



## Modelling disinfection by-products formation in bromide-containing waters

M. Fabbicino<sup>a,\*</sup>, G.V. Korshin<sup>b</sup>

<sup>a</sup> University of Naples Federico II, Department of Hydraulics, Geotechnics and Environmental Engineering, Via Claudio 21, 80125, Naples, Italy

<sup>b</sup> Department of Civil and Environmental Engineering, Box 352700, University of Washington, Seattle, WA 98195-2700, United States

### ARTICLE INFO

#### Article history:

Received 11 November 2008

Received in revised form 16 February 2009

Accepted 17 February 2009

Available online 25 February 2009

#### Keywords:

Bromine  
Chlorination  
DBP  
Modelling  
NOM

### ABSTRACT

A kinetic model capable of simulating by-products formation in bromide-containing waters during disinfection processes is presented in this paper. The model is based on two parallel sequences of incorporation and oxidation reactions induced by bromine or chlorine reacting with natural organic matter (NOM). Each sequence starts from a different type of NOM functionality that has its own set of specific reaction rate. Decay reactions of NOM and halogenated intermediates are assumed to follow a first order kinetic, while disinfection by-product (DBP) generation reactions are simulated introducing so-called splitting coefficients. This approach allows obtaining explicit expressions for DBP species. Model's results are compared with experimental data obtained for seawater samples. Comparison of the data confirms the model's ability to predict DBPs formation with high precision.

© 2009 Elsevier B.V. All rights reserved.

### 1. Introduction

One of the drawbacks of water chlorination is the formation of by-products (DBPs), caused by natural organic matter (NOM) halogenation. Due to the high toxicity of many DBP species, their generation represents a serious threat for human health and environmental quality [1–3]. Therefore the availability of a mathematical model capable of adequately simulating NOM halogenation is very important to predict and control DBP formation.

In prior research, equations with which to predict DBP yield and speciation have been obtained using two approaches. The first one is based on the development of statistic correlations between the concentrations of a single DBP species or their multiple classes and, on the other hand, water quality parameters and/or chlorine dose [4–7]. The second one is based on the examination of specific reaction pathways leading to DBP production through chemical reactions involving NOM and chlorine [8–10].

Research conducted with natural water sources, aquatic humic substances and model compounds, has allowed formulating and testing several hypotheses concerning these pathways. It has been proved that chlorine reacts with NOM through both incorporation and oxidation reactions [11–13]. It has also been found that, in the presence of bromide, bromine competes with chlorine as consequence of the rapid oxidation of bromide to bromine [14–19]. DBP species containing bromine are formed as a result through

the reaction pathway identical to that with chlorine [12,13]. Finally incorporation and oxidation reactions have been shown to involve at least two processes, one occurring much faster than the another [20,21] due to the presence of two distinct types of reactive functionalities of NOM [4,22].

These findings allow formulating a mathematical model that simulates DBP formation in bromide-containing waters. The model presented in this paper was calibrated using experimental data obtained during chlorination of seawater, which is high in bromide. DBPs formed during seawater chlorination are similar to those usually formed during the chlorination of waters of terrestrial provenance [23,24], although in the seawater, due to the high concentration of bromide in it (about  $65 \text{ mg L}^{-1}$ , i.e. one order of magnitude higher than the highest concentration of bromide in drinking water sources, estimated to be  $2 \text{ mg L}^{-1}$ ), chlorobrominated and especially brominated species are more abundant. However, the nature of sites that interact with halogens to form DBPs appears to be largely the same in terrestrial waters and seawater, as has shown by absorbance spectroscopy measurements [25]. It has to be also observed that seawater chlorination is not rare, being used, for example, to control the growth of biofilm on heat exchangers of power station and membranes of desalination plants, or to disinfect ballast water: of course formation of DBP in chlorinated seawater has to be controlled due to the possible adverse effects on marine organisms [26], atmosphere [27] and even humans in case of release of DBPs in drinking water produced in desalination plants [24]. The aim of the paper is therefore to contribute to better understand the mechanism of DBP formation in all kind of waters containing bromine, including seawater, through the elaboration of a mechanistic model able to predict the generation

\* Corresponding author. Tel.: +39 081 7683438; fax: +39 081 5938936.

E-mail addresses: [fabbrici@unina.it](mailto:fabbrici@unina.it) (M. Fabbicino), [korshin@u.washington.edu](mailto:korshin@u.washington.edu) (G.V. Korshin).

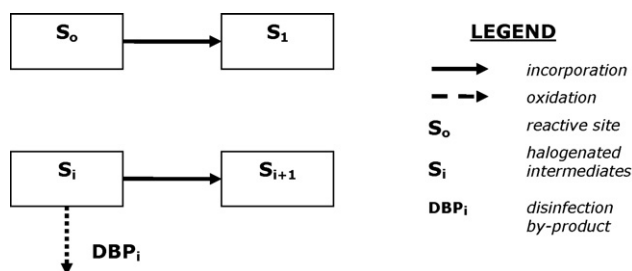


Fig. 1. Schematic pathway of incorporation and oxidation reactions involved in the formation of disinfection by-products.

of chlorinated, brominated and chloro-brominated compounds in chlorinated waters.

## 2. Model formulation

The proposed model is based on the multi-step reaction pathway leading to trihalomethanes (THMs) and haloacetic acids (HAAs) formation that was proposed by Nokes et al. [13].

The pathway includes oxidation and incorporation processes and production of halogenated intermediates (Fig. 1). As a consequence of the instantaneous oxidation of bromide, all processes are attributed to chlorine and/or bromine and assumed to occur simultaneously, although these two species have different characteristic reaction rates. Previous studies [13,15,28,29] showed, in fact, that bromine substitution with NOM can be up to an order of magnitude faster than bromine substitution.

For each halogen two parallel sequences are considered; the first one starts from slow reactive sites of NOM, and the second one starts from fast reactive sites. The two sequences are considered to be mechanistically identical but they have different reaction rates.

In the sequence of relevant transformations, the following reactions are described individually:

- decay of the reactive sites of NOM;
- generation and decay of mono-, di- and tri-halogenated organic intermediates, as a consequence of incorporation reaction;
- generation of disinfection by-products, as a consequence of oxidation reactions.

Decay reactions are assumed to follow a first order kinetic, as indicated by the following relationships:

$$D_{S_0} = \sum_{r=1,2} k_o^r S_o^r \quad (1)$$

$$D_{S_i} = \sum_{r=1,2} k_i^r S_i^r \quad 1 \leq i \leq 3 \quad (2)$$

where  $D_{S_0}$  is the decay rate of NOM ( $\text{mol L}^{-1} \text{min}^{-1}$ );  $D_{S_i}$  is the decay rate of organic intermediates containing  $i$  halogens ( $\text{mol L}^{-1} \text{min}^{-1}$ );  $k_o^r$ ,  $k_i^r$  are the kinetic constants of fast ( $r=1$ ) and slow ( $r=2$ ) decay processes ( $\text{min}^{-1}$ );  $S_o^r$  is the concentration of fast ( $r=1$ ) and slow ( $r=2$ ) reactive site of NOM ( $\text{mol L}^{-1}$ );  $S_i^r$  is the concentration of  $i$ -halogenated intermediates generated by fast ( $r=1$ ) or slow ( $r=2$ ) reactions ( $\text{mol L}^{-1}$ ).

Halogen incorporation reactions to generate halogenated intermediates are obtained assuming that the generation rate of each specie containing  $i$  halogens, is equal to the decay rate of the corresponding specie containing  $i-1$  halogens:

$$G_{S_i} = \sum_{r=1,2} \alpha_i^r k_{i-1}^r S_{i-1}^r \quad 1 \leq i \leq 3 \quad (3)$$

where  $G_{S_i}$  is the generation rate of organic intermediates containing  $i$  halogens ( $\text{mol L}^{-1} \text{min}^{-1}$ );  $\alpha_i^r$  is the splitting coefficient of fast ( $r=1$ ) and slow ( $r=2$ ) intermediate generation reactions.

Finally DBP generation reactions, caused by chlorine- or bromine-driven oxidation, are obtained assuming that the generation rate of each specie is equal to the fraction of the overall decay rate of the intermediate containing the same number of halogens:

$$G_{DBP_i} = \sum_{r=1,2} \beta_i^r k_i^r S_i^r \quad 1 \leq i \leq 3 \quad (4)$$

where  $G_{DBP_i}$  is the generation rate of by-products containing  $i$  halogens ( $\text{mol L}^{-1} \text{min}^{-1}$ );  $\beta_i^r$  is the splitting coefficient of fast ( $r=1$ ) and slow ( $r=2$ ) by-product generation reactions.

Of course if  $n$  is the number of incorporation or oxidation reaction involving a generic intermediate containing  $i-1$  halogens, the following relationship has always to be satisfied:

$$\sum_n (\alpha_i^r + \beta_{i-1}^r) = 1 \quad r = 1, 2 \quad (5)$$

Relevant mass balance equations can be therefore written as

$$\frac{dS_o}{dt} = -D_{S_o} \quad (6)$$

$$\frac{dS_i}{dt} = G_{S_i} - D_{S_i} \quad 1 \leq i \leq 3 \quad (7)$$

$$\frac{dDBP_i}{dt} = G_{DBP_i} \quad 1 \leq i \leq 3 \quad (8)$$

where  $t$  is the time ( $T$ );  $DBP_i$  is the concentration of a generic DBP containing  $i$  halogens ( $\text{mol L}^{-1}$ ).

Assuming that only mono- and di-haloacetic acids are formed by the oxidation of mono- and di-halogenated intermediates, while tri-halogenated HAAs and tri-halomethanes (THMs) are formed via the oxidation of tri-halogenated intermediates and applying Eqs. (6)–(8) to the sequence of reactions involving bromine and chlorine, it is possible to generate a set of differential equations, which can be integrated analytically. This approach also assumes that the initial concentration of the slow and fast reactive sites of NOM can be either determined experimentally or found based on the fitting of model data. This approach allows obtaining the following explicit expressions for the concentrations of chlorinated and brominated organic intermediates and disinfection by-products:

$$S_i = \sum_{r=1,2} \left( S_{o,t=0}^r \cdot \prod_{h=1,i} (\alpha_h^r k_{h-1}^r) \cdot \sum_{j=0,i} \left( \frac{e^{-k_j^r t}}{\prod_{w=0,1:w \neq j} (k_w^r - k_j^r)} \right) \right) \quad 1 \leq i \leq 3 \quad (9)$$

$$H_i = \sum_{r=1,2} \left( \beta_{H_i}^r \cdot S_{o,t=0}^r \cdot k_o^r \cdot \prod_{h=1,i} (\alpha_h^r k_h^r) \cdot \sum_{j=0,i} \left( \frac{1 - e^{-k_j^r t}}{\prod_{w=0,1:w \neq j} (k_w^r - k_j^r)} \right) \right) \quad 1 \leq i \leq 3 \quad (10)$$

$$T = \sum_{r=1,2} \left( \beta_T^r \cdot S_{o,t=0}^r \cdot k_o^r \cdot \prod_{h=1,i} (\alpha_h^r k_h^r) \cdot \sum_{j=0,i} \left( \frac{1 - e^{-k_j^r t}}{\prod_{w=0,1:w \neq j} (k_w^r - k_j^r)} \right) \right) \quad (11)$$

where  $S_{o,t=0}^r$  is the initial concentration of fast ( $r=1$ ) and slow ( $r=2$ ) reactive site of NOM ( $\text{mol L}^{-1}$ );  $H_i$  = concentration of a generic HAA containing  $i$  halogens ( $\text{mol L}^{-1}$ );  $T$  = concentration of a generic THM ( $\text{mol L}^{-1}$ ).

Similar expressions, not reported here for brevity, can be derived for mixed chloro-bromo compounds.

## 3. Materials and methods

Two different seawater samples were used in the experimental study, indicated as S1 and S2. Samples were collected close to

**Table 1**  
Seawater characteristics.

Sample	S1	S2
pH	7.6	7.6
DOC (mg L <sup>-1</sup> )	0.9	1.0
Br (mg L <sup>-1</sup> )	61	60
UV <sub>254</sub> (cm <sup>-1</sup> )	0.024	0.029
SUVA <sub>254</sub> (L mg <sup>-1</sup> m <sup>-1</sup> )	2.7	2.9

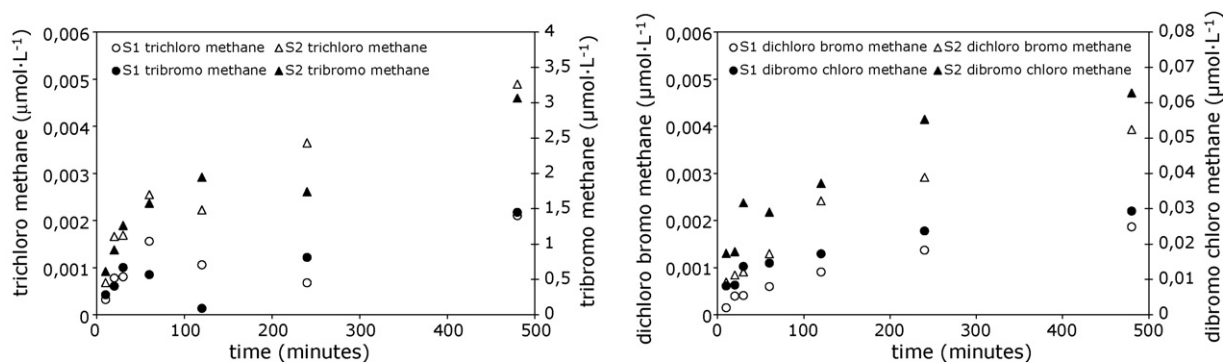
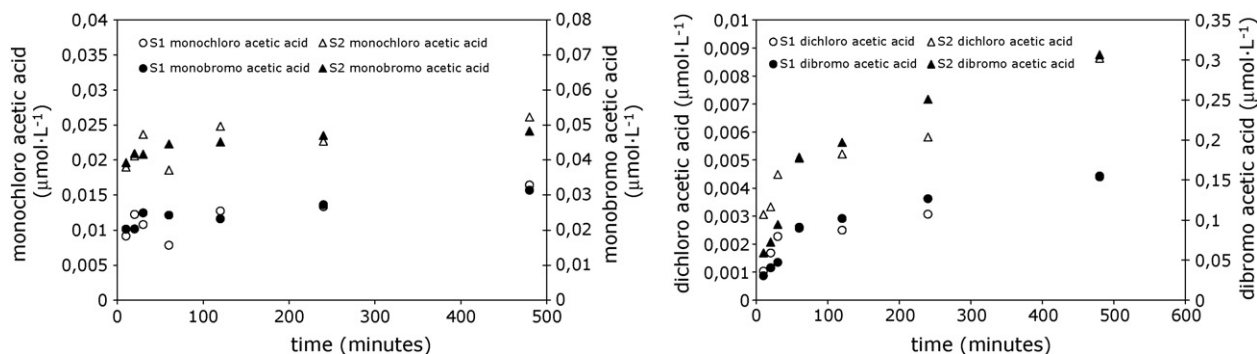
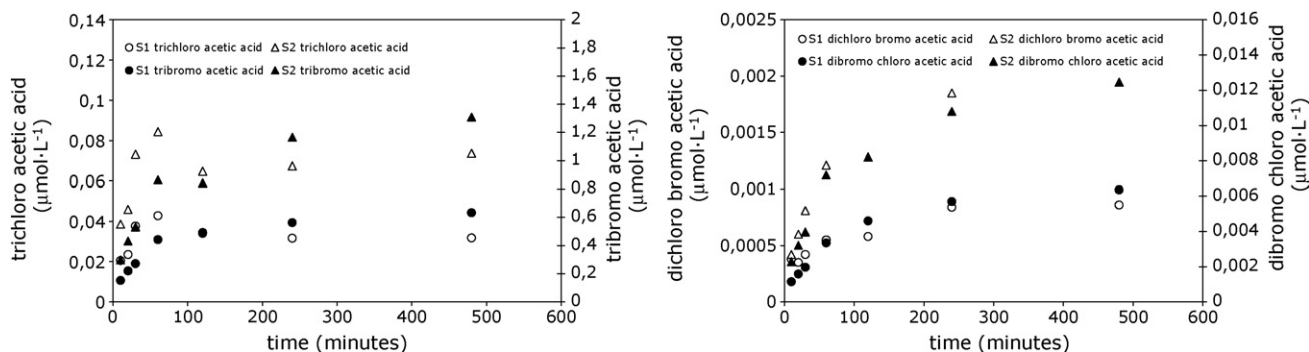
the shoreline in the Gulf of Naples (Italy) and filtered using a polycarbonate filter 0.45  $\mu\text{m}$ . Main characteristics of filtered samples are summarized in Table 1. Chlorination experiments were carried out according to the standard procedures employed in the research of DBP formation and carried out at the Water Quality Laboratory of the University of Washington. These procedures are described elsewhere [30].

After filtration the samples were placed in closed headspace-free reactors, in which chlorine was injected. At different times

(from 10 to 480 min) chlorinated samples were taken from the reactors, quenched with a sodium sulfite solution, dosed in excess respect to the initial chlorine amount, and stored in the dark, at 4 °C. EPA methods 551 and 552 were followed for DBP measurements in chlorinated samples. Standards methods were followed for any other analytical determination. All measurements were performed within 1 week from the experiment start.

THMs and HAAs were measured using a GC HP 5890, equipped with a Ni electron capture detector. Dissolved organic carbon was obtained using a Shimadzu TOC-5000 analyzer which has been shown to yield high quality data for DOC measurements in seawater [31]. Finally bromide content was measured using an IC Metrom 761.

A stock solution of NaClO 0.01N was used as disinfectant agent: selected chlorine dose was equivalent to 1 mg L<sup>-1</sup> (ratio Cl:DOC ~1:1). All reagents used during experiments were high purity grade. Only Millipore MilliQ water was used as reagent water.

**Fig. 2.** Time profiles of the release of trihalomethanes formed in chlorinated seawater samples.**Fig. 3.** Time profiles of the release of mono- and di-halogenated haloacetic acids formed in chlorinated seawater samples.**Fig. 4.** Time profiles of the release of trihalogenated haloacetic acids formed in chlorinated seawater samples.

**Table 2**  
Model's parameters.

Sample	Initial concentration of NOM reactive sites ( $\mu\text{mol L}^{-1}$ )		Ratio between slow and fast reactions		NOM decay kinetic constant ( $\text{min}^{-1}$ )				
	$S_{o,t=0}^1$	$S_{o,t=0}^2$	$s/f$		$k_0^1$				
S1	20	10	0.02		0.6				
S2	40	10			0.5				
	Chlorine induced reactions kinetic constants ( $\text{min}^{-1}$ )			Bromine induced reactions kinetic constants ( $\text{min}^{-1}$ )					
	$k_1^1$	$k_2^1$	$k_3^1$	$k_1^1$	$k_2^1$	$k_3^1$			
S1	0.3	0.07	0.4	0.7	0.02	0.6			
S2	0.4	0.06	0.6	0.4	0.01	0.8			
	Chlorine induced reactions splitting coefficients			Bromine induced reactions splitting coefficients					
	$\alpha_1^1$	$\alpha_2^1$	$\alpha_3^1$	$\alpha_1^1$	$\alpha_2^1$	$\alpha_3^1$			
S1, S2	0.3	0.3	0.3	0.8	0.3	0.6			
	$\beta_{H_1}^1$	$\beta_{H_2}^1$	$\beta_{H_3}^1$	$\beta_T^1$	$\beta_{H_1}^1$	$\beta_{H_2}^1$	$\beta_{H_3}^1$	$\beta_T^1$	
S1, S2	0.0002	0.0002	0.01	0.0003	0.0002	0.006	0.06	0.12	

#### 4. Results and discussion

Experimental results referred to detected DBPs are presented in Figs. 2–4.

Total amount of formed THMs after 8 h was  $3.1 \mu\text{mol L}^{-1}$  in S1 water and  $1.5 \mu\text{mol L}^{-1}$  in S2 water, while total amount of formed HAAs was  $1.8 \mu\text{mol L}^{-1}$  in S1 water and  $0.9 \mu\text{mol L}^{-1}$  in S2 water. DBPs speciation was similar for the two samples. Measured concentrations of single species were in accordance with literature data [23–25]. Brominated DBP were predominant, as expected due to the high bromide concentration. Among THMs, bromoform contributed to about 98% of total formed THMs. Among HAA, the most abundant species was tribromoacetic acid (about 73% of total HAAs for both waters), followed by dibromoacetic acid (17–18%) and trichloroacetic acid (4%), whose concentration was similar to that of monobromoacetic acid. The other species were found only at trace levels. After 480 min of reaction, total incorporated bromide in detected DBPs ranged between 12 and  $14 \mu\text{mol L}^{-1}$  for S1 and between 6 and  $7 \mu\text{mol L}^{-1}$  for S2; total incorporated chlorine was an order of magnitude less important for both waters.

The time profiles of the release for all DBP species, are not markedly different from those observed for fresh water samples [25]. In accord with the hypothesized existence of two distinct types of reactive functionalities of the NOM, one reacting faster than the other, the growth rate was higher during the first 60–90 min, and then it slightly decreased for all DBP species, except for trichloroacetic acid, tri-chloromethane and tri-bromomethane. For these three compounds, in fact, the concentration reached a peak after 60 min, and decreased somewhat, probably because of decay processes, which, in terrestrial water chlorination, are characteristics of tri-bromoacetic acid [30].

The experimental data presented in Figs. 2–4 were used to calibrate the proposed model. Only chlorinated and brominated species were taken into account, excluding mixed chloro-brominated ones, whose concentrations, as mentioned previously, were generally very low.

The ratio of yields of the slow and fast reactions ( $s/f$ ) was assumed to be the same for all decay and DBP generation processes. This assumption was introduced to reduce the number of parameters to be determined through calibration. The latter was performed by minimizing differences between the experimental DBP concentrations and model predictions using for an assigned set of kinetic constants, splitting coefficients, initial concentrations of the fast and slow reactive sites of NOM, and ratios of yields of the fast and slow processes. Splitting coefficients were supposed to

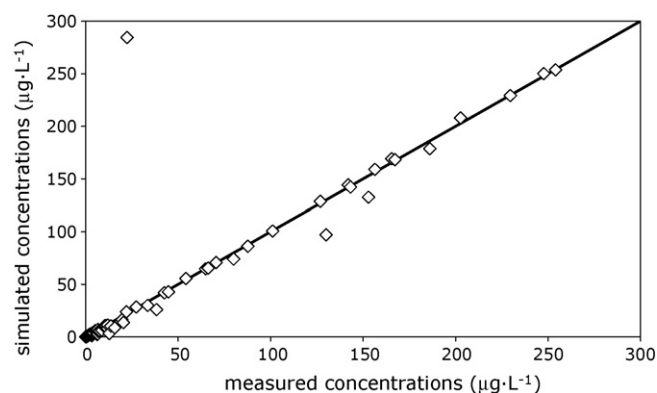


Fig. 5. Correlations between experimentally DBP concentrations and their model predictions.

be independent of NOM characteristics, and therefore equal for the two seawater samples used in the study.

Results of model calibration are summarized in Fig. 5 and Table 2. As it can be seen, the developed model generates high quality simulation data. Almost all points in Fig. 5 are well aligned along the zero-error line, indicating that predicted concentrations are close to the experimental results.

Kinetic constants for the two considered samples are not very different, indicating that NOM characteristics are likely to be similar in these two cases. This is not very surprising given that these parameters are probably affected by chlorine dose, which was the same during the whole study, and by bromide concentration, which was almost the same for the two samples. Further experiments are therefore required to verify the performance of the model in a wider range of experimental conditions.

#### 5. Conclusions

The paper presented an experimental study aimed at investigating and modelling yields and speciation of DBP formed during chlorination of seawater that can be considered a representative example of waters with high bromide levels. The data show that brominated compounds were predominant due to the high bromide concentration in the tested waters while THMs were more abundant than total HAAs.

The experimental data were used to examine the performance of a kinetic model that was based on a multi-step reaction path-

way. The model was calibrated to obtain the values of all kinetic parameters present in the explicit expressions for chlorinated and brominated THMs and HAAs. Although the model is able to fit very well the experimental data, further investigation is necessary to confirm its applicability for different NOM sources.

## References

- [1] S.D. Richardson, Disinfection by-products and other emerging contaminants in drinking water, *Trends Anal. Chem.* 22 (2003) 666–684.
- [2] J.E. Andrews, H.P. Nichols, J.E. Schmid, L.M. Mole, E.S. Hunter, G.R. Klinefelter, Developmental toxicity of mixtures: the water disinfection by-products dichloro-, dibromo- and bromochloro acetic acid in rat embryo culture, *Reprod. Toxicol.* 19 (2004) 111–116.
- [3] R.G. Tardiff, M. Leight Carson, M.E. Ginevan, Updated weight of evidence for an association between adverse reproductive and developmental effects and exposure to disinfection by-products, *Regul. Toxicol. Pharm.* 45 (2006) 185–205.
- [4] D.D. Gang, R.L. Segar, T.E. Clevenger, S.K. Banerji, Using chlorine demand to predict THM and HAA9 formation, *J. AWWA* 94 (2002) 76–86.
- [5] X. Yang, C. Shang, H. Ju-Chang, DBP formation in breakpoint chlorination of wastewater, *Water Res.* 39 (2005) 4755–4767.
- [6] E.E. Chang, P.C. Chiang, S.H. Chao, Y.L. Lin, Relationship between chlorine consumption and chlorination by-products formation for model compounds, *Chemosphere* 64 (2006) 1196–1203.
- [7] N. Ates, M. Kitis, U. Yetis, Formation of chlorination by-products in water with low SUVA—correlations with SUVA and differential UV spectroscopy, *Water Res.* 41 (2007) 4139–4148.
- [8] R.M. Clark, R.C. Thurman, M. Sivaganesan, P. Ringhand, Predicting the formation of chlorinated and brominated DBPs, *J. Environ. Eng.-ASCE* 127 (2001) 493–501.
- [9] A.A. Golfinopoulos, E.G. Arhonditsis, The impact of bromide on the formation of neutral and acid disinfection by-products in Mediterranean chlorinated drinking water, *Water Res.* 36 (2002) 2596–2606.
- [10] S.E. Duijk, R.L. Valentine, Modeling dichloroacetic acid formation from the reaction of monochloramine with natural organic matter, *Water Res.* 40 (2006) 2667–2674.
- [11] W.B. de Leer, J.S. Sinninghe Damste, C. Erkelens, L. de Galan, Identification of intermediates leading to chloroform and C-4 diacids in the chlorination of humic acid, *Environ. Sci. Technol.* 19 (1985) 512–522.
- [12] G.A. Cowman, P.C. Singer, Effect of bromide ion on haloacetic speciation resulting from chlorination and chloramination of aquatic humic substances, *Environ. Sci. Technol.* 30 (1996) 16–24.
- [13] C.J. Nokes, E. Fenton, C.J. Randall, Modelling the formation of brominated trihalomethanes in chlorinated drinking waters, *Water Res.* 33 (1999) 3557–3568.
- [14] G.T.F. Wong, J.A. Davidson, The fate of chlorine in seawater, *Water Res.* 11 (1977) 971–978.
- [15] G. Hua, D.A. Reckhow, J. Kim, Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination, *Environ. Sci. Technol.* 40 (2006) 3050–3056.
- [16] F. Ge, H. Shu, Y. Dai, Removal of bromide by aluminium chloride coagulant in the presence of humic acid, *J. Hazard. Mater.* 147 (2007) 457–462.
- [17] G. Hua, D.A. Reckhow, Comparison of disinfection byproduct formation from chlorine and alternative disinfectants, *Water Res.* 41 (2007) 1667–1678.
- [18] P.M.S.S. Rodrigues, J.C.G. Esteves da Silva, M.C.G. Autunes, Factorial analysis of the trihalomethanes formation in water disinfection using chlorine, *Anal. Chim. Acta* 595 (2007) 266–274.
- [19] S. Chellam, R.R. Sharma, G. Shetty, Y. Wei, Nanofiltration of pretreated Lake Houston water: disinfection by-product speciation, relationships, and control, *Sep. Purif. Technol.* 64 (2008) 160–169.
- [20] R.G. Qualls, J.D. Johnson, Kinetic of the short-term consumption of chlorine by fulvic acid, *Environ. Sci. Technol.* 17 (1983) 692–698.
- [21] P. Westerhoff, J. Debroux, G.L. Amy, D. Gatel, V. Mary, J. Cavard, Applying DBP models to full-scale plants, *J. AWWA* 92 (2000) 89–102.
- [22] L. Heller-Grossman, J. Manka, B. Limoni-Relis, M. Rebhun, THM, haloacetic acids and other organic DBPs formation in disinfection of bromide rich Sea of Galilee (Lake Kinneret) water, *Water Sci. Technol.: Water Supply* 1 (2001) 259–266.
- [23] A.S. Allonier, M. Khalanski, V. Camel, A. Bermond, Characterization of chlorination by-products in cooling effluents of coastal nuclear power stations, *Mar. Pollut. Bull.* 38 (1999) 1232–1241.
- [24] A.G. Dalvi, R. Al-Rasheed, M.A. Javeed, Haloacetic acids (HAAs) formation in desalination processes from disinfectants, *Desalination* 129 (2000) 261–271.
- [25] M. Fabbriano, G.V. Korshin, Formation of disinfection by-products and applicability of differential absorbance spectroscopy to monitor halogenation in chlorinated coastal and deep ocean seawater, *Desalination* 176 (2005) 57–69.
- [26] D.H. Choi, J.S. Park, C.Y. Hwang, S.H. Huh, B.C. Cho, Effects of thermal effluents from a power station on bacteria and heterotrophic nanoflagellates in coastal waters, *Mar. Ecol. Prog. Ser.* 229 (2002) 1–10.
- [27] E. Fogelqvist, M. Krysell, Naturally and anthropogenically produced bromoform in the Kattegatt, a semi-enclosed oceanic basin, *J. Atmos. Chem.* 13 (1991) 315–324.
- [28] P. Westerhoff, P. Chao, H. Mash, Reactivity of natural organic matter with aqueous chlorine and bromine, *Water Res.* 38 (2004) 1502–1513.
- [29] A.D. Nikolaou, T.D. Lekkas, S.K. Golfinopoulos, Kinetics of the formation and decomposition of chlorination by-products in surface waters, *Chem. Eng. J.* 100 (2004) 139–148.
- [30] G.V. Korshin, M.M. Benjamin, O. Hemingway, W. Wu, Development of Differential UV Spectroscopy for DBP Monitoring, AWWA Research Foundation, Denver, 2002.
- [31] J.H. Sharp, A.A. Carlson, E.T. Peltzer, D.M. Castel-Ward, W.B. Sadvige, K.R. Rinker, Final dissolved organic carbon broad community intercalibration and preliminary use of DOC reference materials, *Mar. Chem.* 77 (2002) 239–253.