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Application of UVOX Redox® for swimming pool water treatment: Microbial inactivation, disinfection byproduct formation and micropollutant removal

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HIGHLIGHTS

- UVOX technology can inactivate chlorine-resistant microorganisms.
- In chlorinated pool water, UVOX influenced the formation of brominated DBPs.
- Removal of the selected micropollutants was largely due to chlorination.
- UVOX enhanced the removal of ibuprofen in chlorinated water.

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ABSTRACT

Alternative disinfection technologies may overcome some of the limitations of conventional treatment applied in swimming pools: chlorine-resistant pathogens (e.g. *Cryptosporidium* oocysts and *Giardia* cysts) and the formation of chlorinated disinfection byproducts. In this paper, results of full scale validation of an alternative disinfection technology UVOX Redox® (hereinafter referred to as UVOX) that combines ozonation and UV irradiation are presented. The performance was assessed in terms of microbial inactivation, disinfection byproduct formation and micropollutant removal. UVOX was able to achieve 1.4 −2.7 log inactivation of *Bacillus subtilis* spores at water flows between 20 and 76 m^3/h. Lower formation of trichloromethane and dichloroacetic acid was observed with UVOX followed by chlorination when compared to chlorination alone. However, due to the use of ozone and the presence of bromide in the pool water, the formation of trihalomethanes and haloacetic acids shifted to more brominated byproducts. Chlorine alone was able to remove the target micropollutants: acetaminophen, atenolol, caffeine, carbamazepine, estrone, estradiol, and venlafaxine (>97% removal) after 24 h, with the exception of ibuprofen (60% removal). The application of UVOX in chlorinated water enhanced the removal of ibuprofen. The application of UVOX could lower the usage of chlorine to the level that provides an adequate residual disinfection effect.

1. Introduction

1.1. Swimming pool water disinfection

The main components of a typical water treatment scheme in swimming pools consist of coagulation-flocculation followed by filtration and disinfection (WHO, 2006). Disinfection is applied to ensure microbial inactivation, and the presence of residual disinfectant provides protection against subsequent microbial contamination. Chlorination is widely used for disinfection in swimming pools due to its efficacy against a wide range of pathogens, its availability and cost effectiveness. Chlorine has strong disinfecting power and provides residual disinfectant effects, but some

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pathogens have been proven to be resistant to chlorine, e.g. the faecally-derived protozoa, *Giardia lamblia* cysts and *Cryptosporidium parvum* oocysts (Jarroll et al., 1981; Korich et al., 1990). Additionally, chlorine reacts with organic and inorganic constituents in water to form disinfection byproducts (DBPs) which are associated with adverse health effects (Florentin et al., 2011; Richardson et al., 2010; Xiao et al., 2012; Vlaanderen et al., 2017).

Disinfection technologies, such as UV irradiation and ozonation have been utilized for decades in drinking water and wastewater treatment (Betancourt and Rose, 2004; Bolton and Linden, 2003; USEPA, 1999). UV irradiation has proven to be effective against chlorine resistant pathogens (Clancy et al., 2000; Craik et al., 2000, 2001; Shin et al., 2001). Significant inactivation of *Cryptosporidium* oocysts and *Giardia* cysts was observed at UV fluence <20 mJ/cm^2 (Chevrefils et al., 2006; Hijnen et al., 2006). Ozonation is also a stronger disinfectant than chlorine (Korich et al., 1990). Studies have shown that 99% inactivation of *Cryptosporidium* oocysts and *Giardia* cysts can be achieved at CT (concentration x contact time) values < 10 mg.min/L and <1 mg.min/L at 20 °C pH 7.0, respectively (Jacangelo et al., 2002; Rennecker et al., 1999). Moreover, ozone improves the inactivation of *Cryptosporidium* oocysts in subsequent use of chlorine (Corona-Vasquez et al., 2002; Driedger et al., 2000; Rennecker et al., 2000). In swimming pool water treatment, ozone and UV could be applied to lower the dependency on chlorine as a primary disinfectant.

1.2. DBPs in swimming pool water

The presence of DBPs has been a major concern in disinfected waters. Some DBPs are carcinogenic and mutagenic; and their presence has been associated with asthma, irritation to skin, throat, and eyes (Richardson et al., 2010). Exposure to DBPs due to swimming in chlorinated pool water may cause alterations in serum immune markers (Vlaanderen et al., 2017). The route of exposure to DBPs is not only through ingestion but also through inhalation and dermal absorption (Villanueva et al., 2007). Sources of DBP precursors in swimming pools are organics derived from humans (e.g. urine, sweat) and from the water source itself (Kanan and Karanfil, 2011). Consequently, continuous addition of disinfectant (e.g. chlorine) in the presence of organic loads may lead to high levels of DBPs (Yeh et al., 2014). While more than 700 DBPs have already been identified in disinfected waters, trihalomethanes (THMs) and haloacetic acids (HAAs) are still the most prominent DBPs investigated in swimming pools (Teo et al., 2015). THMs and HAAs are commonly detected in chlorinated waters (Nieuwenhuijsen et al., 2000) while brominated DBPs are also detected during ozonation (Glaze, 1986).

The effect of ozone and/or UV on DBPs formation in swimming pool applications have been demonstrated in many studies (Cheema et al., 2017; Cimetiere and De Laat, 2014; Hansen et al., 2013, 2016; Mao et al., 2014; Spiliotopoulou et al., 2015). Hansen et al. (2016) showed that ozone (0.7–3.4 mg/L) followed by chlorination with sodium hypochlorite (1–3 $mgCl_2$/L of residual chlorine) resulted in lower total THMs formation when compared to chlorination alone (1–3 $mgCl_2$/L of residual chlorine) in batch experiments using body fluid analogue (BFA) to simulate anthropogenic pollutants in swimming pool water. Mao et al. (2014) showed an increase in THM concentrations with an increase in ozone dose from 0 to 2 mg/L during subsequent chlorination. Cimetiere and De Laat (2014) demonstrated an increase in THMs formation and little effect on HAAs by applying high UV doses (23.5 and 47 kJ/m^2) using low-pressure UV in chlorinated water while no effect on THMs was observed using medium-pressure UV with or without free chlorine (Spiliotopoulou et al., 2015). Some studies in real swimming pools investigated the effect of UV followed by chlorination, but the results were contradictory; in fact, this resulted in an increase of THMs (Cassan et al., 2006), a decrease of THMs (Beyer et al., 2004), and no effect (Kristensen et al., 2009). Weng et al. (2012) observed higher formation of dichloroacetonitrile and cyanogen chloride by increasing UV dose while no change was observed in chloroform levels.

1.3. Occurrence and treatment of micropollutants in water

Nevertheless, DBPs are not the only concern in swimming pools. Organic micropollutants (at low concentrations, in the range of μg/L or ng/L) of anthropogenic source, such as pharmaceuticals and endocrine disrupting compounds (EDCs) are of concern due to adverse health effects to wildlife and humans (Richardson and Ternes, 2011). These compounds can enter swimming pools via human body fluids (e.g. urine and sweat) and/or human skin during swimming (some lotions may contain pharmaceuticals). Several commonly used pharmaceuticals, such as acetaminophen, carbamazepine and ibuprofen, have been detected in different swimming pool settings (Ekowati et al., 2016; Suppes et al., 2017; Teo et al., 2016; Weng et al., 2014), while EDCs (e.g. estrone, estradiol) have been mainly investigated in environmental waters (Campbell et al., 2006; Li et al., 2015; Petrovic et al., 2004; Yoon et al., 2010). The European Commission has placed estrone and estradiol on the watch list of substances for Union-wide monitoring in the field of water policy (European Commission, 2018). Pharmaceuticals, such as carbamazepine and venlafaxine, were included in the list of 12 indicator substances established by the Swiss Federal Office of the Environment (FOEN, 2015) for evaluation of upgrading wastewater treatment plant.

Studies have shown that some micropollutants can be either persistent or susceptible to treatment. Weng et al. (2014) shows that acetaminophen reacted fast (less than 5 h of chlorine exposure) to chlorination (12.78 $mgCl_2$/L of initial free chlorine). Acetaminophen, carbamazepine, estrone and estradiol were easily degraded by chlorine (3.5 and 3.8 mg/L) or ozone (Westerhoff et al., 2005). The application of chlorine and UV separately showed only <10% removal of ibuprofen and carbamazepine while the combination of treatments improved the removal to 98% (Wang et al., 2016; Xiang et al., 2016).

1.4. Objectives

Microbial contamination may continuously occur in swimming pools, hence chlorine is still needed to provide residual disinfection in the pool water despite the formation of chlorine-derived DBPs. The application of alternative disinfection technologies, such as ozone and UV, which are effective for microbial inactivation and form little or no DBPs could help in lowering chlorine dosage and eventually minimizing the formation of chlorinated DBPs in swimming pool water. Although many studies have investigated the application of ozone and UV for swimming pool applications, the studies generally targeted microbial inactivation, DBP formation, and removal of micropollutants, separately. Thus, the goal of this research was to assess a commercial technology which combines ozone and UV for all aforementioned objectives. Moreover, the technology was applied in a full scale outdoor swimming pool of a large tourist facility, which then gave the opportunity to observe the overall system performance influenced by hydraulic conditions, longer treatment duration, water recirculation, and continuous disinfection.

2. Materials and methods

2.1. Microorganisms and chemicals

2.1.1. Bacillus subtilis spores

Bacillus subtilis spores have been used as a surrogate for *Cryptosporidium parvum* oocysts in many disinfection studies (Cho et al., 2006; Choi et al., 2007; Driedger et al., 2001; Jung et al., 2008) because of their similar behaviour with respect to disinfection methods such as chlorination, UV and ozonation. *B. subtilis* spores are used as a biodosimeter (a UV calibrated microorganism) for UV reactor validation (Sommer et al., 2004).

UV-253.7 nm calibrated *B. subtilis* spores ATCC 6633 was purchased from HAI-SO GmbH, Austria. The inactivation curve of the spores according to Austrian National Standard ÖNORM M 5873-1:2001 and M 5873-2:2003 was provided by the supplier (Supplementary material Fig. S1).

2.1.2. Body fluid analogue

BFA was added to pool water to simulate the human body fluid released in swimming pool water. BFA solution for spiking the pool water consists of urea, creatinine, histidine, hippuric acid, uric acid, citric acid, sodium phosphate and ammonium chloride. It was prepared using the same composition and proportion as described by Judd and Bullock (2003). All compounds were purchased from Sigma-Aldrich. The concentration of total organic carbon (TOC) in water samples was measured using a TOC-VCSH (Shimadzu) instrument.

2.1.3. Micropollutants

All pharmaceuticals and EDCs: acetaminophen, atenolol, carbamazepine, ibuprofen, venlafaxine hydrochloride, estrone, estradiol, and caffeine were purchased from Sigma-Aldrich. Isotopically labelled compounds were used as internal standards; acetaminophen-d_4, ibuprofen-d_3, and caffeine-d_3, were purchased from Sigma-Aldrich, atenolol-d_7 from Toronto Research Chemicals, carbamazepine-d_{10}, venlafaxine-d_6, estradiol-17β-2,4-D_2, and estrone-2,4,16,16-D_4 from Cluzeau Info Labo. Further details are described in Supplementary material Table S1.

HPLC-grade methanol, acetonitrile, water (LiChrosolv), ammonium acetate, formic acid and Na_2EDTA were purchased from Merck (Germany). Nitrogen (99.995% purity) for drying was obtained from Abelló Linde (Spain). All the samples collected during the experiment were filtered through 0.45 μm polyvinylidene fluoride membrane filters (Merck Millipore, Germany).

2.2. Analytical methods

2.2.1. Enumeration of Bacillus subtilis spores

The freeze dried *B. subtilis* spores were suspended in sterile deionized water for 24 h prior to use. The enumeration of the spores was done by using the pour plate method with Columbia blood agar base (Oxoid). The plates were incubated at 37 °C for 44 ± 4 h.

2.2.2. Analysis of pharmaceutical active compounds

In each sample for pharmaceutical analyses, a suitable volume of 0.1 M Na_2EDTA solution was added to achieve a final concentration of 0.1% (g solute/g solution). Samples were pre-concentrated using Oasis HLB cartridges (60 mg, 3 mL) (Waters Corp., Milford, MA, USA) which were conditioned with 5 mL of methanol followed by 5 mL of HPLC grade water. 25 mL of sample was loaded to the cartridge at 1 mL/min. After sample pre-concentration, cartridges were rinsed with 6 mL of HPLC grade water and were dried with air for 5 min for total water removal. Analytes were eluted with 6 mL of pure methanol. Extracts were evaporated to dryness under a gentle nitrogen stream and reconstituted with 1 mL of methanol. 10 μL of extract were diluted in 1 mL of methanol/water. Finally, 10 μL of an internal standard mixture (at 1 mg/L) were added to the extract. Samples were further analysed using Ultra-Performance™ liquid chromatograph system (Waters Corp. Milford, MA, USA) coupled to a quadrupole-linear hybrid ion trap mass spectrometer (5500 QTRAP, Applied Biosystems, Foster City, CA, USA) with a turbo Ion Spray source. Chromatographic separation was carried out using Acquity HSS T_3 column (for positive electrospray ionization) and Acquity BEH C_{18} column (for negative electrospray ionization) (Waters Corp. Milford, MA, USA). The detailed procedure of the analysis was as described by Gros et al. (2012). The recovery of the analytes is shown in Supplementary material Table S1.

2.2.3. Analysis of endocrine disruptors and related compounds

All samples were filtered through 0.45 μm polyvinylidene fluoride membrane filters. Samples were extracted using Strata-X cartridges (200 mg, 6 mL) (Phenomenex) which were conditioned with 5 mL of methanol followed by 5 mL of HPLC grade water. Samples (50 mL) were loaded at 1 mL/min. Finally cartridges were dried under vacuum conditions in order to carry out the elution with a mixture of dichloromethane:methanol (50:50). The extract was reconstituted with 1 mL of methanol:water and 50 μL of internal standard was added. Samples were analysed by an Ultra Performance Liquid Chromatography (Thermo Fisher Scientific) system coupled to a triple quadrupole mass spectrometer (TSQ Vantage, Thermo Fisher Scientific). Chromatographic separation was carried out using a LUNA OMEGA C_{18} 1.6 μm (100 × 2.1 mm) (Phenomenex) column. The detailed procedure of the analysis was described by Gorga et al. (2013) and Kassotaki et al. (2019). The recovery of the analytes is shown in Supplementary material Table S1.

2.2.4. Analysis of DBPs

Water samples were analysed for THMs, HAAs and bromate content. In the experiments described in section 4.2, four THMs (trichloromethane (TCM), dibromochloromethane (DBCM), bromodichloromethane (BDCM), tribromomethane (TBM)) and bromate levels were analysed by Water Technology Center (TZW), Karlsruhe, Germany using headspace GC/MS (DIN EN ISO 10301) and IC-ICP-MS, respectively. Nine HAAs (monochloroacetic (MCAA), dichloroacetic (DCAA), trichloroacetic (TCAA), monobromoacetic (MBAA), dibromoacetic (DBAA), tribromoacetic (TBAA), bromochloroacetic (BCAA), bromodichloroacetic (BDCAA), chlorodibromoacetic (CDBAA) acids) were analysed by LEITAT Technological Center in Barcelona, Spain based on the US EPA Method 552.2 (USEPA, 1995). The relative standard deviation of DBP analytical methods is shown in Supplementary material Table S2.

2.3. On site measurements

Temperature, pH, free and total chlorine were measured on site, each time a sample was collected. Chlorine concentration was measured using Hach cuvette LCK310 and Hach spectrophotometer DR2800 (Hach Lange GmbH, Germany). Temperature and pH were measured using a portable probe (pH meter 3310 from WTW). Ozone concentration was measured using Hach Ozone AccuVac® (MR) ampules and a portable Hach colorimeter DR890.

3. Study site and equipment

The commercial ozone/UV system was installed in an outdoor swimming pool in a large Mediterranean tourist facility. The

swimming pool is composed of two connecting pools, the main pool has a volume of 560 m^3 and the children's pool has a volume of 10 m^3. The conventional treatment system in the pool consists of two units of rapid sand filtration and chlorination (15% sodium hypochlorite solution is dosed into the recirculated pool water using a membrane dosing pump). The ozone/UV system was placed between the sand filters and the chlorination step (Fig. 1).

The ozone/UV system was provided by Wapure International GmbH, Germany (UVOX Redox® type UVOX-2000, referred to as UVOX). The system is composed of four amalgam low-pressure UV lamps (each 180 W), positioned vertically, each housed in a quartz sleeve located inside a cylindrical reaction chamber (HDPE, dia. 20 cm, net vol. 22 L). The reaction chamber was equipped with a temperature sensor and a UV sensor (D-SiCONORM-LP). The UVOX technology combines ozone generation and UV irradiation in a single unit system. Air suction is created by means of a Venturi and the sucked air travels through the UV reaction chamber (inside the quartz sleeves) where ozone is generated by conversion of oxygen in the air when exposed to UV irradiation at 185 nm. The mixture of water and air flows into the UV reaction chamber, where it is exposed to UV irradiation at 254 nm.

Before starting the experiments, baseline measurements on the UVOX were performed after the pool was filled with municipal tap water. The maximum UV irradiance was 17.47 mW/cm^2. The mixture of ozone and air flow was fixed at 16 L/min in all experiments and the dissolved ozone concentrations in the water before entering the UV chamber varied between 0.01 mg/L and 0.46 mg/L. UV irradiance was monitored during the experiments. The UV doses (IT) reported were calculated as the UV irradiance (I) measured by the UV sensor during the experiment multiplied by the contact time (T).

4. Experimental design

4.1. Microbial inactivation

A stock solution containing *B. subtilis* spores (~10^7 CFU/mL) and BFA was spiked into the water flow from point 2 in Fig. 1 using a dosing pump to achieve a final concentration ~10^4 CFU/mL in the feed water to the UVOX system. Different concentrations of BFA were added to vary the UV transmittance (UVT) of the model water. Water samples for microbial analysis were collected in 50 mL sterile plastic cups from the inlet (point 3 in Fig. 1) and outlet (point 4 in Fig. 1) of the UVOX system. During the experiment, water samples from inlet and outlet of UVOX were collected in triplicates.

Before starting the experiments, a blank experiment was performed in which the UVOX system was switched off; the purpose was to observe the effect of hydraulic conditions on the viability of *B. subtilis* spores. Pool water temperature during the experiments was 12–13 °C and pH was 8.3.

Two experiments were performed by applying UVOX without ozone generation and with ozone generation. The experiments for microbial inactivation were carried out without pool water recirculation and without chlorination since the primary objective of these experiments was to test the microbial inactivation of UVOX alone.

4.2. DBPs and micropollutants

Experiments designed to assess DBPs formation and removal of micropollutants were performed in a recirculating system. The experiment only used 30% of the pool volume (approx. 170 m^3 of water) in order to have an optimum water turn over time of 2.8–3 h as recommended by the UVOX manufacturer. The water flow rate in all experiments was 56.7 ± 0.5 m^3/h which was also the maximum water flow that could be achieved. Water temperature ranged from 10.5 to 12.5 °C and pH 8.0 ± 0.2.

Four different experiments were performed as described in Table 1. Sodium hypochlorite solution (15%) was continuously dosed at a constant rate (1000 mL/h), aiming at 0.3 mgCl_2/L of free residual chlorine (lower limit of free residual chlorine according German standard of water quality in swimming pools (DIN, 2012)). The experiments were conducted sequentially without pool water renewal.

At the start of each experiment, 1 L of BFA stock solution (~170 gC/L) was added to the pool water in order to achieve a final concentration of 1 mgC/L of BFA in the pool. A mixture of pharmaceuticals and EDCs in 150 mL of methanol was added to the pool to achieve a final concentration of ~5 μg/L and ~1 μg/L, respectively. Both BFA and micropollutants were added to the pool water by injecting concentrated solutions into the circulation pipe through point 4 in Fig. 1. Subsequently, the pool water was recirculated for 3 h without inference from the sand filters to ensure proper mixing of added compounds with the pool water. The sand filters were then re-connected before starting the experiment.

Water samples for micropollutant analysis were collected using 100 mL amber PET bottles. Immediately after sample collection, the water samples for pharmaceutical analyses were quenched by adding 1 mL ascorbic acid (25 mg/L). Separately, water samples for DBPs analysis were collected in 250 mL brown glass bottles with no headspace and were kept at 4 °C. Samples for THM analysis were quenched by adding 1 mL of sodium thiosulfate (20 mg/L) and samples for HAA analyses were quenched by adding 25 mg of NH_4Cl in 250 mL sampling bottles.

5. Results and discussion

5.1. Inactivation of Bacillus subtilis spores

The dose response curve (Fig. 2) shows the inactivation of *B. subtilis* spores under different conditions; the curves are compared on the basis of the UV dose applied. The UV disinfection curve showed an increase in removal from 0.9 log at an IT of 5.8 mJ/cm^2 up to 1.3 log at 24 mJ/cm^2, and above this UV dose, the inactivation of *B. subtilis* spores was not optimum. This might be due to the hydraulic conditions as a consequence of lower flow in the

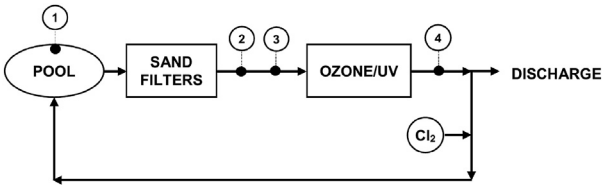

Fig. 1. Schematic of pool water treatment. Point 2: dosing point in microbial inactivation experiments; point 4: dosing point in DBP and micropollutant experiments; point 1, 3 and 4: sampling points.

Table 1
Experimental design for DBPs formation and micropollutants removal.

Exp.	Treatments*	Sampling points**	Sampling period (h)	
			DBPs	Micropollutants
1	SF	1	0, 3, 6, 24	0, 0.5, 1, 1.5, 2, 3, 6, 24
2	SF + UVOX	1, 3, 4		
3	SF + Cl_2	1		
4	SF + UVOX + Cl_2	1, 3, 4		

* SF: sand filtration, Cl_2: chlorination by sodium hypochlorite.
** as shown in Fig. 1.

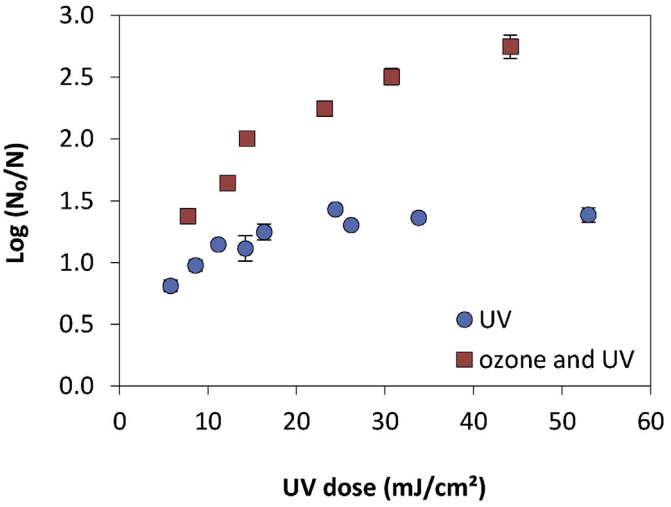

Fig. 2. *Bacillus subtilis* spores inactivation by UVOX. UV is UVOX without ozone generation. Error bars indicate the standard deviations of triplicate samples.

reaction chamber. The UVOX disinfection curve showed enhanced disinfection of *B. subtilis* spores (39%–99%) (Fig. 2). The increase of *B. subtilis* spores inactivation was more substantial at higher UV doses. In UVOX, mixtures of ozone and air are injected to the pool water stream at a constant flow, even when the pool water flow rate changed. Therefore, the amount of ozone injected to the pool water stream at low flow rates (corresponds to high UV doses) will be relatively higher than at high flow rates (corresponds to low UV doses). The experiments using UVOX demonstrated that the addition of ozone significantly enhanced the overall inactivation of *B. subtilis* spores compared to applying UV alone. This result is in agreement with previous studies demonstrating synergistic effects of combined ozone and UV or sequential use of ozone followed by UV on inactivation of microorganisms (*E.coli*, MS2, *B. subtilis* spores, total and faecal coliforms) (Bustos et al., 2010; Fang et al., 2014; Jung et al., 2008; Wu et al., 2015).

Pool Water Treatment and Advisory Group (PWTAG) recommends that the UV dose for UV installation in swimming pools should be able to deliver minimum 3 log inactivation in the viability of *Cryptosporidium parvum* oocysts (PWTAG, 2016). The UV dose required for 3 log inactivation of *C. parvum* oocysts is < 20 mJ/cm^2 (Hijnen et al., 2006). According to the biodosimetry test performed (Cabaj et al., 1996), the actual UV dose of 20 mJ/cm^2 for inactivation *C. parvum* oocysts is equivalent to UV dose of <10 mJ/cm^2 from UVOX which can be achieved at the maximum water flow rate tested (Supplementary material Figs. S2 and S3).

5.2. DBPs and micropollutants experiments

Chlorine was added at a constant rate during the experiments and BFA was only added at the beginning of each experiment. A gradual increase of free chlorine levels was observed and the increase was more evident between 6 and 24 h experiments (Supplementary material Fig. S4). This increase might be due to the absence of photolysis of chlorine during the night (Nowell and Hoigné, 1992).

The experiments were conducted in series and the water was reused hence higher organic carbon concentration was observed in the later experiments.

5.2.1. Formation of DBPs

An increase in THM formation was observed within 24 h in both experiments, applying UVOX followed by chlorination and chlorination alone (Fig. 3). As expected, the increase of THM concentrations observed followed the order TCM > BDCM > DBCM > TBM as reported in other studies (Cassan et al., 2006; Lourencetti et al., 2012; Panyakapo et al., 2008; Weaver et al., 2009) and total THM (TTHM) was highly dominated by TCM. During UVOX followed by chlorination, TCM, BDCM and DBCM were formed at similar concentrations. The increase of TBM formation was negligible in both experiments.

Bromine incorporation factors (BIF) of THMs at sampling period 0, 3, 6, and 24 h with chlorine alone were 0.422, 0.260, 0.246, and 0.260, respectively. Higher BIFs from experiments with UVOX (0.154, 1.098, 1.097, and 0.825, respectively) were observed after 3 h of experiment. Higher BIF values suggest that the formation of DBPs shifted to the brominated species which is attributed to the addition of ozone (Mao et al., 2014). In the presence of bromide, ozone and chlorine in the form of HOCl/OCl oxidized bromide to aqueous bromine (HOBr/OBr) (Farkas et al., 1949; Haag and Hoigne, 1983) which react 10 times faster than chlorine with organic matter (Westerhoff et al., 2004). Consequently, the addition of ozone may have caused the formation of more brominated DBPs. This may explain the results in our study where TCM concentrations observed during experiments with chlorination alone were 2–4 times higher than in experiments with UVOX followed by chlorination. On the other hand, formation of brominated species (BDCM and DBCM) in experiments with UVOX followed by chlorination were observed higher than in experiments with chlorination alone.

Additionally, bromide was already present in the filling water for the pool. During the experiments with chlorination alone and with UVOX followed by chlorination, the initial bromide concentration were 76 μg/L and 160 μg/L, respectively due to decreasing bromide concentration during the period of experiments. As a result, the bromide concentration at the start of experiment with chlorination was half of the initial concentration in the experiment with UVOX followed by chlorination. Since an increasing bromide concentration resulted in higher formation of TTHM (Bond et al., 2014; Chowdhury et al., 2010), higher initial concentration of bromide might also contribute in higher THMs formation in experiment with UVOX, particularly for brominated DBPs.

From the nine HAAs analysed, only DCAA, DBAA and BCAA were detected at concentrations above the limit of quantification (Supplementary material Table S2) and showed noticeable changes in concentration during the experiment. Of the chlorinated HAA species, DCAA, was observed as the dominant HAA formed during experiments with chlorination while in UVOX followed by chlorination, the detected HAAs species were formed at similar concentrations (Fig. 4). The formation of DCAA during experiments with UVOX followed by chlorination was negligible in comparison to the concentrations formed during experiments with chlorination,

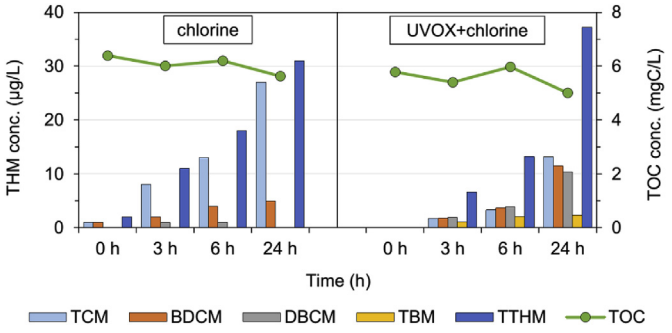

Fig. 3. Increase of THMs in pool water treated with chlorination and UVOX followed by chlorination.

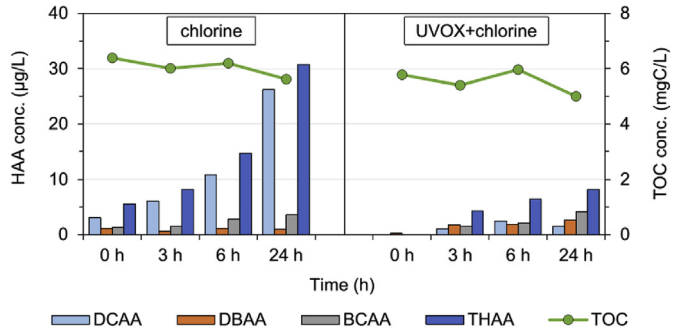

Fig. 4. Increase of HAAs in pool water treated with chlorination and UVOX followed by chlorination.

while the concentrations of brominated species were similar in both experiments.

DCAA and TCAA are the most abundant HAAs detected in chlorinated water (Teo et al., 2015). However, in this study, TCAA detected was below the limit of quantification (<3 µg/L). The reason might be that the model precursors in this study have propensity to form dihaloacetic acids than trihaloacetic acids. As model precursors, some BFA compounds such as citric acid, have shown to generate higher TCM and DCAA, in comparison to other BFA compounds (Kanan and Karanfil, 2011; Yang et al., 2016). The pH used in this study (pH 8) was also not favourable for TCAA formation. It was suggested that THMs and TCAA have a similar precursor structure and in alkali conditions, base-catalysed hydrolysis dominates, leading to formation of THMs while TCAA will be formed in acidic conditions (Liang and Singer, 2003).

BIF of HAAs at sampling period 0, 3, 6, and 24 h with chlorine alone were 0.492, 0.246, 0.252, and 0.128, respectively. Higher BIFs from experiments with UVOX (0, 0.995, 0.735, and 1.013, respectively) were observed after 3 h of experiment. Similarly to THMs, BIF values of HAA suggest that the formation of DBPs shifted to brominated species which is attributed to the addition of ozone (Mao et al., 2014).

Bromate were also present in pool water during experiments with chlorination alone and UVOX followed by chlorination at initial concentrations of 91 µg/L and 33 µg/L, respectively which then increased up to 140 µg/L and 82 µg/L. Chlorination, ozonation, and UV/chlorination can form bromate in the presence of bromide (Fang et al., 2017; Margerum and Huff Hartz, 2002; von Gunten and Hoigne, 1994). However, the increase in bromate observed in both experiments after 24 h was in the same order (49 µg/L) regardless of the treatment applied; with or without UVOX. In chlorination experiments using sodium hypochlorite, bromate may be already present as an impurity from commercial sodium hypochlorite solution (Asami et al., 2009; Garcia-Villanova et al., 2010). This suggests that the increase was likely due to continuous chlorine addition rather than bromide in the water.

5.2.2. Removal of pharmaceuticals and EDCs

The concentration profiles of pharmaceuticals and EDCs in water samples collected from the pool in 24 h experiments are shown in Fig. 5. In chlorinated pool water, most of the selected pharmaceuticals and EDCs were removed after less than 3 h of chlorination except for caffeine, atenolol and ibuprofen. After 24 h of chlorination, 97% removal was achieved for most of the compounds while only 60% of ibuprofen was removed. By adding UVOX to the treatment train, ibuprofen was completely removed after 24 h. It can be concluded that the removal of the target compounds was mostly driven by chlorine except in case of ibuprofen with UVOX enhancing the removal. In both experiments, acetaminophen, venlafaxine, estrone and estradiol were removed faster compared to other compounds (Supplementary material Table S3). Atenolol, carbamazepine, venlafaxine, estrone and caffeine were found to have slower reaction rate when UVOX was used.

High removal of acetaminophen after 24 h of contact time with chlorine and more recalcitrance of ibuprofen and caffeine to chlorination were also observed in the literature (Weng et al., 2014; Westerhoff et al., 2005). Westerhoff et al. (2005) also demonstrated high removals of estrone, estradiol, and carbamazepine. In a study by Wang et al. (2016), only 5.5% degradation of carbamazepine was observed by chlorination. The differences in results are likely due to the experimental protocol (e.g. contact time, pH and dose). The use of UVOX without chlorination has shown partial removal of estrone, estradiol and acetaminophen (<75%) and no effect on other compounds (data not shown) while combining UVOX and chlorination leads to complete removal of ibuprofen. A recent study by Xiang et al. (2016) shows little or no effect of applying UV and chlorine separately in the degradation of ibuprofen while the combination of UV and chlorine significantly increased the degradation rate. The presence of bromide in water also increased the degradation rate of caffeine and carbamazepine but reduced the degradation rate of ibuprofen during UV/chlorine treatment (Cheng et al., 2018). Westerhoff et al. (2005) showed that ozone was able to oxidized >80% of acetaminophen, carbamazepine, ibuprofen, estrone and estradiol. Bromine, chlorine and ozone could effectively oxidize phenolic compounds (Alum et al., 2004; Gallard et al., 2003; Westerhoff et al., 2005). Subsequently, higher degradation rates of micropollutants, such as acetaminophen, estrone and estradiol are expected. However, it should be noted that most

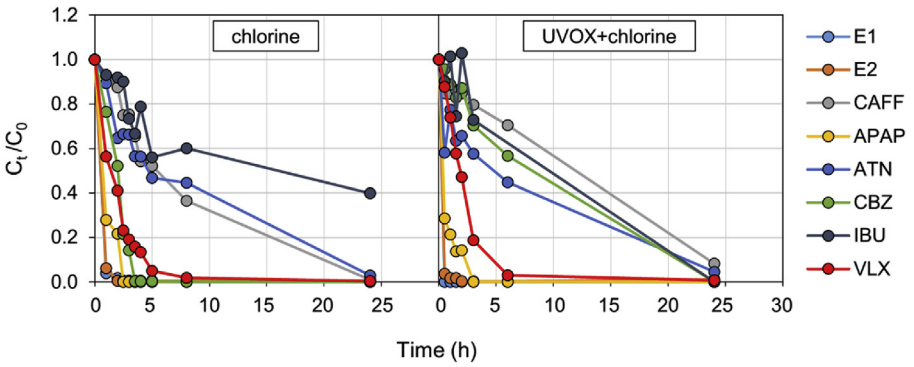

Fig. 5. Concentration profiles for pharmaceuticals and EDCs in pool water treated with chlorine and UVOX followed by chlorination. (E1: estrone, E2: estradiol, CAFF: caffeine, APAP: acetaminophen, ATN: atenolol, CBZ: carbamazepine, IBU: ibuprofen, VLX: venlafaxine).

studies on removal of micropollutants use higher doses of UV and ozone (Wang et al., 2016; Xiang et al., 2016). In this study, the use of low concentrations of ozone and the competition with NOM and BFA, limit the oxidization of pharmaceuticals and EDCs by UVOX.

In this study, chlorine was dosed continuously resulting in continuous elimination of micropollutants. However, bromide might also contributed in the process due to formation of HOBr/OBr which has higher reaction rate compared to HOCl/OCl. These compounds were continuously exposed to chlorine which provides more time for degradation of compounds with lower reaction rates. Regardless of the effectiveness of the treatment, the degradation of pharmaceuticals and EDCs can generate transformation products which may be more hazardous than the parent compounds (Michael et al., 2014; Noguera-Oviedo and Aga, 2016) and should be considered in future studies.

6. Conclusions

UVOX treatment is a promising technology for swimming pool water treatment. It has proven to be effective in inactivation of chlorine resistant microorganisms. In chlorinated pool water, inclusion of UVOX reduced the formation of TCM and DCAA, however, as expected, brominated DBPs (BDCM, DBCM, DBAA and BCAA) were detected at higher concentrations. Consequently, the presence of bromide in water has to be taken into account when using UVOX as pool water treatment, even though low concentrations of ozone were used.

Chlorination was able to remove most pharmaceuticals tested, however, longer contact time was needed for complete removal of caffeine and atenolol while 40% of ibuprofen was still persistent even after 24 h. In treatment combining UVOX and chlorination, the removal of micropollutants was mainly influenced by chlorine. It was observed that UVOX enhanced the degradation of ibuprofen, the most resistant pharmaceuticals in chlorinated water in this study.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.12.126.

References

Alum, A., Yoon, Y., Westerhoff, P., Abbaszadegan, M., 2004. Oxidation of bisphenol A, 17β-estradiol, and 17α-ethynyl estradiol and byproduct estrogenicity. Environ. Toxicol. 19 (3), 257–264.

Asami, M., Kosaka, K., Kunikane, S., 2009. Bromate, chlorate, chlorite and perchlorate in sodium hypochlorite solution used in water supply. J. Water Supply Res. T. 58 (2), 107–115.

Betancourt, W.Q., Rose, J.B., 2004. Drinking water treatment processes for removal of *Cryptosporidium* and *Giardia*. Vet. Parasitol. 126 (1), 219–234.

Beyer, A., Worner, H., Van Lierop, R., 2004. The Use of UV for Destruction of Combined Chlorine [technical note]. Wallace & Tiernan.

Bolton, J.R., Linden, K.G., 2003. Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments. J. Environ. Eng. 129 (3), 209–215.

Bond, T., Huang, J., Graham, N.J.D., Templeton, M.R., 2014. Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water — a case study. Sci. Total Environ. 470–471, 469–479.

Bustos, Y.A., Vaca, M., López, R., Torres, L.G., 2010. Disinfection of a wastewater flow treated by advanced primary treatment using O_3, UV and O_3/UV combinations. J. Environ. Sci. Heal, A 45 (13), 1715–1719.

Cabaj, A., Sommer, R., Schoenen, D., 1996. Biodosimetry: model calculations for UV water disinfection devices with regard to dose distributions. Water Res. 30 (4), 1003–1009.

Campbell, C.G., Borglin, S.E., Green, F.B., Grayson, A., Wozei, E., Stringfellow, W.T., 2006. Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: a review. Chemosphere 65 (8), 1265–1280.

Cassan, D., Mercier, B., Castex, F., Rambaud, A., 2006. Effects of medium-pressure UV lamps radiation on water quality in a chlorinated indoor swimming pool. Chemosphere 62 (9), 1507–1513.

Cheema, W.A., Kaarsholm, K.M.S., Andersen, H.R., 2017. Combined UV treatment and ozonation for the removal of by-product precursors in swimming pool water. Water Res. 110, 141–149.

Cheng, S., Zhang, X., Yang, X., Shang, C., Song, W., Fang, J., Pan, Y., 2018. The multiple role of bromide ion in PPCPs degradation under UV/Chlorine treatment. Environ. Sci. Technol. 52 (4), 1806–1816.

Chevrefils, G., Caron, É., Wright, H., Sakamoto, G., Payment, P., Barbeau, B., Cairns, B., 2006. UV dose required to achieve incremental log inactivation of bacteria, protozoa and viruses. IUVA News 8 (1), 38–45.

Cho, M., Kim, J.-H., Yoon, J., 2006. Investigating synergism during sequential inactivation of *Bacillus subtilis* spores with several disinfectants. Water Res. 40 (15), 2911–2920.

Choi, Y., Cho, M., Lee, Y., Choi, J., Yoon, J., 2007. Inactivation of *Bacillus subtilis* spores during ozonation in water treatment plant: influence of pre-treatment and consequences for positioning of the ozonation step. Chemosphere 69 (5), 675–681.

Chowdhury, S., Champagne, P., James McLellan, P., 2010. Investigating effects of bromide ions on trihalomethanes and developing model for predicting bromodichloromethane in drinking water. Water Res. 44 (7), 2349–2359.

Cimetiere, N., De Laat, J., 2014. Effects of UV-dechloramination of swimming pool water on the formation of disinfection by-products: a lab-scale study. Microchem. J. 112, 34–41.

Clancy, J.L., Bukhari, Z., Hargy, T.M., Bolton, J.R., Dussert, B.W., Marshall, M.M., 2000. Using UV to inactivate *Cryptosporidium*. J. Am. Water Works Assoc. 92 (9), 97–104.

Corona-Vasquez, B., Samuelson, A., Rennecker, J.L., Mariñas, B.J., 2002. Inactivation of *Cryptosporidium parvum* oocysts with ozone and free chlorine. Water Res. 36 (16), 4053–4063.

Craik, S.A., Finch, G.R., Bolton, J.R., Belosevic, M., 2000. Inactivation of *Giardia muris* cysts using medium-pressure ultraviolet radiation in filtered drinking water. Water Res. 34 (18), 4325–4332.

Craik, S.A., Weldon, D., Finch, G.R., Bolton, J.R., Belosevic, M., 2001. Inactivation of *Cryptosporidium parvum* oocysts using medium-and low-pressure ultraviolet radiation. Water Res. 35 (6), 1387–1398.

DIN, 2012. Treatment of the Water of Swimming Pools and Baths - Part 1: General Requirements. Germany Standard DIN 19643-1: 2012-11.

Driedger, A., Staub, E., Pinkernell, U., Mariñas, B., Köster, W., von Gunten, U., 2001. Inactivation of *Bacillus subtilis* spores and formation of bromate during ozonation. Water Res. 35 (12), 2950–2960.

Driedger, A.M., Rennecker, J.L., Mariñas, B.J., 2000. Sequential inactivation of *Cryptosporidium parvum* oocysts with ozone and free chlorine. Water Res. 34 (14), 3591–3597.

Ekowati, Y., Buttiglieri, G., Ferrero, G., Valle-Sistac, J., Diaz-Cruz, M.S., Barceló, D., Petrovic, M., Villagrasa, M., Kennedy, M.D., Rodríguez-Roda, I., 2016. Occurrence of pharmaceuticals and UV filters in swimming pools and spas. Environ. Sci. Pollut. Res. 23 (14), 14431–14441.

European Commission, 2018. 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 Commission Implementing Decision (EU) 2015/495 (notified under document C(2018) 3362).

Fang, J., Liu, H., Shang, C., Zeng, M., Ni, M., Liu, W., 2014. *E. coli* and bacteriophage MS2 disinfection by UV, ozone and the combined UV and ozone processes. Front. Environ. Sci. Eng. 8 (4), 547–552.

Fang, J., Zhao, Q., Fan, C., Shang, C., Fu, Y., Zhang, X., 2017. Bromate formation from the oxidation of bromide in the UV/chlorine process with low pressure and medium pressure UV lamps. Chemosphere 183, 582–588.

Farkas, L., Lewin, M., Bloch, R., 1949. The reaction between hypochlorite and bromides. J. Am. Chem. Soc. 71 (6), 1988–1991.

Florentin, A., Hautemanière, A., Hartemann, P., 2011. Health effects of disinfection by-products in chlorinated swimming pools. Int. J. Hyg Environ. Health 214 (6), 461–469.
FOEN, 2015. Gewässerqualität: Revision der Gewässerschutzverordnung. Erläuternder Bericht zur Änderung der Gewässerschutzverordnung. https://www.bafu.admin.ch/bafu/de/home/themen/bildung/medienmitteilungen.msg-id-59323.html. https://www.newsd.admin.ch/newsd/message/attachments/41551.pdf.
Gallard, H., Pellizzari, F., Croué, J.P., Legube, B., 2003. Rate constants of reactions of bromine with phenols in aqueous solution. Water Res. 37 (12), 2883–2892.
Garcia-Villanova, R.J., Oliveira Dantas Leite, M.V., Hernández Hierro, J.M., de Castro Alfageme, S., García Hernández, C., 2010. Occurrence of bromate, chlorite and chlorate in drinking waters disinfected with hypochlorite reagents. Tracing their origins. Sci. Total Environ. 408 (12), 2616–2620.
Glaze, W.H., 1986. Reaction products of ozone: a review. Environ. Health Perspect. 69, 151.
Gorga, M., Petrovic, M., Barceló, D., 2013. Multi-residue analytical method for the determination of endocrine disruptors and related compounds in river and waste water using dual column liquid chromatography switching system coupled to mass spectrometry. J. Chromatogr. A 1295, 57–66.
Gros, M., Rodríguez-Mozaz, S., Barceló, D., 2012. Fast and comprehensive multi-residue analysis of a broad range of human and veterinary pharmaceuticals and some of their metabolites in surface and treated waters by ultra-high-performance liquid chromatography coupled to quadrupole-linear ion trap tandem mass spectrometry. J. Chromatogr. A 1248, 104–121.
Haag, W.R., Hoigne, J., 1983. Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environ. Sci. Technol. 17 (5), 261–267.
Hansen, K.M., Zortea, R., Piketty, A., Vega, S.R., Andersen, H.R., 2013. Photolytic removal of DBPs by medium pressure UV in swimming pool water. Sci. Total Environ. 443, 850–856.
Hansen, K.M.S., Spiliotopoulou, A., Cheema, W.A., Andersen, H.R., 2016. Effect of ozonation of swimming pool water on formation of volatile disinfection by-products – a laboratory study. Chem. Eng. J. 289, 277–285.
Hijnen, W., Beerendonk, E., Medema, G.J., 2006. Inactivation credit of UV radiation for viruses, bacteria and protozoan (oo) cysts in water: a review. Water Res. 40 (1), 3–22.
Jacangelo, J.G., Patania, N.L., Trussed, R.R., Haas, C.N., Gerba, C., 2002. Inactivation of Waterborne Emerging Pathogens by Selected Disinfectants. AWWA Research Foundation and American Water Works Association, Denver, USA.
Jarroll, E.L., Bingham, A.K., Meyer, E.A., 1981. Effect of chlorine on *Giardia lamblia* cyst viability. Appl. Environ. Microbiol. 41 (2), 483–487.
Judd, S.J., Bullock, G., 2003. The fate of chlorine and organic materials in swimming pools. Chemosphere 51 (9), 869–879.
Jung, Y.J., Oh, B.S., Kang, J.-W., 2008. Synergistic effect of sequential or combined use of ozone and UV radiation for the disinfection of *Bacillus subtilis* spores. Water Res. 42 (6), 1613–1621.
Kanan, A., Karanfil, T., 2011. Formation of disinfection by-products in indoor swimming pool water: the contribution from filling water natural organic matter and swimmer body fluids. Water Res. 45 (2), 926–932.
Kassotaki, E., Pijuan, M., Rodriguez-Roda, I., Buttiglieri, G., 2019. Comparative assessment of endocrine disrupting compounds removal in heterotrophic and enriched nitrifying biomass. Chemosphere 217, 659–668.
Korich, D.G., Mead, J.R., Madore, M.S., Sinclair, N.A., Sterling, C.R., 1990. Effects of ozone, chlorine dioxide, chlorine, and monochloramine on *Cryptosporidium parvum* oocyst viability. Appl. Environ. Microbiol. 56 (5), 1423–1428.
Kristensen, G.H., Klausen, M.M., Andersen, H.R., Erdinger, L., Lauritsen, F., Arvin, E., Albrechtsen, H.J., 2009. Full scale test of UV-based water treatment technologies at Gladsaxe Sport Centre–with and without advanced oxidation mechanisms. In: The 3rd International Swimming Pool and Spa Conference, London.
Li, Z., Xiang, X., Li, M., Ma, Y., Wang, J., Liu, X., 2015. Occurrence and risk assessment of pharmaceuticals and personal care products and endocrine disrupting chemicals in reclaimed water and receiving groundwater in China. Ecotoxicol. Environ. Saf. 119, 74–80.
Liang, L., Singer, P.C., 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. Environ. Sci. Technol. 37 (13), 2920–2928.
Lourencetti, C., Grimalt, J.O., Marco, E., Fernandez, P., Font-Ribera, L., Villanueva, C.M., Kogevinas, M., 2012. Trihalomethanes in chlorine and bromine disinfected swimming pools: air-water distributions and human exposure. Environ. Int. 45 (0), 59–67.
Mao, Y., Wang, X., Yang, H., Wang, H., Xie, Y.F., 2014. Effects of ozonation on disinfection byproduct formation and speciation during subsequent chlorination. Chemosphere 117, 515–520.
Margerum, D.W., Huff Hartz, K.E., 2002. Role of halogen(i) cation-transfer mechanisms in water chlorination in the presence of bromide ion. J. Environ. Monit. 4 (1), 20–26.
Michael, I., Vasquez, M.I., Hapeshi, E., Haddad, T., Baginska, E., Kümmerer, K., Fatta-Kassinos, D., 2014. Metabolites and transformation products of pharmaceuticals in the aquatic environment as contaminants of emerging concern. In: Lambropoulou, D.A., Nollet, L.M. (Eds.), Transformation Products of Emerging Contaminants in the Environment. John Wiley & Sons Ltd.
Nieuwenhuijsen, M.J., Toledano, M.B., Eaton, N.E., Fawell, J., Elliott, P., 2000. Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. Occup. Environ. Med. 57 (2), 73–85.
Noguera-Oviedo, K., Aga, D.S., 2016. Lessons learned from more than two decades of research on emerging contaminants in the environment. J. Hazard Mater. 316, 242–251.
Nowell, L.H., Hoigné, J., 1992. Photolysis of aqueous chlorine at sunlight and ultraviolet wavelengths—II. Hydroxyl radical production. Water Res. 26 (5), 599–605.
Panyakapo, M., Soontornchai, S., Paopuree, P., 2008. Cancer risk assessment from exposure to trihalomethanes in tap water and swimming pool water. J. Environ. Sci. 20 (3), 372–378.
Petrovic, M., Eljarrat, E., Lopez de Alda, M.J., Barceló, D., 2004. Endocrine disrupting compounds and other emerging contaminants in the environment: a survey on new monitoring strategies and occurrence data. Anal. Bioanal. Chem. 378 (3), 549–562.
PWTAG, 2016. 31 Ultraviolet Disinfection: Specification, Maintenance and Validation. Pool Water Treatment Advisory Group.
Rennecker, J.L., Driedger, A.M., Rubin, S.A., Mariñas, B.J., 2000. Synergy in sequential inactivation of *Cryptosporidium parvum* with ozone/free chlorine and ozone/monochloramine. Water Res. 34 (17), 4121–4130.
Rennecker, J.L., Mariñas, B.J., Owens, J.H., Rice, E.W., 1999. Inactivation of *Cryptosporidium parvum* oocysts with ozone. Water Res. 33 (11), 2481–2488.
Richardson, S.D., DeMarini, D.M., Kogevinas, M., Fernandez, P., Marco, E., Lourencetti, C., Ballesté, C., Heederik, D., Meliefste, K., McKague, A.B., Marcos, R., Font-Ribera, L., Grimalt, J.O., Villanueva, C.M., 2010. What's in the pool? A comprehensive identification of disinfection by-products and assessment of mutagenicity of chlorinated and brominated swimming pool water. Environ. Health Perspect. 118 (11), 1523–1530.
Richardson, S.D., Ternes, T.A., 2011. Water analysis: emerging contaminants and current issues. Anal. Chem. 83 (12), 4614–4648.
Shin, G.-A., Linden, K.G., Arrowood, M.J., Sobsey, M.D., 2001. Low-pressure UV inactivation and DNA repair potential of *Cryptosporidium parvum* oocysts. Appl. Environ. Microbiol. 67 (7), 3029–3032.
Sommer, R., Cabaj, A., Haider, T., Hirschmann, G., 2004. UV Drinking water disinfection–requirements, testing and surveillance: exemplified by the Austrian National Standards M 5873-1 and M 5873-2. IUVA News 6 (4), 27–35.
Spiliotopoulou, A., Hansen, K.M.S., Andersen, H.R., 2015. Secondary formation of disinfection by-products by UV treatment of swimming pool water. Sci. Total Environ. 520, 96–105.
Suppes, L.M., Huang, C.-H., Lee, W.-N., Brockman, K.J., 2017. Sources of pharmaceuticals and personal care products in swimming pools. J. Water Health 15 (5), 829–833.
Teo, T.L.L., Coleman, H.M., Khan, S.J., 2015. Chemical contaminants in swimming pools: occurrence, implications and control. Environ. Int. 76 (0), 16–31.
Teo, T.L.L., Coleman, H.M., Khan, S.J., 2016. Occurrence and daily variability of pharmaceuticals and personal care products in swimming pools. Environ. Sci. Pollut. Res. 23 (7), 6972–6981.
USEPA, 1999. Alternative Disinfectants and Oxidants Guidance Manual. U.S. Environmental Protection Agency, Washington DC.
USEPA, 1995. Method 552.2 Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection. National Exposure Research Laboratory Office of Research and Development, Cincinnati, Ohio, USA.
Vlaanderen, J., van Veldhoven, K., Font-Ribera, L., Villanueva, C.M., Chadeau-Hyam, M., Portengen, L., Grimalt, J.O., Zwiener, C., Heederik, D., Zhang, X., Vineis, P., Kogevinas, M., Vermeulen, R., 2017. Acute changes in serum immune markers due to swimming in a chlorinated pool. Environ. Int. 105, 1–11.
Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castano-Vinyals, G., 2007. Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools. Am. J. Epidemiol. 165 (2), 148–156.
von Gunten, U., Hoigne, J., 1994. Bromate formation during ozonization of bromide-containing waters: interaction of ozone and hydroxyl radical reactions. Environ. Sci. Technol. 28 (7), 1234–1242.
Wang, W.-L., Wu, Q.-Y., Huang, N., Wang, T., Hu, H.-Y., 2016. Synergistic effect between UV and chlorine (UV/chlorine) on the degradation of carbamazepine: influence factors and radical species. Water Res. 98, 190–198.
Weaver, W.A., Li, J., Wen, Y., Johnston, J., Blatchley, M.R., Blatchley III, E.R., 2009. Volatile disinfection by-product analysis from chlorinated indoor swimming pools. Water Res. 43 (13), 3308–3318.
Weng, S., Li, J., Blatchley III, E.R., 2012. Effects of UV_{254} irradiation on residual chlorine and DBPs in chlorination of model organic-N precursors in swimming pools. Water Res. 46 (8), 2674–2682.
Weng, S., Sun, P., Ben, W., Huang, C.-H., Lee, L.T., Blatchley III, E.R., 2014. The presence of pharmaceuticals and personal care products in swimming pools. Environ. Sci. Technol. Lett. 1 (12), 495–498.
Westerhoff, P., Chao, P., Mash, H., 2004. Reactivity of natural organic matter with aqueous chlorine and bromine. Water Res. 38 (6), 1502–1513.
Westerhoff, P., Yoon, Y., Snyder, S., Wert, E., 2005. Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. Environ. Sci. Technol. 39 (17), 6649–6663.
WHO, 2006. Guidelines for Safe Recreational Water Environments, vol. 2. Swimming Pools and Similar Environments. World Health Organization, Geneva.
Wu, D., Lu, G., Zhang, R., You, H., Yan, Z., Li, Y., 2015. Disinfection characteristics of the combined ultraviolet radiation and ozone process using *Escherichia coli* as a probe. Water Sci. Technol. Water Supply 16 (1), 163–170.
Xiang, Y., Fang, J., Shang, C., 2016. Kinetics and pathways of ibuprofen degradation

by the UV/chlorine advanced oxidation process. Water Res. 90, 301–308.
Xiao, F., Zhang, X., Zhai, H., Lo, I.M.C., Tipoe, G.L., Yang, M., Pan, Y., Chen, G., 2012. New halogenated disinfection byproducts in swimming pool water and their permeability across skin. Environ. Sci. Technol. 46 (13), 7112–7119.
Yang, L., Schmalz, C., Zhou, J., Zwiener, C., Chang, V.W.C., Ge, L., Wan, M.P., 2016. An insight of disinfection by-product (DBP) formation by alternative disinfectants for swimming pool disinfection under tropical conditions. Water Res. 101, 535–546.
Yeh, R.Y.L., Farré, M.J., Stalter, D., Tang, J.Y.M., Molendijk, J., Escher, B.I., 2014. Bioanalytical and chemical evaluation of disinfection by-products in swimming pool water. Water Res. 59, 172–184.
Yoon, Y., Ryu, J., Oh, J., Choi, B.-G., Snyder, S.A., 2010. Occurrence of endocrine disrupting compounds, pharmaceuticals, and personal care products in the Han River (Seoul, South Korea). Sci. Total Environ. 408 (3), 636–643.