Recommendations for wastewater treatment plants for safe removal of pharmaceuticals and list of pharmaceuticals to be monitored

Report of D.T3.3.1.

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Nature Needs No Pill

Project LLI-527

"Pharmaceuticals in wastewaters – levels, impacts and reduction" MEDWwater

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- Latvian Environment, Geology and Meteorology Centre, ***www.videscentrs.lvgmc.lv***
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Author: Erki Lember, ME Water Consult OÜ

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Introduction

Wastewater has been treated in many parts of the world for more than 100 years. The purpose of wastewater treatment is to protect surface waters from pollution, mainly by reducing organic matter, phosphorus and nitrogen. These pollutants cause a decrease in the concentration of dissolved oxygen in surface waters and eutrophication of water bodies. The municipal wastewater treatment plants (WWTPs) in the Baltics are not yet designed to remove hazardous substances, such as heavy metals, microplastics and micropollutants, including pharmaceutical residues. Though, heavy metals and specific hazardous substances are removed at certain production sites.

EU has authorised more than 100,000 different chemical compounds (including more than 3,600 different active pharmaceutical ingredients or APIs), whereas 1/3 of them producing more than 1 ton per year. Through the production sites and consumers, residues of these compounds can end up at WWTPs, where they cannot be removed by current technologies. Whilst in the case of micropollutants we are talking about concentrations measured in μg/l and ng/l, which in most cases do not pose a hazard, scientists are still concerned about the life cycle of some of these compounds. If these compounds are not biodegradable, they accumulate in the environment and may reach hazardous levels. Also, the combined effect of micropollutants is not entirely clear. Consequently, EU is committed to reducing the environmental burden from micropollutants, including APIs. The best way of doing this is to prevent pollution at source, replace some of the products with environmentally safer ones, etc., but this may not always be possible. Therefore, also municipal WWTPs are seen to have to remove micropollutants.

This guidance material provides an overview of the current state of wastewater treatment and introduces types of technological solutions for the establishment of tertiary wastewater treatment (post-treatment). Increasingly stringent pollution limits and emerging problems, such as micropollutants in wastewater, are the incentives for post-treatment. Since many types of technological solutions allow to solve several problems in one single treatment stage, potential synergies are also discussed that allow to reduce unnecessary investment costs.

Current state of wastewater treatment

In a conventional WWTP, the process starts with a mechanical treatment stage, where floating and suspended matters are removed. This is to prevent pumps from becoming clogged with floating solids and to remove non-settling particles such as plastic that cannot be removed in further steps of the treatment process which mainly use gravity to remove solids from wastewater. Suspended matter such as grit is abrasive and settles to the bottom, causing wear and tear on pumps and waste activated sludge centrifuges, and accumulating, for example, in the bottom of a bioreactor due to settling. Therefore, the

large size suspended and floating matters are often removed by passing wastewater through screens and the small size suspended matters such as grit are removed by using grit traps.

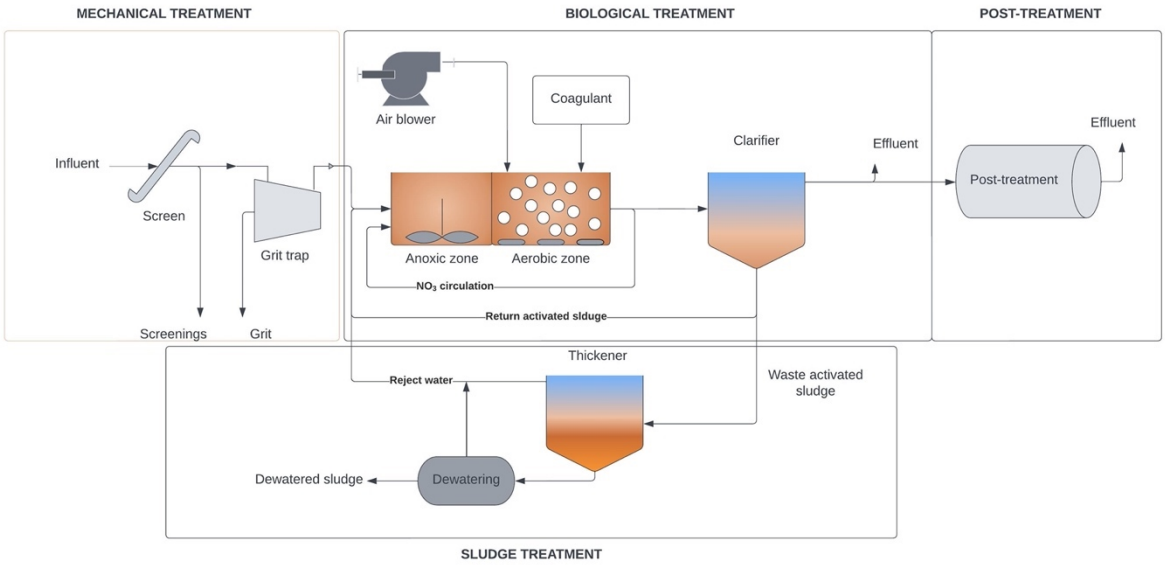

Figure 1. Typical process flowchart of a conventional wastewater treatment plant (WWTP).

Mechanical treatment is followed by biological treatment to remove dissolved pollutants from wastewater. The most common types of biological treatment include the activated sludge process and the biofilm process. In the Baltics, the most common type of treatment is the activated sludge process, which works better in a relatively cold climate. During biological treatment, dissolved pollutants, such as organic matter (measured as COD and BOD), nitrogen and phosphorus are consumed by microorganisms. As a result, the proportion of biomass increases, i.e., dissolved pollutants are transferred from the liquid to the solid state or insoluble particles, which are periodically removed as waste activated sludge. Also, the suspended solids (total solids, TSS), consisting of organic matter, nitrogen and phosphorus, ends up in the biomass. The ratio of pollutants, considered ideal for biological treatment, is 100-5-1, i.e., for each 100 parts of BOD_5 consumed, 5 parts of nitrogen and 1 part of phosphorus (where denitrification is also used then 1.5 parts) is used.

<u>Example 1:</u>

We have a WWTP with the influent characteristics as follows:

BOD_5 350 mg/l

N_{Total} 55 mg/l

P_{Total} 15 mg/l

In this example, to consume all the BOD_5, the microorganisms use up 350 mg/l * 0.05 = 17.5 mg/l of nitrogen, i.e., total nitrogen concentration in the effluent would be 55 mg/l - 17.5 mg/l = 37.5 mg/l, and

for phosphorus, 350 mg/l * 0.01 = 3.5 mg/l, respectively, with phosphorus concentration of 15 mg/l - 3.5 mg/l = 11.5 mg/l in the effluent.

Example 1 shows that a large proportion of pollutants is already used for the growth of microorganisms, however, this is not enough to maintain or improve the status of surface waters. Therefore, in many larger WWTPs, enhanced nitrogen removal or nitrification and denitrification is provided. Since at the inflow to the WWTP, the nitrogen mainly comes in the form of ammonium and organic nitrogen, ammonium (NH_4-N) first needs to be oxidized to nitrate (NO_3-N). This process is called nitrification and it occurs in the presence of dissolved oxygen, i.e., under aerobic conditions. For nitrate removal, denitrification is used, where, under anoxic conditions (i.e., we don't have dissolved oxygen, but we do have chemically bound oxygen), microorganisms use bound oxygen to remove organic matter, i.e., take it from NO_3-N. As a result of this process, N_2 is released as a gas.

Phosphorus is removed from wastewater both biologically and chemically. The most common type of technological solution is chemical coagulation, where, for example, $FeCl_3$ and $Fe_2(SO_4)_3$ based chemicals are added to the biological treatment, which hydrolyse in water and react with orthophosphates (PO_4-P), forming insoluble compounds (salts) that accumulate in waste activated sludge. Biological phosphorus removal is based on microorganisms that are able to accumulate more phosphorus in their cells than they need for life, i.e., in example 1, 2.5% of BOD is counted instead of 1%.

The final step in biological treatment typically includes the removal of biomass from the treated effluent using secondary sedimentation tanks (final clarifiers) (sedimentation phase in batch treatment plant) or membrane filters in a membrane bioreactor. Since the growth of the biomass (hereinafter ‘activated sludge’) needed for biological treatment is relatively slow (it takes 2-3 weeks to start the process in summer, and even several months in winter), a large proportion of the activated sludge has to be pumped back to the beginning of the process. Only a small proportion of the activated sludge is removed as a waste activated sludge which, depending on the WWTP, is thickened, dewatered and stabilised.

Although many WWTPs in the Baltics have a post-treatment in place, in most cases it is not designed to remove micropollutants, but mainly for further removal of nutrients, such as nitrogen and phosphorus. The most common type of post-treatment technology is a disc filter, which removes TSS and thereby reduces the environmental burden from phosphorus. In the following chapters, the API elimination at the WWTP is discussed in more detail and potential synergies are analysed, which would allow using one treatment step to solve a number of problems:

- How to reduce the concentrations of micropollutants, including APIs?
- How to reduce the concentrations of nutrients, such as nitrogen and phosphorus?

1. APIs in wastewater

Since APIs is a relatively narrow concept, the term 'micropollutants' will henceforth be used in discussing the types of technological solutions. This is due to the fact that the types of technological solutions for the removal of APIs and many micropollutants, such as biocides, pesticides, etc., are the same. Micropollutants are hazardous compounds found in concentrations of few μ/l or less. Typically, these are anthropogenic compounds, such as:

- APIs (for human and veterinary consumption);
- industrial chemicals;
- care products;
- hormones (produced and natural);
- plant protection products (pesticides, herbicides).

The main problem with micropollutants is their low adsorption capacity, i.e., many substances pass through the municipal WWTP and end up in the environment. Whilst there are compounds that accumulate, for example, in activated sludge, this again raises problems with the reuse of sewage sludge in agriculture. In the environment, micropollutants reach the water cycle, increasing the concentration of micropollutants in our drinking water over time. However, they have even faster direct impact on surface water organisms, that also end up on our dinner plate.

1.1. Legal incentives for API removal

There will be changes made to the Urban Waste Water Treatment Directive in line with the European Commission's water-related proposals for a zero-emission package in the future. Whilst removing some of the substances at the WWTP would be uneconomical, it is nevertheless proposed to start with post-treatment to reduce the environmental burden from micropollutants. At first, the focus will be on WWTPs of > 100,000 p.e. (population equivalent), which should start with the removal of micropollutants. The proposed requirement is an 80% removal for 6 substances on the list. Later, the same requirement will be applied to WWTPs of > 10,000 p.e or in areas identified as sensitive to pollution with micropollutants, unless Member States demonstrate the absence of risks to the environment or to public health based on a risk assessment. Also, the producer responsibility of pharmaceutical producers, addressed in the *Pharmaceutical Strategy for Europe*, will be increased.

Under the proposed new Urban Waste Water Treatment Directive, water utilities are required to start monitoring the following organic pollutants, including some APIs, and achieve at least 80% removal for 6 of them[1]. Whilst the Directive does not say whether these requirements will be considered as met if

[1]The percentage of removal shall be calculated for at least six substances. The number of substances in category 1 shall be twice the number of substances in category 2. If less than six substances can be measured in sufficient concentration, the competent authority shall designate other substances to calculate the minimum percentage of removal when it is necessary. The average of

the removal is achieved without post-treatment, it is nevertheless assumed that post-treatment will be developed.

Category 1 (substances that can be very easily treated)[2]:

- Amisulpride (CAS No 71675-85-9)
- Carbamazepine* (CAS No 298-46-4)
- Citalopram (CAS No 59729-33-8)
- Clarithromycin* (CAS No 81103-11-9)
- Diclofenac* (CAS No 15307-86-5)
- Hydrochlorothiazide* (CAS No 58-93-5)
- Metoprolol* (CAS No 37350-58-6)
- Venlafaxine* (CAS No 93413-69-5)

Category 2 (substances that can be easily disposed of):

- Benzotriazole (CAS No 95-14-7)
- Candesartan (CAS No 139481-59-7)
- Irbesartan (CAS No 138402-11-6)
- mixture of 4-Methylbenzotriazole (CAS No 29878-31-7) and 6-methyl-benzotriazole (CAS No 136-85-6)

** APIs marked with an asterisk (*) were also investigated at 16 various WWTPs in Latvia and Lithuania as part of the MEDWwater project.*

2. Sampling and analysing micropollutants

the percentages of removal of all substances used in the calculation shall be used in order to assess whether the required 80% minimum percentage of removal has been reached.

[2] Directive of the European Parliament and of the Council concerning urban wastewater treatment (recast). Brussels, 26.10.2022 COM(2022) 541 final ANNEXES 1 to 8.

Micropollutants are already being tested for at WWTPs today, but here are some basics to look out for when sampling. Under the new proposed Urban Waste Water Treatment Directive, micropollutant samples must be taken as follows:

- WWTP of 10,000-49,000 p.e.: 1 sample per month,
- WWTP of > 50,000 p.e.: 2 samples per week.

When sampling micropollutants, it must be taken into account that their concentrations are extremely low, which is why it differs from traditional standardized methodologies. Sadly, today there are no standard methods for sampling micropollutants, but since scientists have been working on this subject for some time, some principles are known that should be followed.

Sampling directly affects the results of the analysis. The results will naturally depend first of all on the type of sampling, whether it is a grab sample or a composite sample, which in turn can be a time-proportional or a flow-proportional composite sample. Here, 24h composite samples (in some cases also 48h and 72h samples, collected as 24h composite samples) rather than grab samples should be preferred. The results are also affected by the sampling instruments used. Some of the micropollutants may be adsorbed to tubes, seals or vessels of automated sampling devices and released again when certain conditions change. This will directly affect the pollutant concentration in the sample. That is why results that are higher than usual must be viewed critically. The concentrations also vary seasonally. In winter, for example, more antibiotics are taken than in summer. Since some of the micropollutants are biodegradable, the reduction in their concentration in the sample should be avoided by filling the sample bottle to the full to avoid excessive aeration, and the sample should be placed immediately in cold, at ca 4° C, freezing of the samples is not recommended.[3,4]

In order to evaluate the micropollutant loads to and the treatment efficiency of the WWTP, samples of influent should be taken preferably from wastewater that has been mechanically treated. This will reduce the proportion of floating and suspended matter that is filtered out during the analysis anyway. At the WWTP without post-treatment, the effluent sample is taken after the final clarifiers. Where post-treatment is available, the samples are taken both after the final clarifiers and after the post-treatment.

[3] Spurenstoffe im Abwasser, eine Handlungsempfehlung for Kommunen, Kompetenzzentrums Spurenstoffe, Oktober 2020.
[4] Möglichkeiten der Elimination von anthropogenen Spurenstoffen, DWA T3/2015, April 2015.

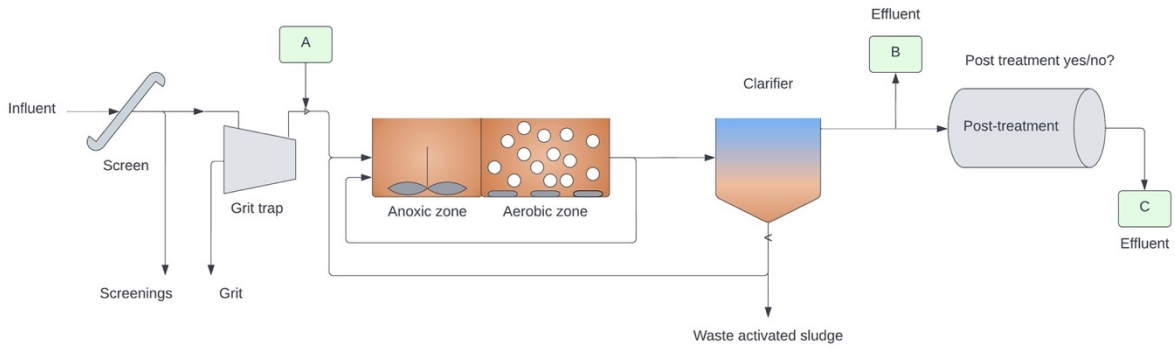

Figure 2. Micro-pollutant sampling points: A - influent, B - effluent and, where post-treatment is available, an additional sample is taken from point C.

As for a sample container, it cannot be avoided that a part of the sample is adsorbed to its walls. However, brown glass bottles, which also reduce the potential degradation of APIs due to light, are best suited for sampling and storage. A plain cap or cap with sealing coated with teflon should be used on the bottle.

The sample can be stored at 4 °C for a short period of time or frozen. When freezing, it should be taken into account that it can affect the API concentrations, because freezing and re-thawing of the sample lead to crystallization processes. If other storage methods are used, such as acidification, it should be taken into account that this also may affect the pollutant concentrations. This particularly affects the adsorption of some of the micropollutants, i.e., the adsorption of micropollutants to the surface of the sampling vessel may increase. Phenols-based acidification, for example, reduces the pH of the sample, which increases the adsorption of some of the APIs. Preservation with biocides, copper salts and sodium azide should be avoided.

Before measuring the micropollutants, the sample often needs to be concentrated. Sample preparation by changing the pH is common. For example, in order to measure diclofenac and ibuprofen, the sample is acidified, carbamazepine and propyphenazone are extracted using, for example, a neutral or alkaline sample. Similarly, matrices that interfere with sample analysis, such as TSS, are removed, which unfortunately can also alter the analytical results.

A large part of the micropollutant concentrations can be measured by chromatography. For this purpose, either gas (GC/MS) or liquid chromatographs (HPLC/MC/MS) are used. Since the results of the samples depend on a large number of factors, it should be taken into account that the variation of the samples exceeding the limit of quantification (LOQ) may be 20-30% and variation of the samples near the LOQ even 50%.

3. APIs in the municipal WWTP

Effluent from WWTPs is one of the important sources of point source pollution of APIs, concentrating both residues of non-prescription medicines and pharmaceutical preparations used in hospitals. However, it certainly cannot be said that WWTPs cause API loads to the environment. Instead, this is one possible point where APIs could be removed. The most appropriate way forward to address this problem would be to stop the use of pharmaceuticals that are hazardous to the environment or replace with those that are less hazardous, but this is not always possible.

In Latvia and Lithuania, APIs at WWTPs have been explored in several projects, in more detail as part of the CWPharma and MEDWwater projects. In addition to influent and effluent loads, API concentrations were also estimated in waste activated sludge, which is important when the sludge is used in the circular economy.

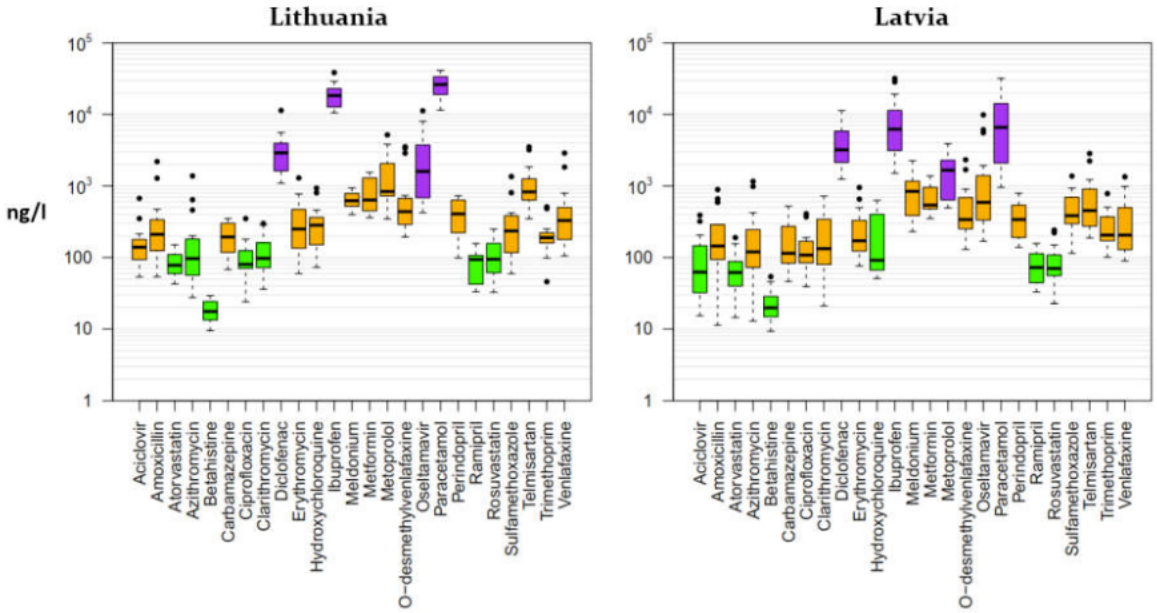

Figure 3. API concentrations measured in the influent of the WWTPs in Lithuania (left) and in Latvia (right). 2 samplings per WWTP at 8 WWTPs per country (n = 16 per country; C < LOQ = LOQ2). Colours highlight different concentration levels with respect to the median concentrations > 1000 ng/l (purple), 100-1000 ng/l (amber), and < 100 ng/l (green).

Figure 3 shows the API concentrations measured at the WWTPs in Latvia and Lithuania (8 WWTPs in each country) as part of the MEDWwater project. The concentrations of 25 different APIs that were analysed, ranged from 10 to 40,000 ng/l. The highest concentrations were found for diclofenac, ibuprofen, and paracetamol (NSAIDs and analgesics), metoprolol, and oseltamivir. The API concentrations overall, however, were found to remain roughly at the same level in both countries. Similar results have been

found also in other countries and as part of other projects, since the guidelines on the use of medicines across the EU are similar. Still, regional differences have been found, for example, in the cities with a number of care facilities and hospitals, where API loads are inevitably higher.[5,6]

3.1. API removal efficiency at municipal WWTPs

Although the WWTPs operated in the Baltics today are not designed to remove APIs, they still succeed in reducing the concentrations of many substances. The extent to which the treatment effect is achieved depends on the biodegradation and sorption properties of the substance. Biodegradable APIs are broken down by microorganisms, while sorbing compounds accumulate in activated sludge. When looking at the API treatment efficiencies achieved at WWTPs, we can mainly point to the following processes:

- stripping: volatile compounds are removed from wastewater during aeration;

- biodegradation: in biodegradation, a distinction is made between two processes. In one case, the microorganisms have the necessary enzymes to break down some of the pollutants and use it for cell construction/energy; in the other case, the organic matter is broken down along with some other compound (e.g., due to the support agent in pharmaceuticals) without special enzymes;

- adsorption to activated sludge/biofilm: many APIs are easily adsorbed due to their surface properties, so the API concentrations in activated substance increase while concentrations in wastewater decrease.

Biodegradation also involves a risk that new transformation products are formed which may affect the environment even more adversely than the original API. So, the existing WWTPs have a hard time with removing APIs, which are not volatile or biodegradable or cannot sorb.

Looking more closely at the various processes of wastewater treatment, such as mechanical treatment, biological treatment and post-treatment to remove TSS and phosphorus, we see that the highest treatment efficiency can be attributed to biological treatment.

[5] Ulvi, A., Aydın, S. & Aydın, M.E. Fate of selected pharmaceuticals in hospital and municipal wastewater effluent: occurrence, removal, and environmental risk assessment. Environ Sci Pollut Res 29, 75609–75625 (2022). https://doi.org/10.1007/s11356-022-21131-y

[6] Takashi Azuma, Natsumi Arima, Ai Tsukada, Satoru Hirami, Rie Matsuoka, Ryogo Moriwake, Hirotaka Ishiuchi, Tomomi Inoyama, Yusuke Teranishi, Misato Yamaoka, Yoshiki Mino, Tetsuya Hayashi, Yoshikazu Fujita, Mikio Masada, Detection of pharmaceuticals and phytochemicals together with their metabolites in hospital effluents in Japan, and their contribution to sewage treatment plant influents, Science of The Total Environment, Volumes 548–549, 2016, Pages 189-197, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2015.12.157.

The API removal efficiency in biological treatment has also been explored in several projects, including the MEDWwater project. However, it is still a challenge to control this process in a targeted manner. Since API concentrations are extremely low, microorganisms rather metabolize them randomly and cannot be assumed to remove APIs in a targeted or optimized way. We now know that the treatment efficiency depends to some extent on the sludge age. The removal in the young sludge is mainly due to adsorption. In the older sludge, at the same time, which is necessary for nitrogen removal, a significantly higher biological removal is already achieved. At the same time, API concentrations in waste activated sludge are also more likely to increase.

Good biodegradation results in activated sludge have been observed for the following APIs[7]:

- ibuprofen at the sludge age of > 2 days;
- bezafibrate (sludge age > 2 days);
- ethinylestradiol (sludge age > 10 days);
- iopromide (X-ray contrast agent, sludge age > 10 days).

However, compounds like carbamazepine and diazepam, are not removed even at the high sludge age, and some treatment efficiencies are only achieved by adsorption.

The use of final filters, such as disc-filters or sand filters, does not particularly affect the API removal. According to various studies, the treatment efficiency has been found to be around 5-15%, but this is also largely due TSS removal and adsorption to filtering media.[7]

The WWTPs analysed as part of the MEDWwater project were found to have the following overall treatment efficiencies, as presented in Figure 4.

[7] Spurenstoffe im Abwasser, eine Handlungsempfehlung for Kommunen, Kompetenzzentrums Spurenstoffe, Oktober 2020.

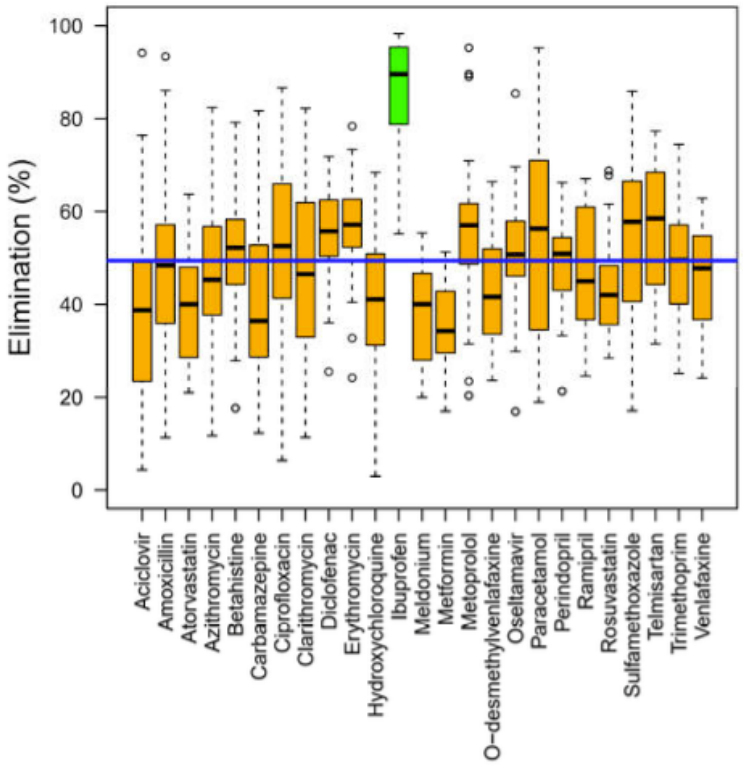

Figure 4. Overall API elimination without distinction between the sampling campaign (summer/winter) and the country (Lithuania/Latvia). 32 data points per API in total (C < LOQ = LOQ). Blue line represents average of the median values.

Figure 4 shows that the median removal rates for all APIs range from 40% to 60% and the average removal is nearly 50%. As part of this project, also the API concentrations in waste activated sludge were estimated and the results suggest that significant API loads actually end up in the sewage sludge. If the sludge is used, for example, in agriculture or as a gardening soil, the API loads can end up in the environment again. It is therefore necessary to consider its whole potential circle when analysing the API routes and selecting treatment technologies. More information about the API concentrations found at the WWTPs in Latvia and Lithuania can be obtained from the MEDWwater reports "*Consultation for selected wastewater treatment plants with suggestions for better treatment of pharmaceuticals"* and *"Data interpretation regarding consumption, WWTPs loads, discharges to water bodies and impact on water environment"*.

Table 1 presents the average API removal rates at the WWTPs analysed as part of the MEDWwater project. The APIs to be reduced by at least 80% in the outflow from the WWTPs, as suggested in the new proposed EU Urban Waste Water Treatment Directive, are highlighted in bold.

Table 1. Average API removal at the WWTPs analysed as part of the MEDWwater project.

API	**Average removal rate at conventional WWTP %**
Acyclovir	40
Amoxicillin	46
Atorvastatin	38
Azithromycin	45
Betahistine	49
Carbamazepine	**41**
Ciprofloxacin	54
Clarithromycin	**48**
Diclofenac	**53**
Erythromycin	56
Hydroxychloroquine	**43**
Ibuprofen	86
Meldonium	37
Metformin	32
Metoprolol	**55**
O-desmethylvenlafaxine	44
Oseltamavir	48
Paracetamol	50
Perindopril	47
Ramipril	44
Rosuvastatin	45
Sulfamethoxazole	54
Telmisartan	52
Trimethoprim	49
Venlafaxine	**44**

4 Planning the technology to remove APIs

An operator of a WWTP, planning to start removing micropollutants, including APIs, should first start from analysing the possible ways of reducing pollution loads from its agglomeration. This can, for example, mean doing a mass balance analysis, mapping out the major sources of pollution, such as hospitals and nursing homes. As the flow rates at the WWTP are hundreds, if not thousands, of times higher than, for example, in hospitals, the investments required to remove APIs at the WWTP are therefore higher. An important advantage of reducing the pollutant concentrations upstream is the reduction of pollutant loads in the sewage sludge, since all types of technological solutions used today at the WWTP remove APIs from the effluent.

Besides upstream analysis, the inflow and outflow of the WWTP need to be monitored. This is necessary to assess the current situation and, consequently, estimate the required treatment efficiency for micropollutants. As a rule, the more source data we have, the more accurately we can design the post-treatment technology. In the absence of earlier micropollutant measurements, the following principles should be applied:

- a minimum of 2 sampling campaigns for the WWTP of < 50,000 p.e.[8];
- a minimum of 3 sampling campaigns for the WWTP of > 50,000 p.e.

During the sampling campaign, it is important that the proportion of non-wastewater (infiltration, stormwater) at the inflow to the WWTP is minimal. For sizing the post-treatment, establishing the highest micropollutant concentrations is crucial.

Also, it is important to establish the hydraulic capacity of the proposed post-treatment during the planning process. A micropollutant removal technology is only feasible when installed for the dry weather flow, not for the maximum flows received at the WWTP. There are different methodologies available for calculating this, but one possible way is to take the flow and precipitation data from the past 3 years and analyse it, by only taking into account flows on days with less than 1 mm of precipitation. Another good analytical methodology is provided in ATV-DVWK-A 198E (*Standardisation and Derivation of Dimensioning Values of Wastewater Facilities*).

[8] One sampling campaign period is a minimum of 1 week, i.e., a total of 7 * 24 h composite samples are taken.

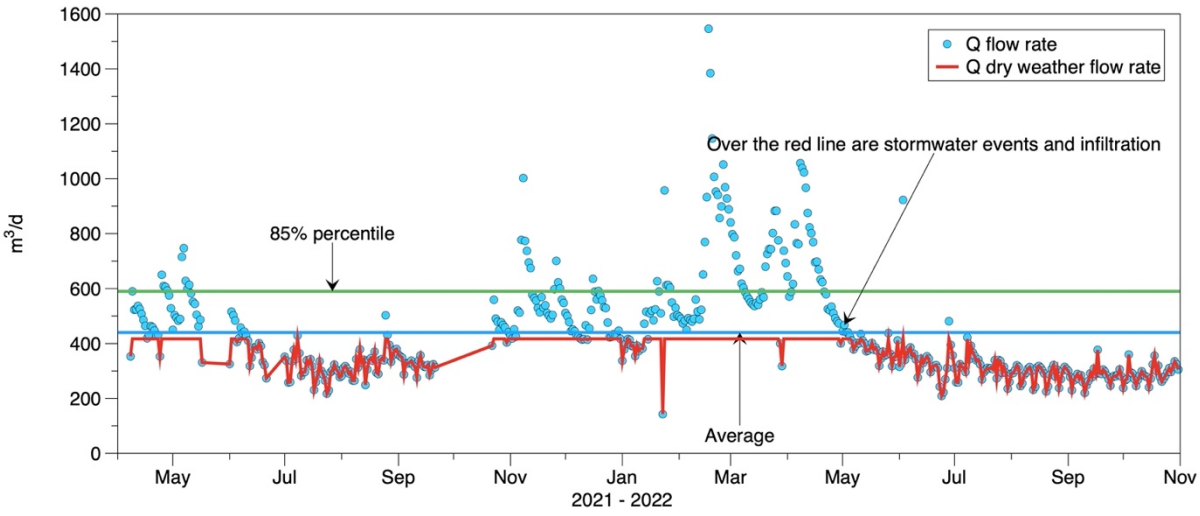

Figure 5. A WWTP flow rate analysis prepared to calculate the hydraulic load underlying the sizing of the post-treatment.

Once the monitoring period is completed, it is time to formulate the targets for the proposed post-treatment, by answering the following questions:

- What are the APIs to be removed?
- What is the expected treatment efficiency?
- What are the hydraulic conditions under which the post-treatment is expected to achieve these treatment efficiencies (at maximum, average, dry weather flows, etc.)?
- Whether the removal rate has to meet the targets set for the expected efficiency at all times, or is the performance of the technology evaluated based on the average annual results?

Once the key questions outlined above have been answered, the next step is to analyse the various technologies to remove micropollutants that are available today. At this point, it is important to find potential synergies with the removal of any other pollutants. For example, ozonation mainly reduces the organic substances, whereas adsorption reduces both heavy metals and APIs, etc. Also, sand filters combined with activated carbon filters help to reduce the TSS and phosphorus loads, but also the API and heavy metal concentrations. If the sewage sludge is to be recovered, it is important to explore the availability of technological solutions to reduce the accumulation of APIs in waste activated sludge. For example, dosing PAC (powdered activated carbon) into the bioreactor will move a large proportion of hazardous substances to activated sludge, so this sludge often has to be incinerated. On the other hand, if the WWTP is incinerating its sludge anyway due to other reasons, then PAC will provide a good, low-cost way of reducing the micropollutant loads. Today, Latvia lacks the possibility of incinerating sewage sludge.

The types of technological solutions considered today to have the highest potential for removing micropollutants are nothing new, but come largely from drinking water treatment. The most common treatment processes include:

- adsorption using activated carbon, either GAC (granular activated carbon) or PAC (powdered activated carbon);
- advanced oxidation, e.g., with ozone or hydrogen peroxide;
- membrane filtration (nanofiltration and reverse osmosis filtration).

Combinations of these technologies are also used. Each of these solutions have their advantages and disadvantages. Sadly, we still lack the best available technology for removing micropollutants. But still, the research and practical experience is enough to find a post-treatment technology suited to remove micropollutants in most cases.

Once a technological solution that suits has been chosen, it must always be piloted because each treatment plant is different, so earlier studies carried out somewhere else cannot be relied on here. Pilot tests can be arranged under laboratory conditions; however, it is recommended that long-term tests be run in a semi-industrial pilot plant to examine the suitability of the selected technology for a minimum of 3 months before the final post-treatment design. This allows enough time to test various operating parameters and opt for the best modes for the given location. Running the pilot tests may seem like a big expense, whereas, in fact, it helps to cut down potentially wrong investment decisions or a missized treatment process that would turn out to be much more expensive in the end.

- when carrying out pilot tests, it is recommended that 24 h composite samples be taken at least 2 times a week. It should be kept in mind that any changes made in the operating modes may not necessarily be seen in the treatment efficiency before several days, or, depending on the process, even several weeks.

After piloting, the design of the actual post-treatment process can be prepared, using the valuable input from the pilot tests. For planning wastewater treatment processes, account should always be taken of possible decrease or increase in hydraulic load, therefore, the processes should be designed as a modular system. That is, if we want to start, for example, with a post-treatment designed for 50,000 m^3/d of wastewater, we will need to set up at least 2 separate treatment lines. That way, when necessary, we can close one of the lines for maintenance or leave it out of operation altogether when the load has dropped. At the same time, we will also leave some room in the plan for a possible extension, i.e., the third treatment line, should the hydraulic load increase.

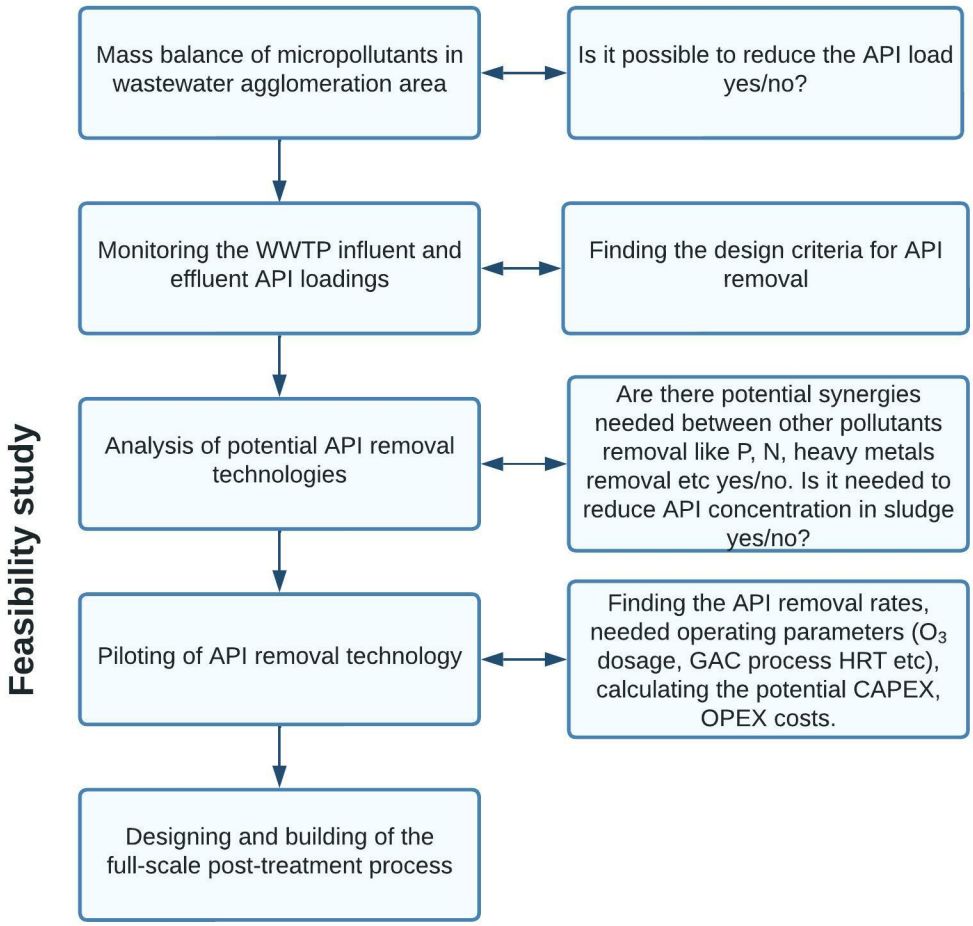

Figure 6. The process of selecting post-treatment technology with emphasis on API removal, while analysing also potential synergies with the treatment of any other pollutants using the same or combined types of solutions.

4.1 Selecting the post-treatment technology

In most cases, both ozonation and activated carbon adsorption can successfully remove > 80% of micropollutants. An exact removal efficiency, however, needs to be established with pilot tests. For example, ozonation has been found to reduce the concentration of micropollutants by 50-65% on average, but to a certain degree, removal is also achieved by conventional biological treatment, so the average removal rate when combined is expected to be 80-90% at the ozone doses that range from 0.4 to 0.7 mgO_3/mgDOC. The ozone dosage depends not only on the DOC concentration but also, for example, on the concentration of NO_2-N oxidised to NO_3-N. Like with ozone, DOC should, in addition to filtering parameters, be used also for sizing the activated carbon process, since by now, quite a lot of data has been gathered on the efficiency of micropollutant removal, depending on DOC.

The removal rates for various APIs when using ozone and activated carbon are compared in Table 2. Here, the removal capacity of the activated sludge process has not been taken into account. [9, 10,11] As presented in the table, most of the APIs behave similarly in both processes and in most cases, a > 70% removal efficiency can be achieved. For substances that are hard to remove, combination of various processes may be required, such as pre-ozonation followed by activated carbon adsorption. An exact need shall be established with pilot tests.

Table 2. Removal efficiency for various APIs when using ozone and activated carbon.[10,11,12]

API	Ozone	Activated carbon
Carbamazepine	very good - good (> 70%)	
Amoxicillin		
Clarithromycin		
Diclofenac		
Ibuprofen		
Hydroxychloroquine		
Metoprolol		
Venlafaxine		
Tramadol	poor-medium 30-70%	good - very good > 70%
Azithromycin		
Benzotriazole	good - very good > 70%	poor-medium 30-70%
Irbesartan		
Candesartan		
Olmesartan	poor-medium 30-70%	
Sulfamethoxazole		
Valsartan		
Valsartan Acid		

[9]Möglichkeiten der Elimination von anthropogenen Spurenstoffen, DWA T3/2015, April 2015.

[10]Aktivkohleeinsatz auf kommunalen Kläranlagen zur Spurenstoffentfernung, Verfahrensvarianten, Reiningungsleistung und betriebliche Aspekte, DWA T1/2019, Mai 2019.

[11]Einsatz der Ozonung zur Spurenstoffentfernung auf kommunalen Kläranlagen – Erfahrungen, verfahrens- technische Aspekte und offene Fragen, DWA T2/2022, November 2022.

Further, Table 3 separately illustrates the sorption properties of various APIs.[10,12] Good removal rates when using activated carbon are guaranteed for all APIs, except gabapentin and metformin. All the micropollutants suggested in the EU Urban Waste Water Treatment Directive are also easily removed when using the activated carbon process.

Table 3. Sorption properties of APIs when using activated carbon.

Very good/good	**Good-poor**	**Barely or nothing**
Azithromycin	Candesartan	Gabapentin
Carbamazepine	4-Formylaminoantipyrin	Metformin
Ciprofloxacin	Guanylurea	
Clarithromycin	Ibuprofen	
Diclofenac	Sulfamethoxazole	
Ibuprofen	Valsartan	
Erythromycin		
Hydroxychloroquine		
Metoprolol		
Venlafaxine		

When using ozonation, consideration should be given to the potential formation of transformation products in case of a number of APIs. In certain cases, the ecotoxicological effects of these transformation products may be much greater than those of the original API. Some examples of APIs that may end up forming transformation products during ozonation include:

- acyclovir;
- acesulfame;
- amoxicillin;
- carbamazepine;
- ciprofloxacin;
- diclofenac;
- metoprolol;
- sulfamethoxazole;
- tramadol
- penicillins;
- cephalexin;

- venlafaxine.

Most of the transformation products are easily removed with sufficient residence time and ozone dose. A number of studies have demonstrated that ozone improves the biological removal of APIs. However, with the exception of tramadol, venlafaxine, metoprolol and ciprofloxacin, which are more difficult to remove than the original APIs.[12], [13]

5 Activated carbon process

Adsorption is a process where the substance to be removed is separated from the water phase and concentrates on the surface of the adsorbent due to physical forces. Adsorption with activated carbon has become one of the most important methods used for removing micropollutants, such as heavy metals and APIs, from wastewater and drinking water. It is also widely used for separating COD that is not readily biodegradable. Earlier experience has shown that the adsorption process is characterised by low operating costs and high treatment efficiency, making it one of the best possible future solutions that can be used for removing micropollutants also at WWTPs. However, adsorption is difficult to use due to its sensitivity to temperature and pH, as it is an equilibrium process where the micropollutants bound can be released again when the point of equilibrium changes. It should also be borne in mind that in wastewater, the micropollutants are present in very low concentrations, while other organic substances, for example, COD, come in high concentrations. In the adsorption process, these two will be competing with each other. The efficiency of adsorption can be improved by selecting the right adsorbent, residence time, etc.

Activated carbon is a form of carbon that has been treated in such a way as to make the material as porous as possible. This is achieved by heating the material to 1000 °C in an oxygen-free environment, while the organic matter in the pores is incinerated and the pores are subsequently cleaned by water vapour. Activated carbon is typically produced from biomass, such as wood, coconut shells, lignite or coal, but scientists keep looking for new materials to produce good absorbent at low cost and high efficiency. The good adsorption properties of activated carbon are mainly due to its large specific surface area, which can even range from 500 to 1,500 m^2/g. Although adsorption to activated carbon is a physical process and there are no chemical bonds, the bond created is very strong. There are mainly two types of activated carbon in use: powdered activated carbon (PAC) and granular activated carbon (GAC). PAC is typically

[12] Einsatz der Ozonung zur Spurenstoffentfernung auf kommunalen Kläranlagen – Erfahrungen, verfahrens- technische Aspekte und offene Fragen, DWA T2/2022, November 2022.

[13] Stapf, M., Miehe, U., Knoche, F., Lukas, M., Bartz, J., Brauer, F., Gutsche, M., Kullwatz, J., Petkow, C., Schneider, M., Winckelmann, D., Bogusz, A., Tomczyk, B., Trzcińska, M., Dworak, A., Chojniak-Gronek, J., Szumska, M., Zieliński, M., Walkowiak, R., Putna-Nimane, I., Liepina-Leimane, I., Dzintare, L., Barda, I., Bester, K., Kharel, S., Sehlén, R., Nilsson J., Larsen, S. B. (2020). Impact of ozonation and post-treatment on ecotoxicological endpoints, water quality, APIs and transformation products. CWPharma project report for GoA3.3: Comparison of post-treatment options.

produced by grinding GAC and it has a larger specific surface area than GAC. Since it takes 2-5 kg of source material to produce 1 kg of activated carbon, preference should be given to activated carbon produced from renewable materials, such as wood, coconut shells, etc.

PAC is a powdered activated carbon which is sometimes also used to remove various hazardous substances. The PAC particle size is typically between 0.005 and 0.1 mm, so it has a larger specific surface area than GAC, i.e., making PAC more efficient at adsorbing most of the substances than GAC that comes in larger particles. The GAC particle size is typically between 0.5 mm and 2.5 mm.

Table 4. Advantages and disadvantages of various types of activated carbon.

	Granular activated carbon GAC	**Powdered activated carbon PAC**
Advantages	- easy to operate; - low-maintenance; - no possible release of activated carbon particles to the effluent; - additional removal of TSS, incl. particular phosphorus; - GAS can be regenerated; - can be operated efficiently, i.e., using the adsorption capacity of GAC to the full.	- relatively low cost of PAC; - easy dosage and control; - no additional PAC separation devices required when dosing directly into activated sludge process; - rapid adsorption due to the small size of PAC particles; - hazardous substances regularly removed with waste activated sludge, making them less likely to release.
Disadvantages	- high investment costs; - slower adsorption due to the size of GAC particles; - in certain cases, the pollutants removed can be released again.	- PAC cannot be regenerated; - the adsorption capacity often not used to the full, since PAC is removed with waste activated sludge; - activated carbon particles, carried out of the process, are released to the effluent; - where PAC is dosed into activated sludge, the reuse of waste activated sludge in agriculture must usually be avoided; - where PAC is dosed after the final clarifiers, large investments are required to establish the PAC separation; - generating ca 4-10% more waste activated sludge.

5.1 Planning the PAC treatment

PAC is widely used because of its simplicity. Where sewage sludge is further incinerated, all that needs to be addressed is the question of how to store and dose PAC, and dosing is done directly into the existing activated sludge process. However, where PAC is used as a post-treatment, a number of problems arise that need to be addressed, because PAC particles are extremely small, making them hard to remove from the effluent. To this end, coagulant must be added before settling/filtration to coagulate small PAC particles into particles that can be settled and filtered out. Without the coagulant, some of the particles could pass through microfilters and sand filters.

Although this guidance material sets out a number of parameters underlying the sizing of the PAC treatment, also the pilot tests should be conducted, because the behaviour of the activated carbon depends on the specific wastewater. Pilot tests should run for at least 3 months to find an optimum dosage, which will serve as the basis for planning the dosing equipment and PAC storage place.

The dosing of PAC into the existing activated sludge process, as illustrated in Figure 7, is a simple and low-cost solution, but less efficient in removing micropollutants than dosing after the sludge process. This is because the adsorption capacity is spent on removing the organic matter that comes at higher concentrations. The advantage, however, is the residence time of the activated carbon in the process which equals to the age of sludge, so that the adsorption capacity can be used to the full. However, PAC dosing results in a 4-10% increase in waste activated sludge. Therefore, the concentration of biomass in the activated sludge process will increase. So, if we continue to operate at the same activated sludge concentration, our actual sludge age will be lower. But so far, the lower age of sludge due to PAC dosing has not been found to have any negative impact on the efficiency of the biological treatment. Plus, earlier research has found that using PAC increases the calorific value of waste activated sludge that is incinerated. A similar technological layout is presented in Figure 8, but here, a final filtration is used to remove all TSS containing PAC, i.e., hazardous compounds.

Sadly, there are no specific principles for sizing when PAC is to be dosed directly into the bioreactor, but experience so far has shown that the doses required to remove micropollutants range from 10 to 30 mg/l.

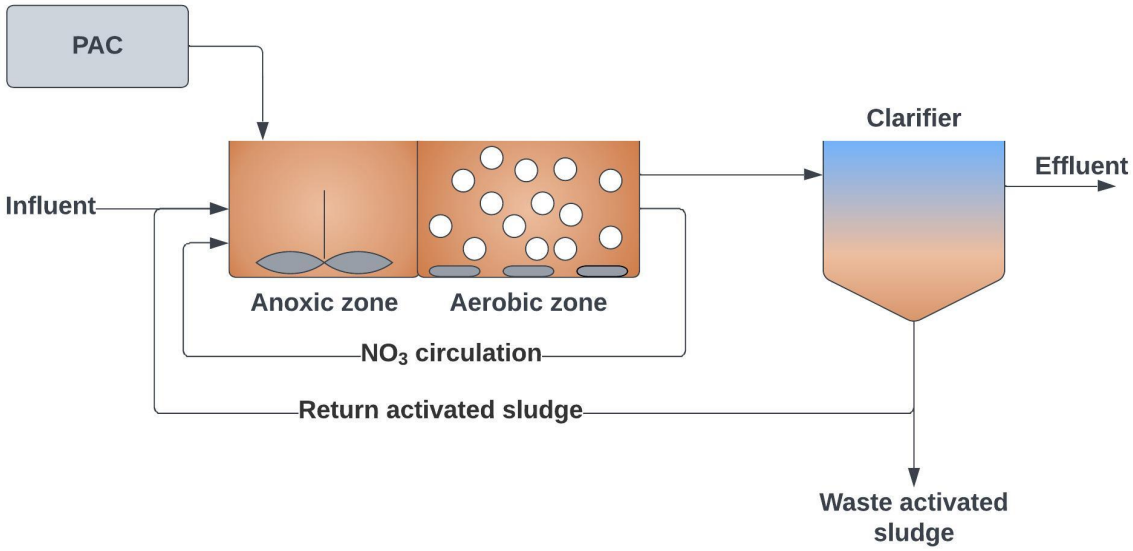

Figure 7. Dosing of PAC directly into the existing activated sludge process. Micropollutants are removed with waste activated sludge.

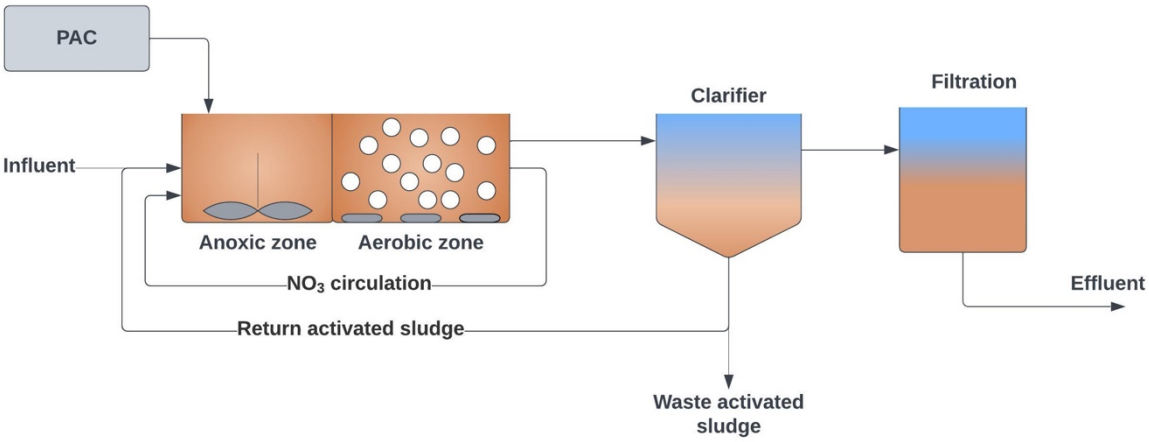

Figure 8. Dosing of PAC directly into the existing activated sludge process. Final filters remove the residues of TSS, which contain also small concentrations of PAC that has adsorbed the micropollutants.

The most efficient method is to dose PAC after the existing treatment process. This ensures that most of the biodegradable organic matter has been removed and the number of substances competing with micropollutants is minimum. Typical process flowchart is presented in Figure 9. In the contact reactor, PAC is provided with sufficient contact time and at the end of the reactor, coagulant is dosed, allowing to remove most of the PAC from the clarifiers. Where waste activated sludge is later incinerated, PAC can be returned to the treatment process (both from the clarifiers and from the filters), where it is later removed along with waste activated sludge. Where waste activated sludge is later recovered, the

removed PAC should be processed separately to reduce the micropollutant concentrations in the sludge. The final filtration is required to remove all TSS, containing PAC with the micropollutants.

For sizing, the following principles should be applied (apply for Figure 9):

- in order to achieve the > 80% micropollutants removal, the PAC dose should be 10-25 mg/l, or, depending on the DOC concentration, 1-2 mgPAC/mgDOC;
- ensure minimum residence time of 30-60 min in the contact reactor, as well as circulation between the clarifiers and the contact reactor, since it takes more than 24 h to use the PAC adsorption capacity to the full;
- parameters for the final clarifiers following the contact reactor: surface loading < 2 m/h, residence time min 2 h;
- add coagulant to remove PAC, coagulant consumption is approx. 0.2-0.5 mg/l for Al and 0.5-1 mg/l for Fe;
- with a sand filter, the maximum filtration rate should be 10-12 m/h, and the filter should have at least one layer of anthracite (1.2-2.5 mm) and one layer of sand (0.65-1.3 mm).

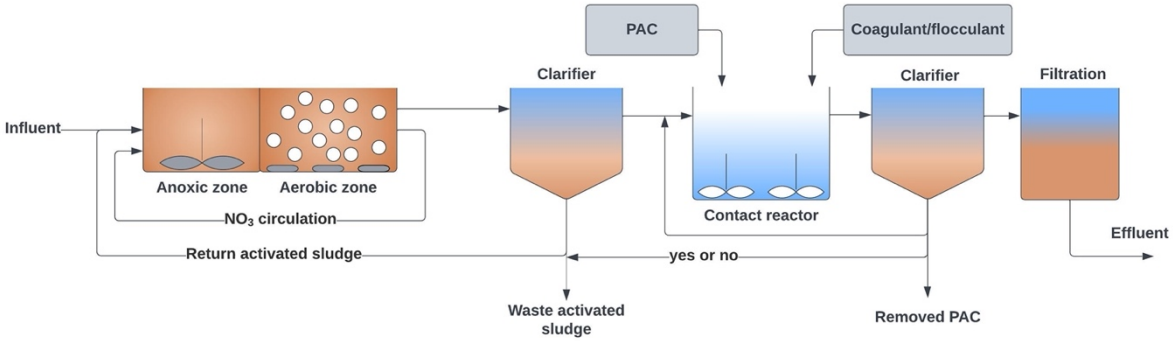

Figure 9. Dosing of PAC into the post-treatment. PAC is dosed into the contact reactor and later bound to coagulant.

Figure 10 illustrates a type of solution for PAC dosing where PAC is dosed after the existing final clarifiers, but the process lacks a contact reactor because it is combined with a filter. As a result, PAC particles get deep into the filtering media (such as sand), forming a so-called combined system of activated carbon/sand filter. In addition, coagulant is dosed along with PAC to form larger PAC particles, or otherwise, some of PAC would pass through the filter. At the top of the filter, a contact reactor is created where the coagulant + PAC react and the micropollutants are adsorbed at the same time.

Based on the experience gained so far, the following principles should be applied for sizing this type of solution:

- residence time at the top of the filter (so-called flocculation chamber) 14-30 min, total residence time in the filter 30-50 min;
- maximum filtration rate 14 m/h;
- PAC dose of 5-20 mg/l depending on the expected treatment efficiency (at least 10 mg/l of PAC where an > 80% micropollutants removal is expected).

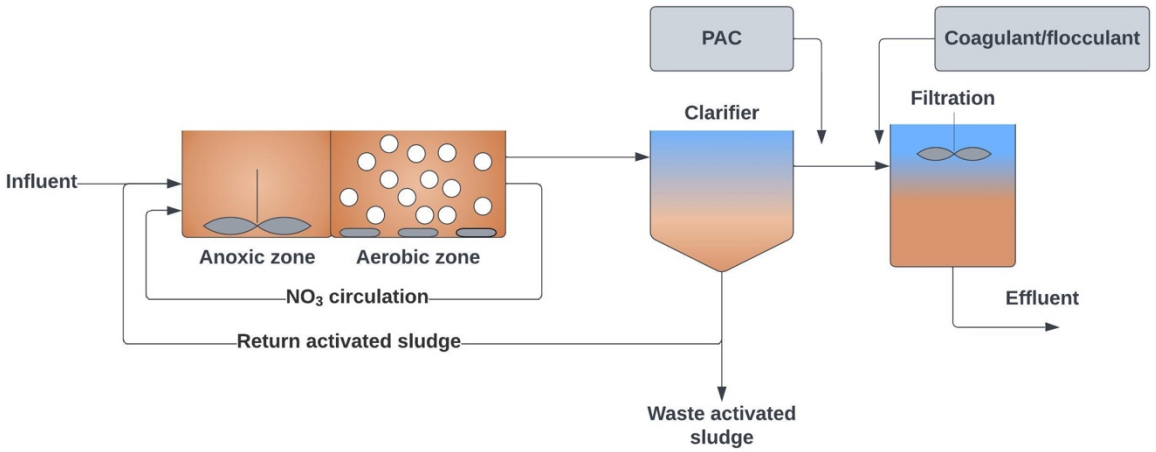

Figure 10. Dosing of PAC after the final clarifiers.

5.1.1 PAC storage

PAC is transported to WWTPs in 'big bags' or, in the case of larger quantities, in tank trucks. In order to facilitate dosing, it is stored in silos, where the potential explosion hazard caused by PAC dust must be taken into account. The expansion of PAC under different conditions must also be taken into account during transport and storage. For dosing, screw conveyors are used or mixing with water and pumping the mixture to the WWTP.

5.1.2 Further handling of PAC

Due to the size of its particles, PAC cannot be regenerated and therefore, PAC containing micropollutants has to be removed from the WWTP and incinerated. As far as we know today, no re-release of micropollutants has been observed from PAC, for example, in waste activated sludge pumped to digesters for stabilisation. If there is no such incineration plant, it is necessary to analyze whether or not the application of this technology is feasible. An alternative is to use regional incineration plants, but it would still lead to high transport costs. This is to say that the comparison of various micro-pollutant

removal technologies must include all necessary processes, including possible transport costs, the construction and operation of an incineration plant, etc.

5.2 Planning the GAC treatment

The GAC filters are most frequently used to remove micropollutants. This is because, unlike PAC, there is no need to tackle the issue of capturing the adsorbent. Two types of GAC filters are mainly known: rapid pressure filters and rapid gravity filters. Pressure filters have already been used for a long time as a pre-treatment option in drinking water treatment and in industrial sector. At the same time, there are still relatively few examples of pressure filters being used at WWTPs. The WWTPs rather tend to prefer open filters for their capacity to treat higher concentrations of TSS. Additionally, in adsorption, the residence time plays an important role, and the residence time in gravity filters is longer.

Figure 11 illustrates a simplified technological layout for integrating the GAC filter to remove micropollutants. In most cases, it is recommended that an additional filtration be established before the adsorption to remove/reduce TSS in wastewater. In certain cases, this process can be combined in a single filter where TSS removal is achieved with layers of different filtering media. Here, particular attention should be paid to the sizing of the filter, as it is extremely difficult to ensure proper backwash with water and air when using different media, without lighter filtering media being washed out.

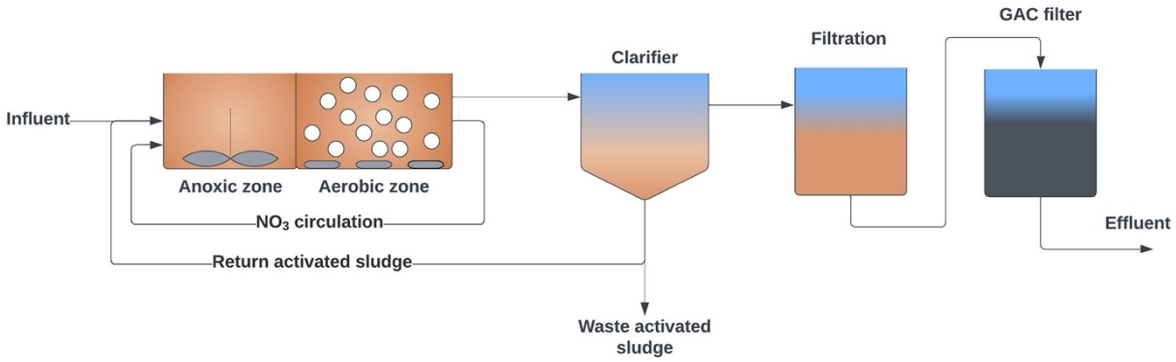

Figure 11. Using the GAC filter to remove micropollutants. The filter before GAC is optional and depends on the local circumstances (e.g., how much of TSS is carried out from the final clarifiers).

Like with a PAC filter, it is important to run pilot tests for a minimum of 3 months for planning the GAC process, allowing to establish the required residence time, wash cycles and adsorption capacity of the process. This is best done on a semi-industrial pilot test device, as illustrated in Figure 12. The pilot tests will reveal any potential problems that are hard to discover during theoretical planning process. For planning the GAC filters, it is also important to analyse the TSS removal efficiencies of the WWTP for the past 2-3 years. This is because piloting can run into a period where, for example, the properties and settling of the activated sludge is good, so the sludge is not carried out of the process. Whereas, at the

time of the test illustrated in Figure 12, the seasonal deterioration of the sludge properties, characteristic to autumn, had just begun, resulting in a shortening of the filter run by almost 3 times. Additionally, this given test period saw the carry out of algae from the final clarifiers, which also caused clogging of the filter. Therefore, it is crucial that the local circumstances are examined and, if necessary, solutions are worked out to protect the GAC filter, by means such as disk or sand filters.

Figure 12. Test device set up as part of the BEST (Better Efficiency for Industrial Sewage Treatment) project funded under INTERREG Baltic Sea Region Programme. The configuration in the picture consists of the sand filter combined with GAC.

In addition, when using GAC, it should be taken into account that due to its large specific surface area, it gets covered with biofilm, increasing the biodegradation of dissolved micropollutants and the adsorption of insoluble particles. This is a process called biological activated carbon filtration (BAC). In certain cases, this biological activity is considered to help in keeping the GAC pores open, as microorganisms gradually break down the organic matter accumulating on pores, provided that the backwash is carried out with air and water, ensuring sufficient oxygen for aerobic processes. However, due to too intense biological growth, all adsorption capacity may also be lost.

The GAC process is often combined with ozonation in order to remove organic matter that is not readily degradable. This is important because ozonation can produce transformation products, which can

pose even more hazard than the original substance. However, the original substance may not become taken up by adsorption before ozonation, whereas during ozonation, it is broken down into smaller compounds that can be removed, for example, by means of a GAC filter. For pre-ozonation and final filtration with GAC, a relatively low ozone dose of ca 0.2 mgO_3/mgDOC can be used to remove micropollutants, whereas for ozonation only, for comparison, doses ranging from 0.3 to 0.9 mgO_3/mgDOC should be considered.

For sizing the GAC filters, the most important parameters are the empty bed contact time (EBCT, min) and the bed volume treated (BV, no unit). To calculate EBCT, the average flow per minute (Q_{av}, m^3/min) and the cross-sectional area of the filter (A_{filter}, m^2) are used, whereas for calculating the cross-sectional area, it is also important to consider the height of the filter h_{GAC}. BV is calculated based on the total amount of wastewater treated by the filter $Q_{treated}$, divided by the volume of the filter ($V_{GAC,}$ m^3).

$$EBCT = \frac{h_{GAC} * A_{filter}}{Q_{av}}, min$$

$$BV = \frac{V_{treated}}{V_{GAC}}$$

For sizing the GAC filter, the following principles should be applied:

- residence time (EBCT) in the GAC filter > 20 min;
- filtering rate 4-7 m/h;
- height of the filter bed 1.5-3 m, the total height of the filter must also allow for filter media expansion by 20-30% during the backwash;
- suited GAC depends on the TSS concentrations: the higher the TSS concentrations at the inflow to the filter, the bigger the GAC fraction should be;
- size of the filter nozzles should be chosen so as to ensure they are not clogged by GAC.

GAC fractions, suited for the TSS concentrations at the inflow to the filter:

- GAC 1.2-2.4 mm for TSS > 10 mg/l;
- GAC 0.8-2 mm for TSS 5-10 mg/l;
- GAC 0.6-2.4 mm for TSS < 5 mg/l.

Where the WWTP already has a sand filter in place for the post-treatment, the contents of that filter can be replaced with GAC. The traditional sand filter is made of layers of gravel, sand and anthracite, and in many cases, all these layers can be partially or fully replaced with activated carbon. Just the backwash intensity and other operating parameters must be adjusted to fit the activated carbon.

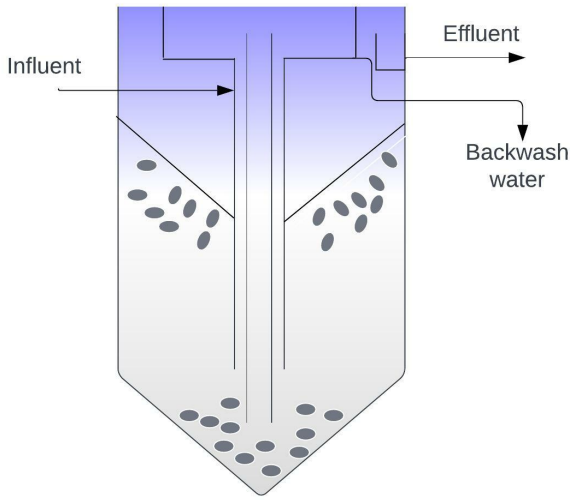

Figure 13. Simplified GAC moving bed reactor.

Figure 13 illustrates a simplified GAC moving bed reactor. Although relatively little is known about this technology today, it is seen as having a potential to remove micropollutants. The same technology is also used with sand to reduce the TSS concentrations, and, depending on the configuration, also for biological treatment to remove, for example, nitrogen and phosphorus. For the micropollutants removal, pre-wetted GAC is dosed at the inflow to the filter for example once a day. The filtration rate of the filter is 7-15 m/h. The required GAC dose is approximately 2 mgGAC/mgDOC. Some of GAC is removed once a week from the bottom of the reactor. Depending on local circumstances, this reactor is sought to operate with GAC aged on average 80-100 days.

5.2.1 GAC regeneration

However, depending on the proposed amount of GAC in the filter, its adsorption capacity will at some point reach its limit where sufficient removal of micropollutants is no longer ensured. At this point, the activated carbon must be replaced or regenerated. At the time of this study, it was not possible to establish any companies operating in Estonia, Latvia or Lithuania performing the regeneration of spent carbon.

Put simply, the regeneration process consists of the following steps:

- drying of GAC at up to 400° C, where desorption, i.e., release of removed micropollutants, is performed;

- pyrolysis at ca 800° C, where compounds that were not released by desorption, are broken down and removed from the surface of GAC by means of pyrolysis gas;

- treating of GAC with water vapour.

Whilst the GAC regeneration is an energy-intensive process, it still comes at lower cost and has sufficient quality to compete with virgin GAC, provided that it can be performed locally. However, transport costs may play a decisive role if GAC has to be transported to another country for regeneration.

5.3 Activated carbon process control

Activated carbon process can be controlled and optimized using various parameters. The most common indicators include:

- UV_{254} online measurements, is correlated to DOC;
- DOC online measurements;
- turbidity measurements;
- TSS measurements.

Although the micropollutants removal efficiency cannot be measured directly online, DOC provides a good indicator. In time, once some data on the actual micropollutants removal have been collected, the link can be established between DOC and the micropollutants under local circumstances, allowing to control the process accordingly. Excessive turbidity and TSS clog the filters, so it is used, if necessary, to bypass the activated carbon filter when the wastewater has too high TSS concentrations.

6 Ozonation

Ozone is a very powerful oxidizer that has long been used in drinking water treatment to improve the properties of water. It is mainly used to remove organic matter causing taste and smell. Ozone also plays an important role in the wastewater treatment, mainly in the pre-treatment of industrial wastewater, where COD, which is not readily degradable, is oxidised so it becomes biodegradable. Ozone is a blue, unstable, poisonous gas with a pungent odour. Ozone is heavier than air, so it can easily accumulate in working areas. However, due to its high reactivity, ozone decays relatively quickly and must be produced onsite.

Ozone has an important role in advanced treatment, where it is applied both for the removal of organic matter that is not readily biodegradable, and for the oxidation of APIs into less hazardous compounds. The consumption or dose of ozone is affected by the various pollutants present in wastewater, such as:

- dissolved organic carbon (DOC) – indicates the concentration of dissolved organic matter that also contains, for example, APIs. During ozonation, this organic matter is broken down along with APIs, so the higher the DOC value, the more ozone it takes to remove APIs;

- chemical oxygen demand (COD) – indicates the amount of oxygen consumed to oxidize the organic and inorganic matter. Ozonation reduces COD by 12-17%; where ozonation is followed by the biological treatment, even by 20-40%;

- nitrite (NO_2) – during ozonation, NO_2 is oxidised into NO_3 and this will use ca 3.43 mgO_3/mg-N;

- suspended solids (total solids, TSS) – high TSS concentrations require higher doses of ozone, since higher TSS means increase in the organic matter content;

- bromide – bromide-ozone reaction produces bromate, which is even more hazardous to the environment than APIs. Therefore, bromide concentrations need to be measured, especially in coastal settlements, before opting for ozone technology. Ozonation should not be used where the bromide concentrations are higher than 0.15 mg/l and the required ozone doses exceed 0.7 mgO_3/mgDOC. Where the bromide concentrations are higher than 0.15 mg/l at the outflow from the WWTP, the pilot tests should be conducted to establish the degree of the bromate formation and to estimate its potential impact on the receiving waters.

Figure 14 illustrates the most common technological layout for the use of ozonation to remove micropollutants. The most commonly used method involves producing ozone from the liquid oxygen (LOX). LOX is fed to an ozone generator, producing O_3 which is then fed to a contact reactor, where it starts to break down the organic matter. Since the residual ozone poses a hazard to the environment and to man, it must be collected and destructed into oxygen again. Due to the potential formation of transformation products, ozonation should always be followed by filtration. For example, in many cases, the biofilm forming in a sand filter and the microorganisms that live in it, are able to bind and break down the transformation products. The safest combination would include the ozonation and the activated carbon filter.

There are also ozone generators that produce O_3 from air. At this point, however, we have to consider higher electricity costs. Whilst producing ozone from LOX takes 8-10 kWh/kg, it takes 12-18 kWh/kg to produce ozone from air. In addition, air requires pre-treatment, i.e., purification and drying. However, in smaller WWTPs, and where the company is reluctant to use LOX due to more stringent occupational safety requirements, producing ozone from air provides a good, simple type of technological solution.

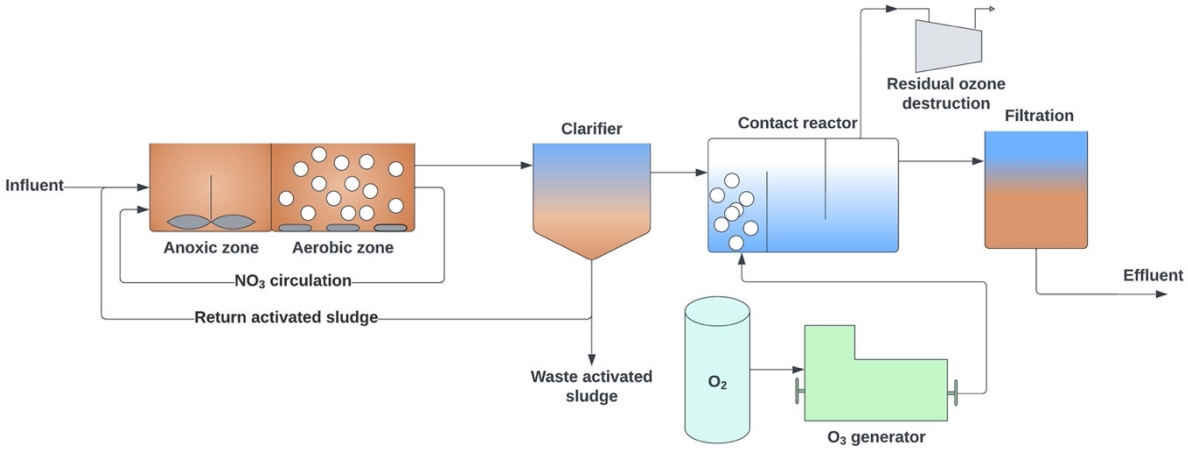

Figure 14. Removal of micropollutants at the WWTP by applying ozonation.

6.1 Planning the ozonation to remove micropollutants

The technological questions that need to be addressed when establishing the ozonation are, broadly speaking, the following:

- whether ozone is to be produced from LOX or air;
- how and where to dose ozone;
- what should be the size of the contact reactor;
- what is the required capacity of the ozone destructor;
- how to remove the transformation products produced during ozonation.

During ozonation, transformation products are formed and organic matter that is not readily degradable can become readily biodegradable, which is why the ozonation also results in an increase in BOD (by even more than 100%). It is therefore required that a biological filter, such as a sand filter, or ideally, an activated carbon filter, working as a BAC (biological activated carbon filter), be installed after the ozonation.

For sizing the process, the following principles should be applied:

- run the pilot tests to establish the required ozone dose; for the micropollutants removal, doses range from 0.3 to 0.9 $mgO_3/mgDOC$;
- select a water-cooled ozone generator, the required capacity of which is also established in pilot tests. In practice, it is possible to produce a maximum of 150-190 g/m^3 of ozone from oxygen and 30-60 g/m^3 of ozone from air;

- ozone dose control should be automated;
- select the storage tank suited for storing LOX, where the ozone is to be produced from liquid oxygen. The required frequency of supply depends on the size of the storage tank, so first, you need to establish the details concerning the required ozone generator;

- plan the contact reactor with the residence time of 15-30 min and select ozone dosing diffusers, taking into account the depth of the contact reactor. Most commonly, ceramic diffusers are used. Ozone can also be dosed before the contact reactor by means of an injector followed by a static mixer;

- select the catalytic ozone destructor, depending on the ozone dose and the proposed ventilation;

- ozone poses a hazard to the environment and to man, so all existing environmental and occupational safety requirements must be followed when using it.

Since the removal of micropollutants directly depends on the ozone dose, automated control is crucial. As the online measurement of micropollutants is not possible yet, so instead, sum parameters or simplified parameters found by research and the links between those are used. One of the parameters in common use is UVA254 adsorption, which is used to estimate the DOC concentrations. However, today, there are also DOC online sensors available, so linking DOC to ozonation is made even easier.

The installation site for an ozone generator should be selected according to the following criteria:[14, 15]

- the room temperature should not exceed 30 °C and the air humidity 60%;

- the room should be as dust-free as possible;

- there should be no other oxidizing substances present in the room (such as coagulants, etc.);

- ozone-resistant materials must be used in construction;

- the residual ozone must be removed from the effluent prior to discharge, the maximum allowed ozone concentration is 0.02 mg/m^3.

Ozone is a gas that poses a hazard to human health and therefore, proper occupational safety methods are extremely important. The effects of ozone appear first in the mucous membranes of the eyes, nose and lungs. Staying longer in rooms where ozone concentrations exceed 0.2 mg/m^3 causes a

[14] Desinfektion von biologisch gereinigtem Abwasser, ATV M 205, 1998, ISBN 3-927729-75-2.
[15] Einsatz der Ozonung zur Spurenstoffentfernung auf kommunalen Kläranlagen – Erfahrungen, verfahrens- technische Aspekte und offene Fragen, DWA T2/2022, November 2022.

coughing fit. From 4 mg/m^3, typical signs of poisoning may be expected, and in rooms where ozone concentrations exceed 20 mg/m^3, a person may die. The following should therefore be considered [13,14]:

- maximum permitted ozone concentration in rooms is 0.2 mg/m^3;
- ventilating the rooms must be possible without entering the room;
- rooms where ozone pollution can occur must be equipped with appropriate hazard alarms;
- ozone equipment can be operated only by professionals who are aware of the hazards and competent to operate the equipment.

For example, DWA rule book T2/2022 *Einsatz der Ozonung zur Spurenstoffentfernung auf kommunalen Kläranlagen – Erfahrungen, Verfahrens-Technische aspects und Offene Fragen* can be used for planning the ozonation aimed at both disinfection and API removal.

6.2 API removal using ozone

The efficiency of ozone in API removal depends on a number of factors. Since ozonation follows the biological treatment, which varies considerably between day and night and is relatively unstable as a whole, we cannot expect the micropollutants removal rates to be stable when the ozone doses remain unchanged. These are the factors that have the greatest impact on the micropollutants removal:

- dissolved organic matter concentration (DOC);
- alkalinity;
- pH value;
- NO_2 concentration; and
- concentrations of any other compounds consuming ozone.

High removal efficiencies can be expected for the following APIs (at pH 7): ethinylestradiol, sulfamethoxazole, clarithromycin, estrone, clindamycin, estradiol, erythromycin, nonylphenol, roxithromycin, trimethoprim, and diclofenac. More than 90% of these APIs are broken down at specific ozone doses of > 0.4 mgO_3/mgDOC because their removal is due to a direct reaction to ozone.

Average removal efficiencies can be expected for acesulfame, bezafibrate, atenolol, gabapentin, isoproturon, mecoprop, metoprolol, and sotalol. The removal of these APIs occurs both as a direct result of ozonation and due to the OH radicals formed. The required specific ozone doses for these APIs need to be established in pilot tests, but range from 0.4 to 1 mgO_3/mgDOC.

The ozone dose for the removal of APIs and other organic matter is established taking into account the concentrations of DOC and NO_2. This is one possible approach:[16]

$D_{dim} = (D_{DOC} \times C_{DOC} + 3.43 \times C_{Nitrit})$

where D_{dim} = required ozone dose mgO_3/l;

D_{DOC} = DOC-specific ozone dose mg/l, typically 0.3-0.9 $mgO_3/mgDOC$;

C_{DOC} = DOC concentration mg/l;

C_{Nitrit} = nitrite concentration mg/l.

Figure 15 provides some indication of the ozone doses required to remove APIs. As we can see, the higher the ozone dose per DOC, the higher the removal efficiency. However, higher doses also mean higher operating costs. Therefore, pilot tests should always be run when planning the ozonation.

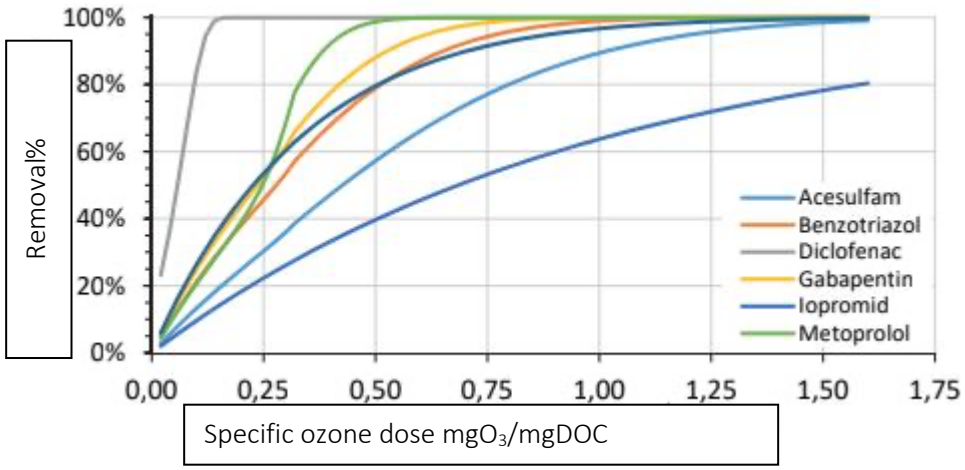

Figure 15. Specific ozone doses to remove certain APIs. (DWA rule book T2/2022 "Einsatz der Ozonung zur Spurenstoffentfernung auf kommunalen Kläranlagen — Erfahrungen, Verfahrens-Technische aspects and Offene Fragen").

[16] Stapf, M.; Miehe, U.; Bester, K.; & Lukas, M. Guideline for advanced API removal. CWPharma project report for GoA3.4: Optimization and control of advanced treatment. December 2020.

6.3 Ozonation process control

The most important parameters to be monitored in ozonation have already been discussed. These include DOC that can be measured either directly or through UVA254 which correlates to DOC. It is also necessary to measure the ozone concentrations at different points in the process. Though it may at first seem that the analysers are extremely expensive, but, in fact, considering the operating costs involved, a properly optimized/controlled process will always save costs. In certain locations, such as working areas, ozone measurements are crucial from a safety at work perspective.

The most important measurement points include:

- measurements of the influent flow to the contact reactor;
- measurements of the amount of ozone produced;
- measurements of the ozone concentrations in the contact reactor;
- measurements of the residual ozone to ensure that the ozone destructor works.

It is possible to automate the removal of micropollutants using ozone to a certain extent, and to this end, a number of control strategies have been developed. Some of them are highlighted here.

A: Constantly the same ozone dose

+ no expensive analysers;

+ easy to operate and maintain;

- does not take into account the actual composition of wastewater;

- does not always guarantee the best possible removal of micropollutants, since the dose does not always meet the needs.

B: Ozone dose control using DOC (measured at the inflow to the contact reactor, establishing the expected DOC)

+ DOC is relatively easy to measure and correlates to micropollutants;

+ optimized ozone consumption by dosing as much as required to remove DOC;

- DOC analysers are simple but relatively expensive;

- need to measure also any other parameters that affect the ozone dosage, such as nitrite.

Control strategy B can also be applied using UV254, which is a lower-cost type of solution. In this case, UV254 should be measured from the inflow to the contact reactor and from the outflow from the final filters. Whilst the outflow from the filters provides information with a certain delay, it is still sufficient to control the treatment process.

Once a week, also the DOC-specific ozone dose (mgO_3/mgDOC) and the ozone production should be analysed, to see whether it remains within normal range. The measurements of micropollutants should be conducted in accordance with national recommendations or based on the guidelines of the new proposed Urban Waste Water Treatment Directive.

7 Advanced oxidation

Advanced oxidation has been widely tested to remove micropollutants. However, this technology has still remained at the level of pilot equipment. Advanced oxidation is an oxidation process that employs hydroxyl radicals. These radicals can be formed by the following processes and combinations thereof:

- ozonation combined with hydrogen peroxide;
- ozonation combined with UV irradiation;
- with hydrogen peroxide and UV irradiation;
- with titanium dioxide and UV light.

Whilst hydrogen peroxide alone does not ensure adequate removal of micropollutants, combining it with ozonation increases the concentration of hydroxyl radicals capable of breaking down organic matter. The UV light has been widely used in the past decade to disinfect wastewater, but these technologies do not remove micropollutants. This would require many times higher radiation, plus the process should combine for example hydrogen peroxide, ozonation or titanium dioxide. However, such combinations of the types of technological solutions have not been used in full-scale WWTPs, since UV light has a high energy consumption and there is also this need for auxiliary processes, which makes it a relatively complex and expensive type of solution.

8 Ferrate

Ferrate is a name for $Fe(VI)O_4^{-2}$, or iron oxide in 6 oxidation state. It is a compound that is relatively unstable in water and rapidly reduces into Fe(III), i.e., adds three electrons, which makes ferrate an interesting oxidiser. Put very simply, the micropollutants are removed in the following way:

$HFe(VI)O_4$ + micropollutant = Fe(III) + oxidised micropollutant

Ferrate is able to oxidize various organic and inorganic matter. So far, it has been applied mainly under laboratory conditions. However, today we know that the removal of micropollutants depends on:

- the concentration of pollutants;
- pH;
- ferrate dose;
- residence time.

Ferrate can be dosed directly into the bioreactor, where it acts, to a certain extent, also as a coagulant, as well as applied as a post-treatment option. Dosing into activated sludge certainly requires higher doses. One possible technological layout applied after the final clarifiers could be as follows:

- 30-60 min residence time in a contact chamber at dry weather flow;
- ferrate dosing;
- final filtration/clarifiers (disc filter, sand filter).

As revealed by the current studies [17], for example, 10 mgFe/l reduced 80% of BOD_5 and 35% of TOC. At the present state of knowledge, ferrate doses of up to 1 gFe/gDOC should be considered to remove micropollutants. This will ensure an > 80% removal for most of the APIs. However, we are not aware of any such full-scale ferrate processes yet, so we lack precise data to establish and operate such type of solution.

9 Membrane filtration

Membrane filtration has been used in medicine and in drinking water treatment for decades. In water treatment, membrane filtration is typically used to remove anthropogenic compounds, such as herbicides and pesticides, that have ended up in groundwater or surface water. Membrane filtration involves a membrane that serves a physical barrier with highly specialized characteristics, which, depending on the size of the filter pores, removes most of the pollutants. The most common types of membrane filtration in drinking water treatment include nanofiltration and reverse osmosis. Reverse osmosis, for example, is widely used to produce drinking water from seawater.

[17] Mikroverunreinigungen aus kommunalem Abwasser, Verfahren zur weitergehenden Elimination auf Kläranlagen, Bundesamt for Umwelt BAFU, Bern 2012.

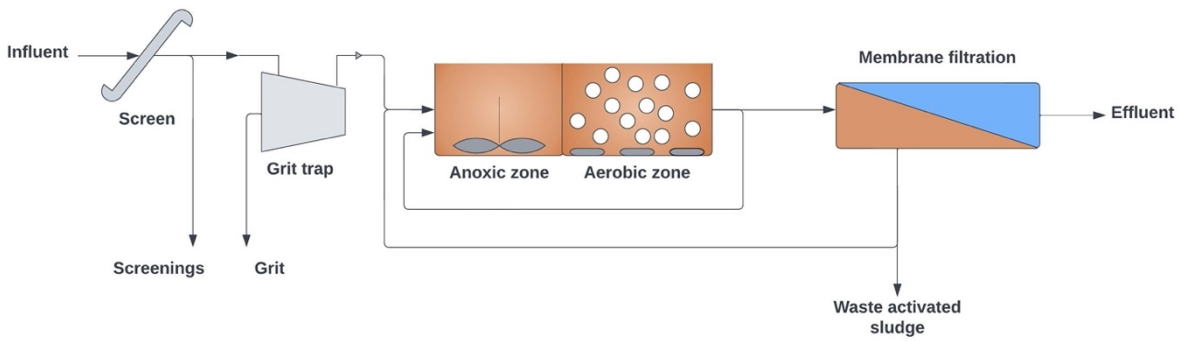

Figure 16. Membrane bioreactor. Activated sludge is separated from wastewater by membrane filtration, not by settling. This process also separates most of the hazardous compounds.

Today, membrane filtration is a growing trend also in wastewater treatment, where conventional activated sludge process is combined with the membrane filtration (ultrafiltration or nanofiltration). The advantage of this process is that we no longer depend on the properties of activated sludge, such as settling, so the WWTP can operate at higher activated sludge concentrations. Consequently, the bioreactor can be smaller in volume. In addition, the membrane filters prevent many hazardous compounds from being carried out to the effluent, including micropollutants when, for example, nanofiltration is used. This makes it easier to recycle the wastewater. However, it should be kept in mind that the membrane filters do not treat, but concentrate the pollutants. Therefore, the problem remains what to do with the concentrate. However, we could benefit from concentrating the micropollutants for example in industrial plants and hospitals, thus reducing the volume of problematic water, so the hydraulic capacity required for further treatment is lower.

10 Other technological solutions for micropollutants removal

The level of micropollutants can be reduced by using various biological processes. This is why in many cases ozonation is followed, for example, by a biofilm process. But even without pre-ozonation, several nature-based treatment processes have the capability of removing some of the micropollutants. Examples of these treatment processes include buried filters with or without reeds, and various other nature-based treatment processes such as wetlands and stabilization ponds.

Buried filter are particularly common at small treatment plants as they are relatively low-maintenance and in many cases do not require electricity to operate. For example, a buried filter can be a gravel and sand filter, with biofilm growing on the top of it, planted with reeds or without it. The

drawback of this solution is the need for a relatively large area, with an average of 1-3 m^2/p.e. or 5-12 m^2/m^3 of wastewater.

Figure 17. Simplified buried filter. Wastewater from biological treatment is discharged into the buried filter for post-treatment.

The most common nature-based wastewater treatment technology is a constructed wetland, also known as a reed bed. This is similar to a buried filter where treatment efficiency is achieved by interaction between various biological processes, carried out by micro-organisms and plants that consume and break down pollutants. Although most research is available on the removal of organic matter and nutrients such as nitrogen and phosphorus, more and more research has also been carried out on the use of constructed wetlands to reduce the level of micropollutants. More than 50 individual case studies have been published to date. [18,19]

The treatment efficiency of constructed wetlands heavily depends on the season, especially in northern Europe. In summer, due to the activity of micro-organisms, better removal of micro-pollutants would be achieved and this process is also supported by sunlight (photodegradation), which can break down certain substances, plus sorption and adsorption. According to various studies, the average removal efficiencies for micropollutants range from 21% to 93%. For example, >70% removal was found for ibuprofen and naproxen, but only <20% for carbamazepine. The highest removal efficiency so far (91%) has been reported for acetaminophen. More detailed information can be found in the published research cited. [19,20]

11 Costs for removing micropollutants

[18] Huma Ilyas, Ilyas Masih, Eric D. van Hullebusch; Pharmaceuticals' removal by constructed wetlands: a critical evaluation and meta-analysis on performance, risk reduction, and role of physicochemical properties on removal mechanisms. *J Water Health* 1 June 2020; 18 (3): 253–291. doi: https://doi.org/10.2166/wh.2020.213

[19]Mikroverunreinigungen aus kommunalem Abwasser, Verfahren zur weitergehenden Elimination auf Kläranlagen, Bundesamt for Umwelt BAFU, Bern 2012.

There is a fair amount of information out there today about the investment and operating costs for technologies to remove micropollutants. Naturally, exact costs depend on the local circumstances in which pilot tests are run to establish the necessary operating parameters and the best suited technological solution. However, there are certain indicators that can be used to estimate the costs.

It is first necessary to analyse the existing situation and to set objectives. Here are some of the factors that should be taken into account:

- whether the WWTP has enough space to build an additional treatment step;
- whether the WWTP has existing old buildings or tanks that can be returned to service;
- how will the hydraulic load change in the future;
- the efficiency of the existing WWTP – whether it is sufficient to start with, for example, ozonation or activated carbon adsorption, or whether a pre-treatment (e.g., a sand filter) needs to be added;
- how is the waste activated sludge stabilised;
- whether the company has or is able to train people capable of operating relatively complex technologies.

The calculation of technology costs may vary from country to country, but on average the following conditions are considered in Europe:

- the lifespan of the structures – 30 years;
- automated control system and parts thereof – 10 years;
- equipment (pumps, screens, feeders, etc.) – 15 years;
- operating costs throughout the lifespan.

The costs may be calculated on the basis (as a percentage of the investment) of:

annual maintenance costs (structures 0.5%, automated control system and parts thereof 2.5%, equipment 2%);

- energy costs (heating, electricity);
- chemicals (LOX for ozonation, activated carbon, coagulant, flocculant, etc.);
- handling of residues (e.g., generation and handling of waste activated sludge);
- costs of tests for micropollutants;

- personnel costs, outsourced services where necessary.

Estimating the exact costs is site-specific, and in addition, input prices change very quickly these days. The processes, however, can be compared, because the percentage breakdowns remain similar. Ozone, for example, is most dependent on the price of electricity, while GAC and PAC depend on its own price.

The following specific costs were found from the published research[20]. All sources confirm the principle that the larger the WWTP, the lower the specific costs for the treatment of one cubic metre of wastewater:

- PAC 10-30 cent/m^3 or 2-14 EUR/population equivalent (p.e) year;
- GAC 10-50 cent/m^3 or 2-14 EUR/p.e./year;
- O_3 5-20 cent/m^3 or 2-16 EUR/p.e./year;
- membrane filtration 0.5-2 EUR/m^3 + GAC 10-50 cent/m^3 per concentrate.

As these figures show, the specific costs for all technologies used today are roughly at the same level. But certainly, for example, the ozonation depends more on electricity prices than the activated carbon adsorption does. It is also more complicated and expensive to maintain ozone technology when there is a lack of required competence among the WWTP staff. In addition, in certain cases it may be necessary to remove the transformation products from the ozonated wastewater using activated carbon, in which case the ozone costs are reduced but, for example, the GAC process and its operating costs are added. Membrane filtration produces a concentrate that requires further treatment, which is why this technology is not suited for municipal WWTPs, but may have a certain potential, for example, in concentrating the wastewater in hospitals, before it is further treated.

12 APIs in sewage sludge

In recent years, the main focus has been on APIs in wastewater, and while the scientists have been engaged in research on sludge, no major targets have been set. Plus, the way of handling the sludge also varies from country to country. In locations with a large number of industries, the sludge is incinerated, making it possible to use all of the above technologies to remove micropollutants. Where, however, the sewage sludge is to be recovered, in particular the nutrients that it contains, such as nitrogen and phosphorus, then the ways of reducing the micropollutant concentrations that are too high still need to be explored.

[20] Treatment installations operated mainly in Germany and Switzerland.

It can be assumed that the most significant increase in the micropollutant concentrations in waste activated sludge is caused by the dosing of PAC, by either injecting directly into the activated sludge or by pumping some of it from the PAC contact reactor to the bioreactor. In this case, waste activated sludge is to be incinerated. If a GAC filter is used, the micropollutant concentrations in waste activated sludge are likely to be lower, but some load is still returned with backwash water from the filters. The lowest micropollutant load in waste activated sludge can be achieved by ozonation combined with a GAC filter. Although the industrial WWTPs sometimes perform pre-ozonation, i.e., ozonation before the biological treatment, which also breaks down some of the APIs, this is not recommended, because of the potential formation of even more hazardous transformation products.

The best way of reducing the micropollutant concentrations in waste activated sludge is to cut the use of micropollutants that are hazardous to the environment (replacing with those that are less hazardous) and process at sources of point pollution, such as hospitals. Whilst non-prescription medicines that people consume at home also have a substantial impact, the pollution loads from hospitals and care facilities are significant.

Possible effects of APIs ending up in the environment have been explored in a number of projects. Whilst most of them consider that micropollutants that come in low concentrations are not directly hazardous, it is recognised that their long-term effects are hard to predict. In soil samples taken in the Netherlands, for example, the incidence of a gene that determines the resistance of soil bacteria to tetracycline had almost 15-fold increased, and this is associated with manure used for fertilization, that came from animals that had been administrated the corresponding compounds. Today, it is also known that APIs can accumulate in plants, and even though APIs mainly concentrate in roots, they can still end up in animal and human diets.[21]

The treatment technologies used today for sewage sludge are mainly composting and anaerobic stabilisation. Incineration is not further addressed here, as the presence of APIs no longer plays a role in that process. Egge Haiba explored various composting technologies in her doctoral research[22] and found that many APIs can be reduced by composting. Optimising the composting process also has an impact on the removal efficiency (such as the support material used, temperature, etc.). Her studies were carried out using pilot tests, which analysed the reduction in APIs under controlled conditions by windrow composting for 30 days, but also assessed the same processes at the operating WWTPs in Tallinn and Tartu. During composting, moisture levels were maintained at 60-70% and sawdust, straw and peat were used as a support agent. The average temperature inside the compost windrow was 23-26 °C. The removal efficiencies revealed that, for example, sawdust accelerated the composting process, including the API removal. The exact length of required composting period depends on local circumstances, but ranges from 1 to 12 months.

[21] Mini-review: Pharmaceuticals in sewage sludge and their degradation during composting – recent studies in Estonia. Nei, L.; Haiba, E.; Lillenberg, M. Agraarteadus 2020. http://doi.org/10.15159/jas.20.02

[22] Egge Haiba, Doctor's Degree, 2017, (sup) Lembit Nei; Merike Lillenberg, Optimization of sewage sludge composting: problems and solutions , Tallinn University of Technology School of Engineering, Tartu College.

Her study was able to reduce the following APIs:

- diclofenac > 90%;
- triclosan > 60%;
- sulfamethoxazole > 80%;
- sulfadimethoxine > 75%
- norfloxacin > 80;
- ciprofloxacin > 90%;
- ofloxacin > 95%.

Anaerobic stabilization can also be expected to result in a reduction in certain APIs, although, like the activated sludge process, it is rather a side process. The microorganisms mainly break down readily degradable organic matter which comes in significantly higher concentrations compared to micropollutants. So, APIs are removed to a certain extent along with readily degradable organic matter. The removal efficiencies vary widely. In a Master's thesis entitled *Removal of pharmaceutical compounds by anaerobic digestion of sewage sludge* by Katrin Asplund written in Novia University of Applied Sciences in 2022, the following results were obtained:

- carbamazepine 52-66%;
- diclofenac 26-45%.

The same thesis points out that other studies have found more than a 70% removal efficiency for both compounds. Since anaerobic stabilisation is often followed by post-composting, the final micropollutant concentrations are lower.

To sum up various scientific works, it can be considered that more than 70% of micropollutants are removed during anaerobic stabilization. The fact whether it is biodegraded, biotransformed or sorbed to sludge/biomass, depends on the pollutant and, to a certain extent, on the operating conditions.

13 Summary of recommendations for removing micropollutants in Latvia and Lithuania

Today, we know that pharmaceutical residues are problematic micropollutants that we need to pay more attention to. The situation, though, including their potential risk to the environment and to man,

varies from country to country. However, it is generally agreed at the EU level that in the future, we should mainly focus on 12 pharmaceutical residues:

1. *amisulpride;*
2. *carbamazepine;*
3. *citalopram;*
4. *clarithromycin;*
5. *diclofenac;*
6. *hydrochlorothiazide;*
7. *metoprolol;*
8. *venlafaxine;*
9. *benzotriazole;*
10. *candesartan;*
11. *irbesartan;*
12. *mixture of 4-methylbenzotriazole and 6-methyl-benzotriazole (CAS no 136-85-6).*

And, it has been agreed that an 80% removal must be achieved for at least 6 from the above-mentioned list. However, as was clear from the previous chapters, there is no way we can remove them API-specifically, but technologies behave relatively similarly in removing all of them, as they do in removing many other hazardous compounds. That means, when choosing API removal technology, we should look at the needs of a particular WWTP and potential risks of APIs which exceed PNEC values. Do we need additional nutrient removal (nitrogen, phosphorus), do we need heavy metal removal, etc., following the process illustrated in Figure 6. Looking more closely at the problematic APIs identified in the MEDWwater project such as ibuprofen, diclofenac, azithromycin and amoxicillin, it can be concluded that most part of these APIs can be removed with both ozonation and activated carbon adsorption, but adsorption is best suited. However, as it has been pointed out on a number of occasions, all the technologies outlined work differently depending on the specific wastewaters, which is why the most accurate estimate can be made in pilot tests, which can be first performed under laboratory conditions when it comes to ozonation and adsorption.

Although, many European countries already have an extensive experience in the removal of APIs at WWTPs, it should be borne in mind that these results cannot be transposed directly to the Baltics. The most similar circumstances to us could be found from Sweden. It is therefore important for each country to develop its own competence. To this end, a semi-industrial piloting that requires operation, is best suited. This will teach how to operate, maintain and identify potential problems, for example due to local climatic conditions. It will also reveal any potential problems. Pilot tests will increase the competence of the staff and provide valuable input in planning the future full-scale treatment processes, training the process operators, etc.

The EU Urban Waste Water Treatment Directive foresees that the micropollutant technology should be first applied to WWTPs of > 100,000 p.e., so these are the first ones to carry out a feasibility study, following, for example, the CWPharma *Guideline for Advanced API removal*. That guidance material mainly focuses on pharmaceutical residues, so it is important to include also the micropollutants as a whole and to analyse any other potential needs, such as the further removal of nitrogen and phosphorus, the limits of which will also be revised in the above directive. After that, the removal of micropollutants at WWTPs of > 10,000 p.e. is to be explored and planned.

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