NTNU – Trondheim
Norwegian University of
Science and Technology

Degradation of DEET and DEP by Ozonation using pCBA as a Hydroxyl Radicals Probe Compound

Aleksandra Malgorzata
Migowska

Civil and Environmental Engineering (2 year)
Submission date: May 2015
Supervisor: Stein Wold Østerhus, IVM

Norwegian University of Science and Technology
Department of Hydraulic and Environmental Engineering

Abstract

The main aim of this master thesis was to examine the process of ozonation of two chosen micopollutants present in grey water. These micropollutants are: n,n-diethyl-m-toluamide (DEET) and diethyl phthalate (DEP). In order to assess the fraction of the compound removed by hydroxyl radicals, degradation of one more compound was studied. This compound was para-chlorobenzoic acid (pCBA) which is known for its specific way of reacting with ozone. Namely, pCBA is removed only by hydroxyl radicals, therefore, is commonly applied as a probe compound in order to measure hydroxyl radicals formation. Series of batch experiments was conducted. Each compound's degradation was studies in two types of permeate coming from the pilot plant applying three ozone doses (5 mg/L, 7.5 mg/L, 10mg/L). Additionally, degradation of pCBA in buffered Milli-Q water was performed for ozone dose of 5mg/L. Every experiment was repeated at least three times. Two studied water types differed in alkalinity and total carbon content. Collected data showed scavenging of ozone by carbonates, therefore, lower removal efficiency in water with higher alkalinity. Moreover, degradation of pCBA and DEET usually proceeded in a similar way with very close removal efficiency values. The lowest removal was noted for DEP. All of studied compound were proved to be removed mostly by radicals. Values of fraction removed by radicals reached 98-100% values. Experiments confirmed described in one of the studies abilities of pCBA to accelerate ozone decomposition. In addition, similar characteristics were observed for DEET as well.

Table of contents

Table of tables

Table of figures

Abbreviations

Acn – acetonitrile

Alk - alkalinity

BDOC – biodegradable organic carbon

C – conductivity

CAS NO. - Chemical Abstracts Service number

DEET- n,n-diethyl-m-toluamide

DEP - diethyl phthalate

DOC – dissolved organic carbon

DOM – dissolved organic matter

EBCT – empty bed contact time

EBNR – enhanced biological nutrient removal

GFT – grey water flow through

IFAS - integrated fixed-film activated sludge

k – reaction rate constant

LD50 - Median lethal dose

MQ – Mili-Q

NOM – natural organic matter

PAO - polyphosphate-accumulating organisms

pCBA - para-chlorobenzoic acid

RGW – recycled grey water

S – substance concentration (micropollutant concentration)

SS – suspended solids

SUVA - Specific Ultraviolet Absorption

TDS – total dissolved solids

TIC – total inorganic carbon

TOC – total organic carbon

TOT-N – Total nitrogen

TOT-P – Total phosphorus

WWTP – wastewater treatment plant

1. Introduction

The term "Micropollutants" describes organic substances occurring in the water in concentrations of a few nanograms or micrograms per liter. Although the concentrations are so low, the presence of those compounds can affect fundamental natural biochemical processes. The group of substances defined as micropollutants include many synthetic substances such as active pharmaceutical ingredients, compounds with biocidal properties (e.g. for material protection or gardening), food additives, cosmetics ingredients or detergents etc. as well as naturally occurring substances such as hormones (Geiger, 2012).

Micropollutants are becoming more and more important issue in water and wastewater treatment field, their toxicity and constant increase in concentration in aquatic environment may become a serious threat in the future. Furthermore, the effect of mixing them all together in the environment and their transformation products impact can cause even bigger damage, which cannot be easily predicted (Beate I. Escher, 2013). Therefore, many studies are focused on potential danger that micropollutats may bring to water systems trying to find the most optimal solution (prevention, removal methods, restrictions in applications etc.) for given conditions.

There are multiple sources of those compounds. Important features that characterizes a compound as a micropollutant is its toxicity and bioaccumulative properties. Depending on which kind of wastewater are we dealing with, other group of micropollutants can be a major issue. In grey water most commonly present are those coming from products that we are applying on our skin, hair, clothes etc. every day, such as: drugs, cosmetics, insecticides etc. Most of these compounds are obviously approved by authorities for usage in cosmetics and all kinds of daily products that humans contact on daily basis, which sometimes seems quite imprudent considering their toxicity.

Although it may seem that these compounds are quite irrelevant due to their extremely low concentrations, we need to remember that they may become greater concern in the future, whenever the up-concentration occur. Lately, due to shrinking water resources, idea of reusing of water is becoming commonly studied area in water and wastewater engineering. For example, grey water reuse treatment technologies are becoming the popular field of research. One of these projects is a pilot plant which is a source of water in the following study on the ozonation of micropollutants. This pilot is a subject of research at the Department of Hydraulic and Environmental Engineering at the Norwegian University of Science and Technology in Trondheim. The pilot plant is designed as a multi-step treatment

plant consisting of a biological step, a membrane filtration step and a ozonation-biofiltration step. The concept is to recycle 80% of grey wastewater adding 20% of fresh water in each cycle. This system requires good removal of micropollutants due to possible up-concentration in the system after several cycles.

According to the studies numerous factors affect the removal of micropollutants via conventional biological treatment. The removal rates in conventional treatment differ due to following factors: hydrophobicity, chemical structure (more complex compounds show higher resistance to biological removal), retention time in bioreactor (the higher retention time, the better removal), the temperature of wastewater, the pH (Magdalena Cirja, 2008). Micropollutants which are not removed in biological step are more likely to be transformed and removed during the ozonation followed by the biofiltration, which is more expensive but also more effective method.

2. Aims and objectives

The aim of performed experiments was to examine and determine the removal efficiency and kinetics of ozonation of three compounds (DEET, DEP and pCBA). The ozonation process was studied in two types of water, which varied in pH, alkalinity and TOC. Each compound and water type was studied with three ozone doses (5 mg/L, 7.5 mg/L, 10mg/L). Two of the compounds (DEET and DEP) are micropollutants present in grey water, whereas pCBA studied as a probe compound used to measure the hydroxyl radicals formation, which was applied in order to determine how much of the compound is removed by the molecular ozone and how much by the hydroxyl radicals.

3. Theoretical introduction to ozonation process

Ozone is commonly known as a strong oxidant. It has been used in the water treatment for about 100 years. Ozone is an unstable gas molecule. It creates the protecting layer of the atmosphere absorbing harmful for people UV radiation, nevertheless, in the lower layer of the atmosphere is unwanted because of the photochemical smog creation and bad influence on human's health. Ozone naturally exist in our environment as a result of lightening storms, but also its presence is a side-effect of human activity and pollution. When needed, for example in water and wastewater treatment, it can be produced commercially under controlled electric discharge (Rakness, 2005).

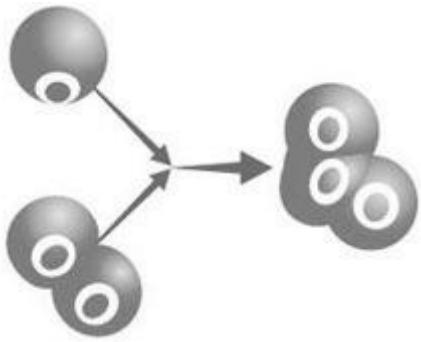


Figure 1. Ozone formation

In the ozonation process, gaseous ozone need to get dissolved in the treated water or wastewater. The dissolved ozone reacts then with the compounds present in the water and oxidize them. Due to the fact that the efficiency of the ozonation process is also dependent on the organic matter concentration, in wastewater treatment, it is most commonly applied after extensive biological treatment. It is generally easy to introduce an ozonation stage at an existing wastewater treatment plant and operate it quite easily. The gross energy consumption of the WWTP (wastewater treatment plant) commonly increases by about 10–30%. An ozone dosage of 3–5gO_3/m³ of wastewater is required for the elimination of the majority of micropollutants (>80%) and this also significantly reduces the ecotoxicological effects (e.g. endocrine effects, algal toxicity etc.). Most pathogens are also destroyed and the wastewater becomes decolorized. Due to the process-related formation of the reactive transformation products, it is recommended to install a stage with biological activity (e.g. sand filter) after ozonation of the wastewater so that these products can fully biodegrade in the WWTP (Geiger, 2012).

Table 1. Selected Physical Properties of Ozone (Rakness, 2005)

Propriety	Value
Molecular weight	48
Specific gravity of gas (air=1)	1.66
Critical temperature	-12.1°C
Critical density	540kg/m^3
Solubility in water, vol/vol at 0°C	0.64

3.1. Ozonation of micropollutants – possibilities in removal

Ozonation in the drinking water technologies is a topic that has been studied since 1970's, whereas wastewater ozonation was not a matter of attention until it was discovered that it can allow to remove some problematic compounds, that could not be efficiently removed before, such as pharmaceuticals and other micropollutants. Nevertheless, in the wastewater treatment, ozonation would be applied only as a polishing step after intensive treatment (for example biological) due to its high cost.

According to the general knowledge about ozone chemistry, it has been proven that ozone decomposes spontaneously by a complex mechanism which involve the hydroxyl free radicals creation. (J. Hoigne, 1981). The hydroxyl free radicals are among the most reactive oxidizing agents in water, with reaction rates on the order of 10^{10} - 10^{13} M^{-1} s^{-1}. "*On the other hand, the half-life of hydroxyl free radicals is on the order of microseconds, therefore concentrations of hydroxyl free radicals can never reach levels above 10 $^{-12}$ M*" (EPA Guidance Manual, 1999). As shown in the figure below, ozone can react with compounds present in the water by either or both pathways:

1. Direct oxidation of a compound by molecular ozone
2. Oxidation of a compound by the free hydroxyl radicals produced during the decomposition of ozone.

The scheme below presents possible ozonation pathway with ozonation by-products production.

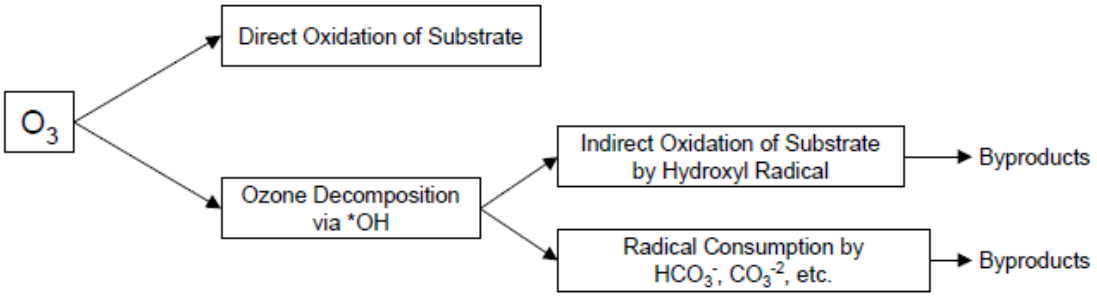


Figure 2. Oxidation reaction of compounds (substrate) during ozonation of water (EPA Guidance Manual, 1999)

According to numerous studies, ozonation is an effective method in improving quality of wastewater by eliminating micropollutants. However, there are still some obstacles that need to be overcame. The design of the process is limited by two major issues according to (Yunho Lee D. G., 2013):

1. The large diversity and number of micropollutants,
2. The variety of water quality and composition that influence ozonation process (especially DOM – dissolved organic matter).

Therefore, a study conducted by (Yunho Lee D. G., 2013) was trying to group micropollutants present in the municipal wastewater into five groups according to their ozone and hydroxyl radical rate constant. This classification allows to find an optimal specific DOM-normalized ozone dose for these groups. Further studies on micropollutants kinetics (from hospital effluent) were conducted and classified more compounds into the same groups later (Yunho Lee L. K., 2014).

Although those two factors mentioned before create some challenges in predicting how the ozonation of micropollutant can proceed, the approach based on chemical kinetics is an useful tool (Chapter: Kinetics of ozonation). According to (Xiaohui Jin, 2012), in order to evaluate the potential of removing micropollutant by ozonation the kinetic data is necessary. The kinetic data for hundreds of compounds has been collected so far by many researchers. Additionally, there has been some models developed incorporating the reaction rate constant, for example (E.J. Rosenfeldt, 2007). Nevertheless, the complexity of the process, high cost of the studies and new micopollutants constantly emerging creates a huge gap and need for further studies.

However, when dealing with waste water, ozonation becomes more complex process with the possibility of production unwanted by-products. According to the study of ozonation of

DEP, "*After the initial hydroxylation and hydrolysis reactions, with increasing ozone dose, the aromatic ring of DEP was opened and some acidic compounds, such as malonic acid, succinic acid and glutaric acid, were formed. In addition, the ozonation of DEP induced the generation of hydrogen peroxide (H_2O_2), at a level six times higher than pure water during ozonation for 18 min*" (Yeon Jung Jung, 2010).

According to (Xinwei Li, 2014), after applying ozonation to reuse wastewater system, toxicity evaluation with *V.fischeri* proved that ozonation can increase toxicity due to unknown micropollutants ozonation by-products. This fact should be taken into account and carefully studied before introducing the ozonation process to existing system.

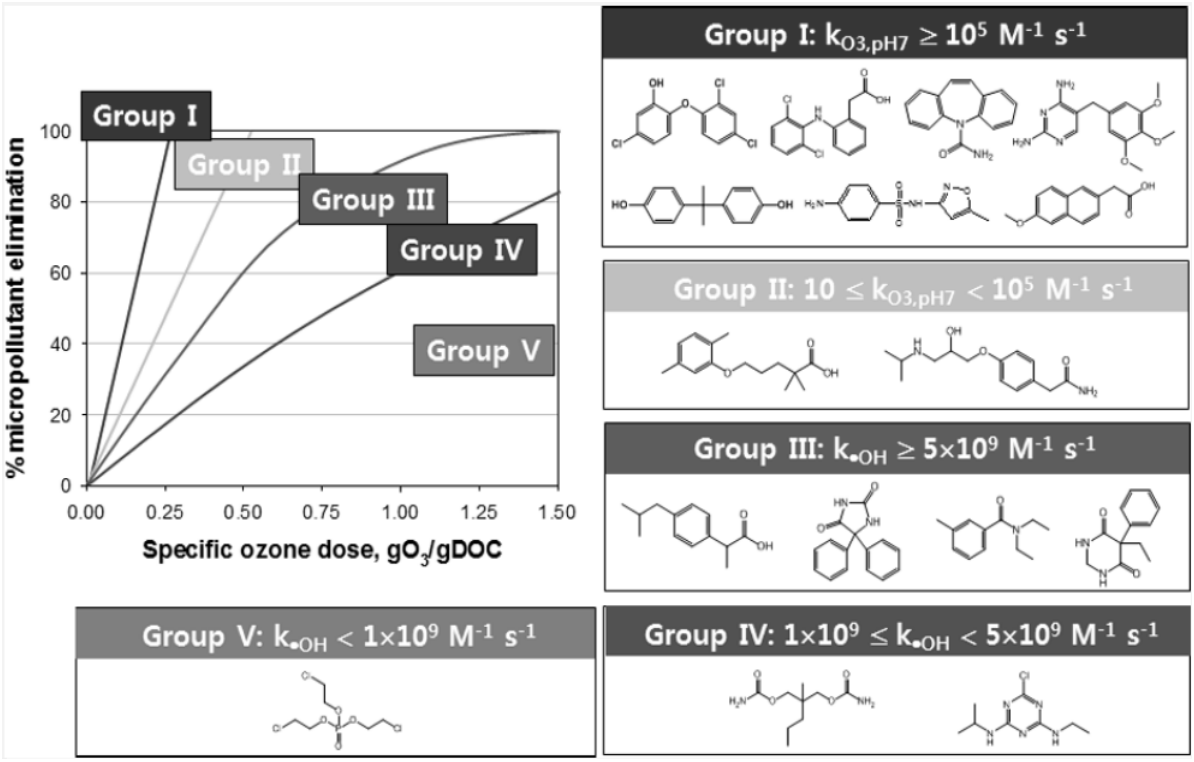


Figure 3. Micopollutants devided into groups according to their ozone and hydroxyl radical rate constants by (Yunho Lee D. G., 2013)

3.2. Influence of ozonation on Biodegradable Dissolved Organic Carbon (BDOC) removal; Ozonation-biofiltration treatment method

DOM (dissolved organic matter) contain a broad range of organic molecules of different origin and composition. Term "dissolved" indicate that the size of those molecules are below 0,45μm. The reaction of ozone with DOM leads to the formation of BDOC. It means that smaller oxygen-rich compounds, such as carboxylic acids, aldehydes, ketones, etc. are formed. These compounds are typically biodegradable and are described together as BDOC. Organic matter present in aqueous solutions can be classified into two main fractions: biodegradable and refractory (ISABEL C. ESCOBAR, 2001). "*The mechanisms and kinetics of the formation of these compounds is governed by the reaction of ozone with DOM moieties such as phenols or other activated aromatic systems. Upon ozonation, this leads to various olefins and eventually small organic acids and aldehydes. Even though this is only a model approximation of the interaction between DOM and ozone, similar processes occur under realistic conditions*" (Urs von Gunten C. v., 2012).

According to the report of RECHNEAU (T. Juhna, 2006), biofiltration is very successfully applied method mostly in drinking water treatment. Biofilters has been proven to remove DOC far beyond the point of theirs adsorption capacity. This observation, together with the low maintenance costs and the effectiveness made this method very commonly applied. The graph below presents the mechanism of biosorption, which is the process found in the biofilters. Biosorption is a combination of adsorption and biological degradation. (Raymond M. Hozalski, 1999)

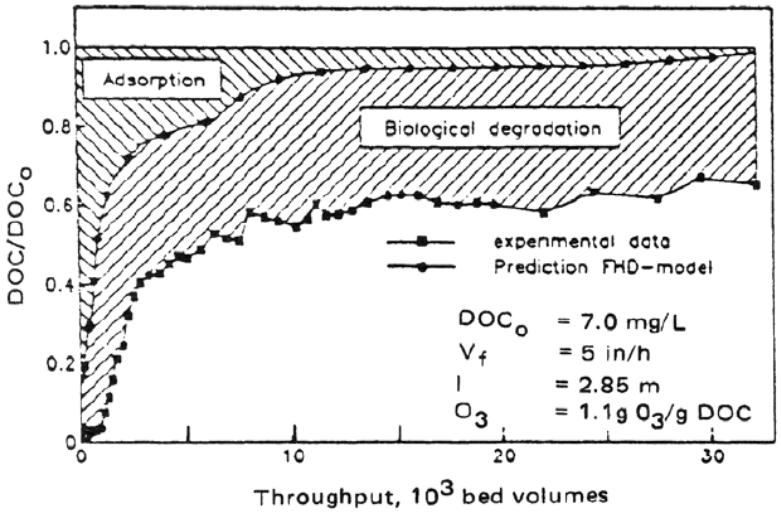


Figure 4. DOC removal by adsorption and biodegradation during biofiltration of an ozonated acid solution (T. Juhna, 2006)

Ozonation-biofiltration process in water treatment can be applied due to following reasons:

1. Disinfection,
2. Color removal,
3. Avoiding biological growth in the network,
4. Enhanced removal of DOC by transforming it into BDOC during ozonation and removing produced BDOC during biofiltration.

The ozonation in drinking water treatment is a promising method to remove DOM from the raw water. The ozonation-biofiltration process is being successfully applied in NOM (natural organic matter) removal. The ozonation step in this kind of treatment is meant to transform DOC into BDOC, however, it has been proven that there is a limitation of this process. According to studies only around 30% of total DOC can be transformed into BDOC during the ozonation process (Wataru Nishijima, 2003). "*The transformation of refractory DOC to BDOC by ozonation may be inhibited by BDOC itself produced by ozonation, because BDOC may also consume ozone*" (Wataru Nishijima, 2003). The aim of the second step, which is most commonly biofiltration, is to remove the BDOC formed during the ozonation (Alex A. Yavich, 2004). The graph below (Figure 5.) shows how ozonation improves the TOC removal in drinking water treatment.

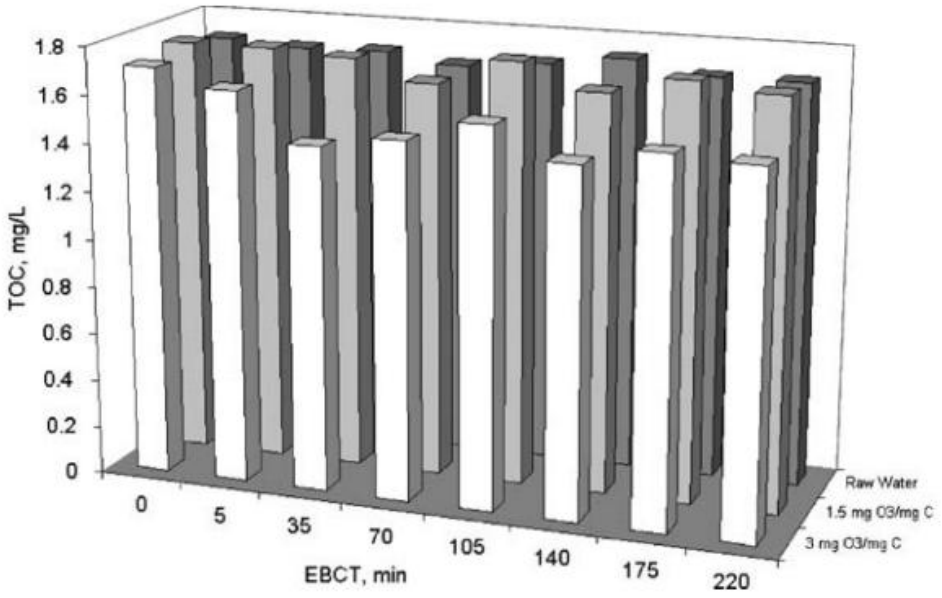


Figure 5. Biodegradation of ozonated Lake Erie water (Alex A. Yavich, 2004)

3.3. Stability of ozone in aqueous solutions; scavenging properties of waters

The main factor affecting the stability of ozone in drinking water and in wastewater is its reaction with the dissolved organic matter (DOM) present in the water. The important fact is that the nature, the composition and the concentration of DOM varies among waters of different sources (Marc-Olivier Buffle, 2006) (Urs von Gunten C. v., 2012). Therefore, each water type has its own specific way of reacting with ozone according to its own unique DOM structure. The type of DOM has an influence on the rate of its reaction with ozone and therefore on the ozone lifetime in these natural waters, drinking waters and wastewaters.

Carbonate alkalinity influences ozone stability by scavenging $OH^{\bullet}$ (Urs von Gunten C. v., 2012). An aspect of considerable consequence in this context is $OH^{\bullet}$ production, resulting from a side reaction of ozone with DOM. The $OH^{\bullet}$ radical is an important intermediate in the decomposition of ozone in water (Urs von Gunten C. v., 2012). It has been proven that both, alkalinity and the DOC content influence ozone decomposition. Therefore, for different types of studied water, which vary in some characteristics, different outcome was expected.

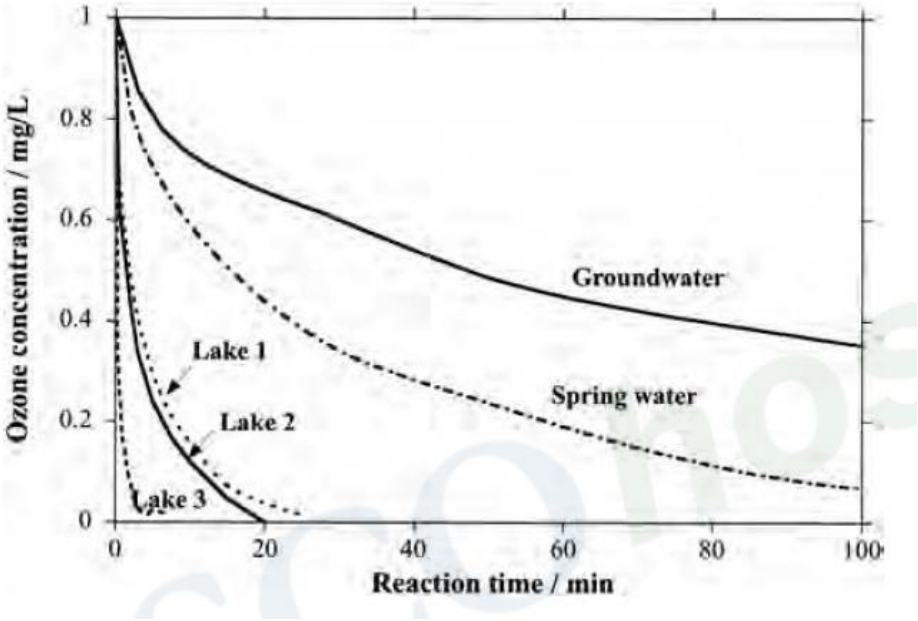


Figure 6. Stability of ozone in various Swiss natural waters at pH 8 and 15°C (ozone dose 1 mg/L). Water quality data: Groundwater (DOC 0.7 mg/L, carbonate alkalinity 6.7 mM); Spring water (DOC 0.9 mg/L, carbonate alkalinity 5.4 mM); Lake 1 (DOC 1.3 mg/L, carbonate alkalinity 2.5 mM); Lake 2 (DOC 1.6mg/L, carbonate alkalinity 3.6 mM); Lake 3 (DOC 3.2 mg/L, carbonate alkalinity 3.4 mM). From Urfer et al., 2001 with permission. (D. Urfer, 2001)

The stability decreases in the sequence groundwater > spring water > lake water 1 and 2 > lake water 3 at pH 8. That corresponds to an increasing DOC concentration and decreasing alkalinity. While keeping the DOC constant, an increase in carbonate alkalinity leads to a significantly lower rate of ozone decomposition (Urs von Gunten C. v., 2012).

Moreover, according to Juan L. Acero, carbonates species (HCO_3^- and CO_3^{2-}) are the promoters accelerating transformation of ozone into $OH^\bullet$ radicals. "*The transformation of O_3 into $OH^\bullet$ radicals as well as the oxidation of a micropollutant, get faster with increasing bicarbonate concentration*" (Juan L. Acero, 2008). Talking about carbonate as an inhibitor that accelerates decomposition of ozone, it is important to note the significance of pH. HCO_3^- and CO_3^{2-} have different reaction rates therefore it is important to know what is the pH of the water to determine present carbonate species. This diversity in reaction rates for carbonates and other scavengers is shown for few examples in the table below.

Table 2. Reactions of OH radical with radical scavengers (Juan L. Acero, 2008)

Reaction	Reaction rate constant k ($M^{-1}s^{-1}$)
$HCO_3^- + OH^\bullet \rightarrow HCO_3^\bullet + OH^-$	$8.5*10^6$
$CO_3^{2-} + OH^\bullet \rightarrow CO_3^{\bullet-} + OH^-$	$3.9*10^8$
$HCO_3^\bullet \leftrightarrow CO_3^- + H^+$	$1*10^{-8}$
$CH_3OH + OH^\bullet \rightarrow {}^\bullet CH_2OH + H_2O$	$9.7*10^8$
$NOM + OH^\bullet \rightarrow xO_2^{\bullet-} + products$	$2.5*10^4$ $(mg/L)^1 s^{-1}$

"*The $OH^\bullet$ scavenging rate of a water can be determined by measuring the rate of the apparent rate constant for the decrease of a probe compound (e.g. pCBA) as a function of varying tBuOH concentrations*" (Urs von Gunten C. v., 2012). "*Without knowing the $OH^\bullet$ scavenging rate of a given water, one can also follow the elimination of an ozone-refractory test compound such as pCBA for which the $OH^\bullet$ rate constant is known ($k= 5*10^9 M^{-1}s^{-1}$) and with the knowledge of the $OH^\bullet$ rate constants of other micropollutants, their degradation can be calculated*" (Urs von Gunten C. v., 2012).

3.4. Kinetics of ozonation

As described in the previous chapter, the oxidation by ozonation proceeds in two parallel ways: as direct and indirect oxidation. The direct oxidation involves molecular ozone, whereas the indirect oxidation is observed due to the $OH^\bullet$ radicals appearance during ozone decomposition. "*To assess ozonation process with respect to oxidation by ozone and $OH^\bullet$ radicals, the concentration or the exposures of both oxidants have to be known*" (Urs von Gunten, 2003). The concentration of ozone can be measured easily by various methods, one of them is precisely described in the method part. On the contrary, the $OH^\bullet$ radicals concentration is extremely difficult to measure. "*This is due to their high reactivity towards the water matrix and ozone, which leads to very low steady-state concentrations, typically below $10^{-12}M$ during ozonation*" (Urs von Gunten, 2003).

Several ways of assessing $OH^\bullet$ radicals concentration are presented in the literature. One of them is a numerical modeling (K.Chelkowska, 1991). However, the modeling is usually quite difficult to apply in natural water and wastewater due to its complex composition. Every model needs to include the fact that the ozone decomposition is always affected by the scavengers present in these water and its consumption of radicals. "*Therefore, model*

predictions of transient $OH^{\bullet}$ radical concentrations are quite arbitrary and generally do not agree well with experimental observation" (Urs von Gunten, 2003).

The most suitable method, for assessing $OH^{\bullet}$ radicals concentration in treated grey water is definitely the method named by Urs von Gunten: "*Experimental calibration of natural waters by indirect measurement of OH• radicals with an ozoneresistant probe compound*". This method allows to track $OH^{\bullet}$ radicals concentration by measuring the removal of the compound that can be only removed by radicals. Commonly, this compound is para-chlorobenzoic acid (pCBA) (Paul Westerhoff, 1999), (Urs von Gunten, 2003), (Juan L. Acero, 2008).

Main purpose of conducting the experiments was to determine the kinetics of the process. In order to do it the differential rate law or the integrated rate law can be used. Often, the exponents in the rate law are the positive integers: 1 and 2 or even 0. Thus the reactions are zeroth, first, or second order in each reactant (CHEMWIKI, UC DAVIS, 2015). According to the literature, ozone decay is expected to proceed as a first order kinetics process and the degradation of micropollutants should show characteristics of a second order kinetics process.

The kinetics of aqueous ozonation process play an important role in assessing the feasibility of treating organic compounds. The careful study of the kinetics of ozonation is immensely important in order to be able to distinguish between the direct ozone reaction and the hydroxyl radical ($HO^{\bullet}$) chain processes that occur in most types of ozonated waters. Such chains can proceed even at low pH, where the $HO^{\bullet}$ initiation is slow, for compounds like formic acid, alcohols, aromatics, and humic acids that release $HO^{\bullet}_2/O_2^-$ following the reaction with $HO^{\bullet}$. It is important to differentiate between the two oxidation pathways because the hydroxyl radical content varies with the type and the concentration of solutes present in the water (C. C. David Yao, 1991).

Additionally, it has been proven that the kinetics of ozonation is affected by other numerous factors such as the temperature, pH, initial concentrations and water composition. For example for DEET according to the study: (Kheng Soo Tay, 2009), the rate of DEET degradation increased exponentially with temperature in the range studied (20–50 °C) and proportionally to the dosage of ozone applied. During the ozonation of DEET under different pH conditions in the presence of phosphate buffer two stages were distinguished. During the first stage, the rate constant, k_{obs}, increased with increasing pH, whereas in the second stage, the rate constant, k_{obs2}, increased from pH 2.3 up to 9.9, however, it decreased when the pH value exceeded 9.9. In the case where buffers were not employed, the k_{obs} were found to

increase exponentially with pH from 2.5 to 9.2 and the ozonation was observed to occur in one stage. The rate of degradation decreased exponentially with the initial concentration of DEET (Kheng Soo Tay, 2009).

According to (Urs von Gunten C. v., 2012), the kinetics of micropollutant ozonation is strongly affected by reaction of ozone with DOM. Therefore, only those micropollutnts that react rapidly with ozone have a chance to be oxidized by ozone via the direct pathway. The elimination of different micropollutants with varying second-order rate constants are presented in the figure below as a function of a specific ozone dose.

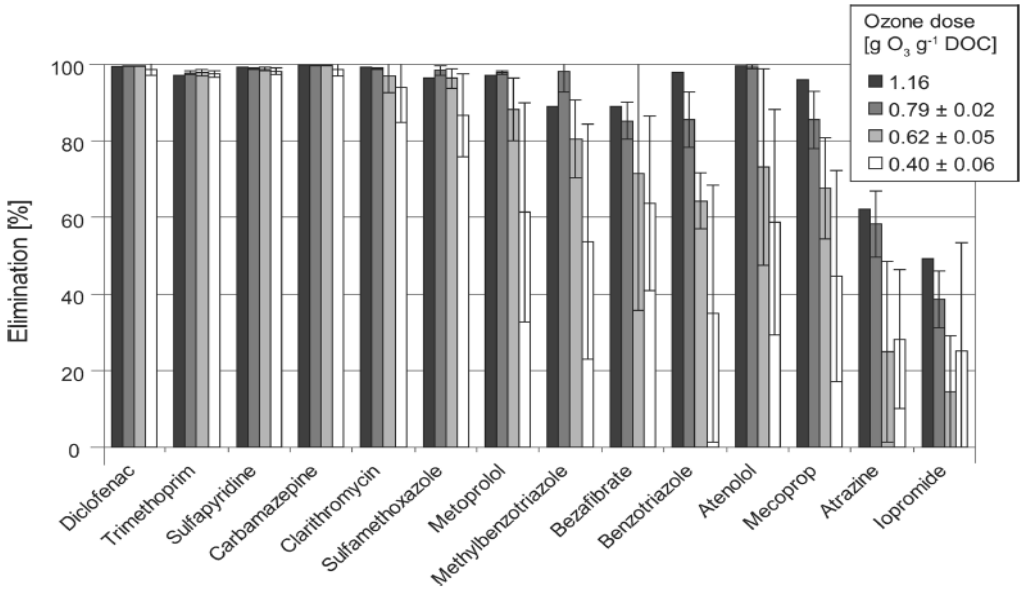


Figure 7. Effect of the ozone dose on the relative elimination of selected micropollutants in the ozone reactor. Results of campaigns with similar ozone doses were averaged (± standard deviation). (Juliane Hollender, 2009)

Some of presented compounds are fast-reacting with ozone directly, they are presented in the beginning – from diclofenac to sulfamethoxazole ($k_{O3} > 10^4 M^{-1}s^{-1}$). Those compounds are fully eliminated even at low specific ozone doses per DOC. For compounds from etoprolol to atenolol ($2*10^2 M^{-1}s^{-1} < k_{O3} < 10^4 M^{-1}s^{-1}$), significantly higher doses are needed. These micropollutants have intermediate ozone reactivity, specific dose of about 1g ozone per g DOC is used for complete elimination. For compounds with second order rate constant near $100 M^{-1}s^{-1}$ and below (mecoprop to iopromide), specific ozone doses of about 1g ozone per g DOC can guarantee elimination of 50-90% only. For these micropollutants the indirect ozonation pathway is taking place. Elimination is dominated by $OH^{\bullet}$ radicals (Urs von Gunten C. v., 2012).

Degradation of micropollutant (*S*) during ozonation can be expressed by following equation (Yunho Lee D. G., 2013):

$$-\ln\left(\frac{[S]}{[S]_0}\right) = k_{O_3}\int [O_3]dt + k_{\bullet OH}\int [OH\bullet]dt. \quad (1).$$

Two constant: k_{O3} and $k_{OH\bullet}$ appearing in the equation describe reactivity of the compound with ozone and hydroxyl radicals. Knowing the k_{O3} and $k_{OH\bullet}$ values the pathway and rate of the degradation can be predicted. As mentioned before, the k_{O3} and $k_{OH\bullet}$ values are currently known for many organic compounds including some micropollutants (a few hundred rate constants for ozone and a few thousand for $OH^{\bullet}$) (Urs von Gunten C. v., 2012), (Yunho Lee D. G., 2013).

Knowing k_{O3} and $k_{OH\bullet}$ from the literature, in the equation 1 the only unknown values would be the ozone exposure $[O_3]$ and hydroxyl radicals exposure $[OH^{\bullet}$. As mentioned before, ozone exposure can be assess easily by measuring ozone concentration (using indigo method described in the method part) and plotting it over time and integrating it by calculating the area under the curve. However, radicals exposure measurements require application of probe compound since it cannot be measured directly. In the method developed by Michael S. Elovitz and Urs von Gunten, the R_{ct} value was introduced in order as the ratio of hydroxyl radicals and ozone exposure ($OH^{\bullet}$-ct and O_3-ct). The R_{ct} value is enough to evaluate fraction removed by radicals. According to (Michael S. Elovitz, 2008):

$$R_{ct} = \frac{\int [\mathrm{OH}\bullet]\mathrm{dt}}{\int [O_3]dt}, \quad (2)\ therefore$$

$$R_{ct} = \frac{[\mathrm{OH}\bullet]}{[O_3]}. \quad (3)$$

In these equations the time-integrated ozone concentration is the ozone exposure O_3-ct, and the time-integrated radicals concentration is the radicals exposure.

3.4.1. pCBA - $OH^{\bullet}$ radicals probe compound

Para-chlorobenzoic acid (pCBA) removal by ozone is being a subject of many studies due to a few reasons. One of them is removal of pCBA as an unwanted micropollutant, nevertheless, this is not the only purpose of studying its degradation. As mentioned before, $OH^{\bullet}$ radicals cannot be measured directly during an ozonation process, therefore, other methods need to be applied. pCBA is an example of a compound that is removed only by radicals, therefore, its removal is studied not only in terms of micropollutant degradation but also it has been used recently as an $OH^{\bullet}$ radical probe compound during ozonation due to its very slow direct reaction with ozone and fast reaction with $OH^{\bullet}$ radicals. The basis of this method is the assumption of the direct ozonation rate constant equal to zero.

The decrease of pCBA can be formulated as (Urs von Gunten, 2003):

$$\frac{-d[pCBA]}{dt} = k_{OH,pCBA} \int [\mathrm{OH}\bullet]dt, \qquad (4)$$

Substitution of the

$$\ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -R_{ct} * k_{OH,pCBA} * \int O_3 dt. \qquad (5)$$

The $OH^{\bullet}$ radical exposure ($\int [\mathrm{OH}\bullet]dt, OHct$) can be measured by the decrease of an ozone-resistant probe compound, such as pCBA according to:

$$\int [OH\bullet]dt = -\ln\left(\frac{[pCBA]}{[pCBA]_0}\right)/k_{OH}, \qquad (6)$$

$$therefore, \qquad [OH\bullet] = d\frac{(\int [OH\bullet]dt)}{dt}. \qquad (7)$$

The ozone exposure can be calculated by the integration of the ozone concentration over time. In natural water studied by Urs von Gunten (2003) a plot of the logarithmic decrease of pCBA ($OH^{\bullet}$ radical ct-value, $OH^{\bullet}$ radical exposure) vs. the measured ozone exposure showed two phases (initial and secondary) for which fairly good linear correlations of the two parameters could be established. The slope of this correlation corresponds to $R_{ct} * k_{OH,pCBA}$. Because $k_{OH,pCBA}$ is constant, this means that the ratio R_{ct} of the exposures (ct-values) of $OH^{\bullet}$ radicals and ozone ($[OH^{\bullet}]/[O_3]$) can also be considered constant. This empirical concept is based on the fact that during an ozonation process, the pseudo first-order rate constant for transforming ozone and scavenging $OH^{\bullet}$ radicals remains constant (Urs von Gunten, 2003).

Moreover, "*in wastewater ozonation, it was recently shown that R_{ct} values and $OH^{\bullet}$ exposures are very high and decrease exponentially during the entire duration of ozone*

decomposition" (Marc-Olivier Buffle, 2006). It indicated that the ozone decomposition kinetics in wastewater is rather similar to the first phase of ozone decomposition in natural water.

Table 3. Hydroxyl radical and ozone rate constants for studied compounds according to (Werner R. Haag, 1992), (Gang Wena, 2011) and (Daniel Gerrity, 2012)

Compound	Hydroxyl radical rate constant [$M^{-1}s^{-1}$]	Ozone rate constant (pH=7) [$M^{-1}s^{-1}$]
pCBA	5×10^9	<0.15
DEET	5×10^9	<10
DEP	$3.98(\pm 0.21) \times 10^9$	0.085±0.021

According to (Daniel Gerrity, 2012), both, pCBA and DEET belong to the group of compounds moderately reactive with both ozone and $OH^{\bullet}$ radicals.

3.4.2. Quantification of oxidation by ozone and by $OH^{\bullet}$ radicals

To quantify the extent of oxidation during an ozonation process, it is necessary to combine the characterization of the ozonation process with the available kinetic information. The oxidation of a micropollutant S during an ozonation process can be formulated as follows (Gunten, 2003):

$$-\frac{d[S]}{dt} = k_{O_3}[S][O_3] + k_{OH}[S][\mathrm{OH}\bullet]. \qquad (8)$$

As shown above, the ratio *Rct* of the concentrations of $OH^{\bullet}$ radicals and ozone can be measured by adding an ozone-resistant probe compound (e.g. pCBA) (Gunten, 2003):

$$R_{ct} = \frac{[\mathrm{OH}\bullet]}{[O_3]}. \qquad (9)$$

Substituting the equation (9) in equation (8) yields (Gunten, 2003):

$$-\frac{d[S]}{dt} = \left(k_{O_3} + k_{OH} * R_{Ct}\right) * [S] * [O_3]. \qquad (10)$$

Integrated for a batch reactor this yields (Gunten, 2003):

$$\ln\left(\frac{[S]}{[S]_0}\right) = -\left(k_{O_3} + k_{OH} * R_{Ct}\right) * \int [O_3]dt, \quad (11)$$

where S is the micropollutant, k_{O3} is the second-order rate constant for the reaction of S with ozone, k_{OH}: second-order rate constant for the reaction of S with $OH^{\bullet}$ radicals.

The fraction $f(\mathrm{OH}\bullet)$of S reacting with $OH^{\bullet}$ radicals can be calculated as (Gunten, 2003):

$$f(\mathrm{OH}\bullet) = \left(k_{OH} * R_{Ct}/(k_{O_3} + k_{OH} * R_{Ct})\right). \quad (12)$$

A summary presented by Kerwin L. Rakness shows the most important features of the R_C concept. R_{Ct} value is a function of pH, temperature, alkalinity and DOC concentration and composition. The main characteristics according to (Kerwin L. Rakness, 2005), are listed below:

- R_{ct} increases with increasing temperature.
- R_{ct} increases with increasing pH.
- R_{ct} decreases with increasing alkalinity (carbonate concentration), therefore, $OH^{\bullet}$ radicals exposure decreases with increasing alkalinity because of the fact that carbonate has a high scavenging rate of $OH^{\bullet}$ radicals.
- R_{ct} increase with increasing DOC concentration, consequently, $OH^{\bullet}$ radicals exposure is grater for higher DOC concentrations.

When applying ozonation as advanced oxidation step in wastewater treatment, it is important to have $OH^{\bullet}$ radicals exposure sufficiently big to oxidize present micropollutants. It may happen that the characteristics of water make it impossible to achieve this sufficient level by spontaneous ozone decomposition and the enhanced $OH^{\bullet}$ exposure is needed. The enhanced $OH^{\bullet}$ radicals exposure can be achieved by addition of hydrogen peroxide or UV irradiation of ozonated water (Kerwin L. Rakness, 2005).

3.4.3. Ozonation of DEET

According to literature, ozonation of DEET has a similar characteristics to the pCBA removal by ozone. Studies have shown that kinetics of the process are very similar and DEET is removed mostly by $OH^{\bullet}$ radicals as well. (Kheng Soo Tay, 2009). "*The low value of the rate constant for the reaction of DEET with molecular ozone indicates that in a real water treatment, where $OH^{\bullet}$ radicals can be generated from ozone decomposition (...), the oxidation of DEET is performed mainly by $OH^{\bullet}$ radicals*" (F. Javier Benitez, 2013).

As shown in the table 3 "Hydroxyl radical and ozone rate constants for studied compounds", the ozone rate constant for DEET is lower then 10, whereas the $OH^{\bullet}$ radicals rate constant is equal to the pCBA rate constant with radicals: $5*10^9$. It means that the rate constant of the reaction with molecular ozone has 8 times lower order of magnitude than the

reaction with $OH^{\bullet}$ radicals. Therefore, the main contribution to the degradation by ozonation of DEET is the indirect ozonation through the $OH^{\bullet}$ radicals pathway (Weihua Song, 2009).

3.4.4. Ozonation of DEP

The values of rate constant of radicals and ozone with DEP are quite different from DEET and pCBA. As shown in the table 3 "Hydroxyl radical and ozone rate constants for studied compounds", the ozone rate constant for DEP is lower than 0.1, whereas the $OH^{\bullet}$ radicals rate constant is close to the value $4*10^9$. It indicates that the degradation of DEP is different from DEET and pCBA. DEP is expected to be less reactive then other compounds with ozone by both oxidation pathways. Therefore, worse removal efficiency is expected. However, similarly to pCBA and DEET, it is still much more reactive with radicals with molecular ozone. The proposed degradation pathways of DEP in literature were divided into hydrolysis of the aliphatic chain and hydroxylation resulting from $OH^{\bullet}$ attack in the aromatic ring. (Yeon Jung Jung, 2010)

4. Characteristics of studied water types

4.1. Permeate from pilot plant

The base of the study was to investigate the feasibility of applying the ozonation step to the pilot scale treatment plant as a final polishing step of treatment combined with biofiltration. This step is expected to remove the problematic micropollutants, as well as, break down DOC into biodegradable BDOC, improve the phosphorus removal and remove color. The pilot plant experiments on the synthetic grey water were the source of water used in the experiment. The pilot plant was designed for enhanced nutrient removal consisted of the Integrated Fixed-film Activated Sludge (IFAS) system operated in the UTC-process mode for enhanced biological nutrient removal (EBNR) with membrane particle separation. Kubota Type 203 flat sheet micro-filtration membranes were applied.

The scheme below shows the pilot plant configuration. First step of the treatment is the enhanced biological treatment. The enhanced biological treatment is designed in order to remove all the nutrients and organics in bioreactors without applying any coagulants or other chemicals. The biological part consist of three tanks: anaerobic, anoxic and aerobic. In two first tanks there is no aeration (only mixing), the third one is aerated. The sludge need to be recycled in order to maintain the process. The sludge need to be returned from anoxic tank to anaerobic and from aerobic to anoxic. The characteristic feature of this type of treatment in comparison to the conventional treatment is the presence of anoxic tank prior to aerobic tank. Under these conditions a group of bacteria present in the sludge called polyphosphate-accumulating organisms (PAO) are accumulating more phosphorus and secondly by separation of the biomass, the phosphorus is removed from water. Following step is the membrane filtration which separates the sludge from the permeate. The ozonation-biofiltration step is planned to be introduced after the membrane filtration (V.A. Bjerkelund)

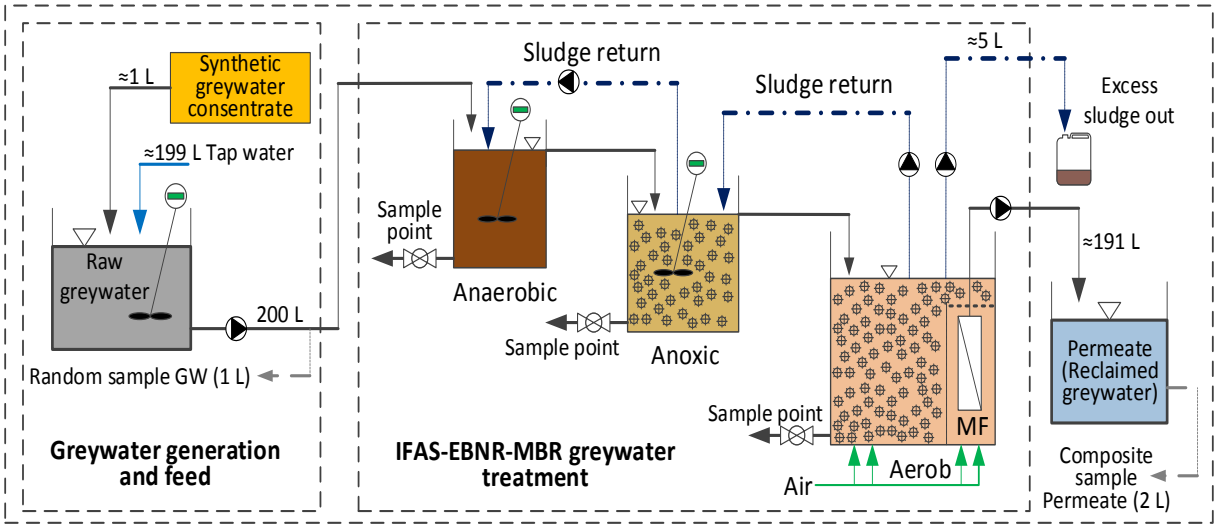


Figure 8. Pilot plant scheme in flow trough system (recycled system turns back 80% of permeate from the last tank into raw gray water after reusing it) (V.A. Bjerkelund)

Grey water is defined as all wastewater from household and office buildings apart from wastewater from toilet. The composition of grey water depends on sources, typical sources are kitchen, bathroom, laundry etc. The main characteristics differentiating grey water from typical wastewater is lower ammonia concentration (in general also lower nutrient concentration) and lower organic carbon content (Eva Eriksson, 2001). The synthetic grey water used in the study was meant to imitate real conditions as precisely as possible. Therefore, the list of cosmetics, detergents etc. was prepared based on the data from "Market Trends 2011 Report" (Nielsen, 2011) and the Norwegian Cosmetics Association. These documents provided the information about the composition of the Norwegian grey water and enabled to recreate typical grey water in the laboratory (V.A. Bjerkelund). Characteristics of raw grey water applied in the pilot plant are presented in the table 4 below.

Table 4. Raw artificial grey water characteristics (V.A. Bjerkelund)

Measured parameter	Raw grey water entering IFAS-EBNR-MBR system
pH	7.6
C (μS/cm)	338
Alk (meq/L)	2
Turbidity (NTU)	80
SS (mg/L)	62
VSS (mg/L)	31
COD (mg/L)	517
FCOD (mg/L)	400
BOD_5 (mg/L)	264
TOT-P (mg/L)	5.67
TOT-N (mg/L)	20
NH_4-N (mg/L)	1.38
NO_3-N (mg/L)	<0.23
Nonion. Sur. (mg/L)	3.78
Anion. Sur. (mg/L)	65
COD:N:P	100:3.5:1.1

Before achieving the stable state in the pilot plant, water has been changing properties and the modification of the system has been changed several times as well. The first type of water used for the study comes from the period when there has been no recycling of permeate yet. This type is called "grey water flow through" (GFT) for the purpose of this study. The second type of water samples were collected in the period of steady state and recycling of the permeate. Water from this period is called "recycled grey water" (RGW). The RGW has some differences in the composition, recycling caused the up-concentration of TOC and carbonates (higher alkalinity). The scheme presented on the previous page (Figure 8.) presents the pilot plant set-up without recycling water. The recycling set-up varies only in the return of the permeate to the raw grey water tank after reusing it. The chart below (Figure 9.) presents properties of permeate in the time period of four months. Water samples used in the study

comes from time period: 28th August–7th September 2014 - GFT and 12th April 2014 – RGW. More detail characteristics are given in the tables below (Tables 5 and 6).

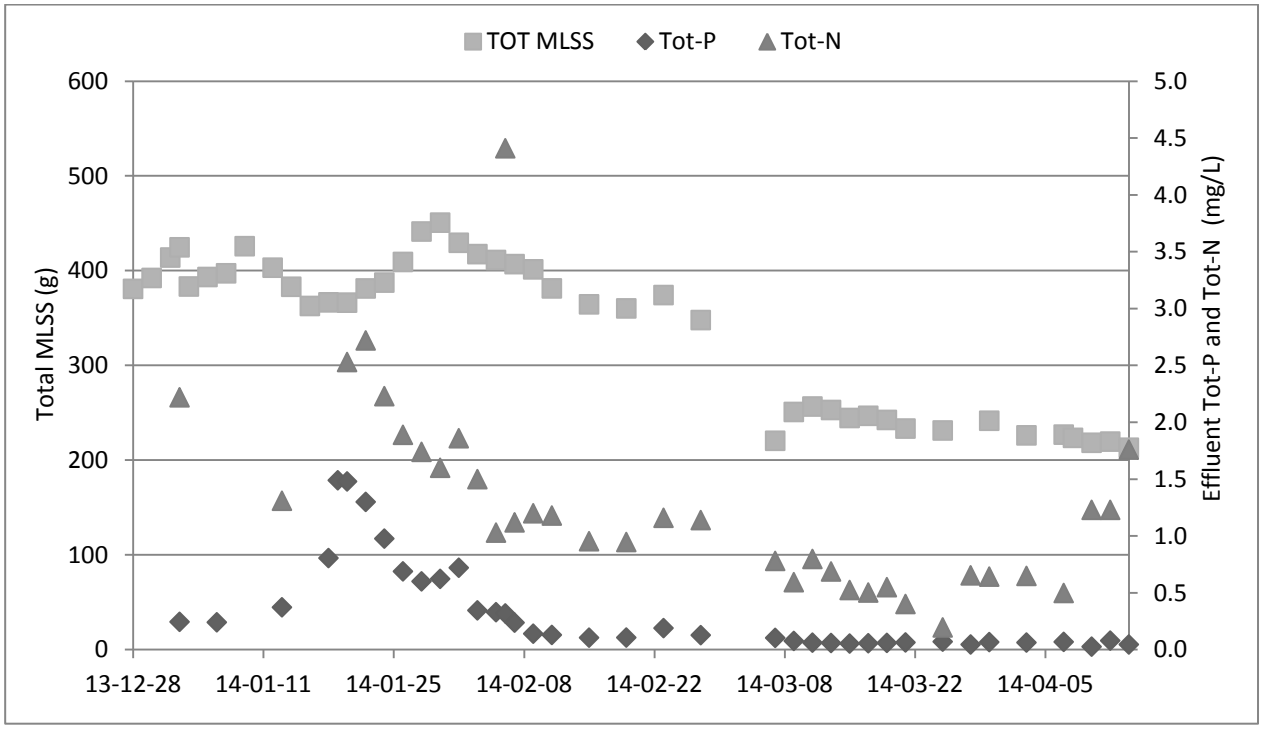


Figure 9. Proprieties variation of permeate from pilot plant during time period of 4 months

Table 5. Properties of GFT water type

Parameter		**Parameter**		**Parameter**	
(unit)	value	(unit)	value	(unit)	value
pH	7.75	**"VTDS"**		**COD/TOC**	
Conductivity		(mg/L)	52.00	(ratio)	2.96
(µS/cm)	353.00	**SUVA**		**C-DOC**	
Alkalinity		(Lm-1 mg-1)	2.07	(mg/L)	3.29
(meq/L)	1.97	**TDS**		**Biopolymers**	
(mg CaCO3/L)	98.50	(mg/L)	206.40	(mg/L)	0.15
UV		**COD**		**Humics**	
(abs/5cm)	0.49	(mg/L)	14.10	(mg/L)	2.08
Color		**TIC**		**TOT-P**	
(mg Pt/L)	15.57	(mg/L)	23.37	(mg/L)	0.08
"TDS" 100		**TOC**		**TOT-N**	
(mg/L)	213.00	(mg/L)	4.77	(mg/L)	1.23

Table 6. Properties of RGW water type

Parameter		**Parameter**		**Parameter**		**Parameter**	
(unit)	value	(unit)	value	(unit)	value	(unit)	value
pH	8.09	**UV**		**SUVA**		**TOT-P**	
Conductivity		(abs/5cm)	0.87	(Lm-1 mg-1)	1.98	(mg/L)	0.48
(µS/cm)	1362.17	**Color**		**TDS**		**TOT-P**	
Alkalinity		(mg Pt/L)	29.34	(mg/L)	790.69	(mg/L)	0.48
(meq/L)	5.18	**"TDS" 100**		**COD**		**PO4-P**	
(mg CaCO3/L)	259.08	(mg/L)	836.00	(mg/L)	27.18	(mg/L)	0.04
Turbidity		**"VTDS"**		**TOC**		**TOT-N**	
NTU	0.17	(mg/L)	136.67	(mg/L)	8.83	(mg/L)	2.42

As shown in the graphs and the tables, studied water types have different characteristics. The most important ones in the research on ozonation, seem to be alkalinity, total carbon concentration and pH. As described before, these are factors mainly affecting ozonation process. The GFT water type characterize in low alkalinity and lower TOC value in comparison with the RGW water type, for which those values are almost doubled. Another difference is pH, however, the difference may be not significant enough to compare the pH influence on the ozonation process.

4.2. Buffered Milli-Q water

For the purposes of the study Milli-Q water was buffered at pH=8 with potassium dihydrogen phosphate (KH_2PO_4) and dipotassium hydrogen phosphate (K_2HPO_4). Phosphates have a very high buffering capacity and are highly soluble in water. This allowed to conduct the ozonation of pCBA in pure water without effect of dropping pH.

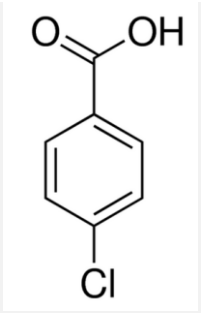
5. Characteristics of studied compounds

The subjects of the study were three micropollutants. Two of them are commonly found in grey water (DEET, DEP). The third one as a pollutant would be found in industrial waste water (pCBA) but it is not studied as a micropollutant most commonly. The specific way of reacting with ozone allows to use it as a probe compound to measure $OH^{\bullet}$ radicals concentration, which is widely described in following chapter.

5.1. PARA-CHLOROBENZOIC ACID (pCBA)

The first studied compound is 4-Chlorobenzoic Acid commonly known as pCBA. This compound is commercially used as an intermediate for manufacturing dyes, fungicides, pharmaceuticals and other organic chemicals. It is used as a preservative in adhesives and paints. This micropollutant is also often used in the ozonation process kinetics research as a $OH^{\bullet}$ radicals probe compound since their concentration cannot be measured directly and pCBA can only be removed by radicals (Yunzheng Pi, 2006).

Table 7. Identification and properties of pCBA

pCBA	
	
FORMULA	ClC_6H_4COOH
CAS NO.	74-11-3
MOLECULAR WEIGHT	156.57
TOXICITY	Oral rat LD50: 1170mg/kg
PHYSICAL STATE	White to off-white crystalline flakes
MELTING POINT	242-245°C
SOLUBILITY	Soluble in hot water

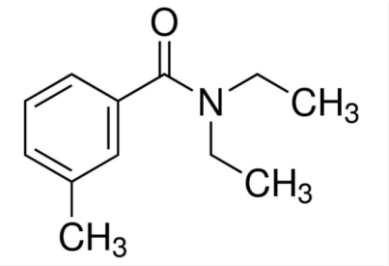
5.2. N,N-DIETHYL-M-TOLUAMIDE (DEET)

N,N-Diethyl-m-Toluamide, commonly known as DEET, is an insect repellent. It is usually applied on human skin directly and on clothing and households. It is primarily used to protect against biting pests such as mosquitoes and ticks (Jackson, Buhl, & Stone, 2008). Because of its low cost and a broad insecticidal spectrum of activity against mosquitoes, flies, fleas, ticks and other biting insects, it has been extensively employed for the protection of humans and animals. The domestic usage of DEET is estimated to be 1800 tons annually and as a consequence DEET has been unintentionally discharged into the environment and become one of the most frequently detected contaminants in water resources in the United States. For example, it has been detected at concentrations up to 1.1 mg/L in 74% of 54 water samples collected from various U.S. streams (Weihua Song, 2009). Formulations of the repellent include liquids, pressurized liquids, lotions, sticks, foams, etc. Uses for the individual products containing DEET vary widely. DEET is a liquid with a distinct, faint odor and is almost colorless. DEET is a plasticizer and can damage certain rubber, plastic, vinyl, or elastic materials such as contact lenses, eyeglass frames and lenses, watch crystals, combs, painted and varnished surfaces, and certain synthetic or treated fabrics. DEET does not damage natural fibers including cotton and wool. It has been previously estimated that approximately 30% of the U.S. population uses DEET annually as a personal insect repellent. Scientists have not definitively determined the exact mode of action of DEET in target organisms. Research indicates that DEET interferes with receptors in a mosquito (and other biting insects) antennae that detect L-lactic acid and carbon dioxide, the primary attractants emitted by humans and other animals. Insects exposed to DEET are thereby unable to effectively locate a host (Jackson, Buhl, & Stone, 2008). DEET has been found in water where wastewater is thought to contribute to stream-flow. The median level found was 0.05 μg/L, with the highest levels (1.10 μg/L) found in streams with urban wastewater (Jackson, Buhl, & Stone, 2008). Contaminations of DEET have been studied and reported in various aquatic environments, such as groundwater, streams, seawater, effluents from sewage plant, and even drinking water treated by conventional water treatment systems.

DEET has been reported to have potential carcinogenic properties in human nasal mucosal cells. Ingestion of low doses of DEET in children has been reported to result in coma and seizures. Currently, there is no legislation controlling the amounts of both usage and discharge of DEET into the environment. Thus, greater attention should be paid to removing this chemical, especially in the production of drinking water (Kheng Soo Tay, 2009).

Regarding its toxicity and mischievousness towards human health, DEET is allowed to use in most of the countries. In all the reports and official websites of organizations as EPA (United States Environmental Protection Agency) DEET is claimed to be safe to use even for small children. Some years ago there was a lot of controversy among applying of this compound due to its potential danger. Concerns regarding DEET emerged in the 1980's after reports about encephalopathy after DEET exposure, particularly among children (Vanessa Chen-Hussey, 2014). However, none of these concerns were successfully confirmed. Moreover, the article by Vanessa Chen-Hussey practically neglect all the accusations against DEET. The medical environment is more concerned about human's health than environment or even slight (not proved yet) negative effect on human's body. Doctors are underlining the positive aspect of preventing spreading diseases distributed by insects by using repellants. Following quote justifies this attitude. "*The theoretical risks associated with wearing an insect repellent should be weighed against the reduction or prevention of the risk of fatal or debilitating diseases including malaria, dengue, yellow fever and filariasis. With over 48 million European residents travelling to regions where vector borne diseases are a threat in 2009, restricting the concentration of DEET containing repellents to 15% or less, as modeled in the 2010 EU directive, is likely to result in extensive sub-therapeutic activity where repellents are infrequently applied. Future European travelers, as a consequence of inadequate personal protection, could potentially be at increased risk of vector borne diseases. Risk assessments of repellents should take these factors into account when setting safe limits"* (Vanessa Chen-Hussey, 2014). Nevertheless, worth mentioning is the fact that apart from all the evidence on safety of DEET, on every product that contain DEET there is a suggestion to wash it from the body as soon as possible, not to apply over irritated or cut skin, not to use under clothes, avoid over-application etc.

Table 8. Identification and properties of DEET

DEET	
	
FORMULA	$CH_3C_6H_4CON(C_2H_5)_2$
CAS NO.	134-149-7
MOLECULAR WEIGHT	191.27
TOXICITY	Oral rat LD50: 1950mg/kg
PHYSICAL STATE	Clear to yellow oily liquid
MELTING POINT	-45°C
SOLUBILITY	Slightly soluble

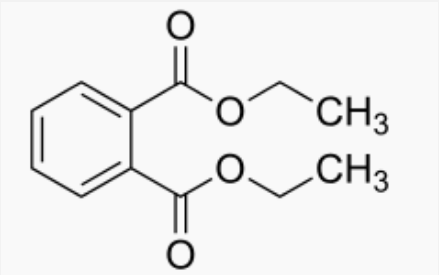
5.3. DIETHYL PHTHALATE (DEP)

Diethyl phthalate is used in a wide range of consumer goods. It has been the subject of great public concern in recent years. Diethyl phthalate is currently used through direct addition in cosmetic products and indirectly in fragrances. The material is listed in the inventory of ingredients employed as a solvent and vehicle in fragrance and cosmetic products, as well as a denaturant, and film former. (SCCNFP, 2002) Small molecule phthalates are used as solvents in perfumes to provide longer linger longer and in nail polish to prevent chipping. They are also used as ingredients of insect repellents, as solvents in lacquer and pesticides, and as dye carrier. Diethyl phthalate is used as a solvent and a vehicle for fragrance and cosmetic ingredients, as well as alcohol denaturant. DEP was reported in 1995 as an ingredient in 67 formulations in the USA at the concentrations ranging from less than 0.1% to 50%. They include bath preparations (oils, tablets, salts), eye-shadows, toilet waters, perfumes and other fragrance preparations, hair sprays, wave sets, nail polish, and enamel removers, nail extenders, nail polish, bath soaps, detergents, after-shave lotions, and skin care preparations. Otherwise, diethyl phthalate is used as a plasticizer for cellulose ester plastic films and sheets (photographic, blister packaging, and tape applications) and molded

and extruded articles (consumer articles such as toothbrushes, automotive components, tool handles, and toys (SCCNFP, 2002).

Regarding human's health, diethyl phthalate is claimed to cause damage to the nervous system as well as to the reproductive system, for both men and women. It has been shown in numerous studies (Amir Miodovnik, 2011), (Ivelisse Colón, 2000), (Shanna H. Swan, 2008). Still very little is known about chronic toxicity, nevertheless, published data about the effects on fertility should be concerning enough to reconsider the addition of DEP to the cosmetics. Although reports usually underline that he uptake of DEP via skin after applying cosmetics is minor, the case of introducing this compound into natural waters via wastewater effluent should be reconsider. Moreover, in the potential reuse of grey water concept this is one of the micropollutants which up-concentration effect is very probable since it is present in numerous cosmetics and daily care products, which after applying on human's skin are eventually flushed down the drain as a grey water.

Table 9. Identification and properties of DEP

DEP	
	
FORMULA	$C_6H_4(COOC_2H_5)_2$
CAS NO.	84-66-2
MOLECULAR WEIGHT	222.24
TOXICITY	Oral rat LD50: 8600mg/kg
PHYSICAL STATE	Clear oily liquid
MELTING POINT	-3°C
SOLUBILITY	Slightly soluble

6. Experiment

The series of experiments were scheduled according to the matrix below. For each type of water degradation of three compounds was studied (pCBA, DEP and DET) for three ozone doses (5mg/L, 7,5mg/L and 10mg/L). Every experiment was conducted in three repetitions. It gave a total number of 54 experiments. After collecting all data, the average from all three trials was calculated and presented partly in the Result section and partly in the Appendix. Three repetitions allowed to estimate errors and all the errors bars are presented on the curved in the Appendix.

Doses of micropollutants varied. For pCBA in GFT and RGW dose of 100μg/L was applied, for buffered MQ water dose of 0.5mg/L, 2.5mg/L and 5mg/L were tried out in order to be able to keep track on the removal. For DEET and DEP dose of 500μg/L was used.

Table 10. Matrix presenting experiment schedule

	pCBA	**DEET**	**DEP**
Grey water flow through (GFT) – 1st type of permeate from the pilot plant, pH 7.8, ALK 2meq/L, low DOC	3 doses of ozone (5 mg/L, 7.5 mg/L, 10mg/L) x 3 trials	3 doses of ozone (5 mg/L, 7.5 mg/L, 10mg/L) x 3 trials	3 doses of ozone (5 mg/L, 7.5 mg/L, 10mg/L) x 3 trials
Recycled grey water (RGW) – 2nd type of permeate from the pilot plant pH 8, ALK 5.1meq/L, high DOC	3 doses of ozone (5 mg/L, 7.5 mg/L, 10mg/L) x 3 trials	3 doses of ozone (5 mg/L, 7.5 mg/L, 10mg/L) x 3 trials	3 doses of ozone (5 mg/L, 7.5 mg/L, 10mg/L) x 3 trials
MQ, pH 8, one ozone dose 5mg/L	1 dose of ozone (5mg/L) x 3 trials		

6.1. Chemicals

Mili-Q

Mili-Q water (MQ) is water used in the laboratory to dilute, clean, prepare samples etc. It is prepared by Mili-Q Q water purification system. According to the Mili-Q© standards used water is called "type 1 Mili-Q water". "*Type 1 water is the grade required for critical laboratory applications such as HPLC mobile phase preparation, blanks and sample dilution in GC, HPLC, AA, ICP-MS and other advanced analytical techniques; preparation of buffers and culture media for mammalian cell culture and IVF; production of reagents for molecular biology applications (DNA sequencing, PCR); and preparation of solutions for electrophoresis and blotting*" (Milli-Q® Water Purification Systems).

Table 11. MQ water characteristics (Milli-Q® Water Purification Systems)

Parameter	Value for Type 1 MQ water
Ions: Resistivity (MΩ•cm @ 25°C)	>18
Organics TOC (ppb)	<10
Pyrogens (EU/mL)	<0.03
Particulates >0,2m (units/mL)	<1
Colloids: Silica (ppb)	<10
Bacteria (cfu/mL)	<1

Micropollutants standards:

- 4-Chlorobenzonic acid (pCBA) 135585 Sigma-Aldrich 99%, Cas Number 74-11-3,
- N,N-Diethyl-3-methylbenzamide (DEET) D100951 Sigma-Aldrich 97%, Cas Number 134-62-3,
- Diethyl phthalate (DEP) A17529 Alfa Aesar 99%, Cas Number 84-66-2,

Other:

- Sodium sulfite 239321 Sigma-Aldrich ≥98%, Cas Number 7757-83-7,
- Sodium dihydrogen phosphate dehydrate 99-100% 106342 Merck Millipore, Cas Number 13472-35-0,
- Ortho-Phosphoric acid 100573 Merck Millipore 85%,
- Potassium dihydrogen phosphate VWR, Cas Number 7778-77-0,
- Di-Potassium hydrogen phosphate VWR, Cas umber 7758-11-4.

6.2. Measures and methods

Full experiment consists of three steps. The first one is the generation of an ozone stock solution which lasted about three hours and needed to be done at most few hours before carrying out the batch experiment. The second one is the batch experiment, which is the ozonation of micropollutants in a mixing "reactor", which was 500-mL beaker. During the batch experiment, samples were taken out at certain time. Thel last step is reading and evaluating the data. The samples of ozone concentration and micropollutants concentration need to be measured. Ozone concentration is measured using an indigo method, which is described in following chapters. Whereas micropollutants concentrations are measured in the HPLC.

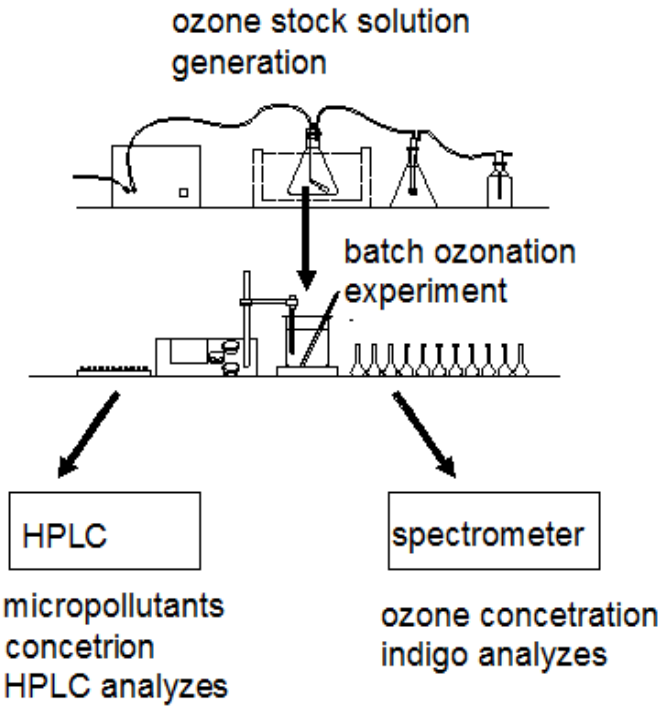


Figure 10. General scheme of experimental procedure

6.2.1. Up-concentration of permeate

In order to conduct the experiment with the up-concentrated permeate water was prepared. This operation was necessary to maintain the characteristics of studied grey water permeate sample. Since ozone used for experiment is a solution, adding it to the sample causes dilution.

The permeate was placed in 1000-mL beakers and heated in the oven for over 24h at the temperature of 65°C. After evaporating more than half of the water, the residue was put into 500-mL volumetric flasks and filled up with the MQ water. The up-concentrated permeate was poured into plastic bottles and stored in a fridge between experiments.

6.2.2. Generation of the ozone

The ozone solution was produced in situ each day of conducting experiments. The production set-up contained the oxygen bottle connected to the ozone generator. The tubing connected the ozone generator with a diffuser that was immersed in a low pH solution, the bottle with solution being ozonated was kept in a cooling bath. The temperature of the ozone solution must have been sustained on the level of about 2°C and pH about 2. Generation of the ozone solution wass carried out by diffusing ozone gas in the low-pH solution. The ozone gas was produced from the oxygen. Gas which did not dissolved need to be caught by KI solution, this is why in the end there are two gas washing bottles with 2% KI solution. The solution being ozonated is kept in the cooling water. During the experiment bottle with the solution was kept on the ice. Although all efforts to keep the conditions as stable as possible, when conducting the experiment repetitively at time intervals, the concentration was dropping and needed to be monitored.

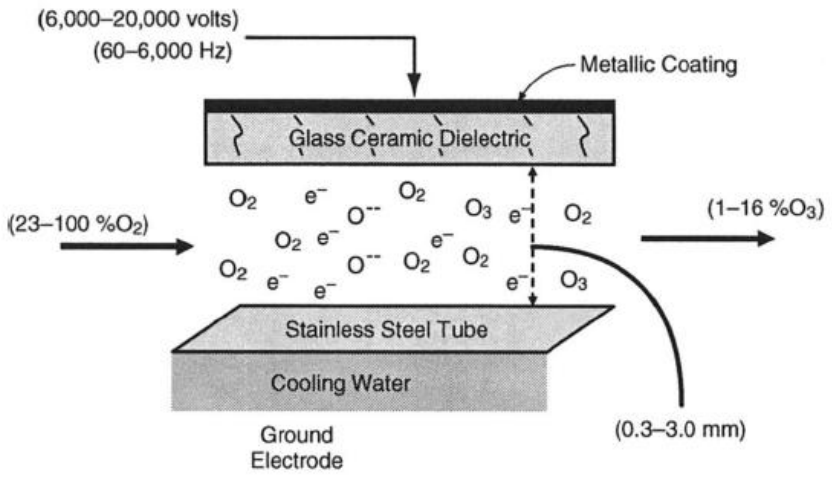


Figure 11. Scheme of commercially available electric-discharge ozone generator (Kerwin L. Rakness, 2005)

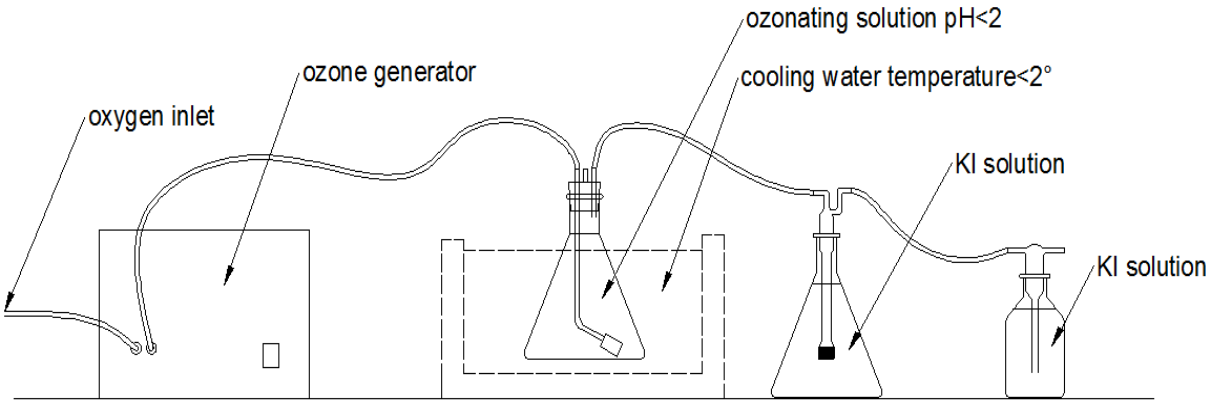


Figure 12. Ozone stock solution generation set-up

6.2.3. Determination of the ozone concentration by the indigo method

Determination of ozone concentration in the stock solution, as well as in the samples taken out during each experiment, was based on the indigo method. An indigo dye is an organic compound with distinctive blue color called indigo. The indigo solution was used to prepare reagents essential for ozone measurements.

The indigo method was developed back in 1854 by Schönbein. "*For the determination of the amount per weight of ozonised oxygen in a given volume of air, I have been using a solution of indigo for years, and many experiments have convinced that this agent leads quickly to the goal; with its help the content of ozonised oxygen can be determined up to a fraction of a milligram within a few minutes, as can be seen from ensuring description*." (Urs von Gunten C. v., 2012) Nowadays, the indigo method is a standard method used in the laboratories. There are two features of the indigo solution that makes it possible to measure ozone concentration. First is the bleaching of indigo in contact with ozone. Secondly, as indigo is a natural dye, the absorbance of this solution can be easily measured and related to certain concentrations of ozone.

The method requires production of two reagents based on indigo solution called in the experiment a reagent I and a reagent II. The reagent I is produced by diluting stock solution of indigo 50 times, whereas the reagent II represents 10 times dilution. Preparation of indigo stock solution and reagents was carried out according to the following instruction.

Indigo stock solution: to the 1-L volumetric flask add 500mL of distilled water and 1mL of phosphoric acid. While stirring, add 770mg of potassium indigo trisulfonate ($C_{16}H_7N_2O_{11}S_3K_3$). Fill to mark with distilled water. Store for at most 4 months in the dark.

Reagent I: to the 250-mL volumetric flask add 5mL of indigo stock solution, 3.25g of sodium dihydrogen phosphate (NaH_2PO_4), 1.75mL of phosphoric acid. After adding all chemicals dilute to the mark with the MQ water.

Reagent II: to the 500-mL volumetric flask add 50mL of indigo stock solution, 6.5g of sodium dihydrogen phosphate (NaH_2PO_4), 3,5mL of phosphoric acid. After adding all chemicals dilute to the mark with MQ water.

Reagents I and II were prepared before running the experiment at most two days in advance and kept in the fridge in dark glass bottles. The reagent I is more diluted and was used to measure lower concentrations, whereas the reagent II was used to measure higher concentrations.

A part of the preparation is also creating the baseline for the spectrometer. Important is to zero the spectrometer with the proper blank each time the reagent in the samples changes. Usually, experiment was started with the baseline created by the reagent II, which is used to measure ozone stock solution concentration and high-concentration samples. In order to zero spectrometer, blanks needed to be prepared. Two 100-mL volumetric flasks were used for each reagent. The blank samples were prepared by diluting reagents 1:10 with distilled water in those flasks. Baseline was created by filling up both cuvettes with the same blanks and creating the baseline for the system in the software.

In order to begin the experiment the concentration of ozone stock solution needed to be measured. To do it precisely, three samples were taken out of the ozone stock solution to three volumetric flasks. Firstly, 10mL of the reagent II to was poured to each one of the 100-mL volumetric flasks. Secondly, 0.4mL of ozone stock solution was poured slowly and precisely into the reagent in the bottom of the flask. Ozone solution rapidly reacts with the reagent bleaching it. Eventually, the flasks could be filled up with the MQ water up to the mark. Sample prepared in that way could be poured into the 10-cm cuvettes to measure absorbance at 600nm wavelength. For each sample three reading were taken, which gave in total 9 results to calculate average.

Ozone stock solution concentration calculations were based on the equation:

$$C = \frac{V_S * \Delta A}{f * b * V_C}, \qquad (13)$$

where: C – concentration of ozone (mg/L) V_s – volume of the sample in volumetric flask (mL), ΔA – difference in the absorbance between a sample and a blank, b – path length of a cell (cm), V_c – volume of sample in a cuvette (mL), f=0.42. Concentration of ozone in the ozone stock solution:

b=10cm

V_c=0.4mL

V_s=100mL

$$C = \frac{100 * \Delta A}{0.42 * 10 * 0.4} = 59.5 * \Delta A. \quad (14)$$

Similar procedure was used to measure the ozone concentration in the samples from the experiment.

6.2.4. Batch experiment

The main part of the laboratory work was the conducted repetitively batch ozonation experiment. The experimental set-up consisted of a beaker, a pH-meter, a thermometer, a mixer, volumetric flasks and HPLC vials. The 50-mL volumetric flasks were used to collect the ozone concentration samples and the HPLC vials to collect micropollutant samples.

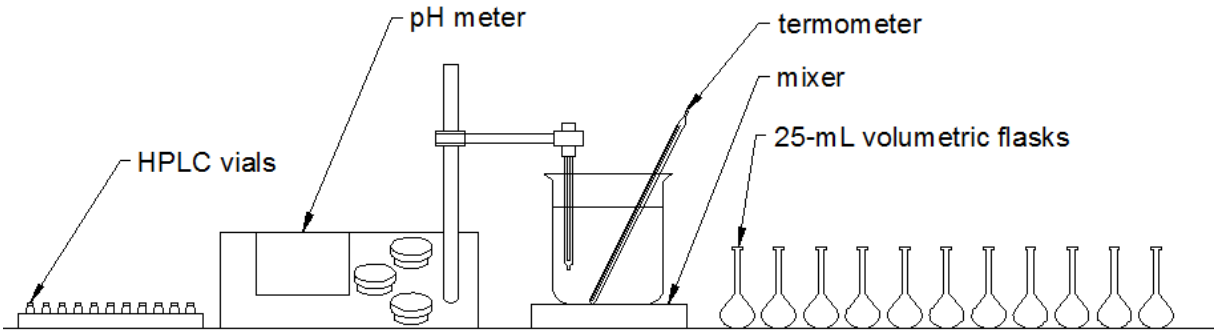


Figure 13. Batch ozonation experiment set-up

Conducting the experiment required very specific preparation. Since ozone was added as a solution with a very low pH, pH and alkalinity adjustment had to be carried out. In order to do it 0.1M HCl and 0.2M $NaHCO_3$ was added in appropriate amounts. The permeate used for the study was up-concentrated two times, therefore if the total volume of batch experiment was 200mL, 100mL of studied up-concentrated water was added. This up-concentration was required due to the fact that ozone was dosed as a solution. It means that quite significant volume of low pH and temperature was added completely changing properties of studied water. Therefore, the pH and temperature adjustments were required. To obtain the total volume of 200mL in a "reactor", the beaker was filled-up with distilled water up to 200mL.

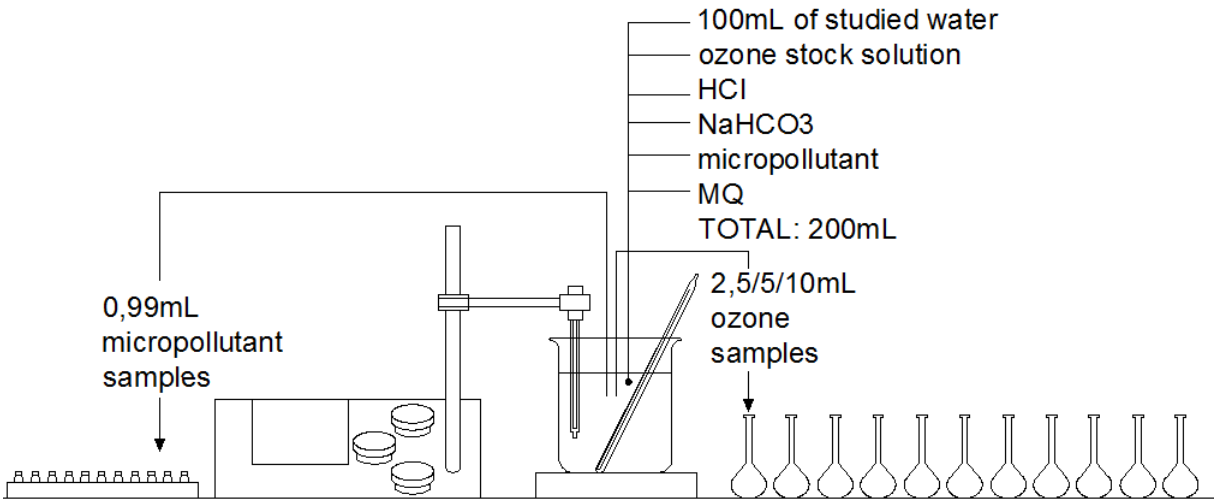


Figure 14. Batch ozonation experiment set-up; doses and pH adjustment

The vials and the volumetric flasks to collect the samples also needed to be prepared basically to stop the ozone degradation and the micropollutant degradation process in the moment of putting samples into the vials. In order to do it 0.01mL of sodium sulfite solution was added into each HPLC vial. In case of ozone measurements, as described before, the indigo reagents were used to preserve ozone concentration by dying indigo. Therefore, in each one of volumetric flasks, 5mL of the reagent I or the reagent II was poured. When very high concentration was expected, the stronger reagent (reagent II) was used and smaller volume of sample was taken out. Sampling was carried out according to the table presented in the Appendix. Experiment's duration varied depending on ozone degradation rate, which proceeds differently according to the water composition. Some experiments lasted 10minutes, some 6minutes, whereas experiments carried out with the buffered MQ water lasted much longer, about 30min.

6.2.5. Ozone samples measurements

Sample collected into 25-mL volumetric flasks were all measured in the same way as described in chapter 7.2.3. Determination of the ozone concentration by the indigo method. Before putting into flasks samples from batch experiment, proper indigo reagent was poured into flask, according to the tables in the Appendix. Secondly, during experiment, proper volume of water was poured to each flask. After finishing the experiment, bottles were filled-up with the MQ water and measured absorbance with spectrometer.

6.2.6. Micropollutants samples HPLC measurements

HPLC stands for high-performance liquid chromatography. The HLPC is today the premier technique for chemical analysis and related applications, with an ability to separate, analyze, and/or purify virtually any sample. This technique is commonly used in the analytical chemistry and it enables measuring concentration down to ppm (depending on the quality of the instrument). It relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Chromatography can be defined as a mass transfer process involving adsorption. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out the column. The sorbent is the active component of the column. Usually, it is a granular material made of solid particles (size 2-50μm). Typical HPLC instrument includes sampler, pumps and detector. The instrument is controlled by the computer and user software. (Lloyd R. Snyder, 2010)

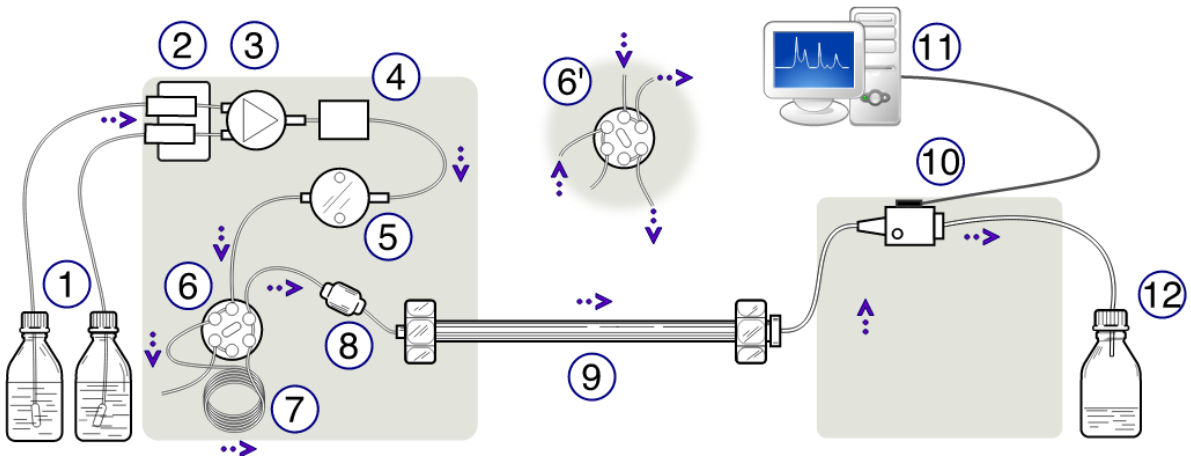


Figure 15. Schematic representation of an HPLC unit. (1) Solvent reservoirs, (2) Solvent degasser, (3) Gradient valve, (4) Mixing vessel for delivery of the mobile phase, (5) High-pressure pump, (6) Switching valve in "inject position", (6') Switching valve in "load position", (7) Sample injection loop, (8) Pre-column (guard column), (9) Analytical column, (10) Detector (i.e. IR, UV), (11) Data acquisition, (12) Waste or fraction collector. (Meyer, 2004)

Methods applied in the study were previously developed. Due to complex composition some samples analyzes were lasting relatively long. Moreover, for purpose of this study it was not necessary to find the detection limits. However, it would be recommended to estimate them for pCBA in the pure MQ water due to high removal and very low concentrations.

Table 12. HPLC methods applied for RGW and GFT water types

	DEET	DEP	pCBA
Flow rate liquid phase	1 mL/min	1.5 mL/min	1 mL/min
Injection volume	500μL	500μL	400μL
Solvent	50% MQ, 50% acn	40% MQ, 60% acn	50% acn, 50% phosphoric acid solution pH2
Wavelength of signal	210nm	226nm	226 nm
Stop time	13min	10min	8min
Time of peak	4.8min	3.2min	4.8 min
Pressure	200bar	200bar	200bar
Temperature	25^{o}C	25^{o}C	30^{o}C
Lamp	UV	UV and visible	UV
Width of slit (B_W)	4 nm	4 nm	4 nm

Table 13. HPLC methods applied in MQ water

	pCBA
Flow rate liquid phase	1 mL/min
Injection volume	300μL
Solvent	42% can, 58% phosphoric acid solution pH2
Wavelength of signal	210nm
Stop time	7min
Time of peak	4.8 min
Pressure	200bar
Temperature	25^{o}C
Lamp	UV
Width of slit (B_W)	4nm

6.2.7. Biofiltration

The biofiltration experiments were conducted before at the Department of Hydraulic and Environmental Engineering as the part of the same project of the pilot plant for grey water reuse. The same types of water ozone doses were studied, therefore, the data is really relevant for this study. The biofiltration experiment was carried out by pumping ozonated water (GFT and RGW) through columns filled with sand. The system consisted of six columns connected in series. It took more than one hour for the water to be pumped through each column, therefore, the whole experiment for each water type lasted about eight hours. Samples were taken out before the first column and after each of the columns. In total seven samples were taken out and the degradation of BDOC in the biofilter of total empty bed contact time of eight hours could be plotted.

The scheme of the system and sampling points (1-7) are presented on the graph below (Figure 16).

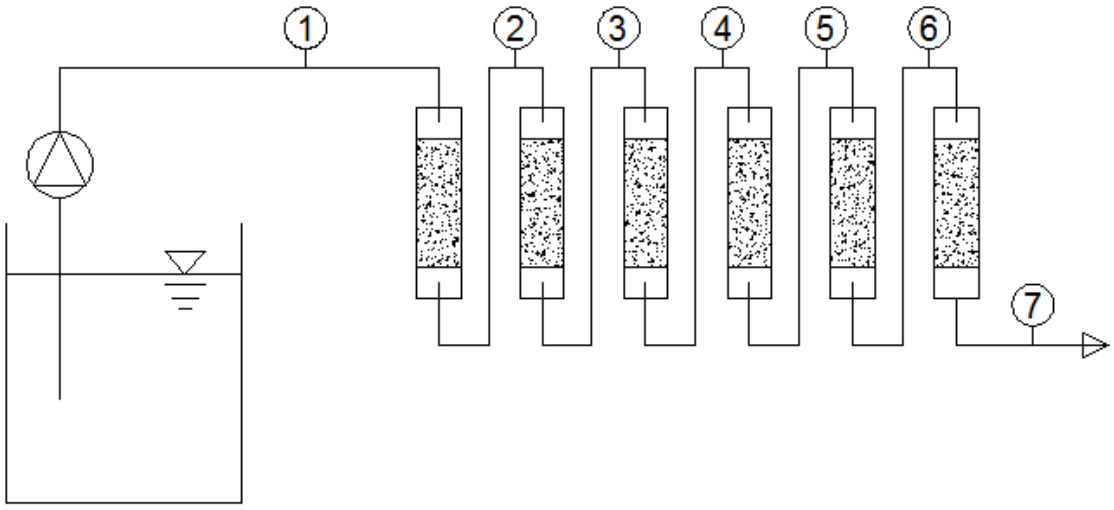


Figure 16. Biofiltration set-up scheme

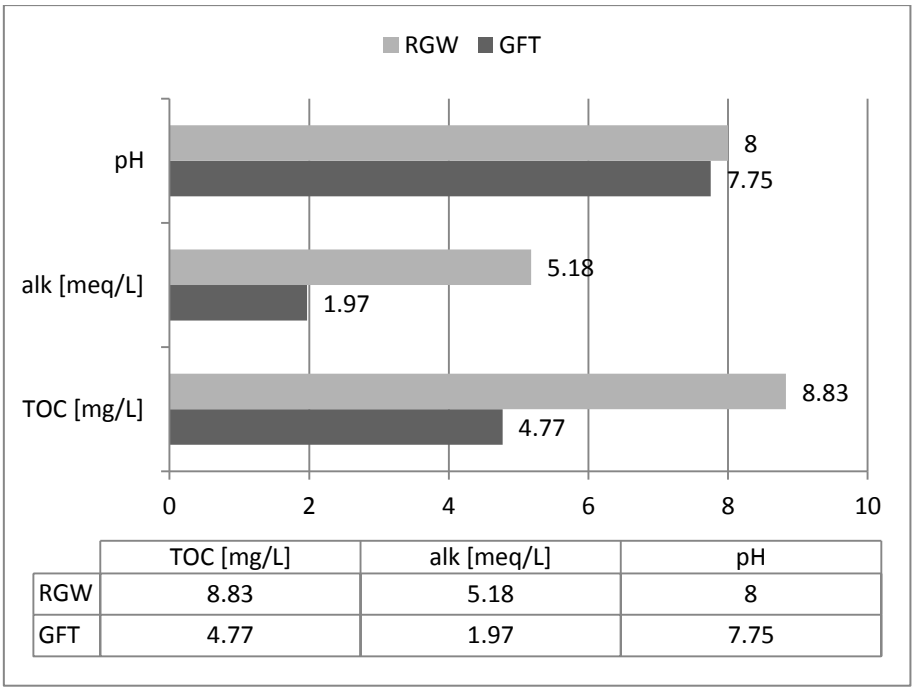
7. Results and discussion

7.1. Removal of micropollutants

The removal data was collected by comparing the final concentration of micropollutant concentration after the ozone was completely degraded in the batch experiment. The values were compared with the initial concentration and presented on the graphs as the average from three trials conducted for each condition. Usually, the degradation of ozone stopped completely after about 4-6 minutes (depending on water type). However, the degradation of the compound very often stopped much sooner, which can be seen on the graphs in the Appendix.

Most obvious and expected observation is an increasing removal efficiency according to the raising ozone dose. However, doubling the dose did not necessarily mean doubling the removal efficiency. Doubled ozone dose (dose of 10mg/L compared to dose 5mg/L) increased the removal by about 20% for RGW and about 21% for GFT.

The most important water properties which can affect ozonation process significantly are compared on the graph below (Figure 17.). As shown, the alkalinity and TOC values are almost double for the RGW compared with the GFT. There is also slight difference in pH, which should not contribute a lot in comparison to alkalinity and TOC.



	TOC [mg/L]	alk [meq/L]	pH
RGW	8.83	5.18	8
GFT	4.77	1.97	7.75

Figure 17. Comparison of water properties of GFT and RGW types

According to the expectations, DEET and pCBA removal efficiency values are very similar. As mentioned in the theoretical introduction, these compound have almost the same reaction rate constants with both, ozone and $OH^{\bullet}$ radicals. Their removal in each type of water is very similar, with a constant tendency of a bit lower removal of DEET in comparison to pCBA.

The lowest removal efficiency was noted for DEP in all kind of water types and ozone doses. The average removal of DEP is always roughly 20% lower than DEET and pCBA. The main difference in kinetic data for DEP was 20% lower reaction rate constant with radicals ($4*10^9$). It may indicate the importance of indirect ozonation by radicals compared to direct ozonation by ozone.

One of the factors most commonly claimed to affect ozonation procedure is pH. In compared water types the difference in pH is quite insignificant. The pH of the RGW was 8, whereas the pH of the GFT was 7.75. In general, higher removal of micropollutants would be expected at higher pH since the higher the pH, the higher R_{ct} value, which means more radicals is produced (Jonas Margota, 2013). Nevertheless, the opposite tendency was observed since there are other much more important factors (as alkalinity and TOC) that could have diminished the pH influence.

In contrast to the difference in pH between the two waters, the difference in alkalinity and TOC is much more significant. Both, alkalinity and TOC values for the RGW is almost double value of the GFT concentrations. Those characteristics seems to be more significantly contributing to the differences in the removal efficiency. Moreover, the difference agrees with the expectations based on the literature values. When alkalinity and TOC values are higher the removal of micropollutants is lower. This phenomenon can be justified by the scavenging properties of carbonate, which as expected lowers the $OH^{\bullet}$ radicals exposure towards micropollutants. Carbonates are known as very strong scavengers of $OH^{\bullet}$ radicals, which means that they react with carbonates immediately before reaching micropollutant. The R_{Ct} value, which describes ratio between $OH^{\bullet}$ and O_3 concentration, decreases with increasing alkalinity (carbonate concentration), therefore, the $OH^{\bullet}$ radicals exposure decreases with increasing alkalinity because of the fact that carbonate has a high scavenging rate of $OH^{\bullet}$ radicals.

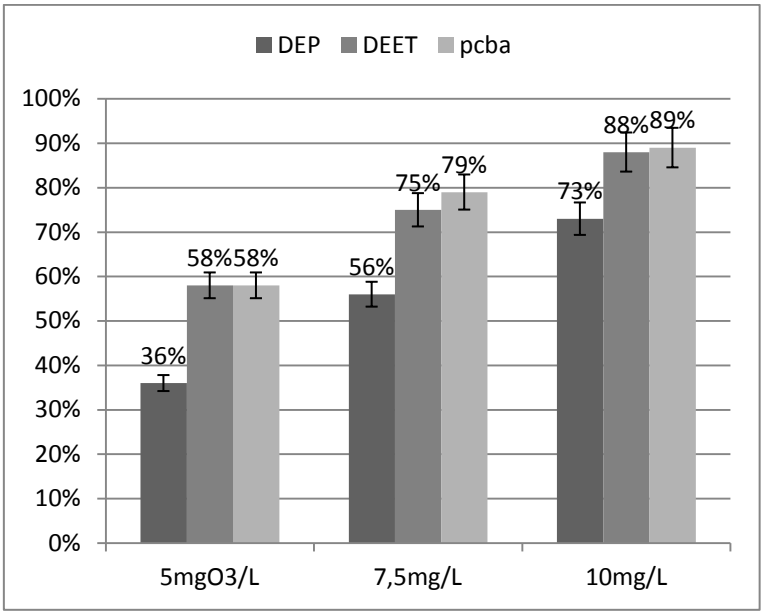


Figure 18. Removal in RGW

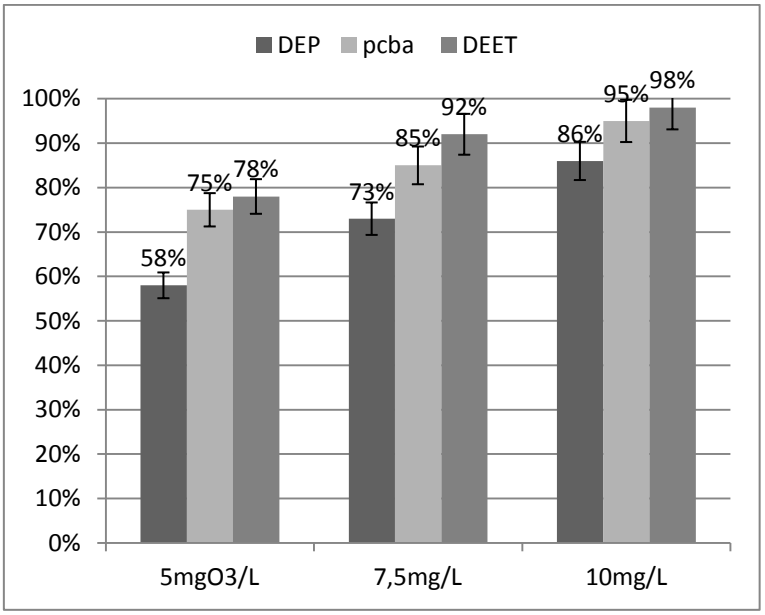


Figure 19. Removal in GFT

7.2. pCBA as a $OH^{\bullet}$ radicals probe compound

The concept of using pCBA as a hydroxyl radicals probe compound is widely introduced in the theoretical part according to the study conducted by Urs von Gunten. According to this method Rct values can be calculated in order to estimate the value of the fraction removed by radicals. Method proved successful for RGW and GFT water types giving reasonable values that agree with characteristics of those waters. pCBA degradation allowed to calculate the $OH^{\bullet}$ radicals contribution into degradation process of DEET and DEP.

The buffered Mili-Q water type occurred problematic. For the pCBA dose of 100μg/L and ozone dose of 5mg/L is was impossible to detect any pCBA in the samples even in the first ones taken out after 15 seconds. The next trial was conducted with 500μg/L of pCBA and the same ozone dose resulted in similar outcome. Very low concentrations were detected in the few samples. However, without determining detection limits for pCBA at the HPLC it is not possible to consider this data. In the next two trials the pCBA dose was raised up to 2.5mg/L and 5mg/L. The outcome was the opposite, no ozone was detected after 20seconds. However, the indigo method set-up for this trial was prepared for quite high concentrations, so the ozone most probably was present longer at much lower concentrations than expected. The higher ozone concentrations were expected basing on the first two trials with lower pCBA dose when the degradation of ozone was really slow. Those results did not allow to examine the pCBA degradation kinetics in pure MQ water. The explanation why it happened was found in the study of Yunzheng Pi. The article extensively describes many aspects of applying pCBA as a probe compound. The study has proven that pCBA in pure water causes a clear acceleration of the ozone decomposition. Shortening the half-life time down to 35sec. The higher was the pH and the pCBA concentration, the stronger was acceleration effect as shown on the graph below. "*In pure water systems pCBA should not be used as a probe compound due to its strong promotion effect on ozone decomposition. Hydrogen peroxide was found to be one intermediate product of ozonation of pCBA. The formed hydrogen peroxide can enhance the ozone decomposition rate*." (Yunzheng Pi, 2006). The study also deeply analyzes the scavenging influence on the pCBA degradation and questions the accuracy of the results for wastewater and artificial waters. The R_{ct} concept was developed for drinking water applications where the scavenging rate of pCBA was below 10%, applying the same concept to water with much different characteristics can prove inaccurate.

Summing up, in experiments of the study (Yunzheng Pi, 2006) it was shown that pCBA accelerated ozone decay (acceleration was observed also in other types of water but not so significant as in pure water). Furthermore, the formation of hydrogen peroxide was observed during this process. The formed H_2O_2 increases the decomposition of aqueous ozone and leads to enhanced formation of $OH^{\bullet}$ radicals. The chain reaction therefore changes to HO^{2-} ion initiated decay of ozone instead of hydroxide ion, OH^-. Thus, an error in applying pCBA as a probe compound in low scavenger containing waters is likely to occur if the scavenging rate of pCBA makes up more than 5% of the total scavenging rate (Yunzheng Pi, 2006). The results achieved during trials of conducting the experiment in the buffered MQ confirmed results of this study. The results from one of the trials are presented in the Appendix.

7.3. Kinetics calculations results

7.3.1. R_{ct} values

The R_{ct} concept was introduced in the theoretical introduction. This method allows to find easily the ratio between $OH^{\bullet}$ radicals and ozone exposures and calculate the fraction removed by $OH^{\bullet}$ radicals. This ratio is described as R_{ct} value. Following equation is given:

$$\ln\left(\frac{[pCBA]}{[pCBA]_0}\right) = -R_{ct} * k_{OH,pCBA} * \int O_3 dt. \qquad (15)$$

According to (Michael S. Elovitz, 2008), By plotting $\ln\left(\frac{[pCBA]}{[pCBA]_0}\right)$ versus $\int O_3 dt$, the R_{ct} value can be found by dividing the slope of the plot by $k_{OH,pCBA}$. It can be easily derived by transforming the formula into linear equation, with constant *a* determining the slope:

$$y = ax$$

$$y = \ln\left(\frac{[pCBA]}{[pCBA]_0}\right)$$

$$x = \int O_3 dt$$

$$a = -R_{ct} * k_{OH,pCBA}$$

$$R_{ct} = -\frac{a}{k_{OH,pCBA}} \qquad (16)$$

Therefore, for known slope value and $k_{OH,pCBA}$, the only unknown is R_{ct} which can be easily calculated. The reaction rate constant of $OH^{\bullet}$ radicals with pCBA is given in the literature as $5*10^9$.

All the R_{ct} values (for each type of water and each dose of ozone), were found basing on this method, the following example presents the method, all the other plots, that allowed to

calculate all values from Table 14 and Table 15, can be found in the Appendix. Following graphs are showing the results for one of the experiment. Studied water was the GFT and ozone dose 5mg/L. The first graph presents first-order kinetic plot of the ozone decomposition. Following one is the ozone and pCBA decay throughout the experiment. Eventually, the third one is the plot described above, which allows to calculate R_{ct} value.

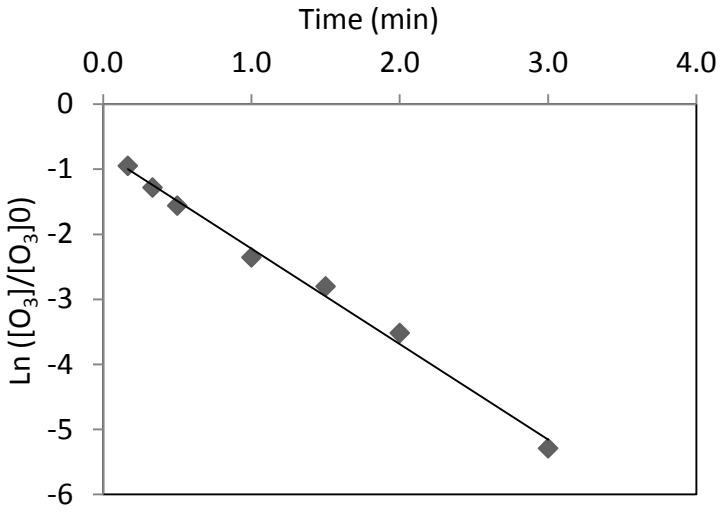


Figure 20. First-order kinetic plot of the ozone decomposition (GFT, 5mgO3/L)

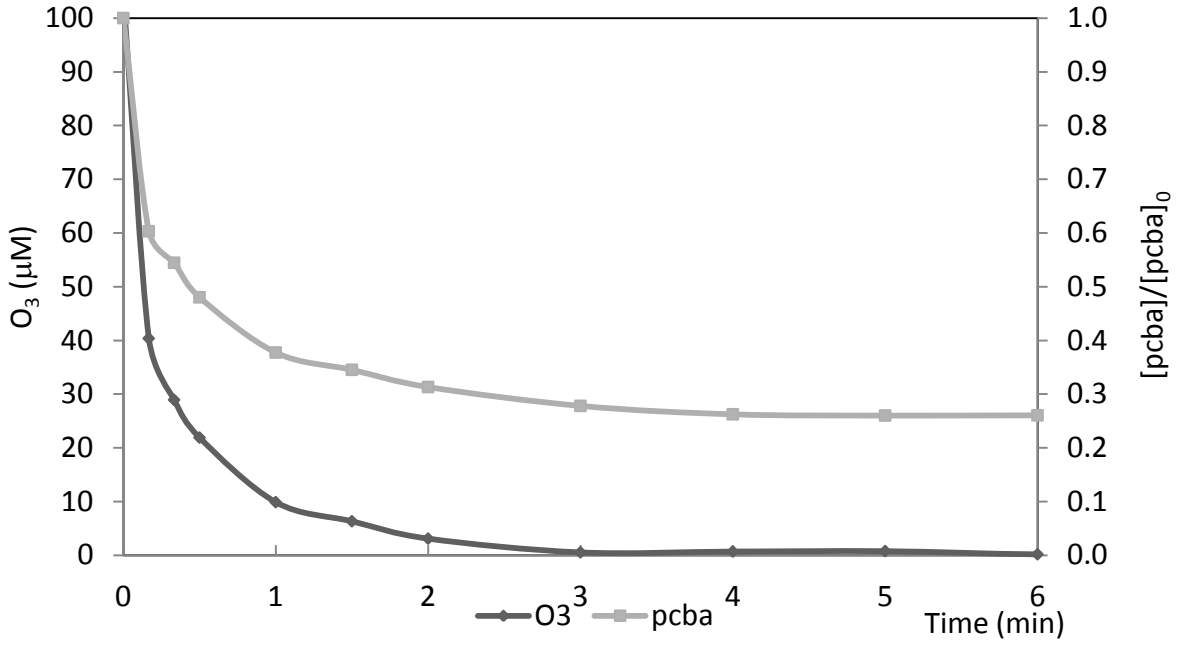


Figure 21. Depletion of ozone and pCBA as a function of reaction time.

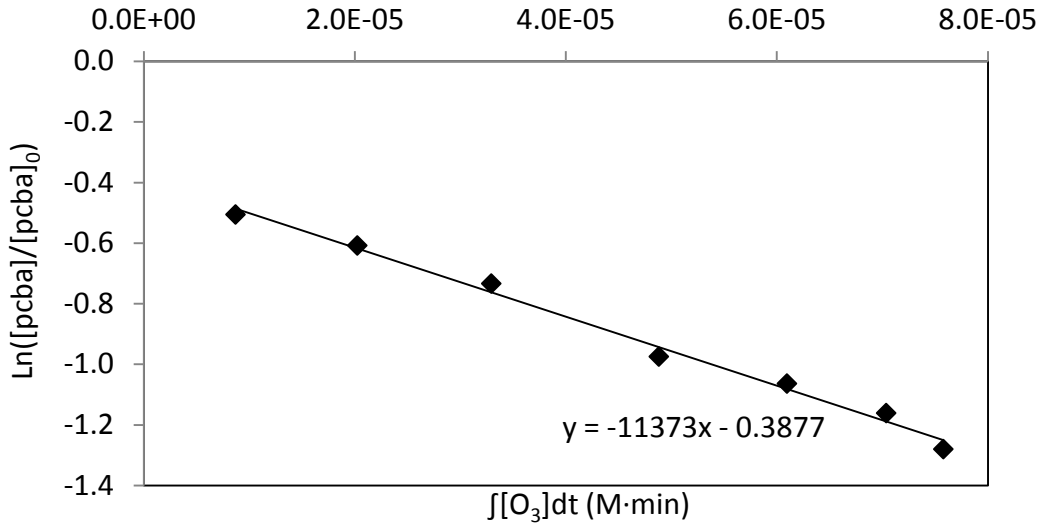


Figure 22. OH-exposure (OH-ct) versus the corresponding O_3-exposure (O_3-ct) for ozonation (GFT, 5mgO3/L)

The value of the slope read from the graph is equal to -11373, therefore after putting the value to the equation 15:

$$R_{ct} = -\left(-\frac{11373}{k_{OH,pCBA}}\right),$$

$$R_{ct} = -\left(-\frac{11373}{5 * 10^9}\right) = 2.27 * 10^{-6}.$$

The values for each water type and for all ozone doses are presented in the table below. According to expectations, for the water with the lower alkalinity and TOC (GFT) the R_{ct} values are higher, which means the greater $OH^{\bullet}$ radicals exposure due to scavenging characteristics.

Table 14. Calculated R_{ct} values for all ozone doses for two types of water

Ozone dose (mg/L)	water type	$k_{OH\ pcba}$	slope	R_{ct} value
5	RGW	$5.00*10^9$	3653	$7.31*10^{-7}$
7.5		$5.00*10^9$	898	$1.80*10^{-7}$
10		$5.00*10^9$	806	$1.61*10^{-7}$
5	GFT	$5.00*10^9$	11373	$2.27*10^{-6}$
7.5		$5.00*10^9$	2836	$5.67*10^{-7}$
10		$5.00*10^9$	1665	$3.33*10^{-7}$

7.3.2. Fraction removed by radicals

Knowing the R_{ct}, the fraction removed by radicals for DEET and DEP ozonation can be calculated according to the formula:

$$f(\mathrm{OH}\bullet) = \left(k_{OH} * R_{Ct}/(k_{O_3} + k_{OH} * R_{Ct})\right). \qquad (16)$$

Using the values of reaction rate constants from the table 3 "Hydroxyl radical and ozone rate constants for studied compounds". Results for all the ozone doses and two water types. Fraction removed by radicals is the amount of removed micropollutant that is oxidized via indirect ozonation, which means that it reacted with hydroxyl radicals.

Table 15. Fraction of DEET and DEP removed by radicals

Ozone dose (mg/L)	water type	R_{ct} value	$k(OH^{\bullet})_{DEET}$	$k_{O3\ DEET}$	$f(OH^{\bullet})_{DEET}$	$k_{OH\ DEP}$	$k_{O3\ DEP}$	$F(OH^{\bullet})_{DEP}$
5	RGW	$7.31*10^{-7}$	$5.00*10^{9}$	10	0.9973	$3.9*10^{9}$	0.09	1.0000
7.5		$1.80*10^{-7}$	$5.00*10^{9}$	10	0.9890	$3.9*10^{9}$	0.09	0.9999
10		$1.61*10^{-7}$	$5.00*10^{9}$	10	0.9877	$3.9*10^{9}$	0.09	0.9998
5	GFT	$2.27*10^{-6}$	$5.00*10^{9}$	10	0.9991	$3.9*10^{9}$	0.09	1.0000
7.5		$5.67*10^{-7}$	$5.00*10^{9}$	10	0.9965	$3.9*10^{9}$	0.09	1.0000
10		$3.33*10^{-7}$	$5.00*10^{9}$	10	0.9940	$3.9*10^{9}$	0.09	0.9999

According to the characteristics described before, the preponderant majority of the removed compounds is removed by radicals via the indirect ozonation pathway. The values for GFT are only slightly higher than for RGW. It means that for those compounds alkalinity and TOC of water do not influence significantly the fraction removed by radicals due to much greater influence of difference between $OH^{\bullet}$ radicals and ozone reactivity with the compound. As for differences between DEP and DEET, slightly higher fraction of DEP, than DEET is removed by radicals due to its really low reaction rate constant with molecular ozone and the same magnitude of the reaction rate constant with hydroxyl radicals.

7.4. Classification of DEP and DEET in terms of ozone reactivity

In the chapter "Ozonation of micropollutants – possibilities in removal" the concept of classifying compounds according to their reaction rate constant with hydroxyl radicals developed by Yunho Lee was described. As presented in the figure 3 "Micopollutants devided into groups according to their ozone and hydroxyl radical rate constants by (Yunho Lee D. G., 2013)", compounds are divided into group regarding their reaction rate constant with hydroxyl radicals. According to this concept, DEET and pCBA should be classified as group III ($k_{OH,pCBA}=5*10^9$, $k_{OH,DEET}=5*10^9$) and DEP as a group IV ($k_{OH,DEP}=3.85*10^9$). It is shown that plotting specific ozone dose versus removal efficiency, depending on the group, the other type of curve is obtained. This method can also be used as a way to find the hydroxyl radical reaction rate constant for the compound when it is unknown according to the slope of the curve.

In studied case, values of the reaction rate constant are very close to each other and close to the group classification limit value. Therefore, the plots have very similar shape for all kind of conditions. Nevertheless, the plots of pCBA in RGW and DEET in GFT, are showing visible change in the shape from linear plot to the curve in accordance with their group. This observation confirms the accuracy of the classification method and the values of reaction rate constant found in the literature. Linear shape of pCBA in GFT plot and DEET in RGW plot can result from the measurement errors.

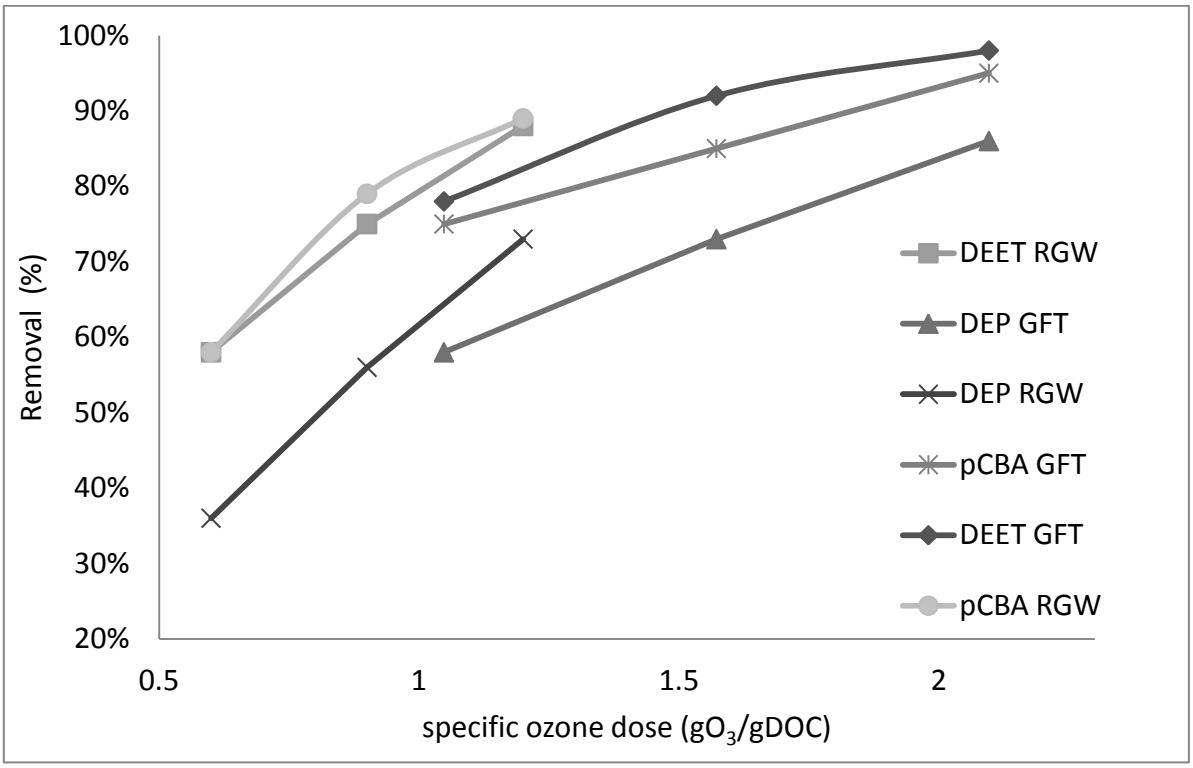


Figure 23. Removal of the compound (DEET, DEP, pCBA) versus specific ozone dose plot

7.5. Ozone decomposition

As described in the theoretical introduction, ozone stability in aqueous solutions depends a lot on the water composition and the compounds with which ozone may react. All of the curves used in this chapter can be found in the Appendix plotted separately for each experiment together with degradation of a compound and error bars. In this section, the shape of the ozone degradation curves is compared for different water types, ozone doses and compound present in the water.

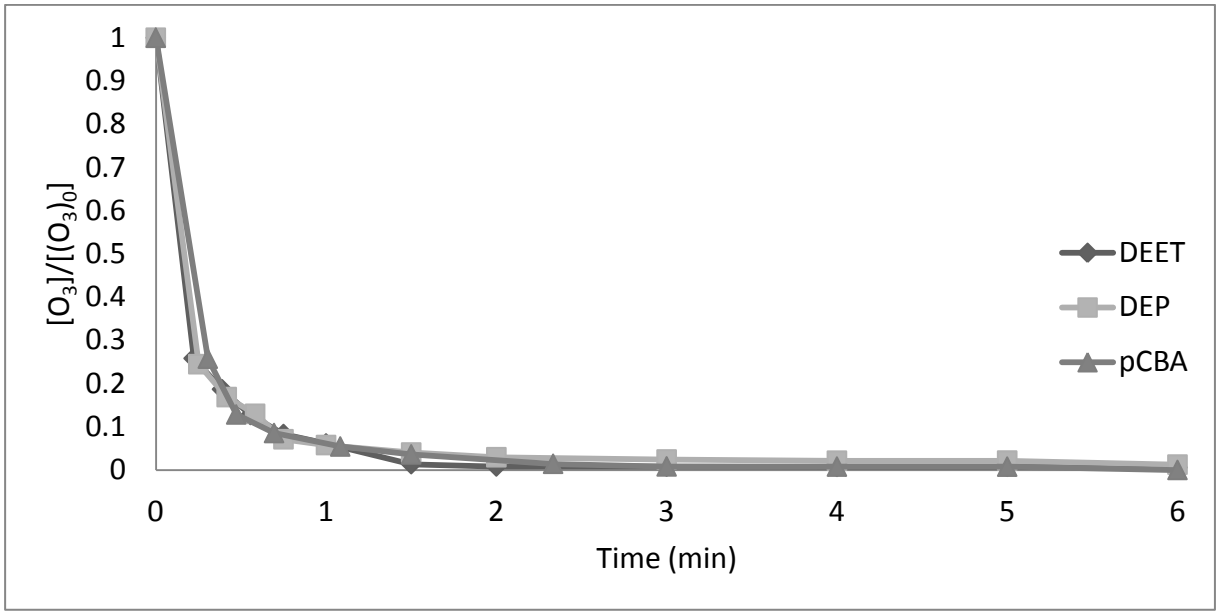


Figure 24. Degradation of ozone in RGW with pCBA, DEET and DEP, ozone dose 5mg/L

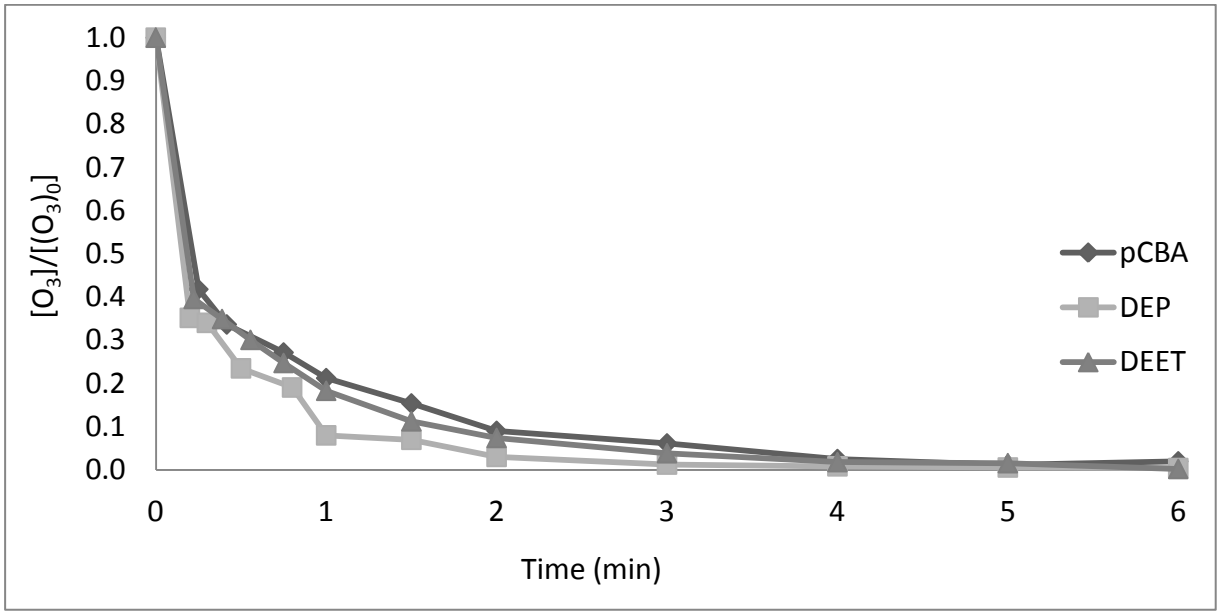


Figure 25. Degradation of ozone in RGW with pCBA, DEET and DEP, ozone dose 7.5mg/L

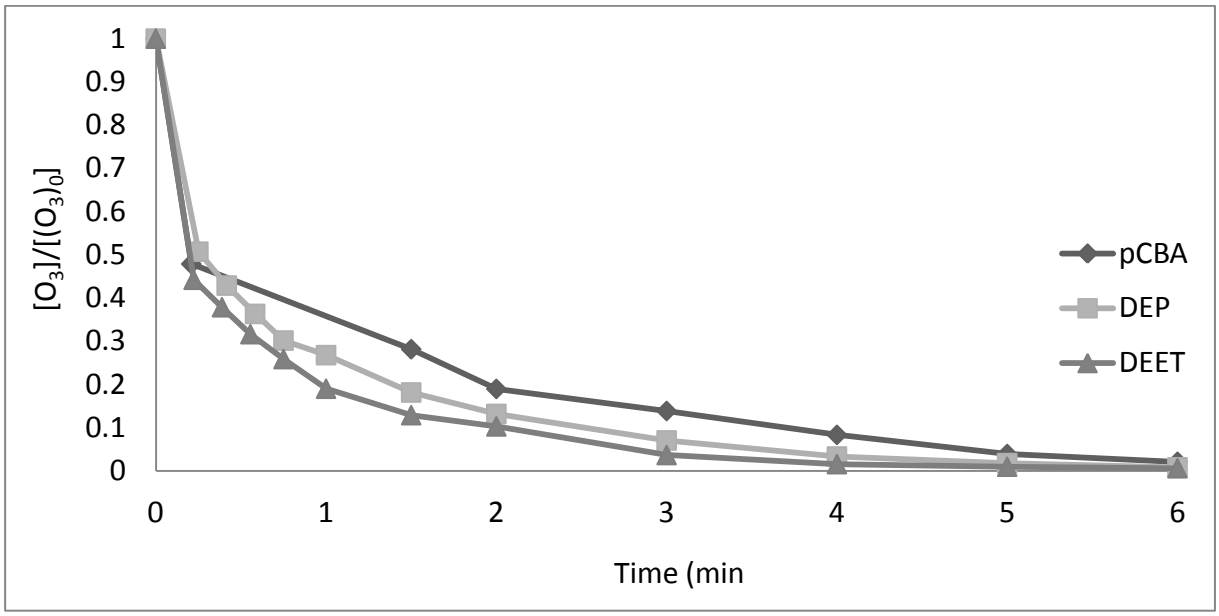


Figure 26. Degradation of ozone in RGW with pCBA, DEET and DEP, ozone dose 10mg/L

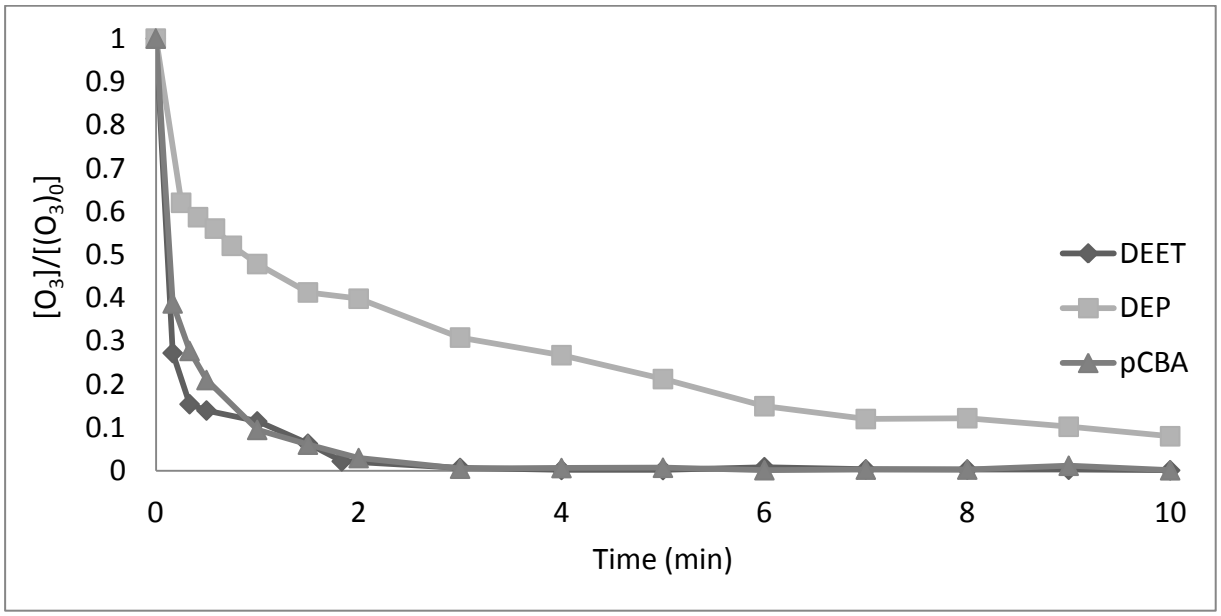


Figure 27. Degradation of ozone in GFT with pCBA, DEET and DEP, ozone dose 5mg/L

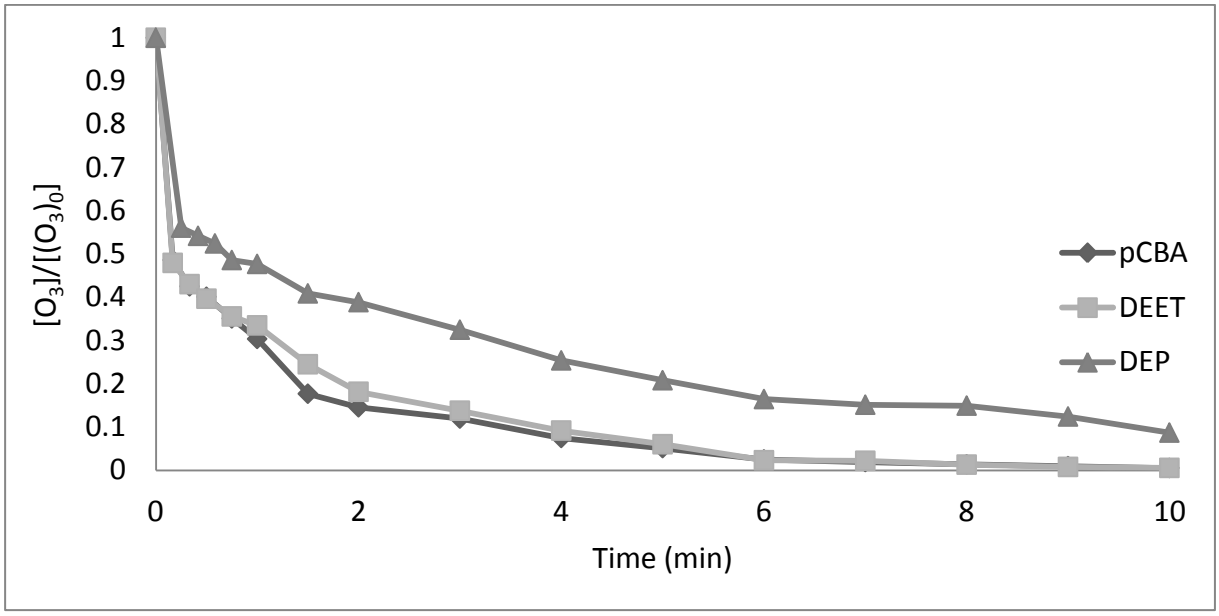


Figure 28. Degradation of ozone in GFT with pCBA, DEET and DEP, ozone dose 7.5mg/L

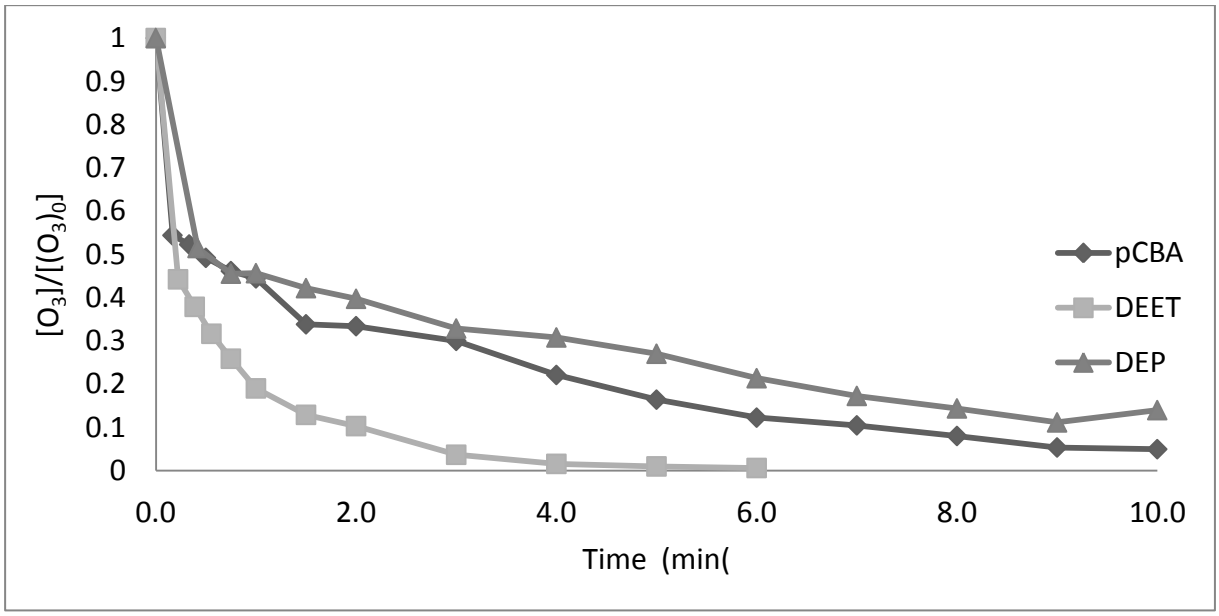


Figure 29. Degradation of ozone in GFT with pCBA, DEET and DEP, ozone dose 10mg/L

Experiments for RGW water type were conducted for 6 minutes. Usually, after this period of time ozone was decomposed completely. The time for GFT was usually about 10 minutes since ozone was decomposing more slowly. This difference may be caused by lower content of TOC and carbonates with which ozone decomposes more quickly. To compare the water types figures 24-26 need to be compared with figures 27-29. On all of the graphs decomposition for all three studied compounds is presented. The ozone doses for all experiments was 5mg/L, 7.5mg/L and 10mg/L. In the figures 24-26, which present ozone decomposition in the RGW water type, decomposition of ozone for all three compounds is very similar. There is no visible influence of the type of the compound on ozone decomposition curve. On the other hand, decomposition in the GFT water type looks quite different. There is very significant difference in decomposition of ozone in the presence of DEP in comparison to DEET and pCBA. One of the reasons may be the inaccuracy in ozone concentration measurements, other may be the influence of DEET and pCBA on the ozone decomposition. The acceleration effect of pCBA was already introduced before. There is possibility that similar acceleration effect is triggered by DEET. Both compounds have very similar reaction rate constants with ozone and with radicals. Therefore, it is possible that they influence ozone decomposition in similar way. Another interesting fact is that this effect is visible only in water with lower TOC and alkalinity values. For the RGW such effect did not occur. Moreover, for all three doses of ozone similar tendency was observed, which indicates that it is not measurement error. Additionally, the tendency is stronger with lower ozone dose. Regarding the fact that concentration of studied compounds was always the same, lower ozone dose means higher molar ratio of ozone and compound, which may make the acceleration effect even more visible. These observations confirm the acceleration effect of pCBA on ozone decomposition as described in the study (Yunzheng Pi, 2006). Moreover, it is possible that similar effect occurs with DEET present in the water, hence, other compounds with the similar reaction rates constant to pCBA and DEET may trigger similar effect. Furthermore, the fact that pCBA influenced the decomposition of ozone differently in different water types, confirms the doubts about accuracy in applying pCBA as a probe compound introduced in study by Yunzheng Pi. It does not mean that pCBA cannot be used as a probe compound, but it is not completely neutral towards the ozone decomposition and radicals concentration measured with this compound may appear different when pCBA is not present in the water and the acceleration effect will not occur, therefore, monitoring ozone decomposition is crucial in understanding if the influence is significant.

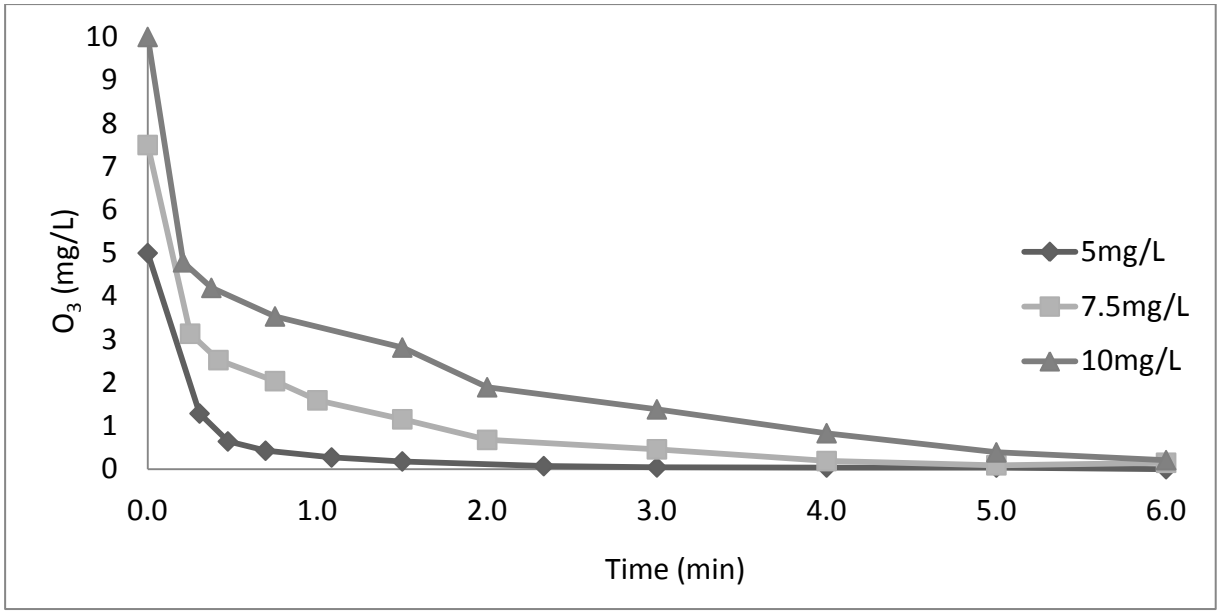


Figure 30. Ozone decomposition curves during ozonation of pCBA in RGW

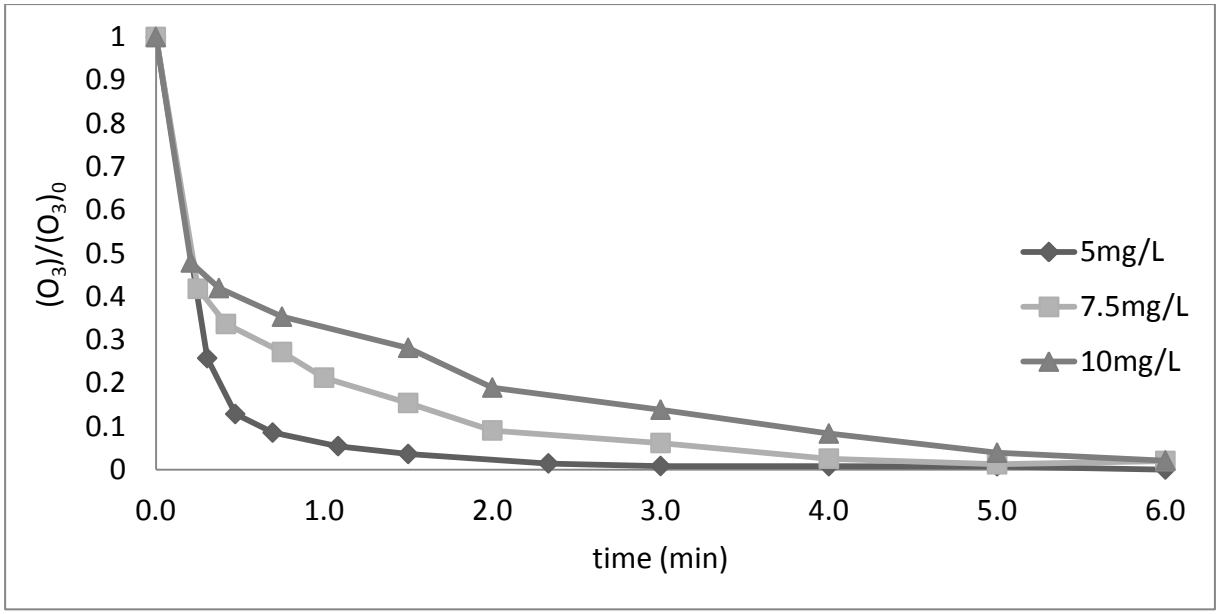


Figure 31. Ozone decomposition curves during ozonation of pCBA in RGW, ozone as a fraction of initial value

On the graphs presented in the figures 30 and 31 the ozone decomposition in the RGW water type was presented for all applied ozone doses (5mg/L, 7.5mg/L, 10mg/L). the graph presented in the figure 30 presents the ozone concentration as a fraction of initial concentration. The half-life time for all the doses is almost the same, however, the further decomposition proceeds quite differently. The similarity in the first phase may be also caused by the fast reaction with pCBA causing the significant drop in the beginning of the decomposition. In particular, this first drop is a drop of a similar number of mg/L (moles/L) as presented in graph 27. For dose of 10mg/L drop is about 5mg/L; for 7.5mg/L – 4.5mg/L; 5mg/L – 4mg/L. It indicates that regardless of the dose, the acceleration of ozone decomposition caused by pCBA is very similar.

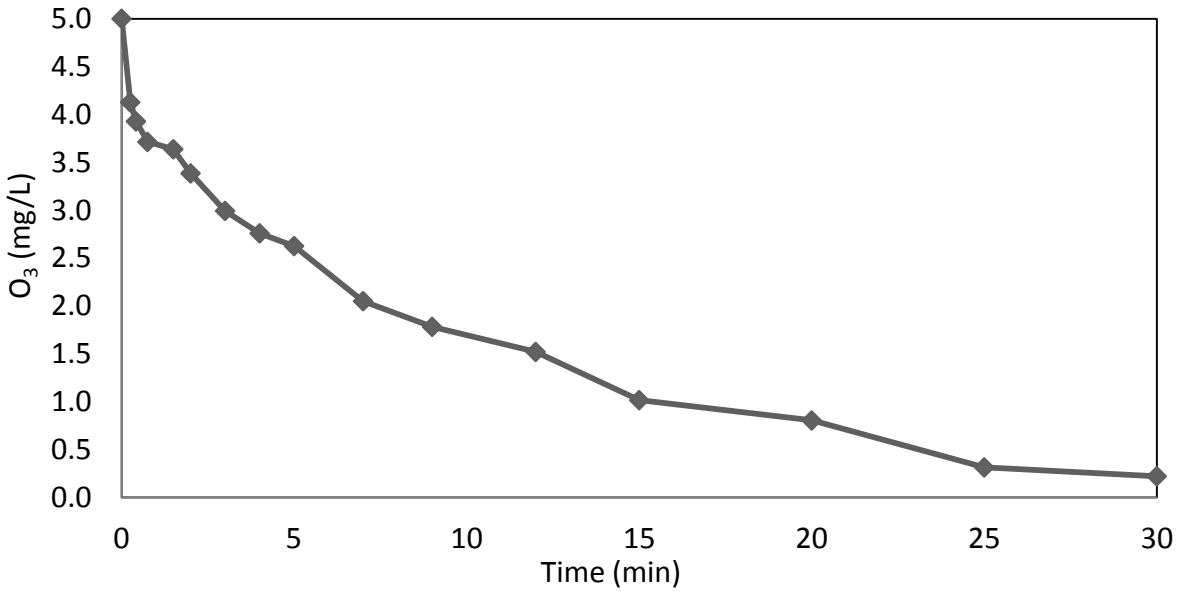


Figure 32. Ozone decomposition in MQ with 500µg/L of pCBA

Figure 32 presents ozone decomposition during the experiment with buffered MQ water. Initial drop in the concentration is probably caused by pCBA which reacted very fast and disappeared completely from the solution. Therefore, further part of this curve (after 1 minute time) can be considered almost as ozone decomposition in pure water. Most importantly, the time of the decomposition increased significantly. From about 6-10 minutes for the RGW and the GFT, ozone degraded almost completely in 30 minutes (5-6 times more longer than the RGW or the GFT). This shows how significant is the contribution of any scavengers present in the water, even when its concentration is not too high (as in the GFT).

7.6. DOC removal during biofiltration preceded by ozonation

The biofiltration experiments were following the ozonation experiments. Results are presented on the graphs below. In accordance to the literature, ozonation visibly enhanced DOC removal during the biofiltration. It happens due to transforming non-biodegradable DOC into BDOC during ozonation. This allows to remove more DOC during the biofiltration process.

As presented on the graphs, the DOC removal increases with raising ozone dose. For both types of water, adding ozone improved removal. Applying 5mgO3/L dropped the value after the biofiltration from about 5mgDOC/L down to about 4DOCmg/L for GFT and from about 9.5DOCmg/L down to about 7.8DOCmg/L for the RGW. Raising the dose of ozone up to 7.5mgO3/L increased removal again by similar value. For the GFT the final value of DOC went down to 3mg/L and for RGW almost down to 5mg/L. Moreover, further increase in the ozone dose up to 10mgO3/L did not improve the DOC removal any more. It indicates that in terms of DOC removal there is a upper limit that ozonation is not able to cross and increasing the dose above some value is a waste of money.

Another important outcome of the experiment is the fact that the decrease in DOC value completely stopped after certain period of time. It indicates that there is no point for conducting biofiltration too long since the DOC drop is quite rapid and nothing more happens after it. This observation is relevant for the design of the biofilter. There is no necessity to design very big biofilters since the empty bed contact time required to remove everything what is possible to remove is relatively short. However, after certain period of time the growth of the biomass in the biofilter may improve the removal more, therefore, some optimal solution must be determined. Regarding the GFT water type, the decrease in DOC value stopped approximately after two hours of the biofiltration and further process did not change this value. Similarly, in RGW water type, the drop in the value ended after about two hours of the process.

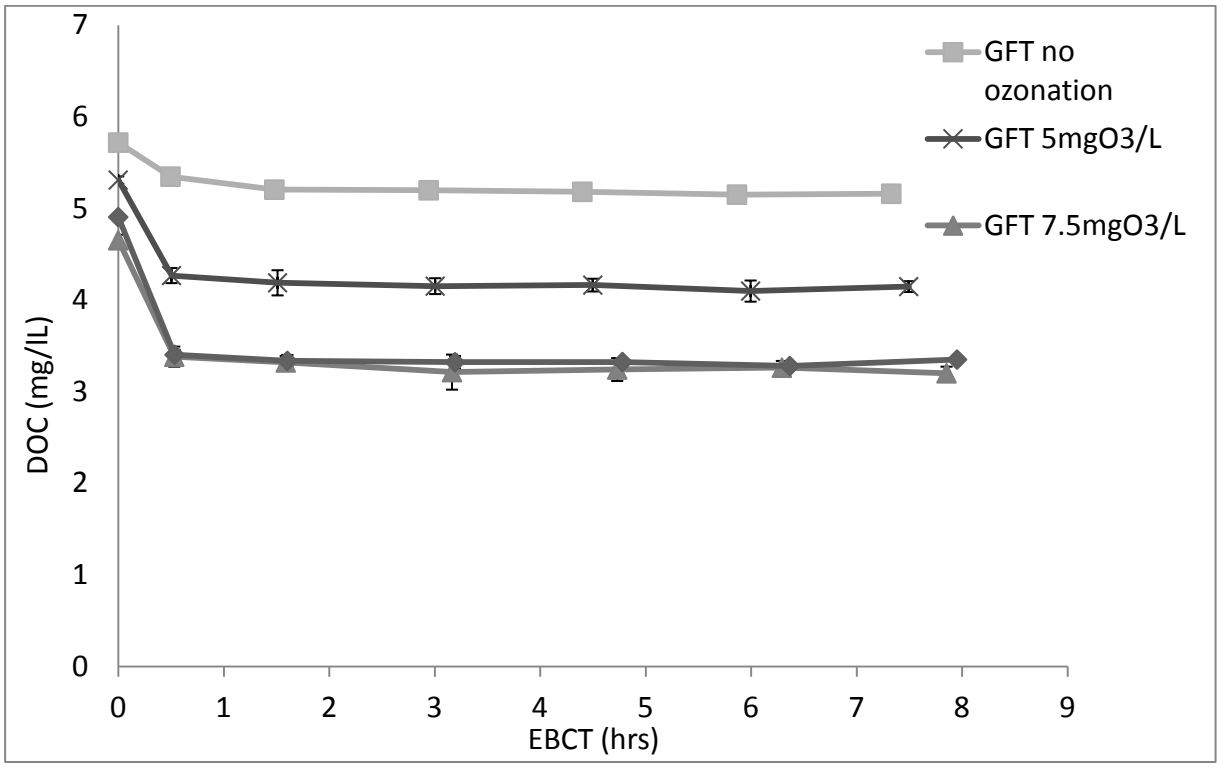


Figure 33. DOC removal during biofiltration preceded by ozonation (GFT, doses of 5, 7.5 and 10mgO3/L)

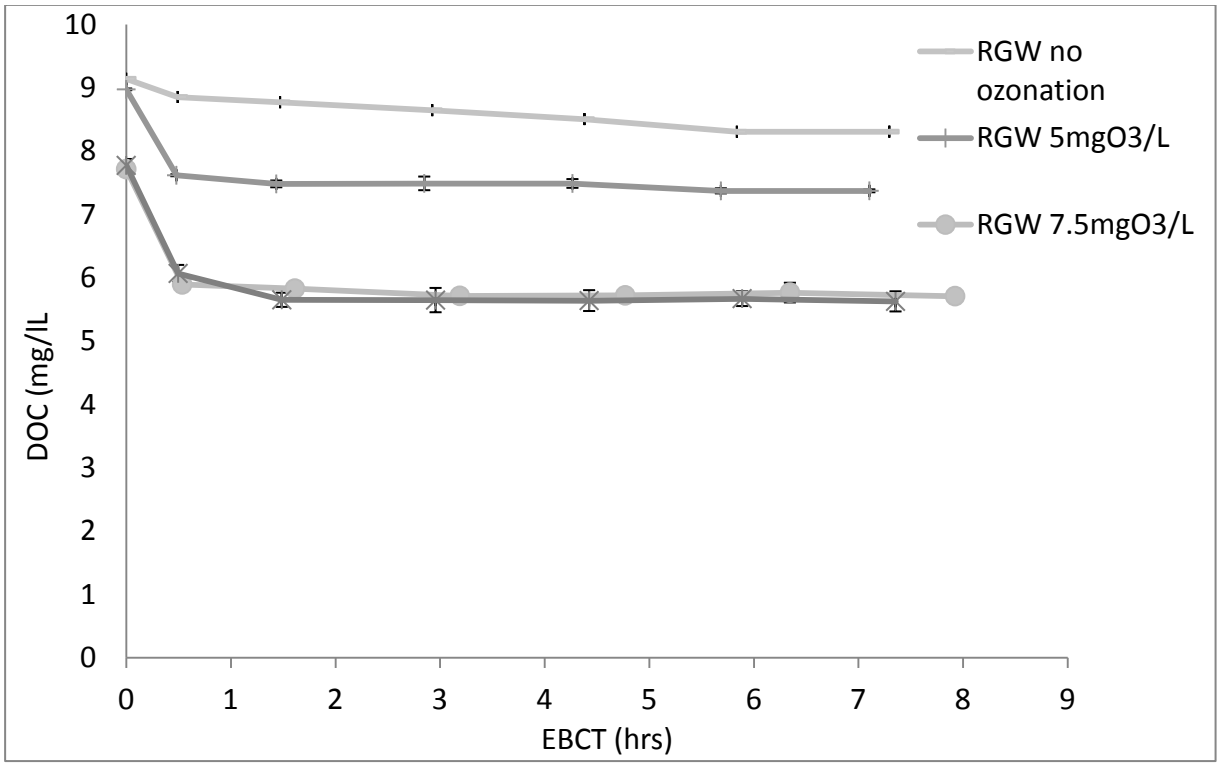


Figure 34. DOC removal during biofiltration preceded by ozonation (RGW, doses of 5, 7.5 and 10mgO3/L)

8. Conclusions

- Collected data allowed to evaluate the removal efficiency of micropollutants by ozonation. Obtained results confirm that success in removal by ozonation depends on many factors, such as water composition, ozone dose, micropollutant type, temperature, pH.
- For the ozone dose of 10mg/L, the removal efficiency was reaching values in the range of 58-98% depending on the compound and the water type. However, for ozone dose of 5mg/L was in the range of 36-86%.
- DEET and pCBA removal efficiency values are very similar and quite high (reaching over 90% for 7.5mgO3/L and 10gO3/L). These compound have almost the same reaction rate constants with both, ozone and $OH^{\bullet}$ radicals. Their removal in each type of water is very similar, with a constant tendency of a bit lower removal of DEET in comparison to pCBA.
- The lowest removal efficiency was noted for DEP in all kind of water types and ozone doses. The average removal of DEP is always roughly 20% lower than DEET and pCBA. The main difference in kinetic data for DEP was 20% lower reaction rate constant with radicals ($4*10^9$). It may indicate the importance of indirect ozonation by radicals compared to direct ozonation by ozone since reactivity of these compounds with molecular ozone is quite close.
- Values of fraction removed by radicals for both studied compounds reached 98-100% values. That means that DEET and DEP are mostly oxidized via indirect ozonation pathway.
- Collected data showed scavenging of hydroxyl radicals by carbonates, therefore, the lower removal efficiency of micropollutants was observed in the water with higher alkalinity. The removal efficiency of micropollutants in the water type with higher alkalinity and TOC (the RGW) was lower compared to water with lower values (the GFT).
- Experiments confirmed described in one of the studies abilities of pCBA to accelerate ozone decomposition. This was clearly observed during the experiment with buffered MQ water. Moreover, the tendency was also visible in the GFT water type (lower alkalinity water). In addition, similar characteristics of ozone decomposition were observed during experiments with DEET as well.

9. Further studies

Further studies on ozonation of micropollutants are still needed to fully understand the process and be able to design it properly in order to achieve satisfying removal of these problematic compounds. More fortunate choice in comparison different ways of reacting with ozone, would be a compound with lower hydroxyl radicals reaction rate constant and higher reaction rate constant with molecular ozone. Furthermore, the observation that DEET accelerates ozone decomposition should be examined in order to understand if this mechanism occurs. Moreover, more experiments should be carried with another compound (with similar reaction rate constants to pCBA and DEET) in order to determine if this effect occur with presence of other compound with similar reaction rate constants. If other compounds do not show this characteristic than in order to study hydroxyl radicals formation in absence of scavengers (for example in buffered MQ water), decomposition of a compound that does not accelerate ozone decomposition but has much higher hydroxyl radicals reaction rate constant than ozone reaction rate constant, should be studied.

In addition, the method of the study could be improved. Sampling manually in the same time samples for measuring ozone decay and micropollutant degradation is very difficult. The indigo method for measuring the ozone concentration requires a lot of precision in choosing proper reagent and volume of the sample. Therefore, often experiments must have been repeated several times.

10. Appendix

10.1. Timing schedule for taking samples during batch experiment

Table 16. Sampling schedule and used reagent during batch experiment for 10 minutes experiment

Time		10mLO_3/L		7.5 mLO_3/L		5 mLO_3/L	
[minutes]	[seconds]	Indigo reagent	Sample volume [mL]	Indigo reagent	Sample volume [mL]	Indigo reagent	Sample volume [mL]
	10	II	2.5	II	5	II	5
	20	II	2.5	II	5	II	5
	30	II	2.5	II	5	II	5
	45	II	2.5	II	5	II	5
	60	II	2.5	II	5	II	5
	90	II	5	II	10	I	5
2	120	II	5	II	10	I	5
3	180	II	5	II	10	I	5
4	240	II	5	II	10	I	5
5	300	II	5	II	10	I	5
6	360	II	10	I	10	I	10
7	420	II	10	I	10	I	10
8	480	II	10	I	10	I	10
9	540	II	10	I	10	I	10
10	600	II	10	I	10	I	10

Table 17. Sampling schedule and used reagent during batch experiment for 6 minutes experiment

Time		10mLO_3/L		7.5 mLO_3/L		5 mLO_3/L	
[minutes]	[seconds]	Indigo reagent	Sample volume [mL]	Indigo reagent	Sample volume [mL]	Indigo reagent	Sample volume [mL]
	15	II	2.5	II	5	II	5
	25	II	2.5	II	5	II	5
	35	II	2.5	II	5	II	5
	45	II	2.5	II	5	II	5
	60	II	2.5	II	5	II	5
	90	II	5	II	10	I	5
2	**120**	II	5	II	10	I	5
3	**180**	II	5	II	10	I	5
4	**240**	II	5	II	10	I	5
5	**300**	II	5	II	10	I	5
6	**360**	II	10	I	10	I	10

Table 18. Sampling schedule and used reagent during batch experiment for 30 minutes experiment for MQ water and dose of ozone 5mg/L

No	Time		5 mLO_3/L	
[-]	[minutes]	[seconds]	Indigo reagent	Sample volume [mL]
1		15	II	1
2		35	II	1
3		60	II	1
4		90	II	1
5	2	120	II	2.5
6	3	180	II	2.5
7	4	240	II	2.5
8	5	300	II	2.5
9	7	420	II	2.5
10	9	540	II	2.5
11	12	720	II	5
12	15	900	II	5
13	20	1200	II	5
14	25	1500	II	5
15	30	1800	II	5

10.2. Tables with data of pCBA experiments

First all results for the GFT are presented, secondly, the RGW results are presented.

Time		pCBA				O3						
(min)	(sec)	µg/L	M/L	[pcba]/[pcba]$_0$	ln([pcba]/[pcba]$_0$)	mgO$_3$/L	M/L	ln([O$_3$]/[O$_3$]$_0$)	k_{exp}	[•OH]	∫[•OH]dt (M·min)	∫[O3]dt (M·min)
0.0	0	100.00	6.39E-07	1.00E+00		5.0	1.04E-04					
0.2	10	60.31	3.85E-07	6.03E-01	-0.506	1.9	4.04E-05	-0.95	0.051	1.01E-11	1.011E-10	8.68E-06
0.3	20	54.44	3.48E-07	5.44E-01	-0.608	1.4	2.89E-05	-1.28	0.030	6.08E-12	1.216E-10	2.02E-05
0.5	30	48.01	3.07E-07	4.80E-01	-0.734	1.1	2.19E-05	-1.56	0.024	4.89E-12	1.468E-10	3.29E-05
1.0	60	37.73	2.41E-07	3.77E-01	-0.975	0.5	9.87E-06	-2.36	0.016	3.25E-12	1.950E-10	4.88E-05
1.5	90	34.51	2.20E-07	3.45E-01	-1.064	0.3	6.32E-06	-2.80	0.012	2.36E-12	2.128E-10	6.10E-05
2.0	120	31.31	2.00E-07	3.13E-01	-1.161	0.1	3.09E-06	-3.52	0.010	1.94E-12	2.323E-10	7.04E-05
3.0	180	27.80	1.78E-07	2.78E-01	-1.280	0.0	5.25E-07	-5.29	0.007	1.42E-12	2.561E-10	7.58E-05
4.0	240	26.23	1.68E-07	2.62E-01	-1.338	0.0	6.83E-07	-5.03	0.006	1.12E-12	2.677E-10	7.82E-05
5.0	300	26.00	1.66E-07	2.60E-01	-1.347	0.0	7.53E-07	-4.93	0.004	8.98E-13	2.694E-10	8.18E-05
6.0	360	26.04	1.66E-07	2.60E-01	-1.346	0.0	1.68E-07	-6.43	0.004	7.48E-13	2.691E-10	8.45E-05
7.0	420	25.99	1.66E-07	2.60E-01	-1.348	0.0	3.08E-07	-5.82	0.003	6.42E-13	2.695E-10	8.62E-05
8.0	480	26.03	1.66E-07	2.60E-01	-1.346	0.0	3.20E-07	-5.79	0.003	5.61E-13	2.692E-10	8.87E-05
9.0	540	25.96	1.66E-07	2.60E-01	-1.349	0.1	1.23E-06	-4.44	0.002	5.00E-13	2.697E-10	9.57E-05
10.0	600	25.54	1.63E-07	2.55E-01	-1.365	0.0	1.44E-07	-6.58	0.002	4.55E-13	2.730E-10	1.03E-04

Table 19. pCBA in GFT, 5mgO$_3$/L

Time		pCBA				O_3						
min	sec	µg/L	M	$[pcba]/[pcba]_0$	$Ln([pcba]/[pcba]_0)$	mgO_3/L	M/L	$ln([O3]/[O_3]_0)$	k_{exp}	[•OH]	∫[•OH]dt (M·min)	∫[O3]dt (M·min)
0.0	0	100.00	6.39E-07	1.00E+00		7.5	1.56E-04					
0.2	10	65.62	4.19E-07	6.56E-01	-0.421	3.6	7.60E-05	-0.72	0.042	8.43E-12	8.43E-11	1.30E-05
0.3	20	56.08	3.58E-07	5.61E-01	-0.578	3.2	6.65E-05	-0.85	0.029	5.78E-12	1.16E-10	3.68E-05
0.5	30	51.16	3.27E-07	5.12E-01	-0.670	3.0	6.27E-05	-0.91	0.022	4.47E-12	1.34E-10	6.90E-05
0.8	45	45.35	2.90E-07	4.53E-01	-0.791	2.6	5.49E-05	-1.05	0.018	3.51E-12	1.58E-10	1.13E-04
1.0	60	40.59	2.59E-07	4.06E-01	-0.902	2.3	4.75E-05	-1.19	0.015	3.01E-12	1.80E-10	1.64E-04
1.5	90	34.03	2.17E-07	3.40E-01	-1.078	1.3	2.77E-05	-1.73	0.012	2.40E-12	2.16E-10	2.21E-04
2.0	120	29.46	1.88E-07	2.95E-01	-1.222	1.1	2.28E-05	-1.93	0.010	2.04E-12	2.44E-10	2.71E-04
3.0	180	23.89	1.53E-07	2.39E-01	-1.432	0.9	1.87E-05	-2.12	0.008	1.59E-12	2.86E-10	3.33E-04
4.0	240	20.41	1.30E-07	2.04E-01	-1.589	0.6	1.17E-05	-2.59	0.007	1.32E-12	3.18E-10	3.94E-04
5.0	300	18.27	1.17E-07	1.83E-01	-1.700	0.4	8.02E-06	-2.97	0.006	1.13E-12	3.40E-10	4.43E-04
6.0	360	17.05	1.09E-07	1.71E-01	-1.769	0.2	3.92E-06	-3.69	0.005	9.83E-13	3.54E-10	4.79E-04
7.0	420	16.28	1.04E-07	1.63E-01	-1.815	0.1	3.00E-06	-3.95	0.004	8.64E-13	3.63E-10	5.03E-04
8.0	480	15.61	9.97E-08	1.56E-01	-1.857	0.1	2.16E-06	-4.28	0.004	7.74E-13	3.71E-10	5.24E-04
9.0	540	15.60	9.96E-08	1.56E-01	-1.858	0.1	1.50E-06	-4.65	0.003	6.88E-13	3.72E-10	5.40E-04
10.0	600	15.55	9.93E-08	1.56E-01	-1.861	0.0	8.42E-07	-5.22	0.003	6.20E-13	3.72E-10	5.52E-04

Table 20. pCBA in GFT, 7.5mgO_3/L

Time		pCBA				O3						
min	sec	µg/L	M/L	$[pcba]/[pcba]_0$	$\ln([pcba]/[pcba]_0)$	mgO_3/L	M/L	$\ln([O_3]/[O_3]_0)$	k_{exp}	[•OH]	∫[•OH]dt (M·min)	∫[O3]dt (M·min)
0.0	0	100.00	6.39E-07	1.00E+00		10.0	2.08E-04					
0.2	10	46.06	2.94E-07	4.61E-01	-0.775	5.4	1.13E-04	-0.61	0.078	1.55E-11	1.6E-10	1.74E-05
0.3	20	41.77	2.67E-07	4.18E-01	-0.873	5.2	1.09E-04	-0.65	0.044	8.73E-12	1.7E-10	5.44E-05
0.5	30	35.27	2.25E-07	3.53E-01	-1.042	4.9	1.02E-04	-0.71	0.035	6.95E-12	2.1E-10	1.07E-04
0.8	45	29.73	1.90E-07	2.97E-01	-1.213	4.6	9.61E-05	-0.77	0.027	5.39E-12	2.4E-10	1.82E-04
1.0	60	26.51	1.69E-07	2.65E-01	-1.328	4.4	9.26E-05	-0.81	0.022	4.43E-12	2.7E-10	2.76E-04
1.5	90	20.78	1.33E-07	2.08E-01	-1.571	3.4	7.05E-05	-1.08	0.017	3.49E-12	3.1E-10	3.98E-04
2.0	120	15.88	1.01E-07	1.59E-01	-1.840	3.3	6.96E-05	-1.10	0.015	3.07E-12	3.7E-10	5.38E-04
3.0	180	10.51	6.72E-08	1.05E-01	-2.252	3.0	6.25E-05	-1.20	0.013	2.50E-12	4.5E-10	7.36E-04
4.0	240	7.88	5.03E-08	7.88E-02	-2.541	2.2	4.61E-05	-1.51	0.011	2.12E-12	5.1E-10	9.53E-04
5.0	300	6.31	4.03E-08	6.31E-02	-2.763	1.6	3.42E-05	-1.81	0.009	1.84E-12	5.5E-10	1.15E-03
6.0	360	5.41	3.45E-08	5.41E-02	-2.917	1.2	2.55E-05	-2.10	0.008	1.62E-12	5.8E-10	1.33E-03
7.0	420	4.79	3.06E-08	4.79E-02	-3.039	1.0	2.18E-05	-2.26	0.007	1.45E-12	6.1E-10	1.50E-03
8.0	480	4.22	2.69E-08	4.22E-02	-3.166	0.8	1.67E-05	-2.53	0.007	1.32E-12	6.3E-10	1.65E-03
9.0	540	4.07	2.60E-08	4.07E-02	-3.202	0.5	1.11E-05	-2.93	0.006	1.19E-12	6.4E-10	1.78E-03
10.0	600	3.93	2.51E-08	3.93E-02	-3.235	0.5	1.03E-05	-3.01	0.005	1.08E-12	6.5E-10	1.88E-03

Table 21. pCBA in GFT, 10mgO_3/L

Time		Pcba				O_3						
min	sec	µg/L	M/L	$[pcba]/[pcba]_0$	$\ln([pcba]/[pcba]_0)$	mgO_3/L	M/L	$\ln([O_3]/[O_3]_0)$	k_{exp}	[•OH]	∫[•OH]dt (M·min)	∫[O3]dt (M·min)
0.0	0	100.00	6.35E-07	1.00E+00		5.0	1.04E-04					
0.2	12	48.67	3.09E-07	4.87E-01	-0.720	1.3	2.68E-05	-1.36	0.062	1.23E-11	1.44E-10	1.01E-05
0.5	28	46.53	2.95E-07	4.65E-01	-0.765	0.6	1.34E-05	-2.05	0.027	5.40E-12	1.53E-10	1.96E-05
0.7	42	46.44	2.95E-07	4.64E-01	-0.767	0.4	8.90E-06	-2.46	0.018	3.68E-12	1.53E-10	2.74E-05
1.5	90	43.76	2.78E-07	4.38E-01	-0.827	0.3	5.65E-06	-2.91	0.009	1.84E-12	1.65E-10	3.83E-05
2.0	120	42.78	2.72E-07	4.28E-01	-0.849	0.2	3.75E-06	-3.33	0.007	1.42E-12	1.70E-10	4.77E-05
3.0	180	42.66	2.71E-07	4.27E-01	-0.852	0.1	1.48E-06	-4.25	0.005	9.47E-13	1.70E-10	5.55E-05
4.0	240	42.17	2.68E-07	4.22E-01	-0.864	0.0	8.55E-07	-4.80	0.004	7.20E-13	1.73E-10	6.02E-05
5.0	300	41.99	2.66E-07	4.20E-01	-0.868	0.0	8.10E-07	-4.86	0.003	5.79E-13	1.74E-10	6.43E-05
6.0	360	42.15	2.68E-07	4.21E-01	-0.864	0.0	7.96E-07	-4.87	0.002	4.80E-13	1.73E-10	6.92E-05

Table 22. pCBA in RGW, 5mgO_3/L

Time		pcba				O_3						
min	sec	µg/L	M/L	[pcba]/[pcba]$_0$	ln([pcba]/[pcba]$_0$)	mgO_3/L	M/L	ln([O_3]/[O_3]$_0$)	k_{exp}	[•OH]	∫[•OH]dt (M·min)	∫[O3]dt (M·min)
0.0	0	100.00	6.35E-07	1.00E+00		7.5	1.56E-04					
0.3	15	29.29	1.86E-07	2.93E-01	-1.228	3.1	6.53E-05	-0.87	0.082	1.64E-11	2.456E-10	1.95E-05
0.4	25	29.40	1.87E-07	2.94E-01	-1.224	2.5	5.26E-05	-1.09	0.049	9.79E-12	2.449E-10	4.41E-05
0.8	45	27.51	1.75E-07	2.75E-01	-1.291	2.0	4.24E-05	-1.30	0.029	5.74E-12	2.581E-10	7.97E-05
1.0	60	27.27	1.73E-07	2.73E-01	-1.299	1.6	3.32E-05	-1.55	0.022	4.33E-12	2.598E-10	1.18E-04
1.5	90	25.82	1.64E-07	2.58E-01	-1.354	1.2	2.40E-05	-1.87	0.015	3.01E-12	2.708E-10	1.60E-04
2.0	120	25.95	1.65E-07	2.59E-01	-1.349	0.7	1.41E-05	-2.40	0.011	2.25E-12	2.698E-10	1.99E-04
3.0	180	23.88	1.52E-07	2.39E-01	-1.432	0.5	9.58E-06	-2.79	0.008	1.59E-12	2.864E-10	2.34E-04
4.0	240	23.77	1.51E-07	2.38E-01	-1.437	0.2	3.93E-06	-3.68	0.006	1.20E-12	2.873E-10	2.61E-04
5.0	300	23.75	1.51E-07	2.37E-01	-1.438	0.1	1.90E-06	-4.41	0.005	9.58E-13	2.875E-10	2.76E-04
6.0	360	23.91	1.52E-07	2.39E-01	-1.431	0.1	3.10E-06	-3.92	0.004	7.95E-13	2.862E-10	2.91E-04

Table 23. pCBA in RGW, 7.5mgO_3/L

Time		pCBA				O_3						
min	sec	µg/L	M/L	$[pcba]/[pcba]_0$	$Ln([pcba]/[pcba]_0)$	mgO_3/L	M/L	$ln([O_3]/[O_3]_0)$	k_{exp}	[•OH]	∫[•OH]dt (M·min)	∫[O3]dt (M·min)
0.0	0	100.00	6.35E-07	1.00E+00		10.0	2.08E-04					
0.2	13	13.41	8.51E-08	1.34E-01	-2.009	4.8	9.97E-05	-0.74	0.161	3.21E-11	4.02E-10	2.17E-05
1.5	90	12.76	8.10E-08	1.28E-01	-2.059	2.8	5.86E-05	-1.27	0.023	4.58E-12	4.12E-10	9.65E-05
2.0	120	11.39	7.23E-08	1.14E-01	-2.172	1.9	3.95E-05	-1.66	0.018	3.62E-12	4.34E-10	1.55E-04
3.0	180	10.84	6.88E-08	1.08E-01	-2.222	1.4	2.88E-05	-1.98	0.012	2.47E-12	4.44E-10	2.14E-04
4.0	240	10.72	6.80E-08	1.07E-01	-2.234	0.8	1.74E-05	-2.49	0.009	1.86E-12	4.47E-10	2.72E-04
5.0	300	10.44	6.63E-08	1.04E-01	-2.259	0.4	8.12E-06	-3.25	0.008	1.51E-12	4.52E-10	3.15E-04
6.0	360	10.56	6.70E-08	1.06E-01	-2.248	0.2	4.36E-06	-3.87	0.006	1.25E-12	4.50E-10	3.40E-04

Table 24. pCBA in RGW 10mgO_3/L

10.3. Depletion of ozone and pCBA as a function of time; Frist order kinetic plot of the ozone decomposition during pCBA degradation; OH-exposure versus O3-exposure plots – enabling Rct value calculation

10.3.1. GFT

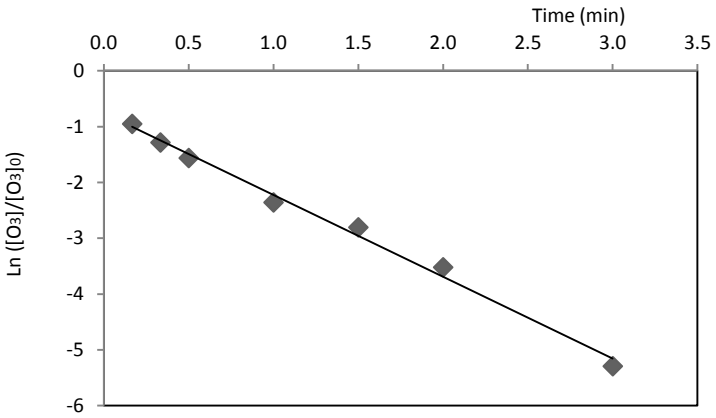


Figure 35. First-order kinetic plot of the ozone decomposition (GFT, 5mgO3/L)

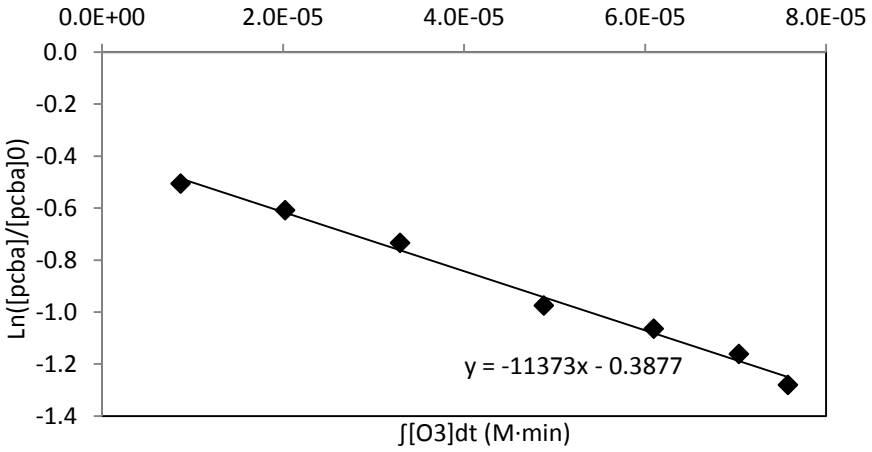


Figure 36. OH-exposure (OH-ct) versus the corresponding O_3-exposure (O_3-ct) for ozonation (GFT, 5mgO3/L)

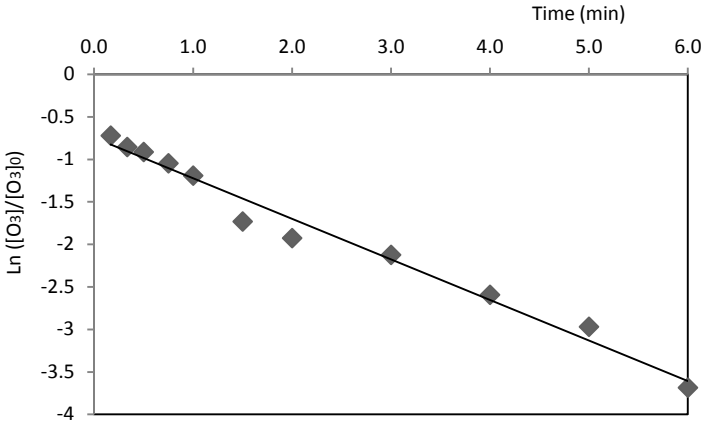


Figure 37. First-order kinetic plot of the ozone decomposition (GFT, 7.5mgO3/L)

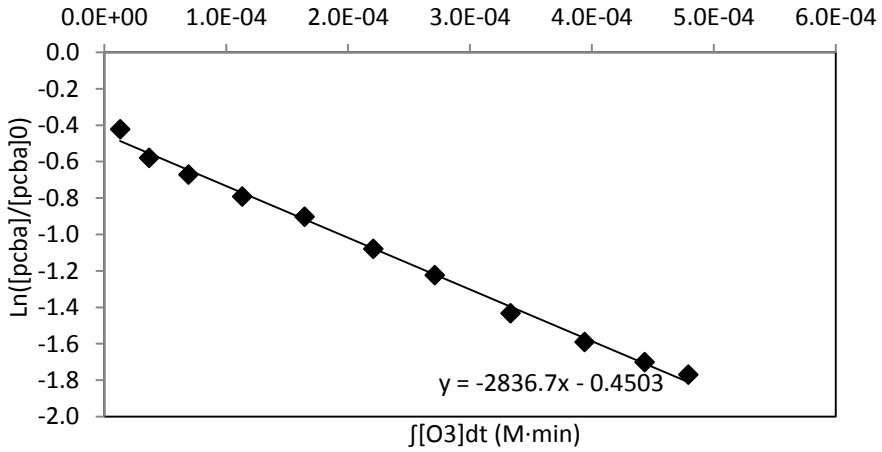


Figure 38. OH-exposure (OH-ct) versus the corresponding O3-exposure (O3-ct) for ozonation (GFT, 7.5mgO3/L)

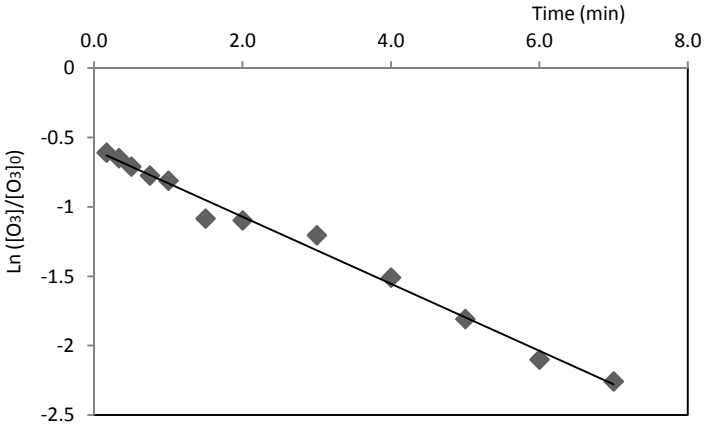


Figure 39. First-order kinetic plot of the ozone decomposition (GFT, 10mgO3/L)

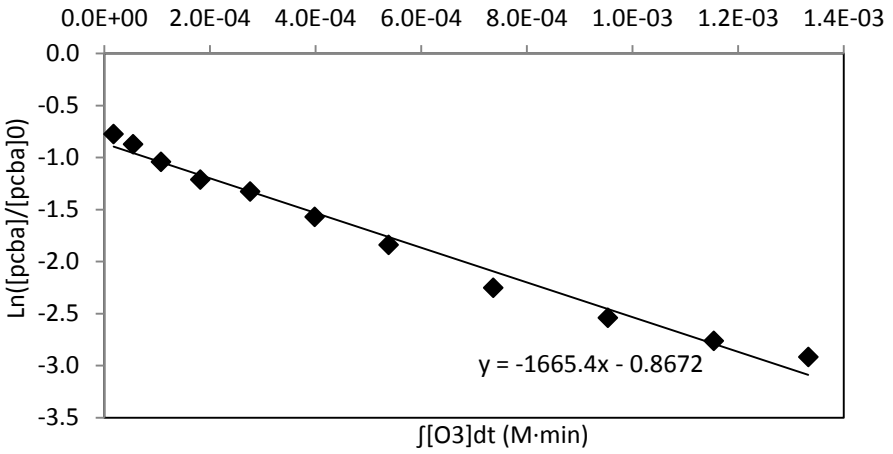


Figure 40. OH-exposure (OH-ct) versus the corresponding O3-exposure (O3-ct) for ozonation (GFT, 10mgO3/L)

10.3.2. RGW

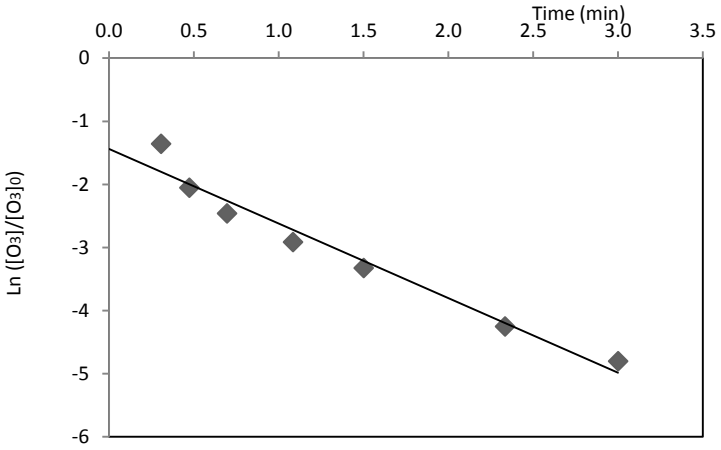


Figure 41. First-order kinetic plot of the ozone decomposition (RGW, 5mgO3/L)

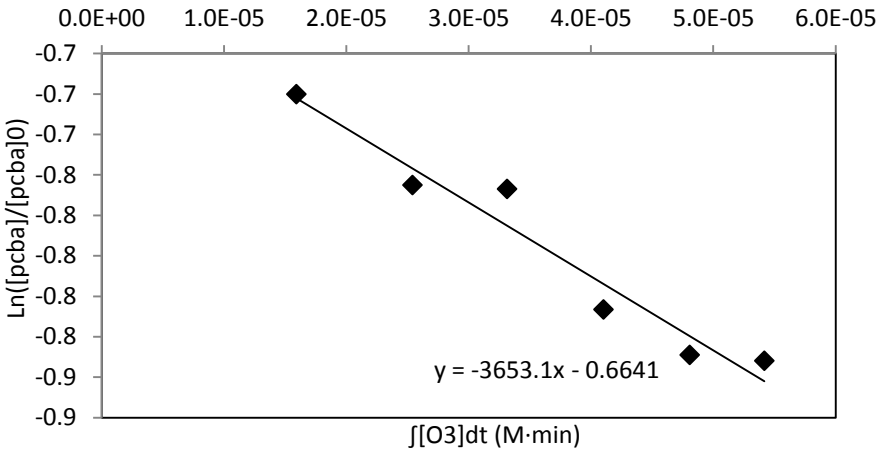


Figure 42. OH-exposure (OH-ct) versus the corresponding O3-exposure (O3-ct) for ozonation (RGW, 5mgO3/L)

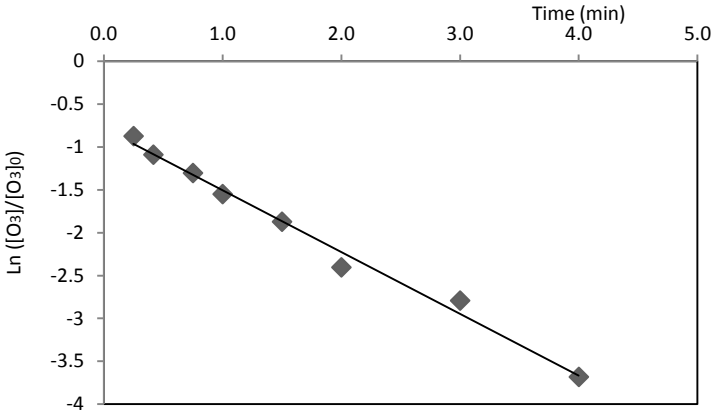


Figure 43. First-order kinetic plot of the ozone decomposition (RGW, 7.5mgO3/L)

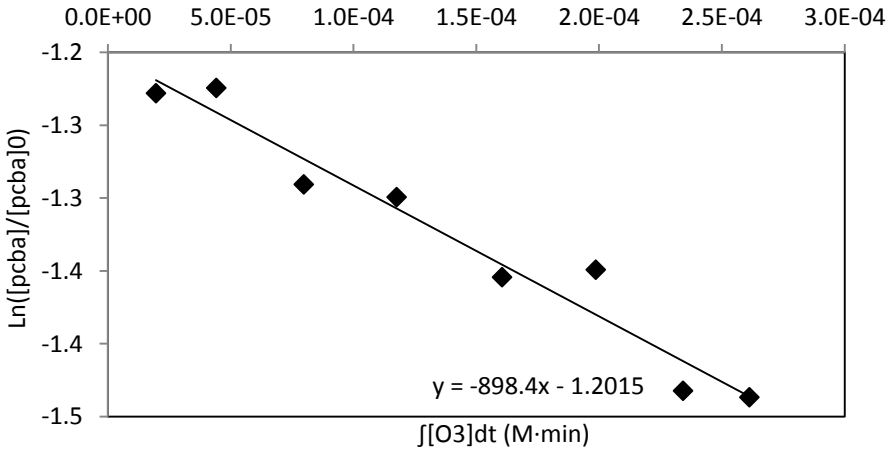


Figure 44. OH-exposure (OH-ct) versus the corresponding O3-exposure (O3-ct) for ozonation (RGW, 7.5mgO3/L)

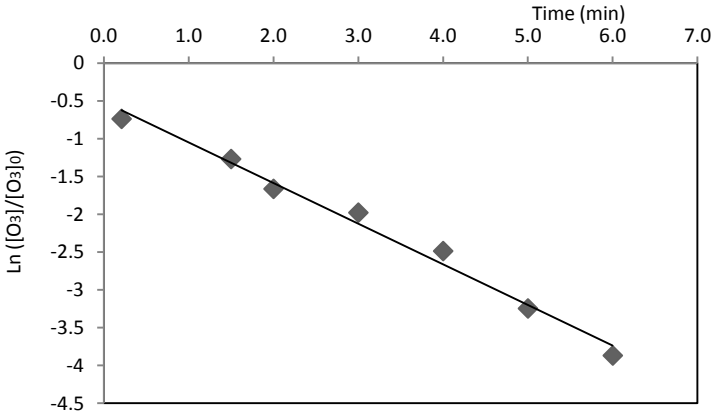


Figure 45. First-order kinetic plot of the ozone decomposition (RGW, 10mgO3/L)

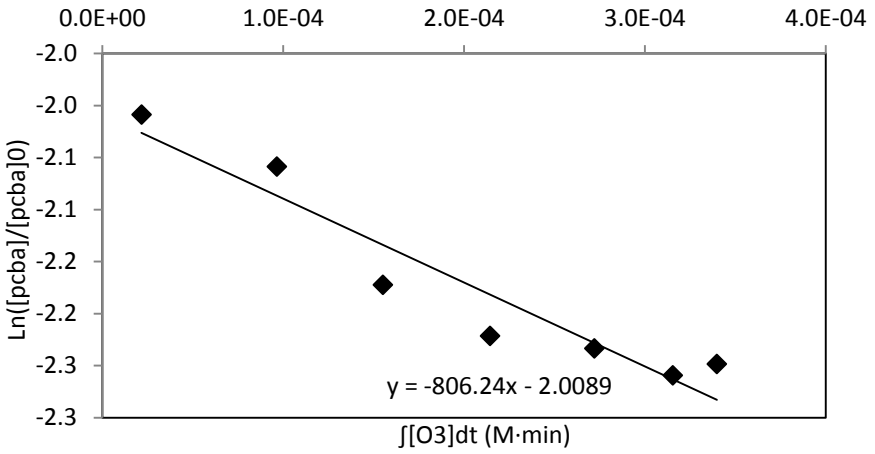


Figure 46. OH-exposure (OH-ct) versus the corresponding O3-exposure (O3-ct) for ozonation (RGW, 10mgO3/L)

10.4. Ozonation of pCBA; degradation of ozone and pCBA curves

10.4.1. RGW – recycled grey water type

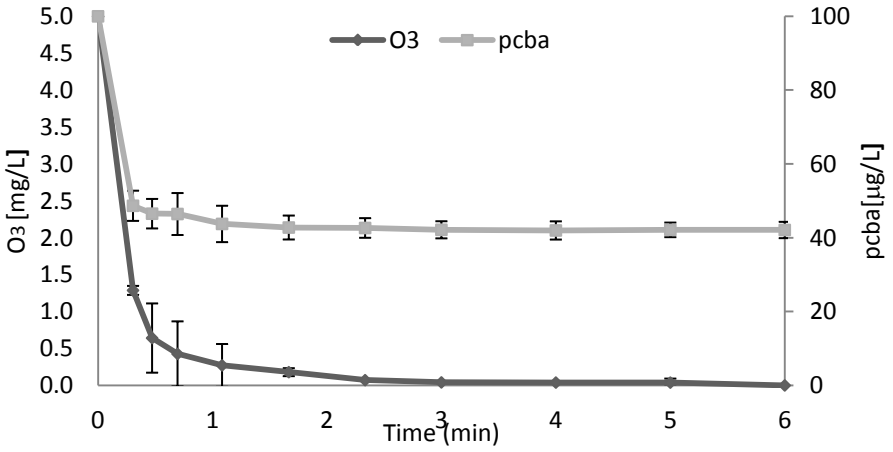


Figure 47. Ozone and pCBA degradation in RGW (ozone dose 5mg/L)

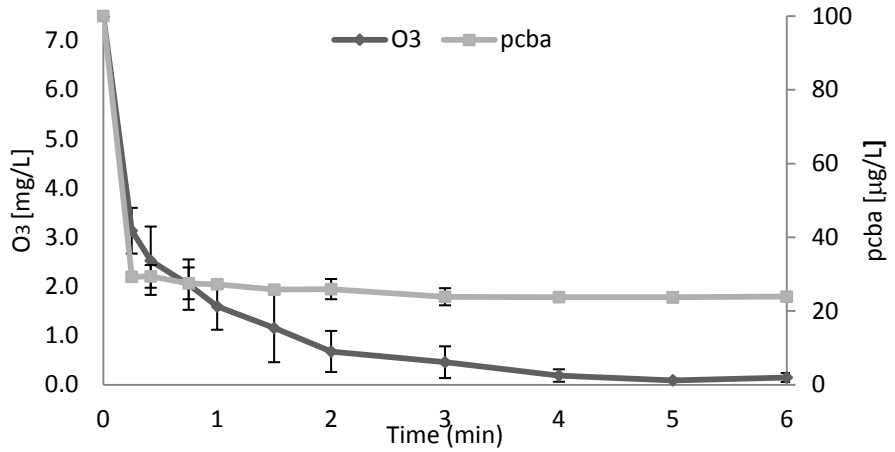


Figure 48. Ozone and pCBA degradation in RGW (ozone dose 7,5mg/L)

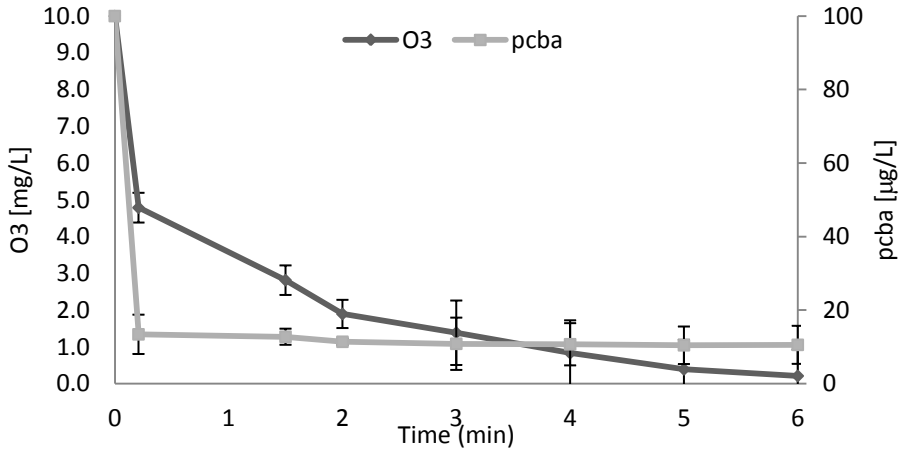


Figure 49. Ozone and pCBA degradation in RGW (ozone dose 10mg/L)

10.4.2. GFT – grey water flow through water type

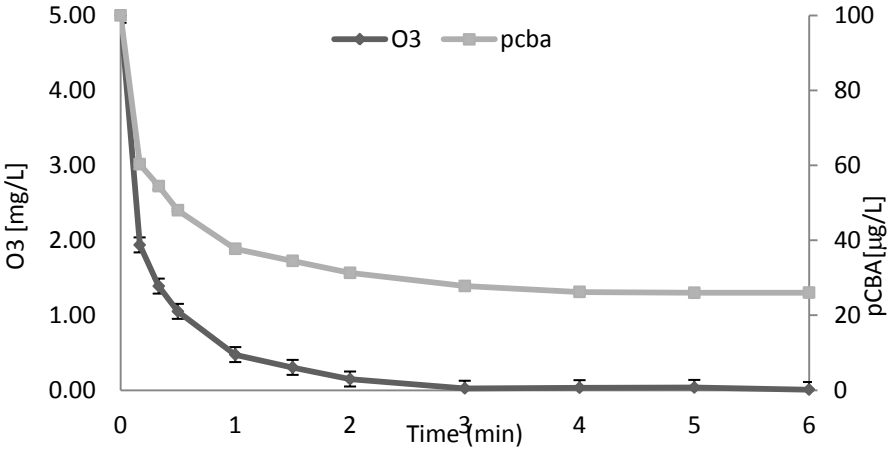


Figure 50. Ozone and pCBA degradation in GFT (ozone dose 5mg/L)

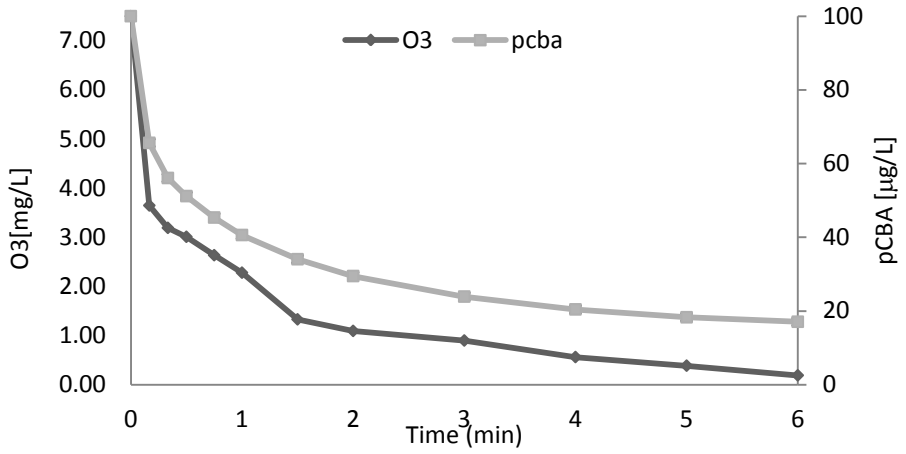


Figure 51. Ozone and pCBA degradation in GFT (ozone dose 7,5mg/L)

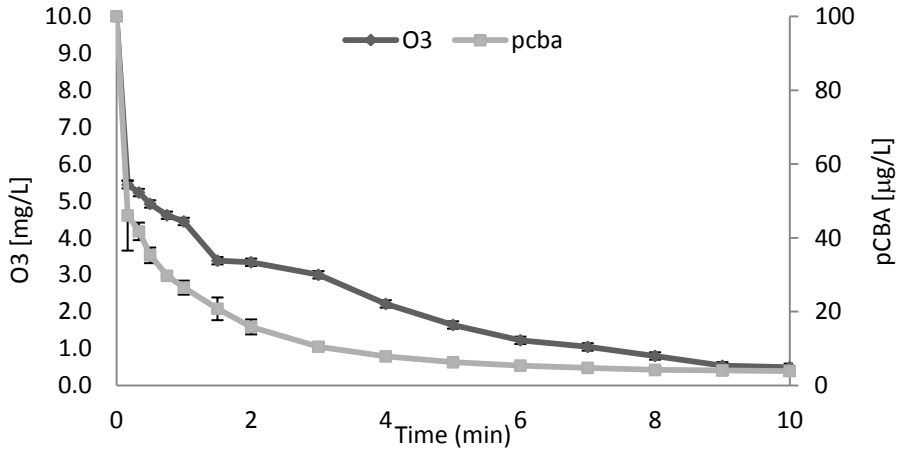


Figure 52. Ozone and pCBA degradation in GFT (ozone dose 10mg/L)

10.4.3. MQ

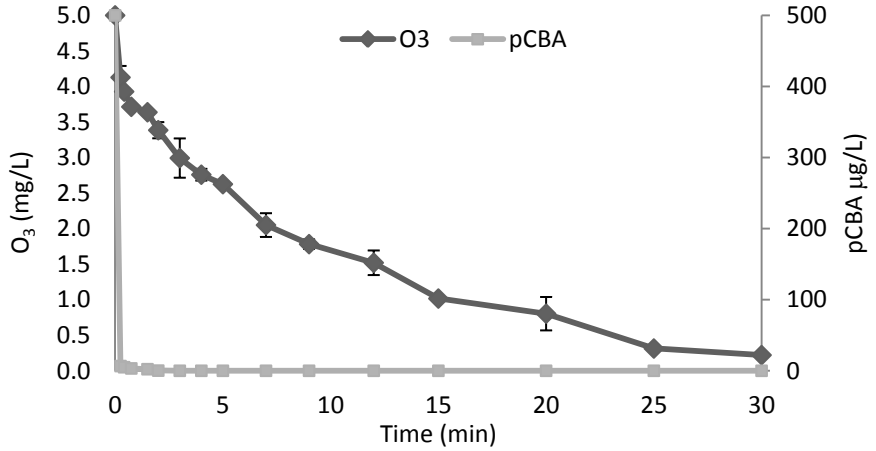


Figure 53. Ozone and pCBA degradation in MQ(ozone dose 5mg/L)

10.4.4. pCBA removal

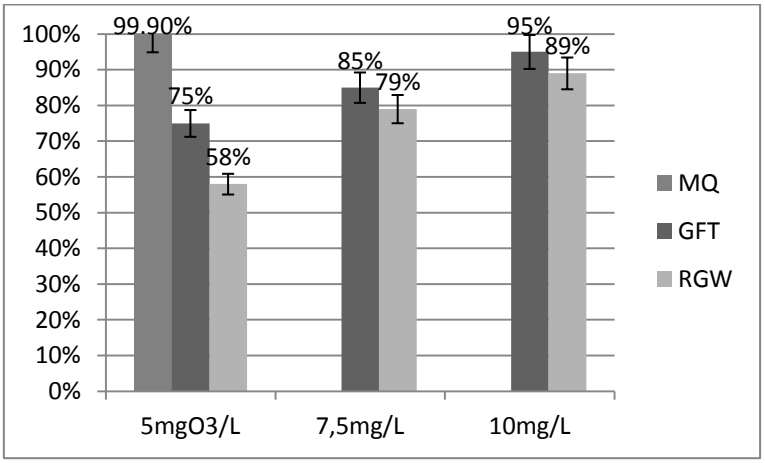


Figure 54. pCBA removal

10.5. Ozonation of DEP; degradation of ozone and DEP curves

10.5.1. RGW – recycled grey water type

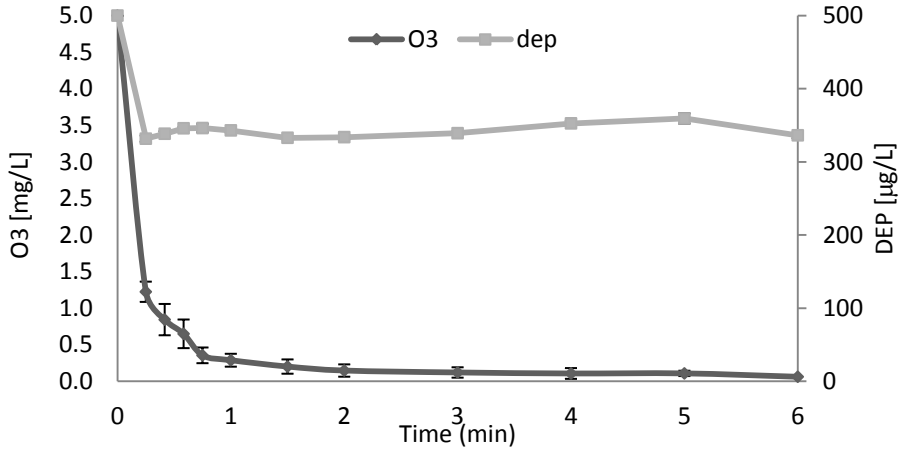


Figure 55. Ozone and DEP degradation in RGW(ozone dose 5mg/L)

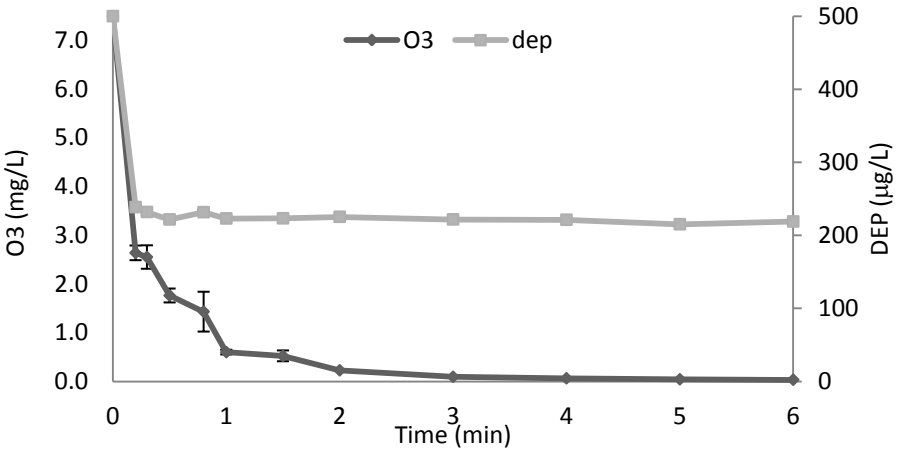


Figure 56. Ozone and DEP degradation in GTF (ozone dose 7,5mg/L)

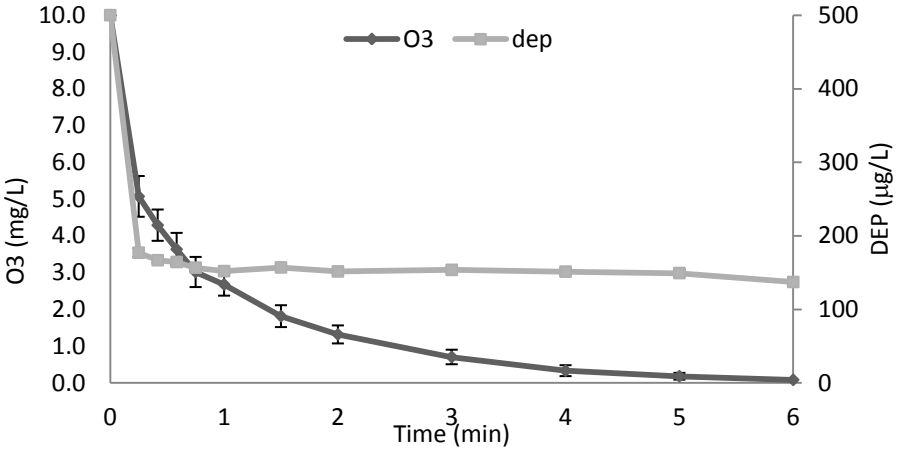


Figure 57. Ozone and DEP degradation in RGW (ozone dose 10mg/L)

10.5.2. GFT – grey water flow through water type

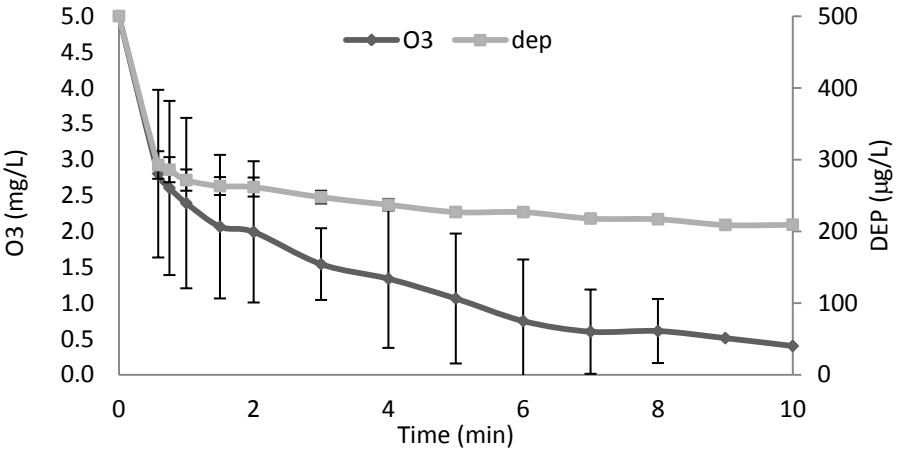


Figure 58. Ozone and DEP degradation in GTF (ozone dose 5mg/L)

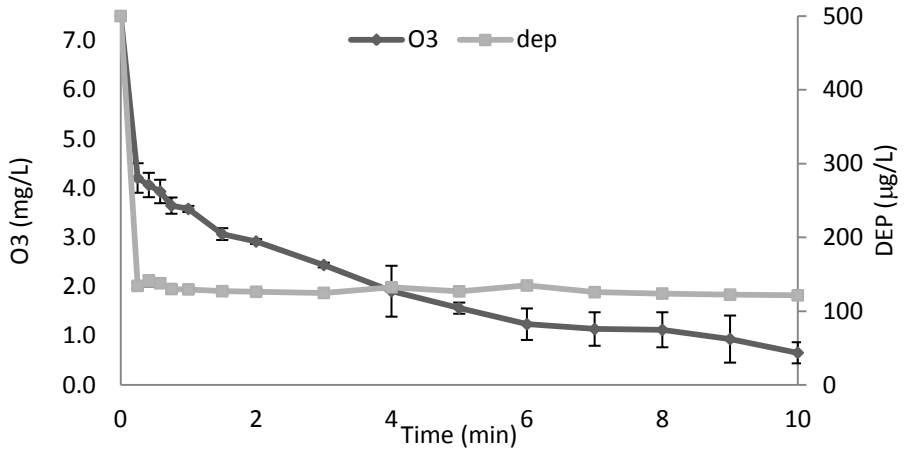


Figure 59. Ozone and DEP degradation in GTF (ozone dose 7,5mg/L)

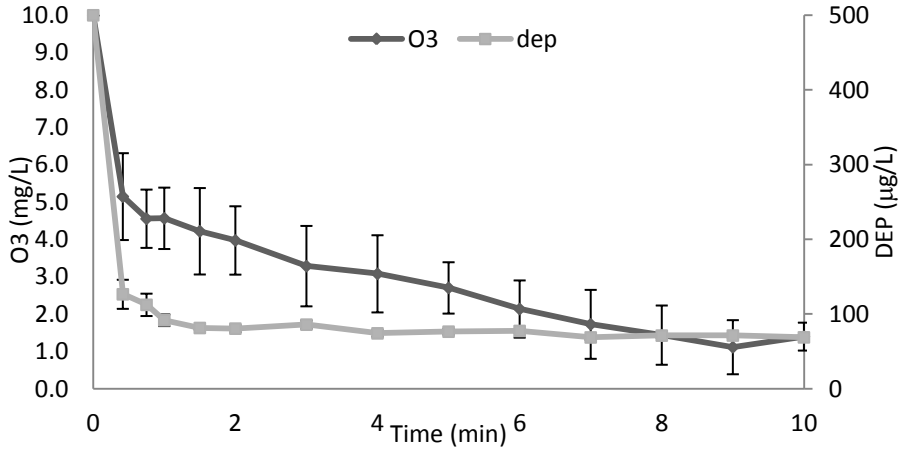


Figure 60. Ozone and DEP degradation in GTF (ozone dose 10mg/L)

10.5.3. Removal of DEP

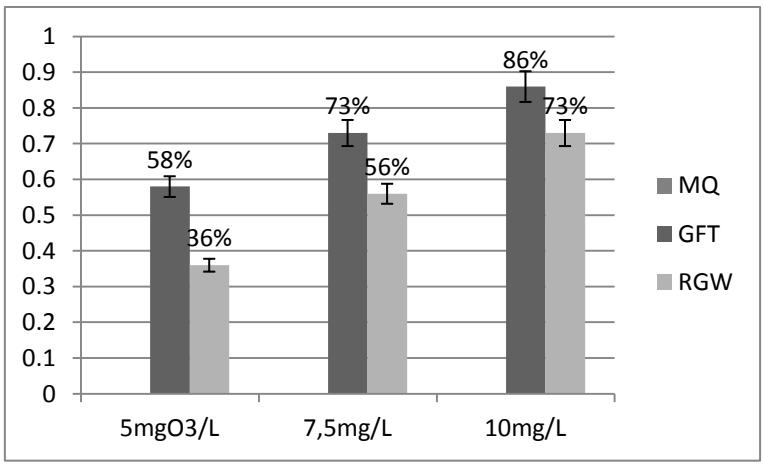


Figure 61. DEP removal

10.6. Ozonationof DEET; degradation of ozone and DEET curves

10.6.1. RGW – recycled grey water type

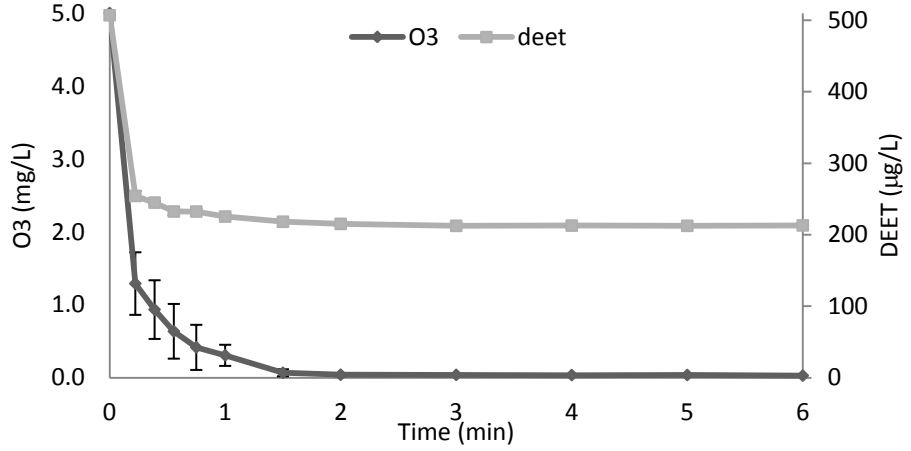


Figure 62. Ozone and DEET degradation in RGW (ozone dose 5mg/L)

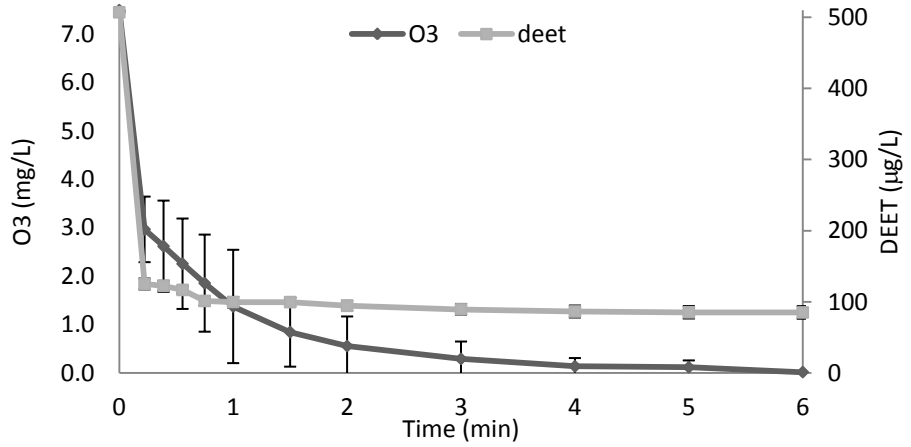


Figure 63. Ozone and DEET degradation in RGW (ozone dose 7,5mg/L)

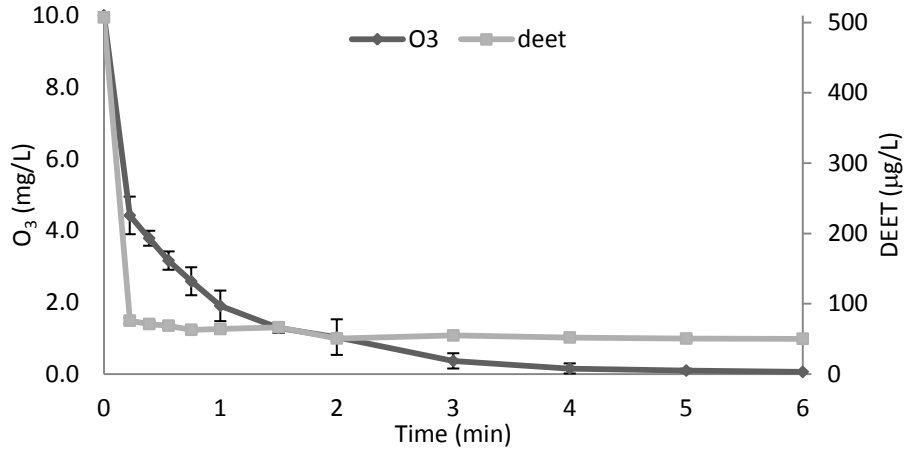


Figure 64. Ozone and DEET degradation in RGW (ozone dose 10mg/L)

10.6.2. GFT – grey water flow through water type

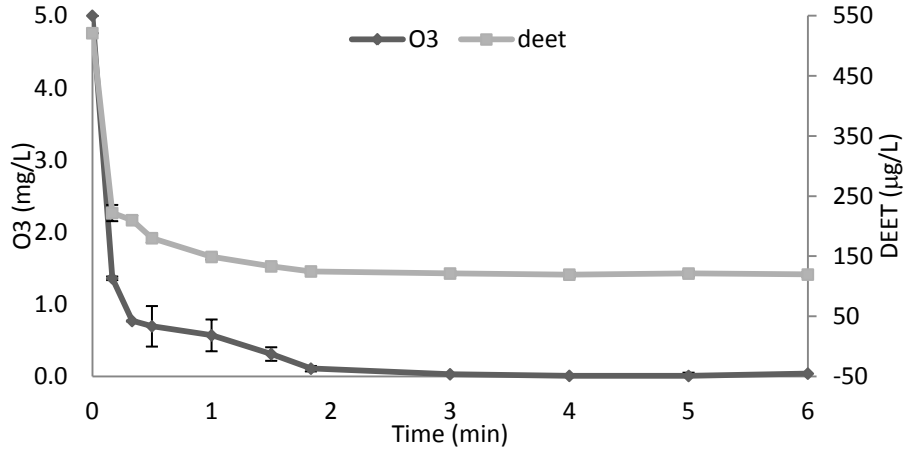


Figure 65. Ozone and DEET degradation in GTF (ozone dose 5mg/L)

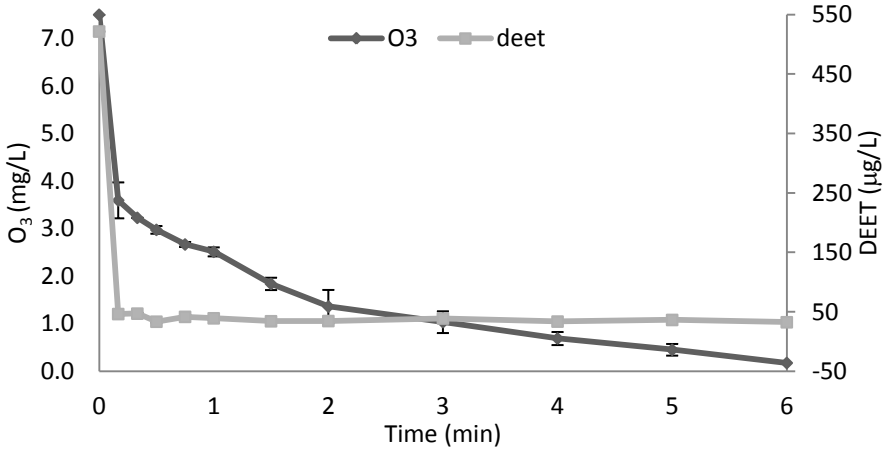


Figure 66. Ozone and DEET degradation in GTF (ozone dose 7,5mg/L)

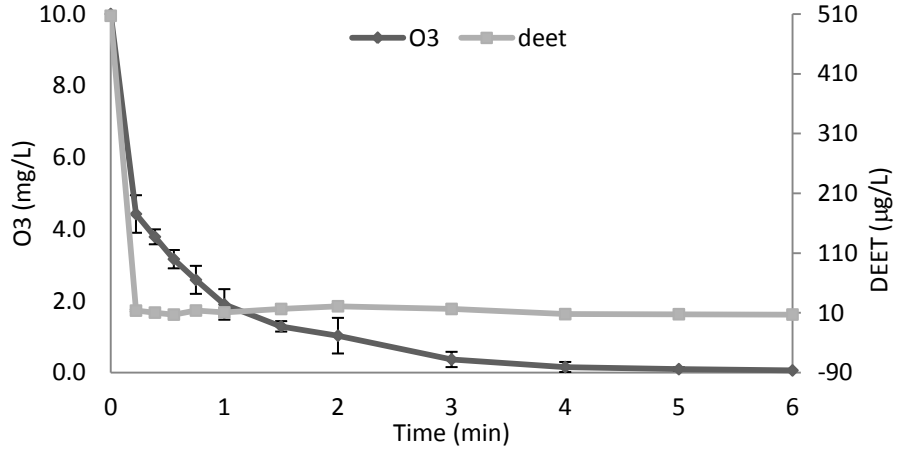
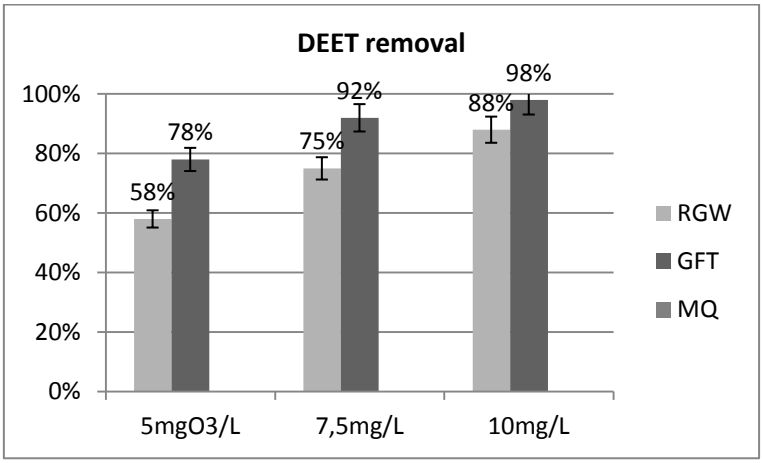


Figure 67. Ozone and DEET degradation in GTF (ozone dose 10mg/L)

10.6.3. Removal of DEET



10.7. Calibration curves

10.7.1. pCBA

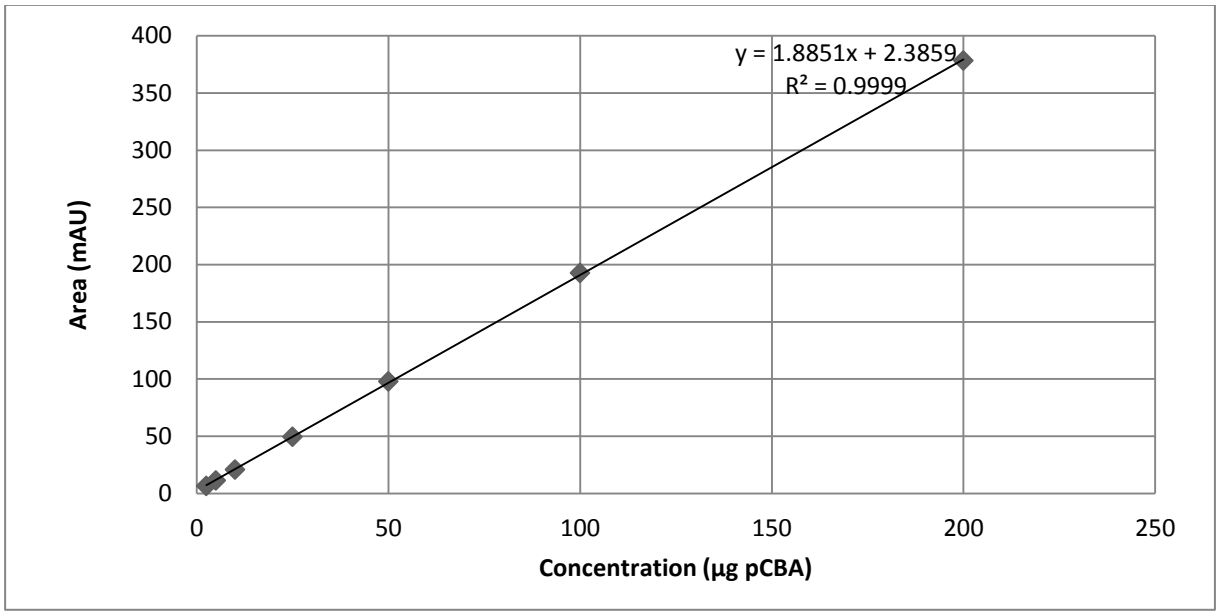


Figure 68. Calibration curve for pCBA in RGW (1)

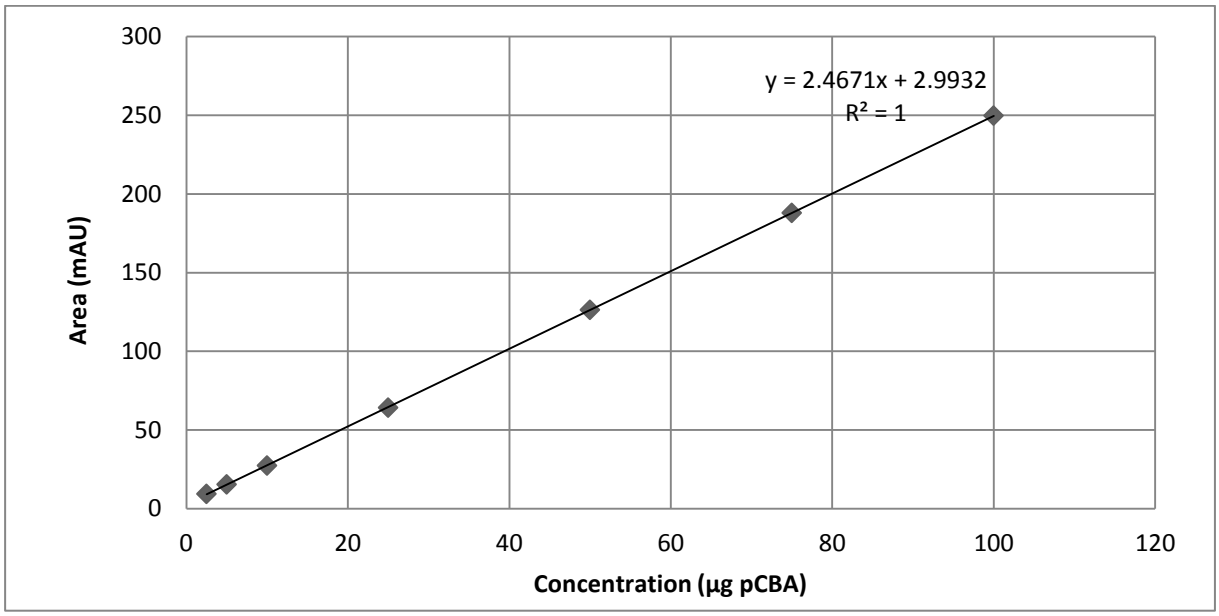


Figure 69. Calibration curve for pCBA in RGW (2)

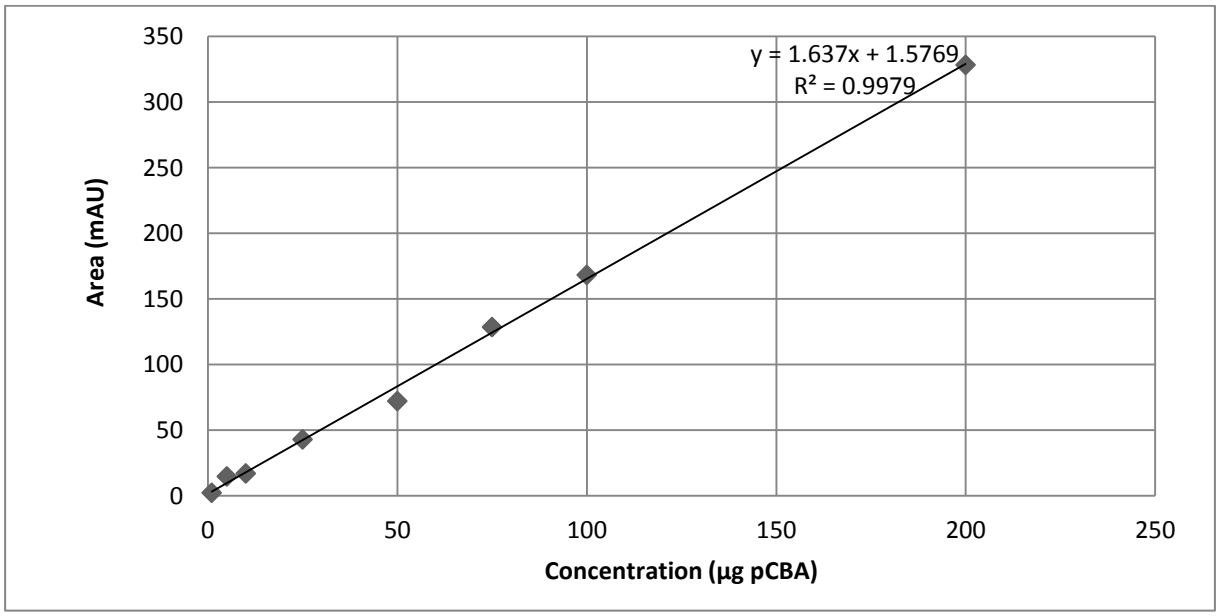


Figure 70. Calibration curve for pCBA in MQ

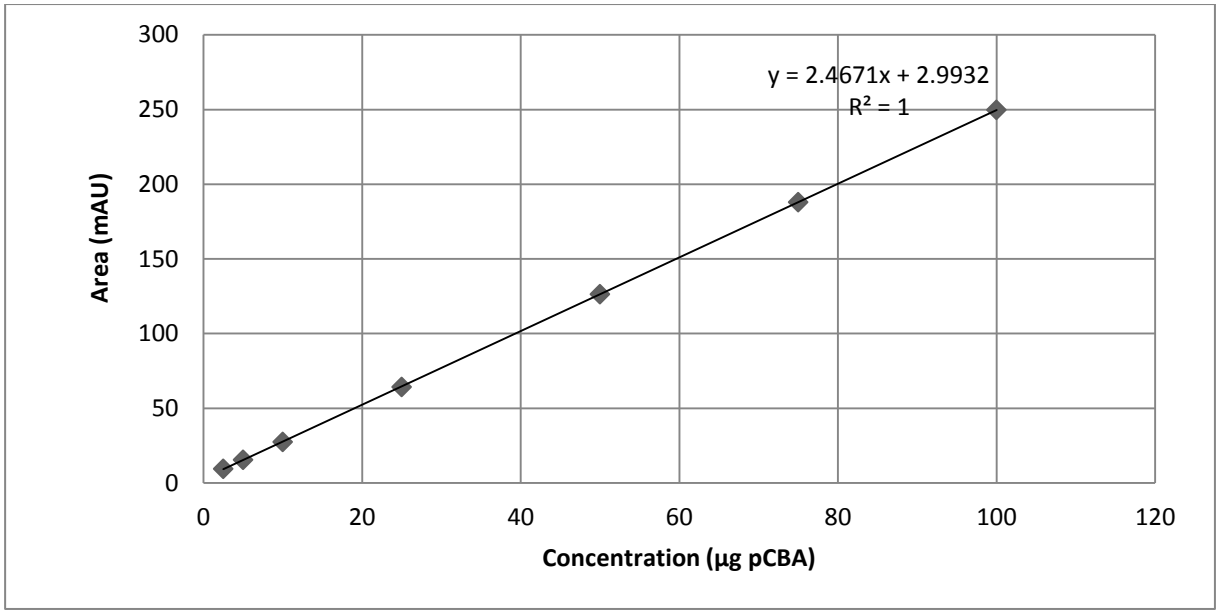


Figure 71. Calibration curve for pCBA in GFT

10.7.2. DEET

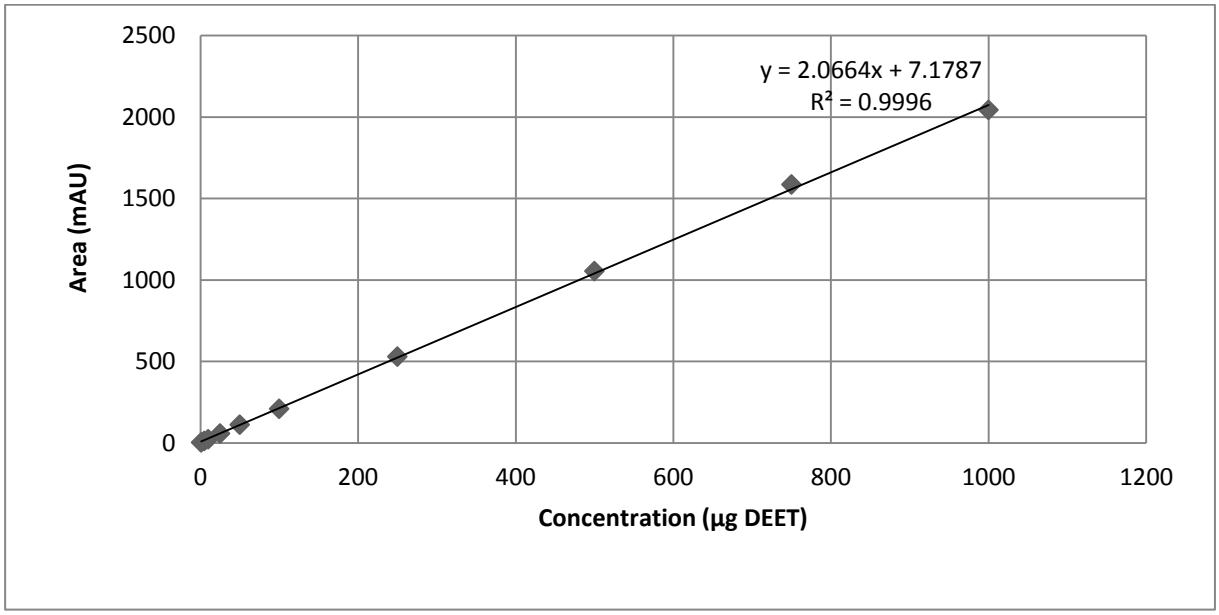


Figure 72. Calibration curve for DEET in RGW (1)

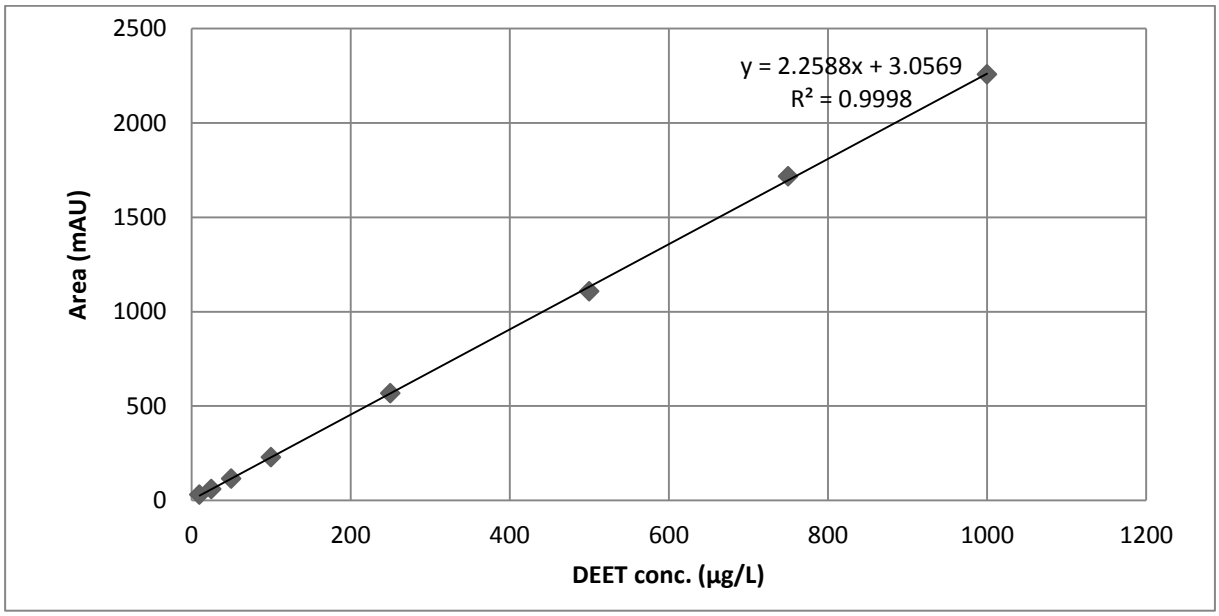


Figure 73. Calibration curve for DEET in RGW (2)

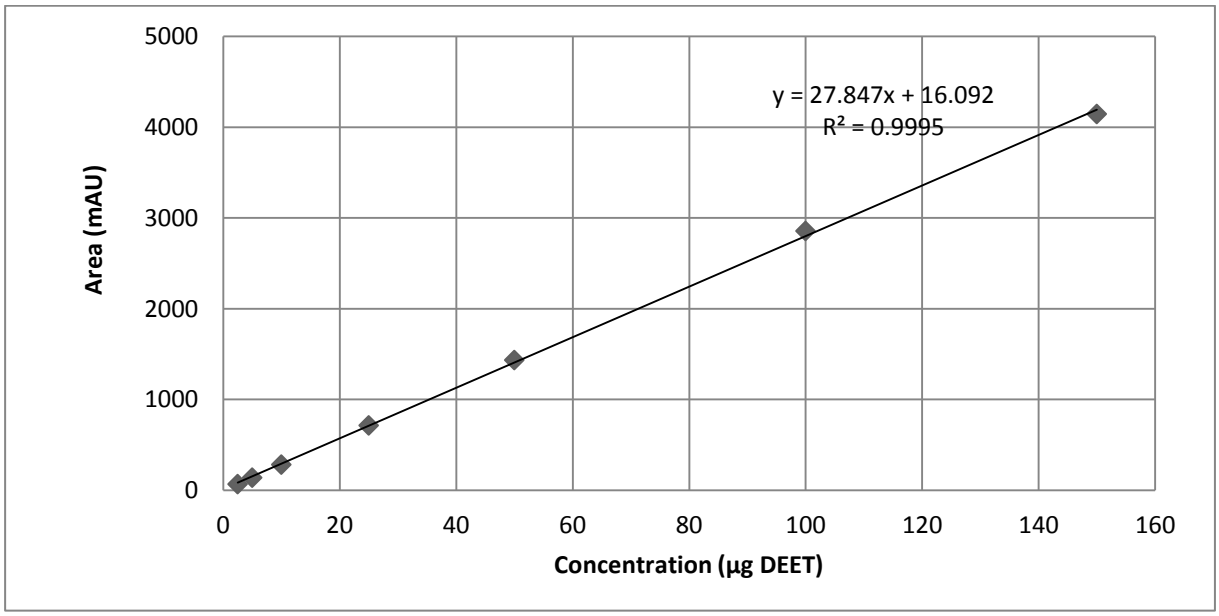


Figure 74. Calibration curve for DEET in GFT

10.7.3. DEP

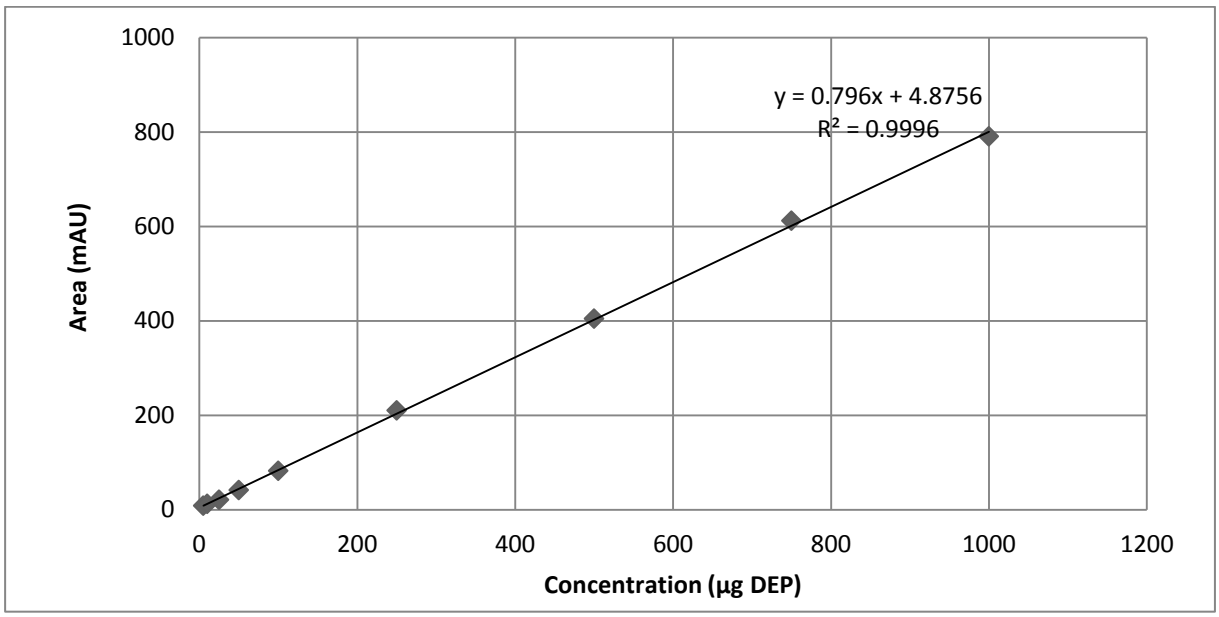


Figure 75. Calibration curve for DEP in GFT

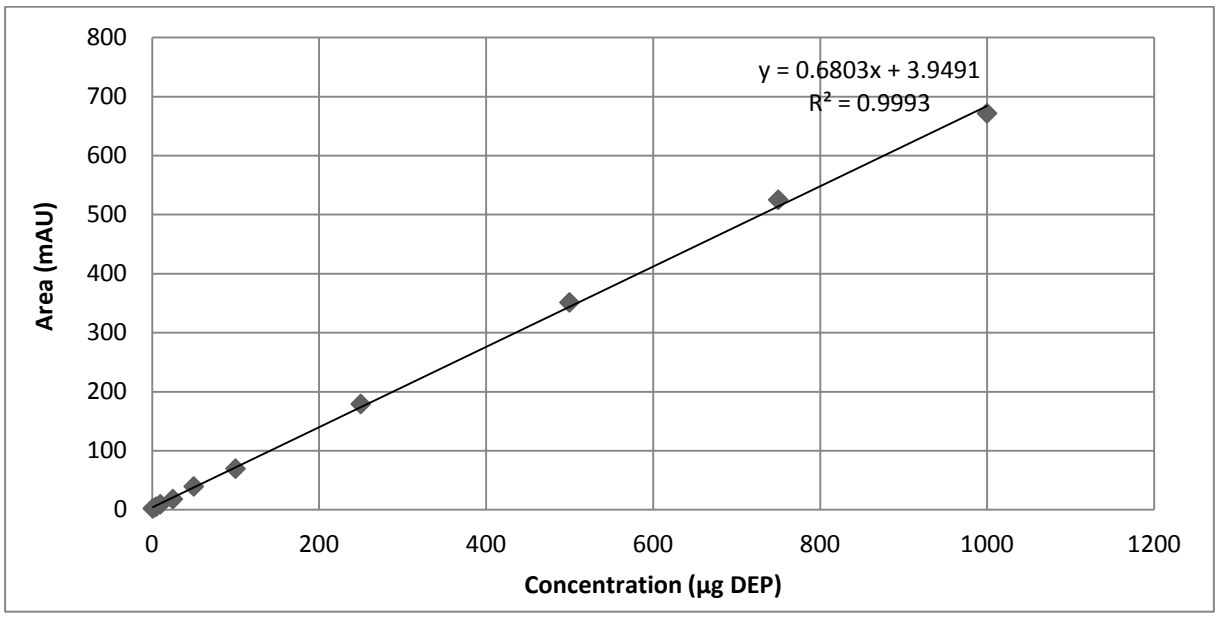


Figure 76. Calibration curve for DEP in RGW

Bibliography

Alex A. Yavich, K.-H. L.-C. (2004). Evaluation of biodegradability of NOM after ozonation. *Water Research*, pp. 2839–2846.

Amir Miodovnik, S. M. (2011). Endocrine Disruptors and Childhood Social Impairment. *Neurotoxicology*, pp. 261-267.

Andreas Peter, U. v. (2007). Oxidation Kinetics of Selected Taste and Odor Compounds During Ozonation of Drinking Water. *Environmental Science & Technology*, pp. 626-631.

Beate I. Escher, M. A. (2013, December 10). Benchmarking Organic Micropollutants in Wastewater, Recycled Water and Drinking Water with In Vitro Bioassays. *Environmental Science and Technology*.

C. C. David Yao, W. R. (1991). RATE CONSTANTS FOR DIRECT REACTIONS OF OZONE WITH SEVERAL DRINKING WATER CONTAMINANTS. *Water Research*, pp. 761-773.

Carson O. Lee, K. J. (2012). Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. *Water Research*, pp. 1005-1014.

CHEMWIKI, UC DAVIS. (2015). *UC DAVIS CHEMWIKI University of California.* Retrieved from http://chemwiki.ucdavis.edu/Physical_Chemistry/Kinetics/Methods_of_Determining_Reaction_Order

D. Urfer, v. G. (2001). Utilisation de l'ozone pour le traitement des eaux potables en Suisse (Use of ozone for treatment of drinking water in Switzerland). 3e partie: etude de cas specifiques. *Gas Wasser Abwasser*, pp. 29–41.

Daniel Gerrity, S. G. (2012, August 24). Development of surrogate correlation models to predict trace organic contaminant oxidation and microbial inactivation during ozonation. *Water Research*, pp. 6257-6272.

E.J. Rosenfeldt, K. (2007). The ROH, UV concept to characterize and the model UV/H2O2 process in natural waters. *Environment Science and Technology*, pp. 2548-2553.

EPA Guidance Manual. (1999). *EPA Guidance Manual Alternative Disinfectants and Oxidants.*

Eva Eriksson, K. A. (2001). Characteristics of grey wastewater. *Urban Water*, pp. 85-104.

F. Javier Benitez, J. L.-R. (2013). Determination of the Reaction Rate Constants and Decomposition Mechanisms of Ozone with Two Model Emerging Contaminants: DEET and Nortriptyline. *Industrial & Engineering Chemistry Research*, pp. 17064-17073.

Gang Wena, J. M.-Q. (2011). Ozonation kinetics for the degradation of phthalate esters in water and the reduction of toxicity in the process of O3/H2O2. *Journal of Hazardous Materials*, pp. 371-377.

Geiger, W. (2012). *Micropollutants in municipal wastewater. Processes for advanced removal in wastewater treatment plants.* Federal Office for the Environment FOEN.

Isabel C. Escobar, A. A. (2001). Assimilable Organic Carbon (Aoc) And Biodegradable Dissolved Organic Carbon (Bdoc): Complementary Measurements. *Water Research*, pp. 4444-4454.

Ivelisse Colón, D. C. (2000). Identification of Phthalate Esters in the Serum of Young Puerto Rican Girls with Premature Breast Development . *CHILDREN'S HEALTH* , pp. 895-900.

J. Hoigne, H. B. (1981). Rate Constants of Reactions of Ozoe with Organic and Inorganic Compounds in Water - I. *Water Research*, pp. 173-183.

Jackson, D. L., Buhl, K., & Stone, D. (2008). DEET technical fact sheets. *U.E.P.A. National Pesticide Information Center*.

Jonas Margota, C. K. (2013). Treatment of micropollutants in municipal wastewater: Ozone or powdered activated carbon? *Science of the Total Environment*.

Juan L. Acero, U. v. (2008). Influence of Carbonate on the Ozone/Hydrogen Peroxide Based Advanced Oxidation Process for Drinking Water Treatment. *Ozone: Science & Engineering: The Journal of the International Ozone Association*, pp. 305-331.

Juliane Hollender, S. G. (2009). Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration. *Environmental Science and Technology*, pp. 7862–7869.

K.Chelkowska, D. I. (1991). Numerical simulations of aqueous ozone decomposition. *Ozone Science & Engineering*, pp. 33-49.

Kerwin L. Rakness. (2005). *OZONE in Drinking Water Treatment: Process Design, Operation and Optimization.* American Water Works Association.

Kheng Soo Tay, N. A. (2009, June 30). Degradation of DEET by ozonation in aqueous solution. *Chemosphere*.

Lloyd R. Snyder, J. J. (2010). *Introduction to Modern Liquid Chromatography, Third Edition.* New Jersey: John Wiley & Sons, Inc.

Magdalena Cirja, P. I. (2008). Factors affecting the removal of organic micropollutants from wastewater in conventional treatment plants (CTP) and membrane bioreactors (MBR). *Rev. Environ. Sci. Biotechnol*, pp. 61-78.

Marc-Olivier Buffle, J. S. (2006). Ozonation and Advanced Oxidation of Wastewater: Effect of O3 Dose, pH, DOM and HO -Scavengers on Ozone Decomposition and HO Generation. *Ozone: Science and Engineering*, pp. 247–259.

Meyer, V. (2004). *Practical High-performance Liquid Chromatography by Veronika Meyer, 4th edition.* John Wiley and Sons.

Michael S. Elovitz, U. v. (2008). Hydroxyl Radical/Ozone Ratios During Ozonation Processes. The Rct Concept. *Ozone: Science & Engineering: The Journal of the International Ozone Association*, pp. 239-260.

Milli-Q® Water Purification Systems. (n.d.). Retrieved from http://www.merckmillipore.com/NO/en/products/water-purification/type-1/5cSb.qB.89EAAAFAJqxkiQpx,nav

Nielsen. (2011). *Market Trends 2011. Fast moving consumer goods in Norway.* Oslo.

Paul Westerhoff, G. A. (1999). RELATIONSHIPS BETWEEN THE STRUCTURE OF NATURAL ORGANIC MATTER AND ITS REACTIVITY TOWARDS MOLECULAR OZONE AND HYDROXYL RADICALS. *Water Research*, pp. 2265-2276.

Rakness, K. I. (2005). *Ozone in Drinking Water Treatment Process Design, Operation, and Optimization.* Denver: American Water Works Association.

Raymond M. Hozalski, E. J. (1999). Removal of Natural Organic Matter (NOM) from Drinking Water Supplies by Ozone-Biofiltration. *Water Science and Technology*, pp. 157-163.

SCCNFP. (2002). *OPINION OF THE SCIENTIFIC COMMITTEE ON COSMETIC PRODUCTS AND NON-FOOD PRODUCTS INTENDED FOR CONSUMERS CONCERNING DIETHYL PHTHALATE* . adopted by the SCCNFP during the 20th Plenary meeting of 4 June 2002 .

Shanna H. Swan. (2008). Environmental phthalate exposure in relation to reproductive outcomes and other health endpoints in humans. *Environmental Res.*, pp. 177-184.

T. Juhna, E. M. (2006). *OZONATION AND BIOFILTRATION IN WATER TREATMENT - OPERATIONAL STATUS AND OPTIMIZATION ISSUES.* TECHNEAU.

Urs von Gunten. (2003). Review: Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Research*, pp. 1443-1467.

Urs von Gunten, C. v. (2012). *Chemistry of Ozone in Water and Wastewater Treatment.* London: IWA Publishing.

V.A. Bjerkelund, S. (n.d.). Pilot scale experiments on enhanced biological nutrient removal from greywater.

Vanessa Chen-Hussey, R. B. (2014). Assessment of methods used to determine the safety of the topical insect repellent N,N-diethyl-m-toluamide (DEET). *Parasites & Vectors*.

Wataru Nishijima, F. T. (2003). DOC removal by multi-stage ozonation-biological treatment. *Water Research*, pp. 150–154.

Weihua Song, W. J. (2009). Free-radical-induced oxidative and reductive degradation of N,N0-diethyl-m-toluamide (DEET): Kinetic studies and degradation pathway. *Water Research*, pp. 635-642.

Werner R. Haag, C. C. (1992). Rate Constants for Reaction of Hydroxyl Radicals with Several Drinking Water Contaminants. *Environmental Scicience and Technology*.

Xiaohui Jin, S. P. (2012). Reaction kinetics of selected micropollutants in ozonation advanced oxidation processes. *Water Research*, pp. 6519-6530.

Xinwei Li, H. S. (2014). Combined process of biofiltration and ozone oxidation as an advanced treatment process for wastewater reuse. *Environmental Science & Engineering*.

Yeon Jung Jung, B. S.-W. (2010, 2 8). The degradation of diethyl phthalate (DEP) during ozonation: oxidation by-products study. *IWA Publishing: Journal of Water and Health*, pp. 290-298.

Yunho Lee, D. G. (2013, May 2). Prediction of Micropollutant Elimination during Ozonation of Municipal Wastewater Effluents: Use of Kinetic and Water Specific Information. *Environmental Science & Technology*, pp. 5872-5881.

Yunho Lee, L. K. (2014). Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent. *Water Research*, pp. 134-148.

Yunho Lee, U. v. (2010). Oxidative transformation of micropollutants during municipal wastewater treatment: Comparison of kinetic aspects of selective (chlorine, chlorine

dioxide, ferrateVI, and ozone) and non-selective oxidants (hydroxyl radical). *Water Research*, pp. 555-566.

Yunho Lee, U. v. (2012). Quantitative structure−activity relationships (QSARs) for the transformation of organic micropollutants. *Water Research*, pp. 6177-6195.

Yunzheng Pi, J. S. (2006, August 18). The Use of para-Chlorobenzoic Acid (pCBA) as an Ozone/Hydroxyl Radical Probe Compound. *Ozone: Science & Engineering: The Journal of the International Ozone Association*.