



Application of Ozone in Wastewater Treatment

For Mitigation of Filamentous Bulking Sludge & Reduction of Pharmaceutical Discharge

FILIP NILSSON

FACULTY OF ENGINEERING | LUND UNIVERSITY



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Reduction of Pharmaceutical Discharge

Filip Nilsson



LUND
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LICENTIATE DISSERTATION

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<p>Abstract</p> <p>Wastewater treatment with activated sludge is the most common way of treating wastewater. The process relies on bacteria converting nutrients, BOD and COD into biomass, CO₂ and N₂. Even though the configuration of activated sludge processes and wastewater treatment plants varies there are common problems which are shared. Filamentous bulking sludge is one problem that is widespread and disturbs the critical sludge separation which can result in reduced throughput, increased cost, sludge release, increased nutrient release and clogging of polishing steps. Another problem is that WWTPs are not designed to reduce the amount of pharmaceuticals commonly found in domestic wastewater and a large portion of them are being released into the environment.</p> <p>Alleviation of filamentous bulking sludge and reduction of pharmaceutical residues are both possible to achieve with ozone. This thesis presents results from two full-scale installations focused on mitigation of filamentous bulking sludge as well as one pilot-scale trial in which ozone was combined with a pre-treatment to remove pharmaceuticals from treated wastewater.</p> <p>Ozone addition into the return activated sludge was very effective in reducing the critical parameters SVI or DSVI to acceptable levels while not affecting the desired biological activity of the main treatment line. The energy consumption of such a system was investigated and found to be 0.044 kWh m⁻³ for a treatment lasting 45 days. This added operating cost should always be compared to the cost of having filamentous bulking sludge problems.</p> <p>A pre-treatment consisting of coagulation/flocculation/disc-filtration was highly effective in reducing the amount of ozone scavenging compounds. When ozone was added at a dose of 5 g O₃ m⁻³ after the pre-treatment, the total pharmaceutical reduction reached 95% compared to 80% without pre-treatment. When ozone was added after pre-treatment the energy consumption reached 0.165 kWh m⁻³ year⁻¹ while without pre-treatment the consumption reached 0.212 kWh m⁻³ year⁻¹.</p>		
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Preface

This thesis is the result of an industrial Ph.D. project cooperation between Primozone Production AB and Water and Environmental Engineering at the Department of Chemical Engineering, Lund University. The work has been conducted within VA-teknik Södra with financial support from Svenskt Vatten.

The study was concentrated to two distinct applications of ozone in wastewater treatment, filamentous bulking sludge reduction and pharmaceutical residue reduction. Two full-scale pilot studies were conducted at Öresundsverket and Klagshamn WWTPs to investigate the feasibility of using ozone for filamentous bulking sludge reduction. One pilot-scale installation to reduce pharmaceutical residues was operated at Lundåkraverket WWTP together with industrial Ph.D. student Janne Väänänen.

The results from this thesis can be used by WWTPs which are considering implementing ozone to either reduce pharmaceutical discharge or controlling filamentous bulking sludge.

Summary

Wastewater treatment with activated sludge has been around for over 100 years, there are however still issues with the process which has not been solved. One of these is filamentous bulking sludge, which is still causing a host of operational problems at wastewater treatment plants (WWTPs). The problems with this sludge stems from its low settling rate which upsets the clarifying process which is integral in wastewater treatment with activated sludge. In an effort to address the problems caused by filamentous bulking sludge, two full-scale trials with ozone were conducted at Klagshamn and Öresundsverket WWTPs. Ozone was injected into the return activated sludge (RAS) at both locations which was then fed into a pressurized reaction vessel. The trials were conducted with essentially identical equipment, the differences between the two trials were reduced to: location of the plant, flow of RAS, specific dosages of ozone and timespan of the trials. The differences were introduced to explore as many aspects of filamentous bulking control with ozone as possible. The specific ozone dosages was not stable at any location, due to the varying SS content in the RAS. At Öresundsverket for instance, the specific ozone dosage ranged from 2.8-5.0 g O₃ kg⁻¹ SS⁻¹ with a constant ozone dosage rate of 900 g O₃ h⁻¹. At Klagshamn WWTP, the variance in specific ozone dosage was greater due to the flow of RAS being changed to investigate how the flow impacted the results. The application of ozone to the RAS did lower the SVI or DSVI significantly at both locations: end SVI at the Klagshamn trials was approximately 100 ml g⁻¹ and end DSVI at Öresundsverket 100 ml g⁻¹. There was a concern that ozone could have a negative impact on the desirable biological processes at the plants, therefore, these processes (nitrification and bio-P release rates) were watched closely throughout the trials with no negative effects discernible. The conclusions from these two full-scale installations are that: ozone can effectively be used to control filamentous bulking sludge with no negative impact on the nutrient removal capabilities of the plant. The economics (energy consumption) of applying ozone for this application was also investigated and did conclude that an ozone plant does impose costs (0.044 kWh m⁻³ for 45 days of operation). However, this cost should be compared to the overall costs of having filamentous bulking sludge causing havoc at the plant.

Another more recent problem at wastewater treatment plants is the discharge of pharmaceutical residues. Pharmaceuticals enters the WWTP through human activity (production, consumption and others) and a large portion of the compounds is simply washed out with the treated wastewater. After that, the pharmaceuticals

enters the environment. At present, there are studies that have clearly shown that fish living in an environment polluted with pharmaceuticals develops numerous problems with their biology. The ability of ozone to reduce the concentration of pharmaceuticals being discharged from WWTPs has been shown numerous times, however, since ozone addition for pharmaceutical reduction is still in its infancy there is potential for advances in how the process is applied at the WWTP. In order to further the understanding of how different process makeups affect the efficiency, a pilot-scale trial was conducted at Lundåkraverket WWTP. The specific avenue of research was to implement a pre-treatment consisting of flocculation, coagulation and disc-filtration prior to ozone being injected. The concentrations of a selection of pharmaceuticals were analyzed after injection of ozone both with and without the pre-treatment. The results clearly showed that the pre-treatment was highly efficient in removing organic substances which in turn increased the pharmaceutical removal efficiency of ozone: 5 g O₃ m⁻³ reached 80% removal without pre-treatment compared to 95% when the pre-treatment was implemented. The economics (energy consumption) was investigated for this application as well and the calculation showed that ozone addition without pre-treatment will impose an extra energy expenditure of 0.212 kWh year⁻¹ m⁻³. When comparing this to the energy requirement of the process when pre-treatment is installed (0.165 kWh year⁻¹ m⁻³), it is clear that installing a pre-treatment is preferable in terms of operating costs.

Scope of the thesis

This licentiate thesis is a compilation of work on the subject of applying ozone in wastewater treatment. Since ozone can be used in a wide range of applications in a WWTP, two main parts were selected: reduce the problems with filamentous bulking sludge and reduce pharmaceutical residue discharge. The work was carried out from 2010 to 2015 at three WWTPs (Klagshamn, Öresundsverket and Lundåkraverket WWTPs), at Water and Environmental Engineering at the Department of Chemical Engineering, Lund University as well as at Primozone Production AB, Sweden.

Two full-scale trials were conducted at Klagshamn and Öresundsverket WWTPs to investigate the feasibility of applying ozone for reduction of filamentous bulking sludge. The biological processes were studied throughout both trials and an attempt to follow possible changes in the biological makeup of the treatment line subjected to ozone was conducted at Öresundsverket WWTP. The results from these two trials have been published at two peer reviewed conferences as well as in one international peer reviewed journal.

Paper I details the trials conducted at Klagshamn WWTP to reduce the problem with filamentous bulking sludge. The paper demonstrates that ozone can indeed be applied in the return activated sludge to improve the settling qualities of the sludge in the main treatment line. The paper also reports that no adverse effects could be detected on the nitrification rate of the activated sludge.

Paper II is very similar to Paper I, as the same type of equipment was used with the same purpose but at another WWTP. The results in this paper corresponds well with the results in Paper I as the settling qualities of the sludge was significantly improved without adverse effect on the biological nutrient removal processes. The paper also reported that no changes could be discerned in the biological makeup of the sludge in the main line after being subjected to ozone.

One pilot-scale experiment was conducted at Lundåkraverket WWTP together with industrial Ph.D. student Janne Väänänen at Hydrotech AB to investigate the impact of pre-treatment on ozone's ability to oxidize pharmaceutical residues. The pre-treatment consisted of chemical coagulation and flocculation followed by filtration to reduce phosphorus, COD and particulate matter before ozonation. Samples were analyzed for pharmaceuticals both with and without pre-treatment before ozonation.

Paper III reports the results obtained at the pilot-scale installation at Lundåkraverket WWTP. The results clearly show that the pre-treatment was highly effective in reducing the amount of phosphorus, COD and particulate matter. The paper also reported that this pre-treatment significantly lowered the amount of ozone needed to achieve the same reduction in pharmaceuticals as without pre-treatment.

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I express my heartfelt gratitude to Karin Jönsson and Åsa Davidsson for accepting me as a Ph.D. student and for your endless support and friendship.

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I am also very thankful for the work by the staff at NSVA and VA SYD for their efforts during the trials with ozone at Klagshamn, Öresundsverket and Lundåkraverket WWTPs.

I wish to express my gratitude to the following individuals:

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Jes la Cour Jansen for our discussions and your work on Paper III.

Maritha Hörsing for your work on Paper III.

Per Halkjær Nielsen and Artur Tomasz Mielczarek for your work and input on Paper II.

My family and friends for their love and support.

About the papers

This thesis comprises of the following original articles which will be referred to in the text by Paper followed by their Roman numerals I-III.

Paper I

Nilsson, F., Jönsson, K. and Dimitrova, I., 2012. "Full-scale ozonation to reduce filamentous sludge at Klagshamn WWTP." Paper presented at the International Ozone Association conference, Toulouse, June 4-6.

Paper II

Nilsson, F., Hagman, M., Mielczarek, A. T., Nielsen, P. H. and Jönsson, K. 2013. "Application of ozone in full-scale to reduce filamentous bulking sludge at Öresundsverket WWTP." *Ozone Science & Engineering* 36 (3): 238-243.

Paper III

Väänänen, J., Nilsson, F., Jansen, J. la C., Hörsing, M., Hagman, M. and Jönsson, K. 2014. "Discfiltration and ozonation for reduction of nutrients and organic micro-pollutants from wastewater – a pilot study." *Water Practice & Technology* 9 (4): 475-482.

Other publications

Along the papers presented above I have also been published along with Marisa Punzi *et al.* in:

Punzi, M., Nilsson, F., Anbalagan, A., Svensson, B.-M., Jönsson, K., Mattiasson, B. and Jonstrup, M. 2015. "Combined anaerobic-ozonation process for treatment of textile wastewater: removal of acute toxicity and mutagenicity." *Journal of Hazardous Materials* 292: 52-60.

My contributions to the publications

Paper I

I wrote the article, helped with the experimental equipment and created the figures. The experiments were designed and conducted by Ivelina Dimitrova and the article is based on her Master of Science thesis from 2011.

Paper II

I planned the experiment together with Karin Jönsson and Marinette Hagman. I conducted the ozone experiments, evaluated the ozone experimental data and wrote the article.

Paper III

I planned the experiments together with Janne Väänänen and Jes la Cour Jansen. I evaluated the ozone experimental data and wrote the ozone parts of the article.

Other publications:

I planned and executed the ozone part of the experiments and wrote the ozone part of the article.

Abbreviations

Abbreviation	Explanation
AWWA Res. F	American Water Works Association Research Foundation
BOD	Biological oxygen demand
COD	Chemical oxygen demand
Dose O ₃	Ozone dose
DMS	N,N-dimethylsulfamide
DSVI	Diluted sludge volume index
EDC	Endocrine disrupting chemicals
EtOH	Ethanol
GAC	Granulated activated carbon
HRT	Hydraulic retention time
LOX	Liquid oxygen
MBBR	Moving bed biological reactor
MO ₃	Ozone needed
NDMA	N-nitrosodimethylamine
NH ₄ -N	Ammonium nitrogen
P	Pressure needed from booster pump
PAC	Powdered activated carbon
PACl	Polyaluminum chloride
PE	Population equivalents
PLC	Programmable logic controller
PO ₄ -P	Phosphate phosphorus
P _{Reactor}	Desired pressure in reactor
PSA	Pressure swing adsorption
P _{Side Stream}	Pressure in side stream
Q _{Design}	Design flow
Q _{Side Stream}	Flow in side stream
Q _{O2}	Oxygen flow
Q _{RAS}	Total RAS flow
Q _{RAS,T}	Treated flow of RAS
RAS	Return activated sludge
R _{RAS}	Ratio of RAS treated
SS	Suspended solids

SV	Sludge volume
SVI	Sludge volume index
TOC	Total organic carbon
Total-N	Total nitrogen
Total-P	Total phosphorus
UCT	University of Cape Town
VSA	Vacuum swing adsorption
VSS	Volatile suspended solids
WWTP	Wastewater treatment plant
[O ₃]	Ozone concentration
[O ₂]	Concentration of oxygen
[SS]	SS concentration in RAS
ΔP_{inj}	Pressure loss in injector
ΔP_{Piping}	Pressure loss in piping

Thesis outline

The introduction section of this work introduces the reader to the subjects of wastewater treatment plants, the history of ozone, ozone applications and ozone reactions. Since ozone can be applied in a wide array of processes, the introduction section also details the two focus areas of the thesis, filamentous bulking control and reduction of pharmaceutical discharge. How ozone can be used to mitigate the problem with filamentous bulking sludge is presented in the section titled “Ozone and filamentous bulking sludge”. The section “Pharmaceuticals in wastewater” deals with the other focus area of this thesis, how the amount of pharmaceuticals being discharged from WWTPs can be reduced with ozone.

The final section “Conclusions” details what deductions can be made from the results obtained in the two focus areas.

Introduction

Ozone has one property in particular which makes it highly useful in wastewater treatment, namely its ability to oxidize organic and inorganic molecules. Oxidation is a chemical reaction in which a substance releases one or more electrons and becomes oxidized, since electrons cannot exist in their lonesome (except as electric current, electron beams or other special cases) they are taken up by another molecule which becomes reduced. Ozone's high tendency to accept electrons from other molecules stems from its inherent instability. The ability of ozone to rapidly oxidize other compounds is the reason why ozone can be utilized in a wide array of applications, ranging from disinfection of potable water to odor reduction in industries. Two different applications of this oxidation capability are investigated in this thesis for use in wastewater treatment.

A wastewater treatment plant is an integral part of everyday life, it does exactly what its name implies, treats wastewater. Wastewater enters the plant and is treated to lower the amount of oxygen scavenging substances (BOD and COD) as well as the amount of nutrients (nitrogen and phosphorus) being discharged into the environment. The treatment of wastewater is today mostly done by a system called activated sludge. Activated sludge is a biological process in which bacteria converts BOD, COD, nitrogen and sometimes phosphorus in wastewater into biomass, CO₂ and N₂. To retain the active bacteria in the process, a gravitational settler is usually employed. The extra biomass created by the bacteria is also removed from the system by the gravitational settler. The settler is by necessity placed close to the final steps in the process and is tailored to a specific flow of sludge entering the settler. If the settler is hindered in its operation by the emergence of a slow settling sludge (filamentous sludge), the throughput of the settler and therefore the plant itself will be affected. There are other problems associated with a slow settling sludge such as surface floating sludge which is costly and time consuming to deal with. There are ways of alleviating the problem with slow settling sludge that ranges from adding chemicals (ozone or PACl) to changing process parameters to make other non-filamentous bacteria grow more dominant.

It has been showed in recent years that rivers and lakes are being polluted by pharmaceutical residues. There are several sources for the pharmaceuticals entering the environment, because most pharmaceuticals are ingested in private homes and those homes are usually connected to a WWTP, the WWTP is a significant source. Since the wastewater treatment system of today is designed to handle a specific task (BOD, COD and nutrients) it is not optimized for removal of pharmaceutical residues finding its way to the plant. A portion of the pharmaceuticals entering the plant are nonetheless removed by the existing processes, however, in order to remove the majority of pharmaceuticals, an additional process has to be implemented. Research of new processes to handle the load of pharmaceuticals has been underway for quite some time, resulting in two preferred ways of tackling the problem, ozone or activated carbon. This work is focused on ozone.

Both filamentous bulking sludge and pharmaceutical residues are issues that affects the operation of WWTPs as well as the environment they are situated in. Both can be remedied with ozone, albeit in different scales of application.

Hypothesis and objectives

The two main hypotheses of this thesis are as follows:

Ozone can be applied in return activated sludge in full-scale to alleviate the problem of poor settling of activated sludge due to filamentous bacteria in a practical and economical manner.

The amount of ozone needed for pharmaceutical reduction in wastewater discharge can be lowered with a pretreatment to lower the organic matter content.

To substantiate the first hypothesis the following questions needs answering:

Can ozone be applied in full-scale to reach acceptable SVI levels?

If acceptable SVI levels can be reached, how long does it take?

Does the flow of return sludge being subjected to ozone have a significant impact on the timeframe and effect of ozone?

Does ozone injection at the rate needed to reach acceptable SVI levels affect the critical biological processes of the WWTP negatively?

Will ozone addition change the microbiological composition of the sludge in the main treatment line?

Is SVI reduction with ozone economically feasible in terms of operating costs?

For the second hypothesis the following questions needs an answer:

If a pretreatment consisting of coagulation/flocculation/disc-filtration is applied, will that lower the amount of ozone needed to reduce the pharmaceutical load significantly compared to the same system without pretreatment?

Is the applied process economically feasible in terms of operating costs?

Ozone and wastewater treatment

Ozone

Ozone was first reported and given its name by Carl Friedrich Schönbein in 1840 at the French academy of science. The name comes from the Greek word ozein, “to smell”, the name is fitting since the smell of ozone is highly characteristic. A high degree of effort went into discerning the true nature of ozone by researchers such as: C. F. Schönbein, J. L. Soret, J. C. G. de Marignac, R. F. Marchand, J. J. Berzelius, A. C. Becquerel, J. A. Houzeau, L. von Babo and others. That ozone was an allotrope of oxygen was discovered in 1865 by J. L. Soret and confirmed by him in 1867. An excellent description of the early years of ozone research has been published by Rubin (2001). The high reactivity of ozone was noted by Schönbein in his early experiments (Rubin, 2001), necessitating a careful choice of materials in which to house the ozone. This high reactivity of ozone derives from its inherent instability which in turn comes from the molecule’s readiness to accept an electron, reducing ozone to O₂, the electron donor then becomes oxidized. This ability of ozone to undergo redox reactions is what gives the ozone molecule its high redox potential of 2.07 V.

Ozone reactions

There are two different pathways for ozone reactions; indirect and direct. The indirect reactions are dependent on radicals formed by the reactions between ozone and an initiator, typically OH[•]. The product of this reaction is called a hydroxyl radical, OH[•]. A hydroxyl radical is characterized as being highly unstable, reacting with electron dense clusters in other molecules (such as amines, double- and triple bonds). The reactions undertaken by hydroxyl radicals are extremely fast, with typical reaction constants in the 10⁸-10¹⁰ M⁻¹ s⁻¹ range (Gottschalk *et al.*, 2010). The formation of hydroxyl radicals are deeply influenced by the pH of the system as well as the concentration of radical scavengers such as carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻). The reactions that make up the indirect pathways are numerous and complex, thus, the overall reaction producing hydroxyl radicals are summarized in Equation 1.



The direct reactions are much slower than the indirect reactions, typically in the $1.0 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$ range (Gottschalk *et al.*, 2010). Ozone reacts selectively with nucleophilic centers, such as unsaturated bonds in the target organic molecule, resulting in ozone being incorporated into the target and breaking of the attacked bond. An example of ozone reacting with an alkene is depicted in Figure 1. Through a complex reaction an ozonide is created, the redox properties of the environment will then induce two different end results; oxidative environment (such as when ozone is present): ketone and carboxylic acid; reductive environment: ketone and aldehyde.

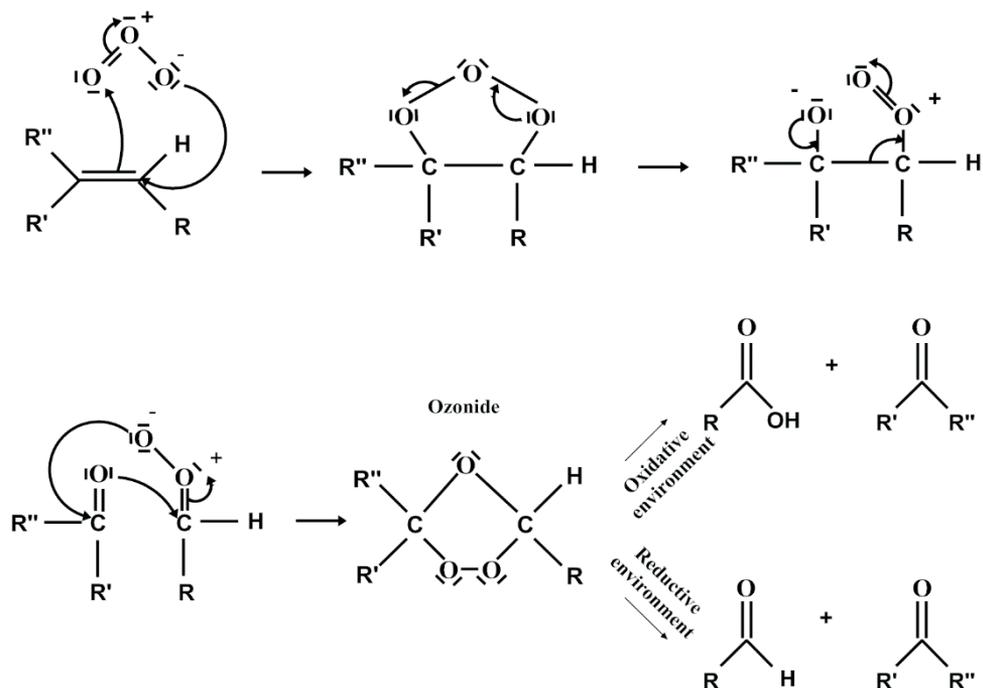
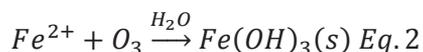


Figure 1.
An example of ozone reacting directly with an alkene.

Direct reactions between ozone and inorganic substances such as Fe^{2+} (Equation 2) and Br^- are generally faster than direct reactions with organic substances ($k = 10^{-3} - 10^9 \text{ M}^{-1} \text{ s}^{-1}$) (Gottschalk *et al.*, 2010). The variance in reactivity is also greater, following the degree of nucleophilicity of the inorganic substances.



The pH and the concentration of scavengers will decide which reaction pathway is dominant; $\text{pH} > 10$ indirect, $\text{pH} < 4$ direct. However, since natural waters are typically in the pH-range of 6-8, both reaction pathways will occur simultaneously (Gottschalk *et al.*, 2010).

Applications of ozone

The first major application of ozone was treatment of drinking water to achieve disinfection. The first ozone installation for inactivation of bacteria in the world was a pilot plant installed in Martinikenfelde in 1891 with equipment from Siemens & Halske, in the then German Empire. A full-scale installation of ozone to treat drinking water followed in 1893 in Oudshoorn, Netherlands. Afterwards, the number of ozone plants in Europe and America continued to rise until 1915, when 49 installations were completed in Europe. The wartime research into poisonous gases for the battlefields in Europe and Russia during World War I however, gave rise to the manufactory of inexpensive chlorine. Chlorine then superseded ozone as the major disinfection agent due mostly to its low price and relative ease of use. Not until after World War II did the construction of new ozone plants reach the same level as prior to 1915 (AWWA *et al.*, 1991). Since the end of World War II, it has been realized that ozone can be utilized for far more than disinfection of drinking water, for example; iron and manganese removal, color removal, turbidity reduction, pesticides degradation, SVI reduction of sludge, excess sludge minimization and disinfection of wastewater (van Leeuwen & Pretorius, 1988; Camel and Bermond, 1998; Xu *et al.*, 2002; Böhler and Siegrist, 2004). Lately, the use of ozone for removal of micro-pollutants, such as pharmaceuticals, biocides and EDCs has gained in interest, especially in Switzerland (Eggen *et al* 2014).

The biological nutrient removal activated sludge plant

The activated sludge system for treatment of wastewater evolved from 1914 and onwards with aeration of Imhoff tanks through blower tanks to recycling of sludge and all the way to today's system. The development of the activated sludge system is a colorful and interesting story, readers interested in the history of the activated sludge system should certainly read the excellent review of the subject by Alleman and Prakasam (1983). The current system of activated sludge treatment varies throughout the world depending on numerous factors such as choice of process, geographical pre-requisites (land availability, climate etc.), loading and suchlike. However, the plant's purpose is to remove BOD, COD and nutrients by utilizing suspended bacteria. Therefore, the plant will need certain unit operations to

function, for example; sufficient HRT, aeration and/or stirring, sludge separation, recycling and disposal. All the unit operations mentioned can possibly be configured in a vast array of manners throughout the world. The removal of phosphorus for instance can be achieved either by utilizing the suspended bacteria, chemical precipitation or a combination of the two. The removal of nitrogen is more uniformly designed through the use of nitrification/denitrification bacteria, which have certain requirements to operate such as aeration and carbon source. Water and Environmental Engineering at Lund University has for many years enjoyed a highly productive cooperation with two large municipal companies running the majority of wastewater treatment plants in southern Sweden, VA-Syd and NSVA. Three WWTPs run by VA-Syd and NSVA were due to their location and disposition chosen as testing facilities for this work, Öresundsverket, Klagshamn and Sjölundaverket WWTPs.

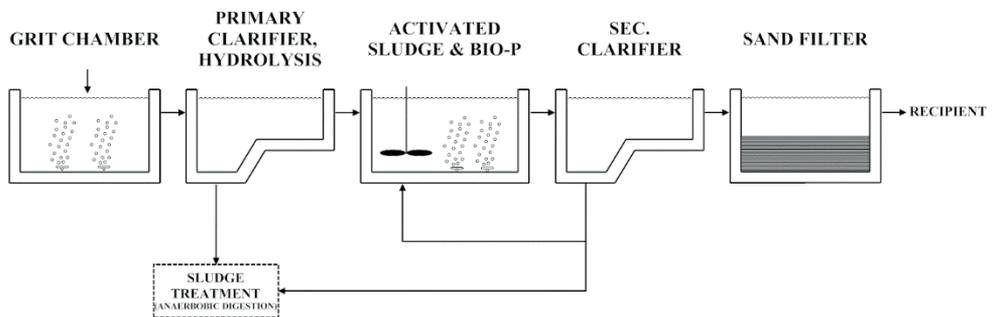


Figure 2.
A schematic overview of the treatment train at Öresundsverket WWTP.

Öresundsverket WWTP in Helsingborg is a 220 000 P.E. fully biological nutrient removal plant (Figure 2). The first step in the treatment at Öresundsverket WWTP consists of screens followed by aerated grit chamber followed by separation into four parallel treatment lines beginning with primary clarification with hydrolysis of primary sludge. The biological stage (with Bio-P) starts with two anaerobic/anoxic volumes followed by three anoxic/aerobic stages and ends with an anoxic zone, also called a UCT-process. The sludge separation is conducted with a secondary clarifier that recycles the major part of the sludge back into the second anaerobic/anoxic zone. The excess sludge is sent into the sludge treatment, consisting of thickening, anaerobic digestion and dewatering. The final stage before the treated wastewater is released into the recipient (Öresund strait) consists of a sand filter (Jönsson *et al.*, 1996).

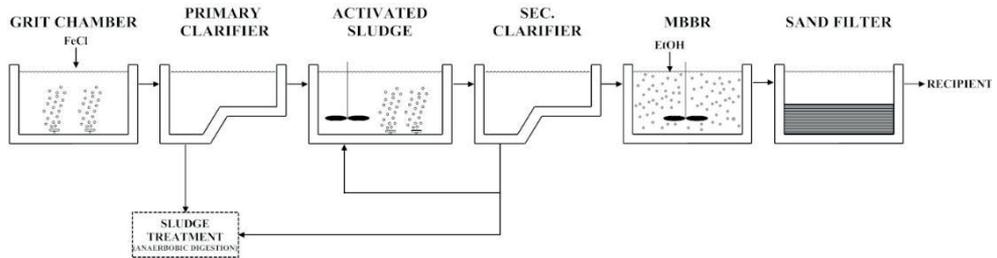


Figure 3.

A schematic overview of the treatment train at Klagshamn WWTP.

The Klagshamn WWTP (Figure 3) in Malmö, Sweden is a 90000 P.E. plant that combines chemical pre-precipitation of phosphorus and biological nitrification/denitrification. The treatment train in Klagshamn WWTP consists of two parallel lines that starts with screens followed by an aerated grit chamber with addition of FeCl for precipitation of phosphorus. The wastewater is then fed to the primary settlers, where primary sludge and wastewater is separated. The following activated sludge process is divided into nine zones that are individually controlled, depending on the desired oxygen level and requirement. From the activated sludge basin, the wastewater is transported to the secondary settler, in which the sludge separation is conducted. The return sludge is cycled back into the beginning of the activated sludge basin and the excess sludge is fed to the anaerobic sludge treatment. Following sludge separation is the post denitrification stirred MBBR with an additional carbon source of ethanol. After the post denitrification MBBR the treatment lines are combined into five sand filters for final polishing prior to release into the recipient (Öresund strait).

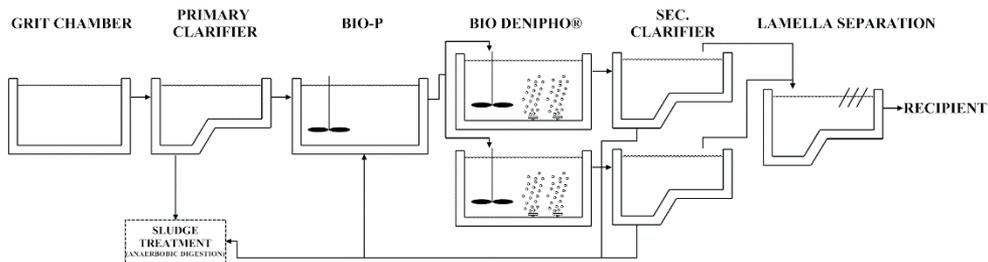


Figure 4.
A schematic overview of the treatment at Lundåkraverket WWTP.

Lundåkraverket WWTP (Figure 4) in Landskrona, Sweden is a 38600 P.E. plant that is a little different compared to Klagshamn and Öresundsverket WWTPs in the regard that it employs a Bio-Denipho® process. The plant is operated as a single line that starts with screens and grit chamber followed by two primary settlers in series. The water is then fed to two anaerobic bio-P basins, followed by the Bio-Denipho® process. The sludge separation takes place in two parallel settlers which then feeds the water phase to the chemical precipitation and lamella separation prior to release into Öresund strait.

Regardless of the exact manner in which these operations are set up, the underlying principles of operation remains the same in terms of the challenges with utilizing bacteria. Therefore, the operational problems faced by one plant can easily be found in another, for instance, filamentous bulking. Filamentous bulking is a phenomenon caused by long filamentous bacteria growing to such an extent as to hinder the separation of sludge from the treated wastewater. The activated sludge system depends on bacteria being present in high enough concentrations in the process for a specified time. If the separation of sludge is hindered, the recycling of sludge from the settler is also hindered, leading to a more inefficient process. Floating sludge in the settler is also a consequence of the filamentous sludge, leading to washing out of sludge and in turn excess nutrient and BOD discharge.

Another problem that has emerged in recent years is the pharmaceutical content of the treated wastewater being discharged from the WWTP's. Since the majority of pharmaceuticals are taken in the home and is transported to the WWTP by wastewater it is challenging to address the issue at the source. Necessitating major efforts at the WWTP instead.

Both these issues are to a high extent possible to address with the application of ozone at the wastewater treatment plant.

Ozone and filamentous bulking sludge

The differing density of activated sludge and wastewater is the driving force in a secondary clarifier. Since the secondary clarifier is one of the critical processes in the WWTP, a disturbance in this process will propagate outwards and cause further problems in the other processes, such as low throughput, sludge release, surface floating sludge etc. Filamentous bacteria are a type of bacteria that forms long web-like structures and causes a phenomenon called filamentous bulking sludge which in turn causes the sludge to be slow-settling (van Leeuwen, 1992; Martins *et al.*, 2004).

There are two different paths available to the operator of the WWTP to remedy the problems caused by filamentous bulking sludge, specific or non-specific. The specific method takes the form of a purposely built selector which, depending on the filamentous species present, imposes ecological regimes designed to inhibit the growth of filamentous bacteria in favor of non-filamentous bacteria. The non-specific methods entail adding a chemical to the sludge, such as chlorine, ozone, aluminium chloride or polyaluminium chloride to either attack the filamentous bacteria directly (ozone and chlorine) or changing the hydrophobicity of the target and thus hindering their uptake of lipid substrate (van Leeuwen, 1988; van Leeuwen & Pretorius, 1988; Saayman *et al.*, 1996; 1998; Paris *et al.*, 2005). Van Leeuwen (1992) proposes that the large surface area of the filaments makes them more susceptible to ozone and other oxidants, however, the exact means by which the mentioned chemicals work is still not completely understood. Since the non-specific measures do not address the cause of the filamentous bacteria, the treatment has to be repeated periodically to ensure adequate settling in the secondary clarifier.

The effective use of ozone to decrease the problem with filamentous bulking sludge has been known for quite some time since van Leeuwen (1988) published an article describing how ozone was applied in a small pilot activated sludge plant installed at the Rooiwal Sewage Works in Pretoria, South Africa. Ozone was applied at two different points in the pilot scale activated sludge plant, directly in the aerated zone and into the return activated sludge. In the aerated zone, ozone was applied at three different doses: 1, 2 and 4 g O₃ kg⁻¹ SS⁻¹, while in the return sludge, a single dose of 2 g O₃ kg⁻¹ SS⁻¹ was used. The results clearly showed that ozone addition lowers the DSVI of the sludge, however, the addition of ozone in the return sludge was more

efficient. An article published by Saayman *et al.*, (1998) shows that when ozone is applied in full-scale to the aerated basin, the SVI is improved even at as low a dose as 0.4-1.4 g O₃ kg⁻¹ SS⁻¹. Wennberg *et al.*, (2009) described the use of ozone to reduce filamentous bulking sludge in full-scale at Klagshamn WWTP, Sweden. Ozone was applied in full-scale on a portion of the return activated sludge at a dosage of 6 g O₃ kg⁻¹ SS⁻¹ and was sufficient to lower the DSVI significantly. A more recent study published by Lyko *et al.*, (2012) details the application of ozone in the return sludge flow in full-scale. Ozone was applied at a dose of 1.6 g O₃ kg⁻¹ SS⁻¹ and approximately 6% of the return sludge flow was treated. The treated line was subjected to ozone for one week every month for approximately 8 consecutive months. The SVI was clearly improved in relation to the control line both initially and throughout the entire trial period. The manner in which ozone is added to the return sludge flow could potentially be of great importance. For instance, ozone can be added at a low constant rate for several weeks/months or for a shorter time but with a higher dosing rate. Due to the limited number of publications on filamentous bulking control with ozone it is not possible at this time to compare different dosing strategies.

The technique of applying ozone specifically to reduce filamentous bulking sludge has not been widely applied nor studied in more than a handful of full/pilot-scale cases found for this thesis. The reason for this is unknown; however, a suggestion is that the method has not been promoted to the same degree as chlorination. The barrier of applying a relatively technology- and knowhow-heavy technique such as ozone can also be a factor in its low usage at WWTPs for filamentous bulking control. A field that has received more attention is the use of ozone to reduce the amount of excess sludge. Ozone was, in most of the cases studied introduced to the return activated sludge albeit with a higher dosage (50 g O₃ kg⁻¹ TSS⁻¹, Dytczak *et al.*, 2007) than for filamentous bulking control. The results obtained by the researchers indicates that ozone can be used to limit or negate the production of excess sludge as well as improve the settling qualities of the sludge (Yasui *et al.*, 1996; Dytczak *et al.*, 2007; Chu *et al.*, 2009).

Filamentous sludge treatment with ozone

The trials that forms a large part of the basis for this thesis were conducted at Klagshamn WWTP in Malmö and Öresundsverket WWTP in Helsingborg in 2011 (Papers I & II). The two plants have been described earlier in this work, however, the plants are both ideally suited to host scientific trials due to their separate treatment lines, providing a real-world reference point, fed with the same influent as the trial line. The scale of the ozone plants used is denoted as full-scale since the equipment were sufficient to treat one treatment line at a time and as will become

apparent further on in this work, one ozone plant can be used for at least two treatment lines. Both WWTPs have experienced problems with their treatment process originating in insufficient settling caused by filamentous sludge. At Klagshamn WWTP the problems caused by filamentous sludge were especially pronounced, causing sludge to be washed out and ending up in the polishing sand filter. Both plants have tried different means to come to terms with the filamentous sludge such as altering the aeration rate and sludge age with varying degree of success. Klagshamn WWTP tested applying PaCl for four consecutive years starting in 2006, the improvement in DSVI was highly varying (Wennberg *et al.*, 2009) causing the plant to look for alternatives. Since neither plant had successfully solved the filamentous sludge problem with specific measures, they decided to try ozone instead. Two mobile, 10-foot containers were constructed in which the ozone production units were housed and installed at both plants. The systems installed at the two WWTPs were identical in terms of equipment inside which consisted of: ozone generator, screw compressor, oxygen generator, chiller, ozone concentration meter and system PLC (Figure 5 and 6).

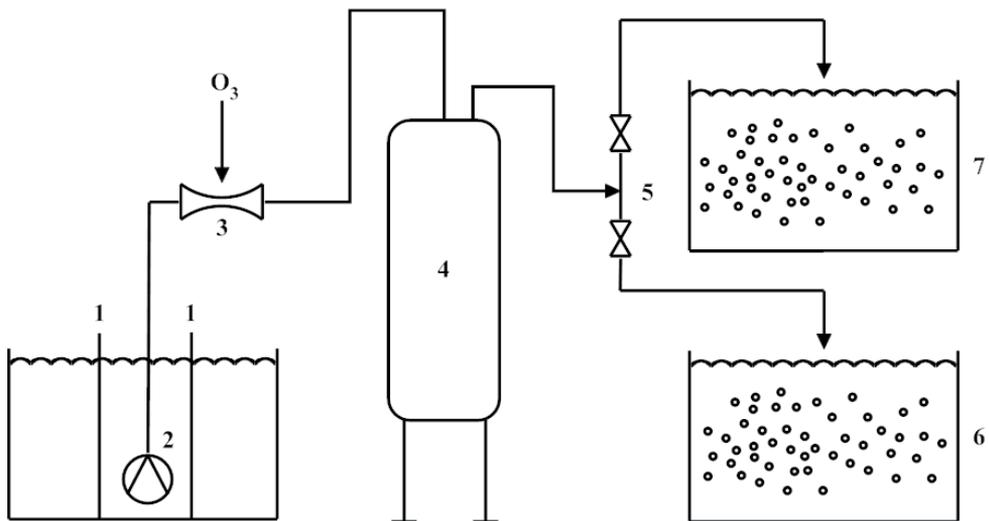


Figure 5. Simplified schematic overview of the experimental setup at Klagshamn WWTP (more details are available in Paper I). 1: Baffles for choosing source of RAS, 2: submerged centrifugal pump, 3: venturi injector, 4: pressurized reaction vessel, 5: valves for choosing destination of treated RAS, 6: aerated zone of treatment line 1, 7: aerated zone of treatment line 2.

At Klagshamn WWTP, the container was installed in such a way as to be able to treat both treatment lines (Figure 5), however, not at the same time. A centrifugal pump was installed at a tactical location in the process train so as to permit return sludge from one line at a time to be pumped ($25\text{-}32\text{ m}^3\text{ h}^{-1}$, $\sim 5\%$ of the total return

sludge flow) through the venturi injector and onwards into the 7.9 m³ pressurized reaction chamber. With the opening and closing of baffles and valves (depicted in Figure 5) the ozone treatment was switched between the two lines. A total of five ozone treatments were conducted at Klagshamn WWTP (Table 1) with alternating flow of return sludge and ozone output (between 620 – 900 g O₃ h⁻¹). The reasoning behind the variation was to find a viable ozone dosing strategy at that particular WWTP, a more detailed description of the trials at Klagshamn WWTP is available in Paper I.

Table 1.
Summary of ozone treatments at Klagshamn WWTP.

Treatment number	WWTP line	Ozone input (g O ₃ h ⁻¹)	Return sludge flow (m ³ h ⁻¹)
I	1	620	25
II	1	620	25
III	1	900	32
IV	2	620	25
V	2	900	32



Figure 6.
Left, outside view of the container and pressurized reactor installed at Klagshamn WWTP. Right, inside view of the same container.

At Öresundsverket WWTP (Figure 7 and 8), the container was installed to treat one line only, the layout of the plant did however necessitate the return sludge to be pumped approximately 60 m prior to injection of ozone. The centrifugal pump was installed in the return sludge basin and delivered $\sim 42 \text{ m}^3 \text{ h}^{-1}$ ($\sim 5\%$ of the total return sludge flow) to the venturi injector and further on into the pressurized reaction vessel (7.9 m^3). From the reaction chamber, the ozone treated return sludge was led back into the aerobic basin. The operation of the ozone unit at Öresundsverket WWTP was more straightforward than at Klagshamn WWTP, ozone was applied at a constant rate of $900 \text{ g O}_3 \text{ h}^{-1}$ to $\sim 42 \text{ m}^3 \text{ h}^{-1}$ of return sludge for 45 days (see Paper II).

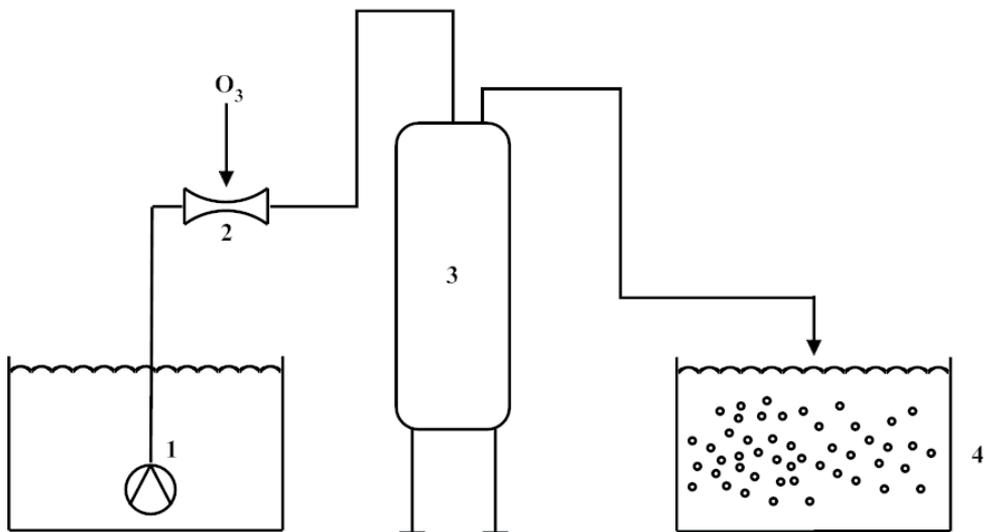


Figure 7.

A simplified schematic of the ozonation system at Öresundsverket WWTP (more details are available in Paper II). 1: Submerged centrifugal pump, 2: venturi injector, 3: pressurized reaction vessel, aerated zone of the chosen treatment line.



Figure 8.
Picture of the container and pressurized reaction vessel installed at Öresundsverket WWTP.

Since it is possible that ozone has a negative impact on the biological nutrient removal capacity of activated sludge it was of utmost importance that the biological activity of the treatment lines were watched closely throughout the trials. The efficiency of the treatment lines at both plants were monitored throughout the ozone trials by a number of parameters, especially the nitrification- and phosphorus release-rates (phosphorus release rate, only at Öresundsverket WWTP) along with normal effluent parameters such as: $\text{NH}_4\text{-N}$, Total-N, Total-P and $\text{PO}_4\text{-P}$. The methods used for nitrification and phosphorus release rates are detailed in Paper II.

Impact on SVI and DSVI

The results from the trials conducted at Klagshamn and Öresundsverket WWTPs are summarized in Table 2. The SVI from both lines at Klagshamn WWTP showed a significant decrease from all ozone treatments reaching an SVI of approximately 100 ml g^{-1} . The different process conditions tried at Klagshamn WWTP (Table 1) did have an impact on the time it took to reach acceptable SVI levels. The higher the flow being treated with ozone the faster did the SVI reach acceptable levels (100 ml g^{-1}). This is not apparent in the summarization of results in Table 2, however, the figures with the SVI results in Paper I provides a clearer picture.

Table 2.

Summary of the results from the ozone trials presented in Paper I and II.

WWTP: Line#: Run#	Days of O ₃	Start SVI or DSVI (ml g ⁻¹)	End SVI or DSVI (ml g ⁻¹)	Flow of RAS (m ³ h ⁻¹)	SS in RAS (kg m ⁻³)	Amount O ₃ (g O ₃ h ⁻¹)	Dose (g O ₃ kg ⁻¹ SS ⁻¹)
Klagshamn: 1: 1	35	SVI: 261	SVI: 86	25	3.1 - 6.7	620	3.7 - 8
Klagshamn: 2: 4	26	SVI: 185	SVI: 78	25	1.9 - 5.3	620	4.7 - 13
Klagshamn: 1: 2	53	SVI: 143	SVI: 96	25	4.3 - 7.9	620	3.1 - 5.8
Klagshamn: 2: 5	32	SVI: 220	SVI: 86	32	4.7 - 6.7	900	4.2 - 6.0
Klagshamn 1: 3	26	SVI: 251	SVI: 73	32	4.3 - 6.1	900	4.6 - 6.5
Öresundsverket 2: 1	45	DSVI: 170	DSVI: 100	42	4.3 - 7.6	900	2.8 - 5.0

A more tangible result is depicted in Figure 9, in which the aerated zones of two parallel treatment lines at Öresundsverket WWTP show a clear difference in the amount of surface floating sludge. The left picture is the treatment line subjected to ozone and the right one is a line without ozone application. The pictures were taken the day after the ozone plant had been running for 45 days. At the start of the treatment with ozone, both treatment lines looked like the left picture.

**Figure 9.**

Pictures of the aerated zones of two parallel treatment lines at Öresundsverket WWTP with (left) and without (right) ozone addition.

At Öresundsverket WWTP it was not possible to measure the SVI directly since the SV of the activated sludge was too high (approximately 800 ml), necessitating measurements of DSVI instead. Starting at a DSVI-value of 170 ml g⁻¹, the DSVI decreased after approximately 10 days and reached a DSVI of 100 ml g⁻¹ after 40 days of ozone addition. What becomes apparent from Table 2 is that the target relative dosage of 5 g O₃ kg⁻¹ SS was difficult to maintain, due to the varying SS-values of the return sludge. Even though the relative dose was not kept in any of the trials, the SVI or DSVI was significantly lowered. Another issue which is not as apparent from Table 2 is the question of how long it takes to reach acceptable SVI or DSVI levels. The number of days of ozonation only specifies the total number of days that ozone was introduced to the return sludge and not how long it took to reach acceptable levels. For instance, the Klagshamn 1:2 run was operated with ozone for a total period of 53 days, however, within 10 days the SVI levels were satisfactory (<100 ml g⁻¹). The run before that, Klagshamn 1:1 was operated with ozone for 35 days, while the SVI reached satisfactory levels within approximately 30 days. The time it took to reach acceptable levels of SVI with ozone application varied substantially throughout the Klagshamn trial (Paper I). The reason for this variance is not known, however, one reason can be that the biological makeup of the sludge is in a state of constant change due to external factors such as influent composition and temperature, causing the impact of ozone to change. Overall, it took approximately 2-6 weeks of ozone addition throughout all trials to reach satisfactory levels of SVI or DSVI.

Impact on biological nutrient removal

Two of the most important measurements in a WWTP are the concentration of nitrogen and phosphorus species being discharged by the plant, especially since those are among the key figures in the plant specific discharge limits. The concentration of these nutrients being discharged is in turn a measurement of how well the plant is operating. A disturbance in the nitrification/denitrification, biological phosphorus removal or sludge being discharged from a secondary settler which is hindered by filamentous sludge will be detected by measuring the concentration of these species being discharged. However, the measurements of discharged nutrients are usually conducted at the combined effluent of the entire plant by stationary in-line meters, to monitor the activated sludge part of one treatment line it is therefore desirable to apply different means of measuring performance. In the case of nitrogen removal performance, the speed by which the sludge is nitrifying NH_4^+ to NO_2^- and NO_3^- (nitrification rate) can be employed. The nitrification rates of the treatment lines subjected to ozonation in Paper I & II are presented in Figures 10 and 11.

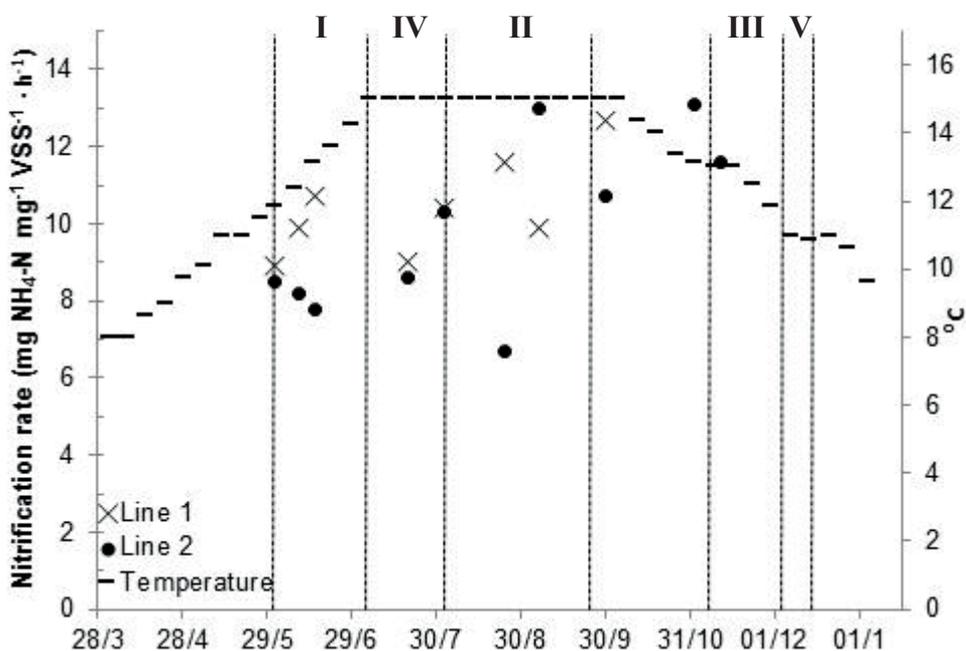


Figure 10.

Nitrification rates of line 1 and 2 together with wastewater temperature in the primary clarifier during the ozone trial period at Klagshamn WWTP (Paper I). The lines and numerals depict the approximate duration of the ozone treatments.

In Paper I, both treatment lines were subjected to ozonation with no adverse effect on nitrification rates as is apparent from the stable nitrification rates. The apparent rise in nitrification rate for those lines can be explained by the increase in water temperature.

The treatment line subjected to ozone at Öresundsverket WWTP were followed for a shorter time than at Klagshamn WWTP (Figure 11), nonetheless, since the nitrification rate remains stable, no adverse effect upon the nitrification rates can be contributed to the addition of ozone.

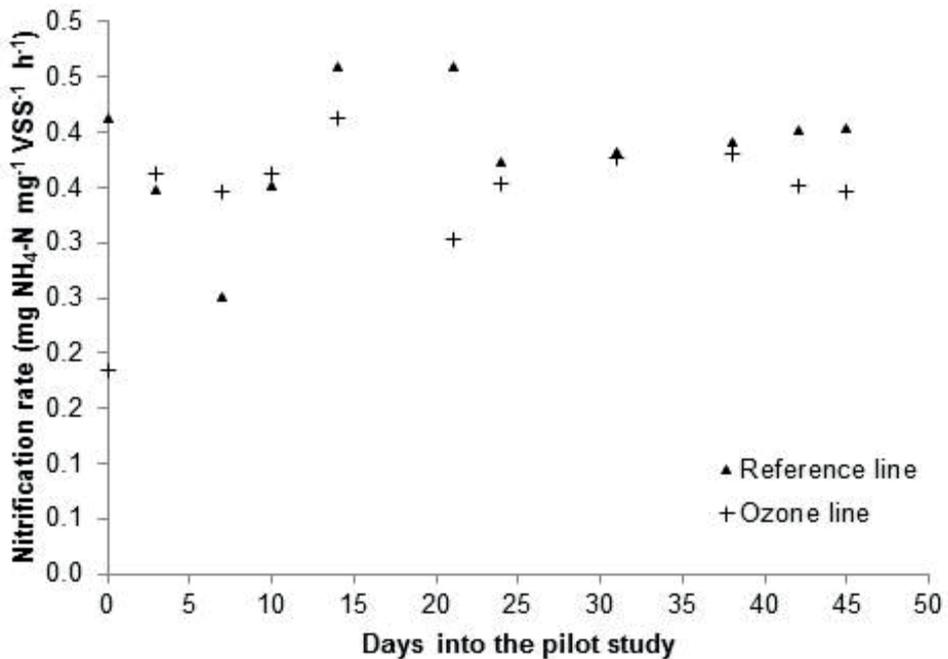


Figure 11. Nitrification rates of the ozone treated and reference lines at Öresundsverket WWTP (Paper II). The ozonation in the ozone line started at day 0.

When it comes to the other nutrient closely followed by WWTP's, phosphorus, the results are similar. Although, since Klagshamn WWTP (Paper I) does not employ biological phosphorus removal, the phosphorus removal performance (Bio-P release rate) was only assessed on sludge from Öresundsverket WWTP (Paper II).

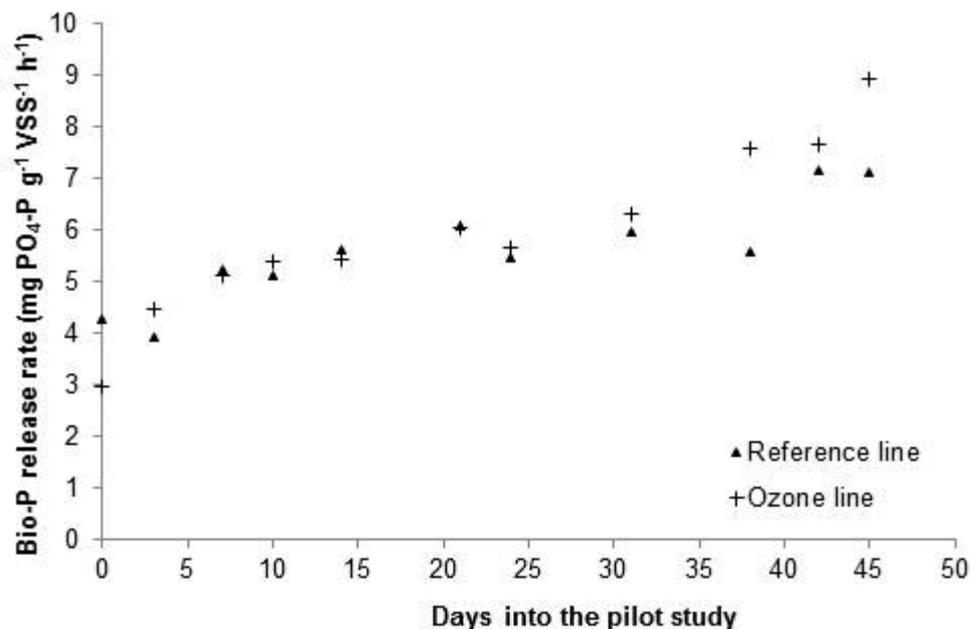


Figure 12. Phosphorus release rates of the ozone treated and reference lines (Paper II).

The phosphorus release rates measured at Öresundsverket WWTP (Figure 12) indicates a slight rise in both the ozone- and reference lines. Since the rise is shared by the two lines, it is reasonable to accredit the rise in performance to an outside factor, such as the rising temperature in southern Sweden during March and April when the ozone treatment was conducted.

Cost of applying ozone for reduction of filamentous bulking sludge

Van Leeuwen and Pretorius (1988) published an article detailing the application of ozone into the aerobic zone in a small pilot-scale system. The application of 4 g O₃ kg⁻¹ SS⁻¹ was efficient in maintaining a low SVI of the ozonated sludge compared to the control. The cost of applying ozone as compared to chlorination was also investigated and the conclusion was drawn that ozone is not significantly more expensive.

An article published by Saayman *et al.*, (1998) shows that when ozone is applied in full-scale to the aerated basin, the SVI is improved even at as low a dose as 0.4-1.4 g O₃ kg⁻¹ SS⁻¹. However, the article also deals with the economics of the application and concludes that chlorination and not ozone is the most cost-effective way to reduce the filamentous bulking sludge with non-specific measures.

The operating cost of an ozone system is dominated by electrical energy input, although additional costs can arise from maintenance. The main contributors to the energy requirements of an ozone system are in this work identified as: ozone generation, feed gas generation, cooling of the ozone generator and the injection system. In order to estimate the amount of energy required and hence the cost of operating an ozone system for reduction of filamentous bulking sludge, an energy calculation has been made (Appendix I). With an ozone system similar to the one described in Paper II, the energy requirements for one hour of operation adds up to 30.7 kWh or 0.044 kWh m⁻³ for the entire treatment lasting 45 days.

Discussion

The addition of ozone investigated in Paper I & II clearly shows that ozone can effectively be used for filamentous bulking control which is comparable to findings published by Lyko *et al.*, (2012). Even though the actual relative dosage (g O₃ kg⁻¹ SS⁻¹) of ozone varied substantially in all trials, the SVI or DSVI was significantly lowered. This indicates that it is not essential, in terms of SVI or DSVI- reduction to adhere to a stable relative dosage of ozone. Additionally, the ozone addition in these trials did not impact negatively on the biological activity in any detectable way.

The investigation into the economy of the treatment revealed that, ozone addition does require a fair amount of electrical energy (30.7 kWh for one hour of operation). However, the cost of having filamentous bulking issues at the WWTP is also significant. For instance, a comparison of cost between adding PAX, adding ozone and using pump trucks to alleviate the problems of floating filamentous sludge was presented by Wennberg *et al.*, (2009). The comparison showed that when considering both investment- and operating costs, ozone was slightly less expensive than using pump trucks, with PAX being the overall cheapest method. However, if a WWTP wishes to reduce their use of chemicals or for some reason chemicals does not work (as in Klagshamn WWTP, Wennberg *et al.*, 2009), ozone can be an advantageous option.

The appearance of filamentous bulking is not consistent throughout the year. This leads to long periods of no ozone application and periods with a sudden need for ozone. This imposes the question whether it is most effective to apply ozone periodically or consistently. Lyko *et al.*, (2012) applied ozone for 1 week every month for approximately 8 months, resulting in the SVI being kept below a value of 100 ml g⁻¹ throughout the trial period. In Paper I, two lines at a WWTP were treated with the same ozone system by alternating the source and end-point of the treated RAS. Ozone was added to one of the treatment lines for approximately two weeks until the SVI of that line had reached satisfactory levels, then the system was switched to the other line and the process repeated. This continued for several weeks until both lines showed satisfactory SVI-levels. Both ways of adding ozone have advantages. If ozone is applied for a short time, the energy requirement will be lower, however, the SVI increases shortly after the system is switched to the other line. When the system is kept running for a longer time with fixed intervals as by Lyko *et al.*, (2012) the SVI is kept low. However, since the ozone system is kept operational for a long time, the energy consumption will be higher than the strategy applied in Paper I. There is also a risk that a dosing strategy that works well at one plant will not be effective at another plant due to the differences in load and microbiology of the plants. This combined with the scarceness of information in the literature necessitates further studies to investigate how to apply ozone in the most economically feasible manner to achieve the desired SVI or DSVI reduction.

Pharmaceuticals in wastewater

To address the contamination of surface waters by pharmaceuticals has gained in importance in recent years especially since it has been shown that pharmaceuticals and other substances are being accumulated in the biosphere and affecting aquatic life forms. A well-known effect of low concentrations of pharmaceuticals in the biosphere are the endocrine disruptions in fish. Endocrine disruptions (reproductive disturbances) have been detected in fish in the wild and in controlled laboratory conditions. These disturbances have been clearly linked to substances causing estrogenic activity in fish such as ethinylestradiol, octylphenol, nonylphenol and many others (Sumpter, 1995; Jobling *et al.*, 1996; 1998; Lange *et al.*, 2001).

There are a number of routes for pharmaceuticals to enter surface waters, among which are manufacturing sites, hospitals and WWTP's. WWTP's are major point sources for pharmaceuticals since people are to a large extent using pharmaceuticals in their homes which are for the most part, at least in the industrialized world, connected to a central WWTP (Ternes *et al.*, 2004; Hollender *et al.*, 2009). Pharmaceuticals and metabolites therefore find their way to the WWTP and enters the treatment train. As described earlier in this work, WWTP's are designed to reduce nutrients, BOD and COD not pharmaceuticals. Although, certain substances such as acetylsalicylic acid, ibuprofen, pyrene, 1-aminopyrene and many others (Matsui *et al.*, 1998; Ternes *et al.*, 2004) are either adsorbed onto sludge or degraded by bacteria either completely or next to. The removal of pharmaceuticals in WWTP's depends on factors such as hydrophobicity and biodegradability of the substance as well as operational parameters such as sludge age (Matsui *et al.*, 1998; Daughton *et al.*, 1999; Clara *et al.*, 2004; Ternes *et al.*, 2004; Falas, 2012). Leading to a portion of the incoming pharmaceutical substances such as carbamazepine, metoprolol, diclofenac and others to pass through the wastewater treatment with little or no degradation or retention.

Pharmaceuticals being discharged from the WWTP ends up in the recipient surface waters. A study published by Ternes (1998) revealed that out of 32 substances screened for, 20 were found in different German streams and rivers. The situation in the United States is similar as a major survey carried out by the U.S. Geological Survey found a number of different organic substances from both industrial and domestic use in 80% of the 139 streams that were screened (Kolpin *et al.*, 2002). A study published by Nakada *et al.* (2006) reported that the treated wastewater in Tokyo, Japan contains several pharmaceuticals albeit in lower concentration than

found in Europe and the United States. While detected concentrations of pharmaceuticals in surface waters are low (ng l^{-1}), the consequences of the contamination may not be evident for a long time.

Considering that the toxicity of pharmaceuticals is normally only assessed with regards to acute toxicity and not chronic exposure to aquatic pharmaceuticals in low concentrations, the ecotoxicity of pharmaceuticals in water bodies may be difficult to assess (Fent *et al.*, 2006). The constant discharge of pharmaceuticals may therefore be a graver problem than we can imagine at the present time.

As these studies shows, the situation with pharmaceuticals being discharged from WWTP's is a global problem and not located to a specific region or country. Neither is the activated sludge process sufficient to remove pharmaceutical substances to a satisfactory degree, therefore it is necessary to implement an additional process stage that can be used all around the world. As of March of 2014, Switzerland has implemented a new water protection act which necessitates WWTPs which falls within certain criteria to be upgraded with a pharmaceutical reduction stage (Eggen *et al* 2014). This decision clearly shows that it is possible to implement measures to limit the pharmaceutical pollution of the environment.

Reduction of pharmaceuticals

There are processes that can be used as a tertiary treatment to reduce the pharmaceutical load entering surface waters, such as: powdered activated carbon (PAC), granulated activated carbon (GAC), UV, hydrogen peroxide (H_2O_2), ozone (O_3) and membrane filtration. However, the two most promising candidates are considered to be ozone and activated carbon (PAC or GAC) (Hollender *et al.*, 2009). Activated carbon acts as a filtering agent, causing the pharmaceuticals to adsorb to the carbon and thereby removing them from the wastewater. Ozone on the other hand works on the principle of oxidation, breaking up substances into smaller organic molecules. The use of ozone to reduce the load of pharmaceuticals being discharged from WWTP's has been investigated in numerous works published since the year 2000 and has been found to be highly effective (Ternes *et al.*, 2003; Huber *et al.*, 2005; Nakada *et al.*, 2007; Hollender *et al.*, 2009; Wert *et al.*, 2009; Hansen *et al.*, 2010; Zimmermann *et al.*, 2011; Katsoyiannis *et al.*, 2011; Hey, 2013; Hey *et al.*, 2014). However, there are still question marks regarding by-product formation when applying ozone

Challenges when applying ozone for reduction of pharmaceutical discharge

As detailed earlier in this work, ozone has been in use for a very long time, mainly to disinfect drinking water. However, the implementation of ozone in full-scale at a wastewater treatment plant to reduce pharmaceutical discharge will present challenges. The water to be treated has for one thing a high concentration of scavenging substances such as TOC, DOC and COD, reacting with the applied ozone instead of the intended pharmaceutical substances (Wert *et al.*, 2009). Another issue is the potential of ozone to create new hazardous substances from the original organic compounds. N-nitrosodimethylamine (NDMA) is one such substance, carcinogenic and formed by ozonation of N,N-dimethylsulfamide (DMS) which in turn is derived from bacterial degradation of the fungicide tolylfluanide. A study published by Schmidt and Brauch (2008) showed that ozonation of drinking water results in 30-50% conversion of the DMS concentration to NDMA. However, NDMA is more biodegradable than DMS and can be removed at least to an extent by biological activity in a sand filter. Several other by-products will be formed or is suspected to be formed by ozonation of pharmaceuticals in wastewater. Studies have shown that organic molecules subjected to ozonation will to a large extent be made more biodegradable by the process, which necessitates a biological treatment after the ozonation stage to mitigate the possible increase in ecotoxicity (Hammes *et al.*, 2006; Hollender *et al.*, 2009; Stalter *et al.*, 2010; Zimmermann *et al.*, 2011).

Pharmaceutical reduction at Lundåkraverket WWTP with ozone

Ozone addition to reduce the amount of pharmaceuticals being discharged from a WWTP have previously been shown to be highly effective (Huber *et al.*, 2003; 2005; Hollender *et al.*, 2009; Hey *et al.*, 2014; Katsoyiannis *et al.*, 2011). The aim of the work presented herein was therefore focused on how to implement ozone addition as an add-on technology in practice.

A pilot plant was set up at Lundåkraverket WWTP (Paper III). The main objectives were to investigate how ozone for pharmaceutical reduction could be combined with another advanced tertiary treatment. It is possible that the discharge limits for phosphorus will be further lowered in Sweden in the near future. Therefore, it was decided to combine the ozone stage with coagulation/flocculation/discfiltration, which not only lowers the concentration of phosphorus but also the COD levels substantially. This process involves adding polyaluminum chloride (PACl) and a polymer to wastewater in order for phosphorus and particulate COD to be

precipitated and/or flocculated prior to removal with a discfilter. For further details regarding this process, see Väänänen (2014).

The pilot installation used in Paper III is depicted in Figure 13. The main feature of the pilot unit was that the order of the treatments could be switched so that ozone addition was either before or after the coagulation/flocculation/discfiltration. The pilot was operated with a wastewater flow of $9.3\text{-}10\text{ m}^3\text{ h}^{-1}$ and a HRT of $5.4\text{-}5.8$ minutes in the coagulation/flocculation stage, where $4\text{ g Al}^{3+}\text{ m}^{-3}$ (PAX XL 36, Kemira Kemi) was added before 1.5 g m^{-3} of high molecular weight and medium-high charge cationic powder polymer was added. After coagulation/flocculation, the water entered a discfilter (Hydrotech HSF1702/1-1F) with $10\text{ }\mu\text{m}$ pores. Either after or before the coagulation/flocculation/discfiltration step the wastewater was subjected to $2, 5$ and $9\text{ g O}_3\text{ m}^{-3}$ in a pressurized reaction vessel with a HRT of 2.6 minutes.

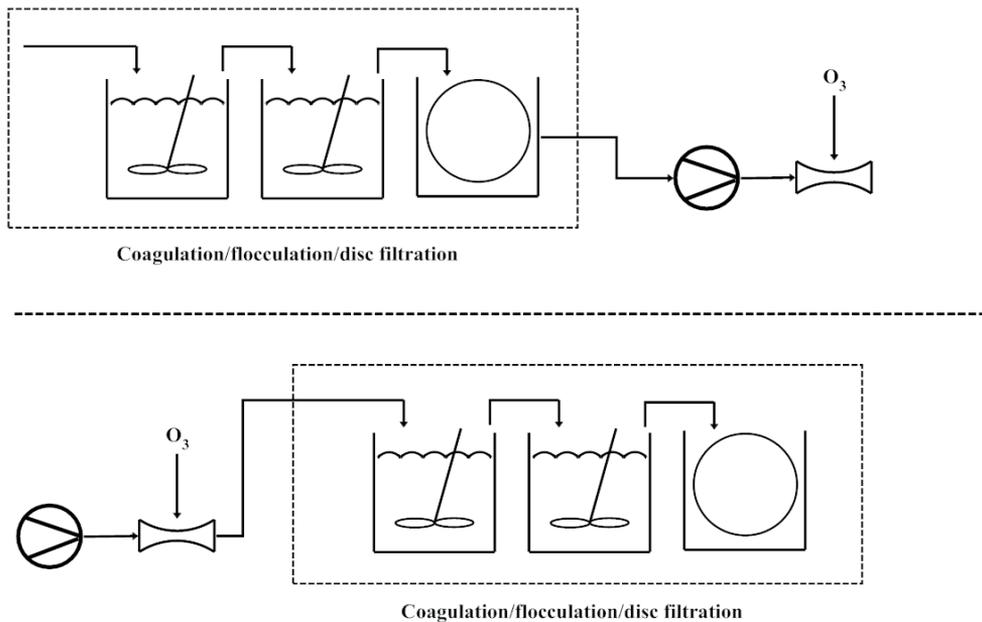


Figure 13.
A simplified schematic diagram of the coagulation/flocculation/discfilter/ozone pilot unit in Paper III.

Pharmaceutical reduction

Out of 46 different substances screened for, 24 were found consistently throughout all experiments, for example carbamazepine, ibuprofen and metoprolol among others. To summarize the results from the ozone trials, the 24 compounds found were combined into a total concentration before and after ozone addition and a reduction percentage was calculated. The reduction of pharmaceuticals by ozone before and after coagulation/flocculation/discfiltration is depicted in Table 3.

Table 3.

Reduction of pharmaceuticals obtained in Paper III.

Ozone dose	Reduction With pre-treatment	Reduction Without pre-treatment
2 g O ₃ m ⁻³	48%	10%
5 g O ₃ m ⁻³	95%	80%
9 g O ₃ m ⁻³	97%	88%

As was expected, the reduction of pharmaceuticals was clearly more efficient when ozone was added after the coagulation/flocculation/discfiltration than when added before said treatment. The reason behind this can be correlated to the reduction of ozone scavenging molecules achieved by the coagulation/flocculation/discfiltration which is detailed in Paper III.

Conclusions

Filamentous bulking sludge

It was proven that ozone has a clear and significant impact on the highly important parameter SVI or DSVI with a relatively low specific dose of approximately $5 \text{ g O}_3 \text{ kg}^{-1} \text{ SS}^{-1}$ in return activated sludge (RAS). Acceptable levels of SVI or DSVI are parameters that needs to be defined at the WWTP prior to ozone addition, the SVI results presented herein reached levels of approximately 100 ml g^{-1} which was deemed acceptable. The results indicated that there is a large variance in the time it takes to reach acceptable levels of SVI or DSVI, approximately 2-6 weeks. As the flow of treated return sludge was altered in Paper I, from 25 to $32 \text{ m}^3 \text{ h}^{-1}$ it was possible to determine that the higher flow of treated RAS decreases the time it takes to reach acceptable SVI or DSVI levels.

As ozone is an oxidant, it was feared that the necessary biological processes in the WWTP could be negatively affected. No such effect was observed in any of the studied WWTPs (Klagshamn and Öresundsverket WWTP) even though the desired effect upon SVI or DSVI was reached. The absence of negative effects on either nitrification/denitrification or biological phosphorus removal leads to the conclusion that the levels of ozone addition utilized in these trials are safe to use.

One of the goals of Paper II was to track changes in the microbial community of the activated sludge as it was subjected to ozonation in full scale. No such change was detected with the means employed (see Paper II).

The cost calculation of the process did reveal that it does require a fair amount of electrical energy to implement (30.7 kWh for one hour of operation). However, the relative high operating cost of the ozone system should be compared to the cost of having pump trucks arriving every time the floating sludge starts to cause problems with the running of the plant.

Pharmaceutical reduction

When ozone was applied after a pre-treatment consisting of coagulation/flocculation/disc-filtration, the total removal of pharmaceuticals was significantly higher with the same ozone dosages as without pre-treatment.

The energy requirement of the process was evaluated for Lundåkraverket WWTP both with and without pre-treatment (Appendix II). When pre-treatment was included in the calculation, $0.165 \text{ kWh m}^{-3} \text{ year}^{-1}$ is estimated to be required to reach 95% reduction in pharmaceuticals. Without pre-treatment, only 88% reduction was reached while it is estimated to require $0.212 \text{ kWh m}^{-3} \text{ year}^{-1}$.

All issues considered, ozone is very capable of improving the efficiency and performance of the wastewater treatment processes considered in this work. Since the main disadvantage of ozone is operating costs, ways to optimize the use of the ozone system should be investigated seriously.

Future studies

To further our understanding of filamentous bulking control with ozone it is desirable to investigate the actual mechanisms involved when ozone reacts with filamentous bacteria in the sludge. Dosing strategies of ozone to reduce filamentous bulking sludge is also an area which warrants further study.

In order to gain a better picture of the feasibility of using ozone to reduce pharmaceuticals in wastewater it would be beneficial to implement ozonation for that purpose on several WWTPs and compare the results.

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Appendix I

Energy consumption calculation for filamentous bulking control

As described earlier in this work, the operating cost of an ozone system is dominated by the energy consumption. Since the maintenance cost is very difficult to estimate it is not included in this calculation. The price of electricity varies between countries and time of the year, therefore, all calculations regarding operating costs are denoted as kWh instead of any currency. To calculate the energy requirements of an ozone system, one first has to decide upon a design of the system since that will have a substantial impact on the operating costs. The design used here is the one described in Paper II, in which one treatment line is treated at a time with oxygen generation on site, side stream injection and closed loop cooling system. With the system decided, the process parameters needs to be set (Table 4).

Table 4.

Process parameters of an ozone system for treatment of filamentous bulking sludge.

Process parameters	Abbreviation	Unit
Ozone dose	Dose O_3	g O_3 / kg SS
Ozone concentration	$[O_3]$	g O_3 / Nm ³ O_2
Ozone needed	M_{O_3}	g O_3 / h
Oxygen flow	Q_{O_2}	Nm ³ O_2 / h
Oxygen concentration	$[O_2]$	% wt
Total RAS flow	Q_{RAS}	m ³ / h
Ratio RAS treated	R_{RAS}	%
Flow RAS treated	$Q_{RAS,T}$	m ³ / h
SS in RAS	$[SS]$	kg SS / m ³
Pressure loss in injector	ΔP_{Inj}	Bar
Pressure loss in piping	ΔP_{Piping}	Bar
Desired pressure in reactor	$P_{Reactor}$	Bar
Pressure needed from booster pump	P	Bar

The flow of sludge to be treated in the side stream injection needs to be decided (Eq. 1) to enable dimensioning of the booster pump and the amount of ozone needed. Additionally, the higher the amount of treated sludge the faster results can be expected, however, the booster pump as well as ozone requirements will increase.

$$Q_{(RAS,T)} = Q_{RAS} \cdot R_{RAS} \text{ Eq. 1}$$

The amount of ozone needed (Eq. 2) is derived from the dose of ozone, the flow of treated sludge and the SS-content.

$$M_{(O_3)} = Dose_{O_3} \cdot Q_{(RAS,T)} \cdot [SS] \text{ Eq. 2}$$

From the amount of ozone needed and concentration of ozone leaving the ozone generator, the flow of oxygen needed can be calculated (Eq. 3).

$$Q_{(O_2)} = M_{(O_3)} / [O_3] \text{ Eq. 3}$$

The last process parameter to calculate is the pressure needed from the booster pump (Eq. 4).

$$P = \Delta P_{Inj} + \Delta P_{Piping} + \Delta P_{Reactor} \text{ Eq. 4}$$

With these calculations made, the requirements of the system are known. In order to reach those requirements, choices has to be made as to what type of equipment to use. What is clear is that there is a wide array of equipment available to achieve the same results, however, the energy requirements do tend to differ.

The electrical energy required to generate ozone varies depending on make of the ozone generator. The concentration of ozone also has a large impact on both ozone

generator efficiency and process efficiency. By increasing the concentration of ozone leaving the ozone generator the required amount of oxygen decreases, however, the energy requirement of the ozone generator increases. The dissolution of ozone into the sludge is also affected by the ozone concentration according to Henry's law. These factors need to be weighed and a compromise settled upon. Therefore, the energy requirement of the ozone generator in this calculation is denoted as kW / kg O₃ at the desired ozone concentration (Table 5).

Ozone generators require cooling in some form, usually water. The amount of cooling needed (kWh) varies widely between different ozone generators on the market. Therefore, the cooling capacity is denoted as a constant, D.

The generation of oxygen on site can be achieved by either Pressure Swing Adsorption (PSA) or Vacuum Swing Adsorption (VSA). Either way requires electrical energy for pressure or vacuum generation which is also influenced by the required flow and concentration of oxygen needed (Table 5).

Table 5.
Energy factors of the ozone system

Equipment	Abbreviation	Unit
Ozone generator	A	kWh kg ⁻¹ O ₃ ⁻¹ at [O ₃]
Oxygen generator + compressor	B	kWh Nm ⁻³ O ₂ at [O ₂]
Booster pump	C	kWh m ⁻³ at P
Cooling system	D	kWh

So the energy requirements divided into process stages can be calculated as follows.

$$\text{Ozone generation} = A \cdot M_{(O_3)} / 1000 \text{ kWh}$$

$$\text{Oxygen generation} = B \cdot Q_{O_2} \text{ kWh}$$

$$\text{Booster pump} = C \cdot Q_{RAS} \text{ kWh}$$

$$\text{Cooling system} = D \text{ kWh}$$

The following cost calculation is an example of how to apply the above mentioned equations with known process parameters (Table 6), equipment and energy factors (Paper II).

Table 6.

Process parameters used in the calculation (Paper II).

Process parameter	Abbreviation	Value
Main line flow	$Q_{\text{Main line}}$	$700 \text{ m}^3 \text{ h}^{-1}$
Ozone dose	Dose O_3	$5 \text{ g } O_3 \text{ kg}^{-1} \text{ SS}^{-1}$
Ozone concentration	$[O_3]$	$200 \text{ g } O_3 \text{ Nm}^{-3} \text{ O}_2^{-1}$
Oxygen concentration	$[O_2]$	95% wt
Total RAS flow	Q_{RAS}	$800 \text{ m}^3 \text{ h}^{-1}$
Ratio RAS treated	R_{RAS}	5%
SS in RAS	$[SS]$	$4.5\text{-}7 \text{ kg } \text{SS } \text{m}^{-3}$
Pressure loss in injector	ΔP_{Inj}	1 Bar
Desired pressure in reactor	P_{Reactor}	1 Bar

The flow of sludge treated is calculated using Equation 1.

$$Q_{\text{RAS},T} = Q_{\text{RAS}} \cdot R_{\text{RAS}} = 800 \cdot 0.05 = 40 \text{ m}^3/\text{h}$$

In Paper II, the SS concentration varied substantially, resulting in a varying relative ozone dose of $2.8\text{-}5 \text{ g } O_3 \text{ kg}^{-1} \text{ SS}^{-1}$ with a constant ozone addition of approximately $900 \text{ g } O_3 / \text{h}$. Since the amount of ozone added in Paper II was $900 \text{ g } O_3 \text{ h}^{-1}$, that figure is used throughout this calculation.

$$M_{(O_3,3,1)} = \text{Dose } O_3 \cdot Q_{(RAS,T)} \cdot [SS] = 5 \cdot 40 \cdot 4,5 = 900 \text{ g } O_3/\text{h}$$

$$Q_{(O_2)} = M_{(O_3)} / ([O_3]) = 900/200 = 4.5 \text{ Nm}^3 / \text{h}$$

$$P = \Delta P_{\text{Inj}} + \Delta P_{\text{Piping}} + \Delta P_{\text{Reactor}} = 1 + 0.2 + 1.2 = 2.4 \text{ Bar}$$

With the requirements calculated, the equipment needs to be specified, the equipment used for this calculations are derived from the system used in Paper II. With the ingoing equipment decided, the energy factors can be specified from the documentation of the equipment (Table 7).

Table 7.
Equipment used in Paper II plus energy factors.

Equipment type	Make	Energy factor	Abbreviation
Ozone generator	Primozone GM18	12 kWh kg ⁻¹ O ₃ ⁻¹ at [O ₃]	A
Oxygen supply + compressor	Oxymat() Kaeser ()	~2 kWh Nm ⁻³ O ₂ ⁻¹ at [O ₂]	B
Booster pump	Flygt 3127.181	~0.15 kWh m ⁻³ at P	C
Cooling	Lauda UC- 0100SP	4.9 kWh at 11.7 kWh cooling	D

The ozone generator requires 10.8 kWh to produce 900 g O₃ h⁻¹ at 200 g O₃ Nm⁻³.

$$\text{Ozone generation} = A \cdot M_{(O_3)} / 1000 = 12 \cdot 900 / 1000 = 10.8 \text{ kWh}$$

At the same time, the ozone generator needs cooling water. Since the ozone generator is decided upon, the cooling need of the generator can be deduced. A Primozone GM18 requires the installed cooling power to be equal to the power of the generator and with one hour of operation this leads to:

$$\text{Cooling system power} = \text{Ozone generation} = 10.8 \text{ kW}$$

However, the active chiller chosen for this calculation delivers 11.7 kW of cooling power at 4.9 kW of electrical power which in turn leads to that the actual energy consumption of the cooling system is:

$$\text{Cooling system} = D = 4.9 \text{ kWh}$$

The specified oxygen generator and compressor requires 9 kWh to produce the needed amount of oxygen (4.5 Nm³ h⁻¹), of which the compressor is by far the largest consumer of energy.

$$\text{Oxygen generation} = B \cdot Q_{O_2} = 2 \cdot 4.5 = 9 \text{ kWh}$$

The specified booster pump requires approximately 6 kWh to lift the treated RAS up to approximately 20 m of head.

$$\text{Booster pump} = C \cdot Q_{RAS} = 0.15 \cdot 40 = 6 \text{ kWh}$$

The sum of the energy required to operate the specified system for one hour can be calculated by adding all the ingoing components.

$$\text{One hour of operation} = 10.8 + 4.9 + 9 + 6 = 30.7 \text{ kWh}$$

The sum of energy requirements is calculated for one hour of operation. As the total time of ozone addition in Paper II was 45 days, the following is the total energy requirement of the treatment.

$$\text{Sum of energy requirements} = 45 \cdot 24 \cdot 30.7 = 33156 \text{ kWh}$$

Divided by the accumulated flow of wastewater throughout the 45 days of ozone treatment, the energy consumption equals:

$$\text{Energy per } m^3 = 33156 / (700 \cdot 24 \cdot 45) = 0.044 \text{ kWh}/m^3$$

Appendix II

Energy consumption calculation for pharmaceutical reduction without pre-treatment

As with the case of applying ozone for filamentous bulking sludge reduction, all costs are expressed as kWh instead of any currency and all maintenance costs are excluded.

To calculate the operating cost of the ozone system needed for pharmaceutical reduction at a WWTP, the overall requirements must be decided (Table 8). In contrast to applying ozone for filamentous bulking sludge, the ozone in this case is applied in the main discharge line. Therefore the most important parameters to decide upon is the design flow of the WWTP and required ozone dose.

Table 8.
Design parameters for pharmaceutical reduction with ozone.

Process parameter	Abbreviation	Unit
Design flow	Q_{Design}	$m^3 h^{-1}$
Side stream flow	$Q_{Side\ Stream}$	$m^3 h^{-1}$ at $P_{Side\ Stream}$
Cooling water flow	$Q_{Cooling}$	$m^3 h^{-1}$
Side stream pressure	$P_{Side\ Stream}$	bar (g)
Ozone dose	Dose O_3	$g\ O_3\ m^{-3}$
Ozone concentration	$[O_3]$	$g\ O_3\ Nm^{-3}\ O_2$
Ozone needed	M_{O_3}	$g\ O_3\ h^{-1}$
Oxygen flow	Q_{O_2}	$Nm^3\ O_2\ h^{-1}$
Oxygen concentration	$[O_2]$	% wt

The first decision to be made is what flow the system should be designed for (Q_{Design}). With that decided upon, the required ozone dose (Dose O_3) needs to be determined, with these overall parameters set, the first calculations can be made.

$$M_{O_3} = Q_{Design} \cdot Dose\ O_3$$

The hourly production of ozone is thereby calculated and that leads to an hourly need for oxygen which is also dependent on the ozone concentration.

$$Q_{(O_2)} = M_{O_3} / [O_3]$$

As in the case with ozone for filamentous sludge reduction, the production of ozone requires oxygen. However, since the application of ozone discussed here is several times larger than the other, it can be beneficial to consider liquid oxygen (LOX) instead of site produced oxygen. If oxygen is to be delivered to the site in liquid form, there will be hardly any energy expenditure for the WWTP, however, the production of liquid oxygen does require energy and the manufacturer will charge for the oxygen delivered. The cost of LOX varies from country to country, as such, the form of oxygen used in this calculation will be either PSA as that is possible to quantify in terms of energy.

The injection system for adding ozone to the main treatment flow can be designed in a variety of ways. The injection system chosen for this calculation is depicted in Figure 14. A portion of the design flow (Q_{Design}) is diverted into a booster pump and then fed to a venturi type injector where ozone is added.

The needed flow in the side stream is decided by the amount of ozone to be added since this decides which injector to use and thereby the needed pressure and flow from the booster pump. The manufacturer of the venturi injector specifies which flow pressure of wastewater is needed for the calculated amount of ozone per hour. Therefore no equation for the calculation of side stream flow is presented.

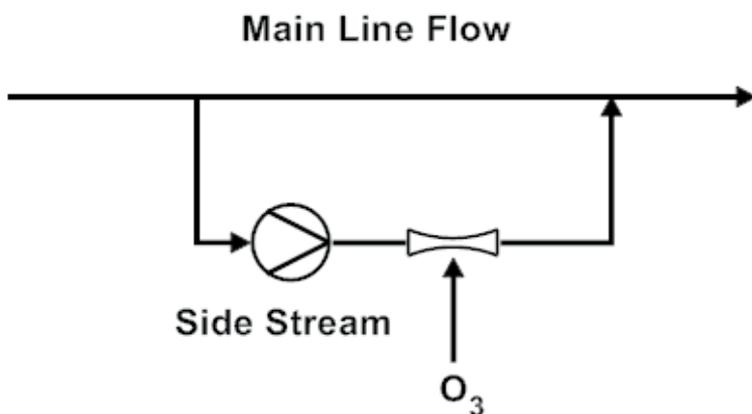


Figure 14.
An example of a side stream injection system for ozone.

The major equipment needed and their energy factors are listed in Table 9.

Table 9.

Energy factors of the ozone system

Equipment	Unit	Abbreviation
Ozone generator	kWh kg ⁻¹ O ₃ ⁻¹ at [O ₃]	A
Oxygen generator + compressor	kWh Nm ⁻³ O ₂ ⁻¹ at [O ₂]	B
Booster pump	kWh m ⁻³ at P	C
Cooling system	kWh	D

So the energy requirements divided into process stages can be calculated as follows.

$$\text{Ozone generation} = A \cdot M_{O_3} / 1000$$

$$\text{Oxygen generation} = B \cdot Q_{O_2}$$

$$\text{Booster pump} = C \cdot Q_{\text{Side stream}}$$

$$\text{Cooling system} = D$$

As an example of the energy requirements for the reduction of pharmaceuticals, a cost calculation is made for Lundåkraverket WWTP below (Table 10). Lundåkraverket WWTP, as described earlier, is designed to handle a peak flow of 3000 m³ h⁻¹ with an average flow of 580 m³ h⁻¹. Therefore the design flow is set to 580 m³ h⁻¹. Since the application of 9 g O₃ m⁻³ was sufficient for 88% reduction in Paper III (without pre-treatment) that is chosen as the required ozone dosage. The other two parameters, ozone and oxygen concentration is set the same as in the energy calculation for filamentous bulking sludge.

Table 10.

Process parameters used in the calculation.

Process parameter	Abbreviation	Value
Design flow	Q _{Design}	580 m ³ h ⁻¹
Ozone dose	Dose O ₃	9 g O ₃ m ⁻³
Ozone concentration	[O ₃]	200 g O ₃ Nm ⁻³ O ₂ ⁻¹
Oxygen concentration	[O ₂]	95 % wt

$$M_{O_3} = Q_{\text{Design}} \cdot \text{Dose } O_3 = 580 \text{ m}^3/\text{h} \cdot 9 \text{ g } O_3/\text{m}^3 = 5220 \text{ g } O_3/\text{h}$$

With the required amount of ozone calculated to 5220 g O₃ / h, the flow of oxygen can be calculated.

$$Q_{O_2} = M_{O_3} / [O_3] = 5220 / 200 = 26.1 \text{ Nm}^3 \text{ O}_2/\text{h}$$

With the amount of ozone and hence flow of oxygen known, the required venturi injector can be decided upon. The venturi injector chosen for this calculation is Mazzei 3090. This injector will be able to inject the calculated amount of ozone if the pressure and flow into the side stream ($P_{\text{Side Stream}}$, $Q_{\text{Side Stream}}$) is 4.22 bar (g) and 57.5 m³/h respectively.

Table 11.
Equipment with known energy factors.

Equipment type	Make	Energy factor	Abbreviation
Ozone generator	2 x Primozone GM48 + 1 x GM18	12 kWh kg ⁻¹ O ₃ ⁻¹ at [O ₃]	A
Oxygen supply + compressor	Oxymat O500 Eco V.3 Kaeser BSD83	1.8 kWh Nm ⁻³ O ₂ ⁻¹ at [O ₂]	B
Injection system	Mazzei 3090 Grundfos MTR 64- 2/2-1	9 kWh at $P_{\text{Side Stream}}$ and $Q_{\text{Side Stream}}$	C
Injection system #2	Mazzei 3090 Grundfos MTR 45- 2/1	3.45 kWh at P_{Side} Stream and $Q_{\text{Side Stream}}$	C ₂
Cooling system	Grundfos CM15-3	2.25 kWh at Q_{Cooling}	D
Cooling system #2	Grundfos CM10-3	1.75 kWh at Q_{Cooling}	D ₂
Pre-treatment	Hydrotech	0.045 kWh m ⁻³	E

The three ozone generators require 62.64 kWh to produce 5.22 kg O₃ h⁻¹.

$$\text{Ozone generation} = A \cdot M_{O_3} / 1000 = 12 \cdot 5220 / 1000 = 62.64 \text{ kWh}$$

The cooling system needs to be designed to handle 100% of that, which results in a cooling need of 62.64 kWh. However, for a system this large it is beneficial to consider an alternative to active cooling with a chiller. A more energy efficient system is to install a heat exchanger and use a source of cool (10-15°C) water available at the WWTP as cooling water. The electrical energy required for cooling the ozone generators will then be restricted to the energy consumption of the pumps needed on both sides of the heat exchanger: Two Primozone GM48 and one GM18 requires:

$$\text{Cooling water flow} = 2 \cdot 5.3 + 2 = 12.6 \text{ m}^3/\text{h}$$

The pumps required for that flow corresponds to two Grundfos CM15-3 centrifugal pumps which equates to:

$$\text{Cooling system} = D \cdot 2 = 2.25 \cdot 2 = 4.5 \text{ kWh}$$

The PSA system chosen for this calculation requires 47 kWh to produce 26.1 Nm³ O₂ h⁻¹.

$$\text{Oxygen generation} = B \cdot Q_{O_2} = 1.8 \cdot 26.1 = 46.98 \text{ kWh}$$

The injection system will require 9 kWh to handle the specified side stream flow and pressure.

$$\text{Injection system} = C = 9 \text{ kWh}$$

The sum of the energy required to operate the specified system can be calculated by adding all the ingoing components.

$$\text{Sum energy requirements} = 62.64 + 4.5 + 46.98 + 9 = 123.12 \text{ kWh}$$

The sum of energy required to operate the ozone system for one hour is 122.9 kWh, considering that the ozone system needs to operate throughout every hour of the year, a yearly energy requirement needs to be calculated.

$$\text{Yearly energy} = 123.12 \cdot 24 \cdot 365 = 1078531 \text{ kWh/year}$$

Using this figure and dividing it by the amount of treated water released by the plant in a year, the specific energy requirement comes to 0.212 kWh / year m³.5080800

$$\text{Yearly energy} / m^3 = 1078531 / (580 \cdot 24 \cdot 365) = 0.212 \text{ kWh/year} \cdot m^3$$

Energy consumption calculation for pharmaceutical reduction with pre-treatment

In Paper III, the required ozone dose to reach 95% reduction was significantly lowered when a pre-treatment consisting of coagulation/flocculation/disc-filtration was applied. It was not even possible with the highest ozone dose (9 g O₃ m⁻³) to reach that high a reduction. An energy calculation with the pre-treatment included is conducted to highlight the benefits of using it.

Since the required ozone dose to reach 95% reduction in Paper III was 5 g O₃ m⁻³ in the case of applied pre-treatment, that dose will be used in this calculation.

Table 12.

Process parameters used in the calculation.

Process parameter	Abbreviation	Value
Design flow	Q _{Design}	580 m ³ h ⁻¹
Ozone dose	Dose O ₃	5 g O ₃ m ⁻³
Ozone concentration	[O ₃]	200 g O ₃ Nm ⁻³ O ₂ ⁻¹
Oxygen concentration	[O ₂]	95 % wt

$$M_{O_3} = Q_{Design} \cdot Dose\ O_3 = 580\ m^3/h \cdot 5\ g\ O_3/m^3 = 2900\ g\ O_3/h$$

The required production of ozone will in this case be 2900 g O₃ h⁻¹ which is substantially lower than the previous case. This amount of ozone will require 34.8 kWh to produce.

$$Ozone\ generation = A \cdot M_{O_3}/1000 = 12 \cdot 2900/1000 = 34.8\ kWh$$

This amount of ozone will in turn require the production of 14.5 Nm³ O₂ h⁻¹.

$$Q_{O_2} = M_{O_3}/[O_3] = 2900/200 = 14.5\ Nm^3\ O_2/h$$

Resulting in an energy expenditure of 26.1 kWh.

$$Oxygen\ generation = B \cdot Q_{O_2} = 1.8 \cdot 14.5 = 26.1\ kWh$$

The injection system will be of the same type as the previous case albeit with a smaller pump which will result in a lower energy consumption.

$$Injection\ system = C_2 = 3.45\ kWh$$

The number of ozone generators needed will also decrease to one GM48 and one GM18, resulting in a cooling water flow of $7.5 \text{ m}^3 \text{ h}^{-1}$.

$$\text{Cooling water flow} = 5.3 + 2 = 7.5 \text{ m}^3/\text{h}$$

Which will in turn require smaller pumps than in the previous case, 2 x CM10-3 with a power requirement of 3.5 kWh.

$$\text{Cooling system} = D_2 \cdot 2 = 1.75 \cdot 2 = 3.5 \text{ kWh}$$

The addition of the pre-treatment will of course add an energy requirement of its own, this amounts to 26.1 kWh.

$$\text{Pre-treatment} = E \cdot Q_{\text{Design}} = 0.045 \cdot 580 = 26.1 \text{ kWh}$$

$$\text{Total energy} = 34.8 + 26.1 + 3.45 + 3.5 + 26.1 = 93.95 \text{ kWh}$$

The sum of energy required to operate the ozone system for one hour is 93.95 kWh, considering that the ozone system needs to operate throughout every hour of the year, a yearly energy requirement needs to be calculated.

$$\text{Yearly energy} = 93.95 \cdot 24 \cdot 365 = 840522 \text{ kWh/year}$$

Using this figure and dividing it by the amount of treated water released by the plant in a year, the specific energy requirement comes to $0.165 \text{ kWh year}^{-1} \text{ m}^{-3}$.

$$\text{Yearly energy} / \text{m}^3 = 840522 / (580 \cdot 24 \cdot 365) = 0.165 \text{ kWh/year} \cdot \text{m}^3$$



My name is Filip Nilsson and I am an engineer and scientist. I have been employed as an industrial Ph.D. student and application engineer at Primozone Production AB since 2010 and have been working with ozone and its applications ever since.

My research has been focused on applying ozone in wastewater treatment to increase the effectiveness of the current treatment process. I have almost exclusively been working with full- or pilot-scale installations of ozone in an effort to obtain experimental data that can be applied in wastewater treatment as straightforwardly as possible.

