The Freshwater Factory: removing organic micro-pollutants with ozonation

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by

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Preface

This document presents the final report for the TU Delft master thesis of Civil Engineering, Watermanagement, specialization Sanitary Engineering. From December 2016 onwards, I have worked both on the master thesis for Watermanagement and the master thesis for SEPAM, at water authority Delfland (HH Delfland).

I would like to thank water authority Delfland (HH Delfland) and more specifically Jouke Boorsma for the opportunity to write my master thesis at HH Delfland. From the beginning, Jouke has been of great help in finishing both theses at HH Delfland.

I am grateful to many other employees of HH Delfland for supporting my research. I would especially like to thank Mark van den Braak for his explanation on all technological aspects of my research and the tours around the wastewater treatment plant. I have greatly appreciated our conversations about the (results of the) pilot experiments. My research has become much more in-depth because of his extensive knowledge on wastewater treatment and ozonation in particular. Also, I would like to thank Erik Knol and Oscar Helsen for their comments on my research during many constructive meetings, both in personal meetings and during meetings of the technological team of the Freshwater Factory.

I would like to thank ozone experts prof. Urs von Gunten, prof. Shane Snyder, Maria Antoniou, Bram Martijn and Mirabella Mulder for their involvement with my research. All of them have been very approachable and willing to help with my research.

Of course, I would like to thank my graduation committee from the TU Delft: prof. Jan Peter van der Hoek, prof. Merle de Kreuk and Erik Mostert. I would like to thank Jan Peter, as chair of my graduation committee, for his explicit involvement in this project and his extensive comments on my report. Furthermore, I would like to thank my first supervisor Merle for her great support during the past year. Merle has introduced me to HH Delfland, supported me in my struggles with TPM and was closely involved in my WM research. I always left our weekly meetings with so much clear answers, ideas and, not unimportantly, motivation. I would like to thank Erik for the substantive meetings we have had and for his comments on my work for both theses.

Finally, I would like to thank my family and friends for their support and interest during the past year and for making all the hours in the library so much more fun.

Ward van Es – October 2017

Summary

In the Netherlands, periods of drought are expected to occur more frequently due to climate change. To cope with expected future water shortages, water authorities and drinking water companies are searching for new freshwater sources. Wastewater is currently a limitedly used fresh water source in The Netherlands. Wastewater reuse, enabled by advanced wastewater treatment, would contribute to closing the regional water cycle.

Water authority Delfland (HH Delfland) expressed its ambition to close the regional water cycle through wastewater reuse in the coalition agreement 2015-2019. The wastewater treatment plants (WWTPs) will have to be used as fresh water source in order to achieve this goal (HH Delfland, 2015). This research studies the Freshwater Factory (FF) pilot of HH Delfland. In this project, wastewater of WWTP De Groote Lucht in Vlaardingen will be reused in the regional water system.

Conventional wastewater treatment plants are designed to remove organic matter (COD & BOD) and nutrients (nitrogen and phosphorous). Advanced wastewater treatment targets organic micro-pollutants (OMPs) in addition to the conventional treatment steps. The term OMPs is used to indicate a wide range of compounds such as pharmaceuticals, biocides and pesticides, corrosion inhibitors and endocrine compounds (Margot et al., 2013).

The need to remove OMPs from wastewater effluent comes from the expected but yet unknown long term effects of OMPs on both the environment and human health (Reungoat et al., 2010). The presence of OMPs endangers reuse of treated wastewater since it can cause chronic toxicity, endocrine disruption and the development of pathogen resistance (Rosal et al., 2010).

This research studies the removal of OMPs and answers the following main research question: *What are the optimal process conditions and corresponding removal in the combination of ozonation and biofilters for the removal of target organic micro-pollutants and toxicity of residual contaminants?* This research can roughly be divided in three parts: 1) introduction (legal and technological context, explanation of OMP removal and treatment steps and pilot configuration), 2) finding and comparing the optimal ozone dosage and 3) analysis and prediction of individual OMP removal.

1. **Introduction**

Legislation on wastewater reuse is drafted on multiple legislative levels, mainly European and nation levels. For instance, the Environmental Quality Standards Directive (2008/105/EC) contains a list of priority (hazardous) substances and other pollutants that are not allowed to be present above a certain concentration in water bodies. The Netherlands has to transpose European Directives into national laws.

Scientific research has identified **three main technologies** with the potential for large-scale application of advanced wastewater reuse in terms of efficiency, costs and energy requirements: adsorption onto activated carbon, size exclusion by reverse osmosis or oxidation of micro-pollutants with ozone (Lee and von Gunten, 2016; Margot et al, 2013; Hollender et al., 2009). This research is focused on the latter treatment technology.

To analyze the presence and activity of OMPs in natural waters and wastewater effluent, two different analyses are used: **chemical and biological analysis**. Chemical analysis is used to quantify concentrations of specific organic micro-pollutants. Biological analysis, in the form of bioassays, provide information on potential effects of the mixture of OMPs on the aquatic ecological system (Margot et al., 2013).

In conventional wastewater treatment, most OMPs are only party removed or even barely affected. Advanced treatment, in this research ozonation, is required to remove these undesired substances. The principle of treatment with ozone is oxidation of OMPs into smaller, biodegradable transformation products (Margot et al., 2013). Ozone in water can react in two different ways with compounds present: direct oxidation by molecular ozone (O_3) or oxidation by hydroxyl radicals ($\cdot OH$), produced during the decomposition of ozone. Biofiltration is recommended for treatment of ozonation effluent to minimize the presence of unknown oxidation products (Lee et al., 2012).

HH Delfland installed a pilot treatment plant with the following treatment scheme: 1) conventional biological treatment, 2) ozonation and 3) (bio)filtration. In the second part, the optimal ozone dosage is determined. In the third part, individual OMP removal in the pilot is evaluated and predicted based on literature and modelling.

2. Finding and comparing the optimal ozone dosage

The optimal ozone dosage depends on 1) effective OMP removal, 2) limiting toxic by-product formation (mainly bromate) and 3) keeping costs within budget. HH Delfland has decided to apply an ozone dosage of 1.0 gO_3/gDOC, which has an average OMP removal efficiency of 92%. This research recommends an ozone dosage of 0.7 gO_3/gDOC, which gives an average removal efficiency of 80%. This ozone dosage is within common limits of ozonation installations currently in use (Mulder et al., 2015) and 80% removal is regarded as effective. Bromate has not been found in the ozone dosage experiments, but it still requires close analysis in the individual OMP removal experiments. Other studies however do find bromate in the ozonation effluent, even at lower ozone dosages and lower bromide concentrations in the ozonation feed water. Operational costs will reach €82.000 per six months for the production of ozone at a dosage of 0.7 gO_3/gDOC. Increasing the dosage to 1.0 gO_3/gDOC would entail a 45% increase in operational costs and 4.0% increase in total costs of the ozone installation and operation.

HH Delfland has based the choice of the optimal ozone on only five measurements. Comparing these results with literature could provide a sounder basis to decide on the optimal ozone dosage. This research has compared studies of Antoniou et al. (2013), Snyder et al. (2006) and Lee et al. (2012) with HH Delfland. These three studies have shown removal efficiency curves that are to a great extend similar to the curve of HH Delfland (see Figure 1). A third order polynomial trend line is drawn through all data points of Antoniou et al. (2013) and Snyder et al. (2006) ($R^2 = 0.92$). It is clearly observable that all data points of HH Delfland are almost exactly located *on* this trend line. The three data points of Lee et al. (2012) are also fairly in line with the trend line. One could argue that HH Delfland could have determined the optimal ozone dosage based on removal efficiencies found in literature, without conducting its own ozone dosage experiments. However, bromate formation and toxicity of residual contaminants are also crucial aspects of determining the optimal ozone dosage. These aspects cannot be predicted by literature.

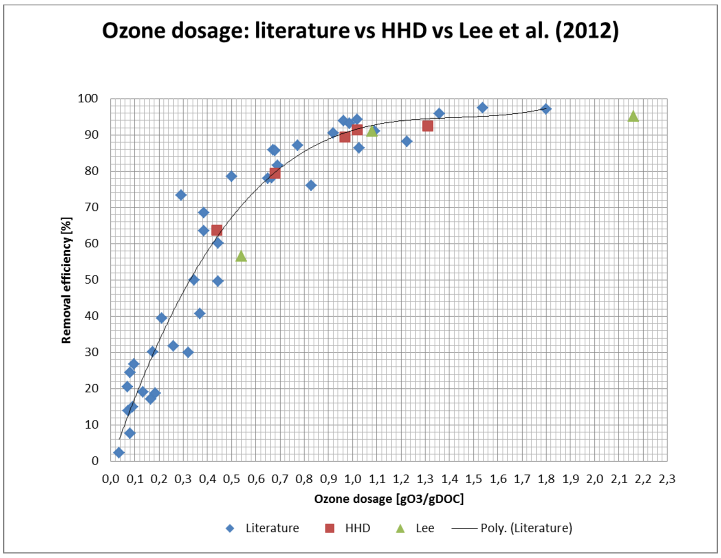


Figure 1 - Comparison of average removal efficiencies

3. Analysis and prediction of individual OMP removal

HH Delfland has conducted a long run test with a fixed ozone dose (1.0 gO_3/gDOC) from July 1, 2017 onwards. This section will analyze the observed removal and predicts the removal based on literature and on modelling.

HH Delfland has provided seven measurements of ozone feed water and ozonation effluent of 423 substances. Of these, only 71 substances have been reported in the measurements. Due to correction for the presence of nitrite, the actual applied ozone dosage was on average 0.95 gO_3/gDOC. The total average removal efficiency of all detected OMPs at all measurements is 91.5%, with an average standard deviation of 3.5%. Figure 2 shows that pharmaceuticals, pesticides and corrosion inhibitors are generally well removed by ozonation. Contrast media show variable removal, which results in high standard deviations. As expected, metals remain untouched by ozonation.

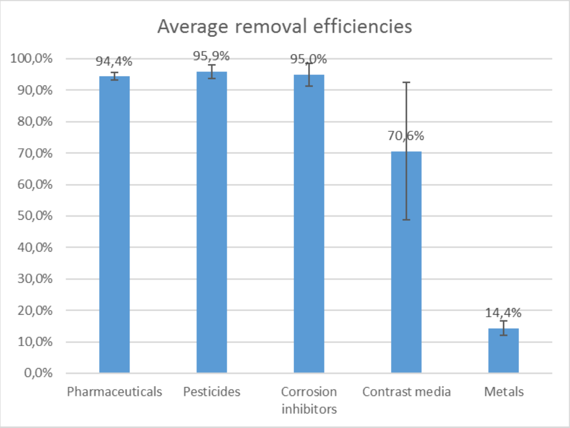


Figure 2 - Average removal efficiencies per group

With the observed removal efficiencies analyzed, the question rises whether these values could have been predicted by literature and modelling. Prediction of OMP removal based on literature is difficult, since different studies use different research set-ups and methods of reporting and comparing. For this reason, OMPs are divided in three categories, to give an *indication* of expected removal efficiencies (removal of >80%, 50-80%, <50%). In total, observed removal efficiency of 12 out of 27 OMPs fall within the range that was expected based on literature. However, observed removal of 15 OMPs do not fall within the expected range. Interestingly, observed removal efficiency is for all these 15 OMPs higher than the expected range. This could be explained by the high ozone dosage at which HH Delfland has conducted the long run test (1.0 $gO_3/gDOC$). Apparently, the categorization of OMPs in three categories, based on findings in scientific literature, **cannot adequately indicate** the removal efficiency.

Table 1 - Comparison of observed removal and predicted removal based on literature

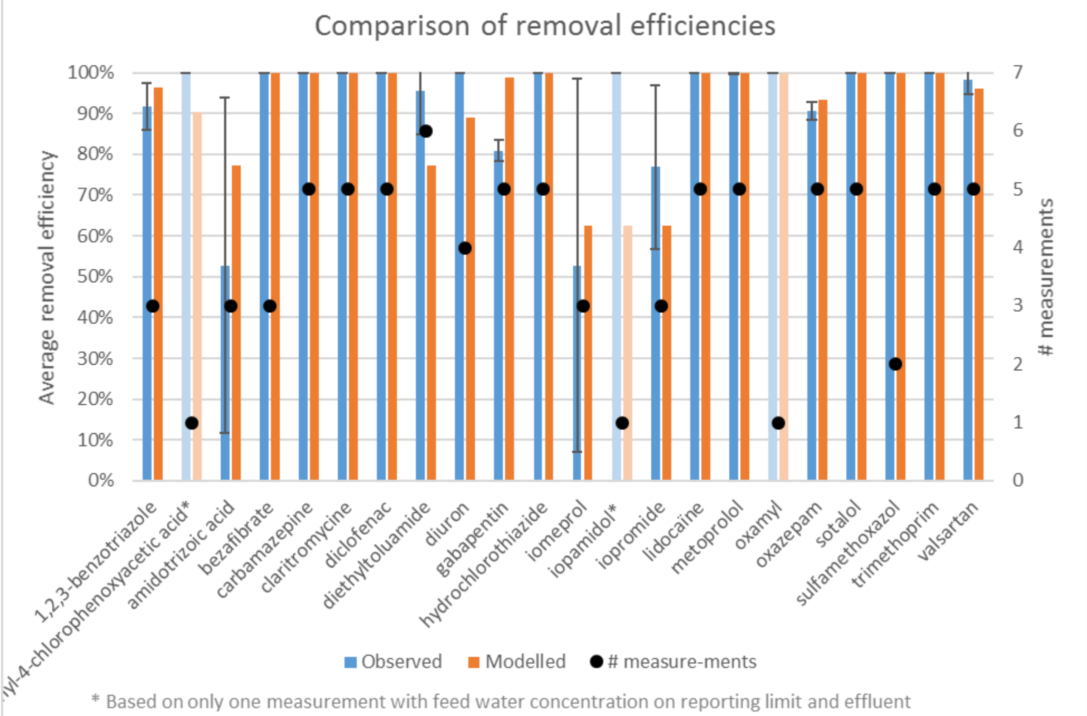
OMP	Group	Observed removal	Removal in literature	In agreement?
1,2,3-benzotriazole	Corrosion inhibitor	91.8%	50-80%	NO
2-methyl-4-chlorophenoxyacetic acid	Herbicide	100.0%	50-80%	NO
bezafibrate	Pharmaceutical	100.0%	>80%	YES
carbamazepine	Pharmaceutical	100.0%	>80%	YES
carbendazim	Fungicide	100.0%	50-80%	NO
claritromycine	Pharmaceutical	100.0%	>80%	YES
clindamycine	Pharmaceutical	100.0%	>80%	YES
diclofenac	Pharmaceutical	100.0%	>80%	YES
diethyltoluamide	Insecticide	95.6%	50-80%	NO
diuron	Herbicide	100.0%	50-80%	NO
gabapentin	Pharmaceutical	80.9%	<50%	NO
hydrochlorothiazide	Pharmaceutical	100.0%	50-80%	NO
iohexol	Contrast media	93.8%	<50%	NO
iomeprol	Contrast media	52.8%	<50%	NO
iopamidol	Contrast media	100.0%	<50%	NO
iopromide	Contrast media	76.9%	<50%	NO
irbesartan	Pharmaceutical	92.7%	50-80%	NO
lidocaïne	Pharmaceutical	100.0%	50-80%	NO
metoprolol	Pharmaceutical	99.9%	>80%	YES
oxamyl	Pesticide	100.0%	>80%	YES
oxazepam	Pharmaceutical	90.5%	<50%	NO
pentoxifylline	Pharmaceutical	100.0%	>80%	YES
phenazone (antipyrine)	Pharmaceutical	100.0%	>80%	YES
sotalol	Pharmaceutical	100.0%	>80%	YES
sulfamethoxazol	Pharmaceutical	100.0%	>80%	YES
trimethoprim	Pharmaceutical	100.0%	>80%	YES
valsartan	Pharmaceutical	98.4%	50-80%	NO

The second method to predict OMP removal is to model the reaction of OMPs during ozonation, based on the equation of Hollender et al. (2009) and Lee and von Gunten (2016). OMP removal efficiency can be predicted if the two second-order rate constants (i.e. k_{O3} and k_{OH}) and the two exposures (i.e. $\int[O_3]dt$ and $\int[OH]dt$) are known (Lee and von Gunten, 2016) (see the equation below).

$$\frac{[S]}{[S_0]} = e^{-k''_{O3}\int[O_3]dt-k''_{OH}\int[OH]dt}$$

This research has made use of the in scientific research empirically determined k_{O3} and k_{OH} values. k_{O3} values have been found in a wide range of $5.0*10^{-2}$ $M^{-1}s^{-1}$ (amidotrizoic acid) to $2.5*10^{6}$ $M^{-1}s^{-1}$ (sulfamethoxazole). k_{OH} values of most OMPs are between 10^{9} and 10^{10}. k_{OH} values are less apparent in scientific literature than k_{O3} values. For eight OMPs of which only k_{O3} values have been found, the k_{OH} values have been estimated based on a rule of thumb provided by Von Gunten (2017). Ozone and hydroxyl radical exposure is defined as the integral of the decay curve of ozone and $^{\cdot}$OH (Hollender et al., 2009). Experiments to determine ozone and hydroxyl radical exposure are complex and are not conducted by HH Delfland. However, Lee and von Gunten (2016) have derived an empirical equation from the fitting of measured ozone exposure from literature. Ozone and $^{\cdot}$OH exposure are both functions of the specific ozone dose. With a specific ozone dosage of 0.95 gO_3/gDOC (corrected for nitrite), the ozone exposure is 8.26 $*10^{-3}$ Ms and the $^{\cdot}$OH exposure is 2.95 $*10^{-10}$ Ms. When the two second-order rate constants (i.e. k_{O3} and k_{OH}) of an OMP and the two exposures (i.e. $\int[O_3]dt$ and $\int[OH]dt$) are known, the removal efficiency of an OMP can be modelled.

Figure 3 shows the observed and modelled removal efficiencies of 22 OMPs. Half of the OMPs have expected removal efficiencies of 100%, which are all confirmed by the observed removal. It can be seen that observed and modelled removal efficiencies for most OMPs do not differ much. Average deviation between the two is only 6.9% point or 8.8%. When the three OMPs that have only one measurement are omitted (light blue and red bars in Figure 3), the average deviation is even as low as 5.6% point or 7.7%. Only 6 out of 22 OMPs have a modelled removal efficiency that is not within the standard deviation of the observed removal. Of these 6 OMPs, two are based on a single measurement (2-methyl-4-chlorophenoxyacetic acid and iopamidol).



* Based on only one measurement with feed water concentration on reporting limit and effluent concentration below reporting limit

Note: light blue and light orange (as oposed to dark blue and dark orange) bars in all graphs emphasize that the observed removal efficiency of the OMP is based on only one measurement.

Figure 3 - Comparison of observed removal and predicted removal based on modelling

Based on comparison between observed and modelled individual OMP removal efficiencies in the pilot of HH Delfland, one could argue that the **model can accurately predict** OMP removal during ozonation. Firstly, the model has showed fairly good results in predicting the removal efficiencies as observed in the pilot and no strong outliers have been observed in the data set. Secondly, ozonation experts agree that OMP removal can be accurately predicted, based on the composition of the molecule (Kruithof, von Gunten).

However, there are also two reasons why the claim that the model works well *in general* to predict OMP removal would not hold. Firstly, this research is not based on sufficient data for such general claim. Secondly, the model seems to especially work well for OMPs with high removal efficiencies, but less for OMPs with lower observed removal.

This research recommends HH Delfland to use a lower ozone dosage of 0.7 gO3/gDOC. This dosage 1) gives an effective removal (80%), 2) has lower energy requirements and thus lower costs and 3) limits bromate formation (found in concentrations up to 56 µg/l with a dosage of 1.0 gO_3/gDOC). Furthermore, this research showed that literature can be used to confirm the average OMP removal efficiencies found in the pilot. The individual removal efficiencies can be modelled with the equation of Hollender et al. (2009) and Lee and von Gunten (2016). A pilot remains useful to gain experience with ozone treatment, to study bromate formation and to study the toxicity of oxidation products. Recommendations for further research are, among others, 1) compare effluent concentrations with background concentrations of receiving waters, 2) analyze substances based on functional groups, 3) expand bromate measurements, 4) analyze bioassays to assess toxicity and 5) use more data to compare modelled and observed OMP removal.

Table of Content

List of abbreviations

BOD	Biological Oxygen Demand
BTPP	Bench-top Pilot Plant
CAS	Conventional Activated Sludge
CFU	Colony Forming Units
COD	Chemical Oxygen Demand
CRW	Colorado River drinking Water intake
DGL	De Groote Lucht
DOC	Dissolved Organic Carbon
EAWAG	Swiss Federal Institute of Aquatic Science and Technology
GAC	Granular Activated Carbon
GCM	Group Contribution Method
FF	Freshwater Factory (at WWTP DGL)
HH	Water Authority (Hoogheemraadschap)
IAD	Institutional Analysis and Development
JRC	Joint Research Centre
MBR	Membrane bioreactor
MDPE	Medium-density polyethylene
OMP	Organic Micro-Pollutant
PAC	Powdered Activated Carbon
PCW	Process, contract and wastewater chain management (department of HH Delfland)
p.e.	People Equivalent
RIVM	National Institute for Public Health and the Environment
R&P	Regulation and plan advising (department of HH Delfland)
SPE	Solid Phase Extraction
STOWA	Dutch Foundation of Applied Water Research
UCT	University of Cape Town
UWM	Urban Water Management
WFD	Water Framework Directive
WSQ	Water System Quality (department of HH Delfland)
WWTP	Wastewater Treatment Plant

1. Introduction

1.1 Problem description

Climate change and urbanization put increasing stress on urban water management (UWM). Climate change will lead to intensified and prolonged periods of both drought and precipitation. Meanwhile urbanization is creating areas with extraordinary high population density, prone to a wide variety of water management challenges (Sun, 2008). These drivers cause water crises to be increasingly viewed as the greatest social risks of coming years by business (World Economic Forum, 2012) and national security communities (Clapper, 2012). The European Commission has expressed its concerns in a Communication on Water Scarcity and Droughts (EC, 2007). Sustainable urban water management has the potential to alleviate these problems by guaranteeing a safe and reliable water system for all inhabitants of urban areas (Kiparsky, 2013). A variety of solutions exist for improving the water balance in vulnerable areas, such as water saving policies and rainwater harvesting (Lafforgue, 2015). A solution with great potential for sustainable urban water management is the reuse of wastewater (Grundmann, 2017). After advanced treatment, wastewater can be reused for a variety of purposes, which will close the water cycle of the urban water system.

The Netherlands is one of the areas prone to the consequences of climate change and urbanization. The western part of The Netherlands is almost completely below sea level, is highly urbanized (504 inhabitants/km^2 (CBS, 2016)) and is situated downstream of freshwater sources, mainly the river Rhine and Meuse. These rivers and regular rainfall (800 mm/year (KNMI, 2016)) (indirectly) supply water for drinking, agricultural and industrial water production and water level management in the polders.

Although the amount of rainfall is considerable in The Netherlands, periods of drought are expected to occur more frequently due to climate change. To cope with expected future water shortages, water authorities and drinking water companies are searching for new freshwater sources. Wastewater is currently a limitedly used fresh water source in The Netherlands. In the south-western part of the country wastewater is treated centrally and subsequently discharged directly into the North Sea, or into large water bodies discharging into the sea. Wastewater reuse would contribute to closing the regional water cycle when adequately treated or when the quality already fits the intended purpose.

1.1.1 Role of water authority Delfland

Water authorities in The Netherlands are crucial actors in the regional water systems. They are the oldest governance bodies in The Netherlands, with history back to the 13th century (Havekes, 2008). The 22 water authorities are responsible for a good water quantity and quality in their service areas. Treatment of municipal and industrial wastewater is part of these responsibilities. Water authorities have to prevent both high and low (ground)water levels in their surface areas.

Water authority Delfland (HH Delfland) expressed its ambition to close the regional water cycle through wastewater reuse in the coalition agreement 2015-2019. HH Delfland has the ambition to be self-sufficient in fresh water needs. The wastewater treatment plants will have to be used as fresh water source in order to achieve this goal (HH Delfland, 2015). The wastewater could be reused for water level management and potentially even for drinking water.

Water authority Delfland is covering the densely populated area spreading from The Hague in the north to Schiedam in the south and from Berkel en Rodenrijs in the east to the North Sea coast in the west (see Figure 4). Wastewater is centrally treated in four treatment plants: Harnaschpolder in Delft (1.2 million people equivalent (p.e.) design capacity, 0.96 million p.e. treated in 2015), Houtrust in The Hague (390.000 p.e. design capacity, 320.000 p.e. treated in 2015), De Groote Lucht (DGL) in Vlaardingen (260.000 p.e. design capacity, 219.000 p.e. treated in 2015) and Nieuwe Waterweg in Hoek van Holland (100.000 p.e. design capacity, 90.000 p.e. treated in 2015) (HH Delfland, 2016a). See Figure 4 for the locations of the wastewater treatment plants. The service area is characterized by intensive greenhouse agriculture, especially around wastewater treatment plant (WWTP) Nieuwe Waterweg.

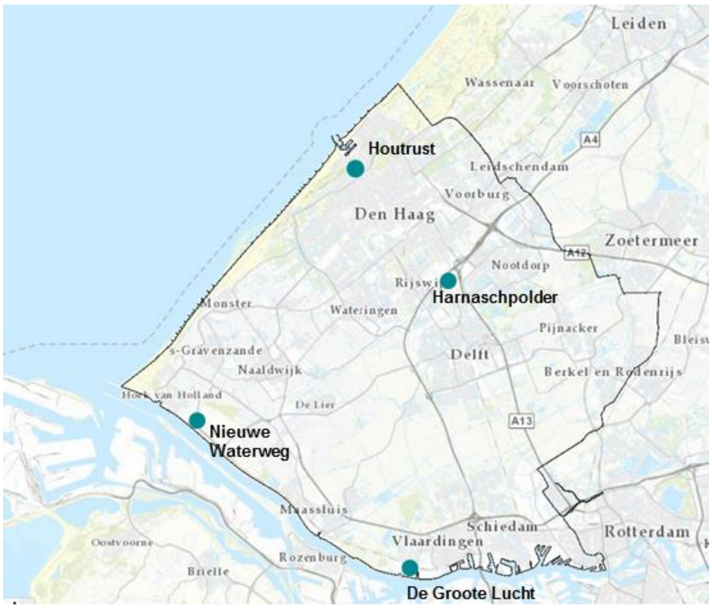


Figure 4 - Service area of HH Delfland and location of the four WWTPs

HH Delfland is currently investigating the potential of wastewater reuse from both treatment plant Harnaschpolder and De Groote Lucht (DGL). Plans to reuse wastewater from the Harnaschpolder are at an early stage of deliberation on the feasibility. Wastewater could be used as a source of drinking water in the region. Advanced treatment would need to be added to the Harnaschpolder to enable reuse.

Potential reuse of wastewater from De Groote Lucht in Vlaardingen is in a further stage of development. The idea is to create a 'Freshwater Factory' (FF) which allows treated wastewater to flow to constructed wetlands (the ‘Water harmonica’) and subsequently into the polders north of the treatment site. The fresh water can support (ground)water levels and enables recreational use of waters by avoiding algae growth in currently (semi) stagnant waters. A pilot of ozonation and biologically active filtration is installed in summer 2016 to gain experience with advanced wastewater treatment on location. This report will focus on the advanced wastewater treatment of the Freshwater Factory. However, for a successful implementation of wastewater reuse projects, a new institutional environment is required. A wide variety of institutional issues are expected in establishing this new environment. Appendix III provides a summary of the research of this author on institutional analysis of a closed water cycle.

In the ‘Plan of Approach’ of the Freshwater Factory, HH Delfland has identified four conditions that together led to the decision to start the pilot plant for advanced treatment of wastewater at WWTP De Groote Lucht (HH Delfland, 2016b). The first general condition is wastewater as currently unused source of fresh water supply, as previously discussed. The second general condition is the expected stricter water quality standards imposed by European and national legislation. Standards for BOD, COD and nutrients of wastewater effluent have already been set (BOD < 25 mg/l, COD < 125 mg/l, P < 1 mg/l (for p.e > 100.000), N < 10 mg/l (for p.e > 100.000) (91/271/EEG)). Although the concentration of pharmaceuticals and endocrine disruptors has come under increasing attention, no standards have currently been set for these compounds. HH Delfland expects that quality standards for wastewater effluent and surface waters will become stricter in the near future. Besides these two general conditions, also two conditions specific to HH Delfland have contributed to the decision to start the pilot. The first is the potential to increase the recreational functionality of the Krabbeplas, which is located in proximity of WWTP DGL. The long residence time of water in this water body (~1 year) and the abundance of nutrients leads to algae growth in summer, limiting recreational activities such as swimming. The Freshwater Factory can supply water to shorten the residence time to a few days which prevents algae growth. The second specific condition is the opportunity for investments in the direct environment provided by extra funding available for quality measures in the area around the Blankenburg-connection. This connection of two highways across the river Nieuwe Waterweg has a significant impact on the environment. To give the region a quality impulse the

Dutch government made €25 million available for quality improvement measures. HH Delfland could partly describe to this funding.

Advanced *wastewater* treatment is relatively unexplored in the field of water management and has its own complexities and peculiarities. *Drinking* water treatment has more experience with advanced treatment technologies. The next section will discuss the complexities in advanced *wastewater* treatment, with a focus on organic micro-pollutant removal.

1.1.2 Complexity in advanced wastewater treatment

Conventional wastewater treatment plants are designed to remove organic matter (COD & BOD) and nutrients (nitrogen and phosphorous). Advanced wastewater treatment targets organic micro-pollutants (OMPs) in addition to the conventional treatment steps. The design of an advanced wastewater treatment plant will always entail a trade-off between costs and benefits. Costs include investment and operation costs, of which energy and chemicals are often the main expenses. Dutch Foundation of Applied Water Research (STOWA) estimates that annual wastewater treatment costs would increase from 1€ billion to 1.8€ billion in case all WWTPs would install an advanced treatment step (ozonation + activated carbon filtration) (STOWA, 2015). Benefits of advanced wastewater treatment are protection of the environment on which effluent is discharged and potentially a new fresh water source which can be reused for the desired purpose. The trade-off is different for various advanced treatment steps. Scientific research has identified three main technologies for advanced wastewater treatment: activated carbon, reverse osmosis or advance oxidation (Margot et al, 2013; Hollender et al., 2009). Chapter 2 discusses the technological context of advanced wastewater treatment in more detail, also regarding the trade-off between costs and benefits.

The main complexity in advanced wastewater treatment is the removal of organic micro-pollutants (OMPs). This term is used to indicate a wide range of compounds such as pharmaceuticals, biocides and pesticides, corrosion inhibitors and endocrine compounds (Margot et al., 2013). This report will use the term organic micro-pollutants (OMPs) but other terms such as emerging pollutants or artificial compounds are also commonly used. More OMPs are expected to end up in the water system due to aging of the Dutch population and increasing use of pharmaceuticals (RIVM, 2016). Temporarily low water levels during dry periods can increase the concentration of OMPs in water bodies significantly (RIVM, 2016).

In The Netherlands, OMPs are generally found in concentrations below 10 µg/l in wastewater treatment plant effluent. Concentrations in surface waters are on average lower than 1 µg/l while concentrations in drinking water are in range of 0.05-0.10 µg/l (RIVM, 2016). In recent years, analytical methods to detect OMPs have improved significantly. OMPs that were previously undetectable are now increasingly measured in wastewater effluent, surface water and groundwater (de Ridder, 2012). Large WWTPs discharging on small water bodies can result in high OMP concentrations. For this reason, the STOWA constructed a methodology to assess the impact of WWTPs on its receiving water bodies and to prioritize so called 'hotspots' (STOWA, 2015). A 'hotspot' is defined as a location where WWTP effluent with a certain OMP load causes problems for the receiving water body (STOWA, 2015).

The need to remove OMPs from wastewater effluent comes from the expected but yet unknown mixture and long term effects of OMPs on both the environment and human health (Reungoat et al., 2010). The presence of OMPs endangers reuse of treated wastewater since it can cause chronic toxicity, endocrine disruption and the development of pathogen resistance (Rosal et al., 2010). OMPs are especially damaging for aquatic organisms since they are subjected to multigenerational exposure (Rosal et al., 2010). Endocrine effects on fish and mussels, such as reproductive disruption, intersex and feminization of males have been observed in water bodies downstream of conventional WWTPs (Margot et al., 2013). For humans, acute health effects are not expected but the mixture and long term effects of exposure even to low concentrations of OMPs is unknown (Webb et al., 2003). This is of particular relevance when wastewater is reused for drinking water production or when indirect potable reuse is considerable (Reungoat et al., 2010). Chapter 3 provides more detailed information on OMPs and their analysis in wastewater treatment.

1.2 Research questions

This research aims to contribute to the development of expertise on OMP removal in advance wastewater treatment. The main research question that will be answered in this research is:

What are the optimal process conditions and corresponding organic micro-pollutants removal efficiencies and toxicity of residual contaminants for the combination of ozonation and biofiltration?

Sub-questions to be answered are:

1. What are the operating parameters and removal mechanisms of ozonation and biofiltration?
2. What is the optimal ozone dosage found during pilot conditions and what does comparison with similar studies in research tell us? Could ozone dosage have been based on literature?
3. What are the expected removal efficiencies based on literature and modelling and what are the observed removal efficiencies in the pilot installation of HH Delfland?
4. Can individual OMP removal be predicted based on literature and/or modelling?
5. Is bromate formed during ozonation? If yes, will it be removed during biological sand filtration?

1.3 Demarcation

As indicated by the research questions stated above, this research focuses on OMPs and toxicity of residual contaminants removal and production by ozonation and biofiltration. This option for advanced wastewater treatment will mainly be applied in developed countries with strict water quality standards. Out of the scope of this research is removal of other undesired substances of wastewater: COD, BOD, nutrients and bacteria and viruses. When removal of OMPs and toxicity affects one of these substances then it will be mentioned. Also out of scope are other options for advanced wastewater treatment, mainly powdered activated carbon and high pressure filtration (nanofiltration and reverse osmosis) (see Chapter 2.1).

1.4 Research method

For this research multiple research methods are used: literature research, data analysis and modelling. At the start of the research an extensive literature review has been conducted to build on knowledge from previous experiments with OMP removal in advanced wastewater treatment. Scientific articles are found in online databases (e.g. Science Direct, NCBI) and/or provided by HH Delfland and have been discussed with process technologists from HH Delfland. The literature review focuses on research in pilots rather than lab scale. It is expected that results from pilot research are more applicable to the situation of HH Delfland. Research of Margot et al. (2013) and Antoniou et al. (2013) have specifically proven to be highly useful. Margot et al. (2013) compare OMP removal by ozone and powdered activated carbon (PAC) pilot scale advanced treatment in Lausanne, Switzerland. Antoniou et al. (2013) investigate the ozone dosage required to remove OMPs from wastewater in bench-scale experiments with conventional WWTP effluent of six Swedish plants.

In the chapters on ozone dosage and observed removal efficiencies, the data of the pilot at WWTP DGL are used. In this research the choice to use the data of the pilot instead of conducting lab experiments in person has deliberately been made. HH Delfland has a budget of €0.4 million for water analysis tests, which yields high quality and extensive data on the performance of ozonation and biofilters. Finally, the modelling research method is used to predict removal efficiencies of ozonation based on the equation of Hollender et al. (2009) and Lee and von Gunten (2016).

1.5 Reading guide

After this introduction, Chapter 2 provides the legal and technological context of wastewater reuse and specifically OMP removal. Chapter 3 describes analytic methods for detection of OMPs and toxicity in more detail. Chapter 4 provides information on OMP and toxicity removal in for this report relevant wastewater treatment steps. Removal mechanisms, configurations and process conditions are discussed for each relevant treatment step. In Chapter 5, the current pilot of HH Delfland at WWTP De Groote Lucht is explained. Chapter 6 provides an analysis of the most optimal ozone dosage based on pilot experiments and a comparison of results with scientific research. Chapter 7 evaluates individual OMP removal, starting with an analysis of the observed removal efficiencies in the long run test of HH Delfland. Also, removal is predicted based on literature and modelling. Finally, Chapter 8 gives conclusions and Chapter 9 recommendations based on this research. Appendix

III will provide a summary of institutional analysis conducted in research of Van Es (2017b). See Figure 5 for a flow chart of this research.

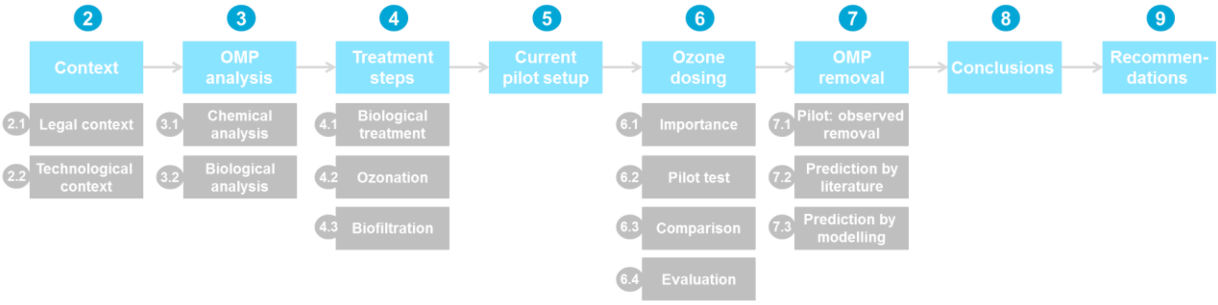


Figure 5 - Flow diagram of research set-up

2. Context

This section starts with a discussion of the legal context which wastewater reuse must conform to. The second part of this Chapter discusses the technological context in which advanced wastewater treatment is embedded. In the demarcation section (1.3) is already stated that this report focuses on the combination of ozonation and biofiltration as advanced treatment step. The second section elaborates on this choice by discussing the wider technological context.

2.1 Legal context

Legislation on wastewater reuse, WWTP effluent standards and surface water standards is drafted on multiple legislative levels. The most relevant legislators for this report are the European Union and the Dutch national government. The European Commission (EC) has expressed its concerns regarding increasingly severe droughts due to climate change. With the combination of an increasing population in highly urbanized areas, the EC warns for increasing water scarcity (EC, 2007). The European Union has adopted five Directives that have a relation with wastewater reuse (see Table 2). Directives are applicable to all member states and set aims that member states need to achieve. Member states are obliged to draft national legislation to meet these aims at a certain date.

The first relevant Directive, applies to the discharge of treated effluent to the water system: the Urban Wastewater Treatment Directive (91/271/EEG). This Directive is relevant to the Freshwater Factory since the discharge of WWTP DGL will be a new discharge. One of the main issues that HH Delfland will have to confront is the discharge of heavy metals on the water system. Heavy metals will only be partly removed by conventional treatment (adsorption to sludge) and not removed by advanced treatment (ozonation and biofiltration) (Margot et al., 2013). This means that heavy metals be present in the effluent. HH Delfland will have to comply with 91/271/EEG in order to be allowed to discharge the effluent on the polder water system.

Table 2 - Five EU Directives applicable to wastewater reuse

EU Directive	Applies to	Description
Urban Wastewater Treatment Directive (91/271/EEG)	Wastewater treatment plant effluent	Includes standards for COD, BOD, N and P
Water Framework Directive (2000/60/EC)	Water bodies	Extensive Directive aimed to improve water quality of European water bodies
Environmental Quality Standards Directive (2008/105/EC)	Water bodies	Contains a list of priority (hazardous) substances and other pollutants with maximum allowable concentrations
Directive 2013/39/EU	Water bodies	Amends Directives 2000/60/EC and 2008/105/EC by extending list of priority substances
Bathing Water Directive (2006/7/EC)	Bathing water bodies	Sets biological standards for bathing water bodies

The other four Directives concern the surface waters that are the receiving water bodies of the wastewater effluent. The Water Framework Directive (WFD) (2000/60/EC) is an extensive Directive aimed to improve water quality of all European water bodies. The Environmental Quality Standards Directive (2008/105/EC) contains a list of priority (hazardous) substances and other pollutants that are not allowed to be present above a certain concentration in water bodies. Directive 2013/39/EU amends Directives 2000/60/EC and 2008/105/EC as regards to priority substances in the field of water policy. This Directive updates the list of priority substances in the WFD (33 substances) with 12 substances (among others cypermethrin).

The WFD has defined a 'water body' as a 'discrete and significant element of surface water' (2000/60/EC). Responsible authorities have to determine the 'water bodies' in its service areas. HH Delfland has distinguished seven water bodies in its service area. The Krabbeplas (on which the Freshwater Factory will discharge, via the Waterhamonica) is not part of a water body but is regarded as 'local water'. However, there are two reasons why EU legislation is still relevant for the Krabbeplas.

Firstly, the *chemical* water quality standards (the priority substances of 2008/105/EC and 2013/39/EU) apply to *all* waters (as opposed to the ecological water quality standards from the WFD). Deterioration of chemical water quality is not allowed according to the 'stand-still principle'. A deterioration of water quality is not allowed to place the chemical water quality in a lower class (e.g. going from a *good* chemical quality to a *moderate* quality). When the chemical water quality is already scored in the lowest class, no deterioration is allowed at all. Increasing the concentration of, for instance, heavy metals by means of a new discharge, could well be seen as a deterioration.

Secondly, HH Delfland has determined that EU standards on water quality apply to *all surface waters* within its service area. HH Delfland uses these standards in permit applications of other actors (e.g. industry), and thus the same standards must be applied to their own discharges.

Finally, the Bathing Water Directive (2006/7/EC) sets biological standards for swimming water bodies. Inland water bodies have 'good quality' when Intestinal enterococci has a concentration below 400 cfu/100 ml[1] and Escherichia coli below 1.000 cfu/100 ml. These standards are relevant since the water body on which effluent is discharged, the Krabbeplas, is designated as bathing water. The European Joint Research Centre (JRC) has recently published a report on minimum water quality requirements for water reuse in agricultural irrigation and aquifer recharge. Standards on COD, BOD, microbiology and macro pollutants (heavy metals, nutrients etc.) have been set. OMPs are not included in these standards. The JRC however emphasizes the need for a framework to guide identification of OMPs to be monitored and if necessary to be regulated (JRC, 2016). When wastewater would be reused for drinking water, then the Drinking Water Directive 98/83/EC is also relevant.

The Netherlands has translated the above described Directives into two laws: Waterwet (2009) and Wet Milieubeheer and two lower level legislative instruments: 'Besluit kwaliteitseisen en monitoring water' (2009) and 'Regeling monitoring Kaderrichtlijn Water' (2010).

These Directives, laws and regulations set standards for maximum allowed concentrations of certain pollutants in water bodies, such as benzene (chemical), lead (heavy metal) and dicofol (pesticide) (2013/39/EU). However, no pharmaceuticals can be found on the priority substances list. They are only listed on the 'Watchlist' which means that no environmental quality standards for these Watchlist substances exist but that member states only have the obligation to monitor occurrence (RIVM, 2016). The pharmaceuticals azitromycin, clarithromycin and diclofenac are, for instance, included on the Watchlist (JRC, 2015).

To date, legislating is not strict for wastewater treatment effluent for two reasons: important OMPs such as pharmaceuticals are missing on the priority substances list and the standards only apply to water bodies and not wastewater treatment plant effluents. Although legislation on pharmaceuticals in wastewater treatment effluent currently does not exist, the subject draws increasing attention from lawmakers at both European and national level. It is expected that the EU priority substances list will be extended by a wider variety of OMPs. In 2014, Switzerland became the first country in Europe to adopt a law requiring 100 of the total 700 WWTPs to remove

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[1] cfu stands for Colony Forming Units and is used to measure the number of viable bacteria cells in a sample per volume (e.g. 100 ml)

80% of OMPs (Mulder et al., 2015). In The Netherlands, the debate continues whether to oblige advanced wastewater treatment to remove OMPs from the water system.

However, governmental bodies such as water authority Delfland, do not only have to comply with existing legislation. The government also has the ‘duty to care’ (in Dutch: zorgplicht). HH Delfland is not allowed to deliberately discharge harmful substances in bathing water, even though there would be no standards for these substances. The ‘duty to care’ is the obligation of the government to carefully fulfill its duties. One of the main duties of HH Delfland is to ensure a good water quality in its service area. Wastewater reuse for the Krabbeplas can only be executed when the HH Delfland is sure that no hazards will occur.

2.2 Technological context

To prevent the above discussed OMPs from accumulating in the water system, either use of OMPs should be decreased, or removal should be achieved somewhere along the water cycle. Decreasing use of pharmaceuticals, pesticides and industrial chemicals will be helpful, but is to a large extent out of influence of water authorities. Water authorities *can* contribute to the removal of OMPs from the water system (Margot et al., 2013). The Netherlands has an ongoing debate on whether removal is most efficient at the point of use (for instance hospitals) or at point of wastewater collection (the wastewater treatment plants). Experiments are conducted with point source removal at Dutch hospitals, for instance using Pharmafilter at the Reinier de Graaf hospital in Delft, The Netherlands. These point source filters can contribute in removing OMPs from the water cycle, since 20% to 45% of pharmaceuticals and endocrine disruptors in Dutch wastewater originate from hospitals (STOWA, 2012). Due to the wide range of OMPs present in the water system and the diffuse sources, point source removal cannot solve the entire problem. Since 90% of wastewater is treated centrally in Europe and 99.5% in The Netherlands (Ministry of I&M, 2016), WWTPs are major point of collection and release into the environment of many OMPs. Not all OMPs are released through WWTPs. Pesticides for instance have a diffuse release into the water system by run-off from agricultural lands. Still, WWTPs make a good location for removal of many undesired substances (Hollender et al., 2009). The Dutch National Institute for Public Health and the Environment (RIVM) estimates that annually 140.000 kg of pharmaceuticals and 17.000 kg of pesticides are discharged into the water system through wastewater treatment plants in The Netherlands (RIVM, 2016).

Advanced treatment steps could be added at wastewater treatment plants to remove OMPs. Scientific research has identified three main technologies with the potential for large-scale application of advanced wastewater reuse in terms of efficiency, costs and energy requirements: adsorption onto activated carbon, size exclusion by reverse osmosis or oxidation of micro-pollutants with ozone (Lee and von Gunten, 2016; Margot et al, 2013; Hollender et al., 2009) (see Table 3). The first option is explored in the ‘Powdered Activated Carbon in Activated Sludge' (PACAS) project of the Dutch Foundation of Applied Water Research (STOWA). Full scale applications are already in use in Germany and Switzerland (Wunderlin, 2017; Mulder et al., 2015).

Table 3 - Three main technologies for advanced wastewater treatment (Vergouwen et al., 2011)

Treatment	Removal mechanism	Removal efficiency	Energy use	Research by
Activated carbon	Adsorption	70%	Low	PACAS project by STOWA Full scale installations in GER & SWI
Reverse osmosis	Size exclusion	95%	High	Baumgarten et al., 2007 Wintgens et al., 2004 Drewes et al., 2002
Ozonation with biofiltration	Oxidation	90%	Medium	Freshwater Factory by HH Delfland Margot et al., 2013 (pilot) Hollender et al., 2009 (full scale)

In the second option, reverse osmosis removes compounds based on size, change and inability to permeate the active RO membrane. Reverse osmosis is found to effectively remove nearly all OMPs in wastewater treatment to a high degree (95-100% removal at 21% recovery) (Baumgarten et al., 2007; Drewes et al., 2002; Wintgens et al., 2004.). However, RO has the disadvantages of higher energy consumption, higher waste production and lower water recovery compare to the other two options (Lee et al., 2012). In The Netherlands there are currently no experiments conducted with reverse osmosis treatment of municipal wastewater.

The options with *powdered* activated carbon and reverse osmosis will not be part of this research. This report will solely focus on the second option: oxidation of OMPs with ozone (in combination with biofiltration with a sand or granular activated carbon (GAC) medium). Decision makers should keep an eye on research to all three treatment options to stay informed on the benefits and disadvantages and costs of both.

The Netherlands can benefit from research conducted in Switzerland and Germany. If The Netherlands wants to remain its global position as country of outstanding water management, it ought to stay ahead in technological developments. Pro-active research and installation of pilot plants will have to be part of these efforts in staying ahead in the field of advanced wastewater treatment.

3. Analysis of organic micro-pollutants

As briefly explained in the introduction, the term ‘organic micro-pollutants’ (OMPs) is used to address a wide range of substances including pharmaceuticals, personal care products, hormones, pesticides, drug metabolites and environmentally persistent chemicals (Antoniou et al., 2013, Margot et al., 2013). The combination and mixture of OMPs present in the natural environment can be different from country to country depending on use in healthcare, farming and industrial activities and removal during wastewater treatment (Margot et al., 2013). OMPs have various pathways towards the water system (e.g. from hospital wastewater or agricultural land run-off), all induced by anthropological activities (Mulder et al., 2015), see Figure 6. Physicochemical properties of OMPs vary widely, being for instance biodegradable or persistent, polar or apolar and hydrohilic or hydrophobic. Compounds can behave differently depending on the physical conditions of the aquatic environment such as pH value (Mulder et al., 2015).

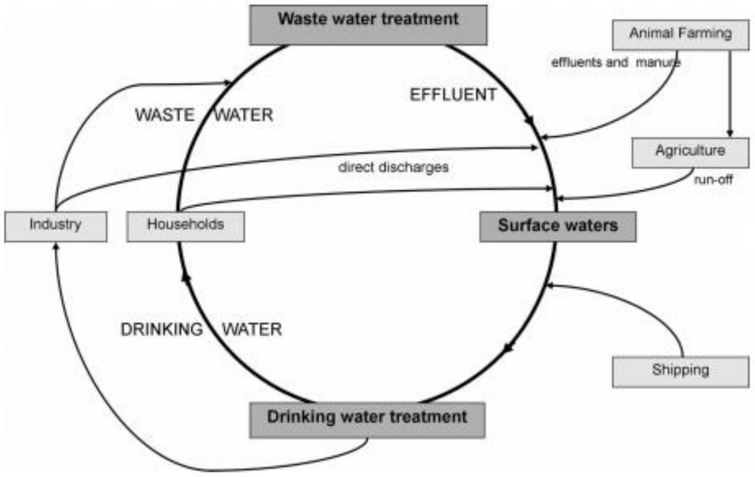


Figure 6 - Schematic representation of the water cycle with pathways of OMPs (Houtman, 2010)

The potential harm of OMPs to the environmental ecology or human health has prompted extensive research on the ability of water and wastewater treatment processes to remove these compounds (Lee et al., 2012). The past years have seen increased scientific and public awareness regarding the contamination of surface waters with OMPs.

To analyze the presence and activity of OMPs in natural waters and wastewater effluent, two different analyses are used: chemical and biological analysis. The next sections will discuss both methods of analysis.

3.1 Chemical analysis

Chemical analysis is used to quantify concentrations of specific organic micro-pollutants. More than 347.000 chemicals are registered and regulated by (inter)national authorities (Fischer et al., 2017). Many of these are present in (waste)water, which makes it impossible to analyze all (European Chemicals Agency, 2016). For this reason, researchers should compose a list of target substances, often the ones indicated as priority substances by respective governments (Margot et al., 2013). These target substances can be used as indicators of presence and removal of OMPs with similar origin or characteristics. Detection methods of OMPs have improved in the past years, allowing to quantify OMP concentrations in micro- and nanograms (De Ridder, 2012). Compounds should have a sufficiently high incoming concentration in order to accurately measure removal efficiencies. When concentrations fall below reporting limits, some researchers take the reporting limit as concentration to calculate removal efficiencies (e.g. Margot et al., 2013; Reungoat et al., 2010), while others take a concentration of half of the reporting limit (Hollender et al., 2009). The STOWA uses the Volkert-Bakker method to uniform analysis of experiments in wastewater treatment (STOWA, 2010). This research uses the term reporting limits, and not detection limits. These terms might seem interchangeable but there is a difference indeed. The difference will be clarified with an example. A laboratory might be able to detect an OMP in concentrations as low as 8 ng/l (detection limit). However, due to margins of error in measurements, the laboratory can decide to set the reporting limit at 10 ng/l for the specific OMP. A measured concentration of for instance 9 ng/l will then be reported as ‘lower than reporting limit of 10 ng/l (< 10 ng/l)’. Laboratories often do not provide information on the *detection limits* and only communicate the *reporting limits*.

In the chemical analysis of OMPs, researchers use solid phase extraction (SPE) under acidified conditions (pH = 2.5 (Margot et al., 2013) or pH = 2.0 (Nakada et al., 2007)). The filtrate is analyzed by a liquid or gas chromatography coupled to tandem mass spectrometer. Margot et al. (2013) use ultra- performance liquid chromatography coupled to tandem quadrupole mass spectrometer (UPLC-MS/MS) while Reungoat et al. (2010; 2012) use liquid chromatography coupled with tandem mass spectrometry (LC/MS/MS). Nakada et al. (2007) use gas instead of liquid chromatography with mass spectrometry (GC-MS).

In chemical analysis, uncertainty regarding recovery and repeatability of the analyses is always present. The uncertainty is compound and concentration dependent, increasing towards the reporting limit of a compound (Margot et al., 2013). Bonvin et al. (2011) find that for the large majority of OMPs analyzed the relative standard deviation was <30% while Reungoat et al. (2010) and Hollender et al. (2009) claim a standard deviation of 20%.

Chemical analysis provides and accurate information on the presence and removal of specific compounds. However, the toxicity of the mixture of thousands of compounds remains unknown with this analysis. For this reason, researchers use biological analysis to assess toxicity of the wastewater. Both methods of analysis are highly relevant in analyzing performance of advanced wastewater treatment.

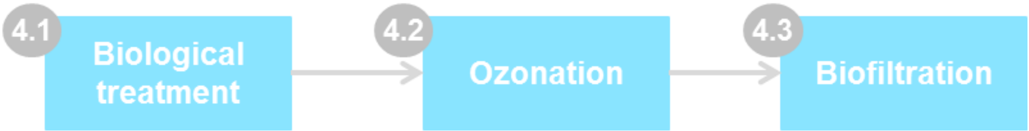
3.2 Biological analysis

Bioassays provide information on potential effects of the mixture of OMPs on the aquatic ecological system (Margot et al., 2013). Research of Reungoat et al. (2010) demonstrates the added value of biological analysis to previously discussed chemical analysis. In his research, estrogenic compounds were not detected in chemical analysis of the advanced treatment effluent, but the samples did have an estrogenic effect. Apparently, one cannot conclude that water doesn't have an estrogenic effect when certain estrogenic compounds cannot be found. The mixture of all transformation products can still show an estrogenic effect. To incorporate mixture effects, researchers use bioassays in their analyses. These bioassays can be seen as sum indicators to detect certain relevant groups of chemicals, such as estrogenic compounds in the example given (Macova et al., 2010; Reungoat et al., 2010). Testing the effect of advanced wastewater treatment with bioassays is currently under development with Macova et al. (2010) demonstrating the ‘first comprehensive application of the bioanalytical tool framework on an advanced water treatment plant’. In the future, bioassays should be used routinely by laboratories or water companies themselves (Macova et al., 2010).

A wide range of bioassays are available that can provide information on groups of chemicals with a common mode of toxic action (Macova et al., 2010). Research of Macova et al. (2010) uses the *Vibrio fischeri* assay to assess baseline toxicity. This assay assesses general toxicity caused by all chemicals by measuring the reduction in luminescence of the naturally bioluminescent marine bacteria *Vibrio fischeri.* Besides general toxicity, specific modes of toxic action can be targeted by bioassays. Macova et al. (2010) target five specific modes of toxic actions with five additional bioassays, including aspects of estrogenicity, genotoxicity, neurotoxicit, phytotoxicity and dioxin-like activity. For the latter aspect Macova et al. (2010) uses the AhR-CAFLUX assay, measuring the induction of fluorescence under the control of Aryl Hydrocarbon Receptor (AhR). Research of Maier et al. (2016) uses the ethoxyresorufin *O*-deethylase (EROD) assay and the reporter gene assay to assess the dioxin-like toxicity. This shows that multiple assays exist to determine general or a specific form of toxicity.

4. Treatment steps

After explaining that OMPs are undesired in the water system and discussing chemical and biological methods of analysis in the previous chapter, this section will discuss the relevant treatment steps to *remove* the OMPs from wastewater. Both conventional treatment and advanced treatment (ozonation and biofiltration) are discussed. This research focuses on the advanced treatment steps since most OMP removal takes place in these steps. The sequence of treatment steps and hence the sequence of discussion in this section is: biological treatment, ozonation, biologically active filtration.



4.1 Biological treatment

Activated sludge (CAS) treatment is a common way of conventional biological wastewater treatment in Europe. This section will not elaborate on all aspects of activated sludge treatment (e.g. COD and BOD removal) but will rather focus on OMP removal during this treatment. Although removal efficiency highly varies per OMP (Reungoat et al., 2010), overall biological treatment does not sufficiently remove OMPs from wastewater (Margot et al., 2013). This is the exact reason that advanced treatment steps are required for the removal. Many OMPs are not biologically degradable because they are developed to illicit a specific biological action (Antoniou et al., 2013). Membrane bioreactors (MBRs) generally have been found to achieve comparable or better OMP removal than the conventional activated sludge process (Kimura et al., 2007; Radjenovic et al., 2007). Radjenovic et al. (2007) find that average removal for 22 OMPs is 75% in MBR and 45% in CAS. A potential explanation could be the greater sludge age in MBR systems, since improved removal is observed with increased solids retention time. Another potential explanation could be the greater adsorption potential to MBR sludge because the organic matter content is greater than for CAS sludge (Radjenovic et al., 2007).

Removal of compounds during conventional treatment can occur for easily biodegradable compounds, for instance paracetamol and ibuprofen (>90% removal) (Hollender et al., 2009; Reungoat et al., 2012). Longer solids retention time has a positive effect on OMP removal, as explained above (Rattier et al., 2014; Radjenovic et al., 2007). Another removal mechanism of OMP removal is due to sorption to the sludge (e.g. hydrophobic musk ketones or zwitterionic fluoroquinolone antimicrobials (Hollender et al., 2009) which is subsequently separated from the treated wastewater. Sorption to sludge of certain OMPs is driven by hydrophobicity of the compounds (Rattier et al., 2014). On the other hand, measured OMP concentrations can also rise during conventional activated sludge treatment due to release from degrading faeces (Margot et al., 2013).

Concluding, most OMPs are only partly removed or even barely affected (e.g. carbamazepine, diclofenac) (Onesios et al., 2009; Margot et al., 2013). Advanced treatment is required to remove these undesired substances. This removal takes place in the subsequent, advanced treatment steps of ozonation and biofiltration. The next sections will discuss these treatment steps in more detail.

4.2 Ozonation

The focus of this report is on advanced treatment with the combination of ozonation and biofiltration. This section will elaborate on the first step, ozonation, while section 4.3 will focus on the second step of biofiltration.

Ozonation has a long history of use for disinfection and trace contaminant removal in drinking and wastewater treatment (Hollender et al., 2009; Lee et al., 2012). It was first used for drinking water treatment in The Netherlands back in 1893, mainly for color removal or taste and odor control (EPA, 1999). However, the potential to remove OMPs with ozonation has only been discussed recently and is not as common (Hollender et al., 2009; Lee et al., 2012). The principle of treatment with ozone is oxidation of OMPs into smaller, biodegradable transformation products (Margot et al., 2013). OMPs are not removed from (waste)water and are not completely mineralized. The latter means that OMPs are not completely converted into inorganic substances such as H_20 and CO_2. This section first discusses the operation of ozone treatment and later the removal mechanisms.

4.2.1 Operation

Ozone is an unstable molecule and should hence be generated at the point of application. The reaction is endothermic and requires a considerable amount of energy (EPA, 1999).

$$3O_2 \overset{\rightarrow}{\underset{\leftarrow}{-}} 2O_3$$

Ozone treatment systems typically consist of four components: gas feed system, ozone generator, ozone dosing, ozone contactor and off-gas destruction (see Figure 7) (EPA, 1999).

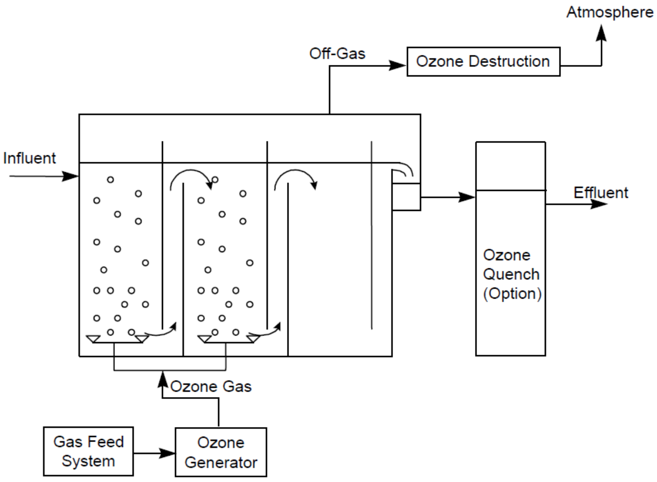


Figure 7 - Four components of an ozone treatment system (EPA, 1999)

The installation requires a **gas feed** flow, which can be high purity oxygen or air. The operation of the first is relatively simple; liquid oxygen is stored in a tank and converted to a gas by an evaporator. The latter is fairly complicated as the air should be properly conditioned with all sorts of air compressors, filters and dryers. The gas feed flows into a generator in which, most commonly by corona discharge, **ozone is generated**. An oxygen-containing gas passes through two electrodes separated by a dielectric and a discharge gap. When voltage is applied to the electrodes, an electron flow across the discharge gap will occur. The oxygen molecules are disassociated by the energy of the electrons, which leads to the formation of ozone (EPA, 1999). Generating ozone requires balancing between ozone yield and operational reliability and reduced maintenance (EPA, 1999).

The ozone gas is transferred (**dosed**) to the water. Two configurations are widely used: bubble diffuser contactors or injectors. The first is depicted in Figure 8 and shows that ozone gas in bubbles contacts co- or counter current flowing water in typically two to six stages. Ozone transfer efficiency depends on the height of the contact tanks and the bubble size. Advantages are process flexibility and operational simplicity, while the required water height and diffuser pore clogging can be regarded as disadvantages (EPA, 1999).

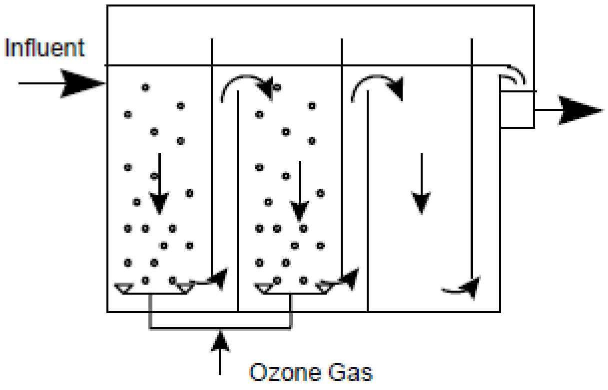


Figure 8 - Bubble diffuser contactor with three stages (EPA, 1999)

The second commonly used configuration is the injector dissolution (see Figure 9). Ozone is injected into water under lower pressure, generated in a venturi section. In this way, ozone is pulled into the water stream. Often a side stream is pumped to a higher pressure to increase the available vacuum for ozone injection. Hereafter the side stream is added to the main flow under high turbulence, enhancing dispersion of ozone in the full flow. The very effective ozone transfer is an advantage of injectors while the complex operation and high costs are downsides.

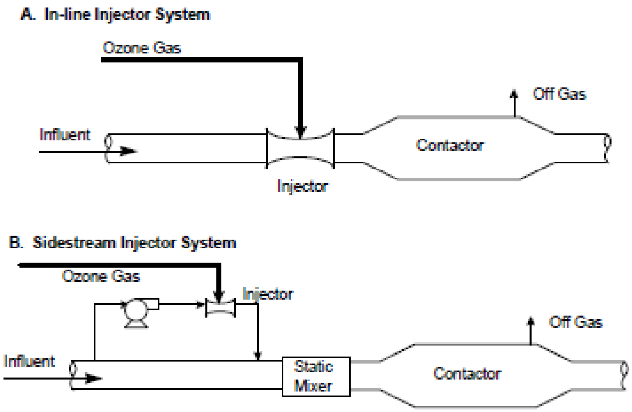


Figure 9 - Injector dissolution, in-line (upper) and sidestream (lower) with a separate contactor (EPA, 1999)

After ozone dosing, a **contactor** is required to allow the ozone to have sufficient contact time with the undesired substances (EPA, 1999). For the bubble diffuser contactor described above, the ozone is dosed at the bottom of the contactor tank. The ozone dosing and ozone contact hence take place in the same reactor. For the venture injector, the ozone contactor is a more separate step in the treatment system.

The final component of an ozone treatment system is the **off-gas destruction**. The off-gas from the installation can have dangerously high concentrations of ozone. For this reason, the gas is collected and ozone is converted back to oxygen by a catalyst before released into the atmosphere (EPA, 1999).

Personnel will require training to safely operate an ozone system at WWTPs. Besides that, specific safety measures should be installed, such as ozone detectors and control schemes. These measures have to prevent the toxic ozone gas to do any damage to equipment and staff. This makes ozonation not suitable for small WWTPs with non-permanent staff (Margot et al., 2013).

4.2.2 Reaction mechanisms

Ozone in water can react in two different ways with compounds present: direct oxidation by molecular ozone (O_3) or oxidation by hydroxyl radicals ($^{\cdot}OH$) produced during the decomposition of ozone (see Figure 10). The decomposition of ozone happens spontaneously during water treatment by a complex mechanism involving the production of hydroxyl radicals (EPA, 1999). The quick transformation of ozone into $^{\cdot}OH$ radicals is due to the reaction of ozone with DOC (Lee and von Gunten, 2016). No scientific study provides an equation for this reaction. This is probably due to the wide variety of forms in which DOC occurs and the complex reaction of ozone with DOC.

Ozone reacts selectively with compounds at a reaction rate from no reaction up to 10^{10} $M^{-1}s^{-1}$ (Hollender et al., 2009). Ozone is particularly reactive to functional groups with high electron density such as double bonds, nonprotonated secondary and tertiary amines, and reduced sulfur species (Hollender et al., 2009). Hydroxyl radicals react strongly and non-selectively with compounds at reaction rates of 10^{10} to 10^{13} $M^{-1}s^{-1}$ (EPA, 1999). The reaction of $^{\cdot}OH$ radicals with compounds occurs by i) addition to an aromatic system, olefin, or lone electron pairs of nitrogen or sulfur, ii) hydrogen abstraction and iii) electron transfer (Lee and von Gunten, 2016). Section 7.3.1 will further elaborate on the reaction rates of ozone and $^{\cdot}OH$ radicals in the attempt to model removal efficiencies of OMPs.

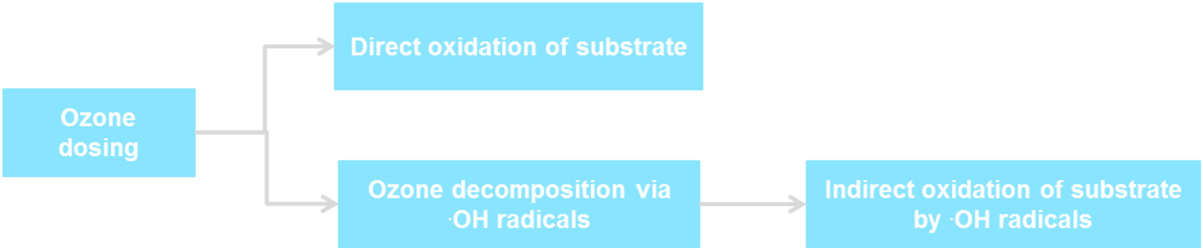


Figure 10 - Two pathways of ozonation: direct and indirect

The two pathways compete for compounds to oxidize. The direct reaction with ozone is relatively slow but the concentration of ozone is relatively high. Reaction with hydroxyl radicals occurs very fast but due to a half-life time in the order of microseconds, the concentration of hydroxyl radicals remains low (EPA, 1999). The interaction between the direct pathway and the indirect pathway (through hydroxyl radicals) is highly complex and not completely grasped by current scientific literature. Lee et al. (2012) find that ozone forms hydroxyl radicals in the presence of natural organic matter (NOM). Given the high concentrations of NOM in wastewater treatment, the hydroxyl radical pathway would be most prevalent in wastewater treatment (Lee et al., 2012). Rosal et al. (2010) also find the hydroxyl radical reaction to be the major pathway for OMP oxidation. The hydroxyl oxidation pathway dominates with the addition of hydrogen peroxide or the exposure to UV during treatment (EPA, 1999).

Oxygen demand of wastewater is determined by dissolved organic carbon (DOC) and nitrite that is left after conventional treatment (Margot et al., 2013). The required dose to oxidize organic micro-pollutants depends on the oxidative demand of water. For this reason, the ozone dose is often mentioned as gram ozone per gram dissolved organic carbon ($gO_3/gDOC$). Higher organic carbon concentration of wastewater can have adverse effects such as higher ozone demand, interference between oxidation of bulk organic matter and target compounds (Lee et al., 2012). In well-functioning wastewater treatment plants, nitrite concentrations are expected to be low (<0.1 mg/l), allowing oxygen consumption by nitrite to be neglected (Antoniou et al., 2013). In case nitrite concentrations *are* significant, the ozone dosage has to be normalized by the weighted sum of DOC and nitrite concentrations ($3.4\ [N\text{-}NO_2] + 0.38\ [DOC]$) (Margot et al., 2013).

Reaction of ozone or hydroxyls does not fully mineralize organics (converting them into inorganic substances such as H_20 and CO_2) or physically removes organics but rather produces smaller organic compounds as product (Lee et al., 2012). These metabolites are typically more polar and biodegradable than their parent compounds (Lee et al., 2012). Biodegradable oxidation products can be (partially) removed during biological post-filtration (Margot et al, 2013). It remains largely unpredictable what oxidation products will be transformed during ozonation, but in general they are expected to have a lower toxic activity than their parent compounds (Hollender et al., 2009; Larcher et al., 2012). However, higher toxicity of the metabolites has also been reported (Larcher et al., 2012; Rosal et al., 2009). Stalter et al. (2010a; 2010b) found that fish toxicity can be increased during ozonation compared to non-ozonated wastewater. The increase in toxicity is probably due to the formation of labile oxidative by-products such as toxic aldehydes and metabolites (Stalter et al., 2010a; 2010b; Margot et al., 2013).

During ozonation the ozone also reacts with non-OMP COD such as natural organic matter (NOM) and humic acids. The most significant risk to the effluent water quality is the transformation of bromide into the carcinogenic bromate (Hollender et al., 2009). Wastewaters with high bromide concentrations are particularly susceptible to bromate formation. A complicating factor is that research of Margot et al. (2013) finds that bromate concentration was not reduced during biofiltration after ozonation as opposed to other undesired transformation products such as nitrosamines (Hollender et al., 2009).

Ozone can be highly effective in breaking up OMPs into smaller biodegradable compounds but the effectiveness can be influenced by a variety of factors. Sorption of OMPs to colloid particles (1 nm to 1 microm) can protect it against the reaction with ozone (Margot et al., 2013). Furthermore, variations in pH give variations in reactivity and hence in removal rates of some substances (Margot et al, 2013).

Recent scientific articles call for additional research to ozonation in wastewater to give insight into the effects on different water characteristics (Lee et al., 2012), potentially increasing toxicity (Stalter et al., 2010a; 2010b) and especially to bromate formation (Margot et al., 2013).

Process conditions

Ozone dosage and ozone contact time are the most important process conditions during the operation of an ozone installation (Lee and von Gunten, 2016). A higher ozone dosage increases the removal of OMPs but does so at higher energy requirements and can also increase concentrations of toxic by-products in the effluent. Determining the ozone dosage will have to be the optimum between effective removal and low side effects. Chapter 6 will elaborate on the ozone dosage used in literature and attempts to find the optimal ozone dosage of HH Delfland.

The ozone contact time will be the other important process condition. When ozone is injected into the wastewater it reacts with organic compounds present. Lee and von Gunten (2016) find two phases of ozone reaction kinetics. The first is a rapid consumption of added ozone within a few seconds to a minute, referred to as instantaneous or spontaneous ozone demand. The second phase is a relatively slower ozone decrease during the remaining reaction time. The first phase is attributed to the reaction of ozone with reactive moieties in DOC such as phenols, neutral amines or olefins. Ozone is usually completely consumed in 5-20 minutes (Lee and von Gunten, 2016). Hollender et al. (2009) find that a significantly reduced contact time (~4 minutes instead of ~10 minutes) does not lead to a different removal efficiency by ozonation. This indicates that in the latter research, most of the ozone has reacted within four minutes of contact time.

During the operation of an ozonation installation, temperature may vary over the seasons. Ozone becomes less soluble and less stable in water at higher temperatures. However, the chemical oxidation rates of OMPs remain relatively stable under temperature change (EPA, 1999).

As explained in this section, ozonation requires a biologically active post-filtration step to remove the biodegradable oxidation products (Hollender et al., 2009). The next section will elaborate on this treatment step.

4.3 Biologically active filtration

Initially, HH Delfland proposed a treatment scheme with two filtration steps, one before ozonation and one after. The first (sand) filtration step would be designed for additional nutrient removal while the second step should biologically degrade transformation products from the ozonation. However, HH Delfland has decided to test whether both processes (nutrient removal and degradation of transformation products) can be achieved in one filtration step, after ozonation. In such a configuration, both nutrient and transformation product removal should take place in one biofiltration step. This section will discuss both processes, with a focus on the degradation of transformation products.

Nutrient removal

Conventional biological treatment as described in section 4.1 is primarily focused on COD and BOD removal. For discharges on vulnerable water bodies nutrient removal is also required to prevent eutrophication of water bodies. In general, nitrogen (N) and phosphorus (P) are the most important nutrients present in wastewater. Nitrogen removal can be achieved by a combination of nitrification and denitrification processes during conventional activated sludge treatment. The challenge for nitrogen removal in a filter *after* ozonation, is the high oxygen concentration of water in the filter. Oxygen concentrations measured by HH Delfland are even above the saturation concentration of oxygen in water (~10 mg/l). Denitrification requires anoxic conditions and hence cannot take place during filtration. To solve this, methanol is added to the filter. Bacteria convert methanol and oxygen into biomass, which lowers the oxygen level to concentrations at which denitrification can take place. In the operation, the amount of methanol is dosed that will remove both oxygen and NO_x-N. The equation below shows that the required dosage of methanol depends on the flow, NO_x-N and oxygen concentration.

$$MeOH\ (g/h) = \mathrm{Q} * (3 * C_{NOx-N} + 1 * C_{O2})$$

In which:

Q = Flow ($\mathrm{m^3/hour}$)
C_{NOx-N} = Concentration $\mathrm{NO_x}$-N (mg/l).
C_{O2} = Oxygen concentration (mg/l).
3 = Dosing rate MeOH/$\mathrm{NO_x}$-N (gMeOH/g$\mathrm{NO_x}$-N).
1 = Oxygen correction (gMeOH/g$\mathrm{O_2}$).

Removal of nitrogen in a post-ozonation filter is quite a challenge and a relatively unexplored area of scientific research. Although it is an interesting topic that is an important part of wastewater treatment, the focus of this research remains on removing OMPs with ozonation. Thus, nitrogen removal will not be further elaborated on.

Phosphorus can be removed by chemical precipitation (by e.g. dosing iron salts) and/or biological phosphorus removal. During this sand filtration step no removal of OMPs (<20%) is expected, except for trimethoprim (80-90%) and gemfibrozil (50-80%) (Nakada et al, 2007). Since this report focuses on OMP removal it will not further elaborated on tertiary treatment by sand filtration.

Degradation of ozonation transformation products

Biofiltration is recommended for treatment of ozonation effluent to minimize the presence of unknown oxidation products (Lee et al., 2012). Without ozonation, many OMPs are hardly biodegradable and hence biofiltration will not remove these compounds. After ozonation, OMPs will have been broken down to more biodegradable compounds, which allows removal of these transformation products during biofiltration. Biofiltration is not expected to achieve major OMP removal. In research of Lee et al. (2012) (ozonation + biofiltration with anthracite filter medium), the biofilter does not provide additional OMP removal. The value of the filter is in removing oxidation products. As explained in the section on OMP analysis, oxidation products can contribute to or even increase toxicity of the effluent and should hence be removed before effluent is discharged to surface waters. This section will first discuss the general removal mechanisms of transformation products in biofiltration, before two options for biofiltration media (activated carbon and sand) will be discussed in more detail.

The idea of biofilters is that bacteria attach to the filter medium to develop a biofilm. These bacteria are responsible for biodegradation of compounds in the feed water (Rattier et al., 2014). For two reasons biomass is expected to grow well on a filter medium after ozonation. Firstly, transformation products of ozonation in the feed water are highly biodegradable providing sufficient substrate for bacteria to grow. BOD concentrations increase during ozonation due to the transformation of chemical compounds (COD) into biodegradable compounds (BOD). Secondly, the production of oxygen due to the reaction of different compounds with ozone, creates an excellent aerobic environment for biological growth on the filter media.

Organic compounds are biodegraded in biofilters by either direct catabolism or cometabolism (Rattier et al., 2014). In biodegradation by direct catabolism, compounds are catabolized by enzymes and used as carbon and energy sources for microorganisms in the biofilm (Rattier et al., 2014). If sufficient substrate (organic compounds) is available, the catabolic activity increases until one of the essential nutrients becomes limiting. Cometabolized compounds are biodegraded by nonspecific enzymes. These enzymes are generated during metabolism of organic compounds (Rieger et al., 2002). In this way the direct catabolism is important for cometabolism to occur. A suitable environment for biological activity is created by a sufficient level of DOC and nutrients in the feed water of the biofilter (Rattier et al., 2014).

All studies examined for this report find that the combination of ozonation and biofiltration decreases the non-specific toxicity and other specific toxic modes of action (among others Reungoat et al., 2010; Margot et al., 2013). This indicates that the mixture of transformation products after ozonation and biofiltration is less toxic than the mixture of their parent compounds.

Multiple filter mediums can be applicable for biofiltration. Activated carbon filtration and sand filtration are most common options, but anthracite could also be used (Lee et al., 2012). The next sections discuss the first two, most common filtration mediums.

4.3.1 Biologically active activated carbon filter

Activated carbon filtration is widely used in drinking water treatment (Margot et al., 2013). The use of activated carbon for advanced wastewater treatment is gaining attention and its performance is now studied widely (Rattier et al., 2014). Activated carbon can be used in a variety of applications and treatment sequences. This report focuses on biologically active post-ozonation filtration with granular activated carbon. Other applications such as powdered activated carbon addition to activated sludge tanks are outside the scope of this report as discussed in section 1.3 on research demarcation. This section discusses operation, configuration and process conditions of activated carbon filtration.

Activated carbon can be produced from medium volatile bituminous coal or lignite (Mulder et al., 2015). Subjecting steam and high temperatures (~1200 degrees C) 'activates' the carbon medium. Activated carbon has a large surface area (~500-1400 m^2/g) which allows adsorption to the medium (Cecen and Aktas, 2012).

When ozonated wastewater is fed to a clean bed activated carbon filter, three phases of operation can be observed (see Figure 11) (Simpson, 2008). In phase A, adsorption of OMPs and DOC to the fresh activated carbon is the dominant process. This phase is characterized by a high removal of organic matter (Reungoat et al., 2012). Over time the adsorption sites of the carbon will be either taken or blocked, leaving no possibilities for further adsorption (Cecen and Aktas, 2012). Removal efficiencies will drop and breakthrough of pollutants will occur (phase B). Meanwhile bacteria attached to the grains will start growing, feeding on the biodegradable matter in the feed water (Reungoat et al., 2012). In the final phase C the activated carbon reaches an equilibrium of substrate (e.g. biodegradable transformation products of the ozonation) consumption by the bacteria on the grains. This equilibrium removal is typically much lower than the removal observed in the first phase of adsorption (Reungoat et al., 2012). This final phase can last for years since carbon grains only need to be renewed due to attrition occurring during backwashing. When the removal efficiencies of the final phase are sufficient to reach desired effluent OMP concentrations and toxicity of residual contaminants, reactivation or renewal of activated carbon grains will hardly be necessary. When the adsorptive capacity of activated carbon *is* required, the grains need to be periodically reactivated.

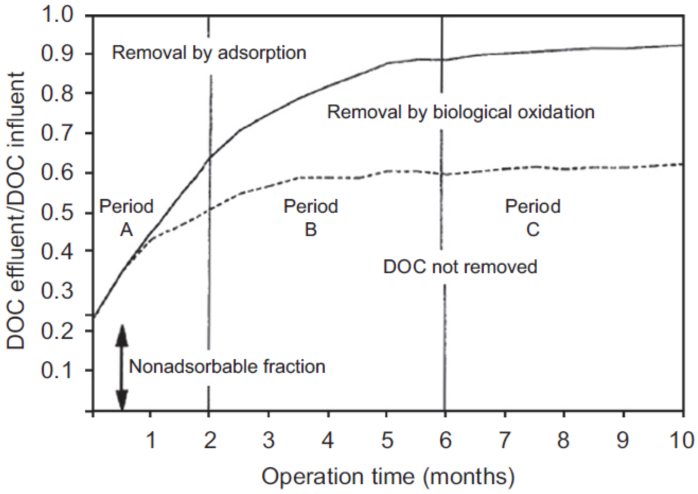


Figure 11 - Three phases of activated carbon filtration operation (Simpson, 2008)

Activated carbon is well known to be a good support medium for microbial growth (Xing, 2008). Biomass develops to higher levels on GAC because of the rougher surface characteristics than on anthracite and sand (Simpson, 2008). Disadvantages are the cost and effort to renew the activated carbon periodically. Besides that, the raw material of carbon, coal or lignite, is fossil material. Water authorities increasingly focus on a sustainable practice of wastewater treatment and might hence be reluctant to use this fossil material.

Configuration

Configuration of activated carbon treatment can either be a fixed bed or a continuous filter, of which the first is most widely used. In a fixed bed filter carbon grains remain in a tank while influent water in flowing downwards through the grains under the force of gravity (see Figure 12). Effluent water flows out from the bottom of the filter bed. To enhance biological degradation, pressurized air can be added to the incoming water. During backwashing the filter is temporarily out of operation, which is required to flush the grains to remove organic matter and to prevent blockage (Mulder et al., 2015). Backwash water is fed back to the wastewater treatment plant to be treated. During backwashing no water can be treated in the filters which requires either redundancy in design by extra filters or storage facilities to overcome backwashing time.

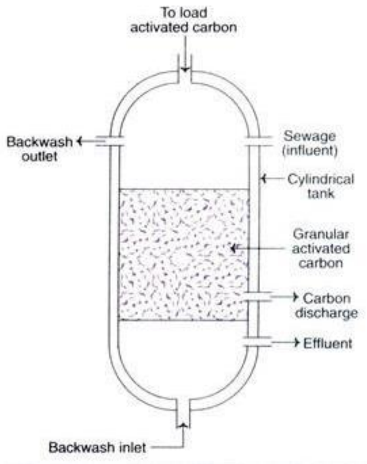


Figure 12 - Schematic representation of a fixed bed (activated carbon) filter (Kumar, 2017)

Continuous filters are up flow, moving bed filters. Water is flowing in from the top and led to the bottom of the activated carbon by a water distributor (see Figure 13). From here water is flowing up through the activated carbon grains. Effluent is flowing out over a weir on top of the tank. Continuous filters do not require temporarily downtime due to backwashing since carbon grains are continually flushed. An air pump is moving grains from the bottom of the filter bed upwards in the washing box. In the carbon washer the carbon grains are separated from the accumulated biomass. The 'clean' carbon grains fall back on top of the filter medium and the backwash water is fed back to the wastewater treatment plant for treatment. Density of the activated carbon grains is important in the upwards flowing continuous filters. When density is too low, grains can ascend and even wash out with higher filtration speeds.

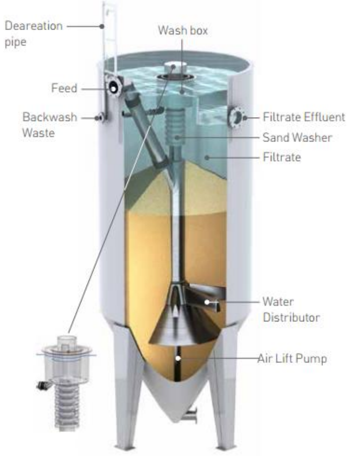


Figure 13 - Continuous (sand) filter (Nordic Waters, 2017)

Process conditions

Contact time, carbon grain renewal and type of carbon are the most important process conditions that can be altered to impact removal efficiency of OMPs and toxicity of residual contaminants. Longer contact time allows the bacteria attached to the grains to degrade more biodegradable compounds (Reungoat et al., 2012). The removal does not increase linearly with contact time. This is caused by difference in rapidly and slowly degrading compounds. With a short contact time the rapidly biodegradable compounds will be removed first and the remaining compounds will have lower biodegradation rates (Reungoat et al., 2012). The consideration whether to renew carbon grains will depend on the need for adsorption during filtration. When OMP concentration has to decrease to lower levels during this treatment step, the adsorptive mode of activated carbon is needed. This asks for carbon grains renewal when adsorption sites on the grains become limited. When activated carbon is only included to the treatment to degrade biodegradable oxidation products of ozonation, the third phase will be sufficient. Grain renewal will have to occur only rarely. Finally, the type of carbon is also an important aspect. For a continuous filter as described in this section, the carbon grains should be sufficiently hard to withstand the mechanical stress of the air lift pump. This pump lifts the carbon grains in the filter to wash the biomass from the grains. When the carbon grains are too soft, the air lift pump could crumble the grains.

4.3.2 Biologically active sand filter

Biologically active sand filtration is to a great extend similar to the above described activated carbon filtration. Configuration of either batch or continuous filters and the contact time as process condition apply in the same way to sand filtration. A major difference is the lack of adsorption to sand grains as opposed to activated carbon grains. This means that the first phase of activated carbon operation (adsorption) will not apply in sand filtration. Sand filtration will hence not (or hardly) contribute to OMP removal but has rather to be seen as a useful additional barrier for elimination of biodegradable compounds formed during ozonation (Hollender et al., 2009). As described before, ozonation is responsible for the majority of OMP removal and biologically active filtration might indeed only be required for removal of oxidation products.

The operation of sand filters starts with the phase B of Figure 11, which is the microbial growth of bacteria attached to the sand grains. The medium will need time to build up biomass before the biodegradable compound removal reaches stable levels. Hollender et al. (2009) finds that biologically active sand filtration removes undesired oxidation products such as NDMA while also improving suspended solids and phosphate removal.

5. Current pilot set-up

HH Delfland has decided to install a pilot at WWTP De Groote Lucht (DGL) to obtain knowledge on technological practices of ozonation and biofiltration and the costs associated with OMP and toxicity removal. A second goal for the pilot is to find design parameters for the desired full scale installation. As explained, HH Delfland has chosen for ozonation but remains interested in pilot experiments with other advanced treatment steps. It has not been decided yet what treatment method the desired full scale installation will consist of – it could for instance still be powdered activated carbon, dosed in the activated sludge system, as currently researched by the PACAS project. This chapter will discuss the treatment scheme of WWTP DGL, the pilot configuration and the OMP analysis.

Treatment scheme

As shortly explained in section 4.3, HH Delfland initially proposed a treatment scheme of 1) conventional biological treatment, 2) sand filtration (for nutrient removal), 3) ozonation and 4) biofiltration with activated carbon or sand as filter medium (for biodegradation of ozone transformation products). With two different filter media in parallel, the performance of both could have been compared. However, during preparation of the long run experiments, it was observed that the activated carbon grains were flushed out of the continuous *up-flow* filter. This is due to the lower density of activated carbon particles, in comparison with sand. The filtration speed could not be sufficiently reduced to prevent operational problems with the filter. Higher flow velocities require a larger surface area of the filter. A prerequisite for the full-scale installation is that only the existing filters can be used. The construction of new filters would require too much investment costs. During preparation of the long run test it was concluded that the minimum required up-flow velocity would already be too high for the activated carbon filter. Thus, the activated carbon filter has been left out of the remainder of the pilot research.

The second adjustment to the initial treatment scheme is to combine nutrient removal and biodegradation of oxidation products in one filter passage. Instead of pre- and post-ozone filtration, this scheme only required post-ozone filtration. The advantage of this scheme is that only one filtration step is required.

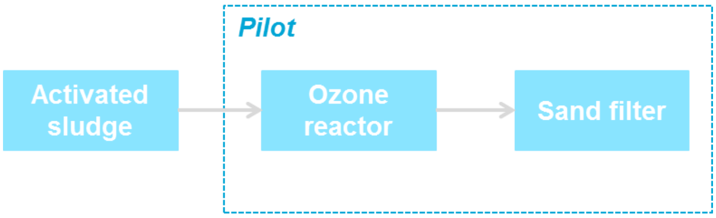


Figure 14 - Treatment scheme of WWTP DGL

Configuration

The treatment scheme of the pilot is 1) conventional biological treatment, 2) ozonation and 3) (bio)filtration (see Figure 14). The first step of treatment at WWTP DGL is the conventional step of activated sludge (CAS) treatment. The configuration of the CAS treatment is according to the University of Cape Town (UCT) Process, which includes biological nitrogen and phosphorous removal, as well as primary and secondary sedimentation.

Ozonation is the second step. For the transfer of ozone, a venturi injector is used (see section 4.3.1). Average Dissolved Organic Carbon (DOC) concentration of the effluent of conventional treatment is 10.5 mg/l (HH Delfland, 2016c). Due to variations in the DOC concentration the ozone dosage will be regulated real time to ensure a constant O_3/DOC ratio. The DOC is measured every minute which smoothens the regulation to some extent.

The sand filter will be a continuous filter (see section 4.4.1) and the contact time (determined by filtration speed) will be around 14 minutes. The pilot is fed with a constant flow of 630 m^3/day. The full-scale installation will be designed to treat 30.000 m^3/day which is half of the normal dry weather flow of WWTP DGL (~60.000 m^3/day). The wet weather flow can be up to ~280.000 m^3/day. The conventionally treated water that is not subject to advanced treatment will be discharged into the Nieuwe Waterweg, as is currently done with all effluent.

OMP analysis

The main purpose of the ozonation and biofiltration is the removal of OMPs and toxicity of oxidation products. Disinfection could also take place during the advanced treatment. This is however not the main purpose of ozonation, since the wetlands (´Water harmonica´) are expected to achieve sufficient levels of disinfection (STOWA, 2012). The aim of the pilot is to produce effluent water that can be discharged on surface water, according to the 'Besluit kwaliteitseisen en monitoring water' (2009) and 'Regeling monitoring Kaderrichtlijn Water' (2010) that are the national regulations to implement the Water Framework Directive as amended by Directive 2013/39/EU. Since pharmaceuticals and hormones are not part of the priority substances lists of the Directive and Regeling, HH Delfland has composed a selection of these substances that are apparent in current wastewater effluent of WWTP DGL. Table 4 shows the ten target substances that HH Delfland will analyze in the pilot experiments. These substances are selected based on their constant presence and high concentrations in WWTP DGL effluent and the different categories of OMPs that they represent (i.e. insecticides, pharmaceuticals, contrast media and corrosion inhibitor). The costs of laboratory analyses have also played a role in choosing these ten target substances. Laboratory analysis uses packages of substances which makes that data on these ten substances come with data of many other substances. This research will make use of the data on these additional substances.

Table 4 - List of target substances of HH Delfland pilot

Target substance	Type of substance	Concentration range in DGL effluent (µg/l)
DEET	Insecticide	0.09 - 0.18
Imidacloprid	Insecticide	0.07 - 0.20
Diclofenac	Pharmaceutical	0.40 - 0.90
Gabapentine	Pharmaceutical	1.50 - 2.80
Irbesartan	Pharmaceutical	0.40 - 2.10
Metformin	Pharmaceutical	0.44 - 1.60
Oxazepam	Pharmaceutical	0.17 - 0.50
Sotalol	Pharmaceutical	0.60 - 2.00
Iopromide	Contrast media	0.06 - 0.39
Benzotriazole	Corrosion inhibitor	2.40 - 2.80

HH Delfland has identified two testing phases during the pilot project. During the first phase the optimal process conditions of ozonation and biofiltration will be determined (see Chapter 6). These ozone dosage tests have taken place from Monday – Wednesday August 1-3 in summer 2016. The ozone production is progressively increased to apply a higher ozone dosage (from 133 g/h to 431 g/h). The third and fourth column show the start and end time of the experiment. During the two hours that an experiment is running, every 10 seconds a small water sample (50 ml) is taken from the in- and outflow of the ozone installation. These samples are collected in two separate medium-density polyethylene (MDPE) tanks, to create a time proportional sample. At the end of one experiment, 36 liters of water has been taken from the pilot. From this storage tank, samples were brought to the laboratory. In the chemical analysis, one sample is taken to measure a compound. It is unknown how often one sample is analyzed. Either one measurement is done, or the average of multiple measurements (e.g. triplicates) is reported.

Table 5 - Information on ozone dosage tests

Date	Day	Start time	End time	Flow [m3/h]	Ozone production [g/h]	Ozone dose [gO3/gDOC]	Flow conventional treatment [m3/h]
8-1-2016	Monday	9:51	11:51	26.2	133	0.48	2,361
8-1-2016	Monday	13:06	15:06	26.2	201	0.74	2,063
8-2-2016	Tuesday	10:26	12:26	26.2	264	1.00	2,965
8-2-2016	Wednesday	14:11	16:11	26.2	320	1.18	4,711
8-3-2016	Wednesday	11:22	13:22	26.2	431	1.49	5,088

In the second phase the removal efficiencies with the determined process conditions are analyzed (see Chapter 7). The first measurement is taken in March 2017 and the rest of the measurements in July-August 2017 (see Table 6). Section 7.1 reflects on the implications of these differences.

Table 6 - Information on long run test

Measurement	#1	#2	#3	#4	#5	#6	#7
Date	3-21-2017	7-1-2017	7-14-2017	7-31-2017	8-8-2017	8-14-2017	8-25-2017
Day	Tuesday	Saturday	Friday	Monday	Tuesday	Monday	Friday

Figure 15 shows the points of measurement and analysis during the second phase of testing. Macro parameters, target substances, bioassays, E.coli and bromate measurements are taken after every treatment step (starting after the CAS treatment). Besides these measurements, focused on the performance of the pilot, HH Delfland is planning to take three measurement campaigns of influent and effluent OMP concentrations during winter, spring and summer to analyze OMP removal during CAS treatment.

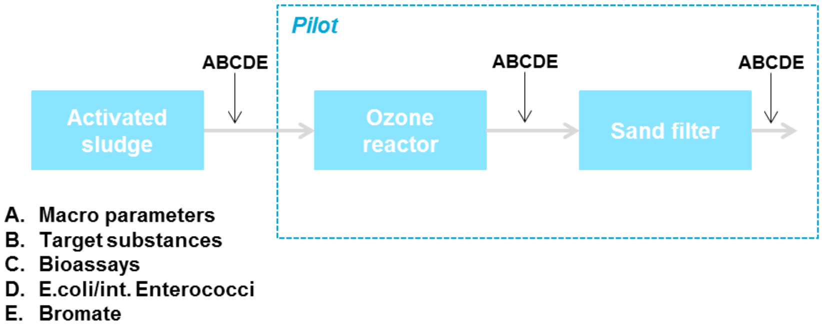


Figure 15 - Points of measuring and analysis during pilot project

In the next chapters, data is analyzed on removal of OMPs and toxicity of residual contaminants from HH Delfland pilot experiments and experiments from scientific literature. The chapters follow the two research phases of HH Delfland, starting with ozone dosing tests to determine the optimal ozone dosage (Chapter 6). In this chapter, it is also discussed what is meant with the term ‘optimal’ ozone dosage. The second phase discusses OMP removal efficiencies during the long run test, with the chosen ozone dosage (Chapter 7).

6. Finding and comparing the optimal ozone dosage

This chapter covers the first test phase, in which the optimal process conditions of the ozonation step are determined. The applied ozone dosage is the main process condition to be discussed. This chapter will answer the second sub question and partially the fifth sub question of this research:

- *What is the optimal ozone dosage found during pilot conditions and what does comparison with similar studies in research tell us? Could ozone dosage have been based on literature?*
- *Is bromate formed during ozonation? If yes, will it be removed during biological sand filtration?*

The term 'optimal ozone dosage' is determined as a dosage at which OMPs are effectively removed, while operation (energy) costs remain within budget and the formation of bromate remains within acceptable range (see section 6.1). In case one of these conditions is not satisfied, the ozone dosage has to be adjusted. In this research phase only OMP removal by ozonation is measured – and not the removal of toxicity of residual contaminants during biofiltration. The implication is that the second sub question only discusses bromate as by-product.

This chapter will first explain the importance of determining the optimal ozone dosage (section 6.1). The remainder of the chapter consists of two parts. Firstly, section 6.2 presents the results of the ozone dosage test as performed by HH Delfland. The final part of section 6.2 provides a choice on the optimal ozone dosage for the full-scale installation (section 6.2.4). Secondly, section 6.3 compares the results of HH Delfland with literature, resulting in an evaluation of the comparison in section 6.4.

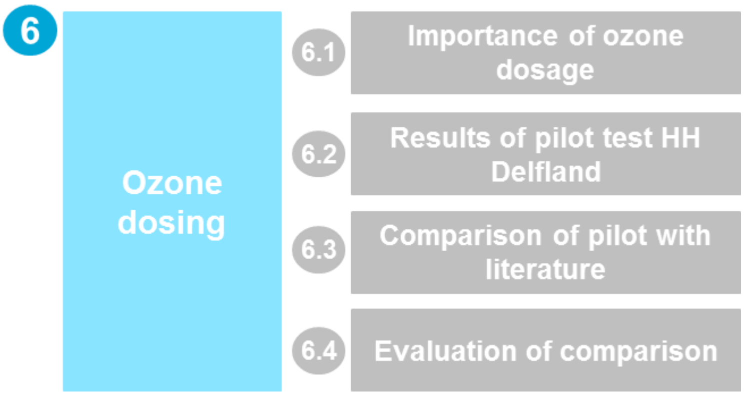


Figure 16 - Flow chart of set-up Chapter 6

6.1 Importance of ozone dosage

The ozone dosage is an important process condition for the performance of the advanced treatment installations. Organic micro-pollutants are generally better removed with higher ozone dosages (Margot et al., 2013). To test this, Margot et al. (2013) have applied an ozone dosage of 2.6 gO_3/gDOC (17.6 mg O_3/l), which is almost two times higher than the highest dosage applied by HH Delfland (1.31 gO_3/gDOC). Recalcitrant OMPs were much better removed at this high ozone dosage. A higher ozone concentrations results in more ozone and hydroxyl radicals ($^{\cdot}OH$) to oxidize OMPs to smaller and more biodegradable compounds. This indicates that it is desirable to apply a high ozone dosage to effectively removal most of the OMPs.

Two constraints however prevent the possibility of applying a very high ozone dosage to remove OMPs to high degree. The first constraint for unlimited ozone application is the formation of *toxic by-products.* Bromate is one of the main by-products of ozonation. In this research only bromate will be analyzed as toxic by-product. Toxicity of other by-products is planned to be analyzed in the long run test of the second phase of the pilot. Unfortunately, the results from the bioassays have not been obtained in time for this research. As explained in section 3.2, bioassays will be used to analyze toxicity of the ozonation effluent. The risk of bromate formation is especially apparent in the presence of high incoming bromide concentrations (Margot et al., 2013; Hollender et al., 2009). Section 6.2.3 will discuss the bromate formation as observed during the ozone dosage experiments in more detail. The second constraint is the fact that ozone production is an *energy intensive process* so costs increase significantly with higher ozone dosages (Antoniou et al., 2013). A general estimation of the costs of ozone production are 2 euros per kilogram ozone (HH Delfland, 2016c). Costs of operation (and investment) should be within range of what is financially acceptable.

The flow diagram of Figure 17 shows that the choice for the applied ozone dosage is a trade-off between OMP removal, energy costs and toxic by-product formation. As mentioned, the performance of biofilters in removing toxicity is not measured in this first research phase. Hence the flow diagram cannot be fully passed through. Section 6.2.4 on the choice of the optimal ozone dosage will further evaluate the determination of the optimal ozone dosage without being able to fully passed through the flow diagram.

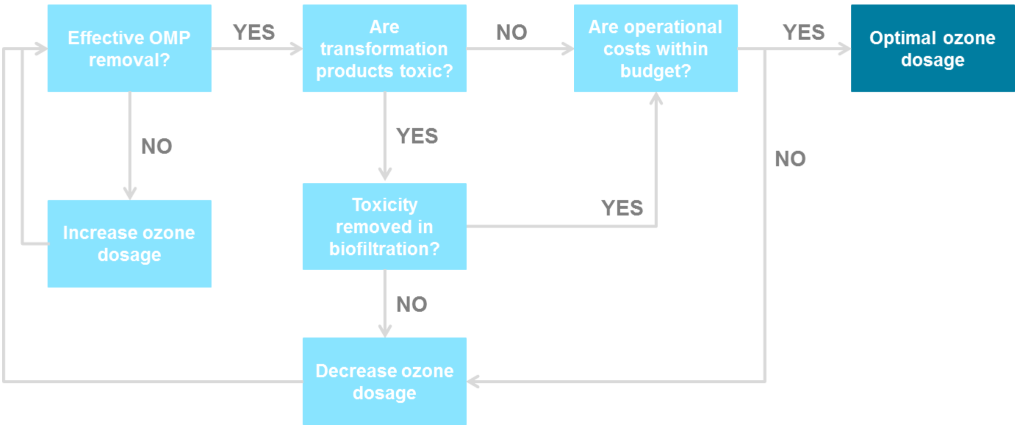


Figure 17 - Flow diagram for determining the optimal ozone dosage

6.2 Ozone dosage tests in pilot HH Delfland

This section will discuss the ozone dosage tests performed at the pilot of HH Delfland. The results on macro parameters (section 6.2.1) and OMP removal (section 6.2.2) are discussed. The latter section contains information on the method, the average OMP removal and individual OMP removal. Section 6.2.3 discusses bromate formation before the decision on the optimal ozone dosage is made in section 6.2.4.

In summer 2016, HH Delfland has conducted experiments with the pilot at wastewater treatment plant De Groote Lucht in Vlaardingen on removal of OMPs at varying ozone dosages. See Table 7 for key figures of the ozone dosage tests. Five different specific ozone dosages have been applied to the ozone feed water (0.44, 0.68, 0.97, 1.02 and 1.31 gO_3/gDOC) with an average DOC concentration of 10.5 mg/l. The tests have been conducted in August 2016 with an average temperature of the pilot influent of 21.5 °C. The flow of ozonated water was kept constant at 26.2 m^3/h, but flow through the conventional treatment differed in the experiments, due to dry or wet weather conditions. Analysis however showed that DOC concentrations at the start of the ozonation did not vary. This means that there was no dilution of the wastewater (HH Delfland, 2016c). This is in contrast with research done by Hollender et al. (2009). This research found ‘significantly lower influent concentrations for most compounds due to the dilution with rain water’ at a twofold increased flow compared to the dry weather flow (Hollender et al., 2009). An explanation of the absence of dilution could be the high recirculation of wastewater within the treatment. The recirculation smoothens the peaks and valleys of the DOC concentration. This could well be the case for the light rain observed during the ozone dosage experiments. For heavy rainfall it is expected that dilution *will* occur, despite the high recirculation of wastewater.

Table 7 - Key figure ozone dosage tests HHD pilot

Key figures HHD pilot			
Water analyzed	WWTP DGL effluent	**Contact time**	14 min
Chemical analysis	129 OMPs	**Ozone generated**	From pure oxygen (corona generator)
Biological analysis	YES	**Ozone dosage range**	4,6-13,8 mg/l
OMPs present	Naturally occurring	**DOC**	10,5 mg/l
OMP concentrations	0 - 2,5 µg/l	**O3/DOC range**	0,44-1,31 O3/DOC (corrected for nitrite)
Set-up	Pilot scale	**NO2-N**	0,07-0,57 mg/l
Ozone contact	Continuous-flow	**Temperature**	21,5 °C
Flow analyzed	26 m^3/h	**Type of ozone injector**	Venturi injector (in main stream)

6.2.1 Macro parameters

Both macro parameters and micro parameters (OMPs) have been analyzed in this experiment. Concentrations of macro parameters in the ozonation feed water and ozonation effluent water are plotted in Figure 18. The feed water of the ozonation step is coming from the conventional wastewater treatment and the ozonation effluent water is going towards the biofilters (see Figure 14 in Chapter 5 for the treatment scheme). As discussed above, the DOC concentration (yellow line) remained at the same level, even though the tests with high ozone dosage have been performed in wet weather operating conditions. The effluent DOC concentration is equal to the feed water since ozonation does not mineralize organics but transforms these into (more biodegradable) compounds. Actual removal of DOC is only expected during the biofiltration step (Margot et al., 2013).

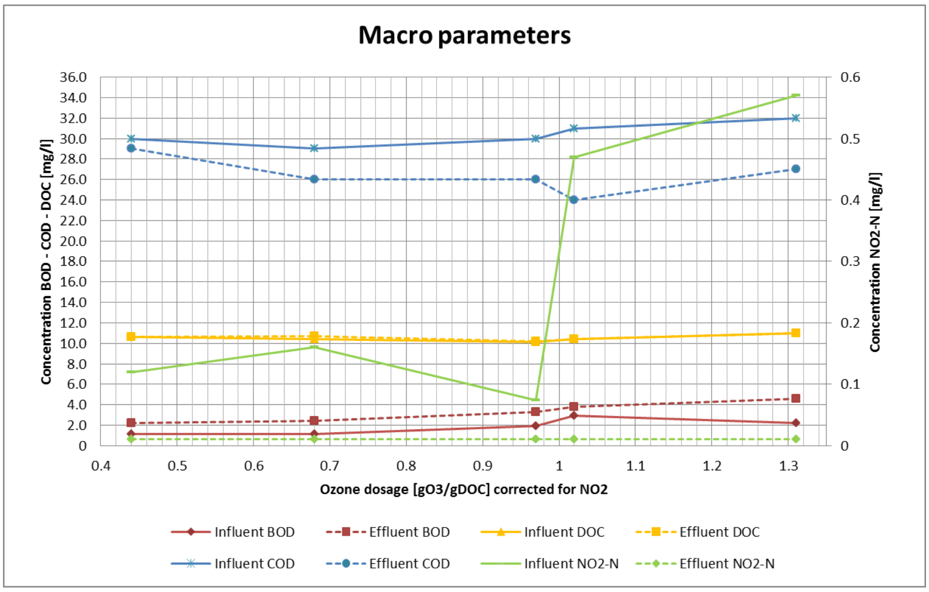


Figure 18 – Ozonation feed water and ozonation effluent concentrations of macro parameters HH Delfland

COD concentrations of the effluent are lower at higher ozone dosages, which can be explained by the fact that more chemical substances are oxidized at higher ozone dosages. These compounds are transformed into biodegradable products, which explains the higher levels of BOD in the effluent than in the feed water. The effect of COD conversion into BOD is stronger with higher ozone dosages. Influent concentrations of nitrite are higher in the experiments with wet weather conditions, potentially caused by incomplete denitrification due to shorter residence times in the conventional treatment. Nitrite reacts rapidly with ozone in a 1 : 1 molar stoichiometry, without generating ·OH radicals (Lee and von Gunten, 2016). The reaction of nitrite and ozone is as follows:

$$NO_2^- + O_3 \rightarrow NO_3^- + O_2$$

The reaction has a high second-order rate constant with ozone (k_{O3}): $3.7 * 10^5\ M^{-1}s^{-1}$. Nitrite is a critical factor in ozone application since it contributes to the ozone demand with 3.4 mgO$_3$/mgN-NO$_2$ (Lee and von Gunten, 2016; Margot et al., 2013). A higher ozone demand of feed water affects the ability of ozone to react with OMPs. HH Delfland currently does not regulate ozone dosage for presence of nitrite as is done for DOC concentration. With up to 13% of ozone required to oxidize nitrite to nitrate this might distort the results on OMP removal (HH Delfland, 2016c). Experiments with ozonation done by Margot et al. (2013) do take the nitrite concentration into account. In this experiment the researchers regulate the ozone dosage to maintain a constant residual ozone concentration near the end of the reactor. Ozone dosage is adjusted to both DOC and NO$_2$ concentrations of the ozonation feed water (Margot et al., 2013). This report will use the ozone dosages corrected for nitrite. Values with the unit gO$_3$/gDOC can be read as “gO$_3$/gDOC, corrected for nitrite”, unless mentioned differently. This means that the ozone that is used to oxidize nitrite is not included in the dosage as mentioned (because this part of the ozone does not react with DOC or OMPs, only with nitrite).

Ammonium (NH$_4$) can also be oxidized by ozone during treatment. The ammonium concentration in the ozone feed water varies with the flow through the conventional treatment plant. In the ‘first flush’ of a rainfall event, the ammonium concentration is usually high. With continuous rainfall, wastewater is diluted and ammonium concentrations usually decrease. It is expected that ammonium does not react very fast with ozone. Scientific literature does not mention the impact of ammonium on the removal of OMPs by ozone. Further research is required to find the role of ammonium during ozone treatment.

6.2.2 OMP removal

With the macro parameters analyzed, this section will discuss the micro parameters measured during the ozone dosage tests. The micro parameters are the organic micro pollutants that this research is focusing on. The method of OMP analysis is presented before the average and individual OMP removal is discussed.

Reporting method

HH Delfland has analyzed ten target substances as formulated in Chapter 5. These target substances occur constantly in (relatively) high concentrations in the effluent of the conventional wastewater treatment plant DGL. HH Delfland uses the Volkert-Bakker method in analyzing pilot data to uniform its analysis with the STOWA (STOWA, 2010). According to this method, concentrations of substances measured below the reporting limit are determined by the following formula:

$$Concentration\ [\mu g l^{-1}] = (100\% - x) * reporting\ limit\ [\mu g l^{-1}]$$

In which:

$$x = \%\ of\ measurements\ below\ reporting\ limit$$

For example, if 60% of measurements are below the reporting limit, then for all measurements below the reporting limit a value of 40% (=100%-60%) of the reporting limit is used (STOWA, 2010). In the ozone dosing experiments of HH Delfland every measurement is treated as a separate series. This means that every measurement is the only one in its series. If one measurement falls below the reporting limit, it means that 100% of the measurements of that series are below the reporting limit (because the series consisted of only one measurement). The formula can then be filled in as follows:

$$Concentration\ [\mu g l^{-1}] = (100\% - x) * reporting\ limit\ [\mu g l^{-1}]$$

With:

$$x = 100\%$$

Gives a concentration of:

$$Concentration\ [\mu g l^{-1}] = (100\% - 100\%) * reporting\ limit\ [\mu g l^{-1}]$$

$$Concentration\ [\mu g l^{-1}] = 0 * reporting\ limit\ [\mu g l^{-1}]$$

$$Concentration\ [\mu g l^{-1}] = 0$$

For the experiment of HH Delfland this means that when a measurement falls below the reporting limit, automatically a value of 0 µg/l is assumed.

In this research, the analysis for the optimal ozone dosage is extended to all 129 OMPs included in the measurement packages of laboratory analysis. However, of the 129 substances only 28 are suitable for analysis: these substances have been detected in concentrations above the reporting limit in the ozonation feed water of (almost) all experiments with different ozone dosages. See Figure 19 for a categorization of the OMPs. Whereas it is unfortunate for this research, it is positive news for HH Delfland that so many OMPs are not detected in significant concentrations in both the ozonation feed water and effluent. Less effort in treatment will be required when many OMPs are not present in wastewater.

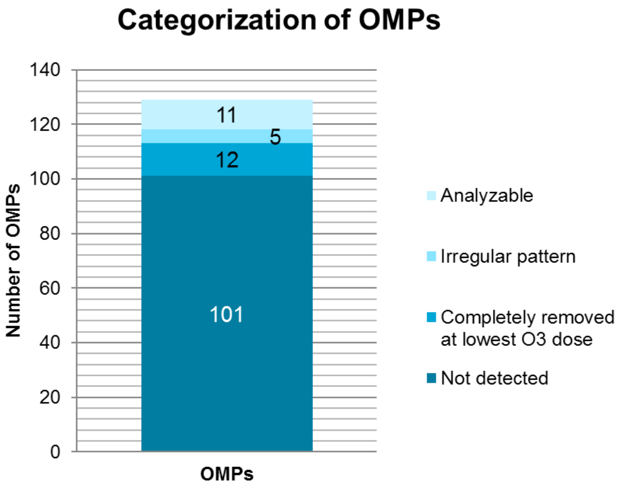


Figure 19 - Categorization of OMPs in HH Delfland ozone dosage experiment

Figure 20 shows the absolute removal (blue diamonds) and percentage removal (red squares) of the 28 analyzable OMPs. The average percentage removal is calculated by:

$$\frac{\sum influent\ concentrations - \sum effluent\ concentrations}{\sum influent\ concentrations} * 100$$

The equation above shows that the average percentage removal is calculated by summing up the ozonation feed water OMP concentrations and summing up the effluent OMP concentrations. This method is regarded more accurate than calculating the average from *individual removal efficiencies*. The latter method would mean that an OMP reduction concentration from 100 ng/l to 10 ng/l (90% removal) would count as much as an OMP reduction from 10 ng/l to 5 ng/l (50% removal). This would give an average removal of 70% ((90%+50%)/2 = 70%). In this way, the reduction from 10 ng/l to 5 ng/l has gotten too much weight in the calculation of the average. In this research it is regarded as more accurate to sum all the influent and all the effluent concentrations and calculate the average removal from there. This would give an OMP reduction from 110 ng/l to 15 ng/l (86.4% removal). However, there are also arguments against this method of summing up the OMP concentrations to calculate the average removal. The main argument would be that the effect of a certain concentration of one OMP on the aquatic system does not have the same effect as same concentration of another OMP. When we desire to include the effect calculation, we will have to turn to the use of bioassays (as explained in section 3.2).

Average OMP removal

Figure 20 shows that both absolute and percentage removal increase with higher ozone dosages. Percentage removal (right axis) follows a curve which flattens around 92% removal. The easily degradable OMPs will react first with ozone, which shows a steep increase in removal efficiency at low ozone concentrations (~0.4-0.8 $gO_3/gDOC$). The removal efficiency curve starts to flatten at ~0.8-1.0 $gO_3/gDOC$ at which harder degradable OMPs have their turn in the water matrix to react with ozone. Apparently 8% of the OMPs are recalcitrant towards ozone, even with high ozone concentrations (>1.0 $gO_3/gDOC$). Absolute removal follows a less smooth curve with a peak at an ozone dosage of 1.02 g $gO_3/gDOC$. Influent OMP concentration was higher during tests with ozone dosages of 0.97 and 1.02 g $gO_3/gDOC$ (13.61 and 13.92 µg/l) compared to influent OMP concentration during tests with an ozone dosage of 1.31 $gO_3/gDOC$ (11.41 µg/l). The absolute removal of ~13 µg/l as observed at the experiments with an ozone dosage of 0.97 and 1.02 $gO_3/gDOC$ could simply not be achieved at the experiment with an ozone dosage of 1.31 $gO_3/gDOC$. The reason is that the ozonation feed water concentration is only 11.41 µg/l at the latter experiment. The results do indicate that absolute OMP removal is higher with higher influent OMP concentrations.

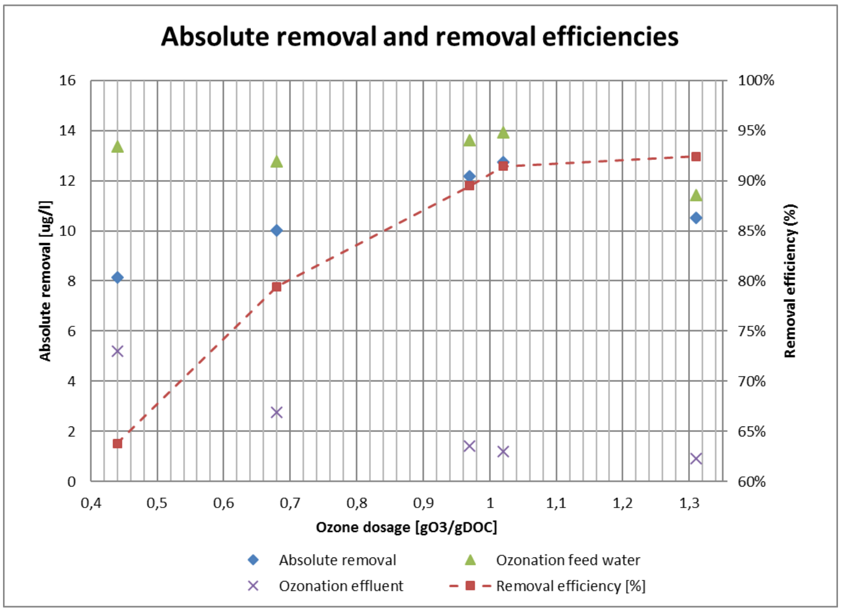


Figure 20 - Absolute and percentage removal of 28 OMPs

Individual OMP removal

With a closer analysis of the 28 analyzable compounds, it can be observed that 12 OMPs are completely (100%) removed at even the lowest ozone dosage of 0.44 g $gO_3/gDOC$. These compounds are apparently easily degraded by ozonation. Left are 16 compounds that show varying removal efficiencies at different ozone dosages. Of these 16 compounds, eight are included in the analyses of HH Delfland while the other eight are currently unanalyzed.

In analyzing the 16 OMPs, we find that five compounds show an irregular removal pattern (i.e. amidotrizoic acid, azoxystrobin, diethyltoluamide, flonicamid and joxitalamine acid, see Figure 21). If we zoom in on amidotrizoic acid (red line in Figure 21), we observe a removal efficiency ranging from 33% at 0.44 $gO_3/gDOC$ to 0% at a higher ozone dosage of 0.68 $gO_3/gDOC$. The next data point (0.97 $gO_3/gDOC$) shows 100% removal while the last two data points are missing. Other OMPs show a similar aberrant though different pattern which makes it hard to draw any conclusions from this data. In the ozone dosage tests of HH Delfland only one measurement per ozone dosage per OMP has been done, so no distribution of measurements for an OMP can be used during analysis. The irregular pattern of removal of these OMPs indicate the complexity of the reactions occurring in ozonation. The difference of the water matrix at different experiments could well have influenced the removal of these OMPs. Also, analysis inaccuracy can be high in the low concentration ranges in which OMPs are present. At the moment, it cannot be explained why these OMPs show this irregular removal pattern.

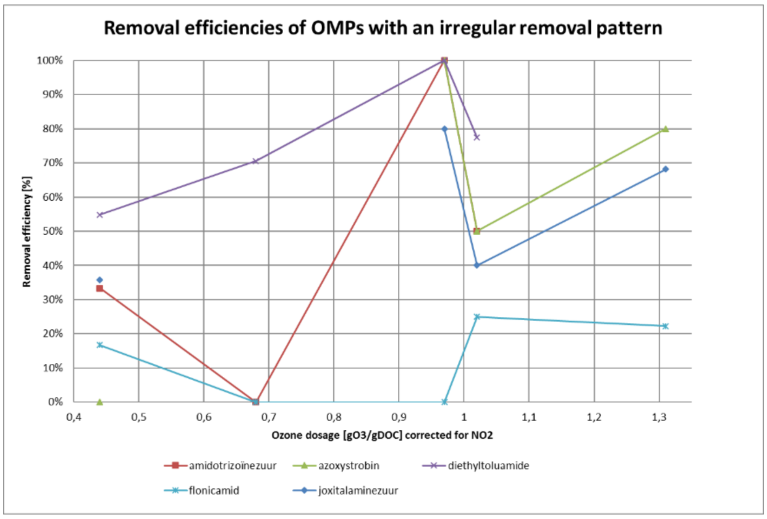


Figure 21 - Removal efficiencies of five OMPs with an irregular removal pattern

When the five OMPs from Figure 21 are excluded, eleven OMPs are left to analyze. Figure 22 shows generally higher removal efficiency at higher ozone dosages. Some of the OMPs are easily degraded by ozone, for instance sulfamethoxazole and valsartan. ~67% of these two OMPs is removed with the lowest ozone dosage tested (0.44 $gO_3/gDOC$) and for ozone dosages of 0.97 $gO_3/gDOC$ and higher, 100% of the OMPs is removed.

Antoniou et al. (2013) classify removal in three ranges: 1) easily degraded: 90% removed with $gO_3/gDOC < 0.70$, 2) moderately degradable: 90% removed with $0.7 < gO_3/gDOC < 1.4$ and 3) recalcitrant: 90% removed with $gO_3/gDOC > 1.4$. When this classification is used, sulfamethoxazole and valsartan, together with methoxyfenozide and metoprolol, can be regarded as easily degradable. The five OMPs with removal curves below the four easily degradable OMPs can be regarded as moderately degradable (Antoniou et al., 2013). These compounds are 1,2,3-benzotriazool, gabapentin, irbesartan, methyl-1H-benzotriazool, oxazepam. Two OMPs are recalcitrant towards ozone treatment according to the classification of Antoniou et al. (2013). Metformin (purple line in Figure 22) is especially recalcitrant, with only 48% removal at the highest ozone dosage applied (1.31 $gO_3/gDOC$). Imidacloprid (dark blue line in Figure 22) is removed for 85% at the maximum ozone dosage.

The dotted black line in Figure 22 is the average removal of 28 analyzable OMPs as previously depicted in .Figure 20. The average removal is in the range of moderately degradable compounds: 90% removal at an ozone dosage of 0.98 $gO_3/gDOC$.

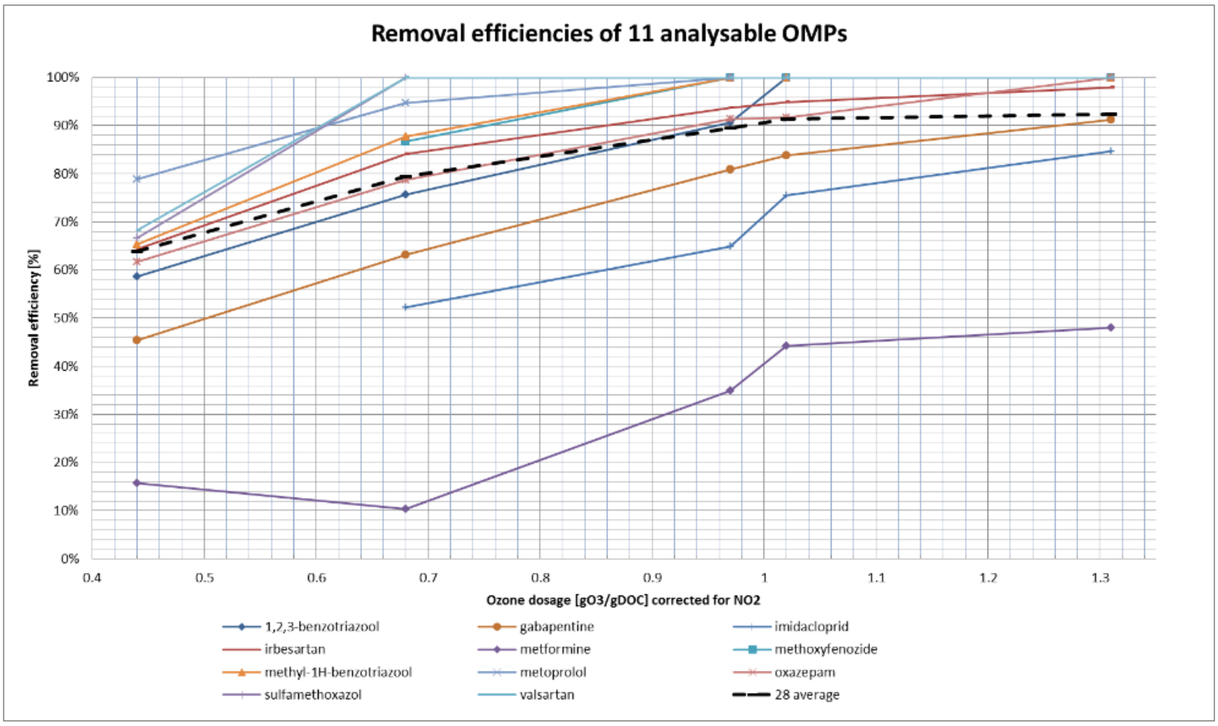


Figure 22 - Removal efficiencies of eleven analyzable OMPs

6.2.3 Bromate formation

Previous sections have discussed OMP removal during ozonation. As explained in section 4.2 on ozonation, toxic transformation products can be formed during treatment. One of the main toxic transformation products is bromate, which is formed by the oxidation of bromide. The main bromide sources are the chemical industry and municipal waste incinerators discharging to WWTPs (Soltermann et al., 2016). The formation of bromate during ozonation has the potential to limit the ozone dosage that can be applied to wastewater. To simplify, bromate is formed by oxidation of bromide by the following reaction (Naumov et al., 2008):

$$Br^{-} + 3O_3 \rightarrow BrO_3^{-} + 3O_2$$

However, the actual pathways of bromate formation are extremely complex. Various factors influence the formation of bromate, for instance DOC concentrations, O_3/DOC ratio, pH and substances that stimulate hydroxyl radical ($^{\cdot}OH$) formation. The mechanisms governing bromate formation during ozonation are presented in Figure

23. Tick lines indicate the main pathways (Antoniou and Andersen, 2012). Although extensive research on bromate formation has resulted in the unravelling of the mechanisms, it remains very hard to predict whether bromate will be formed during ozonation. At the moment, the best way of obtaining insight into bromate formation at a specific ozonation installation is simply conducting experiments to monitor bromate concentrations in the effluent.

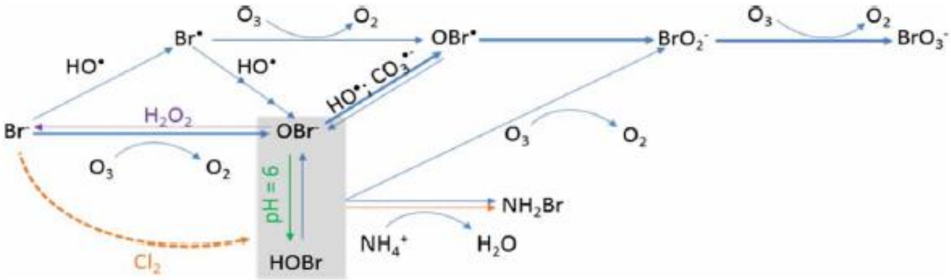


Figure 23 - Reactions that govern bromate formation (Antoniou and Andersen, 2012)

Tests of HH Delfland have shown that with the highest applied ozone dosage, 1.31 $gO_3/gDOC$ (15.6 mg O_3/l) and a bromide concentration of 390 µg/l the bromate concentration in the effluent remained below the reporting limit (and WHO drinking water standard) of 10 µg/l. Dutch drinking water standard for ozone used for oxidation is 1 µg/l, but the analysis does not reach these low levels. When ozone is used for disinfection, the drinking water standard for bromate is 5 µg/l. The Swiss Federal Institute of Aquatic Science and Technology (EAWAG) proposed an environmental quality standard of 50 µg/l to protect aquatic organisms (EAWAG, 2015). The fact that bromate has not been found in the ozone dosage tests in concentrations >10 µg/l, implies that bromate formation will, for now, not be a limiting factor for the determination of the ozone dosage at the ozone installation of HH Delfland. Other researches however do find bromate in the ozonation effluent, even at lower ozone dosages and lower bromide concentrations in the ozonation feed water (see Table 8).

Table 8 - Formation of bromate during ozonation in three researches

Research	Ozone dosage [O3/DOC]	Ozone dosage [mgO3/l]	Bromide influent [µg/l]	Bromate effluent [µg/l]	Bromate yield [% gBrO3/gBr]
HH Delfland	1.31	15.6	390	<10	<2.6
Margot et al. 2013	1.40	7.0	70	>10	>14.3
Gerrity et al. 2011	1.06	7.0	110	>10	>9.1

Margot et al. (2013) finds that bromate concentrations in the ozonation effluent reach levels above the EU drinking water standards (10 µg/l) with a slightly higher ozone dosage of 1.4 $gO_3/gDOC$ (7 mg O_3/l) and a lower bromide concentration of 70 µg/l. Gerrity et al. 2011 also observe bromate in concentrations above 10 µg/l. The latter is especially remarkable since the applied ozone dosage per liter, the ratio of ozone to DOC *and* the bromide concentration of the ozonation feed water is lower in this research (see Table 8).

Although the reaction from bromide to bromate during ozonation is highly complex, Soltermann et al. (2016) conduct empirical research to the formation of bromate. The research addresses ozonation of seven different Swiss wastewaters with a broad range of bromide concentrations (0.034 – 48 mg/l). The treatment with ozone showed bromate formation in a wide range (<2 - >400 µg/l). This transformation corresponds to a bromate yield of 0.3-31.7% mg BrO_3^-/mg Br^-. The term 'bromate yield' provides information on the fraction of bromide that is transformed into bromate. For instance, when 20 µg/l bromate is formed from an influent bromide concentration of 100 µg/l, then the bromate yield can be calculated as:

$$\frac{20\ \mu\text{g BrO}_3^-\ l^-}{100\ \mu\text{g Br}^-\ \text{l}^-} = 20\ \%$$

Using the range of bromate yield found by Soltermann et al. (2016) (0.3-31.7% mg BrO_3^-/mg Br^-), the influent bromide concentration of HH Delfland of 390 µg/l would result in a bromate concentration of 1 – 124 µg/l. According to the current findings of HH Delfland (<10 µg BrO_3^-/l) the bromate yield is <2.6%. This yield is within the range found by Soltermann et al. (2016), although at the bottom of the range. Bromate yield of Margot et al. (2013) and Gerrity et al. (2011) are respectively 14.3% and 9.1% at minimum.

For the moment, three factors can be identified that might explain the absence of bromate formation: 1) the high DOC concentration of the ozonation feed water, 2) a high $^{\cdot}OH/O_3$ ratio and 3) bromide occurring as methylbromide. Firstly, it is expected that ozone will first react with DOC before it reacts with bromide. High DOC concentrations, as observed by HH Delfland in the ozone feed water (10.5 mgDOC/l), could hence reduce bromate formation. Secondly, the $^{\cdot}OH/O_3$ ratio plays a role in the formation of bromate. This ratio is also related to the DOC concentration. Ozone is quickly transformed into $^{\cdot}OH$ radicals due to the reaction of ozone with DOC (Lee and von Gunten, 2016) (see section 4.2 on ozonation). A high DOC concentration will lead to a high transformation of ozone into $^{\cdot}OH$ radicals (i.e. a high $^{\cdot}OH/O_3$ ratio). With a high $^{\cdot}OH/O_3$ ratio the pathway of bromide to bromate is more restricted than with a lower ratio. So, a high DOC concentration leads to a high $^{\cdot}OH/O_3$ ratio, which in turn leads to less bromate formation. The final potential explanation of the absence of bromate has to be seen as a hypothesis. The hypothesis is that in ozonation feed water of HH Delfland, a lot of bromide occurs as methylbromide (CH_3Br). Bromide bounded to the methyl might be less willing to react with ozone toward bromate. Further research is required to find whether this hypothesis indeed plays a role in the absence of bromate formation.

As mentioned, a lot is still unknown regarding the reaction of ozone with bromide to form bromate. For this reason, Lee and von Gunten (2016) advice to test the suitability of ozonation in the planning stage of a WWTP upgrade. HH Delfland does so by closely monitoring the formation of bromate in the second research phase with longer tests. If bromate is indeed found, several strategies are available to lower bromate formation, for instance lowering pH, dosing ammonium or hydrogen peroxide (IJpelaar, 2016).

6.2.4 Choice of ozone dosage

As visualized in the flow diagram of Figure 17 on page 35, the optimal ozone dosage depends on 1) effective OMP removal, 2) limiting toxic by-product formation (bromate) and 3) keeping costs within budget. A complicating factor in the choice of the 'optimal' ozone dosage is that all three criteria mentioned, do not have clear target values. What can be regarded as 'effective' OMP removal – is it >80% or >90%? And what bromate standard should be met – Dutch drinking water standard of 1 µg/l or surface water target of 50 µg/l? Thirdly, the financial budget is also an arbitrary factor that differs for every project. This section attempts to determine reasonable standards for each of the three criteria.

Effective OMP removal

Starting with the first aspect, the question rises on what can be regarded as 'effective' removal. As explained in Chapter 2.1 on the legal context of OMP removal, no clear standards for OMPs discharges and surface water concentrations have been determined yet. HH Delfland has decided on an ozone dosage of 1.0 gO_3/gDOC which on average removes 92% of OMPs present in its wastewater. Figure 22 shows that the curve of the removal efficiency is flattening from 1.0 gO_3/gDOC towards higher ozone dosages. Dosing more than 1.0 gO_3/gDOC will only limitedly increase the removal of OMPs. HH Delfland has chosen this ozone dosage to be sure of high OMP removal while preventing to dose an 'extra' amount of ozone that is ineffective (HH Delfland, 2016c).

However, a removal efficiency of 92% can be regarded as fairly high compared to literature. Margot et al. (2013) state that 80% removal is recommended by the Swiss authorities for being a 'good compromise to reduce load of OMPs significantly while keeping costs in acceptable range'. Nakada et al. (2007) regards 80% removal as 'efficient'. Figure 22 shows that 80% OMP removal is achieved at an ozone dosage of 0.7 gO_3/gDOC at the pilot experiment of HH Delfland.

Also, an ozone dosage of 1.0 $gO_3/gDOC$ can be regarded as high compared to literature. Mulder et al. (2015) finds ozone dosages applied in Germany and Switzerland to be in a range of 0.6-0.9 $gO_3/gDOC$ with an average of 0.7 $gO_3/gDOC$. The dose applied by HH Delfland (1.0 $gO_3/gDOC$) is hence significantly higher and even out of range of operating conditions in Germany and Switzerland. Both the high removal efficiency and the high ozone dosage give rise to the question whether the dosage of 1.0 $gO_3/gDOC$ with removal efficiency of 92% is indeed the ‘optimal’ ozone dosage.

Limiting bromate formation

Before a conclusion on the ‘optimal’ ozone dosage and corresponding removal efficiency can be drawn, the toxic by-product formation must be evaluated. For a sound picture of the formation and elimination of toxicity, biological analysis for both ozonation and biofiltration is required (as explained in Chapter 3.2 on biological analysis). In this first research phase however, biofiltration is not included in the analysis and no bioassays have been used to measure toxicity. The formation of bromate is at this stage the only aspect that provides information on by-product formation. Since bromate is one of the main transformation products, it can still guide us in determining the optimal ozone dosage. As shown in the section above on bromate formation (6.2.3) currently no bromate is found after ozonation in the HH Delfland pilot. This is unexpected given observed bromate formation at lower influent bromide concentrations and lower ozone dosages applied, both in concentration per liter and concentrations per DOC concentration (O_3/DOC ratio). Bromate formation should still be closely monitored in future tests at the pilot. At this moment, we can however say that bromate formation during ozonation does not limit the ozone dosage that can be applied. The relatively high ozone dosage chosen by HH Delfland (1.0 $gO_3/gDOC$) will not lead to unacceptable bromate concentrations in the effluent.

Costs and energy consumption

The final aspect that needs to be addressed is the costs and energy consumption of applying a certain ozone dosage. Figure 24 shows the cost curve in which variable costs are plotted against removal efficiencies, ranging from 70-90%. The graph is based on a flow of 30.000 m^3/day for six months (installation will only be in operation during spring and summer) and costs of ozone production of 2 €/kg. These costs include oxygen and electricity to produce ozone. The graph shows that costs are increasing exponentially towards full OMP removal. 80% OMP removal (at ozone dosage of 0.7 $gO_3/gDOC$) will lead to operational costs of €82.000 per year (i.e. per six months of operation). When the ozone dosage of HH Delfland is applied (1.0 $gO_3/gDOC$) with a removal efficiency of 92%, the operational costs will be €119.000 per year. 92% removal instead of 80% removal leads to an increase of operational costs of 37.000 €/year, which is a 45% costs increase. The variable costs at 0.7 and 1.0 $gO_3/gDOC$ (€82.000 and €119.000 per year) are both within range of the budget available (€150.000 per year) to HH Delfland for variable costs of ozonation.

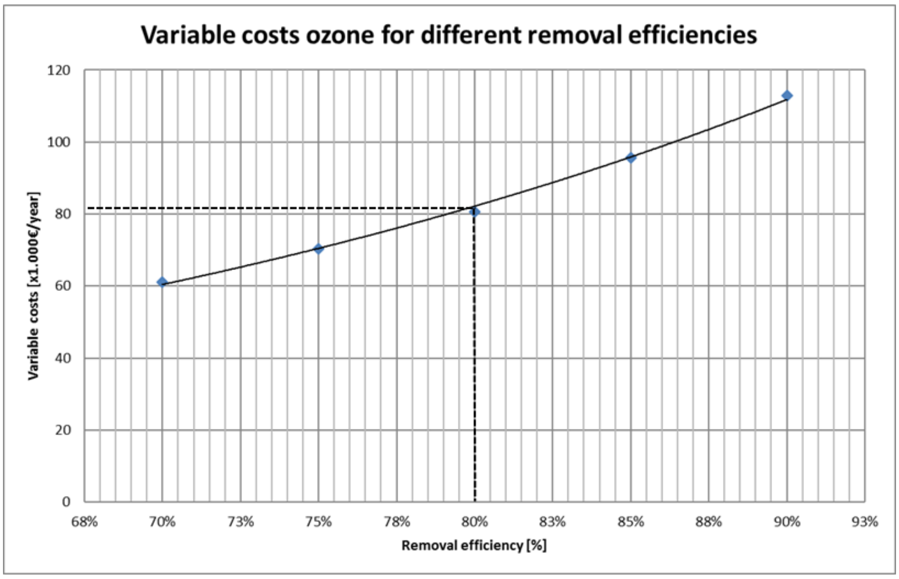


Figure 24 - Variable costs for different removal efficiencies

A 45% variable cost increase for 92% removal instead of 80% is significant. However, the variable costs of ozone dosage are only a fraction of costs of an ozonation installation. Research of Mulder et al. (2015) shows that total costs of ozonation are ~0.17 €/m^3 for an installation of 100.000 p.e., of which only ~0.02 €/m^3 are variable costs for ozonation (see Figure 25). For the full-scale installation of HH Delfland, the variable ozonation costs are 0.022 €/m^3 (92% removal) and 0.015 €/m^3 (80% removal). Saving 0.007 €/m^3 on 0.17 €/m^3 total costs will mean a cost reduction of 4.0%.

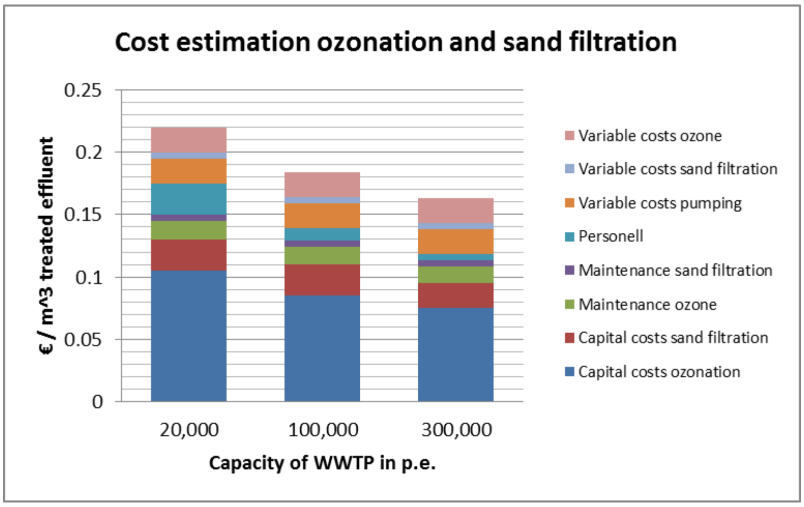


Figure 25 - Estimation of total costs of ozonation and sand filtration Mulder et al. 2015

With the desire of HH Delfland to turn the WWTPs into energy factories, the energy consumption required for ozonation might even be considered more important than the costs. With an energy consumption of 10 kWh/kgO_3 the yearly energy consumption for 80% removal would be ~400.000 kWh and for 92% removal ~600.000 kWh. The energy consumption of the conventional WWTP DGL has been 5.78 million kWh in 2016. The energy required for the ozonation installation would range from 7.0% (at 80% removal) to 10.4% (at 92% removal) of the current energy consumption by WWTP DGL. The energy requirements at both removal efficiencies can be regarded as substantial.

Conclusion on ozone dosage

Now the effectiveness of removal, bromate formation and costs at different ozone dosages have been analyzed, the first part of the second sub question can be answered (*What is the optimal ozone dosage found during pilot conditions?*). This research recommends an ozone dosage of 0.7 gO_3/gDOC, which gives an average removal efficiency of 80%. This ozone dosage is within common limits of ozonation installations currently in use (Mulder et al., 2015) and 80% removal is regarded as effective by Swiss research institute EAWAG and authorities (Margot et al. 2013). To provide a preliminary answer to the fourth research question, it can be concluded that bromate is not found in the ozone dosage experiments. Section 7.1.2 evaluates whether bromate *is* found during the long run test. However, other researches indicate that wastewater of HH Delfland might be susceptible to bromate formation with its high influent bromide concentration.

Operational costs will reach €82.000 per six months for the production of ozone at a dosage of 0.7 gO_3/gDOC. Increasing the dosage to 1.0 gO_3/gDOC would entail a 45% increase in operational costs and 4.0% increase in total costs of the ozone installation and operation.

A major point of discussion that needs to be addressed is the very little measurements in the ozone dosage test that have formed the basis of the determination of the optimal ozone dosage. A large variety of factors can influence performance of ozonation (e.g. varying wastewater matrix, different NO_2-N concentration etc.) so removal efficiencies are expected to vary. In the current experiment, only one data point is obtained for each of the five different ozone dosages. It is now unknown how the removal efficiency curve behaves between an ozone dosage of 0.7 and 1.0 gO_3/gDOC. A measurement at 0.8 gO_3/gDOC could for instance show that the curve is flattening at 0.8 gO_3/gDOC instead of at 1.0 gO_3/gDOC.

The idea of the pilot is that the longer tests will be done with one fixed ozone dosage. It is questionable whether the five data points provide a sufficiently sound basis for the determination of the optimal ozone dosage. However, scientific literature provides extensive information of previously performed experiments with different concentrations of ozone dosed during advanced wastewater treatment. The next section will compare the results of HH Delfland with experiments conducted in literature. The comparison might provide us information that is currently lacking in the experiment conducted by HH Delfland.

6.3 Comparison of HH Delfland and literature

As mentioned in Chapter 5 on the pilot set-up, research of HH Delfland is practically oriented and only covers the results of ten OMPs analyzed in the pilot experiments. This research adds value to the research of HH Delfland by, besides from analyzing a wider set of OMPs, comparing pilot results with scientific research on ozone dosing in advanced wastewater treatment. In the previous section, we have seen that the determination of the optimal ozone dosage is now based on only five measurements. An evaluation of ozone dosage test performed in literature could provide a sounder basis for the determination of the optimal ozone dosage. For a useful comparison with experiments performed in literature, the treatment steps, process configuration and wastewater characteristics must be, to a certain extent, similar to the HH Delfland experiment. This section will elaborate on two researches that are comparable to the pilot of HH Delfland. The first section (6.3.1) will focus on research of Antoniou et al. (2013), providing a research description, comparison of average and individual OMP removal. Section 6.3.2 will discuss similar topics for research of Snyder et al. (2006). The comparison is evaluated in section 6.4.

6.3.1 Comparison with Antoniou et al. (2013)

Research description Antoniou et al. (2013)

Antoniou et al. (2013) devote a full paper to present the results of their experiments to determine the required ozone dosage to remove pharmaceuticals from wastewater. Secondary effluents from six Swedish WWTPs were spiked with 42 pharmaceuticals (nominal concentration 1µg/l) (see Table 9 for key figures) and have undergone the same treatment with ozone. The samples were transferred into borosilicate glass vials with volume of 150 ml. These vials have been placed in a covered water bath at 15 degrees Celsius. The samples were subsequently treated with different ozone dosages (0.5-12.0 mg/l) in bench-scale experiments (Antoniou et al., 2013).

Table 9 - Key figures Antoniou et al. 2013

Key figures Antoniou et al. 2013			
Water analyzed	6 WWTPs Sweden	**Contact time**	10 hours
Chemical analysis	42 pharmaceuticals	**Ozone generated**	From pure oxygen
Biological analysis	NO	**Ozone dosage range**	0.5-12.0 mg/l
OMPs present	Spiked	**DOC range**	5.2-13.7 mg/l
OMP concentrations	1 µg/l	**O3/DOC range**	0.03-1.8 O3/DOC
Set-up	Bench-scale	**NO2-N**	<0.1 mg/l
Ozone contact	In borosilicate glass vials	**Temperature**	15 °C
Volume analyzed	150 ml	**Type of ozone injector**	Stock O3 solution added

Ozone is generated by a 1.0 g/h ozone generator supplied with dry oxygen gas. Contact time with ozone was at least 10 hours, which is longer than the lifetime of O_3 in wastewater. Average concentrations of DOC are given in Table 10. The ozone dosage is expressed as O_3/DOC ratio and the ratio required to remove 90% of the pharmaceuticals can be compared. Antoniou et al. (2013) claim that nitrification was well functioning at all treatment plants (nitrite concentration <0.1 mg/l) and therefor do not correct the ozone dosage for oxidation of nitrite. Antoniou et al. (2013) categorize pharmaceuticals in three groups: 15 out of 42 have shown to be easily degradable (90% removal with O_3/DOC <0.7), 19 moderately degradable (90% removal with 0.7 < O_3/DOC < 1.4) and 8 recalcitrant towards O_3-treatment (90% removal with O_3/DOC >1.4).

Table 10 - Average DOC concentrations in experiments of Antoniou et al. (2013)

	WWTP 1	WWTP 2	WWTP 3	WWTP 4	WWTP 5	WWTP 6
DOC [mg/l]	7.5	6.5	5.2	8.1	13.7	8.4

Comparison of average OMP removal

Figure 26 shows six removal efficiency curves of the average removal of 42 OMPs of six WWTPs analyzed by Antoniou et al. (2013). The averages are determined in the same way as the average of HH Delfland are determined (see section 6.2). The removal curves all follow the same pattern of a flattening curve towards 95-100% removal. The exact path of the removal efficiencies however differs. Effluent 2 (red square in Figure 26) for instance has a lower average removal at ozone dosage of 0.8-0.9 gO_3/gDOC than the other effluents. Reason for this difference can be numerous and are hard to define.

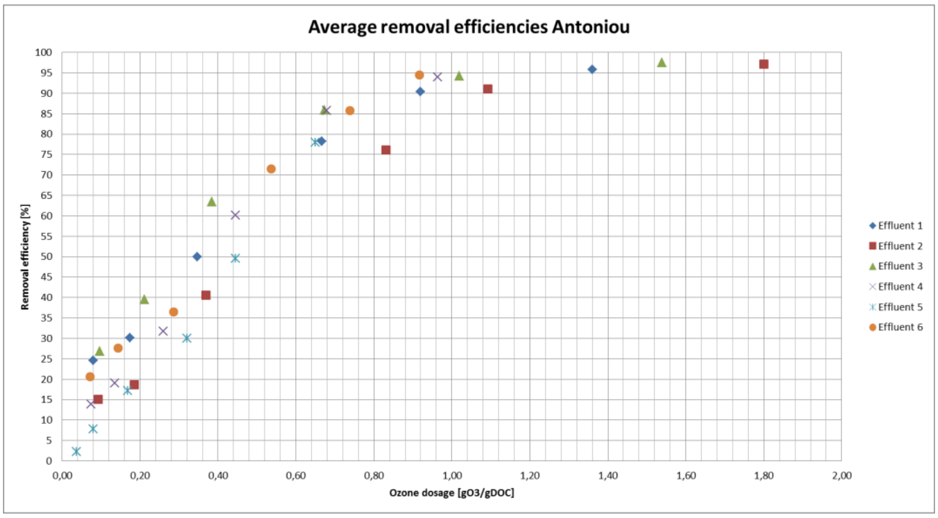


Figure 26 - Six removal efficiency curves (Antoniou et al., 2013)

The thirty data points of Antoniou et al. (2013) come from six different WWTPs, but are all treated in the same ozonation installation. For the sake of comparing the results with HH Delfland, all data points of Antoniou et al. (2013) are regarded as one experiment. This means that all data points (removal efficiency at a certain ozone dosage) from Figure 26 are grouped as one data set (see blue dots in Figure 27). Figure 27 shows the average removal of 28 OMPs of the ozone dosage tests of HH Delfland and the average removal of 42 OMPs found by experiments of Antoniou et al. (2013) plotted in one graph. Of these OMPs analyzed, only six have been included by both HH Delfland and Antoniou et al. (2013). These six OMPs will be discussed in more detail in the next section.

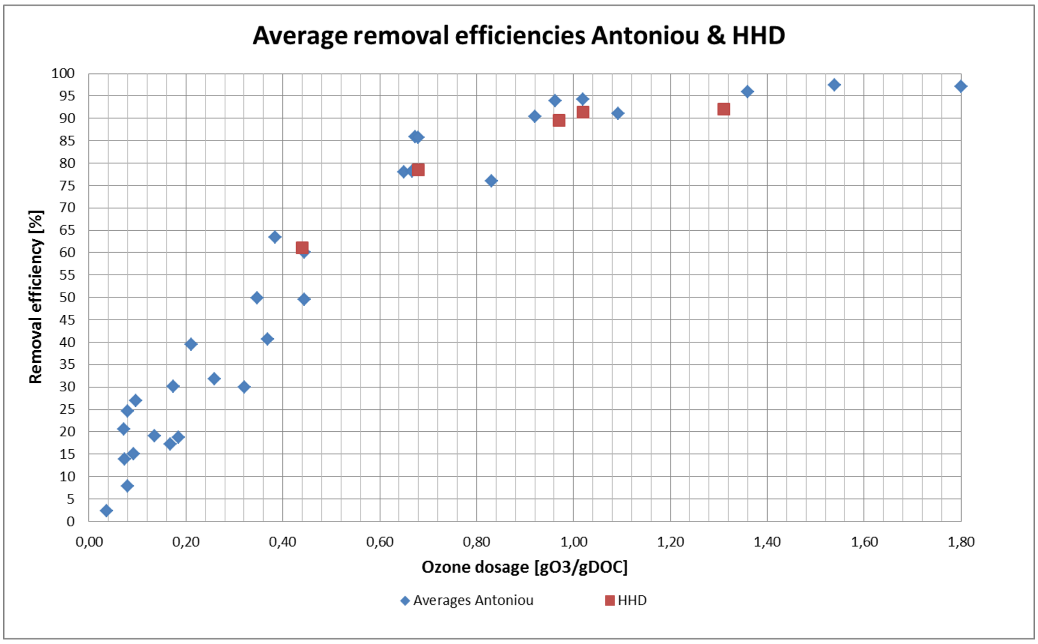


Figure 27 - Average removal of 42 OMPs (Antoniou) and 28 OMPs (HH Defland)

Figure 27 clearly shows that the average removal efficiencies of HH Delfland are within range of results of Antoniou et al. (2013). Although research set-up and OMPs analyzed differ quite substantially, the average results of both researches are within the same range. The next section will evaluate the removal efficiencies of the six OMPs analyzed by both HH Delfland and Antoniou to see whether the individual OMPs also show similar removal efficiencies.

Comparison of individual OMP removal

Analysis of Antoniou et al. (2013) has six OMPs in common with HH Delfland: carbamazepine, diclofenac, irbesartan, metroprolol, oxazepam and trimethoprim. For all six pharmaceuticals the required average ozone dosage to remove 90% of the substance was higher in Antoniou et al. (2013) (column 3 in Table 11) than by HH Delfland (column 4 in Table 11).

Table 11 shows that for instance on average 90% of carbamazepine is removed with an ozone dosage of 0.61 $gO_3/gDOC$ in the research of Antoniou et al. (2013). HH Delfland finds that even with the lowest ozone dosage of 0.44 $gO_3/gDOC$ carbamazepine is removed below reporting limits. Irbesartan falls within range of the six measurements in different WWTPs, so deviation from the average could be within normal ranges. The $gO_3/gDOC$ ratio found by HH Delfland for metoprolol and oxazepam fall below range of measurements by Antoniou et al. (2013). For the other three OMPs no conclusion can be drawn since measurements of HH Delfland (lowest 0.44 $gO_3/gDOC$) do not reach low levels of Antoniou et al. (2013) (0.40-0.44 $gO_3/gDOC$).

Table 11 - O3/DOC ratio required to remove 90% of OMP

OMP	Antoniou et al. 2013		HH Delfland
	Range	Average	
carbamazepine	0,42-0,84	0,61	<0,44
diclofenac	0,43-0,90	0,67	<0,44
irbesartan	0,51-1,41	1,05	0,86
metoprolol	0,73-1,07	1	0,61
oxazepam	1,16-1,64	1,49	0,94
trimethoprim	0,40-0,71	0,55	<0,44

Figure 28 shows the removal efficiencies of the six comparable OMPs as found by experiments by HH Delfland. Carbamazepine, diclofenac and trimethoprim are completely removed with the lowest ozone dosage (0.44 $gO_3/gDOC$) and continue to be so at all higher concentrations tested. In tests of Antoniou et al. (2013) these compounds have lower removal efficiencies at the ozone dosages tested as shown by Table 11. These three

OMPs are however all classified by Antoniou et al. (2013) as easily degradable (90% removal with O_3/DOC <0.7). The other three OMPs (irbesartan, metoprolol and oxazepam) have lower removal efficiencies for the ozone dosages applied, except for metoprolol having an equal (100%) removal efficiency at ozone dosage of 0.97 – 1.02 – 1.31 gO_3/gDOC and oxazepam at 1.31 gO_3/gDOC.

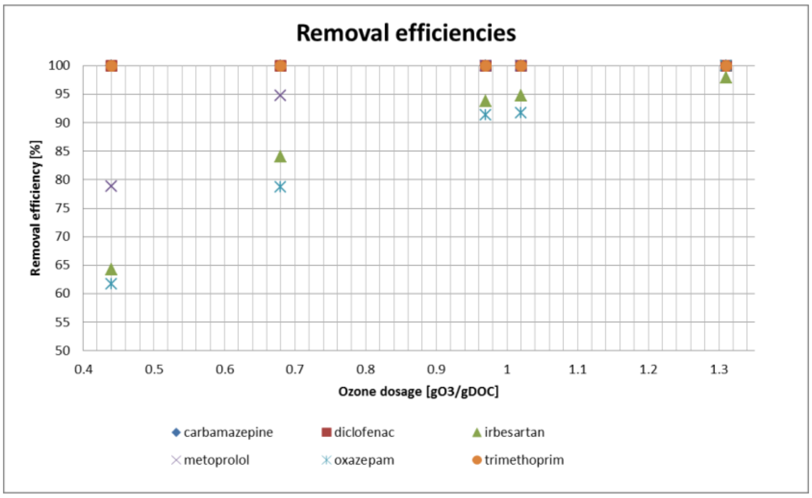


Figure 28 - Removal efficiencies (HH Delfland) of six OMPs analyzed by both researches

The three OMPs in the lower range of removal curves in Figure 28 are interesting to analyze. The first OMP to analyze is the pharmaceutical oxazepam, widely used for treatment of anxiety and insomnia. Figure 29 shows that for every ozone dosage the removal efficiency of oxazepam is higher in the experiment of HH Delfland than in all experiments of Antoniou (effluent 1-6). This raises the question what could have caused this significant difference. DOC concentrations in the influent water of WWTPs analyzed by Antoniou et al. (2013) range from lower (towards 5.2 mgDOC/l) to higher (13.7 mgDOC/l) than concentrations in the HH Delfland pilot (10.5 mg/l). It is hence unlikely that deviating DOC concentrations are the reason for the difference. The next section will elaborate more on potential reasons for difference in results.

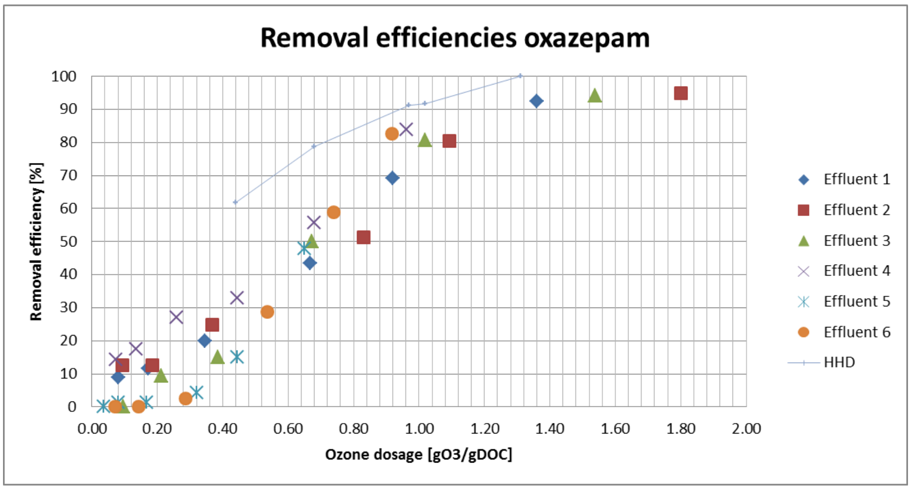


Figure 29 - Removal efficiencies of oxazepam found in research of Antoniou et al. (2013) and HH Delfland

Figure 30 shows the removal efficiency curves of irbesartan for both HH Delfland and Antoniou et al. (2013) (effluent 1-6). The pharmaceutical irbesartan is prescribed to lower blood pressure. The removal efficiency curve of HH Delfland is situated above the curves of effluent 1-5 in the same manner as we have seen for oxazepam. Effluent 6 (orange dots in Figure 30) however has an even higher removal efficiency for all ozone dosages applied. Again, potential reasons for differences are discussed in the next section.

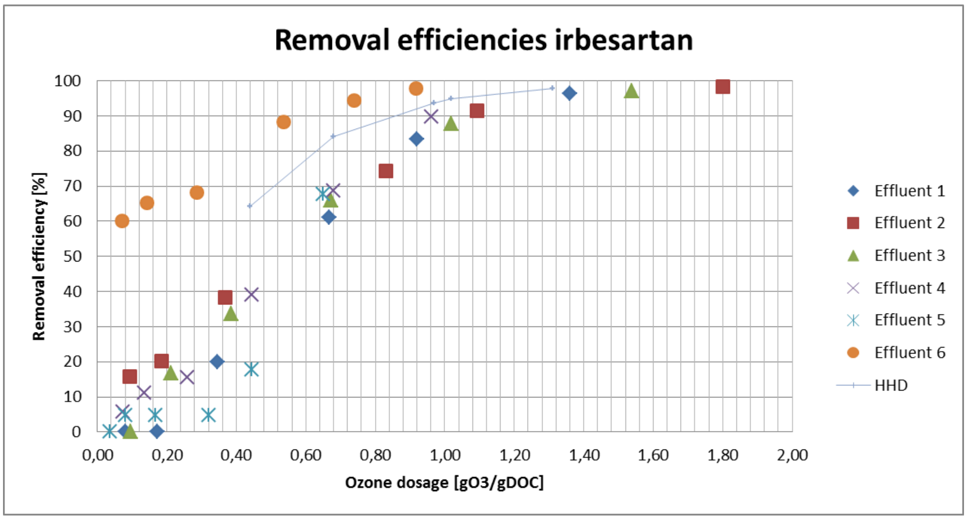


Figure 30 - Removal efficiencies of irbesartan found in research of Antoniou et al. (2013) and HH Delfland

Removal efficiencies of metoprolol in HH Delfland experiments as depicted in Figure 31 are harder to compare with removal efficiencies found by Antoniou et al. (2013). Metprolol is a pharmaceutical that lowers the heart rate and blood pressure. 100% of the OMP is removed in HH Delfland experiments with an ozone dosage of 0.97 $gO_3/gDOC$ and higher. Removal efficiencies for experiments of Antoniou et al. (2013) also reach 100% from ~1.0 $gO_3/gDOC$ onwards. At lower ozone dosage (0.44 $gO_3/gDOC$) HH Delfland has a significantly higher removal efficiency than Antoniou et al. (2013): ~80% compared to ~20-60%.

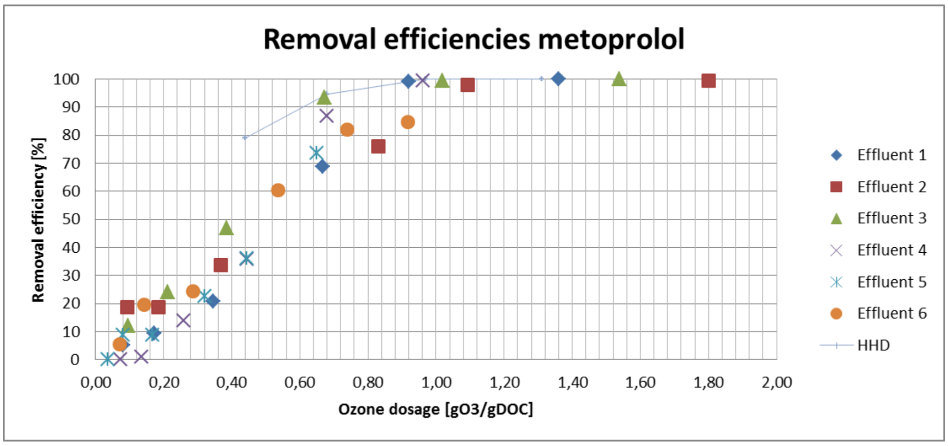


Figure 31 - Removal efficiencies of metoprolol found in research of Antoniou et al. (2013) and HH Delfland

Potential explanation for differences

From the comparison of individual OMPs it becomes clear that removal efficiencies of specific wastewaters and specific treatment can be significantly different than other wastewaters and/or treatment. There are numerous potential reasons why removal efficiencies of individual OMPs could show a different pattern. This section provides a short overview of four potential reasons with a short explanation.

- Spiked OMP concentrations vs. naturally occurring OMPs:

Antoniou et al. (2013) spike wastewater samples with pharmaceuticals. This could give a different situation than pharmaceuticals ´naturally´ occurring in wastewater. Wastewater characteristics are so peculiar that one cannot say with certainty that spiked wastewater will react in the same way with ozone as ‘regular’ wastewater. In case of Antoniou et al. (2013) wastewater is spiked to moderate concentrations (1 µg/l), which are in range of naturally occurring OMP concentrations in HH Deflland influent wastewater (see Table 12). It can however still change the matrix. For instance, if you spike wastewater with the easily oxidized diclofenac then a harder to remove OMP (e.g. iopromide) moves backwards in the reaction sequence to ozone. The removal efficiency of iopromide is in that case affected by the addition of diclofenac.

Solvents are required to spike wastewater (Snyder et al., 2006). The addition of solvents also changes the water matrix and hence changes the complex interactions between ozone, OH radicals and the compounds found in wastewater. Snyder et al. (2006) found that spiked waters have a greater O_3 demand than unspiked water due to the always required solvents contained in the spiking solution. The removal curves of oxazepam, irbesartan and metropolol in Figure 29 - Figure 31 do show generally lower removal efficiencies for the spiked wastewater of Antoniou et al. (2013). The average removal is however in the same range, which indicates that other OMPs than oxazepam, irbesartan and metropolol have lower removal efficiencies at HH Delfland.

Table 12 - Average concentrations of OMPs in ozonation feed water

OMP	Average influent concentration HHD [ug/l]
carbamazepine	0.33
diclofenac	0.36
irbesartan	2.22
metoprolol	1.72
oxazepam	0.45
trimethoprim	0.11

- Different water matrix:

Besides the differences caused by spiking OMPs, the water matrix can differ by many other substances. The sequence of reaction with ozone can be highly different of a certain OMP, depending on other substances. Presence of high concentration of easily degradable DOC can shift an OMP further backwards in the ozone reaction sequence. Presence of recalcitrant OMPs can shift a moderately degradable OMP forward in the reaction sequence.

- Different ozonation installation:

Chapter 4.2 on ozonation has explained that an ozonation installation can take different shapes and forms. Firstly, the scale of the installation can be quite different: from bench- to pilot- to full scale installations. Antoniou et al. (2013) for instance conduct the experiments in bench scale treating only a volume of 150 ml. HH Delfland ozonates a continuous flow (630 m^3/day) of wastewater through the pilot. Ozone production can also differ: Antoniou et al. (2013) uses an ozone generator supplied with dry oxygen gas and HH Delfland uses a corona generator supplied with liquid oxygen.

- Different operating conditions:

The temperature at which experiments of HH Delfland and Antoniou are performed, differ from 21.5 °C to 15 °C. Solubility of ozone and oxygen in water is lower at higher temperatures. According to EPA (1999) chemical oxidation rates do not vary with different temperatures. A lower temperature of Antoniou et al. (2013) would indicate a higher ozone concentration and hence more oxidation of OMPs. Analysis of three individual OMPs in the previous section however show a generally higher removal efficiency for HH Delfland. Ozone contact time also differs at both researches: from 14 minutes (HH Delfland) to 10 hours (Antoniou et al., 2013). For this operating condition the same applies as for temperature: one would expect a higher removal efficiency at longer contact times (Snyder et al. 2006), but removal efficiencies are higher at HH Delfland (with a shorter contact time).

6.3.2 Comparison with Snyder et al. (2006)

After a comparison with Antoniou et al. (2013), this section will compare HH Delfland results in the same way. The research is described in short before average and individual OMP removal are compared. The final section again discusses potential reasons for differences found, in addition to the potential reasons provided in the previous section.

Research description Snyder et al. (2006)

Snyder et al. (2006) evaluate ozonation at bench-, pilot-, and full-scale in both surface water and wastewater. A diverse set of 18-36 OMPs are evaluated, being pharmaceuticals, pesticides, steroids, personal care products etc. Water is collected in Nevada, USA from the Colorado River drinking water intake (CRW) and from a tertiary wastewater treatment plant. Chemical analysis on OMPs has been performed and a human breast carcinoma in vitro bioassay was used to measure estrogenicity. See Table 13 for an overview of the key figures of the research by Snyder et al. (2006).

The research uses total organic carbon (TOC) to provide a O_3/TOC ratio instead of the more commonly used O_3/DOC ratio. See the final part of this section for a discussion on what the implications of this difference might be. The wastewater effluent had nearly twice as high TOC concentration as the river water: 7.15 mg/l compared to 3.23 mg/l. Both CRW and WWTP effluent are treated with ozone in a bench-top pilot plant (BTPP). A continuous flow of 1 l/min was treated by ozone produced from oxygen.

For the comparison with HH Delfland, the pilot scale research of Snyder et al. (2006) on both wastewater and river water is used. The experiments of the bench- and full scale do not vary the ozone dosage, which makes them less useful for this research. The river water is spiked with OMPs in a range of 0.01 – 0.45 µg/l and subsequently treated with two ozone dosages: 0.39 gO_3/gTOC and 0.77 gO_3/gTOC. Reaction time is 14 minutes at an average temperature of 21 °C.

Wastewater is sampled once in June and once in January, which gives a difference in wastewater temperature (27.2 °C in June and 20.4 °C in January). OMPs in the wastewater are naturally occurring. Influent is in both experiments treated with the same three different ozone dosages: 2.1 mgO_3/l, 3.6 mgO_3/l and 7.1 mgO_3/l. With a slightly different TOC concentration (7.1 mgTOC/l in June and 7.2 mgTOC/l in January) this gives slightly different gO_3/gTOC ratios for the experiments conducted in June and January.

Table 13 - Key figures Snyder et al. (2013)

Key figures Snyder et al. 2006			
Water analyzed	River water & WWTP Nevada, USA	**Contact time**	14 min
Chemical analysis	36 OMPs	**Ozone generated**	From pure oxygen
Biological analysis	Human breast carcinoma in vitro bioassay	**Ozone dosage range**	1.25-8.7 mg/l
OMPs present	River water: spiked WWTP: naturally occurring	**TOC range**	River water: 3.23 mg/l WWTP: 7.10-7.20 mg/l
OMP concentrations	0,01-1,2 µg/l	**O3/TOC range**	0.29-1.23 O3/TOC
Set-up	Pilot scale	**NO2-N**	Not present
Ozone contact	Continuous-flow	**Temperature**	20.4-27.2 °C
Flow analyzed	1 l/min	**Type of ozone injector**	Bubble diffuser contactor (counter current)

Comparison of average OMP removal

Research of Snyder et al. (2006) does not show as much data points as the previously discussed research of Antoniou et al. (2013). Results of the pilot experiments on river water (CRW) and on WWTP effluent are shown in Figure 32. Similar to previously analyzed data, the removal efficiencies increase towards ~90-95% at higher ozone dosages. Remarkable is the high removal efficiency of BTPP WWTP in January at a low ozone dosage (0.3 gO_3/gTOC). This makes the removal efficiency curve more linear than exponential. Closer analysis to the data of BTPP WWTP January shows that two recalcitrant OMPs (i.e. estriol and estrone) are not included in January that *are* included in June. This gives a distorted image of an unexpected high average OMP removal at a low ozone dosage.

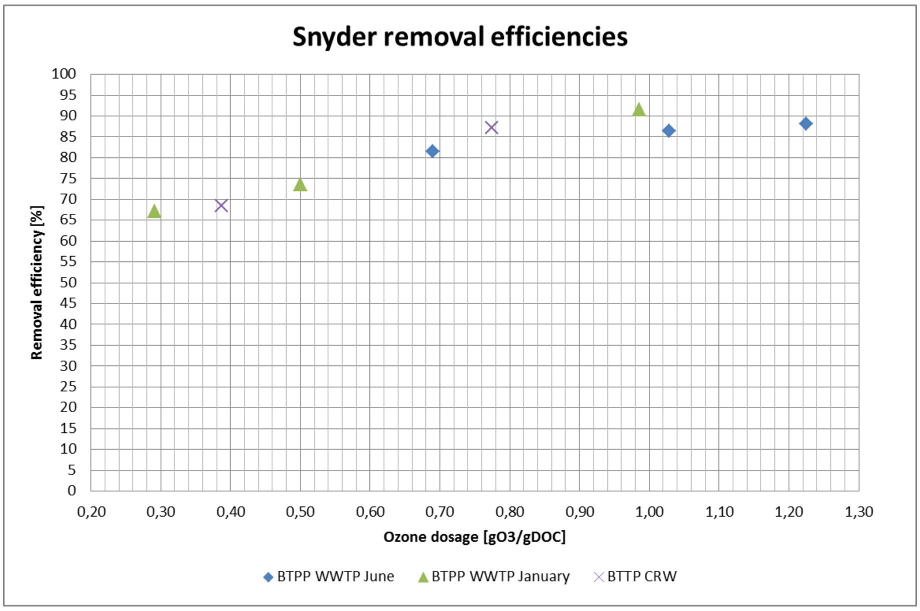


Figure 32 - Removal efficiencies of Snyder et al. (2006)

If the average removal efficiencies of Snyder et al. (2006) are compared with HH Delfland (see Figure 33), it can be observed that at high ozone dosages, the removal efficiencies of HH Delfland are in range of data of Snyder. At lower ozone dosages HH Delfland shows a lower average removal, which can be explained by the biased data as explained above.

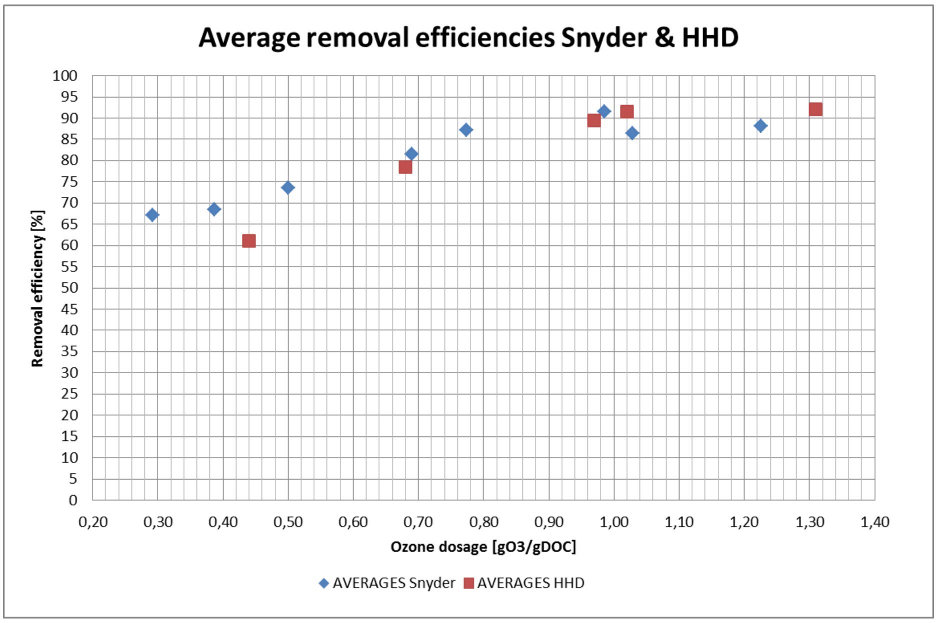


Figure 33 - Average removal efficiencies of Snyder & HH Delfland

Comparison of individual OMP removal

Comparison of individual OMPs is not possible. The two studies have four OMPs in common: carbamazepine, diclofenac, trimethoprim and ibuprofen. The first three are removed at 100% with all ozone dosages applied at experiments of HH Delfland and >97% removal at experiments of Snyder et al. (2006). The forth OMP, ibuprofen, turned out not to be present at HH Delfland wastewater. Ibuprofen is the only OMP of the four OMPs in common that shows less than 97% removal – although the removal pattern is irregular (see Figure 34).

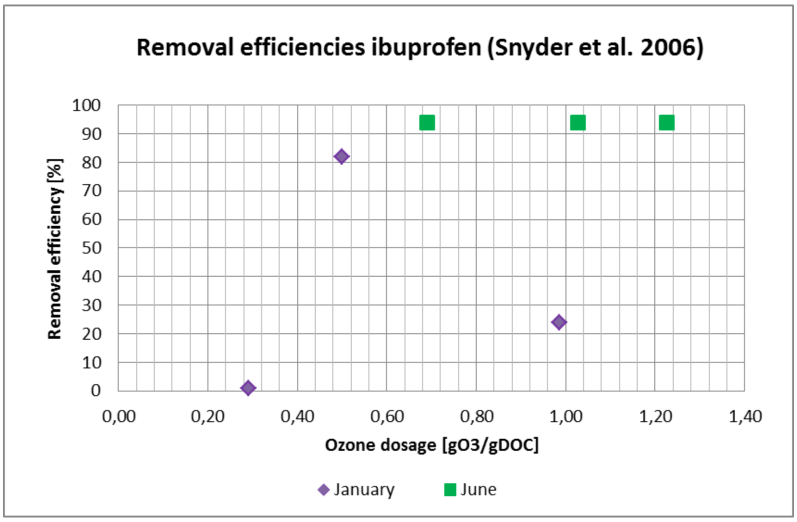


Figure 34 - Removal efficiencies ibuprofen in Snyder et al. (2006)

Potential explanation for differences

The previous sections have showed that average removal efficiencies of HH Delfland and Snyder et al. (2006) seem to be within the same range and no individual OMPs can be compared. The section will still address differences in the researches for the thoroughness of analysis. The same differences that have been addressed in the previous section on differences in research of HH Delfland and Antoniou et al. (2013) apply to the comparison between HH Delfland and Snyder et al. (2006). The section below elaborates on one additional difference and on one difference about which new information is provided.

- TOC vs DOC:

As previously mentioned, Snyder et al. (2006) use *total organic carbon* (TOC) instead of the commonly used *dissolved organic carbon* (DOC). TOC will be higher than DOC since the first includes *all* carbon sources present in wastewater, instead of only dissolved carbon. Unfortunately, Snyder et al. (2006) do not elaborate on DOC concentration. TOC concentration in the research is already in a low range (3.23 mg TOC/l for river water and 7.1-7.2 mg TOC/l) compared to the experiment of HH Delfland (10.5 mg DOC/l). For this reason, it is assumed that the difference between TOC and DOC will not be big and that it will hence not distort the result significantly.

- Temperature:

Similar to research of Antoniou et al. (2013) the temperature of the experiment of HH Delfland differs from the temperature at which research of Snyder et al. (2006) is conducted. Within the different experiments of Snyder et al. (2006) the temperature also varies and the authors are aware of these differences. Interestingly, they find 'quite consistent' removal efficiencies at different temperatures in June and January. The wastewater characteristics were, apart from temperature, also quite similar. This would indicate that the temperature of the influent water has limited effect on the removal efficiency of OMPs.

6.4 Evaluation of comparison

In comparing average removal efficiencies of ozone dosage experiments at HH Delfland with both Antoniou et al. (2013) and Snyder et al. (2006), similar outcomes have been observed. Removal efficiencies of individual OMPs can be different, but average removal of all OMPs analyzed, falls within a similar range. Section 6.4.1 first combines Antoniou et al. (2013) and Snyder et al. (2006) to evaluate the comparison. The second part uses research by Lee et al. (2012) to validate the results (section 6.4.2). The final part discusses the consequences and presents a recommendation to conclude this Chapter on ozone dosage (section 6.4.3).

6.4.1 Combination of literature

In Figure 35, the removal efficiencies of Antoniou et al. (2013) and Snyder et al. (2006) are regarded as one data series: 'literature' (blue diamonds). Data points of Snyder et al. (2006) are mainly located on the right side of the graph at higher ozone dosages. The red squares in Figure 35 depict the removal efficiencies found in the pilot experiment of HH Delfland. If we draw a third order polynomial trend line through all data points of literature (R^2 = 0.92) we find that all data points of HH Delfland are almost exactly located *on* this trend line. This indicates that average removal efficiencies of OMPs is within a similar range, although OMPs analyzed, ozone installations and process conditions are all different in the three studies. In order to further substantiate the finding that all average removal efficiencies are within the same range, this research tries to validate this result by including research of Lee et al. (2012) in the next section.

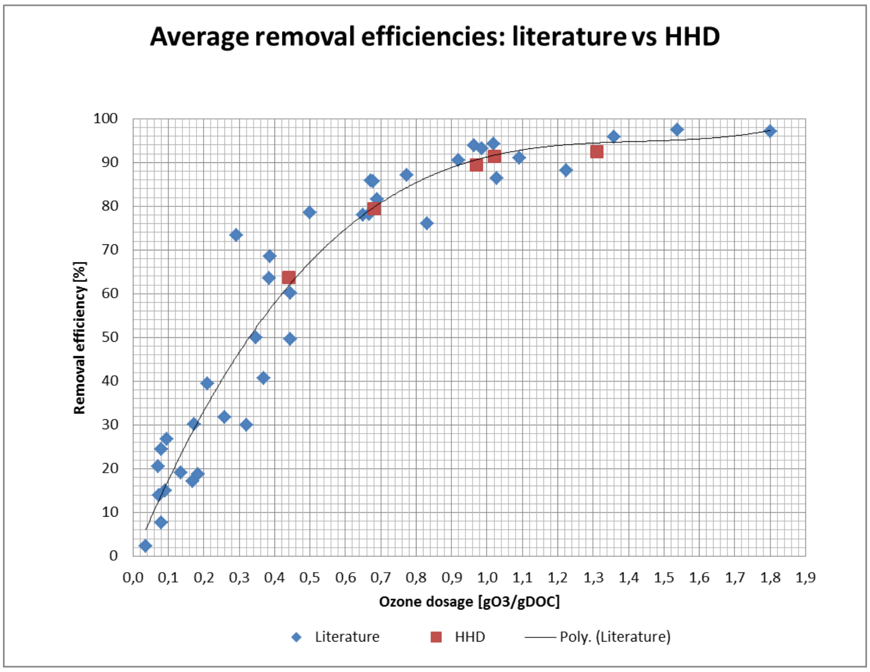


Figure 35 - Average removal efficiencies of combined literature and HH Delfland

6.4.2 Validation with Lee et al. (2012)

In research of Lee et al. (2012) 83 OMPs are analyzed at an advanced wastewater treatment pilot with ozonation and biofiltration in New Mexico, USA. Three different ozone dosages are applied to the wastewater: 2 mg/l, 4 mg/l and 8 mg/l. See Table 14 for key figures of the research and the ozone installation.

Table 14 - Key figures Lee et al. 2012

Key figures Lee et al. 2012			
Water analyzed	WWTP Albuquerque, New Mexico	**Contact time**	15 min
Chemical analysis	83 OMPs	**Ozone generated**	From pure oxygen
Biological analysis	NO	**Ozone dosage range**	0-12 mg/l
OMPs present	Naturally occurring	**DOC range**	3.7 mg/l
OMP concentrations	0.01-1.6 µg/l	**O3/DOC range**	0.54-2.16 O3/DOC
Set-up	Pilot scale	**NO2-N**	Not present
Ozone contact	Continuous-flow	**Temperature**	12-22 °C
Flow analyzed	No information provided	**Type of ozone injector**	Bubble diffuser contactor (counter current)

The average removal efficiencies of the three ozone dosages applied, can be added to Figure 35. This way, it can be checked whether data obtained by Lee et al. (2012) also matches the trend line through all data points of Antoniou et al. (2013) and Snyder et al. (2006). The green triangles in Figure 36 show the three data points of Lee et al. (2012) at ozone dosages of 0.54 gO_3/gDOC, 1.08 gO_3/gDOC and 2.16 gO_3/gDOC. The latter ozone dosage is very high compared to all other ozone dosages applied in previously discussed researches. Only a couple of very recalcitrant OMPs are still detected above the reporting limit at an ozone dosage of 2.16 gO_3/gDOC, such as contrast media iopromide and iohexal.

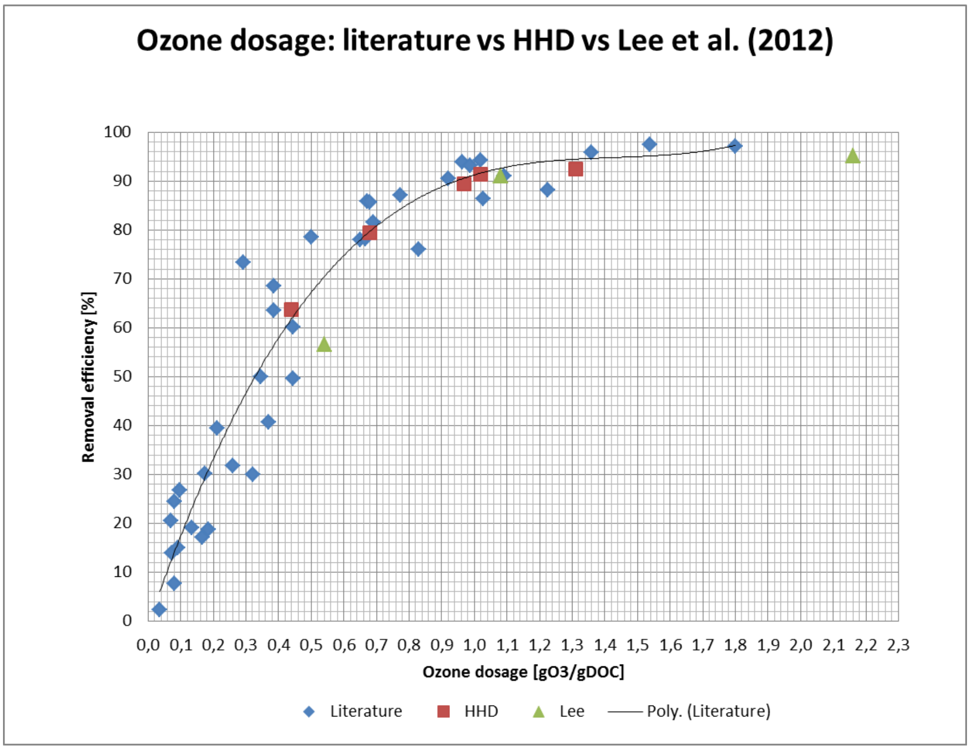


Figure 36 - Three data points of Lee et al. (2012) added to Figure 28

Although Lee et al. (2012) only provide three data points, it can be concluded that the removal efficiencies are fairly in line with the earlier drawn trend line through resource of Antoniou et al. (2013) and Snyder et al. (2006). The highest ozone dosage falls out of range of ozone dosages applied in both researches, but the corresponding removal efficiency is as expected: in the high nineties percentages. The removal efficiency at the middle ozone dosage of 1.08 gO_3/gDOC is almost exactly located on the trend line. The lowest ozone dosage of 0.54 gO_3/gDOC falls somewhat below the trend line, but still seems in range of other data points of research of Antoniou et al. (2013) and Snyder et al. (2006).

We have now seen that the removal efficiencies of yet another ozone dosage experiment follows the trend line to a large extend. This further substantiates the conclusion that average removal efficiencies of different wastewaters and different ozonation installations are within the same range. The next section discusses the consequences of this finding.

6.4.3 Consequences and recommendations

This section answers the second part of the second sub question: *what does comparison with of the ozonation test of HH Delfland with literature on ozone dosage test tell us? Could ozone dosage have been based on literature?* It can be concluded that literature has shown removal efficiency curves that are to a great extend similar to the curve of HH Delfland. HH Delfland could have determined the optimal ozone dosage based on removal efficiencies found in literature, without conducting its own ozone dosage experiments. Table 15 shows the removal efficiencies at the optimal ozone dosage as stated by my research (0.7 gO_3/gDOC) and as stated by HH Delfland (1.0 gO_3/gDOC). The achieved average removal efficiencies are almost equal based on literature or

HH Delfland. This makes sense, since the data points of HH Delfland are almost exactly located at the trend line of removal efficiencies found in literature.

Table 15 - Removal efficiencies based on literature or HH Delfland

Ozone dosage [O3/DOC]	Removal efficiency	
	Literature	HHD
0,7	81%	80%
1,0	91%	91%

In this chapter, the average removal efficiencies have been evaluated. However, HH Delfland is even more concerned with removal efficiencies of individual OMPs. Directive 2013/39/EU has set maximum surface water standards for 45 priority substances. These norms are translated in Dutch legislation ('Besluit kwaliteitseisen en monitoring water'). HH Delfland will have to comply to all norms in order to obtain a permit for discharging into the polder water system. The permit will not be granted based on the effort in removal (e.g. 80% average removal of OMPs), but on quantified norms for a wide range of substances. For this reason, it will be highly relevant to evaluate the removal of individual OMPs for which norms are set or are expected to be set in the near future. Therefore, the next section will examine OMP removal efficiencies based on three sources: 1) ozonation tests in the second research phase of HH Delfland, 2) values presented in literature (of more OMPs and more literature sources than in this chapter) and 3) modelling.

Also, a lot of further research is still required to test other aspects of the performance of ozonation and biofiltration at WWTP DGL. Toxicity tests with bioassays need to closely examine whether ozonation will produce toxic transformation products. If so, the question is whether these toxic products will be removed with biofiltration. With the high bromide concentration of the influent, formation of bromate also needs to be closely monitored. In the full-scale installation, formation of bromate caused by too high ozone dosages applied, must be prevented.

The next chapter will focus on OMP removal with a fixed ozone dosage. The final three sub-questions will be answered in this chapter:

1. What are the expected removal efficiencies based on **literature and modelling** and what are the **observed** removal efficiencies in the pilot installation of HH Delfland?
2. Can individual OMP removal be predicted based on literature and/or modelling?
3. Is bromate formed during ozonation? If yes, will it be removed during biological sand filtration?

7 OMP removal: observation and prediction based on literature data and modelling

The previous chapter has looked at average removal to determine the optimal ozone dosage. This chapter will look at individual OMP removal. HH Delfland has conducted a long run test with a fixed ozone dose (1.0 gO_3/gDOC) from July 1, 2017 onwards. This research evaluates the first seven measurements of the data series, which were available when this report was written. The OMPs that have been measured during this test, will be central in this chapter in prediction by literature and modelling. The first section (7.1) presents the detected OMPs and analyzes the observed removal. The second section (7.2) will predict the removal of these OMPs, based on values found in literature. The section ends with an evaluation of the ability to predict observed OMP removal with values found in literature. Predicted removal efficiency based on modelling is discussed in section 7.3. The ability to predict removal efficiencies by modelling is discussed as final part of section 7.3.

7.1 Actual OMP removal observed

7.1.1 Method of analysis

HH Delfland has provided seven measurements of ozone feed water and ozonation effluent. The first measurement is from March 21, 2017, which was a wide screening measurement. The other measurements have been conducted from July 1 – August 25. Unfortunately, the conditions in all measurements are not completely equal. Differences can occur in numerous variables, for instance water temperature, DOC concentrations, pH, wet/dry weather flow etc. In order determine average removal efficiencies of individual OMPs, the measurements are regarded to have sufficiently equal conditions. The concentrations of 423 substances have been measured. Points of measurement are ozone feed water, ozonation effluent and sand filter effluent. Since the focus of this research is on OMP removal by ozonation, only the first two points of measurement are included.

Values below reporting limit

For measured concentrations below the reporting limit, a value of zero is taken. Since measurements of OMPs is situated at the lowest ranges that current detection methods can reach, the method to deal with concentrations below the reporting limit is an important aspect of a research. Appendix I provides an overview of the possibilities and what method is chosen in relevant scientific research. To summarize, most studies either take the reporting limit as value for concentrations below the reporting limit, or their way of comparing data does not require to determine this value. In the first case, studies calculate removal efficiencies of OMPs that are removed below the reporting limit, with the reporting limit (Margot et al. 2013, Nakada et al. 2007, Snyder et al. 2006). These studies use an '>' (greater than) sign to indicate that the removal is likely to be higher than the calculated removal efficiency with the reporting limit. Secondly, many studies do not present their data in removal efficiencies, but for instance in 'the ozone concentration that is required to remove 90% of the OMP' (Antoniou et al. 2013). In this case, a study avoids to determine values of measurements below the reporting limit.

This research chooses to take a value of zero for concentrations. When methods of detection improve in the future, substances could be measured in even lower concentrations. However, for now this research argues that an OMP is simply not present in wastewater when the concentration falls below the reporting limit.

All methods to cope with values below the reporting limit have advantages and disadvantages. When the value of the reporting limit is taken (as discussed above), the removal efficiency for many OMPs is presented as '>%'. This is not regarded to be suitable for this analysis. Firstly because of the distorted image of low removal efficiencies, when feed water concentrations are just above the detection limit and effluent concentrations are below reporting limit. For this reason, Margot et al. (2013) excludes removal efficiency values that are below 80% (for OMPs with effluent concentrations below reporting limit). This research does not have sufficient data to exclude OMPs. Secondly, concentrations '>%' are hard to compare with expected removal efficiencies based on modelling, since these yields 'exact' removal efficiencies.

The previous chapter in this research has used the Volkert-Bakker method when concentrations fall below the reporting limit. However, data analyzed in this chapter has a matrix disturbance for one measurement (July 1, 2017). This results in reporting limits for this measurement that are ten times higher than for the other measurements. With the Volkert-Bakker method, OMPs from the disturbed measurement that were measured *below* the reporting limit, can have a determined value that is *above* the reporting limit of the other measurements. For this reason, the Volkert-Bakker method cannot be used in this research.

Standard parameters (DOC, ozone dose)
As mentioned, the long run test of HH Delfland is conducted with an ozone dose of 1.0 gO_3/gDOC. The ozone dose in mg/l is regulated by real-time online DOC measurements. However, the previous chapter has discussed the necessity to correct the ozone dose for nitrite. Ozone will be consumed to oxidize nitrite to nitrate and this part of the ozone hence cannot react with OMPs. The idea of the long run test is that it is conducted with a fixed ozone dose (expressed in gO_3/gDOC). However, changing nitrite concentrations can result in different ozone concentrations actually reacting with OMPs. Table 16 below provides the DOC and nitrite concentrations in the seven measurements. DOC concentrations are fairly constant, ranging from 9.9 mg/l to 12.0 mg/l with an average concentration of 10.8 mg/l. Nitrite concentrations range from 0.01 mg/l to 0.35 mg/l. Antoniou et al. (2013) state that nitrification functions well when nitrite concentrations are below 0.1 mg/l. Five of the seven measurements of the HH Delfland experiments have nitrite concentrations higher than or equal to 0.1 mg/l. Ozone dose correction for nitrite is hence required. In Table 16 the ozone consumption to oxidize nitrite is calculated. This allows the calculation of the ozone dose expressed in gO_3/gDOC, corrected for nitrite. This dose ranges from 0.90-1.00 gO_3/gDOC with an average of 0.95 gO_3/gDOC. For the remainder of this chapter, the average ozone dose of 0.95 gO_3/gDOC will be used for all seven measurements. Section 7.3 will elaborate on the sensitivity of the prediction by modelling with an actual ozone dose ranging from 0.90-1.00 gO_3/gDOC.

Table 16 - Overview of DOC and nitrite concentrations to calculate the ozone dose corrected for nitrite

	Unit	Influent 1	Influent 2	Influent 3	Influent 4	Influent 5	Influent 6	Influent 7	Average
DOC	mg/l	9.9	12.0	8.9	12.0	11.5	10.6	10.9	10.8
Nitrite	mg/l	0.05	0.36	0.15	0.35	0.01	0.10	0.10	0.16
O3 dose	gO3/gDOC	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
O3 dose	mg/l	9.9	12.0	8.9	12.0	11.5	10.6	10.9	10.8
Reaction O3-NO2	gO3/gNO2	3.4	3.4	3.4	3.4	3.4	3.4	3.4	3.4
O3 consumption for NO2	mg/l	0.2	1.2	0.5	1.2	0.0	0.3	0.3	0.5
O3 dose (corr for nitrite)	mg/l	9.7	10.8	8.4	10.8	11.5	10.3	10.6	10.3
O3 dose (corr for nitrite)	**gO3/gDOC**	**0.98**	**0.90**	**0.94**	**0.90**	**1.00**	**0.97**	**0.97**	**0.95**

7.1.2 Analysis

In total, 423 substances have been measured in the long run test of HH Delfland. Among these substances are pharmaceuticals, pesticides, contrast media, corrosion inhibitors and metals. Many substances have not been detected in the ozone feed water, nor in the ozonation effluent. For instance, the insecticide carbofuran has not been detected in any of the seven measurements in concentrations above the reporting limit of 0.01 μg/l. Table 17 below provides an overview of the 58 substances that *have* been found at least once with a concentration above the reporting limit. It shows to what group the OMPs belong and what the average removal efficiency is. The average removal efficiency is obtained by taking the average of 1-7 removal efficiencies of the 1-7 measurements in which the OMP has been detected. For instance, the average removal efficiency of biteranol is obtained from only one measurement of feed water and effluent concentrations. The standard deviation of the removal efficiency is hence zero. Diethyltoluamide is for instance detected in six measurements. The standard deviation of the six removal efficiencies that are used to calculate the average removal efficiency, is 10.7%. Standard deviation and number of measurements can be found in the two most right columns of Table 17.

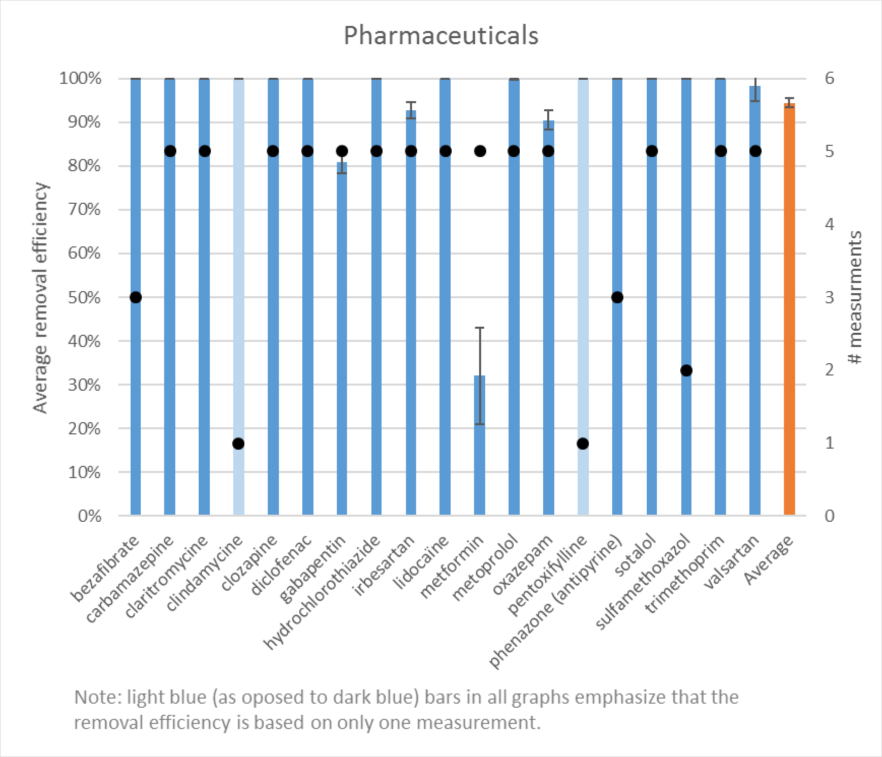
The total average removal efficiency of all detected OMPs at all measurements is 91.5%, with an average standard deviation of 3.8%. This value is in line with the trend line drawn in Figure 36 on page 56. To allow more detailed analysis, the OMPs will be analyzed per group. The final sections will discuss the fate of metals and the formation of bromate.

Table 17 - Overview of detected OMPs

OMP	Group	Average removal efficiency	Standard deviation	# measure-ments
1,2,3-benzotriazole	Corrosion inhibitor	91.8%	5.7%	3
2,6-dichloorbenzamide	Herbicide	100.0%	0.0%	1
2-methyl-4-chlorophenoxyacetic a	Herbicide	100.0%	0.0%	1
acetamiprid	Pesticide	100.0%	0.0%	1
amidotrizoic acid	Contrast media	52.8%	41.1%	3
azoxystrobin	Fungicide	100.0%	0.0%	1
bezafibrate	Pharmaceutical	100.0%	0.0%	3
bitertanol	Fungicide	100.0%	0.0%	1
boscalid	Fungicide	100.0%	0.0%	2
bupirimate	Pesticide	100.0%	0.0%	1
carbamazepine	Pharmaceutical	100.0%	0.0%	5
carbendazim	Fungicide	100.0%	0.0%	6
chloroprofen	Pesticide	100.0%	0.0%	1
claritromycine	Pharmaceutical	100.0%	0.0%	5
clindamycine	Pharmaceutical	100.0%	0.0%	1
clozapine	Pharmaceutical	100.0%	0.0%	5
cyprodinil	Fungicide	100.0%	0.0%	4
diclofenac	Pharmaceutical	100.0%	0.0%	5
diethyltoluamide	Insecticide	95.6%	10.7%	6
diuron	Herbicide	100.0%	0.0%	4
ethofumesate	Pesticide	100.0%	0.0%	1
fenhexamide	Fungicide	100.0%	0.0%	1
flonicamid	Insecticide	26.7%	41.3%	5
gabapentin	Pharmaceutical	80.9%	2.6%	5
hydrochlorothiazide	Pharmaceutical	100.0%	0.0%	5
imazalil	Fungicide	100.0%	0.0%	1
imidacloprid	Insecticide	72.2%	4.9%	6
iohexol	Contrast media	93.8%	8.8%	2
iomeprol	Contrast media	52.8%	45.8%	3
iopamidol	Contrast media	100.0%	0.0%	1
iopromide	Contrast media	76.9%	20.1%	3
ioxitalamic acid	Contrast media	47.5%	15.8%	3
iprodion	Fungicide	100.0%	0.0%	2
irbesartan	Pharmaceutical	92.7%	1.9%	5
lidocaïne	Pharmaceutical	100.0%	0.0%	5
metalaxyl	Fungicide	100.0%	0.0%	1
metformin	Pharmaceutical	32.0%	11.0%	5
methoxyphenozide	Pesticide	100.0%	0.0%	5
methyl-1H-benzotriazole	Corrosion inhibitor	98.2%	1.6%	3
metoprolol	Pharmaceutical	99.9%	0.3%	5
monobutyltin (kation)	Chemical	81.5%	0.0%	1
oxamyl	Pesticide	100.0%	0.0%	1
oxazepam	Pharmaceutical	90.5%	2.2%	5
pentoxifylline	Pharmaceutical	100.0%	0.0%	1
phenazone (antipyrine)	Pharmaceutical	100.0%	0.0%	3
pirimicarb	Insecticide	100.0%	0.0%	4
propamocarb	Fungicide	100.0%	0.0%	6
pymetrozine	Insecticide	100.0%	0.0%	5
sotalol	Pharmaceutical	100.0%	0.0%	5
spinosad	Insecticide	100.0%	0.0%	3
sulfamethoxazol	Pharmaceutical	100.0%	0.0%	2
tetraethyleenglycoldimethylether	Chemical	100.0%	0.0%	3
tetrahydroftaalimide	Chemical	100.0%	0.0%	1
thiamethoxam	Insecticide	100.0%	0.0%	2
tolclofos-methyl	Chemical	100.0%	0.0%	1
trimethoprim	Pharmaceutical	100.0%	0.0%	5
triphenylphosphineoxide	Chemical	23.2%	2.5%	2
valsartan	Pharmaceutical	98.4%	3.6%	5
Average		**91.5%**	**3.8%**	**3.12**

Pharmaceuticals

Figure 37 shows that pharmaceuticals are well removed with the applied ozone dose. For all OMP groups, Appendix II provides the tables on which the figures with removal efficiencies are based. 13 pharmaceuticals are fully removed, i.e. to below reporting limits. Average removal efficiency (orange bar in Figure 37) is as high as 94.4%. The 19 pharmaceuticals have been detected often in the seven measurements. Two pharmaceuticals are detected only once (see light blue bars in Figure 37). The graphs of all OMP groups will emphasize which removal efficiencies have been based on only one measurement, by coloring these bars light blue instead of dark blue.



Note: light blue (as oposed to dark blue) bars in all graphs emphasize that the removal efficiency is based on only one measurement.

Figure 37 - Removal efficiency of 19 pharmaceuticals

If we omit the 100% removed pharmaceuticals in Figure 38, we can further analyze the remaining six pharmaceuticals. Figure 38 shows that only metformin is removed below 80%. All other five pharmaceuticals show high average removals, with small standard deviations (0.3%-3.6%). In the five measurements for each of these pharmaceuticals, deviations in removal efficiencies can be regarded as small.

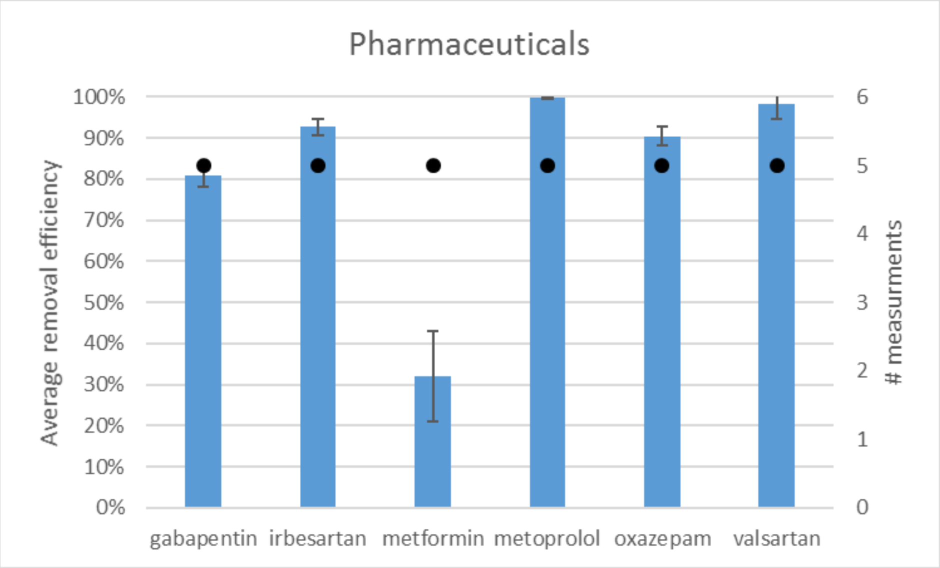


Figure 38 - Removal efficiency of six not completely removed pharmaceuticals

Metformin is only removed 32.0% on average, with a standard deviation of 11.0%. In five measurements, the maximum removal efficiency of metformin has been 40%, with 12.7% as minimum (see Table 18). Interestingly, the lowest removal efficiency of metformin is observed at the fourth measurement, which had the lowest ozone dose (corrected for nitrite (see Table 16)). This could indicate that metformin is highly sensitive to the ozone dose and hence shows lower removal with a lower ozone dosage. However, this statement would be based on only five measurements, which is too little to draw such a general conclusion.

Table 18 - Removal efficiencies of metformin in five measurements

Metformin	# 1	# 2	# 3	# 4	# 5	# 6	# 7
Removal efficiency	37.5%	33.8%	36.1%	12.7%		40.0%	

Pesticides

Pesticides show a similar image to pharmaceuticals. Figure 39 shows that of 26 pesticides detected, 23 have been completely removed. An important notion though is that 12 of these 23 pesticides have only been detected (and fully removed) once (see light blue bars in Figure 39).

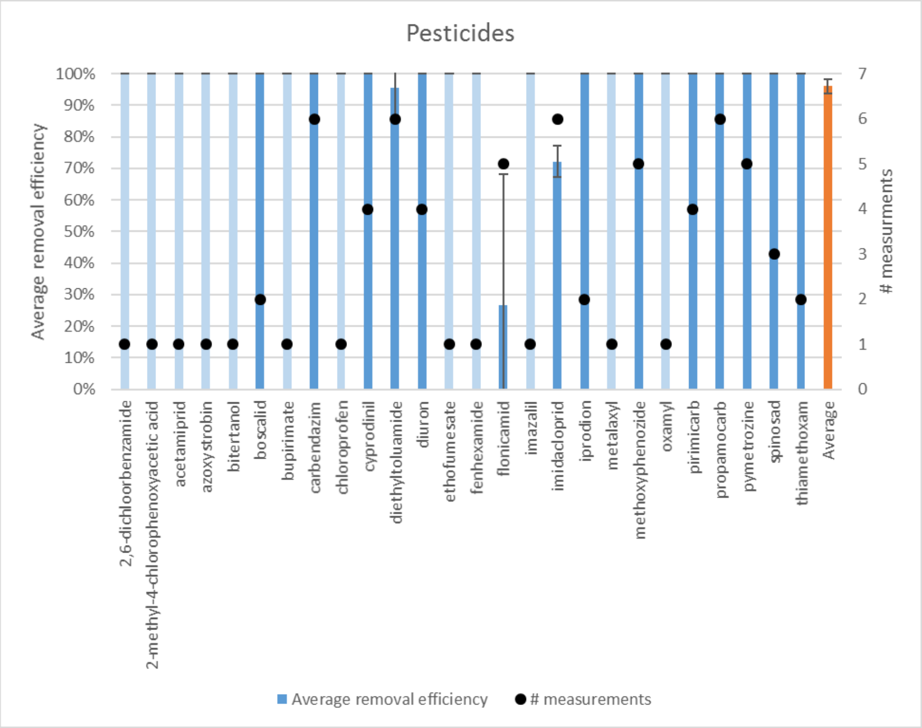
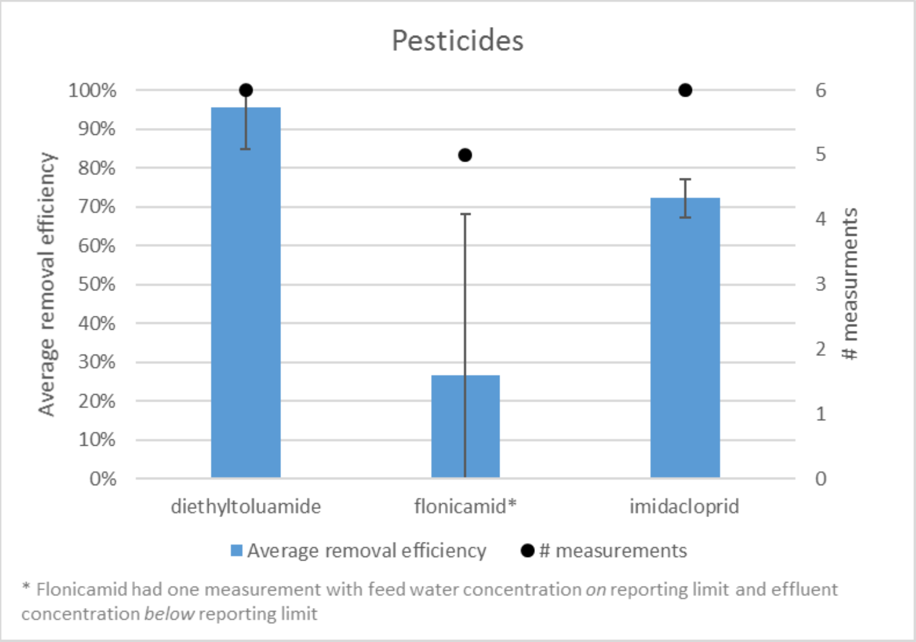


Figure 39 - Removal efficiency of pesticides

When the pesticides that are 100% removed are excluded, only three pesticides are left: diethyltoluamide (DEET), flonicamid and imidacloprid (see Figure 40). With six measurements for both diethyltoluamide and imidacloprid, the standard deviations of 10.7% and 4.9% are relatively small.



* Flonicamid had one measurement with feed water concentration *on* reporting limit and effluent concentration *below* reporting limit

Figure 40 - Removal efficiency of three not completely removed pesticides

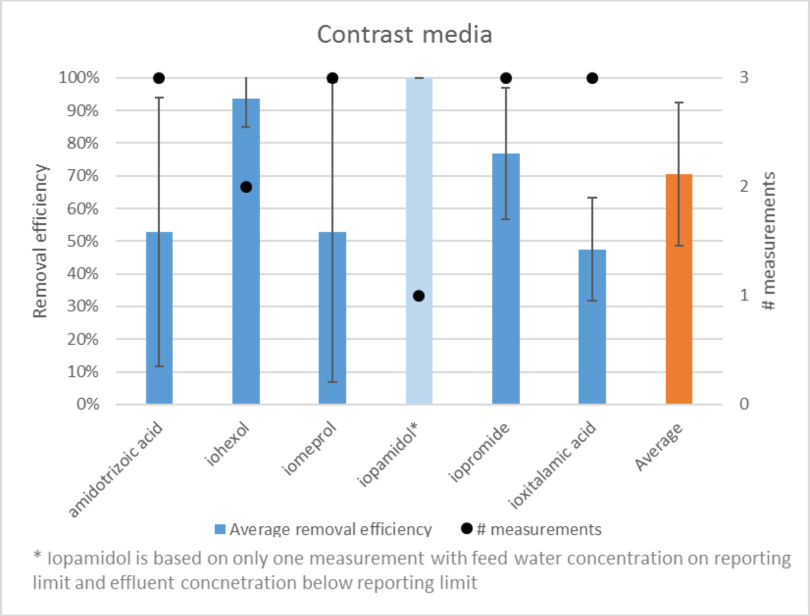
Flonicamid is the only pesticide that is not well removed (26.7% on average). The removal is highly variable with both 0.0% removal and 100% removal observed. As opposed to metformin, the highest removal efficiency is observed with the lowest ozone dose, i.e. in measurement 4 (see Table 19). This removal efficiency is quite distorted. The concentration of the ozonation feed water of measurement four was exactly on the reporting limit (0.02 µg/l) while the concentration of the ozonation effluent was below the reporting limit (<0.02 µg/l). This is a disadvantage of the method to cope with values below the reporting limit, as chosen in section 7.1.1. If we would omit measurement 4, the average removal efficiency would be reduced to 8.3%. Measurements 2, 5 and 6 show more similar removal efficiencies (9-14%).

Table 19 - Removal efficiency of flonicamid per measurement

Flonicamid	# 1	# 2	# 3	# 4	# 5	# 6	# 7
Feed water [ug/l]	0.03	0.22	0	0.02	0.07	0.1	
Effluent [ug/l]	0.03	0.2	0.09	0	0.06	0.09	
Removal efficiency	0.0%	9.1%		100.0%	14.3%	10.0%	

Contrast media

Compared to pharmaceuticals and pesticides, contrast media are only moderately removed by ozonation. Figure 41 shows that the average removal efficiency of six contrast media is 70.6%. Only one contrast medium is 100% removed (iopamidol), which is also the only substance that has been measured only once (light blue bar in Figure 41). Noteworthy is the high standard deviations for all contrast media, except iopamidol (only 1 measurement) and iohexol (standard deviation 8.8%, 2 measurements). The measurements of amidotrizoic acid and iopromide encounter the same situation as flonicamid, with a feed water concentration *on* the reporting limit and an effluent concentration *below* the reporting limit. While amidotrizoic acid is removed with 25% and 33% in the other two measurements, the 100% removal efficiency of the third measurement gives both a higher average removal and a higher standard deviation. Measurements of iomeprol and ioxitalamic acid do not have this problem, but still see high standard deviations. For the three measurements of these two contrast media, the removal efficiency is just highly variable.



* Iopamidol is based on only one measurement with feed water concentration on reporting limit and effluent concnetration below reporting limit

Figure 41 - Removal efficiencies of six contrast media

Corrosion inhibitors

Only two corrosion inhibitors have been analyzed and detected in the long run test. Both 1,2,3-benzotriazole and methyl-1H-benzotriazole are well removed by ozonation (see Figure 42). Standard deviations are low for both substances, indicating that removal efficiencies of different measurements were in the same range.

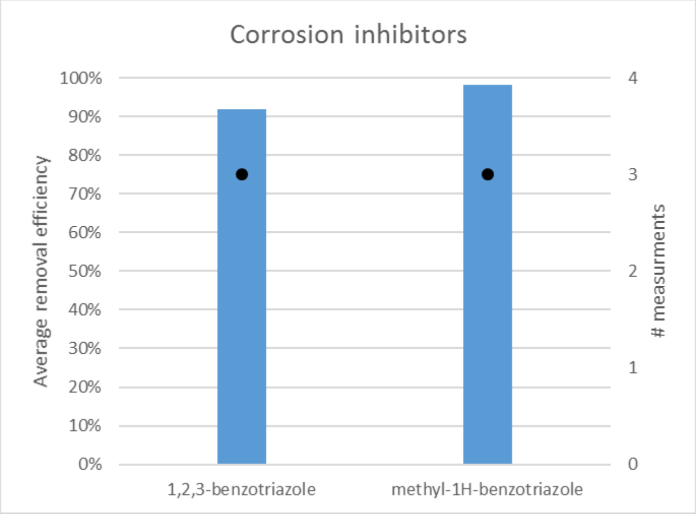


Figure 42 - Removal efficiencies of two corrosion inhibitors

Metals

The previous sections have discussed OMP removal. However, to obtain a discharge permit for the Freshwater Factory, the concentrations of metals and bromate also have to meet the water quality standards (see Appendix III for a case study on the permit application for the Freshwater Factory). This section discusses the fate of metals during ozonation and the next section evaluates the formation of bromate during ozone treatment.

As expected (Margot et al., 2013), metals are not removed by ozonation. Figure 43 shows the removal efficiencies of thirteen metals. Two things are noteworthy in this graph. Firstly, eight of thirteen metals are only detected once in the ozonation feed water of the seven measurements. This can be explained by a different measurement package of the fifth measurement (August 8). During other days of measurements, the samples have not been analyzed for these metals. Removal efficiencies of metals that have only been analyzed once (light blue bars in Figure 43) range from -6.7% to 100%. Therefore, this research can hardly draw any meaningful conclusions on these metals. Secondly, the metals that *have* been analyzed more often (arsenic, cobalt, nickel, uranium and zinc), show very poor removal efficiencies (-4.0%-11.5%). Negative removal efficiencies (i.e. higher concentrations in the ozonation effluent than in the ozonation feed water) could be caused by measuring errors or decomposition of larger molecules during ozonation. Average removal efficiency of all thirteen metals is 14.4%. When only the metals that have been analyzed more often are included, the average removal efficiency is only 3.6%.

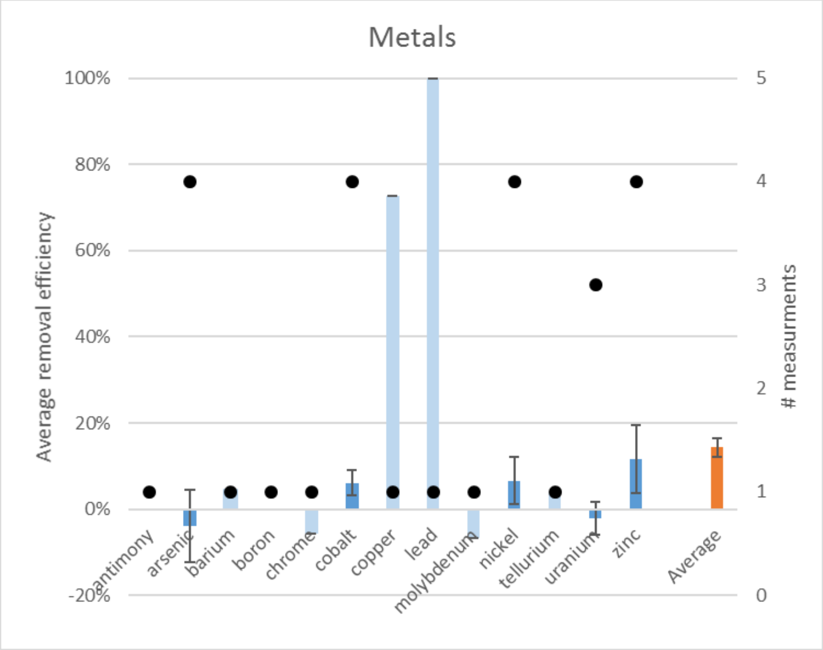


Figure 43 - Removal efficiency of metals

Bromate

This final section answers the fifth research question: *is bromate formed during ozonation? If yes, will it be removed during biological sand filtration?* Since the result of the bioassays are not yet available, this research question only addresses the formation of bromate and not toxicity in general. Section 6.2.3 discussed that no bromate has been reported in the ozone dosage experiments. This was unexpected, since a high ozone dosage has been applied to ozonation feed water with a high bromide concentration (see Table 8 in section 6.2.3).

Table 20 - Bromide and bromate concentrations in long run test

Feed water		#1	#2	#3	#4	#5	#6	#7
bromide	**ug/l**	450	680	400	n/a	600	n/a	n/a
bromate	**ug/l**	n/a*	n/a	n/a	n/a	<1.0	n/a	n/a

Ozonation effluent		#1	#2	#3	#4	#5	#6	#7
bromide	**ug/l**	390	650	370	n/a	560	n/a	n/a
bromate	**ug/l**	<10	n/a	n/a	n/a	63	n/a	n/a

Sand filter effluent		#1	#2	#3	#4	#5	#6	#7
bromide	**ug/l**	390	670	390	310	580	570	n/a
bromate	**ug/l**	n/a	n/a	n/a	8.5	56	37	n/a

**not available, meaning that the measurement has not been done*

In the long run test, bromide concentrations in the ozonation feed water were again relatively high (400-680 µg/l, see Table 8). Interestingly (and for HH Delfland unfortunately), in four out of three out of four measurements, bromate *has* been found. The ozone dosage during the fifth measurement was 0.95 $gO_3/gDOC$.

This dosage is lower than the highest dosage of the ozone dosage experiments, in which no bromate has been found. Bromate is found in the sand filtration effluent in measurement 4, 5 and 6 with a maximum concentration of 63 µg/l (see Figure 44). This concentration is high above the WHO drinking water standard of 10 µg/l and Dutch drinking water standard of 1 µg/l and even above the environmental quality standard of 50 µg/l as proposed by EAWAG (EAWAG, 2015).

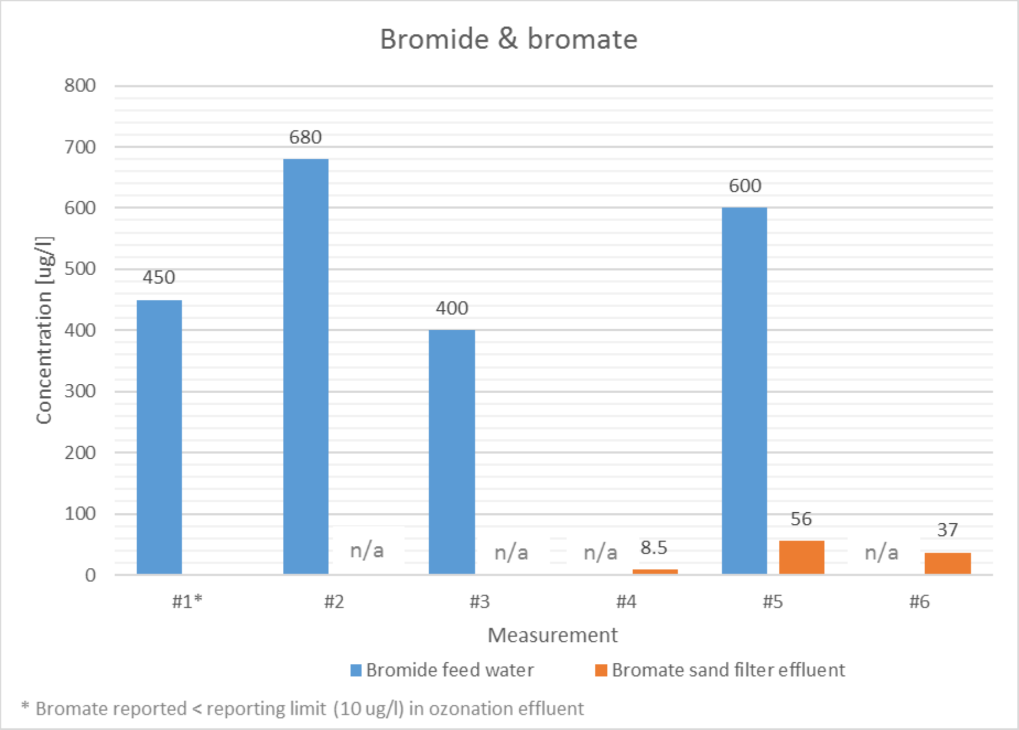


Figure 44 - Bromide and bromate concentrations in the long run test

Figure 44 shows that a lot of information on bromide and bromate is missing. For the first measurement, the feed water bromide concentration is 450 µg/l. The measurement of bromate in the ozonation feed water reported ‘below reporting limit’ of 10 µg/l. In measurement 2 and 3, no measurement on bromate is done. Measurements 4 and 6 do measure bromate (in the sand filter effluent), but do not conduct the measurement on bromide. Measurement 5 provides the most information, with a feed water bromide concentration and bromate concentrations in the ozonation and sand filter effluent (see Figure 45).

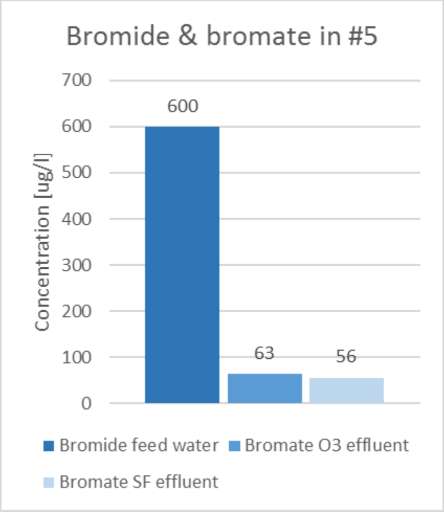


Figure 45 - Bromide and bromate concentrations in measurement 5

Figure 45 shows that the ozonation treatment has a bromate yield of 10.5% µg BrO_3^-/µg Br^-. This bromate yield corresponds with the bromate yield as observed by Margot et al. (2013) and Gerrity et al. (2011) (see Table 8 on page 42). As discussed above, a bromate ozonation effluent concentration of 63 µg/l is quite high. As expected, the concentration of bromate is hardly decreased during biologically active sand filtration. The sand filter effluent concentration is 56 µg/l, still above the proposed environmental quality standard of 50 µg/l (EAWAG, 2015). It remains unknown why no bromate is found in the ozone dosage tests (with maximum 1.31 gO_3/gDOC) while it *is* found in the long run test (0.63 µg/l bromate found with 0.95 gO_3/gDOC).

Measurement 5 gives a clear image of the formation and fate of bromate. However, the resulting image is only based on one measurement. More insight is required into the formation of bromate in the pilot experiments, to decide on a full-scale application.

A concentration of 56 µg/l could be too high to discharge on the internal water system (and eventually on the Krabbeplas). The ozone dosage could be reduced to prevent formation of bromate. Section 6.4 discussed that HH Delfland applies a rather high ozone dosage. However, lowering the ozone dosage will impact the OMP removal efficiency. Other strategies are also available to lower bromate formation, for instance lowering pH, dosing ammonium or hydrogen peroxide (IJpelaar, 2016).

7.1.3 Summary of observed OMP removal

To summarize, the long run test has showed that pharmaceuticals, pesticides and corrosion inhibitors are generally well removed by ozonation (see Figure 46). Contrast media show variable removal which results in high standard deviations. As expected, metals remain untouched by ozonation (see section 2.1). The total average removal efficiency of all detected OMPs is 91.5%. The removal efficiency is in line with the trend line drawn in Figure 36.

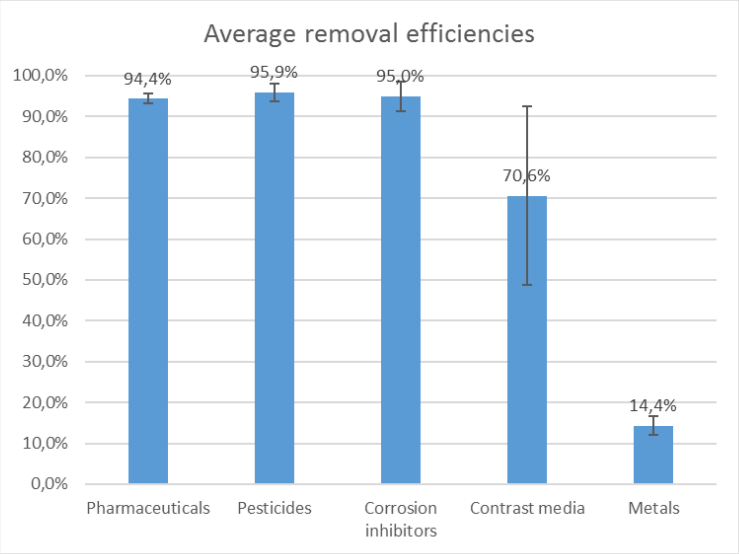


Figure 46 - Average removal efficiencies per group

7.2 Prediction of OMP removal by literature

Section 7.2.1 attempts to predict the removal of the 71 OMPs analyzed in the previous section. Next, section 7.2.2 evaluates the ability to predict the observed OMP removal efficiencies with values found in literature.

7.2.1 Removal efficiencies obtained from literature

Removal efficiencies of 27 OMPs have been found in scientific literature. Table 21 presents an overview of these 27 OMPs with removal efficiencies and the sources in which these are found. While removal efficiencies of 44 OMPs have not been found, some other OMPs have been reported multiple times, e.g. carbamazepine, diclofenac, iopromide and sulfamethoxazole.

The different sources from which removal efficiencies have been obtained, all have different research set-ups and use different ways of reporting. Section 6.3 has discussed differences in research set-up of Antoniou et al.

(2013) and Snyder et al. (2006). A wide variety of aspects can differ in a research, for instance scale (bench scale, pilot scale or full scale), ozone dosing (normally 0.2 – 1.4 $gO_3/gDOC$) or DOC concentrations. Also, the method of reporting and comparing ozonation performance can be completely different. For instance, Margot et al. (2013) report average removal efficiencies with their standard deviations (see Table 21) at ozone doses between 2.3 – 9.0 mg/l with median 5.9 mg/l (0.3-1.2 $gO_3/gDOC$ with median 0.8 $gO_3/gDOC$ (7.3 mg/l DOC)). Antoniou et al. (2013) uses a different method to compare removal of OMPs. The research presents a O_3/DOC ratio required to remove 90% of the pharmaceuticals can be compared. Antoniou et al. (2013) categorize pharmaceuticals in three groups: easily degradable (90% removal of an OMP with $O_3/DOC < 0.7$), moderately degradable (90% removal with $0.7 < O_3/DOC < 1.4$) and recalcitrant towards O_3-treatment (90% removal with $O_3/DOC > 1.4$). Snyder et al. (2006) use four categories for OMPs (>80%, 80-50%, 50-20% and >20%), based on removal with 0.3-1.2 $gO_3/gDOC$.

The different research set-ups and methods of reporting and comparing, makes it virtually impossible to predict one removal rate for an OMP for the situation of HH Delfland. For this reason, this research choses to divide OMPs in three categories to give an *indication* of expected removal efficiencies. The categories are >80% removal, 80-50% removal and <50% removal. This prediction serves to provide an idea whether an OMP is easily removed during ozonation or not. With strict water quality standards and different ozone dosages, prediction based on literature will not suffice to find whether a full scale ozonation installation lead to the desired effluent quality.

Table 21 shows that twelve OMPs are expected to have removal efficiencies higher than 80%. All of these easily degradable OMPs are pharmaceuticals, except for the pesticide oxamyl. Nine pharmaceuticals are expected to be removed for 50-80%. These nine OMPs are pharmaceuticals, pesticides and a corrosion inhibitor. Six OMPs are expected to have a removal efficiency below 50%. Four are contrast media and two are pharmaceuticals (gabapentin and oxazepam). Oxazepam is regarded recalcitrant towards ozone treatment by both Antoniou et al. (2013) and Margot et al. (2013). The latter research even finds a removal efficiency as low as 9%.

Table 21 - Predicted range of removal based on literature

OMP	Group	Removal efficiency reported	Sources	Category removal
1,2,3-benzotriazole	Corrosion inhibitor	64% +/- 14%	Margot 2013	50-80%
2-methyl-4-chlorophenoxyacetic acid	Herbicide	77.0%	Reungoat 2010	50-80%
bezafibrate	Pharmaceutical	81% +/- 8%	Margot 2013	>80%
carbamazepine	Pharmaceutical	>80%, easily degradable, 97% +/- 4%	Snyder 2006, Antoniou 2013, Margot 2013	>80%
carbendazim	Fungicide	79% +/- 17%	Margot 2013	50-80%
claritromycine	Pharmaceutical	93% +/- 4%	Margot 2013	>80%
clindamycine	Pharmaceutical	99% +/- 1%	Margot 2013	>80%
diclofenac	Pharmaceutical	>80%, easily degradable, 94% +/- 3%	Snyder 2006, Antoniou 2013, Margot 2013	>80%
diethyltoluamide	Insecticide	50-80%, 15-65%	Snyder 2006, Nakada 2007	50-80%
diuron	Herbicide	60%, moderately degradable	Reungoat 2012, Lee 2012	50-80%
gabapentin	Pharmaceutical	38% +/- 16%	Margot 2013	<50%
hydrochlorothiazide	Pharmaceutical	40-80%	Reungoat 2012	50-80%
iohexol	Contrast media	38% +/- 16%	Margot 2013	<50%
iomeprol	Contrast media	43% +/- 12%	Margot 2013	<50%
iopamidol	Contrast media	42% +/- 13%	Margot 2013	<50%
iopromide	Contrast media	20-50%, 34% +/- 19%, recalcitrant	Snyder 2006, Margot 2013, Lee 2012	<50%
irbesartan	Pharmaceutical	moderately degradable, 51%	Antoniou 2013, Margot 2013	50-80%
lidocaïne	Pharmaceutical	moderately degradable	Lee 2012	50-80%
metoprolol	Pharmaceutical	moderately degradable, 88% +/- 8%	Antoniou 2013, Margot 2013	>80%
oxamyl	Pesticide	80-100%	Al-Abbas 2014	>80%
oxazepam	Pharmaceutical	recalcitrant, 9%	Antoniou 2013, Margot 2013	<50%
pentoxifylline	Pharmaceutical	>80%	Snyder 2006	>80%
phenazone (antipyrine)	Pharmaceutical	100.0%	Rosal 2010	>80%
sotalol	Pharmaceutical	99% +/- 1%	Margot 2013	>80%
sulfamethoxazol	Pharmaceutical	>80%, moderately degradable, 93% +/- 7%	Snyder 2006, Antoniou 2013, Margot 2013	>80%
trimethoprim	Pharmaceutical	>80%, 99% +/- 2%	Snyder 2006, Margot 2013	>80%
valsartan	Pharmaceutical	61.0%	Margot 2013	50-80%

7.2.2 Ability to predict OMP removal compared to literature range

Table 22 shows the observed removal efficiency (third column) and the removal efficiency obtained from literature (fourth column). As discussed in section 7.2, scientific research uses a wide variety of research set-ups and methods of reporting and comparing of removal efficiencies. For this reason, this research divides OMPs in three categories to give an *indication* of expected removal efficiencies. The fifth column of Table 22 evaluates whether the observed removal falls within the expected range of removal. In total, observed removal efficiency of 12 out of 27 OMPs fall within the range that was expected based on literature. However, observed removal of 15 OMPs do not fall within the expected range. Interestingly, observed removal efficiency is for all these 15 OMPs higher than the expected range. This could be explained by the high ozone dosage at which HH Delfland has conducted the long run test (see a discussion on the choice of the ozone dosage in section 6.2.4). HH Delfland is applying an ozone dose of 0.95 gO_3/gDOC while scientific research often applies lower ozone doses in their experiments.

As a check, the expected removal efficiencies based on literature and the modelled removal efficiencies are compared. This gives a similar image: for only 10 out of 21 OMPs that can be predicted both by literature and by modelling, the modelled removal efficiency falls within the expected range based on literature.

Apparently, the categorization of OMPs in three categories, based on findings in scientific literature, cannot adequately indicate the removal efficiency. Two explanations could be given: that conditions in different scientific researches differ too much to predict individual OMP removal or that individual removal will always show different results based on different water matrixes. It has been discussed that treatment conditions, most importantly ozone dosage, differ a lot in various studies. An OMP that is hardly removed (<50%) with a dosage of, for instance, 0.5 gO_3/gDOC, might be better removed (50-80%) with the ozone dosage applied by HH Delfland (0.95 gO_3/gDOC). Other differences in conditions are DOC concentrations and contact time. The next section will evaluate the ability to predict OMP removal by modelling.

Table 22 – Comparison of observed removal and predicted removal based on literature

OMP	Group	Observed removal	Removal in literature	In agreement?
1,2,3-benzotriazole	Corrosion inhibitor	91.8%	50-80%	NO
2-methyl-4-chlorophenoxyacetic acid	Herbicide	100.0%	50-80%	NO
bezafibrate	Pharmaceutical	100.0%	>80%	YES
carbamazepine	Pharmaceutical	100.0%	>80%	YES
carbendazim	Fungicide	100.0%	50-80%	NO
claritromycine	Pharmaceutical	100.0%	>80%	YES
clindamycine	Pharmaceutical	100.0%	>80%	YES
diclofenac	Pharmaceutical	100.0%	>80%	YES
diethyltoluamide	Insecticide	95.6%	50-80%	NO
diuron	Herbicide	100.0%	50-80%	NO
gabapentin	Pharmaceutical	80.9%	<50%	NO
hydrochlorothiazide	Pharmaceutical	100.0%	50-80%	NO
iohexol	Contrast media	93.8%	<50%	NO
iomeprol	Contrast media	52.8%	<50%	NO
iopamidol	Contrast media	100.0%	<50%	NO
iopromide	Contrast media	76.9%	<50%	NO
irbesartan	Pharmaceutical	92.7%	50-80%	NO
lidocaïne	Pharmaceutical	100.0%	50-80%	NO
metoprolol	Pharmaceutical	99.9%	>80%	YES
oxamyl	Pesticide	100.0%	>80%	YES
oxazepam	Pharmaceutical	90.5%	<50%	NO
pentoxifylline	Pharmaceutical	100.0%	>80%	YES
phenazone (antipyrine)	Pharmaceutical	100.0%	>80%	YES
sotalol	Pharmaceutical	100.0%	>80%	YES
sulfamethoxazol	Pharmaceutical	100.0%	>80%	YES
trimethoprim	Pharmaceutical	100.0%	>80%	YES
valsartan	Pharmaceutical	98.4%	50-80%	NO

7.3 Prediction of OMP removal by modelling

This section aims to predict OMP removal of the 71 OMPs detected in the long run tests. The equation of Hollender et al. (2009) and Lee and von Gunten (2016) is used for this purpose. Section 7.3.1 will first explain the equation, before section 7.3.2 discusses the results of the model. Section 7.3.3 will discuss the ability of the model to predict the observed OMP removal efficiencies.

7.3.1 Explanation of equation

Hollender et al. (2009) and Lee and von Gunten (2016) calculate the predicted removal of OMPs from ozone and hydroxyl radical exposures and second-order rate constants for the reaction with ozone (k_{O3}) and OH radicals (k_{OH}). The kinetics of OMP removal are formulated by equation 1 below:

$$-\frac{d[S]t}{dt} = (k''_{O3}[O_3]_t + k''_{OH}[{}^{\cdot}OH]_t) * [S]_t \qquad (eq.1)$$

Integration of the equation above over the reaction time in an ideal batch or plug-flow reactor yields (Lee and von Gunten, 2016):

$$\frac{[S]}{[S_0]} = e^{-k''_{O3}\int[O_3]dt - k''_{OH}\int[OH]dt} \qquad (eq.2)$$

$In\ which:$

$[S] = concentration\ of\ organic\ micropollutant\ [\mu g/l]$

$[S_0] = ozonation\ feed\ water\ concentration\ of\ organic\ micropollutant\ [\mu g/l]$

$k_{O3} = second - order\ rate\ constant\ of\ compound\ with\ ozone\ [M^{-1}s^{-1}]$

$k_{OH} = second - order\ rate\ constant\ of\ compound\ with\ hydroxyl\ radicals\ [M^{-1}s^{-1}]$

$\int[O_3]dt = ozone\ exposure\ [Ms]$

$\int[OH]dt = hydroxyl\ radical\ exposure\ [Ms]$

OMP removal efficiency can be predicted if the two second-order rate constants (i.e. k_{O3} and k_{OH}) and the two exposures (i.e. $\int[O_3]dt$ and $\int[OH]dt$) are known (Lee and von Gunten, 2016). In order to predict the OMP concentration in the effluent, the OMP concentration of the ozonation feed water should also be known.

7.3.1.1 Second-order rate constants with ozone and hydroxyl radicals

As discussed in section 4.2, OMP removal occurs by oxidation by both ozone and hydroxyl radicals (Lee and von Gunten, 2016). The kinetics of the reactions of ozone with inorganic and organic compounds is typically second order, i.e. first order in ozone and first order in the compound (Von Gunten, 2003). The second order rate constants are independent of the exposures to ozone and $^{\cdot}OH$. This means that they can be obtained independently of the water matrices, for instance in laboratory scale experiments (Lee and von Gunten, 2016).

On the one hand, a lot of research has been done on reaction kinetics and mechanisms, which resulted in elaborate papers on transformation pathways (Von Gunten, 2003) and ‘several hundred’ (Lee, 2017) or even a thousand (Lee and von Gunten, 2016) empirically determined second-order rate constants (among others presented in Hollender et al., 2009). But on the other hand, scholars argue that limited empirical information is available on the kinetics and mechanisms of the reaction of micropollutants with ozone. This would hamper the assessment of the abatement efficiency and the formation of transformation products during ozonation of micropollutants (Lee, 2017). Due to the numerous and ever increasing number of chemicals detected in natural waters, an empirical determination of reaction kinetics and transformation products is a ‘formidable task to be achieved’ (Lee, 2017).

Second order rate constants for the reaction of the OMP with ozone (k_{O3})

As explained in section 4.2.2 on the reaction mechanisms of ozonation, OMPs react selectively with ozone. OMPs with electron-rich moieties, such as phenols, anilines, olefins, reduced sulfur and neutral amine moieties, react rapidly with ozone (Lee and von Gunten, 2016). Hollender et al. (2009) find that activated aromatic moieties, amine functions, or double bonds such as sulfamethoxazole, diclofenac, or carbamazepine are eliminated well by ozone. The rate constants vary widely per OMP. The range of k_{O3} spans over more than 11 orders of magnitude, from $<10^{-2}$ $M^{-1}s^{-1}$ to 10^9 (Lee, 2017). Compounds with k_{O3} values of $>10^4$ M^{-1} s^{-1} are expected to be removed well (Hollender et al., 2009). The k_{O3} values increase for ionizable compounds such as phenols and amines with higher pH, due to the higher ozone reactivity of the deprotonated/neutral forms of phenolic and amine moieties (Lee and von Gunten, 2016). The reaction constant of other functional groups is not dependent on pH. The k_{O3} values are known for a few hundred OMPs (Lee and von Gunten, 2016).

Lee et al. (2017) have developed a prediction platform of reaction kinetics and transformation products [K_{O3}], which can supplement empirical data. The prediction platform is currently not yet online available, but according to professor Von Gunten, a 'web-based version should become available in the near future' (Von Gunten, 2017).

This research has made use of the in scientific research empirically determined k_{O3} values. Literature has provided 24 k_{O3} values of OMPs detected in the long run test of HH Delfland (see Table 23). As expected, k_{O3} values have been found in a wide range of $5.0*10^{-2}$ $M^{-1}s^{-1}$ (amidotrizoic acid) to $2.5*10^{6}$ $M^{-1}s^{-1}$ (sulfamethoxazole). pH values for most measurements are presented in the third column. When possible, the k_{O3} value obtained though experiments with pH values as close to the pH of ozonation feed water in the HH Delfland pilot have been chosen (pH = 7).

Table 23 - kO3 values found in literature

OMP	kO3 [M-1 s-1]	pH	Source
1,2,3-benzotriazole	2.00E+01		Leitner 2010
2-methyl-4-chlorophenoxyacetic acid	4.77E+01	2	Reungoat 2010
amidotrizoic acid	5.00E-02		Lee 2015
bezafibrate	5.90E+02	7	Huber 2003
carbamazepine	3.00E+05	7	Huber 2003
claritromycine	4.00E+04	7	Lee 2014
diclofenac	1.00E+06	7	Huber 2003
diethyltoluamide	5.70E-02	6.5	Tay 2009
diuron	1.47E+01	4	Reungoat 2012
gabapentin	2.20E+02	7	Lee 2014
hydrochlorothiazide	5.11E+03	7	Reungoat 2012
iomeprol	8.00E-01		Lee 2015
iopamidol	8.00E-01		Lee 2015
iopromide	8.00E-01	7	Huber 2003
lidocaïne	7.30E+04	7	Lee 2014
methyl-1H-benzotriazole	1.64E+02		Lee 2015
metoprolol	2.00E+03	7	Lee 2014
oxamyl	6.20E+02		Yao 1991
oxazepam	1.00E+00	7	Lee 2014
phenazone (antipyrine)	5.17E+04	7.9	Miao 2015
sotalol	1.90E+04	7	Lee 2014
sulfamethoxazol	2.50E+06	7	Huber 2003
trimethoprim	2.70E+05	7	Reungoat 2012
valsartan	3.80E+01	7	Lee 2014

Second order rate constants for the reaction of the OMP with hydroxyl radicals (k_{OH})

Hydroxyl radicals react less selectively with OMPs, compared to ozone and react rapidly with most compounds (see section 4.2.2 on ozonation). The three reaction mechanisms of $^{\cdot}OH$ with OMPs have previously been described (see section 4.2.2) as addition, hydrogen abstraction and electron transfer. The first reaction mechanism is usually the fastest with a close to diffusion-controlled rate constant of $>5*10^{9}$ M^{-1} s^{-1} (Lee and von Gunten, 2016; Hollender, 2009).

Three options are available to obtain the k_{OH} values for relevant OMPs. Firstly, the k_{OH} can be predicted by a group contribution method (GCM), in which the k_{OH} is estimated per reaction mechanism. Based on the three mechanisms described above, k_{OH} values have been determined for i) hydrogen abstraction, ii) addition to olefins, iii) addition to aromatic compounds and iv) addition to N, P, and S moieties (Lee and von Gunten, 2016). A 'group rate constant' and a 'group contribution factor' have been assigned to each of the four reaction mechanisms mentioned above. The total k_{OH} value is obtained by the sum of individual k_{OH} values per reaction mechanisms, corresponding to the substructures of an OMP (Lee and von Gunten, 2016). Research of Minakata et al. (2009) has showed that the GCM method can predict the experimental k_{OH} values within a factor of 2 compared to the measured k_{OH} values (Lee and von Gunten, 2016).

Secondly, k_{OH} values have been empirically obtained in scientific research. More than a thousand k_{OH} values have been found for organic components and OMPs (Lee and von Gunten, 2016). This method has been used to find k_{O3} values in the previous section.

Thirdly, Von Gunten (2017) proposes a simpler method to determine k_{OH} values. He mentions the rule of thumb that the larger the molecule, the higher the k_{OH} value will be (Von Gunten, 2017). For large molecules, second order rate constants approach 10^{10} $M^{-1}s^{-1}$, whereas for smaller molecules it is closer to 10^9 $M^{-1}s^{-1}$ or lower. For average sized molecules, a value of about $5*10^9$ $M^{-1}s^{-1}$ is usually a good guess (Von Gunten, 2017).

This research has made use of the in scientific research empirically determined k_{OH} values. The group contribution method is complex to use, since a lot of insight is required into the chemical compositions of OMPs and their reaction mechanisms. Therefore, using the k_{OH} values that have been experimentally determined in scientific research is regarded as more practical. k_{OH} values of 18 OMPs have been found in scientific literature, from sources such as Lee et al. (2014) and Huber et al. (2003). However, it has been noted that k_{OH} values are less apparent in scientific literature than k_{O3} values. For eight OMPs, only the k_{O3} value has been found. Since both the k_{O3} and k_{OH} are required to model the predicted removal efficiency, the missing k_{OH} values for these eight OMPs have been estimated based on the rule of thumb of Von Gunten (2017) (see 'Von Gunten, 2017' in the fourth column of Table 24). Estimation with this rule of thumb provides an acceptable level of accuracy of k_{OH} values for this research.

Table 24 shows that k_{OH} values of most OMPs are between 10^9 and 10^{10}. Three exemptions can be observed: imidacloprid, metformin and metroprolol. These substances have a k_{OH} value of $1.29*10^5$, $1.0*10^7$ and $8.6*10^5$ respectively.

Table 24 - kOH values found in literature

OMP	kOH [M-1 s-1]	pH	Source
1,2,3-benzotriazole	1.07E+10	6.25	Leitner 2010
2-methyl-4-chlorophenoxyacetic acid	6.60E+09	9	Reungoat 2010
amidotrizoic acid	5.00E+09		Von Gunten 2017
bezafibrate	7.40E+09	7	Huber 2003
carbamazepine	8.80E+09	7	Huber 2003
carbendazim	2.20E+09		Minakata [2] 2009
claritromycine	5.00E+09		Lee 2014
diclofenac	7.50E+09	7	Huber 2003
diethyltoluamide	5.00E+09		Von Gunten 2017
diuron	7.10E+09		Minakata 2009
gabapentin	9.10E+09		Lee 2014
hydrochlorothiazide	5.70E+09	3	Reungoat 2012
imidacloprid	1.29E+05		Turabik 2014
iomeprol	3.30E+09		Von Gunten 2017
iopamidol	3.30E+09		Von Gunten 2017
iopromide	3.30E+09	7	Huber 2003
lidocaïne	1.00E+10		Von Gunten 2017
metformin	1.00E+07		Khouri 2004
metoprolol	8.60E+05		Lee 2014
oxamyl	1.00E+10		Von Gunten 2017
oxazepam	9.10E+09		Lee 2014
phenazone (antipyrine)	5.00E+09		Von Gunten 2017
sotalol	1.00E+10		Lee 2014
sulfamethoxazol	5.50E+09	7	Huber 2003
trimethoprim	6.50E+09	7	Reungoat
valsartan	1.00E+10		Von Gunten 2017

7.3.1.2 Exposure of compounds to O_3 and ·OH

OMP removal efficiency depends, next to the reactivity of the OMP towards ozone and ·OH, on the exposure of the OMP to ozone and ·OH. The exposure is captured by $\int[O_3]dt$ and $\int[OH]dt$ and is related to the stability of ozone and ·OH in a given water matrix (Lee and von Gunten, 2016). HH Delfland does not analyze the ozone and hydroxyl radical exposure in the pilot experiment. The only data available on the ozone present in the water is the ozone dosage applied (0.95 gO_3/gDOC). However, this section will discuss extensive efforts of Lee and Von Gunten to predict ozone and ·OH exposure based on the ozone dosage.

Exposure to ozone

Exposure to ozone can be determined by integrating the ozone decay curves over time (Lee and Von Gunten, 2016). Hollender et al. (2009) describe a laboratory analysis to determine the exposure of compounds to ozone. Ozone is added to a sample in a laboratory, after which the residual ozone is measured in time intervals of 10 seconds. Ozone exposure is defined as the integral of the decay curve of ozone (Hollender et al., 2009). The decay of ozone depends on various water quality parameters such as DOC, alkalinity, pH and temperature. As explained in section 4.2.2 on reaction mechanisms of ozone, the decomposition of ozone occurs in two phases: instantaneous ozone demand and remaining demand. Lee and von Gunten (2016) have plotted ozone exposure as function of the specific ozone dose (gO_3/gDOC) as found by five scientific studies (see Figure 47).

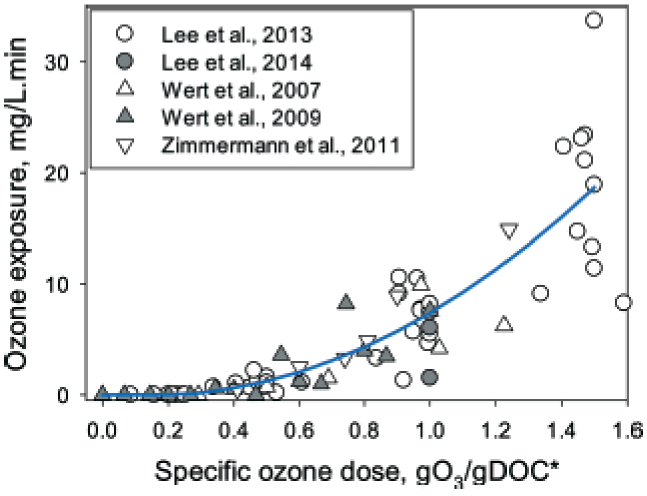


Figure 47 - Ozone exposures as function of specific ozone dose (Lee and Von Gunten, 2016)

Two aspects of Figure 47 are noteworthy: regarding variability and 'zero' ozone exposure at low specific ozone doses. Firstly, the researchers find quite variable (more than a factor 4) ozone exposures for the same specific ozone dose. The variation is caused by differences in DOC, alkalinity and pH (Lee and von Gunten, 2016). Secondly, the graph shows an unexpected ozone exposure of 'zero' with a specific ozone dose <0.3 gO_3/gDOC. The fact that 'zero' exposure is measured is due to the complete ozone consumption (i.e. instantaneous ozone demand, see above) before the first experimental measurement (after 10 seconds). However, at these low specific ozone doses still significant elimination of OMPs is found during wastewater ozonation. This indicates that the actual ozone exposure is not 'zero' at low specific ozone doses. Rather, a more accurate measurement of ozone decay is required (Lee and von Gunten, 2016).

Lee and von Gunten (2016) have derived an empirical equation from the fitting of the measured data from literature (see the line in Figure 47). This equation can be used to roughly estimate the ozone exposure for a given ozone dose. Due to the complex ozone chemistry in wastewater, prediction of ozone exposure is currently only possible by curve fitting with large uncertainty (factor 4) (Lee and von Gunten, 2016). The equation of ozone exposure as function of the specific ozone dose is as follows (fit of Figure 47):

$$O_3 exposure\ [Ms] = f_{O3} * (\frac{gO_3}{gDOC})$$

$$= (1.3 * 10^{-7})\exp(25 * \frac{gO_3}{gDOC})$$

$$for\ 0 < \frac{gO_3}{gDOC} \leq 0.3$$

And:

$$O_3 exposure\ [Ms] = (1.3 * 10^{-2}) * \left(\frac{gO_3}{gDOC} - 0.3\right)^2 + (3.8 * 10^{-3}) * \left(\frac{gO_3}{gDOC} - 0.3\right) + (3.0 * 10^{-4})$$

$$for\ \frac{gO_3}{gDOC} > 0.3$$

The specific ozone dose that HH Delfland is using in the long-run test (0.95 $gO_3/gDOC$) can be filled in in the second equation. This yields an ozone exposure of 8.26 $*10^{-3}$ Ms (7.46 mg/L*min).

As discussed in section 7.1 on data analysis, the initial ozone dose of 1.0 $gO_3/gDOC$ has to be corrected for nitrite concentrations. This yields actual ozone doses ranging from 0.9 – 1.0 $gO_3/gDOC$. A different ozone dose will give a different ozone exposure. However, the impact on the ozone exposure is not extraordinary. Table 25 shows that an ozone dose of 0.9 $gO_3/gDOC$ gives an ozone exposure of $7.26*10^{-3}$ while a dose of 1.0 $gO_3/gDOC$ gives an ozone exposure of $9.33*10^{-3}$. With a dose of 1.0 $gO_3/gDOC$ instead of 0.9 $gO_3/gDOC$, an OMP has 28% more ozone exposure. The next section will evaluate the impact on the prediction of the removal efficiency of an OMP.

Table 25 - Ozone exposure at different ozone dosages

Ozone dose [gO3/gDOC]	0.9	0.95	1.0
Ozone exposure [Ms]	7.26E-03	8.26E-03	9.33E-03

Exposure to hydroxyl radicals

Similar to ozone exposure, hydroxyl radical exposure can be determined by integrating the ·OH concentration over the reaction time (Lee and von Gunten, 2016). Due to the instability of hydroxyl radicals a direct measurement of the presence of OH radicals not possible. Therefore, hydroxyl radical exposure must be indirectly determined by adding the ozone resistant compound p-chlorobenzoic acid (pCBA) to a sample (Hollender et al., 2009). pCBA does not react with ozone, but only with ·OH radicals. Research of Hollender et al (2009) used a HPLC-UV-system is used to analyze the concentration of pCBA. The exposure to hydroxyl radicals is determined from the relative decrease of pCBA in the sample.

$$\int [OH]dt = -\frac{\ln\left(\frac{[pCBA]}{[pCBA]_0}\right)}{k_{OH,pCBA}}$$

In which:

$$k_{OH,pCBA} = 5 * 10^9 M^{-1} s^{-1}$$

Again similar to the determination of the exposure to ozone, empirical data of ·OH exposure from various wastewater effluents as function of the specific ozone dose is analyzed by Lee and von Gunten (2016). Figure 48 shows the data points obtained in six scientific researches. Two phases of ·OH exposure can be identified, although less apparent than in ozone exposure. In the range of 0-0.2 $gO_3/gDOC$ the ·OH exposure increases minimally and with higher specific ozone doses the exposure increases significantly. The ·OH exposures in the low specific ozone dose range (0-0.2 $gO_3/gDOC$) is due to the ozone consumption by DOC moieties with low corresponding ·OH formation, such as olefins or tertiary amines (Lee and von Gunten, 2016). ·OH yields in this range are between 0% - 40% of ozone. The second phase starts at specific ozone doses of > 0.2 $gO_3/gDOC$. For these higher specific ozone doses, the theoretical ·OH yield from the ozone reaction is 100%. This means that the ·OH yield is expected to be higher in the high range of specific ozone doses (> 0.2 $gO_3/gDOC$ – second phase) than in the low range (0-0.2 $gO_3/gDOC$ – first phase).

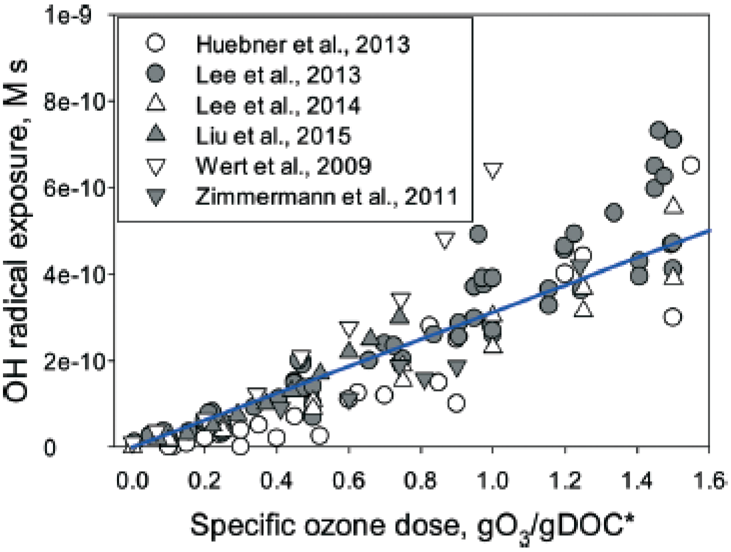


Figure 48 - Hydroxyl exposures as function of specific ozone dose (Lee and Von Gunten, 2016)

Even though Lee and von Gunten (2016) have identified two phases of ·OH exposure, the scholars present one equation to estimate ·OH exposure as a function of the specific ozone dose (see the line in Figure 48 and the equation below).

$$OH\ exposure\ [Ms] = (3.1 * 10^{-10}) * \frac{gO_3}{gDOC}$$

Again the specific ozone dose that HH Delfland is using in the long-run test (0.95 $gO_3/gDOC$) can be filled in in the equation. This yields an ·OH exposure of 2.95 $*10^{-10}$ Ms. Similar to ozone exposure, hydroxyl radical exposure varies at different ozone dosages. The difference between the seven measurements of HH Delfland is 10% at most.

Table 26 - OH exposure at different ozone dosages

Ozone dose [gO3/gDOC]	0.9	0.95	1.0
OH exposure [Ms]	2.79E-10	2.95E-10	3.10E-10

The ·OH/O₃ ratio

The ·OH/O_3 ratio can be used to check the ozone and hydroxyl radical exposure. The ratio of ·OH exposure to O_3 exposure in ozonation installations is extensively researched by Elovitz and von Gunten (1999). The researchers introduce a new parameter R_{ct} to describe the ·OH/O_3 ratio as a function of the reaction time. R_{ct} proved to be a constant value for the majority of the reaction. This results in the expression of R_{ct} as [·OH]/[O_3] (Elovitz and von Gunten, 1999). The R_{ct} is specific to a given water source and can vary from 10^{-7} to 10^{-9} M/M (Von Gunten, 2003).

Given the relatively high DOC concentration in the feed water of the ozonation installation (10.5 mg/l compared to 5.2 ± 0.6 mg/l in research of Hollender (2009)), it is expected that many ·OH radicals are formed. The fact that no measurable bromate is formed, even though incoming bromide concentration is high (see section 6.2.3), is also an indication that the [$^{\cdot}$OH]/[O$_3$] ratio (R_{ct}) is relatively high. The reasoning behind this is that bromide transforms more rapidly to bromate with a high ozone concentration.

Based on the calculations on the ozone and $^{\cdot}$OH exposure, the [$^{\cdot}$OH]/[O$_3$] ratio (R_{ct}) can be determined for the specific wastewater of HH Delfland.

$$\frac{[OH]}{[O_3]} = \frac{(2.9 * 10^{-10} Ms)}{8.26 * 10^{-3} Ms} = 3.56 * 10^{-8}$$

With an R_{ct} value ranging from 10^{-7} to 10^{-9} M/M (Von Gunten, 2003) the Rct found for wastewater of HH Delfland proves to be in range. The R_{ct} of $3.56*10^{-8}$ is somewhat in the higher part of the range, which was expected based on DOC concentrations and the lack of bromate formation.

7.3.2 Results of modelling

Table 27 shows the modelled removed of 22 OMPs. Both the k_{O3} value and k_{OH} value have to be known in order to fill in the equation of Hollender et al. (2009) and Lee and von Gunten (2016). According to this model, most OMPs will be >80% removed with the applied ozone dose in the pilot of HH Delfland. The contrast media iomeprol, iopamidol and iopromide show lower removal efficiencies. These substances both have a low k_{O3} value and k_{OH} value. While metoprolol has a very low reaction rate with hydroxyl radicals, it should still be well removed due to a high reaction rate with ozone.

Table 27 - Predicted removal based on modelling

OMP	Group	kO3 [M-1s-1]	kOH [M-1s-1]	Modelled removal
1,2,3-benzotriazole	Corrosion inhibitor	2.00E+01	1.07E+10	96.4%
2-methyl-4-chlorophenoxyacetic acid	Herbicide	4.77E+01	6.60E+09	90.4%
amidotrizoic acid	Contrast media	5.00E-02	5.00E+09	77.1%
bezafibrate	Pharmaceutical	5.90E+02	7.40E+09	99.9%
carbamazepine	Pharmaceutical	3.00E+05	8.80E+09	100.0%
claritromycine	Pharmaceutical	4.00E+04	5.00E+09	100.0%
diclofenac	Pharmaceutical	1.00E+06	7.50E+09	100.0%
diethyltoluamide	Insecticide	5.70E-02	5.00E+09	77.1%
diuron	Herbicide	1.47E+01	7.10E+09	89.1%
gabapentin	Pharmaceutical	2.20E+02	9.10E+09	98.9%
hydrochlorothiazide	Pharmaceutical	5.11E+03	5.70E+09	100.0%
iomeprol	Contrast media	8.00E-01	3.30E+09	62.5%
iopamidol	Contrast media	8.00E-01	3.30E+09	62.5%
iopromide	Contrast media	8.00E-01	3.30E+09	62.5%
lidocaïne	Pharmaceutical	7.30E+04	1.00E+10	100.0%
metoprolol	Pharmaceutical	2.00E+03	8.60E+05	100.0%
oxamyl	Pesticide	6.20E+02	1.00E+10	100.0%
oxazepam	Pharmaceutical	1.00E+00	9.10E+09	93.2%
sotalol	Pharmaceutical	1.90E+04	1.00E+10	100.0%
sulfamethoxazol	Pharmaceutical	2.50E+06	5.50E+09	100.0%
trimethoprim	Pharmaceutical	2.70E+05	6.50E+09	100.0%
valsartan	Pharmaceutical	3.80E+01	1.00E+10	96.2%

The previous section has discussed the implication of the different ozone dosages (when corrected for nitrite) that are applied in the long run test of HH Delfland. Table 28 shows the result of a small sensitivity check of the modelled removal efficiency of diethyltoluamide (as an example of not fully degraded OMP) at different ozone and hydroxyl radical exposures. As can be seen in Table 27 and Table 28, the average ozone dose of 0.95 gO$_3$/gDOC gives a modelled removal efficiency of 77.1% for diethyltoluamide. The lowest applied ozone dose (0.90 gO$_3$/gDOC) gives 75.2% removal while the highest applied ozone dose gives 78.8% removal (see Table 28). The difference of 3.6 percentage point of the lower and upper bound is something to take in mind, but does not change the average removal efficiency that much. For this research, the average ozone dose of 0.95 $gO_3/gDOC$ will hence be used to compare modelled removal efficiencies with observed efficiencies.

Table 28 - Modelled removal of diethyltoluamide with different exposures

O3 dose [gO3/gDOC]	O3 exposure [Ms]	OH exposure [Ms]	Modelled removal
0.90	7.26E-03	2.79E-10	75.2%
0.95	8.29E-03	2.95E-10	77.1%
1.00	9.33E-03	3.10E-10	78.8%

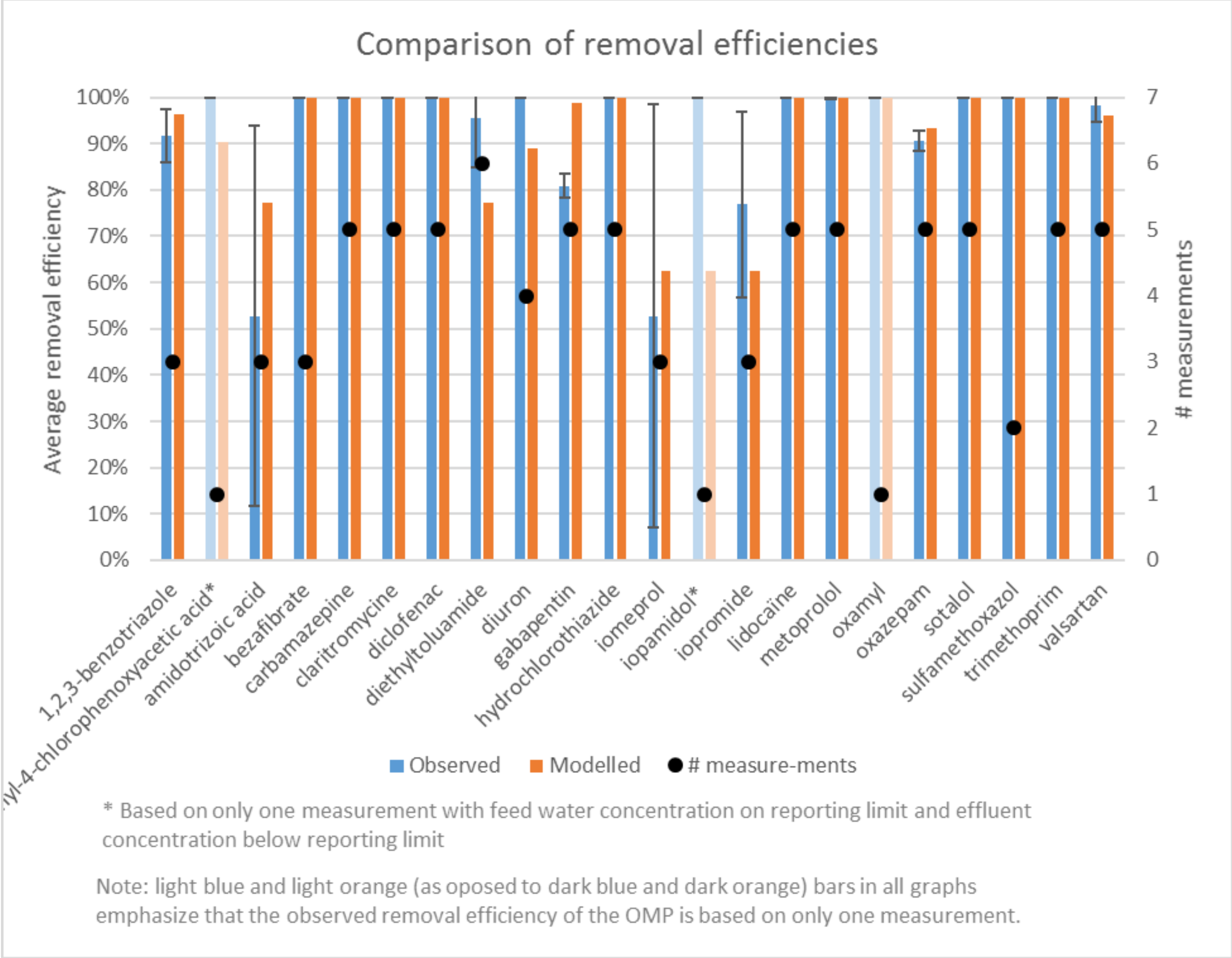
7.3.3 Ability to predict OMP removal compared to modelling

Table 29 and Figure 49 show the observed and modelled removal efficiencies of 22 OMPs. Half of the OMPs have expected removal efficiencies of 100%, which are all confirmed by the observed removal. Two OMPs (2-methyl-4-chlorophenoxyacetic acid and iopamidol) have an observed removal efficiency of 100%, but a lower modelled removal efficiency. However, both observed removal efficiencies have only been determined based on one measurement (see light blue bars in Figure 49). Table 29 also provides the deviation between observed and modelled removal in percentage points and in percentages. Observed and modelled removal efficiencies for most OMPs do not differ much. Average deviation between the two is only 6.9% point or 8.8%. When the three OMPs that have only one measurement are omitted, the average deviation is even as low as 5.6% point or 7.7%.

Only 6 out of 22 OMPs have a modelled removal efficiency that is not within the standard deviation of the observed removal. Of these 6 OMPs, two are based on a single measurement (2-methyl-4-chlorophenoxyacetic acid and iopamidol). For oxazepam, the modelled removal misses the range of standard deviation with 1.5% point (modelled: 96.2%, observed: 98.4% +/- 3.6%). The other 16 OMPs do show similar observed and modelled removal.

Table 29 - Comparison of observed removal and predicted removal based on modelling

OMP	**Observed**	**St. dev.**	**Modelled**	**Deviation (% point)**	**Deviation (%)**
1,2,3-benzotriazole	92%	5.7%	96%	4.6%	5.0%
2-methyl-4-chlorophenoxyacetic acid	100%	0.0%	90%	9.6%	9.6%
amidotrizoic acid	53%	41.1%	77%	24.3%	46.1%
bezafibrate	100%	0.0%	100%	0.1%	0.1%
carbamazepine	100%	0.0%	100%	0.0%	0.0%
claritromycine	100%	0.0%	100%	0.0%	0.0%
diclofenac	100%	0.0%	100%	0.0%	0.0%
diethyltoluamide	96%	10.7%	77%	18.5%	19.3%
diuron	100%	0.0%	89%	10.9%	10.9%
gabapentin	81%	2.6%	99%	18.0%	22.3%
hydrochlorothiazide	100%	0.0%	100%	0.0%	0.0%
iomeprol	53%	45.8%	62%	9.7%	18.4%
iopamidol	100%	0.0%	62%	37.5%	37.5%
iopromide	77%	20.1%	62%	14.4%	18.8%
lidocaïne	100%	0.0%	100%	0.0%	0.0%
metoprolol	100%	0.3%	100%	0.1%	0.1%
oxamyl	100%	0.0%	100%	0.0%	0.0%
oxazepam	90%	2.2%	93%	2.7%	3.0%
sotalol	100%	0.0%	100%	0.0%	0.0%
sulfamethoxazol	100%	0.0%	100%	0.0%	0.0%
trimethoprim	100%	0.0%	100%	0.0%	0.0%
valsartan	98.4%	3.6%	96.2%	2.2%	2.2%



* Based on only one measurement with feed water concentration on reporting limit and effluent concentration below reporting limit

Note: light blue and light orange (as oposed to dark blue and dark orange) bars in all graphs emphasize that the observed removal efficiency of the OMP is based on only one measurement.

Figure 49 - Comparison of observed removal and predicted removal based on modelling

Figure 50 has omitted the OMPs with both 100% observed and 100% modelled removal, to allow a more detailed examination. The figure illustrates that observed and modelled removal are within close range. For five OMPs the modelled removal efficiency is higher than the observed removal. For the other 6 OMPs it is the other way around. It can hence be concluded that the model is not over- or underestimating removal efficiencies compared to the observed removal.

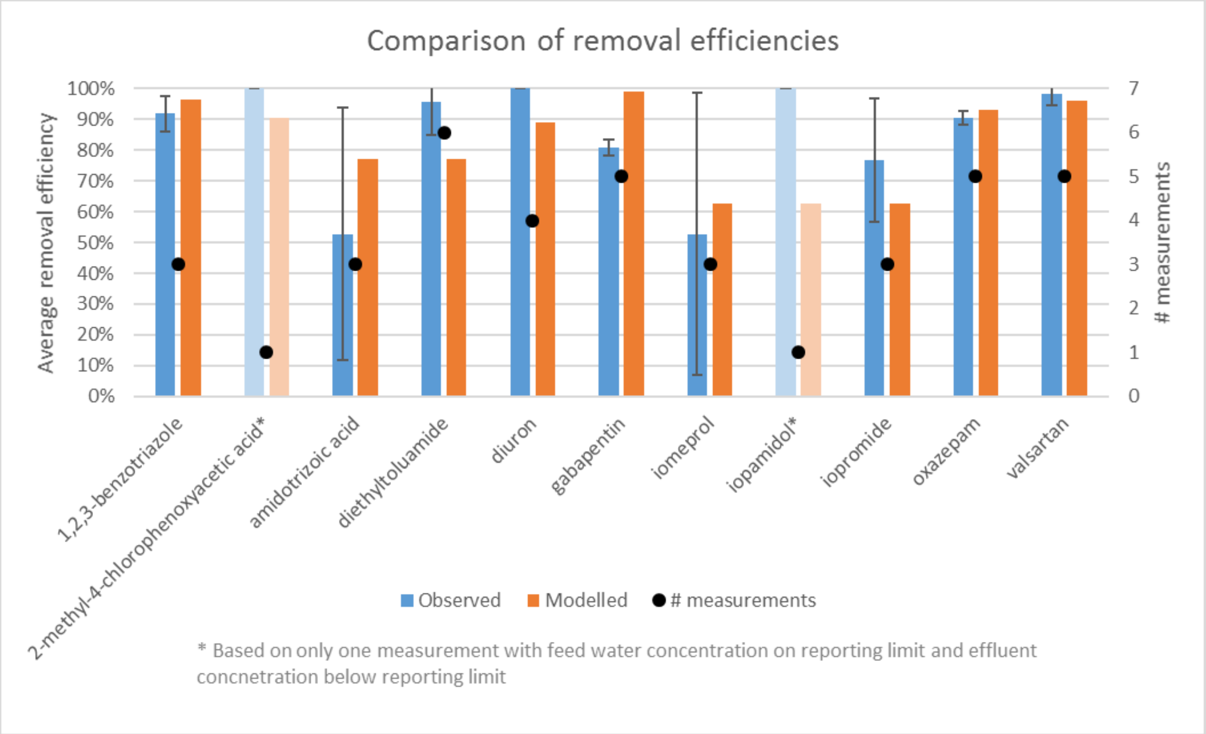


Figure 50 - Observed and predicted removal for not completely removed OMPs

Conclusion

Comparison between modelling and observing individual OMP removal efficiencies has showed that the two methods come up with very similar removal efficiencies. The previous chapter has showed that average removal efficiencies from literature is a good source to determine the average ozone efficiency. The question that is raised in this chapter is whether individual removal efficiencies can be modelled. Based on the data set from the long run test of HH Delfland, it can be concluded that the model gives an adequate prediction of the observed removal efficiencies. This section provides two arguments why removal efficiency *can* be modelled in general. However, there are also three reasons why the claim that the model works well *in general* to predict OMP removal would not hold.

The model *can* accurately predict OMP removal

First, the model has showed fairly good results in predicting the removal efficiencies as observed in the long run test of HH Delfland. The section above has described that modelled removal efficiencies of 16 out of 22 OMPs fall within range of the observed removal efficiency. Also, no strong outliers have been observed in the data set. The modelled prediction of iopamidol has been most far off the observed removal (modelled: 62% removal, observed: 100% removal). However, this comparison is only based on one single measurement and is hence not regarded to be reliable.

Secondly, ozonation experts agree that OMP removal can be accurately predicted, based on the composition of the molecule. Dutch ozone expert Joop Kruithof states that the ability of ozone to remove a compound can be indicated based on the characteristics of the substance (personal communication, June 2017). Lee and von Gunten (2016) find that OMPs with electron-rich moieties, such as phenols, anilines, olefins, reduced sulfur and neutral amine moieties, react rapidly with ozone. Hollender et al. (2009) find that activated aromatic moieties, amine functions, or double bonds are eliminated well by ozone. Also, von Gunten mentioned that second order rate constants of compounds with hydroxyl radicals can accurately be predicted by a simple rule of thumb (personal communication, September 2017). In general, a lot of research on ozonation of OMPs has been conducted in the recent past. These studies have quite similar findings regarding OMP removal by ozonation. It is not likely that one study claims and finds that, for instance, based on substance characteristics, carbamazepine can be easily removed, while another study claims and finds the opposite. With increasing knowledge on reaction mechanisms and second order rate constants, OMP removal efficiency *can* be accurately predicted.

The model *cannot* accurately predict OMP removal

The most important limitation of the claim that OMP removal can be accurately predicted, is that this research is not based on sufficient data for such general claim. Although observed removal efficiencies of 18 out of 22 OMPs is based on three or more measurements (with a maximum of six measurements), it only concerns one ozonation experiment. More data sets are needed to compare modelled and observed removal efficiencies. With comparison with only one research, the agreement between modelled and observed removal could still be based on coincidence. Further research is required to be able to say with more certainty that the model can accurately predict OMP removal.

Secondly, one could argue that the model especially works well for OMPs with high removal efficiencies. All OMPs that were expected to be 100% removed according to the model, did indeed prove to be so by the observed removal. Figure 51 shows that OMPs with high observed removal efficiencies (80-100%) were also accurately predicted, e.g. 1,2,3-benzotriazole (observed: 92%, modelled; 96%), oxazepam (observed: 90%, modelled; 93%) and valsartan (observed: 98%, modelled; 96%). However, OMPs with lower observed removal are less accurately predicted. Figure 51 illustrates that the blue circle in the lower removal efficiency range is a lot wider than the blue circle in the top right corner, with high removal efficiencies. An OMP that is less well predicted by modelling, is for instance amidotrizoic acid (observed: 53%, modelled; 77%).

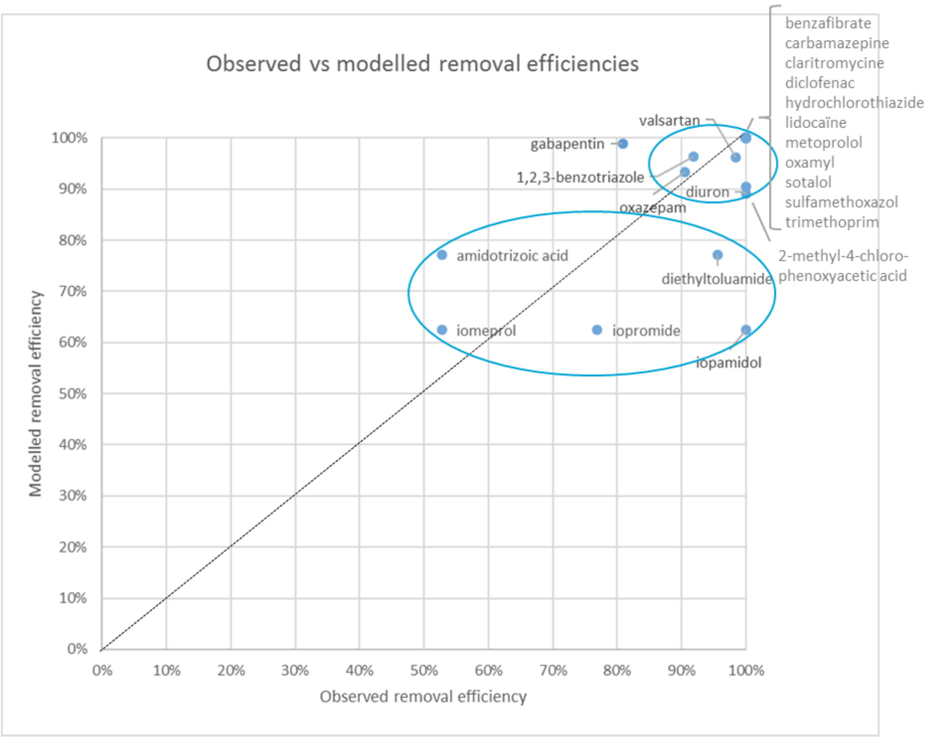


Figure 51 - Modelled vs observed removal efficiency

Finally, water quality standards of priority substance are so strict, that small deviations between modelled and observed removal can matter. Reporting limits of OMPs are in the range of tens of nanograms per liter (0.01 µg/l) and water quality standards are too. A small deviation of modelled and observed removal can determine whether water effluent concentrations meet water quality standards or not. In order to prove that wastewater effluent is of good quality, measurements are still required.

To conclude, the model has showed accurate predictions of observed OMP removal efficiencies for the long run test of HH Delfland. With progressive research on ozonation of treated wastewater, more and more is known about removal mechanisms and efficiencies. However, the model has currently only been tested on one data set from research of HH Delfland. More research is required to extent this claim to other researches. Furthermore, the predictability of easily removed OMPs is especially accurate, while removal efficiencies of recalcitrant OMPs are harder to predict. Finally, to prove that water quality standards of wastewater effluent and surface waters are met, measurements of OMP concentrations will still be required. Chapter 8 will summarize conclusions and provide further recommendations.

8 Conclusions

In this chapter, the answers to the research questions (see section 1.2) are summarized. The first research question, on operating parameters and removal mechanisms of ozonation and biofiltration, has been answered based on literature study. An overview of the parameters and mechanisms can be found in Chapter 4. The other four research questions are answered below.

Research question 2: What is the optimal ozone dosage found during pilot conditions and what does comparison with similar studies in research tell us? Could ozone dosage have been based on literature?

The optimal ozone dose is a balance between effectively removing OMPs (i.e. high ozone dose), preventing toxic by-product formation (i.e. low ozone dose) and limiting the operational costs (energy) (i.e. low ozone dose). Based on the ozone dosage experiments, HH Delfland has chosen an **ozone dosage of 1.0 gO_3/gDOC**. This dosage gives an average removal efficiency of 92% with operational costs of €119.000 per year. This research however proposes a lower **ozone dosage of 0.7 gO_3/gDOC**, which gives a **removal efficiency of 80%** and €82.000 operational costs. The lower ozone dosage still gives an adequate OMP removal (80%), lowers the risk of bromate formation, reduces operational costs with 45% and total costs with 4% and reduces energy consumption (7.0% extra energy consumption of the WWTP instead of 10.4%).

Ozone dosage experiments of Antoniou et al. (2013), Snyder et al. (2006) and Lee et al. (2012) show similar average removal efficiency curves to HH Delfland experiments. Removal efficiencies of individual OMPs can be different, but average OMP removal falls within a similar range. The removal efficiency data points of HH Delfland are almost exactly located on the trend line through all data points obtained from literature. This indicates that average OMP removal efficiency is within a similar range, although OMPs analyzed, ozone installations and process conditions are all different in the four studies.

HH Delfland could have determined the optimal ozone dosage based on removal efficiencies found in literature, without conducting its own ozone dosage experiments. The removal efficiencies found with the ozone dosage experiments of HH Delfland, are similar to the removal efficiencies based on literature. However, bromate formation will always need to be checked (see sub-question 5) and the authorization of a discharge permit will be based on individual OMP quality standards and not on average removal. For this reason, research questions 3 and 4 evaluate individual OMP removal.

Research question 3: What are the expected removal efficiencies based on literature and modelling and what are the observed removal efficiencies in the pilot installation of HH Delfland?

Based on literature, OMPs can be divided in three categories with (>80% removal, 50-80% removal and <50% removal). Due to different research set-ups and different ways of reporting ozonation performance, literature can only give an *indication* of OMP removal. Table 21 on page 68 shows the indicated removal of 27 OMPs, based on different scientific studies.

Modelling the removal efficiencies with the equation of Hollender et al. (2009) and Lee and von Gunten (2016) requires information on second order rate constants of a compound with ozone and hydroxyl radicals and exposure to ozone and hydroxyl radicals. Table 27 on page 76 shows the predicted removal of 22 OMPs, based on modelling.

The long run test of HH Delfland showed that pharmaceuticals, pesticides and corrosion inhibitors are generally well removed by ozonation (94.4% +/- 1.1%, 95.9% +/- 2.2% and 95.0% +/- 3.7% respectively). Contrast media show variable removal, which results in high standard deviations (70.6% +/- 21.9% average removal). As expected, metals are left untouched by ozonation (14.4% +/- 2.2%).

Research question 4: Can individual OMP removal be predicted based on literature and/or modelling?

Division of OMPs in three removal categories (<50%, 50-80%, >80%) **cannot adequately indicate** the removal efficiency as observed in the pilot of HH Delfland. For only half of the analyzed OMPs, the observed removal efficiency falls within the expected range based on literature. The research set-ups of the studies are too different to compare the results. For instance, HH Delfland applies a high ozone dosage (1.0 gO_3/gDOC) compared to literature studies (often between 0.3-0.8 gO_3/gDOC).

The modelled and observed OMPs show **similar removal efficiencies**. Average deviation between the two is only 6.9% point or 8.8%. When the OMPs that are measured only once are omitted, the average deviation is even as low as 5.6% point or 7.7%. For 16 out of 22 OMPs the modelled removal falls within one standard deviation of the observed removal.

The model showed accurate predictions of observed OMP removal efficiencies for the long run test of HH Delfland. With progressive research on ozonation of treated wastewater, more and more is known about removal mechanisms and efficiencies. For these reasons, one can argue that the model ***can*** **accurately predict OMP removal**. However, the model has currently only been tested on one data set from research of HH Delfland. More research is required to extent this claim to other researches. Furthermore, the predictability of easily removed OMPs is especially accurate, while removal efficiencies of recalcitrant OMPs are harder to predict.

Even if the model could can predict OMP removal, there are three reasons why a pilot research will always be of use. Firstly, for the water authority to gain experience with ozone treatment. The Freshwater Factory pilot has showed that a lot can go wrong with an ozone installation. Process technologist can learn from a pilot and get familiar with the treatment. Secondly, the formation of bromate is highly unpredictable (see research question 5). Finally, toxicity of transformation products could not be addressed in this research and is hard to predict. Although never addressed as a problem in scientific literature studied for this research, insight into the toxicity of the residual contaminants is required.

Research question 5: Is bromate formed during ozonation? If yes, will it be removed during biological sand filtration?

Formation of bromate has been studies twice in this research: in the ozone dosage test and in the long run test. **Bromate has not been found during the ozone dosage experiments**. This was unexpected, since feed water bromide concentrations and the applied ozone dosage (max. 1.31 gO_3/gDOC) were high. Other studies (Margot et al. 2013; Gerrity et al. 2011) have found bromate even with lower ozone dosages and lower influent bromide concentrations. The relatively high DOC concentrations and the subsequent high $^{\cdot}OH/O_3$ ratio are two potential explanations for the absence of bromate formation.

During the **long run test, bromate *has* been found**, with a maximum concentration of 0.63 µg/l. Bromate has been found in three out of four measurements (0.085 µg/l, 0.37 µg/l and 0.63 µg/l). Bromate is hardly removed during biofiltration (based on only one measurement: reduced from 0.63 µg/l to 0.56 µg/l). With a drinking water standard of 0.01 µg/l and a surface water standard of 0.50 µg/l, the bromate concentrations are not negligible. When bromate is found more often in high concentrations, the ozone dosage might have to be lowered.

With an ozone dosage of 0.95 gO_3/gDOC in the long run test, it is unexpected that bromate has not been found at a dosage of 1.31 gO_3/gDOC in the ozone dosage test. An obvious explanation for this discrepancy is missing. Further research is required to obtain more insight into the formation of bromate at the pilot of HH Delfland. Also, a discussion with the laboratory is required to obtain more insight into the method of measurement.

9. Recommendations

This chapter will first provide general recommendations based on this research, and subsequently recommendations for further research.

General recommendations

- This research recommends an ozone dosage of 0.7 gO_3/gDOC, which gives an average removal efficiency of 80%. This removal efficiency is regarded as effective by Swiss research institute EAWAG and authorities (Margot et al. 2013). This ozone dosage requires 33% less energy than the currently applied dosage of 1.0 gO_3/gDOC. It also limits bromate formation (effluent concentrations up to 56 µg/l have been found with a dosage of 1.0 gO_3/gDOC).
- Ozone dosage experiments in literature can be used to confirm the average OMP removal efficiencies found in the pilot of HH Delfland.
- The model of Hollender et al. (2009) and Lee and von Gunten (2016) can adequately predict individual OMP removal efficiencies as observed by HH Delfland. However, the ozonation pilot is still of use to gain experience with ozone treatment, to study bromate formation and to study the toxicity of oxidation products.
- HH Delfland should realize that not *everything* can be studied in the ozonation pilot. Advanced wastewater treatment with ozonation is already a novelty in The Netherlands. The pilot of HH Delfland contributes to both the scientific and the practical field of advanced wastewater treatment. However, not all research topics can be addressed in this pilot. HH Delfland should concentrate on those matters that are important for the full-scale installation at WWTP De Groote Lucht. The recommendations for further research below, contain both topics that are important for HH Delfland (e.g. recommendation 1, 4, 5 & 7) and topics that are more academic of nature (e.g. recommendation 3 & 6).

Recommendations for further research

Answering questions in scientific research will always give rise to more questions, and this research is no exception. This section provides seven recommendations for further research in the field of advanced wastewater treatment with the combination of ozonation and biofiltration.

1. Compare effluent concentrations of the long run tests with water quality standards and background concentrations of the receiving water body, in this case the Krabbeplas. This research has studied the performance of the ozonation installation by evaluating removal efficiencies. However, to obtain a permit, the concentrations of the water quality standards must be met. Are the effluent concentrations as measured in the long run test higher or lower than the standards? For the 'stand-still principle' (see section 2.1 on the legal context), the background concentrations of the receiving water body are also important? Will the new discharge cause a deterioration of the water quality (for some substances) or will it be a dilution?
2. If the effluent concentrations of some substances are above the norm, the model of Hollender et al. (2009) and Lee and von Gunten (2016) can calculate what ozone dosage is required to remove the substance below the norm. Is the determined ozone dosage realistic (regarding energy consumption and limiting toxicity and bromate formation)?
3. This research has divided OMPs in compound type (pharmaceuticals, pesticides, corrosion inhibitors, contrast media). Further research could analyze substance by functional groups. A lot of research has been done to what functional groups react well with ozone (e.g. Hollender et al., 2009). The functional groups of OMPs and their corresponding removal efficiencies in the long run test can be studied. Are these results in agreement with previous findings on well reacting functional groups?
4. Bromate formation remains an intricate matter. More bromate measurements are required to find the occurrence and concentration of bromate. Is the measured high bromate effluent concentration (56 µg/l) an exception or does it occur more often? Also, more insight needs to be obtained into the laboratory analysis. Can differences in analysis give different bromate concentrations? This could be a potential explanation that bromate has not been found in ozone dosage test but has been found in the long run test. Finally, the performance of the biologically active sand filter can be

further studied. Currently only one measurement before and after the sand filter has been done (measurement #5).

5. Include bioassays in the analysis, to find whether toxicity is increased during ozonation and whether it is decreased during biofiltration. Similar to recommendation 1, the toxicity of the effluent should also be compared with the toxicity of the receiving water body. This will answer the question whether the new discharge will deteriorate or improve the water quality of the Krabbeplas (regarding toxicity levels). Bioassays have been taken during the long run test, but the data was not yet available at the time of this research.
6. Regarding to modelling the removal efficiencies: use more data from different ozonation experiments to compare modelled and observed removal efficiencies. Further research could confirm or refute the claim that OMP removal efficiencies can be modelled.
7. Further research is required on the role of ammonium during ozone treatment. It is well-known that nitrite oxidizes rapidly with ozone, which reduces the availability of ozone for OMP removal. The effect of ammonium is currently not studied in the Freshwater Factory pilot. Also, explanations on the role of ammonium during ozonation are not apparent in scientific literature.

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Appendix I - Overview values below reporting limit

Goal: provide an overview of methods from scientific literature to cope with concentrations below the reporting limit. In order to compare different studies (e.g. the Freshwater Factory project with the PACAS project), it is important that this issue is handled with care.

There are four options to cope with values below the reporting limit:

1. **Take the reporting limit as value (e.g. 0.01 µg/l)**

- *Three studies use this method.*
- Margot et al. (2013): "In the case when the effluent concentration was below the LOD of the compound, the removal rate was calculated as a minimum value using the LOD as effluent concentration. These minimum removal rates were not integrated into the global removal average unless they were above 80%, in order not to bias the results."
- Nakada et al. (2007) neemt de rapportagegrens om de verwijdering te berekenen, maar vermeldt hierbij met een '>' teken dat de verwijdering waarschijnlijk groter is dan het gegeven percentage. "[Removal efficiency] values with '>' (greater-than sign) mean that the concentration in the effluent was below the limits of quantification, resulting in greater removal efficiencies than the values indicated."
- Snyder et al. (2006): "When compounds were removed to less than the MRL [method reporting limit], percent removals are shown as greater than the value calculated from the MRL."

2. **Take 0.5* reporting limit as value (e.g. 0.5* 0.01 µg/l = 0.005 µg/l)**

- *One study uses this method.*
- Hollender et al. (2009): "concentrations below LOQ [Limit of Quantitation] were set to half of the LOQ value."

3. **Take 0 as value**
    - *Not found in scientific research.*
    - Preference of prof. Merle de Kreuk. If the methods of detection will improve in the near future, that could change the outcome of studies. However, for now it is reasonable to assume that a substance is not present in the water when it cannot be measured above the reporting limit.

4. **Volkert-Bakker method**
    - *Not found in scientific research.*
    - HH Delfland Process Technologist Erik Knol: on 2-2-2017 HH Delfland decided to use the Volkert-Bakker method
    - Problem: measurement 2 of the long rust test of HH Delfland had a matrix disturbance which resulted in a 10x higher reporting limit
        - E.g. for an OMP below the reporting limit, a value is calculated based on the % of measurements below reporting limit: e.g. 0.6*0.01 µg/l = 0.006 µg/l
        - However, for measurement 2 this would mean: 0.6*0.1 µg/l = 0.06 µg/l (which is 6x as high as the reporting limit is all the other measurements!)
    - Discussed with prof. Merle de Kreuk. In her eyes it would be unrealistic to use the Volkert-Bakker method, when this means that a value from measurement #2 would be higher than the reporting limit of the other measurements. See example above.

N.B.

- Many studies do not have to use one of these methods, but report their results in a different way:
    - Huber et al. (2003): "Bezafibrate was oxidized within 5 min to the detection limit"
    - Lee et al. (2012): "with 27 compounds (66%) being removed to below detectable limits"
    - Lee et al. (2014): "Elimination of the remaining 42 compounds could not be determined because their concentrations were below the method quantification limit"
    - Margot et a. (2013): "The very low concentration of this substance in WWTP effluent (2 to 17 ng l^{-1}), close to the limit of quantification, leads however to high analytical uncertainties and could be the cause of the divergences observed."
    - Rosal et al. (2010): "Averages and removal efficiencies have been calculated excluding concentrations below LOQ."
- If an OMP is analyzed that has a ozonation feed water concentration just above the reporting limit, it is not possible to draw a meaningful conclusion on the removal efficiency.
    - Rosal et al. (2010): "Certain compounds such as terbutaline or simazine have been encountered in several samples, but these data have not been considered statistically significant because they were found at concentrations so close to the LOQ that removal efficiency in STP could not be properly assessed and, therefore, they were not included."

Appendix II – Tables long run tests

Table 30 - Overview of metals

Metal	Average removal efficiency	Standard deviation	# measure ments
antimony	0,0%	0,0%	1
arsenic	-4,0%	8,4%	4
barium	4,5%	0,0%	1
boron	0,0%	0,0%	1
chrome	-5,6%	0,0%	1
cobalt	6,1%	2,9%	4
copper	72,7%	0,0%	1
lead	100,0%	0,0%	1
molybdenum	-6,7%	0,0%	1
nickel	6,6%	5,5%	4
tellurium	3,6%	0,0%	1
uranium	-2,2%	3,8%	3
zinc	11,5%	7,9%	4
Average	14,4%	2,2%	2,1

Table 31 - Overview of pharmaceuticals

Pharmaceuticals	Average removal efficiency	Standard deviation	# measure ments
bezafibrate	100,0%	0,0%	3
carbamazepine	100,0%	0,0%	5
claritromycine	100,0%	0,0%	5
clindamycine	100,0%	0,0%	1
clozapine	100,0%	0,0%	5
diclofenac	100,0%	0,0%	5
gabapentin	80,9%	2,6%	5
hydrochlorothiazid	100,0%	0,0%	5
irbesartan	92,7%	1,9%	5
lidocaïne	100,0%	0,0%	5
metformin	32,0%	11,0%	5
metoprolol	99,9%	0,3%	5
oxazepam	90,5%	2,2%	5
pentoxifylline	100,0%	0,0%	1
phenazone (antipy	100,0%	0,0%	3
sotalol	100,0%	0,0%	5
sulfamethoxazol	100,0%	0,0%	2
trimethoprim	100,0%	0,0%	5
valsartan	98,4%	3,6%	5
Average	**94,4%**	**1,1%**	**4,2**

Table 32 - Overview of pesticides

Pesticides	Average removal efficiency	Standard deviation	# measure ments
2,6-dichloorbenzar	100,0%	0,0%	1
2-methyl-4-chlorop	100,0%	0,0%	1
acetamiprid	100,0%	0,0%	1
azoxystrobin	100,0%	0,0%	1
bitertanol	100,0%	0,0%	1
boscalid	100,0%	0,0%	2
bupirimate	100,0%	0,0%	1
carbendazim	100,0%	0,0%	6
chloroprofen	100,0%	0,0%	1
cyprodinil	100,0%	0,0%	4
diethyltoluamide	95,6%	10,7%	6
diuron	100,0%	0,0%	4
ethofumesate	100,0%	0,0%	1
fenhexamide	100,0%	0,0%	1
flonicamid	26,7%	41,3%	5
imazalil	100,0%	0,0%	1
imidacloprid	72,2%	4,9%	6
iprodion	100,0%	0,0%	2
metalaxyl	100,0%	0,0%	1
methoxyphenozide	100,0%	0,0%	5
oxamyl	100,0%	0,0%	1
pirimicarb	100,0%	0,0%	4
propamocarb	100,0%	0,0%	6
pymetrozine	100,0%	0,0%	5
spinosad	100,0%	0,0%	3
thiamethoxam	100,0%	0,0%	2
Average	**95,9%**	**2,2%**	**2,8**

Table 33 - Overview of contrast media

Contrast media	Average removal efficiency	Standard deviation	# measure ments
amidotrizoic acid	52,8%	41,1%	3
iohexol	93,8%	8,8%	2
iomeprol	52,8%	45,8%	3
iopamidol	100,0%	0,0%	1
iopromide	76,9%	20,1%	3
ioxitalamic acid	47,5%	15,8%	3
Average	**70,6%**	**21,9%**	**2,5**

Table 34 - Overview of corrosion inhibitors

Corrision inhibitors	Average removal efficiency	Standard deviation	# measure ments
1,2,3-benzotriazole	91,8%	5,7%	3
methyl-1H-benzotriazole	98,2%	1,6%	3
Average	95,0%	3,7%	3

Appendix III –Institutional analysis of a closed water cycle

This report has discussed the removal of organic micro-pollutants with the combination of ozonation and biofiltration in detail. Removing OMPs in advanced wastewater treatment is crucial in enabling wastewater reuse. The Freshwater Factory aims to close the water cycle by reusing wastewater for recreational purposes in the Krabbeplas. This is not the only wastewater reuse project of HH Delfland that is currently in development. The board of HH Delfland has expressed its ambition to close the regional water cycle. As mentioned in the introduction of this research, a closed water cycle could alleviate stress on urban water management. Climate change is expected to lead to water shortages, due to intensified periods of drought are a great threat in the near future.

Removing OMPs from wastewater is one of the main challenges in wastewater reuse projects. The first seven chapters of this report have solely focused on this challenge. However, for a successful implementation of wastewater reuse projects, a new institutional environment is required. A wide variety of institutional issues are expected in establishing this new environment. Institutional analysis of a closed water cycle has been the subject of the thesis of this author for the master Systems Engineering, Policy Analysis and Management (SEPAM). This chapter will provide a summary of the master thesis, based on Van Es (2017b). The full version of the master thesis can be obtained through TU Delft Repository.

Introduction

The regional water system is a complex socio-technological system. Technology (water treatment, transport etc.) is important for the functioning of the system, but economic, financial, environmental and institutional aspects are just as important. Many different social actors are active in the water system, who hold conflicting interests, objectives and perceptions of a problem situation and act strategically to get the best out of that situation (Enserink et al., 2010). The presence of these actors makes closing the water cycle a complex problem.

Water authorities in the Netherlands are crucial actors in the regional water systems. They are facing the challenge how to close the water cycle by wastewater reuse, to guarantee good water quantity and quality. In the complex policy making process of the multi-actor water system, water authorities would benefit from a comprehensive and sufficiently guiding framework. Literature research (van Es, 2017a) shows that currently, scientific research only provides either too general or too specific frameworks for urban water management. For this reason, Van Es (2017b) aimed to provide such a framework, with the main research question:

How to specify and operationalize an institutional analysis framework to guide actors in closing the regional water cycle?

Proposing a framework for institutional analysis

The Technological, Institutional and Process (TIP) framework of Koppenjan and Groenewegen (2005) has the potential to be both comprehensive and sufficiently guiding. The framework is specified with other frameworks and tools to provide guidance in closing regional water cycles. Functional diagrams are used to provide insight into the required technological changes for a closed water system. The institutional analysis is specified with the four-layer model of Williamson (1998) and the Institutional Analysis and Development (IAD) framework of Ostrom (2011). Concepts of process management that can help in the process towards a closed water cycle, are introduced.

This research focuses on the institutional analysis framework. The term 'institutions' is a broad concept; institutions *influence, guide and limit the behavior of actors and structure political, economic and social interaction* (Ghorbani, 2010; North, 1991). Institutions consist of both informal constraints (sanctions, taboos, customs, traditions, and codes of conduct), and formal rules (constitutions, laws, property rights) (North, 1991).

The **four-layer model of Williamson (1998)** conceptualizes social analysis by categorizing institutions in four different layers (see Figure 52). The first level of the model is the social embeddedness level, in which norms, customs, traditions, mores etc. are located. The second level is the institutional environment in which institutions are the product of politics. These institutions provide the rules of the game within which economic activities are organized. The institutions of governance are located at the third level of the model. The lowest level of institutions concerns marginal analysis; the examination of costs and benefits of individual actions. The **IAD framework of Ostrom (2011)** helps analysts to understand complex social situations and to break these situations down into manageable sets of practical activities. The core of the IAD framework is the 'action situation' (see Figure 52); a conceptual unit that can be utilized to describe, analyze, predict and explain behavior within institutional arrangements. External variables (bottom left in Figure 52) affect the action situation. The core question is what the resulting patterns of interactions and the outcomes of the action arenas are and how they are evaluated by the participants of the action situation.

The IAD framework allows more detailed institutional analysis than the four-layer model of Williamson (1998), by specifying the input and interaction of action situations. An action situation is 'a conceptual space in which actors inform themselves, consider alternative courses of action, make decisions and take action' (Polski and Ostrom, 1999). Ostrom acknowledges that it can be hard to identify relevant action situations in large, complex policy systems (Polski and Ostrom, 1999). To resolve this, the four-layer model of Williamson (1998) can be used to find the critical action arenas in institutional redesign. The model conceptualizes social analysis by categorizing institutions in four different layers (1) cultures & norms, 2) institutional environment, 3) governance and 4) marginal analysis).

Figure 52 provides an overview of the proposed Williamson (1998) – Ostrom (2011) institutional analysis framework. The first step is to find critical issues with Williamson's (1998) framework. Critical issues must be addressed in action situations. The critical action situations are those situations that will be critical to the success of redesigning the urban water cycle towards a closed system. These critical action situations require coordination by the system designer to guide interaction towards desired outcomes. The IAD framework of Ostrom (2011) is well suited to specify key features of the critical action situations to predict interactions and outcomes.

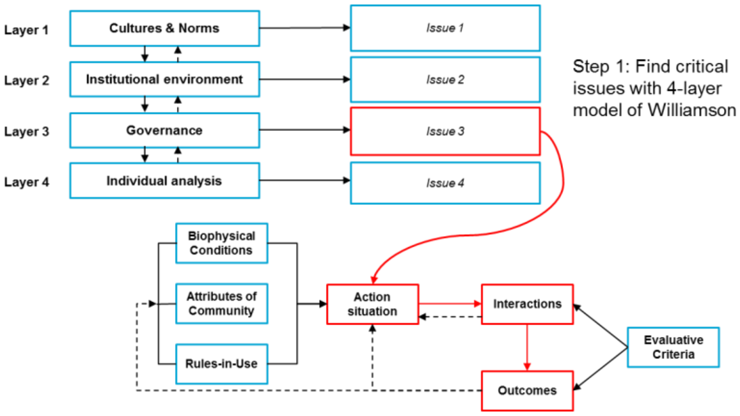


Figure 52 – The Williamson (1998) – Ostrom (2011) institutional analysis framework

To operationalize the proposed institutional analysis framework, a case study of closing the water cycle at HH Delfland is conducted. The first step (finding critical issues) is executed in five parts: 1) technological design, 2) first scan of issues, 3) interviews, 4) analysis of interviews and 5) conclusion on critical action situations. The second step (specifying critical action situations) consists of a description of the 1) external variables, 2) action situation, 3) interaction & outcomes and 4) coordination of the two most critical action situations.

Case study: closing the water cycle in the service area of HH Delfland

Step 1 – Identifying the critical issues

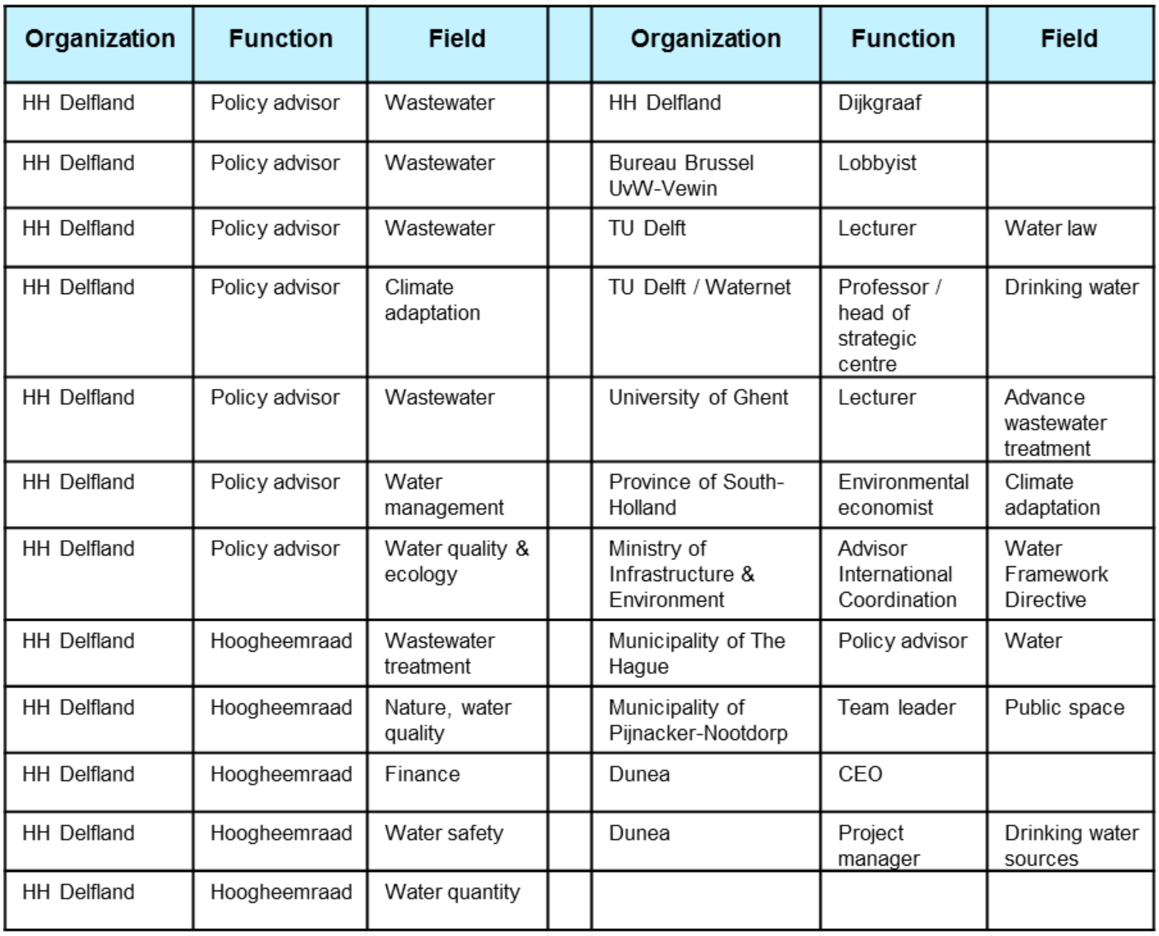
The required **technological changes** for a closed water system are found by constructing function diagrams of the current and desired water system. The main changes to the technological system are 1) addition of advanced wastewater treatment to conventional treatment plants and 2) new infrastructure to transport wastewater treatment effluent to the location of reuse. A wide range of potential issues is found in a **first scan of issues,** based on four projects of wastewater reuse (Belgium, USA, Singapore and Namibia) and a Green Deal. Examples of issues are: public acceptation, adjustment of rules and regulations and the business case of wastewater reuse (see Table 35).

Table 35 - Lessons learned from the analyzed cases on potetial issues for the case of HH Delfland

Case	Lessons learned on potential issues for the case of HH Delfland
Koksijde (Belgium)	• Public acceptation • Health risks • Legislation • Costs • Technology for advanced wastewater treatment
Orange County (USA)	• Business case of wastewater reuse project • No sense of urgency
Singapore and Namibia	• High energy consumption of advanced wastewater treatment • Affordability of reclaimed wastewater • Drinking water and wastewater separated in Dutch organization structure • Adjustment of rules and regulations
Green Deal 'Energy Factories'	• Uncertainty about and ambiguity of rules and regulations • Business case of wastewater reuse project

To find the most critical issues for the case of HH Delfland, **twenty-two interviews** have been conducted with relevant actors in the water system (e.g. HH Delfland, Dunea, ministry, province, municipalities and universities). See Table 36 for an overview of the interviews. The four-layer model of Williamson (1998) is used to structure empirical information from the interviews. In layer 1 (cultures & norms), social acceptability of wastewater reuse and a lack of urgency has been mentioned as issues in closing the water cycle. The issues of difficulty to meet water quality standards and legislation that proves to be conflicting during implementation are mentioned in layer 2 (institutional environment). The wide variety of actors involved in the regional water system and the political nature of the system are issues mentioned in the third layer of governance. The economic feasibility of wastewater reuse is the main issue mentioned in the lowest layer of marginal analysis.

Table 36 - Overview of interviews conducted



Organization	Function	Field		Organization	Function	Field
HH Delfland	Policy advisor	Wastewater		HH Delfland	Dijkgraaf	
HH Delfland	Policy advisor	Wastewater		Bureau Brussel UvW-Vewin	Lobbyist	
HH Delfland	Policy advisor	Wastewater		TU Delft	Lecturer	Water law
HH Delfland	Policy advisor	Climate adaptation		TU Delft / Waternet	Professor / head of strategic centre	Drinking water
HH Delfland	Policy advisor	Wastewater		University of Ghent	Lecturer	Advance wastewater treatment
HH Delfland	Policy advisor	Water management		Province of South-Holland	Environmental economist	Climate adaptation
HH Delfland	Policy advisor	Water quality & ecology		Ministry of Infrastructure & Environment	Advisor International Coordination	Water Framework Directive
HH Delfland	Hoogheemraad	Wastewater treatment		Municipality of The Hague	Policy advisor	Water
HH Delfland	Hoogheemraad	Nature, water quality		Municipality of Pijnacker-Nootdorp	Team leader	Public space
HH Delfland	Hoogheemraad	Finance		Dunea	CEO	
HH Delfland	Hoogheemraad	Water safety		Dunea	Project manager	Drinking water sources
HH Delfland	Hoogheemraad	Water quantity				

Analysis of the interviews shows that the values and drivers of board members of HH Delfland, regarding wastewater reuse, are located at three different levels of the four-layer model of Williamson (see Figure 53). Three groups can be identified. The first group is driven by the values of sustainability and circularity, located at the highest institutional level. The position of the second group corresponds to the third layer of governance, focusing on relations and interactions. The driver of the third group can be found at the forth level of the individual analysis. In their eyes, projects in closing the water cycle should have a positive business case.

An interesting consequence of the difference in institutional level and values is that both groups of board members see the opposite institutional level as issue. To clarify, board members reasoning at the first institutional level (cultures & norms) see the forth level (marginal analysis) as an issue to achieve their goals. The first group argues that investments in a circular water system should be made now, and that (potential) economic benefits will follow later. Focusing too much on the business case at this moment will hinder the implementation of wastewater reuse projects in their eyes. In turn, the third group reasons at the forth institutional level (marginal analysis) and see the values of the first institutional level (culture & norms) as an issue. What some call 'driven by or reasoning from values' is called 'dogmatism' by others. The difference in institutional level of and values and drivers are a potential source of disagreement within the board of HH Delfland.

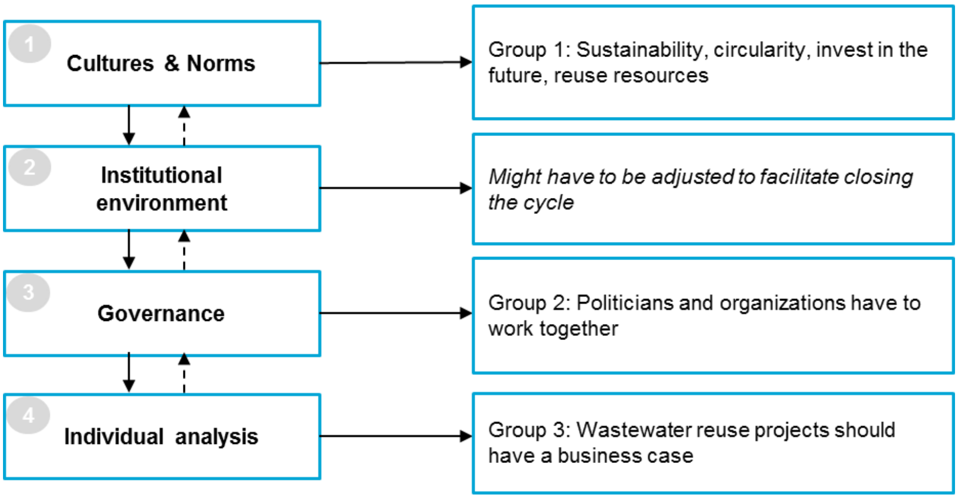


Figure 53 - Overview of levels on which board member argue

This research found that **two of the most critical action situations** are 1) HH Delfland having to obtain a permit to discharge treated wastewater and 2) new arrangements between HH Delfland and Dunea. The first action situation addresses the critical issue of obtaining a discharge permit. The second action situation addresses the critical issues of technological changes, social acceptation and economic feasibility (see Figure 54).

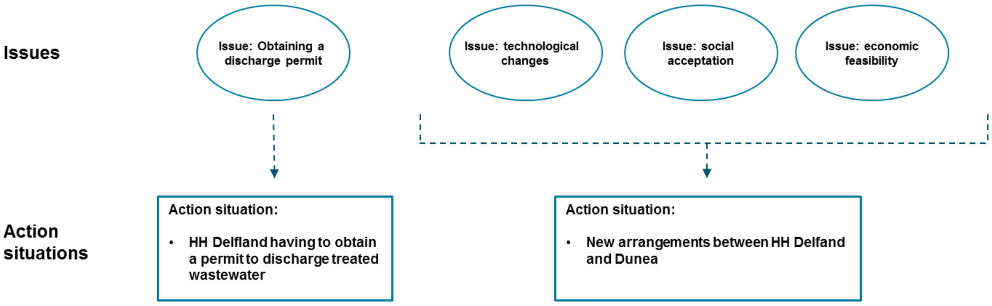


Figure 54 - Overview of issues and action situations

Step 2 – Specifying the critical action situations

The second step of the Williamson-Ostrom framework is to specify the critical action situations as identified in the first step. This section will discuss the two critical action situations.

Action situation 1 – Obtaining a permit to discharge treated wastewater

The 'Freshwater Factory' (FF) pilot project at the wastewater treatment plant 'De Groote Lucht' in Vlaardingen, which tests advanced treated wastewater for recreational reuse, is used to specify the first action situation. Figure 55 shows the nestedness of the action situation. An action situation rarely stands on itself, but is rather embedded in and influenced by other action situations. In turn, interactions and outcomes of the action situation influences the external variables of other action situations.

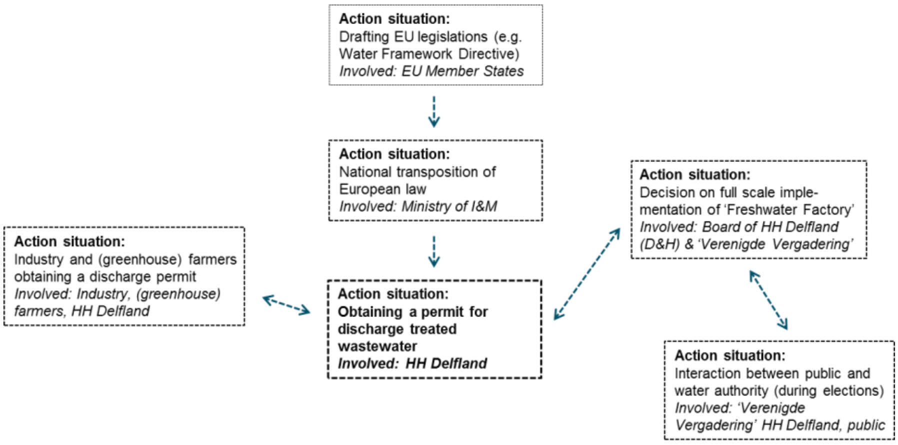


Figure 55 - Overview of nested action situations

HH Delfland is both the applicant and the provider of the discharge permit. Figure 56 shows that three different departments of HH Delfland are involved. The tension in this action situation is between preventing risks for public health (by preventing pollutants to be discharged into surface water) and imposing such strict standards that reuse projects become financially unviable. The three departments together must find a balance between both. With a lenient interpretation of the 'stand-still' principle by Water system quality (WSQ) and Regulation and plan advising (R&P), the FF will obtain a permit with the currently proposed treatment scheme by PCW (ozonation + biofiltration). When the 'stand-still' principle is strictly interpreted, additional advanced treatment is required (e.g. reverse osmosis), which increases costs and energy requirements. With insight into the positions of the board members of HH Delfland (see Figure 53), it is clear that the project will not find support in that case. The licensed FF treatment scheme is part of the *rules-in-use* of the action situation, in which the board of HH Delfland decides on full-scale implementation (see Figure 55).

HH Delfland should stimulate the interaction between the three departments. PCW observes a knowledge gap on what water quality standards must be met, while WSQ has the feeling they have been involved too late in the project. HH Delfland should keep pace in the process of finding a balance between water quality and costs and should dare to move forward. Finding the right balance between water quality and treatment costs can in the end only be achieved by executing the project.

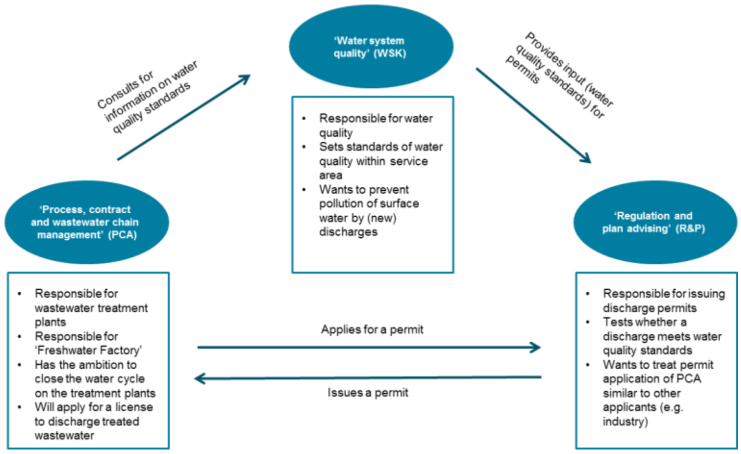


Figure 56 - Overview of actors, relations and responsibilities

Action situation 2 – New arrangements between HH Delfland and Dunea

The second critical action situation, new arrangements between HH Delfland and Dunea for a potable wastewater reuse project, addresses three critical issues in closing the water cycle: technology, social acceptability and finance. HH Delfland and Dunea hardly communicate with each other at the moment. A long road is ahead before both organization can work together in a water reuse project.

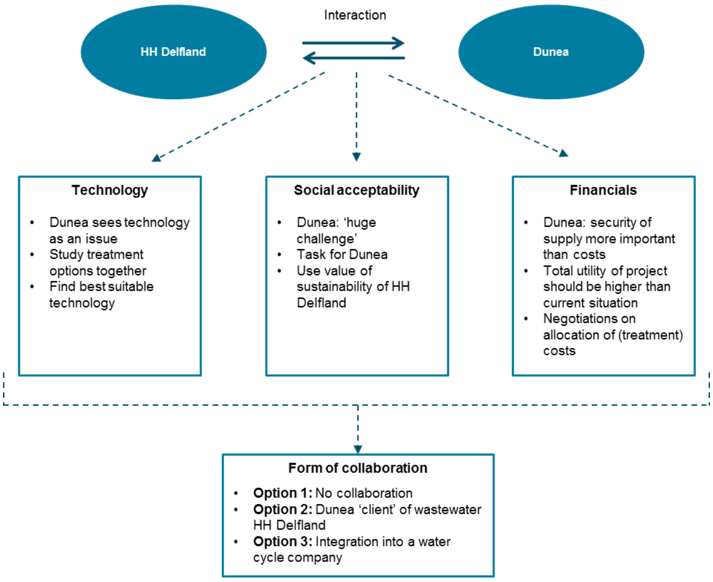


Figure 57 – Overview of critical issues in new arrangements between HH Delfland and Dunea

Firstly, especially Dunea doubts whether **technology** is available that can meet all requirements, with acceptable costs. Installing a pilot project together, can help to exchange information and learn from each other's way of working. Experience with the Freshwater Factory learns that it is highly recommendable to first start a pilot project with the preferred treatment technology. During a pilot project, many technological and institutional issues are expected to surface. With a pilot project, both actors can obtain knowledge and experience with the advanced treatment and the required institutional changes.

Obtaining **social acceptance** of potable wastewater reuse will be a 'huge' challenge (CEO Dunea). Moral, pragmatic and cognitive legitimacy must be acquired for a project to be accepted (Harris-Lovett, 2015). HH Delfland can help to obtain the first, by actively communicating the sustainability and circularity of the project, for instance in a visitors center and guided tours through the plant. For the **financial** issue, the actors need to rise above their own interest. Extra investments in advanced treatment and transport have to be allocated to both organizations. The willingness of Dunea to pay for a reliable and high quality water source, is a great opportunity for this project.

The previously used four-layer model of Williamson (1998) provides an interesting view on the interaction regarding issues of social acceptance and a financial agreement. Figure 58 shows how these two issues can be aligned between HH Delfland and Dunea. The project offers opportunities to address the two main driving values (sustainability and business case) of the board members of HH Delfland. Firstly, HH Delfland can help Dunea to 'sell' the wastewater reuse project to the public as sustainable and circular. Secondly, board members of HH Delfland that are drive by the business case of reuse projects, will be more willing to support the project if Dunea is willing to increase its water tariff to finance the wastewater reuse project.

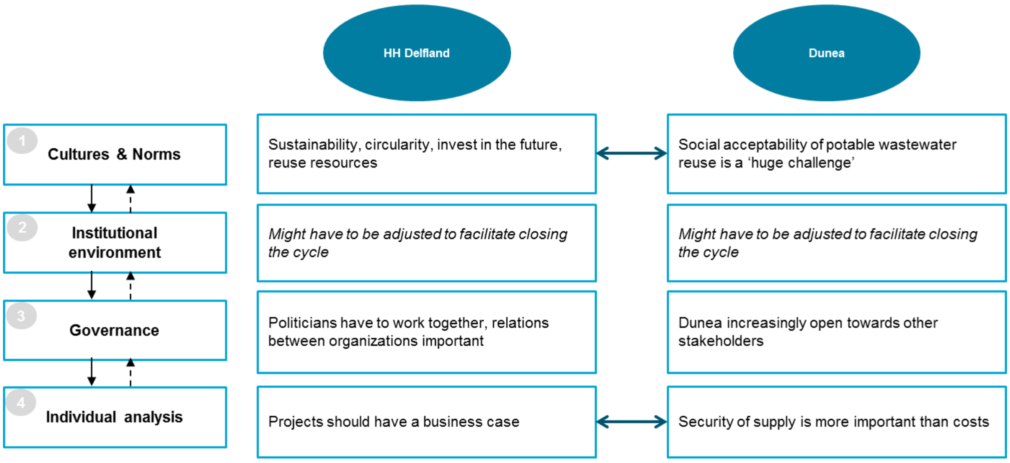


Figure 58 - Overview of four-layer model of Williamson (1998) for both HH Delfland and Dunea

When all issues have been successfully addressed, the actors must find the optimal form of collaboration. This research proposed two options: Dunea to act as a customer of treated wastewater or both actors to merge to a water cycle company. The first is currently the preferred option of the CEO of Dunea.

Evaluation & recommendation

Evaluation of methodology

The research of Van Es (2017b) has provided a comprehensive framework (TIP framework of Koppenjan and Groenewegen (2005)) to start the analysis of the regional water system. The proposed Williamson-Ostrom framework offers the opportunity to further specify and operationalize the institutional analysis. The four-layer model of Williamson (1998) provided clarity in attitudes and positions of actors, and structured critical issues and action situations in closing the water cycle. The IAD framework of Ostrom (2010) has provided further insight into the interaction on the critical issues in the two critical action situations. Further research can contribute to the field of institutional analysis by conducting more case studies with the proposed Williamson-Ostrom framework and execute the case study in a theoretical way instead of an empirical way.

General recommendations

Recommendations for HH Delfland can be given in general, regarding the Freshwater Factory and regarding the potable reuse project with Dunea. In general, the **pioneering role** that HH Delfland has adopted in exploring wastewater reuse projects is commendable and appreciated in the water system. Secondly, while Dunea *is* feeling a **sense of urgency** of freshwater scarcity, the awareness of the vulnerability of freshwater supply should increase at HH Delfland and other governmental bodies. Thirdly, the board of HH Delfland is **internally divided** on whether wastewater reuse projects should be pursued, based on differences in values that drive board members. The division can roughly be explained by values of sustainability versus economic efficiency. Providing insight into the different values, as this research has attempted to do, could help the board members to understand each other's position. It might provide common ground to find agreement within the board. Projects in which the drivers of all board members are aligned have most chance finding approval from the board.

Finally, HH Delfland should be aware of the **heavily politicized nature** of the water authority. Other actors see the political nature not always as beneficial. Both inside and outside HH Delfland, the short-term vision of politicians and the changes in political color are addressed as issues. Dunea even sees the political 'inability' to implement projects as a major issue. HH Delfland should critically examine the political nature of the water authority, to find whether the decision-making process within the water authority has been too heavily politicized.

Recommendations on the Freshwater Factory (FF)

Regarding the Freshwater Factory, piloting and implementing a water reuse project such as the FF needs to be seen as a **learning process** to open new horizons. Politicians have to take (political) risks to find a balance between meeting legislation and limiting costs. A Dutch interpretation of the Water Framework Directive for wastewater reuse projects, is required to find the balance between preserving the 'stand-still principle' in working towards a closed water cycle. The process towards a fully implemented FF will be long, especially when legislation requires adjustments and/or interpretation. HH Delfland should take this into account and be prepared for a long process.

Secondly, **interaction** between the three departments of HH Delfland involved in obtaining a permit (PCW, WSQ, R&P), should be **stimulated**. Interaction will increase the understanding of each other's considerations and trade-offs. Together, the departments should find a balance in the trade-off between water quality and costs. This balance can be presented to the board of HH Delfland, that is eventually responsible for deciding whether the pilot will be upgraded to full-scale.

Thirdly, HH Delfland should **keep pace in the process** of finding the balance in the trade-off and should dare to move forward. HH Delfland has entered unknown grounds with the FF project. It naturally follows that HH Delfland finds knowledge gaps on the way towards a full-scale wastewater reuse project. Finding the balance between water quality of reused wastewater and the costs required can in the end only be achieved by executing the project. The board of HH Delfland will have to show political courage to decide to continue the pilot project towards a full-scale installation. HH Delfland can use the goodwill and momentum of the project (e.g. winning water innovation price) to keep on moving forward.

Recommendations on new arrangements with Dunea for potable reuse

A potable wastewater reuse project in collaboration with Dunea, will require new arrangements between HH Delfland and Dunea. Both actors, and their systems, act almost completely separated at the moment. Implementing a potable wastewater reuse project will be a long process and both actors have to rise above their own interest for a successful implementation. This research found the three main issues in new arrangements between the two actors to be: technology, social acceptability and financials.

Regarding the **technology**, both actors not only need to exchange information, they should experience the way in which both actors work. During a pilot project, many technological and institutional issues are expected to surface. With a pilot project, both actors can obtain knowledge and experience with the advanced treatment and the required institutional changes.

To obtain **social acceptability** for the potable wastewater reuse project, HH Delfland can help Dunea to create moral legitimacy by emphasizing the values of sustainability and circularity. HH Delfland can support Dunea by actively communicating the project through all sort of channels (open days, website, news, information at treatment plants), as is done by Flemish water company IWVA in the Koksijde reuse project.

For the **financial** issue, both actors need to rise above their own interests. Dunea is willing to increase its drinking water tariff, if this is required to guarantee security of supply. This offers an opportunity to obtain support for this project from the part of the board of HH Delfland that is driven by the business case of reuse projects.

In general, HH Delfland could be benefited by approaching the question of circularity in a less political fashion. The discussion within the board of HH Delfland could change when other actors in the water system are consulted. For the potable reuse project, Dunea has a more pragmatic attitude. If wastewater is the most reliable and at the same time financially acceptable (partial) source of drinking water, a wastewater reuse project should be implemented in their eyes.

Chapter 0 has provided a summary of the institutional analysis as conducted in Van Es (2017b). Removing organic micro-pollutants from wastewater is a very important in enabling wastewater reuse. However, this chapter has showed that many more institutional issues will rise with the implementation of wastewater reuse projects. Combining both, i.e. thorough technological and institutional analysis, is a promising strategy to successfully close the regional water cycle.