

IMPACT OF OZONE DOSE ON BROMATE FORMATION IN WATER WITH HIGH BROMIDE CONTENT AND HEALTH EFFECT

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Abstract: Formation of bromate is of a great concern whenever ozonation is used for treating bromide-containing water ever since bromate was classified as a potential carcinogen. This study examines the impact of dose ozone on the bromated formation in groundwater rich in bromide and to estimate the health risks to population due to ingestion. Results of estimated excess cancer risk and chemical toxicity risk to population due to ingestion of treated water were presented and discussed.

Keywords: bromide, bromate, ozonation, drinking water, risk assessment

Introduction

As a powerful oxidant, ozone is becoming increasingly popular in water treatment works because it may efficiently reduce the bacteria, viruses, and protozoans within a short reaction time, reduce or eliminate the color, taste and odor problems in drinking water and effectively remove a variety of organic compounds (Wang et al., 2014). One major drawback of oxidative water treatment is the formation of disinfection byproducts (DBPs), that might be of human or environmental health concern. Ozonation of natural waters in the presence of organic compounds and significant bromide levels can cause the harmful formation of brominated organics and bromate ions (Garcia-Villanova et al., 2014).

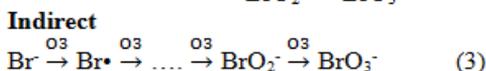
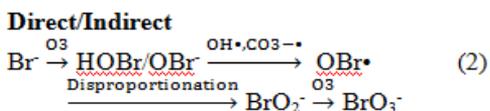
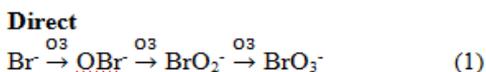
Bromate is the most potent carcinogen among the regulated DBPs and it is considered a possible human carcinogen by some organizations (WHO, USEPA). Its ability to produce oxidative stress, resulting in damage to DNA, may play a role in its ability to induce renal tumors (Rishadson et al, 2007). Bromate is classified as possibly carcinogenic to humans (Group 2B). Several methods of extrapolation permitted the WHO to derive a healthbased value of 2-6 $\mu\text{g L}^{-1}$ in drinking water associated with an upperbound excess cancer risk of 10^{-5} . However, a provisional guideline value of 10 $\mu\text{g L}^{-1}$ is maintained because of limitations in available analytical and treatment methods (WHO, 2008).

If raw water contains bromide, bromate can be formed in the ozonation step via complex mechanism in which molecular ozone and hydroxyl radical ($\text{OH}\cdot$) through three major pathways (reactions (1)-(3)). Bromide is initially oxidized either directly by ozone or indirectly by $\text{OH}\cdot$. Ozone oxidizes Br^- to HOBr/OBr^- , a decisive intermediate in bromate formation. HOBr and OBr^- can be further oxidized by radicals (defined as the direct/indirect pathway), but only OBr^- can be oxidized by ozone (defined as the direct pathway). Hydroxyl radicals oxidize Br^- to $\text{Br}\cdot$, which is either oxidized by

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ozone or converted to OBr⁻ and subsequently oxidized by radical or ozone, collectively defined as indirect pathway (Parrino et al., 2014). In addition, the bromated content in water is determinate by a number of factors, such as the initial bromide and ammonia content, ozone dose and the exposure time, pH, total alkalinity and many others.



Low levels of bromide (< 20 µg L⁻¹) are found unproblematic for bromine-derived byproducts. For bromide levels in the range 50-100 µg L⁻¹, excessive bromate formation may already become a problem. Depending on the treatment goals, bromate formation can become a serious problem for bromide levels above 100 µg L⁻¹ (von Gunten, 2003). A lot of authors showed that the production of bromate increases with increasing ozone dose and concentrations of bromide present in water (von Gunten, 2003, Legube et al., 2004).

The main goal of this research was to investigate under laboratory conditions the effect of ozonation process on the bromate formation in water with high bromide content. At the same time, the potent health risk to population due to ingestion of treated water was investigated.

Materials and methods

Experimental procedures: Ozonation was carried out at the natural pH in a 2 L glass column, 85 mm in diameter. Ozone was generated electrochemically by *Argentox* ozone generator with a capacity of 1 g h⁻¹, and introduced to the water via a diffuser at the bottom of the column at a flow rate of 7 L h⁻¹, in order to achieve the transferred ozone concentrations of 0.5-3.0 mg O₃ mg DOC⁻¹. After ozonation, excess ozone was removed by nitrogen flow. The ozone doses were chosen to investigate the influence of lower and higher ozone doses on mechanism of bromide oxidation and bromate formation in groundwater.

Analytical methods: Water samples were analyzed for dissolved organic carbon (DOC) content on an Elementar LiquiTOC II, which uses combustion at 850 °C to oxidize the carbon. The UV₂₅₄ absorbance measurements were performed in accordance with standard methods (APHA, 2012) on a PG Instruments LtdT80+ UV/VIS spectrophotometer at a wavelength of 254 nm, with a 1cm quartz cell, and the specific ultraviolet absorbance values (SUVA, defined as 100xUV₂₅₄xDOC⁻¹, expressed in L mg⁻¹ m⁻¹) was calculated. pH measurements were carried out on a WTW InoLab portable instrument. Water alkalinity was measured by standard volumetric method

(APHA, 2012). Bromide and bromate content was measured according to USEPA methods 317 and 326 on a DIONEX ICS-3000 Ion Chromatography System (USEPA, 2000b, 2002). The concentration of ozone transferred to the water was calculated from the difference in the input and output ozone concentrations in the gas phase, which were measured under standard conditions (273 K and 101.3 kPa) by iodometric titration (APHA, 2012).

Risk Assessment

For this study, two types of risks were evaluated, separately, because the human health effects can be classified as carcinogenic risk and chemical toxicity risk. Firstly, the excess cancer risk due to ingestion of bromate in ozonated water was evaluated based on the general US EPA standard method. After ozonation process bromate content was determined and such a risk assessment is carried out under the assumption that the bromate contents will not changed significantly after further water treatment.

Methodology of Excess Cancer Risk Assessment: The Individual excess cancer risk (IECR) can be evaluated by the following expression where UR_0 is the risk factor expressed as $(\mu\text{g L}^{-1})^{-1}$ due to ingestion of drinking water and US EPA, has considered the toxicological values of inorganic bromate for the cancer risk calculation at the case-study area, $UR_0 = 2 \times 10^{-5} (\mu\text{g L}^{-1})^{-1}$. C_{bw} is the estimated concentration of bromate in ozonated water, expressed as $\mu\text{g L}^{-1}$ (Kumar et al., 2011).

$$IECR = UR_0 \cdot C_{bw} \quad \text{(Equation (1))}$$

Methodology of Chemical Risk Assessment: Secondly, to evaluate the hazard quotient for bromate, the chemical toxicity risk as lifetime average daily dose (LADD) was estimated with the help of Equation (3) (USEPA, 2000) and was compared with the reference dose (RfD) of $0.372 \mu\text{g kg}^{-1} \text{day}^{-1}$ which is calculated on the basis of maximum acceptable level of bromate ($10 \mu\text{g L}^{-1}$) in drinking water. Here, the water ingestion rate was set as 2 L day^{-1} which is similar to the upper-bound level of adult daily intake recommended by US EPA (1991). 350 days for exposure frequency (US EPA, 1991) and 75 years for total exposure duration i.e. the average all Serbia life expectancy for both males and females, 27375 days for average time and 70 kg for body weight (Sohn et al., 2006). The hazard quotient (HQ) and chemical toxicity risk (LADD) was calculated through ingestion of bottled water by the following formula (Kumar et al., 2011):

$$HQ = \frac{LADD}{RfD} \quad \text{(Equation (2))}$$

$$LADD (\mu\text{g/kg/dan}) = \frac{Ci \times IR \times EF \times LE}{AT \times BW} \quad \text{(Equation (3))}$$

where, Ci = Concentration of bromate in bottled water ($\mu\text{g L}^{-1}$), IR = Ingestion rate (L day^{-1}), EF = Exposure frequency (days year^{-1}), LE = Life expectancy (years), AT = Average Time (days), BW = Body Weight (kg), RfD = Reference Dose ($\mu\text{g kg}^{-1} \text{day}^{-1}$), $LADD$ = lifetime average daily dose, ($\mu\text{g kg}^{-1} \text{day}^{-1}$).

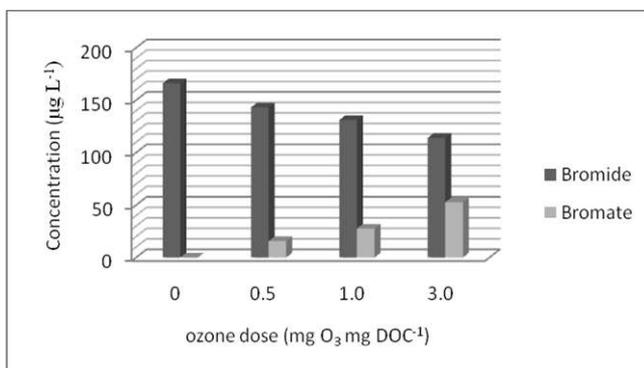
Results and discussion

A summary of the chemical characteristics of these groundwater from Serbia are presented on Figure 1. The results showed that groundwater has low values of DOC and UV₂₅₄ (Table 1), what means that investigated water contained a low organic matter content. The raw water has moderate SUVA value (3.23 L mg⁻¹ m⁻¹) suggesting this water contains a mixture of hydrophilic and hydrophobic organic matter different molecular weight (Croué et al., 2000). The high bromide content present in water (160 µg L⁻¹) allows the formation of high concentrations of brominated DBPs and bromate during oxidation water treatment.

Table 1. Characterisation of the raw groundwater

Parameter	Unit of measurement	Mean value
pH	-	7.7±0.2
Total alkalinity	mg CaCO ₃ L ⁻¹	1016±36
DOC	mg L ⁻¹	2.50±0.22
UV ₂₅₄	cm ⁻¹	0.08±0.01
SUVA	L mg ⁻¹ m ⁻¹	3.23±0.11
Bromide	mg L ⁻¹	0.16±0.10

Effects of ozone dose on bromate formation in water are shown in Graphic1. Ozonation of groundwater leads to the formation of bromate, whose content in water increases with increasing ozone dose (up to 52.6 µg L⁻¹). At the same time, bromide content decreased as a result of bromate formation. To the same conclusions, that the production of bromate increases with increasing ozone dose and concentrations of bromide present in water, reached by the other authors (von Gunten, 2003). In investigated water the bromate content after ozonation exceeds the maximum value in the drinking water of 10 µg L⁻¹ at all tested ozone doses.



Graph. 1. The impact of ozone dose on bromate formation in groundwater during ozonation

The individual excess cancer risk due to ingestion of bromate in ozonated water at an average of 2 L day⁻¹ over the lifetime expectancy of 75 years for a Serbian adult are present in Table 2. The values for excess cancer risk increased with increasing ozone dose during treatment and showed about one order of magnitude higher than the maximum acceptable level (2×10^{-5}) as per guide lines of US EPA. In the worst case, when the highest ozone dose was used, the excess cancer risk was expected to be about 9.5 per ten thousand people. In Sohn et al (2006) study, the calculated health risk for bromate ranged from 1.4×10^{-4} to 1.3×10^{-3} (average of 4.3×10^{-4}) for the ten source waters.

Table 2. Health risks (excess cancer risk and chemical toxicity risk) (procentile 95th) due to ingestion of bromate in ozonated water

Ozone dose (mg O ₃ mgDOC ⁻¹)	Excess cancer risk (x 10 ⁻⁴)	Chemical Toxicity risk (LADD)	Hazard Quotient (HQ)
0.5	2.96	0.400	1.0
1.0	5.22	0.715	1.9
3.0	9.50	1.368	3.6

To evaluate the chemical toxicity risk of bromate, the lifetime average daily dose (LADD) of bromate through ingestion was estimated at different ozone doses and compared it with the reference dose (RfD) of 0.372 µg kg⁻¹ day⁻¹ and thereby produced a hazard quotient (Table 2). The life time average daily dose (LADD) increased (0.400 - 1.368 µg kg⁻¹ day⁻¹) during ozonation, by considering the body weight as 70 kg of an adult Serbian reference man. The mean of hazard quotient (LADD/RfD) was also found to be slightly greater than unity indicating that bromate in drinking water is under alarming situation from the chemical toxicity point of view. In the worst case, the exposure dose determined to be 3.6 µg kg⁻¹ day⁻¹ which is 3 - 4 times higher than RfD. Approximately, the same number of times bromate content is higher than the reference value of 10 µg L⁻¹. All conclusions are in accordance with the regulations, the risk is significantly increased because the bromate content is up to five times higher than the exposure limits, which are also based on health risks.

Conclusion

In the studied water during ozonation leads to the bromate formation, whose content increases with increasing ozone dose. Bromate concentration exceeds the maximum allowed value in drinking water of 10 µg L⁻¹ at all tested doses of ozone. The exposure level of bromate was comparatively high and the chemical toxicity in turn is also presumed to be greater. Therefore, it is suggested that either bromide (precursor of bromate) should be removed using different techniques. Because of the large number of factors that influence bromate production, it will be necessary to optimize treatment by balancing the advantages and disadvantages of various measures on an individual basis for each water supply.

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