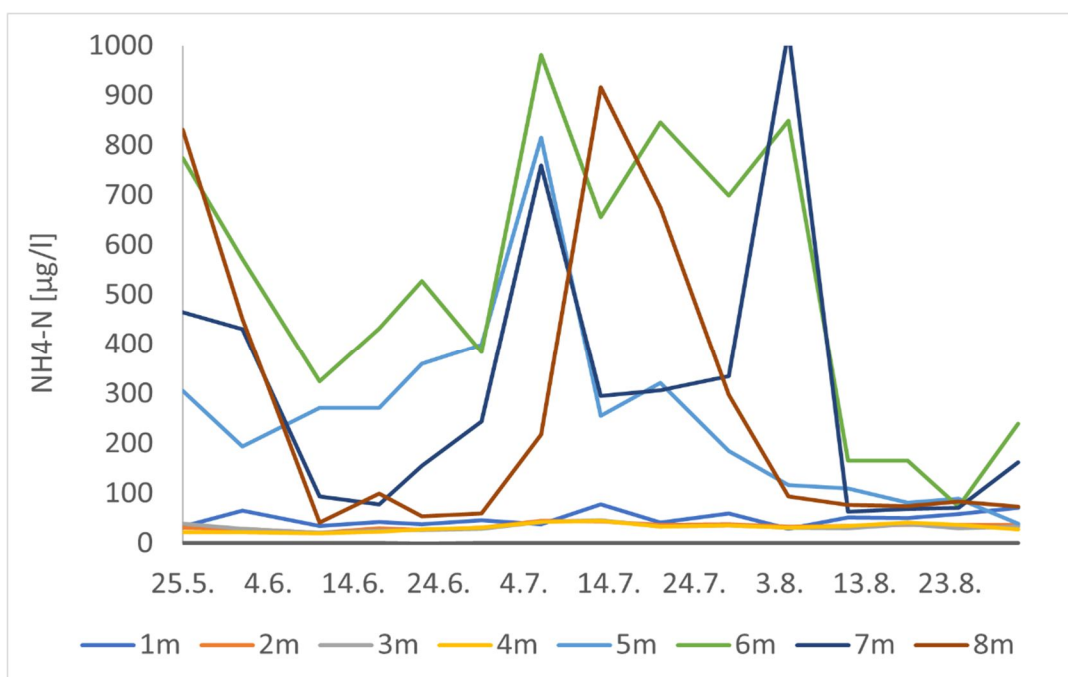


Figure 16 – NH₄-N concentrations measured for every meter of depth in lake Kutjern.

Sulfate

Concentration of this element was found at large scale in metalimnion, just around the top the layer of stratification. There was little to less sulfate at the bottom. Some days had high concentrations in epilimnion, where the values were highest at 2 m – 3 m. There were overall slightly decrease in sulfate during the sampling period (figure 18).

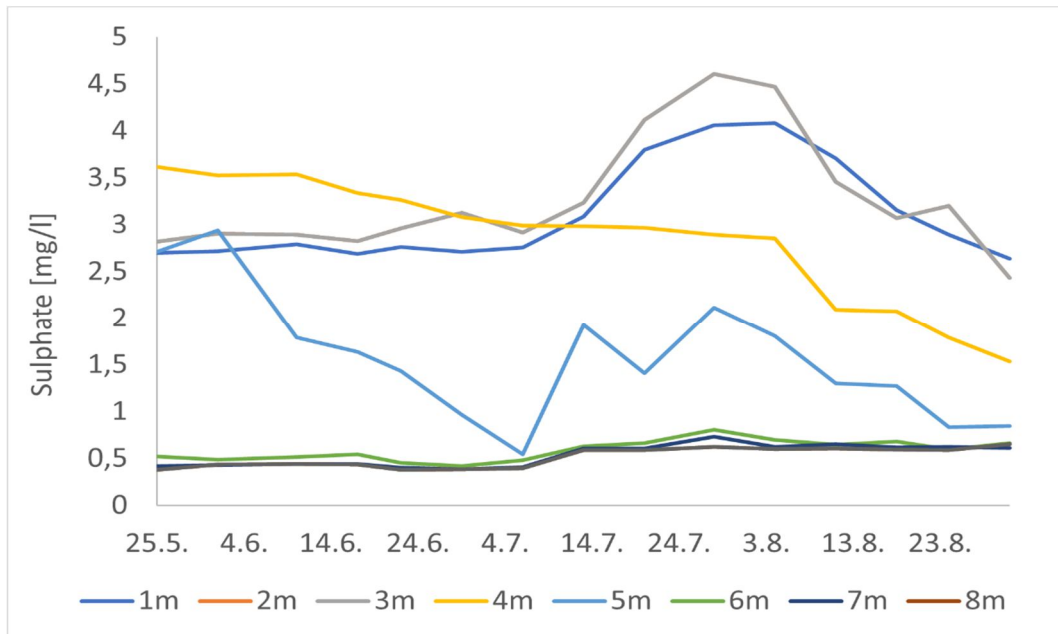


Figure 18 – Sulfate concentrations measured in every meter of depth in lake Kutjern.

Total Nitrogen (TN)

Amount of total nitrogen increased with depth. The stratification layer kept most of the total nitrogen in the range 5 m – 7 m. This substance was measured to higher concentrations in the water column compared to the other elements (Figure 19).

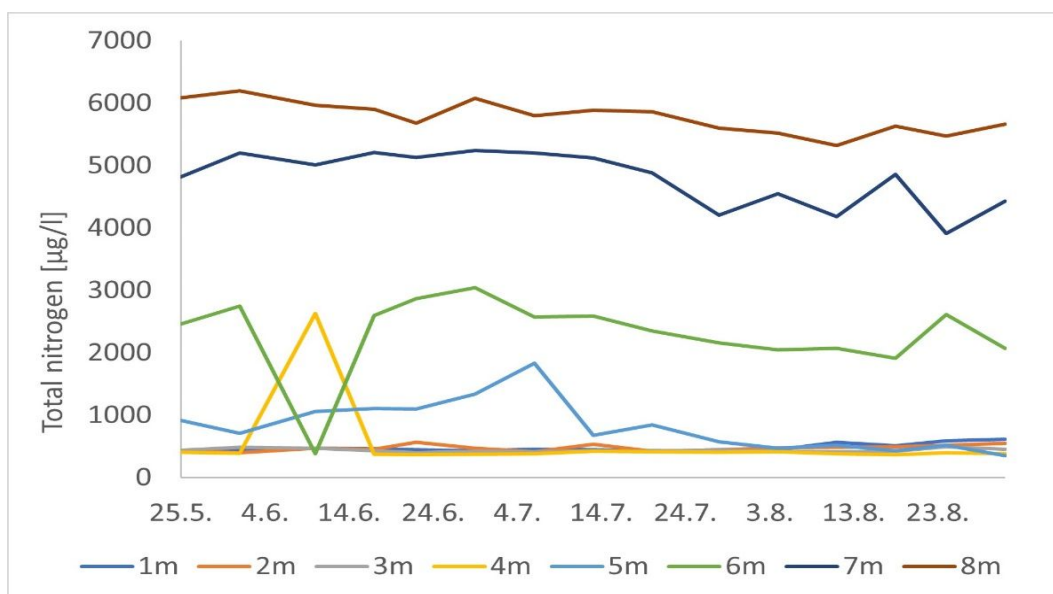


Figure 19 – TN concentrations measured for every meter of depth in lake Kutjern.

3.7 Heavy metals

Cadmium

Values of cadmium were decreasing towards the bottom. Overall, through the weeks of sampling there was a downfall for each meter of depth. Values of Cadmium increased in the transition from June to July, before decreasing slightly again, in the end of August. The maximum value was 0,28 µg/l at 8 m depth the 06th of July (Figure 20). 6 m of depth had 9,9 µg/l at 18th of August 2023.

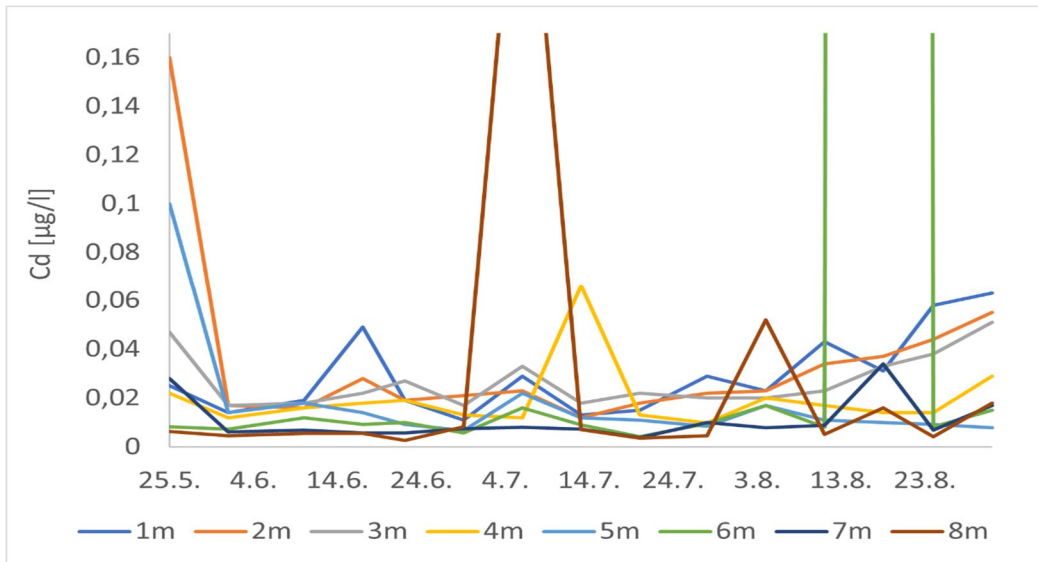


Figure 20 – Cd concentrations measured for every meter of depth in lake Kutjern.

Chromium

Results show very remote concentrations of Chromium. They were below harmful concentrations, and barely reached class II according to Attachment S1. The concentrations increased with depth and was highest above the sediment surface at 8 m of depth (Figure 21). Medio July had deviations at 5 m of depth.

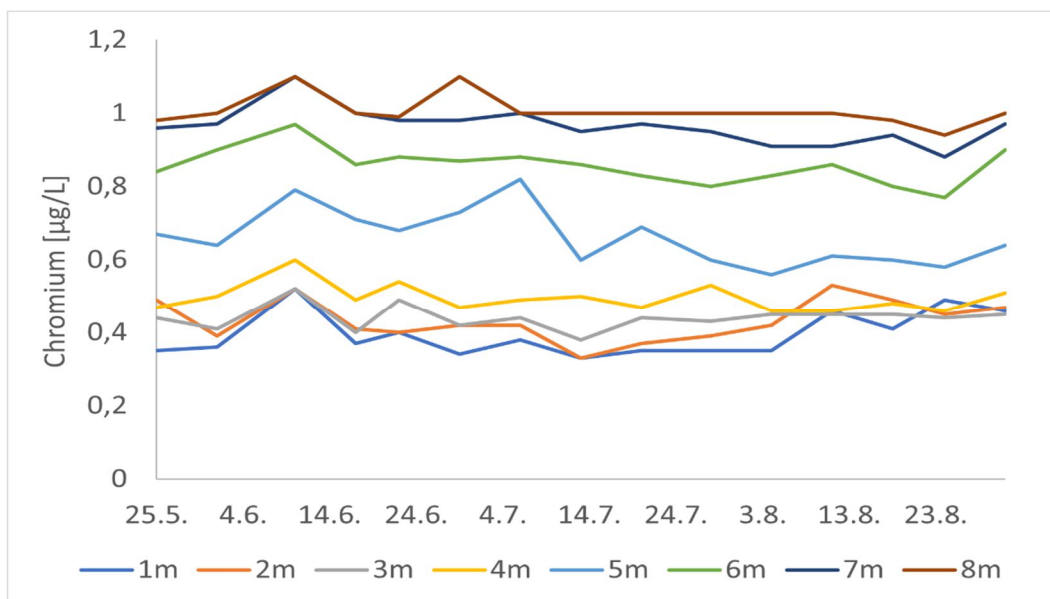


Figure 21 – Cr concentrations measured for every meter of depth in lake Kutjern.

Cobalt

Expressed the same behavior as Lead. Relative stable levels with a slight increase towards the end of the season. Some days had a sudden bloom. Concentration of cobalt was highest at 6 m the 27th of July (Figure 22).

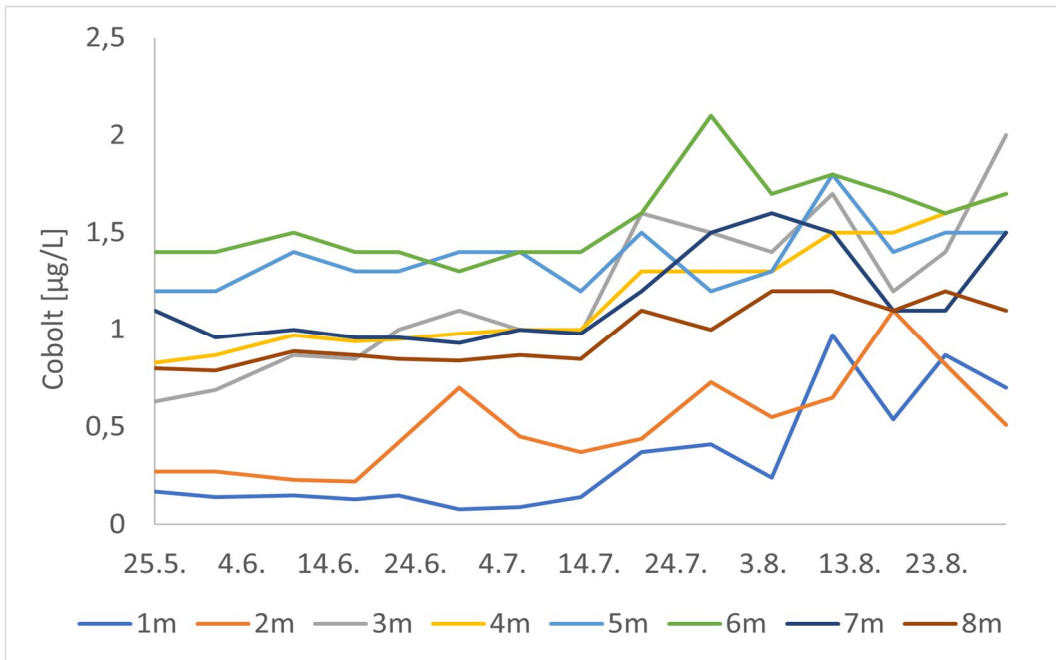


Figure 22 – Co concentrations measured for every meter of depth in lake Kutjern.

Copper

Copper had intervals of changing concentrations through most parts of the sampling period. The highest concentrations were found in epilimnion, but the element had smaller distribution deviations in all depths of the water column (Figure 23).

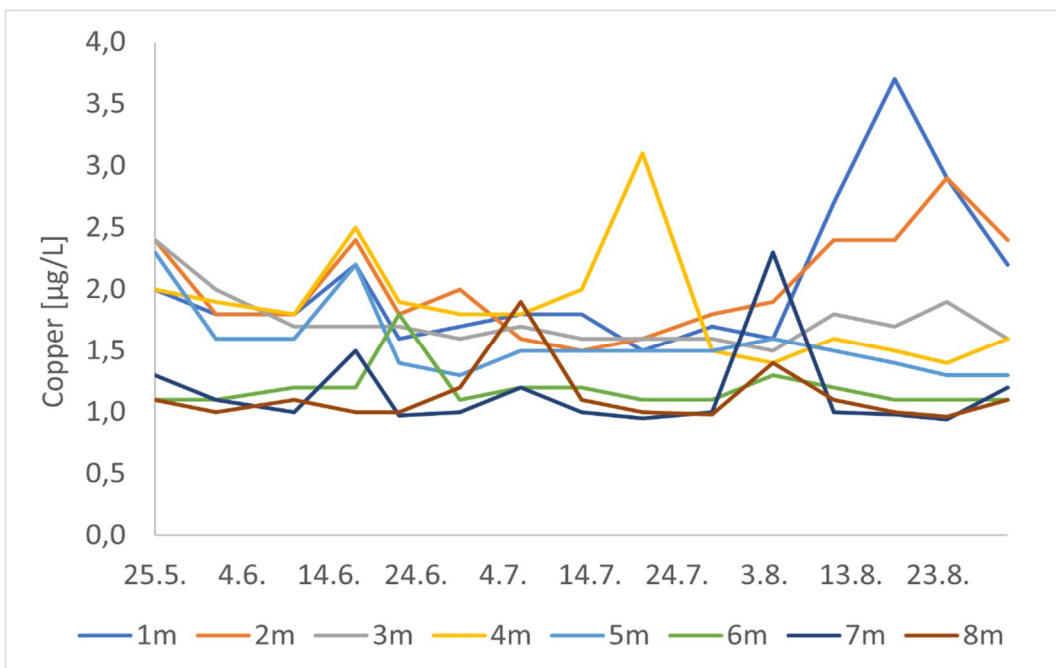


Figure 23 – Cu concentrations measured for every meter of depth in lake Kutjern.

Iron

Concentrations of iron varied with depth. The concentration increased towards the bottom. Values increased drastically from 5 m. A drop in concentration at 5m of depth, were found in the middle of July (Figure 24).

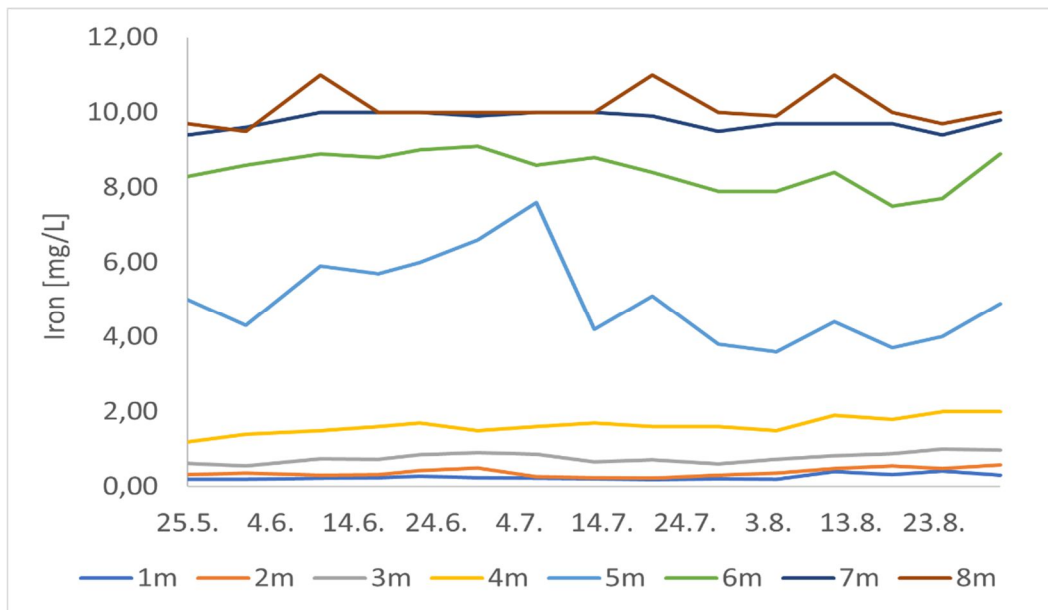


Figure 24 - Fe concentrations measured for every meter of depth in lake Kutjern.

Lead

The highest values of lead were found in the stratification layer, with increasing concentrations down towards the salt layer and decreasing further from 5m and down towards 8 m. At four meters there were measured an extreme value of 39 $\mu\text{g/l}$ (Figure 25).

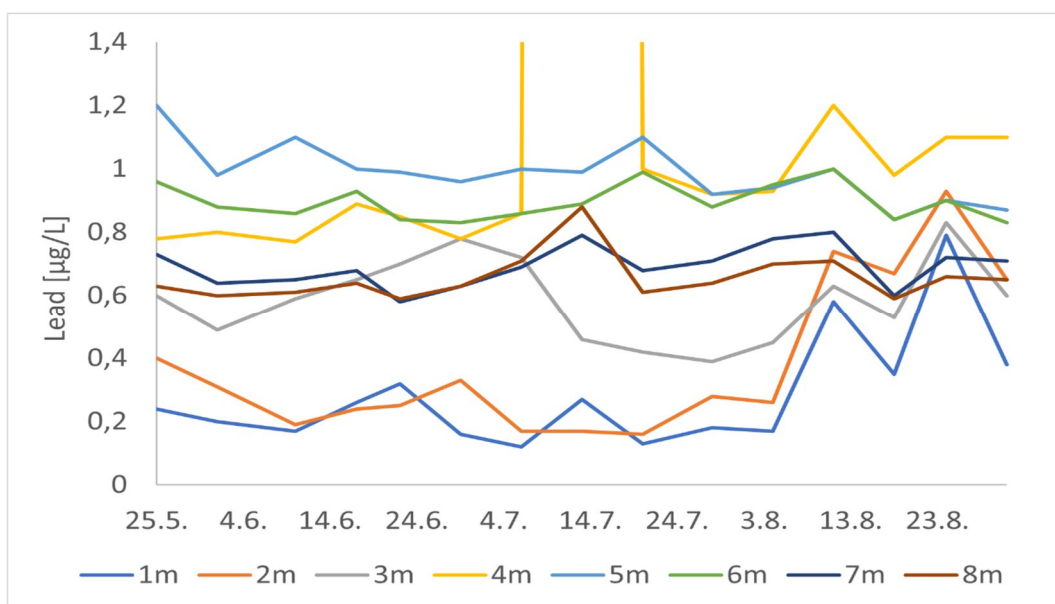


Figure 25 – Pb concentrations measured for every meter of depth in lake Kutjern.

Manganese

Had great increase in concentration with increased depth. 630 µg/L were found at most at 8 m of depth. The lowest concentration was found at 1 m with 9,4 µg/L (Figure 26). There was great increase in concentrations from 4 m and down.

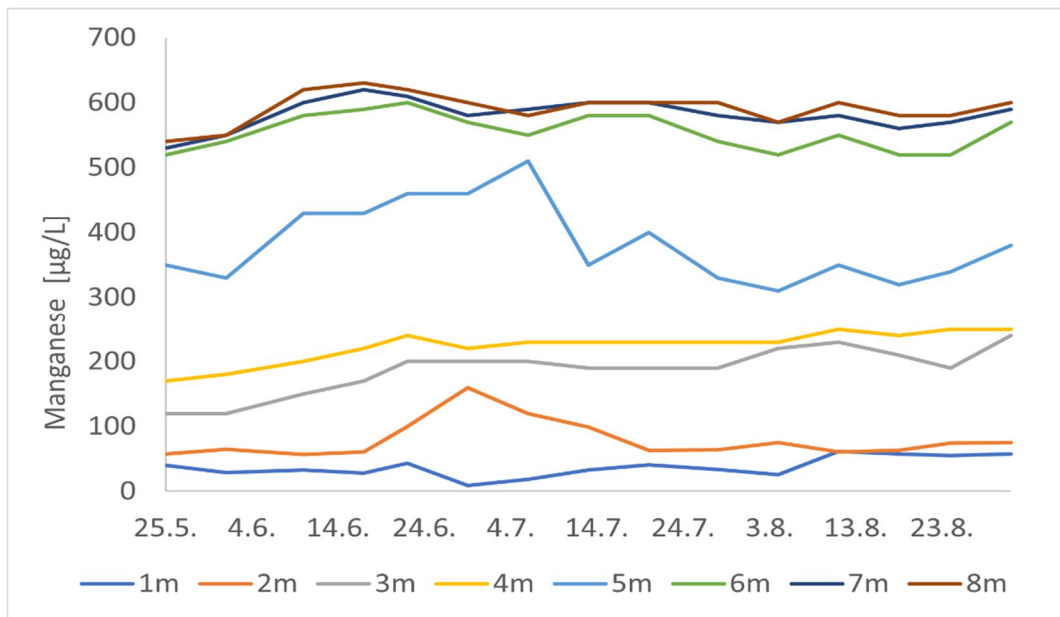


Figure 26 – Mn concentrations measured for every meter of depth in lake Kutjern.

Nikkel

Values rised towards the bottom, and through the season. Nikkel increased with a significant concentration through the whole water column in the end of august (Figure 27). Concentrations were ranging from 0,5 µg/L till nearly 3,0 µg/L during the sampling period.

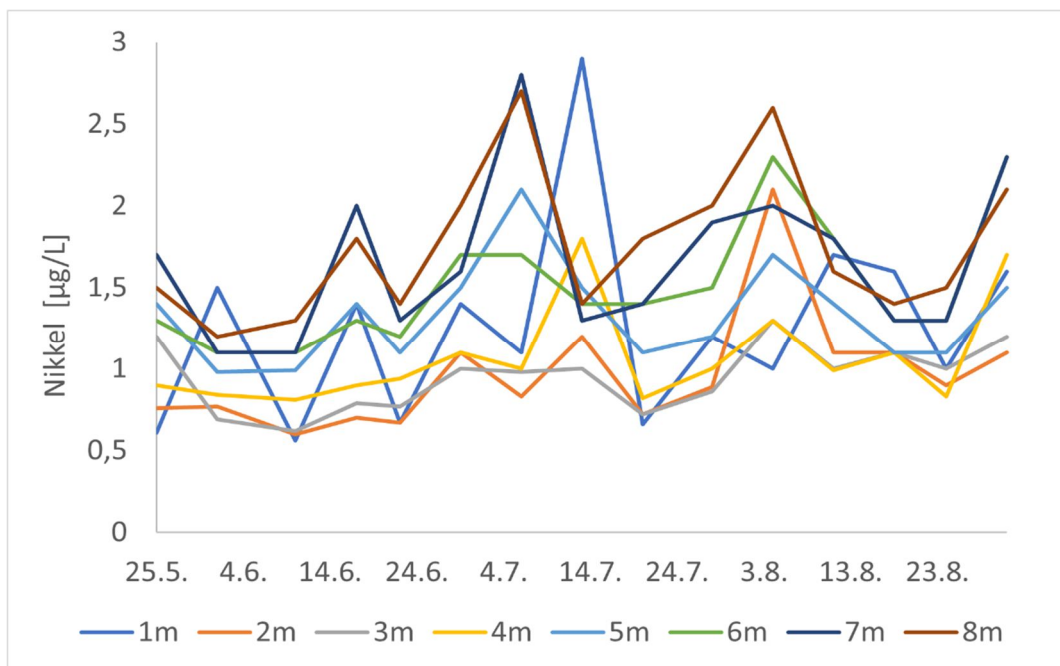


Figure 27 – Ni concentrations measured for every meter of depth in lake Kutjern.

Sulphur

Concentrations increased towards stratification layer from the top, but not all the way to the bottom. Allochthonous supplies were likely concentrated in epilimnion. Smell of H₂S gas occurred during water sampling from 4 m depth and down (Figure 28).

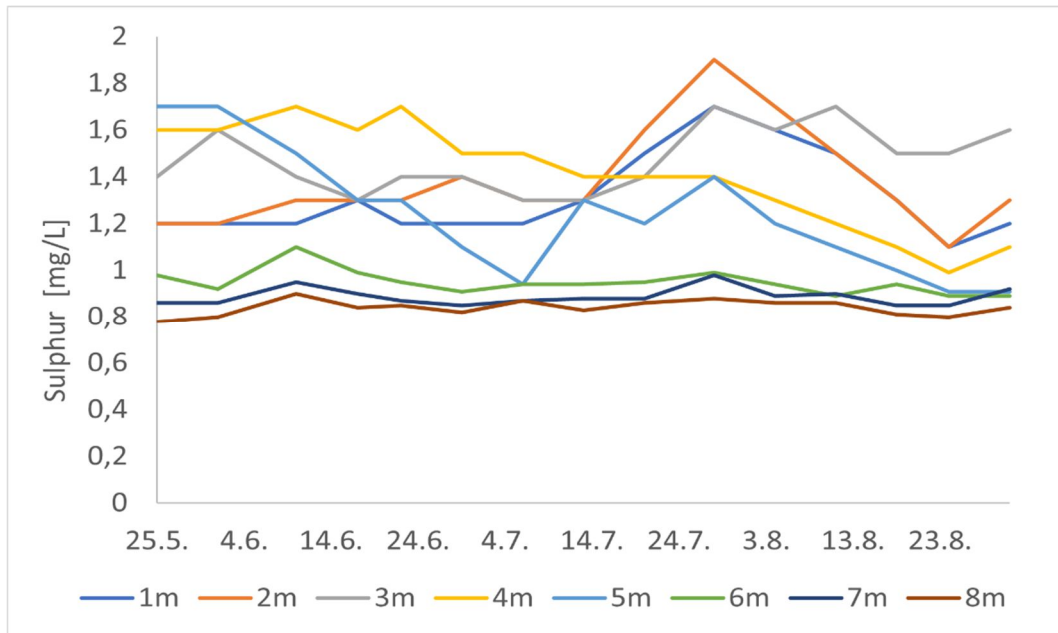


Figure 28 - Sulphur concentrations measured for every meter of depth in lake Kutjern.

Zink

Had relatively high concentrations. With a maximum value of 400 µg/L at 4 m depth the 13th of July. There were also intervals with changing concentrations. At the end of June and first period of July the concentrations of Zink were at its lowest. At 7 m the measurements showed close to 90 µg/L 11th of August (Figure 29).

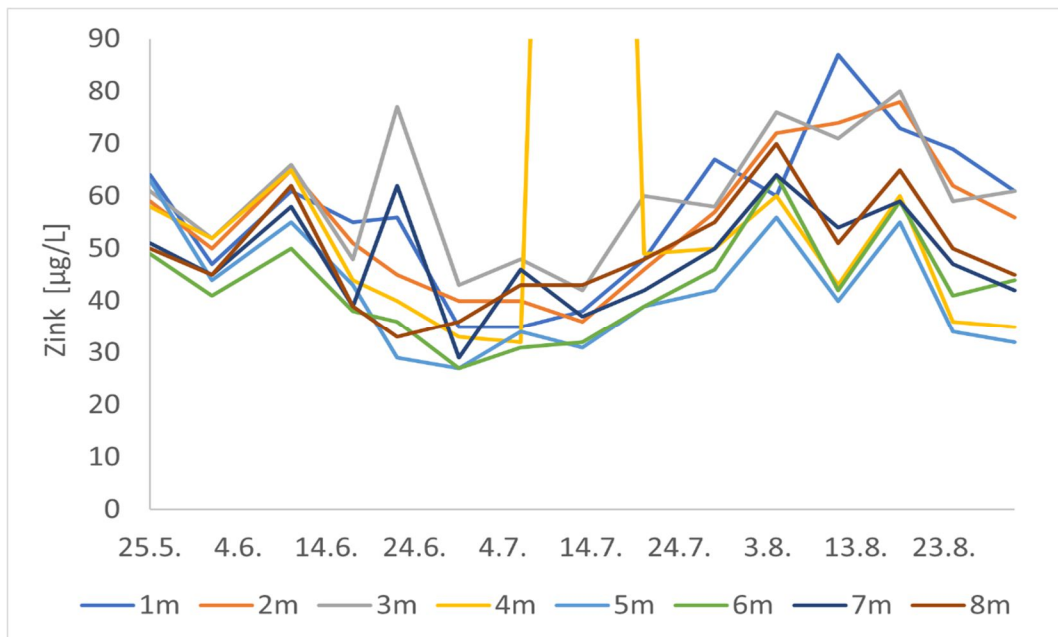


Figure 29 – Zn concentrations measured for every meter of depth in lake Kutjern.

3.8 Principal Component Analysis (PCA)

PCA of Kutjern visualize high correlation between two components, and together about 70% of variety in gathered data. In 0 – 4 m of depth Mn, Fe and Co correlated well. Together with Cr and DOC these metals correlated good with pH and specific conductivity. Pb, Zn and Cd correlated with O₂ concentration and ORP. To some degree also temperature. S and Cu correlated negatively with most other metals. S was found in high concentrations from the layer of stratification and up towards the surface, while most of the Cu concentrations was found in epilimnion (*Figure 30*).

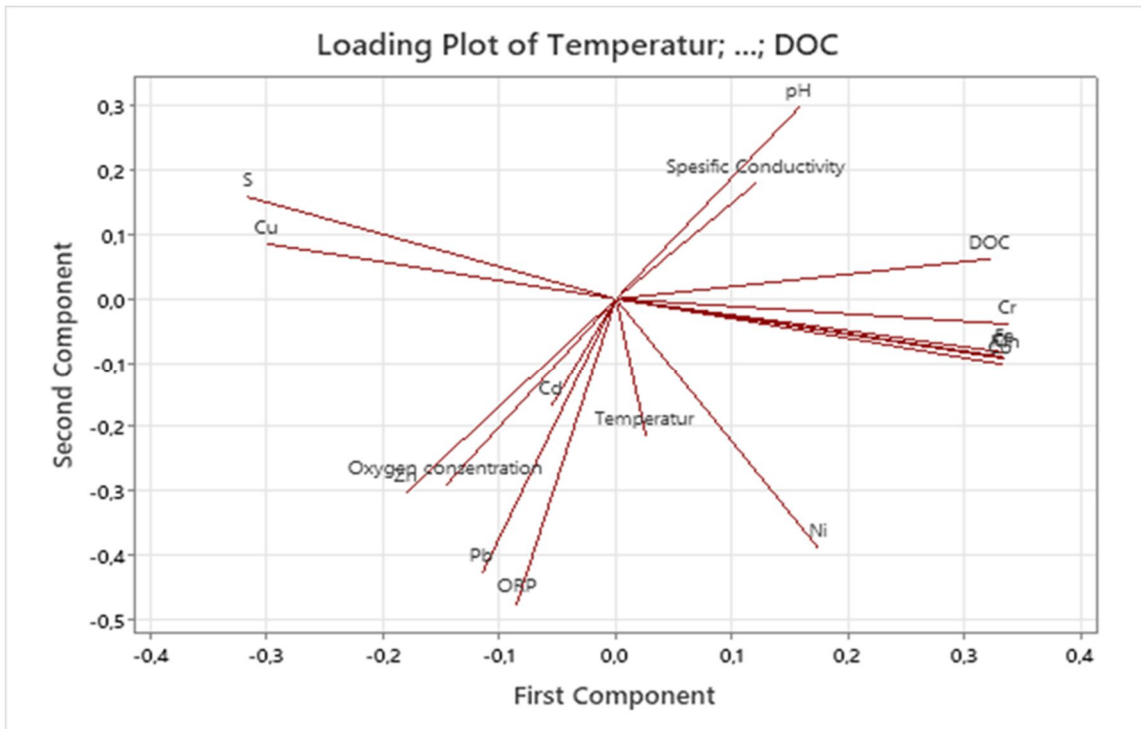


Figure 30 – Metal correlation analysis from 0 – 4 m.

In 4 - 8 m of depth, Pb, Ni, Co, Cr, Cl, Fe, Mn and DOC correlated more with oxygen concentration, temperature and pH. Unlike Cu, Zn and S. Specific conductivity and ORP correlated oppositely, with negative correlations to oxygen concentration, temperature, and pH (Figure 31). Cu correlated with Zn and S, but not with any other substances. These substances had negative correlation with Pb, Ni, Co, Cr, Cl, Fe and Mn under the circumstances these measurements were made. Specific conductivity had negative correlation with oxygen concentration and temperature.

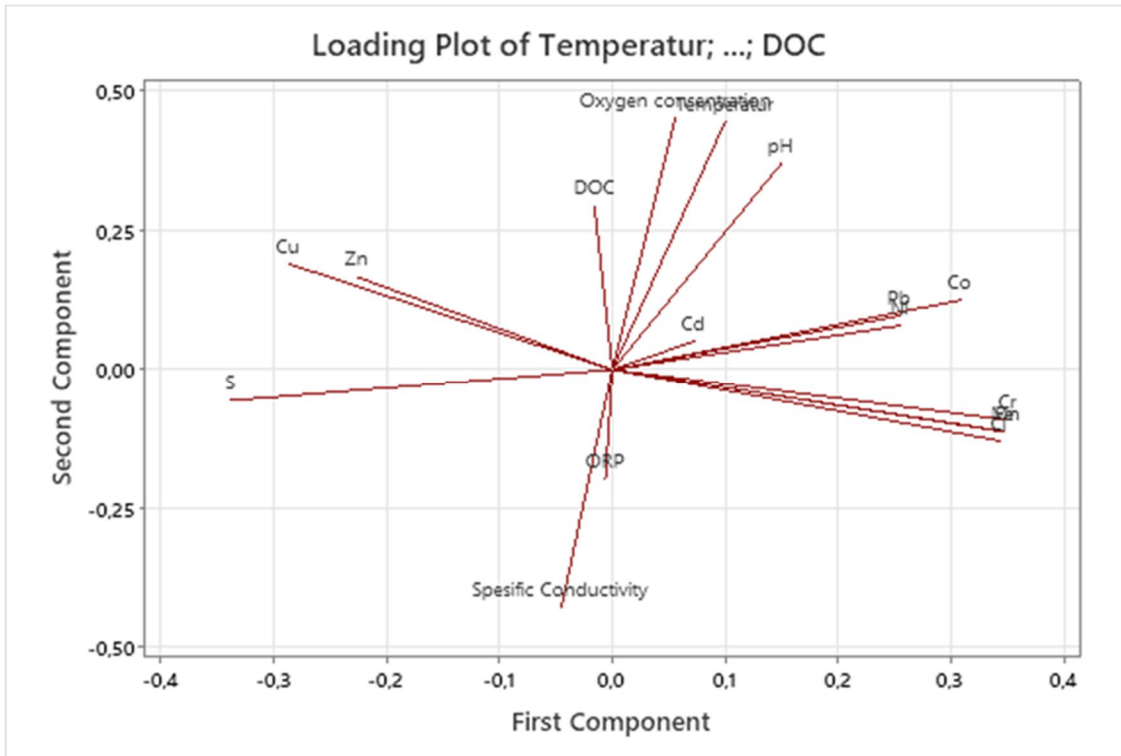


Figure 31 – Metal correlation analysis from 4-8m.

3.9 SPCR-analysis

A Spearman's rank correlation analysis was conducted in addition to the PCA-analysis previously mentioned, to visualize further correlation between the measured coefficients. Mn and Fe by example was experienced with high correlation, while pH had low correlation to most metals except for Mn, Zn and Cd. ORP (redox potential) correlated more with Cd and Ni, than other metals. There was high correlation between several heavy metals according to the analysis.

Table 1 - SPCR-analysis (Spearman's rank correlation coefficient), in which the relationship between two variables is valued in a monotonic function. Because the Spearman method is either linear or not, the perfect value of correlation is 1 or -1. Green marked numbers indicate high probability of correlation in the environment the parameters are measured.

	Con	pH	ORP	O ₂	S	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Cl	DOC
Con																
pH	0,252															
ORP	-0,795	-0,186														
O ₂	-0,332	0,121	0,246													
S	0,354	-0,203	-0,293	0,183												
			-0,290	-0,514												
Cr	0,293	0,204	-0,218	-0,582	-0,711											
			-0,435	0,023	0,003											
Mn	0,013	0,504	0,046	-0,298	0,803	0,756										
			-0,869	-0,280	0,000	0,001										
Fe	0,048	0,475	0,039	-0,389	0,794	0,832	0,935									
			-0,889	-0,152	0,000	0,000	0,000									
Co	0,054	0,343	0,046	-0,393	0,774	0,793	0,949	0,950								
			-0,869	-0,147	0,001	0,000	0,000	0,000								
Ni	-0,502	0,136	0,493	0,050	-0,799	0,339	0,649	0,636	0,661							
			-0,062	0,860	0,000	-0,216	0,009	0,011	0,007							
Cu	-0,032	-0,208	0,115	0,324	0,804	-0,744	-0,813	-0,830	-0,812	-0,611						
			-0,684	0,238	0,000	0,001	0,000	0,000	0,000	0,016						
Zn	0,366	-0,461	-0,282	0,246	0,519	-0,264	-0,517	-0,518	-0,436	-0,439	0,353					
			-0,308	0,376	0,047	-0,341	0,049	0,048	-0,104	0,101	-0,197					
Cd	-0,316	-0,450	0,496	0,279	0,233	-0,325	-0,493	-0,325	-0,329	-0,086	0,520	0,307				
			-0,060	0,315	0,402	-0,237	-0,062	0,237	0,232	0,761	-0,047	0,265				
Pb	-0,184	0,075	0,357	0,111	-0,670	0,396	0,622	0,629	0,664	0,811	-0,622	-0,043	0,043	0,043		
			-0,191	0,694	0,006	-0,143	0,013	0,012	0,007	0,000	0,013	0,879	-0,879	-0,879		
Cl	0,039	0,386	0,079	-0,436	-0,803	0,811	0,890	0,943	0,904	0,671	-0,875	-0,539	-0,379	-0,661	0,661	
			-0,781	-0,104		0,000	0,000	0,000	0,000	0,006		0,038	-0,164	-0,007	-0,007	
DOC	0,452	0,364	-0,393	-0,400	-0,592	0,871	0,647	0,704	0,689	0,257	-0,710	-0,121	-0,354	0,432	0,711	
			-0,147	-0,140	0,020	0,000	0,009	0,003	0,004	0,355		0,666	0,196	-0,108	-0,003	

4. Discussion

4.1 Climatic data

The concentration of metals and salts available in the lake was composed by ecological functions and properties of the catchment. Physical events like rain, wind (turbulence) and temperature affected the metallic composition in Kutjern. By example the salt stratification layer, where measurements of conductivity varied through the season. That's most likely because some days in June and July were casting great amounts of precipitation over Kutjern. Therefore, concentrations and values of each depth were different from time to time.

4.2 Comparable results

According to earlier investigations of Kutjern done by COWI on behalf of Statens vegvesen (Saunes & Værøy 2017), tests of salt intrusion and its effects was conducted. Their top & bottom sampling in November, indicated higher values of metals Pb, Cd, Cu, Zn and Ni than the results of this study. Reasonable, due to Statens vegvesen regulations of salt applications on E18. Less amounts of salt have intruded the lake by runoff since then. The research done by COWI was done over the 2015/2016 season and compared to our values of 2023. COWI predicted that Kutjern had clear stratification of salt, depletion of O₂ and that the lake's ecological situation had worsened from 2010 to 2015. Most metal concentration were found to tolerable or at least below toxic levels, except for copper that was found in levels with potentially severe toxic effects (Saunes & Værøy 2017).

A study done by *Daria Dedikova*, by the Norwegian university of life sciences in 2023, showed how salt stratification and meromixis affected metal and phosphate availability in Kutjern. Physical conditions varied a bit from our study, including weather like wind and rain. Overall pH, O₂ concentration, specific conductivity, productivity, and redox potential were similar to the result of this study. The values of her study were higher in epilimnion and lower in hypolimnion. Same for manganese and Cr values was significantly overall higher. Up to 2,5 times as high in hypolimnion. Cobalt concentrations were slightly higher in our study, especially in epilimnion. Nikkel was preliminary found in hypolimnion but increased significantly overall from mid-July throughout the sampling period. The results in this study showed reasonably higher values of Nikkel both in epilimnion and hypolimnion in this period than the study by *Dedikova* 2023. Copper had quite similar values and was decreased through the season. Values of Zink was 5 – 8 times as high in this study. Cadmium values were similar and relatively low compared to other metals. Lead was similar and higher values occurred in metalimnion occurred in this study. Same values were represented for Sulphur.

Another study done by *Vilde Steiro* (2022) measured some of the same metals and by comparing them to our results we found: Higher values of Manganese. Especially towards the last period of sampling. Iron values was higher in epilimnion and lower in hypolimnion. Physical conditions like O₂ concentration, temperature and specific conductivity were quite equal. All of them indicated stratification with ripple effects

equal to our results. *Steiro* 2022 had measurements of 1503.7 $\mu\text{S}/\text{cm}$ at most in the bottom of chemocline. That means there had been a slightly decrease in specific conductivity at the bottom layer in Kutjern. Temperatures in *Steiro's* study had variations within 2 – 3 °C in epilimnion, and even less variation in hypolimnion.

Earlier studies by Statens vegvesen, classified the water quality of Kutjern in 2015. By comparing their results to the results of this study, copper values have lowered 10 times, even though sink has increased in epilimnion since 2016. Chloride concentrations were equally high, and there were found toxic amounts of lead in equal concentrations in epilimnion. Another study by *Rishatt* 2018 had measurements of specific conductivity at 1547 $\mu\text{S}/\text{cm}$ at most, compared to 1325 $\mu\text{S}/\text{cm}$ in this study. Both with a sudden increase from 4 m of depth and down. Heavy metals and stratification have therefore been persistent in Kutjern for several years, even though deviations have occurred (Saunes & Værøy 2017).

Early studies revealed that the lake experienced significant impacts from road salt, exhibiting a distinct chemocline and salt-induced oxygen gradient at a depth of 2 meters in June 2016. The chloride concentration measured for their study reached 400 mg/L at the depth of 8 meters, an unusually high concentration for a freshwater lake. Additionally, a pronounced H_2S odor emanated from the lake's bottom water (Bækken & Haugen 2011; Saunes & Værøy 2017).

4.3 Stratification

In terms of discussing the distribution of saline stratification, we need to establish the fact that a diffuse layer of salty water is covering the majority of hypolimnion. Application of road salt has been reduced in the last years, considering earlier studies that had great values of conductivity and chloride in Kutjern. As the results visualize, there is a clear range of chloride concentration starting in between 4 and 5 m of depth. Chloride concentration is also increasing towards the bottom and there is reason to believe that the chloride comes from road runoff. The same area had high levels of ORP, which dropped drastically below 3.2 m. Negative correlation between oxygen and specific conductivity, and positive correlation between ORP and specific conductivity is therefore likely and reasonable in such a stratified lake. Without any drastic turbulence or intervention these processes have been ongoing for years and will continue.

Temperature measurements also indicated thermal stratification over the sampling period. There were preliminary temperatures between 20 – 15 °C degrees in the first meter, 15 - 10 °C from 1 – 2 m and then rapidly down to from 2 m and deeper. That was the case through the whole season, which means there were little to less mixing of temperatures through the water column. Thermal stratification can be discussed when there are a few degrees Celsius difference from top to bottom of a lake (Yu et. al 2010) With Kutjern having close to 20 degrees Celsius difference in different parts of the lake, we can establish the fact that thermal stratification occurred during the sampling period and the reason for that is most likely ripple effects of saline stratification which have prevented circulation over time.

The air temperature around Kutjern, had increased according to meteorological data from Norsk Klimaservicesenter, which means more of the lake should have been heated with normal circulation or turbulence. Because sunlight only reached through the first two meters, photosynthesis likely occurred in epilimnion, creating more organic material at this depth and again absorbing more sunlight and preventing heat from stretching down in the water column (Wetzel 2001).

4.4 O₂ & DOC

Diffusion of oxygen into water takes time, and to saturate water with oxygen from the atmosphere, the water must circulate. Ideal saturation is based on control of diffusion, mixing and saturation. Deviation in form of dissolved oxygen from photosynthesis or biochemical oxidations, can slightly impact the saturation (Wetzel 2001). Lake Kutjern has limited circulation due to stratification and limited primary production mostly in epilimnion, which is the reason to believe the lake is undersaturated (Bækken 2012). Extreme clinograde oxygen profiles can occur in meromictic lakes with stratification. When monimolimnion receives organic material or even sulfates from saline water, the oxygen intrusion depletes (Wetzel 2001).

Degradation of organic matter consume oxygen wherever it proceeds in the water. When oxygen is consumed, labile organic matter is oxidized anaerobically by other electron acceptors in order of an energetic yield. Denitrification is followed by reduction of manganese and iron due to reductive dissolution of iron and manganese oxyhydroxides. This process releases aqueous Fe(II), Mn(II) and heavy metals. Sulfate reduction produces hydrogen sulfide, as we experienced when taking water samples from 4 m – 8 m. It may even react with dissolved iron to produce iron sulfides. When these terminal electron acceptors are depleted, the remaining organic matter is stored as methane, acetate or sedimented. The speed of this process is determined by redox potential in the lake (Sibert 2015).

Productivity by biota, and respiration is determining the total concentration of O₂ (Wetzel 2001). The reason ammonia values were drastically changing in June was due to its increasing primary production. June and some days of July, like the 25th, had higher temperatures with great sunlight intrusion, which made primary production more applicable in epilimnion. Oxygen concentrations were close to zero from around 2 – 3 m depth. So photosynthetic activity was firstly conducted in epilimnion, where oxygen was available. This means that respiration consumed oxygen in hypolimnion, and eventually made it anoxic. The temperatures indicated that epilimnion was heated, while most of the lake is below 10 °C. This correlates with the fact that the lake lack of turbulence and the stratification prohibits photosynthesis and primary production through the entire water column.

According to the PCA-analysis, O₂ is negatively correlated with specific conductivity and redox potential, which indicates that salt intrusion and runoff from the road has negative impacts on O₂ concentration and partly the reason why Kutjern became anoxic in hypolimnion and established a chemocline around 3 - 4 m.

Dissolved organic carbon increased during the season. The input of DOC probably increased with rain and temperature, which makes sense considering the correlation between these parameters. Total Nitrogen increased with depth and probably because the available nitrogen was easiest consumed in epilimnion, while the remains were deposited in the sediments due to anoxic conditions. Chlorophyll a increased drastically in the third week of July until the second week of August. The same goes for total nitrogen. Temperature also rise at this point, which means pre-conditions for algae growth was good (Wetzel 2001)

4.5 Redox & pH

Redox potential was never stable at any point, even though the variation within each depth had similar redox potentials most of the season. The first three meters had oxidizing conditions, but below 3.5 m it converted into more reducing conditions. The chemocline moved up and down through the sampling period, but from 4 m and down there were reducing conditions through the entire season. This shift was controlled by the chemocline and equivalent to its ripple effects. In oxygen rich environments, oxidation is favored, while in anaerobic conditions reducing conditions dominate (Wetzel 2001).

Redox conditions were affected by breakdown of organic matter. Microbial activity plays a crucial role for determining redox potential, because decomposition enhance consumption of electron acceptors (such as O_2 , nitrate, sulfate) leading to reducing conditions. Oxygen demand leads to anaerobic respiration, which involves alternative electron acceptors like nitrate or sulfate to proceed degradation of organic matter. Sulfate concentration was lower at 8 m, where conditions were mostly anoxic and reducing. Which perquisitions for development and fluctuation of H_2S gas throughout the water column. Water depth and meromixis prevent distribution of heat towards the bottom, which effects primary production and oxygen distribution towards the bottom, favoring reducing conditions (Wetzel 2001).

The pH measurements indicate several shifts throughout the summer. Firstly, there was extending values from 5,0 till 6,6 down through the water column, with different values at different depths. The first meter had the highest pH around 6, before lowering into acidic values around the bottom of epilimnion. Down under epilimnion there was mostly levels of pH about 5.6, before hypolimnion became more basic at pH values around 6,0. The main reason for this shift is due to concentration of CO_2 in the water column. CO_2 dissolved in water give carbonation or acids like HCO_3^- , H_2CO_3 , which lowers the pH. In epilimnion photosynthetic bacteria consumed CO_2 in primary production, while in hypolimnion where there was less photosynthesis due to limited sunlight, the CO_2 concentration naturally increased. Respiration and decomposition of organic material resulted in increased concentrations of CO_2 as well. As Kutjern is related to a larger bog, the geological properties of the catchment may contribute to allochthonous supplies of DOM and humic acid (Wetzel 2001).

4.6 Iron/Manganese distribution.

Because iron/manganese correlated with most of the heavy metals we studied (*Table 1*), there is reasonable to discuss how these metals behaved in Kutjern in terms of mobility and speciation. Like manganese, iron species is pH and redox dependent. Therefore, Fe complexes may mostly be Fe^{2+} or $\text{Fe}(\text{OH})_2$ in more reducing conditions. Since Manganese is like iron in species appearance, the Mn^{2+} will be the most prevalent form. Manganese is basically controlled by pH and change between Mn^{2+} and MnCO_3 in pH 6 - 8, which is the shift of some of our samples. The most common species of ferric iron in lakes is $\text{Fe}(\text{OH})_3$.

At equilibrium in pH between 5 - 8 $\text{Fe}(\text{OH})_3$ is hardly soluble. By having Fe^{2+} available in higher parts of the water column, bioavailability may increase even though iron is not directly toxic. In flowing systems, substances like lead might be more toxic than Fe but is often bound to organic substances or adsorbed to particles (Wetzel 2001). Mn and Fe correlated with Co, Pb, Ni and Cr according to the PCA analysis (*Table 1*). Mn and Fe concentrations increased simultaneously with decreasing oxygen concentrations towards the end of august. Release from sediment surface because of anoxic conditions, was therefore more likely to occur towards the end of the season.

4.7 Heavy metals

The composition of heavy metals in Kutjern was related to traffic pollution and runoff, but their mobility and bioavailability in Kutjern was reasonably low, even though redox conditions and pH that controls the solubility of metals, was found at different levels through the whole sampling period. Copper was mostly bound to organic material, while some was bound as $\text{Cu}(\text{OH})_2$ and CuCO_3 . This means that DOC controls pH that again controls the mobility of copper. By increasing conductivity and lowering pH, more Cu^{2+} ions were solved. Increased conductivity and lowered pH mobilize organic material and therefore copper. Which is why copper was found in higher concentrations in epilimnion and generally mobile in the aquatic phase (Balistrieri et al., 1992). Rapid changes in concentration occurred through the season and may be related to the DOM supplies coming from the bog nearby.

A cluster analysis done by Kasem et. Al (2020) revealed that Cu, Zn, Pb, Fe, Co, Cr, and Ni exhibit comparable patterns, with Eh serving as a significant factor in regulating them within water systems. Meanwhile our study shows that Mn and Fe demonstrate a strong correlation coefficient, while Cr, Mn, Fe and Co show correlation with specific conductivity and pH, and less correlation with ORP in 1 – 4 m of depth (Kasem et. Al 2020).

Cr speciation is by example more determined by reducing conditions, where $\text{Cr}(\text{OH})_4^-$ and CrH are most prevalent under pH 6 - 8. Co is also redox dependent, forming Co^{2+} ions and therefore reactive in our pH range with reducing conditions. Cd as Cd^{2+} and nikkell as NiH under the same set of physical parameters. That means particle bound heavy metals are less soluble in oxidizing environments like we measured at 1 – 4 m but are likely to increase mobility and change speciation in reducing conditions.

According to the PCA-analysis S and Cu were negatively correlated DOC, Cr, Mn, Fe, Co, and partly Ni, in 0 – 4 m. Which indicates different behavior and speciation in epilimnion. DOC was positively correlated with Cr, Mn, Fe, Co and partly Ni, which indicates solubility of these metals. DOC adsorbs some of these metals during transportation into the lake and may also be able to sediment metals and prevent distribution directly when entering the lake. S and Cu have higher concentrations in epilimnion than hypolimnion, which indicates less sedimentation and more mobility. In 4 – 8 m there was quite a different spectrum of metals due to different behavior. In this range Cu, S and Zn are negatively correlated with Pb, Ni, Co, Cr, Fe, Mn. Again, the metal speciation is dependent on chemical composition of the metal. Some relation to pH is found for the recent mentioned metals at certain depths, but pH does not change enough to influence all of them directly (Balistrieri et al., 1992).

The current metal speciation per given time is therefore dependent on redox conditions, pH, and the chemical properties of the metal. Some metals are stable, and some are more reactive at different pH values. The highest toxicity of metals was found in S, Fe and Zn. These substances are less toxic than for example Co, Ni and Cr (Wetzel 2001). Mobility of metals increased by the change of redox conditions and pH because those factors lead to heavy metal release from the sediments surface and increases bioavailability in the aquatic phase. Depending on the toxicity of the released metal, it could potentially be harmful to organisms when made bioavailable. If the heavy metals are particularly bound when transported into the lake, there is reason to believe most of them are sedimented and made unavailable for microorganisms directly, by the redox potential and pH equivalent to the results of this study (Kasem et. Al 2020).

4.8 Limitations

This study does not include:

- A) Groundwater impacts
- B) Industrial attributes
- C) Internal pollution by fish or biota
- D) Sewage or wastewater treatment of runoff
- E) Soil measurements of salt between the road and lake

5. Conclusion

By measuring temperature, oxygen, specific conductivity, redox potential, pH as well as a large spectrum of metals and salts, there was found a discernible correlation between these parameters and meromixis. Mobilization of iron and manganese from sediment, coupled with lack of nitrogen and sulfate in epilimnion indicates together with large amounts of dissolved organic carbon hypoxic conditions in lake Kutjern. The salt intrusion has therefore instigated a distinct layer of stratification, delineating a chemocline below epilimnion.

Comparative assessment against antecedent investigations reveals that Kutjern maintains a layer of stratification akin to previous studies, even though salt application and runoff from the nearby road has been reduced together with heavy metal discharge. According to Miljødirektoratets Veileder (*Attachment S1*) of water quality the metal composition in Kutjern falls below toxic thresholds and thereby indicating a classification of good water quality, without underestimating the deleterious effects of increased conductivity and ionic water (Norconsult 2023).

H_0 is therefore confirmed and H_1 is discarded.

For future studies, it is advisable to conduct sediment and soil analyses in between the road of E18 and Kutjern, to ascertain the total presence of particle-bound heavy metals. Such endeavors would offer further insights in road salt contamination and its ramifications on the surrounding environment and enrich already existing knowledge of roadside pollution.

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7. Appendix

Table S1 – Classification of metal toxicity (([M608.pdf \(miljodirektoratet.no\)](#) read: 03.04.2024)

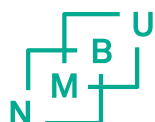
Navn på stoff	Klasse I	Klasse II	Klasse III	Klasse IV	Klasse V
	Bakgrunn	God	Moderat	Dårlig	Svært dårlig
Metaller					
Arsen	0 - 0,15	0,15 - 0,5	0,5 - 8,5	8,5 - 85	> 85
Bly	0 - 0,02	0,02 - 1,2	1,2 - 14	14 - 57	> 57
Kadmium	0 - 0,003	Fotnote 1	Fotnote 2	Fotnote 3	Fotnote 3
Kobber	0 - 0,3	0,3 - 7,8		7,8 - 15,6	> 15,6
Krom	0 - 0,1	0,1 - 3,4			> 3,4
Kvikksølv	0 - 0,001	0,001 - 0,047	0,047 - 0,07	0,07 - 0,14	> 0,14
Nikkel	0 - 0,5	0,5 - 4	4 - 34	34 - 67	> 67
Sink	0 - 1,5	1,5 - 11		11 - 60	> 60
PAH					
Naftalen	0 - 0,00066	0,00066 - 2	2 - 130	130 - 650	> 650
Acenaftalen	0 - 0,00001	0,00001 - 1,28	1,28 - 33	33 - 330	> 330
Acenaften	0 - 0,000034	0,000034 - 3,8		3,8 - 382	> 382
Fluoren	0 - 0,00019	0,00019 - 1,5	1,5 - 34	34 - 339	> 339
Fenantren	0 - 0,00025	0,00025 - 0,5	0,5 - 6,7	6,7 - 67	> 67
Antracen	0 - 0,004	0,004 - 0,1		0,1 - 1	> 1
Fluroanten	0 - 0,00029	0,00029 - 0,0063	0,0063 - 0,12	0,12 - 0,6	> 0,6
Pyren	0 - 0,000053	0,000053 - 0,023		0,023 - 0,23	> 0,23
Benzo(a)antracen	0 - 0,000006	0,000006 - 0,012	0,012 - 0,018	0,018 - 1,8	> 1,8

Table S4 – Average data from 0 – 4 m & 4 – 8 m of Kutjern physical measurements, used for PCR analysis.

Prøver tatt rundt kl.10:00	Temperatur	Spesific Cond	pH	ORP	Chl A	Oxygen concentration		
0-4m	24.05.2023	8,52364706	126,894118	5,92505882	-18,1788235	15,0247059	3,30858824	2,12651092
	30.05.2023	8,30835294	146,752941	5,97305882	-27,5082353	16,0811765	2,85764706	2,12651092
	07.06.2023	9,45592593	147,592593	5,93049383	-69,6	17,9074074	2,25691358	2,23953421
	14.06.2023	10,1853086	138,987654	5,90518519	-39,017284	21,4592593	1,73728395	2,23953421
	21.06.2023	9,94216216	157,297297	5,88986486	-46,0081081	29,2540541	0,80337838	2,39174366
	28.06.2023	9,69390909	436,181818	5,94618182	-47,8336364	31,8790909	0,93981818	1,94144146
	04.07.2023	11,8166667	138,925926	6,01296296	-6,21234568	39,5641975	2,17987654	2,2395344
	10.07.2023	12,5498765	140,123457	6,0191358	-1,34567901	43,3320988	2,01925926	2,2395344
	17.07.2023	11,607284	173,679012	6,05148148	-34,5209877	40,8925926	2,37	2,2395344
	24.07.2023	12,4211111	130,271605	6,09851852	-36,2246914	45,7469136	2,74518519	2,2395344
	31.07.2023	12,7797531	125,555556	6,0208642	-6,98888889	45,3814815	2,30814815	2,2395344
	06.08.2023	12,7646914	130,271605	6,06098765	-20,0209877	45,2790123	2,08246914	2,2395344
	13.08.2023	12,5564198	119,82716	5,87641975	3,21481481	44,4802469	2,12777778	2,2395344
	20.08.2023	12,8683951	118,938272	5,93024691	48,8493827	43,0567901	1,70185185	2,2395344
	27.08.2023	12,5461728	96,8888889	5,66283951	131,420988	36,9135802	4,01666667	2,2395344
4-8m	24.05.2023	3,84067568	1060,77027	5,92148649	-134,358108	19,0243243	-0,18824324	5,58383517
	30.05.2023	3,84591549	1109,47887	5,91788732	-146,176056	19,6464789	-0,14183099	5,51860264
	07.06.2023	3,88405405	1092,01351	5,91918919	-147,677027	19,6391892	-0,11851351	5,60988175
	14.06.2023	3,92913043	1035,07246	5,89623188	-153,74058	20,1231884	-0,11362319	5,50116086
	21.06.2023	3,98441176	1068,08824	5,94691176	-167,876471	19,9220588	-0,12279412	5,47941722
	28.06.2023	4,04271429	1031,28571	5,94928571	-163,16	19,76	-0,11914286	5,52290558
	04.07.2023	4,11304348	1002,78261	5,93956522	-162,434783	20,3507246	-0,10652174	5,5011614
	10.07.2023	4,1315942	1031,66667	5,94144928	-165,568116	20,2724638	-0,09376812	5,5011614
	17.07.2023	4,15912281	1090	5,95368421	-180,712281	19,2859649	-0,09298246	5,24023124
	24.07.2023	4,30753623	938,84058	5,95724638	-153,52029	21,3449275	-0,08028986	5,5011614
	31.07.2023	4,41710145	890,492754	5,95898551	-160,07971	22,1492754	-0,0884058	5,5011614
	06.08.2023	4,47753623	897,57971	5,9626087	-171,281159	21,9130435	-0,07217391	5,5011614
	13.08.2023	4,585	898,671429	5,94857143	-165,068571	24,2785714	-0,07114286	5,52290558
	20.08.2023	4,67728571	810,157143	5,94328571	-159,867143	24,2228571	-0,072	5,52290558
	27.08.2023	4,961	826,957143	6,00942857	-143,474286	25,7771429	-0,031	5,52290558

Table S5 – Average data from 0 – 4 m & 4 – 8 m data of metals, Cl and DOC measured in Kutjern, used for PCR analysis.

S	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb	Cl	DOC
1,35	0,4375	97	0,585	0,475	0,8675	2,2	60,5	0,0635	0,505	18,847525	16,7575
1,08	0,8625	485	8,1	1,125	1,475	1,45	53,25	0,035625	0,88	238,052925	19,5575
1,4	0,415	98,5	0,6275	0,4925	0,95	1,875	50,25	0,015	0,45	19,6271	16,4675
1,07	0,8775	492,5	8	1,0875	1,095	1,2	43,75	0,008	0,775	239,0227	19,2925
1,4	0,54	110	0,69	0,555	0,6475	1,775	64,25	0,01725	0,43	21,205425	17,7225
1,1125	0,99	557,5	8,95	1,1975	1,1225	1,225	56,25	0,010625	0,805	241,4896	20,3325
1,375	0,4175	119,75	0,7225	0,535	0,9475	2,2	49,5	0,02925	0,51	21,10245	16,6475
1,0075	0,8925	567,5	8,625	1,1325	1,625	1,475	39,75	0,00865	0,8125	248,224075	18,9625
1,4	0,4575	145,75	0,815	0,63	0,7625	1,75	54,5	0,021	0,53	22,698675	16,675
0,9925	0,8825	572,5	8,75	1,1275	1,25	1,2925	40	0,006925	0,75	179,13875	18,5175
1,375	0,4125	147,35	0,7825	0,7145	1,15	1,775	37,75	0,0155	0,5125	22,5638	16,5175
0,92	0,92	552,5	8,9	1,1175	1,7	1,15	29,75	0,00705	0,7625	257,855825	19,535
1,325	0,4325	142,25	0,74	0,6345	0,9775	1,725	38,75	0,02425	0,4675	21,969275	16,2
0,905	0,925	557,5	9,05	1,1675	2,325	1,45	38,5	0,0815	0,815	256,68195	18,4825
1,325	0,385	138	0,7025	0,6225	1,725	1,725	129	0,02725	9,975	21,6904	15,6525
0,9875	0,8525	532,5	8,25	1,1075	1,4	1,2	35,75	0,0088	0,8875	237,11255	18,885
1,475	0,4075	131	0,685	0,9275	0,73	1,95	50,75	0,017	0,4275	20,679025	16,1975
0,9725	0,8725	545	8,6	1,35	1,425	1,1375	42	0,005675	0,845	238,970975	19,5875
1,675	0,425	129,5	0,6775	0,985	0,9875	1,65	58	0,0202	0,4425	19,24025	17,1875
1,0625	0,8375	512,5	7,8	1,45	1,65	1,145	48,25	0,008125	0,7875	231,33365	18,9375
1,55	0,42	137,75	0,6975	0,8725	1,425	1,6	67	0,0215	0,4525	19,8328	17,49
0,9725	0,825	492,5	7,775	1,45	2,15	1,65	63,5	0,02345	0,8425	222,252925	18,595
1,475	0,475	150,75	0,9	1,205	1,1975	2,125	68,75	0,02925	0,7875	19,632475	20,33
0,9375	0,845	520	8,375	1,575	1,65	1,2	46,75	0,008275	0,8775	225,378525	18,795
1,3	0,4575	142,75	0,8875	1,085	1,225	2,325	72,75	0,02875	0,6325	18,24995	20,6875
0,9	0,83	495	7,725	1,325	1,275	1,12	59,5	2,49	0,7175	219,12515	17,77
1,1725	0,46	142,25	0,975	1,1725	0,9325	2,275	56,5	0,0385	0,9125	19,408775	21,2025
0,8625	0,7925	502,5	7,7	1,35	1,3	1,075	43	0,0071	0,795	238,386375	18,825
1,3	0,4725	155,75	0,965	1,2275	1,4	1,95	53,25	0,0495	0,6825	16,917675	22,535
0,89	0,8775	535	8,4	1,45	2,05	1,175	40,75	0,01445	0,765	220,0513	17,9125



Norges miljø- og biovitenskapelige universitet
Noregs miljø- og biovitenskapelige universitet
Norwegian University of Life Sciences

Postboks 5003
NO-1432 Ås
Norway