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Modelling Bromate Formation During Ozonation

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Abstract

Bromate formation has been identified as a significant barrier in the application of ozone during water treatment for water sources that contain high levels of bromide. Bromate has been identified as a possible human carcinogen and bromate levels in drinking water are strictly controlled at 10 μg/L in most developed countries. Various models have been proposed to model bromate formation during ozonation based on raw water quality, ozone dose and contact time. Two main approaches for modelling have been used: an empirical regression modelling methodology and kinetic based methodology. Currently, the benefit of the bromate models lies in their ability to show how process parameters may impact on the amount bromate formed.

Keywords – Ozone; Bromate; Kinetics; Modelling; Multiple Linear Regression.

Introduction

In recent years, bromate has become known as a contaminant of potable water supplies and in aquariums due to its formation from naturally occurring bromide during ozonation. Evidence supports the view that bromate is a possible human carcinogen and is therefore strictly controlled in drinking water (Weinberg *et al*, 1993; Bull and Cottruvo, 2006). Ozonation has become increasingly important in water treatment across the world as an oxidising agent and disinfectant due to its strong oxidation potential (von Gunten, 2003a). Ozone is used as a disinfectant in the water industry that is active against a wide range of microbes including more effective treatment of *Cryptosporidium* oocysts and *Giardia* over conventional chlorine due to the increased oxidation potential of ozone (Bull and Cottruvo, 2006). Ozone is also used at water treatment works (WTW) for oxidising organic molecules such as pesticides and taste, odour and colour causing compounds and oxidising inorganics such as iron and manganese to their insoluble form (Kasprzyk-Hordern *et al.*, 2003).

Disinfection by-product (DBP) formation is associated with all disinfectants and oxidants, however, the major DBP of concern when using ozone is bromate (BrO_3^-), a DBP that forms from naturally occurring bromide (Br^-) in raw water (Legube *et al.*, 2004). Toxicity testing on experimental animals has consistently shown bromate to induce cancer in rats, mice and hamsters through damage to genetic material (Chipman *et al.*, 1998 and Bull and Cottruvo, 2006). Whilst there is no data demonstrating that bromate is carcinogenic to humans, it is plausible to assume that the mechanisms resulting in tumour formation in laboratory animals could occur in humans. For this reason the World Health Organisation (WHO) has set a provisional guideline concentration of 10 μg/L bromate in drinking water (WHO, 2004). European Union law specifies that all member states must enforce a maximum bromate concentration of 10 μg/L by 2008 (European Drinking Water Directive). In the UK, the legislation enforcing this standard came into effect in 2003. In the US, regulations also specify a maximum value of 10 μg/L (United States Environmental Protection Agency (USEPA) Stage 1 Disinfectants and Disinfection By-products Rule, 1998).

There is some evidence showing that water utilities using hypochlorite solids or liquids for disinfection purposes may add up to 3 μg/L of bromate in to drinking water as a result of the formation of bromate during the manufacture of hypochlorite products (Weinberg et al., 2003). However, the formation of bromate during disinfection and oxidation is generally only associated with the use of ozone as it has superior oxidising ability over other commonly used disinfectants. In the presence of ozone, the conversion of bromide to bromate occurs via two complex pathways (Figure 1). The first is through the direct oxidation of bromide from molecular ozone (O_3) to hypobromite (BrO^-), which is then further oxidised to bromate (Haag and Hoigne, 1998). The second pathway occurs from the formation of the hydroxyl radical (OH•) from the decomposition of molecular ozone in water. The hydroxyl radical has an even greater oxidation potential than molecular ozone (Balakrishnan *et al.*, 2002). The hydroxyl

radical converts the bromide ion to the bromide radical (Br•) which is then converted to BrO_3^- through further reactions with OH• or molecular ozone.

Bromate formation has been the major barrier in the use of ozone for water treatment where the source water contains bromide, particularly given the challenging targets set for the maximum allowable bromate concentration (Magazinovic *et al*., 2004). A number of bromate modelling tools have been developed for predicting bromate formation in order to provide a better understanding of when bromate regulations may be exceeded at WTWs. From a health and water utility perspective, the ultimate goal of such models would be to provide a bromate formation tool capable of accurately controlling bromate formation by changing operational conditions during ozonation to bring bromate formation below the maximum allowable concentration.

The objectives of this review were to:

- determine the important operational parameters for modelling bromate formation
- describe and discuss empirical regression, kinetic and artificial neural network (ANN) bromate modelling efforts that have been developed for predicting bromate formation.
- Use real historical data from a full scale WTW to determine the applicability of bromate formation models at full scale.

Factors influencing bromate formation

The formation of bromate during ozonation is strongly dependent on the characteristics of the water to be treated and the amount of ozone contacting the water. The following lists the important variables for bromate formation:

1) *Bromide concentration*

   Given that bromide is oxidised by ozone to bromate, an increase in bromide inevitably leads to an increase in bromate for a constant ozone dose and contact time (Legube *et al*., 2004). Conversion of bromide to bromate is usually between 10-50 % during ozonation (Song *et al*., 1996). Typical concentrations of bromide in natural waters usually range from 30-200 μg/L, with an average of 100 μg/L (Amy *et al*., 1994), however this can be greater than 500 μg/L (Legube *et al*., 2004). Amy *et al*. (1994) have suggested that up to 30 μg/L of bromate can form from an average bromide concentration of 100 μg/L – significantly above the target bromate concentration of 10 μg/L. This equates to a 20.5 % conversion rate of bromide to bromate in terms of Br. Groundwater sources can have particularly high bromide concentrations due to ingress by salt water, road run-off following the salting of roads in winter and also as a result of dissolution from sedimentary rocks (Magazinovic *et al*., 2004; Butler *et al*., 2005). A general conclusion by von Gunten (2003b) was that waters containing <20 μg/L of bromide do not present a problem for bromine-derived DBPs, whilst waters containing >100 μg/L of bromide are likely to cause significant bromate problems. The propensity to form bromate from bromide is therefore highly dependent on the raw water quality and source and the goals of disinfection.

2) pH

As the ozonation pH of the water is increased, the rate of bromate formation increases (Pinkernell and von Gunten, 2001). In part, this is as a result of the formation of the more unstable and reactive BrO^- compound at high pH as the equilibrium between $HBrO \Leftrightarrow BrO^- + H^+$ shifts to the right as the concentration of hydrogen ions decreases. In addition to this, hydroxyl radical formation is promoted at high pH due to the increased concentration of hydroxyl ions present and the lower stability of ozone at high pH (Song *et al*., 1997; Siddiqui *et al*., 1998). Bromate formation has been shown to increase from 10 μg/L at pH 6.5 to 50 μg/L at pH 8.2 (Legube *et al*., 2004) whilst Krasner *et al*. (1994) observed a 60 % decrease in bromate formation for each drop in pH unit. The ozonation pH is widely regarded as being the most effective bromate control strategy at WTW and should be considered the best available treatment for bromate control (Ozekin and Amy, 1997). However, this must be balanced by the increased formation of brominated organic compounds as pH is reduced (USEPA, 1999a). Additionally, the cost of pH reduction may be prohibitive for high alkalinity waters due to the volume of acid required (von Gunten, 2003b).

3) Applied ozone concentration and contact time

An important consideration in the conversion of bromide to bromate is the specific goal of disinfection (von Gunten *et al*., 2001). For example, if bacteria and viruses are being targeted, the conversion of bromide to bromate is low. However, if *Cryptosporidium parvum* oocysts are being treated, the conversion of bromide to bromate is high. This relates to the concentration of applied ozone (*C*) and the residence time of the ozone (*t*). The efficiency of any disinfectant may be characterised by the '*Ct*' factor (USEPA, 1999b). The relationship between bromate formation and *Ct* follows a linear function with an increase in *Ct* leading to an increase in bromate formation (von Gunten and Hoigne, 1996 and Legube *et al*., 2004). Due to its low solubility, typical residual concentrations of ozone found at WTW are in the range 0.1-1 mg/L. In order to achieve 99 % inactivation of *C. parvum* oocysts typical *Ct* of 3.1-48.0 mg min/L are recommended by the USEPA (USEPA, 2006). The range of *Ct* was temperature dependent with the *Ct* increasing with temperature (<0.5-30 ºC). For bacteria and virus inactivation, the *Ct* required to achieve a similar inactivation is much less. For example the *Ct* required to achieve a 2-log inactivation of *Escherichia coli* is five orders of magnitude less than for *C. parvum* (von Gunten *et al*., 2001). However, *Ct* is dependent on temperature and the log inactivation of microorganisms required. For example at 13 °C, a 3-log inactivation of *Cryptosporidium* requires a *Ct* of 22 mg min/L whilst at 22 °C a similar inactivation requires a *Ct* of 8 mg min/L (Galey *et al*., 2004). Any change in *Ct* for bromate control must therefore also ensure that adequate disinfection is maintained.

4) DOC concentration

Both the concentration and nature of organic material in water can affect bromate formation. During ozonation, any natural organic matter (NOM) present in the water generally reduces bromate formation. This is because ozone and hydroxyl radicals are consumed by the oxidation of organic molecules and therefore taken away from

the bromate formation pathways. However, this is not always the case because if a residual ozone concentration is required for disinfection, more ozone may need to be added resulting in similar or in some cases increased concentrations of bromate. The presence of NOM and bromide during ozonation can also lead to the formation of brominated organics. The exact identity of all of these brominated compounds has yet to have been fully established (and are not currently regulated for), but they are believed to be a higher risk to health than chlorine based DBP's (Song *et al*., 1997). From a bromate modelling point of view, the presence of NOM can be the principle stumbling block in producing accurate bromate formation models due to the complexity and site specific nature of NOM and its complex interactions with ozone (Westerhoff *et al.*, 1998; Sohn *et al*., 2004). This prevents accurate knowledge of the precise reactions between ozone and NOM difficult.

5) Alkalinity

The presence of inorganic carbon (IC) species increases bromate formation because both carbonate (CO_3^{-2}) and bicarbonate (HCO_3^-) species can form the carbonate radical ($CO_3^{-}\bullet$) as a result of oxidation by hydroxyl radicals (von Gunten, 2003a). Once the carbonate radical has been formed, this can convert hypobromite into the hypobromite radical ($BrO^{-}\bullet$) and then bromate (Kim *et al*., 2004).

6) Ammonia concentration

The presence of ammonia in water acts as a scavenger of hypobromous acid (HOBr) during ozonation, an important intermediate in the formation pathway of bromate (Pinkernell and von Gunten, 2001; von Gunten, 2003a). HOBr reacts with ammonia to form bromamine compounds, which, in turn, can be converted back to bromide through oxidation by ozone. Ammonia can therefore remove a significant intermediary from the bromate formation path and reduce the amount of bromate formed (Song *et al*., 1997). Ammonia may be present naturally in waters to be ozonated, or alternatively can be added prior to ozonation as a bromate prevention strategy. The addition of a high concentration of ammonia (1.5 mg/L) has been shown to reduce bromate formation by around 5 μg/L when applied to water containing 100 μg/L Br^- under constant conditions (Ozekin and Amy, 1997). This reduction, although small, may be critical for those WTW where bromate levels are around the maximum permitted concentration. However, this must be tempered by the fact that above a certain concentration, the addition of ammonia has no further effect on bromate reduction. Therefore, for waters that contain naturally high to medium concentrations of ammonia, the addition of further ammonia may offer no further benefit (von Gunten, 2003b). Furthermore, any un-removed ammonia may act as a nutrient for nitrifying bacteria once in distribution (USEPA, 1999a). An additional strategy for bromate control using ammonia is combined pre-chlorination/ammonia addition before ozonation. This has been shown to reduce bromate formation in lake Zurich water from 10 μg/L to 2 μg/L (conditions: Cl_2 0.7 mg/L; NH_3 400 μg/L; 1.5 mg/L O_3; Br^- 90 μg/L) and may be a promising control strategy involving lower ammonia addition to drinking water (Buffle *et al*., 2004).

7) Temperature

Increased temperature has been shown to increase the rate of bromate formation as a result of increased reaction kinetics and because the equilibrium between $HBrO \Leftrightarrow BrO^- + H^+$ shifts to the right as the temperature increases due to a commensurate increase in the acidity constant (Legube *et al*., 2004). The effect of temperature has been shown to be more pronounced at higher ozone doses. For example, Galey *et al*. (2004) observed that at an ozone dose of 1 mg/L the bromate formation was 8 μg/L at both 5 and 24 °C whilst at 2.5 mg/L the bromate formation was 22 μg/L at 5 °C and 37 μg/L at 24 °C. Bromate formation is therefore dependent on water temperature and remediation strategies may only need to be considered seasonally where there are big differences in the temperature of the water to be treated. However, it must also be considered that ozone disinfection efficacy is also dependent on temperature. There is evidence showing that for some microorganisms, increased temperature results in reduced inactivation (bacteria and bacterial spores) whilst for *C. Parvum*, inactivation increased with increasing temperature (von Gunten, 2001b). The proposed purpose of ozonation therefore needs consideration. Increased ozone may need to be added for bacteria inactivation when the temperature is high whilst for *C. Parvum* lower ozone doses may be applied. The two different goals of disinfection will therefore also result in different levels of bromate formation.

Modelling approaches

Previous bromate modelling papers have concentrated on empirical modelling using multiple linear regression (MLR) or kinetic based models. The following section will review and evaluate each of these approaches in turn.

Empirical models and multiple linear regression

Empirical modelling from existing bromate formation data has been the most widely applied approach to bromate formation modelling. The variables important for bromate formation are those mentioned previously: bromide, DOC or UV_{254}, pH, O_3 dose, NH_3, alkalinity and temperature. The relationship of each of these variables to the output bromate concentration is then found experimentally by fixing all variables but one. The change in bromate formation is then observed with the random variable. By carrying out MLR on the data (or log transformed data), the cumulative relationship and significance of each of the variables can be found. MLR was first applied to bromate formation by Ozekin (1994) and, to date, most bromate formation models using MLR have been of the form:

$$\log Y = b_0 + b_1 \log x_1 + b_2 \log x_2 + b_3 \log x_3 \ldots\ldots + b_n \log x_n$$

Equation [1]

where Y is the dependent variable, x_i is an independent variable and b_i is the regression coefficient. The following example shows the bromate formation regression model from Song *et al*. (1996):

$$\log [BrO_3^-] = -6.11 + 0.880 \log[Br^-] - 1.180 \log[DOC] + 5.110 \log[pH] + 1.420 \log[O_3] + 0.270 \log[t] - 0.180 \log[NH_3\text{-}N] + 0.180 \log[IC]$$

Equation [2]

A range of bromate formation models found in the literature of the form shown in (1) are included in Table 1. An alternative form of the equation has been developed by Ozekin and Amy (1997), where not all the variables in the equation have been log transformed:

$$\log[BrO3\text{-}] = -3.361 + 1.136 \log[Br\text{-}] - 1.267 \log[DOC] + 0.249 [pH] + 1.575 \log[O3] + 0.006 [t]$$

Equation [3]

Not all of the developed models include every one of the variables. For example, Ozekin's original model incorporated bromide, DOC, pH, O_3 dose and contact time with alternative models for waters with and without ammonia addition. DOC has been replaced with ultra-violet absorbance at 254 nm (UV_{254}) in the model of Sohn *et al*. (2004). This was because there has been shown to be a strong correlation between the organic content of raw water and the UV_{254}. Using UV_{254} is of advantage because UV_{254} is regarded as being an easier measurement to make on-line A number of the regression models also include ammonia. This gives flexibility to water utilities depending on whether they add ammonia as a bromate control measure or routinely measure ammonia as a water quality parameter (Ozekin and Amy, 1997).

For a number of the predictive regression models, bromate formation is limited in application to water temperatures of 20 °C because the original experiments were carried out at 20 °C (Ozekin, 1994; Song *et al*., 1996). Due to the reduced stability of dissolved ozone with increasing temperature, bromate formation increases as temperature increases. Temperature is therefore of real concern for drinking water production at WTW where there is a risk of bromate formation. A survey of 47 small WTW in France found that 49 % of drinking water contained ≥10 μg/L bromate in July in comparison to 7 % in December (Legube *et al*., 2002). In order for bromate formation models to be successfully applied at WTW, temperature must be factored into the model given that variations in water temperature received by a WTW can vary from season to season by more than 20 °C in extreme climates (Serodes *et al*., 2003). Sohn *et al*. (2004) report on a temperature correction factor for bromate formation (see Table 1) that was deemed to satisfactorily adjust the bromate formation from that found at 20 °C to that at temperatures between 2-24 °C. An alternative approach to this has been to incorporate temperature into the regression model as an independent variable by carrying out bromate formation experiments at a range of temperatures (Galey *et al*., 1997 and Legube *et al*., 2004).

The relative importance of each of the variables that determine bromate formation can be identified by comparison of the regression co-efficient (Song *et al*., 1996). A higher positive value gives an increased effect on bromate formation whilst an increasing

negative co-efficient value has a more reducing effect on bromate formation based on similar incremental contributions to the model from each variable. Analysis of the co-efficients presented in Table 1 shows that the parameters are of the following order of importance:
Increase in bromate formation: pH > O_3 dose > Br^- > IC > time
Decrease in bromate formation: DOC > NH_3-N

Evidently, the higher concentrations of OH^- and BrO^- ions at high pH are of more importance than the other variables contributing to the regression equations. Because temperature has only been considered in two models (Table 1), there is less certainty of the overall impact that it has on bromate formation. The regression equation from Siddiqui *et al.* (1994) suggests that an increase in temperature has more of an impact on bromate formation than both bromide concentration and ozone dose. Work from Galey *et al.* (1997) implies that it has less of a bearing than ozone dose, but more of an effect than bromide concentration. However due to the increased bromate formation observed at WTW during summer, temperature should always be included in bromate formation models

Validation of developed models

In order for bromate formation models to be considered for application at WTW, the models must be validated with real data. During most model development, the models have been applied to the same type of water to those with which the models have been developed. Although from a limited database, in these instances good correlation has been seen between the observed and predicted bromate concentrations. For example, Song *et al.* (1996) had an average R^2 value of 0.93 for validation of bromate models on water sources that were used to develop the model for predicted against measured bromate concentrations, with the regression line close to the y=x line that is indicative of a perfect model. Similarly good correlation was seen by Siddiqui *et al.* (1994) and Ozekin and Amy (1997) with R^2 values of 0.98 and 0.91 respectively. There is little information available in the literature for models applied to different waters from where the model was developed. However, those that have carried out this type of 'external validation' have seen mixed results The data shown in Figure 2 shows the predicted bromate against the observed bromate from three studies (Siddiqui *et al*., 1994; Song *et al*., 1996; Ozekin and Amy, 1997). The authors have assessed the predicted bromate to the actual bromate formation from a water that was different to that from which the model was developed. The model of Song *et al*. (1996) had data points very close to y=x, but there were only a few data points and only concentrations >20 μg/L bromate have been considered. At low concentrations, the model of Ozekin and Amy (1997) was not very accurate with most bromate predictions significantly over the observed bromate.

Validation of MLR models to a full scale WTWs

There are only a few examples in the literature of externally validating MLR models. For this reason, further elucidation is required in order to assess the more widespread

applicability of these models at full scale. In the following section, a number of bromate MLR models have been applied to a common data set from a WTW in the UK.

The data available from the works consisted of 36 complete data sets taken over a one year period for the following water and ozonation parameters: raw water bromide and DOC concentration, raw water UV absorbance at 254 nm (UV_{254}); ozonation pH, contact time, transferred ozone dose, water temperature and final water bromate concentration. Samples were taken by site scientists and sent to an accredited laboratory for analysis of bromide, bromate, DOC concentration and UV_{254}. Ozonation pH, ozone dose and contact time and temperature were taken from the WTWs on-line monitors and automated control systems. For the model of Song *et al*. (1996) and Sohn *et al*. (2004) the alkalinity of the water was estimated to be 100 mg/L as $CaCO_3$. This data was input in to the bromate formation models in Table 1 with the exception of the two ammonia models which were not assessed firstly because ammonia was not added as a bromate reduction strategy at the WTW and secondly the background ammonia concentration in the water to be ozonated was very low (≤0.04 mg/L N). The output bromate concentrations from the models were then plotted against the observed bromate concentrations for each of the models. As can be seen from Figure 3, the predictive ability varied from model to model.

From this data, the models can be classified into three categories: models that tend to under predict bromate formation (models of Siddiqui *et al*., 1994 and Song *et al*., 1996); models that tend to over predict (models of Ozekin, 1994 and Sohn *et al*., 2004) and models that are scattered around the observed=predicted curve (y=x) (models of Galey *et al*., 1997 and Ozekin and Amy, 1997). This agrees with the validation efforts on 'real' waters that have been presented in Figure 2. The models of Galey *et al*. (1997) and Ozekin and Amy (1997) gave the most accurate predictions as the linear regression line through the data was close to the y=x line and the scatter around the regression line much less than that for the other two models. However, the correlation coefficients for the 'good' models were low (R^2 values of 0.34 for Galey *et al*. (1997) and 0.40 for Ozekin and Amy (1997)).

Taking the best two models in Figure 3, the models were able to follow the general trend in bromate formation (as shown in Figure 4), however as shown in Figure 3, the main disadvantage of the models being that individual estimates on bromate formation could be very inaccurate, with some estimates approaching a difference of ±100 %. The inaccuracy of the models was confirmed statistically using a chi-squared test to compare the prediction of the models with the observed data. For both the models there was a very significant difference between the modelled and actual bromate concentrations (Galey *et al*. model: $\chi^2 = 70.4$, $p = 0.00036$, Ozekin and Amy model: $\chi^2 = 92.1$, $p = 0.0000005$) indicating that the model is a very poor fit to the data.

Whilst the individual estimates were inaccurate even for the best fitting model, an indication of the model being able to assess more general trends rather than individual

estimates was given by considering how the models predict values over and under the current EU drinking water standard for bromate (10 μg/L) (regardless of the difference in individual estimates). During the actual experimental period the observed number of bromate values ≥10 μg/L was 13/36 (36.1 %). Both of the selected models were very accurate, with the model of Galey *et al.* (1997) exactly matching the observed number of bromate failures. The model of Ozekin and Amy (1997) was still very accurate with only one extra bromate failure predicted.

MLR summary

The assessment of different MLR models in this study showed that they were able to follow the general trend in bromate formation well but individual estimates could be very inaccurate when applied to different data sets. This tends to agree with previous conclusions that as the MLR models are applied to increasing numbers of raw waters, the accuracy of the models decreases (Legube *et al*., 2004; Kim *et al*., 2004). The reasons for this may be fourfold:

1) *Models have been derived from specific waters and reactor configurations*.
Bromate formation has been shown to be highly influenced by NOM, not only in terms of its concentration, but also in its source and nature. Song *et al*. (1996) have added NOM isolates to model waters and found that different source waters and different MW organics produced different bromate formation models. However, there was no consistent relationship for specific MW giving rise to increased/decreased bromate formation when compared from source to source. The fact that NOM is highly variable from site to site has lead to the conclusion that the type of NOM is more important than its concentration for bromate formation (Song *et al*., 1996; Ozekin and Amy, 1997). The available information on the relative reactivity of ozone with different types of organic compounds is limited. However, activated aromatic moieties in organic pollutants have been shown to have low direct reactivity with ozone (von Gunten, 2003a; Buffle and von Gunten, 2006). This suggests that waters containing highly aromatic NOM may have increased bromate formation due to the reduced ozone consumption of these compounds. NOM is therefore likely to be a significant source of error in bromate formation models during more widespread application of the models. In addition, most MLR models have been developed from waters that have been spiked with bromine (Ozekin and Amy, 1997). Often the bromine concentrations added are unnaturally high and therefore bear little relationship to those found in the field. In light of the fact that permitted bromate concentrations in drinking water are heading towards 10 μg/L worldwide (if they are not already at this level), increased definition and accuracy of MLR models are required at these low concentrations which is not currently present.

2) *Boundary conditions of models may be exceeded*
Each of the MLR models was developed within a set of boundary conditions. Outside these ranges, the accuracy of the models has not been experimentally validated. Therefore, when the models have been applied to different data sets, there can be no guarantee that the data lies within the required range. For example, in all of the models in Table 1, the lowest raw water bromide concentration boundary was

70 μg/L, whilst for the utility data presented in Figure 3, the lowest bromide concentration went as low as 43 μg/L. This helps explain the inaccuracies of the models, but also highlights the need for future models to consider lower bromide concentrations to improve their applicability at WTW. A further consideration must also be given to WTW sites where a sidestream ozone dose is applied at high concentration and then diluted in a contact tank. In these instances, the applied ozone dose can be up to 20 mg/L prior to dilution. The implications for bromate formation both in the sidestream and the contact tank have yet to have been analysed, but it has been shown previously that MLR models do not accurately predict bromate for sidestream ozone dosing (Smith, 2002).

3) *Reactor configuration*
The reactor configuration used in the model development tend to be different from study to study and to those utilised at WTW. In most instances, configurations have been true batch or semi-batch reactors (Siddiqui *et al*., 1994). In the true batch mode, ozone is administered into a sidestream and then introduced to the reactor for a set period of time. In this way, all of the applied ozone is in the aqueous phase. In semi-batch mode, the ozone is applied for a set amount of time directly into the reactor. Adopting these models for a WTW is therefore likely to lead to some error as ozonation is operated in the continuous mode; the scale is much greater and the efficiency of ozone transfer into the reactor may be different depending on diffuser configuration and operation. However, as only a small percentage of bromide is converted to bromate, the reactor configuration is likely to be of less importance than the previous two factors.

4) Uncertainty in the measured variables
It must also be considered that there was some error associated with the actual measurements taken from the WTWs for variables that went in to the models and the actual bromate measured exiting the site. This may result from natural drift of on-line monitors, variations in flow through the WTWs, difficulties in measuring ozone concentration and error in instruments. However, due to routine site quality controls and laboratory auditing it is unlikely that this had a significant impact on model accuracy.

In order to provide accurate bromate formation predictions, the empirically based models must therefore be derived experimentally for a specific water (or set of waters). Alternatively, given that the best selected models were able to show more general trends in bromate formation for a different water source to that used in the model development, the models can be used as a more qualitative demonstration of the change in bromate formation when the input variables are changed (Ozekin and Amy, 1997; Galey *et al*., 2002). The example in Figure 5 shows the water utility data used previously, however here the pH has been fixed at either pH 6, 7 or 8. This highlighted how a reduction of pH from 8 to 6 could lead to significant reductions in bromate formation using the model of Galey *et al*. (1996). The decrease in bromate values >10 μg/L was from 47 % at pH to 0 % at pH 6. The impact on bromate reduction was less when the ozone contact time was changed from 20 to 5 minutes (Figure 6). Reducing the contact time from 20

to 5 minutes reduced the proportion of bromate failures above 10 μg/L from 64 to 34 %. This highlights the increased benefit of reducing pH over contact time as previously identified from comparison of the co-efficients from the regression model. Using the models in this manner could prove to be an important tool for water treatment managers in order to prioritise bromate remediation strategies.

Kinetic and ozone decomposition rate modelling

It has been shown above that empirical modelling of bromate formation is highly dependent on the specific nature of the water (Kim *et al*., 2004). Mechanistic models incorporating the fundamental chemical reactions in the formation of bromate have been developed in an attempt to overcome this problem (Westerhoff *et al*., 1998, Hassan *et al*., 2003; Sohn *et al*., 2004). Essentially, a kinetic approach models the reactions and rate constants (obtained experimentally or from the literature) involved in:

1) the consumption of ozone and the conversion of ozone to radicals, and
2) bromate formation from both direct and indirect oxidation.

The modelling of ozone consumption has taken a number of different approaches. A basic model assumes that the hydroxyl radical alone is responsible for the conversion of bromide to bromate as it has been estimated that the hydroxyl radical contributes between 70-100 % of the total bromate formation (Mizuno *et al*., 2007). This relationship is dependent on the conversion of ozone to hydroxyl radicals at different pH:

$$O_3 \rightarrow 0.5OH\bullet + O_2$$

Equation [4]

Accurate bromate prediction has been simulated using this type of model for synthetically prepared waters. However, this does not consider that other radical species can form that may become available for bromate formation. A second approach increases the complexity by considering all the known reactions of ozone in water at neutral pH, including those involving inorganic and organic carbon which consider all oxidant radical formation (Westerhoff *et al*., 1998).

The ozone consumption models can then be combined with bromide oxidation reaction kinetics to predict bromate formation. During the modelling process, the reactions involved (both direct and indirect) during the bromate formation pathways and the rate constants for the reaction must be identified. Increased accuracy has been achieved by considering as many possible reactions as possible that may influence bromate formation. Different modellers have previously used differing numbers of reactions. For example Hassan *et al*. (2003) listed 72 separate reactions that may occur, Kim *et al*. (2004) listed 68 whilst Westerhoff *et al*. (1998) considered 46.

Differential equations for each of the reactions and the associated reaction rate constants are then input into a computer programme along with the initial concentrations of the important chemical species involved in bromate formation. The programme then integrates the differential equations together and gives solutions for the concentration of each species with time for ozone decay and bromate formation (von Gunten, 2003b).

Validation of kinetic models

The validations of the kinetic model when NOM is absent have been shown to be comparable to validations of MLR models. Westerhoff *et al*. (1998) compared two models: firstly, a basic model based on a single equation for the formation of hydroxyl radicals from ozone and secondly a more complex model involving 12 reactions for ozone consumption and radical generation. For both models, 34 reactions were then subsequently considered for bromate formation. Good fits were seen for both models when used on synthetic waters, with both having regression lines with an $R^2 \geq 0.98$ and slopes very near to a value of 1 and an intercept close to 0. However, once NOM isolates were added to the water, the accuracy of the models broke down with bromate concentrations being over-predicted. This can be seen in Figure 7, where the predicted and observed bromate concentrations over time have been taken for the basic and simple models. This was after the addition of three equations for NOM reacting with OH• radicals and hypobromite and hypobromous acid in the models.

Validation of kinetic models on different water from that which the model has been developed has been carried out for a synthetic water in the absence of organic material (Hassan *et al*., 2003). As can be seen in Figure 8, there was a general tendency for the model to over predict bromate formation when compared to actual values. Given that a satisfactory prediction for kinetics models has currently been considered as ±100 % (von Gunten, 2003; Hassan *et al*., 2004), there is still considerable work required in order to improve the accuracy of kinetic based models. Additionally, there is a paucity of detail available for low bromate concentrations that are critical for because they are likely to be experienced at low concentrations at WTW.

Kinetics summary

The kinetics based model have shown similar or worse levels of performance to the MLR models giving high levels of accuracy for synthetic water in the absence of NOM. A more simple kinetic model has recently been developed that predicts bromate formation from the concentration of hydroxyl radical to dissolved ozone ratio (Mizuno *et al*., 2007). Once NOM has been added to the water, the models have been ill-equipped to deal with the increased complexity of the systems (Westerhoff *et al*., 1998). Given that all natural waters contain NOM, further research is required on quantifying the reactions between NOM and the oxidising species present during ozonation before kinetic based models can be considered for application at WTW.

Artificial neural networks

Finally, there has been one example in the literature of modelling bromate formation using the relatively new modelling strategy of artificial neural networks (ANN) (Legube *et al*., 2004). Whilst it is beyond the scope of this work to go into ANN with any great detail, the following briefly summarises the basic steps involved in ANN modelling (from Lek *et al*., 1996). The modelling principle is based upon human neurone operation, with three types of neurone layers: the input layer, one or more hidden layers and an output layer. Each neurone of the input layer is connected to the neurones of the hidden layer, which in turn are connected to the output neurone that corresponds to the value to be predicted. The initial input layer comprises as many neurones as there are variables in the system (e.g. bromine, pH, ozone dose etc). Using computer modelling software, the hidden and output neurones evaluate the stimulation from the previous neurones based on the weighting of the connections between neurones (defined by the modeller). Through a series of algorithms and back-propagation, the network is trained until there is minimum error in the expected and observed values of the model. The model is then validated and tested using randomly selected data not used in the model development.

ANN models have the advantage of being able to consider complex input variables that may not be independent of one another and where relationships between variables may not be linear. Whilst there has been limited work on bromate formation using ANN, work completed has shown that ANN increases the accuracy over MLR of predicting bromate formation for comparison of the same 20 data points by increasing the R^2 co-efficient from 0.94 to 0.98 (Legube *et al*., 2004). Further work is therefore required for bromate formation using ANN as a useful predictive tool on real waters.

Summary

As has been shown both kinetic and MLR models have limited applicability to accurately predict bromate formation when applied to waters that are different from where they have been developed due to the inherent variability in raw water quality from site to site. The real benefit in the general application of the models at present, particularly for the MLR models, lies in a more qualitative demonstration of how changing process variables such as ozone dose/contact time, pH or ammonia addition can impact on bromate formation. Rather than provide absolute bromate concentrations, a more realistic outcome of using the models is to state that reducing a controllable parameter (e.g. pH, ozone contact time or dose) from x to y at a WTW will reduce the proportion of bromate failures (i.e. those above 10 μg/L). However, before process variables are changed, some caution is needed to ensure that the primary function of the ozonation does not become compromised. For example, reducing ozone contact time may impact on disinfection efficacy and pH changes could affect oxidation and precipitation of iron and manganese.

Each of the different bromate modelling techniques has advantages and disadvantages for application to real waters at WTW (Table 2). The most accurate results to date have

been seen with MLR models, but this technique requires considerable time and effort investment in order to independently assess all of the variables of the model. An alternative approach in the development of an accurate site specific model may be to build a regression model directly from the full scale water treatment system. However, the implication of not being able to control water quality variables and the limited scope for changing ozonation parameters needs to be quantified using such an approach. Kinetic models have struggled to meet the accuracy required when NOM has been present in the raw water. The ANN model has shown promise, but large volumes of data are required to 'train' the model and remains an unexplored technique at present.

Conclusions

None of the models can be considered accurate for generically predicting bromate formation at WTW. Unless investment is made to develop empirical models for specific waters, the current benefit of bromate formation models lie in their ability to show the likely change in bromate formation when process variables are changed rather than precise and highly accurate bromate predictions.

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Table 1. Regression coefficient values for bromate formation from various locations

Regression coefficient values for listed variables from bromate prediction models (number of variables included is dependent on particular model)										**Boundary conditions**	**Notes**	**Source**
Constant	**Br^- (μg/L)**	**DOC (mg/L)**	**pH**	**O_3*[1] (mg/L)**	**t*[2] (mins)**	**NH_3-N (mg/L N)**	**UV_{254} (cm^{-1})**	**Alkalinity (mg/L as $CaCO_3$)**	**Temp (°C)**			
1.55×10^{-6}	0.730	-1.260	5.820	1.570	0.280	-	-	-	-	$70 \leq \mathbf{Br^-} \leq 440$ $1.1 \leq \mathbf{DOC} \leq 8.4$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.1 \leq \mathbf{O_3} \leq 10.0$ $1 \leq \mathbf{t} \leq 120$	Model developed from 10 raw waters. For raw waters with no ammonia. Limited to 20 °C.	Ozekin (1994)
1.63×10^{-6}	0.730	-1.300	5.790	1.590	0.270	-0.033	-	-	-	$70 \leq \mathbf{Br^-} \leq 440$ $1.1 \leq \mathbf{DOC} \leq 8.4$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.1 \leq \mathbf{O_3} \leq 10.0$ $1 \leq \mathbf{t} \leq 120$ $0.02 \leq \mathbf{NH_3\text{-}N} \leq 3.0$	Model developed from 10 raw waters. For raw waters with ammonia. Limited to 20 °C	Ozekin (1994)
1.19×10^{-7}	0.960	-	5.680	1.307	0.336	-	0.623	-0.201	*[3]	$70 \leq \mathbf{Br^-} \leq 440$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.1 \leq \mathbf{O_3} \leq 10.0$ $1 \leq \mathbf{t} \leq 120$ $0.010 \leq \mathbf{UV_{254}} \leq 0.280$ $13 \leq \mathbf{Alkalinity}$	Developed from Ozekin (1994). For raw waters with no ammonia. Limited to 20 °C.	Sohn *et al.* (2004)
8.71×10^{-8}	0.944	-	5.810	1.279	0.337	-0.051	0.593	-0.167	*[3]	$70 \leq \mathbf{Br^-} \leq 440$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.1 \leq \mathbf{O_3} \leq 10.0$ $1 \leq \mathbf{t} \leq 120$ $0.02 \leq \mathbf{NH_3\text{-}N} \leq 3.0$ $0.010 \leq \mathbf{UV_{254}} \leq 0.280$ $13 \leq \mathbf{Alkalinity} \leq 316$	Developed from Ozekin (1994). For raw waters with ammonia. Limited to 20 °C.	Sohn *et al.* (2004)

(continued)

Table 1 (continued)

Constant	Br^- (μg/L)	DOC (mg/L)	pH	O_3*[1] (mg/L)	t*[2] (mins)	NH_3-N (mg/L N)	UV_{254} (cm^{-1})	Alkalinity (mg/L as $CaCO_3$)	Temp (°C)	Boundary conditions	Notes	Source
7.76×10^{-7}	0.880	-1.180	5.110	1.420	0.270	-0.180	-	0.180 [says IC]	-	$2 \leq \mathbf{BrO_3^-}$ $100 \leq \mathbf{Br^-} \leq 1000$ $1.5 \leq \mathbf{DOC} \leq 6.0$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.5 \leq \mathbf{O_3} \leq 6.0$ $0 \leq \mathbf{t} \leq 30$ $0.02 \leq \mathbf{NH_3\text{-}N} \leq 3.0$ $1 \leq \mathbf{Alkalinity} \leq 216$	Model developed from 4 different model waters. Limited to 20 °C	Song *et al.* (1996)
5.41×10^{-5}	0.040	-1.080	4.700	1.120	0.304	-	-	-	0.580	$70 \leq \mathbf{Br^-} \leq 440$ $1.1 \leq \mathbf{DOC} \leq 8.4$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.1 \leq \mathbf{O_3} \leq 10.0$ $1 \leq \mathbf{t} \leq 120$		Galey *et al.* (1997)
1.5×10^{-3}	0.610	-0.740	2.260	0.640	-	-	-	-	2.030	$250 \leq \mathbf{Br^-} \leq 1500$ $3.0 \leq \mathbf{DOC} \leq 7.0$ $6.5 \leq \mathbf{pH} \leq 8.5$ $1.5 \leq \mathbf{O_3} \leq 17.5$ $20 \leq \mathbf{Temp} \leq 30$	Model developed from 5 surface and ground waters	Siddiqui *et al.* (1994)

*[1]Utilised/transferred ozone

*[2]Time in ozone contactor

*[3]Temperature correction factor can be applied for variations in temperature: $[BrO_3]_{@tempT} = [BrO_3]_{@temp20\ °C}\ (1.035)^{T-20}$

Table 2. The advantages and disadvantages of each of the bromate formation modelling techniques.

Model	Advantages	Disadvantages
MLR	- Bromate formation can be predicted accurately for real waters from which model developed. - Relatively simple technique to apply to individual WTW once model has been developed	- Empirically derived therefore models are site specific. Generic model inapplicable across all types of water. - Labour intensive to develop models - No evidence available suggesting the technique can be applied to high rate side stream ozone dosing and subsequent blending.
Kinetics	- Accurate results achieved when applied to model waters not containing NOM.	- Complex understanding of the reactions that occur during ozonation required - Reactions of NOM can interfere with predicted kinetic equations to an unknown degree due to the complexity of organics.
ANN	- Does not assume a linear relationship between input variables (transformed or otherwise) - Does not assume variables are independent of one another	- Relatively unexplored technique for bromate formation - Large amounts of data are required to 'train' the models. - Model is only as good as the assumptions made by the modeller.

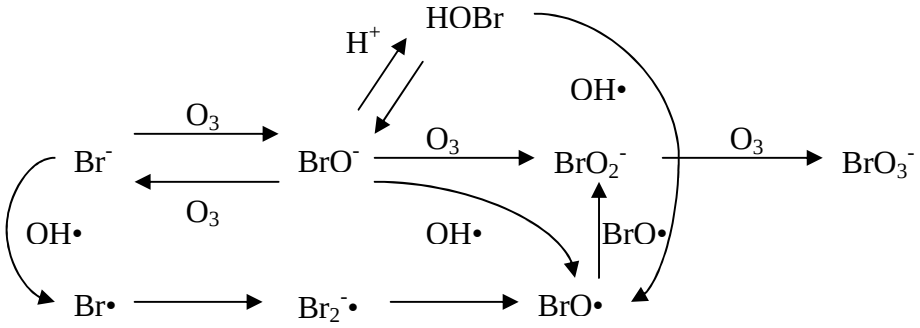


Figure 1. The pathways for bromate formation from bromide (adapted from Legube *et al*., 2004).

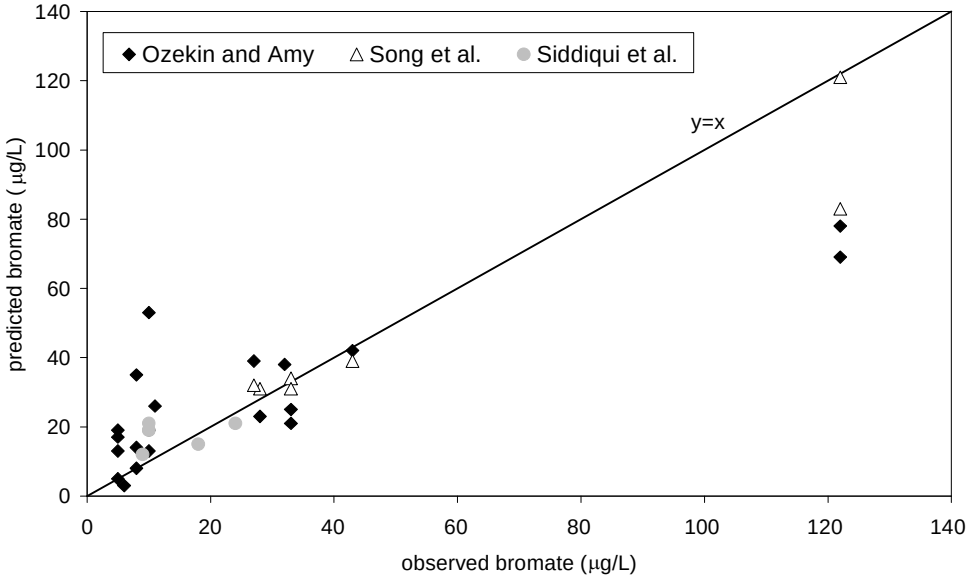
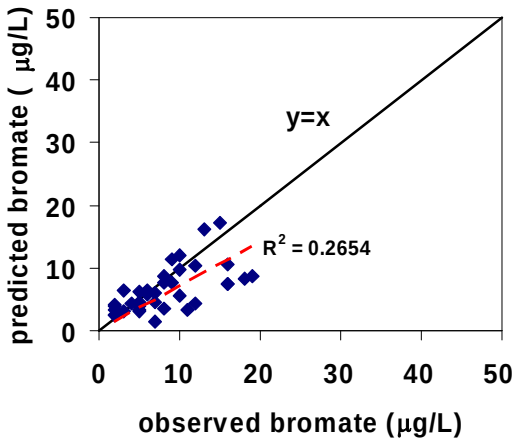
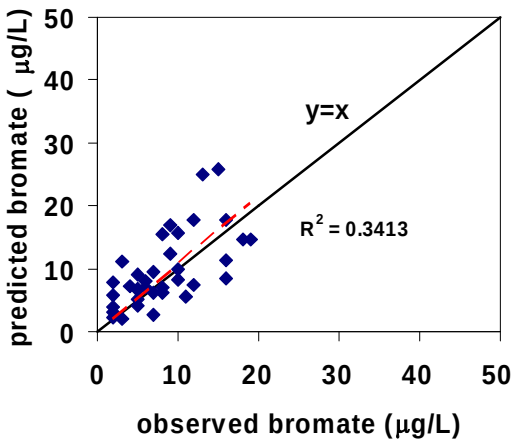


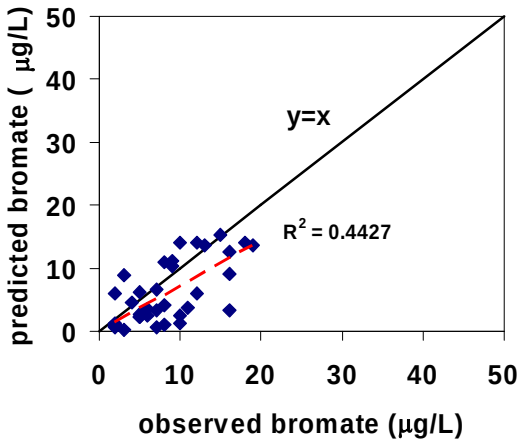
Figure 2. Predicted bromate against observed bromate for external validation of model prediction models (from the models of Siddiqui *et al*., 1994; Song *et al*., 1996 and Ozekin and Amy, 1997).



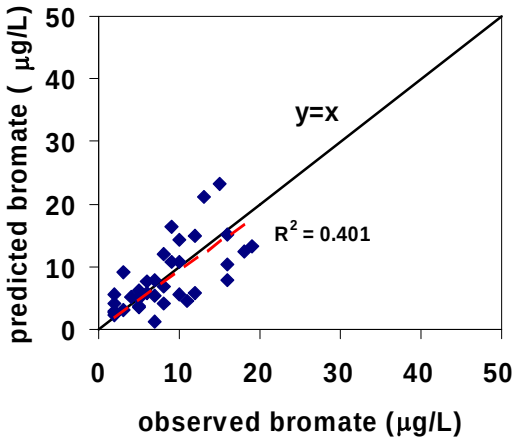
Song *et al.* model



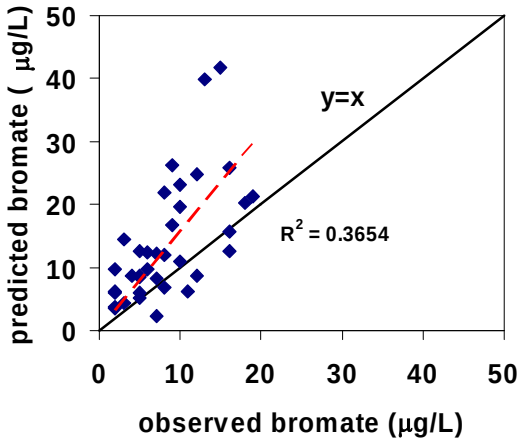
Galey *et al.* model



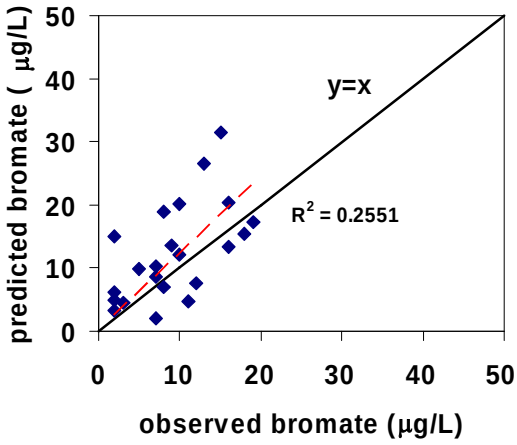
Siddiqui *et al.* model



Ozekin and Amy model



Ozekin model



Sohn *et al.* (UV) model

Figure 3. Water utility data applied to MLR bromate prediction models

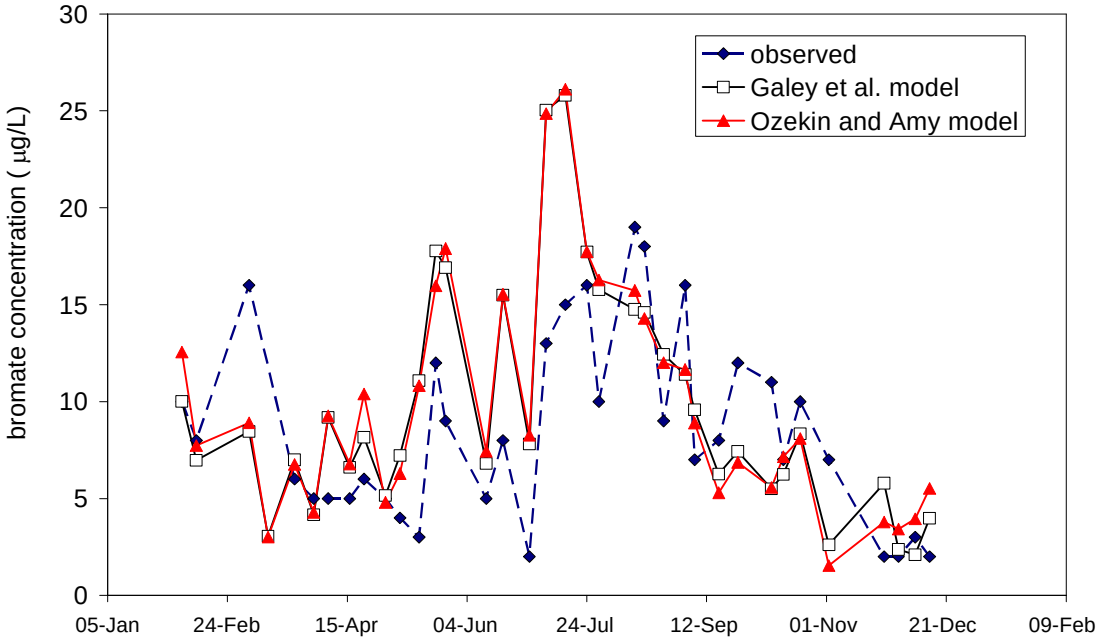


Figure 4. Observed bromate against predicted bromate using the models of Galey *et al*. (1997) and Ozekin and Amy (1997).

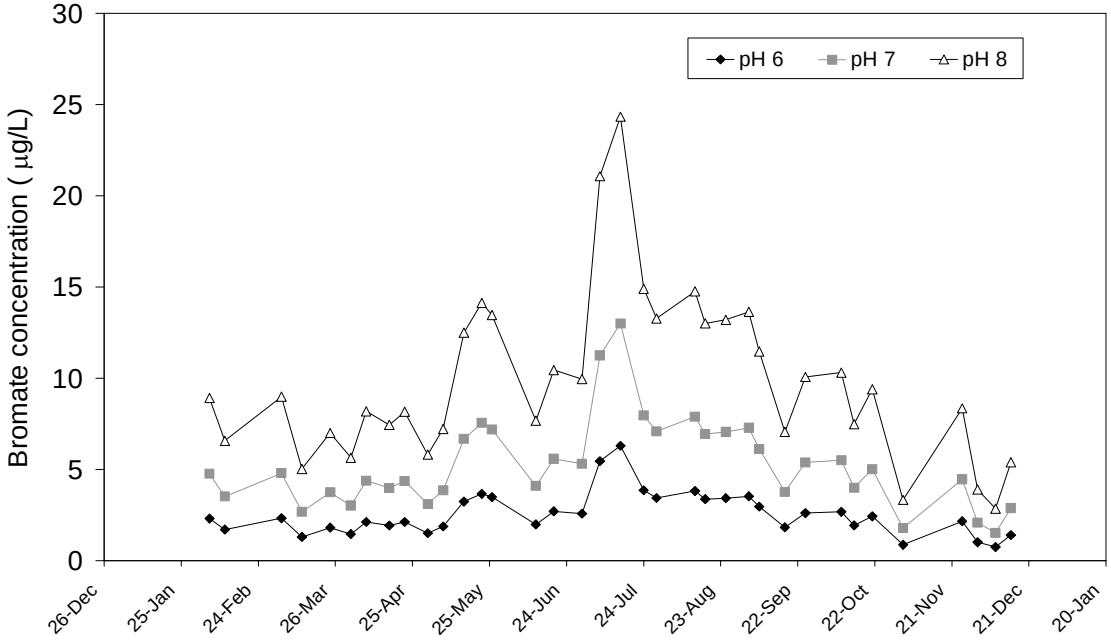


Figure 5. How the bromate formation models change with increasing pH.

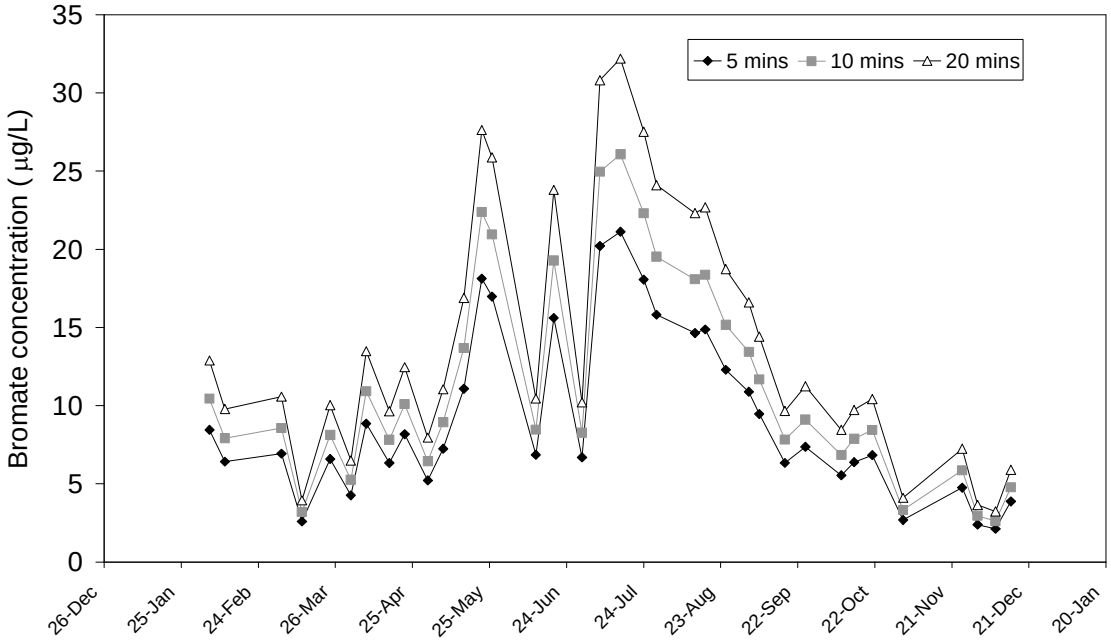


Figure 6. How the bromate formation models change with ozone contact time.

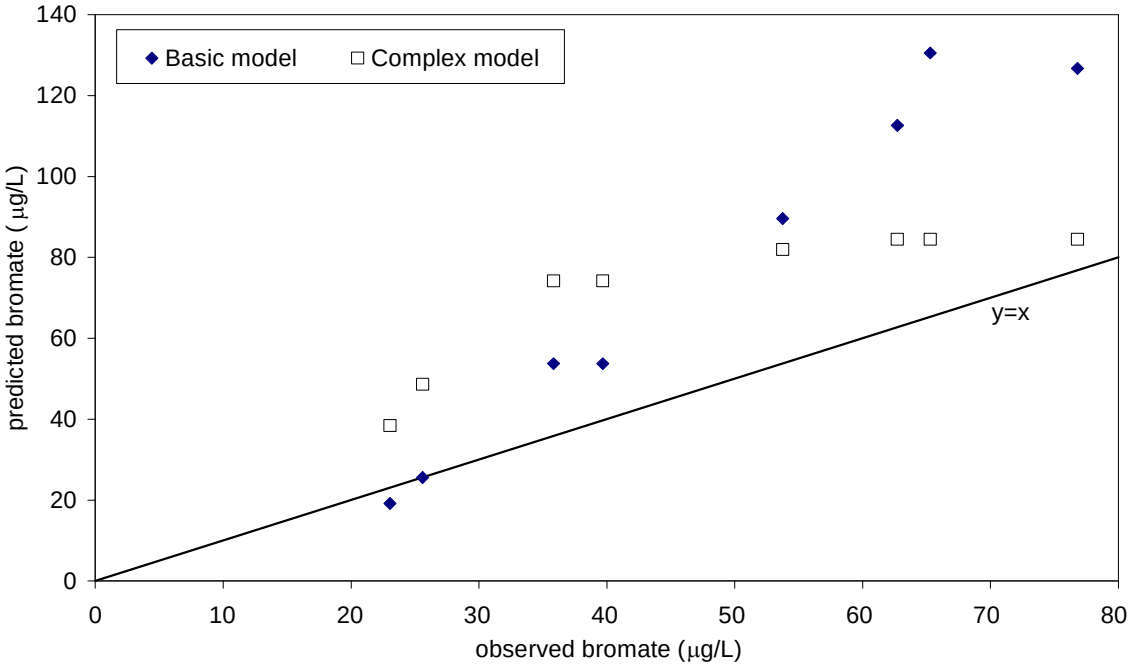


Figure 7. The observed and predicted bromate formation for two kinetic based models for synthetic waters with added NOM isolates (data taken from Westerhoff *et al*., 1998).

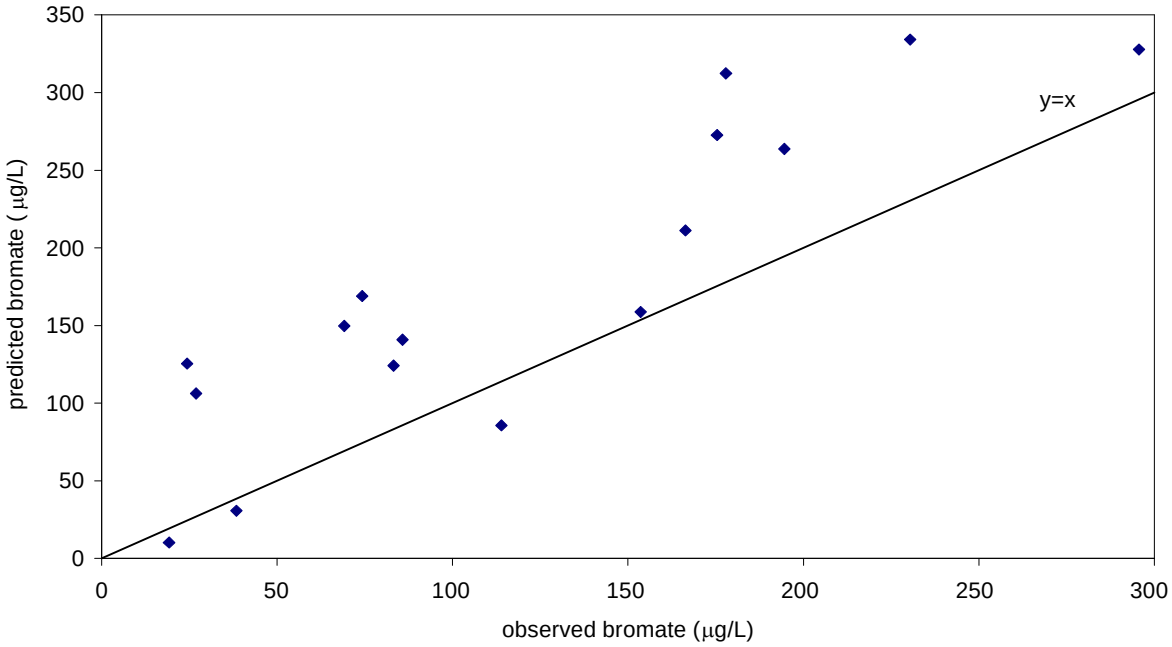


Figure 8. External validation effort of kinetic model (data taken from Hassan *et al.*, 2003).