



**CWPharma**  
CLEAR WATERS FROM PHARMACEUTICALS

# Guideline for advanced API removal

**GoA3.4: Optimization and control of advanced treatment**

**December 2020**



EUROPEAN  
REGIONAL  
DEVELOPMENT  
FUND

## **Authors**

Stapf, Michael (KWB – Berlin Centre of Competence for Water)

Miehe, Ulf (KWB)

Bester, Kai (AU – Aarhus University)

Lukas, Marcus (UBA – German Environment Agency)

## **Contributors**

Zhiteneva, Veronika (KWB)

Sehlén, Robert (TVAB – Tekniska verken i Linköping AB)

Larsen, Sille Bendix (KU – Kalundborg Utility)

Lember, Erki (EVEL – Estonian waterworks association)

## **Chapter contributions (institution):**

- At a glance (AU, KWB)
- Introduction (KWB, AU)
- Ozonation (KWB, UBA, AU)
- Activated carbon (KWB)
- Moving bed biofilm reactors (AU)
- Monitoring of ozonation and AC processes (KWB, UBA)
- API removal by ozone and activated carbon (KWB)
- Implementation of an API elimination stage (KWB, AU)

## **Financing**

This report was financed by the European Union, Interreg Baltic Sea Region, European Regional Development Fund.

# List of abbreviations

AC	Activated carbon
API	Active pharmaceutical ingredient
AWT	Advanced wastewater treatment
BOD	Biochemical oxygen demand
BV	Bed volume
CAPEX	Capital expense
CAS	Conventional activated sludge
CFD	Computational fluid dynamics
CO <sub>2,eq</sub>	Carbon dioxide equivalent
COD	Chemical oxygen demand
COD <sub>dis</sub>	Dissolved chemical oxygen demand
DOC	Dissolved organic carbon
DPD	N,N-Diethyl-p-phenylendiamin
EBCT	Empty bed contact time
fDOM	Fluorescent dissolved organic matter
GAC	Granular activated carbon
GWP	Global warming potential
HRT	Hydraulic retention time
K <sub>O<sub>3</sub></sub>	Reaction rate constant with ozone
K <sub>OH</sub>	Reaction rate constant with hydroxyl radicals
LOX	Liquid oxygen
MBBR	Moving bed biofilm reactor
MTZ	Mass transfer zone
NDMA	N-Nitrosodimethylamine
NF	Nanofiltration
NO <sub>2</sub> <sup>-</sup>	Nitrite ion
OBP	Oxidation by-product
OH-radicals	Hydroxyl radical
OPEX	Operating expense
PAC	Powdered activated carbon
PE	People equivalent
PSA	Pressure swing adsorption
RO	Reverse osmosis
RSSCT	Rapid small-scale column tests
TP	Transformation product
TSS	Total suspended solids
UVA <sub>254</sub>	Ultraviolet absorbance at 254 nm
WWTP	Wastewater treatment plant
ΔUVA <sub>254</sub>	Relative reduction of UVA <sub>254</sub>

# Table of contents

At a glance.....	5
Introduction.....	6
Ozonation .....	7
Basics .....	7
Relevant water quality parameters .....	8
Transformation and oxidation by-products .....	9
Ecotoxicity.....	9
Full-scale ozonation at WWTPs.....	11
Operational aspects .....	13
Activated carbon.....	15
Basics .....	15
Relevant water quality parameters for activated carbon processes.....	15
Full-scale PAC at WWTPs .....	16
Full-scale GAC at WWTPs.....	19
Moving bed biofilm reactors (MBBR).....	22
Basics .....	22
Relevant water quality parameters .....	22
Full-scale MBBR at WWTPs.....	22
Monitoring of ozonation and AC processes .....	24
API removal by ozone and activated carbon.....	26
Process combinations .....	26
Carbon footprint .....	27
Costs .....	27
Implementation of an API elimination technology .....	29
WWTP fitness check .....	29
Feasibility study .....	30
Detailed planning .....	31
Optimizing existing systems .....	32
References .....	34
Appendix.....	38

# At a glance

## Ozonation

Relies on the substance specific reaction with ozone in the water phase. Typical applied ozone doses used for the elimination of active pharmaceutical ingredients (APIs) alter the molecule structure of the organic compounds, but do not result in their mineralisation. Formed transformation and oxidation by-products are often associated with negative ecotoxicological effects (e.g. mutagenic effects). However, many of the formed substances are more biodegradable than the original substance and can be removed by a mandatory biological post-treatment.

## Activated carbon

Relies on the adsorption of APIs onto the very large inner surface of activated carbon (AC). Activated carbon can be used in either a powdered (PAC) or granulated (GAC) form, which require different process schemes. PAC is directly mixed into the water flow and requires a final filtration stage to avoid any PAC entering the receiving water body. For a more efficient usage, PAC that is rejected by the filtration stage can be transferred to the main biological treatment stage, where it is removed along with the excess sludge. In that case, excess sludge cannot be applied on agricultural land, and must be incinerated instead. GAC treatment is very common in drinking water production and can be applied as filter material in filters. When treating WWTP effluent, GAC will become loaded with the APIs and over time API removal efficiency will decrease. When the API elimination target cannot be achieved anymore, loaded GAC material has to be replaced by new GAC. The loaded GAC can either be regenerated or incinerated. The production of activated carbon is associated with a high carbon footprint.

## Biofilm (e.g., moving bed biofilm reactors (MBBR))

Biofilms are able to metabolise APIs including many that are not degradable in conventional WWTPs. Similar to ozonation, this technology is a reactive technology, meaning that APIs can be either mineralised, incorporated in the biomass or released as transformation products. MBBRs consume energy only via aeration, but require large basins to provide sufficient time for biological processes. So far, full-scale MBBRs in the context API removal are only used as ozonation post-treatment and require further development before they can be recommended as a standard option for API removal.

Table 1: Schematic evaluation of the different API removal technologies: ozonation, granular activated carbon (GAC), powdered activated carbon (PAC), and moving bed biofilm reactor (MBBR). Categories are very good (++), good (+), average (0), and bad/negative (-). It should be noted that API removal with the different technologies is always substance specific, thus, evaluation will strongly depend on the targeted substances. #Final costs are very site specific.

Category	Ozone	GAC	PAC	MBBR	
API removal	++	++	++	0	+
Technology maturity for API elimination	++	++	++	-	
Process complexity	+	++	0	+	
Reaction products from the water matrix	-	++	++	++	
Transformation products or metabolites	-	++	++	-	
Costs <sup>#</sup>	+	+	+	0	
Operational energy required	-	+	0	+	+
Carbon footprint	0	0	-		+
Space requirement	++	+	-	++	-
Subsequent sludge application in agriculture	++	++	-		++

# Introduction

The overall aim of the “Clear Waters from Pharmaceuticals” (CWPharma) project, which was funded by EU’s Interreg Baltic Sea Region programme, is to provide guidance on how to reduce the load of active pharmaceutical ingredients (APIs) entering the aquatic environment and especially the Baltic Sea. Even though different methods for reducing the amount of APIs entering the wastewater exist<sup>1, 2</sup>, API usage cannot be completely avoided and, thus, “end-of-pipe” measures are also necessary.

Municipal wastewater treatment plants (WWTPs) are relevant point sources of APIs as they treat the wastewater from public households, hospitals, and industry of the connected catchment area. However, conventional “state-of-the-art” WWTPs can only remove APIs that are either easily biodegradable and/or absorbable to activated sludge, whereas others can pass the treatment process with no or only minor reductions. Therefore, reduction of a broad range of APIs can only be achieved by using targeted advanced wastewater treatment (AWT) techniques, such as ozonation or application of powdered and granular activated carbon. All of these technologies for API removal are already used at full-scale WWTPs and have proven their practical and economical suitability.

This guideline is meant to provide an overview on how to plan, start, and operate AWT technologies for API elimination. The recommendations are based on the experiences and results from the CWPharma project, but also on the available knowledge from Germany and Switzerland, which is collected and distributed by competence centres such as the German Micropollutants Competence Centre Baden-Württemberg (KomS)<sup>1</sup> and the Swiss Plattform Verfahrenstechnik Mikroverunreinigungen<sup>2</sup> as well as by expert groups from the related water associations.

Membrane separation via dense membrane such as nanofiltration (NF) or reverse osmosis (RO) was not considered in this guideline, as both technologies produce a brine with high API concentrations. At coastal WWTPs, this brine might be discharged directly to the sea in order to protect fresh water ecosystems, but this would not reduce the API load to the Baltic Sea. Thus, the brine also requires treatment, which makes this approach less economical in comparison to the other established API removal technologies.

---

<sup>1</sup> Kompetenzzentrum Spurenstoffe Baden-Württemberg, <https://koms-bw.de/en/>

<sup>2</sup> VSA Plattform Verfahrenstechnik Mikroverunreinigungen, <https://micropoll.ch/>

# Ozonation

The following sections give a brief overview on the basics of ozonation, relevant water quality parameters, and the formation of transformation and oxidation by-products. In addition, ecotoxicological aspects are addressed. Finally, technical application of ozonation at full-scale is described along with details regarding operational aspects.

## Basics

Ozone is a powerful oxidant, 10-times more soluble in water than oxygen<sup>3</sup>, and is widely used during drinking water treatment. Ozone can be used for the elimination of APIs and other xenobiotic substances, disinfection, as well as for odour and colour removal. Due to its high reactivity, ozone is not stable over a long period of time, and must be produced on site. The application of ozone in water also results in the formation of hydroxyl-radicals ( $\cdot\text{OH}$ ), which are an even more powerful oxidant than ozone. In general, higher ozone doses result in an increased formation of OH-radicals. Although both oxidants are linked to each other they exhibit different behaviour. Ozone reacts primarily with molecule structures that have a high electron density (e.g. double bonds, amines, etc.), which is also reflected in reaction rate constants ( $K_{\text{O}_3}$ ), which vary over several magnitudes ( $< 1$  to  $10^6 \text{ M}^{-1}\text{s}^{-1}$ ). In contrast, OH-radical reactions are much faster, but less specific. Thus, reaction rate constants ( $k_{\text{OH}}$ ) of most APIs are in the same order of magnitude ( $10^9 \text{ M}^{-1}\text{s}^{-1}$ ). The overall API elimination by the ozonation is therefore the combined result of individual APIs reacting with both ozone and OH-radicals. Generally, APIs can be grouped according to their reaction rate constants (Table 2), which can be found in the literature for many APIs<sup>3</sup>. Reasonable elimination can be expected for APIs that show a sufficient reactivity with ozone (group I and II) and/or OH-radicals (group III). APIs in groups IV and V should not be targeted by ozonation.

Table 2: Example of APIs grouped by their reactivity with ozone ( $K_{\text{O}_3}$ , here at pH 7) and OH-radicals, respectively<sup>4</sup>.

Group	Compound	$K_{\text{O}_3} (\text{M}^{-1}\text{s}^{-1})$	$K_{\text{OH}} (\text{M}^{-1}\text{s}^{-1})$	Reactant
I	Carbamazepine Diclofenac Sulfamethoxazole Trimethoprim	$K_{\text{O}_3} \geq 10^5$	-	Primarily ozone
II	Benzotriazole Bezafibrat Clarithromycin Gabapentin	$10 \leq K_{\text{O}_3} < 10^5$	-	Ozone as well as OH-radicals
III	Ibuprofen Oxazepam Phenytoin Primidon	$K_{\text{O}_3} < 10$	$K_{\text{OH}} > 5 \cdot 10^9$	Primarily OH-radicals
IV	Fluconazole Iopromide Levetiracetam	$K_{\text{O}_3} < 10$	$10^9 \leq K_{\text{OH}} < 5 \cdot 10^9$	Primarily OH-radicals, but less reactivity with APIs than APIs of group III
V	TCEP	$K_{\text{O}_3} < 10$	$K_{\text{OH}} < 10^9$	No relevant reactivity with ozone or OH-radicals

Wastewater ozonation is distinct from the ozonation used for drinking water, groundwater or surface water due to different water matrices and targets (e.g. API elimination or disinfection). Ozone depletion in wastewater is much faster and OH-radicals are primarily formed from the reaction with the bulk organic background. Therefore, wastewater ozonation is intrinsically a so-called advanced oxidation process, even without addition of hydrogen peroxide<sup>5</sup>.

## Relevant water quality parameters

In this section, the impact of select water quality parameters on wastewater ozonation are briefly described.

**Dissolved organic carbon (DOC)** reflects the overall amount of dissolved organic compounds in the wastewater, which also includes the target APIs. Required ozone dose for API elimination depends on the DOC concentration at the ozonation influent, which can be estimated online by using  $UVA_{254}$  as surrogate parameter. At commonly applied ozone doses for API elimination, ozonation increases the biodegradability of the DOC, but does not result in its mineralization (no significant change by ozonation alone). In combination with biological post-treatment, DOC reductions of about 15 - 20% have been observed (deep-bed filters)<sup>6</sup>.

**Chemical oxygen demand (COD)** represents the amount of oxygen that can be consumed by the oxidation of organic and inorganic compounds. In contrast to the DOC, ozonation can reduce the COD by 12% - 17%<sup>6</sup>. In combination with biological post-treatment, an overall COD reduction of 20% - 40% can be achieved<sup>6</sup>.

**Nitrite ( $NO_2^-$ )** is transformed into nitrate during the ozonation process. The reaction is very fast ( $K_{O_3} \approx 4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ ) and consumes about 3.43  $\text{mgO}_3/\text{mg-N}$  that is then no longer available for the oxidation of the organics. Thus, the ozone dose needs to be increased accordingly to ensure that the desired API removal is achieved.

**Total suspended solids** remaining after a properly-functioning clarifier have only a limited impact on the ozone consumption and API elimination. Thus, pre-filtration of the water is usually not necessary. However, increased ozone dose might be required at high TSS concentrations. Also, reported foaming issues have been attributed to high TSS concentrations<sup>7</sup>, which, however, might be site-specific.

The **pH** of the wastewater can have an impact on the rate of ozone depletion, the reactivity of some APIs with ozone (APIs in their deprotonated state react faster with ozone), as well as on the OH-radical consumption by the water matrix (scavenging). In practice, the overall impact of the pH on the API elimination is low.

**Water temperature** affects the rate of ozone depletion. Higher water temperature accelerates ozone depletion and vice-versa and, thus, can be relevant when dimensioning the ozone reactor.

**Dissolved oxygen** is massively increased during ozonation and can reach concentrations around 20  $\text{mg/L}$  at the ozonation effluent. This can negatively impact post-denitrification processes<sup>7, 8</sup>. Note that the increase of oxygen is related to the application of technical oxygen and is not a result of the ozone reactions.

**Bromide** is a precursor of bromate, a cancerogenic oxidation by-product. Bromate formation chemistry is very complex and involves multiple intermediate products. In general, the higher the bromide concentration and the specific applied ozone dose, the higher the bromate formation. At bromide levels up to 150  $\mu\text{g/L}$  and applied ozone doses up to 0.7  $\text{mgO}_3/\text{mgDOC}$ , bromate formation is not expected to be critical. At higher bromide levels a bromide source tracking can be conducted and bromate formation should be checked in lab-scale experiments. Relevant bromide sources can be municipal waste incinerators, chemical industries, geogenic sources, marine aerosols, and infiltration of seawater into the sewer systems of coastal cities<sup>8, 9</sup>. Bromate can be reduced back into bromide under anoxic conditions (e.g. denitrification).



## Transformation and oxidation by-products

Besides the desired effects (e.g. API elimination, disinfection, discolouration, etc.), ozonation also results in the formation of transformation products (TPs) and oxidation by-products (OBP). TPs are formed from the reaction with the target substances (here APIs), whereas OBPs are formed from the reaction with the non-targeted organic and inorganic compounds.

The analytical monitoring of TPs is very challenging, since even one API (parent) can end up in several TPs which themselves can be further converted into additional TPs. A comprehensive overview on what TPs can be expected with ozonation is not available at the current status. Depending on the functional group (attacking point of ozone) of the parent compound, the resulting TPs are expected to either be more (e.g. double bonds, aromatic compounds) or less (e.g. amines) biodegradable<sup>11</sup>. The amount of TPs in the ozonation effluent depends on the presence of the parent compound as well as the applied specific ozone dose<sup>10, 12</sup>. An overview of the TPs measured in the CWPharma project can be found in the GoA3.3 report<sup>10</sup>. An example of parent compounds and their TPs is shown for tramadol and venlafaxine in Figure 1.

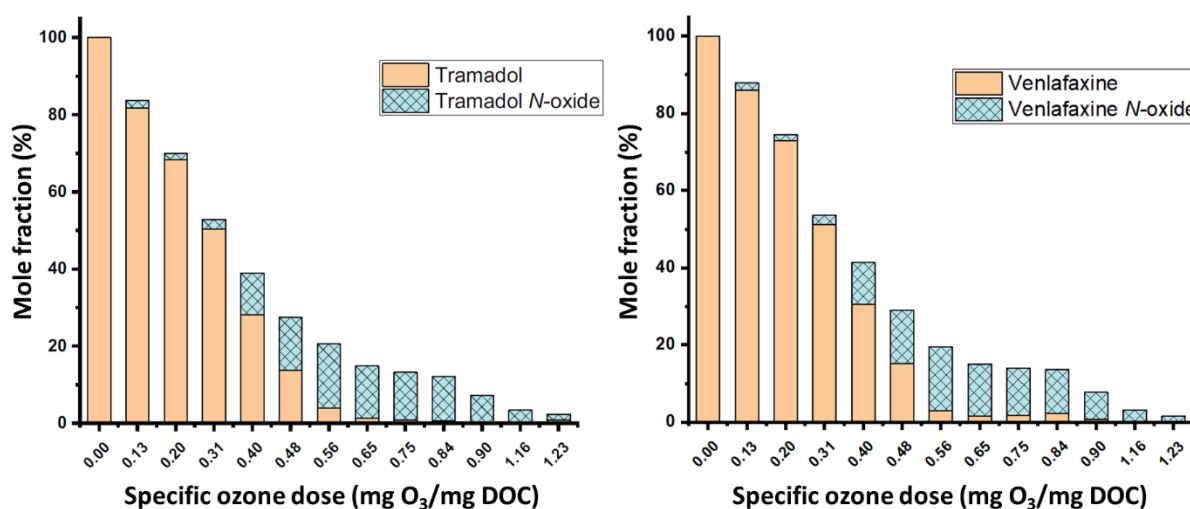


Figure 1: Impact of ozonation on tramadol and venlafaxine as well as the formation and reduction of their N-Oxides at varying specific ozone doses (adapted)<sup>12</sup>.

Some well-known OBPs formed during ozonation of inorganic compounds are nitrate and bromate. Nitrate is formed quickly by the oxidation of nitrite and results in an increased ozone consumption (3.43 mgO<sub>3</sub>/mg-N). Bromide present in the water can be oxidized to bromate (see water quality section).

Most relevant OBPs from organic compounds are nitrosamines and low-molecular compounds formed from the oxidation of the bulk DOC. The most famous nitrosamine formed by ozonation is N-Nitrosodimethylamine (NDMA), which can also already be present in the secondary effluent. However, it has been shown that NDMA formed by ozonation can be removed by biological post-treatment<sup>13</sup>. Formation of low-molecular compounds such as aldehydes and ketones increase with the specific ozone dose, but can easily be biodegraded by biological post-treatment<sup>14</sup>.

## Ecotoxicity

Municipal wastewater is a reservoir for many potentially toxic substances that can cause ecotoxicological effects even in low concentrations (µg/L to ng/L). Such substances can originate from pharmaceuticals, pesticides, chemicals, washing agents or other sources and may alter the regulation of sexual development and function of female vertebrates (estrogenic substances) or cause alterations in the genome of organisms (mutagenic substances). WWTPs can remove many of these substances as well as their associated transformation and/or degradation products (metabolites). However, some of these compounds are poorly removed and, thus, can enter the aquatic environment. Even though chemical analysis can quantify single substances in the ng/L

range, analytical methods only cover a small fraction of the known substances. In contrast, ecotoxicological tests (bioassays) allow an integral assessment of the negative effects (including potential mixture effects) of environmental samples on specific test organisms, which are assumed to be representative for the respective environmental compartment. Bioassays can either be conducted with aquatic species from different trophic levels (*in-vivo* tests e.g., with algae or aquatic plants, small crustaceans, or fish) or with cells/cell cultures (*in-vitro* tests e.g., with genetically modified yeast cells, human cell cultures or bacteria). Bioassays can be conducted with either native or enriched samples (e.g. by using solid phase extraction).

Wastewater treatment with ozonation results in the oxidation of APIs and other potential ecotoxicologically relevant substances, and can result in a reduction of toxicological properties. For example, it is well known that ozonation results in a strong decrease of estrogenic potential (up to 100%), which can be caused by e.g. hormones<sup>15</sup> and can be seen in Figure 2 (left). However, ozonation can also create TP and OBPs that might be even more toxic than the original (parent) substance. Some studies have shown a negative impact of ozonation when using specific bioassays (e.g. mutagenic effects in bacterial genomes with the Ames YG7108 test)<sup>15</sup>, which was also observed in the CWPharma project when using strongly enriched samples (Figure 2, right). However, such negative effects can be reduced/removed by a biological post-treatment<sup>15</sup> such as deep-bed filters, constructed wetlands or a GAC filter (Figure 2, right)<sup>10</sup>. Thus, it is recommended to operate an ozonation plant only in combination with a suitable biological or adsorptive post-treatment.

For assessing the impact of single treatment stages (ozonation, post-treatment), it is recommended to only use ecotoxicological tests that can provide reliable systematic results. Based on the evaluation of 17 different bioassays within the CWPharma project, it is recommended to use a set of bioassays that covers mutagenic effects, estrogenicity, and bioluminescence inhibition (unspecific toxicity). Especially when comparing different post-treatment types, 100- or 1,000 fold sample enrichment is recommended to obtain clearer results. More details on this topic are available in the GoA3.3 CWPharma report<sup>10</sup>.

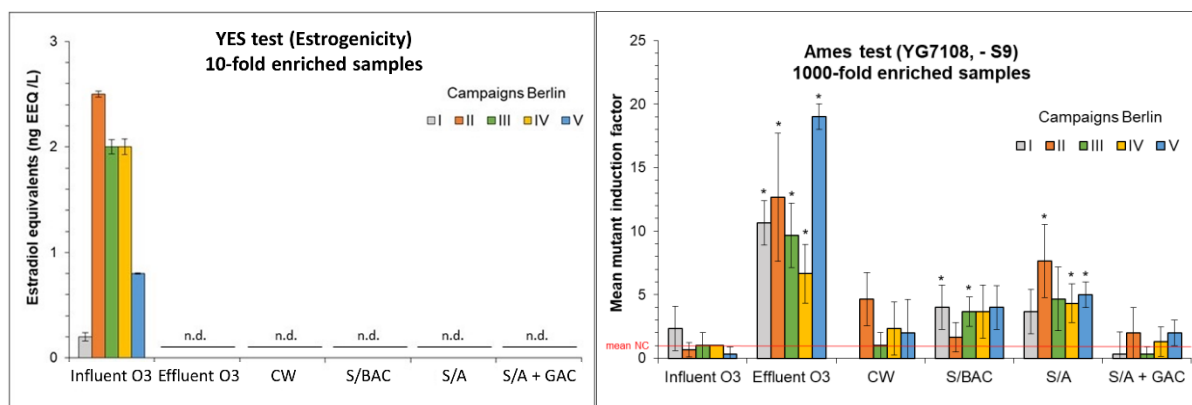


Figure 2: Estrogenic (left) and mutagenic potential (right) determined from samples of the Berlin ozone pilot-plant with different post-treatments: constructed wetland (CW), sand/biological activated carbon filter (S/BAC) as well as a sand/anthracite filter (S/A) that was followed by a granular activated carbon filter (GAC). Adapted from GoA3.3 report<sup>10</sup>.

## Full-scale ozonation at WWTPs

Ozonation plants are located after the secondary clarifier and consist of an ozone production unit, an ozone injection and reactor, an offgas-treatment, and a post-treatment (see Figure 3).

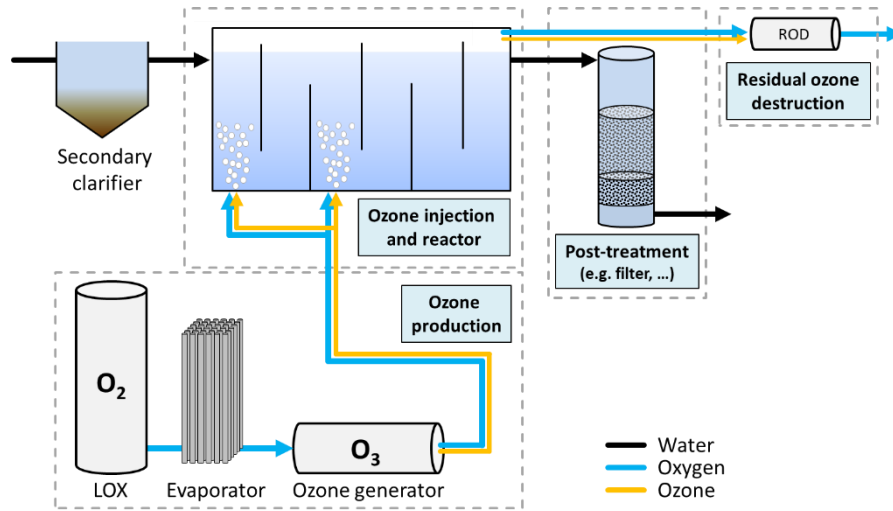


Figure 3: Scheme of a full-scale ozonation plant that consist of an ozone production unit, an ozone injection and reactor, an offgas-treatment, and a post-treatment.

### Ozone production

Ozone is always produced on-site by an ozone generator that transforms oxygen molecules into ozone (e.g. principle of silent electrical discharge). Typically, ozone concentrations of up to 15 wt% (225 gO<sub>3</sub>/Nm<sup>3</sup>) can be achieved, meaning that the product gas still mainly contains oxygen. The ozone production is energy intensive (10 kWh/kgO<sub>3</sub>) and exothermic. Thus, about 90% of the used energy is converted into heat that has to be removed by a cooling system. At full-scale, oxygen supply is usually covered by liquid oxygen (LOX) provided by an external supplier and stored on-site in insulated tanks. Prior to its use in the ozone generator, LOX is converted into its gaseous state in an evaporator. In some cases oxygen concentrators, which extract the oxygen directly from the local ambient air by pressure swing adsorption (PSA), can also be used. Compared to PSAs, LOX requires less space, allows a higher flexibility of the gas flow, has a better process stability, and is often preferable from an economical point of view.

However, LOX has to be delivered on a regular basis, whereas PSA units are independent of external deliveries. Oxygen purity needs to be in line with the specifications of the ozone generator. Traces of nitrogen (0.1 – 1.0 vol%) might also be added to the oxygen to maintain efficient ozone generation.

The design ozone dose ( $D_{dim}$ , mgO<sub>3</sub>/L) can be determined by the DOC specific ozone dose ( $D_{DOC}$ , typically between 0.3 and 0.9 mgO<sub>3</sub>/mgDOC) and the DOC concentration ( $C_{DOC}$ , mg/L) at the ozonation influent (Eq. 1). Additional ozone consumption by nitrite can be considered by filling in the expected nitrite levels ( $C_{Nitrite}$ , mg-N/L). The range of the required ozone production capacity ( $\dot{m}_{O_3}$ , gO<sub>3</sub>/h) can be determined by applying the minimum and maximum water flow ( $Q_{water}$ , m<sup>3</sup>/h), and the design ozone dose at Eq. 2. Likewise, the range of the oxygen gas flow ( $\dot{Q}_{O_2}$ , m<sup>3</sup>/h) can be determined by applying the ozone production range and the ozone concentration in the product gas ( $C_{O_3,productgas}$ , gO<sub>3</sub>/m<sup>3</sup>) at Eq. 3.

$$\text{Design ozone dose} \quad D_{dim} = (D_{DOC} \times C_{DOC} + 3.43 \times C_{Nitrite}) \quad \text{Eq. 1}$$

$$\text{Ozone production} \quad \dot{m}_{O_3} = Q_{water} * D_{dim} \quad \text{Eq. 2}$$

$$\text{Oxygen flow} \quad \dot{Q}_{O_2} = \dot{m}_{O_3} / C_{O_3,productgas} \quad \text{Eq. 3}$$

For easier adaptation to different flow ranges and redundancy, the overall ozone production can be provided by several ozone generators that are operated in parallel.

## Ozone injection and reactor

The ozone containing product gas is typically injected into the water via diffusors or a side-stream (venturi) injection. Ozone resistant diffusors (e.g. ceramic) are located at the bottom of the ozone reactor, similar to the aeration tank of a CAS-system. The ozone containing product gas is then introduced into the water via fine bubbles. For good gas-water transfer, the reactor depth should be at least five meters. To design the diffusor injection system, the range of the gas flow at the lowest and highest ozone demand must be known. During low ozone demand (e.g. night time), gas flow can be significantly lower than usual. As diffusors require a minimal gas flow, it might be necessary either to shut off some diffusors (risk of water and/or suspended solids intrusion) or to lower the ozone concentration of the product (increase specific oxygen and energy consumption). At a side-stream injection system, a booster pump pushes a part of the ozonation influent (or effluent) into the ozone injection system, where a local low pressure is created by the venturi principle sucking in the product gas. The ozone containing side-stream is then mixed with the full-stream. For good mixing, either static mixers (e.g. WWTP Kalundborg) or radical diffusors (e.g. WWTP Linköping) can be used. Side stream injection allows higher flexibility of the gas flow and can be easier to maintain, as the most relevant parts of the system are located outside of the ozone reactor. However, venturi systems have a higher energy consumption (booster pump) and are associated with the risk of increased bromate formation due to higher local dissolved ozone concentrations.

The main purpose of the ozone reactor is to provide a sufficiently long hydraulic retention time (HRT) for the ozone reaction to be completed so that no gaseous and residual dissolved ozone<sup>3</sup> can leave the reactor uncontrolled. Thus, the reactor must be gas tight and all materials in contact with ozone must be ozone resistant (e.g. stainless steel, concrete without an organic coating). It should be highlighted that the reactor volume and the HRT do not have an effect on the overall API elimination. However, insufficient mixing of the product gas with the water stream and short circuits in the reactor should be avoided, otherwise some water may be insufficiently ozonated (reducing the overall API elimination) or dissolved ozone may be present in the reactor effluent (e.g. at high flow situations). The overall ozone reactor volume ( $V_{reactor}$ , m<sup>3</sup>) can be calculated based on the maximal flow ( $Q_{max}$ , m<sup>3</sup>/h) and the minimum HRT ( $HRT_{min}$ , h) that is sufficient for a complete ozone depletion:

$$\text{Reactor volume} \quad V_{reactor} = Q_{max} * HRT_{min} \quad \text{Eq. 4}$$

Minimal HRT is typically between 15 and 30 minutes. For ozone reactors with a common reactor design (e.g. existing plants) a minimal HRT of 20 minutes is recommend. However, as time for complete ozone depletion depends on multiple parameters such as the applied ozone dose, DOC, nitrite, pH and water temperature, also a lower minimal HRT is possible (e.g. WWTP Aachen-Soers (DE): 12 min HRT at 0,5 mgO<sub>3</sub>/mgDOC). A higher pH and water temperature will result in a faster ozone depletion and vice versa. Thus, the ozone depletion rate will be different in the summer than in the winter. When aiming for a low HRT (< 20 minutes) it is recommended to perform lab-scale tests with the local water matrix to determine the time for complete ozone depletion ( $t_{depl.}$ , min) at varying boundary conditions. The minimal HRT can be derived by dividing  $t_{depl.}$  by the empirically determined factor of 0.35<sup>16</sup>. Additionally, computational fluid dynamics (CFD) simulations can be used to identify the optimal ozone reactor design (see also GoA3.1 report<sup>7</sup>). Even though most full-scale plants use a reactor with multiple compartments (e.g. WWTP Linköping (SE), WWTP Neugut (CH)), other reactors without them do exist (e.g. WWTP Aachen-Soers (DE) or WWTP Duisburg-Vierlinden (DE)). So far, there is no agreement on what reactor design is the most optimal.

---

<sup>3</sup> This is in contrast to the application of ozone for e.g. drinking water disinfection, where a certain residual dissolved ozone concentration in the reactor effluent can be desired.

## Residual ozone destruction

Due to the toxic nature of ozone, all gas that leaves the ozone reactor (offgas) must be treated by an ozone destructor that converts the residual ozone to elemental oxygen. Ozone destructors use either heat or a catalyst material. In a thermic ozone destructor, offgas must have a temperature of 350°C for at least 2 seconds. In a catalytic ozone destructor, offgas is preheated (40° - 80°C) to avoid condensation of water vapour on the catalytic material (e.g. metal oxides with a Cu/MnO basis or palladium), which could destroy it. Both ozone destructor types can destroy safely ozone and require low maintenance. Differences between them are that more energy and more effort for insulation is required for the thermic ozone destructor, whereas the catalyst ozone destructor can be negatively impacted by water vapour or other substances that are toxic to the catalyst (e.g. halogens, sulphur-containing substances, nitrogen oxides).

For safety, offgas should be evacuated from the ozone reactor by maintaining a low-pressure after the ozone destructor. However, if the flow of the product gas is lower than the flow of the offgas, ambient air will enter the ozone reactor via the mandatory safety valve and dilute the ozone concentration of the offgas. If the flow of the offgas is not measured, then it is not possible to precisely calculate an ozone mass balance<sup>7</sup>.

## Ozonation post-treatment

Besides the desired API elimination, disinfection, and reduction of certain ecotoxicological endpoints (e.g. estrogenic activity), wastewater ozonation also results in the formation of OBPs (e.g. bromate, NDMA) and TPs. Occasionally, an increased ecotoxicological potential (e.g. mutagenic effects) has also been reported<sup>10, 15</sup>. To reduce possible ecotoxicological effects<sup>10, 15</sup> and the concentration of certain OBPs (e.g. NDMA), an ozonation plant must be followed by a post-treatment, either biological or adsorptive. A biological post-treatment can be achieved by different options, such as deep-bed filters (e.g. sand/anthracite, biological activated carbon), MBBRs, or constructed wetlands. Alternatively, an adsorptive post-treatment (e.g. GAC) can be used, which usually outperforms biological filters regarding the removal of TPs but is associated with higher costs.

An overview of WWTPs with full-scale ozonation along with their post-treatment options is shown in SI-Table 1, but it should be kept in mind that sometimes post-treatment already existed prior to the construction of the ozonation plant.

## Operational aspects

In this section, certain operational aspects that should be considered during the planning and operation of an ozonation plant are briefly described.

### Operational safety

Given the properties of ozone (inhalation of more than 10 ppm can be lethal) and oxygen (supports combustion), ensuring a safe working environment is very important. Relevant places (e.g. room with ozone generator), should be equipped with ambient ozone and oxygen sensors. In case leakage is detected, safety measures must be triggered (e.g. audible and visible alarms, forced ventilation, shut down of ozone generation, etc.). Additionally, staff working at the ozonation plant need to wear portable ozone gas sensors. The power transformer of the ozone generator creates a high pitched noise and a magnetic field, therefore ear protection is required and people with pacemakers must stay away<sup>7</sup>.

All materials that may come in contact with ozone must be ozone resistant (e.g. stainless steel and PTFE). LOX can strongly react with fatty compounds (e.g. bitumen in asphalt). Thus, LOX tanks have to be mounted on a suitable support (e.g. concrete plate surrounded by gravel and grass)<sup>7</sup>.

### **Cooling system**

If process water is used for the cooling of the ozone generation system, biofilm growth and particles can significantly decrease the cooling water flow and reduce the heat transfer capacity of the heat exchanger. As a result, energy consumption increases while ozone production decreases. To avoid blockages, a strainer and a self-cleaning filter system can be installed. Small amounts of ozone can also be added to reduce biofilm growth in the heat exchanger<sup>7</sup>.

### **Foaming**

At the WWTP Linköping, foaming problems occurred in the pilot- and full-scale plant operation during periods of high turbidity. The foam was assumed to consist of lysed biomass and dissolved foam-forming compounds. Therefore, a water spray was installed in the offgas pipe to avoid its filling with foam<sup>7</sup>. Foaming issues also occasionally occurred at WWTP Kalundborg and therefore an anti-foaming agent is added to the influent chamber of the MBBR.

### **Online measurements**

Ozone concentration in gas (e.g. product gas, offgas) can be measured by UV absorption (e.g. 254 nm) and usually do not require regular maintenance. Dissolved ozone can be measured with amperometric electrodes or by color abatement of substances like N,N-Diethyl-p-phenylendiamin (DPD) or indigo. However, online sensors for dissolved ozone at WWTP ozonation plants often require notable maintenance and sometimes do not work as intended. Thus, considering their integration into the ozonation system should be checked carefully.

# Activated carbon

The following sections give a brief overview on the basics of activated carbon and relevant water quality parameters. Additionally, the technical application of activated carbon processes at full-scale is described along with details regarding operational aspects to consider.

## Basics

Activated carbon (AC) is used for decades in the drinking water production to remove xenobiotics such as pesticides or chlorinated solvents and can be used to remove APIs at WWTPs through interactions of the compounds with the hydrophobic AC surface (adsorption). AC is commercially available as granulated (GAC) or powdered (PAC) products, which differ in the size of the AC grains. A typical range for the diameter of a GAC grain is 0.5 – 2.5 mm, whereas PAC grains are much smaller (0.005 – 0.1 mm). AC is generated from carbon-containing raw material (e.g. coal, lignite, wood, etc.) by chemical or thermal activation, which creates a structured inner pore system containing micropores (0.4 – 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm). In general, micropores contribute the most to the overall high specific inner surface (500 – 1500 m<sup>2</sup>/g AC). However, a certain amount of macropores is also required to enable the target substances to physically reach the micropores. The distribution between the different pore sizes depends on the activation process as well as on the raw material used, and is therefore product specific. In contrast to PAC, which is always incinerated, loaded GAC can also be reactivated. During the reactivation process, about 10 - 20 % of the GAC is lost (e.g. fine fractions from de-dusting and sieving) and must be replaced with fresh GAC.

The overall API removal by AC depends on multiple parameters: (1) the concentrations and chemical characteristics of the APIs, (2) the dosage and the characteristics of the activated carbon used (e.g. pore size distribution, spec. surface), (3) the contact time between water and activated carbon, and to a lesser extent (4) the water temperature and pH value. Whether a PAC or GAC process is more appropriate for a specific WWTP depends on several local specific aspects, such as existing / unused infrastructure, sludge disposal routes, water matrix, and API elimination target. Non-polar, hydrophobic, and small molecules (e.g. carbamazepine, benzotriazole) are usually well adsorptive, in contrast to polar molecules (e.g. gabapentin, sulfamethoxazole). Substances with a high molecular mass, such as x-ray contrast media, are also poorly adsorptive, as their size prevents them from reaching the micropores. To characterise the adsorption capacity of the different AC products, indicator parameters such as the BET surface, iodine number, nitrobenzene number, and adsorption of methylene blue or molasses onto the AC can be quantified. However, studies have shown that these indicators only provide a very rough estimate of the actual adsorbability of APIs onto the AC in the complex wastewater matrix<sup>17</sup>. Thus, to determine the required dosage, lab-scale experiments with the local water matrix and different AC products are recommended. Adsorption tests for PAC can be conducted in simple batch tests<sup>17-19</sup>, whereas GAC products can be evaluated in rapid small-scale column tests (RSSCT)<sup>20</sup>.

## Relevant water quality parameters for activated carbon processes

The most important water quality parameter is the DOC, as other organic substances compete with the APIs for the activated carbon adsorption sites. Thus, the PAC dosage can be normalized to the DOC concentration (typical range is 1 – 2 mg PAC/mg DOC). Likewise, GAC must be more frequently replaced in the presence of elevated DOC concentrations. Depending on PAC dosage and if PAC is returned to the CAS, DOC at the WWTP effluent can be reduced by 30% – 50%<sup>21</sup>.

Nitrogen compounds such as ammonia, nitrite, and nitrate as well as phosphate are not absorbed by AC. However, phosphate concentrations in the WWTP effluent can be impacted by the coagulant used to improve the PAC retention. Total suspended solids will also be reduced

by the final PAC retention (filtration) stage. Treatment with AC also results in a decolourisation of the wastewater due to the organics removed.

### Full-scale PAC at WWTPs

Generally, PAC treatment consists of a PAC storage and dosing station, a contact tank where the PAC is mixed into, and a separation stage where the loaded PAC is extracted from the water. As a contact time of more than 24 h is necessary to utilise the full adsorption capacity in a single-stage PAC process, a decoupling of the hydraulic and PAC retention time is required. This can be achieved either by PAC enrichment within the separation stage (e.g. filter) or by PAC separation and recirculation back into the contact tank. PAC recirculation results in a very efficient use of the PAC due to higher loading, when the partially loaded PAC is transferred to water containing a higher organic background, which causes additional adsorption due to the increased concentration gradient. When PAC is recirculated into the main biological treatment, PAC particles will end up in the activated sludge. Therefore, excess sludge cannot be disposed on agricultural fields and must be incinerated. The final PAC separation stage must be designed for a full-stream treatment to avoid PAC particles in the WWTP effluent, even if the PAC stage itself is only designed for treatment of a partial flow (e.g. maximal dry weather flow). Based on reported experiences<sup>22</sup>, PAC in the activated sludge does not negatively impact the biological processes. The sludge volume index was either not affected or showed slight improvement, which was attributed to the density increase caused by the attached PAC particles. Depending on the applied PAC dosage, an increase of the overall sludge amount by 4 – 10% (dry matter) can be expected. No significant impacts were reported on the dewatering of the PAC-containing excess sludge or on the overall biogas production of the digester.

As indicated in the schematic overview (Figure 4), three different PAC processes are currently used at full-scale: simultaneous PAC dosage, PAC dosage prior to a filter, and using a separate PAC contact reactor (“Ulmer process”).

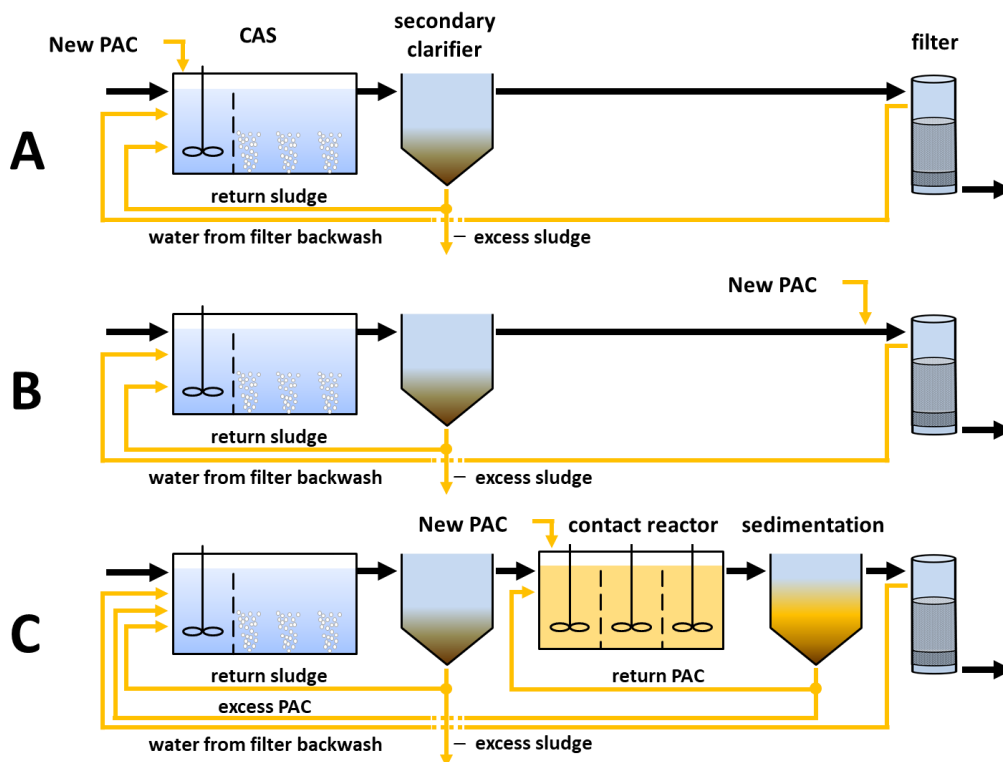


Figure 4: Schematic overview of different PAC processes that have been applied at full-scale plants: A) simultaneous PAC dosage, B) PAC dosage prior to a filter, and C) separate PAC contact reactor (“Ulmer process”).



**Simultaneous PAC dosage** into the biological treatment stage is an easy way to implement a single-stage PAC treatment and can be an option for small WWTPs or WWTPs with very limited space. PAC attaches to the sludge flocks so that it is not freely floating around in the water. Therefore, PAC can only reach the WWTP effluent when there is insufficient sludge retention. However, for safety, a final polishing filtration can be implemented. Loaded PAC is removed along with the excess sludge, so the average contact time of the PAC is similar to the sludge age. There is no need for a coagulant to enhance the settling of PAC/sludge flocks in the secondary clarifier. Backwash water from the final filtration process is sent back to the biological treatment stage. Compared to other PAC processes, investment costs are low, as no additional contact tanks are required. Compared to the other two processes, a higher PAC dosage is required to achieve a similar API removal. This process was investigated at full-scale at two WWTPs, but is currently used in only one WWTP (SI-Table 4).

**PAC dosage prior to a filter** is a two-stage PAC process in which PAC is added prior to the final filtration process, with or without using a separate contact tank. In case a deep-bed filter is used, PAC accumulates within the filter bed over the filter runtime, which increases the PAC contact time. For a more efficient PAC usage, filter backwash water can be transferred into the main biology where it is removed via the excess sludge. This process was tested at full-scale at four WWTPs and is currently used at three WWTPs in Germany and Switzerland (SI-Table 4). Typical PAC dosage is 1 – 2 mg PAC/mg DOC.

**Separate PAC contact reactor (“Ulmer process”)** uses an additional separate PAC circulation system and is thus the most elaborate but also most space consuming PAC process. In principle, fresh PAC is continuously added into the contact tank, remains there for a certain time (minimal HRT varies in the range of 30 to 60 minutes<sup>22</sup>), and is then usually extracted by a sedimentation stage and recirculated back into the contact tank. Due to the recirculation, high PAC concentrations of 1 – 10 g PAC/L can be achieved within the contact tank<sup>21</sup>. The PAC sludge remains in the contact tank for several days, until the excess PAC sludge is sent back to the main biological treatment stage. There, the PAC is extracted from the system along with the excess sludge of the secondary clarifier. Currently, the *Ulmer process* is used in 16 WWTPs in Germany and Switzerland (SI-Table 4). In most cases a combination of clarifier and dual-media filter (sand/anthracite) is used for PAC separation. Typical PAC dosage is 1 – 2 mg PAC/mg DOC.

### PAC separation

Independent of the PAC process used, discharge of PAC from the WWTP into the aquatic environment must be avoided at all times. Depending on the process used, one or two PAC separation systems are required that can handle different total suspended solids (TSS) concentrations (e.g. 5 – 30 mg PAC/L at the final filtration stage or 1 – 10 g PAC/L at to *Ulmer process* contact reactor<sup>21</sup>). Separation systems can generally be classified into: sedimentation, deep-bed filtration (e.g. dual-media filter, continuously operated filter), and surface filtration (e.g. membranes, cloth filters, microsieves). The subsequent section provides a brief description of the suitability of the different PAC separation systems, which is also summarized in Table 3.

**Sedimentation** in a clarifier can be used in the *Ulmer process* after the PAC contact tank but not as final filtration stage because small amounts of PAC will always slip through. The clarifier should be able to maintain a minimum HRT of more than 2 hours at maximal flow (specific vertical flow < 2 m/h). If lamella separators are applied in the clarifier, the minimum HRT can be lower. For improved settling of the PAC, a coagulant and polymer dosing are used.

**Deep-bed filtration** includes conventional filters with single (e.g. sand) or dual media (e.g. sand and anthracite) as well as continuously operated filters (e.g. DynaSand®). Deep-bed filters can be used as a final polishing stage, but are not able to handle the high TSS concentrations of the contact reactor of the *Ulmer process*. For sufficient PAC separation in these filters, a continuous addition of coagulant (e.g. 0.2 – 0.5 mg Al/L or 0.5 – 1.0 mg Fe/L) is required, which also results in an enhanced phosphorous removal<sup>22</sup>. Depending on the local boundary

conditions, filter velocities and the filter runtime until backwash vary between 5 – 16.5 m/h and 1 – 3 days, respectively<sup>3</sup>.

**Ultrafiltration membranes** do not require any additional chemicals (e.g. coagulants) for complete PAC removal and can also reject microorganisms. Thus, membranes can be used as a single stage filtration after the contact tank of the *Ulmer process* instead of e.g. a clarifier / filter combination (submerged membrane) or could also be used as final polishing stage (pressurized membrane, dead-end modus). Until now, PAC rejection by membranes at WWTPs has only been tested at pilot-scale<sup>21</sup>.

**Cloth filtration** is available as a disc or drum filter and can be used as a final polishing stage if very fine fibres are used. Adding coagulant prior to the cloth filter results in a lower turbidity, but decreases filter runtime due to more frequent flushing. However, cloth filtration cannot be used directly after the PAC contact tank at the *Ulmer process*, as it cannot handle the high TSS concentrations.

**Microsieves** can neither handle the high TSS concentrations in the effluent of the contact tank of the *Ulmer process* nor can they achieve the required retention as a final filtration stage<sup>23</sup>.

*Table 3: Overview of the suitability of technologies that can be used for PAC separation at the effluent of the “Ulmer process” contact tank and as a final polishing stage at the WWTP effluent. \* currently not used in full-scale.*

Technology	At effluent of the <i>Ulmer process</i> contact reactor	At the WWTP effluent (final polishing)
Sedimentation	+	-
Deep-bed filtration	-	+
Membranes*	+	+
Cloth filtration	-	+
Microsieves	-	-

### Operational aspects for PAC processes

Even though PAC itself is flame-resistant, there is a risk that the fine PAC powder can cause a dust explosion if there is also an ignition source. Potential explosive conditions can occur e.g. during filling/emptying of the PAC silo, wetting of the PAC, or during cleaning. In big PAC silos, the steady exothermic PAC oxidation reaction can create embers and form carbon monoxide<sup>22</sup>. Thus, appropriate measures and according national regulations must be carefully adhered to. Potential sources of ignition should be avoided (e.g. no open flames, lightning protection, grounding of the PAC truck via the PAC silo during the filling procedure, etc.). PAC silos can also be monitored (e.g. temperature, carbon monoxide at the offgas) and measures to ensure an inert atmosphere inside the silo (e.g. flooding with carbon dioxide or nitrogen) can be taken<sup>22</sup>.

At full-scale, PAC is usually stored in silos that should have at least a size of 85 m<sup>3</sup> to be able to store the full load of a PAC delivery truck even if there is still some PAC left over in the silo<sup>22</sup>. For the dimensioning of the silo volume, it should be kept in mind that the density of the filled in PAC is usually lower than the storage density provided by the supplier. A PAC density of 0.3 kg/L can be assumed as a reference value<sup>22</sup>. After filling in the PAC, a free space of 10% - 15% of the silo height (cylindrical part) should remain on top of the PAC<sup>22</sup>.

The silo is filled using pressurized air. It is possible for foreign matter to be in the PAC of the PAC delivery truck, which can cause damages/clogging of the PAC dosing unit. Thus, it should be possible to insert a sieve between the filling hose of the PAC truck and the fill-in connection pipe of the silo. The silo should be equipped with a level sensor to avoid overfilling the PAC silo and the display of the filling height should be visible close to the fill-in connection pipe<sup>22</sup>.

PAC is hydrophobic and thus must be wetted prior to introduction into the WWTP via a water-jet pump. The water velocity of the PAC dosing pipe should be > 1 m/s to prevent PAC

sedimentation. For a precise PAC dosage, PAC feeding should be done by mass (gravimetrically) and not by volume, as the PAC density can vary by a factor of 2<sup>22</sup>.

For the PAC tender procedure at full-scale, requesting a sample reference and defining clear quality criteria for the PAC is recommended, since adsorption characteristics might differ even for the same PAC product type. Quality criteria can be the water content of PAC (dried at 150°C) or the reduction of DOC and/or UVA<sub>254</sub> in a 24-h batch test. A quick quality check can be done by determining the removal of UVA<sub>254</sub> by the PAC in the local water matrix, as this surrogate correlates well with API reduction<sup>17, 24, 25</sup> and the test can be conducted at an on-site laboratory using a simple UV photometer. Each PAC delivery should be crosschecked with the PAC sample reference and, if quality criteria are not met, the vendor should be liable for compensation.

### Full-scale GAC at WWTPs

GAC is mainly used in deep-bed filters, which are a simple and robust process that does not impact other parts of the WWTP. In theory, GAC adsorption capacity for a certain APIs decreases with a gradient in the flow direction of the filter<sup>22</sup>. The API adsorption occurs primarily in the mass transfer zone (MTZ), which is located between the loaded (influent) and unloaded (effluent) GAC. In the MTZ a sufficient concentration gradient as well as adsorption sites remain so that the APIs can attach onto the GAC. Unless the MTZ has reached the end of the GAC filter, the API in question will be completely removed from the water. It should be noted that the GAC is mixed during filter backwash and therefore the loading zones are disturbed. Thus, GAC filters should be operated with water containing low amounts of suspended solids (< 20 mg/L) to reduce backwash intervals. As soon as the MTZ has reached the end of the GAC filter, the API breaks through and its removal will continue to decrease until the GAC is replaced by fresh or regenerated GAC. Based on experiences in Switzerland, GAC filter material should be exchanged after 20,000 to 30,000 bed volumes to meet the Swiss API elimination goal (80 %removal of indicator substances in the overall WWTP process)<sup>26</sup>. No significant differences regarding API elimination and exchange frequency are expected between fresh and reactivated GAC, but the latter is usually cheaper and has a lower carbon footprint<sup>26</sup>. GAC exchange frequency depends on various factors such as the target API, GAC characteristics (e.g. type, size distribution, etc.), and the DOC content of the water. Rapid small-scale column tests (RSSCT)<sup>20</sup> can be used to identify differences between GAC types (e.g. API elimination). However, some aspects that are relevant for a full-scale application might not be covered sufficiently by the RSSCTs (e.g. biological processes, impact of overall filter runtime). Thus, piloting activities with a filter (same layers than the full-scale filter, 20 – 40 cm inner diameter, test of new and reactivated GAC) can provide useful results<sup>22</sup>.

The two most important parameters for the design and operation of a GAC filter are the empty bed contact time (EBCT, min) and the bed volumes treated (BV, no unit). The EBCT represents the average time the water flow ( $Q$ , m<sup>3</sup>/min) needs to pass through the (empty) filter bed volume that is defined by its filter surface area ( $A_{\text{filter}}$ , m<sup>2</sup>) and height ( $h_{\text{GAC}}$ , m). The BV is determined by dividing the cumulated water volume treated with the same GAC ( $V_{\text{treated}}$ , m<sup>3</sup>) by the volume of the GAC ( $V_{\text{GAC}}$ , m<sup>3</sup>) and represent a normalised filter runtime that can be used to compare between various GAC filters in different WWTPs. Both parameters can be calculated using the following equations:

$$\text{Empty bed contact time (EBCT)} \quad EBCT = \frac{h_{\text{GAC}} * A_{\text{filter}}}{Q} = \frac{V_{\text{GAC}}}{Q} \quad \text{Eq. 5}$$

$$\text{Bed volumes (BV)} \quad BV = \frac{V_{\text{treated}}}{V_{\text{GAC}}} \quad \text{Eq. 6}$$

In principle, GAC filters can be designed as gravity driven filters (discontinuously or continuously) or as pressurized filters, and are employed after the secondary clarifier (Figure 5).

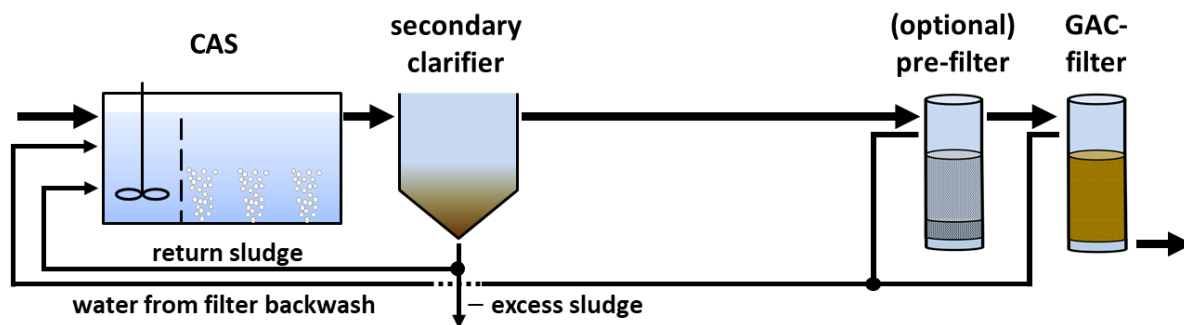


Figure 5: Scheme of a full-scale GAC process.

With a filter bed height between 1.5 and 2.5 m and a filter velocity between 4 and 7 m/h, the EBCT should be at least 20 minutes<sup>26</sup>. The total height of the filter must provide sufficient space for 20% to 25% expansion of the filter bed and some safety buffer (e.g. 20 – 40 cm) during backwash<sup>22, 26</sup>. The GAC grain size should be adjusted to the TSS level of the water. The higher the TSS concentrations, the coarser the GAC grain size should be to avoid filter clogging and more frequent back flushing. Suitable grain size distributions are: 0.6 – 2.4 mm (TSS < 5 mg/L), 0.8 – 2 mm (TSS between 5 – 10 mm), and 1.2 – 2.4 mm (TSS > 10 mg/L)<sup>26</sup>. Alternatively, a pre-filtration stage can be considered. Usually, the filtration stage is subdivided into several filter cells with an additional filter cell for backup (e.g. maintenance, during GAC exchange at another cell). Having at least four filter cells (incl. backup) will allow adjustment of filter operation to varying flow conditions<sup>26</sup>. GAC exchange frequency can be reduced if GAC filters are operated in parallel at different bed volumes (time shifted start-up of the GAC filters). The reduced performance of one filter cell can then be compensated by the other ones and the overall API elimination at the effluent of the GAC filtration stage can still be within the defined target. In case pressurized GAC filters are used, filters can be operated in series to obtain simultaneous TSS removal (primarily at first filter cell) and API elimination<sup>22</sup>.

Another interesting but yet not well-investigated option is the use of GAC in a moving bed reactor (e.g. CarboPlus®)<sup>4</sup>. In principle, pre-wetted GAC with an average size of 0.5 mm is added batch-wise (e.g. once a day) into a reactor that is operated in an upflow direction with a velocity between 7 – 15 m/h (max. 20 m/h). Due to the flow, a moving GAC bed of about 2.2 m establishes. Typical GAC dosage is 2 mg GAC/mg DOC. Loaded GAC is removed from the bottom of the reactor weekly, which results in a GAC age between 80 and 100 days. Elevated TSS concentrations (e.g. sludge drift) can result in its accumulation in the moving bed and should be avoided. As the fine fraction of the GAC is removed before GAC addition to the reactor, it is not expected that an additional post-filtration is necessary. Nevertheless, bed height and turbidity in the effluent should be monitored online. Even though only one full-scale plant is in operation so far, several WWTPs apparently intend to use this process in the future (SI-Table 3).

### Operational aspects for GAC processes

GAC filters can be operated top-down or bottom-up, which also affects the choice of the filter nozzles. In the first case, big particles cannot reach and clog the nozzles so their slits should be smaller than the smallest GAC grain size. In the other case, nozzle slits must be wider (e.g. 1 – 2 mm) to avoid clogging by particles from the secondary effluent and the filter should be operated with a support layer to avoid fine GAC particles slipping through backwards. Coarse GAC should be used for that support layer instead of gravel, as it might eventually end up in the GAC reactivation process<sup>22</sup>.

In principle, existing filters can be changed into GAC filters. However, filter modifications as well as adaptations of the back-flush procedure with air and water can be required. If new filters are constructed, it should be checked how the future filling and emptying procedure can be

<sup>4</sup> <https://micropoll.ch/verfahren/aktivkohle/gac-verfahrensfuehrungen>, accessed 26.11.2020

conducted in the best way to reduce required personnel effort (e.g. by integration of required pipes and connectors for injector systems used to extract the GAC from the filters)<sup>22</sup>. From the practical point of view, filter cells should be adapted to the load capacity of the GAC trucks that will transport the GAC (delivering, disposal). Note that the specific weight of wet GAC is about double that of dry GAC<sup>26</sup>. Each filter cell should be equipped with a flow meter to determine the treated bed volumes accordingly. Level sensors can be used to adjust the water level within the filters and can be used in combination with pressure sensors to measure the pressure difference within the filter. The pipe for the pressurized air should be equipped with a central pressure sensor<sup>22</sup>.

After filling the filter with new, dry GAC, the GAC should be wetted for several days so that the pores will be filled up with water before the first backwash with water is conducted<sup>22</sup>. Some parts of the GAC might swim up and have to be removed by the flushing procedure, which should be pre-emptively specified by the suppliers. Water used for wetting can have a high pH due to the ashes in the GAC (especially GAC reactivates).

Operation of the GAC filters as a coagulation filtration stage for an enhanced phosphorus removal is not recommended, as it has a negative impact on the GAC reactivation process and the TSS load is strongly increased, which results in more frequent filter flushing<sup>26</sup>.

GAC tender/billing should be done by volume instead of mass by using the following procedure<sup>22</sup>: fill GAC in the filter, water it for up to three days, and conduct a light filter-flushing with water to remove very small GAC particles. After that: GAC volume is calculated by filter surface area and filter bed height (either by operator and/or vendor). This procedure has some advantages for the WWTP operator: dust, too small grains and GAC swimming on top are removed and therefore not billed. Also, water content of GAC is than not relevant.

# Moving bed biofilm reactors (MBBR)

## Basics

MBBRs can remove APIs from wastewater via metabolic reactions within the biofilm. Ideally, APIs are either mineralised or incorporated into the biomass. The biomass in the biofilm is considerably more able to remove APIs than the sludge biomass from a CAS and can degrade APIs that are believed to be non-degradable such as carbamazepine<sup>27</sup> and iodinated x-ray contrast media<sup>28</sup>. In MBBRs the biofilms are located on plastic carriers (diameter is typically 1 to 5 cm) suspended in the water. In this way, MBBR operation is similar to active sludge reactors. The operation of an MBBR depends on the biomass/volume and the surface area/volume. The higher the biomass and the surface area, the higher the expected API removal, compared to otherwise similar reactors. However, balancing the feeding to build-up and maintain the biomass and not to supply too much biochemical oxygen demand (BOD) can be challenging. Compared to ozonation and treatment with activated carbon, MBBR operation has a relatively low carbon footprint, as its operation requires energy primarily for the aeration.

## Relevant water quality parameters

MBBRs are relative robust against usual wastewater parameter fluctuations (e.g. BOD, COD, TSS, ammonia, nitrate, nitrite). However, high alkalinity can result in scaling on some MBBR carriers (increasing weight), which then have a tendency to sediment in the tanks. The negative impact of scaling seems to be less relevant for the most recent developed carriers (Z series of AnoxKaldnes<sup>TM</sup> in contrast to K<sub>1</sub> and K<sub>5</sub>, Figure 6).

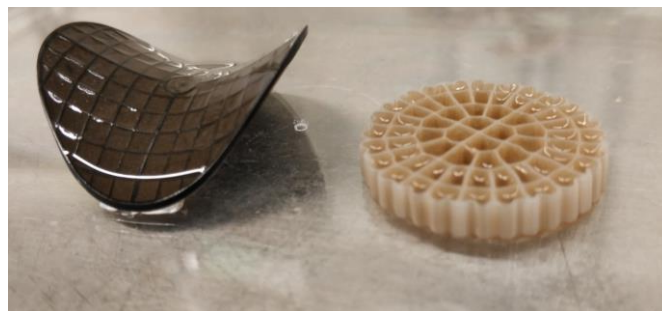


Figure 6: Z200 and K5 (AnoxKaldnes<sup>TM</sup>) carriers for MBBR (Diameter 2-5 cm)

Usually MBBRs require the addition of BOD (methanol, ethanol, or raw wastewater) to support the biomass growth. However, some studies investigated if MBBRs that are operated after a CAS and ozonation can also use hard COD as carbon source and removed APIs and/or ozonation products successfully<sup>29, 30</sup>.

## Full-scale MBBR at WWTPs

Usage of MBBRs at full-scale is common in Scandinavia for nitrification and denitrification. As shown in Figure 7, MBBRs in the context API removal could be applied as:

- **post-treatment** after a high loaded CAS, which is used for BOD and N management. In this setup, the focus of the MBBR would be additional nitrification and API removal;
- **mainstream** substitute of a CAS to treat BOD, ammonia and APIs at the same time. However, this setup would require an additional low loaded polishing MBBR; or
- **ozonation post-treatment** to reduce OBPs and TPs formed (see also ozonation section).

So far, full-scale MBBRs in the context of API removal are only used as ozonation post-treatment (e.g. Kalundborg (DK)<sup>8</sup>, Linköping (SE)<sup>7</sup> or Warburg (DE)<sup>30</sup>). Configurations 1 (CAS post-treatment) and 2 (mainstream MBBR) have only been demonstrated at pilot-scale.

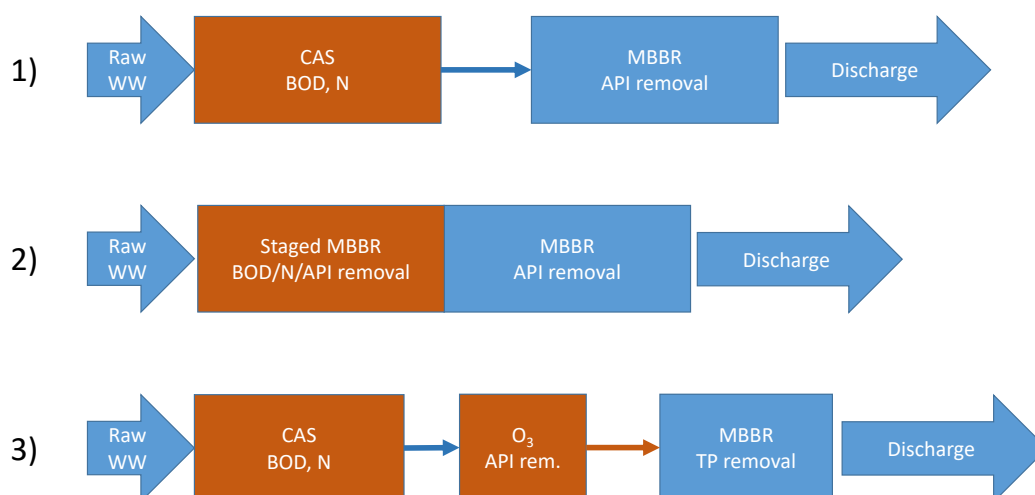


Figure 7: Potential setups of MBBR reactors in the context of API removal: 1) CAS post-treatment, 2) mainstream MBBR, and 3) ozonation post-treatment.

A HRT of 6 to 10 hours in the MBBR is necessary to achieve a quantitative compound-specific API removal<sup>27, 31-34</sup> and only in a very few cases HRTs of 4 h or less than 2 h were successful in removing APIs<sup>30</sup>. Individual studies have also reported a 90% removal of diclofenac during a 4 hour treatment in a pilot-scale sequencing batch reactors: however, the same reactors were less successful for other APIs<sup>35, 36</sup>. Interestingly, API removal is often similar under aerated and denitrification conditions<sup>27</sup>. MBBR lab-scale tests conducted within the CWPharma project also confirmed that APIs such as ibuprofen, valsartan, candesartan, and gabapentin have a half-life (time to reduce API by 50%) of less than 5 hours<sup>8</sup>. In contrast, half-lives of other APIs such as venlafaxine, tramadol, and diclofenac were more than 100 hours under the investigated settings.

Similar to ozonation, MBBR is a reactive process that eliminates target API via a transformation process. Thus, metabolites formed in MBBRs are only incorporated in biomass or mineralized at a later metabolic step.

In conclusion, MBBRs need further development before they can be recommended as a standard option for API removal.

# Monitoring of ozonation and AC processes

This section briefly summarizes the usage of surrogate parameters for monitoring and process control of API elimination technologies, discusses how to monitor PAC retention, and lists which bioassays should be used for an ecotoxicological assessment.

## Surrogate parameters for monitoring and process control

Besides direct measurement of APIs at the influent and effluent of the API elimination technology, surrogate parameters can be used for process control and monitoring. The easiest way to monitor the performance of PAC and ozonation processes is to determine the relative UVA<sub>254</sub> reduction ( $\Delta UVA_{254}$ ), which can be calculated using Eq. 7:

$$\Delta UVA_{254} = \frac{UVA_{254,influent} - UVA_{254,effluent}}{UVA_{254,influent}} = 1 - \frac{UVA_{254,effluent}}{UVA_{254,influent}} \quad \text{Eq. 7}$$

Even though many studies show a clear correlation of the API elimination with the  $\Delta UVA_{254}$  (see also Figure 8), the slopes and intercepts can vary due to local boundary conditions. Therefore, conducting dose-response tests to get site specific correlations with the local water matrix is recommended<sup>7, 8</sup>. Within the CWPharma project, the reduction of fluorescence ( $\Delta fDOM$ ) was determined to be a possible interesting alternative to the usage of  $\Delta UVA_{254}$  (Figure 8).

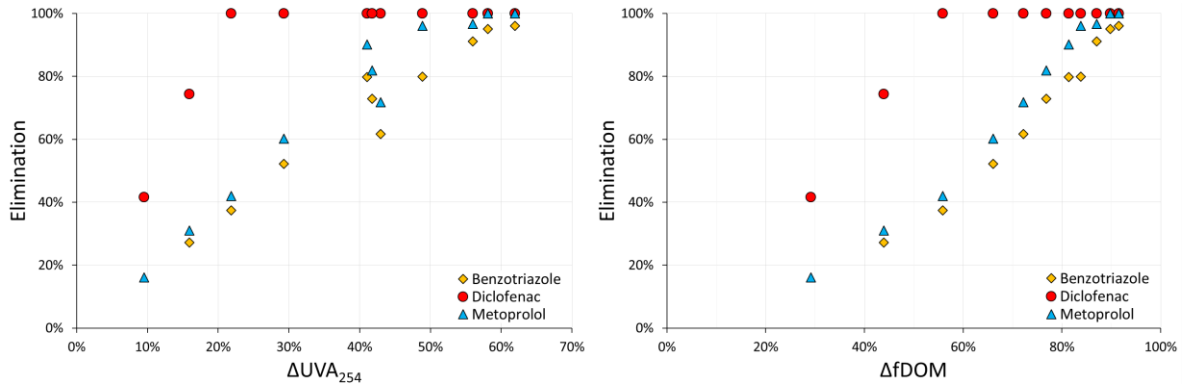


Figure 8: Elimination of diclofenac, metoprolol and benzotriazole compared to the reduction of UVA<sub>254</sub> ( $\Delta UVA_{254}$ , left) and the reduction of fluorescence ( $\Delta fDOM$ , right) at the ozonation pilot plant in Berlin. Elimination was set to 100% in case effluent concentration was below the limit of quantification.

The  $\Delta UVA_{254}$  only depends on the measurement of UVA<sub>254</sub> (1/m) at the influent and effluent of the API elimination stage and does not require any knowledge of the current process conditions (e.g. ozone or PAC dosage).  $\Delta UVA_{254}$  is linked to changes in the organic background and not to the APIs themselves, as their concentrations are very low. Therefore,  $\Delta UVA_{254}$  is a suitable surrogate for ozonation, PAC and probably also for the GAC moving bed process, however, it is not suitable for long-term monitoring of API elimination in a GAC filter.

The UVA<sub>254</sub> itself can be measured either online or in a laboratory, as it requires only a UV photometer. Prior to measurement in the laboratory, samples must be filtered (e.g. 0.45  $\mu\text{m}$  cellulose syringe filter) to remove particles which influence the UVA<sub>254</sub>. UVA<sub>254</sub> online sensors usually have an automatic turbidity compensation that can be calibrated based on samples that have been taken on-site and measured in the laboratory. UVA<sub>254</sub> online sensors do not require a pre-filtration per-se, but it might help reduce issues related to high TSS concentrations or algae present in the water. The previously mentioned surrogate parameters can also be used in a feedback control strategy that adjusts the dosage (e.g. ozone, PAC) in a way that stable reduction of the surrogate parameter and, consequently, the API elimination, is achieved. However, even though tests at pilot- and full-scale plants successfully demonstrated the use of  $\Delta UVA_{254}$  in a feedback control, often the simple flow proportional dosage is used instead as potential benefits (e.g. more efficient dosing) were not high enough to compensate additional maintenance efforts (e.g. regular cleaning of sensors to avoid measurement errors due to fouling).



## **PAC retention**

Besides the TSS measurement, turbidity can be used as surrogate parameter for online process monitoring of PAC retention. Considering varying turbidity behaviours of different PAC products, monitoring the combination of TSS and turbidity is recommended. A TSS concentration of < 1 mg/L and a turbidity of < 1 FNU should be achieved in the WWTP effluent<sup>21</sup>. Samples from the WWTP effluent can be filtered with e.g. 0.5 µm glass fibre filters and then simply visually controlled or compared to a reference (filtration of samples with defined PAC concentrations)<sup>23, 37</sup>.

## **Ecotoxicological monitoring**

Based on the findings in the CWPharma project, using a set of ecotoxicological tests that can provide reliable systematic results for the evaluation of ozonation and post-treatments is recommended. The set should cover the evaluation of mutagenic effects, estrogenicity, and bioluminescence inhibition. Especially when comparing different post-treatment types, using a final enrichment factor of 100 or 1,000 to obtain clearer results can be recommended. More details can be found in the GoA3.3 CWPharma report<sup>10</sup>.

# API removal by ozone and activated carbon

Besides the water quality at the WWTP (e.g. DOC, nitrite, etc.) and its biodegradability (potential removal through biological treatment), overall elimination of an API at a WWTP with an API elimination technology depend also on

- the chemical characteristics (e.g. polar/non-polar, reactivity with ozone and OH-radicals);
- the chosen API elimination technology (e.g. ozonation, PAC or GAC); and
- the specific dosage of PAC, ozone, or bed volumes treated (GAC)

In Table 4, the expected elimination for some micropollutants by PAC and ozone is shown. Even though some substances are well removed by both technologies, removal of other substances will strongly depend on the chosen technology. Thus, the API elimination technology must be individually chosen according to the target of the specific WWTP.

Table 4: Expected elimination of micropollutants for specific doses of 1 mg PAC/mg DOC and 0.7 mg O<sub>3</sub>/mg DOC based on lab-scale, pilot-scale and full-scale applications as summarized in prior work<sup>38</sup>. Note that the dosages will change the removal. An asterisk (\*) indicates that the substance is a metabolite/transformation product.

API / micropollutant	Activated carbon	Ozonation
Amisulpride Carbamazepine Citalopram Clarithromycin Diclofenac Hydrochlorothiazide Metoprolol Tramadol Venlafaxine	good – very good (> 70%)	
Benzotriazole Irbesartan Oxipurinol*	good – very good (> 70%)	moderate – average (≈ 30 – 70 %)
Candesartan Formylaminoantipyrine* Olmesartan Sulfamethoxazole	moderate – average (≈ 30 – 70 %)	good – very good (> 70%)
Valsartan Valsartan acid*	moderate – average (≈ 30 – 70 %)	
Gabapentin	none – low (< 30 %)	moderate – average (≈ 30 – 70 %)

## Process combinations

The combination of ozonation and AC processes is possible and can be beneficial as the AC can reduce certain TPs and OBPs formed by the ozonation process. In addition, ozonation reduces the aromaticity, molecular size and hydrophobicity of the bulk DOC, which in turn reduces the competition with APIs for adsorption sites at the AC (less AC required)<sup>39</sup>. In addition, the combination of ozonation and GAC filtration can significantly reduce the required GAC exchange frequency. In this combination, ozonation can be operated at a lower dosage, which also reduces the formation of undesired OBPs. Combining two processes can affect the overall complexity, costs, carbon footprint, and workload for maintenance and needs to be assessed site-specifically. Currently, process combinations (ozonation + GAC-filter) are used at full-scale in two WWTPs (SI-Table 2).

## Carbon footprint

Implementation and operation of API elimination technologies will increase the WWTP's carbon footprint. Within the CWPharma project, a generic evaluation of the implementation of an ozonation, PAC and GAC process (each in combination with sand filtration) was evaluated<sup>40</sup>. In brief, overall global warming potential (GWP) can be subdivided into the impact of the infrastructure (e.g. production of construction material), the electricity production as well as the production of LOX and activated carbon. In Figure 9, the country and technology specific differences in the GWP can be seen. The differences in electricity production (e.g. hard coal, natural gas, nuclear, wind) and DOC load of the WWTPs explain the differences. In brief, GWP of ozonation relates primarily to the carbon footprint represented by carbon dioxide equivalents ( $\text{CO}_{2,\text{eq}}$ ) of the electricity production, whereas GWP for activated carbon processes depend on the DOC load of the WWTP, the PAC dosage, and the exchange frequency of the GAC, respectively. As it was assumed in the evaluation that the GAC is regenerated, it has a lower carbon footprint than the fresh PAC as overall energy consumption of the reactivation process is lower than for the creation of new activated carbon.

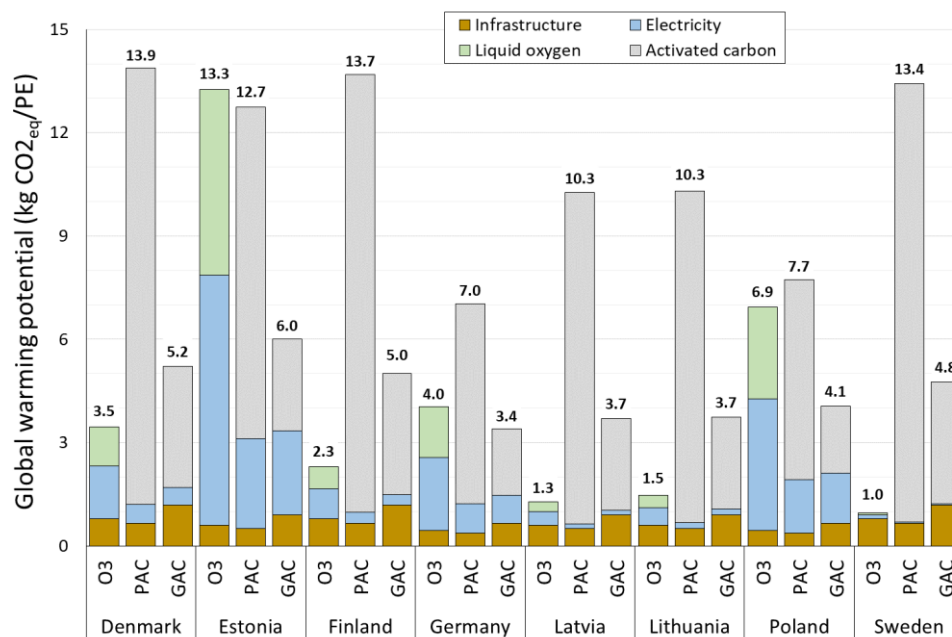


Figure 9: Global warming potential per country normalized on load (PE) for ozonation, PAC and GAC (each in combination with a sand-filtration)<sup>40</sup>.

## Costs

The costs of an advanced treatment technology can be divided into capital expense (CAPEX) and operating expense (OPEX). CAPEX includes costs for e.g. buying land, site preparation, construction work, equipment, and capital interest, whereas OPEX includes costs for e.g. supplies (e.g. liquid oxygen, activated carbon), energy consumption, and maintenance of equipment. Cost evaluations are available for some countries (e.g. Germany, Switzerland, and Sweden). However, costs related to construction (e.g. land, material, transport, labours, and professionals) and operation (e.g. supplies, electricity, labours) can be distinctly different between the countries. In addition, annual amount of wastewater per PE varies strongly between the countries (e.g. median for South Baltic region:  $44 \text{ m}^3/\text{PE} \cdot \text{a}$  and Nordic region:  $80 \text{ m}^3/\text{PE} \cdot \text{a}$ <sup>41</sup>).

Based on a compilation of feasibility studies and operating full-scale plants in Germany and Switzerland, it was shown in a study<sup>42</sup> that the specific annual costs ( $\text{€}/\text{m}^3$ ) of WWTPs with a similar size in the same country can vary by more than a factor of two.

Differences were often not due to the choice of technology (e.g. ozonation, PAC or GAC), but attributed to site-specific boundary conditions, such as:

- site conditions (space available, ground conditions, construction above / below surface);
- water matrix (e.g. DOC, nitrite, etc.);
- already available equipment / constructions (e.g. filters that can be used as post-treatment);
- treatment of the full-stream or a partial-stream; or
- whether additional pumping is required

Specific annual costs per treated  $m^3$  (including OPEX and CAPEX, without VAT) that are shown in Figure 10 (left) are based on studies from Germany (that also includes data from Switzerland)<sup>42</sup> and Sweden<sup>43</sup>. For the German study, no differentiation between the technologies (ozone, PAC and GAC) were made for the cost function. It should be mentioned that the calculation basis (e.g. amortisation period, post-treatment already existed) for the WWTPs that have been included in the studies were not harmonized, which prevents a direct comparison. Nevertheless, a general decrease of the specific costs with the WWTP size can be seen. The significant lower costs per  $m^3$  in Sweden might be related to the comparable high amount of wastewater per people equivalent (PE) as estimation of the specific annual costs per PE changes the picture (see Figure 10, right).

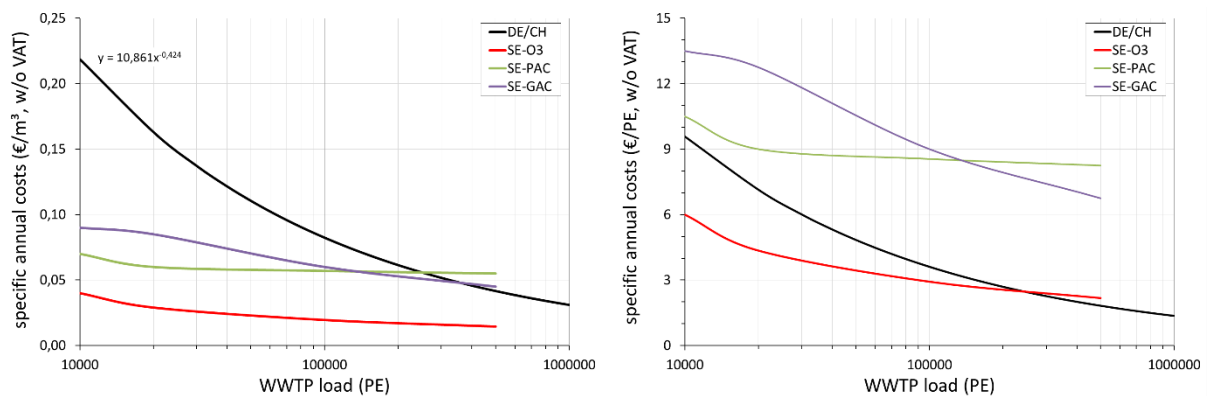


Figure 10: Average annual costs including OPEX and CAPEX normalized for  $m^3$  treated (left) and PE (right), respectively. Cost per PE were estimated based on the specific annual amount of wastewater ( $DE = 44 m^3/PE \cdot a^{41}$  and  $SE = 150 m^3/PE \cdot a^{43}$ ). Note that specific costs are always site specific and, thus, can vary strongly even for WWTPs with the same load.

# Implementation of an API elimination technology

Additional removal of APIs at municipal WWTPs can be achieved by using mature technologies such as ozonation, powdered activated carbon, and/or granular activated carbon. Basics, process schemes as well as advantages and disadvantages of the different technologies have been briefly described in this report. However, each WWTP is unique and, thus, the choice of the most suitable advanced wastewater treatment (AWT) technology depends on many variables. Besides costs for construction and operation (e.g. energy, oxygen, activated carbon) as well as available structures in the WWTP, also legal boundary conditions and the choice of targeted APIs can be relevant. For a successful implementation and operation of an AWT, the following four modules can be used as a guidance (Figure 11).



Figure 11: Four modules for a successful implementation and operation of an AWT.

## WWTP fitness check

Before conducting a feasibility study and more detailed planning, a brief check of the current WWTP situation should be undertaken to define the overall targets of the AWT, to identify potential barriers that might rule out certain technologies, and determine additional data or monitoring campaign needs.

The fitness check can contain a brief evaluation of the following points.

### Define overall target of AWT technology

Unless targets are defined by the appropriate authority, the focus of the API elimination might be e.g. reduction of overall API emission from WWTPs, surface water protection or securing water sources used for drinking water. Potential synergies of AWT with other targets of the WWTP (e.g. reduction of phosphorous and/or COD emissions, disinfection (ozone), heavy metals (AC), etc.) should be checked.

### Check availability of water quality parameters

Relevant parameters include DOC, nitrite, bromide, and TSS at the influent of the AWT stage (in most cases, secondary effluent). As DOC is not a common parameter measured at WWTPs, establishing a correlation between the dissolved chemical oxygen demand ( $\text{COD}_{\text{dis}}$ ) and DOC might help to make use of available COD time series.

### Identify potential barriers

Local water quality and boundary conditions can favour or prevent application of certain AWT technologies. Potential handicaps could be the desired application of excess sludge disposal in agriculture (with PAC it would have to be incinerated), elevated bromide concentrations ( $> 150 \mu\text{g/L}$ ) can pose a risk of increased bromate formation at an ozonation, and nitrite can increase the ozone demand. Elevated DOC concentrations will result in higher doses of AC and ozone. If the WWTP has a high share of industrial wastewater (e.g. distinctly higher DOC), results from other WWTPs with AWT might not be transferable and, thus, pre-evaluation with the local water matrix (e.g. lab-tests) should be conducted. In addition, insufficiently working clarifiers

and elevated TSS concentration might affect AWT stages (e.g. more frequent flushing of GAC filters, increased dosage, etc.).

Identified barriers must not automatically result in exclusion of the affected technologies, but could be a starting point for more detailed investigation on how to overcome them, if required.

### **Feasibility study**

Based on the considerations and assessments of the “fitness-check” module, a feasibility study should be conducted to assess the practicability of an AWT for API elimination, estimate costs for construction and operation, and evaluate different scenarios (e.g. using different technologies).

In order to facilitate comparison between different feasibility studies<sup>5</sup>, they should contain at least the following items:

#### **Ambition of the API elimination technology**

Besides outlining the ambitions / targets of the API elimination technology, a brief summary of the current impact of the WWTP operation on sources used for drinking water, bathing waters and ecological status of the receiving water body can be added, if relevant.

#### **Status of the WWTP**

This includes a description of the catchment area (incl. potentially relevant hotspots such as hospitals or industry), design and actual loading of the WWTP, description of the treatment processes (incl. process schemes), overview of flows, and concentrations (load) of relevant water quality parameters (e.g. DOC, COD, TSS, nitrite, bromide).

#### **API monitoring campaigns**

If not already available, sampling campaigns for relevant APIs should be conducted at the WWTP effluent (e.g. 24h composite samples) for at least three days with dry-weather conditions. Note that concentrations of some API vary over the span of the week. Additional sampling campaigns can be conducted at the influent of the biological treatment and influent of the planned AWT technology, to evaluate the effect of the biological treatment on the overall API removal, and, if relevant, during rainy weather conditions.

#### **State of the art / knowledge of AWT**

A brief description of the available AWT technologies for API elimination along with an overview of reference WWTPs with the existing AWT in operation (if possible, highlight WWTPs in the same country or region) should be compiled.

#### **Preliminary design of AWT technology**

Outline a concept for integrating the planned AWT process into the existing WWTP processes considering country-specific standards, if available. For this evaluation, following criteria should be considered:

Define the design flow of the AWT (e.g. dry-weather peak, maximal flow of the WWTP) according to the target of the API elimination stage. In case the design flow is smaller than the maximal flow of the WWTP, evaluate whether all water can be directed through the AWT stage (taking into account the reduced API removal efficiency) or whether it must be by-passed. Planning the AWT with a design flow of less than the maximal flow might significantly reduce space and investment costs of the AWT without affecting the average annual API elimination in the same order of magnitude.

---

<sup>5</sup> In case national knowledge platforms exist, it is recommended that they provide a template for the conduction of feasibility studies to increase information exchange. Public reposts should be collected and identified (linked) on a homepage along with a summary of the most relevant indicator parameters for the according WWTP.

Determine dosages (PAC, ozone) and GAC exchange frequency required to meet the API elimination target. This evaluation can be based on lab-scale experiments, experiences of similar WWTPs (in the same country), or using a range of commonly applied dosages (PAC, ozone) or maximum treated bed volumes (GAC).

Evaluate potential integration of existing infrastructure (e.g. unused tanks, filter) and determine space requirements (e.g. additional tank volume).

Consider limitations of AWT technologies (e.g. bromate formation potential for ozonation, sludge disposal for PAC, etc.), but also potential positive side effects (e.g. advanced phosphorous removal at a filtration stage, disinfection by ozone, improvement of other water quality parameters such as COD, DOC, TSS, heavy metals, etc.).

### **Costs**

Estimate investment (CAPEX) and operational costs (OPEX) based either on (national) reference values, if available, or on the local boundary conditions. For the latter, CAPEX and OPEX of the different AWT technologies need to be evaluated including potential required infrastructure (e.g. ozonation post-treatment, pumps, pre-filtration for GAC, etc.) according to the local/national cost evaluation procedure.

### **Overall evaluation**

Choosing the most suitable AWT technology for a specific WWTP should not only consider investment and operational costs, but could also include other criteria. Such criteria could be maturity and available experiences with the according technology (national, but also international), space requirements, carbon footprint, efforts for maintenance, required staff qualification, robustness of the process (especially relevant for small/remote WWTPs where staff is not always present) or ecotoxicological considerations.

### **Detailed planning**

After finalizing the feasibility study and selecting the favoured API elimination technology, a more in-depth planning is recommended to prepare the final tendering documents. The aim of this step is to reduce uncertainties regarding the final design and to build-up detailed knowledge for the targeted AWT technology. The detailed planning can consist of:

#### **Conduction of lab-scale tests**

If not already conducted in the course of the feasibility study, lab-scale experiments should be conducted with representative water samples from the according WWTP. The lab-tests can be used to determine dose-dependent correlations with API removal, suitable surrogate parameters relevant for defining the future setpoint of the AWT, and to derive robust design parameters for the chosen AWT technique without piloting activities.

Besides the API removal and bromate formation potential, lab-scale tests for ozonation<sup>44-46</sup> should focus on the ozone decay at different boundary conditions (e.g. water quality, pH, water temperature) to evaluate and optimize the reactor size with<sup>7</sup> or without CFD modelling.

Regarding PAC processes, batch lab-scale<sup>17-19</sup> experiments can be used to identify the optimal PAC type, determine the required dosage and the associated  $UVA_{254}$  reduction that can be used to monitor the PAC process and PAC quality control. Similar evaluation of different GAC types can be done with rapid small-scale column tests (RSSCT)<sup>20</sup>.

#### **On-site piloting**

In most cases, costly and time-consuming on-site piloting of mature technologies such as ozonation or activated carbon is not necessary, as many relevant design parameters can be derived from lab-scale tests. However, most experiences with AWT for API elimination come from WWTPs in central Europe (e.g. Germany, Switzerland, etc.). Thus, it cannot be ruled out that these experiences do not completely cover the different boundary conditions (e.g.

differences in the water matrix, water temperature variations) at WWTPs in other countries. Therefore, (short-term) piloting activities might be used to validate results from lab-scale experiments, build up knowledge for the operation of an AWT plant and for promotion/knowledge transfer purposes. Piloting activities might also be useful if e.g. results of lab-scale experiments differ strongly from other references, large hospitals or pharmaceutical industries are within the WWTP catchment area and cause unusual high API concentrations, or if the WWTP has a high share of industrial wastewater. Piloting activities can also be accompanied by an assessment of the formation of TPs/OPBs as well as ecotoxicological impacts of the ozonation and its biological post-treatment.

### **Additional monitoring, need for process control**

Depending on the amount of available data, additional monitoring of flows (average, range between min. and max.) as well as water quality parameters relevant for the design of the AWT process (e.g. DOC, nitrite, TSS) might be required.

These data can also be used to assess if the commonly used flow proportional dosage of ozone and PAC will be sufficient or a more advanced process control (e.g. load proportional,  $\Delta\text{UVA}_{254}$ , etc.) is required to meet the defined API target. Online sensors must be maintained on a regular basis, thus, they should be installed in a way that they can be easily accessed and maintained. Acceptance of the new technology can be increased by including local WWTP staff at planning process.

For ozonation only: If a relevant bromate formation is expected at the targeted specific ozone dose, a bromide source tracking can be conducted to identify hot spots for bromide emissions within the WWTP catchment area (see ozonation chapter) and to assess potential mitigation strategies. As usually no target value for bromate emissions from WWTP exist, acceptable discharge limits (e.g. linked e.g. to acute and chronic quality standards in the receiving water body (e.g. 50  $\mu\text{g}/\text{L}$ <sup>6</sup>) have to be agreed upon with the responsible water authority.

### **Optimizing existing systems**

After construction and commissioning of the AWT stage, several aspects can be evaluated to optimize AWT operation and to maintain a stable API elimination:

#### **Benchmarks for energy and liquid oxygen demand**

Especially for ozonation, energy and LOX consumption can be evaluated on a regular basis (e.g. every year) to identify trends and optimization potential. In addition, purchase of LOX and electricity can be re-evaluated regularly to reduce operational costs<sup>7, 8</sup>.

#### **Monitoring of bromide concentration**

When running a full-scale ozonation, bromide concentration could be measured at the influent of the ozonation on a regular basis (e.g. monthly) to identify potential increases due to changes within the catchment area. In case of high bromide concentrations and elevated bromate formation, bromide source tracking as well as bromate formation suppression strategies can be conducted.

#### **Variations of API elimination**

In case of unexpected variations of the API elimination, AWT stage should be monitored more frequently using surrogate parameters (e.g.  $\Delta\text{UVA}_{254}$ ) to identify potential disturbances. These might be caused by changes of the water quality (e.g. DOC, nitrite, etc.), the AWT process itself (e.g. dosing of PAC, reduced gas-water mass transfer in the ozonation, etc.) or the used AC material (e.g. changes on quality of PAC/GAC regarding API elimination). When using PAC for API elimination, quality checks should be conducted for each PAC delivery (e.g. using surrogate

---

<sup>6</sup> <https://www.ecotoxcentre.ch/expert-service/quality-standards/proposals-for-acute-and-chronic-quality-standards/>



parameters) and the PAC dose adapted in case PAC shows a lower API elimination capacity. GAC exchange frequency of can be optimized for parallel operated filters by (re-)starting the filters time-shifted.

### **PAC retention**

Regular measurements of the TSS and turbidity at the WWTP effluent are necessary to check the PAC retention by the final filtration. If the PAC retention is not sufficient, it should be checked if the coagulation process could be optimized.

# References

1. Zhiteneva, V.; Thisgaard, P.; Miehe, U.; Stapf, M.; Perkola, N.; Mehtonen, J.; Äystö, L.; Ek Henning, H. *Joint Conclusions for API Emission Reductions. CWPharma Activity 5.2 output*; 2020.
2. Thisgaard, P.; Zhiteneva, V.; Miehe, U.; Stapf, M.; Perkola, N.; Mehtonen, J.; Äystö, L.; Ek Henning, H. *Action Plan for API Emission Reductions. CWPharma Activity 5.3 output*; 2020.
3. von Sonntag, C.; von Gunten, U., *Chemistry of Ozone in Water and Wastewater Treatment. From Basic Principles to Applications*. IWA Publishing: 2012.
4. Lee, Y.; Gerrity, D.; Lee, M.; Bogeat, A. E.; Salhi, E.; Gamage, S.; Trenholm, R. A.; Wert, E. C.; Snyder, S. A.; Von Gunten, U., Prediction of micropollutant elimination during ozonation of municipal wastewater effluents: Use of kinetic and water specific information. *Environmental Science and Technology* **2013**, *47*, (11), 5872-5881.
5. Buffle, M.-O.; Schumacher, J.; Meylan, S.; Jekel, M.; von Gunten, U., Ozonation and Advanced Oxidation of Wastewater: Effect of O<sub>3</sub>Dose, pH, DOM and HO•-Scavengers on Ozone Decomposition and HO•-Generation. *Ozone: Science & Engineering* **2006**, *28*, (4), 247-259.
6. Stapf, M.; Schumann, P.; Völker, J.; Miehe, U. *Studie über Effekte und Nebeneffekte bei der Behandlung von kommunalem Abwasser mit Ozon*; Kompetenzzentrum Wasser Berlin: Berlin, 2017.
7. Sehlén, R.; Nilsson, J. *Evaluation and experiences of full-scale ozonation followed by MBBR post-treatment and comparison with previous pilot tests. GoA3.1: Pharmaceutical removal at full scale*; 2020.
8. Bregendahl, J.; Larsen, S. B.; Stapf, M.; Bester, K.; Kharel, S.; Svendsen, S. B.; Lukas, M.; Putna-Nimane, I.; Bogusz, A. *Evaluation and experiences of full-scale ozonation followed by MBBR post-treatment at Kalundborg wastewater treatment plant. CWPharma project report for GoA3.2: Flexible use of existing infrastructure*; 2020.
9. Soltermann, F.; Abegglen, C.; Gotz, C.; von Gunten, U., Bromide Sources and Loads in Swiss Surface Waters and Their Relevance for Bromate Formation during Wastewater Ozonation. *Environ Sci Technol* **2016**, *50*, (18), 9825-34.
10. Stapf, M.; Miehe, U.; Knoche, F.; Lukas, M.; Bartz, J.; Brauer, F.; Gutsche, M.; Kullwatz, J.; Petkow, C.; Schneider, M.; Winckelmann, D.; Bogusz, A.; Tomczyk, B.; Trzcińska, M.; Dworak, A.; Chojniak-Gronek, J.; Szumska, M.; Zieliński, M.; Walkowiak, R.; Putna-Nimane, I.; Liepina-Leimane, I.; Dzintare, L.; Barda, I.; Bester, K.; Kharel, S.; Sehlén, R.; J., N.; Larsen, S. B. *Impact of ozonation and post-treatment on ecotoxicological endpoints, water quality, APIs and transformation products. CWPharma project report for GoA3.3: Comparison of post-treatment options*; 2020.
11. Hübner, U.; von Gunten, U.; Jekel, M., Evaluation of the persistence of transformation products from ozonation of trace organic compounds - a critical review. *Water research* **2015**, *68*, 150-170.
12. Kharel, S.; Stapf, M.; Miehe, U.; Ekblad, M.; Cimbritz, M.; Falås, P.; Nilsson, J.; Sehlén, R.; Bester, K., 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* **2020**, *731*, 139064.
13. Bourgin, M.; Beck, B.; Boehler, M.; Borowska, E.; Fleiner, J.; Salhi, E.; Teichler, R.; von Gunten, U.; Siegrist, H.; McArdell, C. S., 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* **2018**, *129*, 486-498.

14. Sauter, D.; Dąbrowska, A.; Bloch, R.; Stapf, M.; Miehe, U.; Sperlich, A.; Gnirss, R.; Wintgens, T., Deep-bed filters as post-treatment for ozonation in tertiary municipal wastewater treatment: impact of design and operation on treatment goals. *Environmental Science: Water Research & Technology* **2021**.
15. Völker, J.; Stapf, M.; Miehe, U.; Wagner, M., Systematic Review of Toxicity Removal by Advanced Wastewater Treatment Technologies via Ozonation and Activated Carbon. *Environ Sci Technol* **2019**, *53*, (13), 7215-7233.
16. Maus, C.; Herbst, H.; Ante, S.; Becker, H. P.; Glathe, W.; Börgers, A.; Türk, J., Hinweise zu Auslegung und Design von Ozonanlagen zur Mikroschadstoffelimination. *Korrespondenz Abwasser, Abfall* **2014**, *61*, (11).
17. Zietzschmann, F.; Altmann, J.; Ruhl, A. S.; Dünnbier, U.; Dommisch, I.; Sperlich, A.; Meinel, F.; Jekel, M., Estimating organic micro-pollutant removal potential of activated carbons using UV absorption and carbon characteristics. *Water research* **2014**, *56*, 48-55.
18. Zietzschmann, F.; Altmann, J.; Hannemann, C.; Jekel, M., Lab-testing, predicting, and modeling multi-stage activated carbon adsorption of organic micro-pollutants from treated wastewater. *Water research* **2015**, *83*, 52-60.
19. Böhler, M. *Laborversuche zur Bestimmung der Reinigungsleistung von Pulveraktivkohle zur Entfernung von Mikroverunreinigungen auf Kläranlagen*; VSA, Eawag, 2019.
20. Zietzschmann, F.; Müller, J.; Sperlich, A.; Ruhl, A. S.; Meinel, F.; Altmann, J.; Jekel, M., Rapid small-scale column testing of granular activated carbon for organic micro-pollutant removal in treated domestic wastewater. *Water Science and Technology* **2014**, *70*, (7), 1271-1278.
21. Thomann, M.; Abegglen, C.; Baggenstos, M.; Bangerter, B.; Bleny, H.; Böhler, M.; Frei, R.; Sommer, M.; Thonney, D.; Wintgens, T.; Wunderlin, P.; Meier, A.; Grelot, J. *Pulveraktivkohle: Verfahren und Abtrennstufen*; VSA, Plattform „Verfahrenstechnik Mikroverunreinigungen“, 2019.
22. Metzger, S.; Alt, K.; Biebersdorf, N.; Böhler, M.; Bornemann, C.; Hiller, C.; Jedele, K.; Jekel, M.; Lyko, S.; Nahrstedt, A.; Wintgens, T.; Krahnstöver, T.; Mätzig, H.; Remy, C.; Rößler, A.; Zietzschmann, F.; Wilhelm, C. *Aktivkohleeinsatz auf kommunalen Kläranlagen zur Spurenstoffentfernung – Verfahrensvarianten, Reinigungsleistung und betriebliche Aspekte –*; Deutsche Vereinigung für Wasserwirtschaft, Abwasser und Abfall e. V. (DWA): Hennef, Mai 2019, 2019.
23. Lindell, P. *PAC retention by microsieve. Piloting at Viikinmäki WWTP.*; Helsinki Region Environmental Services Authority, 2019.
24. Altmann, J.; Ruhl, A. S.; Zietzschmann, F.; Jekel, M., Direct comparison of ozonation and adsorption onto powdered activated carbon for micropollutant removal in advanced wastewater treatment. *Water research* **2014**, *55*, 185-193.
25. Altmann, J.; Zietzschmann, F.; Geiling, E. L.; Ruhl, A. S.; Sperlich, A.; Jekel, M., Impacts of coagulation on the adsorption of organic micropollutants onto powdered activated carbon in treated domestic wastewater. *Chemosphere* **2015**, *125*, 198-204.
26. Böhler, M.; Joss, A.; McArdell, C.; Meier, A. *Hinweise zur Planung und Auslegung von diskontinuierlich gespülten GAK-Filtern zur Elimination organischer Spurenstoffe aus kommunalem Abwasser. Konsenspapier zum Ergebnis eines Workshops mit Fachexperten aus der Schweiz und Deutschland*; Eawag und VSA: Dübendorf, 2020.
27. Torresi, E.; Escolà Casas, M.; Polesel, F.; Plósz, B. G.; Christensson, M.; Bester, K., Impact of external carbon dose on the removal of micropollutants using methanol and ethanol in post-denitrifying Moving Bed Biofilm Reactors. *Water research* **2017**, *108*, 95-105.

28. Hapeshi, E.; Lambrianides, A.; Koutsoftas, P.; Kastanos, E.; Michael, C.; Fatta-Kassinou, D., Investigating the fate of iodinated X-ray contrast media iohexol and diatrizoate during microbial degradation in an MBBR system treating urban wastewater. *Environ Sci Pollut R* **2013**, *20*, (6), 3592-3606.
29. El-taliawy, H.; Casas, M. E.; Bester, K., Removal of ozonation products of pharmaceuticals in laboratory Moving Bed Biofilm Reactors (MBBRs). *Journal of Hazardous Materials* **2018**, *347*, 288-298.
30. Itzel, F.; Baetz, N.; Hohrenk, L. L.; Gehrman, L.; Antakyali, D.; Schmidt, T. C.; Tuerk, J., Evaluation of a biological post-treatment after full-scale ozonation at a municipal wastewater treatment plant. *Water research* **2020**, *170*, 115316.
31. Casas, M. E.; Chhetri, R. K.; Ooi, G.; Hansen, K. M. S.; Litty, K.; Christensson, M.; Kragelund, C.; Andersen, H. R.; Bester, K., Biodegradation of pharmaceuticals in hospital wastewater by staged Moving Bed Biofilm Reactors (MBBR). *Water research* **2015**, *83*, 293-302.
32. Polesel, F.; Torresi, E.; Loreggian, L.; Casas, M. E.; Christensson, M.; Bester, K.; Plósz, B. G., Removal of pharmaceuticals in pre-denitrifying MBBR – Influence of organic substrate availability in single- and three-stage configurations. *Water research* **2017**, *123*, 408-419.
33. Falås, P.; Baillon-Dhumez, A.; Andersen, H. R.; Ledin, A.; la Cour Jansen, J., Suspended biofilm carrier and activated sludge removal of acidic pharmaceuticals. *Water research* **2012**, *46*, (4), 1167-1175.
34. Falås, P.; Jewell, K. S.; Hermes, N.; Wick, A.; Ternes, T. A.; Joss, A.; Nielsen, J. L., Transformation, CO<sub>2</sub> formation and uptake of four organic micropollutants by carrier-attached microorganisms. *Water research* **2018**, *141*, 405-416.
35. Tang, K.; Spiliotopoulou, A.; Chhetri, R. K.; Ooi, G. T. H.; Kaarsholm, K. M. S.; Sundmark, K.; Florian, B.; Kragelund, C.; Bester, K.; Andersen, H. R., Removal of pharmaceuticals, toxicity and natural fluorescence through the ozonation of biologically-treated hospital wastewater, with further polishing via a suspended biofilm. *Chemical Engineering Journal* **2019**, *359*, 321-330.
36. Ooi, G. T. H.; Tang, K.; Chhetri, R. K.; Kaarsholm, K. M. S.; Sundmark, K.; Kragelund, C.; Litty, K.; Christensen, A.; Lindholst, S.; Sund, C.; Christensson, M.; Bester, K.; Andersen, H. R., Biological removal of pharmaceuticals from hospital wastewater in a pilot-scale staged moving bed biofilm reactor (MBBR) utilising nitrifying and denitrifying processes. *Bioresource Technology* **2018**, *267*, 677-687.
37. Lindell, P. *PAC retention by Mecana pile cloth filter. Piloting at Viikimäki WWTP.*; Helsinki Region Environmental Services Authority, 2019.
38. Metzger, S.; Barjenbruch, M.; Beier, S.; Miehe, U.; Nafu, I., Statusbericht „Spurenstoffentfernung auf kommunalen Kläranlagen in Deutschland“. *Korrespondenz Abwasser, Abfall* **2020**, *67*.
39. Zietzschmann, F.; Mitchell, R. L.; Jekel, M., Impacts of ozonation on the competition between organic micro-pollutants and effluent organic matter in powdered activated carbon adsorption. *Water research* **2015**, *84*, 153-60.
40. Äystö, L.; Stapf, M. *Scenarios for reducing pharmaceutical emissions -Estimated load reductions, greenhouse gas emissions & costs. CWPharma project report for GoA5.1.*; 2020.
41. Rettig, S.; Schulz, K.; Barjenbruch, M.; Al-Zreiqat, I. *Key Figure Data For Energy Efficiency. Benchmarking the Baltic Sea Region in the project IWAMA – Interactive Water Management.*; 2018.
42. Herbst, H.; Antakyali, D.; Sasse, R.; Ante, S.; Schulz, J., Kosten der Elimination von Mikroschadstoffen und mögliche Finanzierungsansätze. *Korrespondenz Abwasser, Abfall* **2016**, *63*, 2, 124-130.

43. SEPA *Advanced wastewater treatment for separation and removal of pharmaceutical residues and other hazardous substances - Needs, technologies and impacts. A government-commissioned report. Report number: 6803; 6803; The Swedish Environmental Protection Agency, 2017.*
44. Schindler Wildhaber, Y.; Mestankova, H.; Schärer, M.; Schirmer, K.; Salhi, E.; von Gunten, U., Novel test procedure to evaluate the treatability of wastewater with ozone. *Water research* **2015**, *75*, 324-335.
45. Zietzschmann, F.; Stapf, M.; Sperlich, A.; Ruhl, A.-S.; Miehe, U.; Gnirß, R.; Jekel, M. *TestTools – Entwicklung und Validierung von schnellen Testmethoden zum Spurenstoffverhalten in technischen und natürlichen Barrieren des urbanen Wasserkreislaufs; 21.12.2018, 2018.*
46. Zappatini, A.; Götz, C. *Testverfahren zur Beurteilung der Behandelbarkeit von Abwasser mit Ozon; Verband Schweizer Abwasser- und Gewässerschutzfachleute: Zofingen, 2015; p 36.*

# Appendix

The following compilation of full-scale plants that plan or already operate an ozonation, PAC or GAC process for API elimination is based mainly on the work of the German and Swiss competence centres (KomS<sup>7</sup>, VSA<sup>8</sup>).

*SI-Table 1: Overview of WWTPs with full-scale ozonation plants that are in operation or in the planning/construction phase, respectively. No claim to completeness.*

#	Country	WWTP	Post-treatment	Status
1	Denmark	Kalundborg	MBBR	In operation
2	Germany	Aachen-Soers	MBBR + sand filtration	In operation
3	Germany	Bad Sassendorf	Polishing pond	In operation
4	Germany	Duisburg-Vierlinden	MBBR	In operation
5	Germany	Eriskirch	Sand filtration	In operation
6	Germany	Warburg	MBBR	In operation
7	Sweden	Linköping	MBBR	In operation
8	Switzerland	Neugut	Sand filtration	In operation
9	Switzerland	Reinach	Sand filtration	In operation
10	Switzerland	Werdhölzli	Sand filtration	In operation
11	Switzerland	Bassersdorf	Sand filtration	In operation
12	Switzerland	Porrentruy	Sand filtration	In operation
13	Germany	Friedrichshafen	Sand filtration	Planning/construction
14	Germany	Herrenberg	Filtration	Planning/construction
15	Germany	Schloß Holte-Stukenbrock	Sand filtration	Planning/construction
16	Germany	Tübingen	Sand filtration	Planning/construction
17	Switzerland	Birsig	Sand filtration	Planning/construction
18	Switzerland	Furthof	Sand filtration	Planning/construction
19	Switzerland	Kloten Opfikon	Sand filtration	Planning/construction
20	Switzerland	Lützelmurgtal	Sand filtration	Planning/construction
21	Switzerland	Morgental (+ Hofen)	Sand filtration	Planning/construction
22	Switzerland	Neuchâtel	Sand filtration	Planning/construction
23	Switzerland	Seeland Süd	Sand filtration	Planning/construction
24	Switzerland	Birmensdorf	Sand filtration	Planning/construction
25	Switzerland	Birsig	Sand filtration	Planning/construction
26	Switzerland	Sierre	Sand filtration	Planning/construction
27	Switzerland	Aigle	Sand filtration	Planning/construction

*SI-Table 2: Overview of WWTPs with full-scale plants with combination processes that are in operation or in the planning/construction phase, respectively. No claim to completeness.*

#	Country	WWTP	Process option	Status
1	Germany	Weißenburg in Bayern	Ozone + sand-/GAC-filter (in parallel)	In operation
2	Switzerland	Altenrhein	Ozone + GAC-filter	In operation
3	Switzerland	ProRheno	Ozone + PAC prior to sand filtration	Planning/construction
4	Switzerland	Glarnerland	PAC + GAC	Planning/construction

<sup>7</sup> Kompetenzzentrum Spurenstoffe BW, <https://koms-bw.de/en/>

<sup>8</sup> VSA Plattform Verfahrenstechnik Mikroverunreinigungen, <https://micropoll.ch/>

SI-Table 3: Overview of WWTPs with full-scale GAC plants that are in operation or in the planning/construction phase, respectively. No claim to completeness.

#	Country	WWTP	Process option	Status
1	Germany	Bad Oeynhausen	GAC-filter	In operation
2	Germany	Gütersloh-Putzhagen	GAC-filter (2 / 9)	In operation
3	Germany	Obere Lutter	GAC-filter	In operation
4	Germany	Rietberg	GAC-filter (continuously operated)	In operation
5	Germany	Westerheim	GAC-filter	In operation
6	Switzerland	Penthaz	Moving bed GAC	In operation
7	Germany	Darmsheim	GAC-filter	Planning/construction
8	Switzerland	Delémont	Moving bed GAC	Planning/construction
9	Switzerland	Le Locle	Moving bed GAC / GAC filter	Planning/construction
10	Switzerland	Moos, Amriswil	GAC filter	Planning/construction
11	Switzerland	Muri	GAC filter	Planning/construction
12	Switzerland	Villette (+ Ocybèle)	Moving bed GAC / GAC filter	Planning/construction
13	Switzerland	Winterthur	GAC filter	Planning/construction
14	Switzerland	Luzern	Moving bed GAC	Planning/construction
15	Switzerland	Niederglatt	Moving bed GAC	Planning/construction
16	Switzerland	Val-de-Ruz	Moving bed GAC / GAC filter	Planning/construction
17	Switzerland	Rosenbergsau	Moving bed GAC	Planning/construction
18	Switzerland	La Saunerie	Moving bed GAC	Planning/construction
19	Switzerland	Brig	GAC filter	Planning/construction
20	Switzerland	Yverdon	Moving bed GAC	Planning/construction

SI-Table 4: Overview of WWTPs with full-scale PAC plants that are in operation or in the planning/construction phase, respectively. No claim to completeness.

#	Country	WWTP	Process option	Status
1	Germany	Albstadt-Ebingen	Ulmer process	In operation
2	Germany	Albstadt-Lautlingen	Ulmer process	In operation
3	Germany	Barntrup	PAC dosage prior to a filter	In operation
4	Germany	Böblingen-Sindelfingen	Ulmer process	In operation
5	Germany	Dülmen	Ulmer process	In operation
6	Germany	Hechingen	Ulmer process	In operation
7	Germany	Kressbronn-Langenargen	Ulmer process	In operation
8	Germany	Lahr	Ulmer process	In operation
9	Germany	Laichingen	Ulmer process	In operation
10	Germany	Langwiese	Ulmer process	In operation
11	Germany	Mannheim	Ulmer process	In operation
12	Germany	Öhringen	Ulmer process	In operation
13	Germany	Steinhäule	Ulmer process	In operation
14	Germany	Stockacher Aach	Ulmer process	In operation
15	Germany	Wendlingen am Neckar	Ulmer process	In operation
16	Switzerland	Herisau	Ulmer process	In operation
17	Switzerland	Thunersee	Ulmer process	In operation
18	Switzerland	Schönau	PAC dosage prior to a filter	In operation
19	Switzerland	Flos	Simultaneous PAC dosage	In operation
20	Switzerland	Egg-Oetwil am See	PAC dosage prior to a filter	In operation
21	Germany	Pforzheim	Ulmer process	Planning/construction
22	Germany	Stuttgart-Mühlhausen	PAC dosage prior to a filter	Planning/construction
23	Switzerland	Bioggio	PAC dosage prior to a filter	Planning/construction
24	Switzerland	Ecublens	PAC dosage prior to a filter	Planning/construction
25	Switzerland	Ergolz 1	PAC dosage prior to a filter	Planning/construction
26	Switzerland	Fehraltorf	Ulmer process	Planning/construction
27	Switzerland	Gossau-Grüningen	PAC dosage prior to a filter	Planning/construction
28	Switzerland	La Chaux-de-Fonds	PAC dosage prior to a filter	Planning/construction
29	Switzerland	Lachen-Untermarch	PAC dosage prior to a filter	Planning/construction
30	Switzerland	Oberglatt	Ulmer process	Planning/construction
31	Switzerland	Zimmerberg	PAC into MBR	Planning/construction
32	Switzerland	Falkenstein	PAC into MBR	Planning/construction