Assessment and management of risk associated with bromate formation in drinking water

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ABSTRACT

The objective of this work is the development of a global methodology for the evaluation and management of the risk of bromate formation associated with the ozonation of drinking water in order to anticipate the upcoming regulation in 2008 regarding the bromate content in water of 10 μg/l. An aid decision tool was developed for the calculation of the risk of bromate formation using water quality data and plant operational conditions which helped to develop operational recommendation guide for ozonation process on the basis of different treatment scenario simulations. The model was adapted, tested and validated on six full scale plants located near Paris area, and can be easily used by the operators in their everyday work. The tool has shown to be efficient in prediction of the bromate risk in treated water for different water qualities and operating conditions and allowed to establish the levels of risk (low, medium and high). It can be used successfully as support to establish guidelines for risk management focusing on optimization of disinfection and oxidation processes involving ozone.

Key words | aid-decision tool, bromate formation model, disinfection by-products, ozonation of drinking water, risk assessment, treatment plant operation

INTRODUCTION

The status of the current drinking water regulation is focusing on the preventive management of health risk and obligation of means rather than obligation of results. In this context all the processes used for drinking water treatment have to be critically assessed regarding both their benefits and shortcomings. One major inconvenient of the ozonation and advanced oxidation processes used for micro-pollutants removal and disinfection is the formation of by-products such as bromates. Bromate is a genotoxic carcinogen inducing renal cell tumors in rats and therefore was declared as a potential human carcinogen (WHO 1995/2004). Bromates are not naturally present in water but they are formed when ozonating bromide-containing waters (highly variable content in a range of 10 to 1,000 μg/l). They also could be contained as impurities in sodium hypochlorite used for final disinfection. In most countries, and in particular in USA and in the European countries, drinking water standards for bromate have been set to 10 μg/l. The compliance with these standards could be sometimes a real challenge for the operators who have to maintain and optimize the performance of ozonation in order to ensure the adequate disinfection level and limit bromate formation (Galey et al. 2001; Von Gunten & Pinkernell 2000). The recent research studies showed that benefits of preventing gastroenteritis by proper disinfection (risk of infection by C. parvum cryptosporidiosis or severe gastroenteritis) outweighs by a factor of 10 the health losses by premature death from renal cancer due to bromate formation (Havelaar et al. 2000). Therefore the key question which the water treatment operators are facing is how to ensure adequate disinfection of Cryptosporidium using ozone (Amy et al. 2000; Rennecker et al. 1999) without compromising compliance with bromate levels targets? In this context it becomes crucial for drinking water operators to follow a methodology helping them to better assess and...
manage the bromate-related risk and establish a decision tree tool to give recommendations regarding the water treatment processes optimization, accounting for the current and future water quality regulation.

In response to this growing concern and need, a predictive aid-decision tool has been developed estimating the bromate potential formation and providing the required elements to anticipate the risks and establish the adequate plant operating conditions. The tool is based on the requirements of the HACCP (Hazard Analysis Critical Control Point) risk assessment approach.

**APPLICATION OF THE HACCP APPROACH FOR DEVELOPMENT OF A METHODOLOGY AND A TOOL FOR ASSESSMENT AND MANAGEMENT OF RISK OF BROMATE FORMATION**

The 3rd edition of the Guidelines for drinking water quality from the World Health Organization have introduced a preventive approach for the water quality management. This approach, based on the HACCP principles, requires the identification of the site-specific hazards and of the associated control measures. In the case of bromates, even though parametric values exist, the current knowledge on the type of raw water resource and the presence of different treatment strategies allow today to apply such an approach and control the bromate formation by using appropriate water quality monitoring and aid decision tool for plant operation.

Developing a water safety plan requires the identification of the site-specific hazards, the implementation of on-line monitoring (focused on critical points) and the establishment of management procedures (for routine and crisis). The available knowledge on the formation pathways of bromate during drinking water ozonation, and on the performance of the treatment steps applied for drinking water production, allow today to apply such an approach. One of the most important steps of a water safety plan is hazard analysis, which includes hazard identification, hazard prioritization, and identification of control measures. It is important to underline that without any value on the maximum acceptable concentration for the human, no precise or quantitative objective of treatment performance can be defined, and this approach can only be qualitative.

**Exposure of the consumer**

Research is being conducted to determine whether BrO$_3^-$ is a direct or indirect carcinogen and the findings could change the risk assessment. Several studies have been conducted in Europe, USA and in Japan. The conclusion of these studies is that there is no argument to question the bromate ion carcinogenicity. The WHO and USEPA classifications regarding bromate ion are not questionable. The major limitation of the hazard characterization is the lack of data on the effects of long-term exposure in humans. The value of the dose of bromate associated with the upper-bound lifetime cancer risk of $10^{-5}$ depends on the mathematical/extrapolation model used. A provisional guideline value of 10 µg/l recommended by WHO (2004) is associated with an upper-bound excess lifetime cancer risk of $5 \times 10^{-5}$. The weight of evidence from the rat bioassays indicates that bromate has the potential to be a human carcinogen. The provisional guideline value of 10 µg/l recommended by WHO (2004) is associated with an upper-bound excess lifetime cancer risk of $5 \times 10^{-5}$. However, there are still remaining questions. The first one relates to what is carcinogenic: bromate or potassium? The mostly available data concerns potassium bromate, while little data is available on sodium bromate. At the same time the occurrence of sodium bromate is more significant. And it is supposed that sodium bromate and potassium bromate have similar behavior and effects.

The second question is about the mechanism of cancer genesis: genotoxic effect or indirect effect? It is still unknown how to extrapolate data from high doses in experimental animals to low doses in humans.

Therefore, for the moment, and based on the provisional guideline value of 10 µg/l recommended by WHO, drinking water standards for bromate have been set to this value (10 µg/l) in Europe and USA.

**Identification and prioritization of hazards**

Bromate is formed by a complicated mechanism including both reactions with molecular ozone and with OH...
radicals (Von Gunten & Hoigne 1994; Von Gunten & Oliveras 1998). These authors showed that both mechanisms contribute in an equal manner to the formation of bromate for waters with low content of organic matter. For waters with higher levels of DOC the contribution of each mechanism can be variable. However, the authors stated that the contribution of the molecular mechanism was 30 to 80% according to the type of water and the conditions of ozonation. The molecular mechanism is more selective than the radical one and it contributes mainly to the initial oxidation of bromides and the final oxidation of \( \text{BrO}_2 \) ions.

- The occurrence and formation of bromate is affected by the water quality and the ozonation process treatment objectives. The parameters influencing the water quality are: bromide content, the natural organic matter (NOM) type and level, pH, ammonia, alkalinity, ammonia, and temperature. The formation of bromate increases with the increase of the temperature. The effect of the temperature on the kinetics of the chemical reaction follows the Arrhenius law: it is critical to take it into account for surface waters exposed to seasonal variations as the higher is the temperature, the higher is the risk of bromate formation (usually occurring in summer).
- The operational parameters influencing the ozonation process are: the transferred ozone dose (TOD), the residence time in the contactor, the type of contactor, the ozone residual, the total applied CT value.

Identification of control measures

The large amount of available data on the efficiency of the different treatment steps applied for drinking water production allowed to identify the appropriate BAT (best available technologies) for minimizing the risk for the consumer regarding pathogen removal and by-products formation control. When ozone is used to target inactivation credit higher than 1 log of more resistant pathogens like Cryptosporidium the applied doses can appear to be critical in relation to bromate formation. Therefore, the key control parameters and solutions for bromate minimization are determined on the basis of the kinetics of the first oxidation step in the bromate formation mechanism, i.e. the oxidation from bromide to hypobromous acid (\( \text{HOBr} \)). This step is controlled by the bromide content, the pH and the presence of ammonia.

- **pH decrease** can influence bromate formation by shifting of \( \text{HOBr}/\text{OBr}^- \) equilibrium to \( \text{HOBr} \). For moderate amount of bromides in surface waters at \( \text{pH} = 8 \) bromates are formed at levels well in excess of the MCL for 1 log of Cryptosporidium inactivation while at \( \text{pH} = 7 \) a 1.5 log inactivation of Cryptosporidium can be achieved without exceeding the MCL of 10 \( \mu \text{g/l} \) for bromate. Lowering the pH to minimize bromate formation has the added cost benefit of decreasing the ozone dosage.
- **Ammonia** present in water helps to selectively scavenge \( \text{HOBr} \) under formation of \( \text{NH}_2\text{Br} \), because ammonia reacts quickly with \( \text{HOBr} \) but not with ozone. Some authors (Buffle & Von Gunten 2004) found that ammonia addition could reduce bromate formation in some cases by 40%. The efficacy of this reaction is strongly influenced by NOM, bromide and ozone dosage. However, ammonia addition in drinking water treatment plants is not allowed in France (Buffle & Von Gunten 2004).
- Control of the bromide level can be achieved through accurate management of the resource. For example, blending of waters if different resources are available with various bromide concentrations can be adopted to reduce the maximal bromide level in the feed source.

Methodology for critical control points (CCP) identification

The main control points have been established:

- Definition of the treatment goal of the ozonation step on the treatment line (targeted pollutant removal, treatment objectives) and the expected performances (removal credit) on the basis of the acceptable risk level.
- Data base constitution using existing and/or newly generated data for raw and treated water quality (temperature, pH, bromides, bromate, specific parameters such as micro-organisms or micro-pollutants) and ozonation process operational data (contactor design, hydraulic conditions, ozone generation and transfer, flow rate production, applied ozone and targeted residual ozone, CT).
Control of purity of liquid chlorine chemical added before or after ozonation (limit trace of brominated pollutants).

The risk assessment tool development

The tool is based on a model for bromate formation reaction simulation and prediction of the risk to get non-compliance with the 10 µg/l target for bromate in the treated water. The bromate formation modelling has been extensively studied by different researchers (Haag 1983; Von Gunten & Hoigné 1994). To date, a complex model based on the various identified kinetic rates is being proposed (Von Gunten & Oliveras 1998). However, the ozonation process is also driven by the hydraulics and variable contactor operating conditions (Roustan et al. 1991). Therefore, in order to better predict the bromate level formation, it appeared necessary to combine both kinetics and hydraulic models. Recent works by Kim et al. (2007) and Tang et al. (2005) simulate bromate formation in a full scale ozone contactor.

The model which has been used in this study has been previously published (Roustan et al. 1996) and further improved (Do-Quang et al. 1999). Integrating recently published in the literature findings, newly collected operational data and full scale feedback, the accuracy of the bromate formation model has been further enhanced and a predictive tool for the bromate risk control developed. The model is able to predict the maximum CT value (ozone residual × contact time) to be applied to comply with the 10 µg/L MCL for bromate in the treated water. A specific database integrated in the model and containing relevant information (such as inactivation constants, concentrations) on different micro-pollutants (e.g. pesticides, taste and odor compounds) and micro-organisms (e.g. Cryptosporidium) allows to relate the CT value to the respective disinfection/oxidation efficiency. The model integrates inactivation kinetics data within a continuous flow reactor taking into account the specific hydrodynamic model established from the specified geometrical characteristics and operational conditions of the reactor. The input parameters for the model are the different water quality data (ozone demand, ozonation kinetic, temperature, pH, bromide), the ozone contactor data (dimensions, inlet/outlet water and gas locations, ozone concentration in the gas phase, gas flow rate, water flow rate). The output parameters from the model are: ozone treatment rate, ozone residual evolution in the reactor (profile in space or time), profile of the CT value in the reactor, micro-organisms inactivation or micro-pollutant oxidation profiles, bromate concentration evolution between the inlet and the outlet of the reactor. The model was adapted, tested and validated on six full scale water treatment plants potentially exposed to the bromate risk, over the past 2 years period.

APPLICATION ON FULL-SCALE WATER TREATMENT PLANTS

Site description and water quality issues

Assessment and management of bromate risk using the previously described methodology have been implemented on 6 big drinking water production sites (using groundwater or surface water) near Paris. All of the six water treatment plants have a conventional treatment line composed of a full clarification step (coagulation/flocculation/settling), followed by a first stage filtration, post-ozonation step, second stage GAC filtration and final chlorination. Table 1 summarizes the most relevant data for this study on the different sites. Pre-ozonation is applied without ozone residual on sites 2 and 3, for algae control without specific effect on bromate formation. The clarified waters before post ozonation on these six sites have near average composition: average alkalinity 15–20 µequiv/L, ammonium concentration = 0.1 mg/L, DOC = 2–2.5 mg/L. Bromide level is variable and higher for the ground waters than this observed for the studied surface waters; pH of the clarified water is variable on the sites, depending on the raw water seasonal composition (presence of algae) and on the operating way of the clarification processes and specially when acidification is applied for enhanced coagulation.

Different ozone contactors are designed on these sites (Deep U Tube, in-line ozone injection, bubble diffuser contactor). On all the sites, ozonation is used to reach a disinfection goal of 0.5 to 1.5 log inactivation of Cryptosporidium. The ozonation is used as well to oxidize the natural organic matter, in particular on site 4, and to oxidize micro-pollutants (phenol, taste- and odor-causing...
Table 1 | Summary of the studied water treatment plants

<table>
<thead>
<tr>
<th>Site</th>
<th>Capacity (m³/h)</th>
<th>Bromide (μg/l), T (°C)</th>
<th>Water quality parameters (Min/Max)</th>
<th>pH raw water, pH water before ozonation</th>
<th>Goal for ozone use</th>
<th>Ozonation process, Ozone residual (mg/l)</th>
<th>Bromate risk</th>
<th>Bromate control strategy</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,000/4,000</td>
<td>(Br⁻): 50/70, T: 5/28</td>
<td>Surface water, 7.5, 7.8</td>
<td>0.5 to 1 log Crypto inactivation</td>
<td>Deep U Tube, 0.2/0.6</td>
<td>Low to medium</td>
<td>Bisulfite, or PAC addition After contactor</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1,500/3,000</td>
<td>(Br⁻): 50/70, T: 5/28</td>
<td>Groundwater &amp; reservoir 7.2, 8</td>
<td>1.5 log Crypto inactivation</td>
<td>Large scale bubble diffuser contactor</td>
<td>Medium</td>
<td>pH control</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>500/2,500</td>
<td>(Br⁻): 50/80, T:5/28</td>
<td>Surface water, 7.4, 8</td>
<td>0.5 to 1 log Crypto inactivation</td>
<td>In-line ozone injection</td>
<td>Medium to high</td>
<td>pH control and CT regulation</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>3,000/9,000</td>
<td>(Br⁻): 50/70, T:5/28</td>
<td>Surface water, 7.2, 7.6</td>
<td>UV absorbance value reduction, 0.5 log Crypto inactivation</td>
<td>Optimized plug flow bubble diffuser contactor, 0.3–0.6</td>
<td>Medium</td>
<td>CT control</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>500/1,200</td>
<td>(Br⁻): 100/250, T: 12/20</td>
<td>Ground water (wells) 7.4, 7.8</td>
<td>Micro-pollutant oxidation, 0.5 to 1 log Crypto inactivation</td>
<td>In-line ozone injection</td>
<td>Medium to High</td>
<td>Bromide control in the raw waters. Ozone residual</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1,500/6,000</td>
<td>(Br⁻): 100/250, T: 12/20</td>
<td>Ground water (wells) 7.4, 7.8</td>
<td>Phenol oxidation, disinfection</td>
<td>Large volume bubble diffuser contactor</td>
<td>High</td>
<td>Bromide control in the raw waters. Ozone residual</td>
<td></td>
</tr>
</tbody>
</table>
compounds) in particular on sites 5 and 6. The difference between the six WTPs lies mainly in the bromide content of the raw water (ground water or surface water) and in the applied CT values (depending on the type of reactor).

For all sites, the ozonation process regulation is based on the on-line control of the dissolved ozone residual at the reactor outlet. On all the sites, an increase of the bromate concentration between the reactor outlet and the granular activated carbon (GAC) step inlet has been observed, due to the presence of significant ozone residual and high contact time. Bromate level in the final treated water is close to the concentration measured at the GAC inlet which means that no more bromates are formed after the GAC.

For these sites, the bromate risk levels have been defined, as a function of the measured bromate concentration in final treated water for 2005–2006 period collected from monthly (from November to April) and weekly (from May to October) sampling. The three risk levels have been defined as:

- Low risk = bromate concentration in final treated water lower than 10 μg/l.
- Medium risk = bromate concentration in final treated water between 10 and 25 μg/l.
- High risk = bromate concentration in final treated water higher than 25 μg/l.

**Risk assessment results**

On all these sites, the risk of bromate formation has been identified through simulations made by the predictive tool adapted for each case. The model simulations and predictions were in agreement with the measured experimental data as shown on Figure 1 (example given for site 2). Similar correlations have been obtained for all the sites, allowing to validate the model and achieve a confidence interval for the predicted risk values of 20% on average.

Example of bromate and *Cryptosporidium* risk evaluation is illustrated Figure 2 for site 6. Bromates concentration is given versus the production flowrate on this site, for a constant applied ozone residual, corresponding to a variable applied CT or *Cryptosporidium* inactivation. This illustration is given for a constant level of bromide, a constant pH and temperature. This figure illustrates the optimal operation condition in terms of production flow rate, (1,700 < Q m³/h < 3,200), linked with no risk to form bromate and no risk to have less than 1 log inactivation of *Cryptosporidium* on this site.

**CONCLUSION**

To compare the positive and negative health effects of drinking water disinfection it is accepted today to apply the DALYs (disability adjusted life-years) measure. Studies show that benefits of preventing cryptosporidiosis or severe gastroenteritis by proper disinfection outweighs health losses by premature death from renal cancer by a factor of 10 (Havelaar et al. 2000). On the other hand, ozonation in combination with chlorination decreases the concentration of trihalomethane in treated water and eliminates some of the mutagenicity of raw water, thus reducing the risk of
bladder cancer (Chevrier et al. 2004). This is the basic approach used in the development of the tool for bromate risk assessment: different strategies have been applied to control bromates by optimizing disinfection and oxidation. Operating conditions (pH regulation, applied ozone residual) have been established based on measured and simulated bromate values, depending on water quality variation (temperature, bromide level) and production flow rate. For each of the six sites, accurate recommendations and best practices have been given for operators to manage ozonation depending on disinfection objectives for water quality and condition of production variable with time. Different solutions have been applied on full-scale sites for consensus between proper disinfection for Crypto-
sporidium and compliance with bromate MCL with the help of the risk assessment tool. Site specific bromate formation control strategies have been identified for each plant (CT control, pH control, bromide content control).

ACKNOWLEDGEMENTS

The authors would like to acknowledge the water treatment plant operators Antony Corbin, Pierre Pierronne and Michel Conan from Lyonnaise des Eaux Group for their significant contribution to the success of this project, namely in the application and validation of the developed tool on the different full-scale water treatment plants.

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