Oxygen and its impact on nitrification rates in aquatic sediments

Tina Liesirova

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Cover Picture: Conduction of sediments in Roskilde Fjord. Picture taken by Daniel Conley, April 2016

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Abstract: Eutrophication, the undesired phenomenon of high nutrient loads in an aquatic system, is mostly caused by human impact: industrial and urban waste water discharge, run-off of fertilizers from agricultural use, and combustion of fuels. The study of eutrophications' main participants such as the nitrogen cycle, are necessary to prevent it. Environmental parameters have an impact onto the effectivity of the subprocesses of the nitrogen cycle. Research by Jianlong and Ning (2004) suggests hypoxic conditions to be more favorable for nitrification than normoxic ones. In order to test this hypothesis aquatic sediments from the Roskilde Fjord in Denmark were collected on the 5th and the 26th of April 2016 (apr5, apr26) to determine their nitrification rates in differing oxygen environments. In addition, the samples were compared to see if there was a significant contrast between the dates of sample retrieval. The nitrification rates of apr5 (0-1cm depth; 1-2cm depth) and apr26 (0-2cm depth) were established by measuring the NO_X (NO_2^- and NO_3^-) concentrations with help of a spectrophotometer. Apr5 samples were measured twice (t0h, t24h), whereas the apr26 sediments were measured five times (t0h, t4h, t8h, t16h, t23h). Furthermore, the apr26 samples were treated either with air to generate normoxic conditions, or with nitrogen gas to generate hypoxic and anoxic conditions.

The results from apr5 show highest NO_X rates in 1-2cm depth, beneath the OPD (2.7mm). The results from apr26 under normoxic/hypoxic/anoxic treatment suggest hypoxic conditions to be more favorable for nitrifying processes. Despite apr26 samples having had hypoxic benthic conditions, nitrification rates were lower than from apr5. It is likely the influence of additional parameters such pH and sulfides to be responsible for the comparably low nitrification rates from apr26, despite the hypoxic benthic environment.

Keywords: Eutrophication, nitrification, hypoxic, normoxic, Roskilde Fjord

Supervisor(s): Jane Caffrey, Daniel Conley, Stefano Bonaglia

Subject: Biogeochemistry

Tina Liesirova, Department of Geology, Lund University, Sölvegatan 12, SE-223 62 Lund, Sweden. E-mail: tina.liesirova@gmail.com

Syre och dess inverkan på nitrifieringshastigheter i akvatiska sediment

TINA LIESIROVA

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Sammanfattning: Eutrofiering det oönskade fenomenet av hög näringstillförsel i ett akvatiskt system, är för det mesta ett resultat av mänsklig påverkan: industriellt och urbant avloppsvatten, avrinning av gödningsmedel från odlad mark, och förbränning av fossila bränslen. Studien av de främsta faktorerna som bidrar till eutrofiering (t. ex. variationer i kvävets kretslopp), är viktigt för förståelsen av dess negativa påverkan på miljön och hur man kan motverka det. Olika miljöparametrar påverkar effektiviteten av delprocesser i kvävets kretslopp. Forskning av Jianlong och Ning (2004) föreslår att hypoxiska förhållanden är mer gynnsamma för nitrifiering än normoxiska förhållanden. För att testa denna hypotes hämtades akvatiska sediment från Roskilde Fjorden i Danmark den 5:e och den 26:e April 2016 (prover apr5, apr26) så att variationer i nitrifieringen beroende på skillnader i syre mängden kunde fastställas. Dessutom, gjordes en jämförelse mellan olika prover för att se om signifikanta skillnader kunde påträffas beroende på vilket datum proverna hämtades. Nitrifieringshastigheten av prov apr5 (0-1 cm djup; 1-2 cm djup) och apr26 (0-2 cm djup) fastställdes genom att mäta koncentrationerna av NO_X (NO_2^- och NO_3^-) med hjälp av en spektrofotometer. Apr5 delprover mättes två gånger (t0h, t24h), medan prov apr26 mättes fem gånger (t0h, t4h, t8h, t16h, t23h). Dessutom behandlades prov apr26 antingen med luft för att generera normoxiska förhållanden, eller med kväve (gas) för att generara hypoxiska och anoxiska förhållanden.

Resultaten från apr5 visar högsta NO_X hastighetsvärden på 1-2 cm djup, under OPD (2.7 mm). Resultaten från apr26 under normoxiska/hypoxiska/anoxiska behandlingar visar på att hypoxiska förhållanden är mer gynnsamma för nitrifieringsprocesser. Trots att apr26 proven hade hypoxiska bentiska förhållanden, så var nitrifieringshastigheterna lägre än för apr5. Det är möjligt att ytterligare parametrar så som pH och sulfider kan ha bidragit till den förhållandevis låga nitrifieringshastigheten för apr26, trots den hypoxiska bentiska miljön.

Nyckelord: Eutrofiering, nitrifiering, hypoxisk, normoxisk, Roskilde Fjord

Handledare: Jane Caffrey, Daniel Conley, Stefano Bonaglia

Ämnesinriktning: Biogeokemi

Tina Liesirova, Geologiska institutionen, Lunds universitet, Sölvegatan 12, 223 62 Lund, Sverige. E-post: tina.liesirova@gmail.com

1 Introduction

Eutrophication is a phenomenon of high nutrient loads in an ecosystem. In aquatic environments eutrophication often has a damaging effect, which in the worst case can lead to large changes in biodiversity (Chislock et al. 2013). One of the main participants of eutrophication is the nitrogen cycle (Bernhard 2010).

The nitrogen cycle is the key process to transforming nitrogen into accessible inorganic nitrogen, which then can be taken up by the environment's living organisms (Bernhard 2010; Bock & Wagner 2006). The converting processes in the cycle are performed by different microbial groups (Bernhard 2010). However, the processing rates are not continuously stable, because the nitrogen cycle and its participants are greatly influenced by alternating environmental conditions (Kemp et al. 1990). These environmental conditions are amongst others physical and chemical parameters like pH, salinity, temperature, and oxygen which have a shaping influence onto the mentioned microbial groups (Erguder et al. 2009; Jin et al. 2010; Kemp et al. 1990; Rinkes 2015). Oxygen is the main driver for aerobic metabolism (respiration), which is considered to be the strongest/most convenient energy source for organisms and therefore has a significant importance (Dickens 1964). The microbial groups responsible for the nitrifying processes perform under oxic conditions making oxygen availability obviously one of the control factors of the nitrogen cycle (Bernhard 2010). However, studies from both, Stenstrom and Poduska as well as Jianlong and Ning suggest the microbial groups from the nitrifying processes perform preferably under hypoxic conditions rather than normoxic conditions (Jianlong & Ning 2004; Stenstrom & Poduska 1980). By understanding the details of these complex environmental processes and implementing effective sewage regulations accordingly, risky accumulations of nitrogen concentrations in waters could be avoided, which in itself would avoid eutrophication (Clarke et al. 2003).

The aim of this bachelor thesis is the study and comparison of production rates of nitrifying processes under differing oxygen conditions in aquatic sediments taken from the Roskilde Fjord in Denmark on the 5th and the 26th of April 2016.

1.1 Background

1.1.1 Eutrophication

Even though eutrophication is a natural phenomenon, it is mostly undesired and mostly caused by human impact (Bernhard 2010). This so called “cultural” eutrophication has its cause in the run-off of fertilized agricultural areas, both industrial and urban waste water discharge, and the accelerated deposition of nitrogen by combustion of fuels (de Jonge et al. 2002). Eutrophication occurs in waters and wetlands and is defined as the unproportional increase of plant and algal growth due to high nutrient loading. Sunlight cannot pass the density of this growth, so light dependent organisms (plants, predators) in littoral zones suffer reduced growth or die (Andersen et al. 2010). Furthermore, the rising photosynthesis of plants and algae leads to depletion of inorganic carbon in the system, which in turn increases pH conditions with lethal consequence for aquatic organisms (Alabaster et al. 1980; Chislock et al. 2013; Committee on Water Quality et al. 1972; Doudoroff & Katz 1950; European Inland Fisheries Advisory Commission Working Party on Water Quality Criteria for European Freshwater 1969; McKee & Wolf 1963; Thurston 1979). With the death of the algal bloom, decomposition of the organic material sets in. Hence the concentration of dissolved oxygen (DO) drops drastically leading to hypoxic or anoxic water conditions and most oxygen depending organisms suffocate (Chislock et al. 2013). A present example of large-scale eutrophication is the Baltic Sea (Carstensen et al. 2014). Changes to the nitrogen cycle due to human impact are considered to be - amongst others - a cause of it (Andersen et al. 2010; Clarke et al. 2003) The outcome of eutrophication are enormous cyanobacteria blooms during rising temperatures in summer resulting eventually in hypoxia or anoxia, so called “dead zones” (Carstensen et al. 2014; Jianlong & Ning 2004).

1.1.2 Nitrogen cycle

All living organisms depend on the supply of primary nutrients to build up biomolecules (e.g. proteins, DNA) and nitrogen is one of them (Bernhard 2010; Bock & Wagner 2006; Osman 2012; Rinkes 2015). The air is enriched in atmospheric nitrogen (N_2). However, in this form it is not accessible to most organisms which require inorganic compounds of nitrogen ($NH_4 NO_2^-$, NO_3^-). The nitrogen cycle (figure 1) is able to convert atmospheric nitrogen into inorganic compounds which then are absorbed by organisms (Bernhard 2010; Rinkes 2015). The nitrogen cycle is a set of processes and the major pathways are divided into nitrogen fixation, nitrification, denitrification, and ammonification (Bernhard 2010; Jorgensen & Fath 2008). In the following the thesis focuses on nitrification.

1.1.3 Nitrification

During nitrification ammonia oxidizers convert NH_3 into nitrite (NO_2^-) and afterwards into nitrate (NO_3^-). The whole reaction usually takes place under oxic conditions. Archaea and bacteria performing the conversion from NH_3 to NO_2^- (1) are called ammonia-oxidizers. The conversion from NO_2^- to NO_3^- (2) is performed by nitrite-oxidizing bacteria. Nitrification is important, because it can remove damaging amounts of NH_3 from the water system by the following reaction which otherwise could result in eutrophication (Bernhard 2010; Jorgensen & Fath 2008; Rinkes 2015; Schmidt & Schaechter 2011) :

$$(1)\ NH_3 + O_2 \rightarrow NO_2^- + 3H^+$$

$$(2)\ NO_2^- + \tfrac{1}{2}\, O_2 \rightarrow NO_3^-$$

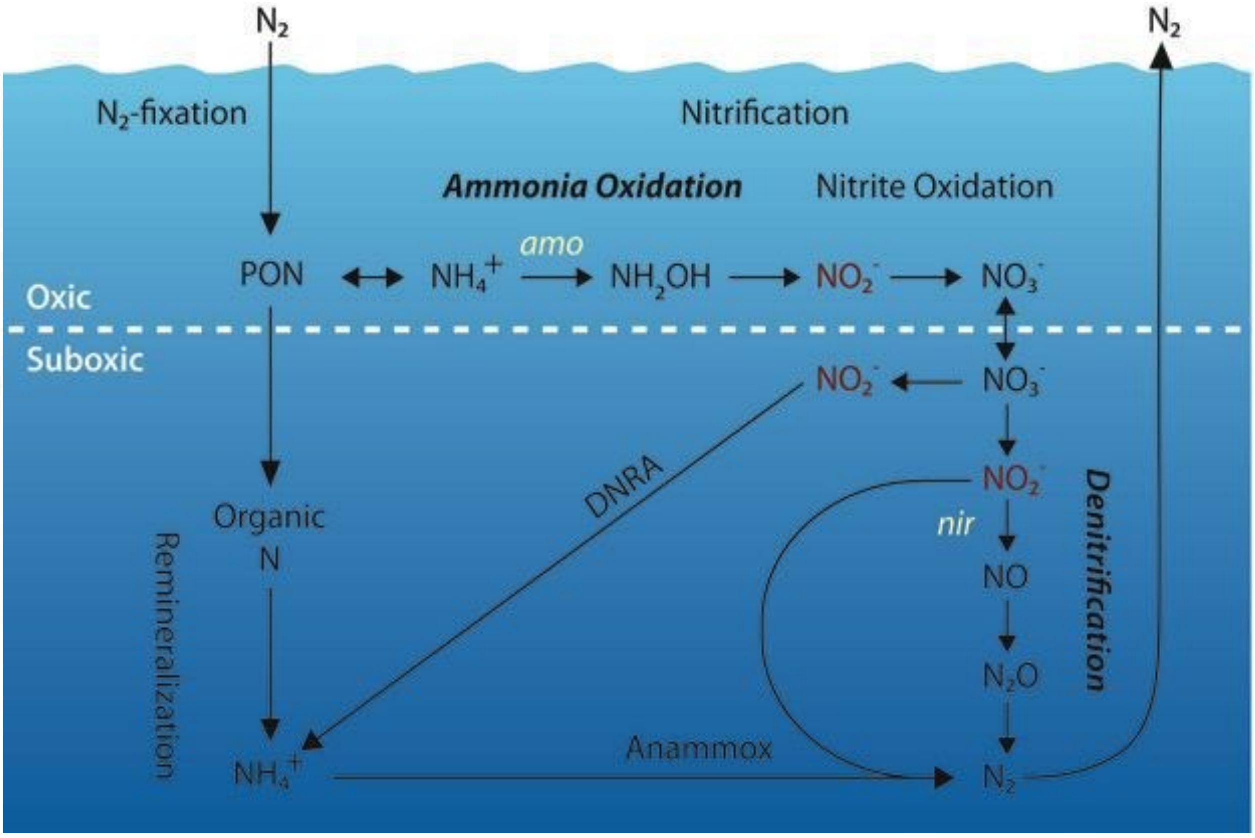


Figure 1. Major transformations in the nitrogen cycle, appeared in Francis et al., 2007.

2 Location of study

Adjacent to the Baltic Sea, Denmark's coastal shelf offers an environment of interest for studies in the changes of nutrient concentrations. Measurements revealed the Danish coastal waters having undergone a 3-fold increase in nitrogen loading due to agricultural waste water discharge between 1950 and 2003 (Clarke et al. 2003). In the wake of these findings, improvements in agricultural regulations were suggested for Danish ecosystems and estuaries. One of these estuaries which received these regulations is the Roskilde Fjord (Clarke et al. 2003). The Roskilde Fjord is part of the Sjælland region in Denmark, situated close to the town Roskilde, the only bigger city in the area (figure 2). The fjord is a shallow estuary with an average depth of 3m and a total surface area of 122km^2 (Clarke et al. 2003; Kamp-Nielsen 1992). The inner bay is mainly surrounded by land used for agriculture. In the 19th century, the agronomical and local industry wastewater discharge was directly inserted into the fjord which lead to a strong nutrient gradient decreasing towards the opening of the Kattegat (Clarke et al. 2003). The mentioned sewerage regulations were ineffective until the late 1950s and renewed in the 1990s, but in summer 2000 the total nitrogen supply in Roskilde Fjord was still 494,9t (Adser 1999). Due to this high number after more than 50 years of sewerage regulations (Clarke et al. 2003), it was chosen as the study of interest for this thesis.

3 Materials and Methods

3.1 Hydrography and sampling

On the 5th of April (apr5) and 26th of April 2016 (apr26), samples were collected in Kattinge Vig (KV_05; KV_26) in the Roskilde Fjord. A kajak corer was used to gather the upper 15cm of the sea bottom sediments in tubes. The hydrography of the water column was determined on-site using a YSI multimeter (Pro Plus), which measured temperature in °C, pH, salinity in PSU, and dissolved oxygen in mg/l (picture 3).

3.2 Oxygen analysis in sediment

In the lab, the sediment porewater oxygen content of the coretubes was measured in a temperature controlled room (17 °C) using oxygen microelectrodes with 100um tip di-

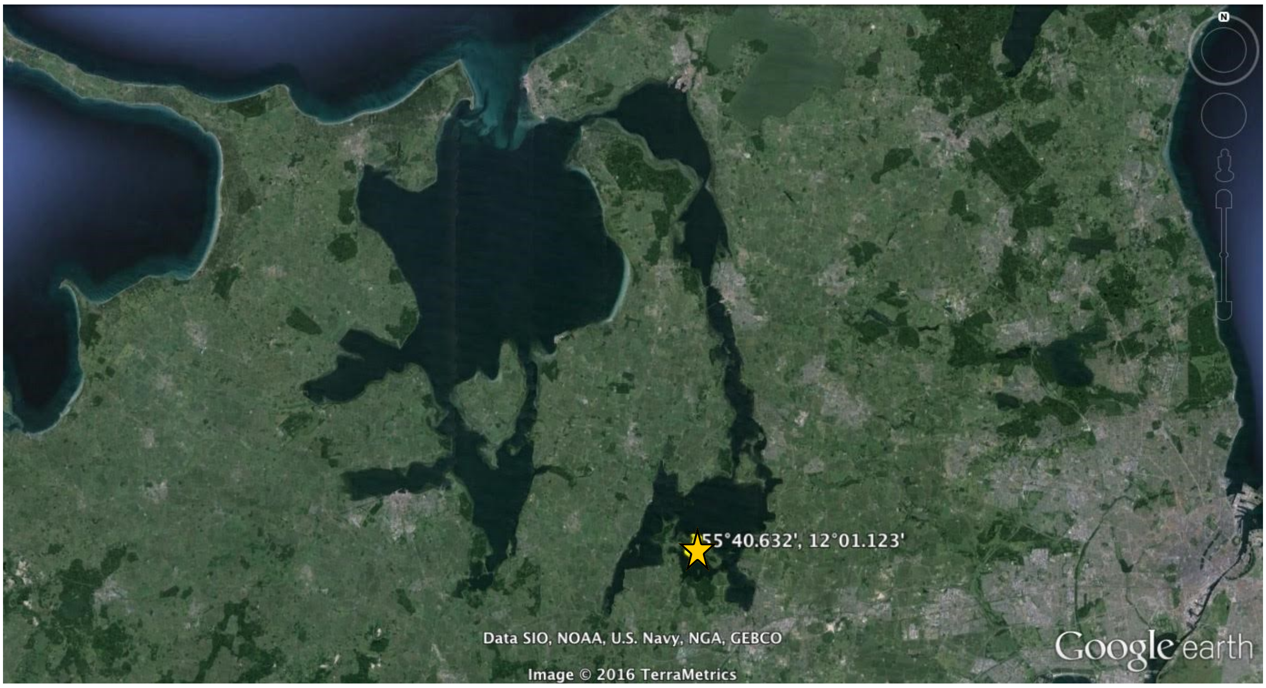
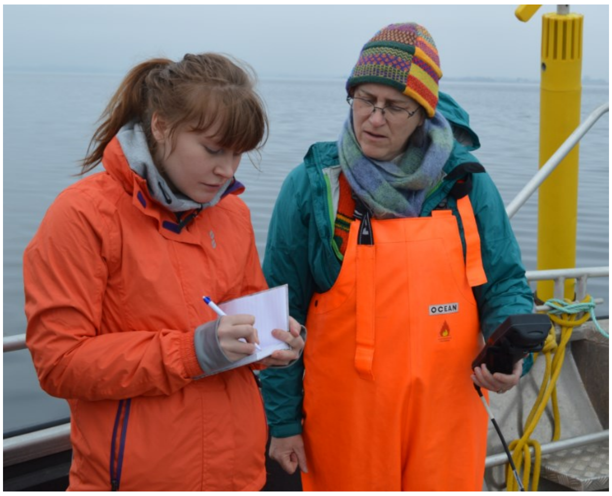


Figure 2. Map of the Roskilde Fjord, Denmark. Station Kattinge Vig marked.Taken from Google Earth.



Picture 3. Hydrography determination.

ameter (Unisense) as described and modified by Schulz and Zabel (Lohse et al. 1997; Schulz & Zabel 2006).

3.3 Potential nitrification
- NOx concentration and production rate

The potential nitrification for KV_05 and KV_26 was determined in two single experiments. At first sediments were made slurry with GF/F (Whatman®) filtered water from the fjord. On the 5th of April 1-2 g of slurry sediment from 0-1cm (KV_05_0-1), and 1-2 cm depth (KV_05_1-2) and 50 ml of site water were extracted. Triplicates were prepared for each depth. Two time points in a 24h interval were set to measure concentration and calculate potential nitrification rate (t0, tf). On the 26th of April, 5 cm^3 sediment from the upper 2cm depth were mixed (KV_26_0-2cm) with 250ml of site water. Six replicates were prepared. In a 24h interval five measurements were taken (T1-0; T-2-1; T3-2; T4-3; T5-4). The nitrite and nitrate analysis was performed as described in Schnetger and Lehners (Schnetger & Lehners 2014). For the NO_2^- analysis the samples were treated with Griess reagents (Doane & Horwáth 2003) naphthyl-ethylene-diamine-dihydrochloride (NED) and sulfanilamide (SAM) in 10ml vials. For the NO_3^- analysis the reduction from nitrate to nitrite was forced by adding a surplus of vanadium chloride. Standards out of a $NaNO_2$ stock were generated from 0uM, 1uM, 5uM, and 10uM. The R^2 for all standard curves was greater than 0,99. Concentration was then determined through spectrophotometric absorbance at λ=543nm using a spectrophotometer (CADAS 100, Dr Lange) (Miranda et al. 2001). The total potential production rate was calculated as the change of NO_2^- and NO_3^- concentrations over time accounting for the volume of water and amount of sediment in the incubation.

3.4 NOx prod. rates under normoxic, hypoxic and anoxic conditions in sediments, 26th April

Slurry samples (picture 4) were treated for four hours with oxygen to create normoxic conditions, or with nitrogen to create hypoxic (28% saturation) and anoxic (0% saturation) conditions. Afterwards, all samples were exposed to oxygen. The experiment was carried out over a 24h interval with five conducted measurements (t0, t4h, t7h, t16h, t23h). The slurry samples were filtered using GF/F filters.

3.5 Statistical analysis

Statistical analysis with analysis of variance (ANOVA) and statistical errors was performed using Sigmaplot 13.0. To test significant differences between sample groups apr5

Picture 4. Slurry samples

and apr26, the apr5 rates were converted from umol/g/d to umol/cm^3 based on the water content of the sediments. Graphical plotting was performed using MS Excel and Plot2.

4 Results (on site)

4.1 Hydrography

4.1.1 Temperature

On April 5th the sea surface temperature was about 8.7°C and decreased evenly to 7.2°C in 8m depth (figure 5). The thermocline was situated in the following 2m, which was represented by a sudden decrease to 4°C at 10m depth. The temperature stayed constant until 14 m depth and decreased then slightly to 3.6°C. The benthic waters had a temperature of 4°C.

On April 26th, sea surface temperatures were also about 8.7°C, but warmed up to 8.9°C until 9m depth. The following meter, water temperature increased relatively rapid to 9.2°C, which lasted until 14m depth. At the sea bottom the temperature decreased to 9°C.

4.1.2 Salinity

In the beginning of April the salinity at the sea surface was about 11.5 PSU (figure 6). The values increased constantly until 8m depth to 12.5 PSU. The following two meters the halocline was observable between 8 – 10m depth, reflected by a rapid increase to 14 PSU. Between 10m and the sea bottom the salinity rose at first slightly to 14.3 PSU and dropped afterwards again to 14 PSU.

On April 26th, the salinity at the sea surface was about 11.7 PSU and increased evenly to 12 PSU in 9m depth. The following two me-

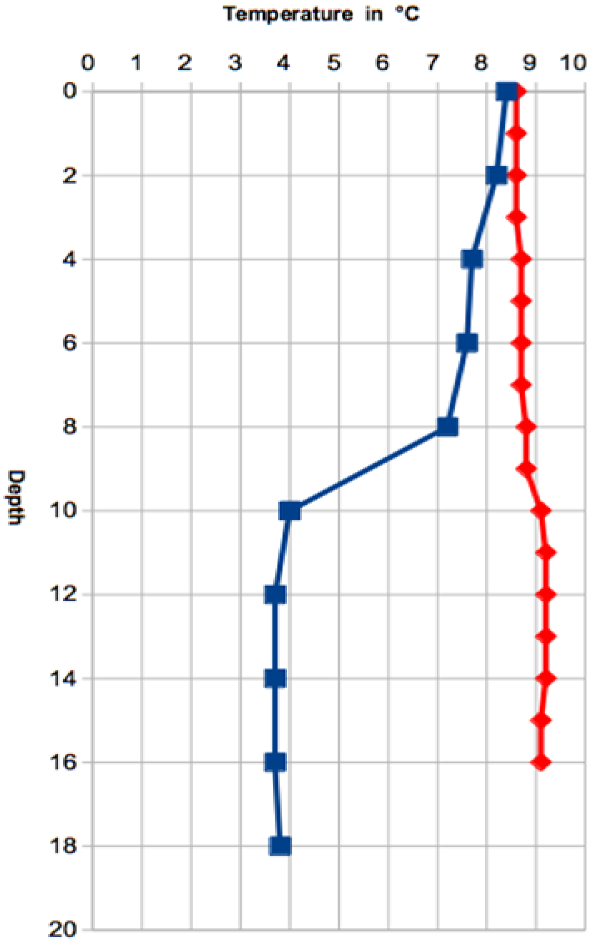


Figure 5. Temperature graph.

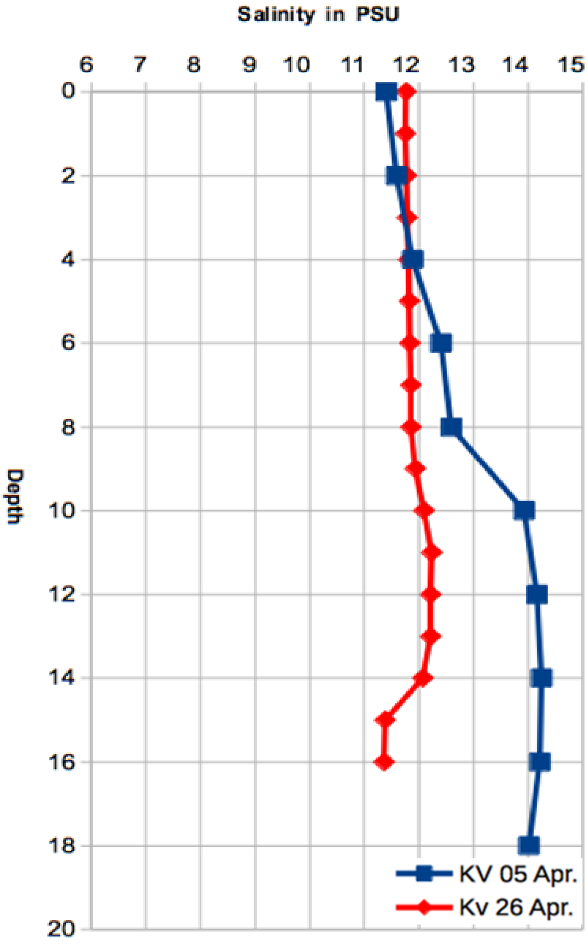


Figure 6. Salinity graph.

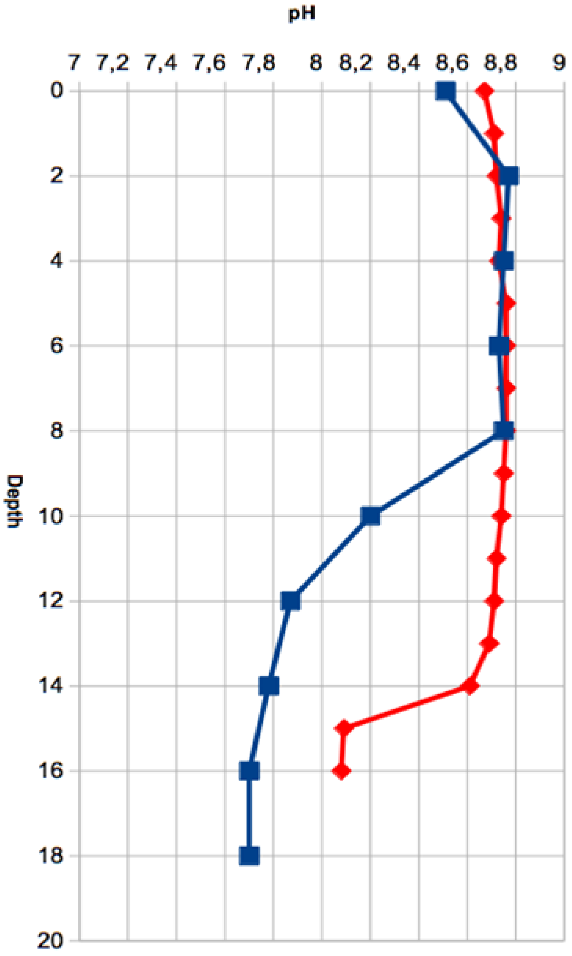


Figure 7. pH graph

ters the steady line bent slightly and the salinity reached 12.2 PSU, which potentially indicated a halocline. Between 11 and 14m depth the value remained constant, but decreased rapidly to 11.4 PSU in the benthic water column, which suggests a second halocline.

4.1.3 pH

On April 5th, the surface water had a pH value of 8.5 (figure 7). In the first two meter of depth the pH increased to 8.8 and remained stable until 8m depth. Afterwards the pH dropped rapidly to 7.8 (12 m depth) and continued reducing moderately to 7.7 in the benthic water column.

At the end of April, the pH at the sea surface was about 8.65. The value rose slowly up to 8.75 (8 m depth) and decreased afterwards to 8.6 (14m depth). Thereupon the pH dropped rapidly to 8.1 followed in the bottom water column.

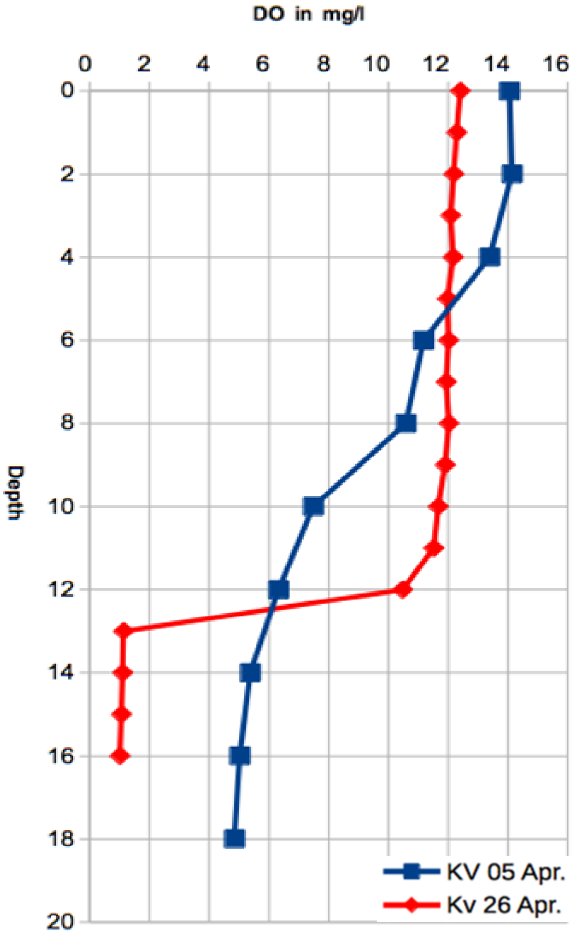


Figure 8. DO graph

4.1.4 Dissolved Oxygen (DO)

The first two meters of the sea surface water column in the beginning of April had an DO value of 14 mg/l (figure 8). The concentration dropped to 13.2 mg/l (4m depth), followed by a steeper decrease to 10.4 mg/l (8m depth). Between 8 and 10m the DO dropped rapidly to 7.5 mg/l. The decrease continued but decelerated until it reached the bottom water column with a value of 4.9 mg/l.

On the 26th April the sea surface had a DO value of 12.4 mg/l, which lowered minimal to 11.5 mg/l in 11m depth. The decrease accelerated and between 12m and 13m the oxicline is situated and the DO concentration dropped drastically to 1 mg/l (hypoxic condition) and remained in the benthic water column.

5 Results (laboratory)

5.1 Oxygen content in pore water

All oxygen profiles in this study had a reversed s-shape as a graph. Important measurement points were the sediment surface oxygen values, which are observable by a significant decrease in concentration due to the diffusion boundary layer. Furthermore, there were two depths which confined the steepness of the linear oxygen decreased throughout the depth. Subsequently the slope decelerated and approached tangentially the y-axis, representing the oxygen penetration depth.

5.1.1 Oxygen profile, apr5 sample

The sediment surface had a concentration of 250umol/l, before it started decreasing. The linear reduction was observable between 50um (about 250umol/l) and 1400um depth (50 umol/l). The oxygen penetration depth (OPD) was located in 2700 um depth. The second profile showed similar results.

5.1.2 Oxygen profiles, apr26 sample

Profile 1 showed the oxygen concentration at the sediment surface was about 226 umol/l and the OPD was situated in 2200um depth (figure 9).

The second profile showed similarities to the first profile. However, the surface oxygen concentration was slightly higher with about 230 umol/l and the OPD was positioned in 2100um depth (figure 9).

The last profile had the highest surface oxygen concentration with about 236 umol/l. It had the lowest OPD situated in 2300um (figure 9).

5.2 Nitrification measurements

5.2.1 NO$_X$ concentration, apr5 and apr26

The NO$_X$ (NO$_2^-$ plus NO$_3^-$) concentration measurements were taken twice in a 24 hours experiment (t0 and tf) from two different depths of the same sample (KV_Depth 0-1cm; KV_Depth 1-2cm).

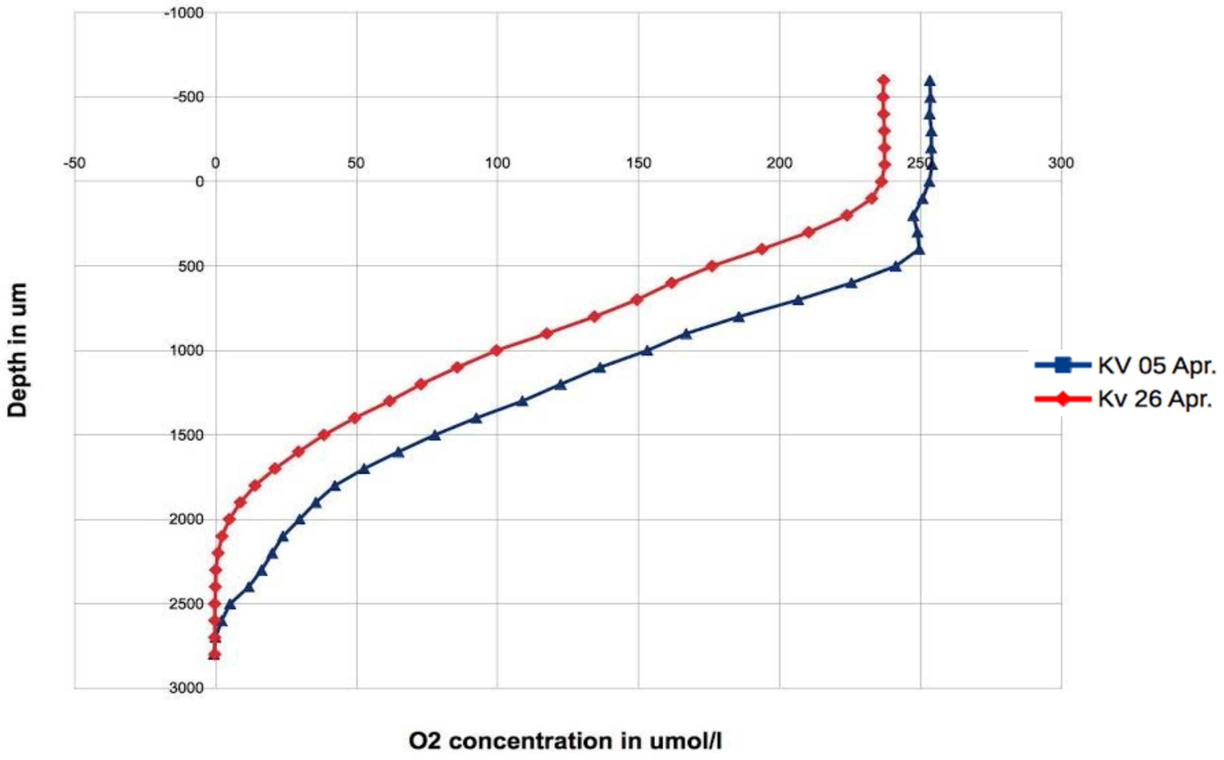


Figure 9. Oxygen profiles from 5th and 26th of April.

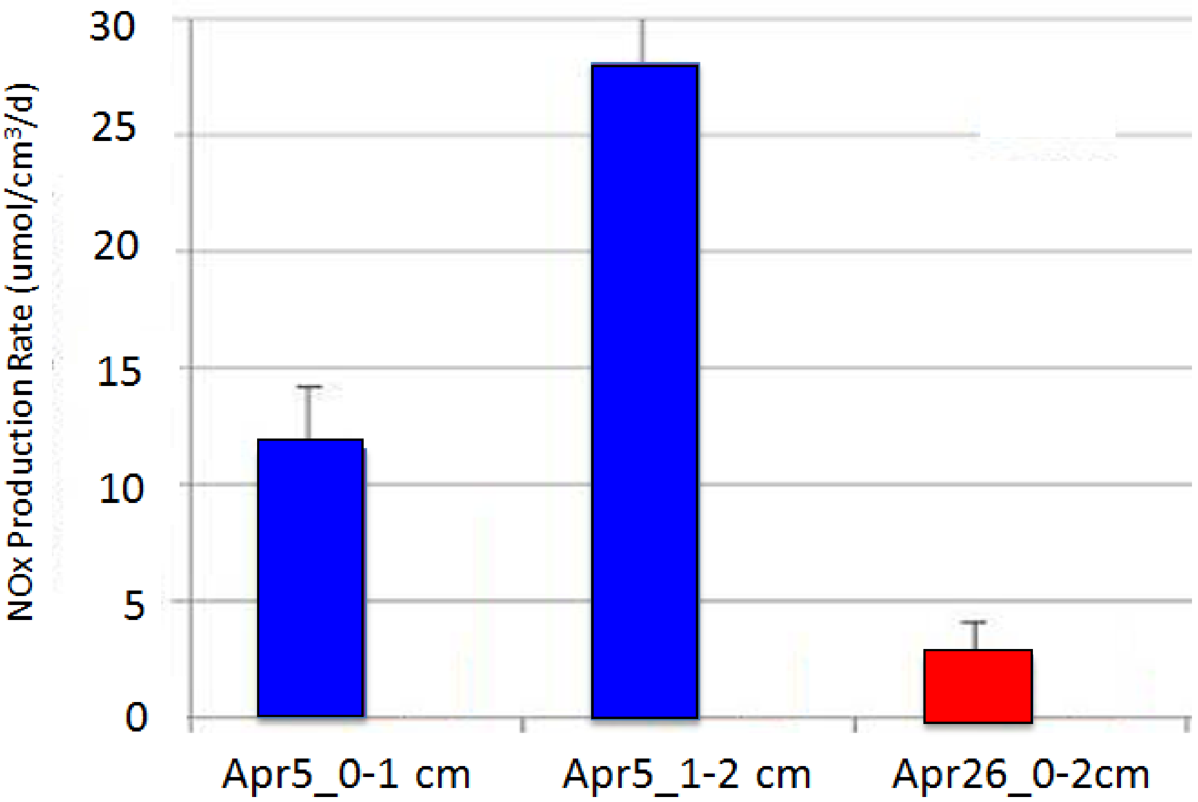


Figure 10. NOx production rates from both apr5 samples and apr26.

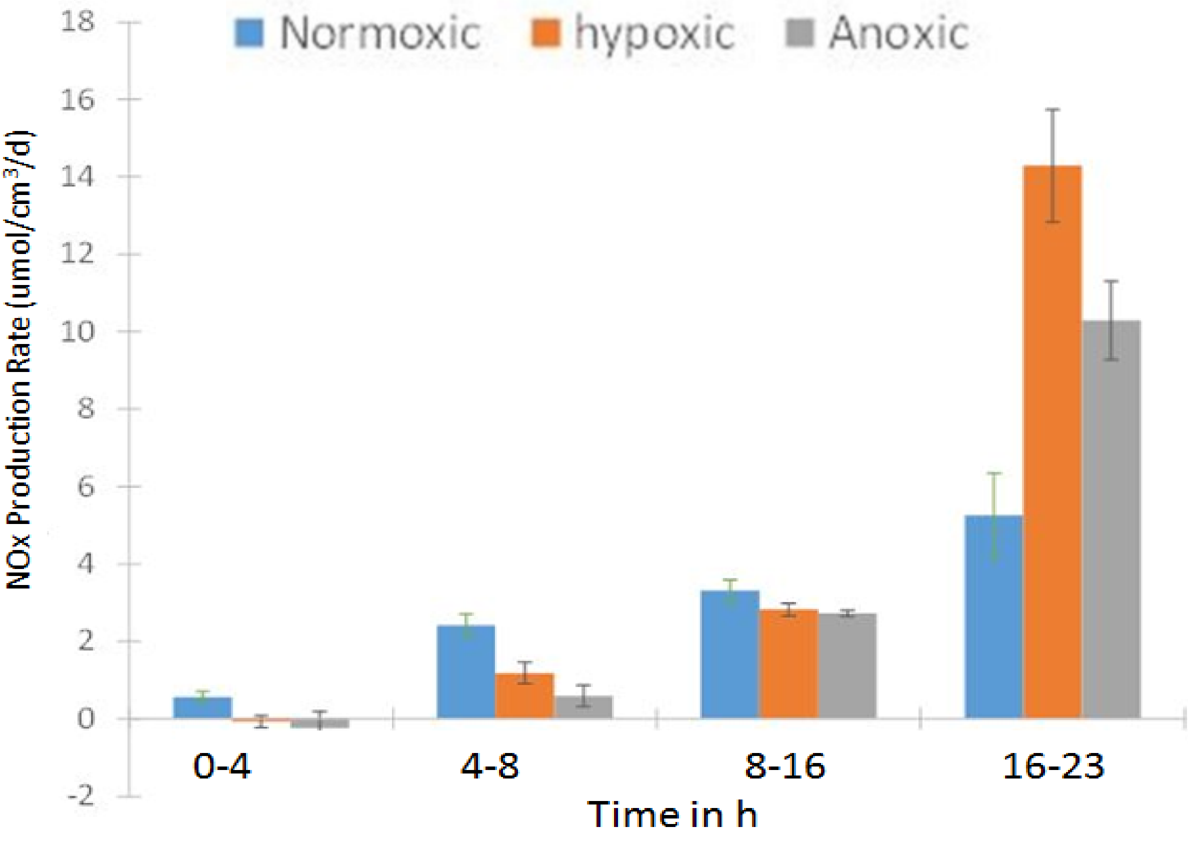


Figure 11. NOx production rate under normoxic/hypoxic/anoxic conditions.

At both depths a considerable increase in concentration was observable after one day, however the concentrations from the deeper sample were significantly higher than from the upper one.

The NO_X concentrations from apr26 were measured under normoxic/hypoxic/anoxic treatment during a 24h experiment. The concentrations of the different treatment showed all exponential increase. Hereby the hypoxic conditions provided after 24h the highest values, whereas the normoxic treatment provided the lowest ones (compare production rates in figure 11).

5.2.2 NOx production rate - Statistical comparison from 5th and 26th of April

Figure 10 compares the potential nitrification production rate between the samples from the 5th of April (KV_05_0-1cm depth; KV_05_1-2cm depth) and the 26th of April (KV_26). A statistically significant difference was determined between KV-05_1-2 and KV_26.

Nitrifying processes were highest in early April in the deeper sediment samples (1-2cm depth) with about 27 umol/cm3/d compared to sediment surface samples at the end of April with about 4 umol/cm3/d.

6 Discussion

Comparing nitrifying rates in the sediment from the 5th of April with the rates from the 26th of April reveals higher NO_X production and concentrations in the beginning of the month. This is in accordance with normoxic conditions in the water column in early April and higher O_2 values in the pore water. The highest production rates in KV_05 were measured in 1-2cm depth although the OPD in the pore water was reached in 2.7mm (2700um) depth. The sediment surface should have higher nitrification rates if O_2 conditions are more favorable for nitrification.

The apr26 experiment, which treated samples under normoxic, hypoxic, and anoxic conditions revealed higher values in the hypoxic treatment group than in the normoxic one. This is in accordance with the results from Sibag and Kim (2014) (Sibag & Kim 2014). However, it has to be taken into account that there was a hypoxic benthic environment (1 mg/l) on the 26th of April during stormy conditions. The question arises why the potential nitrification rates from apr26 had been lower than in the beginning of the month (DO of about 4.8 mg/l), if hypoxic conditions are preferred by nitrifiers.

Therefore we conclude that other parameters affecting nitration must be taken into account. Jianlong and Ning (2004) report of the influence of DO, pH, and temperature onto ammonia oxidation and nitrite accumulation with optimal conditions being DO = 1.5 mg/l (hypoxic), pH = 7.5, and temperature = 30°C (Jianlong & Ning 2004).

The laboratory, in which the experiments were conducted, was not temperature controlled. This means there were no *in situ* conditions when measuring NO_X concentrations, which leaves only pH and DO as possible parameters to compare. On the 5th of April the pH was 7.7 and on the 26th of April it was 8.1. The pH conditions beginning of April are closer to Jianlong and Ning's (2004) results and seem to be more favorable for the experiments, suggesting pH to having a sufficient influence onto nitrification and thus affecting the results.

Another study by Berg et al. (Berg et al. 2015) implies sulfides to having an inhibiting effect onto nitrification by damaging the metabolism of the microbial groups. There are sulfides present in the Roskilde Fjord (Holmer & Nielsen 1997), which could have disturbed the nitrifiers. During temporary mixing events, toxic sulfides could mix up with upper sediment/ water layers and affect the nitrifying processes (Berg et al. 2015). This could explain why the apr26 nitrification rates were significantly lower compared to early April despite the hypoxic benthic environment.

In conclusion, the impact of hypoxic or normoxic conditions onto nitrification rates is not possible by simply comparing total production rates and concentrations from the samples taken on the 5th and the 26th of April due to the possible impact of other parameters. However, the results from the normoxic/ hypoxic/anoxic conditions (apr26) indicates hypoxic conditions are more favorable for nitrifying processes than normoxic conditions.

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I would like to thank my thesis advisors Jane Caffrey, Daniel Conley, and Stefano Bonaglia from the geological department in Lund University. All of them were very considerate towards my concerns and questions throughout my thesis. My special gratitude goes to Jane, who led me with a lot of patience through the main experiments in the laboratory, beginning with fundamental processes in a chemistry lab. She explained the geochemistry on which this thesis is based on step by step and supported me during the whole writing process.

Despite his full schedule, Daniel took his time to help me to get onto the right course with my project and management. He constantly encouraged my work, even during my deepest hours of panic.

Under Stefano's supervision I gained a lot of experience during the practical process of sediment conduction under almost critical environmental conditions in the fjord.

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Illustrations

Fig. 1

Francis, C. A., J. M. Beman, and M. M. M. Kuypers. 2007. “New processes and players in the nitrogen cycle: the microbial ecology of anaerobic and archaeal ammonia oxide tion”. *ISME Journal* 1: 19-27.

Fig. 2

Source: “Roskilde Fjord.” N55°40.632’ and E012°01.123’.Google Earth. July 2, 2015. May 26, 2016.

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