Chlorothalonil transformation products in drinking water resources: Widespread and challenging to abate

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ABSTRACT

Chlorothalonil, a fungicide applied for decades worldwide, has recently been banned in the European Union (EU) and Switzerland due to its carcinogenicity and the presence of potentially toxic transformation products (TPs) in groundwater. The spread and concentration range of chlorothalonil TPs in different drinking water resources was examined (73 groundwater and four surface water samples mainly from Switzerland). The chlorothalonil sulfonic acid TPs (R471811, R419492, R417888) occurred more frequently and at higher concentrations (detected in 65–100% of the samples, $\leq$2200 ngL^{-1}) than the phenolic TPs (SYN507900, SYN548580, R611968; detected in 10–30% of the samples, $\leq$130 ngL^{-1}). The TP R471811 was found in all samples and even in 52% of the samples above 100 ngL^{-1}, the drinking water standard in Switzerland and other European countries. Therefore, the abatement of chlorothalonil TPs was investigated in laboratory and pilot-scale experiments and along the treatment train of various water works, comprising aquifer recharge, UV disinfection, ozonation, advanced oxidation processes (AOPs), activated carbon treatment, and reverse osmosis. The phenolic TPs can be abated during ozonation (second order rate constant k_{O3} ~10^4 M^{-1}s^{-1}) and by reaction with hydroxyl radicals (•OH) in AOPs (k_{OH} ~10^9 M^{-1}s^{-1}). In contrast, the sulfonic acid TPs, which occurred in higher concentrations in drinking water resources, react only very slowly with ozone (k_{O3} <0.04 M^{-1}s^{-1}) and •OH (k_{OH} <5.0 × 10^7 M^{-1}s^{-1}) and therefore persist in ozonation and •OH-based AOPs. Activated carbon retained the very polar TP R471811 only up to a specific throughput of 25 m^{3}kg^{-1} (20% breakthrough), similarly to the X-ray contrast agent diatrizoic acid. Reverse osmosis was capable of removing all chlorothalonil TPs by $\geq$98%.

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1. Introduction

Chlorothalonil, a broad-spectrum fungicide, has recently been banned in the EU and Switzerland because of its carcinogenic properties, the risks to fish and amphibians, and the expected contamination of groundwater with chlorothalonil TPs (BLW, 2019a; European Commission, 2019). In Switzerland, chlorothalonil had predominantly been used for grain and vegetable cultivation, but its use had also been approved for viticulture and non-agricultural land. Chlorothalonil has been applied in high

amounts for decades (first registration in the USA in 1966) (EPA, 1999), as shown by the sales data in Switzerland (45 t/a, 2017) and Germany (1000–2500 t/a, 2017), where chlorothalonil was among the ten most sold pesticides in 2017 (BLW, 2019b; BVL, 2018).

Due to the toxicity of the parent compound and insufficient toxicological data for the TPs, the European Food Safety Agency (EFSA) recommended to provisionally classify chlorothalonil TPs as relevant pesticide TPs in 2018 (EFSA, 2018), implying an EU drinking water standard of 100 ngL^{-1} (European Commission, 1998). To our knowledge, the EU member states have not yet decided on the drinking water relevance of chlorothalonil TPs; e.g. in Germany the previous classification as non-relevant or not evaluated still applies, resulting in a higher drinking water standard. However, some European countries, such as Denmark and France, apply the same

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drinking water standard of 100 ngL^{-1} to all pesticide TPs. Some non-European countries, e.g. Australia and the USA, define individual, risk-based thresholds, but so far only for a limited number of pesticides and TPs (Laabs et al., 2015). As recommended by the European Commission (2019), Switzerland recently classified chlorothalonil as carcinogen category 1B, thereby declaring all groundwater TPs as relevant (irrespectively of their toxicity), following the EU guidance document Sanco/221/2000 –rev.10-final (European Commission, 2003).

To reduce drinking water contamination with organic micropollutants, various treatment processes exist, such as (i) managed aquifer recharge (Hollender et al., 2018; Maeng et al., 2011), (ii) activated carbon treatment (Delgado et al., 2012; Westerhoff et al., 2005), (iii) ozonation (Hübner et al., 2012; von Gunten, 2003; von Sonntag and von Gunten, 2012; Westerhoff et al., 2005), (iv) AOPs, e.g. UV/H$_2$O$_2$, O$_3$/H$_2$O$_2$, UV/Cl$_2$ (Chuang et al., 2017; Guo et al., 2018; Huber et al., 2003; Miklos et al., 2018; Stefan, 2018; von Gunten, 2018), and (v) membrane processes such as nanofiltration and reverse osmosis (Taheran et al., 2016). Treatment efficiency strongly depends on physical-chemical properties of a compound. Managed aquifer recharge is most effective for less polar and well-degradable compounds (Benotti et al., 2012; Maeng et al., 2011); similarly, activated carbon filtration retains especially semi- to non-polar micropollutants (Westerhoff et al., 2005). While the oxidant ozone (O$_3$) selectively transforms mainly electron-rich compounds (e.g. phenols), •OH produced during ozone decomposition and in AOPs are less selective and react with a broader spectrum of organic compounds (von Sonntag and von Gunten, 2012). While these oxidative methods may only partially abate the micropollutant load and can produce reaction products, reverse osmosis is capable of removing most micropollutants to a large extent. However, operational costs of reverse osmosis systems are high (Taheran et al., 2016) and the highly-concentrated reject water that is produced requires disposal (Umar et al., 2014).

In a recent suspect screening for more than 1000 pesticide TPs (including >25 chlorothalonil TPs) in Swiss groundwater, we have detected eight different chlorothalonil TPs, six of them reported for the first time (Kiefer et al., 2019). The chlorothalonil TP R471811 was even found in all 31 groundwater samples with concentrations up to 2700 ngL^{-1}. Due to the high usage of chlorothalonil worldwide, chlorothalonil TPs may be a widespread threat for drinking water quality. However, the efficiency of water treatment processes to abate chlorothalonil TPs from drinking water have not yet been evaluated.

Therefore, we aimed to investigate the abatement of sulfonic acid- and phenol-containing chlorothalonil TPs from water in full-scale waterworks, pilot plants, and laboratory experiments. Our hypothesis was that the more electron-poor and more polar sulfonic acid TPs (exhibiting at least one sulfonic acid group; R471811-SA, R419492-SA, R417888-SA, and two isomers of R417888-SA; "SA" for sulfonic acid) are probably more recalcitrant during oxidative or adsorptive treatment. In contrast, the less polar phenolic TPs (SYN507900-Ph, SYN548580-Ph, R611968-Ph, "Ph" for phenol) are probably abated more efficiently by oxidation or adsorption, as previously shown for other phenolic compounds (Kovalova et al., 2013a; Lee et al., 2005). First, chlorothalonil TPs were monitored in different drinking water resources such as in lakes, rivers, and groundwater to obtain more information on the scope of chlorothalonil TPs contamination. Second, the fate of chlorothalonil TPs in a full-scale water treatment train consisting of activated carbon, ozonation, and UV disinfection was investigated. Additional laboratory and pilot-scale experiments were carried out to supplement the full-scale observations regarding activated carbon, ozonation, and UV disinfection and to test additional advanced treatment processes (AOPs, reverse osmosis).

2. Materials and methods

2.1. Drinking water resources and waterworks

To investigate the fate of chlorothalonil TPs in water treatment, samples were taken along the treatment train of eight waterworks (Table SI-A1) in February 2019. Waterworks A abstracts raw water from the river Rhine. Suspended matter is removed in a settling pond followed by a rapid sand filter. Then, the clarified water is infiltrated into the aquifer, abstracted again (average residence time: days to two months) and filtered via three granular activated carbon filters (specific throughput at the time of sampling: 25, 55, 305 m^{3}kg^{-1}). A final disinfection is performed with a medium pressure UV lamp. Waterworks B treats raw water from a karstic spring with ozonation (0.8 g O$_3$ g^{-1} DOC (dissolved organic carbon)) followed by two granular activated carbon filters (specific throughput at the time of sampling: 23, 215 m^{3}kg^{-1}). Waterworks C uses Lake Zurich water (abstraction point 30 m below the lake surface), which is ozonated in two steps (pre- and intermediate ozonation) with different specific ozone doses (0.3 and 0.6 g O$_3$ g^{-1} DOC). Ozonation is followed by twelve granular activated carbon filters (average specific throughput at the time of sampling: 1200 m^{3}kg^{-1}, i.e. mainly biological and not adsorptive filters) and slow sand filtration. Waterworks D abstracts river bank filtrate from the river Limmat (outflow of Lake Zurich, Switzerland). The bank filtrate is disinfected (Cl$_2$/ClO$_2$), infiltrated into the aquifer and abstracted again. In addition, seven groundwater abstraction wells and four springs were sampled in Switzerland. The water from these wells or springs is delivered to the consumer as drinking water either without further treatment, with only minor treatment (UV disinfection), or after mixing with water from other sources (Table SI-A1, waterworks E-I).

Samples were collected in laboratory glass bottles (previously annealed at 500 °C; 500 mL bottles, SIMAX Kavalier, Czech Republic) in February 2019 and then frozen at −20 °C until sample enrichment and measurement. Six field blanks, consisting of ultrapure water (>18 MΩcm, Barnstead Nanopure Diamond system and Elga Purelab Chorus) filled in sampling bottles, transferred to a second bottle during sampling, and frozen until enrichment and measurement, did not show detectable concentrations of the target analytes, demonstrating that no contamination occurred during sample handling and analysis. Furthermore, rain water from Dübendorf (vicinity of Zurich, 431 m above sea level, Switzerland) and Jungfraujoch (3571 m above sea level, Switzerland) was collected and analysed as background controls from hypothetically uncontaminated field sources. Since evian® water is used in many laboratories for calibration standard preparation, additionally evian® water (bottled in polyethylene terephthalate, PET) was enriched and analysed as a blank sample.

To investigate the occurrence of chlorothalonil TPs in groundwater (the major drinking water resource in Switzerland), we also present semi-quantitative data for 60 groundwater samples, collected in May and August 2018 within the Swiss National Groundwater Monitoring NAQUA (www.bafu.admin.ch/naqua). The 60 groundwater monitoring sites were selected based on long-term monitoring data. Twenty sites were known to have very low overall micropollutant concentrations, whereas 40 sites were chosen because micropollutants from urban or agricultural sources had been detected in the past. These samples were analysed using a comparable analytical method as described in section 2.4.

2.2. Stock solutions and chemicals

Stock solutions for liquid chromatography high-resolution tandem mass spectrometry (LC-HRMS/MS) analyses were prepared

depending on compound solubility in ethanol, methanol or ethanol/water (1:1, volumetrically) at a concentration of 0.1 or 1 gL^{-1}. As organic solvents may influence ozonation and photo-degradation experiments, stock solutions for laboratory experiments (except for activated carbon) were prepared in water (20−100 μM corresponding to 0.005−0.035 gL^{-1}). For details, see SI-A2.

Six chlorothalonil TPs (Fig. 1), reported by Kiefer et al. (2019) in groundwater and for which reference material was available (ASCA GmbH, Germany; Syngenta, Switzerland), were analysed in the environmental water samples (section 2.1). The TPs differ in their functional groups (Fig. 1). All TPs contain at least one amide group, three of the TPs have at least one hydroxyl group (phenolic TPs), whereas the other three TPs are characterized by at least one sulfonic acid group (sulfonic acid TPs). For the laboratory experiments, two phenolic TPs (R611968-Ph, SYN507900-Ph) and two sulfonic acid TPs (R471811-SA, R417888-SA) were selected as test compounds and it was assumed that structurally related TPs would behave similarly during water treatment. The four TPs were selected due to lower measurement uncertainty compared to R419492-SA and SYN548580-Ph.

2.3. Laboratory and pilot-scale experiments

Abatement of micropollutants with ozone or to a lesser extent with ·OH or degradation by UV photolysis can depend on the speciation of organic compounds such as phenols. For the phenolic TPs considered here (R611968-Ph and SYN507900-Ph), experimentally determined acid-base equilibrium constants (pK$_a$) were not available, so the exact speciation under environmentally relevant pH values is not known. However, the predicted pK$_a$ values (4.1

and 4.7, Fig. 1; predicted with JChem for Office, version 17.1.2300.1455, ChemAxon Ltd.) are more than two units below environmentally relevant pH values, indicating the dominance of the anionic phenolate species (>99%). To obtain data applicable to most waterworks, all laboratory experiments were conducted at pH 7.5 using a 5 mM phosphate buffer, unless stated otherwise. Laboratory experiments were performed individually for each compound, unless stated otherwise. Samples from laboratory or pilot-scale experiments were analysed without prior enrichment.

2.3.1. UVC irradiation

Photodegradation under UVC irradiation (four RPR-2537A lamps centered around 254 nm, Rayonet, Southern New England Ultraviolet Company, Branford, USA, emission spectrum in Fig. SI-A1) was carried out in a merry-go-round photoreactor (Rayonet, Southern New England Ultraviolet Company, Branford, USA) and by back-to-front light exposure. Temperature was kept constant (12 ± 2 °C, typical for groundwater in Central Europe). Depending on the reactivity, TPs (0.1 μM, pH 7.5) were irradiated for 40−150 min in quartz test tubes (diameter: 1.3 cm, length: 7 cm). Photon fluence rates were determined by chemical actinometry using atrazine as described by Zepp, 1978 (pH 7.0, 5 mM phosphate buffer; quantum yield: 0.046 molE^{-1}, Hessler et al. (1993), molar absorption coefficient: 3860 M^{-1}cm^{-1} at 254 nm, Nick et al. (1992)). Atrazine shows similar phototransformation rates as the phenolic TPs, is easy to handle and analyse, and was successfully tested and compared to the actinometer hydrogen peroxide by Canonica et al. (2008). The photon fluence rate was 4.0−5.3 × 10^{-5} Em^{-2}s^{-1} (determined on different days). For details, including light emission spectra and absorbance spectra of
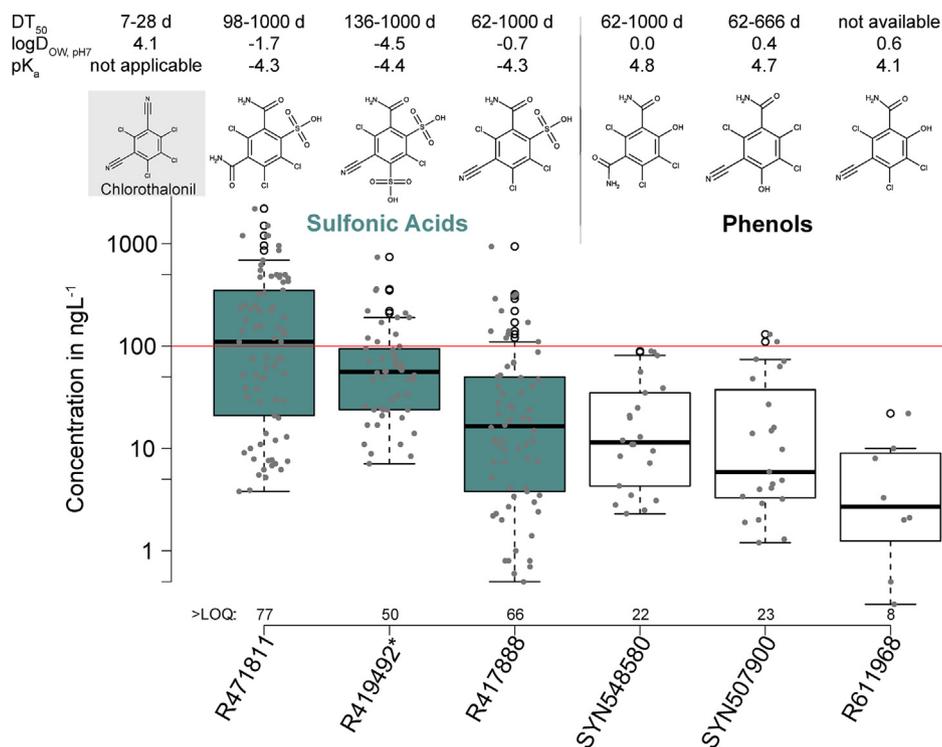

Fig. 1. Concentration distribution of different chlorothalonil TPs in 77 samples (73 x groundwater, 4 x surface water). Non-detects (LOQs: 0.2−5 ngL^{-1}) are not included in the boxplots. The sulfonic acid-containing TPs (on the left in green) were more frequently detected and at higher concentrations than the phenol-containing TPs (on the right in white). The red line marks the Swiss drinking water standard. The open circles represent outliers. The gray solid circles show the concentrations of individual samples. Dissipation time DT$_{50}$ from EFSA (2018), logD$_{OW, pH7}$ (water-n-octanol distribution coefficient considering the speciation at pH 7) and pK$_a$ (acid dissociation constant) were predicted with JChem for Office (Version 17.1.2300.1455; ChemAxon Ltd.). *R419492: high measurement uncertainty (~0.5-2 × reported concentration). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

chlorothalonil TPs and data analysis for photon fluence rates, quantum yields, and photon fluence-based rate constants, see SI-A5.

2.3.2. Ozonation

To determine the second order rate constant (k_{O3}) for the reaction of ozone with the slowly-reacting sulfonic acid TPs (R471811-SA, R417888-SA), TPs were exposed to ozone in excess at pH 2.3 (0.1 μM TP, 100 μM ozone, 10 mM phosphoric acid, 10 mM tert-butanol to scavenge •OH) in a 250 mL glass bottle with a dispenser system (Hoigné and Bader, 1994). Acidic conditions were selected as ozone is more stable at low pH (von Sonntag and von Gunten, 2012) and the sulfonic acid TPs do not change their speciation over a wide pH range (predicted pK_a −4.3, Fig. 1). The ozone concentration and TP abatement were monitored over 15 h (for details, see SI-A6).

The reaction kinetics for the faster reacting phenolic TPs (SYN507900-Ph, R611968-Ph) were investigated by competition kinetics using salicylic acid as a competitor ($k_{O3} = 2.8 \times 10^4 \, M^{-1}s^{-1}$, Hoigné and Bader (1983)). Phenolic TPs (1 μM) and salicylic acid (1 μM) were exposed to varying ozone doses (0–4.5 μM) at pH 7.5 in 10 mL glass vials in presence of tert-butanol (50 mM, to scavenge •OH) (for details, see SI-A7). Other compounds for which reliable second order rate constants were reported (e.g. carbamazepine, clarithromycin) were also tested or considered as competitors but finally not used, either due to higher reactivity with ozone (carbamazepine, $k_{O3} = 3 \times 10^5 \, M^{-1}s^{-1}$, Huber et al. (2003)) or analytical problems (clarithromycin). Direct measurement of the second order rate constant with ozone (similar approach as for the sulfonic acid TPs) was not feasible for the phenolic TPs because these reactions are too fast to be observed in batch reactors at environmentally relevant pH values.

2.3.3. Advanced oxidation

To evaluate the potential of AOPs, the second order rate constants were determined for the reactions of •OH (k_{OH}) with the TPs. •OH can be produced by a combination of hydrogen peroxide (H_2O_2) with UV irradiation or ozone, or at high pH directly from ozone (Rosenfeldt and Linden, 2004; Staehelin and Hoigne, 1982). Here, TPs (0.1 μM) were exposed to H_2O_2 (1 mM) at pH 7.5 in a comparable reactor set-up as for UVC photodegradation experiments (section 2.3.1; here: UVA light with emission peak at 367 nm). To reduce the experimental effort, R471811-SA and SYN507900-Ph, and R417888-SA and R611968-Ph, respectively, were exposed to UVA/H_2O_2 in the same vials. The second order rate constant k_{OH} was determined by competition kinetics using benzoic acid as a reference compound exhibiting similar reactivity as the TPs (10 μM, $k_{OH} = 5.9 \times 10^9 \, M^{-1} s^{-1}$, Buxton et al. (1988)) (for details, see SI-A9).

Using this experimental set-up, the sulfonic acid TPs showed no degradation, probably because the •OH concentration was too low (10^{-15} M). Thus, the second order rate constants for sulfonic acid TPs were determined by exposure to higher •OH concentrations produced from ozone (0–80 μM) under alkaline conditions (pH ~10, 0.3 mM NaOH), with the X-ray contrast agent diatrizoic acid as a competitor. Diatrizoic acid was selected as a competitor due to its low reactivity ($k_{OH} = 5.4 \times 10^8 \, M^{-1}s^{-1}$, Real et al. (2009)), which is of similar order of magnitude as that expected for the sulfonic acid TPs. Degradation by ozone could be excluded due to the low stability of ozone at pH ~10 and the very low ozone reactivity of both diatrizoic acid (k_{O3} 0.05 $M^{-1}s^{-1}$, Real et al. (2009)) and sulfonic acid TPs (<0.04 $M^{-1}s^{-1}$, see section 3.3.1 and Table 1). For details, see SI-A8.

2.3.4. Activated carbon

The potential of adsorption to activated carbon was evaluated by conducting powdered activated carbon batch experiments. As the experimental set-up does not take into account kinetic effects, adsorption might be overestimated compared to granular activated carbon filters. In order to compare not only the adsorption behaviour between the chlorothalonil TPs but also relative to other micropollutants present in many waterworks, the herbicide atrazine and the X-ray contrast agent diatrizoic acid were also included in the experiments as reference compounds. Adsorption to activated carbon is affected by the water matrix and micropollutant concentration (Delgado et al., 2012; Knappe et al., 1998). To simulate real water conditions as closely as possible, groundwater (DOC 1.1 mgL^{-1}, electrical conductivity 840 μScm^{-1}) was spiked to a target concentration of ~500 ngL^{-1} for each TP (test solution <0.05% MeOH). Adsorption experiments were not performed for each chlorothalonil TP individually because it was assumed that the competition for adsorption sites between the chlorothalonil TPs and natural organic matter (NOM; low mgL^{-1} range) and further anthropogenic micropollutants affects the adsorption to a larger extent than the competition between the individual chlorothalonil TPs (ngL^{-1} range). The test solution (17 mL spiked groundwater, 34−680 μL activated carbon suspension, 0−646 μL ultrapure water) was stirred for 42 h in closed glass vials with varying powdered activated carbon doses (0−40 mgL^{-1}, Eurocarb CC PHO 8x30, added as suspension). The chlorothalonil TP concentration in the supernatant solution was determined after filtration (Chromafil® Xtra RC-20/13, 0.2 μm).

2.3.5. Reverse osmosis

Reverse osmosis was investigated in a pilot-scale experiment at the waterworks E (Table SI-A1). Raw water originated from groundwater that was highly contaminated with chlorothalonil TPs (total concentration ~2000 ngL^{-1}). The raw water was pumped through a spiral wound reverse osmosis membrane (TMG20D-400, Toray Membrane Europe AG, Switzerland) with a pre-filter (PP95BL5L2005, Everblue, Italy), recovering 38−65% as permeate (permeate flow rate 12.9−14.0 Lmin^{-1}, for details, see SI−B10). Within a period of fourteen weeks, five raw water, five permeate, and three reject water samples were taken. Between sampling campaign two and three, the membrane was exchanged due to clogging because the antiscalant (ROPUR RPI-3000A, Toray Membrane Europe AG, Switzerland) had not correctly been dosed.

2.4. Analytical methods

2.4.1. Enrichment of environmental samples

Environmental samples were enriched via vacuum-assisted evaporative concentration using a Syncore® Analyst (BÜCHI, Switzerland) according to the method validated by Mechelke et al. (2019) with slight modifications. A sample volume of 120 mL was spiked with 221 isotope-labelled internal standards (100 ngL^{-1}) and evaporated into BÜCHI glass vials (1 mL appendix cooled at 7−10 °C) at 20 mbar and 45 °C to ~1 mL using a back-flush unit. The sample volume was adjusted to 1.2 mL with ultrapure water. To reduce analyte loss by sorption to the glass surface, the BÜCHI vials were rinsed thoroughly with the sample. Then, the sample was centrifuged at 3720 g (Heraeus Megafuge 1.0 R, Thermo Fisher Scientific, U.S.) for 15 min in annealed centrifuge vials. The supernatant was transferred to 1.5 mL vials (with screw caps; BGB Analytik AG, Switzerland) and kept at 8 °C until measurement. Analogous to the environmental samples, 17 calibration standards (0.1−2000 ngL^{-1} in ultrapure water), seven laboratory and field

blank samples, one evian®, two rain water samples, and nine spiked samples (10, 100, 250, 500 ngL^{-1}) were prepared and analysed.

2.4.2. HPLC-MS/MS and HPLC-UV analyses

2.4.2.1. Environmental samples.
Analytes were separated with high-performance LC (HPLC) on a reverse phase C18 column (Atlantis® T3 3 μm, 3.0 × 150 mm; Waters, Ireland) with water and methanol as eluents, both modified with 0.1% concentrated formic acid. The injection volume was 150 μL corresponding to 15 mL of the original water sample. Samples were analysed in sequence, first in negative, then in positive electrospray ionization mode (−2.5/3.5 kV) on an Orbitrap high-resolution mass spectrometer (Fusion Lumos, Thermo Fisher Scientific, U.S.).

2.4.2.2. Laboratory and pilot experiments.
Samples from ozonation, UV irradiation and advanced oxidation experiments were spiked with isotope-labelled internal standards (2500 ngL^{-1}) and then measured with the same analytical method as the environmental samples, except for a lower injection volume (100 μL). Additionally, the first 5 min of the HPLC run were directed to the waste to reduce interferences from the phosphate buffer. Samples from experiments conducted at elevated TP concentration (1 μM) were diluted by a factor of ten.

The adsorption experiments with activated carbon (section 2.3.4) were measured with another analytical method at the Laboratory for Operation Control and Research (Zweckverband Landeswasserversorgung, Germany). For chromatographic separation an Ultra Aqueous C18 column (5 μm, 4.6 × 250 mm; Restek, U.S.) was used with an injection volume of 100 μL and with water and acetonitrile as eluents, each acidified with 0.1% concentrated formic acid. Analytes were ionized using electrospray (4.5/-4.5 kV) in switching mode and detected with a triple quadrupole mass spectrometer (API 5500 Qtrap, Sciex, U.S.).

Samples from the reverse osmosis pilot plant were analysed at the Water and Soil Protection Laboratory (Office of Water and Waste Management of the Canton of Berne) for four pesticide TPs with high concentrations (chlorothalonil TPs R471811-SA and R417888-SA, chloridazon-desphenyl, chloridazon-desphenyl-methyl) using a comparable LC-HRMS/MS method (injection volume 100 μL; Atlantis® T3 3 μm, 3.0 × 150 mm; Waters, Ireland; QExactive, Thermo Fisher Scientific, U.S.). Selected samples were additionally measured at Eawag (comparable method to environmental samples, without enrichment). Major cations and anions were analysed at the Eawag apprenticeship laboratory.

The actinometer atrazine (section 2.3.1) was analysed on a Dionex UltiMate 3000 RS HPLC system coupled to a diode array detector (Thermo Fisher Scientific, U.S.) using a reverse phase C18 column (Atlantis® T3 3 μm, 3.0 × 150 mm; Waters, Ireland). Data was processed with the Chromeleon 7.2.1 Software. For details on HPLC-MS/MS and HPLC-UV analyses, see SI-A3.

2.4.3. Quantification

Samples measured with HPLC-MS/MS were quantified using TraceFinder 4.1 (Thermo Fisher Scientific, U.S.) and MultiQuant 3.0.3 (Sciex, U.S.), as appropriate. For each analyte and measurement, an isotope-labelled internal standard was selected for quantification that eluted at a similar retention time as the analyte and resulted in a relative recovery close to 100% and high reproducibility across different spiked samples (for more details, see Kiefer et al. (2019) or SI-A4). Quantification results including limits of quantification (LOQs, 0.2–10 ngL^{-1} in environmental samples), relative recoveries (average 85–110% and relative standard deviation <20% across spiked samples in environmental samples) and isotope-labelled internal standards are provided in SI−B1 and

SI−B2.

The chlorothalonil TPs R419492-SA and SYN548580-Ph were quantified retrospectively because reference material was received after analysis. For quantification and quality control, eleven calibration standards, one blank sample, six samples from drinking water treatment and six corresponding spiked samples were enriched and analysed (section 2.4.1 and 2.4.2). This calibration model was applied to the previously measured samples. The concentration of SYN548580-Ph deviated less than 20% in the six samples, which were measured twice. However, in case of R419492-SA, the concentration results differed by a factor of two. Due to the early retention time of R419492-SA, a suitable internal standard was not available. Therefore, R419492-SA concentrations were multiplied by two in the retrospectively quantified samples. It should be noted that measurement uncertainty for R419492 is expected to be higher (~0.5-2 × reported concentration) than in case of the other chlorothalonil TPs (~0.7-1.5 × reported concentration). The abatement of chlorothalonil TPs in the waterworks was compared to the abatement of the sweetener acesulfame and the X-ray contrast agent diatrizoic acid. In contrast to acesulfame, diatrizoic acid could not be quantified because reference material for diatrizoic acid was not included in the multi-component standard solution for quantification of the environmental samples. However, abatement was calculated from differences in the response ratios of diatrizoic acid and its structurally identical isotope-labelled internal standard before and after treatment.

To estimate the error of the calculated abatement efficiencies in water treatment due to measurement uncertainty, each sample taken along the treatment train was measured in triplicate. The uncertainty in removal was calculated based on the standard deviation of the measurement triplicates using Gaussian error propagation. In addition, three samples were enriched and measured in triplicate to assess the reproducibility of sample enrichment. The standard deviations of the triplicate measurement concentrations and the enrichment triplicates was comparable.

To determine the extent of chlorothalonil TPs in groundwater, concentrations were quantified in 60 groundwater samples (section 2.1) that have been analysed using a comparable method as the one used for the environmental samples in this study. The major differences were a lower enrichment factor (75 instead of 100) and a lower injection volume (140 instead of 150 μL), corresponding to 10.5 mL of the original sample (instead of 15 mL). Additionally, only 35 isotope-labelled internal standards were spiked. The samples were analysed together with four calibration standards (1, 10, 100, 1000 ngL^{-1}) and three spiked samples (10, 100, 250 ngL^{-1}), containing among other compounds the chlorothalonil TPs R471811-SA, R417888-SA, SYN507900-Ph and R61198-Ph. The concentrations of the chlorothalonil TPs R419492-SA and SYN545850-Ph were estimated based on the calibration standards measured separately (see above).

3. Results and discussion

3.1. Chlorothalonil TPs in drinking water resources

Fig. 1 illustrates the concentration ranges of the chlorothalonil TPs in different drinking water resources. In addition to the TPs presented in Fig. 1, the TPs R611965 (carboxylic acid) and R418503-SA were investigated with reference material (LOQ 10 ngL^{-1}) but never detected. SYN548581-SA, which is the R417888-SA isomer that we previously identified only tentatively based on comparison of the isotope pattern, predicted MS/MS spectrum and retention time (Kiefer et al., 2019), was now confirmed with reference material (Fig. SI-A9). As expected, none of the TPs were found above the LOQ of 0.2–10 ngL^{-1} in rain water or ultrapure water. TP

R471811-SA was detected in all other samples, even in groundwater with very low anthropogenic impact, in surface water (river Rhine: 53 ngL^{-1}, Lake Zurich: 5 ngL^{-1}), and in bottled water (evian® water: 6 ngL^{-1}). The two other sulfonic acid TPs, R417888-SA and R419492-SA, were detected in 86% and 65% of samples (without rain and ultrapure water), whereas the phenols (R611968-Ph, SYN507900-Ph, SYN548580-Ph) were detected less frequently (in 10−30% of the samples) and at lower concentrations (Fig. 1). In the four surface waters investigated (3 rivers, 1 lake), all TPs had concentrations below 100 ngL^{-1}; whereas at least one TP was above 100 ngL^{-1} in 40 out of 73 groundwater samples. It should be noted that concentrations in rivers may be subject to stronger seasonal fluctuations compared to concentrations in groundwater (for a compilation of all quantitative data, refer to SI−B1 and SI−B2).

Based on long-term monitoring data, the 60 groundwater monitoring sites were pre-classified as influenced by agricultural micropollutants (20 sites), micropollutants from wastewater (20 sites, often influenced by river bank filtration), or with only low anthropogenic influence (20 sites, section 2.1). As expected, the median concentration of the chlorothalonil TPs was higher in groundwater samples influenced by agriculture (515 ngL^{-1}) than in groundwater samples pre-classified as wastewater-impacted (99 ngL^{-1}) or in samples with only low anthropogenic influence (19 ngL^{-1}). The phenols play a minor role for the drinking water quality, since they exceeded 100 ngL^{-1} in only 3% of samples, whereas the sulfonic acids R471811-SA, R417888-SA, and R419492-SA exceeded 100 ngL^{-1} in 52%, 14%, and 14% of samples, respectively.

The concentration ratios between the TPs vary strongly from sample to sample (SI−B1). For example, TP R471811-SA was found at 2−50 times (median: 7.4) higher concentrations compared to its direct precursor compound, TP R417888-SA. These differences could be related to a different formation rate and/or transport behavior. The less polar TP R417888-SA is more affected by sorption than the more polar TP R471811-SA. Therefore, in case of TP R417888-SA, the degree of retardation during transport through the unsaturated zone might depend more strongly on the site-specific soil/sediment characteristics (e.g. organic carbon) than in the case of TP R471811-SA. In addition, more R417888-SA will be oxidized to R471811-SA with increasing residence time (depending e.g. on size of soil/sediment particles) in the biologically more active aerobic top soil. Therefore, we speculate that the concentration ratio between the TPs R471811-SA and R417888-SA will increase with increasing organic carbon content and residence time in the unsaturated zone.

3.2. Abatement of chlorothalonil TPs during drinking water treatment

Fig. 2 provides an overview of the abatement by granular activated carbon filtration, ozonation and UV disinfection in different waterworks, while Fig. 3 illustrates the abatement of the three sulfonic acid TPs along the treatment train of waterworks A and B (phenolic TPs were not detected). Waterworks C and D showed only very low concentrations of chlorothalonil TPs in the raw water and were therefore not discussed in detail (Lake Zurich and river Limmat both ≤7 ngL^{-1}, see SI−B2 for all quantitative data). Sand filtration and subsequent infiltration to the aquifer followed by abstraction did not lead to a decrease of the concentrations (Fig. 3, left), which is in accordance with the high mobility and persistence of the sulfonic acid TPs (EFSA, 2018).

Whereas the sulfonic acid TPs were stable during ozonation and UV disinfection, granular activated carbon filtration led to an abatement (Fig. 3). However, only very fresh activated carbon (specific throughput 23 and 25 m^{3}kg^{-1}, waterworks A and B) was capable of sufficiently abating all sulfonic acid TPs (R471811-SA:

80% abatement; R417888-SA, R419492-SA: below LOQ). For slightly older activated carbon (specific throughput 55 m^{3}kg^{-1}, waterworks A), no retention of R471811-SA was observed, whereas R419492-SA was still abated by 55% and R417888-SA was below LOQ. An activated carbon filter with a specific throughput of 215 m^{3}kg^{-1} (waterworks B) retained only the sulfonic acid TP with the highest water-n-octanol distribution coefficient considering the speciation at pH 7 (log D$_{OW\ pH7}$; R417888-SA, 58% abatement). The oldest activated carbon filter (specific throughput 305 m^{3}kg^{-1}, waterworks A) had higher effluent than influent concentrations for all sulfonic acid TPs, indicating slight leaching from the filter.

The poor retention behaviour for R471811-SA was comparable to the breakthrough behaviour of the X-ray contrast agent diatrizoic acid (Fig. 2). Whereas both compounds were still abated by 80% by fresh activated carbon (specific throughput 25 m^{3}kg^{-1}), neither R471811-SA nor diatrizoic acid were abated by slightly older activated carbon (specific throughput 55 and 305 m^{3}kg^{-1}; diatrizoic acid was not present in the raw water of waterworks B). It should be noted that the results from the two waterworks A and B are in good agreement, although different granular activated carbons were used (waterworks A: bituminous coal, Filtrasorb® 400, Calgon Carbon Corporation; waterworks B: bituminous coal, Hydraffin® XC 30, Donau Carbon).

In intensively used agricultural areas, managed aquifer recharge can decrease groundwater contamination with chlorothalonil TPs by dilution because surface waters are usually less polluted with chlorothalonil TPs (section 3.1). Three of the investigated groundwater abstraction wells were close to a river (40−730 m), which was only slightly contaminated (concentration sum of chlorothalonil TPs 100 ngL^{-1} in a grab sample). With increasing distance to the river, the concentration sum of the chlorothalonil TPs in the abstracted groundwater increased (2 abstraction wells 40 m from river: 85 and 220 ngL^{-1}, concentrations may differ due to a different pumping regime before sampling, leading to different proportions of river water in the abstracted sample; abstraction well 730 m from river: 420 ngL^{-1}; SI−B2). However, managed aquifer recharge may introduce other organic micropollutants such as wastewater-derived compounds (Hollender et al., 2018). Accordingly, we observed higher concentrations of the sweetener acesulfame in abstraction wells close to the river compared to an abstraction well with larger distance to the river (grab sample in river: 280 ngL^{-1}; 2 abstraction wells 40 m from river: 120 and 34 ngL^{-1}, concentrations may differ due to a different pumping regime before sampling; abstraction well 730 m from river: 11 ngL^{-1}; SI−B2).

The phenolic TPs were partly abated by UV disinfection with a large variability (57 ± 43%, Fig. 2, SI−B3, waterworks E and F). No clear difference in abatement between the UV disinfection systems with low pressure Hg lamps (monochromatic UV light, 254 nm) or medium pressure Hg lamps (polychromatic UV light) was observed (Fig. 2). UV systems at waterworks are usually installed for disinfection, requiring only low fluences, i.e. ≥400 Jm^{-2} according to German, Austrian and Swiss legislation (DVGW, 2006; ÖNORM, 2001; SVGW, 2010). Despite the low fluences, abatement of some organic micropollutants has been reported. Scheurer et al. (2014) observed 30% abatement of the sweetener acesulfame at a waterworks in Basel, Switzerland, and similar acesulfame abatement (30−50%, Fig. 2) was observed at the UV disinfection systems in this study. In addition to acesulfame, we also observed partial abatement of diatrizoic acid (30−40%, Fig. 2). In contrast, UV disinfection did not affect the concentration of the sulfonic acid TPs (waterworks A, Fig. 3). The slight abatement or formation observed at three other UV systems (Fig. 2) likely reflects uncertainty from sampling and sample analysis.

It can be asked whether the investigated TPs may also be formed in the waterworks from chlorothalonil or chlorothalonil TPs.
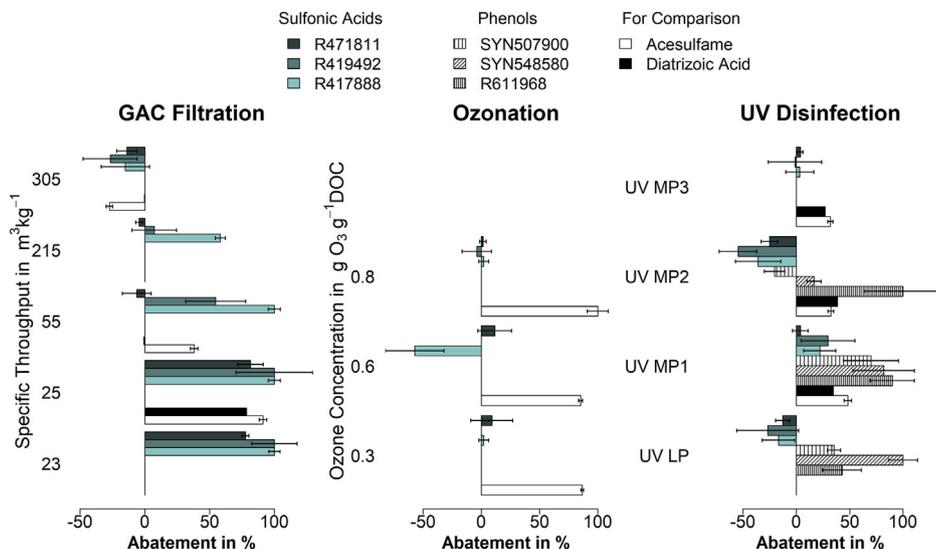
Fig. 2. Abatements of chlorothalonil TPs by different treatment processes across multiple waterworks; for comparison acesulfame and diatrizoic acid are also included. Error bars indicate measurement uncertainty propagated from standard deviation of measurement triplicates (no triplicate measurements for diatrizoic acid). Uncertainty from sampling is not included. Abatement <LOQ is reported as 100%. The apparent formation of R417888-SA in ozonation was only observed in one sample with concentrations close to the LOQ (SI−B2) and is probably related to measurement uncertainty. GAC: granular activated carbon; LP: low pressure Hg lamp; MP: medium pressure Hg lamp; MP1&2: waterworks E, MP3: waterworks A, see Table SI-A1; (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Chlorothalonil itself was not analysed in this study as it does not ionize sufficiently in electrospray. However, based on laboratory and lysimeter experiments performed within the EU pesticide registration process (EFSA, 2018) and a German groundwater monitoring program (LUBW, 2011), the presence of chlorothalonil in the raw waters in relevant concentrations is unlikely. Accordingly, the water supplier operating waterworks B regularly checks for chlorothalonil in the raw water using gas chromatography electron ionization mass spectrometry, but has never detected this compound (LOQ = 20 ngL^{-1}). Furthermore, a formation of one target TP from another target TP was only observed in small amounts in the laboratory experiments, i.e. 2% R471811-SA was formed from R417888-SA at pH 10 (for each ozone dose, including the control without ozone, SI-A8), indicating very slow basic hydrolysis (section 3.3). Therefore, we expect that the results of our study are not influenced by chlorothalonil TPs formed in the waterworks.

3.3. Laboratory experiments

Table 1 provides the results from laboratory experiments with ozone, UV and AOPs and corresponding literature data for common micropollutants for comparison. SI−B4 to SI−B10 show the experimental data, SI−A5 to SI−A10 describe the calculations of the reported values.

3.3.1. UV irradiation

In full-scale water treatment, the phenolic TPs were partially abated by UV disinfection (57 ± 43%), whereas the sulfonic acid TPs were persistent (section 3.2, Fig. 2). The UVC irradiation experiments confirmed the higher photodegradability at 254 nm of the phenolic TPs, exhibiting higher photon fluence-based rate constants (Table 1). The fast decay of the phenolic TPs relates to their higher quantum yields compared to the sulfonic acid TPs, while all TPs have moderate to high molar absorptivities (Table 1, Fig. SI-A1 and SI-A2). Using the photon fluence-based rate constants determined, we calculated the theoretical abatement by UV disinfection (SI-A5), assuming an applied UV dose of 400 Jm^{-2} as prescribed in

Switzerland, Germany and Austria (DVGW, 2006; ÖNORM, 2001; SVGW, 2010). Theoretically, <0.2% of the sulfonic acids and <2.5% of the phenols should be abated under such UV disinfection conditions (Table. SI-A10). However, abatement in full-scale treatment (Fig. 2) was higher compared to the estimates from UVC treatment alone. This difference might be explained by indirect phototransformation due to production of reactive intermediates that can contribute to the removal of micropollutants, i.e. reactions with radicals or triplet states generated by photoexcitation of dissolved organic matter or nitrate (Canonica et al., 1995; Mark et al., 1996; Zepp et al., 1987). Especially nitrate may play an important role, because groundwater polluted with chlorothalonil TPs often has elevated nitrate concentrations, since both originate from mainly agricultural sources (median of nitrate concentration in groundwater samples with phenolic TPs: 20 mgL^{-1}, SI−B1). In contrast, dissolved organic matter concentrations are usually low in groundwater (DOC in the 60 groundwater samples ≤ 2.1 mgL^{-1}). Indirect phototransformation is especially important for compounds susceptible to oxidation such as phenols (Canonica et al., 2008).

In addition to disinfection, UV irradiation is used to generate •OH in UV-based AOPs. The fluence applied in UV-based AOPs (5000−10000 Jm^{-2}, Chuang et al. (2017)) are about 10−25 times higher compared to UV disinfection, so also direct phototransfomation can become relevant in case of the phenols. An abatement of 24% for R611968-Ph and 37% for SYN507900-Ph is estimated for a UV dose of 7500 Jm^{-2} and the respective rate constants. For 90% abatement of the phenolic TPs by direct photolysis, 38000−64000 Jm^{-2} would be required; for the sulfonic acid TPs UV doses would need to be even ten times higher (Table SI-A10).

3.3.2. Ozonation

In the ozonation step of waterworks B, the sulfonic acid TPs were not degraded (section 3.2). This is in agreement with the very low second order rate constant for the reaction with ozone (k_{O3} <0.04 $M^{-1}s^{-1}$, Table 1). Only micropollutants with second order rate constants $\gg 10$ $M^{-1}s^{-1}$ are significantly abated during ozonation (von Sonntag and von Gunten, 2012); e.g. acesulfame
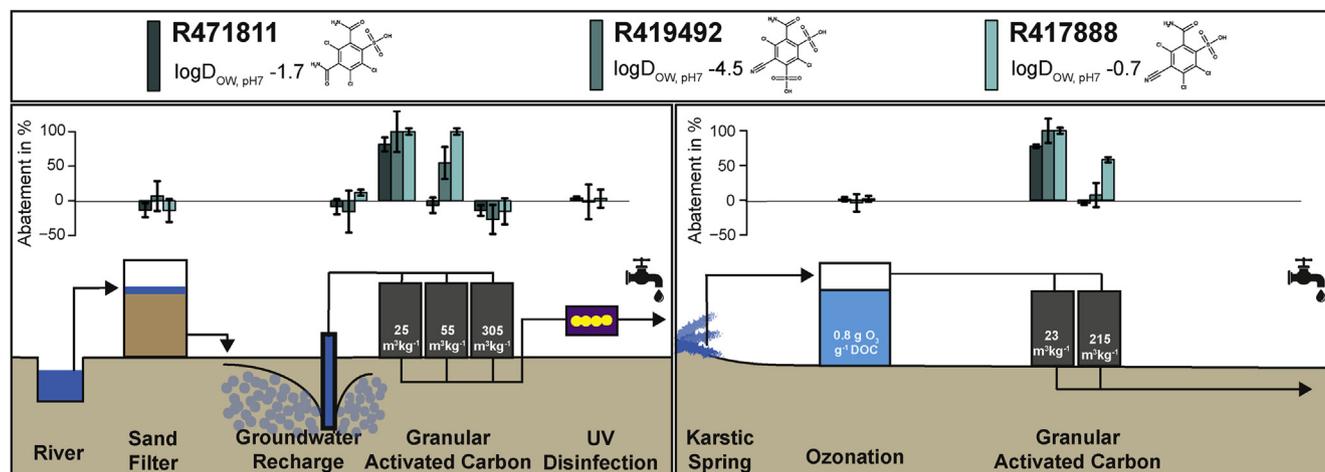
Fig. 3. Abatement of sulfonic acid chlorothalonil TPs along the treatment train of waterworks A (left) and B (right; calculated from one step to the next step). The UV disinfection system was equipped with a medium pressure Hg lamp. Phenolic TPs were not detected. $logD_{OW, pH7}$ (water-n-octanol distribution coefficient considering the speciation at pH 7) predicted with JChem for Office (Version 17.1.2300.1455; ChemAxon Ltd.).

($k_{O3} = 88$ $M^{-1}s^{-1}$, Table 1) was abated by > 85% during ozonation (waterworks B and C; Fig. 2). The measured second order rate constants support our hypothesis that ozone only minimally reacts with the sulfonic acid TPs, because the benzene rings have six electron-withdrawing substituents such as chlorine, sulfonic acid, cyano- and/or amide-groups (Fig. 1). Ozone-refractory compounds (e.g. atrazine, Table 1) are mostly abated by •OH that are formed from ozone decay and ozone reactions with dissolved organic matter as secondary oxidants (von Sonntag and von Gunten, 2012). However, the sulfonic acid-containing TPs are also very refractory against •OH ($k_{OH} < 5.0 \times 10^7$ $M^{-1}s^{-1}$, Table 1), explaining why no abatement was observed in waterworks B for these compounds.

In contrast, the more electron-rich phenolic TPs are clearly more reactive, as expected, both with ozone and •OH ($k_{O3} > 10^4$ $M^{-1}s^{-1}$, Table 1). To what extent the phenolic TPs will be abated in full-scale treatment cannot be concluded from the data presented here because the concentrations of the phenolic TPs were <LOQ in the raw water of waterworks B and C. However, Hollender et al. (2009) showed for a wastewater treatment plant with 5.2 ± 0.6 mgL^{-1} DOC and hydraulic retention times of 3.7−10.1 min in the ozone reactor that micropollutants with $k_{O3} > 10^4$ $M^{-1}s^{-1}$ are fully abated at ozone doses >0.4 g ozone g^{-1} DOC. Therefore, we assume that the phenols will be fully abated in waterworks B (0.8 g O$_3$ g^{-1} DOC, contact time > 10 min) and C (pre-ozonation: 0.3 g O$_3$ g^{-1} DOC, contact time >25 min; intermediate ozonation 0.6 g O$_3$ g^{-1} DOC;

contact time >10 min).

For phenolic compounds, Lee and von Gunten (2012) developed quantitative structure-activity relationships (QSARs) based on substituent descriptors (Hammett constants) to predict the second order rate constants for the reactions with ozone. The proposed QSAR was applied to predict the second order rate constants of R611968-Ph and SYN507900-Ph, and in addition, of the phenolic TP, which was not investigated in laboratory experiments (SYN548580-Ph, see SI-A7). The second order rate constants of R611968-Ph and SYN507900-Ph predicted by QSAR were on average 2.4 times higher than the measured values. A factor 2.4 is within the uncertainty described by Lee and von Gunten (2012). The predicted second order rate constant of SYN548580-Ph was three to five times higher than the predicted second order rate constants of SYN507900-Ph and R611968-Ph, indicating higher abatement.

3.3.3. Advanced oxidation

Overall, a broader range of micropollutants can be transformed in AOPs compared to ozonation because the •OH generated in AOPs is a less selective oxidant (von Gunten, 2018). Moreover, direct phototransformation by UV irradiation can contribute to micropollutant abatement depending on the AOP applied (e.g. UV/H$_2$O$_2$, UV/free chlorine) (Katsoyiannis et al., 2011).

The second order rate constant for the reaction of R611968-Ph

Table 1
Rate constants and photochemical parameters determined in laboratory experiments in this study (chlorothalonil TPs) or from literature (other micropollutants): second order rate constant for the reactions of target compounds with ozone (k_{O3}) or •OH (k_{OH}), photon fluence-based rate constant k_E, molar absorptivity ε_{254nm}, and the quantum yield Φ; $\pm$ standard deviation or as reported in respective study.

Compound	Ozone k_{O3} in M^{-1}s^{-1}	•OH k_{OH} in M^{-1}s^{-1}	UVC k_E in m^{2}einstein^{-1}	UVC ε_{254nm} in M^{-1} cm^{-1}	UVC Φ in mol einstein^{-1}
R471811-SA	<0.04	$<5.0 \times 10^7$	1.1 ± 0.1	710	$(0.7 \pm 0.1) \times 10^{-2}$
R417888-SA	<0.04	$<5.0 \times 10^7$	1.9 ± 0.1	8000	$(0.10 \pm 0.01) \times 10^{-2}$
SYN507900-Ph	4.1×10^{4}*	not determined	30 ± 1	6900	$(1.8 \pm 0.1) \times 10^{-2}$
R611968-Ph	$(2.6 \pm 0.3) \times 10^{4}$*	$(2.7 \pm 0.6) \times 10^9$	17 ± 1	5400	$(1.4 \pm 0.1) \times 10^{-2}$
Acesulfame	88 (a)	4.55×10^9 (a); $(3.8 \pm 0.3) \times 10^9$ (b)	130** (c)	not reported	26-33 (d)
Atrazine	6 (e)	3×10^9 (e)	41 ± 1	3860 (f)	$(4.6 \pm 0.4) \times 10^{-2}$ (g)
Carbamazepine	~3×10^5 (h)	$(8.8 \pm 1.2) \times 10^9$ (h)	1.0 (i)	6070 (i)	0.06×10^{-2} (i)
Diatrizoic Acid	0.05 ± 0.01 (j)	$(5.4 \pm 0.3) \times 10^8$ (j)	251 ± 22 (j)	31200 (j)	$(3.5 \pm 0.3) \times 10^{-2}$ (j)

* Value might be smaller (factor 10) due to conflicting values for k_{O3} of the competitor salicylic acid in Hoigné and Bader (1983), for details see SI-A7; ** calculated according to equation (SI-9) using values from Fu et al. (2019).
(a) Kaiser et al. (2013), (b) Toth et al. (2012), (c) Fu et al. (2019) (d) Scheurer et al. (2014), (e) Acero et al. (2000), (f) Nick et al. (1992), (g) Hessler et al. (1993), (h) Huber et al. (2003), (i) Pereira et al. (2007), (j) Real et al. (2009).

with •OH was $(2.7 \pm 0.6) \times 10^9$ $M^{-1}s^{-1}$, which is similar to e.g. atrazine and many other micropollutants (Table 1; von Sonntag and von Gunten (2012)). For SYN507900-Ph, the second order rate constant could not be determined because it was already reacting by direct photochemical reactions during UVA irradiation and an enhancement of the decay rates could not be observed in UVA/H_2O_2 (SI-A9, SI–B8). However, because of their similar structures, we assume that the second order rate constant for the reaction of SYN507900-Ph with •OH is in the same range as for R611968-Ph. For a treatment plant with reverse osmosis followed by UV/H_2O_2, Marron et al. (2019) calculated pollutant abatement depending on their second order rate constants for the reaction with •OH, whereby they assumed that the UV/H_2O_2 reactor is designed to remove 1,4-dioxane by 70% through reactions with •OH (i.e. 4×10^{-10} Ms •OH exposure). Under these comparably favourable conditions (low •OH scavenging due to low DOC: <0.5 mgL^{-1}), R611968-Ph (k_{OH} $(2.7 \pm 0.6) \times 10^9$ $M^{-1}s^{-1}$) would be abated by 60–70% due to reaction with •OH. In contrast to the phenolic TPs, the abatement of the sulfonic acids ($k_{OH} < 5.0 \times 10^7$ $M^{-1}s^{-1}$) is expected to be negligible in O_3/H_2O_2 or UV/H_2O_2. Based on these low reactivities both with the rather unselective oxidant •OH and the selective oxidant ozone, it is likely that sulfonic acids are also persistent towards other oxidants such as HOCl, ClO_2 or sulfate radicals.

3.3.4. Activated carbon

Adsorption to powdered activated carbon was investigated in a natural groundwater (DOC 1.1 mgL^{-1}) spiked with four chlorothalonil TPs and, for comparison, with diatrizoic acid (anionic at pH 7; predicted log $D_{OW\ pH7}$ -0.6) and atrazine (neutral at pH 7; predicted log $D_{OW\ pH7}$ 2.2), two micropollutants with well-known adsorption behaviour. Fig. SI-A7 and SI-A8 show the abatement as a function of the powdered activated carbon dose. According to this, the affinity to activated carbon decreases in the following order: atrazine > R611968-Ph > R417888-SA ≈ SYN507900-Ph > R4718111-SA ≈ diatrizoic acid.

The laboratory experiments showed a higher activated carbon affinity of R417888-SA compared to R471811-SA, which was confirmed by the better retention of R417888-SA in the waterworks (section 3.2) and is in accordance with the higher hydrophobicity (Fig. 1, higher log $D_{OW\ pH7}$). However, hydrophobicity is not the only parameter governing adsorption to activated carbon (Kovalova et al., 2013b). Diatrizoic acid, which has a predicted log $D_{OW\ pH7}$ comparable to R417888-SA, showed similar adsorption behaviour to R471811-SA. This was observed as well in full-scale (section 3.2), i.e. diatrizoic acid can be used in waterworks as predictor for the expected breakthrough of R471811-SA.

3.3.5. Reverse osmosis

The reverse osmosis pilot plant was sampled five times over a period of fourteen weeks. The corresponding results are summarized in SI–B10. Chemical analyses focused on the two chlorothalonil TPs with the highest concentrations (R471811-SA, R417888-SA). Two additional pesticide TPs (chloridazon-desphenyl, log $D_{OW\ pH7}$ -0.8; chloridazon-desphenyl-methyl, log $D_{OW\ pH7}$ -0.6) and nitrate, which are typical groundwater contaminants in many agricultural areas, were also investigated.

The phenolic TPs were completely removed (not detectable in permeate, i.e. <10 ng/L, raw water: ~30–100 ng/L). Furthermore, the chlorothalonil TP R417888-SA and chloridazon-desphenyl-methyl were not detectable in the permeate (raw water: 200–280 ngL^{-1} and 30–33 ngL^{-1}), whereas the chlorothalonil TP R471811-SA was abated by ≥98% (raw water: 1200–2100 ngL^{-1}; permeate: 15–20 ngL^{-1}), nitrate by 95–98% (raw water: 16.5–18.6 mgL^{-1}; permeate: 0.4–0.9 mgL^{-1}), and the pesticide TP chloridazon-desphenyl was only abated by 87–94% (raw water: 440–560 ngL^{-1}; permeate: 30–63 ngL^{-1}). The lower removal of chloridazon-desphenyl compared to the chlorothalonil TPs may be related to differences in the molecular properties. In contrast to the chlorothalonil TPs, chloridazon-desphenyl is uncharged and has a smaller molecular mass and volume (R471811-SA: 348 gmol^{-1}, 23 nm^3; chloridazon-desphenyl: 146 gmol^{-1}, 11 nm^3; predicted by JChem for Excel, Version 17.1.2300.1455, ChemAxon Ltd.).

3.4. Practical implications

The sulfonic acid TPs are detected more frequently in drinking water resources than the phenolic TPs and exhibit higher concentrations, often exceeding the Swiss drinking water standard of 100 ngL^{-1}. Chlorothalonil has recently been banned in the EU and in Switzerland (BLW, 2019a; European Commission, 2019), so chlorothalonil will no longer be applied in large parts of Europe. However, it is difficult to predict how long these TPs will continue to be present in groundwater and for how long water suppliers will face raw water polluted with chlorothalonil TPs. The duration depends on various factors such as the exact dissipation time, groundwater recharge rate, groundwater residence time, and dilution with other water sources in the respective aquifer. Experience from other pesticides with similar properties related to biodegradability and application periods and polar TPs is scarce. However, studies in Germany and Switzerland showed no concentration decline for the TPs of the herbicide chloridazon within five years after the last application in two shallow aquifers with average groundwater residence times <15–20 years (Hintze and Hunkeler, 2019; Neukum and Meyer, 2019). Model predictions are uncertain but indicate that a decrease in chloridazon TP concentration by 90% will take more than 20 years (Neukum and Meyer, 2019).

Both sampling along water treatment trains and laboratory experiments indicate that the sulfonic acid TPs of chlorothalonil are persistent in most water treatment processes. Photochemical and oxidative processes (UV irradiation, ozonation, and AOPs based on •OH) are not able to abate the sulfonic acid-containing TPs. In contrast, activated carbon may offer a chance to abate the sulfonic acid TPs to a certain extent, but efficiency varies strongly among TPs. To remove all chlorothalonil TPs, activated carbon needs to be exchanged or regenerated very frequently, approximately as often as for the removal of the X-ray contrast agent diatrizoic acid, causing high economic and ecological costs. Reverse osmosis abated ≥98% of chlorothalonil TPs; however, this is an energy intensive process and the reject water (20–30% of treated water) needs to be treated or disposed. Efficient post-treatment processes are not known and disposal to lakes and rivers is questionable because the pollutants are returned to the water cycle.

4. Conclusions

- Chlorothalonil TPs are widespread in drinking water resources. One TP (R471811-SA) was detected in all 77 samples, even in groundwater with low anthropogenic impact. The sulfonic acid containing TPs (R471811-SA, R419492-SA, R417888-SA) exceeded concentrations of 100 ngL^{-1} in 14–52% of the samples, while the phenol-containing TPs (SYN507900-Ph, SYN548580-Ph, R611968-Ph) were less frequently detected; in 97% of samples the phenol-containing TPs were below concentrations of 100 ngL^{-1}.
- Although chlorothalonil has recently been banned in Europe, the TPs of chlorothalonil are expected to challenge drinking water suppliers for many years due to their persistence in the environment and in water treatment processes.

- The phenolic TPs can be removed by various treatment techniques such as ozonation, AOPs, and activated carbon. Even UV disinfection may lead to a certain extent of removal.
- In contrast to the phenolic TPs, the less electron-rich sulfonic acids are more persistent and can be removed neither by ozonation nor by •OH-based AOPs under typical water treatment conditions. The sulfonic acids adsorb to activated carbon to varying extents, depending on their polarity. For an efficient removal of the TP with the highest concentrations, granular activated carbon needs to be exchanged more frequently than for other common micropollutants.
- Reverse osmosis was able to abate the chlorothalonil TPs by ≥98%. However, the reject water needs to be disposed.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.116066.

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