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Balancing effectiveness, costs and implications

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Treatment of micropollutants in wastewater: balancing effectiveness, costs and implications


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Treatment of micropollutants in wastewater: balancing effectiveness, costs and implications

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Abstract

In this contribution, we analyse scenarios of advanced wastewater treatment for the removal of micropollutants. We refer to current mainstream, broad spectrum processes including ozonation and sorption onto activated carbon. We argue that advanced treatment requires properly implemented tertiary (nutrient removal) treatment in order to be effective. We review the critical aspects of the main advanced treatment options, their advantages and disadvantages. We propose a quantification of the costs of implementing advanced treatment, as well as upgrading plants from secondary to tertiary treatment when needed, and we illustrate what drives the costs of advanced treatment for a set of standard configurations. We propose a cost function to represent the total costs (investment, operation and maintenance) of advanced treatment. We quantify the implications of advanced treatment in terms of greenhouse gas emissions. Based on the indicators of total toxic discharge, toxicity at the discharge points and toxicity across the stream network discussed in Pistocchi et al., 2022, we compare costs and effectiveness of different scenarios of advanced treatment. In principle the total toxic load and toxicity at the points of discharge could be reduced by about 75% if advanced treatment processes were implemented virtually at all wastewater treatment plants, but this would entail costs of about 4 billion euro/year for the European Union as a whole. We identify a “compromise” scenario where advanced treatment is required at plants of 100 thousand population equivalents (PE) or larger, or at plants between 10 and 100 thousand PE if the dilution ratio at the discharge point is 10 or less. Under this scenario, the extent of the stream network exposed to high toxicity would not increase, and the other indicators would not deteriorate significantly, while the costs would remain at about 1.5 billion Euro/year. Arguably, costs could be further reduced, without a worsening of water quality, if we replace a local risk assessment with the above criteria of plant capacity and dilution to determine if a WWTP requires advanced treatment.
Keywords

Introduction
In the past decades, urban wastewater treatment plants (WWTPs) have been designed for the removal of organic carbon, nitrogen and phosphorus with effluent standards depending on the permitting rules in place. In the European Union (EU), these conform to the Urban Wastewater Treatment Directive (UWWTD) 91/271/EEC. Although WWTPs are able to remove many pollutants through sorption and biodegradation, they remain an important point of entry into the aquatic environment for the more persistent and mobile contaminants. A demand has grown over time to address in particular organic trace compounds of emerging concern such as pharmaceuticals, biocides and pesticides, and other household and industrial chemicals, collectively referred to as micropollutants (MPs), besides constituents such as microplastics, engineered nanoparticles and pathogens.

An appreciable removal of MPs at a WWTP usually requires more advanced treatment processes than conventional pollution, and may imply higher resource intensity and associated greenhouse gas (GHG) and other emissions. Most obviously, an advanced treatment implies higher investment and operational costs, and may require more skilled operators compared to a conventional treatment.

Establishing an appropriate level of wastewater treatment entails balancing the reduction of MP concentrations in effluents, on the one side, and resource intensity, emissions and costs, on the other. As the marginal removal of MPs decreases with the intensity of treatment, arguably it would not be convenient to push the treatment beyond a certain level. Finding a trade-off between costs, impacts and benefits is key to sustainable wastewater treatment.

In this contribution, we consider the mainstream options currently available for the removal of MPs from wastewater beyond the performance of conventional WWTPs. We focus on two broad families

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of processes, namely activated carbon (AC, in powdered (PAC) or granular (GAC) form) and chemical oxidation with ozone (O$_3$).

A plethora of specific processes has been developed to address particular classes of contaminants. Moreover, disinfection processes already applied in WWTPs discharging to water bodies used for bathing or aquaculture, not falling into one of the above categories, may also have in principle an effect on MPs.

All these processes have usually shown to remove contaminants to a similar extent, but at higher costs or with more severe constraints (e.g. regeneration of alternative adsorbents, security problems with the storage of hazardous reagents, by-products, energy consumption, availabilities of resources or catalysts etc.) in comparison with AC and O$_3$ (Abegglen, 2012; Miklos et al., 2018). Therefore, solutions at the full scale are mainly limited to the abovementioned processes alone or in combination.

Applying AC or O$_3$ to the effluents of conventional biological treatment plants enables in principle a substantial removal of the majority of MPs from wastewater. However, we need to compare this positive effect with the costs of investment and operation, increased consumption of energy and other resources, and associated greenhouse gas (GHG) emissions, both directly during the process, and embedded in the process input (e.g. Jekel et al. 2015; Meier and Remy 2020).

Moreover, advanced treatment of MPs may have unintended negative effects on the effluents due to the formation of by-products (e.g. bromates during O$_3$ if bromide is appreciably present in the influent), or undermine the reuse of sludge in agriculture (e.g. when PAC is applied in the activated sludge bioreactor and cannot be separated from the excess sludge).

This paper addresses the technical and economic conditions that make advanced urban wastewater treatment for MP removal a cost-effective solution.

After discussing the preconditions required on biological treatment before implementing advanced treatment, we examine the different options available, the costs of their implementation depending on the desired removal of MPs, their energy and GHG emissions and subsequent implications, and
other factors that may hamper or enable the incorporation of advanced treatment processes in existing WWTPs. In this, we take into account the initial conditions of a given WWTP and the possible synergies with disinfection processes for the removal of MPs. On this basis, we explore the trade-offs between costs and benefits of implementing advanced wastewater treatment in the European context, with the aim of identifying an acceptable, cost-effective strategy for the end-of-pipe control of MPs in wastewater. Throughout this contribution, we regard end-of-pipe treatment as complementary to the control of micropollutants at the source. Consequently, our analysis does not endorse end-of-pipe treatment as the only, or even the most important component of an overall approach to MP pollution control.

The importance of conventional biological treatment performance

The quantification of MP removal within a conventional activated sludge (CAS) wastewater treatment process, as obtained by the existing models applied in practice, considers three types of removal processes: sorption to suspended solids, volatilization, and degradation (e.g. Pomiès et al., 2013). Volatilization is usually less uncertain than other mechanisms as it depends on the air-water partition coefficient (Henry’s constant) and the air flow in the bioreactor, which are relatively simple to quantify. Volatilization can be important for highly volatile chemicals (such as synthetic musks and cyclic silicones), but usually a marginal mechanism for less volatile chemicals, typically of more direct concern for water pollution.

Sorption and degradation, on the contrary, depend on partitioning coefficients and degradation rates subject to the effect of several mechanisms of physicochemical interactions at the surface of suspended solids and kinetics of microorganisms (ibid.). Sorption of MPs may occur onto primary or secondary sludge, and in some cases on digested sludge.

The removal of MPs by sorption occurs in stages: first, readily sorbed MPs are removed from the influent with primary sludge; subsequently, the remaining mass of the MPs is partly adsorbed on the
active biomass in the bioreactor, where degradation also occurs (Hoersing et al., 2011; Andersen et al., 2005).

Degradation may consist of biodegradation (when a MP is fully mineralized), or more often of biotransformation (when a MP is converted to a metabolite). Usually, because of their low concentration, MPs are a co-substrate of the biodegradation of organic matter rather than a specific substrate.

The individual mechanisms of biodegradation are often still poorly understood. However, there is a general agreement on the fact that in conventional activated sludge (CAS) processes a longer hydraulic retention time (HRT) provides more time for biodegradation, and a longer sludge residence time (SRT) enables the development of slow-growing bacterial biomass, hence a higher diversity of organisms to attack the chemicals more effectively (Martin Ruel et al., 2010; Dytczak et al., 2008). Long SRT has been suggested as a generally representative parameter when designing biological processes for the biological removal of biodegradable MPs (Kreuzinger et al., 2004, Clara et al., 2005).

As a longer SRT is required for nitrification, we usually expect a higher removal of MPs in nitrifying plants than in plants designed only for the removal of organic carbon.

The further extension of the SRT beyond what is needed for nitrification brings limited benefits (e.g. up to a few percent of additional degradation for some highly biodegradable MPs: Choubert et al., 2011, Falas et al., 2016), and has potentially negative impacts on the energy balance.

An effect similar to extending the SRT in a CAS can be obtained with biofilm carriers added to a bioreactor (the so-called moving-bed bioreactor configuration, MBBR), combinations of CAS with fixed biofilms (integrated fixed film activated sludge - IFAS), membrane aerated bioreactors (MABR) or biofiltration systems. In these configurations, the biofilm that develops enables the growth of microorganisms usually not present in a conventional bioreactor designed with low SRT. Krzeminski et al., 2019, review the role and mechanisms of biological treatment processes for the removal of MPs. They highlight that the adoption of an MBBR configuration does not seem to bring other clear
advantages over a nitrifying-denitrifying CAS process designed with a sufficient SRT, although improved removal have been documented for specific substances (Falas et al., 2012, 2016). Another popular variant to the CAS is the membrane bioreactor (MBR), whereby a membrane replaces the secondary settler after the bioreactor. Arguably, an MBR achieves similar performances compared to CAS, if both systems are operated under the same temperature, sludge age and redox conditions, although bioassays have sometimes shown a higher capability of MBR to reduce the oestrogenic activity of the effluent (Bertanza et al., 2011). It has been suggested that the presence of dispersed bacteria and the smaller diameter of flocs in an MBR compared to a CAS bioreactor may favour mass transfer and degradation of highly soluble MPs. Advantages and disadvantages of converting CAS into MBR are site specific depending on various technical and economic implications (Bertanza et al., 2017).

The role of denitrification is less clear. Denitrification is often co-implemented with nitrification by varying the redox conditions within the reactor, which may enable the growth of a more diversified community of microorganisms and pool of active enzymes, thus promoting the removal of a broader spectrum of MPs. However, improvements over oxic plants have proven quite limited (Falas et al., 2016), hence denitrification seems to be less critical than nitrification for the biological removal of MPs.

Besides controlling the extent to which biodegradation of MPs can occur, the plant’s biological removal performance with conventional pollutants has also important economic implications, because it may affect the consumption of reagents. In particular, nitrites (NO2-) compete with MPs for oxidants such as ozone, hence nitrification should be effective and the concentration of NO2- at the end of biological treatment should be checked at the design stage. Nitrite reacts very quickly with ozone and is almost completely oxidised to nitrate (Liu 2001). If the wastewater contains a lot of nitrite, the ozone is rapidly depleted and less ozone is available for the degradation of MPs.
The oxidation of ammonium with ozone does not take place to a significant extent (Hoigné and Bader, 1983).

The dissolved organic carbon (DOC) and NH₄ compete for adsorbents such as AC. Phosphate (PO₄) can also be adsorbed to AC to some extent, and even more strongly with other sorbents (such as expanded clay). In the case of adsorption on GAC beds, low concentrations of total suspended solids (TSS) are also important in order to limit clogging and the need of backwash. Finally, dissolved organic matter (measured as dissolved organic carbon -DOC) competes for both oxidants and sorbents and should be as low as possible in order to reduce the dose of both O₃ and PAC (or to ensure a sufficient lifespan of a GAC contactor) required for the removal of MPs.

Based on the above considerations, we may conclude that lower concentrations of conventional pollutants imply a better operation operation of advanced treatment, and we can regard good biological removal of carbon and nutrients as a technical prerequisite before implementing any more advanced treatment. Table 1 summarizes indicative biological treatment effluent quality requirements that can be recommended in order to make MP removal cost-effective (see Phan et al., 2022; Juaréz et al., 2021).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Requirement s for AC</th>
<th>Requirement s for O₃</th>
<th>Typical in plants with COD removal only</th>
<th>Typical in plants with Nitrification only</th>
<th>Typical in plants with Denitrification and P removal</th>
<th>Typical in plants with Filtration (sand filtration, drum or dish filters, MF/UF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>&lt;30 mg/L in order to limit the need to backwash the GAC bed</td>
<td>&lt;30 mg/L</td>
<td>150 mg/L – 70% reduction</td>
<td>100 mg/L – 80% reduction</td>
<td>50 mg/L – 90% reduction</td>
<td>-</td>
</tr>
<tr>
<td>TSS</td>
<td>&lt;20 mg/L in order to limit O₃ dosage and risks of Bromate formation</td>
<td>&lt;20 mg/L</td>
<td>45 mg/L – 85% reduction</td>
<td>30 mg/L – 90% reduction</td>
<td>15 mg/L – 95% reduction</td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Total N</td>
<td>NNH4&lt; 2 mg/L</td>
<td>NNO2&lt;1 mg/L</td>
<td>45 mg/L – 10% reduction</td>
<td>35 mg/L – 30% reduction</td>
<td>15 mg/L – 70% reduction</td>
<td>-</td>
</tr>
<tr>
<td>---------</td>
<td>--------------</td>
<td>-------------</td>
<td>--------------------------</td>
<td>-------------------------</td>
<td>--------------------------</td>
<td>---</td>
</tr>
<tr>
<td>Total P</td>
<td>9 mg/L – 10% reduction</td>
<td>9 mg/L – 10% reduction</td>
<td>2 mg/L – 80% reduction</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>E.Coli</td>
<td>3 log-reduction</td>
<td>3 log-reduction</td>
<td>3 log-reduction</td>
<td>4 log-reduction</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Indicative removal of micropollutants</td>
<td>20% reduction</td>
<td>30% reduction</td>
<td>60% reduction</td>
<td>70% reduction</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SRT</td>
<td>3 to 5 days</td>
<td>8-12 days</td>
<td>15-25 days</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Table 1 – Indicative quality requirements for effluents for well-functioning advanced treatment. We assume COD ~3 x DOC.

Options for the advanced treatment of wastewater micropollutants

Processes based on oxidation

Ozonation entails a direct pathway consisting of the reaction of the MP with ozone (O₃) and a pathway by radical reactions, mostly driven by hydroxyl radical (OH) (von Sonntag and von Gunten, 2012 and von Gunten 2018). The dosage of O₃ needed to abate MPs depends largely on the dissolved organic carbon (DOC) of the influent (Antoniou et al., 2013 and Lee and von Gunten 2016 and Bourgin et al. 2018), as well as on NO₂⁻ and to a lesser extent the suspended solids. Besides NO₂⁻, other chemical species found in wastewater can react with ozone and/or OH, including bromide (Br⁻) and iodide (I⁻) (Gottschalk et al., 2009). Other species consume OH (e.g. carbonate (CO₃²⁻) dissolved organic matter (DOM) (von Sonntag and von Gunten 2012 and Gottschalk et al., 2009) resulting in a limitation of the OH-induced pathway of oxidation. The reactivity of a compound with O₃ depends on functional groups rather than the entire structure. Activated aromatic moieties, olefins, neutral amines and reduced sulfur moieties make compounds particularly reactive to ozone (von Sonntag and von Gunten, 2012 and Lee and von Gunten, 2016 and von Gunten, 2018). The extent of transformation of MPs in...
Ozonation strongly depends on their chemical structure. Many MPs are abated at extents >80% for an average ozone dose of 0.5-0.9 gO₃/gDOC⁻¹ (e.g. Penru et al., 2018 and Hollender et al., 2009, Lee et al., 2013 Bourgin et al., 2018, El-taliawy et al., 2017).

A typical configuration of an ozonation process entails equipment for on-site generation of O₃, a reactor where O₃ comes into contact with the influent, and an ozone destruction unit to treat the off-gas. The feedstock for O₃ generation may be pure oxygen or air, and the process most commonly used in wastewater treatment plants is electrical discharge (Metcalf & Eddy, 2014). When using air, the generation of O₃ requires 1.5 to 2 times as much energy as from pure oxygen. The latter, though, needs to be prepared at another industrial facility and transported in liquefied form, so the impact of both feedstocks is arguably comparable and the choice between the two depends on practical factors, such as the availability of space, plant size, safety requirements on the site, etc. (Abegglen C. et al., 2012).

The contact time with O₃ and the configuration of the reactor play an important role. It is generally recommended to work at low ozone dosage with a contact time of 10-14 minutes for maximum flow. Not every wastewater is suitable for treatment with ozone. In some cases, harmful non-degradable reaction products can form by oxidation (for instance, high concentrations of bromide in the influent yield potentially carcinogenic bromate). The safety of ozonation has to be tested in an early stage of planning, and specific procedures exist on purpose (VSA, 2021).

Moreover, oxidation may cause only a partial oxidation of compounds, generating some transformation products that can be potentially harmful. Many studies indicate that oestrogenicity is efficiently abated during ozonation and with other oxidants (Huber et al., 2004 and Lee et al., 2008 and Escher et al., 2009 and Schindler et al, 2015). In some cases, though, biological essays have shown that a reduced concentration of certain target MPs in ozonation effluents from real wastewater did not correspond to a reduction of oestrogenicity, which could be attributed to transformation products (Bertanza et al, 2011, 2013). It has been also shown that effects such as antibiotic activity and algal
In order to limit risks from transformation products, it is good practice to polish ozonation effluents via sand filtration or biological treatments (see e.g. Tang et al., 2020). Polishing processes may include biofiltration, MBBR and GAC besides sand filtration. The main effect of the biological post-treatment is the degradation of the oxidation by-products formed from the dissolved organic matter matrix, as transformation products are usually not biodegradable (Gulde et al., 2021). Typical polishing processes include biological sand or activated carbon filtration, biofiltration (Bourgin et al., 2018).

Processes based on adsorption

Adsorption of hydrophilic MPs occurs when the treated effluent is put in contact with solids of very high specific surface, and is primarily due to electrostatic interactions. AC is widely adopted for the purification of water and other fluids in many industrial applications. While alternative sorbents have been developed, such as zeolites or expanded clay (e.g. Tahar et al., 2014), AC remains to date the most cost-effective option for the removal of wastewater MPs. AC is produced from an appropriate thermal processing of a carbonaceous feedstock, yielding a carbon structure with very high micro-porosity, hence very large specific surface. The latter enables the capture of dissolved MPs from the influent, until the available adsorption sites are saturated. The feedstock may be virtually any material containing carbon, including hard coal, lignite, charcoal of wood or other ligno-cellulosic materials, or biochar (Gu et al., 2018). The typical configurations of AC include powder (PAC), fluidized granular grains (micro-grains), or a granular fixed bed (GAC) (Metcalf & Eddy, 2014).

PAC can be dosed directly into or after the biological reactor. Direct dosing of PAC has primarily been studied in suspended sludge processes (Serrano et al., 2011; Boehler et al., 2012; Meinel et al., 2016), with or without membranes for biomass separation, but the possibility has also been demonstrated for biofilm processes (Cimbritz et al., 2019). Dosing after the biological treatment entails separate contact reactors and various separation methods (Boehler et al., 2012, Altmann et al., 2015; Margot
et al., 2011; Löwenberg et al., 2013; Kårelid et al., 2017). It is possible to dose the PAC directly before a sand filter to keep the system compact (Löwenberg et al., 2016 and Boehler et al., 2011).

When the process configuration allows, PAC can be recirculated in order to maximize its utilization (counter current principle).

After treatment, PAC must be separated from the effluent either through settling and/or through filtration (e.g. membrane ultra-filtration, UF, sand filtration or cloth filters).

When the ambition is to remove 80% of certain indicator substances, a HRT of 30min should be ensured according to DWA, 2021. As for oxidation, the quality of the influent for an AC process is critical. DOC, that has affinity with AC, must be therefore as low as possible in order to reduce the dose of sorbent, hence costs. A typical dosage is 1.5 g PAC/gDOC to treat a secondary effluent, while it must be higher (2-2.5gPAC/gDOC) if the PAC is added directly in the biological treatment.

PAC added into the biological system makes the quality of the sludge unfit for reuse through spreading on farmland due to the presence of the adsorbed MPs. It also increases the volume of sludge produced by 20-30% depending on the dosage. On the contrary, PAC is beneficial for sludge incineration, as it increases its energy content. When PAC is obtained from biogenic feedstock, its combustion is also climate-neutral, but this is not the case when PAC derives from fossil feedstock.

The appraisal of PAC as a solution requires a broader consideration of the sludge handling strategy applied. At present, the agricultural use of sludge is heavily debated, and some countries are virtually phasing it out (e.g. Germany’s regulation, BGB I Nr. 65 S. 3465 ff., 2017) also considering that part of the agricultural value of sludge (particularly phosphorus) may be recovered through specific processes compatible with incineration.

GAC entails a separate reactor where the influent comes into contact with the granules forming a fixed bed. This avoids the need for settling. However, not only requires GAC a low influent DOC content, but also lower suspended solids (usually <20 mg/L) to enable a smooth operation by limiting clogging and reduced backwash frequency, hence costs. For an effective removal of MPs, the hydraulic
retention time (or “empty bed contact time”, EBCT) of the reactor should be of 20-30 minutes (Böhler et al. 2020, Fundneider et al. 2020) for the maximum flow that has to be treated. Shorter contact times were also found effective in some cases (Besnault et al., 2015). When the GAC filter is saturated, it requires regeneration of the sorbent. The time before a GAC bed requires regeneration, usually expressed as the volume of influent treated divided by empty bed volume, i.e. number of bed volumes (BV), is a critical parameter driving the costs and impacts associated to a GAC treatment. Swiss recommendations (Böhler et al. 2020) indicate a GAC duration of 20,000 – 30’000 BV when treating urban wastewater, although the variation observed in practice is very large (e.g. Benstoem et al., 2017). This is dependent on the concentration of DOC and the general composition of the wastewater. Regeneration requires transport of used GAC to a factory, and its exposure to high temperature (1200°C). During this step, a loss of 10 to 20% of GAC occurs requiring the addition of new GAC, so called “make up”. The possibility of regeneration is an advantage of GAC over PAC, potentially reducing GHG emissions (Meier and Remy, 2020).

GAC can be used also in a fluidized bed system. This type of solution uses a smaller grain size of GAC compared to a fixed bed, and leaves the grains fluidized in a reactor. Fresh GAC is added regularly (e.g. once a day) and used GAC is removed about once a week and stored for regeneration. So the dosage is more flexible compared with a conventional GAC filter and the smaller grain size allows higher reaction rates. The GAC stays in the system for about 100 days. This enables installations with lower reactor volume compared to conventional GAC filtration, and lowers risks of clogging.

For both PAC and GAC, the production or regeneration of the sorbent accounts for a significant part of the treatment costs and impacts because of the energy and chemicals use it entails.

Role of membrane filtration and constructed wetlands

The ultrafiltration or microfiltration membranes used in MBR as a replacement for secondary settlers may in principle achieve a good removal of certain MPs, but in general there seems to be no evidence of a better performance of MBR systems compared to conventional plants. However, for the removal
of molecules with a size of a few hundred daltons (Da) or less, as is the case for many MPs, membranes need to have a proportionately small pore size (molecular cut-off), which makes them fall in the realm of nanofiltration, if not even reverse osmosis. Use of these techniques for secondary urban wastewater effluents entails relatively high investment costs as well as high operating pressures, hence energy, which makes them expensive for ordinary wastewater treatment if compared to AC and O$_3$. Membrane filtration may become more affordable if the effluents are intended for water reuse, and could be an option for new plants. Moreover, nanofiltration and reverse osmosis generate a concentrate (brine) that must be treated in a sidestream process before it can be released to surface water.

Constructed wetlands (CW) are systems adapted for the wastewater treatment in small communities, involving filtration and biological degradation processes, or even photodegradation. The reactor is filled with gravel (when raw wastewater is applied) or sand (when primary treated wastewater is applied) or consists of a free surface pond. Removal efficiencies by these processes are in the same range as those of activate sludge process for most substances (Choubert et al., 2011). Ilyas et al., 2020, review a considerable number of case studies concerning the removal of pharmaceuticals in constructed wetlands and highlight that removal efficiencies may be rather high. However, they also point at a large variability stemming from the variable operational conditions of CW, the properties of the chemicals, and the variety of biophysical processes involved (including biodegradation, photodegradation, plant uptake and sorption). Overall, our understanding of the relationships between design parameters of CW and removal efficiency is still rather limited (Ilyas and van Hullebusch, 2019), although retention times and design parameters seem capable to explain the observed removal of various organic contaminants (Ilyas et al., 2021). The performance of CW seems consistent with that of biological treatment processes, while space requirements for CW can be limiting for their development in urban areas.
Recently, constructed wetlands processes have been increasingly proposed as a polishing stage also for the secondary effluents of larger plants (Papias et al., 2018). High hydraulic retention time (several days), low water level and solar-radiation are operating conditions that can explain their good polishing performances (Gabet-Giraud et al., 2010).

The role of disinfection processes for the removal of micropollutants

At present, more than 10% (by capacity) of the European wastewater treatment plants includes a disinfection stage. This is usually required when effluents are discharged to waters assigned to bathing or aquaculture, or reused. The most common disinfection processes are based on chlorination (not relevant for MP control), ultraviolet (UV) radiation or chemical oxidation.

UV radiation (in the form of UV-B from sunlight, or as engineered light enriched as UV-C) can directly transform some organic compounds (Fatta-Kassinos et al., 2011). Additionally, the presence of photosensitizers (e.g., nitrate, dissolved organic matter) can generates reactive transient species that oxidize organic compounds through indirect photodegradation (Mathon et al., 2019). The structure of the molecule (absorption spectrum and quantum yield) and the physicochemical conditions of the water determines the efficiency of both direct and indirect photodegradation, particularly in secondary WWTP effluents. The kinetic constants and half-life for the photodegradation of various micropollutants have been extensively reported, although most studies report data for pure water or synthetic wastewater: only very few studies addressed real secondary treated wastewaters, and none under full-scale conditions (Mathon et al., 2016).

UV radiation is usually unable to significantly transform organic micropollutants in WWTP effluents at the dose level used for disinfection (Paredes et al., 2018). At much higher (e.g. 100x) dose, though, it could abate micropollutants. Still, the contact time required for this would be of at least 1 hour (Paredes et al., 2018), compared to the contact time for disinfection (typically <10-15 minutes), and this would require 4 to 6 times larger volumes for the treatment. The additional cost due to the increased energy demand and infrastructure upgrading is likely not to make UV alone a competitive
alternative to other advanced treatment processes. Nevertheless, UV irradiation can be effective at removing certain substances, such as diclofenac, acid fenofibric or propranolol, in systems with high hydraulic retention time (> 5 days) and less than 20 cm water depth (Mathon et al., 2019).

Conventional chemical oxidation processes include chlorination (either with hypochlorous acid, HOCl or hypochlorite, ClO\textsuperscript{-}) and peracetic acid (PAA) treatment of secondary effluents (Deborde, 2008). Hypochlorous acid and PAA are selective oxidants at the low concentrations applied, and form organic compounds which may be undesirable. Hypochlorous acid can attack a broader range of organic chemicals than PAA, but is very sensitive to pH because the more strongly oxidizing form, HOCl, has a pKa of 7.4 (Deborde, 2008, Kim and Huang 2021).

Chemical oxidation is widely used for the control of pathogens (bacteria, viruses, protozoa and helminths) and antimicrobial resistance genes (ARGs). The oxidant doses for inactivation of oxidant-resistant microorganisms (protozoa, bacterial spores, ARGs) are higher than for most MPs (von Sonntag und von Gunten, 2012 and Czekalski et al., 2016), so these treatments may have a sizable effect on most MPs.

In conclusion, the presence of a disinfection stage does not necessarily add a significant contribution in terms of MP removal, and at the same time a process of advanced treatment for micropollutants may not be sufficient for disinfection purposes. However, depending on the disinfection targets there may be synergisms that need to be appraised on a case by case basis.

Life-cycle impacts of advanced treatment

The removal of MPs from wastewater using PAC, GAC or O\textsubscript{3} implies a more complex treatment plant with a potentially larger use of materials, process inputs, and energy. All this entails supply chains with the associated impacts, and calls for a life-cycle analysis (LCA) perspective (Risch et al., 2021). LCA must considers all greenhouse gas (GHG) and other emissions causing acidification, ozone depletion, toxicity and eutrophication, and resource use of all material and energy flows associated to the inputs.
processes and outputs of wastewater treatment. In this way, it can unveil the environmental implications of alternative treatment options in a holistic perspective. Application of LCA to wastewater treatment can be very challenging. Reliance on existing databases for the so-called characterization factors, representing parametric impacts of wastewater inputs (such as the energy and chemicals used for a treatment process) on various environmental dimensions, may not provide a correct account of the specific conditions of each plant, e.g. when energy or chemicals are derived from circular processes and may have a peculiar impact profile. Process innovation and optimization may also play a substantial role in mitigating the impacts of advanced treatment. For instance, using energy from renewable resources may significantly reduce the GHG emissions of O₃, and use of non-fossil feedstock for the sorbent may reduce the GHG emissions of GAC and PAC (Joseph et al., 2020). Several studies have addressed the LCA of solutions for the removal of MPs from wastewater. Rahman et al. (2018) and Risch et al. (2021), consider GAC, O₃ and other advanced treatment options for a list of usual wastewater MPs in the American and French contexts, and conclude that the reduced ecological and human toxicity due to lower discharges of MPs may be comparable with, or even outweighed by the toxicity caused by additional treatment. However, GAC and O₃ perform far better than other solutions (membranes or other AOPs). While MP removal by GAC and O₃ cause slight increases in other impact categories (eutrophication, global warming potential, acidification and ozone depletion), Rahman et al. (2018) show that the effects attributable to GAC or O₃ alone are small compared to the overall impacts of wastewater treatment (including nutrient removal).

Tarpani and Azapagic, 2018, show better performances for GAC than for O₃ under the point of view of greenhouse gas emissions, mainly associated to energy demand, but the differences among the two are relatively small.

Pesqueira et al., 2020, in their systematic review note that LCA studies on MP removal processes are relatively consistent and show that energy and chemicals used for MP removal drive the bulk of the impacts. The production of both energy and chemicals may cause impacts in terms of all types of...
emissions. However, Pesqueira et al. 2020 point out that such studies may generally suffer from an underestimation of the benefits associated to the removal of MPs, because they consider a reduction of toxicity with reference to a limited set of contaminants. As broad-spectrum advanced treatment processes typically remove a range of chemicals, the reduction of effluent toxicity is expected to exceed by far the additional toxicity associated to reagents and energy for GAC and O₃, contrary to the findings of Rahman et al., 2018. A more realistic picture of the extent to which advanced treatment reduces effluent toxicity may stem from the deployment of bioassays for a more suitable characterisation (Pedrazzani et al., 2019a, Escher and Leusch, 2011; Gonzalez-Gil et al., 2016; Papa et al. 2016a, Pedrazzani et al., 2020; see also Phan et al., 2021). Use of results of bioassays in LCA requires their conversion into equivalent pollutant mass flows (as suggested by Pedrazzani et al., 2018 and Pedrazzani et al., 2019b; see also Papa et al. 2013, 2016b).

The GHG emissions associated to advanced treatment, due to the use of energy and reagents, remain an important issue to consider. Recent LCA studies (Tarpani and Azapagic, 2018, Li et al., 2019) indicate a relatively narrow range of emissions between 0.15 and 0.3 kg CO₂e/m³ of wastewater treated for AC and O₃ as well as for membrane filtration. Collin et al., 2020, based on Georges et al., 2009, also consider emissions from sand filters around 7.5 kg CO₂e/PE/year, or roughly 0.1 kg/m³.

**Modelling the costs of advanced wastewater micropollutant removal**

The implementation of an advanced treatment level for wastewater MPs entails (1) costs for the retrofitting of the existing biological (secondary and tertiary) treatment in order to ensure sufficient effluent quality, and (2) costs for the implementation of new treatment processes. The costs of retrofitting of existing plants depend on their initial operating conditions and margins of improvement, on the available space and reactor volumes, and several other site-specific factors. In this section, we propose a schematic quantification of the implementation of advanced treatment only, with the sole purpose of a screening-level calculation to compare strategic investment alternatives at the
continental scale. The Supplementary information illustrates an additional calculation including an estimate of the costs to retrofit the existing plants. The costs of new treatment processes depend largely on the type of process and design configuration adopted, and in any case the specific conditions of a plant may cause a considerable variation. Therefore it is difficult to correctly compare the costs of projects at different WWTP.

The costs of advanced treatment include the CAPEX for additional infrastructure, as well as the O&M, energy costs and costs of consumables employed in the processes (i.e. the operational expenditure, OPEX). For ozonation, the infrastructure includes the contactor as well as the ozone generation and quenching equipment. Moreover, ozonation needs post-treatment, e.g. with a GAC, sand filter or polishing biological treatment in order to remove by-products. If a filtration stage is already in place ozonation can be quite convenient, whereas if a new filtration is needed, the costs for advanced treatment are considerably higher. Also PAC added directly in the biological treatment may require a filtration to minimize AC loss. PAC may entail a lower CAPEX if it can be dosed directly in the bioreactor. GAC requires a dedicated contactor. The OPEX of ozonation is driven by the energy demand of O3 generation, while that of PAC and GAC is driven by the sorbent and/or its regeneration. The costs of advanced treatment may vary considerably depending on the initial conditions of a plant. Indicative ranges of costs and cost functions proposed in the grey literature in various contexts in Europe are summarized in Table 3 and Table 2, typically highlighting highest costs for GAC, followed by PAC and ozonation, also rather consistently with Rizzo et al. (2019). These authors report a CAPEX in the range of 0.035 - 0.05 Euro/m3 of treated wastewater (30 years depreciation for civil works and 15 years for mechanical equipment, 10 for electrical equipment), and an OPEX of 0.04 Euro/m3 of treated wastewater (including electric energy, maintenance, additional analyses and workload, oxygen input), practically independent of the process adopted. The operational cost of O3 and AC depends on the dose, in turn very sensitive to NO2 and DOC. For instance, a technical and economic assessment of ozonation in France (Choubert et al., 2017) calculated a cost of 0.1-0.2 Euro/m3 for ozonation and 0.2-
0.3 Euro/m³ for activated carbon, depending on the size of the plant and its initial and operating conditions and the supply chain of reagents.

<table>
<thead>
<tr>
<th>Type of treatment</th>
<th>Source</th>
<th>Expenditure function</th>
<th>Costs included and units</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC + SF</td>
<td>BG Ingenieure und Berater AG, 2012</td>
<td>48234.9679*PE^-0.4786</td>
<td>investment costs CHF/PE</td>
</tr>
<tr>
<td>PAC + SF</td>
<td>BG Ingenieure und Berater AG, 2012</td>
<td>179.4029*PE^-0.2225</td>
<td>operation cost CHF/PE/Y</td>
</tr>
<tr>
<td>O3 + SF</td>
<td>BG Ingenieure und Berater AG, 2012</td>
<td>26889.5261<em>PE^-0.5078 + 21424.4602</em>PE^-0.5733</td>
<td>investment costs CHF/PE</td>
</tr>
<tr>
<td>O3 + SF</td>
<td>BG Ingenieure und Berater AG, 2012</td>
<td>367.5990*PE^-0.3528</td>
<td>operation cost CHF/PE/Y</td>
</tr>
<tr>
<td>O3</td>
<td>Türk et al., 2013</td>
<td>2261.9*V^0.4417</td>
<td>investment cost before VAT (approximate function); V=water volume treated, m³/a</td>
</tr>
<tr>
<td>O3</td>
<td>Türk et al., 2013</td>
<td>0.0147*V+46081</td>
<td>operation cost; V=water volume treated, m³/a</td>
</tr>
<tr>
<td>O3</td>
<td>Türk et al., 2013</td>
<td>0.0073*V+9322</td>
<td>energy cost; V=water volume treated, m³/a</td>
</tr>
<tr>
<td>O3</td>
<td>Antakyali, 2017, cit. in Rizzo et al., 2019</td>
<td>5.68 PE^-0.38</td>
<td>Investment cost Euro/m³</td>
</tr>
<tr>
<td>PAC</td>
<td>Antakyali, 2017, cit. in Rizzo et al., 2019</td>
<td>6.23 PE^-0.36</td>
<td>Investment cost Euro/m³</td>
</tr>
<tr>
<td>GAC</td>
<td>Antakyali, 2017, cit. in Rizzo et al., 2019</td>
<td>143.23 PE^-0.63</td>
<td>Investment cost Euro/m³</td>
</tr>
<tr>
<td>Ensemble curve</td>
<td>Herbst et al 2016</td>
<td>10.861 PE^-0.424</td>
<td>Total cost Euro/m³</td>
</tr>
</tbody>
</table>

Table 2 – cost functions from Switzerland (CH) and Germany (DE). O3=ozonation; SF=sand filter; PAC, GAC =powdered, granular activated carbon.
<table>
<thead>
<tr>
<th>type of treatment</th>
<th>Source</th>
<th>cont ext</th>
<th>Units</th>
<th>for 10000 PE</th>
<th>for 20000 PE</th>
<th>for 50000 PE</th>
<th>for 100000 PE</th>
<th>for 500000 PE</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3 + SF</td>
<td>Baggenstos, 2019</td>
<td>CH</td>
<td>Euro per PE per year</td>
<td>25.38</td>
<td>2.25E+01</td>
<td>13.724</td>
<td>12.596</td>
<td></td>
</tr>
<tr>
<td>PAC in CAS + SF</td>
<td>Baggenstos, 2019</td>
<td>CH</td>
<td>Euro per PE per year</td>
<td>27.26</td>
<td>24.722</td>
<td>17.108</td>
<td>16.074</td>
<td></td>
</tr>
<tr>
<td>PAC + SF</td>
<td>Baggenstos, 2019</td>
<td>CH</td>
<td>Euro per PE per year</td>
<td>30.08</td>
<td>26.884</td>
<td>17.296</td>
<td>15.792</td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td>Baggenstos, 2019</td>
<td>CH</td>
<td>Euro per PE per year</td>
<td>31.96</td>
<td>29.093</td>
<td>20.492</td>
<td>17.39</td>
<td></td>
</tr>
<tr>
<td>O3**</td>
<td>Baresel et al., 2017</td>
<td>SE</td>
<td>Euro per m3</td>
<td>0.04</td>
<td>0.029</td>
<td>0.0195</td>
<td>0.0145</td>
<td></td>
</tr>
<tr>
<td>BAF(GAC)**</td>
<td>Baresel et al., 2017</td>
<td>SE</td>
<td>Euro per m3</td>
<td>0.085</td>
<td>0.065</td>
<td>0.0475</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>O3+BAF(GAC)**</td>
<td>Baresel et al., 2017</td>
<td>SE</td>
<td>Euro per m3</td>
<td>0.11</td>
<td>0.075</td>
<td>0.05</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>PAC-UF**</td>
<td>Baresel et al., 2017</td>
<td>SE</td>
<td>Euro per m3</td>
<td>0.21</td>
<td>0.16</td>
<td>0.13</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>UF-BAF(GAC)**</td>
<td>Baresel et al., 2017</td>
<td>SE</td>
<td>Euro per m3</td>
<td>0.21</td>
<td>0.155</td>
<td>0.11</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>GAC</td>
<td>STOWA, 2017</td>
<td>NL</td>
<td>Euro per PE per year</td>
<td>14.8</td>
<td>13.7</td>
<td>12.6 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAC+SF</td>
<td>STOWA, 2017</td>
<td>NL</td>
<td>Euro per PE per year</td>
<td>13.8</td>
<td>10.5</td>
<td>8.4 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3+GAC</td>
<td>STOWA, 2017</td>
<td>NL</td>
<td>Euro per PE per year</td>
<td>15.9</td>
<td>10.0</td>
<td>9.5 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3</td>
<td>STOWA, 2017</td>
<td>NL</td>
<td>Euro per PE per year</td>
<td>4.8</td>
<td>3.2</td>
<td>2.6 *</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O3+SF</td>
<td>STOWA, 2017</td>
<td>NL</td>
<td>Euro per PE per year</td>
<td>10.6</td>
<td>8.9</td>
<td>7.9 *</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 – ranges of costs of advanced treatment for Switzerland (CH), the Netherlands (NL) and Sweden (SE). O3=ozonation; SF=sand filter; PAC, GAC=powdered, granular activated carbon; BAF=biologically active filter; CAS=conventional activated sludge; UF= ultrafiltration. (* capacity 300,000 PE; **referred to specific flow of 150 m3 per PE per year)

The variability of costs among different treatment options seems to be comparable with the variability within a certain treatment option depending on the specific plant conditions. Consistently, some authors have suggested that the specific costs of advanced treatment (including CAPEX and OPEX) could be represented as a first approximation by a single expenditure function (e.g. Herbst et al., 2016).

In order to define an appropriate expenditure function for advanced wastewater MP removal in Europe, we compiled a dataset of actual or accurately estimated costs for advanced treatments in...
European WWTPs (the dataset is provided and documented as Supplementary information). By plotting the levelized costs of advanced treatment as a function of plant capacity, we show (Figure 1) that indeed the variability among technical solutions is comparable with the variability depending on plant conditions. While the heterogeneity of the data hampers a conventional statistical analysis, we observe that costs can be captured within a factor 2 by the simple function:

\[ C_{\text{adv}} = 1000 \text{ PE}^{-0.45} \]

Equation 1

where \( C \) represents the levelized cost (Euro/PE/year) of advanced treatment. This expenditure function, plotted in Figure 1, should not be regarded as a statistical model, but as a practical working assumption.

In order to better understand the drivers of the total cost of advanced treatment, let us consider a set of nine typical treatment process configurations with AC, \( O_3 \) or a combination thereof, as shown in Table 4. A detailed discussion of the rationale for selecting those nine configurations is provided as Supplementary information. We refer to a wastewater treatment plant of medium capacity (50,000 PE) with a dry weather flow of 0.2 m\(^3\) day\(^{-1}\) PE\(^{-1}\). We assume a concentration of DOC in secondary
effluent equal to 10 mg/L. We design the PAC and ozonation treatment configurations with a contact
time of 60 and 10 minutes respectively, and the GAC configuration with an EBCT of 20 minutes. We
further assume a GAC mass equal to 0.625 kg/PE and GAC losses in regeneration/reactivation equal
to 20%. Maintenance and operation costs other than energy are assumed to be equal to 3% of the
investment every year, and we assume a write-off time of 20 years with a discount rate of 3% for
investments. We further assume a cost of other unspecified chemical additives of 0.01 Euro/m3 for
all treatment processes. All other design and costing parameters are calculated or provided in Table
4. Based on the assumptions made, the total costs of the various configurations would be broken
down as shown in Figure 2.

It appears that the various configurations reflect trade-offs between energy and process inputs. Due
to the variability of cost items depending on the context, the ranking of alternatives may completely
change compared to this example. Arguably, all configurations are rather similar to each other,
although ozonation features consistently lower costs.
Figure 2 - breakdown of costs of the nine representative configurations of advanced treatment, based on the specific assumptions of Table 4. Labels of the categories axis correspond to codes in Table 4.
<table>
<thead>
<tr>
<th>code</th>
<th>PAC1</th>
<th>PAC2</th>
<th>GAC</th>
<th>O31</th>
<th>O32</th>
<th>O33</th>
<th>O3GAC</th>
<th>PAC+UF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAC (kg/PE/y)</td>
<td>1.095</td>
<td>2.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.095</td>
</tr>
<tr>
<td>O3 (kg/PE/y)</td>
<td></td>
<td></td>
<td>0.292</td>
<td>0.438</td>
<td>0.584</td>
<td>0.1825</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC replacement (kg/PE/y)</td>
<td></td>
<td></td>
<td>1.314</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PAC contactor volume (m3/PE)</td>
<td>0.008333</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ozone contactor volume (m3/PE)</td>
<td></td>
<td></td>
<td>0.0014</td>
<td>0.0014</td>
<td>0.0014</td>
<td>0.0014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GAC contactor volume (m3/PE)</td>
<td></td>
<td></td>
<td>0.002778</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>energy use for O3 production from pure O2 (kWh/kgO3)</td>
<td></td>
<td></td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
<td>12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>energy use for external pure O2 production kWh/kgO3</td>
<td></td>
<td></td>
<td>8.2</td>
<td>8.2</td>
<td>8.2</td>
<td>8.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pumping and other energy use kWh/m3</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
<td>0.07</td>
<td>0.2</td>
</tr>
<tr>
<td>cost of UF membrane modules (Euro/(m3/day))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost of GAC Euro/kg</td>
<td></td>
<td></td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost of PAC Euro/kg</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost of pure oxygen Euro/kg</td>
<td></td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>investment for contactor vessels Euro/m3</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td>500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investment for sand filters Euro/PE</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Investment for O3 production equipment (Euro/PE)</td>
<td></td>
<td></td>
<td>6.5</td>
<td>6.5</td>
<td>6.5</td>
<td></td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>cost of GAC regeneration Euro/kg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 4 – design and operating parameters for 9 typical configurations of advanced treatment for wastewater MPs.

Electronic copy available at: https://ssrn.com/abstract=4052482
Energy requirements

The removal of micropollutants with O3, AC or membrane filtration entails an increased use of energy, either directly in the process, or indirectly as embedded in the process input. Production of ozone, in particular, is more energy intensive compared to AC, requiring about 0.3 kWh per m³ of treated wastewater (Rizzo et al., 2019) as the sum of energy use for ozone generation from oxygen (about 0.05 kWh per m³), and the preparation of oxygen (about 0.25 kWh per m³). Their figures are confirmed by the findings of Bertanza et al (2018) who, for an ozone dose of 8 g/m³, report an energy consumption for a tertiary ozonation stage (all equipment included) of 0.05 - 0.08 kWh/m³ of treated wastewater (excluding the energy required for liquid oxygen production). Hansen et al., 2010, find an overall energy demand of about 0.1 kWh/m³ per g of O3 used in the process. For comparison, membrane nanofiltration requires about 0.5 to 1 kWh/m³ (Rizzo et al., 2019). A sand filter downstream of ozonation usually requires 0.01 – 0.05 kWh/m³ according to Büeler et al. (2018).

Compared to a typical energy use of less than 0.5 kWh/m³ of wastewater treated in conventional plants, the additional energy consumption represents an increase in excess of 10%. Experience in Switzerland shows an increased power demand of 10-30% in WWTPs upgraded with ozonation (Rizzo et al., 2019). Data from the Sophia-Antipolis plant in France (Choubert et al. 2017) indicate that ozonation has caused a 25% increase of the total energy consumption due to under-load and thermal destruction of O3 in excess. The destruction of ozone in excess contributes to the overall energy demand of ozonation, and can be made less energy-intensive by using a catalytic rather than thermal excess O₃ quenching.

While the AC process in itself requires only limited energy (see Risch et al., 2021), the production of activated carbon is also energy intensive, and so is the process of GAC reactivation. Among the case studies that we have compiled for the present analysis, energy use ranges from less than 1 to more than 12 kWh per PE per year (Figure 3). Although ozonation alone or in combination with GAC shows higher energy intensity compared to GAC and PAC, the patterns are rather complex and not clear, anyway not suggesting any economy of scale.
Identification of optimal treatment scenarios at the European scale

The considerations presented above enable an appraisal of advanced wastewater treatment scenarios for the removal of MPs at the European scale. In this section, we systematically explore scenarios of advanced wastewater treatment in order to identify cost-effective combinations enabling the highest removal of pollution at the lowest cost or GHG emission. Pistocchi et al., 2022, present an analysis of three indicators of impact by MPs at the European scale, namely:

- the total load of MPs, $L$, defined as the toxicity-weighted sum of mass discharges of a list of MPs representing a proxy of “total pollution”.
- Near field pollution at the discharge point $LT$, defined as the cumulative toxicity of the same list of MPs, computed at the discharge points of wastewater treatment plants.

Figure 3 – energy use for advanced treatment of MPs at the plants whose costs are displayed in Figure 1, plotted as a function of the treated population equivalents – PE. Data in detail are provided as Supplementary information.
Far field pollution CT, defined as the cumulative toxicity of the same list of MPs, computed for the whole European stream network.

Indicators LT and CT are computed as the toxic units or risk quotients (sum of concentrations normalized by appropriate reference risk thresholds) resulting from the discharge of the WWTP effluents in the European surface waters. They depend on the concentration of contaminants in the effluents and, unlike indicator L, on the dilution occurring in the ambient waters.

Details on the three indicators are described in Pistocchi et al., 2022. The indicators are computed for various scenarios: in each scenario, it is assumed that all plants above a certain capacity or treated volume of wastewater (P, expressed in population equivalents: PE), and/or discharging in water bodies with a dilution ratio D below a certain threshold are required to implement an advanced treatment process. D is the ratio of effluent to ambient concentrations, assuming the WWTP discharge is the only source of pollution, i.e. the receiving water body is initially free of pollution. In Pistocchi et al., 2022, the dilution ratio is evaluated under average flow conditions in the water body.

While the removal efficiency of each MP varies from one process configuration to another, the cumulative toxicity of the effluents is shown to depend only weakly on the type of advanced treatment.

Indicator L is an aggregated indicator for the EU, indicator LT is computed at every WWTP, and indicator CT is a map covering the whole stream network. The value of the indicators changes with the intensity of wastewater treatment that is required under a given scenario.

Here we compare L, LT and CT, with an estimation of the corresponding costs and GHG emissions.

We consider the WWTPs existing in the EU as per the 10th UWWTD Implementation Report (EC, 2020). When a plant is required to perform advanced treatment, we estimate the corresponding cost based on Equation 1. Figure 4 plots as a function of annual treatment costs the reduction, compared to a baseline scenario of full compliance with the UWWTD, of the total load indicator L achieved with various combinations of D and P. For a given threshold D, L is progressively reduced at lower thresholds P, with apparent marginally decreasing effectiveness. This indicates that it is more cost-effective to require advanced treatment at larger plants than at smaller plants. The higher the dilution threshold D, the more cost-effective it is to implement advanced treatment. When we consider no threshold for D, i.e. an advanced treatment is required for all plants above a threshold P irrespective of the dilution ratio in the
receiving water bodies, we obtain the highest reduction of $L$ for a given total annual cost. Conversely, while advanced
treatment at all plants with $P \geq 100,000$ PE allows a reduction of $L$ of about 38% and a cost of about 840 million Euro
per year, the same reduction can be obtained with advanced treatment at all plants of 50,000 PE if $D=100$, or 5000 PE
if $D=20$, at higher costs. This means that, when it comes to the total load, it is more cost-effective to implement
advanced treatment only at larger plants than based on the dilution of the receiving water bodies.

The indicator of near field pollution, $L_T$, is reduced mainly by lowering the plant threshold $P$, and the improvements
are marginally decreasing with increasing dilution threshold $D$ (Figure 5). Typically, there is not additional benefit
beyond $D=10$.

![Figure 4 – Plot of indicator $L$ as a function of the implementation cost (total annual costs as per Equation 1), for different combinations of $D$ and $P$. The continuous lines in colour correspond to a given value of $D$, while the data points along these lines represent each a threshold $P$ (increments of 100,000 PE above 100,000 PE, and 10,000 PE below). The dashed black lines connect points with the same value of $P$. "All" denotes the case of $D$ set to infinity (all plants irrespective of $D$). The black dot represents the "compromise" scenario.](https://ssrn.com/abstract=4052482)
Figure 5 – average across the EU of indicator LT as a function of the implementation cost (total annual costs as per Equation 1), for different combinations of D and P. The continuous lines in colour correspond to a given value of D, while the data points along these lines represent each a threshold P (increments of 100,000 PE above 100,000 PE, and 10,000 PE below). The dashed black lines connect points with the same value of P. “All” denotes the case of D set to infinity (all plants irrespective of D). The black dot represents the “compromise” scenario.

The indicator of cumulative pollution in the stream network (CT) may be used to map how the percentages of the stream network in a given risk category change as a consequence of implementing advanced treatment. Pistocchi et al., 2022, propose to classify the European stream network in four categories with high, medium-high, medium-low and low risk of exceeding risk thresholds. In Figure 6, we plot the percentage of the European stream network falling in each of these categories under each of the scenarios of D and P considered here, as a function of the cost of the corresponding scenario. Each point in the graphs is therefore a scenario. It is apparent that advanced treatment may reduce by almost a half the percentage of the stream network at high risk (Figure 6 A), and that at medium-high risk (Figure 6 B). Usually the reduction of the high and medium-high risk causes an increase of the percentage at medium-low risk. When advanced treatment is implemented at most plants (i.e. in scenarios with low P and high D), though, there can be a significant increase of the percentage of the network at low risk, while that at medium-low risk decreases (Figure 6 C, D). The decrease of the percentage at high risk and, less apparently, of the percentage at medium-high risk show a decreasing marginal effectiveness of the investments. On the contrary, significant increases in the percentage at low risk require high investments.
Figure 6 – percentage of the stream network under four toxicity risk categories (high, medium-high, medium-low and low) under each advanced treatment scenario, as a function of the corresponding costs. Each point in the graph is a scenario (not labelled for the sake of readability). The black dot represents the “compromise” scenario.

The three indicators describe the response of MP pollution to investments in advanced wastewater treatment. Looking at the total toxic load discharged in the environment (indicator L), it is most cost-effective to require advanced treatment at larger plants irrespective of the dilution in the receiving water bodies. Looking at the near field toxicity (indicator LT) it appears that requiring advanced treatment where dilution exceeds 10 brings little marginal improvements. Looking at the overall conditions of the stream network (indicator CT), most of the reduction in high and medium-high risks would be achieved with annual costs below 1.5 billion Euro/year, indicating that advanced treatment at larger plants and/or at plants with low dilution is cost-effective. However, if the target is to bring the whole stream network to low risk conditions, it is necessary to target as many plants as possible, including those with
lower capacity and/or discharging at higher dilution. Based on these considerations, we suggest a “compromise”
scenario where advanced wastewater treatment is prescribed at all plants above 100,000 PE irrespective of dilution,
and at all plants above 10,000 PE when the dilution ratio at discharge is 10 or less. This scenario is represented by a
black dot in Figure 4, Figure 5 and Figure 6. The graphs show how this scenario performs reasonably well in terms of
all three indicators, although it may not be strictly optimal according to each of them.

The costs discussed above do not include the upgrade of WWTPs from carbon removal to denitrification, which is de 
facto a prerequisite of advanced treatment. We estimate the costs of upgrade for the above “compromise” scenario
(Figure 7), following the conservative approach illustrated in the Supplementary information. Under these
assumptions, the costs may be up to about four times as high as the costs of advanced treatment, on a PE basis. Hence
even if the total capacity of plants requiring an upgrade to nitrogen removal is relatively small, the total cost of upgrade
may be comparable to the total cost of advanced treatment alone in many cases. It should be also stressed that the
costs of upgrade may vary very significantly from case to case, and in various circumstances denitrification could be
implemented at plants presently required to remove only carbon, through relatively inexpensive improvements in the
operation of the process, particularly based on instrumentation, control and automation. Our estimated cost of
upgrade varies significantly among countries, depending on the current level of wastewater treatment. Countries
where virtually all WWTPs perform nitrogen removal already (such as Germany and Austria) are bound to face lower
overall costs. On the contrary, in countries like Spain, Italy, Ireland, Portugal and, to a lesser extent, France and
Hungary, the upgrade costs may be large. In any case, even accounting for these differences, they would remain below
0.5% of the annual income even for the less privileged population in the lowest-income countries of the EU, as shown
in Figure 7.

In the estimation of costs, we neglected the presence of advanced treatment/disinfection in existing plants. When
disinfection is present, advanced treatment for MPs could offer opportunities for synergies and economies.
We can also estimate the corresponding GHG emissions from the population equivalents (PE) undergoing advanced treatment under that scenario. As a first approximation, we may consider GHG emissions proportional to cumulative PE subject to advanced treatment. We assume an emission of 0.225 kg CO2e/m³ of treated wastewater (midrange of literature values) and a wastewater discharge of 0.2 m³/day per PE for a first quantification, obtaining for the above “compromise” scenario the GHG emissions by country as shown in Figure 8.

The average GHG emissions vary by country depending on the cumulative PE subject to advanced treatment. Emissions represent always less than 1% (and mostly between 0.2 and 0.3%) of the total national emissions of GHG for 2019, and are highest in countries with a less carbon-intensive electric system.

The GHG emission factors estimated here do not take into account the improvement of GHG emissions due to the upgrade of existing plants (potentially lower CH4 and NO2 emissions, see Parravicini et al., 2021), which are expected even net of possible additional energy requirements for aeration.

Figure 7 – Costs of advanced treatment (absolute and as a % of the annual income of the poorest 5% of the population).
Conclusions

MPs used in urban areas and conveyed by wastewater pose a concern, and discharges of WWTPs are, and will likely remain, their key entry point to the environment. Therefore, removing MPs during wastewater treatment is an essential component of pollution control. This does not diminish the importance of other actions, such as measures at the source or a mitigation of storm overflows (whose relative contribution to pollution increases when removal of MPs at the WWTP is effective). Control at the source is usually the most cost-effective measure when addressing a specific substance or class of substances (e.g. PFAs). However, it is very likely that a broad spectrum of substances will continue to leak from the technosphere and flow through our WWTPs in the short and mid-term, before we can complete a full ecological transition in our production and use of chemicals. In this perspective, we need a strategic approach to the treatment of MPs at WWTPs. Among the available options for the removal of MPs, mainstream cost-effective solutions are limited to activated carbon, ozonation or their combination in various process configurations. These are largely equivalent in terms of costs, energy use and GHG emissions, and a decision on the solution to adopt necessarily depends on the specific conditions of each case. In specific cases, membrane filtration processes may prove a cost-effective alternative, especially when effluent quality standards need to be high (e.g. for direct or indirect potable reuse of waters). Nature-based solutions such as constructed wetlands (CW) are attractive because of their low energy demand, their operational simplicity and many possible co-benefits including on landscape and biodiversity. On the other hand, CW require spaces that may not be available for WWTPs, particularly in urban contexts, and may struggle with the most recalcitrant chemicals. The suitability and sustainability of an advanced treatment process must be evaluated based on many criteria, such as plant reliability, process flexibility, need of skilled personnel, administrative...
constraints, availability of space, residual capacity and adaptability of existing biological treatment, etc. Procedures for the integration of these items in a general evaluation and decision making framework have been proposed e.g. for MBR (Bertanza et al., 2017) and for sludge disposal routes (Bertanza et al. 2016).

In this contribution, we have shown that widespread implementation of advanced treatment can reduce total toxic discharge and toxicity at the point of discharge by about 75%. The percentage of the length of the stream network exposed to medium-high toxicity (based on the indicators defined in Pistocchi et al., 2022) can be reduced from about 7% to about 3.5%, and the percentage exposed to high toxicity from about 0.9% to about 0.5%. However, achieving these objectives would cost about 4 billion euro/year for the whole EU. Implementing advanced treatment at all plants larger than 100,000 PE, or between 10,000 and 100,000 PE when the dilution rate is below 10, enables a reasonable compromise, in the range of solutions with the highest effectiveness while preventing costs to increase excessively. At the same time, the capacity of the target plants is sufficient to support the management complexity of advanced treatment.

Under this “compromise” scenario of advanced treatment, we would achieve a reduction by about 50% of the total toxic discharge, 40% of the toxicity at the point of discharge, a percentage of the stream network exposed to high toxicity of about 0.5%, and a percentage exposed to medium-high toxicity of about 5%. The costs would remain at about 1.5 billion euro/year for the whole EU. Limiting the total PE undergoing advanced treatment enables a proportional limitation of GHG emissions. Under the above “compromise” scenario, the estimated total GHG emission is about 5.4 million tonnes CO2e/year, approximately 0.15% of the EU total GHG emissions in 2019. The increasing decarbonisation of power generation and the development of low-carbon AC, e.g. from biochar including from circular industrial processes, may contribute to further reduce, or even neutralize the GHG footprint of advanced treatment. The costs of the “compromise” scenario appear affordable even compared to the standards of the lowest incomes in the European context, and part of those costs could be required anyway for reasons of nutrient removal or disinfection. Opportunities for synergistic solutions may particularly arise in this respect from fixing non-performing WWTPs, achievement of full compliance with the UWWTD, replacement of existing disinfection/filtration etc. In some cases, a site-specific risk assessment may unveil opportunities for more cost-effective solutions (e.g. source control of hazardous releases from industrial facilities). Therefore the costs estimated for the “compromise” scenario could be further reduced while achieving the same water quality standards.
References


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https://doi.org/10.1016/J.JENVMAN.2020.111563


35. STOWA (2017). Verkenning technologische mogelijkheden voor vermijdering van geneesmiddelen uit afvalwater. Rapport 2017, Amersfoort, the Netherlands. Available at:
https://www.stowa.nl/sites/default/files/assets/PUBLICATIES/Publicaties%202017/STOWA%202017-36%20%20defversie.pdf

https://www.ivl.se/download/18.34244ba71728fcb3f3f8e2/1591705071470/B2288.pdf

https://micropoll.ch/Mediathek/abkläerungen-verfahrenseignung-ozonung-empfehlung/?search=abkläraungen


kostenstudie/?media_filter_one=kosten


53. Meier, A., Remy, C., Klimafreundlich Gewässer Schützen – Co2-Fussabdruck Verkleinern Bei Der Elimination Organischer Spurenstoffe Auf Kläranlagen. Aqua & Gas N° 2, 2020


65. Hansen, Kamilla M.S., Aikaterini Spiliotopoulou, Ravi Kumar Chhetri, Mònica Escolà Casas, Kai Bester, Henrik R. Andersen, Ozonation for source treatment of pharmaceuticals in hospital wastewater – Ozone lifetime and


community shifts and change trophic status. Water Research, 200, 117206. 

https://doi.org/10.1016/J.WATRES.2021.117206
Costs for the upgrade of an existing WWTP

The effluent of a biological treatment should meet the discharge quality of a well-functioning nitrifying plant, before we implement an advanced treatment in a cost-effective way. Denitrification may not be required, although it can be further contribute to the removal of certain MPs. Denitrification may not be required, although it can be further contribute to the removal of certain MPs.

The required effluent quality may be achieved in several different ways, and the design of a solution is necessarily site-specific. Plants originally designed only for carbon removal require extending the SRT, and the presence of appropriate anoxic conditions in order to achieve denitrification. Longer SRT may entail larger volumes of the bioreactor and/or the secondary settler. When volumes cannot be increased, converting the existing biological reactors to other processes (e.g. MBBR, IFAS, MBR, submerged biofilters, MABR) may be an option. Plants operating nitrification but not denitrification require introducing an appropriate alternation of aerobic and anoxic conditions. This can be achieved by adding an anoxic tank besides the aerated CAS bioreactor, or by appropriately configuring a single CAS bioreactor with intermittent aeration.

Nitrification requires a higher input of oxygen in the bioreactor compared to carbon removal only, hence more intense aeration entailing higher power consumption and associated GHG emissions. Denitrification, on the other hand, generally reduces the direct emissions of nitrous oxide (Valkova et al., 2021), potentially offsetting those of nitrification. Another advantage of denitrification is the improvement of sludge settleability. Denitrification, though, may require additional exogenous carbon sources, hence additional energy use and GHG emissions. When this is not the case, a fully denitrifying plant may be a no-regret solution that a plant manager may be willing to implement (e.g. in order to stabilize the pH) even if not strictly required by the permit in place.

The removal of P at a plant may not be an essential prerequisite of advanced treatment, except when PO4 may compete with micropollutants in adsorption. This circumstance should be checked at the design stage. Usually P removal is obtained through chemical precipitation, which may also enhance the removal of certain less soluble MPs (Comber et al., 2021). The cost of upgrading of an existing WWTP must be evaluated case by case, because it may vary largely depending on site-specific conditions. However, we may expect a need for approximately doubling the reactor...
and settler volumes. Nitrification requires also a higher oxygen input. However, the energy demand for aeration can
be approximately the same as the transfer efficiency of oxygen is much higher in long SRT systems thanks to the finer
bubbles and the intermittent aeration compared with short SRT systems with medium size bubbles and continuous
aeration.

For the sake of an indicative calculation at European scale, we consider the expenditure functions of the FEASIBLE
model (OECD, 2004) as updated by COWI, 2010. In FEASIBLE, the capital expenditure (CAPEX) of wastewater treatment
plants (in Euro/PE) is given as a function of the plant capacity (PE) and treatment level (carbon, N and P removal). We
might assume that the costs of retrofitting may be approximated by the difference between the costs of a plant at a
given level and those of a plant performing nitrification/denitrification. This assumption neglects all possible
economies (e.g. the possibility to exploit available infrastructure, piping, pumping equipment and instrumentation) or
diseconomies (e.g. demolition and reconstruction), and should be regarded only as a rough first approximation. Based
on the FEASIBLE expenditure functions, the upgrade would entail a differential CAPEX of about 160 Euro/PE for a
capacity of 12,000 PE (see Figure 9). In many cases, however, upgrading a plant from carbon removal only to nitrogen
removal entails higher costs than the mere difference between CAPEX of carbon and of N removal plants, due to
diseconomies related to the rearrangement of a plant. As a practical upper limit for the cost of upgrade, we assume
the CAPEX is equal to the differential CAPEX between carbon removal and N removal plants, added to 50% of the
CAPEX of a carbon removal plant, all costs being calculated using the respective expenditure functions of the FEASIBLE
model. Under this assumption, the cost of upgrade is described by the following function (see Figure 9):

\[ C = 0.23 \times 10^{(0.25-0.002\log(PE))} \times PE \]  
Equation 2

The ratio between this cost and the differential cost is on average 1.63, which can be regarded as an engineering safety
factor for the purposes of our calculations. With these assumptions, upgrading is less expensive than building a new
plant with denitrification, but more expensive than building a new plant for carbon removal only.
The levelized cost of upgrading of the biological treatment (Euro/PE/year) is given by:

$$C_{up} = \frac{1}{pva(n, r)} + \omega C + C_{el}E$$  \hspace{1cm} \text{Equation 3}$$

where:

- $C$ = assumed investment cost of the upgrade (Euro/PE) as shown in Figure 9;
- $C_{el}$ = cost of electricity (Euro/kWh)
- $E = \text{incremental energy requirement } \frac{\text{kWh}}{\text{PE}}$
- $\omega$ = annual operation and maintenance (O&M) costs (excluding energy) as a % of investment costs
- $pva(n, r) = \frac{1 - \left(\frac{1}{1 + r}\right)^n}{r}$ is the present value of annuities for an investment, with
- $r$ = discount rate and $n$ = assumed lifetime of the investment (years).
We assume a lifetime of 20 years and a discount rate of 3% (hence pva of about 15 years), an O&M cost of 3% of the investment per year, and an additional electricity demand of 15 kWh/PE/year at a cost of 0.1 Euro/kWh when upgrading a plant from carbon removal only to nutrient removal. This assumption ignores the possible savings on energy allowed by introducing denitrification, adding to the precautionary nature of the estimate.

**Calculation sheets**

The following material is provided as separate files:

1) Excel workbook containing:
   - Database of case studies with energy use and costs data
   - Derivation of the cost functions

2) Excel workbook containing:
   - Data on EU WWTPs as reported under the UWWTD (10th implementation report), dilution rates etc.
   - Calculations for the cost-effectiveness analysis

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