

## Trihalomethane, chlorite and bromate formation in drinking water oxidation of Italian surface waters

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### ABSTRACT

Recent regulations on drinking water have introduced very restrictive limits for oxidation/disinfection by-products (DBPs), particularly total trihalomethane concentrations (TTHMs), chlorite and bromate. Consequently many utilities are closely optimizing their disinfection practices in order to meet the regulation standards. This study evaluates DBPs formation and suggests some applicability criteria for chlorine, chlorine dioxide and ozone for different waters.

Different oxidation batch tests with chlorine, chlorine dioxide and ozone were performed on some raw water samples coming from ten representative sources in Italy: seven artificial lakes and three rivers. TTHMs, chlorite and bromate increase with increasing chlorine, chlorine dioxide and ozone dose, respectively. The Italian standard for TTHMs ( $30 \mu\text{g l}^{-1}$ ) is fulfilled by 50% of the waters for chlorine doses of  $1.1\text{--}1.2 \text{ mg l}^{-1}$ . Because chlorite concentration is about 60% of chlorine dioxide dose, the Italian standard for chlorite ( $200 \mu\text{g l}^{-1}$ ) is fulfilled for chlorine dioxide doses lower than  $0.3\text{--}0.4 \text{ mg l}^{-1}$ . The maximum concentration of  $10 \mu\text{g l}^{-1}$  for bromate can be respected only for waters with very low bromide concentration (lower than  $20 \mu\text{g l}^{-1}$ ) (von Gunten 2003).

**Key words** | bromate, chlorine, chlorine dioxide, chlorite, ozone, trihalomethane

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### INTRODUCTION

The recent 98/83 EU Directive on drinking water for human consumption and its accomplishment in the Italian Legislative Decree 31/2001 have introduced very restrictive limitations particularly for the disinfection by-products, commonly called DBPs, that are usually formed in oxidation/disinfection treatments.

Although in recent years chlorine has been increasingly abandoned in Italy because of the high formation of organo-halogenated by-products, today chlorine is applied in final disinfection for about 63% of the distributed water, chlorine dioxide for 31% and the remaining 6% by gaseous chlorine and UV radiation (Conio 1999).

When chlorine-based disinfectants are used, water in the most distant part of the network has to maintain a stable residual of free chlorine around  $0.2 \text{ mg l}^{-1}$ , according to Italian legislation (Decree of the Republic President 236/1988; Legislative Decree 31/2001).

The main chlorine disinfection by-products, known as trihalomethanes (TTHMs), which are generated by

chlorine reactions with organic matter and bromide, were regulated with a maximum concentration of  $30 \mu\text{g l}^{-1}$  by Decree of the Republic President 236/1988. This value was confirmed in the Legislative Decree 31/2001, in place of the higher limit of  $100 \mu\text{g l}^{-1}$  introduced by the European Directive, because of the toxic and mutagenic effects of TTHMs on humans (Lilly *et al.* 1997; Nobukawa and Sanukida 2001). Moreover, some authors have recently observed that inhalation instead of ingestion is an important pathway for exposure and that TTHMs can pose a serious threat for spontaneous abortion in pregnant women (Miles *et al.* 2002). For this reason, alternative oxidants such as chlorine dioxide and ozone have been introduced. However, their application can produce other by-products, such as chlorite and chlorate, generated from chlorine dioxide oxidation (Vel Leitner *et al.* 1996), and bromate, generated from ozone oxidation of bromide-containing waters (Siddiqui and Amy 1995).

For bromate, classified by the United States Environmental Protection Agency (USEPA) as potentially carcinogenic and genotoxic for humans (Wilbourn 1995), both the 98/83 EU Directive and the Italian Legislative Decree 31/2001 have introduced a maximum concentration of  $10 \mu\text{g l}^{-1}$ . For chlorite, which is not considered in the European Directive, a drinking water standard of  $200 \mu\text{g l}^{-1}$  has been introduced by the Italian Decree (with a transitory limit of  $800 \mu\text{g l}^{-1}$  from December 2003 to December 2006), as it may lead to haemolytic anaemia at low levels of exposure and to an increase in methaemoglobin at high levels of exposure (Gallagher *et al.* 1994).

These low standards could be fulfilled by removing DBPs after their formation with specific treatments or by reducing DBPs formation during the oxidation–disinfection process, as explained in the following paragraphs. The mechanisms of DBPs formation and the specific treatments for their removal have been investigated in many studies during recent years.

Trihalomethanes increase with organic matter and bromide concentration, chlorine dose, contact time, temperature and pH, while they decrease with increasing ammonia concentration (Clark *et al.* 1996; Casey and Chua 1997). Their control can be achieved by removing the main organic precursors with specific physical (coagulation/flocculation, filtration, GAC/BAC filtration) and chemical (oxidation with alternative oxidants, such as ozone, hydrogen peroxide and UV radiation) treatments before water chlorination (Kusakabe *et al.* 1990; Galapate *et al.* 2001) or by removing TTHMs with air stripping (Umphres *et al.* 1983) and activated carbon adsorption (Morawski and Inagaki 1997), which offer unsatisfactory removal efficiencies.

Chlorite occurs as the first by-product in oxidation reactions with chlorine dioxide (Korn *et al.* 2002). Approximately 60–70% of chlorine dioxide consumed is converted to chlorite. Different treatments for chlorite removal have been studied, showing satisfactory results: adding reduced-sulphur compounds, such as sulphur dioxide and sodium sulphite (Dixon and Lee 1991); adding ferrous chloride and ferrous sulphate (Katz and Narkis 2001); and applying powdered (PAC) or granular (GAC) activated carbon (Dixon and Lee 1991).

Bromate is the main by-product produced during ozone oxidation; its formation depends on ozone exposure and it generally increases with ozone dose, bromide concentration (Ozekin and Amy 1997), pH and contact time, while it decreases with organic matter, ammonia and alkalinity (Siddiqui and Amy 1993). The best bromate control strategies are pH reduction and ammonia addition (Pinkernell and von Gunten 2001). Good control of bromate formation could be obtained with the advanced oxidation of ozone combined with hydrogen peroxide, although results have been controversial (Croué *et al.* 1996; von Gunten *et al.* 1996; von Gunten and Oliveras 1998; Collivignarelli *et al.* 2000), depending on treatment goals and water quality. Also, the combination of ozone with UV radiation, though not a common practice in drinking water treatment, can reduce bromate formation (Siddiqui *et al.* 1996). However, ozone in combination with UV does not reduce bromate formation if a certain oxidation target is to be achieved. Bromate removal can also be obtained by fresh GAC adsorption (Bao *et al.* 1999), with different efficiencies depending on water quality, GAC type and loading time, and BAC filtration, particularly with low dissolved oxygen and nitrate concentrations (Kiristis *et al.* 2001).

Another interesting way to control DBPs concentration, studied in this work, is to reduce their formation by optimizing the oxidation process; this means to choose the best reagent and to optimize the process conditions (dose and contact time) based on the characteristics and DBPs precursors (organic matter, bromide, pH, alkalinity, etc.) of the raw water.

The aim of this study is to investigate the disinfection by-products (TTHMs, chlorite and bromate) formation during the oxidation of ten surface waters with chlorine, chlorine dioxide and ozone and to evaluate the reagents' applicability for different water precursors (TOC and bromide).

## MATERIAL AND METHODS

### Water characteristics

The experimental tests were performed on surface waters from ten different treatment facilities in Italy:

**Table 1** | Chemical characteristics of raw waters analysed in the experiment

Water	pH (–)	Alkalinity (meq l <sup>-1</sup> )	Turbidity (NTU)	TOC (mg l <sup>-1</sup> )	UV254 (1 cm <sup>-1</sup> )	Bromide (µg l <sup>-1</sup> )	NH <sub>3</sub> (mg l <sup>-1</sup> )	NO <sub>2</sub> <sup>-</sup> (mg l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> (mg l <sup>-1</sup> )	Chloride (mg l <sup>-1</sup> )
Lake waters										
1	8.50	2.0	7.0	3.3	0.0711	150	0.1	< DL	2.9	56.0
2	8.26	1.8	11.0	3.1	0.0675	160	0.2	< DL	3.0	67.2
3	7.60	1.2	16.0	6.3	0.3154	150	0.3	< DL	3.1	88.5
4	7.75	1.5	17.0	6.0	0.2623	190	0.2	< DL	0.6	103.5
5	8.16	3.6	4.0	4.9	0.0633	120	0.1	–	5.9	41.5
6	7.95	3.4	4.0	2.4	0.0358	30	< DL	–	2.0	11.8
7	8.30	–	8.9	5.0	0.2090	220	0.5	< DL	0.5	87.6
River waters										
8	7.95	2.8	5.5	2.7	0.0150	< DL	0.5	0.10	11.7	10.0
9	8.40	4.3	8.0	5.5	0.1373	30	0.8	–	9.9	48.0
10	8.08	1.7	13.0	2.7	0.1100	< DL	0.4	0.15	11.0	6.0
Average										
Lake water	8.07	2.3	9.7	4.4	0.1463	146	0.2*	< DL	2.6	65.2
River water	8.14	2.9	8.8	3.6	0.0874	10*	0.6	0.13	10.9	21.3
All waters	8.10	2.5	9.4	4.2	0.1287	105*	0.3*	0.04*	5.1	52.0

DL: detection limit; \*the average value is calculated considering a concentration of 0 mg l<sup>-1</sup> instead of <DL; – not detected.

- seven artificial lakes (waters 1–7);
- three rivers (waters 8–10).

As shown in Table 1, raw waters contained an average concentration of organic matter (TOC = 4 mg l<sup>-1</sup>), medium-high concentrations of bromide and ammonia and low concentration of nitrate. In particular, waters from artificial lakes were characterized by higher concentrations of organic matter, bromide, chloride and turbidity, while nitrogen compounds were higher in river waters.

## Experimental

Different oxidation batch tests were performed on raw waters with chlorine, chlorine dioxide and ozone with different concentrations and contact times (Table 2).

Chlorine oxidation was performed by adding an aliquot of sodium hypochlorite solution diluted from a commercial 4% solution. Chlorine dioxide was produced from sodium chlorite activated by a 10% HCl solution. The chlorine dioxide was sparged using air bubbling and absorbed into a distilled water-cooled ice bath. The ClO<sub>2</sub> solution obtained (freshly formed twice a week) was placed in brown bottles and kept in a refrigerator in the dark. The concentration was measured using the N,N-diethyl-*p*-phenylenediamine (DPD) method just before application (IRSA method—CNR no. 4060).

During the oxidation treatments with chlorine and chlorine dioxide, a glass bottle was filled with 1 litre of raw water sample to which sodium hypochlorite solution or chlorine dioxide was added in order to reach the required reagent concentration. The sample was mixed with a

**Table 2** | Reagents concentration and contact time applied in the oxidation tests

Water	Contact time (min)	Chlorine (mg l <sup>-1</sup> )	Chlorine dioxide (mg l <sup>-1</sup> )	Ozone contact time (min)	Ozone (mg l <sup>-1</sup> )
Lake waters					
1	60	2.4	2.4	10	—
2	60	0.5, 0.9, 1.3, 1.7	0.6, 1.1, 1.7, 2.2	10	1.1, 1.7, 3.2, 5.0
3	60	0.6, 1.3, 1.9, 2.5	0.8, 1.6, 2.3, 3.1	10	0.4, 1.7, 2.6
4	60	2.8	2.9	10	1.4–3.2
5	60–120	0.8–1.3	0.5–1.0	10	1.1–2.1
6	60–120	0.5–0.9	0.4–0.8	10	1.1–2.0
7	60	0.9–1.8	0.9–1.8	10	1.5, 2.0, 3.5
River waters					
8	60	0.6, 1.3, 1.9, 2.6	0.3, 0.6, 0.9, 1.3	10	0.6, 1.6, 3.2
9	60	1.9–3.7	1.5–2.9	10	3.1–5.2
10	60	1.7–3.5	1.0–2.0	10	1.0–2.0

magnetic stirrer bar during the whole test duration (of 1 or 2 hours) and, finally, the necessary volume was collected for analysis.

The laboratory scale ozonation system (Figure 1) included a 7-litre column reactor (140 cm high and 8 cm diameter) with a diffuser for ozone introduction and internal baffles to improve ozone–water mixing. Ozone, generated from air with an Ozon lab OL 0.5/50A-Prominent generator (with a flow rate of 684 mgO<sub>3</sub> h<sup>-1</sup>), was injected at the base of the column and diluted in water; ozone in the offgas was kept from the top of the column, trapped in iodide solution and quantified with iodometric titration. The effective ozone dosage was determined by the iodometric method: a solution of potassium iodide (KI) was ozonated, acidified with sulphuric acid and titrated with 0.1 N sodium thiosulphate. The applied ozone dosage is referred to as ozone production (kgO<sub>3</sub> h<sup>-1</sup>)/water flux (m<sup>3</sup> h<sup>-1</sup>). The transferred ozone dosage is the ozone actually absorbed in the water and is about 80–90% of the applied ozone dosage.

For each water sample the chlorine and chlorine dioxide demand was calculated for different contact times (15, 30, 60, 90 and 120 minutes).

For each contact time the oxidant demand is evaluated by dosing an oxidant concentration so that, after the required contact time, a minimum residual concentration of 0.5 mg l<sup>-1</sup> is detected. The oxidant demand at each contact time is calculated as the difference of the oxidant dose and the residual concentration. For all the analysed waters the oxidant demand increases with increasing contact time and reaches a maximum at 60–120 minutes, showing the behaviour of water 2 represented in Figure 2. This is called total demand and is the oxidant dose able to fulfil the reagent request for oxidation and disinfection needs.

During the experimental oxidation tests different doses (25, 50, 75 and 100% of total demand) were applied, while the contact time was 60 minutes (and 120 minutes only in some tests) to complete the oxidation process (this is the conventional contact time applied for pre-oxidation).

Ozone oxidation tests were performed applying different ozone doses with low, medium and high concentration (with concentrations from 0.4 to 5.2 mg l<sup>-1</sup>) in a batch reactor with a contact time of 10 minutes to complete the ozone oxidation reactions (this was demonstrated by the fact that during these tests the ozone effectively

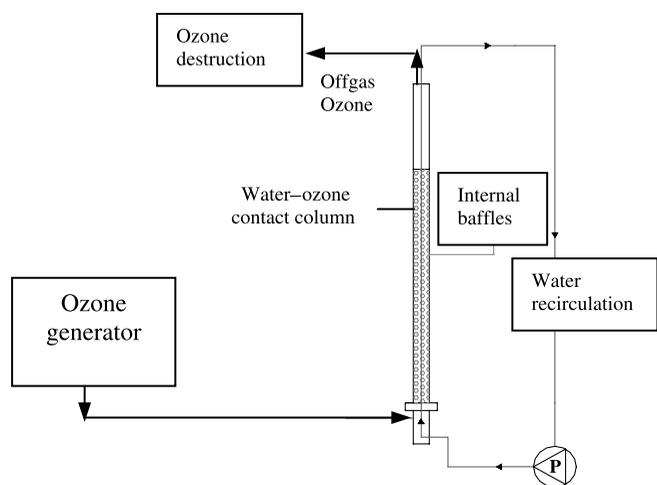


Figure 1 | Experimental plant for ozone oxidation.

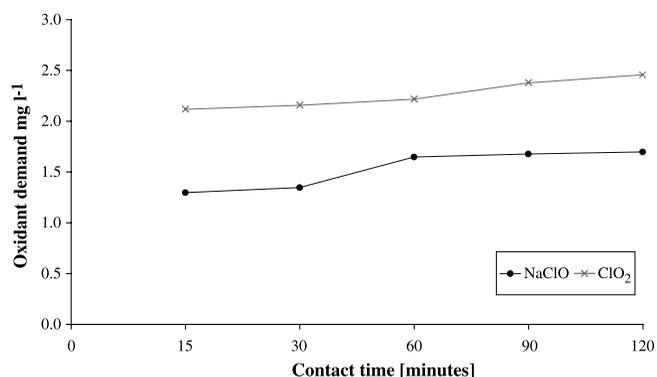


Figure 2 | Chlorine and chlorine dioxide demand with time (water 2).

transferred into the water was entirely consumed in 10 minutes).

The  $C \cdot t$  values applied during the oxidation tests were determined as follows: for chlorine and chlorine dioxide the applied reagent dose was 25, 50, 75 and 100% of the total demand, while the contact time ( $t$ ) was 60 minutes (120 minutes only in some tests); for ozone the applied dose was chosen with low and high concentrations (from 0.4 to 5.2 mg l<sup>-1</sup>) with a contact time ( $t$ ) of 10 minutes. The reagent concentration  $C$  is the residual concentration of the oxidant at the end of the contact time. Depending on water matrices and applied oxidant dose, the residual concentration ( $C$ ), expressed as a percentage of the

applied dose, is 30–60% for chlorine, 10–25% for chlorine dioxide and 2–8% for ozone.

### Analytical methods

For each sample, pH, alkalinity, TOC, UV absorbance at 254 nm wavelength, bromide, ammonia, nitrite, nitrate, trihalomethanes, chlorite, chlorate and bromate were analysed. The ion analysis was performed by direct injection into an ion chromatograph (Dionex, 4500 series, column AS9, pre-column AS9SC, with an eluent solution of Na<sub>2</sub>CO<sub>3</sub> 0.002 M, NaHCO<sub>3</sub> 0.00075 M and with conductivity detector); the four trihalomethanes (chloroform, bromodichloromethane, dibromochloromethane and bromoform) were analysed with a gas chromatograph (Perkin-Elmer 8600 with ECD detector) with the static head space method. DBPs detection limits were 3 µg l<sup>-1</sup> for TTHMs and bromate and 2 µg l<sup>-1</sup> for chlorite while the quantification limit for bromide was 3 µg l<sup>-1</sup>. TOC was analysed with a total carbon monitor (Carlo Erba) and the UV-absorbance on raw and filtered water with a UV-visible spectrophotometer (Beckman DU 70) with a 1 cm quartz cell.

## RESULTS AND DISCUSSION

### Oxidant demands

The disinfectant demand, after 1-h contact time for chlorine and chlorine dioxide and after 10 minutes for ozone, is defined as the oxidant concentration necessary to satisfy the demand of the matrix and to give a significant inactivation of microorganisms, which must be analysed according to the Italian legislation on drinking water (Decree of the Republic President 236/1988): total and faecal coliforms, total bacteria count at 22 and 36°C, spores of *Clostridium perfringens*, *Enterococcus* and *Escherichia coli* (the last two parameters must be evaluated according to the future Italian legislation, Legislative Decree 31/01, which came into force after 25 December 2003).

The concentrations indicated in Table 3 show that the analysed waters have very different oxidant demands

**Table 3** | Disinfectant demand evaluated at 1 h contact time for chlorine and chlorine dioxide and 10 min for ozone

Water	Chlorine		Chlorine dioxide		Ozone	
	Demand (mg l <sup>-1</sup> )	MgNaClO per mgTOC	Demand (mg l <sup>-1</sup> )	mgClO <sub>2</sub> per mgTOC	Applied dose (mg l <sup>-1</sup> )	mgO <sub>3</sub> per mgTOC
Lake waters						
1	2.4	0.7	2.4	0.7	—	—
2	1.7	0.5	2.2	0.7	3.2	1.0
3	2.5	0.4	3.1	0.5	2.6	0.4
4	2.8	0.5	2.9	0.5	3.2	0.5
5	1.3	0.3	1.0	0.2	2.1	0.4
6	0.9	0.4	0.8	0.3	2.0	0.8
7	1.8	0.4	1.8	0.4	2.0	0.4
River waters						
8	2.6	1.0	1.3	0.5	1.6	0.6
9	3.7	0.7	2.9	0.5	3.1	0.6
10	3.5	1.3	2.0	0.8	2.0	0.7

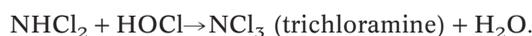
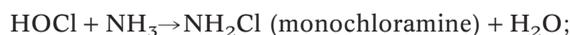
because of the high variability of their characteristics: from 0.9 to 3.7 mg l<sup>-1</sup> for chlorine; from 0.8 to 3.1 mg l<sup>-1</sup> for chlorine dioxide and from 1.6 to 3.2 mg l<sup>-1</sup> for ozone.

The highest oxidant demand (Table 3) is shown by waters 4 and 9 (respectively lake and river waters), which had the highest concentrations of water matrix components (Table 1), particularly natural organic matter (NOM), TOC, UV absorbance and turbidity. The lowest oxidant demand is shown by water 6, with a low concentration of NOM.

The achieved C\*t values (C\*t is 45 mg min l<sup>-1</sup> for chlorine, about 30 mg min l<sup>-1</sup> for chlorine dioxide and 1.6 mg min l<sup>-1</sup> for ozone) are sufficient for good removal of total and faecal coliforms, total bacteria count at 22 and 36°C, spores of *Clostridium perfringens*, *Enterococcus* and *Escherichia coli*, which should comply with a zero level in 100 ml water according to Italian legislation (EPA 1999).

Although it is not possible to generalize, it can be observed that a higher demand is shown by river waters

for chlorine, probably due to the higher ammonia concentration which reacts with free chlorine forming three types of chloramines, according to the following reactions:



These reactions compete with each other and are heavily dependent on initial chlorine to ammonia nitrogen ratio, pH, temperature and contact time (EPA 1999). At molar ratios of chlorine to ammonia-N of up to 1:1, the first reaction will dominate while further increases in molar ratio, such those calculated for the analysed waters (2.1 Cl<sub>2</sub>/N-NH<sub>3</sub> for lake waters and 1.4 Cl<sub>2</sub>/N-NH<sub>3</sub> for river water) may result in the formation of dichloramine and trichloramine, with reaction rates depending mainly on

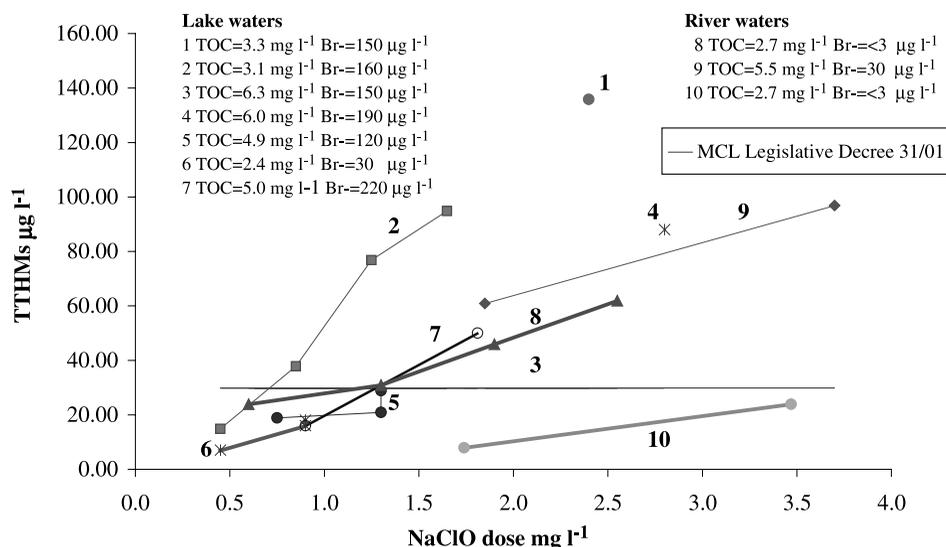


Figure 3 | Trihalomethanes formation versus chlorine dose for different surface waters (1 h contact time).

pH (White 1999). For ozone, the higher demand is shown by lake waters, because of the different type of organic matter present, while no differences between river and lake waters are shown for chlorine dioxide.

## DISINFECTION BY-PRODUCTS FORMATION AND MINIMIZATION

### Chlorine

The results of chlorine oxidation tests show an increasing trihalomethanes formation with increasing chlorine dose with a constant contact time of 60 minutes (Figure 3); for doses higher than 1.0–1.5 mg l<sup>-1</sup>, TTHMs concentration is over the Italian maximum concentration level (MCL) of 30 µg l<sup>-1</sup> for most of the treated waters.

The cumulative probability function has been plotted in Figure 4 for waters with TTHMs formation lower than 30 µg l<sup>-1</sup> (Figure 4a), the Italian standard indicated in the Legislative Decree 31/01, and 100 µg l<sup>-1</sup> (Figure 4b), the 98/83/EU standard.

In each graph the observed probability has been evaluated for the experimental reagent concentrations (respectively 13 and 26 values for Figure 4a and 4b),

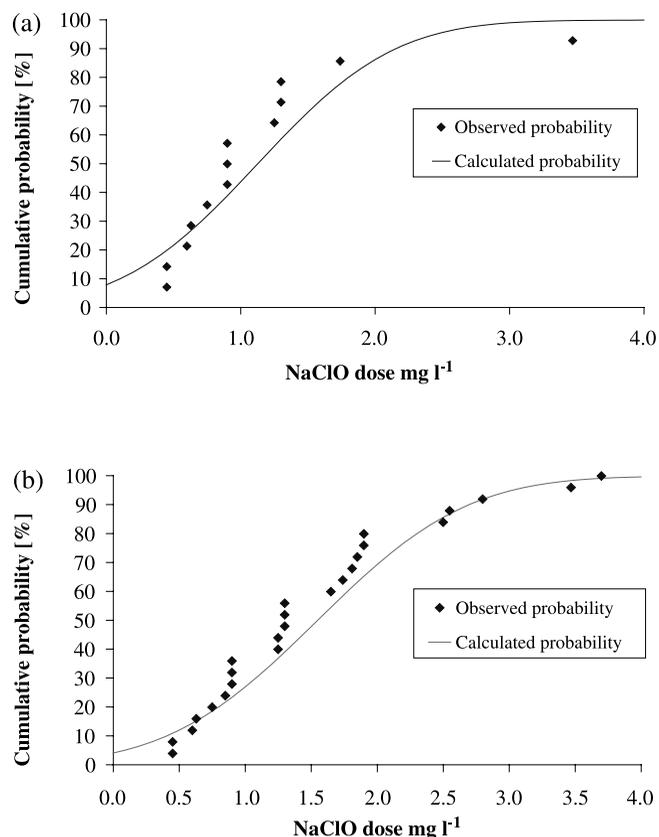


Figure 4 | Cumulative probability function of waters with TTHMs formation lower than (a) 30 µg l<sup>-1</sup> and (b) 100 µg l<sup>-1</sup>.

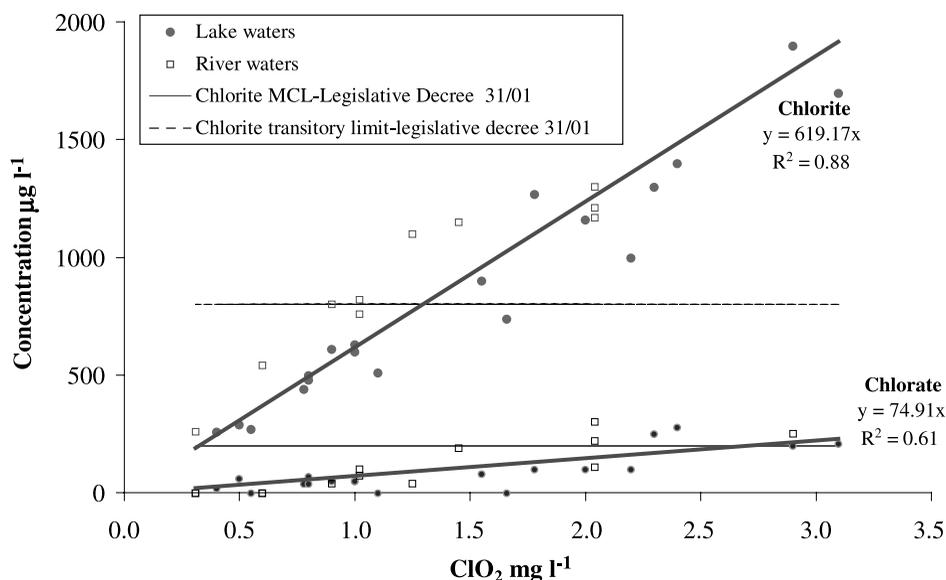


Figure 5 | Correlation of chlorite and chlorate with chlorine dioxide dose during the oxidation treatment (1 h contact time).

while the calculated probability has been determined with a normal distribution function applied for increasing reagents concentrations with an average concentration of 1.13 and a standard deviation of 0.79 for Figure 4a, and a media of 1.55 and a standard deviation of 0.89 for Figure 4b.

The results show that the chlorine concentration for which 50% of the waters are below the Italian limit of  $30 \mu\text{g l}^{-1}$  is  $1.1\text{--}1.2 \text{ mg l}^{-1}$  (Figure 4a), while the concentration for which 50% of the waters are below the EU limit of  $100 \mu\text{g l}^{-1}$  is  $1.5 \text{ mg l}^{-1}$  (Figure 4b).

### Chlorine dioxide

Chlorine dioxide dramatically reduces TTHMs formation in comparison with chlorine treatments (about 80–100%), but other specific by-products, mainly chlorite and chlorate, are generated. Both chlorite and chlorate show a reasonable linear correlation (the linear regression coefficients  $R^2$  are, respectively, 0.88 and 0.61) with chlorine dioxide dose. Chlorite formation is about 62% and chlorate is 7–8% of chlorine dioxide dose (Figure 5).

The maximum allowed concentration for chlorite is  $200 \mu\text{g l}^{-1}$  according to the Italian regulation, with a

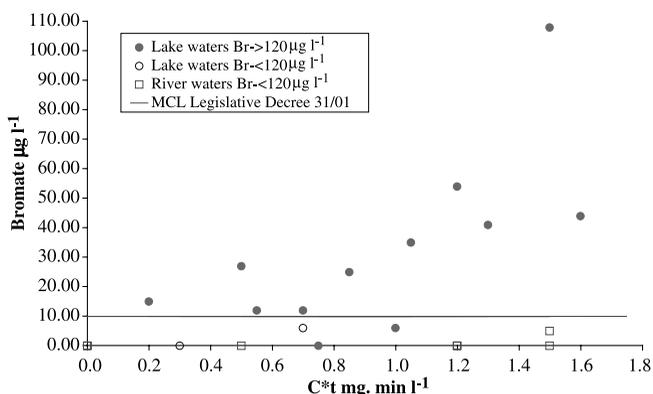
transitory limit of  $800 \mu\text{g l}^{-1}$  from 2003 to 2006; this means that the chlorine dioxide applied dose should be lower than  $0.3 \text{ mg l}^{-1}$  (after 2006) and  $1.4\text{--}1.5 \text{ mg l}^{-1}$  (from 2003 to 2006).

The main consequence is that the use of chlorine dioxide in pre-oxidation produces a chlorite concentration generally higher than  $800 \mu\text{g l}^{-1}$ ; this is clear if we consider that chlorine dioxide demand is about  $0.5 \text{ mg ClO}_2$  per  $\text{mg TOC}$  (Table 3) and the average TOC concentration for the analysed waters is  $4 \text{ mg l}^{-1}$  (Table 1). In this case the application of specific treatments (such as activated carbon absorption and ferrous salts coagulation) after pre-oxidation is necessary for chlorite removal.

### Ozone

One of the main by-products of ozonation is bromate, which must be strictly limited to the maximum concentration of  $10 \mu\text{g l}^{-1}$ , according to the Italian Legislative Decree.

Bromate formation depends on both the process parameters (mainly ozone dose) and water quality (bromide and organic matter): bromate formation increases obviously with ozone dose and bromide concentration in raw



**Figure 6** | Correlation of bromate with ozone dose (C) x contact time (t) (10 minutes contact time).

water (bromide is the main bromate precursor) while it decreases with organic matter, if a constant ozone dose is applied. These results agree with the main findings of other researchers (Legube *et al.* 1995; Croué *et al.* 1996).

The experimental data represented in Figure 6 show that bromate concentration increases with increasing C\*t for lake waters characterized by a higher bromide concentration. In contrast, no bromate is formed in river waters due to the lack of bromide in raw water. This means that ozone can be applied without restriction to low bromide waters (such as the river waters analysed in this experiment). However, many difficulties can be experienced for ozone application to waters with high bromide concentration, such as the water samples from the artificial reservoirs, which have an average bromide concentration of 140 µg l<sup>-1</sup> (from 30 to 220 µg l<sup>-1</sup>).

## CONCLUSIONS

The oxidation batch tests with chlorine, chlorine dioxide and ozone on raw waters from ten different surface water sources show the following results:

- The analysed waters have very different oxidants demands due to the high variability of their characteristics: from 0.9 to 3.7 mg l<sup>-1</sup> for chlorine; from 0.8 to 3.1 mg l<sup>-1</sup> for chlorine dioxide and from 2.0 to 3.2 mg l<sup>-1</sup> for ozone;

- During the oxidation treatments with chlorine, TTHMs increase with the reagent dose and the Italian limit of 30 µg l<sup>-1</sup> for TTHMs can be fulfilled by 50% of the waters with a chlorine concentration of 1.1–1.2 mg l<sup>-1</sup>;
- During the oxidation with chlorine dioxide, significant chlorite concentrations, about 60% of chlorine dioxide dose, are produced and they are not influenced by water matrix parameters. Consequently, the limit of 200 µg l<sup>-1</sup> for chlorite can be fulfilled only with chlorine dioxide doses lower than 0.3–0.4 mg l<sup>-1</sup>. Otherwise, specific treatments for chlorite removal should be applied.
- During the oxidation with ozone, bromate formation increases with ozone dose and bromide concentration. The maximum concentration of 10 µg l<sup>-1</sup> for bromate can be fulfilled only for water with low bromide concentration (0–30 µg l<sup>-1</sup>).

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