

Ministry of Environment and Food of Denmark Environmental Protection Agency

N₂O Emissions from Ejby Mølle Full-Scale Evaluation of Conventional Activated Sludge and MABR N₂O emissions

MUDP report August 2020

Publisher: The Danish Environmental Protection Agency

Editors: Nerea Uri Carreño (VCS), Per Henrik Nielsen (VCS) Nina Almind-Jørgensen (VCS)

ISBN: 978-87-7038-216-8

The Danish Environmental Protection Agency publishes reports and papers about research and development projects within the environmental sector, financed by the Agency. The content of this publication do not necessarily represent the official views of the Danish Environmental Protection Agency. By publishing this report, the Danish Environmental Protection Agency and the content represents an important contribution to the related discourse on Danish environmental policy.

Sources must be acknowledged

Contents

1.	Summary	4
2.	Resumé	5
3.	Introduction	6
3.1	Motivation for this project	6
4.	Method	7
4.1	Ejby Mølle process description	7
4.1.1	Operational conditions	7
4.1.2	Data acquisition	8
4.1.3	Data analysis	8
4.2	MABR	12
4.2.1	Process description	12
4.2.2	Data acquisition	12
4.2.3	Data analysis	13
5.	Results	14
5.1	Activated sludge	14
5.2	MABR	17
6.	Conclusion and perspectives	19
7.	References	20

1. Summary

Nitrous oxide (N_2O) is a greenhouse gas with a global warming potential 265 times stronger than carbon dioxide on a 100-year time horizon (Eickemeier et al., 2014) and therefore, even emitted in small amounts, it can contribute significantly to global warming. In addition, nitrous oxide is acknowledged as an important threat to the ozone layer (Ravishankara et al., 2009). N_2O is an undesired bioproduct emitted during the biological nitrogen removal process in wastewater treatment systems and despite the recent efforts in understanding nitrous oxide emissions from wastewater treatment, data from full-scale plants is still scarce.

VandCenter Syd is the third largest provider of water and wastewater services in Denmark. The largest water and resource recovery facility operated by VandCenter Syd in Odense is Ejby Mølle, with treatment capacity of 410.000 population equivalents. Innovation and sustainability are two key values for VandCenter Syd, and therefore, quantification and mitigation of nitrous oxide emissions is a high priority.

VandCenter Syd partnered in 2017 with Aarhus Vand to implement full-scale demonstration of membrane aerated biofilm reactor (MABR) technology at Ejby Mølle. This technology, besides other potential benefits, is believed to have the capability of reducing nitrous oxide emissions compared to conventional activated sludge (CAS).

In this project, a monitoring camping of nitrous oxide emissions was carried out at Ejby Mølle from January to June 2019. We measured nitrous oxide emissions from the conventional activated sludge surface-aerated reactors and the MABR demonstration reactors. Liquid phase sensors were used in two of the activated sludge tanks and the MABR tanks, and a gas analyser was used to measure nitrous oxide concentrations in the exhaust gas of the MABR units.

The nitrous oxide emissions from the activated sludge reactors, which use surface aerators for aeration, were calculated using the N₂O concentration measured with the sensor and a mass transfer coefficient, K_La . The mass transfer coefficient was difficult to estimate, two different methods were applied with significantly different results, and we believe it introduced a high degree of uncertainty in the results.

Seasonal changes in temperature and a change in the operational conditions in the activated sludge from parallel to series operation at the end of April 2019, caused a great increase in nitrous oxide emissions from the CAS.

Overall, nitrous oxide emissions from the MABR reactors were on average an order of magnitude lower than those from the CAS.

2. Resumé

Lattergas (N₂O) er en drivhusgas med en effekt 265 gange større end kuldioxid (CO₂) på en 100 års tidshorisont. Derfor selv med en lille emission frigivet til luften, har lattergas en signifikant virkning på den globale opvarmning. Lattergas er anerkendt som en stor trussel for ozonlaget. Lattergas er et uønsket biprodukt, som frigives fra rensningen af kvælstof i spildevand på renseanlæggene. Der er i den seneste tid blevet forsket en del i lattergas emissioner fra spildevandsrensning, men der mangler data fra fuld skala anlæg.

VandCenter Syd er den 3. største forsyning af drikkevand samt rensning af spildevand i Danmark. Ejby Mølle i Odense er med en kapacitet på 410.000 PE (person ækvivalenter) det største spildevand og ressourcegenindvindingsanlæg som VandCenter Syd driver. Innovation og bæredygtighed er vigtige værdier for VandCenter Syd, og derfor arbejder vi på at kunne kvantificere og mindske emissioner fra renseanlæg.

I et samarbejde med Aarhus Vand blev der i 2017 implementeret et membrane aerated biofilm reactor (MABR) fuld skala demonstrations anlæg på Ejby Mølle renseanlæg. MABR skulle ifølge teorien kunne fjerne kvælstof fra spildevand med et mindre energiforbrug samt et mindre udslip af lattergas, sammenlignet med et konventionelt aktivt slam anlæg.

I dette projekt er der fra januar til juni 2019, blevet målt og overvåget produktionen af lattergas fra et konventionelt overflade beluftet anlæg samt et MABR anlægget. I to af aktiv slam tankene er der blevet installeret sensorer til måling af koncentrationen af opløst lattergas i vandet. I MABR anlægget er koncentrationen af opløst lattergas målt samt koncentrationen af lattergas i ventilationsgassen fra anlægget.

Lattergasemissionen fra det konventionelle aktivt slam anlæg, er beregnet på baggrund af målingerne fra sensorerne installeret i tankene samt en K_La koefficient. Det er svært at estimere en nøjagtig K_La værdi, hvilket kan ses i denne rapport, hvor flere metoder anvendes med deraf forskellige resultater. Det kan konkluderes at der derfor er usikkerhed i resultaterne i denne rapport.

Det kan konkluderes at sæson ændringer i temperaturen samt ændringer fra parallel drift til serie drift af CAS i slutningen af april, medførte en markant øgning af lattergas emission fra Ejby Mølle.

Overordnet kan det konkluderes at lattergasemissionerne fra MABR i gennemsnit over den målt periode var en størrelsesorden lavere end emissionerne fra atkivt slam anlægget.

3. Introduction

VandCenter Syd is working on quantifying, understanding, and mitigating their greenhouse gas emissions at the Ejby Mølle WRRF, being nitrous oxide (N₂O) one of the most important to consider. Vandcenter Syd partnered with Aarhus Vand in 2017 to demonstrate MABR technology at the Ejby Mølle WWRF. The demonstration started in the summer 2018 and N₂O emissions are being monitored since then. The full-scale demonstration of MABR at Ejby Mølle will allow the comparison of N₂O emissions from MABR and conventional activated sludge treatment. To investigate all of this, an application for MUDP (Miljøteknologisk Udviklings- og Demonstrationsprogram) was applied.

Membrane aerated biofilm reactors (MABR) is a new and upcoming technology that has the potential to help utilities achieve intensive nutrient removal treatment with low energy consumption. This disruptive technology delivers oxygen directly to the active biomass through oxygen permeable membranes, which increases dramatically the oxygen transfer efficiency (Syron & Casey, 2008)The membranes serve also as the biofilm support, which creates a unique counter-diffusional profile. The MABR technology brings together several aspects beneficial for facilities striving to become energy and carbon neutral. The increased oxygen transfer efficiency reduces energy consumption, the fixed biofilm reduces the amount of sludge produced and the combination of both makes possible the intensification of the biological processes, increasing the capacity of the plant and/or reducing its footprint. Moreover, one of the key traits of MABR is its potential to mitigate nitrous oxide emissions, as demonstrated by (Kinh, Suenaga, et al., 2017) and previously by (Pellicer-Nàcher et al., 2010). Its counter-diffusional profile provides a niche for N₂O-reducing bacteria (Kinh, Riya, et al., 2017). The consumption of N₂O by heterotrophs in the outer layers of the biofilm and the bulk liquid, where high carbon concentrations are expected, is where the main mitigation potential of MABR relies.

In 2019, nitrous oxide sensors were also installed in two of the aeration basins of Ejby Mølle for the quantification of nitrous oxide emissions from the conventional activated sludge part of the treatment plant. This report presents results from monitoring nitrous oxide emissions at Ejby Mølle in 2019 from the activated sludge basins and the MABR demonstration pilot.

3.1 Motivation for this project

The purpose of the project is to quantify and understand nitrous oxide emissions from the biological nutrient removal processes at Ejby Mølle. With better understanding of the operations influence on N_2O emissions, better control parameters can be produced.

For utilities, it is no longer enough to reach the required effluent quality, but also to look at overall carbon footprint. Therefore, it is important to develop technologies or/and control parameters to clean the wastewater to the required effluent quality with minimum emissions. The full-scale demonstration of MABR at Ejby Mølle is a potential technology that could remove nitrogen with less use of energy, but also less release of N₂O.

4. Method

4.1 Ejby Mølle process description

The Ejby Mølle WRRF is the largest treatment plant operated by VandCenter Syd. It is located in Odense and was designed for a treatment capacity of 410.000 population equivalents. The treatment consists, among others, in chemically enhanced primary clarification with iron dosage, followed by secondary treatment with activated sludge and tricking filters. In dry weather conditions only a small portion of the flow is treated by the trickling filters. The activated sludge treatment consists on phase-isolated carrousel type of basins for nitrification, denitrification and phosphorus removal. The waste activated sludge passes through mainstream hydrocylones, that separate the light fraction from the heavier fraction (which is returned to the activated sludge system). The final waste activated sludge is treated in mesophilic anaerobic digesters, the reject water from these digesters is treated in a sidestream deammonification reactor and later discharged to the activated sludge basins. Effluent from the activated sludge basins and trickling filters is further treated with sand filtration and re-aerated (if necessary) before its discharge to Odense Å.



Figure 1. Schematic of Ejby Mølle WWTP – not including MABR test facilities

4.1.1 Operational conditions

4.1.1.1 Phase 1 – Operation before the 27th April 2019

Nitrous oxide emissions from the activated sludge treatment were monitored from January to June in 2019. The operational conditions in the basins changed the 27th of April, due to reasons outside of the scope of this project. Phase 1 is the operation of the basins in parallel as described below:

- The four phase-isolated carrousels called LT1, LT2, LT3 and LT4 are operated in two parallel pairs: LT1 and LT2, and LT3 and LT4. We assume the operation of the two pairs is very similar and will focus the study and the rest of this report on LT1 an LT2 only.
- Only one of the two reactors is fed at any given time, it is mainly the ammonia concentration in the tank that defines which of the two reactors gets the feed (there are other parameters that will affect this decision). The feed contains mixed liquor from

the anaerobic zones (return activated sludge and primary effluent), sidestream anammox effluent and trickling filter effluent.

- The reactor getting feed is in "denitrification mode" and therefore aeration is off.
- The reactor not getting feed is in "nitrification mode" and therefore aeration is on. Two dissolved oxygen sensors control the number of rotors in operation, there are six rotors in each tank.
- The reactor in denitrification mode is also the reactor with the outlet weir open, sending the mixed liquor to the secondary clarifiers.
- The reactor in nitrification mode has both inlet and outlet weirs closed.

4.1.1.2 Phase 2 – Operation after the 27th April 2019

During the second phase, after the 27th of April 2019, the conventional activated sludge treatment was changed to run in series mode, as described below:

- The inlet weir at LT1 is open and in LT2 is closed, all the time. The outlet weir is open in LT2 and closed in LT1, all the time. The mixed liquor flows from LT1 to LT2 through internal openings in the walls that separate them.
- This change in operation means both tanks are continuously fed, but aeration is intermittent. Both tanks perform nitrification and denitrification, although LT1, which has the highest ammonia concentrations is aerated most of the time.

4.1.2 Data acquisition

Unisense sensors were installed in LT1 and LT2, one in each tank, in January 2019. They were calibrated every two months following Unisense instructions. The location of the sensors in the basins can be seen in figure 2. Dissolved oxygen, temperature, ammonia, and nitrate concentrations were continuously monitored using online sensors.

To calculate the emissions as percentage of the nitrogen load and nitrogen removal, we used data from the laboratory analysis of 24-hour composite samples of inlet and outlet samples.



Figure 2. Schematic of the aeration tanks at Ejby Mølle and sensor location. (Rotors only shown in the picture on the left, for clarity).

4.1.3 Data analysis

Nitrous oxide emissions were calculated using the methods recommended by Unisense in (Unisense Environment, 2019).

The dataset includes measurements from online sensors at the aeration basins in Ejby Mølle, LT1 and LT2, from the 21st of January 2019 until the 20th of June 2019 recorded every second. Mathematical analysis of the data was performed using R programming software.

The volumetric transfer rates for oxygen and nitrous oxide (g / m^3 / h) are calculated as follows:

$$OTR = \frac{dC_{O_2}}{dt} = K_L a_{O_2} * \left(C_{O_2}^{sat} - C_{O_2}^i \right)$$
(1)

$$NTR = \frac{dC_{N_2O}}{dt} = K_L a_{N_2O} * \left(C_{N_2O}^i - \frac{C_{N_2O}^{iir}}{H_{N_2O}} \right)$$
(2)

Knowing the oxygen concentration and nitrous oxide concentration at any given time, the only unknown parameter is the mass transfer coefficient (Kla), and they are both related to each other as follows:

$$K_L a_{N_2 O (T \ 20 \ ^\circ C)} = K_L a_{O_2 (T \ 20 \ ^\circ C)} * \sqrt{\frac{D_{N_2 O}}{D_{O_2}}} = K_L a_{O_2} * \sqrt{\frac{1.77 \times 10^{-9} \ m^2 s^{-1}}{2.12 \times 10^{-9} \ m^2 s^{-1}}}$$
(3)

$$K_{L}a_{N_{2}O(T \ process)} = K_{L}a_{O_{2}(T \ process)} * \sqrt{\frac{D_{N_{2}O}}{D_{O_{2}}}}$$
(4)

Different ways of calculating this parameter are possible, in this report we tested two methods suggested in (Unisense Environment, 2019).

In a first attempt to calculate the K_La coefficient for N₂O we used the method based on online K_La estimation from dissolved oxygen concentrations. We identified a case where the dissolved oxygen concentration had remained steady for a few minutes before the rotors were turned off, as can be seen in the figure 3 below. We calculated the slope of the curve using linear regression, to determine how much oxygen was used by microorganisms and then assumed than when the oxygen concentration is steady, the oxygen consumption and transfer are equal, therefore being able to calculate oxygen transfer rate (OTR) and K_La for oxygen. According to this method, the K_La for nitrous oxide in the example (from the 25th of January at 11 degrees Celsius) was 0,75 h-1. Which is in the very low range of what we would expect, based on previous experiences at WWTP with surface aerators. The problem with this method in our case, is probably the location of the oxygen sensors. They are far away from the rotors and there is a time delay, as can be seen in figure 3, it takes almost two minutes for the oxygen to start decreasing after the rotors have been turned off. There is also a large gradient of dissolved oxygen (DO) concentrations along the tank, and we calculate K_La using the lowest concentrations possible (furthest away from the rotors), which give us the lowest possible K_La.



Figure 3. Dissolved oxygen concentration in LT1 the 25th January, used to estimate KLa coefficient. Colors represent whether the aeration (rotors) was on or off.

The second and final method, which we have used to report our emissions is based on power consumption.

Based on the general formula for oxygen transfer:

$$OTR = K_L a * (C^* - C_L) \tag{5}$$

Instead of trying to calculate OTR like in the previous method, we used OTR measurements from a previous study done by DHI at Ejby Mølle (Andreasen & DHI, 2010). According to this report, we assume that the actual oxygen transfer only depends on the number of rotors in operation and their depth of submersion.



Figure 4. Oxygen transfer efficiency at different rotor submersion depths. From (Andreasen & DHI, 2010)

Table 1. Summary of results from (Andreasen & DHI, 2010)

%, neddykning	56	51	46.5	42.5	39	33
Neddykning, cm	29.5	27	24.75	22.75	21	18
kW, sum	241	217	208	190	184	153
kW/rotor	40	36	35	32	31	26
IE, kg O2/kWh	1.27	1.36	1.43	1.39	1.45	1.56
OC, kg O2/time	305	296	298	265	266	239
% nedsat effektivitet ift 24.75 cm	12	5	0	3	-1	-9

Tabel 2. Samlet oversigt over effektivitetsmålingerne. kW/rotor er gennemsnit af de 6 rotorer. IE er iltningseffektivitet. OC er iltningskapacitet. Neddykningen er målt under omrøring. Med rotorerne i drift ses en stigning på neddykningen på ca. 1 cm, som skal lægges til styringen under drift.

Again, following the report from DHI, the kW use per rotor (all six) depending on the submersion level follows the next formula:



Figure 5. Correlation between submersion and kW use from the 6 rotors at Ejby Mølle. From (Andreasen & DHI, 2010).

$$y = 3.6182 * x + 37.222 \tag{6}$$

Therefore, the KW per rotor can be calculated dynamically for the whole data set as follows:

$$kW_rotor = \frac{3.6182*\%_{submersion} + 37.222}{6}$$
(7)

The Standard Aeration Efficiency (SAE kg O2/ kWh) can also be found in the report. However, in this case, the SAE was not linear, therefore we will use the value reported for the average submersion level (51%) which is 1.36 kg O2/kWh

The alpha Oxygen Transfer Rate can then be calculated as:

$$\alpha OTR = SAE * number of rotors * kW pr.rotor$$
(8)

Knowing the alpha OTR we can go back to the general formula:

$$\alpha OTR = K_L a * (C^* - C_L) * V \tag{9}$$

And we can calculate dynamically an oxygen K_La value for every data point depending on submersion of the rotor, number of rotors in operation, oxygen saturation concentration (calculated based on temperature) and the actual concentration of oxygen in the process. In this case again, we are using a single value of K_La that should be representative for the whole tank. We know that this is not realistic, but we assume that this value is representative enough.

The following graph (figure 6) shows daily average K_La (h⁻¹) calculated values during the study period in 2019 using two different methods: based on observed oxygen concentrations, the first method described previously; and based on power consumption, which will be used from now on in the report. The great differences in Kla using different methods reveal the high level of uncertainty in the reported emissions from this report.





To calculate the emissions using the K_La values, we used the following formula: $N_2 O \ emissions = K_L a \ _{N2O \ Process \ temp} * C_{N2O} * V$ (10)

We calculated K_La for every data point where the air is on, and we assigned a value of 0.125 h^{-1} when the aeration was off.

4.2 MABR

4.2.1 Process description

The MABR demonstration set up consists of two full-scale MABR units from two different manufacturers. The units are installed in separate tanks next to the aerobic selectors for biological phosphorus removal and fed continuously with mixed liquor from the basins and operated as continuous stirred-tank reactors, as shown in figure 7.

Air for oxygen transfer through the membranes and mixing and scouring of the units is delivered with separate blowers. Air passes through the hollow-fiber membranes, which allow for gas transfer to the biofilm that grows on top of the membranes. The gas transfer across the membranes includes oxygen transfer from the interior of the membranes to the biofilm, and the back diffusion into the membranes of nitrogen gas, carbon dioxide and nitrous oxide. The exhaust air from the membranes is continuously collected for online analysis of the gas.

The MABR tanks perform total nitrogen removal under continuous aeration: nitrification occurs within the biofilm and denitrification occurs partly in the biofilm and partly in the surrounding mixed liquor. Both MABR reactors were operated under similar loading conditions, much higher than the volumetric load in the CAS.



Figure 7. The MABR demonstration setup at Ejby Mølle.

4.2.2 Data acquisition

Nitrous oxide in the MABR reactors is measured in two different fractions: dissolved in the mixed liquor and in the exhaust gas from the membranes.

Dissolved N₂O is measured using Unisense sensors as described previously. Nitrous oxide in the exhaust gas after the membranes is measured using an ABB Gasloq analyser. Ammonia, temperature, and redox potential are also continuously monitored.



Figure 8. Diagram of the sensors at the MABR reactors.

4.2.3 Data analysis

_

Nitrous oxide emissions from the MABR emissions were calculated differently for the two different fractions:

- Mixed liquor nitrous oxide emissions were calculated using the N₂O liquid concentration, a K_La for a non-aerated reactor and the tank volumes, using the formula:

$$NTR = \frac{dC_{N_2O}}{dt} = K_L a_{N_2O} * \left(C_{N_2O}^i - \frac{C_{N_2O}^{dir}}{H_{N_2O}} \right)$$
(11)

Nitrous oxide emissions from the exhaust were calculated using the measured nitrous oxide concentration in parts per million, airflow, temperature and pressure.

5. Results

5.1 Activated sludge

The overall results from the calculation of the nitrous oxide emissions from the activated sludge can be seen in table 2. This table shows the nitrous oxide emissions from all four aeration basins, extrapolated from the results from LT1 and LT2. The results are expressed as percentage of nitrogen in the load and as percentage of nitrogen removed. The nitrogen mass balance was done with official laboratory data from composite samples from the inlet and outlet of the wastewater treatment plant under different assumptions:

- The nitrogen load to the activated sludge equals the nitrogen concentration in the inlet times the flow from the primary clarifier effluent.
- It does not consider the nitrogen removal in the primary clarifier or the nitrogen load to the aeration tanks from the recirculating streams: trickling filter effluent and side-stream anammox effluent.

The average nitrous oxide emissions from the aeration tanks were $13,67 \pm 18,30$ % of the nitrogen load and $15,37 \pm 19,94$ % of the nitrogen removal. A great variation in the data was observed. A more detailed discussion of the results for LT1 and LT2 will be done within the rest of this section.

The resulting N₂O emissions from LT1 and LT2 were very similar during phase 1 and later diverged significantly during phase 2. As can be seen in table 3 the N₂O emissions as kg of nitrogen emitted per day, remained constant in LT2 (approx. 7 kg N per day). In contrast, emissions in LT1 changed from very low values at the beginning of 2019, similar to LT2 (15 kg N per day) to much higher values after the 27th April (262 kg N per day in average). The nitrous oxide concentration in the tanks changed from very low values, less than 0.1mg N/ L in both LT1 and LT2 to much higher values (0,61 mg N / L on average) with a great variability in LT1.

This change appears to correspond to the change in the operational control of the tanks that happened the 27th of April 2019, as was described in the methodology section. Normally, the four aeration basins in Ejby Mølle are operated as phase-isolated reactors (similar to Biodenipho[™]). Tanks LT1 and LT2 are operated in parallel, with only one of the two tanks being fed at the time. The 27th of April, operation control changed to "in series" operation. From that day on, LT1 was fed continuously and the mixed liquor ran from LT1 to LT2 through the internal wall openings and left LT2 towards the secondary clarifiers. Therefore, the tanks changed from receiving the same load and having aeration on a similar fraction of the time, to LT1 receiving all the load and having air on most of the time, passing later to LT2 where the air was mostly off and the tank was in denitrification mode most of the time. As can be seen in table 3 (percentage of time with aeration), both tanks LT1 and LT2 used to have aeration on less than half of the time (approx. 30 % of the time), after the 27th of April, LT1 was aerated (nitrification mode) on average 60 % of the time, and LT2 was only aerated 10 % of the time. However, despite having aeration on more time, the dissolved oxygen concentration was lower in LT1 (0,3 mg /L) than in LT2 (0,9 mg /L) after the 27 of April. This can seem counterintuitive but can be explained by the higher oxygen demand created by feeding LT1 all the time. Operating in series also had an effect in the daily ammonia concentration, from a very steady set-point at approx. 1.3 mg/L, to a higher and more unstable value after May.

As we have seen, all these changes in the operational conditions could be responsible for the changes in N_2O emissions, however, it is also well known, that N_2O emissions are subjected to seasonal variations, with expected higher emissions when the water temperature increases

(Chen et al., 2019). In this case, the higher temperatures coincided with the series operations of the tanks, and it is therefore not possible to quantify the contribution of the temperature increase in the N₂O emission. In future work, we will try to compare the emissions from this study with older data sets from Ejby Mølle, to be able to quantify the season variation expected at this specific location.

An initial exploratory analysis of the data from LT1 using principal component analysis (PCA) can be seen in figure 9, confirms a positive correlation between ammonia concentration, temperature and N₂O concentration, and inverse correlation with DO concentrations. It is also possible to clearly cluster the two groups of data points according to whether the reactor was in parallel or in series operation. However, as explained before, since the changes in operation occurred simultaneously to the changes in temperature, it is not possible to distinguish from this data set what is the contribution from each.

Looking closer at the dynamics on how N_2O was produced in the tanks in figure 10, we can try to understand the production pathways that were predominant at Eiby Mølle. The pattern in the graphs from March in LT1 and LT2 is very similar, both showing very low concentrations of nitrous oxide; in these graphs, nitrous oxide is accumulated during the anoxic periods, but the concentration decreases before the next aeration cycle despite nitrate accumulating in the tank. In the graphs from May 2nd , which correspond to the second phase of operation the patterns are completely different: LT1 has high concentrations of nitrous oxide, which is accumulated during the anoxic periods and it is not denitrified before the next aeration cycle, therefore, when the aeration is turned back on, nitrous oxide is stripped. However, in LT2, which was in denitrification mode most of the time, nitrous oxide concentrations remained very low. We can see in the figures how the N2O concentration decreases when the aeration is on and increases as soon as aeration stops, possibly due to nitrifier denitrification or hydroxylamine production pathways. When the air is off for a sufficient amount of time, as in the 2nd of March in LT1 and LT2 and the 2nd of May in LT2, N₂O concentration decreases again. This nitrous oxide "sink" effect has been widely reported in literature as attributed to heterotrophic denitrification using nitrous oxide as an electron acceptor (Conthe et al., 2019). The PCA analysis also confirmed that the concentration of NO₃ seems to be independent in this case, from the N₂O concentrations and emissions.

Date Temp		Total N ₂ O emissions				
	Celsius	N ₂ O (kg N ₂ O-N/d)	N ₂ O % N load	N ₂ O % N Re- moved		
21-01-2019	10	4,42	0,32	0,36		
05-02-2019	10	7,13	0,39	0,43		
21-02-2019	11	15,23	0,87	0,97		
06-03-2019	10	175,92	18,12	25,98		
13-03-2019	9	1,78	0,17	0,23		
31-03-2019	12	9,00	0,80	0,87		
24-04-2019	13	181,50	10,67	11,26		
02-05-2019	13	768,99	50,27	53,02		
21-05-2019	15	1.206,59	49,39	54,24		
03-06-2019	16	341,61	18,06	20,29		
13-06-2019	16	30,25	1,31	1,36		
Average			13,67	15,37		
Stand. Dev.			18,30	19,94		

Table 2. Results from all four	CAS tanks at Ejby Mølle,	extrapolated from the results
from LT1 and LT2.		

		Days	DO conc	NH4-N	Temp	N ₂ O conc	Time aeration	N ₂ O emissions
				conc			on	
			mg/L	mg N/L	Celsius	mg N L	%	kg N per day
LT1	Phase 1	96	0,59 ± 0,20	1,33 ± 0,13	12	0,07 ± 0,11	33,47 ± 6,94	15,08 ± 37,07
	Phase 2	55	0,32 ± 0,10	1,90 ± 0,72	16	0,61 ± 0,44	57,01 ± 13,99	262,17 ± 208,66
LT2	Phase 1	96	0,73 ± 0,21	1,26 ± 0,12	12	$0,04 \pm 0,06$	29,00 ± 6,52	7,40 ± 10,96
	Phase 2	55	0,87 ± 0,71	1,52 ± 1,17	16	0,06 ± 0,16	11,95 ± 7,82	6,73 ± 15,39

Table 3. Comparison of LT1 and LT2 in the two operation phases of the study.



Figure 9. Principal component analysis of the main variables: ammonia concentration, nitrous oxide concentration, dissolved oxygen concentration and nitrate concentration. The different colors correspond to the two different periods of operation. And cluster plot using the k-means clustering method.



Figure 10. Concentration profiles in LT1 and LT2 the 2nd of March and May of 2019. Ammonia concentration in mg N/L in green, dissolved oxygen in mg /L in orange, nitrate concentration in mg N/L in blue and nitrous oxide concentration in mg N /L in pink.

5.2 MABR

The results presented below are still preliminary and under current investigation. The results show average values from the two demonstration reactors. During the time of this study, January to June 2019, the performance of the reactors was not stable. The ammonia sensors had several technical issues; therefore, the nitrogen removal rates were not fully representative. Moreover, when comparing the emissions from the conventional activated sludge to those of the demonstration study, it worth noting that the MABR was operated under much higher loading rates. The activated sludge had an average hydraulic retention time (HRT) of 26 hours, and the MABR was operated at an average of 3 hours HRT, which means the MABR treated on average more than 8 times more load per m³ than the activated sludge reactors.

Table 4, shows average data from the two reactors for the six months study period in 2019. The average temperature in the reactors was 13 degrees and the hydraulic retention time was 3 hours. The nitrous oxide emissions were measured both in the exhaust gas from the membranes and the mixed liquor in the MABR reactor. The nitrous oxide emissions results are expressed as percentage of the nitrogen load and percentage of the nitrogen removal. The high standard deviation in the results could indicate the presence of errors and outliers in the data. As described before, the ammonia sensors had several technical issues during the study period that affected the nitrogen load and removal rates.

The results, however, reflect the great potential for MABR to achieve very intensive total nitrogen removal with low nitrous oxide emissions. The average N₂O emissions from the mixed liquor were $0,11 \pm 0,30$ percent of the nitrogen load and $0,47 \pm 0,96$ percent of the nitrogen removed; and $0,17 \pm 0,10$ percent of the nitrogen load and $0,77 \pm 1,58$ percent of the nitrogen removed in the exhaust gas. The results from the MABR reactors were on average one order of magnitude lower than those from the activated sludge. Ammonia concentration

Dissolved Oxygen concentration Nitrate concentration

Nitrous Oxide concentration

Table 4. Average N_2O emissions from the MABR reactors from January to June 2019.

	Temp	HRT	N ₂ O emissions		
	Celsius	h	% N Load	% N removal	
Mixed Liquor	10	2	0,11 ± 0,30	0,47 ± 0,96	
Exhaust gas	15	3	0,17 ± 0,10	0,77 ± 1,58	

6. Conclusion and perspectives

The project at Ejby Mølle forms part of a larger investigation performed under the MUDP project. The following findings summarize and represent the investigation performed at Ejby Mølle. The overall conclusion can be summarised in two findings; the emissions from surface aerated CAS systems can be significant, but very difficult to quantify accurately; and MABR technology would appear to have significantly lower emissions compared to CAS systems.

- Nitrous oxide emissions were monitored at Ejby Mølle from January to June 2019 in two different locations: the activated sludge basins and the MABR demonstration pilot reactors.
- Nitrous oxide emissions from the activated sludge basins were calculated from measurements of nitrous oxide concentration in the liquid phase and a mass transfer coefficient parameter: K_La. Two methods were used to calculate the K_La value with different results, there is therefore, a high degree of uncertainty in the results.
- Nitrous oxide emissions from the aeration tanks averaged 13,67 ± 18,30 percentage of the nitrogen load and 15,37 ± 19,94 percentage of the nitrogen removal. A great variation in the data was observed.
- A great increase in nitrous oxide emissions was observed in the data at the end of April 2019, which coincides with both a change in the operation of the tanks from parallel to series and a seasonal increase in the water temperature.
- Principal component analysis of the data was able to explain 73% of the variability in the data within the first two components. Nitrous oxide concentration was positively correlated to the water temperature and the ammonia concentration and negatively to dissolved oxygen concentrations. Nitrate seemed to be independent from nitrous oxide concentration. It was possible to cluster the data in two different groups according to the operational conditions: parallel or series.
- The performance of the MABR reactors during the study period was not stable and there were technical issues related to instrumentation.
- Nitrous oxide emissions from MABR were monitored in the exhaust gas from the membranes and the mixed liquor in the tank and averaged 0,11 ± 0,30 percent of the nitrogen load and 0,47 ± 0,96 percent of the nitrogen removed in the mixed liquor; and 0,17 ± 0,10 percent of the nitrogen load and 0,77 ± 1,58 percent of the nitrogen removed in the exhaust gas.
- Nitrous oxide emissions were on average one order of magnitude lower than those in the conventional activated sludge plant under much higher loading conditions.
- More work in this field is need before accurate emissions from surface aerated CAS systems can be determined.

7. References

- Andreasen, P., & DHI. (2010). Målinger Ejby Mølle Renseanlæg Energibesparelser ved optimering af rotorneddykning og pausedrift på omrører. 37057819.
- Chen, X., Mielczarek, A. T., Habicht, K., Andersen, M. H., Thornberg, D., & Sin, G. (2019). Assessment of Full-Scale N2O Emission Characteristics and Testing of Control Concepts in an Activated Sludge Wastewater Treatment Plant with Alternating Aerobic and Anoxic Phases. *Environmental Science and Technology*, *53*(21), 12485–12494. https://doi.org/10.1021/acs.est.9b04889
- Conthe, M., Lycus, P., Arntzen, M., Ramos da Silva, A., Frostegård, Å., Bakken, L. R., Kleerebezem, R., & van Loosdrecht, M. C. M. (2019). Denitrification as an N2O sink. *Water Research*, 151, 381–387. https://doi.org/10.1016/j.watres.2018.11.087
- Eickemeier, P., Schlömer, S., Farahani, E., Kadner, S., Brunner, S., Baum, I., & Kriemann, B. (2014). Climate Change 2014 Mitigation of Climate Change Working Group III Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.
- Kinh, C. T., Riya, S., Hosomi, M., & Terada, A. (2017). Identification of hotspots for NO and N2O production and consumption in counter- and co-diffusion biofilms for simultaneous nitrification and denitrification. *Bioresource Technology*. https://doi.org/10.1016/j.biortech.2017.08.051
- Kinh, C. T., Suenaga, T., Hori, T., Riya, S., Hosomi, M., Smets, B. F., & Terada, A. (2017). Counter-diffusion biofilms have lower N2O emissions than co-diffusion biofilms during simultaneous nitrification and denitrification: Insights from depth-profile analysis. *Water Research*, *124*, 363–371. https://doi.org/10.1016/j.watres.2017.07.058
- Pellicer-Nàcher, C., Sun, S., Lackner, S., Terada, A., Schreiber, F., Zhou, Q., & Smets, B. F. (2010). Sequential aeration of membrane-aerated biofilm reactors for high-rate autotrophic nitrogen removal: Experimental demonstration. *Environmental Science and Technology*, *44*(19), 7628–7634. https://doi.org/10.1021/es1013467
- Syron, E., & Casey, E. (2008). Membrane-Aerated Biofilms for High Rate Biotreatment: Performance Appraisal, Engineering Principles, Scale-up, and Development Requirements. *Environmental Science & Technology*, *42*(6), 1833–1844. https://doi.org/10.1021/es0719428
- Unisense Environment. (2019). Estimation of mass transfer coefficient and emission of N2O from surface aerator systems.

N2O Emissions from Ejby Mølle - Full-Scale Evaluation of Conventional Activated Sludge and MABR N2O emissions

Vandcenter Syd har på Ejby Mølle i Odense fra januar til juni 2019 målt og overvåget produktionen af lattergas fra et konventionelt anlæg med overflade rotorer samt et MABR-anlæg ("Membrane Aerated Biofilm Reactor"). I to af aktiv slam tankene er der blevet installeret sensorer til måling af koncentrationen af opløst lattergas i vandet. I MABR anlægget er koncentrationen af opløst lattergas samt koncentrationen at lattergas i udløbsgasen fra anlægget målt.

Der er betydelig usikkerhed i resultaterne, men det kan konkluderes, at vandtemperaturen og mængden af ammonium havde en positiv korrelation med lattergaskoncentrationen, og at ændringer fra parallel drift til seriedrift af det konventionelle anlæg medførte en markant forøgelse af lattergasemissionen fra Ejby Mølle.

Samtidig kan det konkluderes, at lattergasemissionerne fra MABR anlægget i gennemsnit over den målte periode var en størrelsesorden lavere end emissionerne fra det konventionelle anlæg med overflade rotorer.



The Danish Environmental Protection Agency Tolderlundsvej 5 5000 Odense C

www.mst.dk