Chlorate formation in water distribution systems: a modeling study

Fulvio Boano, Silvia Fiore and Roberto Revelli

ABSTRACT

Chlorine-based disinfection agents are known to favor the production of disinfection by-products (DBPs), whose concentrations are restricted by international guidelines to ensure a safe consumption of drinking water. Hence, it is important to understand the behavior of DBPs within water distribution networks (WDNs) to avoid users' exposure to concentrations higher than guideline values. The build-up in chlorate concentration resulting from chlorinated disinfectants is here simulated with the EPANET 2.0 software for one benchmark WDN serving about 130,000 inhabitants. Chlorate generation was accounted by means of an empirical model, considering different boundary conditions (physicochemical features of raw water, disinfectant dose). The gathered results indicate that increases in chlorate concentration within the considered WDN are narrow. Chlorate neo-formation in the WDN is, however, strictly related to the initial amount of chlorate released by the water treatment plant, i.e., to the input value in the WDN. If chlorate concentration in treatment plants is kept below 700 μg/L (i.e., World Health Organization guideline), depending on the mixing conditions in tanks, the simulation results referred to the considered WDN show that the DBP build-up within the network is limited (in any case lower than 5–7% of the threshold value).

Key words | chlorate, disinfection by-products, drinking water, water distribution network

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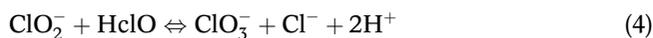Italy
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INTRODUCTION

Chlorine-based chemicals are commonly employed in water treatment plants (WTPs) to oxidize organic and inorganic pollutants, to remove microbial pathogens, and to improve water organoleptic features. While these compounds are very effective as oxidants/disinfectants, their application is known to promote the production of pollutants defined as disinfection by-products (DBPs), which have potential harmful effects on humans and are, therefore, a main public health concern (US EPA 2011; WHO 2011). The concerns about the presence of DBPs in drinking water and their possible negative effects, also related to congenital anomalies (Righi *et al.* 2012), have led to the development of regulations (Directive 98/83/CE is in force in EU) and international guidelines to identify threshold values of DBP concentration to avoid possible harmful effects for water consumption (US EPA 2011;

WHO 2011). Chlorate, supposed to act as an endocrine disrupting compound, is not yet regulated in the EU. The World Health Organization (WHO) guidelines define 700 μg/L as a limit for chlorate in drinking water and an acceptable daily intake equal to 30 μg/kg of body weight, considering a consumption of 2 L/d of water and a 60 kg adult individual (WHO 2011).

DBPs mostly derive from chlorine reaction with natural organic matter and other precursors (Hua & Reckhow 2007; Goslan *et al.* 2009), therefore the physicochemical properties of raw water are of main importance (Sorlini & Collivignarelli 2005). Other crucial issues about DBP generation are type and dose of disinfectant. While in small WTPs, particularly the ones dedicated to groundwater treatment, a single-phase disinfection (i.e., by means of hypochlorite) is usually adopted, large installations

generally perform multiple-step disinfection processes. A primary disinfection, aimed at the removal of pollutants and pathogens (i.e., by means of ozone, chlorine gas or chlorine dioxide), is commonly followed by a secondary disinfection, which has the main goal of assuring drinking water quality along the water distribution network (WDN) to final users. As a result, both primary and secondary disinfectants ought to be considered as DBP potential sources, and their interaction should be taken into account as well (US EPA 2011).

In the last decades chlorine dioxide has been extensively employed, particularly in surface water potabilization processes, because it is able to avoid the generation of trihalomethanes (THMs). Yet, chlorine dioxide can support the formation of chlorite and chlorate ions, that may derive from hypochlorite as well, and also from the interaction between chlorine dioxide (ClO_2) and hypochlorite (OCl^-), according to the following reactions (Gates *et al.* 2009; Snyder *et al.* 2009):

$$2\,OCl^- \rightarrow O_2 + 2\,Cl^- \tag{1}$$

$$3\,OCl^- \rightarrow ClO_3^- + 2\,Cl^- \tag{2}$$

$$2\,ClO_2 + HClO + H_2O \Leftrightarrow 2\,ClO_3^- + Cl^- + 3H^+ \tag{3}$$

$$ClO_2^- + HClO \Leftrightarrow ClO_3^- + Cl^- + 2H^+ \tag{4}$$

Chlorine dioxide, in contact with organic and inorganic oxidizable substances, degrades to chlorite, chlorate, and chloride (Cl^-) ions. Chlorite (ClO_2^-) is rapidly formed as an intermediate between hypochlorite and chlorate (ClO_3^-) during reaction (2) (Snyder *et al.* 2009). Moreover, chlorine dioxide, in the presence of hypochlorite, may undergo a disproportionation reaction to form chlorate as in reaction (3) (Gates *et al.* 2009). Several reactions may take place, as mentioned before, with different relative contributions during the overall chlorate formation process. However, (Gordon & Tachiyashiki, 1991) suggested that the direct reaction of hypochlorous acid (which is the dominant species at pH 5–7) with chlorite ion could be the main reaction responsible for chlorate

generation. Therefore, reaction (4) is assumed to contribute during the whole range of the reaction, while reaction (2) becomes relevant at the beginning of the process for pH values below 8. In general, the parameters mainly influencing chlorate neo-formation are both water features (temperature increase, pH, dissolved organic matter) and operational boundary conditions, such as coagulant and disinfectant doses (Korn *et al.* 2002; Zanetti *et al.* 2008). Temperature is a key factor in DBPs' formation (usually determining an increase of concentration), and disinfectant dose as well. Chlorite levels may vary between 10 and 20% of ClO_2 dose in winter and 40 and 70% in summer, while chlorate levels usually are between 10 and 30% of ClO_2 dose (Gates *et al.* 2009).

Potabilization treatments are specifically designed to ensure that DBPs' concentrations in WTPs outflow are below the international guidelines values. The most common approach in DBP control is a minimization of organic and inorganic precursors: coagulation, anion exchange, membranes, activated carbon, ozone, are technical solutions regularly implemented at full scale in WTPs. THMs and chlorite ions are effectively removed by active carbon (Sorlini *et al.* 2014), usually foreseen in WTPs' upstream secondary disinfection, although chlorate is not. Moreover, DBPs can still form within the WDN as a consequence of disinfectant reaction in pipes and tanks (Baribeau *et al.* 2002). Therefore, particularly in the case of chlorate, it is necessary to understand whether DBP build-up in WDNs can result in concentration values that significantly exceed guideline values.

The aim of this work is to analyze the net amount of chlorate produced in a water distribution system along the path between WTPs and users, taking into account raw waters having dissimilar physicochemical characteristics and different disinfection operative conditions. Although very few studies have been performed regarding the presence of DBPs in WDNs (e.g., Kim *et al.* 2002), none of them involved chlorate; therefore, this research is the first one to address the evaluation of chlorate neo-formation and dynamics within a WDN. The EPANET 2.0 model of the benchmark WDN Anytown (Walski *et al.* 1987) was analyzed as an iconic case study, and water quality simulations have been run to evaluate maximum chlorate concentrations in different flow conditions.

METHODOLOGY

The benchmark WDN

Anytown WDN was chosen in the present research because despite its simple structure it represents a benchmark case that has often been considered in modeling studies of water supply systems (Walski *et al.* 1987; Farmani *et al.* 2005; Herstein & Filion 2011; Fu *et al.* 2012; Atkinson *et al.* 2014; Basupi *et al.* 2014). The complete description of the WDN was reported by Walski *et al.* (1987), and only its main features are summarized here. The network structure is composed of 34 pipes (for a cumulative length of approximately 70 km) and 16 demand nodes with a daily average demand of 404 L/s comprehensive of residential and industrial users, corresponding to a population of about 130,000 inhabitants. Water is provided by a single reservoir connected to a pumping station, and two tanks whose sizes are 15,000 and 1,600 m^3, respectively, are included. Water demand values at single nodes ranged between 12.6 and 63.1 L/s, and the highest and lowest nodes had elevations equal to 6.1 and 36.6 m. The minimum and maximum values due to temporal variations in water demand were 0.6 and 1.3 times the mean daily values, respectively.

Evaluation of chlorate neo-formation

In-depth scientific activity has been devoted in the past decades to the development of models able to predict THMs and haloacetic acids' formation in drinking water (Sadiq & Rodriguez 2004; Chowdhury *et al.* 2009), although most models are based on multiple regressions and reaction kinetics are usually not considered. Only few researches are available at the moment about chlorate predictive models (Korn *et al.* 2002; Zanetti *et al.* 2008), and they are based on empirical equations as well. As discussed before, many different chemical reactions are involved in chlorate build-up, and their relative influence is not constant over the whole process. Therefore, the evaluation of zero-order or first-order kinetic expressions could be quite difficult (Boano *et al.* 2014), and the huge variance of raw water pH and its high influence on chlorate generation kinetics (Gordon & Tachiyashiki 1991) should also be considered.

In this study, the overall chlorate generation process was considered. Consequently, an empirical equation based on raw water features and on disinfection boundary conditions was preferred because it is able to describe the temporal dynamics of chlorate production in a more complex and flexible way compared to a kinetic approach. Specifically, the predictive equation developed by Korn *et al.* (2002) (see Equation (5)) from regression analysis of raw water disinfected with chlorine dioxide in eight Canadian WTPs, was considered in the present research. The Korn model was preferred to the one proposed by Zanetti *et al.* (2008), because the second was obtained from a single WTP. The Korn model predicts the amount of generated chlorate as a function of water physicochemical properties, reaction time, and ClO$_2$ dose:

$$\begin{aligned}
\log(\mathrm{ClO_3^-}) &= -1.99 + 0.621\log(\mathrm{pH}) - 0.090\log(T) \\
&\quad + 0.698\log(\mathrm{ClO_2}+1) - 0.104\log(t+1) \\
&\quad + 0.0460\log(\mathrm{NPOC}\times\mathrm{UV_{254}}) + 0.389\log(T)\log(\mathrm{ClO_2}+1) + \\
&\quad 0.346\log(\mathrm{ClO_2}+1)\log(t+1) + 0.486\log(\mathrm{NPOC}\times\mathrm{UV_{254}}) \\
&\quad \log(\mathrm{ClO_2}+1) - 0.119\log(\mathrm{NPOC}\times\mathrm{UV_{254}})\log(t+1)
\end{aligned}$$

(5)

where T ($^\circ$C) is water temperature, t (h) is water age, *NPOC* (mg/L) is non-purgeable organic carbon content (i.e., the organic fraction of total organic carbon (TOC), whose analytical measure also includes inorganic carbon), and UV_{254} (cm^{-1}) is the specific absorbance of UV light at 254 nm. In Equation (5), ClO$_3^-$ and ClO$_2$ concentrations are expressed in mg/L.

The aim of the work is to evaluate the formation of chlorate only in the WDN, beside the amount formed within the WTP. Hence, the value predicted by Equation (5) at $t = 0$ (i.e., at the entrance of the WDN) was subtracted from the calculated chlorate concentrations, and the net increments in chlorate concentrations caused by ClO$_2$ decay in the WDN were thus determined.

Raw water features and disinfection operative parameters

The values of the physicochemical characteristics of raw water employed in this study were gathered considering a critical analysis of literature data (see Table 1), in which

Table 1 | Raw water features and disinfection operative parameters derived from literature survey (n.a.: not available)

Reference	Type of raw water (no. of case studies)	Location	Parameter (measure unit)	Values (min–max)	Average value
Sorlini & Collivignarelli (2005)	Groundwater (1)	Italy	TOC (mg/L)	4.10	
			UV_{254} (1/cm)	0.0786	
			pH (pH units)	8.0	
			ClO_2 dose (mg/L)	1.18	
Nissinen *et al.* (2002)	Groundwater (6)	Finland	TOC (mg/L)	1.5–9.5	3.7
			UV_{254} (1/cm)	n.a.	n.a.
			pH (pH units)	6.3–7.3	6.85
			Cl_2 dose (mg/L)	0.12–0.73	0.41
Korn *et al.* (2002)	Groundwater (1)	Canada	NPOC (mg/L)	0.60	
			UV_{254} (1/cm)	0.009	
			pH (pH units)	7.57	
			ClO_2 dose (mg/L)	1.51	
Korn *et al.* (2002)	Surface water (7)	Canada	NPOC (mg/L)	2.03–5.96	4.26
			UV_{254} (1/cm)	0.034–0.212	0.118
			pH (pH units)	7.21–8.11	7.87
			ClO_2 dose (mg/L)	1.51	1.51
Sorlini *et al.* (2014)	Surface water (13)	Italy	TOC (mg/L)	2.4–6.3	4.0
			UV_{254} (1/cm)	0.015–0.315	0.118
			pH (pH units)	7.60–8.50	8.13
			ClO_2 dose (mg/L)	0.40–3.10	1.48
Kim *et al.* (2002)	Surface water (4)	Korea	TOC (mg/L)	2.35–5.12	3.06
			UV_{254} (1/cm)	0.072–0.116	0.085
			pH (pH units)	7.7–8.2	7.95
			ClO_2 dose (mg/L)	n.a.	n.a.
Nissinen *et al.* (2002)	Surface water (24)	Finland	TOC (mg/L)	2.6–11.9	7.36
			UV_{254} (1/cm)	n.a.	n.a.
			pH (pH units)	6.0–7.5	6.78
			Cl_2 dose (mg/L)	0.3–3.33	1.86
Wei *et al.* (2010)	Mixed (15)	China	TOC (mg/L)	0.27–7.75	1.88
			UV_{254} (1/cm)	n.a.	n.a.
			pH (pH units)	6.97–8.60	7.60
			ClO_2 dose (mg/L)	n.a.	n.a.

either NPOC or TOC values are shown according to data availability. Table 2 summarizes the values of the physico-chemical and operative parameters considered by the Korn model (see Equation (5)) that were used as boundary conditions for the simulations in the present research. The data reported in Table 2 were derived from the ones shown in Table 1 by means of their aggregation in three categories, defined on the grounds of raw water origin: surface water, groundwater, and mixed water. Cl_2 dose values in Table 1 were converted in ClO_2 ones considering a stoichiometric factor equal to 1.05. Mixed water values were gathered as average values of groundwater and surface water. The data in Table 2 are consistent regarding two

Table 2 | Raw water features and disinfection operative parameters employed for the simulations

Reference	Type of raw water	Parameter (measure unit)	Value
This study	Groundwater	TOC (mg/L)	2.80
		UV_{254} (1/cm)	0.044
		pH (pH units)	6.81
		ClO_2 dose (mg/L)	1.03
	Surface water	TOC (mg/L)	4.67
		UV_{254} (1/cm)	0.107
		pH (pH units)	7.68
		ClO_2 dose (mg/L)	1.62
	Mixed	NPOC (mg/L)	3.12
		UV_{254} (1/cm)	0.076
		pH (pH units)	7.36
		ClO_2 dose (mg/L)	1.32

aspects. First, they reliably describe the quality of surface raw water towards that of groundwater. Second, this approach consistently describes the real situation about WTPs and WDNs, which may be fed by a single or multiple types of raw water.

No hypotheses were made about the nature of primary and secondary disinfection in the WTP feeding the considered WDN. A single water reservoir and therefore a single disinfectant input in the WDN were hypothesized in the simulations.

In buried pipelines, the presence of soil limits heat exchange and temperature fluctuations of water within pipes. For this reason, in this modeling analysis, water temperature was considered constantly equal to 14 °C throughout the WDN (see Table 1) and the influence of heat exchange on chlorate production rate was hence assumed to be negligible. Chlorate production may decrease with increasing distance from the WTP because production rates are proportional to disinfectant concentration, which in turn progressively decays as water travels through the WDN. However, the effect of this decrease in disinfectant concentration was not considered because (i) it was expected to be limited and (ii) the slight overestimation of DBP production in the WDN resulting from the assumption of constant disinfectant concentration led to a conservative estimate of chlorate exposure from drinking water consumption.

Modeling approach

The network model was analyzed with the EPANET 2.0 software (Rossman 2000). Numerical simulations were run considering three scenarios representing a wide array of different mixing conditions of water in the two tanks. Tank mixing is a crucial issue because tanks are often characterized by high water residence times that enhance disinfectant decay and formation of DBPs. The three considered scenarios were useful to evaluate the impact on chlorate production of three different mixing models, i.e., fully mixed, first-in-first-out (FIFO) plug flow, and last-in-first-out (LIFO) plug flow. The fully mixed model is most suited for tanks with frequent filling and emptying that enhance water mixing, while FIFO and LIFO plug flow models describe tanks with negligible mixing potential and either with separate inlet/outlet pipes (FIFO) or with a single pipe for both inflow and outflow (LIFO). Further mixing scenarios were not considered because alternative descriptions of water mixing would require the introduction of model parameters which are difficult to estimate (e.g., Clark *et al.* 1996). Moreover, the three considered scenarios already represent very different ways of water recirculation, and hence provide different estimates of water residence times in tanks.

Values of water age (*t* parameter in Equation (5)) were derived from the hydraulic model of the WDN. A water quality simulation with duration of 120 days was performed because it was seen that after this duration values of water age attained stable periodic conditions that were no longer affected by the initial conditions. Values of water age were hence obtained discarding this initial transient. Water age in the WDN followed a periodic daily pattern induced by the temporal demand of network users, and the maximum value for each node was thus extracted to represent the conditions that led to the highest chlorate production. Maximum chlorate concentrations were then considered for critical points that exhibited the maximum concentrations within the WDN.

RESULTS AND DISCUSSION

The simulations presented in the foregoing sections have been performed, and the main results are reported below focusing on chlorate concentrations in nodes and tanks of Anytown network.

Spatial variations of chlorate concentrations arise in the WDN because of differences in water age among network nodes. Water age is strongly influenced by the temporal dynamics of the system, and it varies during the simulation due to the influence of the intensity and direction of pipe flow rates, which in turn depend on time-variable user demands. Figure 1 shows an example of the water age evolution predicted by EPANET for Node 80 and Tank 65 (Mixed mode). The water age behavior reflects the typical daily pattern given by user demands, with Tank 65 displaying milder variations because the large water volume stored in the tank results in a high inertia that dampens the fluctuations of water age.
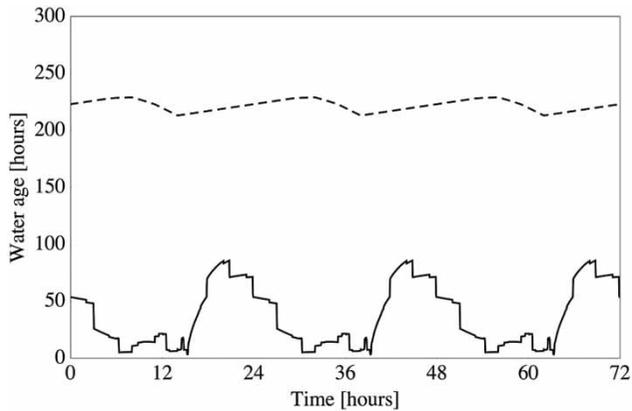
Figure 1 │ Temporal dynamics of chlorate concentrations at Node 80 (continuous line) and Tank 65 (dashed line). The time origin represents the midnight of a day for which the simulation attained periodic conditions.

Temporal patterns of water age shown in Figure 1 result in variations over time of chlorate concentration at each point of the WDN. In the remainder of this analysis, only the peak value of the water age for each node and tank has been taken into account because these peak values are associated with the maximum exposure of WDN users to chlorate.

Figure 2 shows the configuration of the Anytown network with labels that identify the nodes and the tanks. The figure reports maximum water age for Mixed tank conditions (see Table 3 and discussion below). Water ages increase with distance from the input point (Node 10), and the highest values are found in tanks as well as in nearby nodes. In particular, for Mixed tank conditions the water age exhibits its highest value at Tank 65 (which is much larger than Tank 165), in Node 60 and Node 80.

Results of the maximum water ages obtained from the EPANET simulations are displayed in Table 3 for the three different scenarios with respect to mixing conditions in tanks (Mixed, FIFO, and LIFO) and for the three different types of raw water. As anticipated by Figure 2, for Mixed and FIFO modes, water age values are highest in Tank 65 and Node 160 (the nearest to Tank 65), while in LIFO mode, the values in nodes are more homogeneous and very high in the two tanks. The longest time spent by water in the WDN is predicted for the LIFO case and it corresponds to 514 and 655 h (i.e., about 3–4 weeks) for the two tanks. These values are lower for the Mixed and FIFO scenarios, but even in these cases the long permanence in Tank 65 results in water ages that are higher than 1 week (229 and 290 h for Mixed and FIFO, respectively).

Table 3 also displays the chlorate concentration increments calculated with the Korn model (Equation (5)) with respect to the chlorate concentration calculated in Node 10. As stated in the section 'Evaluation of chlorate
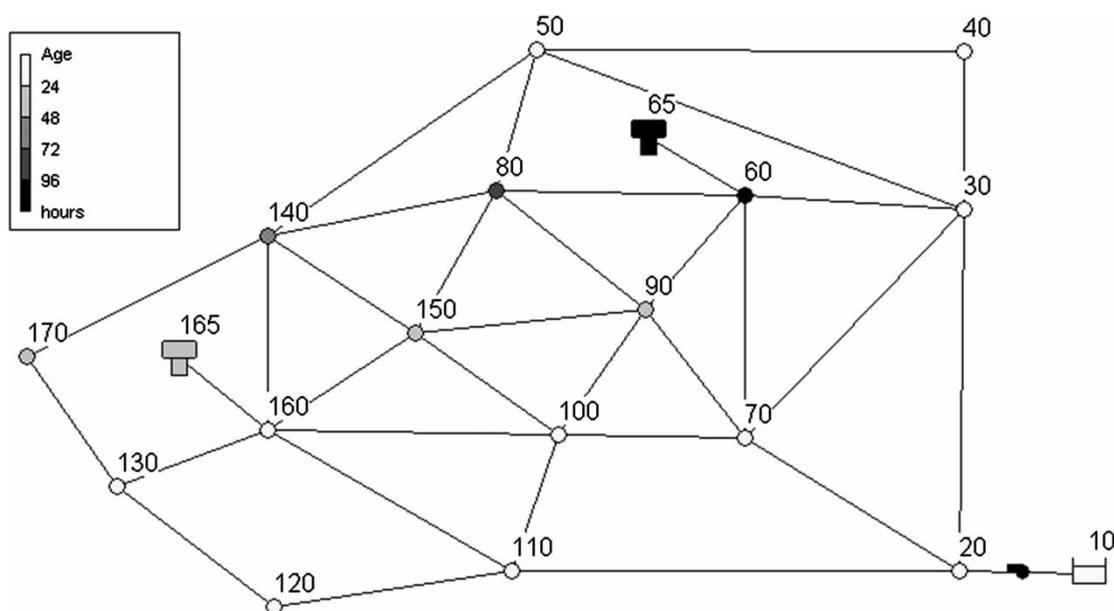
Figure 2 │ Spatial distribution of water age over the WDN for the Mixed tank scenario.

Table 3 | Water age and chlorate concentrations increment with respect to input Node 10

| | Water age [hours] | | | ClO$_3$ increments [µg/L] | | | | | | | | |
| | | | | GW source | | | SW source | | | Mixed source | | |
	Mixed	FIFO	LIFO	Mixed	FIFO	LIFO	Mixed	FIFO	LIFO	Mixed	FIFO	LIFO
Node 20	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Node 30	1.57	1.57	1.57	4.36	4.36	4.36	5.43	5.43	5.43	9.34	9.34	9.34
Node 40	2.55	2.55	2.55	5.96	5.96	5.96	7.38	7.38	7.38	10.93	10.93	10.93
Node 50	3.58	3.58	3.58	7.27	7.27	7.27	8.96	8.96	8.96	12.00	12.00	12.00
Node 60	115.59	118.8	8.97	27.46	27.67	11.48	31.86	32.08	13.95	20.25	20.30	14.64
Node 70	0.73	0.73	0.73	2.48	2.48	2.48	3.11	3.11	3.11	6.78	6.78	6.78
Node 80	85.83	88.19	9.27	25.31	25.51	11.65	29.54	29.75	14.15	19.70	19.75	14.73
Node 90	44.82	48.00	4.78	20.88	21.33	8.49	24.66	25.16	10.42	18.41	18.55	12.87
Node 100	1.55	1.55	1.55	4.33	4.33	4.33	5.39	5.39	5.39	9.30	9.30	9.30
Node 110	0.84	0.84	0.84	2.77	2.77	2.77	3.46	3.46	3.46	7.25	7.25	7.25
Node 120	1.81	1.81	1.81	4.80	4.80	4.80	5.97	5.97	5.97	9.81	9.81	9.81
Node 130	19.04	25.63	12.14	15.59	17.35	13.07	18.70	20.71	15.80	16.53	17.21	15.43
Node 140	48.20	49.10	10.03	21.36	21.48	12.06	25.19	25.33	14.63	18.56	18.60	14.94
Node 150	35.39	36.00	9.73	19.35	19.46	11.90	22.96	23.09	14.44	17.92	17.95	14.86
Node 160	19.48	27.27	13.63	15.72	17.73	13.70	18.85	21.14	16.53	16.58	17.35	15.72
Node 170	40.62	42.00	13.37	20.24	20.45	13.59	23.95	24.19	16.41	18.21	18.28	15.67
Tank 65	229.11	290.00	514.66	32.71	34.61	39.46	37.44	39.44	44.45	21.46	21.86	22.79
Tank 165	35.48	34.73	655.23	19.37	19.24	41.60	22.98	22.83	46.63	17.92	17.88	23.16

neo-formation', the main goal of the present analysis is the evaluation of the chlorate production within the WDN. To this aim, the concentration of chlorate for water entering the network from the WTP in Node 10 is set to zero to exclusively focus on the chlorate build-up in the WDN. Hence, we have considered the chlorate concentration in Node 10 as the reference level against which the increments in the rest of the network are determined. The increments listed in Table 2 range between a few micrograms per liter for nodes that are close to the WTP up to approximately 40 µg/L for tanks and nearby nodes. Such values are comparable with the amount of chlorate that is generated in WTPs when groundwater is disinfected (50–100 µg/L) and much smaller than chlorate concentrations that are found at the entrance of the WDN fed with treated surface water (200–1,000 µg/L), which typically requires a higher disinfectant dose (Fiore *et al.* 2012; Sorlini *et al.* 2014).

The parameter values used for the application of Equation (5) are reported in Table 2. With these values,

Equation (5) can be rewritten in different forms depending on the raw water type:

$$GW: ClO_3 = 0.03965(1 + t)^{0.1106} \tag{6}$$

$$SW: ClO_3 = 0.07245(1 + t)^{0.0766} \tag{7}$$

$$Mixed: ClO_3 = 0.05290(1 + t)^{0.0968} \tag{8}$$

where t is the reaction time (in hours) that was assumed equivalent to the maximum water age. Figure 3 displays the behavior of the increments in chlorate concentration (i.e., $ClO_3|_t - ClO_3|_{t=0}$) over the WDN, with markers denoting the increment values at the corresponding nodes and tanks. The figure shows that the amount of produced chlorate is mainly controlled by differences in water age among WDN nodes. The physicochemical properties of raw water also affect chlorate production, but their influence is less
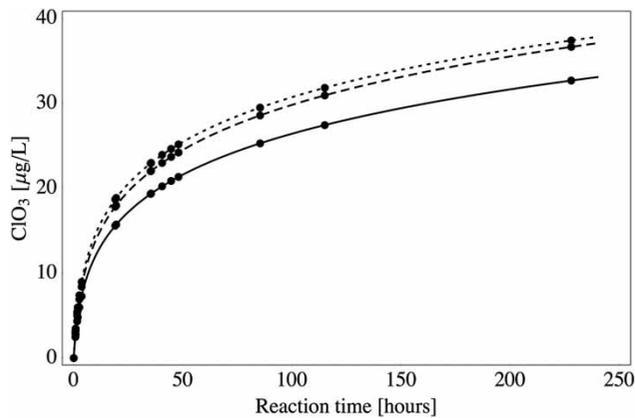
Figure 3 | Increments in chlorate concentration predicted by Equation (5) (groundwater: continuous line, surface water: dotted line, mixed water: dashed line) and for the network nodes (dots).

remarkable compared to the reaction time. As expected, the highest chlorate production occurs when surface water is considered while the lowest one corresponds to groundwater, with mixed water representing an intermediate case.

The level of risk for the users that is associated with chlorate formation in the WDN is strictly related to the amount of chlorate that is already present in drinking water from the WTP, i.e., to the input chlorate concentration. Most countries have not imposed any restrictions on maximum chlorate concentration in drinking water yet. Hence, the value of 700 µg/L suggested by the WHO guidelines for drinking water quality (WHO 2011) is here considered as a reference level to assess the relevance of chlorate build-up. The calculated increments in chlorate concentrations were hence compared to the WHO reference level, and the resulting values are reported in Table 4 for the different raw water types and tank mixing scenarios. The relative increments vary within a relatively narrow range, comprising between 0.4 and 6.7% of the WHO threshold value. The highest values always occur at the tanks in LIFO scenarios, and correspond to 5.9, 6.7, and 3.3% when the raw water source is represented by groundwater, surface water, and mixed water, respectively. Beside

Table 4 | Relative increments (%) of chlorate concentrations with respect to the reference value of 700 µg/L (WHO 2011)

| | ClO$_3$ increments [%] | | | | | | | | |
| | GW source | | | SW source | | | Mixed source | | |
	Mixed	FIFO	LIFO	Mixed	FIFO	LIFO	Mixed	FIFO	LIFO
Node 20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Node 30	0.6	0.6	0.6	0.8	0.8	0.8	1.3	1.3	1.3
Node 40	0.9	0.9	0.9	1.1	1.1	1.1	1.6	1.6	1.6
Node 50	1.0	1.0	1.0	1.3	1.3	1.3	1.7	1.7	1.7
Node 60	3.9	4.0	1.6	4.6	4.6	2.0	2.9	2.9	2.1
Node 70	0.4	0.4	0.4	0.4	0.4	0.4	1.0	1.0	1.0
Node 80	3.6	3.6	1.7	4.2	4.3	2.0	2.8	2.8	2.1
Node 90	3.0	3.1	1.2	3.5	3.6	1.5	2.6	2.7	1.8
Node 100	0.6	0.6	0.6	0.8	0.8	0.8	1.3	1.33	1.3
Node 110	0.4	0.4	0.4	0.5	0.5	0.5	1.0	1.0	1.0
Node 120	0.7	0.7	0.7	0.9	0.9	0.9	1.4	1.4	1.4
Node 130	2.2	2.5	1.9	2.7	3.0	2.3	2.4	2.5	2.2
Node 140	3.1	3.1	1.7	3.6	3.6	2.1	2.7	2.7	2.1
Node 150	2.8	2.8	1.7	3.3	3.3	2.1	2.6	2.6	2.1
Node 160	2.3	2.5	2.0	2.7	3.0	2.4	2.4	2.5	2.3
Node 170	2.9	2.9	1.9	3.4	3.5	2.3	2.6	2.6	2.2
Tank 65	4.7	5.0	5.6	5.4	5.6	6.4	3.1	3.1	3.3
Tank 165	2.8	2.8	5.9	3.3	3.3	6.7	2.6	2.6	3.3

tanks, the maximum relative increments at WDN nodes can be found in the FIFO and, to a slightly lower extent, in the Mixed scenario (4.0%, 4.6%, and 2.9% for groundwater, surface water, and mixed water, respectively).

The previous results show that the increments of chlorate concentration within the network resulting from disinfectant reaction in tanks are very limited (<7%) compared to the concentration limit proposed by WHO. Since tanks do not represent points of water consumption by users, it is worth stressing that this increment is even lower (<5%) for WDN nodes where the actual user demand of water is located.

CONCLUSIONS

The production of DBPs in WDNs is expected after the application of chlorine-based disinfection agents. International guidelines (WHO 2011) suggest limiting the concentrations of DBP values in order to guarantee the safety of drinking water. Among possible disinfection methods, chlorine-based ones are widely employed because of their cost-effectiveness ratio. It is thus necessary to evaluate the production of DBPs in WDNs and their dynamical behavior.

This study has focused on the formation of chlorate in a benchmark WDN. Chlorate build-up in the WDN has been evaluated by coupling an EPANET-based model of the network to determine water residence times in the WDN and an empirical equation (Korn *et al.* 2002) to calculate the amount of produced chlorate over the wide range of residence times in the network. The results show that the increments in chlorate concentrations are limited (i.e., lower than concentrations typically found in WTPs) and that, in the investigated conditions, the DBP production is much lower (<5–7%) of the values suggested by commonly accepted international guidelines (WHO 2011). Even though these values are specific for the benchmark network that was considered here, it is expected that the results are also representative of similar medium-sized WDNs, for which the neo-formation of chlorate in WDN pipes and tanks should not represent a health concern provided that chlorate concentration is kept below suggested guideline values at treatment plants.

A simplifying assumption that has been made in the present analysis is related to the influence of pipe conditions on chlorate dynamics. In real networks, spatial variations of the pipe properties such as type of material, age, and roughness influence chlorine dynamics (Al-Jasser 2007; Fuchigami *et al.* 2012) and may thus also affect chlorate formation within the WDN. However, these effects are typically neglected in modeling studies because detailed information about pipe characteristics are usually unavailable and including the influence of pipe wall conditions would introduce a high level of uncertainty that would make results less reliable. Moreover, the predictive equation employed in the present analysis is already one of the most detailed ways to estimate chlorate formation, and it does not include the influence of wall materials which were considered less important than the other factors considered here. Another practical issue that has been disregarded is the presence of water leakages. While this assumption is not realistic, it is important to stress that leakages would result in a less critical situation for DBP formation. On the one hand, low water velocities generally occur during the night when user demands are low, resulting in higher water age that favors DBP production. On the other hand, leakage intensity is also highest during the night because of high pressure levels. The inclusion of leakage in the model would hence lead to a small increase in velocities at night that would reduce water age in the system and also chlorate production, partially balancing the effect of low night-time velocities. These changes in water age are expected to be small and probably not relevant compared to the residence time in tanks, but they would, anyway, make the situation less critical for chlorate production. Nonetheless, future insights on pipe wall influence on chlorine-based disinfectants and the development of more realistic and refined WDN models may lead to more precise predictions of DBP production in water networks.

Given the increasing attention received by DBP control to ensure safety of drinking water, it is expected that the formation of DBPs in water within WDNs will represent an active research topic for future studies about drinking water quality. Future developments will likely better analyze the controlling factors for the kinetics of formation of chlorate and other DBPs. In this context, our study has shown the importance of an accurate description of the multiple factors

that affect DBP formation. In particular, the residence time of drinking water in WDNs should not be neglected when DBP formation is assessed because of the remarkably long times spent by water in storage tanks.

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