



**CWPharma2**  
CLEAR WATERS FROM PHARMACEUTICALS

## O2.2 Bromate Mitigation

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## 1. Introduction

This CWPharma2 report focusses on the work being done in Kalundborg as part of the CWPharma2 project concerning bromate mitigation. The intention has been to evaluate the possibility of achieving a reduction of the bromate content in the effluent following ozonation in the Kalundborg wastewater treatment plant.

Firstly, the Kalundborg wastewater treatment plant is briefly introduced (section 3). The issue of bromide and bromate and the environmental consequences are put into perspective based on the results of CWPharma and research from the University of Lund, Sweden (sections 4 to 7). Then the actual work in Kalundborg is described and details of measurements etc. are given illustrated and commented (sections 8 to 11).

Finally, actual work in Kalundborg to reduce bromide content are explained, alternative solutions to technical bromate removal/mitigation are mentioned and finally the conclusions and results (sections 12 to 13).

## 2. Summary

The full-scale MBBR facility in Kalundborg was originally not build for this purpose but is has always been a possibility to use the MBBR facility for a post-ozonation bio-based polishing of the ozonated effluent. Substantial support and assistance to Kalundborg Utility was rendered by the partners of KWB and Aarhus University. In spite of this support the goal of performing bromate mitigation by a full-scale MBBR was not achieved. However, valuable experience with the operation of an MBBR facility as a post-ozonation treatment was indeed achieved.

Kalundborg Utility has continued the work with bromate mitigation in the MBBR Kalundborg facility on the basis of the results and experience gained during CWPharma2. Progress has been made and the first test measurements of possible bromate reduction in the MBBR are expected to be during the spring of 2022.

### 3. Introduction to the KCR WWTP

Kalundborg Municipal WWTP (Kalundborg Centrale Renseanlæg) is originally designed to a 50.000 PE capacity. However, due to the high (from about 25 to max. 35 °C) temperature of the incoming industrial wastewater, the max. capacity is probably closer to 148.000 PE.

With variations caused by rainwater in the municipal system around 60 – 70% of the flow to the WWTP originates from local industries. Hence, the wastewater composition is heavily affected by the substantial industrial in-flow to the plant and therefore quite different from traditional WWTP serving only municipal wastewater.

The WWTP is a classical BIO-DENITRO plant with a hydrolysis side stream for biological phosphorus removal. An overview of the plant is seen on the following **Figure 1**.



**Figure 1.** Aerial image of Kalundborg WWTP

The plant consists of a mechanical pre-treatment with a grid and sand filter starting the treatment of the municipal wastewater. Hereafter the water is pumped to the anaerobic pre-tanks in front of the alternating aeration tanks. From the anaerobic pre-tanks, the wastewater and the return sludge are directed to the aeration tanks. In this part of the process the industrial wastewater is now added and therefore bypasses the unnecessary mechanical pre-treatment with grid and sand filter. Originally, the municipal wastewater were mixed with the industrial wastewater before the mechanical pre-treatment. The new process layout started in 2021.

Originally, the aeration tanks were operated as two sets of alternating tanks with two tanks in each set. However, due to hydraulic challenges, the alternating operation has been omitted and the plant is now operated as four tanks in parallel with an equal flow directed to each tank. From the aeration tanks, the total flow is collected in a well, where it is divided for the three secondary clarifiers.

From the clarifiers, the sludge is directed to the sludge pumping station, where both the return sludge pumps and activated sludge pumps are located. The return sludge pumps return the sludge to the side-stream hydrolysis and the anaerobic pre-tanks. The activated sludge pumps direct the activated sludge to the sludge dewatering where it is dewatered to a concentration of about 22 % DS content.

The dewatered sludge is tested and classified as A-sludge and spread on agricultural land and/or woodland as fertilizer. After the secondary clarifiers, the water can be directed to tertiary treatment, which includes the ozonation and a MBBR plant used as post-treatment. Kalundborg WWTP also hold a possibility presently not used of adding Hydrogen Peroxide as an oxidation step to the post treatment following the CAS and the secondary clarifiers. Finally, WWTP effluent is pumped to the other side of the road and from thereon, pumped to the recipient at Sea (The Great Belt/Baltic Sea) by a pipeline.

Due to the nature of the COD received from the industries (mainly inert), the COD/BOD ratio of 4.2 is comparably high. However, nitrogen removal is not affected by this and the effluent demand for 8 mg/l TN is fulfilled. The explanation is probably the sludge age in the plant (> 30 days), which gives the hydrolysis process time to convert the slowly degradable parts of the organic matter into more easily degradable COD.

The ozonation plant, originally designed for COD reduction, consists of two parallel lanes and can treat, in total, up to 1,200 m<sup>3</sup>/h. The two ozone generators, individually coupled to each line, can produce between 7.2 and 90 kg O<sub>3</sub>/h, an ozone dosage between 12 and 150 mg O<sub>3</sub>/l, which, with a DOC content around 15-17 mg/l, corresponds to a specific ozone dose between 0.75 and 9.4 mg O<sub>3</sub>/mg DOC.

Within CWPharma and ever since when the Kalundborg plant has been performing full-stream API removal, liquid oxygen (LOX, 3 x 50 m<sup>3</sup> tanks) was used as the oxygen supply of the ozone generators and the ozone was injected via a pump-injection system.



Ozone reactions take place in three 50 m<sup>3</sup> tanks operated in series (150 m<sup>3</sup> reactor volume per lane), providing a minimum hydraulic retention time of 15 minutes. Automatic process control is used to define a setpoint (constant ozone dose) of the flow-proportional ozone dosage.

Residual ozone in the off gas of the tanks is removed by an ozone destructor unit so it only contains oxygen, which is later used in the hydrolysis tanks for aeration. The intention is that the ozonation effluent is then treated in the MBBR reactor.

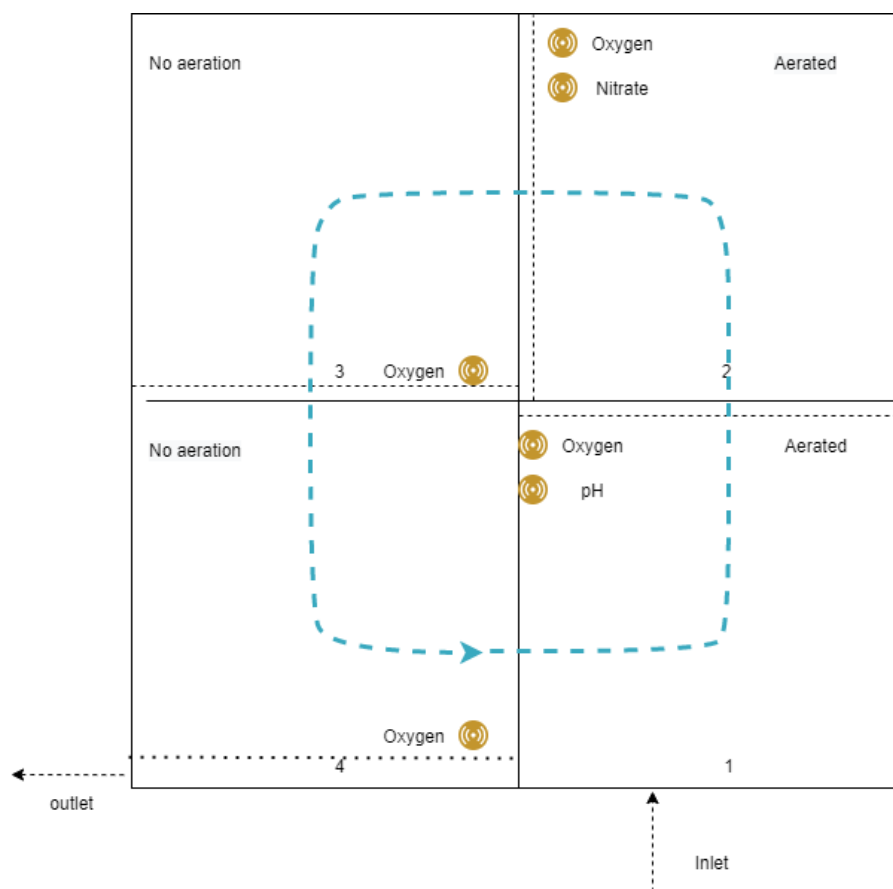
The moving bed bioreactor (MBBR) originally intended for COD removal has a total volume of 1,200 m<sup>3</sup> filled to 25 Vol% with Kaldnes K1 carriers (600 m<sup>3</sup>/t surface area).



**Figure 2.** Picture of the Kalundborg MBBR facility (Picture: Kalundborg Utility)

Total reactor volume is divided into four zones/tanks of 300 m<sup>2</sup>. The inlet of the MBBR is situated in zone one which along with zone two is mechanically aerated. The aeration is designed to strip off residual oxygen in the wastewater. Zone three and four is intended to accommodate for growth of denitrifying bacteria by achieving anaerobic conditions aided by dosing external carbon into tank two.

A schematic overview of the plant is seen in **Figure 3**.



**Figure 3.** Schematic drawing of the Kalundborg MBBR facility with position of online sensors (Kalundborg Utility)

## 4. Bromide in Wastewater and Formation of Bromate

It is well established that if water contains bromide and ozone treatment is used, thus in this process bromate will be produced. The amount of bromate produced will depend on bromide concentration in the water being ozonated and the dose of ozone added in the process.

During the CWPharma project, a dose-response trial <sup>1</sup> was performed in Kalundborg and supplemented with bromide source tracking in the catchment area of the wastewater processed by the Kalundborg WWTP<sup>2</sup>.

<sup>1</sup> Page 18 – CWPharma Report GoA3

<sup>2</sup> Pages 19 – 23 – CWPharma Report GoA3

The investigations revealed that relative high concentrations of bromide<sup>3</sup> are present in the wastewater of Kalundborg and the issue of bromate formation was of importance in Kalundborg. The two main sources of bromide in Kalundborg were an area in the old harbour area in Kalundborg where saltwater intrusion into the old sewage system were documented and residues from industrial processes probably with a main component from biocides added in cooling towers of the industry in Kalundborg. Seasonal variation would apply and the water level in the harbour, which is dependent on weather and tide condition. In broad terms it can be concluded, that on a yearly basis the saltwater intrusion stands for about 60% of the bromide and the rest from the industry about another 40% at present.

Kalundborg Utility has started a dialog with the industry to possibly reduce bromide content in the industrial wastewater. The effect of this endeavour might further be enhanced if the old traditional cooling towers are replaced with the planned District Cooling project presently being set-up as a new part of the Industrial Symbiosis in Kalundborg.

Furthermore, Kalundborg Utility has performed a re-lining and renovation of the sewage system in the specific part of the old harbour to reduce saltwater intrusion substantially into the sewage system also in the event of high-water levels in the harbour.

The area is illustrated in **Figure 4** – the yellow circle markings in the upper left area.



**Figure 4.** Wastewater collection system of Kalundborg with possible bromide sources

<sup>3</sup> 1.73 – 2.68 ppm measured during CWPharma campaigns



These measures will probably substantially reduce the amount of bromide in the wastewater treated at the Kalundborg Plant.

## 5. Bromate, PNEC-values and Toxicity

During ozonation, bromide is converted into bromate and possible bromated halogens. Bromate is known to be carcinogenetic for human beings.<sup>4</sup>

Bromate PNEC values are in general quite low due to high uncertainty and lack of data regarding the toxicity of bromate to aquatic environments. It seems also to be of importance to distinguish with different values to an inland freshwater recipient and outlet of ozone treated water to a saltwater marine environment.

There are few official references to Bromate concentration and PNEC values.

Switzerland operates with a concentration of 50 µg/l in water, which is outlet into freshwater lakes and rivers. Another reference regards bromate as toxic to aquatic organisms, with PNEC(M) = 1.1 µg/l and PNEC(F) = 110 µg/l (uncertainty factor of 1,000 for marine waters and 10 for freshwater).<sup>5</sup>

Following experiments conducted with *acartia tonsa* the marine PNEC value could be increased to 11 µg/l. These figures are still affected by substantial uncertainty on the toxicity of bromate to marine environments. The “safety factor” in the PNEC marine values was reduced from 1000 to 100. However, a security factor of 100 is still substantial.

Kalundborg Utility has established a collaboration project with other utilities and know-how centres as part of the Danish VUDP research and development program, which eventually after much more thorough test procedures will be able to access a bromate PNEC marine value which is significantly less affected by uncertainty and hence could be the future standard. The results from this project would be available probably in the spring of 2022.

## 6. Ozonation, Bromide and Bromate

Ozonation is considered to be one of the rather few reliable methods of treating wastewater for API and micropollutants. The technology used to both produce and inject ozone is reasonably well known, as well as knowledge and operational experience. While ozonation has high consumption of electricity, it is worth mentioning that it can still be both economically- and environmentally favourable if the electricity is produced with sustainability in mind. Dependent on how the electricity being used to produce the ozone and run ozone wastewater treatment

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<sup>4</sup> [https://www.who.int/water\\_sanitation\\_health/dwq/chemicals/bromate030406.pdf](https://www.who.int/water_sanitation_health/dwq/chemicals/bromate030406.pdf)

<sup>5</sup> Steward, M.E., W.J. Biogoslowski, R.Y. Hsu and G.R. Helz (1979) Bt-Products of Oxidative Biocides: Toxicity to Oyster Larvae. (Marine Pollution Bulletin 10(6): 166-169

facilities, the carbon footprint and the economy from choosing ozonation as the wastewater treatment method can be rather favourable.<sup>6</sup>

As part of CWPharma 2, sampling 81 WWTP in the Baltic Sea area was conducted. 34 of these samples were from Danish Wastewater Plants. In this respect, it is remarkable that coastal (less than 5 km from the Sea) WWTP shows a significant higher level of bromide in the inlets to the plants. For the Danish WWTP the median value is 0.43 mg/L with top levels above 0.6 mg/L. For the Kalundborg Plant levels in the inlet has been measured to be between 2.68 and 1.6 mg/L.<sup>7</sup>

Seawater contains an average of 65 mg Br-/l.<sup>8</sup> Saltwater intrusion in a catchment area of a WWTP could with reason be suspected to be the origin of high bromide concentrations in the inlets to a WWTP situated near the coast.

It might be that e.g. the CAS wastewater treatment method is capable of reducing bromide content in wastewater. Anyhow, the levels measured for coastal WWTP is a severe problem in relation to the use of ozonation as a method to reduce API content in wastewater outlet to a marine recipient.

## 7. The Rationale of an MBBR as Post-ozone Treatment

Based on the results of the CWPharma project<sup>9</sup> and research from University of Lund<sup>10</sup> CWPharmaz included a post-ozone treatment stage after the ozone facility at the Kalundborg Plant with a dual purpose.

Firstly, to achieve full-scale replication of the bromate reduction achieved in MBBR laboratory conditions by Lauren Dell at all referred to above.

Secondly, to investigate and optimize in full-scale the possibility of reducing API's further after ozonation as the lab-scale experiments in CWPharma performed by Aarhus University has indicated to be possible.

Examples of the MBBR laboratory experiments in Lund (Laureen Dell)

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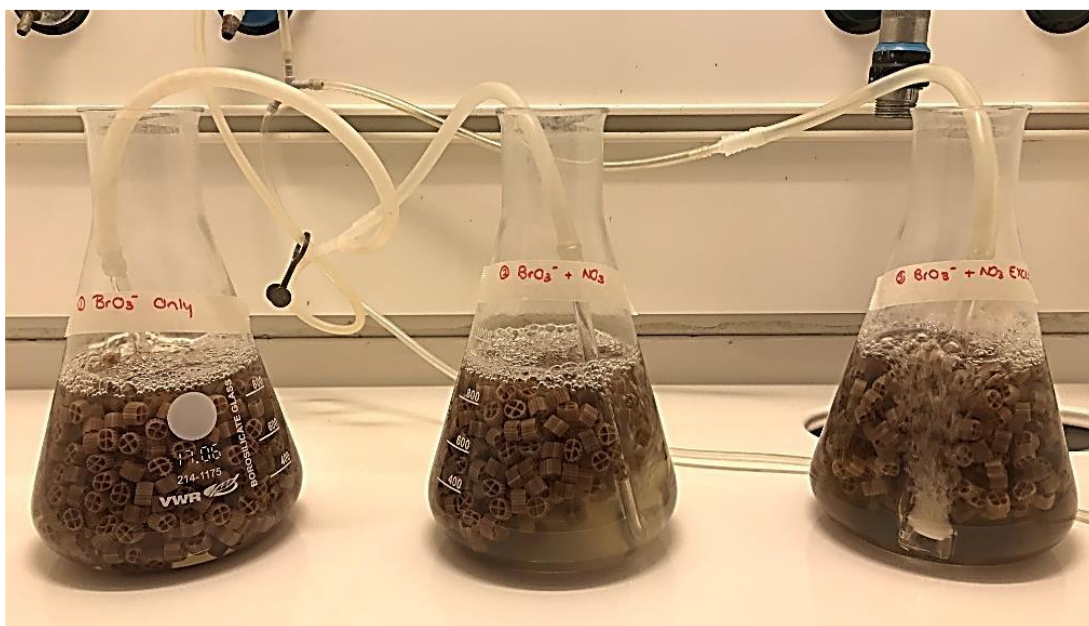
<sup>6</sup> "Äystö, L. & Stapf, M. 2020. Scenarios for reducing pharmaceutical emissions – Estimated load reductions, greenhouse gas emissions & costs. Project CWPharma Activity 5.1 + 5.2 report. Page 35 f.f.

<sup>7</sup> Page 19 – CWPharma Report GoA3

<sup>8</sup> Page 20 – CWPharma report GoA3

<sup>9</sup> Pages 25 – 35 CWPharma report GoA3

<sup>10</sup> In press but not published by Michael Cimbritz, Per Fälas and Lauren Dell



**Figure 5.** Laboratory denitrifying MBRR for bromate reduction

As a first step to achieve bromate reduction, it is necessary to strip-off excess oxygen in the first tank of the MBRR facility. Therefore, this was one of the goals of the CWPharma2 bromate mitigation efforts at the Kalundborg WWT plant.



**Figure 6.** Tank 1 – Kalundborg MBRR facility (Picture: Kalundborg Utility)

## 8. Design of BOD dosing for the Kalundborg MBBR

In a scenario analysis, the amount of BOD needed to achieve a full nitrate removal with and without ozonation was calculated using the water quality parameters at the MBBR influent shown in **Table 1**.

**Table 1.** Concentrations of ammonium (NH<sub>4</sub>), nitrate (NO<sub>3</sub>), and total nitrogen (TN) at the influent of the MBBR between 17.08.2021 and 30.09.2021 (Lab-data).

Date	NH <sub>4</sub> (mg-N/L)	NO <sub>3</sub> (mg-N/L)	TN (mg-N/L)
17.08.2021	1.73	1.10	7.88
19.08.2021	0.77	1.51	7.16
20.08.2021	0.52	1.75	6.41
23.08.2021	0.66	1.41	7.74
26.08.2021	0.89	1.09	8.24
06.09.2021	0.65	9.60	17.04
07.09.2021	1.97	1.10	20.60
08.09.2021	1.77	0.96	12.40
09.09.2021	1.81	1.15	10.40
10.09.2021	1.30	1.29	9.21
15.09.2021	0.34	0.98	6.40
16.09.2021	0.81	0.96	6.27
17.09.2021	0.73	0.75	5.86
20.09.2021	1.00	0.58	7.26
24.09.2021	0.79	1.30	7.28
27.09.2021	1.11	1.48	7.04
30.09.2021	0.76	0.52	5.56
<b>Average</b>	1.04	1.62	8.99

It was assumed that remaining ammonium at the influent of the MBBR (average  $\approx 1$  mg-N/L, **Table 1**) is oxidized to nitrate by consuming 4.3 mgO<sub>2</sub>/mg NH<sub>4</sub>-N. DO concentration at the MBBR with deactivated ozonation was determined to be  $\approx 2$  mgO<sub>2</sub>/L and  $\approx 15$  mgO<sub>2</sub>/L if the ozonation was active. Consequently, only parts of the ammonium can be converted to nitrate ( $\approx 0.5$  mg-N/L) in the first case, whereas all of it can be converted if the ozonation is turned on. Without ozonation, around 10 mg/L of easy degradable COD would be required to remove all nitrate, whereas around 24 mg/L of COD would be required with active ozonation due to the increases DO. At a MBBR flow of 400 m<sup>3</sup>/h, these concentrations would translate to a total C-dosing of 0.86 m<sup>3</sup>/d and 1.95 m<sup>3</sup>/d, respectively (Table 2).

**Table 2.** Expected C-dosing with and without ozonation. Calculations are based on a flow of 400 m<sup>3</sup>/h at the MBBR

Parameter	Unit	w/o ozonation	with ozonation
NH <sub>4</sub> at MBBR influent	mg-N/L	1.0	1.0
DO at MBBR influent	mg O <sub>2</sub> /L	2.0	15.0
NO <sub>3</sub> at MBBR influent	mg-N/L	1.6	1.6
Max. NO <sub>3</sub> increase by nitrification	mg-N/L	0.5	1.0
Max. NO <sub>3</sub> at MBBR	mg-N/L	2.1	2.7
Remaining DO after potential nitrification	mg O <sub>2</sub> /L	0.0	10.5
COD required for denitrification	mg COD/L	10.4	13.3
COD required for DO depletion	mg COD/L	0.0	10.5
Required COD dosing	mg COD/L	10.4	23.8
Required COD mass flow	g COD/h	4169	9529
Required C-dosing, hourly	L/h	35.6	81.4
Required C-dosing, daily	m <sup>3</sup> /d	0.86	1.95

## 9. Results from MBBR operation with and without ozonation

In this chapter, results of the MBBR operation between June 2021 and mid of September 2021 are shown. This period can roughly be divided into two operational conditions:

- MBBR operation without ozonation (01. June – 22. July)
- MBBR operation with ozonation (22. July – 13. September)

Due to the lower DO concentrations at the influent of the MBBR, it was expected that anoxic conditions / denitrification could be reached, whereas more external carbon dosing would be required to keep these anoxic conditions (see also previous chapter).

### Dissolved oxygen:

An overview on the DO concentrations in the different chambers of the MBBR is given in **Figure 7**. During the first phase, DO concentration at the MBBR influent (chamber 1) was on average 1.1 mgO<sub>2</sub>/L and increased to about 2.1 mgO<sub>2</sub>/L in the second chamber, due to a minimal aeration in chamber 1 that keeps the carriers floating. In the last chambers, the measured DO was around 0.5 mgO<sub>2</sub>/L.

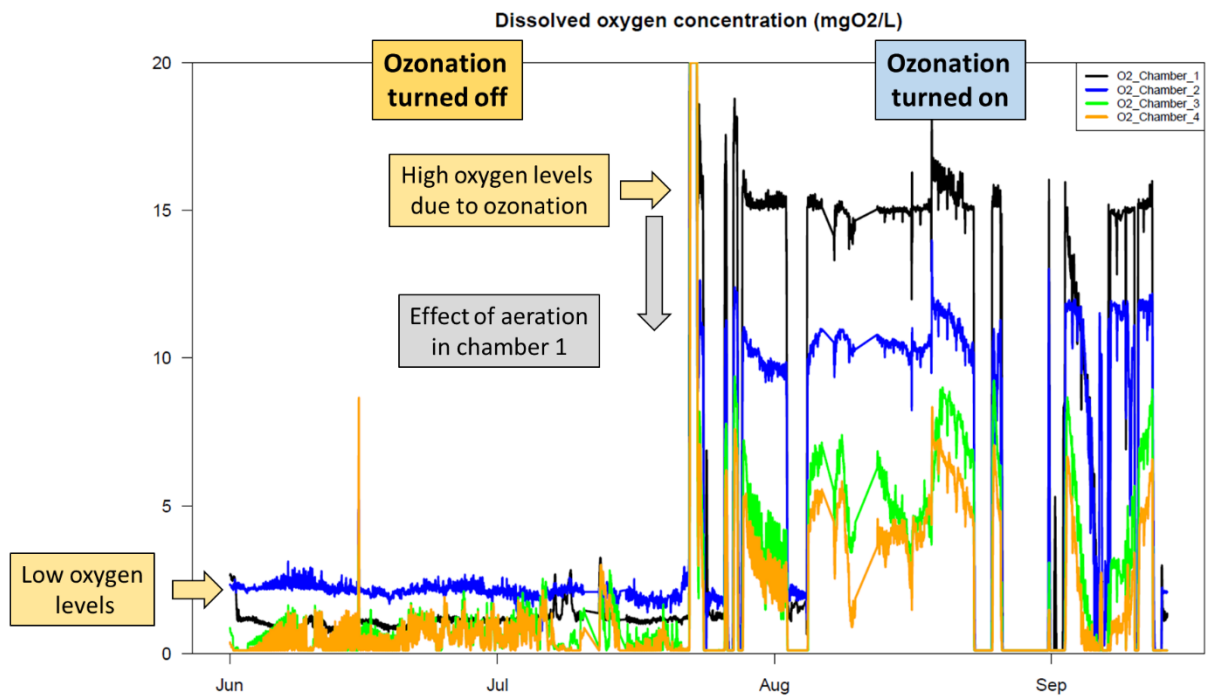
In contrast, in the phase with active ozonation, DO at the influent of the MBBR was about 15 mgO<sub>2</sub>/L. Therefore, aeration of the first chamber was turned on to strip out parts of the oxygen. As a result, DO at the second chamber was at about 10 mgO<sub>2</sub>/L. The DO in chambers 3 and 4



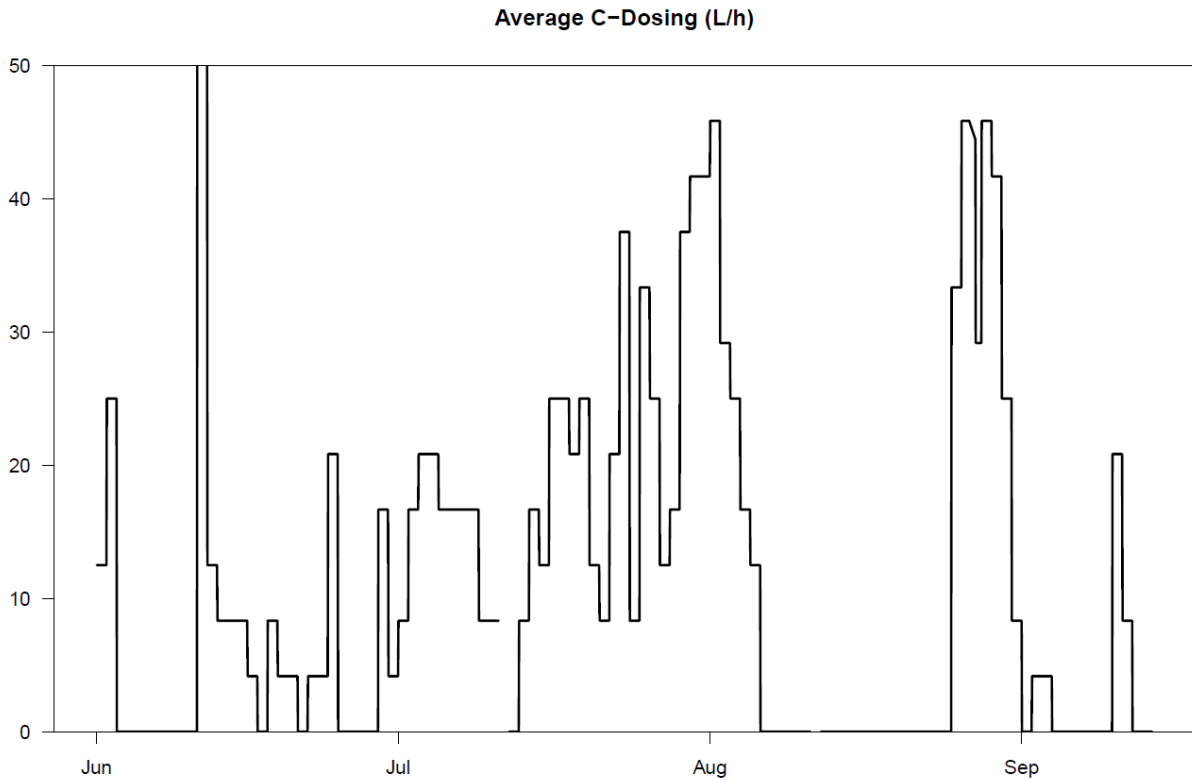
decreased further, however, during this test phase and with active ozonation, it was not possible to reduce the DO below 2 mgO<sub>2</sub>/L due to an insufficient dosing of carbon.

### Carbon dosing:

The real dosing of the external carbon source (10% sugar solution) was not measured online (e.g. flow meter). Consequently, it was not possible to monitor the real dosing and compare it with the according set point during the operation. For the assessment of the MBBR operation, the level sensor (remaining volume of sugar solution in the storage tank) was used to estimate the average carbon dosing per day (**Figure 8**). In the first period (without ozonation), carbon dosage was on around 23 L/h, but with strong variations between the days. During most of August, no carbon was dosed because the storage tank ran empty. In September, also almost no real carbon dosing occurred (e.g. due to technical issues with the pumping / dosing system).



**Figure 7.** Dissolved oxygen concentrations (online measurements) in the different chambers of the MBBR (1 = influent, 4 = effluent).



**Figure 8.** Average daily C-dosing estimated based on the remaining volume in the storage tank.

Comparison of the required carbon dosage with the apparent carbon dosage is shown in **Figure 9**. For that, the following formula was used, which is implemented in the MBBR process control:

$$A = 1000 * \frac{(B + 0.35 * C) * D}{E}$$

With:

A = C-source dose (mL/m<sup>3</sup>)

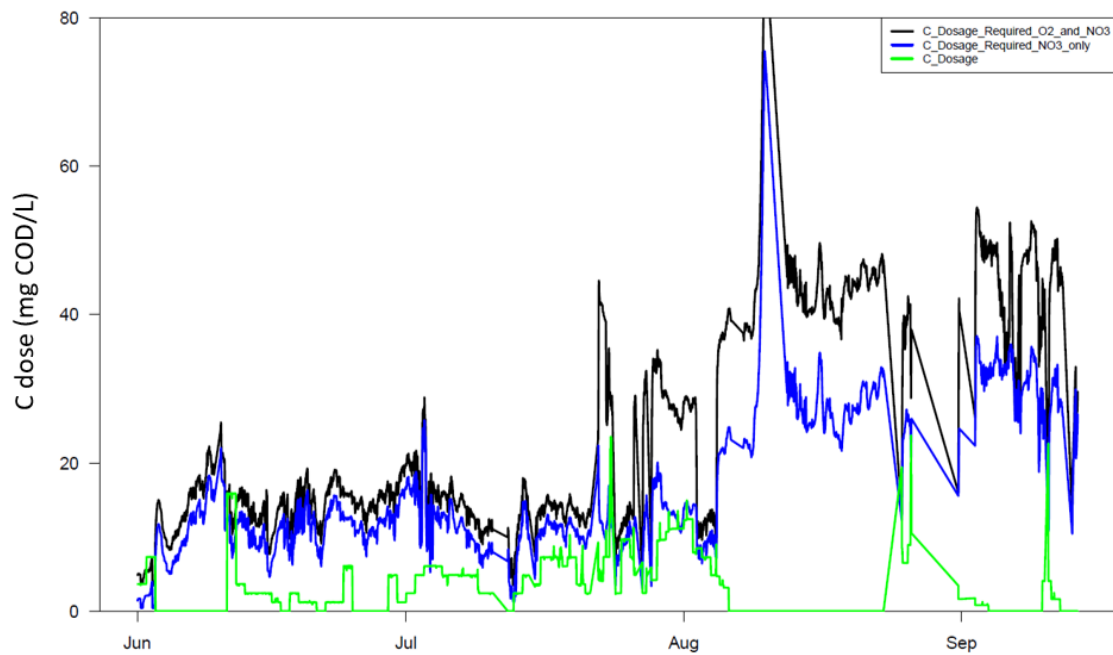
B = Nitrate at the MBBR influent (mg-N/L; online sensor in chamber 2)

C = dissolved oxygen at the MBBR influent (mgO<sub>2</sub>/L; online sensor)

D = C/N ratio (manual input = 4.2 g COD /g NO<sub>3</sub>-N)

E = C-source concentration (= 117 g COD/L, sugar solution)

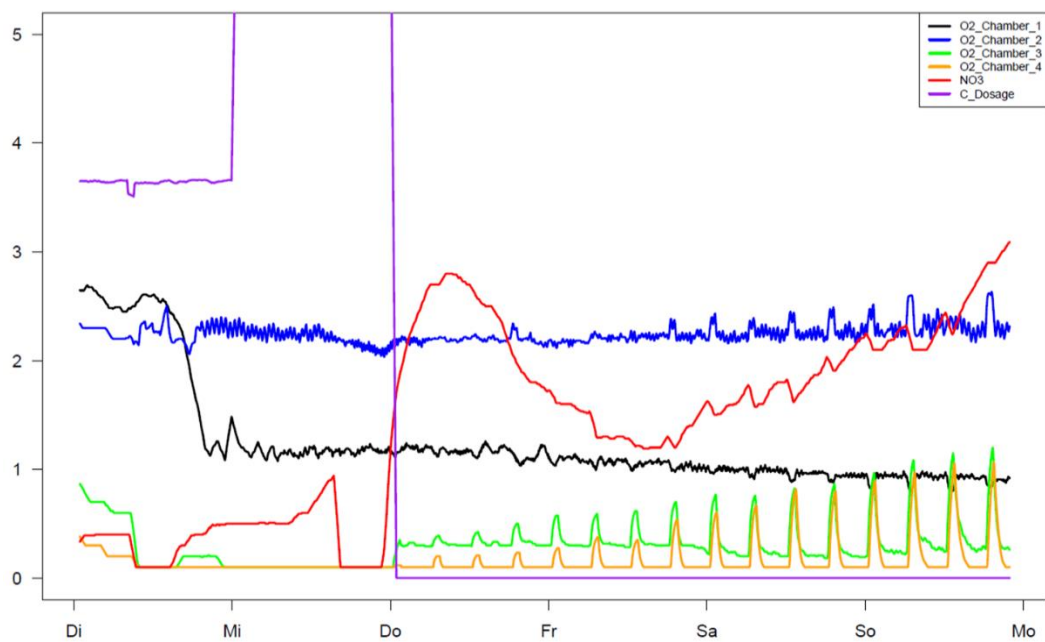
Based on the before mentioned issues, it is not surprising that almost always carbon dosage was too low or even no dosing occurred. Consequently, no anoxic conditions / denitrification was reached. Note that the calculated required carbon doses are here higher than it was estimated in Table 2 especially because of higher concentrations of nitrate measured by the online sensor in chamber 2 with median values of around 2.7 mg-N/L (June – August) and 6 mg-N/L (August – Mid September), respectively.



**Figure 9.** Comparison of the required carbon dosage (blue = only denitrification, black = denitrification and consumption of DO) with the apparent carbon dosage.

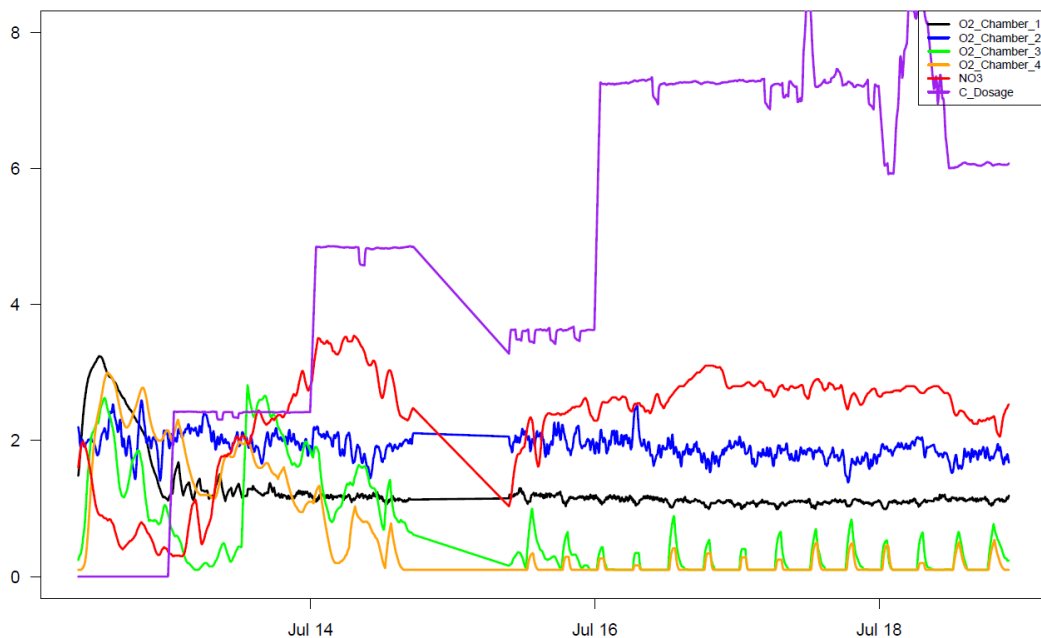
## 10. Some details of the MBBR operation

As shown in **Figure 10**, DO concentrations in chamber 3 and 4 increase simultaneously at a regular interval. This can be attributed to the “grid aeration” that serves the purpose to push back carriers that might be stuck at the grids between the different chambers. In doing so, they increase the DO concentration in the water and contradict the denitrification process. Thus, even though this might only affect local parts of the according MBBR chambers, the grid aeration intervals should be reduced as possible.



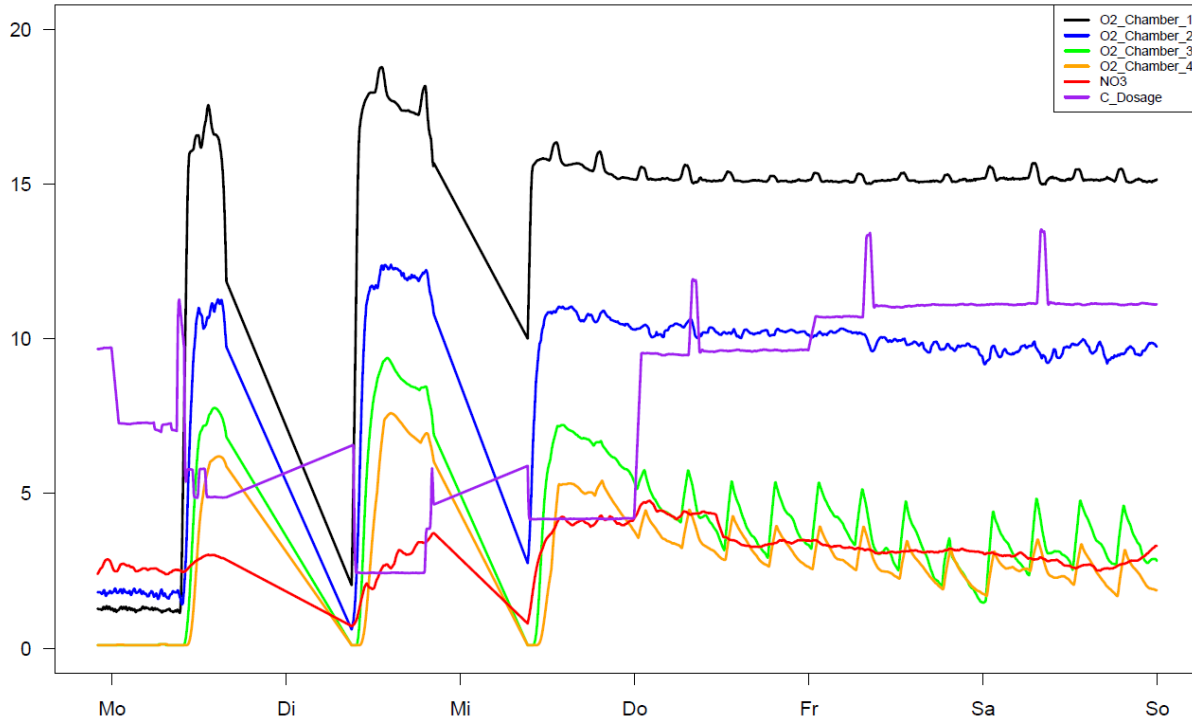
**Figure 10.** DO (mgO<sub>2</sub>/L) and online nitrate (mg-N/L) concentrations along with the estimated carbon dosage (mg COD/L) in the period 01.06.2021 and 06.06.2021.

An example of the impact of the carbon dosage on the remaining DO concentrations during times without ozonation can be seen in **Figure 11**. Over time and with a steady carbon dosing, all DO was consumed in the MBBR besides of the times with an active grid aeration. However, it has to be noted that the influent DO concentration was already very low.



**Figure 11.** DO (mgO<sub>2</sub>/L) and online nitrate (mg-N/L) concentrations along with the estimated carbon dosage (mg COD/L) in the period 12.07.2021 and 19.07.2021.

An example of the impact of the carbon dosage on the remaining DO concentrations during times with ozonation can be seen in **Figure 12**. As mentioned in the beginning of this chapter, DO concentrations at the influent of the MBBR increase from around 1 mgO<sub>2</sub>/L to 15 mgO<sub>2</sub>/L due to the technical oxygen at the ozonation. Aeration in the first chamber strips out parts of the DO, so around 10 mgO<sub>2</sub>/L are present in chamber 2 into which the external carbon was given. The added carbon resulted in a further reduction of the DO to around 2 to 4 mgO<sub>2</sub>/L in chamber 3 and 4, respectively. However, DO could not completely be removed in the MBBR. The up and down of the DO can be attributed to the grid aeration.



**Figure 12.** DO (mgO<sub>2</sub>/L) and online nitrate (mg-N/L) concentrations along with the estimated carbon dosage (mg COD/L) in the period 26.07.2021 and 31.07.2021.



## 11. Measurement and Results from Sampling Campaigns

The wastewater at Kalundborg Utility has an approximately 70% fraction of industrial wastewater, where inert organic compounds are plenty and temperature is high. While the present sludge culture is widely adjusted to this type of wastewater, growing biofilm on the carriers in the MBBR has proven to be a cumbersome task associated with multiple problems.

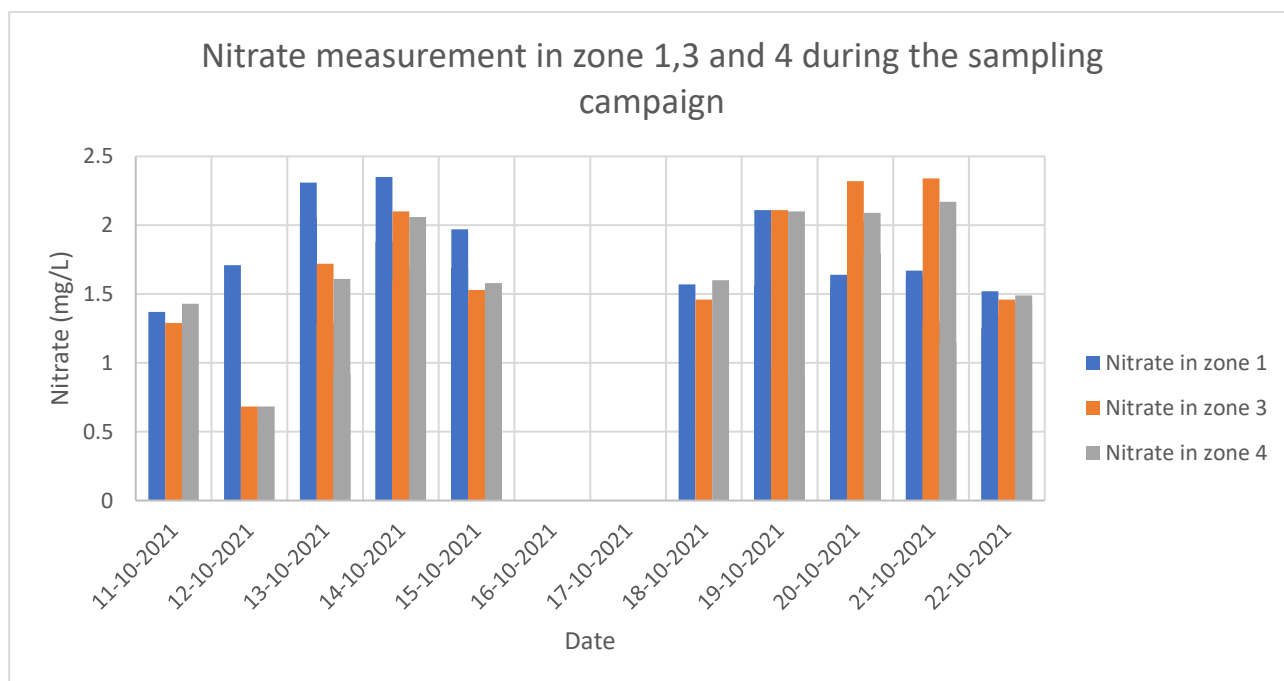
An example of the issues faced at Kalundborg Utility was the carbon dosing. The pumps used to supply external carbon is originally designed for ethanol 23,5% solution containing 471 g COD/L. Ethanol as carbon source was at the time of construction of the MBBR plant supplied through the members of the Kalundborg Industrial Symbiosis at a very reasonable price. However, from 2017 the “waste ethanol” was to be supplied to the biogas industry instead. In the duration of CW-pharma2, ethanol was in high demand due to corona outbreak where disinfectant was produced at a rapid pace to keep up with the excessive demand. In economic terms, ethanol was not only hard to get but also very expensive making long term full scale operation unfeasible, and therefore other options for a carbon source to the MBBR facility were explored.

A waste stream from glucose polymer production diluted into 10% solution containing roughly 117 g COD/L eventually became available. As COD content of the 10% sugar water solution was 4 times lower than the originally intended ethanol source, the original ethanol-dosing pump was required to deliver 4 times the amount of liquid.

After 4-5 months trial and troubleshooting the output of the pump resulted in acquiring a new temporary pump where the carbon dosing was controlled manually. In this trial a 2 week sampling campaign was conducted and early-stage biofilm on the carriers was observed as small filamentous hair strains.

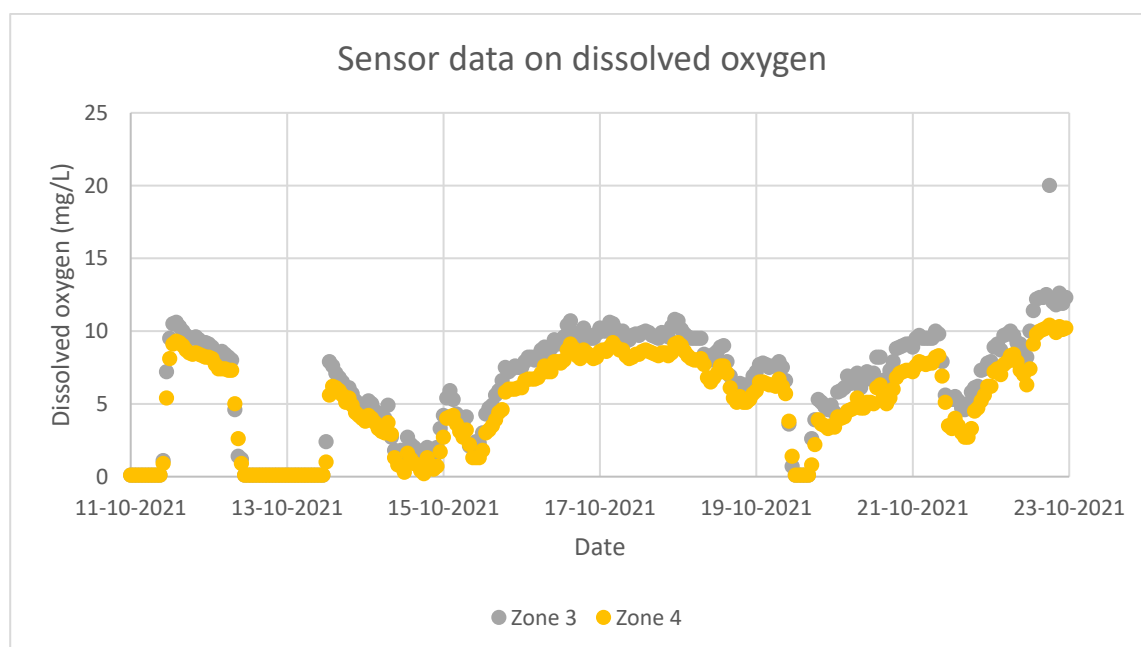
As bromate reduction is dependent on de-nitrifying conditions, the onsite sensing and testing capabilities from Kalundborg utility was used to test whether denitrifying conditions have been reached. Prerequisite for that is the absence of molecular oxygen in the respective tanks and thus nitrate can be reduced to elemental nitrogen. It is especially challenging to reach absence of oxygen as the MBBR is placed downstream to the ozonation plant, which is delivering water over saturated with oxygen.

Thus, the sampling campaign was intended to document denitrification conditions and also to store additional samples for eventual bromate measurement. During the trial campaign grab-samples was taken every morning and late afternoon and COD, ammonium and Nitrate was measured in zone 1,3 and 4. The results of nitrate measurements are seen in **Figure 13**.



**Figure 13.** Nitrate concentrations in the MBBR during the first campaign with dosing of sugar. – Denitrification could not be achieved.

The nitrate level was generally lower in zone 4 compared to zone 1. In-order to tell whether the decrease in nitrate was due to denitrification process, dissolved oxygen level in zone 3 and 4 was also evaluated. (see the results in **Figure 14**)



**Figure 14.** Oxygen concentrations in the MBBR during the first campaign with dosing of xxx sugar. – Denitrification conditions could not be achieved.

When comparing the DO level with nitrate removal there is little evidence documenting the denitrification process. As the DO level was generally quite high in zone 3 and 4. Thus, the results from the two-week sampling campaign did not yield information that could sufficiently document nitrate removal by denitrification. Previous attempts at conducting sampling campaigns were discarded due to unstable supply and function of the ozonation plant caused by a series of unfortunate issues occurring with the transformers of the plant. The combined operational problems with the ozonation plant and the difficulty in finding a suitable carbon source resulted in unstable operation of the ozonation plant and ultimately also the MBBR facility. The “stop-and-go” situations are a severe problem to a biological process, which require stability as a key process element. Dosing enough carbon (BOD) into the MBBR to achieve denitrifying conditions could not be achieved during the test periods.

## 12. Alternative Solutions to Achieve Bromate Mitigation

There has been a focus of handling the issue of bromate in wastewater outlet with attempts to treat or eliminate the bromate. This is the traditional way of handling wastewater issues.

Another possibility would be to prevent the bromide to enter the ozonation tanks. In other words to treat the wastewater for bromide before it is converted to bromate. This can be done either by tracking down and by elimination the sources of bromide and/or to add a specific treatment step elimination the bromide in the inlet to ozonation.

First of all, it is possible to reduce the inflow of wastewater containing bromide. This is done in Kalundborg based on the bromide source tracking which revealed that in Kalundborg there were only two major sources of bromide.

Therefore, Kalundborg Utility has engaged in a dialog with the industry to reduce bromide content and with the municipality to pose legal demands to the industry in relation to connection permits to the public wastewater and sewage system.

Secondly, Kalundborg Utility is also relining the old sewage line in the old harbour area and securing the inlet wells in the same area to resist inflow of saltwater.

Given the high content of bromide to many coastal situated wastewater treatment plants, it seems to highly likely, that this inflow of bromide is caused by intrusion of saltwater to the sewage system. To secure a sewage system against intrusion of saltwater makes sense in many ways and not only as a prerequisite to allow ozonation treatment of the wastewater outlet. Intrusion of seawater causing the levels indicated by the levels of bromide also is a sign of quite significant volumes of seawater, which in many ways would be both a hydraulic and also an economic unnecessary burden for a wastewater treatment plant.

Therefore, the issue of preventing seawater to enter the sewage system seem to be relevant to all wastewater systems near to the coast.

There are strict limits to bromide content in drinking water. Therefore, in this part of the water sector there has been developed methods to reduce or almost totally eliminate bromide. This is done, e.g., when saltwater/seawater is desalinated.

Reverse osmosis is possible method. Also the specific “ion exchange” treatment is offered by the Pyrolite company and other advanced “mechanical” filters might be a possibility. However, this has not been part of this project, but should be mentioned as a possibility worth pursuing further in both practical, operational and economic terms.

## 13. Conclusions and Results

The work with the Kalundborg full-scale MBBR facility during the 12 months of the CWPharma 2 project has given valuable experience on how to operate such a facility and has made it possible to narrow the issues, which have to be solved in order to possibly achieve bromate reduction on the Kalundborg site and in MBBR facilities in general.

A better result would of course have been full-scale operation with actual bromate reduction measured, and a guideline of how to optimize bromate reduction in a MBBR facility. However, as it often has been proved there is a significant difference between Lab-scale test/Lab-scale results and full-scale operation.

In relations to the goals set-up for this part of the project it can be concluded, that:

- A. It has been possible and without major problems to strip the leftover oxygen in the effluent from ozonation. This has been proven to be efficient in the first chamber of the Kalundborg MBBR facility. This has been achieved with retention times of a 1-few hours in the chamber and with aeration and circulation of the effluent in the first chamber. All measures follow the needs of an actual and realistic day-to-day operational situation.
- B. During CWPharma2, it has been possible to expand the collaboration between the partners and use the gained experience during CWPharma about using ozonation as a vehicle for API removal and further optimizing this endeavour both in terms of economy and in terms of technological optimization. During the CWPharma 2 period, substantial fluctuations in electricity prices have occurred and e.g. changed the economy feasibility of making changes and non-technical optimizations in the operation of an ozone facility for wastewater treatment.
- C. Overall, the activities at the Kalundborg MBBR plant have added to the knowledge of how to run an MMBR facility on highly treated effluent. There is very limited operational experience available when it comes to running a full-scale MBBR facility on effluent already treated with a highly optimized BIODENITRO process and then further supplemented with ozonation. Such a running situation is substantially different from the original intentions of the operation of an MBBR plant. The test carried out in

Kalundborg has not led to a final conclusion of how to run an MBBR facility and achieved bromate reduction but has during a trial-and-error process eliminated strategies with now can be exclude and gradually narrowed the possible operational strategies down to a limited set of possibilities. If it has been possible to run this process further for a few months, or if the project has not been affected by the difficulties and abnormal prices for a relevant carbon source, then it is likely, that the CWPharma 2 project would have been able to achieve a conclusion on bromate mitigation and MBBR facilities. In this respect, it must be noted that it is not given that lab results can be replicated to full-scale situation – and it is a possibility, that it is too difficult under practical operational situations to achieve the necessary bromate reduction in a full-scale MBBR facility. Sometimes very long retention times have proved to be a possibility to make MBBRs to function. However, a retention time above 3-4 hours is not a de facto operation possibility, as it would result in the need to build much larger and therefore more expensive MBBR plants.

- D. It was not possible during the CWPharmaz period to make the MBBR running with a stable and sufficient bacteria film on the carriers of the MBBR plant. Without such a stable bacteria film it is not possible to establish the circumstances necessary to have bromate reduction in the MBBR plant.

The Kalundborg team continued to work with the issues of the MBBR facility based on the experience during the project. In the later phase of writing this report, the Kalundborg Team achieved a stable and documented bacteria film on the carriers in all four tanks of the Kalundborg MBBR facility. Kalundborg utility will be continuing the work on a possible bromate reduction and doing this in collaboration with Anox-Kaldnes and a Swedish WWTP also attempting to use MBBR as a post ozonation treatment possibility and are in regular contact with the partners of the CWPharmaz project.