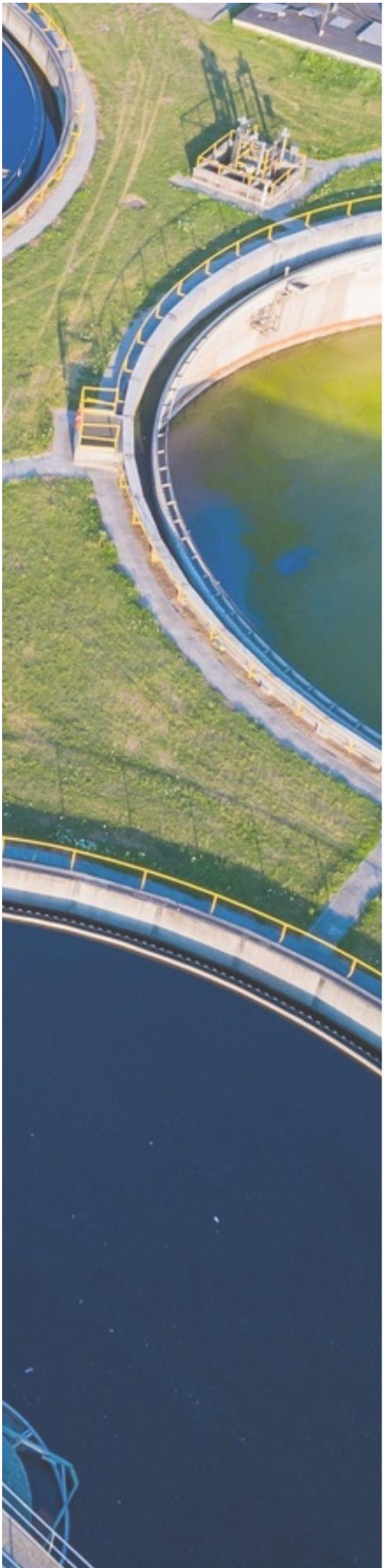

European Regional Development Fund

EUROPEAN UNION

Less is More

Energy-efficient technologies for removal of pharmaceuticals and other contaminants of emerging concern

Deliverable 4.1 - Part II, Danish national report

Specific expert paper on treatment technology/efficiency for the Danish pilot plant

Deliverable 4.2

Specific expert paper on reuse of treated water

June 2021

CONTENTS

1 Foreword

This report is part of the project LESS IS MORE - Energy-efficient technologies for removal of pharmaceuticals and other contaminants of emerging concern. The project was financed by the Interreg South Baltic Programme 2014-2020 through the European Regional Development Fund.

Partners in the project were: Lund University, Department of Chemical Engineering; Sweden Water Research AB, Kristianstad University, Slagelse Utility (SK Forsyning), Slagelse Municipality, JSC "Kretinga Water" and Gdansk Water Fund.

The project started 1st of January 2018 and completion date was 30th of June 2021.

The specific project objective was to demonstrate, test and validate - new technological solutions for removing pharmaceuticals and other CECs as well as antibiotic-resistant bacteria that are suitable for small and middle sized WWTPs, and to disseminate information on new technologies to the end-users.

This paper is reporting the treatment technology/efficiency for the Danish pilot plant which is one out of three national reports within Deliverable 4.1. This paper also includes the reporting of the expert paper for reuse of treated water (see Chapter 11), which is one out of two deliverables within Deliverable 4.2.

The activities in Slagelse have been carried out by:

- Jan Jørgensen (Slagelse Utility)
- Lillian Pia Munkholm Wismann (Slagelse Utility)
- Anders Mark Jensen (Slagelse Utility)
- Nikolaj Mikkelsen (Municipality of Slagelse)
- Bodil Mose Pedersen (DHI)
- Ulf Nielsen (DHI and Ultraaqua after December 2020)

This report was prepared by Ulf Nielsen, DHI/Ultraaqua and Bodil Mose Pedersen, DHI in close collaboration with Slagelse Utility and Slagelse Municipality.

Copenhagen, March 23, 2020

2 Summary

Slagelse WWTP is a conventional urban WWTP (125,000 PE) based on activated sludge with N and P removal, which treats all wastewater from Slagelse City (34,000 inhabitants). The treated wastewater is released to a small stream (Tude Å), which runs 10 km before it ends up in The Great Belt. Several micropollutants in the treated wastewater are exceeding the predicted no-effect concentrations ($PNEC_{Freshwater}$) in the stream. Among these are benzotriazole, diclofenac, tramadol and venlafaxine.

On this basis, Slagelse WWTP has decided to implement full-scale advanced treatment to remove micropollutants and pathogens before 2025. In 2019, as part of the present project, Slagelse WWTP constructed a large-scale pilot plant to pre-test methods for the future full-scale solution. The objective was to clarify whether a relatively simple post-treatment, based on particle filtration followed by a granular activated carbon (GAC) filter and UV, could reduce the micropollutant concentrations below the effect levels.

The construction of the large-scale pilot plant and the testing of methods were carried out within the present EU Interreg South Baltic project: LESS is MORE. Within the project experiences have been shared between pilot plants in Sweden and Lithuania.

The large-scale pilot plant is treating the conventional WWTP effluent. The pilot plant process train consists of a drum filter (10 µm) followed by a GAC filter (bed volume: 17 m^3) and finalised by UV treatment (> 40 mJ/m^2). The plant was put in operation in January 2019. The 1.5-year test period ended in August 2020. The plant is in ongoing operation (December 2020).

The plant treats 30 m^3/h, which corresponds to 8% of the average dry weather effluent from Slagelse WWTP. Empty bed contact time (EBCT) in the GAC filter was between 34 and 41 minutes. During the test period, 253,000 m^3 or 14,882 bed volumes (BV) were treated by the pilot plant GAC filter. DOC was measured between 7-9 mg/l in the Slagelse WWTP effluent. The GAC filter was loaded with reactivated GAC (0.42-2.8 mm), which has a CO_2-footprint 6 times smaller than conventional virgin GAC.

The wastewater was analysed for conventional wastewater parameters, micropollutants (44 selected pharmaceuticals, industrial pollutants and pesticides) and bacteria (total counts, *E. coli*, enterococcus) plus antibiotic resistant bacteria (Vancomycin resistant enterococci (VRE), carbapenem resistant enterobacteria (CPE) and cephalosporin resistant *E. coli* (CEF)) before and after treatment. The 44 micropollutants were analysed by Kristianstad University (34 parameters) and Institut für Energi- und Umwelttechnik e.V. (10 parameters).

All 44 analyzed micropollutants were measured above the limit of quantification in the effluent from the conventional Slagelse WWTP during the test period. 14 micropollutants[1] were measured above the $PNEC_{Freshwater}$ in the WWTP effluent. These 14 substances were considered as main target for the pilot plant treatment.

Figure 2-1 illustrates the overall removal of the 14 substances from the inlet of the conventional WWTP to the outlet of the pilot plant after UV treatment. It was observed that the removal rate of these substances was 46% in the conventional WWTP. After the pilot plant, a removal of more than 99% was measured with fresh GAC (BV 969), and after 1.5-year and BV 14,882 a total removal rate above 90% was still observed.

[1] Azithromycin, benzotriazole, bisphenol A, ciprofloxacin, clarithromycin, diclofenac, estrone, methylbenzotriazole, oxazepame, PFOS, propranolol, sertraline, tramadol and venlafaxine.

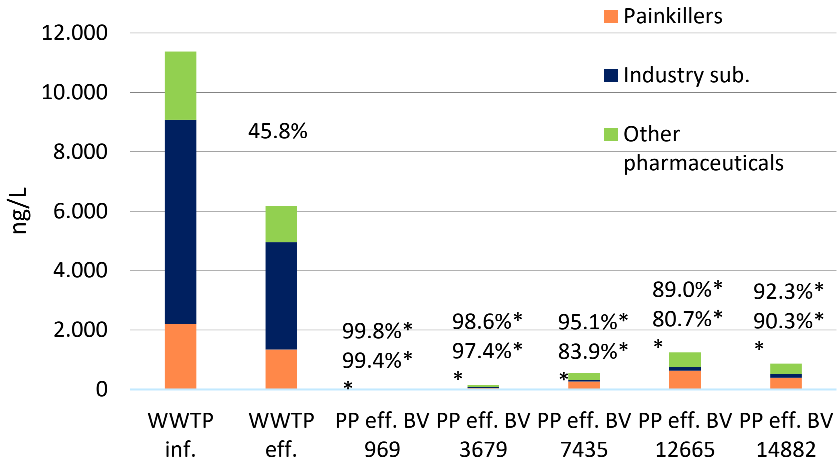

Figure 2-1: Sum of concentrations of the 14 critical micropollutants from influent to conventional WWTP to effluent of pilot plant after growing number of BV through GAC filter. * Reduction of total concentration relative to WWTP inf. ** Reduction relative to WWTP eff.

Six substances (azithromycin, diclofenac, PFOS, tramadol, sertraline, and venlafaxine) were measured above the $PNEC_{Freshwater}$ values during the 1.5-year test period. No substances were measured above $PNEC_{Freshwater}$ when the activated carbon was all fresh (BV 969). The six substances broke through the GAC filter step wisely. Finally, at BV 14,882 five substances were measured above $PNEC_{Freshwater,}$

Common to the six substances, except sertraline and only partly PFOS, was that at the last two sampling times (from 14,192 BV to 14,882 BV) the removal rates increased. The same pattern was observed for the sum of concentrations of the 14 substances (See Figure 2-1).

The observations during the test period did not give any clear explanations of the mechanisms involved with improved GAC removal. The EBCT was not increased during the last period and could not explain the improvement. A possible explanation could be increased biofilm growth in the GAC. The last two samplings took place in July to August 2020, when temperature increased and might have initiated enhanced biofilm growth leading to changed adsorption capabilities or possible biological degradation. More investigations are needed to clarify further.

DOC equivalent (DOCeq) was measured by an online optical sensor. DOCeq results followed the removal rate of the majority of the critical micropollutants. DOCeq measurements might be used as a rough surrogate parameter to monitor the removal of micropollutants.

The analysis of microbial parameters showed that total counts, *E. coli* and enterococcus were reduced to below the Danish drinking water quality criteria /12/ in the pilot plant effluent. Antibiotic resistant bacteria (VRE, CPE and CEF) were reduced to below limit of detection. The pilot plant effluent also complies with class A (the tightest requirements) of the EU regulation for water reuse for agricultural irrigation /13/.

The average energy consumption during operation of the pilot plant was 0.24 kwh/m^3. The total investment for the pilot plant, including carbon usage, was 210,000 EUR. The number of man-hours spent for maintenance of the pilot plant was approximately four hours per week.

The present large-scale pilot plant is to be seen as a pre-test and development for implementation of the future full-scale solution. In November 2020, Slagelse Utility has received approval for funding from the Danish EPA to establish an expansion of the pilot plant. The expansion will cover testing and development of advanced oxidation processes (AOP) and ozonation in combination with the existing process train. The objective is to develop targeted processes to remove the few last micropollutants, which break through the GAC filter, and hereby extend the performance and lifetime of the GAC filter.

Seen in this perspective it is not possible now to lay down a fully covering estimate of the future economy for polishing wastewater at Slagelse WWTP. But based on the present preliminary experiences it is possible to give an estimate for the future costs of the full-scale implementation. The estimate is based on a linear write-off of the investment cost over 15 years. Including electricity consumption and manpower for maintenance, the total estimate sums to 0.088 EUR/m^3 (0.66 DKK/m^3).

The project has shown that it is possible by a relatively simple post-treatment setup based on particle filtration, GAC (with low CO_2-footprint reactivated GAC) and UV to reduce the critical micropollutants by more than 90%. But in order to steadily and cost-efficiently reduce all micropollutants to the no-effect-concentrations ($PNEC_{Freshwater}$) it is suggested to supplement the process setup with AOP and ozonation processes before and after GAC. This will be developed and tested in a follow-up project in 2021.

3 Introduction

3.1 Slagelse wastewater treatment plant

Municipality of Slagelse is situated in West Zealand as illustrated in Figure 3-1. The municipality has 79,000 inhabitants.

Figure 3-1: Municipality of Slagelse (from Google Maps)

Slagelse WWTP is owned and operated by Slagelse Utility (SK Forsyning A/S). Slagelse Utility is a public owned multi-utility company delivering power, gas, district heating, water and wastewater treatment. Slagelse Utility operates three large scale WWTPs as well as 24 smaller WWTPs.

Slagelse WWTP treats all wastewater from Slagelse City, which has 32,000 inhabitants. Slagelse WWTP is a conventional WWTP with activated sludge with nitrogen and phosphorous removal. The capacity is 125,000 PE, and the daily load is approximately 60,000 PE. Total flow per year is typically 4,000,000 m^3.

An overview process diagram is shown in Figure 3-2 and aerial photo in Figure 3-3. The average sludge retention time is 13 days, and the hydraulic retention time in the biological step is about 49 hours. An extra separate biological step – the Activated Return sludge Process (ARP) - treats the reject water. The ARP consists of concentrated activated sludge, and the retention time in the ARP is estimated to about 30 days.

The conventional biological Slagelse WWTP reduces COD by 97%, BOD by 99%, total nitrogen by 91% and total phosphorous by 94%.

Biogas is produced from primary and surplus sludge, and the dewatered sludge is disposed in agriculture.

The treated wastewater is discharged to the nearby stream, Tude Å (for more details, see section 7.7)

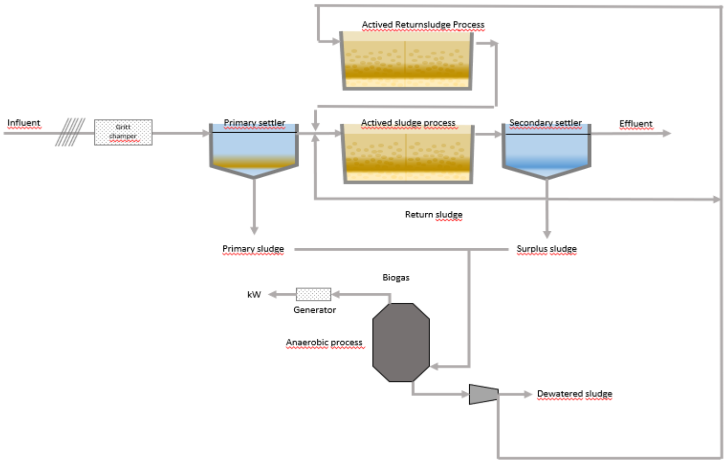

Figure 3-2: Overview process diagram of Slagelse WWTP

Figure 3-3: Aerial photo of Slagelse WWTP (from www.krak.dk)

3.2 Water area Tude Å

The treated wastewater from Slagelse WWTP is discharged to the stream named Tude Å. Before discharge to Tude Å the treated wastewater runs through a lagoon area which also contains urban run-off from Slagelse City.

From Slagelse City the stream runs approximately 10 km to the marine area, The Great Belt. Figure 3-4 shows photos from the stream.

Figure 3-4: Photos from the water area named Tude Å. The stream winds its way to The Great Belt.

4 Chemical analysis for pharmaceuticals and industrial chemicals

Pharmaceuticals constitute a large group of substances, and there are several hundred approved active substances (APIs) on the market. To be able to analyse and identify drugs in environmental samples, a number of different techniques and methods have been developed at different laboratories. Over the years the list has grown, and methods have been added. It is not uncommon for a method to involve analysis of up to 100 substances. The consequence of these so-called multi-methods is on one hand more results that describe the presence of drugs in the environment, on the other hand the many substances to be analysed leading to increased complexity, which can cause higher measurement uncertainty and lower method sensitivity in turns. The comparability of different analysis can also be made more difficult if the same substances are not measured in the different methods.

Within this project a number of micropollutant were selected to be analysed. The chosen substances were selected based on the answers given to the following questions:

- What are the typical concentrations of pharmaceuticals emerging from a sewage treatment plant?
- Which pharmaceuticals should be monitored in the present project?

The discussions emerged in a list of 35 compounds, which was the starting point for the analysis task. During the project the list was somewhat modified.

4.1 Analytical method

Special sample preparation and analysis techniques are required to be enable analysis of pharmaceutical residues and other organic micropollutants (OMPs) in water samples, which often occur in low to very low concentrations. During sample preparation, the OMPs are separated and concentrated. Furthermore, background-disrupting substances such as humic acid are separated from the sample.

Two common sample preparation techniques in environmental analysis are LLE (Liquid Liquid Extraction) and SPE (Solid Phase Extraction). In organic trace analysis of polar to semipolar micro-pollutants, it has almost become standard to use SPE. When SPE is used, the micro-contaminants are transferred to an adsorbent consisting of a polymer enclosed in a sample cartridge. After extraction, the samples are eluted with a suitable organic solvent(s). The samples are then evaporated and transferred to special sample vials pending final analysis.

Analysis of the samples is done by chromatography in combination with mass spectrometry, called HPLC-MS/MS or GC-MS/ MS, depending on whether the chromatography takes place with a liquid column (HPLC) or a gas column (GC). Within this project only HPLC-MS/MS was used. In the literature, the analytical chain is often shortened to SPE-HPLC-MS/MS.

4.2 Sample preparation

At MoLab, Kristianstad University specific techniques for sample preparation have been invented, and unique analysis methods have been developed for optimized analysis of polar to semipolar micro-pollutants /22/.

The special sample processing technology, which has been developed and used in the analysis in this project, enables analysis of the entire water sample, without filtration through a 0.45 µm filter which is otherwise usually the case /24/. A detail in the developed technology is a sand filter which is placed in the SPE column and which is then kept throughout the analysis chain. The EU's watch list states that "In order to ensure comparable results from different Member States, all substances must be monitored in whole water samples.". The method, which includes analysis of most of the constituent micro-pollutants in the study and which is based on the technology above, was published in its entirety in the work “High Flow-Rate Sample Loading in Large Volume Whole Water Organic Trace Analysis Using Positive Pressure and Finely Ground Sand as a SPE-Column In-Line” /24/.

4.3 Final analysis UPLC MS/MS

As previously mentioned, so-called multi-methods developed for the final analysis in HPLC-MS/MS risk being subject to a number of analytical compromises because they have to handle a large number of substances with large chemical differences. A large part of the compromise ends up in the chromatography part (HPLC) when only one method and column is used, almost exclusively performed using an acidic buffer. To reduce the element of compromise, MoLab's UPLC-MS/MS method is instead based on three individual chromatographic methods - an acidic-, a basic- and a neutral method, each of which has its own column. During method development, each compound is evaluated for chromatographic conditions and mass spectrometric optimization. The strategy makes better use of the full potential of a UPLC-ESI-MS/MS system and is thus better adapted to cover assorted chemical differences, which minimizes the number of compromises and contributes to more robust and more flexible methods with higher analytical sensitivity.

Each sample is injected three times (1 + 1 +10 µl), and the total analysis time is 6.5 + 6.5 + 8 = 21 min, including washing of the system and equilibration of the column between individual injections. The method for the UPLC MS/MS part is published in the work “Increased electrospray ionization intensities and expanded chromatographic possibilities for emerging contaminants using mobile phases of different pH” /23/. The methods are validated according to the standard method, 1694 /25/,

5 Slagelse WWTP - Characterization of wastewater

The measured effluent flow from Slagelse WWTP in one year from September 2019 to the end of August 2020 is illustrated in Figure 5-1. Measured precipitation in the same period is illustrated for comparison. High effluent flows follow large amounts of precipitation. This is due to combined sewer system in the old parts of Slagelse City.

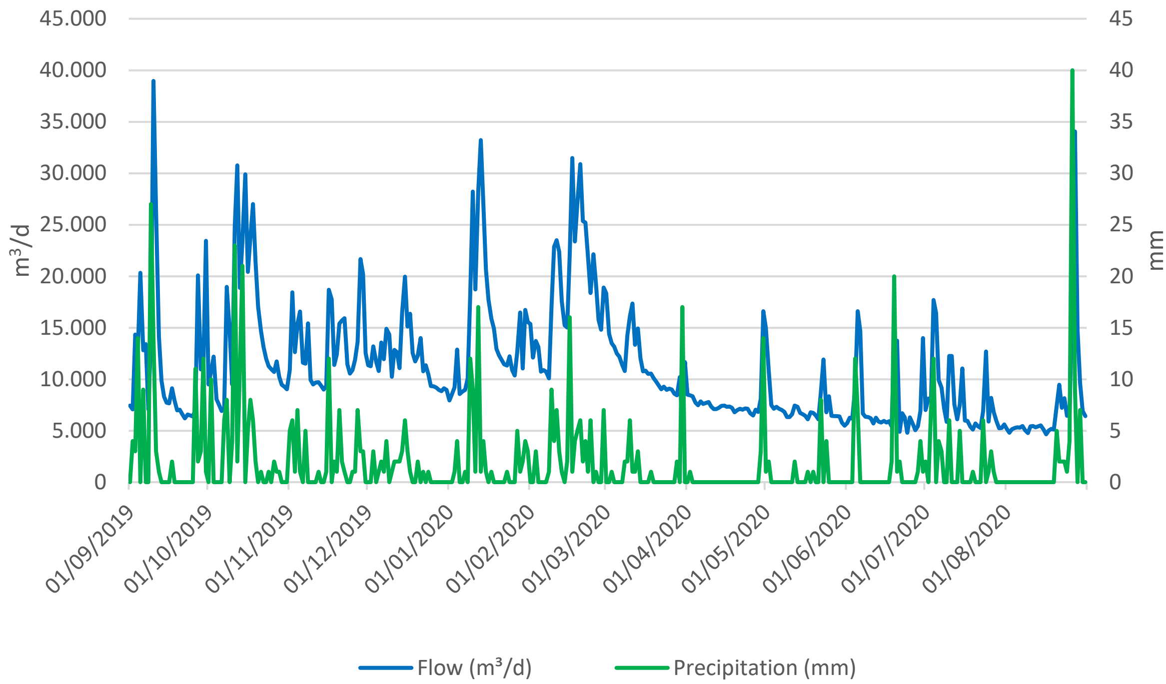

Figure 5-1: Measured effluent flow (m^3/d) and precipitation (mm) from Slagelse WWTP from September 2019 to August 2020.

Table 5-1 shows data for the effluent water flow from Slagelse WWTP. The average daily dry weather flow in this period was 8,843 m^3. The minimum dry weather daily flow was 4,647 m^3. The pilot plant treats approximately 720 m^3/d. This is between 6.5 and 16% of the daily dry weather flow and 8,1% of the average dry weather flow.

Table 5-1: Effluent flow from Slagelse WWTP from September 2019 to August 2020 (m^3/d). Dry weather flow only includes days without registered precipitation (= 0 mm)

m^3/d	Average	Min.	Max.	Std.d.
Dry weather	8,843	4,647	29,900	3,585
All year	11,275	4,647	38,964	5,909

The analysed operational parameters (BOD, COD, Total-N and Total-P) in effluent from Slagelse WWTP are illustrated in Figure 5-2 and Figure 5-3. The daily flow is illustrated for comparison in both figures. Summary numbers are shown in Table 5-2, where the observed numbers also are compared with the Danish quality standards for discharge to fresh water areas /16/.

COD and BOD are observed to comply with the Danish quality standards all year round. COD is observed in a higher level in the spring and summer period where the wastewater is more concentrated. Low values are observed in relation to high flows due to dilution from urban runoff. BOD is observed in stable low concentration with an average of 2.9 mg/l.

Total-N and Total P are observed to comply with the Danish quality standards on average but to exceed the standards in peak values. The exceeding's are primarily due to a large reconstruction of the aeration systems in the process tanks from February to September 2020. From time to time the volume of the process tanks has been half of its normal volume.

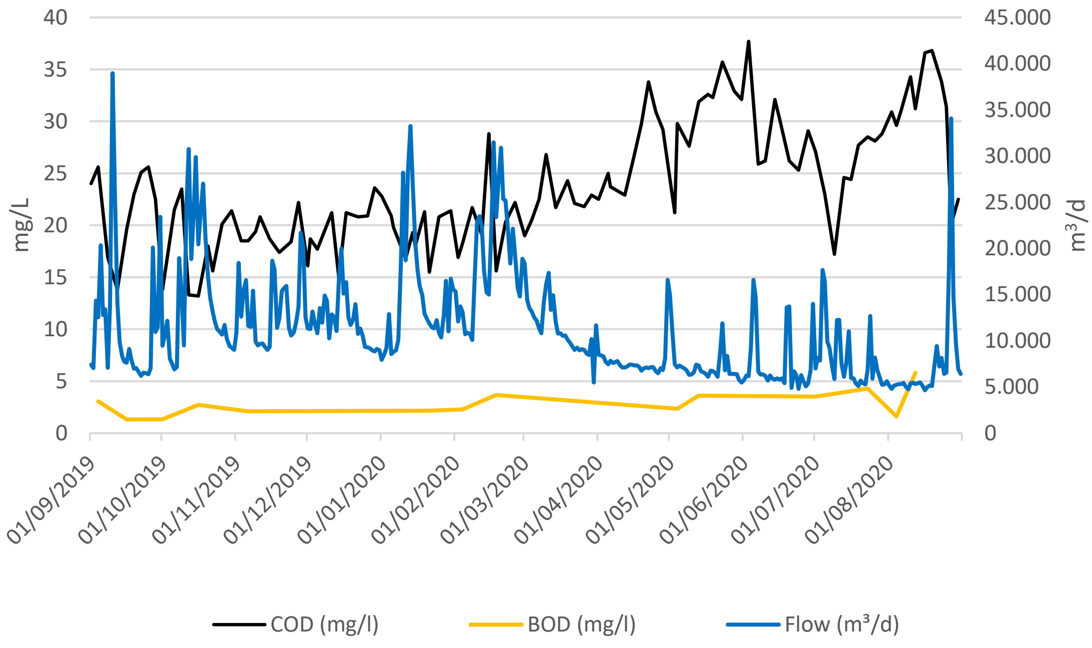

Figure 5-2 Measured COD and BOD (mg/l) in effluent from Slagelse WWTP from September 2019 to August 2020. Effluent flow (m^3/d) is illustrated for comparison

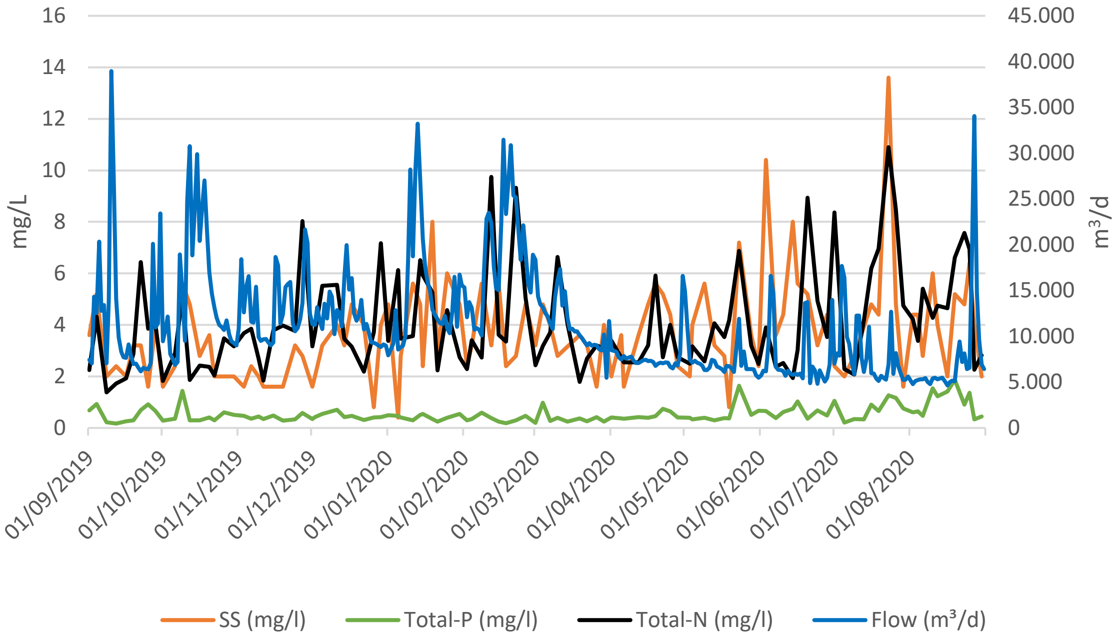

Figure 5-3 Measured SS, Total-N and Total-P (mg/l) in effluent from Slagelse WWTP from September 2019 to August 2020. Effluent flow (m^3/d) is illustrated for comparison

From Table 5-2 it appears that from time to time Total-N and Total-P concentrations in the effluent exceed the Danish quality standards. The reason can be explained by precipitation in the catchment, which is followed by high influent flow, reduced treatment efficiency and probably sludge drift.

Table 5-2: COD, BOD, SS, Total-N and Total-P in effluent from Slagelse WWTP from September 2019 to August 2020 (mg/l). Values above general Danish quality standards are highlighted /16/.

mg/l	Samples (n)	Average	Min.	Max.	Std.dev.	Quality standards
COD	108	23.8	13.2	37.7	5.8	75
BI_5	14	2.9	1.3	5.8	1.3	15
SS	107	4.0	0.4	33.2	3.4	-
Total-N	108	4.1	1.4	10.9	2.0	8
Total-P	108	0.54	0.17	1.9	0.34	1*

‘) >100.000 PE the concentration must not prevent compliance with environmental standards for the water area

Four times during the test period a sample was taken from the influent and analyses of 44 micropollutants including four neonicotinoids and six contrast media were carried out (see Table 5-3). Twenty parameters exceed on average, $PNEC_{Fresh\ water}$. The maximum concentrations were exceeded for 21 parameters.

Table 5-3: Concentrations of pharmaceuticals in influent to Slagelse WWTP. Concentrations exceeding $PNEC_{freshwater}$ are in orange colour.

ng/l	Number	Number> LOQ	Average	Min	Max	Std.dev.	LOQ	PNEC
Amisulprid	1	1	271	271	271		1	5,000
Atenolol	4	4	415	67	618	258	2	100,000
Azithromycin	4	4	205	9	530	225	2	19
Benzotriazole	4	3	4,634	2,406	8,885	3,683	2	900
Bisphenol A	4	4	409	62	726	274	10	100
Carbamazepine	4	4	390	210	551	139	1	500
Ciprofloxacin	4	4	358	13	565	259	10	89
Citalopram	4	4	326	152	550	190	1	8,000
Clarithromycin	4	4	424	48	774	320	2	120
Diclofenac	4	4	517	381	740	156	2	50
Erythromycin	4	3	66	n.d.	156	72	1	200
Estrone	4	4	44	3.8	90	36	0.2	3.6
Fluconazole	4	4	361	230	595	167	0.3	57,000
Furosemide	4	4	3,710	100	8,579	3,601	5	31,300
Hydrochlorothiazide	1	1	52	52	52	n.r.	10	143,000
Ibuprofen	4	3	26,591	n.d.	88,883	41,787	100	4,000
Irbesartan	1	1	412	412	412	n.r.	2	704,000
Ketoconazole	4	4	83	4	202	87	10	100
Losartan	4	4	1,975	867	3,551	1,186	1	245,000
Methotrexate	4	3	11	n.d.	25	11	2	260,000
Methylbenzotriazol	1	1	1,800	1.800	1,800	n.r.	20	1,000
Metoprolol	4	4	1,174	828	1,916	500	2	62,000
Naproxen	4	4	2,898	185	5,733	2,298	10	1,700
Oxazepame	4	4	575	343	752	202	1	500
Paracetamol	4	4	52,408	7	109,626	44,838	2	9,200
PFOA	4	4	6.9	1.1	13	6	1	48
PFOS	4	4	31	6,5	69	27	2	0.65
Propranolol	4	4	98	23	189	69	2	20
Sertraline	4	4	104	2,7	207	93	1	1
Sulfamethoxazole	4	4	152	31	214	82	2	118
Tramadol	4	4	1,688	874	3,781	1,399	1	100
Trimethoprim	4	4	593	201	1.462	585	1	62,000
Venlafaxine	4	4	489	182	1.190	476	1	100
Zolpidem	4	3	2.1	n.d.	5.5	2	1	2,200
Acetamiprid	4	2	0.8	n.d.	2.3	1.1	0.2	500
Clothianidin	3	1	8.2	n.d.	25	14	1	130
Imidacloprid	4	4	49	13	76	27	2	8.3
Thiamethoxam	3	1	145	n.d.	434	251	1	42

(cont'd)

ng/l	Number	Number> LOQ	Average	Min	Max	Std.dev.	LOQ	PNEC
Amidotrizoic Acid	1	0	< 30	< 30	< 30	n.r.	30	143,000
Iohexol	1	1	85,000	85,000	85,000	n.r.	90	1,000,000
Iomeprol	1	1	5,700	5,700	5,700	n.r.	50	1,000,000
Iopamidol	1	0	< 50	< 50	< 50	n.r.	50	410,000
Iopromide	1	0	< 50	< 50	< 50	n.r.	50	1,360,000
Ioversol	1	1	2,600	2,600	2,600	n.r.	50	3,686,000

n.d. not detected
n.r. not relevant

6 Pilot Plant

6.1 Plant layout, processes, and sampling points

A large-scale pilot plant for polishing of biological treated wastewater has been established at Slagelse WWTP. The location of the pilot plant at the WWTP site is shown in Figure 6-1 (red circle at the figure).

Figure 6-1: Location of the large-scale pilot plant at Slagelse WWTP

Form the outside, the large-scale pilot plant consists of a 17 ft. container and an 8.7-meter-high cylinder, which contains the GAC (granular activated carbon). The pilot plant is shown in Figure 6-2.

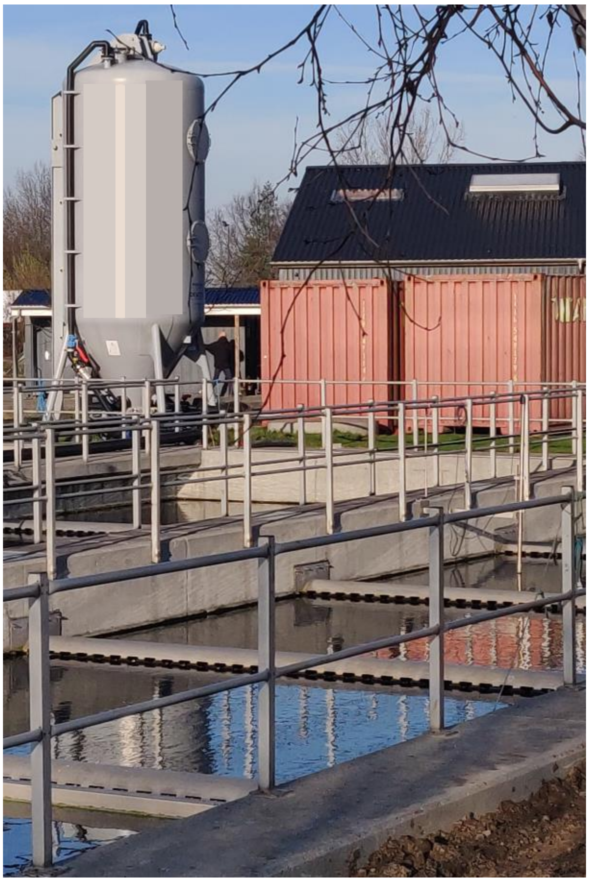

Figure 6-2: Large-scale pilot plant at Slagelse WWTP

The overall treatment concept consists in polishing of the biologically treated wastewater through adsorption of pharmaceuticals and other micro pollutants in a column packed with granular activated carbon (GAC). The GAC column is sensitive to SS (suspended solids) in the feed water, as SS can more or less clog the column, reducing the capacity for adsorption of micropollutants. Even at treatment plants with good performing secondary sedimentation tanks, a level of 10-15 mg SS/l would be typical, and at increased flows during rain the concentration of SS in the overflow may increase. An important part of the treatment concept is therefore to pretreat the wastewater with the aim of intensive removal of SS prior to GAC treatment.

The pilot plant is dimensioned to treat 30 m^3/h or 720 m^3/d. The plant consists of a drum filter with a micro screen (10 µm) followed by a GAC-filter and UV-radiation. Figure 6-3 shows a schematic process diagram of the plant. The wastewater is pumped from the secondary sedimentation tank to the drum filter. The screenings are pumped back to the WWTP inlet.

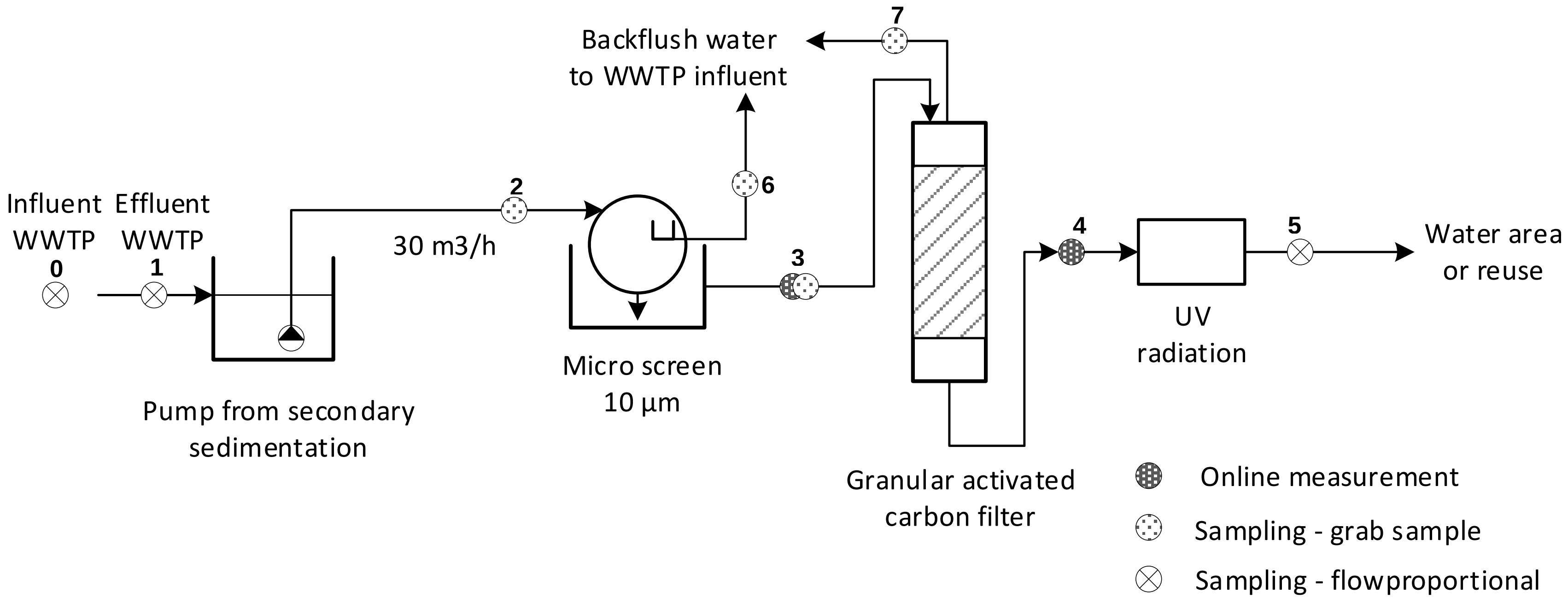

Figure 6-3: Outline of pilot plant in Slagelse including sampling points from 0 to 7.

The GAC filter dimensions and specifications are described in Table 6-1. The GAC-filter was supplied by Desotec. The filter was filled with reactivated Organosorb 20 from Desotec. The GAC-filter was backwashed with water from the secondary clarifiers. In the last part of the test period also pressurized air was added to the backwash water. See description of backwash-history in Section 6.2.

Table 6-1 Geometrical dimensions, hydraulic loading and GAC properties of the Mobicon 100 filter unit.

Mobicon 100 Design data	Properties	Unit
Design Flow	30.0	m^3/h
Filtration velocity	6.1	$m^3/m^2 \cdot h$
Empty Bed Volume	17.0	m^3
Empty Bed Contact Time	34.00	min
Cross sectional area	4.9	m^2
Bed height	3.5	m
Mass of Carbon	7480	kg
Bulk density of Carbon	480	kg/m^3
Particle density of Carbon	795	kg/m^3
Bed porosity	0.45	-
Organosorb 20 Particle Size	1.7 (0.42-2.8)	mm

The UV treatment system was supplied by Ultraaqua A/S. The reactor has 4 lamps (Model: MonoRay, 4-220 SS SwirlFlow LUVT). The design flow rate is 30 m^3/h, and the design UV dose was > 40 mJ/cm^2. The measured UV transmittance (UVT) of the Slagelse WWTP effluent was 70-75%.

6.2 Backwash and operational incidents

Backwash of the GAC filter took place six times during the test period from January 2019 to August 2020 (see Table 6-2). The backwash procedure takes between 30 and 45 minutes. 20 to 30 m^3 backwash water taken from WWTP effluent (from secondary clarifiers) was used. The last backwash on 07.07.2020 included flushing with pressurized air. The aim was to efficiently remove possible filter-channels, which develop with high certainty in GAC filters after longer periods of operation (see section 7.2). The procedure for flushing with air starts with 10 minutes backwashing with water followed by about 15 minutes with a combination of water and air. Finally, the filter is backwashed with water for 10-15 minutes.

Table 6-2: Backwash of the GAC filter during the test period

Backwash	BV	Comments
03-06-2019	2,323	Treated wastewater. Sampling of backwash water after 15 minutes
31-07-2019	3,769	Treated wastewater.
11-11-2019	5,987	Treated wastewater. Sampling of backwash water after 5 and 10 min.
04-03-2020	10,482	Treated wastewater
17-03-2020	11,044	Treated wastewater
07-07-2020	14,066	Treated wastewater and air

At Slagelse WWTP algae started to grow in the secondary clarifiers when the temperature increases in the spring. This resulted in blockage of the drum filter placed before the GAC filter. The filter cloth was cleaned every two weeks with acetic acid in periods where algae presence was a problem. In the summer 2020 a filter (2 mm pore size) was placed around the pump intake. Blocking of the drum filter was in this way reduced considerably, and clean of the drum filter cloth was not necessary thereafter.

6.3 Flow and bed volumes

During the test period from January 2019 to August 2020 about 253,000 m^3 wastewater from Slagelse WWTP was treated in the pilot plant. The volume equalizes nearly 14,900 bed volumes which have passed the GAC filter (see Table 6-3 and Figure 6-4). Most of the time the flow through the pilot plant varied between 25 and 30 m^3/h.

Table 6-3: Sampling date, bed volumes (BV) and accumulated flow on sampling date

Date	BV	Acc. Flow [m^3]
11-03-2019	969	16,481
05-04-2019	1,375	23,373
15-05-2019	2,054	34,916
06-06-2019	2,442	41,520
31-07-2019	3,769	64,074
09-09-2019	4,541	77,200
23-10-2019	5,498	93,461
12-11-2019	6,026	102,438
25-11-2019	6,521	110,862
18-12-2019	7,435	126,400
26-01-2020	8,944	152,047
27-01-2020	8,986	152,761
13-02-2020	10,322	175,470
11-03-2020	11,971	203,514
14-05-2020	12,665	215,301
10-06-2020	13,423	228,185
11-07-2020	14,192	241,267
25-08-2020	14,882	252,999

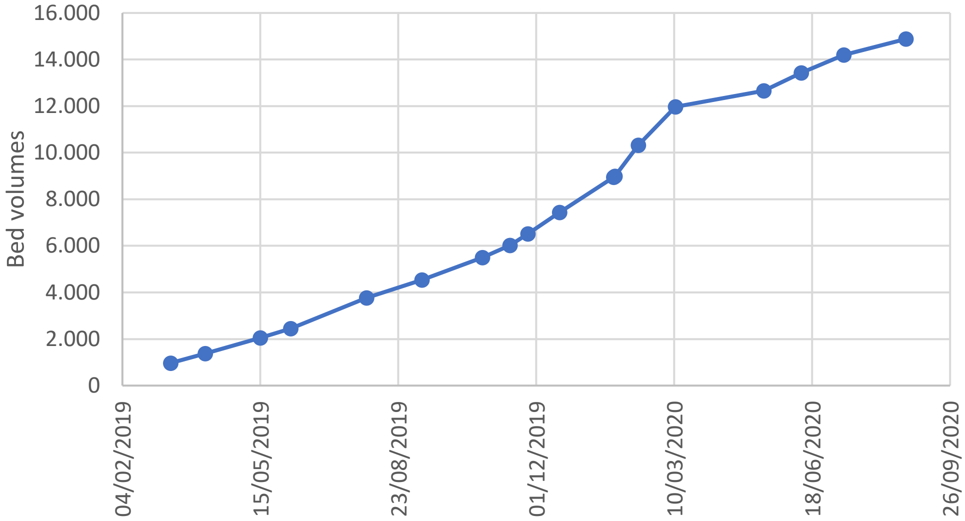

Figure 6-4: Accumulated flow during test period from January 2019 until end of August 2020.

6.4 Wastewater parameters

The pilot plant performance concerning the traditional wastewater parameters COD, Total-N and Total P is evaluated below. Measured COD in effluent from traditional WWTP (influent to pilot plant) and effluent from pilot plant is illustrated in Figure 6-5. It was observed that the influent to the pilot plant varied between 13 and 55 mg COD/l with an average of 25 mg/l and that the effluent was stabilized between 9 and 32 mg/l with an average of 18 mg/l.

Figure 6-6 shows the removal percentage of COD during the test period. During the test period the removal percentage of COD in the pilot plant was reduced by approximately 30% (from 50% to 18%, see Figure 6-6). In this period from February 2019 to August 2020 a total of 253.000 m^3 was treated, which corresponds to a load of14,882 bed volumes to the GAC filter. The pilot plant breakthrough is further discussed in Section 7.4.

It is observed that Total-N and Total-P are only slightly reduced in the pilot plant, as expected (see Figure 6-7 and Figure 6-8). The Total-N is reduced from an average of 4.1 mg/l to 3.5 mg/l in the effluent from the pilot plant. Peak values are reduced from above the environmental quality standard (8 mg/l – see Chapter 5) to below or close to the quality standard value.

The Total-P is also slightly reduced from an average of 0.5 mg/l to 0.4 mg/l in influent and effluent respectively. Until June 2020 peak values are reduced to below the environmental quality standard (1 mg/l). After June 2020, which is after treatment of approximately 220,000 m^3 or 13,000 BV, it is observed that the peak values are not reduced to the same degree.

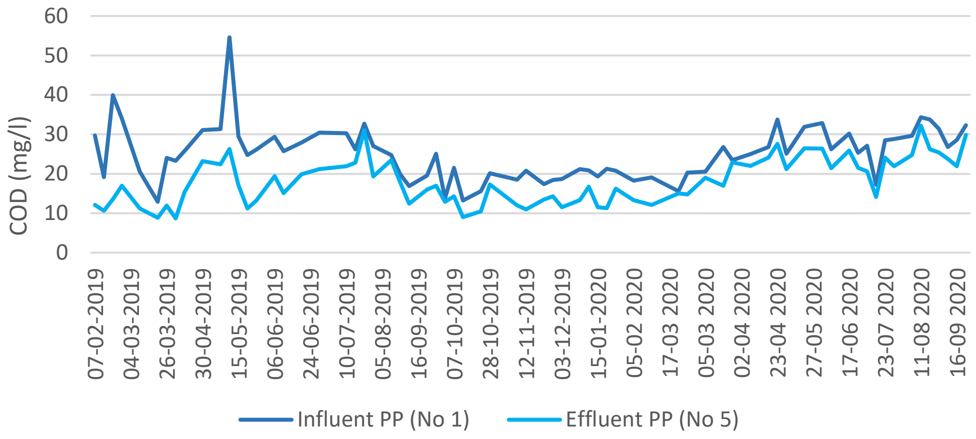

Figure 6-5: COD in influent (conventional WWTP effluent) and effluent from pilot plant

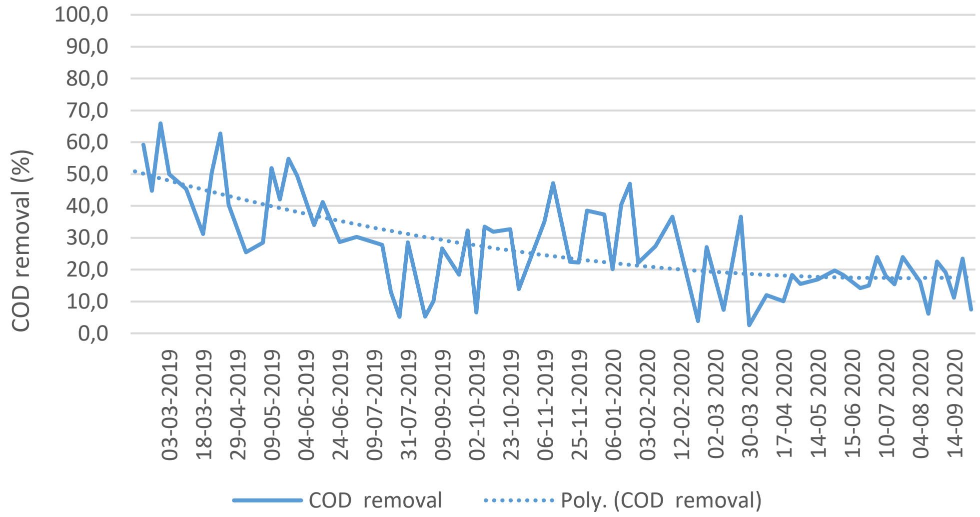

Figure 6-6: COD removal percentage in pilot plant. A polynominal (second order) trendline is illustrated by dotted line

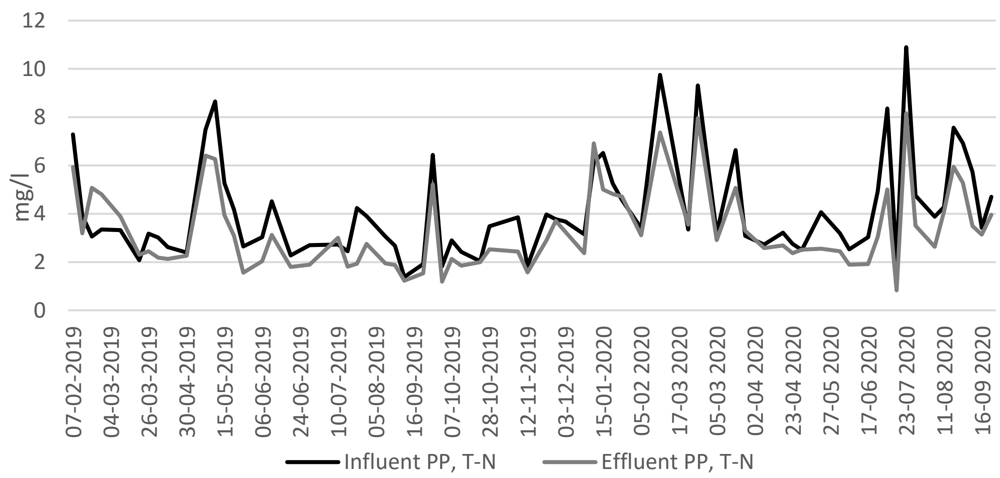

Figure 6-7: Total-N in influent (conventional WWTP effluent) and effluent from pilot plant

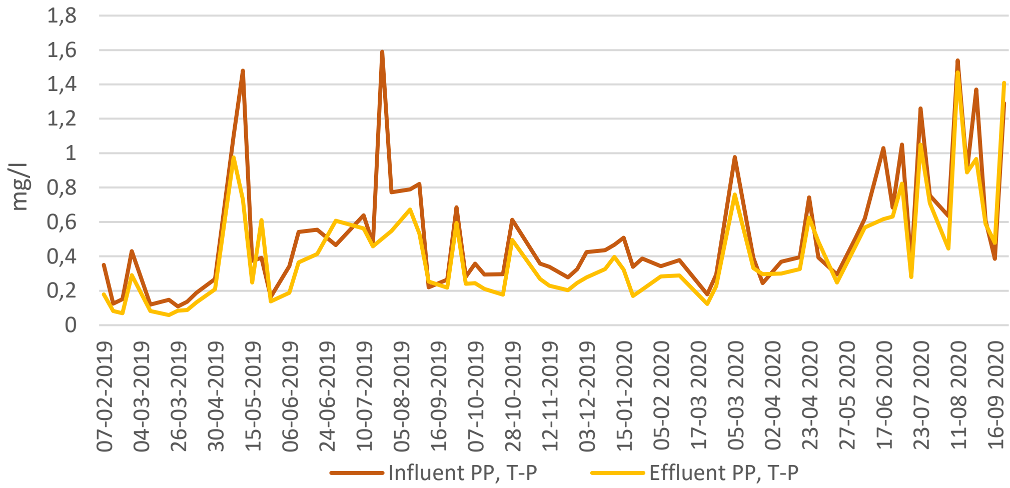

Figure 6-8: Total-P in influent (conventional WWTP effluent) and effluent from pilot plant

6.5 Measurements of DOC and $UV_{250\text{-}260}$

An online optical sensor manufactured by s::can Messtechnik GmbH was installed to measure at the inlet and outlet of the GAC filter. The sensor can measure an equivalent to DOC (DOC_{eq}) and can also measure traditional UV absorbance[2] The $UV_{250\text{-}260}$ was measured as an average of the wavelengths between 250 and 260 nm. To obtain the DOC_{eq} measurement, the absorbance of several specific wavelength(s) is transformed into concentrations through algorithms and calibration against data obtained by chemical analysis. The wavelengths and algorithms used for the different parameters (e.g. DOC_{eq}) are considered confidential and are only known by the manufacturer.

The water was collected by a Nuert volumetric rotary vane pump from sampling Point 3 and 4 (see Figure 6-3). A switch valve system secured that the water was passing the spectrophotometric measurement in 45 minutes or in 1-hour intervals. Figure 6-9 shows the online measurement setup at the pilot plant.

[2] The optical sensor also measured turbidity, $NO3_{eq}$, TOC_{eq} and “fingerprint” scan from 190-720 nm. These measurements are not included in this report

Figure 6-9: Pilot plant setup for online measurement of DOC (equivalent) and $UV_{250-260}$

Three measurement campaigns for DOC were carried out for the calibration of s::can measurements in January 2019, February 2019 and March 2020. Samples were collected as grab samples before and after the GAC filter. $UV_{250-260}$ and DOC_{eq} was measured by s::can. Table 6-4 presents the results and the calculated average removal of DOC in the GAC filter. The table also shows the calculated specific UV absorbance (SUVA[3]).

As expected, Table 6-4 shows that DOC was efficiently removed (by 91 and 64% respectively) at the beginning of the test period in January and February 2019 where the GAC was new. A year and 12,000 BV's later, the DOC removal was measured to 1%. This was also expected at this point due to GAC filter DOC saturation.

A preliminary laboratory scale test with the same GAC as used in the pilot plant was carried out as an RSSCT (Rapid Small-Scale Column Test) in January 2019 /6/. The RSSCT tests showed that DOC breakthrough reached 85% already at 1,800 BV, and the full DOC breakthrough was predicted to take place between 2,000 and 2,500 BV.

It can be stated that the specific UV absorbance (SUVA) is lower in the March 2020 sample (SUVA: 2.4 compared to 3.3 in the January and February 2019 samples), which indicates lower hydrophobicity. Changes in influent SUVA – which indicates the aromaticity of the DOC in the influent - might explain why GAC filter removal can vary also after expected filter saturation. If SUVA gets lower in the influent, the adsorption of DOC is also most likely to be reduced.

[3] SUVA = $UV_{250-260}$ divided by DOC and multiplied by 100

Table 6-4: External laboratory DOC measurements of samples from before and after GAC filtration. $UV_{250-260}$ was measured by s::can. Specific UV absorbance (SUVA) is calculated by dividing $UV_{250-260}$ by DOC.

			Before GAC (Po. 3)			After GAC (Po. 4)			Average
	Unit	Date	N	Average	Min-max	N	Average	Min-max	removal
DOC	mg/l	18.01.19	4	8.0	7.8 -8.2	4	0.75	0.7-0.8	91%
$UV_{250-260}$	cm-1	18.01.19	4	0.26	0.26-0.26	4	0.07	6.6-0.07	
SUVA	l/(mgDOC m)	18.01.19		3.3			9.3		
DOC	mg/l	07.02.19	2	8.9	8.7-9	2	3.2	3-3.4	64%
$UV_{250-260}$	cm-1	07.02.19	2	0.29	0.28-0.29	2	0.11	0.10-0.11	
SUVA	l/(mgDOC m)	07.02.19		3.3			3.4		
DOC	mg/l	05.03.20	2	7.1	6.8-7.3	2	7	6.4-7.5	1%
$UV_{250-260}$	cm-1	05.03.20	2	0.17	0.17-0.18	2	0.15	0,15	
SUVA	l/(mgDOC m)	05.03.20		2.4			2.1		

Figure 6-10 to Figure 6-12 shows examples of the online s::can measurement of DOCeq and $UV_{250-260}$ during the test period. The examples illustrate measurements from May 2019, May 2020 and August 2020. Table 6-5 summarises the removal rates of DOCeq and $UV_{250-260}$.

DOCeq was reduced from 40% in May 2019 to 14% in May 2020 and increased again to 21% in August 2020. $UV_{250-260}$ removal was reduced from 36% to 15% and did not increase again in August 2020 as clearly as DOCeq.

Figure 6-13 illustrates the development of DOCeq and $UV_{250-260}$ through the test period.

It is not possible to explain more exactly why removal of DOCeq and $UV_{250-260}$ differs. It is clear that the absorbance of the different wavelengths, which are used for DOCeq and $UV_{250-260}$, give different results in these water matrixes. The measurements of micropollutants shows that the removal rates for several of the critical substances were increased by the end of the test period (see Section 7.4). The measurement of DOCeq follows this pattern more clearly than $UV_{250-260}$. It can be concluded that the DOCeq seems to be a marginally better indicator for micropollutant breakthrough than $UV_{250-260}$.

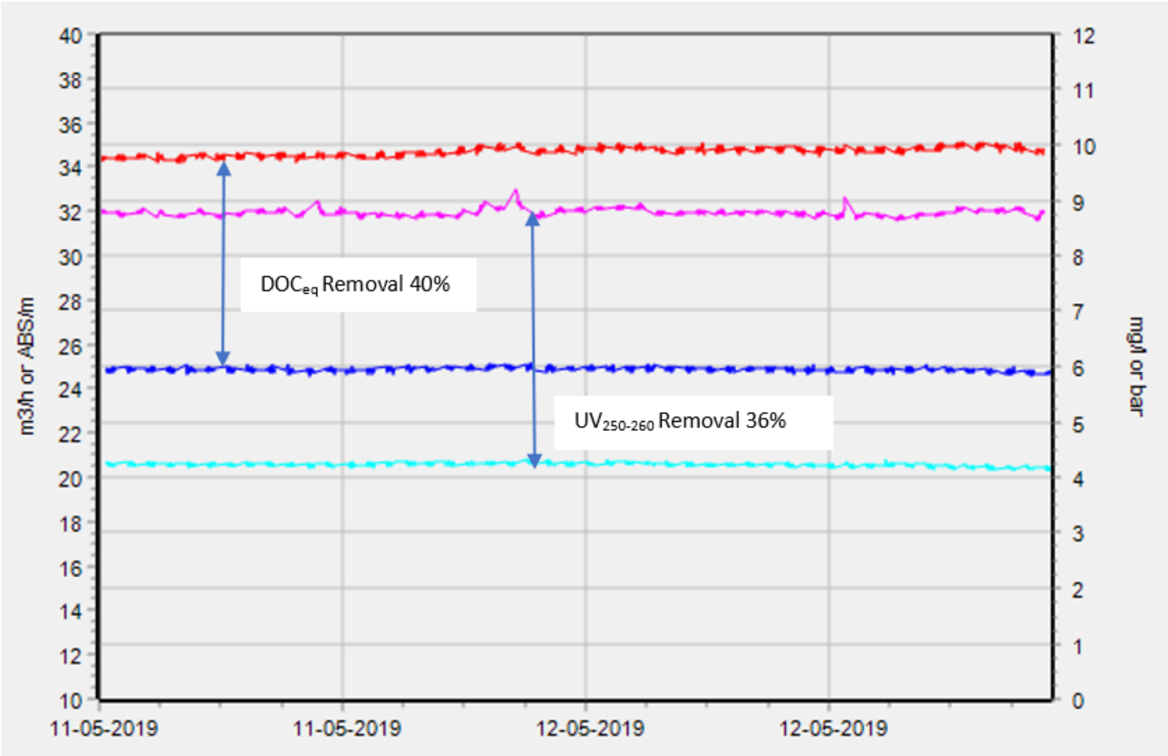

Figure 6-10: S:can measurements (DOCeq and $UV_{265\text{-}260}$ on 11.05.2019 after 1,917 Bed Volumes. Red=DOCeq in, blue= DOCeq out, violet= $UV_{250\text{-}260}$ in, turquoise=$UV_{250\text{-}260}$ out

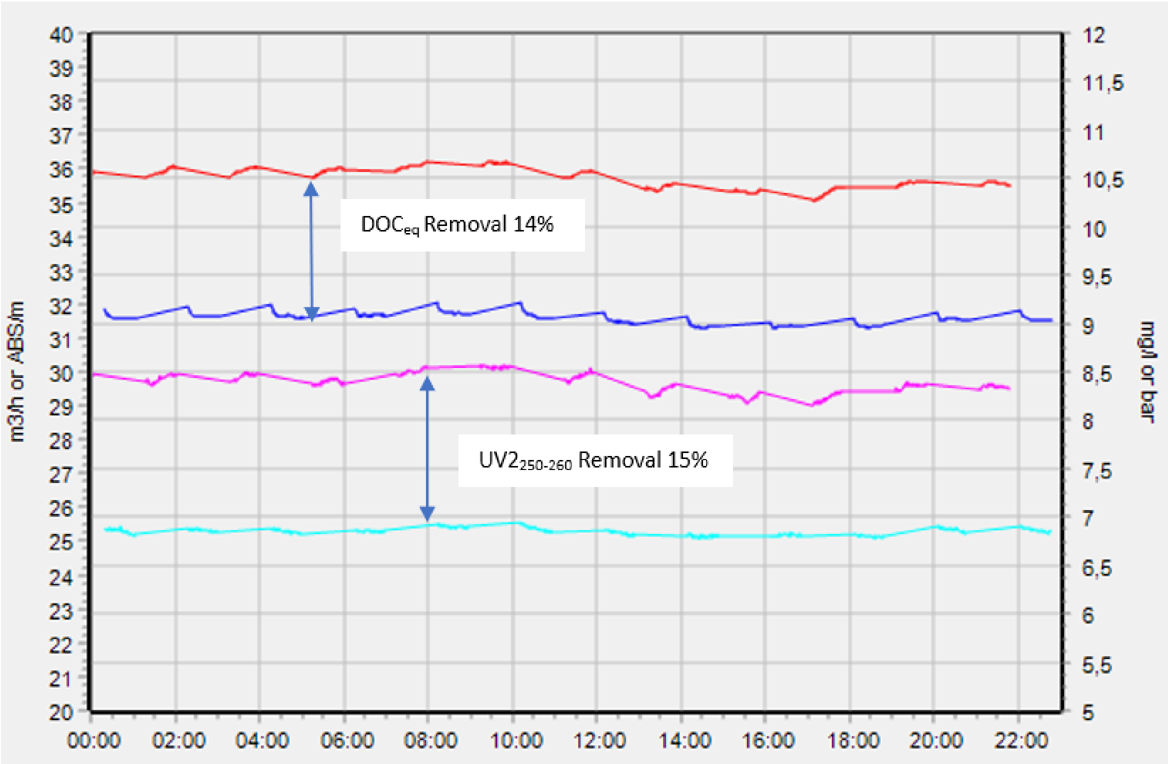

Figure 6-11: S:can measurements (DOC eq and $UV_{250\text{-}260}$) on 24.05.2020 after 12,932 Bed Volumes. Red=DOC_{eq} in, blue= DOC_{eq} out, violet= $UV_{250\text{-}260}$ in, turquoise=$UV_{250\text{-}260}$ out

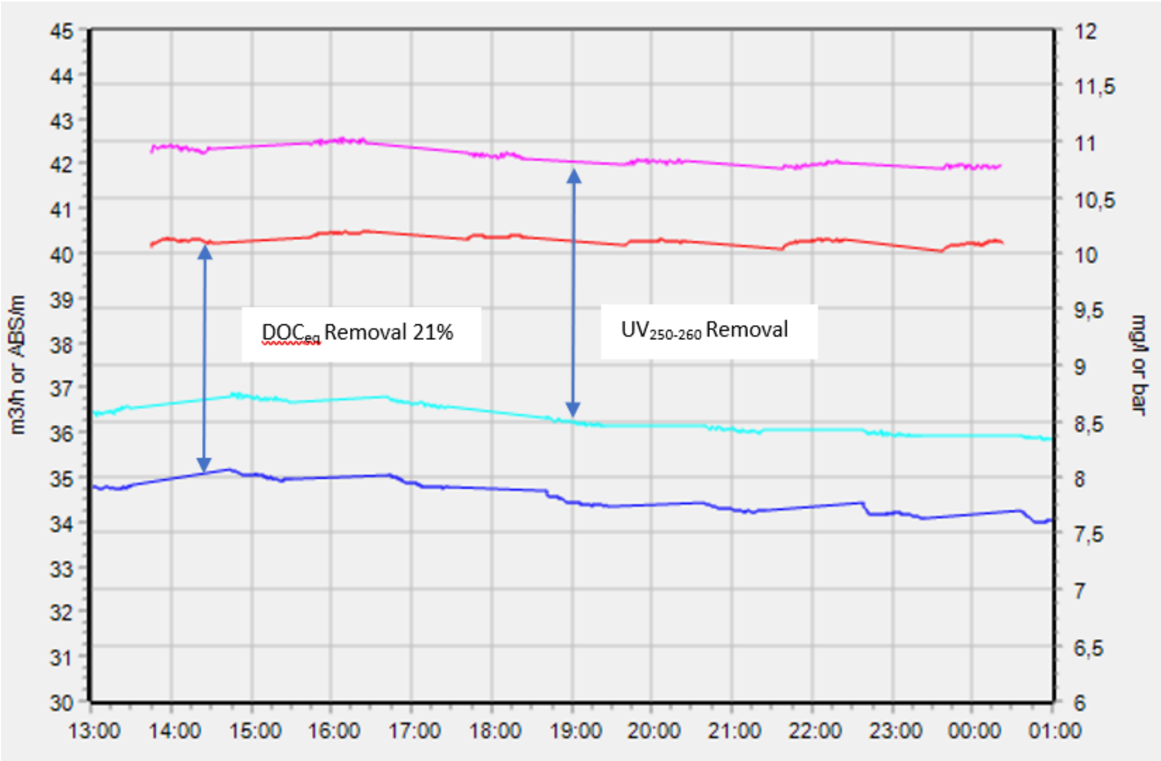

Figure 6-12: S:can measurements (DOC eq and $UV_{250-260}$) on 25.08.2020 after 14,882 Bed Volumes)

Table 6-5: S:can measurements (DOCeq and $UV_{250-260}$) and removal ratios shown in Figure 6-10, Figure 6-11, and Figure 6-12

Date	DOCeq % removal	UV250-260 % removal	Bed Volumes % removal
11.05.2019	40	36	1,917
24.05.2020	14	15	12,932
25.08.2020	21	15	14,882

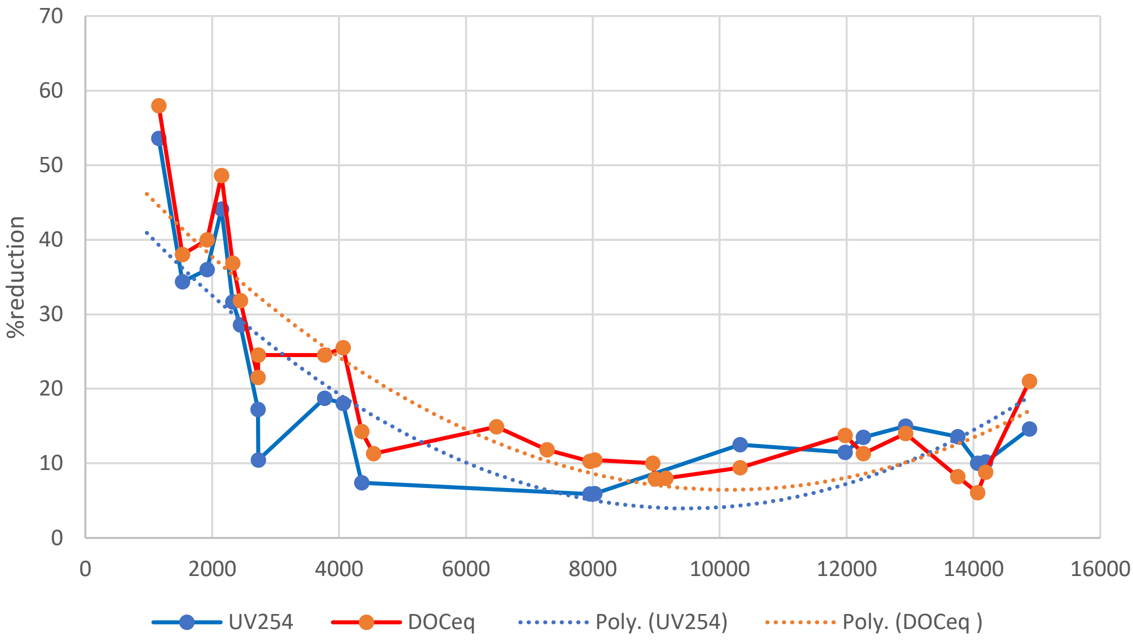

Figure 6-13: Development of reduction of $UV_{250-260}$ and DOC_{eq} are shown as a function of bed volumes. The dotted lines are trendlines shown as polynomials.

7 Pharmaceuticals and industrial chemicals

The analysis for pharmaceuticals and industrial chemicals were carried out during the test period from January 2019 to August 2020. Wastewater samples were collected from the sampling points described in Figure 6-3.

The wastewater sampling included 24-hours automatic flow proportional sampling of the influent to the WWTP (Point 0), effluent from the WWTP, which is also the influent to the pilot plant (Point 1) as well as the effluent of the pilot plant (Point 5). Sampling before GAC (Point 3) and backwash water from the GAC filter (Point 7) were carried out as spot sampling.

Altogether 44 different pharmaceuticals, industrial chemicals, pesticides and contrast media were analysed which led to 2,296 results (See Table 7-1). The sampling frequency varied through the test period. Kristianstad University analysed 37 parameters and Institut für Energi- und Umwelttechnik e.V. (IUTA) analysed 7 parameters, including contrast media.

Table 7-1: Analyses for micropollutants. Total number of samples analysed, and analysis carried out by Kristianstad University and IUTA. The number of analyses include influent to Slagelse WWTP, pilot plant,

	Number
Total number of analyses	2,296
Total number of analyzed parameters	44
Kristianstad parameters	37
IUTA parameters	7

7.1 Effluent from conventional WWTP (influent to pilot plant)

The influent to the pilot plant is the same water as the effluent of the WWTP. The sampling was carried out by the existing flow proportional sampler in Point 1 (see Figure 6-3). The measured influent quality is presented in Table 7-2.

Sooner or later, all parameters were measured to be higher than LOQ (Limit of Quantification). The measured concentrations are compared to PNECs for freshwater ($PNEC_{Freshwater}$). Numbers higher than $PNEC_{Freshwater}$ are highlighted. In total 16 substances were measured above $PNEC_{Freshwater}$. For 12 substances (including neonicotinoids) the average was higher than $PNEC_{Freshwater,}$ and for 3 substances only the maximum concentration was higher the $PNEC_{Freshwater}$.

A major industrial pollution incident resulted in momentarily very high concentrations of neonicotinoids. These substances are presented independently at the bottom of Table 7-2, and the results are discussed in Section 7.8.

Substances analysed by IUTA are marked with * in Table 7-2.

Table 7-2: Effluent from conventional WWTP (influent to pilot plant). Concentrations of pharmaceuticals and industrial pollutants. Neonicotinoids and contrastmedia are situated together in the bottom of the table.

Substance [ng/L]	Number >MLQ	Number	Average	Min.	Max.	Std.dev	MLQ	PNEC
Amisulprid	6	6	119.5	24.3	190.2	63.2	1	5,000
Atenolol	18	18	101.2	45.5	197.4	40.9	2	100,000
Azithromycin	18	18	179.8	67.4	432.6	110.9	2	19
Benzotriazole	18	18	2,773.5	1,227.8	4,570.0	940.7	2	900
Bisphenol A	18	18	54.6	19.3	133.3	26.4	10	100
Carbamazepine	18	18	280.1	145.3	493.0	110.8	0.5	500
Ciprofloxacin	16	18	63.4	0.0	138.4	38.8	10	89
Citalopram	18	18	138.3	59.1	295.4	61.3	1	8,000
Clarithromycin	18	18	100.8	38.9	256.4	53.5	2	120
Diclofenac	18	18	441.0	199.6	862.4	210.2	2	50
Erythromycin	18	18	69.2	15.8	191.3	55.3	0.5	200
Estrone	18	18	5.1	0.9	13.6	4.1	0.2	3.6
Fluconazole	18	18	229.9	101.2	345.6	78.2	0.3	57,000
Furosemide	18	18	1,631.7	696.8	3,121.4	717.9	5	31,300
Hydrochlorothiazide	6	6	43.9	22.4	67.0	18.2	10	143,000
Ibuprofen	7	18	153.1	n.d.	576.1	200.2	100	4000
Irbesartan	6	6	35.2	11.5	52.0	16.7	2	704,000
Ketoconazole	17	18	3.8	<LOQ	9.6	2.1	10	100
Losartan	18	18	822.2	398.4	1,427.1	328.5	1	245,000
Methotrexate	2	18	0.3	n.d.	3.0		2	260,000
Methylbenzotriazol*	8	8	876.3	140	3100	18	10	1,000
Metoprolol	18	18	832.9	492.5	1,361.9	256.7	2	62,000
Naproxen	18	18	243.9	53.9	478.9	119.6	10	1,700
Oxazepame	18	18	366.3	182.5	683.4	170.3	1	500
Paracetamol	13	18	175.5	n.d.	1944.6	467.4	2	9,200
PFOA	18	18	5.9	1.7	11.5	2.5	1	48
PFOS	18	18	15.4	3.3	38.9	10.0	2	0,65
Propranolol	18	18	43.5	26.7	66.1	11.2	2	20
Sertraline	18	18	15.2	3.5	35.5	9.7	0.5	0.52
Sulfamethoxazole	18	18	53.7	17.7	93.2	21.9	2	118
Tramadol	18	18	908.7	466.2	1,380.4	239.4	1	100
Trimethoprim	18	18	82.6	36.1	129.0	27.5	1	62,000
Venlafaxine	18	18	326.0	169.4	536.9	114.5	1	100
Zolpidem	14	18	1.0	n.d.	2.3	0.7	0.5	2,200
Acetamiprid	10	18	1.0	n.d.	4.9	1.5	0.2	500
Clothianidin	4	15	293.0	n.d.	2,515.6	666.6	1	130
Imidacloprid	18	18	268.3	n.d.	2,805.7	689.8	2	8.3
Thiamethoxam	14	15	3,911.3	n.d.	18,406.2	6834.6	1	42

(cont'd)

Substance [ng/L]	Number >MLQ	Number	Average	Min.	Max.	Std.dev	MLQ	PNEC
Amidotrizoic Acid*	2	9	27.0	<LOQ	62	1,057	10	,
Iohexol*	6	9	816.1	<LOQ	2,100	41	50	1,000,000
Iomeprol*	9	9	1,522.2	1100	3,300	0	10	1,000,000
Iopamidol*	3	9	211.7	<LOQ	660	21	10	410,000
Iopromide*	2	9	45.6	<LOQ	150	730	20	1,360,000
Ioversol*	9	9	11,566.7	7,500.0	15,000	701	90	3,686,000

The average effluent concentrations (influent to pilot plant) of the 14 substances measured above $PNEC_{Freshwater}$ (excluding neonicotinoids) are illustrated in Figure 7-1. Corrosion inhibitor benzotriazoles, which is analysed both as benzotriazole and methylbenzotriazole, represents the highest and third highest concentration of the critical measured substances. Benzotriazoles are followed by the painkillers tramadol and diclofenac as well as the antipsychotics oxazepame and antidepressant venlafaxine.

The same critical substances are presented in Figure 7-2, but here they are related to the effect level of $PNEC_{Freshwater}$. The ratio between measured concentrations (MEC) and predicted no-effect concentrations ($PNEC_{Freshwater}$) is presented. $MEC/PNEC_{Freshwater} = 1$ is illustrated by the red line. Figure 7-2 shows that antidepressant sertraline and the fluorosurfactant PFOS are the most environmentally critical substances. They are measured 29 and 24 times above $PNEC_{Freshwater}$ respectively. Both sertraline and PFOS are measured in low concentrations compared to the other critical substances (see Figure 7-1), which highlights that even very low concentrations of pollutants can be very critical.

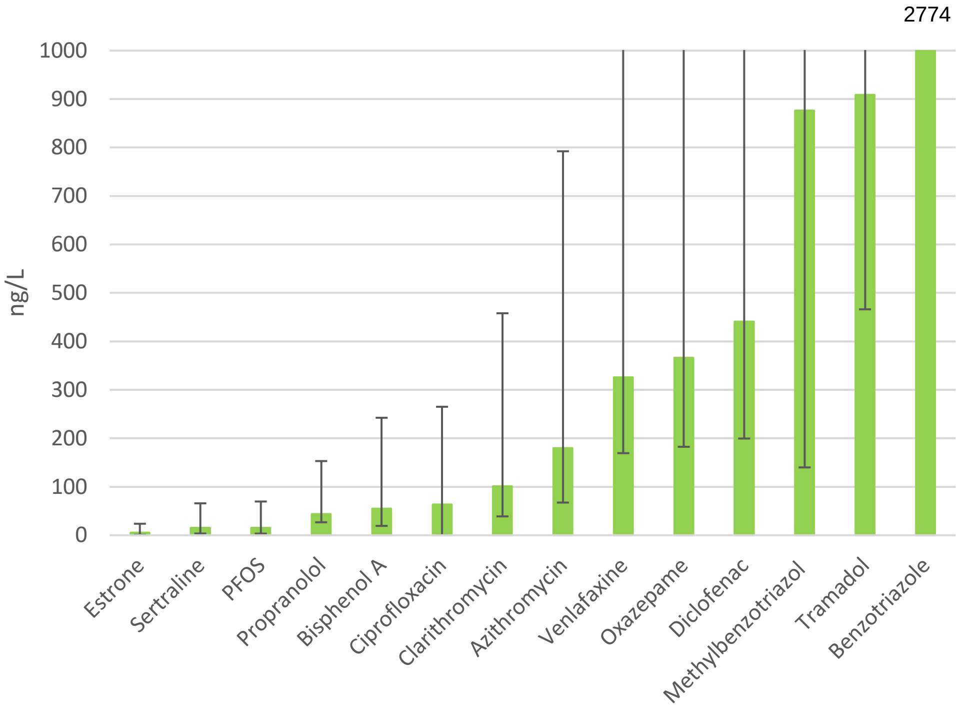

Figure 7-1: Effluent from conventional WWTP (influent to pilot plant). Average concentrations of pollutants measured above $PNEC_{Freshwater}$. Minimum and maximum values are shown as a bar at each column.

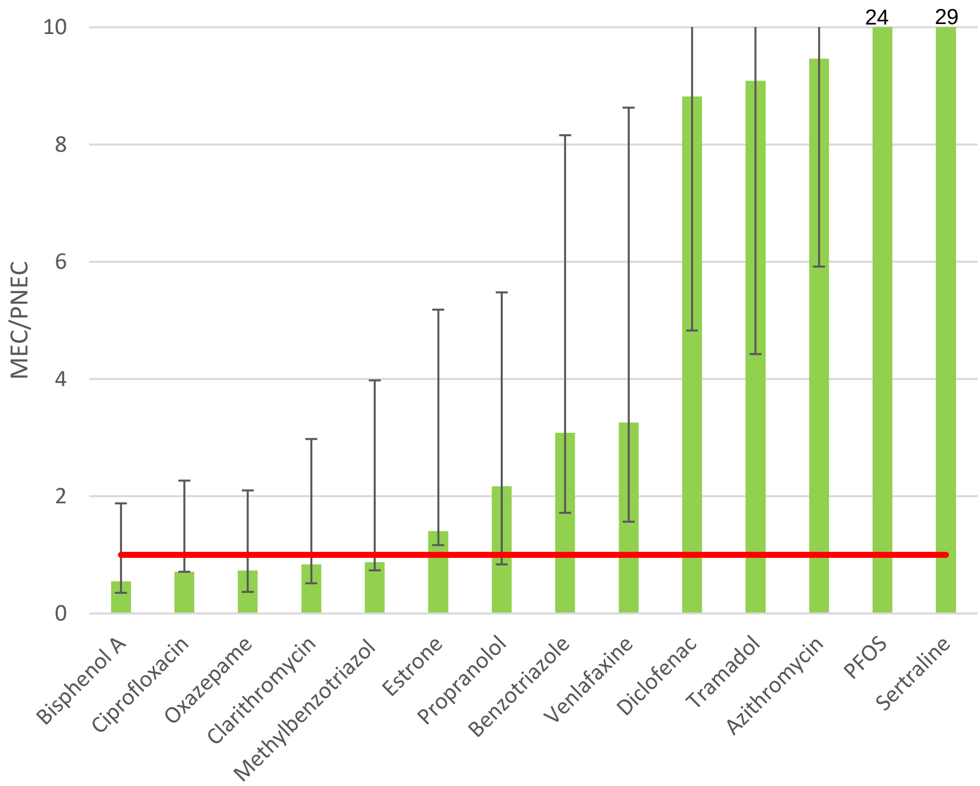

Figure 7-2: Environmental risk ratio in effluent from conventional WWTP (influent to pilot plant). Ratio between measured average concentrations (MEC) and predicted no-effect concentrations ($PNEC_{Freshwater}$). The $PNEC_{Freshwater}$ is illustrated by the red line ($MEC/PNEC_{Freshwater} = 1$). Minimum and maximum values are shown as a bar at each column.

7.2 Pilot plant effluent quality

The effluent quality for the total test period is summarized in Table 7-3. The effluent quality is highly dependent on loading of the GAC filter, i.e. how many bed volumes (BV) the filter has been loaded with. Assessment of the effluent quality is to be viewed in this perspective. Table 7-3 shows that only six substances (excluding neonicotinoid thiamethoxam which is discussed in Section 7.8) have been measured above the $PNEC_{Freshwater}$ values during the total test period.

Table 7-3 Summarized pilot plant effluent quality of the total sampling period from March 2019: (BV 969) to August.2020 (BV 14.882).

Substance	Number >MLQ	Number	Average	Min	Max	MQL	Std. Dev.	PNEC
Amisulprid	6	6	15.6	6.9	29.2	1	7.8	5,000
Atenolol	11	18	8.8	n.d.	32.2	2	10.9	100,000
Azithromycin	16	18	38.8	n.d.	86.4	2	24.6	19
Benzotriazole	18	18	36.6	1.5	110.8	2	37.9	900
Bisphenol A	17	18	22.6	n.d.	44.9	10	11.6	100
Carbamazepine	16	18	40.2	n.d.	130.5	0.5	41.5	500
Ciprofloxacin	7	18	3.3	n.d.	16.8	10	4.9	89
Citalopram	15	18	9.4	n.d.	28.1	1	9.8	8,000
Clarithromycin	18	18	48.2	7.9	164.8	2	35.0	120
Diclofenac	18	18	110.0	2.1	538.8	2	131.3	50
Erythromycin	17	18	39.9	n.d.	114.7	0.5	36.5	200
Estrone	12	18	0.3	n.d.	1.3	0.2	0.4	3.6
Fluconazole	18	18	80.6	0.3	187.2	0.3	61.0	57,000
Furosemide	17	18	366.4	n.d.	1,234.0	5	349.8	31,300
Hydrochlorothiazide	4	5	8.8	<LOQ	22.0	10	8.5	143,000
Ibuprofen	5	18	48.8	n.d.	418.6	100	106.3	4,000
Irbesartan	6	6	25.5	11.6	45.4	2	12.2	704,000
Ketoconazole	0	18	n.d.	n.d.	0.0	10		100
Losartan	18	18	312.9	6.1	909.2	1	260.5	245,000
Methotrexate	0	18	n.d.	n.d.	0.0	2		260,000
Methylbenzotriazol	1	9	10.8	<LOQ	52	10	7.8	1,000
Metoprolol	14	18	61.9	n.d.	186.6	2	67.6	62,000
Naproxen	14	18	69.6	n.d.	265.3	10	77.5	1,700
Oxazepame	17	18	72.3	n.d.	251.8	1	72.4	500
Paracetamol	12	18	20.3	n.d.	94.8	2	27.8	9,200
PFOA	17	18	3.2	n.d.	7.3	1	1.8	48
PFOS	18	18	6.7	0.2	26.2	2	7.7	0.65
Propranolol	9	18	0.9	<LOQ	5.0	2	1.4	20
Sertraline	4	16	1.6	<LOQ	24.5	0.5		0.52
Sulfamethoxazole	17	18	21.6	n.d.	46.4	2	15.0	118
Tramadol	18	18	142.8	0.5	371.8	1	134.9	100
Trimethoprim	13	18	6.7	n.d.	19.9	1	7.1	,
Venlafaxine	17	18	77.1	n.d.	217.9	1	74.0	100
Zolpidem	0	18	n.d.	n.d.	n.d.	0.5		2,200

(cont'd)

Substance	Number >MLQ	Number	Average	Min	Max	MQL	Std. Dev.	PNEC
Acetamiprid	5	18	0.2	n.d.	1.3	0.2	0.4	500
Clothianidin	1	18	0.0	n.d.	0.3	1		130
Imidacloprid	17	18	2.1	n.d.	4.7	2	1.7	8.3
Thiamethoxam	18	18	86.3	1.9	477.6	1	116.8	42
Amidotrizoic Acid	3	9	76.4	<LOQ	500	10	2	.
Iohexol	3	9	130.0	<LOQ	460	50	7	1,000,000
Iomeprol	8	9	267.2	<LOQ	580	10	0	1,000,000
Iopamidol	3	9	57.2	<LOQ	280	10	159	410,000
Iopromide	2	9	21.9	<LOQ	47	10	155	1,360,000
Ioversol	8	9	2.522.8	<LOQ	6.300	90	201	3,686,000

Figure 7-3 presents the effluent quality of the 14 critical substances that were measured above $PNEC_{Freshwater}$ in the pilot plant influent (effluent of WWTP). The figure shows that tramadol, diclofenac, venlafaxine, oxazepame, benzotriazole, azithromycin and clarithromycin are measured in the highest concentrations after 14,882 BV. This corresponds to the substances measured in the highest concentrations in the influent (see Figure 7-1).

The environmental risk ratios (MEC/ $PNEC_{Freshwater}$) for the same 14 critical substances are presented in Figure 7-4. The figure shows that no substances are measured above $PNEC_{Freshwater}$ when the activated carbon is all fresh at BV 969. At BV 3769 the first break throughs are measured for two substances: Fluorosurfactant PFOS and antibiotic azithromycin. At BV 7,435 two additional substances are measured above $PNEC_{Freshwater}$: Painkillers diclofenac and tramadol. And at BV 12,665 five substances, including antidepressant venlafaxine, are measured above $PNEC_{Freshwater}$. Finally, at BV 14,882 five substances are still measured above $PNEC_{Freshwater}$. but venlafaxine is swapped by antidepressant sertraline which is measured in low concentrations (1.1 ng/l), but the risk ratio is two.

If the effluent risk ratio is compared with the influent risk ratio (Figure 7-2), it can be noted that the substance which poses the highest risk, antidepressant sertraline, is almost completely removed by the GAC treatment. This is also the situation after BV 12,665.

The other 8 substances, which are also measured above $PNEC_{Freshwater}$ in the effluent from the conventional WWTP, are reduced to a risk level below 1 during the whole test period.

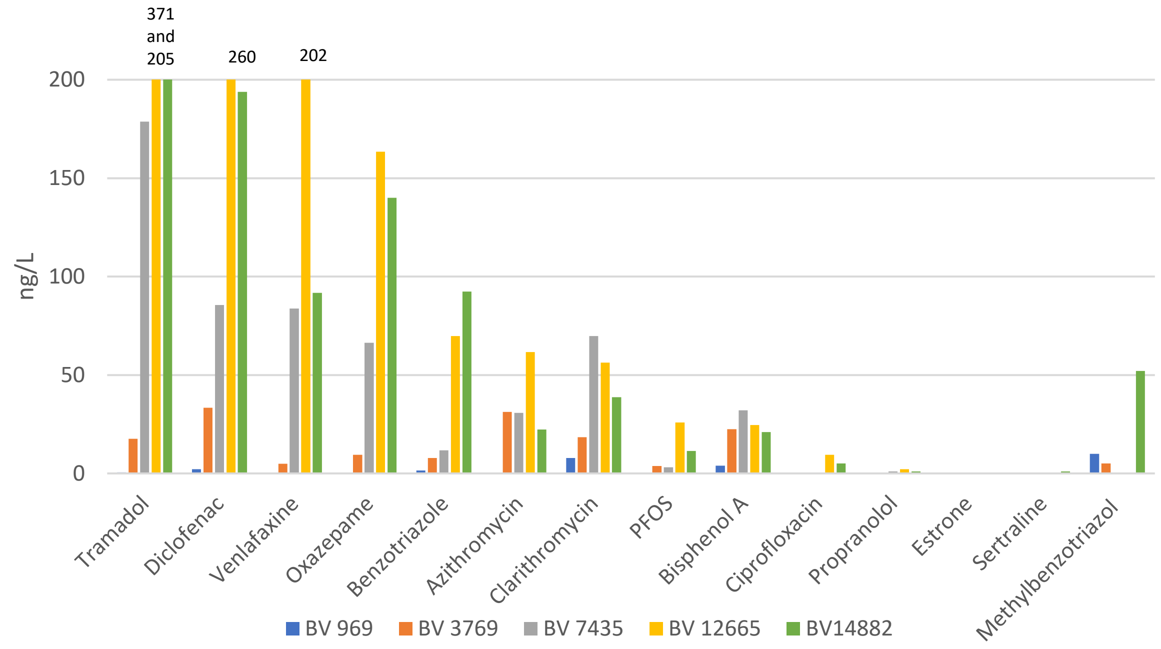

Figure 7-3: Pilot plant effluent quality of selected critical substances measured at different bed volumes (BV).

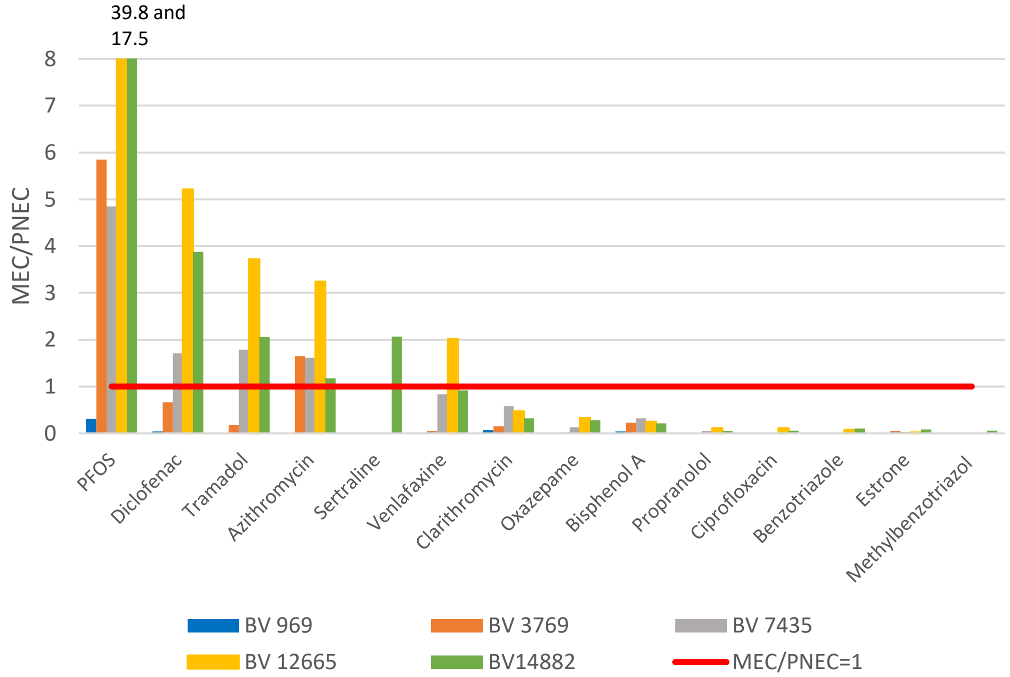

Figure 7-4: Effluent environmental risk ratio. Ratio between measured concentrations (MEC) and predicted no-effect concentrations ($PNEC_{Freshwater}$). The $PNEC_{Freshwater}$ is illustrated by the red line ($MEC/PNEC_{Freshwater}$ = 1).

7.3 Removal efficiency

The micropollutant removal efficiency of the conventional WWTP is illustrated in Figure 7-5. It is observed that chemotherapy methotrexate and painkillers ibuprofen and paracetamol are efficiently (>99%) removed in the conventional plant. Ibuprofen and paracetamol are measured in high concentrations in the influent to the WWTP (each measured to around 50 mg/l. see Table 5-3).

For erythromycin, a negative reduction was observed. This is likely to be explained by conjugation and deconjugation. Conjugation is a process by which a compound is made water soluble by the binding of a functional group to the parent compound. Conjugation occurs in the human body, primarily in the liver, and is one of the ways in which the human body excretes pharmaceuticals. When a pharmaceutical is conjugated, it is not detected and identified as the parent compound in chemical analyses because of the functional group. During biological treatment, the pharmaceutical can deconjugate, meaning that the functional group is removed. Without the functional group, the pharmaceutical is instead detected and identified via chemical analysis.

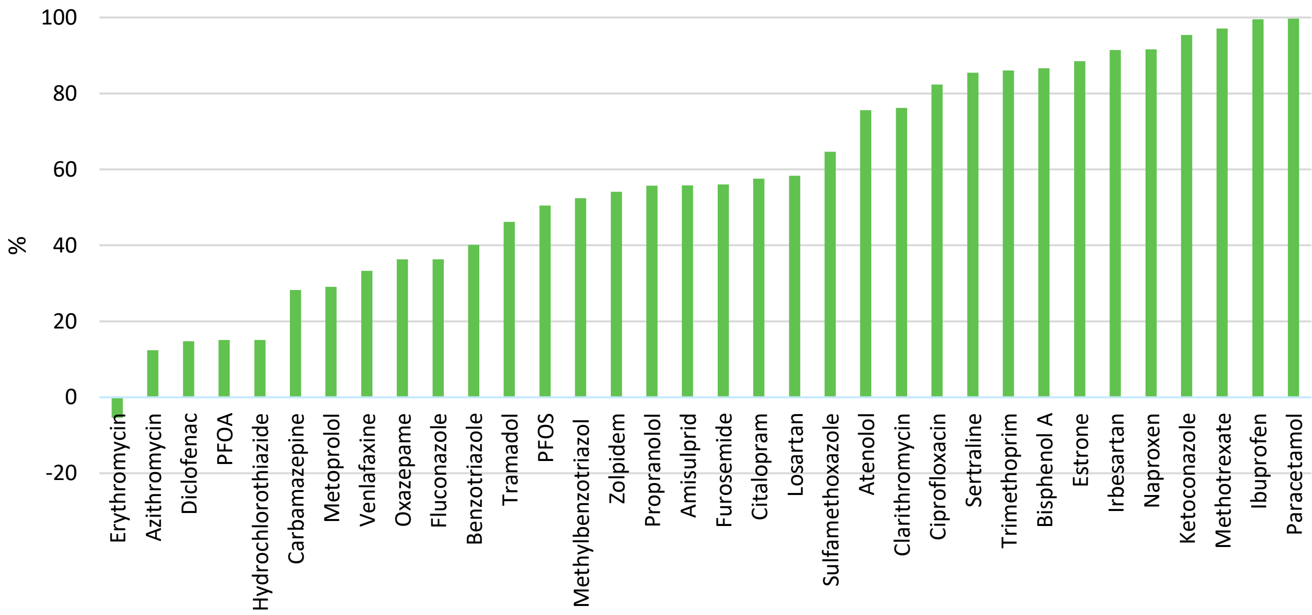

Figure 7-5: Micropollutant removal in conventional WWTP: The influent is characterized by 4 samples, the effluent by 18 samples except for irbesartan, hydrochlorothiazide and amisulpid that were analysed in 6 samples in the effluent from the WWTP.

The overall WWTP (including pilot plant) removal efficiency of the sum of concentrations of 34 micropollutants is illustrated in Figure 7-6. Neonicotinoids and contrast media are handled separately because the substances occur in different concentration levels. The figure illustrates the overall removal from the inlet of conventional WWTP (Po. 0) to the outlet of the pilot plant after UV treatment (Po. 5) (see sampling points in Figure 6-3).

Figure 7-6 shows that the conventional treatment plant removes approximately 89%. This high removal rate is primarily due to the dominating high concentrations of painkillers ibuprofen and paracetamol, which are effectively removed (>99.7%) in the conventional WWTP. With the fresh GAC at BV 969, an almost complete removal of all 34 micropollutants is measured (99.97%). After BV 12,665 the reduction drops to 96.7% due to substances like the blood pressure drugs furosemide and losartan which start to break through the GAC filter in the highest concentrations. After 14,000 BV the sorption increased again, which might be due to an effective backwash of the GAC filter just before 14,000 BV or to a biological growth in the filter, which might change the adsorption capabilities of the filter. At the end of the test period at 14,882 BV, removal efficiency was increased to 97.7%.

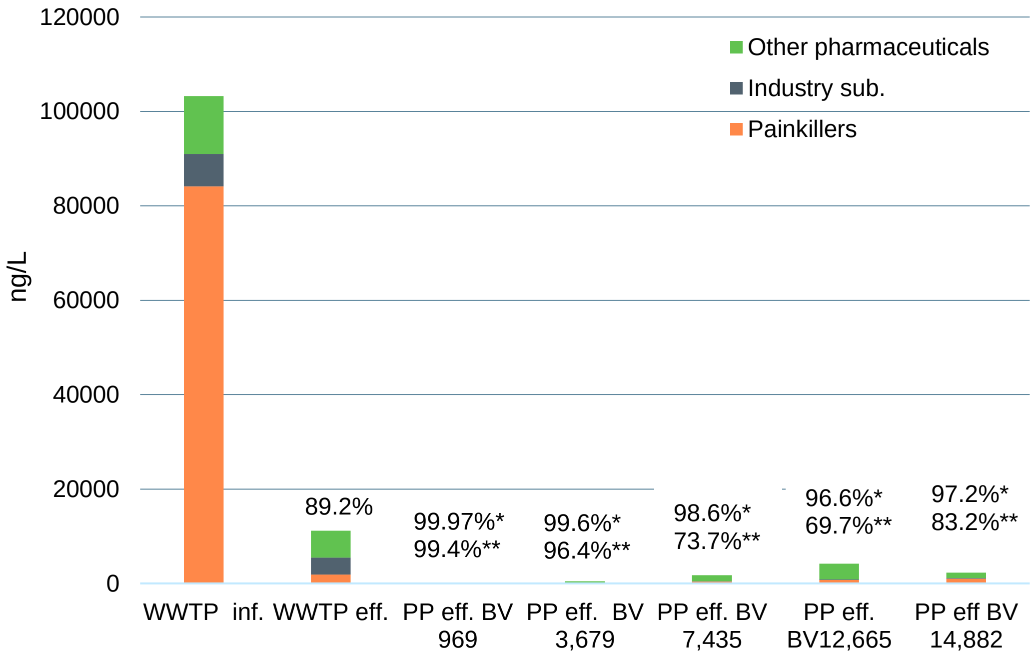

Figure 7-6 Sum of concentrations of 34 micropollutants from sampling points in influent to conventional WWTP (Point 0.), in effluent from conventional WWTP (Point 1.) and in effluent from pilot plant after a growing number of BV through GAC filter (Point 5.).* Reduction of total concentration relative to WWTP inf. ** Reduction relative to WWTP eff.

To focus on the 14 critical substances, which are measured above $PNEC_{Freshwater}$ in the conventional WWTP effluent, the same illustration of overall WWTP removal is shown in Figure 7-7. It was observed that the removal of these 14 substances was much lower (37.7%) in the conventional WWTP. Here the high removal was observed after the pilot plant treatment. With fresh GAC (BV 969), a removal of >99% was measured, and after BV 12,665 a total removal rate of 86.4% was observed from inlet of the conventional WWTP to outlet of the pilot plant. The Swiss target is 80% removal.

For international comparison, the removal efficiency of Swiss indicator substances is illustrated in Figure 7-8. The Swiss aim is to remove the organic micropollutants by 80% on average over the whole WWTP from influent to effluent. The Swiss Federal Office for the Environment (FOEN) has established a shortlist of 12 indicator substances[4], which must be reduced by 80% (FOEN. 2017). The 12 substances were specifically chosen as non-easily degradable substances and are therefore normally not well removed during

[4] The 12 Swiss indicator substances are: Amisulpride, benzotriazole, candesartan, carbamazepine, citalopram, clarithromycin, diclofenac, hydrochlorothiazide, irbesartan, metoprolol, methylbenzotriazole and venlafaxine.

conventional wastewater treatment. In this project 11[5] out of the 12 substances were analysed.

Figure 7-8 illustrates that Swiss substances are weakly removed in the conventional biological plant (by 30%) as expected. As opposed to this it was observed that the pilot plant removes the 11 substances very efficiently. The 11 substances are reduced by 99.8% with fresh GAC at BV969 and by 91.8% after BV14,882.

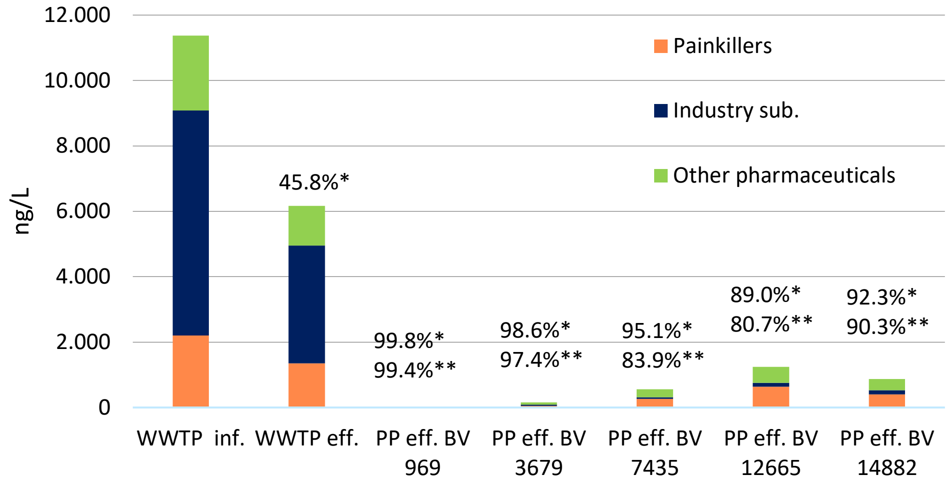

Figure 7-7 Sum of concentrations of the 14 critical micropollutants from sampling points in influent to conventional WWTP (Point 0.), in effluent from conventional WWTP (Point 1.) and in effluent from pilot plant after a growing number of BV through GAC filter (Point 5.).* Reduction of total concentration relative to WWTP inf. ** Reduction relative to WWTP eff.

[5] 11 of the 12 Swiss indicator substances are analysed in this project. Blod pressure drug candesartan has not been measured. Candesartan is used in low amounts in the catchment area of Slagelse WWTP. The total consumption of candesartan in 2017 was 390 g.

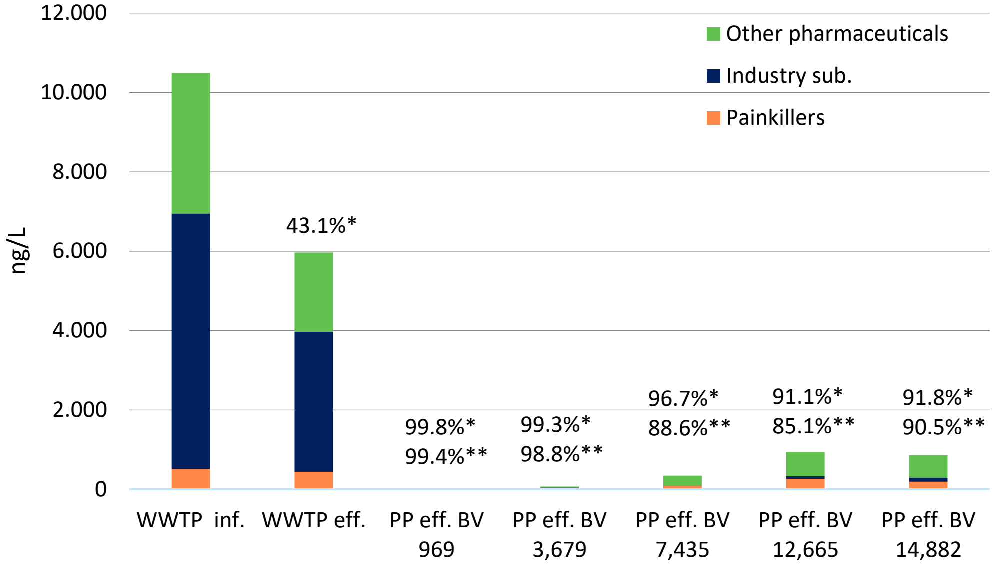

Figure 7-8 Sum of concentrations of the 11 Swiss indicator substances from sampling points in influent to conventional WWTP (Point 0.), in effluent from conventional WWTP (Point 1.) and in effluent from pilot plant after a growing number of BV through GAC filter (Point 5.).* Reduction of total concentration relative to WWTP inf. ** Reduction relative to WWTP eff.

The removal percentages from influent to WWTP to effluent from pilot plant of each of the 14 critical substances plus the extra analysed Swiss substances (carbamazepine. citalopram and metoprolol) are illustrated in Table 7-4. The table shows that most of the critical substances are reduced by more than 80%.

The five substances measured above $PNEC_{Freshwater}$ in the effluent from the pilot plant after 14,882 BV are highlighted in Table 7-4. The lowest removal rate (16%) is observed for PFOS at 12,665 BV. This low removal rate is due to the fact that the average PFOS WWTP influent concentration is low (31 ng/l based on an average of four samples) compared to both influent to, and effluent from, the pilot plant at that specific day (38.9 ng/l and 25.9 ng/l respectively). This results in a very low removal rate although the removal rate in the pilot plant is 33% (see Table 7-5).

Two of the five highlighted critical substances are also the substances with the lowest reduction percentage after 14,882 BV. The other three – tramadol, azithromycin and sertraline - are removed by more than 88% although they were measured above $PNEC_{Freshwater}$ in the effluent from the pilot plant (see Figure 7-4). This highlights that more than 80% removal is not always enough to comply with PNEC limits.

Table 7-4 Removal percentages of 14 critical micropollutants and three Swiss pharmaceuticals (clarithromycin, metoprolol and citalopram) from conventional WWTP influent to effluent from pilot plant.

	Conventional WWTP plus pilot plant removal percentage							
BV	**969**	**2442**	**4541**	**6026**	**8986**	**10322**	**12665**	**14.882**
Diclofenac	100	98	92	92	80	79	50	63
PFOS	99	97	75	73	92	90	16	63
Oxazepame	100	100	98	96	85	79	72	76
Venlafaxine	100	100	99	94	72	73	59	81
Carbamazepine	100	100	98	98	87	81	73	83
Tramadol	100	100	99	98	85	86	78	88
Azithromycin	100	91	88	70	68	88	70	89
Clarithromycin	98	95	89	90	86	82	87	91
Metoprolol	100	100	99	100	91	86	86	93
Bisphenol A	99	97	96	91	96	89	94	95
Citalopram	100	100	100	100	96	92	92	97
Methylbenzotriazol	98	98	99					97
Benzotriazole	100	100	100	100	99	98	98	98
Ciprofloxacin	100	100	100	99	100	98	97	99
Sertraline	100	100	100	100	100	100	100	99
Propranolol	100	100	100	100	99	95	98	99
Estrone	100	100	100	100	100	97	100	99
Total removal 14 substances	100	98	95	92	89	89	78	88

≥80%
50-80%
20-<50%
<20%

7.4 Pilot plant breakthrough

The removal percentages in the pilot plant of each of the 14 critical substances are illustrated in Table 7-5. Clarithromycin, PFOS and azithromycin are observed to have the highest breakthrough after BV 14,882. It should be noted that clarithromycin and bisphenol A are relatively efficiently removed at the conventional WWTP (with 77% and 88% respectively, see Figure 7-5). This results in relatively high total abatement for these substances across the whole WWTP (see Table 7-4). PFOS is observed to have highly variable reduction rates in the WWTP.

The five substances that are measured above $PNEC_{Freshwater}$ in the pilot plant effluent are highlighted in Table 7-5. Among these, PFOS has the highest breakthrough at 14,822 BV with a 46% reduction. PFOS is followed by diclofenac, azithromycin, venlafaxin and tramadol.

Table 7-5: Pilot plant removal percentages (from effluent conventional WWTP to effluent pilot plant) for 14 critical substances and three Swiss pharmaceuticals (clarithromycin, metoprolol and citalopram). Substances measured above $PNEC_{Freshwater}$ are highlighted.

	Pilot plant removal percentage							
Bed Volumes	**969**	**2,442**	**4,541**	**6,026**	**8,986**	**10,322**	**12,665**	**14,882**
PFOS	98	89	64	64	22	34	33	46
Clarithromycin	95	76	49	43	29	31	15	49
Azithromycin	100	95	85	61	35	70	56	75
Bisphenol A	91	82	67	42	21	30	41	77
Diclofenac	99	98	90	88	66	47	55	78
Oxazepame	100	100	96	93	60	34	64	80
Venlafaxine	100	99	98	90	56	41	62	82
Carbamazepine	100	100	98	97	72	49	74	82
Tramadol	100	100	99	96	70	55	69	85
Ciprofloxacin	100	n.d.	100	100	100	75	76	85
Metoprolol	100	100	99	100	84	66	84	92
Citalopram	100	100	100	99	77	74	85	93
Sertraline	100	100	100	100	100	100	100	95
Benzotriazole	100	100	100	100	98	95	98	97
Methylbenzotriazol	98	100	97					97
Estrone	100	100	99	100	85	73	99	98
Propranolol	100	100	100	100	100	90	100	98
Total removal 14 substances	99	95	89	83	65	60	67	82

≥80%
50-80%
20-<50%
<20%

The breakthrough curves for the critical substances are shown in Figure 7-9. It is observed that azithromycin and PFOS starts to break through first and that they have varying reduction rates through the test period. Tramadol, diclofenac and venlafaxine have slower and much more stable breakthrough curves. Sertraline is very effectively removed. After 14,000 BV sertraline starts to break through although the removal is still >95%.

Common to the six substances, except sertraline and only partly PFOS, is that at the last two sampling (from 14,192 BV to 14,882 BV) the sorption increases again resulting in higher removal rates. Comparison with the physical and chemical properties of the six substances (see Table 7-6) does not give any clear explanations of the mechanisms involved with the GAC removal. The removal patterns cannot be explained by Log K_{ow} values or water solubility. This indicates that the observed removal is based on mechanisms other than hydrophobic interaction or water solubility. Microbiological degradation might also take place in the GAC. It is not possible to distinguish between sorption and degradation by just measuring changes in concentrations.

Table 7-6 Physical and chemical data for six critical micropollutants /8//9//21/

Substance	CAS Number	Solubility in water mg/l /26/	Log Kow /26/	MW g/mol	Charge /21/	Aromatic ring /21/
Azithromycin	83905-01-05	0.062	4.02	749	++	0
Diclofenac	15307-86-5	4.5	3.9	296.15	-	2
PFOS *)		680	n.a.	500.126	-	0
Sertraline	79559-97-0	94	2.18	342.7	+	2
Tramadol	27203-92-5	1,200	2.4	263.38	+	1
Venlafaxine	99300-78-4	4,400	0.43	313.87	+	1

n.a. not available

Figure 7-10 illustrates the summarised removal of the 14 critical substances and 11 Swiss substances. The final removal rate of both groups of substances at 14,882 BV is very close to 80%. It is 82% for the sum of the 14 critical substances measured above $PNEC_{Freshwater}$ in the effluent from the conventional plant and 79% for the 11 Swiss substances.

It is observed that the removal rate is decreasing until 10,300 BV after which it is stable until 13,400 BV, and finally the removal rate is increasing in the last two samplings. It is expected that the summarized removal rate will decrease gradually during the test period because of the growing filter breakthrough of each substance. But it is unexpected that the removal increases by the end of the test period.

Possible explanations of the final increase of the removal rate can be divided into:

- Change in backwash method (including air)
- Biofilm growth
- Change in EBCT

The backwash method was changed as described in Section 6.2 before the last two sampling times. The backwash carried out on July 7th. 2020 was combined with compressed air. Until then, backwash was only carried out with water (pumped from the secondary clarifiers). The intension was to remove particles and sediment more thoroughly in the filter which caused growing pressure drop. The backwash was effective on the pressure drop issue, but it might also have resulted in more efficient removal of the micropollutants. The backwash might have destroyed channels, which have been formatted since last backwash, and resulted in better water distribution in the GAC leading to more effective utilisation of the GAC. The backwash might also remove particles which blocked the entrances (macropores) to the micropores in the GAC. The adsorption of micropollutants primarily takes place in the micropores, and blockage could have resulted in less effective adsorption of micropollutants.

But this does not explain why the removal rate gets even better at the second sampling time after the backwash. One explanation could be that biofilm growth changes the adsorption capabilities of the GAC and in this case leads to enhanced adsorption. The last two samplings took place in July to August where temperatures were rising which increased the biological growth in the secondary clarifiers. Biofilm growth might also have been initiated by the rising water temperature.

The empty bed contact time (EBCT) in the GAC filter changed according to the water flow. The water flow through the filter was adjusted by the GAC inlet pump (see Figure 6-3). The adjustment of the pump during the test period is shown in Figure 7-10. At 30 m^3/h the EBCT is 34 minutes. Due to periods with high pressure drop in the GAC filter the flow was adjusted to 25 m^3/h and down to 15 m^3/h. This results in EBCT of 41 and 68 minutes respectively. Figure 7-10 shows that the removal rate of micropollutants does not follow the change in flow. The changes in EBCT do not seem to be a decisive factor. The lowest EBCT (34 minutes) is relatively high, and even higher EBCT is not expected to result in more efficient micropollutant removal. Swiss studies have demonstrated that EBCT below 10 minutes (often because of high flow due to heavy rain events) results in reduced removal rates of micropollutants /4/. Danish experience from GAC treatment at Herlev Hospital shows efficient removal of pharmaceuticals at an EBCT of 41 minutes /10/. According to Swiss experiences, a minimum EBCT for efficient micropollutant removal is 25 minutes /11/ at low DOC (4-6 mg/l). Higher levels of DOC are expected to require longer EBCT.

Observations of increasing sorption after long operation of the GAC filter were also done in a Swiss study from 2018 /2/. This Swiss GAC filter was also fed by secondary clarified wastewater, and the water was prefiltered by a textile filter (instead of the 10 µm drum filter used in the Slagelse test). Here, increasing sorption (70-80% removal) was observed at the last two sampling times (at 22,000 and 28,000 BV) for e.g. diclofenac, metoprolol, venlafaxine and benzotriazole. The study stated that a clarification would require more investigations.

DOC was measured with conventional analytical method as well as DOC equivalents (DOCeq). DOCeq was measured by an online optical sensor (see description in Section 6.5). The conventional measurements showed values of the Slagelse secondary clarified water between 7 and 9 mg/l (see Section 6.5). This is lower than the Swedish Svedala WWTP (11 mg/l) and higher than conventional Swiss plants (4-7 mg/l) /2/.

The results of the optical sensor measurements of DOCeq are illustrated in Figure 7-9 and Figure 7-10. The figures show that as an overall picture, the sensor measured DOCeq follows the same trend as the majority of the critical micropollutants. Therefore, it is concluded that the DOCeq measurements can be used as a rough surrogate parameter to monitor the removal of micropollutants. Other studies have shown similar results with optical sensor measurements of UV_{254} /1/. As described in Section 6.5 the sensor-measured $UV_{250-260}$ in this study shows almost the same patterns as DOCeq. It is concluded that the DOCeq measurement fits the micropollutants' removal marginal better than the $UV_{250-260}$ measurements.

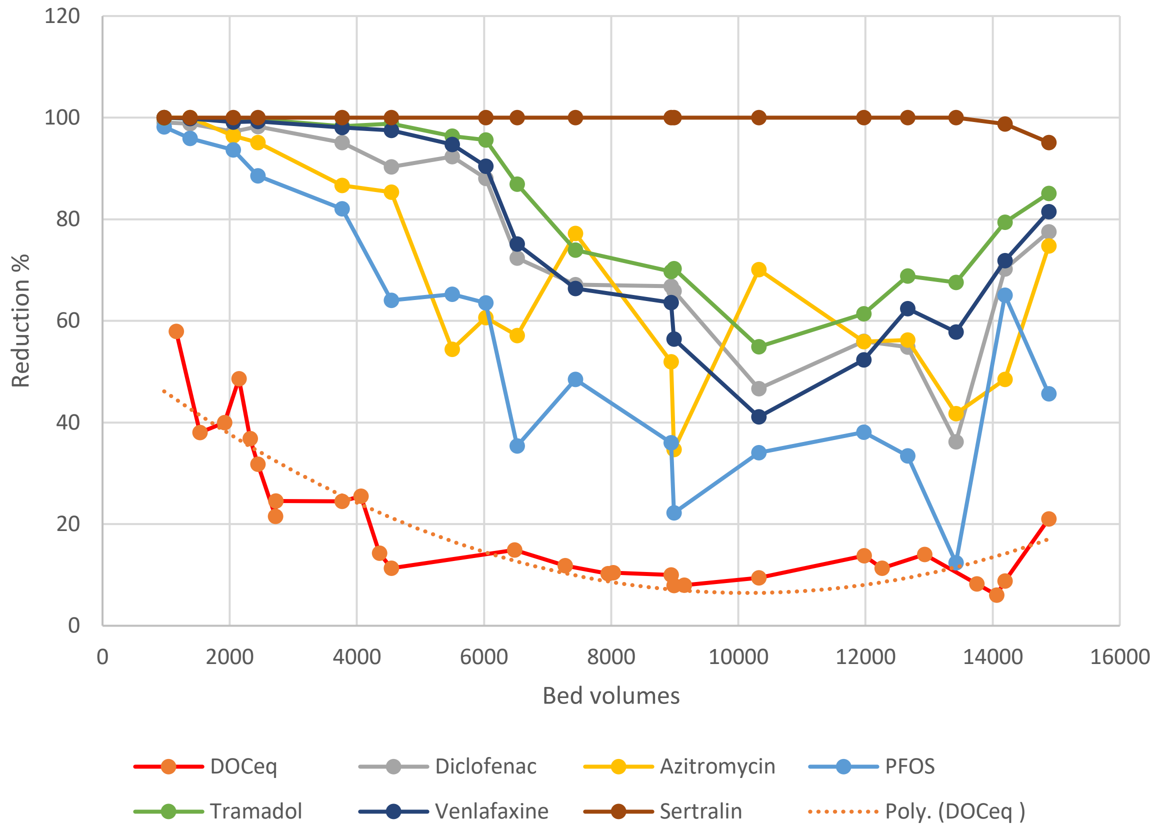

Figure 7-9: Relative reduction of selected pharmaceuticals. PFOS and DOC_{eq} in the pilot plant. The dotted line indicates the trend for the development of the DOC_{eq}.

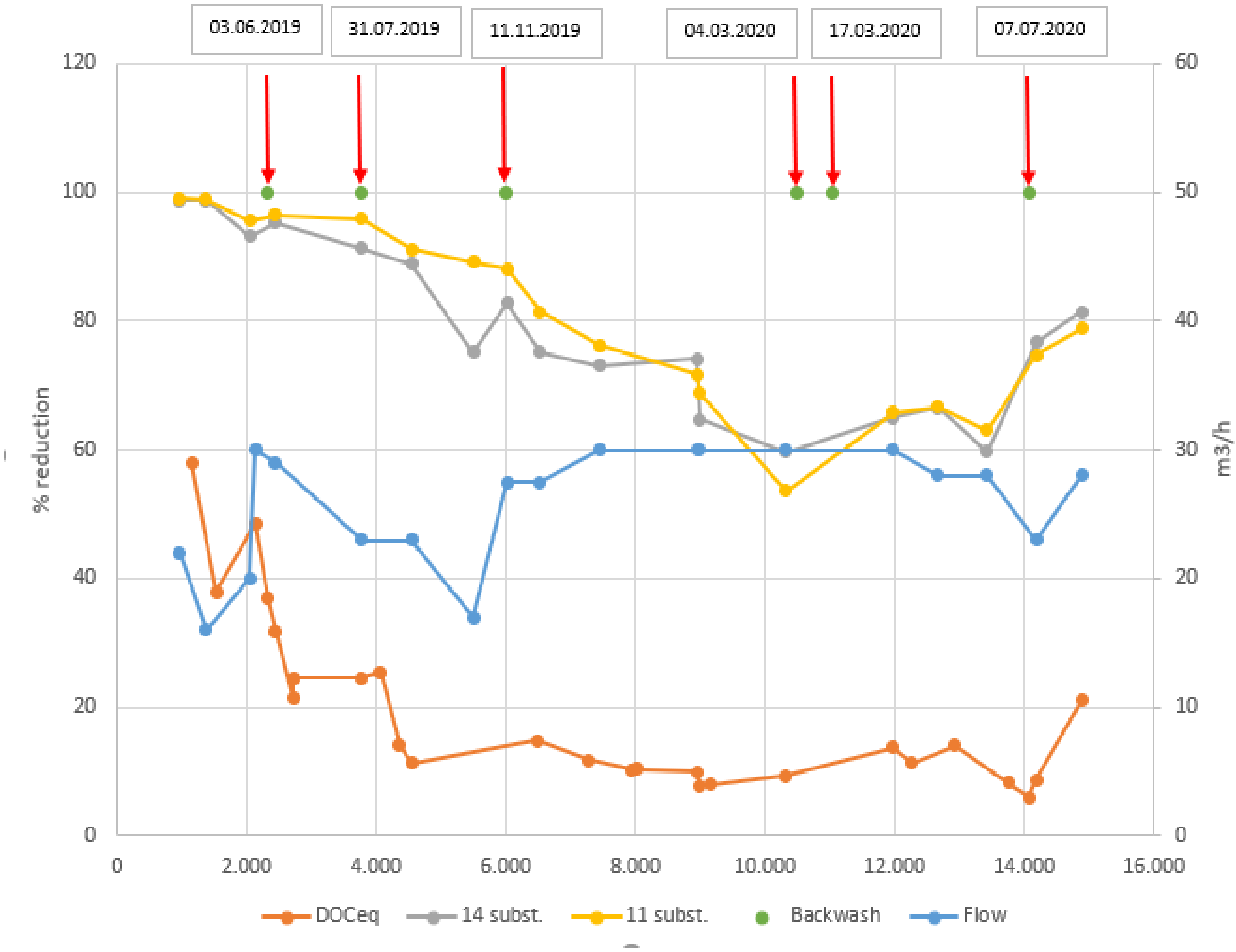

Figure 7-10: Development of removal of DOC_{eq}. sum of 14 pharmaceuticals and industrial chemicals. and 11 swiss focus substances. The flow through the GAC filter corresponds to the adjustment of the pump. The red arrows indicate when the backwash was performed.

7.5 Contrast media

Six contrast media (amidotrizoic acid, iohexol, iomeprol, iopamidol, iopromide, ioversol) have been analysed in the influent and effluent of the conventional Slagelse WWTP, and in the effluent from the pilot plant Iohexol, Iomeprol and ioversol were analysed in concentrations higher than the detection limits (10 – 90 ng/L) in each monitoring campaign. All contrast media measurement results are presented in Table 5-3, Table 7-2 and Table 7-3. Ioversol was present in the highest concentrations in the influent to Slagelse WWTP and in the effluent from the pilot plant. Figure 7-11 shows the total concentration of contrast media and the removal after four selected numbers of bed volumes (BV) compared to the effluent from Slagelse WWPT. At the beginning of the test period (after 969 BV), the sum of contrast media was removed by 99% compared to the influent concentration to the pilot plant.

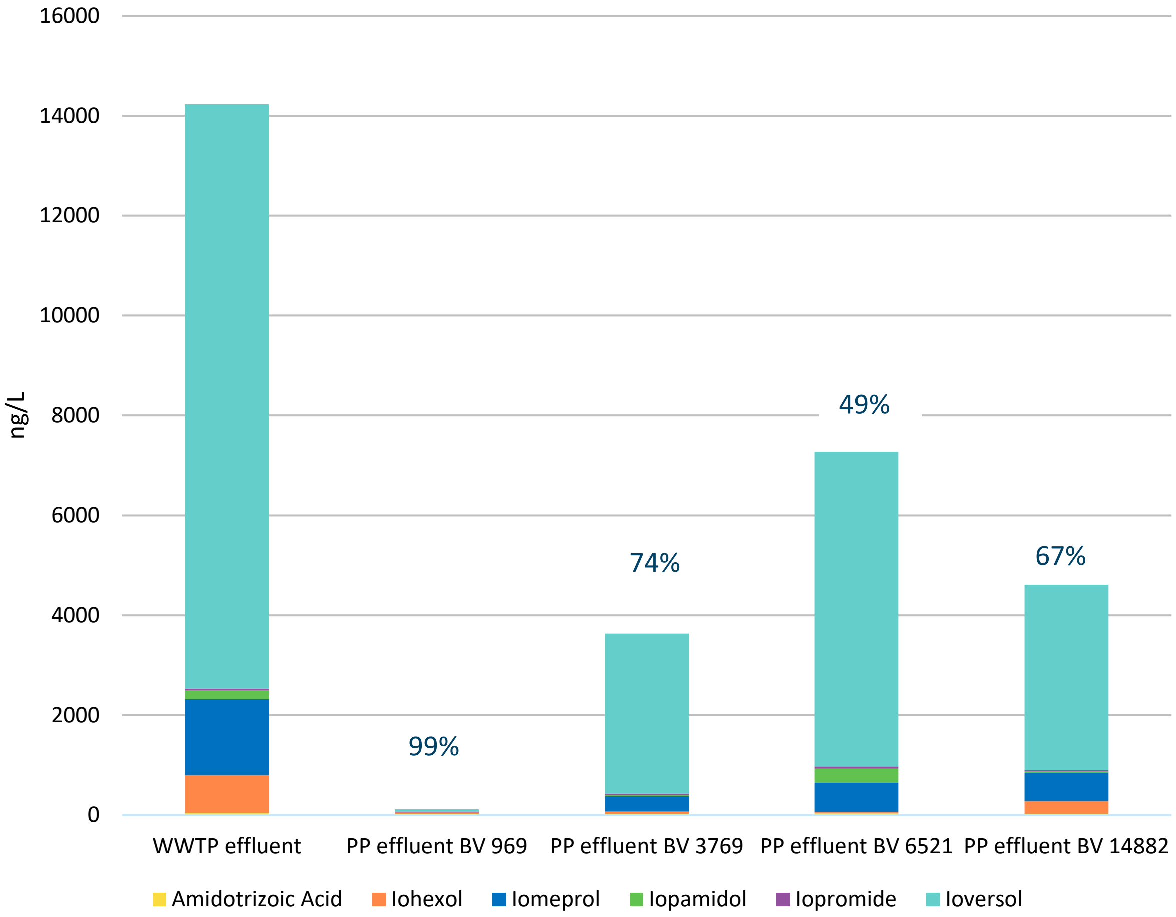

Figure 7-11: Reduction of total concentration of contrast media relative to the effluent from Slagelse WWTP The total contrast media concentrations are measured after 969. 3,769. 6,521 and 14,882 bed volumes.

Subsequently, (BV 3,769, 6,521, 14,882) the removal in the pilot plant was less efficient (74%, 49% and 67%). The contrast media concentrations did not at any time exceed the $PNEC_{Freshwater}$ in the effluent from the pilot plant.

7.6 Backwash water

Three samples of the backwash water were analysed to verify which substances are released from the GAC filter when backwash takes place. The backwashes were performed with secondary clarified wastewater from the conventional WWTP (same as effluent from the WWTP), see Section 6.2 for description of the backwash procedure. Table 7-7 shows that substances like benzotriazole, furosemide, tramadol, metoprolol, losartan, venlafaxine and diclofenac are present in the highest concentrations in the backwash water. These are the same substances that are present in the highest concentrations in the effluent from the WWTP (influent to GAC filter).

When the first backwash took place, the GAC filter had been loaded for nearly five months. The data shows that higher concentrations are washed out in the beginning of the backwash procedure and that the concentrations decrease to the end of the backwash period, which takes 30 to 45 minutes in total.

Table 7-7: Concentrations of pharmaceutical and industrial chemicals measured in backwash water after variable backwash period.

Date	03-06-2019	13-11-2019	
ng/l	After 15. min backwash	After 5 min backwash	After 10 min. backwash
Zolpidem	n.d.	0.8	n.d.
Estrone	n.d.	2.5	0.5
Ketoconazole	7.4	2.7	0.7
PFOA	3.6	4.7	5.0
Erythromycin	14.9	33.5	24.7
Bisphenol A	9.3	34.9	24.1
PFOS	5.7	39.9	17.2
Sertraline	5.2	44.2	5.1
Propranolol	1.3	59.3	2.6
Clarithromycin	87.9	67.3	41.0
Sulfamethoxazole	9.4	97.0	50.0
Atenolol	n.d.	97.1	16.5
Ciprofloxacin	21.5	102.5	22.2
Naproxen	22.7	106.8	28.8
Trimethoprim	1.8	118.8	17.2
Fluconazole	82.5	120.2	98.1
Citalopram	3.4	178.6	17.5
Carbamazepine	32.1	209.4	54.4
Azithromycin	76.6	284.7	75.6
Oxazepame	48.6	307.5	97.3
Diclofenac	87.1	314.1	156.8
Venlafaxine	15.7	354.8	123.0
Metoprolol	28.8	817.9	153.1
Losartan	200.6	915.3	394.7
Tramadol	47.9	1,056.6	284.0
Furosemide	101.9	1,449.9	910.3
Benzotriazole	73.4	4,637.4	365.9

7.7 Pharmaceuticals in water area (Tude Å)

Wastewater from Slagelse WWTP is discharged to Tude Å via a lagoon and a small channel/ditch (see Figure 7-12). Upstream (Tude Å position 2, Årslevvej) and downstream (Tude Å position 1, Ådalen) the discharge point samples were taken in summer and winter time. During the summer the water level in Tude Å decreases, and in the winter the water level increases due to more precipitation and less evaporation during winter.

The water level at two measuring points up- and downstream the discharge point appears from Table 7-8. The measuring points are not the same as the sampling points. The measuring points for water level are placed about 7 km from the discharge point.

The water level in Tude Å is low, and the stream is only 2.5 m wide. Therefore, the wastewater load from Slagelse WWTP (6,000 – 14,000 m^3/d) affects the flow and the concentration of pollutants in the stream considerably. However, the discharge of wastewater also has a positive impact on Tude Å because the stream does not dry out in the summer.

Table 7-8: Water level in Tude Å up- and downstream the discharge point for Slagelse WWTP

Station	Name	Kote Zero level	Up or downstream	Water level [m]		
				Nov. 2019	Ultimo Jan. 2020	Ultimo Aug. 2020
56.06	Tude Å. Ørslev	16.9 m	Up	1.5-1.7	1.7-2.1	1.1
56.11	Tude Å. Valbygaard	1.92 m	Down	0.6-1	0.5-1.5	0.2-0.3

From Figure 7-13 and Figure 7-14 it appears that the concentrations of pharmaceuticals (diclofenac, tramadol, venlafaxine, propranolol, estrone and sertraline) and industrial chemicals (benzotriazole, bisphenol A, PFOS) are higher downstream than upstream, which indicates a significant load impact from Slagelse WWTP. The higher flow after the discharge point indicates that the concentrations of the pollutant become more notable. The increase in concentrations applies to all substances. Sampling and analyses forming the basis for Figure 7-13 and Figure 7-14 were carried out on a summer day (17.07.2019) where the flow in Tude Å was low compared to wintertime, and this implies an increasing difference between the upstream and the downstream concentrations.

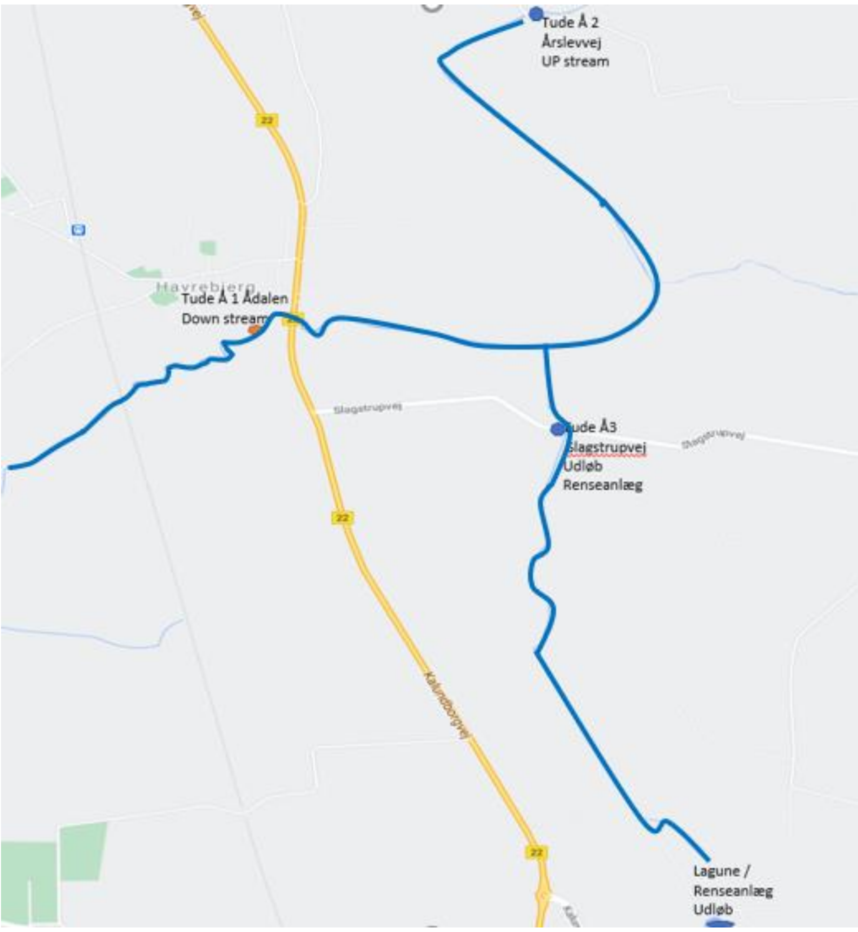

Figure 7-12: Position of sampling along Tude Å. Position 1 is downstream the discharge point from Slagelse WWTP. Position 2 is upstream, and position 3 is outlet from Slagelse WWTP.

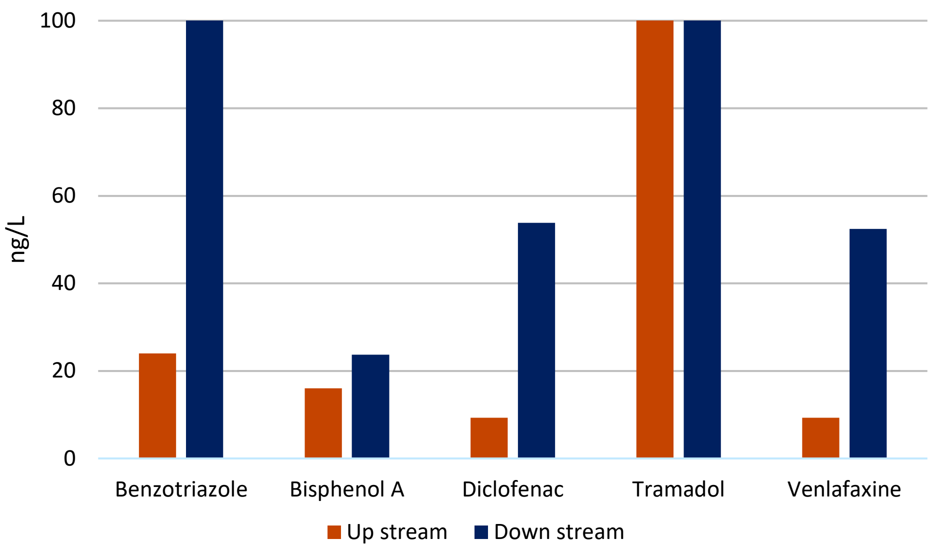

Figure 7-13: Concentrations of benzotriazole, bisphenol A, diclofenac, tramadol and venlafaxine measured on a summer day (17.07.2019) in Tude Å up- and downstream the discharge position of wastewater.

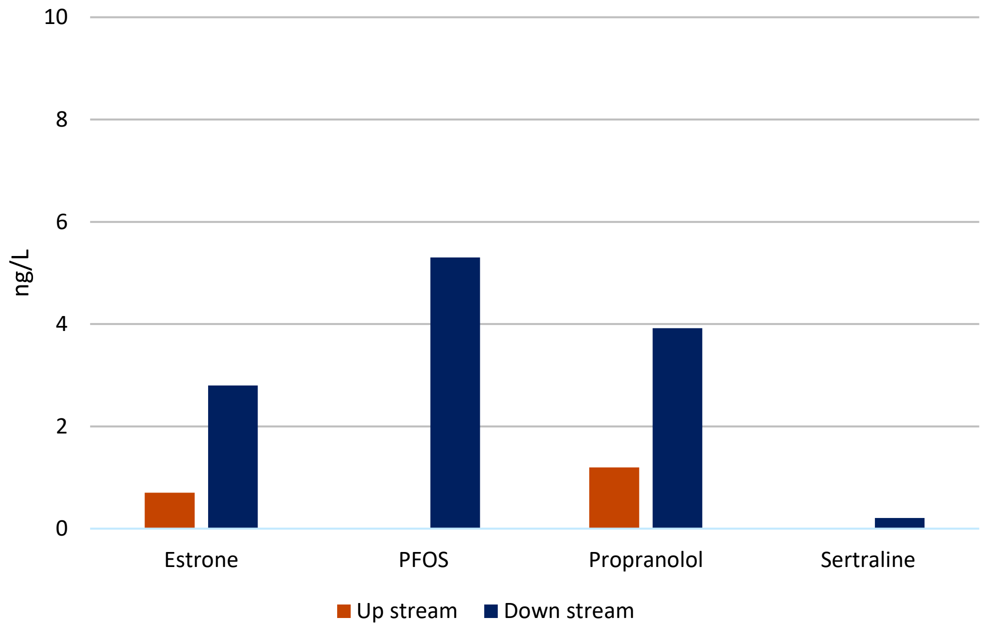

Figure 7-14: Concentrations of estrone, PFOS, propranolol and sertraline measured on a summer day (17.07.2019) in Tude Å up- and downstream the discharge position of wastewater.

Figure 7-15 shows concentrations of benzotriazole, bisphenol A, diclofenac, tramadol and venlafaxine measured in seven samples taken downstream the discharge point during the test period. The wastewater treated in the pilot plant represents between 6.5% and

16% of the wastewater treated by Slagelse WWTP (wet weather) and about 8% during dry weather.

The samples collected on summer days (green colours) contain the highest concentrations of pollutants. Contrary to that. the winter samples (blue colours) contain the lowest concentrations. which reflects the higher water flow in Tude Å during winter.

Estrone, PFOS, propranolol and sertraline (Figure 7-16) show the same trend as the substances mentioned above - high concentrations on summer days and lowest concentrations in Tude Å (downstream) on winter days.

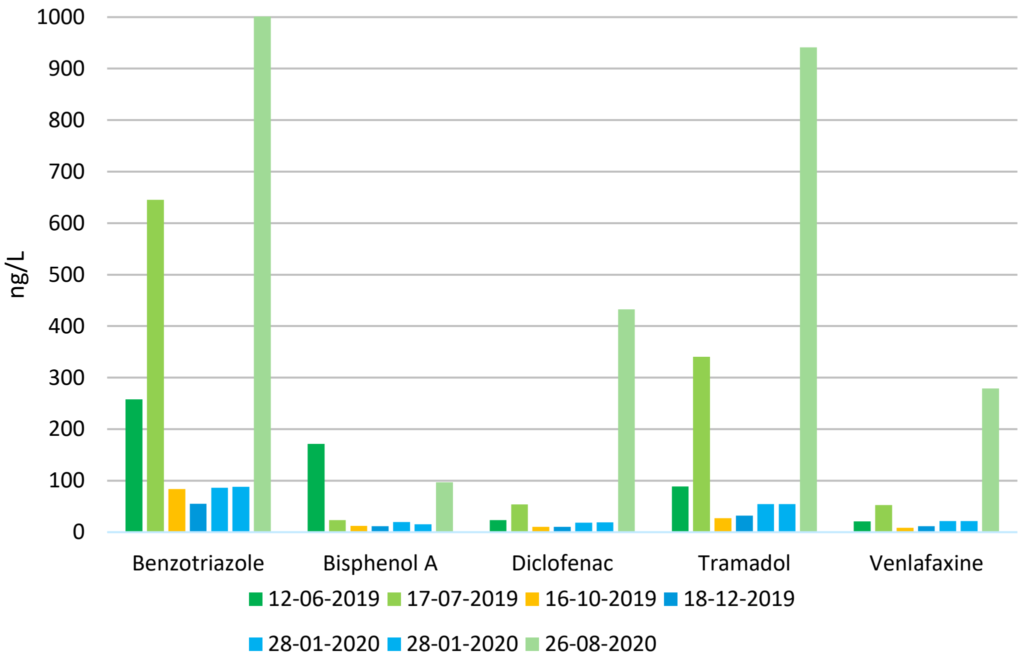

Figure 7-15: Concentrations of benzotriazole, bisphenol A, diclofenac, tramadol and venlafaxine measured on summer days (shade of green). winter days (shade of blue) and on one autumn day (orange) in Tude Å downstream the discharge position of wastewater.

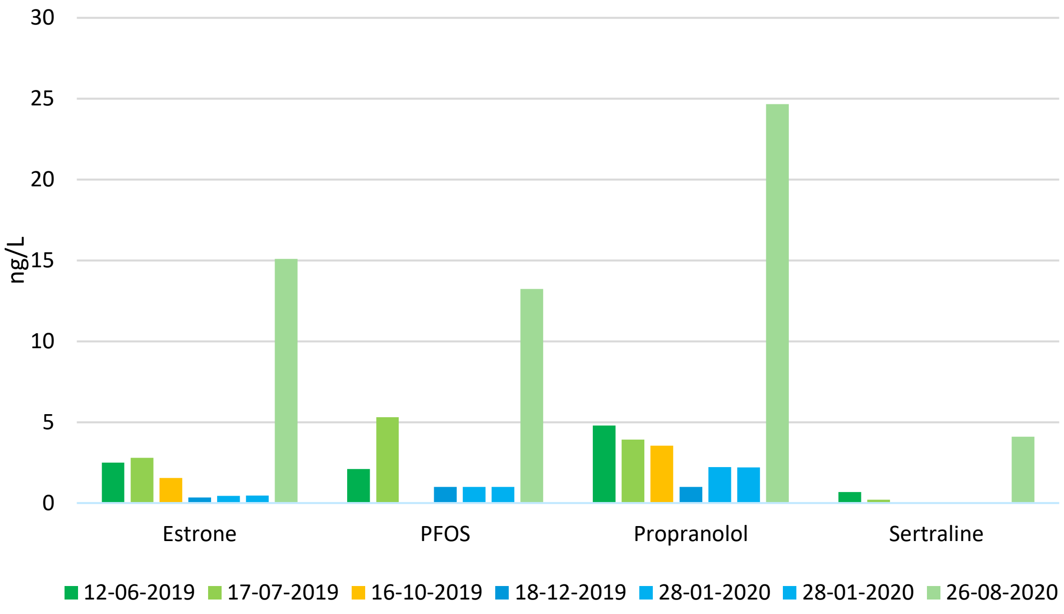

Figure 7-16: Concentrations of estrone, PFOS, propranolol and sertraline measured on summer days (shade of green), winter days (shade of blue) and on one autumn day (orange) in Tude Å downstream the discharge position of wastewater.

In Figure 7-17 the measured pollutant concentrations (MEC) in Tude Å are compared to PNEC. The MEC/PNEC=1 is exceeded more often on summer days than on winter days. All pollutants exceed MEC/PNEC=1 at least once in the summer, while in the winter only PFOS exceed MEC/PNEC=1.

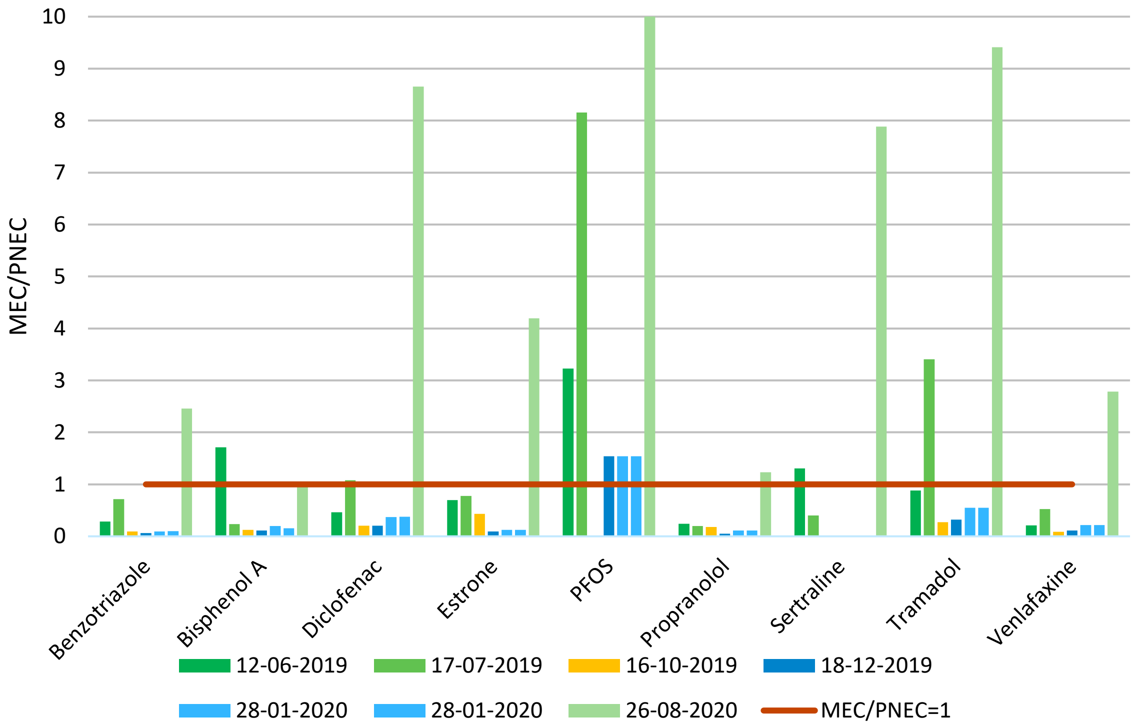

Figure 7-17: MEC/PNEC of benzotriazole, bisphenol A, diclofenac, tramadol, venlafaxine estrone, PFOS, propranolol and sertraline measured on summer days (shade of green), winter days (shade of blue) and on one autumn day (orange) in Tude Å downstream the discharge position of wastewater.

7.8 Major pollution event with neonicotinoids

Measurement results from analysis of neonicotinoids in the influent and effluent of the conventional Slagelse WWTP and in the effluent from the pilot plant are presented in Table 5-3, Table 7-2 and Table 7-3. Data are summarized in Table 7-9.

When the test period started in January 2019, a company called Flux Water operated on the WWTP Slagelse site. The company operated as a waste handling plant treating liquid hazardous waste. The liquid waste treatment processes included separation/filtration and chemical precipitation. The treated waste/wastewater was discharged to Slagelse WWTP, and the average wastewater flow was 4 m^3/h and maximum 100 m^3/d.

After the first sampling of the test period on 11.03.2019 it was realized that the effluent samples from Slagelse WWTP contained very high concentrations of three out of four analyzed neonicotinoids (acetamide, clothianidin, imidacloprid and thiamethoxam). Clothianidin, imidacloprid and thiamethoxam exceeded $PNEC_{Freshwater}$ 5 338 and 438 times respectively.

Neonicotinoids are insecticides which can be fatal to domesticated honeybees and wild pollinators. In 2018, the EU banned the three main neonicotinoids (clothianidin, imidacloprid and thiamethoxam) for all outdoor uses. Although EU tightened the ban in 2019, which means that use of all neonicotinoids was banned, the Danish Environmental Agency authorized use of neonicotinoids in beet fields to avoid loss of harvested crops. The authorization was given because the beet plants do not flower, and bees do not visit the beet plants. Seed companies treat beet seeds with neonicotinoids. The specific origin of neonicotinoids in the liquid waste handled by Flux Water is not clear. But it has been confirmed that specific liquid waste batches handled at Flux Water caused the major pollution of Slagelse WWTP.

By analyzing samples of wastewater discharged from Flux Water to Slagelse WWTP it was verified that the company was the neonicotinoid source. From Table 7-9 it appears that the concentration of clothianidin, imidacloprid and thiamethoxam exceeds the PNEC (19,133 and 296 times) on 06.06.2019. By the next sampling on 31.07.2019 the concentrations of neonicotinoids had decreased to a level below PNEC except for imidacloprid. However, the concentration had decreased from 1,112 to 40 ng/L. The handling of wastewater containing neonicotinoids at Flux Water stopped in June 2019 by intervention from the local environmental authorities.

Table 7-9: Neonicotinoid concentrations in effluent from Slagelse WWTP and after pilot plant. Concentrations which exceed PNEC are marked with orange

Date Total Flow PP Bed Volumes PP		11.03.2019 16,473 969		06.06.2019 41,514 2,442		31.07.2019 64,073 3,769		13.02.2020 175,474 10,322		25.08.2020 252,999 14,882	
ng/l	PNEC Freshwater	Effluent WWPT	Effluent PP	Effluent WWPT	Effluent PP	Effluent WWPT	Effluent PP	Effluent WWPT	Effluent PP	Effluent WWPT	Effluent PP
Acetamiprid	500	n.d	n.d	0.56	0.32	0.13	n.d	n.d	n.d	4.9	1.3
Clothianidin	130	648.6	n.d	2,515	0.33	n.d	n.d	n.d	n.d	n.d	n.d
Imidacloprid	8.3	2,805	0.1	1,112	0.51	40	0.47	7.5	1.9	23.9	4.2
Thiamethoxam	42	18,406	1.9	12,434	23.8	18	42	2.9	74.4	8.2	135

n.d. not detected

From the start of the test period until February 2020 the pilot plant removed the neonicotinoids, and the concentrations in the effluent was below PNEC. At the end of the test period (Feb – Aug 2020) the concentrations of thiamethoxam increased indicating that the GAC filter leaked thiamethoxam which gave rise to concentrations (74.4 and 135ng/L) higher than PNEC (42 ng/L).

8 Microbiology and antibiotic resistance

During the test period, culturable bacteria (22 and 37 ºC), *E. coli* and enterococci were analysed in samples from WWTP effluent (position 1), after GAC filter (position 4) and the effluent from the pilot plant (position 5). WWTP Slagelse analysed the samples. The number of culturable bacteria were counted on embedded wastewater samples on agar plates. The agar plates were cultivated at 22 and 37 ºC. *E. coli* and enterococci were measured by using Tecta™. The methods utilize the fact that bacteria produce enzymes which interact with a substrate that colours *E. coli* and enterococci. Afterwards the coloured colonies can be counted (colilert® or enterolert®) or the colour of the wastewater suspension can be detected by spectroscope measurements (Tecta™).

The results appear from Table 8-1 and show that the pilot plant removes bacteria and that the water quality meet the Danish Drinking Water Act /12/.

Table 8-1 Bacteria measured in effluent from Slagelse WWTP (1), after GAC filter (4) and in effluent from the pilot plant after UV radiation (5).

Parameter	Unit	N	Effluent WWPT (1)	N	After GAC (4)	N	N higher than requirement	Effluent pilot plant (5)	DK Drinking Water Act /12/ (user's tap)
Culturable bacteria 22 °C	CFU/mL	25	72 - >1,000	13	157 - >200	32	0	0 -180	200
Culturable bacteria 37°C	CFU/mL	26	6 ->1,000	15	56 - >200	33	-	0-63	
Escherichia coli	CFU-EQV/100 mL	24	<1 ->100,000	15	784 ->10,000	34	1	<1 - 1	N.m.
Enterococci	CFU-EQV/100 mL	22	<1 ->10,000	15	483 ->10,000	31	2	<1 - 1	N.m.

N.m.: Not measurable

The GAC filter removes *E. coli* corresponding to 1 log unit (see Figure 8-1). After the UV radiation (design dose > 40 mJ/cm^2), the concentration of *E. coli* in effluent from the pilot plant decreased to below 1 CFU-EQV/100 mL and fulfils the requirement for *E. coli* in drinking water. The Danish Drinking Water Act requires that the concentration of *E. coli* should not be measurable. During the test period, 34 *E. coli* analyses were carried out, and only once *E.coli* concentration was 1 CFU-EQV/100 mL. All other samples showed *E. coli* <1 CFU-EQV /100 mL in the effluent from the pilot plant. Enterococci have been detected to 1 CFU-EQV/100 mL twice in the test period.

When the flow through the UV-system stops, the UV radiation also stops. The water coming out immediately after a stop might not have been disinfected sufficiently. Three times (*E. coli* once; enterococci twice) the drinking water requirements have not been met, and that could be explained by previous short term stop of the UV-system. Generally, the UV system demonstrates stable operation.

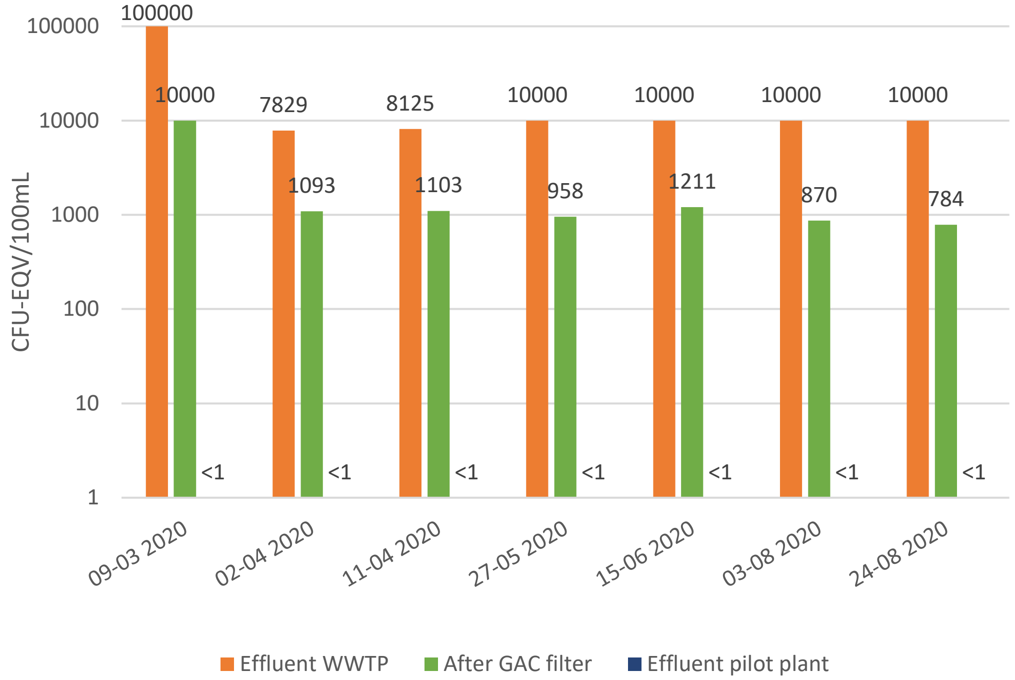

Figure 8-1: *E.coli* analysed in six samples from Slagelse WWTP effluent, after GAC filter and from effluent of pilot plant. Data labels show the concentrations of *E. coli* [CFU-EQV/100 mL].

Culturable bacteria measured at 22 ºC were analysed 32 times in the effluent from the pilot plant, and the concentration varied between 0 and 180 CFU/mL which is lower than the limit (200 CFU/mL) given in the Danish Drinking water Act /12/. Culturable bacteria at 37 ºC are reduced by UV radiation, and 33 samples were below 63 MPN/100 mL – no drinking water requirement has been given. Enterococci should not be measurable in drinking water. In 29 samples out of 31 the effluent concentrations of enterococci were below 1 MPN/100 mL, and in two samples the concentration was 1 MPN/100mL. These results show that the UV radiation ensures that discharged wastewater from the pilot plant meets the requirements for culturable bacteria 22 °C. *E. coli* and enterococci in drinking water.

One effluent sample from Slagelse WWTP and one effluent sample from the pilot plant were taken on 16.09.2020, and the samples were analysed by Eurofins related to intestinal worms. No intestinal worms were found, nor viable intestinal worms. In addition, nematodes and nematodes eggs (Ascaris, Toxocara, Trichuris, Capillaria) as well as cestodes and cestodes eggs (Taenia, Hymenolepis) were analysed. None of these parameters were detected. The legionella spp. concentration was <1000 CFU/L.

A regulation from the European Commission includes minimum requirements applicable to reclaimed water destined to be used for agricultural irrigation /13/. Reclaimed water quality class A (highest quality class) corresponds to secondary treatment filtration and disinfection. In that situation quality requirement for *E. coli* is <10 CFU/100 mL or below detection limit. Legionella spp. requirement says <100 CFU/L when there is a risk of aerosolization in greenhouse.

Reclaimed water will be considered compliant with the requirements for the parameters mentioned above when values for *E. coli*, *Legionella spp.* and Intestinal nematodes are met in 90% or more of the samples. None of the values of the samples can exceed the maximum deviation limit of 1 log unit from the indicated value for *E. coli* and *Legionella* and 100 % of the indicated value for intestinal nematodes. The treated water from the pilot plant complies with these requirements for reclaimed water (see section 11.1).

8.1.1 Antibiotic resistance

Samples collected 27.02.2020 from influent to Slagelse WWTP (primary settle tank), effluent from WWTP, after the GAC filter and effluent from the pilot plant were analysed related to the number of enterococci, *E. coli* and coliform bacteria. In continuation hereof, the following resistant bacteria were estimated: vancomycin-resistant enterococci (VRE), carbapenem-resistant Enterobacteriaceae (CPE) and third generation Cephalosporin-resistant *E. coli* (CEF-EC).

A number of coliform bacteria were estimated by embedment of wastewater or diluted wastewater in Brilliance agar (BRA) from Oxoid (2018). Agar was produced as described by the supplier. After the agar was cooled down, it was mixed with the wastewater. CPE was determined by adding Meropenem to the cooled agar. The agar plates were incubated at 36 °C ± 2 °C for 24 hours ± 1 hour. Violet colonies were interpreted as *E. coli,* and light red colonies were coliform bacteria (other than *E. coli*).

Determination of resistance against third generation cephalosporine has been carried out in the same way as CPE but by adding cefotaxime representing third generation cephalosporine. Only results from *E. coli* have been counted, i.e. violet colonies and dark blue colonies. All the bacteria analyses have been carried out twice, and the numbers shown in Table 8-2 are the averages.

Table 8-2: Measured concentrations of enterococci, coliform*, and E. coli* including resistant bacteria on 27.02.2020. Samples were collected at four places: Influent to the Slagelse WWTP (primary settle tank), effluent from WWPT, after GAC filtration, and effluent from pilot plant. Analysis were carried out by DHI.

	Enterococci		Coliform			*E.coli*		
Unit	Total MPN/100 mL	VRE CFU/100 mL	Total MPNCFU/100 mL	CPE CFU/100 mL	CEF CFU/100 mL	Total MPNCFU/100 mL	CPE. CFU/100 mL	CEF CFU/100 mL
Influent WWTP	950,000	13,000	42,500,000	455	369,500	1,690,000	182	92,350
Effluent WWTP	10,750	424	292,500	<20	12,500	17,950	<20	1,325
After GAC	1,520	49	17,500	<20	673	2,185	<20	237
Effluent PP	<1	<1	<50	<20	<20	<50	<20	<20

VRE: Vancomycin resistant enterococci
CPE: carbapenem resistant Enterobacteria
CEF: Cephalosporin resistant *E. coli*

There is very clear concentration decrease of enterococci, coliform and *E. coli* from the influent to the effluent from the WWTP and further decrease through the pilot plant. Carbapenem resistant Enterobacteria (CPE) and *E. coli* were not present in the effluent from the WWTP. After the particle filtration and GAC-filtration in the pilot plant more microorganisms have been removed, and none of the measured microorganisms (Total and resistant) were present in the effluent from the pilot plant after the water had passed the UV-system. The results indicate that the pilot plant equipped with particle filtration, GAC filter and an UV-system is an efficient barrier when it comes to microorganisms.

9 Resource consumption and overall economy

9.1 Energy and GAC consumption

The average energy consumption during operation of the pilot plant was 0.24 kwh/m^3. This covered the total pilot plant consumption, including inlet pump (pumping from secondary clarifiers), drum filter operation, pumping to GAC filter and UV disinfection.

The effectiveness of the GAC filtration can be evaluated through the total amount of GAC used and the treated amount of water. An average removal rate of 80% of critical micropollutants can be used as an efficiency target. The average removal rate of the 14 critical substances (measured above $PNEC_{Freshwater}$ in the effluent from the conventional WWTP) as well as the Swiss substances were very close to 80% in the final measurement time (see Section 7.4). At this point the filter had treated 253,000 m^3 or 14,882 BV.

The GAC filter has a volume of 17 m^3 and a filling of 7,480 kg (see Section 6.1). This corresponds to a carbon usage of 30 mg GAC/l, when the test period ended. Further measurements, after additional treatment of water, are needed to fully evaluate the potential of the present GAC filter.

To be comparable to the removal efficiency of powdered activated carbon (PAC[6]) about 10-20 mg/l activated carbon should be reached. A carbon usage of 15 mg/l will correspond to approximately 30,000 BV in the present GAC-filter. However, a full-scale implementation of GAC will most probably be designed with serial GAC filter cells. Here, renewal of GAC filter cells will take place stepwise securing an optimised micropollutant saturation and a longer lifetime of the GAC filters. And if a low dose of ozonation (0.2 g ozon/g DOC) is added before GAC filtration, it is realistic to expect filter lifetime above 50,000 BV /4/. This corresponds to a carbon usage of 10 mg/l. Ozonation is also planned to be tested in combination with GAC in Slagelse WWTP within 2021 (See Section 10).

Experience from a full-scale advanced treatment plant at Herlev Hospital in Copenhagen also shows that serial GAC filters can easily reach a GAC consumption of 10-12 mg/l. In Herlev Hospital three GAC filters are renewed in steps to secure a constant high removal rate of the critical hospital micropollutants /14/. It should be noted that ozonation and microfiltration (200 nm) are done prior to GAC treatment at Herlev Hospital.

Production of conventional activated carbon based on fossil precursors is well known to cause environmental pollution. Mining of fossil coal, the activation process and transportation of activated carbon cause considerable amounts of energy use and CO_2-emissions. The production of conventional virgin activated carbon is quantified to cause consumption of 109-124 GJ per tons activated carbon and emission of 11-18 tons of CO_2-equivalents per tons activated carbon. The production of reactivated carbon is quantified to cause 17-29 GJ per tons product and emission of 2-3 tons of CO_2-equivalents per tons reactivated carbon produced /15/.

In other words, production of reactivated carbon causes six times less CO_2-emissions than production of virgin activated carbon. On this background it was decided to use reactivated carbon in the present study. Reactivated carbon from Desotec (Organosorb 20) was used, and the amount for filling was 7,480 kg. Compared to the use of virgin

[6] PAC has the important disadvantage that it is not possible to recycle and reactivate. PAC is normally disposed with the sludge when used in urban WWTP's.

activated carbon this results in a total saving of approximately 90 tons CO_2-equivalents in the present study.

9.2 Pilot plant costs

The original total investment budget for the pilot plant, including carbon usage, was 104,000 EUR. Not unexpected for a research and development project, the total final investment cost ended up in 210,000 EUR. This has covered e.g. reconstruction and installation of new larger pumps for feeding of the GAC filter, installation of pressurized air setup for backwash of GAC-filter and new influent pump.

The number of man-hours used for maintenance of the pilot plant was approximately 4 hours per week. Especially the drum filter needed maintenance and cleaning during summer because of algae growth in the secondary clarifiers, where the influent to the pilot plant was collected.

9.3 Input for estimate of overall future costs for full scale implementation

Slagelse Utility has decided to install full-scale advanced treatment to remove micropollutants and pathogens before 2025. The present large-scale pilot plant is to be viewed as a pre-test and development project for implementation of the future full-scale solution. The present testing of the process train: Particle filtration -> GAC filter -> UV is the first step to narrow down the most optimised solution for Slagelse WWTP.

In November 2020, Slagelse Utility has received approval for funding from the Danish EPA to establish an expansion of the pilot plant. The expansion will cover testing and development of oxidation processes (ozonation and AOP) in combination with the existing process train. The objective is to develop targeted processes to remove the few last micropollutants which break through the GAC filter and hereby extend the performance and lifetime of the GAC filter.

From this perspective it is not possible now to lay down a fully covering estimate of the future economy for polishing the wastewater at Slagelse WWTP. But based on the present preliminary experiences it is possible to describe an estimate for the future costs of the full-scale implementation.

The estimate is based on an assessment of a cost per m^3 treated water based on the pilot plant scale (30 m^3/t). Slagelse WWTP has an average dry weather flow of 370 m^3/h, so upscaling of the treatment is certainly expected to result in benefits from economies of scale.

The estimate is based on a linear write-off over 15 years and assuming a GAC-filter loading of 46,000 BV (five filter shifts) which corresponds to a carbon usage of 10 mg/l. Total investment costs for drum filter, building, pumps & pipes, GAC filter unit and UV are estimated to 120,000 EUR, and each GAC filter filling (including GAC transport costs) is estimated to 16,200 EUR. This accounts to 0.056 EUR/m^3 (0.42 DKK/m^3). Including electricity consumption (0.013 EUR/m^3) and manpower for maintenance (0.019 EUR/m^3) the total estimate amounts to 0.088 EUR/m^3 (0.66 DKK/m^3).

10 Evaluation of the concept

Different polishing processes for removal of micropollutants from urban WWTPs are currently being tested all over Europe. Also, full-scale implementations of mainly ozonation and powdered activated carbon (PAC) are seen, especially in Germany and Switzerland. Sweden has now a full-scale implementation of ozonation in Lidköping and a couple of granulated activated carbon (GAC) installations. Still Denmark has not got any full-scale WWTP implementation of processes designed for removal of micropollutant.

In the present study we have tested a WWTP polishing process train consisting of (see details in Figure 6-3):

Particle filtration (10 µm) → GAC → UV

Particle filtration (10 µm)

The drum filter was installed to protect the GAC filter against suspended solids from the secondary sedimentation. Elevated concentrations of suspended solids can occur after secondary sedimentation during e.g. rain events. The installed drum filter worked as planned and prevented especially string algae during spring and summer of reaching the GAC filter. Installation of a prefiltration (2 mm pore size) before the influent pump in the last part of the test period prevented a large part of the string algae to get into the drum filter. This reduced the need for maintenance to a minimum.

GAC filter

The background for the present testing of WWTP polishing through GAC filter was:

- In several international tests GAC has shown a very broad range and effectful removal of micropollutants.
- Adsorption in activated carbon does not result in any potential critical reaction products like NDMA or bromate. This is a risk when using ozonation.
- GAC can be reactivated and recycled after use. This is contrary to PAC which is disposed after use.
- Because GAC can be recycled it has a lower CO_2-footprint than PAC.
- When biofilm is established in a GAC-filter, supplementary biological degradation of micropollutants can potentially take place.
- GAC works as a supplementary particle filtration.

Disadvantages can be that GAC filters tend to use more activated carbon than PAC processes (in mg AC per litre). This may lead to a risk that GAC causes higher costs.

Therefore, the important question was: How to operate GAC to keep the consumption of activated carbon low and still achieve high removal rates?

The present GAC filter is a standard commercial large-scale filter (8 m high cylinder and 2.6 meter in diameter). Several commercial activated carbon suppliers deliver similar filters. During operation the most important issue was the building up of high pressure drop across the filter. This was most likely caused by suspended solids smaller than 10 µm. To prevent the high pressure drop, backwash was carried out six times during the 1.5 years test period. The commercial GAC filters are designed to be easily transported on large trucks. They are not optimised to prevent high pressure drop. In a future full-scale installation at Slagelse WWTP it might be an advantage to design the GAC filters with higher surface area compared to bed hight. This may help to reduce the pressure drop issue.

The GAC filter was filled with reactivated carbon (0.42-2.80 mm). The production of reactivated carbon causes six times less CO_2-emissions than production of virgin activated carbon This was used to clarify whether the low CO_2-footprint carbon could reduce the critical micropollutants efficiently.

Testing of GAC filtration is challenged by the fact that it takes long to reach a high number of bed volumes and to get the chance to make long-term evaluation of the filter performance. In the present 1.5-year test period, 14,882 bed volumes were reached. In comparison, European references often reach 30,000 to 50,000 BV. After 14,882 BV the average removal rate of the critical substances was still 83%. Five substances were exceeding the $PNEC_{Freshwater}$.

The monitoring campaigns showed that the removal efficiency was improving during the last phase of the test period which might be explained by biofilm growth (see section 7.4). This tells us that the removal efficiency may develop even more positively over time, but we need to follow the GAC filter over a longer period to clarify this. For now, we can conclude that the removal efficiency concerning selected pharmaceuticals and industrial chemicals was high (>80%) in the final part of the test period.

The high removal efficiency also showed that reactivated/recycled GAC worked satisfactorily. This conclusion is the same as conclusions from Swiss studies where reactivated and virgin carbon has been compared /4/. No significant difference in treatment performance was observed.

The empty bed contact time (EBCT) was between 34 and 43 minutes in most of the test period. In short periods, EBCT was even as high as 1 hour. This EBCT (above 34 minutes) is a little higher than the general recommended minimum EBCT above 25 minutes for effective micropollutant removal (see e.g. /17/). We registered that heightening the EBCT to one hour did not increase the removal rate.

However, the exceeding of $PNEC_{Freshwater}$ for five substances (azithromycin, PFOS, diclofenac, tramadol and sertraline) is still considered critical by Slagelse Utility and Slagelse Municipality. Therefore. Slagelse Utility has now planned to test additional polishing techniques to remove this last exceeding of $PNEC_{Freshwater}$. It is planned to test combinations of GAC with different oxidation steps before or/and after the GAC filter. The tests of oxidation will cover ozonation and advanced oxidation processes (AOP) and are planned to be carried out in 2021.

By future testing of combination of ozonation/AOP before and after GAC it is expected that the GAC filter can reach above 50,000 BV or even change into a biological activated carbon (BAC) filter, which could have much higher life expectancy (>100.000 BV) /18/ – and concurrently potentially remove the critical substances below $PNEC_{Freshwater}$.

UV

The UV treatment finalised the polishing process train that the pilot plant consists of. A swirl flow UV reactor with a dose of 40 mJ/cm^2 secured a very stable disinfection after GAC filter treatment.

E. coli and enterococci were reduced to below detection limit (<1 MPN/100 mL) in all the weekly samples in the test period except for three times where values of 1 MPN/100 mL were measured once for *E. coli* once and twice for enterococci. These three values could all be explained by prior flow stops.

When the flow through the UV-system stopped, the UV radiation also stopped. The UV system only started up when the flow was above 12 m^3/h. Due to this, this first water was not disinfected. And the three times with measurable *E. coli* and enterococci were all linked to flow-stops and the subsequent insufficient disinfection. The future UV-setup will ensure that the UV-radiation will start up immediately when flow is measured. This can prevent non-disinfected water to leave the WWTP in the future.

11 Reuse of treated wastewater

The water quality of the effluent from the pilot plant is documented to be very high, and that leads to more options for reuse. The options are very often linked to drinking water standard and standards for irrigation, but several applications have their own parameters and concentrations to be met. Here, focus is on standards for drinking water and irrigation.

In the following, the new EU regulation on minimum requirements for water reuse for agricultural irrigation /13/ will be used for comparison. The new regulation will apply from 26 June 2023 in the member states and include an authority permit process, where the responsible parties (including the end-user) for the water reuse system will have to apply for a permit to the competent authority.

11.1 Quality of treated water

The possibility for reusing the treated water is closely related to the water quality. 30 parameters were analysed twice in the effluent from the pilot plant (10.09.2019 and 25.11.2019) and compared with Danish drinking water requirements (see Table 11-1).

Table 11-1: Drinking water parameter measured in effluent from the pilot plant and in water from the water works Valbygaard in Slagelse. The Danish drinking water standards refer to water quality at consumer's tap. Concentrations exceeding drinking water standards are in orange colour

Parameter	Unit	Effluent Pilot plant. 10.09. 2019	Effluent Pilot plant. 25.11. 2019	Waterworks Valbygaard 2019	DK drinking water standard /12/
pH	pH	8	8.1	7.3	7.0-8.5
Temperature	°C	17	17	10.2	12 (aim)
Evaporation residue	mg/l	590	660	600	
Conductivity	mS/m	99	110	106	>300 – 25,000
Colour	mg Pt/l	26	36	4.7	15
Turbidity	FNU	0.48	0.34	0.15	<1
Hardness	°dH	12	15.7	17	
Calcium (Ca)	mg/l	72	94	95	
Magnesium (Mg)	mg/l	9.3	10	17	
Ammonium (NH_4^+)	mg/l	0.26	0.065	< 0.005	<0.05 (0.5)
Nitrite	mg/l	0.102	0.12	< 0.004	0.10
Nitrate	mg/l	1.95	13	3.4	50
Chloride	mg/l	130	150	120	250
Fluoride	mg/l	0.24	0.29	0.38	1.5
Sulphate. filtrated	mg/l	33	40	29	250
Aggressive carbon dioxide	mg/l	< 2	<2	< 5	
Hydrogen carbonate	mg/l	323	384	390	
NVOC	mg/l	5.8	7.5	1.9	4
VOC	mg/l	< 0.5	<0.5	1	

(cont'd)

Parameter	Unit	Effluent Pilot plant. 10.09. 2019	Effluent Pilot plant. 25.11. 2019	Waterworks Valbygaard 2019	DK drinking water standard /12/
TOC	mg/l	5.8	7.5		
Iron (Fe)	mg/l	0.073	0.069	0.0074	0.2
Kalium (K)	mg/l	22	20	5	
Mangan (Mn)	mg/l	0.048	0.033	0.00065	50
Natrium (Na)	mg/l	120	130	110	175
Arsenic (As)	µg/l	0.88	0.96	0.92	5
Cadmium (Cd)	µg/l	0.03	<0.003	< 0.003	3
Chrome (Cr)	µg/l	0.2	0.035	< 0.03	50
Copper (Cu)	µg/l	0.73	2.4	2.2	2,000
Nickel (Ni)	µg/l	1.3	1.2	0.076	20
Zinc (Zn)	µg/l	95	86	3.3	3,000

Ammonia concentrations up to 0.50 mg/L is accepted at the tap, but simultaneously the nitrite requirement (0.10 mg/L) must be met. Twice the nitrite concentration (0,102 mg/L and 0,12 mg/L) show minor exceeding of the requirement. Nitrite and nitrate requirements also include that: (nitrate conc./50) + nitrite conc./3) ≤1. The two water samples from the effluent of the pilot plant meet this requirement.

In addition, the Danish drinking water Act includes quality requirements related to PFAS compounds, and the individual compounds must not exceed 0.1 mg/l. Two of the PFAS compounds are PFOS and PFOA, which were analyzed in the effluent from the pilot plant, and the average concentrations were 0.0067 and 0.0032 µg/l. The concentrations meet the quality standard.

Compared to the microbiological requirements, the effluent water meets the Danish drinking water Act (see Chapter 8).

Based on the knowledge about the water quality found in this project, reuse of pilot plant effluent in technical processes, which need drinking water quality, is in principle possible.

The EU regulation for water reuse for agricultural irrigation /13/ contains minimum requirements. Reclaimed water quality requirements are divided into four classes (A-D), but in this report only class A is described (the tightest requirements). Class A water is allowed for irrigation of all food crops, including root crops consumed raw, and food crops where the edible part is in direct contact with reclaimed water.

From Table 11-2 it appears that effluent water from the pilot plant meet the water quality requirements for agricultural irrigation concerning the parameters BOD, TSS and Turbidity. In most cases the measurement for turbidity FNU and NTU can be compared.

The indicated values for BOD, TSS and turbidity in Class A shall be met in 90% or more of the samples. None of the values of the samples can exceed the maximum deviation limit of 100% of the indicated value.

Table 11-2: Water quality in effluent from pilot plant and reclaimed water quality requirements for agricultural irrigation.

Parameter	Unit	Average effluent of pilot plant	EU irrigation requirements
BOD	mg/l	2.9	<10
TSS	mg/L	4	<10
Turbidity	FNU/NTU	0.48*	<5**
E. coli	CFU/100 mL	<1 – 1***	<10
Legionella spp.	CFU/100 mL	<1,000	<1,000 Where there is risk of aerosolization in greenhouses
Intestinal nematodes (helminth eggs):	egg/l	n.d.	≤1 For irrigation of pastures or forage

n.d. not detected

*Single measurement FNU (Nephelometric Turbidity Unit (white light 400-680 nm)

**Formazin Nephelometric Unit (infrared light 780-900 nm)

*** for more details seeTable 8-2

Compared to the microbiological requirements, the effluent water meets the EU requirements for reclaimed water for agriculture (see Chapter 8).

The EU regulation also sets requirements to water quality A with regard to performance target for treatment facilities which produce reclaimed water (see /13/ for details about monitoring requirements). The validation of treatment facilities appears from Table 11-3.

Table 11-3: Validation monitoring of reclaimed water for agricultural irrigation /13/.

Indicator bacteria	Performance target Log_{10} reduction	Performance Pilot Plant Log_{10} reduction
E. coli	≥5.0	≥5.0 Tecta-method ≥6.0 Plate count method

When the concentration of *E. coli* in the influent to Slagelse WWTP was >100,000 CFU-EQV/100 mL (Tecta-method), total *E. coli* reduction was more than a 5 log_{10} reduction, which indicates that the WWTP including the pilot plant meets the EU requirements for quality of water to be used for agricultural irrigation (see Chapter 8). Sampling on 27.02.2020 of influent to the WWTP showed *E. coli* concentration of 1,690,000 CFU/100 mL (plate count method) and <50 CFU/100 mL in the effluent from the pilot plant which indicates a >6 log_{10} reduction.

The regulation also includes performance targets for Total coliphages or similar coliphages (≥6.0 log_{10} reduction) and *Clostridium perfringens* spores/spore-forming sulphate-reducing bacteria (≥4.0 log_{10} reduction and ≥5.0 log_{10} reduction respectively). Analyses of Total coliphages and *Clostridium perfringens* spores have not been carried out during the test period.

11.2 Possible reuse of treated water in Slagelse

When application of treated wastewater is considered, several topics must be handled including:

- Risk assessment related to water quality and application (see section 11.1)

- Monitoring programs
- Collection, handling and transport of the water
- Authority approval

Sometimes overcoming of prejudice related to quality of treated wastewater is needed when drinking water is replaced although the water has a better quality in general compared to most drinking water.

Below, several sectors/activities or professions placed around Slagelse are mentioned, which could profitably use treated wastewater, save drinking water resources and water/discharge taxes. The yearly consumption of drinking water is estimated based on common knowledge about the sectors/activities.

Golf courses

It is very often necessary to irrigate golf courses, but only a minor part of the golf course is irrigated, i.e. greens and tee sites to keep them in good condition. In dry summers the fairways are sometimes irrigated, too, and more water is needed. Water consumption for irrigation at three Danish golf courses has been estimated to 4,500 to 8,000 m^3/year, and the courses cover between 56 and 95 ha /20/.

Garden centers

In the catchment area to Slagelse, there are some garden centers that grow vegetables, e.g. strawberries, blue berries and different sorts of cabbage used for human consumption. Most of the crops grow outdoor, but strawberries also grow in green house and in tunnel houses. Therefore, different irrigation systems are used. A strawberry field needs about 1000 m^3 per ha during one season /19/.

Garden centers selling ornamental plants and other plants for private customers very often use drinking water for irrigation, but here use of treated wastewater could be an alternative.

Combined heating and power plants and combined incineration and heat plants

The nearby placed incineration plant for waste uses conventionally treated wastewater from Slagelse WWTP for irrigation of incineration slag.

The distribution system for heat to the households and companies using district heating must be fed with make-up water, which today consists of drinking water, but an alternative could be effluent water from the pilot plant. The water is softer than the drinking water which is an advantage. The combined heating plants in the Slagelse catchment area each consumes about 5,000 m^3 make-up water per year.

Slagelse WWTP

Slagelse Utility uses about 21,000 m^3 per year of conventionally treated wastewater from Slagelse WWTP to cleaning processes related to grit removal, pre-dewatering and end dewatering of sludge. Today conventional effluent wastewater is also used for cleaning of filters and production of polymer solutions. By substituting conventional effluent wastewater with pilot plant treated water (with drinking water quality), problems with blocking of filters due to too much suspended solids can be avoided, and better hygiene can be attained when producing polymer solutions.

Slagelse WWTP uses 1,000 to 1,100 m^3 drinking water per year of which 300 to 350 m^3 goes to cleaning of offices or is used in the canteen and to toilets etc. The remaining 700 to 750 m^3 is used as technical water for other purposes and could be substituted with water from the pilot plant.

Other applications

Concrete production companies very often use drinking water in the concrete production. Instead they could use polished wastewater. Today the concrete production company Unicon, situated nearby Slagelse WWTP, uses 1,800 m^3 drinking water per year, which could potentially be replaced by water from the pilot plant.

During summer, hot dry periods very often occur, and limitations concerning use of drinking water for irrigation might be introduced. Slagelse Utility is considering supplying polished water from a water station (corresponds to a gas station), where private people and companies can collect water for purposes where drinking water quality is not legislatively required.

Slagelse Municipality Contractor carries out wet road salting, dust control and street cleaning, where polished water could also easily be used.

12 References

/1/ Johannes Altmann et al., 2016: *UV254 absorbance as real-time monitoring and control parameter for micropollutant removal in advanced wastewater treatment with powdered activated carbon*. Water Research 94 (2016) 240-245.

/2/ Marc Bourgin et al., 2018: *Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products.* Water Research 129 (2018) 486-498.

/3/ Federal Office for the Environment (FOEN). 2017: *Gewässerqualität: Revision der Gewässerschutzverordnung* (accessed 1 august 2017).

/4/ Christa McArdell, EAWAG, 2020: *Pilotversuche mit GAK und Kombiverfahren Ozon + GAK auf Schweizer Kläranlagen*. 4. WebSeminar KomS-VSA am 10.09.2020.

/5/ Danish Ministry of Food and Environment, 2019: *Act on wastewater permits etc. according to law on environmental protection.* Consolidation Act no. 1317. 4 December 2019.

/6/ Slagelse Utility and Slagelse Municipality (SUSM), 2019: *Rapid Small Scale Column Test (RSSCT) of Organosorb 10 and 20 with effluent water from Slagelse WWTP. Pre-test for construction of pilot plant at Slagelse WWTP.* Interreg South .Baltic Less is More-project. Report by DHI. January 2019.

/7/ European Medicines Agency, 2006: *Guideline on the environmental risk assessment of medicinal products for human use*. June 2006.

/8/ PubChem Open Chemistry Database https://pubchem.ncbi.nlm.nih.gov. October 2020.

/9/ DHI, 2020: *Database on Physical Chemical data*. October 2020

/10/ DHI, 2016: *Full scale advanced wastewater treatment at Herlev Hospital*. Prepared by DHI, May 2016.

/11/ P. Wunderlin, A. Joss und J. Fleiner, 2017: *Elimination von spurenstoffen durch granulierte aktivkohle (gak) filtration: grosstechnische untersuchungen auf der ara bülach-furt – zwischenbericht.* EAWAG 2017.

/12/ Miljø- og Fødevareministeriet, 2019: *Bekendtgørelse om vandkvalitet og tilsyn med vandforsyningsanlæg*. BEK nr. 1070 28/10/2019

/13/ Regulation (EU) 2020/741 of the European Parliament and of the Council of 25 May 2020 on Minimum Requirements for Water Reuse.

/14/ Herlev Hospital, 2020: *Self-control of treated wastewater from Herlev Hospital*. June 2020.

/15/ DWA, 2016: *Aktivkohleeinsatz auf kommunalen Kläranlagen zur Spurenstoffentfernung –Arbeitsbericht der DWA-Arbeitsgruppe KA-8.6 "Aktivkohleeinsatz auf Kläranlagen".* Korrespondenz Abwasser. Abfall 63 (12). 1062–1067.

/16/ Miljø- og Fødevareministeriet, 2019: *Bekendtgørelse om spildevandstilladelser m.v. efter miljøbeskyttelseslovens kapitel 3 og 4.* BEK1317 04/12/2019.

/17/ EAWAG, 2017: *Elimination von Spurenstoffen durch granulierte Aktivkohle (GAK) Filtration: Grosstechnische Untersuchungen auf der ARA Furt-Bülach*. Zwischenbericht Dübendorf. January 2017.

/18/ Reungoat. J. *et al*., 2012: *Ozonation and biological activated carbon filtration of wastewater treatment plant effluents*. Water Research. Volume 46. Issue 3. 1 March 2012. Pages 863-872.

/19/ Gartnerirådgivning (2016) IPMjordbr.pdf (hortiadvice.dk)

/20/ Københavns Universitet, 2011: Opsamling af regnvand på golfbaner – Københavns Universitet (ku.dk) 2011 | Videnblad nr. 07.03-04

/21/ Chemicalize.com

/22/ Svahn. O., 2016: *Tillämpad miljöanalytisk kemi för monitorering och åtgärder av antibiotika- och läkemedelsrester i Vattenriket*. Lund University. 2016.

/23/ Svahn. O. & Björklund. E., 2016: *Increased electrospray ionization intensities and expanded chromatographic possibilities for emerging contaminants using mobile phases of different pH.* Journal of Chromatography B. 1033, 128-137.

/24/ Svahn. O. & Björklund. E., 2019: *Simple, fast and inexpensive large "whole water" volume sample SPE-loading using compressed air and finely ground sand.* Anal. Methods VL IS 2019, 1431, 64–73.

/25/ US Environmental Protection Agency (US EPA): *Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC / MS / MS*. 2007.

/26/ US EPA Epi Suite Exp data EPI Suite™-Estimation Program Interface | Predictive Models and Tools for Assessing Chemicals under the Toxic Substances Control Act (TSCA) | US EPA