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Abstract
This article presents a calibration procedure for a model describing the role of NOM during ozonation. Calibration has been conceived as practical tool for engineering purpose. Using a single-phase batch protocol, two waters were investigated following experimental plans comprising 32 and 14 experiments. Results of the simulations show that the calibration procedure enables the model, for both waters, to predict well changes in ozone dose, temperature and pH, even when a radical scavenger, *tert*-butanol, is added. More than 70% of the experiments could thus be modelled satisfactorily (predictions statistically classified as "good" or "very good"), having used only 26% of the experiments in calibrating the model. Results obtained for experiments performed at low NOM concentration are more contrasted, however the model is able to account for most changes in sub listed experimental parameters.
Keywords
Calibration; Ozonation; SimOx; Modelling; Natural Organic Matter

INTRODUCTION

Facing stringent regulations on ozonation by-products as bromate ions, operators of water services are increasingly turning towards modelling. In recent years, an important effort has therefore been devoted to the understanding and modelling of complex phenomena involved in ozonation (see *e.g.* (Mizuno *et al.*, 2007)). Handling on-site specificities, current modelling approaches often fail. This encouraged the development of a new simulator, **SimOx**, which has been especially designed to cope with real situations providing the user with indications on disinfection, by-product formation and micropollutant fate (Mandel *et al.*, 2008). Although using mechanistic models, SimOx tackles parameter fitting incorporating an optimisation feature that allows an easy calibration of the implemented chemical models.

Quality calibration is crucial when modelling ozonation. Adequately simulated concentration profiles for ozone and radical species as hydroxyl radical indeed will enable SimOx to precisely calculate disinfection and simulate the removal of micropollutants (pharmaceuticals, pesticides, additives…). Linked to the model implemented in the simulator, a normalised calibration procedure for engineering purpose and with determined performances shall therefore be defined for site implementation. Basing on the results of two experimental plans, this article presents a modelling procedure to calibrate a given model accounting for the effects of NOM during ozonation. The calibration steps are detailed, thus setting guidelines for a practical application of the model used herein. Validation results are given to assess the quality of the calibration.

METHODS

Gas-tight syringe set-up

Focusing on chemical phenomena related to NOM ozonation, a single-phase experimental set-up has been developed. A solution of dissolved ozone is prepared, letting an ozone flow bubble in a specially conceived 2L reactor filled with ultra pure water (left hand side of figure 1: ozone comes in the reactor *via* a glass tube (a), bubbles into ultra pure water through a sintered glass diffuser (b)

and goes to the ozone destructor *via* an exhaust glass tube (c)). 10 mL gas-tight syringes are used to withdraw predetermined quantities of ozonated water (d) and to inject them in the 100 mL gas-tight syringe (e) or take samples from the 100 mL gas-tight syringe, which is held horizontally in a thermostatic water bath (right hand side of figure 1). Ozone remaining in samples for pCBA (*para* chlorobenzoic acid, used as hydroxyl radical probe compound) concentration measurement is quenched using fresh concentrated sodium thiosulfate. Similar protocols have already been used by several researchers; see *e.g.* (Kim *et al.*, 2004). The same effort was devoted in this study to avoid any ozone stripping and to assure reproducible experimental conditions (Mandel, 2008). All materials in contact with ozone have been specially selected according to their chemical compatibility.

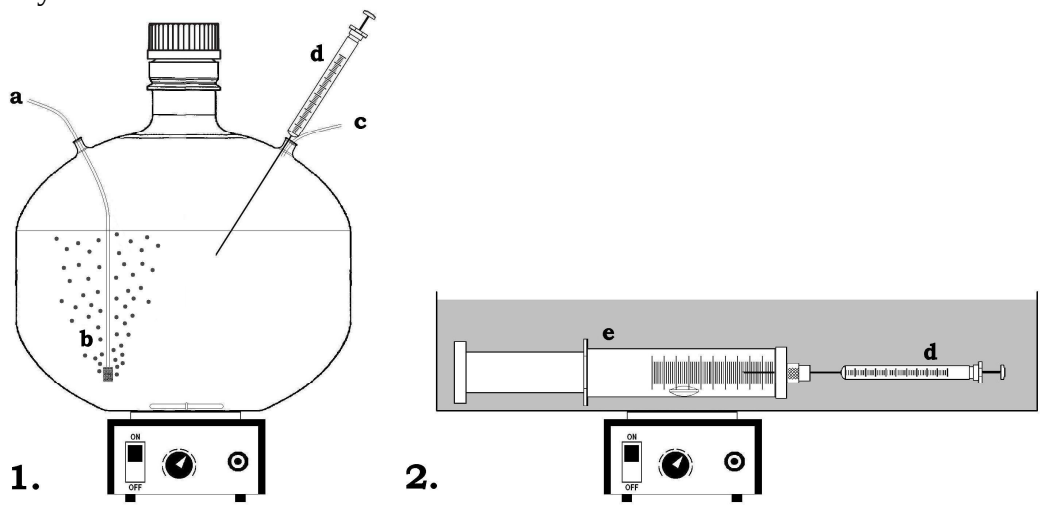

Figure 1. Schematic of the experimental set-up used in this study

Reactants and water characteristics

A Trailigaz ozonator working with pure oxygen was used to saturate ultra pure water. UVOzon 200.125 and UVOzon 200.200 analysers measured gaseous ozone concentration (always kept at 90 ± 5 $mg.L^{-1}$). All other reactants used in this study were reagent grade or analytical grade. Natural waters exhibiting different mineral and organic contents were selected: dam water originating from VI (Vitré, Brittany) and surface water from the river Oise, MSO (Méry-sur-Oise, Parisian suburban area) were chosen (see characteristics in table 1).

Table 1. Main characteristics of the waters investigated

Water	Origin	pH	TOC* ($mg.L^{-1}$)	Alkalinity ($meq.L^{-1}$)	Bromide ($mg.L^{-1}$)
MSO	River	7.8 – 8	2.7 – 3.2	4.7 – 4.9	0.05 – 0.06
VI	Dam	7.3 - 7.5	1.9 – 2.1	0.95-1.05	0.12 – 0.17

*TOC: Total Organic Carbon

Analyses

A Thermo Spectronic Helios Gamma spectrophotometer was used to determine aqueous ozone concentrations with Carmin-Indigo method (Bader & Hoigné, 1981). pCBA was analysed with UltraPerformance Liquid Chromatography coupled to mass detection, using a Waters Acquity column. Quantification limit was below 1 $\mu g.L^{-1}$. TOC was measured on each matrix before ozonation. The measurements were performed at CAE (Veolia Water Analyses Centre), and confirmed by additional analyses carried out in the lab.

Experiments performed

Following experimental control parameters were chosen according to their influence on ozone decomposition: pH, radical-scavenger *tert*-butanol adding (in excess), temperature, ozone dose, NOM concentration. Two levels were defined for each parameter. A first experimental design was built up to explore every combination of experimental control parameters. This experimental plan was applied to investigate MSO and Maisons-Laffitte (results not presented in this paper) waters and represented $2^5 = 32$ experiments per water. Basing on the analysis of the results, it was decided to alter the first experimental plan (i) increasing the interval of temperature between level 1 and 2 from 5.5 to 15°C, (2) suppressing from validation group the experiments, for which a good agreement could easily be obtained after calibration. This plan was then applied to investigate VI water. The experimental conditions are summarised in table 2.

Table 2. Levels of the parameters explored in the experimental plans

Experimental parameter	Level 1	Level 2
pH	Natural pH	Natural pH – 1
Tert-butanol initial concentration (mM)	0	10
Temperature (°C)	19 *then* 20	13.5 *then* 5
Ozone dose ($mg.L^{-1}$)	1.7	2.4
NOM dilution factor	1 (*no dilution*)	2

pH adjustment was performed adding nitric acid. NOM concentration variation was achieved through dilution with ultra pure water, ozonated and deozonated beforehand; alkalinity was then re-adjusted to its original value adding carbonate and bicarbonate ions. The levels of the experimental parameters {pH, ozone dose, temperature} were chosen in accordance with engineering issues, so that experimental conditions could always be encountered on-site. In total, both experimental plans represented 46 experiments, conducted within three weeks.

Chemical models used

Reactions with NOM. On one hand, it is well known that a great part of NOM found in natural waters is composed by organic acids (humic, fulvic, tannic acids etc.). On the other hand, NOM can play different roles reacting with molecular ozone as consumer or radical initiator and also reacting with radicals as chain-promoter or chain-scavenger. The model used in this study is based on these observations and can be seen as a new version of the model for NOM presented in (Savary, 2002). Three fractions of NOM were defined: NOM_d, NOM_i and NOM_p. The scavenging effect of NOM was considered negligible compared to that of carbonate/bicarbonate in the waters investigated. The reactions of NOM are summarised in table 3.

Table 3. Reactions of the fractions of NOM distinguished in this study

Type	Reaction
Direct consumption	$NOM_d + O_3 \rightarrow products$
Chain initiation	$NOM_i + O_3 \rightarrow {}^{\bullet}OH + products$
Chain promotion	$NOM_p + {}^{\bullet}OH \rightarrow {}^{\bullet}O_2^- + products$

In order to describe the acid character of the NOM fractions presented in table 3, a pKa was defined for each fraction. Each fraction was thus distributed over two species (acid or base), one of the species having a negligible reactivity. Moreover, temperature effects were modelled through the adjustment of three activation energies. In the end, 12 model parameters have to be adjusted to fit experimental data: 3 kinetic constants, 3 initial concentrations, 3 pKa and 3 activation energies.

Other reactions. Reactions for alkaline species were taken from (Westerhoff *et al*. 1997); the ozone self-decomposition model was taken from (Mizuno *et al*., 2007).

SimOx

SimOx is the new simulator commonly developed by Veolia and ENSCR for oxidation steps in potable water treatment works (Mandel *et al.*, 2008). Very flexible in use, it freely accepts all types of chemical reactions, thus allowing testing and evaluating various chemical pathways. The hydraulic flow conditions are described through the use of systemic schemes, consisting in an assembling of ideal reactors (de Traversay *et al.*, 1999). Conceived as decision-helping tool, it handles on-site specificities as residual oxidant concentration management. SimOx incorporates a parameter fitting module as well. The results presented in the following were obtained with a commercial optimisation tool implementing Nelder-Mead method, which was imbedded within SimOx.

RESULTS AND DISCUSSION

Qualitative analysis of the experimental results

Qualitative analysis showed that the experimental data set was consistent with already observed phenomena: if pH, ozone dose or temperature increases, so will the ozone decomposition rate; if *tert*-butanol is added or NOM is diluted, the ozone depletion will occur more slowly. The most significant change in the depletion curves for ozone and pCBA was observed when *tert*-butanol was added with a simultaneous pH drop. This led in all experiments to a considerable decrease of the initial slope steepness. The variation of one of the experimental parameters (pH or *tert*-butanol) had also important consequence on ozone and pCBA profiles. Whereas a drop of temperature of 5.5 °C had almost no effect (MSO water), a drop of 15°C had a major effect on depletion curves for both ozone and pCBA. The changes in ozone dose and NOM concentration had less significant consequences.

Calibration procedure

Defining calibration group. Conceived as modelling procedure for engineering purpose, a practical approach in calibrating the model for NOM is discussed in this section. Calibration should only require a limited number of experiments, enabling the model to account for the main experimental influences determined in the previous paragraph.

First, a reference experiment is chosen as the most likely to happen in real conditions encountered on-site; the parameters are: temperature = 13.5 °C (MSO water) or 20°C (VI water), [*tert*-butanol] = 0, no NOM dilution, natural pH, O_3 dose = 1.7 $mg.L^{-1}$. Three other experiments are considered to calibrate the model at reference experiment temperature. Following the conclusions of the qualitative analysis, these experiments are:

- Reference experiment with [*tert*-butanol] = 10 mM
- Reference experiment at $pH_{natural} - 1$
- Reference experiment with [*tert*-butanol] = 10 mM at $pH_{natural} - 1$

Two other experiments are incorporated if temperature effect is sought to be modelled: Reference experiment with [*tert*-butanol] at 19 °C (MSO water) or 5 °C (VI water) and Reference experiment at 19 or 5°C. All other experiments not included in the calibration set are used for validation.

Building up the calibration procedure. Given the small amount of experiments used for calibration, it was decided not to optimise all model parameters at the same time. Because some parameters are

correlated - *i.e.* have influence over same observed data (ozone and/or pCBA concentrations) - their simultaneous determination should be avoided. For example, both fractions NOM_i and NOM_p have, directly or indirectly, influence over both concentrations of ozone and pCBA. This explains why parameters referring to NOM_p were systematically determined apart from those referring to NOM_i. A convenient way to "de-correlate" the model parameters for NOM_i and NOM_p then consists in using an experiment done with *tert*-butanol where radical promotion is blocked to the same experiment done without *tert*-butanol. Furthermore, parameters referring to the same NOM fraction as k_i, $[NOM_i]_0$, Ea_i and pKa_i are strongly correlated because each of these model parameters acts on same experimental data. Hence, Ea_i and pKa_i were determined using separate experiments done at another temperature and pH, respectively.

Table 4. Calibration procedure overview

Experiment	Parameter determined	Comments
Ref. + *tert*-butanol	k_d, k_i	*1. Alternately determined*
	$[NOM_d]_0$, $[NOM_i]_0$	*2. Commonly determined*
Ref.	k_p, $[NOM_p]_0$	*Same as first optimisation*
Ref + *tert*-butanol + pH	pKa_d, pKa_i	-
Ref. + pH	pKa_p	-
Ref. + *tert*-butanol + 19 °C	Ea_d, Ea_i	-
Ref. + 19 °C	Ea_p	-

The calibration procedure design is sequential, so that a determined parameter is fixed after its optimisation. This kind of determination is easy to implement but can induce errors because the value of a fixed parameter may influence the next optimisation. This has been avoided as possible, (i) setting boundaries of physical relevance for the parameters to be optimised and (ii) separating optimisation for the kinetic constant values and the initial concentrations in a first time (see Table 4) before proceeding to global optimisation on all variables.

Validation results

Major results from an engineering point of view. Validation results showed globally good agreement of the simulations to experimental data. The calibrated model was able to account for most of the experimental changes and especially to the changes that preferentially may occur during on-site ozonation management: Temperature (see figure 2); Ozone dose (see figure 3); pH (see figure 4). The changes when adding *tert*-butanol and diluting NOM were also satisfactorily simulated (see next paragraph) but do not appear on the following figures since these phenomena are not likely to be encountered on site. Results presented in figure 2 regard VI water; figures 3 and 4 regard MSO water. Results are discussed in detail in the next sections.

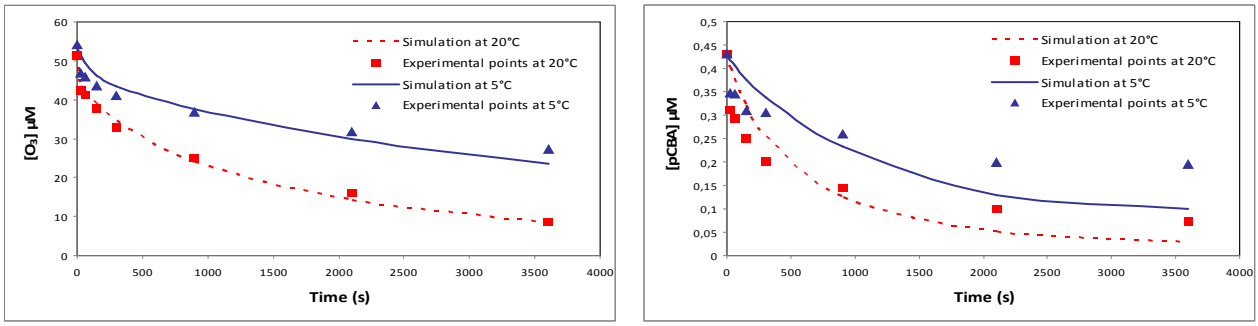

Figure 2. Ozone and pCBA profiles for experiments # 5 and # 14. Other parameters is kept constant: large ozone dose. VI water

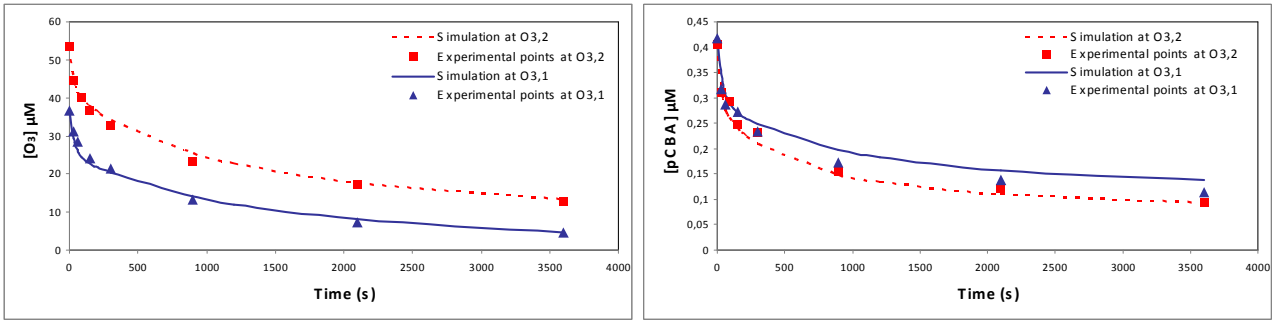

Figure 3. Ozone and pCBA profiles for experiments # 9 and # 13. Other parameter is kept constant: NOM is diluted. MSO water

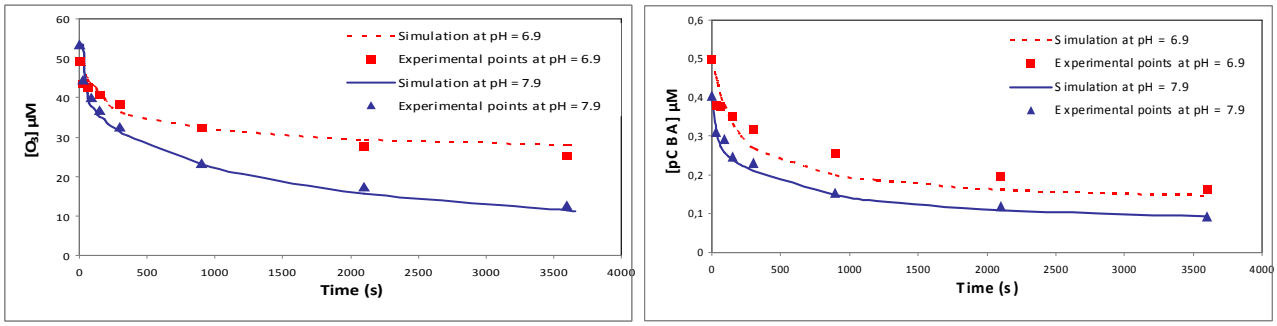

Figure 4. Ozone and pCBA profiles for experiments # 13 and # 15. Other parameters are kept constant: NOM is diluted, large ozone dose. MSO water

Statistical parameters. A statistical analysis was carried out to assess the calibration and validation qualities. Following the definition of calibration groups for MSO water, 16 - 4 = 12 experiments were used for validation at 13.5 °C and 16 – 2 = 14 experiments were used for validation at 19 °C. In the case of VI water, 14 – 6 = 8 experiments were used for validation. Two common statistical parameters were used to determine the quality of the fit for the model implemented in SimOx: the reliability factor r and the coefficient of determination R^2. Their definitions are given in equation 1 for n experimental points noted x_{exp} and n simulated points x_{sim}. Simulated points are in good agreement with experimental points when r is close to 0 and R^2 is close to 1. In the following, R^2 will be expressed in percent.

$$r = \sqrt{\frac{\sum_i^n \left(x_{\exp} - x_{sim}\right)^2}{\sum_i^n x_{\exp}{}^2}} \qquad R^2 = 1 - \frac{\sum_i^n \left(x_{\exp} - x_{sim}\right)^2}{\sum_i^n \left(x_{\exp} - \overline{x_{\exp}}\right)^2} \tag{1}$$

MSO water. All results at 13.5 °C are gathered in figure 5. For all experiments, the values of r and R^2 are represented by histogram bars. The taller bars represent R^2.

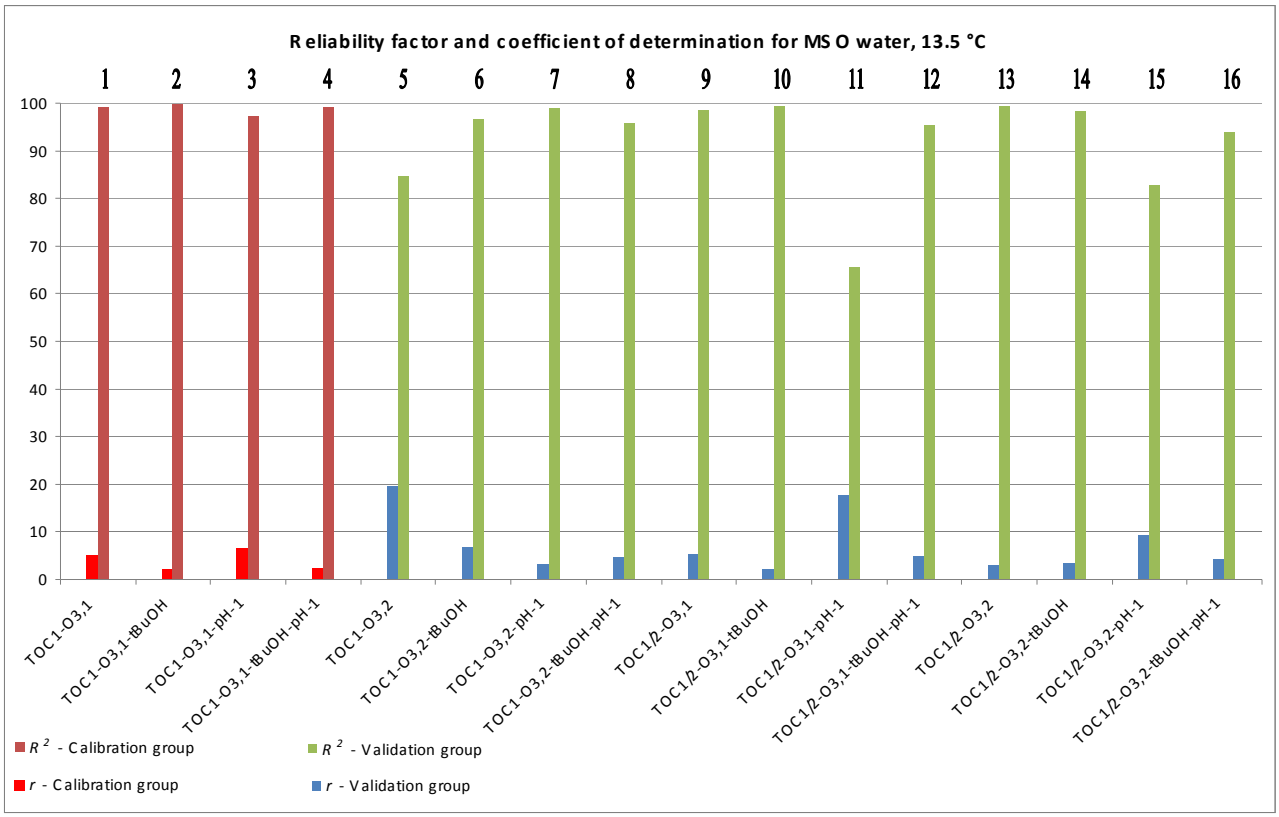

Figure 5. Statistical evaluation of the simulations done for MSO water, 13.5 °C

Obviously, results for calibration data (4 first bars) are better than those for validation data. Nevertheless, one can observe a good agreement of simulation to experiments for most of the validation experiments. It is interesting to analyse results on the base of the experiments that were selected in the calibration group. In this way, it appears that *tert*-butanol effect is satisfactorily simulated (compare experiment # 6 to # 5, # 8 to # 7 etc.). pH effect is also well simulated when NOM is not diluted (compare experiments # 7 and 8 to # 5 and 6). This can be attributed to the calibration group as it was constructed. On the other hand, it has to be mentioned that the absence of experiments performed at higher ozone dose was not problematic (except for one experiment out of eight - experiment # 5). The experiments with NOM dilution were diversely simulated: whereas the deviation to experimental data was found small on the majority of these experiments, the model failed on experiment # 11. Moreover pH effect was not predicted satisfactorily for experiments at TOC/2: a systematic worsening of simulation quality is observed when comparing experiments # 11 and 12 to # 9 and 10; # 15 and 16 to # 13 and 14. Even though being weaker, the quality of the results at 19 °C (not presented) remains acceptable and homogeneously distributed over the experiments. At that temperature, only 2 experiments were used for calibration and 14 for validation.

VI water. The results of the two statistical factors for VI water are given in figure 6.

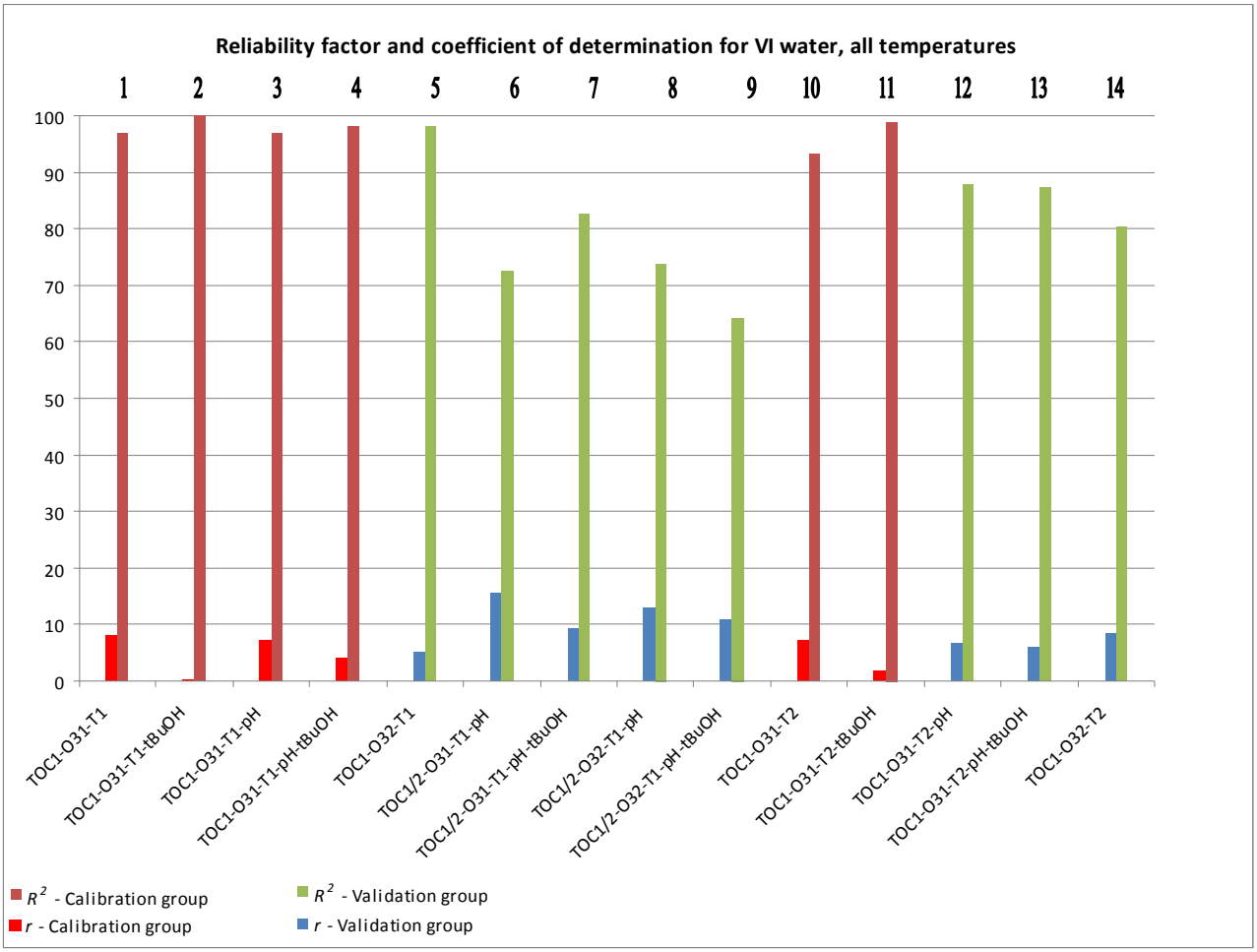

Figure 6. Statistical evaluation of the simulations done for VI water, all temperatures

Results presented in figure 6 are globally good, not as homogeneous as those obtained with MSO water, though. In fact, the validation group for VI water solely comprised experiments that had been difficult to model for MSO and Maisons-Laffitte waters (VI experiments # 5 to 9 respectively correspond to MSO experiments # 5, 11, 12, 15 and 16). Contrary to MSO water, experiment # 5 (large ozone dose) is correctly modelled.

Summary. Simulation results for both waters globally show good agreement with experimental data. However experiments performed with simultaneous pH drop and NOM dilution cannot adequately be modelled, although validation results of the separate phenomena give satisfaction. For the relative average quality of these results, two hypotheses can be asserted:

- The model may be unsuitable to adequately simulate important changes in NOM concentration when lowering pH. Due to the intricate nature of NOM, important physicochemical modifications could occur that are beyond the scope of the model.
- The calibration group of experiments or the calibration procedure itself is not *ad hoc*: the group of experiments for which the simulation failed is clearly to be seen on figure 5 and comprises all experiments with NOM dilution at $pH_{natural} - 1$. The results may change if one of these experiments is included into the calibration group, originally to small to describe all phenomena susceptible to occur.

However, as average simulation results are to be found for certain experiments performed with NOM dilution, one has to keep in mind that VI water stems from a dam. This implies relatively small variations in water quality over the time, meaning that in practice, such variations in NOM

concentration are rarely encountered. From an engineering point of view, the discrepancies between simulation and experiments at TOC/2 can thus be regarded as secondary: considering only the experiments done without NOM dilution, simulation quality is always acceptable for VI (penultimate row in table 5). A simplified reading of figures 5 and 6 is proposed in table 5, where the simulations have been classified in three groups according to the quality of the simulation proposed by the calibrated model.

Table 5. Quality distribution of the simulated experiments

Water		Very good (R^2 > 95 and 0 < r < 5)	Good (80 < R^2 and r < 10)	Mediocre (rest)
MSO	13.5 °C	8	6	2
	19 °C	0	8	8
MSO total		8	14	10
VI total		4	7	3
VI not diluted		4	6	0
Both waters (%)		**26**	**46**	**28**

Parameter values determined for both MSO and VI waters are summarised in table 6. Some values did change in a sensitive way between MSO and VI waters, reflecting differences in organic content. These values are difficult to compare with the very few similar data available in scientific literature. Pointing out the differences, it can be said that (i) the reactivity of NOM_d in VI was found to be slightly higher than in (Bezbarua, 1997); (ii) the reactivity of NOM_i in MSO was found to be significantly high (Bezbarua, 1997); (iii) the reactivity of NOM_p in VI was superior to what observed (Kim, 2004).

Table 6. Model parameter values for investigated waters

Water	NOM fraction	Kinetic constant k_0 ($M^{-1}.s^{-1}$)	Initial concentration at natural pH (µM C)	Water TOC (µM C)	pKa	Ea ($kJ.mol^{-1}$)
MSO	NOM_d	$1.07.10^3$	5.5	$1.9.10^2$	6.54	1.14
	NOM_i	$1.89.10^8$	26.69		6.84	$3.78.10^1$
	NOM_p	$3.96.10^8$	$1.1.10^2$		7.38	0
VI	NOM_d	$4.58.10^{35}$	5.10	$1.43.10^2$	8.00	$1.78.10^5$
	NOM_i	$3.27.10^9$	43.29		8.74	$4.84.10^4$
	NOM_p	$2.43.10^{14}$	22.65		6.22	$2.68.10^4$

CONCLUSIONS

Calibrating NOM models for ozonation is a major step in the process modelling: good calibration leads to precise concentration profiles for ozone and hydroxyl radicals that can in turn be used to calculate disinfection and micropollutant removal. Considering a chemical model accounting for the effects of NOM during ozonation, a calibration procedure designed for engineering purposes has been defined. Associated with the presented protocol, experiments intended to calibrate specified water only represent one and a half day of experimental work. The quality of this modelling procedure has been assessed basing on a large experimental plan comprising 46 experiments performed on two waters exhibiting different characteristics. The results showed that:

- A good agreement of the model with experimental data can be found on both waters if calibration is done on 6 specified experiments. The calibrated model is able to describe changes in ozone dose, pH, temperature, and to a smaller extent, in NOM concentration – even when a radical scavenger is added. More than 70% of the experiments could thus be

modelled satisfactorily, having used only 26% of the experiments in calibrating the model.

- Results were generally less accurate when modelling experiments performed with different NOM concentrations. It although remains questionable whether NOM dilution is relevant for waters exhibiting very stable characteristics over time (VI water).

Future work will consist in collecting experimental data with other types of water, in order to widen the scope of this study, testing the NOM model and its calibration procedure. In parallel, other calibration groups of experiments will be used to assess what could be the best possible calibration procedure. Finally, this approach shall be up-scaled to real ozonation units.

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