



Determination of oxidant exposure during ozonation of secondary effluent to predict contaminant removal



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ABSTRACT

The use of kinetic models to predict oxidation performance in wastewater is limited due to fast ozone depletion during the first milliseconds of the reaction. This paper introduces the Quench Flow Module (QFM), a bench-scale experimental technique developed to measure the first 5–500 milliseconds of ozone depletion for accurate determination of ozone exposure in wastewater-ozonation processes. Calculated ozone exposure in QFM experiments was up to 24% lower than in standard batch experiments, strongly depending on the initial sampling point for measurement in batch experiments. However, oxidation rates of slowly- and moderately-reacting trace organic compounds (TrOCs) were accurately predicted from batch experiments based on integration of ozone depletion and removal of an ozone-resistant probe compound to calculate oxidant exposures. An alternative concept, where ozone and hydroxyl radical exposures are back-calculated from the removal of two probe compounds, was tested as well. Although the QFM was suggested to be an efficient mixing reactor, ozone exposure ranged over three orders of magnitude when different probe compounds reacting moderately with ozone were used for the calculation. These effects were beyond uncertainty ranges for apparent second order rate constants and consistently observed with different ozone-injection techniques, i.e. QFM, batch experiments, bubble columns and venturi injection. This indicates that previously suggested mixing effects are not responsible for the difference and other still unknown factors might be relevant. Results furthermore suggest that ozone exposure calculations from the relative residual concentration of a probe compound are not a promising option for evaluation of ozonation of secondary effluents.

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1. Introduction

Ozonation reduces the concentrations of many trace organic compounds (TrOCs) from secondary wastewater effluent (Hollender et al., 2009; Huber et al., 2005; Ternes et al., 2003; Wert et al., 2009b; Zucker et al., 2015b) via direct and indirect oxidation reactions. Optimization of ozone dosing in tertiary treatment is commonly based on selected fast-, moderately- and slowly-reacting TrOC elimination requirements (e.g. Lee et al., 2013). Hence, modeling and predicting the elimination of TrOCs is an essential tool for controlling ozonation systems. The relative

residual compound concentration (c) following ozonation can be determined by second-order kinetics with ozone and hydroxyl ($\cdot\text{OH}$) radicals, using second-order rate constants $k(\text{O}_3)$ and $k(\cdot\text{OH})$, ozone exposure ($\int(\text{O}_3)dt$) and $\cdot\text{OH}$ -radical exposure ($\int(\cdot\text{OH})dt$), as expressed in Eq. (1) (von Gunten and von Sonntag, 2012). Oxidation of TrOCs can be adequately predicted when the rate constants are known – either derived from the literature (e.g. Huber et al., 2003) or determined based on direct measurements or competition kinetics method (von Gunten and von Sonntag, 2012). Oxidant exposures are determined specifically for every application since they are directly affected by water quality parameters. However, oxidant exposure measurement is a significant obstacle due to low $\cdot\text{OH}$ -radical concentration and fast ozone depletion during ozonation.

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$$\frac{c}{c_0} = \exp\left(-k_{O_3} \int [O_3] dt - k_{\cdot OH} \int [\cdot OH] dt\right) \quad (1)$$

Oxidation performance in drinking and surface waters can be predicted from batch experiments by calculating ozone and $\cdot OH$ -radical exposures (Elovitz and von Gunten, 1999). $\cdot OH$ -radical exposure can be back-calculated from the removal of an ozone-resistant probe compound (e.g. pCBA) (Elovitz and von Gunten, 1999; Pi et al., 2005; Wert et al., 2009a). The direct reaction of the resistant probe compound with ozone is negligible, hence its contribution to compound removal can be eliminated from the equation, according to Eq. (2). This method can be referred as ' $\cdot OH$ -radical probe method'. Ozone exposure can be determined by integrating measured ozone concentrations in batch experiments over time (referred here as 'direct indigo method'). Hence, the evaluation of oxidation performance can be determined from the ozone depletion in conjunction with removal of the probe compound.

$$\frac{c}{c_0} = \exp\left(-k_{\cdot OH} \int [\cdot OH] dt\right) \quad (2)$$

However, an accurate ozone exposure measurement in wastewater effluents is problematic. The rapid reaction of effluent organic matter and even effluent particles (Zucker et al., 2015a) with ozone results in very rapid ozone depletion in the first milliseconds of the reaction and hence inaccurate determination of the ozone exposure (Buffle et al., 2006b; Schindler Wildhaber et al., 2015). Thus, sensitive and advanced methods, such as quench- or stopped-flow systems (Buffle et al., 2006b; Nöthe et al., 2009), are required to determine the accurate ozone exposure.

An alternative concept suggests that ozone exposure can be back-calculated from the removal of a probe compound that reacts with both ozone and $\cdot OH$ -radicals (Huber et al., 2005; Hübner et al., 2013). This concept involves indirect determination of oxidant exposures; where $\cdot OH$ -radical exposure is back-calculated from the removal of ozone-resistant probe compound (i.e. ' $\cdot OH$ -radical probe method'), and ozone exposure is back-calculated from removal of moderately- (or fast-) reacting probe compound (referred here as 'ozone probe method') following ozonation of wastewater effluents. The methods suggested to determine oxidant exposure are summarized in Table 1. However, predicting the elimination of fast-reacting TrOCs ($k(O_3) > 10^4 \text{ M}^{-1} \text{ s}^{-1}$) was not feasible. The reasons suggested for the poor prediction were either selective TrOC sorption to wastewater particles leading to some protection against ozone attack (Huber et al., 2005), mixing effect of aqueous ozone to the entire water (in batch systems), or gas-liquid mass-transfer limitation (in diffuser-based systems) which may lead to a similar oxidation degree for all fast-reacting TrOCs despite the different rate constants (Hübner et al., 2013). However, diffusion (i.e. gas-liquid mass-transfer) limitation was ruled out based on film theory by Huber et al. (2005). Consequently, it is assumed that the consumption of low ozone dosages is faster than the time required for volumetric sample homogenization in the experimental batch, semi-batch or diffuser-based pilot systems. To overcome this

limitation, other mixing alternatives in ozone systems must be taken into consideration, such as venturi ozone-injection or quench-flow systems.

In the present study, a quench-flow system was used to determine ozone exposure in wastewater effluents using the two proposed methods: (1) the quench-flow system is used as a tool to measure ozone depletion in the first milliseconds (5–500 ms) of the reaction in the 'direct indigo method' and (2) the system is used as an efficient mixing tool to overcome limitation through mixing in the 'ozone probe method'. Then, the feasibility of predicting oxidation of TrOCs by these methods was evaluated. Finally, different ozone-injection techniques were compared (stock solution mixing, diffusion, venturi injection) with respect to mixing and mass-transfer efficiency.

2. Materials and methods

2.1. Standards and reagents

Eleven TrOCs were selected for this study, based on the availability of established rate constants with ozone and $\cdot OH$ -radicals and their occurrence and concentration in secondary effluents. The TrOCs were separated according to their apparent second order rate constants at pH 8 for the reaction with ozone into fast-reacting ($k(O_3) > 10^4 \text{ M}^{-1} \text{ s}^{-1}$), moderately-reacting ($10 \text{ M}^{-1} \text{ s}^{-1} < k(O_3) < 10^4 \text{ M}^{-1} \text{ s}^{-1}$) and slowly-reacting ($k(O_3) < 10 \text{ M}^{-1} \text{ s}^{-1}$) compounds (Table 2). Stock solutions ($2\text{--}10 \text{ mg L}^{-1}$) were prepared separately for each TrOC in ultrapure water and kept in the dark at $4 \text{ }^\circ\text{C}$.

2.2. Experimental procedures

Six sets of experiments were conducted using a Quench Flow Module (QFM-400, Bio-Logic, Tennessee, USA) and an ozone batch reactor to evaluate the determination of oxidant exposure by the two concepts. Quench-flow experiments using similar system were described earlier by Lee et al. (2013). Experiments were performed in triplicates and conducted at room temperature ($\sim 22 \text{ }^\circ\text{C}$) with grab samples of secondary effluent from a wastewater treatment plant in Berlin (Ruhleben). General effluent parameters were: pH = 7.94 ± 0.05 , dissolved organic carbon (DOC) = $11.4 \pm 0.6 \text{ mg L}^{-1}$, nitrite (NO_2^-) = $72.8 \pm 29.8 \text{ } \mu\text{g L}^{-1}$, UV absorbance at 254 nm (UV_{254}) = $30.3 \pm 3.3 \text{ m}^{-1}$, TIC = $63.9 \pm 5.4 \text{ mg L}^{-1}$. A concentration of $10 \text{ } \mu\text{g L}^{-1}$ for all TrOCs (with the exception of para-chlorobenzoic acid [pCBA] at $100 \text{ } \mu\text{g L}^{-1}$) was spiked directly before starting the experiments to ensure reliable analysis of removal rates.

An ozone stock solution ($\sim 70 \text{ mg L}^{-1}$) was prepared by continuously bubbling ozone gas, produced from a pure oxygen-fed generator (Modular 8 HC generator, Wedeco (Xylem), Herford, Germany), in a stirred glass reactor filled with chilled ($4 \text{ }^\circ\text{C}$) ultrapure water to improve ozone solubility.

In the QFM, three syringes driven by independent motors introduce ozone stock solution, effluent and ultrapure water at different ratios into a mixing chamber. The reacting mixture then

Table 1
Summary of methods suggested for oxidant-exposure determination.

Exposure	$\cdot OH$ -radical	Ozone	
Method name	$\cdot OH$ -radicals probe method	1. Direct indigo method	2. Ozone probe method
Technique	Back-calculation from the removal of a probe compound	Integration of ozone depletion over time	Back-calculation from the removal of a probe compound
Probe compound used	Ozone-resistant TrOCs (pCBA, IOP or PRI)	Indigo quenching	Moderately-reacting TrOCs (ACS, BTA, MTP, BZF or VLX)

Table 2
Summary of second-order rate constants of analyzed TrOCs.

Compound	$k(\text{O}_3)^a$ pH 8 in $\text{M}^{-1}\text{s}^{-1}$	$k(\text{O}_{3,ss})^b$ in $\text{M}^{-1}\text{s}^{-1}$ (protonated/deprotonated)	$k(\cdot\text{OH})^c$ in $10^9 \text{M}^{-1}\text{s}^{-1}$	Reference
Para-chlorobenzoic acid (pCBA)	0.15	0.15	5.2	(Yao and Haag, 1991)
Iopromide (IOP)	0.8	0.8	3.3	(Baus et al., 2004)
Primidone (PRI)	1 ^d	<10 ^e	6.7 ^d	^d (Real et al., 2009)
Acesulfame (ACS)	88	88	4.5	^e (Lee et al., 2014)
Benzotriazole (BTA)	398 ^f	20/2.0·10 ³ ^f 3.5·10 ³ ^g (deprotonated)	14.2 ^h	(Kaiser et al., 2013) ^f (Benitez et al., 2015) ^g (Lee et al., 2014) ^h (Vel Leitner and Roshani, 2010)
Bezafibrate (BZF)	590	590	7.4	(Huber et al., 2003)
Metoprolol (MTP)	4·10 ⁴	330/8.6·10 ⁵	7.3	(Benner et al., 2008)
Venlafaxine (VLX)	5.6·10 ⁴ ⁱ	3.2·10 ³ /1.3·10 ⁶ ⁱ	8.8 ^j	ⁱ calculated based on Lee et al. (2014) ^j (Wols et al., 2013)
Carbamazepine (CBZ)	3·10 ⁵	3·10 ⁵	8.8	(Huber et al., 2003)
Diclofenac (DCF)	6.8·10 ⁵ ^k *1·10 ⁶ ^l	1·10 ⁶ ^l	7.5 ^l	^k (Sein et al., 2008) ^l (Huber et al., 2003)
Sulfamethoxazole (SMX)	5.7·10 ⁵ ^m (pH = 7.7) *2.5·10 ⁶ ⁿ (pH = 7)	4.7·10 ⁴ /5.7·10 ⁵ ^m	5.5 ⁿ 8.5 ^o	^m (Dodd et al., 2006) ⁿ (Huber et al., 2003) ^o (Mezyk et al., 2007)

^aapparent k -value for the reaction of O_3 at pH 8; ^bspecies-specific k -value for the reaction of O_3 ; ^c k -value for the reaction of OH radicals, * used for calculations in this study. Letters are for referring to specific comments or references.

passes through a single delay line, used as a contact chamber to control aging times, which were varied from 5 ms to 500 ms. The reaction was stopped by injecting an indigo solution with a fourth syringe into a second mixing chamber to quench any residual ozone, and the final solution was flushed through an exit line to a collection device. An automated program started all QFM experiments with a system rinse and determination of the ozone concentration in the stock solution by mixing with defined amount of ultrapure water in the first mixing chamber and quenching with indigo solution. It is worth noting that the time frame for handling ozone stock prior experiment was about 20 s in total, where 15–18% decrease in stock concentration was observed due to the auto decomposition rate of ozone and losses in the system. Hence, determination of ozone stock concentration prior to any experiment was vital to ensure reliability of applied ozone dosages.

For the evaluation of ozone exposure based on an accurate measurement of ozone depletion using the QFM, the spiked effluent was treated with moderate ($8.3 \pm 0.8 \text{ mg L}^{-1}$) and high ($13.2 \pm 0.8 \text{ mg L}^{-1}$) ozone dosages (to achieve ratios of applied ozone dosage to initial DOC (mg O_3 /mg DOC) of 0.73 and 1.16, respectively), at aging times of 5 ms–500 ms. For longer aging times, batch experiments were carried out in a 0.5-L magnetic-stirred reactor, by adding concentrated stock solutions of ozone to the effluent. Ozone dosage (at $t = 0$) was determined by measurement of ozone stock concentration and its relative volume in final working solution. Samples were taken after 10 s–600 s and immediately quenched with indigo solution.

To evaluate the ozone probe method, spiked effluent was mixed in the QFM with different amounts of ozone to obtain ozone dosages of 1.2 mg L^{-1} to 13.5 mg L^{-1} (specific ozone dosages of 0.1–1.1 mg O_3 /mg DOC). Ultrapure water was added from the third syringe to compensate for the different volumes of added ozone stock solution. Samples were analyzed after complete depletion of dissolved ozone (>0.5 h).

In addition, the effect of mass-transfer was evaluated in a venturi ozone-injection system using data from an ongoing pilot system treating secondary effluent (i.e., natural concentrations of TrOCs) by biofiltration, ozonation and short soil aquifer treatment at the Shafdan wastewater treatment plant in Israel (more details can be found in Zucker et al. (2015b)). Ozone was produced from pure oxygen (15 L min^{-1}) and introduced by venturi injection into the effluent stream. The ozonation unit (100 g h^{-1} , OCS GSO 30,

Xylem, Herford, Germany) was operated in continuous mode with a specific ozone dosage of 0.1–1.0 mg O_3 /mg DOC. General effluent parameters (prior ozonation) were: $\text{pH} = 7.81 \pm 0.05$, $\text{DOC} = 9.11 \pm 1.5 \text{ mg L}^{-1}$, $\text{NO}_2^- = 90.0 \pm 15.5 \mu\text{g L}^{-1}$, $\text{UV}_{254} = 17.1 \pm 1.2 \text{ m}^{-1}$, $\text{alkalinity} = 207 \pm 2 \text{ mg L}^{-1}$ as CaCO_3 . It should be noted that for both effluents, nitrite residues (less than 0.1 mg L^{-1}) had only minor effect on ozone consumption during experiments.

2.3. Analytical methods

Ozone concentrations in the gas stream were measured by an ozone gas analyzer (BMT 963, Berlin, Germany). O_3 stock solution concentrations and dissolved ozone residuals were measured according to indigo standard method 4500B (APHA et al., 2005). Temperature and pH were measured directly after the experiments using a WTW 357 pH meter (Germany). Samples for analysis of bulk parameters and TrOC concentrations were filtered through a 0.45- μm cellulose nitrate filter (Sartorius, Göttingen, Germany). DOC was measured on a varioTOC and a highTOC II analyzer (Elementar, Hanau, Germany). Analysis for UV_{254} was conducted on a Lambda 12 photometer (Perkin-Elmer, Rodgau, Germany). Other wastewater parameters were analyzed using standard methods (APHA et al., 2005).

TrOCs were measured by HPLC–MS/MS with electro-spray ionization after filtration. Analytical details are summarized in Table S1 in supporting information for all analyzed compounds. All TrOCs (other than pCBA) were detected by HPLC (Hewlett Packard 1100 Series, CA, USA) on a TSQ Vantage (Thermo Scientific, MA, USA) mass spectrometer. Separation was achieved using a 2.5 μm Acquity XSelect HSS T3 column (50 mm \times 2.1 mm, Waters, MA, USA) at a flow rate of $500 \mu\text{L min}^{-1}$ with a linear gradient from 98% eluent A (ultrapure water with 5% methanol and 0.5% formic acid) to 100% methanol (B). Analysis was performed with mass fragments chosen according to the DAIOS MS/MS database (Wasserchemische Gesellschaft, 2013). Deuterated internal standards (see Table S1, TRC, Toronto, Canada) were used for quantification. Data were evaluated using Xcalibur 2.1 (Thermo Scientific, MA, USA).

pCBA was detected by HPLC (Hewlett Packard 1100 Series, CA, USA) with a 3 μm Luna C18 column (150 mm \times 2.0 mm, Phenomenex, CA, USA) equipped with a Micromass Quattro LC 9037

(Waters, MA, USA) mass spectrometer. Separation was achieved at a flow rate of $250 \mu\text{L min}^{-1}$ with a gradient program with ultrapure water (A) and acetonitrile (B), adjusted to pH 3 with formic acid. Eluent B was increased from 25% to 95% within 6 min, held for 2 min, reduced back to 25% within 4 min and stabilized for an additional 10 min. A concentration of $50 \mu\text{g L}^{-1}$ of 2,4-dichlorobenzoic acid was added prior to analysis as an internal standard.

3. Results and discussion

3.1. Ozone exposure determination using ozone-depletion curves

The degradation of TrOCs and the ozone-depletion kinetics were determined during the first 5–500 milliseconds of ozonation using the QFM. The kinetics of ozone depletion was compared with published values to verify the compatibility of the QFM with advanced systems used in previous studies (Buffle et al., 2006b; Nöthe et al., 2009). Fig. 1 shows ozone depletion in secondary effluent as a function of time during the first 500 ms using the QFM (inset), and up to 3 min using a batch reactor (recorded to complete ozone depletion). Given the high DOC concentration in the effluents, ozone reacts rapidly and its consumption in the first 0.5 s was found to be 3.2 mg L^{-1} and 4.6 mg L^{-1} for moderate and high ozone dosages, respectively, equal to ~35% consumption for both dosages. The amount of ozone consumed during the first 20 s is defined as the instantaneous ozone demand (IOD) and was found to be 5.6 mg L^{-1} and 9.4 mg L^{-1} for moderate and high ozone dosages, respectively. IOD results from other studies are presented in Table 3. At low ozone dosages ($<0.5 \text{ mg O}_3/\text{mg DOC}$), ozone was consumed during the IOD phase of ozone. In moderate and high ozone dosages, high variations in IOD were observed at different dosages and wastewater matrix characteristics. Hence, ozone decay patterns within the first 20 s vary, as was previously observed by Buffle et al. (2006a).

Ozone exposures were calculated by integrating the respective depletion curves over time and compared to values reported in the literature (Table 3). The latter were calculated mostly in batch experiments, as the initial sampling point varied between 10 s and

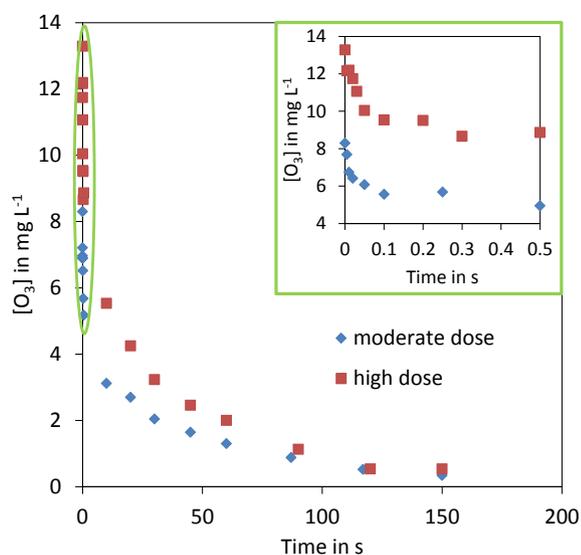


Fig. 1. Ozone depletion during the first 3 min of reaction in Ruhleben effluents (pH=8.0) with moderate (8.3 mg L^{-1}) and high (13.2 mg L^{-1}) ozone dosages. Inset: ozone depletion during the first 500 ms. Measurements were taken by both QFM ($<0.5\text{s}$) and batch experiments ($>10 \text{ s}$)

30 s. Few papers used advanced methods, quench- or stopped-flow systems (Buffle et al., 2006a, 2006b; Lee et al., 2013; Nöthe et al., 2009), for accurate determination of ozone exposure via addition of initial phase measurements and could be compared to the results from this study. Similar ozone exposures ($4.2 \cdot 10^{-3} \text{ M s}$ and $4.1 \cdot 10^{-3} \text{ M s}$) were obtained at a moderate specific ozone dosages of 0.73 and 0.74 $\text{mg O}_3/\text{mg DOC}$ in batch measurements for two different WWTP effluents (Ruhleben in this study and Wueri in Zimmermann et al. (2011)). In both batch studies, samples were withdrawn following ozone addition at intervals starting from 10 s until complete ozone consumption. Ozone exposures in Ruhleben effluents calculated by batch mode starting from 10 s were found to be 10% higher than exposures for batch mode determined with integration of the initial phase by QFM measurements. However, when ozone-depletion measurements started at 20 s (commonly used initial measurement point in batch experiments) or even 30 s, this overestimation increased to 16% and 24%, respectively, at a moderate specific ozone dosage of 0.73 $\text{mg O}_3/\text{mg DOC}$ in the Ruhleben effluents. Such an overestimation was also demonstrated by Buffle et al. (2006b), suggesting higher differences of 50% between ozone exposures for a Swiss WWTP effluent determined with and without initial phase measurements (first batch samples were taken after 30 s) at a specific ozone dosage of 0.88 $\text{mg O}_3/\text{mg DOC}$. This higher difference might be explained by the relatively low ozone exposure ($1.2\text{--}2.2 \cdot 10^{-3} \text{ M s}$) compared to the present study, which may involve inaccuracies due to fast ozone depletion.

For high ozone dosages ($>1.0 \text{ mg O}_3/\text{mg DOC}$), high variability (by a factor of 5) of ozone exposures was observed, with results from this study being within the range of reported values (as can be also observed in Fig. S1 in supporting information). This high variability in ozone decomposition kinetics can be attributed to influencing wastewater characteristics such as organic matter, carbonate concentration and even temperature. In comparison to the moderate dosage, overestimation of ozone exposure was less pronounced (6%, 14% and 22% with sampling after 10 s, 20 s and 30 s, respectively), indicating a more accurate exposure determination from batch experiments with increasing ozone dosages. This was confirmed by results calculated from depletion kinetics described by Nöthe et al. (2009) at the even higher specific ozone dosages of 1.38 $\text{mg O}_3/\text{mg DOC}$ (Table 3) and can be explained by the relatively high (66%) of residual ozone concentration after 20 s. At lower dosages, higher proportion of ozone is consumed within 20 s (which is not measured in batch experiments) resulting in inaccurate exposure determination. Consequently, determination of ozone exposure from batch experiments provides sufficient accuracy to predict compound removal at moderate to high ozone dosages. However, automatization of batch experiments to reduce the lag time to the first ozone-depletion measurement might help improve prediction accuracy. Towards the lower ozone dosages, exposure determination may become less accurate and the use of advanced methods, such as quench- or stopped-flow systems, should be considered. At these dosages, ozone exposure determination for prediction of fast-reacting TrOC elimination is less important, as they are typically eliminated below LOQ for specific ozone dosages, which are optimized for slowly- to moderately-reacting compounds. Hence, accurate ozone exposure determination is mainly critical for the elimination of moderately-reacting TrOCs, microbial inactivation, or effluent organic matter transformation. For example (Wert et al., 2007), showed that 2-logs of fecal coliform inactivation can be achieved in wastewater in very low specific ozone dosages ($\sim 0.3 \text{ mg O}_3/\text{mg DOC}$), at the absence of stable ozone residual.

•OH-radical exposures with the moderate and high ozone dosages were back-calculated (using Eq. (2)) from the removal of the ozone-resistant probe compounds primidone (PRI) or iopromide

Table 3
Literature review of ozone-exposure calculations with and without initial phase measurement.

Dose in mg O ₃ /mg DOC	DOC in mg L ⁻¹	Ozone exposure in M·s				Error (%)	IOD in mg L ⁻¹	Effluent origin	Reference
		Batch mode	Sampling from	Initial phase measurements + batch mode					
0.25	6.0	~9.9·10 ⁻⁵	10s	1.5·10 ^{-5a}	84%		LaWWTP (CH)	(Lee et al., 2013)	
0.33	4.5	–	–	~0.2·10 ^{-4b}	–		Opfikon (CH)	(Buffle et al., 2006a)	
0.40	6.6 (TOC)	6.2·10 ⁻⁴	10s	–	–	2.5	LVNV (USA)	(Wert et al., 2009b)	
	10.3	–	–	–	–	4.5	RMCO (USA)		
0.41	2.4	6.9 ± 0.7·10 ⁻⁴	10s	–	–		Wueri (CH)	(Zimmermann et al., 2011)	
0.44	4.5	–	–	~0.7·10 ^{-4b}	–		Opfikon (CH)	(Buffle et al., 2006a)	
0.50	4.7–26.0	0.2–2.8·10 ⁻³	10s	–	–		10 secondary wastewater effluents	(Lee et al., 2013)	
0.55	4.5	–	–	~1.7·10 ^{-4b}	–		Opfikon (CH)	(Buffle et al., 2006a)	
0.60	7.1 (TOC)	~2.1·10 ⁻³	10s	–	–	~1.5	Clark (USA)	(Wert et al., 2007)	
0.60	6.6 (TOC)	1.5·10 ⁻³	10s	–	–	2.9	LVNV (USA)	(Wert et al., 2009b)	
	10.3	7.5·10 ⁻⁴	–	–	–	5.6	RMCO (USA)		
	10.3	–	–	–	–	6.8	PCFL (USA)		
0.60	4.4	3.1 ± 0.6·10 ⁻³	10s	–	–		Wueri (CH)	(Zimmermann et al., 2011)	
0.73	11.4 ± 0.6	4.2 ± 0.7·10^{-3d}	10s	3.7 ± 0.6·10^{-3c}	10 (p-value = 0.14)	5.6	Ruhleben (DE)	This study	
		4.4 ± 0.5·10⁻³	20s		16 (p-value = 0.07)				
		4.9 ± 0.5·10⁻³	30s		24 (p-value = 0.05)				
0.74	3.4	4.1 ± 0.4·10 ⁻³	10s	–	–	2.5	Wueri (CH)	(Zimmermann et al., 2011)	
0.80	6.6 (TOC)	5.0·10 ⁻³	10s	–	–	3.3	LVNV (USA)	(Wert et al., 2009b)	
	10.3	4.5·10 ⁻³	–	–	–	6.3	RMCO (USA)		
	10.3	1.2·10 ⁻³	–	–	–	7.8	PCFL (USA)		
0.81	4.7	6.1 ± 0.4·10 ⁻³	10s	–	–	3.3	Wueri (CH)	(Zimmermann et al., 2011)	
0.88	4.5	~2.2·10 ⁻³	30s	~1.3·10 ^{-3b}	~50	~3.0	Opfikon (CH)	(Buffle et al., 2006b)	
0.90	4.8	1.1 ± 0.1·10 ⁻²	10s	–	–	4.0	Wueri (CH)	(Zimmermann et al., 2011)	
0.97	7.1 (TOC)	~5.4·10 ⁻³	10s	–	–	~2.3	Clark (USA)	(Wert et al., 2007)	
1.00	6.6 (TOC)	9.5·10 ⁻³	10s	–	–	3.7	LVNV (USA)	(Wert et al., 2009b)	
	10.3	1.0·10 ⁻²	–	–	–	6.6	RMCO (USA)		
	10.3	4.4·10 ⁻³	–	–	–	8	PCFL (USA)		
1.00	4.7–26.0	0.4–1.3·10 ⁻²	10s	–	–	–	10 secondary wastewater effluents	(Lee et al., 2013)	
1.16	11.4 ± 0.6	7.5 ± 0.6·10⁻³	10s	7.0 ± 0.6·10^{-3c}	6 (p-value < 0.05)	9.4	Ruhleben (DE)	This study	
		8.2 ± 0.7·10⁻³	20s		14 (p-value < 0.05)				
		9.0 ± 1.0·10⁻³	30s		22 (p-value < 0.05)				
1.24	4.1	1.90 ± 0.1·10 ⁻²	10s	–	–	4.8	Wueri (CH)	(Zimmermann et al., 2011)	
1.38	7.2	~7.2·10 ⁻³	20s	~6.8·10 ^{-3d}	4.9	6.4	Bottrup (DE)	(Nöthe et al., 2009)	
1.50	4.7–26.0	1.10	10s	–	–	–	10 secondary wastewater effluents	(Lee et al., 2013)	
		~4.20·10 ⁻²	–	–	–	–			
1.54	7.2 (TOC)	~1.03·10 ⁻²	10s	–	–	~3.4	Clark (USA)	(Wert et al., 2007)	

Bold represent this study (and not data from literature).

^a Time range: initial phase measurements (QFM): 22 ms-2s; batch measurements: ≥ 7 s.

^b Time range: initial phase measurements (CQFS): 350 ms-21s; batch measurements: ≥ 30 s.

^c Time range: initial phase measurements (QFM): 2ms-0.5 s; batch measurements: ≥ 10 s; Standard deviation based on two laboratory experiments with the same wastewater.

^d Time range: initial phase measurements (SF3): 40 ms-9 s; batch measurements: ≥ 20s; Calculated by three phases of ozone depletion (ln c/c₀) over time.

(IOP). The •OH-radical exposures were 0.25·10⁻⁹ M s and 0.34·10⁻⁹ M s at moderate and high ozone dosages, respectively. Small differences of 6% and 9% between exposure determination from PRI and IOP are within the uncertainty of second order rate constants for reactions with hydroxyl radicals. In Fig. 2, the removal of slowly- and moderately-reacting TrOCs is accurately predicted by integrating the ozone-depletion curves without initial phase measurements by QFM. Fast-reacting TrOCs are not shown, as they were removed below LOQ at the applied ozone dosages. However, removal below LOQ was also predicted based on calculation. It should be noted that evaluation of ozone exposure with initial

phase measurements of ozone depletion (using QFM) gave similar removal predictions. This may be due to two reasons: the relatively high accuracy of the ozone exposure calculation from batch experiments, and the limited contribution of ozone to slowly- and moderately-reacting TrOCs.

3.2. Ozone exposure determination using probe compounds

Predicting the degradation of a TrOC by determining •OH-radical and ozone exposures from second-order kinetics with two probe compounds, as suggested by Hübner et al. (2013), was tested using

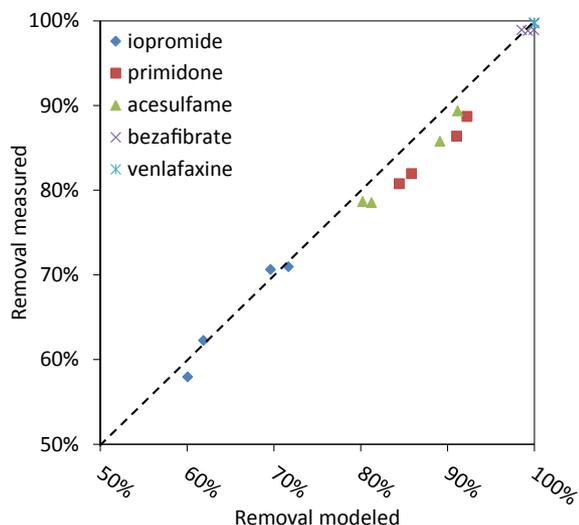


Fig. 2. Comparison of the measured and modeled relative elimination for the oxidation of slowly- and moderately-reacting TrOCs at moderate and high ozone dosages (without using the QFM). Ozone exposures were determined via 'direct indigo method' while $\cdot\text{OH}$ -radical exposures were determined by ' $\cdot\text{OH}$ -radical probe method'.

the QFM. With the $\cdot\text{OH}$ -radical probe method, $\cdot\text{OH}$ -radical exposure is back-calculated from the removal of ozone-resistant probe compound, whereas in the ozone probe method, ozone exposure is back-calculated from the removal of moderately-reacting probe compound following ozonation of wastewater effluents. QFM experiments were conducted with different specific ozone dosages in the range of 0.1–1.1 mg $\text{O}_3/\text{mg DOC}$. pCBA, PRI and IOP were chosen as ozone-resistant probe compounds for the calculation of $\cdot\text{OH}$ -radical exposure in this concept as well. Their relative removals, obtained during ozonation, differed (Fig. 3a) due to their rate constants in the reaction with $\cdot\text{OH}$ -radicals. $\cdot\text{OH}$ -radical exposures were back-calculated from the removal of pCBA, PRI and IOP by Eq. (2), where the direct reaction with ozone is neglected. As can be noted in Fig. 3b, $\cdot\text{OH}$ -radical exposures were similar for all probe compounds at the different ozone dosages. A linear correlation of $\cdot\text{OH}$ -radical exposure with ozone dosage was observed, including a lag in ozone consumption (~ 0.12 mg $\text{O}_3/\text{mg DOC}$) with no significant formation of $\cdot\text{OH}$ -radicals. A similar correlation (lag and curve) was reported previously (Hübner et al., 2013) using batch and semi-batch systems, indicating comparable efficiency of $\cdot\text{OH}$ -radical formation with the different systems and a negligible mixing effect on the efficiency of $\cdot\text{OH}$ -radical formation. These results show that both PRI and IOP are suitable internal tracers for determining $\cdot\text{OH}$ -radical exposure, without the need to spike the effluent with external probe compound (i.e. pCBA). This finding contradicts a previous study (Huber et al., 2003), which showed underestimation in prediction using IOP in natural waters. It should be noted, however, that determination of $\cdot\text{OH}$ -radical exposure using naturally existing internal tracers (i.e. without spiking) requires sensitive analytical methods to evaluate accurately the elimination following ozone treatment. In this study, PRI and IOP were spiked at environmentally relevant concentration (10 $\mu\text{g L}^{-1}$) to allow accurate comparability of pCBA with other probe compounds.

For moderately- and fast-reacting TrOCs, the direct reactions with ozone cannot be neglected. Ozone exposure was calculated using moderately-reacting TrOCs (acesulfame [ACS], benzotriazole [BTA], metoprolol [MTP], bezafibrate [BZF] or venlafaxine [VLX]) as probe compounds. Since analytical accuracy at low levels can be a critical factor for exposure determination (elimination levels of up to 99% could be observed for TrOCs), fast-reacting TrOCs were not

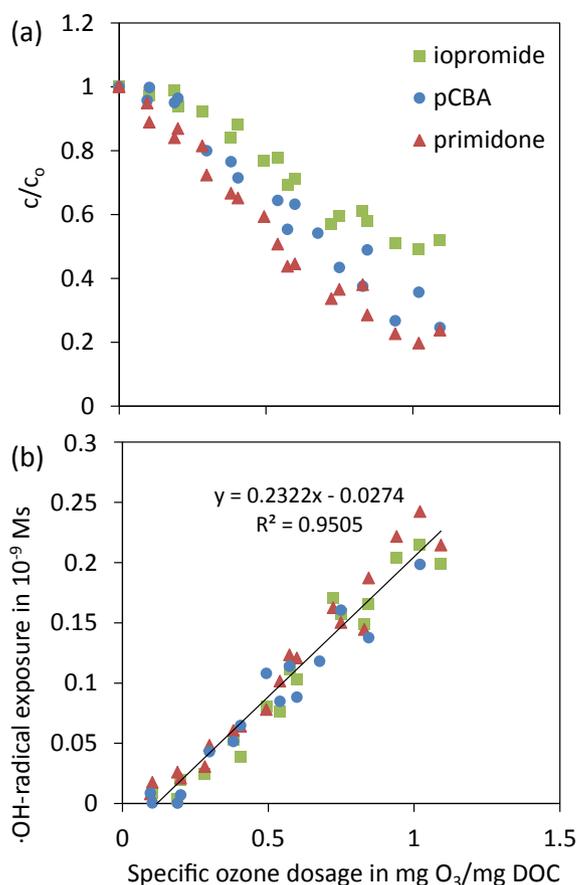


Fig. 3. (a) Relative removal for pCBA, IOP and PRI as ozone-resistant probe compounds following ozonation of Ruhleben effluent using QFM. (b) Determination of $\cdot\text{OH}$ -radical exposure using probe compounds.

used as ozone probe compounds (removed below the LOQ at specific ozone dosages of 0.3 mg $\text{O}_3/\text{mg DOC}$). Calculated ozone exposure from different relative removal rates of probe compounds using Eq. (1) at a specific ozone dosage of 0.1 mg $\text{O}_3/\text{mg DOC}$ ranged between $1.13 \cdot 10^{-4}$ (ACS) to $4.90 \cdot 10^{-7}$ (VLX), and decreased with increasing rate constants for the reaction of probe compounds with ozone. This effect was previously observed and explained by mixing effects and/or mass-transfer limitation (Hübner et al., 2013). Ozone exposures determined using the direct indigo method of ozone-depletion measurements (section 3.1) at moderate and high specific ozone dosages (0.73 and 1.16 mg $\text{O}_3/\text{mg DOC}$, respectively) were similar to the exposures obtained using the ozone probe method with ACS as the probe compound ($k(\text{O}_3) = 88 \text{ M}^{-1} \text{ s}^{-1}$). ACS is considered a moderately-reacting compound, and has the lowest rate constant in the group used for the evaluation. In Fig. 4, measured and modeled relative eliminations for the oxidation of different TrOCs were compared based on models with ACS (Fig. 4a) and VLX (Fig. 4b) as the probe compounds. When ACS was used as an ozone probe compound, overestimation was observed for MTP, VLX, and the fast-reacting compounds carbamazepine (CBZ), sulfamethoxazole (SMX) and diclofenac (DCF). In contrast, prediction using VLX resulted in underestimation for most TrOCs, also demonstrating that the use of QFM with highly efficient mixing chambers does not enable accurate ozone exposure calculations from probe compounds.

It should be noted that in addition to inefficient mixing, the accuracy of rate constants can be a major obstacle for using the ozone probe method. For many compounds, literature data only

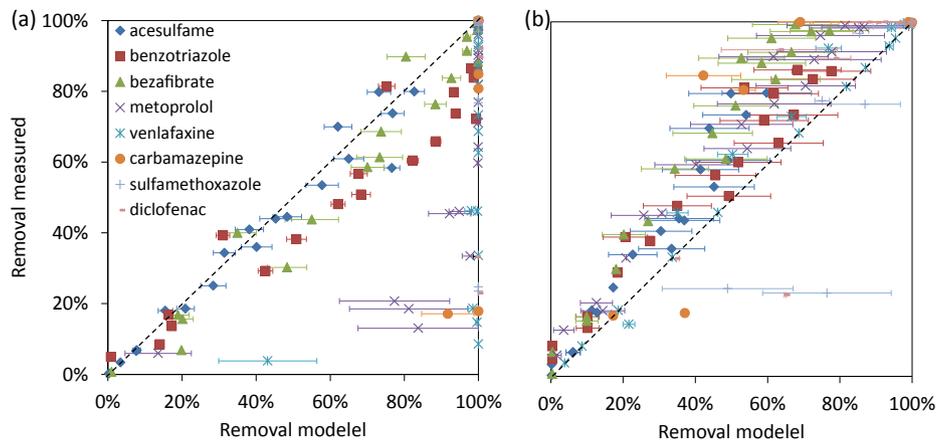


Fig. 4. Comparison of the measured and modeled relative elimination for the oxidation of several TrOCs by ozone and \bullet OH-radicals at different dosages; ozone exposures were calculated by the 'ozone probe method' using (a) ACS and (b) VLX as the probe compound. Error bars represent the uncertainty range in modeled removal associated with rate constants inaccuracies (minimum and maximum uncertainty factors for rate constants were 2/3 and 4/3 of literature values, respectively).

provide apparent second-order rate constants for a particular pH without considering the different reactivities of each individual acid–base species of an ionizable TrOC (von Gunten and von Sonntag, 2012). In other words, small differences in pH can dramatically affect a compound's reactivity with ozone. For example, the rate constants for the reaction of MTP, VLX and BTA with ozone increase by over one order of magnitude when increasing pH from 7 to 8.5 (Lee et al., 2014). Even species-specific k -values were reported differently in literature for BTA as can be observed in Table 2 (Benitez et al., 2015; Lee et al., 2014). Furthermore, the determination of rate constants, even at the same pH, is not always accurate; reported constants for the reaction of SMX with ozone at pH 7, for example, differ by one order of magnitude (Dodds et al., 2006; Huber et al., 2003). Two rate constants were reported also for DCF, which have pH-independent ozone reactivity (Huber et al., 2003; Sein et al., 2008). Error bars in Fig. 4 provides the uncertainty range in modeled removal associated with rate constants inaccuracies (minimum and maximum uncertainty factors for rate constants suggested by Neumann et al. (2009) as 2/3 and 4/3 of literature data, respectively). However, the quantitative assessment showed that even within the uncertainty ranges of k , accurate prediction from probe compounds cannot be made.

Quantified approaches suggested also water characteristic parameters and interaction of TrOCs with aquatic colloids as possible attributers for the uncertainty in predicting TrOC elimination (Neumann et al., 2009; Zimmermann et al., 2011). Specifically, water characteristics were quantified as the main influencing factor for the prediction of slowly-reacting TrOCs, while both water characteristics and uncertainties in rate constants values were the dominant source for uncertainty in predicting the elimination of moderately-reacting TrOCs. Only for the fast-reacting TrOCs, both mixing effects (i.e. hydraulic parameters) and uncertainties in rate constants derived the poor prediction.

3.3. Comparison of different ozone injection systems

The feasibility of overcoming the mixing and mass-transfer limitation using three different ozone-injection techniques was tested with respect to TrOC removal. Stock solution mixing (i.e. batch) experiments and ozone-diffusion (i.e. semi-batch and pilot) experiments were presented previously by our research group (Hübner et al., 2013). QFM experiments involve efficient mixing of low volumes of ozone stock and effluents. Pilot experiments

performed by venturi injection of ozone are additionally compared in this study.

\bullet OH-radical exposure was calculated using IOP as the probe compound for all ozone systems. A linear correlation of \bullet OH-radical exposure with ozone consumption was observed with batch, semi-batch and bubble-column pilot experiments (Hübner et al., 2013), in the QFM (Fig. 3) and during venturi injection (Fig. S2). The lag in ozone consumption without significant formation of \bullet OH-radicals, as well as the slope of the correlation, depend on effluent quality and differ between experiments. Reliable modeling of the removal of other ozone-resistant compounds indicates that the efficiency of \bullet OH-radical formation is not affected by mixing and mass-transfer limitations.

Fig. 5 compares measured and modeled $\ln c/c_0$ of fast-reacting TrOCs in QFM, batch and venturi injection experiments with a specific ozone dosage of up to 0.35 mg O_3 /mg DOC, since most fast-reacting TrOCs ($k(O_3) > 10^4 \text{ M}^{-1}\text{s}^{-1}$) were removed below LOQ at higher ozone dosages. Modeled values were calculated by the

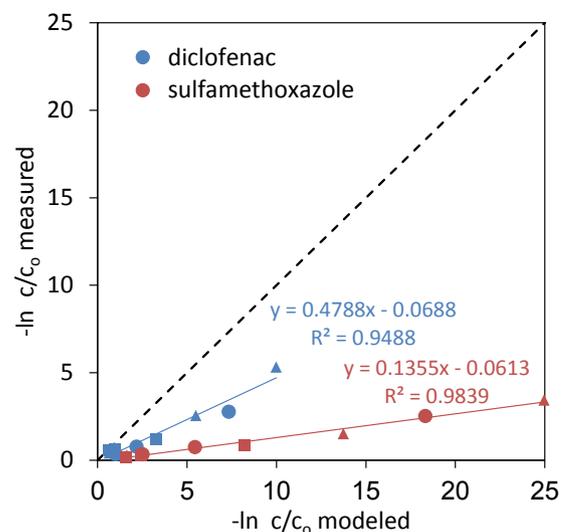


Fig. 5. Comparison of measured and modeled $\ln c/c_0$ of fast-reacting SMX and DCF by the 'ozone probe method' (ozone exposure calculated from relative residual concentration of CBZ; \bullet OH-radical exposure neglected) following batch (circles), venturi injection (square) and QFM (triangle) experiments.

ozone probe method, where CBZ was used for ozone exposure determination, and $\bullet\text{OH}$ -radical exposure was neglected at these low dosages. Low (<20%) to negligible contribution of $\bullet\text{OH}$ -radicals to the elimination of fast-reacting TrOCs during ozonation was previously reported in literature (Hollender et al., 2009; Lee et al., 2013). Although specific ozone dosages and initial TrOC concentrations varied between the experiments (due to variations in experimental conditions, effluent quality, and TrOC presence in the effluents), and despite the use of different techniques, systematic overestimation of the removal of fast-reacting compounds was observed in all systems. The consistent data among batch, venturi injection, and QFM indicates that mass transfer or mixing are not the source for the difference. Based on competition kinetics and the assumption of correct rate constant for CBZ, apparent second order rate constants were calculated from the experiments for SMX ($3.9 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$) and DCF ($4.8 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$). These constants are lower than rate constants reported in literature for both compounds ($6.8 \cdot 10^5 - 1 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ for DCF and $5.7 \cdot 10^5 - 2.5 \cdot 10^6 \text{ M}^{-1}\text{s}^{-1}$ for SMX) and it seems that other, unknown factors might play a role during ozonation of secondary effluents. Systematic experiments would be needed to identify these effects. However, results demonstrated that the determination of ozone exposure from residual concentration of probe compounds and second-order rate constants is critical for modeling ozonation of secondary effluents.

4. Conclusions

Prediction of TrOC removal during ozonation of secondary effluents based on kinetic models strongly depends on the accuracy of the determination of ozone and $\bullet\text{OH}$ -radical exposure. In this study, two different concepts for determining oxidant exposures were evaluated based on QFM experiments and compared with other ozonation systems. In the first concept, ozone depletion is measured in combined QFM and batch experiments and integrated over time. The second proposed concept involves ozonation at different ozone dosages and measurement of probe compounds after complete reaction with ozone; ozone exposure is then back-calculated from residual concentration using second-order kinetics. Both concepts utilize the measurement of an ozone-resistant compound to determine exposure of highly reactive $\bullet\text{OH}$ -radicals.

To validate the first concept, accurate ozone exposures were determined in combined QFM and batch experiments for moderate and high ozone dosages. Determination of exposure from single-batch experiments with sampling initiated at 10 s, 20 s and 30 s resulted in respective overestimations of ozone exposure by 11%, 16% and 24% for moderate and 6%, 14% and 22% for high ozone dosages compared to exposures determined by combined QFM and batch experiments. Predicting the removal of slowly- and moderately-reacting compounds, however, showed adequate results. At low ozone dosages, however, higher uncertainties can be expected due to overall lower ozone exposures, hence more accurate measures might be needed for exposure determination. With the second concept, ozone exposures ranged over three orders of magnitude when different moderately-reacting compounds were used for the calculation. The minimum ozone exposure value (calculated with ACS) was the most accurate. In previous studies, mixing effects have been suggested as a major obstacle for exposure determination, but other effects, such as inaccuracy of second-order rate constants at different pHs, might also play a key role. However, consistent deviation of measured and modeled removal in different ozonation systems, including batch and semi-batch experiments (Hübner et al., 2013), QFM experiments and venturi injection (this study), indicate that other still unknown factors

besides mixing affect exposure calculation. As a consequence, it can be concluded that ozone exposure calculations from probe compounds is not a promising option for ozonation of secondary effluents.

Determination of $\bullet\text{OH}$ -radical exposure was accurate with both concepts. However, the probe concept provides additional information on dosage dependency of oxidant exposure. The comparability of pCBA and other (PRI and IOP) substances as suitable probe compounds was shown. Therefore, although addition of pCBA has become a standardized method for $\bullet\text{OH}$ -radical exposure determination in lab-experiments, we propose using naturally existing internal tracers in pilot and full-scale applications without the need for spiking with external probe compounds such as pCBA. In order to overcome limitations of inaccurate kinetic data and analytical inaccuracy at low compound concentrations, a combination of 2–3 internal tracers for accurate and reliable $\bullet\text{OH}$ -radical exposure determination can be applied.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.05.049>.

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