BONUS CLEANWATER PROJECT

Final publishable summary report 1st April 2017 to 31st March 2020

1 Project outline of goals and results envisaged at the beginning of the project cycle

CLEANWATER focused on developing ecotechnologies for removing microplastics and organic micropollutants, such as pharmaceuticals, biocides, flame retardants, and personal care products, from wastewater to reduce the inputs into the Baltic Sea. Additionally CLEANWATER delivered an assessment of the predominant ways of input of microplastics and micropollutants (MP) as well as advances in analytical processes.

Organic micropollutants are contained in wastewater with up to several µg/L concentrations per compound. Usually municipal wastewater contains several thousands of different compounds that are used in everyday life.

- Biocides are used in cosmetics, paints, clothes and a lot of other utilities.
- Flame retardants are used in furniture, clothes and others.
- Personal care compounds including fragrances are used in our daily hygiene.
- Detergents are used in all kinds of washing/cleaning activities.
- Pharmaceuticals are used mostly at home by all kinds of people.

This is just to name but a few compounds groups and usages. On top of the micropollutants, wastewater also contains microplastic particles. They either originate from various deterioration processes of polymeric materials, or are functional additives in consumer products such as in cosmetics (peeling).

Most of these micropollutants are not very well removed in conventional activated sludge (CAS) wastewater treatment plants, as residence time (typically below 20 h) is too short to allow for the biodegradation of most of these compounds. In addition, the sorption of the target compounds to sludge is minor and the partitioning equilibrium tends for the water phase. To some extent, microplastic particles can be removed from the wastewater together with the sludge. Thus, these micropollutants and microplastics are released via wastewater treatment plants into the recipients. This can result in ng to µg/L concentrations in the receiving waters. In Figure 1 typical inflow and outflow concentrations of a multitude of compounds in a Danish wastewater treatment plant are shown.

It is also known that the removal for the classical easily degradable compounds, like Ibuprofen, usually ends in primary metabolites formation (e.g. Hydroxy- and Carboxy Ibuprofen) and full mineralization is not achieved. Therefore, there is an increasing concern regarding the formation of transformation products in wastewater treatment systems.

BONUS CLEANWATER has focused but not worked exclusively on pharmaceuticals, as they usually are the compounds most complicated to manage: they are designed to leave the human body after 1-2 days and thus, to sorb very little. On the other hand, they are designed to be stable (persistent) in the human body, therefore making biodegradation processes in the treatment plants very difficult.

Generally, it is perceived that concentrations in highly loaded surface waters are too high to achieve good ecological status and not regarded as a safe resource for drinking water production. In Germany, Switzerland, and emerging in Sweden, programmes are launched to remove organic micropollutants at the wastewater treatment plants to achieve lower pollutant loads in the surface waters.

Considering the urban water system, it is clear that WWTPs are a large source of such micropollutants to the environment. However, there are also other parts of the urban sewer system that can play a role in introducing micropollutants into the environment.

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Work carried out in the project

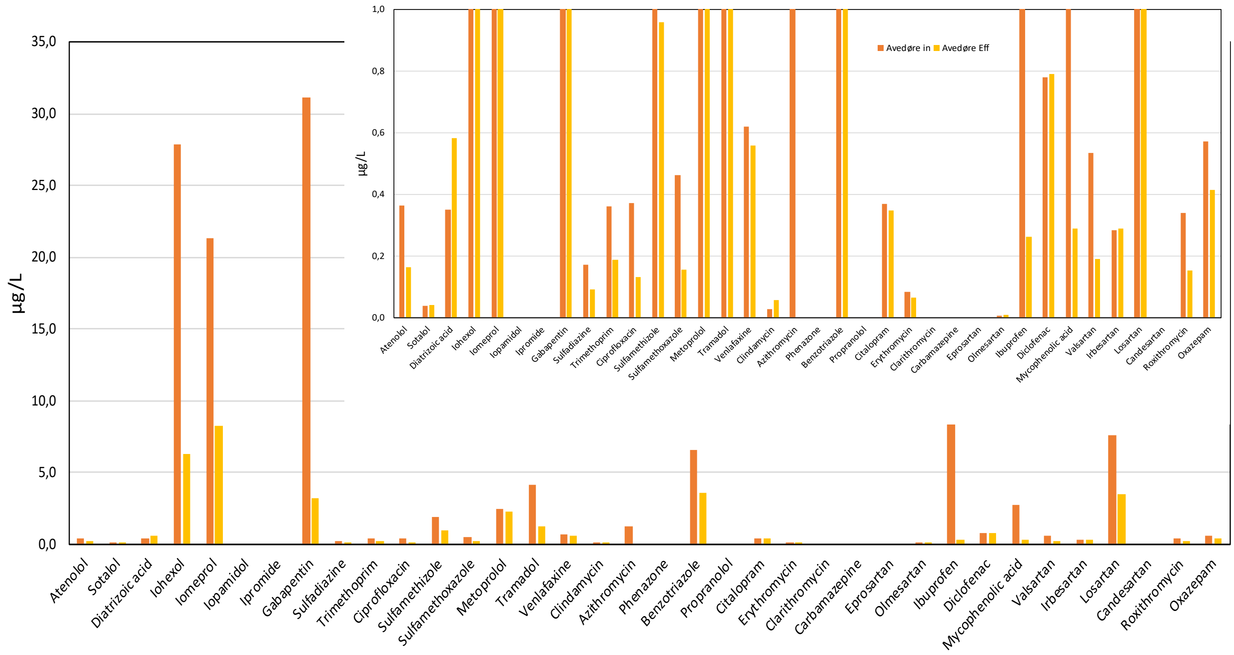

Figure 1 concentrations of compounds measured at the in- and outflow of a typical conventional activated sludge treatment plant in Denmark (Avedøre) (24h composite samples).

Combined sewer overflows (CSO) occur after torrential rains in urban areas drained by combined sewer systems (rainwater and wastewater in the same pipes). In Scandinavia and Germany this is typically city quarters established before 1970. These systems are designed to drain a certain amount of rainfall. Once that is exceeded (often the design value is three times dry weather flow), the systems overflow and discharge the mixed water into the recipients without any treatment.

Pure stormwater is any rainwater flowing off an urban surface. *A priori* this water has been considered as pure rainwater and has been discharged in separated sewer systems directly into surface waters. However, since the 1980s it became clear that these urban surfaces often emit compounds into the stormwater that can cause pollution. The main load of the pesticide mecoprop in, e.g., lake Zurich is not from agricultural use but from roof run-off from impregnated polymeric flat roofs.

Though the situation for single compounds is well understood, and before CLEANWATER, there was no holistic assessment on which emission pathway contributed with which compound and to which extent, (concentration/load) to the pollution of the Baltic Sea. CLEANWATER did not only provide a quantitative analysis of the pathways but also an assessment on the respective loads to the whole catchment and a rough estimate on which concentrations to expect in the Baltic Sea.

CLEANWATER explored the possibilities of removing micropollutants by advanced biological as well as advanced chemical means, with focus on both effluent water from larger urban wastewater treatment plants, and decentralized treatment of smaller rural wastewater treatment plants. CLEANWATER focused on eco-technologies, meaning technologies that can be used with low energy usage, and without just moving the problem (the micropollutants) from one compartment (water) to another (as done in sorption techniques making use of activated carbon). As planned, CLEANWATER has worked with:

1. making ozonation energy efficient,
2. optimizing moving bed biofilm reactors and membrane bioreactors for micropollutant removal from urban wastewater treatment plants effluents,
3. establishing biomimetic forward osmosis as a tool for zero emissions into seawater, and
4. establishing biofilters for decentralized treatment for both combined sewer overflow and for polishing effluents from small wastewater treatment plants.

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CLEANWATER has not only focused on removing micropollutants from water but has also tested whether problematic or persistent compounds are formed in the various reactors (formation of metabolites and other transformation products). This is very important, as only a minor change of the molecule will usually not change the toxicity and thus not change the assessments of the emissions loads much. There are a few cases, though, e.g., the steroid hormones for which small changes in structure has massive impact on their effects.

CLEANWATER also aimed for enhancing analytical capabilities, which was extremely needed for the analysis of microplastics but also for some issues on micropollutants.

2 Main results achieved during the project

Emissions to the Baltic

CLEANWATER focused on urban aquatic emissions of microplastics and micropollutants and considered the following pathways: treated (and untreated) wastewater, stormwater and combined sewer overflow. It was concluded that:

- the removal rates of these compounds are diverse and range from 0% to 98%
- most of the considered compounds, mainly pharmaceuticals, show low removal (< 20%) in conventional wastewater treatment
- 1-10 t of each individual compound is emitted to the Baltic Sea (considering the multitude of compounds about 10.000 t micropollutants will reach the Baltic Sea annually)
- for those compounds that are introduced to wastewater, treated wastewater is the main transfer route to the Baltic Sea
- combined sewer overflow is the dominant source for those compounds that are removed in conventional wastewater treatment (>99%)
- stormwater is only relevant for those compounds that are in direct contact with rainwater (e.g., biocides from construction materials or PAH and rubber from traffic emissions)
- the considered compounds are, on average, expected to reach concentrations of 0.1 to 20 ng/L in the open sea, though concentrations close to the discharge points (inner fjords, mouths of the rivers) are expected to exceed these values by 1-3 orders of magnitude
- effects are predominantly expected at these costal hotspots.

Removing micropollutants and microplastics from urban water emissions will thus especially increase water quality in those hot spot areas (wastewater discharge areas, inner fjords, estuaries and mouths of big rivers).

Removal technologies

There are two main approaches for removal of micropollutants. Either compounds are undergoing a reaction (being purely chemical or biochemical) in which the compounds are transformed over multiple steps into other compounds until they are mineralised or incorporated into the biomass, or there is a phase transfer in which the compounds are removed from the water and transferred into another medium. For the reactive approaches the transformation products are critical, while, for the phase transfer approaches, the main issue is how to handle the phase to which the compounds are accumulated. CLEANWATER assessed ozonation, moving bed biofilm reactors (MBBRs), membrane bioreactors (MBRs), biofiltration and biomimetic forward osmosis (BMFO) – all but BMFO based on the reactive approach. Activated carbon, applied in the form of dosing of powder or filtration through granules, was not included in CLEANWATER as energy consumption for the production is externalised (occurring elsewhere). Furthermore, powdered activated carbon is no option for those countries that want to close the nutrient cycle by utilising the sludge on agricultural land (with potential pollutant transfer from water to food). Some technologies are ready to be used in full-scale to remove a multitude of micropollutants.

Ozonation is based on oxidation of organic matter including pharmaceuticals and other organic micropollutants. Ozonation is currently the most established technology and has been applied in a multitude of wastewater treatment plants for micropollutant removal. Most micropollutants are transformed into new compounds, transformation products, in contact with ozone rather than being mineralized. At the same time various oxidation by-products can be formed depending upon the content of the water. Considering the formation of by- and transformation products, ozonation is typically combined with a biological post-treatment

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to reduce toxicity following ozonation. Ozonation is applied in full-scale for removal of micropollutants with advantages like low foot-print and the possibility to control removal through varying dosing. Generation of ozone is however energy intensive and must be done on-site. Ozonation is widely applied partly due to the fact that a wide range of substances can be effectively removed. However, CLEANWATER has determined that there are more regions (coastal) in Scandinavia that have bromide concentrations in the wastewater, which is triggering production of unwanted bromate during ozonation, than is relevant in central Europe. Ozonation does not remove microplastics, as plastic materials are very resilient towards chemical breakdown.

Moving bed biofilm reactors (MBBRs), with biofilms growing on suspended carriers, are applied in full-scale for BOD and nutrient removal. In recent years, MBBRs have been successfully tested and showing potential to remove also micropollutants. The removal mechanisms are, similar to biofiltration, based on microbial communities that metabolise the micropollutants. With an innovative approach on feeding the microorganisms a high biofilm activity can be maintained to promote increased removal of organic micropollutants. MBBRs have shown potential to transform some organic micropollutants, like for example diclofenac, to a higher degree than previously demonstrated in activated sludge systems. MBBRs proved to have a relative low climate change impact and low operation cost, but on the other hand investment costs are somewhat higher than ozonation. However, the high removal reported by other studies could not be reproduced with the CLEANWATER version of the MBBR process, which was significantly different. MBBR is capable to retain microplastics in the biofilm matrix and transfer the microplastics to the excess sludge for final management. Due to low plastic loads in the water to be treated, this could however not be experimentally verified. The carriers themselves were of plastics, and could hence give off some microplastics during their life time. The relative contribution was though low and below the detection limit of the applied analytical method.

Membrane bioreactors (MBR) are based on the principle of activated sludge with the possibility to work with higher biomass concentrations, long sludge ages and with the settler replaced for a micro- or ultrafiltration membrane which allows for a low foot-print. Highly efficient biomasses and operation conditions for micropollutant removal have been described in laboratory scale and in single cases in in pilot scale. There is not one finished MBR system that is operating micropollutant removal in full-scale. However 90% removal for a multitude of compounds has been published with very high HRTs in laboratory reactors. cMBR (MBRs with ceramic membranes) in CLEANWATER has shown under some conditions high removal rates, but costs and energy usage made this also a very costly approach in comparison. MBR systems are based on filtration with low filter pore sizes, and will hence retain microplastics particles down to the pore size and even below (due to cake filtration). Opposite to the conventional polymeric membrane based MBRs the ceramic cMBRs tested will not give off plastic particles and have very small pore sizes. Their potential at retaining microplastics is hence high. This could however not be experimentally verified due to operational issues affecting the performed tests.

Biofiltration is similar to slow sand filtration. Treatment is based on biofilm microbial communities that metabolise the micropollutants, with the biofilms being allocated in porous media (natural or synthetic). Biofiltration is seen as an option for decentralised treatment (CSO, stormwater) and for very small WWTPs (<1000 persons). Similar systems are in use for stormwater treatment (Germany) and bank filtration (all over the world). Dependent on residence time (up to 20h) and the shaping of the microbial community, the removal of certain micropollutants can be high (> 95%). However, establishing the right microbial community can take a long time (months). The installations need considerable space and are therefore only suited for decentralised treatment and can be expected to run on a very low level of maintenance and interventions. Biofiltration is seen by the consortium as suitable for decentralised treatment, including very small wastewater treatment facilities, stormwater treatment and tackling of combined sewer overflow. Some of the tested variant had quite reasonable removal rates. LCA and cost assessment showed this as s relatively efficient approach. Biofiltration will remove significant amounts of microplastics by physically retaining them in the biofilms and, depending on the pore size of the media used for biofiltration, also by physical filtration processes. The microplastics will accumulate in the filters and have finally to be managed.

Biomimetic forward osmosis (BMFO) relies (similar to reverse osmosis) on membranes that are able to separate micropollutants from water. Opposite to reverse osmosis, for which the driving force is physical pressure, the driving force for forward osmosis is osmotic pressure. The main innovation in CLEANWATER was the use of a biomimetic membrane that includes the aquaporin molecule in the membrane, which makes it considerable easier for water to pass the membrane. All compounds that were tested in CLEANWATER were

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rejected by more than 94% and often the rejection rate was up to 99%. BMFO could thus decrease emissions considerably or produce water with drinking water quality. No research was done on how to deal with the concentrated stream of MP. BMFO is expected to fully retain microplastics. This could however not be experimentally verified due to operational issues affecting the performed tests.

Comparison of technologies

The different technologies come with advantages and disadvantages reflecting differences in removal, carbon footprint, costs and space demands to name but a few. Technology readiness level (TRL) is also different as some technologies are available in full-scale, for example ozonation, and others are under development in various pilot studies, as in the CLEANWATER project. Table 1 provides and overview and indication of some key aspects, primarily based on results from the project. Granular Activated Carbon (GAC) and Powdered Activated Carbon (PAC) have been added for comparison. If removal is based, partly or entirely, on reactions (degradation), various transformation products will be formed. Such transformation products might influence toxicity in different ways but are not necessarily considered a problem.

Removal is classified as *specific* or *broad*. Broad means that removal (80-90% or more) can be expected for a wide spectrum of substances. Specific means that removal can be expected but not necessarily to the same degree, at least not for substances commonly analysed and for design conditions applied so far.

The different technologies can and should be combined in different ways, for example to maximize removal of various substances or transformation products. Ozonation *should* be combined with biological post-treatment, for example an MBBR, to reduce toxicity. It should be noted that the various technologies have been assessed in different scales with MBR, biofiltration and BMFO evaluated for small-scale installations and ozonation and MBBR being evaluated also for large scale plants (>100 000 pe). Each case and each technology must be evaluated based on local conditions and the existing infrastructure.

	Ozonation	MBBR	MBR	PAC[1]	GAC[1]	Biofilter	BMFO
Costs	Low	Low[2]	High	Low	Medium	Low	High
CO_2-footprint	Medium	Low	High	High	High	Low	Low
Removal	Broad	Specific	Specific	Broad	Broad	Specific	Broad
Transformation products	Yes	Yes	Yes	No	Yes	Yes	No
Foot-print	Low	Medium	Medium	Low	Low	High	Low
TRL							
Nutrient recycling on agricultural land	Yes	Yes	Yes	No	Yes	Yes?	Yes
Target	Wastewater post CAS	Wastewater post CAS	Wastewater post CAS	Wastewater post CAS	Wastewater post CAS	CSO/ rainwater	Drinking water

[1]Information on cost and CO_2-footprint from Baresel (2018) and *Anleitung zur Planung und Dimensionierung von Anlagen zur Mikroschadstoffelimination* (2016)
[2]Based on a hydraulic retention time of 2 hours
Costs: Low: <0.05 €/m³, Medium: <0.1 €/m³, High: >0.1 €/m³
TRL: Red; 1-3, Orange; 4-6 (piloting), Green 7-9 (full-scale implementation)

General outcomes

CLEANWATER assessed that the costs of removing micropollutants and microplastics will be between 0.03 €/m^3 (Biofilters) and 0.2 €/m^3 (ozonation, advanced biofilm treatment). CLEANWATER assessed the energy use related CO_2 emission of advanced treatment to be between 0.03 kg CO_2/m^3 (Biofilter) and 0.140 kg CO_2/m^3 (ozonation). These parameters are vastly dependent on which technology is used and on how electric power in the respective region is generated. All in all, CLEANWATER has achieved significant technical progresses and new knowledge on all the involved five very different technologies. Moreover, CLEANWATER delivered an energy based live cycle assessment and cost assessment for the respective technologies for the Baltic Sea catchment.

Recommendations and lessons learnt

BONUS CLEANWATER has gained new critical knowledge on how ecotechnologies can be used for removing organic micropollutants and microplastics from wastewater in order to reduce the inputs into the Baltic Sea.

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1) there is not yet one technology that solves the micropollutant removal completely without creating new environmental disadvantages. All technologies proved to improve the micropollutant removal, which is acknowledged to be critical in order to meet good ecological status in the Baltic Sea. However, all technologies have had their own pros and drawbacks, from high energy requirements, creating new toxic compounds or transformation products, high capital costs or large footprint to just not being capable of removing some of the micropollutants. However, it should be clear that reducing the concentrations of micropollutants by one decade (>90% reduction) for a wide range of compounds is possible.
2) different requirements, locally as well as regional, will favour or disfavour some technologies due to present conditions, such as wastewater characteristics, existing process technology, excess sludge handling, cost of land, energy prices and legislation. The best choice for one wastewater treatment plant may therefore not necessarily be the best for another one, even within the same region, which is why each discharge source to the Baltic Sea needs to be evaluated separately.
The combination of the two above mentioned lessons means, that utilities have several options to select the right technology meeting the local demands. The choice of each utility will be a balance between environmental responsibility and cost.
The recommendation is therefore to start investigating how each wastewater plant, based on opportunities, restrictions and priorities, can best integrate different micropollutant removal technologies. The BONUS CLEANWATER project, has contributed with knowledge to the overall jigsaw-puzzle on microplastic and micropollutant removal that each wastewater treatment plant needs to complete.

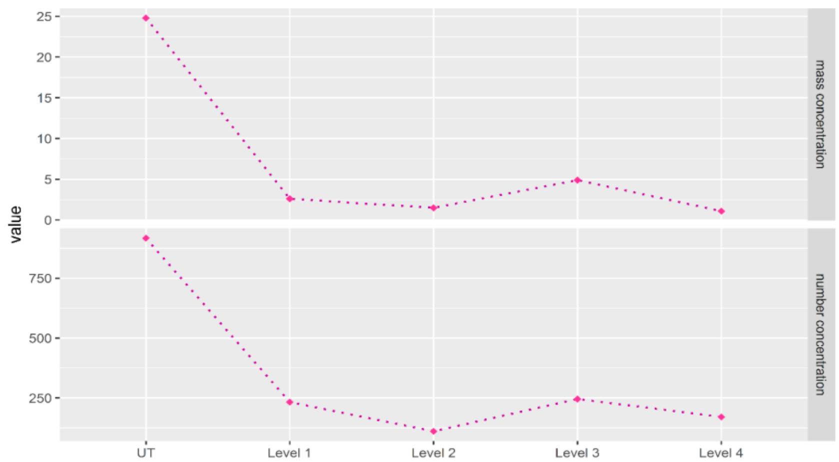

Fig 2 Successful removal of microplastic particles in the multilayer biofilter pilot. (UT=inlet) from Liu et al., How well can microplastics be removed from treated wastewater? A pilot study of biofilters polishing treatment plant effluents, Water, 12, 1085.

3 The continuity plan of the project

The project is following its initial plan. The final report has been submitted end of May 2020.
Beyond the runtime of the project:
Future activities have been discussed and agreed upon in the last steering committee meetings of the project. Several initiatives have emerged, especially one for the JPI call on aquatic pollutants is worth mentioning.

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