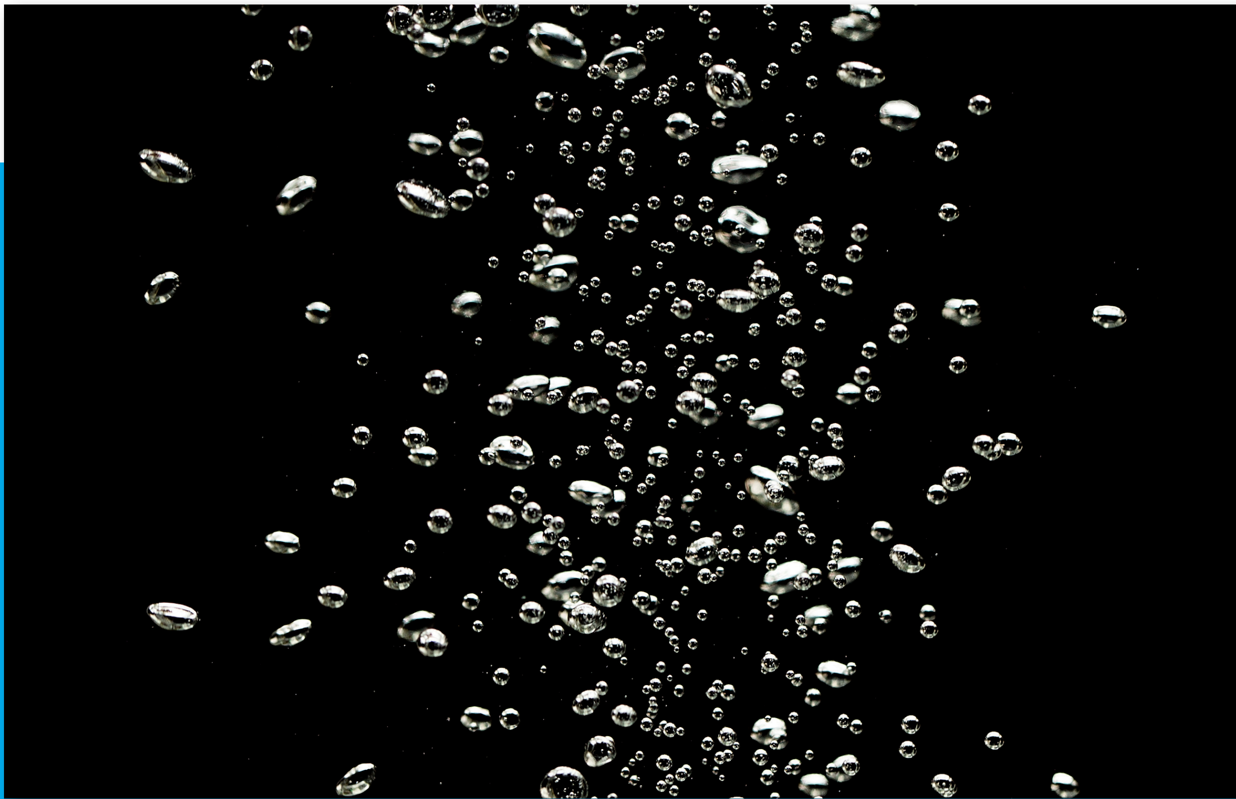
Large scale water treatment and the implications for the water cycle

Ozonation, waste water, advanced treatment, micropollutants



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1 Introduction

Next to our familiarity with all sorts of technology, we are also familiar to use of a large range of chemicals. This has clearly resulted in increased welfare and well-being but has also led to consequences. Complex mixtures of anthropogenic substances are now known to exist in the environment. While the compounds in production may be known or not, the environmental mixtures are often chemically and toxicologically poorly characterized. Legislation and companies are seeking ways to minimize the impact but despite these efforts, the number and concentration of chemicals in the environment is expected to rise in the near future. This is due to continuous development and production of new chemical substances by chemical industry (van Wezel et al. 2017a). Of particular interest in this paper is the suspected increase of emissions via industrial and domestic waste water. This increase may be a consequence of economic and population growth and/or demographic changes, while in addition, climate change is causing more extreme river discharges, with the possible result that low river discharges may lead to concentrated flow and higher compound concentrations. These developments are asking for measures to mitigate negative effects.

It is also clear that innovations in chemical analytics allow detection of a wider range of chemicals; these techniques may detect compounds down to ng/l and lower (Richardson and Ternes 2014). In previous years, studies on hormones and pharmaceuticals showed that wildlife can be affected even at these low concentrations (Guillette et al. 2000, Jobling et al. 1996, Tyler et al. 1998). Nowadays, a substantial body of evidence exists that compounds may have ecological and potential human effects, even at the low environmental concentrations. However, some researchers doubt whether these effects are detectable in the environment and advocate that monitoring of wildlife populations should be included in evaluating environmental protection strategies (Johnson and Sumpter 2016).

Due to these developments and increased awareness, emission sources of a diverse range of anthropogenic substances to the environment are gaining increased attention in legislation and public perception. Reduction of the emission of hazardous chemicals into the water cycle and prevention of human exposure to such substances via drinking water is nowadays part of the WHO Sustainable Development Goals (SDGs). Measures to reduce the concentrations of chemicals in the water cycle may be curative or preventive in nature and may differ in the time to yield results. For example, changes in legislation may be preventive and give results in the long term, while some technological interventions could have more short term results. For the latter, governments are mostly considering technological options (Eggen et al. 2014, Joss et al. 2008). In the Rhine basis in particular, treatment of effluent by the application of ozone is discussed as one option, based on the fact that is was considered cheap and effective (Eggen et al. 2014).

In light of the intended wide application of advanced treatment steps, there is a need for an overview of the available knowledge on existing regulations driving mitigation and monitoring efforts in the EU. Here, we focus on emerging compounds and their transformation products. More specifically, we explore potential consequences of applying ozonation as a technological intervention on a large scale. We discuss how this treatment upstream may have benefits but also drawbacks for the receiving areas downstream. From this overview, research questions are identified.

From priority substances to emerging compounds 2

Environmental monitoring and the subsequent awareness of the occurrence of a wide range of micropollutants is a main driver for regulation on chemical emissions and further monitoring. Currently, the production, emission and safe usage of chemicals is being regulated by different types of policies. More specifically, emissions to waters are controlled by waste regulations, agriculture rules and product directives. An overview of this framework is described before, while figure 1 is taken from this article (Munthe et al. 2017).

Besides this type of regulations that are focusing on the emissions, other types of regulation are more specifically aimed to safeguard the quality of waters. For example, WHO drinking water guidelines and the US Water Act contain several aspects of water quality issues, including safety thresholds and monitoring aspects. Directive 2010/75/EU of the European Parliament includes monitoring as part of the permits for industrial emissions. Next, also in Europe, the Water Framework Directive (WFD) and Drinking Water Directive (DWD) contain thresholds on safe concentrations for humans and the environment, while these regulations also prescribe monitoring of compounds in different waters.

In the Water Framwork Directive (2008/105/EC), environmental quality standards (EQS) were set for 33 priority substances (groups) to achieve a good chemical status of surface waters. These substances were selected as they pose a clear threat to the environment due to their intrinsic substance characteristics, as these were Persistent, Bioaccumulative and/or Toxic (PBT characteristics). Member States have agreed to implement measures to reduce or avoid substance emissions if these targets are exceeded. In 2013, these standards were adjusted and 12 other substances were included as new priority substances in Directive 2013/39/EC amending Directives 2000/60/EC and 2008/105/EC. In all, the focus is strongly on 'relevant pollutants' or groups of pollutants. A recent paper shows that mitigation options on the control of emissions to the environment can also start from the system perspective and not from compounds (van Wezel et al. 2017b).

However, while the current focus is still on substances, the focus is not only on 'priority compounds' but also on 'emerging compounds' or 'compounds of emerging concern' (Halden 2014). These compounds are either new on the market or their occurrence in the environment has been recently discovered. The reason to emerge is their harmfulness or that they are detected due to advances in analytical chemistry (Richardson and Ternes 2014). Yet, these compounds all lack a legal and policy framework for monitoring and/or emissions reduction measures. In the European NORMAN network of laboratories and knowledge institutes, two types of definitions were defined: emerging pollutants or emerging substances (www.norman.net). The NORMAN definitions imply that emerging pollutants may be regulated after some time, while emerging substances imply that information is not always leading to further concern and legislative action. It may be therefore better to use a term that includes the perspective of society, as 'compounds of emerging concern'. These may sometimes be abbreviated to CECs (Halden 2014).

Emerging pollutants - A substance currently not included in routine environmental monitoring programs and which may be candidate for future legislation due to its adverse effects and / or persistency.

Emerging substance - A substance that has been detected in the environment, but which is currently not included in routine monitoring programs and whose fate, behavior and (eco)toxicological effects are not well understood.

Source: www.norman-network.net

In the EU-WFD, monitoring is now implemented for some compounds of emerging concern: the 'watch list of substances' for European Union-wide monitoring is described in Directive 39/2013/EU and in the Decision 2015/495/EU. The list contains two pharmaceuticals (diclofenac and the synthetic hormone 17-alpha-ethinylestradiol (EE2)), two natural hormones (estrone (E1), and 17-betaestradiol (E2)), the macrolide antibiotics (azithromycin, clarithromycin and erythromycin), several pesticides (methiocarb, oxadiazon, imidacloprid, thiacloprid, thiamethoxam, clothianidin, acetamiprid and triallate), an UV filter (2-ethylhexyl-4-methoxycinnamate) and an antioxidant (2,6-di-tert-butyl-4-methylphenol) which is commonly used as food additive. Based on this list of compounds, monitoring data are now collected across Europe. In case pollution of the aquatic environment is confirmed across the whole of Europe, these substances may be added to the list of priority substances when these lists are reviewed and updated.

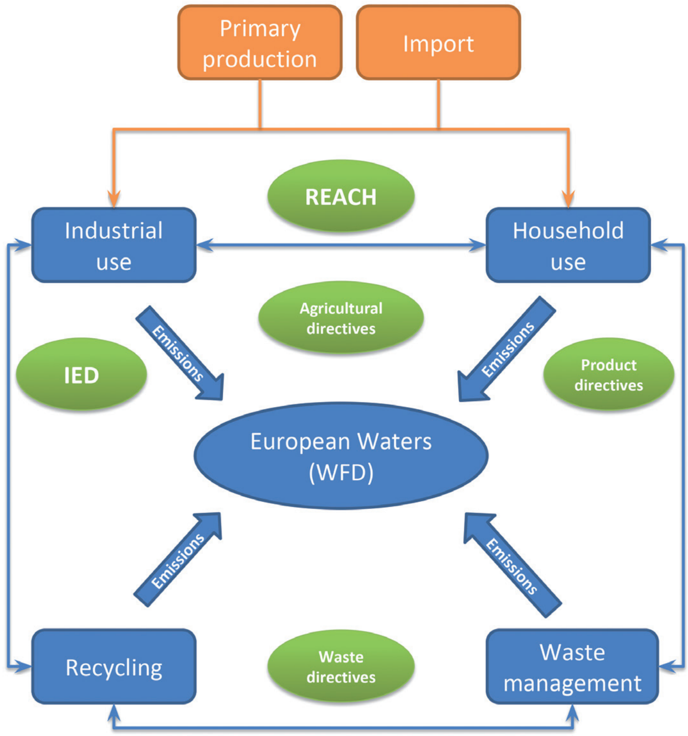

Figure 1: Schematic substance flow analysis for chemicals including examples of where policies interact in the system. From different use (blue coloured objects) of produced or imported chemicals (orange coloured objects) and the emissions generated to the receiving waters and were in this system different policies interacts (green coloured objects). IED Industrial emissions directive, Directive 2010/75/EU on industrial emissions; REACH Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), Regulation (EC) No 1907/2006. Reproduced from (Munthe et al. 2017), originally published in Environmental Sciences Europe by Springer publishers.

3 Reduction of micropollutants in the water cycle

Regulations and Green chemistry

While the legal frameworks develop and monitoring activities detect new compounds, solutions to reduce emissions of chemicals to the water cycle are asked for, e.g. by adopting green chemistry. The principle of green chemistry is based on the enhanced integration across disciplines – amongst which are toxicologists and chemists. Green chemistry may lead to compounds on the market that are less hazardous and/or easier to remove in the water treatment (van Wezel et al. 2017b). This process of the incorporation of new design principles on compounds may only give results in the long term. Indeed, existing regulations such as REACH has shown that no trend toward an elimination of chemicals with inherent environmentally hazardous properties is visible in the PBT characteristics of the new chemicals introduced to the market between 1982 and 2007 (Strempel et al. 2012).

Other strategies exist that may result on shorter terms, such as totally banning use of the most hazardous chemicals or strict control via emission permits of industry. Next, specific end-of pipe treatment solutions may be effective since a major source of chemicals in the water cycle is coming via waste water treatment systems, especially household chemicals, such as pharmaceuticals and biocides. For example, a European-wide monitoring study on the occurrence of micropollutants in 90 different waste water treatment effluents showed that 131 organic compounds were present in European wastewater effluents, in concentrations ranging from low nanograms to milligrams per liter (JRC 2012).

Technology to reduce micropollutants

In light of the impact of waste water treatment effluents on water quality, technological intervention in the (municipal) waste water system are investigated, including studies on costs efficiency and potential reduction of the emissions of substances (Eggen et al. 2014, Oulton et al. 2010). Also, water reuse concepts are asking for treatment of compounds in the waste stream to fuel new water usage, e.g. in farming (Dong et al. 2016). Next, researchers describe treatment options by focusing on the compounds on the monitoring list (Barbosa et al. 2016). Their conclusion is that treatment of waste waters using several technological options is decreasing the emissions. However, they also stated that knowledge is limited on the removal efficiencies in realistic settings since much of the work is based on small lab scale studies. Next, efficiencies of several treatment processes can decrease considerably when realistic water matrices are used instead of simulated ones.

Ozonation

In drinking water production, ozonation is mainly used for microbial removal and established for many years now. In waste water treatment, ozonation is not only used to disinfect the waters but also used to oxidize the compounds of emerging concern. The mechanism is based on the fact that ozone is a reactive molecule, an oxidizing agent. In general, ozone reacts with electron rich chemical structures such as double bonds while the efficiency strongly depends on pH, type and amount of organic matter, and other parameters (Von Gunten 2003, Wert et al. 2009).

Ozonation may affect a wide range of compounds and literature is full of examples, including de-colorization of dye-polluted waters (Khamparia and Jaspal 2017), oil fractions (Garoma et al. 2008, Huang et al. 2015, Shi et al. 2015) and studies on the degradation of micropollutants such as pesticides and pharmaceuticals (Eggen et al. 2014, Gomes et al. 2017, Joss et al. 2008). Examples of substances that are readily oxidized by ozonation are HHCB (musks) (Liu et al. 2012), bisphenol A (de Leon-Condes et al. 2017, Garoma et al. 2010a), diclofenac, carbamazepine, metoprolol and bezafibrate (Dantas et al. 2007, Hollender et al. 2009, Huber et al. 2005b, Klavarioti et al. 2009, Ternes et al. 2002, Ternes et al. 2003, Zimmermann et al. 2011). Next to that, the efficiency of ozonation towards antimicrobials is investigated, such as sulfamides (Feng et al. 2016, Garoma et al. 2010b, Homem and Santos 2011). Other compounds of interest are 1H-Benzotriazoles

(Alotaibi et al. 2015, Hollender et al. 2009, Stasinakis et al. 2013). Most recent, the attention is on the inactivation of both antibiotic resistant bacteria as resistance genes by ozone treatment (Czekalski et al. 2016, Sharma et al. 2016, Sousa et al. 2017). This overview shows that the outcome may vary and that removal efficiencies may be location and system specific. This is clearly showed by a recent study aimed to combine this with quantitative literature and experimental data, see figure below. Here, 12 xenobiotics in particular were selected to show removal efficiencies of parent compounds, including variation in a specific ozone dose range. Note that the kO3 is the second order rate constant for exposure to ozone, which is also regarded as the direct oxidation, while exposure to hydroxyl radicals is regarded as the indirect oxidation (k OH) (Mathon et al. 2017).

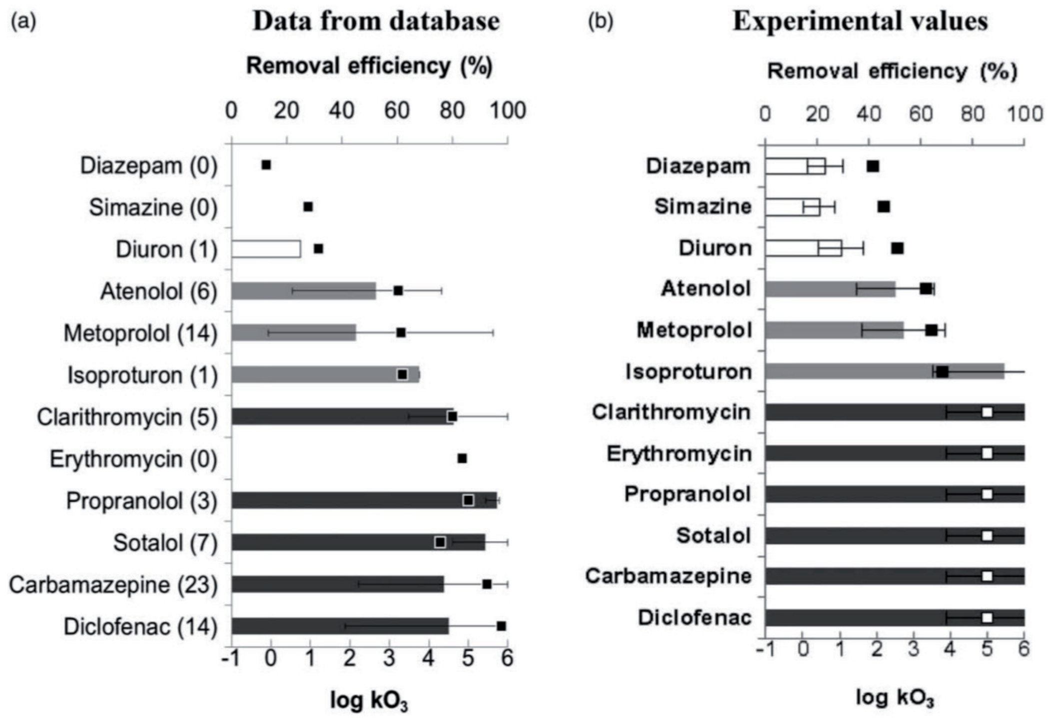

Figure 2: Removal efficiencies (bar) and kO3 (square) for 12 xenobiotics: (a) from the database (ozone dose between 0.2 and 0.4 gO3 gDOC–1), standard deviation with black line, number of data available in brackets; (b) from our experiments (one value measured with ozone dose: 0.2 gO3 gDOC–1), the error bars are determined as described in Choubert et al. (2012), full squares for accurately measured kO3, empty squares for the minimal estimate. The colors of the bars identify the three groups: low-oxidizable (white), medium-oxidizable (light gray) and high-oxidizable (dark gray) xenobiotics. Figure taken from (Mathon et al. 2017) in Water Science and Technology by IWA publishing.

Next, another example is a full-scale ozonation followed by sand filtration, in which a large group of compounds was studied and some 'generic' conclusions were presented. Most of the compounds with a double bond or an aromatic structure (e.g., phenol, alkyl, methoxy, or non-protonated amine) were susceptible to ozonation. Less susceptible were compounds with amide structures (Ahmed et al. 2010, Hollender et al. 2009). The combination of ozonation and sand filtration with activated sludge treatment gave reduction percentages above 80%. In contrast, X-ray contrast media, acidic pharmaceuticals, pesticides (atrazine), and the artificial sweetener sucralose are not fully transformed by ozonation (Huber et al. 2005a). Other classes of compounds may show similar varying removal efficiencies, e.g. also depending on ozone dosage. It should be noted here that the terminology of 'removal' is not accurate, since most of the technologies including ozonation compounds 'transform' rather than remove from the waters.

Transformation

4

Transformation products in waste water treatment plants

Although several pilots are developed in the Rhine catchments, the knowledge of the formation of transformation products in waste water treatment plants is quite limited compared to studies on drinking water production processes using similar techniques. While the intention is to lower the burden of contaminants of concern, the resulting transformation products may be harmful as well. In this respect, these compounds are called “disinfection by-products (DBPs)”. Drinking water companies use UV or ozone treatment and include activated carbon reduce transformation products before supplying tap water (WHO 2000). A review paper described several aspects of chemical and biological assessment options for several waste water treatment technologies and highlighted that “elimination is not mineralization” (Prasse et al. 2015). Another paper specifically highlights ozonation of waste water treatment (Lee and Von Gunten 2016). While several known transformation products exist, also largely unidentified compounds will be likely to occur (Hollender et al. 2009, Klavarioti et al. 2009) and their potential effects are subject of study (Hübner et al. 2015, Macova et al. 2010, Rahman et al. 2014, Ribeiro et al. 2015). Two well-known examples are described below, bromate and NDMA (see box).

Bromate

Among the products that may be formed, formation of bromate from bromine containing waters is of particular concern. During ozonation, the formation of bromate is based on a reaction with O3 and OH-radicals (Heeb et al. 2014, Richardson et al. 2007, Soltermann et al. 2016, Wert et al. 2007) (Gomes et al. 2017). Bromate formation is to be avoided as it has been classified as a potential carcinogen. The exact level of toxicity is still a matter of debate as bromate may be rapidly decomposed in stomach acid. In general, bromate formation depends upon the concentration of ozone used, the bromide ion concentration, pH and contact time. Bromide can be removed prior to ozonation, but that is expensive. Bromide concentration in sewage waters will therefore limit the dosage of ozone as formation of bromate is depending on the dosage. In addition, presence of bromate and intermediates may also lead to the formation of bromo-organic by-products, such as bromoform (Heeb et al. 2014, Von Gunten 2003). Concentrations in the low mg/L-range are described in the literature (Soltermann et al. 2016, Zimmermann et al. 2011). Swiss researchers have calculated that – even in the worst case – bromate concentrations in major Swiss rivers will increase by 0.35 µg/L for the Rhine at Basel and 0.27 µg/L for the Rhône at Geneva (Soltermann et al. 2016).

In the case of smaller waterbodies, however, increased bromate levels could pose problems for drinking water use. In the Netherlands, bromide concentrations the river Rhine range between 90 and 320 µg/l (RIWA Rijn Rapport, 2015). Not many data are available on effluent from Dutch sewage treatment plants, as normally would be available via the Dutch Watson database. Here, values were reported for the year 2008 as high as 280 µg/L (RWZI Leiden Zuid-West, The Netherlands) [Watson online database, accessed June 2017]. In more recent studies, the influent concentration of bromide appeared to be 50 µg/L at Panheel (Hofman-Caris et al. 2016), while effluent in Tilburg contains 50-150 µg/L, in Eindhoven 90-150 µg/L, and in Leiden <10 µg/L(STOWA 2015).

Halonitroalkanes, halonitriles, haloamides, and N-nitrosamine (NDMA)

Other compounds that may be relevant transformation products are the halonitroalkanes, halonitriles, haloamides, and N-nitrosamine (NDMA), as their formation is associated with several techniques including ozone and others such as chlorine dioxide, UV, chloride and chloramine disinfection (Shah and Mitch 2012). N-nitrosodimethylamine (NDMA) is a strong carcinogen. Several ‘mother compounds’ (precursors) have been correlated to form NDMA during ozonation, such as pharmaceuticals, amine-based polymers and NOM (Gerrity et al. 2015, Leavey-Roback et al. 2016, Mitch et al. 2003, Najm and Trussell 2001, Schmidt and Brauch 2008, Sgroi et al. 2016, Sgroi et al. 2015, Shah et al. 2012).

Toxicity

Effluent quality is improved considering several studies on ozonation of sewage waters. An overview by Prasse et al., 2015 describes several cases in which ozonation decreased the biological activity of toxicants, such as >90% removal of estrogenic activity (Escher et al. 2009), (Stalter et al. 2010a, Stalter et al. 2013, Stalter et al. 2011). A genotoxicity removal of 80 to 98% was shown by (Magdeburg et al. 2012, Reungoat et al. 2010). Furthermore, anti-androgenicity and aryl-hydrocarbon receptor (AhR) agonistic activity is reduced by 96% (Stalter et al. 2011). Studies on receiving waters showed that macroinvertebrate abundance data was showing significant improvement after installing an upgraded municipal wastewater treatment plant (WWTP) with full-scale ozonation, followed by sand filtration (Ashauer 2016). Also, studies on the ecosystem functions in receiving water showed improvements using in situ bioassays with Gammarus fossarum (Bundschuh et al. 2011).

On the other side, the paper of Prasse et al. (Prasse et al. 2015) also highlights that transformation products of compounds may increase toxicity in bioassays and that these should get attention. For example, studies using standardized organism tests, Vibrio fischeri and Daphnia magna showed that transformation products of clofibric acid and monochlorophenols significantly increased toxicity resulting from exposing compounds to ozonation (Rosal et al. 2009, Shang et al. 2006). Other studies found that the oxidized products of clofibric acid, propranolol, acyclovir, and metoprolol were showing more (eco)toxicity effects than the parent compound (Dantas et al. 2007, Prasse et al. 2012, Rosal et al. 2009, oji et al. 2012) or that ozone may contribute to effects (Bertanza et al. 2013, Park et al. 2016). Several papers describe the human and ecological risks of the formation of substances under the influence of ozone treatment, while most attention is on the potential ecological effects, e.g. (Fatta-Kassinos et al. 2011, Loeb 2011, Macova et al. 2010, Magdeburg et al. 2014, Mohapatra et al. 2014, Prasse et al. 2015, Ribeiro et al. 2015, Stalter et al. 2010b, Umar et al. 2015, Verlicchi et al. 2015a, Vom Eyser et al. 2013).

Persistence

So, while toxicity can be decreased or increased, little is known about the biodegradability of individual transformation products resulting from ozonation ((Hübner et al. 2015), see also figure 3). Based on their review of studies and an evaluation of the biodegradability of transformation products with the biodegradability probability program (BIOWIN) and the University of Minnesota Pathway Prediction System (UMPPS), they have shown that transformation products may not necessarily be better removed in biological posttreatment. Ozonation of olefinic compounds (alkenes) seems to lead to degradable products, while ozonation of amines may lead to less degradable compounds than parent amines. For aromatic compounds, diverse reactions are predicted and observed. However, these estimations using calculations may not be accurate enough. Yet, formation of persistent transformation products is of particular interest in view of water cycles and treatment options and drinking water production downstream of ozonation plants.

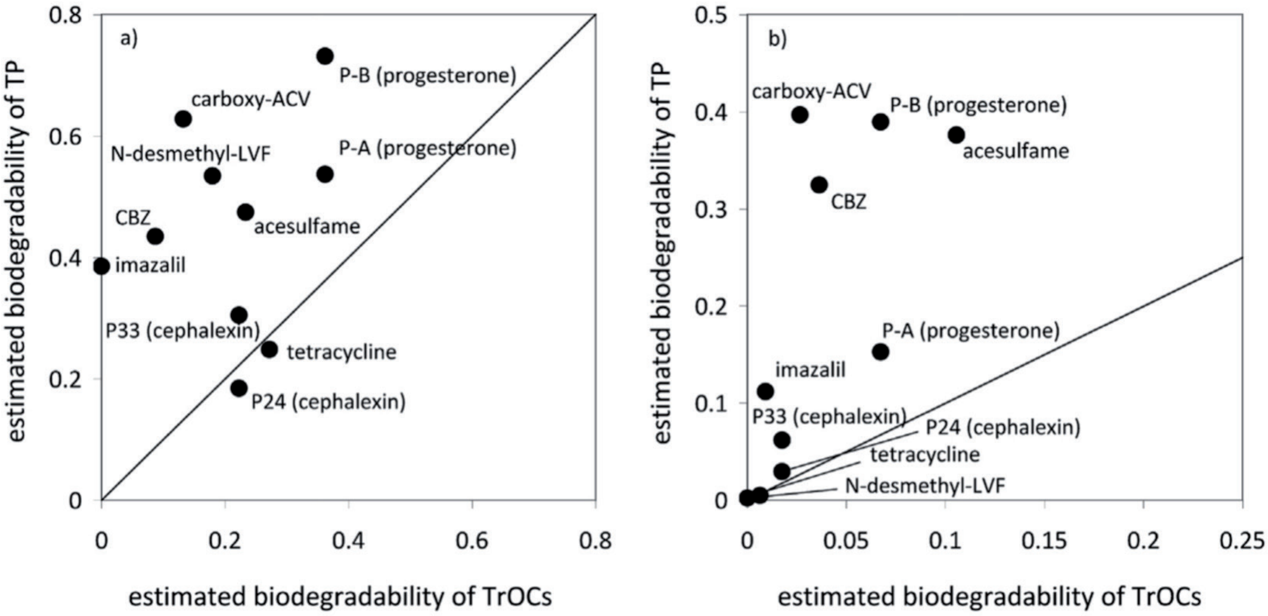

Figure 3: Assessment of the biodegradation of transformation products in comparison to parent compounds as taken from article (Hübner et al. 2015) as published in Water Research by Elsevier. Assessment of the biodegradation of olefinic trace organic compounds (TrOCs): using (a) the linear MITI model and (b) the non-linear MITI model from BIOWIN (predicted probability of biodegradation in the range of 0 (persistent) to 1 (readily biodegradable).

Post treatment

The reactive products in effluent from installation may be prevented from reaching the receiving waters . Sand filtration or activated carbon treatment is usually implemented after ozonation (Ahn et al. 2015, Magdeburg et al. 2014, Prasse et al. 2015). Sand filtration is capable of blocking most products (Hollender et al. 2009, Nakada et al. 2007). However, as described above, persistent pollutants may remain, and not fully removed by this step. Examples of sand filtration as post-treatment options showed that aldehyde concentrations and NDMA removal was measured (Schmidt and Brauch 2008, Wang and Summers 1996). Biologically active activated carbon filters or membrane bioreactors can also act as efficient barriers for oxidation by-product removal.

Drinking water companies use, for example, activated carbon after UV or ozone treatment to remove transformation products of advanced oxidation processes (also referred to as disinfection byproducts) before supplying tap water (WHO 2000) (Macova et al. 2010) Ozonation as an effective treatment step is also included in the Dutch Pharmafilter® concept, using a MBR pre-treatment and GAC post ozone treatment of hospital effluents (Verlicchi et al. 2015b). It was also shown that biological activated carbon treatment prior and post ozonation did not result in increased DOC removal (Reungoat et al. 2011). This can most likely be attributed to the low molecular weight and high polarity of many OPs, which are formed as ozonation significantly shifts the molecular size distribution to smaller sizes (Wang et al. 2008).

5

The Rhine catchment and technological interventions

Already during some years now, improvements on reducing known priority compounds have been made in reducing chemical emission in the Rhine and reports show subsequent biodiversity restoration, e.g. reflected by the international committee for the Rhine. Part of these efforts were the installation of sewage treatment plants, reducing the inflow of untreated waste water into the river Rhine. Nowadays, over 5000 treatment plants exist in the Rhine catchment area. These plants treat over 96% of the households of the about 58 million in habitants connected to municipal waste water treatment plants (www.iksr.org). The total treatment capacity of these wastewater treatment plants is about 100 million inhabitant equivalents. These plants treat wastewater not only from households but also partly from industries. About half of the total amount of waste water of the Rhine catchment is treated in wastewater treatment plants with a capacity beyond 100,000 inhabitant equivalents (less than 4% of all 5,000 treatment plants). As described below, several communal waste water treatment plants are currently being upgraded or are planned to be upgraded, including the installation of ozonation to further reduce the emissions of compounds, including compounds of emerging concern. Some developments in Switzerland, Germany and the Netherlands are described, while information from Luxembourg, Belgium and France is not included in this overview.

Switzerland

To start upstream in the Rhine catchment, Switzerland has decided that circa 100 sewage plants of the total 700 will be upgraded, treating about 50–60% of the Swiss wastewater released to sensitive surface waters. In Switzerland, a Water Protection Act has been in force since January 2016, basically a law on compounds of emerging concern. The law describes that 80% of the micropollutants will be removed from sewage. The energy consumption is expected to increase by 5–30% in a WWTP, and nationally by 0.1% (Eggen et al. 2014). The increase in costs for wastewater treatment due to this law has been estimated at 130 million US$ per year, which is equal to about 10–15% of the current costs of wastewater treatment (15 US$ per capita per year). The upgrading of the treatment plants is realized by a tax based on the polluter-pays principle, in effect until 2040. Every sewage treatment plant pays 9 Swiss francs per connected resident to the federal government. The tax finances 75 per cent of this investment. In case the plant is upgraded with the additional purification stage and it meets the treatment requirements, it is exempted from the tax. For the treatment requirements, a list of indicator compounds is developed, including easy removable compounds and more resistant ones.

In these plans, additional treatment steps have been proposed, and most focus lies on the use of (advanced) oxidation processes - (A)OPs - and/or in combination with Granular Activated Carbon (GAC) (Eggen et al. 2014, Margot et al. 2013). The Neugut wastewater treatment plant is considered to have a pioneering role in Swiss water protection efforts (www.neugut.ch). After this installation, other facilities are being upgraded on a short term. Other systems will make use of ozone, while some may include powered coal systems only and no ozone. The Neugut facility (150,000 population equivalents) has a full-scale ozonation installation and discharges into the Glatt river, discharging into the Rhine.

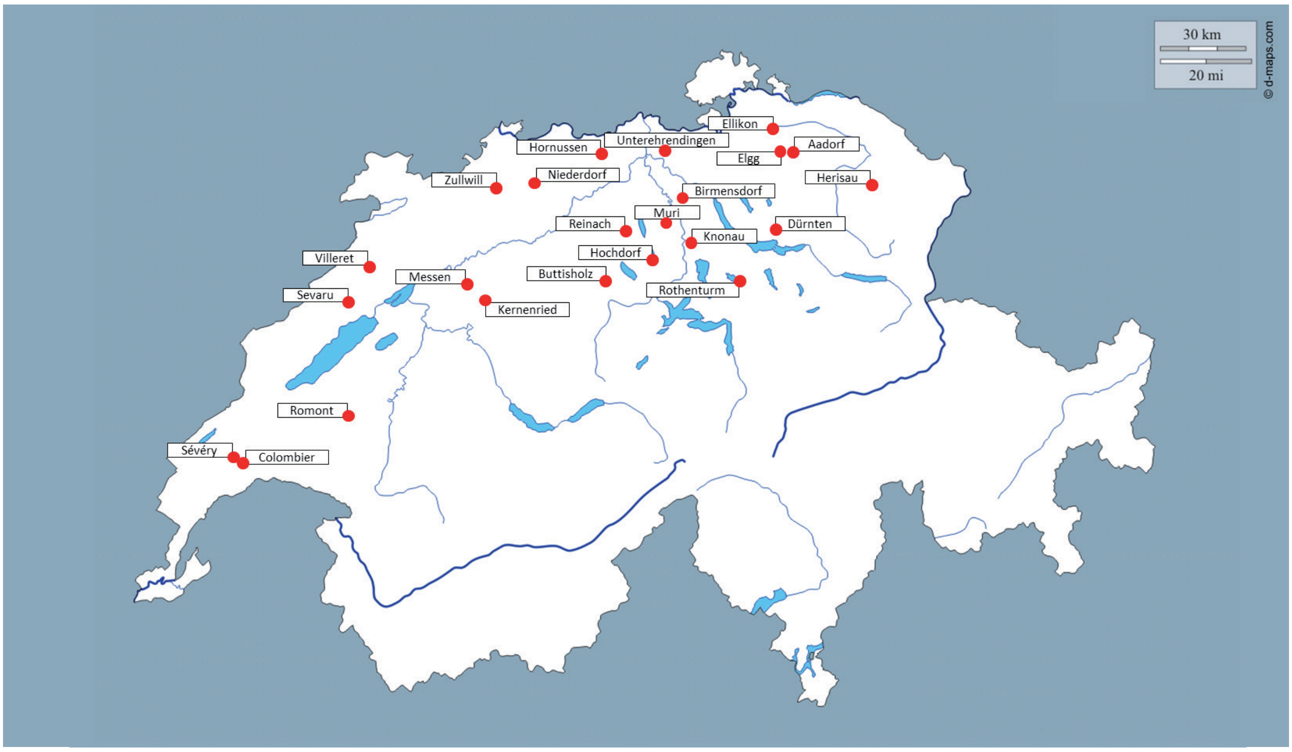

Figure 4: Sewage treatment plants studied in the ECOIMPACT project, Switzerland. Reproduced from http://www.eawag.ch/en/research/water-for-ecosystem/pollutants/ecoimpact/

Germany

Germany will also perform an upgrading of several treatment plants. A good example of a large-scale project is the waste water treatment installation at Duisburg-Vierlinden. Some other projects started in the federal states of Nordrhein-Westfalen (North Rhine-Westphalia) and Baden-Württemberg.

"Um unsere Gewässer aktiv zu schützen, bedarf es eines Multibarrierenschutzes, angefangen bei den Quellen, über die Kläranlagen bis hin zu den Wasserwerken", erklärte Umweltminister Johannes Remmel zur Veröffentlichung des Fortsetzungsberichts Reine Ruhr.

A full-scale municipal ozonation plant without research purposes in Germany started operation in November 2016 at the city of Warburg (40,000 PE) and three others will follow. In Nordrhein-Westfalen (NRW), the strategy is laid out in the "Program Reine Ruhr", part of the Rhine basin. Following that strategy, the elimination of compounds in the water is tackled at the source, the sewage treatment plants and the drinking water production installations. Next, in this project, ozonation is investigated as one of the barriers to reduce the chemical emissions to the environment. In several regions, financial incentives are given to invest in advanced treatment installations. Yet, no specific treatment requirements are established yet. Currently in NRW alone, at least 28 installations are in progress of being upgraded with 6 plants already in use (Figure 5). Next to that over 100 plants are being studied (see the current status at www.masterplan-wasser.nrw.de).

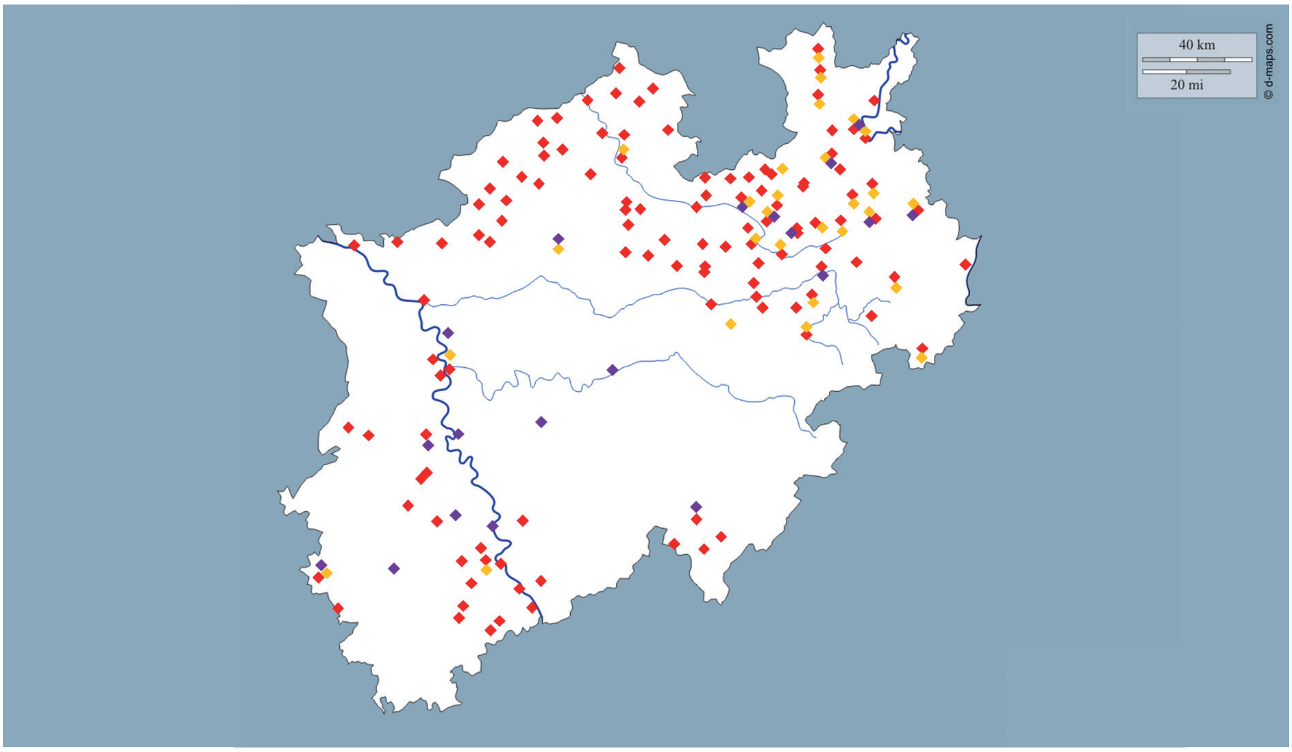

Figure 5: Water treatment installations subject to the Masterplan Wasser in Nordrhein-Westfalen, Germany. Status as of May 2017, reproduced from http://www.masterplan-wasser.nrw.de

The Netherlands

In the Netherlands, the discussion on upgrading sewage treatment plants is going on for some time. Some argue that the effects of chemicals on the environment would not justify the costs of implementing new treatment options, while others state that the contribution of bordering countries to the emission of chemicals may outweigh that of the Netherlands. A recent study on the emissions of pharmaceuticals have indicated that emission do come from Rhine and Meuse bordering countries upstream. However, also the emission via the Dutch sewage treatment plants contributes significantly (Coppens et al. 2015). The foreseen upgrading of several plants in the bordering countries may shift the contribution towards a higher influence of Dutch treatment plants.

Ahead of these discussions, water boards already investigate options to reduce emissions of micropollutants by using technology. In the Dutch study report, three treatment options were described for which large scale installations exist to treat waste water. Here, ozonation, Powdered Activated Carbon (PAC) dosage and Granular Activated Carbon (GAC) filtration were evaluated (STOWA 2015). Ozonation with sand filtration was seen as the cheapest option in this study. In the Dutch PACAS project, dosing of powered active coal to conventional active sludge systems is investigated (www. stowa.nl). Here, the study monitors a list of indicator substances to assess the performance of emission reduction.

Only few water authorities in the Netherlands seem to consider ozone treatment technology. Currently, one water board (Hoogheemraadschap Delfland) is performing such a pilot installation under the name “Waterfabriek Groote Lucht”. The installation uses ozone to treat water after which sand or carbon filtration is used before a polishing step in an ecological zone, as described in an article as a ‘waterharmonica’ (Llorens et al. 2009).

The formation of toxic transformation products during ozonation is described in the STOWA study from 2015 to be a 'topic of discussion' and it refers to studies in Germany and Switzerland (STOWA 2015). It states that in these countries, it is advised to implement a filtration step after ozonation by using sand filtration or active carbon, to remove any biodegradable transformation products formed during ozonation. Moreover, the Dutch study shows that knowledge is limited to whether sand filtration after ozonation is sufficiently adequate to remove the potential transformation products entering the environment. "This should be further researched for the Dutch situation", this study states. Hence, the monitoring of the pilot scale study at the pilot scale study in Delfland focuses on a similar list of indicator substances as the PACAS study (personal communication, Hoogheemraadschap Delfland). These substances should give information on the reduction efficiencies in different configuration settings and/or treatment technology. Next, the assessment of the efficacy using bioassays is foreseen, aimed at answering whether biological effects of effluents is reduced or that biological effects may be increased by the treatment. Other water boards were still planning studies at the time of writing the report, so a comprehensive list is not available.

6

Discussion on implications for technology and research

While the “benefits” from ozone treatment are promoted “as a cost-effective measure to reduce micropollutants in the water” (Eggen et al. 2014), the decision for upgrading of waste water treatment in Switzerland was criticized by other researchers (Johnson and Sumpter 2015). Arguments from these researchers was that too little evidence is available to justify spending public money. As a reaction, Swiss researchers replied by stating that enough evidence was gathered on removal efficiencies, costs, energy demand and the feasibility of implementing the recommended technologies at existing waste water treatment plants (Stamm et al. 2015). They further argue that parallel studies have been or are being performed in other countries like Germany and France, confirming results on the removal efficiencies. Next, they described that in the direct democracy system in Switzerland, decisions were made after consultation with relevant stakeholders (authorities, industry, professionals in the field, fishermen, environmental NGOs, etc.) (Stamm et al. 2015). In this scientific discussion, the formation of by-products, post treatment options and its implications for research and policy is not a prominent discussion point. A range of studies do underline the need for post-treatment installations, such as sand filters or GAC filtration, as they seem to be enhance the reduction efficiencies due to the sorption of formed transformation productions to the activated carbon (Knopp et al. 2016). However, no clear statement by authorities is yet given whether these are necessary or mandatory. Some scientific studies describe the “need for post-treatment”; some “recommend” post treatment, see e.g. (Hollender et al. 2009) . Others state more strongly that ozonation should only be established in combination with a bioactive post treatment such as sand filtration, e.g. (Prasse et al. 2015).

In a Dutch overview report, it was described that post-treatment should be chosen as a precautionary measure, since no clear conclusion is available on the nature of transformation products and/or toxicity of ozonated waters (STOWA 2015). Sand filtration is most often chosen in Germany and Switzerland (references in (STOWA 2015)). The configuration of these systems is comparable to existing Dutch systems, as stated in the STOWA report.

Assessment on the upgrading of sewage treatment plants

In addition, a recent pragmatic approach is proposed to include in the decision making process for upgrading of waste water treatment systems, based on laboratory studies and field work (Schindler Wildhaber et al. 2015), see figure 4. The assessment of four parameters is proposed: the matrix effects on ozone stability, the efficiency of micropollutant elimination, the formation of oxidation by-product (bromate and N-nitrosodimethylamine) and bioassays to measure specific and unspecific toxicity of the treated wastewater. If criteria are not fulfilled, activated carbon may be the better choice. So, by using a range of techniques (chemistry, bioassays), a well-informed decision can be made on the potential by-effects, these authors state. However, the approach may be laborious. The question arises whether in-depth research is needed for each sewage treatment or that generic conclusions may be drawn after a nation-wide research. The latter seems feasible since waste waters may not vary that much in chemical composition. Regular monitoring may be included to check after upgrading for unwanted effects.

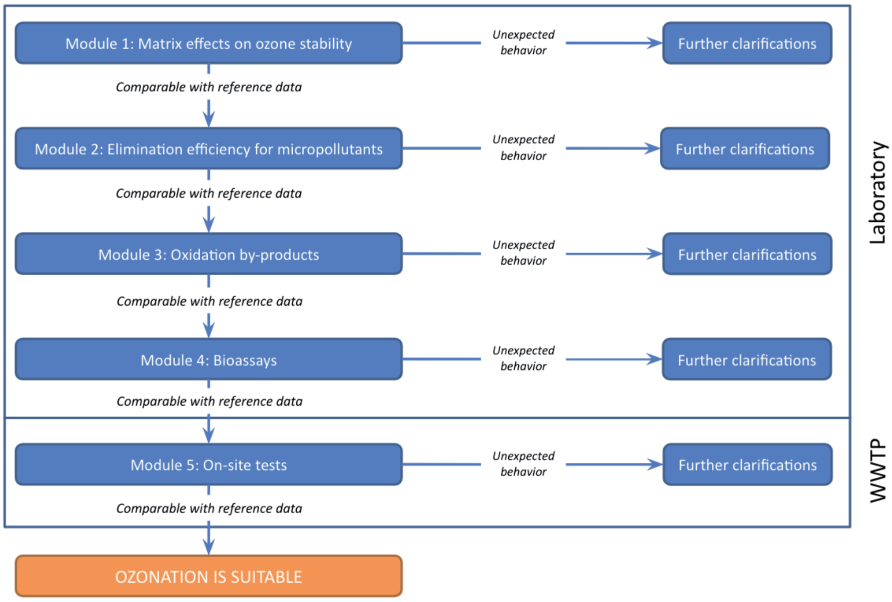

Figure 6: Approach to include in the decision for upgrading of waste water treatment systems, based on laboratory studies and field work. Reproduced from Schindler Wildhaber et al. (2015), originally published in Water Research by Elsevier.

Assessment tools and aspects of concern

The approach in Figure 6 was developed to aid decision making but raised some questions on the implications for the tools and information needed in this flow diagram. Again, the focus is on the “elimination” of certain indicator compounds, with less focus on the transformation products. Next, bioassays and chemical methods are needed to assess the water quality. However, questions were raised whether these bioassays (ecotoxicological perspective) and chemical analyses (the chemical perspective) are suitable to study the transformation products of ozonation (Prasse et al. 2015).

Biological and toxicological assessment

In a study using bioassays, it was observed that aqueous samples showed higher anti-estrogenic and reproductive toxicity than extracted samples, indicating that the causative compounds are not extractable or were lost during extraction (Giebner et al. 2016). So, it is evident that sample enrichment methods and bioassays should be carefully selected to avoid false-negative results (Prasse et al. 2015). From several papers, it can be learned that increase in toxic potential after ozonation is most probably the result of introduction of a nonspecific reactive MoA. It was advocated to especially use reactive toxicity assays, in particular the Ames assay for an effect-directed identification of mutagenic ozonation by-products (Magdeburg et al. 2014), similar as shown by research on other AOP techniques such as UV and ozone (Brack 2003, Fatta-Kassinos et al. 2011, Heringa et al. 2011, Kolkman et al. 2013, Spira et al. 2013, Vughs et al. 2016). This all underlines the importance of using toxicity assays covering several reactive toxicity endpoints is essential or showing an integrated (whole organism) response. For example, in the study by Prasse, the bioluminescence inhibition assay using the marine bacteria Vibrio fischeri and the fresh water cladoceran Daphnia magna is described (Petala et al. 2006) (Rosal et al. 2009). Daphnia may be less susceptible than Vibrio fisheri (Petala et al. 2006). In Stalter et al. (Stalter et al. 2010b) and Magdeburg et al. (Magdeburg et al. 2012), the fish early life stage test (FELST) using rainbow trout showed effects after ozonation of waste water. Next, genotoxicity is a well-investigated aspect of disinfection by-products. For example, genotoxicity was detected with the comet assay (Stalter et al. 2010a) and rainbow trout (Magdeburg et al. 2014) after application of ozonation and not before. Prasse et al. (2015) gives a further overview of several assays and responses and not only adverse effects, also a reduction in toxicity after ozonation is reported here (Prasse et al. 2015).

Next to that, identification of the causes of (increased) toxicity after ozone treatment by using EDA (Effect Directed Analysis) is valuable tool fueling research with options to control these potential harmful transformation products entering the environment (Brack 2003, Prasse et al. 2015). An important approach in Effect Directed Analysis is the fractionation of effluent (extracts) and test for toxicity. The fraction with the effect is then analyzed further to identify the compounds that show effects. Nevertheless, also in these applications, advances in chemistry are needed to analyze transformation products.

Chemical analytical tools

Existing models allow for the estimation of removal efficiencies but not for the formation of transformation products (Prasse et al. 2015). Expectations are large on the application of non-target analysis, also to help to identify unknown sources and compounds, e.g. (Ruff et al. 2015; Schlüsener et al 2016). Yet, these advanced analytical techniques also depend on sample pre-treatment technology. Solid Phase Extraction (SPE) is most often used as sample pretreatment, aimed to increase sensitivities. However, polarities of most organic pollutants result in substantially low affinity for SPE sorbents. Prasse et al (2015) compared DOC fractions retained on SPE materials with significantly lower DOC fractions absorbed in ozone treated wastewater samples, even if activated carbon is used as sorbent (see figure 7). Therefore, the development of extraction procedures is needed. Alternative (chromatographic) separation methods such as HILIC is crucial. Chemically, the challenges lie in the polar region, as described recently by e.g. (Reemtsma et al. 2006)). addressing the occurrence of PMOCs: polar mobile organic compounds. Yet, identifying compounds is not a solution, as the currently observed compounds may not be present in the future, so post treatment is to be advised.

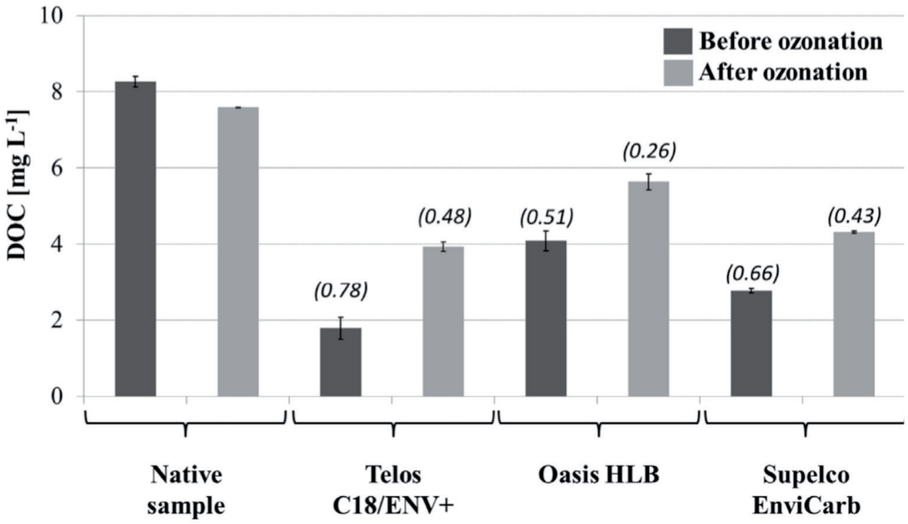

Figure 7: DOC fractions in ozone treated waste water adsorbed on SPE material. Graph taken from Prasse et al (2015), originally published in Water Research by Elsevier.

7 Conclusion

As described in this and other reviews, researchers have proven that ozonation is successful in reducing most organic micropollutants, including many compounds of emerging concern, e.g. (Gomes et al. 2017). Yet, ozonation does not eliminate chemicals complete but creates transformation products. As these products may cause adverse effects, effective measures should be taken to identify, characterize and avoid the emissions of harmful and persistent transformation products. From this review, it became also clear that a pragmatic, yet quite laborious, approach can be followed in choosing whether not to upgrade by using ozone (Schindler Wildhaber et al. 2015). In some circumstances it is yet very difficult to reduce the formation of by-products, especially when identification and risk assessment are lacking. For example, options to reduce bromate formation exist, but they are not straightforward and have sometimes little efficiency (Soltermann et al. 2016), especially in sewage waters compared to surface and drinking water.

Challenges for drinking water suppliers

Upgrading of sewage treatment plants is currently in progress in the Rhine catchment. Drinking water companies are abstracting water from this river. They, in a sense, 'reuse' the treated water for drinking water. The foreseen large scale upgrading of sewage treatment plants may reduce micropollutants entering the waters. However, the formation of transformation products may also lead to unknown and yet not easy detectable and removable compounds, including persistent and mobile compounds. In all, these developments may lead to new challenges in future drinking water production.

Chemically, the challenges lie in analysis of the transformation products, mostly highly polar substances. Recently, researchers have addressed these compounds as PMOCs: polar mobile organic compounds (Reemtsma et al. 2006). Toxicologically, there is a clear need for selection of adequate bioanalytical tools to assess the effect of ozonation on biological activity and the potential health effects of transformation products (Prasse et al. 2015). Technically, the challenges are that the formation of transformation products is not yet fully understood and cannot be predicted with accuracy (e.g. (Hübner et al. 2015)). Yet, no literature highlights the fact that large scale treatment with ozone upstream may have implications on the abstraction of water for drinking water production downstream. The latter asks for specific studies on that matter, next to the necessary developments in chemical and toxicological tools.

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