

# NUMERICAL MODELLING OF OZONATION PROCESS WITH RESPECT TO BROMATE FORMATION. PART I – MODEL DEVELOPMENT

Urszula Olsińska\*

AQUA SEEN Spółka z o.o., ul. Siennicka 29, 04-394 Warszawa, Poland

The paper focuses on the modelling of bromate formation. An axial dispersion model was proposed to integrate the non-ideal mixing, mass-transfer and a kinetic model that links ozone decomposition reactions from the Tomiyasu, Fukutomi and Gordon (TFG) ozone decay model with direct and indirect bromide oxidation reactions, oxidation of natural organic matter and its reactions with aqueous bromine. To elucidate the role of ammonia an additional set of reactions leading to bromamine formation, oxidation and disproportionation was incorporated in the kinetic model. Sensitivity analysis was conducted to obtain information on reliability of the reaction rate constants used and to simplify the model.

**Keywords:** model, ozonation, bromate, hydrodynamics, kinetics

## 1. INTRODUCTION

Ozone based water treatment technologies are widely used for disinfection and oxidation processes. However, drawbacks to ozone utilisation exist. The desired effects of ozonation must be confronted by the formation of by-products that might be of human health concern, and among others bromate formation. The formation of bromate during ozonation of bromide-containing waters became an issue for drinking water production since it was classified as a potential carcinogen (WHO, 1993). Consequently, in many countries drinking water guidelines or standards were set to  $10 \mu\text{g BrO}_3^-/\text{dm}^3$  (e.g. Council Directive 98/83/EC; US Environmental Protection Agency, 2009).

The oxidation of bromide by ozone was studied in the context of bromate formation by several researchers (Fischbacher, 2015; Haag and Hoigné, 1983; Siddiqui et al., 1995; von Gunten and Hoigné, 1994). Empirical modelling from existing bromate formation data using multiple linear regression has been the most widely applied approach to bromate formation modelling. As an effort to predict the formation of bromate ions, some semi-empirical and numerical kinetic models have been developed as well (Hassan et al., 2003; Kim et al., 2007; Mizumo et al., 2007; Pinkernell and von Gunten, 2001; Song et al., 1996; Westerhoff et al., 1998). Bromate formation pathways are commonly considered in the kinetic-based models, but specific reactions varied between each of them. In addition, they do not include reactions recently reported for bromate formation. Values of the reaction rate constants taken from the literature were often fitted to the experimental results.

\* Corresponding author, e-mail: urszula.olsinska@gmail.com

Bromate is formed by a complex mechanism comprising both reactions with molecular ozone and hydroxyl radicals (Haag and Hoigné, 1983; Hoigné, 1998; von Gunten and Hoigné, 1994; von Sonntag and von Gunten, 2012). Thus, a kinetic model of the ozonation process must include reactions of ozone self-decomposition, direct and indirect reactions of bromide oxidation, and competitive reactions of dissolved ozone and radicals with various constituents present in natural waters (e.g. carbonate species, natural organic matter, phosphates, ammonia). Apart from the kinetic model, several phenomena which occur simultaneously during ozonation must be considered when its mathematical description is developed. These phenomena are: convection in a liquid and gas phase, ozone mass transfer from the gas to the liquid phase and, mixing in both fluids. In simulations of the bubble column performance the reactor hydrodynamics plays a key role. The models previously employed to predict the formation of bromate in bubble-column contactors assumed either a plug flow or complete mixing (Roustan et al., 1996). However, the axial dispersion model was successfully adapted for estimation of ozone self-decomposition kinetics in a semi-batch bubble column reactor (Kuosa et al., 2005) and in flow-through ozone bubble columns (El Din and Smith, 2001; Zhou et al. 1994).

The objective of this study was to develop a mechanistic model of the ozonation process that combines the stiff system of kinetic reactions with a hydrodynamic reactor model, to gain an insight into bromate formation under different operational conditions.

## 2. MODEL DEVELOPMENT

### 2.1. Reaction pathways

The proposed kinetic model was based on a multistep reaction pathway leading to bromate formation in natural waters containing bromide ions. The latter are oxidised by both ozone molecules and  $\cdot\text{OH}$  radicals, so radical formation must be included in the model. However, as hydroxide radicals can also be formed in the reaction of water molecules with ozone, it was decided to neglect this reaction in the developed model as being very slow ( $k = 1.1 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ ). To describe the decomposition of an aqueous ozone the TFG mechanism was adapted. The fundamental reactions incorporated in the TFG model are listed in Table 1.

Table 1. Ozone self-decomposition according to TFG mechanism

Reaction	Rate constant ( $T = 293 \text{ K}$ )	Reference	Eq.
Initiation			
$\text{O}_3 + \text{OH}^- \xrightarrow{k_1} \text{HO}_2^- + \text{O}_2$	$k_1 = 40 \text{ M}^{-1}\text{s}^{-1}$ $k_1 = 70 \text{ M}^{-1}\text{s}^{-1}$ $k_1 = 120 \text{ M}^{-1}\text{s}^{-1}$  $k_1 = 140 \text{ M}^{-1}\text{s}^{-1}$	Tomiyasu et al., 1985 Lovato et al., 2009 Chelkowska et al., 1992; Gordon, 1995 Nemes et al., 2000	(1)
$\text{O}_3 + \text{HO}_2^- \xrightarrow{k_2} \text{O}_3^{\cdot-} + \text{HO}_2^{\cdot}$	$k_2 = 1.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ $k_2 = 1.8 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ $k_2 = 2.2 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Chelkowska et al., 1992 Gordon, 1995 Tomiyasu et al., 1985	(2)
Propagation			
$\text{HO}_2^{\cdot} + \text{OH}^- \xrightarrow{k_3} \text{O}_2^{\cdot-} + \text{H}_2\text{O}$	$k_3 = 3.2 \times 10^5 \text{ s}^{-1}$ $k_3 = 7.9 \times 10^5 \text{ s}^{-1}$	Tomiyasu et al., 1985 Beltrán et al., 1998	(3)
$\text{H}_2\text{O} + \text{O}_2^{\cdot-} \xrightarrow{k_4} \text{HO}_2^{\cdot} + \text{OH}^-$	$k_4 = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ $k_4 = 5.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Tomiyasu et al., 1985 Beltrán et al., 1998	(4)

Reaction	Rate constant ( $T = 293$ K)	Reference	Eq.
$O_3 + O_2^{\cdot-} \xrightarrow{k_5} O_3^{\cdot-} + O_2$	$k_5 = 1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_5 = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Bühler et al., 1984 Nemes et al., 2000	(5)
$O_3^{\cdot-} + H_2O \xrightarrow{k_6} O_2 + OH^- + \cdot OH$	$k_6 = 15 \text{ s}^{-1}$ $k_6 = 20 \div 30 \text{ s}^{-1}$	Chelkowska et al., 1992 Tomiyasu et al., 1985	(6)
$O_3^{\cdot-} + \cdot OH \xrightarrow{k_7} HO_2^{\cdot} + O_2^{\cdot-}$	$k_7 = 6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_7 = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_7 = 8.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_7 = 2.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Tomiyasu et al., 1985 Chelkowska et al., 1992 Schedsted et al., 1984b Nemes et al., 2000	(7)
$O_3 + \cdot OH \xrightarrow{k_8} HO_2^{\cdot} + O_2$	$k_8 = 1.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ $k_8 = 5.0 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ $k_8 = 3.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_8 = 2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Schedsted, 1984a; Chelkowska et al., 1992; Gordon, 1995 Tomiyasu et al., 1985 Acero and Gunten, 2000	(8)
Termination			
$O_3^{\cdot-} + \cdot OH \xrightarrow{k_9} O_3 + OH^-$	$k_9 = 1.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ $k_9 = 2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_9 = 8.3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Chelkowska et al., 1992 Schedsted et al., 1984b Nemes et al., 2000	(9)

The TFG model provides only a simplified description of a chain-reaction sequence initiated by an oxygen atom transfer from ozone to hydroxide ion/a two-electron transfer process. As it seems to be somewhat incomplete and requiring refinement, several known reactions between the intermediate species (e.g. hydroxyl radicals, hydroperoxide radicals and superoxide anion radicals) were incorporated in the basic model. However, they may represent minor pathways only. The reactions added to the TFG model are presented in Table 2.

Table 2. Supplementary reactions to the basic ozone self-decomposition model

Reaction	Rate constant ( $T = 293$ K)	Reference	Eq.
Decay slow-down step			
$HO_2^- + \cdot OH \xrightarrow{k_{10}} O_2^{\cdot-} + H_2O$	$k_{10} = 7.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Christensen et al., 1982	(10)
$H_2O_2 + \cdot OH \xrightarrow{k_{11}} O_2^{\cdot-} + H_2O + H^+$	$k_{11} = 2.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Christensen et al., 1982	(11)
$H_2O_2 + HO_2^{\cdot} \xrightarrow{k_{12}} \cdot OH + O_2 + H_2O$	$k_{12} = 3.0 \text{ M}^{-1}\text{s}^{-1}$	Koppenol et al., 1978	(12)
$H_2O_2 + O_2^{\cdot-} \xrightarrow{k_{13}} \cdot OH + OH^- + O_2$	$k_{13} = 0.13 \text{ M}^{-1}\text{s}^{-1}$	Weinstein et al., 1979	(13)
Termination			
$\cdot OH + O_2^{\cdot-} \xrightarrow{k_{14}} OH^- + O_2$	$k_{14} = 7.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_{14} = 9.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Beck, 1969 Schedsted et al., 1968	(14)
$2\cdot OH \xrightarrow{k_{15}} H_2O_2$	$k_{15} = 5.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton, et al., 1988	(15)
$\cdot OH + HO_2^{\cdot} \xrightarrow{k_{16}} H_2O + O_2$	$k_{16} = 6.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Schedsted et al., 1968	(16)
$2HO_2^{\cdot} \xrightarrow{k_{17}} H_2O_2 + O_2$	$k_{17} = 8.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al., 1985	(17)
$HO_2^{\cdot} + O_2^{\cdot-} \xrightarrow{k_{18}} HO_2^- + O_2$	$k_{18} = 9.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al., 1985	(18)

Reaction	Rate constant ( $T = 293\text{ K}$ )	Reference	Eq.
Acid-base equilibrium ( $pK_A = 11.6$ )			
$\text{HO}_2^- + \text{H}^+ \xrightarrow{k_{19}} \text{H}_2\text{O}_2$	$k_{19} = 2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ $k_{19} = 5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Tomiyasu et al., 1985 Weast and Selby, 1971	(19)
$\text{H}_2\text{O}_2 \xrightarrow{k_{20}} \text{HO}_2^{\cdot} + \text{H}^+$	$k_{20} = 4.5 \times 10^{-2} \text{ s}^{-1}$ $k_{20} = 0.125 \text{ s}^{-1}$	Tomiyasu et al., 1985 Weast and Selby, 1971	(20)
Dissociation equilibrium			
$\text{H}_2\text{O} \xrightarrow{k_{21}} \text{H}^+ + \text{OH}^-$	$k_{21} = 1 \times 10^{-3} \text{ s}^{-1}$	Weast and Selby, 1971	(21)
$\text{H}^+ + \text{OH}^- \xrightarrow{k_{22}} \text{H}_2\text{O}$	$k_{22} = 1 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$	Weast and Selby, 1971	(22)

Other reactions reported in the literature (Buxton et al., 1988; Nemes et al., 2000) appropriate to use in case of waters of  $\text{pH} > 9.5$  were decided to be neglected in the model derived for drinking water.

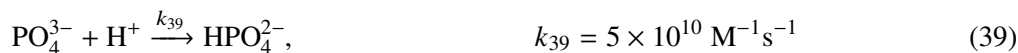
It was also found that the ozone decomposition rate is influenced by inorganic and organic admixtures of the water. Bicarbonate and carbonate ions, phosphates, and natural organic matter are considered to be the most important  $\cdot\text{OH}$  scavengers (Chelkowska et al., 1992; von Gunten, 2003). Since hydroxyl radicals contribute to  $\text{BrO}_3^-$  formation, the scavenging of the  $\cdot\text{OH}$  radicals should lead to a reduced bromate yield (von Gunten and Hoigné, 1994; von Gunten, 2003). However, carbonate species cannot be considered simply to be ozone decomposition inhibitors, since they can contribute to bromate formation via the radical pathway as well, which is reflected in Table 3.

Table 3. Main reactions involving carbonate species

Reaction	Rate constant ( $T \approx 293\text{ K}$ )	Reference	Eq.
Acid-base equilibria			
$\text{H}_2\text{CO}_3 \xrightarrow{k_{23}} \text{HCO}_3^- + \text{H}^+$	$k_{23} = 1 \times 10^5 \text{ s}^{-1}$ $k_{23} = 2.25 \times 10^4 \text{ s}^{-1}$	Weast and Selby, 1971 Westerhoff et al., 1997	(23)
$\text{HCO}_3^- + \text{H}^+ \xrightarrow{k_{24}} \text{H}_2\text{CO}_3$	$k_{24} = 2 \times 10^{11} \text{ M}^{-1}\text{s}^{-1}$ $k_{24} = 5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Weast and Selby, 1971 Westerhoff et al., 1997	(24)
$\text{HCO}_3^- \xrightarrow{k_{25}} \text{CO}_3^{2-} + \text{H}^+$	$k_{25} = 2.2 \text{ s}^{-1}$ ; $k_{25} = 2.5 \text{ s}^{-1}$	Chelkowska et al., 1992 Weast and Selby, 1971	(25)
$\text{CO}_3^{2-} + \text{H}^+ \xrightarrow{k_{26}} \text{HCO}_3^-$	$k_{26} = 4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$ $k_{26} = 5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Chelkowska et al., 1992 Weast and Selby, 1971	(26)
Direct reactions with ozone molecules			
$\text{HCO}_3^- + \text{O}_3 \xrightarrow{k_{27}} \text{products}$	$k_{27} = 0.001 \text{ M}^{-1}\text{s}^{-1}$	Hoigné et al., 1985	(27)
$\text{CO}_3^{2-} + \text{O}_3 \xrightarrow{k_{28}} \text{products}$	$k_{28} = 0.01 \text{ M}^{-1}\text{s}^{-1}$	Hoigné et al., 1985	(28)
Indirect reactions with $\cdot\text{OH}$ radicals			
Initiation			
$\text{CO}_3^{2-} + \cdot\text{OH} \xrightarrow{k_{29}} \text{OH}^- + \text{CO}_3^{\cdot-}$	$k_{29} = 3.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al., 1988	(29)
$\text{HCO}_3^- + \cdot\text{OH} \xrightarrow{k_{30}} \text{H}_2 + \text{CO}_3^{\cdot-}$	$k_{30} = 8.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Daiton, 1968	(30)

Reaction	Rate constant ( $T \approx 293$ K)	Reference	Eq.
Propagation			
$\text{CO}_3^{\cdot-} + \text{H}_2\text{O}_2 \xrightarrow{k_{31}} \text{HCO}_3^- + \text{HO}_2^{\cdot}$	$k_{31} = 8.0 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ $k_{31} = 4.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$	Glaze and Kang, 1988 Acero and Gunten, 2000	(31)
$\text{CO}_3^{\cdot-} + \text{HO}_2^- \xrightarrow{k_{32}} \text{CO}_3^{2-} + \text{HO}_2^{\cdot}$	$k_{32} = 5.6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff et al., 1997	(32)
Termination			
$\text{CO}_3^{\cdot-} + \text{CO}_3^{\cdot-} \xrightarrow{k_{33}} \text{CO}_2 + \text{CO}_4^{2-}$	$k_{33} = 2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff et al., 1997	(33)
$\text{CO}_3^{\cdot-} + \text{O}_3^{\cdot-} \xrightarrow{k_{34}} \text{CO}_3^{2-} + \text{O}_3$	$k_{34} = 6.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Chelkowska et al., 1992	(34)
$\text{CO}_3^{\cdot-} + \cdot\text{OH} \xrightarrow{k_{35}} \text{CO}_2 + \text{HO}_2^-$	$k_{35} = 3 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff et al., 1997	(35)
$\text{CO}_3^{\cdot-} + \text{O}_2^{\cdot-} \xrightarrow{k_{36}} \text{CO}_3^{2-} + \text{O}_2$	$k_{36} = 4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ $k_{36} = 7.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff et al., 1997 Perkowski et al., 2005	(36)
Chain branching			
$\text{CO}_3^{\cdot-} + \text{OBr}^- \xrightarrow{k_{37}} \text{CO}_3^{2-} + \text{BrO}^{\cdot}$	$k_{37} = 4.3 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Kläning and Wolff, 1985	(37)
$\text{CO}_3^{\cdot-} + \text{BrO}_2^- \xrightarrow{k_{38}} \text{CO}_3^{2-} + \text{BrO}_2^{\cdot}$	$k_{38} = 1.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Daiton, 1968	(38)

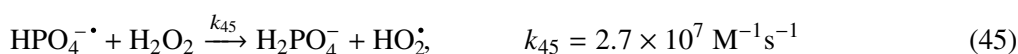
Other scavengers of  $\cdot\text{OH}$  radicals considered in the model are  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ . These ions are commonly present in natural waters of a typical pH range (pH = 6.5–8.5), thereby influencing system performance. To determine their equilibrium concentrations, equations proposed by Weast and Selby (1971) were introduced in the model:



Both  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  may react with  $\cdot\text{OH}$  radicals (Maruthamuthu and Neta, 1978):



and further formation of hydroxyl radicals is terminated. However,  $\text{HO}_2^{\cdot}$  radicals may be formed in the presence of hydrogen peroxide (Beltrán, 2005):

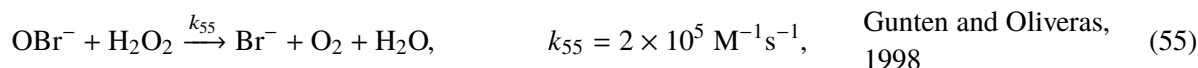
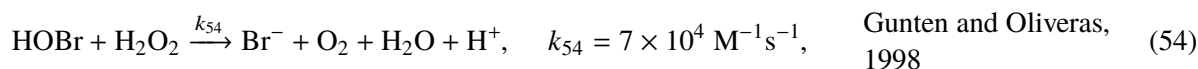
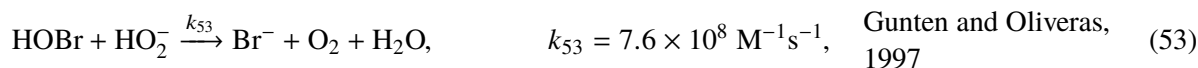


The reaction pathway leading from bromide to bromate in the presence of both ozone and  $\cdot\text{OH}$  radicals is very complex and involves many brominated species with oxidation states between (I) and (V), while the most frequently reported are:  $\text{BrO}^-/\text{HBrO}$ ,  $\text{BrO}_2^-$ ,  $\text{Br}^{\cdot}$ ,  $\text{BrO}^{\cdot}$ ,  $\text{BrOH}^-$ ,  $\text{Br}_2^{\cdot}$ . The reactions controlling the well-known mechanism for direct interaction of molecular ozone with bromide are given in Table 4. It is important to notice that oxidation of bromate(III) to bromate(V) may not as previously assumed be an O-transfer reaction (Eq. (50a)) but rather an electron-transfer reaction (Eq. (50b)) (Fischbacher et al., 2015).

Table 4. Bromate formation – molecular mechanism

Reaction	Rate constant ( $T = 293$ K)	Reference	Eq.
$\text{Br}^- + \text{O}_3 \xrightarrow{k_{46}} \text{OBr}^- + \text{O}_2$	$k_{46} = 160 \text{ M}^{-1}\text{s}^{-1}$ $k_{46} = 258 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigné, 1983 Liu et al., 2001	(46)
$\text{OBr}^- + \text{O}_3 \xrightarrow{k_{47}} 2\text{O}_2 + \text{Br}^-$	$k_{47} = 300 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigné, 1983	(47)
$\text{OBr}^- + \text{O}_3 \xrightarrow{k_{48}} \text{O}_2 + \text{BrO}_2^-$	$k_{48} = 100 \text{ M}^{-1}\text{s}^{-1}$ $k_{48} = 25 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigné, 1983 Song et al., 1996	(48)
$\text{HOBr} + \text{O}_3 \xrightarrow{k_{49}} \text{O}_2 + \text{BrO}_2^- + \text{H}^+$	$k_{49} \leq 0.013 \text{ M}^{-1}\text{s}^{-1}$	Haag et al., 1982	(49)
$\text{BrO}_2^- + \text{O}_3 \xrightarrow{k_{50a}} \text{BrO}_3^- + \text{O}_2$	$k_{50a} \geq 10^5 \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigné, 1983	(50a)
$\text{BrO}_2^- + \text{O}_3 \xrightarrow{k_{50b}} \text{BrO}_2^{\cdot} + \text{O}_3^{\cdot}$	$k_{50b} = 8.9 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$	Fischbacher et al., 2015	(50b)
Acid-base equilibrium ( $pK_A = 8.9$ )			
$\text{HOBr} \xrightarrow{k_{51}} \text{OBr}^- + \text{H}^+$	$k_{51} = 79 \text{ s}^{-1}$	Calculated value	(51)
$\text{OBr}^- + \text{H}^+ \xrightarrow{k_{52}} \text{HOBr}$	$k_{52} = 5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Haag and Hoigné, 1983	(52)

Since hypobromous acid/hypobromite ions ( $\text{HOBr}/\text{OBr}^-$ ) are the most important intermediates in the multistep bromate formation process (von Gunten, 2003), their reactions with hydroperoxide ions and hydrogen peroxide were presumably included in the model:



Bromate ions can also be formed due to the oxidation of bromide ions by hydroxyl radicals, via the formation of the bromine atom ( $\text{Br}^{\cdot}$ ) (Eq. (56)) (von Gunten and Oliveras, 1998). The radical reactions considered within the bromate formation pathway are listed in Table 5.

Table 5. Radical reactions within bromate formation pathway

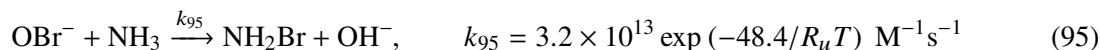
Reaction	Rate constant ( $T = 293\text{--}298$ K)	Reference	Eq.
$\text{Br}^- + \cdot\text{OH} \xrightarrow{k_{56}} \text{Br}^{\cdot} + \text{OH}^-$	$k_{56} = 1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	von Gunten, 2003	(56)
$\text{Br}^- + \cdot\text{OH} \xrightarrow{k_{57}} \text{BrHO}^{\cdot}$	$k_{57} = 1.06 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Zehavi and Rabani, 1972	(57)
$\text{BrHO}^{\cdot} \xrightarrow{k_{58}} \text{Br}^- + \cdot\text{OH}$	$k_{58} = 3.3 \times 10^7 \text{ s}^{-1}$		(58)
$\text{BrHO}^{\cdot} + \text{H}^+ \xrightarrow{k_{59}} \text{Br}^{\cdot} + \text{H}_2\text{O}$	$k_{59} = 4.4 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$		(59)
$\text{BrHO}^{\cdot} \xrightarrow{k_{60}} \text{Br}^{\cdot} + \text{OH}^-$	$k_{60} = 4.2 \times 10^6 \text{ s}^{-1}$		(60)
$\text{Br}^{\cdot} + \text{OH}^- \xrightarrow{k_{61}} \text{BrHO}^{\cdot}$	$k_{61} = 1.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$		(61)
$\text{BrHO}^{\cdot} + \text{Br}^- \xrightarrow{k_{62}} \text{Br}_2^{\cdot} + \text{OH}^-$	$k_{62} = 1.9 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$		(62)
$\text{Br}^- + \text{Br}^{\cdot} \xrightarrow{k_{63}} \text{Br}_2^{\cdot}$	$k_{63} = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$		(63)
$\text{Br}_2^{\cdot} \xrightarrow{k_{64}} \text{Br}^- + \text{Br}^{\cdot}$	$k_{64} = 1 \times 10^5 \text{ s}^{-1}$		(64)

Reaction	Rate constant ( $T = 293\text{--}298\text{ K}$ )	Reference	Eq.
$2\text{Br}_2^{\cdot-} \xrightarrow{k_{65}} \text{Br}^- + \text{Br}_3^-$	$k_{65} = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Sutton et al., 1965	(65)
$\text{Br}_3^- \xrightarrow{k_{66}} \text{Br}_2 + \text{Br}^-$	$k_{66} = 8.3 \times 10^8 \text{ s}^{-1}$	Sutton et al., 1965	(66)
$\text{Br}_2 + \text{Br}^- \xrightarrow{k_{67}} \text{Br}_3^-$	$k_{67} = 1 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	Sidgwick, 1952	(67)
$2\text{Br}^{\cdot} \xrightarrow{k_{68}} \text{Br}_2$	$k_{68} = 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Kläning and Wolff, 1985	(68)
$\text{Br}_2 + \text{H}_2\text{O} \xrightarrow{k_{69}} \text{HOBr} + \text{H}^+ + \text{Br}^-$	$k_{69} = 8.24 \text{ s}^{-1}$ $k_{69} = 110 \text{ s}^{-1}$	Sutton et al., 1965 Gordon, 1995	(69)
$\text{HOBr} + \text{H}^+ + \text{Br}^- \xrightarrow{k_{70}} \text{Br}_2 + \text{H}_2\text{O}$	$k_{70} = 8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Gordon, 1995	(70)
$\text{Br}^{\cdot} + \text{O}_3 \xrightarrow{k_{71}} \text{BrO}^{\cdot} + \text{O}_2$	$k_{71} = 1.5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Gunten & Oliveras, 1998	(71)
$\text{Br}^{\cdot} + \text{OBr}^- \xrightarrow{k_{72}} \text{Br}^- + \text{BrO}^{\cdot}$	$k_{72} = 4.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Kläning and Wolff, 1985	(72)
$\text{Br}_2^{\cdot-} + \text{OBr}^- \xrightarrow{k_{73}} \text{BrO}^{\cdot} + 2\text{Br}^-$	$k_{73} = 8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Daiton, 1968	(73)
$\text{HOBr} + \cdot\text{OH} \xrightarrow{k_{74}} \text{BrO}^{\cdot} + \text{H}_2\text{O}$	$k_{74} = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al., 1988	(74)
$\text{OBr}^- + \cdot\text{OH} \xrightarrow{k_{75}} \text{BrO}^{\cdot} + \text{OH}^-$	$k_{75} = 4.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Daiton, 1968	(75)
$2\text{BrO}^{\cdot} + \text{H}_2\text{O} \xrightarrow{k_{76}} \text{OBr}^- + \text{BrO}_2 + 2\text{H}^+$	$k_{76} = 4.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$		(76)
$\text{Br}_2^{\cdot-} + \text{BrO}_2 \xrightarrow{k_{77}} \text{OBr}^- + \text{BrO}^{\cdot} + \text{Br}^-$	$k_{77} = 8 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$		(77)
$\text{BrO}_2^- + \cdot\text{OH} \xrightarrow{k_{78}} \text{BrO}_2^{\cdot} + \text{OH}^-$	$k_{78} = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$		(78)
$\text{BrO}_2^- + \text{BrO}^{\cdot} \xrightarrow{k_{79}} \text{OBr}^- + \text{BrO}_2^{\cdot}$	$k_{79} = 3.4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$		(79)
$\text{BrO}_2^{\cdot} + \cdot\text{OH} \xrightarrow{k_{80}} \text{BrO}_3^- + \text{H}^+$	$k_{80} = 2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al., 1988	(80)
$\text{BrO}_3^- + \cdot\text{OH} \xrightarrow{k_{81}} \text{BrO}^{\cdot} + \text{OH}^- + \text{O}_2$	$k_{81} = 3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Amichai et al., 1969	(81)
$2\text{BrO}_2^{\cdot} \xrightarrow{k_{82}} \text{Br}_2\text{O}_4$	$k_{82} = 1.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Daiton, 1968	(82)
$\text{Br}_2\text{O}_4 \xrightarrow{k_{83}} 2\text{BrO}_2^{\cdot}$	$k_{83} = 7 \times 10^7 \text{ s}^{-1}$		(83)
$\text{Br}_2\text{O}_4 + \text{OH}^- \xrightarrow{k_{84}} \text{BrO}_3^- + \text{BrO}_2^- + \text{H}^+$	$k_{84} = 7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$		(84)
$2\text{BrO}^{\cdot} \xrightarrow{k_{85}} \text{Br}_2\text{O}_2$	$k_{85} = 2.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton and Daiton, 1968	(85)
$\text{Br}^{\cdot} + \text{HO}_2 \xrightarrow{k_{86}} \text{Br}^- + \text{HO}_2^{\cdot}$	$k_{86} = 4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Song et al., 1996	(86)
$\text{Br}^{\cdot} + \text{BrO}^{\cdot} \xrightarrow{k_{87}} 2\text{HOBr}$	$k_{87} = 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Kläning and Wolff, 1985	(87)
$\text{HOBr} + \text{O}_2^{\cdot-} \xrightarrow{k_{88}} \text{Br}^{\cdot} + \text{O}_2 + \text{OH}^-$	$k_{88} = 3.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	Schwarc and Bielski, 1986	(88)
$\text{OBr}^- + \text{O}_2^{\cdot-} \xrightarrow{k_{89}} \text{BrO}^{\cdot} + \text{O}_2$	$k_{89} > 10^8 \text{ M}^{-1}\text{s}^{-1}$		(89)
$\text{Br}_2^{\cdot-} + \text{O}_2^{\cdot-} \xrightarrow{k_{90}} 2\text{Br}^- + \text{O}_2$	$k_{90} = 1.7 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$		(90)
$\text{Br}_3^- + \text{O}_2^{\cdot-} \xrightarrow{k_{91}} \text{Br}_2^{\cdot-} + \text{O}_2 + \text{Br}^-$	$k_{91} = 1.5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$		(91)

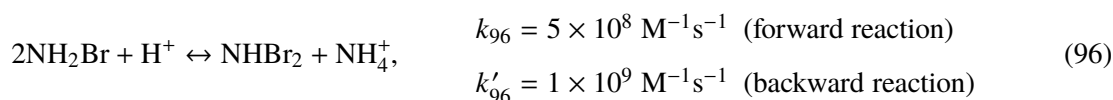
If ammonia is present in water (or added prior to ozonation process), bromamines are formed in the reactions with free bromine (Galal-Gorchev and Morris, 1965):



The reaction of  $\text{NH}_3$  with  $\text{HOBr}$  (Eq. (92)), which is an electrophilic substitution of  $\text{H(I)}$  in ammonia by  $\text{Br(I)}$ , leads to the formation of monobromamine. Once formed,  $\text{NH}_2\text{Br}$  can react further with bromine to form dibromamine (Eq. (93)) and eventually tribromamine (Eq. (94)). The reactions (92)–(94) were found to be reversible (Sugam and Helz, 1981), but judging from equilibrium constants that have been reported:  $3.0 \times 10^{10}$ ,  $4.7 \times 10^8$  and  $5.3 \times 10^6$  respectively, the rate constants for the backward reactions are very small. Thus, it does not seem appropriate to incorporate the backward reactions in the overall mass balance equations. The second-order rate constants (Galal-Gorchev and Morris, 1965; Wajon and Morris, 1982) were considered for further calculations. The rate constant for the reaction (92) is approximately three orders of magnitude higher than the corresponding rate constant for hypobromite (Eq. (93)), which is due to higher electrophilicity of  $\text{HOBr}$  compared to  $\text{OBr}^-$  (Wajon and Morris, 1982; Haag et al., 1984):



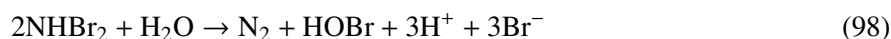
Dibromamine is also formed through the disproportionation of  $\text{NH}_2\text{Br}$  (Heeb et al., 2014; Inman and Johnson, 1984; Lei et al., 2004):



The formation of dibromamine due to the disproportionation of monobromamine was found to be catalysed by phosphate buffer. Therefore, the following rate law proposed by Inman and Johnson (1984) for the pH range of 7.5–8.5 was incorporated in the kinetic model:

$$\frac{d[\text{NHBBr}_2]}{dt} = 2.4 \times 10^8 [\text{H}^+] [\text{Br}_{tot}]^2 + 9.9 \times 10^{11} [\text{H}^+] [\text{PO}_4] [\text{Br}_{tot}]^2 \quad (97)$$

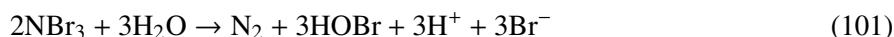
Dibromamine is even less stable in aqueous solutions than monobromamine. The mechanism of dibromamine decomposition elaborated by Cromer et al. (1978) was adapted:



with the second-order apparent rate constant for the decomposition of  $\text{NHBBr}_2$  proposed by Johnson and Overby (1971):

$$k_{98} = 1.38 \times 10^7 \exp[-7510/(1.987T)], \text{ M}^{-1} \text{ s}^{-1} \quad (100)$$

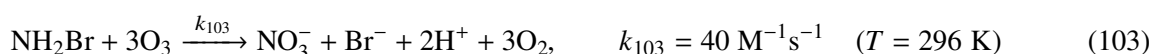
Similar to the reaction (98), the decomposition of tribromamine was found to be irreversible (La Pointe et al., 1975):



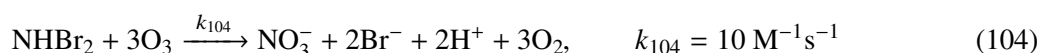
and to follow the rate law (Eq. (102)), which was introduced into the proposed model:

$$-\frac{d[\text{NBr}_3]}{dt} = \frac{9.7 \times 10^{-11} [\text{NBr}_3]^{3/2}}{[\text{H}^+] [\text{OBr}^- + \text{HOBr}]^{1/2}} \quad (102)$$

Moreover, oxidation of both monobromamine and dibromamine was considered. The reaction of  $\text{NH}_2\text{Br}$  with ozone yields bromide and nitrate (Eq. 103) (Berne et al., 2004; Hoigné et al., 1985):

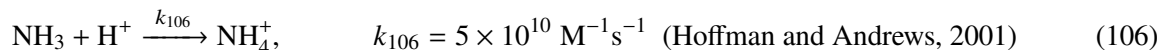


Analogous products are formed in the reaction of dibromamine with ozone. However, oxidation proceeds four times more slowly (Haag et al., 1984):





Despite the reactions of bromamines with molecular ozone, the reaction between  $\text{NH}_2\text{Br}$  and  $\cdot\text{OH}$  radical was introduced with the rate constant estimated at a level of  $6 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  (Song et al., 1997). A set of reactions engaging ammonia also required addition of the reactions describing acid base equilibrium for ammonia/ammonium system:



Another important aspect to be considered when modelling ozonation process is the presence of natural organic matter, usually measured as a dissolved organic carbon. Because of a complex, not well-defined structure and chemistry of NOM, it is still difficult to assess/predict precisely ozone stability in natural waters or the formation of different ozonation by-products (Mandel et al., 2012). On one hand, NOM may affect ozone stability in two ways: (1) it can directly react with dissolved ozone (Eq. (107) in Table 6) or (2) indirectly through scavenging hydroxyl radicals (Eq. (108) in Table 6). The latter reaction is a chain reaction. After reaction of  $\cdot\text{OH}$  with NOM, a fraction of NOM is transferred into carbon-centred radicals, which in the presence of oxygen subsequently form superoxide radicals (von Gunten, 2007; Hoigné, 1998).  $\text{O}_2\cdot^-$  radicals react quickly with ozone to form  $\cdot\text{OH}$  radicals (Eq. (14) in Table 2). This chain reaction leads to ozone depletion, which may be only terminated by inhibitors. In natural waters they mainly consist of a fraction of NOM and carbonate/bicarbonate (Buxton et al., 1988). On the other hand, in bromide-containing waters bromide ions are transformed into intermediate species, which are reactive towards NOM (Eqs. (110)–(112) in Table 6). It has been recognized that hypobromite/hypobromous acid may react with NOM to form bromoorganic compounds (e.g. tribromomethane) (von Sonntag and von Gunten, 2012). In addition, a part of the organic bromine may bind to higher molecular organic matter from NOM (Westerhoff et al., 1998). To simplify a mathematical description of ozonation process only selected reactions were incorporated in the proposed model (Table 6).

Table 6. Selected reactions in the presence of NOM

Reaction	Rate constant	Reference	Eq.
$\text{O}_3 + \text{DOC} \rightarrow \cdot\text{OH} + \text{products}$	$k_{107} = 1 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$	Siddiqui et al., 1995	(107)
$\cdot\text{OH} + \text{DOC} \rightarrow \text{O}_2\cdot^- + \text{products}$	$k_{108} = 5 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ $k_{108} = 3.96 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$	Siddiqui et al., 1995 Song et al., 1997	(108)
$\text{CO}_3^{\cdot-} + \text{DOC} \rightarrow \text{DOC} + \text{HCO}_3^-$	$k_{109} = 5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	Siddiqui et al., 1995	(109)
$\text{HOBr} + \text{DOC} \rightarrow \text{products} + \text{Br}^-$	$k_{110} = 5 \text{ M}^{-1}\text{s}^{-1}$	Westerhoff et al., 1998	(110)
$\text{OBr}^- + \text{DOC} \rightarrow \text{products} + \text{Br}^-$	$k_{111} = 5 \text{ M}^{-1}\text{s}^{-1}$		(111)
$\text{BrO}\cdot + \text{DOC} \rightarrow \text{products} + \text{HOBr}$	$k_{112} = 5 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$		(112)

## 2.2. Mass transfer modelling

As mentioned before, despite the chemical reaction system and water matrix the three other processes may affect the ozonation process: convection, mixing, ozone transfer from the gas to the liquid phase. The two-phase axial dispersion model was chosen to describe the reactor hydrodynamics – particularly backmixing phenomena of the gas and liquid phases (Levenspiel, 1999), while a two-film theory of mass transfer (Lewis and Whitman, 1924) was applied to describe the ozone mass transfer from the gas phase to the liquid phase. Thus, the rate of an overall ozone mass transfer from the gas phase to the liquid phase was expressed as:

$$\Psi = E_p k_L a \left( [\text{O}_3]_L^* - [\text{O}_3]_L \right) \quad (113)$$

Consequently, the ozone mass balance equations for the liquid (Eq. (114)) and the gas phase (Eq. (115)) may be written for the differential fluid element as follows:

$$\varepsilon_L \frac{\partial [\text{O}_3]_L}{\partial t} = I_{uL} \frac{\partial [\text{O}_3]_L}{\partial z} + \varepsilon_L D_{LL} \frac{\partial^2 [\text{O}_3]_L}{\partial z^2} + E_p k_{La} ([\text{O}_3]_L^* - [\text{O}_3]_L) + \varepsilon_L r_{\text{O}_3} \quad (114)$$

$$\varepsilon_G \frac{\partial [\text{O}_3]_G}{\partial t} = \frac{\partial (u_G [\text{O}_3]_G)}{\partial z} + \varepsilon_G D_{LG} \frac{\partial^2 [\text{O}_3]_G}{\partial z^2} - E_p k_{La} ([\text{O}_3]_L^* - [\text{O}_3]_L) \quad (115)$$

where the reaction rate of ozone consumption (e.g. in the absence of ammonia) equals:

$$\begin{aligned} r_{\text{O}_3} = & -k_1[\text{O}_3][\text{OH}^-] - k_2[\text{O}_3][\text{HO}_2^-] - k_5[\text{O}_3][\text{O}_2^{\cdot-}] - k_8[\text{O}_3][\text{HO}^\bullet] + k_9[\text{O}_3^{\cdot-}][\text{HO}^\bullet] - k_{27}[\text{HCO}_3^-][\text{O}_3] \\ & - k_{28}[\text{CO}_3^{2-}][\text{O}_3] + k_{34}[\text{CO}_3^{\cdot-}][\text{O}_3^{\cdot-}] - k_{46}[\text{Br}^-][\text{O}_3] - k_{47}[\text{OBr}^-][\text{O}_3] - k_{48}[\text{OBr}^-][\text{O}_3] \\ & - k_{49}[\text{HOBr}][\text{O}_3] - k_{50a}[\text{BrO}_2^-][\text{O}_3] - k_{50b}[\text{BrO}_2^-][\text{O}_3] - k_{71}[\text{Br}^\bullet][\text{O}_3] - k_{107}[\text{DOC}][\text{O}_3] \end{aligned} \quad (116)$$

The value of enhancement factor depends on a chemical reaction regime, which can be deduced from the Hatta number defined for the 2<sup>nd</sup> order irreversible reaction (Biń and Roustan, 2000):

$$Ha = \frac{\sqrt{D_{\text{O}_3} k [B]}}{k_L} \quad (117)$$

The molecular diffusivity of ozone gas in water was determined using the equation recommended by Johnson and Davis (1996), while the local mass transfer coefficient was assumed to be in the order of  $(1.9\text{--}3.0) \times 10^{-4} \text{ m}\cdot\text{s}^{-1}$  for water containing organic substances (Beltrán, 2005).

A term  $k [B]$  was calculated based on chemical analysis of source waters and relevant reaction rate constants, which are available in the literature. In the case of source waters used in this study, the resultant values of the Hatta number ranged from  $10^{-4}$  to  $10^{-2}$ . Since  $Ha < 0.02$ , the slow kinetic regime can be assumed so the reactions take place in a bulk of the liquid. Under these conditions the enhancement factor is equal to 1 (Biń and Roustan, 2000). Thus, this value was introduced into the model, and consequently the reaction rates were calculated according to standard kinetics valid for the bulk liquid phase. Therefore, the mass balance equations for each of the chemical moieties ( $X_i$ ) considered in the model were set as:

$$\varepsilon_L \frac{\partial [X_i]}{\partial t} = I_{uL} \frac{\partial [X_i]}{\partial z} + \varepsilon_L D_{LL} \frac{\partial^2 [X_i]}{\partial z^2} + \varepsilon_L r_{X_i} \quad (118)$$

The development of any mathematical model involves a compromise to balance conflicting needs. On one hand, a model must incorporate the major processes/phenomena anticipated within the system in a manner which is consistent with established knowledge about the system. On the other hand, model equations must be solvable within the reasonable computational time. To compromise between the need to pursue reality and the need to limit complexity of the problem to make the model tractable, additional assumptions were made:

- backmixing in the gas phase can be neglected if the gas superficial velocity takes the values lower than  $0.1 \text{ m}\cdot\text{s}^{-1}$  thus a plug flow ( $D_{LG} = 0$ ) can be assumed for the gas phase;
- there are no radial concentration gradients;
- temperature, gas holdup and volumetric ozone transfer coefficient remain constant along the height of reactor;
- the reactor is operated under steady-state conditions, which is a common design practice in engineered ozonation units.

Thus, the system of non-linear partial differential equations can be transformed to the system of non-linear ordinary differential equations:

$$I_{uL} \frac{d[\text{O}_3]_L}{dz} + \varepsilon_L D_{LL} \frac{d^2[\text{O}_3]_L}{dz^2} + k_{La} ([\text{O}_3]_L^* - [\text{O}_3]_L) + \varepsilon_L r_{\text{O}_3} = 0 \quad (119)$$

$$\frac{d(u_G[\text{O}_3]_G)}{dz} k_{La} ([\text{O}_3]_L^* - [\text{O}_3]_L) = 0 \quad (120)$$

$$Iu_L \frac{d[X_i]}{dz} + \varepsilon_L D_{LL} \frac{d^2[X_i]}{dz^2} + \varepsilon_L r_{X_i} = 0 \quad (121)$$

The equilibrium concentration of dissolved ozone was determined by applying Henry's law

$$[\text{O}_3]_L^* = \frac{p\text{O}_3}{H_e} = \frac{p \times x}{H_e} \quad (122)$$

To account for hydrostatic effect on superficial gas velocity, mass balance over inert constituents in the gas phase was considered as proposed by Zhou et al. (1994):

$$\frac{d(u_G c_n)}{dz} = 0 \quad (123)$$

After integration Eq. (123) is equivalent to:

$$u_G p(1 - x) = u_{G_0} p_0(1 - x_0) \quad (124)$$

in which pressures are expressed following a definition of hydrostatic pressure:

$$p = p_T + \gamma \varepsilon_L (H - z) \quad \text{and} \quad p_0 = p_T + \gamma \varepsilon_L H \quad (125)$$

### 2.3. Mathematical approach

The proposed ADM for a two-phase absorption with chemical reactions in the bulk of the liquid phase comprises a system of non-linear ordinary differential equations with boundary conditions at two points:

- for the co-current flow mode:

$$z = 0; \quad x = x_0; \quad [\text{O}_3]_G = [\text{O}_3]_{G,0}; \quad (126)$$

$$[\text{O}_3]_L = [\text{O}_3]_{L,0} + LD \left. \frac{d[\text{O}_3]_L}{dz} \right|_{z=0}; \quad [\text{O}_3]_{L,0} \rightarrow 0; \quad [X] = [X]_0 + LD \left. \frac{d[X]}{dz} \right|_{z=0}$$

$$z = H; \quad \left. \frac{d[\text{O}_3]_L}{dz} \right|_{z=H} = 0; \quad \left. \frac{d[X]}{dz} \right|_{z=H} = 0 \quad (127)$$

- for the counter-current flow mode:

$$z = 0; \quad x = x_0; \quad \left. \frac{d[\text{O}_3]_L}{dz} \right|_{z=0} = 0; \quad \left. \frac{d[X]}{dz} \right|_{z=0} = 0 \quad (128)$$

$$z = H; \quad [\text{O}_3]_L = [\text{O}_3]_{L,0} - LD \left. \frac{d[\text{O}_3]_L}{dz} \right|_{z=H}; \quad [\text{O}_3]_{L,0} \rightarrow 0; \quad [X] = [X]_0 - LD \left. \frac{d[X]}{dz} \right|_{z=H} \quad (129)$$

The solution of the ADM equations needs a numerical method to transform them into non-linear algebraic equations. In this study, the finite-difference method was chosen. Basically, a uniform discretisation was applied. A non-uniform mesh was executed adaptively changing parameters Step Monitor and Working Precision in the Find Root toolbox. Numerical optimisation was conducted with the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm assuming a function tolerance at the level of  $10^{-8}$ . All calculations were performed with a software package "Mathematica". It should be noted that all the 2<sup>nd</sup> order reaction rate constants were expressed in the right units ( $\text{mol}^{-1} \text{m}^3 \text{s}$ ) before substituting them to the reaction rate equations.

The relative sensitivity function was adopted to evaluate the sensitivity of the model output (concentration of bromate formed during the simulated ozonation process) to a change of each of the published value of

the kinetic constants. The values of *RSF* were estimated from the sensitivity function by a finite forward difference method following Eq. (130):

$$RSF = \frac{w' \times k_i}{y(z, k_i)} \quad (130)$$

and raising the nominal  $k_i$  value with a perturbation factor  $\zeta = 2; 3; 4; 5$  as follows:

$$w' = \frac{\hat{y}(z, k_i + \zeta k_i) - \hat{y}(z, k_i)}{\zeta k_i} \quad (131)$$

The value of  $RSF < 0.25$  indicates that the tested parameter is not influential. The parameter is considered moderately influential when  $0.25 < RSF < 1$ , very influential if  $1 < RSF < 2$ , and extremely influential when  $RSF$  takes values higher than 2 (Audenaert et al., 2010). The rate constants, which exerted at least a moderate influence on the model output, were then modified within their reported range of values to select the values that best fitted the model.

The goodness-of-fit between experimental and simulated values was quantified by calculating Theil's inequality coefficient (Theil, 1961) expressed by the equation:

$$TIC_j = \frac{\sqrt{\sum_i (y_i - \hat{y}_i)^2}}{\sqrt{\sum_i y_i^2} + \sqrt{\sum_i \hat{y}_i^2}} \quad (132)$$

A value of the *TIC* equal to zero implies a perfect fit (Theil, 1961), while the value lower than 0.3 indicates a good agreement with measured data (Audenaert et al., 2010).

### 3. RESULTS AND DISCUSSION

#### 3.1. Sensitivity analysis

Qualitative effect on the overall bromate formation by changing separately each of the published values of the rate constants was assessed based on simulations carried out with II data set presented in Table 1 published elsewhere (Olsińska, 2019). Table 7 gives a summary of sensitivity analysis results performed for the basic model (in the absence of ammonia).

Table 7. Sensitivity of the model towards changes in the values of the rate constants

<i>RSF</i>	Effect	Equation number
< 0.25	Almost none/small	(6)–(9), (11)–(13), (19), (20), (25)–(28), (45), (54)–(80), (85)–(91);
$0.25 < RSF < 1$	Moderate	(3), (10), (14), (17), (18), (23), (24), (29)–(35), (36)–(38), (43), (44), (49), (53), (81)–(84), (108)–(112);
$1 < RSF < 2$	Significant	(2), (4), (15), (16), (47), (50a), (50b), (107);
> 2	Extremely significant	(1), (5), (46), (48).

Following sensitivity analysis, it can be concluded that the model is very sensitive to changes in the rate constants of the direct oxidation of bromide and hypobromite ions. These results proved the findings presented by Hassan et. al (2003).

Similar sensitivity analyses were performed for the model, which included reactions taking place in the system if ammonia was present. It was found that in water of nearly neutral pH, bromate formation is moderately affected by the rate constants of the reactions: (93), (94), (98), (99), and (104).

The rate constants written in bold (Tab. 7) were then modified within their reported range of values. Computed values were confronted with the experimental data to select the optimum values that give the smallest deviation from the measured concentrations of bromates. The rate constants that fitted the model best are shown in Table 8.

Table 8. Rate constants selected on basis of sensitivity analysis

Equation number	$k$	Equation number	$k$
(1)	$120 \text{ M}^{-1}\text{s}^{-1}$	(23)	$2.25 \times 10^4 \text{ s}^{-1}$
(2)	$1.5 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$	(24)	$5 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$
(3)	$3.2 \times 10^5 \text{ s}^{-1}$	(36)	$4 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
(4)	$2 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}$	(46)	$160 \text{ M}^{-1}\text{s}^{-1}$
(5)	$1.6 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	(48)	$100 \text{ M}^{-1}\text{s}^{-1}$
(14)	$7.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$	(108)	$3.96 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$

These chemical reaction rate constants were further used at the stage of model simplification and validation.

### 3.2. Simplifying the basic model

To rationalise the reaction system, additional numerical investigations were performed. In subsequent simulations one reaction was omitted, while the set of other reactions was left unchanged. The obtained results proved that the model can be simplified by neglecting the reactions (11)–(18) when the bromate formation is modelled for water with pH of 6.98, as there was no change in its resultant concentration. At pH of 7.85 the relative deviation between the measured and computed concentration reached 4% and increased up to 12% in case of water of higher pH.

A similar tendency was observed when the indirect reactions (88)–(91) were neglected. Thus, the model can be simplified by these reactions when bromate formation in water of nearly neutral pH is predicted.

## 4. CONCLUSIONS

The availability of a model like one presented herein, may allow the engineers to explore, through simulations, a very broad range of system configurations, inputs, and operational strategies. Since a few assumptions and simplification of the process were made, the proposed model must be validated before using it for prediction of bromate formation in natural waters (containing bromide ions) ozonated under full scale conditions.

## SYMBOLS

ADM axial dispersion model  
 $[B]$  concentration of any compound B

$[\text{Br}_{\text{tot}}]$	sum of molar concentrations of species encountered as free bromine
$c_n$	concentration of an inert constituent in the gas phase, $\text{mol}\cdot\text{m}^{-3}$
$D_{\text{O}_3}$	molecular diffusion coefficient, $\text{m}^2\cdot\text{s}^{-1}$
$D_L$	axial (longitudinal) dispersion coefficient, $\text{m}^2\cdot\text{s}^{-1}$
$\text{DOC}$	dissolved organic carbon, $\text{mol}\cdot\text{C}\cdot\text{m}^{-3}$
$E_p$	enhancement factor, –
$H$	water head measured from the level of ozone diffuser to water surface
$Ha$	Hatta number, –
$H_e$	Henry's law constant, $\text{Pa}\cdot\text{mol}^{-1}\cdot\text{m}^3$
$I$	denotes the flow direction in the liquid phase ( $I = +1$ counter-current; $I = -1$ co-current flow mode)
$k$	chemical reaction rate constant, $\text{M}^{-1}\cdot\text{s}^{-1}$ , $\text{s}^{-1}$
$k_L$	liquid phase mass transfer coefficient, $\text{m}\cdot\text{s}^{-1}$
$k_L a$	liquid phase volumetric mass transfer coefficient, $\text{s}^{-1}$
$LD$	vessel dispersion number, –
$\text{NOM}$	natural organic matter
$[\text{O}_3]_L$	concentration of dissolved ozone in the bulk liquid, $\text{mol}\cdot\text{m}^{-3}$
$[\text{O}_3]_L^*$	equilibrium interfacial ozone concentration, $\text{mol}\cdot\text{m}^{-3}$
$p$	pressure, Pa
$pK_A$	negative logarithm of acid-base equilibrium constant, –
$r$	chemical reaction rate, $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$
$R_u$	universal gas constant; $8,3143 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$\text{RSF}$	relative sensitivity function
$t$	time, s
$T$	temperature, K
$\text{TFG}$	Tomiyasu, Fukutomi and Gordon
$\text{TIC}$	Theil's inequality coefficient, –
$u$	superficial velocity, $\text{m}\cdot\text{s}^{-1}$
$w'$	sensitivity function
$x$	gas molar fraction in the gas phase, –
$y$	measured concentration, $\text{mol}\cdot\text{m}^{-3}$
$\hat{y}$	simulated concentration, $\text{mol}\cdot\text{m}^{-3}$
$[X]$	concentration of any reaction substrate, $\text{mol}\cdot\text{m}^{-3}$
$z$	distance measured from ozone inlet (diffuser), m

*Greek symbols*

$\varepsilon$	hold-up coefficient, –
$\Psi$	rate of overall ozone mass transfer from gas phase to liquid phase, $\text{mol}\cdot\text{dm}^{-3}\cdot\text{s}^{-1}$
$\zeta$	perturbation factor, –
$\gamma$	specific weight, $\text{N}\cdot\text{m}^{-3}$

*Superscripts*

*	refers to gas–liquid equilibrium conditions
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*Subscripts*

i	parameter number
L	refers to the liquid phase
G	refers to the gas phase
0	refers to initial values
T	refers to reactor top

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Received 18 November 2018

Received in revised form 14 January 2019

Accepted 15 January 2019