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Preventing **R**ecalcitrant **O**rganic **M**obile **I**ndustrial chemical**S** for **C**ircular **E**conomy in the soil-sediment-water **S**ystem

Start date of the project: **1st November 2021**

Duration: **42 months**

D4.4: Guidance document for upgrade and optimization of advanced wastewater treatment

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Executive Summary

Micropollutants such as pharmaceuticals, biocides, per- and polyfluoroalkyl substances (PFAS) and others can have adverse effects on the aquatic environment and human health. Common and mature technologies for the removal of micropollutants in wastewater treatment plants (WWTPs) include ozonation or powdered (PAC) and granular activated carbon (GAC). So far, more than 50 WWTPs in Europe (mainly in Germany and Switzerland) use such advanced treatment technologies at full-scale.

The recently published proposal to amend the Urban Wastewater Treatment Directive (UWWTD) proposes requirements for the removal of micropollutants in municipal WWTPs, depending on the treatment capacity and the local risks posed by micropollutants. The requirements for such quaternary treatment include 12 indicator substances which must be removed by at least 80% on average.

As knowledge of the removal efficiency of these advanced wastewater treatment (AWWT) technologies with respect to PFAS and other industrial persistent and mobile (iPM) compounds at dosages applied in practice is limited, for this deliverable, short-term sampling campaigns were carried out at five WWTPs equipped with different treatment technologies. With one exception, the AWWT processes were operated in such a way that they would have met the UWWTD treatment goals.

Of the 20 PFAS analysed, 13 PFAS were detected at least once above the limit of quantification (LOQ) in the secondary effluent. The PFAS always detected were PFBA, PFHxA, PFOA, PFPeA and PFHpA (1 - 25 ng/l). Median removals for pharmaceuticals (46% - 78%) and industrial chemicals (42% - 79%) by the AWWT processes were in a similar range, while PFAS were not significantly removed. In the best case (WWTP with PAC) a median removal of 25% was achieved for the five PFAS that were present in the samples and could be evaluated.

The very low concentrations of PFAS and some iPMs in the water samples lead to high analytical uncertainties that hinder the evaluation of the AWWT processes. For a more robust assessment, long-term monitoring (about 1 year) is needed, to account for seasonal variations and changes in operational regimes.

Even though the results of this study are limited in regards to PFAS elimination, they indicate that AWWTs implemented for micropollutant removal are not an effective barrier for PFAS. Consequently, catchment areas that have elevated PFAS concentrations won't be able to rely on such end-of-pipe measures at municipal WWTPs and might need to focus on PFAS source control.

PROMISCES

Table of content

1 Introduction and scope of the guideline

Micropollutants such as pharmaceuticals, biocides, per- and polyfluoroalkyl substances (PFAS) and others can cause adverse effects on the aquatic environment and human health. Consequently, the European Commission strives to reduce the amount of micropollutants in the aquatic environment as one main goal of the European Green Deal's zero pollution ambition, which is reflected by the proposed adaptions of several water-related EU directives listed below:

- Water Framework Directive (WFD)[1]
- Groundwater Directive (GWD)[1]
- Environmental Quality Standards Directive (EQSD)[1]
- Urban Wastewater Treatment Directive (UWWTD)[2]

The recent proposed revisions of the GWD and the EQSD include (environmental) quality standards for several pharmaceuticals, pesticides and several industrial substances including PFAS. Among other changes, the proposed UWWTD revision includes a mandatory implementation of a quaternary treatment for micropollutants removal at municipal wastewater treatment plants (WWTPs), depending on the WWTP treatment capacity (population equivalents) as well as on local risks posed by micropollutants. The requirements for quaternary treatment (control of the treatment efficiency) is similar to the Swiss law[3] (enforced since 12/2016) and outlines the removal of 12 indicator substances which must be removed by at least 80% on average. Details on the indicator substances and the calculation process of the average removal can be found in the according references.

Despite potential differences between the proposed and final version of the amended UWWTD, a growing number of municipal WWTPs will likely implement advanced wastewater treatment (AWWT) technologies for micropollutant removal anyway (e.g. due to local risks posed by micropollutants, available public funding, as demonstration projects for national strategies …). Common and mature technologies for micropollutant removal at WWTPs are ozonation or adsorption onto powdered and granulated activated carbon. Details on the benefits and trade-offs of the application of these technologies are available in the CWPharma project guideline (Stapf et al., 2020). So far, more than 30 WWTPs in Germany (Metzger et al., 2020), 19 WWTPs in Switzerland[4], and an increasing number of WWTPs in other European countries (e.g. Denmark, Sweden) use such technologies at full-scale.

Most of these AWWT processes are specifically designed to reduce emissions of a given set of (indicator) substances. As removal efficiency of the AWWT processes is very substance specific (Altmann et al., 2016; Sauter et al., 2020), they may also be able to reduce concentrations of PFAS and industrial (potentially) persistent and mobile substances (iPM). However, knowledge on the removal efficiency of PFAS and other industrial substances at typical dosages applied in practice at these AWWT technologies is still limited.

For example, Rößler and Launay (2019) showed that overall removal of four PFAS in the WWTP increased after the implementation of a full-scale PAC treatment, but these findings were based on a few samples. PFAS removal via GAC filtration depends strongly on PFAS chain length and the treated

[1] https://environment.ec.europa.eu/publications/proposal-amending-water-directives_en (accessed 17.03.2023)

[2] https://environment.ec.europa.eu/publications/proposal-revised-urban-wastewater-treatment-directive_en (accessed 17.03.2023)

[3] https://www.fedlex.admin.ch/eli/cc/2016/671/de (accessed 17.03.2023)

[4] https://micropoll.ch/Mediathek/liste-der-aras-mit-mv-stufe/ (accessed 17.03.2023, list status: 22.12.2022)

bed volumes. Experiments by Park et al. (2020) show that PFAS removal via GAC decreases with the PFAS chain length. Thus, the shorter the chain length of the PFAS in the treated water, the more often GAC must be exchanged to maintain a relevant PFAS removal. Regarding ozonation, no significant impact on PFAS removal is expected, as most PFAS show a poor reactivity with ozone and OH-radicals (Franke et al., 2019; Trojanowicz et al., 2018).

Considering the expected changes in EU-wide legislation, it is important for utilities to know whether and to what extent these AWWT technologies can also remove such substances, and to determine whether additional measures are required for their local situations. Therefore, sampling campaigns at five selected WWTPs using different AWWT processes at full-scale were carried out to fill current data gaps, to evaluate the impact on the different targets, and to derive recommendations for operators, utilities and engineering companies/consultants.

2 Overview WWTPs and sampling campaigns

Sampling campaigns were conducted at a total of 5 WWTPs located in Germany, Switzerland and Sweden. The technologies employed at the selected WWTPs are:

- 2 WWTPs with ozonation and biological post-treatment,
- 2 WWTPs with powdered activated carbon prior to filtration,
- 1 WWTP with a combination of ozonation and granular activated carbon filtration.

The WWTPs were selected without any prior assessment of whether specific PFAS and/or industrial substances could be expected in the WWTP influent. To evaluate the processes performance under normal, current operating conditions, no specific operating conditions were specified during the sampling campaigns. Three sampling campaigns were carried out at each WWTP, with two (PAC processes) and three sampling points (ozonation with post-treatment), respectively. Samples were collected as 24-hour mixed samples, except for WWTP E (grab samples). Samples were frozen until they were sent to the laboratories by overnight transport. Sample analysis was carried out by the Berliner Wasserbetriebe (BWB) in Berlin and the Bundesanstalt für Gewässerkunde (BfG) in Koblenz.

BWB quantitatively analysed the samples for general water quality parameters such as dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm (UVA_{254}), nitrite, and other nitrogen and phosphorous species. The samples were also analysed for a total of 122 micropollutants, which can be roughly divided into three categories based on their substance classes and application fields: pharmaceuticals (n = 45; DIN EN ISO 21676:2021), PFAS (n = 20; DIN 38407-F42 2011-03), and pesticides / industrial chemicals (n = 57; DIN 38407-F36 2014-09, DIN ISO 16308 (F45) 2017-09).

BfG qualitatively analysed the samples for more than 1500 organic micropollutants using a database-assisted suspect screening approach. According to Jewell et al. (2020), suspect screening was performed with a quadrupole-time-of-flight (qTOF) mass spectrometer, and results were subsequently compared with an in-house database. The database (>1500 entries as of 03/2023) was fed with authentic reference standards, resulting in instrument specific retention times and fragmentation patterns. For identification, features detected in the WWTP samples were matched to database entries by exact mass (+/- 10 mDa), retention time (+/- 1 min) and MS^2 spectrum. Further details of the method can be found in Nürenberg et al. (2015).

The AWWT specifications (dosages and water quality parameters) during the sampling campaigns can be found in Table 1, whereas a more detailed description of the WWTPs and the sampling points can be found in appendix 0.

Table 1: Overview of selected water quality parameters and dosages of each WWTP. A minus (-) indicates not measured. # Dosage refers either to mg O_3/l or mg PAC/l. Specific ozone doses marked with * were corrected for the ozone consumption due to nitrite oxidation (3.43 mg O_3/mg NO_2-N). Prior to the sampling campaign, the GAC filter at WWTP B had already treated ≈ 30,000 bed volumes.

WWTP	Country	AWWT type	Sampling type	DOC (mg/L)	UVA_{254} (1/m)	Nitrite (mg-N/l)	Dosage# (mg/l)	Specific dosage# (mg/mgDOC)
A	SE	O_3	24h	12.8	22.0	0.66	5.1	0.42 (0.24*)
B	CH	O_3+GAC	24h	7.6	13.9	0.05	1.1	0.15 (0.13*)
C	CH	O_3	24h	5.7	12.0	-	2.2	0.39
D	CH	PAC	24h	5.9	12.2	-	5.8	0.99
E	DE	PAC	grab	6.0	14.7	-	13.2	2.21

3 Micropollutants measured in the secondary effluent

57 out of the 122 micropollutants in the target analysis were detected above the LOQ in at least two WWTPs. The median concentrations of all secondary effluent samples are shown in Figure 1. Pharmaceuticals and some of their metabolites (e.g. guanylurea, valsartan acid) were detected in a broad concentration range (0.03 – 75 µg/l). The median concentrations of both industrial chemicals and pesticides varied between 0.1 – 5 µg/l. 12 of the 20 PFAS were detected at median concentrations between 1 and 15 ng/l. An overview of PFAS detected can be found in the appendix (SI-Table 1). Compared with other studies (Appleman et al., 2014; Barisci and Suri, 2021; Phong Vo et al., 2020; Stoiber et al., 2020), PFOA, PFOS and PFHxS were measured in lower concentrations, whereas the other PFAS substances as well as the total sum of PFAS were within the expected range. Also measured concentrations of pharmaceuticals were in the same range as other municipal WWTPs (Stapf and Zhiteneva, 2021).

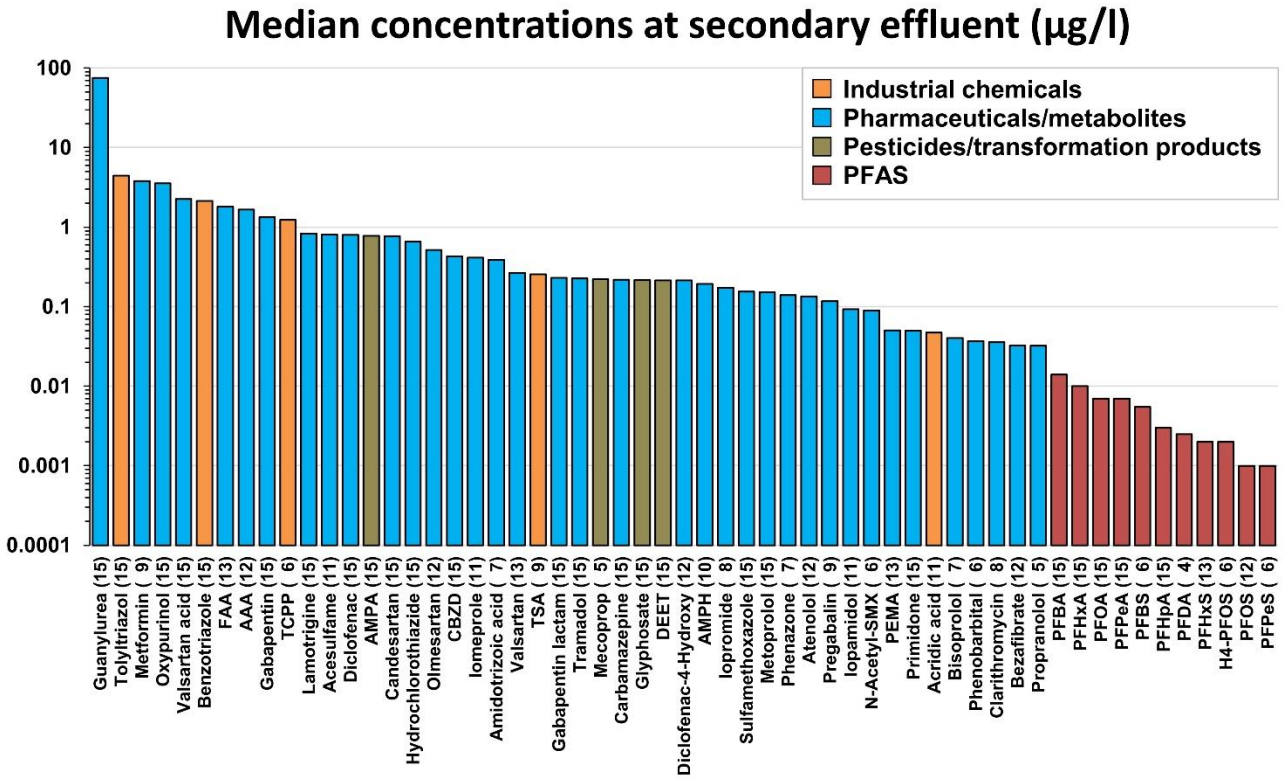

Figure 1: Median concentrations of compounds in all secondary effluent samples. Substances which were only detected at one WWTP have been excluded. Substances were clustered in four groups (pharmaceuticals, industrial chemicals, pesticides, PFAS), which include also some metabolites/transformation products that were not marked specifically. The number of samples above the limit of quantification is shown in parentheses.

4 Assessment of the sampling campaigns

Each of the five WWTPs was checked for whether it met the requirements of the quaternary treatment according to the UWWTD proposal (at least 80% removal of a set of indicator substances). The following assumptions and boundary conditions were used:

- Only 7 of the 12 indicator substances were included in the target analysis method (included: carbamazepine, diclofenac, hydrochlorothiazide, metoprolol, benzotriazole, candesartan, methylbenzotriazole; not included: amisulpride, citalopram, clarithromycin, venlafaxine and irbesartan)
- For calculating the average removal, a ratio of 2:1 between category 1 and 2 substances must be used. Therefore, one category 2 substance had to be excluded (candesartan)
- No reference point for the 80% removal is given in the UWWTD proposal, so it is assumed that the removal must be achieved between the influent and the effluent of the WWTP (similar to the Swiss regulation). As no samples were taken in the influent of the WWTP, the effect of the biological treatment was estimated by using substance specific reductions based on measurements at WWTPs in Switzerland (Götz et al., 2015).

Results shown in Table 2 indicate that four out of the five WWTPs would meet the micropollutant removal requirements in the UWWTD proposal. Additionally, the overall removal at WWTPs D and E is expected to be even higher, as the impact of the PAC recirculation into the biology was not considered. The comparably poor micropollutant removal performance at WWTP A can be explained by the presence of nitrite (0.66 mg-N/l) in the ozonation influent, which reduces the (effective) specific ozone dose from 0.42 to 0.24 mg O_3/mg DOC. Otherwise, a similar removal to what was seen at WWTP C would have been expected. For WWTP B, the low specific ozone dosage of 0.13 mg O_3/mg DOC is compensated by the subsequent GAC filter.

Table 2: Average removal of indicator substances according to UWWTD proposal. Expected micropollutant reduction by the biology is based on Götz et al. (2015). Asterisk (*) indicates that elimination is expected to be higher due to the recirculation of the PAC in the biology. The colours indicate whether the treatment goal of 80% removal throughout the WWTP was achieved (green) or not (red).

Category	Substance	Biology (literature)	Average removal in the advanced treatment only (measured, n = 3)					Average removal in the whole WWTP (estimated)				
			A	B	C	D	E	A	B	C	D	E
			O_3	O_3 + GAC	O_3	PAC	PAC	O_3	O_3 + GAC	O_3	PAC	PAC
1	Carbamazepine	0%	77%	84%	92%	81%	82%	77%	84%	92%	81%	82%
1	Diclofenac	29%	83%	98%	96%	74%	61%	88%	99%	97%	81%	72%
1	Hydrochlorothiazide	9%	48%	92%	78%	70%	77%	53%	93%	80%	73%	79%
1	Metoprolol	24%	44%	89%	71%	91%	93%	57%	92%	78%	93%	95%
2	Benzotriazole	31%	47%	56%	60%	65%	83%	64%	69%	73%	76%	88%
2	Methylbenzotriazole	41%	33%	66%	55%	69%	65%	60%	80%	73%	82%	79%
	Average removal	**22%**	**55%**	**81%**	**75%**	**76%**	**77%**	**66%**	**86%**	**82%**	**81%***	**83%***

5 Target analysis

The impact of the different advanced treatment processes on pharmaceuticals, industrial chemicals and PFAS analysed by the target method is summarised in Figure 2. To minimise the impact of analytical uncertainties, only substances with concentrations equal to or higher than five times the limit of quantification in the influent of the advanced treatment process (= secondary clarifier effluent) were included. Although the number of substances varied greatly between categories and WWTPs (pharmaceuticals: n = 15 - 25, industrial chemicals: n = 2 - 3 and PFAS: n = 1 - 5), some trends were observed:

- Pharmaceuticals and industrial chemicals were reduced by a similar extent.
- In most cases, the median removal of both pharmaceuticals and industrial chemicals was lower than the average removal of the UWWTD indicator substances.
- Due to the limited data, the highly variable removal and the different types of PFAS at the WWTPs, it is not possible to make a robust assessment of the impact of the different treatment technologies in regards to PFAS. The available data indicate that PFAS are poorly removed, with only one WWTP (WWTP D) showing a median removal of 25%.

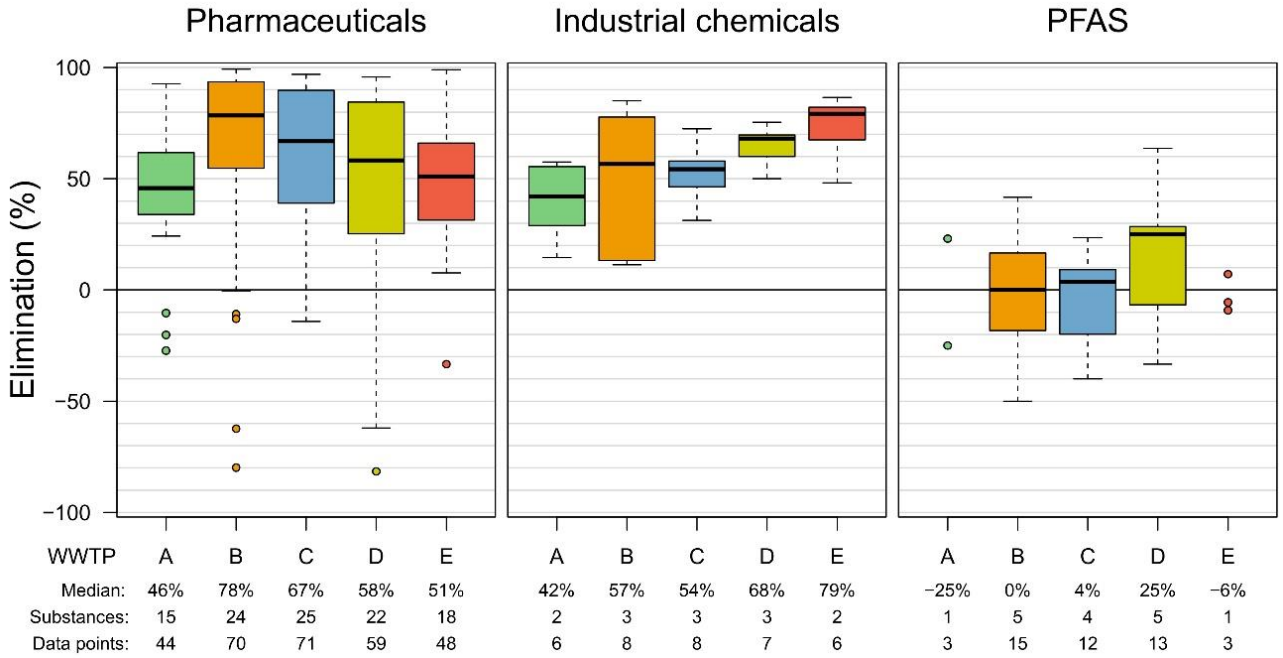

Figure 2: Elimination of substances by the entire advanced treatment process chain grouped in pharmaceuticals, industrial chemicals and PFAS. Note that only substances with an advanced treatment process influent concentration (= secondary clarifier effluent) equal to or higher than five times the limit of quantification are presented. Some data points might be outside the plotting area (e.g. elimination below -100%).

6 Database assisted suspect screening

The screening resulted in the identification of 202 substances present in at least one sample from the WWTPs investigated. It should be noted that this screening does not provide absolute concentrations. In analogy to the approach already described by Bader et al. (2017), the evaluation is based on a relative change of signal intensities before and after the respective treatment. For this, only compounds detected in the influent of the respective treatment stages (= secondary effluent) were considered. Thus, identified compounds which were not found in the samples before AWWT were not included in the following evaluation.

For a relatively large share of substances identified by the suspect screening, lower signal intensities were observed after the treatment, resulting in a relative reduction in intensity. Between 15 - 43% of the compounds could not be detected after the treatment (evaluated as 100 % reduction), which could be due either to complete removal/transformation of the substance or an incomplete removal resulting in an intensity < LOD. On the other hand, higher signal intensities were detected for 7 - 16% of the compounds at least at one sampling date after the AWWT.

In Figure 3, the relative reduction in signal intensity is shown for each WWTP. Substances were grouped into pharmaceuticals, industrial chemicals or other chemicals. In contrast to the results from the target analysis, lower intensity reductions were observed for industrial chemicals. It should be noted at this point that data for from target analysis is based on 2-3 industrial chemicals while suspect screening data includes 11-21 substances of this class underlining the added benefit from suspect screening for the assessment.

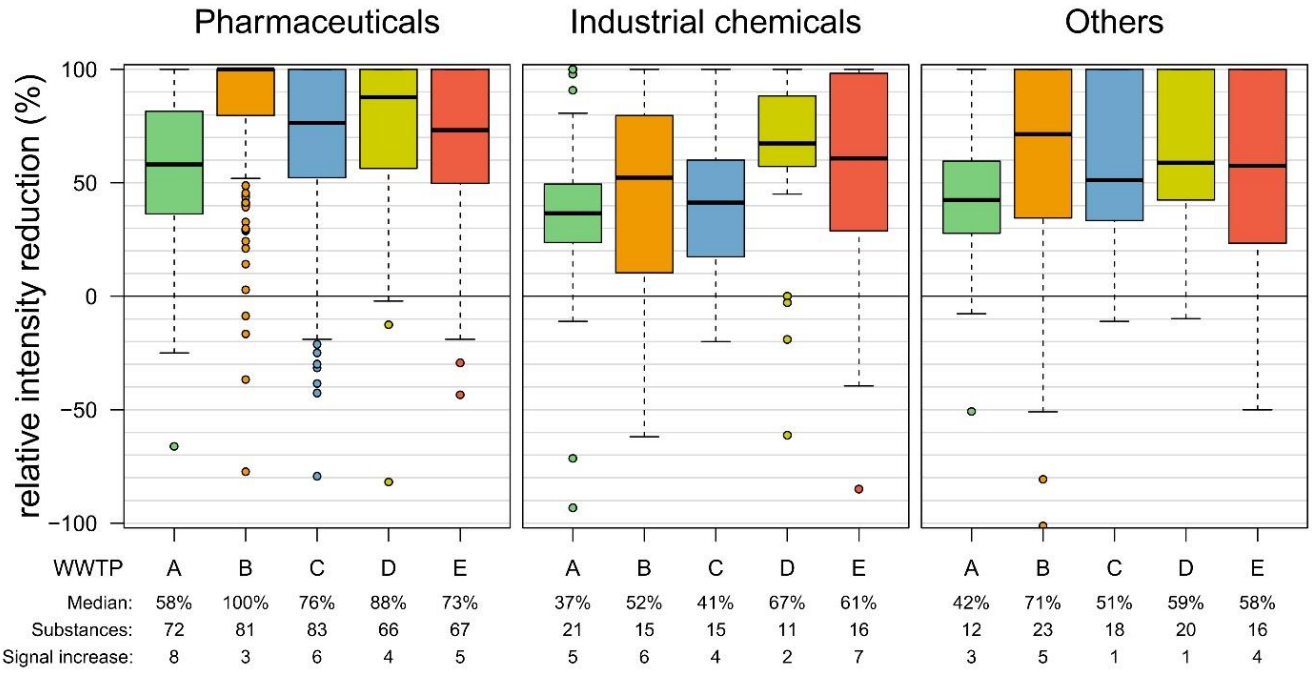

Figure 3: Impact of the advanced treatment process chains on substances, grouped into pharmaceuticals, industrial chemicals and other substances. A positive reduction of the signal intensity indicates that the concentration of the substance is reduced, whereas a negative reduction indicates a concentration increase. The number of substances indicates the number of different substances for which a change of intensity could be calculated. The signal increase indicates the amount of different substances for which a signal increase occurred at least once.

7 Summary and recommendations

Except for one WWTP, all WWTPs investigated would have met the treatment targets defined in the UWWTD proposal. The reason why WWTP A did not achieve the 80% removal target was because the effective specific ozone dose was reduced by almost half due to nitrite present in the ozonation influent during the sampling days.

Out of the 20 PFAS analysed, 12 PFAS were detected at least once above LOQ prior to the AWWT (= secondary effluent). The PFAS which were always detected were PFBA, PFHxA, PFOA, PFPeA, and PFHpA (1 – 25 ng/l). Target as well as the database suspected screening methods highlight that the removal is very substance specific. Based on the quantitative target analysis, the median removal of pharmaceuticals (46% – 78%) and industrial chemicals (42% - 79%) was in a similar range, whereas PFAS were not significantly affected. The greatest PFAS removal (median removal of 25%) was seen in WWTP D, which used PAC.

The qualitative suspect screening for about 1500 substances revealed that about 200 different substances could be detected above the detection limit. Even though no conclusive statements about the performance of the different AWWT types can be drawn based on the limited data, the results show that all of the investigated technologies are able to reduce a broad range of micropollutants (reduction was very compound specific). In contrast to target analysis data, suspect screening data indicates a significantly lower removal of industrial compounds compared to pharmaceuticals. Especially for the assessment of WWTP receiving a large share of industrial wastewater, suspect screening might be used to extend the list of target indicator substances by a larger number of industrial chemicals to gain more robust results.

The very low concentrations of PFAS and some iPMs in the water samples resulted in high analytical uncertainties which hindered the evaluation of the AWWT processes. Consequently, the sampling and analyses performed in this work provide an initial indication of removal, but do not address the impact of different operational conditions. For a more robust evaluation, long-term monitoring (approx. 1 year) is needed to account for seasonal variations and changes in operational conditions.

Although the results of this study regarding PFAS elimination are limited, they indicate that AWWT implemented for micropollutant removal are not effective barriers for PFAS. Consequently, catchment areas that have elevated PFAS concentrations will not be able to rely on such end-of-pipe measures at municipal WWTPs and may need to focus their efforts on PFAS source control.

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Appendix A: WWTP descriptions and sampling points

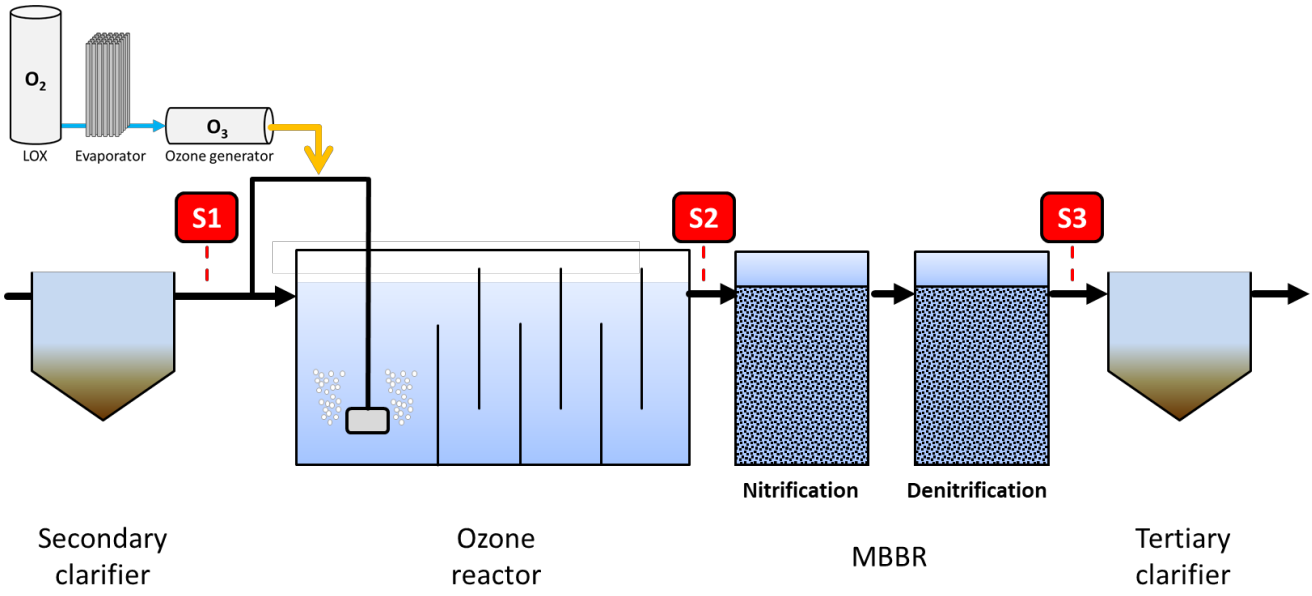
WWTP A

The WWTP A is located in Sweden and has a load of about 210,000 people equivalents (PE). The WWTP treats about 40,000 m^3/d and has an average flow of 1,700 m^3/h. The wastewater treatment consists of the following steps:

- mechanical treatment (grid), sand and grease removal, primary aeration, primary clarifier
- activated sludge process with nitrification (N) and denitrification (DN), secondary clarifier
- ozonation using a moving bed biofilm reactor (N / DN) as post-treatment
- tertiary clarifier

The ozonation plant is designed for treatment of up to 3,000 m^3/h and has a total ozone production capacity of 20 kgO_3/h. The ozone reactor has a volume of 524 m^3 and can provide a hydraulic retention time between 10 and 60 minutes (~ 18 minutes at average flow). Ozone is applied in the first chamber of the ozone reactor using a side-stream injection system with a radial diffuser. The ozone dose can be controlled by ΔUVA_{254} (UVA_{254} measured at sampling points S1 and S2, respectively). However, typically, a fixed ozone dose of 8 mgO_3/L is used.

The MBBR post-treatment consists of two zones: nitrification followed by denitrification. The HRT varies between 0.75 – 4.5 hours (~ 80 minutes at average flow).



SI-Figure 1: Schematic overview of the ozonation plant and the MBBR post-treatment at WWTP A. Phosphoric acid can be added at the MBBR influent to enhance growth of biomass at low P concentrations. Ethanol is used as carbon source for the denitrification stage, whereas aluminium chloride is added at the end of the MBBR to precipitate phosphorous and to improve flocculation of suspended solids. Sampling points used in PROMISCES are S1 (influent ozonation), S2 (effluent ozonation), and S3 (effluent post-treatment).

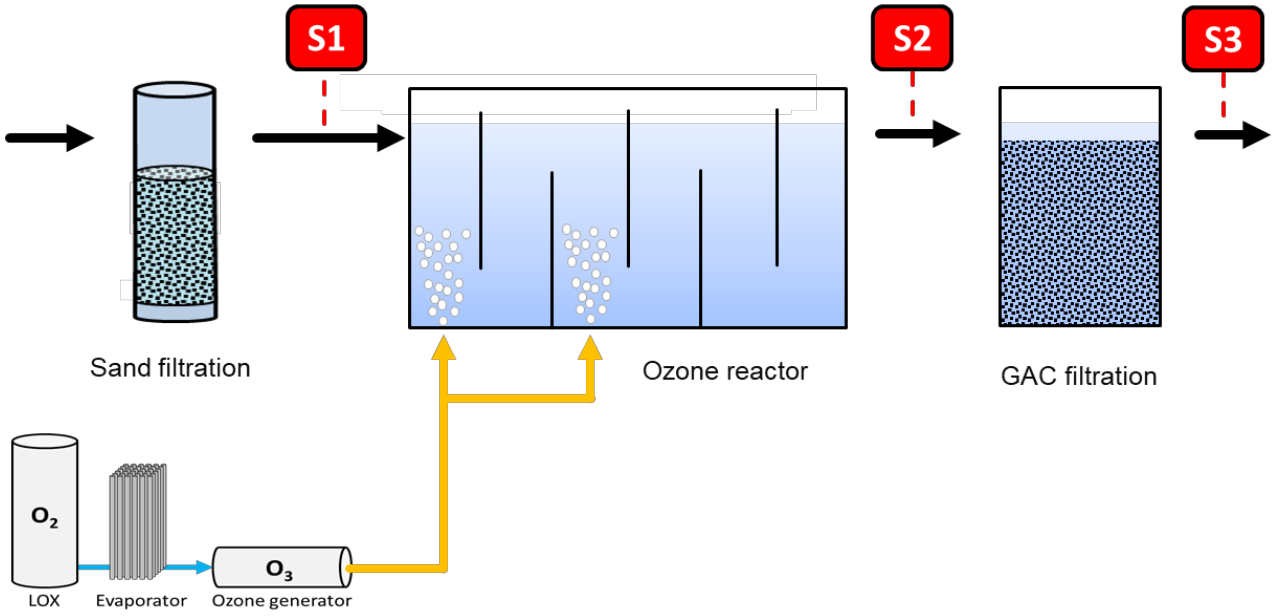
WWTP B

WWTP B is located in Switzerland is designed for a load of about 120,000 population equivalents (PE) and also treats wastewater from the nearby industry. It treats about 30,000 m^3/d (2021) and has an average flow of 950 m^3/h.

Wastewater treatment consists of the following steps:

1. mechanical treatment (grid), sand and grease removal, and primary clarifier
2. two parallel biological treatment lines with nitrification/denitrification zones:
    a. conventional activated sludge (CAS) system followed by a clarifier
    b. fixed bed biology with styrofoam pellets
3. sand filtration
4. ozonation
5. granular activated carbon (GAC) filtration

The ozonation plant has two ozone reactors (385 m^3, each) and is designed to treat up to 1700 m^3/h. The hydraulic retention time is about 30 minutes on average. The ozone dose is controlled by ΔUVA_{254} (UVA_{254} measured at sampling points S1, S2, and S3). The typical setpoint is a ΔUVA_{254} of 10%, which corresponds to a specific ozone dose of 0.1 g O_3/g DOC. Additionally, nitrite is also measured and considered in the ozone control. The ozone treatment is followed by the GAC filter. It consists of 8 chambers, one of which is always on stand-by and ready for backwashing, maintenance etc. The empty bed contact time of the GAC filter is on average two hours.



SI-Figure 2: Schematic overview of the ozonation plant and the GAC post-treatment at WWTP B. Sampling points used in PROMISCES were S1 (influent ozonation), S2 (effluent ozonation), and S3 (effluent post-treatment).

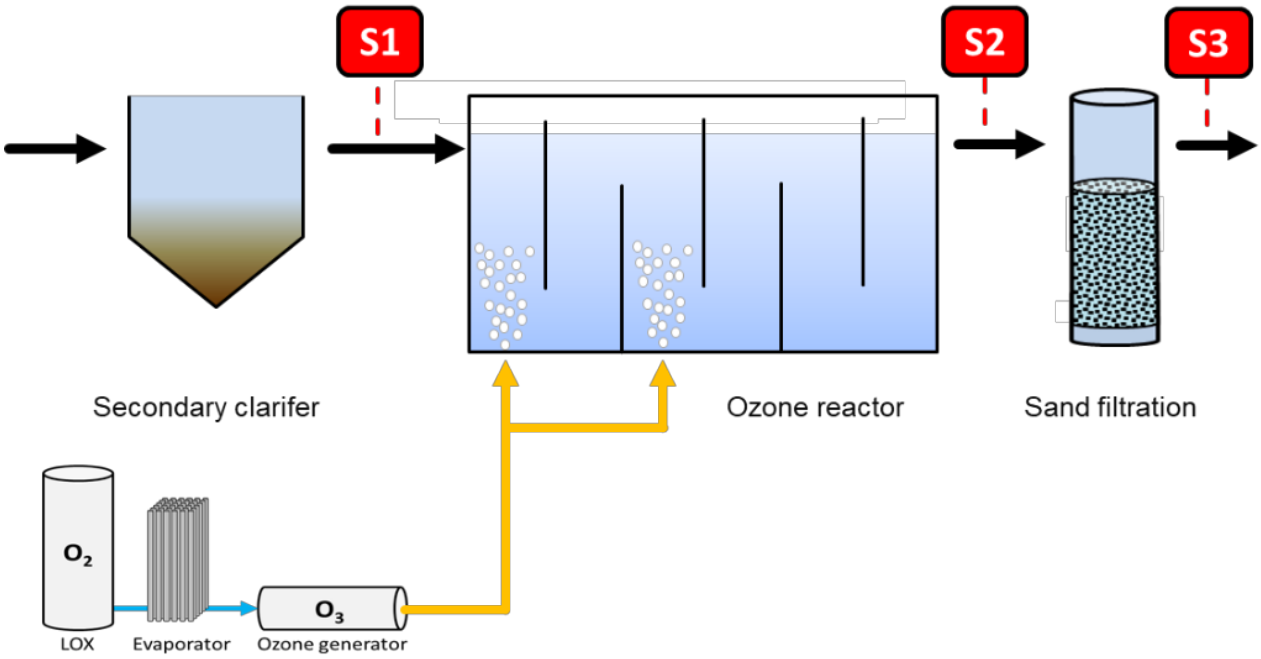
WWTP C

WWTP C is located in Switzerland and has a load of about 150,000 population equivalents (PE). It treats between 13,000 and 57,000 m^3/d and has an average flow of 720 m^3/h.

Wastewater treatment consists of the following steps:

1. mechanical treatment (grid), sand and grease removal and primary clarifier
2. CAS with nitrification/denitrification, secondary clarifier
3. ozonation
4. sand filtration

The ozonation plant is designed for the treatment of up to 2,375 m^3/h and has a total ozone production capacity of 2 x 5.5 kgO_3/h. The ozone reactor has a volume of 530 m^3. The average hydraulic residence time is about 37 minutes. Ozone is introduced into the water via diffusors. The ozone dose is controlled by ΔUVA_{254} (UVA_{254} measured at sampling points S1 and S2). The typical setpoint is a ΔUVA_{254} of 42%, which corresponds to a specific ozone dose between 0.33 and 0.5 g O_3/g DOC (1.6 – 2.7 g O_3/m^3). Additionally, nitrite is also measured and considered in the ozone control. The ozone treatment is followed by a sand filter.



SI-Figure 3: Schematic overview of the ozonation plant and the sand filtration at WWTP C. Sampling points used in PROMISCES were S1 (influent ozonation), S2 (effluent ozonation), and S3 (effluent ozonation post-treatment).

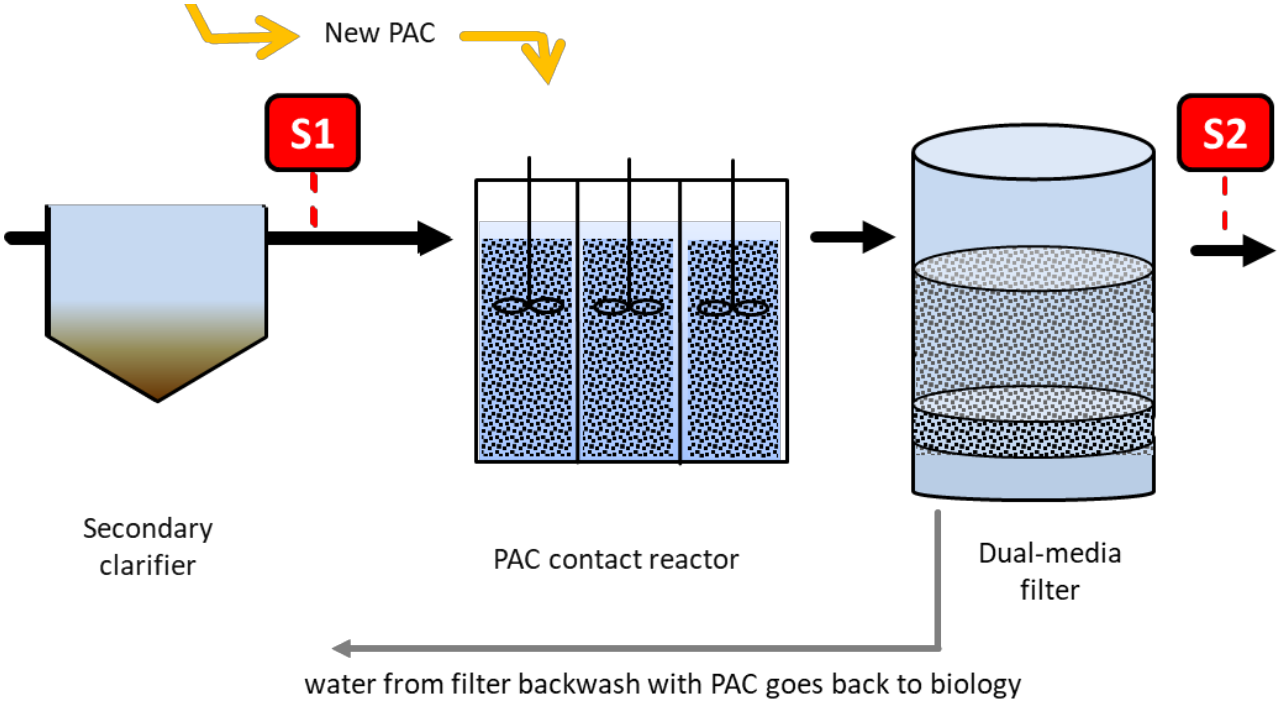
WWTP D

WWTP D is located in Switzerland and has a load of about 17,000 population equivalents (PE). It treats between 4,100 and 17,300 m^3/d and has an average flow of 300 m^3/h.

Wastewater treatment consists of the following steps:

1. mechanical treatment (grid), sand removal and primary clarifier
2. CAS with nitrification/denitrification, chemical phosphorus removal, secondary clarifier
3. powdered activated carbon (PAC) dosing prior to a coagulation filtration (dual-media filter)

The PAC contact reactor and the dual-media filter were designed for treatment up to 750 m^3/h. The contact reactor has a volume of 240 m^3 to maintain a hydraulic retention time of at least 19 minutes. PAC is stored in a PAC silo and is pre-wetted prior to usage. The PAC suspension is then introduced to the contact reactor at a dose of about 6 mg PAC/L. PAC retention is achieved by the subsequent coagulation filtration (coagulant = 1 mg Fe/L, $FeCl_3$; average filter velocity = 10 m/h). The PAC is recirculated along with the filter backwash water to the biological treatment stage, where it is eventually removed together with the excess sludge.



SI-Figure 4: Schematic overview of the PAC treatment and the coagulation filtration (dual-media filter) at WWTP D. Sampling points used in PROMISCES are S1 (influent PAC contact reactor) and S2 (effluent of dual-media filtration).

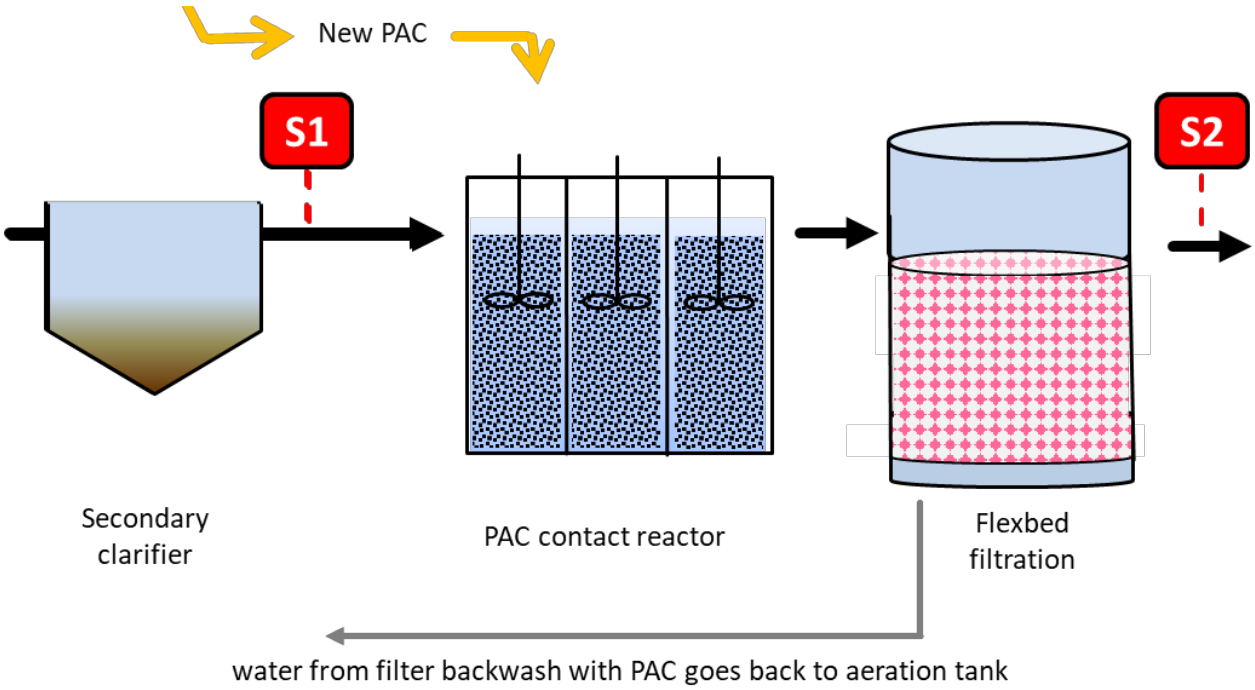
WWTP E

WWTP E is located in Germany and has a load of about 12,000 population equivalents (PE). It treats between 1,200 and 11,000 m^3/d and has an average flow of 85 m^3/h.

Wastewater treatment consists of the following steps:

1. mechanical treatment (grid), sand and grease removal, and primary clarifier
2. CAS, secondary clarifier
3. treatment with PAC
4. Flexbed filter (filtration with a compressible filter medium)

The PAC stage has a treatment capacity up to 290 m^3/h. The PAC contact tank has a volume of 135 m^3 to maintain a hydraulic retention time between 19 and 25 minutes. The PAC storage and dosing is similar to WWTP D, but with an average dosage of 10 mg PAC/L. PAC retention is achieved by a Flexbed filter with an average flow of 85 m^3/h. PAC is recirculated along with the filter backwash water to the biological treatment stage, where it is eventually removed together with the excess sludge.



SI-Figure 5: Schematic overview of the PAC treatment and the Flexbed filtration at WWTP E. Sampling points used in PROMSICES are S1 (influent PAC contact reactor) and S2 (effluent Flexbed filtration).

Appendix B: PFAS detected at WWTP secondary effluents

SI-Table 1: Overview of PFAS detected at sampling point 1 (= secondary effluent) of the five WWTPs investigated. The numbers represent how often the PFAS were measured ≥ LOQ, whereas the number in brackets indicate how often the PFAS were measured ≥ 5 * LOQ. Minus sign (-) indicates that the compound was not detected above LOQ in any of the samples (n = 3 per WWTP).

Substance	Chain length	WWTP A	WWTP B	WWTP C	WWTP D	WWTP E	Total
PFBA	4	3 (3)	3 (3)	3 (3)	3 (3)	3 (3)	15 (15)
PFBS	4	-	3 (0)	-	3 (0)	-	6 (0)
PFPeA	5	3 (0)	3 (3)	3 (3)	3 (3)	3 (0)	15 (9)
PFPeS	5	1 (0)	2 (0)	-	3 (0)	-	6 (0)
HFPO-DA	6	-	-	-	1 (0)	-	1 (0)
PFHxA	6	3 (0)	3 (3)	3 (3)	3 (3)	3 (0)	15 (9)
PFHxS	6	3 (0)	3 (0)	3 (0)	3 (0)	1 (0)	13 (0)
PFHpA	7	3 (0)	3 (0)	3 (0)	3 (1)	3 (0)	15 (1)
PFHpS	7	-	-	-	-	-	-
H4-PFOS	8	1 (0)	3 (0)	2 (0)	-	-	6 (0)
PFOA	8	3 (0)	3 (3)	3 (3)	3 (3)	3 (0)	15 (9)
PFOS	8	3 (0)	3 (3)	3 (0)	3 (0)	-	12 (3)
PFOSA	8	-	-	-	-	-	-
PFNA	9	-	-	-	-	-	-
PFNS	9	-	-	-	-	-	-
PFDA	10	1 (0)	1 (0)	-	-	2 (0)	4 (0)
PFDS	10	-	-	-	-	-	-
PFUnA	11	-	-	-	-	-	-
PFDoDA	12	-	-	-	-	-	-
PFTrDA	13	-	-	-	-	-	-