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How Bromate and Ozone Concentrations can be Modelled at Full Scale based on Lab-Scale Experiments – A Case Study

Running head title

How to model bromate & ozone at full scale based on lab tests

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Abstract

This article presents a full-scale modelling study of an industrial ozonation unit for practical application. The modelling framework combines an integrated hydraulic model (systematic network) with a quasi-mechanistic chemical model. Dealing with natural water, the chemical model has to be parameterised, and the parameters calibrated. This was done based on lab-scale experiments. The calibration results showed that the chemical model is able to account for changes in contact time with ozone, pH, temperature, ozone dose, NOM concentration, bromide concentration. Comparison of Residence Time Distributions showed that the hydraulic model accurately reproduces flow conditions. Six sampling points were installed along an industrial ozonation unit of 487 m³ consisting of two baffled tanks in series. Bromate and ozone concentrations were monitored under varying operational process conditions. After the selection of a value for the k_{La} , simulations were run. Using the lab-scale calibrated models, simulated and experimental data were found in close agreement: 84% of the simulated concentrations for ozone matched measurements (\pm experimental error), 60 % for bromate. A readjustment of the kinetics of a single reaction (out of 65) showed that seasonal changes in NOM activity may easily be taken into account based on regular concentration measurements (90% of the bromate concentrations were then modelled accurately).

Keywords: Ozone; Bromate; Natural Organic Matter; Modelling; Hydraulics; Chemical Kinetics; Drinking Water; Hydroxyl Radicals; Ozonation Plant.

Introduction

Besides disinfection, management of ozonation processes in potable water treatment has to deal with new constraints: on one hand, regulations on disinfection by-products became very restrictive (10 $\mu\text{g}\cdot\text{L}^{-1}$ for bromate ions since 2008 in the EU); on the other hand, the occurrence and fate of micropollutants in aquatic environments represent matters of increasing concern (Huber et al., 2003; Mompelat et al., 2009). Modelling appears to be one possible solution to face the challenge of managing the ozonation process (Rietveld et al., 2009).

Modelling of ozonation units, however, has to adapt to site-specific conditions. Considering natural water, Natural Organic Matter (NOM) interactions with ozone may vary seasonally, when studying the same water source throughout the year; or locally, when studying water samples from different sources. In addition, flow conditions impact for a large part on disinfection efficiencies and bromate formation levels (Roustan et al., 1996a; Do-Quang et al., 1999). Being adaptive, models for industrial ozonation units therefore need to be calibrated. While calibration can rely on data collected on-site – for chemical kinetics (Audenaert et al., 2010) or hydraulics (Gujer & von Gunten, 2003) – it is of advantage to use instead lab-scale experiments or numerical studies (perfectly known process conditions, experimental ease). In the latter case, modellers nevertheless have to deal with upscaling. In

both cases, the model is finally validated at full-scale with data that were not used for calibration purposes.

Many modelling studies of industrial ozonation units can be found in the literature, but a model validated on a large experimental dataset predicting ozone and bromate concentrations at full-scale remains, to our knowledge, unpublished. Most studies have dealt with disinfection efficiency, especially since the popularisation of Computational Fluid Dynamics (CFD), (Murrer et al., 1995; Do-Quang et al., 1996; Cockx et al., 1999); fewer studies have dealt with bromate formation. Besides, modelling studies of full-scale ozonation processes often rely on empirical or semi-empirical chemical modelling. As a consequence, guidelines for the use of quasi-mechanistic predictive models integrating chemical pathways for ozone self-decomposition, influence of inorganic carbon, formation of bromate etc. are rarely published. Aiming at practical application, we asked whether a model calibrated at lab-scale (chemical kinetics) and with numerical data (hydraulics) can be validated with full-scale data (ozone and bromate concentrations).

Since hydraulic and chemical phenomena can be completely decoupled, modellers typically develop two models: one for hydraulics and another for chemical kinetics. Moreover, attempts to model ozonation with a unique model – e.g. with statistical models (Sohn et al., 2004) or artificial neural network models (Heck et al., 2001) – were not validated at full-scale. On one hand, different modelling frameworks have been developed for hydraulics. From the less to the most detailed, they are: Axial Dispersion Models (ADMs), systematic networks (patterns of ideal reactors), stochastic models (systematic networks where individual particles are followed through the tank) and CFD. On the other hand, different models for the chemistry of aqueous ozone have been developed in controlled laboratory conditions. Ranking these model from the least detailed to the most detailed, they are: correlations, simplified mechanisms (with less than 10 chemical reactions) and quasi-mechanistic. Different combinations of hydraulic and chemical models have been studied to model industrial ozonation units; we present in Figure 1 a selection of papers proposing full-scale modelling. Some studies that were done using CFD on disinfection efficiency were not included as they are only marginally related to the present study, see (Dong et al., 2007; Bolaños et al., 2008; Wols et al., 2010).

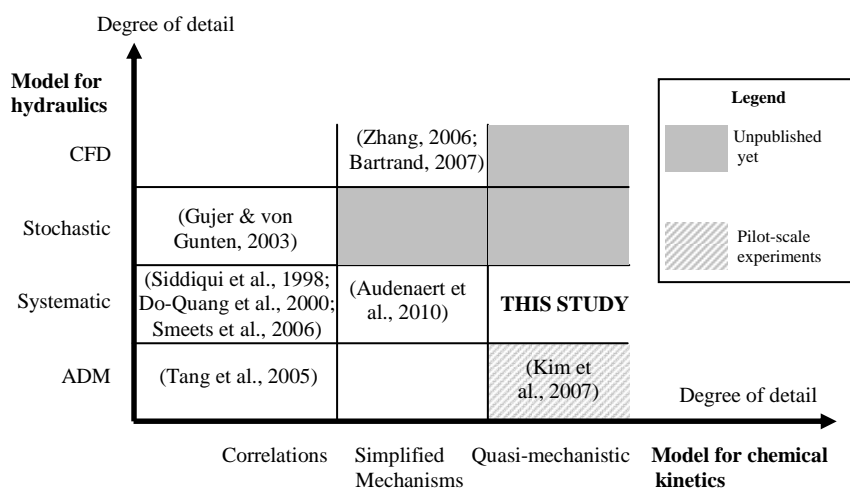


Figure 1 Modelling frameworks of previous full-scale studies

The modelling framework designed for this study combines a hydraulic systematic network with a quasi-mechanistic model for chemical kinetics. Aiming at providing operators with an operational modelling procedure, the following constraints were taken into account: (i) to use no or very few full-scale experimental data to calibrate the models; (ii) to explore the models robustness to seasonal variations and changes in operational conditions.

Material and Methods

Chemical Models

The models used in this study originate from the literature, whether it be for ozone self-decomposition (Mizuno et al., 2007), or inorganic carbon influence (Westerhoff et al., 1997). These models are mechanistic pathways with Arrhenius-law temperature dependence. The model for the influence of NOM on ozone and hydroxyl radicals was proposed in (Mandel et al., 2009); three fractions of NOM-reactive entities are distinguished: ozone consumers, hydroxyl radical initiators and hydroxyl radical promoters. Each fraction is then distributed over two species, with acidic or basic character. The model for the influence of NOM on ozone and hydroxyl radicals is parameterised, so that it requires the calibration of 12 parameters before being implemented. More details on the model can be found in (Mandel et al., 2009). For the formation of bromate, a mechanistic pathway has been derived from previously published results. It is graphically depicted in Figure 2 and detailed in Table 1 and 2. In total, 65 chemical reactions were considered.

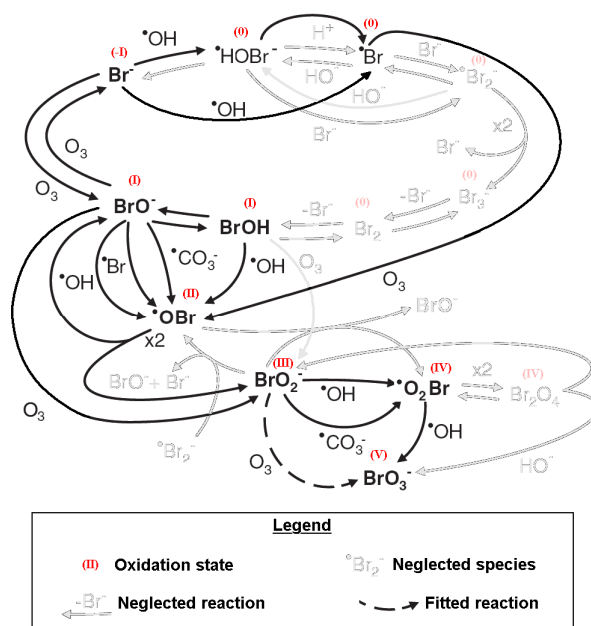


Figure 2 Bromate formation pathway used in this study

Numerous reactions may be involved in bromate formation and the most commonly encountered in published studies are represented in Figure 2. However, some reactions are not likely to occur due to their relative low kinetics or the weak probability for their reactants to be formed. As a result, they were neglected and are shown in grey in Figure 2. These assumptions were confirmed by numerical tests comparing the modelling results with and without the grey reactions of Figure 2 (Mandel, 2010).

NOM is known to alter bromate formation by lowering the amounts formed, see e.g. (Westerhoff et al., 1998). However, the presence of NOM can be the principle stumbling block in producing accurate bromate formation models (Jarvis et al., 2007; Westerhoff et al., 1998; Sohn et al., 2004). Consequently, there is no unified model for bromate formation in natural waters yet. In order to take into account the effect of NOM on bromate formation, the isothermal kinetics (*i.e.* the frequency factor) of the last molecular oxidation step leading to bromate was optimised (Figure 2). Most authors consider instead (i) possible reduction of hypobromous acid or hypobromite ions to bromide ions by NOM reactive species (Westerhoff et al., 1998), and/or (ii) substitution reactions leading to organo-bromine, e.g. (Siddiqui & Amy, 1993; Huang et al., 2004). Implementing these reactions may be chemically more accurate, initial concentrations of the reactive NOM species remain nevertheless to be determined. Seeking a model easy to calibrate, we selected one particular reaction, which drives the formation of bromate (results of a sensitivity analysis): the molecular oxidation

$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$, which is usually considered as unlimitedly fast. A drastic drop in the kinetics of this reaction may yield abnormally high concentrations of BrO_2^- in the system. Such accumulation however should not destabilise other kinetics since BrO_2^- only reacts to form bromate ions (directly or indirectly, *via* $\cdot O_2Br$). A similar approach was proposed by (Westerhoff et al., 1998), with molecular oxidation $Br^- + O_3 \rightarrow BrO^- + O_2$. The values for kinetic constants are presented in Table 1 and Table 2, for radical and molecular reactions respectively.

Table 1 Radical reactions within bromate formation pathway

Reaction	Kinetic constant value (293K)	Reference
$BrO^- + \cdot OH \rightarrow \cdot OBr + HO^-$	$4.5 \cdot 10^9 M^{-1} \cdot s^{-1}$	(Buxton & Dainton, 1968)
$BrOH + \cdot OH \rightarrow \cdot OBr + H_2O$	$2 \cdot 10^9 M^{-1} \cdot s^{-1}$	(Buxton & Dainton, 1968)
$BrO_2^- + \cdot OH \rightarrow \cdot O_2Br + HO^-$	$2 \cdot 10^9 M^{-1} \cdot s^{-1}$	(Buxton & Dainton, 1968)
$2 \cdot OBr + H_2O \rightarrow BrO_2^- + BrO^- + 2H^+$	$5 \cdot 10^9 M^{-1} \cdot s^{-1}$	(Buxton & Dainton, 1968)
$\cdot O_2Br + \cdot OH \rightarrow BrO_3^- + H^+$	$2 \cdot 10^9 M^{-1} \cdot s^{-1}$	(Buxton et al., 1988)
$Br^- + \cdot OH \rightarrow \cdot Br + HO^-$	$1.1 \cdot 10^9 M^{-1} \cdot s^{-1}$	(von Gunten & Hoigné, 1996)
$Br^- + \cdot OH \rightarrow \cdot HOBr^-$	$10^{10} M^{-1} \cdot s^{-1}$	(Zehavi & Rabani, 1972)
$\cdot HOBr^- \rightarrow \cdot Br + HO^-$	$4.2 \cdot 10^6 s^{-1}$	(Zehavi & Rabani, 1972)
$\cdot Br + O_3 \rightarrow \cdot OBr + O_2$	$1.5 \cdot 10^8 M^{-1} \cdot s^{-1}$	(von Gunten & Hoigné, 1994)
$\cdot Br + BrO^- \rightarrow \cdot OBr + Br^-$	$4.1 \cdot 10^9 M^{-1} \cdot s^{-1}$	(Kläning & Wolff, 1985)
$\cdot CO_3^- + BrO^- \rightarrow CO_3^{2-} + \cdot OBr$	$4.3 \cdot 10^7 M^{-1} \cdot s^{-1}$	(Kläning & Wolff, 1985)
$\cdot CO_3^- + BrO_2^- \rightarrow CO_3^{2-} + \cdot O_2Br$	$1.1 \cdot 10^8 M^{-1} \cdot s^{-1}$	(Buxton & Dainton, 1968)

Table 2 Molecular reactions within bromate formation pathway

Reaction	Kinetic constant value (293K)	Reference
$Br^- + O_3 \rightarrow BrO^- + O_2$	$1.6 \cdot 10^2 M^{-1} \cdot s^{-1}$	(Haag & Hoigné, 1983)
$BrO^- + O_3 \rightarrow Br^- + 2O_2$	$3.3 \cdot 10^2 M^{-1} \cdot s^{-1}$	(Haag & Hoigné, 1983)
$BrO^- + O_3 \rightarrow BrO_2^- + O_2$	$10^2 M^{-1} \cdot s^{-1}$	(Haag & Hoigné, 1983)
$BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$	$> 10^5 M^{-1} \cdot s^{-1}$ $4.6 \cdot 10^4 M^{-1} \cdot s^{-1}$	(von Gunten & Hoigné, 1994) This study, fitted value
$BrO^- + H^+ \rightarrow BrOH$	$5 \cdot 10^{10} M^{-1} \cdot s^{-1}$	(Westerhoff, 1995)
$BrOH \rightarrow BrO^- + H^+$	$7.9 \cdot 10^1 s^{-1}$	Calculated with $pK_a = 8.8$ and protonation reaction kinetics

Laboratory Experiments

Two separate chemical models were calibrated based on experimental results: (i) a model for the influence of NOM on ozone and hydroxyl radicals and (ii) a model for the influence of NOM on bromate formation. The experiments were done separately, on two different water samples – both originating from the water works studied at full-scale (Annet-sur-Marne). The 500 mL required for bromate concentration measurement was not compatible with the experimental set-up used for characterising the influence of NOM on ozone and hydroxyl radicals (reactor volume=100 mL).

Calibration of the model for the influence of NOM on ozone and hydroxyl radicals was based on the results of fourteen experiments. The experiments are presented in Table 3. Five experimental conditions were explored: changes in temperature, pH, ozone dose, nature of NOM – with and without radical-scavenger – and concentration of NOM. Ozone and *para*-chlorobenzoic acid (*p*CBA) concentrations were measured for seven contact times with

ozone (30''; 1'; 2'30''; 5'; 15'; 35' and 60'). *p*CBA was chosen as hydroxyl radical "tracer", due to its kinetics. No *p*CBA was added when the radical-scavenging species *tert*-butanol had already been added, because *p*CBA concentration had been found constant in that case (results of previous experiments not shown here). A specially conceived single-phase set-up was used. The set-up is detailed – including chemical analyses – with a calibration procedure for the model for the influence of NOM on ozone and hydroxyl radicals in (Mandel et al., 2009). The water sample studied was withdrawn at the inlet of the ozonation unit of Annet-sur-Marne water works (sand-filtered water). The experiments were done in February 2009. The characteristics of the water sample were as follows: pH=7.4; alkalinity (A_T)=2.82 meq.L⁻¹; TOC=1.3 mgC.L⁻¹; SUVA(254 nm)=1.43 L.m⁻¹.mgC⁻¹.

Table 3 Experiments done for calibrating the model for the influence of NOM on ozone and hydroxyl radicals

Experiment #	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Scavenger adding (10mM <i>tert</i> -butanol)		X		X				X		X		X		X
pH drop (7.4→6.4)			X	X					X	X	X	X	X	X
Large O ₃ dose (1.4 mg.L ⁻¹ →2.3 mg.L ⁻¹)					X	X							X	X
Temperature drop (20°C →5°C)						X	X	X	X	X				
NOM dilution (with ultra-pure water)											X	X	X	X

Calibration of the model for the formation of bromate ions was based on the experimental results of fifteen experiments: bromate formation was followed under changing initial bromide concentrations: five levels, from 48 µg.L⁻¹ (natural concentration) to 128 µg.L⁻¹; and ozone doses: three levels, 0.9 mg.L⁻¹; 1.6 mg.L⁻¹; 2.3 mg.L⁻¹. A full factorial approach was chosen for the design of experiments. Contrary to the experiments presented in Table 3, the contact time with ozone was kept constant at 10 min. Classical single-phase batch experiments were done in 500 mL glass bottles. The solution of aqueous ozone injected in the bottles was prepared as in (Mandel et al., 2009). Samples were analysed using ion chromatography and conductimetric detection; quantification limit was 2 µgBrO₃⁻.L⁻¹. The water sample studied was withdrawn at the inlet of the ozonation unit (sand-filtered water). The experiments were done in the first days of July 2009. The characteristics of the water sample were: pH=8.05; A_T =4.24 meq.L⁻¹; TOC=1.6 mgC.L⁻¹; SUVA(254 nm)=1.03 L.m⁻¹.mgC⁻¹; [Br⁻]=48 µg.L⁻¹.

Full-scale Experiments at the Ozonation Unit of Annet-sur-Marne Water Works

Annet-sur-Marne ozonation unit consists of two tanks linked by a pipe of diameter 800 mm as depicted in Figure 3. The transfer chambers are shown in yellow and the contact chambers in blue. The two linked tanks have approximately the same volume: 235 m³ and 252 m³, respectively for the first and the second tank. Six sampling points were installed along the tank baffles to follow the profiles for ozone and bromate concentrations. The location of each point was chosen in order that the sampling took place in the main flow, where water velocity was high. Sampling points are also represented on Figure 3; for each sampling point, the time indication corresponds to the hydraulic retention time under nominal flow conditions (1600 m³.h⁻¹).

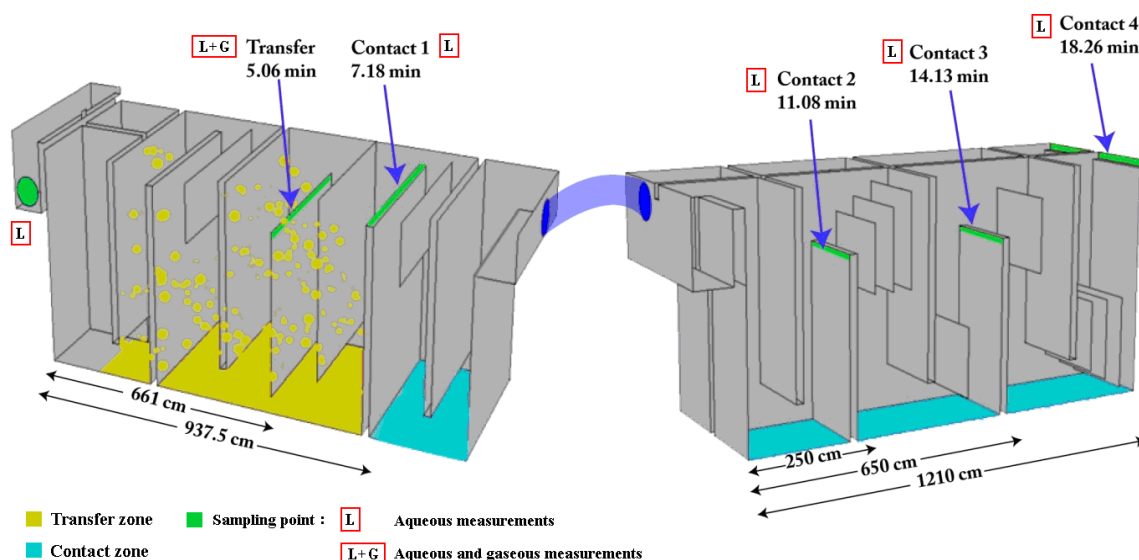


Figure 3 View of the ozonation unit investigated in this study (Mandel, 2010)

Aqueous ozone concentration was measured with on-line analysers directly connected to the sampling points. Two types of analysers were used: Solu Comp II (Rosemount Analytical, Chanhassen, USA) and Q 45H/64 (ATI, Colleagueville, USA). Gaseous ozone concentration in the exhaust gas at *Transfer* sampling point was measured with a 964 BT analyser (BMT, Berlin, Germany) connected to a blind flange located on the roof of the unit. Bromate concentration was analysed with ion chromatography and conductimetric detection; quantification limit was $1 \mu\text{gBrO}_3^- \cdot \text{L}^{-1}$.

For each experiment, the water quality was characterised by the following parameters: pH, A_T , TOC, SUVA(254 nm), temperature and bromide concentration. Bromide concentrations were measured using ion chromatography and conductimetric detection. pH, A_T , UVA(254 nm) and temperature were directly measured at the ozonation unit during the experiments; TOC was analysed by combustion catalytic oxidation and non-dispersive infrared method. Finally, the following operational process conditions were recorded by the Supervisory Control And Data Acquisition (SCADA) system of the plant: water flow rate (Q_w), ozonated air flow rate (Q_g), aqueous ozone concentrations and ozone concentration in the ozonated air ($[\text{O}_3]_g$).

Operational process conditions have been divided into two types: the main conditions, water flow rate and setpoint for concentration of residual ozone (called "setpoint" herein), could be manually changed *via* the SCADA system; secondary conditions, ozonated air flow rate and ozone concentration in the ozonated air, were set by the Programmable Logic Controller. An experimental planning was designed, based on the main operational process conditions: 2 levels were defined for the water flow rate and 3 levels for the setpoint. Accordingly, 17 experiments were scheduled from July to October 2009. Moreover, the experiments were done during two experimental periods (the first period lasting from July 21st to August 14th 2009; the second period lasting from September 2nd to October 10th 2009). Whereas water characteristics did not vary significantly during the study, many operational process conditions were tested. These conditions and the water characteristics are summarised in Table 4.

Table 4 Summary of the experimental conditions of the case study

Water characteristics						
	pH	A_T ($\text{meq} \cdot \text{L}^{-1}$)	TOC ($\text{mg} \cdot \text{L}^{-1}$)	SUVA ($\text{L} \cdot \text{m}^{-1} \cdot \text{mgC}^{-1}$)	T ($^{\circ}\text{C}$)	$[\text{Br}^-]$ ($\mu\text{g} \cdot \text{L}^{-1}$)
Minimum	7.2	3.58	1.5	1.17	16.6	30
Median	7.5	3.67	1.7	1.35	20.6	32
Maximum	7.5	3.78	1.8	1.53	22.8	41

Operational process conditions

	<i>Directly controlled</i>		<i>Set by Programmable Logic Controller</i>		
	Q_1 ($m^3 \cdot h^{-1}$)	Setpoint ($mg \cdot L^{-1}$)	$[O_3]_g$ ($g \cdot Nm^{-3}$)	Q_g ($Nm^3 \cdot h^{-1}$)	O_3 dose ($mg \cdot L^{-1}$)
Minimum	990	0.2	10.2	61.3	0.73
Median	1661	0.3	19.8	73.1	0.83
Maximum	1851	0.4	19.9	149.0	1.12

Results and Discussion

Calibration of the Chemical Models Using Lab-Scale Experiments

The model for the influence of NOM on ozone and hydroxyl radicals was calibrated based on the agreement of experimental (observed) and simulated (predicted) concentrations for ozone and *p*CBA. The comparison of experimental and simulated concentrations is given in Figure 4 and Figure 5, for ozone and *p*CBA respectively. The coefficient of determination R^2 and the number of points comprised within experimental uncertainty, *i.e.* for which prediction does not significantly differ from observation, are displayed on each figure. The quality of the results obtained with Annet-sur-Marne water is comparable with that obtained with other water samples (Méry-sur-Oise and Vitre, see (Mandel et al., 2009)). The good agreement observed for all those water samples confirms the soundness of the chemical model.

The experimental uncertainty was determined by calculating the standard deviation of concentration measurements for replicate experiments; it takes therefore into account the experimental uncertainty of the whole experimental setup, not only the analytical uncertainty. A constant error, whatever the concentration value, has been hypothesised since the analytical methods employed (colorimetry for ozone, mass detection for *p*CBA, ion chromatography for bromates) rely on the homogeneity of the variance of the measurements over the concentration range for their own calibration (hypothesis of homoscedasticity). Finally, at lab-scale, the experimental uncertainties were found to be: $\pm 0.1 \text{ mgO}_3 \cdot \text{L}^{-1}$; $\pm 4 \text{ } \mu\text{g}p\text{CBA} \cdot \text{L}^{-1}$ and $\pm 3 \text{ } \mu\text{gBrO}_3^- \cdot \text{L}^{-1}$.

The values of the 12 parameters of the model describing the influence of NOM on ozone and hydroxyl radicals are given in Table 5. These values should not be considered *per se* since numerical tests showed that, even leading to excellent simulation results, they may be far from the optimum (Mandel, 2010). As a result, physicochemical interpretation based on these values should be avoided. Similar reservations about parameter values are generally expressed by process modellers, see *e.g.* (Jeppsson, 1996).

Table 5 Values of the parameters of the model for the influence of NOM on ozone and hydroxyl radicals (NOM model presented in Mandel et al., 2009)

Fraction	Type of parameter	Value
Initiation	pK_A for:	6.4
Consumption	$NOM_a \leftrightarrow NOM_b + H^+$	5.5
Promotion		4.3
Initiation		$2.2 \cdot 10^1$
Consumption	Kinetic constant rate at $T=293K$ ($M^{-1} \cdot s^{-1}$)	$4.9 \cdot 10^5$
Promotion		$5.9 \cdot 10^8$
Initiation		83.5
Consumption	Energy of activation for initiation, consumption or promotion ($kJ \cdot mol^{-1}$)	8.5
Promotion		57.3
Initiation	Initial concentration for the considered fraction ($mg \text{ C} \cdot L^{-1}$) at $pH=7$	0.4
Consumption		0.1
Promotion		0.8

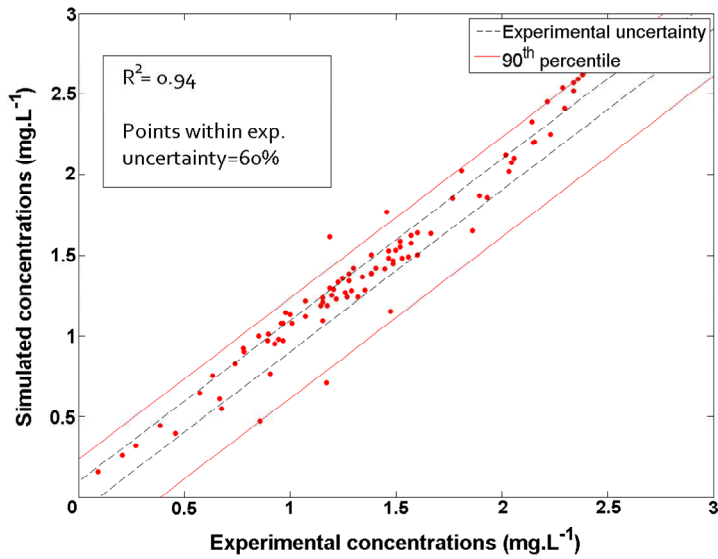


Figure 4 Comparison of experimental and simulated ozone concentrations, lab-scale

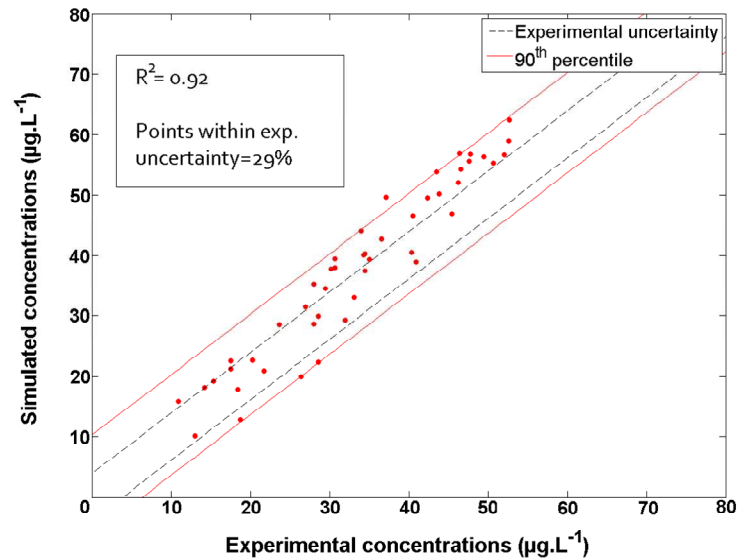


Figure 5 Comparison of experimental and simulated pCBA concentrations, lab-scale

The model for the influence of NOM on bromate formation was calibrated based on the agreement of experimental and simulated bromate concentrations. The results are presented in Figure 6. The bromate concentrations increased with initial bromide concentrations and ozone doses. Note however that the model tends to underestimate the impact of an increase in ozone dose and to overestimate the impact of an increase in initial bromide concentration (compare the slope of the points with the same ozone dose to that of the points with the same initial bromide concentration). The model for bromate formation is found to be robust, given that, for a wide range of experimental conditions, predictions are close to observations.

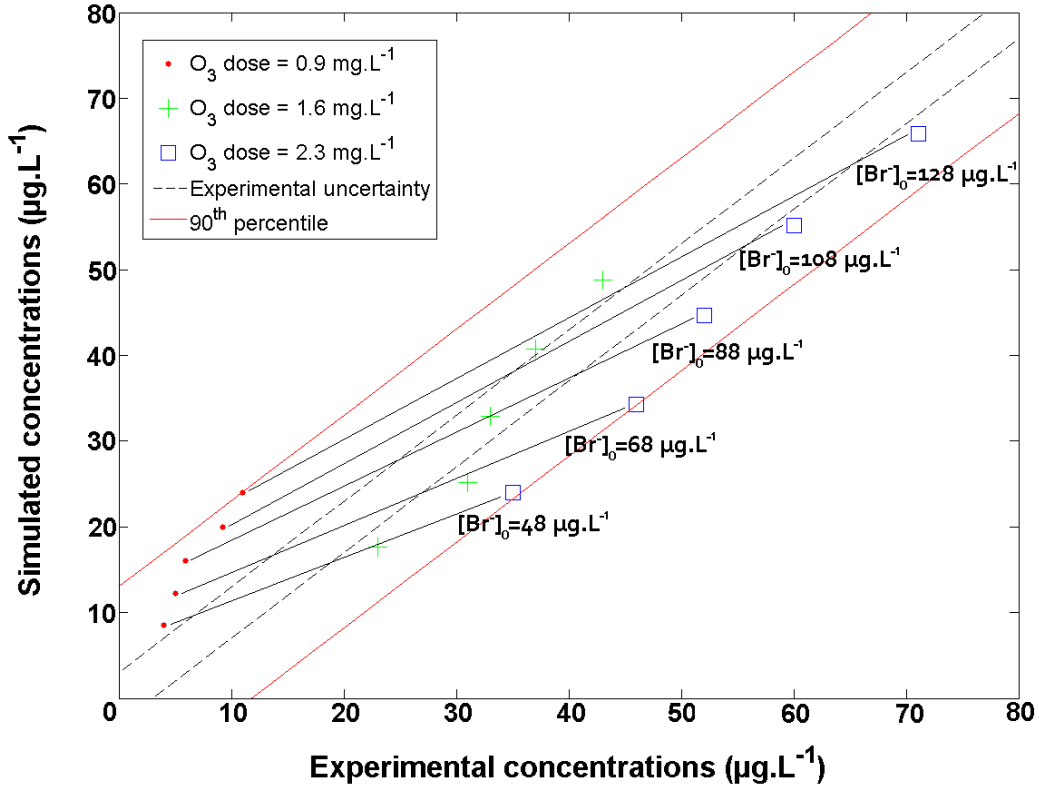


Figure 6 Comparison of experimental and simulated bromate concentrations, lab-scale

The final value for the kinetic constant of reaction $BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$ was set at $4.6 \cdot 10^4 \text{ M}^{-1} \cdot \text{s}^{-1}$ at 293K, assuming energy of activation of $42 \text{ kJ} \cdot \text{mol}^{-1}$. This value is slightly smaller than what is observed in NOM-free water ($\geq 10^5 \text{ M}^{-1} \cdot \text{s}^{-1}$). Such negative influence of NOM on bromate formation is in good agreement with already reported observations, see e.g. (Siddiqui & Amy, 1993).

Calibration of the Hydraulic Model Using CFD

Using the results of a previous CFD study of the ozonation unit, a systematic network was proposed to describe the hydraulics of the unit. A systematic network is a pattern of ideal reactors: for this study, single-phase Plug Flow Reactors (PFRs) and Continuously Stirred Tank Reactors (CSTRs) were used; two-phase CSTRs were also considered (two-phase PFRs were modelled by co- or counter-current cascades of two-phase CSTRs). Residence Time Distributions (RTDs) and turbulence analysis by means of CFD were used to calibrate the network, according to the procedure proposed by (de Traversay et al., 2001). The two RTDs, for the CFD study and the systematic network, are drawn on Figure 7. The systematic network was designed in two steps by fitting successively the RTD of the first and the second tanks. The resulting systematic network is schematised in Figure 8; it comprises 46 reactors or blocks of reactors.

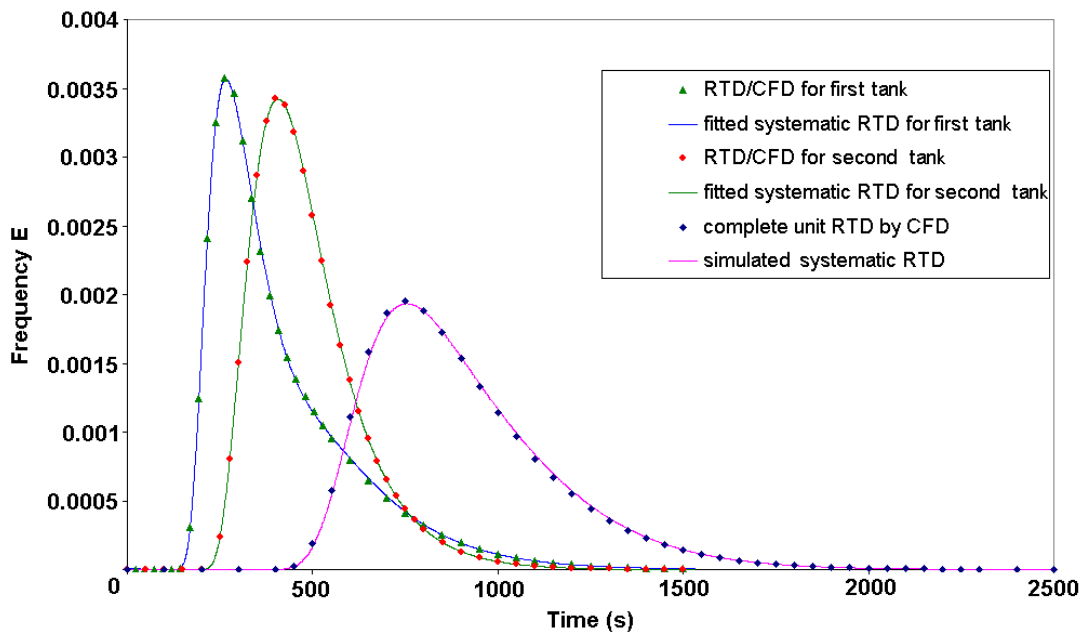


Figure 7 RTDs obtained with CFD and with the systematic network developed

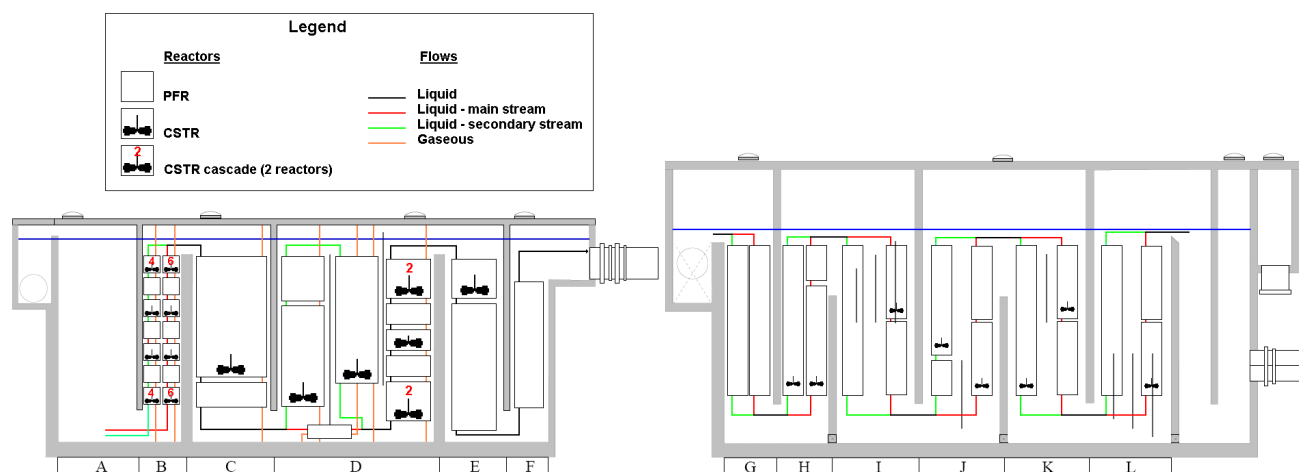


Figure 8 Systematic network proposed for the hydraulics of Annet-sur-Marne ozonation unit

Validation at Full-Scale (with Lab-Scale Calibration)

A classical two-film approach was implemented to model mass transfer, see e.g. (Langlais et al., 1991). Values for the mass transfer coefficient $k_L a$ generally range from $5 \cdot 10^{-4} \text{ s}^{-1}$ to 0.02 s^{-1} for similar reactors or tanks (Laplanche et al., 1991; Roustan et al., 1996b; Siddiqui et al., 1998). Given that ozone dissolution is mostly kinetics-driven, a large value for the $k_L a$ was selected: 0.04 s^{-1} . Preliminary simulation runs showed that a lower value for the $k_L a$ would have resulted in worse predictions for ozone concentrations.

Full-scale validation results of the two models are gathered in Figure 9 and Figure 10, for ozone and bromate respectively. As for lab-scale experiments, the experimental uncertainty was determined with replicate experiments on the unit; experimental uncertainties were $\pm 0.09 \text{ mgO}_3 \cdot \text{L}^{-1}$ and $\pm 1.9 \text{ } \mu\text{gBrO}_3^- \cdot \text{L}^{-1}$. The 17 experiments (complete dataset) are presented in Figure 9; only the 8 experiments from the first period are presented in Figure 10. Bromate concentrations had namely become considerably lower in the second period; this was assessed by comparing replicate experiments from one period to another: ozone profiles were found identical at $\pm 0.04 \text{ mg} \cdot \text{L}^{-1}$, whereas bromate had decreased by more than $4 \text{ } \mu\text{g} \cdot \text{L}^{-1}$.

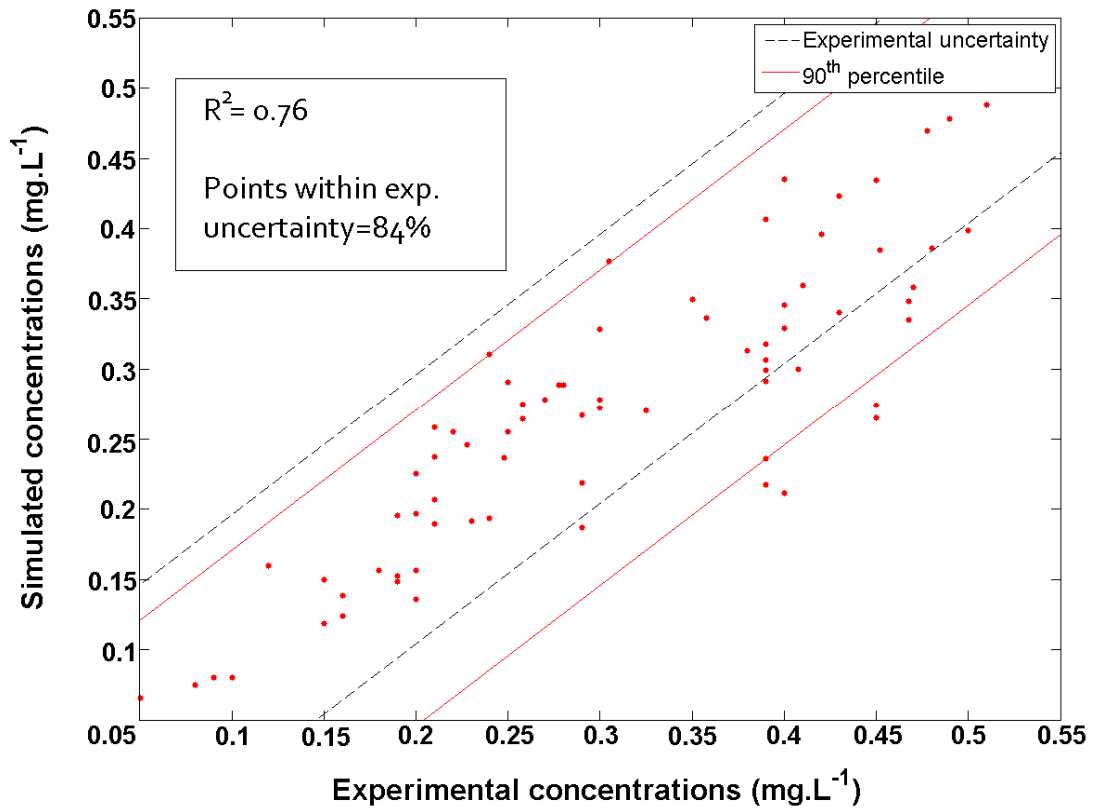


Figure 9 Comparison of experimental and simulated ozone concentrations, validation at full-scale

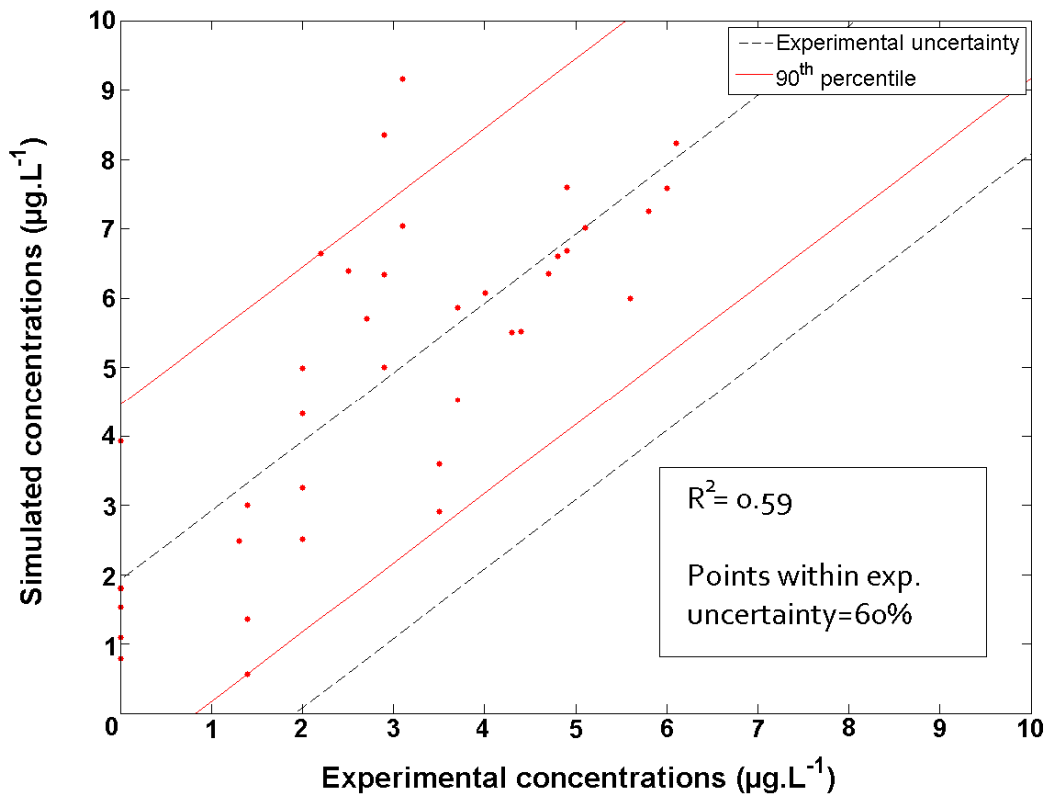


Figure 10 Comparison of experimental and simulated bromate concentrations, first period experiments, validation at full-scale

Obviously, the results of the full-scale validation presented in Figure 9 and Figure 10 are not as good as for lab-scale calibration (Figure 4 to Figure 6). However the major part of the

simulated concentrations is in close agreement with experimental measurements: 84 % of the concentrations for ozone, 60% for bromate. Besides, the simulation results show that the model may slightly under-predict ozone concentrations and over-predict bromate formation. Considering the experiments individually, and comparing experimental and simulated data, one can notice two phenomena:

- a constant prediction quality for ozone concentration. Experimentally, ozone decomposition rates were found to be stable, so that the modelling results adequately matched the experimental measurements over both experimental periods;
- a systematic over-prediction of bromate concentrations. Already observed at the beginning of the study, the phenomenon was enhanced in the meantime separating the first from the second period.

Ozone decomposition and hydroxyl radical generation appear to be stable throughout the year as suggested by the fact that a model calibrated with experimental results obtained in February 2009 remains valid with data collected in July 2009. Moreover, other seasonal comparisons with water samples from Annet-sur-Marne and other water works showed the relative stability of the ozone demand (Mandel, 2010).

Inversely, bromate formation appears more sensitive to seasonal changes. Already reported in (Westerhoff et al., 1998; Kim et al., 2007), NOM strongly influences bromate formation. Consequently, the overprediction in bromate concentrations may be explained by changes in the nature of NOM that would have occurred during the time interval between lab-scale calibration for the bromate formation model (first days of July) and full-scale experiments, which began on July 21st. Indeed, it appears from the recordings of concentration measurements stored in the SCADA system of the water works that bromate formation has a seasonal character: bromate formation levels generally increase by the beginning of May; they reach their maximum at the end of June and decrease till November. This variation can be repeatedly observed and is not solely due to changes in temperature, since July and August are generally the two warmest months in Annet-sur-Marne. Moreover, physicochemical properties or operational process conditions are generally constant (pH, A_T , $[Br^-]$, TOC, flow rates, ozone dose...). Calibrated in August, it is therefore likely that the model would have given more accurate results (see also the change in the SUVA values: 1.03 L.m⁻¹ for calibration; from 1.17 L.m⁻¹ to 1.53 L.m⁻¹ during the case study).

Considering that (i) seasonal variations altered much more predictions for bromate ions than for ozone; (ii) the predictions for ozone concentration were matching observations for the two experimental periods; (iii) no molecule could be used to assess hydroxyl radical concentration; it was decided not to modify the values of the parameters presented in Table 5 (model for the influence of NOM on ozone and hydroxyl radicals).

Validation at Full-Scale (with a Readjusted Model for Bromate Formation)

In order to test the possibility of a calibration bias for the bromate formation model, a smaller value for the kinetic constant rate of the molecular oxidation $BrO_2^- + O_3 \rightarrow BrO_3^- + O_2$ was determined (see Table 6). The value was optimised based on the bromate concentrations of the first full-scale experiment (chosen so as to reproduce the use of a simulation software tool by the operators at the water works), then injected in the model and finally used to model and to be validated by the 7 remaining experiments of the first period. A similar approach was applied for the second experimental period. In this case however, the model for bromate formation was calibrated based on a single measurement: the outlet bromate concentration of the first experiment of the second period. Validation examples are given in Figure 11 to Figure 14. In these figures, temporal concentration profiles are given for ozone and bromate, for the different sampling points of the tank and for different operational process conditions. The global results for ozone and bromate concentrations are gathered in Figure 15 and Figure 16, respectively.

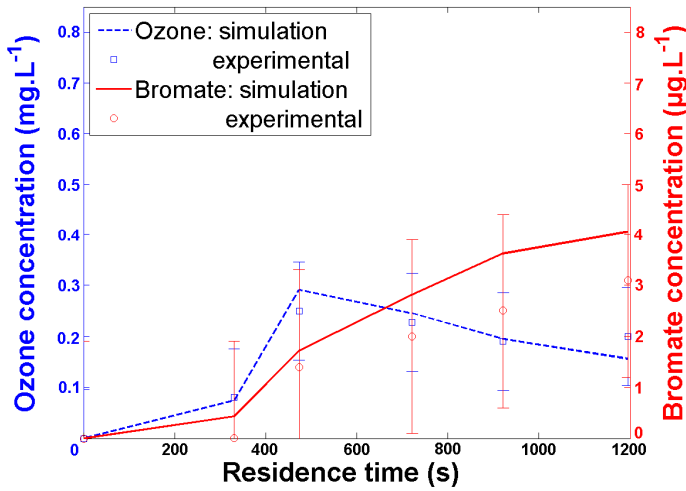


Figure 11 First period experiment ($[O_3]_g=13.5 \text{ g.Nm}^{-3}$; $Q_g=84.4 \text{ Nm}^3.\text{h}^{-1}$; $Q_f=1481 \text{ m}^3.\text{h}^{-1}$; setpoint= 0.2 mg.L^{-1})

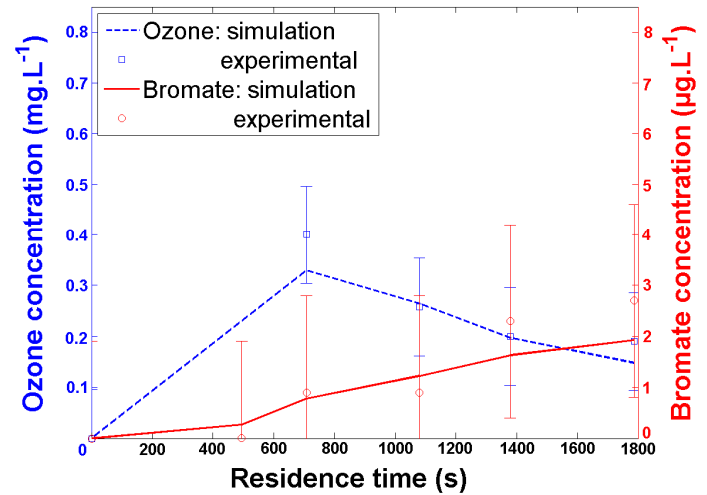


Figure 12 Second period experiment ($[O_3]_g=10.2 \text{ g.Nm}^{-3}$; $Q_g=80.2 \text{ Nm}^3.\text{h}^{-1}$; $Q_f=990 \text{ m}^3.\text{h}^{-1}$; setpoint= 0.2 mg.L^{-1})

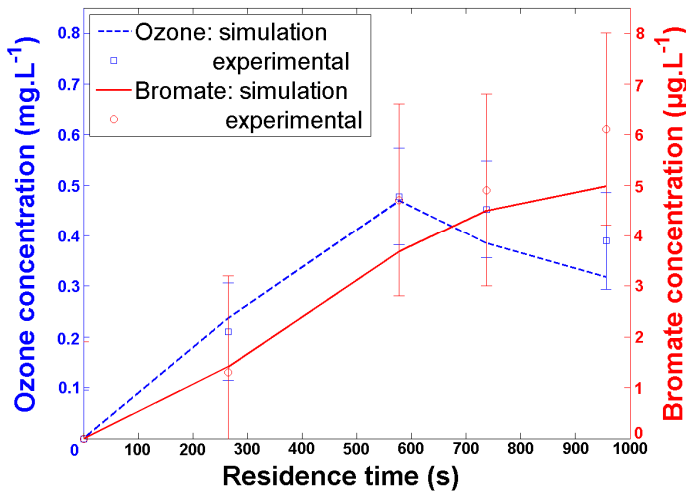


Figure 13 First period experiment ($[O_3]_g=13.9 \text{ g.Nm}^{-3}$; $Q_g=149 \text{ Nm}^3.\text{h}^{-1}$; $Q_f=1851 \text{ m}^3.\text{h}^{-1}$; setpoint= 0.4 mg.L^{-1})

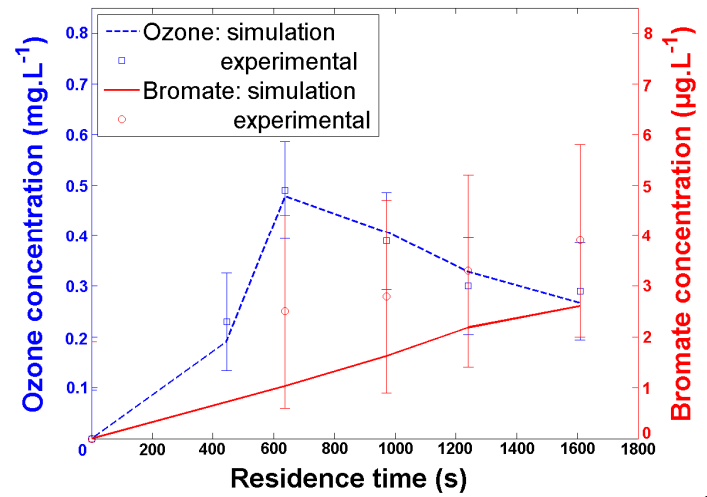


Figure 14 Second period experiment ($[O_3]_g=13.1 \text{ g.Nm}^{-3}$; $Q_g=81.6 \text{ Nm}^3.\text{h}^{-1}$; $Q_f=1100 \text{ m}^3.\text{h}^{-1}$; setpoint= 0.3 mg.L^{-1})

Table 6 Kinetic parameters for bromate formation, first and second experimental periods

	BrO ₃ ⁻ concentrations used for adjustment (%)	k(293 K) (M ⁻¹ .s ⁻¹)	E _A (kJ.mol ⁻¹)	BrO ₃ ⁻ concentrations within uncertainty (%)
Period 1	12.5	2.1.10 ⁴	42	92
Period 2	3	5.9.10 ³	42	97

As it appears from the comparison of the concentration profiles obtained with lab-scale calibration or with on-site readjustment, the formation of bromate and the decomposition of ozone may be simultaneously predicted. This observation confirms that the model for bromate formation may be applied to simulate industrial ozonation units. However, it should periodically be readjusted (this was done here by considering only isolated concentration measurements) on the basis of a regular sampling (monthly for example). The frequency of the sampling / readjustment has to be determined. Regarding ozone decomposition, the model appears to be more stable, but this has to be confirmed over a longer period of testing.

The modelling procedure (systematic network associated to quasi-mechanistic chemical models) developed in this study presents several advantages over other approaches used for modelling full-scale ozonation units:

- Contrary to studies coupling simple chemical kinetics with accurate hydraulic description by CFD (Zhang, 2006; Bartrand, 2007; Wols et al., 2010), calculations are quite fast (~1 s) and parameter values can easily be changed, for example water flow rates. The long computational time required for simulation explains for a large part that very few studies consider the effects of water quality or operational conditions on CFD models (Zhang, 2006).

- Hydraulic flow conditions can also be modelled by stochastic models and coupled with chemical models, for example with pseudo first-order ozone decomposition and with disinfection kinetics with lag-phase, as in (Gujer & von Gunten, 2003). Such models are well suited to reproduce tank behaviours, both globally – RTDs – and locally – by tracking particles. However, the high computational cost here also prohibits the refinement of chemical models (Gujer & von Gunten, 2003). Additionally, this approach has not yet been supported by full-scale experimental validation.

- Some authors couple one-dimensional ADMs with chemical correlations (Tang et al., 2005) or with quasi-mechanistic models (Kim et al., 2007). ADMs describe non-ideal tubular reactors and can be applied to model bubble columns. Extrapolating to other geometries is difficult (Cockx et al., 1999), but results were promising in terms of predictions for inactivation of *Cryptosporidium parvum* oocysts and gave interesting insights in bromate formation pathway for NOM-containing water. These results need however to be extended, either by considering larger ozonation units (Kim et al., 2007), or longer experimental periods (Tang et al., 2005).

- Systematic networks were generally coupled with simplified chemical approaches: chemical correlations (Siddiqui et al., 1998; Do-Quang et al., 2000; Smeets et al., 2006) or simple mechanisms (Audenaert et al., 2010). Bromate formation was modelled by multiple linear correlation (Siddiqui et al., 1998) or by a single chemical reaction (Audenaert et al., 2010). The results presented at full-scale were promising in terms of predictions for disinfection and ozone concentrations, but remain limited for bromate concentrations.

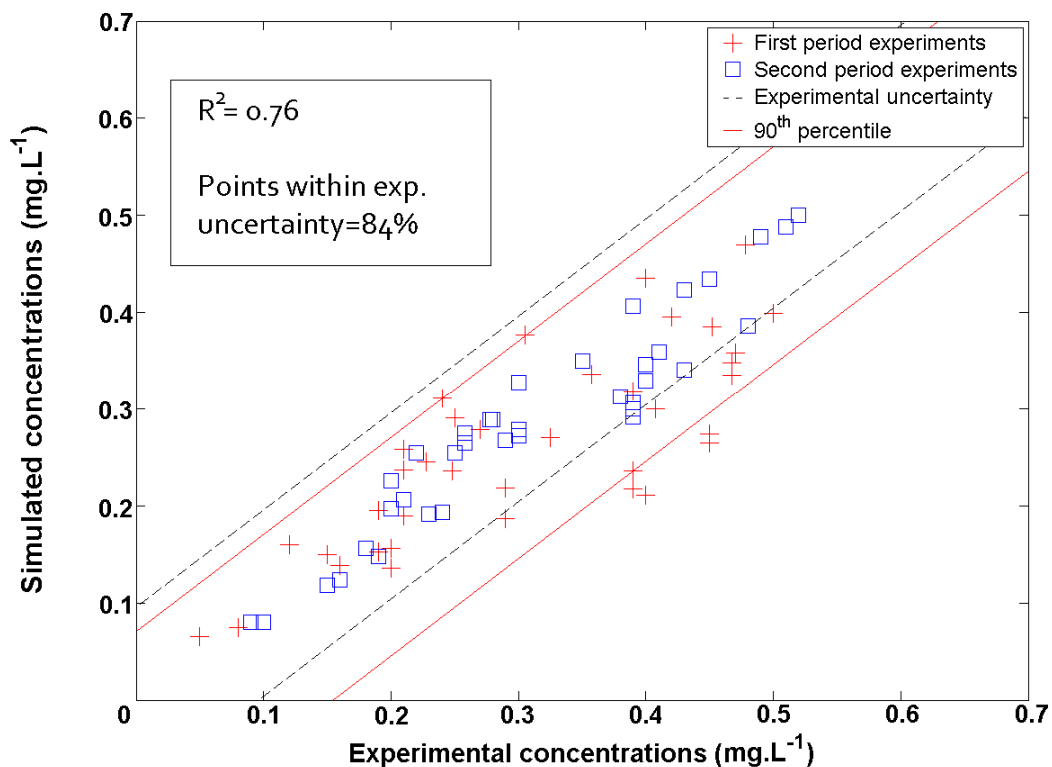


Figure 15 Experimental and simulated ozone concentrations, validation at full-scale

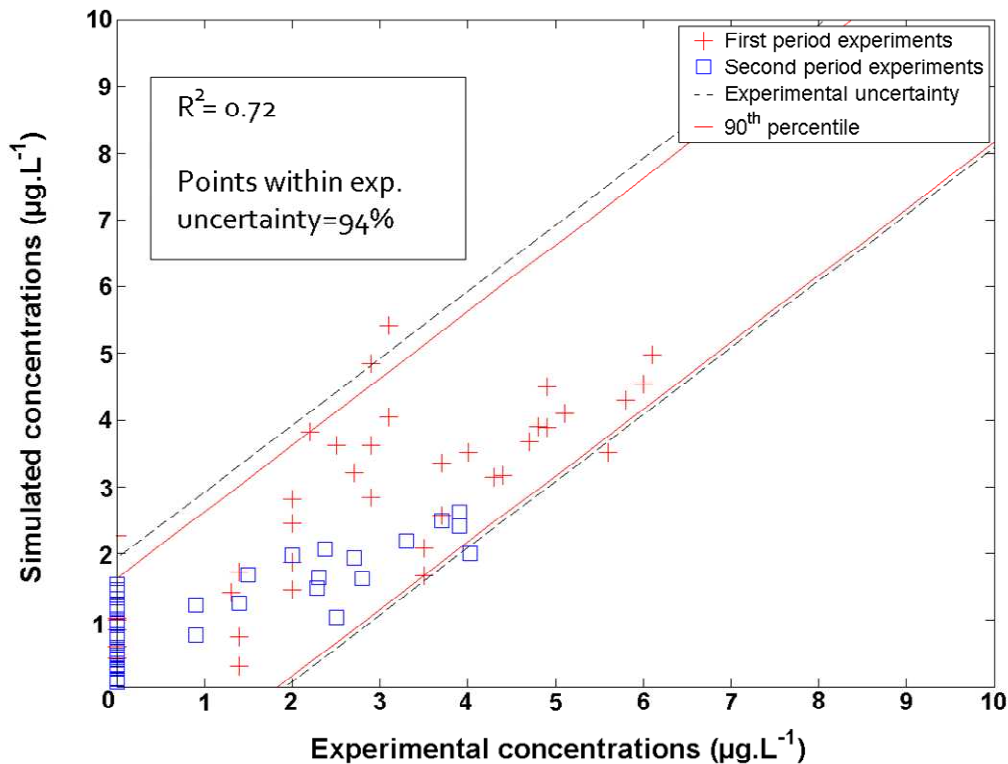


Figure 16 Experimental and simulated bromate concentrations, full-scale

One possible limitation of this study is the poor quality of the modelling of gaseous ozone concentrations. Experimental gaseous ozone concentration measurements were used to assess the transfer efficiency of the unit. Experimental efficiencies were high: for the four first experiments, a value of 83 % was calculated. The simulations overestimated this parameter: the calculations gave an efficiency of 97 %. This discrepancy may partly arise from the geometry of the unit, since gaseous ozone is sampled in a headspace common to several chambers (chambers D and E in Figure 8) whereas modelling is specific to individual chambers (Siddiqui et al., 1998). This discrepancy may also arise from an overconsumption of ozone in the model. Three main explanations can be given to this overconsumption:

- The ozone doses used for calibrating the model for the influence of NOM on ozone and hydroxyl radicals are much larger than those encountered on-site;
- The CFD study used to calibrate the systematic network was calculated for a single-phase problem (no gaseous ozone). Gaseous flow rate may impact on water hydraulics and mass transfer.
- Differences in the behaviour of NOM towards ozone may have caused the model not to be exactly calibrated for the experimental conditions of the case study.

If the predictions for ozone concentrations are generally well predicted (84% of predictions matching observations) over a practical working domain (0-0.5 mg.L⁻¹), the experimental values observed for bromate ions could not be used to fully check the validity of the model. A reduced domain (0-6 µg.L⁻¹) could be considered. Still, the amount of data remains appreciable with respect to other full-scale modelling studies.

Conclusion

The modelling framework of this study relies on the combination of a quasi-mechanistic chemical reaction pathway with a hydraulic systematic network. The reaction pathway consists of reaction sets from previous studies for: ozone self-decomposition, influence of inorganic carbon and influence of NOM on ozone and hydroxyl radicals. In addition, a

simplified reaction pathway comprising 18 reactions was proposed to model bromate formation. In total, 65 chemical reactions were considered.

Based on lab-scale experiments, kinetic parameters were adjusted in order to account for the influence of NOM on ozone and hydroxyl radical (12 parameters) and on bromate concentrations (1 parameter). The modelling results adequately reproduced the phenomena observed at lab-scale (concentration profiles) or generated numerically (RTDs).

Chemical models were applied to simulate full-scale experiments. The majority of the modelled concentrations matched measurements (\pm experimental error): 84% and 60% of the concentrations for ozone and bromates, respectively. Moreover, the model can adapt to different operational process conditions: changes in liquid flow rate, gaseous ozone concentration and gaseous ozone flow rate. The validity of the model was confirmed in the case of bromate ions by a local adjustment, which led to a considerable improvement of the simulation results: more than 90% of the modelled bromate concentrations were found in agreement with measurements.

The modelling approach presented in this paper was conceived as a procedure for practical application. Calibration is based on the results of classical lab experiments (chemical models) and of CFD studies (hydraulic model), which are now commonly performed. If a continuous use of the models throughout the year is sought, it is likely that the chemical model may have to be regularly readjusted. This should represent, however, only a limited task (one sampling every two months in this study). Prospects for this work involve the extension of the full-scale study over a longer time period in order to assess the robustness of the model. Moreover, the modelling framework developed in this study may be applied to simulate disinfection efficiencies and micropollutant removal. The possibilities of model parameter readjustments shall also be considered in future work (e.g. sensitivity analysis of the model parameters).

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