Juliane Hollender,
chemist and head of the
Environmental Chemistry
department.
Co-author: Beate Escher

Eliminating micropollutants: efficiency assessment

Various ways of upgrading wastewater treatment plants so as to enhance the elimination of micropollutants are currently being considered. But what chemical and biological indicators can be used to evaluate the effectiveness of additional treatment steps?

To eliminate micropollutants at wastewater treatment plants (WWTPs), it is not sufficient merely to install appropriate systems (see the article by Christian Abegglen on p. 25) – their effectiveness and any shortcomings need to be assessed in order to optimize the processes. In the case of WWTPs, it is necessary to define chemical and biological measurement methods that can be used to evaluate the efficiency of the additional treatment steps. To date, individual substances or selected biological effects have been measured in a relatively arbitrary manner. Our aim, therefore, was to propose a set of general, cost-efficient methods of evaluation providing meaningful results for future assessments of treatment performance. Our work was carried out as part of a pilot study on ozonation with subsequent sand filtration at the Wüeri WWTP in Regensdorf [1]. At the same time, our study was designed to estimate the elimination efficiency of the additional ozonation step.

Parameters determined in the ozonation pilot study at the Wüeri WWTP in Regensdorf.

Parameters	Test substances/assays	Function/indicator substances/toxicity endpoints
General WWTP parameters	Chemical and biological oxygen demand, undissolved substances, DOC, nitrogen species	WTTP characterization
Micropollutants	▶ 53 substances with continuous input	Pharmaceuticals, biocides
	▶ Biologically active substances	Estrogens (estrone)
	▶ Additional 180 substances	Broad spectrum
	▶ Reaction products of ozonation	Nitrosamines, bromate
Toxicity (mode of action-based assays)	▶ Bioluminescence assay	Non-specific toxicity
	▶ Combined algal assay	Non-specific (growth inhibition) and specific (photosynthesis inhibition) toxicity
	▶ Yeast estrogen screen	Estrogenic effects
	▶ Acetylcholinesterase inhibition	Neurotoxic effects
	▶ umuC assay	Genotoxic effects

Broad range of parameters. In defining the parameters to be assessed, the approach we adopted was to start with a broad range of measurements and then narrow these down for future assessments on the basis of the experience accumulated (Table). As well as general WWTP parameters, therefore, we determined firstly the concentrations of a wide variety of micropollutants, e.g. pharmaceuticals and biocides, which enter the WWTP continuously in wastewater and whose loads are influenced by the newly installed treatment processes. We also investigated the formation of two known by-products of ozonation – nitrosamines and bromate. Secondly, we used various bioassays to determine the general and specific toxicity of the micropollutants contained in the water [2–3]. This makes it possible not only to gain an impression of how overall contamination with micropollutants is reduced, but also to identify specific, particularly problematic effects, such as estrogenicity, neurotoxicity and genotoxicity.

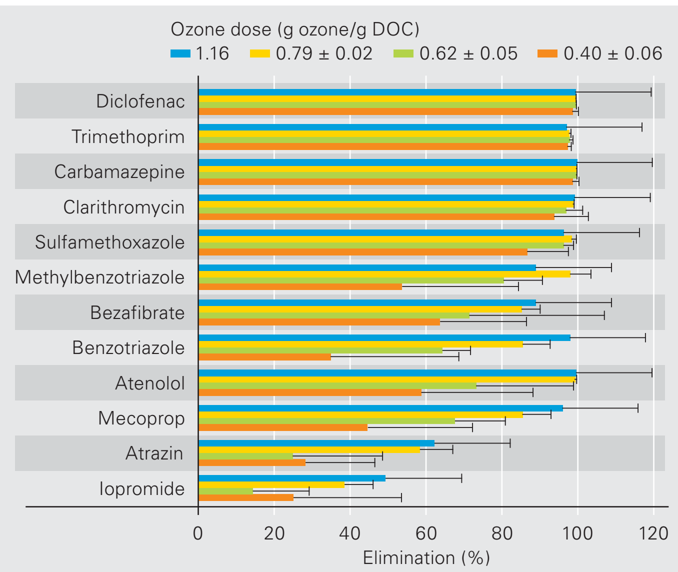
Reduction of micropollutants in the Furtbach due to ozonation. Initially, we studied a total of 53 indicator substances. On account of their polarity, these are mainly found in the aqueous phase, they are highly persistent in the WWTP and in some cases they have been shown to be biologically active. Substances were selected which are oxidized by ozone at different rates, owing to their different functional groups. The degree of oxidation depends on the reactivity of a substance with ozone and on the ozone dose (Fig. 1) which is available for oxidation and does not react with other constituents of wastewater. As well as ozone itself, continuously generated OH radicals play an important role as oxidizing agents. They are less specific oxidants than ozone and generally exhibit very high rate constants for reactions with micropollutants. Accordingly, in spite of their short lifetime and low concentrations, they can contribute markedly to the oxidation of a micropollutant. This applies in particular to micropollutants that lack a high degree of reactivity with the highly selective ozone.

The intermediate ozone dose (0.6 g O_3 per gram dissolved organic carbon (DOC)) leads to a significant reduction in the number of substances detected above the limit of quantification in the WWTP effluent. Only 16 of the 53 substances studied were found in concentrations of more than 15 ng/l. In the case of substances which are more recalcitrant to ozone (e. g. mecoprop, benzotriazole and atenolol), concentrations were clearly reduced. The antibiotics investigated were eliminated completely, but contrast agents only partly. After the biological step, estrogens only occur in concentrations below 6 ng/l and were completely eliminated with the intermediate ozone dose (detection limit 0.1–2.5 ng/l). This is in agreement with the ecotoxicological analysis based on the yeast estrogen screen (YES), which indicates a substantial reduction of estrogenic activity (see below).

In order to gain an overview of the behaviour of an even broader spectrum of micropollutants during ozonation, screening – using high-resolution mass spectrometry – was expanded to cover approximately 180 additional substances. The range of compounds studied comprises of pesticides, pesticide transformation products, biocides, anticorrosive agents, pharmaceuticals and their metabolites, and food additives – all substances that are used in relatively large quantities in Switzerland or the EU and thus potentially to be found in the environment.

Of the 180 substances, 25 were detected in concentrations of more than 15 ng/l in the secondary effluent, but most of these were effectively eliminated in the course of ozonation with the intermediate ozone dose. Among the substances less well removed were the artificial sweetener sucralose and the antiepileptic drug levetiracetam.

Fig. 1: Influence of ozone dose on the elimination of selected persistent micropollutants in the ozonation step.



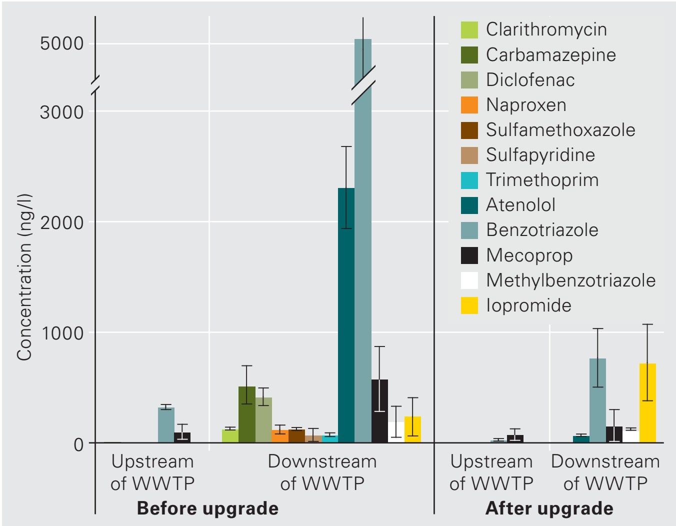


Fig. 2: Comparison of dry-weather water quality in the Furtbach upstream and downstream of the WWTP before and after installation of the ozonation system. The dose applied in the ozonation step was 0.62 ± 0.05 g ozone per gram DOC.

The additional treatment step thus substantially improves water quality in the Furtbach stream (Fig. 2). As a result of ozonation, input of micropollutants to the Furtbach from the WWTP are reduced by 70 %. The total reduction in input of micropollutants to the stream amounts to 27 kg per year, with benzotriazole accounting for 7.5 kg, atenolol 2.6 kg, diclofenac 2.4 kg, mecoprop 1.3 kg and carbamazepine 1.1 kg.

Nitrosamines and bromate: problematic by-products of ozonation? It is known that, during the ozonation process, carcinogenic nitrosamines can be formed from organic nitrogen compounds, and bromate from bromide. For this reason, concentrations of eight nitroso compounds over time were studied at the WWTP. Of the nitrosamines measured, three were not found above the detection limit of approx. 1 ng/l, while the rest were detected in the low nanogram-per-litre range. Significant quantities of NDMA (5–15 ng/l) are formed during ozonation, but on average 50 % is eliminated again in the subsequent sand filtration step.

As yet, no generally accepted limits exist for nitrosamines in surface, ground or drinking water. Based on toxicology data, the concentration of NDMA in drinking water associated with a lifetime cancer risk of one in one million is 0.7 ng/l (EPA, IRIS database). At the same time, however, depending on food composition, significant amounts of nitrosamines can also be formed in the body and excreted in urine [4].

Concentrations of bromide in wastewater at the Wüeri treatment plant were found to be typical of municipal wastewater – under dry weather conditions, ≤30 µg/l after the ozone step. Samples collected at various points in the ozone reactor showed that even with an ozone dose of 1.2 g O_3 per gram DOC the limit of 10 µg/l specified for bromate in drinking water is not exceeded.

In conclusion, it can be said that both nitrosamines and bromate are formed during the ozonation of municipal waste-

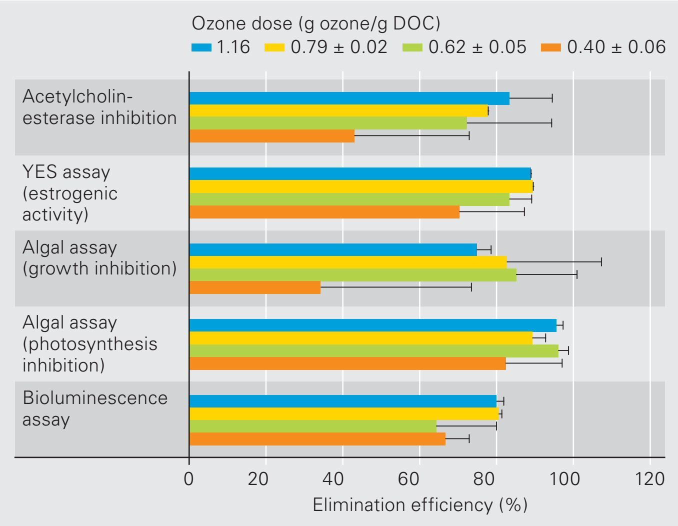


Fig. 3: Elimination efficiency of ozonation (including sand filtration), as determined by various mode of action-based test systems.

water. However, the concentrations of these problematic products are very low and thus do not raise any concerns; nonetheless, they should be assessed again for wastewater of different composition.

Toxicity reduced by ozonation. The fact that ozonation including sand filtration improves the treatment performance of the WWTP is also demonstrated by the toxicity tests (Fig. 3) [2–3]. As the ozone dose increases, the toxicity of the water studied is reduced. Thus, with the bioluminescence and the algal growth inhibition tests, non-specific toxicity was found to decrease by 40–80 %. In addition, specific toxic effects are also reduced: inhibition of photosynthesis (combined algal assay) – as induced by atrazine, for example – is reduced by 70–90 %, and neurotoxicity (acetylcholinesterase inhibition) – caused by insecticides such as diazinon – decreases by 60–80 %.

Before ozonation, the YES assay indicates concentrations of over 1 ng/l estradiol equivalents in water – a level proposed as a mode of action and bioassay-based limit for estrogenicity. Ozonation reduced the estrogenic effects by more than 95 %, which correlates well with the results of trace analysis. It would even be worth considering whether costly trace analysis for estrogenic substances cannot be replaced by a sensitive and inexpensive bioassay procedure.

All the samples from the primary clarifier showed marked genotoxicity, although the samples had to be highly concentrated. While this effect is already reduced in the biological step, it only disappears almost completely after ozonation. This also shows that ozonation does not lead to the formation of significant amounts of genotoxic substances.

As well as these test batteries focusing on micropollutants, the University of Frankfurt carried out tests involving aquatic organisms as part of the EU project Neptune. In rainbow trout and annelids, adverse effects on development, reproduction and biomass production were observed after ozonation; however, these disappeared after subsequent sand filtration. Ozonation should therefore always be followed by a sand filtration step as an additional barrier [1].

Future evaluation: trace analysis for selected substances combined with toxicity tests. The installation of the ozonation system enhanced the reduction of organic micropollutant concentrations and effects in WWTP effluents. Even an ozone dose of 0.6 g O_3 per gram DOC (approx. 3 mg/l) increased the elimination efficiency of the WWTP for the broad range of substances investigated by an average of 40–50 %. As a result, toxicity detected with the aid of bioassays was also reduced.

While screening for more than 200 substances was worthwhile and relevant in the context of this research project, it would generally be too costly for monitoring purposes. Based on consumption data, the properties of micropollutants and their behaviour in the various WWTP treatment steps, a subset of six substances was selected for integration into future assessment efforts – i. e. carbamazepine, diclofenac, sulfamethoxazole, benzotriazole, mecoprop and estrone. These substances are particularly suitable for the evaluation of additional measures such as ozonation and powdered activated carbon adsorption.

Although the results of trace analysis often correlated well with less costly mode of action-based bioassays, chemical analysis remains indispensable. It makes it possible to calculate reductions in pollutant loads – values that could subsequently be relevant for the specification of legal requirements. To gain a better overall evaluation and ensure that substances with significant effects are not overlooked, selected bioassays should be used in combination with trace analysis for the assessment of effectiveness. ○ ○ ○

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