Environmental Science
Water Research & Technology

PAPER

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Cite this: *Environ. Sci.: Water Res. Technol.*, 2019, **5**, 1709

Surface water treatment by UV/H_2O_2 with subsequent soil aquifer treatment: impact on micropollutants, dissolved organic matter and biological activity†

Robin Wünsch,[ab] Julia Plattner,[c] David Cayon,[a] Fabienne Eugster,‡[c] Jens Gebhardt,[d] Richard Wülser,[c] Urs von Gunten[be] and Thomas Wintgens*[a]

Received 28th June 2019,
Accepted 14th August 2019

DOI: 10.1039/c9ew00547a

rsc.li/es-water

Because organic micropollutants (MP) are frequently detected in river waters that are used as drinking water sources, combining a relatively cost-efficient natural treatment with upstream advanced oxidation processes (AOP) appears promising for their efficient abatement. Such a multi-barrier system can be integrated in drinking water production schemes to minimize risks from potentially hazardous MPs. This study investigates the impact of an UV/H_2O_2 AOP before soil aquifer treatment (SAT) on the abatement of selected MPs (EDTA, acesulfame, iopamidol, iomeprol, metformin, 1*H*-benzotriazole, iopromide), dissolved organic matter (DOM) (apparent molecular size distribution, specific UV absorbance at 254 nm – SUVA) and microbial parameters (intact cell count, cell-bound ATP). A pilot plant consisting of an AOP (0.5 m^3 h^{-1}, 4 mg L^{-1} H_2O_2, 6000 J m^{-2}) and two parallel soil columns (filtration velocity: 1 m d^{-1}, column height: 1 m) was continuously operated over a period of 15 months with Rhine river water pre-treated with rapid sand filtration. The investigations revealed a shift towards longer retention times of the humic substances peak in LC analysis of DOM, lower SUVA and higher biodegradability of DOM after UV/H_2O_2 treatment. In addition, an overall higher abatement of all investigated MPs by the combined treatment was observed (AOP with subsequent SAT) compared to either process alone. This observation could be explained by an addition of the single treatment effects. The strong primary disinfection effect of the AOP was detectable along the first meter of infiltration, but did not lead to any change in the column performance (*i.e.*, similar abatement of dissolved organic matter).

Water impact

Drinking water resources around the world are polluted with organic micropollutants, having potential adverse effects on human health upon long-term ingestion. This study demonstrates that these substances can be abated in a multi-barrier treatment, deploying an UV/H_2O_2 oxidation process with subsequent soil aquifer treatment. Combining such engineered ("grey") and nature-based ("green") treatment infrastructures can provide drinking water of high quality.

Introduction

Synthetic organic micropollutants (MP), such as residuals from pharmaceuticals, pesticides or personal care products, are frequently detected in surface water and groundwater.[1–4] These substances should be prevented from entering in the environment in the first place and kept as low as possible in drinking water (if necessary by treatment) to avoid adverse health effects (considering also the precautionary principle[5] and consumer perception[6]). Resource protection and control are the most important measures to avoid persistent substances entering in the aquatic environment.[7–11] This includes managing the disposal of MPs as much as possible,

[a] *FHNW University of Applied Sciences and Arts Northwestern Switzerland, School of Life Sciences, Institute for Ecopreneurship, Hofackerstr. 30, 4132 Muttenz, Switzerland. E-mail: thomas.wintgens@fhnw.ch*
[b] *School of Architecture, Civil and Environmental Engineering (ENAC), Ecole Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland*
[c] *IWB (Industrielle Werke Basel), Margarethenstrasse 40, 4002 Basel, Switzerland*
[d] *Xylem Services GmbH, Boschstraße 4, 32051 Herford, Germany*
[e] *Eawag, Swiss Federal Institute of Aquatic Science and Technology, Überlandstrasse 133, 8600 Dübendorf, Switzerland*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ew00547a

‡ Present address: F. Hoffmann-La Roche AG, Sicherheit, Gesundheits- und Umweltschutz, Grenzacherstrasse 124, 4070 Basel.

e.g., by collection and proper treatment of contaminated waste streams. Nevertheless, MPs are detected in surface water and groundwater bodies,[1–4] as conventional wastewater treatment plants cannot sufficiently address some of these target substances.[12,13] Additionally, diffuse sources contribute to the prevalence of MPs in water bodies.[14,15]

One efficient technology to abate MPs during the drinking water production is the application of low pressure (LP) ultraviolet light (UV)-based advanced oxidation processes (AOPs).[16–19] UV/H_2O_2 processes abate MPs typically by two parallel mechanisms, *i.e.*, direct photolysis and reactions with hydroxyl ($^{\cdot}OH$) radicals.[19]

For direct photolysis, in a first step, the target molecule has to absorb the emitted light.[19,20] The ability to absorb light of a specific wavelength (λ) is expressed in the molar absorption coefficient (ε_λ). In a second step, the energy taken up by a molecule through the absorbed light can partly result in a photochemical change of the molecule, *e.g.*, breaking of covalent bonds, abstraction of an electron, *etc.* The fraction of photons that lead to a transformation of the MP is the quantum yield (Φ_λ).[19,20]

In the UV/H_2O_2 process, $^{\cdot}OH$ radicals are produced by photolysis of hydrogen peroxide:

$$H_2O_2 + h\nu \rightarrow 2\,{}^{\cdot}OH$$

At 254 nm (λ at which LP-UV lamps primarily radiate), ε_{254} of H_2O_2 is ~18.6–19.2 M^{-1} cm^{-1},[19,21] and Φ_{254} is 1.0.[19] $^{\cdot}OH$ radicals react almost diffusion controlled with a large spectrum of MPs.[19]

However, UV/H_2O_2 oxidation processes usually do not lead to a full mineralization of the MPs. Instead, potentially toxic transformation products (TP) can be formed.[22] In addition, the dissolved organic matter (DOM) is transformed to products, which are partially bioavailable,[16,17,23,24] and an increased formation potential for disinfection by-products upon post-chlorination was observed.[16,24] Therefore, AOP treated water should be biologically treated before its distribution.[22,25]

Soil aquifer treatment (SAT) systems are applied in integrated water management systems for the removal of dissolved organic carbon (DOC) and pathogens,[26,27] but MPs have also been demonstrated to be partially degraded during SAT.[27–31] Yet during SAT, full mineralization of MPs is often not accomplished and (partly stable) metabolites are formed. Approaches to combine technical and natural treatment systems are considered highly useful, *e.g.*, by the UNESCO to ensure good water quality and robust treatment systems at reasonable costs.[32] Ozonation and AOPs before natural and/or technical biological treatment systems have been considered in many previous studies,[17,22,24,29,33–48] However, currently predominantly in the fields of enhanced wastewater treatment[34,38,39,48] or indirect potable reuse schemes.[39,43,49] Nevertheless, implementations of treatment schemes combining technical and natural treatment systems in full-scale are still scarce, especially for drinking water production from conventional water sources, *i.e.*, surface water or groundwater.

In a previous study the combination of H_2O_2, O_3 and UV was investigated to treat river water after coagulation, flocculation, sedimentation, micro-sieving and dual media filtration before dune infiltration for an improved abatement of MPs.[35,50–54] In comparative pilot tests with different treatment combinations (O_3, UV/H_2O_2, UV/O_3 and O_3/H_2O_2), all investigated MPs except methyl *tert*-butyl ether (MTBE) were abated by >90% with UV/H_2O_2. However, the O_3/H_2O_2 process showed similar or better efficiency, apart from the X-ray contrast media amidotrizoic acid, and that limited bromate formation was found.[35] Different AOP combinations (O_3/H_2O_2/LP-UV) were compared with respect to MP removal efficiency, investment and operational costs. For the specific treatment case, a combination of 2 mg L^{-1} O_3, 6 mg L^{-1} H_2O_2 and LP-UV at 6500 J m^{-2} yielded the best abatement per € treatment costs.[51] This is probably due to the "bleaching effect" by O_3/H_2O_2 (decrease in UV absorption at 254 nm), which makes subsequent UV/H_2O_2 treatment more efficient. In laboratory experiments, spiked MPs showed a similar biodegradation in an ozonated water matrix as in a non-oxidized matrix, except for naproxen, ibuprofen and gemfibrozil, which had a lower extent of abatement in the oxidized matrix.[52]

In another study, urban surface water was treated either with ozonation before SAT column treatment, or bank filtration and aeration before SAT column treatment.[24] The authors concluded that O_3-SAT is a feasible option for water treatment due to the overall higher abatement of MPs and removal of precursors for disinfection by-products, but did not investigate bromate formation.[24] Similar results were also obtained with municipal wastewater effluents.[38,39]

Despite these previous studies, no long-term data are currently available for a UV/H_2O_2 treatment of surface water with subsequent SAT. The aim of this study was to evaluate the performance of a UV/H_2O_2 – SAT column treatment system in comparison to SAT column treatment only. Selected MPs were analyzed to investigate their abatement by the different treatment steps. Measurements by liquid chromatography coupled with an organic carbon detector (LC-OCD) were conducted to study the impact of distinct treatment steps on the molecular size distribution of the dissolved organic matter (DOM). Microbiological parameters, such as intact cell counts and cell-bound ATP, were analyzed to investigate their evolution along the treatment train. With this approach, this study provides an assessment of the performance and impacts of UV/H_2O_2 treatment with subsequent SAT for drinking water production.

Materials and methods

Pilot plant

A scheme of the continuously operated pilot plant is presented in Fig. 1. Water from the river Rhine after full-scale rapid sand filtration (used for full-scale soil infiltration) was used as feed water for the pilot plant. H_2O_2 was dosed at a target concentration of 4 mg L^{-1} from a stock solution (35% food-grade H_2O_2, diluted to 2 g L^{-1} with ultrapurified water, >18 MΩ). A constant UV dose of 6000 J m^{-2} was

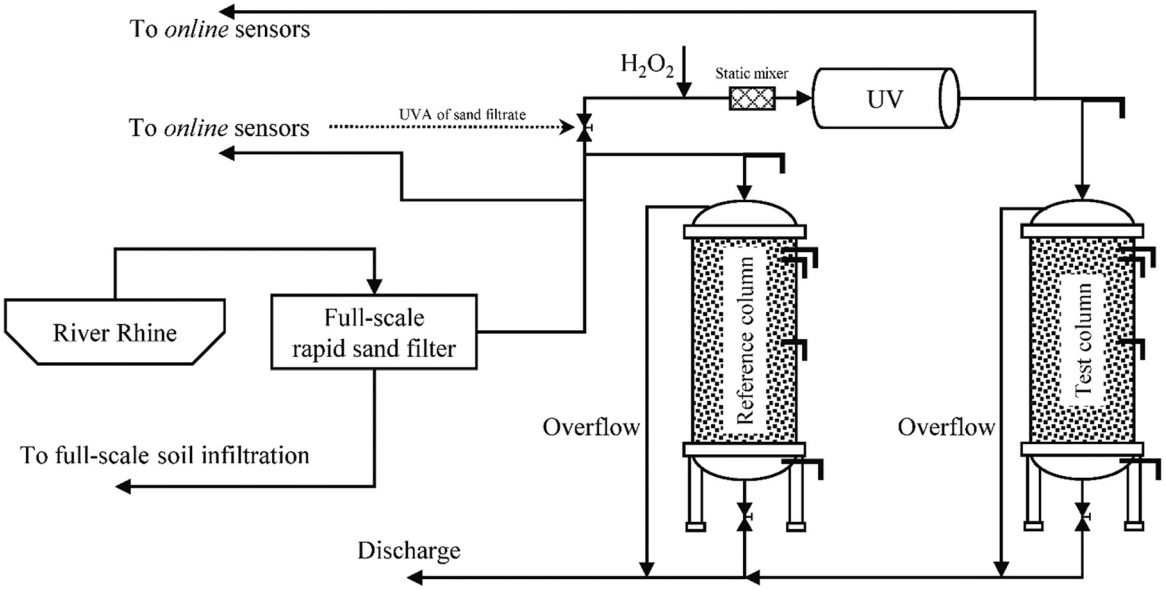

Fig. 1 Scheme of the continuously operated pilot plant. After full-scale rapid sand filtration, 4 mg L^{-1} H_2O_2 was dosed before a static mixer and irradiated with low pressure UV light (radiation maximum: 254 nm) with a dose of 6000 J m^{-2}. Soil columns were operated in constant overflow at an infiltration velocity of 1 m d^{-1}.]: sampling point.

applied by controlling the flow through the low pressure UV reactor (Spectron 6, Xylem Inc., Germany). The UV absorption at 254 nm (UVA) of the sand filtrate was measured online. The soil columns were filled with a disturbed soil sample from the Lange Erlen (Basel, Switzerland) infiltration site (first meter, sieved fraction <2 cm) and sand from the rapid sand filters for enhanced permeability in a 1 : 1 volumetric ratio. They were operated in continuous overflow and manually adjusted to a target flow of 6 L h^{-1} (EBCT = 24 h, *i.e.*, infiltration velocity = 1 m d^{-1}) by a needle valve at the respective column outlet. The continuous operation was divided in a start-up phase (March 2017–October 2017) and a test phase (November 2017–August 2018). The pilot plant operation monitoring online sensors and probes, as well as operation parameters of the AOP and soil columns during the test phase are summarized in ESI† Tables S1–S3.

Feed water

Rhine river sand filtrate characteristics (influent for AOP and reference soil column) during the test phase (November 2017–August 2018) were: DOC = 1.3 ± 0.1 mg L^{-1}, pH = 8.1 ± 0.1, alkalinity = 221 ± 54 mg L^{-1} as $CaCO_3$, UVA = 3.6 ± 1.4 m^{-1}, turbidity = 0.25 ± 0.60 FNU, temperature = 13.6 ± 7.0 °C, dissolved oxygen (DO) = 9.8 ± 2.0 mg L^{-1}, nitrate (NO_3^-) = 6.5 ± 1.2 mg L^{-1}, iron (as total iron): 5 ± 1 μg L^{-1}. Total copper in the Rhine river water was 25.2 ± 1.9 μg L^{-1}, measured by the local authority in a nearby observation station (January 2017–May 2018).[55] DOM, carbonate and bicarbonate were the only relevant $^{\bullet}OH$ radical scavengers of the background matrix. The *pseudo* first-order scavenging rate constant of the water background matrix for reactions with $^{\bullet}OH$ radicals ($k_{OH,S}$) can be calculated by:[56]

$$k_{OH,S} = \sum_i k_{OH,i} \times [S_i]$$

$k_{OH,i}$ is the second order rate constant for the reaction of scavenger i with $^{\bullet}OH$ radicals, $[S_i]$ is the concentration of the respective scavenger. $k_{OH,i}$ for DOC, CO_3^{2-} and HCO_3^- are 2.3 × 10^4 L mg C^{-1} s^{-1},[57] (average value of five surface water sources[57]), 3.9 × 10^8 L mol^{-1} s^{-1},[58] and 8.5 × 10^6 L mol^{-1} s^{-1},[58] respectively which leads to $k_{OH,S}$ of about 5.3 × 10^4 s^{-1} for the tested water. This is in the order of 10% of $k_{OH,S}$ of a tertiary effluent from a municipal wastewater treatment plant.[59] Considering the quenching by H_2O_2 ($k_{OH,\ H_2O_2}$ = 2.7 × 10^7 L mol^{-1} s^{-1} (ref. 58)) at the target dose of 4 mg L^{-1}, $k_{OH,S}$ increases to 5.6 × 10^4 s^{-1}, *i.e.*, the fraction of $^{\bullet}OH$ radicals reacting with H_2O_2 is low (6%).

Micropollutants and reagents

An overview on selected properties of the investigated MPs is given in Table S4† along with details on the respective measurement range and analytical uncertainty. All MP samples were prepared by addition of sodium thiosulfate ($Na_2S_2O_3$, purum p.a., anhydrous, ≥98%) to a final concentration of 0.25 mM for H_2O_2 quenching,[60] providing a reaction time of at least two hours (samples were usually measured 24–72 h after sampling). With an estimated half-life time of H_2O_2 under these conditions of about four hours,[61] this means quenching was relatively slow. However, the resulting H_2O_2 concentrations of <3 mg L^{-1} did not affect the analysis of MPs. In addition, possible abatement of MPs during sampling storage due to Fenton-like reactions with Fe(III) and Cu(II) can very likely be neglected under the given circumstances.[62,63] 1*H*-Benzotriazole (BTZ) and metformin (MET)

were measured after direct injection (250 μL) by HPLC-MS/MS (Qtrap 5500, AB Sciex) with electro-spray ionization according to a modified standard method (DIN 38407-47). Separation was achieved using an Acquity UPLC HSS T3 column (3.0 mm × 150 mm, 1.8 μm, Waters, MA, USA) in an UltiMate 3000 HPLC (Thermo Scientific, MA, USA). Acesulfame (ACE), iomeprol (IME), iopamidol (IPA) and iopromide (IPR) were analyzed by the same system but using an Eclipse XDB-C18 pre-column (12.5 mm × 4.6 mm, 5 μm, Agilent Technologies, CA, USA) and an Eclipse XDB-C18 column (50 mm × 4.6 mm, 1.8 μm, Agilent Technologies, CA, USA). Samples were prepared by evaporation to dryness under vacuum at 54 °C and then reconstituted with eluent and filtered (0.2 μm), resulting in a concentration factor of 10. Ethylenediaminetetraacetic acid (EDTA) was analyzed according to a modified method from Geschke and Zehringer[64] as Fe(III)–EDTA after SPE using a Bakerbond spe Quaternary Amine (N+) column (Avantor, PA, USA). Samples were biologically stabilized by the addition of 7 mL formaldehyde (37%) to 500 mL of sample, as EDTA samples were prepared and measured usually about two weeks after sampling. Substances were eluted with formic acid, achieving a concentration factor of 800. Separation was achieved by an UltiMate 3000 HPLC (Thermo Scientific, MA, USA), equipped with a Superspher 60 RP-select B (Merck, Germany) column. Signals were detected by a Dionex DAD-3000RS (Thermo Scientific, MA, USA) diode array detector at 258 nm.

Bulk organic matter

DOC was analyzed on a LC-OCD analyzer (DOC Labor Dr. Huber, Germany) with 2000 μL injection volume, deploying an isocratic elution method (phosphate buffer at pH 6.85).[65] Separation was achieved by a size exclusion column (250 mm × 20 mm, Toyopearl HW-50S, Tosoh Bioscience, Japan).[65] Biodegradable dissolved organic carbon (BDOC) was determined according to the French norm AFNOR XP T90-319 in duplicate batches as the difference in DOC before and after a seven-day incubation at 25 °C using a washed sand inoculum. Before setting up the BDOC batches, all samples were treated with catalase immobilized on a resin (Sepabeads EC-EP, particle size: 200–500 μm) for quenching residual peroxide.[66] 1–2 g L^{-1} catalase resin were added to the samples, placed on a shaker for 1 h at 100 rpm and separated by sedimentation. Quenching success was confirmed by H_2O_2 quantification. H_2O_2 was quantified photometrically by titanium oxalate.[67,68] In brief, 0.5 mL of a titanium(IV) oxysulphate solution in concentrated sulphuric acid (~1.3% Ti) is added to 10 mL of a sample. After about five minutes of reaction, the absorbance at 420 nm is measured (see Table S5† for details). Soil respiration was measured in triplicates along the Swiss reference method Agroscope B-BA-IS.[69,70] In brief, produced CO_2 is trapped in 25 mM NaOH within 72 h incubation at 25 °C. Then, CO_3^{2-} is precipitated with 0.5 M $BaCl_2$ and residual NaOH determined by titration with 25 mM HCl, using a phenolphthalein indicator. Produced CO_2 is calculated from the used volume of HCl. Details on the performance of all applied analytical methods other than for MPs are provided in Table S5.†

Microbial parameters

Intact cell counts (ICC) were measured along an adopted method from Prest *et al.*[71] In brief, 10 μL of a SYBR® Green I (SG) stain stock solution and 20 μL of 30 mM propidium iodide in dimethyl sulfoxide (DMSO, ≥99.9%) were mixed, then filled up to 1 mL with DMSO (ICC stain working solution). Samples were prepared by 1 : 10 dilution in 0.22 μm-filtered bottled water before staining and then heated to 37 °C for 3 minutes. Subsequently, 10 μL of the ICC stain working solution was added to 990 μL of the sample. Samples were incubated in the dark (37 °C, 10 minutes) before the measurement with an Accuri C6 (BD Biosciences, NJ, USA) flow cytometer. Total adenosine tri-phosphate (ATP) of the samples was measured in duplicates according to a protocol adopted from Hammes *et al.*[72] In brief, 1.6 mL sample was incubated (38 °C, 5–10 minutes) in parallel to 50 μL aliquots of prepared ATP reagent (10 mL ATP reagent with 1.6 mL of 1 M $MgCl_2$). Then, 500 μL of the heated sample was transferred to the ATP reagent and incubated for exactly 20 seconds before measuring the luminescence at 490–575 nm on a GloMax 20/20 (Promega, WI, USA) luminometer. Quantification was done by a calibration with pure ATP standards. Free ATP was measured by the same method after filtration of the samples with 0.22 μm syringe filters. Bacterial, *i.e.*, cell-bound ATP was calculated by subtracting free ATP from total ATP.

Results and discussion

Abatement of selected target micropollutants

By the treatment with UV/H_2O_2, all MP abatements were found to be statistically significant in paired two-sided *t*-tests, except for MET (Fig. 2). The results agree very well with published data on the MPs, *e.g.* ACE, IME, IPA and IPR are known to be well abated by direct photolysis.[73–76] BTZ is known to be primarily abated by hydroxyl radicals ($^{\bullet}OH$).[77] Neglecting direct photolysis[78,79] and assuming a second order rate constant for the reaction of BTZ with $^{\bullet}OH$ radicals of $k_{OH,BTZ} = 8.34 \times 10^9$ M^{-1} s^{-1},[77] the abatement of BTZ indicates an average $^{\bullet}OH$ radical exposure of $(1.5 \pm 0.1) \times 10^{-10}$ M s. This is in the range of previously reported $^{\bullet}OH$ radical exposures for a comparable UV/H_2O_2 treatment in a similar surface water (1.8×10^{-10} M s).[80] EDTA and MET are relatively recalcitrant substances even in reactions with $^{\bullet}OH$ radicals.[73,81] However, depending on the complexed metal ion, direct photolysis of EDTA complexes can proceed quickly, *e.g.*, with Fe(III).[82] Calculations with the average molar concentrations of the sand filtrate's cations in the ChemEQL chemical speciation software[83] confirmed that EDTA should be prevalent as $[Fe(III)OH(EDTA)]^{2-}$ (57%), $[Fe(III)(EDTA)]^{-}$ (39%) and $[Ca(EDTA)]^{2-}$ (3%). Therefore, the relatively strong abatement is attributed to direct photolysis of the predominant

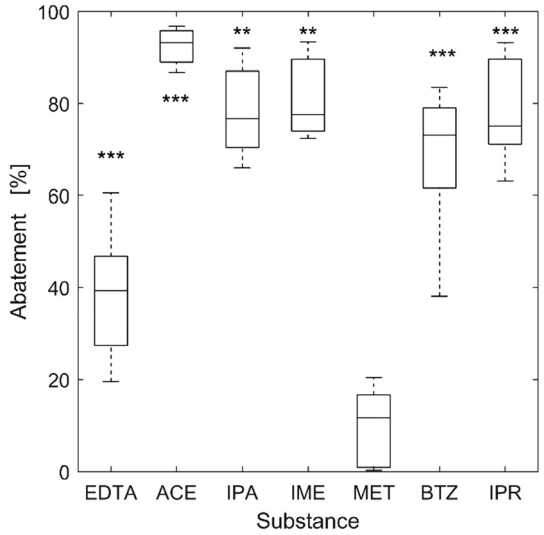

Fig. 2 Abatement of the selected micropollutants by the UV/H_2O_2 treatment. Abatement calculated relative to the LOQ, if effluent concentration was below the LOQ. n = 7 for all MPs. Central mark of boxes: median; lower and upper edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Significance of abatement in paired two-sided t-tests (sand filtrate and after AOP treatment) are marked with "★★" and "★★★" for $p < 0.01$ and $p < 0.001$, respectively.

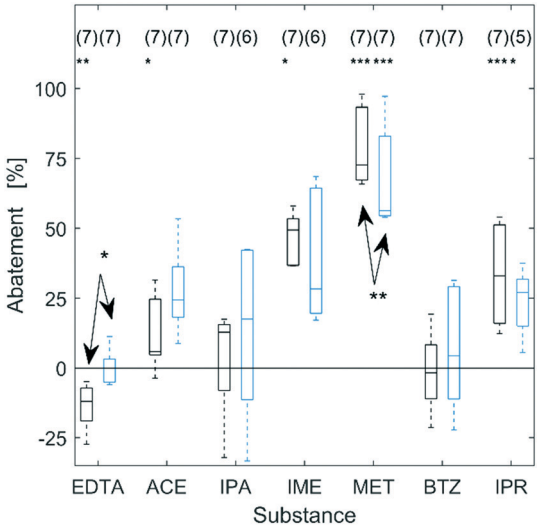

Fig. 3 Abatement of micropollutants along the soil columns, calculated relative to the influent concentration of the respective column receiving Rhine river sand filtrate (black) or UV/H_2O_2 treated Rhine river sand filtrate (blue). Abatement calculated to the LOQ, if effluent concentration was below the LOQ. n indicated by numbers in brackets. Central mark of boxes: median; lower and upper edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Significance of abatement along columns and significance of difference between groups in paired two-sided t-tests are marked with "★", "★★" and "★★★" for $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

Fe(III)EDTA complexes.[82] For MET, with a $^{\bullet}OH$ radical exposure of 1.5×10^{-10} M s and $k_{OH,MET} = 1.4 \times 10^{9}$ M^{-1} s^{-1},[84] a UV dose of 6000 J m^{-2}, $\varepsilon_{254,MET}$ = 940 M^{-1} cm^{-1},[84] and $\Phi_{254,MET}$ = 0.014 mol per einstein,[84] an abatement of around 22% was expected, which is close to the measured range of 0–20%.

The water temperature of Rhine river filtrate ranged from 3.2–27.0 °C during the experiments. It is known that both $^{\bullet}OH$ radical reactions[19,85–87] and photo-physical properties[19,88] can be temperature dependant, while the influence of the latter is expected to be minimal.[87] In addition, the efficiency of the UV lamps also changes with temperature.[89] This might translate into a lower applied UV dose in low water temperatures than at elevated temperatures, consequently in lower direct photolysis of target MPs and generation of $^{\bullet}OH$ radicals, and finally in lower observed reaction rates. However, our study was not designed to systematically investigate the temperature effects; hence, the impact of the water temperature on the observed reaction rates are not evaluated.

After the soil column treatment of Rhine river sand filtrate, five substances were prevalent in median concentrations >0.1 μg L^{-1}. These were EDTA (Swiss drinking water threshold 200 μg L^{-1} [90]), ACE, IPA, IME, and BTZ (Fig. S1†). Abatement during soil treatment alone was statistically significant for ACE, IME, MET and IPR (Fig. 3). In contrast, the abatement of IPA and BTZ were negligible by the column receiving Rhine river sand filtrate. IPA and BTZ are known to be recalcitrant in biological wastewater treatment.[91–93] Overall, the soil treatment alone does not appear to be very effective for the removal of the investigated MPs, except for MET.

After pre-treatment with UV/H_2O_2, only MET and IPR abatements were found to be statistically significant in the column fed with the AOP effluent. In contrast to the column receiving Rhine river sand filtrate, the abatements of ACE and IME were probably not significant in the column receiving the AOP effluent because of the often very low influent concentrations (Fig. S1†).

Statistically significant differences between the performances of the soil columns were only found for EDTA and MET. EDTA concentrations in the raw water were often higher in the past years than during the test phase and tended to decrease throughout the last years (Fig. S2†). We hypothesize that the soil material is likely saturated with EDTA, leading to a leaching due to competitive adsorption of DOM (Fig. 3). As further discussed below, the organic matter in the AOP effluent tends to be more hydrophilic. Hence, its lower adsorption on the soil column might provide an explanation for the lower leaching of EDTA after the AOP.

MET is known to be well biodegradable.[91,94–99] Differences between the soil column performances for MET are explained by a lower biological activity in the water phase receiving UV/H_2O_2 effluent. The strong primary disinfection effect in combination with the residual H_2O_2 may hamper the biological regrowth in the water phase along the top few centimetres, as further discussed below. However, the lower removal of MET in the soil column after UV/H_2O_2 due to less co-metabolism or less enzymatic diversity as a consequence of increased

concentrations of biodegradable DOM cannot be ruled out completely (see discussion below).[100]

Temperatures were controlled neither in the column influents, nor along the columns. The effluent temperatures, measured in grab samples, were 1.0–1.5 °C above the sand filtrate's temperature due to temperature equilibration with the environment. They ranged between 7.9–27.3 °C and 8.0–27.6 °C for the column receiving Rhine river sand filtrate and AOP effluent, respectively (n = 14 for both). The varying temperature is expected to impact the performance of the soil columns as well, in terms of removal of both bulk organic matter and MPs.[30] However, for the soil columns as well, the study was not designed to assess the impact of temperature on the removal efficiency; hence, it is not further evaluated.

The combined treatment (AOP with subsequent SAT) led to higher abatements for the majority of the investigated substances compared to soil or UV/H_2O_2 treatment alone. By the use of the selected UV/H_2O_2 process, it was possible to abate all investigated MPs to below 0.1 μg L^{-1} after subsequent soil treatment, except for EDTA. Such an extent of abatement could not be accomplished by soil treatment alone (Fig. S1†). It is hence concluded that the combined treatment can be a useful approach to reach a certain treatment goal. Furthermore, the AOP can act as an additional barrier to avoid target MPs to accumulate in the soil. The overall abatement can be explained by the sum of the effects of UV/H_2O_2 and soil treatment and the soil column performance did not significantly change due to AOP pre-treatment (Fig. 3). Therefore, no enhanced or synergistic abatement of target substances in the soil column was observed after the AOP for the investigated compounds. This confirms previous results for a surface water matrix, which was treated by 1 mg O_3 mg^{-1} DOC before a biodegradation batch test with an adapted sand inoculum to remove various spiked MPs.[52] Transformation products of the MPs are formed upon the UV/H_2O_2 treatment and they are typically are more polar than their parent compounds. Hence, they less efficiently sorb onto the soil material.

In addition, the biological stability of TPs is mostly unknown and not explored in this study. A theoretical assessment of TPs from ozonation indicated that some TPs might be better removed in subsequent biological treatment steps, whereas others would be recalcitrant, depending on the type of ozonated parent compound.[101] Only very limited information from pilot or full-scale applications is available on this topic. Results from wastewater ozonation indicate that some TPs are relatively stable in subsequent biological treatments.[34,102] Therefore, it is uncertain whether a higher degree of MPs' mineralization can be expected from a combined AOP-SAT treatment.

Nevertheless, AOP treated water should be biologically restabilized before its distribution to remove biologically available organic matter formed during the AOP.[103] Therefore, the proposed configuration appears particularly interesting for surface waters with low background scavenging rates, $k_{OH,S}$.[36] In addition, previous studies demonstrated an increase of the disinfection by-product formation potential upon chlorination in AOP treated water, which was lowered again by a biological post-treatment,[16,104,105] *e.g.*, a SAT.

A previous study was able to link lower concentrations of primary substrate and a higher share of its refractory substances with a higher biological abatement of MPs in laboratory-scale column tests.[100] As during the AOP treatment parts of the DOM became more biodegradable, *i.e.*, less refractory,[16,17,23,24] this might imply a worse performance of the combined treatment (AOP + soil column) than the sum of the single treatment steps in certain waters. However, the small differences of the soil column performances with or without AOP pre-treatment in our study does not confirm these previous observations (Fig. 3).

Impact on bulk organic parameters

In natural waters, DOM is prevalent at concentrations several orders of magnitude higher than MPs. As the generated $^{\bullet}OH$ radicals react relatively unselectively, DOM is one of their major sinks: based on the estimated $k_{OH,S}$, the fraction of $^{\bullet}OH$ radical reacting with DOM is about 60% and with bicarbonate about 40%. As expected,[16,23,106] the applied UV/H_2O_2 process did not lead to mineralization of the DOM (Fig. S3†), but DOM becomes more biodegradable by the application of an AOP.[16,17,23,24] Laboratory measurements of the BDOC (n = 3, March 2018–June 2018) confirmed an increase of the biodegradable fraction by the AOP treatment from an average of 0.1 mg L^{-1} (sand filtrate) to 0.5 mg L^{-1} BDOC (UV/H_2O_2 effluent, $p < 0.05$). However, this did not lead to an increased abatement of the DOC by the soil column treatment after AOP and the difference between the performances of the tested columns was statistically not significant (Fig. S3†). In fact, both soil columns (with and without AOP pre-treatment) did not contribute much to the DOC removal (median removal of 0.2 mg L^{-1} (18%) and 0.3 mg L^{-1} (23%) without and with AOP pre-treatment, respectively). This is in contrast to full-scale SAT applications, where DOC removals between 33–88% were reported.[28] However, in our study, the utilized columns had a much lower residence time (24 h) and shorter travelling distance (1 m) compared to the reviewed full-scale applications (residence times: 3 days–96 months, travelling distance: 6–2700 m).[52] In addition, the sand filtrated feed water was biologically already very stable in terms of low BDOC values (see above), which might explain the overall low DOC removal.

Fig. 4 shows LC-OCD chromatograms of the different treatment steps. The peak around 44 minutes (associated with humic substances, HS[65]) was abated, while a peak at around 48 minutes (associated with building blocks[65]) was built up. On average, the HS peak maximum was slightly shifted ($p < 0.01$) from 43.9 ± 0.5 min (Rhine river sand filtrate) to 44.5 ± 0.5 min (Rhine river sand filtrate after UV/H_2O_2 treatment). Our measurements cannot exclude that this results from a matrix effect of the changed background matrix after the AOP. However, along with the

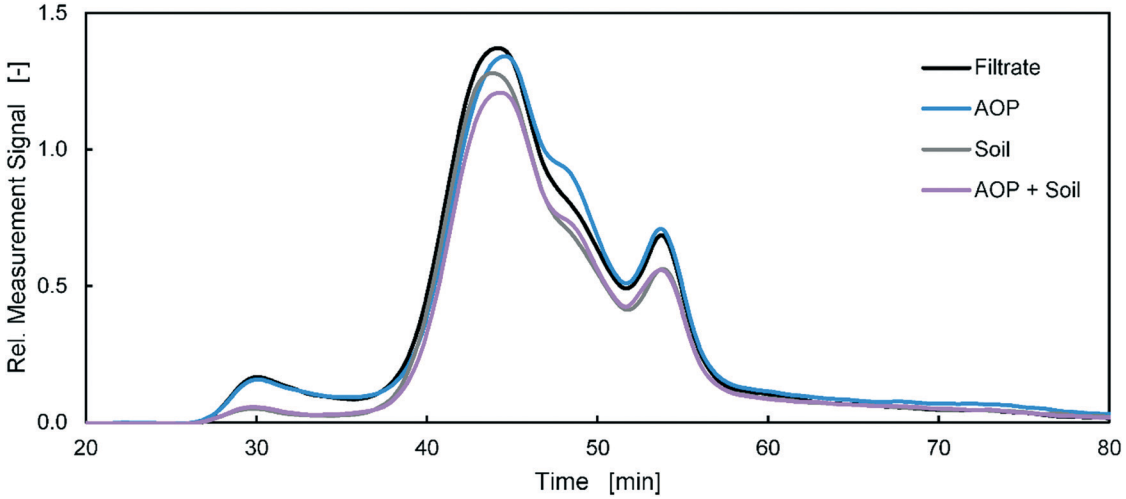

Fig. 4 LC-OCD chromatograms of the dissolved organic matter after the indicated treatments, averages from measurement campaigns (n = 7, November 2017–August 2018, one outlier measurement after a rain-event was excluded). Black line: Rhine river sand filtrate. Blue line: AOP. Grey line: soil column. Lavender line: AOP and soil column.

slight increase of the peak around 48 minutes, this indicates a slight shift towards smaller molecules, which is in line with the widely assumed de-polymerization mechanism of DOM upon UV/H_2O_2 treatment.[107] Subsequent soil column treatment led to a decrease of all peaks, indicating that all fractions were removed by the SAT treatment, regardless of the AOP pre-treatment. In fact, the slightly shifted HS peak was the only parameter in LC-OCD measurements that differed between the two soil column influents and effluents (Tables S6 and S7†).

The AOP also decreased the specific UV absorbance at 254 nm (SUVA = UVA/DOC), an indicator for aromaticity of the DOM and, by that, for hydrophobicity. Median SUVA values significantly ($p < 0.01$, n = 3) decreased from 2.0 L mg^{-1} m^{-1} after sand filtration to 1.7 L mg^{-1} m^{-1} after AOP treatment. This indicates that AOP reaction products tended to be less aromatic. It is known that $^{\bullet}$OH radicals react readily with DOM by $^{\bullet}$OH addition to C–C double bonds and aromatic rings, H-abstraction and to a minimal extent by electron transfer.[108] It is known that UV/H_2O_2 treatment can lead to ring opening reactions, *e.g.*, of phenols.[109] In addition, studies on direct photolysis of natural DOM confirmed that irradiation at 254 nm is able to reduce the SUVA values even at doses comparable to those applied in this study (6000 J m^{-2}).[110,111] Therefore, the decrease in SUVA by the AOP treatment is attributed to both direct photolysis of DOM and its reactions with $^{\bullet}$OH radicals. Soil column treatment resulted in an increase of the SUVA value in both treatment lines (2.4 L mg^{-1} m^{-1} and 1.9 L mg^{-1} m^{-1} for the columns receiving Rhine river sand filtrate without and with UV/H_2O_2 treatment, respectively). It has been demonstrated previously that an increase of SUVA during soil passage is due to an accumulation of slowly- and non-biodegradable DOM in the water phase, as this fraction of DOM is typically associated with a higher molecular weight and SUVA.[24,112]

Impact on microbial activity

UV irradiation during water treatment is known to effectively inactivate microorganisms.[113] The applied AOP utilizes UV doses that are about 15–20 times higher than those commonly used for drinking water disinfection.[114] This leads to a strong primary disinfection effect of the water during AOP treatment. This is reflected by the ICC measurements in the water phase at the column influent (Fig. 5). The corresponding cell-bound ATP in the water phase is shown in Fig. 6 and supports this observation. ICC measurements along the columns showed that the disinfection effect of the AOP was still detectable throughout the subsequent column receiving the AOP effluent.

Of note, ICC measurements are not a proper method to distinguish between living and dead cells after UV/H_2O_2 treatment. As UV irradiation primarily targets the DNA of cells, the cell membrane might still be intact after treatment. Hence, the reduction of ICC by UV/H_2O_2 is not discussed (travel distance = 0 cm). However, lower ICC values in the water phase along the column after the UV/H_2O_2 treatment remained visible and probably contributed to the lower values of bacterial ATP, as discussed below. Overall, the filter effect of the soil columns for the removal of intact cells was relatively low (0.3 ± 0.1 $\log_{10}$ for both columns).

A median reduction of 1.5 ± 0.6 $\log_{10}$ in bacterial ATP was observed by the UV/H_2O_2 treatment (Fig. 6). Residual ATP in inactivated (but still intact) cells might explain the low reduction values of bacterial ATP. However, heterotrophic plate counts (HPC) before and after the AOP treatment during the start-up phase showed a relatively low reduction of only 1.3 ± 0.4 $\log_{10}$ (n = 5, March 2017–July 2017). This is less than expected, as the UV dose (6000 J m^{-2}) should be high enough for an inactivation of more than 4 $\log_{10}$ for bacteria, viruses and protozoa.[113,115] The similar $\log_{10}$ reduction values of bacterial ATP and HPC is probably fortuitous because there is no

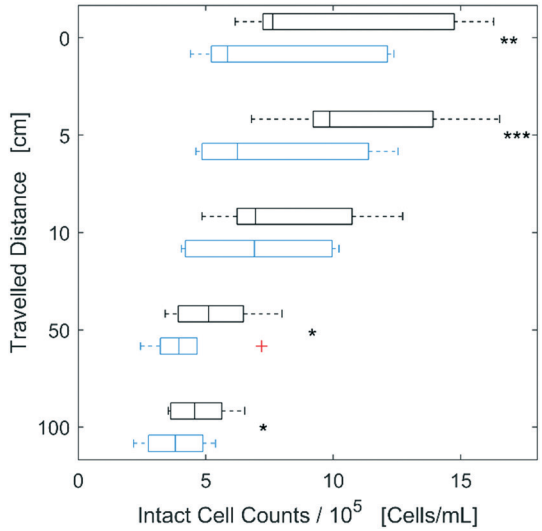

Fig. 5 Intact cell counts in the water phase along the columns receiving Rhine river sand filtrate (black) and AOP effluent (blue). n = 6 for all. Central mark of boxes: median; left and right edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Outliers, *i.e.*, values outside ±2.7 standard deviations from median (99.3% coverage of normally distributed data), marked as a red cross. Significant differences between groups in paired two-sided t-tests are marked with "★", "★★" and "★★★" for $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively.

general correlation between cell-bound ATP and HPC.[72] The soil column receiving Rhine river sand filtrate was able to reduce the bacterial ATP concentrations by 0.6 ± 0.4 $\log_{10}$, which falls in a similar range as the removal of ATP of slow sand filters in previous studies (about 0.2 $\log_{10}$ [116]).

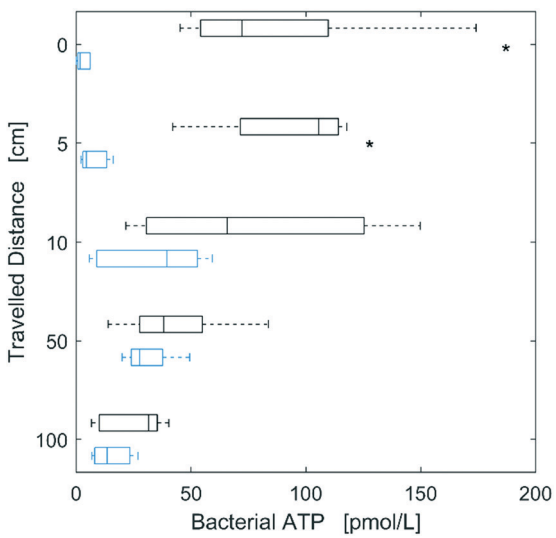

Fig. 6 Bacterial ATP in the water phase along the columns receiving Rhine river sand filtrate (black) and AOP effluent (blue). n = 5 for all, except n = 4 for Rhine river sand filtrate after 5 cm travel distance. Central mark of boxes: median; left and right edges of boxes: 25th and 75th percentiles, respectively; whiskers: minimum and maximum values. Significant differences between groups in paired two-sided t-tests are marked with "★" for $p < 0.05$.

The bacterial activity in the water phase was consistently higher along the column receiving Rhine river sand filtrate compared to the column receiving the AOP effluent (Fig. 6). In the Rhine river sand filtrate column, the bacterial ATP peaked after 5 cm (110 pM). After that, the concentration of the bacterial ATP constantly decreased towards the column effluent. In the column after AOP pre-treatment, the bacterial ATP increased from around 0 pM at the column influent to a maximum of about 40 pM after a filtration distance of 10 cm. At the same time, the median residual H_2O_2 concentration after the AOP was 3.6 ± 0.7 mg H_2O_2 L^{-1} (Table S3†). Along the subsequent column receiving the AOP effluent, hydrogen peroxide was still present in low concentrations after 5 cm (0.2 ± 0.1 mg H_2O_2 L^{-1}, *i.e.* partially <LOQ, n = 3) and was completely depleted (<LOD) after 10 cm (*i.e.*, contact time around 2 hours), which is in good agreement with published results from laboratory batch tests.[117] The increase in bacterial ATP is explained by detachment of soil bacteria. However, as H_2O_2 inhibits microbial activity even at 1 mg H_2O_2 L^{-1},[117] the residual hydrogen peroxide can serve as an explanation for the slow recovery of bacterial ATP along the first centimeters in the column after the AOP treatment.

Respiratory measurements of soil samples from the columns' tops confirmed that both column materials were biologically active, *i.e.*, the residual H_2O_2 did not inhibit biological activity at the influent zone of the column. The soil respiration of the column material receiving AOP pre-treated water was much higher (30 μg CO_2 per g dry mass soil per 24 h) than the material in the column receiving Rhine river sand filtrate (17 μg CO_2 per g dry mass soil per 24 h). This finding is not necessarily in contradiction to the ATP data, as the ATP values were measured for the water phase only. The observation might be related to the higher availability of BDOC after the AOP treatment. In addition, the decay of H_2O_2 gives rise to additional O_2, stimulating additional bacterial activity. However, as the water along both SAT columns was fully oxic at all times and almost oxygen saturated in the sand filtrate, the latter hypothesis is considered more relevant for full-scale applications with different redox conditions along the infiltration path.

The specific cell activity (*i.e.*, bacterial ATP/ICC) in the water phase along the column receiving the AOP effluent never exceeded the activity of the Rhine river sand filtrate column at the sampling points in a statistically significant way (Fig. S4†). As more BDOC was produced by the AOP, it was expected that the specific cell activity might be higher due to the additional substrate available. However, this could not be demonstrated in this study. It is known that the microbial density is orders of magnitudes higher on the soil compared to the water phase. For the soil, a higher activity could be demonstrated in the top layer after the AOP treatment (see above).

Conclusions

• A combination of UV/H_2O_2 with a subsequent soil aquifer treatment (SAT) is a feasible process combination for micropollutant abatement in drinking water production. Residual

hydrogen peroxide hampers microbial regrowth in the water phase unless it is depleted to below 0.3 mg L^{-1} (5–10 cm infiltration depth in this study). Despite this, the soil was still biologically active.

• Micropollutant abatement by the UV/H_2O_2 process with subsequent SAT is generally higher than by UV/H_2O_2 or SAT only. However, the abatement could be well explained by an additive effect of the unit processes. The investigated substances (EDTA, acesulfame, iopamidol, iomeprol, metformin, 1*H*-benzotriazole, iopromide) were primarily abated by the UV/H_2O_2 process and metformin mainly during SAT.

• A slight shift of the humic substances peak maximum towards longer retention times, along with a small build-up of the building blocks fraction, indicates a shift towards smaller substances as a consequence of UV/H_2O_2 treatment. This is accompanied with an increase of the biodegradable fraction of the dissolved organic matter (DOM). In addition, a loss in specific UV absorbance of the DOM (SUVA) by the oxidation process was observed. However, the investigated soil columns did not contribute much to the removal of DOC, probably due to the relatively short residence time compared to full-scale SAT systems.

• The UV/H_2O_2 process had a strong primary disinfection effect on the suspended microorganisms, mainly due to the high UV doses applied. This effect was conserved in the water phase, likely due to the inhibitory effect of the residual H_2O_2 within the first 10 cm. Along the full length of the investigated columns (1 m), both intact cell counts and cell-bound ATP measurements were lower in the column with compared to without UV/H_2O_2 treatment.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was conducted within the AquaNES project, which received funding from the European Union's Horizon 2020 program (Grant Agreement No. 689450). Jan Svojitka, Rita Hochstrat and Nadja Rastetter (all FHNW) are thanked for their practical help and support in results interpretation. Pascal Temmler, Pascal Brand and their teams (all iwb) are acknowledged for their support in continuous operation and maintenance of the pilot plant and online sensors.

References

1 B. Petrie, R. Barden and B. Kasprzyk-Hordern, A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring, *Water Res.*, 2015, **72**, 3–27, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0043135414006307.

2 J. C. G. Sousa, A. R. Ribeiro, M. O. Barbosa, M. F. R. Pereira and A. M. T. Silva, A review on environmental monitoring of water organic pollutants identified by EU guidelines, *J. Hazard. Mater.*, 2018, **344**, 146–162, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0304389417307483.

3 F. Desbiolles, L. Malleret, C. Tiliacos, P. Wong-Wah-Chung and I. Laffont-Schwob, Occurrence and ecotoxicological assessment of pharmaceuticals: Is there a risk for the Mediterranean aquatic environment?, *Sci. Total Environ.*, 2018, **639**, 1334–1348, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969718315341.

4 S. Fekadu, E. Alemayehu, R. Dewil and B. Van der Bruggen, Pharmaceuticals in freshwater aquatic environments: A comparison of the African and European challenge, *Sci. Total Environ.*, 2019, **654**, 324–337, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969718344243.

5 *The Council of the European Union. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption*, Official Journal of the European Communities European Union, 1998, pp. 1–23, Available from: http://data.europa.eu/eli/dir/1998/83/oj.

6 R. Tobias, Communication About Micropollutants in Drinking Water: Effects of the Presentation and Psychological Processes, *Risk Anal.*, 2016, **36**(10), 2011–2026, DOI: 10.1111/risa.12485.

7 *Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment*, Available from: http://data.europa.eu/eli/dir/1991/271/oj.

8 *Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy*, Available from: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:32000L0060.

9 *Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy Text with EEA relevance*, Available from: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32013L0039.

10 *Commission Implementing Decision (EU) 2018/840 of 5 June 2018 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council and repealing Comm*, Available from: https://eur-lex.europa.eu/legal-content/en/TXT/?uri=CELEX:32018D0840.

11 *US EPA. Toxic Substances Control Act (TSCA) Chemical Substance Inventory*, Available from: https://www.epa.gov/tsca-inventory.

12 P. Verlicchi, M. Al Aukidy and E. Zambello, Occurrence of pharmaceutical compounds in urban wastewater: Removal, mass load and environmental risk after a secondary treatment-A review, *Sci. Total Environ.*, 2012, **429**, 123–155, DOI: 10.1016/j.scitotenv.2012.04.028.

13 Y. Luo, W. Guo, H. H. Ngo, L. D. Nghiem, F. I. Hai and J. Zhang, *et al.* A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, *Sci. Total Environ.*, 2014, **473–474**, 619–641, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969713015465.

14 R. P. Schwarzenbach, B. I. Escher, K. Fenner, T. B. Hofstetter, C. A. Johnson and U. von Gunten, *et al.* The Challenge of Micropollutants in Aquatic Systems, *Science*, 2006, **313**(5790), 1072–1077, DOI: 10.1126/science.1127291.

15 S. J. Stangroom, C. D. Collins and J. N. Lester, Sources of Organic Micropollutants to Lowland Rivers, *Environ. Technol.*, 1998, **19**(7), 643–666, DOI: 10.1080/09593331908616722.

16 S. R. Sarathy, M. I. Stefan, A. Royce and M. Mohseni, Pilot-scale UV/H2O2 advanced oxidation process for surface water treatment and downstream biological treatment: effects on natural organic matter characteristics and DBP formation potential, *Environ. Technol.*, 2011, **32**(15), 1709–1718, DOI: 10.1080/09593330.2011.553843.

17 K. Lekkerkerker-Teunissen, *Advanced oxidation and managed aquifer recharge - A synergistic hybrid for organic micropollutant removal*, TU Delft, 2012, p. 208.

18 J. C. Kruithof, P. C. Kamp and B. J. Martijn, UV/H2O2 treatment: A practical solution for organic contaminant control and primary disinfection, *Ozone: Sci. Eng.*, 2007, **29**(4), 273–280, Available from: http://linkinghub.elsevier.com/retrieve/pii/S1369703X07002409.

19 M. I. Stefan, *Advanced Oxidation Processes for Water Treatment*, IWA Publishing, London, 2018, p. 686, DOI: 10.1021/jz300929x.

20 J. R. Bolton, I. Mayor-Smith and K. G. Linden, Rethinking the Concepts of Fluence (UV Dose) and Fluence Rate : The Importance of Photon-based Units – A Systemic Review, *Photochem. Photobiol.*, 2015, **91**, 1252–1262.

21 D. B. Miklos, C. Remy, M. Jekel, K. G. Linden, J. E. Drewes and U. Hübner, Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review, *Water Res.*, 2018, **139**, 118–131, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135418302380.

22 U. von Gunten, Oxidation Processes in Water Treatment: Are We on Track?, *Environ. Sci. Technol.*, 2018, **52**(9), 5062–5075, DOI: 10.1021/acs.est.8b00586.

23 K. E. Black and P. R. Bérubé, Rate and extent NOM removal during oxidation and biofiltration, *Water Res.*, 2014, **52**, 40–50, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135413010166.

24 H. C. Kim, W. M. Lee, S. Lee, J. Choi and S. K. Maeng, Characterization of organic precursors in DBP formation and AOC in urban surface water and their fate during managed aquifer recharge, *Water Res.*, 2017, **123**, 75–85, DOI: 10.1016/j.watres.2017.06.038.

25 S. A. Parsons, in *Advanced Oxidation Processes for Water and Wastewater Treatment*, ed. S. A. Parsons, IWA Publishing, London, 2004.

26 *Water Reclamation Technologies for Safe Managed Aquifer Recharge*, ed. C. Kazner, T. Wintgens and P. Dillon, IWA Publishing, London, 2012, p. 460.

27 S. Grünheid, G. Amy and M. Jekel, Removal of bulk dissolved organic carbon (DOC) and trace organic compounds by bank filtration and artificial recharge, *Water Res.*, 2005, **39**(14), 3219–3228.

28 S. K. Maeng, S. K. Sharma, K. Lekkerkerker-Teunissen and G. L. Amy, Occurrence and fate of bulk organic matter and pharmaceutically active compounds in managed aquifer recharge: A review, *Water Res.*, 2011, **45**(10), 3015–3033, DOI: 10.1016/j.watres.2011.02.017.

29 M. K. Yoon, J. E. Drewes and G. L. Amy, Fate of bulk and trace organics during a simulated aquifer recharge and recovery (ARR)-ozone hybrid process, *Chemosphere*, 2013, **93**(9), 2055–2062, DOI: 10.1016/j.chemosphere.2013.07.038.

30 M. Alidina, J. Shewchuk and J. E. Drewes, Effect of temperature on removal of trace organic chemicals in managed aquifer recharge systems, *Chemosphere*, 2015, **122**, 23–31, DOI: 10.1016/j.chemosphere.2014.10.064.

31 J. Regnery, J. Barringer, A. D. Wing, C. Hoppe-Jones, J. Teerlink and J. E. Drewes, Start-up performance of a full-scale riverbank filtration site regarding removal of DOC, nutrients, and trace organic chemicals, *Chemosphere*, 2015, **127**, 136–142, DOI: 10.1016/j.chemosphere.2014.12.076.

32 WWAP (United Nations World Water Assessment Programme)/UN-Water, *The United Nations World Water Development Report 2018*, Nature-Based Solutions for Water. Paris, 2018.

33 J. Schumacher, Y. Z. Pi and M. Jekel, Ozonation of persistent DOC in municipal WWTP effluent for groundwater recharge, *Water Sci. Technol.*, 2004, **49**(4), 305–310, Available from: https://iwaponline.com/wst/article/49/4/305/10649/Ozonation-of-persistent-DOC-in-municipal-WWTP.

34 M. Bourgin, B. Beck, M. Boehler, E. Borowska, J. Fleiner and E. Salhi, *et al.* Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products, *Water Res.*, 2018, **129**, 486–498, DOI: 10.1016/j.watres.2017.10.036.

35 K. Lekkerkerker-Teunissen, J. Scheideler, S. K. Maeng, A. Ried, J. Q. J. C. Verberk and A. H. Knol, *et al.*, Advanced oxidation and artificial recharge: A synergistic hybrid system for removal of organic micropollutants, *Water Sci. Technol.: Water Supply*, 2009, **9**(6), 643–651.

36 S. Sudhakaran, S. K. Maeng and G. Amy, Hybridization of natural systems with advanced treatment processes for organic micropollutant removals: New concepts in multi-barrier treatment, *Chemosphere*, 2013, **92**(6), 731–737, DOI: 10.1016/j.chemosphere.2013.04.021.

37 J. E. Drewes and M. Jekel, Behavior of DOC and AOX using advanced treated wastewater for groundwater recharge, *Water Res.*, 1998, **32**(10), 3125–3133, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135498000645.

38 U. Hübner, U. Miehe and M. Jekel, Optimized removal of dissolved organic carbon and trace organic contaminants during combined ozonation and artificial groundwater recharge, *Water Res.*, 2012, **46**(18), 6059–6068, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135412006434.

39 I. Zucker, H. Mamane, H. Cikurel, M. Jekel, U. Hübner and D. Avisar, A hybrid process of biofiltration of secondary

effluent followed by ozonation and short soil aquifer treatment for water reuse, *Water Res.*, 2015, **84**(August), 315–322, DOI: 10.1016/j.watres.2015.07.034.

40 A. Lakretz, H. Mamane, H. Cikurel, D. Avisar, E. Gelman and I. Zucker, The Role of Soil Aquifer Treatment (SAT) for Effective Removal of Organic Matter, Trace Organic Compounds and Microorganisms from Secondary Effluents Pre-Treated by Ozone, *Ozone: Sci. Eng.*, 2017, **39**(5), 385–394, DOI: 10.1080/01919512.2017.1346465.

41 Y. Lester, D. S. Aga, N. G. Love, R. R. Singh, I. Morrissey and K. G. Linden, Integrative Advanced Oxidation and Biofiltration for Treating Pharmaceuticals in Wastewater, *Water Environ. Res.*, 2016, **88**(11), 1985–1993, DOI: 10.2175/106143016X14504669767454.

42 H. C. Kim, S. H. Park, J. H. Noh, J. Choi, S. Lee and S. K. Maeng, Comparison of pre-oxidation between O3 and O3/H2O2 for subsequent managed aquifer recharge using laboratory-scale columns, *J. Hazard. Mater.*, 2019, **377**(March), 290–298, DOI: 10.1016/j.jhazmat.2019.05.099.

43 U. Hübner, S. Kuhnt, M. Jekel and J. E. Drewes, Fate of bulk organic carbon and bromate during indirect water reuse involving ozone and subsequent aquifer recharge, *J. Water Reuse Desalin.*, 2016, **6**(3), 413–420, DOI: 10.2166/wrd.2015.222.

44 K. Hellauer, D. Mergel, A. Ruhl, J. Filter, U. Hübner and M. Jekel, *et al.* Advancing Sequential Managed Aquifer Recharge Technology (SMART) Using Different Intermediate Oxidation Processes, *Water*, 2017, **9**(3), 221, Available from: http://www.mdpi.com/2073-4441/9/3/221.

45 J. Regnery, A. D. Wing, J. Kautz and J. E. Drewes, Introducing sequential managed aquifer recharge technology (SMART) - From laboratory to full-scale application, *Chemosphere*, 2016, **154**, 8–16.

46 M. K. Yoon and G. L. Amy, Reclaimed water quality during simulated ozone-managed aquifer recharge hybrid, *Environ. Earth Sci.*, 2015, 7795–7802, DOI: 10.1007/s12665-014-3412-5.

47 S. Echigo, M. Nakatsuji, Y. Takabe and S. Itoh, Effect of preozonation on wastewater reclamation by the combination of ozonation and soil aquifer treatment, *Water Sci. Technol.: Water Supply*, 2015, **15**(1), 101–106.

48 J. Hollender, S. G. Zimmermann, S. Koepke, M. Krauss, C. S. McArdell and C. Ort, *et al.* Elimination of Organic Micropollutants in a Municipal Wastewater Treatment Plant Upgraded with a Full-Scale Post-Ozonation Followed by Sand Filtration, *Environ. Sci. Technol.*, 2009, **43**(20), 7862–7869, DOI: 10.1021/es9014629.

49 J. E. Drewes and N. Horstmeyer, Strategien und Potenziale zur Energieoptimierung bei der Wasserwiederverwendung, *Österreichische Wasser- und Abfallwirtschaft.*, 2016, **68**(3–4), 99–107, DOI: 10.1007/s00506-016-0298-3.

50 C. Bertelkamp, K. Lekkerkerker-Teunissen, A. H. Knol, J. Q. J. C. Verberk, J. C. Van Dijk and C. J. Houtman, *Granular activated carbon filtration or ion exchange as pre-treatment option for the advanced oxidation process; advantages and limitations. In: American Water Works Association WQTC Conference Proceedings*, AWWA, Savannah, Georgia, 2010.

51 J. Scheideler, K. Lekkerkerker-Teunissen, T. Knol, A. Ried, J. Q. J. C. Verberk and H. C. Van Dijk, Combination of O3/H2O2 and UV for multiple barrier micropollutant treatment and bromate formation control – an economic attractive option, *Water Pract. Technol.*, 2011, **6**(4), 1–2, DOI: 10.2166/wpt.2011.0063.

52 K. Lekkerkerker-Teunissen, E. T. Chekol, S. K. Maeng, K. Ghebremichael, C. J. Houtman and A. R. D. Verliefde, *et al.*, Pharmaceutical removal during managed aquifer recharge with pretreatment by advanced oxidation, *Water Sci. Technol.: Water Supply*, 2012, **12**(6), 755–767.

53 K. Lekkerkerker-Teunissen, A. H. Knol, L. P. Van Altena, C. J. Houtman, J. Q. J. C. Verberk and J. C. Van Dijk, Serial ozone/peroxide/low pressure UV treatment for synergistic and effective organic micropollutant conversion, *Sep. Purif. Technol.*, 2012, **100**, 22–29.

54 K. Lekkerkerker-Teunissen, A. H. Knol, J. G. Derks, M. B. Heringa, C. J. Houtman and R. C. H. M. Hofman-Caris, *et al.*, Pilot Plant Results with Three Different Types of UV Lamps for Advanced Oxidation, *Ozone: Sci. Eng.*, 2013, **35**(1), 38–48, DOI: 10.1080/01919512.2013.721317.

55 *Schweizerische Eidgenossenschaft Bundesamt für Umwelt, Land Baden-Württemberg Ministerium für Umwelt Klima und Energiewirtschaft / Landesanstalt für Umwelt Baden-Würtemmberg. Rheinüberwachungsstation, Weil am Rhein*, [cited 2019 Jun 14], Available from: https://www.aue.bs.ch/umweltanalytik/rheinueberwachungsstation-weil-am-rhein.html.

56 J. R. Bolton, K. G. Bircher, W. Tumas and C. A. Tolman, Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Processes, *J. Adv. Oxid. Technol.*, 1996, **1**(1), 2548–2553, DOI: 10.1021/es062353p.

57 P. L. Brezonik and J. Fulkerson-Brekken, Nitrate-Induced Photolysis in Natural Waters: Controls on Concentrations of Hydroxyl Radical Photo-Intermediates by Natural Scavenging Agents, *Environ. Sci. Technol.*, 1998, **32**(19), 3004–3010, DOI: 10.1021/es9802908.

58 G. V. Buxton, C. L. Greenstock, W. P. Helman and A. B. Ross, Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O − in Aqueous Solution), *J. Phys. Chem. Ref. Data*, 1988, **17**(2), 513–886, DOI: 10.1063/1.555805.

59 D. B. Miklos, R. Hartl, P. Michel, K. G. Linden, J. E. Drewes and U. Hübner, UV/H2O2 process stability and pilot-scale validation for trace organic chemical removal from wastewater treatment plant effluents, *Water Res.*, 2018, **136**, 169–179, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0043135418301519.

60 W. Liu, S. A. Andrews, M. I. Stefan and J. R. Bolton, Optimal methods for quenching H2O2 residuals prior to UFC testing, *Water Res.*, 2003, **37**(15), 3697–3703.

61 M. R. Hoffmann and J. O. Edwards, Kinetics of the oxidation of sulfite by hydrogen peroxide in acidic solution, *J. Phys. Chem.*, 1975, **79**(20), 2096–2098.

62 H. Gallard and J. De Laat, Kinetic modelling of Fe(III)/H2O2 oxidation reactions in dilute aqueous solution using

atrazine as a model organic compound, *Water Res.*, 2000, **34**(12), 3107–3116.

63 A. L.-T. Pham, F. M. Doyle and D. L. Sedlak, Kinetics and efficiency of H2O2 activation by iron-containing minerals and aquifer materials, *Water Res.*, 2012, **46**(19), 6454–6462, Available from: http://linkinghub.elsevier.com/retrieve/pii/S004313541200663X.

64 R. Geschke and M. Zehringer, A new method for the determination of complexing agents in river water using HPLC, *Fresenius' J. Anal. Chem.*, 1997, **357**(6), 773–776, DOI: 10.1007/s002160050247.

65 S. A. Huber, A. Balz, M. Abert and W. Pronk, Characterisation of aquatic humic and non-humic matter with size-exclusion chromatography - organic carbon detection - organic nitrogen detection (LC-OCD-OND), *Water Res.*, 2011, **45**(2), 879–885, DOI: 10.1016/j.watres.2010.09.023.

66 M. M. Bazri, B. Barbeau and M. Mohseni, Impact of UV/H2O2 advanced oxidation treatment on molecular weight distribution of NOM and biostability of water, *Water Res.*, 2012, **46**(16), 5297–5304, DOI: 10.1016/j.watres.2012.07.017.

67 USP technologies, *Titanium Oxalate (Spectrophotometric)*, [cited 2019 Apr 10], Available from: http://www.h2o2.com/technical-library/analytical-methods/default.aspx?pid=71&name=Titanium-Oxalate-Spectrophotometric.

68 G. Eisenberg, Colorimetric Determination of Hydrogen Peroxide, *Ind. Eng. Chem., Anal. Ed.*, 1943, **15**(5), 327–328, DOI: 10.1021/i560117a011.

69 W. Jäggi, Die Bestimmung der CO2-Bildung als Mass der bodenbiologischen Aktivität, *Schweiz. Landwirtsch. Forsch.*, 1976, **15**, 371–380.

70 Agroscope, Band 2: Bodenuntersuchungen zur Standort-Charakterisierung, in *Schweizerische Referenzmethoden der Eidg landwirtschaftlichen Forschungsanstalten*, 2015th edn, 1996.

71 E. I. Prest, F. Hammes, S. Kötzsch, M. C. M. van Loosdrecht and J. S. Vrouwenvelder, Monitoring microbiological changes in drinking water systems using a fast and reproducible flow cytometric method, *Water Res.*, 2013, **47**(19), 7131–7142, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0043135413008361.

72 F. Hammes, F. Goldschmidt, M. Vital, Y. Wang and T. Egli, Measurement and interpretation of microbial adenosine triphosphate (ATP) in aquatic environments, *Water Res.*, 2010, **44**(13), 3915–3923, DOI: 10.1016/j.watres.2010.04.015.

73 B. A. Wols, D. J. H. Harmsen, J. Wanders-Dijk, E. F. Beerendonk and R. C. H. M. Hofman-Caris, Degradation of pharmaceuticals in UV (LP)/H2O2 reactors simulated by means of kinetic modeling and computational fluid dynamics (CFD), *Water Res.*, 2015, **75**, 11–24, DOI: 10.1016/j.watres.2015.02.014.

74 T. E. Doll, Photochemischer und photokatalytischer Abbau von Carbamazepin, Clofibrinsäure, Iomeprol und Iopromid, ed. Fritz H. Frimmel, Lehrstuhl für Wasserchemie und DVGW-Forschungsstelle am Engler-Bunte-Institut der Universität Karlsruhe (TH), Karlsruhe (Germany), 2004, vol. 42, p. 172.

75 F. X. Tian, B. Xu, Y. L. Lin, C. Y. Hu, T. Y. Zhang and N. Y. Gao, Photodegradation kinetics of iopamidol by UV irradiation and enhanced formation of iodinated disinfection by-products in sequential oxidation processes, *Water Res.*, 2014, **58**, 198–208, DOI: 10.1016/j.watres.2014.03.069.

76 S. Canonica, L. Meunier and U. von Gunten, Phototransformation of selected pharmaceuticals during UV treatment of drinking water, *Water Res.*, 2008, **42**(1–2), 121–128.

77 S. Bahnmüller, C. H. Loi, K. L. Linge, U. Gunten and S. Canonica, Degradation rates of benzotriazoles and benzothiazoles under UV-C irradiation and the advanced oxidation process UV/H2O2, *Water Res.*, 2015, **74**, 143–154, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135414008719.

78 I. Zucker, D. Avisar, H. Mamane, M. Jekel and U. Hübner, Determination of oxidant exposure during ozonation of secondary effluent to predict contaminant removal, *Water Res.*, 2016, **100**, 508–516, Available from: https://linkinghub.elsevier.com/retrieve/pii/S004313541630375X.

79 U. Hübner, S. Keller and M. Jekel, Evaluation of the prediction of trace organic compound removal during ozonation of secondary effluents using tracer substances and second order rate kinetics, *Water Res.*, 2013, **47**(17), 6467–6474.

80 E. J. Rosenfeldt and K. G. Linden, The R OH,UV Concept to Characterize and the Model UV/H2O2 Process in Natural Waters, *Environ. Sci. Technol.*, 2007, **41**(7), 2548–2553, DOI: 10.1021/es062353p.

81 J. Lati and D. Meyerstein, Oxidation of first-row bivalent transition-metal complexes containing ethylenediaminetetraacetate and nitrilotriacetate ligands by free radicals: a pulse-radiolysis study, *J. Chem. Soc., Dalton Trans.*, 1978(9), 1105–1118.

82 M. Sörensen, S. Zurell and F. H. Frimmel, Degradation Pathway of the Photochemical Oxidation of Ethylenediaminetetraacetate (EDTA) in the UV/H2O2-process, *Acta Hydrochim. Hydrobiol.*, 1998, **26**(2), 109–115, Available from: http://doi.wiley.com/10.1002/%28SICI%291521-401X%28199803%2926%3A2%3C109%3A%3AAID-AHEH109%3E3.0.CO%3B2-C.

83 *Müller B. ChemEQL (V. 3.2.1)*, Eawag, Dübendorf (Switzerland); 2015 [cited 2019 Apr 10], Available from: https://www.eawag.ch/en/department/surf/projects/chemeql/.

84 B. A. Wols, R. C. H. M. Hofman-Caris, D. J. H. Harmsen and E. F. Beerendonk, Degradation of 40 selected pharmaceuticals by UV/H2O2, *Water Res.*, 2013, **47**(15), 5876–5888, DOI: 10.1016/j.watres.2013.07.008.

85 J. M. Gleason, G. McKay, K. P. Ishida and S. P. Mezyk, Temperature dependence of hydroxyl radical reactions with chloramine species in aqueous solution, *Chemosphere*, 2017, **187**, 123–129, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0045653517312754.

86 H. Herrmann, D. Hoffmann, T. Schaefer, P. Bräuer and A. Tilgner, Tropospheric Aqueous-Phase Free-Radical Chemistry: Radical Sources, Spectra, Reaction Kinetics and Prediction Tools, *ChemPhysChem*, 2010, **11**(18), 3796–3822, DOI: 10.1002/cphc.201000533.

87 B. A. Wols, D. J. H. Harmsen, J. Wanders-Dijk, E. F. Beerendonk and C. H. M. Hofman-Caris, Degradation of pharmaceuticals in UV (LP)/H2O2 reactors simulated by means of kinetic modeling and computational fluid dynamics (CFD), *Water Res.*, 2015, 75(0), 11–24, DOI: 10.1016/j.watres.2015.02.014.

88 R. Zellner, M. Exner and H. Herrmann, Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H2O2 at 308 and 351 nm in the temperature range 278?353 K, *J. Atmos. Chem.*, 1990, **10**(4), 411–425, DOI: 10.1007/BF00115783.

89 Z. He, *UV Lamp Temperature Characteristics*, IUVA News, 2012, vol. 144, pp. 13–7, Available from: https://iuvanews.com/stories/pdf/archives/140401He_Article_2012.pdf.

90 Eidgenössische Departement des Innern (EDI), *Verordnung des EDI über Trinkwasser sowie Wasser in öffentlich zugänglichen Bädern und Duschanlagen (TBDV)*, 817.022.11, Switzerland, 2018, [cited 2019 Ar 10], pp. p1–24, Available from: https://www.admin.ch/opc/de/classified-compilation/20143396/index.html.

91 C. Götz, J. Otto and H. Singer, Überprüfung des Reinigungseffekts, *Aqua Gas*, 2015, **2**, 34–40.

92 J. L. Kormos, M. Schulz and T. A. Ternes, Occurrence of Iodinated X-ray Contrast Media and Their Biotransformation Products in the Urban Water Cycle, *Environ. Sci. Technol.*, 2011, **45**(20), 8723–8732, DOI: 10.1021/es2018187.

93 A. G. Asimakopoulos, A. Ajibola, K. Kannan and N. S. Thomaidis, Occurrence and removal efficiencies of benzotriazoles and benzothiazoles in a wastewater treatment plant in Greece, *Sci. Total Environ.*, 2013, **452–453**, 163–171, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0048969713002234.

94 S. Tisler and C. Zwiener, Formation and occurrence of transformation products of metformin in wastewater and surface water, *Sci. Total Environ.*, 2018, **628–629**, 1121–1129, DOI: 10.1016/j.scitotenv.2018.02.105.

95 C. Trautwein and K. Kümmerer, Incomplete aerobic degradation of the antidiabetic drug Metformin and identification of the bacterial dead-end transformation product Guanylurea, *Chemosphere*, 2011, **85**(5), 765–773, DOI: 10.1016/j.chemosphere.2011.06.057.

96 M. Markiewicz, C. Jungnickel, S. Stolte, A. Białk-Bielińska, J. Kumirska and W. Mrozik, Primary degradation of antidiabetic drugs, *J. Hazard. Mater.*, 2017, **324**, 428–435.

97 B. Blair, A. Nikolaus, C. Hedman, R. Klaper and T. Grundl, Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment, *Chemosphere*, 2015, **134**, 395–401, DOI: 10.1016/j.chemosphere.2015.04.078.

98 A. Kot-Wasik, A. Jakimska and M. Śliwka-Kaszyńska, Occurrence and seasonal variations of 25 pharmaceutical residues in wastewater and drinking water treatment plants, *Environ. Monit. Assess.*, 2016, **188**(12), 1–13, DOI: 10.1007/s10661-016-5637-0.

99 M. Scheurer, A. Michel, H. J. Brauch, W. Ruck and F. Sacher, Occurrence and fate of the antidiabetic drug metformin and its metabolite guanylurea in the environment and during drinking water treatment, *Water Res.*, 2012, **46**(15), 4790–4802.

100 J. E. Drewes, D. Li, J. Regnery, M. Alidina, A. Wing and C. Hoppe-Jones, Tuning the performance of a natural treatment process using metagenomics for improved trace organic chemical attenuation, *Water Sci. Technol.*, 2014, **69**(3), 628–633.

101 U. Hübner, U. von Gunten and M. Jekel, Evaluation of the persistence of transformation products from ozonation of trace organic compounds – A critical review, *Water Res.*, 2015, **68**, 150–170, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135414006939.

102 U. Hübner, B. Seiwert, T. Reemtsma and M. Jekel, Ozonation products of carbamazepine and their removal from secondary effluents by soil aquifer treatment – Indications from column experiments, *Water Res.*, 2014, **49**(1), 34–43, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135413009275.

103 *Biodegradable Organic Matter in Drinking Water Treatment and Distribution*, ed. M. Prévost, P. Laurent, P. Servais and J.-C. Joret, AWWA, Denver (CO), 2005, vol. xiii, p. 300.

104 H.-C. Lin and G.-S. Wang, Effects of UV/H2O2 on NOM fractionation and corresponding DBPs formation, *Desalination*, 2011, **270**(1–3), 221–226, DOI: 10.1016/j.desal.2010.11.049.

105 A. D. Dotson, O. S. Keen, D. Metz and K. G. Linden, UV/H2O2 treatment of drinking water increases post-chlorination DBP formation, *Water Res.*, 2010, **44**(12), 3703–3713, DOI: 10.1016/j.watres.2010.04.006.

106 R. Toor and M. Mohseni, UV-H2O2 based AOP and its integration with biological activated carbon treatment for DBP reduction in drinking water, *Chemosphere*, 2007, **66**(11), 2087–2095.

107 S. R. Sarathy, M. M. Bazri and M. Mohseni, Modeling the Transformation of Chromophoric Natural Organic Matter during UV/H2O2 Advanced Oxidation, *J. Environ. Eng.*, 2011, **137**(10), 903–912.

108 C. von Sonntag and U. von Gunten, *Chemistry of Ozone in Water and Wastewater Treatment: From Basic Principles to Applications*, ed. C. von Sonntag and U. von Gunten, Water Intelligence Online, IWA Publishing, London, 2012, p. 302, Available from: http://wio.iwaponline.com/cgi/doi/10.2166/9781780400839.

109 C. Prasse, B. Ford, D. K. Nomura and D. L. Sedlak, Unexpected transformation of dissolved phenols to toxic dicarbonyls by hydroxyl radicals and UV light, *Proc. Natl. Acad. Sci. U. S. A.*, 2018, **115**(10), 2311–2316, DOI: 10.1073/pnas.1715821115.

110 A. Parkinson, M. J. Barry, F. A. Roddick and M. D. Hobday, Preliminary toxicity assessment of water after treatment with uv-irradiation and UVC/H2O2, *Water Res.*, 2001, **35**(15), 3656–3664, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0043135401000963.

111 E. H. Goslan, F. Gurses, J. Banks and S. A. Parsons, An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes, *Chemosphere*,

2006, **65**(7), 1113–1119, Available from: http://linkinghub.elsevier.com/retrieve/pii/S0045653506005042.

112 K. Hellauer, J. Uhl, M. Lucio, P. Schmitt-Kopplin, D. Wibberg and U. Hübner, *et al.*, Microbiome-Triggered Transformations of Trace Organic Chemicals in the Presence of Effluent Organic Matter in Managed Aquifer Recharge (MAR) Systems, *Environ. Sci. Technol.*, 2018, **52**(24), 14342–14351.

113 W. A. M. Hijnen, E. F. Beerendonk and G. J. Medema, Inactivation credit of UV radiation for viruses, bacteria and protozoan (oo)cysts in water: A review, *Water Res.*, 2006, **40**(1), 3–22.

114 US EPA, *Ultraviolet Disinfection Guidance Manual for the Final Long Term 2 Enhanced Surface Water Treatment Rule (EPA 815-R-06-007)*, 2006 [cited 2019 Apr 10], Available from: https://nepis.epa.gov.

115 G. Chevrefils, É. Caron, H. Wright, G. Sakamoto, P. Payment and B. Barbeau, *et al.*, *UV Dose Required to Achieve Incremental Log Inactivation of Bacteria, Protozoa and Viruses*, IUVA News, 2006, vol. 81, pp. 38–45.

116 K. Lautenschlager, C. Hwang, F. Ling, W.-T. Liu, N. Boon and O. Köster, *et al.* Abundance and composition of indigenous bacterial communities in a multi-step biofiltration-based drinking water treatment plant, *Water Res.*, 2014, **62**, 40–52, Available from: https://linkinghub.elsevier.com/retrieve/pii/S0043135414003960.

117 F. Wang, D. van Halem, G. Liu, K. Lekkerkerker-Teunissen and J. P. van der Hoek, Effect of residual H2O2 from advanced oxidation processes on subsequent biological water treatment: A laboratory batch study, *Chemosphere*, 2017, **185**, 637–646, DOI: 10.1016/j.chemosphere.2017.07.073.

