CWPharma

CLEAR WATERS FROM PHARMACEUTICALS

Evaluation and experiences of full-scale ozonation followed by MBBR post-treatment and comparison with previous pilot tests

GoA3.1: Pharmaceutical removal at full scale

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Introduction

Background

This study was conducted within the framework of the project Clear Waters from Pharmaceuticals (CWPharma) that was funded by EU's Interreg Baltic Sea region programme. Overall aim of CWPharma is to provide tools and recommendations to policy makers, authorities and municipalities on how to reduce the load of active pharmaceutical ingredients (APIs), which enter the aquatic environment and especially the Baltic Sea.

Municipal wastewater treatment plants (WWTPs) are relevant point sources of APIs as they treat wastewater from public households, hospitals and industry of the connected catchment area. Conventional "state-of-the-art" WWTPs can only remove APIs that are either easily biodegradable and/or absorbable to activated sludge, whereas persistent APIs can pass the WWTP with minor or no reduction. Main technologies for the reduction of a broad range of APIs are treatment with activated carbon (powdered or granular) or ozonation. Ozone is a strong oxidising agent with a high reactivity that has to be produced on site. At usual applied ozone doses, ozonation of secondary effluent does not result in a mineralization (conversion of an organic substance into inorganic matter) but in a transformation of organic compounds into smaller and (usually) easier biodegradable compounds. Thus, for their degradation, ozonation plants are commonly operated in combination with a biological post-treatment.

Objective of CWPharma's work package 3 is the demonstration of advanced treatment techniques and to provide knowledge on how to operate them in the best way. This report summarizes the experiences from the operation of a full-scale ozonation plant with moving bed bioreactor (MBBR) at the Swedish WWTP Nykvarnsverket in Linköping.

From pilot to full-scale ozonation at Nykvarnsverket

In 2014 Tekniska verken i Linköping AB (TVAB) conducted a pilot study (Sehlén et al., 2015) at the WWTP Nykvarnsverket in Linköping in order to investigate the potential for an ozonation process to remove pharmaceuticals. A significant reduction of pharmaceuticals was obtained and neither major adverse effects on the post-denitrification MBBR process nor ecotoxicological effects on the wastewater were observed. This contributed to the decision of the board of TVAB to build a full-scale ozonation plant at WWTP Nykvarnsverket.

During 2015 discussions with ozone equipment suppliers and study visits at existing ozonation plants (e.g. Bad Sassendorf and Duisburg-Vierlinden, Germany) were conducted. Due to earlier problems with iron deposits on online sensors and diffusers, it was decided to use a side stream ozone injection instead of diffusers. Based on results from the pilot study, the nominal ozone production capacity was set to 20 kg ozone/h. It was also decided to use secondary effluent as cooling water for the ozone generator and to by-pass the ozonation plant when the concentration of suspended solids (SS) exceeded a certain limit. It was decided during projecting to set the limit to 10 mg SS/L in order to avoid excess foaming in the reactor and off-gas system and also to avoid a possible blockage of the cooling water filter and the ozone injection system. It is not considered a problem with 10 mg/L soft particles but the injection system can be blocked by larger debris.

In 2015 the post-denitrification MBBR was rebuilt to increase the nitrogen removal capacity. The total reactor volume was increased by 166 % split into three lines with 4 reactors in series. The total carrier volume was increased by 156 %. The two first reactors, in each line was designed for post nitrification using residual dissolved oxygen from the ozonation plant. Pump capacity, valves and pipes was prepared to be able to connect the ozonation plant when it was constructed.

In parallel, different ozone reactor designs were evaluated by CFD simulations in order to obtain an optimal process solution to dissolve ozone as efficiently as possible and to create a plug flow ensuring that all ozone will completely depleted before reaching the reactor effluent.

There was not enough power supply at the wastewater treatment plant to supply the ozone plant and a new power supply unit had to be built (300 kW).

Procurement of the ozone process, construction work and power supply was done in parallel.

In 2016, the construction work on the ozone reactor and the machine house started and in September 2017 the full-scale plant was inaugurated by the minister of environment in Sweden.

Activities

The main objective of CWPharma's group of activity (GoA) 3.1 was the evaluation and process optimization of the full-scale ozonation system at the wastewater treatment plant in Linköping. This objective has been conducted with the following activities:

- Evaluation of a full-scale ozonation system and validation of the prior pilot study
- Demonstration and optimization of different control strategies for a stable and economic pharmaceutical removal
- Monitoring of relevant pharmaceuticals
- Conduction of sampling campaigns for an ecotoxicological assessment of the ozonation and MBBR post-treatment
- Close co-operation with the local water authority in order to evaluate the outcomes in respect of adequate risk reduction
- Exchange of information with operators of other full- or large-scale ozonation systems

Description of the wastewater treatment plant in Linköping

The full-scale ozonation plant is a part of the WWTP Nykvarnsverket that is located in Linköping next to the river Stångån. Nykvarnsverket treats about 40,000 m³/d with an average flow of 1,700 m³/h and a load equivalent to 211,000 PE. In 2019, an average BOD_7 of 350 mg/L, TOC of 180 mg/L, P-tot of 5.2 mg/L and N-tot of 52 mg/L was measured in the influent water to the WWTP. The treatment process consists of mechanical treatment (screens, grit chamber, pre-aeration and pre-sedimentation), biological treatment (activated sludge process), ozonation, nitrogen treatment (MBBR reactors for nitrification and denitrification) and chemical treatment (phosphorous removal). An overview of the plant is shown in Figure 1.

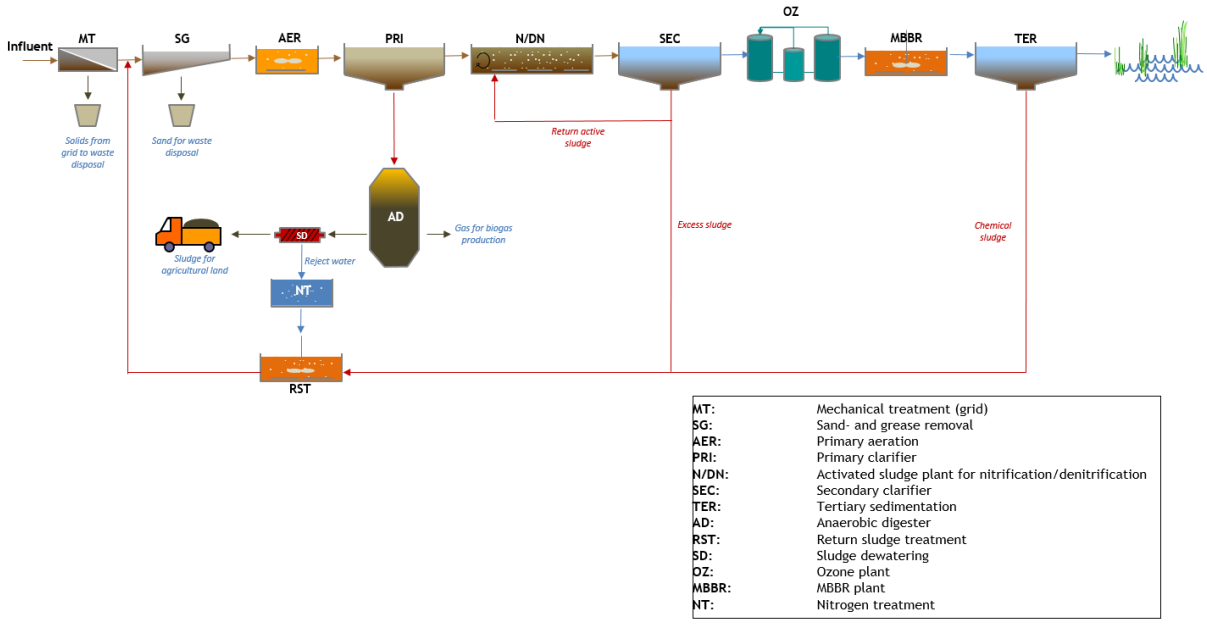

Figure 1: Overview of the WWTP Nykvarnsverket in Linköping.

Ozonation and MBBR plant

An overview of the ozonation plant and the MBBR post-treatment is shown in Figure 2.

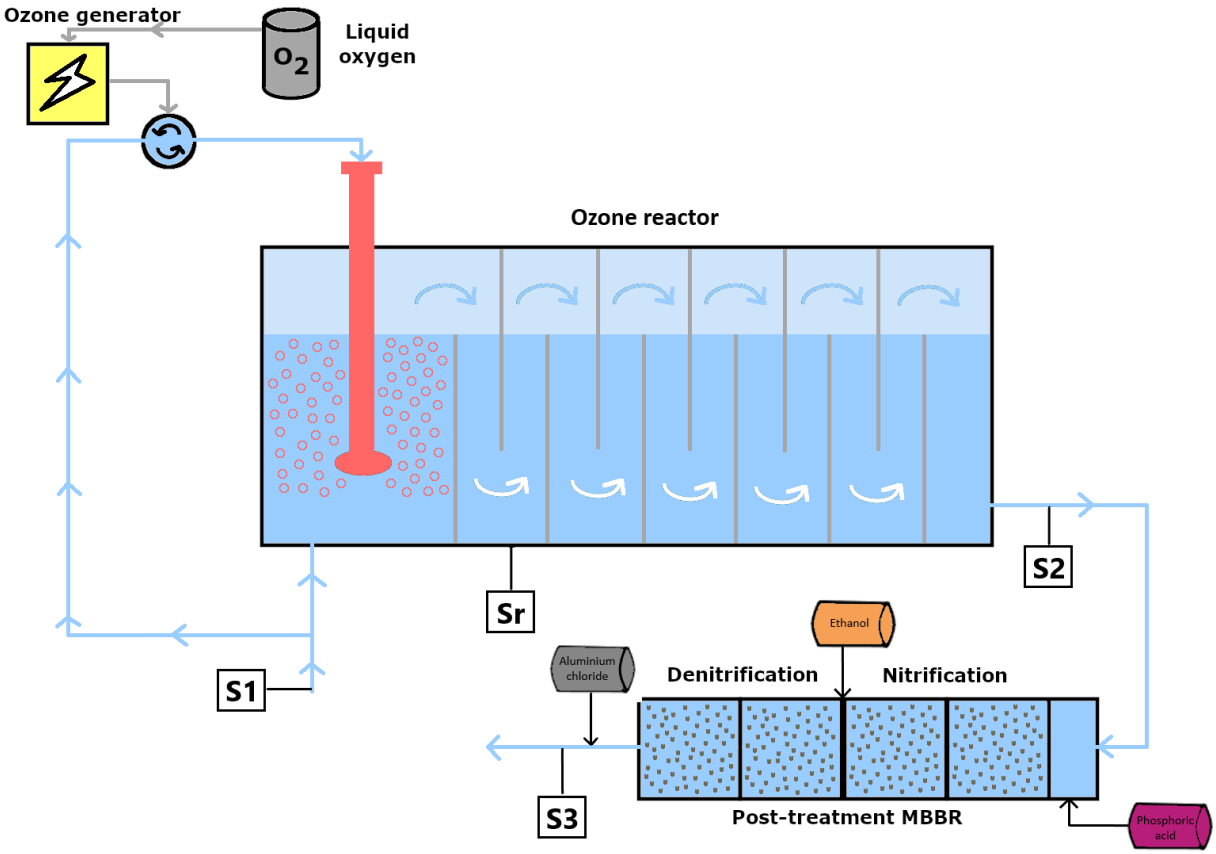

Figure 2: Overview of ozonation and MBBR process in Linköping. Four different sampling points are marked: S1 (before ozonation), S2 (after ozonation), S3 (after MBBR post-treatment) and Sr (first chamber of the ozone reactor).

The ozonation plant can treat up to 3,000 m³/h of secondary effluent with a maximum ozone production of 20 kg O_3/h (CFV30, Ozonia, Figure 3(b)). The volume of the ozone reactor is 524 m³, with a hydraulic retention time (HRT) between 10-60 min depending on the flow (yearly average water flow of 1700 m³/h contributes to a HRT of 18 min). Ozone is generated from liquid oxygen and is mixed into a side-stream from the secondary effluent that has a constant flow of around 140 m³/h. The ozone enriched water is injected into the ozone reactor by a radial diffuser (Ozonia patent) and mixed with the mainstream of the secondary effluent. Most of the ozone reactions occur immediately after injection. The ozonized wastewater then flows through a series of chambers while the dissolved ozone concentration is declining. No measurable concentration of dissolved ozone has been detected at the effluent of the ozone reactor. Several sensors are placed before and after the ozone reactor as well as after the first chamber of the ozone reactor to measure parameters online , e.g. water flow (S1), turbidity (S1), pre-filtered UVA_{254} (S1 and S2), dissolved ozone (Sr) and oxygen concentration (S2). There are also sensors necessary for the operation of the ozone reactor, e.g. to measure gas flow, ozone concentration in the process gas and off-gas as well as gas and water pressures. A description of the online sensors is in Table 9 in Appendix.

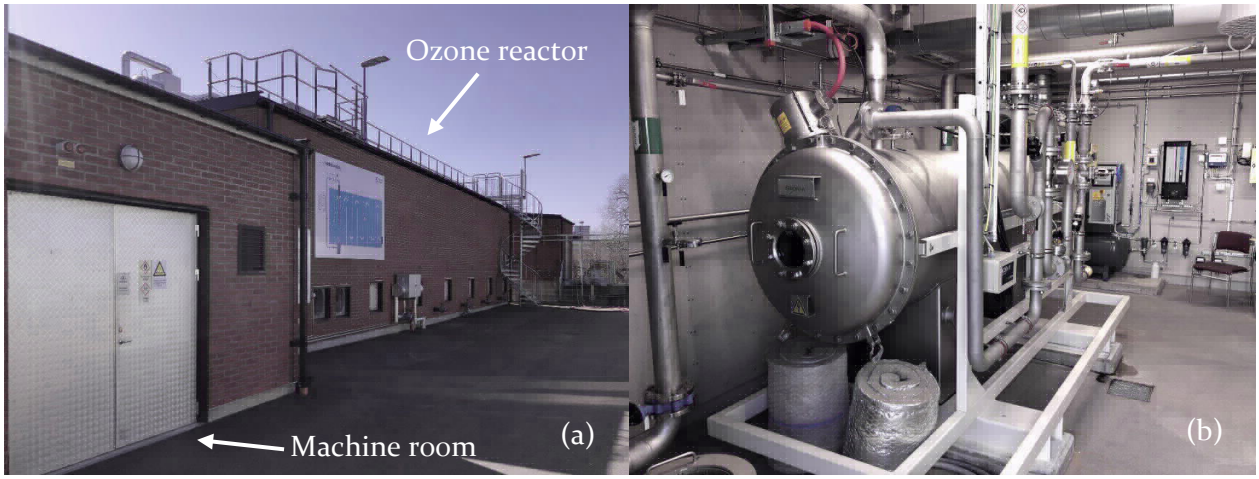

Figure 3: (a) Ozonation plant in Linköping. (b) Ozone generator model CFV30 from Ozonia.

The MBBR plant (Figure 4) consists of three separate lines with four reactors in each line. In total, the MBBR contains around 600 million carriers contributing to a surface of 520,000 m^2 with a filling ratio of 39 % (70 % HXF 12 KLL carriers and 30 % K1 carriers). The total volume is 3 x 740 m^3 = 2,200 m^3, giving a HRT between 45 min – 4.5 hours (yearly average water flow of 1700 m^3/h contributes to a HRT of about 80 min). Since the MBBR is located directly after the ozonation, the dissolved oxygen concentration is high (15- 20 mg O_2/L) in the first MBBR reactors. Generally, nitrification and other oxygen-consuming reactions occur in the two first reactors of each line. When the phosphate concentration in the secondary effluent is low, phosphoric acid is added at the influent of the MBBR to supply the growth of nitrification bacteria. Denitrification occurs in the two last reactors and ethanol is added as carbon source. Aluminium chloride is added directly after the last reactors in MBBR (before the sampling point S3) to precipitate remaining phosphorous and to flocculate suspended solids, which are removed in the tertiary clarifier.

Figure 4: Panorama view of the MBBR plant in Linköping consisting of three separate lines with four reactors (2 x nitrification, 2 x denitrification) in each line.

Evaluation of a full-scale ozonation system

The ozonation plant in Linköping was the first full-scale facility in Sweden. There are no standard operating procedures for API elimination at WWTPs. Therefore, the full-scale ozonation plant has not only been studied in order to investigate the reduction of APIs and other substances but also to evaluate the plug flow and other properties of the plant.

Dose-response test

Three different sampling campaigns with dose-response tests have been performed during autumn 2018, spring 2019 and summer 2019. In each test, the ozone doses ranged from 4 to 10 mg O_3/L in order to evaluate the impact of the ozone dose on the API elimination.

Besides API elimination, several water quality parameters have been measured: dissolved organic carbon (DOC), total organic carbon (TOC), chemical oxygen demand (COD), suspended solids (SS), nitrite, nitrate, phosphate, pH, conductivity, alkalinity, ultraviolet absorbance (UVA_{254}), fluorescence (fDOM), bromide and bromate. Methods used for analysis of the different parameters are highlighted in Table 8 in the appendix.

Nitrite and nitrate

Nitrite (NO_2-N) is formed during incomplete nitrification or denitrification in the biological treatment process prior to the ozonation. Nitrite consumes ozone and is oxidized to nitrate (NO_3-N) at a much faster reaction rate (~10^5 $M^{-1}s^{-1}$) compared to many of the investigated APIs. Thus, parts of the applied ozone are consumed if nitrite is present in the ozonation influent (3.43 mg O_3 is required to oxidize 1 mg NO_2-N) and less ozone is left for API elimination. Usually, no nitrite can be detected in the ozonation effluent. Surprisingly, during the operation of the ozonation plant all the effluent samples of the ozonation plant (S2) contained nitrite in the range between 0.2 and 0.8 mg NO_2-N/L. Thus, corresponding grab samples were taken before, in and after the ozone reactor. Results showed that nitrite present at the reactor influent (S1) was removed at the end of the first chamber of the ozone reactor (Sr). Still nitrite could be detected at the effluent of the ozone reactor (S2). These findings either indicate that nitrite is formed in the last chambers of the ozone reactor or that a part of the wastewater passed through the reactor without a reaction with ozone. Tracer tests showed that the plug flow in the ozone reactor is efficient and, thus, no large amount of wastewater should pass through the reactor without an ozone reaction. It is therefore more likely that a formation of nitrite occurred in the last chambers, which is not inconceivable since the wastewater contains ammonia and the oxygen concentration in the ozone reactor is high. Additional investigations were conducted to ensure that sample handling or storage has not influenced the results. Since nitrite was always removed at sampling point Sr, only nitrite concentration in the secondary effluent was considered for the evaluation of the nitrite corrected ozone dose (instead of the difference between influent and effluent of the ozonation plant).

DOC, TOC and COD

DOC and TOC represent the amount of organic compounds in the wastewater. DOC is often used to normalize the ozone dose when comparing results from different studies and facilities because DOC contributes to the ozone demand. COD is a parameter to measure the oxygen demand in the water which includes the oxidability of both organic and inorganic compounds. However, no clear pattern could be observed when measuring COD at the full-scale plant. DOC concentrations measured during the dose-response sampling campaigns are plotted in Figure 5.

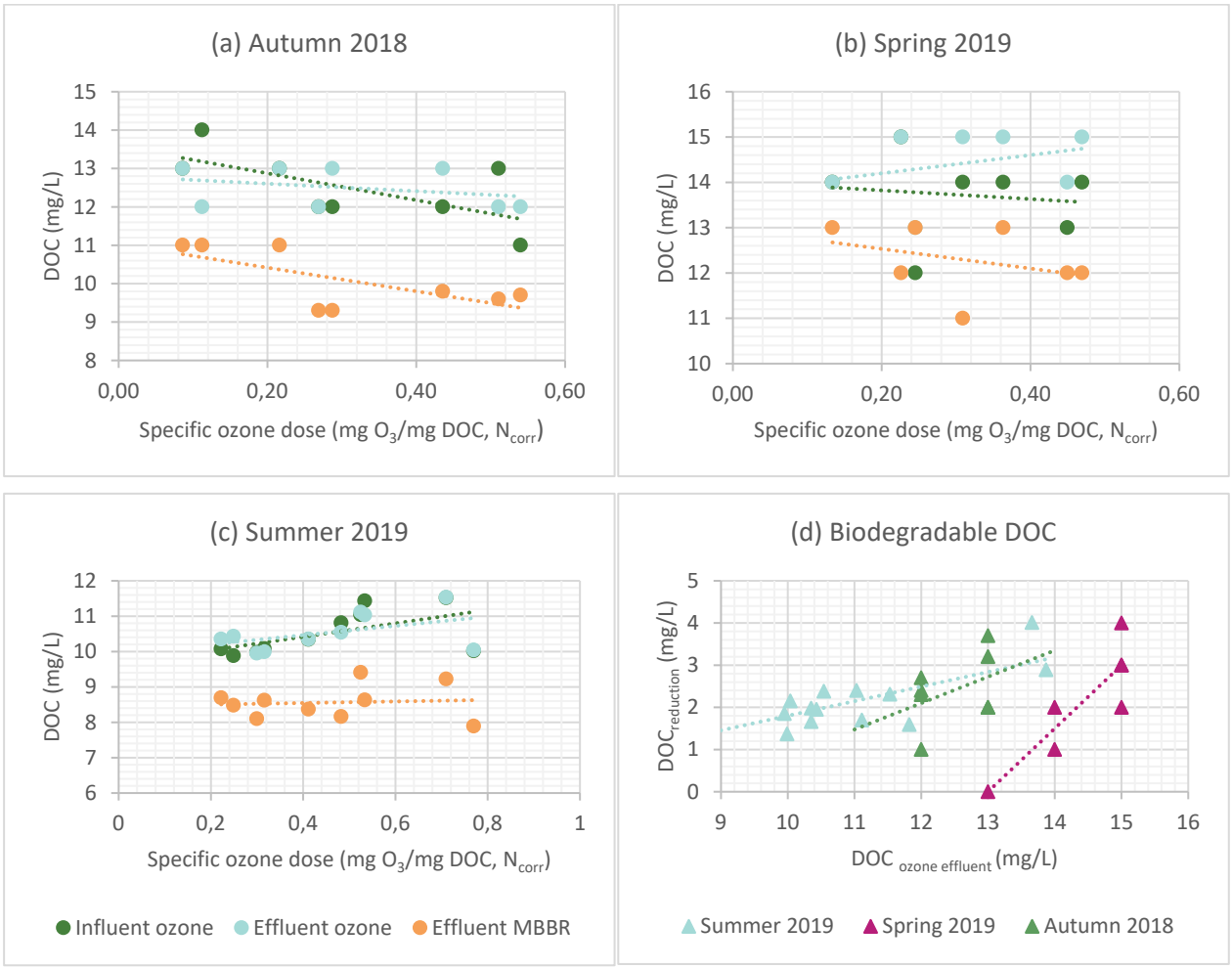

Figure 5: DOC concentrations at the ozonation influent, ozonation effluent, and MBBR effluent measured in the three sampling campaigns during autumn 2018 (a), spring 2019 (b) and summer 2019 (c). The specific ozone concentration on the X-axis only relates to effluent ozone and effluent MBBR. In figure (d) the absolute reduction of DOC concentration by the MBBR process is plotted against the DOC concentration at the ozonation effluent.

The concentration of DOC in the ozone influent (secondary effluent) varies quite much over the seasons (10-14 mg/L) and has also a weekly and diurnal variation. The variation of the DOC concentration in the secondary effluent is related to the variation in biological activity in the upstream activated sludge process, due to temperature and flow variations, and also the variation of the DOC load entering the WWTP.

It is a known fact that DOC consumes ozone, but no significant changes in DOC concentration can be seen when comparing the concentrations at the influent and effluent of the ozonation plant (Figure 5 (a)-(c)). However, at the applied ozone doses neither a transition of particulate TOC into DOC (would result in an increase) nor a mineralization (would result in a decrease) was expected. In autumn 2018 and spring 2019, DOC seemed to decrease with increasing ozone dose after the MBBR, whereas in summer 2019 the DOC concentration in the effluent of the MBBR did not seem to depend on the ozone dose (Figure 5 (c)). During summer, effluent BOD and DOC are normally very low. The remaining DOC might be more inert, which would explain why there was no ozone dose dependency in the effluent MBBR concentration in summer. In Figure 5 (d) the absolute DOC reduction over the MBBR process is plotted against the ozone effluent concentration for all three seasons. The absolute reduction of DOC seems to depend on the amount of DOC in the ozone reactor effluent.

Ultraviolet absorbance and fluorescence

Various aromatic compounds that ozone react with, e.g. bulk DOC or APIs, absorb ultraviolet light. The presence of organic material can also affect the fluorescence intensity. Therefore fluorescent dissolved organic material (fDOM) and UVA_{254} were measured. Correlations between ozone dose and reduction of UVA_{254} and fluorescence were observed in the dose-response tests. The results are presented in section "Process control strategies".

Suspended solids

Grab samples collected before and after ozonation indicated that the ozonation process decreased the concentration of suspended solids (SS), but no correlation with the ozone dose was observed. Foaming problems occur in the ozone reactor when the wastewater has high concentration of SS. Therefore, the ozonation plant is automatically shut down when the concentration exceeds a chosen set point of 10 mg SS/L. See also separate chapter about foaming.

Phosphate

During the pilot study, the concentration of dissolved total phosphorous increased after ozonation at high ozone doses (10 – 23 mg O_3/L). When organic material is degraded by ozonation, it can be expected that organic bound compounds such as phosphate are dissolved in the water. However, no increase of phosphate during ozonation could be observed with the ozone doses produced at the full-scale facility.

Alkalinity and conductivity

Alkalinity is the pH-buffer capacity of water. It is an important water quality parameter to measure as it can give an indication of process disturbances. However, in this study alkalinity was not affected or did affect the ozonation process. Conductivity is the capacity of water to conduct electricity, which is related to the amount of dissolved inorganic salts. However, no interaction between ozonation and conductivity could be observed.

Comparison of different sampling campaigns

Table 1 shows a selection of water quality parameters measured in the secondary effluent and the applied ozone doses in pilot and full-scale that can be taken into account when comparing the API reduction in different sampling campaigns.

Table 1: Parameters measured in the secondary effluent and applied ozone doses during the different sampling campaigns in pilot and full-scale.

	DOC (mg/L)	Nitrite NO_2-N (mg/L)	UVA_{254} (m^{-1})	UVA_{254}/DOC (L/mg*m)	Water temperature (°C)	Ozone dose (mg O_3/L)	Specific ozone dose (mg O_3/mg DOC, N corr)
Pilot summer 2014	10 ± 1	0.4 ± 0.2	24 ± 9	2.4 ± 0.9	21 ± 1	2-23	0.14-2.30
Pilot autumn 2014	10 ± 1	0.5 ± 0.1	25 ± 4	2.5 ± 0.4	19 ± 2	5-8	0.44-0.74
Full-scale autumn 2018	13 ± 1	0.9 ± 0.2	34 ± 5	2.7 ± 0.4	19 ± 1	4-10	0.22-0.67
Full-scale spring 2019	14 ± 1	0.8 ± 0.2	30 ± 2	2.2 ± 0.2	13 ± 1	4-10	0.24-0.54
Full-scale summer 2019	11 ± 2	0.6 ± 0.2	26 ± 2	2.4 ± 0.2	21 ± 1	4-10	0.40-0.84
Full-scale summer 2019 grab samples	11 ± 1	0.4 ± 0.2	28 ± 3	2.5 ± 0.3	21 ± 1	4-10	0.40-0.86
Average pilot	10 ± 1	0.5 ± 0.2	25 ± 7	2.5 ± 0.7	20 ± 2	2-23	0.14-2.30
Average full-scale	12 ± 2	0.7 ± 0.3	30 ± 4	2.5 ± 0.3	19 ± 4	4-10	0.22-0.86

In Figure 6, the API reduction in the full-scale study is compared with the pilot study.

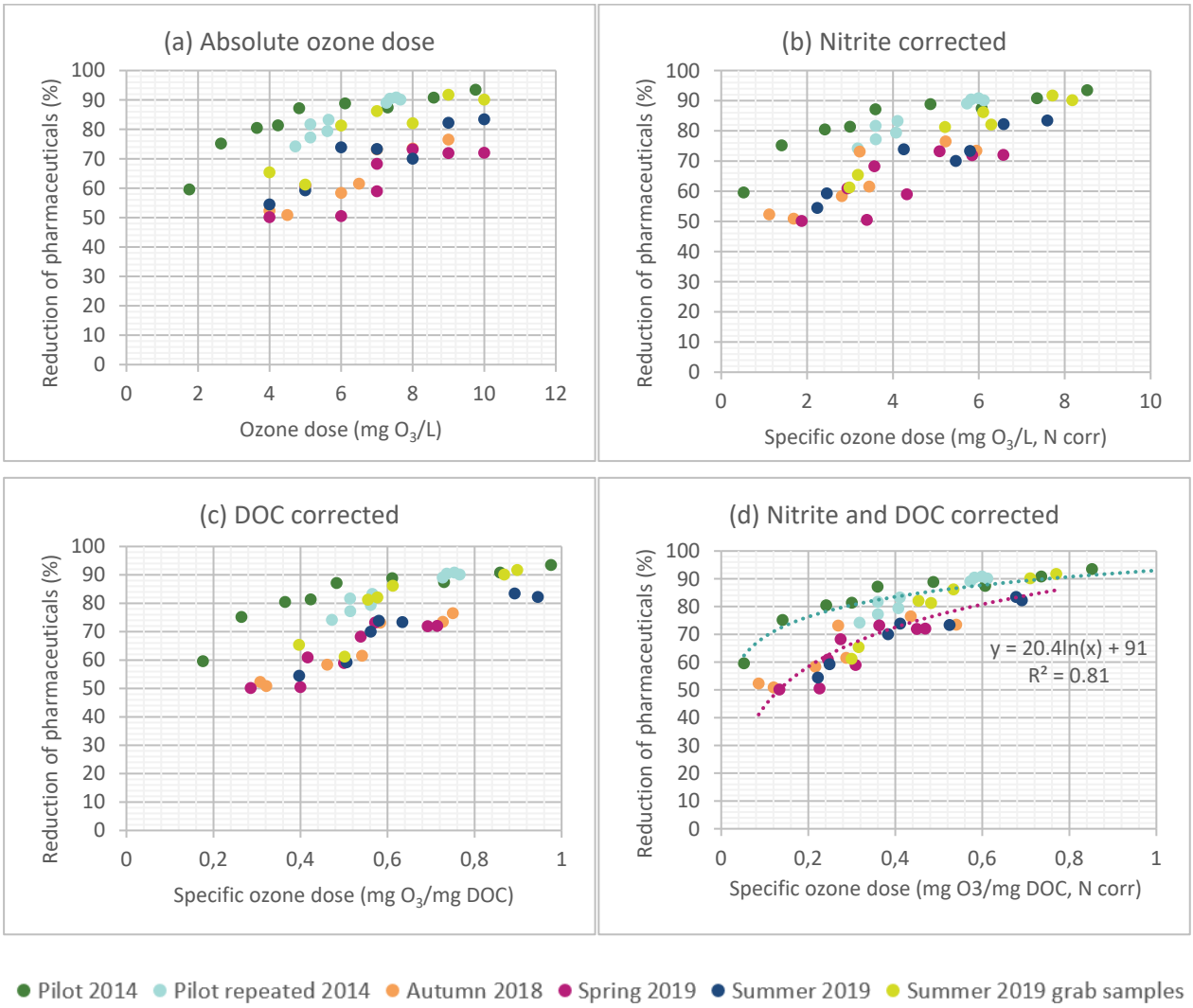

Figure 6: Average API reduction for different ozone doses in full-scale study compared to the pilot study. In (a), the API reductions are plotted against the absolute ozone dose applied. In (b), the ozone dose is corrected for nitrite concentration in the secondary effluent. In (c), the ozone dose is corrected for DOC concentration in the secondary effluent. In (d), the ozone dose is corrected for both nitrite and DOC in the secondary effluent. The dotted lines are log-fits based on the results from the pilot-scale and full-scale studies. For the full-scale study, the ozone dose was corrected using the concentration of DOC and nitrite in the secondary effluent for each measurement. For the pilot study, the corrected doses were calculated using the average DOC and nitrite concentrations in Table 1. The equation represents the log-fit of the data from the full-scale study. The average API reduction was calculated for atenolol, citalopram, diclofenac, metoprolol, sulfamethoxazole, oxazepam, trimethoprim and propranolol.

Due to the differences in nitrite and DOC concentration, normalization of the ozone dose was done according to these. The results of different sampling campaigns correlate better with each other when the ozone dose is normalized by both nitrite and DOC concentration in the secondary effluent.

However, in all the graphs it is clear that the reduction of APIs was better during the first trials in the pilot study compared to all the other sampling campaigns.

Since similar results have been observed in all other sampling campaigns, these are assumed to be relevant to use to describe the efficiency for API removal at the WWTP in Linköping. The log-fit based on all full-scale sampling campaigns correlates well with all the tests when normalizing the ozone dose based on DOC and nitrite concentration in the secondary effluent. According to this log fit data 0.6 mg O_3/mg DOC would be required in order to remove an average of 80 % APIs.

The first pilot sampling campaign was conducted during the summer 2014. During the autumn, the tests were repeated for ozone doses of 5 and 7.5 mg O_3/L. Before starting the repeated tests, the gas flow and the generator pressure were adjusted. The gas flow in the ozonation pilot was adjusted manually by a needle valve so there are some uncertainties in the accuracy of the gas flow settings.

If the actual gas flow was higher than expected during the first pilot trials it could explain the difference in API reduction between the studies.

When repeating the tests in pilot-scale autumn 2014 the ozone residual concentration in the off-gas was much lower than during the first pilot-scale tests and the reduction of UVA_{254} and API was lower. It was assumed then that this was due to an increased load of organic material and nutrients to the WWTP after the summer test period. However, the specific ozone dose, which considers the most ozone consuming compounds nitrite and DOC, did not indicate a large load increase.

If the actual ozone dose during the first pilot-scale dose-response test is assumed higher than the set point, and the specific ozone dose is adjusted to fit the residual off-gas concentration and residual UVA in Table 2, the data set from the first dose-response test in pilot-scale lines up with the repeated pilot-scale test and the full-scale test results (Figure 7).

Table 2. Ozone dose, specific ozone dose, residual ozone concentration in the off-gas and residual UVA_{254} during the pilot tests 2014. The adjusted ozone dose corresponds to a probable actual ozone dose due to inaccurate gas flow settings.

Test period during the pilot tests	Ozone dose (mg O_3/L)	Specific ozone dose (mg O_3/mg DOC, N corr)	Ozone residual in the off-gas (g/Nm^3)	Residual UVA_{254} (%)	Adjusted specific ozone dose (mg O_3/mg DOC, N corr)
Dose response test	4.8	0.36	0.4-0.7	29	0.58 (7 mg O_3/L)
Repeated test	4.7	0.32	0.1	48	0.32
Dose response test	7.3	0.61	0.9-1	7	0.83 (9.5 mg O3/L)
Repeated test	7.3	0.58	0.4	25	0.58

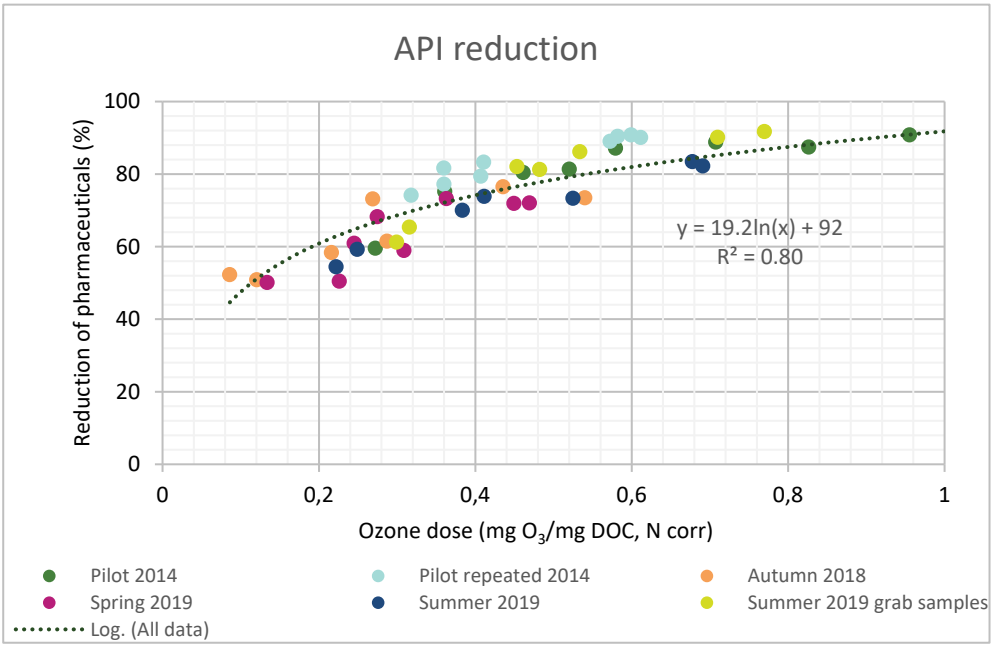

Figure 7: Average API reduction for different nitrite and DOC corrected ozone doses with an adjusted ozone dose for the first pilot tests. The dotted line and the equation represent the log-fit for all the data (both pilot and full-scale).

The specification of the ozone production capacity of the full-scale plant was based on the pilot study results. The inaccurate pilot gas flow rotameter provided wrong information, for the tender specification, regarding the nominal full scale ozone generator capacity. This highlights the importance of accurate settings and analysis, during a pilot study, in order to draw correct conclusions for upscaling based on pilot test results. It is also essential to take into account that an increased load to the WWTP, over time, can increase the concentration of DOC and nitrite to the ozonation plant and thus the need of higher ozone production capacity (Table 1).

Performance tests

Performance tests were conducted in order to evaluate the energy requirements as well as consumption of LOX during different operational modes. The ozone production was increased at different ozone concentrations. Four performance series were tested with ozone concentrations 10, 11, 12 and 13 % in the product gas. For each concentration, ozone production ranging from 2 kg/h to 16 kg/h was tested with an increase of 2 kg/h in each 15 minutes step.

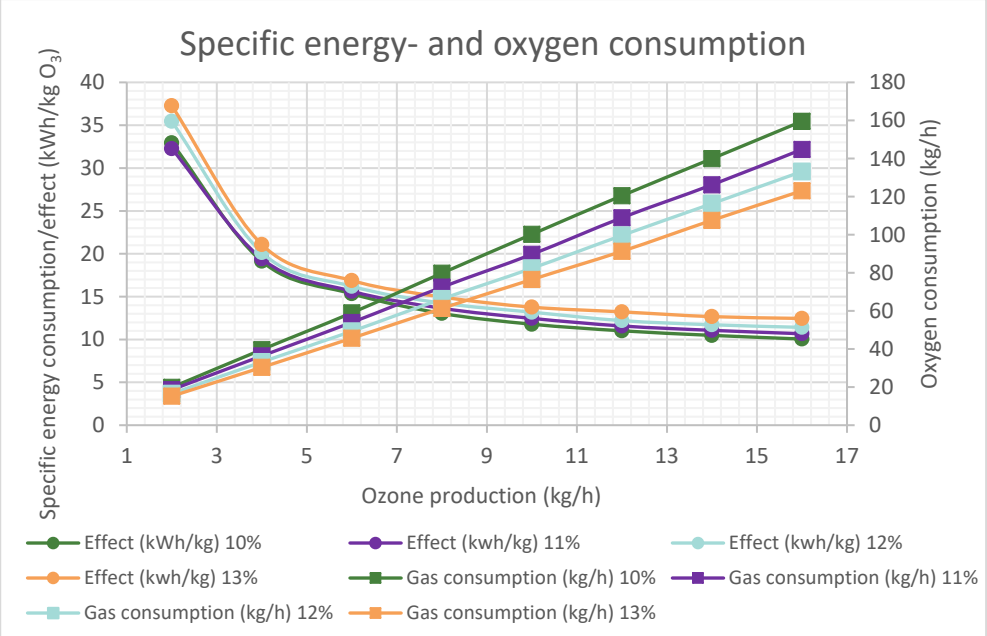

Figure 8: Specific energy consumption (effect) and oxygen consumption with increasing ozone production.

The specific required energy consumption for operating the ozone reactor decreased exponentially with an increasing ozone production. At 16 kg O_3/h, the specific energy consumption was in the range between 10.05 and 12.46 kWh/kg O_3, where the variation depended on the ozone concentration. The high specific energy consumption at low ozone production can be explained by the fixed required energy consumption by pumps and other equipment which run at the same effect independent of the ozone production. The total oxygen consumption increased linearly with increasing ozone production.

Evaluation of the ozone reactor design

CFD-simulations

Before the reactor was built, different reactor designs were evaluated by CFD simulations in order to design an optimal process solution to inject ozone as efficiently as possible, to create a plug flow to avoid short circuits and dead zones and to ensure that the ozone residual concentration will be completely depleted in the reactor outlet.

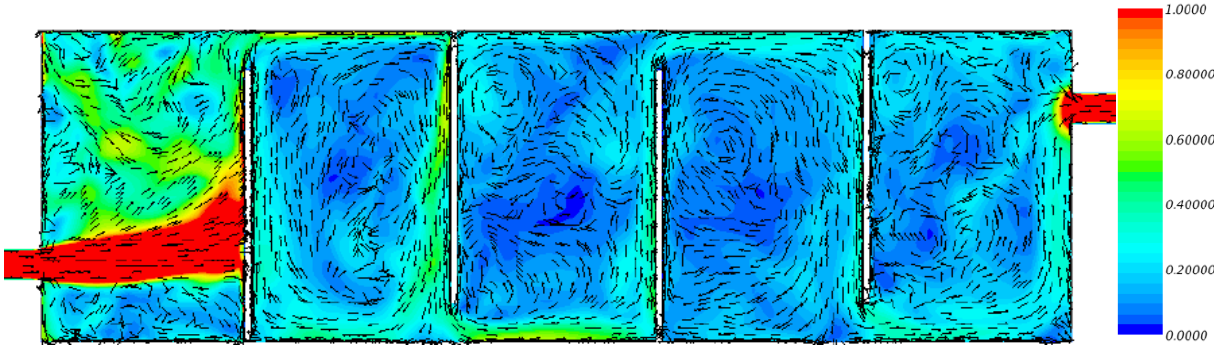

Figure 9: The first CFD flow simulation with the reactor volume distributed in five equally sized compartments. The arrows are showing the direction of the flow. The colour represents the velocity were red is the highest velocity and dark blue represents zero velocity.

In the first simulation the reactor was divided into five equally sized compartments with inlet and outlet on each short side of the reactor. This configuration creates high turbulence in the inlet chamber, back flows, large dead volumes and short circuiting.

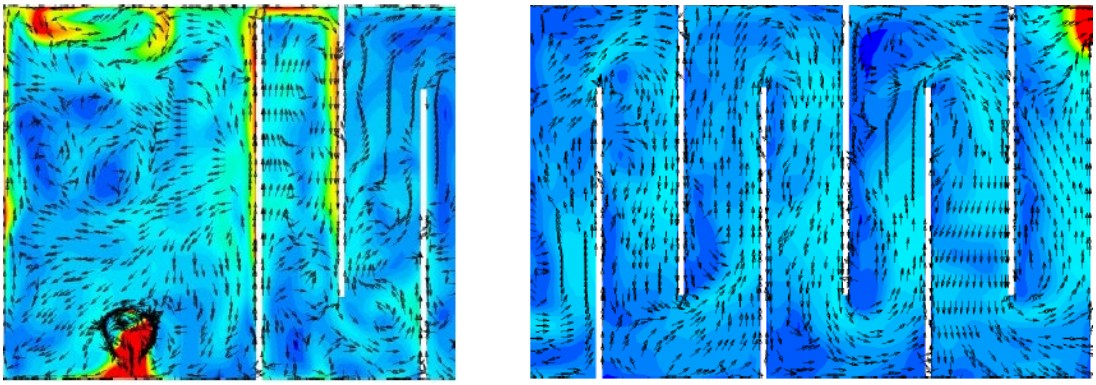

Figure 10: CFD simulation with the final reactor design. The figure is split in the first and the last part of the reactor.

In the final reactor design the inlet comes in from the long side distributing the flow towards the bottom of the inlet chamber which reduces turbulence and short circuiting. The following chambers was divided in narrow compartments, which creates a plug flow with a narrow residence time distribution in the CFD-simulation.

The simulation results indicated a residence time distribution included within ± 6 % around the nominal HRT indicating a very good plug flow.

Tracer tests

Tracer tests were performed in the full-scale ozone reactor in order to evaluate the plug flow and mixing in the ozone reactor. When the ozone facility is in operation, the concentration of dissolved oxygen increases from approximately 6 mg DO/L to 15 – 20 mg DO/L. The reactor effluent DO concentration depends on the ratio between gas- and water flow.

The tracer tests were conducted by measuring the oxygen concentration in the water at the outlet of the ozone reactor at different time-points after starting-up the ozone production. The results are shown in Figure 11.

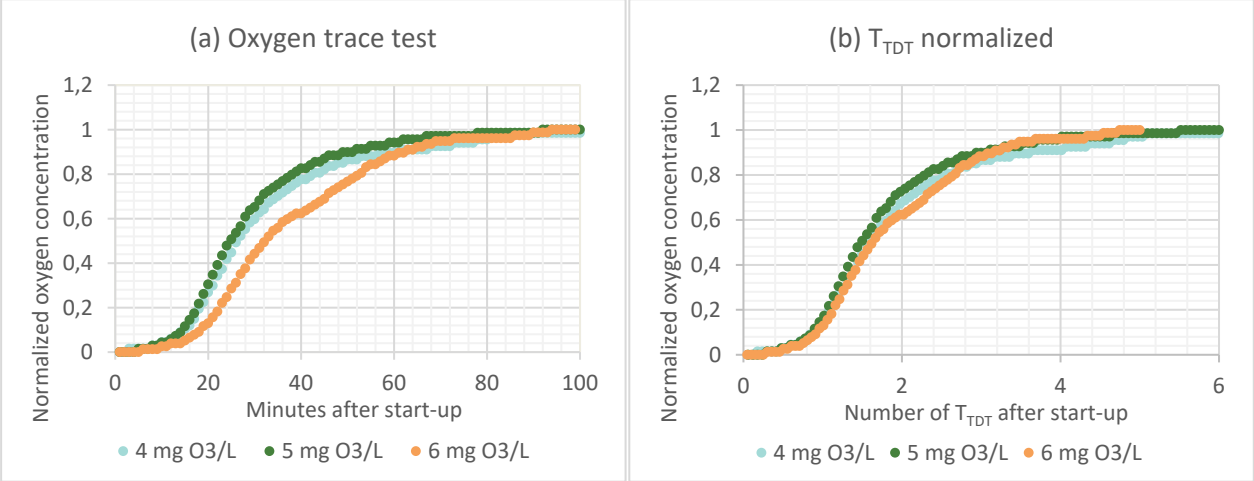

Figure 11: Normalized oxygen concentration in the water at the outlet of the ozone reactor after start-up of ozone production with the ozone doses 4, 5 and 6 mg O_3/L. In (a), the normalized oxygen concentration in S2 are plotted against minutes after start-up of the ozone production. In (b), the x-axis are normalized on the T_{TDT} calculated for each test based on the water flow.

The theoretical detention time (T_{TDT}) was calculated from the reactor volume of 524 m^3 and the average water flow for the different measurements. When normalizing the x-axis depending on the T_{TDT} for the different measurements, no difference was observed for the different ozone doses indicating that the test could be performed for different doses with similar results. In all tests, the oxygen concentration started to increase linearly after about one T_{TDT}. After two T_{TDT}, about 70 % of the max oxygen concentration was achieved. 90 % of the oxygen increase was achieved after about three T_{TDT}.

Two parameters that can be used to describe the plug flow and mixing in the reactor are baffling factor (BF) and Morrill index (MI).

To increase the contact time, baffling is used in many reactors meaning that the water flow goes in a certain direction through different lines instead of straight through the reactor tank. The BF is calculated as the ratio of T_{10} to T_{TDT}, were T_{10} is the time required for the first 10 % of a tracer to travel to the outlet of the reactor. A baffle factor of less than 0.3 indicates a large amount of mixing or short-circuiting, values above 0.7 indicate a more equal flow and 1.0 indicates an ideal plug flow in the reactor (Benjamin and Lawler, 2013).

The MI is calculated as the ratio of T_{90}, the time when 90 % of the tracer element has travelled through the reactor, to T_{10}. MI can give an indication of the mixing efficiency in the reactor and a higher value means more mixing. An ideal plug flow reactor has an MI of 1, a continuous flow stirred tank reactor with total mixing has a MI above 20. In order to improve the plug flow, reactors can be placed in series, giving an increased BF and decreased MI (Gualtieri, 2012).

Table 3: Parameters measured and calculated in the trace tests with the ozone doses 4, 5 and 6 mg O_3/L.

Parameter	4 mg O3/L	5 mg O3/L	6 mg O3/L	Average
T_{10} (min)	15	15	19	16 ± 2
T_{90} (min)	61	52	63	59 ± 6
Average water flow (m^3/h)	1884	1886	1588	1786 ± 170
T_{TDT} (min)	16.7	16.7	19.8	17.7 ± 1.8
Baffle factor BF	0.90	0.90	0.96	0.92 ± 0.03
Morrill index MI	4.1	3.5	3.3	3.6 ± 0.4

The BF was in all three trials close to 1 indicating an equal flow similar to plug flow in the ozone reactor and that a large part of the reactor volume is used for the water flow. An MI about 3-4 indicates some mixing or short-circuiting in the reactor, however, the value is far away from a reactor with total mixing that has an MI above 20.

The results from the full-scale tracer tests confirmed the plug flow simulation results from the CFD design model.

Variations of ozone consuming substances in the secondary effluent

During the pilot study 2014, diurnal variations of the concentration in the secondary effluent were observed for some APIs. For APIs that are dosed several times per day, the concentration in the secondary effluent was decreased due to dilution during the day when the water flow increased. For APIs with daily intake, e.g. anti-depressive and cardiovascular agents, the concentrations were more constant during the day. No large diurnal variations were observed for UVA_{254} or DOC, however, the nitrite concentration increased every afternoon when there was a higher load to the biological treatment.

In order to evaluate diurnal variations in the full-scale facility, grab samples were taken before and after ozonation every hour between 8:00-17:00 during one day, while a constant ozone dose of 8 mg O_3/L was applied. The average concentrations of the investigated APIs and UVA_{254} before ozonation indicated a small variation during the day (Figure 12 (a)).

In both studies there was an API peak in the afternoon which was probably due to a morning peak in the WWTP inlet due to accumulated APIs in urine during the night (Coutu et al., 2013). The delay of the API peak through the plant is related to the retention time in the upstream processes.

Similar to the pilot study, variations in the amount of the ozone consuming substances (DOC and nitrite) were observed during the operation of the full-scale plant, which resulted in a varying ozone demand during the day (Figure 12 (a)).

Variations in nitrite and DOC concentration were also observed for different periods over the year. At WWTP Nykvarnsverket, the DOC and nitrite concentration are measured in the secondary effluent once a week and the results from 2018-2019 can be seen in Figure 12 (b). The variation of DOC and nitrite depends on different load to the WWTP but also on occasional disturbances of the biological treatment process. Since both DOC and nitrite consume ozone, the variations cause differences in ozone dose requirements to obtain a specific API reduction. During periods with high DOC and nitrite concentration in the secondary effluent, a higher absolute ozone dose is required to obtain the same specific ozone dose compared to periods with lower amounts of nitrite and DOC.

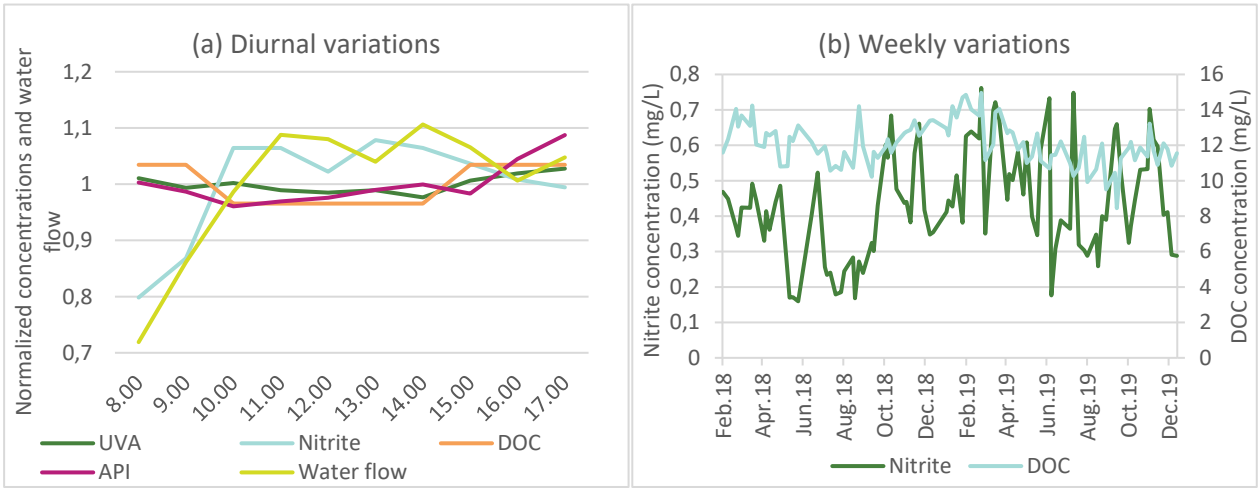

Figure 12: Diurnal and weekly variations in the secondary effluent. (a) Normalized concentrations of APIs, nitrite and DOC in the secondary effluent for grab samples collected before and after ozonation every hour between 8:00–17:00 and the water flow during one day. (b) Weekly variations of nitrite and DOC concentrations in the secondary effluent at WWTP Nykvarnsverket 2018-2019.

The results indicate that it would be necessary to adapt the ozone dose in order to maintain a stable specific ozone dose and to obtain a constant API reduction.

Costs

Operational costs (OPEX)

Operational costs of the ozone reactor were analysed based on the two major variable costs of operation: cost of energy and cost of liquid oxygen (LOX). When the test was performed in autumn 2018 the energy price was 0.07 €/kWh and the LOX price 0.085 €/kg. In addition, 1200 €/month was charged for LOX services.

A cost analysis was performed based on the costs for energy and LOX for the different ozone concentrations (Figure 13).

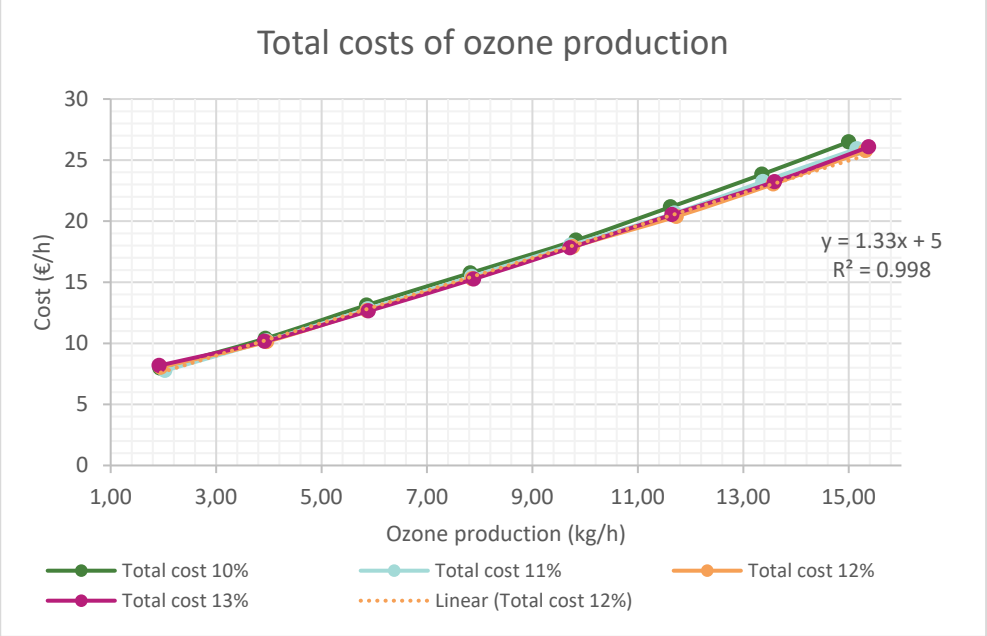

Figure 13: The total operational cost of the ozone reactor at different operational modes (ozone concentration in the gas) based on the prices for energy and LOX during the autumn 2018. The equation is a linear regression for the ozone concentration 12 %.

There were no major differences between the operational costs for different ozone concentrations, but for ozone doses above 4 kg O_3/h, an ozone concentration of 12 or 13 % is more cost effective. The specific energy consumption is different depending on the type of equipment and configuration. It is therefore important for other operators to investigate the costs that are relevant for the specific facility and not draw too much conclusions from the graphs that are only specific for the ozone facility in Linköping.

The cooling water temperature for the ozone generator is also an important factor that affects the energy consumption. Ozone degrades faster with higher temperature which requires an increased ozone production resulting in an increased energy consumption. A cooling water temperature above 20 °C is not recommended. The temperature increase over the heat exchanger (delta T) is 3 °C in Linköping so the cooling water temperature at the generator inlet would then be 23 °C. At higher temperatures the maximum capacity of the ozone generator is reduced, and the energy consumption increases substantially.

OPEX also depends very much on the energy and liquid oxygen (LOX) prices. Operating at high ozone concentration in the process gas is favourable when the price of LOX is high. The LOX price in Linköping is however very low and will probably increase in the future. In this case only the energy price has an effect when optimizing the total OPEX cost. With a slight increase in energy cost lower ozone concentration would be more favourable. However, a lower ozone concentration results in an increased gas flow which reduces the mass transfer efficiency so less ozone is transferred to water. It also results in higher dissolved oxygen concentration in the MBBR inlet which has a negative effect on the denitrification rate and the consumption of carbon source in the last two reactors of the MBBR.

OPEX calculation

An example of OPEX calculation can be seen in Table 5 based on average concentrations of the ozone consuming compounds DOC and nitrite, water flow, costs and ozone concentration (Table 4). In the calculation, a required specific ozone dose of 0.55 mg O_3/mg DOC, N corr is assumed.

Table 4: Parameters and data used for OPEX calculation in Table 5. A required ozone dose of 0.55 mg O_3/mg DOC, N corr is assumed. Average DOC concentration, nitrite concentration and water flow are based on full-scale sampling campaigns. The prices for energy and LOX are the exact prices during the autumn 2018.

Parameter	Abbreviation	Value	Unit
Required specific ozone dose	$E_{DOC,\ corr}$	0.55	mg O_3/mg DOC, N corr
Average DOC concentration	c_{DOC}	12.1	mg DOC/L
Average nitrite concentration	$c_{NO2\text{-}N}$	0.43	mg NO_2-N/L
Average water flow	Q	1700	m^3/h
Ozone consumption by nitrite	N_{corr}	3.43	mg O_3/mg NO_2-N
Energy price	$price_{energy}$	0.07	€/kWh
LOX price (fixed)	$price_{LOX,\ fixed}$	40	€/d
LOX price (variable)	$price_{LOX,\ variable}$	0.085	€/kg LOX
Ozone concentration in process gas	$c_{O3,\ process\ gas}$	12	%

Table 5: OPEX calculation based on data in Table 4.

Parameter	Short	Formula	Values	Result
Required ozone dose	$c_{O3,\ water}$	$E_{DOC,\ corr} \cdot c_{DOC} + N_{corr} \cdot c_{NO2\text{-}N}$	= 0.55 · 12.1 + 0.43 · 3.43 =	8 g/m^3
Ozone consumption	p_{O3}	$c_{O3,\ water} \cdot Q$	= 8 · 1700 =	13.6 kg O_3/h
LOX consumption	p_{LOX}	p_{O3} / $c_{O3,\ process\ gas}$ · 24 h	= 13.6 / 12 % · 24 h=	2717 kg LOX/d
LOX cost	$cost_{LOX}$	$price_{LOX,\ variable} \cdot p_{LOX} + price_{LOX,\ fixed}$	= 0.085 · 2717 + 40 =	271 €/d
Specific energy consumption	$spec_{energy}$	14 kg O_3/h, 12 wt. %, from Figure 8	=>	11.72 kWh/kg O_3
Energy consumption	p_{energy}	$spec_{energy} \cdot p_{O3} \cdot 24$ h	= 11.72 · 13.6 · 24 =	3825 kWh/d
Energy cost	$cost_{energy}$	$price_{energy} \cdot p_{energy}$	= 0.07 · 3825 =	268 €/d
Total operational cost	$cost_{tot}$	$cost_{LOX} + cost_{energy}$	= 271 + 268 =	539 €/d = 197 k€ /annually
Cost per m^3 treated water		$cost_{tot}$ / (Q · 24 h)	= 539 / (1700 · 24) =	0.013 €/m^3
Nitrite oxidation	N_{ox}	$c_{NO2\text{-}N} \cdot N_{corr}$	= 0.43 · 3.43 =	1.47 mg O_3/L
Cost for nitrite oxidation		N_{ox} / $c_{O3,\ water} \cdot cost_{tot}$	= 1.47 / 8 · 539 =	99 €/d = 36 k€ /annually

In this case 18,4 % of the produced ozone (1,47/8) is consumed by nitrite alone, which highlights the necessity of reducing nitrite formation in the upstream process.

Note that OPEX in the calculation example does not include investment cost, maintenance, post treatment and staff cost.

Capital costs (CAPEX)

The transferability of the capital cost for the investment of the ozone treatment system at WWTP Nykvarnsverket in Linköping is limited as parts of the existing infrastructure could be used and some costs have been charged to other projects. Inlet pumps, valves and the MBBR post-treatment system was already in place. The power supply needed for the ozone production had to be upgraded but the cost was charged to another project for power supply of future upgrade of the treatment plant. With these limitations the capital cost was approx. 25 MSEK (approx. 2.5 M €). Comparing this cost with the calculated cost for an ozone plant in Sweden with similar capacity the price in Linköping is very low.

Process control strategies

Controlling the ozone dose is important because underdosing results in an insufficient API reduction, while overdosing contributes to unnecessarily high consumption of energy and chemicals and may increase the risk for formation of undesired ozonation by-products. The amount of ozone consuming substances, DOC and nitrite, varies in the secondary effluent and it might be relevant to change the ozone dose depending on those variations. There are no standard operating procedures or limit values for API elimination at WWTPs in Sweden, making it difficult to decide a set-value for an optimal ozonation process. Furthermore, it is not possible to measure concentrations of APIs online. Therefore, other parameters (surrogates) were investigated in order to find a correlation with the API elimination and to monitor or control the ozonation process.

Investigation of process control parameters

Ozone concentration in the off-gas, UVA_{254}, fDOM, dissolved ozone and redox potential were investigated as possible control parameters.

Ozone concentration in the off-gas

The ozone concentration in the off-gas is the amount of the produced ozone that has not been dissolved in the wastewater. In drinking water disinfection, this parameter has been used for feedback process control since it has some correlation with the amount of ozone consuming substances in water.

In order to evaluate the potential for the off-gas concentration to be used as control parameter, the off-gas concentration and mass transfer efficiency were measured at different ozone doses (Figure 14).

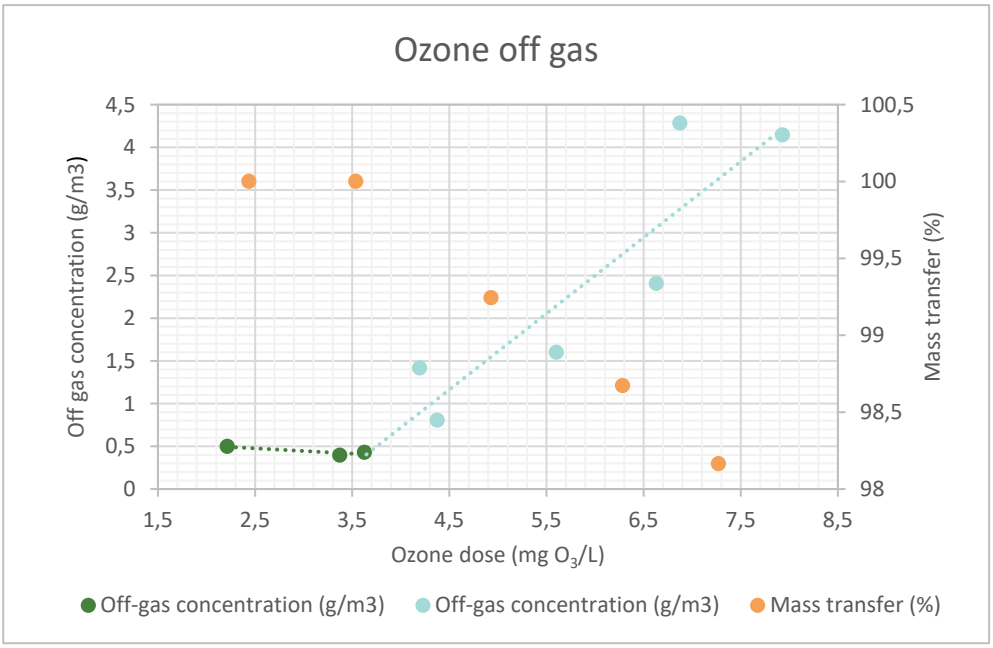

Figure 14: Ozone off-gas concentration and mass transfer for different ozone doses.

Both the ozone off-gas concentration and the mass transfer rate can be fitted as two separate lines depending on the ozone dose. In Figure 14 both parameters are almost constant until an ozone dose of approximately 3.6 mg O_3/L. For higher doses the gas flow was too high to obtain a 100 % mass transfer contributing to more ozone in the off-gas. This indicated that the off-gas concentration could be used as control parameter to ensure a high mass transfer efficiency and minimizing the amount of unutilized ozone in the process.

The mass transfer efficiency is a calculated function based on the process gas concentration and the off-gas concentration, assuming that the gas flow in and out is equal. However, there is an uncertainty in the accuracy of the off-gas concentration measurement due to dilution during periods

of low production. The off-gas fan runs at a constant speed/flow. When the process gas flow is lower than the off-gas flow, a safety valve opens resulting in a dilution of the off-gas concentration with air. There is only a mass flow measurement in the process gas flow so the measurement of mass transfer is only valid when the off-gas flow is equal to the process gas flow.

Step response tests were conducted to create a model over the response in off-gas concentration with varying ozone dose, from which a PI-controller was designed and implemented in the control system. The controller was designed to decrease the ozone dose at high off-gas concentration and increase the ozone dose when the off-gas concentration is low. However, when testing the controller it turned out that it was difficult to use for the full-scale facility due to large variations in wastewater flow through the ozone reactor. When the wastewater flow increases, more ozone is produced to obtain the ozone concentration in the water. Higher ozone production increases the gas flow and reduces the mass-transfer efficiency which in turn increases the ozone concentration in the off-gas. The controller then responds with a decrease of the ozone production when it actually should be higher. The opposite reaction occurs when the wastewater flow decreases. Less ozone will end up in the off-gas and the controller responds with an increased ozone production when it instead should be lower.

With a constant wastewater flow and a constant gas flow this type of controller might be useful. This was the case during the pilot test where this control strategy was tested with reasonably good results.

The off-gas controller has however been implemented in the control system for the full-scale plant, as a quick response controller to avoid overdosing during a sudden dilution at rain events. The set point for the max off-gas concentration has to be adapted depending on the specific ozone dose set point and the normal dry weather water flow.

Ultraviolet absorbance at 254 nm (UVA_{254})

Light adsorption at 254 nm (UVA254) is a common surrogate parameter for DOC that contains aromatic rings or unsaturated double/triple carbon bonds. Changes at these molecule structures, e.g. by reaction with ozone, result in a change of the UVA254.

This relative UVA254 reduction (1-UVA254,out/ UVA254,in) can be used as simple surrogate parameter to identify the overall impact of ozone on the organic background matrix (specific ozone dose, incl. nitrite correction) as well as on the API elimination (Figure 15).

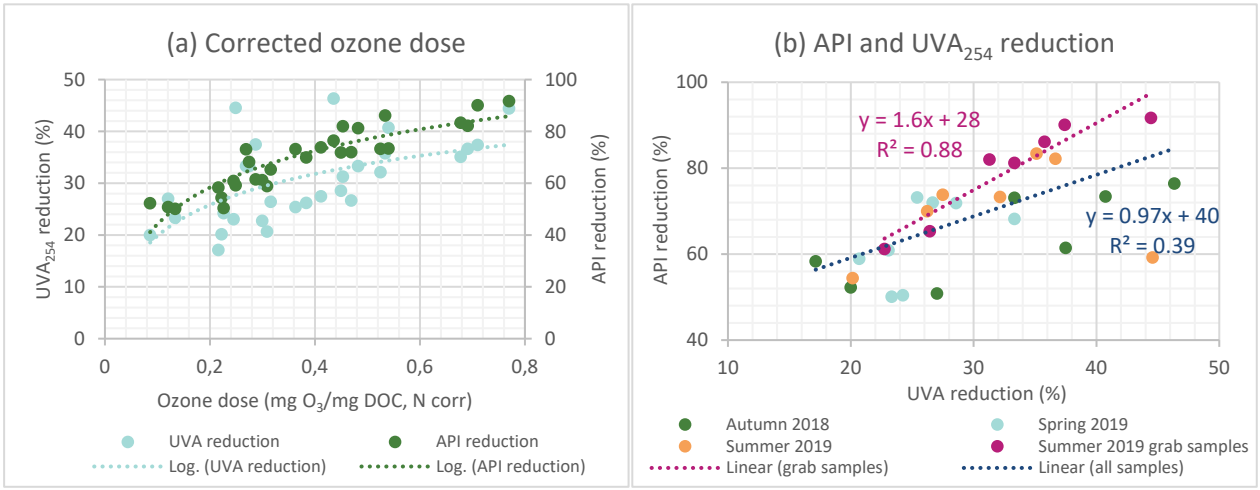

Figure 15: Reduction of APIs and UVA_{254} lab measurements in the dose-response tests. In (a), the reduction of APIs and UVA_{254} are plotted against the corrected ozone dose. (b) shows the correlation between API and UVA_{254} reduction in the different dose-response tests. The blue equation represents the linear regression for all samples. The purple equation represents the linear regression for the grab samples. The average API reduction was calculated for atenolol, citalopram, diclofenac, metoprolol, sulfamethoxazole, oxazepam, trimethoprim and propranolol. UVA_{254} was measured for unfiltered samples.

When studying Figure 15 there is a relation between specific ozone dose, API reduction and UVA_{254} reduction. The best correlation between the reduction of APIs and UVA_{254} was observed for the grab samples (purple in Figure 15 (b)) indicating that UVA_{254} can be a good ozone dose control parameter or an indication of the API reduction in the ozonation system.

Process control of the ozone dose with UVA_{254} as control parameter have been tested using an UVAS online meter from Hach. Only one sensor is used to measure the UVA_{254} both before and after ozonation, so two pumps are alternately pumping influent and effluent water to the sensor. The pumps are switched between influent and effluent water once during each HRT of the flow through the ozone reactor. A new value of the UVA_{254} reduction is provided every time a flow equal to the reactor volume has passed through the ozone reactor.

API-controller was designed based on step-response tests of the UVA_{254} reduction over the ozonation reactor. Unfortunately, the PI-controller worked poorly since the reduction is linked to both inlet and outlet UVA_{254}. Noise in the measured process value (UVA_{254}-reduction) created large fluctuations in the error value (set value – process value). When the PI-controller was responding to the error by adjusting the control variable (ozone dose) the process was destabilized creating very large fluctuations in the process (Figure 16).

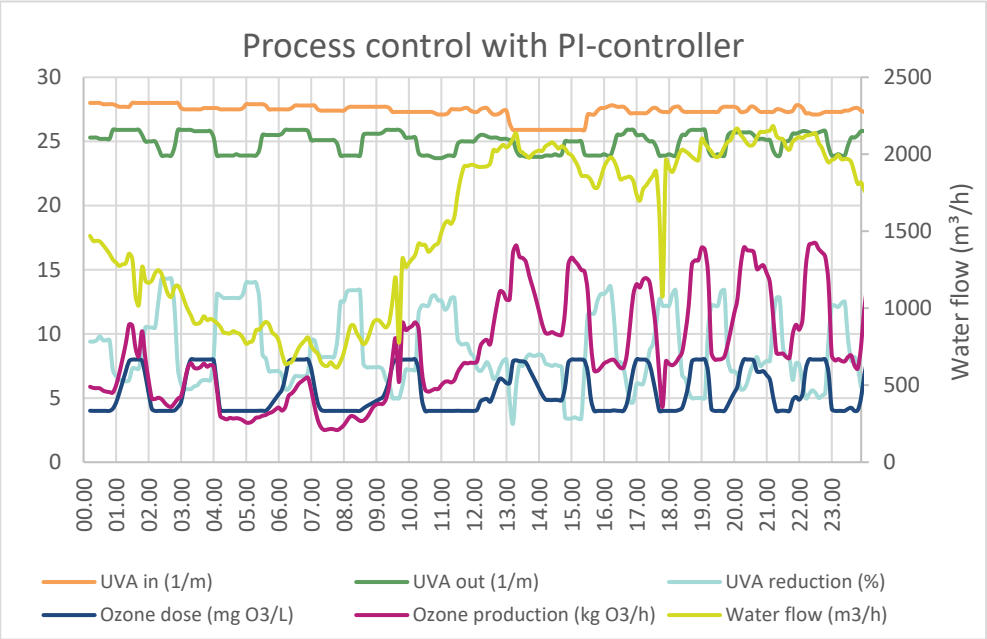

Figure 16: Ozone dose process control by a PI-controller using UVA_{254} reduction as process value.

Instead a proportional controller was created, similar to the one used in Berlin for ozonation in pilot-scale (Stapf et al., 2016). The design of the controller is to select a base value of the ozone dose (for example 7 mg O_3/L) and a set point of the UVA_{254} reduction (for example 30 %). The ozone dose is adjusted proportionally to the deviation from the set point with a certain percentage factor. In order to avoid unreasonable changes of the dose, minimum and maximum limitations of the added dose can be set. Filtration of the measurement noise is done by choosing a minimum deviation from the set point before the ozone dose is changed. When starting up the ozonation process there is an instability in the UVA_{254} readings during approximately one hour. In order to stabilize the signal a holding time, before starting up the dose controller, can be selected.

A schedule of the parameters that can be changed in the implemented UVA_{254} controller is shown in Figure 17.

If the strategy would have been targeting a constant outlet UVA concentration a PI-controller should probably be stable, if using the feed-back signal from the UVA_{254} sensor in the ozonation effluent.

UVA_{254}-controller	ON	OFF			
Base dose	7	mg O_3/L			
Setpoint of UVA_{254} reduction	30	%			
% difference measured value/setpoint	140	%	change dose	-2.0	mg O_3/L
% difference measured value/setpoint	60	%	change dose	+2.0	mg O_3/L
Min. limit added dose	-3.0	mg O_3/L			
Max. limit added dose	+3.0	mg O_3/L			
+/- % difference measured value/setpoint to change the dose	110	%			
Run time of the ozone generator before the controller is turned on after shut down	60	min			

Figure 17: Schedule of the parameters that can be changed in the UVA_{254} process controller implemented in Linköping. The values in the yellow boxes are examples and can be changed by the operators at the WWTP.

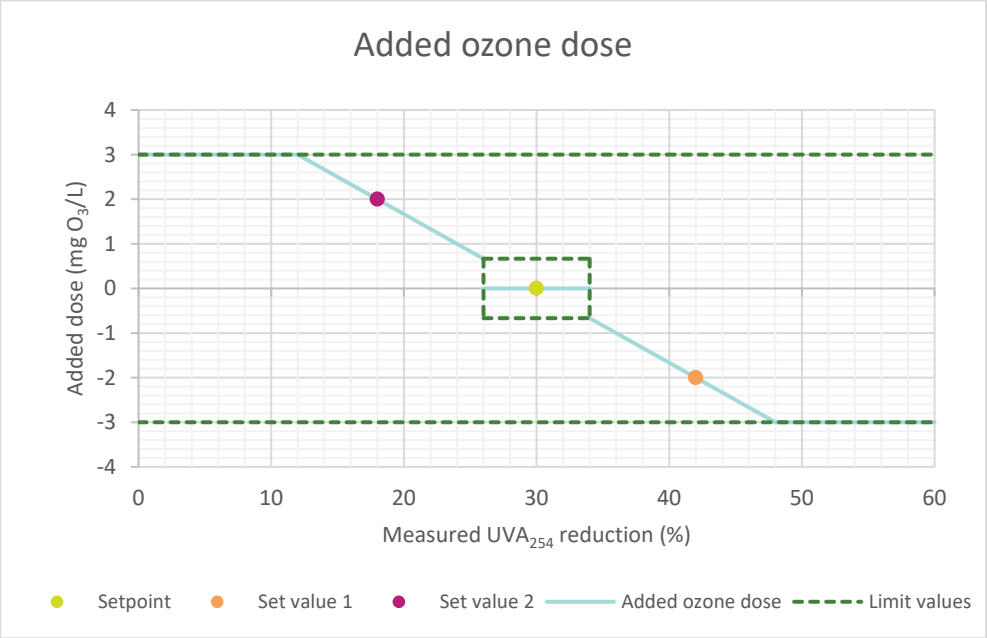

Figure 18: Added ozone dose for different measured UVA_{254} reductions when the parameters in Figure 17 are input to the controller. The set point of UVA_{254} reduction is 30 %. When the quote between measured UVA_{254} reduction and set point is 140 %, the ozone dose is decreased with -2 mg O_3/L (Set value 1). When the quote is 60 %, the ozone dose is increased with 2 mg O_3/L (Set value 2). For other measured UVA_{254} reductions, the added dose is calculated proportional to the set values. The quote must be at least ± 110 % to change the dose, which contributes to the UVA_{254} reduction in the interval 27–33 %. The min and max limitations of added dose are ± 3 mg O_3/L.

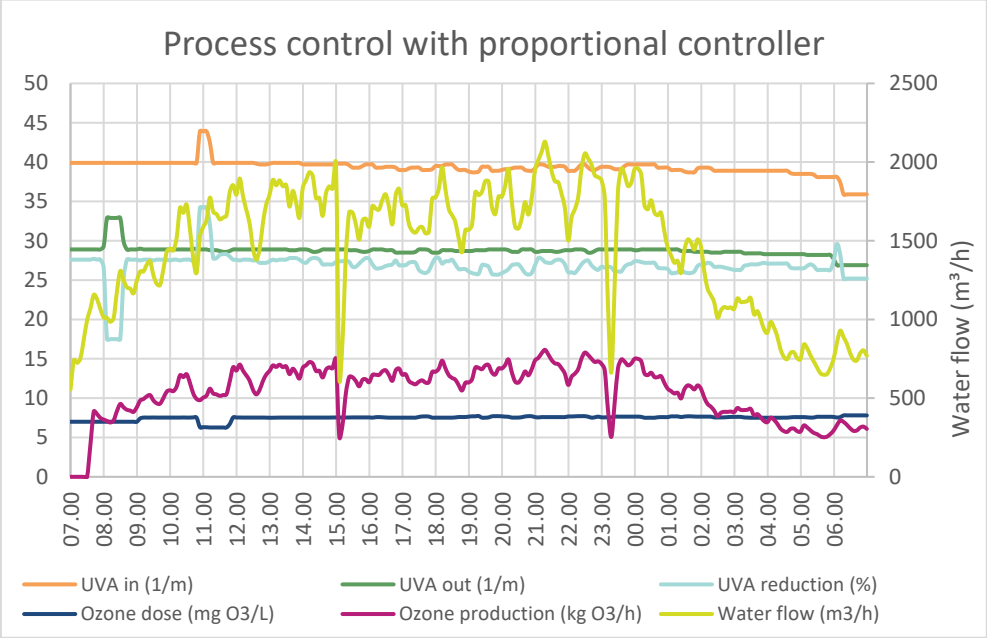

Figure 19: Ozone dose process control by a proportional controller with the settings in Figure 17.

The proportional controller in Figure 19 works more stable compared to the PI-controller. When testing the controller, samples were collected at periods with low and high load and the UVA_{254} was filtered and measured at the lab. However, it turned out that at least during dry weather conditions, the variation in UVA_{254} was smaller than the uncertainty between the lab and online measurement. Due to the small variations, it is uncertain whether it is worth to use the UVA_{254} online sensor for process control of diurnal variations. The UVA reduction can, however, be useful in order to observe major changes in the influent water quality and in the process efficiency that affects the API reduction.

Other parameters

Dissolved ozone was investigated as possible control parameter by measuring the concentration of dissolved ozone in the first chamber of the ozone reactor. Some ozone was detected when using AccuVac® Ampules (Hach) and a spectrophotometric method (Indigo), but the installed online meter could not detect any dissolved ozone. However, no relationship could be observed between applied ozone dose and dissolved ozone measured with the ampules, and no conclusion could be drawn whether dissolved ozone is useful as control parameter.

Another parameter that was tested as control parameter is redox potential, which describes the ability to reduce or oxidize compounds in the water. Ozone and hydroxyl radicals are strong oxidants. Thus their presence should increase the oxidation potential in the water. Redox potential was measured in water from the first chamber in the ozone reactor, the same measurement point as for dissolved ozone. No correlation was observed between applied ozone dose and redox potential, maybe because there were too many contaminants that altered the redox potential in wastewater or simply due to lack of dissolved ozone in the water.

Similar to UVA_{254}, the amount of organic material such as APIs can be indicated by measuring the fluorescence intensity in the water. Therefore, some samples of dose-response experiments at WWTP Linköping were sent to Berlin Centre of Competence for Water for the measurement of fluorescent dissolved organic matter (fDOM) with the EXO fDOM online sensor (YSI). The results indicated a correlation to the API reduction, which can be used similar to the UVA_{254} reduction (Figure 19).

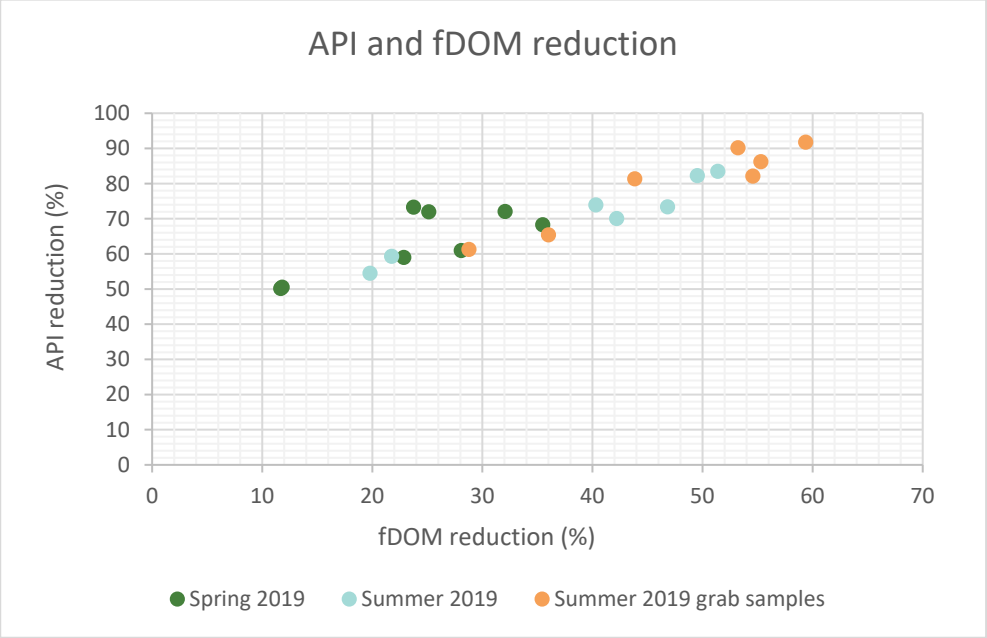

Figure 20: Correlation between the reduction of APIs and fluorescent dissolved organic matter (fDOM) measured in spring and summer full-scale sampling campaigns.

Application of process control

If the controller works ideally, a certain specific ozone dose can be achieve based on the control parameter and thereby a certain API reduction. Based on the correlations between specific ozone dose and API reduction, a constant average water flow and measurements of DOC and nitrite in the secondary effluent during 2018-2019, an estimation of the API reduction, ozone production and costs with/without process control are shown in Figure 20.

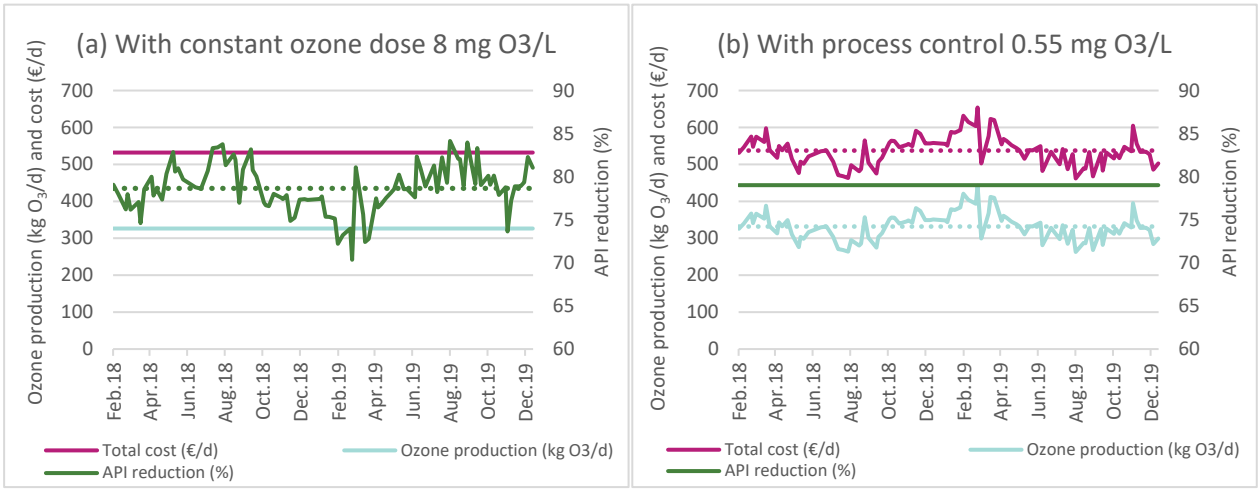

Figure 21: API reduction, ozone production and cost if a constant ozone dose of 8 mg O_3/L is applied (a) compared to when a specific ozone dose of 0.55 mg O_3/mg DOC, N corr, is applied (b). The data is based on weekly measurement of DOC and nitrite in the secondary effluent and an average water flow of 40,800 m³/d. The correlation between API reduction and specific ozone dose in Figure 6 (d) is used for calculations. The dotted lines represent the average of the parameters.

When a constant ozone dose of 8 mg O_3/L is applied, the API reduction varies at different periods during the year and some overdosing may occur during the summer and underdosing during the winter. With process control, a more constant API reduction can be obtained, assuming that the controller works ideally. However, when comparing the average values, they are almost the same for both cases. It is therefore difficult to evaluate which way to go. If there is a requirement saying that for each day/month, a certain API reduction must be obtained, then an advanced process control would be required. On the other hand, if the requirement states a yearly average of the API reduction, the controller may be redundant in this case. However, these results are based on the specific conditions in Linköping with the ozone reactor and the energy/LOX prices, thus the situation can be different at other facilities. It is also important to keep in mind that the parameters in the graphs

were calculated using a constant average water flow and DOC and nitrite concentrations measured as 24 h composite samples once per week. Both the water flow and the concentrations of DOC and nitrite actually varies during a diurnal cycle and at different periods during the year (Figure 12).

The calculations above assume that the controller works ideally, which probably not always is the case. For example, deposits on the UVA_{254} online probe often result in a higher UVA_{254}. If the measured value of UVA_{254} is higher than the real value, the calculated UVA_{254} reduction will be lower, and the controller suggest a higher ozone dose than required. This in turn leads to higher ozone consumption and a higher cost.

Environmental effects

Effect on the aquatic environment

Figure 22 shows a summary of the measured API concentrations in the secondary effluent.

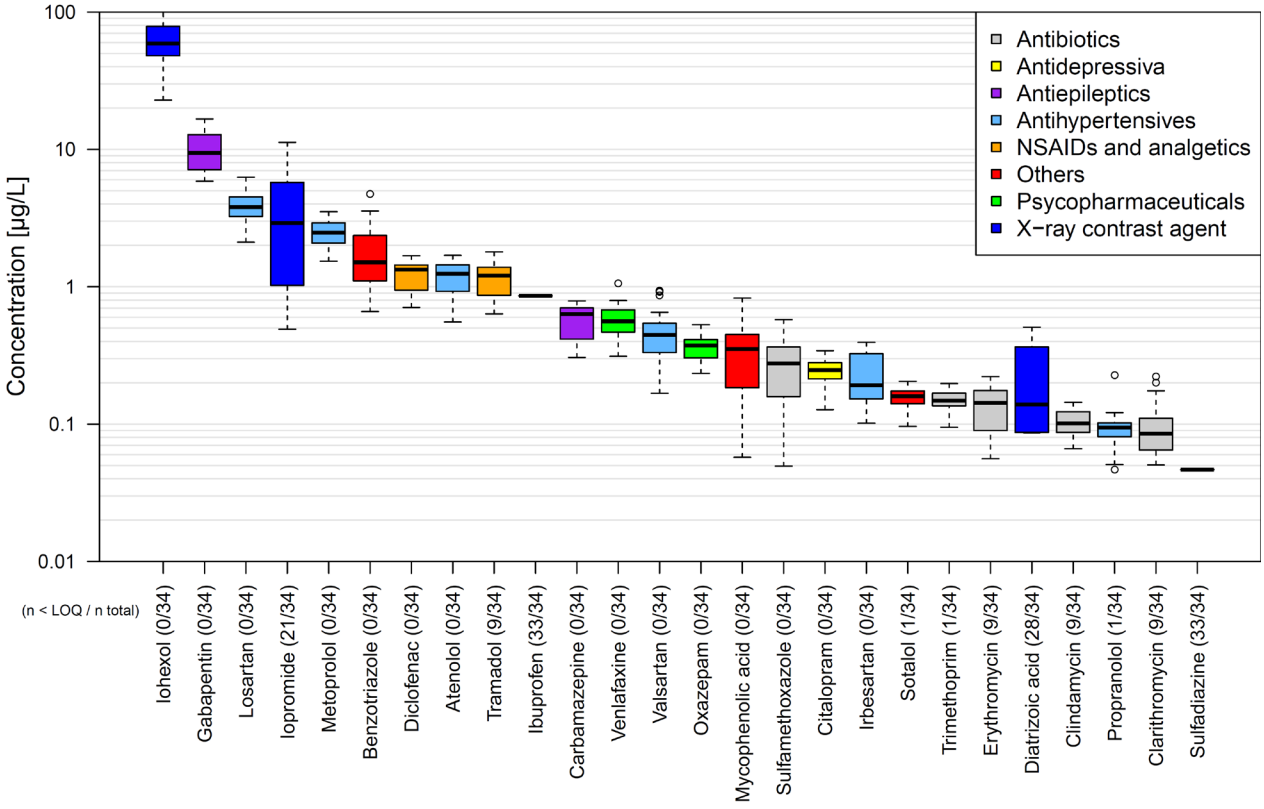

Figure 22: Concentrations of APIs measured in the secondary effluent (ozonation influent) in the full-scale sampling campaigns.

The x-ray contrast agent's iohexol and iopromide are found in high levels in the secondary effluent. X-ray contrast agents are designed to be poorly biodegradable. Since there is a large hospital in Linköping the high levels of x-ray contrast agents in the wastewater were expectable. However, there are no known effects from the contrast media on the aquatic environment and no ecotoxicological data are available. Therefore, no further evaluation of the environmental effect of the x-ray contrast was performed.

For the other APIs, evaluation about if the compounds may affect the aquatic environment was performed using the measured concentrations of the APIs in the dose-response sampling campaigns and the predicted no effect concentration (PNEC) values in Table 6 in Appendix. The results are shown in Figure 23.

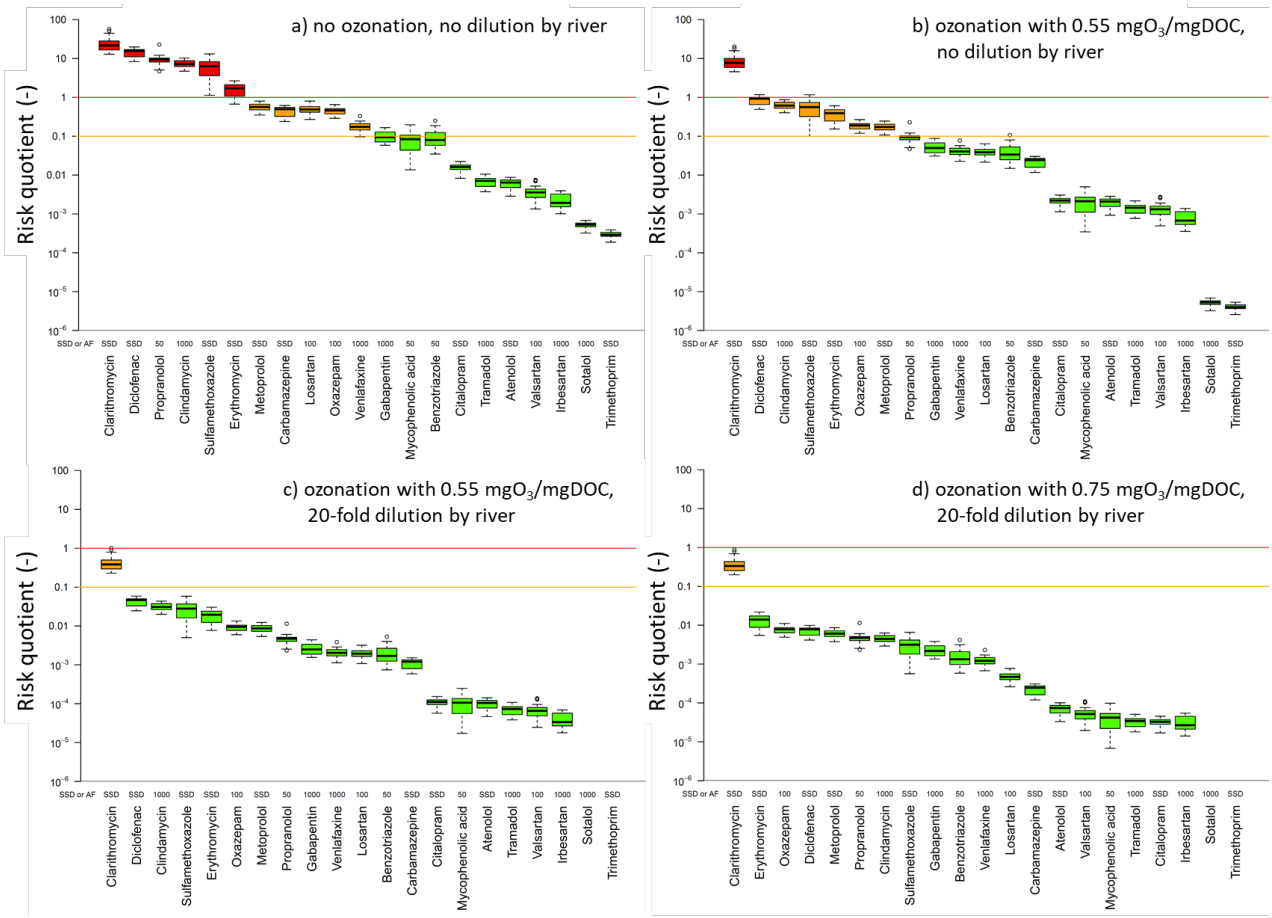

Figure 23: Risk quotients calculated based on the measured concentrations of APIs in the dose-response sampling campaigns and the PNEC values in Table 6 in Appendix. In (a), the risk quotients if no ozone is applied and no dilution by river. In (b), the specific ozone dose of 0.55 mg O3/mg DOC is applied but no dilution by river. In (c), the specific ozone dose of 0.55 mg O3/mg DOC is applied and dilution factor by the river is 20. In (d), the specific ozone dose of 0.75 mg O3/mg DOC is applied and dilution factor 20.

Without ozonation, six of the investigated APIs in Figure 23 are in levels posing a risk for the aquatic environment (risk quotient > 1.0) and five APIs in levels posing a potential risk (between 0.1 and 1.0). When applying a specific ozone dose of 0.55 mg O_3/mg DOC, N corr, the risk quotient is decreased for all the APIs but there is still some risk. When calculating with the average dilution factor in the recipient (20-fold dilution), all the investigated APIs are below the risk limit. The risk quotients are even lower when applying 0.75 mg O_3/mg DOC, but according to these results it is uncertain whether it is worth to have a higher ozone dose since all the APIs in both cases are in levels posing a low risk for the aquatic environment.

The dilution in the recipient entails low risk quotients. However, the dilution factor varies seasonally and even if the dilution contributes to low risk quotas, the mass flow of APIs to the environment decreases if higher amounts are reduced at the WWTP. This in turn leads to a decreased amounts of APIs ending up in the Baltic Sea, which is the focus for the CWPharma project and the API load to the Baltic Sea is not influenced by river dilution. However, as concluded in this report, the energy and LOX consumption as well as the cost also increases with a higher ozone dose, which also contributes to a cost for the environment. By taking this into account, it is difficult to state which ozone dose to use.

It is important to mention that the method with risk quotients, PNEC and river dilution are useful to conclude the environmental effects from APIs in the case for Linköping WWTP, where the dilution factor is about 20 in the immediate recipient water. For other WWTPs the dilution factor can be irrelevant, for example if the recipient is the Baltic Sea where the dilution factor is basically infinite.

Bacteria reduction

During the pilot study and in previous literature it has been shown that ozonation reduces the amount of bacteria. The amount of bacteria before and after ozonation and after MBBR was measured for different ozone doses in the full-scale study (Figure 24).

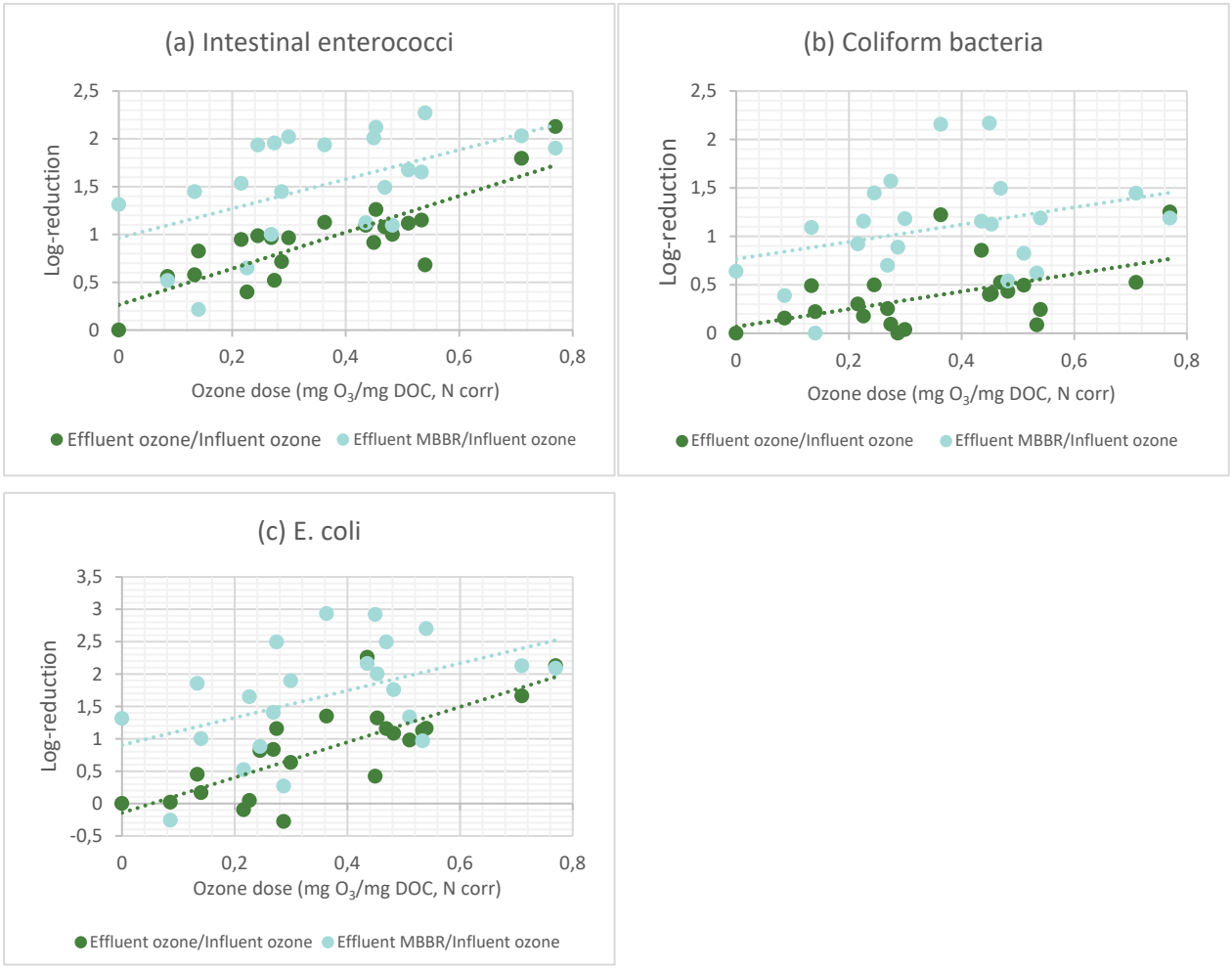

Figure 24: Bacteria reduction during ozonation and MBBR. The reduction is calculated as $-\log_{10}(out/in)$.

As can be seen in Figure 24, intestinal enterococci, coliform bacteria and E. coli are for most of the samples reduced by ozonation. The reduction proceeds during the MBBR post treatment. It seems like the reduction depends on the ozone dose, even though there were variations in the results.

Although the quantification of bacteria surviving the different treatment did not consider their resistance pattern, it is reasonable to assume that the reduction of antibiotic resistant bacteria is of the same magnitude as for antibiotic sensitive counterparts of the same species. It is still an open question if or to what extent antibiotics in effluents and receiving waters contribute to the development and spread of antibiotic resistance. In any case, the parallel reduction of antibiotics by the ozonation will reduce the risks for such selection to occur in effluents and receiving waters. The possibility cannot be excluded that gene fragments from bacteria that were killed during the ozonation could be taken up and incorporated in other, living bacteria. However, uptake of naked DNA is only common in a minor fraction of bacterial species, and under rather special conditions. Also a selection pressure would be needed to provide cells that have acquired resistance a sufficiently strong growth advantage. The reduction of antibiotics further limits this risk scenario (Bengtsson-Palme et al., 2017) .

Effect on the MBBR

The concentration of ozone in the process gas is between 10-14 wt. % ozone. Thus, 86 – 90 % of the injected gas consists of pure oxygen. When injecting pure oxygen the concentration of dissolved oxygen (DO) will be much higher compared to injecting air. Shortly after starting the ozone

production, DO concentration in the MBBR influent increases from 6-8 mg O_2/L to 15-20 mg O_2/L. Most of the DO is consumed quite rapidly by nitrifying bacteria and heterotrophic bacteria in the two first reactors in the MBBR. However, besides dissolved oxygen concentration, the nitrifying reaction rate depends on several parameters like ammonia concentration and temperature. The capacity also depends on the retention time in the reactors and the amount of biofilm present on the carriers. During periods with high flow and ozone production, low temperature and low ammonia concentration, there are high peaks of residual DO remaining in the inlet to the denitrifying reactors. Denitrifying bacteria need an external carbon source to reduce nitrate and nitrite to nitrogen gas. However, the bacteria prefer using oxygen instead of nitrate and nitrite as an electron acceptor. In order to achieve the same reduction, during periods with high DO, more carbon source has to be dosed because the oxygen must first be consumed. There is a possibility to dose reject water with high ammonia concentration to the ozone reactor effluent during periods with low ammonia concentration in the nitrification reactors. The nitrification reaction rate can thereby be increased to reduce more DO and more of the carbon source is used for denitrification. But at the same time more nitrogen is added to the MBBR process. During summer periods the ammonium concentration after nitrification can be close to zero which means that there may be a nitrogen shortage for the bacteria in the subsequent denitrification process. Some studies claim that bacteria can adapt by using nitrate as a nitrogen source but there is a lag period of about two weeks (Zhang et al., 2020). When needed the reject water was added with a proportional dose of 1 L/m³ which increased the ammonium concentration by 1 mg/L. API concentration in the reject water was very low and the addition increased API-concentrations only marginally (approx. 2 ng/L in average).

To conclude, if the ozone dose can be reduced it not only reduces the energy and liquid oxygen consumption for ozone production, but it also reduces the consumption of carbon source for nitrogen removal in the MBBR.

Ozonation by-products

A critical compound when studying ozonation of wastewater is bromide, which can be oxidized to carcinogenic bromate. Analyses of bromide and bromate was performed during both the pilot- and the full-scale study. Neither bromide nor bromate were detected over the detection limits, 1 mg/L for bromide and 5 µg/L for bromate. The Swedish limit value for bromate in drinking water is 10 µg/L.

Transformation products

Ozone reacts with several organic micropollutants resulting in formation of several transformation products (TPs). Analysis of selected transformation products was performed on grab samples from the summer sampling campaign and the results are shown in Figure 25.

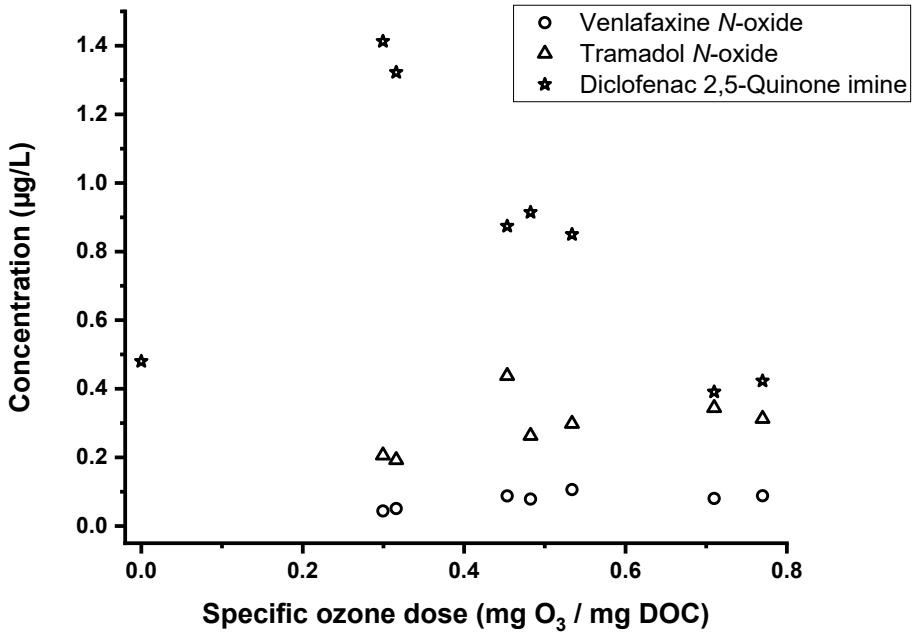

Figure 25: Concentration of N-oxide of tramadol and venlafaxine and Diclofenac 2,5-Quinone imine in the ozonation effluent.

Diclofenac 2,5-Quinone imine was formed from carbamazepine during ozonation as shown in Figure 25. This compound was present also in the influent to ozonation indicating its formation either during human metabolism or in biological treatment step in WWTP. Its concentration increases in the ozonation effluent with increasing ozone dose and reaches maximum at specific ozone dose of 0.3 mg O_3/mg DOC, N corr. Further, its concentration starts to gradually decrease above 0.3 mg O_3/mg DOC specific ozone dose. At a specific ozone dose of about 0.7-0.8 mg O_3/mg DOC, N corr its concentration was lower in the ozonation effluent compared to the ozonation influent.

N-oxides of tramadol and venlafaxine were below LOQ in the ozonation influent. Their concentration increased after ozonation as shown in Figure 25. A clear trend of formation and removal was not visible in this plant (also due to limited range of specific ozone dose applied during the experiment). More details about the formation and removal of these N-oxides was published by Kharel et al., 2020.

Ecotoxicity test

Three sampling campaigns were conducted at Linköping WWTP to investigate the impact of ozonation and MBBR post-treatment on a broad range of toxicological endpoints such as neurotoxicity, mutagenicity, genotoxicity, endocrine effects, growth and reproduction. Samples were taken at the ozonation influent as well as the effluents of the ozonation and MBBR, respectively. At all sampling campaigns an ozone dose of 8 mg O3/L was applied that corresponds to a specific ozone dose between 0.49 and 0.57 mg O3/mg DOC, N corr. Most of the 17 ecotoxicological tests were conducted with a final enrichment factor of 10 based on extracts from a solid phase extraction (1000-fold enrichment). Samples were filtered prior to the solid phase extraction. Therefore, particles as well some dissolved compounds (according to their physical and chemical properties) were removed from the samples. Therefore, the ecotoxicity results of enriched samples cannot be compared one-to-one to those which used native samples. Details on the ecotoxicological evaluation can be found in the CWPharma GoA3.3 report (Stapf et al., 2020).

For most of the investigated ecotoxicological endpoints (neurotoxicity, mutagenicity, genotoxicity and androgenic activity) no effects were found. Also, no negative effects were observed for growth inhibition of the bacteria *Pseudomonas putida* and the algae *Desmodesmus subspicatus*. For other tests, e.g. YES/YAS antagonistic properties, no systematic trend was observed, which prevented further evaluation and conclusions from the results obtained. Likewise, results of *Ceriodaphnia dubia*

reproduction inhibition indicated in one of two cases a negative impact of the ozonation process that could be removed by the MBBR post-treatment. However, more sampling campaigns would be required to confirm this finding. Beneficial impact of the ozonation was observed for the reduction of estrogenic activity that was occasionally present in the secondary effluent but below the limit of detection at the ozonation effluent. Also, *Aliivibrio fischeri* bioluminescence inhibition tests indicated slight toxic effects in samples of the ozonation influent that could be significantly reduced by the ozonation process, whereas the MBBR post-treatment had no significant impact.

In summary, advanced wastewater treatment with a combination of ozonation and MBBR post-treatment has shown a beneficial impact towards estrogenic potential and *Aliivibrio fischeri* bioluminescence inhibition. Also, results indicate that the ozonation process is not forming compounds that can cause negative effects on the majority of the evaluated toxicological endpoints.

Practical experiences from full-scale ozonation

Design of the ozonation plant

Specification of the ozone production equipment

The ozone generator capacity was specified by using data from the dose response test in the pilot study and a maximum flow of 3000 m^3/h, which allows treatment of up to 95 % of the flow on a yearly basis. The nominal production capacity was specified to be 20 kg ozone/h. The minimum flow and dose requirement specified the minimum production capacity to 2 kg ozone/h. In order to have the possibility to optimize the operation of the plant depending on operating conditions and the price of energy and oxygen, the ozone generator was specified to operate within a concentration span between 10 – 14 wt. %. The specification of the concentration span was based on input from different suppliers of ozone generators.

In order to have an energy efficient plant, there was a requirement on the mass transfer efficiency of the injection system of minimum 95 %.

It was decided not to pre-filter the ozone reactor inlet water. Instead the plant is by-passed during periods with suspended solids concentration above 10 mg/L.

Secondary effluent water is also used as cooling water.

Due to a possible risk of iron fouling of an installation with ceramic diffusers the injection system was specified to be a side stream injection.

Design of the reactor

During discussions with suppliers at the first part of the procurement process it turned out that the suppliers did not have the possibility to design the ozone reactor. Therefore, TVAB worked together with a consultant to test different configuration in a CFD-simulation. The target was to achieve efficient injection and homogenous mixing in the inlet chamber to achieve a high mass transfer efficiency in the inlet chamber and a plug flow through the following compartments to minimize the retention time distribution to avoid short circuiting.

Comments on the operating conditions and operating experiences

The large operating span of 2 – 20 kg ozone/hour and concentration span 10 – 14 wt. % set a requirement for the gas control valve to operate in a large span between 14 – 200 kg oxygen/h which was difficult to achieve especially at 14 kg oxygen/h were the control valve is almost closed.

At high ozone concentrations and gas temperature in the generator ozone degrades at a higher rate. The reaction is exothermic creating heat which speeds up the self-degradation rate even more. Therefore, it is crucial to have a good cooling capacity and operate at lower ozone concentration in the process gas for an energy efficient operation.

When using process water for cooling the system it is important to consider that particles and biofilm growth can considerably decrease the cooling water flow and reduce the heat transfer capacity of the heat exchanger. Higher cooling water temperature within the ozone generator increases the energy consumption and reduces the ozone production capacity.

The cooling water system in Linköping has been rebuilt by changing the cooling water source to the WWTP plant effluent water instead of secondary effluent water, installation of a self-cleaning filter system and injection of a small amount of ozone in the heat exchanger inlet to reduce biofilm growth.

Also a strainer was installed in the side stream to avoid blockage in the ozone injection system.

Foaming

During the pilot study, foaming problem during periods with high turbidity was obvious. The pilot off-gas system was filled with foam at several occasions. In the full-scale installation there is foam dampening spray water in the off-gas pipe inlet tube.

The ozone reactor effluent contains foam which can be seen at the surface of the inlet chamber of the MBBR-system. The concentration of suspended solids decreases by approximately 10 % over the ozone reactor. The foam probably consists of lysed biomass and dissolved foam-forming compounds.

Figure 26: Foaming in the ozone reactor effluent. Picture taken at the MBBR inlet compartment.

Working environment

Constructing a safe plant

It is very important to address the working environment when projecting an ozone plant, taking in consideration the tendency of ozone and oxygen to react with some construction material and other surrounding materials and compounds. Leakage during filling of the liquid oxygen (LOX) tank can result in a reaction with the fatty compound bitumen in asphalt. In Linköping the LOX-tank is mounted on a concrete plate surrounded by gravel and grass. Asphalt cannot be used because oxygen reacts explosively with fatty compounds.

Figure 27: LOX tank mounted on a concrete plate surrounded by gravel and grass for a safe work environment.

When ozone is handled it is important to use ozone resistant materials like stainless steel and PTFE gaskets. Rubber is degraded by ozone.

Operating safety

In the machine room double ambient ozone and oxygen sensors are installed. If a leakage is detected, ozone generation shuts down, oxygen gas valves close, audible and visible alarms and an alarm to the SCADA system are triggered and forced ventilation starts at 10-fold room volume change/h.

When entering the plant during operation it is mandatory to carry a portable ozone gas sensor.

Outside the machine room there is a locker with a gas mask with a filter which is specific for acid gases and organic fumes. It is only used to save a person from the machine room in the event of an accident with personal injury and ozone leakage in the room.

There is a catalytic ozone destructor on the off-gas line. The ozone concentration is measured before and after the destructor securing the function and shutting down operation if there is ozone detected in the destructor outlet.

Dissolved ozone is measured in the reactor effluent. If dissolved ozone is detected, the ozone production and flow shuts down and a dosage of digester centrate, with high concentrations of organic material, starts, which consumes residual ozone rapidly.

The ozone generator power transformer creates a high pitch noise and a magnetic field. Ear protection is necessary. People wearing pacemakers are not allowed to be near the power transformer.

Figure 28: Machine room.

Conclusions

Water quality parameters

- DOC and TOC represent the amount of organic compounds in the wastewater.
- The commonly applied ozone doses used for API elimination resulted in a very small impact on DOC and no significant reduction of COD. A further COD and DOC reduction impact of MBBR post-treatment on DOC and COD was limited.
- Nitrite present at the ozonation influent increases the ozone demand or, in case a constant ozone dosage is used, reduces the ozonation performance.
- Due to the differences in nitrite and DOC concentrations, normalization of the ozone dose was done according to these. The results from different sampling campaigns were more congruent when the ozone dose was normalized based on both nitrite and DOC.
- Both grab samples and 24 h composite samples were collected for the evaluation. The correlations between ozone dose, API reduction and other water quality parameters correlated better in the grab samples compared to the 24 h samples. The conclusion is that grab samples are useful to evaluate correlations between parameters, but 24 h composite samples are more representative in order to monitor the total influent and effluent load of APIs and other compounds.

API reduction

- The full-scale ozonation plant in Linköping reduces the amount of APIs in the wastewater when an ozone dose between 4-10 mg O_3/L is applied.
- Average API reduction for different applied ozone doses was calculated for atenolol, citalopram, diclofenac, metoprolol, sulfamethoxazole, oxazepam, trimethoprim and propranolol.
- A log-fit based on the results from the full-scale sampling campaigns was done giving the equation $y = 20.4 * ln(x) + 91$, where y is the average API reduction (%) and x the specific ozone dose (mg O_3/mg DOC, N corr) ($R^2 = 0.81$).
- To obtain averagely 80 % API reduction for the investigated APIs, a required specific ozone dose of 0.55 mg O_3/mg DOC, N corr was determined from the equation.

OPEX & CAPEX

- The specific energy consumption depends on the type of equipment and configuration. It is therefore important for other operators to investigate the costs that are relevant for the specific facility and not draw too much conclusions from the numbers that are specific for the ozone facility in Linköping.
- The cooling water temperature has a great impact on the energy consumption. At higher temperatures the maximum capacity of the ozone generator is reduced and the energy consumption increases substantially.
- OPEX also depends very much on the energy and liquid oxygen (LOX) prices.
- Calculated OPEX for the ozonation plant in Linköping is 197 k€ /annually if a specific ozone dose of 0.55 mg O_3/mg DOC, N corr is applied. The OPEX per m^3 treated water is 0.013 €/m^3.
- In Linköping around 18 % of the produced ozone is consumed by nitrite alone, which costs around 36 k€ /annually.
- The capital cost for the investment of the ozone treatment system in Linköping was limited by the existing infrastructure and costs that were charged to other projects. Inlet pumps, valves and the MBBR post-treatment system were already in place. The power supply needed for the ozone production had to be upgraded but the cost was charged to another project for power supply of future upgrade of the treatment plant. With these limitations the capital cost was approx. 25 MSEK (approx. 2.5 M €).

Variations of ozone consuming substances and ozone dose control

- The average concentration of the investigated APIs and UVA_{254} before ozonation indicated a variation during the day.
- Diurnal and weekly variations in the amount of the ozone consuming substances DOC and nitrite result in a varying ozone demand.
- This indicates that it would be necessary to adapt the ozone dose in order to maintain a stable specific ozone dose at all times to obtain a constant API reduction.
- An off-gas controller has been implemented in the control system in the full-scale plant as a quick response controller to avoid overdosing during a sudden dilution at rain events.
- A PI-controller for UVA_{254} reduction was tested and worked poorly due to noise in the measured process value resulting in very large fluctuations in the process. Instead a proportional controller for UVA_{254} reduction was designed and adjusted proportionally to the deviation from the set point with a certain percentage factor.
- When a constant ozone dose of 8 mg O_3/L is applied, the API reduction varies at different periods during the year and some overdosing of ozone may occur during the summer and underdosing during the winter. With process control, a more constant API reduction can be obtained, assumed that the controller works ideally. However, when comparing the average API reduction values, they are almost the same in both cases. It is therefore difficult to evaluate which way to go. If there is a requirement to achieve a constant API reduction, then process control would be needed. On the other hand, if the requirement states a yearly average of the API reduction, the controller may be redundant in this case.

Environmental effects

- A risk evaluation of how APIs would affect the aquatic environment was performed by calculating a risk quotient from the measured concentrations of selected APIs in the dose-response sampling campaigns and the predicted no effect concentration (PNEC).
- When applying a specific ozone dose of 0.55 mg O_3/mg DOC, N corr and an average dilution factor in the recipient the risk quotient is decreased below the high risk quotient limit 1.
- The method with risk quotients is useful to conclude the environmental effects of APIs downstream Linköping WWTP, where the dilution factor is about 20 in the immediate recipient water. For other WWTPs the dilution factor can be irrelevant, for example if the recipient is the Baltic Sea where the dilution factor is too high.
- A certain wastewater disinfection by the ozonation process can be achieved. When a specific ozone dose of 0.55 mg O_3/mg DOC, N corr was applied, 1 – 2 log reduction of *E. coli* and *Enterococci* could be achieved. The MBBR post-treatment further increased the reduction of pathogens.
- Advanced wastewater treatment with a combination of ozonation and MBBR post-treatment had a beneficial impact towards estrogenic potential and *Aliivibrio fischeri* bioluminescence inhibition. Furthermore, the results indicate that the ozonation process does not form compounds that can cause negative effects on the majority of the evaluated toxicological endpoints.

Effect on the downstream process

- The ozonation process results in an oversaturation of the water with oxygen (up to 20 mg/L), which is beneficial for nitrification processes in the MBBR, but can also have a negative impact on denitrifying post-treatment stages when the oxygen is not completely consumed during nitrification.
- If the ozone dose can be reduced it not only reduces the energy and liquid oxygen consumption for ozone production, but it also reduces the consumption of carbon source for nitrogen removal in the MBBR.

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Appendix

Table 6: Overview on evaluated APIs as well as other substances such as x-ray contrast agents or corrosion inhibitor, which are highlighted in italic. If not stated otherwise, PNEC and assessment factors are based on GoA2.2 report.

Active pharmaceutical ingredient	LOQ (µg/L)	PNEC (µg/L)	Assessment factor	CAS Number	Typical API usage
Atenolol (ATE)	0.025	194	SSD	29122-68-7	antihypertensive
Azithromycin (AZI)	10	N/A	N/A	83905-01-5	antibiotic
Benzotriazole (BTZ)	0.025	19[a]	50[a]	95-14-7	corrosion inhibitor, antifreezes
Candesartan (CSC)	0.025	0.42	1000	139481-59-7	antihypertensive
Carbamazepine (CBZ)	0.05	1.28	SSD	298-46-4	antiepileptic
Ciprofloxacin (CFX)	1	0.00511	SSD	85721-33-1	antibiotic
Citalopram (CIT)	0.05	15.4	SSD	59729-33-8	antidepressant
Clarithromycin (CLM)	0.0125	0.00391	SSD	81103-11-9	antibiotic
Clindamycin (CDM)	0.0125	0.014[b]	1000[b]	18323-44-9	antibiotic
Diatrizoic acid (DZA)	0.06	N/A	N/A	117-96-4	x-ray contrast agent
Diclofenac (DCF)	0.025	0.0852	SSD	15307-86-5	analgesic and anti-inflammatory
Eprosartan (ESM)	0.05	100	1000	133040-01-4	antihypertensive
Erythromycin (ERY)	0.00625	0.0835	SSD	114-07-8	antibiotic
Gabapentin (GPN)	0.05	100	1000	60142-96-3	antiepileptic
Ibuprofen (IBP)	0.1	0.00012	SSD	15687-27-1	analgesic and anti-inflammatory
Iohexol (IHX)	0.12	N/A	N/A	66108-95-0	x-ray contrast agent
Iomeprol (IMP)	0.12	N/A	N/A	78649-41-9	x-ray contrast agent
Iopamidol (IPD)	0.25	N/A	N/A	60166-93-0	x-ray contrast agent
Iopromide (IPR)	0.25	N/A	N/A	73334-07-3	x-ray contrast agent
Irbesartan (IBS)	0.00625	100	1000	138402-11-6	antihypertensive
Losartan (LSP)	0.0125	7.8	100	114798-26-4	antihypertensive
Metoprolol (MET)	0.05	4.38	SSD	51384-51-1	antihypertensive
Mycophenolic acid (MPA)	0.025	4.2[b]	50[b]	24280-93-1	immunosuppressant
Olmesartan (OLS)	0.025	N/A	N/A	144689-63-4	antihypertensive
Oxazepam (OXA)	0.025	0.81	100	604-75-1	treatment of anxiety, insomnia, and alcohol withdrawal syndrome
Phenazone (PNZ)	0.05	N/A	N/A	60-80-0	anti-inflammatory
Propranolol (PRO)	0.025	0.01[b]	50b	525-66-6	antihypertensive
Roxithromycin (RXM)	0.3	N/A	N/A	80214-83-1	antibiotic
Sotalol (SOT)	0.025	300	1000	3930-20-9	antiarrhythmic agent
Sulfadiazine (SDZ)	0.025	0.135	1000	68-35-9	antibiotic
Sulfamethizole (SMZ)	0.1	N/A	N/A	144-82-1	antibiotic
Sulfamethoxazole (SMX)	0.025	0.0438	SSD	723-46-6	antibiotic
Tramadol (TRA)	0.00625	170	1000	27203-92-5	analgesic and anti-inflammatory
Trimethoprim (TRI)	0.023	508	SSD	738-70-5	antibiotic
Valsartan (VLS)	0.05	125	100	137862-53-4	antihypertensive
Venlafaxine (VLX)	0.0125	3.22	1000	93413-69-5	antidepressant

LOQ = limit of quantification of the analytical method used at Aarhus University, PNEC = predicted no effect concentration, SSD = Species Sensitivity Distribution
a) based on European Chemicals Agency (ECHA), date: 14. April 2020. https://echa.europa.eu/registration-dossier/-/registered-dossier/14234/6/1
b) based on Ågerstrand, M. Derivation of PNECs for 39 pharmaceutical substances. ACES report number 36. Stockholm University. Table 4.

Table 7: Overview on evaluated transformation products, with the according limit of quantification (LOQ) of the analytical method used at Aarhus University.

Parent API	Transformation product	Abbreviation	LOQ (µg/L)
Azithromycin	Azithromycin N-oxides	AZI-NOX	0.2
Carbamazepine	1-(2-benzoic acid)-(1H,3H)-quinazoline-2,4-dione	BaQD	0.05
	CBZ 10,11 epoxides	CBZ-EPX	0.0125
	rac trans 10,11 (dihyro, dihydroxy) CBZ	CBZ-RTN	0.0125
Clarithromycin	Clarithromycin N-oxides	CLM-NOX	0.0125
Diclofenac	Hydroxy diclofenac (mix of 3,4,5)	DCF-OH	0.075
	DCF 2,5 quinone imine	DCF-QIM	0.1
	DCF amide	DCF-AMD	0.05
	DCF benzoic acid	DCF-BZA	0.05
	1-(2,6-dichlorophenyl)indolin-2,3-dione	DCPID	0.5
	2,6-dichlorodiphenylamine	DCPA	0.2
Erythromycin	Erythromycin N-oxides	ERY-NOX	0.05
Tramadol	Tramadol N-oxide	TRA-NOX	0.0125
	N-Desmethyl tramadol	N-DES-TRA	0.0125
Venlafaxine	Venlafaxin N-oxide	VLX-NOX	0.00625

Table 8: Parameters analysed for samples, methods and laboratory performing the analysis.

Parameter	Method	Laboratory for analysis
Pharmaceutical residues	HPLC-MS/MS	Aarhus University
DOC	SS-EN 1484, utg 1	TVAB laboratory
TOC	SS-EN 1484, utg 1	TVAB laboratory
COD	ISO 15705:2002	Synlab analytics Sweden AB
Suspended solids	SS-EN 872:2005	TVAB laboratory
Nitrite	ISO 15925-1:2013	TVAB laboratory
Nitrate	ISO 15925-1:2013	TVAB laboratory
Phosphate	ISO 15925-1:2013	TVAB laboratory
Conductivity	SS-EN 27888, utg 1	TVAB laboratory
Alkalinity	SS-EN ISO 9963-1, utg 1	TVAB laboratory
Dissolved ozone	Indigo method, AccuVac ampules (Hach)	TVAB laboratory
Ultraviolet absorbance (UVA_{254})	Spectrometry (UV-1700 PharmaSpec)	TVAB laboratory
Fluorescence (fDOM)	EXO fDOM sensor (YSI)	Berlin Centre of Competence for Water
Redox potential	Redox electrode (827 pH lab meter)	TVAB laboratory
E. coli	SS 028167-2	Synlab analytics Sweden AB
Intestinal enterococci	SS-EN ISO 7899-2	Synlab analytics Sweden AB
Coliform bacteria	SS 028167-2	Synlab analytics Sweden AB
Bromide	SS-EN ISO 10304-1:2009	ALS
Bromate	EN ISO 15061/EN ISO 10304-4	ALS

Table 9: Parameters measured online, instrument and manufacturer.

Parameter	Instrument	Manufacturer
Water flow	Sitrans FM	Siemens
Product gas flow	Rosemount 3051 differential pressure flow transmitter	Emmerson process management
Off-gas ozone concentration	Ozone analyser BMT 964	BMT Messtechnik GMBH
Dissolved oxygen	LDO2	Hach
Nitrate	Nitrax	Hach
Temperature	PT100	Hach
Turbidity	Solitax SC	Hach
Dissolved ozone	Aqueous ozone monitor UV-106-W	2B Technologies
Ultraviolet absorbance (UVA_{254})	UVAS	Hach