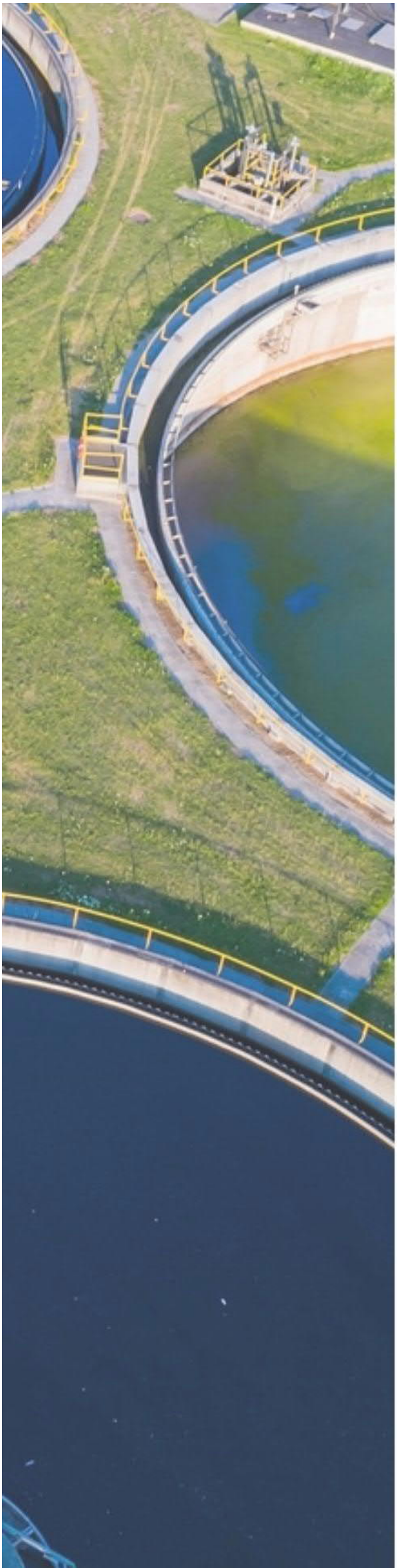


Interreg South Baltic

EUROPEAN UNION

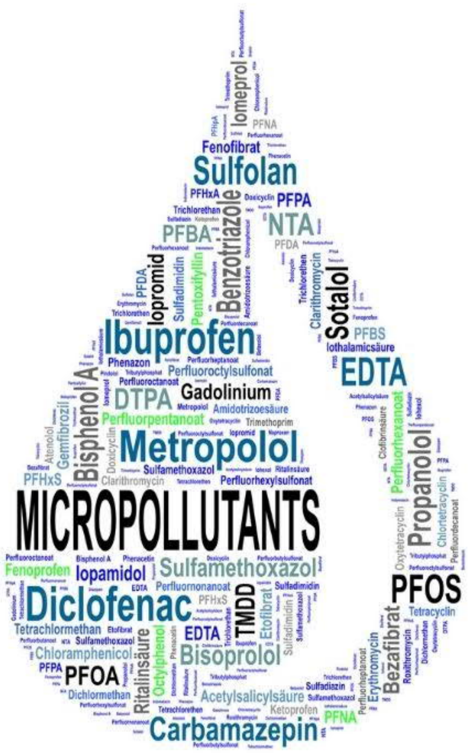
European Regional Development Fund

Less is More

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

Deliverable No: 4.1 (part I)

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



Summary

The objective of this part of the LESS IS MORE project was to test and evaluate a process-driven innovation for wastewater treatment including removal of organic micropollutants; direct membrane filtration (DMF) followed by granular activated carbon (GAC) filtration. By introducing microsieving and membranes early in the process line an improved treatment process and enhanced potential for reuse of energy and water could be expected. In addition, a parallel pilot plant was constructed with GAC-filtration as a fourth treatment step treating the biologically and chemically treated effluent from the full-scale Svedala WWTP.

GAC filtration following DMF showed a very high potential for removal of organic micropollutants. All substances studied were initially removed to at least 97%. Long term effects and breakthrough behaviour could however not be analysed, since severe fouling of the membranes only permitted short time operation, in the range of a few days, before substantial cleaning was needed to continue operation. Further development of membrane operation on raw wastewater is needed in order to evaluate and potentially establish a full-scale concept based on DMF and GAC filtration. Tests in laboratory and pilot scale showed that approximately 90% of COD could be removed with DMF and preceding coagulation/flocculation with microsieving. Most of the reduction was attributed to the microsieve with preceding coagulation/flocculation. Moreover, the DMF concept provides opportunities for reuse of wastewater and control of P-removal with potential for >95% phosphorus removal.

The full-scale treatment at Svedala WWTP, with biological and chemical treatment, is only removing organic micropollutants to a limited extent. However, adding advanced treatment with GAC filtration makes it possible to accomplish high removal. This was demonstrated by pilot-scale operation during a period of 10 months, resulting in operation corresponding to 30 000 bed volumes (BV). Breakthrough of UVA254 and DOC occurred after a few thousand bed volumes while reduction in removal efficiency for several micropollutants was noted at a later stage which is in accordance with previous studies. At 3000 BV basically all substances showed a reduction of more than 80%. Between 8000 and 18000 BV, the removal efficiency was deteriorated (to less than 50%) for several compounds. Removal efficiency is likely affected by the applied EBCT (10 minutes in this study) and might be improved by increasing the contact time.

An important part of the LESS IS MORE project has been dedicated to laboratory studies of separation mechanisms in GAC filters. Differentiation between separation and degradation using radiolabelled substances, model prediction of GAC performance using batch tests with PAC and extraction of previously adsorbed micropollutants are examples of methods and procedures that have been established. They will be used in future studies of the complex removal mechanisms in GAC-filters in order to find improvements in design as well as operation of filters. Also, analytical procedures have been developed enabling more rapid analysis, yet at the same time avoiding cross contamination, of whole water samples. During the project several new compounds have been added to the plethora of analytes. At an early state benzotriazole was identified as an important compound, and later on the reminding majority of the Swiss indicator substances. Finally a whole new method for analysing the compounds on EUs watchlist 3 was developed.

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. The Swedish partners' participation in the project was co-financed by the Swedish Agency for Marine and Water Management.

Partners in the project were: Lund University, Department of Chemical Engineering; Sweden Water Research AB, Kristianstad University, Slagelse Utility, 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 Swedish pilot plant which is one out of three national reports within Deliverable 4.1. This deliverable also includes one consolidated summary report.

The main work within this part of the project deliverable has been carried out by Alexander Betsholtz, Simon Gidstedt, Ola Svahn, Federico Micolucci, Åsa Davidsson and Michael Cimbritz.

Thank you to Tobias Hey, Janne Väänänen, Basel Al-Rudainy, Emmanuel Joncquez, Ann-Sofi Jönsson and Frank Lipnizki for guidance and for lending us your expertise. Thank you to Per Falås, Stina Karlsson, Ellen Edefell, Maria Takman and Gertrud Persson, for valuable support and help at the pilot scale plant and in the laboratory. Thank you to Svedala municipality for hosting the plant and a special thank you to the staff at Svedala WWTP - without your help the pilot scale plant would still be in its construction phase.

This report was written by Michael Cimbritz, Åsa Davidsson, Ola Svahn, Simon Gidstedt and Alexander Betsholtz.

Lund, April 20th, 2021

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Introduction

Organic micropollutants (OMP), for example pharmaceutical residues, can cause negative effects in lakes and rivers, already at very low concentrations (see, for example, Fick et al., 2010, Larsson et al., 1999). The Swedish government has concluded that advanced wastewater treatment is one of the measures needed in order to limit negative effects from organic micropollutants in receiving waters. Therefore, the Swedish Agency for Marine and Water Management, on behalf of the government, has funded several projects during the last years with the purpose of evaluating and developing techniques to be applied at municipal wastewater treatment plants. The projects were finished by 2017 and are described by Cimbritz & Mattson (2018). Following these projects, The Swedish Agency for Marine and Water Management decided to support LESS IS MORE financially.

Since 2019 the Swedish Environmental Protection Agency supports pre-studies and actual upgrades of Swedish wastewater treatment plants, meaning that several municipalities have received funding and that their wastewater treatment plants are under construction or in the planning phase. A few are also in operation, either with ozonation or granular activated carbon or both. At the moment these plants are not regulated by legal permits, but rather taken into operation to reduce loading of organic micropollutants and to protect sensitive recipients and future drinking water resources. The Water Framework Directive (2000/60/EC), with the Priority Substances Directive (2013/39/EU) and the watch list (article 8b), are driving forces for regulation and actual measures for countries within the European Union. Some of the substances included in the watch list have been recorded as river basin-specific pollutants (RBSP) according to The Swedish Agency for Marine and Water Management regulations on classification and environmental quality standards for surface water (HVMFS 2015:4). In practice this means that Sweden became one of the first countries to introduce environmental quality standards for these substances. However, yet there is no, standard procedure on how to regulate discharge of organic micropollutants, neither in Sweden nor in other member states.

Implementing existing technologies (like activated carbon) for removal of organic micropollutants is expected to increase the energy consumption at the WWTP. Conventional wastewater treatment (including biological treatment) already struggles with a high energy consumption due to the aeration needed for oxidation of organic matter. If this organic matter instead could be separated from the wastewater and used for generation of energy, e.g. by biogas production, the energy balance could be improved. One innovative process for separation of organic matter is a physico-chemical process including chemically enhanced microsieving and direct membrane filtration (DMF). This process was introduced by Ravazzini et al. (2005) and further tested and developed by Hey (2016). The DMF concept shows a high potential for reduced foot-print and increased biogas production, the latter by >30 % compared to conventional wastewater treatment (Hey et al., 2017). High retention of particulate phosphorus and organic carbon makes the DMF-concept interesting also as treatment preceding granular activated carbon (GAC) filtration for removal of organic micropollutants. However, the combined concept (DMF + GAC) has previously not been tested. Within the Swedish part of the LESS IS MORE project this concept was further tested and evaluated.

Objective

The specific objective of this part of the project was to test and evaluate a process-driven innovation; chemically enhanced microsieving and subsequent direct membrane filtration followed by granular activated carbon filtration. By introducing microsieving and membranes early in the process line an improved treatment process and enhanced potential for reuse of energy and water could be expected. This innovative process was evaluated together with GAC as a fourth treatment step proceeding biological treatment.

Chemical analysis of organic micropollutants

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, several 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, and on the other hand the many substances to be analysed lead to increased complexity, which in turn can cause greater analytical uncertainty and lower method sensitivity. The comparability between different analyses can also be made more difficult if the same substances are not measured in the different methods.

Within this project several organic micropollutants, including pharmaceuticals, were selected to be analysed. The substances were selected based on the following questions:

- What are the typical concentrations of organic micropollutants (OMPs), preferably pharmaceuticals, emerging from a sewage treatment plant?
- Which substances 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.

Analytical method

To be able to analyse pharmaceutical residues and other organic micropollutants in water samples, which often occur in low to very low concentrations, special sample preparation and analysis techniques are required. During sample preparation, the OMPs are separated and concentrated. Furthermore, background-disrupting substances, such as humic acids, 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 LESS IS MORE only HPLC-MS/MS was used. In the literature, the analytical chain is often shortened to SPE-HPLC-MS/MS.

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 (Svahn, 2016). The special sample processing technology that has been developed and used in the analysis in LESS IS MORE enables analysis of the entire water sample, without filtration through a 0.45 µm filter that is otherwise usually the case (Svahn & Björklund, 2019). 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 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 (Svahn & Björklund, 2019).

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 huge number of substances with a huge variety of chemical properties. 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, each of which has its own column linked to; an acidic-, a basic- and a neutral method. During method development, each compound is evaluated for chromatographic conditions and mass spectrometric optimization. The uniqe set up enables new compounds to be added at their required analytical optimum with relatively ease, as has been the case in LESS IS MORE. The strategy also 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 (Svahn & Björklund, 2016). The methods are validated according to the standard method, 1694, published in 2007 by the US Environmental Protection Agency (US EPA), Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC / MS / MS (EPA, 2007).

The pilot site

The pilot plant was placed indoors at Svedala wastewater treatment plant (WWTP), in Scania in Southern Sweden, see Figure 1

Figure 1. The Swedish pilot plant was placed at Svedala WWTP in Svedala. The picture also shows the location of the other two pilot plants in the LESS IS MORE project; Kretinga (outside Klaipeda in Lithuania) and Slagelse (on the west side of Sjaelland in Denmark).

Svedala WWTP

Svedala WWTP was built in 1974 and re-constructed in 1996 for additional nitrogen removal. Approximately 12 000 persons are connected. In addition, minor industries are connected. Figure 2 illustrates the process configuration at the plant.

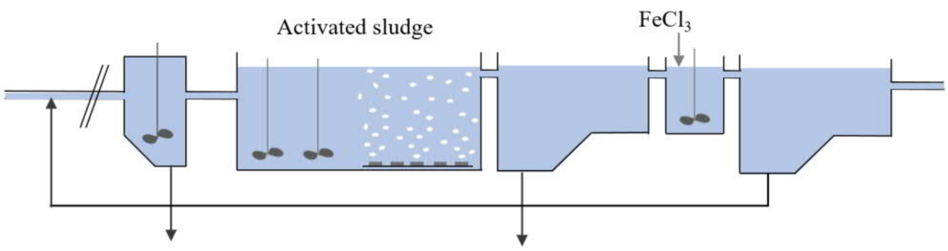


Figure 2. The process layout at Svedala WWTP.

After screening (3 mm) and grit removal in an aerated sand trap, water is directed to an activated sludge process (no primary settling) configurated for pre-denitrification with swing zones for adjustment of aeration with respect to variations in loading. After secondary settling follows post-precipitation (iron chloride) and tertiary settling before water is discharged to Sege å. Waste sludge is dewatered through centrifugation and stabilized by lime addition.

In the LESS IS MORE project, wastewater was pumped from the end of the aerated grit chamber and directed to the direct membrane filtration (DMF) pilot plant and from the effluent of the WWTP to a GAC pilot plant with a sand filter and a GAC filter.

Influent wastewater

Influent wastewater at Svedala WWTP (after screening and grit removal) corresponds to the influent to the DMF-GAC pilot. Table 1 summarizes influent characteristics.

Table 1. Influent characteristics at Svedala WWTP (November 2019 – May 2020).
(Grab samples; n=16 for SS, TOC, n=5 for Tot-N, DOC, n=10 for Tot-P)

	Average concentrations (mg/L)
Suspended solids (SS)	435
Total organic carbon (TOC)	187
Dissolved organic carbon (DOC)	52
Total nitrogen (Tot-N)	81
Total phosphorus (Tot-P)	9.5

Composite samples were collected during a sampling campaign in May 2020 showing comparable, although somewhat lower, concentrations. The concentrations are typical for municipal wastewater treatment plants in Sweden.

Effluent wastewater

Effluent wastewater at Svedala WWTP (after pre-tretment, biological treatment and post-precipitation) corresponds to the influent to the effluent GAC-pilot. Average concentrations of SS, DOC and ammonium nitrogen in the effluent water during 10 months are shown in Table 2.

Table 2. Effluent characteristics at Svedala WWTP (September 2019 – June 2020).
(24-hour composite samples; n=21)

	Average concentrations (mg/L)
Suspended solids (SS)	6.7
Dissolved organic carbon (DOC)	12
Ammonium nitrogen (NH_4-N)	1.6

Svedala wastewater treatment plant is designed for nitrogen removal and nitrification is close to complete as indicated by the low levels of ammonium. DOC and SS-levels in the effluent are typical for Swedish wastewater treatment plants.

The pilot plant

To test the DMF-concept in combination with GAC, a pilot plant was constructed at Svedala WWTP where influent wastewater was pumped directly from the existing sand trap.

In addition, the pilot plant included a parallel line with GAC-filtration as a fourth treatment step treating the (tertiary) effluent from the WWTP.

Layout

Figure 3 presents a simplified schematic overview of the pilot plant and Figure 4 shows a side-view of the pilot plant.

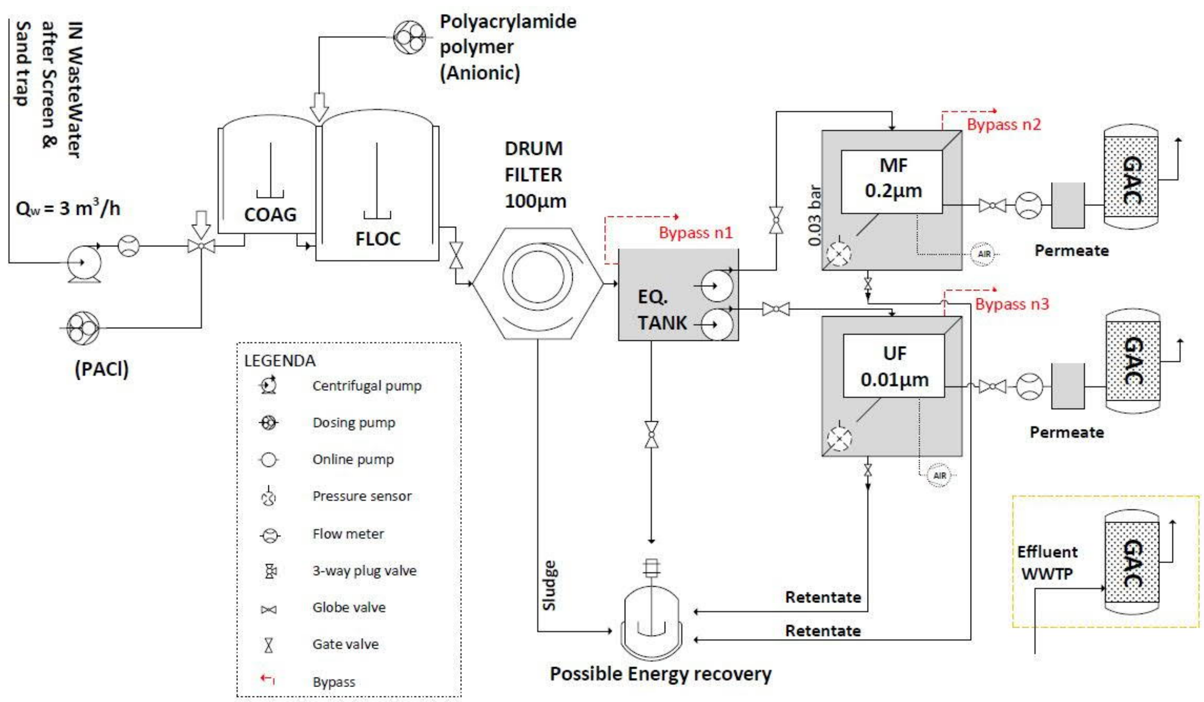


Figure 3. The pilot plant at Svedala WWTP.

Coagulation and flocculation were applied to precipitate phosphorous and enhance particle separation in the microsieve (MS; 100 µm) prior to membrane filtration. Microfiltration (MF; 0.2 µm) and ultrafiltration (UF; 0.01 µm) were operated in parallel for comparison, using MS filtrate as feed. After membrane filtration, each generated permeate was filtered through a GAC filter for MP abatement.

Pre-treatment before GAC-filtration on effluent water (biologically and chemically treated) consisted of a sand filter (not indicated in Figure 3). The sand filter had the purpose of reducing the concentration of suspended solids (SS) entering the GAC-filter in order to reduce the backwash frequency and facilitate operation.

Figure 4. Pilot plant including coagulation/flocculation tank (left side), drum sieve, retention tank, membrane unit (middle, black).

Design data

Design data for the plant is summarized in Table 3. More information about considerations during planning and design phase can be found in Deliverable 3.1– Peer review report.

Table 3. Design data for the pilot plant at Svedala WWTP.

	Direct membrane filtration + GAC-filtration	Effluent GAC-filtration
Coagulation tank (m^3)	0.2	
Flocculation tank (m^3)	0.8	
Coagulant dosing	In pipe (5-15 mg Al^{3+}/L)	
Coagulant[a]	Polyaluminium chloride	
Polymer dosing	Overflow to floc. tank (1-4 mg/L)	
Polymer[b]	Anionic	
Drum filter[c] area (m^2)	0.33	
Pore filter opening (um)	100	
Filtration rate[d] (m/h)	8-9	
Equalization tank volume (m^3)	0.6	
Membrane tank dimensions (m)	H: 2.35, W: 0.5, D: 1.5	
Membrane surface area (m^2)	40	
Cut-off (MWCO) UF[e] (Da)	10 000	
Pore size MF[f] (µm)	0.2	
Design flux[d] (L/m^2h^{-1})	25	
GAC column height (m)	0.54	0.54
GAC column volume (L)	19	19
GAC cross section area (m^2)	0.04	0.04
Mass of carbon[g] per column (kg)	5.98	5.98
EBCT[d] (min)	10	10

[a]PAX XL-60, Kemira
[b]Hydrex 6161, Veolia (high molecular weight, weakly anionic)
[c]Hydrotech, HDF-801
[d]Filtration rate, flux and empty bed contact time varied during the tests.
[e]UFX10 pHt™, hydrophilic polysulphone type, Alfa Laval
[f]MFP2, hydrophopic fluoro polymer type, Alfa Laval
[g]Aquasorb 5000, Jacobi Carbons

It should be noted that the pilot plant was designed for two treatment options; one for direct membrane filtration utilizing the influent wastewater at Svedala WWTP and one for treatment of the effluent wastewater, biologically and chemically treated, at the plant. The same type of GAC-filtration columns were used for the two set-ups. The effluent GAC-filter was operated continuously for 10 months while the DMF-plant was operated in shorter campaigns.

Operation, automation and control

Basic operation modes and details related to operation are described in the following sections. A control system for monitoring and regulation of chemical dosing and flow was installed, see Figure 5.

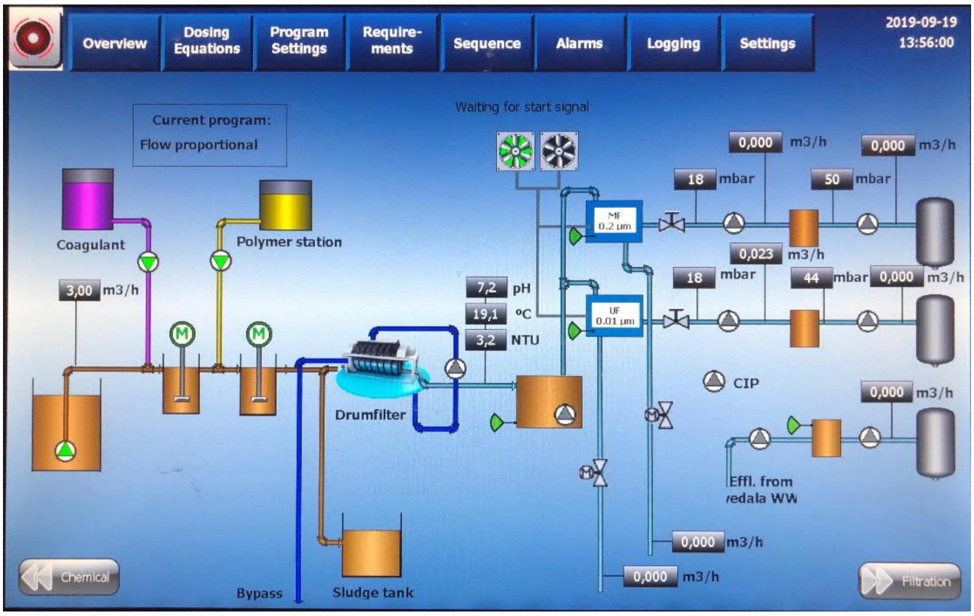


Figure 5. Overview of the control system.

Primary filtration

Both membranes received water from the primary filtration unit based on coagulation/flocculation and microsieving. The typical dosing (flow proportional) was 12 mg Al^{3+}/L and 3 mg/L polymer. Different polymer types were tested and the best results, in terms of the highest SS-reduction, were achieved with a high molecular weight, anionic, polymer. The set-up for primary filtration with pre-precipitation is based on Väänänen et al. (2016). Figure 6 shows the coagulation/flocculation tank.

Figure 6. Coagulation/flocculation tank with drum filter in the background (left picture). The right picture shows the coagulation chamber and the flocculation chamber with mixers.

Following coagulation/flocculation and drum filtration effluent SS concentration was in the order of 10-24 mg/L. TS-content in the sludge was in the order of 0.5-1 % TS. Figure 7 shows the drum filter.

Figure 7. The drum filter with the back wash ramp and spray nozzles in the front. Influent water is fed in the grey pipe (left) and sludge is withdrawn in the orange pipe (left).

Membrane filtration

After the primary filtration a 600 L tank for equalization, with overflow, was placed for control of the water to the membrane tank. About 1 m^3/h was directed to each membrane line. Figure 8 shows the membrane unit.

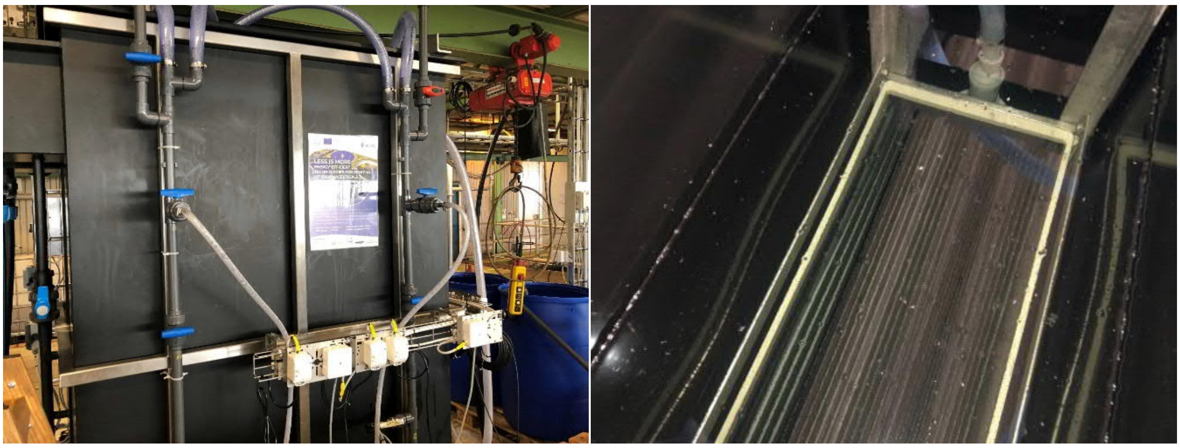
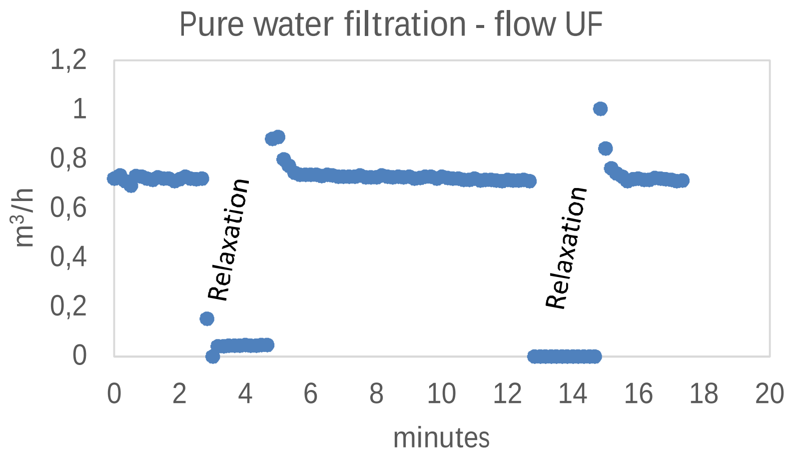


Figure 8.The membrane tank (left) and a top-view of the membranes (right).

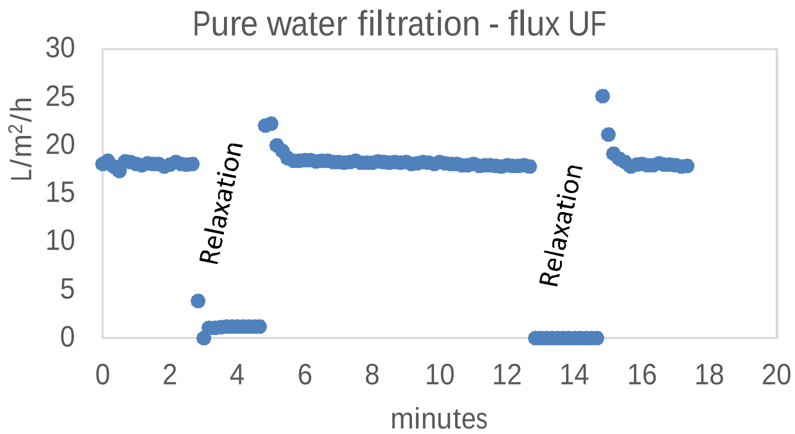
The membrane tank was divided in two tanks (1 m^3 each) and the membranes were submerged in about 600-700 L of water. The HRT was in the order of 40 minutes in the membrane tank but varied due to high variations in flux. A retentate amount of 150 litres was discharged from the membrane tank every 15 minutes to prevent growth in the tank.

To prevent fouling, the tanks were aerated, and a permeation/relaxation method was applied in which permeate pumps were on for 8 minutes and then off for 2 minutes. This relaxation would enhance the removal of a possible fouling-cake formed on the membrane surface. Pure water filtration results for the UF membrane are shown in Figure 9a-c.

a.



b.



c.

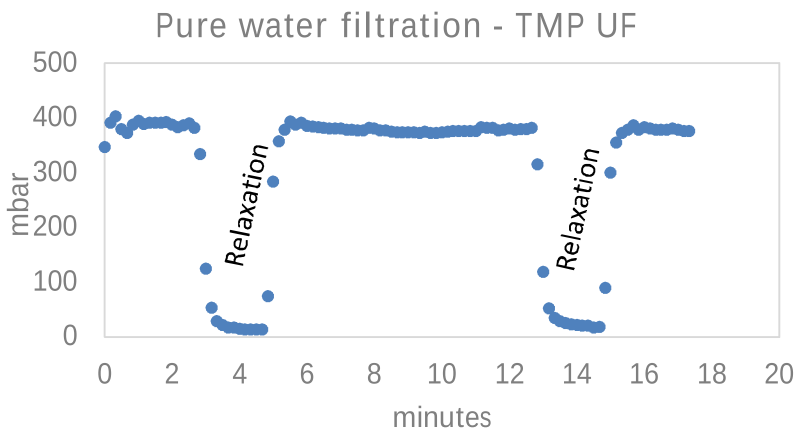


Figure 9. Pure water filtration results for the UF membrane, flow (a), flux (b) and transmembrane pressure, TMP (c).

The operation was supposed to promote a constant flux of 25 L/m^2h^{-1} (LMH) with varying transmembrane pressure (TMP). For the MF, flux rapidly decreased during operation, due to fouling, and dropped from 25 LMH to 9 LMH in three days. During the same period TMP increased from 90 to 740 mbar. For the UF, flux decreased from 27 to 9 LMH and TMP increased from 340 to 640 mbar. Typical variations of flux and TMP during a 15-hours-period is shown in Figure 10.

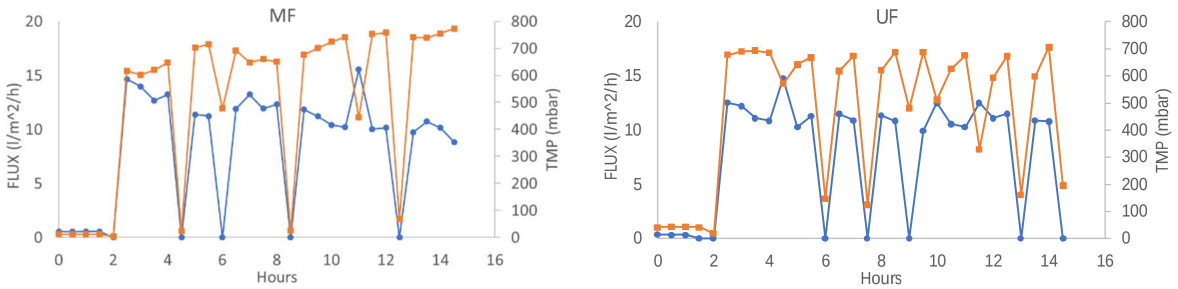


Figure 10. Flux (blue) and TMP (orange) variations during membrane filtration (MF and UF in parallel) of chemically pre-treated wastewater in the DMF pilot plant. The drops in TMP and flux represent relaxation phases.

Membranes were continuously operated in a period of maximum four days before cleaning, both in terms of backwash with chemicals, but also by soaking the membranes in chemicals for 24-48 hours. Hydrogen peroxide (1.2 g/L) combined with high pH (10-11) and 10-20 g/L citric acid together with low pH (2.0) were applied.

GAC-filtration

The same type of GAC-filtration columns were used for the two set-ups (DMF + GAC and effluent GAC). The effluent GAC-filter was operated continuously for 10 months while the DMF-plant was operated in shorter campaigns. The GAC-filter contained 6.0 kg of GAC (Aquasorb 5000, Jacobi), corresponding to a volume of around 19 liters. The filter was operated in a downflow mode with a flowrate of 114 L/h, corresponding to an empty bed contact time (EBCTs) of 10 minutes and a hydraulic loading rate of 3 m/h. Pre-treatment before GAC-filtration (only used in the Effluent polishing line) consisted of a sand-filter, identical in type to the GAC-filter and operated with the same flow rate, hydraulic loading rate and EBCT, see Figure 11. The sand-filter had the purpose of reducing the concentration of suspended solids (SS) entering the GAC-filter in order to reduce the backwash frequency.

Figure 11. GAC columns used both in the DMF line and the effluent line of the pilot plant.

The GAC and sand filters were operated at constant flowrates (114 L/h), except for minor disturbances early on (<5000 bed volumes), which led to slight reductions (<10 %) in the flow rates (see Figure 12). At certain bed volumes, the flowrates were also varied during a few hours in order to investigate how changes in EBCTs influenced treatment performance.

The GAC-filter pressure build-up (Figure 12, right axis) was recorded and used to determine backwash initiation. The backwash was conducted in a separate backwash-station, with the flowrate velocity manually set to allow a careful mixing of the granules while preventing the loss of activated carbon granules with the backwash water. Backwashing was initiated when the pressure loss was between 1.5-3 bars, depending on the total pressure loss (sand filter + GAC-filter). Backwashing was conducted 12 times over the study period (30 000 BV). The water volumes used for each backwash was around 150 liters, corresponding to around 8 BV volumes, which also corresponds to the minimum backwash tank capacity in corresponding large-scale systems. On average, the volume required for backwash was in the order of 0.3 % of the total flow treated by the GAC-filter.

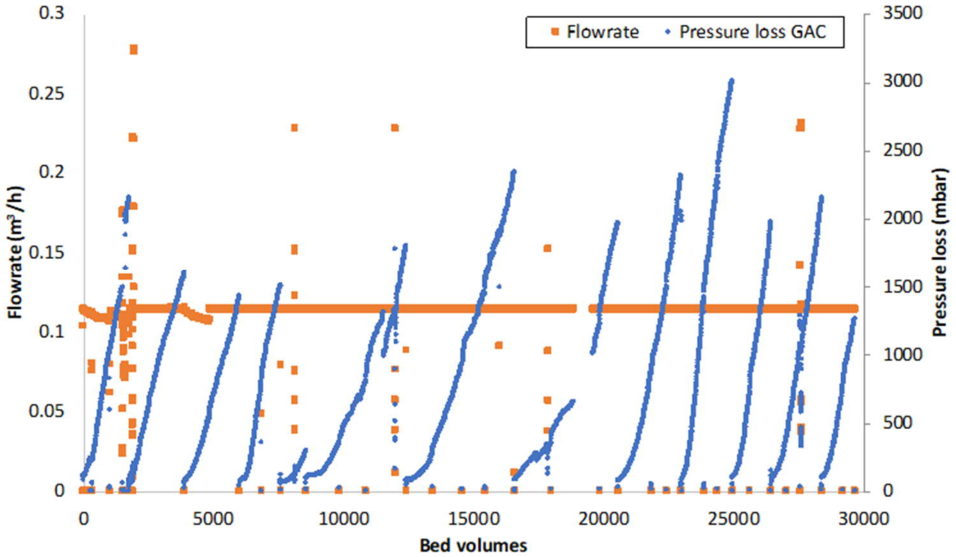


Figure 12. Pressure build-up in the GAC filter

Direct membrane filtration – organic matter and nutrients

Removal of organic matter and nutrients is of great importance for the evaluation of the DMF concept. A substantial removal efficiency is needed to comply with effluent demands but also to facilitate the removal of organic micropollutants in the GAC-filter.

The direct membrane filtration unit included chemical precipitation, microsieving and two parallel membrane filtration lines. From the initiation of membrane filtration, operation problems related to fouling were experienced for both membrane filtration lines, MF and UF, resulting in need for backwashing and extensive cleaning of the membranes after maximum four days of continuous operation. An installation fault on the MF module construction resulted in breakdown of the MF line. Hence, continued evaluation focused on the UF line. Removal (average values) of organic matter, phosphorus and nitrogen by chemically enhanced microsieving with and without additional ultrafiltration membranes are shown in Figure 13. A comparison of the achieved water quality in the DMF pilot line with the full-scale WWTP effluent is found in Table 4.

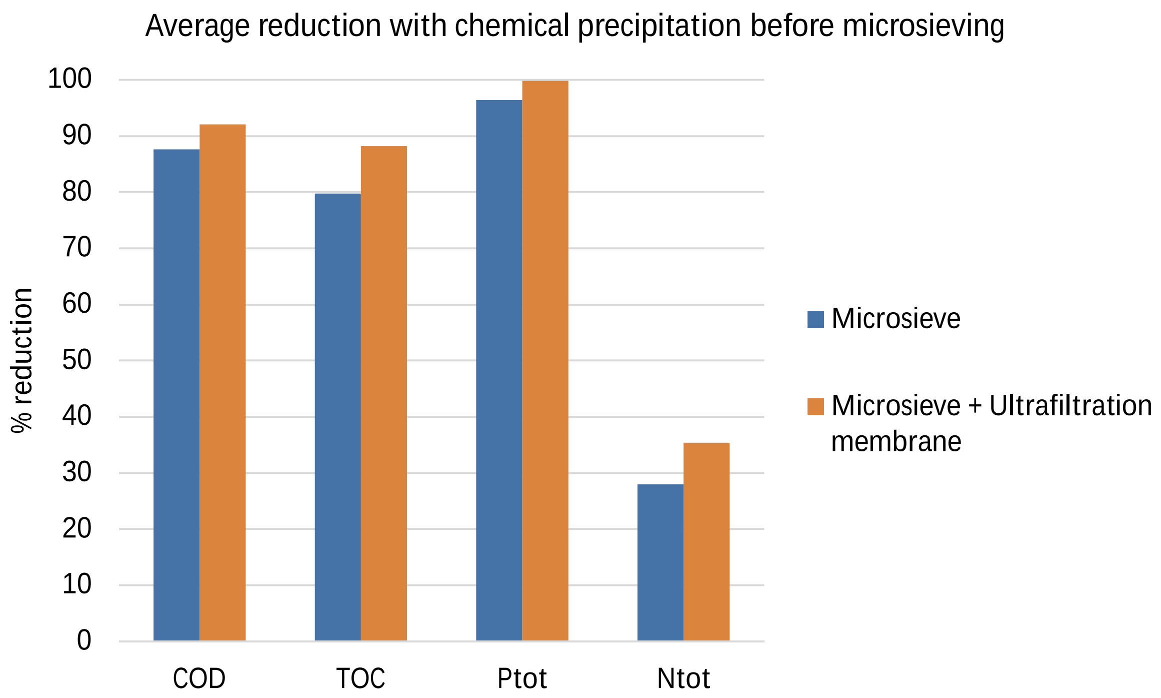


Figure 13. Average reduction of COD, TOC, total-P and total-N (dosing 12 mg/L Al and 3 mg/L polymer) after microsieving and after microsieving + ultrafiltration.

In total a high removal of both particulate matter, organic matter and phosphorus were achieved. The majority of the reduction is a result of the chemically enhanced primary filtration with microsieving. The membrane filtration contributes with a minor additional removal of organic matter, SS and phosphorus. Nitrogen is, as expected, not removed to a level that would be accepted for treatment plants with demands on nitrogen removal, but still 35% of nitrogen was removed in total. Higher removal would require biological treatment (nitrification and denitrification).

Table 4. Average concentrations of SS, COD, TOC, Total-N and total-P measured in the influent wastewater (after grit and sand removal), after microsieving, MS (chemical dosing 12 mg/L Al and 3 mg/L polymer) and after the ultrafiltration membrane. For comparison the average concentration in effluent wastewater from the full-scale plant is also given.

	Influent WW	After MS	After UF	Effluent WW (full-scale plant)
SS (mg/L)	371	16	2	7
COD (mg/L)	665	87	58	Not analysed
TOC (mg/L)	161	37	21	13
P-tot (mg/L)	10.0	0.37	0.05	<0.1
N-tot (mg/L)	72	48	43	5

The results show that >80% of the organic matter (measured as TOC and COD) and >95% of total phosphorus could be removed. Previous research (Väänänen et al., 2016) has demonstrated that phosphorus removal can be controlled in a corresponding set-up but without membranes. In Table 5 treatment options and results for different abiotic process configurations with and without membranes are summarized.

Table 5. Treatment options, expected removal and objectives using different abiotic process configurations.

Process configuration	Expected removal	Treatment objectives and options
Microsieving (MS)	SS: 50% COD: 20% TP:20%	Saving space (replacing primary clarifiers)
Cationic polymer coagulation + MS	SS: 70-90% COD:70-80% TP: 50-90%	Increased gas production potential Increase reduction of P Minimized tertiary chemical sludge production
Coagulation/flocculation +MS	SS: >95% COD: 70-90% TP: >95%	Optimization of SS, COD and P removal Storm water treatment
Coagulation/flocculation + MS + MF	SS: 100%	Further optimization of SS, COD and P removal
Coagulation/flocculation + MS + UF	SS: 100%	Further optimization of SS, COD and P removal Reuse of permeates (e.g. for irrigation)

Abiotic treatment based on microsieving, with options for coagulation and flocculation, and membrane post-treatment gives great flexibility in terms of meeting expectations on removal of organics, phosphorus and suspended solids. Nitrogen is not expected to be removed, although minor effects can be noticed, in the order of 20-40%, depending upon wastewater characteristics. With the use of membranes important options for reuse can be added to the treatment objectives.

Micropollutants

Removal of micropollutants were studied both in laboratory and pilot-scale set ups with activated carbon, with and without preceding biological treatment.

Pilot plant influents

In the initial phase of the LESS IS MORE project, sampling of influent and effluent wastewater were performed to get an indication of the content of organic micropollutants in the wastewater before and after treatment at the full-scale WWTP in Svedala. Influent concentrations are summarized in Figure 14. Figure 15 shows a close up of substances found in lower concentrations.

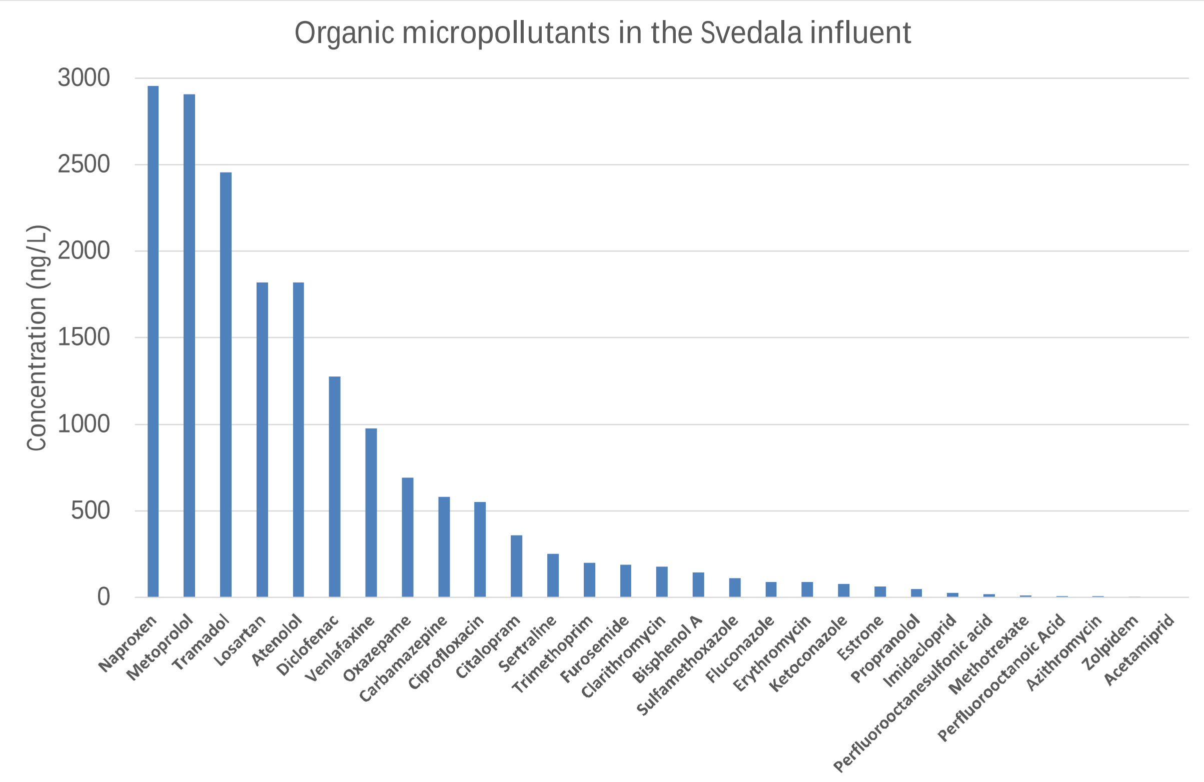


Figure 14. Influent concentrations of organic micropollutants to Svedala WWTP. Measurements are based on a single grab sample. Paracetamol and ibuprofen (not included in the figure) were quantified in concentrations >10 µg/L.

Paracetamol and ibuprofen were, by far, the most prevalent organic micropollutants and they were quantified in concentrations >10 µg/L. These substances were excluded from the figure for clarity. Several of the pharmaceuticals found in the Svedala influent are also found in similar concentrations in influents to other Swedish wastewater treatment plants. The concentrations in the Svedala influent gives an impression of the content of organic micropollutants going to the direct membrane filtration pilot.

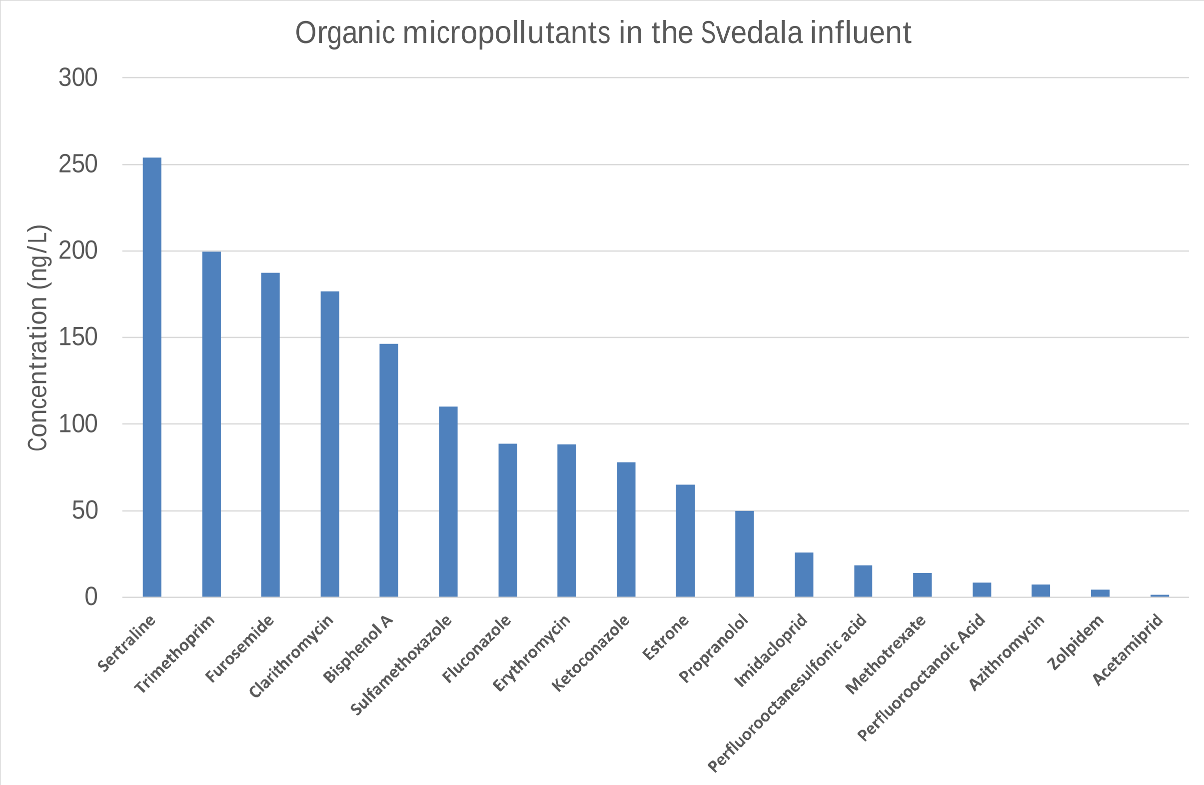


Figure 15. Influent concentrations of organic micropollutants (only substances found in lower concentrations) to Svedala WWTP. Measurements are based on a single grab sample.

From Figure 15 it can be noted that several antibiotics (chlarithromycin, sulfamethoxazole and erythromycin) could be quantified in concentrations in the order of 100 ng/L. Imidacloprid, a neonicotinoid, and perfluorooctanesulfonic acid (PFOS) were also detected and quantified. Both substances are recorded as river basin specific pollutants with environmental quality standards stated by the Swedish Marine Water Agency.

Effluent concentrations, following mechanical, biological and chemical treatment, are summarized in Figure 16, and Figure 17 shows a close up of substances found in lower concentrations. The concentrations in the Svedala effluent gives an impression of the content of organic micropollutants going to the GAC filter treating biologically and chemically treated wastewater.

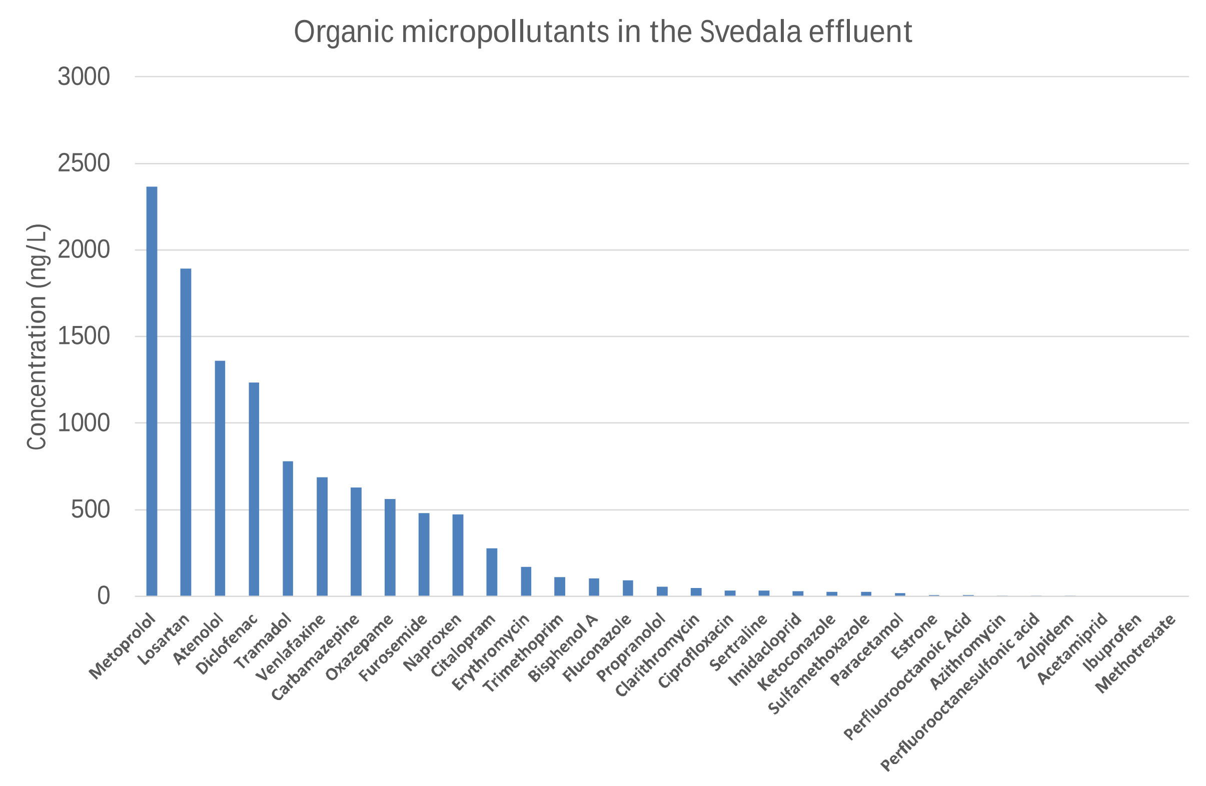


Figure 16. Effluent concentrations of organic micropollutants from Svedala WWTP. Measurements are based on a single grab sample.

The concentration of diclofenac (>1000 ng/L), also typical for other Swedish wastewater effluents, was 10 times higher than the environment quality standard (100 ng/L) for surface waters (HVFMS 2019:25). Downstream analysis of a grab sample from February 2020 showed a diclofenac concentration of 43 ng/L. It could be noted that the concentration was similar to the influent concentration.

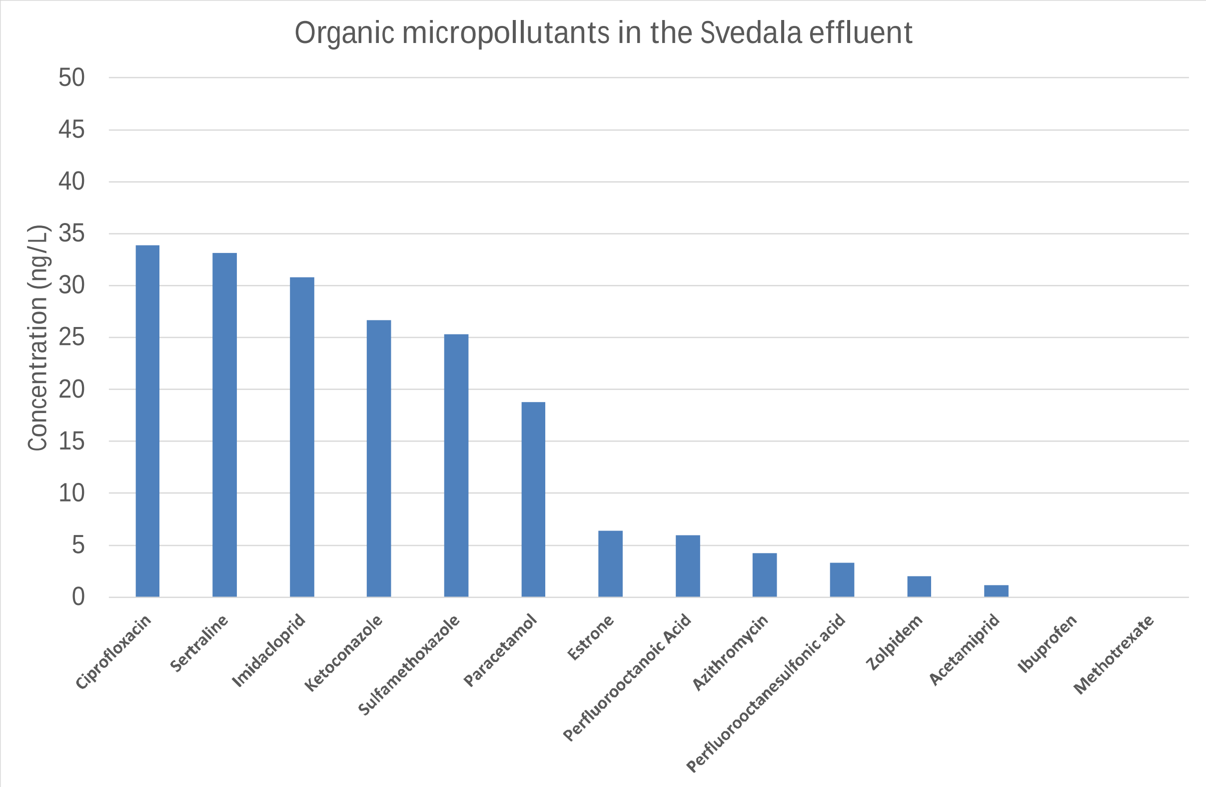


Figure 17. Effluent concentrations of organic micropollutants (only substances found in lower concentrations) from Svedala WWTP. Measurements are based on a single grab sample.

From Figure 17 it can be noted that Imidacloprid (31 ng/L) are present in concentrations higher than 5 ng/l which is the environment quality standard (100 ng/L) for surface waters (HVFMS 2019:25). Downstream analysis of a sample from February 2020 showed an Imidacloprid concentration of 2 ng/L.

Removal at Svedala WWTP

Figure 18 illustrates removal efficiency at Svedala WWTP without advanced treatment in the form of GAC-filtration. Removal can preferably be attributed to degradation and sorption in the activated sludge process.

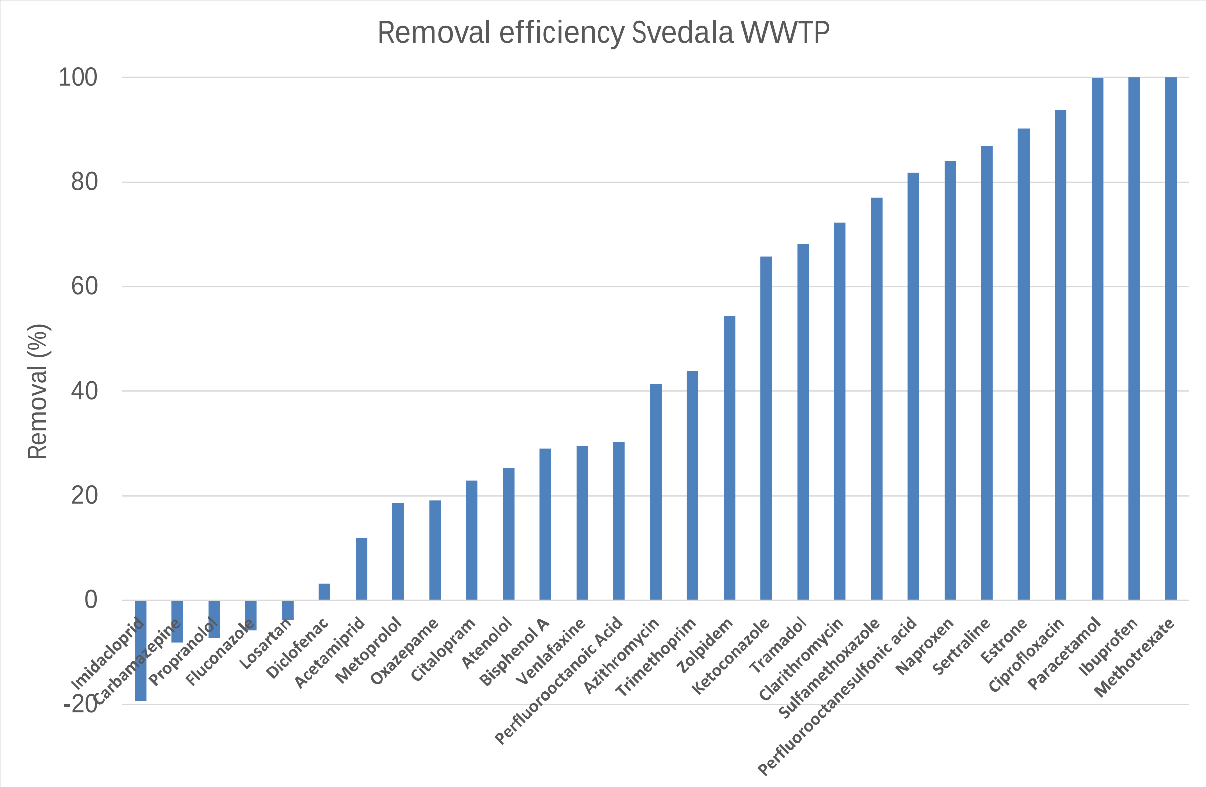


Figure 18. Removal efficiency at Svedala WWTP.

As can be seen, 8 out of 31 substances were reduced by >80%, for example naproxen, paracetamol, ibuprofen, estrone, ciprofloxacin and sertraline. This is in accordance with results from other activated sludge plants with nitrogen removal (Falås, 2012). In the case of naproxen, paracetamol and ibuprofen removal can be explained by biological transformation and degradation primarily in the activated sludge process. Ciprofloxacin and sertraline can be recovered in substantial amounts from sewage sludge, which is also the case for ketoconazole and citalopram. Removal of estrone appears to be a combination of both removal processes (Svahn & Björklund, 2019). Most substances are however only partially removed and some substances can be considered as persistent, for example carbamazepine and diclofenac. Thus, advanced treatment is necessary to accomplish removal of a broad spectrum of organic micropollutants.

Removal efficiency – GAC on membrane filtrated influent wastewater

The potential for GAC filtration following direct membrane filtration was investigated primarily in laboratory scale (see Supplementary test in laboratory and bench scale) but also in a 3-day campaign in the pilot plant. Figure 19 illustrates removal efficiency for one of the days based on 24-hour sampling.

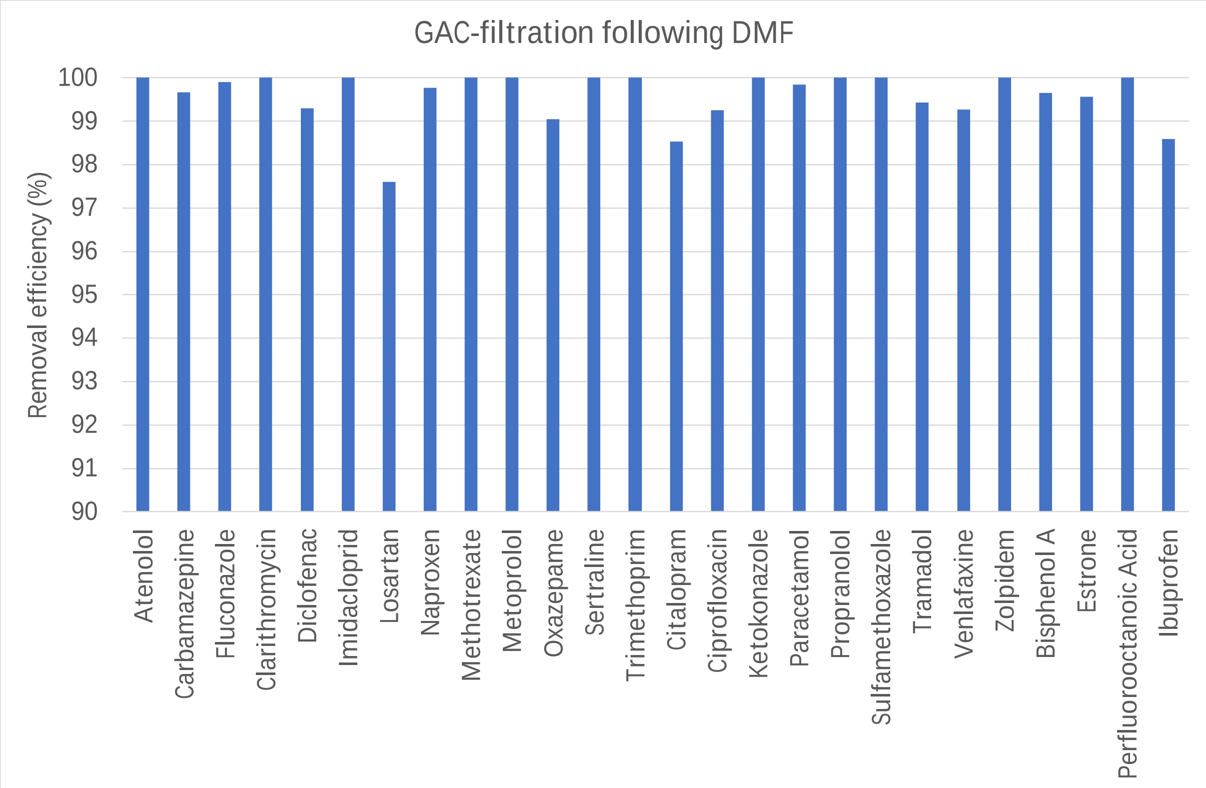


Figure 19. Removal efficiency over the GAC-filter following direct membrane filtration.

All substances were removed to at least 97% indicating a high removal potential for the combination of DMF and GAC. Breakthrough behaviour remains to be studied since long term operation of the preceding membranes could not be achieved.

Removal efficiency – GAC on biologically treated effluent wastewater

GAC filtration was tested on long-term basis on biologically treated wastewater. The empty bed contact time (EBCT) was kept at 10 minutes, which is at the lower end according to literature, often suggesting 20-30 minutes (Fundneider et al., 2020). However, this allowed for consecutive operation corresponding to more than 30 000 bed volumes. During the operation period test campaigns were conducted with varying EBCTs. Figure 20 illustrates influent and effluent concentrations after 3000 bed volumes.

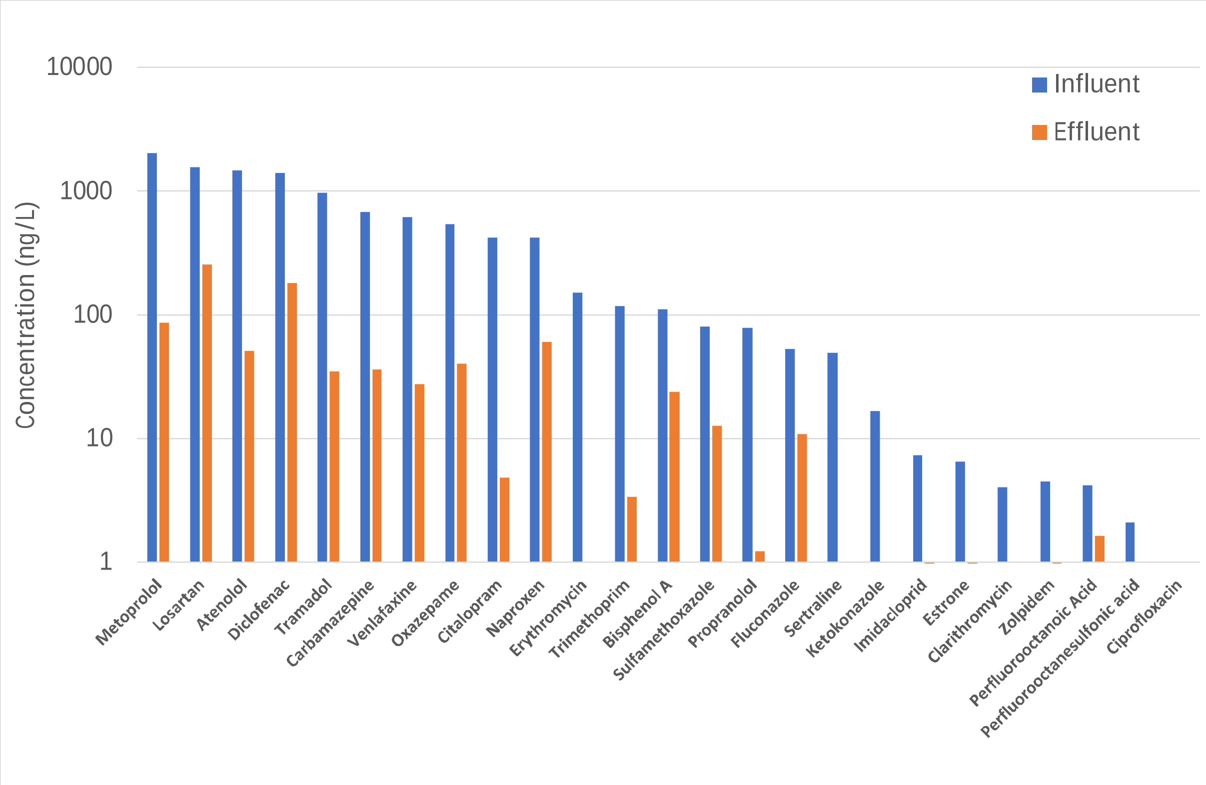


Figure 20. Influent and effluent concentrations to and from the GAC filter (3000 BV) treating biologically treated wastewater.

At this stage the GAC filter results in high removal corresponding to at least 90% for most substances. It should be noted that removal, especially for some substances susceptible to sorption or degradation in preceding treatment steps, also should be studied considering removal prior to the GAC-filter. Sulfamethoxazole is such an example. Already after 3000 BV removal is in the order of 80% but in fact probably higher since significant amounts must have already been transformed or degraded in the biological treatment since it can´t be recovered from sewage sludge (Svahn & Björklund, 2019)..

Figure 21 shows removal as a function of treated bed volumes for three key substances; carbamazepine, diclofenac and sulfamethoxazole as well as reduction of DOC and UVA254.

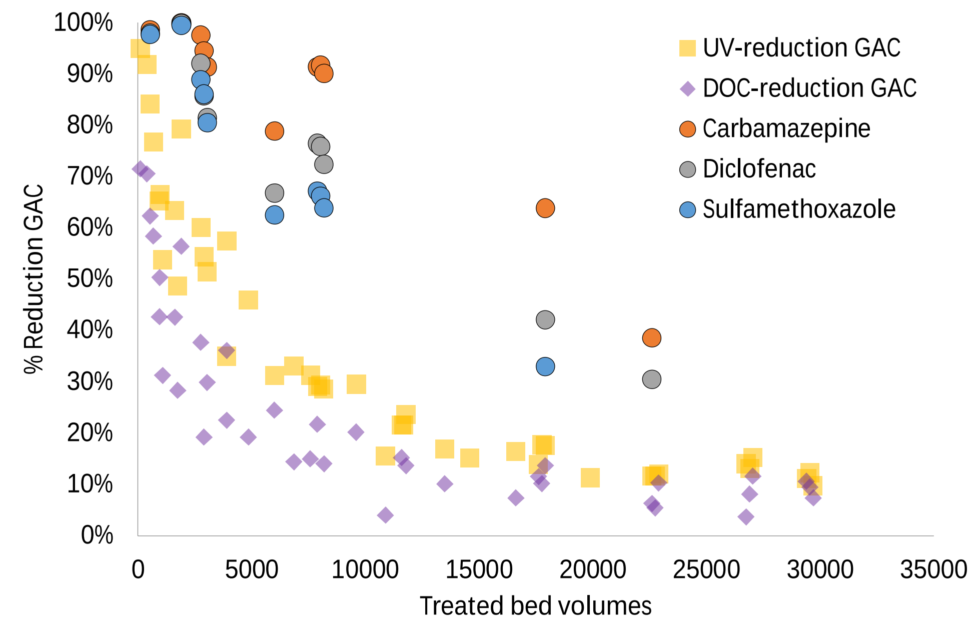


Figure 21. Removal of carbamazepine, diclofenac, sulfamethoxazole, DOC and UV (UVA254-signal) as a function of treated bed volumes.

Breakthrough of UV and DOC occurs relatively early and already after a few thousand bed volumes. DOC breakthrough was initially around 30 %, suggesting that a significant amount of the DOC does not adsorb to GAC. Breakthrough, or at least a clear reduction in removal efficiency for the micropollutants, is noted at a later stage which is in accordance with previous studies.

Table 6 summarizes removal of the different substances at different time points, bed volumes. At 3000 BV basically all substances show a reduction of more than 80%. From 8000 BV, the removal of a few substances is below 80%; fluconazole, sulfamethoxazole and diclofenac together with erythromycin and losartan are showing deteriorated removal. At 18 000 BV, the removal is below 60% for the same substances and also for naproxen and venlafaxine. At 22 600 BV, only two substances are removed to a higher degree and at that point, indications of desorption, with negative removal, is seen for some single substances.

Another way of looking at removal in a GAC filter would be to consider accumulated removal. Such an approach will be relevant if substances would be regulated on annual basis.

Table 6. Removal of the different substances at different bed volumes.

	3000 BV	8000 BV	18000 BV	22600 BV
Metoprolol	96%	97%	81%	50%
Losartan	84%	72%	42%	27%
Atenolol	97%	97%	75%	48%
Diclofenac	87%	74%	47%	27%
Tramadol	96%	94%	60%	37%
Carbamazepine	95%	91%	63%	40%
Venlafaxine	96%	92%	58%	38%
Oxazepame	93%	86%	60%	34%
Citalopram	99%	98%	88%	71%
Naproxen	86%	80%	48%	25%
Erythromycin	100%	69%	29%	-18%
Trimethoprim	97%	97%	91%	51%
Bisphenol A	79%	87%	71%	35%
Sulfamethoxazole	84%	60%	17%	-44%
Propranolol	98%	98%	94%	74%
Fluconazole	79%	65%	38%	19%
Sertraline	100%	100%	100%	100%
Ketokonazole	100%	100%	100%	85%
Imidacloprid	91%	93%	65%	38%
Clarithromycin	100%	80%	72%	-13%

Reduction can be affected by the applied EBCT. Figure 22 illustrates how removal can be improved by increasing the contact time in the filter. Small variations in removal was observed for micropollutants which generally were adsorbed to a high extent (Table 6), such as trimethoprim and atenolol. The removal of diclofenac, naproxen and sulfamethoxazole generally showed a higher dependence on empty bed contact time, suggesting that the adsorption of these compounds is, to a higher extent, limited by adsorption kinetics

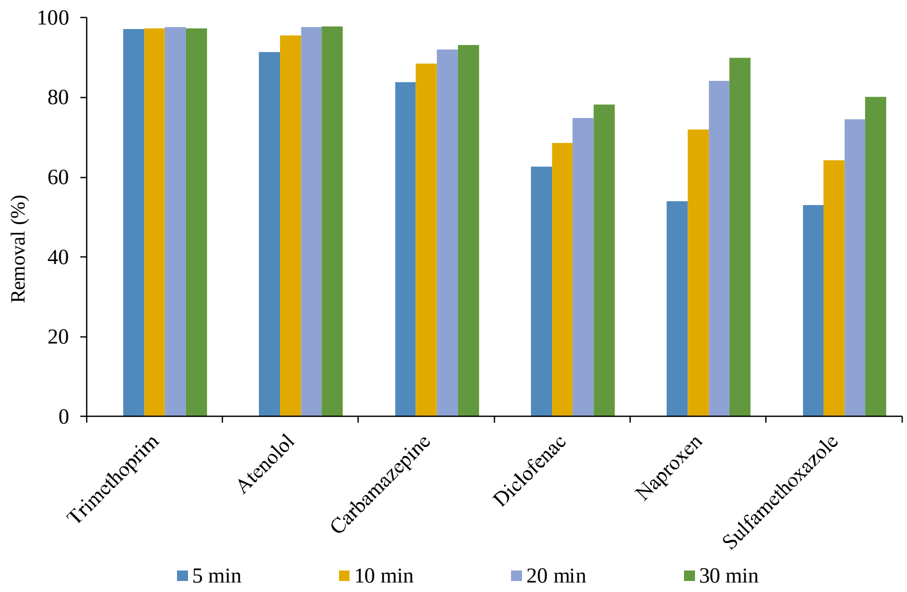


Figure 22. Removal as a function of EBCT.

Supplementary tests in laboratory and bench scale

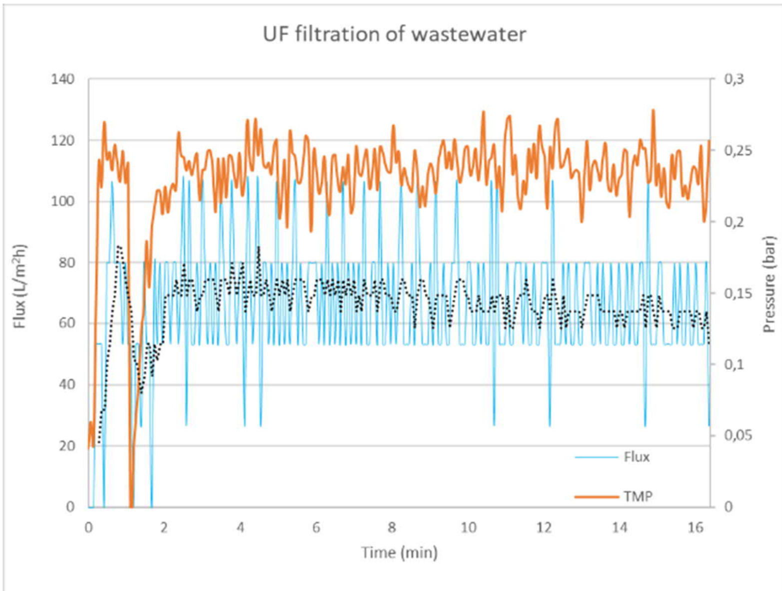
In connection with the work of designing, building and operating the pilot plant, various supplementary studies and tests were carried out. For example, initial lab work was done to simulate the chemical and mechanical separation in the DMF pilot and to be able to partially select dosages and operating modes even before the pilot was built. Furthermore, lab studies were used to study what happens to the micro-pollutants in contact with activated carbon. As it was not possible to run longer periods of membrane filtration followed by GAC filtration, lab studies were used as a complement. Another side project studied the GAC filter media in-depth. As part of the evaluation of energy efficiency, biogas potential measurements were made on sludge from the DMF pilot on repeated occasions. An evaluation of the potential for reuse of water from the DMF process was also done.

These studies are briefly described below in the subsections and references to other reports or coming scientific publications are given for more information.

Initial lab tests

Initial lab work was done in parallel to the DMF pilot, simulating the chemical-mechanical treatment including coagulation, flocculation, microsieving and membrane filtration.

Laboratory DMF experiments using UF showed reduction of total organic carbon and total phosphorus with 75% and >99%, respectively. The flux was around 66 L/m^{2}h at 0.2 bar transmembrane pressure (TMP) with low flux decline (Figure 23). A flux around 74 L/m^{2}h was obtained at 0.5 bar TMP and fouling resulted in decreasing flux (Figure 23). Chemical membrane cleaning in the laboratory could restore permeability completely.



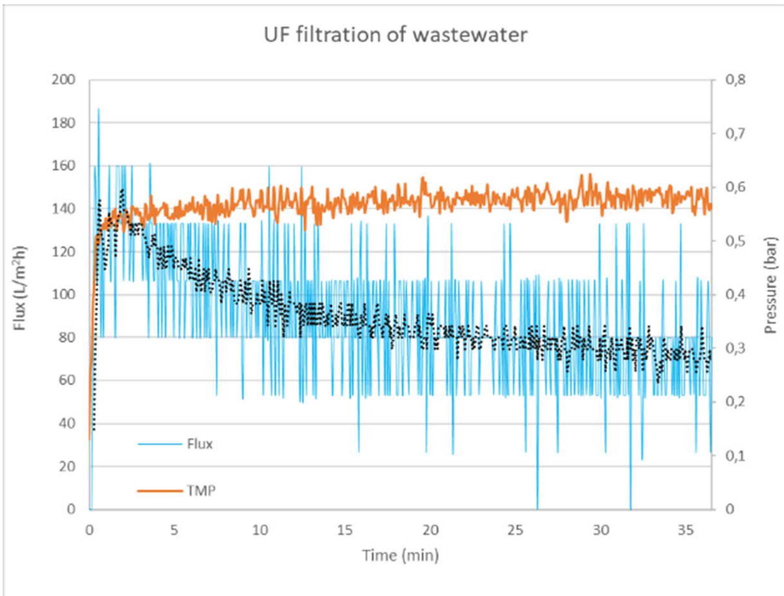


Figure 23. Membrane flux at 0.2 and 0.5 bar.

Different GAC-filter pre-treatment methods (resulting in different DOC-concentrations and DOC characteristics) and their effect on the adsorption of micropollutants were tested. Four differently pre-treated water types were spiked with two micropollutants (Mecoprop and Sulfametoxazole) and the adsorption to powdered activated carbon was evaluated, see Figure 24.

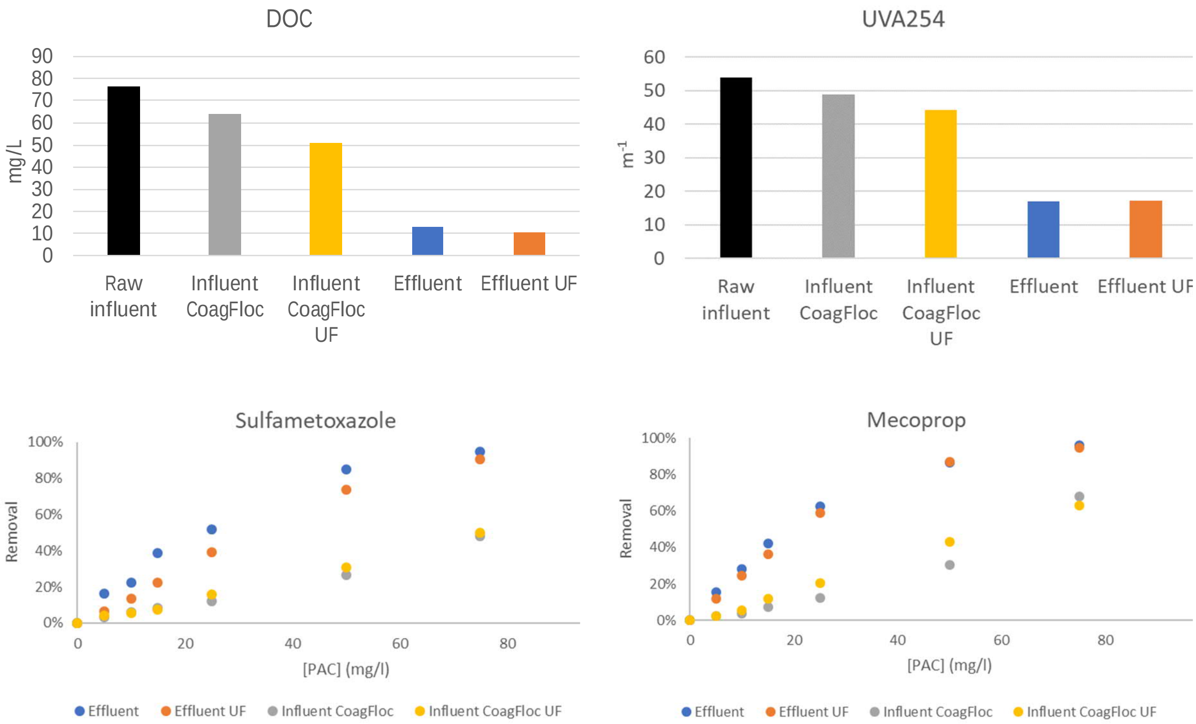


Figure 24. DOC and UVA254 results from lab-scale tests of different pre-treatment methods and removal of sulfametoxazole and mecoprop when combining the pre-treatment with adsorption to activated carbon.

The tests show a difference in levels of DOC (and UVA254) comparing influent wastewater treated with coagulation/flocculation, microsieving and ultrafiltration with effluent, biologically and chemically treated, wastewater with and without ultrafiltration. Consequently, when testing adsorption capacity the effluents result in higher reduction for the same PAC-dose.

Differentiation between adsorption and degradation

By better understanding what is happening in the granular activated carbon (GAC)-filters, we can contribute to safer dimensioning, better cost calculations and hopefully to the development of more efficient filter operation. GAC-filters can be used to reduce the content of organic micropollutants in wastewater, but it is uncertain to which extent biological degradation contributes to their removal. In this study (Betsholtz et al, 2021), ^{14}C-labeled organic micropollutants were therefore used to distinguish degradation from adsorption in a GAC-filter media with associated biofilm, see Figure 25.

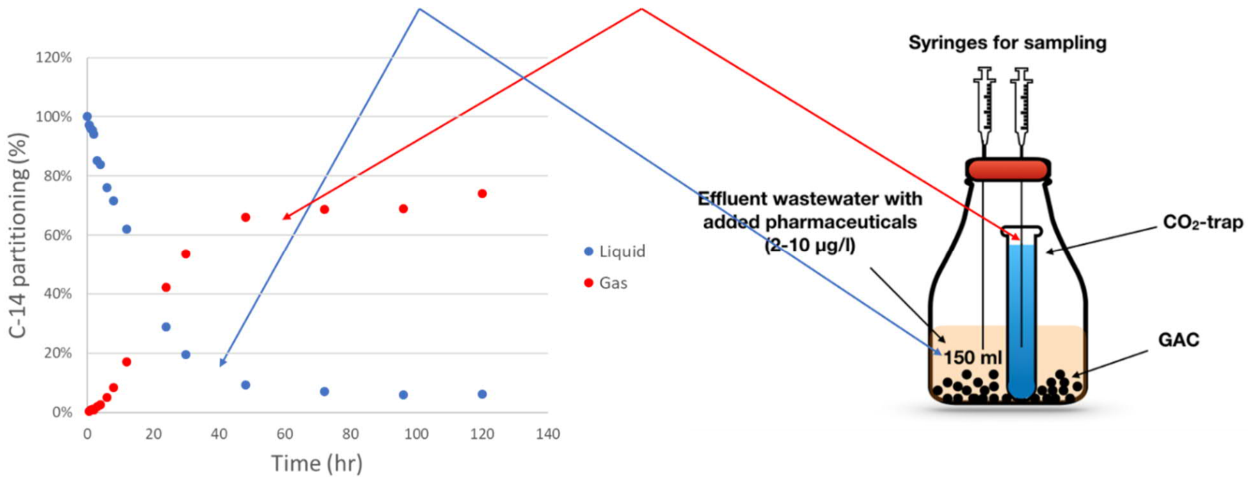


Figure 25. Study of adsorption and biological degradation using liquid scintillation and ^{14}C-labeled organic micropollutants.

Competition for adsorption onto activated carbon

The objective of this study was to investigate organic micropollutant competition for adsorption sites on activated carbon by using the permeates from the DMF pilot process in laboratory adsorption tests with powdered activated carbon. Adsorption in the DMF permeate was compared with adsorption in the biologically treated tertiary effluent from Svedala full-scale WWTP. Correlations between removal and organic micropollutants molecular properties as well as characteristics of the different wastewater streams were evaluated to explain competition and adsorption capacity. These lab-scale results using PAC were verified against the pilot-scale GAC-filtration results showing that removal in the GAC filter could be estimated, see Figure 26. More can be found in Gidstedt et al. (2021a).

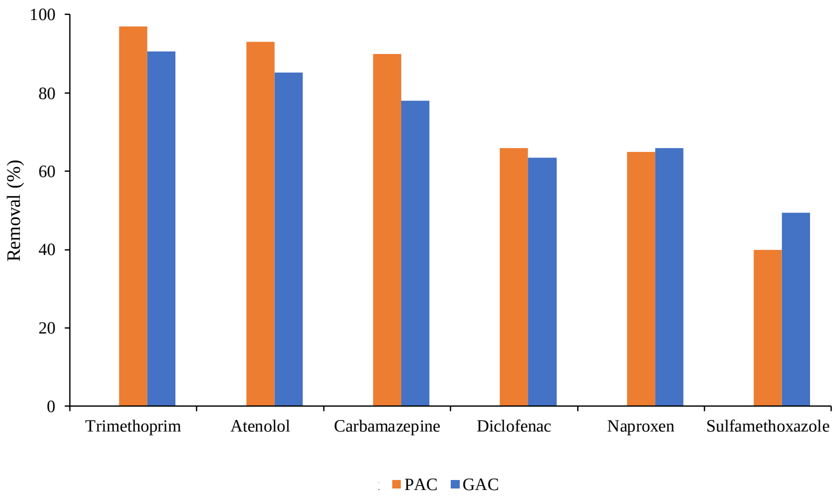


Figure 26. Comparison of achieved removal of selected OMPs in laboratory PAC tests and pilot-scale GAC filtration.

In-depth of a GAC filter

With the development of analytical methods, refined in the LESS IS MORE project, new possibilities for in-depth analysis of filters have emerged. Previously adsorbed micropollutants can be extracted and quantified. With sampling of a filter at different depths and times unique profiles can be created reflecting spatial and temporal variations of removal organic micropollutants. This type of analysis has increased our understanding of the complex removal mechanisms in GAC-filters. The results can potentially be used for improvements in design as well as operation of filters. Figure 27 illustrates concentration profiles from extraction of GAC filter media.

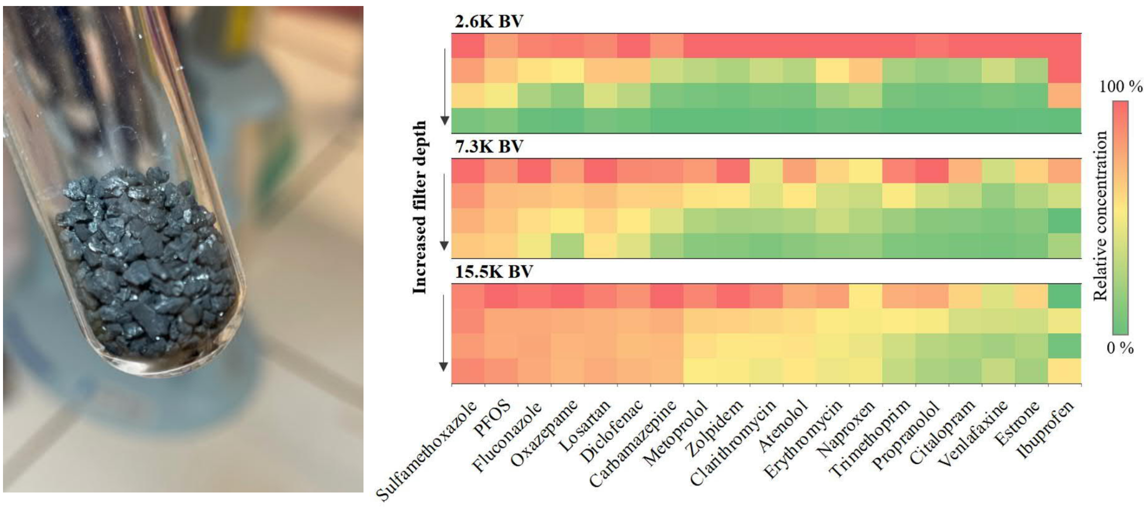


Figure 27. Concentration profiles resulting from extraction of GAC filter media at different time points, bed volumes.

The results, see also Edefell et al. (2021), indicate that certain micropollutants, such as sulfamethoxazole and fluconazole, are found at relatively high concentrations also at the bottom of the filter while others compounds are found in much lower concentrations in the lower layers. The result is a function of several parameters including various adsorption patterns, differences in development of mass transfer zones and biological degradation for different micropollutants.

Evaluation of energy re-use

An evaluation of the enhanced energy re-use potential within the DMF concept has been done as part of the Deliverable 4.2. The idea of the DMF concept is to replace the primary clarification and activated sludge step usually found in conventional wastewater treatment plants. The expected benefits of this concept is increased recovery of organic matter and a potential increase in biogas production by anaerobic digestion of the organic matter (Figure 28). By the additional use of chemically enhanced primary treatment the separation efficiency can be further enhanced. Laboratory biogas potential tests were performed to evaluate the energy content of the sludge from the DMF pilot process. Results and more information can be found in the Deliverable 4.2.

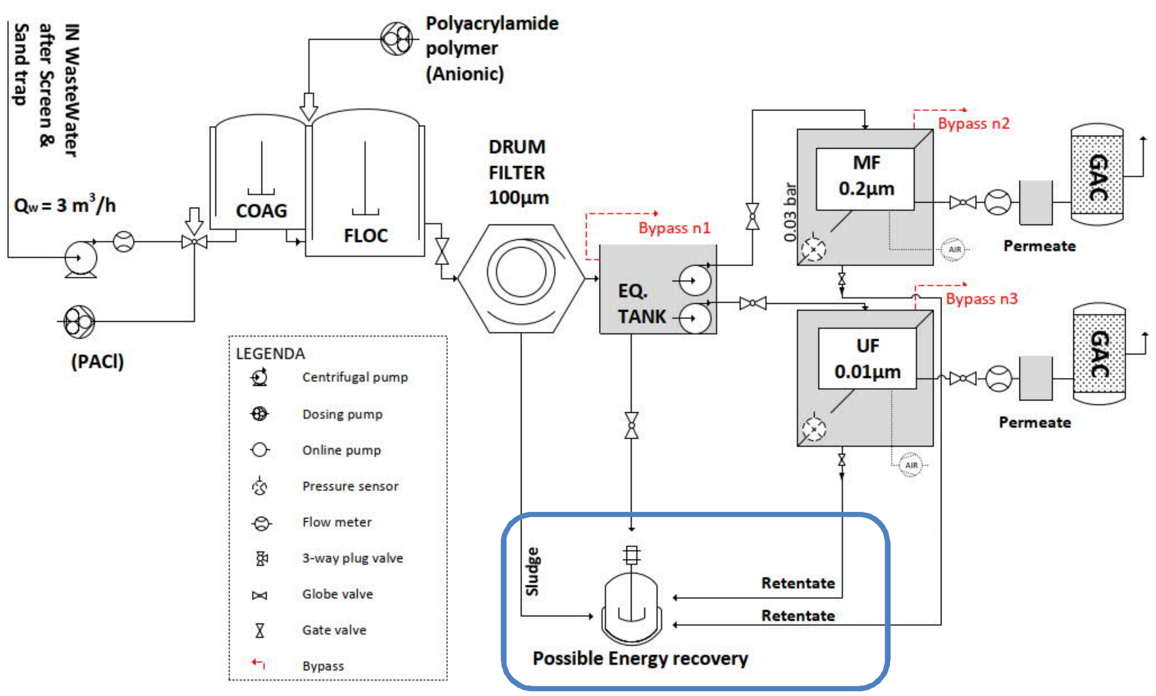


Figure 28. Process scheme for the Svedala pilot plant including chemical-mechanical treatment followed by GAC filtration. Possible energy recovery indicated with the blue frame.

Water re-use potential

To evaluate the re-use potential of treated wastewater from the pilot plant, E.coli was analysed for both treatment lines, Figure 29. Not surprisingly, the GAC-filter operated on biologically treated wastewater only had a small reducing effect, 43%. The reduction of E.coli over the DMF-pilot was larger, 99.7% in total when ultrafiltration was applied, i.e. almost 3 log-reductions. The results will be found in Gidstedt et al. (2021b).

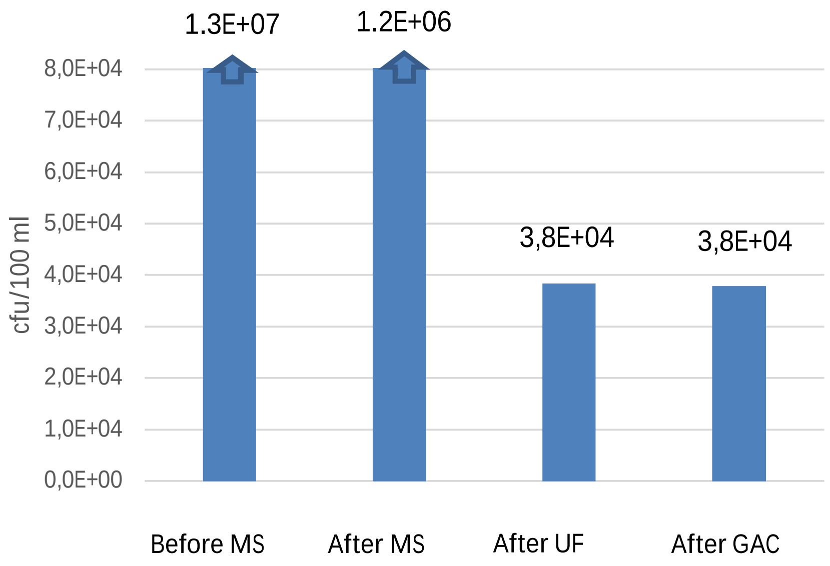


Figure 29. E.coli in samples from the DMF-pilot plant at Svedala before and after microsieving (MS), after ultrafiltration (UF) membrane and after GAC filtration.

Conclusions

To test a direct membrane filtration (DMF) concept in combination with GAC, a pilot plant was constructed at Svedala WWTP in Sweden where raw wastewater was directly pumped from the existing sand trap. In addition, a parallel pilot was constructed with GAC-filtration as a fourth treatment step treating the (tertiary) effluent from the WWTP. Main conclusions from the pilot results supplemented by laboratory studies are found below.

GAC filtration following DMF showed a very high potential for removal of micropollutants. All substances studied were removed to at least 97%. Long term effects and breakthrough behaviour could however not be analysed, since severe fouling of the membranes only permitted short time operation, in the range of a few days, before substantial cleaning was needed to continue operation. Further development of membrane operation on raw wastewater is needed in order to evaluate and potentially establish a full-scale concept based on DMF and GAC filtration. Tests in laboratory and pilot scale showed that approximately 90% of COD could be removed with DMF and preceding coagulation/flocculation with microsieving. Most of the reduction was attributed to the microsieve with preceding coagulation/flocculation. Moreover, the DMF concept provides opportunities for reuse of wastewater and control of P-removal with potential for >95% phosphorus removal.

The full-scale treatment, with biological and chemical treatment, at Svedala WWTP is only removing organic micropollutants to a limited extent. Most substances are only partially removed and some substances can be considered as persistent, for example carbamazepine and diclofenac. Thus, advanced treatment is necessary to accomplish removal of a broad spectrum of organic micropollutants.

Advanced treatment with GAC filtration of the effluent was successfully demonstrated during a period of 10 months, resulting in operation corresponding to 30 000 bed volumes (BV). Breakthrough of UVA254 and DOC occurred after a few thousand bed volumes while reduction in removal efficiency for several micropollutants was noted at a later stage which is in accordance with previous studies. At 3000 BV basically all substances showed a reduction of more than 80%. Between 8000 and 18000 BV, the removal efficiency was deteriorated (to less than 50%) for several compounds e.g. fluconazole, sulfamethoxazole, diclofenac, erythromycin and losartan. Removal efficiency is likely affected by the short applied EBCT (10 minutes in this study) and might be improved by increasing the contact time.

An important part of the LESS IS MORE project has been dedicated to laboratory studies of separation mechanisms in GAC filters. Differentiation between separation and degradation using radiolabelled substances, model prediction of GAC performance using batch tests with PAC and extraction of previously adsorbed micropollutants are examples of methods and procedures that have been established. They will be used in future studies of the complex removal mechanisms in GAC-filters in order to find improvements in design as well as operation of filters. Also, analytical procedures have been developed enabling more rapid sample preparation of whole water samples, and at the same time minimizing cross contamination of samples. During the project several new compounds have been added to the plethora of analytes such as benzotriazole and the majority of the Swiss indicator substances. A novel method for analysing the compounds on EUs watchlist 3 was also developed.

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