Modelling Micropollutant Removal Through Ozonation in Wastewater

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Modelling Micropollutant Removal Through Ozonation in Wastewater

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Preface

Thank you to my supervisors Fabio Polesel and Ramesh Saagi, for their continuous support through my work, for sharing their valuable knowledge and for their overall willingness to offer help whenever I needed it. Thank you to my examiner Michael Cimbritz for his guidance and opportune feedback, and also thank you to him and Åsa Davidsson for introducing me to Wastewater Treatment Engineering.

Thank you to DHI A/S for providing me with the WEST® licence and the guides and tutorials to dive into the software.

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Abstract

Proper management of water resources is a key to climate change adaptation and resilience in modern societies. Adequate treatment of wastewater is essential for ensuring the sustainability of the water cycle and the health of the environment and the ecosystems that inhabit it. It can also contribute to water supply needs in regions facing issues stemming from water stress. In this context, computer models can play an important role in assisting wastewater treatment systems facing growing populations and more stringent demands.

This study proposes the combined use of an ozone decomposition model and a micropollutant model to simulate micropollutant removal through ozonation. The model is based on the use of second-order rate constants, denominated kinetic coefficients, and it solves a continuity equation that describes the dynamics of compounds over time. It is developed from the work of Audenaert et al. (2013), which includes the presence of Dissolved Organic Matter (DOM), and adds the effect of Total Suspended Solids (TSS). It also considers fractionation steps for the Chemical Oxyen Demand (COD) and the conjugated, particulate and soluble fractions of a sample of micropollutants, to enable it to be used in combination with other treatment configurations.

The model is calibrated by using two sets of data, one from batch experiments carried out by Juárez et al. (2021) and the other from the operation of an ozonation pilot plant (Ekblad et al., 2021). The validation is then performed by comparing to experimental data from Lee et al. (2014), and achieved with an average coefficient of determination (r^2) of 0.89.

Overall, the model presents a good fit for simulations with values based on batch experimentation, and to a lesser extent in comparison to the data from the pilot plant. Moreover, when the model diverges from the source data it does so with an underestimation in most cases. It also shows lower removal performance with the addition of H_2O_2, and better removal capacity with higher Hydraulic Retention Time (HRT). It responds, however, with negligible sensitivity to variations in pH.

This research offers many possibilities for future work, as it could be applied into risk impact studies, expanded to other micropollutant species, or improved by deepening the work on the effect of TSS, pH, nitrogen species, particulate organic matter, inorganic matter, or others.

The model can also be tested in combination with other treatment configurations and hybrid systems, or together with Computational Fluid Dynamics (CFD). Lastly, there could be a way to put the emerging potential of Artificial Intelligence (AI) to the benefit of wastewater treatment modelling.

Keywords: Micropollutants, water reuse, wastewater treatment models, ozonation, computer modeling.

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1 Introduction

1.1 Overview

Water resources in modern society are of paramount importance to achieve development, climate adaptation and overall well-being (Directorate-General for Environment, 2022; Shestakova et al., 2020). At the same time, these resources are used unevenly across the globe and are subjected to stress and scarcity in certain regions, rendering populations vulnerable to a lack of safe and clean water. Such issues commonly stem from mismanagement, climate change and population growth, and push forward the need for more efficient water management on all scales (Aqueduct Alliance, 2019; Duong and Saphores, 2015; Shestakova et al., 2020; von Sonntag and von Gunten, 2012).

In light of the latter, efforts towards circular economy call upon the idea of wastewater as a water source, with the added benefit of retrieving nutrients and energy as well (Directorate-General for Environment, 2022; Juárez, 2021; Salgot et al., 2006; Shestakova et al., 2020). Wastewater reclamation has been thus gaining momentum as a solution for increasing water demands in water stressed areas, mainly for non-potable applications (Alfiya et al., 2017; Salgot et al., 2006; von Sonntag and von Gunten, 2012). The range of this reuse encompasses irrigation for agriculture, groundwater recharge, industrial processes and urban consumption (Dalahmeh and Baresel, 2014; Duong and Saphores, 2015; United Nations, 2014; von Sonntag and von Gunten, 2012). Hence, different uses of reclaimed wastewater demand different qualities and proper risk management in order to maintain an adequate level of safety to the consumers and the environment (Salgot et al., 2006).

It is therefore a key role what wastewater treatment plants (WWTPs) presently do in providing for the opportunity to effectively reclaim wastewater, as their performance conditions its feasibility. Challenges arise from this situation, with the need for adequate treatment of a wide variety of pollutants, and in present times a particular group of them, called micropollutants (MPs), has been gathering significant attention (Luo et al., 2014). They consist of different types of compounds, among them pesticides, flame retardants, pharmaceuticals and personal care products (Stasinakis and Gatidou, 2010). MPs are present in water at very low concentrations and their effects on both human health and biodiversity are not yet fully understood (Grandclément et al., 2017). Evidence has revealed the presence of MPs in urban systems, groundwater and surface reservoirs all over the world, becoming an environmental concern at an international scale and a high priority topic of research and policy (Carvalho et al., 2015; Ekblad et al., 2021; Directive 2000/60/EC, 2000; Grandclément et al., 2017; Nguyen et al., 2021; von Sonntag and von Gunten, 2012). A particularly pervasive trait of MPs is their tendency to bioaccumulate to toxic levels, either for humans or other species, and to move up the food chain (Burkhardt-Holm, 2011; Grandclément et al., 2017; Salgot et al., 2006).

To worsen the matter, many conventional treatment practices are currently not being able to efficiently remove micropollutants, and WWTPs may be failing to act as a barrier between pollution and the environment (Alfiya et al., 2017; Grandclément et al., 2017; Luo

et al., 2014). WWTPs consider primary, secondary and often times tertiary processess in their operations, incurring in such cases higher costs and more sophisticated technologies. These tertiary treatments are applied for more stringent effluent demands, and thus it can potentially offer better performance in the removal of MPs (Davis, 2010; Luo et al., 2014). Therefore, developing optimal removal methods for pollutants has become a high priority that requires a collaborative effort between operators, designers, modellers, policy and decision makers (Luo et al., 2014).

In all evidence, caring for the water cycle becomes a critical role that water treatment systems fulfill. Providing with advanced processes that go beyond standard practice is a need that arises from increasing pollutant loads from growing populations, more strict environmental demands and water reclamation potential (Davis, 2010; Shestakova et al., 2020). Among these advanced processes is ozonation, where its application in WWTPs has already been tested in full-scale in some opportunities (Bourgin et al., 2018; Hollender et al., 2009; Itzel et al., 2020; Zimmermann et al., 2011). Despite the fact that most plants use ozonation for its disinfecting properties, it is also capable of reducing MPs in wastewater. This dual capacity actually renders ozonation as an attractive practice for water reclamation efforts (Blackbeard et al., 2016; Hernández-Leal et al., 2011).

On the other hand, computer models capable of generating predictions on MP removal performance have established themselves as a fundamental tool for making water treatment operations more efficient, that offer engineers and decision makers ways to better assess and optimize the processes involved, and understand the possible consequences on the surrounding environment (Audenaert et al., 2013; Bezbarua and Reckhow, 2004; Clouzot et al., 2013). With evolving technologies being tested and implemented in WWTPs, and more stringent regulations being put in place, many challenges have arisen for modellers to confront (Clouzot et al., 2013). Therefore, modelling MP removal is a contribution to keep up the pace with modern water quality needs that leads to better environmental care and management of water and reclaimed water resources.

1.2 Aim

A commercial software presently available for modelling wastewater treatment systems is WEST®, developed by the engineering consultancy firm DHI A/S. It consists of a simulation tool for the optimization, operation and automation of treatment plants, and it was developed to perform dynamic modeling and simulation of water quality systems.

The software does not currently have an available ozonation model in their new library, and the aim of this project is to propose a model that predicts the removal of micropollutants in wastewater through ozonation, and make it readily available to be included in the new model library.

1.3 Research Problem

The problem that motivates this research can be divided into two questions:

- What is the best modelling approach to encompass the relevant phenomena involved in micropollutant removal with ozone dosing?

- How could this model adapt to different wastewater effluents and treatment configurations?

2 Background

2.1 Wastewater characteristics

A stream of wastewater is typically composed of domestic and industrial effluents that originate from homes, offices, commercial and institutional buildings in the first case, and factories, manufacturing and chemical processes on the other hand. In addition, there can usually be stormwater, melted snow and ice in the mix, together with infiltration and inflow from groundwater. On average, the temperature in wastewater usually varies between 10 to 20°C, and the pH gravitates around 6.5 to 8.5 (Davis, 2010; Shestakova et al., 2020).

Traditionally, wastewater is characterized in terms of biochemical oxygen demand (BOD), chemical oxygen demand (COD) (both to indicate presence of organic matter), total nitrogen (TN) or total Kjeldahl nitrogen (TKN), and total phosphorus (TP). On top of that, industrial activities contribute with a significantly diverse range of pollutants associated with the different process that can be involved (Davis, 2010). From such characterizations, water treatment targets the removal of waste to increase water quality to admissible standards. One of the main motivators is the concern for environment protection, as contamination of water bodies pose a dangerous threat to the ecosystems and their biodiversity, including human well-being (Salgot et al., 2006; Shestakova et al., 2020). In the case of industrial effluents, the treatment often times takes place at the source, as local collection systems and wastewater treatment plants may not be prepared to handle industry-specific water matrices and thus discharge streams with remaining contaminants (Davis, 2010; Shestakova et al., 2020).

Generally speaking, wastewater can be treated by a variety of methods, which can be physical, biological, chemical and physico-chemical. Physical processes involve the separation of solid particles, biological processes rely on microorganic action to consume dissolved pollutants, chemical treatment induces chemical reactions on pollutants, and physico-chemical methods combine the first and the last mentioned (Shestakova et al., 2020).

2.2 What are micropollutants

Micropollutants are organic and inorganic compounds found in concentrations in the nano and microgram scales, that pose a threat to the ecosystems in the form of behavioral changes, impacts on anatomy and reproduction, antibiotic resistance and even higher mortality in living organisms that can be long term (Brodin et al., 2013; Clouzot et al., 2013; Kidd et al., 2007; Qiao et al., 2018; Schultz et al., 2011; Stasinakis and Gatidou, 2010). Examples of these contaminants are pharmaceuticals, illicit drugs, surfactants, industrial chemicals, flame retardants, pesticides, metallic trace elements, steroid hormones, microbial pathogens and personal care products, and can be grouped by application, molecular similarity and biochemical activity, among other categories (Clouzot et al., 2013; Grandclément et al., 2017; Juárez, 2021; Luo et al., 2014; Kasprzyk-Hordern et al., 2009; Loos et al., 2013; Ternes and Joss, 2007; Stasinakis and Gatidou, 2010). Out of all MPs, compounds from industrial activities, pharmaceuticals and personal care products are the most present in wastewater

(Alfiya et al., 2017; Undeman et al., 2022). Figure 2.1 depicts (*a*) the concentration ranges of certain micropollutants in contrast with common macropollutants (Stamm et al., 2016; Undeman et al., 2022) and (*b*) their presence in WWTP effluents within the Baltic Sea drainage basin, gathered from a database built by Undeman et al. (2022). PFASs, PAHs and PCBs stand for per- and poly- fluoroalkyl substances, polyaromatic hydrocarbons and polychlorinated biphenyls, respectively (Ibid.).

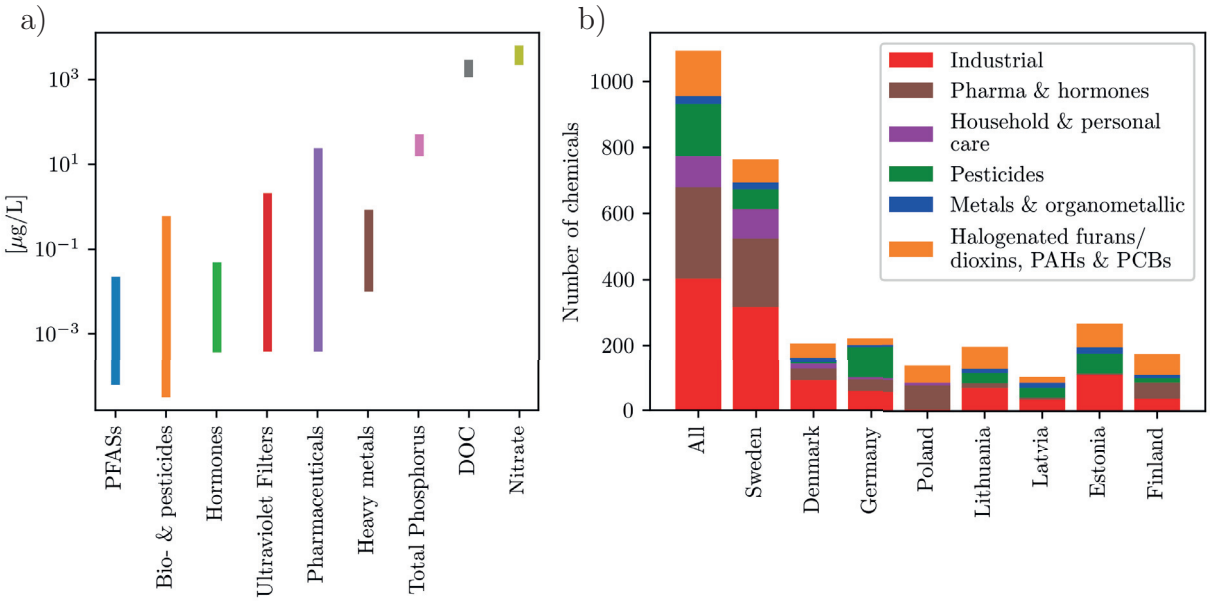

Figure 2.1: a) Concentration ranges of certain micropollutants in contrast with Total Phosphorus, DOC and Nitrate. The ranges cover from the 25^{th} to the 75^{th} percentiles (Stamm et al., 2016; Undeman et al., 2022). b) Compilation of observed concentrations of MPs in WWTP effluens within the Baltic Sea drainage basin, gathered from a database built with literature search from sources published between the years 2000 and 2020 (Undeman et al., 2022).

In addition, there is the possibility of MPs being precursors of other types of products, some of them originated from metabolic processes that may take place in the human body. These can lead to metabolized compounds to be excreted and ultimately enter the environment (Juárez, 2021; Kasprzyk-Hordern et al., 2009; Dorado et al., 2003; Miao et al., 2005; Testa et al., 2012). Apprehensions like the ones mentioned and the threat they represent are also brought to the discussion over wastewater reclamation (Duong and Saphores, 2015).

The vast diversity of MPs arises from the different usage and consumption that they are made for, and has a direct impact on the complexity of the challenges that treatment processes have to face (Luo et al., 2014). MPs have been observed to be discharged through WWTPs, as mentioned earlier, and are carried to the treatment plants through domestic, industrial, agricultural (e.g.: containing manure) and hospital discharges, landfill leachate and stormwater runoff (Luo et al., 2014; Juárez, 2021; Stangroom et al., 1998). Furthermore, these streams are subjected to spatial and temporal variations depending on local practices,

industrial rates of production, metabolisms, water consumption and performance of WWTPs (Jelić et al., 2012; Luo et al., 2014; Petrović et al., 2009). Lastly, when MPs reach water bodies, they are subjected to processes that will depend on both their physico-chemical properties (e.g.: solubility, polarity, etc.) and the characteristics of the receiving bodies (i.e.: whether it is a groundwater or surface water reservoir, if there is sediment present, etc.) (Stasinakis and Gatidou, 2010).

Much is still unknown regarding the effects that MPs can have on the environment and human health, and their diversity only complicates things, as it becomes unfeasible to target them one by one (Grandclément et al., 2017; Lee et al., 2014; Loos et al., 2013; Luo et al., 2014; Ternes and Joss, 2007).

2.3 The treatment of micropollutants

Wastewater containing micropollutants has to be adequately treated to improve its quality and to avoid potential hazardous impacts, as mentioned in the previous section, whether the intention is to reclaim it or to discharge it into a receiving body (Alfiya et al., 2017; Juárez, 2021).

Micropollutant treatment is affected by the contaminants' physico-chemical properties and by the conditions of the treatment processes (Luo et al., 2014). And the processes themselves should be designed in order to attain the desired quality of the effluent. From a historical perspective, the configuration of WWTPs have mostly aimed at the removal of organic matter, nitrogen and phosphorus with primary, secondary and - sometimes - tertiary processes, resulting in the partial treatment of certain MPs (Falås et al., 2016; Luo et al., 2014). For example, fragrances, pharmaceuticals, hormones and endocrine disruptive compounds have been found to have removal rates varying between 10 to 40% in primary treatment, according to a recount made by Luo et al. (2014). In more general terms, MPs can be removed when primary and activated sludge capture compounds before being removed as waste, or when compounds are transformed or volatilized, or when they experience dispersion, dilution, biodegradation or biotransformation, with the last two mentioned being the main responsible for removal in biological treatment (Clara et al., 2005; Luo et al., 2014). Still, many contaminants remain unaltered (Choubert et al., 2011; Clara et al., 2005).

Thus, advanced treatment has better performance when dealing with MPs, and is more broadly implemented when the goal is to produce high effluent quality, which in turn often implies higher costs, and are intended for specific purposes (e.g.: reuse) (Luo et al., 2014). A broad catalogue of alternatives can be considered to upgrade a WWTP, which include processes that rely on biological treatment, activated carbon-based treatment, membrane filtration, advanced oxidation processes (AOPs), or hybrid configurations, each with their own set of pros and cons to their application (Al-Rifai et al., 2011; Altmann et al., 2014; Juárez, 2021; Falås et al., 2013, 2016; Huber et al., 2003; Nowotny et al., 2007). So far, there is no single specific treatment configuration that guarantees complete MP removal, but AOPs, activated carbon adsorption, reverse osmosis and membrane bioreactors (MBRs) are generally regarded as high performing alternatives (Luo et al., 2014). Particularly activated carbon and ozonation are believed to show the most promise (Altmann et al., 2014; Huber et al., 2003; Nowotny et al., 2007; Ternes et al., 2002).

2.3.1 Membrane filtration

Filtration with the use of membranes is accomplished when compounds are too big to go through its pores, are adsorpted into the membrane or are repelled by charge. The efficiency depends on the characteristics of the membrane itself, but also on the conditions it operates and the rate at which its pores clog (i.e.: fouling). Nanofiltration (NF) and reverse osmosis (RO) show good potential for micropollutant treatment and have higher removal efficiency than their coarser counterparts (microfiltration (MF) and ultrafiltration (UF)) because of their smaller pore size (Chang, 2010; Luo et al., 2014; Schäfer et al., 2011).

2.3.2 Membrane bioreactors (MBRs) and biofiltration

MBRs consist of biological treatment through activated sludge in conjunction with membrane filtration. In this case, membrane interception can target compounds that adhere to the activated sludge but are resistant to its effects. Complementarily, the sludge retention time (SRT) can be adjusted in order to enhance their microbial degradation (Luo et al., 2014; Radjenović et al., 2009; Spring et al., 2007). In a 2012 resarch by Trinh et al., removal of MPs was observed in a full-scale MBR with a performance that was resilient to seasonal variations, thanks to the combined action of biotransformation and adsorption. The overall performance of MBRs may vary depending on sludge age and concentration, anoxic and anaerobic stages, wastewater characterization, temperature, pH and conductivity (Kovalova et al., 2012; Trinh et al., 2012).

Biofiltration, on the other hand, includes techniques such as sand and trickling filters and beds of activated carbon. In this settings, attached growth takes place for biological treatment and their performance appears to be notable for micropollutant removal, despite it not being widely tested yet (Luo et al., 2014).

2.3.3 Activated carbon

Activated carbon is an adsorbent material that has the capability to remove contaminants, and is applied either as powdered activated carbon (PAC) or granular activated carbon (GAC). Until recent times it was mostly used for drinking water treatment, due to its application on odor and taste control. Now, its use in wastewater treatment has brought new challenges due to the different nature of the processes and flow qualities involved (Ekblad et al., 2021; Luo et al., 2014; Nowotny et al., 2007).

The application of PAC has yielded a removal rate of 80% and more, and is being considered effective in adsorbing recalcitrant and non-biodegradable micropollutants. GAC, in turn, shows similar results yet it demands additional care to avoid saturation over time, which would affect its efficiency. These techniques can also be hindered in the presence of highly contaminated waters or organic matter, due to the generation of competition for binding sites and consequent appearance of blockage (Luo et al., 2014).

2.3.4 Ozonation and other advanced oxidation processes

These technologies rely on redox reactions that oxidize micropollutants and have demonstrated high degradation rates. Traditionally used for their disinfecting properties, it highlights their appeal as a wastewater treatment process for this dual function, even more so when dealing with water reuse efforts (Blackbeard et al., 2016; Hernández-Leal et al., 2011).

As previously mentioned, ozonation in particular is presently being applied at full scale in WWTPs and a general focus of study (Bourgin et al., 2018; Hollender et al., 2009; Huber et al., 2003; Itzel et al., 2020; Juárez, 2021; Luo et al., 2014; Nakada et al., 2007; Zimmermann et al., 2011).

Ozonation degrades compounds by dissolving highly reactive ozone molecules into the water stream, that trigger chain chemical reactions in the solution. Thus, the reactivity of the targeted pollutants, together with the wastewater characteristics, play an important role on removal efficiency, which evidences its dependence to the specific substances present in the process (Ekblad et al., 2019, 2021; Hansen et al., 2016; von Sonntag and von Gunten, 2012; Zucker et al., 2015). A collection of works mentioned in Lee et al. (2013) shows that contemporary research in different countries has shown MP elimination of 80% and over in wastewater, and similar results for the case of biologically treated greywater. However, limitations still remain given the diversity of micropollutants and wastewater matrices to be dealt with (Hernández-Leal et al., 2011; Lee et al., 2013).

An example of other AOPs that have been a subject of interest are UV-based processes. The exposition to UV has been reported to remove up to 90% of selected MPs if combined with the addition of hydrogen peroxide (H_2O_2) (Kim et al., 2009).

2.3.5 Considerations regarding micropollutant removal

The measurement of percent removal of MPs is commonly used to describe treatment performance and characterize their reduction from wastewater (Stadler et al., 2012). A research done by Luo et al. (2014), which gathered the average removal of a sample of micropollutants in WWTPs located in 14 countries and regions, revealed differences between compounds of the same usage class, and inconsistencies between measurements for the same contaminant at different locations.

However, arguments have come up to push forward the need to additionally consider by-products and transformation products, as they contribute to toxicity too. By-products can result from reactions originated by a treatment process being applied to wastewater. Transformation products (TPs), on the other hand, consist of conjugated forms of the parent compound caused by human and microbial metabolism. Furthermore, their conjugation and de-conjugation dynamics can even cause for negative removal observations. Pharmaceuticals enveloped in organic matter that are later released during treatment are another source of increase in parent compounds' concentration along a wastewater treatment line (Kharel et al., 2021; Luo et al., 2014; Polesel et al., 2016; Stadler et al., 2012).

The existence of TPs adds another layer to the complexity of micropollutant treatment systems, and reporting removal rates without tracking the mechanisms of TP formation and elimination might generate an inaccurate picture of the reality of effluent quality and environmental management (Stadler et al., 2012). To continue with the case of ozonation, hybrid systems are encouraged to address the issue with by-products and transformation products, although which ones to pick is not a trivial decision and should be addressed in future research (Kharel et al., 2020, 2021; Stadler et al., 2012).

An alternative to hunt every possible by-product or TP would be to perform a risk evaluation, that would require the identification and priorization of the most hazardous contaminants, to link them to potential vulnerable zones and the consequential impact they

would induce (Stadler et al., 2012).

2.4 Current and future regulations

There are regulations at present times that set standards and define targets for water quality demands in the effluents from wastewater treatment plants. Notably in Europe, a Directive was put forward in 1991 to avoid adverse effects on the environment generated by urban and industrial wastewater discharge, called Urban Wastewater Treatment Directive (UWWTD) (Directive 91/271/EEC, 1991; Directorate-General for Environment, 2022). It has been amended since then, and together with additional European legislation, more specific issues regarding wastewater quality have been added, like the Directive amendment targeting eutrophication in 1998 (Directive 98/15/EC, 1998; European Commission, 2023), the EU Water Framework Directive adding a list of 45 priority substances in the year 2000 (Directive 2000/60/EC, 2000), the European Parliament Directive defining quality standards for 33 priority substances in 2008 (Directive 2008/105/EC, 2008), the Decision on a watch list of micropollutants for EU-wide monitoring in 2015 - updated in 2020 and in 2022 (Commission Implementing Decision (EU) 2015/495, 2015; Commission Implementing Decision (EU) 2020/1161, 2020; Commission Implementing Decision (EU) 2022/1307, 2022) - and the Council Directive regulating bromate levels in drinking water in 2020, among others (Council Directive 2020/2184, 2020; Directorate-General for Environment, 2022; Juárez, 2021). Similar examples can be gathered from countries outside the EU, like the Clean Water Act in the United States and the Canadian Environment Protection Act (Canadian Environmental Protection Act, 1999; Davis, 2010; Luo et al., 2014; U.S. House of Representatives Congress, 2018).

The present regulatory framework demands more information about chemicals of high concern, which in turn affect how they are handled. In Europe, water supply and sanitation is receiving €2 billion a year in investment on average, and at the same time new pollutants are emerging that have a hazardous potential at low concentrations (Clouzot et al., 2013; Directorate-General for Environment, 2022). And more efforts are expected to come up in the near future. There is a new revision of the UWWTD in the works to aim at reducing even more the levels of urban pollution, with special emphasis on pharmaceuticals and personal care products. In the face of this dynamic scenario, it is of utmost importance that researchers, engineers, modelers and decision makers stay up to date with the social and environmental needs in order to tackle these issues head on (Clouzot et al., 2013; Directorate-General for Environment, 2022).

2.5 Computational tools for wastewater treatment systems

The development of computational tools during the past century, together with increasingly stringent demands for nutrient removal at WWTPs in the 80's pushed for improvements in existing treatment systems that were backed by computer-based simulation models. Like in present times, they allowed for optimization in the design and operation of plants, for

better understanding of experimental work and to support the role of operators (Dupont and Sinkjær, 1994).

As quoted by Dupont and Sinkjær (1994), WWTP optimization with computational tools normally requires choosing an adequate model, characterising the influent wastewater and the treatment processes considered, calibrating and validating the model, optimizing what is intended to be improved, implementing the results, and subsequently monitoring the processes' performance in light of the new findings.

There have been several models and iterations of models being developed over the years, most notably the Activated Sludge Model (ASM), which has gone through many versions and modifications and still is being frequently used (Gujer et al., 1999; Henze et al., 2006; Iacopozzi et al., 2007; Polesel et al., 2016; Zhou et al., 2013). On the other hand, the Integrated Urban Wastewater and Stormwater system (IUWS) model is an example of a larger scale model that includes different systems, namely drainage networks, stormwater, wastewater and sludge treatment, and water recipients. Its use has allowed, among other things, for the modelling of micropollutant fluxes (Vezzaro et al., 2014).

In present times, several software tools have been developed by engineering and consulting companies to provide for wastewater treatment services, such as BioWin, STOAT, Sumo© and WEST® (*BioWin*, 2023; *STOAT*, 2023; *Sumo*, 2023; *WEST*, 2023)(DHI A/S, 2023; Dynamita Process Modeling, 2023; EnviroSim, 2023; WRc, 2023).

3 Ozonation

Ozone is among the strongest oxidizers applicable to the treatment of water due to its high reactivity. It has been historically used for disinfection purposes for the most part, but also as an alternative for the removal of pollutants such as metals, pharmaceuticals, microorganisms, and dissolved organic matter either as a stand-alone application or in combination with other technologies (Audenaert et al., 2010; Camel and Bermond, 1998; Elovitz and von Gunten, 1999; Huber et al., 2005; Juárez, 2021; Rodríguez et al., 2008; Tuhkanen and Mariñosa, 2010).

3.1 The ozonation process in wastewater treatment

The advanced oxidation processes (AOPs) that take place with the degradation or transformation of compounds by reactive chemical species, in addition to disinfection, makes ozonation an appealing and economically feasible alternative for the treatment of micropollutants in wastewater and water reuse efforts, specially if implemented as an advanced treatment step (Audenaert et al., 2010; Bourgin et al., 2018; Grandclément et al., 2017; Huber et al., 2005; Rodríguez et al., 2008; Shestakova et al., 2020; von Sonntag and von Gunten, 2012).

3.1.1 Ozone decomposition and other reactions in the water matrix

The ozone molecule (O_3) reacts with other species by oxidizing certain moieties, that is, parts of other molecules that are common within groups of compounds. Ozone is a selective oxidant that only interacts with amino groups, activated aromatic systems and a specific type of hydrocarbons called olefins (Ekblad et al., 2021; McNaught and Wilkinson, 2019; Rokhina and Virkutyte, 2010; von Sonntag and von Gunten, 2012). However, ozone action is complemented by a second phenomenon centered around hydroxyl radicals (OH·). These are formed in side reactions from the decomposition of ozone in water (Juárez, 2021; Rodríguez et al., 2008; von Sonntag and von Gunten, 2012).

Hydroxyl radicals are also highly reactive, but in contrast to ozone's selective quality, they are non-selective and can target the compounds that show resistance to ozone (Elovitz and von Gunten, 1999; Minakata et al., 2009; Rokhina and Virkutyte, 2010; Virkutyte and Rokhina, 2010). Their formation is favored with the presence of hydrogen peroxide (H_2O_2) and in environments with high pH. Individually, the oxidation potential of both O_3 and OH· is notoriously higher than other oxidizing agents, hence the ozonation process profits from both of their oxidizing effects for the removal of micropollutants (Lee et al., 2014; Luo et al., 2014; Juárez, 2021; Rodríguez et al., 2008; von Sonntag and von Gunten, 2012).

Ozone is generated by exciting oxygen molecules (O_2) with the use of an energy source. The oxygen molecules are brought to a higher energy state and then split into two oxygen radicals (O·). These radicals are then free to bind to another O_2 molecule with the aid of a collision partner (A) to form O_3, as displayed in the following reactions (Kogelschatz, 2003; von Sonntag and von Gunten, 2012):

$$O_2 + \overline{e} \longrightarrow 2O\cdot \tag{3.1}$$
$$O_2 + O\cdot + A \longrightarrow O_3 + A \tag{3.2}$$

While reaction 3.2 is taking place, other instances of O· consumption compete with the ozone formation. This competition becomes accentuated if air is fed as the gas source, since nitrogen species come into play as well and make the reaction system more complex, as reviewed by Kogelschatz (2003).

On the other hand, once ozone is formed and exposed to a water matrix for treatment, it begins its decomposition in the presence of electron-rich moities of dissolved organic matter (DOM) and pollutants by means of a chain reaction. As a result, OH· radicals emerge and together with O_3 they react with DOM and other oxidizable compounds as new species get formed and subsequently consumed in the reaction system. Thus, reactions take place that involve the water matrix (M) - which includes DOM and other compounds - and the micropollutants (MP) competing for ozone and the hydroxyl radicals, as shown below (Juárez, 2021; von Sonntag and von Gunten, 2012):

$$M + O_3 + OH\cdot \longrightarrow M_{\text{ox}} \tag{3.3}$$
$$MP + O_3 + OH\cdot \longrightarrow MP_{\text{ox}} \tag{3.4}$$

The reactivity of a micropollutant is a crucial factor that characterises how rapidly and efficiently it is eliminated by ozonation, and those with high reactivity with ozone get quickly oxidized (von Sonntag and von Gunten, 2012). In parallel, a fraction of the hydroxyl radicals are usually scavenged (i.e.: consumed by interacting with other substances) by other compounds present in the water matrix, but they contribute to the removal of micropollutants too. In other words, the presence of dissolved organic and inorganic matter - and other species - affect ozone decomposition dynamics. More precisely, it impacts the amount of ozone needed for treatment, the rate at which OH· forms and depletes and the rate at which O_3 is decomposed. This translates into ozone decreasing more rapidly in wastewater than in higher quality streams (Buffle et al., 2006b; Juárez et al., 2021; McNaught and Wilkinson, 2019; von Sonntag and von Gunten, 2012; Zucker et al., 2015). Furthermore, DOM's characterisation varies among different streams depending on their origin and affects the overall water matrix, which is also influenced by the vast diversity of micropollutants that could be present in the mix. Thus, the nearly infinite combinations of compounds that conform the water matrix, and the abundance of the ozone molecule itself, have an additional and crucial impact on the effectiveness of the ozonation process (Lee et al., 2013; Rodríguez et al., 2008; von Sonntag and von Gunten, 2012).

3.1.2 Design and operational aspects

To cope with the different characteristics of the effluents being treated with ozonation, ozone doses are commonly normalized with respect to the amount of dissolved organic carbon (DOC) contained in them. This term can be likened to DOM, and both are treated as equivalent in the present study (Hopkinson and Vallino, 2005). Normalized ozone dose is referred

to as 'specific ozone dose' and expressed in grams of ozone per grams of DOC, although some other parameters are also known to be used for standardizing purposes (Altmann et al., 2014; Ekblad et al., 2021; Juárez et al., 2021; Kharel et al., 2020; Lee et al., 2013, 2014). Despite this convention, and because of the sensitivity of ozonation to the reactivity of each micropollutant, the removal performance is specific to each substance, so the quality of a treated water sample would show different rates of removal for different micropollutants at a same ozone dose (Ekblad et al., 2021; Lee et al., 2014).

Aside from the specific dosing, other design and operational parameters can be tuned in order to modify the ozonation performance. For instance, the temperature, the ozone dispersion method, the hydraulic retention time (HRT), previous coagulant addition and as previously mentioned, the pH and direct application of H_2O_2 could potentially be used to impact the outcome of the treatment, some with higher impact than others (Ekblad et al., 2021; Hansen et al., 2016; Juárez, 2021; Lee et al., 2013, 2014)(Ekblad et al., 2021; Hansen et al., 2016; Juárez et al., 2021a, Lee et al., 2013; Lee et al., 2014). To exemplify, the solubility of ozone in water decreases as temperature rises, and its concentration is more stable at lower pH values, decreasing faster in neutral or alkaline environments. Whereas with regards to HRT, higher periods maximize the oxidation of micropollutants but also increase the chances of causing some of the ozone to remain as a residual in the ozonation unit (von Sonntag and von Gunten, 2012).

Moreover, energy consumption from the application of ozone into the wastewater stream can be optimized in order to make the process economically or energetically feasible. When the ozone molecules are excited (i.e.: subjected to high voltage) they may or may not be exposed to oxygen, since the solubility of the former is much higher than that of the latter, so its presence is not a detriment to the process. Also, the discharge method may vary as it can be infused into the water through bubbles, static mixers or Venturi injectors. Thus, some decisions need to be made on this topic (Ekblad et al., 2021; Liu et al., 2020; Juárez, 2021; von Sonntag and von Gunten, 2012).

3.1.3 Additional considerations

Aside from the aforementioned relevance of the different phenomena and parameters involved in the ozonation process, there is even more research to perform to continue refining the knowledge of this treatment alternative. Currently, the effect of particulate matter is still to be thoroughly considered as most times it is left out of calculations for ozone dosing (Juárez, 2021; Juárez et al., 2021; Zucker et al., 2015).

Even more so, metabolites, which result from a living being's metabolism modifying micropollutants (e.g.: pharmaceuticals), have to be considered when dealing with wastewater treatment (Kharel et al., 2021; McNaught and Wilkinson, 2019). Lastly, the appearance of transformation products and oxidation by-products downstream of an ozonation treatment unit is of utmost importance and necessary to consider as well. Some additional treatment steps could be added to improve the system's performance, like biological post-filtration with sand or activated carbon filter (Audenaert et al., 2010; Clouzot et al., 2013; Esplugas et al., 2007; Hollender et al., 2009; Kharel et al., 2021; Luo et al., 2014).

All things considered, there is still substantial research to be made to better understand the dynamics involved in the application of ozonation for the removal of micropollutants in

wastewater (Kharel et al., 2021).

3.2 Computer modelling of ozonation

Computer models are an essential tool for the design, optimization and control of water treatment systems and the overall engineering of the processes involved (Audenaert et al., 2013). When dealing with the treatment of micropollutants, models help decision-makers and engineers better comprehend the fate of these substances and their trace constituents (i.e. transformation products), how to optimize their removal and potentially reduce the impact they may generate on the environment (Bezbarua and Reckhow, 2004; Clouzot et al., 2013; Stadler et al., 2012). In the case of ozonation procedures, they contribute to set adequate ozone doses for a given treatment process (Rodríguez et al., 2008).

Nervertheless, the large number of micropollutants pose difficulties to modellers not only due to their diversity, but also because of the constant updates on MP behaviour and dynamics, treatment technologies and regulatory targets (Clouzot et al., 2013). Clouzot et al. (2013) propose that MPs should be addressed by groups based on common characteristics between them instead of individually, and search for ways to mathematically represent their transformations in various treatment contexts, such as the effects of activated sludge, to better control that toxicity values are never met in the outflows of wastewater treatment plants.

Ozonation modelling essentially replicates the reduction of one or several pollutants (it may include other parameters as well, such as COD) as a response to ozone supply. It relies upon process conditions and kinetic parameters (Audenaert et al., 2010; Rodríguez et al., 2008)(Audenaert et al., 2010; Rodríguez et al., 2008), and has been mostly tackled with mechanistic, empirical and semi-empirical approaches (Audenaert et al., 2010; Westerhoff et al., 1997).

- **Mechanistic approaches:** the extent of their usefulness in the engineering field depends on the knowledge of kinetic constants and stoichiometry of the ozone reactions, thus they are affected by the complexity of addressing said parameters in wildly different contexts (Audenaert et al., 2010, 2013; Juárez et al., 2021; Lee et al., 2014; Liu et al., 2020; Rodríguez et al., 2008).

- **Empirical approaches:** based mostly on measured and experimental data, they have been developed as a predicting tool for the removal of micropollutants with ozonation. They may be less flexible depending on how tailored they are conceived from the empirical data gathered (Ekblad et al., 2021; Juárez et al., 2021; Westerhoff et al., 1997).

- **Semi-empirical approaches:** Usually stem from recalibration of mechanistic parameters or modifications not rooted on chemical or kinetic principles or phenomena, in order to fill in for lacking knowledge that would otherwise hinder a mechanistic model (Audenaert et al., 2013; Elovitz and von Gunten, 1999).

A semi-empirical model based on chemical kinetics and highlited in this research has been used in several previous studies. It is based on micropollutant removal by the combined

effect of ozone and the hydroxyl radical, and can be applied if the O_3 and OH· concentrations and rate constants are known (Audenaert et al., 2013; Buffle et al., 2006a; Elovitz and von Gunten, 1999; Lee et al., 2013, 2014; Rodríguez et al., 2008; von Sonntag and von Gunten, 2012; Zimmermann et al., 2011). Elovitz and von Gunten (1999) presented equation 3.5, which describes the decrease of a given micropollutant's concentration over time:

$$-\frac{d[MPo]}{dt} = k_{O_3} \times [O_3] \times [MPo] + k_{OH\cdot} \times [OH\cdot] \times [MPo] \tag{3.5}$$

The coefficients k_{O_3} and $k_{OH\cdot}$ are second-order rate constants associated to the respective chemical reactions between MPo and O_3, and MPo with OH· (Elovitz and von Gunten, 1999; Lee and von Gunten, 2010; Lee et al., 2013, 2014).

The use of this equation and a normalized ozone dosage (i.e. in g O_3/g DOC) allows for a fairly versatile removal model, although continuous and further research should help increase its reliability (Lee et al., 2013; Liu et al., 2020).

4 Materials and Methods

The process of construction of the model for micropollutant removal through ozonation involves the use of a commercial software and data from academic sources to build and calibrate its performance. The methodology employed is detailed in the present section.

4.1 The WEST® software

This study uses a sophisticated commercial software called WEST®, a simulation tool for the optimization, operation and automation of treatment plants. It was developed by the consultancy firm DHI A/S as part of the company's software portfolio for hydraulic and hydrological engineering to perform dynamic modeling and simulation of water quality systems. It offers great adaptability to custom scenarios, with a variety of useful tools in a user-friendly interface and built-in advanced experiments that allow for model calibration, scenario analyses, uncertainty analyses, local and global analyses, among others (DHI A/S, 2022; *WEST Getting Started*, 2022; *WEST Models Guide*, 2023).

The simulations carried out in this research use the variable-coefficient ODE (VODE) solver (Brown et al., 1989) with a variable step size, an absolute tolerance of 1×10^{-20} and a relative tolerance of 1×10^{-5}.

4.2 The ozonation model

The ozonation model proposed in this study solves a continuity equation that describes the change in mass over time for all the species involved, and can be divided into two parts: transport and conversion. Given an ozonation chamber with fixed volume in which the ozonation process takes place, the rate of change of the mass of each compound is described by the equation shown below.

$$\frac{dMass}{dt} = Transport + Conversion \times Volume \tag{4.1}$$

The $Transport$ element from equation 4.1 is simply the difference between the mass that enters the volume and the mass that leaves it over time, while $Conversion$ stands for the change in concentration of each compound over time. The latter being multiplied by the fixed volume of the chamber, equation 4.1's units are mass over time.

The solution to the $Conversion$ part of the equation is the core of the model, and is conformed of essentially two parts, namely an ozone decomposition model and a micropollutant removal model, both based on constant rates referred as kinetic coefficients. The ozonation model is integrated and stored in an 'Ozonation block' within the software.

4.2.1 Ozone decomposition

As mentioned earlier in this study, the ozone molecule decomposes once in contact with an aqueous medium, and a set of chain reactions produces various radical oxidizing species. Said

equations can and have been modelled in order to describe the varying concentrations of O_3 and the radicals over time. A mass balance of ozone accounting for its solubility in water is also often included, and these type of models for ozone decomposition have been available in literature for many years now (Bezbarua and Reckhow, 2004; Bühler et al., 1984; Rodríguez et al., 2008; Staehelin et al., 1984).

The SHB model

The model selected for this work is a modification to the SHB model, which has shown good performance and accurate component reactions and rates from previous evaluations (Bezbarua and Reckhow, 2004). This original model, named after J. Staehelin, J. Hoigné and R.E. Bülher, was developed through a study on ozone decomposition by pulse radiolysis and published in two parts in 1984. In their work, they propose a chain mechanism with initiation, promotion and termination steps as the best reaction model to describe ozone decomposition in pure water (Bezbarua and Reckhow, 2004; Bühler et al., 1984; Staehelin et al., 1984).

Audenaert et al. (2013) version

The version used is the one proposed by Audenaert et al. (2013), which also includes the effect of DOM in the matrix. DOM is divided into four groups with similar properties: DOM_1, DOM_2, DOM_3 and DOM_4. Groups 1 and 2 can be represented by compounds to the likes of formic acid and tertiary butanol, respectively, and only react with the HO· radical, while tertiary amines and olefins would be representative of groups 3 and 4, which react with both O_3 and HO· (Audenaert et al., 2013; Westerhoff et al., 1997).

The complete model portrayed in Audenaert et al. (2013) work consists of a series of 33 second order differential equations and involves the use of 29 kinetic coefficients. However, after a sensitivity analysis it was concluded that just a small fraction of the original composition had an effective impact on the modelling of O_3 and OH· concentrations (Audenaert et al., 2013). This simplified model is represented by the Gujer Matrix shown in Table 4.1. Such a notation serves as a means of representing a system of ordinary differential equations (ODEs) in a simplified and intelligible manner (Ibid.). The table contains the model's reactions, plus a few additions described in the following sections. In this matrix, each column accounts for a component present in the water, and each row shows a reaction taking place. The stoichiometric factors filling the matrix are multipliers of the reaction rates, so the change in concentration over time for each component can be written as the sum of the product between all the stoichiometric factors and the corresponding rates, within the respective column. Equation 4.2 shows how the change over time in concentration C_j of a compound j can be obtained from a Gujer matrix, where f_{ij} is the stoichiometric factor of reaction i towards compound j, R_i is the product of reaction i's reactants' concentrations, and k_i is the rate constant for reaction i.

$$\frac{dC_j}{dt} = \sum_{i=1}^{reactions} f_{ij} \times k_i \times R_i \tag{4.2}$$

4.2.2 Micropollutant removal

Equation 3.5 reviewed in section 3.2 can be easily implemented into the ozone decomposition model mentioned earlier. Thus, an additional pair of differential equations with its corresponding rate constants k_{O_3} and $k_{OH\cdot}$ can describe the concentration of a specific micropollutant in the wastewater stream. The complete set of equations is presented in the Gujer matrix of Table 4.1, with the last two rows accounting for micropollutant removal.

Effect of suspended solids

Two experimental studies reviewed for this research have demonstrated a scavenging effect of suspended solids (SS) in the overall removal performance of ozonation treatment (Ekblad et al., 2021; Juárez et al., 2021), which motivate the inclusion of two more reactions to the Gujer matrix (see Table 4.1). These attempt to simulate the scavenging of O_3 and of OH· by total suspended solids (TSS). They are assigned a kinetic coefficient each and are also subjected to calibration.

Table 4.1: Gujer matrix used to model ozone decomposition and micropollutant removal (Audenaert et al., 2013; Elovitz and von Gunten, 1999).

Reactions	CO_2	$CO_3^{-}\cdot$	H_2O_2	H^+	HCO_3^-	$HCO_3\cdot$	HO^-	$HO\cdot$	HO_2^-	$HO_2\cdot$	Reaction rates
Chain initiation											
$O_3 + HO^- \longrightarrow HO_2^- + O_2$							-1		1		$k_1 \times [O_3] \times [HO^-]$
$O_3 + HO_2^- \longrightarrow HO_2\cdot + O_3^-\cdot$									-1	1	$k_2 \times [O_3] \times [HO_2^-]$
Chain propagation											
$O_3 + HO\cdot \longrightarrow HO_2\cdot + O_2$								-1		1	$k_9 \times [O_3] \times [HO\cdot]$
$H_2O_2 \longrightarrow HO_2^- + H^+$			-1	1					1		$k_{11} \times [H_2O_2]$
$HO_2^- + H^+ \longrightarrow H_2O_2$			1	-1					-1		$k_{12} \times [HO_2^-] \times [H^+]$
Carbonate reaction											
$HO\cdot + HCO_3^- \longrightarrow HCO_3\cdot + HO^-$					-1	1	1	-1			$k_{17} \times [HO\cdot] \times [HCO_3^-]$
DOM reactions											
$CO_3^-\cdot + HO\cdot \longrightarrow CO_2 + HO_2^-$	1	-1						-1	1		$k_{26} \times [CO_3^-\cdot] \times [HO\cdot]$
$HO\cdot + DOM_1 \longrightarrow$ products								-1			$k_{28} \times [HO\cdot] \times [DOM_1]$
$HO\cdot + DOM_2 \longrightarrow$ products								-1			$k_{28} \times [HO\cdot] \times [DOM_2]$
$HO\cdot + DOM_3 \longrightarrow$ products								-1			$k_{28} \times [HO\cdot] \times [DOM_3]$
$HO\cdot + DOM_4 \longrightarrow$ products								-1			$k_{28} \times [HO\cdot] \times [DOM_4]$
$O_3 + DOM_3 \longrightarrow$ products											$k_{29} \times [O_3] \times [DOM_3]$
$O_3 + DOM_4 \longrightarrow$ products											$k_{29} \times [O_3] \times [DOM_4]$
Mass transfer											$k_La \times ([O_3^*] - [O_3])$
Effect of TSS											
TSS scavenging of O_3											$k_{TSS\text{-}O_3} \times [O_3] \times [TSS]$
TSS scavenging of HO·								-1			$k_{TSS\text{-}OH\cdot} \times [HO\cdot] \times [TSS]$
Micropollutant reactions											
$O_3 + MPo \longrightarrow$ products											$k_{O_3} \times [O_3] \times [MPo]$
$HO\cdot + MPo \longrightarrow$ products								-1			$k_{OH\cdot} \times [HO\cdot] \times [MPo]$

Table 4.1: Gujer matrix used to model ozone decomposition and micropollutant removal (Audenaert et al., 2013; Elovitz and von Gunten, 1999) (Continued).

Reactions	O_2	$O_2^{-}\cdot$	O_3	$O_3^{-}\cdot$	DOM_1	DOM_2	DOM_3	DOM_4	TSS	MP	Reaction rates
Chain initiation											
$O_3 + HO^- \longrightarrow HO_2^- + O_2$	1		-1								$k_1 \times [O_3] \times [HO^-]$
$O_3 + HO_2^- \longrightarrow HO_2\cdot + O_3^-\cdot$			-1	1							$k_2 \times [O_3] \times [HO_2^-]$
Chain propagation											
$O_3 + HO\cdot \longrightarrow HO_2\cdot + O_2$	1		-1								$k_9 \times [O_3] \times [HO\cdot]$
$H_2O_2 \longrightarrow HO_2^- + H^+$											$k_{11} \times [H_2O_2]$
$HO_2^- + H^+ \longrightarrow H_2O_2$											$k_{12} \times [HO_2^-] \times [H^+]$
Carbonate reaction											
$HO\cdot + HCO_3^- \longrightarrow HCO_3\cdot + HO^-$											$k_{17} \times [HO\cdot] \times [HCO_3^-]$
DOM reactions											
$CO_3^-\cdot + HO\cdot \longrightarrow CO_2 + HO_2^-$											$k_{26} \times [CO_3^-\cdot] \times [HO\cdot]$
$HO\cdot + DOM_1 \longrightarrow$ products		1			-1						$k_{28} \times [HO\cdot] \times [DOM_1]$
$HO\cdot + DOM_2 \longrightarrow$ products						-1					$k_{28} \times [HO\cdot] \times [DOM_2]$
$HO\cdot + DOM_3 \longrightarrow$ products							-1				$k_{28} \times [HO\cdot] \times [DOM_3]$
$HO\cdot + DOM_4 \longrightarrow$ products								-1			$k_{28} \times [HO\cdot] \times [DOM_4]$
$O_3 + DOM_3 \longrightarrow$ products			-1	1			-1				$k_{29} \times [O_3] \times [DOM_3]$
$O_3 + DOM_4 \longrightarrow$ products			-1					-1			$k_{29} \times [O_3] \times [DOM_4]$
Mass transfer			1								$k_La \times ([O_3^*] - [O_3])$
Effect of TSS											
TSS scavenging of O_3			-1						-1		$k_{TSS\text{-}O_3} \times [O_3] \times [TSS]$
TSS scavenging of $HO\cdot$									-1		$k_{TSS\text{-}OH\cdot} \times [HO\cdot] \times [TSS]$
Micropollutant reactions											
$O_3 + MPo \longrightarrow$ products			-1							-1	$k_{O_3} \times [O_3] \times [MPo]$
$HO\cdot + MPo \longrightarrow$ products										-1	$k_{OH\cdot} \times [HO\cdot] \times [MPo]$

Sample of micropollutants

Among many criteria that could have been used for selecting a handful of micropollutants to test in this study, nine micropollutants were chosen which where most frequently found in the references gathered for experimental data. The sample consists of Benzotriazole, Carbamazepine, Diclofenac, Gabapentin, Metoprolol, Oxazepam, Sulfamethoxazole - included in the latest watch list added for monitoring substances accross the European Union (Commission Implementing Decision (EU) 2022/1307, 2022), Valsartan and Venlafaxine. Table 4.2 lists their molar masses (Kim et al., 2023) and the corresponding values for k_{O_3} and $k_{OH\cdot}$.

4.2.3 Assumptions on compound fractionation

In order to disaggregate commonly used influent species for wastewater characterization, three main assumptions must be considered to 'translate' them into the compounds that form part of the model, listed across the columns in Table 4.1. This section of the model is all stored in a 'Transformation block' and made available for the integration of the 'Ozonation block' to any WWTP model in WEST®.

Table 4.2: Micropollutant sample used in this study. Values for k_{O_3} and $k_{OH\cdot}$ are obtained from Lee et al. (2013), (Lee et al., 2014) and (Liu et al., 2020) either as averages or stand-alone values.

Micropollutant	Molar mass [gr/mole]	k_{O_3} [M^{-1} d^{-1}]	$k_{OH\cdot}$ [M^{-1} d^{-1}]
Benzotriazole[a]	119.12	2.1×10^7	6.6×10^{14}
Carbamazepine[b]	236.27	2.6×10^{10}	7.6×10^{14}
Diclofenac[c]	296.15	8.6×10^{10}	6.5×10^{14}
Gabapentin[a]	171.24	1.9×10^7	4.8×10^{14}
Metoprolol[a]	267.36	1.7×10^8	6.3×10^{14}
Oxazepam[a]	286.71	8.6×10^4	7.9×10^{14}
Sulfamethoxazole[c]	253.28	4.8×10^{10}	6.0×10^{14}
Valsartan[a]	435.52	3.3×10^6	8.6×10^{15}
Venlafaxine[a]	277.40	7.3×10^8	8.6×10^{15}

[a] From Lee et al. (2014).
[b] Average from Lee et al. (2013), (Lee et al., 2014) and (Liu et al., 2020).
[c] Average from Lee et al. (2013) and (Lee et al., 2014).

Ozone decomposition species

The initial conditions for the ozone decomposition species CO_2, $CO_3^{-}\cdot$, H_2O_2, H^+, HCO_3^-, $HCO_3\cdot$, $HO\cdot$, HO_2^-, HO^-, $HO_2\cdot$, $O_2^{-}\cdot$, O_3 and $O_3^{-}\cdot$ are taken from Audenaert et al. (2013), which in turn were obtained from Bezbarua and Reckhow's work in 2004. It should be noted that O_3 concentration is initially 0 gr/m^3 but is later modified by ozone dosage during simulations. In addition, O_2 initial concentration is also assumed to be 0 gr/m^3.

COD to DOC

The amount of organic matter, measured in chemical oxygen demand (COD), is assumed to be divided into particulate and soluble fractions. The soluble COD is then fractionated again into fermentation products, readily biodegradable organic matter and inert soluble matter (*WEST Models Guide*, 2023).

The main assumptions taken are how these soluble COD groups are associated with the DOM groups. According to Phan et al. (2022), the overall quantity of COD divided by DOC - that is, the COD/DOC ratio - represents on average the degree of oxidation of organic compounds. For this study, a ratio of 3 is picked as representative of wastewater treatment plant effluents (Nöthe et al., 2009). The latter means that total DOM (or DOC) is estimated as one third of the total soluble COD. Lastly, it is assumed that fermentation products compose DOM_1, while readily biodegradable organic matter, on the other hand, is assigned to DOM_2. The inert soluble matter is equally distributed to DOM_3 and DOM_4. The concentration of each of these DOM groups is thus calculated as a third part of the concentration of the compounds respectively associated with each. A diagram of this fractionation scheme better explains it, and can be appreciated in Figure 4.1. Table 4.3 lists the values of each fraction shown in the diagram.

The value of f_TSS_COD is estimated based on the assumption that there are few sludge

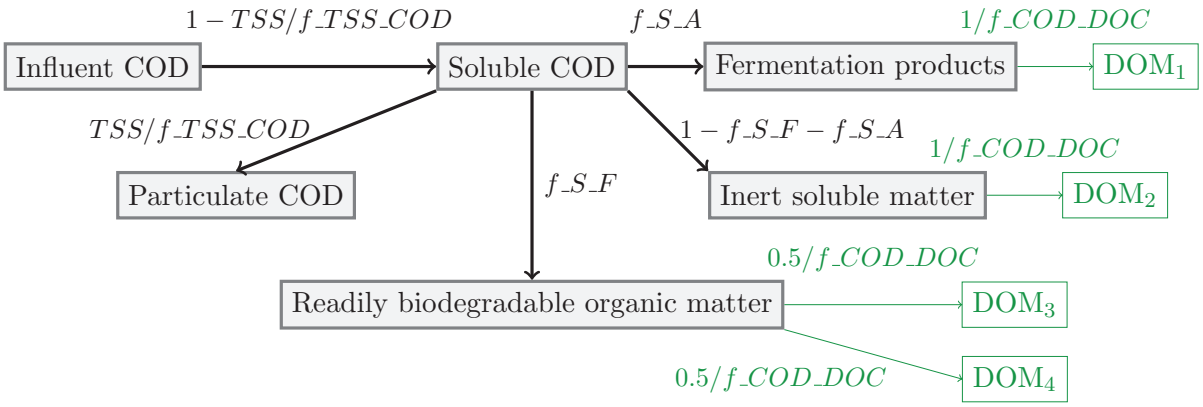

Figure 4.1: Fractionation of chemical oxygen demand (COD) into dissolved organic matter (DOM).

Table 4.3: Values for fractions used in COD to DOC fractionation (Phan et al., 2022; WEST, 2023).

Fraction	Value
f_TSS_COD	0.95
f_S_A	0.25
f_S_F	0.375
f_COD_DOC	3

residues after secondary treatment in comparison to a generally conventional influent into a wastewater treatment plant. The other fractions f_S_A and f_S_F are taken from established values used within WEST® applications (*WEST*, 2023).

Micropollutants' conjugate, particulate and soluble fractions

A major assumption agreed upon during the elaboration of the present research, is the fractionation of micropollutants into three species: soluble, particulate and conjugate. The first two, as their names suggest, reffer to the amount of a compound to dissolve in the aqueous media and the amount that precipitates. The conjugate fraction refers to a micropollutant going through human metabolism, where a hydrophilic moiety is added to its composition to facilitate excretion (Delli Compagni et al., 2020; Polesel et al., 2016; Testa et al., 2012).

Thus, the scope of the present model only considers the soluble fraction of the micropollutants analyzed, and does not consider the phenomena involving the metabolized conjugates or the precipitates (see Figure 4.2). To reasonably calculate the soluble fractions (f_S), an expression that employs their respective sorption coefficients (K_d) and the total amount of suspended solids (TSS) is used. This is exemplified in Equation 4.3, where the sorption coefficient, also known as solid-water partition coefficient, is commonly used to account for sorption and desorption dynamics of compounds in the presence of suspended solids (Delli Compagni

et al., 2020; Joss et al., 2005, 2006).

$$f\_S = \frac{1}{1 + K_{\mathrm{d}} \times TSS} \tag{4.3}$$

Table 4.4 shows the values for f_conj and K_d used for the estimation of the soluble concentration of micropollutants in the model. The values are based off previous works with applied fractionations (Delli Compagni et al., 2020; Joss et al., 2005, 2006; Mazioti et al., 2015; Polesel et al., 2016).

Table 4.4: Values for fractions used for micropollutant fractionation, based off previous exemplary works(Delli Compagni et al., 2020; Joss et al., 2005, 2006; Mazioti et al., 2015; Polesel et al., 2016).

Micropollutant	f_conj	K_d
Benzotriazole	0	0.22
Carbamazepine	0.92	0.1
Diclofenac	0.76	0.1
Gabapentin	0	0.1
Metoprolol	0.1	0.1
Oxazepam	0.1	0.1
Sulfamethoxazole	0.8	0.1
Valsartan	0	0.1
Venlafaxine	0	0.1

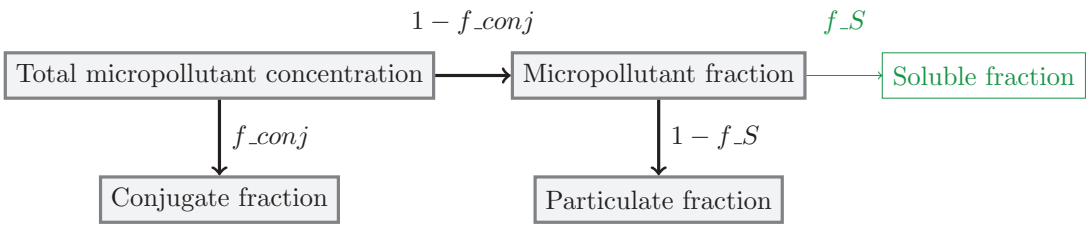

Figure 4.2: Fractionation of a Micropollutant.

4.2.4 Other assumptions and limitations

A few other assumptions and limitations worth mentioning are the following:

- Any form of data collection relies solely on literature review instead of laboratory experiences, and in turn is subjected to each sources' own boundaries and limitations.
- Modelling results are subjected to both the computational capacity and software limitations inherent to the tools utilized.

- Due to time constrains it was preferred to work with micropollutants that are most frequently mentioned in the literature instead of working with representative groups of micropollutants.
- The testing of the model in combination with an existing WWTP configuration is left out of scope.
- No fractionation and transformation products from the ozonation process are taken into account.
- Since for the time being the model is thought for advanced treatment, sufficiently low concentrations of nitrogen species are expected so that their effect on ozone decomposition and micropollutant removal is negligible.
- The kinetic coefficients shown in Table 4.2 were obtained at a pH of 7 and some of them change in more basic environments, but for the purpose of this research they were assumed constant.
- The effects of pressure and temperature are not considered.

4.3 Calibration procedure

The calibration procedure focuses solely on the values of the kinetic coefficients for O_3 and OH· exposures in the equations for micropollutants' reactions (k_{O_3} and $k_{OH\cdot}$, respectively), and for the scavenging effect of TSS on O_3 and OH· ($k_{TSS\text{-}O_3}$ and $k_{TSS\text{-}OH\cdot}$, respectively). This means that only the reactions under the rows titled "Effect of TSS" and "Micropollutant reactions" in Table 4.1 are affected by the calibration.

There are two main sources of experimental data used for the calibration of the model, Juárez et al. (2021) that employed laboratory-scale procedures to measure micropollutant removal in the presence of suspended solids (SS), and Ekblad et al. (2021) that operated an ozonation pilot plant and measured its removal performance under different variations as well. No data is used to evaluate the performance of the ozonation model in combination with another treatment configuration. Consequently, the sources previously mentioned are replicated using the ozonation model where only the MP removal from ozonation itself is taken into account.

The calibration procedure is performed based on ozone dosage and percentage of removal of soluble micropollutants in the wastewater stream.

4.3.1 Batch experimentation

The batch experiments performed by Juárez et al. (2021) consisted of different wastewater samples from six wastewater treatment plants (WWTPs) kept in bottles for at least an hour. Micropollutants were artificially added to the samples to match a desired initial concentration, and then each sample was ozonated by adding an ozone stock solution. Later, different concentrations of SS were also added to samples from the Lundåkra WWTP in Landskrona, Sweden. The SS was added as a suspension of thickened sludge, and several ozone-response curves were obtained from all cases evaluated (Juárez et al., 2021). For the calibration

process, only the batch samples from Lundåkra for various SS concentrations are considered. The model layout consists of an isolated 'Ozonation block' represented by an ozonation chamber in the software, as protrayed in Figure 4.3.

Figure 4.3: Ozonation block represented by an ozonation chamber in WEST®.

The characterization of the different wastewater samples for each degree of SS presence are shown in the table below.

Table 4.5: Wastewater effluent data from batch experiments. Values are given for parameters and compounds under each of the effluents from 0 to 200 g SS/m^3 (Juárez et al., 2021).

	0	10	25	50	75	100	200
COD_{Cr}[a][gr/m^3]	17.2	28.7	46.4	77	99	125.4	214.6
SS [gr/m^3]	0	12	26	48	80	102	196
pH [-]	8	7.8	7.8	7.8	7.8	7.8	7.8
Benzotriazole [μg/L]	1.905	1.833	1.724	1.743	1.844	2.071	1.874
Carbamazepine [μg/L]	2.414	-	-	2.531	2.695	3.007	2.917
Diclofenac [μg/L]	2.884	2.717	2.792	2.651	2.775	2.684	2.580
Gabapentin [μg/L]	5.211	-	5.982	8.481	8.906	10.123	8.744
Metoprolol [μg/L]	4.112	3.877	4.150	3.986	3.934	3.937	3.975
Oxazepam [μg/L]	2.713	2.344	2.330	1.850	1.927	2.097	2.019
Sulfamethoxazole [μg/L]	1.505	1.671	1.465	1.286	1.323	1.373	1.150
Valsartan [μg/L]	3.464	3.352	3.403	3.080	3.192	3.409	3.474
Venlafaxine [μg/L]	2.748	2.923	3.094	2.754	2.773	2.980	2.954

[a] COD measured with the dichromate method (Juárez et al., 2021).

A particular assumption is taken for the calibration using this source. The mass balance equation shown in the Gujer matrix of Table 4.1 is assumed to not contribute to the ozone dynamics in the samples, as the initial ozone doses are considered high enough so that the effect of the mass balance is comparatively negligible.

4.3.2 Ozonation pilot plant

The operation of an ozonation pilot plant performed by Ekblad et al. (2021) was carried out during a period of 7 months. Installed at the Lundåkra WWTP the pilot plant treated wastewater samples extracted both before and after a post-precipitation stage of the treatment plant. Ozonation was achieved with an ozone generator and either a static mixer or

a Venturi injector, and the reaction took place in a pressurized environment with an HRT of 10 minutes. They later proceeded to operate the pilot plant while changing the HRT, the ozone dispersion method and the wastewater temperature, and added precipitation with aluminum chloride to test different treatment scenarios (Ekblad et al., 2021). Only the initial results with the streams after post-precipitation with 10 minutes of HRT are considered for the calibration process. The layout of the model in WEST® is shown in Figure 4.4.

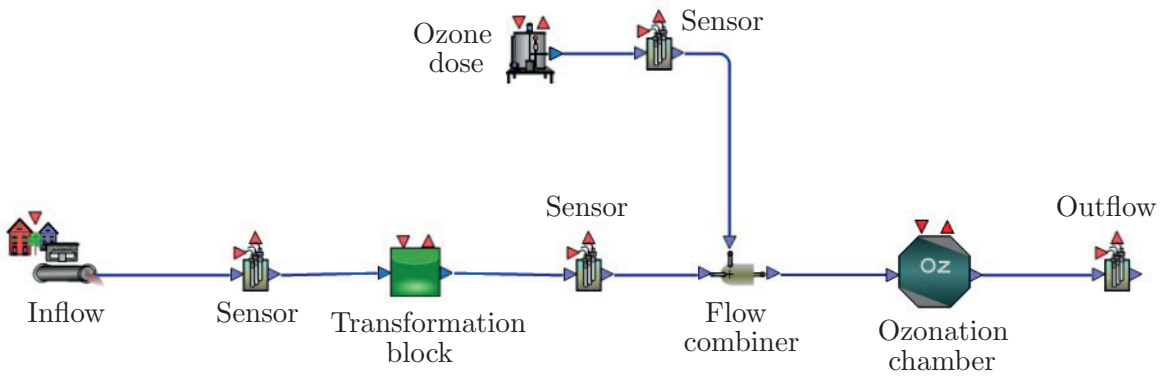

Figure 4.4: Layout of the ozonation treatment model in WEST®.

Table 4.6 lists the characteristics of both wastewater streams before and after post-precipitation.

Table 4.6: Wastewater effluent data from the operation of the pilot plant. Values are given for both before and after post-precipitation (Ekblad et al., 2021).

	Before post-precipitation	After post-precipitation
COD [gr/m^3]	35.1	27.5
DOC [gr C/m^3]	10.6	10.0
SS [gr/m^3]	7.5	1.8
pH [-]	7.6	7.6
Benzotriazole [μg/L]	0.535	
Gabapentin [μg/L]	2.280	
Metoprolol [μg/L]	3.900	
Oxazepam [μg/L]	0.560	
Valsartan [μg/L]	1.350	
Venlafaxine [μg/L]	1.225	

4.3.3 The calibrating sequence

The calibration procedure is separated into three stages. The first two stages use the data from the batch experiments, starting with the calibration of the kinetic coefficients of the

sample of micropollutants, and following with the calibration of the kinetic coefficients associated with the scavenging effect of TSS. The third stage is to calibrate the micropollutants' kinetic coefficients in the context of continuous operation, and thus the model is put to the test in two different modelling scenarios.

The way the coefficients are calibrated is by changing the exponent of a multiplying factor, as expressed by Equation 4.4. The calibrating factor is expressed by x.

$$k_{\text{calibrated}} = k_{\text{original}} \times 10^{x} \tag{4.4}$$

This calibration, as mentioned before, is applied to k_{O_3} and $k_{OH\cdot}$ for each micropollutant, and to $k_{TSS\text{-}O_3}$ and $k_{TSS\text{-}OH\cdot}$ to adjust the ozone-response curves for the removal performance that the model simulates.

4.4 Validation procedure

Validation is performed with the use of Lee et al. research (2014), where laboratory experimentation was carried out to study the removal of micropollutants with varying doses of ozone at two different pH values and with the addition of hydrogen peroxide (H_2O_2). The wastewater sample used was an effluent from a membrane bioreactor (MBR) pilot plant that treated a hospital wastewater in the Swiss city of Baden (Lee et al., 2014). Table 4.7 shown next characterizes the MBR effluent.

Table 4.7: Hospital wastewater effluent after MBR treatment (Lee et al., 2014).

	Value
DOC [gr C/m^3]	5.1
Alkalinity [gr HCO_3^-/m^3]	469.85
pH [-]	7
Benzotriazole [μg/L]	14.30
Carbamazepine [μg/L]	236.27
Diclofenac [μg/L]	1.11
Gabapentin [μg/L]	2.40
Metoprolol [μg/L]	0.29
Oxazepam [μg/L]	0.25
Sulfamethoxazole [μg/L]	1.47
Valsartan [μg/L]	0.18
Venlafaxine [μg/L]	0.19

As in the calibration process, the validation is done by comparing the resulting removal of the soluble fractions of micropollutants with respect to the dose of ozone added to the water sample. Only the results at a pH of 7 and without any addition of H_2O_2 are considered for the validation process.

Additionally, the assumption about the mass balance mentioned in section 4.3.1 is kept for this procedure.

It is also worth mentioning that the simulations in this case are performed with the same VODE solver and absolute tolerance of 1×10^{-20}, but a relative tolerance of 1×10^{-4} to adjust for computational capacity.

4.5 Sensitivity analysis

A brief analysis of sensitivity to certain parameters is considered in this study. There is available data that measured changes in MP removal from differences in pH and addition of H_2O_2 (Lee et al., 2014) and variations of the HRT (Ekblad et al., 2021), albeit not always for all 9 micropollutants. Additional runs are therefore performed to test the behaviour of the model in light of such changes.

5 Results and Discussion

The resulting values for the kinetic coefficients of each micropollutant, together with the values for the coefficients for TSS scavenging are shown in Table 5.1. As previously stated, there are two sets of results, one from calibrating with batch data (Juárez et al., 2021), and one from calibrating with data from an ozonation pilot plant (Ekblad et al., 2021). A common phenomena found during the whole calibrating process, is a low sensitivity of the model to variations of the $k_{OH\cdot}$ coefficient in contrast with k_{O_3}. The model is hence calibrated by only changing the kinetic coefficients associated to O_3 exposure.

As seen in Table 5.1, the multiplying factors for both sets of data are similar, and in some cases the kinetic coefficients change significantly. Oxazepam is the most extreme case, that originally had the lowest coefficients but it is then adjusted to an order of magnitude closer to the other micropollutants' coefficients. Figure 5.1 provides a more clear view of the change that the coefficients undergo after calibration.

Table 5.1: Calibration results from batch data (Juárez et al., 2021) and ozonation pilot plant data (Ekblad et al., 2021). The multiplying factor is written as 10^x, where x is the exponent which value is used for the calibration as shown in the third and fifth columns.

	Original values	Batch data		Pilot plant data	
Micropollutant	k_{O_3} [M^{-1} d^{-1}]	$\times 10^x$	k_{O_3} [M^{-1} d^{-1}]	$\times 10^x$	k_{O_3} [M^{-1} d^{-1}]
Benzotriazole	2.1×10^7	0.90	1.6×10^8	0.42	5.5×10^7
Carbamazepine	2.6×10^{10}	-1.90	3.3×10^8		
Diclofenac	8.6×10^{10}	-2.40	3.4×10^8		
Gabapentin	1.9×10^7	0.30	3.8×10^7	0.42	5.0×10^7
Metoprolol	1.7×10^8	0.10	2.2×10^8	0.15	2.4×10^8
Oxazepam	8.6×10^4	3.25	1.5×10^8	3.00	8.6×10^7
Sulfamethoxazole	4.8×10^{10}	-2.01	4.8×10^8		
Valsartan	3.3×10^6	1.75	1.8×10^8	1.65	1.5×10^8
Venlafaxine	7.3×10^8	-0.70	1.5×10^8	-0.50	2.3×10^8
TSS			2.0×10^3		

After calibrating the different target parameters, simulation results are plotted and contrasted with their respective reference data. The plots, displayed in the following sections, show the micropollutant removal from ozonation measured in percentage, and the ozone dose in grams of ozone per grams of either COD or DOC, depending on the source data.

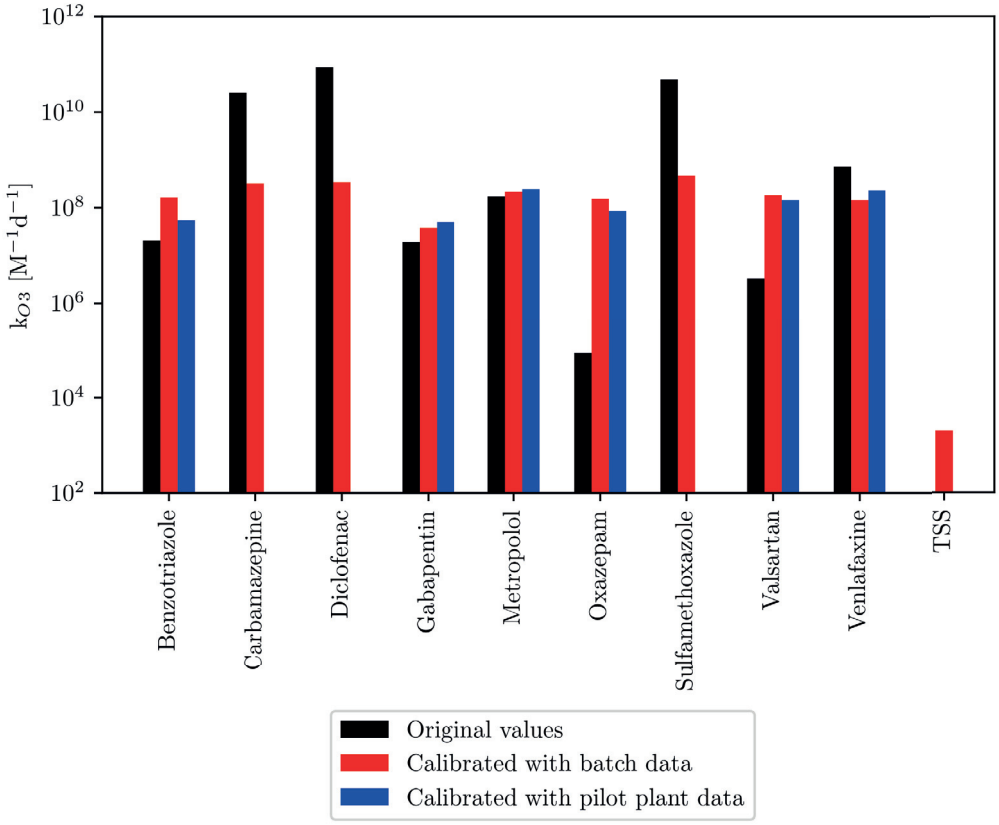

Figure 5.1: Values for k_{O_3} after calibration with batch data in red (Juárez et al., 2021) and ozonation pilot plant data in blue (Ekblad et al., 2021).

5.1 Calibration with batch data

Simulation results are shown in contrast to the data retrieved from the batch experiments performed by Juárez et al. (2021). The wastewater stream characterized in the second column of Table 4.5, with no presence of suspended solids (SS) is taken as input. The ozone dose in this research was administered in g O_3/g COD.

5.1.1 Calibration of kinetic coefficients for micropollutant removal

Figure 5.2 shows the comparison between the simulation and reference data with no TSS.

From the results, it can be appreciated that the model is able to adjust rather satisfactorily for most of the micropolluntants, with a slightly more notorious divergence in the cases of Benzotrizole, Gabapentine, Metoprolol and Venlafaxine. For the former and the latter, the curves fall short to estimate the removal before reaching the plateau at 100 %, as the reference data indicates a steeper removal curve. In the case of Gabapentin, the removal is characterized by an 'S' shape, which if looked attentively is also the shape of the reference data in the plot, though the bends occur in different places. The simulated results match the reference data for low ozone doses ($\leq$ 0.25 g O_3/g COD), then underestimates the removal

capacity for doses between 0.25 and 0.5 g O_3/g COD, to later slightly overestimate the removal when reaching 0.6 g O_3/g COD. A possible explanation for this, is the fact that Gabapentin is administered at a higher concentration than the rest of the compounds (Table 4.5), while also having the smallest k_{O_3} value. This would explain why the removal is comparatively lower at the beginning, as the rate of removal given by equation 3.5 is proportionally lower to Gabapentin's initial concentration. In the case of Metoprolol, the reference data shows unexpected removal values for the last two points, so those are not considered when judging the model's fit.

5.1.2 Calibration of the scavenging effect of TSS

Figure 5.3 shows the comparison between the simulation and reference data including the scavenging effect of TSS at two different concentrations of 50 and 200 g TSS/m^3.

The quality of the model's performance decreases with the addition of suspended solids. The calibration of $k_{TSS\text{-}O_3}$ attempts to match the removal reported by Juárez et al. (2021) at 200 g TSS/m^3, and then simulations are tested for lower TSS concentrations. With the exception of Gabapentin, the model is shown to replicate the data adequately at low ozone doses but then underestimates the removal of Carbamazepine, Diclofenac, Metoprolol, Sulfamethoxazole and Venlafaxine. It does however fit the curve for Valsartan from beginning to end, with just a slight over estimation towards the highest removal values. In the case of Oxazepam, the overestimation is higher at higher ozone doses, and in the case of Gapapentin the model is not able to correctly describe the shape of the curve and consistently underestimates its removal.

In contrast, the curves at 50 g TSS/m^3 reveal a lower sensitivity of the model to TSS, in comparison to the reference data. It consistently simulates lower removal performance for all micropollutants, and ultimately begs the question of whether the proposed representation of the scavenging effect is good enough. The structure of this effect is modelled using the same approach as the one for micropollutant removal, as written in equation 3.5. Nonetheless, a different mathematical representation could potentially yield better results.

On the other hand, some phenomena currently left out of scope could actually be indirectly represented by this 'TSS effect'. For example, the effect of nitrogen species could be skewing the results and suggesting the need to include them in a future iteration of the model.

5.2 Calibration with pilot plant data

The resulting simulation of MP removal is shown here against the data retrieved from the operation of the ozonation pilot plant by Ekblad et al. (2021). As Figure 5.4 shows, the ozone dose in this case was measured in g O_3/g DOC.

As the data after post-precipitation is the one used for the calibration, the model shows a better fit with those points. Nevertheless, there is a prevalent underestimation of the removal performance with the exception of Valsartan. Also, contrary to the previous calibration, Gabapentin shows the best fit out of the micropollutants tested (with the stream after post-precipitation).

Overall, the model shows better agreement at lower doses of ozone, but also the reference data used is more scattered than the match data. This is expected given the sources of uncertainty from the operation of the pilot plant are more complex. In addition, these simulations include the equation for mass transfer for ozone, shown in Table 4.1. As reported by Audenaert et al. (2013), the values for k_La and $[O_3^*]$ are very influential in the model's performance, and thus better results could potentially be achieved by further calibrating them. This can also explain the lower quality of the simulation fit with respect to the reference data.

The model is consistent in estimating a poorer performance with the stream before post-precipitation, which also agrees with the remarks posed by the authors of the source research (Ekblad et al., 2021).

5.3 Validation of the model

The model parameters obtained from the calibration with batch data are applied without any changes to the data from Lee et al. (2014) (See Table 4.7). The result of the validation is displayed in Figure 5.5. The coefficient of determination (r^2) is included for each plot, which in turn is calculated by equation 5.1.

$$r^2 = 1 - \frac{SSE}{SST} \tag{5.1}$$

The terms SSE and SST refer to the error sum of squares and the total sum of squares, respectively Devore (2011). The average value of r^2 for all micropollutants is 0.89.

The validation achieved is deemed satisfactory. With five out of the nine micropollutants tested, the r^2 value is equal or higher than 0.94, and with only two it is lower than 0.8. In most cases, and in line with the calibration process, the removal is underestimated. The exceptions are Metoprolol, Gabapentin and Valsartan, which seem to reach a plateau lower than a 100% removal.

Valsartan results show the best fit, followed by Oxazepam and Bezotriazole, that reveal a slightly lower simulated removal with the addition of 1 g O_3/g DOC. With Carbamazepine, Diclofenac, Sulfamethoxazole and Venlafaxine, the model underestimates the removal until matching the reference data at their plateaus, least in the case of Sulfamethoxazole and most accentuated with Venlafaxine. Lastly, Gabapentin is again the worst fit as it displays its 'S' shape, that in this case is not correspondent to the shape of the curve formed by the reference data.

Altogether, the model is able to give a sound estimation of the expected removal performance of micropollutants from an ozonation treatment. It is calibrated using data from the Lundåkra WWTP and validated with a hospital effluent treated with a MBR, and is able to produce consistent results given the different origins and characterizations of the two water streams. Moreover, when the model diverges from the source data it does so with an underestimation in most cases, which could be even considered as a safety factor from a conservative point of view.

5.4 Sensitivity to selected parameters

To test the sensitivity of the model to pH and H_2O_2, the parameters obtained with the calibration with batch data (Lee et al., 2014) are used. The sensitivity to HRT is tested with the calibration with the pilot plant data (Ekblad et al., 2021).

5.4.1 pH

Figure 5.6 shows how the model reacts at two different pH values: 7 and 8.5. From the results it is apparent that the model has marginal sensitivity to the variations in pH. As previously stated, the main reason for this is that the values for k_{O_3} are assumed constant, whereas Lee et al. (2014) use higher values at a pH of 8.5 for Benzotriazole, Gabapentin, Metoprolol, Sulfamethoxazole and Venlafaxine. Variations in removal performance of these compounds would thus be expected by employing a pH-sensitive k_{O_3} coefficient. In spite of this, the only variations that the pH produces in this model so far are from the different concentrations in the H^+ and OH^- ions.

From the source data, however, it can be appreciated that also Valsartan shows to be quite sensitive to pH variations, and even Oxazepam to a lesser extent. This kind of behaviour might suggest that a pH-sensitive k_{O_3} coefficient could be used to model the removal of these compounds too.

5.4.2 H_2O_2

The plots in Figure 5.7 display how the removal of micropollutants is affected by an increasing dose of hydrogen peroxide (H_2O_2), corresponding to 0, 0.25 and 0.5 in moles of H_2O_2 per moles of O_3. The ozone dose reported for this data set is 1 g O_3/g DOC, and is kept accordingly for these simulations.

It is unclear from the Gujer matrix of Table 4.1 how H_2O_2 would impact on MP removal. As said in section 3.1.1, H_2O_2 favors the formation of hydroxyl radicals (Luo et al., 2014) but this relationship is not translated into a reaction equation in the model being used. From the plots, the model actually shows a negative response from removal in the presence of H_2O_2, which agrees with the trend that the source data shows for Benzotriazole, Gabapentin, Oxazepam and Sulfamethoxazole.

The simulated removal curve only fits the data well for Benzotriazole and Oxazepam at a pH of 8.5. For the other compounds it just highlights the difference between the reference data and the simulated data at 1 g O_3/g DOC previously evidenced in Figure 5.6.

5.4.3 HRT

The hydraulic retention time (HRT) is adjusted between 5 and 40 minutes and the changes in removal performance of the model are plotted in Figure 5.8.

Not much agreement is met between the simulated curves and the reference data. The model reveals a high sensitivity to HRT, and in Ekblad et al. (2021) they report that the impact of HRT is not significant enough to prove itself relevant.

The effect of HRT remains nevertheless consistent accross the micropollutants tested, and it's relevance in the model can be explained by the fact that the main dynamics are represented by Equation 3.5, where the MP concentration is inversely proportional to time.

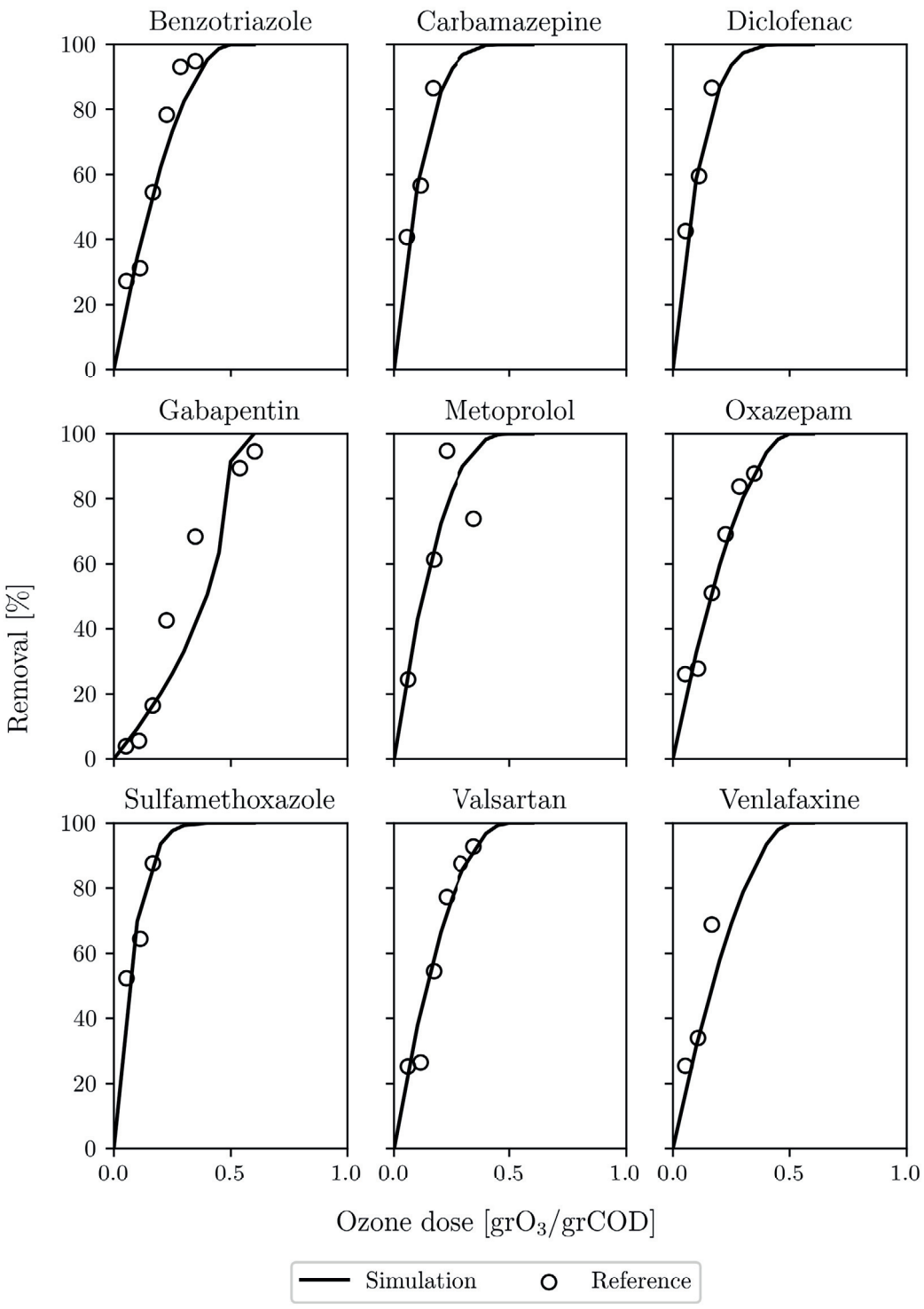

Figure 5.2: Removal performance of the model simulation after calibrating for the kinetic coefficients of the micropollutant sample in comparison to the reference data from Juárez et al. (2021). The wastewater stream used does not contain TSS.

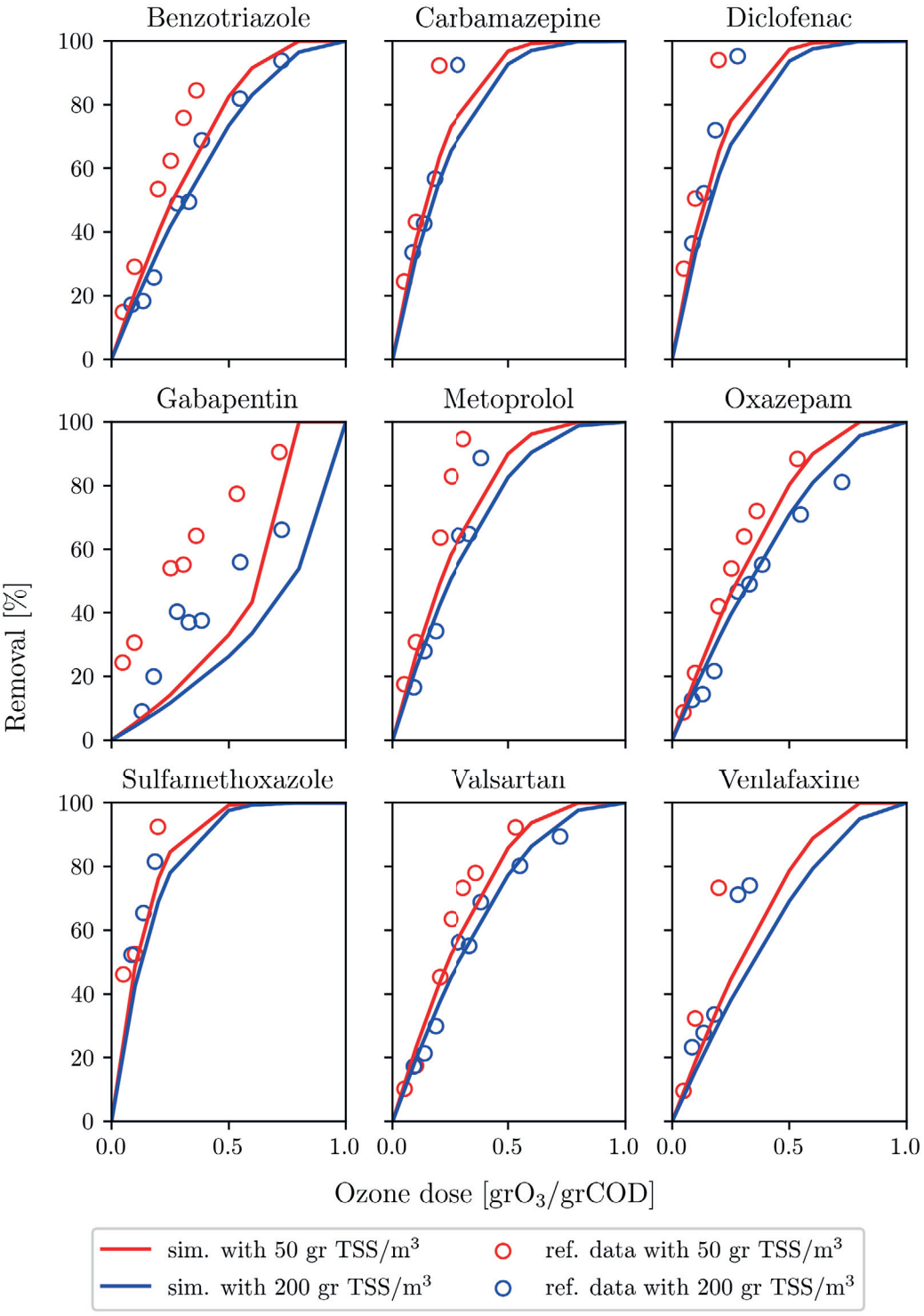

Figure 5.3: Removal performance of the model simulation after calibrating for the scavenging effects of TSS in comparison to the reference data from Juárez et al. (2021).

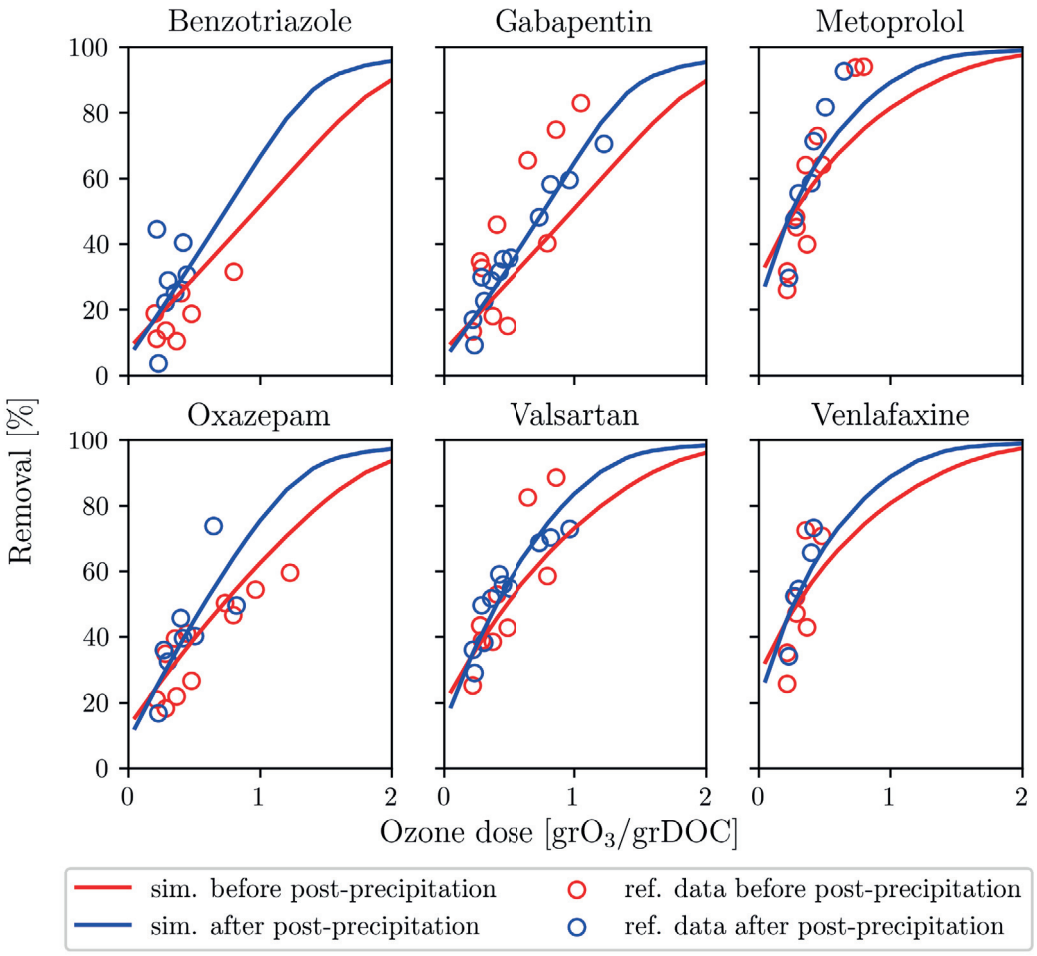

Figure 5.4: Removal performance of the model simulation after calibrating for the kinetic coefficients of the micropollutant sample in comparison to the reference data from Ekblad et al. (2021).

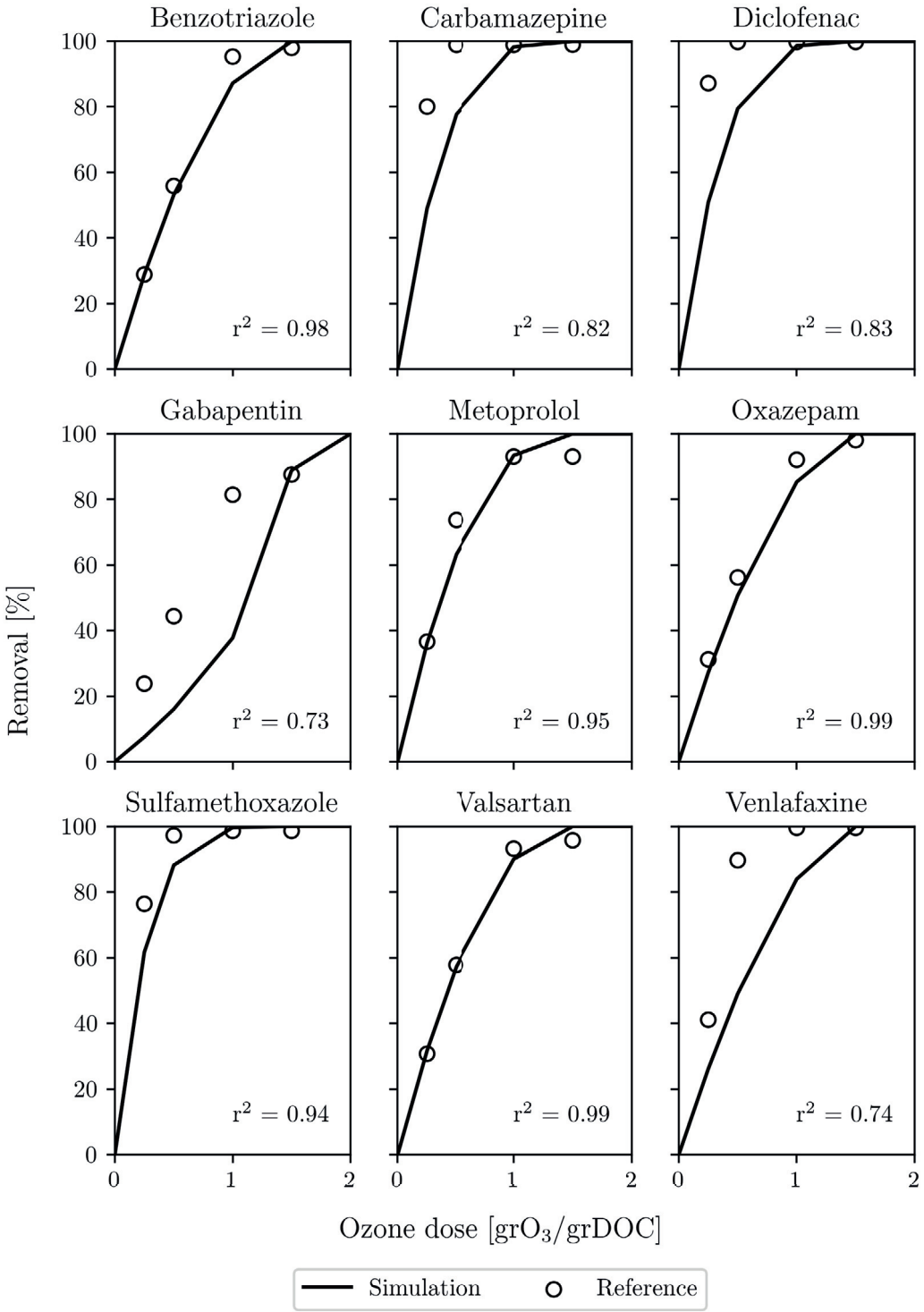

Figure 5.5: Removal performance of the calibrated model contrasted with reference data from Lee et al. (2014). Values for the r^2 is added for each micropollutant.

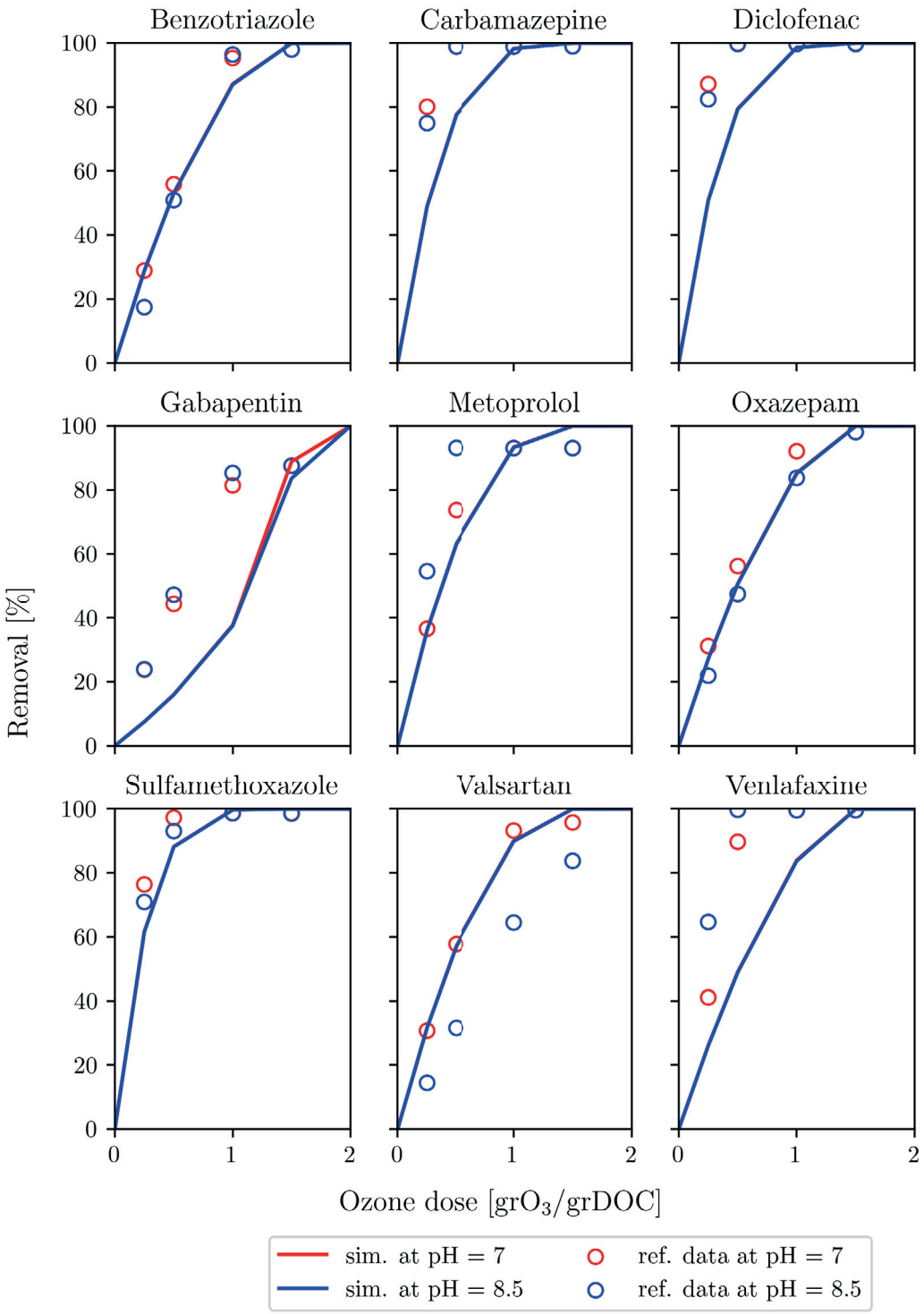

Figure 5.6: Model sensitivity to pH in contrast with reference data from Lee et al. (2014).

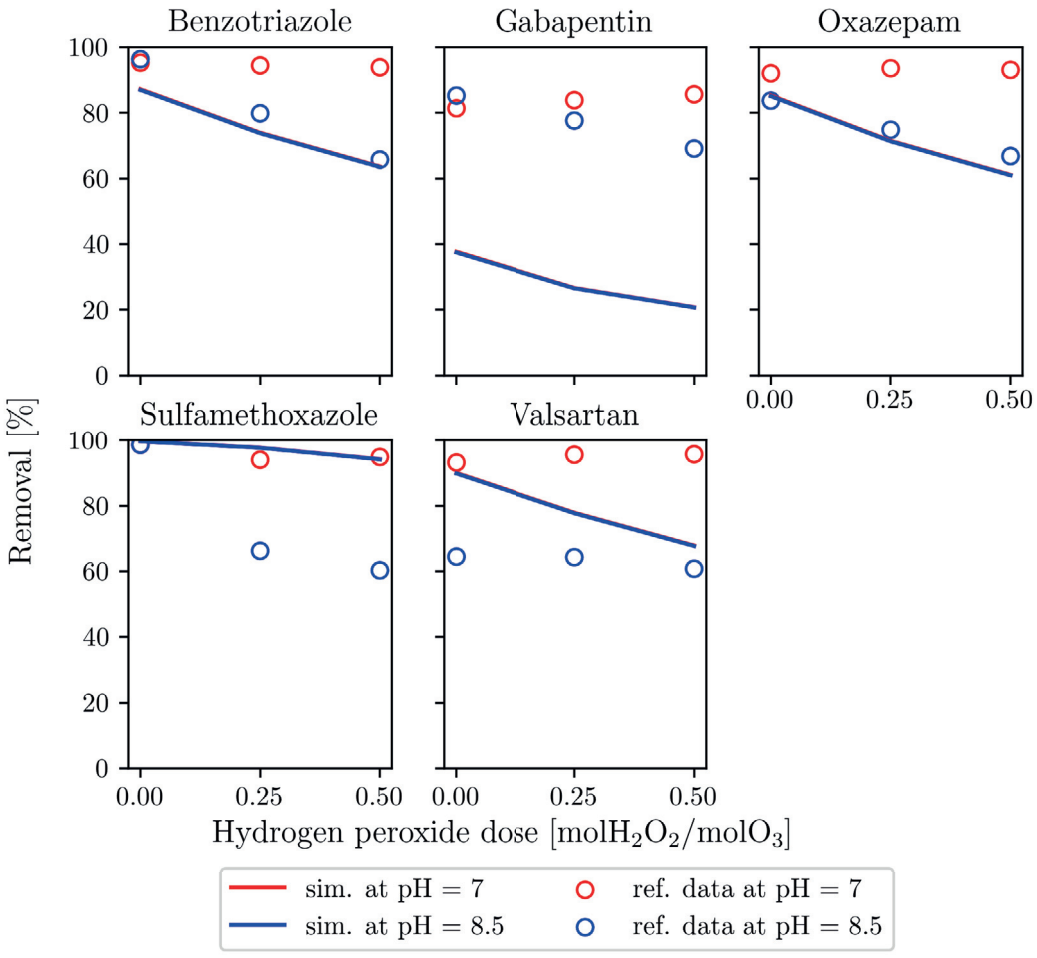

Figure 5.7: Model sensitivity to addition of H_2O_2 in contrast with reference data from (Lee et al., 2014).

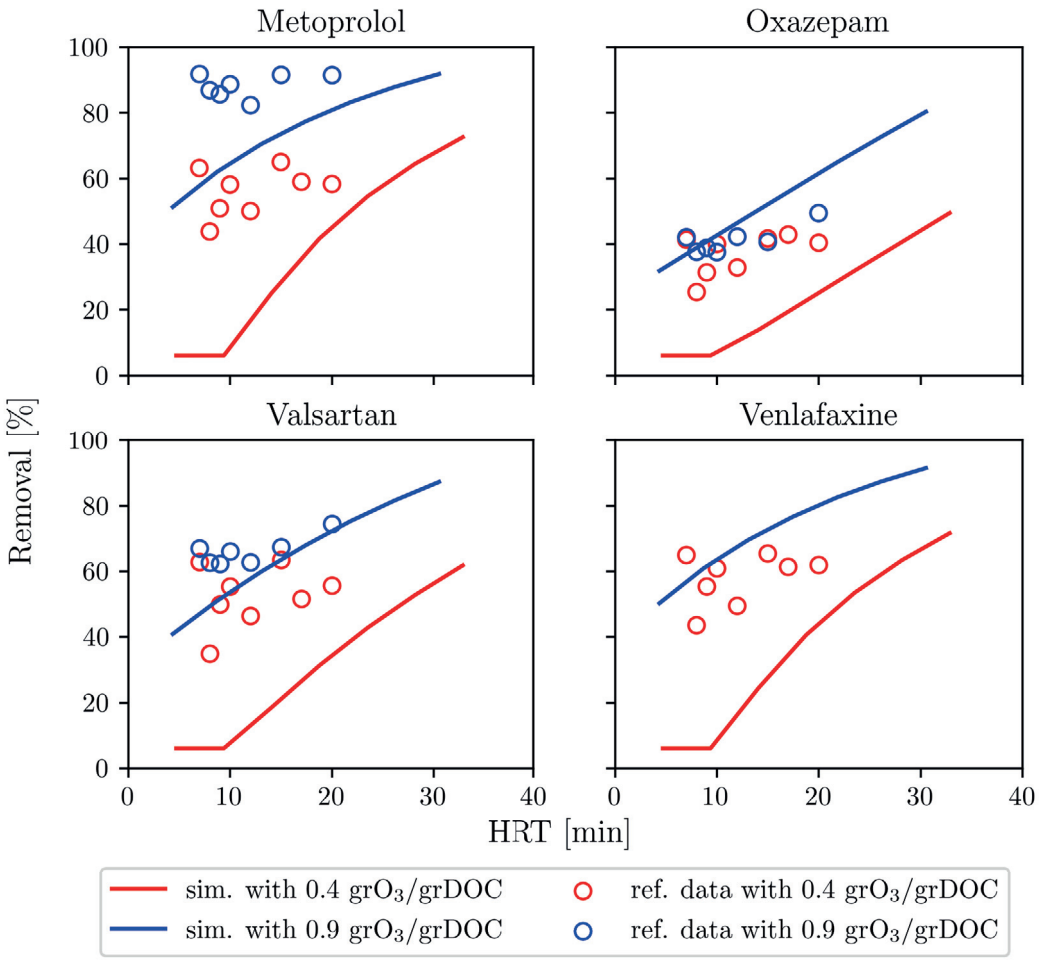

Figure 5.8: Model sensitivity to variations in HRT in contrast with reference data from Ekblad et al. (2021).

6 Conclusions

This study aims at combining an ozone decomposition model and a micropollutant removal model to simulate micropollutant removal through ozonation. It uses and approach based on second-order rate constants, denominated kinetic coefficients, to solve a continuity equation that describes the dynamics of compounds over time. The conclusions obtained are listed as follows:

- The model has low sensitivity to variations of the $k_{OH\cdot}$ coefficient in contrast with k_{O_3}. The model is hence calibrated by only changing the kinetic coefficients associated to O_3 exposure.
- The model presents a good fit for simulations with values based on batch experimentation, and to a lesser extent in comparison to the data from the pilot plant.
- The latter could be explained by the fact that k_La and $[O_3^*]$ are very influential in the model's performance, and might thus need a more adequate calibration.
- Findings show a lower sensitivity of the model to TSS in comparison to the reference data. It consistently simulates lower removal performance for all micropollutants, which might suggest other alternatives to representing the scavenging effect.
- Alternatively, other phenomena currently left out of scope could actually be indirectly represented by the 'TSS effect'. For example, the effect of nitrogen species could be skewing the results and suggesting the need to include them in a future iteration of the model.
- The validation is achieved with an average coefficient of determination (r^2) of 0.89.
- When the model diverges from the source data it does so with an underestimation in most cases.
- There is a lower removal performance observed with the addition of H_2O_2, and better removal capacity with higher Hydraulic Retention Time (HRT). It responds, however, with negligible sensitivity to variations in pH.
- The model can be expanded to include other dynamics and phenomena originally left out of scope.

7 Future Work

The extent of additional work that can be addressed in the future can be divided into micropollutant groups, fragmentation and dynamics, scavengers and catalysts, and some additional computer-related tools. A key aspect common to most continuation alternatives for this research is pilot experimentation and/or laboratory work. This would yield more varied and tailored empirical data from which the model could benefit greatly. If this research were to be continued by another student, a concrete suggestion would be to include conjugate, deconjugate and particulate dynamics and to orient the model to receive a representative micropollutant to simulate the removal of a group or class of micropollutants, rather than having to add individual micropollutants to the model.

7.1 Micropollutant groups, fragmentation and dynamics

The need to work with representative groups of micropollutants becomes apparent when considering the wide spectrum of different types that exist. Even more so, the most hazardous can continue to be identified and catalogued to facilitate the implementation of risk impact studies (Stadler et al., 2012). A move towards a grouping approach would help make this model easier to implement to different cases and a wider variety of studies.

Also, a next iteration would be to include at least to some extent the dynamics of the conjugate and particulate fractions of the micropollutants. The fractionation aspect is already considered on the model, but more information - and possibly assumptions - would need to be gathered for an adequate addition of this kind. But this need not be limited to conjugate and particulate fractions, as the same strategy can be extended to transformation and deconjugation as well. The faith of transformation products has already been established as fundamental to accurately portray the presence of micropollutants in WWTP effluents (Stadler et al., 2012).

7.2 Scavengers and catalysts

The scavenging effect of TSS in the performance of micropollutant removal is something that can continue to be improved in this model. A better mathematical representation can be achieved if laboratory experiments similar to the ones performed by Juárez et al. (2021) are replicated and possibly extended to a pilot plant operation, as shown in (Ekblad et al., 2021).

Nonetheless, not only TSS can be extended on, but also other agents like the presence of nitrogen species, particulate organic matter and even inorganic matter under certain conditions (Audenaert et al., 2013). The study of pH is another route to follow, with the implementation of pH-sensitive kinetic coefficients either just for ozone exposure or for hydroxyl radical exposure as well.

7.3 Additional computer-related tools

This model could profit greatly if tested in combination with an Activated Sludge Model (ASM) or as a hybrid advanced system. Even more so if it is part of a complete WWTP with all its treatment stages included. With the aid of telemetry, it could become part of a digital twin of a plant that already operates with ozonation treatment, and the calibration possibilities would be much greater.

On the other hand, a complete version of the SHB model could be tested instead of the simplified one used in this research, to elucidate how much more would the model gain in performance and if it would be a worth modification or not.

One could also hypothesize that the use of Computational Fluid Dynamics (CFD) could eventually enrich the model, however it would have to be backed up by robust empirical data and a good notion of which parameters might be of interest in this sort of evaluation.

Lastly, Artificial Intelligence (AI) seems to be a ubiquitous topic in present times, and naturally leads to wonder about the applications it can have on water and wastewater treatment models. Targeting some of the most challenging aspects of these activities with AI-based resources could become a fruitful endeavor in the nearby future.

References

Al-Rifai, J. H., Khabbaz, H. and Schäfer, A. I. (2011), 'Removal of pharmaceuticals and endocrine disrupting compounds in a water recycling process using reverse osmosis systems', *Separation and Purification Technology* **77**(1), 60–67.
URL: *https://www.sciencedirect.com/science/article/pii/S1383586610004855*

Alfiya, Y., Friedler, E., Westphal, J., Olsson, O. and Dubowski, Y. (2017), 'Photodegradation of micropollutants using v-uv/uv-c processes; triclosan as a model compound', *Science of The Total Environment* **601-602**, 397–404.
URL: *https://www.sciencedirect.com/science/article/pii/S0048969717312792*

Altmann, J., Ruhl, A. S., Zietzschmann, F. and Jekel, M. (2014), 'Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment', *Water Research* **55**, 185–193.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135414001419*

Aqueduct Alliance (2019), 'Aqueduct water risk atlas'.
URL: *https://www.wri.org/applications/aqueduct/water-risk-atlas/#/?advanced=false&basemap=hydro&indicator=w_awr_def_tot_cat&lat=45.18826782404264&lng=-305.15625000000006&mapMode=view&month=1&opacity=0.5&ponderation=DEF&predefined=false&projection=absolute&scenario=optimistic&scope=baseline&timeScale=annual&year=baseline&zoom=2*

Audenaert, W. T. M., Callewaert, M., Nopens, I., Cromphout, J., Vanhoucke, R., Dumoulin, A., Dejans, P. and Van Hulle, S. W. H. (2010), 'Full-scale modelling of an ozone reactor for drinking water treatment', *Chemical Engineering Journal* **157**(2), 551–557.
URL: *https://www.sciencedirect.com/science/article/pii/S1385894710000112*

Audenaert, W., Vandevelde, M., Van Hulle, S. and Nopens, I. (2013), 'Impact of dissolved organic matter (dom) on parameter sensitivity of a kinetic ozone decomposition model', *Ozone: Science and Engineering* **35**, 338–349.
URL: *https://www.researchgate.net/publication/236633323_Impact_of_Dissolved_Organic_Matter_DOM_on_Parameter_Sensitivity_of_a_Kinetic_Ozone_Decomposition_Model*

Bezbarua, B. K. and Reckhow, D. A. (2004), 'Modification of the standard neutral ozone decomposition model', *Ozone: Science & Engineering* **26**(4), 345–357. doi: 10.1080/01919510490482179.
URL: *https://doi.org/10.1080/01919510490482179*

BioWin (2023).
URL: *https://envirosim.com/*

Blackbeard, J., Lloyd, J., Magyar, M., Mieog, J., Linden, K. G. and Lester, Y. (2016), 'Demonstrating organic contaminant removal in an ozone-based water reuse process at full scale', *Environmental Science: Water Research & Technology* **2**(1), 213–222.
URL: *http://dx.doi.org/10.1039/C5EW00186B*

Bourgin, M., Beck, B., Boehler, M., Borowska, E., Fleiner, J., Salhi, E., Teichler, R., von Gunten, U., Siegrist, H. and McArdell, C. S. (2018), 'Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products', *Water Research* **129**, 486–498.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135417308734*

Brodin, T., Fick, J., Jonsson, M. and Klaminder, J. (2013), 'Dilute concentrations of a psychiatric drug alter behavior of fish from natural populations', *Science* **339**(6121), 814–815. doi: 10.1126/science.1226850.
URL: *https://doi.org/10.1126/science.1226850*

Brown, P. N., Byrne, G. D. and Hindmarsh, Alan, C. (1989), 'Vode: a variable-coefficient ode solver', *SIAM journal on Scientific and Statistical Computing* **10**(5), 1038–1051.
URL: *https://computing.llnl.gov/sites/default/files/ODEPACK_pub4_207532.pdf*

Buffle, M. O., Meylan, S., Von Gunten, U., Schumacher, J. and Jekel, M. (2006b), '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* **28**(4), 247–259–259.
URL: *https://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&AuthType=ip,uid&db=edselc&AN=edselc.2-52.0-33645212175&site=eds-live&scope=site*

Buffle, M.-O., Schumacher, J., Salhi, E., Jekel, M. and von Gunten, U. (2006a), 'Measurement of the initial phase of ozone decomposition in water and wastewater by means of a continuous quench-flow system: Application to disinfection and pharmaceutical oxidation', *Water Research* **40**(9), 1884–1894.
URL: *https://www.sciencedirect.com/science/article/pii/S004313540600131X*

Burkhardt-Holm, P. (2011), 'Linking water quality to human health and environment: the fate of micropollutants', *Inst Water Policy Natl Univ Singapore* pp. 1–62.
URL: *https://www.researchgate.net/profile/Patricia-Burkhardt-Holm/publication/268328108_Linking_Water_Quality_to_Human_Health_and_Environment_The_Fate_of_Micropollutants/links/552e2d130cf2acd38cb900f9/Linking-Water-Quality-to-Human-Health-and-Environment-The-Fate-of-Micropollutants.pdf*

Bühler, R. E., Staehelin, J. and Hoigné, J. (1984), 'Ozone decomposition in water studied by pulse radiolysis. 1. perhydroxyl (ho2)/hyperoxide (o2-) and ho3/o3-as intermediates', *The Journal of Physical Chemistry* **88**(12), 2560–2564.
URL: *https://pubs.acs.org/doi/abs/10.1021/j150656a026*

Camel, V. and Bermond, A. (1998), 'The use of ozone and associated oxidation processes in drinking water treatment', *Water Research* **32**(11), 3208–3222.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135498001304*

Canadian Environmental Protection Act (1999), 'Priority substances list assessment report: Nonylphenol and its ethoxylates'.
URL: *https://laws-lois.justice.gc.ca/eng/acts/c-15.31/*

Carvalho, R. N., Ceriani, L., Ippolito, A. and Lettieri, T. (2015), 'Development of the first watch list under the environmental quality standards directive', *JRC Science Hub* .
URL: *https://edisciplinas.usp.br/pluginfile.php/5548876/mod_resource/content/1/Watch%20List.pdf*

Chang, C. Y. (2010), *Nanofiltration membranes and nanofilters*, IWA Publishing, book section Chapter 4.
URL: *http://library.oapen.org/handle/20.500.12657/25913*

Choubert, J. M., Martin Ruel, S., Esperanza, M., Budzinski, H., Miège, C., Lagarrigue, C. and Coquery, M. (2011), 'Limiting the emissions of micro-pollutants: what efficiency can we expect from wastewater treatment plants?', *Water Science and Technology* **63**(1), 57–65.
URL: *https://doi.org/10.2166/wst.2011.009*

Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. and Kroiss, H. (2005), 'Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants', *Water Research* **39**(19), 4797–4807.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135405005178*

Clouzot, L., Choubert, J.-M., Cloutier, F., Goel, R., Love, N. G., Melcer, H., Ort, C., Patureau, D., Plósz, B. G., Pomiès, M. and Vanrolleghem, P. A. (2013), 'Perspectives on modelling micropollutants in wastewater treatment plants', *Water Science and Technology* **68**(2), 448–461.
URL: *https://doi.org/10.2166/wst.2013.272*

Commission Implementing Decision (EU) 2015/495 (2015), 'Commission implementing decision (eu) 2015/495 of 20 march 2015 establishing a watch list of substances for union-wide monitoring in the field of water policy pursuant to directive 2008/105/ec of the european parliament and of the council'.
URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv%3AOJ.L_.2015.078.01.0040.01.ENG*

Commission Implementing Decision (EU) 2020/1161 (2020), 'Commission implementing decision (eu) 2020/1161 of 4 august 2020 establishing a watch list of substances for union-wide monitoring in the field of water policy pursuant to directive 2008/105/ec of the european parliament and of the council (notified under document number c(2020) 5205) (text with eea relevance)'.

URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2020.257.01.0032.01.ENG&toc=OJ:L:2020:257:TOC*

Commission Implementing Decision (EU) 2022/1307 (2022), 'Commission implementing decision (eu) 2022/1307 of 22 july 2022 establishing a watch list of substances for union-wide monitoring in the field of water policy pursuant to directive 2008/105/ec of the european parliament and of the council (notified under document c(2022) 5098) (text with eea relevance)'.
URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32022D1307*

Council Directive 2020/2184 (2020), 'Directive (eu) 2020/2184 of the european parliament and of the council of 16 december 2020 on the quality of water intended for human consumption (recast)'.
URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32020L2184*

Dalahmeh, S. and Baresel, C. (2014), 'Reclaimed wastewater use alternatives and quality standards: From global to country perspective: Spain versus abu dhabi emirate'.
URL: *https://sjostad.ivl.se/download/18.1f96676d145d7c937412444/1400791505237/C24.pdf*

Davis, M. L. (2010), 'Water and wastewater engineering'.
URL: *https://www.accessengineeringlibrary.com/binary/mheaeworks/aae8f5df02e7aa86/b45f6e6c17b039fdc147a0a2e900b88f959c465de4d153ea6dd48cc89f774dc1/book-summary.pdf*

Delli Compagni, R., Polesel, F., von Borries, K. J. F., Zhang, Z., Turolla, A., Antonelli, M. and Vezzaro, L. (2020), 'Modelling the fate of micropollutants in integrated urban wastewater systems: Extending the applicability to pharmaceuticals', *Water Research* **184**, 116097.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135420306345*

Devore, J. L. (2011), *Probability and Statistics for Engineering and the Sciences*, 8th edn, Brooks/Cole.
URL: *https://www.bibsonomy.org/bibtex/2c194dd98c9ba0f074329fe35d72a7a5b/dzeneralen*

DHI A/S (2022), 'Om dhi'.
URL: *https://worldwide.dhigroup.com/se/om-dhi*

Directive 2000/60/EC (2000), 'Directive of the european parliament and of the council of 23 october 2000 establishing a framework for community action in the field of water policy.'.
URL: *https://eur-lex.europa.eu/eli/dir/2000/60/oj*

Directive 2008/105/EC (2008), 'Directive 2008/105/ec of the european parliament and of the council on environmental quality standards in the field of water policy'.
URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A32008L0105*

Directive 91/271/EEC (1991), 'Council directive 91/271/eec of 21 may 1991 concerning urban waste-water treatment'.
URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A31991L0271*

Directive 98/15/EC (1998), 'Commission directive 98/15/ec of 27 february 1998 amending council directive 91/271/eec with respect to certain requirements established in annex i thereof'.
URL: *https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A31998L0015*

Directorate-General for Environment (2022), 'Directive of the european parliament and of the council concerning urban wastewater treatment (recast)'.
URL: *https://environment.ec.europa.eu/publications/proposal-revised-urban-wastewater-treatment-directive_en*

Dorado, P., Berecz, R., Norberto, M.-J., Yasar, U., Dahl, M.-L. and Llerena, A. (2003), 'Cyp2c9 genotypes and diclofenac metabolism in spanish healthy volunteers', *European Journal of Clinical Pharmacology* **59**(3), 221–225.
URL: *https://doi.org/10.1007/s00228-003-0588-0*

Duong, K. and Saphores, J.-D. M. (2015), 'Obstacles to wastewater reuse: an overview', *WIREs Water* **2**(3), 199–214. https://doi.org/10.1002/wat2.1074.
URL: *https://doi.org/10.1002/wat2.1074*

Dupont, R. and Sinkjær, O. (1994), 'Optimisation of wastewater treatment plants by means of computer models', *Water Science and Technology* **30**(4), 181–190.
URL: *https://doi.org/10.2166/wst.1994.0186*

Ekblad, M., Falås, P., El-taliawy, H., Nilsson, F., Bester, K., Hagman, M. and Cimbritz, M. (2019), 'Is dissolved cod a suitable design parameter for ozone oxidation of organic micropollutants in wastewater?', *Science of The Total Environment* **658**, 449–456.
URL: *https://www.sciencedirect.com/science/article/pii/S0048969718349258*

Ekblad, M., Juárez, R., Falås, P., Bester, K., Hagman, M. and Cimbritz, M. (2021), 'Influence of operational conditions and wastewater properties on the removal of organic micropollutants through ozonation', *Journal of Environmental Management* **286**, 112205.
URL: *https://www.sciencedirect.com/science/article/pii/S030147972100267X*

Elovitz, M. S. and von Gunten, U. (1999), 'Hydroxyl radical/ozone ratios during ozonation processes. i. the rct concept', *Ozone: Science & Engineering* **21**(3), 239–260. doi: 10.1080/01919519908547239.
URL: *https://doi.org/10.1080/01919519908547239*

Esplugas, S., Bila, D. M., Krause, L. G. T. and Dezotti, M. (2007), 'Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (edcs) and pharmaceuticals and personal care products (ppcps) in water effluents', *Journal of Hazardous Materials* **149**(3), 631–642.
URL: *https://www.sciencedirect.com/science/article/pii/S0304389407011028*

European Commission (2023), 'Environment'.
URL: *https://ec.europa.eu/environment/water/water-urbanwaste/legislation/directive_en.htm*

Falås, P., Longrée, P., la Cour Jansen, J., Siegrist, H., Hollender, J. and Joss, A. (2013), 'Micropollutant removal by attached and suspended growth in a hybrid biofilm-activated sludge process', *Water Research* **47**(13), 4498–4506.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135413004181*

Falås, P., Wick, A., Castronovo, S., Habermacher, J., Ternes, T. A. and Joss, A. (2016), 'Tracing the limits of organic micropollutant removal in biological wastewater treatment', *Water Research* **95**, 240–249.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135416301361*

Grandclément, C., Seyssiecq, I., Piram, A., Wong-Wah-Chung, P., Vanot, G., Tiliacos, N., Roche, N. and Doumenq, P. (2017), 'From the conventional biological wastewater treatment to hybrid processes, the evaluation of organic micropollutant removal: A review', *Water Research* **111**, 297–317.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135417300052*

Gujer, W., Henze, M., Mino, T. and Loosdrecht, M. v. (1999), 'Activated sludge model no. 3', *Water Science and Technology* **39**(1), 183–193.
URL: *https://www.sciencedirect.com/science/article/pii/S0273122398007859*

Hansen, K. M. S., Spiliotopoulou, A., Chhetri, R. K., Escolà Casas, M., Bester, K. and Andersen, H. R. (2016), 'Ozonation for source treatment of pharmaceuticals in hospital wastewater – ozone lifetime and required ozone dose', *Chemical Engineering Journal* **290**, 507–514.
URL: *https://www.sciencedirect.com/science/article/pii/S1385894716000449*

Henze, M., Gujer, W., Mino, T. and van Loosedrecht, M. (2006), 'Activated sludge models asm1, asm2, asm2d and asm3'.
URL: *https://doi.org/10.2166/9781780402369*

Hernández-Leal, L., Temmink, H., Zeeman, G. and Buisman, C. J. N. (2011), 'Removal of micropollutants from aerobically treated grey water via ozone and activated carbon', *Water Research* **45**(9), 2887–2896.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135411001205*

Hollender, J., Zimmermann, S. G., Koepke, S., Krauss, M., McArdell, C. S., Ort, C., Singer, H., von Gunten, U. and Siegrist, H. (2009), 'Elimination of organic micropollutants in a municipal wastewater treatment plant upgraded with a full-scale post-ozonation followed by sand filtration', *Environmental Science & Technology* **43**(20), 7862–7869. doi: 10.1021/es9014629.
URL: *https://doi.org/10.1021/es9014629*

Hopkinson, Charles S., J. and Vallino, J. J. (2005), 'Efficient export of carbon to the deep ocean through dissolved organic matter', *Nature (London)* **433**(7022), 142–145. Language: English; Coden: NATUAS; Collation: 4; Publication Types: Serial; Updated

Code: 200605; Illustration(s): illus. incl. 1 table; Number of References: 30; Reviewed Item: Analytic.
URL: *https://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&AuthType=ip,uid&db=geh&AN=2006-012619&site=eds-live&scope=site*

Huber, M. M., Canonica, S., Park, G.-Y. and von Gunten, U. (2003), 'Oxidation of pharmaceuticals during ozonation and advanced oxidation processes', *Environmental Science & Technology* **37**(5), 1016–1024. doi: 10.1021/es025896h.
URL: *https://doi.org/10.1021/es025896h*

Huber, M. M., GÖbel, A., Joss, A., Hermann, N., LÖffler, D., McArdell, C. S., Ried, A., Siegrist, H., Ternes, T. A. and von Gunten, U. (2005), 'Oxidation of pharmaceuticals during ozonation of municipal wastewater effluents: A pilot study', *Environmental Science & Technology* **39**(11), 4290–4299. doi: 10.1021/es048396s.
URL: *https://doi.org/10.1021/es048396s*

Iacopozzi, I., Innocenti, V., Marsili-Libelli, S. and Giusti, E. (2007), 'A modified activated sludge model no. 3 (asm3) with two-step nitrification–denitrification', *Environmental Modelling & Software* **22**(6), 847–861.
URL: *https://www.sciencedirect.com/science/article/pii/S1364815206001228*

Itzel, F., Baetz, N., Hohrenk, L. L., Gehrmann, L., Antakyali, D., Schmidt, T. C. and Tuerk, J. (2020), 'Evaluation of a biological post-treatment after full-scale ozonation at a municipal wastewater treatment plant', *Water Research* **170**, 115316.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135419310905*

Jelić, A., Gros, M., Petrović, M., Ginebreda, A. and Barceló, D. (2012), *Occurrence and Elimination of Pharmaceuticals During Conventional Wastewater Treatment*, Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 1–23.
URL: *https://doi.org/10.1007/978-3-642-25722-3_1*

Joss, A., Keller, E., Alder, A. C., Göbel, A., McArdell, C. S., Ternes, T. and Siegrist, H. (2005), 'Removal of pharmaceuticals and fragrances in biological wastewater treatment', *Water Research* **39**(14), 3139–3152.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135405002733*

Joss, A., Zabczynski, S., Göbel, A., Hoffmann, B., Löffler, D., McArdell, C. S., Ternes, T. A., Thomsen, A. and Siegrist, H. (2006), 'Biological degradation of pharmaceuticals in municipal wastewater treatment: Proposing a classification scheme', *Water Research* **40**(8), 1686–1696.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135406001126*

Juárez, R. (2021), Ozonation in Advanced Wastewater Treatment, Licentiate thesis.
URL: *https://lup.lub.lu.se/search/publication/3489206c-07b9-434b-a686-cf3ed9397836*

Juárez, R., Karlsson, S., Falås, P., Davidsson, A., Bester, K. and Cimbritz, M. (2021), 'Integrating dissolved and particulate matter into a prediction tool for ozonation of organic

micropollutants in wastewater', *Science of The Total Environment* **795**, 148711.
URL: *https://www.sciencedirect.com/science/article/pii/S0048969721037839*

Kasprzyk-Hordern, B., Dinsdale, R. M. and Guwy, A. J. (2009), 'The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters', *Water Research* **43**(2), 363–380.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135408005010*

Kharel, S., Stapf, M., Miehe, U., Ekblad, M., Cimbritz, M., Falås, P., Nilsson, J., Sehlén, R. and Bester, K. (2020), 'Ozone dose dependent formation and removal of ozonation products of pharmaceuticals in pilot and full-scale municipal wastewater treatment plants', *Science of The Total Environment* **731**, 139064.
URL: *https://www.sciencedirect.com/science/article/pii/S004896972032581X*

Kharel, S., Stapf, M., Miehe, U., Ekblad, M., Cimbritz, M., Falås, P., Nilsson, J., Sehlén, R., Bregendahl, J. and Bester, K. (2021), 'Removal of pharmaceutical metabolites in wastewater ozonation including their fate in different post-treatments', *Science of The Total Environment* **759**, 143989.
URL: *https://www.sciencedirect.com/science/article/pii/S0048969720375203*

Kidd, K. A., Blanchfield, P. J., Mills, K. H., Palace, V. P., Evans, R. E., Lazorchak, J. M. and Flick, R. W. (2007), 'Collapse of a fish population after exposure to a synthetic estrogen', *Proceedings of the National Academy of Sciences* **104**(21), 8897–8901. doi: 10.1073/pnas.0609568104.
URL: *https://doi.org/10.1073/pnas.0609568104*

Kim, I., Yamashita, N. and Tanaka, H. (2009), 'Performance of uv and uv/h2o2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in japan', *Journal of Hazardous Materials* **166**(2), 1134–1140.
URL: *https://www.sciencedirect.com/science/article/pii/S0304389408018505*

Kim, S., Chen, J., Cheng, T., Gindulyte, A., He, J., He, S., Li, Q., Shoemaker, B. A., Thiessen, P. A., Yu, B., Zaslavsky, L., Zhang, J. and Bolton, E. E. (2023), 'Pubchem 2023 update', *Nucleic Acids Research* **51**(D1), D1373–D1380.
URL: *https://doi.org/10.1093/nar/gkac956*

Kogelschatz, U. (2003), 'Dielectric-barrier discharges: Their history, discharge physics, and industrial applications', *Plasma Chemistry and Plasma Processing* **23**(1), 1–46.
URL: *https://doi.org/10.1023/A:1022470901385*

Kovalova, L., Siegrist, H., Singer, H., Wittmer, A. and McArdell, C. S. (2012), 'Hospital wastewater treatment by membrane bioreactor: Performance and efficiency for organic micropollutant elimination', *Environmental Science & Technology* **46**(3), 1536–1545. doi: 10.1021/es203495d.
URL: *https://doi.org/10.1021/es203495d*

Lee, Y., Gerrity, D., Lee, M., Bogeat, A. E., Salhi, E., Gamage, S., Trenholm, R. A., Wert, E. C., Snyder, S. A. and von Gunten, U. (2013), 'Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: Use of kinetic and water specific information', *Environmental Science & Technology* **47**(11), 5872–5881. doi: 10.1021/es400781r.
URL: *https://doi.org/10.1021/es400781r*

Lee, Y., Kovalova, L., McArdell, C. S. and von Gunten, U. (2014), 'Prediction of micropollutant elimination during ozonation of a hospital wastewater effluent', *Water Research* **64**, 134–148.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135414004564*

Lee, Y. and von Gunten, U. (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* **44**(2), 555–566.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135409008008*

Liu, Z., Yang, Y., Shao, C., Ji, Z., Wang, Q., Wang, S., Guo, Y., Demeestere, K. and Hulle, S. V. (2020), 'Ozonation of trace organic compounds in different municipal and industrial wastewaters: Kinetic-based prediction of removal efficiency and ozone dose requirements', *Chemical Engineering Journal* **387**, 123405.
URL: *https://www.sciencedirect.com/science/article/pii/S1385894719328189*

Loos, R., Carvalho, R., António, D. C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T., Blaha, L., Jarosova, B., Voorspoels, S., Servaes, K., Haglund, P., Fick, J., Lindberg, R. H., Schwesig, D. and Gawlik, B. M. (2013), 'Eu-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents', *Water Research* **47**(17), 6475–6487.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135413006647*

Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J., Liang, S. and Wang, X. C. (2014), 'A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment', *Science of The Total Environment* **473-474**, 619–641.
URL: *https://www.sciencedirect.com/science/article/pii/S0048969713015465*

Mazioti, A. A., Stasinakis, A. S., Gatidou, G., Thomaidis, N. S. and Andersen, H. R. (2015), 'Sorption and biodegradation of selected benzotriazoles and hydroxybenzothiazole in activated sludge and estimation of their fate during wastewater treatment', *Chemosphere* **131**, 117–123.
URL: *https://www.sciencedirect.com/science/article/pii/S0045653515002398*

McNaught, A. D. and Wilkinson, A. (2019), 'Compendium of chemical terminology'.
URL: *https://goldbook.iupac.org/*

Miao, X.-S., Yang, J.-J. and Metcalfe, C. D. (2005), 'Carbamazepine and its metabolites in wastewater and in biosolids in a municipal wastewater treatment plant', *Environmental*

Science & Technology **39**(19), 7469–7475. doi: 10.1021/es050261e.
URL: *https://doi.org/10.1021/es050261e*

Minakata, D., Li, K., Westerhoff, P. and Crittenden, J. (2009), 'Development of a group contribution method to predict aqueous phase hydroxyl radical (ho•) reaction rate constants', *Environmental Science & Technology* **43**(16), 6220–6227. doi: 10.1021/es900956c.
URL: *https://doi.org/10.1021/es900956c*

Nakada, N., Shinohara, H., Murata, A., Kiri, K., Managaki, S., Sato, N. and Takada, H. (2007), 'Removal of selected pharmaceuticals and personal care products (ppcps) and endocrine-disrupting chemicals (edcs) during sand filtration and ozonation at a municipal sewage treatment plant', *Water Research* **41**(19), 4373–4382.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135407004010*

Nguyen, P. Y., Carvalho, G., Reis, M. A. M. and Oehmen, A. (2021), 'A review of the biotransformations of priority pharmaceuticals in biological wastewater treatment processes', *Water Research* **188**, 116446.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135420309817*

Nowotny, N., Epp, B., von Sonntag, C. and Fahlenkamp, H. (2007), 'Quantification and modeling of the elimination behavior of ecologically problematic wastewater micropollutants by adsorption on powdered and granulated activated carbon', *Environmental Science & Technology* **41**(6), 2050–2055. doi: 10.1021/es0618595.
URL: *https://doi.org/10.1021/es0618595*

Nöthe, T., Fahlenkamp, H. and Sonntag, C. v. (2009), 'Ozonation of wastewater: Rate of ozone consumption and hydroxyl radical yield', *Environmental Science & Technology* **43**(15), 5990–5995. doi: 10.1021/es900825f.
URL: *https://doi.org/10.1021/es900825f*

Petrović, M., de Alda, M. J. L., Diaz-Cruz, S., Postigo, C., Radjenović, J., Gros, M. and Barcelo, D. (2009), 'Fate and removal of pharmaceuticals and illicit drugs in conventional and membrane bioreactor wastewater treatment plants and by riverbank filtration', *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* **367**(1904), 3979–4003. doi: 10.1098/rsta.2009.0105.
URL: *https://doi.org/10.1098/rsta.2009.0105*

Phan, L. T., Schaar, H., Saracevic, E., Krampe, J. and Kreuzinger, N. (2022), 'Effect of ozonation on the biodegradability of urban wastewater treatment plant effluent', *Science of The Total Environment* **812**, 152466.
URL: *https://www.sciencedirect.com/science/article/pii/S0048969721075446*

Polesel, F., Andersen, H. R., Trapp, S. and Plósz, B. G. (2016), 'Removal of antibiotics in biological wastewater treatment systems—a critical assessment using the activated sludge modeling framework for xenobiotics (asm-x)', *Environmental Science & Technology* **50**(19), 10316–10334. doi: 10.1021/acs.est.6b01899.
URL: *https://doi.org/10.1021/acs.est.6b01899*

Qiao, M., Ying, G.-G., Singer, A. C. and Zhu, Y.-G. (2018), 'Review of antibiotic resistance in china and its environment', *Environment International* **110**, 160–172.
URL: *https://www.sciencedirect.com/science/article/pii/S0160412017312321*

Radjenović, J., Petrović, M. and Barceló, D. (2009), 'Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (cas) and advanced membrane bioreactor (mbr) treatment', *Water Research* **43**(3), 831–841.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135408005642*

Rodríguez, A., Rosal, R., Perdigón-Melón, J. A., Mezcua, M., Agüera, A., Hernando, M. D., Letón, P., Fernández-Alba, A. R. and García-Calvo, E. (2008), *Ozone-Based Technologies in Water and Wastewater Treatment*, Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 127–175.
URL: *https://doi.org/10.1007/978-3-540-79210-9_4*

Rokhina, E. V. and Virkutyte, J. (2010), *Advanced catalytic oxidation of emerging Micropollutants* , IWA Publishing, book section Chapter 10.
URL: *http://library.oapen.org/handle/20.500.12657/25913*

Salgot, M., Huertas, E., Weber, S., Dott, W. and Hollender, J. (2006), 'Wastewater reuse and risk: definition of key objectives', *Desalination* **187**(1), 29–40.
URL: *https://www.sciencedirect.com/science/article/pii/S0011916405007186*

Schultz, M. M., Painter, M. M., Bartell, S. E., Logue, A., Furlong, E. T., Werner, S. L. and Schoenfuss, H. L. (2011), 'Selective uptake and biological consequences of environmentally relevant antidepressant pharmaceutical exposures on male fathead minnows', *Aquatic Toxicology* **104**(1), 38–47.
URL: *https://www.sciencedirect.com/science/article/pii/S0166445X11000907*

Schäfer, A. I., Akanyeti, I. and Semião, A. J. C. (2011), 'Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens', *Advances in Colloid and Interface Science* **164**(1), 100–117.
URL: *https://www.sciencedirect.com/science/article/pii/S0001868610001739*

Shestakova, M., Hansen, B., Valanko, R., Pekonen, P., Hesampour, M., Halttunen, S., Hofmann, R., Pretorius, R., Penttinen, M., Recktenwald, M., Karpova, T., Rossum, R., Grönfors, O., Mattsson, E., Ahlgren, J., Nilsson, B., Leen, P., Havansi, H. and Abinet, R. (2020), 'About water treatment'.
URL: *https://www.kemira.com/insights/water-handbook-2020/*

Spring, A. J., Bagley, D. M., Andrews, R. C., Lemanik, S. and Yang, P. (2007), 'Removal of endocrine disrupting compounds using a membrane bioreactor and disinfection', *Journal of Environmental Engineering & Science* **6**(2), 131–137.
URL: *https://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&AuthType=ip,uid&db=a9h&AN=26232542&site=eds-live&scope=site*

Stadler, L. B., Ernstoff, A. S., Aga, D. S. and Love, N. G. (2012), 'Micropollutant fate in wastewater treatment: Redefining "removal"', *Environmental Science & Technology*

46(19), 10485–10486. doi: 10.1021/es303478w.
URL: *https://doi.org/10.1021/es303478w*

Staehelin, J., Buehler, R. E. and Hoigné, J. (1984), 'Ozone decomposition in water studied by pulse radiolysis. 2. hydroxyl and hydrogen tetroxide (ho4) as chain intermediates', *The Journal of Physical Chemistry* **88**(24), 5999–6004.
URL: *https://pubs.acs.org/doi/pdf/10.1021/j150668a051?casa_token=CEMLNryTph8AAAAA:DE2tIuz4HqYE8LoF0-d3v_KthuAiBedvNRiMb5RhPMDKRVmXUfy9OMWAhHN77oSkyENXtl-_dLikYg*

Stamm, C., Räsänen, K., Burdon, F. J., Altermatt, F., Jokela, J., Joss, A., Ackermann, M. and Eggen, R. I. L. (2016), *Chapter Four - Unravelling the Impacts of Micropollutants in Aquatic Ecosystems: Interdisciplinary Studies at the Interface of Large-Scale Ecology*, Vol. 55, Academic Press, pp. 183–223.
URL: *https://www.sciencedirect.com/science/article/pii/S0065250416300150*

Stangroom, S. J., Collins, C. D. and Lester, J. N. (1998), 'Sources of organic micropollutants to lowland rivers', *Environmental Technology (United Kingdom)* **19**(7), 643–666–666. Environmental Technology (United Kingdom) (Environmental Technology (United Kingdom), 1 July 1998, 19(7):643-666) Publication Type: Academic Journal; Rights: Copyright 2017 Elsevier B.V., All rights reserved.
URL: *https://ludwig.lub.lu.se/login?url=https://search.ebscohost.com/login.aspx?direct=true&AuthType=ip,uid&db=edselc&AN=edselc.2-52.0-0031683967&site=eds-live&scope=site*

Stasinakis, A. S. and Gatidou, G. (2010), *Micropollutants and Aquatic Environment*, IWA Publishing, book section Chapter 1.
URL: *http://library.oapen.org/handle/20.500.12657/25913*

STOAT (2023).
URL: *https://www.wrcgroup.com/services/stoat-wastewater-works-modelling-freeware/*

Sumo (2023).
URL: *https://dynamita.com/products.html*

Ternes, T. A., Meisenheimer, M., McDowell, D., Sacher, F., Brauch, H.-J., Haist-Gulde, B., Preuss, G., Wilme, U. and Zulei-Seibert, N. (2002), 'Removal of pharmaceuticals during drinking water treatment', *Environmental Science & Technology* **36**(17), 3855–3863. doi: 10.1021/es015757k.
URL: *https://doi.org/10.1021/es015757k*

Ternes, T. and Joss, A. (2007), *Human pharmaceuticals, hormones and fragrances*, IWA publishing.
URL: *https://doi-org.ludwig.lub.lu.se/10.1021/jf049228m*

Testa, B., Pedretti, A. and Vistoli, G. (2012), 'Reactions and enzymes in the metabolism of drugs and other xenobiotics', *Drug Discovery Today* **17**(11), 549–560.
URL: *https://www.sciencedirect.com/science/article/pii/S1359644612000359*

Trinh, T., van den Akker, B., Stuetz, R. M., Coleman, H. M., Le-Clech, P. and Khan, S. J. (2012), 'Removal of trace organic chemical contaminants by a membrane bioreactor', *Water Science and Technology* **66**(9), 1856–1863.
URL: *https://doi.org/10.2166/wst.2012.374*

Tuhkanen, T. A. and Mariñosa, P. C. (2010), *UV irradiation for Micropollutant removal from aqueous solutions in the presence of H2O2*, IWA Publishing, book section Chapter 8.
URL: *http://library.oapen.org/handle/20.500.12657/25913*

Undeman, E., Rasmusson, K., Kokorite, I., Leppänen, M. T., Larsen, M. M., Pazdro, K. and Siedlewicz, G. (2022), 'Micropollutants in urban wastewater: large-scale emission estimates and analysis of measured concentrations in the baltic sea catchment', *Marine Pollution Bulletin* **178**, 113559.
URL: *https://www.sciencedirect.com/science/article/pii/S0025326X22002417*

United Nations (2014), World urbanization prospects — the 2014 revision, highlight, Report.
URL: *https://population.un.org/wup/Publications/Files/WUP2014-Highlights.pdf*

U.S. House of Representatives Congress (2018), '33 u.s.c. - navigation and navigable waters.'.
URL: *https://www.govinfo.gov/app/details/USCODE-2018-title33/*

Vezzaro, L., Benedetti, L., Gevaert, V., De Keyser, W., Verdonck, F., De Baets, B., Nopens, I., Cloutier, F., Vanrolleghem, P. A. and Mikkelsen, P. S. (2014), 'A model library for dynamic transport and fate of micropollutants in integrated urban wastewater and storm-water systems', *Environmental Modelling & Software* **53**, 98–111.
URL: *https://www.sciencedirect.com/science/article/pii/S1364815213002910*

Virkutyte, J. and Rokhina, E. V. (2010), *Hybrid Advanced Oxidation techniques based on cavitation for Micropollutants degradation*, IWA Publishing, book section Chapter 9.
URL: *http://library.oapen.org/handle/20.500.12657/25913*

von Sonntag, C. and von Gunten, U. (2012), 'Chemistry of ozone in water and wastewater treatment: From basic principles to applications'.
URL: *https://doi.org/10.2166/9781780400839*

WEST (2023).
URL: *https://www.mikepoweredbydhi.com/products/west*

Westerhoff, P., Song, R., Amy, G. and Minear, R. (1997), 'Applications of ozone decomposition models', *Ozone: Science & Engineering* **19**(1), 55–73. doi: 10.1080/01919519708547318.
URL: *https://doi.org/10.1080/01919519708547318*

WEST Getting Started (2022), Report, DHI A/S.
URL: *https://manuals.mikepoweredbydhi.help/latest/WEST.htm*

WEST Models Guide (2023).
URL: *https://manuals.mikepoweredbydhi.help/latest/Cities/TornadoModels/index.htm*

Zhou, M., Gong, J., Yang, C. and Pu, W. (2013), 'Simulation of the performance of aerobic granular sludge sbr using modified asm3 model', *Bioresource Technology* **127**, 473–481.
URL: *https://www.sciencedirect.com/science/article/pii/S0960852412014265*

Zimmermann, S. G., Wittenwiler, M., Hollender, J., Krauss, M., Ort, C., Siegrist, H. and von Gunten, U. (2011), 'Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: Micropollutant oxidation, by-product formation and disinfection', *Water Research* **45**(2), 605–617.
URL: *https://www.sciencedirect.com/science/article/pii/S0043135410005634*

Zucker, I., Lester, Y., Avisar, D., Hübner, U., Jekel, M., Weinberger, Y. and Mamane, H. (2015), 'Influence of wastewater particles on ozone degradation of trace organic contaminants', *Environmental Science & Technology* **49**(1), 301–308. doi: 10.1021/es504314t.
URL: *https://doi.org/10.1021/es504314t*

A Popular Science summaries

A.1 Popular Science summary

How can computers help clean our waters?

Computer models to the service of water treatment

Water is running out in many places. Why? Because of inadequate management of water resources, because of climate change, because of population growth, or a little bit of everything. When this happens, reusing the water that comes out as waste from human activities might just as well become an interesting alternative. If you don't believe this, you are late to the party. Drinking water and even *beer* have already been made from treated wastewater (check out the examples of Windhoek, NEWater and Epic OneWater Brew). So, one might think that from here on it will be easy to secure water supply wherever we need it. To get there, however, there's still a lot of work to do when it comes to cleaning water - work made easier with the help of computers.

This might sound alarming, but we still don't know exactly what is hiding in our wastewaters. The more we improve our measuring technologies, the more components we find that can harm the environment and, therefore, us. A name coined for a notorious group of them is "micropollutants". These are sneaky compounds that are present in the tiniest of concentrations, but that tend to accumulate over the years and cause mayhem wherever they land. They come from personal care products, drugs, pesticides, hormones, pathogens and a bunch of other stuff, and are super tricky to remove. A great deal of effort has gone into researching how to handle this problem, and many technologies have been identified and developed for this very purpose. Among those, it's ozonation.

Ozonation, as its name hints, means using ozone to remove micropollutants from water. It is a very popular technology due to its effectiveness, but it still needs to be implemented very carefully so there are not unwanted results. Here is where computers play a very big role, as they help us simulate a lot of complex phenomena when we apply them to assist treatment processes.

In this research, a model is proposed that can be used to simulate the removal of micropollutants from ozonation in wastewater. Nine micropollutants are selected to test the model, and results are compared with data found in research papers. The model shows a good agreement with the data, and offers a starting point to keep building and expanding its capabilities. The aim is to help water engineers that are implementing ozonation, and to keep expanding what we know about its effects. Water regulations are going to keep getting ever more strict (and rightly so), and it is good that we use everything we have to continue improving the quality of the water we treat. That includes all the computer power we can harness.

A.2 Resumen de Divulgación Científica

¿Cómo pueden los computadores ayudarnos a limpiar nuestras aguas?

Modelos computacionales al servicio del tratamiento de aguas

El agua se está acabando en muchos lugares. ¿Por qué? Por la gestión inadecuada del recurso, por el cambio climático, por el crecimiento poblacional, o por una mezcla de todo lo anterior. Cuando esto ocurre, el reúso de agua producida como residuo de actividades humanas puede ser perfectamente considerada como una alternativa interesante. Y esto ya se ha implementado, por si creías que no era posible. Agua para beber e incluso *cerveza* ya se han producido a partir de aguas residuales (puedes revisar los ejemplos de Windhoek, NEWater y Epic OneWater Brew). Entonces, uno podría pensar que ya con esto va a ser fácil garantizar el abastecimiento de agua donde sea que se necesite. Para llegar a eso, no obstante, aún hay mucho trabajo por hacer cuando hablamos de limpiar nuestras aguas - trabajo que puede ser facilitado con la ayuda de computadores.

Esto puede sonar alarmante, pero todavía no sabemos exactamente qué es lo que se esconde en nuestras aguas residuales. Cada vez que nuestros aparatos de medición mejoran, encontramos nuevos contaminantes que pueden dañar el medio ambiente y, por consiguiente, a nosotros. A un notorio grupo de éstos se les ha llamado "microcontaminantes". Estos son compuestos sigilosamente presentes en concentraciones ínfimas, pero que tienden a acumularse a través de los años y causar todo tipo de daños donde sea que caigan. Provienen de productos de aseo personal, drogas, pesticidas, hormonas, patógenos, y muchas otras fuentes, y son muy difíciles de remover. Ya se han hecho grandes esfuerzos en investigar cómo lidiar con este problema, y varias tecnologías han sido identificadas y desarrolladas para este propósito. Entre ellas se encuentra la ozonización.

La ozonización se refiere a la aplicación de ozono para la remoción de microcontaminantes del agua. Es una tecnología bastante popular debido a su efectividad, pero aún necesita implementarse con cuidado para que no genere resultados no deseados. Aquí es donde los computadores juegan un gran papel, ya que nos ayudan a simular una gran cantidad de fenómenos complejos cuando los aplicamos a procesos de tratamiento.

En esta investigación, se propone un modelo que puede utilizarse para simular la remoción de microcontaminantes por medio de la ozonización de aguas residuales. Son nueve los microcontaminates que se eligen para evaluar el modelo, y se comparan los resultados con datos obtenidos de publicaciones académicas. El modelo muestra un buen ajuste con los datos, y ofrece un punto de partida sobre el cual construir y expandir sus capacidades. El objetivo es ayudar a ingenieros hidráulicos que implementen ozonización, y continuar expandiendo lo que sabemos sobre sus efectos. Las regulaciones en torno al agua se vuelven cada vez más exigentes (y con justa razón), y es bueno usar todo lo que tenemos a disposición para mejorar la calidad del agua que tratamos. Esto incluye toda la capacidad computacional que podamos aprovechar.

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