



# QUATERNARY TREATMENT FOR WASTEWATER TREATMENT PLANTS IN LIGHT OF THE PROPOSED NEW URBAN WASTEWATER TREATMENT DIRECTIVE

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## Abstract

The proposed new Urban Wastewater Treatment Directive imposes quaternary treatment to ensure the elimination of a large spectrum of micropollutants. Accordingly, WWTPs  $\geq 100,000$  p.e. as well as WWTPs  $\geq 10,000$  p.e. that discharge to micropollutant-sensitive areas have to be upgraded to reach 80% elimination calculated for specific indicators over the entire wastewater treatment process. Estimations for Austria range from 56 to 241 WWTPs to be upgraded. The interrelationship with other EU legislation bears both synergies, e.g., for water reuse, and challenges, e.g., for the newly proposed stricter environmental quality standards for the forever chemicals PFAS.

**Keywords:** activated carbon treatment, micropollutants, ozonation, quaternary treatment, risk-based approach, urban wastewater treatment directive.

## 1. INTRODUCTION

The proposed new Urban Wastewater Treatment Directive (UWWTD) (COM(2022) 541 final) published in October 2022 sets stricter rules for wastewater treatment in Europe. Amongst others, quaternary treatment is required to eliminate the broadest possible spectrum of micropollutants. The treatment is imposed both on a precautionary (Art. 8.1) and risk-based (Art. 8.2 and 8.4) approach. Consequently, large wastewater treatment plants treating a load of 100,000 population equivalents (p.e.) and above, as well as plants  $\geq 10,000$  p.e. that discharge to micropollutant-sensitive areas, shall be upgraded following an ambitious implementation plan. Micropollutant-sensitive areas have to be identified by the Member States, and unless disproved by risk assessment the list of areas shall cover water bodies used for the abstraction of water for human consumption, bathing waters, lakes, rivers with a dilution ratio below 10, areas with aquaculture, and water bodies where the environmental quality standards are exceeded (link to water framework directive: Directives 2000/60/EC and 2008/105/EC), compare Table 1.



A minimum of 80% elimination over the entire treatment process, i.e., conventional (biological) and advanced (quaternary) treatment, has to be achieved. The elimination is determined based on at least six out of twelve indicator substances, primarily pharmaceuticals, listed in Table 3 of Annex I (part B). The twelve substances are equal to the indicators applied in Switzerland and accordingly, indicators are categorized based on their removal potential: category 1 covers eight substances that can be very easily eliminated and category 2 covers four substances that can be easily eliminated, see Table 1. When calculating the average removal, the number of substances from category 1 should be twice the number of substances from category 2.

## 2. ESTABLISHED TREATMENT TECHNOLOGIES

Ozonation and activated carbon treatment proved to be established methods for micropollutant removal during numerous pilot studies and meanwhile also full-scale applications (Mišik et al., 2020; Pistocchi et al., 2022; Rizzo et al., 2019; Schaar et al., 2010; Slipko et al., 2022). Platforms in Switzerland<sup>1</sup> and in Germany, Baden Württemberg<sup>2</sup>, offer visualizations of the implementation status distinguishing between ozonation and activated carbon as well as plants operation, under construction, and in the planning phase, respectively. Both activated carbon and ozone are suitable to remove a large spectrum of micropollutants and indicators are removed very easily (category 1) and easily (category 2), cp. Table 1.

**Table 1:** Indicator substances categorised according to their removal potential during quaternary treatment.

Category	Indicator substance	Elimination by AC	Elimination by O <sub>3</sub>
Category 1: very well adsorbable and oxidizable	Amisulpride	Blue	Blue
	Carbamazepine	Blue	Blue
	Citalopram	Blue	Blue
	Clarithromycin	Blue	Blue
	Diclofenac	Blue	Blue
	Hydrochlorothiazide	Blue	Blue
	Metoprolol	Blue	Blue
	Venlafaxine	Blue	Blue
Category 2: well adsorbable and oxidizable	Benzotriazole	Green	Green
	Candesartan	Green	Green
	Irbesartan	Green	Blue
	Mix of 4-Methyl- and 6-Methylbenzotriazole	Green	Green

Legend: AC - activated carbon treatment; O<sub>3</sub> - ozonation.  
 Colour legend: blue... > 80%; green... 50-80% removal during quaternary treatment).

Activated carbon is characterized by a high adsorption capacity due to its high inner surface (600-1,500 m<sup>2</sup>/g) and high porosity (300-1,500 mm<sup>3</sup>/g). More polar substances have a higher affinity due to the hydrophobic surface of the activated carbon. Non-polar substances are less adsorbed as well as high molecular substances that are too big for the micropores.

Activated carbon can be applied in two forms, as a powder (PAC) and in granular form (GAC). PAC can be added to the biological reactor or the secondary clarifier of WWTPs. GAC is usually applied as a fixed-bed filter after the secondary or tertiary treatment of WWTPs, but can also be applied as a pressure filter. GAC can be regenerated to extend its service life and reduce operational costs.

Ozonation is a chemical oxidation process, which can effectively oxidize a wide range of organic micropollutants acting via two major oxidants: directly via the selective oxidation of ozone, and indirectly via unselective hydroxyl radicals generated during the direct oxidation of the organic matrix. The formation of oxidation by-products or transformation products is regarded as potentially problematic and consequently, it is recommended to be coupled with a biologically active post-treatment. NDMA, one of the relevant oxidation by-products can be degraded in a biological post-treatment. Bromate is another relevant oxidation by-product, however, it cannot be removed by post-treatment. Thus, wastewater should be analysed for bromide before implementing ozonation. At bromide concentrations above 150 µg/L, bromate formation can become an issue and should be investigated in advance.

<sup>1</sup> <https://micropoll.ch/Mediathek/karte-der-ara-mit-mv-stufe/>

<sup>2</sup> <https://dwa-bw.maps.arcgis.com/apps/webappviewer/index.html?id=2428880b396f4a21a6123b3fb87feb8b>



A multibarrier approach, combining ozonation with a subsequent GAC filter entails synergies for micropollutant removal and biological post-treatment.

Costs vary depending on treatment size and applied technologies. Based on published costs data Pistocchi et al. (2022) suggested an estimation of the total annualized costs in [€/p.e./yr] as  $1,000 \times p.e.^{-0.45}$ , with p.e. representing the plant capacity. This simple function can capture the costs within a factor of 2.

### 3. ESTIMATIONS FOR AUSTRIA

Estimations on the number of Austrian WWTPs to be upgraded for compliance with Article 8.1 and 8.2 and 8.4, respectively, are presented in Table 2. The data is extracted from the electronic register for the determination of essential surface water body pollutants emitted by specified point sources (data from 2020, EMREG-OW database). The numbers are estimated based on the design capacity. According to Art. 8.1, 37 large WWTPs have to be upgraded. For micropollutant-sensitive areas (Art. 8.2a-f) two scenarios were calculated with regard to the environmental quality standards (EQS) directive (2008/105/EC), Art. 8.2f. While the current EQS do not require additional treatment, the proposed new EQS<sup>3</sup> will result in a nationwide upgrade of 241 WWTPs due to the exceedance of certain substances and substance groups, amongst others e.g., bisphenol A or PFAS. Summing up Art. 8.1 and 8.2 requirements, 93 and 278 WWTPs will have to be upgraded, depending on the EQS considered. This corresponds to 65 and 92% of the Austrian WWTP capacity, of which 57% is covered by large WWTPs.

**Table 2:** Estimations on the number of Austrian WWTPs to be upgraded with quaternary treatment.

WWTPs $\geq$ 100,000 p.e. design capacity (Art. 8.1)	37
WWTP $\geq$ 10.000 – 99,999 p.e. design capacity (Art. 8.2a-f)	
a) drinking water supply	0 / 8*
b) bathing waters	19
c) lakes	5
d) dilution ratio $<10$	37
e) aquaculture activities	no data
f1) areas with EQS-exceedance (current EQS-directive)	0
f2) areas with EQS-exceedance (proposal 2022)	241
<b>Sum Art. 8.1 + 8.2 (current EQS)</b>	<b>93</b>
<b>Sum Art. 8.1 + 8.2 (EQS-proposal 2022)</b>	<b>278</b>

\* 8 WWTPs when the river Rhine catchment is taken into account. To date, river bank filtration is not accounted for in the estimations

3 Proposal for a Directive amending the Water Framework Directive, the Groundwater Directive and the Environmental Quality Standards Directive: [https://environment.ec.europa.eu/publications/proposal-amending-water-directives\\_en](https://environment.ec.europa.eu/publications/proposal-amending-water-directives_en).

In order to guarantee effective measures to tackle the issue of micropollutants in the aquatic environment, the final decision on the WWTPs to be upgraded (number and location) will need further consideration on the catchment area level. In this context, emission modelling of micropollutants in river basin catchment areas e.g., as demonstrated by Zoboli et al. (2019), is a necessary tool to assess the effectiveness of measures such as quaternary treatment on the immission situation. It can help to reveal the cumulative effect of upgrading multiple WWTPs but also distinguish between diffuse versus point sources.

### 4. OUTLOOK AND CONCLUSIONS

The interrelationship with other current water-related EU legislation and proposals bears both synergies and challenges.

Synergies occur e.g., with regulation (EU) 2020/7411 on minimum requirements for water reuse (for agricultural irrigation) since to date, micropollutant removal is not intrinsically required by this regulation.

Considering the contribution of WWTPs to climate and energy goals, the biological methanation of CO<sub>2</sub> from biogas using hydrogen can play a significant role. Hydrogen is produced by electrolysis and the simultaneously produced oxygen could act as a feed gas for ozone generation.

Challenges have been mentioned in the context of the newly proposed EQS for PFAS. PFAS are not removed during biological treatment and the forecasted EQS exceedance will require additional treatment (Art. 8.2f). Ozonation, however, does not eliminate PFAS, while activated carbon is more suitable. While both technologies have their strengths and weaknesses, this is a further argument to follow the multibarrier approach of ozonation combined with granular activated carbon. The impact of quaternary treatment on PFAS concentrations in surface waters presents a suitable example for emission modelling.

In conclusion, quaternary treatment for WWTPs is a necessary and feasible option to meet the challenges posed by the proposed new UWWTD (COM(2022) 541 final), which aims to protect the environment and human health from the adverse effects of wastewater discharge. Ozonation and activated carbon are two effective quaternary treatment technologies that can remove a wide range of micropollutants from wastewater, but they also have some drawbacks that need to be addressed by further research and optimization. Quaternary treatment should be integrated with other conventional and innovative processes to achieve a holistic and sustainable wastewater management system.

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