Norwegian University of Life Sciences

Master's Thesis 2024 60 ECTS
Faculty of Environmental Sciences and Natural Resource Management
Gunnhild Riise and Thomas Rohrlack

The importance of thermal stratification and oxygen conditions for internal cycling of nitrogen and release of phosphorus in Lake Årungen

Andreas Gustav Mandelid Meyer
Master of Science in Environmental Science

Acknowledgements

I want to thank my supervisors Gunnhild Riise & Thomas Rohrlack for their guidance during field work, laboratory work and writing. Further I would like to express gratitude to PURA who supported the laboratory analyses and field work financially. And I would like to thank my fellow students for support during the days at the study room.

Abstract

Eutrophication together with its subsequent effects, increased levels of phytoplankton, algae, decreased water transparency and oxygen depletion poses a significant threat to our limnic systems. Cultural eutrophication, in particular, significantly shortens the lifespan of freshwater bodies compared to natural processes. Lake Årungen, a dimictic lake, undergoes seasonal mixing, impacting its oxygen levels and nutrient distribution. During stratification, the lake experiences anoxic conditions in the hypolimnion, affecting the nitrogen and phosphorus cycles. The presence of nitrate in the hypolimnion can buffer against phosphorus release from sediments, mitigating eutrophication. The degree of mixing in Lake Årungen, influenced by wind and weather conditions, is crucial for maintaining water quality. Increased air temperatures due to climate change are contributing to the earlier onset and greater stability of thermal stratification in lakes such as Lake Årungen. This prolonged stratification period can lead to extended anoxic conditions in the hypolimnion and increases chances of internal phosphorus loading. Effective management of nutrient inputs, particularly from agriculture, is essential to counteract eutrophication and preserve freshwater ecosystems. Increased thermal stratification stability from increased air temperatures early in the season reduces oxygen distribution, increasing anoxia duration and necessitating higher nitrate levels to prevent reducing conditions. Comparative data from previous years (2017, 2013, and 2009) indicated that sufficient nitrate levels are critical in buffering phosphorus release from sediments. In 2023, nitrate levels at the onset of anoxia were 2.6 mg/l, maintaining a high redox potential and preventing significant internal phosphorus loading. In contrast, lower nitrate levels in earlier years led to substantial phosphorus release. Threshold levels for nitrate concentration, crucial in preventing internal phosphorus loading, are influenced by various biogeochemical and environmental factors, including sediment composition, pH, and microbial activity. Effective management strategies should focus on reducing external nitrate inputs and maintaining higher nitrate levels to mitigate the impacts of prolonged thermal stratification and prevent eutrophication in Lake Årungen.

Contents

Introduction

Amongst environmental issues, one that is considered a significant threat concerning the freshwater systems, is eutrophication. Eutrophication is observed to be the cause of multiple unfavourable effects on any limnic waterbody, e.g., increased biomass of phytoplankton, periphyton, and suspended algae, decreased water column transparency, depletion of deep-water oxygen levels and problems with taste, odour, and filtration in drinking water (Smith, 2013). Eutrophication can happen from both natural and cultural origin. The former being a slow process where increased primary production, increased organic matter content and increased sedimentation rate forms a slow positive feedback-loop that ensures shallower water and accumulation of nutrients and biomass over longer periods of time (Sawyer, 1966; Wetzel, 2001). Cultural eutrophication is affected by anthropogenic influence that changes the availability of nitrogen and phosphorus, which is known as growth-limiting nutrients, hence accelerating the speed of the process. This in turn leads to a significantly shorter lifespan for the freshwater in question, than if it would be affected purely by natural eutrophication. The main reason for the rise of cultural eutrophication is the rapid advancement in agricultural practices starting in the second half of the 20th century (Smith, 2013). Global production of agricultural fertilizers released under 10 million metric tons of nitrogen in 1950, but this number may surpass 135 million tons by the year 2030 (Vitousek et al., 1997). Pollution to these waterbodies from both agriculture and other sources must be identified and limited in order to counteract such widespread cultural eutrophication.

Lake Årungen is under the category of dimictic lakes (Romarheim & Riise 2009), meaning it undergoes two periods of full mixing during a year, one in the autumn and one in the spring season. Usually, when there is not full circulation, there is a layer between epilimnion and hypolimnion, metalimnion, in which there will be formed a thermocline. Thermocline is a relatively "shallow" layer in the lake where the temperature changes greatly. When summer is close, the heating of mostly the surface water creates a warm water layer, epilimnion. Since the heating from solar radiation is primarily affecting the surface water, and less downwards in the water column, there will be a layer of warm and less dense water lying over the colder, more dense water, the hypolimnion. These differences in density help prevent the water from mixing. A metalimnion layer is formed between the epilimnion and hypolimnion, where this thermocline with rapid temperature change is found. At this point there is complete stratification with three distinct layers with each having their temperature range. The wind can contribute to some mixing of the water, but it will be limited to the epilimnion due to the temperature and subsequent density-differences. When such stratification occurs, there is a high probability of the hypolimnion reaching anoxic conditions, because stratification hinders supply of oxygenated water from top to bottom and the consumption of oxygen is ongoing, caused by the decaying of organic detritus downwards to the bottom of the lake (Chapman, 2019). This decay happens through microbial degradation and consumes oxygen. When the season changes to autumn, the colder air temperature will decrease the depth of epilimnion, and hypolimnion will increase, to the point where the stratification is lost. When the temperature differences in the whole lake is uniform throughout the depths of the lake, there will be full circulation. Here we will see oxygenated water being transported downwards into the bottom layers because of water mixing. Wind will contribute more to the mixing at this point, as the water that is directly in contact with the cold air will sink down relatively quickly and further contribute to the lake mixing. Closer to winter season, the surface water will slowly get colder and turn into ice. As the water molecules have solidified, the air and wind conditions over the ice layer will have no mixing effect on the lake. Stratification will be able to form, with a thin layer just under the ice with temperature between 0 and 4 degrees Celsius. Under this layer the remaining water lies, with temperatures usually at approximately 4 degrees or just above. As spring arrives the ice will slowly melt away and since the temperature differences throughout the water column are relatively small, mixing will be allowed to begin. Once the ice cover is gone, the warm air, and especially the wind, will again contribute further to the mixing, enabling the supply of oxygen to the bottom of the lake. This continues until the air temperatures rise again towards summer (Chapman, 2019).

Wetzel (2001) explains how nitrogen can take various chemical forms when entering freshwaters. It occurs as dissolved molecular nitrogen (N_2), many different organic compounds like amino acids, amines, proteins, recalcitrant humic compounds, ammonia (NH_4^+), nitrite (NO_2^-) and nitrate (NO_3^-). The amount of available nitrogen in the waterbody is primarily being regulated by the processes of denitrification, sedimentation of nitrogen-associated matter, and uptake by the organisms living there, though this is a simplification of the complex system. Effluent outflow, bacterial denitrification and sedimentation of both inorganic and organic compounds may lead to both permanent and temporary loss of nitrogen from the lake. So, Wetzel

(2001) emphasizes that much of, not only the load of nitrogen, but also the metabolism of nitrogen happens in the sediments. Nitrogen fixation, which is normally a minor component of the total nitrogen input, can role as major driving source of nitrogen into the system at the times of year where agricultural applications of fertilizer is at its most. These outputs, together with the inputs, are all important to understand for a complete measurement of total nitrogen retention (Wetzel, 2001).

As mentioned, there is a high probability for lakes to form an anoxic hypolimnion during lake stratification, where the dissolved oxygen has been depleted. In the Central Basin of Lake Erie in the 1960s, lake stratification led to such anoxic conditions and accumulation of phosphorus in the lake. This led to the initiation of control programs to monitor the lake and its phosphorus levels. This lake is a dimictic lake in a cold temperate area, comparable with Lake Årungen (Chapman, 2019). The state of the redox conditions will somewhat determine to which degree the phosphorus will be released from the sediments, because decreased redox conditions will in turn mean less reduction of nitrate to molecular nitrogen gas, which in turn will mean more nitrate available in the lake. Frostad (2018) found that there is an important relation between the concentration of nitrate and concentration of phosphate, in Lake Årungen. She studied how nitrate can act as a phosphorus-buffer. This is because when there is no oxygen present, nitrate can work as an electron-acceptor, hence it is oxidizing some metals, like the iron that exists in the upper layers in the lake sediments. Internal loading of phosphorus is primarily linked to happen because of reduction of this iron in the upper sediment layers (Frostad, 2018), therefore nitrate in the hypolimnion is a potential buffer to phosphorus loading.

Because of the size and the north-south direction of Lake Årungen, it is especially prone to having its degree of mixing greatly affected by wind and other weather conditions (Frostad, 2018). In the watercourse of Ytre Oslofjord, the degree of retention of nitrogen and phosphorus in the freshwaters in the watercourse is the factor associated with the most uncertainty (Staalstrøm et al 2022), explaining that the presence of nitrate in the hypolimnion, is crucial for mitigating increased phosphorus loading and the consequences this potentially can lead to.

In this master thesis I want to find study the stratification in Lake Årungen, linked to the levels of nitrogen and phosphorus, together with other variables, and to find out more about:

1) How the changes in climate and weather conditions are affecting the thermal stratification in Lake Årungen,

   and

2) How this thermal stratification and the distribution of oxygen in the water column will impact the levels of nitrate and release of phosphorus in the lake.

Materials and methods

Study system

Area of the study is limited to the Årungen catchment area, and the focus is set on Lake Årungen. Lake Årungen is located in Akershus county, specifically in the municipality of Ås, though the catchment includes areas within Frogn and Nordre Follo municipalities as well. The lake lies approximately 29 kilometers south of the capital, Oslo, and around one kilometer northwest of NMBU. The surrounding landscape around both the lake and the catchment in general is filled with agricultural lands, forests, and some urban areas. Most of the surrounding areas are heavily impacted by anthropogenic sources.

The whole Årungen catchment covers an area of approximately 52 square kilometers. Agricultural lands occupy 53%, while forests cover 34%, and urban areas make up for the last 10%, as reported by Hongve et al.(1980). The urban areas in the catchment are mainly the center of Ås and Ski, in which you have the highest population density. Besides the Ski center, there is not much industrial activity.

Lake Årungen itself is an oblong lake that stretches 3 kilometers in length and it's around 450 meters broad. The total size of the lake is approximately 1.3 square kilometers and the deepest point in the lake is 13 meters deep. The global retention time of the lake is estimated to be 4.5 months (Hongve et al., 1980). The coordinates of Lake Årungen are 59.6848 North and 10.7489 East, specifically the deepest point in Lake Årungen (WQDataLIVE).

Field work

The field work consisted of conducting in-situ measurements, collecting water samples and analyzing samples in the laboratory. The first field work involved taking initial in-situ measurements and water samples and commenced on the 24th of May 2023. From there, new samples were generally taken every other week (every 14th day) and continued until sometime in October. Sampling date varied some due to practical reasons. Sampling over the summer made it possible to observe the effects of the stratification that usually occurred in August.

The water samples consisted of 8 samples from each of 7 different depths, taken from a vertical line at the deepest point in the lake (13 meters), and 8 samples from the stream Årungselva which goes by “outlet” in the dataset, totaling 64 samples. For practical reasons, primarily for avoiding disturbance of the sediment surface and sample contamination, the most bottom water samples are taken from 12 meters, instead of right above the lake bottom at 13 meters. Therefore, the depths where the samples were taken were: 0.5m, 1m, 3m, 5m, 8, 11m and 12 meters.

In-situ measurements included water temperatures (°C) and oxygen levels, which was measured in dissolved oxygen concentration (mg/l) and oxygen saturation (%). These included more frequent measurements than the main depths: 0.5m, 1m, 2m, 3m, 4m, 5m, 6m, 7m, 8m, 9m, 10m, 11m, and 12m. These measurements were not optimal for lab analysis as the storage of the samples could to some degree affect these values. These measurements were collected using a handheld Optical Dissolved Oxygen Instrument logger (Pro-series, from YSI). Absorbance was measured at 254 nm the same day as sampling (UV-VIS Spectrophotometer UV1201, from Shimadzu). Additionally, water transparency was measured in the field, using a standard white Secchi disc, and was later used to calculate an estimate for the euphotic depth in the lake.

Lab analysis

pH was measured by analyzing unfiltered samples at room temperature with a pH meter (pHenomenal 1100 pH /mV /C Meter, from VWR) and analysis was executed according to Norwegian Standard NS4720. The pH meter was calibrated with the use of two reference solutions at pH 4 and pH 7 prior to analyzing the water samples.

Chlorophyll *a* was measured through pigment analysis in accordance with NS4767. They were filtered by vacuum filtration with a glass microfiber filter with 1.2 micrometers in pore diameter (Whatman grade GF/C, from VWR) extracted by adding 3ml aceton, and then freeze dried in a dark vacuum. The samples were centrifuged at 3000rpm for 15 minutes and the absorbance at wavelength 665 nm and 750 nm was determined in a 1 cm cuvette. The samples were transferred to brown glass tubes, to minimize the risk of light penetration. It was then run through a high-performance liquid chromatography instrument (UltiMate 3000 HPLC, from Thermo Scientific), which has been calibrated with known solutions to ensure the instruments accuracy.

Tot-P, total phosphorus concentration, was measured through NS-EN 1189. What was really measured here was the concentration of orthophosphate. 2ml potassium peroxydisulfate was added as an oxidizing agent, converting the phosphorus to orthophosphate. The sample was autoclaved at 1 ATM and 121 degrees Celsius for 30 minutes. After cooling down, the samples of orthophosphate were added 20microliters antimony-molybdate, causing the formation of an antimony phosphomolybdate complex. Further 20microliters of an ascorbic acid were added, which reduced the complex and gave it a blue color., and it was measured at the absorbance at 880 nm, which gave the concentrations of the orthophosphate (UV-VIS Spectrophotometer UV1201, from Shimadzu).

Phosphate-P concentration was measured as orthophosphate in accordance with NS-EN ISO 10304-1. The sample was analyzed through a single column ion chromatography machine (Dionex ICS-6000DP, from Thermo Scientific). The phosphate goes through a low-capacity anion-exchanger as a stationary phase, while the mobile phase includes a carbonate/bi-carbonate buffer. The solution passes through a suppressor which reduces the conductivity of the mobile phase, and the phosphate concentration peaks are registered by a conductivity detector.

Tot-N, total nitrogen concentration, was measured in accordance with NS 4743, and done through a FIA, flow injection analysis. Total nitrogen was analyzed quickly, as this is important to avoid changes in the sample and it should therefore be stored in a dark and cold storage space for not more than 3 days, if stored. A solution of potassium peroxydisulfate together with NaOH, "Alkaline activated potassium peroxydisulfate", (to ensure a basic solution) was added as an oxidizing agent, and the sample was autoclaved at 1 ATM 121 degrees Celsius for 30 minutes. The solution then went through an FIA analysis (FIAstar 5000 analyzer). By going through a cadmium column in this apparatus, the nitrate was reduced to nitrite and coupled with a N-(1-naphthyl) ethylenediamine dihydrochloride solution and turned the sample into magenta, and the absorbance was measured at 540 nm.

Nitrate-N concentration was measured in accordance with NS-EN ISO 10304-1. The sample was analyzed through single column ion chromatography (Dionex ICS-6000DP). The nitrate goes through a low-capacity anion-exchanger as a stationary phase, while the mobile phase includes a carbonate/bi-carbonate buffer. The solution passes through a suppressor which reduces the conductivity of the mobile phase, and the nitrate concentration peaks are registered by a conductivity detector.

Ammonium-N concentration was measured in accordance with NS 4746. The ammonium was put in a weak alkaline solution (pH=10.8-11.4) and reacted with hypochlorite to form monochloramine, which was then added salicylate that gives a blue color. This reaction is a slow process, and therefore it could take around an hour to measure. After an hour the sample was measured at 655 nm. This method can detect levels between 0.02 mg/l and 2.0 mg/l, with an accuracy of 5%.

Data processing

All sets of data were organized and stored in Microsoft Excel (version 2404, build 17531.20000). Figures were produced in both Excel and Rstudio (R, R-4.4.0 Windows). The climate date, euphotic depth, water temperatures and oxygen concentration were processed and visualized in Excel. Oxygen saturation, pH, nutrients, chlorophyll-*a* and water temperatures across the different depths over the study period were worked on in Rstudio and presented as contour plots/isopleth diagrams. There were also executed a simple regression analysis in Microsoft Excel to calculate a decomposition rate of nitrate available in the hypolimnion during anoxic conditions.

Results

Climatic factors

Air temperature and precipitation over the study period is retrieved from the data collection at BIOKLIM, located at Søråsjordet in Ås, Akershus county, with permission from Signe Kroken at BIOKLIM. This data is complete for the entire study period from May to October 2023. Datasets for the three earlier normal periods 1991-2020, 1961-1990 and 1931-1960 have also been retrieved, with mean values of air temperature and precipitation (source BIOKLIM).

Air temperatures increased at the start of May and went through some minor fluctuations up till the change of month before it had a significant increase again during June. The warmest temperature was measured in the middle of June, 22.5 degrees. After this increase, the temperature stayed relatively steady until the beginning of October. October was the month with the largest differentiation, ranging from –1 degree, to 13 degrees Celsius.

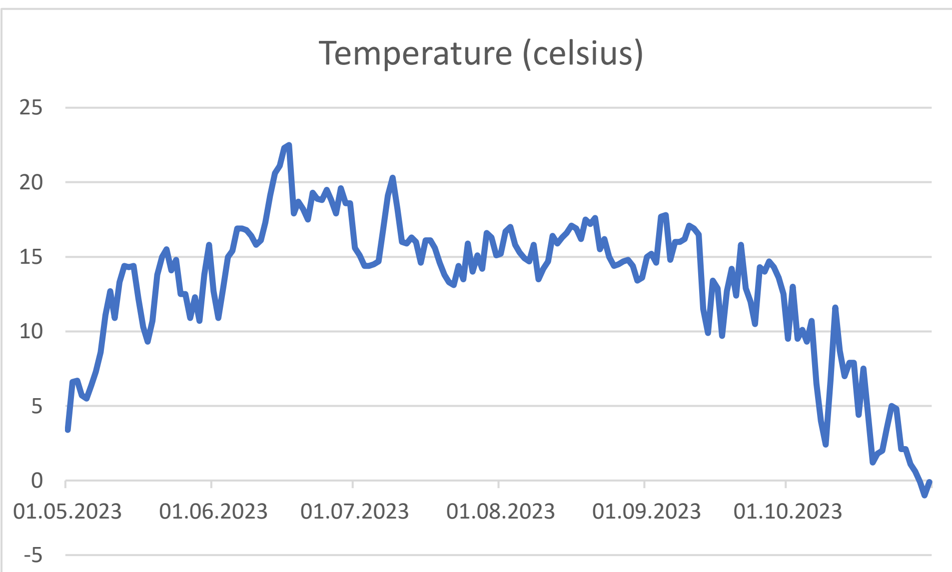


Figure 1: Air temperatures at the BIOKLIM weather station at Søråsjordet, Ås (BIOKLIM 2023)

Precipitation measurements were low in the months of May and June. During May there were three days which measured over 1mm, and double that for June. Between July and October, it showed greater variations and several peak events, less during October. August included the three highest values, the highest reaching 46.0mm.

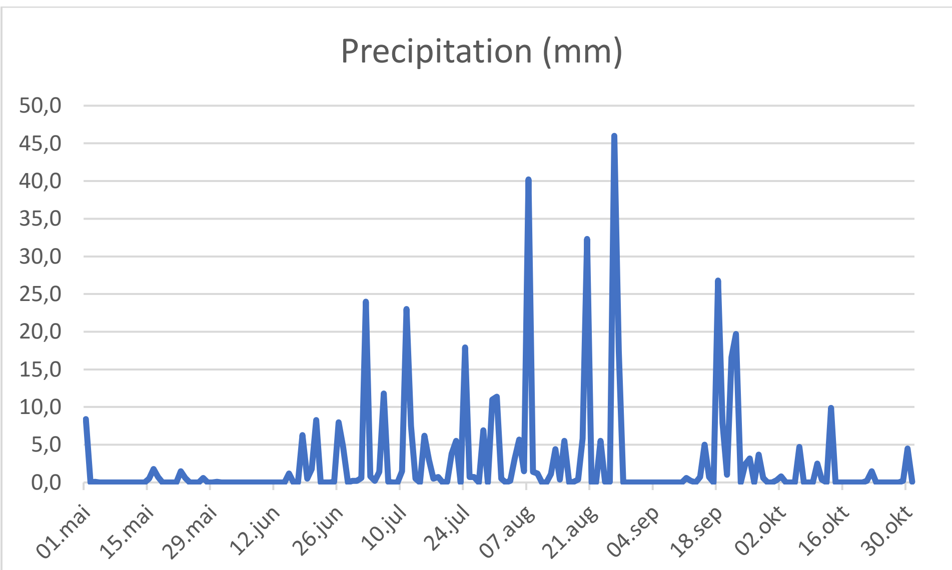


Figure 2: Precipiation amounts measured at the BIOKLIM weather station at Søråsjordet, Ås (BIOKLIM, 2023)

In comparison to the three earlier climate normals, the measurements during the study period showed a significantly higher mean temperature during the months of June and September.

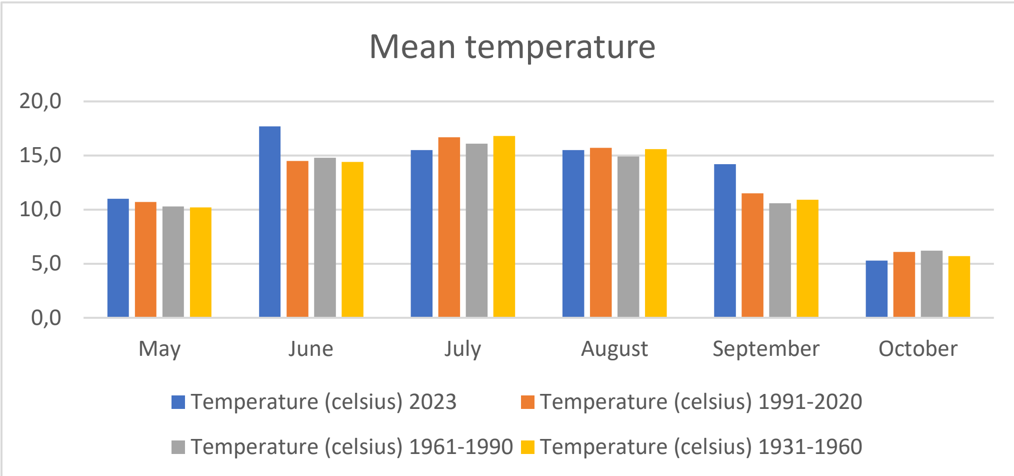


Figure 3: Comparison of mean values of air temperatures from the study period of 2023 and the three earlier climate normals on a monthly basis, from the BIOKLIM weather station at Søråsjordet, Ås (BIOKLIM 2023)

Regarding the precipitation measurements, there are significant differences between the study period and all the historical normals, for all the months except for September which has been stable over all periods. May, June, and October showed half or less than half of the precipitation of earlier periods. July and August showed high amounts compared to the earlier periods.

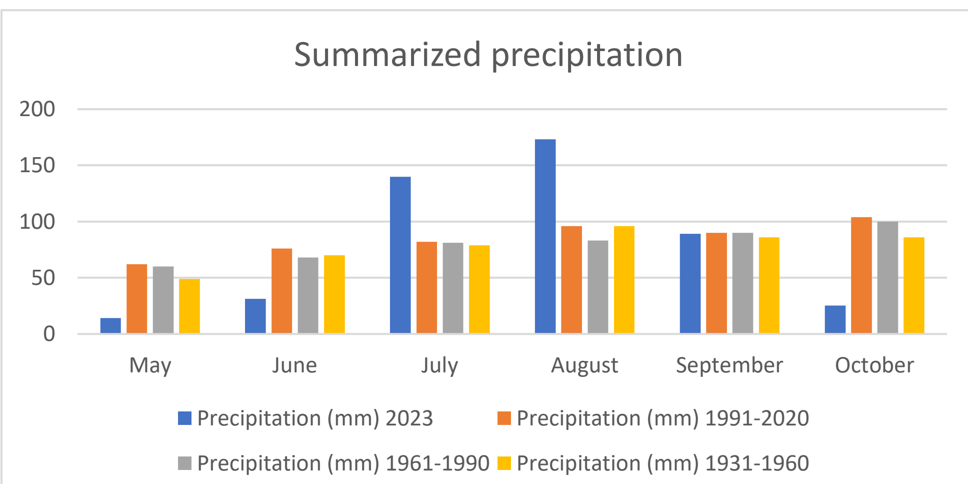


Figure 4: Comparison of summarized amount of precipitation from the study period of 2023 and the three earlier climate normals on a monthly basis, from the BIOKLIM weather station at Søråsjordet, Ås (BIOKLIM 2023)

Secchi depth and euphotic zone depth

The euphotic depth is constantly relative to the depth measured with the Secchi disc; therefore, they will stay relative to each other throughout the dataset. The first two sampling dates gave the same measurement, at 225cm in euphotic zone depth. Then it was nearly a doubling in the depth in the middle of June, reaching a maximum the study period of 400cm. This increase, compared to the initially measured depth, lasted throughout July and past half of August before it was, in the beginning of September, approximately back to the depth that was measured before the increase.

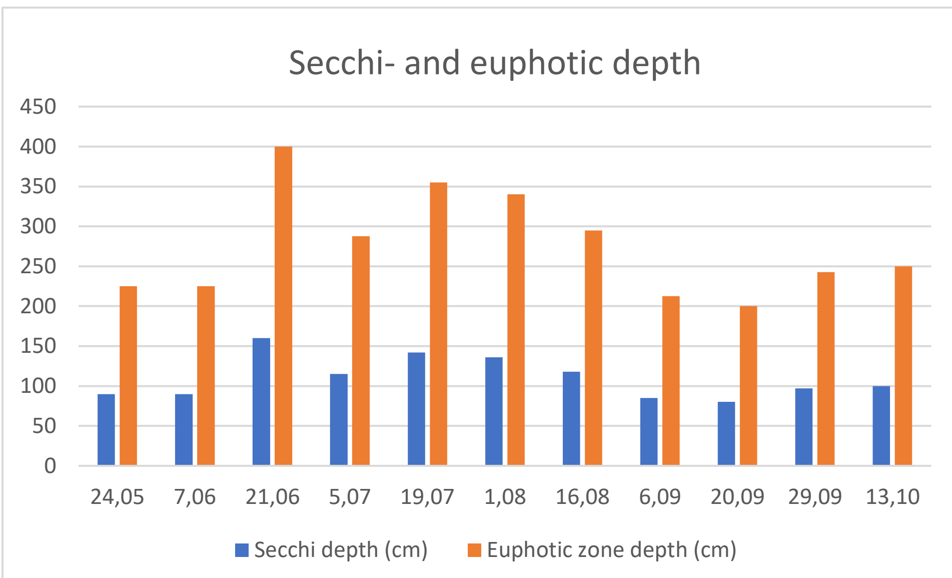
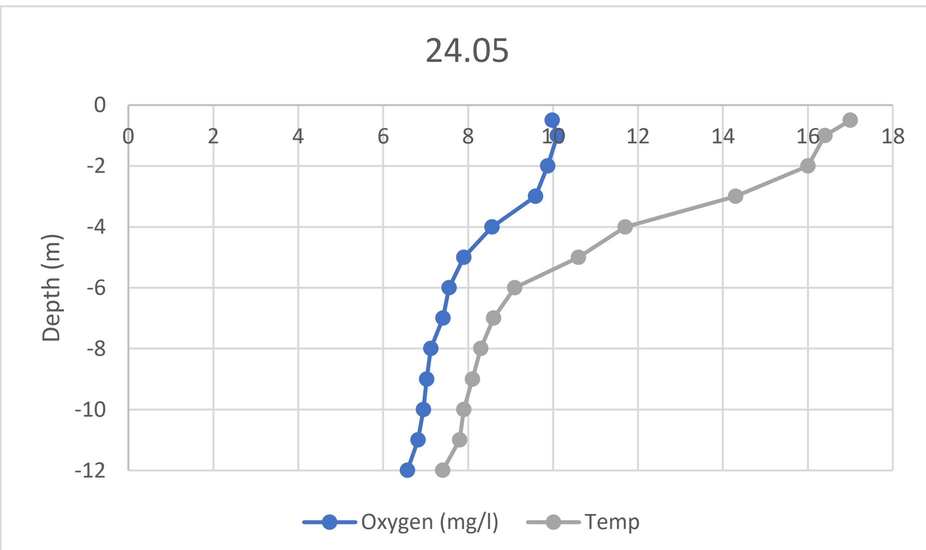
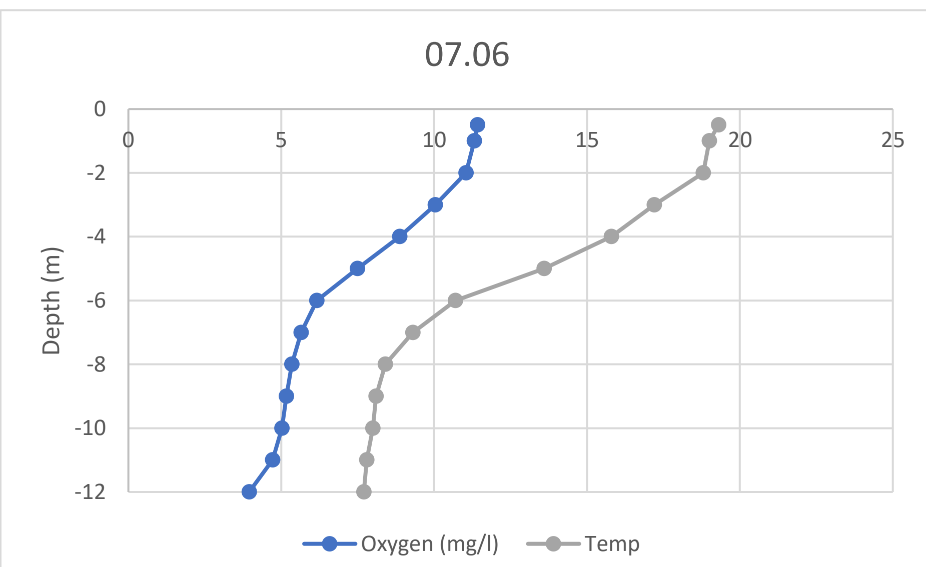


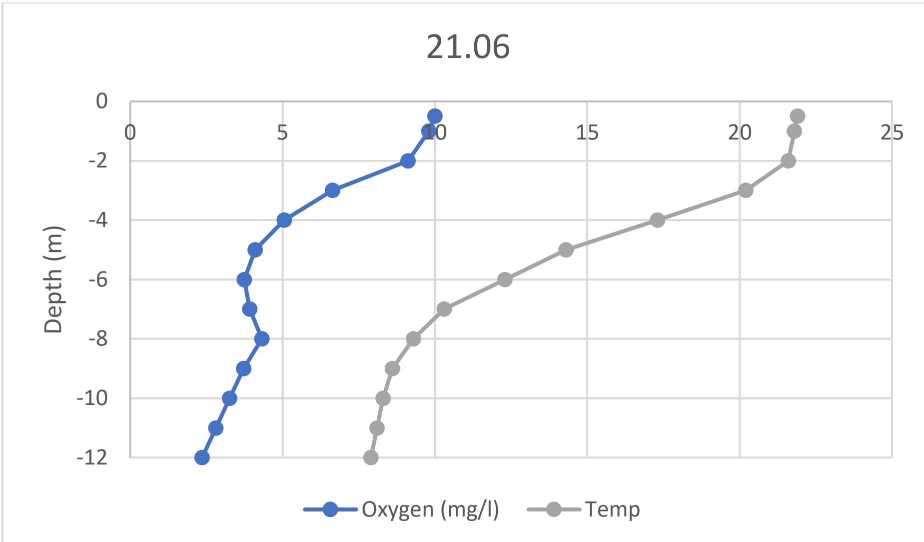
Figure 5: Secchi-depth and euphotic zone calculated from the secchi-depth, measured in-situ.

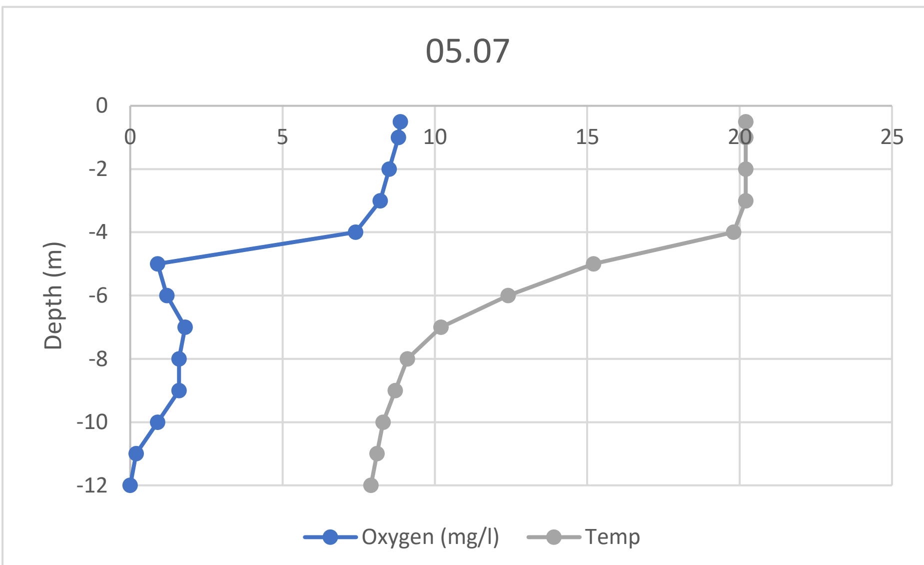
Water temperatures and oxygen concentration in the water column

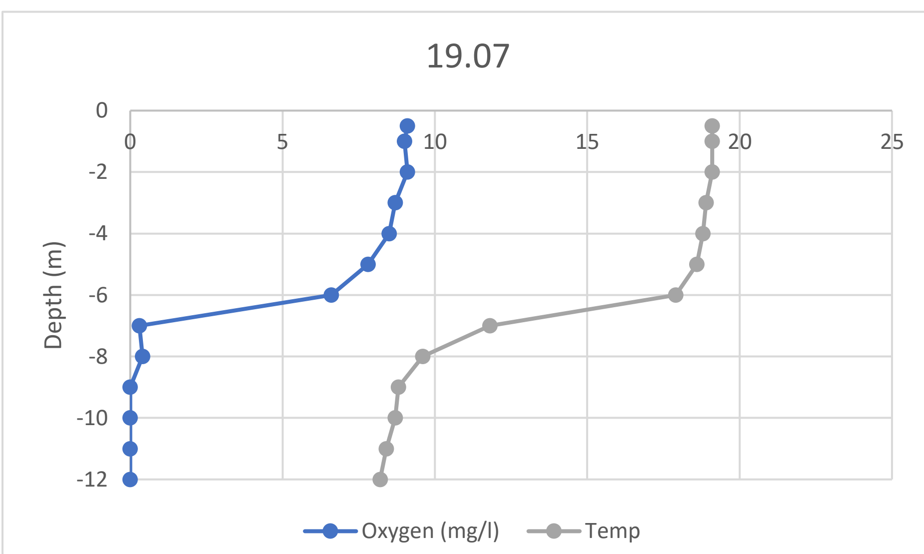
The measurements showed signs of thermal stratification at the very start of the study period, on the 24th of May, with oxygen values slowly decreasing along with increasing depth. Full thermal stratification with a clear thermocline was observed at the start of July. The first occurrence of an anoxic hypolimnion was measured at the beginning of July, at the same time the full stratification was observed, and this lasted throughout the entire rest of the study period. At that sampling date, only the top 4 meters showed oxygen concentrations above 1.8 O_2 mg/l. The thermal stratification did exhibit a loss of stability on the sampling dates of the 16th of August and the 6th of September. The thermocline can be observed moving downwards in the water column, and the initiation of lake mixing is clear at the last sampling date, on the 13th of October. The water temperatures were close to uniformly distributed throughout the water column, the recorded exception being a slightly colder measurement at 12 meters. The oxygen levels were exhibiting signs of the lake mixing, although the anoxia above the sediment lasted the entire period, with oxygen levels at 0.1 mg/l at 12 meters during the last sampling date.

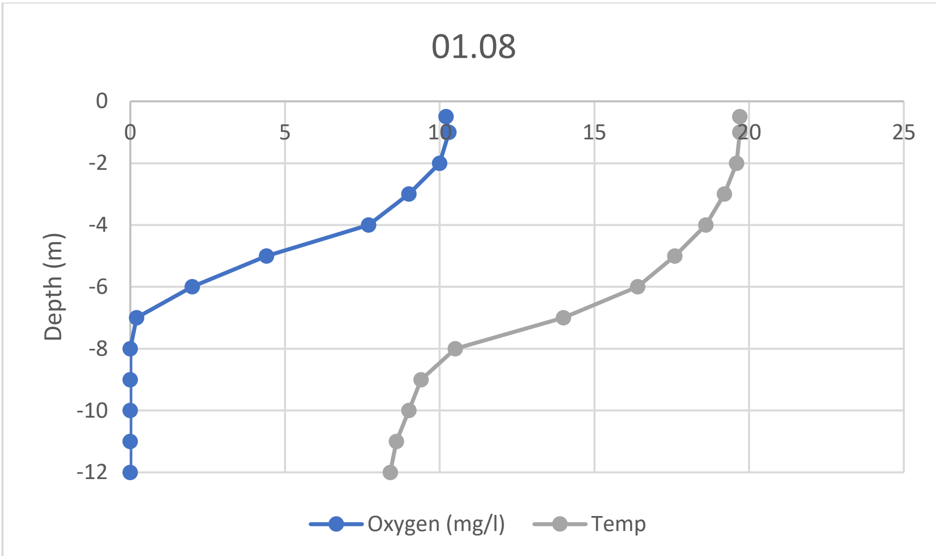




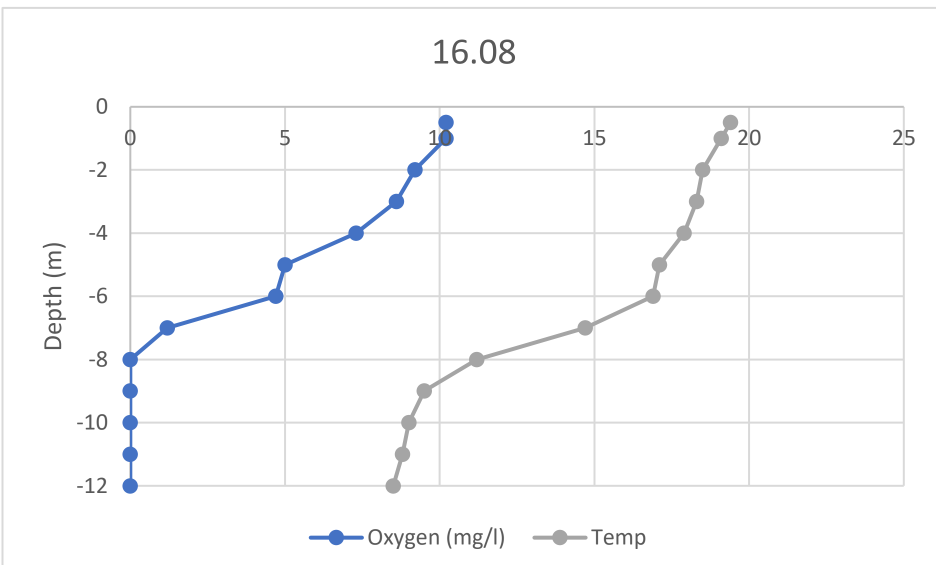

21.06
Depth (m)
0
-2
-4
-6
-8
-10
-12
0
5
10
15
20
25
Oxygen (mg/l)
Temp


05.07
Depth (m)
0
-2
-4
-6
-8
-10
-12
0
5
10
15
20
25
Oxygen (mg/l)
Temp

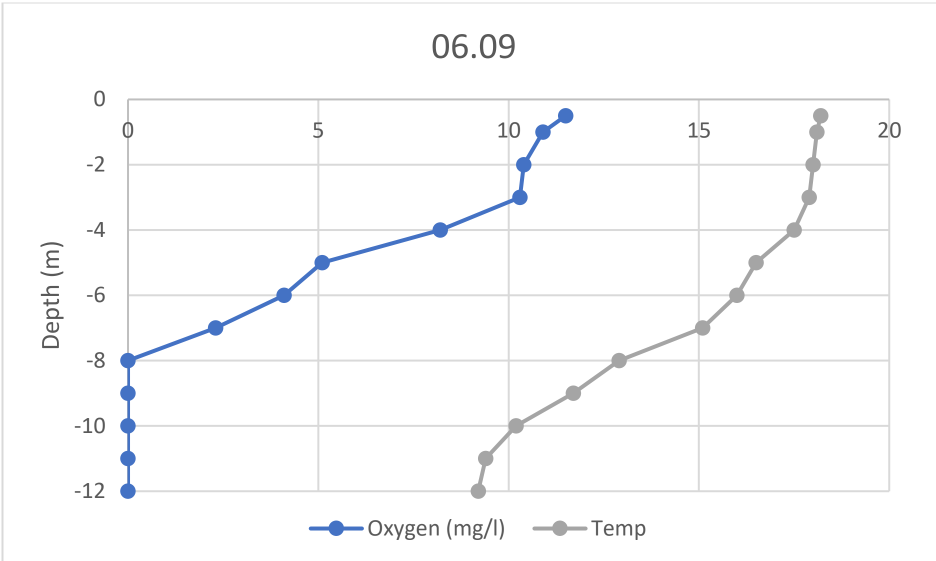

19.07
Depth (m)
0
-2
-4
-6
-8
-10
-12
0
5
10
15
20
25
Oxygen (mg/l)
Temp



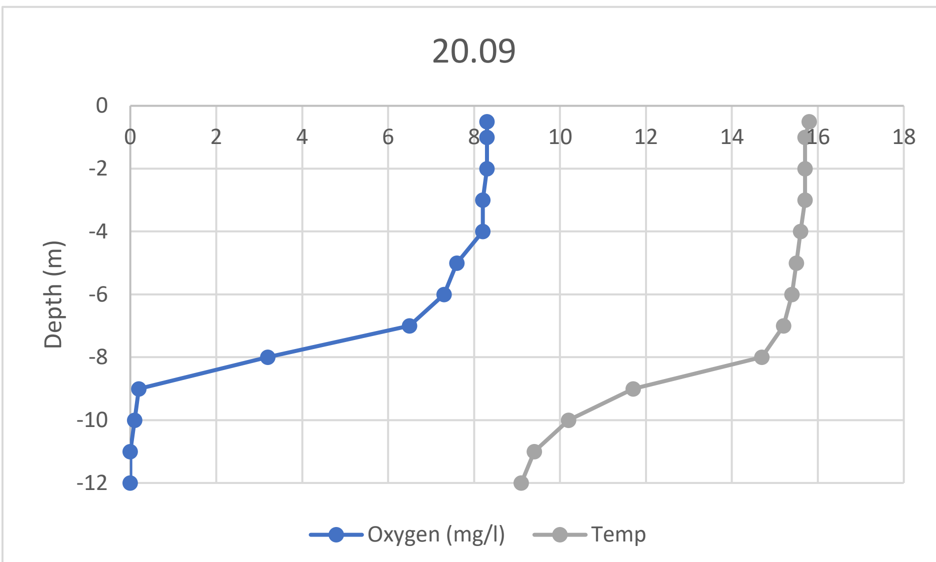
01.08
Depth (m)
0
-2
-4
-6
-8
-10
-12
0
5
10
15
20
25
Oxygen (mg/l)
Temp



16.08
Depth (m)
0
-2
-4
-6
-8
-10
-12
0
5
10
15
20
25
Oxygen (mg/l)
Temp



06.09
0
-2
-4
-6
-8
-10
-12
0
5
10
15
20
Depth (m)
Oxygen (mg/l)
Temp



20.09
0
-2
-4
-6
-8
-10
-12
0
2
4
6
8
10
12
14
16
18
Depth (m)
Oxygen (mg/l)
Temp

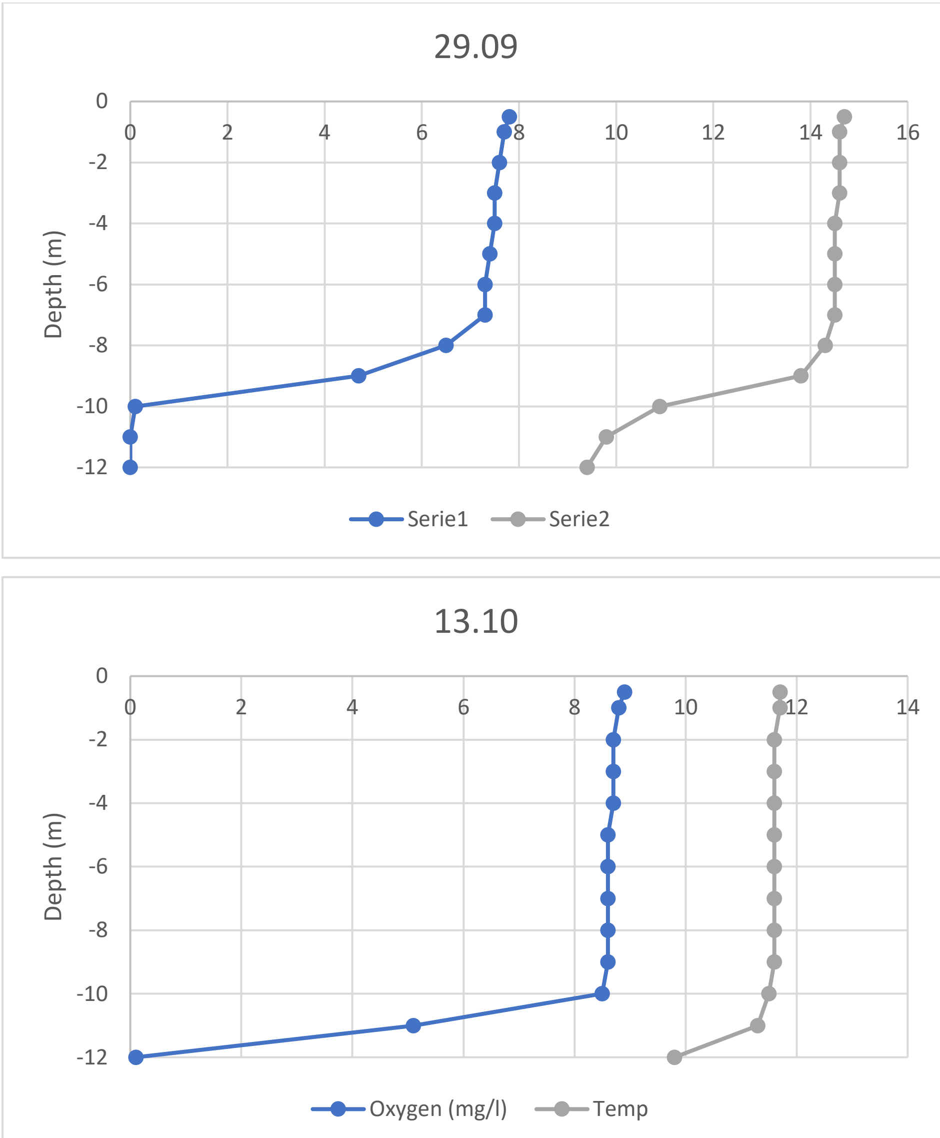


Figure 6: Water temperatures (Celsius) and oxygen concentrations (mg/l) downwards in the water column over the different sampling dates along the study period of late May till middle of October 2023 in Lake Årungen.

Isopleth/contourplots

Data collected in-situ and data from the analysed water samples have been processed and visualized in contourplots through Python.

Temperature and oxygen

It is visible from figure 7, from the first sampling date in May, that lake mixing was no longer occurring this season. In the figure the increase in water temperature in the upper layers is prominent, with the highest water temperature measured was 21.9 degrees Celsius at 0.5 meters depth, on the 21st of June. From this sampling date and until the study period ended, the thermocline can be observed as it moved continuously further down in the water column, ending in the initiation of lake circulation during the last sampling on the 13th of October, visible to the right in the figure.

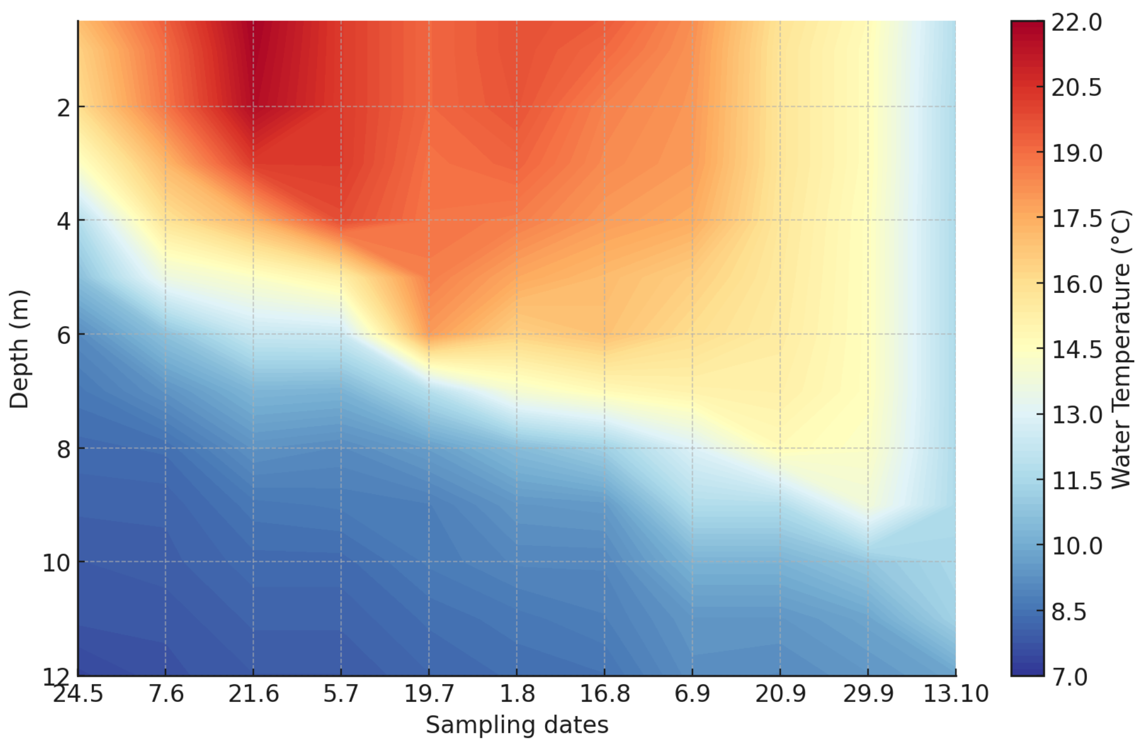


Figure 7: Isopleth diagram showing water temperature (Celsius) across time and depth in Lake Årungen from late May till middle of October 2023

The figure shows the oxygen saturation levels (%O_2) changing rapidly in the top layer during the first half of June, before it shows that the onset of anoxic conditions was simultaneous as the thermal stratification at the start of July, from which point the oxygen levels stay relatively stable above and below the thermocline as it moves downwards (the only rapid change is the at the thermocline..). The low oxygen values appearing in July lasted throughout the rest of the study period, with anoxia still visible on the 13th of October, although the last sampling date shows a redistribution of oxygen downwards the water column affecting all depths except 11- and 12meters depth. The highest oxygen saturation levels were measured at 0.5 meters depth on the 7th of June and the 6th of September, they showed 124% and 122% respectively.

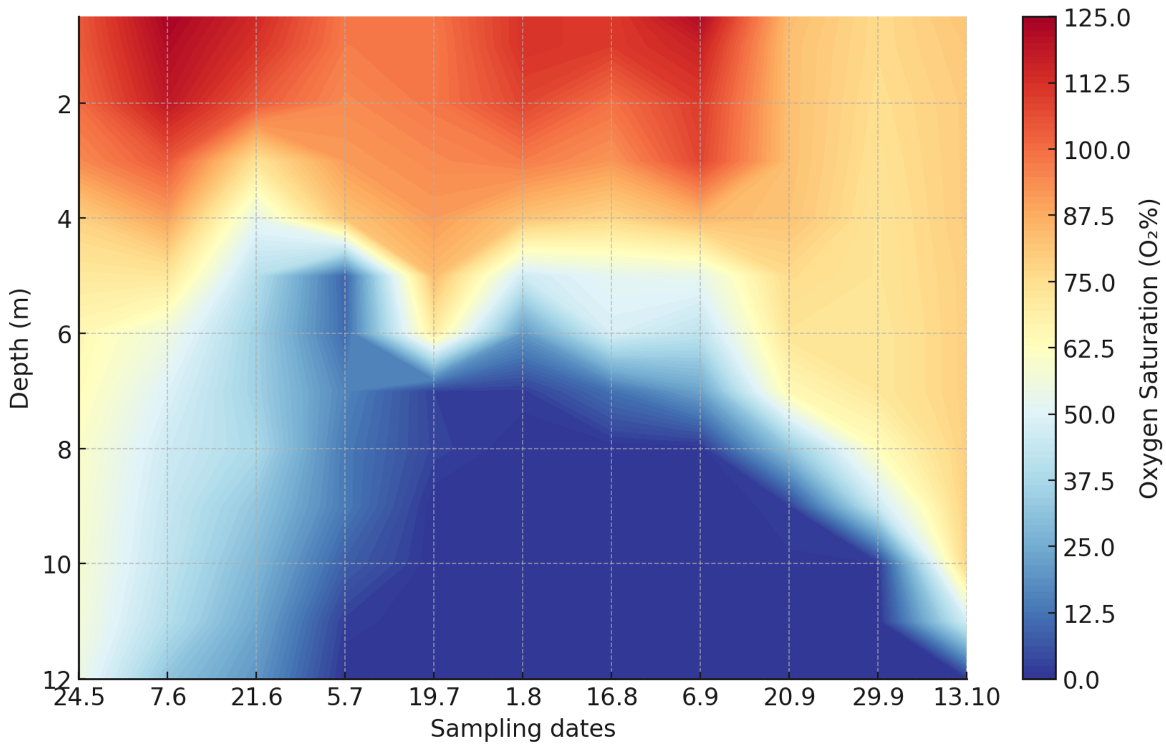


Figure 8: Isopleth diagram showing oxygen saturation (%) across time and depth in Lake Årungen from late May till middle of October 2023

Nutrients

TP showed two high measurements on the first sampling date, 24th of May, at 0.5 and 3 meters, with respectively 199 and 142 µg/l. From the start of June until mid-August, there were little variations in TP, except for a slight increase downwards in the lake, and one anomaly. The abnormal value was measured at 8 meters depth, on the 19th of July, which showed 119 µg/l. From August and the rest of the study period, the samples showed an increase of TP in hypolimnion. Both days in September showed significant increase at both 11 and 12 meters.

PO_4 measurements showed no phosphate present in approximately every sampling over the entire period (Appendix, Table A1).

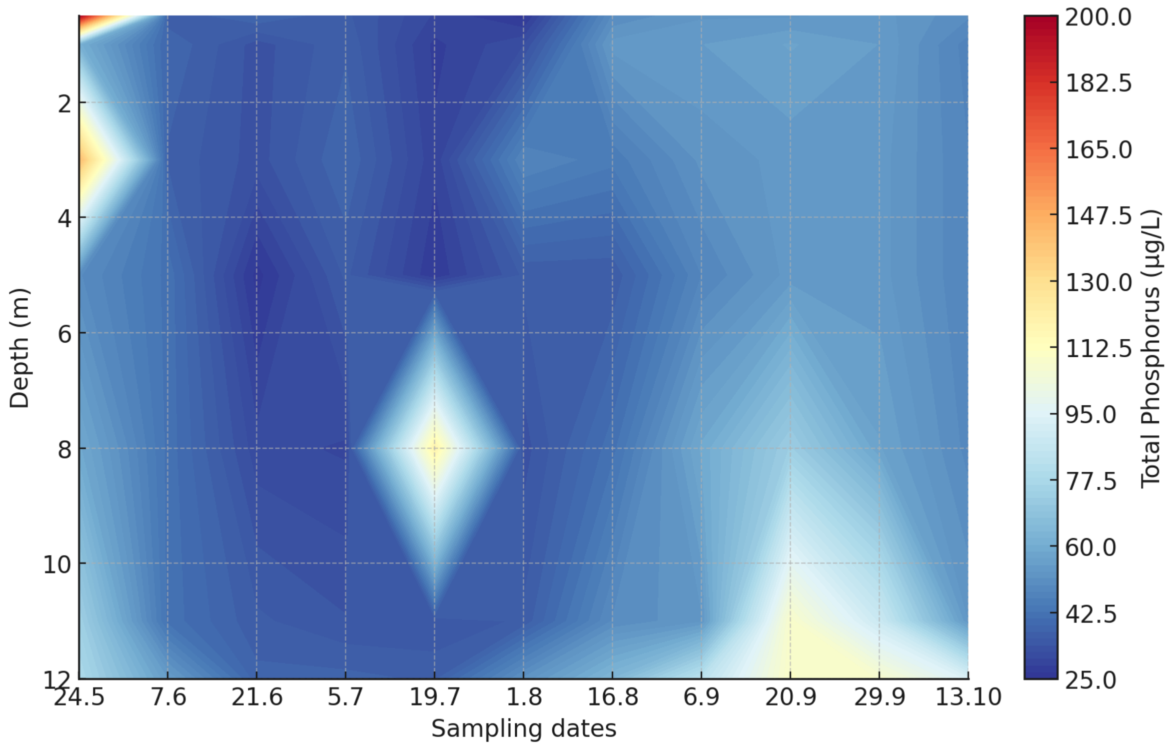


Figure 9: Isopleth diagram showing TP - total phophorus concentration (µg/l) across time and depth in Lake Årungen from late May till middle of October 2023

TN levels were measured the highest for all depths in the start of the study period, with a peak of 4.4mg/l at 3 meters depth, 24th of May. In general, the nitrate levels were elevated at 8 meters depth throughout most of the study period. Most of the sampling dates showed decreased values in the top layers, compared to the bottom layers, until the middle of August when this trend shifted and decreased values could be seen at the bottom instead. The lowest value measured was 2.1 mg/l on the 29th of September. On the last sampling date, the levels have spread evenly throughout the water column, except for a reduced concentration at 1 meter depth.

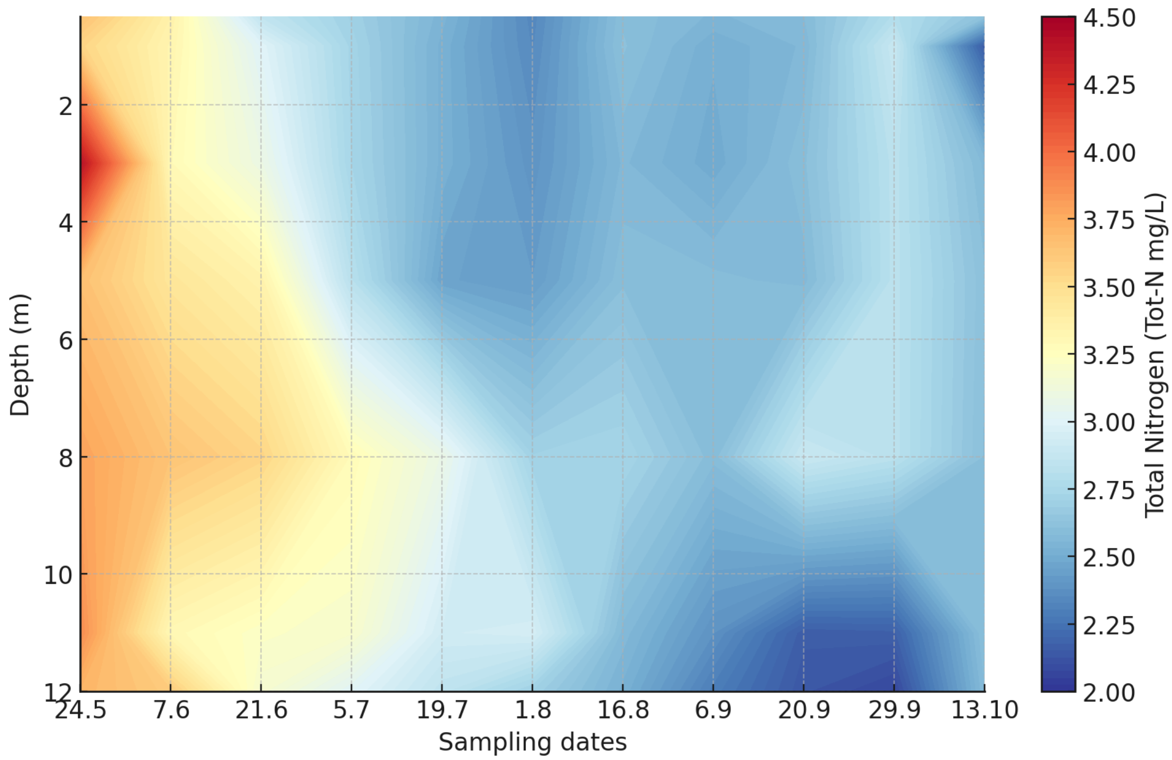


Figure 10: Isopleth diagram showing TN - total nitrogen concentration (mg/l) across time and depth in Lake Årungen from late May till middle of October 2023

Primarily following the same trends as Tot-N, the highest nitrate levels was measured at 8 meters depth for most of sampling dates. Peak nitrate concentration was measured to 3.1 mg/l at 8 meters depth the first sampling date. The concentrations were measured the highest at the first sampling date, after which they generally decreased. There was observed high concentrations in the lower depths until approximately the middle of August when, instead of accumulation in the bottom layers, the values from especially the two lowest depths started to decrease at a faster rate than the upper layers in the water column. In contradiction to the Tot-N levels, the nitrate values spreading around the time of lake mixing did not include the layer above the sediment, which measured the lowest value at 0.7 mg/l.

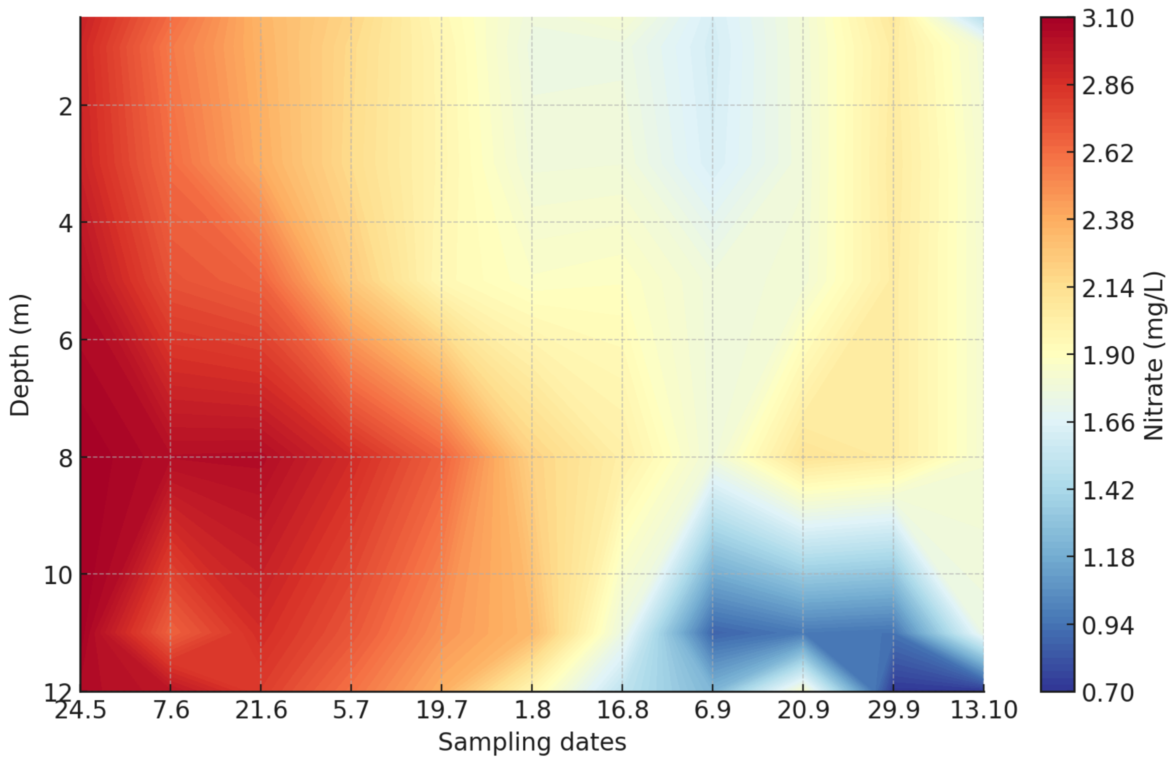


Figure 11: Isopleth diagram showing nitrate concentration (mg/l) across time and depth in Lake Årungen from late May till middle of October 2023

The first sampling date showed increased value at 12 meters depth and slightly increased values in the top layer. In general, the values for ammonium were low in samples from June and July, relative to the rest of the dataset, all samples in this period measuring below 53 µ/l. From the beginning of August until the end of the study period, the ammonium concentrations are accumulated at the bottom layers of the lake, measuring no values below 92 µgrams/l at 12 meters depth. The highest concentration was measured at 12 meters on the last sampling date, 13th of October, and measured 146m µgrams/l.

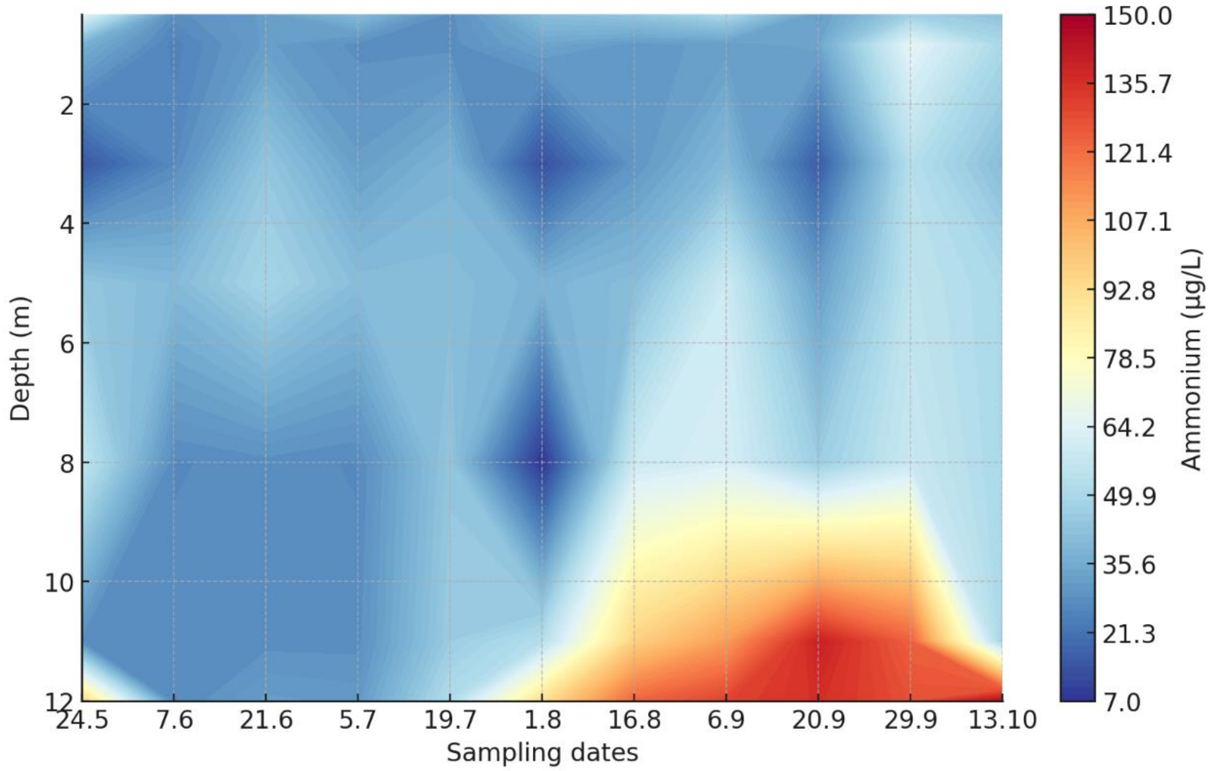


Figure 12: Isopleth diagram showing ammonium concentration (µg/l) across time and depth in Lake Årungen from late May till middle of October 2023

pH og chlorophyll-*a*

Measurements of pH showed a general trend of higher values in epilimnion than in hypolimnion for the whole study period. The highest value was measured on the 7th of June, reaching a pH of 9.4 at 1 meter's depth. The lowest value recorded was at 12 meters on the 21st of June, measuring a pH of 6.7. Except for an increase at 11 meters on the 7th of June, the measurements on 8, 11 and 12 meters showed stable, continuous levels of pH throughout the study period.

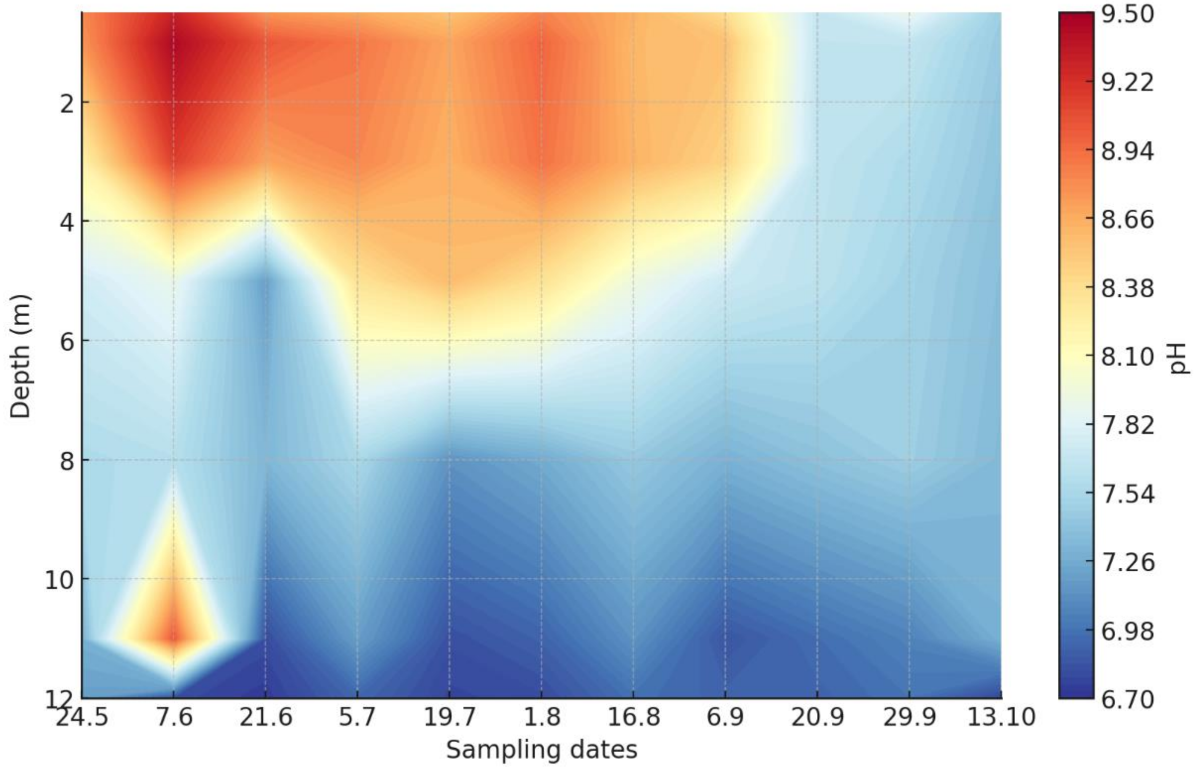


Figure 13: Isopleth diagram showing pH across time and depth in Lake Årungen from late May till middle of October 2023

Chlorophyll-*a* values showed great variation along the study period. At the beginning of the study period, the first sampling measured the peak of Chlorophyll-*a* levels, reaching 115 µgrams/l at 3 meters depth. Generally, measurements throughout the entire study period shows low levels of Chlorophyll-*a* at the bottom layers. For 12 meters depth, close to the lake sediment, measurements only showed existence of Chl-*a* at the last sampling date when lake mixing was initiated. 0.5, 1 and 3 meters were the depths which showed any level on all sampling dates.

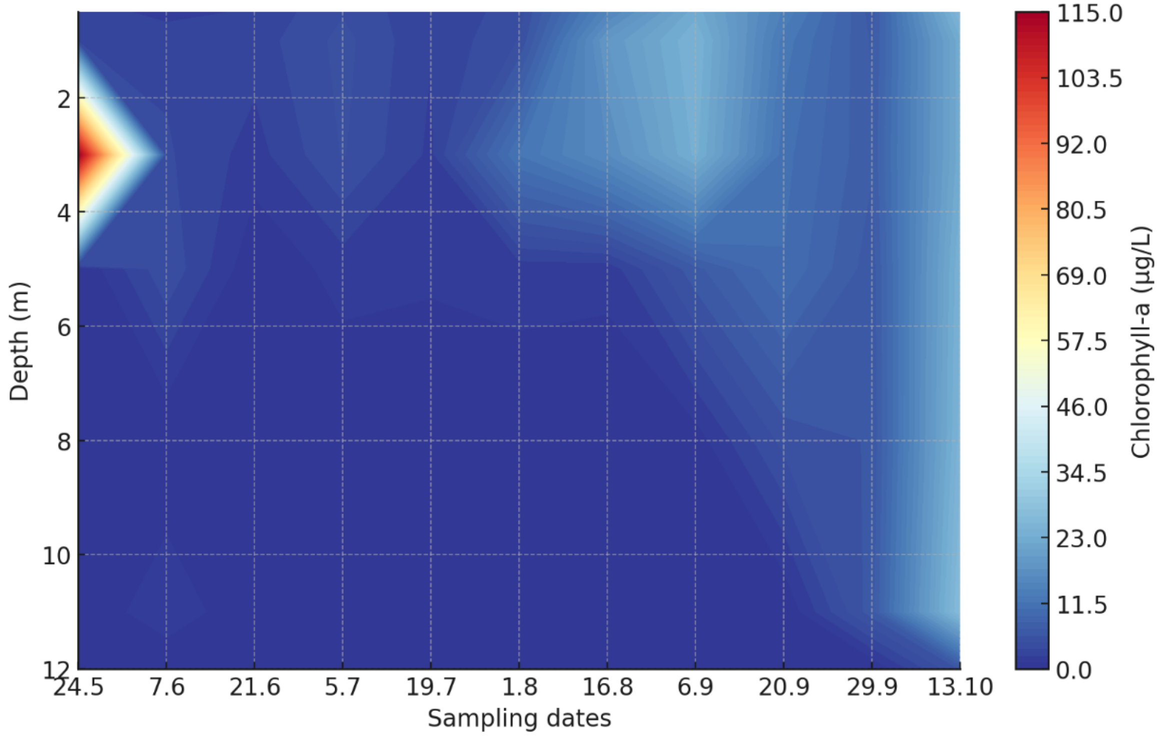


Figure 14: Isopleth diagram showing chlorophyll-a concentration (µg/l) across time and depth in Lake Årungen from late May till middle of October 2023

d

Nitrate levels above the sediment and decomposition rate

The rate of nitrate decomposition was calculated by a simple regression analysis, which included the levels of nitrate at 12 meters for the period of thermal stratification and anoxic conditions at 12 meters depth. This is done to most accurately present the consumption of nitrate caused by microbial respiration and to limit the effects of external nitrate input to this depth.

Nitrate concentration was at 2.6 mg/l at the onset of thermal stratification and anoxic conditions above the sediment. It slowly decreased during the rest of the period, except for an elevated level on the 20th of September. On the next two sample dates, the last two, the nitrate levels were at the lowest, 0.71 mg/l and 0.70 mg/l.

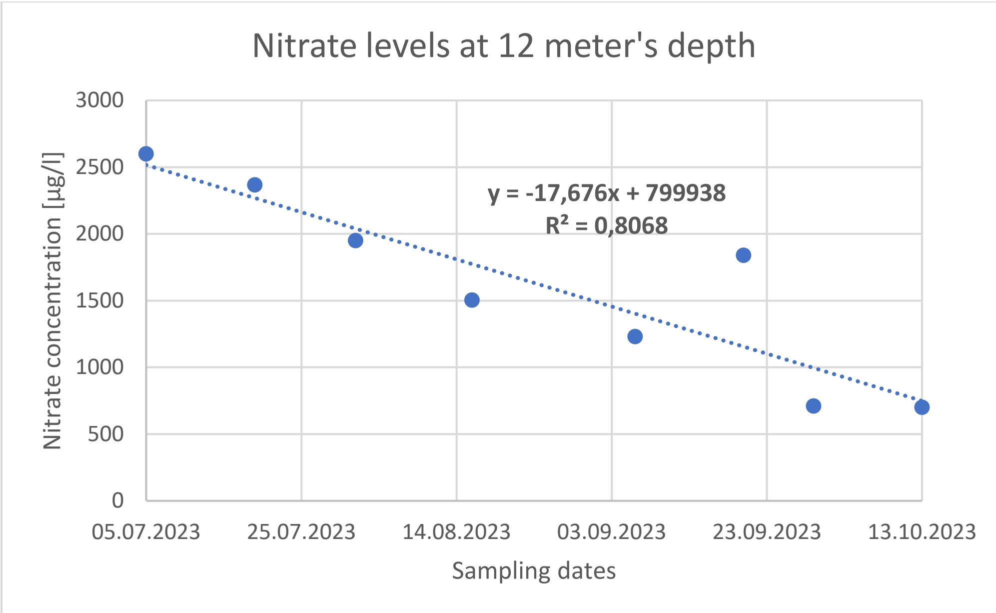


Figure 15: Nitrate values [µg/l] above the sediment (12 meters) during the period of thermal stratification and anoxia in hypolimnion with an executed linear regression showing the decreasing trend.

Discussion

Weather conditions affecting thermal stratification formation.

Increased air temperatures, and an earlier seasonal increase, will help initiate the onset of thermal stratification, as well as contributing to the stability of the stratification. The effects of air temperatures on thermal stratification in lakes like Lake Årungen has been well established in scientific literature. Climate change, global warming and subsequent increase in air temperatures and solar radiation contribute further to an earlier and prolonged period of thermal stratification and anoxia. A study from (Magee & Wu, 2017) showed increased temperatures in epilimnion and decreased temperatures in hypolimnion, therefore increased stratification stability and duration, from three lakes when there was an increase in air temperature.

During my study period of 2023, the mean air temperature of June was 17.7 compared to Frostad's (2018) 14.5 degrees Celsius. Both years showed a full onset of thermal stratification around the beginning of July. Although more prominent signs of stratification are visible from earlier on in the year of 2023. From 3 meters down to 8 meters depth, the temperature spans from respectively 20.2 to 9.3 degrees Celsius. At the same time in 2017, the temperature span from 16.4 to 9.6 degrees Celsius. Although it is mostly the upper layers that show the largest difference, the stability of the stratification could seem strengthened during 2023 compared to 2017. Earlier onset and increased duration of the thermal stratification in turn increases time without addition and distribution of oxygen, which increases chances of longer periods of anoxia in the hypolimnion. In such scenarios, nitrate levels would have to be higher than normal to sufficiently suppress reducing conditions in the absence of oxygen.

(Magee & Wu, 2017) also explained that wind speed could potentially be of extensive importance when studying stratification on larger surface area lakes, and it is known that Årungen's north-south orientation also makes it prone to the impact of wind mixing. Perturbation scenarios in their study indicate that the degree of wind speed and subsequent mixing could be the primary driver in determining how the hypolimnion temperature will fluctuate. This is however most important for more shallow lakes.

Stratification and distribution of oxygen affecting levels of nitrate and release of phosphorus from the sediments.

The data from this study was compared to Frostad's (2018) values from 2017, and data from two earlier years, 2013 and 2009. The nitrate levels above the sediment in Lake Årungen during my study period were 2.6 mg/l at the start of anoxic conditions in hypolimnion, which was 5^{th} of July. The nitrate concentration decreased and hit the threshold level on 29^{th} of September, though a significant phosphorus loading did not occur. Therefore, it appears as though nitrate concentrations have been sufficient in keeping a high enough redox potential to have buffered any possible, substantial internal phosphorus loading event.

During Frostad's (2018) research, anoxia also occurred at the start of July, and the concentration of nitrate above the sediment was 3.1 mg/l. Although it is not considered significant phosphorus loading, there were signs of leakage of phosphate above the sediment when nitrate levels approached 1.5 mg/l in the middle of September, reaching a maximum of 47.8 µg/l in phosphate concentrations in the beginning of October.

In 2013, the initial nitrate values measured 2.5mg/l after spring turnover and were in a steady decline during the whole time of stratification. The nitrate concentration approached 1.5mg/l approximately one and a half month earlier than the case was in 2017. The nitrate concentration dropped below the 1.0 mg/l threshold in the beginning of September, and could not buffer the internal loading sufficiently, causing phosphate to peak at over 400 µg/l later that month.

For 2009, the nitrate concentration after the spring turnover was at 1.7 mg/l and measured around 1.2mg/l when stratification and an anoxic hypolimnion occurred. Therefore, the nitrate levels went below the threshold early in July that year, earlier than the later years, and peaked at 286.7 µg/l after a delayed phosphorus loading event in September. For the year of 2013 and 2009, there were approximately depletion of all available nitrate above the sediment.

For the earlier years there can be observed lower initial nitrate concentrations, resulting in significant internal phosphorus loading. To reduce, ultimately prevent, major internal phosphorus loading events, nitrate concentrations available in the lake at the start of stratification periods should not be substantially lower than the values measured in 2023, despite the fact that there was no internal loading that year. Therefore, measures to reduce external loading of nitrogen from the agricultural lands surrounding the lake should be closely and continuously monitored as a higher reduction also provides higher potential for internal phosphorus loading.

A threshold level for nitrate concentration in the hypolimnion initiating leaking of phosphate have been suggested, based on several earlier studies (Andersen 1982; Jensen & Andersen 1992; Tirén & Pettersson 1985; Wetzel 2001) and further supported in a study by Frostad (2018). This suggestion is 1 NO3 mg/l, although the concentration on nitrate in hypolimnion required to initiate internal phosphorus loading from the lake sediment is proven to vary from 0.5 mg/l to 1.0 mg/l, therefore it is an estimated upper threshold level.

The nitrate threshold is impacted by several biogeochemical and environmental factors. There could be potential leakage of phosphate from the sediments prior to hitting the nitrate threshold, or in scenarios that does not result in nitrate levels below the threshold, like the situation in 2017 with elevated phosphate levels as nitrate concentration reached approximately 1.5 mg/l. The threshold levels could be affected by the composition of the sediment, in particular the content and reactivity of iron oxides which efficiently binds the phosphorus in the lake. Lower iron content in the sediments could mean smaller reductions could lead to a significant phosphate release. pH could influence the redox conditions (Quesheng & Kirk, 2018). The composition of active microbial organisms plays a crucial role in the efficiency of nitrate reduction processes. Different microbial compositions' impact on both phosphate leakage and denitrification could however be more difficult to assess as it would have to include collection of the different microorganisms in the aquatic community to study these differences. Higher organic matter content in the lake can enhance the microbial respiration process and possibly lowering the nitrate threshold due to increased demand for electron acceptors (Albina et al, 2019).

Although a small portion, partial oxygenation of the deeper water layers could oxidize the reduced iron and therefore the phosphate bound there could potentially be captured or recaptured into the sediments. Since the oblong Lake Årungen is located in a north-south direction, vertical mixing of the water is thought to have greater impact than lakes with different orientations. This may possibly have contributed to lessen the stability and duration of thermal stratification in the lake, although the oxygen concentrations do not show any signs of oxygenation penetrating the thermocline.

A decomposition rate of nitrate was calculated to 0.018 mg/l for my period of study. In a hypothetical scenario that measures were taken to reduce the external input of nitrate by 50%, the nitrate concentration at the initiation of anoxic conditions above the sediment would be 1.3 mg/l. This would mean that all the nitrate present above the sediment would get consumed and emptied around the middle of September, 15th of September if calculating using these numbers exactly. In this scenario, substantial quantities of phosphate may escape from the sediment prior to the fall turnover, occurring around mid-October. The resulting elevated phosphate concentrations under such conditions have the potential to trigger the onset of algal blooms in the subsequent growth season, with an increased degree of eutrophication happening and possibly including potentially dangerous cyanobacteria, which is a phenomenon observed in previous instances.

Conclusion

Earlier rise in air temperatures could mean a continuously earlier stratification formation, leading to prolonged anoxia in the hypolimnion. Finding practical and accurate methods for conducting studies on the effect from wind mixing could be of significant contribution to understanding thermal stratification stability on lakes like Lake Årungen. It is crucial to find a way to look at all climatic factors together to understand how onset and duration of thermal stratification is going to impact our lakes in the future. Threshold levels for nitrate concentration, crucial in preventing internal phosphorus loading, are influenced by various biogeochemical and environmental factors, including sediment composition, pH, and microbial activity. Effective management strategies should focus on reducing external nitrate inputs and maintaining higher nitrate levels to mitigate the impacts of prolonged thermal stratification and prevent eutrophication in Lake Årungen.

References

Andersen, J. M. (1982). Effect of nitrate concentration in lake water on phosphate release from the sediment. Water Research, 16 (7): 1119-1126

Albina, P., et al. "Influence of Hydrogen Electron Donor, Alkaline PH, and High Nitrate Concentrations on Microbial Denitrification: A Review." *International Journal of Molecular Sciences*, vol. 20, no. 20, 18 Oct. 2019, p. 5163, https://doi.org/10.3390/ijms20205163.

Chapman, D.V., Unesco, World Health Organization and United Nations Environment Programme (1992). Water quality assessments. Published On Behalf Of UNESCO, WHO, UNEP [By] Chapman & Hall.

Frostad, P. (2018). Coupling between nitrate input and phosphorus retention in lake sediments – A case study from Lake Årungen. [online] Available at: https://nmbu.brage.unit.no/nmbu-xmlui/bitstream/handle/11250/2565314/PiaFrostad_Masteroppgave2018_2.pdf?sequence=1&isAllowed=y.

Hongve, D., Skogheim, O.K., Hindar, A. and Abrahamsen, H. (1980). Effects of heavy metals in combination with NTA, humic acid, and suspended sediment on natural phytoplankton photosynthesis. Bulletin of Environmental Contamination and Toxicology, 25(1), pp.594–600. doi:https: //doi.org/10.1007/bf01985577. (

Jensen, H. S., & Andersen, F. O. (1992). Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of four shallow, eutrophic lakes. *Limnology and Oceanography*, *37*(3), 577–589. https://doi.org/10.4319/lo.1992.37.3.0577

Magee, M. R., & Wu, C. H. (2017). Response of water temperatures and stratification to changing climate in three lakes with different morphometry. *Hydrology and Earth System Sciences*, *21*(12), 6253–6274. https://doi.org/10.5194/hess-21-6253-2017

Qusheng, J. & Kirk, M. F. "PH as a Primary Control in Environmental Microbiology: 1. Thermodynamic Perspective." *Frontiers in Environmental Science*, vol. 6, 1 May 2018, https://doi.org/10.3389/fenvs.2018.00021.

Romarheim, A.T. and Riise, G. (2009). Development of cyanobacteria in Årungen. Norsk vannforening, [online] 04, pp.384–393. Available at: https://vannforeningen.no/wp-content/uploads/2015/06/2009_794728.pdf.

Sawyer, C.N. (1966). Basic Concepts of Eutrophication. Water Pollution Control Federation, [online] 38(5), pp.737–744. Available at: https://www.jstor.org/stable/25035549.

Smith, V.H. (2003). Eutrophication of freshwater and coastal marine ecosystems a global problem. Environmental Science and Pollution Research, 10(2), pp.126–139. doi: https://doi.org/10.1065/espr2002.12.142

Staalstrøm, A., Mats Walday, Vogelsang, C., Frigstad, H., Borgersen, G., Albretsen, J. and Lars-Johan Naustvoll (2021). Utredning av behovet for å redusere tilførslene av nitrogen til Ytre Oslofjord. 214.

Tirén, T. & Pettersson, K. (1985). The influence of nitrate on the phosphorus flux to and from oxygen depleted lake sediments. Hydrobiologia, 120 (3): 207-223

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H. and Tilman, D.G. (1997). HUMAN ALTERATION OF THE GLOBAL NITROGEN CYCLE: SOURCES AND CONSEQUENCES. Ecological Applications, [online] 7(3), pp.737–750. doi: https://doi.org/10.1890/1051-0761

Wetzel, R.G. (2001). Limnology : Lake and River Ecosystems. Burlington: Elsevier Science.

WQData LIVE. Available at: https://www.wqdatalive.com/public/v3/1247?dashboardId=19&panels%5B0%5D%5Bid%5D=164&panels%5B0%5D%5Bparams%5D=31647%2C31648%2C31659

Appendix

Table A1: Complete dataset

Sample	Depth (m)	Date	Water temp (C)	O2 conc.(mg/l)	O2 saturation(%)	TP(µg/l)	PO4(µg/l)	TN(mg/l)	NO3(mg/l)	NH4(µg/l)	pH	Chlorophyll-a (µg/l)	Absorbance
1	0,5	24.05.2023	17	9,98	103,8	199	0	3,65	2,931	65	8,81	3,004495965	0,129
2	1	24.05.2023	16,4	10,1	103,2	61	3	3,55	2,902	37	8,758	2,669135939	0,131
3	3	24.05.2023	14,3	9,59	94,1	142	0	4,40	2,92	15	8,211	114,7541532	0,136
4	5	24.05.2023	10,6	7,9	71,4	50	0	3,66	3,02	44	7,744	0	0,147
5	8	24.05.2023	8,3	7,12	60,4	59	0	3,79	3,101	56	7,563	0,088513056	0,166
6	11	24.05.2023	7,8	6,82	57,1	74	0	3,87	3,093	28	7,281	0	0,178
7	12	24.05.2023	7,4	6,57	54,4	78	0	3,71	3,04	96	7,192	0	0,186
8	Outlet	24.05.2023				75	0	3,67	2,746	34			
9	0,5	07.06.2023	19,3	11,42	124	36	0	3,36	2,624	28	9,3	1,849977845	0,116
10	1	07.06.2023	19	11,31	121,89	39	0	3,33	2,572	25	9,445	3,159531255	0,034
11	3	07.06.2023	17,2	10,04	104,4	37	0	3,29	2,624	27	9,15	3,657623358	0,036
12	5	07.06.2023	13,6	7,49	72	42	0	3,45	2,723	40	7,9	4,426752334	0,068
13	8	07.06.2023	8,4	5,35	45,7	42	0	3,64	3,03	27	7,6	0	0,037
14	11	07.06.2023	7,8	4,72	39,7	42	0	3,30	2,66	28	9,034	2,124313341	0,062
15	12	07.06.2023	7,7	3,95	31,3	55	0	3,60	2,986	27	6,8	0	
16	Outlet	07.06.2023				47	0	3,32	2,701	41			
17	0,5	21.06.2023	21,9	10	114	39	0	2,85	2,343	32	8,768	2,498707074	0,075
18	1	21.06.2023	21,8	9,8	111,7	33	0	3,00	2,353	32	9,04	2,870901725	0,079
19	3	21.06.2023	20,2	6,64	73,3	33	0	3,09	2,376	44	8,701	1,801048267	0,081
20	5	21.06.2023	14,3	4,1	40	26	0	3,35	2,658	49	7,188	0,122598829	0,105
21	8	21.06.2023	9,3	4,32	37,7	31	0	3,55	3,038	28	7,325	0	0,132
22	11	21.06.2023	8,1	2,81	23,8	36	0	3,22	2,876	28	6,802	0	0,122
23	12	21.06.2023	7,9	2,36	19,9	38	0	3,17	2,804	32	6,737	0	0,122
24	Outlet	21.06.2023				48	0	2,93	2,248	61			
25	0,5	05.07.2023	20,2	8,86	97,6	36	0	2,70	2,188	40	8,681	4,550450704	0,123
26	1	05.07.2023	20,2	8,8	97,2	37	0	2,72	2,165	28	8,896	5,034248774	0,082
27	3	05.07.2023	20,2	8,2	91	39	0	2,73	2,153	32	8,821	4,751666719	0,075
28	5	05.07.2023	15,2	0,9	9,3	36	0	2,81	2,247	41	8,348	1,660856781	0,104
29	8	05.07.2023	9,1	1,6	13,6	30	0	3,28	2,882	27	7,542	0	0,107
30	11	05.07.2023	8,1	0,2	2	34	0	3,19	2,708	28	7,186	0	0,116
31	12	05.07.2023	7,9	0	0	38	0	3,01	2,599	31	6,92	0	0,123
32	Outlet	05.07.2023				42	8	2,67	2,013	35			
33	0,5	19.07.2023	19,1	9,1	98,3	30	0	2,54	1,949	28	8,545	2,412942871	0,075
34	1	19.07.2023	19,1	9	97,5	28	0	2,52	1,967	28	8,695	2,377757557	0,075
35	3	19.07.2023	18,9	8,7	94,1	29	0	2,52	1,971	38	8,64	2,049544548	0,076
36	5	19.07.2023	18,6	7,8	84	27	0	2,46	1,949	41	8,577	1,311202722	0,076
37	8	19.07.2023	9,6	0,4	3,2	119	0	3,08	2,663	44	7,134	0,438716886	0,101
38	11	19.07.2023	8,4	0	0	34	0	2,93	2,474	46	6,82	0,049479348	0,116
39	12	19.07.2023	8,2	0	0	37	0	2,84	2,367	52	6,774	0	0,119
40	Outlet	19.07.2023				30	0	2,53	1,932	37			
41	0,5	01.08.2023	19,7	10,2	112	26	0	2,34	1,772	41	8,841	4,132075328	0,116
42	1	01.08.2023	19,7	10,3	112	32	0	2,35	1,754	34	8,975	4,71153347	0,081
43	3	01.08.2023	19,2	9	97	48	0	2,39	1,784	13	8,915	11,71341098	0,082

44	5	01.08.2023	17,6	4,4	46	36	0	2,43	1,868	38	8,356	1,637216648	0,089
45	8	01.08.2023	10,5	0	0	33	0	2,71	2,2	7	7,255	0,317217598	0,09
46	11	01.08.2023	8,6	0	0	36	0	2,95	2,323	53	6,906	0	0,109
47	12	01.08.2023	8,4	0	0	52	0	2,70	1,951	92	6,804	0	0,129
48	Outlet	01.08.2023				30	0	2,42	1,744	49			
49	0,5	16.08.2023	19,4	10,2	110	50	0	2,60	1,821	44	8,639	14,96365438	0,104
50	1	16.08.2023	19,1	10,2	110	54	0	2,61	1,757	31	8,6	18,6311736	0,104
51	3	16.08.2023	18,3	8,6	92	45	0	2,56	1,79	30	8,63	16,26441146	0,103
52	5	16.08.2023	17,1	5	52	36	0	2,60	1,885	41	7,94	1,529461624	0,108
53	8	16.08.2023	11,2	0	0	42	0	2,73	2,019	59	7,44	0,139091945	0,103
54	11	16.08.2023	8,8	0	0	50	6	2,57	1,744	97	7,131	0	0,123
55	12	16.08.2023	8,5	0	0	64	0	2,52	1,504	123	6,97	0	0,114
56	Outlet	16.08.2023				38	0	2,54	1,833	38			
57	0,5	06.09.2023	18,2	11,5	122	53	0	2,55	1,618	50	8,378	22,78414021	0,149
58	1	06.09.2023	18,1	10,9	116	55	0	2,51	1,607	32	8,556	24,3889204	0,151
59	3	06.09.2023	17,9	10,3	108	52	0	2,49	1,623	40	8,447	23,57031207	0,151
60	5	06.09.2023	16,5	5,1	53	48	0	2,59	1,778	59	7,714	6,595047318	0,152
61	8	06.09.2023	12,9	0	0	59	0	2,59	1,779	62	7,293	0,528329483	0,14
62	11	06.09.2023	9,4	0	0	53	0	2,38	0,878	111	6,845	0	0,127
63	12	06.09.2023	9,2	0	0	83	0	2,29	1,23	131	6,909	0	0,156
64	Outlet	06.09.2023				54	0	2,50	1,677	43			
65	0,5	20.09.2023	15,8	8,3	84	53	3	2,58	1,798	32	7,68	13,63156037	0,14
66	1	20.09.2023	15,7	8,3	83	57	7	2,56	1,795	34	7,66	12,24723817	0,142
67	3	20.09.2023	15,7	8,2	83	54	0	2,60	1,788	16	7,648	10,86456528	0,142
68	5	20.09.2023	15,5	7,6	76	54	0	2,57	1,8	32	7,631	10,35382845	0,15
69	8	20.09.2023	14,7	3,2	32	73	0	2,89	2,108	46	7,392	5,08207881	0,161
70	11	20.09.2023	9,4	0	0	109	0	2,16	0,964	140	6,952	0	0,182
71	12	20.09.2023	9,1	0	0	110	0	2,13	1,839	136	6,913	0	0,188
72	Outlet	20.09.2023				51	0	2,41	1,616	43			
73	0,5	29.09.2023	14,7	7,8	76	54	0	2,79	2,074	47	7,9	6,363593923	0,154
74	1	29.09.2023	14,6	7,7	76	55	0	2,88	2,045	66	7,665	6,787467004	0,159
75	3	29.09.2023	14,6	7,5	74	54	0	2,82	2,056	53	7,565	7,153064409	0,159
76	5	29.09.2023	14,5	7,4	73	54	0	2,82	2,045	55	7,5	6,275080867	0,158
77	8	29.09.2023	14,3	6,5	63	57	0	2,82	2,046	58	7,47	5,913331856	0,162
78	11	29.09.2023	9,8	0	0	88	0	2,17	0,939	124	7,051	6,46365216	0,173
79	12	29.09.2023	9,4	0	0	108	1	2,07	0,71	128	6,982	0	0,195
80	Outlet	29.09.2023				54	2	2,79	1,999	41			
81	0,5	13.10.2023	11,7	8,9	82	50	0	2,62	1,46	43	7,466	25,65229308	0,145
82	1	13.10.2023	11,7	8,8	81	47	0	2,15	1,793	50	7,44	22,90014179	0,148
83	3	13.10.2023	11,6	8,7	80	48	0	2,57	1,816	41	7,404	22,79843425	0,15
84	5	13.10.2023	11,6	8,6	79	48	0	2,61	1,819	50	7,372	24,33064472	0,15
85	8	13.10.2023	11,6	8,6	79	49	0	2,60	1,819	50	7,339	25,04259756	0,151
86	11	13.10.2023	11,3	5,1	47	53	5	2,61	1,751	47	7,284	26,96899351	0,151
87	12	13.10.2023	9,8	0,1	1	93	0	2,58	0,7	146	6,779	5,918279791	0,193
88	Outlet	13.10.2023				53		2,63	1,839	47			

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

Postboks 5003
NO-1432 Ås
Norway