Impact of secondary disinfection on corrosion in a model water distribution system

John D. Eisnor and Graham A. Gagnon

ABSTRACT

The objective of this project was to evaluate the impact of secondary disinfectants on internal corrosion and water quality in old, unlined cast-iron water distribution system pipes. The disinfectants evaluated for this study were free chlorine, chloramines, chlorine dioxide and chlorite. The investigation was conducted with five recirculating pipe loops, one for each disinfectant and one control, to observe the impacts of corrosion. The loops were evaluated over a period of 220 days. Collected samples were evaluated for corrosion rate, total and dissolved iron, and turbidity. Results indicate that monochloramine and free chlorine increase corrosion rate within distribution systems, with average rate of 5.9 and 3.3 ml per year (mpy), respectively. Chlorine dioxide, at levels used for drinking water treatment, did not impact corrosion, as the rates were similar to those observed in the control loop, with an average rate of 2.2 mpy. The average corrosion rate in the control loop was 2.1 mpy. Corrosion rates decreased, with respect to the control, when chlorite was used, with an average rate of 0.9 mpy over the course of experimentation. Similar trends were observed for total and dissolved iron. Iron levels were higher for free chlorine, monochloramine and chlorine dioxide (2.82, 1.36 and 0.72 mg I^{-1}, respectively), with respect to the control (0.11 mg I^{-1}). However, iron levels were lower when chlorite was used (0.03 mg I^{-1}). It is hypothesized that chlorite was reacting with soluble Fe^{2+} and other metals and thereby reducing corrosion and red water. Overall, these findings indicate that disinfection with chlorite decreased the corrosion rate within the distribution system and chlorine dioxide produced corrosion rates comparable to the control pipe loop.

Key words | chlorine dioxide, corrosion, disinfection, distribution systems, free chlorine, polyphosphate

John D. Eisnor
Nova Scotia Department of Environment
   and Labour,
Halifax,
Nova Scotia,
Canada

Graham A. Gagnon (corresponding author)
Department of Civil Engineering,
Dalhousie University,
Halifax,
Nova Scotia,
Canada
E-mail: *graham.gagnon@dal.ca*

INTRODUCTION

The drinking water industry is striving to implement new regulations for secondary disinfection to prevent unwanted microbial contamination in the distribution system while minimizing the formation of disinfectant by-products (DBPs). From a public health perspective the need to increase disinfectant residual concentrations and/or switch disinfectants will be a critical factor in developing these regulations. However, these decisions can potentially lead to significant degradation of both water quality and distribution system materials via corrosion. The results generated from this study will provide the water industry with critical data that will allow

development of strategies for mitigating iron and copper corrosion, thereby improving disinfectant efficacy.

It is widely accepted in the literature that disinfectant residuals increase corrosion rates (AWWA 1999; McNeill and Edwards 2001), as secondary disinfectant serves as potential oxidants for distribution system pipe and related plumbing material. Furthermore there is a lack of direct comparison under controlled conditions among disinfectants and their relative corrosivity on pipe surfaces and scales. Previous studies that have examined disinfectants in relation to iron pipes have obtained indirect assessments of their impact on corrosion by evaluating other

aspects of secondary disinfection, such as the efficacy of disinfectants to control microbial pathogens on various pipe surfaces (LeChevallier et al. 1993), or the impact of disinfectants and pipe material on DBP formation in distribution systems (Tuovinen et al. 1984; Valentine et al. 1999). Moreover, other studies have found that increased disinfectant levels can lead to higher corrosion rates and metal by-product concentrations for both copper (Reiber 1989; Hong and Macauley 1998; Boulay and Edwards 2001) and iron (Treweek et al. 1985; Pisigan and Singley 1987). However these studies were primarily focused on the oxidation of metallic copper or iron by the disinfectant and typically only evaluated effects of free chlorine. Furthermore, many bench-scale experiments geared for developing corrosion control strategies are conducted in the absence of a disinfectant or with a constant disinfectant residual (e.g. McNeill and Edwards 2000). Few studies have rigorously compared the impact of secondary disinfectants in pilot-scale distribution systems.

In terms of market share free chlorine is the most commonly used disinfectant in North America (AWWA Water Quality Division Disinfection Systems Committee 2000). However to remain in compliance with current and future regulations concerning trihalomethanes (THMs) and/or haloacetic acids (HAAs) many utilities have switched to chloramines for secondary disinfection. Chloramines have historically been considered desirable because they provide a stable and persistent residual along the distribution system, and can penetrate deeper into the biofilm layer to limit its growth (Kirmeyer et al. 1993). Unfortunately, previous work has shown that approximately two-thirds of medium and large systems in the US that chloraminate experience nitrification to some degree (Kirmeyer et al. 1995; LeChevallier et al. 1996).

Chlorine dioxide has been used as an alternative to free chlorine because of its ability to inactivate *Cryptosporidium* (Chauret et al. 2001) and control nitrification (McGuire et al. 1999). Chlorine dioxide has been shown to have a higher disinfecting capacity than free chlorine (Galvin and Mellado 1993), and is a viable option for controlling regrowth in distribution systems (Gagnon et al. 2004). In a full-scale study Volk et al. (2002) found that chlorine dioxide lowered the total number of cells in the distribution system by one order of magnitude and produced significantly less THMs than free chlorine. Chlorine dioxide can produce chlorite and chlorate and their degradation in distribution systems is relatively low (Baribeau et al. 2002), although chlorite can also function as a disinfectant. For the purposes of this investigation chlorite will be presented as a disinfectant rather than a by-product of chlorine dioxide as it was not generated as a by-product, but intentionally from sodium chlorite. The impact that chlorine dioxide, or its chemical by-products, has on corrosion in the distribution system is poorly documented.

The objective of this research was to evaluate the impact of secondary disinfectants on internal corrosion and water quality in old, cast-iron water distribution system pipes. In particular, the disinfectants evaluated for this study were free chlorine, chloramines, chlorine dioxide and chlorite. The investigation was conducted using five recirculating pipe loops to observe the impacts of corrosion. Pipe loop systems are ideal for studying the impacts of corrosion in distribution systems as opposed to full-scale distribution system studies because the latter can be costly, difficult to perform and may have negative effects on water quality (Kirmeyer et al. 1993).

MATERIALS AND METHODS

Pipe loop set-up

The pilot-scale study was located at the J.D. Kline Water Supply Plant (JDKWSP), which is a 110 Mld direct filtration plant that obtains its water from Pockwock Lake, Halifax, Nova Scotia. The raw water is characterized by relatively low pH, hardness and alkalinity (Table 1).

Post-filtered water from the JDKWSP was used as the feed water to the model distribution system. The filtered water has a pH of 6 and a total chlorine residual of approximately 0.05 mg l^{-1}. The filtered water was treated to have no chlorine residual, a pH of 8 and a polyphosphate concentration of 0.8 mg l^{-1} (as polyphosphate) prior to entering the model distribution system, which is consistent with the corrosion control strategy for the JDKWSP at the time of this study. To reach the desired

Table 1 | Raw and finished water quality at the JDKWSP (1999–2000)

Parameters	Raw water	Filtered water	Treated water
Alkalinity (as mg l^{-1} CaCO$_3$)	< 1.0	> 10	33.0
Colour (TCU)	7.5	2.5	2.5
Conductivity (μmho cm^{-1})	35.0	110.0	110.0
Hardness (mg l^{-1} as CaCO$_3$)	4.4	10.0	44.4
Iron (mg l^{-1})	0.03	0.02	0.02
Langelier index @ 5°C	− 6.1	− 5.1	0.1
pH	5.4	6.0	8.8
TDS (mg l^{-1})	27.0	40.0	85.0
Turbidity (NTU)	0.33	0.03	0.28
Total organic carbon (mg l^{-1})	2.3	1.4	1.4

water characteristics, chlorine residual was removed using a granular activated carbon (GAC) column, sodium hydroxide was added to adjust the pH to 8 and polyphosphate (Virchem 937, Carus Corp.) was added for corrosion control. Maddison *et al.* (2001) found that polyphosphate addition was an optimal corrosion control method for the Pockwock Lake treated water.

A recirculating pipe loop was selected because previous work with similar pipe rigs (e.g. Maddison *et al.* 2001) found that disinfectant decay was minimal in a once-through pipe rig configuration. Furthermore it was felt that a continuously flowing model system would not confound the experiment, as previous studies (e.g. Lytle and Schock 2000) have demonstrated the importance of water stagnation on corrosion. The other key design parameters (e.g. flow rate, pipe diameter) were selected on the basis of a comprehensive review and framework of pipe rigs and pilot distribution systems (Eisnor and Gagnon 2003).

Five recirculating pipe loops (Figure 1) were used in parallel to test each of the four disinfectants, with an additional pipe loop to serve as a control which did not

receive any disinfectant. The pipe loop consisted of a test pipe that was a 1.5 m (5 feet) length of 100 mm (4 inches) cast-iron pipe sampled from a low flow area of the Halifax regional water distribution system. The cast-iron pipe was approximately 100 years old and was heavily tuberculated. The nominal diameter of the pipe was found to be approximately 60 mm (2.4 inches).

Water was recirculated using a centrifugal pump rated at 53.8 l min^{-1} (14.2 gpm (US)) at 7.4 m (24.3 feet) of head in 75 mm (3 inches) flexible, reinforced PVC tubing. The pump size was based on a desired velocity of approximately 0.30 m s^{-1} (1 fps) in the cast-iron section, which is typical of actual velocities in a distribution system (McAnally and Kumaraswamy 1994; MacKoul *et al.* 1995; Camper 1996).

The water supply for the project flowed by gravity from the filters of the JDKWSP through the GAC column into a 20 l plastic reservoir. A diaphragm pump transferred the water to a second 20 l plastic reservoir, to which sodium hydroxide and zinc polyphosphate were added. A variable speed multicartridge peristaltic pump (Masterflex®, Vernon Hills, Illinois) lifted the water to the influent port of each of the pipe loops. The disinfectants were applied to the influent flow using another variable speed multicartridge peristaltic pump, such that five distinct pipe loops could be operated in parallel each containing different disinfectant.

Experimental design

A two-step conditioning period was completed. To condition the pipes to water matrix conditions, source water at a pH of 8 (no polyphosphate) was supplied to the pipes for approximately two months starting in December 2000, to flush out and acclimatize the pipes to pH adjusted water. In late January 2001, the second phase of conditioning commenced when polyphosphate was introduced to the loops for a period of two weeks. This phase was completed to introduce the test water that would be used for the rest of the study. Upon completion of conditioning, the pilot-scale experiments started by adding secondary disinfectants to the parallel pipe loops.

The experimental design matrix for the pilot-scale study is shown in Table 2. The experiment examined two
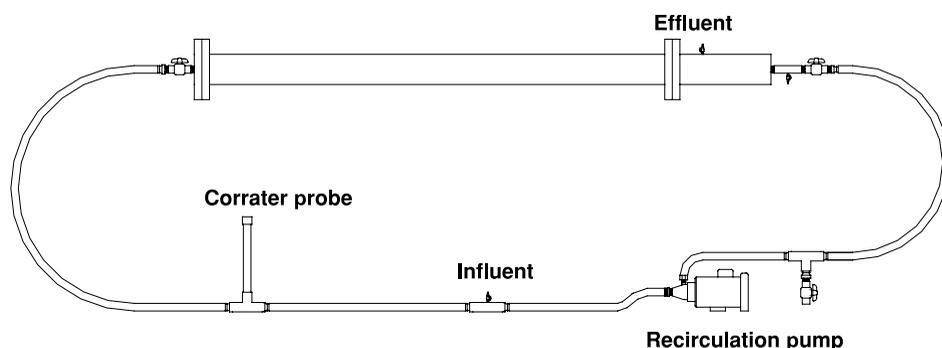
Figure 1 | Schematic of pipe loop employed by this project.

Table 2 | Experimental design matrix

Retention time (h)	Disinfectant residual concentration (mg l^{-1})				
	Control: no disinf.	Chlorine dioxide	Chlorite	Free chlorine	Monochloramine
6	0.0/0.0	0.25/0.5*	0.1/0.2	0.5/1.0	1.0/2.0
12	0.0/0.0	0.25/0.5	0.1/0.2	0.5/1.0	1.0/2.0

*Low/high target effluent residual concentrations.

retention times (i.e. 6 and 12 h) within the loop and a high and low effluent disinfectant residual for each of the four disinfectants. For both retention times the water in the pipe loop had a constant internal velocity of 0.3 m s^{-1}, as described previously, and the overall pipe loop system had a retention time of 6 or 12 h. The target disinfectant values were chosen to be within minimum and maximum limits that have been established by regulatory agencies. The Ontario Drinking Water Guidelines (Ontario Ministry of the Environment 2001) have set a minimum free chlorine residual of 0.2 mg l^{-1} and a minimum combined chlorine residual of 1.0 mg l^{-1} to be measured at all points in a distribution system. The USEPA drinking water standard for chlorine dioxide is a maximum of 0.8 mg l^{-1} (USEPA 1999). Knowing that a certain percentage of chlorine dioxide may form the chlorite ion, target values for chlorite were set to be less than that of chlorine dioxide.

The intent of the experimental design is to enable utilities to directly compare corrosion rates among disinfectants, as very little information has been reported

on the impact of disinfectant residuals on corrosion in iron pipe (McNeill and Edwards 2001). In particular, free chlorine and monochloramine act as benchmarks in the present investigation because there is a general lack of published data for chlorine dioxide in distribution systems.

In addition to new corrosion data, the experimental design examines the possible interaction and main effects of water age (i.e. retention time) and disinfectant residual on corrosion. The impact of stagnation on corrosion is complex and is highly dependent on pipe material, water chemistry and temperature of the pipe rig. Lytle and Schock (2000) found that metal levels increased exponentially with respect to stagnation time, particularly for stagnation times in the 20–24 h range, which is outside the range of the present investigation. For a full-scale system it is very difficult to determine the effect of water age, as the disinfectant residual will decay as the water ages. The effect of water ageing in relation to water quality has been demonstrated in several studies (e.g. Prévost *et al*. 1997)

and in particular was demonstrated previously for the Halifax regional distribution system for retention times of 30–55 h (Maddison *et al.* 2001). The pipe loops in the present study were operated with retention times of 6 and 12 h, which is short relative to full-scale systems. However these times were selected as several studies (Prévost *et al.* 1998; Lu *et al.* 1999; Gagnon and Huck 2001) have demonstrated the impact of high surface area to volume ratios or small pipes as important factors affecting disinfectant decay and other undesirable water quality outcomes in the distribution system.

Analytical methods

The corrosivity of the water in each of the loops was measured using linear polarization probes that were equipped with carbon steel electrodes (Corrater® 6112 probes, Rohrback Cosasco Systems, Santa Fe Springs, California). Carbon steel electrodes were selected because other research of similar nature used the same material (LeChevallier *et al.* 1990, 1993; Volk *et al.* 2000). The corrosion rate data may be slightly accelerated in relation to the pipe section tested as the carbon steel electrodes were freshly installed at the beginning of the testing programme, whereas the cast-iron pipe had been in service for over 100 years. Nevertheless the corrosion rate data presented herein provides an easily standardized benchmark for comparison by others. The corrosion rate was measured using a hand held corrosion measurement system (RCS 9000, Rohrback Cosasco Systems, Santa Fe Springs, California). Corrater probes were placed in-line on each of the five pipe loops. In addition, an influent Corrater was placed in-line on the influent water pipe following chemical treatment for corrosion control (i.e. after NaOH and polyphosphate addition) and prior to the addition of any disinfectants.

Bulk water quality was measured according to *Standard Methods* (1995). The parameters that were monitored were alkalinity, colour, dissolved iron, dissolved oxygen, pH, phosphorus, temperature, total iron and turbidity. The pH and temperature were measured using an Orion model 230A pH meter (Thermo Orion, Beverly, Massachusetts). Dissolved oxygen was measured using a VWR model 4000 portable D.O. meter (VWR International, So. Plainfield, New Jersey). The turbidity was measured using a HACH Ratio Turbidimeter (HACH Co., Loveland, Colorado). Apparent colour was measured using a spectrophotometer (HACH DR/3000, HACH Co., Loveland, Colorado). Total iron and total dissolved iron were measured using the HACH FerroVer Method with a HACH DR/3000 spectrophotometer. The dissolved iron sample was filtered through a 0.45 μm membrane filter prior to analysis. Phosphorus was measured as (PO_4^{3-}) colorimetrically with a spectrophotometer. Both orthophosphate (reactive) and total phosphate of the sample was measured. The total phosphate was measured following an acid digestion step, as described in standard method 4500P-E. Phosphate was quantified at a wavelength (λ) 890 ηm. Typically the orthophosphate measured in the system was very low (<0.05 mg l^{-1}) indicating little reversion in the system.

Both free chlorine and monochloramine residuals were measured using the DPD colorimetric method. In this research it was necessary to measure chlorine dioxide residual concentrations as low as 0.050 mg l^{-1}. A spectrophotometric method employing lissamine green was used as previously described by Chiswell and O'Halloran (1991). Lissamine green is both selective and sensitive for the determination of low levels of chlorine dioxide. This method has been examined extensively and found not to suffer from interferences caused by other chlorine species in the water (Hofmann *et al.* 1998). A LKB Biochrom Ultrospec 4051 spectrophotometer (Biochrom Limited, Cambridge, UK) was used to analyse for chlorine dioxide. Chlorite was measured according to EPA Method 5510 using a Dionex 500 ion chromatograph.

Sampling for analysis was performed a minimum of two times per week while pH and disinfection residuals for operational control were monitored on a more frequent basis.

Chemical preparation

Chlorine dioxide was generated according to a method presented in *Standard Methods* (1995). The generator consists of a bench-top apparatus, in which a 25% sodium

chlorite solution is slowly added to an 18N sulfuric acid solution, producing chlorine dioxide. The chlorine dioxide is purged from the mixture in a gas-washing bottle, and trapped in water surrounded by an ice bath. Off-gas from this bottle is directed to a potassium iodide trap to prevent the release of chlorine dioxide into the air. The resulting chlorine dioxide solution is approximately 2 g l^{-1}.

Concentrated disinfectant solutions of chlorine and monochloramine were produced in halogen-demand-free water. Free chlorine was produced using a 5% solution of analytical grade sodium hypochlorite.

Monochloramine was produced by combining sodium hypochlorite and ammonium chloride at a ratio of 1 ml NaOCl to 216 mg NH_4Cl in phosphate buffered saline (PBS) (pH 9.5). The resulting monochloramine solution was diluted to the desired concentration.

The chlorite ion was prepared using 80% sodium chlorite that was recrystallized three times from water below 40°C under minimal light. This solution was then diluted to the desired concentration.

Statistical analysis

Statistical tests were repeated for the various combinations of disinfectant dose (high and low), disinfectant type (control, chlorine, chlorite, chlorine dioxide, chloramines) and retention time (6 and 12 h). In addition, statistical tests compared the significant differences between the average influent and effluent values for the water quality parameters measured. The level of significance that was used for all tests was $\alpha = 0.05$. Statistical procedures followed were an analysis of variance (ANOVA) test or student t-tests, as described by Box $et\ al$. (1978).

RESULTS AND DISCUSSION

### Comparison of treatment conditions on corrosion rate

The influent and effluent corrosion rate for the control loop over the entire experimental programme is provided in Figure 2. The influent corrosion rate showed a gradual
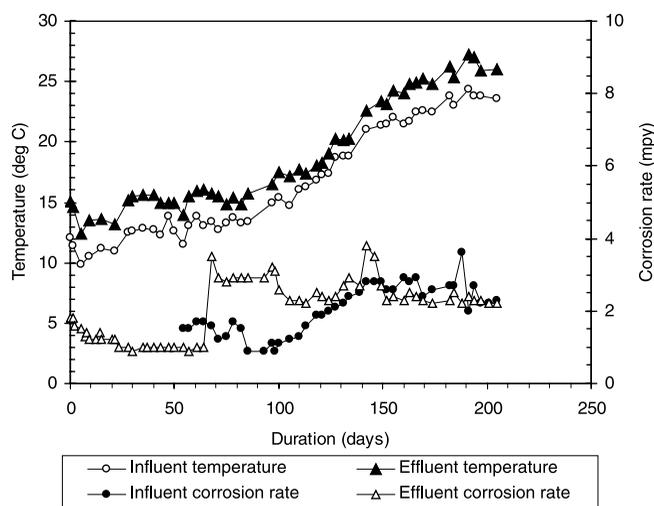
Figure 2 | Influent and effluent corrosion rates and temperatures for the control pipe loop.

increase in corrosion rate between days 90 and 140. Over that period the water temperature in the control loop increased by approximately 6°C. It is suspected that the increase in corrosion rate was linked to the temperature increase as corrosion rates are affected by temperature (Schock 1999). A regression analysis completed showed that the influent corrosion rate was correlated to the influent temperature ($r^2 = 0.72$). However, the effluent corrosion rate remained relatively constant and independent of temperature. The effluent corrosion rate increased sharply at day 65 because of a physical change resulting from a pipe tubercle that blocked the influent line to the control loop preventing fresh water from entering it. After the problem was identified on day 65 the water in the control loop was continually recirculated for approximately 24 hours until the problem was fixed. After the physical problem was fixed the corrosion rate did not return to the level it was at before, but remained constant at this higher value.

The average corrosion rates for the five pipe loops for each disinfectant dose and hydraulic retention time are shown in Figure 3. Regardless of hydraulic retention time or disinfectant dose, monochloramine had the highest corrosion rate. However it is noteworthy that maintaining a constant chloramine residual was more difficult than for either free chlorine or chlorine dioxide. Because of the low
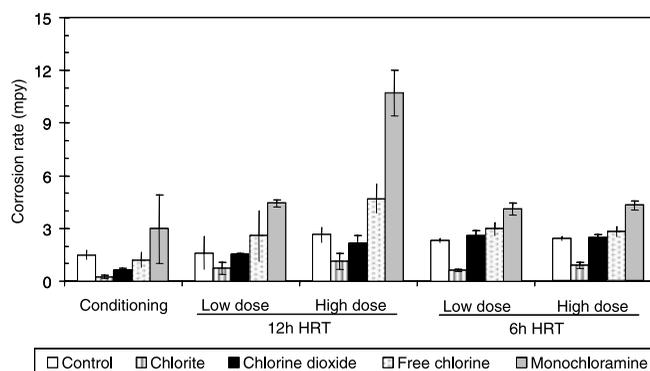
Figure 3 │ Average corrosion rates for the different phases (error bars indicate standard deviations).

alkalinity of the filtered water from the water treatment plant, any minor changes in buffering capacity had substantial impacts on chloramine stability. Iron corrosion was, in turn, indirectly affected as the chloramine dose was adjusted more frequently to compensate for the minor pH fluctuations that occurred at the water treatment plant.

Furthermore, there was other qualitative evidence that indicated that chloramine was more corrosive than the other disinfectants. It was observed that severe pitting corrosion was occurring on the stainless steel tubing used to draw chloramine out of its supply bottle. The attack was concentrated near the rubber stopper used to cork the bottle in an area that was not immersed in the monochloramine solution. The pitting corrosion eventually got to the point where it penetrated the stainless steel, rendering it useless. The stainless steel tubing in the bottles for chlorite, chlorine dioxide and free chlorine did not experience any corrosion.

Free chlorine had the next highest corrosion rate although, during the 6 hour retention time phases, it was very close to the corrosion rate in the chlorine dioxide loop. From a statistical perspective there was no significant difference between the chlorine dioxide and control pipe loop. Of the four disinfectants, chlorite had the lowest corrosion rate followed by chlorine dioxide, free chlorine and monochloramine.

Interestingly, the corrosion rate in the chlorite loop was lower than the corrosion rate of the control loop. This lower corrosion rate may be attributed to reactions with ferrous iron (Fe^{2+}) from the pipe material. Baribeau et al. (2002) found that chlorite (ClO_2^-) levels decrease within distribution systems. These decreases have been attributed to various factors including reactions with ferrous iron (Fe^{2+}) from pipe material. Iaturu and Knocke (1992) found that can oxidize Fe^{2+} into ferric iron (Fe^{3+}) and follows the oxidation-reduction reaction in Equation (1).

$$4Fe^{2+} + ClO_2^- + 10H_2O = 4Fe(OH)_3\ (s) + Cl^- + 8H^+\ (1)$$

Statistical analyses were performed to compare the mean corrosion rates for each of the five pipe loops during each combination of retention and disinfectant dose. Regardless of the retention time, the average corrosion rate for monochloramine was always significantly greater than the corrosion rates of the other loops ($\alpha < 0.0001$), which is contrary to other studies that have reported that free chlorine is more corrosive than monochloramine (e.g. Reiber 1993). The corrosion rates in the free chlorine and monochloramine loops were significantly greater than the corrosion rate in the control pipe loop ($\alpha < 0.05$). The average corrosion rate in the chlorine dioxide loop was statistically the same as the average corrosion rate in the control loop for each hydraulic retention time studied. The corrosion rate in the chlorite loop was also significantly less than that for the other disinfectants ($\alpha < 0.001$) and less than the corrosion rate in the control loop ($\alpha < 0.002$). Overall, of the treatment conditions studied, the corrosion rates can be ranked from a statistical comparison as: $NH_2Cl > Cl_2 > ClO_2 = No$ disinfectant $> ClO_2^-$. Because iron corrosion would be lower in a system with chlorine dioxide, regardless of generation quality, than in a system with free chlorine there should be more disinfectant available for disinfection of microorganisms in the distribution system. Interestingly, Volk et al. (2002) reported on a full-scale system that temporarily switched from free chlorine to chlorine dioxide over a 2.5 month period. In that study it was reported that the total number of cells was reported to decrease by 1-log during the switch to chlorine dioxide, although the value for the combination of disinfection concentration and contact time (C.t)

for primary disinfection remained similar for both disinfectants.

Comparison of treatment conditions on iron release

The concentration of iron in samples of water from distribution systems can be used as a rough estimate for corrosion, although actual corrosion rates cannot be determined (Schock 1999). Elevated concentrations of metals in solution are indicative of relatively high rates of corrosion in new pipe or the release of metal deposits on old pipe walls back into solution. In old, cast-iron pipes, the source of iron is usually from the thick layer of scale that contains various iron compounds that have built up over the years. Changes in flow patterns or water chemistry may loosen or dissolve the scale, resulting in elevated iron concentrations in the treated water. In the present investigation, linear velocities through the test section were kept constant to focus specifically on the impact of disinfectant chemistry on iron release.

The influent total iron concentrations for the control loop were consistently less than 0.06 mg l^{-1}. This value reflected the iron concentration of the filtered water at the JDKWSP and was the same for all five pipe loops. Effluent total iron concentrations from the control loop were stable during the entire experiment, averaging 0.06 mg l^{-1} with a standard deviation of 0.02 mg l^{-1}. Low iron values in the influent water were anticipated, as previous research (Maddison *et al.* 2001) on this water demonstrated the benefits of polyphosphate for minimizing iron concentrations in distributed water. In addition Lytle and Snoeyink (2002) showed that polyphosphates reduced apparent colour and turbidity of iron suspensions. It was found that the decreased turbidity was attributed to the reduction in particle size by the polyphosphates on the iron-based particle, which led to a decrease in light-scattering properties.

Results reported in Figure 4 indicate that both the control loop effluent and chlorite loop effluent had very small average total iron concentrations. Regardless of retention time or dose the overall average iron release from the chlorite pipe loop was 0.04 mg l^{-1} with a
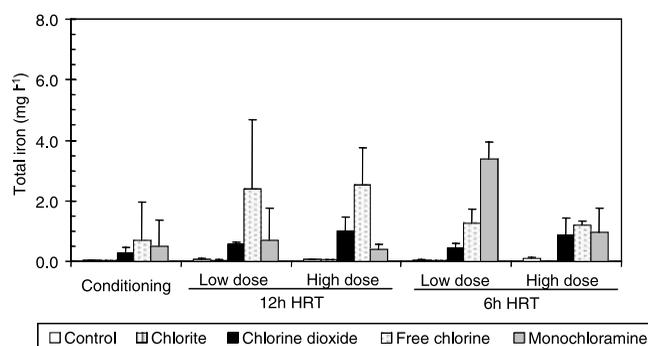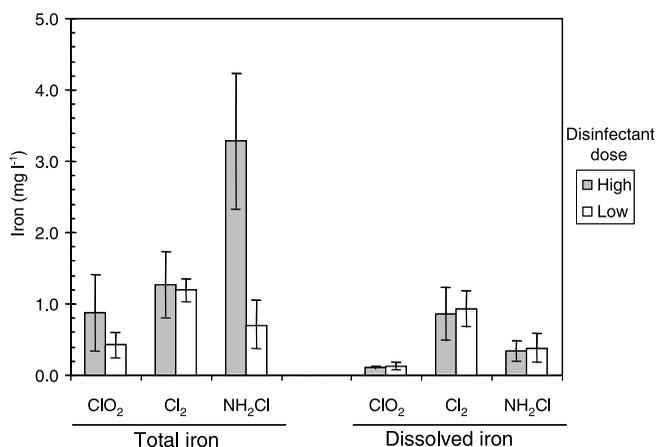

Figure 4 | Total iron concentrations for the different phases (error bars indicate standard deviations).

standard deviation of 0.02 mg l^{-1}. Similar to the corrosion rate data, the iron release data for the chlorite pipe loop was on average always lower than the control pipe loop, although from a statistical perspective the mean values from these two pipe loops were not significantly different from each other.

A comparison of the chlorite and the control pipe loops with the other disinfection conditions is provided in Figure 4. On average, the free chlorine pipe loop and monochloramine loop had the highest effluent total iron concentrations, with overall average (and standard deviation) iron concentrations of 2.02 mg l^{-1} ($\pm$ 1.6) and 1.25 mg l^{-1} ($\pm$ 1.0), respectively. During the 12-h retention time, the free chlorine pipe loop had the highest total iron concentration of 2.40 mg l^{-1} ($\pm$ 1.9) regardless of disinfectant dose. The standard deviations for the iron data were large for some of the disinfectants because three samples had iron concentrations ranging from 5.65 to 8.30 mg l^{-1}. Figure 4 also shows that the chlorine dioxide pipe loop had lower effluent total iron concentrations than both the free chlorine and chloramine pipe loops. Overall, there was a statistically significant difference between the iron release from the chlorine dioxide pipe loop and the iron release from either the chloramine or the free chlorine pipe loop. The only treatment period when the average effluent total iron concentration from the chlorine dioxide pipe loop was not significantly different from the free chlorine pipe loop was during the low disinfection dose with a 6-h hydraulic retention time (HRT). However, during this low disinfectant phase, the

Figure 5 | Total and dissolved iron concentrations for a 6-h retention time for the ClO_2, Cl_2 and NH_2Cl pipe loops (error bars indicate standard deviations).

Table 3 | P-value comparison of 6 and 12-h retention time

Treatment	Corrosion rate	Total iron	Turbidity
Control	0.061	0.288	0.004
ClO_2^-	0.046	< 0.001	< 0.001
ClO_2	< 0.001	0.329	0.367
Cl_2	0.085	0.004	0.002
NH_2Cl	0.001	0.002	0.007

average free chlorine residual was less stable and disinfectant residuals of less than 0.1 mg l^{-1} were recorded over a 1-week period.

For a hydraulic retention time of 12 h, it was observed that iron concentrations increased substantially in the free chlorine pipe loop (Figure 4). Visually the effluent appeared red and contained fine pipe tubercles. There was concern that this water quality may continue for the entire experiment and that the high suspended solids may make measuring an accurate total iron concentration difficult. Thus dissolved iron concentrations, as quantified after filtration through a 0.45 μm filter, were also quantified to determine the difference between particulate iron and dissolved iron. It is recognized that Lytle and Snoeyink (2002) have shown that iron colloids may be smaller than 0.45 μm in the presence of polyphosphate; however the dissolved iron measurements were consistent with *Standard Methods* for quantifying dissolved iron.

Figure 5 provides a comparison of the total and dissolved iron concentrations for the three treatment conditions that caused the greatest increase in corrosion rate (i.e. ClO_2, Cl_2, NH_2Cl). The dissolved iron concentration measured in the control and the chlorite pipe loops were at or below the method detection limit (MDL = 0.02 mg l^{-1}), as was shown previously in Figure 4. The free chlorine pipe loop had the highest average dissolved iron concentration of 0.86 mg l^{-1} during low disinfectant dose

and 0.94 mg l^{-1} during the high disinfectant dose. Similar to the total iron concentrations, the chlorine dioxide loop had the lowest effluent dissolved iron concentrations, which were statistically different from the dissolved iron concentrations from the chloramine and free chlorine pipe loops.

Impact of hydraulic retention time and dose on iron corrosion

Table 3 illustrates the statistical differences between pipe retention times from pooled corrosion rate, iron and turbidity data for each pipe loop. Table 3 generally indicates that at a retention time of 6 hours the water was less corrosive and there was less red water, which follows a similar trend to results reported by Lohmann *et al.* (1997) and to stagnation results presented by Lytle and Schock (2000). In particular, the average iron values for the free chlorine pipe loop for the 6-h and 12-h retention times were 1.23 and 2.43 mg l^{-1}, respectively, which were statistically different from each other (Table 3). Although corrosion rates for the chlorine dioxide pipe loop were statistically different, other parameters (e.g. total iron) were not. The average iron values for the chlorine dioxide pipe loop for the 6-h and 12-h retention times were 0.67 and 0.83 mg l^{-1}, respectively.

Similarly, the corrosion rate and iron release from the chlorine dioxide pipe loop were not sensitive to the applied disinfectant dosages, as show in Table 4. Interestingly, a higher dose in the chlorite pipe loop had a

Table 4 | P-value comparison of the low and high disinfectant dosages for each disinfectant

Treatment	Corrosion rate	Total iron	Turbidity
ClO_2^-	0.010	0.273	0.023
ClO_2	0.182	0.642	0.655
Cl_2	< 0.001	0.583	0.824
NH_2Cl	0.001	0.063	0.094
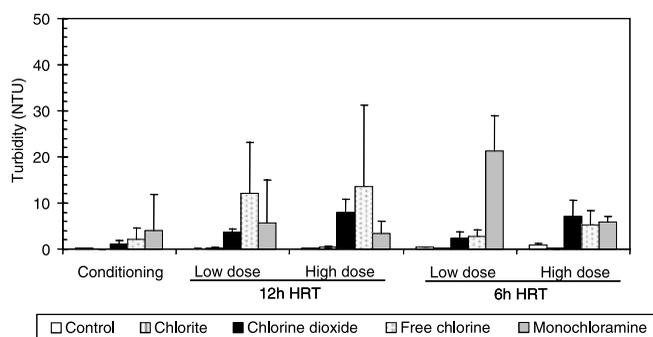
Figure 6 | Average effluent turbidity for the different phases (error bars indicate standard deviations).

significantly higher corrosion rate than the lower dose. In particular the average corrosion rate in the chlorite pipe loop for the higher and lower dose was 0.6 and 1.0 ml per year (mpy), respectively. Although the corrosion rate values for the chlorite pipe were statistically different from each other for the applied dosages studied, the corrosion rates from the chlorite pipe loop were much lower than those from any of the other disinfectants studied (Figure 3). The data from the chloramine and free chlorine pipe loops indicate that the dose from these disinfectants will strongly impact corrosion rate (Table 4). The average corrosion rate from the chloramine pipe loop for the pooled low and high dose data was 4.3 and 7.7 mpy, respectively.

Comparison of influent to effluent water quality

Another method used to determine the impact disinfectants had on corrosion rate and water quality was to compare the net difference between influent and effluent values. The control pipe loop was analysed first to determine if a significant change between influent and effluent was observed in that loop, which could be caused by other water quality factors (e.g. temperature). The effluent corrosion rates in the control pipe loop (average of 2.1 mpy) were normally slightly greater than the influent corrosion rate (average 2.0 mpy). However, statistical tests revealed that the control loop did not experience significant changes over the entire duration of the experiment ($p = 0.624$).

Similarly, the statistical analysis revealed that there was no significant difference between influent and effluent corrosion rate ($p = 0.311$) in the chlorine dioxide loop over the entire duration of the experiment. When average influent and effluent corrosion rates were compared for the individual phases, effluent corrosion rates for the free chlorine and monochloramine loops were significantly higher than the influent corrosion rates for the majority of the time. The chlorite loop had significantly lower corrosion rates than the influent corrosion rates for the entire experimental run.

The influent total iron concentrations were lower than effluent total iron concentrations for the chlorine dioxide, free chlorine and monochloramine loops. The statistical analysis revealed that, during the majority of the phases for these three pipe loops, the influent and effluent average total iron concentrations were significantly different. Turbidity levels were higher in the effluent than in the influent for all of the pipe loops, even the control (Figure 6). The significantly higher effluent turbidity level indicates that something in the pipe loops system was affecting turbidity. Because influent and effluent total iron levels were not significantly different in the control pipe loop, the material causing the increase in turbidity was not detectable as an iron-based corrosion product. The source may have been an iron or metal complexed with an organic colloidal material from the pipe walls.

CONCLUSIONS

This study examined the impact of four disinfectants on internal corrosion and water quality in old, cast-iron water

distribution pipes. Overall, chlorite and chlorine dioxide resulted in decreased or similar corrosion rates with respect to those observed in the control experiments. Monochloramine and free chlorine increased corrosion rates within the pipe loops. Chlorite has low corrosion rates, which were affected both by the hydraulic retention time and the disinfectant dose. Similar to the other pipe loops, lower retention times and low disinfectant doses produced the lowest corrosion rates in the chlorite pipe loop. The chlorine dioxide loop produced corrosion rates and red water similar to the control loop, average corrosion rates were 2.2 and 2.1 mpy, respectively. In contrast the monochloramine and free chlorine loops had statistically higher corrosion rates for most of the study in comparison with the chlorine dioxide loop. Practically, these results indicate that water utilities should examine the impact of corrosion and red water in addition to other water quality parameters when selecting their secondary disinfectants, as results presented in this paper indicate the impact disinfectant residuals can have on iron corrosion.

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