

Advanced Wastewater Treatment by Ozonation for Abatement of Micropollutants from Municipal Wastewater Effluents

Urs von Gunten*, Christa S. McArdell*, Christian Abegglen, Marc Böhler, Juliane Hollender, Adriano Joss, and Hansruedi Siegrist

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Abstract: Municipal wastewater treatment plants are important contributors to the discharge of micropollutants to the aquatic environment. Therefore, in Switzerland it has been decided to treat the water at these point sources to reduce the discharge of micropollutants from municipal wastewater effluents. A team of scientists at Eawag has evaluated treatment options, which need to be readily available, easily applicable, and cheap. Based on a rigorous assessment, activated carbon-based processes and ozonation were selected. In this paper the focus is on ozonation, and the different aspects of its application are discussed, including kinetics and mechanisms for ozone reactions with micropollutants and matrix components, formation, and fate of transformation products in biological post-filtration and toxicological aspects. Finally, upgrading of ozonation is described including outreach of this approach to other countries.

Keywords: Ecosystem health · Enhanced municipal wastewater treatment · Micropollutant abatement · Ozonation



Photo taken at the Swiss Chemistry Night 2024 on the occasion of the celebration of the SCS Sandmeyer Award 2024. From left to right Christian Abegglen, Christa McArdell, Hansruedi Siegrist, Juliane Hollender, Urs von Gunten, Marc Böhler. Adriano Joss was not at the event. Photo credit, André Maurer, Steffisburg (<https://www.andremaurer.ch>), ©Swiss Chemical Society, Bern.

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Dr. Christa S. McArdell is a group leader at the Department of Environmental Chemistry, Eawag. She is specialized in target analysis of micropollutants and suspect screening of transformation products in the environment. She was involved in numerous

pilot- and full-scale studies for micropollutant abatement from wastewater.

Prof. Hansruedi Siegrist is a retired group leader from the Engineering Department at Eawag and an adjunct professor from ETHZ. He is a process engineer and developed concepts for enhanced wastewater treatment, worked on upscaling to full-scale ozonation, including process control.

Prof. Juliane Hollender is a group leader at the Department of Environmental Chemistry at Eawag and an adjunct Professor at ETHZ. She is specialized in environmental analytical chemistry and particularly in target and non-target analysis of micropollutants and their fate in natural and engineered aquatic systems.

Prof. Urs von Gunten is a retired group leader from the Department of Water Resources and Drinking Water and is a professor emeritus at EPFL. He is an environmental chemist and performed kinetic and mechanistic studies for micropollutant abatement and transformation product formation during ozonation. He also investigates reactions of ozone with matrix components and develops mitigation strategies.

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1. Introduction

The contamination of the aquatic environment by synthetic organic compounds is a major problem for the ecosystem and potentially human health if water resources are used for drinking water and food production.^[1] Many anthropogenic activities lead to the discharge of organic micropollutants to aquatic systems by point or diffuse sources, including domestic use, industries, agriculture, traffic and urban water management.^[1]

Based on an initiative from the Swiss Federal Office for the Environment and several European projects, a multidisciplinary Eawag team consisting of environmental chemists, ecotoxicologists and environmental engineers have shown early on by a rigorous assessment of fluxes of organic chemicals that municipal wastewaters are an important source of synthetic organic compounds in receiving water bodies with diverse impacts on aquatic organisms.^[2,3] This was the starting point of an Eawag-based research initiative to develop concepts for mitigation of wastewater treatment plant effluents to protect aquatic ecosystems and drinking water resources from an important source of contaminants such as pharmaceuticals, personal care products, endocrine disruptors, pesticides and industrial chemicals. Many of the chemicals are not or only partly biodegradable in conventional wastewater treatment.^[4-6] It was demonstrated that a more advanced treatment is needed to abate a broad selection of micropollutants.^[7] To this end, the Eawag team tested activated carbon-based adsorption processes^[8] and many different chemical oxidants such as chlorine, chlorine dioxide, ferrate(VI), iron complexes of tetra-amido macrocyclic ligands (TAML), hydroxyl radicals ($\cdot\text{OH}$) formed by the Fenton process or a combination of ultraviolet irradiation and H_2O_2 , and ozonation.^[9] Activated carbon-based processes and ozonation were found to be feasible and economic solutions. The focus of this paper is oxidation because it involves chemical transformation reactions that need more in-depth evaluation.

In compliance with various criteria, such as availability of oxidants, kinetics for the reaction with a broad selection of organic contaminants, energy demand/costs and the potential to form toxic products from the reaction with the organic matrix, ozonation was selected as the most suitable oxidation process. Ozone itself has significant reactivity with many functional groups that have high electron density and are present in bioactive compounds, such as activated aromatic moieties, olefins, neutral amines and reduced sulfur groups,^[10,11] and additionally it decomposes in water to the hydroxyl radical which reacts with most compounds at near diffusion-controlled rates.^[10]

2. Assessment of Ozonation for Micropollutant Abatement

Fig. 1 shows the different aspects that need to be considered during oxidation (ozonation) of micropollutants. They will be discussed in the following subsections.

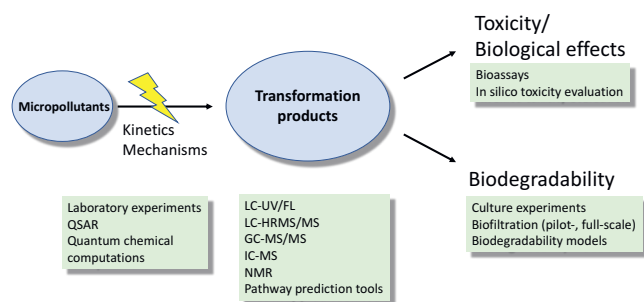


Fig. 1. Oxidation of micropollutants during ozonation with the crucial aspects and tools, from left to right: Reaction kinetics; Formation of transformation products (TPs); Biological effects of TPs; Biodegradability of TPs during biological post-treatment. Fig. 1 from *Water Res.* **2024**, 253, 121148, published under licence CC BY 4.0. Copyright the authors, ref. [12].

2.1 Reaction Kinetics

Bench-scale experiments were performed to determine second-order rate constants for the reactions of a large number of chemicals including pharmaceuticals, endocrine disruptors and personal care products with ozone and hydroxyl radicals.^[10,13,14] The second-order rate constants were measured by various methods including quench-flow, stopped-flow, and competition kinetics.^[14] The selected organic contaminants were previously detected in municipal wastewater effluents by analytical methods developed by the team and others with liquid chromatography mass spectrometry (LC-MS)^[15,16] and they were grouped based on their oxidant reactivities with oxidants, rather than the applications of the compounds. To extrapolate kinetic information to other compounds, we developed Quantitative Structure Activity Relationships (QSAR) based on Hammett-type parameters^[17] and orbital energies derived by quantum chemical computations.^[18] By the combination of kinetic information with measurements of the ozone and hydroxyl radical exposures in wastewaters, the abatement efficiency of micropollutants can be estimated, which is crucial for the feasibility of ozonation.^[19] Based on the developed kinetic database for ozone and the hydroxyl radical, we concluded that ozonation is a suitable process for the effective removal of a broad range of diverse micropollutants.

2.2 Product Formation

During ozonation, micropollutants are only partially modified and not fully mineralized. Therefore, the elucidation of the formation of any transformation products (TPs) and the fate of micropollutants and their TPs, especially related to their toxicity and biodegradability, has to be assessed (Fig.1). For this step, advanced analytical techniques such as high resolution mass spectrometry (HRMS) are required in combination with methods like NMR for product identification.^[20-22] There is already a significant knowledge base for transformation product formation during ozonation, which is based on reactions of ozone with organic functional groups (Fig. 2).

However, under realistic conditions, both ozone and $\cdot\text{OH}$ react in parallel or in sequence with micropollutants and this has to be considered for TP formation. Therefore, we performed an ozonation study with a large number of compounds (>50) with different functional groups by tentatively identifying the corre-

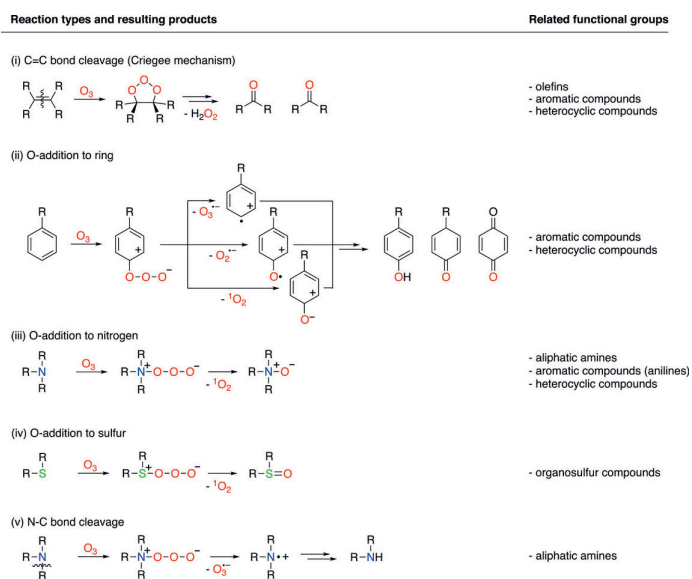


Fig. 2. Primary reactions of ozone with the main ozone-reactive functional groups: Olefins, activated aromatic compounds, amines, and sulfur-containing compounds. Fig. 2 from *Water Res.* **2022**, 213, 118053, published under licence CC BY 4.0. Copyright the authors ref. [11].

sponding ozonation TPs through a combination of non-target LC-HRMS data and kinetic/mechanistic considerations, which were derived from a large body of experimental and quantum chemical based fundamental studies performed in the Eawag team. 227 TPs were detected from 39 target compounds which corresponds to an average of >5 TPs per target compound.^[23] No TPs were detected from 12 target compounds, which is due to limitations of the analytical approach. It can be hypothesized that the detected TPs make up only a fraction of the formed compounds. The identified TPs could be explained by general mechanisms for ozone and $\cdot\text{OH}$ reactions with organic compounds. One example is the transformation of flecainide, a human pharmaceutical for heart beat control (Fig. 3).^[23] The primary product of ozone attack on the secondary amine function is a transient imine *N*-oxide (two isomers), which then further reacts with ozone at the double bond by ring opening, resulting in formation of nitro compounds with a carbonyl group. The $\cdot\text{OH}$ can further react at one of the carbonyl groups to form an acid.

These results, along with other studies performed in wastewater matrices,^[22] demonstrate that a large number of TPs can be formed during ozonation.^[23] Since there are mostly no commercial standards available to assess the toxicity of TPs, methods have been developed to determine the biological effects of mixtures; this will be discussed in the next section.

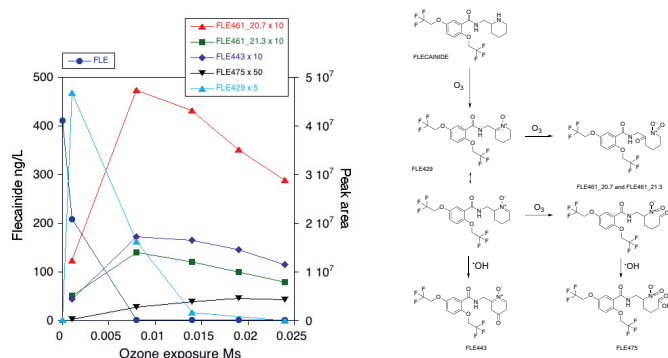


Fig. 3. Pilot-scale ozonation of spiked Lake Zürich water. Left: Evolution of flecainide and the transformation products as a function of the ozone exposure. Right: Potential reaction mechanism involving ozone and $\cdot\text{OH}$ with the structures of flecainide and the detected transformation products. Fig. 3 from *Water Res.* **2021**, *207*, 117812, published under licence CC BY 4.0. Copyright the authors ref. [23].

2.3 Biological Effects and Toxicity

During oxidation of micropollutants, mineralization rarely occurs, and the main question is whether the ensuing transformation products still contain the initial biological activity. It was demonstrated by the team that estrogenic compounds lost their biological effects in parallel to the abatement of the target compound. One case in point is the estrogen 17α -ethinylestradiol (EE2) which has been shown to cause fish population decline at ng/L levels.^[24] Fig. 4 shows that the abatement of 17α -ethinylestradiol (EE2), the active ingredient of the contraceptive pill, by ozone and $\cdot\text{OH}$, occurs in parallel to the reduction of estrogenicity (EEQ) measured by the Yeast Estrogen Assay (YES).^[25] This means that the primary attack of the oxidants on this compound leads to a complete loss of the estrogenicity. Therefore, ozonation is well suited to abate the effects of EE2 in municipal wastewater effluents.

Effect-based studies for micropollutant ozonation have also been performed with other bioactive compounds, such as pesticides and antimicrobial compounds, and generally an efficient abatement of the original biological activities has been observed.^[26–30] Overall, this means that for these classes of com-

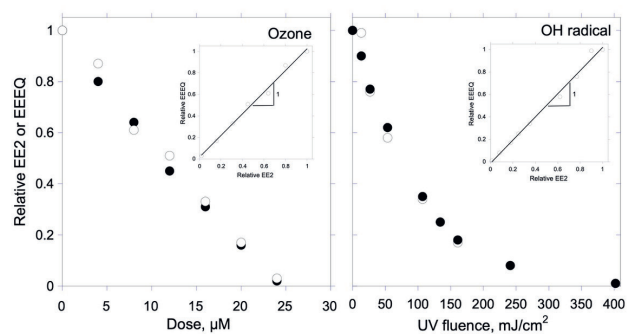


Fig. 4. Relative abatement of 17α -ethinylestradiol (EE2) by ozone (left panel, closed circles) and hydroxyl radicals produced by the UV/H₂O₂ process (right panel, closed circles). The relative abatement of the estrogenicity, measured by the Yeast Estrogen Assay (EEQ), is shown with the open circles. Reprinted (adapted) with permission from Lee *et al.* ref. [25], Copyright (2008) American Chemical Society.

pounds the original biological effects are mostly abated, so are not preserved in the transformation products. Nevertheless, there are also cases, in which more toxic compounds are formed during ozonation. One case in point is the formation of the mutagenic *N*-nitrosodimethylamine (NDMA) from the ozonation of *N,N*-dimethylsulfamide, a metabolite of the fungicide tolylfluanide during ozonation of bromide-containing waters.^[31,32] In another study the formation of estrogenicity (YES) was observed by $\cdot\text{OH}$ -induced oxidation of quinoline.^[33] However, the estrogenic potency of the hydroxylated quinoline is very low and not relevant under realistic conditions. In conclusion, a careful assessment needs to be performed to evaluate ozonation, including several biotests (see below).

2.4 Biodegradability

To degrade potentially toxic TPs and oxidation products from the matrix (see below), ozonation needs to be followed by a biological post-treatment. The fate of TPs was investigated in a pilot-scale ozonation of water from Lake Zurich by dosing 51 compounds with different ozone-reactive functional groups.^[23] Transformation products were identified by LC-HRMS (see above) and their fate was investigated in a post-treatment with a biological sand filter. It could be demonstrated that only a small portion of the detected transformation products were biodegradable or showed a higher degree of biodegradability than their parent compounds. These TPs contained carbonyl, carboxylic acid and amide groups, and were mostly derived from activated aromatic compounds and/or olefins (Figs. 2 and 5). TPs derived from amine-type compounds such as *N*-oxides, nitro or nitroso compounds did not show significant biodegradability in the sand filter (Fig. 5). This was also confirmed in a parallel study in a municipal wastewater effluent.^[22] Even though this shows that many of the observed transformation products are quite stable, the abatement of the observed toxicity/biological effects of parent compounds as well as of the oxidized matrix constituents warrants an improved quality of the discharged wastewater if a biological post-treatment is implemented after ozonation^[34] (see also Section 2.5).

2.5 Reactions with Dissolved Organic Matter

One of the limiting factors of water treatment and in particular for oxidation processes is the presence of dissolved organic matter (DOM) (natural origin or wastewater-derived). Since micropollutant concentrations are in the ng/L–μg/L range and DOM is in the mg/L range (as DOC), there is a huge competition between the targets and DOM. It can be assumed that >95% of the ozone and even a higher fraction of $\cdot\text{OH}$ are consumed by DOM, making this process inherently inefficient. Fig. 6 shows the competing

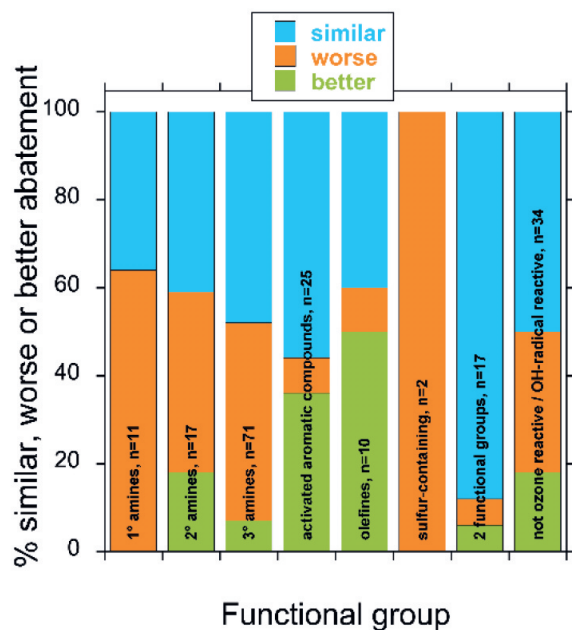


Fig. 5. Biological post-treatment in a pilot-scale biological sand filtration after ozonation of Lake Zurich water. Effect of functional groups of target compounds on the biodegradability by comparison of target compounds with transformation products. Orange: TPs are less efficiently biodegraded than parent compounds; blue: similar biodegradability for parent and TPs; green: better biodegradability of TPs compared to the parents. Fig. 5 from *Water Res.* **2021**, *207*, 117812, published under licence CC BY 4.0. Copyright the authors ref. [23].

scheme for oxidants, on the one hand the desired abatement of targets (micropollutants, microorganisms) and on the other hand reactions with DOM and some inorganic constituents (bromide, iodide, nitrite).

The reactions of oxidants with DOM leads to a lower abatement of micropollutants but also influences the relative contribution of ozone and $\cdot\text{OH}$ to the oxidation of the targets.^[35–38] In addition, disinfection by-products are formed from the reactions of these oxidants with DOM. They consist of oxygen-containing compounds such as aldehydes, ketones and carboxylic acids.^[39] To detect carbonyl compounds after ozonation of lake water and wastewater, a derivatization method with *p*-toluenesulfonylhydrazine (TSH) coupled to LC-HRMS was developed.^[40,41] 178 carbonous and nitrogenous carbonyl compounds were detected during bench-scale ozonation of two lake waters and three secondary wastewater effluents, and during full-scale ozonation of a secondary wastewater effluent. A subset of carbonyl compounds

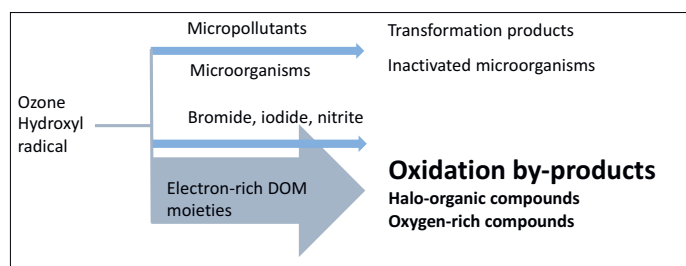


Fig. 6. Ozonation during water treatment. Reactions of ozone and hydroxyl radical with the targets (micropollutants and microorganisms) and the side reactions with dissolved organic matter (DOM) and the inorganic constituents, bromide, iodide, and nitrite. Fig. 6. from *Water Res.* **2024**, *253*, 121148, published under licence CC BY 4.0. Copyright the authors from ref. [12].

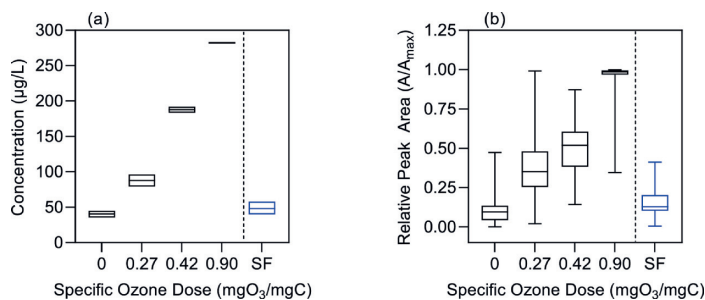


Fig. 7. Fate of (a) target and (b) non-target carbonyl compounds during full-scale wastewater ozonation (Werdhölzli, Zürich, Switzerland) as a function of increasing specific ozone doses and after biological sand filtration (SF, effluent samples for all specific ozone doses). (a) Total concentration of 8 target carbonyl compounds. Boxes show the concentration range and the lines inside the mean concentrations. (b) Relative peak areas (A/A_{\max} , with A = area in each sample type and A_{\max} = highest area measured in all samples) of 40 non-target carbonyl compounds. Lines inside the boxes correspond to the first quartile and the whiskers correspond to the minimum and maximum concentrations (including outliers). Fig. 7 from *Water Res.* **2023**, *237*, 119751, published under licence CC BY 4.0. Copyright the author from ref. [40].

(20%) was detected in all water types.^[41] 8 out of 17 target carbonyl compounds were detected above limits of quantification (LOQs) in most ozonated samples. The concentrations of the 8 identified target compounds decreased in the order: formaldehyde > acetaldehyde > glyoxylic acid > pyruvic acid > glutaraldehyde > 2,3-butanedione > glyoxal > 1-acetyl-1-cyclohexene.^[40] Fig. 7 shows the formation of target (Fig. 7a) and non-target (Fig. 7b) carbonyl compounds as a function of the specific ozone dose for full-scale ozonation of a municipal wastewater. The degradation of the carbonyl compounds in the biological post-sand filtration is also shown. It could be demonstrated that carbonyl compounds are well biodegradable, which is also in line with the observation that occasional toxicity after ozonation is abated during post-filtration.^[42–44] In addition, non-target screening showed that 50–80% of the signals that appeared in LC-HRMS after ozonation are TPs or oxidation by-products and were removed in post-treatments with granular activated carbon filtration performing the best.^[45,46]

2.6 Reactions with Bromide, Iodide and Nitrite

The water matrix also contains inorganic ions, which can be oxidized by ozone and $\cdot\text{OH}$ (Fig. 6). Bromide is present in low concentrations in natural waters in Switzerland (< 20 µg/L) but its concentration may be much higher in municipal wastewaters mainly due to industrial discharges.^[47] Bromide can be oxidized to bromate during ozonation in a complex mechanism including ozone and $\cdot\text{OH}$.^[48] This is problematic and often the limiting factor for ozonation, because bromate is a possible human carcinogen with a strict drinking water standard of 10 µg/L.^[48] Since bromate is difficult to remove after its formation, chemical and hydraulic strategies have been developed to avoid its formation.^[48,49] Since bromate formation is a relatively slow process, its formation in wastewater effluents can be typically minimized for specific ozone doses < 0.6 gO₃/gDOC.^[47] Iodide is typically present in fresh waters at very low concentrations (<< 20 µg/L).^[50] During oxidative water treatment iodide can be oxidized to iodine, which then may lead to the formation of potentially toxic iodo-organic compounds.^[50,51] However, during ozonation iodide is readily oxidized to the non-toxic iodate, which is the desired inert sink for iodine.^[52,53] Therefore, in contrast to other oxidants, ozonation can be applied to avoid the formation of iodo-organic compounds. Finally nitrite, which may be present in wastewaters due to insufficient nitrification,^[54] is problematic during ozona-

tion. First, it consumes ozone in a fast 1:1 reaction,^[55] leading to a loss of efficiency and the formation of nitrate. However, even though nitrate is the final oxidation product from an oxygen atom transfer, a side reaction produces NO_2^{\cdot} by an electron transfer. It has been demonstrated, that this leads to nitro compounds, which are potentially toxic.^[56] Therefore, complete nitrification is a critical pre-requisite for the ozonation of municipal wastewater effluents.

2.7 Assessment of Feasibility of Ozonation for Municipal Wastewater Treatment

As outlined above, ozonation of municipal wastewater effluents is complex because of the many facets that need to be assessed. Therefore, a tiered test system was developed to determine the feasibility of ozonation for specific wastewater effluents.^[57,58] An outline of this procedure is provided in Fig. 8. It starts with an assessment of the catchment, especially the presence of industrial activities, which may lead to unexpected by-products during ozonation. As discussed above, monitoring of bromide is a central task, because ozonation may be limited due to undesired bromate formation.

In the next step, the ozone stability and formation of $\cdot\text{OH}$ are determined and compared to previous data sets to detect potential unexpected matrix effects. In the next module, bromate and *N*-nitrosamines are measured before and after ozonation. Bromate should not exceed $5 \mu\text{g/L}$ since pollution of receiving waters is not allowed in the water protection act. Then the abatement of micropollutants is determined and it should be in the typical range of previously ozonated wastewater effluents. The last module consists of biotests (Ames (mutagenicity), algal and daphnia toxicity). If there are unexpected findings in any of the modules, further tests need to be done. If a wastewater is not suitable for ozonation, this is often already manifested in the chemical tests which means that the biotest can be omitted.

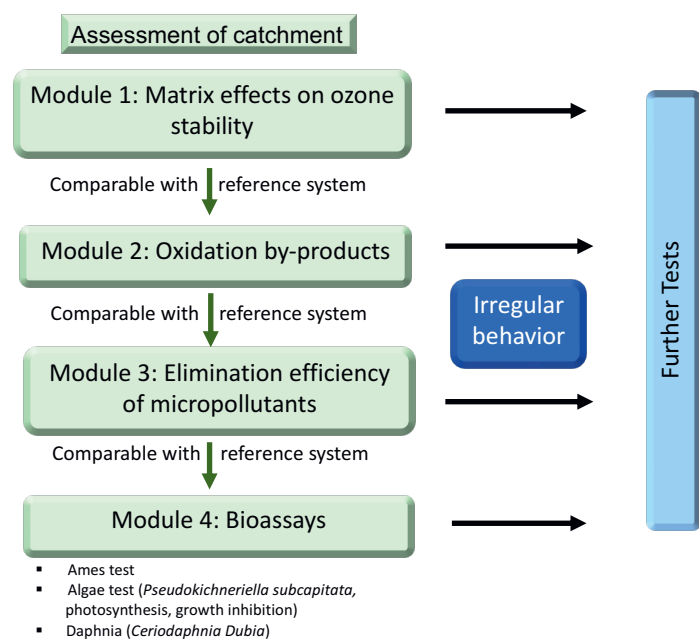


Fig. 8. Test procedure to assess the feasibility of ozonation of municipal wastewater. The tiered approach includes an assessment of the catchment, (1) test of the ozone stability, (2) determination of formation of the oxidation by-products bromate and *N*-nitrosodimethylamine (NDMA), (3) abatement efficiency of micropollutants, and (4) bioassays. Fig. reprinted (adapted) with permission from Schindler Wildhaber *et al.* [57], Copyright (2015) Elsevier.

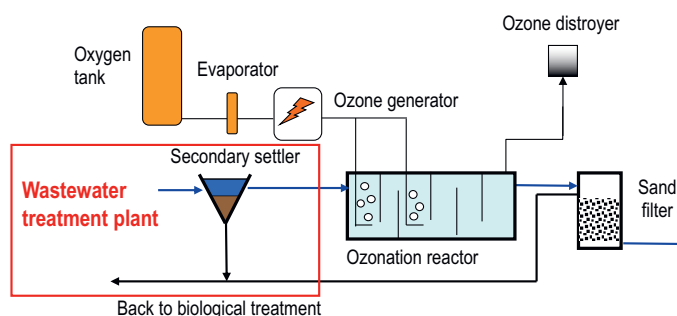


Fig. 9. Typical municipal wastewater treatment scheme including an ozonation step. Secondary treatment effluent is treated with an ozonation followed by a biological sand filtration step. Ozone is produced on site from oxygen, which is evaporated from liquid oxygen. Fig. adapted from ref. [59].

3. From Laboratory to Full-scale Implementation

3.1 Full-scale Tests

The assessment of ozonation processes for micropollutant abatement was based initially on laboratory experiments. However, there are several issues to upscale this process: (i) transferability of kinetics and mechanisms, (ii) positioning of ozonation and reactor hydraulics, (iii) energy and logistics. To get this information, pilot-scale and full-scale data need to be generated. Fig. 9 shows a typical scheme of a municipal wastewater treatment with an ozonation step.^[59] It consists of a full wastewater treatment unit followed by ozonation and biological sand filtration, which degrades biodegradable organic reaction products (see above).

Fig. 10 shows the relative abatement of selected micropollutants as a function of the specific ozone dose for ozonation at a full-scale wastewater treatment plant (Wüeri, Regensdorf, Switzerland). Compounds with high second-order rate constants ($k > 10^5 \text{ M}^{-1}\text{s}^{-1}$) for the reactions with ozone are readily abated ($> 80\%$) even at the lowest applied specific ozone dose of $0.4 \text{ gO}_3/\text{gDOC}$. For compounds with an intermediate ozone reactivity ($k: 10^2 - 10^5 \text{ M}^{-1}\text{s}^{-1}$), specific ozone doses of $0.62 - 0.79 \text{ gO}_3/\text{gDOC}$ are required for $> 80\%$ abatement and for compounds with low ozone reactivities ($k < 10^2 \text{ M}^{-1}\text{s}^{-1}$), an 80% abatement cannot be reached even for the highest ozone dose ($1.18 \text{ gO}_3/\text{gDOC}$).

The full-scale data shown in Fig. 10 could be predicted within a factor 1.5 by laboratory experiments with the same ozone doses and the same water quality.^[61] This demonstrates that upscaling of the ozonation step is possible based on laboratory experiments within certain limits. To quantify the efficiency of ozonation, 12 indicator substances with different ozone-reactivities were selected. On an average abatement of 80% should be achieved for all 12 substances (or for at least for six of them according to their categories) in case not all 12 can be measured in sufficient concentration^[62,63] over the whole wastewater treatment plant including biological treatment and ozonation. Fig. 11 shows the abatement of the 12 indicator substances for 4 upgraded wastewater treatment plants (WWTPs) with ozonation. The required average 80% elimination of indicator substances over the whole plant was reached.

To further test these results, a campaign in a full-scale WWTP including biological treatment and ozonation was performed for a target list of 550 micropollutants (including metabolites) at a specific ozone dose of $0.55 \text{ gO}_3/\text{gDOC}$. In total, 175 compounds were found in the influent of the WWTPs, and Fig. 12 shows their average abatement in biological treatment (BIO, 34%), and ozonation (OZO, $> 67\%$).^[65] Over the whole plant, the average abatement of all substances was $> 80\%$.

For full-scale implementation, aspects such as hydraulic retention times, reactor hydraulics, ozone control, dosing and

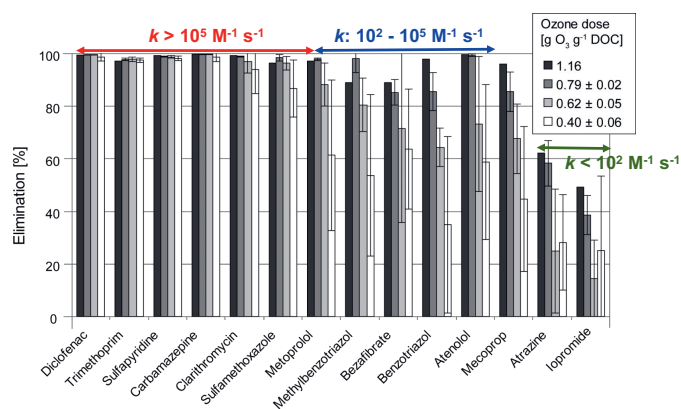


Fig. 10. Abatement of selected micropollutants during ozonation at the full-scale wastewater treatment plant Wüeri (Regensdorf, Switzerland) as a function of the specific ozone doses. Reprinted (adapted) with permission from Hollender *et al.* ref. [60], Copyright (2008) American Chemical Society.

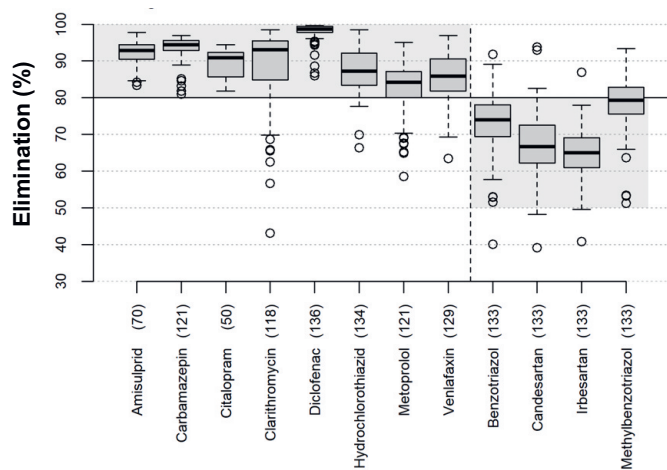


Fig. 11. Abatement of the selected Swiss indicator substances over the whole wastewater treatment plant including biological treatment and ozonation applying a specific ozone dose of 0.4 – 0.6 gO₃/gDOC for 4 upgraded full-scale wastewater treatment plants in Switzerland. Fig. from ref. [64].

monitoring, safety and reliability were developed and tested by the Eawag team. Since it is time-consuming and costly to monitor micropollutant abatement in real time, proxies were developed based on bulk parameters. Correlations between abatement of micropollutants and the difference of the UV absorbance and electron donating capacity (EDC) before and after ozonation were established and they allow the estimation of the efficiency of the ozonation process in terms of micropollutant abatement.^[66,67] Based on full-scale experiments, cost and energy estimates could be made for the planned upgrade of wastewater treatment plants in Switzerland with ozonation.^[68] It was estimated that the energy demand for ozonation (0.5 gO₃/gDOC, 5 mg/L DOC) including production of pure oxygen is ~0.05 kWh/m³, which is in the order of 10% of the total energy consumption of a municipal wastewater treatment plant.^[60] The cost for the upgrade is mostly covered by a tax of 9 CHF per person in Switzerland and the increase of cost at municipal wastewater treatment plants is about 10–15% (0.02–0.25 CHF/m³). Furthermore, a cost-benefit analysis revealed that the Swiss population showed high willingness to pay for the reduction of micropollutants in wastewater.^[69] All these factors showed that ozonation in wastewater treatment is economic, technically feasible, robust in operation and acceptable by the public.

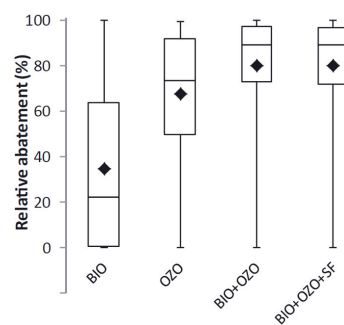


Fig. 12. Distribution of abatement of 175 compounds in biological wastewater treatment (BIO), ozonation (OZO), both together and over the whole plant including sand filtration (SF). Box-whisker plot (minimum, 25th percentile, median, 75th percentile, maximum and (♦) average). Specific ozone dose 0.55 mgO₃/gDOC, two 48 h composite samples, wastewater treatment plant Neugut, Dübendorf, Switzerland. Reprinted with permission from Bourgin *et al.* ref. [65], Copyright (2018) Elsevier.

3.2 Current Situation and Outlook

The upgrade of the selected ~120 Swiss municipal wastewater treatment plants, covering around 70% of Swiss inhabitants, started in 2016 and is ongoing. The implementation of a new Water Protection Ordinance in such a short time was only possible thanks to the good collaboration of researchers with authorities and all relevant stakeholders from the very beginning. Fig. 13 shows the current situation at the end of 2024 with 33 wastewater treatment plants upgraded already and with another 42 plants in the construction or planning phase for the different processes.

As illustrated in Fig. 13, about 30% of the municipal wastewater treatment plants have been upgraded with ozonation. Typically, these are the larger plants and they make up about > 50% of the connected residents of the upgraded plants. A similar proportion of plants are under construction or in the planning phase for the addition of an ozonation step. Research is still ongoing with regard to combined treatments of ozonation with activated carbon, and optimal design of GAC filtration.

Based on political interpellations, there might be a larger number of municipal wastewater treatment plants that need to be upgraded. For diclofenac (active anti-inflammatory ingredient of *e.g.* Voltaren), the environmental quality standard of 0.05 µg/L as recorded in the Swiss water protection ordinance since 2020, has been exceeded in many river stretches, which might necessitate more WWTPs with advanced treatment processes in the future.^[71]

The efforts in Switzerland also have a strong influence and outreach on the global situation regarding abatement of micro-

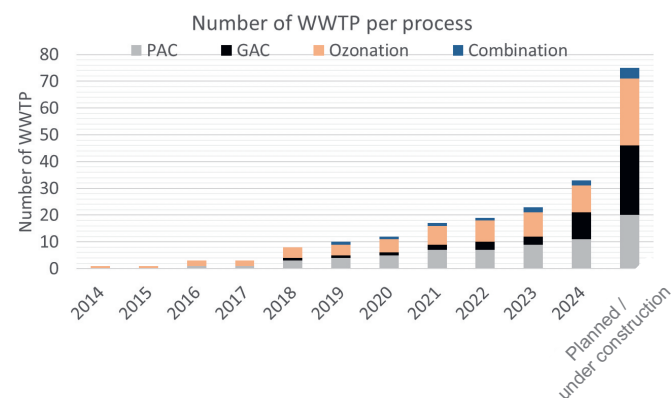


Fig. 13. Number of operational Swiss municipal wastewater treatment plants and plants under construction/planned in December 2024 with the different processes. From micropoll.ch.

pollutants during municipal wastewater treatment. The European Union has adopted a very similar strategy in the new Urban Wastewater Treatment Directive which entered into force at the beginning of 2025 (European Union, 2024).^[72] In addition, the findings from this study are also applicable in the context of potable water reuse, where municipal wastewater effluents are treated to drinking water quality. This approach becomes more important due to enhanced water scarcity with climate change.

4. Conclusions

The application of ozonation has been investigated for micropollutant abatement from municipal wastewater effluents in various projects for more than 10 years. This required advanced analytical tools and detailed chemical knowledge of reaction kinetics, mechanisms of ozone reactions with micropollutants and inorganic and organic matrix components, toxicological assessment of transformation products and disinfection by-products. In addition, know-how on upscaling and process control for full-scale application of ozone to municipal wastewater treatment plants had to be developed. Overall, these projects required an interdisciplinary team of chemists, ecotoxicologists, and environmental engineers.

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- [1] R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson, U. von Gunten, B. Wehrli, *Science* **2006**, *313*, 1072, <https://doi.org/10.1126/science.1127291>.
- [2] C. Ort, J. Hollender, M. Schaerer, H. Siegrist, *Environ. Sci. Technol.* **2009**, *43*, 3214, <https://doi.org/10.1021/es802286v>.
- [3] B. I. Escher, R. Baumgartner, M. Koller, K. Treyer, J. Lienert, C. S. McArdell, *Water Res.* **2011**, *45*, 75, <https://doi.org/10.1016/j.watres.2010.08.019>.
- [4] P. Falås, A. Wick, S. Castronovo, J. Habermacher, T. A. Ternes, A. Joss, *Water Res.* **2016**, *95*, 240, <https://doi.org/10.1016/j.watres.2016.03.009>.
- [5] J. Benner, D. E. Helbling, H.-P. E. Kohler, J. Wittebol, E. Kaiser, C. Prasse, T. A. Ternes, C. N. Albers, J. Aamand, B. Horemans, D. Springael, E. Walravens, N. Boon, *Water Res.* **2013**, *47*, 5955, <https://doi.org/10.1016/j.watres.2013.07.015>.
- [6] A. Joss, E. Keller, A. C. Alder, A. Göbel, C. S. McArdell, T. Ternes, H. Siegrist, *Water Res.* **2005**, *39*, 3139, <https://doi.org/10.1016/j.watres.2005.05.031>.
- [7] A. Joss, H. Siegrist, T. A. Ternes, *Water Sci. Technol.* **2008**, *57*, 251, <https://doi.org/10.2166/wst.2008.825>.
- [8] M. Boehler, B. Zwickelpflug, J. Hollender, T. Ternes, A. Joss, H. Siegrist, *Water Sci. Technol.* **2012**, *66*, 2115, <https://doi.org/10.2166/wst.2012.353>.
- [9] T. Ternes, A. Joss, 'Human Pharmaceuticals, Hormones and Fragrances - The Challenge of Micropollutants in Urban Water Management' IWA, London, **2006**, <https://doi.org/10.2166/9781780402468>.
- [10] C. von Sonntag, U. von Gunten, 'Chemistry of ozone in water and wastewater treatment. From basic principles to applications', IWA, London, **2012**, <https://doi.org/10.2166/9781780400839>.
- [11] S. Lim, J. L. Shi, U. von Gunten, D. L. McCurry, *Water Res.* **2022**, *213*, 118053, <https://doi.org/10.1016/j.watres.2022.118053>.
- [12] U. von Gunten, *Water Res.* **2024**, *253*, 121148, <https://doi.org/10.1016/j.watres.2024.121148>.
- [13] M. M. Huber, S. Canonica, G. Y. Park, U. von Gunten, *Environ. Sci. Technol.* **2003**, *37*, 1016, <https://doi.org/10.1021/es025896h>.
- [14] M. C. Dodd, M. O. Buffle, U. von Gunten, *Environ. Sci. Technol.* **2006**, *40*, 1969, <https://doi.org/10.1021/es051369x>.
- [15] T. A. Ternes, *Water Res.* **1998**, *32*, 3245, [https://doi.org/10.1016/S0043-1354\(98\)00099-2](https://doi.org/10.1016/S0043-1354(98)00099-2).
- [16] W. Giger, A. C. Alder, H.-P. E. Kohler, C. S. McArdell, E. Molnar, H. R. Siegrist, M. J.-F. Suter, *CHIMIA* **2003**, *57*, 485, <https://doi.org/10.2533/000942903777679064>.
- [17] Y. Lee, U. von Gunten, *Water Res.* **2012**, *46*, 6177, <https://doi.org/10.1016/j.watres.2012.06.006>.
- [18] M. Lee, S. G. Zimmermann-Steffens, J. S. Arey, K. Fenner, U. von Gunten, *Environ. Sci. Technol.* **2015**, *49*, 9925, <https://doi.org/10.1021/acs.est.5b00902>.
- [19] Y. Lee, U. von Gunten, *Environ. Sci. Technol.* **2016**, *2*, 421, <https://doi.org/10.1039/C6EW00025H>.
- [20] M. C. Dodd, D. Rentsch, H. P. Singer, H.-P. E. Kohler, U. von Gunten, *Environ. Sci. Technol.* **2010**, *44*, 5940, <https://doi.org/10.1021/es101061w>.
- [21] C. Prasse, M. Wagner, R. Schulz, T. A. Ternes, *Environ. Sci. Technol.* **2012**, *46*, 2169, <https://doi.org/10.1021/es203712z>.
- [22] R. Gulde, M. Rutsch, B. Clerc, J. E. Schollée, U. von Gunten, C. S. McArdell, *Water Res.* **2021**, *200*, 117200, <https://doi.org/10.1016/j.watres.2021.117200>.
- [23] R. Gulde, B. Clerc, M. Rutsch, J. Helbing, E. Salhi, C. S. McArdell, U. von Gunten, *Water Res.* **2021**, *207*, 117812, <https://doi.org/10.1016/j.watres.2021.117812>.
- [24] K. A. Kidd, P. J. Blanchfield, K. H. Mills, V. P. Palace, R. E. Evans, J. M. Lazorchak, R. W. Flick, *Proc. Natl. Acad. Sci. U. S. A.* **2007**, *104*, 8897, <https://doi.org/10.1073/pnas.0609568104>.
- [25] Y. Lee, B. I. Escher, U. von Gunten, *Environ. Sci. Technol.* **2008**, *42*, 6333, <https://doi.org/10.1021/es7023302>.
- [26] S. Suarez, M. C. Dodd, F. Omil, U. von Gunten, *Water Res.* **2007**, *41*, 2481, <https://doi.org/10.1016/j.watres.2007.02.049>.
- [27] M. C. Dodd, H.-P. E. Kohler, U. von Gunten, *Environ. Sci. Technol.* **2009**, *43*, 2498, <https://doi.org/10.1021/es8025424>.
- [28] H. Mestankova, B. Escher, K. Schirmer, U. von Gunten, S. Canonica, *Aquat. Toxicol.* **2011**, *101*, 466, <https://doi.org/10.1016/j.aquatox.2010.10.012>.
- [29] H. Mestankova, K. Schirmer, B. I. Escher, U. von Gunten, S. Canonica, *Environ. Pollut.* **2012**, *161*, 30, <https://doi.org/10.1016/j.envpol.2011.09.018>.
- [30] F. Lange, S. Cornelissen, D. Kubac, M. M. Sein, J. von Sonntag, C. B. Hannich, A. Golloch, H. J. Heipieper, M. Moder, C. von Sonntag, *Chemosphere* **2006**, *65*, 17, <https://doi.org/10.1016/j.chemosphere.2006.03.014>.
- [31] C. K. Schmidt, H.-J. Brauch, *Environ. Sci. Technol.* **2008**, *42*, 6340, <https://doi.org/10.1021/es7030467>.
- [32] U. von Gunten, E. Salhi, C. K. Schmidt, W. A. Arnold, *Environ. Sci. Technol.* **2010**, *44*, 5762, <https://doi.org/10.1021/es1011862>.
- [33] H. Mestankova, A. M. Parker, N. Bramaz, S. Canonica, K. Schirmer, U. von Gunten, K. G. Linden, *Water Res.* **2016**, *93*, 110, <https://doi.org/10.1016/j.watres.2015.12.048>.
- [34] C. Kienle, I. Werner, S. Fischer, C. Lüthi, A. Schifferli, H. Besselink, M. Langer, C. S. McArdell, E. L. M. Vermeirssen, *Water Res.* **2022**, *212*, 118084, <https://doi.org/10.1016/j.watres.2022.118084>.
- [35] S. A. Rath, U. von Gunten, *Water Res.* **2024**, *261*, 121917, <https://doi.org/10.1016/j.watres.2024.121917>.
- [36] M. S. Elovitz, U. von Gunten, H.-P. Kaiser, in 'Natural organic matter and disinfection by-products, Characterization and control in drinking water', Vol. ACS Symposium Series 761 (Eds.: S. E. Barrett, S. W. Krasner, G. Amy), American Chemical Society, Washington, DC., **2000**, <https://doi.org/10.1021/bk-2000-0761.ch016>.
- [37] M. S. Elovitz, U. von Gunten, H.-P. Kaiser, *Ozone Sci. Eng.* **2000**, *22*, 123, <https://doi.org/10.1080/01919510008547216>.
- [38] M. S. Elovitz, U. von Gunten, *Ozone Sci. Eng.* **1999**, *21*, 239, <https://doi.org/10.1080/01919519908547239>.
- [39] F. Hammes, E. Salhi, O. Koster, H. P. Kaiser, T. Egli, U. von Gunten, *Water Res.* **2006**, *40*, 2275, <https://doi.org/10.1016/j.watres.2006.04.029>.
- [40] T. Manasfi, J. Houska, I. Gebhardt, U. von Gunten, *Water Res.* **2023**, *237*, 119751, <https://doi.org/10.1016/j.watres.2023.119751>.
- [41] J. Houska, T. Manasfi, I. Gebhardt, U. von Gunten, *Water Res.* **2023**, *232*, 119484, <https://doi.org/10.1016/j.watres.2022.119484>.
- [42] D. Stalter, A. Magdeburg, J. Oehlmann, *Water Res.* **2010**, *44*, 2610, <https://doi.org/10.1016/j.watres.2010.01.023>.
- [43] J. Reungoat, B. I. Escher, M. Macova, F. X. Argaud, W. Gernjak, J. Keller, *Water Res.* **2012**, *46*, 863, <https://doi.org/10.1016/j.watres.2011.11.064>.

- [44] D. Stalter, A. Magdeburg, M. Wagner, J. Oehlmann, *Water Res.* **2011**, *45*, 1015, <https://doi.org/10.1016/j.watres.2010.10.008>.
- [45] J. E. Schollée, M. Bourgin, U. von Gunten, C. S. McArdell, J. Hollender, *Water Res.* **2018**, *142*, 267, <https://doi.org/10.1016/j.watres.2018.05.045>.
- [46] J. E. Schollée, J. Hollender, C. S. McArdell, *Water Res.* **2021**, *200*, 117209, <https://doi.org/10.1016/j.watres.2021.117209>.
- [47] F. Soltermann, C. Abegglen, C. Götz, U. von Gunten, *Environ. Sci. Technol.* **2016**, *50*, 9825, <https://doi.org/10.1021/acs.est.6b01142>.
- [48] C. M. Morrison, S. Hogard, R. Pearce, A. Mohan, A. N. Pisarenko, E. R. V. Dickenson, U. von Gunten, E. C. Wert, *Environ. Sci. Technol.* **2023**, *57*, 18393, <https://doi.org/10.1021/acs.est.3c00538>.
- [49] F. Soltermann, C. Abegglen, M. Tschui, S. Stahel, U. von Gunten, *Water Res.* **2017**, *116*, 76, <https://doi.org/10.1016/j.watres.2017.02.026>.
- [50] H. MacKeown, U. von Gunten, J. Criquet, *Water Res.* **2022**, *217*, 118417, <https://doi.org/10.1016/j.watres.2022.118417>.
- [51] S. D. Richardson, T. A. Ternes, *Anal. Chem.* **2022**, *94*, 382, <https://doi.org/10.1021/acs.analchem.1c04640>.
- [52] Y. Bichsel, U. von Gunten, *Environ. Sci. Technol.* **1999**, *33*, 4040, <https://doi.org/10.1021/es990336c>.
- [53] H. Bürgi, T. Schaffner, J. P. Seiler, *Thyroid* **2001**, *11*, 449, <https://doi.org/10.1089/105072501300176408>.
- [54] W. Gruber, L. von Känel, L. Vogt, M. Luck, L. Biolley, K. Feller, A. Moosmann, N. Krähenbühl, M. Kipf, R. Loosli, M. Vogel, E. Morgenroth, D. Braun, A. Joss, *Water Res.* **2021**, *13*, 100122, <https://doi.org/10.1016/j.wroa.2021.100122>.
- [55] J. Hoigné, H. Bader, W. R. Haag, J. Staehelin, *Water Res.* **1985**, *19*, 993, [https://doi.org/10.1016/0043-1354\(85\)90368-9](https://doi.org/10.1016/0043-1354(85)90368-9).
- [56] T. Manasfi, U. von Gunten, in prep.
- [57] Y. Schindler Wildhaber, H. Mestankova, M. Schärer, K. Schirmer, E. Salhi, U. von Gunten, *Water Res.* **2015**, *75*, 324, <https://doi.org/10.1016/j.watres.2015.02.030>.
- [58] P. Wunderlin, H. Mestankova, E. Salhi, Y. Schindler Wildhaber, M. Schärer, K. Schirmer, U. von Gunten, *Aqua Gas* **2015**, *28*, https://www.eawag.ch/fileadmin/Domain1/News/2015/0805/ozonierungstest_a_g.pdf.
- [59] C. Abegglen, M. Böhler, J. Hollender, S. G. Zimmermann, B. Zwicklenpflug, U. von Gunten, H. Siegrist, D. Thonney, *Gas Wasser Abwasser* **2010**, 587.
- [60] J. Hollender, S. G. Zimmermann, S. Koepke, M. Krauss, C. S. McArdell, C. Ort, H. Singer, U. von Gunten, H. Siegrist, *Environ. Sci. Technol.* **2009**, *43*, 7862, <https://doi.org/10.1021/es9014629>.
- [61] S. G. Zimmermann, M. Wittenwiler, J. Hollender, M. Krauss, C. Ort, H. Siegrist, U. von Gunten, *Water Res.* **2011**, *45*, 605, <https://doi.org/10.1016/j.watres.2010.07.080>.
- [62] Swiss Federal Authorities, https://www.fedlex.admin.ch/eli/cc/1998/2863_2863_2863/en, 2025.
- [63] Swiss Federal Authorities, <https://www.fedlex.admin.ch/eli/oc/2016/671/de>, 2016.
- [64] P. Wunderlin, R. Gulde, J. Bossard, *Aqua Gas* **2024**, *1*, 46, https://micropoll.ch/wp-content/uploads/2024/02/2024_AG_MV-aus-dem-haueslichenAbwasser_entfernen.pdf.
- [65] M. Bourgin, B. Beck, M. Boehler, E. Borowska, J. Fleiner, E. Salhi, R. Teichler, U. von Gunten, H. Siegrist, C. S. McArdell, *Water Res.* **2018**, *129*, 486, <https://doi.org/10.1016/j.watres.2017.10.036>.
- [66] A. Wittmer, A. Heisele, C. S. McArdell, M. Böhler, P. Longree, H. Siegrist, *Water Sci. Technol.* **2015**, *71*, 980, <https://doi.org/10.2166/wst.2015.053>.
- [67] N. Walpen, A. Joss, U. von Gunten, *Water Res.* **2022**, *209*, 117858, <https://doi.org/10.1016/j.watres.2021.117858>.
- [68] C. Abegglen, S. Beier, J. Pinnekamp, C. Mauer, H. Siegrist, *Gas Wasser Abwasser* **2011**, 479.
- [69] I. Logar, R. Brouwer, M. Maurer, C. Ort, *Environ. Sci. Technol.* **2014**, *48*, 12500, <https://doi.org/10.1021/es502338j>.
- [70] VSA Platform Process Engineering Micropollutants: www.micropoll.ch.
- [71] R. Gulde, P. Wunderlin, I. Wittmer, T. Doppler, *Aqua Gas* **2024**, *3*, 36, https://www.aquaetgas.ch/wasser/gew%C3%A4sser/20240229_arzneimittel-in-gew%C3%A4ssern/
- [72] EUR-Lex, <https://eur-lex.europa.eu/eli/dir/2024/3019/oj>, **2024**.

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