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The effect of chloride, sulfate and dissolved inorganic carbon on iron release from cast iron

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Abstract

Iron corrosion in drinking water distribution systems causes water discoloration, water quality deterioration, hydraulic loss, and even pipe failures, which are usually influenced by pipe scale structure, water hydraulics, water chemistry, and other factors. This work evaluated the effects of chloride, sulfate, and dissolved inorganic carbon (DIC) on iron release from a 90-year-old cast iron pipe section at water pH 8.0 under stagnant conditions. Experimental results showed that the addition of 150 mg/L sulfate to water significantly increased the mean total iron concentrations to 1.13–2.68 mg/L, relative to 0.54–0.79 mg/L for the baseline water with only 10 mg C/L DIC. Similar results were observed under conditions when chloride was added, and when sulfate and chloride were added together. In contrast, the mean total iron concentrations were significantly reduced by 53–80% in waters with higher DIC of 50 mg C/L, as compared to similar waters with lower DIC of 10 mg C/L. The Larson Ratio could be a good indicator for iron release depending on the circumstances. Iron release was predicted by molecular radial diffusion modelling that accounted for water quality, scale characteristics, hydraulics, and other condition-related information. The results provided insightful information for water systems that have cast iron pipes and galvanized iron pipes and that might encounter changes in water treatment and water sources. More studies are needed to better understand the cast iron corrosion mechanisms under the examined water chemistries.

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Appendix A. Supplementary data Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.116037>.

Keywords

Iron corrosion; Water discoloration; Chloride; Sulfate; Dissolved inorganic carbon; Molecular diffusion model

1. Introduction

Corrosion control of water distribution system materials, including premise plumbing, is of high priority for water utilities in the United States (U.S.) to maintain acceptable chemical and microbial drinking water quality (EPA, 1991a). A recent survey showed that 31% of water mains are comprised of old cast iron pipes or galvanized iron pipes (Folkman, 2018). It is difficult to estimate the number of galvanized iron pipes in service lines and premise plumbing systems because of the efforts to remove galvanized iron materials due to its strong association with discoloration water complaints and unpredictable nature regarding corrosion (Tang et al., 2018). However, many water utilities still have aged cast and galvanized iron pipes in their water systems that can be heavily tuberculated with complicated layered scale structures developed over decades (Sarin et al., 2004a; Gerke et al., 2008; Little et al., 2014).

Although not a direct public health risk like leaded materials, corrosion of iron-based materials is of concern as the tubercles or scales on the iron pipe surface exert a disinfectant demand, harbor biofilm, create head-loss build-up, accumulate trace contaminants, and produce discolored water due to iron release (McNeill and Edwards, 2001; LeChevallier et al., 1993; Benjamin et al., 1996; Lytle et al., 2004a, 2014; Imran et al., 2005a). Iron release refers to the movement of soluble or particulate iron from the corroded iron pipe wall to the bulk drinking water. Iron can cause variations in water color ranging from yellow to dark red and imparts a metallic taste and smell to the water (EPA, 1991b). In order to minimize aesthetic issues related to iron in drinking water, the U.S. Environmental Protection Agency (EPA) has set a secondary maximum contaminant level for a total iron of 0.3 mg/L (EPA, 1991b) that applies to iron in the source water. Previous studies have explored the relationship between iron release from iron pipe scale and pipe age, pipe scale structure, water quality, flow conditions and other factors (McNeill and Edwards, 2001; DeBerry et al., 1982; Blengino et al., 1995; Benjamin et al., 1996; Sarin et al., 2001, 2003; 2004a, 2004b; Zhang and Edwards, 2007; Tang et al., 2018).

The structure and properties of iron corrosion by-product scales or tubercles are critical to understanding iron release (Sarin et al., 2001, 2003, 2004a). Iron pipe scales start from the pipe wall and grow radially inwards toward the center of a corroded site; the scales vary by water distribution systems and iron pipe samples but share somewhat similar structures (Sontheimer et al., 1981; Herro and Port, 1993; Herro, 1998; Sarin et al., 2001, 2003; Ray et al., 2010). Typical iron scales have four distinct layered structures: (1) a corroded floor which is located on the corroded pipe metal surface, (2) a porous core layer that is closest to the corroded floor dominated by reduced ferrous iron [Fe(II)] minerals such as Fe(OH)₂, green rusts and FeCO₃, (3) a middle hard shell-like layer that covers the inner layer dominated by magnetite (Fe₃O₄) and goethite (α-FeOOH) minerals, and (4) a relatively

loosely held top surface layer dominated by ferric [Fe(III)] oxy-hydroxides minerals such as Fe(OH)₃ and lepidocrocite (γ-FeOOH) (Sarin et al., 2004a; Herro and Port, 1993). The formation of Fe(III) minerals increases as the distance from the iron metal increases, whereas Fe(II) minerals tend to form close to iron metal surface reflecting a redox gradient. The siderite conceptual model (Sontheimer et al., 1981) and Kuch corrosion model (Kuch, 1988) described the major pathways of iron release into the bulk water under different conditions, which were later expanded by Sarin et al. (2001, 2004a). Generally, iron release from iron pipe scale is controlled by oxidation-reduction corrosion of iron metal and developed Fe(II and III) minerals, dissolution of Fe(II and III) scale minerals, velocity-induced erosion and scouring, and other mechanisms (Benson et al., 2012). The porosity of scale layers is one factor determining the diffusion processes between scale layers (Benjamin et al., 1996). As a result, the porous inner layer promotes the migration of Fe(II) and other ions within the middle hard-shell layer, which isolates the porous core layer from the bulk water and minimize corrosion and iron release into the bulk water (Sarin et al., 2003; Benson et al., 2012). Therefore, the thickness and properties of the hard-shell layer play an important role in controlling iron release into the bulk water, which is highly influenced by water chemistry.

Water chemistry (e.g., oxidants, pH, alkalinity, chloride, sulfate, corrosion inhibitors) affects the water-scale interface interactions and reactions, scale microstructure, and iron release by changing water redox and corrosivity (Baylis, 1926; Larson and Skold, 1958; DeBerry et al., 1982; Sarin et al., 2003, 2004b; Lytle et al., 2005a; Imran et al., 2005a; Zhang and Edwards, 2007; Yang et al., 2014; Tang et al., 2018). The presence of important oxidants such as dissolved oxygen (DO) and free chlorine increases the oxidation of iron metal to Fe(II) and then to Fe(III) ions, which would hydrolyze to form denser and less permeable Fe(III) minerals within scales, resulting in an overall decrease of iron release relative to when there were no water oxidants (Lytle et al., 2004b; Sarin et al., 2003; Zhang and Edwards, 2007). The decrease of iron release due to the presence of oxidants in water could also be enhanced with flowing water conditions resulting from increasing transport of oxidants to the surface of the iron pipe scale (Sarin et al., 2004b). Increase of water pH decreased iron release, particularly alkaline, environments promoted Fe(II) oxidation rates and formation of the denser Fe(III) oxy-hydroxides minerals within the scale, which resisted the diffusion of iron into the bulk water; in contrast, lower pH led to the formation of more porous Fe(II) layer (Baylis, 1926; Cornell and Schwertmann, 2003; Benson et al., 2012). Similarly, higher alkalinity could maintain a more robust scale structure that was resistant to iron release by providing a higher buffering capacity that prevented pH changes (Sarin et al., 2004a). Corrosion inhibitors such as orthophosphate reduced iron release, and the exact mechanisms were uncertain (McNeill and Edwards, 2000, 2001; Benson et al., 2012; Lytle et al., 2005a), but Sarin et al. (2003) indicated that phosphate inhibitors helped to form an insoluble and less permeable phosphate scale layer that resisted iron release into the bulk water. Other important water parameters chloride and sulfate were shown to have mixed results on iron release (McNeill and Edwards, 2001; Lytle et al., 2005a; Benson et al., 2012; Tang et al., 2013), and the presence of sulfate could change the composition of iron scale when sulfate-reducing bacteria were present, reducing sulfate to sulfide-based precipitates (Lytle et al., 2005b; Burlingame et al., 2006). Even though Larson and Skold (1957, 1958) showed that

chloride and sulfate increased the water corrosivity to iron and bicarbonate protected iron pipe as indicated by the Larson Ratio (Equation (1)), more research is still needed to explore the impact of bicarbonate, chloride and sulfate on iron release from iron pipe scale, along with its associated mechanisms.

$$\text{Larson Ratio (LR)} = \frac{[Cl^-] + 2[SO_4^{2-}]}{[HCO_3^-]} \quad (1)$$

where $[Cl^-]$, $[SO_4^{2-}]$, and $[HCO_3^-]$ were milliequivalents per liter. $LR < 0.8$ indicates low corrosion rate, $0.8 < LR < 1.2$ indicates moderate corrosion, and $LR > 1.2$ indicates high corrosion rate.

Minimizing iron release in water distribution systems is important for improving water aesthetic concerns (Zhang and Edwards, 2007) and mitigating associated toxic substances such as lead and arsenic that can readily adsorb onto corroding iron surface scale minerals (Dixit and Hering, 2003; Lytle et al., 2010; Masters and Edwards, 2015; Pieper et al., 2017). An improved understanding of iron scale-drinking water interactions may lead to adoption of more comprehensive drinking water practices that improve distribution system water quality, protect human health, and predict distribution system responses to source water or treatment changes. The objective of this work was to examine the impact of changes in chloride, sulfate, and dissolved inorganic carbon (DIC) on iron release from a 90-year-old cast-iron pipe section under stagnant conditions. Specifically, (1) the impact of the water quality parameters on iron release, pH changes, and DO depletion was examined; (2) the relationship between the Larson Ratio and iron release was investigated; and (3) the actual iron release from stagnation studies and the predicted iron release from a molecule diffusion model were compared.

2. Material and methods

2.1. Experimental apparatus

A 15.6 cm long 90-year-old cast iron pipe section [10.2 cm inside diameter (ID)] was removed from the City of Cincinnati, Ohio drinking water distribution system (Supporting Information Fig. S1). The inner pipe wall diameter measured approximately 1.3 cm less than its original specifications, indicating corrosion-related tuberculation. The pipe was positioned vertically, and each end of the pipe was fitted with two airtight clear acrylic plexiglass plates that were bolted to rings that supported the pipe section and prevented air (i.e., oxygen) from interacting with the pipe interior. The bottom plate was fitted with an inlet port connected to a 6.4 mm ID plastic tube used to pump water from a 4-Liter water reservoir into the pipe. The top plate also had a water outlet port as well as three additional sampling ports from which water could be sampled, and other water quality could be measured

2.2. Testing water conditions and analyses

Four-liters of test water for the nine different test conditions (assigned as A-I) was prepared from laboratory double distilled water, which referred to the water generated by slowly

boiling the condensed water vapor from a prior slow boiling (Table 1). The nine testing water conditions were comprised of water pH 8.0, DIC of 10 or 50 mg C/L (or 42 or 210 mg/L alkalinity as CaCO_3), chloride of 0 or 150 mg/L, and sulfate of 0 or 150 mg/L (Table 1; SI-1). With exception of pH, the range of test water conditions encompassed values in the original drinking water from the community where the cast iron pipe was harvested (Lytle et al., 2005a). The pH was approximately 0.5–1.0 pH unit lower than the original source, however, the pipe section has been conditioned at pH 8.0 for years prior to this study. In total, twenty-two water condition changes were made to the iron pipe apparatus to represent water treatment and source water changes in chloride, sulfate and DIC parameters in practice. The 4-Liter test water was completely mixed with a magnetic stir plate after appropriate amounts of chemicals were added to achieve desired water quality.

After the 4-Liter fresh water preparation, a 200 mL water sample was collected to record the initial temperature, pH, DO, DIC, and metal measurements. Next, 1.5-Liters of test water was pumped through the inlet port into the pipe section at a rate of 50 mL/min. Excess water flowed out the top outlet to waste, and the remaining 2.5-Liter water was used to fill the pipe section. The water was then allowed to stagnate 24 h during the week and 48 h + over the weekend. Following each stagnation period, water samples were drawn by syringe through one of the top sampling ports. The syringe was inserted in the center of the pipe so that the tip was approximately 4 cm from the bottom plexiglass plate. The samples were analyzed for water pH, water temperature, and DO levels upon collection (SI-1). Meanwhile, collected water samples were also appropriately preserved for metal analyses.

Total iron and Fe(II) were measured using a spectrophotometric method per Ferron method (method 8008) and per 1, 10 phenanthroline (method 8146) on the HACH Model 2700 (Loveland, CO), respectively (APHA, AWWA, & WEF, 1995). The difference between the total iron and Fe(II) represented the Fe(III) species. The detection limit of the HACH spectrophotometric method for total iron was 0.03 mg/L and for Fe (II) was 0.008 mg/L. In order to confirm the HACH spectrophotometric results, metals including total iron in the majority of water samples were also analyzed with a Thermo Jarrel Ash (Franklin, MA) 61E purged inductively coupled plasma atomic emission spectrometry (ICP-AES) per standard method 200.7 (APHA, AWWA, & WEF, 1995). Ultrapure 16N nitric acid (Ultrax, J. T. Baker Chemical Company, Phillipsburg, NJ) was used to preserve samples at 0.15% v/v for metals analysis. The detection limit of ICP-AES for total iron was 0.001 mg/L. For data quality assurance and quality control, standards, blanks and spikes of known concentrations accounted for 10% of the measured samples.

2.3. Stagnation studies and molecular diffusion model

Representative water conditions A-D were selected to examine the relationship between total iron release and DO depletion during up to 72 h of stagnation time using the same pipe apparatus. The total iron levels were measured using the spectrophotometric method and DO levels were measured as indicated above. In order to validate the results of the experiment and have more confidence in the data obtained, a radial molecular diffusion model was employed (Kuch and Wagner, 1983). The model was originally developed to describe lead release from lead pipe walls, and it was adapted to model the release of iron from cast iron

pipe scale. This model assumed that iron concentration was constant along the pipe, and the transfer of iron from cast iron pipe was controlled by diffusion across a thin layer adjacent to the pipe wall (Equations (2)–(4)) (Kuch and Wagner, 1983; Green and Southard, 2019) and can be described by:

$$R_{Fe} = \frac{[Fe]^t - [Fe]^0}{[Fe]^\infty - [Fe]^0} = 1 - \exp \frac{-4Fo'}{\frac{1}{Bi'} + \frac{1}{\sqrt{(5.78)^2 + \frac{1}{\pi Fo'}}}} \quad (2)$$

where Fo' is the Fourier number:

$$Fo' = \frac{Dt}{4a^2} \quad (3)$$

and Bi' is the Biot number that serves as a correction factor for additional diffusion barriers present on the pipe scale:

$$Bi' = \frac{\beta_a \cdot 2a}{D} \quad (4)$$

Note that a = internal radius of the pipe (cm), which was 4.45 cm after excluding the tubercle layers, D = diffusion coefficient for iron in water (cm^2/s), t = stagnation time (s), and β_a = mass transfer coefficient of an additional resistance due to iron corrosion deposits (cm/s). A detailed description of the model and related parameters was described in the Supporting Information Calculation S1.

2.4. Statistical analysis

All statistics were performed in the SigmaPlot 14.0 Notebook (Systat Software, Inc). An alpha value (α) of 0.05 was selected to determine the statistical significance (Dalgaard, 2008). The normality of the data was determined using the Shapiro-Wilk test. For parametric or normally distributed data (Shapiro-Wilk test, $p > 0.05$), t -test or one-way ANOVA was used to compare the mean iron concentrations among different water conditions; for non-parametric or non-normally distributed data (Shapiro-Wilk test, $p < 0.05$), rank tests including Mann-Whitney test, Kruskal-Wallis, and Spearman's rank correlation were used to compare the median iron concentrations among iron data groups and the associations between different parameters. For validation purposes, a linear regression was conducted between measured iron levels from stagnation studies and modeled iron levels from the molecular diffusion model.

3. Results

Nine water conditions representing different combinations of chloride, sulfate, and DIC concentrations were evaluated for 801 days at an initial water pH 8.0 and temperature of 23 ± 1.2 °C (Table 1; Fig. S4). Twenty-two water condition changes were made to the 90-year-old cast iron pipe section apparatus over the study period. Alternating conditions allowed for the evaluation of the impact of rapid water quality change on iron release, water pH change,

and DO depletion over 24-hr stagnation periods. Although water samples were collected after 48-hr and 72-hr stagnation periods, they were not statistically different from 24-hr samples, therefore were not discussed.

3.1. Total iron and Fe(II) release

Out of the total 328 collected water samples, 176 water samples were measured for total iron levels by both spectrophotometric and ICP-AES methods. For the 176 water samples, the total iron release throughout the 801-day study ranged from below detection limit level (BDL) (0.03 mg/L) up to 4.1 mg/L by spectrophotometric method and from BDL (0.001 mg/L) up to 3.95 mg/L by ICP-AES method. The average and median levels were 0.90 mg/L and 0.84 mg/L by spectrophotometric method, and 0.62 mg/L and 0.57 mg/L by ICP-AES method and the total iron by both methods was in good agreement when both analyses were on the same sample (Spearman's $\rho = 0.79$, $p < 0.001$) (Fig. S2). Since iron results by the spectrophotometric method were available for all collected water samples as compared to only 54% by ICP-AES, the iron results by the spectrophotometric method were reported below.

As the speciation of iron released into water indicates redox reaction phases, the total Fe(II) in 326 out of 328 collected water samples was measured and ranged from 0.008 to 0.30 mg/L, with an average and median of 0.07 mg/L and 0.06 mg/L, respectively (Figs. S3-a). The ratio between Fe(II) and total iron ranged from 0 to 0.52, with a median of 0.06 (Figs. S3-b). This finding indicates that Fe(III) was the prevalent iron form in the collected water samples. This information was consistent with established knowledge that at alkaline pH of 8.0, oxidation of Fe(II) to Fe(III) is very fast when sufficient DO is present in water (Kester et al., 1975; Millero, 1985; Li et al., 2016). As all samples were taken from the center of the vertical cast iron pipe section, better sampling and preservation methods might be necessary to identify the Fe(II) and Fe(III) species in water both near and far away from the pipe wall. The iron species profile across the pipe radius could be critical in understanding the mechanisms associated with iron release under each water quality.

3.2. The effect of chloride and sulfate

To examine the effect of sulfate, conditions A and B were alternated repeatedly for the first 134 days. The cast iron pipe section was first filled with baseline water (condition A) containing 10 mg/L DIC for 49 days (Table 1; Fig. 1). The total iron concentration (or iron indicated later) remained relatively constant, with an average of 0.79 ± 0.19 mg/L for the first 49 days. Between days 50–112, 150 mg/L sulfate was added to the pipe section (condition B) and the average iron was 1.13 ± 0.06 mg/L, resulting in an immediate 0.34 mg/L increase in iron levels with a statistically significant difference (Mann-Whitney test, $p < 0.001$). Water conditions A and B were executed again during days 113–134. A similar trend was observed when adding sulfate to condition B during days 127–134. The average iron increased to 1.07 mg/L, compared to 0.62 ± 0.22 mg/L for condition A, during days 113–126 (t -test, $p < 0.001$). Additionally, the increase in average iron, due to the addition of sulfate during the second alternation, almost doubled during days 50–112. This indicated that sulfate could have a lasting effect on scale structure that impacted the scales ability to increase the diffusion of iron into the bulk water.

The impact of chloride and sulfate was examined by alternating conditions A-E multiple times (Table 1; Fig. 1). The baseline condition A was resumed between days 135–147 resulting in an average iron concentration of 0.65 ± 0.11 mg/L, similar to that of the previous two time periods in which condition A was tested (Kruskal-Wallis test, $p = 0.40$). On day 148, condition C water containing 100 mg/L chloride was added to the pipe section until day 162. This experiment resulted in an immediate and significant increase in the average iron concentration by 1.23 mg/L, relative to the baseline (t -test, $p < 0.001$). On day 162, condition D water containing 100 mg/L chloride and 150 mg/L sulfate was tested for 21 days until day 182, and the average iron was 2.11 ± 0.36 mg/L. Then condition B, without chloride, was resumed on day 183, until day 216, resulting in a further increase in the average iron concentration to 2.68 ± 0.34 mg/L. The average iron concentration for condition B was significantly higher than that found in conditions C or D (t -test, $p = 0.034$), but condition C was statistically similar to condition D (Mann-Whitney test, $p = 0.69$). This change indicates that the addition of both chloride and sulfate to the test water did not severely alter the iron release comparative to the addition of chloride alone.

In order to validate the above observations, the alternations between conditions A-D was executed again between days 217–266, but in a slightly different order. Specifically, the cast iron apparatus was resumed with the baseline of condition A on day 217, then followed by condition B on day 231, condition D on day 245, and condition C on day 259. The average iron levels for conditions A, B, D, and C were 0.54 ± 0.12 mg/L, 1.41 ± 0.17 mg/L, 1.68 ± 0.14 mg/L, and 1.83 ± 0.10 mg/L, respectively. Similar results were obtained with the addition of both chloride and sulfate. The iron release in condition D increased significantly as compared to the baseline condition A (t -test, $p < 0.001$), which was not worse than condition C with chloride only (t -test, $p = 0.13$). However, condition C was significantly worse than when water was added with sulfate only in condition B (Mann-Whitney test, $p = 0.017$).

Another group of alternation among conditions B-E was followed between days 267–441. On day 267, condition E with 10 mg/L chloride, was introduced to the apparatus for 36 days, and the average iron concentration was 0.59 ± 0.12 mg/L, similar to previous periods with condition A that did not have chloride (Kruskal-Wallis test, $p = 0.33$). Then the same apparatus was tested with condition C on day 303, condition D on day 322, and condition B on day 403. The average iron levels for conditions C, D, and B were 1.53 ± 0.39 mg/L, 1.53 ± 0.19 , and 1.13 ± 0.22 mg/L, respectively. The iron release from conditions B-D was significantly higher relative to E without any chloride or sulfate ($p = 0.002$). In this case, iron release in condition D with both chloride and sulfate was not worse than condition C with chloride only or condition B with sulfate only (Kruskal-Wallis test, $p = 0.073$).

3.3. Effect of increasing DIC concentration

The baseline condition A was resumed on day 442 for 13 days with an average iron of 0.58 ± 0.02 mg/L, and the remainder of conditions F–I were run using 50 mg C/L DIC as opposed to 10 mg C/L between days 455–608 (Table 1; Fig. 1). Condition F with only 50 mg C/L DIC was studied between days 454–498, and it significantly reduced the average iron concentration by 57% to 0.25 ± 0.08 mg/L relative to condition A (t -test, $p < 0.001$).

Adding 150 mg/L of sulfate to condition G resulted in an average iron of 0.37 ± 0.09 mg/L between days 499–539. The additions of 100 mg/L of chloride and 150 mg/L of sulfate to condition H resulted in an average iron of 0.43 ± 0.21 mg/L between days 540–548. Adding 150 mg/L of chloride and 150 mg/L of sulfate in condition I resulted in an average iron of 0.51 ± 0.21 mg/L between days 549–608. These additions resulted in an insignificant increase of iron release for conditions G-I that contained sulfate and/or chloride in them, relative to F, that contained only DIC (Kruskal-Wallis test, $p = 0.073$). However, the average iron release for waters with higher DIC of 50 mg C/L in G and H was significantly lower than waters with lower DIC of 10 mg C/L (B and D) that were run previously (G vs B, H vs D, $p < 0.001$). These findings indicate the beneficial impact of DIC resisting iron release from the iron scale. Repeating condition D on days 609–801 resulted in a significant increase in average iron to 0.63 ± 0.06 mg/L (Mann-Whitney test, $p < 0.001$). The change in average iron might be caused by the decrease of DIC which could have outweighed the benefit due to the decrease of chloride.

3.4. Larson Ratio, DO depletion, and pH changes

It was apparent that chloride, sulfate, and DIC impacted iron release in different ways. Iron release was divided into eight groups according to the Larson Ratio ranging from 0 to 7.13 (Table 1). Observations to examine if adding DIC had a lasting effect in resisting iron release, the relationship between iron release and the Larson Ratio, consisted of three phases. These phases were: 1) when DIC = 10 mg C/L during elapsed time 1–454 days (Fig. 2a), 2) when DIC = 10 and 50 mg C/L during elapsed time 1–608 days (Fig. 2b), and 3) when DIC = 10 and 50 mg C/L during elapsed time 1–801 days (Fig. 2c).

The Larson Ratio moderately predicted iron release levels when water conditions contained low levels of DIC - that is, a measurement of 10 mg C/L (Spearman's $\rho = 0.61$, $p < 0.001$) (Fig. 2a). When waters were switched to higher levels of DIC of 50 mg C/L, there was a slightly stronger association between iron release and the Larson Ratio (Spearman's $\rho = 0.68$, $p < 0.001$) (Fig. 2b). This observation supported the idea that changes in the Larson Ratio could be qualitative indicator of iron release. However, when water conditions switched from higher DIC of 50 mg C/L to lower DIC of 10 mg C/L, the overall association between iron release and the Larson Ratio greatly decreased (Spearman's $\rho = 0.32$, $p < 0.001$) (Fig. 2c). We speculate that the DIC had a long-lasting effect on promoting the scale stability and resisting iron release. As the Larson Ratio does not account for the structure of the pipe scale or the effect of previous water chemistries, the Larson Ratio could be limited in predicting iron release depending on the order of water treatment changes.

The changes in other important water parameters such as pH and DO were consistent to the observations by Li et al. (2016) (Table 1; Figs. S5 and S6). In general, the pH increased, and the DO depleted over time. The initial and final average pH ranged from 7.39–8.36, and 8.28–9.39, respectively. The pH increase was 0.94 ± 0.38 unit, which could have been a result of the pipe metal or scale corroding and producing hydroxide ions (Sarin et al., 2004b). In contrast, the initial DO was 6.69–9.37 mg/L and decreased by 5.25 ± 1.55 mg/L after 24 h of stagnation due to the oxidation of Fe(II) and pipe scale, and iron corrosion.

3.5. Stagnation studies and molecular diffusion model

Representative water conditions A-D were used for stagnation studies that were carried out for up to 72 h of stagnation periods (Fig. 3a–d). The iron release for the baseline condition A had a relatively “linear” upward trend over time. Specifically, the iron release was 0.58 mg/L after 24 h, and it increased to 1.14 mg/L after 48 h; it kept increasing to 1.86 mg/L after 72 h of stagnation. In contrast, with the addition of chloride or sulfate, the iron release for conditions B-D had a relatively more rapid increase and reached a “steady” state after 24 h of stagnation. After 16–19 h of stagnation, the iron release for conditions B, C, and D was 1.39 mg/L, 0.53 mg/L, and 1.45 mg/L, respectively. After 24 h of stagnation, the iron release for B, C, and D at the “steady” state measured 1.6 mg/L, 2.0 mg/L and 2.0 mg/L, respectively. The increase in iron release suggested the addition of chloride and sulfate enhanced the kinetics of iron release from the scale into water. To validate the measured iron levels, the molecular diffusion model was adapted, and the iron levels obtained from the model suggested a favorable agreement with the experimental results with a R^2 of 0.89–0.97 (linear-regression, $p < 0.001$) (Calculation S1; Fig. 3e; Table S1). The mass transfer coefficients (β_a) indicate the additional resistance layer of iron pipe scale was different, measuring 2.04×10^{-5} cm/s, 3.51×10^{-4} cm/s, 7.69×10^{-5} cm/s, and 2.49×10^{-4} cm/s for A, B, C, and D, respectively.

4. Discussion

4.1. Impact of chloride, sulfate and DIC

The release of iron from the cast iron pipe apparatus was a function of chloride, sulfate and DIC levels in the water. Additionally, the changes in iron release were rapid and instantaneous in response to the changes in chloride, sulfate, and DIC levels. The rapid response without a lingering impact suggested that the likelihood of damage to the iron pipe scale integrity was low. It consistently showed that upon the addition of chloride and/or sulfate, the total iron concentration immediately elevated relative to iron levels in waters containing only DIC, particularly for waters with lower DIC. In contrast, waters with higher DIC (50 mg C/L vs. 10 mg C/L) reduced iron release even when high concentrations of chloride and sulfate were present, countering their negative impact.

The detrimental effect of chloride on iron release was found in other studies (Lytle et al., 2005a; Peng et al., 2013; Pieper et al., 2018; Hu et al., 2018), and could be explained by the conceptual iron release model developed by Sarin et al. (2004b). In short, chloride may promote local pH drops and the formation of electrolytic cells, encouraging the dissolution of Fe(II); both changes gradually help form a porous scale that assists with the diffusion of dissolved Fe(II) into water. Liu et al., 2013 showed that increasing chloride levels favored the formation of loose and porous microcrystalline lepidocrocite on the iron scale surface. Meantime, the Fe(II) ions formed within the inner porous scale attract negatively charged ions such as chloride and sulfate, which results in further corrosion. Additionally, chloride slows down the oxygenation rate of Fe(II) to Fe(III) such that Fe(II) can diffuse further distances through the pipe scale before its oxidation to Fe(III) (Tamura et al., 1976). This finding also explains the correlation between higher levels of DIC or bicarbonate assists in reducing iron release. The increasing levels of DIC could provide increasing buffering

capacity, resist pH ranges within the tubercle, and limit the mobility of Fe(II), chloride and sulfate anions, and impact Fe(II) solubility.

Though other studies showed that sulfate increased total iron release (Liu et al., 2013; Peng et al., 2013; Zhang et al., 2014; Hu et al., 2018), the impact of sulfate on iron release was inconsistent in this study. Iron release in water containing sulfate alone, could increase or decrease in waters with chloride, (and sulfate) depending on the circumstances and the associated mechanisms remained unresolved. It was speculated that sulfate ions in water possibly impacted the iron scale structure, iron solubility or bacterial community in scale. Increasing sulfate was shown to favor the formation of hard shell goethite (Liu et al., 2013), and was also associated with sulfur-oxidizing bacteria, sulfate-reducing bacteria and iron-reducing bacteria present in scale, influencing iron release into water (Lytle et al., 2005b; Yang et al., 2014).

The Larson Ratio has long been used to indicate the severity of iron corrosion. The water samples with a larger Larson Ratio of > 1.2 , indicating high corrosivity of iron had statistically higher iron levels relative to those with Larson Ratio of < 0.8 (Mann-Whitney test, $p < 0.001$). Though a higher Larson Ratio can successfully predict a higher iron release, the association between the Larson Ratios and iron concentrations was dependent on the circumstances, in this case, the water treatment changes (Fig. 2). It might be necessary to incorporate other water parameters not considered in this work that are important to iron scale build-up and release into the Larson Ratio for better prediction. For example, Imran et al. (2005b) incorporated water temperature and hydraulic residence time or water age parameters into the equation to give better results.

4.2. Molecular diffusion model

The molecular radial diffusion model reasonably predicted the release of total iron under stagnation periods based on the regression results despite complexities and uncertainties regarding the true nature of iron (i.e., soluble versus particulate iron, and ferrous versus ferric iron). It was noteworthy that the mass transfer coefficients reflecting the resistance layer composed of iron scale solids were calculated based on measured iron levels during stagnation studies due to the lack of information on scale characteristics (Calculation S1). As water conditions B-D reached equilibrium after 24 h of stagnation, based on the βa values, the calculated thickness of the resistance layer for 24 h of stagnation time, was 1.76 cm, 30.28 cm, 6.65 cm, and 21.52 cm for A, B, C and D water conditions, respectively. These calculated βa values for resistance layers were considerably high relative to the effective cast iron diameter of 8.9 cm. Although the model provides quantitative experimental data, it failed to capture the iron mass transfer from the resistance layer mechanistically.

It might be necessary to re-evaluate the assumption about molecular diffusion being the controlling mechanism for iron release. Instead, the iron pipe scale porosity, structure, composition, thickness and other properties were likely to play a critical role in controlling the iron release, and therefore, should be incorporated in the model. Including more information about water hydraulics involvement in predicting iron release from real water distribution systems is another consideration. One study showed that the mass transfer

coefficient for chlorine dissipation in drinking water systems was a function of water flow, pipe length, and pipe diameter for galvanized iron pipe and unlined cast iron pipe (Mutoti et al., 2007). The reported coefficients continuously increased from 1.2×10^{-5} – 6.7×10^{-4} cm/s as water velocity increased from 1.00×10^{-4} – 9.19×10^{-1} m/s for galvanized iron pipe, and from 5.79×10^{-6} – 3.62×10^{-4} cm/s as water velocity increased from 7.00×10^{-5} – 2.29×10^{-2} m/s for unlined cast iron pipe. Therefore, a better understanding of iron diffusion processes, pipe scale characteristics, and water hydraulics is necessary for more accurate model prediction.

4.3. Implications and limitations

The results from this study provide useful information for water utilities who may be considering making changes or are experiencing changes in their water treatment (e.g., switch to chloride or sulfate-based coagulants) and/or water sources (e.g., switch from ground water to surface water). The control of iron release, addition of buffering capacity, or reduction of chloride or sulfate may help stabilize the water quality in the distribution system. However, in order to mitigate contaminants in each water system, the control of lead, copper, and other unique contaminants needs to be assessed and prioritized based on the water quality and corrosion control needs.

This study gives some insight into iron release and corrosion, but there are still many limitations. First, the water conditions were tested at pH 8.0, which was considered likely to exacerbate iron corrosion relative to other pHs (Masters and Edwards, 2015; Tang et al., 2018). Additionally, the examined waters sometimes contained higher levels of chloride (100–150 mg/L) and sulfate (150 mg/L) comparative to what is generally found in water distribution systems. Cincinnati tap water had an average chloride of 34 mg/L and sulfate of 65 mg/L in previous work (Lytle et al., 2005a). The 2–3 times higher chloride and sulfate concentrations examined in this study had the potential to be more aggressive toward iron release than Cincinnati tap water. Second, it would be unlikely to have 24–72 h of stagnation time in water mains under normal operating conditions, and similar stagnation time is more likely in residential distribution lines, often highly dependent on water demand and uses. Third, all nine water conditions were examined using the cast iron pipe section consecutively and the uptake of DIC by the pipe was not monitored. Additionally, inner pipe surface analyses to identify changes in pipe scale properties including mineralogy, elemental make-up, and structural integrity could not be performed because the pipe section remains in use for other investigations. Therefore, the associated mechanisms for elucidating the impact of each individual parameter demand further study. Future examination of iron species in collected water samples and pipe scale samples could give insight into the issue. Future experiments could also feature a pipe loop that models variable flows present in real distribution systems and contain typical levels of constituents. There could also be pipes made from various materials, so that differences in materials can be studied.

5. Conclusions

Iron corrosion and iron release are relevant problems in all water distribution systems. The results show that bicarbonate helps reduce iron release while chloride and sulfate are linked

to increased iron release. The extent to which these components affect iron release is not completely understood. The results discussed in this paper provide insight for water utilities considering making changes to the treatment of source water in water distribution systems operating with cast iron or aged galvanized iron pipe materials. The Larson Ratio could be an effective predictor of iron release, although it should be used with caution. While the molecular diffusion model had the potential to be used for predicting iron release, more research is needed to understand iron release and its associated mechanisms entirely. would like to thank the assistance of the City of Cincinnati Water Works for providing the experimental pipe section.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- APHA AWWA and WEF, 1995 American Public Health Association (APHA), American Water Works Association (AWWA). In: Eaton L.S.C. Andrew D., Greenberg Arnold E. (Eds.), Water Environment Federation (WEF). Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Atlanta, GA.
- Baylis JR, 1926 Factors other than dissolved oxygen influencing the corrosion of iron pipes. Ind. Eng. Chem. 18 (4), 370–380.
- Benjamin MM, Sontheimer H, Leroy P, 1996 Corrosion of iron and steel In: Chemistry of Corrosion Inhibitors in Potable Water, 2 ed., vol. 586 AWWARF & DVGW-TZW, Denver, CO.
- Benson AS, Dietrich AM, Gallagher DL, 2012 Evaluation of iron release models for water distribution systems. Crit. Rev. Environ. Sci. Technol. 42 (1), 44–97.
- Blengino JM, Keddah M, Labbe JP, Robbiola L, 1995 Physico-chemical characterization of corrosion layers formed on iron in a sodium carbonate-bicarbonate containing environment. Corrosion Sci. 37 (4), 621–643.
- Burlingame GA, Lytle DA, Snoeyink VL, 2006 Why red water? Understanding iron release in distribution systems. J. Am. Water Works Assoc. Opflow 32 (12), 12–16.
- Cornell RM, Schwertmann S, 2003 The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses, 2 ed. Wiley-VCH.
- Dalgaard P, 2008 Introductory Statistics with R, second ed. Springer Science + Business Media, LLC, New York, NY.
- DeBerry DW, Kidwell JR, Malish DA, 1982 Corrosion in Potable Water Systems: Final Report. U.S. E.P.A., Washington DC. February.
- Dixit S, Hering JG, 2003 Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. Environ. Sci. Technol. 37 (18), 4182–4189. [PubMed: 14524451]
- EPA, 1991a U.S. Maximum contaminant level goals and national primary drinking water regulations for lead and copper. final rule. Fed. Regist. 56, 26460.

- EPA, 1991b U.S. EPA national secondary drinking water regulations. final rule. Fed. Regist. 56 (20), 3526.
- Folkman S, 2018 Water Main Break Rates in the USA and Canada: a Comprehensive Study. Utah State University: Buried Structures Laboratory. March.
- Gerke TL, Maynard JB, Schock MR, Lytle DL, 2008 Physiochemical characterization of five iron tubercles from a single drinking water distribution system: possible new insights on their formation and growth. Corrosion Sci. 50 (7), 2030–2039.
- Green DW, Southard MZ, 2019 Perry's Chemical Engineer's Handbook, 9 ed. McGraw-Hill Education.
- Herro HM, Port RD, 1993 The Nalco Guide to Cooling Water System Failure Analysis. McGraw-Hill, New York, NY.
- Herro HM, 1998 MIC myths-does pitting cause MIC. Corr. NACE Int. 98, 1–20.
- Hu J, Dong H, Xu Q, Ling W, Qu J, Qiang Z, 2018 Impacts of water quality on the corrosion of cast iron pipes for water distribution and proposed source water switch strategy. Water Res. 129, 428–435. [PubMed: 29179122]
- Imran SA, Dietz JD, Mutoti G, Taylor JS, Randall AA, Cooper CD, 2005a Red water release in drinking water distribution systems. J. Am. Water Works Assoc. 97 (9), 93–100.
- Imran SA, Dietz JD, Mutoti G, Taylor JS, Randall AA, 2005b Modified Larsons ratio incorporating temperature, water age, and electroneutrality effects on red water release. J. Environ. Eng. 131 (11), 1514–1520.
- Kester DR, Byrne RH, Liang YJ, 1975 Redox reactions and solution complexes of iron in marine systems. Marine Chem. Coast. Environ. 18 (56–79).
- Kuch A, Wagner I, 1983 A mass transfer model to describe lead concentrations in drinking water. Water Res. 17 (10), 1303–1307.
- Kuch A, 1988 Investigations of the reduction and re-oxidation kinetics of iron (III) oxide scales formed in waters. Corrosion Sci. 28 (3), 221–231.
- Larson TE, Skold RV, 1957 Corrosion and tuberculation of cast iron. J. AWWA (Am. Water Works Assoc.) 49 (10), 1294–1302.
- Larson TE, Skold RV, 1958 Laboratory studies relating mineral quality of water to corrosion of steel and cast iron. Corrosion 14 (6), 285–288.
- LeChevallier MW, Lowry CD, Lee RG, Gibbon DL, 1993 Examining the relationship between iron corrosion and the disinfection of biofilm bacteria. J. AWWA (Am. Water Works Assoc.) 85 (7), 111–123.
- Li M, Liu Z, Chen Y, Hai Y, 2016 Characteristics of iron corrosion scales and water quality variations in drinking water distribution systems of different pipe materials. Water Res. 106, 593–603. [PubMed: 27776308]
- Little BJ, Gerke TL, Lee JS, 2014 Mini-review: the morphology, mineralogy and microbiology of accumulated iron corrosion products. Biofouling 30 (8), 941–948. [PubMed: 25271874]
- Liu H, Schonberger KD, Peng CY, Ferguson JF, Desormeaux E, Meyerhofer P, et al., 2013 Effects of blending of desalinated and conventionally treated surface water on iron corrosion and its release from corroding surfaces and pre-existing scales. Water Res. 47 (11), 3817–3826. [PubMed: 23651514]
- Lytle DA, Sorg TJ, Frietch C, 2004a Accumulation of arsenic in drinking water distribution systems. Environ. Sci. Technol. 38 (20), 5365–5372. [PubMed: 15543738]
- Lytle DA, Magnuson ML, Snoeyink VL, 2004b Effect of oxidants on the properties of Fe(III) particles and suspensions formed from the oxidation of Fe(II). J. AWWA (Am. Water Works Assoc.) 96 (8), 112–124.
- Lytle DA, Sarin P, Snoeyink VL, 2005a The effect of chloride and orthophosphate on the release of iron from a cast iron pipe section. J. Water Supply Res. Technol. - Aqua 54 (5), 267–281.
- Lytle DA, Gerke TL, Maynard DJB, 2005b Effect of bacterial sulfate reduction on iron-corrosion scales. J. AWWA (Am. Water Works Assoc.) 97 (10), 109–120.
- Lytle DA, Sorg TJ, Muhlen C, Wang L, 2010 Particulate arsenic release in a drinking water distribution system. J. AWWA (Am. Water Works Assoc.) 102 (3), 87–98.

- Lytle DA, Sorg T, Wang L, Chen A, 2014 The accumulation of radioactive contaminants in drinking water distribution systems. *Water Res.* 50 (1), 396–407. [PubMed: 24275108]
- Masters S, Edwards M, 2015 Increased lead in water associated with iron corrosion. *Environ. Eng. Sci.* 32 (5), 361–369.
- McNeill LS, Edwards M, 2000 Phosphate inhibitors and red water in stagnant iron pipes. *J. Environ. Eng.* 126 (12), 1096–1102.
- McNeill LS, Edwards M, 2001 Iron pipe corrosion in distribution systems. *J. Am. Water Works Assoc.* 93 (7), 88–100.
- Millero FJ, 1985 The effect of ionic interactions on the oxidation of metals in natural waters. *Geochem. Cosmochim. Acta* 49 (2), 547–553.
- Mutoti G, Dietz JD, Arevalo J, Taylor JS, 2007 Combined chlorine dissipation: pipe material, water quality, and hydraulic effects. *J. Am. Water Works Assoc.* 99 (10), 96–106.
- Peng CY, Ferguson JF, Korshin GV, 2013 Effects of chloride, sulfate and natural organic matter (NOM) on the accumulation and release of trace-level inorganic contaminants from corroding iron. *Water Res.* 47 (14), 5257–5269. [PubMed: 23863395]
- Pieper KJ, Tang M, Edwards MA, 2017 Flint water crisis caused by interrupted corrosion control: investigating “ground zero” home. *Environ. Sci. Technol.* 51 (4), 2007–2014. [PubMed: 28145123]
- Pieper KJ, Tang M, Jones CN, Weiss S, Greene A, Mohsin H, Parks J, Edwards MA, 2018 Impact of road salt on drinking water quality and infrastructure corrosion in private wells. *Environ. Sci. Technol.* 52 (24), 14078–14087. [PubMed: 30407803]
- Ray RI, Lee JS, Little BJ, Gerke TL, 2010 The anatomy of tubercles: a corrosion study in a fresh water estuary. *Mater. Corros.* 61 (12), 993–999.
- Sarin P, Snoeyink VL, Bebee J, Kriven WM, Clement JA, 2001 Physico-chemical characteristics of corrosion scales in old iron pipes. *Water Res.* 35 (12), 2961–2969. [PubMed: 11471696]
- Sarin P, Clement JA, Snoeyink VL, Kriven WM, 2003 Iron Release from corroded, unlined cast-iron pipe. *J. AWWA (Am. Water Works Assoc.)* 95 (11), 85–96.
- Sarin P, Snoeyink VL, Lytle DA, Kriven WM, 2004a Iron corrosion scales: model for scale growth, iron release, and colored water formation. *J. Environ. Eng.* 130 (4), 364–373.
- Sarin P, Snoeyink VL, Bebee J, Jim KK, Beckett MA, Kriven WM, Clement JA, 2004b Iron release from corroded iron pipes in drinking water distribution systems: effect of dissolved oxygen. *Water Res.* 38 (5), 1259–1269. [PubMed: 14975659]
- Sontheimer H, Kölle W, Snoeyink VL, 1981 The siderite model of the formation of corrosion-resistant scales. *J. AWWA (Am. Water Works Assoc.)* 73 (11), 572–579.
- Tamura H, Goto K, Nagayama M, 1976 Effect of anions on the oxygenation of ferrous ion in neutral solutions. *J. Inorg. Nucl. Chem.* 38 (1), 113–117.
- Tang M, Triantafyllidou S, Edwards M, 2013 In situ remediation of leaks in potable water supply systems. *Corrosion Rev.* 31 (3–6), 105–122.
- Tang M, Nystrom V, Pieper K, Parks J, Little B, Guillems R, Esqueda T, Edwards M, 2018 The relationship between discolored water from corrosion of old iron pipe and source water conditions. *Environ. Eng. Sci.* 35 (9), 943–952.
- Yang F, Shi B, Bai Y, Sun H, Lytle DA, Wang D, 2014 Effect of sulfate on the transformation of corrosion scale composition and bacterial community in cast iron water distribution pipes. *Water Res.* 59, 46–57. [PubMed: 24784453]
- Zhang X, Mi Z, Wang Y, Liu S, Niu Z, Lu P, et al., 2014 A red water occurrence in drinking water distribution systems caused by changes in water source in Beijing, China: mechanism analysis and control measures. *Front. Environ. Sci. Eng.* 8 (3), 417–426, 2014.
- Zhang Y, Edwards M, 2007 Anticipating effects of water quality changes on iron corrosion and red water. *J. Water Supply Res. Technol. - Aqua* 56 (1), 55–68.

Fig. 1. Total iron concentration and Larson Ratio as a function of elapsed time (top: 0–400 days, bottom: 400–801 days) during 24 h of stagnation periods.

Fig. 2.

Correlation between total iron concentration and Larson Ratio during 24 h stagnation periods for (a) when DIC = 10 mg C/L for elapsed time 1–454 days (Spearman's $\rho = 0.61$, $p < 0.001$), (b) when DIC = 10 & 50 mg C/L for elapsed time 1–608 days (Spearman's $\rho = 0.68$, $p < 0.001$), and (c) when DIC = 10 & 50 mg C/L for elapsed time 1–801 days (Spearman's $\rho = 0.33$, $p < 0.001$).

Fig. 3.

Total measured iron concentrations and dissolved oxygen levels present in water for conditions A-D (a-d) during stagnation studies. The normalized ratio of total iron concentrations from stagnation studies and from the molecular diffusion model was compared for conditions A-D (e) (Calculation S1).

Table 1

Summary of average water quality parameter values for 24 h of stagnation periods.

Water Condition	ET (day)	DIC (mg/L)	Chloride (mg/L)	Sulfate (mg/L)	Larson Ratio	Sample Size	pH I		pH F		DO I (mg/L)		DO F (mg/L)		Fe (II) (mg/L)		Total Fe (mg/L)	
							Ave	CI	Ave	CI	Ave	CI	Ave	CI	Ave	CI	Ave	CI
A	1-49	10	-	-	0	21	8.28	0.06	9.26	0.07	6.93	0.39	2.60	0.34	0.04	0.01	0.79	0.19
B	50-112	10	-	150	3.75	33	8.36	2.82	9.34	3.22	6.39	2.21	2.49	0.99	0.08	0.03	1.13	0.06
A	113-126	10	-	-	0	7	8.28	0.06	9.24	0.03	8.27	0.52	4.88	1.38	0.03	0.02	0.62	0.22
B	127-134	10	-	150	3.75	5	8.19	0.02	9.05	0.09	7.65	0.23	3.85	0.40	0.09	0.04	1.69	0.38
A	135-147	10	-	-	0	6	8.23	0.08	9.16	0.06	7.42	0.33	3.27	0.76	0.05	0.03	0.65	0.11
C	148-161	10	100	-	3.38	7	8.14	0.08	8.84	0.08	7.73	0.31	2.43	0.35	0.15	0.03	1.88	0.12
D	162-182	10	100	150	7.13	8	8.09	0.06	8.88	0.06	7.55	0.25	2.75	0.44	0.16	0.04	2.11	0.36
B	183-216	10	-	150	3.75	17	8.02	0.13	8.28	0.20	6.99	0.44	1.85	0.23	0.17	0.02	2.68	0.34
A	217-230	10	-	-	0	8	7.39	0.14	8.40	0.14	7.00	0.17	1.90	0.33	0.06	0.03	0.54	0.12
B	231-244	10	-	150	3.75	7	7.73	0.08	8.51	0.14	6.69	0.16	1.62	0.69	0.21	0.08	1.41	0.17
D	245-258	10	100	150	7.13	6	7.89	0.15	8.61	0.25	7.75	1.07	1.68	0.34	0.18	0.07	1.68	0.14
C	259-266	10	100	-	3.38	3	7.83	0.12	8.78	0.14	7.67	0.19	1.96	0.33	0.12	0.03	1.83	0.10
E	267-302	10	10	-	0.34	13	8.10	0.20	9.25	0.12	7.41	0.35	2.83	0.33	0.05	0.03	0.59	0.12
C	303-321	10	100	-	3.38	10	8.18	0.02	9.22	0.12	8.35	0.65	3.00	0.82	0.10	0.03	1.53	0.39
D	322-402	10	100	150	7.13	20	8.09	0.05	9.13	0.07	8.30	0.27	2.09	0.21	0.10	0.02	1.53	0.19
B	403-441	10	-	150	3.75	11	8.08	0.07	9.39	0.06	9.37	0.48	2.63	0.78	0.09	0.02	1.13	0.22
A	442-454	10	-	-	0	3	8.08	0.02	9.38	0.12	8.73	0.12	2.22	0.34	0.11	0.07	0.58	0.02
F	455-498	50	-	-	0	15	8.12	0.04	8.81	0.05	8.42	0.33	2.67	0.41	0.02	0.01	0.25	0.08
G	499-539	50	-	150	0.75	19	8.11	0.03	8.76	0.03	8.35	0.19	1.91	0.16	0.01	0.01	0.37	0.09
H	540-548	50	100	150	1.43	3	8.16	0.05	8.78	0.05	8.74	0.56	1.39	1.44	0.00	0.00	0.43	0.21
I	549-608	50	150	150	1.76	27	7.98	0.04	8.63	0.06	7.18	0.17	2.23	0.12	0.02	0.01	0.51	0.21
D	609-801	10	100	150	7.13	79	7.81	0.06	9.02	0.08	8.30	0.34	2.88	0.18	0.05	0.01	0.63	0.06

ET = elapsed time, DIC = dissolved inorganic carbon as C, pH_I = initial pH, pH_F = final pH, DO_I = initial dissolved oxygen, DO_F = final dissolved oxygen; Ave = average, CI = 95% confidence interval, Fe(II) = ferrous iron.