Modeling and analysis of chlorine dioxide, chlorite, and chlorate propagation in a drinking water distribution system

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ABSTRACT

The drinking water distribution system of Cremona, in the north of Italy, was monitored for 6 years (2006–2011) analyzing chlorine dioxide, chlorite, and chlorate concentrations. The software Epanet 2.0 (USEPA) was applied to the distribution system. The mixing zone of the water coming from the two drinking water treatment plants, respectively located to the west and east of the city, was estimated using the software. Propagation of chlorine dioxide, chlorite, and chlorate was simulated with the software. Measured and simulated results were compared. The results of the distribution system monitoring showed a high chlorine dioxide consumption, since residual chlorine concentration was always below 0.12 mg L⁻¹. Chlorite concentration was over 700 μg L⁻¹ for 12–16% of results in the first 2 years, for 48% of results in 2008, and for 1–8% of results from 2009 to 2011. In particular, chloride concentration was always below 200 μg L⁻¹. The mixing zone of the water in the distribution system was determined, and the comparison between measured and simulated concentrations showed the usefulness of the model for predicting disinfectant and by-product propagation in the distribution system.

Key words | chlorate, chlorine dioxide, chlorite, drinking water, modeling, water distribution system

INTRODUCTION

Disinfection is applied in drinking water treatment plants (DWTPs) to ensure water quality and to avoid bacterial contamination in drinking water distribution systems (DWDSs). However, disinfectant concentration in DWDSs decreases with time, while disinfection by-product (DBP) formation increases; this is due to chemical reactions of the disinfectant with dissolved and particulate matter in water, biofilm, and pipe wall material (Wable et al. 1991; Zhang et al. 1992; Kiéné et al. 1998; Al-Jasser 2007).

If chlorine dioxide (ClO₂) is used as a disinfectant, chlorite (ClO₂⁻) and chlorate (ClO₃⁻) can be produced as DBPs. In fact, ClO₂ and ClO₃ can be produced during the ClO₂ generation process in the DWTP (Equations (1) and (2)), during water treatment and in the DWDS. Concerning the ClO₂ generation process in DWTPs, ClO₂ can be used as a reagent to produce ClO₂ in DWTPs. In particular, ClO₂ can be generated by ClO₂ oxidation with chlorine. Moreover, ClO₂ and ClO₃ can be produced from the interaction between ClO₂ and hypochlorite (OCl⁻) (Equation (3)) (Gates et al. 2009):

\[
\begin{align*}
2\text{NaClO}_2 + \text{Cl}_2 & \rightarrow 2\text{ClO}_2 + 2\text{NaCl} \\
2\text{ClO}_2 + 2\text{OH}^- & \rightarrow \text{H}_2\text{O} + \text{ClO}_2^- + \text{ClO}_3^- \\
\text{ClO}_2 + \text{HClO} & \rightarrow \text{ClO}_3^- + \text{Cl}^- + 2\text{H}^+
\end{align*}
\]
During water treatment, ClO₂ can react with natural organic matter (NOM) in water, producing ClO₂ and ClO₃⁻. The main parameters that influence ClO₂ and ClO₃⁻ formation are water quality parameters such as pH, temperature, and NOM content, and operating conditions such as the disinfectant dosage (Korn et al. 2002). In particular, studies showed that ClO₂ concentration, temperature, and NOM content are the most significant parameters influencing ClO₂ and ClO₃⁻ formation (Korn et al. 2002; Collivignarelli & Sorlini 2004; Gates et al. 2009).

In DWDSs, ClO₂ can still react with organic and inorganic compounds, degrading ClO₂, ClO₃⁻, and chloride (Cl⁻) as a consequence of reactions in pipes and tanks (Baribeau et al. 2002). Studies showed that iron corrosion scales in DWDS pipes generally contain reduced iron, which can react with oxidative disinfectants (Sarin et al. 2001, 2004a, 2004b) such as ClO₂, with undesirable losses in the disinfectant residual (Zhang et al. 2008).

The main factors that can influence ClO₂ and ClO₃⁻ formation in a DWDS are the ClO₂ residual concentration, pipe material and diameter, corrosion by-products and biofilm, water residence time and water temperature. Concerning the fate of ClO₂ and its DBPs in DWDSs, some researchers found that ClO₂ concentration decreases with increasing residence time (Oliivieri et al. 1986; Thompson 1988). Concerning corrosion by-products and biofilm, the reaction between ClO₂ and Fe²⁺, which is the main corrosion by-product in metallic pipes, leads to a ClO₂ decrease (Zhang et al. 2008). Moreover, ClO₂ decreases with increasing water residence time in DWDSs, while ClO₃⁻ increases or remains stable (Thompson 1988; McGuire et al. 1990; Lafrance et al. 1992).

Therefore, it is important to evaluate spatial and temporal variation in residual chlorine, chlorite (ClO₂⁻), and chlorate (ClO₃⁻) within DWDSs. In fact, the World Health Organization (WHO) recommends a free residual chlorine concentration of 0.2 mg L⁻¹ in DWDSs (WHO 2011); moreover, since ClO₂ and ClO₃⁻ can cause oxidative damage to human red blood cells, each compound should not exceed the WHO guideline value (GV) of 700 μg L⁻¹ in drinking water (WHO 2011). The Italian regulation limit exists only for ClO₂ (700 μg L⁻¹), while ClO₃⁻ is not regulated (Italian Legislative Decree 37/2001).

Prediction of the disinfectant residual and DBP propagation in a DWDS can be achieved using water distribution modeling (WDM), which allows simulation and evaluation of a DWDS under different operating conditions. For example, the software Epanet 2.0 is a WDM in the public domain, developed by the United States Environmental Protection Agency (USEPA), which models the hydraulic and water quality behavior of water distribution piping systems (Rossman 2000).

In the literature, several studies are available on the measurement and modeling of chlorine and chlorate in DWDSs (Clark et al. 1994; Rossman et al. 1994; Islam et al. 1997; Rodriguez & Sérodes 1998, 2001; Li & Zhao 2006; Al-Jasser 2007; Courtis et al. 2009; Mohamed & Abozeid 2011; Boano et al. 2016). Some researchers modeled chlorine residual propagation in DWDSs with the Epanet software and obtained good agreement with observed chlorine levels at locations where the hydraulics were well characterized (Rossman et al. 1994). Other researchers studied the chlorine residual propagation in DWDSs and found that residuals varied widely both spatially and temporally; moreover, they observed that long residence times in storage tanks caused low or nonexistent residual disinfectant concentrations in the DWDS; further, they found that supply system operation has a significant effect on the distribution and concentration of chlorine residuals in the DWDS (Clark et al. 1993). Since chlorine is the most popular and traditional disinfectant, most modeling efforts have been focused on trihalomethanes (THMs) (Sadiq & Rodriguez 2004). Some researchers studied THM reaction kinetics and developed a model for predicting their formation in DWDSs. They found that a second-order reaction is a good predictor of THM formation, and they observed good agreement between calculated and measured values, confirming that the model is applicable to an actual DWDS (Li & Zhao 2006). However, since few studies are available on ClO₂, ClO₂⁻, and ClO₃⁻ propagation in DWDSs by means of WDM, the kinetic reactions of ClO₂, ClO₂⁻, and ClO₃⁻ and the simulation of their propagation in DWDSs by means of WDM must be further investigated.

This novel work is aimed at understanding ClO₂, ClO₂⁻, and ClO₃⁻ propagation in a DWDS by means of WDM software. It studies the DWDS of Cremona, in the north of Italy, fed by two treatment plants in which ClO₂ disinfection is applied, respectively located to the west and east of the city. The DWDS was monitored for 6 years (2006–2011)
analyzing residual chlorine, ClO₂, and ClO₃ concentrations at 26 points of the network. The Epanet 2.0 software (USEPA) was applied to the DWDS in order to estimate the mixing zone of the water coming from the west and east treatment plants, and in order to simulate the propagation of ClO₂, ClO₂⁻, and ClO₃⁻. The measured and simulated results were compared in order to evaluate the applicability of the model to the DWDS.

**MATERIAL AND METHODS**

**Drinking water supply system of Cremona (Italy)**

The drinking water supply system studied is located in the city of Cremona (76,000 inhabitants), in the north of Italy. Groundwater is withdrawn by two well fields, respectively consisting of nine wells and ten wells, and respectively located in the north-west and east of the city; each well field is capable of providing a maximum flow rate of 38.9 ML d⁻¹ and each well withdraws water at a depth between 160 and 200 m. Groundwater contains methane (CH₄), hydrogen sulfide (H₂S), ammonia (NH₄⁺), iron (Fe), manganese (Mn), and arsenic (As(III)). The main raw water quality characteristics (average values) are: CH₄ 5 mg L⁻¹, H₂S 0.15 mg L⁻¹, NH₄⁺ 1.4 mg L⁻¹, Fe 57 µg L⁻¹, Mn 51 µg L⁻¹, As 15 µg L⁻¹, pH 8.0, temperature 17 °C, Kubel index 2.5 mg O₂ L⁻¹, bromide <0.005 mg L⁻¹, ultraviolet absorption at 254 nm (UV254) 0.0786 cm⁻¹, and TOC 4.10 mg L⁻¹. The well fields feed two equal DWTPs, respectively located to the east and west of the city, each using the following treatment train: aeration, biofiltration, chemical oxidation with potassium permanganate and coagulation with ferric chloride, sand filtration, and final disinfection with ClO₂. The disinfectant dosage is 0.8 mg ClO₂ L⁻¹ (0.42 mg Cl₂ L⁻¹) in each DWTP. After treatment, water is supplied to the DWDS by means of pumps with inverters. The east DWTP has three output sections, and the west DWTP has five output sections. The east DWTP supplies a reservoir located in the center of the city, after which a pumping station delivers water to the city. The pumping station has two output sections.

The DWDS is 259 km in length, 65% of the pipes are steel, 19% cast iron, 6% HDPE (high-density polyethylene), 10% other materials, and the diameters vary from approximately 60 to 800 mm.

**Evaluation of the disinfectant and DBP concentrations in the distribution system**

Data of the residual Cl₂, ClO₂, and ClO₃ concentrations measured at 26 points of the DWDS (Figure 1) from 2006 to 2011 (monthly) were collected in order to evaluate the disinfectant and DBP concentrations in the DWDS.

**Modeling of the drinking water supply system**

**Model development**

The model of the DWDS was developed with the USEPA software, Epanet 2.0. According to the DWDS cartography, the altimetry of each junction and the length, material, and roughness coefficient of each pipe were inserted in the software model. The modeled DWDS was simplified in order to simulate only a part of the system, and pipes below 150 mm were not considered. However, the discharge related to each removed part of the system was inserted into the appropriate junction in the model (see ‘Development of the hydraulic model’). The simplified scheme, characterized by five closed paths, 144 junctions, and a 23 km total length, was used for all the subsequent simulations (Figure 2).

![Figure 1](https://iwaponline.com/aqua/article-pdf/65/8/597/398264/jws0650597.pdf)
Development of the hydraulic model. In order to develop the hydraulic model, the daily trends of pressure and discharge in the DWDS were analyzed. These trends were elaborated using pressure and discharge values measured at the outlet of each DWTP and at the outlet of the pumping station located in the city center (Figure 3). The average pressure and discharge values were calculated from these trends (at each output section: average daily discharge ranges from 17 to 50 L/s and average daily pressure varies from 3.8 to 5.1 bar) and, then, used in the model. Since all the pumps at the outlet of the DWTPs and the pumping station are equipped with inverters, pressure and discharge are controlled at the output section (pump head and related discharge are managed and regulated). Pumping operating point is regulated as time function. Therefore, to simulate this behavior, pressure reduction valves and discharge reduction valves were inserted in the model at the junctions downstream of each pump; the measured average pressure and discharge values were inserted in these valves in the model at the output section of the DWTPs and the pumping station.

The users of the DWDS are 84% civil, 15% industrial, and 1% public. In the DWDS, time varying demand was implemented using direct discharge metering at all users for each category. Therefore, each junction has a certain water demand. Temporal variation in water demand at each junction depends on users’ number and related category. Furthermore, water demands higher than 10,000 m$^3$/year (industries) were concentrated in a single junction of the model. The total water demand of the removed zone was considered located in a single junction of the model.

In order to model the daily water discharge at different points of the DWDS, the daily trend of the discharge in each junction was estimated considering 154 users/km, a total delivered water volume of about 7,800,000 m$^3$, and a 32% distribution loss. Different hourly coefficients were applied to the daily average discharge measured at the output section of the two DWTPs and the pumping station (Figure 4(a)–4(c)). Different hourly coefficients were applied to the daily average discharge of industries located at different points of the DWDS (Figure 4(d)). Therefore, the demand pattern (daily water discharge trend) was inserted at each junction in the modeled DWDS (Figure 5).

Modeling the water mixing zone. The chemical validation of the model was carried out in order to determine the water mixing zone in the DWDS and to simulate the disinfectant and DBP propagation in the DWDS.

In order to determine the mixing zone of the water coming from the two DWTPs, the propagation of a salt in the modeled system was simulated with the software Epanet 2.0. The aim was to evaluate the propagation in the system of a substance without decay or growth. The initial salt concentration in the water was considered zero. A salt concentration of 70,000 mg L$^-1$, twice that of seawater, was dosed in the model continuously for 24 hours, at first only in the east DWTP and in the central pumping station and then only in the west DWTP. The salt concentration in the junctions of the modeled system was evaluated. In particular, in the case where salt was dosed only in the east DWTP and pumping station, the salt propagation was evaluated during 24 h simulation. The pipes in which salt was never detected in 24 h and the pipes located farthest from the east DWTP and from the central pumping station were determined. The same evaluation was carried out in the case where salt was dosed in the west DWTP. In particular, the water mixing zone was defined as the modeled DWDS zone constituted by the pipes where a salt concentration diverse from
zero was observed during the 24 h simulation in both cases, dosing salt in the east and the west DWTP, at certain times of the day.

**Chemical validation.** In order to simulate the disinfectant and DBP propagation in the DWDS, the ClO₂, ClO₂⁻, and ClO₃⁻ reaction kinetics were studied at laboratory scale.

Batch experiments were carried out by treating water samples collected at the outlet of the sand filter of the full-scale DWTP with ClO₂. Each 2 L water sample was divided into smaller samples of 100 mL. Each water sample was put in a graduated cylinder and treated with 5 mg L⁻¹ of ClO₂. The ClO₂ dosage is higher than the one employed in the DWTP final disinfection, because
the aim of this test was to evaluate the ClO₂ consumption and the DBP formation in the presence of a residual ClO₂ concentration. Then, each cylinder was plugged, manually stirred to homogenize the solution and kept in dark conditions. The residual ClO₂, ClO₂⁺, and ClO₃⁻ concentrations were analyzed after 0, 4, 10, 30, 60, 79, 120, 160, 180, 360, 670, 1,440, and 2,280 minutes water-disinfectant contact time. Tests were carried out at a temperature of 22–24°C and pH 8.0. Water samples were stored in a fridge at 4°C in dark conditions. The ClO₂ solution (concentration of 250 mg ClO₂/L) was directly collected from the ClO₂ generator used in the DWTP and it was stored in a fridge at 4°C in dark conditions before use.

The interpolation of the residual concentrations versus time allowed determining the order of each reaction kinetic and the bulk reaction coefficient (kₜ) for ClO₂, ClO₂⁺, and ClO₃⁻. The reaction kinetic for ClO₂ is described by a first-order reaction:

\[ C = C_0 \cdot e^{k_b t}, \quad k_b < 0 \]

\[ C = \text{concentration at } t \text{ time (mg L}^{-1}) ; \quad C_0 = \text{initial concentration (1 mg L}^{-1}) ; \quad k_b = \text{bulk reaction coefficient (1 s}^{-1}) ; \quad t = \text{contact time (s)}. \]

The reaction kinetics for ClO₂⁺ and ClO₃⁻ are described by zero order reactions:

\[ C = C_0 + k_p t, \quad k_p > 0 \]

The ln(residual ClO₂) versus time determined by batch experiments at laboratory scale is shown in Figure 6(a). The exponential function well approximates the distribution of the residual ClO₂ concentrations, with a correlation close to 80%. Therefore, the first-order equation showed a linear ClO₂ decay versus time and \( k_b \) was equal to \(-0.0002\) min⁻¹, thus \(-0.288\) d⁻¹.

The ClO₂ and ClO₃⁻ concentrations versus time determined by batch experiments at laboratory scale are shown, respectively, in Figure 6(b) and 6(c). The linear function well approximates both the distributions of the ClO₂ and ClO₃⁻ concentrations, with a correlation close to 80% in both cases. Therefore, the zero-order equation represented both the ClO₂ and ClO₃⁻ growth versus time,
and $k_b$ was respectively equal to 0.0004 mg L$^{-1}$ min$^{-1}$, thus 0.576 mg L$^{-1}$ d$^{-1}$, and 0.00007 mg L$^{-1}$ min$^{-1}$, thus 0.101 mg L$^{-1}$ d$^{-1}$.

In the model, initial Cl$_2$, ClO$_2$, and ClO$_3$ concentrations at the DWTPs and at the pumping station were the average annual concentrations measured in the real system at these points. In particular, in the model, the initial concentration of residual Cl$_2$ was 0.42 mg L$^{-1}$ and 0.02 mg L$^{-1}$, respectively, at the outlet of both the DWTPs and the pumping station, ClO$_2$ was 0.680 mg L$^{-1}$ and 0.733 mg L$^{-1}$, respectively, at the outlet of the east and west DWTP, and ClO$_3$ was 0.081 mg L$^{-1}$ and 0.082 mg L$^{-1}$, respectively, at the outlet of the east and west DWTP.

After inserting the initial disinfectant and DBP concentrations, Cl$_2$, ClO$_2$, and ClO$_3$ kinetics were defined in the model, assigning the reaction kinetic order and the $k_b$ to each parameter. The order of the reaction kinetics and $k_b$ inserted in the model for residual Cl$_2$, ClO$_2$, and ClO$_3$ were the ones determined at laboratory scale, respectively, for the residual ClO$_2$, ClO$_2$, and ClO$_3$.

Comparison between measured and simulated data

Different simulations of the residual Cl$_2$, ClO$_2$, and ClO$_3$ propagation in the DWDS were carried out on the modeled system. The pressure, flow, residual Cl$_2$, ClO$_2$ and ClO$_3$ measured at different points of the system were compared.

Figure 5 | Water demand (L s$^{-1}$) at each numbered junction of the modeled DWDS.
to the simulated values. The measured values were the average values measured at each sampling point of the system (Figure 1) at 10.00 a.m. during the monitoring campaign from 2006 to 2011 (see section ‘Evaluation of the disinfectant and DBP concentrations in the distribution system’). The simulated values were evaluated at the same sampling points (Figure 1) at 10.00 a.m. after one month from the start of the disinfectant dosing in the DWTPs in the model. The period of one month was chosen because after one month a stable water quality condition was achieved in the model simulation.

### Analytical methods

The ClO₂ residual concentration during the batch experiments was determined with a residual chlorine analyzer (Cl₂ detection limit = 0.05 mg L^{-1}) (APAT IRSA CNR 4080 2005). Since the chlorine analyzer measured the Cl₂ concentration, the ClO₂ concentration was calculated from the detected Cl₂ values with a conversion factor: ClO₂ = 1.9 Cl₂. The ClO₂ and ClO₃⁻ concentrations were determined using Ion Chromatography Dionex ICS 5000 (detection limit ClO₂ = 0.05 mg L^{-1} and ClO₃⁻ = 0.03 mg L^{-1}) (UNI EN ISO 10504-4).

### RESULTS AND DISCUSSION

#### Analysis of the residual chlorine, chlorite, and chlorate concentrations in the real distribution system

The residual Cl₂, ClO₂⁻, and ClO₃⁻ concentrations were analyzed at 26 points of the DWDS from 2006 to 2011 (Figure 7).

The results show that the residual Cl₂ was always below the WHO GV of 0.2 mg L^{-1} and sometimes was absent (Figure 7(a)). This is a negative aspect, since the chlorine absence implies a null protection from bacterial contamination at these points of the DWDS, so water safety cannot be ensured.

The ClO₂⁻ concentration from 2006 to 2008 often exceeded the WHO GV of 700 μgL^{-1}, in particular at the points of the system more distant from the DWTPs (Figure 7(b)). From 2009 to 2011, the ClO₂⁻ concentration was below the GV. The data showed significant variability before 2008, which subsequently decreased; this trend was probably due to the reduction of the ClO₂ dosage in the DWTP after a gradual cleaning of the DWDS pipes in 2008. Overall, the ClO₂⁻ concentration exceeded the WHO GV for 12–16% of results in the first 2 years, for 48% of results in 2008, and for 1–8% of results from 2009 to 2011.

The ClO₃⁻ concentration was significantly below the WHO GV of 700 μgL^{-1} throughout the monitoring period (Figure 7(c)).
Figure 7 | Residual Cl$_2$ (a), ClO$_2$ (b), and ClO$_3$ (c) versus time measured in the distribution system of Cremona (Italy) from 2006 to 2011 (sampling point position is shown in Figure 1).
**Determination of the mixing zone**

The simulations aimed at determining the water mixing zone showed that, dosing salt in the east DWTP and pumping station, a salt concentration diverse from zero in the modeled DWDS reached the junctions more distant from the east DWTP and from the pumping station for the first time at 6.00 a.m. and at 7.00 a.m. The salt concentration in the modeled DWDS after 6 and 7 hours from the start of the salt dosing (70,000 mg L$^{-1}$) in the east DWTP is reported in Figure 8. After 6 and 7 hours, the farthest points of the DWDS reached by the salt were junctions a, c, e, g, h, and i.

Dosing salt in the west DWTP, a salt concentration diverse from zero in the modeled DWDS reached the junctions more distant from the west DWTP for the first time at 7.00 p.m. and at 11.00 p.m. The

![Figure 8](https://iwaponline.com/aqua/article-pdf/65/8/597/398264/jws0650597.pdf)

![Figure 9](https://iwaponline.com/aqua/article-pdf/65/8/597/398264/jws0650597.pdf)
propagation of the salt was evaluated in the modeled DWDS after 19 and 23 hours from the start of the salt dosing (70,000 mg L\(^{-1}\)) in the west DWTP (Figure 9). After 19 and 23 hours, the farthest points of the DWDS reached by the salt were junctions a, b, d, e, f, and h.

The DWDS zone where water coming from the east and west DWTP is mixed was determined by comparing the results of the two simulations of the salt propagation (Figures 8 and 9). The mixing zone is constituted by the pipes of the DWDS between junctions a–b, c–d, e–f, and g–h (Figure 10).

**Residual chlorine, chlorite, and chlorate propagation in the modeled distribution system**

The Cl\(_2\) residual in the modeled DWDS at 10 a.m. after one month from the start of the disinfectant dosing in both the DWTPs is reported in Figure 11(a). This time was chosen since the water sampling at the different points of the DWDS usually takes place at 10 a.m. for the laboratory analysis. The results of the residual Cl\(_2\) propagation modeling showed that the Cl\(_2\) residual concentrations were still high at points near the two DWTPs (0.42 mg L\(^{-1}\)), due to a very slow disinfectant consumption; with an increase in the distance from the DWTPs, a sharp residual Cl\(_2\) decay was observed. Moreover, in the mixing zone of the DWDS the residual Cl\(_2\) concentrations were still high, while low values were registered in the peripheral pipes of the modeled system. Furthermore, since the residual Cl\(_2\) concentration at the central pumping station was low, low concentrations were observed at the near junctions.

The correlation between the measured and modeled residual Cl\(_2\) concentrations was evaluated (Figure 11(b) and Table 1). The model tends to overestimate the residual Cl\(_2\) concentrations in 67% of the cases, compared to the measured concentrations in the real DWDS.
the root mean square error (Table 1), half the results showed a high error value (>0.100). This result can be due to the fact that the pipe wall effect was not evaluated in the simulation, because of the difficulty in simulating this effect at laboratory scale, while in the real system the additional reactions at pipe walls could influence water quality and, therefore, the disinfectant consumption. For instance, pipe material and biofilm in pipes could affect the water quality, determining a high ClO2 consumption. Moreover, it is possible that in the real system, a residual contaminant in water (e.g., NOM) can react with the disinfectant, determining a higher ClO2 consumption and, consequently, lower Cl2 residual concentrations. These aspects, which were not evaluated in the model, should be further investigated in future studies.

Table 1 | Comparison between measured and modeled residual Cl2 concentrations, mean absolute error, and root mean square error, at 10 a.m. after one month from the start of the disinfectant dosing in both the DWTPs

<table>
<thead>
<tr>
<th>Junction number (sampling point)</th>
<th>Residual Cl2 (mg L⁻¹)</th>
<th>Measured</th>
<th>Modeled</th>
<th>Mean absolute error</th>
<th>Root mean square error</th>
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<tbody>
<tr>
<td>79</td>
<td>0.035</td>
<td>0.08</td>
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<td>0.35</td>
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</tbody>
</table>

The ClO2 concentration in the modeled DWDS at 10 a.m. after one month from the start of the disinfectant dosing in both the DWTPs is reported in Figure 12(a). The results show that the ClO2 concentrations at points near the two DWTPs were close to those from the outlet of the DWTPs (close to 0.70 mg L⁻¹), since the ClO2 formation was very slow; with an increase in the distance from the DWTPs, a gradual ClO2 concentration increase was registered. Moreover, in the peripheral pipes and in the mixing zone of the modeled DWDS the ClO2 concentrations were over the WHO GV of 700 μg L⁻¹.

The correlation between the measured and modeled ClO2 concentrations was evaluated (Figure 12(b)). The model tends to overestimate the residual ClO2 concentrations in 75% of the cases, compared to the measured concentrations in the real DWDS. Considering the root mean square error (Table 2), only a few results showed a high error value (>0.100). As for the Cl2 results, the differences between the modeled and measured ClO2 concentrations were due to the aspects previously explained.

The ClO3 concentration in the modeled DWDS at 10 a.m. after one month from the disinfectant dosing in both the DWTPs is reported in Figure 13(a). The results showed a
very low ClO$_3^-$ concentration gradient. Near the two DWTPs, ClO$_3^-$ formation was negligible, since the concentrations were close to those from the outlet of the DWTPs (close to 0.10 mg L$^{-1}$); with an increase in the distance from the DWTPs, a slow and gradual ClO$_3^-$ concentration increase was observed, with values always below the WHO GV of 700 $\mu$g L$^{-1}$.

The correlation between the measured and modeled ClO$_3^-$ concentrations was evaluated (Figure 13(b)). As for ClO$_2^-$, the model tends to overestimate the residual ClO$_3^-$ concentrations in 75% of the cases, compared to the measured concentrations in the real DWDS. Considering the root mean square error (Table 3), only one result showed a high error value (>0.100). Also in this case, the differences between the modeled and measured ClO$_3^-$ concentrations were probably due to the aspects previously explained.

### CONCLUSIONS

In this work the distribution system of Cremona, in the north of Italy, was monitored for 6 years (2006–2011) analyzing residual chlorine, chlorite, and chlorate concentrations. The USEPA software Epanet 2.0 was applied to the distribution network in order to simulate the propagation of residual chlorine, chlorite, and chlorate, and in order to estimate the mixing zone of the water coming from the west and east treatment plants. The measured and simulated concentrations were compared.

The results of the network monitoring showed a high chlorine dioxide consumption and a significant chlorite formation. Predictably, this occurred mainly at the points of the network more distant from the treatment plants, where it exceeded the GV. Conversely, a low chlorate formation was registered. The propagation of chlorine and DBPs was simulated with the software, and the correlation was evaluated between the measured and the modeled results. Moreover, the water mixing zone in the distribution network was determined.
Table 3 | Comparison between measured and modeled residual ClO₃⁻ concentrations, mean absolute error, and root mean square error, at 10 a.m. after one month from the start of the disinfectant dosing in both the DWTPs

<table>
<thead>
<tr>
<th>Junction number (sampling point)</th>
<th>ClO₃⁻ (mg L⁻¹)</th>
<th>Measured</th>
<th>Modeled</th>
<th>Mean absolute error</th>
<th>Root mean square error</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>0.073</td>
<td>0.100</td>
<td>0.024</td>
<td>0.026</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>0.091</td>
<td>0.090</td>
<td>0.001</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>145</td>
<td>0.068</td>
<td>0.090</td>
<td>0.023</td>
<td>0.023</td>
<td></td>
</tr>
<tr>
<td>137</td>
<td>0.083</td>
<td>0.100</td>
<td>0.014</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>0.061</td>
<td>0.100</td>
<td>0.043</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>0.084</td>
<td>0.100</td>
<td>0.013</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>0.093</td>
<td>0.150</td>
<td>0.053</td>
<td>0.053</td>
<td></td>
</tr>
<tr>
<td>121</td>
<td>0.070</td>
<td>0.220</td>
<td>0.145</td>
<td>0.145</td>
<td></td>
</tr>
<tr>
<td>148</td>
<td>0.063</td>
<td>0.160</td>
<td>0.099</td>
<td>0.099</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>0.094</td>
<td>0.090</td>
<td>0.007</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td>116</td>
<td>0.102</td>
<td>0.100</td>
<td>0.006</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>0.096</td>
<td>0.150</td>
<td>0.054</td>
<td>0.054</td>
<td></td>
</tr>
</tbody>
</table>

This study shows how ClO₂, ClO₂⁻, and ClO₃⁻ kinetic reactions determined at laboratory scale can be used to describe the rates of reaction of these compounds in the DWDS. However, the differences between some of the measured and modeled concentrations were probably due to the kinetic study carried out at the laboratory scale in batch conditions and to the pipe wall effect, which was not evaluated in this study because of the difficulty in simulating it at laboratory scale. Moreover, it is possible that in the real system, a residual contaminant in water (e.g., NOM) can react with the disinfectant, determining a higher ClO₂ consumption and, consequently, lower Cl₂ residual concentrations. Therefore, further modeling should be carried out to determine the chlorine and DBP reaction kinetics, considering the pipe wall effect, in order to optimize the model. Notwithstanding, the proposed model is a useful tool since it is personalized for the studied drinking water distribution network, as specific disinfectant and DBP kinetics for the water distributed were determined at laboratory scale and were applied to the specific system. The model has proved to be a useful instrument for the prediction of the disinfectant and DBP propagation in the drinking water distribution network and is a valid support for water utility management.

**ACKNOWLEDGEMENTS**

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