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Formation and Reverse Osmosis Removal of Bromate Ions during Ozonation of Groundwater in Coastal Areas

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Abstract: The generation of bromate ions during ozonation of groundwater samples affected by seawater intrusion was investigated. The ozone-water contact times studied were 2.5, 5, 10, 15, and 30 min, while the applied ozone rate was 4.5 mg/min. Generation of bromate ions started right after the application of ozone. The level of bromates increased with time as more ozone was added to the reactor. Even after 30 min of ozonation, the concentration of bromates kept rising without reaching a plateau. The higher the initial concentration of bromide ions, the higher the level of bromate ions in the ozonated water sample. The experimental results obtained during ozonation of the specific groundwater samples (low TOC and low ammonia concentrations) were used in order to develop a mathematical model capable of forecasting the generation of bromate ions. The empirical model containing two independent variables, conductivity and contact time, was:

$$\lfloor BrO_3^- \rfloor = e^{-10,157} * [\text{Conductivity}]^{1,5466} * [\text{Contact Time}]^{0,94031}, R^2 = 0.8568$$

This model allows the prediction of bromate ion generation, when the groundwater conductivity and the contact time are known, for an ozone application rate around 4.5 mg/min. Finally, the ozonated water was treated by reverse osmosis. The removal of bromate ions reached 96.1%. Equivalent reduction in the conductivity of the water was also achieved.

Keywords: Bromate, ozonation, reverse osmosis

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INTRODUCTION

In coastal areas, seawater intrusion into the groundwater table may result in significant deterioration of groundwater quality. This phenomenon may be intensified during the summer months, when increased water requirements (both for drinking purposes and irrigation) result in increased pumping and therefore, in further deterioration of the groundwater quality. In addition to the increase of the salinity of groundwater, enrichment of the groundwater with specific substances and ions present in seawater may result in the generation of undesired chemicals during disinfection intended for drinking purposes. Such an undesirable substance is the bromate ion, which may be produced during ozonation of groundwater, which has been enriched with bromide ions from sea water.

The application of ozone in drinking water treatment has been increasing, since its use does not promote the formation of trihalomethanes inherent in chlorination. However, ozone is also responsible for the formation of various organic and inorganic by-products (1). The bromate ion (BrO_3^-) is the most important by-product, because it has been classified as a genotoxic human carcinogen (2). It is formed as a result of oxidation of bromide ions (Br^-) and a maximum contaminant level has been set both by the EPA and the European Commission at 10 μg/L. The generation of bromates during ozonation of bromide containing water has been attributed to a mechanism that involves both molecular ozone and hydroxyl radical reactions (3–7). Factors affecting the generation of bromate ions include the bromide concentration, the organic matter content, the ozone dose, the pH, temperature, alkalinity, and the ammonia concentration (5, 8–10). Control of the bromate level may be possible by means of activated carbon adsorption, UV radiation, pH reduction, or ammonia addition (11–14). There are limited studies examining the use of membrane processes, such as reverse osmosis or electrodialysis, on bromate ion removal (13). More recently, membrane biofilm reactors have demonstrated the ability to reduce bromate ions, as well as other oxidised contaminants (15, 16).

One particular application of ozone disinfection is in the bottled water industry. In tourist areas, bottled water is a major water product during the summer months. In many countries, most of the bottle water industries are small enterprises and they do not have the personnel and analytical infrastructure to monitor the generation of bromate ions. It is therefore important that in these cases simpler methods of bromate ion prediction and monitoring be developed. In a previous study, bromate formation due to ozonation of groundwater in coastal areas was satisfactorily modeled by an empirical exponential model (17). The measurements of conductivity, ozone dose, and time were sufficient for the estimation of bromate ion production during ozonation of water containing low DOC and ammonia concentrations.

The aim of this work was to evaluate the formation of bromate ions during ozonation of groundwater coming from coastal areas in Western Greece. In addition, an empirical model based on easily-measured variables was developed in order to assess the influence of water quality characteristics and treatment conditions on bromate formation during ozonation. Finally, the removal of bromate ions by means of Reverse Osmosis was investigated, since there is limited relevant information on the application of this method for bromate removal from water.

EXPERIMENTAL

Water Samples

Water samples were collected from 7 wells from the plains of Arta (Samples A1 to A7) in the vicinity of Amvrakikos bay, and 2 wells from the island of Zakynthos (Samples Z1 and Z2). Sampling took place in October 2004. The sampling period was at the end of the dry season and therefore, the effect of seawater intrusion on the quality of groundwater was expected to be most severe. The samples were analyzed for Br^-, Cl^-, pH, conductivity, turbidity, alkalinity, DOC and NH_4-N (Table 1). In addition, a synthetic water sample (S1) was prepared by mixing seawater with unchlorinated drinking water (1:15 volume ratio). This latter sample was used for the study of bromate ions removal after ozonation and reverse osmosis.

Experimental Set-up

Ozonation Experiments

Ozone was produced by supplying dry air to an Aqua-Flo CD1B ozone generator. The air flowrate was 140 L/h. The ozonator outlet was connected to the ozonation reactor through Teflon tubing. The ozonation reactor was a glass cylindrical reactor with a volume of 500 mL. The operation of the ozonation reactor was in the semi-batch mode, i.e. the water sample was introduced into the reactor in the beginning of the operation, while the addition of ozone took place continuously during the experimental run through a stone diffuser. The ozone stream leaving the reactor was trapped in two glass traps containing a solution of 2% KI. Prior to each ozonation experiment, the ozone application rate was measured by directing the ozone stream into two KI traps in series for a period of 10 min.

During each ozonation experiment, 250 mL of water was placed in the ozonation reactor and ozone generated in the ozonator was bubbled through. For each water sample a series of ozonation experiments took place by varying the contact time. Contact times studied were 2.5, 5, 10, 15, and 30 min. When the desired contact time had been reached, the supply of ozone was stopped and a sample was taken for the measurement

Table 1. Characteristics of water samples

Constituent	A1	A2	A3	A4	A5	A6	A7	Z1	Z2	S1	Legislation
Cl^- (mg/L)	12	12	12	128	57	55	14	455	216	1622	250[a]
Br^- (mg/L)	<0.1	<0.1	0.1	0.5	0.3	0.1	<0.1	1.5	1.3	6.87	
SO_4^{2-} (mg/L)	96.3	111.6	118.3	2	77.5	66.9	132.3	206	125.1	235.5	250[a]
NO_3^- (mg/L)	6.6	0.1	<0.05	0.5	<0.05	<0.05	6.2	213	17.5	76.3	50[b]
Ammonia-N (mg/L)	<0.01	0.015	0.084	4.60	2.07	0.50	<0.01	0.05	0.13	<0.01	0.50[a]
pH at 20°C	7.40	7.72	7.40	7.32	7.35	7.88	7.55	7.12	7.23	6.81	
Conductivity (μS/cm)	509	554	566	10499	850	810	547	2370	1800	4960	2500[a]
DOC (mg/L)	0.70	0.44	0.55	1.53	1.26	1.06	0.45	1.82	1.91	1.79	
Alkalinity (mg/L $CaCO_3$)	163	183	184	386	302	290	147	402	560	126	

[a] Indicative value.

[b] Maximum limit.

of the residual ozone. Then, the residual ozone in the reactor was destroyed by adding 0.25 mL of a 5% ethylenediamine solution, and an appropriate amount of ozonated water sample was withdrawn for bromate analysis.

Reverse Osmosis Experiments

The Reverse Osmosis (RO) pilot unit used for the evaluation of the removal of bromate ions was manufactured by GE-OSMONICS (model RO-E2-O375-DLXS). The membrane of the pilot unit was a 1.2 m^2 spiral wound synthetic membrane. The operating conditions of the RO unit are presented in Table 2. The RO pilot unit was fed with the synthetic groundwater S1, which had undergone ozonation under intense ozonation conditions (ozone application rate 12.84 mg/min, contact time 10 min). Prior to feeding the RO unit, the water sample was allowed to stand for 24 h in order to allow complete decomposition of all residual ozone.

Analytical Methods

Residual ozone was measured spectrophotometrically according to standard method 4500-O_3, "Indigo Colorimetric Method" (18). Ozone gas-phase concentration, or equivalently ozone application rate, was determined by bubbling ozone for 10 min through two serial traps containing a solution of 2% potassium iodide. The content of each trap was then titrated with a sodium thiosulfate solution, according to the method 4500-Cl (19).

Ammonium concentrations were measured by the colorimetric method of Merck, with a detection limit of 0.01 mg/L. Measurement of the absorbance was done at 692 nm with a SHIMADZU UV1200 spectrophotometer. Alkalinity was measured according to the standard method 2320-B (19). Dissolved Organic Carbon (DOC) measurements were conducted with a Shimadzu 5000A TOC Analyser.

Bromide, Chloride, and Bromate ions were analyzed by Ion Chromatography (Dionex DX−500). An Ionpac AS9-HC analytical and an Ionpac AG9-HC guard column were used. The detection was accomplished by

Table 2. Operating conditions of the RO pilot unit

Technical parameter	Value
Operating pressure	$15 \cdot 10^5$ N/m^2 (15 bar)
Feed flowrate	0.136 m^3/h
Flux	113.3 m^3/m^2h
Recovery	50%
Permeate flowrate	0.07 m^3/h

conductivity measurement after suppression. The eluent was 9 mM Na_2CO_3. Bromide and Chloride were analyzed with a 25 μL injection loop, changing the sensitivity, as their concentrations varied (20). To eliminate poor separation problems between bromate and chloride ions, each sample was first filtered through an Ag cartridge, in order to eliminate the concentration of chloride, and then through a H cartridge. Depending on the range of concentration of bromates, injection loops of 200 μL and 500 μL were used. Quantitative measurements of bromate were considered those at concentrations higher than 2 μg/L.

RESULTS AND DISCUSSION

Water Characteristics

The quality characteristics of the water samples are presented in Table 1. Water samples A1, A2, A3, and A7 were characterized by low conductivity and a low chloride content. These water samples came from irrigation wells near the Amvrakikos coast line, yet they were not affected by seawater intrusion. These results indicated that there was sufficient groundwater flow, even during the dry season of the summer months, that prevented seawater intrusion in the plains of Arta near the Amvrakikos bay. In terms of overall assessment, these water samples had the best quality characteristics and, as far as the chemical analysis was concerned, they could be considered proper for drinking purposes. Samples A4, A5, A6, and Z2 contained higher concentrations of chloride ions and equivalently higher values of conductivity, indicating some degree of seawater intrusion. Yet, their quality characteristics are in general within regulations as far as drinking water is concerned. Water sample Z1 had a high concentration of chloride ions and a high level of conductivity, indicating severe seawater intrusion. For comparison purposes, the quality characteristics of the synthetic water sample (mixture of seawater and unchlorinated drinking water) is also presented in Table 1.

The level of bromide ions in these water samples ranged from less than 0.1 mg/L (detection limit) to 6.87 mg/L for the synthetic water. The correlation between chloride and bromide ions in the various water samples is shown in Fig. 1. There was a linear relationship between these two ions. The slope of the straight line, indicating the ratio of Cl^-/Br^- in the water samples, was 236. This value is close to the reported ratio of Cl^-/Br^- in seawater (290) (21). This indicates that the groundwater samples had been enriched in ions as a result of seawater intrusion. Furthermore, a linear correlation existed between the bromide ion concentration and conductivity (Fig. 1). This linearity is due to the chloride ion, which constitutes the main ionic form in the water samples affected by seawater intrusion.

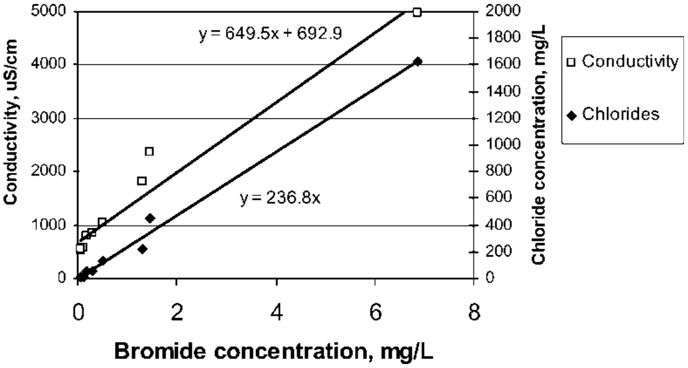

Figure 1. Correlation between bromide ion concentration with chloride ion concentration and conductivity.

Ozonation Treatment

In order to study the effect of ozonation on the formation of bromate ions, three water samples were used, namely A3, A4 and Z1. Selection of these samples was made based on their level of conductivity and concentration of bromide ions, which are precursors of bromate ions. The ozone application rate was around 4.5 mg/min (4.47 mg/min, 4.51 mg/min, and 4.66 mg/min for the ozonation of water samples A3, A4, and Z1, respectively). Figure 2 presents the concentration of bromate ions after ozonation as a function of the applied ozone dose for the three water samples. The applied ozone dose was defined as: [(Inlet ozone concentration—Outlet ozone concentration) $*$ Flowrate $*$ Contact time]/Vsample and it represents the ozone dose transferred to the water sample.

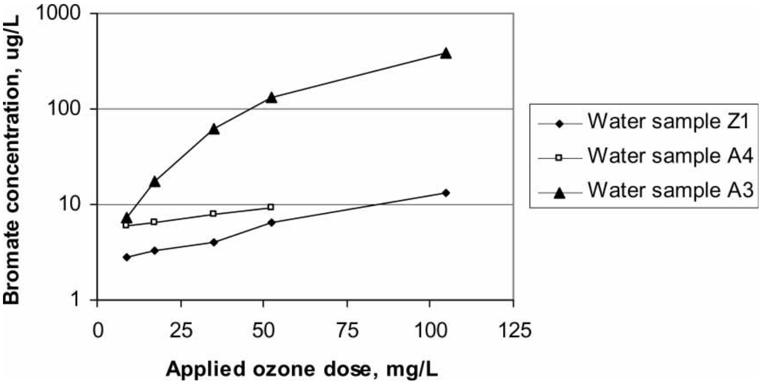

Figure 2. Effect of applied ozone dose on bromate ion generation.

Generation of bromate ions started right after the application of ozone. The level of bromates increased with time as more ozone was added to the reactor. Even after 30 min of ozonation (corresponding to an applied ozone dose of 105 mg/L), the concentration of bromates kept rising without reaching a plateau. The maximum permissible bromate concentration in drinking water of 10 μg/L was achieved in 15–25 min contact time for the water samples A3 and A4, while for sample Z1 at around 2.5 min of ozonation time. The difference among the three samples is related to the specific characteristics of the three samples, and most importantly to the initial level of bromide ions. The effect the initial concentration of bromide ions had on the formation of bromate ions is presented in Fig. 3, where it is shown that the higher the initial concentration of bromide ions, the higher the level of bromate ions in the ozonated water sample.

The product C∗T = (Concentration of Disinfectant)∗(Disinfection Time) is known as the Disinfection Criterion or Factor, and it is used by many agencies (e.g. U.S. EPA) for the effective control of disinfection. In case ozone is used as the disinfectant, this Criterion is:

$$C * T = (\text{Concentration of Residual Ozone}) * (\text{Contact Time})$$

The U.S. EPA has recommended appropriate values of the Disinfection Criterion for efficient disinfection of pathogenic micro-organisms, such as bacteria, viruses and protozoa (oocysts). This is particularly important for oocysts, such as *Giardia Lamblia* and *Cryptosporidium*, for which chlorine is not an effective disinfectant, but ozone is. Figure 4 presents the generation

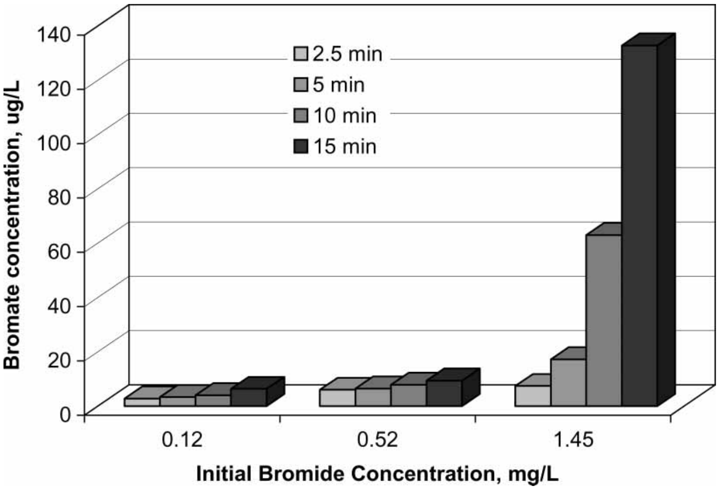

Figure 3. The effect of the initial bromide concentration on the formation of bromates during ozonation.

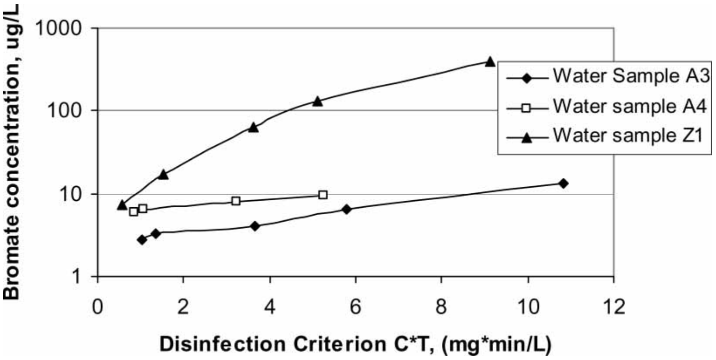

Figure 4. Bromate formation in relation to the Disinfection Criterion.

of bromate ions as a function of the Disinfection Criterion for the three water samples, respectively. As can be seen from this figure, as the Disinfection Criterion (efficiency of disinfection) increased, so did the level of bromate ions produced. Low values of the Criterion, which correspond to inactivation of viruses and Giardia, produced low levels of bromates; however, values around 10 (sometimes used for inactivation of Cryptosporidium) produced bromates at levels at or above the maximum permissible concentration, even for the low bromide water.

The experimental results obtained during ozonation of the groundwater samples were used to develop a mathematical model capable of forecasting the generation of bromate ions. Since the concentrations of ammonia and dissolved organic carbon were low, four independent variables were considered: Ozone application rate, Contact time; Conductivity; and pH. Conductivity was preferred over bromide concentration for two reasons: First, because of the linearity observed between bromide concentration and conductivity, and second, because for a small water company it would be easier to monitor water conductivity as opposed to bromide concentration. Based on Principal Component Analysis (PCA) it was found that the main variables affecting the formation of bromate ions were Conductivity and Contact Time (64,8% and 34,3% explanation of the variance, respectively). The effects of pH and ozone application rate were not significant, since these two variables did not vary much for these water samples. Following PCA, an empirical model was developed. The model contained two independent variables, conductivity and contact time. Based on regression analysis, the following mathematical expression was obtained:

$$\lfloor BrO_3^- \rfloor = e^{-10,157} * [\text{Conductivity}]^{1,5466} * [\text{Contact Time}]^{0,94031},$$
$$R^2 = 0,8568$$

This model allows the prediction of bromate ion generation, when the groundwater conductivity and the contact time are known, for an ozone application rate around 4.5 mg/min. It should be mentioned that in these experiments the ozone application rate was constant at 4.5 mg/min. The effect of varying the ozone application rate had been studied in a previous study (17). It was found that ozone application rate affected bromate formation by an additional term where the applied ozone rate was raised to 1.26.

Reverse Osmosis Treatment

There is limited information on the removal of bromate ions by Reverse Osmosis. In order to examine the efficiency of RO for bromate ion removal, the synthetic water sample S1 was intensely ozonated (ozone application rate = 12.84 mg/min, ozonation time: 10 min). This led to the generation of bromate ions at a concentration of 190.5 μg/L. This ozonated water was further treated by reverse osmosis. The treatment results are presented in Table 3. The bromate ion concentration in the permeate was 7.4 μg/L reaching a removal of bromate ions 96.1%. This bromate concentration is below the maximum permissible level of 10 μg/L. The bromate removal efficiency by reverse osmosis was similar to the one observed by van der Hoek et al. (13) for a full scale RO unit and higher for an electrodialysis membrane system (retention 64%) (13). In addition to the bromate ion level, an equivalent reduction in the conductivity of the waster was also achieved. The initial conductivity of the water (4690 μS/cm) was reduced to 217 μS/cm resulting in a reduction of 95%.

These results indicate that for a maximum level of bromates equal to 10 μg/L, the initial ozonated water could have a concentration of bromates around 250 μg/L. However, it should be emphasized that the water used for the RO study had a very high initial conductivity. If a low conductivity (salinity) water resource is used, then the high degree of conductivity removal would render it inappropriate for drinking. In this case, proper mixing of RO-treated and plain ozonated water should take place, while re-mineralization by dilution of ions from minerals is an alternative solution.

Table 3. Water characteristics during RO treatment

Water characteristic	Feed	Permeate		Concentrate	
		Concentration	%Reduction	Concentration	%Increase
BrO_3^- (μg/L)	190	7.4	96	NM	NM
Conductivity (μS/cm)	4690	217	95	10000	113

NM: Not measured.

CONCLUSIONS

According to the previous results, the following conclusions can be drawn:

- Ozonation of groundwater coming from coastal areas in Western Greece resulted in the formation of undesirable bromate ions. The bromate ion concentration increased with the applied ozone dose as ozonation proceeded. The higher the initial concentration of bromide ions, the higher the level of bromate ions in the ozonated water sample.
- For the water samples affected by seawater intrusion, ozonation resulted in the formation of bromate ions at concentrations at or higher than the maximum permissible limits at C∗T values recommended for deactivation of Cryptosporidium (5–10 mg/L min).
- An empirical model was developed that can predict the formation of bromate ions during ozonation of the specific groundwater samples. The independent variables of the model are the contact time and the conductivity of groundwater, which can be easily measured. Since the samples were characterized by low TOC and ammonia concentrations, the empirical model is expected to perform satisfactorily for these kinds of groundwater.
- The use of Reverse Osmosis proved to be very effective in removing bromate ions from ozonated water, since the rejection of bromate ions was 96%.

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