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Study of the Formation-Distribution of Chlorite and Chlorate from Chlorine Dioxide in a Water Distribution Network: the Case Study of Udine

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Abstract. To ensure water quality and to avoid bacterial contamination in Drinking Water Distribution Systems (DWDS), disinfection is conducted in drinking awater treatment plants. Disinfectant concentration in DWDS decreases with time while, due to chemical reactions with dissolved and particulate matter, biofilm and pipe wall material, disinfection by-product (DBP) formation increases. Chlorine-based disinfection methods are the most commonly used and, if chlorine dioxide is used as a disinfectant, chlorite and chlorate can be produced as DBPs. This study evaluates with a simulation model (EPANET-MSX) the formation and distribution of chlorite and chlorate in the water distribution system of Udine, which is disinfected with chlorine dioxide. Having an integrated chemical-hydraulic model can, in fact, improve water utilities network management both in standard and special conditions. The results obtained with the simulation model were only minimally different to the concentration values measured on site, hence it can be assumed that they may be used for several conditions in order to make predictions.

Key words. Disinfection by-products, Chlorine dioxide, EPANET-MSX.

1. Introduction. Disinfection is conducted in drinking water treatment plants (DWTPs) to ensure water quality and to avoid bacterial contamination in drinking water distribution systems (DWDS). However, while the disinfectant concentration in DWDS decreases with time, disinfection by-product (DBP) formation increases; this is due to chemical

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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). The most commonly used disinfection methods are chlorine-based and, if chlorine dioxide is used as a disinfectant, chlorite and chlorate can be produced as DBPs.
Therefore, it is important to evaluate spatial and temporal variation in residual chlorine, chlorite (ClO2-), and chlorate (ClO3-) within DWDS. In fact, the World Health Organisation (WHO) recommends a free residual chlorine concentration of 0.2 mg L^{-1} in DWDS (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). Prediction of the disinfectant residual and DBP propagation in DWDS can be achieved using water distribution modelling (WDM), which allows simulation and evaluation of a DWDS under different operating conditions.

In this study, water distribution is modelled with the software EPANET, developed by the United States Environmental Protection Agency (USEPA), which models the hydraulic and water quality behaviour of water distribution piping systems (Rossman 2000). Since few studies using WDM are available on ClO2, $ClO2^{-}$ and $ClO3^{-}$ propagation in DWDS (Korn et al. 2002, Sorlini et al. 2016, Boano et al. 2016), the kinetic reactions of ClO2, $ClO2^{-}$ and $ClO3^{-}$ and the simulation of their propagation in DWDS using WDM must be further investigated. This novel work is aimed at understanding ClO2, $ClO2^{-}$ and $ClO3^{-}$ propagation in a DWDS using WDM software, more specifically, the DWDS of Udine, in the north-east of Italy.

2. Chlorine dioxide, chlorite and chlorate. Chlorine dioxide disinfection is mainly used for its many advantages. It quickly penetrates bacteria biofilm, which makes it very reactive and efficient, meaning a low concentration is sufficient for bacteria inactivation. It also has a wide range of action (reacting with bacteria, viruses and algae), exhibits a stable oxidation and disinfection strength across a wide pH range from pH 2.0 to 10.0, and causes a reduction in the formation of halogenated DBPs, such as trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs). On the other hand, chlorine dioxide generates chlorite and chlorate as disinfection by-products. As seen before, considering the adverse health risks of chlorite and chlorate (i.e., haemolytic anaemia and liver damage), the level of these anions is restricted in drinking waters. In particular, the 2020 EU Directive imposes a limit of 700 micrograms per litre for each by-product. For this reason, it is important to have a model that predicts their concentrations.

3. Udine water distribution system. Udine, which is located in north-east Italy, has a DWDS that supplies

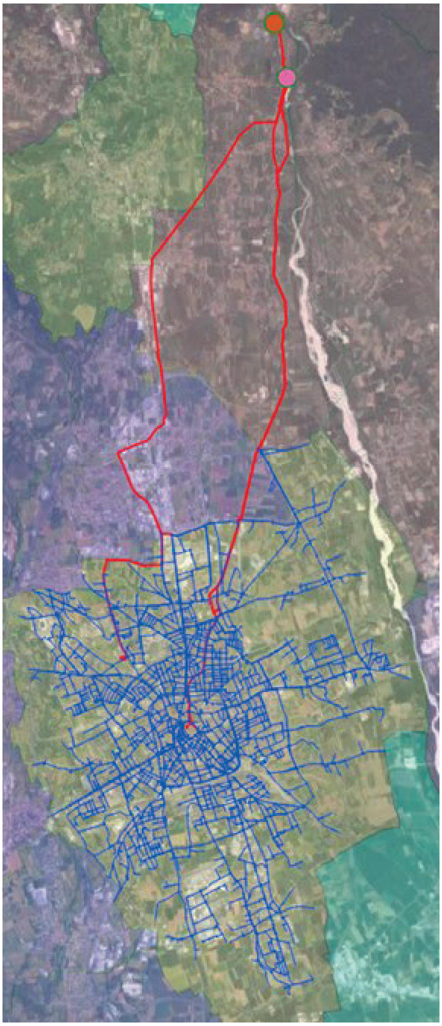
Figure 1. Water distribution system of Udine.

approximately 100,000 inhabitants, has an overall length of 416 km and is disinfected with ClO2. The network is mainly supplied by the Zompitta wells that are located north of the city (Fig. 1) and by 3 wells inside the city which are used when needed. Due to the high water quality, the disinfection required is minimal. In fact, the water utility maintains a constant concentration of chlorine dioxide of 0.15 mg/L in the Zompitta tank, while, when the city wells are activated, their disinfection is carried out with sodium hypochlorite at a concentration of 0.07 mg/L. The Udine WDN has been modelled in detail using the EPANET software. The model, that counts 5793 nodes, 6466 pipes, 5 tanks and 6 reservoirs has been calibrated and validated with an on-site measurement campaign.

4. Analytical procedure. After the validation of the hydraulic model, batch experiments were carried out by treating raw water samples with ClO2. 100 ml of the Zompitta well's raw water was put in a graduated cylinder and treated with 5 mg/L of ClO2. The ClO2 dosage is higher than the one employed in the DWTP disinfection, because the aim of this test was to evaluate the ClO2 consumption and subsequent DBP formation. Each cylinder was then plugged, stirred and stored in the dark. The residual ClO2, $ClO2^-$ and $ClO3^-$ concentrations were analysed after 0, 20, 40, 80, 120, 240, 360, 1440, 2880 and 4320 minutes of water:disinfectant contact time. Tests were carried out at a temperature of 17-20°C and a pH of 7.7. (Water samples were stored in a fridge in dark conditions). The ClO2 solution was produced in a laboratory (mixing hydrochloric acid and sodium chlorite).

Figure 2. Spectrophotometer.

5. Instruments used. Measurement of the ClO2 concentration was performed indirectly, multiplying by 1.9 the free chlorine concentration measured with the spectrophotometer (Fig. 2). In contrast, the chlorite and chlorate concentrations were measured using an ion chromatographer (IC) (Fig. 3). The IC measurement required a certain amount of time, as it was necessary to identify the retention time of every anion using their standards and to construct calibration lines in order to determine their concentrations (Fig. 4). The IC chromatograms for raw and treated water are reported in Figure 5, and we can see, for the raw water, the presence of four peaks related to 4 different species: chloride, nitrate, sulphite and sulphate. For the treated water, two new peaks, corresponding to chlorite and chlorate, appear.

6. Results and discussion. The concentrations measured at the different time-steps allowed the determination of the reaction kinetics for the three species of interest. In Figure 6, the three graphs representing, respectively, ClO2 decay and $ClO2^-$ and $ClO3^-$ formation are reported.

These laws have been applied in the EPANET-MSX software to couple the chemical reactions with the hydraulic simulation. Using EPANET-MSX, it was possible to simultaneously model the concentrations of the three species using both 0 order and first order kinetics. To assess the laws' quality, the concentration of the species was measured at 30 points of the network: eighteen were measured in the last two years by the water utility and the remaining measurements were done in the university laboratory. In this table, the modelled and measured values for each species are reported with their absolute and root mean square error. The low error values, near the instrument detection limit of 50 micrograms/L confirm the laws' effectiveness; moreover, we can appreciate that the maximum values of $ClO2^-$ and $ClO3^-$ measured and calculated are three times lower than the limit. The correlation between modelled and measured concentrations is reproduced for both species in Figure 7. The main differences are due to the linearity of the equation adopted and their dependence on ClO2 concentration.

In conclusion, through the hydraulic simulation paired with chemical reactions based on batch

Figure 3. Ion chromatographer.

experiments, a qualitative model of the Udine WDN has been created. This model, having as input the initial concentration of ClO_2, provides as output the concentrations of ClO_2, ClO_2^- and ClO_3^- in every network node. The small difference between real and simulated values confirms the equation's quality and, thus, its possible use in several conditions for predictive purposes. It is important to highlight that the entire methodology is based on a robust and detailed hydraulic modelling, difficult to find in other works, without which chemical models would find little application.

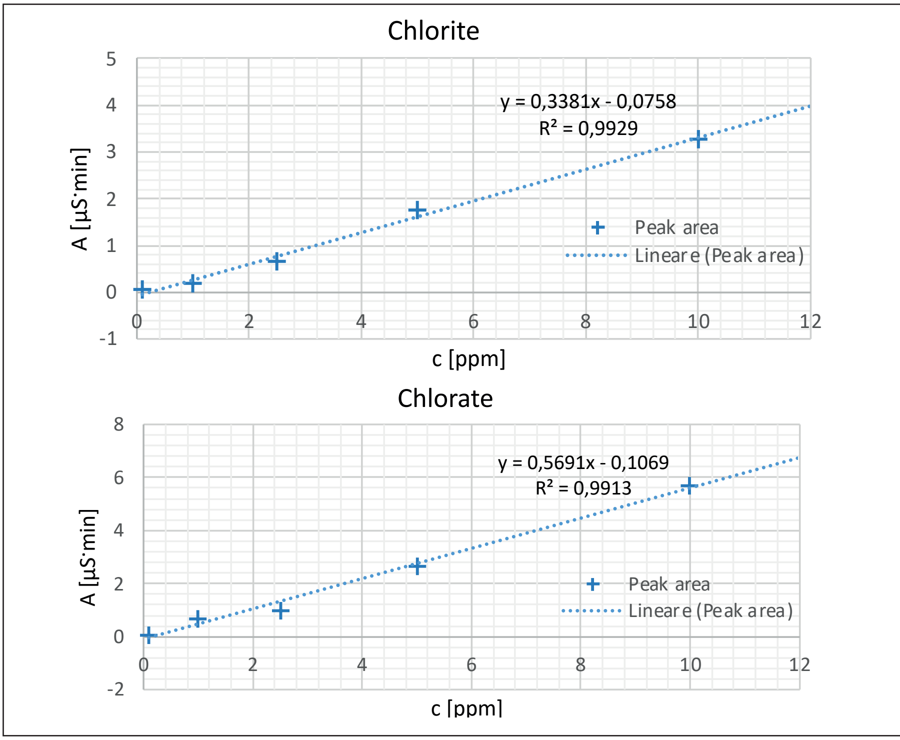

Figure 4. Chlorite and chlorate calibration lines.

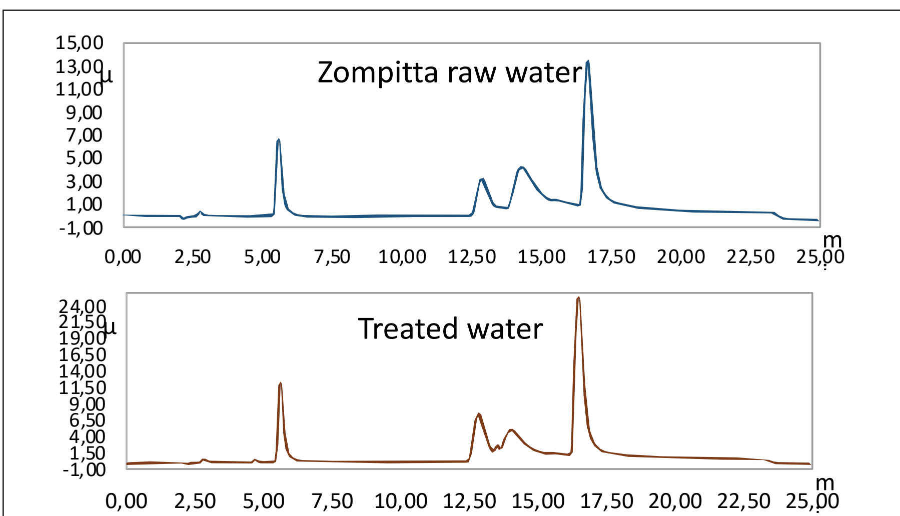

Figure 5. IC chromatograms for raw and treated water.

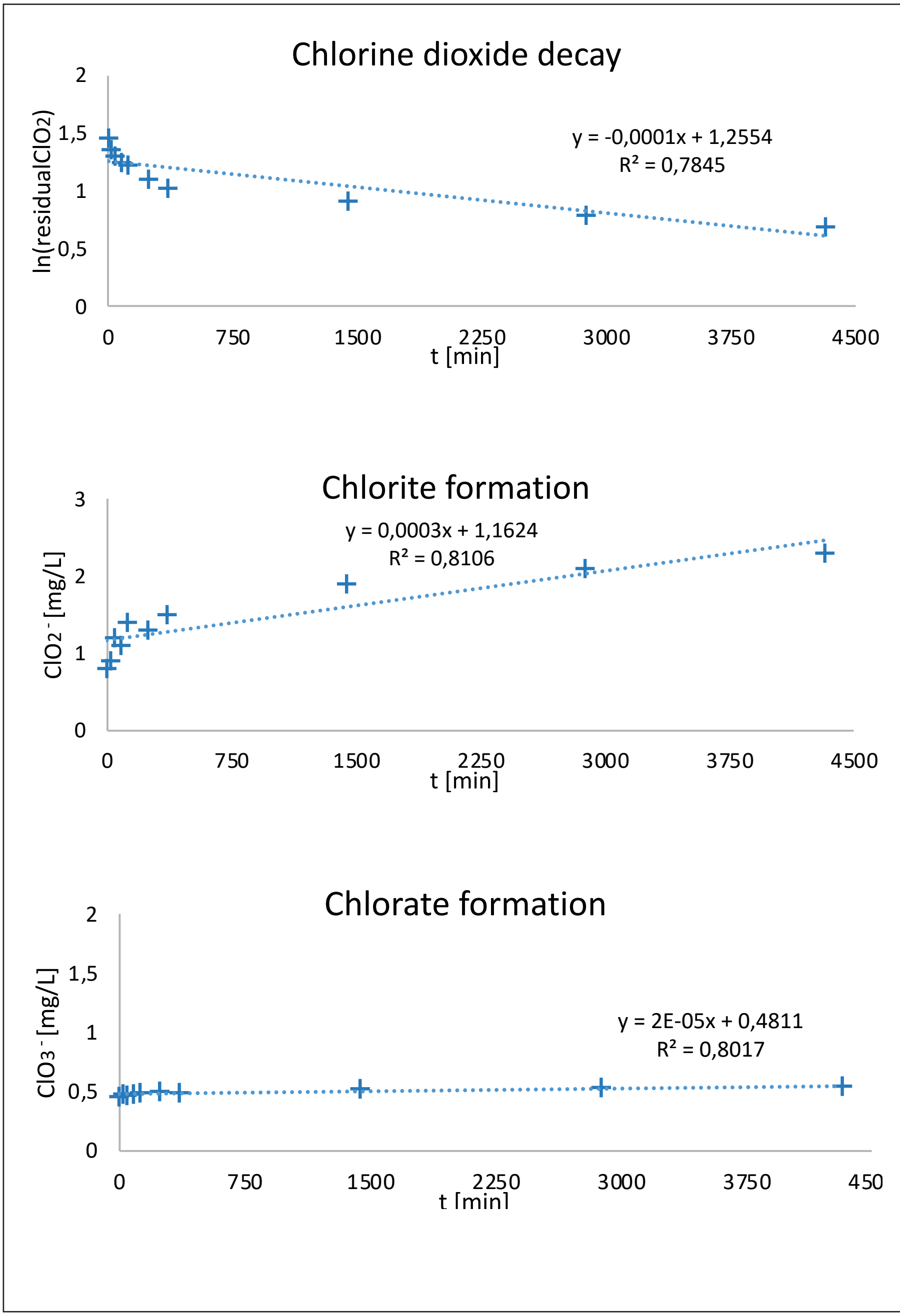

Figure 6. Chlorine dioxide decay law and chlorite and chlorate formation laws.

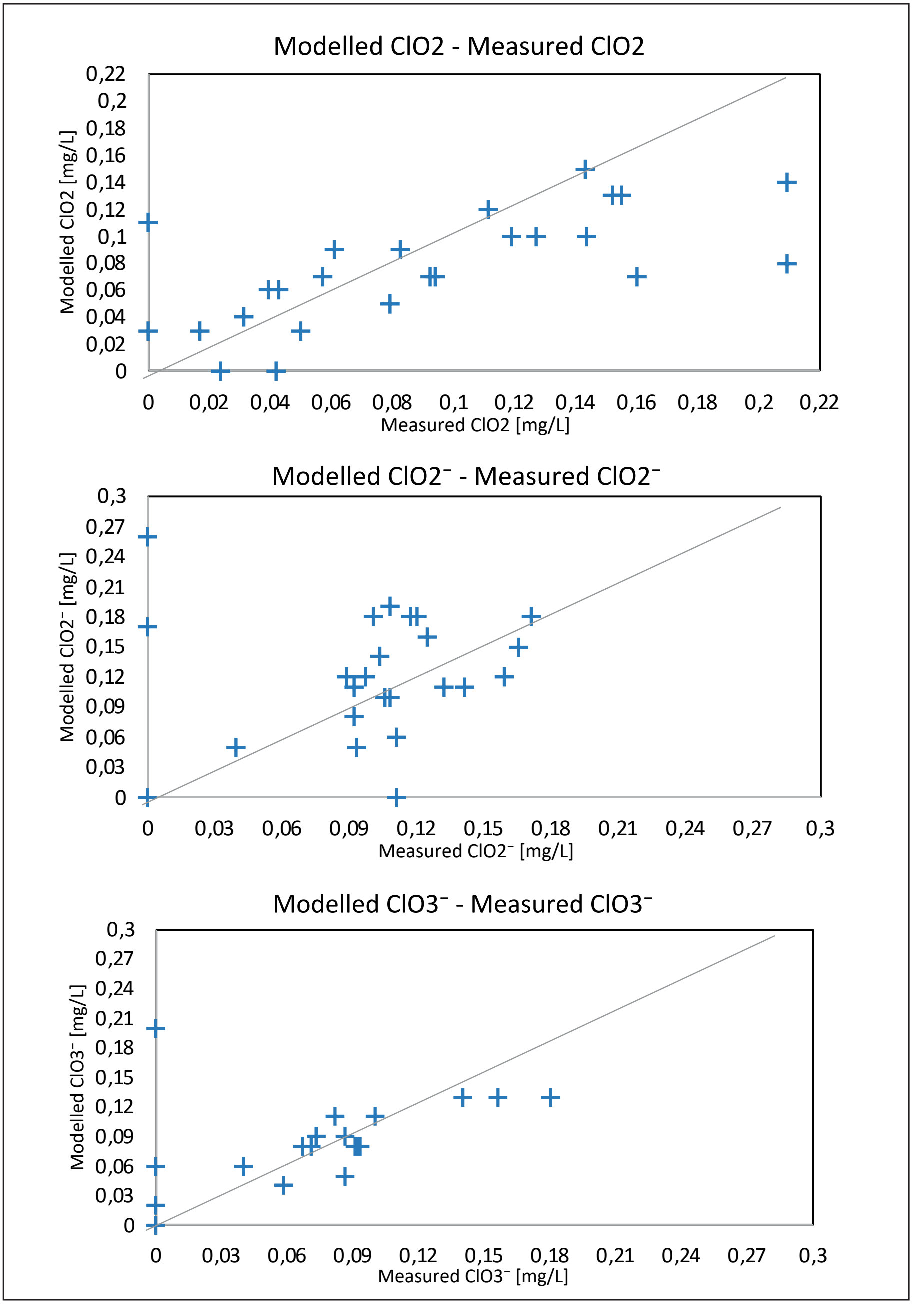

Figure 7. Correlation between modelled and measured concentrations of ClO2, $ClO2^{-}$ and $ClO3^{-}$.

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