Baltic Marine Environment Protection Commission

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Background

HOD 49-2015 agreed on a new HELCOM action on micropollutants in effluents from wastewater treatment plants to be included in the Pressure WG work plan (Outcome of HOD 49-2015, para 4.69).

The action implies compilation of knowledge on wastewater from treatment plants as sources of micropollutants in the environment and evaluation of existing and novel WWT techniques by compiling existing information on e.g. feasibility, costs, and good practice.

The document summarizes some preliminary results of the ongoing project "Advanced wastewater treatment as a measure to reduce chemical pollution of the Baltic Sea" run by Baltic Eye, Baltic Sea Centre, Stockholm University. It contains a quick overview of the mechanisms of contaminant removal for the most commonly applied technical solutions in large scale applications and discussion and testing of a strategy for evaluation of benefits of an unselective end-of-pipe measure like wastewater treatment for reduction of hazardous substances in the Baltic Sea.

The attachment contains extended information on the preliminary project findings.

Action requested

The Meeting is invited to take note of the information and utilize it for the implementation of the HELCOM action on micropollutants in effluents from wastewater treatment plants.

Summary

Advanced wastewater treatment as a measure to reduce chemical pollution of the Baltic Sea – first results from pilot project

Background

Source control is the preferred solution to reduce chemical pollution. It is, however, commonly perceived as unlikely that current regulations, campaigns and economic incentives to substitute or reduce emissions of substances identified as hazardous will suffice to reduce the ever increasing flow of thousands of chemicals to the aquatic system. In particular negative effects related to pharmaceuticals are problematic since environmental risks must be weighed against human health benefits. Because of these circumstances, advanced wastewater treatment has gained much attention in the last decade as part of the strategy to protect the aquatic environment.

Practically any contaminant can be removed by advanced treatment methods; however this is a question of energy consumption and hence costs. A range of technologies exist that remove micropollutants from wastewater via physical separation, biological degradation and adsorption. Oxidation of micropollutants with ozone or adsorption onto activated carbon (PAC or GAC) are the two technologies mainly tested/implemented in full scale (Margot et al 2013, Cimbritz et al 2016). Compilations of available technologies, configurations and costs have been reviewed recently / are underway e.g. in Sweden.

Question: How can we evaluate the benefit of advanced wastewater treatment from a Baltic Sea perspective? (Pilot project)

When considering upgrading WWTPs to remove micropollutants, it is necessary not only to estimate the feasibility of technology and costs, but also the benefits. Estimating the benefit is not an easy task for any compound specific measure, and certainly not for advanced wastewater treatment since the benefit is, apart from removal of known contaminants, the removal of substances we are not aware of in the effluents.

We have identified three general approaches that may be tested that can help assessing the benefit:

1. Reduction of total chemical mass emitted from WWTPs (consideration of known and unknown contaminants): How much can the general (unspecific) chemical exposure be lowered in the Baltic Sea?

2. Reduction of concentrations of priority/indicator chemicals (consideration of contaminants we are aware of prioritize): Worst case/best case estimation of to what extent advanced treatment of the wastewater could lower environmental concentrations exceeding toxicity thresholds. What conclusions can be drawn based on field data about the adequacy of advanced wastewater treatment as a measure to reduce chemical pollution in the Baltic Sea?

3. Reduction of toxic effects (consideration of known and unknown contaminants): Assess outcomes of ecotoxicological tests (test batteries) assessing differences in toxicity before/after additional treatment steps. Can this be used to assess reduction of emissions of toxic substances to the Baltic Sea?

Here we describe the first "total mass-removal/transformation" approach, and some preliminary results.

Method

- Data on removal efficiencies from various scientific publications were compiled, all reporting results from full scale or large scale pilot implementations of O3 or AC treatments.
- The average removal efficiencies were calculated 1) for all compounds compiled in the literature (Litt-dataset) and 2) a separate dataset containing the compounds in the Swedish screening database measured (and exceeding detection limits) for which removal efficiencies were reported

(SE-dataset). For the latter dataset (SE), the average yearly mass per connected person (ng/person) in effluent was calculated based on measurements from years 2003 – 2014. The removal efficiencies of these compounds were then weighted according to this mass (i.e. more weight was given to compounds that occur in higher concentrations in the total average). The same was done for the compounds for which a "typical effluent concentration" was reported in the literature (Litt) based on that concentration.

- The weighted average removal rates based on the SE-dataset was used to calculate the total mass removal from the largest WWTPs along the Baltic Sea coast. We make the assumption that chemical emissions per capita in Sweden are representative for all countries, as a first estimate, and that the chemicals in this dataset are representative of all micropollutants in the wastewater with respect to distribution of loads and removal efficiencies. All WWTPs closer than 20 km (ca 615 WWTPs) from the Baltic Sea are included in the calculations.

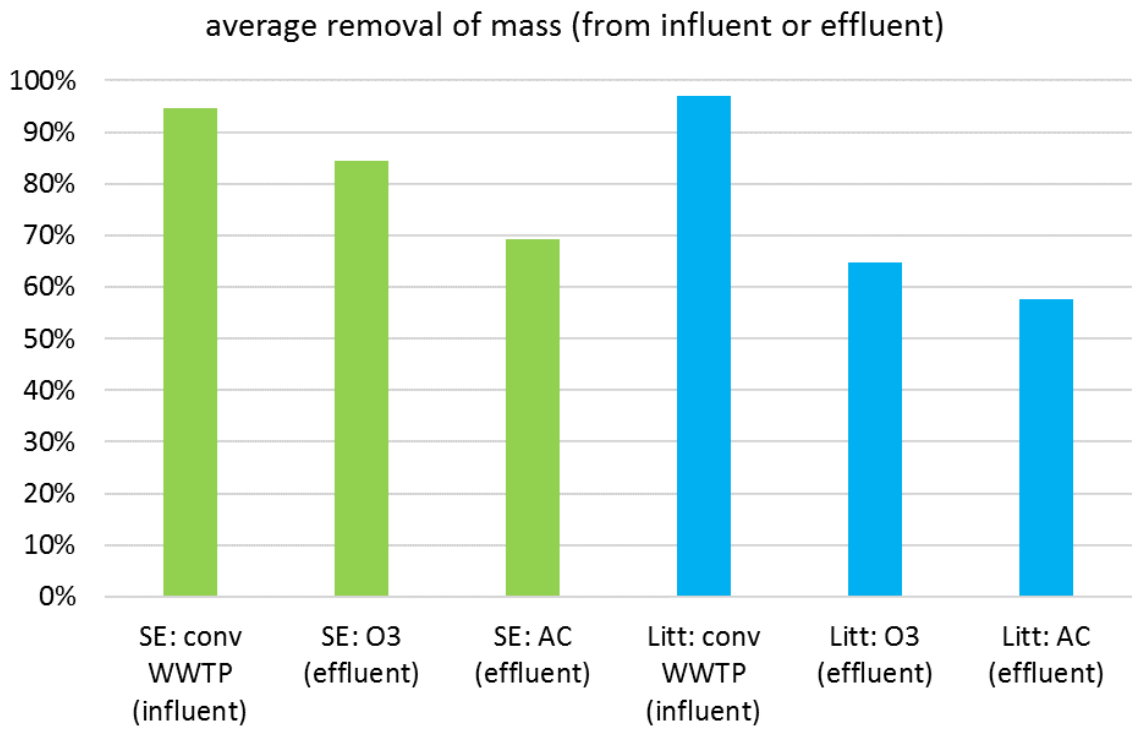

Figure 1. Average removal efficiencies for (green bars) compounds measured in Swedish effluents with conventional treatment, O3 or AC removal efficiency reported in the literature, weighted to measured per capita emissions in effluent; average removal efficiencies in full literature compilation, weighted to typical influent (conventional) or effluent (O3, AC) concentrations reported in the literature (European data).

Results: Evaluation of potential to reduce total chemical load (mass based) from coastal WWTPs

How much could the total chemical load of chemicals be reduced/transformed to presumably less stable compounds by upgrading all coastal WWTPs >100 000 PE?

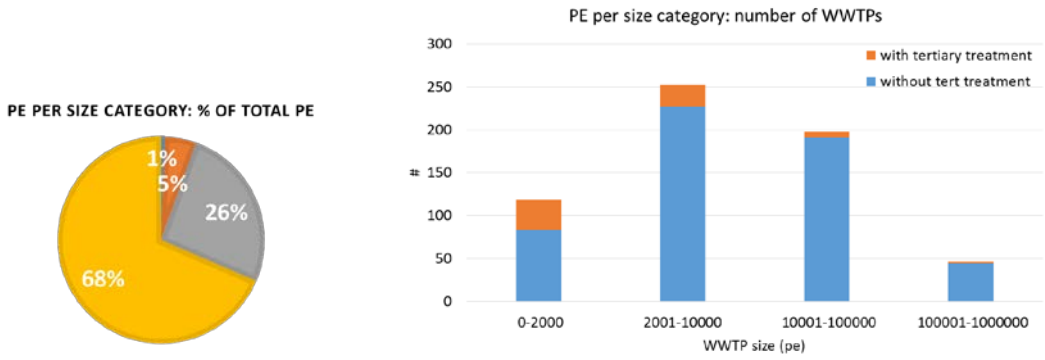

Figure 2. Contribution of coastal WWTPs in different size categories to total load (PE) and number of WWTPs in each size category. Pie chart: size categories clock-wise 0-2000, 2001-10000, 10001-100000, >100000.

- Ca 615 WWTPs are located < 20 km from the coast. 46 of these have reported loads >100 000 PE. The total loads from these 46 WWTPs contribute ca 68% of the total load (PE) from the 615 WWTPs closest to the coast. Two of the 46 largest coastal WWTPs do not have tertiary treatment, according to the databases and (in the case of Russia) as far as we could find out. Note that chemicals emitted from non-coastal WWTPs also reach the sea, but we did not attempt to quantify this mass at this point.
- Upgrading the 46 largest WWTPs closest to the coast would result in a ca 40-45% reduction of the total chemical load (mass) (using average removal efficiencies SE in Figure 1). Whereas AC-based methods remove the chemicals from the effluent, ozonation leads to transformation, and hence no mass reduction. However, the transformation products are in many cases more easily degraded in the environment. The formation of unknown transformation products is, however, the major disadvantage of oxidative treatments.

References

Cimbritz et al., Rening från läkemedelsrester och andra mikroföroreningar En kunskapssammanställning, Svenskt vatten utveckling report, 2016

Margot, J., et al., Treatment of micropollutants in municipal wastewater: ozone or powdered activated carbon? Science of the total environment, 2013. 461: p. 480-498.

Attachment

Advanced wastewater treatment as a measure to reduce chemical pollution of the Baltic Sea –first results from pilot project.

Emma Undeman, Baltic Sea Centre, Stockholm University

Background

Although acute or chronic effects on Baltic Sea wildlife populations of chemical pollution are not clearly distinguishable from other environmental stressors today, various ecotoxicological indicators (e.g. EROD activity, lysosomal membrane stability, occurrence of micronuclei, imposex, embryo aberrations and reproductive disorders) show impaired health status of various fish species and lower trophic organisms in many coastal areas. At the same time, we know that the use pattern of chemicals in society has changed over time, going from use of few chemicals in large quantities, often emitted from point sources, to use of many chemicals in small quantities (e.g. chemicals in consumer products) and many diffuse sources ("chemical intensification" of our society). Whereas many point sources for chemical pollution have been identified over the years, the diffuse sources are more difficult to handle. The most efficient and sustainable measure to reduce chemical pollution is source control (e.g. regulation of use), but this type of measure relies on various priority lists of identified hazardous substances or focus on specific chemicals that are in the spotlight. It is unlikely that compound-specific individual regulations and e.g. campaigns to change consumer behaviour will suffice to reduce the ever increasing flow of thousands of chemicals with a wide variety of usage and transport pathways to the aquatic system. Many chemicals used in everyday life are, however, collected in sewage that passes through wastewater treatment plants. The WWTPs are hence nodes for chemical flows in society. Advanced wastewater treatment has therefore gained much attention in the last decade as part of the strategy to protect the aquatic environment, in particular from pharmaceuticals for which a regulation of use can in many cases be inconceivable.

Advanced treatment options and removal mechanisms – brief overview

Practically any organic contaminant can be removed by advanced treatment methods; however this is a question of energy consumption and hence costs. A range of technologies exist that remove micropollutants from wastewater via physical separation (membrane technologies: ultrafiltration, nanofiltration, reversed osmosis), biological degradation (i.e. degradation by metabolic activity mainly of microorganisms), oxidation (ozone O3, hydrogen peroxide H2O2, chlorine dioxide ClO2, ferrates), and adsorption to activated carbon AC. Oxidation of micropollutants with ozone or adsorption onto activated carbon are the two technologies mainly tested/implemented in full scale (Margot et al 2013, Cimbritz et al 2016). Ozonation leads to degradation of the pollutants (usually not full mineralization, to what extent depends on the ozone dose), with the drawback that toxic oxidation by-products may be formed (bromate, nitrosamines, folmaldehyde) as well as (unknown) transformation products. A polishing step after the ozonation step (e.g. sand filtration, AC) is hence often required. The oxidation products are, however, often more easily biodegradable than the mother substances and may hence be partly removed in post-filtration steps or downstream (Oller et al 2011, Margot et al 2013). Activated carbon can be used either in powdered form (PAC dosed to the water) or as a filter of granulated activated carbon (GAC). Adsorption to AC separates the pollutants from the wastewater. The micropollutants are not transformed, and hence no by-products are formed. However, regeneration of the AC, which is gradually saturated over time, is required. In the regeneration/destruction process (burning) the adsorbed chemicals are mineralized (Cimbritz et al 2016).

The choice of AC or ozone is case dependent, e.g. depending on existing infrastructure, how sludge is to be treated, composition of the wastewater (DOC, TOC, bromide concentrations, pH). The reduction of micropollutants (MPs) depends on water quality, dose of AC or ozone, and also the physical chemical properties of the MPs.

Both ozone and the hydroxyl radicals formed when ozone reacts with the organic wastewater matrix in the water attacks MPs. OH radicals are unselective, but to a large extent disarmed by the many kinds of radical scavengers (e.g. carbonate) present in the wastewater and hence compounds mainly oxidized by the OH radicals are more affected by the quality of the wastewater, explaining a rather high variation in removal rates observed for some substances (Nakada 2007, Margot et al 2013). Molecular structures with high electron density (C=C double bonds, activated aromatic systems and non-protonated amines) are susceptible to ozone attacks. Electron donating structures in the molecule (e.g. aliphatic functional groups, hydroxyl groups) enhances reactivity. Electron withdrawing groups (e.g. ethynyl, amide or carboxyl groups) can reduce electron density and make the molecules less reactive (Nakada et al 2007). Chemicals such as sulfamethoxazole (antibiotic), propranolol (beta-blocker), diclofenac (anti-inflammatory drug), carbamazepine (anti-epilepticum), bisphenol A are examples of chemicals with high ozone reactivity. Ibuprofen (NSAID), ketoprofen, metronidazole (antibiotic), primidone (antiepileptic), mecoprop ("household" herbicide) and benzotriazole (e.g. corrosion inhibitor) have low reactivity with ozone and show moderate removal efficiencies due to reaction with OH radicals. Gabapentin (anti-epeleticum), atrazine (herbicide), irgarol (algicide, antifouling agent) and many contrast media are resistant to both ozone and OH radical attacks (Margot et al 2013).

Activated carbon is a selective sorbent. The interactions between MPs and the AC surface are controlled mainly by non-specific dispersive interactions (van der Waals interactions) and hence the molecular volume, and also by electrostatic interactions (Coulombic interactions) i.e. like charges repel, unlike charges attract one another (Dickenson and Drewes 2010). The adsorption is influenced by organic matter in the wastewater, which compete for adsorption sites or block pores in the carbon particles. The charge of AC is pH dependent. In the study by Margot et al 2013, the PAC was neutral or slightly positively charged when loaded (point of zero charge pH >7.3), but because of adsorption to the positively charged PAC of negatively charged organic matter present in the wastewater, the surface charge of PAC became negative. Cationic compounds were hence expected to adsorb to the PAC surface. Anionic substances would be repelled; however, this effect can be offset by hydrophobic partitioning onto the PAC. In summary, hydrophobicity plays a more significant role for negatively charged MPs than for neutral and positively charged molecules. For hydrophilic substances, the PAC affinities can be expected to be highly variable due to variable hydrogen bond formations and pi-pi interactions between MPs and PAC surfaces (Margot et al 2013).

Pilot project: How can we evaluate the benefit of advanced wastewater treatment from a Baltic Sea perspective?

We have identified three general approaches:

1. Reduction of total chemical mass *emitted from WWTPs*: Make an estimation of total chemical emissions (total mass) from coastal WWTPs in the Baltic Sea catchment. How much could the total chemical load of these known chemicals be reduced/transformed to presumably less stable compounds by upgrading all coastal WWTPs, or e.g. only the largest ones? If we treat the water motivated by the precautionary principle (without knowing the exact benefit, here without knowing the reduction of negative effects), how much can the general (unspecific) chemical exposure be lowered in the Baltic Sea?
2. Reduction of concentrations of priority chemicals: Summarize reported surface water concentrations in the Baltic Sea or fresh water systems in the catchment of chemicals with measured removal efficiencies and their toxicological thresholds (e.g. EQS and/or PNECs). Make a worst case/best case estimation of to what extent advanced treatment of the wastewater could lower environmental concentrations exceeding these thresholds (if any). What conclusions can be drawn based on field data about the adequacy of advanced wastewater treatment as a measure to reduce chemical pollution in the Baltic Sea?
3. Reduction of toxic effects: Compile literature data on outcomes of ecotoxicological tests (test batteries) assessing differences in toxicity before/after additional treatment steps.

In this document, we describe the first “mass-removal/transformation” approach, and some preliminary results.

Removal efficiencies reported in literature from full scale or large pilot scale compiled in this study

In this project, we compiled data on removal efficiencies from various scientific publications, either review articles or publications including a wide range of compounds, all reporting results from full scale or large scale pilot implementations of O3 or AC treatments, all with some variation in applied doses and technical set up and treatment combinations. This introduces variability (not yet quantified) in removal efficiencies. However, this compilation indicates the expected magnitude of removal efficiency for the individual substances. The column-charts below (Figure 1) show the average removal efficiencies in typical conventional WWTPs (tertiary treatment) and the *additional* removal (calculated in this study) that can be expected when adding an additional treatment step. Hence, if the removal in conventional WWTPs is large, the *additional* removal will be small, although the removed fraction of what remained in the effluent from the conventional treatment may be large (this is often the number reported in the literature).

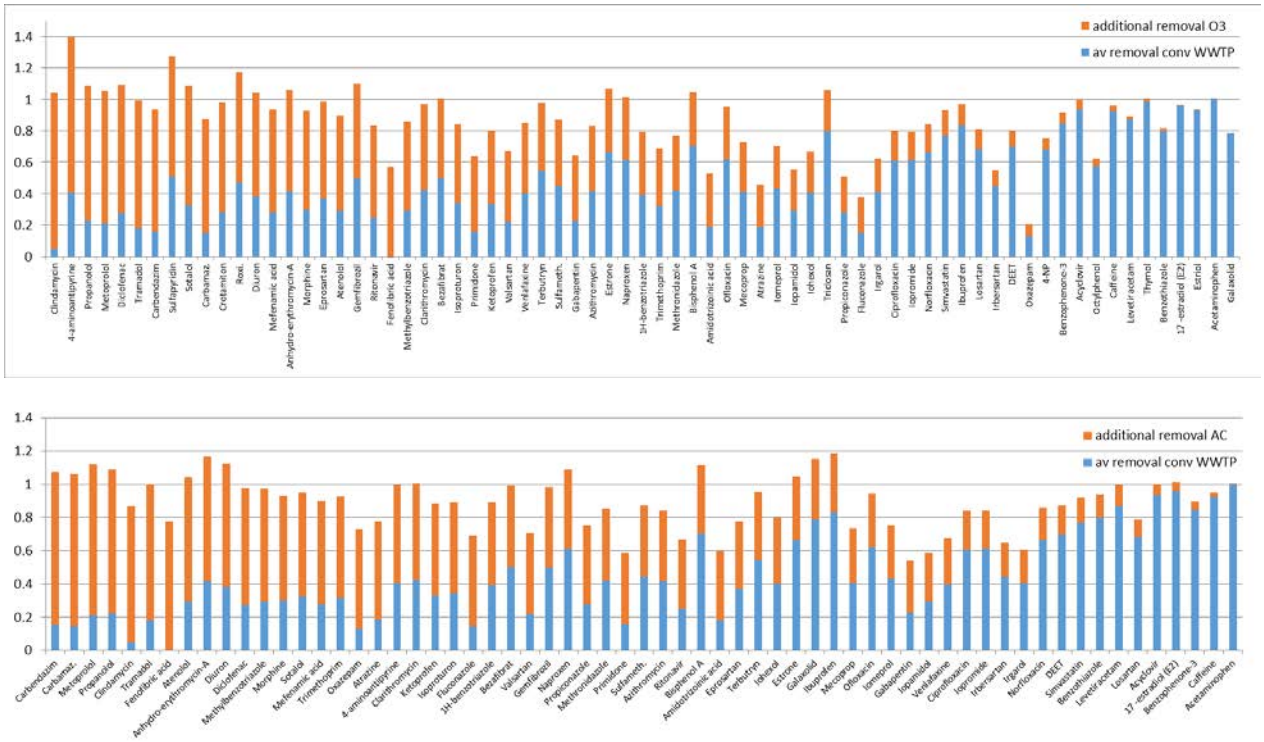

Figure 1. Removal efficiencies in conventional WWTPs ($mass_{influent}$ – $mass_{effluent}$) / $mass_{influent}$) and additional removal in advanced treatment (O3 or AC) ($mass_{effluent}$ – $mass_{after\_treatment}$)/$mass_{influent}$). Based on literature data.

These figures hence indicate what fraction of the total mass in *influent* that can be removed by additional treatment

Removal efficiencies relative chemical mass in conventional WWTP effluent

The average removal efficiencies were calculated 1) for all compounds compiled in the literature and 2) for the compounds in the Swedish screening database measured (and exceeding detection limits) for which removal efficiencies were reported. Simple averages are presented in the figure below (“not weighted”). For the compounds in the Swedish screening database with matching removal efficiency found in the literature (SE), the average yearly mass per connected person (ng/person) in effluent was calculated based on

measurements from years 2003 – 2014. The removal efficiencies of these compounds were then weighted according to this mass (i.e. more weight was given to compounds that occur in higher concentrations in the total average). The same was done for the compounds for which a "typical effluent concentration" was reported in the literature (Litt) based on that concentration. The mass/concentration-weighted and non-weighted average removal efficiencies deviated mainly for conventional WWTP-removal, indicating high emissions of chemicals that are also efficiently removed without advanced treatment technologies.

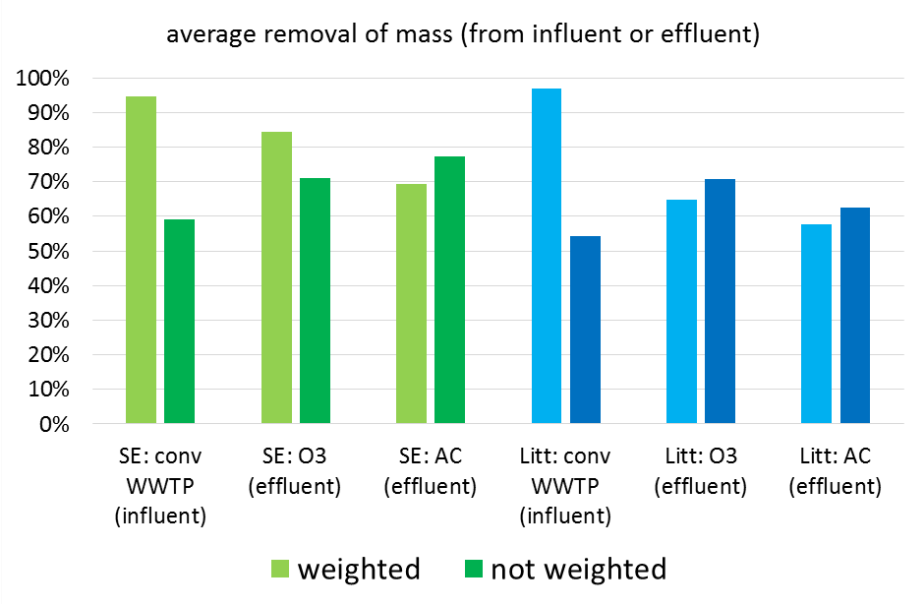

Figure 2. Average removal efficiencies for (green bars) compounds measured in Swedish effluents with an O3 or AC removal efficiency reported in the literature, un-weighted or weighted to measured per capita emissions in effluent; average removal efficiencies in full literature compilation, un-weighted or weighted to typical effluent concentrations reported in the literature (European data).

Evaluation of potential to reduce total chemical load (mass based) from coastal WWTPs

Based on the mass-weighted average removal efficiencies for chemicals measured in the Swedish monitoring program, we try to answer the following question: How much could the total chemical load of chemicals that *we know are emitted* be reduced/transformed to presumably less stable compounds by upgrading all coastal WWTPs, or e.g. only the largest ones (>100 000 PE)? In other word, if we treat the water motivated by the precautionary principle (without knowing the exact benefit, here without knowing the reduction of negative effects), how much can the general (unspecific) chemical exposure be lowered in the Baltic Sea?

We make the assumption that chemical emissions per capita in Sweden are representative for all countries, as a first estimate. All WWTPs closer than 20 km from the Baltic Sea are included (Figure 3). This distance was arbitrarily selected as a first test-cut off to partly avoid overestimations from treating all river transport of chemicals as through a "passive pipe" (i.e. no dissipation in rivers), still representing a worst case scenario (all molecules survive river transport to the Baltic Sea). Data from Russia is a combination of old data from PLC-5 and estimations based on data from the water company managing WWTPs in St Petersburg and Kaliningrad. Data for other countries is from EU's Waterbase and Swedish EPA (Svenska miljöportalen).

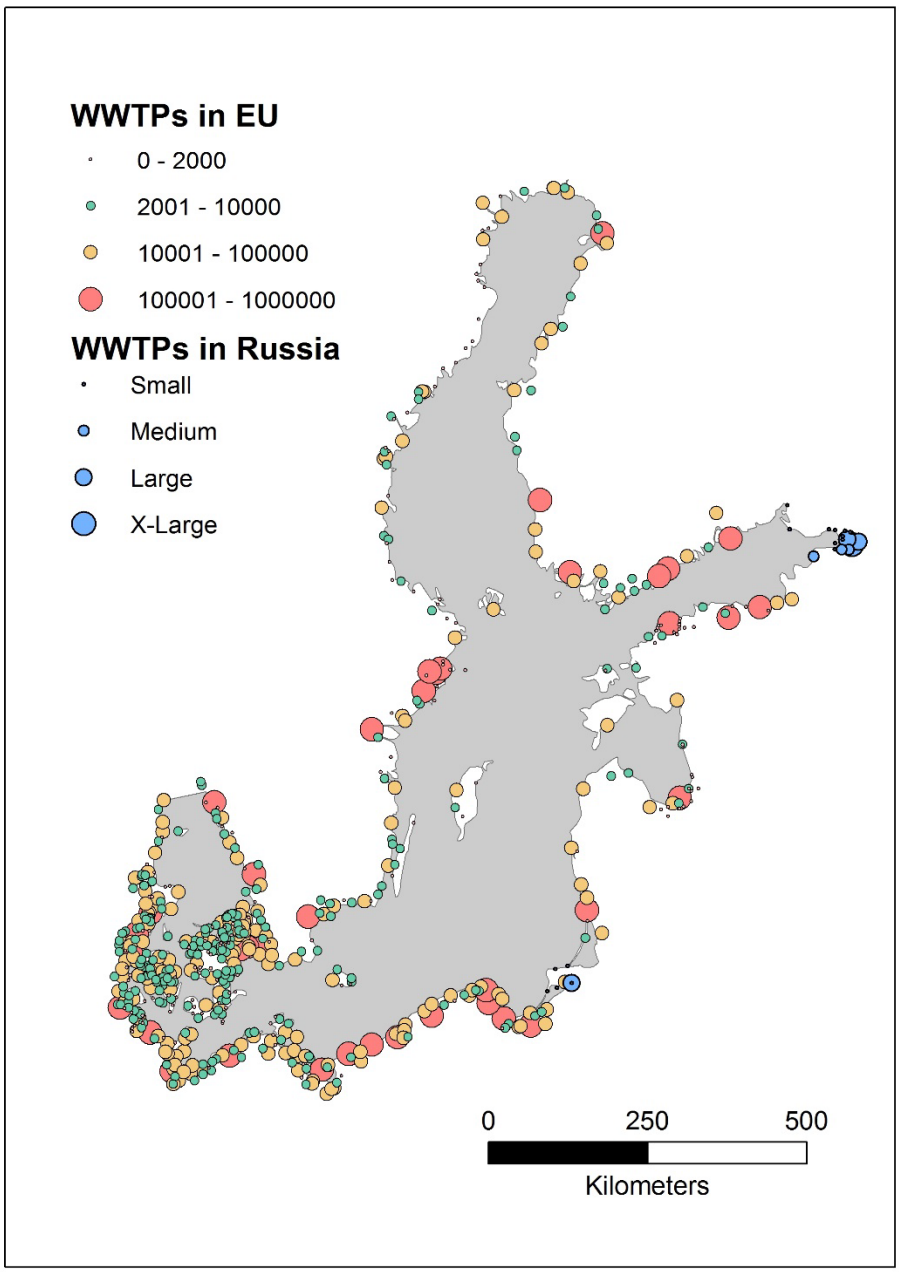

Figure 3. Map showing WWTPs in the Baltic Sea closer than 20 km from the coast. Russia: Size scaled to total P-loads reported in PLC-5. Other countries: size scaled to PEs (person equivalents).

There are 615 WWTPs shown on the map. The number and location of WWTPs operating in Russia is uncertain at this point because a lot of WWTPs have been re-built, closed or merged since PLC-5, and we did not have access to more recent data. Therefore, only 8 Russian WWTPs are included (the largest in St Petersburg and Kaliningrad) in these first calculations.

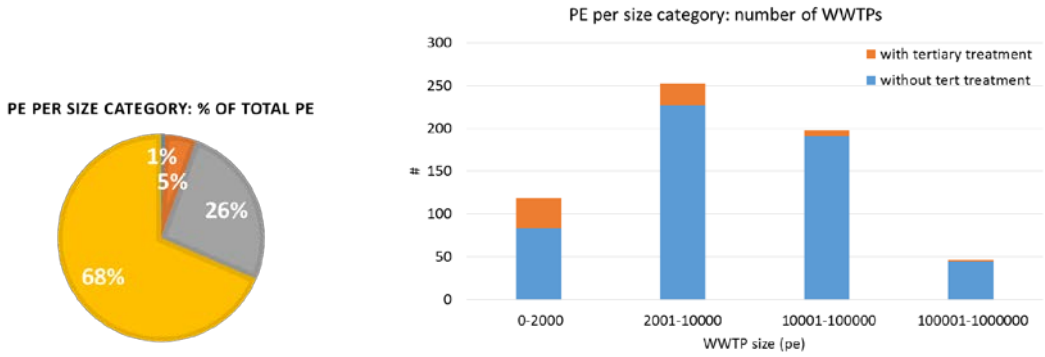

Figure 4. Contribution of coastal WWTPs in different size categories to total load (PE) and number of WWTPs in each size category. Pie chart: size categories clock-wise 0-2000, 2001-10000, 10001-100000, >100000.

The 46 largest WWTPs (i.e. all with reported loads >100 000 PE) contribute 68% of the total load (PE) from the 615 WWTPs closest to the coast. Two of these do not have tertiary treatment, according to the databases and (in the case of Russia) as far as we could find out at this point.

Assuming that all chemical emissions per PE are equal, and that the mass-weighted average removal efficiencies (Figure 2) are representative for all known and unknown substances in the effluents, upgrading the 46 largest WWTPs closest to the coast would result in a ca 40-45% reduction of the total chemical load (mass). Whereas AC-based methods remove the chemicals from the effluent, ozonation leads to transformation, and hence no mass reduction. However, the transformation products are in many cases more easily degraded in the environment. The formation of unknown transformation products is, however, the major disadvantage of oxidative treatments.

Summary of major arguments for and against advanced wastewater treatment as a measure to remove micropollutants

So called advanced waste water treatment technologies can be implemented in existing waste water treatment plants to enhance removal of micropollutants, the technology exists and costs are reasonable. Since wastewater is already collected in society for a number of reasons (hygiene, nutrient removal), additional treatment provides an opportunity to remove a wide range of known and unknown contaminants from the system flowing from our society and reduce the chemical load to both the fresh water systems (including drinking water reservoirs) and the Baltic Sea. Compared to the slow process of regulating and phasing out individual chemicals, the treatment technology can be implemented relatively fast and will reduce emissions of a wide range of chemicals simultaneously. Removing a wide spectrum of contaminants also reduces the risk of combination effects in the aquatic systems, simply because loads of most compounds from the WWTPs are reduced. It is, however, difficult to estimate the total benefit of implementing advanced treatment since major pathways for all chemicals we use are difficult and costly to determine (e.g. it is very difficult to estimate the total load reduction to the Baltic Sea for chemicals with multiple pathways), and no-effect levels (in various chemical mixtures) are difficult to establish. This also means that the cost of inaction is difficult to estimate. Additional treatment can possibly be viewed as following the precautionary principle and may be **a good complement** to other actions as it is (relatively) unselective and effective compared to the single chemical approach. Beneficial side effects is a general improved wastewater quality with respect to pathogens and DOC. Implementing advanced treatment may also create a market for technical solutions

of this type, and could help the technology move forward, hopefully reduce costs and energy requirement, and also create work opportunities.

Because of difficulties of valuing the benefits of advanced treatment, there is a risk that this is an unnecessary action with small effect. Advanced treatment of wastewater will only have a significant impact on chemicals coming mainly via WWTPs, other routes are more important for many pollutants. It is not the final solution, and there is worry that this solution may discourage upstream control actions. The fundamental principle that the polluter should pay is not followed (and is hence something that should be elaborated on). Not all chemicals can be removed, and 100% removal is seen for very few compounds. Hence large chemical emissions to WWTPs can still result in large loads to the environment. Another disadvantage is the increased energy use which impacts climate if non-renewable energy sources are used. Maybe most important is the extra treatment costs in money and energy, resources that could be spent on other, perhaps more relevant, actions to reduce chemical pollution.

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