Christian Abegglen, environmental engineer and postdoc in the Process Engineering department.
Co-authors: Adriano Joss and Hansruedi Siegrist

Eliminating micro-pollutants: wastewater treatment methods

In many cases, micropollutants are only partly eliminated at wastewater treatment plants. The remaining fraction, together with any transformation products, enters receiving waters with the treated effluents. What options can modern process engineering offer to improve elimination performance?

In recent years, organic micropollutants such as pharmaceutical residues or hormones have been detected in various lakes and rivers in Switzerland [1]. They mainly enter surface waters via domestic wastewater and – not surprisingly – wastewater treatment plant (WWTP) effluents have been identified as the main source of these substances. This is because existing treatment plants were not designed to eliminate substances of this kind, but to reduce input of solids, organic material and nutrients. Even so, modern treatment plants remove a large proportion of micropollutants, either by means of sorption to activated sludge or by biological degradation/transformation [2]. However, residual contamination with pharmaceuticals, hormones or other micropollutants can still cause problems in aquatic ecosystems. One way of minimizing input of organic micropollutants to surface waters is to integrate an additional treatment step at WWTPs.

What options are available? An additional process that can be used to upgrade treatment plants needs to meet various requirements:

► Broad spectrum of action: it must be possible for a wide range of problematic substances to be largely eliminated.

► No problematic by-products: the formation of toxic or otherwise problematic products in the additional step must be avoided.

► Ease of use: it must be straightforward to operate and should not call for specialist staff.

► Cost/benefit ratio: the use of resources (materials, energy, staff, costs) must be reasonable and provide appropriate benefits.

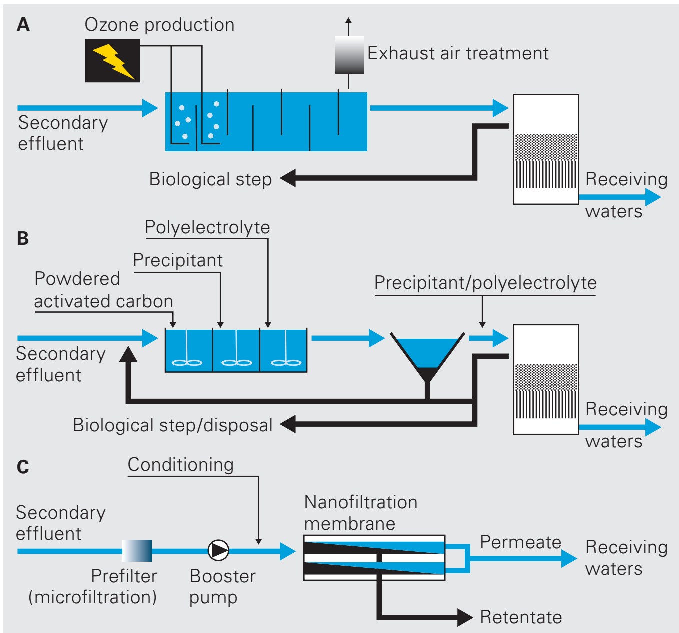
In fact, a number of existing methods make it possible to eliminate micropollutants effectively. Some of these are already used in the treatment of drinking water, although the requirements differ markedly in the case of wastewater treatment:

► Background contamination: the concentration of organic substances in treated wastewater is around 5–50 times higher than in drinking water. Micropollutants account for less than 1 % of this total – i.e. more than 99 % consists of "harmless", natural substances. At the same time, these natural substances influence the effectiveness of the methods under consideration, thus often leading to reduced efficiency and increased costs.

► Inflow variation: both the volumes of wastewater to be treated and the composition can vary significantly (by a factor of 10). The process in question has to be able to respond appropriately to such fluctuations.

When all these aspects are taken into account, three methods emerge as suitable candidates for advanced wastewater treatment – ozonation, powdered activated carbon adsorption and "dense membrane" technologies (especially nanofiltration).

Fig. 1: Schematic flow charts for the ozonation (A), powdered activated carbon adsorption (B) and nanofiltration (C) processes. Other options are available (in particular for activated carbon).



These methods are being investigated more closely, from different perspectives, in various departments of Eawag.

Ozonation: feasible at a large scale. As part of the "MicroPoll strategy" project, Eawag has been closely involved in studying large-scale ozonation of treated wastewater at the Regensdorf plant [3]. Ozone has a strong oxidizing action – i.e. many substances are attacked and transformed by this agent. Since ozone is highly unstable, it has to be generated at the site of application – in an energy–intensive process – from dry air or from liquid oxygen. It is added in gaseous form to the wastewater stream, and sufficient time must then be available for it to react with the wastewater constituents (Fig. 1A). The amount of ozone required depends on various parameters, such as the level of background dissolved organic matter and wastewater pH and alkalinity, as well as the desired elimination performance (see the article by Juliane Hollender on p. 28). The concentration of many organic micropollutants is substantially reduced even with relatively low doses of ozone (see Fig. 1 on p. 29).

One problem with ozonation is that in general the target compounds are not fully mineralized, but merely transformed, and so even more harmful substances may be produced as a result. Accordingly, experience at Regensdorf indicated that after ozonation an additional step is required – e.g. sand filtration – to break down reactive oxidation products.

However, as well as removing micropollutants, ozone reduces not only the microbial count but also odour, colour and foam. Because ozone is a potent irritant, safety measures are also required to protect staff in the event of malfunctions. In the Regensdorf pilot study, however, it was shown that the application of ozonation at a WWTP is technically and operationally feasible. At the same time, it is associated with increases of around 10–20 % in both energy consumption and costs, although these figures depend on various factors, including the size of the plant (cf. Table).

Powdered activated carbon adsorption: effective, but slow. Treatment with powdered activated carbon (PAC) is being studied – also as part of the "MicroPoll strategy" project – in small-scale pilot plants at Eawag. In this process, PAC (particle diameter 10–50 μm) is added to the wastewater. Thanks to the huge surface area (1000 m^2/g) and other specific chemical properties (e.g. charge, arrangement of molecules), many substances adsorb onto the particles. Activated carbon adsorption is a highly promising method for the removal of numerous micropollutants (Fig. 2): elimination rates of more than 80 % are achieved for many (but not all) substances in treated wastewater with a dose of 10–20 mg PAC per litre. In contrast to ozonation, activated carbon adsorption is a slow process. For many substances, equilibrium concentrations are only attained after several hours. One way of accelerating and optimizing the adsorption process is to circulate the carbon so that – as with activated sludge – it remains in the system longer than the water (Fig. 1B). The general difficulty with PAC treatment lies in separating the carbon from the water. Various options are available: it can be done either via sedimentation, which necessitates the use of precipitants, or via (membrane) filtration, which requires additional energy. With sedimentation, a downstream sand filter is needed to retain carbon that has not been removed. The used carbon is then incinerated, and the sorbed organic substances are thus completely mineralized.

Another way of improving the effectiveness of activated carbon adsorption would be to recycle the carbon to the biological step of the treatment plant. As activated carbon is normally only used after the biological step – i.e. when concentrations of contaminants are already very low – its surface is only partly loaded and its full purification potential is not effectively exploited. When carbon is recycled to the biological step, where contaminant concentrations are higher, additional loading occurs. This approach is currently being investigated at Eawag, but it is not yet clear whether activated carbon will adversely affect degradation proc-

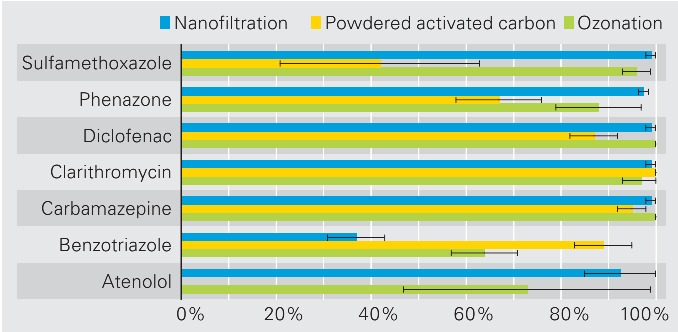


Fig. 2: Elimination rates for selected micropollutants with the three processes. The data, collected by Eawag, are applicable for the following operating conditions: ozonation – dose 0.6 g O_3 per gram dissolved organic carbon (Regensdorf); powdered activated carbon – dose 10 mg PAC per litre (Eawag pilot plant); nanofiltration – Dow Filmtec NF90 membrane operated at 5 bar (Eawag pilot plant).

Overview of energy consumption and costs for downstream ozonation or PAC adsorption. The values include sand filtration except otherwise noted. Primary energy represents total energy consumption, including production and transport of the agents required (oxygen, PAC). The costs are given for small (< 15,000 PE = population equivalents) and large (> 100,000 PE) wastewater treatment plants (WWTP) and comprise investment and operating costs [4].

	Unit	Ozonation	PAC
Additional energy consumption WWTP (without sand filtration)	kWh/m^3	0.05–0.15	< 0.005
Additional energy consumption WWTP	kWh/m^3	0.1–0.2	0.05
Increase in energy consumption WWTP	%	20–50	10–20
Primary energy	kWh/m^3	0.3–0.5	0.4–0.7
Costs small WWTP < 15,000 PE	CHF/m^3	0.32–0.36*	0.42–0.47*
Costs small WWTP < 15,000 PE	CHF/PE/a	32–36	42–47
Costs large WWTP > 100,000 PE	CHF/m^3	0.09–0.11*	0.15–0.20
Costs large WWTP > 100,000 PE	CHF/PE/a	10–15	15–20

*Average wastewater volume per PE: 100 m^3 per year.

esses in activated sludge and whether a significant benefit can be achieved. With this set-up, the carbon would be continuously removed from the system with the activated sludge.

The additional energy required for activated carbon adsorption at the treatment plant is low. However, as the production of activated carbon is highly energy-intensive, primary energy consumption is higher than with ozonation (Table). The costs are also estimated to be slightly higher than for ozonation and are largely dependent on the costs of powdered activated carbon (likely to rise sharply in the future).

Dense membranes: an option for water-stressed areas. Dense membranes (as used in nanofiltration and reverse osmosis) are made of a material that is much more permeable to water than to dissolved substances, while particles are fully retained. At an operating pressure of 5–40 bar, relatively pure water can thus be obtained from feed water rich in dissolved substances and particles (Fig. 1C). After biological treatment, the wastewater generally has to be prefiltered (microfiltration) and the pressure boosted before it passes through the filter modules. The water is circulated several times so as to increase the flow rate across the membrane, wash away deposits and thus slow down the formation of a cake layer. Depending on the composition of the wastewater and the type of membrane, conditioning – i. e. the addition of chemicals – will also be needed to prevent precipitation and membrane fouling. Even so, membranes will require regular chemical cleaning.

The concentrate held back by the membrane is known as the retentate, while the treated water is known as the permeate. The yield, i. e. the permeate/wastewater ratio, typically lies between 75 % and 80 %. Consequently, between 20 % and 25 % of the wastewater – in the form of contaminated retentate – has to be further treated and disposed of. In addition, both the energy requirements (due to the high operating pressure) and the costs are substantially higher than with ozonation or PAC adsorption. The energy required is estimated at 1–2 kWh/m^3. Given the energy and cost considerations and the lack of disposal options for the retentate, dense membrane technologies do not appear to be suitable for municipal wastewater treatment in Switzerland. However, in areas of water scarcity, where drinking water is to be prepared directly or indirectly from treated wastewater, these technologies – especially nanofiltration – are certainly an option to be considered.

Additional treatment steps: important, but not sufficient. If input of organic micropollutants from municipal wastewater to surface waters are to be reduced in Switzerland, ozonation and PAC adsorption are particularly suitable options. They make it possible to remove a substantial proportion of these contaminants. While ozonation performs somewhat better in terms of costs, the micropollutants are merely transformed rather than being fully retained. With the PAC process, the substances end up bound to the surface of the carbon. The residual carbon (together with the residual sludge) then has to be dewatered, dried and incinerated. With regard to energy consumption, the two methods are comparable, although in the case of ozonation the energy requirement mainly arises at the treatment plant itself, whereas large amounts of energy are required for the production of powdered activated carbon. In the current state of knowledge, the two processes are thus about equally well suited.

However, treatment plants are not the only sources of micropollutants from urban drainage systems. These substances also enter natural waters via surface runoff, combined sewer overflows or leaking sewers. Input pathways also include agriculture, industrial emissions and other diffuse sources (see the article by Irene Wittmer on p. 8). Input of micropollutants to surface waters can be substantially reduced, but not wholly eliminated, by means of additional treatment steps at WWTPs. The problem of micropollutants in Swiss waters, therefore, cannot be solved – even if it is considerably alleviated – merely by adopting end-of-pipe measures. At-source measures (e. g. replacement of critical chemicals, reduced consumption) should continue to be pursued as the top priority.

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