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Gunnhild Riise and Thomas Rohrlack

Coupling between nitrate input and phosphorus retention in lake sediments – A case study from Lake Årungen

Pia Frostad
Master of Science in Ecology
Environmental Sciences and Natural Resource Management

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Abstract

Cultural eutrophication represents one of the greatest threats to freshwater systems, with lowland streams and lakes being especially vulnerable in areas that receive an increased supply of nutrients from human activity. Internal phosphorus loading can cause implications in the restoration of a lake that suffer from the detrimental effects of eutrophication, delaying the time from implementation of restorative actions to significant improvement over a period of several years. The presence of nitrate in the hypolimnion during summer stagnation can act as a phosphate buffer by suppressing the internal loading of phosphorus. Thus, establishing a relationship between the concentration of nitrate in the hypolimnion and internal loading of phosphate is a key factor in mediating the potential detrimental effects of eutrophication in a lake. In situ and laboratory analyses on water samples collected from the eutrophic, dimictic Lake Årungen in 2017, 2013 and 2009 were used to investigate the coupling between nitrate and phosphorus, and to what extent nitrate input from the catchment affects nitrates ability to control internal phosphorus loading in lake. Results from this study show that there was a coupling between nitrate and phosphate concentrations in the hypolimnion during anoxic conditions. In 2017 the nitrate levels were sufficiently high in protecting the lake from internal phosphorus loading. In 2013 and 2009, nitrate levels were depleted before the fall turnover, resulting in extensive leaking of phosphate from the sediment. With a nitrate decomposition rate of 0.02 mg/l a day above the sediment, a 50% reduction in the external input of nitrate in 2017 could have produced a similar outcome to what was seen in 2013 and 2009. Based on results from this study, attention should be focused on the start concentration of nitrate above the sediment at the onset of anoxic conditions in the hypolimnion. One should be cautious against measures that can potentially decrease the external input of nitrate to Lake Årungen, as this can, under given conditions, initiate internal phosphorus loading.

1 Introduction

Eutrophication, a process where nutrient enrichment causes increased primary production, is today a widespread environmental problem, and represent one of the greater threats to freshwater systems (Smith 2003). Both natural and cultural processes can cause eutrophication. Natural eutrophication is a slow, continuous process in which the addition of organic matter causes an increase in primary production and sedimentation rate (Wetzel 2001). On the other hand, cultural eutrophication is a result of human-induced pollution that speeds up the natural eutrophication process, shortening the life span of a lake (Hasler 1947; Sawyer 1966; Smith 2003). With regard to eutrophication, the aim of freshwater management is to restore a water body back to its natural trophic status by limiting the causes and effects of cultural eutrophication. Being located in areas that receive an increased supply of nutrients from human activity, lowland streams and lakes are especially vulnerable to cultural eutrophication (Wetzel 2001). Both urbanization and agriculture generate elevated loading of nutrients into the catchment (de Jonge et al. 2002; Wetzel 2001). Nutrient concentration and availability is a critical factor in primary production, which is fundamental for a healthy freshwater ecosystem. However, enhanced nutrient concentrations can deteriorate the ecosystem by causing eutrophication. An increase in nutrient concentration generally causes altered community structure through favoring certain phytoplankton species (Schindler 1977), such as dominance of cyanobacteria (Smith 2003). Among other detrimental effects are anoxic conditions and increased probability of internal loading of nutrients stored in the sediment (Søndergaard et al. 2003). It is not only freshwater biota that is affected by these consequences, harmful algal blooms caused by eutrophication can also become a risk to human health (Anderson et al. 2002; Codd et al. 1997).

Identifying the sources of nutrient loading in freshwater systems is of great importance in the efforts to improve water quality problems associated with eutrophication. One study from 2005 examining lowland catchment systems in the UK show that point sources (sewage effluent) of phosphorus poses a greater risk than diffuse sources such as agricultural runoff (Jarvie et al. 2006). However, in Norway, measures to improve sewage treatment and leaking pipes have reduced the significance of such point sources. We now see that agriculture is an important source of phosphorus (pura.no 2015). In the process of improving the water quality of a lake, internal phosphorus loading can cause serious problems. Due to a high storage capacity of phosphorus in the sediments, the time from implementation of restorative actions to improvement can be delayed over a period of several years (Ryding 1985). Retention and release of phosphorus from the sediment is influenced by a number of factors, and will vary according to different lake categories (Sondergaard et al. 2001). It is therefore essential to identify all factors that can be of significance in achieving an improved water status.

Internal loading of phosphorous has been demonstrated to be caused mainly by reduction of iron in the upper sediment layers, a process which is strongly influenced by redox conditions (Boström & Pettersson 1982; Hansen et al. 2003; Mortimer 1942; Wetzel 2001). During summer stratification in an eutrophic lake, the oxygen content of the sediment-water interphase can be drastically reduced by microbial degradation of organic matter (Wetzel 2001). As the hypolimnion becomes anoxic, nitrate serves as an alternative oxidizing agent. In this way, nitrate is acting as a redox buffer by maintaining a high redox potential above the sediment (Tirén & Pettersson 1985). Oxidized iron (Fe_2O_3) adsorbs phosphate strongly, and is an important factor in retaining phosphorus in the sediment (Drever 1982). The redox potential in an anoxic hypolimnion declines upon the consumption of nitrate, and reducing conditions arise. When the oxidized iron is reduced (to Fe^{2+}, FeS_2 or $FeCO_3$), the iron associated phosphate in the upper sediment layer is released into the water phase (Drever 1982; Wetzel 2001).

As nitrate acts as a redox buffer in the hypolimnion, knowledge about the nitrogen cycle in a lake that is prone to internal loading of phosphorus is of great value. Nitrogen can enter a lake in numerous chemical forms (Wetzel 2001). In general, the amount of available nitrogen is mainly controlled by denitrification, sedimentation of nitrogen-associated substances, and uptake by biota. Nitrogen can be lost, either permanently or temporary, through effluent outflow from the lake, bacterial denitrification, and sedimentation of inorganic or organic compounds. Differences in nitrogen inputs and outputs determine the total nitrogen retention in a lake. Hence, knowledge about these parameters is crucial in assessing the likelihood of a situation with internal phosphorus loading in a lake. In regard to nitrate, Wetzel (2001) remarks that there is no release of iron-bound phosphate from the sediments in an anoxic hypolimnion as long as there is an abundancy of nitrate (ca. > 0.1-1 mg NO_3^- mg/l) in the water phase above the sediments (Wetzel 2001). A study on 31 eutrophic Danish lakes from 1981 showed that the release of phosphate from the sediments is highly dependent on the nitrate concentrations in the hypolimnion (Andersen 1982). In stratified lakes with an anoxic hypolimnion, there was no release of phosphate from the sediments if the concentration of nitrate in the hypolimnion was above 1 mg/l. Despite being a phosphorus buffer, it is also important to remember that nitrogen can be a contributing factor in the intensification of the eutrophication process if it is a limiting factor in the primary production.

In 2008 the Water Framework Directive (WFD) was implemented in Norway with the aim of improving and securing a good status in all surface waters within 2021 (Vannportalen 2014b). The general purpose of the regulations that followed the enforcement of the WFD is to obtain a holistic protection and promote sustainable use of water bodies through implementation of surveillance plans for each individual water body and its catchment (Vanndirektivet 2009; Vannportalen 2014b). Based on the surveillance plans, necessary measures are to be carried out in order to achieve good ecological and chemical status in all natural surface waters (Vannportalen 2014a). One frequently used measure to improve the ecological status of a water body is to reduce the nutrient input from sewage and agricultural runoff, often with phosphorus being the main target. The important role of phosphorus as a major driver of eutrophication in lakes was illustrated in the large-scale fertilization experiments conducted by Schindler in Lake 226 of northwestern Ontario (Schindler 1974). Techniques that aid in reducing internal loading of phosphorus have also been explored, such as physically removing the phosphorus-rich sediments or changing the sorption capacity by adding oxygen, nitrate, iron, alum or calcium (Faafeng 1996; Ripl 1976; Sondergaard et al. 2001). Several studies have shown that nitrate addition can improve water quality by serving as a mechanism that suppress internal phosphorus loading (Hansen et al. 2003; Ripl 1976; Søndergaard et al. 2000; Wauer et al. 2005). In Lake Kolbotnvannet, restoration methods included a modified version of the “Riplox-method” (Ripl 1976) where calcium nitrate is introduced in the hypolimnion. Addition of nitrate resulted in increased sorption of phosphorus in the sediment and improved redox status (Faafeng 1996). The same was discovered in an experimental addition of nitrate in Lake Lyng in Denmark, where the addition of nitrate resulted in a 48-77% reduction in total phosphorous compared to non-treatment years (Søndergaard et al. 2000).

Lake Årungen is a shallow lake in the southeast of Norway, located in a lowland area dominated by agriculture. The catchment is in a region that has a high proportion of marine deposits, thus making the lake nutrient rich through deposition of marine clay and fine sediments. Historically, in the years before the late 1800’s, the lake experienced little impact by human activity and is believed to have been mesotrophic. Following the 2nd world war, changes in agricultural practices and increased runoff from untreated sewage lead to periods of anoxic conditions, formation of H_2S gas and subsequent fish deaths. As a consequence of this, the sewage system was improved, and effort was put into reducing nutrient runoff from agriculture. This greatly improved the water quality during the 1980's and 1990's (Borch et al. 2007). As of today, the water quality of the lake is not suited for bathing, despite numerous attempts to reduce the eutrophication. These weak results might partly be explained by internal phosphorus loading. Due to its geographical position, the sediment in Årungen is high in phosphorus, and previous estimates show that the lake has a retention factor for phosphorus of 0.5 (Riise et al. 2010b). This storage can function as an internal source of phosphorus, and it is controlled by certain factors such as circulation patterns, oxygen concentrations in the hypolimnion and sediment redox conditions. In addition to external loading of phosphorus, Lake Årungen also receives large amounts of nitrate from agricultural runoff and sewage. During summer stagnation, when the lake is stratified, this incidental addition of nitrate can serve as a phosphorus buffer by suppressing the internal loading of phosphorus (Beutel et al. 2016).

As of the most recent report from PURA, "poor" status has been signed to lake Årungen in accordance to the WFD regarding the evaluation of eutrophication parameters (physio-chemical elements), while ecological status is set to "moderate" (pura.no 2015). According to the WFD, Lake Årungen is to achieve "good" ecological status, and thus function as a recreational bathing spot, within 2021. For this to be accomplished the total phosphorus (TP) concentration in the water has to be reduced to below 15 μg/l (Borch et al. 2007). Prioritizing measures that aim at reducing the input of phosphorus in the catchment, from both agriculture and urban activity, may imply that external sources of nitrate will also become reduced. Consequently, the lake can suffer from more frequent episodes of internal phosphorus loading, causing a situation where it becomes more difficult to control the algal blooms through measures in the catchment.

The aim of this study is to evaluate the effect of human activity upon internal phosphorus loading through input of nitrate from sewage and agricultural runoff. The unique history of Lake Årungen have seemingly caused it to become dependent upon external input of nitrate as means of preventing leaking of phosphorus from the sediment. The lake has been given much public attention as it is home to an international rowing station, and it is undeniably of great interest to the public that the water quality is improved. The relationship between nitrate and internal phosphorus loading should be considered as managers and politicians set future goals for improving the water quality in the lake.

I will in this thesis investigate the relationship between nitrate and phosphorus in Lake Årungen and examine to what extent internal phosphorus loading is regulated by nitrate levels. The collected data from 2017 will be used in combination with data collected in 2013 and 2009 by the hydrology and limnology group at NMBU to evaluate the following hypotheses:

1) In the situation of anoxic conditions in the hypolimnion, there exists a coupling between nitrate concentrations and internal phosphorus loading.

2) Input of nitrate from the catchment is sufficiently high in protecting the lake from internal phosphorus loading.

3) Reducing the nutrient input (especially nitrate) to the lake, as decided by managers and regulators, can potentially cause increased phosphorus leaking from the sediment.

2 Methods

2.1 Study area

Lake Årungen is situated in the municipalities Ski and Ås in Akershus county, and is part of the Årungen watercourse. Frogn municipality is also a part of its catchment. It is located west of the Oslo fjord, and is approximately 30 km south of Oslo (6624684.14N, 260227.91E). The landscape surrounding the lake and its catchment is highly influenced by human activity and comprised of agricultural fields combined with forests and urban areas that are scattered throughout the catchment.

2.1.1 The catchment

The total area of the catchment is 52 km^2, consisting of 53% agriculture, 34% forest and 10% urban settlement (Skogheim & Abrahamsen 1980). There are several streams in the catchment that discharge into the lake, with Bølstadbekken having the greatest contribution (Gunnarson 2007) (Figure 1). The main outlet is in the northern part of the lake where it goes though Årungenelva into Bunnefjorden, a part of Oslofjorden. The center of Ås and Ski are the two urban areas that has the highest population density in the catchment area. Aside from Ski center there is little industrial activity in the catchment area.

Figure 1 Overview of lake Årungen and its sub catchments (Borch et al. 2007).

2.1.2 Lake Årungen

Lake Årungen is a shallow lowland lake with a total surface area of 1.2 km^2. It stretches in a north-south direction with a length of 3 km and an average width of 450 m. Its maximum and mean depth is 13 m and 8 m respectively, and it has a global retention time of 4.5 months (Skogheim & Abrahamsen 1980). Årungen is classified as a dimictic lake with two full circulations in spring and autumn (Romarheim & Riise 2009). The lake is oriented approximately in a north-south direction, and is therefore highly exposed to wind that causes mixing of the water. The catchment area is located below marine limit, and the lake receives large amounts of erosion material from the catchment. Based on estimates on allochthonous input from the catchment and sediment samples from the lake, the total retention factor for dry matter has been calculated to be 0.75 (Reierstad 2010). Thus, the sediments in the lake are storing large amounts of nutrients.

2.2 Data collection

2.2.1 Field work

The field work was carried out in the period between the 2nd of May and the 23rd of October in 2017. The general frequency of the sampling was every three weeks, with a period of increased sampling frequency during the summer stratification in August. A total of 10 series of water samples were collected and analyzed during this period.

2.2.2 Water samples and analyses

Water samples for physical and chemical analyses were collected along a vertical profile at the deepest part of the lake (13.2 m) using a Swedaq Hydro-X water collector. One exception was made during the last sampling day on the 23rd of October due to the removal of a buoy that was used for anchoring. This was resolved by collecting the 13m sample at the regular location, whilst collecting the remaining samples at a shallower location (< 13 m) that had a buoy. Measurements were performed at 10 different depth increments of the water column, with most being concentrated in the hypolimnion (0.5m, 1m, 3m, 5m, 8m, 9m, 10m, 11m, 12m and 13m). Temperature (°C), dissolved oxygen (DO concentration (mg/l), oxygen saturation (%), and conductivity (μS/cm) were measured in the field as storage of the samples may influence some of the results. Light conditions in the lake were examined by measuring the secchi depth with a white 13x18cm secchi disk, and photosynthetically active radiation (PAR) from the surface down to the depth with 0.1 % relative irradiance using a light meter sensor (LI-COR LI250A).

2.3 Laboratory analyses

On the day of sampling subsamples from all depths were prepared and stored cold prior to further analysis. For each sample, phosphorus and nitrogen were separated into the different fractions total phosphorus (TP), phosphate (PO_4^{3-}), total nitrogen (TN), ammonium (NH_4^+) and nitrate (NO_3^-). Samples for water color and absorbance at 254 nm, turbidity, pH, alkalinity and chlorophyll a (Chla) were analyzed at the day of sampling. Total organic carbon (TOC), dissolved organic carbon (DOC) and seston were analyzed the following day. Analyses performed on samples from depth 0.5m, 1m, 3m, 5m, 8m, 12m and 13m will be referred to as main depths from here on.

Turbidity

Determination of turbidity were performed according to the Norwegian Standard (NS-ISO 7072) with a turbidimeter model 2100AN IS (Hach, Loveland, CO, USA). Unfiltered samples from the main depths were analyzed at room temperature, and turbidity were expressed in formazin nephelometric units (FNU). In this method, scattered light from the sample at a 90° angle from the incident light is measured by a single detector in the instrument.

pH

Determination of pH were performed on all samples according to the Norwegian Standard (NS 4720). Unfiltered samples were analyzed at room temperature with a potentiometric PHM210 standard pH meter in combination with a Orion 8172BNWP pH electrode. The pH meter was calibrated against two reference solutions at pH 4 and pH 7 prior to use.

Alkalinity

Measurements of alkalinity were performed on the samples for the main depths according to the Norwegian Standard (NS-EN ISO 9963-1). All samples were unfiltered and at room temperature prior to titration with an automatic titrator (665 Dosimat Methrom), and the endpoint of pH 4.5 were measured with a PHM210 standard pH meter in combination with a Orion 8172BNWP pH electrode. Total alkalinity was calculated using the following equation:

$$A_T = \frac{c(HCl) \times V_6 \times 1000}{V_4}, \qquad (1)$$

where A_T is the total alkalinity (mmol/l), c(HCl) is the concentration of the hydrochloric solution (mol/l), V_4 is the volume of the sample (ml) and V_6 is the volume of HCl (ml) used to reach pH 4.5.

Water color and absorbance at 254 nm

Filtered samples from the main depths were analyzed spectrophotometrically (Shimadzu UV-1201) for determination of water color and absorbance at 254 nm according to the Norwegian Standard (NS 4748). This method allows for determination of water color that is due to dissolved substances. Absorbance was measured at 410 nm in 5 cm cuvettes, and the results are presented as true color units (TUC, mg l^{-1} Pt). Absorbance at 254 nm were measured using 1 cm cuvettes. Deionized water was used as reference solution for all measurements.

Chlorophyll a

Chlorophyll a was analyzed for the main depths according to the Norwegian Standard (NS4767). 500 ml of the sample was filtrated by vacuum filtration with a glass microfiber filter (Whatman GF/C, dimeter?). Extraction of chlorophyll a were carried out by adding 7 ml of methanol and letting the filters soak in the solution for 20 hours in a dark environment. The samples were centrifuged at 4000 rpm for 10 minutes before the absorbance at 665 nm and 750 nm were determined by using 1 cm cuvettes, with methanol as the reference solution. Chlorophyll a concentration was calculated using the following equation:

$$A_{665\,K} = A_{665} - A_{750}, \tag{2}$$

where A_{665} and A_{750} is the absorbance at 665 nm and 750 nm, respectively.

$$C_v = \frac{10^4 e \times A_{665\,K}}{77\,V\,l}\,\mu g L^{-1}, \tag{3}$$

where C_v is the concentration of chlorophyll a, e is the volume of methanol extract (ml), l is the length of the cuvette (mm), V is the filtrated sample volume (l), and 77 is the chlorophyll a absorption coefficient in 100% methanol.

Suspended solids

Determination of suspended solids was performed according to the Norwegian Standard (NS-EN 872). 500 ml from samples from the main depths was filtrated by vacuum filtration with a glass microfiber filter (Whatman GF/C). The microfiber filters were left to dry for 30 minutes in room temperature prior to drying at 105 °C for 1 hour. Filters were weighted before filtration and after drying, and concentration of suspended solids were calculated using the following equation:

$$p = \frac{1000 \times (b-a)}{V}, \tag{4}$$

with p being the content of suspended solids (mg/l), b the mass of the filter after filtration and drying (mg), a the mass of the filter before filtration (mg) and V is the volume of the sample (ml).

Total organic carbon and total dissolved carbon

Total organic carbon (TOC) and total dissolved carbon (DOC) was analyzed with a Shimadzu organic carbon analyzer (ASI-V and TOC-V CPN) (detection limit: 0.2 mg/l) in accordance with the Norwegian Standard (NS-EN 1484). This was performed by trained personnel at the soil and water laboratories at NMBU

Ammonium

The concentration of ammonium-N (NH_4-N) was measured for all depths according to a modified version of the Norwegian Standard (NS 4746). In a weak alkaline solution, ammonium will react with hypochlorite to form monochloramine, which in turn will produce a blue color in the presence of salicylate. Filtered samples were transferred to FIA test tubes, and salicylate and hypochlorite were added separately after consecutive mixing of the solution. The samples were let to rest for minimum one hour in a dark environment prior to being measured spectrophotometrically at 655 nm. The detection limit is 0.02 mg/l NH4-N.

Phosphate

Phosphate (PO_4^{3-}) was determined in accordance with the Norwegian Standard (NS 4724). Phosphate reacts with molybdate to create a yellow-colored antimony-molybdate phosphate complex. When reduced by ascorbic acid, a blue colored complex is formed that can be measured spectrophotometrically at 880 nm (detection limit: 1 $\mu g\ l^{-1}$). Filtered samples from all depths were transferred to FIA test tubes, and ascorbic acid and molybdate were added between mixing the solution. The samples were analyzed after 10 minutes.

Nitrate

Nitrate (NO_3-N) was determined according to the Norwegian Standard (NS-EN ISO 10304-1). Samples were analyzed using single column ion chromatography (XYZ auto sampler, ASX-500 series, Zellweger analytics IC 5000). The sample solution is passed through a low capacity anion exchanger column as the stationary phase. The mobile phase contains a carbonate/bicarbonate buffer, and the sample is therefore also passed through a suppressor column that decrease the conductivity of the mobile phase. A conductive detector measured the nitrate concentration.

Total nitrogen

Total nitrogen (TN) concentrations were determined by flow injection analysis (FIA). Samples were prepared according to the Norwegian Standard (NS 4743). An oxidizing agent (potassium persulfate in a sodium hydroxide solution) was added to the samples and autoclaved at 200 kPa for 30 minutes. The autoclaved samples were mixed with a buffer solution, and nitrate is reduced to nitrite when flowed through a cadmium column. The nitrate is then converted into a diazo compound on the addition of a sulphanilamide solution. When coupled with N-(1-naphthyl)ethylenediamine dihydrochloride the solution turn magenta in color and is measured at 540nm.

Total phosphorus

Total phosphorus (TP) was determined according to the Norwegian Standard (NS-EN 1189). Potassium peroxydisulfate were added to the samples as an oxidizing agent, converting all phosphorus into orthophosphate when autoclaved for 30 minutes at 200 kPa. Addition of ascorbic acid and antimony-molybdate caused an atimony phosphomolybdate complex to form that produce a strongly colored molybdenum blue complex in reducing conditions. Absorbance of this complex were measured at 880 nm to determine the concentrations of orthophosphate.

Calculation of euphotic depth

The secchi depth measurements were used as a proxy for the estimation of the euphotic depth. A conversion factor of 2.5 was chosen as the water in lake Årungen in general has high turbidity. The correlation between secchi depth and euphotic depth is described in the following equation:

$$Z_{eu} = m \times Z_{SD}, \tag{5}$$

where Z_{eu} is the euphotic depth, m is the conversion factor, and Z_{SD} is the secchi depth.

2.4 Treatment and analysis of data

In addition to the data collected in Lake Årungen in 2017, analyses also include data collected by the hydrology and limnology group at NMBU in 2013 and 2009. Data collected in situ and on the laboratory were organized in Microsoft Excel 2016 (version 1701). R Studio (Studio 2012) were used in the data analyses and construction of figures. Linear interpolation was applied on data for nitrate (NO_3-N), phosphorus (PO_4-P) and oxygen (O_2) for data collected in 2013 and 2009 as these years did not contain measurements from depths of 9, 10 and 11 meters. Linear regression was used to calculate the nitrate decomposition rate above the sediment for all years. Selection of data for these analyses were based on the period when the conditions above the sediment were anoxic. This is to ensure that external sources of nitrate are limited, and that the consumption of nitrate is due to reduction of nitrate by microbial respiration.

3 Results

3.1 Weather

Temperature and precipitation data have been obtained through the BIOKLIM field station at Sørås in Ås, Akershus (NMBU 2017). Registration of temperature and precipitation have been retrieved for the entire sampling period, with the exception of precipitation measurements that have not been performed during weekends in July and August. Temperature measurements show that there were great fluctuations in May, with temperatures reaching from 1.7 °C to 16.9 °C (Figure 2). This was followed by a steady temperature increase until mid-July, and a temperature decrease during the rest of the sampling period. From mid-September and throughout October there were once again additional fluctuations in temperature. Regarding precipitation there has been high peaks during each month, with an exception being July with moderate precipitation (Figure 2). It must however be taken into consideration that there is a lack of information during the months of July and August.

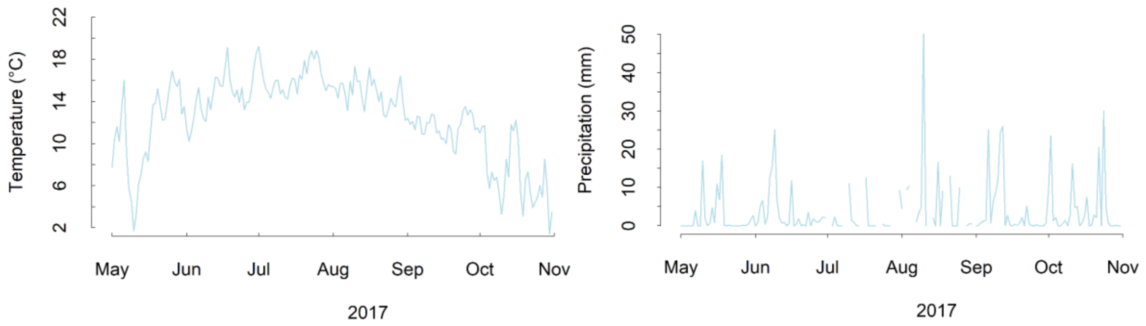


Figure 2 Temperature and precipitation measurement at the BIOKLIM field station in Sørås, 2017 (NMBU 2017).

Compared to mean values from the period between 1969 and 1990 the mean temperature for each month during the sampling period is slightly higher, except for June and August where the temperature is 0.3 °C and 0.2 °C lower, respectively (Figure 3). The greatest discrepancies are found in May and September where there has been an increase of 0.8 °C and 1.1 °C, respectively. The mean precipitation measured during the sampling period is substantially higher than the 1969-1990 mean values (Figure 3). However, during the month of June the mean precipitation was almost 40 % lower compared to the historical mean, making it an unusually dry month.

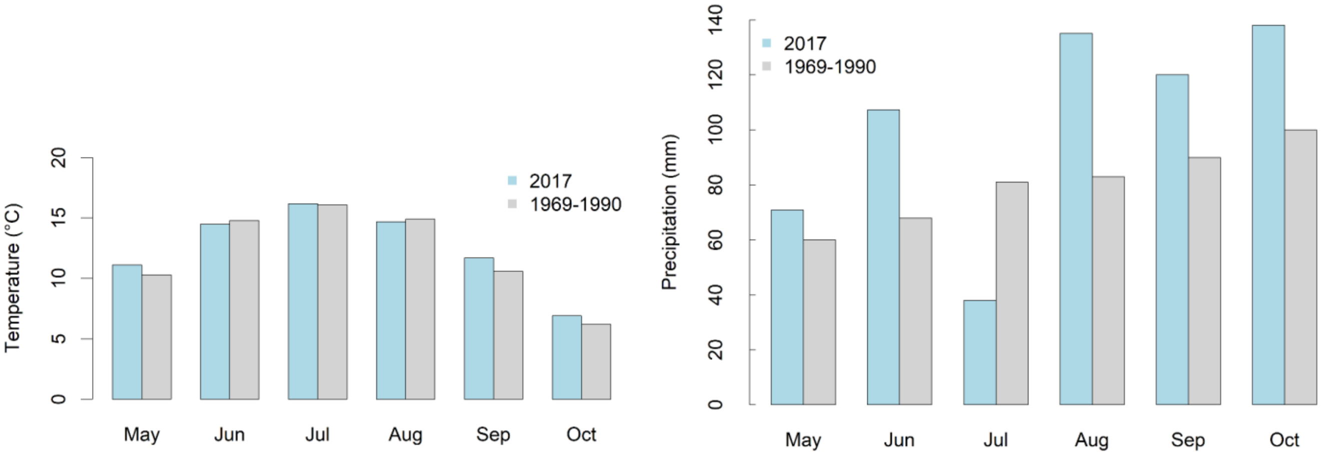


Figure 3 Mean temperature and mean precipitation measurements at the BIOKLIM field station in Sørås (NMBU 2017). Blue bars show mean values for 2017, grey bars show mean values for the 1969-1990 period.

3.2 Light characteristics and suspended solids

Secchi depth measured at each consecutive sampling date shows that it was stable from May to June (Figure 4). It was followed by an increase to a maximum of 1.65 m in August, before it continued to decline from late August to the last sampling date in October. Being a function of the secchi depth, the euphotic depth follows the same trend throughout the whole sampling period, with a maximum of 4.13 m in mid-August (Figure 4). Suspended solids (seston) for the upper 3 meters in the water column was at a maximum in May, followed by a decline in mid-June (Figure 4). Throughout the remainder of the sampling period the measures were relatively stable, with a minimum of 3.5 mg/l on the 23rd of October.

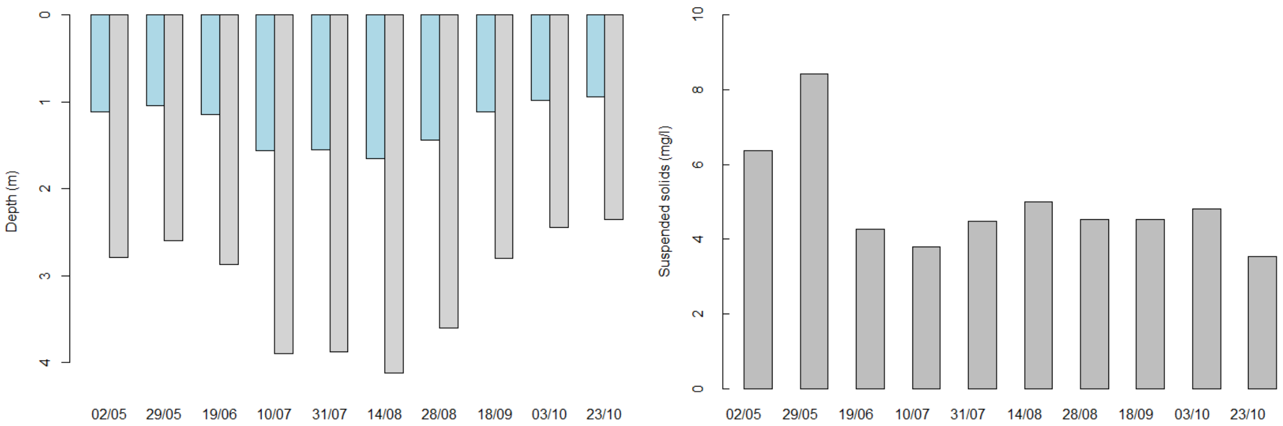
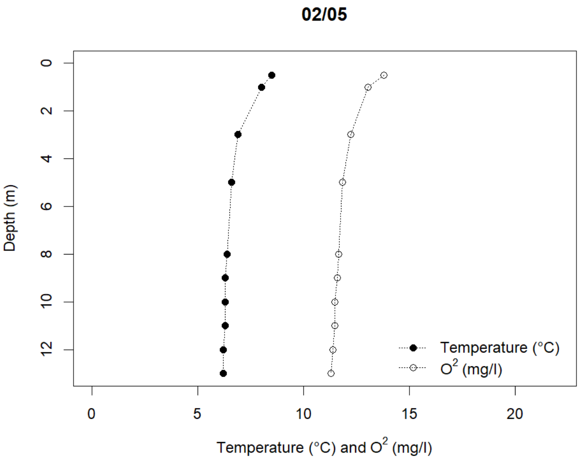


Figure 4 Left: Secchi (blue bars) and euphotic (grey bars) depth measured at each sampling date. Right: Mean suspended solids (mg/l) for the upper 3 meters in the water column.

3.3 Temperature and oxygen

The lake was in full circulation on the first day of sampling the 2nd of May (Figure 5). Signs of stratification could be seen in June, and in July it was fully stratified. The thermocline moved downwards from July to October until the lake was once again fully stratified on the 23rd of October. Values of 0 mg/l (O_2) appeared in the hypolimnion at the 10th of July and continued until the 3rd of October. An anomaly appeared in the measurements from the 18th of September where the oxygen concentration increased to 5.45 mg/l at 12 meters.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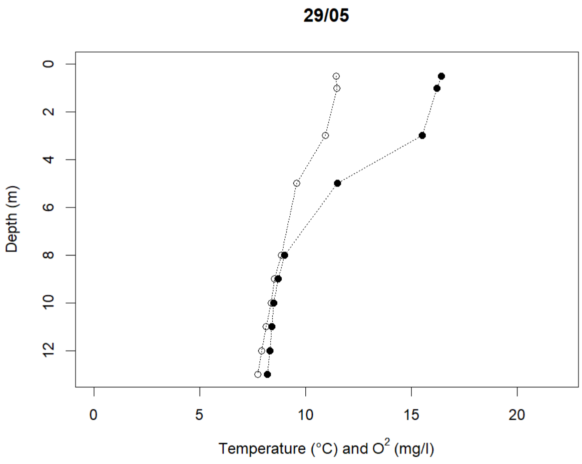
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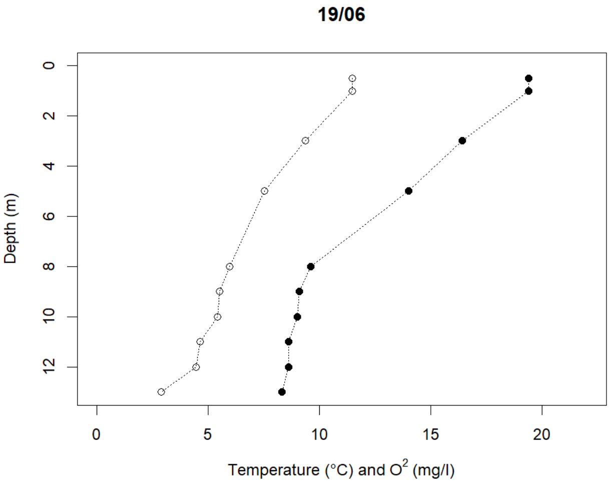
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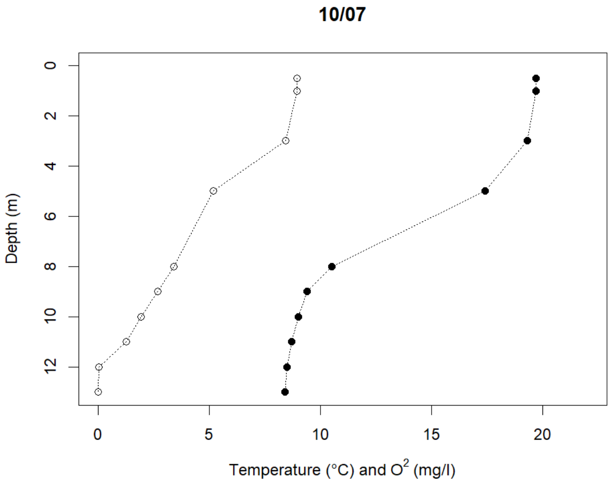
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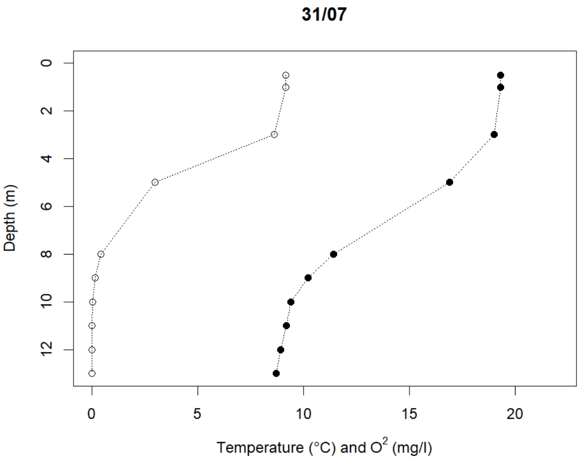
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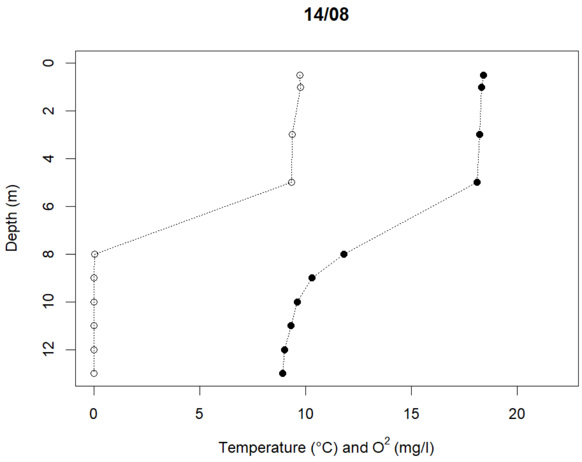
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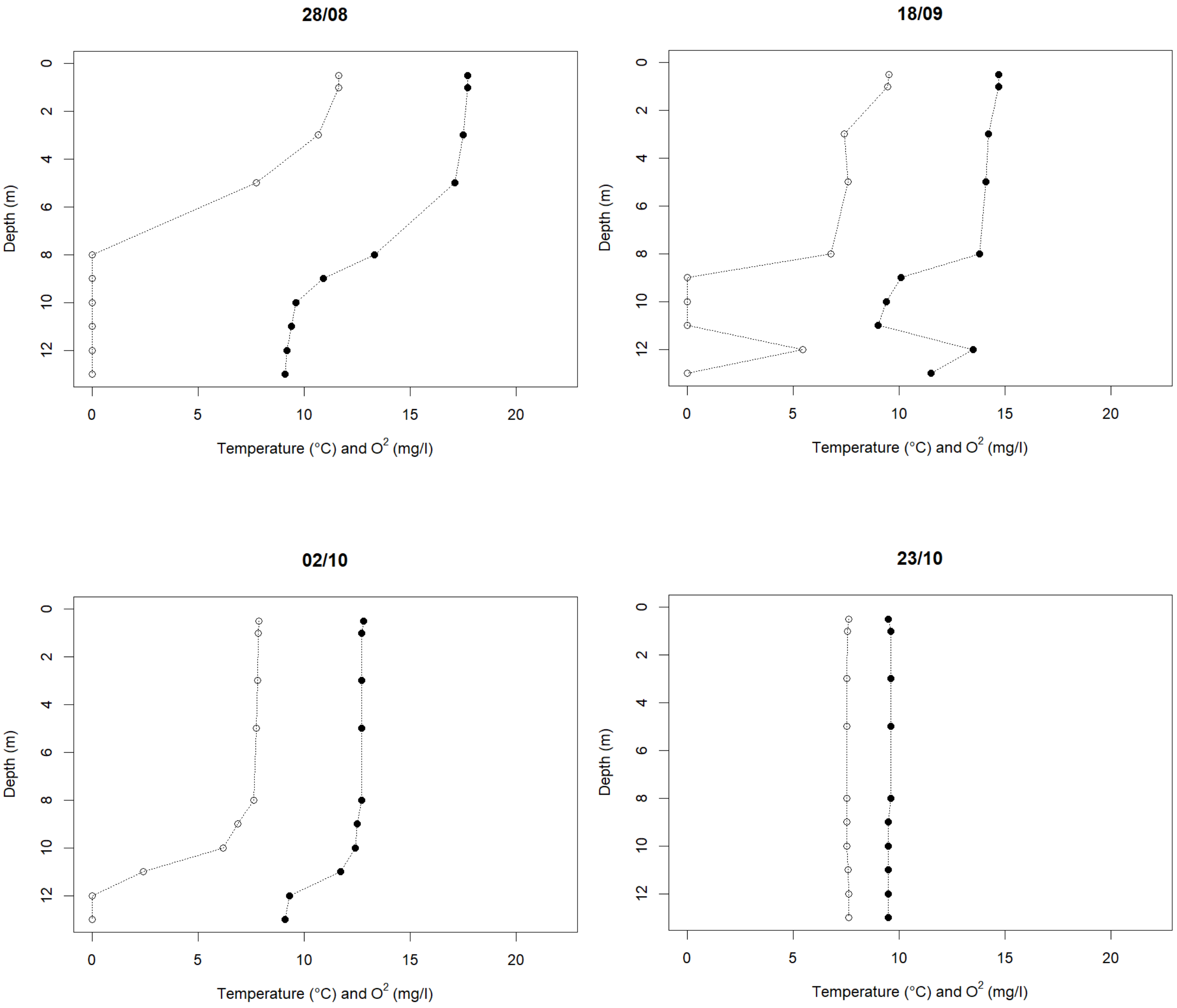
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Figure 5 Water column temperature (°C) (open markers) and oxygen concentration (mg/l) (grey markers) series in Årungen from May to October 2017.

3.4 Isopleth diagrams of water parameters

Time-depth isopleths diagrams are based on in-situ data and laboratory analyses for all samples collected during the period May to October 2017.

3.4.1 Temperature and oxygen

Temperature data indicate that the lake was in full circulation in May and late October. Heating of the upper water column started in May, peaking at 19.7 °C at the 10th of July

(Figure 6). During the whole of the stratified period the thermocline descended. Oxygen saturation was at its highest on the 19th of June and 28th of August (125 % and 123 %, respectively). Anoxic condition in the hypolimnion were observed in the period between the 7th of July to the 2nd of October (Figure 6). The anomaly on the 18th of September can be seen in measurements of both temperature and oxygen, as shown in figure 5.

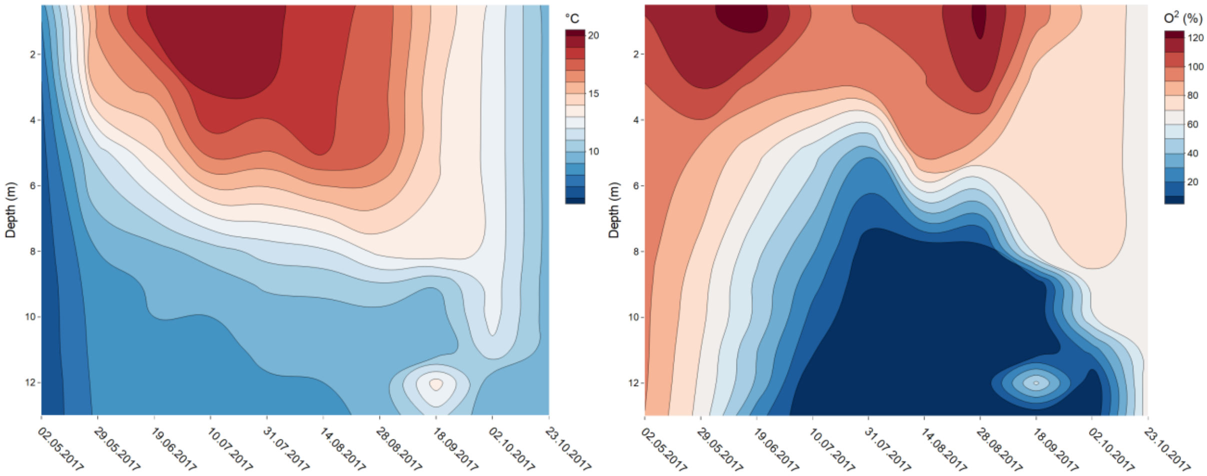

Figure 6 Time-depth isopleth diagram of temperature (°C) (left) and oxygen saturation (%) (right) in lake Årungen from May to October 2017.

3.4.2 pH, color and turbidity

There was an increase in pH in the epilimnion from May to late August as primary production increased (Figure 8). Peaking at pH 9 at the 28th of August, it declined to pH 7.5 at the end of October. Apart from a slight decrease during the stratification period, pH remained more stable in the hypolimnion. Measurements of color show that there was a minor increase in color units in mid-June, followed by a slight decrease in August (Figure 7). From September onwards, the color increased in the entire water column, peaking at 41 color units at 13 meters in September. Measurement on turbidity show a general positive trend between turbidity and depth for all samples (Figure 7). It was further evident that turbidity was at its lowest during July and August, with a minimum value on the 31st of July (2.7 FNU at 5 m). An abrupt increase in turbidity was observed at a depth of 9 to 11 meters the 2nd of October.

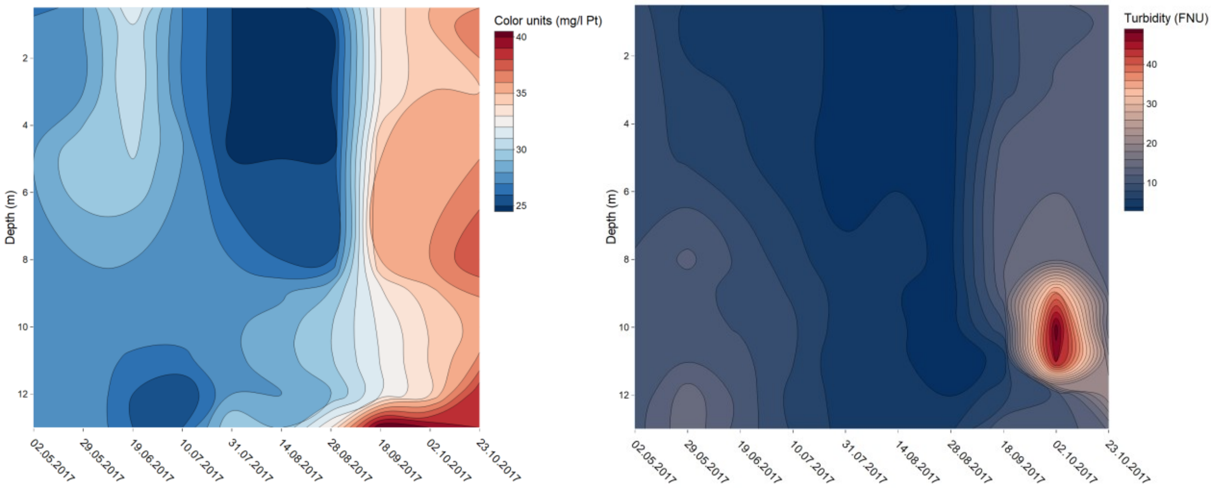

Figure 7 Time-depth isopleth diagram of color units (mg/l Pt) (left) and turbidity (FNU) (right) in lake Årungen from May to October 2017.

3.4.3 Organic material and chlorophyll a

Total organic and total dissolved carbon both showed a general tendency of increasing throughout the sampling season (Figure 9). TOC concentrations ranged from 5.8 to 7.8 mg/l and DOC concentrations ranged from 5.7 to 7.7 mg/l.

Chlorophyll a concentrations showed high time-depth variation, ranging from 1.3 to 29.1 µg/l (Figure 8). The highest concentrations were measured in the upper 3 meters at the 31st of July, coinciding with the high temperatures that was recorded in July (Figure 6). In August the concentration at 5 meters was between 15 and 20 µg/l, which corresponds with the euphotic depth at that point of time (Figure 4).

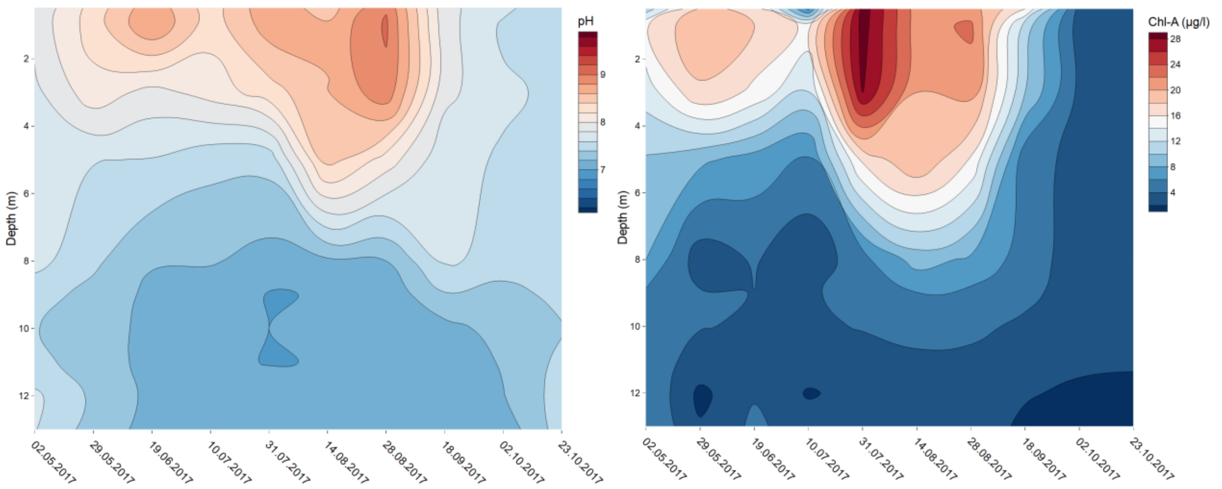

Figure 8 Time-depth isopleth diagram of pH (left) and chlorophyll A (µg/l) (right) in lake Årungen from May to October 2017.

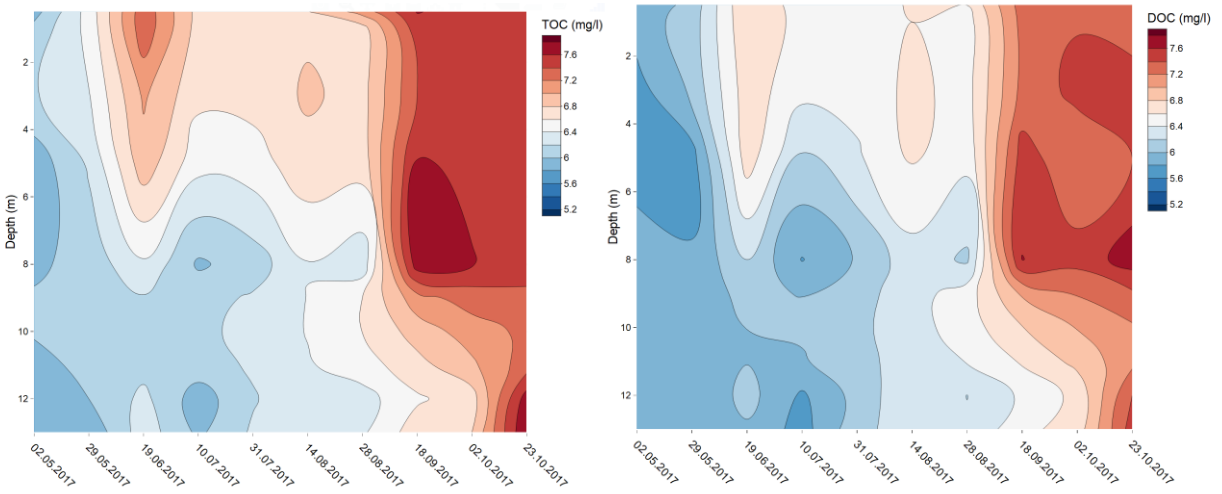

Figure 9 Time-depth isopleth diagram of total organic carbon (TOC, mg/l) (left) and total dissolved carbon (DOC, mg/l) (right) in lake Årungen from May to October 2017.

3.4.4 Nutrients

After the spring turnover the TP concentration in the lake ranged between 36 and 44 µg/l (Figure 10). There was a period with slightly lowered concentrations in the upper 9 meters of the water column during the duration of the stratified period. From late August onwards, the concentrations increased in the hypolimnion, peaking at 118 µg/l at 12 meters on the 2nd of October. Phosphate concentrations were in general low in the uppermost part of the water column during the stratification, and increasing with depth (Figure 11). The lowest concentrations were recorded in the epilimnion at the 10th and 31st of July (< 0.5 µg/l). Above the sediment the concentrations were fluctuating between 19 µg/l and 2.5 µg/l from May to

August. In late September and October there seemed to be a leaking of phosphate from the sediment, as the lake was still stratified. Concentrations above the sediment peaked at 47.5 µg/l on the 2nd of October.

As with TP, TN was relatively evenly distributed in the water column after the spring turnover, with concentrations fluctuating between 4.1 mg/l and 4.7 mg/l (Figure 10). The highest concentration measured was at 5 meters the 19th of July (5.8 mg/l). As the period of stratification advanced, concentrations decreased in the hypolimnion, with a minimum of 2.6 mg/l at the 2nd of October. Nitrate concentrations followed the same time-depth pattern as TN (Figure 11). After spring turnover, the concentrations ranged between 3.5 mg/l and 4 mg/l. Concentrations peaked at 5.1 mg/l at the same depth and date as TN. There was a declining trend in concentrations above the sediment throughout the stratified period, with the lowest concentration measured at the 2nd of October (1.4 mg/l). After the fall turnover, nitrate was once again evenly distributed in the whole water column, only varying by 0.3 mg/l.

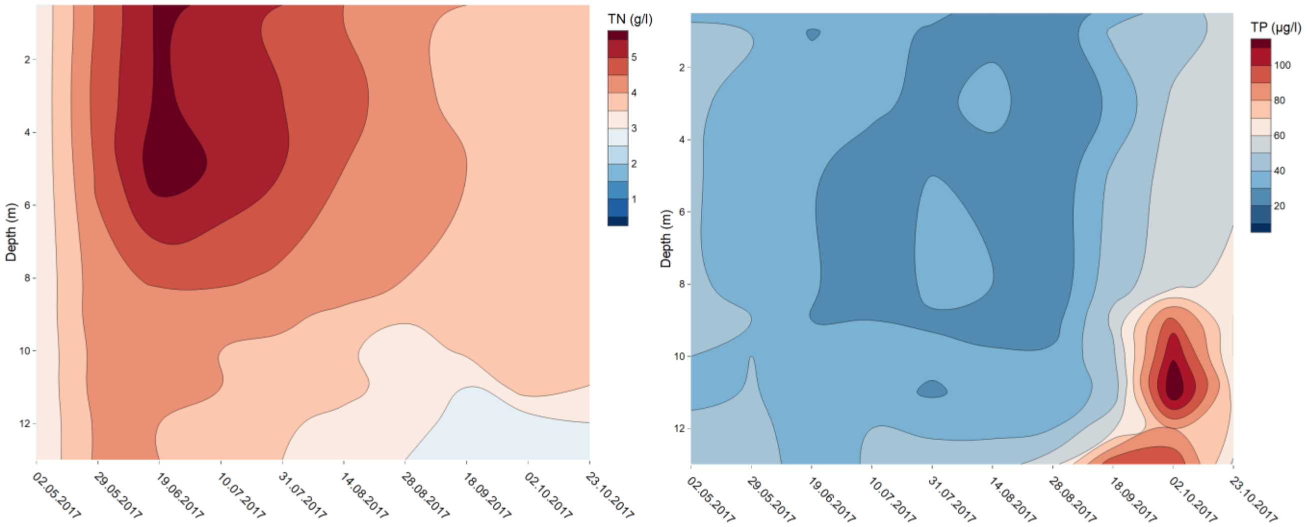

Figure 10 Time-depth isopleth diagram of total nitrogen (TN, left) and total phosphorous (TP, right) in lake Årungen from May to October 2017.

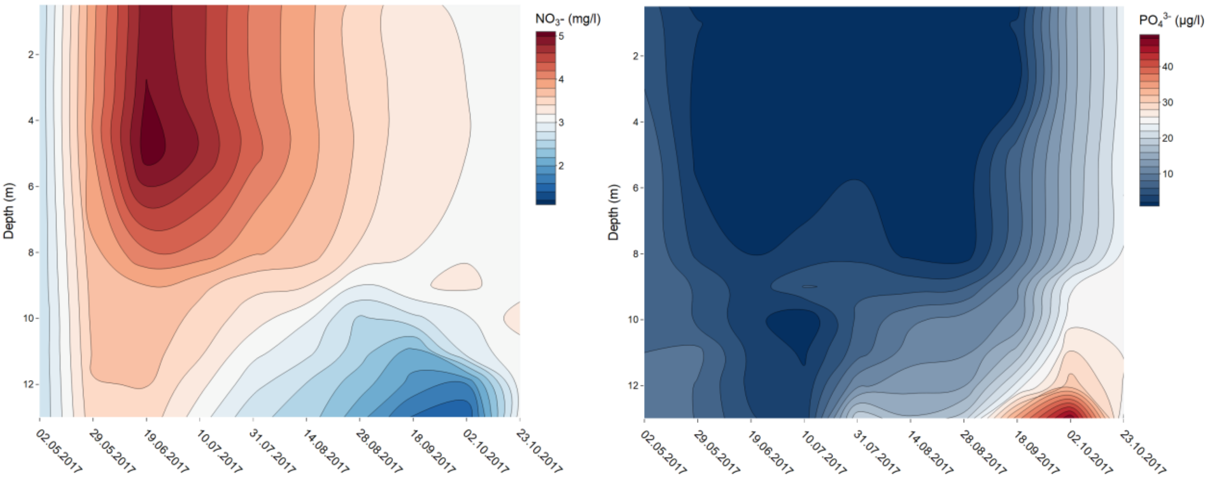

Figure 11 Time-depth isopleth diagram of nitrate (mg/l) (left) and phosphate (µg/l) (right) concentrations in lake Årungen from May to October 2017.

3.5 Comparisons of nitrate and phosphate above the sediment

Data from three years (2017, 2013, 2009) were used to examine the trends of nitrate (mg/l) and phosphate (µg/l) concentrations above the sediment. Based on previous findings on the coupling between nitrate concentrations in the hypolimnion and leaking of phosphate from the sediments (Andersen 1982; Tirén & Pettersson 1985; Wetzel 2001), an upper threshold level of 1 NO_3-N mg/l is used as a visual guide in the representation of these results.

In 2017 nitrate levels over the sediments were 2.6 mg/l before the spring turnover (2nd of May) and increased to 3.5 mg/l after the spring turnover (29th of May) (Figure 12). After the fall turnover the concentration was 3.1 mg/l. Phosphate concentrations were below 1 µg/l until mid-July (Figure 12). They increased until the beginning of October, peaking at 47.8 µg/l.

In 2013 the nitrate concentration had only a slight increase after the spring turnover (Figure 13). During the period of stratification it steadily declined, reaching a concentration less than 1 mg/l on the 1st of October. Phosphate concentrations were steady when nitrate concentrations were over 1 mg/l, but increased rapidly to over 400 µg/l on the 1st of October when nitrate levels went below the threshold of 1 mg/l (Figure 13).

In 2009 nitrate concentrations were at 1.1 mg/l in late-April, and it increased to 1.7 mg/l after the spring turnover (Figure 14). The concentrations decreased steadily during the stratification period, reaching levels under 1 mg/l on the 8th of July. Concentrations above the threshold level were not recorded again until the 11th of November. Concentrations of phosphate did not show an abrupt increase after nitrate concentration went below the threshold level of 1 mg/l. Instead there was a lag in the response of phosphate, differing from was seen in 2013. The concentrations slowly increased from the 22nd of July, peaking at 286.7 µg/l on the 30th of September (Figure 14). After the fall turnover the concentrations were below 15 µg/l.

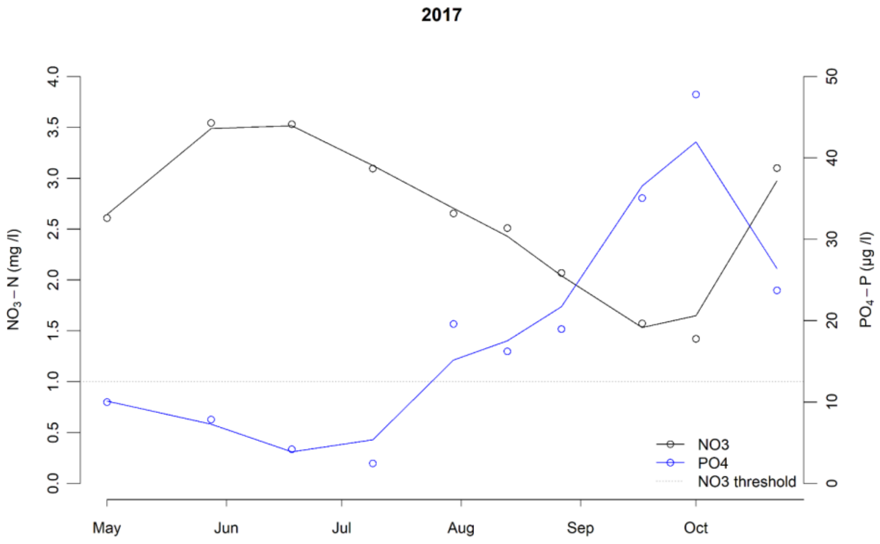

Figure 12 Nitrate (black) and phosphate (blue) at 13 meters in lake Årungen from May to October 2017.

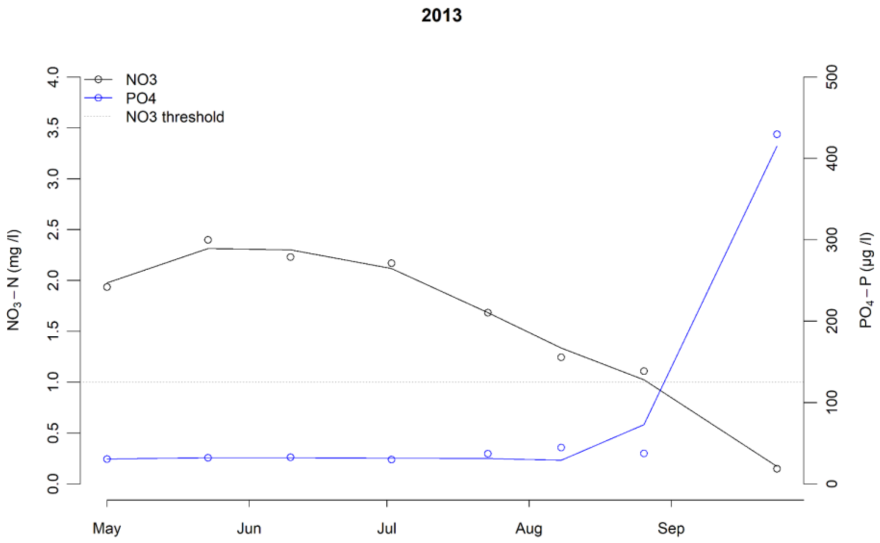

Figure 13 Nitrate (black) and phosphate (blue) at 13 meters in lake Årungen from May to October 2013.

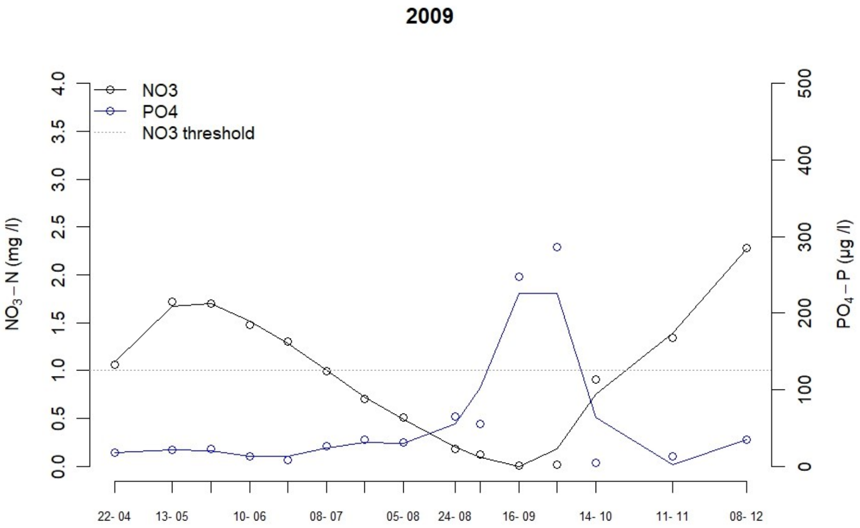

Figure 14 Nitrate (black) and phosphate (blue) at 13 meters in lake Årungen from April to December 2009.

4 Discussion

In the following section, the general conditions of Lake Årungen during the season of 2017 will be described before the discussion on the results according to the three stated hypotheses.

4.1 General conditions in Lake Årungen 2017

In general, the season of 2017 was atypical in terms of weather conditions. Air temperatures were mostly below normal values (1969-1990) (Figure 3), which may have contributed to lowered rates of primary production during the growth period. The catchment received large amounts of precipitation compared to normal values (1969-1990) (Figure 3), likely causing increased runoff into Lake Årungen. As seen in the results, the secchi depth never exceeded 2 meters during the sampling period (Figure 4), which can be explained by the increased input of matter through runoff from the catchment. Apart from a small increase in late May, primary production remained relatively low up until August (Figure 8). Temperature and oxygen measurements show that the lake was fully stratified in the beginning of July, with signs of anoxic conditions above the sediment (Figure 5). Following the onset of anoxic conditions in the hypolimnion, the results show that nitrate consumption in the hypolimnion increased until the fall turnover (Figure 11). The combination of the different conditions in 2017 are likely to have contributed to increased levels of nitrate in Lake Årungen, protecting the lake from internal phosphorus loading.

4.2 Coupling between nitrate and phosphate

Analyses on samples collected in this study establish a significant, negative correlation (-77) between nitrate and phosphorus (Appendix 1, figure A1). Time-depth isopleth diagrams show that during the period with a stable thermal stratification and high nitrate concentration (>2 mg/l) in the hypolimnion, the concentration of phosphate remained at a level below 20 μg/l (Figure 11). Signs of internal phosphorus loading appeared as nitrate concentrations dropped below 1.5 mg/l at 13 meters depth on the 18th of September (Figure 12). However, in 2017 the hypolimnion never reached levels of nitrate below the estimated upper threshold of 1 mg/l, despite oxygen levels being below the detection limit of 0 mg/l for approximately 114 days. Consequentially, a situation of extensive internal phosphorus loading never occurred.

The results from samples collected and analyzed in 2013 and 2009 supply further proof of the coupling between concentrations of nitrate and phosphorus. The development in Lake Årungen in both years demonstrate how internal phosphorus loading can be initiated in a situation with anoxic conditions and low levels of nitrate (< 1mg/l) in the hypolimnion. In 2013 there was a clear relationship between the two nutrients: phosphate concentrations above the sediment had an eleven-fold increase from the 2nd of September to the 1st of October as nitrate concentrations decreased from 1.1 mg/l to 0.2 mg/l, respectively (Figure 13). The response in 2009 was similar to that of 2013, yet a delay was observed in time from when nitrate concentrations fell below the estimated upper threshold to the peak in phosphate leakage (Figure 14). Nitrate concentrations above the sediment fell below 1mg/l on the 8th of August, and continued to decline until reaching the lowest measured value of 0.01 mg/l on the 16th of September. Simultaneously, signs of phosphate leakage from the sediment did not appear until nitrate concentrations fell below 0.5 mg/l.

These results coincide with previous findings on the coupling between nitrate concentrations and internal phosphorus loading in the hypolimnion (Andersen 1982; Boström & Pettersson 1982; Hemond & Lin 2010; Musolff et al. 2017). Through experimental addition of nitrate on collected sediment samples from seven Swedish lakes and the Hungarian lake Balaton, Bostrøm and Pettersson wanted to determine the differences in phosphorus release upon addition of nitrate of sediment from different lake types (Boström & Pettersson 1982). Though the aim of the study was not to quantify the relationship between nitrate concentrations and phosphorus release, it is nevertheless interesting that the addition of nitrate to the water above the sediment lead to improved redox conditions, thus preventing phosphorus release, in all lake types. Although there are similarities between the results from this study on Lake Årungen and the findings of Bostrøm and Petterson, attention must be brought to the discrepancy in methods. Whilst they performed analyses on water in direct contact with the sediment surface, analyses in this study were based on samples collected as close as possible to the sediment. The water collector was not allowed to fully descend to the sediment surface as the shape of the bottom weight could disturb the sediment surface, interfering with the sample. Hence, measurement of nitrate concentration above the sediment can deviate from the exact concentration that were in the lake. Results from 2017 show that there were signs of phosphate leaking from the sediment when nitrate concentrations were at 1.5 mg/l (Figure 12), but due to the imprecise sampling method this concentration could be lower right above the sediment. Musolff et al. discovered through analyses on long-term data from 110 mountainous streams leading into German drinking waters that changes in nitrate concentrations were linked to the release of dissolved iron and adsorbed compounds such as phosphate (Musolff et al. 2017). Declining nitrate concentrations were linked to strong positive trends of reduced iron and a significant increase in phosphorus. Evidence of how nitrate can suppress internal phosphorus loading were also made by Hemond and Lin on their study of the dimictic Upper Mystic Lake (Hemond & Lin 2010).

4.3 Nitrates ability to buffer leaking of phosphate from the sediment

Measurements from the lake in all three years showed a correlation between the depletion of nitrate and the release of phosphorus in the hypolimnion: depths where nitrate concentrations approached zero were predictors of the depths of phosphate increase (Figure 12, 13 and 14). Regarding this study, the findings of Andersen from 1981 mentioned in the introduction chapter is of particular interest. Detailed description of two of the 31 lakes that were investigated (Knud Sø and Fussing Sø) show that there was a significant release of phosphorus from the sediments as nitrate concentrations were below 1 mg/l several meters above the sediment (Andersen 1982). It is therefore plausible to assume that the nitrate concentrations above the sediment surface were relatively lower, perhaps close to zero, resulting in a very low redox potential. Results from the study on Lake Årungen indicate that the onset of phosphorous release from the sediment coincides with approximately 1 mg/l in 2013 and 0.5 mg/l in 2009 (Figure 13 and 14). There was no leakage of phosphorous from the sediments in 2017 when nitrate concentrations in the hypolimnion remained above 1 mg/l (lowest reading was 1.4 mg/l on the 2nd of October). The nitrate concentration at which phosphorus start leaking from the sediment varies from 0.5 mg/l to 1 mg/l, suggesting that an assumed threshold of 1 NO_3-N mg/l is fitting, although a rough upper estimate.

As conditions become anoxic, nitrate is the preferred oxidation agent in microbial decomposition processes. Concentration of nitrate in the hypolimnion at the onset of anoxic conditions during the summer stratification is an important factor that influences the potential of internal phosphorus loading. In 2017, the decomposition rate of nitrate above the sediment during anoxic conditions was 0.02 mg/l a day (Appendix 2, figure A2). Hence, nitrate consumption did not exceed the amount of available nitrate, as the initial nitrate concentration at 13 meters depth at the onset of anoxic conditions were approximately 3 mg/l. Interestingly, in 2013 the decomposition rate of nitrate was identical to that in 2017, but the start concentration of nitrate differed (Appendix 2, figure A3). Having an initial nitrate concentration of only 1.7 mg/l, the rate of consumption was sufficient in depleting nitrate concentrations to a level below 0.2 mg/l within the fall turnover. In 2009, the decomposition rate of nitrate during the period of anoxic conditions was lower compared to 2017 and 2013, being only 0.01 mg/l a day (Appendix 2, figure A4). However, with a start concentration of nitrate at 1.3 mg/l, nitrate levels above the sediment were depleted within mid-September. These findings suggest that input of nitrate from the catchment is not always sufficient in protecting the lake from internal loading of phosphorus.

The year-to-year variation in lake dynamics in Lake Årungen are likely to affect the nitrate concentration in the hypolimnion at the onset of anoxic conditions. Identifying these factors, and to which extent they affect this process, can aid our understanding on the onset and duration of internal phosphorus loading.

The onset and duration of the thermal stratification is highly influenced by weather conditions. As previously mentioned, the season of 2017 can be characterized by low temperatures and increased precipitation compared to normal values (1969-1990) (Figure 3). The month of May was slightly warmer (0.8 °C), which probably aided in the onset of a thermal stratification though rapid warming of the upper water column. In late May the lake showed signs of thermal stratification, and on the 10th of July it was fully stratified with a thermal gradient of over 5 °C between 5 and 8 meters (Figure 5). The average temperature in the hypolimnion was at approximately 9 °C from late May and throughout the growth season, indicating that there was limited mixing between deep and shallow water. Anomalies in temperature and oxygen measurements were observed at 12 meters depth on the 18th of September. It is believed that this can be explained by certain qualities, i.e. temperature and density, in the runoff that produced a layer at 12 meters with heightened oxygen concentrations (Figure 5 and 6). In both 2013 and 2009 the temperature average in May were 1.8 °C and 0.8 °C warmer, respectively (Appendix 3, figure A5 and A6). As with 2017, this can have caused a rapid establishment of the thermal stratification. The increased temperature that was observed in May for all years is believed to have positively affected the primary production. Analyses on chlorophyll a, pH and oxygen saturation from 2017 coincide with the elevated temperature values in May (Figure 6 and 8). It is presumed that a similar situation occurred in both 2013 and 2009. Establishment of the thermal stratification lake Årungen causes isolation of the hypolimnion. When this process is initiated early in the season, the potential of nitrate depletion and internal phosphorus loading increases.

Except for July, all months had periods with increased precipitation in 2017. Receiving under 50 % of mean precipitation, July was the only month with lowered precipitation values. Precipitation patterns in 2013 and 2009 years were fluctuating a lot compared to normal values (Appendix 3, figure A5 and A6). The trends for 2013 and 2009 are quite the opposite of one another. In 2013, lake Årungen received a lot of precipitation in May and June (> 100% increase), whilst June was unusually dry, receiving less than 20% of normal precipitation. Precipitation in 2009 were below the normal values in May and June, but the lake received almost 100% more in July and August.

Precipitation in the catchment, followed by increased runoff, is a factor that contributes to nutrient loading in a lake. Since being surrounded by agricultural land, Lake Årungen is sensitive to fluctuations in nutrient loading caused by year-to-year variations in precipitation (Romarheim et al. 2015). Large amounts of soil bound nitrate and phosphorus can be mobilized upon events of increased precipitation and surface runoff in the catchment (Wetzel 2001). With increased nutrient loading, particularly nitrogen and phosphorus, primary production can remain at a high level, assuming that potentially limiting factors such as light and temperature remains at a sufficient level for photosynthesis. In addition to nutrient loading, surface runoff caused by precipitation events in the catchment also carry organic and inorganic matter. Riise et al. stated in a study from 2013 that Lake Årungen has had a yearly mean sedimentation rate of 7.5 mm since 1986 (Riise et al. 2013), meaning that a large amount of autochthonous and allochthonous matter sediments to the bottom. This is one of several factors that contributes to the microbial decomposition in the hypolimnion, which eventually can cause hypolimnetic anoxia and internal phosphorus loading. In 2013, the combination of increased air temperature and high amount of precipitation may explain the low nitrate concentrations in the hypolimnion. A warm climate during spring can promote terrestrial plant growth, resulting in a high plant nitrogen uptake, whilst extreme precipitation events can act as a diluting agent in the lake. In 2009, the reduced precipitation received by the catchment in May and June can have caused a low input of nitrate to the lake, resulting in a low nitrate concentration in the hypolimnion as the lake became stratified.

Temperature and oxygen are two important factors governing several processes that can lead up to a situation of internal phosphorus loading in a lake. Increased temperature in the hypolimnion can stimulate the microbial activity in and above the sediment. This can lower the redox potential though utilization of nitrate as an electron donor, thus inducing mobilization of iron-bound phosphate. Jensen and Andersen discovered that temperature alone explained over 70% of the seasonal variation in internal phosphorus loading (Jensen & Andersen 1992). In a more recent study by Solim and Wanganeo, temperature in the hypolimnion had a significant correlation with increased phosphorus concentrations in the hypolimnion (Solim & Wanganeo 2009). However, in this study, the results on monthly temperature averages in the hypolimnion for all three years do not seem to explain the discrepancy in nitrate consumption rates or the amount of phosphate released from the sediment (Appendix 4, table A1). The highest average temperature measured in lake Årungen during these three years was 11.5 °C at 13 meters depth in September 2017. Average temperatures of the whole season in the hypolimnion did not exceed 10 °C in 2017, 2013 and 2009. In a study on Lake Esrom, Kamp-Nielsen observed that there was no significant increase in release of phosphorus as temperatures remained below 10 °C (Kamp-Nielsen 1975). This can explain the limited effect of temperature on nitrate consumption and phosphate release in this study.

4.4 The effect of a reduction in nitrate input

The findings on nitrate consumption rate and its coupling with internal phosphorus loading imply that, in a management perspective, it is important to acknowledge the role of nitrate in protecting Lake Årungen from internal phosphorus loading. Knowledge about the input of nitrate from the catchment and the rate of nitrate decomposition in the hypolimnion can be valuable tools in the assessment of future mitigation efforts in Lake Årungen. The estimated nitrate decomposition rate in 2017, 2013 and 2009 was 0.02, 0.02 and 0.01 mg/l a day, respectively (Appendix 2, figure A2, A3 and A4). In 2017 and 2013, the decomposition of nitrate appears as a linear process with a constant rate of 0.02 mg/l a day. As with 2017 and 2013, the estimation of the decomposition rate in 2009 is based on the period when there is a stable thermal stratification and the hypolimnion is anoxic. However, the results from 2009 show that the rate of decomposition decreased as nitrate levels above the sediment fell below 0.2 mg/l (Appendix 2, figure A3). A simple linear regression may therefore not have been a suitable model in assessing the true rate of nitrate decomposition that year, and it is likely that the rate was greater than 0.01 mg/l a day up until nitrate concentrations fell below 0.2 mg/l.

Until further studies are carried out, the decomposition rate of nitrate in 2017 and 2013 can be used as a general estimate on the lakes ability to consume nitrate in the hypolimnion during anoxic conditions. In 2017 the input of nitrate from the catchment was sufficient in protecting the lake from internal phosphorus loading as it exceeded the consumption of nitrate in the hypolimnion during the thermal stratification. How will a reduction in the nitrate input to Lake Årungen affect the protective function of nitrate? In 2017, if the input of nitrate was to be reduced by 50%, the start concentration of nitrate above the sediment at the onset of anoxic conditions in the hypolimnion would be 1.5 mg/l. With a decomposition rate of 0.02 mg NO_3^- /l a day, the water above the sediment would be depleted of nitrate in late September. In this scenario, large amounts of phosphate could potentially leak from the sediment before the fall turnover in mid-October. The elevated levels of phosphate that would appear in a situation like this can cause the outbreak of algal blooms in the following growth season, as has been the case earlier.

Although the results indicate that levels of nitrate should not be reduced in Lake Årungen, it is important to keep in mind that elevated levels of nitrate can have several detrimental effects in the lake, as well as the marine environment of Bunnefjorden. If being a limiting factor in the primary production in Lake Årungen, increased concentrations of nitrate can contribute to eutrophication of the lake. However, according to a recent report from PURA (2016), nitrogen concentrations in Lake Årungen are high, thus not limiting primary production (pura.no 2016). Being in direct connection with Bunnefjorden, the nitrate concentration in Lake Årungen can also have unwanted effects on the coastal marine environment. It is today a widespread agreement that nitrogen is one of the primary limiting factors in marine environments (Herbert 1999). In light of this, caution should be taken against restoration measures that focus on direct input of nitrate compounds in the lake, such as the "Riplox-method" (Ripl 1976). As observed in 2017, Lake Årungen has the ability to self-regulate the leaking of phosphate from the sediment with sufficient input of nitrate from the catchment. Focus should therefore be directed towards a management that take into account how a reduction in nutrient input from agriculture and urban activity affects Lake Årungen's ability to avoid phosphate leakage from the sediment. I.e. the positive effects of decreased nitrate levels must be balanced against increased risk of internal phosphorus loading.

The processes affecting the input of nitrate into Lake Årungen and the nitrate decomposition rate in the hypolimnion are complex. Multiple factors such as climate, activities in the catchment, primary production, and temperature in the hypolimnion all contribute to the variation in nitrate input and consumption in the hypolimnion. It is recognized that climatic conditions are highly influential upon the sediment's role of being a source of phosphorus in Lake Årungen (Riise et al. 2010a). With milder winters and periods with more intense precipitation, future climate changes are expected to cause implications in the management of Lake Årungen. It is beyond the scope of this study to identify the specific factors, and to which extent they have a significant effect on the levels of nitrate in Lake Årungen. Further research into how different factors affect the nitrate dynamics in Lake Årungen and its catchment is necessary and will be of great value in the process of finding appropriate mitigation measures in this lake.

5 Conclusion

The findings in this study show that there is a coupling between nitrate and phosphorus in Lake Årungen. It is apparent that nitrate concentrations in the hypolimnion have a direct influence on the leakage of phosphate from the sediment. In 2017, high concentrations of nitrate in the hypolimnion protected the lake from internal phosphorus loading. In 2013 and 2009, there was extensive leakage of phosphate from the sediment in the situation of anoxic conditions with low nitrate concentrations in the hypolimnion.

Establishing a relationship between the concentration of nitrate in the hypolimnion and internal loading of phosphate is a key factor in mediating the potential detrimental effects of eutrophication in Lake Årungen. Based on results from this study, attention should be focused on the start concentration of nitrate above the sediment at the onset of anoxic conditions in the hypolimnion. One should be cautious against measures that can potentially decrease the external input of nitrate to Lake Årungen, as this can, under given conditions, initiate internal phosphorus loading. This could lead to a situation where it becomes more difficult to control the algal blooms through measures in the catchment. This study did not aim at explaining how nitrate input and nitrate decomposition rate in the hypolimnion are affected by different factors. The discrepancy in start concentration of nitrate and nitrate decomposition rate in the hypolimnion during anoxic in 2017, 2013 and 2009 could not be explained by any of the investigated factors. Future studies are therefore required to address this connection in order to develop our understanding of this complex process.

6 Literature

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7 Appendices

Appendix 1 – Correlation matrix

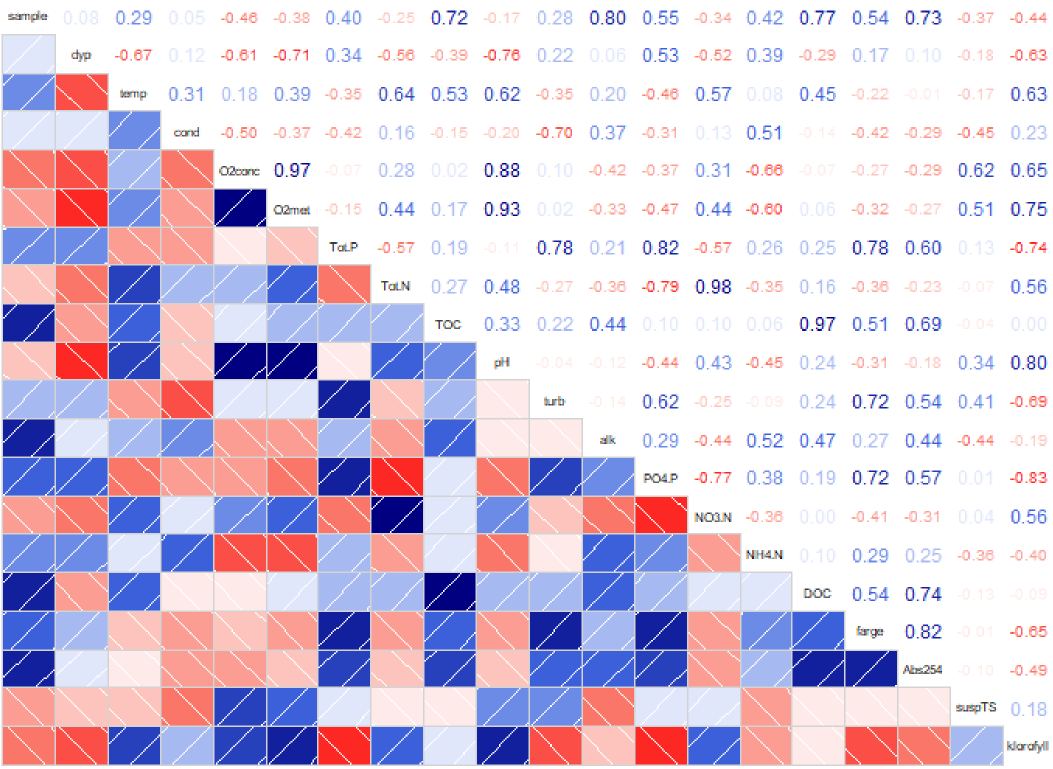


Figure A1 Correlation matrix with correlation values for all parameters that were measured from samples collected in lake Årungen in 2017. The correlation coefficient for nitrate (NO_3-N) and phosphate (PO_4-P) has a significant p-value of < 0.05.

Appendix 2 – Nitrate decomposition rate

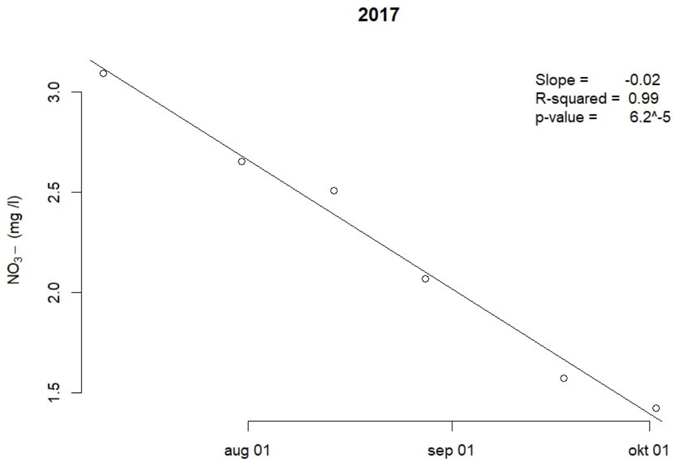


Figure A2 Nitrate decomposition rate (mg/l day) at 13 meters depth during the period with thermal stratification and anoxic conditions in the hypolimnion during 2017. Rate parameters are based upon simple linear regression on data collected in 2017.

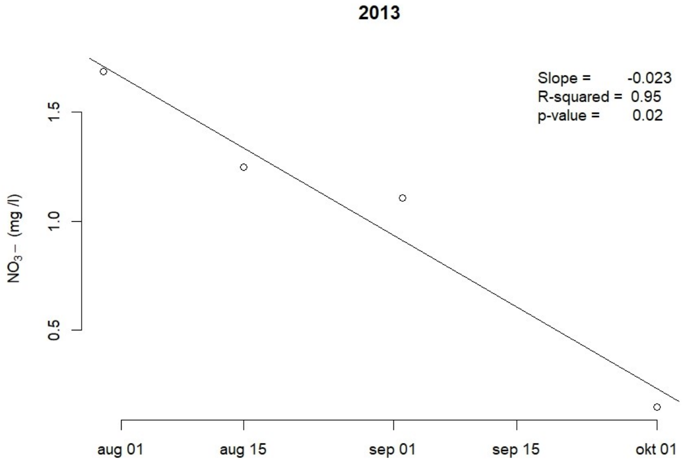


Figure A3 Nitrate decomposition rate (mg/l day) at 13 meters depth during the period with thermal stratification and anoxic conditions in the hypolimnion during 2013. Rate parameters are based upon simple linear regression on data collected in 2013.

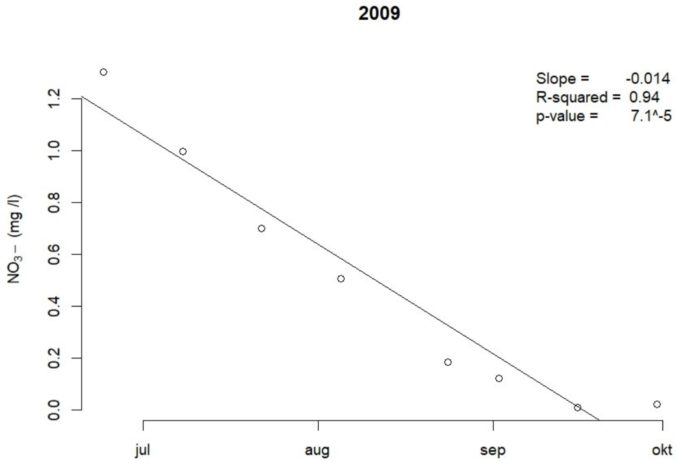


Figure A4 Nitrate decomposition rate (mg/l day) at 13 meters depth during the period with thermal stratification and anoxic conditions in the hypolimnion during 2009. Rate parameters are based upon simple linear regression on data collected in 2009.

Appendix 3 – Climate data for 2013 and 2009

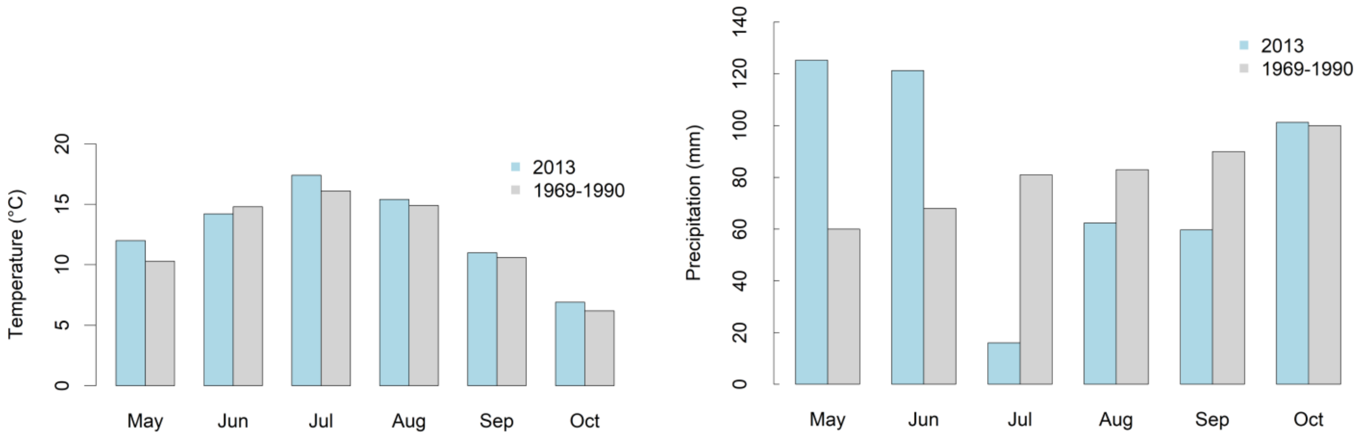


Figure A5 Mean temperature (left) and mean precipitation (right) measurements at the BIOKLIM field station in Sørås (NMBU 2013). Blue bars show mean values for 2013, grey bars show mean values for the 1969-1990 period.

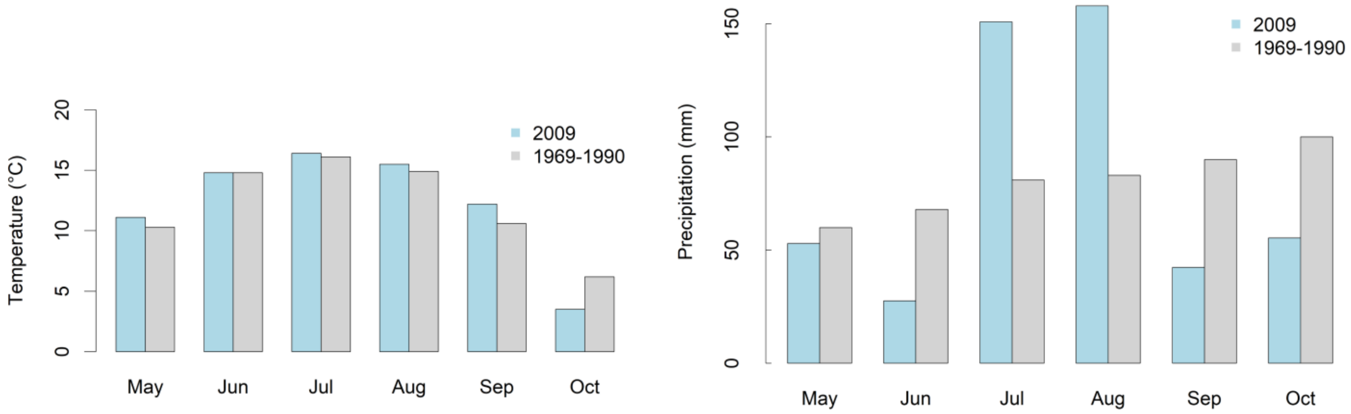


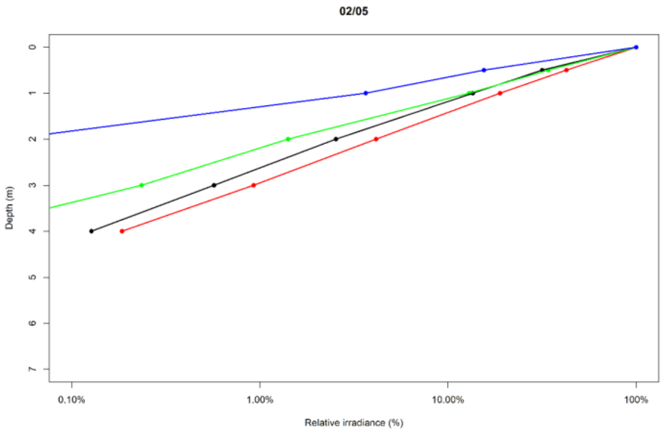
Figure A6 Mean temperature (left) and mean precipitation (right) measurements at the BIOKLIM field station in Sørås (NMBU 2017). Blue bars show mean values for 2009, grey bars show mean values for the 1969-1990 period.

Appendix 4 – Temperature data in the hypolimnion

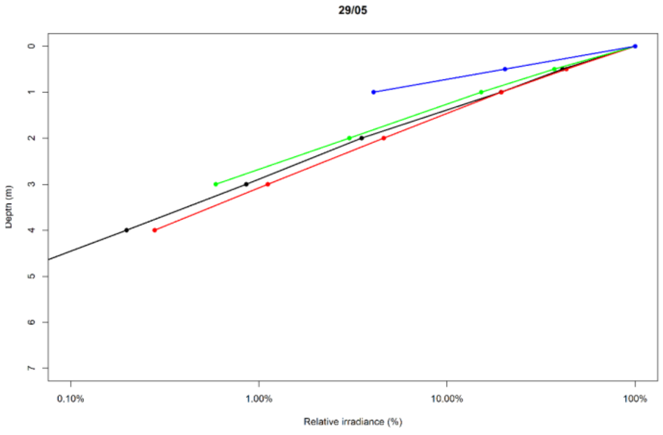
Table A1 Mean temperature (℃) in the hypolimnion (8-13 meters) and mean temperature (℃) above the sediment surface (13 meters) for May to October in 2017, 2013 and 2009. Mean temperature values for the whole period are also calculated for each year.

	Temperature 8m-13m (°C)			Temperature 13m (°C)		
Period	2017	2013	2009	2017	2013	2009
May	7.4	7.0	7.5	7.2	6.7	7.0
Jun	8.9	8.0	8.3	8.3	7.7	7.7
Jul	9.4	8.7	8.6	8.6	8.0	7.9
Aug	10.0	8.8	9.2	9.0	8.1	8.2
Sep	11.2	9.6	10.8	11.5	8.5	8.9
Oct	10.4	9.8	9.5	9.3	8.2	9.5
Whole period	10.0	8.7	9.0	9	7.9	8.2

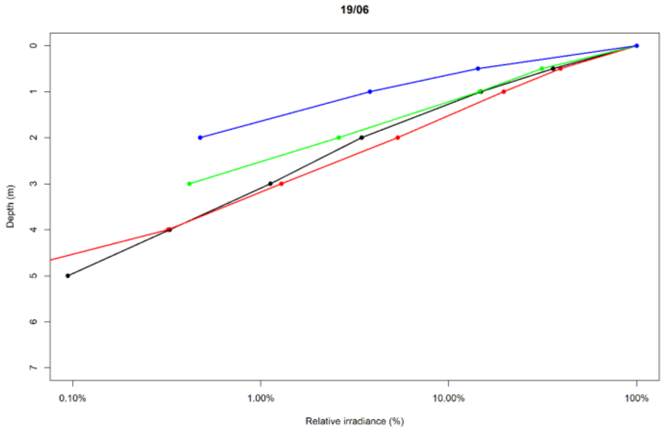
Appendix 5 – Light characteristics



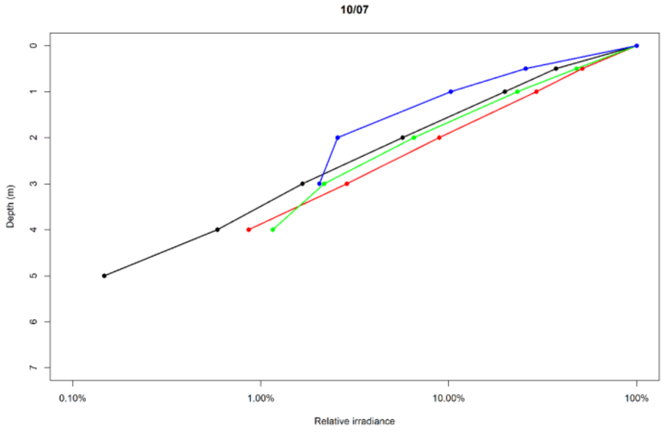
02/05



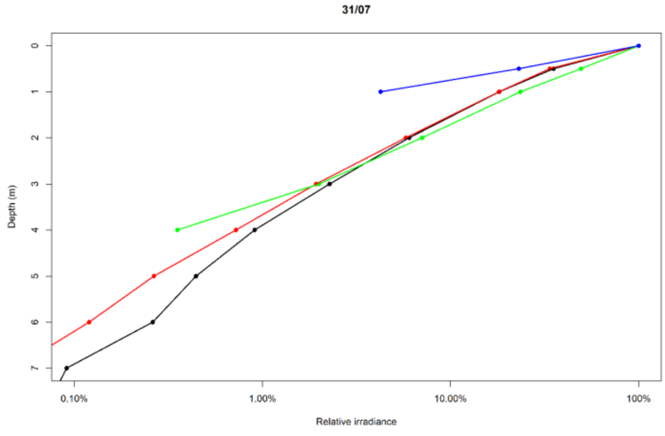
29/05



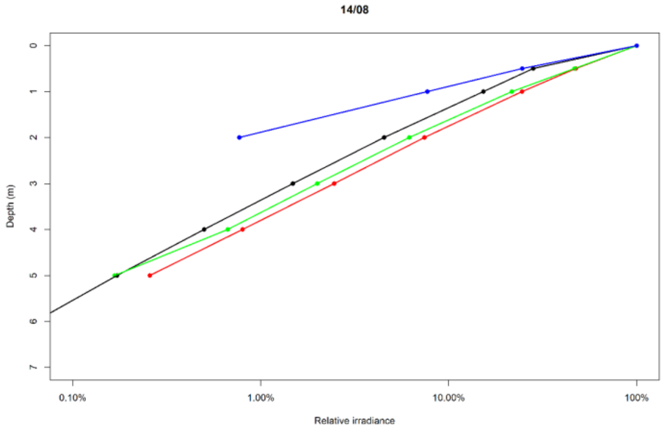
19/06



10/07



31/07



14/08

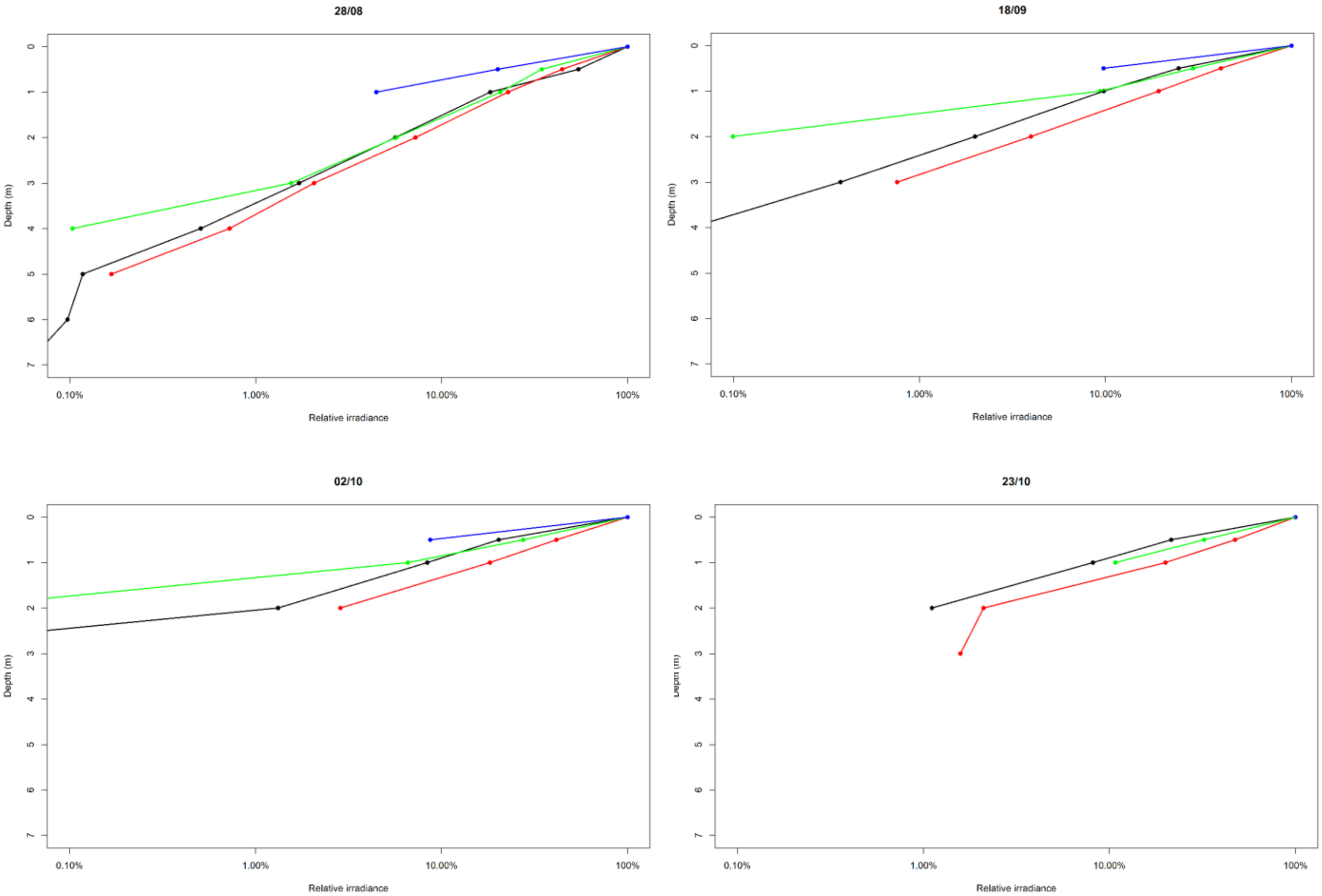


Figure A7 Relative irradiance (x-axis) of PAR (black line), green (green line), red (red line) and blue light (blue line), measured for each depth down to 1 % relative irradiance in lake Årungen. The relative irradiance is presented on a logarithmic scale for each series.

Appendix 6 – Data from in-situ measurements and laboratory analyses on lake Årungen in 2017

Sample	Depth	Date	Temp (°C)	Cond (µS/cm)	O_2 (mg/l)	O_2 (%)	TP (µg/l)	TN (mg/l)	TOC (mg/l)	pH	Turb (FNU)	Alk (mmol/l)	PO4-P (µg/l)	NO3-N (mg/l)	NH4-N (mg/l)	DOC (mg/l)	Color	Abs254	suspTS (mg/l)	Chla
1	0.5	02.05.2017	8.5	264	13.8	111.5	37	3.10	5.92	7.84	8.8	967.44	5	2.62	0.008	5.83	26	0.190	5.5	10.9
2	1	02.05.2017	8	265	13.05	109.2	43	3.10	6.06	7.87	9.4	1011.45	5	2.63	0.008	5.89	28	0.193	6.5	15.8
3	3	02.05.2017	6.9	265	12.23	99.4	42	3.10	6.18	7.75	9.6	989.00	6	2.65	0.008	5.72	27	0.192	7.1	12.9
4	5	02.05.2017	6.6	265	11.83	95.3	41	3.10	5.88	7.70	9.2	983.61	8	2.63	0.010	5.67	28	0.194	6.5	9.8
5	8	02.05.2017	6.4	265	11.64	93.7	41	3.10	5.96	7.67	10.1	988.10	8	2.63	0.011	5.94	27	0.192	6.3	8.0
8	9	02.05.2017	6.3	266	11.59	92.6	42	3.10					8	2.63	0.012					
9	10	02.05.2017	6.3	266	11.48	91.9	40	3.10					8	2.60	0.012					
10	11	02.05.2017	6.3	266	11.47	91.7	36	3.10					8	2.62	0.014					
6	12	02.05.2017	6.2	266	11.38	91.1	44	3.10	5.81	7.64	10.4	973.73	10	2.61	0.014	5.94	27	0.193	7.9	6.0
7	13	02.05.2017	6.2	267	11.28	89.8	45	3.10	6.00	7.61	11.2	968.34	10	2.61	0.014	5.95	28	0.194	8.3	6.0
11	0.5	29.05.2017	16.4	276	11.45	118.3	36	4.60	6.48	8.28	5.7	993.49	1.43	3.94	0.017	6.07	28	0.195	8.3	18.4
12	1	29.05.2017	16.2	276	11.46	117.5	41	4.60	6.46	8.30	5.3	985.40	2.14	3.95	0.017	6.10	28	0.197	8.5	19.8
13	3	29.05.2017	15.5	277	10.94	111.1	36	4.70	6.39	8.12	6.6	980.91	1.43	3.98	0.018	6.05	28	0.196	8.5	17.6
14	5	29.05.2017	11.5	277	9.59	88.7	36	4.60	6.23	7.61	7.6	989.90	1.43	3.97	0.030	5.72	30	0.196	8.5	8.5
15	8	29.05.2017	9	276	8.84	77.5	38	4.30	6.08	7.44	12.5	977.32	3.56	3.76	0.026	5.82	28	0.196	9.3	2.9
18	9	29.05.2017	8.7	275	8.52	74	40	4.30					5.70	3.70	0.023					
19	10	29.05.2017	8.5	275	8.38	72.4	40	4.20					5.70	3.67	0.024					
20	11	29.05.2017	8.4	275	8.13	70	41	4.20					8.55	3.63	0.024					
16	12	29.05.2017	8.3	275	7.91	68.2	43	4.10	6.00	7.36	15.1	978.22	7.84	3.59	0.026	5.80	28	0.193	9.9	1.5
17	13	29.05.2017	8.2	275	7.74	66.5	44	4.10	5.84	7.31	15.4	987.20	7.84	3.54	0.029	5.81	28	0.196	10.1	2.2
21	0.5	19.06.2017	19.4	277	11.46	124.6	37	5.60	7.33	8.74	5.4	994.39	0.49	4.93	0.009	6.79	32	0.211	4.4	17.6
22	1	19.06.2017	19.4	277	11.46	124.6	29	5.60	7.33	8.79	5.4	990.79	0.49	4.93	0.008	6.77	31	0.211	4.2	18.0
23	3	19.06.2017	16.4	280	9.36	96.1	37	5.60	7.03	7.93	5.8	990.79	0.49	5.01	0.024	6.71	31	0.222	4.2	15.5
24	5	19.06.2017	14	280	7.53	73.3	31	5.80	6.92	7.59	6.3	966.54	1.23	5.11	0.051	6.70	30	0.211	3.6	7.1
25	8	19.06.2017	9.6	277	5.95	52.4	31	4.60	6.37	7.22	9.5	970.14	1.98	4.17	0.014	6.20	28	0.202	4.4	4.2
28	9	19.06.2017	9.1	276	5.5	47.9	30	4.20		7.15	9.3		2.72	3.80	0.006					
29	10	19.06.2017	9	276	5.43	47.6	32	4.20		7.14	9.8		2.72	3.79	0.011					
30	11	19.06.2017	8.6	277	4.64	40.5	34	4.20		7.13	10.6		3.46	3.69	0.009					
26	12	19.06.2017	8.6	277	4.45	38.4	35	4.00	6.25	7.15	11.3	1006.47	3.46	3.61	0.014	6.07	26	0.206	5.8	3.8
27	13	19.06.2017	8.3	278	2.89	24.5	36	4.00	6.31	7.13	11.2	1012.35	4.20	3.53	0.020	5.97	26	0.192	6.0	4.4
31	0.5	10.07.2017	19.7	286	8.94	98.6	32	5.40	6.73	8.30	5.1	1048.26	0.24	4.66	0.037	6.50	27	0.192	4.0	5.5

Sample	Depth	Date	Temp (°C)	Cond (µS/cm)	O_2 (mg/l)	O_2 (%)	TP (µg/l)	TN (mg/l)	TOC (mg/l)	pH	Turb (FNU)	Alk (mmol/l)	PO4-P (µg/l)	NO3-N (mg/l)	NH4-N (mg/l)	DOC (mg/l)	Color	Abs254	suspTS (mg/l)	Chla
32	1	10.07.2017	19.7	286	8.94	98.6	36	5.20	6.72	8.29	5.1	1030.31	0.98	4.66	0.035	6.53	27	0.195	3.6	15.5
33	3	10.07.2017	19.3	286	8.42	92.1	32	5.20	6.65	8.08	5.3	1054.10	0.24	4.67	0.039	6.46	27	0.207	3.8	11.6
34	5	10.07.2017	17.4	285	5.17	54.5	25	5.40	6.47	7.46	5.0	1018.18	0.98	4.78	0.036	6.18	28	0.196	3.2	5.8
35	8	10.07.2017	10.5	278	3.42	31	24	4.60	5.97	7.22	6.7	994.39	2.45	4.12	0.012	5.79	28	0.190	2.6	2.5
38	9	10.07.2017	9.4	277	2.68	23.4	30	4.20		7.08	7.8	1004.26	6.12	3.66	0.013					
39	10	10.07.2017	9	278	1.93	16.8	32	4.00		7.05	8.3	1006.96	0.24	3.52	0.013					
40	11	10.07.2017	8.7	278	1.27	11	33	4.00		7.05	8.1	1011.45	1.71	3.44	0.010					
36	12	10.07.2017	8.5	280	0.05	0.5	40	3.80	5.90	7.05	7.3	1042.88	2.45	3.26	0.019	5.77	25	0.196	3.4	1.8
37	13	10.07.2017	8.4	281	0	0	41	3.60	5.96	7.06	7.7	1055.45	2.45	3.09	0.046	5.72	26	0.184	3.6	2.9
41	0.5	31.07.2017	19.3	288	9.15	100.6	33	5.00	6.67	8.75	3.1	1098.54	-0.24	4.16	0.029	6.40	25	0.179	4.8	29.1
42	1	31.07.2017	19.3	288	9.14	100.4	28	4.90	6.78	8.70	3.2	1069.81	0.49	4.15	0.029	6.58	25	0.184	4.6	28.9
43	3	31.07.2017	19	288	8.6	94.2	27	5.00	6.67	8.31	3.0	1087.76	-0.24	4.17	0.040	6.47	25	0.196	4.0	28.0
44	5	31.07.2017	16.9	287	3	31.3	30	5.00	6.51	7.47	2.7	1074.30	-0.24	4.27	0.089	6.37	25	0.185	2.8	16.5
45	8	31.07.2017	11.4	280	0.42	4	32	4.40	6.10	7.12	4.5	1034.80	3.43	3.83	0.033	6.02	27	0.188	1.0	5.3
48	9	31.07.2017	10.2	280	0.17	1.7	29	4.10		6.99	5.0		5.63	3.45	0.025					
49	10	31.07.2017	9.4	281	0.03	0.2	32	3.90		7.00	4.8		6.37	3.30	0.043					
50	11	31.07.2017	9.2	282	0	0	29	3.70		6.99	4.1		7.10	3.06	0.068					
46	12	31.07.2017	8.9	286	0	0	36	3.60	6.18	7.09	5.2	1110.65	11.51	2.87	0.137	6.07	28	0.192	3.0	2.7
47	13	31.07.2017	8.7	288	0	0	50	3.50	6.23	7.11	5.3	1153.29	19.60	2.65	0.218	6.13	30	0.215	3.6	2.9
51	0.5	14.08.2017	18.4	284	9.74	103.6	24	4.50	6.79	8.50	4.1	1101.68	0.74	3.86	0.012	6.64	24	0.192	5.4	21.1
52	1	14.08.2017	18.3	284	9.76	103.5	27	4.50	6.77	8.63	3.8	1090.46	0.74	3.86	0.010	6.60	25	0.194	5.0	21.1
53	3	14.08.2017	18.2	284	9.36	99	34	4.70	6.83	8.59	3.9	1061.28	1.48	3.85	0.012	6.65	25	0.198	4.6	20.0
54	5	14.08.2017	18.1	285	9.33	98.5	24	4.50	6.73	8.50	3.7	1072.05	0.74	3.87	0.016	6.63	25	0.194	4.0	20.0
55	8	14.08.2017	11.8	282	0.04	0.4	30	4.30	6.39	7.16	4.6	1072.50	1.48	3.71	0.061	6.32	26	0.197	3.8	8.9
58	9	14.08.2017	10.3	281	0	0	27	3.90		7.01	4.1		5.17	3.41	0.056					
59	10	14.08.2017	9.6	282	0	0	31	3.60		7.02	4.2		9.59	3.03	0.108					
60	11	14.08.2017	9.3	284	0	0	33	3.70		7.01	4.3		11.07	2.86	0.149					
56	12	14.08.2017	9	286	0	0	38	3.30	6.37	7.12	4.8	1165.85	13.28	2.59	0.242	6.37	28	0.209	2.8	3.3
57	13	14.08.2017	8.9	288	0	0	45	3.30	6.40	7.11	5.1	1180.21	16.24	2.51	0.273	6.32	29	0.208	2.6	3.3
61	0.5	28.08.2017	17.7	282	11.63	122.6	21	4.20	7.08	8.98	3.6	1145.21	0.73	3.51	0.008	6.60	26	0.193	4.8	20.9
62	1	28.08.2017	17.7	282	11.63	122.6	21	4.20	6.72	9.03	3.3	1143.86	0.73	3.47	0.007	6.51	25	0.199	4.4	22.4
63	3	28.08.2017	17.5	283	10.67	113	21	4.20	6.73	8.94	3.3	1124.57	0.73	3.52	0.010	6.51	25	0.200	4.4	20.9
64	5	28.08.2017	17.1	286	7.73	80.6	22	4.20	6.69	8.11	3.1	1120.98	0.00	3.56	0.045	6.45	25	0.193	3.2	15.8
65	8	28.08.2017	13.3	284	0	0	22	4.00	6.27	7.20	3.5	1123.67	0.73	3.37	0.102	6.16	26	0.203	2.4	7.6
68	9	28.08.2017	10.9	284	0	0	26	3.60		7.06	2.9		5.83	3.00	0.141					

Sample	Depth	Date	Temp (°C)	Cond (µS/cm)	O2 (mg/l)	O2 (%)	TP (µg/l)	TN (mg/l)	TOC (mg/l)	pH	Turb (FNU)	Alk (mmol/l)	PO4-P (µg/l)	NO3-N (mg/l)	NH4-N (mg/l)	DOC (mg/l)	Color	Abs254	suspTS (mg/l)	Chla
69	10	28.08.2017	9.6	286	0	0	32	3.20		7.06	3.0		10.94	2.56	0.232					
70	11	28.08.2017	9.4	287	0	0	33	3.20		7.06	3.0		11.66	2.49	0.253					
66	12	28.08.2017	9.2	289	0	0	40	3.20	6.32	7.17	3.8	1240.32	13.85	2.29	0.338	6.20	29	0.214	2.0	3.6
67	13	28.08.2017	9.1	292	0	0	56	3.00	6.37	7.19	5.6	1265.89	18.96	2.07	0.434	6.22	33	0.215	1.0	3.1
71	0.5	18.09.2017	14.7	275	9.53	94.6	35	4.00	7.61	7.86	9.4	1146.11	1.46	3.26	0.020	7.30	33	0.225	4.8	16.0
72	1	18.09.2017	14.7	275	9.46	93.8	42	3.80	7.51	7.88	9.5	1132.20	2.19	3.29	0.016	7.27	33	0.239	4.8	11.1
73	3	18.09.2017	14.2	272	7.42	72.5	32	3.80	7.40	7.86	9.3	1103.02	1.46	3.29	0.021	7.26	33	0.236	4.0	10.0
74	5	18.09.2017	14.1	272	7.58	74.1	42	4.00	7.62	7.66	13.0	1094.95	7.31	3.23	0.072	7.50	35	0.242	4.8	4.7
75	8	18.09.2017	13.8	273	6.77	65.9	47	4.00	7.71	7.63	13.9	1094.95	8.04	3.20	0.088	7.61	35	0.253	5.2	5.1
78	9	18.09.2017	10.1	289	0	0	52	4.00		7.38	13.0		11.69	3.18	0.116					
79	10	18.09.2017	9.4	294	0	0	48	3.60		7.13	9.5		12.42	2.75	0.181					
80	11	18.09.2017	9	306	0	0	44	3.00		7.06	4.5		16.81	2.12	0.356					
76	12	18.09.2017	13.5	274	5.45	52.5	59	2.80	6.57	7.19	7.5	1291.45	22.66	1.93	0.474	6.43	32	0.225	2.0	2.2
77	13	18.09.2017	11.5	285	0	0	98	2.60	6.71	7.18	11.5	1383.82	35.08	1.57	0.670	6.54	41	0.233	2.8	1.6
81	0.5	02.10.2017	12.8	272	7.86	76.2	45	3.75	7.52	7.65	11.9	1151.49	15.04	3.15	0.096	7.22	35	0.242	4.6	3.3
82	1	02.10.2017	12.7	272	7.83	76.1	45	3.70	7.52	7.57	11.3	1120.98	15.04	3.17	0.095	7.38	35	0.244	4.8	3.1
83	3	02.10.2017	12.7	272	7.79	75.6	52	3.70	7.54	7.63	12.4	1098.54	15.04	3.20	0.092	7.46	35	0.248	5	3.5
84	5	02.10.2017	12.7	272	7.73	75.1	54	3.67	7.56	7.58	13.2	1106.17	15.77	3.20	0.095	7.24	36	0.246	5.4	3.5
85	8	02.10.2017	12.7	271	7.63	74	55	3.70	7.61	7.53	15.5	1101.23	17.22	3.18	0.101	7.47	36	0.252	6.6	2.9
88	9	02.10.2017	12.5	267	6.86	66.4	95	3.98		7.31	38.1		23.77	3.24	0.123					
89	10	02.10.2017	12.4	267	6.17	59.5	109	3.85		7.28	48.9		25.23	2.97	0.134					
90	11	02.10.2017	11.7	280	2.4	23.9	118	3.76		7.22	46.6		28.14	2.91	0.191					
86	12	02.10.2017	9.3	302	0	0	80	2.70	6.71	7.19	10.3	1357.82	31.05	1.79	0.583	6.66	34	0.241	6.4	1.6
87	13	02.10.2017	9.1	312	0	0	98	2.56	6.80	7.07	10.4	1454.65	47.79	1.42	0.798	6.70	40	0.247	4.6	1.3
91	0.5	23.10.2017	9.5	266	7.63	66.1	55		7.40	7.43	12.3	1114.69	22.99	3.00	0.016	7.3	36	0.255	3.8	2.0
92	1	23.10.2017	9.6	266	7.56	66	54		7.50	7.54	12.3	1094.05	22.99	3.20	0.010	7.3	37	0.251	3.6	2.0
93	3	23.10.2017	9.6	266	7.54	65.9	54		7.50	7.56	12.3	1080.58	22.99	3.10	0.016	7.5	35	0.253	3.2	2.0
94	5	23.10.2017	9.6	266	7.53	65.7	55		7.50	7.56	12.8	1064.42	23.71	3.10	0.008	7.4	36	0.258	3.8	2.0
95	8	23.10.2017	9.6	266	7.52	65.9	66		7.50	7.54	13.4	1076.99	24.43	3.10	0.027	7.7	38	0.259	4.0	2.0
98	9	23.10.2017	9.5	266	7.52	65.7	59			7.47	13.8		25.87	3.10	0.046					
99	10	23.10.2017	9.5	265	7.54	65.8	60			7.38	14.6		24.43	3.30	0.008					
100	11	23.10.2017	9.5	261	7.59	66.3	67			7.45	18.7		25.87	3.10	0.012					
96	12	23.10.2017	9.5	261	7.61	66.4	69		7.70	7.49	21.7	1077.89	25.87	3.10	0.023	7.4	39	0.264	10.6	1.6
97	13	23.10.2017	9.5	260	7.62	66.5	58		7.80	7.50	14.2	1089.56	23.71	3.10	0.014	7.5	39	0.262	3.6	1.6

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

Postboks 5003
NO-1432 Ås
Norway