MICROPOLLUTANTS IN THE AQUATIC ENVIRONMENT AND THEIR REMOVAL IN WASTEWATER TREATMENT WORKS

Antakyali, D.[1], Morgenschweis, C.[2], de Kort, T.[2], Sasse, R.[1] Schulz, J.[1] and Herbst, H.[1]
[1] Grontmij GmbH, Germany, [2] Grontmij B.V., Netherlands
Corresponding Author Email demet.antakyali@grontmij.de

Abstract

Micropollutants are known for their potential to significantly affect the aquatic environment. The environmental impact of these substances is expressed particularly by their persistency, bioaccumulation potential and toxicity. Effective test methods regarding their ecological toxicity are currently under research. Municipal wastewater treatment works (WWTWs) are among the most important entry paths of micropollutants into surface water bodies. Recent investigations proved that oxidative and adsorptive methods can be applied cost-effectively for micropollutant removal. Various removal units have been already implemented in full-scale in municipal WWTWs in Germany, Switzerland and France. In the Netherlands treatment units including micropollutant removal have been constructed in hospitals. Further full-scale plants are currently being planned. The paper presents an overview on the general impacts of micropollutants, effective techniques for their removal and current implementations in Europe.

Keywords

activated carbon, adsorption, micropollutant removal, ozonation, wastewater treatment

Introduction

The term “micropollutants” basically represents the residues of chemicals occurring in the water-soil-air matrix in trace amounts from microgram to pictogram per litre and literally underlines the low concentration range of the substances. Pharmaceuticals, cosmetic products, artificial musk, industrial auxiliary chemicals, pesticides and biocides are among the substance groups considered as micropollutants. These are released into the hydrological cycle through urban and agricultural sources.

The effects of micropollutants in aquatic ecosystem are not very well known yet. However, there are clear indications for their significant impact potential, particularly considering the long-term impacts. Reasons for this are (1) their potential to accumulate into aquatic organisms and human bodies (bioaccumulation), (2) their toxicity and (3) their resistance to degradation in the environment (persistency). Regulations on their emission and discharge are thus decisive for improving the aquatic environment and surface water quality.

The Water Framework Directive 2000/60/EC (CEC, 2000) is the European-wide legislation tackling the hazards and risks arising from priority substances. It aims for good ecological and chemical conditions in surface water bodies and regulates the monitoring and measures of the EU Member States towards improving the surface water quality. In 2013, the new Directive 2013/39/EC (CEC, 2013) came into force, amending the Directives 2000/60/EC and 2008/105/EC (CEC, 2008), which previously amended the Directive 2000/60/EC, as regards to the list of priority substances. More specifically, twelve new substances were introduced and thus, 45 compounds are now classified as priority substances. A remarkable number of the substances given in the priority list, particularly biocides and industrial auxiliary chemicals are considered as micropollutants due to their nature, impact and concentration range. There is a waiting list with another 100 substances that will be assessed for inclusion during the next review process. Regarding the known effects of micropollutants and the expected future developments such as increased consumption of the chemicals associated with the demographic rise, intensified actions shall be taken towards minimising the release of micropollutants into surface water bodies (ARGE KOM-M.NRW, 2015).

The entry pathways of micropollutants into surface water bodies are diverse. Current findings about the hazardous feature of these chemicals first raise the question whether they can be replaced by harmless alternatives. This is partly possible and should be a primary goal for the policy makers. However, it is very unlikely that a full replacement of these chemicals by the harmless ones will be possible, as certain hazardous features, such as endocrine manipulation (hormonal pharmaceuticals) or fatal effects (antibiotics, pesticides) are desired effects. Thus to prevent the release of micropollutants in the aquatic environment, a multi-barrier concept is required. This implies actions towards preventing micropollutants from entering the hydrological cycle at the source as well as elimination measures. Regarding the latter, a broad spectrum of micropollutants enter surface water bodies through municipal wastewater treatment works (WWTWs), making them an important source for micropollutant release. Thus, advanced wastewater treatment technologies can contribute to the micropollutant removal significantly.

Micropollutants in surface waters

Wastewater-relevant micropollutants

The number of compounds introduced into the environment by humans is in the thousands (Rosi-Marshall and Royer, 2012). However, not all of them are relevant for wastewater. Common micropollutants found in municipal wastewater are discussed in this report as general pharmaceuticals, endocrine disrupting compounds (EDCs) and biocides. Some sample wastewater-relevant substances are given in Table 1.

Table 1: Sample micropollutants found in municipal wastewater

Substance	Utilisation purpose
Carbamazepine	Antiepileptic (pharmaceutical)
Diclofenac	Anti-inflammatory (pharmaceutical)
Propyphenazone	Analgesic, antipyretic (pharmaceutical)
Caffeine	Stimulant (food & pharmaceutical)
AHTN & HHCB	Fragrance (personal care product)
Benzophenone	Sun blocking crèmes, plastics (industrial auxiliary chemical)
Bisphenol A	Basic component for plastics (industrial auxiliary chemical)
TCEP & TCPP & TDCPP	Flame retardant (industrial auxiliary chemical)
DEET	Insect repellent (biocide)
4-nonylphenoles	Industrial surfactant, pesticide (biocide)
Terbutryn	Algicide, herbicide (biocide)
2-hydroxybiphenyl	Disinfectant, fungicide (biocide)

Pharmaceuticals

The group includes a wide variety of substances, e.g., cardiovascular, antiepileptic, analgesic, and cytostatic pharmaceuticals, antibiotics, antidepressants, X-ray contrasting agents and sexual enhancement drugs. The major part of research on pharmaceuticals in the aquatic environment has focused on occurrence and concentration of the compounds in the surface water, and a number of studies has investigated the short term effects of individual pharmaceuticals on aquatic organisms under laboratory conditions and in higher doses. On the way how pharmaceuticals in low concentrations affect ecosystem functioning, literature is scarce (Rosi-Marshall and Royer, 2012; STOWA, 2015).

Endocrine disrupting compounds

Endocrine disrupting compounds (EDCs) are a group of substances that exert hormonal activity in organisms and/or interfere in a different way with the endocrine system in organisms. This group includes hormone preparations (e.g. synthetic oestrogens like ethinyl estradiol used in birth control pills), a number of industrial auxiliary chemicals (e.g. perfluorinated compounds like PFOS, plasticizers like phthalates and Bisphenol-A), organotin compounds (e.g. TBT), pesticides (e.g. DDT), synthetic fragrances (e.g. musks) and personal care products.

Biocides, including pesticides and disinfectants

This group includes pesticides, disinfectants and anti-fouling agents. Disinfectants are intended to kill off microorganisms that are present on surfaces. Anti-fouling agents are used on surfaces to prevent growth of organisms. These are used, for instance, on ship hulls and in piping of cooling water systems. Pesticides are a wide variety of biologically active substances exterminate in general specific groups of organisms such as insects (insecticides), algae (algaecides), weeds (herbicides), fungi (fungicides), etc. Pesticides are mainly used in agriculture, but also to preserve materials in storage and in the killing of plagues that pose threats to human health.

Ecological effects of common groups of micropollutants

The ecological impact of the micropollutants depends basically on their concentrations, persistence and the accumulation tendency in living organisms. The impact can be chronic or acute[1] and is to be expected on individual organisms or community and ecosystem level. In general, chronic effects occur at lower concentrations than acute effects. Table 2 gives an overview on the known effects.

Substances that have hormone-like behaviour (endocrine disrupting compounds) can cause effects at very low concentrations, as hormones are messenger agents functioning at low concentration range. The same holds true for a wide variety of pharmaceuticals that are specifically designed to be biologically active in target organisms. Persistent compounds – like some pesticides - are known to accumulate in ecosystems, so even if concentrations in the effluent are relatively low, they may rise over time. Also, if there is a continuous input of less persistent micropollutants into the aquatic ecosystem, this may cause negative chronic effects as well, as organisms are continuously exposed to a certain concentration of (a mixture of) micropollutants.

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[1] Acute effects are effects that have a direct impact on the organism, like mortality. Chronic effects are more subtle – reduced reproduction, behavioural changes or feminisation of populations – and show at lower concentrations. Effects on individual level can have significant effects on population and community level, and hence, on the stability of aquatic ecosystems.

Table 2: Overview on the impact of selected micropollutant groups on living organisms

Group	Class	Examples of specific effects
Pharmaceuticals	Antibiotics	- Inhibition of growth of certain (micro)algae in 72 and 96 h experiments starting at 6 µg/L (Santos *et al.,* 2010; Kümmerer, 2009) - Effects on nitrification activity (at 9 mg/L) (Klaver and Matthews, 1994) - Effects on reproduction, hatching and viability of juvenile stages of crustaceans (e.g. water fleas) at conc. < 1 mg/L (Kümmerer, 2009) - Secondary effects in crustaceans by alteration of associated microbiota due to effects of antibiotics (Kümmerer, 2009)
	Antihistamines	- Effects on activity and behavior (reduced fleeing response) of damselfly larvae starting at concentrations of 0.4 µg/L, due to neurotransmitter-like behavior of antihistamines (Jonsson *et al*., 2014)
	Antidepressants and anti-anxiety medication	- Behavioral changes in fish at environmentally relevant concentrations: e.g. aggressive behavior and increased activity in perch exposed to 1.8 µg oxazepam/L; impact on mating behavior of fathead minnows starting at conc. of 1 µg Prozac/L (Brodin *et al*., 2013; Weinberger and Klaper, 2014)
	Anti-inflammatory drugs	- Cell damage in trouts after 3-week exposure to concentrations >0.5 µg diclofenac/L (Mehinto et al., 2010)
Endocrine disrupting compounds	(Synthetic) hormones	- The threshold value for endocrine disrupting effects is ~ 0.5 ng 17a-ethinylestradiol/L. Effects range from lower egg production in female fish, to growth reduction, increased liver size, feminisation of young male fish to overall disruption of the natural hormonal balance. Similar effects occur in molluscs (ICPR, 2011; STOWA, 2015; Jobling and Tyler, 2003)
	Synthetic musk fragrances	- Larval development in certain crustaceans (copepods) is affected at concentrations of 20 µg HHCB/L; at concentrations of 200 20 µg/L, proteins involved in excretion of xenobiotic compounds are inhibited (Walters *et al*., 2005; Peck and Hornbuckle, 2006).
	Antifoulants	- Development of male sex organs in female sea snails (imposex) at concentrations of 1 ng TBT/l and total reproductive failure in sea snails at concentrations of 6-8 ng TBT/l (Sumpter, 2002).
	Plasticizers	- Effects of bisphenol-A on egg production in aquatic snails starting at 8 ng/l; effects on reproduction in daphnids starting at 3 to 30 µg DEHP/l (Jobling *et al*., 2004; OEHHA, 2009)
Biocides	Desinfectants	Triclosan and triclocarban affect the growth of algae and fresh water crustaceans from concentrations <0.1 µg/l; decreased aggression (nest protection behavior) in Fathead minnows at concentrations of 1.6 µg triclosan/L (STOWA, 2015; Brausch and Rand, 2011)
	Pesticides	Very wide range of effects on target and non-target species, including acute (e.g., mortality) and chronic effects (reduced reproduction, behavioral changes, growth inhibition, endocrine disruption). Also higher food chain effects may occur: decline of farmlandbird populations in the vicinity of surface waters with imidacloprid concentrations >20 µg/L has been observed in a long-term study (Hallmann et al., 2014).
	Antifoulants	*see antifoulants in the endocrine disrupting compound section*

Another possible scenario is incidental input in the surface water of high concentrations of micropollutants through effluent discharge. In fact, the exposure to a single micropollutant may not have an effect on the ecosystem, but the combined exposure to numerous micropollutants at low concentrations may have a negative impact. This may lead to acute effects on the ecosystem, from which populations and communities need to recuperate. However, if this recuperation takes longer than time between incidental discharges, or if the impact is too hard to recuperate from, the negative impacts on the aquatic ecosystem may be long-lasting (EU, 2009; EU, 2012).

Finally, the relevance of micropollutants to a surface water ecosystem also depends on the sensitivity of the ecosystem and the input of specific compounds or groups of compounds in the system, both in terms of concentration and duration between inputs. This makes the question of micropollutants also a location-specific issue.

Determination of the ecological impact of micropollutants

Biological test methods

Ecotoxicological testing in addition to chemical analyses

Chemical analyses of micropollutants give insight in the presence or absence of these compounds in surface water, waste water and effluent above a compound-specific limit of detection. Therefore, it is a useful way to look at removal efficiency of micropollutants by WWTWs with or without advanced techniques. However, this insight is limited to the compounds that are analysed. In some cases, the metabolites of a micropollutant are more toxic than the initial compound. In chemical analyses this may not show up.

Translation of concentrations of micropollutants to the effects on organisms is a challenge in itself. In environmental samples complex mixtures of micropollutants may be present. With the current state of knowledge on effects of complex mixtures of micropollutants in the aquatic environment, it is hard to predict whether certain groups of substances add to, enhance or diminish each other’s effect. Especially persistent (not easily degradable) micropollutants deserve attention, as those may accumulate in the environment.

Because of aforementioned reasons, ecotoxicological analyses of discharged wastewater (Whole Effluent Testing) may be a valuable addition to chemical analyses. By an effect-based approach (bioassays) the effects of all toxic substances in an environmental sample can be investigated.

Bioassays

Exposing well-studied organisms under controlled conditions in a laboratory to (an extract of) waste water samples, gives insight in the ecotoxicity of the mixture of micropollutants in discharge or surface water. The effects are a measure for the toxicity of the sample: the lower the concentration at which negative effects occur, the more toxic the sample. Tests are generally performed with at least three functional groups of organisms (e.g., algae, crustaceans, insects, bacteria), as each (group of) organism(s) may react differently to a (mixture of) substance(s). They can be short and focusing on acute effects (e.g., mortality) or long-term and focusing on chronic effects (e.g. growth, reproduction). Chronic tests are in general more sensitive than acute tests. Effects in chronic bioassays tend to be at concentrations one to three orders of magnitude lower. With different solid phase extraction methods micropollutants in water samples can be preconcentrated. Testing these preconcentrated samples with acute bioassays is a way to get information on chronic effects in organisms. Table 6 gives an overview on the biotests applied to determine the micropollutant toxicity.

Table 3: Available bioassays categorized according to the indicator organism

Regular aquatic bioassays*	**Acute**	**Chronic**
Plants	Algae - 72hrs growth rate and biomass (e.g., ISO 8692) Duckweed - 7 days growth rate and biomass (e.g., OECD 221)	Algae - 96 hrs growth rate and biomass (e.g., OECD 201)
Crustaceans	Daphnids (water fleas) - 48hrs mobilisation and behavior (e.g., ISO 6341)	Daphnids (water fleas) - 21 day survival and reproduction (e.g., OECD 211)
Rotifers	*Brachionus* sp. - 24 hrs survival (e.g., ASTM E1440)	*Brachionus* sp. - 48 hrs survival and reproduction (e.g., ISO 20666)
Insects	Chironomid (non-biting midge) larvae - 2 or 7 day mobilisation (e.g., OECD 235)	Chironomid (non-biting midge) larvae - 28 day survival, development and growth (e.g., RIZA 93.027)
Bacteria	Bioluminescence (Microtox assay) - 30 min bioluminescence inhibition of *Vibrio fisheri* (e.g., ISO 11348) Respiration test - inhibition of respiration of bacteria from activated sludge after 30 min or 3 hrs (e.g., OECD 209) Nitrification test - nitrification inhibition with bacteria from activated sludge after 4 hrs (e.g., ISO 9509)	-
Fish	Fish test - 96hrs survival and behavior in adult fish (e.g., OECD 203) Fish egg test - 48hrs embryonic survival and development (e.g., OECD 236)	Early Life Stage test - 30-35 days larval hatching, survival, development, behavior and/or growth (e.g., OECD 210) Juvenile growth test - 28 days growth, development and behavior (e.g., OECD 215) Life cycle test - hatching success, embryo, larval and juvenile development, adult development and reproduction in parent and first generation - this may include effects of endocrine disruption (e.g., OECD ENV/JM/MONO(2008)22)

*focus on fresh water tests and species

Bioassays can also be used to test the efficiency of advanced treatment techniques to eliminate micropollutants from waste water. By testing the toxicity of effluent from a regular WWTW and comparing that to the toxicity of effluent from a WWTW using advanced techniques, the removal efficiency to ecotoxicity can be investigated. The influents of those WWTWs must be similar to make a relevant comparison.

Certain (chronic) effects do not show up easily in regular ecotoxicity tests. This may be the case for endocrine disruptors, as the effects of these compounds at low concentrations are subtle and may not show up during the test time of relatively short bioassays. This would require very costly bioassays that test the effect on multiple generations. However, with relatively simple in-vitro tests on the cellular level (e.g., CALUX assays), effects of micropollutants – e.g., endocrine disruption - can be investigated in (waste) water samples (Table 4). For the testing of removal efficiency of micropollutants in an effect-based manner, the use of multiple species and effect-analyses is advisable.

Table 4: Other sample bioassays available for testing of toxicity of micropollutants

Other bioassays	Examples of tests
Genotoxicity and mutagenicity	Ames test - induction of DNA damage and mutations to specifically modified bacterial strains (*Salmonella* or *E. coli*) (e.g., OECD 471) umuC test - DNA damage to repair systems of cell of specifically modified *Salmonella* strains (e.g., ISO 13829)
Calux Assays	Wide range of specific assays, e.g.: DR CALUX and PAH CALUX - Xenobiotics metabolism / dioxin receptor activation; ER CALUX - Estrogen signalling; ERα CALUX - Estrogen receptor α-mediated signalling; ERα-anti CALUX - Repression of estrogen receptor α-mediated signalling; ERβ CALUX - Estrogen receptor β-mediated signalling; ERβ-anti CALUX - Repression of estrogen receptor β-mediated signalling; AR CALUX - Androgen receptor activation; AR-anti CALUX - Repression androgen receptor activation; PR CALUX - Progesterone receptor-mediated signalling; PR-anti CALUX - Repression of progesterone receptor-mediated signalling; GR CALUX - Glucocorticoid receptor-mediated signalling; P53 CALUX - p53-dependent pathway activation / genotoxicity response; genotox CALUX - p53-dependent pathway activation; ER stress CALUX - Endoplasmic reticulum stress response; cytotox CALUX - Repression of constitutive transcriptional activation See: http://www.biodetectionsystems.com/products/bioassays/available-assays.html

The development of high-throughput in-vitro bioassays is ongoing at the moment. In the future, these will be an instrument to screen (eco)toxicological effects of micropollutants in waste- and surface water in a relatively inexpensive way.

Ecological field studies

Another way to look at ecological effects of micropollutants, is to look at the ecosystem itself. If shifts the ecological communities at downstream of the effluent discharge. The advantage of looking at the ecosystem under natural conditions is to see the actual effects on the system. A recent Dutch study showed that decline in aquatic invertebrate communities and in farmlandbird populations that depend on those species, is strongly related to the use of imidacloprid – a neonicotinoid insecticide – in the studied areas (Hallman et al., 2014). These kinds of studies are long-term studies, but incorporated in regular monitoring programs of the chemical and ecological status of surface water, give insight in long-term effects of surface water quality, with effects of micropollutants being a part of that.

The advance of ecotoxicity testing in addition to chemical analysis is that the effect of all micropollutants and its metabolites present in the effluent are incorporated.

Comparative assessment of the methods

Each method to determine the impact of the micropollutant has its strengths and weaknesses. Table 5 presents an overview on the advantages and disadvantages of chemical, biological and ecosystem analyses.

Table 5: Other sample bioassays available for testing of toxicity of micropollutants

	Advantages	Disadvantages
Chemical analysis	+ Gives information on concentrations of micropollutants in effluent + Relatively inexpensive for the regular groups of pollutants	- Information limited to compounds that are analysed. No information on metabolites - No direct relation with effects on ecosystem, especially in cases with complex mixtures of pollutants
Ecotoxicological analysis	+ Information on the effects of the total amount of bioavailable pollutants in an environmental sample + Insight in the specific group(s) of organisms that may be at risk	- No direct insight in the specific compound(s) that cause the effect - Chronic tests may be relatively expensive
Ecosystem studies	+ The full scope of the ecosystem is being investigated: seemingly small effects may have significant effects at other places in the ecosystem - Site-specific information is gathered, making site-specific measures possible	- It may be difficult to isolate the effects caused by pollution from effects caused by other factors such as the suitability of the habitat, the absence or presence of certain key species, or water quality parameters like pH and conductivity - Effects may be site-specific and therefore may be hard to extrapolate to other sites

In general, combination of monitoring with different analytical methods (chemical and ecotoxicological) and monitoring of the ecological quality of the surface water near WWTWs, gives the best insight in the effect WWTW discharge (including removal of micropollutants) has on the ecosystem. Pilot studies for Waterboards in the Netherlands look into combinations of all three or two (chemical and ecotoxicological) methods for monitoring purposes. This effect-based and chemical monitoring can be used as a prioritization and measures selection tool. The ecological and ecotoxicological monitoring may give insight in which (parts of) waterbodies may be negatively influenced by micropollutants while the chemical analyses can point to the substances (and possible sources) at which measures should be focussed.

Micropollutant entry pathways into surface water bodies

There are different pathways for micropollutants entering surface waters. Figure 1 presents the common sources and routes of micropollutants into surface water.

Wastewater treatment work effluents constitute a very significant pathway, for containing the micropollutants which were consumed in build-up areas, mainly pharmaceuticals, personal care products and household chemicals. In fact, whilst relatively concentrated sources of pharmaceuticals and hormones originate from hospitals, the majority of the load of these substances is released by domestic households (STOWA, 2011). Also the residues of industrial chemicals enter the surface waters through WWTW effluents. Combined sewer overflows as well as surface runoff from urban areas with separate storm water collection system can transport an important load of micropollutants such as biocides within a short time.

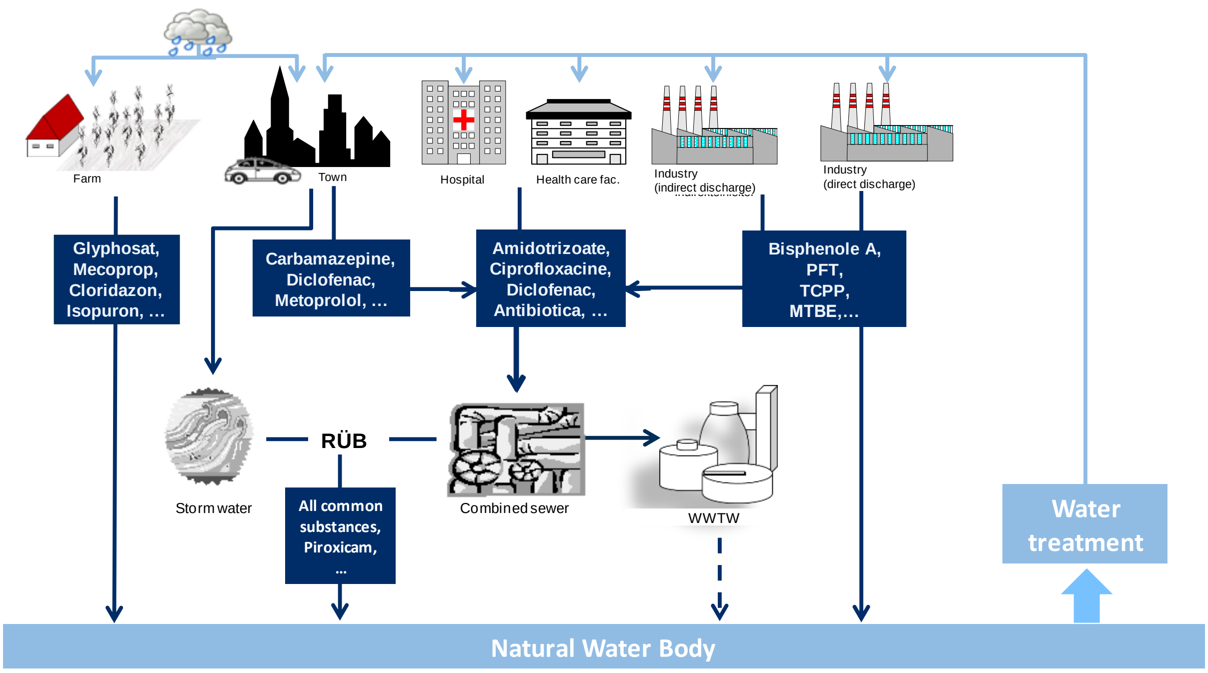

Figure 1: Different pathways of micropollutants entering the environment (WWTP: wastewater treatment plant)

Agricultural areas constitute another important entry pathway for veterinary pharmaceuticals and pesticides as a diffuse source, yet rather difficult to control by technical installations. WWTWs present here a concentrated point source, where a large spectrum of micropollutants can be removed at once.

State of the technology in micropollutant removal

Target group for removal processes

Wastewater relevant micropollutants have been discussed in previous sections. The persistence of the substances to natural and technical degradation processes varies with their physicochemical properties. Some of the pharmaceuticals can be removed by > 99 % (e.g. Ibuprofen), where some other are found in the effluent with almost no change (Carbamazepine). It is stated that conventional biological treatment plants can remove overall half of the micropollutants (Luo *et al.*, 2014). However, the other half is sufficient to cause the observed impacts. Thus the focus of the micropollutant removal processes lies on the substances, which cannot be removed through conventional treatment processes.

Potential techniques for the cost effective removal of micropollutants

Biological treatment can accomplish more, if optimised for enhanced removal of the micropollutants through membrane bioreactors, biofiltration systems and coagulation-flocculation (e.g. Luo *et al.*, 2014). Furthermore, wetlands have the potential to remove micropollutants from wastewater (e.g. Carranza-Diaz *et al.*, 2014) and there is ongoing research in this field. However, there are already proven technical processes for efficient micropollutant removal. Figure 2 presents an overview on these processes, being oxidative, adsorptive and physical methods.

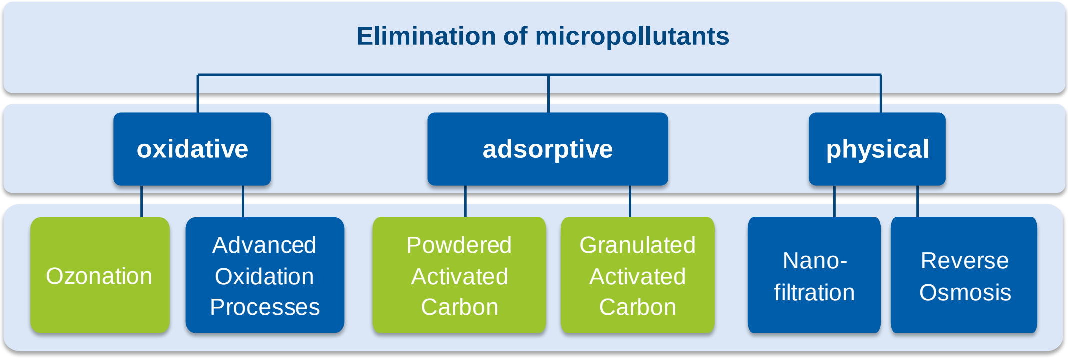

Figure 2: **Practically tested techniques for the removal of micropollutants; the most cost-effective methods operating at full scale marked in green**

The physical methods are based on filtration processes using membrane technology. With respect to the small particle size of micropollutants, nanofiltration and reverse osmosis are the most effective physical techniques using membrane filtration. However, neither nanofiltration nor reverse osmosis offer cost-effective solutions due to high operating pressures and the associated energy demand. Oxidative processes can generally offer a significant elimination of micropollutants. Advanced Oxidation Process (AOP) combines the UV treatment and oxidation processes using hydrogen peroxide (H_2O_2) or ozone. The AOP is faster than ozonation alone, however, also less cost-efficient. Adsorptive processes are known from drinking water treatment and can also remove a remarkable portion of micropollutants.

It must be stated that there is no particular treatment process to remove all different micropollutants at once. However, from the present state of the art, the ozonation process and the adsorption by means of powdered activated carbon (PAC) as well as granulated activated carbon (GAC) are considered as the cost-effective methods for micropollutant removal for full scale applications (e.g. Hernández-Leal *et al.*, 2011; Margot *et al.*, 2013; Altmann *et al.*, 2014).

Ozonation

Ozone (O_3) is an unstable gas and a very strong oxidant, which quickly decomposes to the more stable gaseous oxygen (O_2). Due to its high reactivity, ozone is capable of oxidizing persistent organic substances to more easily degradable substances (Barjenbruch *et al.* 2014). The ozonation is an already well-established process in the drinking water treatment and is particularly beneficial for

- the reduction of bacteria and viruses, and disinfection,
- the oxidation of the organic and inorganic components of water and
- the elimination of odour and colour.

Ozone oxidizes pollutants either directly or indirectly through the generation of hydroxyl (OH) radicals. In general, both reaction paths can occur. However, depending on the substance characteristics and the wastewater composition, one of the two processes will predominate. Further influences may arise from the reactive conditions such as temperature and pH value (Barjenbruch *et al.*, 2014).

The ozonation process is applied to the effluent of the biological treatment in a separate reaction tank, where ozone is fed through air diffusers or injector systems. Ozone is not easily transportable and thus must be produced on-site. In order to prevent the release of excess ozone to the final effluent, an ozone destruction unit is set at the outflow of the reaction tank. The ozonation step is followed by a biological post-treatment for the removal of possible breakdown products of the oxidation process, which may still pose a significant danger for living organisms. Biologically activated filtration systems or maturation ponds as well as fluid-bed or fixed-bed reactors can be implemented for this purpose. (ARGE KOM-M.NRW, 2015).

The efficiency of the ozone for micropollutant removal may be reduced by any oxisidable matter in the wastewater due to competition. Regarding the WWTP effluent, dissolved organic carbon (DOC) is assumed to be the indicator parameter and thus the ozone dosage is set according to the DOC concentrations. Also nitrite is recommended to determine, as it can increase the ozone demand in the wastewater.

Adsorption by activated carbon

In the adsorption process gas or liquid molecules are adhered on a solid surface by electrostatic interaction. Adsorption by activated carbon implies that the adsorbed compounds are completely removed from the wastewater. If more than one contaminant is present, hydrophobic substances will be absorbed by carbon more efficiently and, thus, will be removed in larger quantities than hydrophilic substances. In particular, activated carbon is appropriate for adsorbing non-polar, organic substances due to its large specific surface that ranges from 500 to 1500 m^2/g (Barjenbruch *et al.*, 2014).

Activated carbon is produced from natural materials such as wood, coconut shell, peat, lignite, bituminous coal and petroleum residues. The carbon medium is activated by exposing it to steam and high temperatures of about 1200 °C. The heating causes cracks, gaps and pores which are associated with surface increases. In general, two different types of carbon are used: Powdered activated carbon (PAC) with grain sizes below 0,045 mm and granulated activated carbon (GAC) with grain sizes in the range of 0,5-4,0 mm (Barjenbruch *et al.*, 2014).

PAC treatment is generally implemented after the biological stage, where it is dosed into the WWTW effluent in a separate contact tank and separated afterwards again in a settling tank. The sludge from the settling tank can be recirculated into the contact tank or into the activated sludge tank before withdrawn from the system for disposal. The fine PAC particles require an additional filtration step following the settling tank (ARGE KOM-M.NRW, 2015).

In GAC applications, GAC is used as filling material in so called fixed-bed filters. The application can be rather cost-effective in WWTWs with readily existing flocculation filters, since the filling material in use can be easily replaced by GAC (ARGE KOM-M.NRW, 2015). Unlike PAC, GAC can be reactivated for reuse. However, compared to PAC, the filters may need larger space due to the smaller surface area of GAC.

Important factors for the process selection and design

A functioning WWTW is the prerequisite for an efficient micropollutant removal. Organic matter, especially particles in the effluent can reduce the efficiency of the micropollutant removal processes or require a larger dimensioning. Instead of enlarging the micropollutant removal step, it may be less expensive to improve the conventional treatment process or to install a pre-filtration unit before the oxidation and adsorption steps.

Wastewater flow and composition can play an important role on the selection of the most suitable process, thus they should be analysed for each plant individually through a screening. Due to the high number of chemicals considered as micropollutants, the substance selection for the screening may be challenging at first sight. Local conditions should be considered for each plant, depending on the potential micropollutant sources within the WWTW catchment. ARGE KOM-M.NRW (2015) presents a comparative overview on the substance selection by different professional groups.

Both processes can remove a broad spectrum of substances, yet removing efficiencies of adsorption and oxidation differ slightly with the substance groups. A comparison of the elimination rates between ozone oxidation and adsorption by Fahlenkamp *et al.* (2008) indicates that the removal of oestrogens such as 17β-Estradiol is very high for both techniques. Carbamazepine (antiepileptic), Diclofenac (painkiller), Sulfamethoxazole (antibiotic) can be more efficiently eliminated by ozonation than by PAC, while PAC yields better elimination rates for Nonylphenols, Bisphenol A and musks.

The removal efficiency for both of the processes depends on the retention time of the wastewater in the reaction tank and the dosage of ozone or activated carbon. In general, higher ozone and PAC doses or frequent exchange of GAC will increase the removal efficiency. However, the design must be economically optimised. Thus lab-scale tests are recommended to determine the optimum dosage. Another important factor, which may help reducing the construction costs, is the availability of any structures to be used for the micropollutant removal step.

The competence centre for micropollutants suggests that the micropollutant removal step should be designed to eliminate at least 80 % of the sum of the significant micropollutants (ARGE KOM-M.NRW, 2015).

Implemented removal-sites in Europe

Current state of implementations

An adsorption step in a municipal WWTW has already been constructed in 1992 in southern Germany (state of BW), which was designed for the removal of colour originated from textile dyes. The first municipal WWTW extension for a targeted micropollutant removal is located in Bad Sassendorf, in the NRW state of Germany. The plant has been taken into operation in 2009 following a series of lab and pilot scale investigations. Today, there are 17 municipal WWTWs running a micropollutant removal unit in Europe. Figure 3 presents the distribution of the operating units according to the size of the WWTWs.

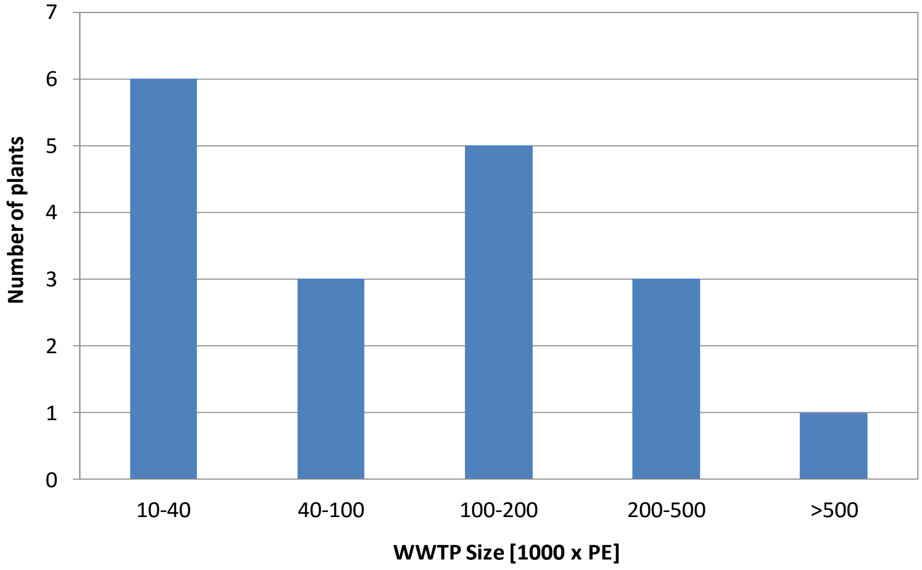

Figure 3: **Number of implemented micropollutant removal units in municipal WWTWs in Europe according to the size of the WWTW (by June 2015)**

Of the 17 municipal WWTWs with a micropollutant removal unit, 14 are located in Germany, two in France and one in Switzerland. In another Dutch WWTW a special process is applied achieving a partial removal of micropollutants.

Country	Size of WWTW [PE]	Process in application	Source
Germany (NRW)	30 000	Ozonation	KomM.NRW, 2015
Germany (NRW)	13 000	Ozonation	KomM.NRW, 2015
Germany (NRW)	50 000	Ozonation and PAC	KomM.NRW, 2015
Germany (NRW)	380 000	GAC	KomM.NRW, 2015
Germany (NRW)	150 000	GAC	KomM.NRW, 2015
Germany (BW)	725 000	PAC	KomS, 2015
Germany (BW)	440 000	PAC	KomS, 2015
Germany (BW)	250 000	PAC	KomS, 2015
Germany (BW)	43 000	PAC	KomS, 2015
Germany (BW)	24 000	PAC	KomS, 2015
Germany (BW)	125 000	PAC	KomS, 2015
Germany (BW)	57 000	PAC	KomS, 2015
Germany (BW)	36 000	PAC	KomS, 2015
Germany (BW)	184 000	PAC	KomS, 2015
Switzerland	150 000	Ozonation	Micropoll, 2014
France	26 000	Ozonation	Degremont, 2013
France	15 000	Ozonation	Micropoll, 2014
Netherlands	165 000	1-STEP©, GAC (partial)	Micropoll, 2014

Table 6 gives an overview on the permanent applications including the size of the WWTW and implemented process. It is seen that both activated carbon adsorption and ozone oxidation processes found full-scale applications. Of note is the frequency of PAC plants in the state Baden-Württemberg, which is to be justified by the existing experience in the region with activated carbon plants descended from past applications with textile dying wastewater.

Table 6: Permanent implementations for micropollutant removal in municipal WWTWs in Europe (NRW = North Rhine Westphalia; BW = Baden-Württemberg; PAC = powdered activated carbon; GAC = granulated activated carbon; MBR = membrane bioreactor)

Country	Size of WWTW [PE]	Process in application	Source
Germany (NRW)	30 000	Ozonation	KomM.NRW, 2015
Germany (NRW)	13 000	Ozonation	KomM.NRW, 2015
Germany (NRW)	50 000	Ozonation and PAC	KomM.NRW, 2015
Germany (NRW)	380 000	GAC	KomM.NRW, 2015
Germany (NRW)	150 000	GAC	KomM.NRW, 2015
Germany (BW)	725 000	PAC	KomS, 2015
Germany (BW)	440 000	PAC	KomS, 2015

Germany (BW)	250 000	PAC	KomS, 2015
Germany (BW)	43 000	PAC	KomS, 2015
Germany (BW)	24 000	PAC	KomS, 2015
Germany (BW)	125 000	PAC	KomS, 2015
Germany (BW)	57 000	PAC	KomS, 2015
Germany (BW)	36 000	PAC	KomS, 2015
Germany (BW)	184 000	PAC	KomS, 2015
Switzerland	150 000	Ozonation	Micropoll, 2014
France	26 000	Ozonation	Degremont, 2013
France	15 000	Ozonation	Micropoll, 2014
Netherlands	165 000	1-STEP©, GAC (partial)	Micropoll, 2014

The tendency for new constructions of micropollutant removal steps in WWTWs is ongoing in central Europe, in particular in Germany and Switzerland. In Germany micropollutant removal steps are in the construction or design phase at more than 10 WWTWs. Also in Switzerland the extension of several other WWTWs with micropollutant removal has been initiated as a consequence of the introduction of the legal enforcement. One plant is in operation since 2014, and a second one is about to be taken into full operation. The selection of plants to be extended is based on the WWTW size and feature or the sensitivity of the receiving water body.

Besides the applications in municipal WWTWs, decentralized plants have been implemented in several hospitals for hospital wastewater being a hot-spot for pharmaceutical residues. Table 7 presents the basic features of the plants in operation.

Table 7: Permanent decentralised WWTWs including a micropollutant removal step in hospitals in Europe.

Country	**Capacity**	**Process in application**	**Source**
Germany (NRW)	340 beds, 32 m³/h	MBR and Ozonation	KomM.NRW 2015
Germany (NRW)	560 beds, 25 m³/h	MBR, Ozonation and PAC	PILLS 2009
Netherlands	200 beds, 10 m³/h	MBR, Ozonation and GAC	E. Koetse (Pharmafilter) 2014 (personal communication)
Netherlands	400 beds, 10 m³/h	MBR, Ozonation and GAC	E. Koetse (Pharmafilter) 2014 (personal communication)
Denmark	900 beds, 15 m³/h	MBR, Ozonation and GAC	Nielsen *et al.* 2013

Two plants in Germany, two in Netherlands and one in Denmark are known to the authors. Two more plants are currently under construction in the Netherlands. The common feature of the implemented hospital plants is that the plants combine the biological wastewater treatment with a post-treatment micropollutant removal step in decentralized units.

Cost of the micropollutant removal step

The costs associated with micropollutant treatment will vary dependent upon the availability of existing assets, the substances to be removed and the flow to be treated. Figure 4 summarises the specific costs of the implemented plants in Germany and Switzerland (by March 2015).

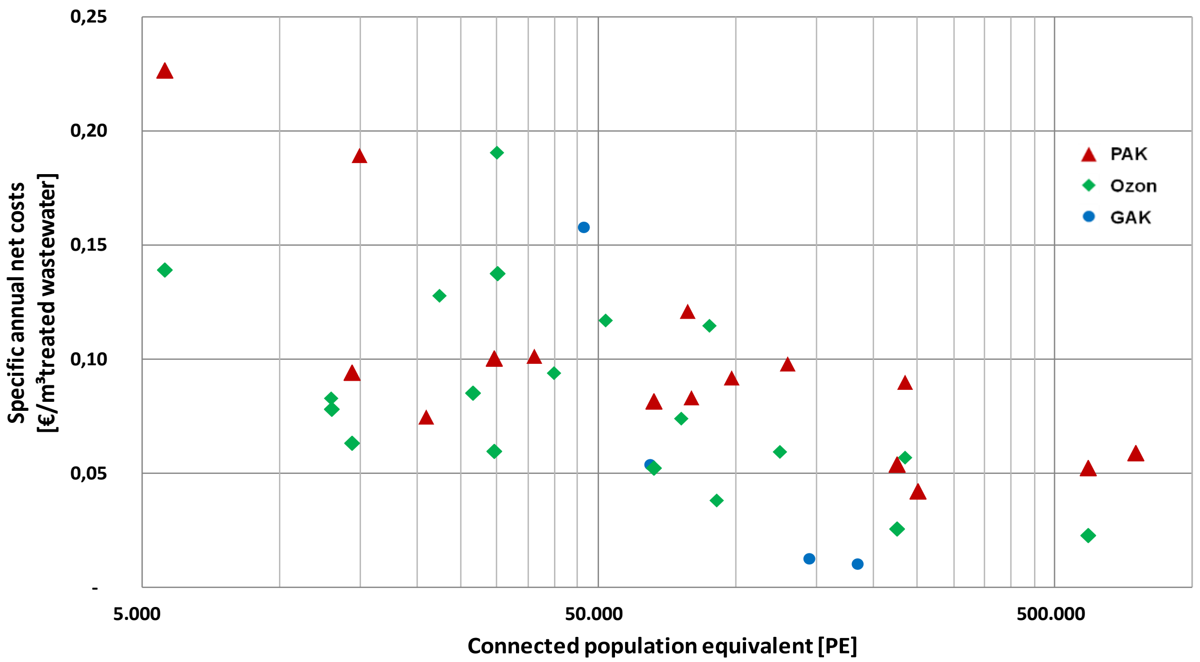

Figure 4: Specific costs of ozonation and activated carbon processes for different WWTPs in Germany and Switzerland (source: KOM-M.NRW)

In line with the expectations, larger plants result in the lower specific costs. No clear cost advantage between PAC, GAC or ozone can be observed. The data contains plants, where existing structures have been used and also those only with new installations. Thus an exact cost comparison is not possible. However, a general tendency around 10 Euro cents per m³ treated wastewater can be recognised.

Conclusions

Types, entry pathways and impact of the micropollutants were discussed. Typical substances released by municipal wastewater treatment works (WWTW) were presented. Biological test methods to determine the toxicity of micropollutants were demonstrated. Technical measures to remove the micropollutants from wastewater were explained and some details on the process selection and design were given. Finally the state of the full scale implementations in Europe for micropollutant removal in WWTWs was displayed.

Micropollutants such as pharmaceutical residuals, biocides, industrial auxiliary chemicals, hormones etc. are likely to have a significant impact on the aquatic environment due to their bioaccumulation potential, toxicity and persistency. For preventing the entry of micropollutants into surface water bodies, a multi-barrier concept is needed. Municipal wastewater treatment works (WWTWs) are among the most important entry pathways for micropollutants into the aquatic environment. As point sources they technically enable actions to prevent the micropollutant release. Thus they can act as an important component of a multi-barrier concept.

A significant rejection of micropollutants can be accomplished in WWTWs through the extension with ozonation or activated carbon adsorption. These techniques are applied subsequent to the conventional biological treatment step (includes final sedimentation tank). Both techniques can achieve good results, yet their efficiency on different group of substances can be variable. Oxidation requires a biological post-treatment process to remove any breakdown products. Considering micropollutant removal by means of adsorption, both granulated activated carbon (GAC) and powdered activated carbon (PAC) can be used. PAC step should be finalised by an additional filtration to reject the very fine carbon particles. The adsorption via GAC is particularly suitable for WWTWs which already have a filtration system. The design of the plants should consider the wastewater characteristics and the vulnerability of the receiving water bodies. A preliminary screening of the incoming wastewater should be conducted prior to the design of a micropollutant removal step.

The costs associated with micropollutant treatment will vary dependent upon the availability of existing assets, the substances to be removed and the flow to be treated.

Current research focuses on the determination of the efficiency of micropollutant removal and on the cost-efficient combination of different processes for an optimised process design.

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